Dedication

Dedicated to that most capricious

Never to be understood

Weather cocky incorruptible and absolutely

Necessary person

The gentle readers

Preface

The explosive scientific revolution is the result of a number of factors that complement one another. These factors include a better understanding of the science of materials. These advances are often based on new and extended understanding and application of basic principles initially presented in all the core chemistry courses. Polymer Chemistry complies with the advanced course definition building on the foundations laid in general, organic, physical, analytical, and inorganic chemistry. The text integrates and interweaves the important core topic areas. The core topics are interrelated with information that focuses on polymer advance topics. This assists students in integrating their chemical knowledge and illustrates the connection between theoretical and applied polymer information. It is written so that chapters can be taken in order and all the chapters need to be covered to gain an adequate appreciation of the science of polymers. Some readers will elect to read the more descriptive chapters dealing with polymer types before looking at the chapters. This book is user friendly, it is appropriate as an advanced course text of BS (honor) an introductory-level graduate-level classes. This book reflects the growth and the continually expanding role of polymers. There is an increased emphasis on pictorializing, reinforcing, integrating, and interweaving the basic polymer concepts. Each chapter is essentially self-contained, but each relates to the other chapters. Whenever possible, difficult concepts are distributed and reinforced over several chapters. This is true for all the various important and critical types of polymers including synthetic, biological, physical, organometallic, and inorganic polymers. The principle that the basic concepts that apply to one grouping of polymers apply to all the other types of polymers is emphasized. The updating of analytical, physical, and spectral characterization techniques continues, including expanded coverage of the theory and results arising from atomic force microscopy and scanning probe microscopy. As before, the interplay between natural and synthetic polymers is emphasized. A number of miscellaneous topics have been drawn together in one chapter, which includes sections on conductive polymers, smart materials, proteomics, biopolymer, classification. Stereo geometry of polymers has been added.

This unified approach to publish my first book, covers the wide range of underlying principles: from molecular structure to material properties; from the relationships between part design, processing and performance to mechanical properties and mechanisms of polymer. The book stands out with many full-color graphs and figures that visually convey what polymers can--and cannot--accomplish in a world that relies on this class of materials. Two principles are key to the textbook's appeal: 1) Students learn that, independent of the origin of the polymer, synthetic or native, the same general laws apply, and 2) students should benefit from the book without an extensive knowledge of polymer chemistry. Taking the reader from the basics to an advanced level of understanding, the text meets the needs of a wide range of students in polymer chemistry, and is suitable for both BS (honor) - and master-level students. This book uses an interdisciplinary approach to provide insight into the most important uses of synthetic polymers: elastomers, fibers, and plastics. It introduces polymer science in a straight forward, rigorous, and practical way that cover the chemistry, physical chemistry and technology of polymers. Whenever possible, physical equations are not just presented but are derived step-by-step from first principles.

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Acknowledgments

I gratefully acknowledge the completion of this taking into consideration book could for not have been possible without participation and assistant of so many people whose names may not all the enumerated.

Their contributions are sincerely appreciated and gratefully acknowledged.

However, the group would like to express their deep appreciation and indebtedness particularly my honorable teachers and mentors. Writing a book is not too much easy as I thought. None of this would be possible without help and guide of my seniors and coworkers.

To all relative, friends and others who is one way or another shares their support, either morally, financially and physically…thanks a lot

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CONTENT

Chapter 1
Introduction to Polymers
1.0 Definition

Polymer, any of a class of natural or synthetic substances composed of very large molecules, called **macromolecules** that are multiples of simpler chemical units called **monomers**. A **polymer** is a large molecule made up of chains or rings of linked repeating subunits, which are called monomers. A polymer is made up of many (“poly” = many) repeated units (= “mer”) of a monomer (mono = one). Consequently, polymer molecules are composed of a large number of identical building blocks, labeled as macromolecules. The length of the polymeric chain is specified by the number of repeat units in the chain. This is called the 'degree of polymerization' (DP). Therefore, the molecular weight (MW) of a polymer is defined by:

MW = Degree of polymerization x molecular weight of repeat unit

All processes used in polymer production lead to chains of varying lengths and hence with different molecular weights. Accordingly, there is not a single molecular weight in a given polymer but a distribution of molecular weights that is more or less broad depending upon uniformity in length of chains that composed its macromolecules. Consequently, molecular weights of polymers are represented as average molecular weights. Optimum molecular weight for a polymer depends on the structure and its end use. It has to be said that polymers with very high molecular weights are difficult to process.

1.1 History

The word polymer comes from the Greek prefix poly-, which means "many," and the suffix -mer, which means "parts." The word was coined by Swedish chemist Jons Jacob Berzelius (1779–1848).Since most materials are polymeric and most of the recent advances in science and technology involve polymers, some have called this the polymer age. Actually, we have always lived in a polymer age. The ancient Greeks classified all matter as animal, vegetable, and mineral. Minerals were emphasized by the alchemists, but medieval artisans emphasized animal and vegetable matter. All are largely polymeric and are important to life as we know it. Most chemists, biochemists, and chemical engineers are now involved in some phase of

polymer science or technology. The word “polymer” is derived from the Greek poly and meros, meaning many and parts, respectively. Some scientists prefer to use the word macromolecule, or large molecule, instead of polymer. Others maintain that naturally occurring polymers, or biopolymers, and synthetic polymers should be studied in different courses. Others name these large molecules simply “giant molecules.” However, the same principles apply to all polymers. If one discounts the end uses, the differences between all polymers, including plastics, fibers, and elastomers, or rubbers, and natural and synthetic, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, and by the functional groups present, and most of all, by their size allowing an accumulation of these forces. In addition to being the basis of life itself, protein is used as a source of amino acids and energy. The ancients degraded or depolymerized the protein in meat by aging and cooking, and they denatured egg albumin by heating or adding vinegar to the eggs. Early humans learned how to process, dye, and weave the natural proteinaceous fibers of wool and silk and the carbohydrate fibers from flax and cotton. Early South American civilizations, such as the Aztecs, used natural rubber (Hevea brasiliensis) for making elastic articles and for waterproofing fabrics. There has always been an abundance of natural fibers and elastomers but few plastics. Of course, early humans employed a crude plastic art in tanning the protein in animal skins to make leather and through heating created somewhat “plastic” tortoise shells. They also used naturally occurring tars as caulking materials and extracted shellac from the excrement of small coccid insects (Coccus lacca).

The modern understanding of polymers as macromolecules was proposed by German organic chemist Hermann Staudinger .Polymers usually have high melting and boiling points. Because the molecules consist of many monomers, polymers tend to have high molecular masses. Polymers make up many of the materials in living organisms, including, for example, proteins, cellulose, and nucleic acids. Moreover, they constitute the basis of such minerals as diamond, quartz, and feldspar and such man-made materials as concrete, glass, paper, plastics, and rubbers.

The word polymer designates an unspecified number of monomer units. When the number of monomers is very large, the compound is sometimes called a high polymer. Polymers are not restricted to monomers of the same chemical composition or molecular weight and structure.

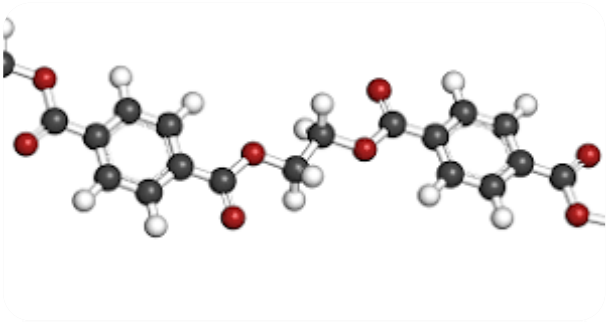
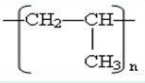
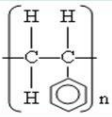
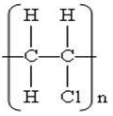
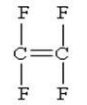
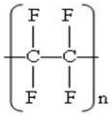


Figure 1.1Polymers structures

1.2 Nomenclature

The fact that synthetic polymer science grew in many venues before standard nomenclature groups were present to assist in standardization of the naming approach resulted in many popular polymers having several names including common names. Many polymer scientists have not yet accepted the guidelines given by the official naming committee of the International Union of Pure and Applied Chemistry, IUPAC, because the common names have gained such widespread acceptance. Although there is a wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

Table 1.1 List of polymers with their monomers and uses

Name of Polymer	Monomer	Repeating Structural Unit	Uses
polypropylene	$CH_2=CHCH_3$ propylene		Molded and extruded plastics, film, fibers for garments and carpeting
polystyrene	 styrene		Styrofoam, foam insulation, breakage-proof packaging, inexpensive molded articles.
Polyvinyl chloride (PVC)	 Vinyl chloride		Electrical insulation, film, rubber-like articles, synthetic leather, floor covering, raincoats, shower curtains, plastic plumbing pipes
Polyfluoroethylene (TeflonTM, PTFE)	 tetrafluoroethene		Heat and stick resistant coating that is resistant to high temperatures and inert to almost all solvents and other chemicals

1.3 **Common Names**

Little rhyme or reason is associated with many of the common names of polymers. Some names are derived from the place of origin of the material, such as Hevea brasilliensis— literally “rubber from Brazil”—for natural rubber. Other polymers were named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905. For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called nylon 66. Even here, there is no set standard as to how nylon 66 is to be written with alternatives including nylon 66 and nylon 66.

1.4 **Source-based Names**

Most common names are source based, that is, they are based on the common

name of the reactant monomer, preceded by the prefix “poly.” For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.

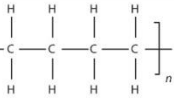
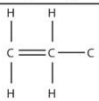
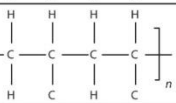
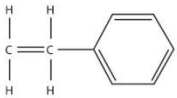
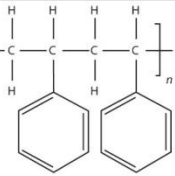
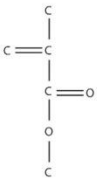
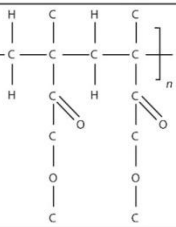
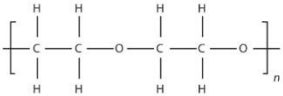
The majority of polymers based on the vinyl group (H2C=CHX) or the vinylidene group (H2C=CX2) as the repeat unit are known by their source-based names. Thus, polyethylene is the name of the polymer synthesized from the monomer ethylene; poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate. Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a source-based and a structure-based name. This polymer is well known by a number of trade names, such as Dacron, its common grouping, polyester, and by the abbreviation PET.

Although it is often suggested that parentheses be used in naming polymers of more than one word, for example, poly(vinyl chloride), but not for single word-polymers, such as polyethylene, some authors entirely omit the use ofparentheses for either case (polyvinyl chloride).

1.5 Linkage-based Names

Many polymer “families” are referred to by the name of the particular linkage that connects the polymers. The family name is “poly” followed by the linkage name. Thus, those polymers that contain an ester linkage are known as polyesters, those with an ether linkage are called polyethers.

Table 1.2 Polymer details with their monomers

Monomer	Monomer Name	Polymer	Polymer Name
	ethylene		poly(ethylene)
	propylene		poly(propylene)
	styrene		poly(styrene)
	methyl methacrylate		poly(methyl methacrylate)
	ethylene oxide		poly(ethylene oxide)

1.5 Trade Names

Tradenames are used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the tradename given for the phenol-formaldehyde condensation product developed by Baekeland. A sweater whose contents are described as containing Orlon contains polyacrylonitrile fibers that are “protected” under the Orlon trademark and produced or licensed to be produced by the holder of the Orlon trademark. Carina, Cobex, Dacovin, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all tradenames for poly(vinyl chloride) manufactured by different companies. Some polymers are better known by their tradename than their generic name. For instance,

polytetrafluoroethylene is better known as Teflon, the tradename held by Dupont.

1.6 Polymers in Life

Polymers are widely used advanced materials, which are found almost in every material used in our daily life. To date, the importance of polymers has been much more highlighted because of their applications in different dominions of sciences, technologies and industry – from basic uses to biopolymers and therapeutic polymers. They serve as the very basis of both plant and animal life as proteins, nucleic acids, and polysaccharides. In construction, they serve as the basic building blocks as concrete, insulation, and wooden and composite beams. At home, they are found as the materials for our rugs, curtains, coatings, wastepaper baskets, water pipes, window glass, ice cube trays, and pillows. In transportation, they are present in ever-increasing amounts in our aircraft, automobiles, ships, and trucks. In communication, they form critical components in our telephones, TVs, computers, CDs, newspaper, optical fibers, and cell phones. Plastics act as favorite materials for our toys such as toy soldiers, plastic models, toy cars, dolls, skip ropes, hula hoops, and corvettes. Our food is polymer intense as meats, vegetables, breads, and cookies. In history, polymers have been the vehicle for the Magna Carta, Torah, Bible, Koran, and our Declaration of Independence. Outside our homes, they are present in our flowers, trees, soil, spider webs, and beaches. In fact, it is improbable that a polymer is not involved in your present activity—reading a paper book, holding a plastic-intense writing device, sitting on a cloth-covered chair or bed, and if your eyes need corrective vision, glasses, and contact lenses of one variety or another. Polymers gain their importance because of their size. Some polymers are stronger on a weight basis than steel. Most are resistant to rapid degradation and rusting.

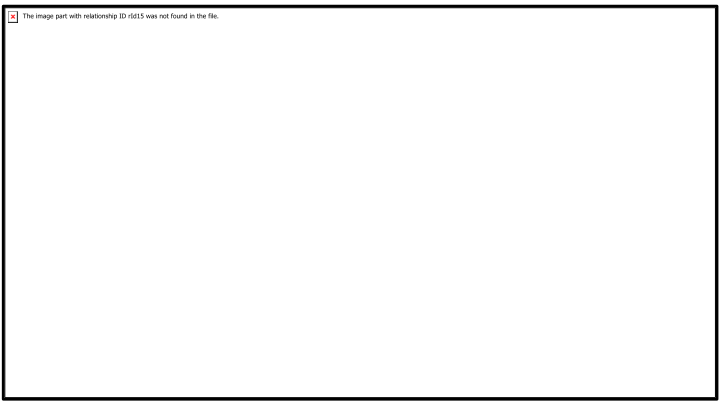


Figure 1.1 Uses of synthetic polymers

CHAPTER 2

Polymerization Process

2.0 Classification of Polymerization

I. Based on molecular forces

The most common way of classifying polymers is to separate them into groups based on molecular forces - thermoplastics, thermosets, and elastomers. The thermoplastics can be divided into two types - those that are crystalline and those that are amorphous**.**

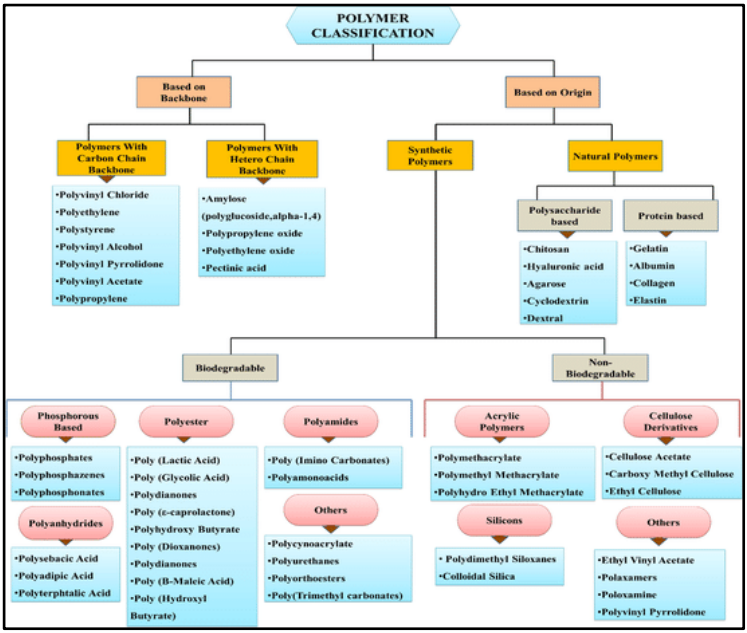


Figure 2.1 Classification of polymers

- **Thermoplastics**

Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled. Thermoplastic polymers can be repeatedly softened by heating and then solidified by cooling - a process similar to the repeated melting and cooling of metals. Most linear

and slightly branched polymers are thermoplastic. All the major thermoplastics are produced by chain polymerization. These are the liner or slightly changed to branched polymers that can be softened on continues heating and hardening on cooling. Their intermolecular force lying in between the fibers and elastomers. Polyvinyl, polystyrene etc. are examples of thermoplastic polymers. Thermoplastics have a wide range of applications because they can be formed and reformed in so many shapes. Some examples are food packaging, insulation, automobile bumpers, and credit cards.

- **Thermosets**

A thermosetting plastic, or thermoset, solidifies or "sets" irreversibly when heated; they cannot be reshaped by heating. Thermosets usually are three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. The cross-linking restricts the motion of the chains and leads to a rigid material. A simulated skeletal structure of a network polymer with a high cross-link density is shown below. Polymers comes under the category of heavily branched or cross-linked, which can mould on heating and can't regain the original shape. So these cannot be reused. Bakelite

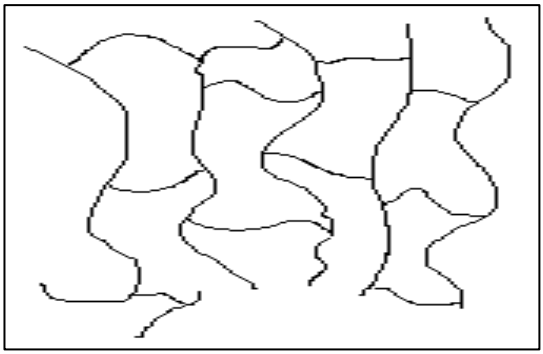


Figure 2.2 polymer Bakelite structure

Thermosets are strong and durable. They primarily are used in automobiles and construction. They also are used to make toys, varnishes, boat hulls, and glues.

- **Elastomers**

Elastomers are rubbery polymers that can be stretched easily to several times their unstretched length and which rapidly return to their original dimensions when the applied stress is released. Elastomers are cross-linked, but have a low cross-link density. The polymer chains still have some freedom to move, but are prevented from permanently moving relative to each other by the cross-links. To stretch, the polymer chains must not be part of a rigid solid - either a glass or a crystal. An elastomer must be above its glass transition temperature, Tg, and have a low degree of crystallinity. Rubber bands and other elastics are made of elastomers. Polymers that are rubber-like solids and having elastic properties. Here the polymer bonds are held together by weak intermolecular forces and that allows these polymers to stretch. The cross-links present in the polymer between the chains helps to retrace the original position after the removal of the applied force. Examples are Buna-s and Buna-s

Figure 2.3 Buna-s rubber

- **Fibers**

They are polymers having strong intermolecular forces like hydrogen bonding. Due to this strong force molecules are kept closer, that is they are closely packed. Because of this property, they are crystalline in nature. Polyamide and polyesters are examples.

II. Based on Source

They are again divided into three subcategories:

- **Natural polymers**

They are found naturally in plants and animals. Resins, starch and rubber are examples of this.

- **Semi-synthetic polymers**

This is a modified version of natural rubber. That means natural rubbers are treated with chemicals to make them semi-synthetic. Cellulose acetate and cellulose nitrate are the examples come under this subcategory.

- **Synthetic polymers**

Polymers which are completely man-made are called synthetic polymers. Polythene, Nylon 66, synthetic rubber are the widely used synthetic polymers

III. Based on the Structure of Polymers

There are three different types.

- **Linear polymers**

Consists of a long and straight-chain of monomers. PVC is a linear polymer

- **Branched polymers**

They are linear polymers containing some branches. Low-density Polythene is an example.

- **Network or cross-linked polymer**

Polymers having cross-linked bonds with each other is called cross-linked or network polymer. Generally, they are formed from bi-functional or tri-functional monomers. Bakelite and melamine are examples of this type of polymer.

IV. Based on Mode of Polymerization

They are divided into two subcategories:

- **Addition Polymers**

Polymers formed by the repeated addition of monomers by possessing the double or triple bonds. If the addition is of the same species they are called

homopolymers and if the addition is of different monomers they are called copolymers. Examples are polythene and Buna-s respectively.

- **Condensation polymers**

These polymers are formed by repeated condensation of tri or bifunctional monomeric units. In this reaction elimination of some small molecules like water and hydrogen chloride etc. will take place. Terylene and Nylon 6,6 are examples.

Table 2.1 Types of bio degradeable polymer

Base polymer	Source type	Advantages	Disadvantages	Potential applications	Suppliers
Starch	Renewable	Lower cost Fast biodegradation	Poor mechanical properties Hydrophillicity	Foams Films and bags Moulded items	Novamont (Materbi) Plantic Technologies Rodemberg (Solanyl) Biotec (Bioplast) National starch (ECO-FOAM)
Polyhydroxyalkalonates (PHA)	Renewable	Rapid biodegradation Water soluble	High costs	Moulded items	Biomer (Biomer) Metabolix P&G
Cellulose and cellulose acetates	Renewable	High strength Water stable	Difficult to process Very low biodegradability	Composites fibre-board	UCB (Naturyflex) Mazzuchelli (Bioceta)
Fatty acid (triglyceride oil based) polymers	Renewable	High strength	Brittle Low biodegradability	Composites Adhesives Compatibilizers	Dow U Delaware (Research)
Lignin polymers	Renewable	High strength	Brittle Low biodegradability	Composites Adhesives Compatibilizers	Borregard (Lignopol)
Protein polymers	Renewable	High strength	Non-reproducible properties	Films	
Polylactic acid (PLA)	Renewable and non-renewable	High strength	Brittle	Injection Moulding Fibres	Cargill-Dow (NatureWorks) Boehringer

While condensation polymers account for only a modest fraction of all-synthetic polymers, most natural polymers are of the condensation type. The first all-synthetic polymer, Bakelite, was produced by the stepwise polycondensation of phenol and formaldehyde. As shown by Carothers in the 1930s, the chemistry of condensation polymerizations is essentially the same as classic condensation reactions leading to the formation of monomeric esters, amides, and so on. The principal difference is that the reactions used for polymer formation are bifunctional instead of monofunctional.

2.1 Comparison between polymer type and kinetics of polymerization

There is a large, but not total, overlap between the terms condensation polymers and stepwise kinetics and the terms addition (or vinyl) polymers and chain kinetics. In this section, we will look at each of these four terms

and illustrate the similarities and differences between them. The terms "addition" and "condensation" polymers were first proposed by Carothers and are based on whether the repeat unit of the polymer contains the same atoms as the monomer. An addition polymer has the same atoms as the monomer in its repeat unit. Since many of the important addition polymers are formed from vinyl reactants, many addition polymers are also referred to as "vinyl polymers"

Condensation polymers generally contain fewer atoms in the polymer backbone than in the reactants because of the formation of by-products during the polymerization process and the backbone contains non-carbon atoms.

X–A–R–A–X + Y–B–R′–B–Y → –(A–R–A–B–R′–B–)– + XY

The term "stepwise kinetics," or "step-growth kinetics," refers to polymerizations in which the polymer's molecular weight increases in a slow, stepwise manner as reaction time increases.

Table 2.2 Comparison between stepwise and chain wise polymerization

Addition Polymerization	Condensation Polymerization
monomers must have either a double bond or triple bond	Monomer must have two similar or different functional groups
Produces no by-products	By-products such as ammonia, water and HCl are produced
Addition of monomers results in polymers	Condensation of monomers result in polymers
The molecular weight of the resultant polymers is a multiple of monomer's molecular weight	The molecular weight of the resultant polymers is not a multiple of monomer's molecular weight

2.2Process of polymerization

2.2.1-Step Growth Polymerization(condensation polymerization)

Condensation polymers account for only a small percentage of all synthetic polymers, most natural polymers are of the condensation type. The first all-synthetic Bakelite, was produced by the stepwise condensation of phenol and

formaldehyde, and many of the other synthetic polymers available before World War II were produced using stepwise polycondensations of appropriate reactants. As shown by Carothers in the 1930s, the chemistry of condensation polymerizations is essentially the same as classic condensation reactions leading to the formation of monomeric esters, amides, and so on. The principal difference is that the reactants used for polymer formation are bifunctional instead of monofunctional. The kinetics for stepwise polycondensation reactions and the kinetics for monofunctional aminations and esterification's, for example, are similar.

With most collisions of proper orientation being effective in lengthening the chain. This is in agreement with the slowness of stepwise processes compared with radical chain processes. The rate constant of individual polycondensation steps is essentially independent of chain length, being similar to that of the "small-molecule" condensation. This is responsible for the stepwise growth pattern of polycondensations, since addition of a unit does not greatly increase the reactivity of the growing end, whereas for radical and ionic vinyl polymerizations the active radical and ionic site is transmitted to the growing chain end, giving a reactive end group. In step-growth polymerization, the polymers are formed by the independent reaction between the functional groups of simple monomer units. In step-growth, each step may consist of a combination of two polymers having a different or same length to form a longer length molecule.The reaction is a lengthy process and the molecular mass is increased at a very slow rate. An example of step-growth polymerization is condensation polymerization where a water molecule is evolved in the reaction when the chain is lengthened.

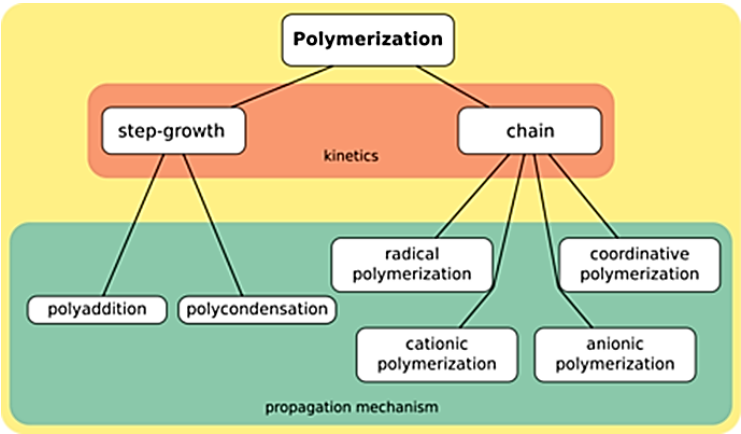


Figure 2.4 polymerization process

2.2.2 Mechanism of condensation polymerization

It is a form of a step-growth polymerization where smaller molecules or monomers react with each other to form larger structural units (usually polymers) while releasing by products such as water or methanol molecule.

2.2.3 Principles of condensation polymerization

A condensation polymerization is a form of step-growth polymerization in which monomers and/or oligomers react with each other to form larger structural units while releasing smaller molecules as a byproduct such as water or methanol. A well-known example of a condensation reaction is the *esterification* of carboxylic acids with alcohols. If both moieties are difunctional, the condensation product is a linear polymer, and if at least one of the moieties is tri- or tetra-functional, the resulting polymer is a crosslinked polymer (i.e. a three-dimensional network). Adding monomers with only one reactive group will terminate a growing chain, and consequently lower the (average) molecular weight. Thus, the average molecular weight and the crosslink density will depend on the functionality of each monomer involved in the condensation polymerization and on its concentration in the mixture.

A classic step-growth condensation is the reaction between a dibasic acid and a glycol, shown below:

$HOOC–(CH_2)_n–COOH + HO–(CH_2)_m–OH \rightarrow HOOC–(CH_2)_n–COO–(CH_2)_m–OH + H_2O$

The resulting polymer is called a polyester. The water is continuously removed from the reaction system because it is reactive with ester linkages to reverse the reaction. One of the most common thermoplastic polyesters is poly(ethylene terephthalate), often abbreviated PET or PETE:

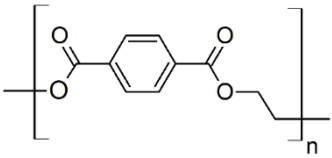
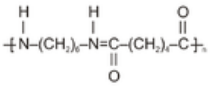
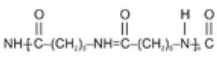
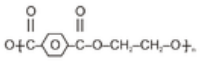
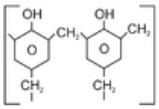
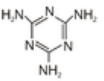
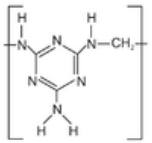


Figure 2.5polyester structure (ester linkage example)

In condensation polymerization, the formation of the polymer occurs when there is a loss of some small molecules as byproducts through the reaction where molecules are joined together. The byproducts formed may be water or hydrogen chloride. Polyamide and proteins are examples of condensation polymers. Some of the different types of condensation polymerization are given below

Table 2.3 Examples and uses of condensation polymers

POLYMER	MONOMER	STRUCTURE	USES
1. Nylon 6, 6	a) Adipic acid HOOC-$(CH_2)_4$-COOH b) Hexamethylene diamine NH_2-$(CH_2)_6$-NH_2		For making fabrics, for clothing, sports wear, combs, bristles of brushes.
2. Nylon 6	Caprolactum 		Mainly used for making cords for types, ropes and fabrics.
3. Polyester	a) Ethyleneglycol CH_2OH CH_2OH b) Terephthalic acid HOOC-C$_6$H$_4$-COOH		Crease resistant fibres, safety helmets.
4. Phenol - formaldehyde Resin (Bakelite)	a) Phenol  b) Formaldehyde HCHO		Manufacture of switches, plugs, cooker handles, Iron handles and parts.
5. Melamine-Melamine - formaldehyde Polymer	a) Melamine  b) Formaldehyde CH_2O or HCHO		In the manufacture of unbreakable tableware, trays clocks, knobs, litensil handles etc.

2.2.4 Examples of condensation polymers

- **Polyethene**

Polyethylene is a member of the important family of polyolefin resins. It is the most widely used plastic in the world.Ethylene molecules are essentially composed of two methylene units (CH_2) linked together by a double bond between the carbon atoms—a structure represented by the formula CH_2=CH_2. Under the influence of polymerization, the double bond can be broken and the resultant extra single bond used to link to a carbon atom in another ethylene molecule

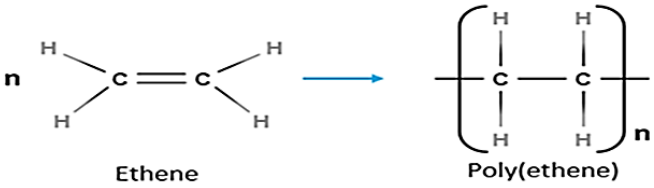


Figure 2.6 Poly ethylene structure

- **Polyamides**

They are synthetic fibres and are called as nylons. These polymers have an amide linkage between them. Condensation polymerization of di-amines with di-carboxylic acid and also of amino acids and their lactams will create a polyamide.

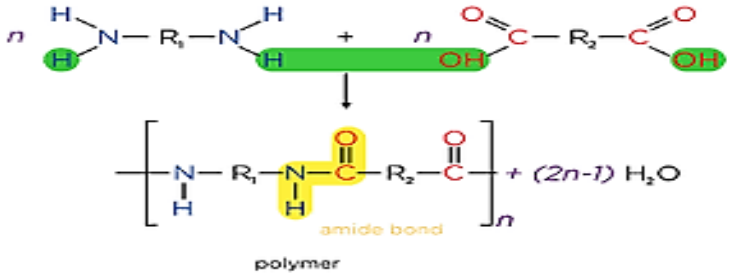


Figure 2.7Amide bond formation

- **Nylon 66**

This polymer is prepared under the condition of high pressure and temperature by the condensation polymerization of hexamethylenediamine with adipic acid.

Nylon 6: Prepared by heating of caprolactam with water under high temperature. It is used for tyre cords, fabrics and ropes.

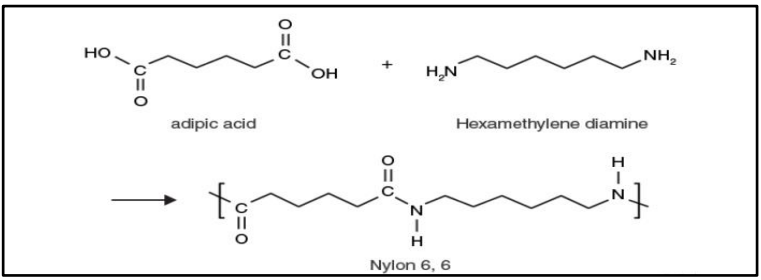


Figure 2.8 Structure of Nylon 6,6

- **Polyesters**

When dicarboxylic acids and diols undergo polycondensation, polyesters are formed. Prepared by heating a mixture of terephthalic acid and ethylene glycol at 460 k by using zinc acetate antimony trioxide as a catalyst. Dacron or terylene are the best-known examples for polyesters. And also they are used for glass reinforcing materials in safety helmets.

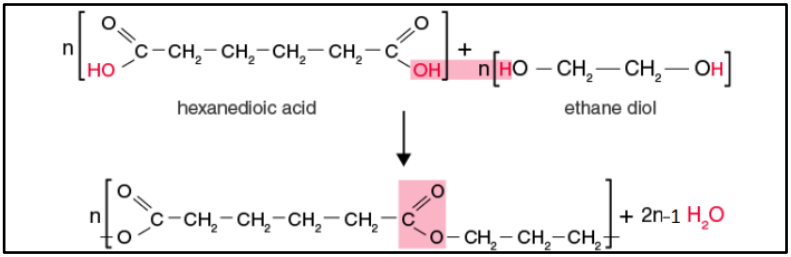


Figure 2.9Reaction of hexanedioic acid and ethane diol

- **Phenol – Formaldehyde Polymer**

Novolac on heating with formaldehyde undergoes crosslinking and forms an infusible sold mass named as Bakelite. They are used for combs, electric switches and phonograph records.

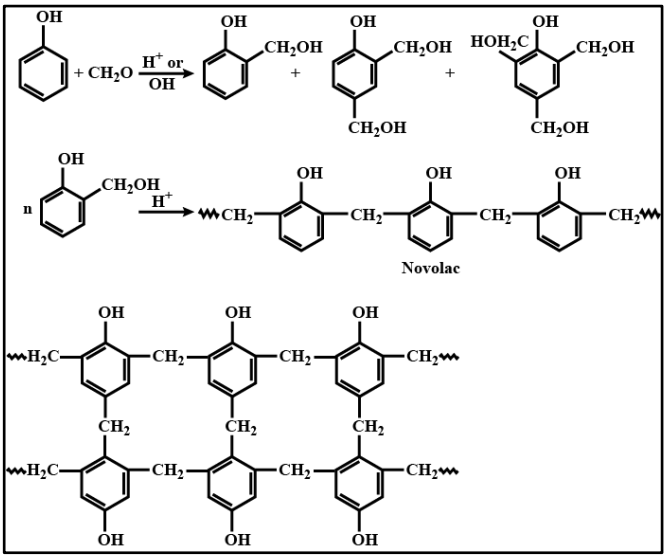


Figure 2.10 Structure of Bakelite

- **Melamine – Formaldehyde Polymer**

It is formed by the condensation polymerization of melamine and formaldehyde in certain conditions. They are used for the manufacture of unbreakable crockery.

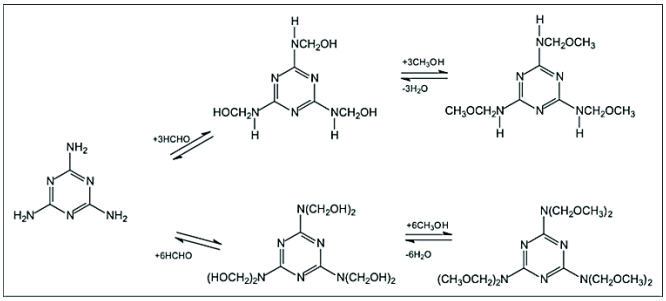


Figure 2.11 Melamine formaldehyde polymer

2.2.4 Stepwise kinetics

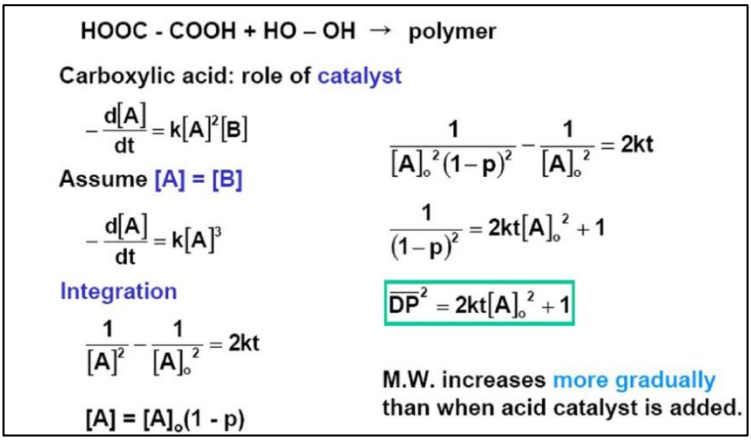
While more complicated situations can occur, we will consider only the kinetics of simple polyesterification. The kinetics of most other common

condensations follows an analogous pathway. For uncatalyzed reactions where the diacid and diol are present in equimolar amounts, one diacid is experimentally found to act as a catalyst. The experimental rate expression dependencies are described in the usual manner as follows:

Rate of polycondensation = d[A] /dt = k[A]^2 [D]

Where [A] represents the diacid concentration and [D] the diol concentration. Where [A] = [D], we can write as described below

Table 2.4 Steps of kinetics of condensation polymerization



2.2.5 Degree of polymerization

The number-average degree of polymerization DP_N can be expressed as

DP_N =number of original molecules /number of molecules at a specific time t

N0/ N orA0/ At

2.2.6Carothers equation

DP_N = A0 /At = A0 /A0(1- P) = 1 /1 -P

The relationship is called the Carothers equation because it was first found by Carothers while working with the synthesis of nylons (polyamides). For an essentially quantitative synthesis of polyamides where p is 0.9999, the DP

was found to be approximately equal to 10,000, the value calculated

DPN = 1 /1- p = 1/ 1 0.9999 = 1 0.0001 = 10,000

The DP of 10,000 calculated above for nylon-610 is more than adequate for a strong fiber. Actually, it would be difficult to force such a high molecular weight polymer through the small holes in the spinneret in the melt extrusion process used for fiber production. The many possible nylons are coded to show the number of carbon atoms in the amine and acid repeat units, respectively. The most widely used nylon fiber is nylon-66. The high value of p would be decreased and the value of DP also decreased accordingly if a competing cyclization reaction occurred.

Useful high molecular weight linear polymers are not obtained unless the value for the fractional conversion p is at least 0.990, i.e., a DP greater than 100. It is important to note that the rate constant k for reactions of monofunctional compounds is essentially the same as that for difunctional compounds, and hence these k values, which are essentially unchanged during the reaction, can be used for polycondensation reactions.

2.3 Chain Growth Polymerization (Step reaction polymerization)

Addition polymerization

In chain-growth polymerization, the molecules of the monomers are added together to form a large chain. The monomers adding maybe the same type or different. Generally, alkenes, alkadienes and their derivatives are used. In this mode, lengthening of chains occurs as a result of the formation of either free radicals or ionic species.chain-reaction polymerization is usually rapid, and the initiated species continue to propagate until termination. Thus, in the extreme case, one initiating species could be produced which would produce one high molecular weight polymer molecule, leaving all of the other monomer molecules unchanged. In any case, the concentration of the monomer, which is usually a derivative of ethylene, decreases continuously throughout the reaction. In contrast to stepwise polymerization, the first species produced is a high molecular weight polymer. A kinetic chain reaction usually consists of at least three steps, namely, initiation, propagation, and termination. The initiator may be an anion, a cation, a free radical, or a coordination catalyst. While coordination catalysts are the most important commercially, the ionic initiators will be discussed first in an

attempt to simplify the discussion of chain reaction polymerization.Cationic polymerizations require monomers that have electron-releasing groups such as an alkoxy, a phenyl, or a vinyl group. Anionic polymerization occurs with monomers containing electron-withdrawing groups such as carboxyl, nitrile, or halide. This selectivity is due to the strict requirements for stabilization of anionic and cationic species. Compared with free radical polymerizations, ionic polymerizations are not as well defined. Reactions can use heterogeneous initiators and they are usually quite sensitive to the presence of impurities. Thus, kinetic studies are difficult and the results sensitive to the particular reaction conditions. Furthermore, the rates of polymer formation are more rapid. Cationic and anionic polymerizations are similar. Both involve the formation and propagation of ionic species. While high-energy, low-stability ions would be expected to react with most double bonds, ionic species that are stable enough to propagate are difficult to form and are easily destroyed. The "energenic window" that allows the formation of such charged species is narrow. While polar solvents might be desirable to solvate the ions and hence help stabilize them, they often cannot be used. Some polar solvents, such as water and alcohols, react with and destroy most ionic initiators. Other polar solvents, such as ketones, prevent initiation because of the formation of stable complexes with the initiators. Ionic polymerizations are therefore conducted in low or moderately polar solvents, such as hexane and ethylene dichloride.Chain growth polymerization is also called addition polymerization and is based on free radical, cationic, anionic, and coordination reactions where a single initiating species causes the growth of a polymer chain.The kinetic chain reaction typically consists of three steps: initiation, propagation, and termination.

Unsaturated monomers (monomers with double or triple bonds) are usually used in addition polymerization. During the addition polymerization, all monomers are consumed and no byproducts are formed. Common examples of addition polymerization are polyethylene, polyvinyl chloride (PVC), acrylics, polystyrene, polytetrafluoroethylene, and polyoxymethylene (acetal).

It could be observed that the polymer on the right of the arrow sign is formed by addition of the repeating units on the left of the arrow. In this illustration, R_1 and R_2 represent functional groups or other group of atoms

Functional groups are specific groups of atoms that determine the characteristics and chemical reactivity of the polymer influencing the processability and application of plastic products. In the example of a bicycle chain, a necklace, or even a charm bracelet, let us consider that each link in the chain has a hanging pendant or a charm. These pendants could be different in structure and could be attached distinctly to the chain providing unique characteristics and appearance. Similarly, functional groups are attached to the polymer backbone providing unique features to the polymer and plastics application.

In addition polymerization the polymerization reaction occurs through three distinctive steps as

1.Chain initiation: In this step the polymerization reaction is initiated usually by means of an external initiator which creates a reactive site. The initiator could be a radical (free radical polymerization), cation (cationic polymerization, applicable to monomers with electron donating groups such as isobutylene), anion (anionic polymerization, applicable to monomers with electron withdrawing groups such as styrene, acrylonitrile, butadiene, acrylates, ethylene oxide, and lactones), and organometallic complex (coordination polymerization with Ziegler-Natta catalysts).

2.Chain propagation: In this step monomers or repeating units attach to the molecular chain, propagating the chain length.

3.Chain termination: In this step the chain growth is terminated through neutralization of the reactive center.

The simplest type of addition polymerization is free radical polymerization in which a polymer is formed by successive addition of free radical building block.

The initiators for free radical, anionic and cationic polymerizations are organic radicals, carbanions, and carboniums. Chain growth is exothermic with the polymerization is mainly controlled by steric and resonance factors of the monomer. Generally, the less resonance stabilization the more exothermic the reaction and the greater the steric factors, the less exothermic the polymerization. For high polymer to be formed, the activated monomer and growing polymer chain must be stable and growth rapid enough to allow

long chains to be formed. Stability of the activated monomer or growing end is primarily dependent on resonance, polar, and inductive effects. Thus, a vinyl monomer with electron donating groups is more apt to polymerize through a cationic route because the active carbonium site is stabilized inductively and through resonance. Styrene can be polymerized by either cationic, anionic, or free radical polymerization because all three active forms are resonance stabilized.

Table 2.5Major techniques used in production of important vinyl polymers

Free radical	Cationic	Anionic	Complex
(LDPE) polyproplene	polystyrene		polyacetal
Poly(vinyl chloride) polybutadiene	polyisobutylene		Thermoplastic olefin
Poly(vinyl acetate) polyisoprene	butyle rubber		isoprene
Polyacrylonitrile			styrene
Poly(methyl methacrylate)			
Polyacrylamide			
Polychloroprene			
Poly(vinyl pyridine)			
(SAN)			
Polytetrafluoroethylene			
Poly(vinylene fluoride)			
(ABS)			
Ethylene-methacrylic acid			
(SBR)			
Nitrile rubber (NBR)			

2.4-Cationic polymerization

Cationic polymerization is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes reactive. This reactive monomer goes on to react similarly with other monomers to form a polymer. The types of monomers necessary for cationic polymerization are limited to alkenes with electron-donating substituents and heterocycles. Styrene, isobutylene, and ethyl vinyl ether were polymerized over a century ago by the use of cationic initiators such as sulfuric acid, tin(IV) chloride, boron trifluoride, and iodine. The first species produced in these reactions are carbocations, and these were unknown as such prior to World War II. It is now known that pure Lewis acids, such as boron trifluoride or aluminum chloride, are not effective as initiators. A trace of a protoncontaining Lewis base, such as water, is also required. The Lewis base coordinates with the electrophilic Lewis acid, and the proton is the actual initiator. Since cations cannot exist alone, they are always accompanied by a counterion, also called a gegenion.

2.4.1 Monomers

Monomer scope for cationic polymerization is limited to two main types: alkene and heterocyclic monomers. Cationic polymerization of both types of monomers occurs only if the overall reaction is thermally favorable. In the case of alkenes, this is due to isomerization of the monomer double bond; for heterocycles, this is due to release of monomer ring strain and, in some cases, isomerization of repeating units. Monomers for cationic polymerization are nucleophilic and form a stable cation upon polymerization.

2.4.2 Alkene

Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electron-donating groups make the olefin nucleophilic enough to attack electrophilic initiators or growing polymer chains. The electron-donating groups attached to the monomer must be able to stabilize the resulting cationic charge for further polymerization. Some reactive olefin monomers are shown below in order of decreasing reactivity, with heteroatom groups being more reactive than alkyl or aryl groups. Note, however, that the reactivity of the carbenium ion formed is the

opposite of the monomer reactivity.

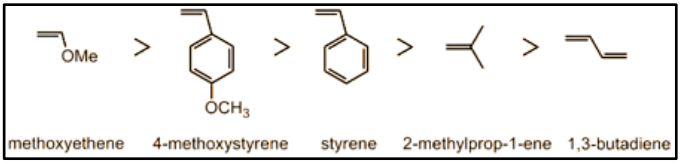


Figure 2.12 Decreasing reactivity of alkene monomers

2.4.3 Heterocyclic monomers

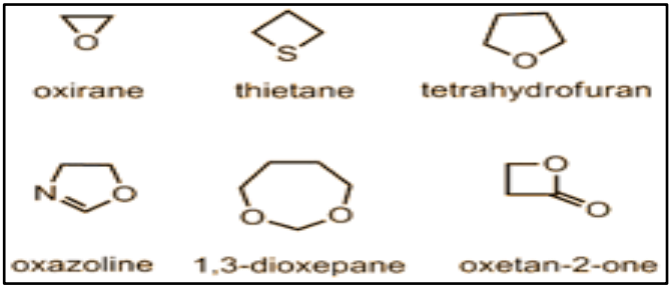


Figure 2.13 Examples of heterocyclic monomers

Heterocyclic monomers that are cationic ally polymerized are lactones, lactams and cyclic amines. Upon addition of an initiator, cyclic monomers go on to form linear polymers. The reactivity of heterocyclic monomers depends on their ring strain. Monomers with large ring strain, such as oxirane, are more reactive than 1,3-dioxepane which has considerably less ring strain. Rings that are six-membered and larger are less likely to polymerize due to lower ring strain.

2.4.4 Mechanism

- **Initiation**

Initiation is the first step in cationic polymerization. During initiation, a carbenium ion is generated from which the polymer chain is made. The counterion should be non-nucleophilic, otherwise the reaction is terminated instantaneously. There are a variety of initiators available for cationic polymerization, and some of them require a coinitiator to generate the needed cationic species.

- **Protic acids**

Strong protic acids can be used to form a cationic initiating species. High concentrations of the acid are needed in order to produce sufficient quantities of the cationic species. The counterion (A^-) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated alkene. Common acids used are phosphoric, sulfuric, fluoro-, and triflic acids. Only low molecular weight polymers are formed with these initiators.

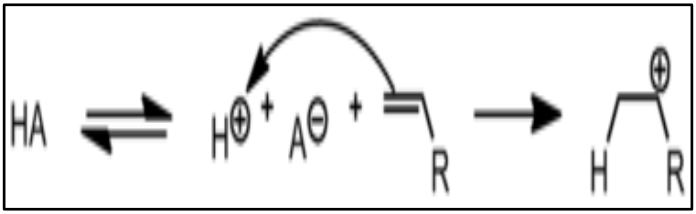


Figure 2.14Initiation by protic acid

- **Lewis acids/Friedel-Crafts catalysts**

Lewis acids are the most common compounds used for initiation of cationic polymerization. The more popular Lewis acids are $SnCl_4$, $AlCl_3$, BF_3, and $TiCl_4$. Although these Lewis acids alone are able to induce polymerization, the reaction occurs much faster with a suitable cation source. The cation source can be water, alcohols, or even a carbocation donor such as an ester or an anhydride. In these systems the Lewis acid is referred to as a coinitiator while the cation source is the initiator. Upon reaction of the initiator with the coinitiator, an intermediate complex is formed which then goes on to react with the monomer unit. The counterion produced by the initiator-coinitiator complex is less nucleophilic than that of the Bronsted acid A^- counterion. Halogens, such as chlorine and bromine, can also initiate cationic polymerization upon addition of the more active Lewis acids.

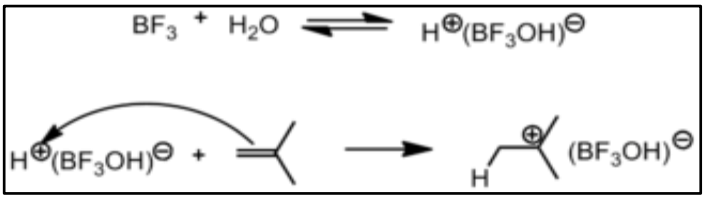


Figure 2.15 Initiation with boron tri fluoride (co initiator) and water (initiator)

- **Carbenium ion salts**

Stable carbenium ions are used to initiate chain growth of only the most reactive alkenes and are known to give well defined structures. These initiators are most often used in kinetic studies due to the ease of measuring the disappearance of the carbenium ion absorbance. Common carbenium ions are trityl and tropylium cations.

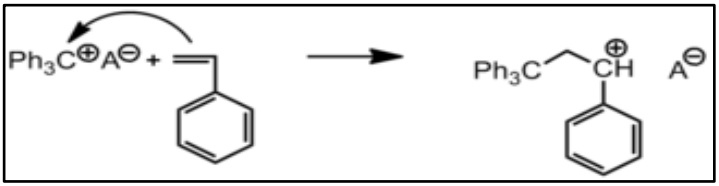


Figure 2.16Initiation with trityl carbenium ion

- **Ionizing radiation**

Ionizing radiation can form a radical-cation pair that can then react with a monomer to start cationic polymerization. Control of the radical-cation pairs is difficult and often depends on the monomer and reaction conditions. Formation of radical and anionic species is often observed.

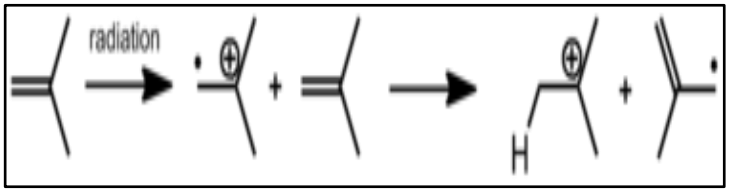


Figure 2.17Initiation using ionizing radiation

- **Propagation**

Propagation proceeds by addition of monomer to the active species, i.e. the carbenium ion. The monomer is added to the growing chain in a head-to-tail fashion; in the process, the cationic end group is regenerated to allow for the next round of monomer addition.General propagation pathway

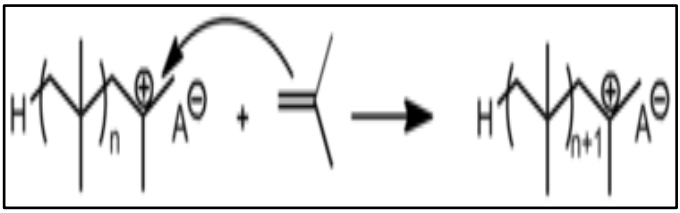


Figure 2.18 propagation by active site species

- **Effect of temperature**

The temperature of the reaction has an effect on the rate of propagation. The overall activation energy for the polymerization is based upon the activation energies for the initiation , propagation, and termination steps.Chain length is also affected by temperature. Low reaction temperatures, in the range of 170–190 K, are preferred for producing longer chains.This comes as a result of the activation energy for termination and other side reactions being larger than the activation energy for propagation.As the temperature is raised, the energy barrier for the termination reaction is overcome, causing shorter chains to be produced during the polymerization process.

The more polar the solvent used in the reaction, the better the solvation and separation of the ions. Since free ions are more reactive than ion pairs, the rate of propagation is faster in more polar solvents.The size of the counterion is also a factor. A smaller counterion, with a higher charge density, will have stronger electrostatic interactions with the carbenium ion than will a larger counterion which has a lower charge density.[1] Further, a smaller counterion is more easily solvated by a polar solvent than a counterion with low charge density. The result is increased propagation rate with increased solvating capability of the solvent.

- **Termination**

Termination generally occurs by unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex.

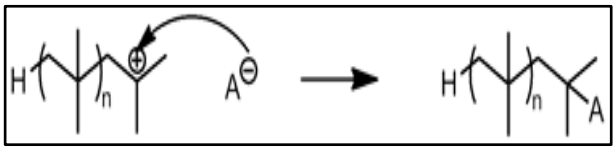


Figure 2.19 Termination by combination with an anionic fragment from the counterion

- **Chain transfer**

Chain transfer can take place in two ways. One method of chain transfer is hydrogen abstraction from the active chain end to the counterion.In this process, the growing chain is terminated, but the initiator-coinitiator complex is regenerated to initiate more chains.

Figure 2.20 Chain transfer by hydrogen abstraction to the counter ion

The second method involves hydrogen abstraction from the active chain end to the monomer. This terminates the growing chain and also forms a new active carbenium ion-counter ion complex which can continue to propagate, thus keeping the kinetic chain intact.

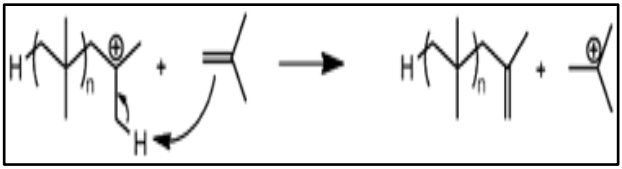


Figure 2.21 Chain transfer by hydrogen abstraction to the monomer

- **Cationic ring-opening polymerization**

Cationic ring-opening polymerization follows the same mechanistic steps of initiation, propagation, and termination. However, in this polymerization reaction, the monomer units are cyclic in comparison to the resulting polymer chains which are linear. The linear polymers produced can have low ceiling temperatures, hence end-capping of the polymer chains is often necessary to prevent depolymerization.

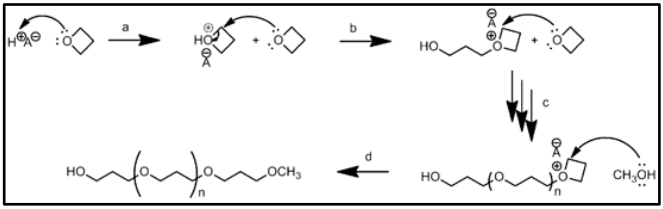


Figure 2.22 Cationic ring-opening polymerization of oxetane involving (a and b) initiation, (c) propagation, and (d) termination with methanol

2.4.5 Kinetics

The rate of propagation and the degree of polymerization can be determined from an analysis of the kinetics of the polymerization. The reaction equations for initiation, propagation, termination, and chain transfer can be written in a general form:

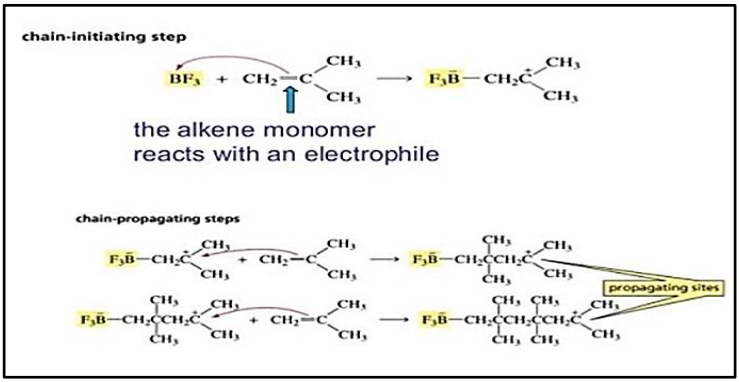


Figure 2.23 Assuming steady-state conditions, i.e. the rate of initiation = rate of termination

This equation for $[M^+]$ can then be used in the equation for the rate of

propagation

From this equation, it is seen that propagation rate increases with increasing monomer and initiator concentration.The degree of polymerizationcan be determined from the rates of propagation and termination

2.4.6 Living cationic polymerization

In 1984, Higashimura reported the first living cationic polymerization for alkyl vinyl ethers. This type of polymerization has allowed for the control of well-defined polymers. A key characteristic of living cationic polymerization is that termination is essentially eliminated, thus the cationic chain growth continues until all monomer is consumed.

- **Commercial applications**
  PIB

The largest commercial application of cationic polymerization is in the production of polyisobutylene (PIB) products which include polybutene and butyl rubber. These polymers have a variety of applications from adhesives and sealants to protective gloves and pharmaceutical stoppers. The reaction conditions for the synthesis of each type of isobutylene product vary depending on the desired molecular weight and what typeof monomer is used. The conditions most commonly used to form low molecular weight. Polyisobutylene are initiation with $AlCl_3$, BF_3, or $TiCl_4$ at a temperature range. These low molecular weight polyisobutylene polymers are used for caulking and as sealants. These polymers are used to make rubber products and are additives for certain thermoplasts. Another characteristic of high molecular weight PIB is its low toxicity which allows it to be used as a base for chewing gum.

- **Butyl rubber gloves**

Butyl rubber, in contrast to PIB, is a copolymer in which the monomers isobutylene and isoprene are polymerized in a process similar to high molecular weight PIBs. Butyl rubber polymerization is carried out as a continuous process with $AlCl_3$ as the initiator. Its low gas permeability and good resistance to chemicals and aging make it useful for a variety of applications such as protective gloves, electrical cable insulation, and even basketballs.

- **Polybutene**

polybutene is another copolymer, containing roughly 80% isobutylene and 20% other butenes (usually 1-butene). The production of these low molecular weight polymers (300–2500 Da) is done within a large range of temperatures (−45 to 80 °C) with $AlCl_3$ or BF_3. Depending on the molecular weight of these polymers, they can be used as adhesives, sealants, plasticizers, additives for transmission fluids, and a variety of other applications. These materials are low-cost and are made by a variety of different companies including BP Chemicals, Esso, and BASF.

- **Copolymers of polyterpenes**

polymers formed by cationic polymerization are homopolymers and copolymers of polyterpenes, such as pinenes (plant-derived products), that are used as tackyfiers. In the field of heterocycles, 1,3,5-trioxane is copolymerized with small amounts of ethylene oxide to form the highly crystalline polyoxymethylene plastic. Also, the homopolymerization of alkyl vinyl ethers is achieved only by cationic polymerization.

2.5Anionic Polymerization

Anionic addition polymerization is a form of chain-growth polymerization or addition polymerization that involves the polymerization of monomers initiated with anions. The type of reaction has many manifestations, but traditionally vinyl monomers are used. Often anionic polymerization involves living polymerizations.

2.5.1 History

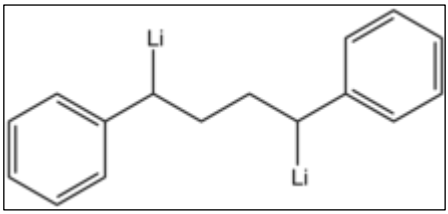


Figure 2.24 two ended living polymer

Product of the reductive coupling of styrene with lithium, 1,4-dilithio-1,4-diphenylbutane.As early as 1936, Karl Ziegler proposed that anionic polymerization of styrene and butadiene by consecutive addition of

monomer to an alkyl lithium initiator occurred without chain transfer or termination. Twenty years later, living polymerization was demonstrated by Michael Szwarc and coworkers. In one of the breakthrough events in the field of polymer science, Szwarc elucidated that electron transfer occurred from radical anion sodium naphthalene to styrene. The results in the formation of an organo sodium species, which rapidly added styrene to form a "two – ended living polymer." An important aspect of his work, Szwarc employed the aprotic solvent tetrahydrofuran.

2.5.2 Monomer characteristics

Two broad classes of monomers are susceptible to anionic polymerization.

Vinyl monomers have the formula CH_2=CHR, the most important are styrene (R= C_6H_5), butadiene (CH=CH_2), and isoprene (R = C(Me) =CH_2). A second major class of monomers are acrylate esters, such as acrylonitrile, methacrylate, cyanoacrylate, and acrolein. Other vinyl monomers include vinyl pyridine, vinyl sulfone, vinyl sulfoxide, vinyl silanes.

Figure 2.25 vinyl pyridine and butadiene structure

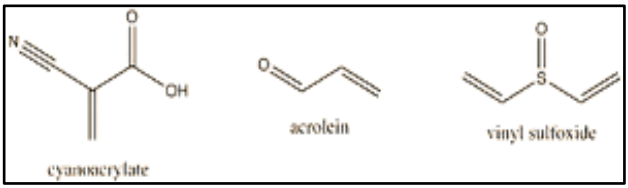


Figure 2.26 Anionic polymer examples

2.5.3 Examples of polar monomers

2.5.4 Examples of vinyl monomers

- **Cyclic monomers**

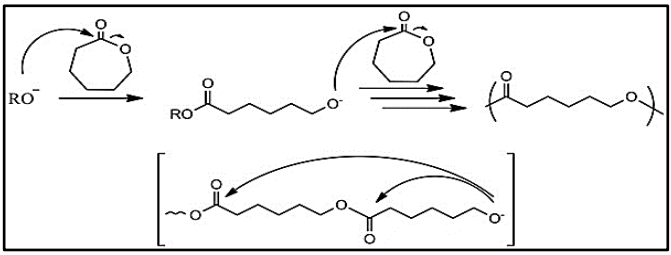


Figure 2.27 Anionic ring-opening polymerization of ε-caprolactone, initiated by alkoxide

- **Hexamethylcyclotrisiloxane**

This is a cyclic monomer that is susceptible to anionic polymerization to siloxane polymers. Many cyclic compounds are susceptible to ring-opening polymerization. Epoxides, cyclic trisiloxanes, some lactones, lactides, cyclic carbonates, and amino acid N-carboxyanhydrides.

In order for polymerization to occur with vinyl monomers, the substituents on the double bond must be able to stabilize a negative charge. Stabilization occurs through delocalization of the negative charge. Because of the nature of the carbanion propagating center, substituents that react with bases or nucleophiles either must not be present or be protected.

2.5.5 Initiation

Initiators are selected based on the reactivity of the monomers. Highly electrophilic monomers such as cyanoacrylates require only weakly nucleophilic initiators, such as amines, phosphines, or even halides. Less reactive monomers such as styrene require powerful nucleophiles such as butyl lithium. Reactions of intermediate strength are used for monomers of intermediate reactivity such as vinyl pyridine.

The solvents used in anionic addition polymerizations are determined by the reactivity of both the initiator and nature of the propagating chain end. Anionic species with low reactivity, such as heterocyclic monomers, can use

a wide range of solvents .For example, the initiation and polymerization of styrene with potassium amide proceeds as follows:

$KNH_2 \Leftrightarrow K^+ + NH_2^-$

$$NH_2^- + M \rightarrow NH_2M^-$$

$$NH_2M_n^- + M \rightarrow NH_2M_{n+1}^-$$

$$NH_2M_n\text{-} + NH_3 \rightarrow NH_2M_nH + NH_2^-$$

The "Gegen" ion, K^+, has been omitted from the scheme above, because it is dissolved ("free") in a media of comparatively high dielectric constant.

2.5.6 Initiation by electron transfer

Initiation of styrene polymerization with sodium naphthalene proceeds by electron transfer from the naphthalene radical anion to the monomer. The resulting radical dimerizes to give a disodium compound, which then functions as the initiator. Polar solvents are necessary for this type of initiation both for stability of the anion-radical and to solvate the cation species formed. The anion-radical can then transfer an electron to the monomer. Initiation can also involve the transfer of an electron from the alkali metal to the monomer to form an anion-radical. Initiation occurs on the surface of the metal, with the reversible transfer of an electron to the adsorbed monomer.

2.5.7 Initiation by strong anions

Nucleophilic initiators include covalent or ionic metal amides, alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds (alkyl lithium compounds and Grignard reagents). The initiation process involves the addition of a neutral (B :) or negative ($:B^-$) nucleophile to the monomer. The most commercially useful of these initiators has been the alkyl lithium initiators. They are primarily used for the polymerization of styrene's and dienes.

Monomers activated by strong electronegative groups may be initiated even by weak anionic or neutral nucleophiles (i.e. amines, phosphines). Most prominent example is the curing of cyanoacrylate, which constitutes the basis for superglue. Here, only traces of basic impurities are sufficient to induce an anionic addition polymerization or zwitterion addition polymerization,

respectively.

2.5.8 Propagation

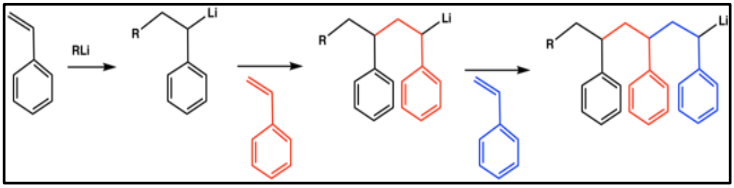


Figure 2.28 Anionic addition polymerization

2.5.9 Organo lithium-initiated polymerization of styrene

Propagation in anionic addition polymerization results in the complete consumption of monomer. This stage is often fast, even at low temperatures.

2.5.10 Living anionic polymerization

Living anionic polymerization is a living polymerization technique involving an anionic propagating species. One of the remarkable features of living anionic polymerization is that the mechanism involves no formal termination step. In the absence of impurities, the carbanion would still be active and capable of adding another monomer. The chains will remain active indefinitely unless there is inadvertent or deliberate termination or chain transfer. This gave rise to two important consequences:

1. The number average molecular weight, M_n, of the polymer resulting from such a system could be calculated by the amount of consumed monomer and the initiator used for the polymerization, as the degree of polymerization would be the ratio of the moles of the monomer consumed to the moles of the initiator added.
2. All the chains are initiated at roughly the same time. The final result is that the polymer synthesis can be done in a much more controlled manner in terms of the molecular weight and molecular weight distribution (Poisson distribution).

2.5.11 kinetics

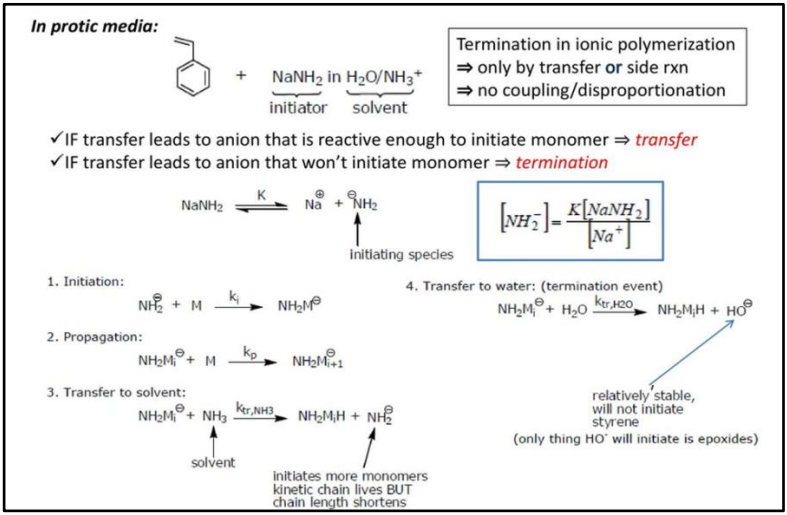


Figure 2.29 kinetic steps of anionic polymerization

2.5.12 Consequences of living polymerization

- **Block copolymers**

Synthesis of block copolymers is one of the most important applications of living polymerization as it offers the best control over structure. The nucleophilicity of the resulting carbanion will govern the order of monomer addition, as the monomer forming the less nucleophilic propagating species may inhibit the addition of the more nucleophilic monomer onto the chain. An extension of the above concept is the formation of triblock copolymers where each step of such a sequence aims to prepare a block segment with predictable, known molecular weight and narrow molecular weight distribution without chain termination or transfer.Sequential monomer addition is the dominant method, also this simple approach suffers some limitations. Moreover, this strategy, enables synthesis of linear block copolymer structures that are not accessible via sequential monomer addition. For common A-b-B structures, sequential block copolymerization gives access to well defined block copolymers only

if the crossover reaction rate constant is significantly higher than the rate constant of the homopolymerization of the second monomer, i.e., $k_{AA} >> k_{BB}$.

- **End-group functionalization/termination**

One of the remarkable features of living anionic polymerization is the absence of a formal termination step. In the absence of impurities, the carbanion would remain active, awaiting the addition of new monomer. Termination can occur through unintentional quenching by impurities, often present in trace amounts. Typical impurities include oxygen, carbon dioxide, or water. Termination intentionally allows the introduction of tailored end groups.

Living anionic polymerization allow the incorporation of functional end-groups, usually added to quench polymerization. End-groups that have been used in the functionalization of α-halo alkanes include hydroxide, -NH_2, -OH, -SH, -CHO,-$COCH_3$, -COOH, and epoxides.

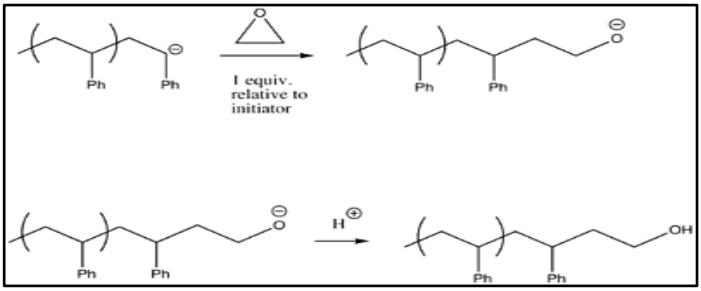


Figure 2.30Addition of hydroxide group through an epoxide.

An alternative approach for functionalizing end-groups is to begin polymerization with a functional anionic initiator. In this case, the functional groups are protected since the ends of the anionic polymer chain is a strong base. This method leads to polymers with controlled molecular weights and narrow molecular weight distributions.

It is an addition polymerization that involves the polymerization of monomers that are initiated with anions. This polymerization will be initiated by the transfer of electrons from the ion to the monomer.

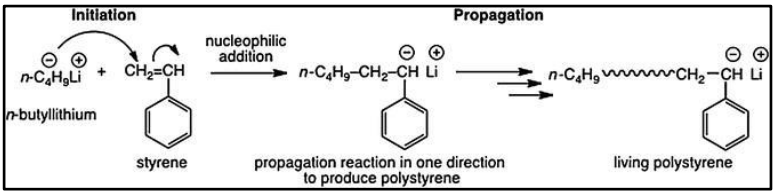


Figure 2.31Addition anionic polymerization

2.6 Free radical polymerization

In polymer chemistryFree-radical polymerization (FRP) is a method of polymerization, by which a polymer forms by the successive addition of free-radical building blocks. Free radicals can be formed by a number of different mechanisms, usually involving separate initiator molecules. Following its generation, the initiating free radical adds (nonradical) monomer units, thereby growing the polymer chain.

Free-radical polymerization is a key synthesis route for obtaining a wide variety of different polymers and materials composites. The relatively non-specific nature of free-radical chemical interactions makes this one of the most versatile forms of polymerization available and allows facile reactions of polymeric free-radical chain ends and other chemicals or substrates. Free-radical polymerization is a type of chain-growth polymerization, along with anionic, cationic and coordination polymerization

2.6.1 Initiation

Initiation is the first step of the polymerization process. During initiation, an active center is created from which a polymer chain is generated. Not all monomers are susceptible to all types of initiators. Radical initiation works best on the carbon–carbon double bond of vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones.Initiation has two steps. In the first step, one or two radicals are created from the initiating molecules. In the second step, radicals are transferred from the initiator molecules to the monomer units present. Several choices are available for these initiators.

2.6.2 Types of initiation and the initiator

- **Thermal decomposition**

The initiator is heated until a bond is homolytically cleaved, producing two radicals. This method is used most often with organic peroxides or azo

compounds.

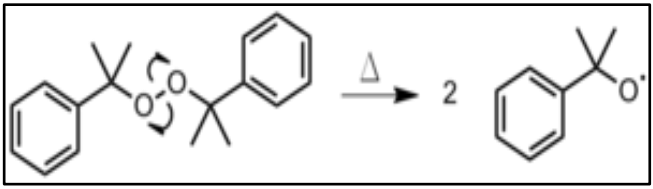


Figure 2.32 Thermal decomposition of dicumyl peroxide

- **Photolysis**

Radiation cleaves a bond homolytically, producing two radicals. This method is used most often with metal iodides, metal alkyls, and azo compounds.

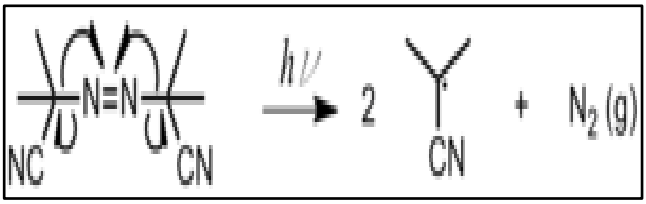


Figure 2.33Photolysis of azoisobutylnitrile (AIBN)

Photoinitiation can also occur by bi-molecular H abstraction when the radical is in its lowest triplet excited state.An acceptable photoinitiator system should fulfill the following requirements

1. High absorptivity in the 300–400 nm range.
2. Efficient generation of radicals capable of attacking the alkene double bond of vinyl monomers.
3. Adequate solubility in the binder system (prepolymer + monomer).
4. The photoinitiator and any byproducts resulting from its use should be non-toxic.

- **Redox reactions**

Reduction of hydrogen peroxide or an alkyl hydrogen peroxide by iron. Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, and Cu^{+} can be employed in place of ferrous ion in many instances.

- **Persulfates**

The dissociation of a persulfate in the aqueous phase. This method is useful in emulsion polymerizations, in which the radical diffuses into a hydrophobic monomer-containing droplet.[3]

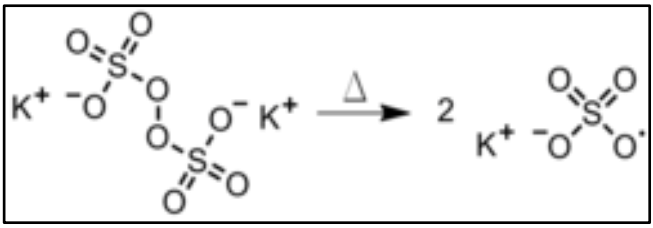


Figure 2.34 Thermal degradation of a persulfate

- **Ionizing radiation**

α-, β-, γ-, or x-rays cause ejection of an electron from the initiating species, followed by dissociation and electron capture to produce a radical.

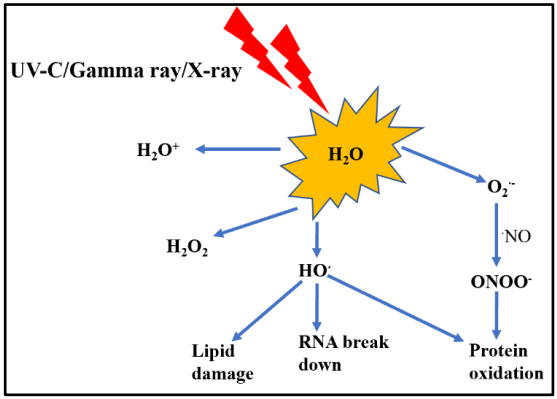


Figure 2.35 Ionizing radiation generate free radicals

The three steps involved in ionizing radiation: ejection, dissociation, and electron-capture

- **Electrochemical**

Electrolysis of a solution containing both monomer and electrolyte. A monomer molecule will receive an electron at the cathode to become a radical anion, and a monomer molecule will give up an electron at

the anode to form a radical cation . The radical ions then initiate free radical (and/or ionic) polymerization. This type of initiation is especially useful for coating metal surfaces with polymer films.

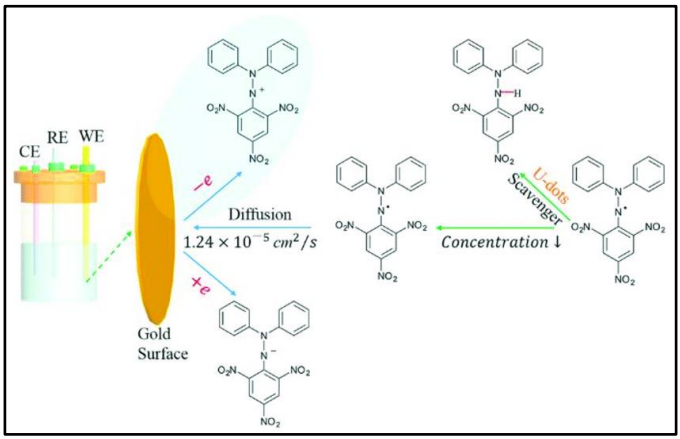


Figure 2.36 Electrochemical mechanism CNDs scavenging free radical.

Formation of radical anion at the cathode; (bottom) formation of radical cation at the anode

- **Plasma**

A gaseous monomer is placed in an electric discharge at low pressures under conditions where a plasma (ionized gaseous molecules) is created. In some cases, the system is heated and/or placed in a radiofrequency field to assist in creating the plasma.

- **Sonication**

High-intensity ultrasound at frequencies beyond the range of human hearing (16 kHz) can be applied to a monomer. Initiation results from the effects of cavitation (the formation and collapse of cavities in the liquid). The collapse of the cavities generates very high local temperatures and pressures. This results in the formation of excited electronic states, which in turn lead to bond breakage and radical formation.

2.6.3 Ternary initiators

A ternary initiator is the combination of several types of initiators into one

initiating system. The types of initiators are chosen based on the properties they are known to induce in the polymers they produce. For example, poly(methyl methacrylate) has been synthesized by the ternary system.

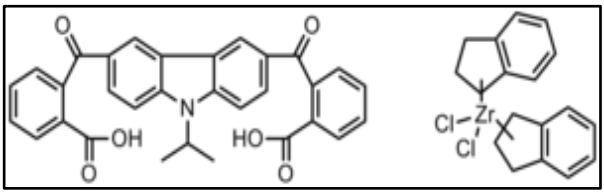


Figure 2.37Benzoyl peroxide-3,6-bis(*o*-carboxybenzoyl)-*N*-isopropylcarbazole-di-η^5-indenylzicronium dichloride

The combination of all of these components—a metallocene, an initiator, and a heteroaromatic diketo carboxylic acid—yields a ternary initiating system that was shown to accelerate the polymerization and produce polymers with enhanced heat resistance and regular microstructure.

- **Initiator efficiency**

Due to side reactions and inefficient synthesis of the radical species, chain initiation is not 100%.The efficiency factor *f* is used to describe the effective radical concentration. The maximal value of *f* is 1, but typical values range from 0.3 to 0.8. The following is a list of reactions that decrease the efficiency of the initiator.

- **Primary recombination**

Two radicals recombine before initiating a chain. This occurs within the solvent cage, meaning that no solvent has yet come between the new radicals.

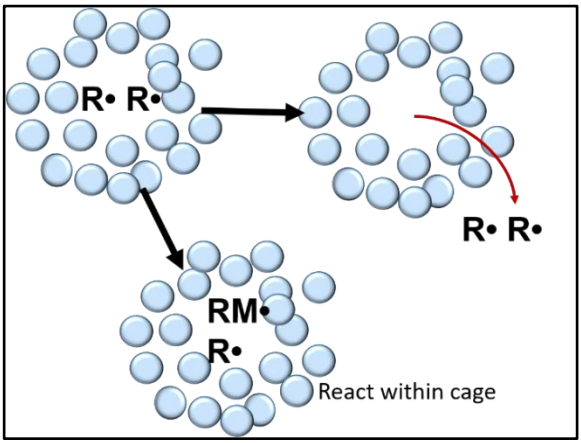


Figure 2.38 Cage effect within solvent

Other recombination pathways

Two radical initiators recombine before initiating a chain, but not in the solvent cage .

Figure 2.39Recombination of phenyl radicals from the initiation of BPO outside the solvent cage

- **Side reactions**

One radical is produced instead of the three radicals that could be produced

2.6.4 Propagation

During polymerization, a polymer spends most of its time in increasing its chain length, or propagating. After the radical initiator is formed, it attacks a monomer . In an ethene monomer, one electron pair is held securely between the two carbons in a sigma bond. The other is more loosely held in a pi bond. The free radical uses one electron from the pi bond to form a more stable bond with the carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical. This begins the polymer chain.

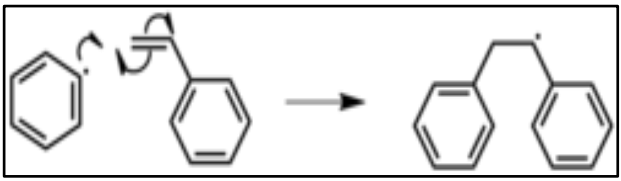


Figure 2.40Phenyl initiator from benzoyl peroxide (BPO) attacks a styrene

Benzoyl peroxide (BPO) attacks a styrene molecule to start the polymer chain.Once a chain has been initiated, the chain propagates until there are no more monomers (living polymerization) or until termination occurs. There may be anywhere from a few to thousands of propagation steps depending on several factors such as radical and chain reactivity, the solvent, and temperature. The mechanism of chain propagation is as follows

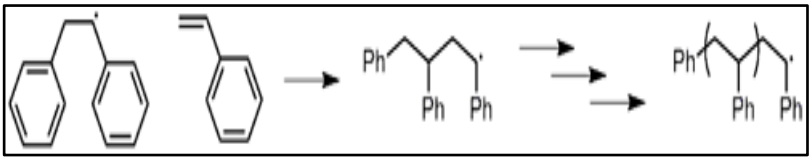


Figure 2.41Propagation of polystyrene with a phenyl radical initiator.

2.6.5 Termination

Chain termination is inevitable in radical polymerization due to the high reactivity of radicals. Termination can occur by several different mechanisms. If longer chains are desired, the initiator concentration should be kept low; otherwise, many shorter chains will result.Combination of two active chain ends: one or both of the following processes may occur.

1-Combination of two active chain ends

Two chain ends simply couple together to form one long chain . One can determine if this mode of termination is occurring by monitoring the molecular weight of the propagating species: combination will result in doubling of molecular weight. Also, combination will result in a polymer that is C_2 symmetric about the point of the combination.

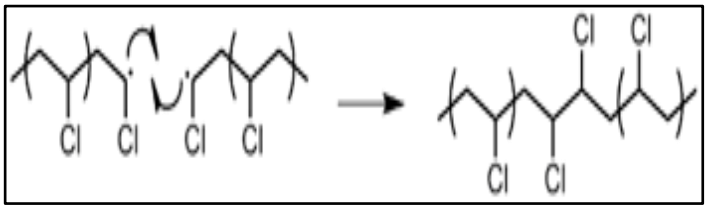


Figure 2.42Termination by the combination of two poly(vinyl chloride) (PVC) polymers.

- **Radical disproportionation**

Hydrogen atom from one chain end is abstracted to another, producing a polymer with a terminal unsaturated group and a polymer with a terminal saturated group

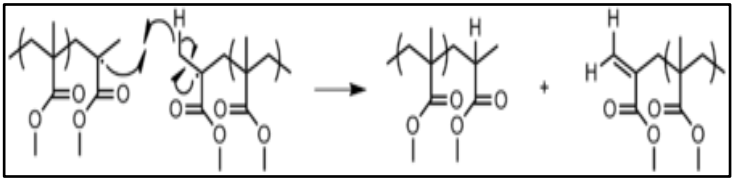


Figure 2.43Termination by disproportionation of poly(methyl methacrylate).

2-Combination of an active chain end with an initiator radical

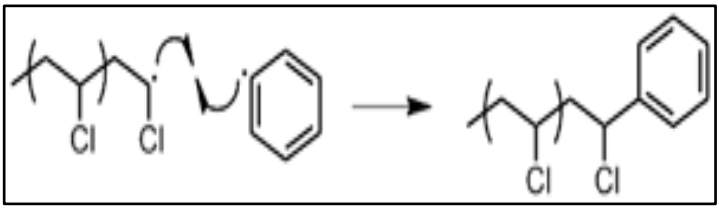


Figure 2.44Termination of PVC by reaction with radical initiator.

- **Interaction with impurities or inhibitors**

Oxygen is the common inhibitor. The growing chain will react with molecular oxygen, producing an oxygen radical, which is much less reactive. This significantly slows down the rate of propagation.

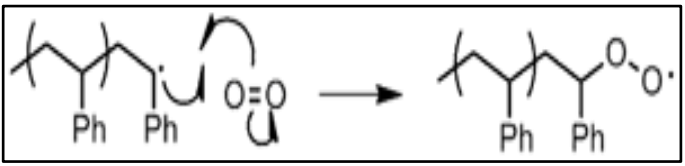


Figure 2.45Inhibition of polystyrene propagation due to reaction of polymer with molecular oxygen.

Nitrobenzene, butylated hydroxyl toluene, and diphenyl picryl hydrazy are a few other inhibitors. The latter is an especially effective inhibitor because of the resonance stabilization of the radical.

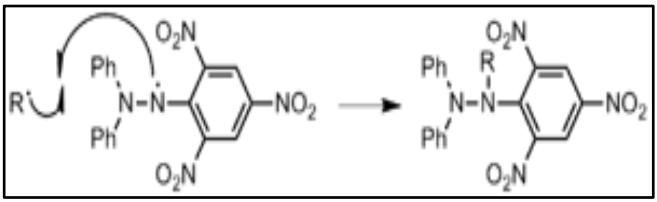


Figure 2.46 Inhibition of polymer chain, R, by DPPH.

2.6.6 Chain transfer

Contrary to the other modes of termination, chain transfer results in the destruction of only one radical, but also the creation of another radical. This newly created radical is not capable of further propagation. Similar to disproportionation, all chain-transfer mechanisms also involve the abstraction of a hydrogen or other atom. There are several types of chain-transfer mechanisms.

1-Solvent

Hydrogen atom is abstracted from a solvent molecule, resulting in the formation of radical on the solvent molecules, which will not propagate further

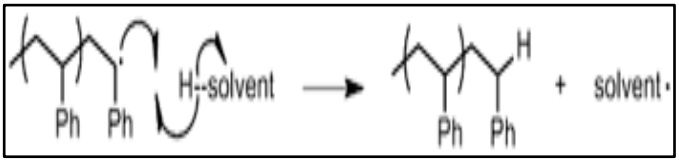


Figure 2.47Chain transfer from polystyrene to solvent.

The effectiveness of chain transfer involving solvent molecules depends on the amount of solvent present (more solvent leads to greater probability of transfer), the strength of the bond involved in the abstraction step (weaker bond leads to greater probability of transfer), and the stability of the solvent radical that is formed (greater stability leads to greater probability of transfer). Halogens, except fluorine, are easily transferred.

2-monomer

Hydrogen atom is abstracted from a monomer. While this does create a radical on the affected monomer, resonance stabilization of this radical discourages further propagation

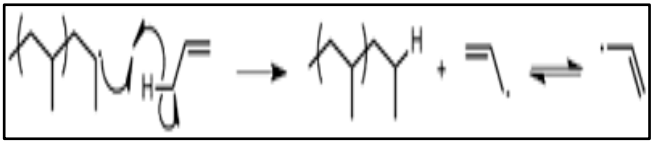


Figure 2.48Chain transfer from polypropylene to monomer.

3-initiator

Polymer chain reacts with an initiator, which terminates that polymer chain, but creates a new radical initiator. This initiator can then begin new polymer chains. Therefore, contrary to the other forms of chain transfer, chain transfer to the initiator does allow for further propagation. Peroxide initiators are especially sensitive to chain transfer.

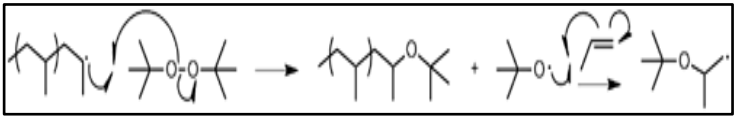


Figure 2.49Chain transfer from polypropylene to di-t-butyl peroxide initiator.

4-polymer

Radical of a polymer chain abstracts a hydrogen atom from somewhere on another polymer chain. This terminates the growth of one polymer chain, but allows the other to branch and resume growing. This reaction step changes neither the number of polymer chains nor the number of monomers which have been polymerized, so that the number-average degree of

polymerization is unaffected.

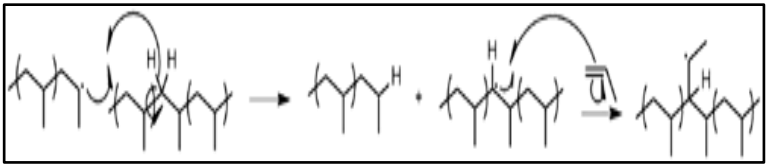


Figure 2.50Chain transfer from polypropylene to backbone of another polypropylene.

2.6.7 Effects of chain transfer

The most obvious effect of chain transfer is a decrease in the polymer chain length. If the rate of transfer is much larger than the rate of propagation, then very small polymers are formed with chain lengths of 2-5 repeating units (telomerization).

2.6.8 Methods

There are four industrial methods of radical polymerization

- **Bulk polymerization**: reaction mixture contains only initiator and monomer, no solvent.
- **Solution polymerization**: reaction mixture contains solvent, initiator, and monomer.
- **Suspension polymerization**: reaction mixture contains an aqueous phase, water-insoluble monomer, and initiator soluble in the monomer droplets (both the monomer and the initiator are hydrophobic).
- **Emulsion polymerization**: similar to suspension polymerization except that the initiator is soluble in the aqueous phase rather than in the monomer droplets (the monomer is hydrophobic, and the initiator is hydrophilic). An emulsifying agent is also needed.

Other methods

- **Template polymerization**: In this process, polymer chains are allowed to grow along template macromolecules for the greater part of their lifetime. A well-chosen template can affect the rate of polymerization as well as the molar mass and microstructure of the

daughter polymer. template after reaching the end of a template polymer.

- **Plasma polymerization**: The polymerization is initiated with plasma. A variety of organic molecules including alkenes, alkynes, and alkanes undergo polymerization to high molecular weight products under these conditions. The propagation mechanisms appear to involve both ionic and radical species. Plasma polymerization offers a potentially unique method of forming thin polymer films for uses such as thin-film capacitors, antireflection coatings, and various types of thin membranes.
- **Sonication:** The polymerization is initiated by high-intensity ultrasound. Polymerization to high molecular weight polymer is observed but the conversions are low. The polymerization is self-limiting because of the high viscosity produced even at low conversion. Reversible deactivation radical polymerization.

2.6.9Reversible-deactivation radical polymerization

Also known as living radical polymerization, controlled radical polymerization, reversible deactivation radical polymerization (RDRP) relies on completely pure reactions, preventing termination caused by impurities. Because these polymerizations stop only when there is no more monomer, polymerization can continue upon the addition of more monomer.

- Atom transfer radical polymerization **(ATRP):** based on the formation of a carbon-carbon bond by atom transfer radical addition. requires reversible activation of a dormant species (such as an alkyl halide) and a transition metal halide catalyst (to activate dormant species).
- Reversible Addition-Fragmentation Chain-Transfer Polymerization **(RAFT):** requires a compound that can act as a reversible chain-transfer agent, such as dithio compound.
- Stable Free Radical Polymerization **(SFRP):** used to synthesize linear or branched polymers with narrow molecular weight distributions and reactive end groups on each polymer chain. The process has also been used to create block co-polymers with unique

properties.

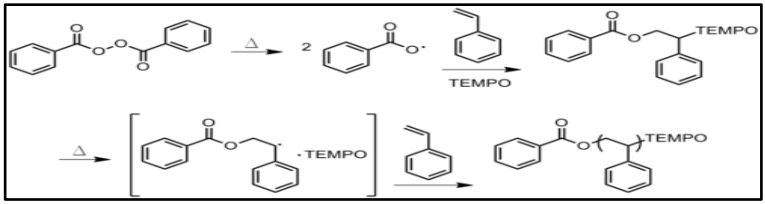


Figure 2.51formation of block copolymers by SFRP

2.6.10 Kinetics

In typical chain growth polymerizations, the reaction rates for initiation, propagation and termination can be described as follows:

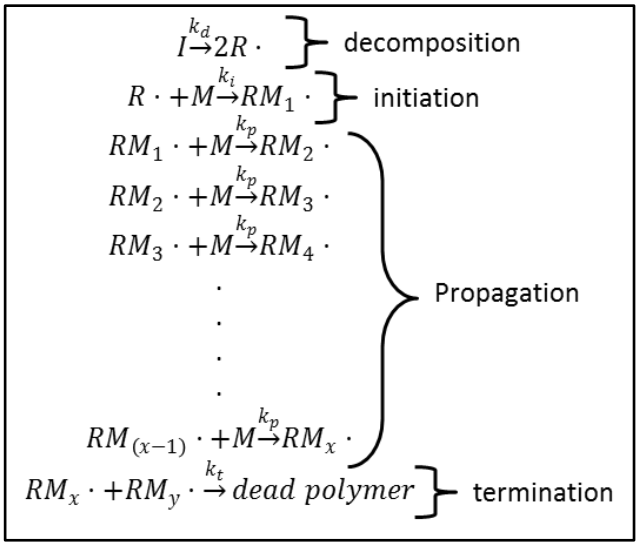


Figure 2.52 Kinetic steps of free radical polymerization

The kinetic equation for coupling termination is shown below. Unlike ionic polymerizations, the termination of the growing free radical chains usually takes place by coupling of two macro radicals. Thus, the kinetic chain length (v) is equal to DP/2.

Rt = d[M·]/ dt = 2kt[M·][M·] = 2kt[M·] ^{2}

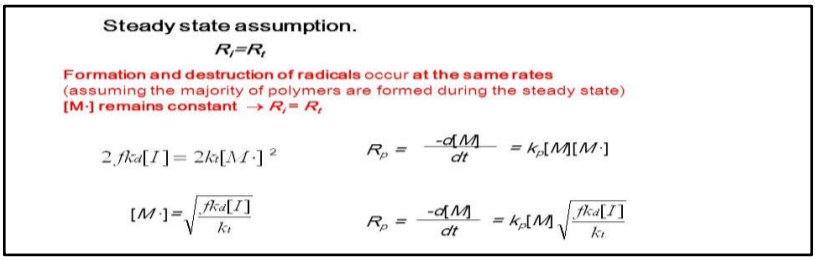


Figure 2.53 at steady state polymerization kinetics of FRP

where *f* is the efficiency of the initiator and k_d, k_p, and k_t are the constants for initiator dissociation, chain propagation and termination, respectively. [I] [M] and [M•] are the concentrations of the initiator, monomer and the active growing chain.

Under the steady-state approximation, the concentration of the active growing chains remains constant, i.e. the rates of initiation and of termination are equal. The concentration of active chain can be derived and expressed in terms of the other known species in the system.In this case, the rate of chain propagation can be further described using a function of the initiator and monomer concentrations.The kinetic chain length v is a measure of the average number of monomer units reacting with an active center during its lifetime and is related to the molecular weight through the mechanism of the termination. Without chain transfer, the kinetic chain length is only a function of propagation rate and initiation rate.Assuming no chain-transfer effect occurs in the reaction, the number average degree of polymerization P_n can be correlated with the kinetic chain length. In the case of termination by disproportionation, one polymer molecule is produced per every kinetic chain.Termination by combination leads to one polymer molecule per two kinetic chains

If chain transfer is considered, the kinetic chain length is not affected by the transfer process because the growing free-radical center generated by the initiation step stays alive after any chain-transfer event, although multiple polymer chains are produced. However, the number average degree of polymerization decreases as the chain transfers, since the growing chains are terminated by the chain-transfer events.

2.6.11Applications

Free radical polymerization has found applications including the manufacture of polystyrene, blockcopolymer elastomers, cardiovascular stents, chemical surfactants and lubricants. Block copolymers are used for a wide variety of applications including adhesives, footwear and toys.Free radical polymerization has uses in research as well, such as in the functionalization of carbon nanotubes. CNTs intrinsic electronic properties lead them to form large aggregates in solution, precluding useful applications. The use of polymers instead of smaller molecules can modify CNT properties (and conversely, nanotubes can modify polymer mechanical and electronic properties). Purification of the polymer can be used to obtain a more uniform length distribution before grafting. The radical polymer glass PTMA is about 10 times more electrically conductive than common semiconducting polymers. PTMA is in a class of electrically active polymers that could find use in transparent solar cells, antistatic and antiglare coatings for mobile phone displays, antistatic coverings for aircraft to protect against lightning strikes, flexible flash drives, and thermoelectric devices, which convert electricity into heat and the reverse. Widespread practical applications require increasing conductivity another 100 to 1,000 times.

2.7 Copolymerization

A copolymer is a polymer derived from more than one species of monomer. The polymerization of monomers into copolymers is called copolymerization. Copolymers obtained by copolymerization of two monomer species are sometimes called **biopolymers**. Those obtained from three and four monomers are called terpolymers and quaterpolymers, respectively.

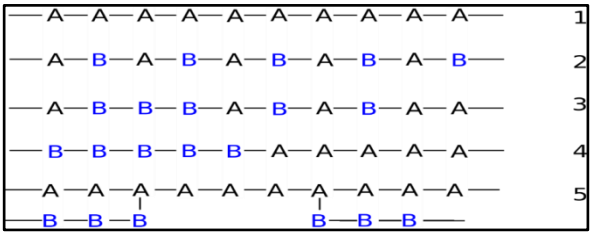


Figure 2.54 Types of copolymers

2.7.1 Commercial copolymers

Copolymer include acrylonitrile butadiene styrene (ABS), styrene/butadiene co-polymer (SBR), nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate, all formed by chain-growth polymerization. Another production mechanism is step-growth polymerization, used to produce the nylon-copolymer of nylon 12, nylon 6 and nylon 66, as well as the copolyester family.

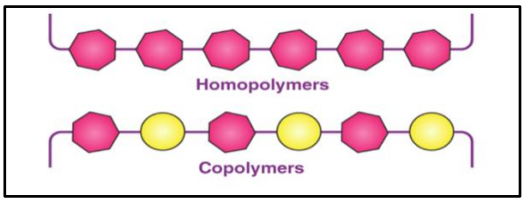


Figure 2.55 difference of copolymer and homopolymers

2.7.2Reactivity ratios

The reactivity ratio of a growing copolymer chain terminating in a given monomer is the ratio of the reaction rate constant for addition of the same monomer and the rate constant for addition of the other monomer. For example the rate constant for propagation of a polymer chain ending in monomer 1 (or A) by addition of monomer 2 (or B).

2.7.3 Kinetics

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}\right)$$

$d[M_1]/d[M_2]$: molar ratio of repeat units in copolymer
$[M_1]/[M_2]$: molar ratio of monomers in initial feed
$r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$r_1 > 1 \rightarrow M_1$ tends to self-propagate
$r_1 < 1 \rightarrow$ copolymerization is preferred

- Knowing r_1 and $r_2 \rightarrow$ can project the desired $d[M_1]/d[M_2]$ (for conversion <10%)
- f_1 and f_2: molar fractions of M_1 and M_2 in the initial feed
- F_1 and F_2: molar fractions of M_1 and M_2 in the final copolymer

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1]+[M_2]} \qquad F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1]+d[M_2]}$$

Figure 2.56 kinetic steps of copolymerization

2.7.4Copolymers

Copolymers are composed of two or more monomers. Source-based names are conveniently used to describe copolymers using an appropriate term between the names of the monomers. Any of a half dozen or so connecting terms may be used, depending on what is known about the structure of the copolymer. When no information is known or intended to be conveyed, the connective term “co” is employed in the general format poly(A-co-B), where A and B are the names of the two monomers.

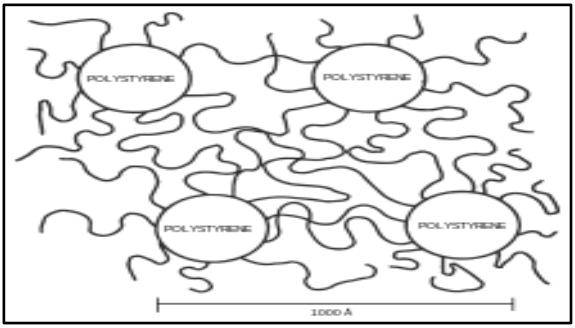


Figure 2.57 SBS block copolymer schematic microstructure

2.7.5 Block copolymers

comprise two or more homopolymer subunits linked by covalent bonds. The union of the homopolymer subunits may require an intermediate non-repeating subunit, known as a junction block. Diblock copolymers have two distinct blocks; triblockcopolymers have three. Technically, a block is a portion of a macromolecule, comprising many units, that has at least one feature which is not present in the adjacent portions. A possible sequence of repeat units A and B in a triblock copolymer might be

~A-A-A-A-A-A-A-B-B-B-B-B-B-B-A-A-A-A-A~.

Block copolymers are made up of blocks of different polymerized monomers. For example, polystyrene-b-poly(methyl methacrylate) or PS-b-PMMA (where b = block) is usually made by first polymerizing styrene, and then subsequently polymerizing methyl methacrylate (MMA) from the reactive end of the polystyrene chains. This polymer is a "diblock copolymer" because it contains two different chemical

blocks. Triblocks, tetrablocks, multiblocks, etc. can also be made. Diblock copolymers are made using living polymerization techniques, such as atom transfer free radical polymerization (**ATRP**), reversible addition fragmentation chain transfer (RAFT), ring-opening metathesis polymerization (ROMP), and living cationic or living anionic polymerizations.An emerging technique is chain shuttling polymerization.

The synthesis of block copolymers requires that both reactivity ratios are much larger than unity ($r_1 >> 1$, $r_2 >> 1$) under the reaction conditions, so that the terminal monomer unit of a growing chain tends to add a similar unit most of the time.

2.7.6 Blockiness

The "blockiness" of a copolymer is a measure of the adjacency of comonomers vs their statistical distribution. Many or even most synthetic polymers are in fact copolymers, containing about 1-20% of a minority monomer. In such cases, blockiness is undesirable. A block index has been proposed as a quantitative measure of blockiness or deviation from random monomer composition.

2.5.7Alternating copolymers

An alternating copolymer has regular alternating A and B units, and is often described by the formula: -A-B-A-B-A-B-A-B-A-B-, or $-(-A-B-)_n-$. The molar ratio of each monomer in the polymer is normally close to one, which happens when the reactivity ratios r_1 and r_2 are close to zero.

A step-growth copolymer formed by the condensation of two bifunctional monomers

$-(-A-A-B-B-)_n-$

A–A and B–B is in principle a perfectly alternating copolymer of these two monomers, but is usually considered as a homopolymer of the dimeric repeat unit A-A-B-B. An example is nylon 66 with repeat unit $-OC-(CH_2)_4-CO-NH-(CH_2)_6-NH-$, formed from a dicarboxylic acid monomer and a diamine monomer.

2.5.8 Periodic copolymers

Periodic copolymers have units arranged in a repeating sequence. For two

monomers A and B, for example, they might form the repeated pattern

$(A-B-A-B-B-A-A-A-A-B-B-B)_n$

2.5.9 Random copolyme

If the probability of finding a given type monomer residue at a particular point in the chain is equal to the mole fraction of that monomer residue in the chain, then the polymer may be referred to as a truly random copolyme.Statistical copolymers are dictated by the reaction kinetics of the two chemically distinct monomer reactants, and are commonly referred to interchangeably as "random" in the polymer literature.

2.5.10 Mayo-Lewis equation

The Mayo-Lewis equation can be used to predict the composition of the polymer product for all initial mole fractions of monomer. This equation is derived using the Markov model, which only considers the last segment added as affecting the kinetics of the next addition.

The composition and structural type of the copolymer depend on these reactivity ratios r_1 and r_2 according to the Mayo–Lewis equation, also called the **c**opolymerization equation or copolymer equation, for the relative instantaneous rates of incorporation of the two monomers.

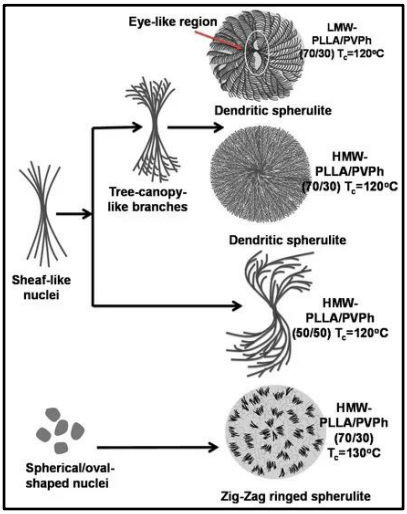


Figure 2.58 Composition and type of copolymers

2.5.11 Mechanism random copolymer

There are several ways to synthesize random copolymers. The most common synthesis method is free radical polymerization; this is especially useful when the desired properties rely on the composition of the copolymer rather than the molecular weight, since free radical polymerization produces relatively disperse polymer chains. Free radical polymerization is less expensive than other methods, and produces high-molecular weight polymer quickly.Several methods offer better control over dispersity. Anionic polymerization can be used to create random copolymers, but with several caveats: if carbanions of the two components do not have the same stability, only one of the species will add to the other. Additionally, anionic polymerization is expensive and requires very clean reaction conditions, and is therefore difficult to implement on a large scale. Less disperse random copolymers are also synthesized by ″living″ controlled radical polymerization methods, such as atom-transfer radical-polymerization (ATRP), nitroxide mediated radical polymerization (NMP), or Reversible addition−fragmentation chain-transfer polymerization (RAFT). These methods are favored over anionic polymerization because they can be performed in conditions similar to free radical polymerization. The reactions require longer experimentation periods than free radical polymerization, but still achieve reasonable reaction rates.

2.5.12 Stereoblock copolymers

In stereoblock copolymers the blocks or units differ only in the tacticity of the monomers.

2.5.13 Gradient copolymers

In gradient copolymers the monomer composition changes gradually along the chain.

2.5.14 Branched copolymers

There are a variety of architectures possible for nonlinear copolymers. Beyond grafted and star polymers discussed below, other common types of branched copolymers include brush copolymers and comb copolymers.

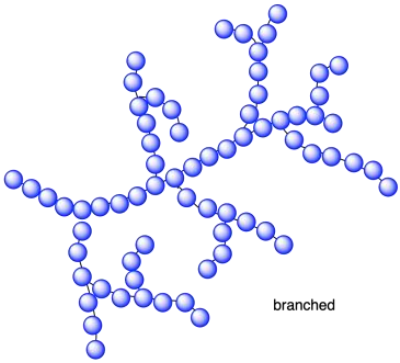


Figure 2.59 branched shaped copolymer

2.5.15 Graft copolymers

Graft copolymers are a special type of branched copolymer in which the side chains are structurally distinct from the main chain. Typically the main chain is formed from one type of monomer (A) and branches are formed from another monomer (B), or else the side-chains have constitutional or configurational features that differ from those in the main chain.

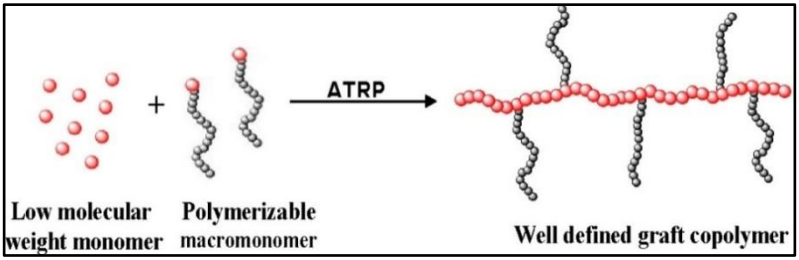


Figure 2.60 graft copolymer shaped copolymer

The individual chains of a graft copolymer may be homopolymers or copolymers. Note that different copolymer sequencing is sufficient to define a structural difference, thus an A-B diblock copolymer with A-B alternating copolymer side chains is properly called a graft copolymer.

2.5.16 Star copolymers

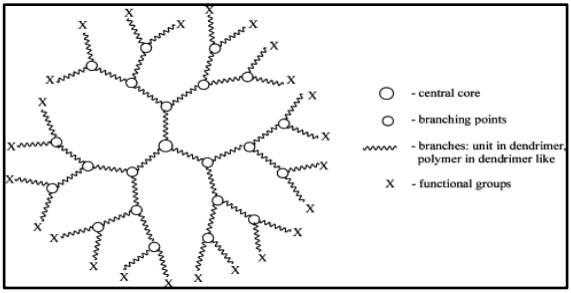


Figure 2.61Star shaped polymers or copolymers

Star copolymers have several polymer chains connected to a central core.

2.5.16 Microphase separation

Block copolymers are interesting because they can "microphase separate" to form periodic nanostructures, as in the styrene-butadiene-styrene block copolymer. The polymer is known as Kraton and is used for shoe soles and adhesives.

this.

2.5.17 Copolymer engineering

Copolymerization is used to modify the properties of manufactured plastics to meet specific needs, for example to reduce crystallinity, modify glass transition temperature, control wetting properties or to improve solubility. It is a way of improving mechanical properties, in a technique known as rubber toughening. Elastomeric phases within a rigid matrix act as crack arrestors, and so increase the energy absorption when the material is impacted for example. Acrylonitrile butadiene styrene is a common example.

2.6 Emulsion polymerization

Emulsion polymerization is a free-radical polymerization in which a monomer or mixture of monomers is polymerized in an aqueous surfactant solution to form a latex**.**Many water-soluble vinyl monomers may be polymerized by the emulsion polymerization technique. This technique, which differs from suspension polymerization in the size of the suspended particles and in the mechanism, is widely used for the production of a number

of commercial plastics and elastomers. While the particles in the suspension range from 10 to 1000 nm, those in the emulsion process range from 0.05 to 5 nm in diameter. The small beads produced in the suspension process may be separated by filtering, but the latex produced in emulsion polymerization is a stable system in which the charged particles cannot be recovered by ordinary separation procedures. Since relatively stable macroradicals are produced in the emulsion process, the termination rate decreases and a high-molecular-weight product is rapidly produced. It is customary to use a water-soluble initiator such as potassium persulfate, an anionic surfactant such as sodium stearate, and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40°C–70°C. When the concentration of soap exceeds the critical micelle concentration, the molecules are present as micelles in which the hydrophilic carboxylic acid ends are oriented toward the water–micelle interface and the lyophilic hydrocarbon ends are oriented toward the center of the micelle. The micelles are present as spheres with a diameter of 5–10 nm when the soap concentration is less than 2%. However, with the higher concentrations typically employed, the micelles resemble aggregates of rods that are 100–300 nm in length.The water-insoluble monomer, M, is attracted to the lyophilic ends in the micelles, causing the micelles to swell. The number of swollen micelles per milliliter of water is on the order of 1018. However, at the initial stages of polymerization (phase I) most of the monomer is present as globules that resemble those observed in suspension polymerization. Since the initiation of polymerization takes place in the aqueous phase, essentially no polymerization occurs in the globules. Thus, they serve primarily as a reservoir of monomer supplied to the micelles to replace monomer converted to polymer.

2.6.1 Advantages

Advantages of emulsion polymerization include:

- High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free-radical polymerization, there is a tradeoff between molecular weight and polymerization rate.
- The continuous water phase is an excellent conductor of heat, enabling fast polymerization rates without loss of temperature control.

- Since polymer molecules are contained within the particles, the viscosity of the reaction medium remains close to that of water and is not dependent on molecular weight.
- The final product can be used as is and does not generally need to be altered or processed.

2.6.2 Disadvantages

Disadvantages of emulsion polymerization include:

- Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove
- For dry (isolated) polymers, water removal is an energy-intensive process
- Emulsion plymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer

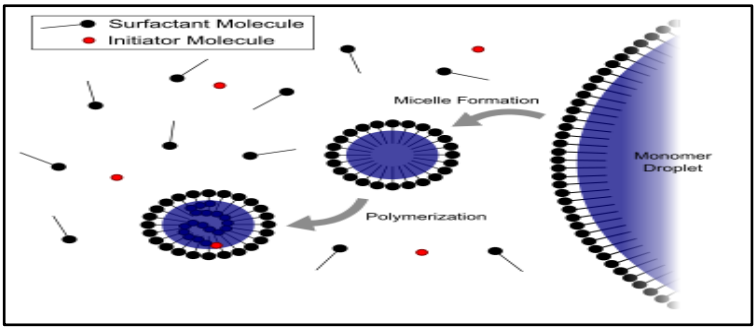


Figure 2.62Mechanism of emulsion polymerization

2.6.3 Stages of propagation

According to Smith and Ewart, the first stages of propagation in an emulsion system also take place in the aqueous phase to produce a more lyophilic surface oligoradical. When the DP of the PS oligoradical is 3–5, its solubility is much like that of styrene, and it migrates to the swollen micelle where propagation continues with the styrene molecules already present. According to the accepted theories, each micelle can accommodate only one free radical, as noted before, and until a second one enters and terminates the

propagation reaction through coupling, propagation continues to take place in the micelles. From a statistical point of view, only one-half of the micelles (N/2) will contain growing chains at any one time. It should also be noted that since propagation occurs in the micelles, the rate of polymerization will be proportional to the number of micelles present, that is, the rate is proportional to the soap concentration. As the micelles grow by absorption of more monomer and formation of polymer, they become relatively large particles that absorb soap from micelles that have not been inoculated or stung by oligo radicals. Thus, in stage II, when about 20% of the monomer has been converted to polymer, the micelles disappear and are replaced by large, but fewer, monomer–polymer particles. Polymerization continues in stage II, and monomer continues to be supplied to the particles by the droplets in the aqueous phase. These droplets disappear when about 30% of the monomer has been converted to polymer. Polymerization continues in stage III after about 60% conversion, but all monomer must now be supplied to the macroradicals by a diffusion process in the micelles. The rate of propagation in the micelles is similar to that described for other free radical chain growth, but since the free radical concentration is equal to the number of active micelles, the value of N/2 is used instead of [M]. Thus, the rate of propagation is dependent on the number of micelles present.

$Rp = kp[M][M\cdot] = kp[M]\ (N/2)$

Hence, since propagation is a very fast reaction, long chains are produced before termination by coupling, which takes place as the result of the entrance of a new oligoradical in the active micelle. The DP is also proportional to the number of active micelles.

- **Advantages**
  Gives potential for rapid polymerization to yield high molecular weight polymer with low polydispersity. Viscosity of polymer emulsion is much lower than that of straight polymer in melt phase. Easier to process but also allows production of polymers that are extremely sticky as 100% polymer. Final product can easily be removed from reactor due to lower viscosity (and can be washed out with water).Continuous phase (water) acts as a heat sink and allows temperature to be much better controlled, avoiding dangerous overheating.

- **Disadvantages**
  Polymer can easily become contaminated with traces of the emulsifier. This can lead to poor transparency which can often be an important property. Unless the finished polymer is to be supplied as an emulsion, the final stage requires coagulation and removal of the aqueous phase. This can generate very large amounts of water - not necessarily a disadvantage but it does have been adequately treated and disposed of.

CHAPTER 3

Morphology of polymers

3.0 Disordered polymers

Polymers may consist of both crystalline and amorphous regions, and polymer morphology describes the arrangement and microscale ordering of polymer chains in space. Disordered polymers: In the solid state, a tactic polymers, polymers with a high degree of branching and random copolymers form amorphous polymer structure.

3.1 Chemical Configuration and Conformation.

Polymer morphology is a physical phenomenon that focuses on studying the structures and relationships of polymers. Importance of this phenomenon is the capability of describing the arrangement of molecules on a large scale. Such an arrangement can be classified either amorphous, crystalline, or semi-crystalline. Often, polymers have a semi-crystalline arrangement. This arrangement consists of small crystalline portions (domains) (crystallites) surrounded by domains of amorphous phase.The terms configuration and conformation are often used interchangeably. It is important to make a distinction between the chemical configuration of a polymer chain which includes block distribution, facticity groupings and branching as a separated topic from coil conformation which has to do the chain dimensional scaling and size. Local conformation includes helical coiling of the chains (secondary structure in proteins) and formation of larger partially collapsed structures (tertiary structures in proteins). The structure of a chain is intimately tied to the crystalline unit cell and the colloidal shape of crystallites in polymers. The structure of a synthetic polymer chain is polydisperse in all aspects. Structure is built up from,

1) Chemical Configuration- The arrangement of chemical units in the chain. This is known as chain primary structure in proteins.

2) Local Conformation- Rotational states of chemical bonds, formation of helical structures. This is know as chain secondary structure in proteins.

3) Larger scale conformation such as helix folding and formation of "blob" substructures. This is known as tertiary structure in proteins.

4) Global Chain Conformation which is governed by entropy. This

dominates the structural scaling of chain size with molecular weight.

3.2 Helical structures

Formation of Helical structures is usually required for polymers to crystallize. The formation of long sequences of helical structures requires long sequences of uniform tacticity in chain units.

3.3 Trans Gauche conformations in simple vinyl polymers

Polyethylene is the most common commercial polymer. The secondary structure required for PE to crystallize is a planar zigzag conformation with no helical twist. Polyethylene does not possess tacticity since all substitutent groups are the same. If we consider a Neuman Projection along the chain for two carbons it can be seen that rotation about the C-C bond leads to variable energy states.

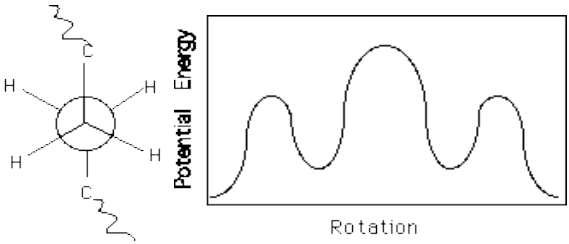


Figure 3.1 trans and gauche conformation

The minimum in this energy diagram (shown to the left) is the trans state. The sub minima are the gauche states. The planar zigzag conformation is produced by all trans states.

3.4 Structure of materials

Linus Pauling, in 1954, received the Nobel Prize for his insights into the structure of materials, mainly proteins. Pauling showed that only certain conformations are preferred because of intramolecular and intermolecular hydrogen bonding.

3.5 Stereochemistry of polymers

The terms “memory” and “to remember” are similar and used by polymer chemists in similar, but different ways. The first use of the terms memory and to remember involves reversible changes in the polymer structure usually

associated with stress–strain deformation of a rubber material where the dislodged, moved polymer segments are connected to one another through chemical and physical cross-links so that once the particular stress–strain is removed the polymer returns to its original, prestress–strain arrangement of the particular polymer segments.

Table 3.1 principle stereochemistry and uses of polymers

Polymer	*Principal Stereochemistry*	*Typical Uses*
Plastics		
Polyethylene, high density (HDPE)	-	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polyethylene, ultrahigh molecular weight (UHMWPE)	-	Surgical prostheses, machine parts, heavy, heavy-duty liners
Polypropylene	Isotactic	Automobile and appliance parts, rope, cordage, webbing, carpeting film
Poly(1-butene)	Isotactic	Film, pipe
Poly(4-methyl-1-pentene)[a]	Isotactic	Packaging, medical supplies, lighting
Polystyrene	Syndiotactic	Specialty plastics
1,4-Polybutadiene	*trans*	Metal cam coatings, potting compounds for transformers
1,4-Polyisoprene	*trans*	Golf ball covers, orthopedic devices
Ethylene-1-alkene[b] copolymer (linear low-density polyethylene, LLDPE)	-	Blending with LDPE, packaging film, Bottles
Ethylene-propylene block copolymers (polyallomers)	Isotactic	Food packaging, automotive trim, toys, bottles, film, heat-sterilizable containers
Polydicyclopentadiene[c]	-	Reaction injection molding (RIM) structural plastics

Thus, the polymer "remembers" its initial segmental arrangement and returns to it through the guiding of the cross-links. The second use involves nonreversible changes of polymer segments and whole chain movements also brought about through stress–strain actions. These changes include any synthetic chain and segmental orientations as well as post synthesis changes including fabrication effects. These changes involve "permanent" differences in chain and segmental orientation and in some ways these changes represent the total history of the polymer materials from inception (synthesis) through the moment when a particular property or behavior is measured. These irreversible or nonreversible changes occur with both cross-linked and non-cross-linked materials and are largely responsible for the change in polymer property as the material moves from being synthesized, processed, fabricated, and used in whatever capacity it finds itself. Thus, the polymeric material "remembers" its history with respect to changes and forces that influence chain and segmental chain changes.

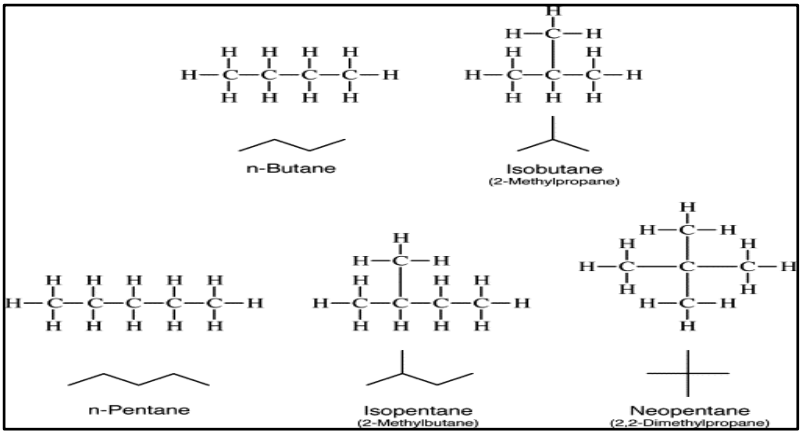


Figure 3.2Stereo chemistry of hydrocarbons

For hydrocarbons composed of low numbers of carbons, such as methane, ethane, propane, and butane, the materials are gases at room temperature. For the next grouping such as hexane and octane, the materials are liquids. The individual hydrocarbon chains are held together by dispersion forces that are a sum of the individual methylene and end group forces.

Here, the total dispersion forces are sufficient to be greater than individual carbon–carbon bond strengths so the chains decompose prior to their evaporation. These linear chains are sufficiently long to be crystalline waxy solids but not sufficiently long to allow the chains to interconnect various crystalline groupings. Thus, they are brittle solids with little physical strength. As the chains increase in length, the chain irreversible and, when appropriate cross-linking is present, reversible memory because of their size. High-density polyethylene (HDPE), formerly called low-pressure PE, [H (CH2CH2)n)H], like other alkanes [H(CH2)nH], may be used to illustrate a lot of polymer structure. As in introductory organic chemistry, we can understand the properties and chemical activities of many complex organic compounds if we understand their basic chemistry and geometry. HDPE, like decane [H(CH2)8H] or paraffin [H(CH2)about 50H], is a largely linear chainlike molecule consisting of catenated carbon atoms bonded covalently. The carbon atoms in all alkanes, including HDPE, are joined at characteristic tetrahedral bond angles of approximately 109.5°.

While decane consists of 10-methylene groups, HDPE may contain more

than 1000 of these methylene units. While we use the term normal or linear to describe non branched chains, we know that because of the tetrahedral bond angles and ability for twisting that the chains are zigzag shaped with many possible structural variations. The distance between the carbon atoms is 1.54 angstroms or 0.154 nanometers (nm). The apparent zigzag distance between carbon atoms in a chain of many carbon atoms is 0.126 nm. Thus, the length of an extended nonane chain is 8 units times 0.126 nm/units = 1.008 nm. For PE, the repeat unit has two methylenes so that the apparent zigzag is 0.252 nm for each "ethylene" unit. The zigzag or contour length of an HDPE chain 1000 units long, [H (CH2CH2)1000H], is 1000 units times 0.252 nm/units or 252 nm. However, because of rotations about the carbon atoms, chains seldom extend to their full extended contour length but are present in many different shapes or conformations. The full contour length of a polymer is obtained by multiplying the apparent repeat unit length (l), that is, the length of each mer or unit, by the number of units (n); contour length = nl.

The classical statistical approach may be used to show the distance traveled by a blindfolded person taking n number of steps of length l in a random walk or the distance flown by a confused moth, bird, or bee. The distance traveled from start to finish is not the straight-line path measured as nl but the root-mean-square distance ((r2) 1/2), which is equal to ln1/2. Thus, the root-mean-square length of a flexible PE chain with 1000 units is 0.252 nm times (1000)1/2 = 7.96 nm or about 3% of the contour length. Nobel Laureate Paul Flory and others have introduced several corrections so that this random flight technique could be applied to polymer chains approaching a full contour length of nl, that is, rigid rod structures. Each specific protein molecule has a specific chain length, like classical small molecules, and are said to be monodisperse with respect to chain length or molecular weight. However, most synthetic commercial polymers such as HDPE are composed of molecules of different lengths. In polymer chemistry scientists use the term "pendant group" to label any group present on the repeat unit of isobutane. Thus, polypropylene (PP)CH3 –(–CH2–CH–)– has a methyl group as a pendant unit, but PP is designated as a linear polymer

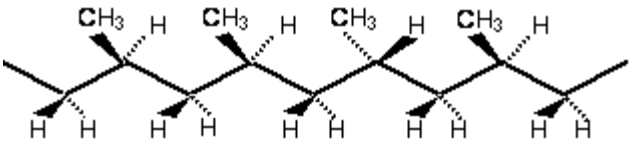


Figure 3.3 linear polymer polypropylene structure

In contrast, lowdensity polyethylene (LDPE), formally called high-pressure polyethylene, is a branched polymer because chain extensions or branches of methylene units are present coming off of branch points along the typically linear backbone chain . The linearity provides strength while the branching provides flexibility and toughness.

The size and shape of polymers are intimately connected to their properties. The shape of polymers is also intimately connected to the size of the various units that comprise the macromolecule and the various primary and secondary bonding forces that are present within the chain and between chains.

A most important aspect of secondary structures is supercoiling. Supercoiling simply is the coiling of the already helical DNA. The typical DNA structure is the thermally stable form. Two divergent mechanisms are believed responsible for supercoiling. The first, and less prevalent, is illustrated by a telephone cord. The telephone cord is typically coiled and represents the “at rest” or “unstressed” coupled DNA. The more common form, involves the presence of less than normal coiling. This can be illustrated by taking a rubber band, breaking one end and then attaching it about a stationary object. Begin braiding the two ends until just prior to a bunching or formation of supercoiling through over coiling. Then separate the two ends pulling them apart. The resulting strain produces supercoiling and illustrates supercoiling resulting in under coiling or under winding. Thus, under winding occurs when there are fewer helical turns than would be expected. Purified DNA is rarely relaxed. Supercoiling with bacterial DNA gives a largely open, extended, and narrow rather than compacted, multibranched structure.

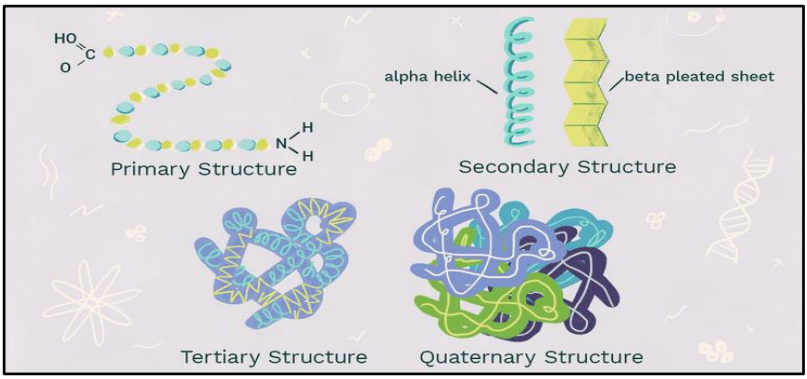


Figure 3.4differentiate b/w primary,secondary and tertiary structures

By comparison, the DNA in eukaryotic cells is present in very compacted packages. Supercoiling forms the basis for the basic folding pattern in eukaryotic cells that eventually results in this very compacted structure. Subjection of chromosomes to treatments that partially unfold them shows a structure where the DNA is tightly wound about "beads of proteins" forming a necklace-like arrangement where the protein beads represent precious stones imbedded within the necklace fabric . This combination forms the nucleosome, the fundamental unit of organization upon which higher-order packing occurs. The bead of each nucleosome contains eight histone proteins. Histone proteins are small basic proteins with molecular weights between 11,000 and 21,000 and specified by names such as H1 and H2. H1 is especially important and its structure varies to a good degree from species to species, whereas some of the other histones, such as H3 and H4, are very similar. Histones are rich in the amino acid residues from arginine and lysine. Wrapping of DNA about a nucleosome core compacts the DNA length about sevenfold. The overall compacting though is about 10,000 fold. Additional compacting of about 100-fold is gained from formation of the so-called 30 nm fibers. These fibers contain one H1 within the nucleosome core. This organization does not occur over the entire chromosome but rather is punctuated by areas containing sequence-specific (non-histone containing) DNA-binding proteins. Histone core spaced nucleosomes consisting of histone protein bound to supercoiled deoxyribonucleic acid (DNA) with DNA links between the histone bound units forming a 30 nm higher-order fiber. The additional modes of compaction are just beginning to be

understood but may involve scaffold assisting. Thus, certain DNA regions are separated by loops of DNA with about 20,000–100,000 base pairs with each loop possibly containing sets of related genes. The scaffold contains several proteins, especially H1 in the core and topoisomerase II. Both appear important to the compaction of the chromosome. In fact, the relationship between topoisomerase II and chromosome folding is so vital that inhibitors of this enzyme can kill rapidly dividing cells, and several drugs used in the treatment of cancer are topoisomerase II inhibitors.

The central theme concerning the major secondary structures found in nature is also illustrated with the two major polysaccharides derived from sucrose, that is, cellulose and a major component of starch, amylose. Glucose exists in one of two forms—an alpha and a beta form where the terms alpha and beta refer to the geometry of the oxygen connecting the glucose ring to the fructose ring.Cellulose is a largely linear homosaccharide of the beta-d-glucose. Because of the geometry of the beta linkage, individual cellulose chains are generally found to exist as sheets, the individual chains connected through hydrogen bonding. The sheet structure gives cellulose-containing materials good mechanical strength allowing them to act as structural units in plants.

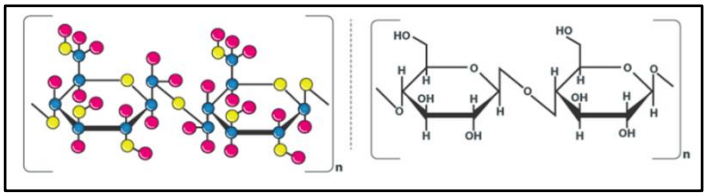


Figure 3.5 Cellulose linear homo saccharide of glucose structure

Amylose, by comparison, is a linear poly(alpha-d-glucose). Its usual conformation is as a helix with six units per turn. Amylose is a major energy source occurring in plants as granules.

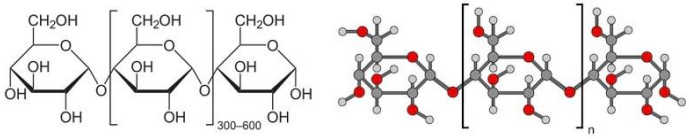


Figure 3.6 amylose linear polymer structure

Polymer morphology generally describes the arrangement and microscale ordering of polymer chains in space. The macroscopic physical properties of a polymer are related to the interactions between the polymer chains.

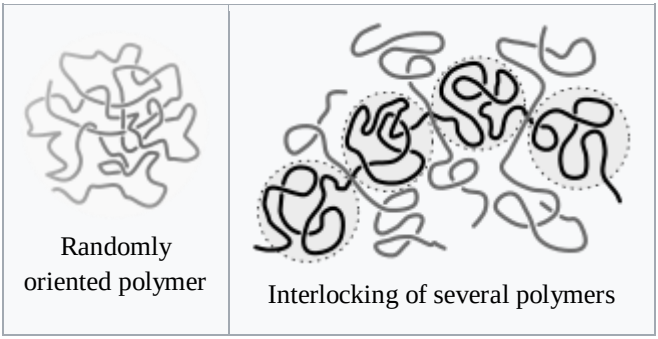
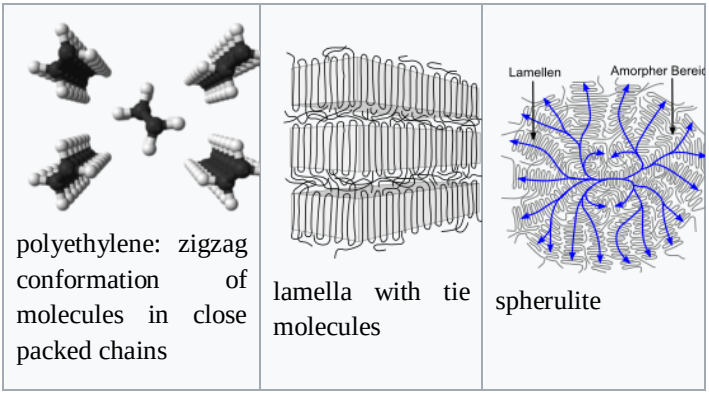
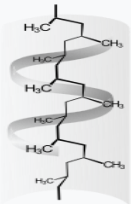


Figure3.7 randomly oriented polymer structure

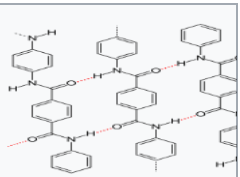
- **Disordered polymers**

In the solid state, atactic polymers, polymers with a high degree of branching and random copolymers form amorphous (i.e. glassy structures). In melt and solution, polymers tend to form a constantly changing "statistical cluster", see freely-jointed-chain model. In the solid state, the respective conformations of the molecules are frozen. Hooking and entanglement of chain molecules lead to a "mechanical bond" between the chains. Intermolecular and intramolecular attractive forces only occur at sites where molecule segments are close enough to each other. The irregular structures of the molecules prevent a narrower arrangement.





polypropylene h elix



p-Aramid, red dotted: hydrogen bonds

Figure3.8 examples of disordered polymers

- **Linear polymers**

Linear polymers with periodic structure, low branching and stereo regularity (e. g. not atactic) have a semi-crystalline structure in the solid state. In simple polymers (such as polyethylene), the chains are present in the crystal in zigzag conformation. Several zigzag conformations form dense chain packs, called crystallites or lamellae. The lamellae are much thinner than the polymers are long (often about 10 nm). They are formed by more or less regular folding of one or more molecular chains. Amorphous structures exist between the lamellae. Individual molecules can lead to entanglements between the lamellae and can also be involved in the formation of two (or more) lamellae (chains than called tie molecules). Several lamellae form a superstructure, a spherulite, often with a diameter in the range of 0.05 to 1 mm.

The type and arrangement of (functional) residues of the repeat units effects or determines the crystallinity and strength of the secondary valence bonds. In isotactic polypropylene, the molecules form a helix. Like the zigzag conformation, such helices allow a dense chain packing. Particularly strong intermolecular interactions occur when the residues of the repeating units allow the formation of hydrogen bonds, as in the case of *p*-aramid. The formation of strong intramolecular associations may produce diverse folded states of single linear chains with distinct circuit topology. Crystallinity and superstructure are always dependent on the conditions of their formation, see also: crystallization of polymers. Compared to amorphous structures, semi-crystalline structures lead to a higher stiffness, density, melting temperature and higher resistance of a polymer.

- **Cross-linked polymers:** Wide-meshed cross-linked polymers are elastomers and cannot be molten (unlike thermoplastics); heating cross-linked polymers only leads to decomposition. Thermoplastic elastomers, on the other hand, are reversibly "physically crosslinked" and can be molten. Block copolymers in which a hard segment of the polymer has a tendency to crystallize and a soft segment has an amorphous structure are one type of thermoplastic elastomers: the hard segments ensure wide-meshed, physical crosslinking.

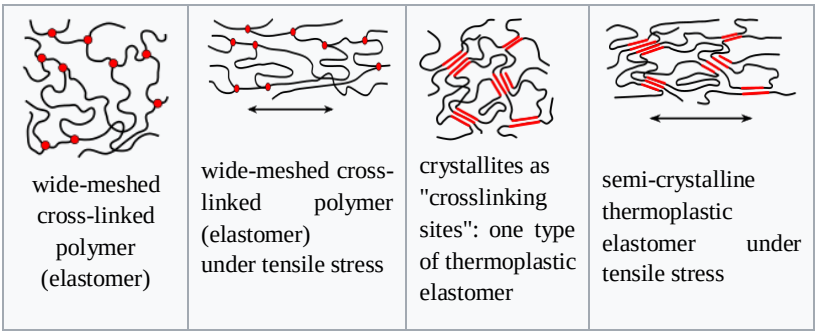


Figure3.9 examples of cross linked polymers

3.6 Crystallinity

For polymers, the term crystalline has a somewhat ambiguous usage. In some cases, the term crystalline finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for x-ray crystallography, may be defined in terms of a conventional unit cell composed of one or more polymer molecules with cell dimensions of hundreds of angstroms or more. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely

crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. For many polymers, crystallinity may also be associated with decreased transparency.

Table 3.2 polymers crystallinity and density

Polymer type	Density (g cm^{-3})	Crystallinity
Natural rubber	0.92	Low
Polyethylene–low density	0.91–0.93	45–60%
Polyethylene–high density	0.94–0.97	70–95%
Polypropylene	0.85–0.94	50–80%
Polystyrene	0.96–1.05	Low
Polyamide (PA6 and PA66)	1.12–1.14	35–45%
Polycarbonate	1.20	Low
Cellulose acetate	1.28	High
Polyvinyl chloride	1.38	High
Polylactic acid	1.21–1.43	37%

CHAPTER 4

Natural polymers

4.0 What are natural polymers?

Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.Polymers are of two types: naturally occurring and synthetic or man made.

- **Natural**

Natural polymeric materials such as hemp, shellac, amber, wool, silk, and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

- **Synthetic**

The list of synthetic polymers, roughly in order of worldwide demand, includes polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyacrylonitrile, PVB, silicone, and many more.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeat unit or monomer is ethylene. Many other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

4.1 History

Polymers have been essential components of commodities since the early days of humankind. The use of wool (keratin), cotton and linen fiber's (cellulose) for garments, paper reed (cellulose) for paper are just a few examples of how our ancestors exploited polymer-containing raw materials

to obtain artefacts. The latex sap of "caoutchouc" trees (natural rubber) reached Europe in the 16th century from South America long after the Olmec, Maya and Aztec had started using it as a material to make balls, waterproof textiles and containers. The chemical manipulation of polymers dates back to the 19th century, although at the time the nature of these species was not understood. The behavior of polymers was initially rationalized according to the theory proposed by Thomas Graham which considered them as colloidal aggregates of small molecules held together by unknown forces. Notwithstanding the lack of theoretical knowledge, the potential of polymers to provide innovative, accessible and cheap materials was immediately grasped. The work carried out by Braconnot, Parkes, Ludersdorf, Hayard and many others on the modification of natural polymers determined many significant advances in the field. Their contributions led to the discovery of materials such as celluloid, galalith, parkesine, rayon, vulcanized rubber and, later, Bakelite: all materials that quickly entered industrial manufacturing processes and reached households as garments components (*e.g.*, fabrics, buttons), crockery and decorative items.

After the 1930s polymers entered a golden age during which new types were discovered and quickly given commercial applications, replacing naturally-sourced materials. This development was fuelled by an industrial sector with a strong economical drive and it was supported by a wide academic community that contributed with innovative synthesis of monomers from cheaper raw materials, more efficient polymerization processes, improved techniques for polymer characterization and advanced theoretical understanding of polymers.

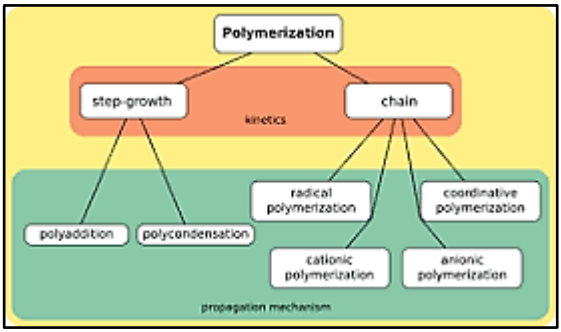


Figure 4.1 types of polymerization

4.2 Study of bio polymers

Biological polymers represent successful strategies that are being studied by scientists as avenues to different and better polymers and polymer structure control. Sample “design rules” and approaches that are emerging include the following:

 Identification of sequences that give materials with particular properties

 Identification of sequences that cause certain structural changes

 Formation of a broad range of materials with a wide variety of general/specific properties and function (such as proteins/enzymes) through a controlled sequence assembly from a fixed number of feedstock molecules (proteins, about 20 different amino acids; five bases and two sugar units for nucleic acids)

 Integrated, in situ (in cells), polymer productions with precise nanoscale control Repetitive use of proven strategies with seemingly minor structural differences but resulting in quite divergent results (protein for skin, hair, and muscle)

 Control of polymerizing conditions that allow steady-state production far from equilibrium.

There often occurs a difference in “mind-set” between the nucleic acid and protein biopolymers. Nucleic acids and proteins are site specific with one conformation. Generally, if it differs in structure or geometry from the specific macromolecule needed, it is discarded. Nucleic acids and proteins are not a statistical average, but rather a specific material with a specific chain length and conformation. By comparison, synthetic and many other biopolymers are statistical averages of chain lengths and conformations. All of these distributions are often kinetic and/or thermodynamic driven.

4.3 Importance of biopolymers

This difference between the two divisions of biologically important polymers is also reflected in the likelihood that there are two molecules with the exact same structure. For molecules such as polysaccharides and those based on terpene-like structures, the precise structures of individual molecules vary, but for specific proteins and nucleic acids, the structures are identical from molecule to molecule. This can be considered a consequence

of the general function of the macromolecule. For polysaccharides, the major, though not the sole function, are energy and structure. For proteins and nucleic acids, main functions include memory and replication, in addition to proteins sometimes also serving a structural function. Another difference between proteins and nucleic acids and other biopolymers and synthetic polymers involves the influence of stress–strain activities on the material properties. Thus, application of stress on many synthetic polymers and some biopolymers encourages realignment of polymer chains and regions often resulting in a material with greater order and strength. Counter, application of stress to certain biopolymers, such as specific proteins and nucleic acids, causes a decrease in performance (through denaturation, etc.) and strength. For these biopolymers, this is a result of the biopolymer already existing in a compact and "energy favored" form and already existing in the "appropriate" form for the desired performance. The performance requirements for the two classifications of polymers are different. For one set, including most synthetic and some biopolymers, performance behavior involves response to stress–strain application with respect to certain responses such as chemical resistance, absorption enhancement, and other physical properties. By comparison, the most cited performances for specific nucleic acids and proteins involve selected biological responses requiring specific interactions occurring within a highly structured environment with specific shape and electronic requirements.

4.4 Carbohydrates

Carbohydrates are the most abundant organic compounds, constituting three-fourths of the dry weight of the plant world. They represent a great storehouse of energy as a food for humans and animals. About 400 billion tons of sugars are produced annually through photosynthesis, dwarfing the production of other natural polymers, with the exception of lignin. Much of this synthesis occurs in the oceans, pointing to the importance of harnessing this untapped food, energy, and renewable feedstocks storehouse. The potential complexity of even the simple aldohexose monosaccharides is indicated by the presence of five different chiral centers, giving rise to 25 or 32 possible stereo isomeric forms of the basic structure, two of which are glucose and mannose. While these sugars differ in specific biological activity, their gross chemical reactivities are almost identical, permitting one to often employ mixtures within chemical reactions without regard to actual

structure. Their physical properties are also almost the same, again allowing for the mixing of these structures with little loss in physical behavior. But their biological properties are markedly different.

4.4.1 Polysaccharide

One of the most rapidly growing areas of science and polymers involves natural polymers. Our bodies are largely composed of polymers: deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, and polycarbohydrates. The "health" of these polymers is related to aging, awareness, mobility, strength, and so on, that is, all the characteristics of being alive. Many medical, health, and biological advances focus on polymers. There is an increasing emphasis on such natural polymers. The emphasis on the human genome and relationships between genes and proteins, and our health underlies much of this movement. Thus, an understanding of polymeric principles is advantageous to those desiring to pursue a career related to their natural environment, be it medicine, biomedical, biological, bioengineering, etc. Physically, there is no difference in the behavior, study, or testing of natural and synthetic polymers. The techniques suitable for application to synthetic polymers are equally applicable to the study and behavior of natural polymers.

Many renewable feedstocks are currently summarily destroyed (through leaving them to rot or burning) or utilized in a non-economical manner. Thus, leaves are "ritualistically" burned each fall. A number of these seemingly useless natural materials have already been utilized as feedstock sources for industrial products with more becoming available.

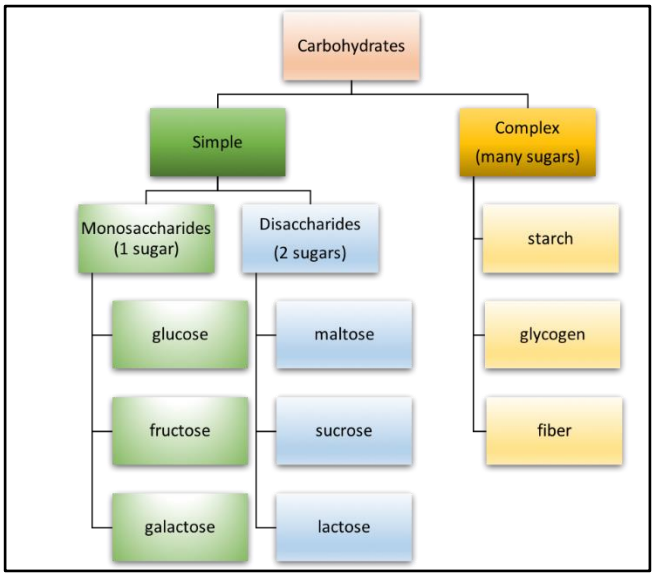


Figure 4.2 carbohydrates classification

4.4.2Sources

Carbohydrates are diverse with respect to occurrence and size. Familiar mono- and disaccharides include glucose, fructose, sucrose and mannose. The most important polysaccharides are cellulose and starch. These may be hydrolyzed to lower-molecular-weight carbohydrates (oligosaccharides) and finally to d-glucose. Glucose is the building block for many carbohydrate polymers. It is called a monosaccharide since it cannot be further hydrolyzed while retaining the ring.

Figure 4.3 natural sources of carbohydrates

4.4.3 Structure

Simple sugars exist in both cyclic and linear forms. Intramolecular nucleophilic reactions occur creating equilibrium combinations of these linear and cyclic forms. Monosaccharides are classified according to certain characteristics. Here, we will deal only with the cyclic designations since the polysaccharides are cyclic in nature.

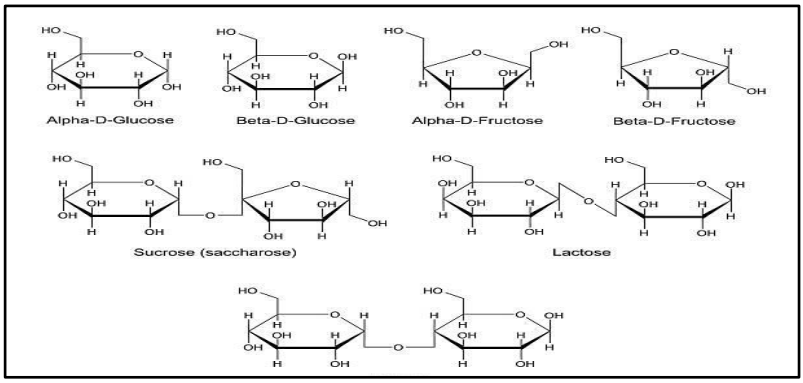


Figure 4.4 Structure of glucose, lactose and sucrose molecules

The only exception is the nature of the end groups that may be cyclic or linear. For our purposes, these classification characteristics are the stereo placement of the alcohol groups on the ring, the size of the ring, and the placement of the ether linkage. With the exception of carbons 1 and 6, the carbons are stereo centers or stereo genic making d-glucose one of 24 = 16

possible stereoisomers.

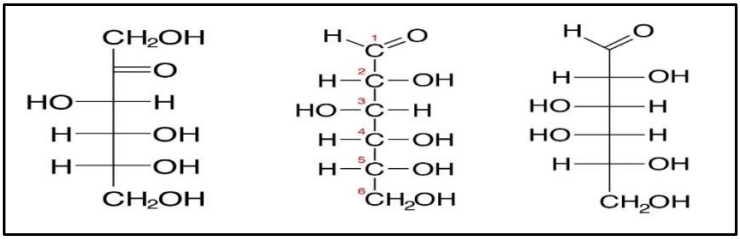


Figure 4.5 Structure of monosaccharides

4.4.5 Cellulose

Cellulose is a polydisperse polymer with an average DP in the general range of 3,500–36,000. Native cellulose is widely distributed in nature and is the principal constituent of cotton, kapok, flax, hemp, jute, ramie, and wood. Cellulose comprises more than one-third of all vegetable matter and is the world's largest renewable resource. Much cellulose is derived from woody plants as trees, but more is found as grasses and plants . Approximately 50 billion tons is produced annually by land plants, which absorb 4 × 1020 cal of solar energy. Natural cotton fibers, which are the seed hairs from Gossypium, are about 1–2 cm in length and about 5–20 μm in diameter. The molecules in native cellulose are present in threadlike strands or bundles called fibrils. Cellulose is not found in a pure form but rather it is associated with other materials such as lignin and hemicelluloses. Cotton contains the purest form of cellulose. Wood, in its dry state, contains 40%–55% cellulose, 15%–35% lignin, and 25%–40% hemicellulose.

Figure 4.6 Sources of cellulose

- **Pulping**

Plant pulp is the major source of commercial cellulose. The extraction of cellulose from plants is called pulping. Pulping is achieved using thermomechanical, chemical, or mechanical approaches. Plant pulp, from wood, is the major source of nontextile fibers while cotton is the major source of textile fibers.

- **Cotton**

Cellulose in the form of cotton is used in the textile industry in cloths, cartons, carpets, blankets, and sheets. While cotton was once the king of fabrics, it is still the material of choice for two of the most recognized clothing items—the T-shirt

- **Paper**

Paper is made from cellulose. Cellulosic fibers are also used as filter materials in artificial kidneys and reverse osmosis though today most kidney dialysis units use cuprammonium tubular films derived from cellulose rather than cellulose itself. While the celluloses are often largely linear, they are not soluble in water because of the presence of strong intermolecular hydrogen bonding and sometimes the presence of a small amount of cross-linking. Most of these cellulosic fibers are randomly oriented, but a small percentage are preferentially oriented in one direction because the paper is made from a cellulose-derived watery slurry with the water largely removed through the use of heated rollers that somewhat orient the fibers. Modern paper is made from wood pulp, largely cellulose, which is obtained by the removal of lignin from debarked wood chips by use of chemical treatments with sodium hydroxide, sodium sulfite, or sodium sulfate.

- **Inorganic esters**

The most widely used so-called inorganic ester of cellulose is “cellulose nitrate” (CN), also called nitrocellulose and gun cotton. Celluloid is produced from a mixture of CN and camphor. It was the first “synthetic” cellulose recognized product. Initially, CN was used as a military explosive and improvements allowed the manufacture of smokeless powder

- **Organic esters**

The most important cellulose ester is “cellulose acetate” because of its use in

fibers and plastics. They were first made in 1865 by heating cotton with acetic anhydride. Varying properties are achieved by varying the amount of substitution. The melting point generally decreases with decreasing acetylation..

4.4.6Starch

Cellulose is the major structural polysaccharide, plant energy storage and regulation utilizes a combination of similar polysaccharides that combined are referred to as starch. Starch can be divided into two general structures:

- Branched amylopectin
- Linear amylose.

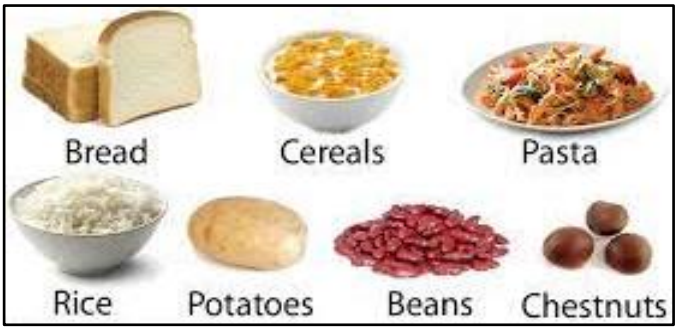


Figure 4.7 Sources of starch

Linear amylose Most starches contain about 10%–20% amylose and 80%–90% amylopectin though the ratio can vary greatly. While cellulose can be considered a highly regular polymer of d-glucose with units linked through a β-1,4 linkage, amylose is a linear polysaccharide with glucose units linked in an α-1,4-fashion while amylopectin contains glucose units with chains of α-1,4 glucopyranosyl units but with branching occurring every 20–30 units, with the chain branch occurring from the 6 position. While this difference in orientation is how the glucose units are connected appears small, it causes great differences in the physical and biological properties of cellulose and starch. People contain enzymes that degrade the α-glucose units but we are unable to digest β units. Thus, starch is a food source for us, but cellulose is not.

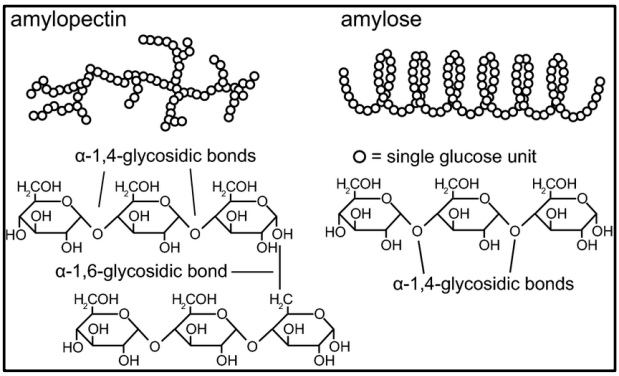


Figure 4.8 Structure of amylose and amylopectin

4.4.7Other polysaccharides

The best-known homopolysaccharides are derived from d-glucose and known as glucans. Glucose has a number of reactive sites and a wide variety of polymers formed utilizing combinations of these reactive sites are found in nature

- **Glycogen**

Glycogen is a very highly branched glucan or polysaccharide formed from glucose. It is structurally similar to amylopectin though more highly branched. This greater branching gives glycogen a greater water solubility. Glycogens are the principal carbohydrate food reserve materials in animals. They are found in both invertebrates and vertebrates and likely found in all animal cells. The highest concentration of glycogen is found in muscle with the greatest amount found in our liver, the tissue from which it is most often isolated.

- **Dextrans**

Dextrans are high-molecular-weight-branched extracellular polysaccharides synthesized by bacteria. These bacteria are found in many places including the human mouth where they flourish on sucrose-containing food that becomes trapped between our teeth.

- **Chitin**

Chitin is generally a homopolymer of 2-acetamido-2-deoxy-d-glucose (N-

acetylglucosamine) 1 → 4 linked in a β configuration; it is thus an amino sugar analog of cellulose.Naturally Occurring Polymers distributed in bacteria and fungi, the major source is crustaceans. In fact, chitin is the most abundant organic skeletal component of invertebrates.

- **Chitosan**

Chitosan is produced from the deacetylation of chitin. Chitosan is employed in the food industry. It is a hemostatic from which blood anticoagulants and antithrombogenic agents have been formed. It is often sold as a body fat reducing agent or to be taken along with eating to encapsulate fat particles.

- **Heparin**

Glycosaminoglycans are polysaccharides that contain amino sugar units. Most are of animal origin. Heparin is complex containing d-glucuronic acid, l-iduronic acid, and d-glucosamine units. It is found in the lung, liver, and arterial walls of mammals

- **Hyaluronic acid**

Hyaluronic acid is found in the connective tissues, umbilical cords, and skin, and it is the synovial fluid of joints. It can have very large molecular weights, to 107 Da making solutions of hyaluronic acid quite viscous. They can form gels. As a synovial fluid in joints, it acts as a lubricant and in the cartilage, it may also act, along with chondroitin sulfates, as a shock absorber.

- **Chondroitin sulfates**

Chondroitin sulfates are found in the bone, skin, and cartilage but not as a free polysaccharide. Rather, it exists as proteoglycan complexes where the polysaccharide is covalently bonded to a protein. The proteoglycan of cartilage contains about 10% protein, keratan sulfate, and chondroitin sulfate, mainly the 4-sulfate in humans. The function of proteoglycan in cartilage is similar to that of noncellulosic polysaccharides and protein in plant cell walls.

- **Arabinogalactans**

Arabinogalactans contain unmodified galactose and is contained in many plant gums and carrageenan and agar. Seaweeds represent a source of many polysaccharides including alginic acid, agar, and carrageenan.

Table 4.1 Different food examples containing different sugars components

Class (no. of sugar units)	Subgroup	Components	Food examples
Sugars (1-2)	Monosaccharides	Glucose Galactose Fructose	Honey, agave, molasses, fruit juice
	Disaccharides	Sucrose Lactose Maltose	Sugar cane, milk, yoghurt, germinating grains
	Polyols (sugar alcohols)	Sorbitol Mannitol	Button mushrooms, snow peas, sweet potatoes
Oligosaccharides (3 - 9)	Malto-oligosaccharides	Maltodextrins	Produced by industrial hydrolysis of starch
	Other Oligosaccharides	Raffinose Stachyose Fructooligosaccharides	Plant seeds (e.g., peas, beans, lentils), wheat, rye, asparagus, onions
Polysaccharides (>9)	Starch	Amylose Amylopectin Modified starches	Maize, rice, sorghum, barley
	Nonstarch polysaccharides	Cellulose (insoluble) Hemicellulose (insoluble) Pectins Hydrocolloids	Soluble forms pectins, beta-glucans, mucilates, gums

4.5 Proteins

Many different monodisperse polymers of amino acids, which are essentially components of plants and animals, are called “proteins.” This word is derived from the Greek porteios, “of chief importance.” Twenty different α-amino acids are joined together by peptide linkages and are also called polyamides or polypeptides. The latter term is often used by biochemists to denote oligomers or relatively low-molecular-weight proteins. They are all alpha-amino acids with the amine and acid moieties occurring on the same alpha carbon.

4.5.1 Isoelectric point

The net ionic charge of an amino acid varies with the charges in the solution pH. The pH at which an amino acid is electrically neutral is called the “isoelectric point.” For simple amino acids (containing only one acid and one

amine), this occurs at a pH of about 6 with the formation of a dipolar or zwitterion . Hence, α-amino acids, like other salts, are water-soluble, high-melting, polar compounds that migrate toward an electrode at pH values other than that of the isoelectric point in a process called electrophoresis.

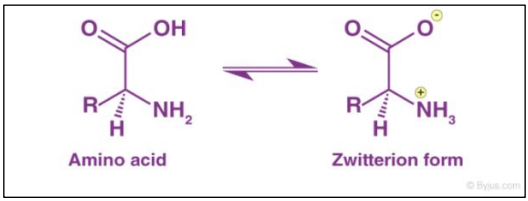


Figure 4.9 Zwitter ion formation

4.5.2 Polypeptides

Sequences for polypeptides, it is usual to use a three-letter abbreviation or a one-letter abbreviation starting with the N-terminus to the left and going to the C–O terminus to the right. It is important to remember that all proteins are polypeptides. The size of proteins is generally noted in either the number of amino acid units or more likely the molecular weight in kilo Daltons (kDa).

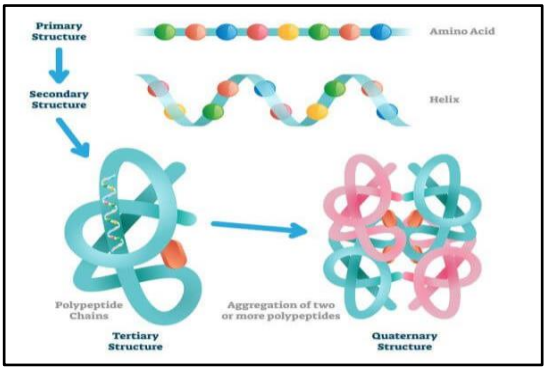


Figure 4.10 polypeptide structure

4.5.3 Synthesis of protein

Proteins are synthesized in nature from the N-terminus to the C-terminus. The amino acids may be neutral, acidic, or basic, in accordance with the relative number of amino and carboxylic acid groups present. Cations can be

formed with amino acids like tryptophane, lysine, histidine, and arginine that have "additional" amine groups, while others that contain "additional" acid groups can be hydrolyzed to form anions like aspartic acid and glutamic acid. The presence of varying amounts of these amino acid moieties within a protein is primary a driving force for the separation of proteins using electrophoresis and results in polypeptides having different isoelectric points. If there are a number of acidic and/or basic groups on the polypeptide, the molecule is said to be a polyampholyte or if they contain only positive or negative charges, they are called "polyelectrolytes." The behavior of these charged polypeptides is similar to the behavior of other charged polymers. Thus, a fully hydrolyzed poly(acrylic acid) acts as a rod because the negative sites repeal one another while a polypeptide with a large number of negative sites will also be elongated. The spacing and number of these charged sites helps determine the tertiary structure of such polypeptides. Even though the atoms within a peptide bond are coplanar, they can exist in two possible configurations, cis and trans. The trans form is usually favored whenever there is a bulky group on the adjacent alpha carbon(s) because the bulky groups offer less steric hindrance in the trans structure. While humans synthesize about a dozen of the 20 amino acids needed for good health, the other 8 are obtained from outside our bodies, generally from eating foods that supply these essential amino acids.

4.5.4 Sources

Different foods are good sources of different amino acids. Cereals are generally deficient in lysine. Thus, diets that emphasize cereals will also have other foods that can supply lysine.

4.5.5 Primary structure

The term primary structure is used to describe the sequence of amino acid units (configuration) in a polypeptide chain.

4.5.6 Secondary structure

The term "secondary structure" is used to describe the molecular shape or conformation of a molecule. For proteins, it is the amino acid sequence. Hydrogen bonding is also an important factor in determining the secondary structures of natural materials and synthetic materials that can hydrogen bond. In fact, for proteins, secondary structures are generally those that allow

a maximum amount of hydrogen bonding. This hydrogen bonding also acts to stabilize the secondary structure, while cross-linking acts to lock in a structure. In nature, the two most common secondary structures are helices and sheets. In nature, extended helical conformations appear to be utilized in two major ways: to provide linear systems for the storage, duplication, and transmission of information (DNA, RNA) and to provide inelastic fibers for the generation and transmission of forces (F-actin, myosin, and collagen). Generally, these helices are readily soluble in dilute aqueous solution. Often, solubility is only achieved after the inter- and intra-hydrogen bonding is broken. There are a variety of examples in which linear or helical polypeptide chains are arranged in parallel rows.

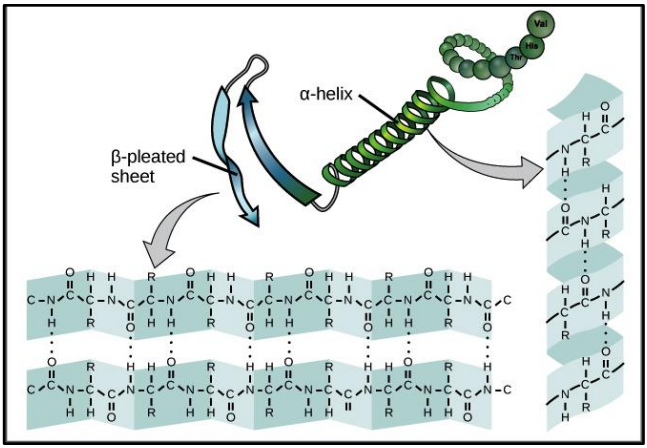


Figure 4.11 Secondary structure of protein

The structure of proteins generally falls into three groupings: fibers, membrane, and globular. The structural proteins such as the keratins, collagen, and elastin are largely fibrous. A reoccurring theme with respect to conformation is that the preferential secondary structures of fibrous synthetic and natural polymers approximate that of a pleated sheet (or skirt) or helix.For proteins, that configuration is described as an l-configuration, with the helix being a “right-handed” helix. This right-handed helix is referred to as an “alpha helix.”

- **Keratins**

Keratins are structural proteins. As noted earlier, two basic “ordered”

secondary structures predominate in synthetic and natural polymers. These are the helices and the pleated sheet structures. Hydrogen bonding occurs within a single strand, whereas in the sheets, the hydrogen bonding occurs between adjacent chains. Helices are often described in terms of a repeat distance, the distance parallel to the axis in which the structure repeats itself; pitch, the distance parallel to the helix axis in which the helix makes one turn; and rise, the distance parallel to the axis from the level of one repeat unit to the next . Helices generally do not have an integral number of repeat units or residues per turn. The alpha helix repeats after 18 amino acid residues taking five turns to repeat. Thus, the number of residues per turn is 18/5 = 3.6 residues/turn. For some polypeptides, each carbonyl oxygen is hydrogen bonded to the amino proton on the fourth residue giving a "hydrogen-bonded loop" with 13 atoms. Helices are often described in terms of this number, n. Because hydrogen bonds tend to be linear, the hydrogen bonding in proteins approximate this with the –N–H…… O=C in a straight line. The "rise," h, of alpha-keratin is found by x-ray spectroscopy to be about 0.15 nm for each amino acid residue. The pitch, p, of a helix is given by p = nh. For alpha-keratin, p = 3.6 amino acid residues/turn × 0.15 nm/amino acid residue = 0.54 nm/turn. Hair and wool are composed of alpha-keratin. A single hair on our head is composed of many strands of keratin. Coiled, alpha helices, chains of alpha-keratin intertwine to form protofibrils that in turn are clustered with other protofibrils forming a microfibril. Hundreds of these microfibrils, in turn, are embedded in a protein matrix giving a macrofibril that in turn combines giving a human hair. While combing will align the various hairs in a desired shape, after a while, the hair will return to its "natural" shape through the action of the sulfur cross-links pulling the hair back to its original shape. Secondary bonding is involved in forming the helical structures allowing the various bundles of alpha-keratin to be connected by weak secondary interactions that in turn allow them to readily slide past one another. This sliding or slippage along with the "unscrewing" of the helices allows our hair to be flexible. Some coloring agents and most permanent waving of our hair involve breakage of the sulfur cross-links and a reforming of the sulfur cross-links at new sites to "lock in" the desired hair shape. Only a fraction of the sulfur cross-links are reformed by the "permanent" so that after some time, the original nonreformed cross-linked sites prevail and the hair returns to its original shape. Our fingernails

are also composed of alpha-keratin, but keratin with a greater amount of sulfur cross-links giving a more rigid material. In general, for both synthetic and natural polymers, increased cross-linking leads to increased rigidity. The other major structural feature of proteins is **pleated sheets**. Two kinds of pleated sheets are found. When the chains have their N → C directions running parallel, they are called parallel beta-sheets. The N → C directions can run opposite to one another giving what is called an antiparallel beta-sheet. The beta-keratin that occurs in silk produced by insects and spiders is of the antiparallel variety. While alpha-keratin is especially rich in glycine and leucine, beta-keratin is mostly composed of glycine and alanine with smaller amounts of other amino acids including serine and tyrosine. Size-wise, leucine offers a much larger grouping attached to the alpha carbon than does alanine. The larger size of the leucine causes the alpha-keratin to form a helical structure to minimize steric factors.

By comparison, the smaller size of the alanine allows the beta-keratin to form sheets. This sheet structure is partially responsible for the "softness" felt when we touch silk. While silk is not easily elongated because the protein chains are almost fully extended, beta-keratin is flexible because of the low secondary bonding between sheets allowing the sheets to flow past one another.

In the silk fibroin structure, almost every other residue is glycine with either alanine or serine between them allowing the sheets to fit closely together. While most of the fibroin exists as betasheets, regions that contain more bulky amino acid residues interrupt the ordered beta-structure. Such disordered regions allow some elongation of the silk. Thus, in the crystalline segments of silk fibroin, there exists directional segregation using three types of bonding: covalent bonding in the first dimension, hydrogen bonding in the second dimension, and hydrophobic bonding in the third dimension. The polypeptide chains are virtually fully extended; there is a little puckering to allow for optimum hydrogen bonding. Thus, the structure is not extensible in the direction of the polypeptide chains.

By comparison, the less specific hydrophobic (dispersive) forces between the sheets produce considerable flexibility. The crystalline regions in the polymers are interspersed with amorphous regions in which glycine and alanine are replaced by amino acids with bulkier pendant groups that prevent

ordered arrangements from occurring. Furthermore, different silkworm species spin silks with differing amino acid compositions and thus, with differing degrees of crystallinity.

The composition within a spider web is not all the same. We can look briefly at two of the general types of threads. One is known as the network or frame threads also called the dragline fabric. It is generally stiff and strong.

- **Kevlar**

The second variety is the catching or capture thread that is made of viscid silk that is strong, stretchy, and covered with droplets of glue. which is used in bullet-resistant clothing, has less energy-absorbing capacity in comparison to either frame or capture threads. In fact, when weight is dropped onto frame silk, it adsorbs up to ten times more energy than Kevlar.

- **Wool**

Wool, while naturally existing in the helical form, forms a pleated skirt sheetlike structure when stretched. If subjected to tension in the direction of the helix axes, the hydrogen bonds parallel to the axes are broken and the structure can be irreversibly elongated to an extent of about 100%. Wool is the fiber from members of the Caprinae family that includes sheep and goats.

4.5.7 Tertiary structure

The term “tertiary structure” is used to describe the shaping or folding of macromolecules. These larger structures generally contain elements of the secondary structures. Often, hydrogen bonding, salt bridges, post-translational modifications, and disulfide cross-linking lock in such structures. As noted earlier, proteins can be divided into three broad groups—fibrous or fibrillar proteins, membrane proteins, and globular proteins.

4.5.8Globular proteins

There is a wide variety of the so-called globular proteins. Almost all globular proteins are soluble in acidic, basic, or neutral aqueous solutions. Many globular proteins are enzymes. Many of these have varieties of alpha- and beta-structures imbedded within the overall globular structure. Beta-sheets are often twisted or wrapped into a “barrel-like” structure. They contain portions that are beta-sheet structures and portions that are in an alpha-

conformation. Further, some portions of the globular protein may not be conveniently classified as either an alpha- or beta-structure. These proteins are often globular in shape so as to offer a different "look" or polar nature to its outside.

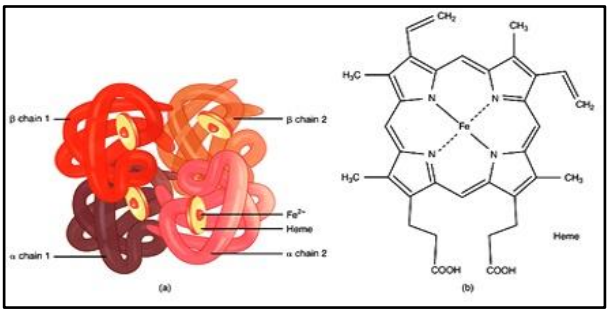


Figure 4.12 Globular protein structure

The energy factors include charge–charge interactions, hydrogen bonding, van der Waals interactions, and hydrophilic/hydrophobic effects. Within a particular globular polymer, there may be one or more polypeptide chain folded backward and forward forming quite distinct structural domains. Each domain is characterized by a particular style of coiling or "sheeting" that may be nonrepetitive with respect to its peptide chain geometry or may be repetitive, conforming to one of several now well-recognized patterns. The specific chain conformations are determined by the side-chain interactions of the amino acids superimposed on intra-peptide hydrogen bonding along the chain. The form of chain folding is thus ultimately determined by the amino acid sequence and the polymeric nature of the polypeptide chains and is fundamental to the specific geometry of the given protein. Protein units can be either negatively or positively charged. Attractions between unlike charges are important as are the repulsions between like changed units. As expected, these associations are pH dependent and are one route for conformation changes to occur.

The ability to hydrogen bond is also an important factor with respect to the internal folding scheme. Because the proteins are tightly packed, the weak van der Waals interactions can also play an important role in determining chain folding. The tendency for polarity-like segments to congregate can also be an important factor in chain folding. Thus, hydrophilic groupings

generally are clustered to the outside of the globular protein allowing them to take advantage of hydrogen bonding and other polar-bonding opportunities, while hydrophobic clusters of amino acid units occupy the internal regions of the protein taking advantage of hydrophobic interactions. Globular proteins act in maintenance and regulatory roles—functions that often require mobility and thus some solubility. Included within the globular grouping are enzymes, most hormones, hemoglobin, and fibrinogen that are changed into an insoluble fibrous protein fibrin that causes blood clotting. Denaturation is the irreversible precipitation of proteins caused by heating, such as the coagulation of egg white as an egg is cooked, or by addition of strong acids, bases, or other chemicals.

4.5.9 Fibrous proteins

Fibrous proteins are long macromolecules that are attached through either inter- or intrahydrogen bonding of the individual residues within the chain. Solubility, partial or total, occurs when these hydrogen bonds are broken. In general, they confer stiffness and rigidity to biological systems that are themselves fluid. Fibrous proteins are found in animals. They appear as filaments and are often formed from a limited number of amino acid units. They are generally insoluble in water with hydrophobic portions protruding from the central core. Examples are collagen, elastin, and keratin. Actin and tubulin are globular soluble monomers that polymerize forming long stiff structures that make up the cytoskeleton that allows cells to maintain their shape. Structural proteins are used to construct tendons, bone matrices, connective tissues, and muscle fiber. They can also be used for storage. They are not as easily denatured as globular proteins. Some structural proteins, such as kinesin, dynein, and myosin, serve as the so-called motor proteins that can generate mechanical forces as muscles and are involved in allowing the movement of cells such as the sperm cell involved in sexual reproduction in multicellular organisms.

Collagen is the most abundant single protein in vertebrates making up to one-third of the total protein mass. Collagen fibers form the matrix or cement material in our bones where mineral materials precipitate. Collagen fibers constitute a major part of our tendons and act as a major part of our skin. Hence, it is collagen that is largely responsible for holding us together. Collagen is also widely used in foods under the name gelatin . The basic

building block of collagen is a triple helix of three polypeptide chains called the "tropocollagen unit." Each chain is about 1000 residues long. The individual collagen chains form left-handed helices residues per turn. In order to form this triple-stranded helix, every third residue must be glycine because it offers a minimum of bulk. Another interesting theme in collagen is the additional hydrogen bonding that occurs because of the presence of hydroxyproline derived from the conversion of proline to hydroxyproline. The conversion of proline to hydroxyproline involves vitamin C. Interestingly, scurvy, the consequence of a lack of vitamin C, is a weakening of collagen fibers giving way to lesions in the skin and gums and weakens blood vessels. Collagen fibers are strong. In tendons, the collagen fibers have strength similar to that of hard-drawn copper wire. Much of the toughness of collagen is the result of the cross-linking of the tropocollagen units to one another through a reaction involving lysine side chains. Lysine side chains are oxidized to aldehydes that react either with a lysine residue or with one another lysine through an aldol condensation and dehydration resulting in a cross-link. This process continues throughout our life resulting in our bones and tendons becoming less elastic and more brittle. Again, a little cross-linking is essential, but more cross-linking leads to increased fracture and brittleness. Collagen is a major ingredient in some "gelation" materials.

- **Elastin**

Collagen is found where strength is needed, but some tissues, such as arterial blood vessels and ligaments, need materials that are elastic. Elastin is the protein of choice for such applications. Elastin is rich in glycine, alanine, and valine and it is easily extended and flexible. Its conformation approaches that of a random coil so that secondary forces are relatively weak allowing elastin to be readily extended as tension is applied. The structure also contains some lysine side chains that are involved in cross-linking. The cross-linking is accomplished when four lysine side chains are combined to form a desmosine cross-link. This cross-link prevents the elastin chains from being fully extended and causes the extended fiber to return to its original dimensions when tension is removed. One of the areas of current research is the synthesis of polymers with desired properties based on natural analogs.

4.5.10 Membrane proteins

Membrane proteins are attached to or associated with the membrane of a cell.

More than half of the proteins interact with these membranes. Membrane proteins are generally divided according to their attachment to a membrane. Transmembrane proteins span the entire membrane. Integral proteins are permanently attached to only one side of membranes. Peripheral membrane proteins are temporarily attached to integral proteins or lipid bilayers through combinations of noncovalent bonding such as hydrophobic and electrostatic bonding. These membranes often act as receptors or provide channels for charged or polar molecules to pass through them.

4.5.11 Quaternary structure

The term quaternary structure is employed to describe the overall shape of groups of chains of proteins or other molecular arrangements. For instance, hemoglobin is composed of four distinct but different myoglobin units, each with its own tertiary structure that comes together giving the hemoglobin structure. Both synthetic and natural polymers have superstructures that influence/dictate the properties of the material. Many of these primary, secondary, tertiary, and quaternary structures are influenced in a similar manner. Thus, primary structure is a driving force for secondary structure. Allowed and preferred primary and secondary bonding influence structure. For most natural and synthetic polymers, hydrophobic and hydrophilic domains tend to cluster. Thus, most helical structures will have either a somewhat hydrophobic/hydrophilic inner core or the opposite outer core resulting from a balance between secondary and primary bonding factors and steric and bond angle constraints. Globular proteins have irregular 3D structures that are compact but which when brought together form quaternary structures that approach being spherical. While the overall structure is spherical, the surface is irregular, with the irregularity allowing the proteins to perform specific biological functions. The preferred folding confirmation is again influenced by the same factors of bonding type, polarity, size, flexibility, and preferred bond angles. The folded conformations are possible because of the flexibility of the primary bonding present within proteins. Thus, polar portions, namely, the amine and carbonyl moieties, are more fixed, but the carbon between them is more flexible. Again, the folding characteristic conformations are driven by secondary bonding. Some folding is chemically “fixed” through use of cross-links. In hair, these cross-links are often disulfides, –S–S–. As noted before, the flexibility of proteins allows them to carry out a wide variety of tasks and the building sites of proteins

produce a variety of different proteins. Our cells often build about 60,000 different kinds of proteins. By comparison, a bacterial cell will synthesize only a little over 1000 different kinds of proteins. When a protein contains roughly more than about 200 amino acid groups, it often assumes two or more somewhat spherical tertiary structural units. These units are often referred to as domains. Thus, hemoglobin is a combination of four myoglobin units with each of the four units influenced by the other three and where each unit contains a site to interact with oxygen. The specificity of enzymatic catalytic activity is dependent on tertiary structure. Phosphoglycerate kinase is a protein composed of 415 amino acids. The protein chain is folded back and forward forming a claw-like structure that has two rigid domains divided by a more flexible hinge region.

4.6 Nucleic acids

The name "nuclein" was coined by Miescher to describe products isolated from the nuclei in pus. This name was later changed to nucleic acid. Our modern knowledge of heredity and molecular biology is based on our knowledge of nucleic acids. The human genome is composed of nature's most complex, exacting, and important macromolecule. It is composed of nucleic acids that appear complex in comparison to simpler molecules such as methane and ethylene. Major part of skin, teeth, bones, cartilage, and tendon Fibroin Varies with source, fibrous linear with cross-links.

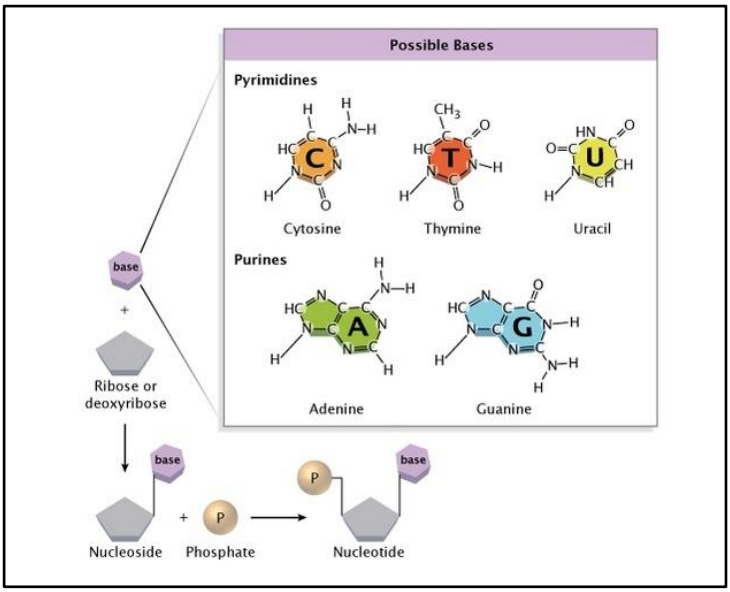


Figure 4.13 structure of DNA

4.6.1 Structure

Each unit is essentially the same containing a phosphate and a deoxyribose sugar and one of four bases with each base typically represented by the capital of the first letter of their name, G, C, A, and T. In fact, the complexity is less than having four separate and independent bases because the bases come in matched sets, they are paired. The mimetic Gee CAT allows an easy way to remember this pairing (G-C and A-T). The base, sugar, and phosphate combine forming nucleotides such as adenylic acid, adenosine-5′-phosphate, and represented by the symbols A, dA, and dAMP. The backbone of nucleic acids is connected through the 3′ and 5′ sites on the sugar with the base attached at the 1′ site. Because the sugar molecule is not symmetrical, each unit can be connected differently, but there is order (also called sense or directionality) in the sequence of this connection so that phosphodiester linkage between units is between the 3′ carbon of one unit and the 5′ carbon of the next unit. Thus, nucleic acids consist of units connected so that the repeat unit is a 5′–3′ (by agreement, we consider the start to occur at the 5′ and end at the 3′ though we could just as easily by agreement gone in the

opposite direction for our description) linkage. Thus, the two ends are not identical—one contains an unreacted 5′-phosphate and the other an unreacted 3′-unrected hydroxyl. A shorthand is used to describe nucleic acid sequences.

Laureates Watson and Crick correctly deduced that DNA consisted of a double-stranded helix in which a pyrimidine base on one chain or strand was hydrogen bonded to a purine base on the other chain. The bonding distances are not the same with the GC paring more compact. These uneven pairing distances result in a DNA with a characteristic twisting giving unique structures. It is this twisting, and the particular base sequence, that eventually results in the varying chemical and subsequently biological activities for various combinations.

4.6.2 Stability

The stability of the DNA is due to both internal and external hydrogen bonding as well as ionic and other bonding. First, the internal hydrogen bonding is between the complementary purine–pyrimidine base pairs. Second, the external hydrogen bonding occurs with the polar sites along exterior sugar and phosphate moieties and water molecules. Third, ionic bonding occurs between the negatively charged phosphate groups situated on the exterior surface of the DNA and electrolyte cations such as Mg^{2+}. Fourth, the core consists of the base pairs, which, along with being hydrogen bonded, stack together through hydrophobic interactions and van der Waals forces. In order to take good advantage of pi-electron cloud interactions, the bases stack with the flat "sides" over one another so that they are approximately perpendicular to the long axis. The AT and CG base pairs are oriented in such a manner that the sugar-phosphate backbones of the two twined chains are in opposite or antiparallel directions with one end starting at the 5′ and ending at the 3′, and the starting end of the other across from the 5′ end being a 3′ end and opposite the other 3′ end is a 5′ end. Thus, the two chains "run" in opposite directions. The glucose bonds holding the bases onto the backbone are not directly across the helix from one another. Thus, the sugar-phosphate repeat units are not the same. This dislocation creates structures referred to as major and minor grooves. It is known that at least some proteins that bind to DNA recognize the specific nucleotide sequences by "reading" the hydrogen bonding pattern presented by the edges of these grooves. In solution, DNA is a dynamic, flexible molecule. It undergoes

elastic motions on a nanosecond time scale most closely related to changes in the rotational angles of the bonds within the DNA backbone. The net result of these bendings and twistings is that DNA assumes a roughly globular or spherical tertiary shape. The overall structure of the DNA surface is not that of a reoccurring “barber pole” but rather because of the particular base sequence composition, each sequence will have its own characteristic features of hills, valleys, bumps, etc. As the two strands in a double helix separate, they act as a template for the construction of a complementary strand. This process occurs enzymatically with each nucleotide being introduced into the growing chain through matching it with its complementary base on the existing chain. Thus, two identical strands are produced when one double-helix combination replicates. DNA chains can contain 1 million subunits with an end-to-end contour length of about 1 mm. Even with the complexity of these large macromolecules, synthesis of new chains generally occurs without any change in the molecule.

The transcription product of DNA is always single-stranded RNA. The single strand generally assumes a right-handed helical conformation mainly caused by base-stacking interactions also present in the DNA. The order of interaction is purine–purine ≫ purine–pyrimidine > pyrimidine–pyrimidine. The purine–purine interaction is so strong that a pyrimidine separating two purines is often displaced from the stacking order to allow the interaction between the two purines to occur. Base paring is similar to that of the DNA except that uracil generally replaces thymine. For coupled RNA, the two strands are antiparallel as in DNA. Where complementary sequences are present, the predominant double-stranded structure is an A form right-handed double helix. Many RNAs are combinations of complementary two-stranded helices, singlestranded segments, and other complex structures. Hairpin curves are the most common type of more complex structure in RNA. Specific sequences, such as UUCG, are generally found at the ends of RNA hairpin curves. Such sequences can act as starting points for the folding of an RNA into its precise 3D structure. where the protein can act as a clamp or vice holding the various important members involved with the particular reproduction step in place. Thus, the protein complex acts as an assembly line tunnel or doughnut with the reactants present within the interior. There are two types of cells. Prokaryote cells lack a cell nucleus or any other membrane-bound organelles. Most organisms possessing prokaryote cells

are single celled. Bacteria and archaea are examples of organisms with prokaryote cells. Eukaryote cells possess enclosed membranes and form the basis of animals, plants, and fungi. In prokaryote cells, the mRNA can be used immediately after it is produced or it may be bound to a ribosome. In comparison, in eukaryote cells, mRNA is made in the cell nucleus and it can be moved across the nuclear membrane after it is synthesized into the cytoplasm where protein synthesis occurs.

4.6.3 Flow of biological information

Nucleic acids, proteins, some carbohydrates, and hormones are informational molecules. They carry directions for the control of biological processes. With the exception of hormones, these are macromolecules. In all these interactions, secondary forces such as hydrogen bonding and van der Waals forces, and ionic bonds and hydrophobic/hydrophilic character play critical roles. Molecular recognition is the term used to describe the ability of molecules to recognize and interact (bond) specifically with other molecules. This molecular recognition is based on a combination of these interactions just cited and on structure. Molecular recognition interactions have several common characteristics. First, the forces that are involved in these interactions are relatively weak and they are noncovalent. They are on the order of about 1–8 kcal/mol (4–30 kJ/mol) compared to covalent bonds of the order of about 80 kcal/mol (300 kJ/mol) for a C–C sigma bond. A single secondary bond is generally not capable of holding molecules together for any length of time. But for macromolecules, there is a cumulative effect so that the forces are not singular but are multiplied by the number of such interactions that are occurring within the particular domain. Second, these interactions are reversible. Initial contact occurs as the molecules come into contact with one another often through simple diffusion or movement of the molecules or segments of the molecules. These initial contacts are often not sufficient to cause the needed binding though some transitory interactions occur. Even so, in some cases, the cumulative bonding is sufficient to allow a transient but significant interaction to occur. This complex can then begin a specific biological process. Eventually, thermal motions and geometrical changes cause the complex to dissociate. Ready reversibility is an important key that allows a relatively few “signaling” molecules to carry out their mission. Third, bonding between the particular molecular sites is specific. There must exist a combination of complementary bonding,

hydrophobic/hydrophilic sites, ionic charge, and geometry that allow effective long-term (generally no more than several seconds) interactions to occur. In general, the flow of biological information can be mapped as follows: DNA → RNA → Protein → Cell structure and function The total genetic information for each cell, called the "genome," exists in the coded two-stranded DNA. This genetic information is expressed or processed either through duplication of the DNA so it can be transferred during cell division to a daughter cell or it can be transferred to mRNA that in turn transfers the information to proteins that carry out the activities of the cell. Duplication of double-stranded DNA is self-directed.

Table 4.1applications of DNA

Purpose	Target sample	Multiplexed reactions	Demultiplexing probes on array
Expression profiling	mRNA or totRNA from relevant cell cultures or tissues	Amplification of all mRNAs via some combination of RT/PCR/IVT	Single- or double-stranded DNA complementary to target transcripts
Pathogen detection and characterization	Genomic DNA from microbes	Random-primed PCR, or PCR with selected primer pairs for certain target regions	Sequences complementary to preselected identification sites
Genotyping	Genomic DNA from humans or animals	Ligation/extension for particular SNP regions, and amplification	Sequences complementary to expected products
Resequencing	Genomic DNA	Amplification of selected regions	Sequences complementary to each sliding N-mer window along a baseline sequence and also to the three possible mutations at the central position
Find protein-DNA interactions	Genomic DNA	Enrichment based on transcription factor binding	Sequences complementary to intergenic regions

The DNA, along with accessory proteins, directs the replication or construction of two complementary strands forming a new, exact replicate of the original DNA template. As each base site on the DNA becomes available through the unraveling of the double-stranded helix, a new nucleotide is brought into the process held in place by hydrogen bonding and van der Waals forces so that the bases are complementary. It is then covalently bonded through the action of an enzyme called DNA polymerase. After

duplication, each DNA contains one DNA strand from the original double-stranded helix and one newly formed DNA strand. This is called "semiconservative replication" and increases the chance that if an error occurs, the original base sequence will be retained. How is DNA suitable as a carrier of genetic information? While we do not entirely understand, several features are present in DNA. First, because of the double-stranded nature and mode of replication, retention is enhanced. Second, DNA is particularly stable within both cellular and extracellular environments, including a good stability to hydrolysis within an aqueous environment. Plant and animal DNA have survived thousands of years. Using polymerase chain reactions (PCRs), we can reconstruct DNA segments allowing comparisons to modern DNA. The genome is quite large, on the order of a millimeter in length if unraveled, but within it exists coding regions called genes.

CHAPTER 5

Inorganic polymers

5.0 Physical aspects of polymers Molecular forces and chemical bonding in polymers

Inorganic polymer, any of a class of large molecules that lack carbon and are polymers—that is, made up of many small repeating units called monomers. The word polymer is derived from the Greek term poly, meaning many, and meros, which means part. Nature abounds with carbon-based (that is, organic) polymers, such as wool, silk, proteins, starch, and cellulose. In addition, rubber and plastic are made of a wide variety of man-made organic polymers. But many inorganic compounds, such as oxyacids and oxy-anions, also form polymers. This is especially true of weak acids, such as boric acid, H3BO3, and silicic acid, H4SiO4. In the anions of weak acids, a high density of negative charge resides on the oxygen atoms. This charge density can be reduced by the process of polymerization.

5.1 Examples

Examples of inorganic polymers include polysilanes (Si–Si bonds), polysiloxanes (Si–O bonds, or silicones), polysilazanes (Si–N bonds), polysulfides (S–S bonds), polyphosphazenes (P–N bonds), polyborazylenes (B–N bonds), and polythiazyls (S–N bonds)

5.2 Polyphosphazenes

Poly phosphorene's include a wide range of hybrid inorganic-organic polymers with a number of different skeletal architectures with the backbone P-N-P-N-P-N-. In nearly all of these materials two organic side groups are attached to each phosphorus center. Linear polymers have the formula $(N=PR^1R^2)_n$, where R^1 and R^2 are organic . Other architectures are cyclolinear and cyclomatrix polymers in which small phosphazene rings are connected together by organic chain units. Other architectures are available, such as block copolymer, star, dendritic, or comb-type structures. More than 700 different polyphosphazenes are known, with different side groups (R) and different molecular architectures.

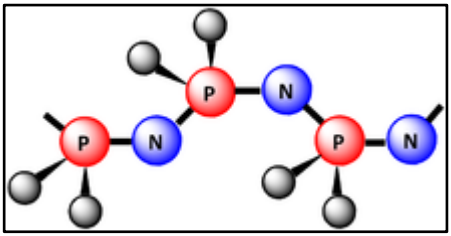


Figure 5.1 structure of polyphosphazene

5.2.1 Synthesis

The method of synthesis depends on the type of polyphosphazene. The most widely used method for linear polymers is based on a two-step process. In the first step, hexachlorocyclotriphosphazene$(NPCl_2)_3$ is heated in a sealed system at 250 °C to convert it to a long chain linear polymer with typically 15,000 or more repeating units. In the second step the chlorine atoms linked to phosphorus in the polymer are replaced by organic groups through reactions with alkoxides, aryl oxides, amines or organometallic reagents.

Because many different reagents can participate in this macromolecular substitution reaction.

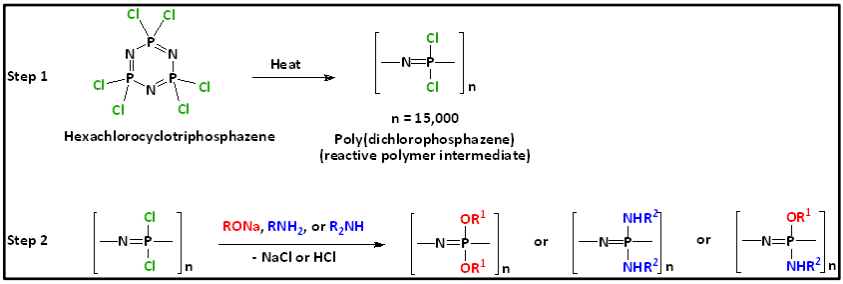


Figure 5.2 poly phosphazene synthesis

5.2.2 Properties and uses

More than 700 different macromolecules that correspond to e groups or combinations of different side groups. In these polymers the properties are defined by the high flexibility of the backbone. Other potentially attractive properties include radiation resistance, high refractive index, ultraviolet and visible transparency, and its fire resistance. The side groups exert an equal

or even greater influence on the properties since they impart properties such as hydrophobicity, hydrophilicity, color, useful biological properties such as bio erodibility, or ion transport properties to the polymers

- **Thermoplastics**

The first stable thermoplastic poly(organophosphazenes), isolated by Allcock, Kugel, and Valan, were macromolecules with trifluoroethoxy, phenoxy, methoxy, ethoxy, or various amino side groups. Of these early species, poly[bis(trifluoroethoxyphosphazene], $[NP(OCH_2CF_3)_2]_n$, has proved to be the subject of intense research due to its crystallinity, high hydrophobicity, biological compatibility, fire resistance, general radiation stability, and ease of fabrication into films, microfibers and nanofibers. It has also been a substrate for various surface reactions to immobilize biological agents.

- **Phosphazene elastomers**

The first large-scale commercial uses for linear polyphosphazenes were in the field of high technology elastomers, with a typical example containing a combination of trifluoroethoxy and longer chain fluoroalkoxy groups. The mixture of two different side groups eliminates the crystallinity found in single-substituent polymers and allows the inherent flexibility and elasticity to become manifest. Glass transition temperatures as low as -60 °C are attainable, and properties such as oil-resistance and hydrophobicity are responsible for their utility in land vehicles and aerospace components. They have also been used in bio stable biomedical devices.

- **Polymer electrolyte**

Linear polyphosphazenes with oligo-ethyleneoxy side chains are gums that are good solvents for salts such as lithium triflate. These solutions function as electrolytes for lithium ion transport, and they were incorporated into fire-resistant rechargeable lithium-ion polymer battery. The same polymers are also of interest as the electrolyte in dye-sensitized solar cells. Other polyphosphazenes with sulfonated aryloxy side groups are proton conductors of interest for use in the membranes of proton exchange membrane fuel cells.

- **Hydrogels**

Water-soluble poly(organophosphazenes) with oligo-ethyleneoxy side chains can be cross-linked by gamma-radiation. The cross-linked polymers absorb water to form hydrogels, which are responsive to temperature changes, expanding to a limit defined by the cross-link density below a critical solution temperature, but contracting above that temperature.

- **Bioerodible polyphosphazenes**

The ease with which properties can be controlled and fine-tuned by the linkage of different side groups to polyphosphazene chains has prompted major efforts to address biomedical materials challenges using these polymers. Different polymers have been studied as macromolecular drug carriers, as membranes for the controlled delivery of drugs, as biostable elastomers, and especially as tailored bioerodible materials for the regeneration of living bone.Nanofibers and porous constructs of these polymers assist osteoblast replication and accelerate the repair of bone in animal model studies.

- **Commercial aspects**

No applications are commercialized for polyphosphazenes. The cyclic trimer hexachlorophosphazene ($(NPCl_2)_3$) is commercially available. It is the starting point for most commercial developments. High performance elastomers known as PN-F or Eypel-F have been manufactured for seals, O-rings, and dental devices. An aryloxy-substituted polymer has also been developed as a fire resistant expanded foam for thermal and sound insulation.

5.3 Polysiloxane

polysiloxane is a polymer made up of siloxane ($-R_2Si-O-SiR_2-$, where R = organic group). They are typically colorless oils or rubber-like substances. Silicones are used in sealants, adhesives, lubricants, medicine, cooking utensils, thermal insulation, and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk

5.3.1 Chemistry

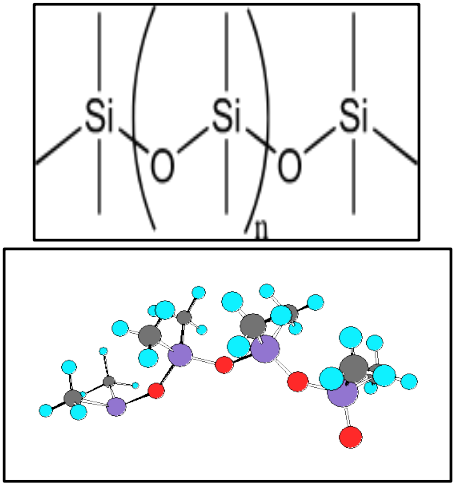


Figure 5.3 structure of polysiloxane

More precisely called polymerized siloxanes or polysiloxanes, silicones consist of an inorganic silicon–oxygen backbone chain (···−Si−O−Si−O−Si−O−···) with two organic groups attached to each silicon center. Commonly, the organic groups are methyl. The materials can be cyclic or polymeric. By varying the −Si−O− chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil. The second-largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligo siloxanes

5.3.2Terminology and history

F. S. Kipping coined the word silicone in 1901 to describe the formula of polydiphenylsiloxane, Ph_2SiO (Ph denoting phenyl, C_6H_5), by analogy with the formula of the ketone benzophenone, Ph_2CO (his term was originally silicoketone). Kipping was well aware that polydiphenylsiloxane is polymeric whereas benzophenone is monomeric and noted the contrasting

properties of Ph_2SiO and Ph_2CO.The discovery of the structural differences between Kipping's molecules and the ketones means that silicone is no longer the correct term (though it remains in common usage) and that the term siloxane is preferred according to the nomenclature of modern chemistry.

5.3.3 Synthesis

Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:

$$n\ Si(CH_3)_2Cl_2 + n\ H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\ HCl$$

The polymerization typically produces linear chains capped with **Si−Cl** or **Si−OH** (silanol) groups. Under different conditions, the polymer is a cyclic, not a chain.

For consumer applications such as caulks silyl acetates are used instead of silyl chlorides. The hydrolysis of the acetates produces the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

$$n\ Si(CH_3)_2(CH_3COO)_2 + n\ H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\ CH_3COOH$$

Branches or crosslinks in the polymer chain can be introduced by using organosilicons precursors with fewer alkyl groups,

5.3.4 Properties

This silicone rubber folding chessboard resists creasing and wrinkling.

Silicones exhibit many useful characteristics, including

- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of −100 to 250 °C)
- The ability to repel water and form watertight seals.

- Does not stick to many substrates, but adheres very well to others, e.g. glass
- Does not support microbiological growth
- Resistance to oxygen, ozone, and ultraviolet (UV) light. This property has led to the widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).
- Electrical insulation properties. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
- High gas permeability: at room temperature (25 °C), the permeability of silicone rubber for such gases as oxygen is approximately 400 times that of butyl rubber, making silicone useful for medical applications in which increased aeration is desired. Conversely, silicone rubbers cannot be used where gas-tight seals are necessary such as seals for high-pressure gasses or high vacuum.

5.3.5 Applications

Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g. insulation), electronics , household (e.g., sealants and cooking utensils), automobile (e.g. gaskets), airplane, office machines (e.g. keyboard pads), medicine and dentistry (e.g. tooth impression molds), textiles and paper (e.g. coatings).

- **Automotive**

Silicone caulks and rubber components are increasingly used in automotive applications.In the automotive field, silicone grease is typically used as a lubricant for brake components since it is stable at high temperatures, is not water-soluble, and is far less likely than other lubricants to foul.

- **Aerospace**

Silicone is often used to seal maintenance access openings in aerospace equipment.

Silicone is a widely used material in the aerospace industry due to its sealing properties, stability across an extreme temperature range, durability, sound dampening and anti-vibration qualities, and naturally flame retardant properties. Maintaining extreme functionality is paramount for passenger safety in the aerospace industry, so each component on an aircraft requires high-performance materials.

- **Building construction**

The strength and reliability of silicone rubber are widely acknowledged in the construction industry. One-part silicone sealants and caulks are in common use to seal gaps, joints and crevices in buildings. One-part silicones cure by absorbing atmospheric moisture, which simplifies installation. In plumbing, silicone grease is typically applied to O-rings in brass taps and valves, preventing lime from sticking to the metal.

- **Coatings**

Silicone films can be applied to such silica-based substrates as glass to form a covalently bonded hydrophobic coating. Such coatings were developed for use on aircraft windshields to repel water and to preserve visibility, without requiring mechanical windshield wipers which are impractical at supersonic speeds. Similar treatments were eventually adapted to the automotive market in products marketed by Rain-X and others.Many fabrics can be coated or impregnated with silicone to form a strong, waterproof composite such as silnylon.

- **Cookware**

As a low-taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cookware industry, particularly bakeware and kitchen utensils. Silicone is used as an insulator in heat-resistant potholders and similar items; however, it is more conductive of heat than similar less dense fiber-based products. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), making it possible to reach into boiling water.

Other products include molds for chocolate, ice, cookies, muffins, and various other foods; non-stick bakeware and reusable mats used on baking sheets; steamers, egg boilers or poachers; cookware lids, pot holders, trivets,

and kitchen mats. Flexible ice cube trays made of silicone allow easy extraction of ice.

- **Defoaming**

Silicones are used as active compounds in defoamers due to their low water solubility and good spreading properties.

- **Dry cleaning**

Liquid silicone can be used as a dry cleaning solvent, providing an alternative to the traditional chlorine-containing perchloroethylene (perc) solvent. The use of silicones in dry cleaning reduces the environmental effect of a typically high-polluting industry.

- **Electronics**

Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration, a process called "potting". Silicones are used where durability and high performance are demanded of components under extreme environmental conditions, such as in space (satellite technology). They are selected over polyurethane or epoxy encapsulation when a wide operating temperature range is required (−65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties, and high purity.

- **Firestops**

Silicone-foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage, and cracking. These problems have led to reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC).Silicone firestops are also used in aircraft.

- **Jewelry**

Silicone is a popular alternative to traditional metals (such as silver and gold) with jewelry, specifically rings. Silicone rings are commonly worn in professions where metal rings can lead to injuries, such as electrical conduction and ring avulsions.

- **Lubricants**

Silicone grease is often used with laboratory glassware to prevent seizing.

Silicone greases are used for many purposes, such as bicycle chains, airsoft gun parts, and a wide range of other mechanisms.

- **Medicine and cosmetic surgery**

Silicone is used in microfluidics, seals, gaskets, shrouds, and other applications requiring high biocompatibility. Additionally, the gel form is used in bandages and dressings, breast implants, testicle implants, pectoral implants, contact lenses, and a variety of other medical uses.

- **Personal care**

Silicones are ingredients widely used in skincare, color cosmetic and hair care applications. Some silicones, notably the amine functionalized amodimethicones, are excellent hair conditioners, providing improved compatibility, feel, and softness, and lessening frizz. The phenyl dimethicones, in another silicone family, are used in reflection-enhancing and color-correcting hair products, where they increase shine and glossiness .

- **Toys and hobbies**

Baby toys made of nontoxic silicone rubber.Silly Putty and similar materials are composed of silicones dimethyl siloxane, polydimethylsiloxane, and decamethyl cyclopentasiloxane, with other ingredients. This substance is noted for its unusual characteristics, e.g., that it bounces, but breaks when given a sharp blow; it will also flow like a liquid and form a puddle given enough time.

CHAPTER 6

Molecular weight determination of polymers

6.0 Molecular weight determination of polymers

There are two possibilities: one has to do with the number of repeat units and the other to the spatial extent. In the former case, the standard term is molecular weight.The degree of polymerization is also commonly used in this context. A variety of experimental techniques are available for determining the molecular weight of a polymer. We shall discuss a few such methods in Section 1.8 and postpone others until the appropriate chapters. The expression molecular weight and molar mass should always be modified by the word average. This too is something we shall take up presently. For now, we assume that a polymer molecule has a molecular weight M, which can be anywhere in the range 10^3—10^7 or more. Since polymer molecules are made up of chains of repeat units, after the chain itself comes the repeat unit as a structural element of importance. Many polymer molecules are produced by covalently bonding together only one or two types of repeat units. These units are the parts from which chains are generated; as a class of compounds they are called monomers.

6.1 Degree of polymerization

The degree of polymerization of a polymer is simply the number of repeat units in a molecule. The degree of polymerization N is given by the ratio of the molecular weight of the polymer to the molecular weight of the repeat unit: M N — M0 .One type of polymerization reaction is the addition reaction in which successive repeat units add on to the chain. No other product molecules are formed, so the molecular weight of the monomer and that of the repeat unit are identical in this case. A second category of polymerization reaction is the condensation reaction, in which one or two small molecules such as water or HCl are eliminated for each chain linkage formed. In this case the molecular weight of the monomer and the repeat unit are somewhat different. For example, suppose an acid (subscript A) reacts with an alcohol (subscript B) to produce an ester linkage and a water molecule. The molecular weight of the ester the repeat unit if an entire chain is built up this way, differs from the combined weight of the reactants by twice the molecular weight of the water; therefore,

$$\mathbf{N} = \frac{\boldsymbol{M}}{\boldsymbol{M0}}$$

6.2 Introduction to Chain Molecules

The end units in a polymer chain are inevitably different from the units that are attached on both sides to other repeat units. We see this situation in the n-alkanes: each end of the chain is a methyl group and the middle parts are methylene groups. Of course, the terminal group does not have to be a hydrogen as in alkanes; indeed, it is often something else. Our interest in end groups is concerned with the question of what effect they introduce into the evaluation of N.

The following example examines this through some numerical calculations. As a polymer prototype consider an n-alkane molecule consisting ofN—2 methylene's and 2 methyl groups. How serious an error is made in M for different Ns if the difference in molecular weight between methyl and methylene groups is ignored? Solution The effect of different end groups on M can be seen by comparing the true molecular weight with an approximate molecular weight, calculated on the basis of a formula (CH2)N.

Table 6.1These Me and the percentage difference between them are listed here for several values of N

N	**M**	**Mapprox**	**% Difference**
3	44	42	4.5
7	100	98	2.0
12	170	168	1.2
52	730	728	0.3
102	1,430	1,428	0.14
502	7,030	7,028	0.028
1002	14,030	14,028	0.014

Although the difference is almost 5% for propane, it is closer to 0.1% for the case of N m 100, which is about the threshold for polymers. The precise

values of these numbers will be different, depending on the specific repeat units and end groups present.

6.3Molecular weight of polymer

It is the size of macromolecules that gives them their unique and useful properties. Size allows polymers to act more as a group so that when one polymer chain moves, surrounding chains are affected by that movement. Size also allows polymers to be nonvolatile since the secondary attractive forces are cumulative (for instance, London dispersion forces are about 8 kJ/mol per repeat unit), and because of the shear size, the energy necessary to volatilize them is sufficient to degrade the polymer. Generally, the larger the polymer, the higher the molecular weight.

The average molecular weight (M) of a polymer is the product of the average number of repeat units or mers expressed as DP times the molecular weight for the repeating unit. Thus, for polyethylene (PE) with an average DP of 100, the average molecular weight is simply 100 units times 28 Daltons/unit = 2800 Dalton's (Da). Note that amu and Dalton's refer to equivalent units.

6.4 Molecular weight distribution

Polymerization reactions, both synthetic and natural (but not for all natural materials such as proteins and nucleic acids), lead to polymers with heterogeneous molecular weights, that is, polymer chains with different numbers of mers. Molecular weight distributions (MWDs) may be rather broad may be mono-, bi-, tri-, or polymodal. A bimodal curve is often characteristic of a polymerization occurring under two different environments. Polymers consisting of chains of differing lengths are called polydisperse, while polymers containing only one chain length, such as specific nucleic acids, are called monodisperse.

6.5 Physical properties and molecular weight relation

Many physical properties are related to molecular weight. The melt viscosity is typically proportional to the 3.4 power of the average chain length; so melt viscosity, η, is proportional to M. Thus, the melt viscosity increases rapidly as the chain length increases, and more energy is required for the processing and fabrication of large molecules.

However, there is a trade-off between molecular weight–related properties

and chain size such that there is a range where acceptable physical properties are present but the energy required to cause the polymers to flow for processing is acceptable. This range is called the "commercial polymer range." Many physical properties tend to level off at some point and increased chain length gives little increase in that physical property. Thus, most commercial polymer ranges include the beginning of this leveling off threshold. While a value above the threshold molecular weight value (TMWV; lowest molecular weight where the desired property value is achieved) is essential for most practical applications, the additional cost of energy required for processing extremely high polymer molecular weights is seldom justified. Accordingly, it is customary to establish a commercial polymer range above the TMWV but below the extremely high-molecular-weight range.

However, it should be noted that since toughness increases with chain length, extremely high-molecular-weight polymers, such as ultrahigh molecular weight polyethylene (UHMPE), are used for the production of tough articles such as waste barrels. Some properties are not as sensitive to molecular weight such as heat capacity, refractive index, and density. Even so, many important properties are related to chain length. Oligomers and other low-molecular-weight polymers are not useful for applications where high strength is required. The value of TMWV is dependent on Tg, the cohesive energy density (CED) of amorphous polymers, the extent of crystallinity in crystalline polymers, and the effect of reinforcements in polymeric composites. Thus, while a low-molecular-weight amorphous polymer may be satisfactory for use as a coating or adhesive, a chain length generally above 100 may be required if the polymer is to be used as an elastomer or plastic.

6.6 Average molecular weight values

Small molecules, such as benzene and glucose, have precise structures such that each molecule of benzene has six carbon atoms and six hydrogen atoms. By comparison, each molecule of poly-1,4-phenylene may have a differing number of benzene-derived units, while single molecules (single chains) of PE may vary in the number of ethylene units, the extent and frequency of branching, the distribution of branching, and the length of branching.

A few polymers, such as nucleic acids and many proteins, consist of

molecules, individual polymer chains that must not vary, so they have a precise molecular weight. The concept of averaging in chemistry is not new. The atomic weights that appear in the periodic table are averages dependent on the natural abundances of various isotopes. In a similar way, the molecular weights of polymeric materials that contain chains of varying chain lengths is also an average dependent on the abundance of the various chain lengths present in the mixture.

While there are several statistically described averages dependent on how we calculate the final average molecular weight from the chain lengths of the individual molecules within the polymer sample, we will concentrate on the two that are most germane to polymers.The number-average value, corresponding to a measure of chain length average, is called the number-average molecular weight, Mn. Physically, the number-average molecular weight can be measured using any technique that counts the molecules, that is, is directly dependent on the number of chains. The number-average value, corresponding to a measure of chain length average, is called the number-average molecular weight, Mn. Physically, the number-average molecular weight can be measured using any technique that counts the molecules, that is, is directly dependent on the number of chains. Here, each capsule contains one polymer chain. All of the capsules are the same size, regardless of the size of the polymer chain. Capsules are then withdrawn, opened, and the individual chain length measured and recorded. A graph can be constructed from the data with the maximum value being the numberaverage molecular weight. The probability of drawing a particular capsule is dependent on the number of each capsule and not on the size of the chain within the capsule.

6.7 Weight-average molecular weight

The weight-average molecular weight, Mw, is similarly described, except that the capsule size corresponds to the relative size of polymer chain contained within it. In this approach, the probability of drawing out a particular chain length is dependent on the size of the capsule as well as the number of capsules of that size. Larger chains have a greater probability (at least in this exercise) of being drawn out because they are larger and are contained within larger capsules. Again, a graph is constructed and the maximum value is the weight-average molecular weight. Notice that the maximum occurs at a higher molecular weight for the weight-average

situation.

The area of the curve should be the same and the Mi ordinate is longer reflecting the extension to a greater molecular weight for the weight-average situation. Several mathematical moments (about a mean) can be described using the differential or frequency distribution curve, and these can be described by equations. The first moment is thenumber-average molecular weight, Mn. Any measurement that leads to the number of molecules, functional groups, end groups, or particles that are present in a given weight of sample allows the calculation of Mn. The Mn is calculated like any other numerical average by dividing the sum of the individual molecular weight values by the number of molecules.

Mn= Total weight of sample /Number of molecules of N

Most thermodynamic properties are related to the number of particles present and thus are dependent on Mn. Colligative properties are dependent on the number of particles present and are thus related to Mn. Mn values are independent of molecular size and are highly sensitive to small molecules present in the mixture. Values of Mn are determined by Raoult's techniques that are dependent on colligative properties. These techniques include ebulliometry (boiling point elevation), cryometry (freezing point depression), osmometric, and end-group analysis. Weight-average molecular weight, Mw, is determined from experiments in which each molecule or chain makes a contribution to the measured result relative to its size. This average is more dependent on the number of longer chains than is the number-average molecular weight, which is dependent simply on the total number of each chain.

Mw=WM/W

Bulk properties associated with large deformations, such as viscosity and toughness, are most closely associated with Mw. Mw values are most often determined by light-scattering photometry. However, melt elasticity is more closely related to the third moment known as the z-average molecular weight, Mz. The Mz is most often determined using either light-scattering photometry or ultracentrifugation. It is shown mathematically as

$Mz=M^3 N/M^2N$

6.8Calculation of the MWD

6.8.1 Ion-exchange chromatography

There are a wide variety of chromatography techniques including paper and column techniques. Chromatographic techniques involve passing a solution containing the to-be-tested sample through a medium that shows selective absorption for the different components in the solution.

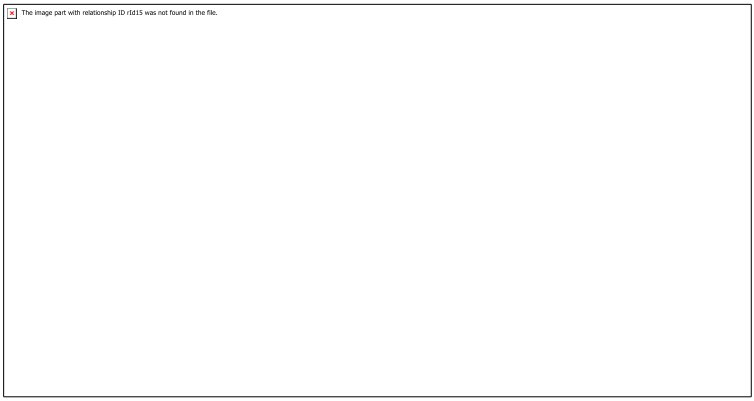


Figure 6.1Ion exchange chromatography

Ion-exchange chromatography separates molecules on the basis of their electrical charge. Ionexchange resins are either polyanions or polycations. For a polycation resin, those particles that are least attracted to the resin will flow more rapidly through the column and be emitted from the column first. This technique is most useful for polymers that contain changed moieties.

6.8.2Affinity chromatography

In affinity chromatography, the resin contains molecules that are especially selected that will interact with the particular polymer(s) that is being studied. Thus, for a particular protein, the resin may be modified to contain a molecule that interacts with that protein type. The solution containing the mixture is passed through the column and the modified resin preferentially means that the molecular weight of the largest particles soluble in a suitable solvent can be, in theory, determined associates with the desired protein allowing it to be preferentially removed from the solution. Later, the protein is washed through the column by addition of a salt solution and collected for

further evaluation.

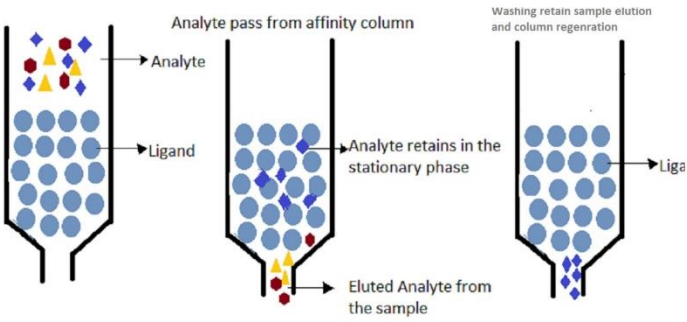


Figure 6.2 affinity chromatography

6.8.3 High-performance liquid chromatography

In high-performance liquid chromatography (HPLC), pressure is applied to the column that causes the solution to rapidly pass through the column allowing procedures to be completed in a fraction of the time in comparison to regular chromatography.

6.8.4 Electrophoresis

When an electric field is applied to a solution, polymers containing a charge will move either toward the cathode (positively charged species) or toward the anode (negatively charged species). This migration is called electrophoresis. The velocity at which molecules move is mainly dependent upon the electric field and change on the polymer driving the molecule toward one of the electrodes and a frictional force dependent on the size and structure of the macromolecule that opposes the movement. In general, the larger and more bulky the macromolecule, the greater the resistance to movement, and the greater the applied field and charge on the molecule, the more rapid the movement. While electrophoresis can be conducted on solutions it is customary to use a supporting medium of a paper or gel. For a given system, it is possible to calibrate the rate of flow with the molecular weight and/or size of the molecule.

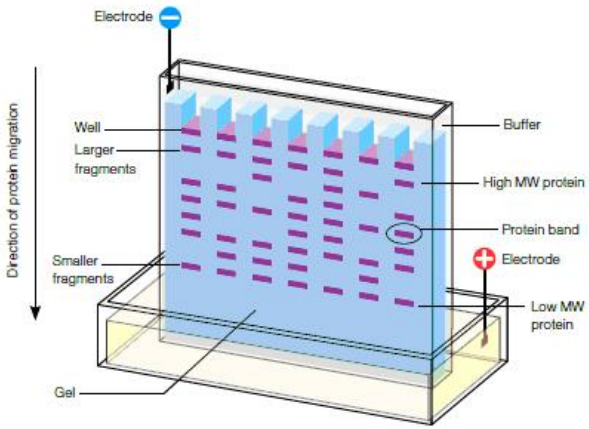


Figure 6.3 protein electrophoresis method

Here, the flow characteristics of the calibration material must be similar to those of the unknown. Generally though, electrophoresis is often employed in the separation of complex molecules such as proteins where the primary factor in the separation is the charge on the species. Some amino acids such as aspartic acid and glutamic acid contain an additional acid functional group, while amino acids such as lysine, arginine, and histidine contain additional basic groups. The presence of these units will confer to the protein tendencies to move toward the anode or cathode. The rate of movement is dependent on a number of factors including the relative abundance and accessibility of these acid and base functional groups.

6.8.5 Gel permeation chromatography

Gel permeation chromatography (GPC) is a form of chromatography that is based on separation by molecular size rather than chemical properties. GPC or size exclusion chromatography (SEC) is widely used for molecular weight and MWD determination.

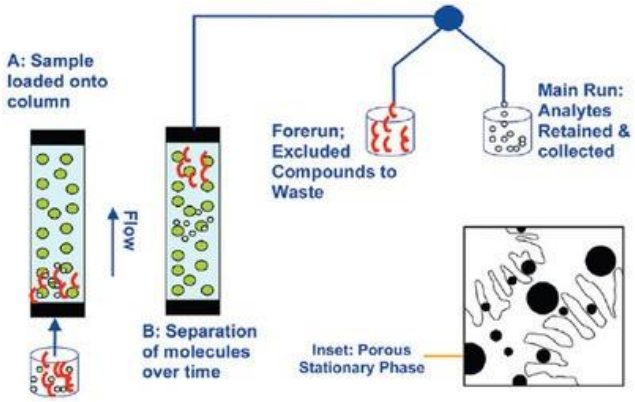


Figure6.4 Gel permission chromatography procedure

In itself, SEC does not give an absolute molecular weight and must be calibrated against polymer samples whose molecular weight has been determined by a technique that does give an absolute molecular weight.

6.8.6 Size exclusion chromatography

SEC is an HPLC technique whereby the polymer chains are separated according to differences in hydrodynamic volume. This separation is made possible by the use of special packing material in the column. The packing material is usually polymeric porous spheres often composed of polystyrene cross-linked by addition of varying amounts of divinylbenzene. Retention in the column is mainly governed by the partitioning (or exchanging) of polymer chains between the mobile (or eluent) phase flowing through the column and the stagnate liquid phase that is present in the interior of the packing material. Through control of the amount of cross-linking, nature of the packing material, and specific processing procedures, spheres of widely varying porosity are available. The motion in and out of the stationary phase is dependent on a number of factors including Brownian motion, chain size, and conformation.

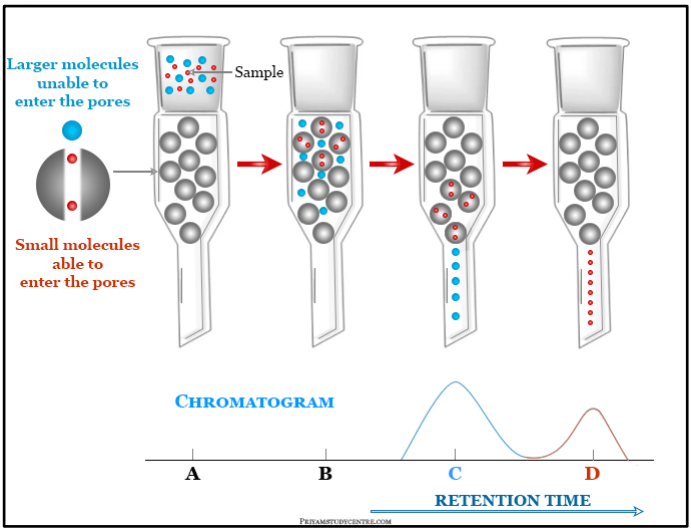


Figure 6.5 size exclusion chromatography principle and column

The latter two are related to the polymer chain's hydrodynamic volume—the real, excluded volume occupied by the polymer chain. Since smaller chains preferentially permeate the gel particles, the largest chains are eluted first. As noted earlier, the fractions are separated on the basis of size. The resulting chromatogram is then a molecular size distribution. The relationship between molecular size and molecular weight is dependent on the conformation of the polymer in solution.

CHAPTER 7

Colligative properties

7.0 What is colligative properties?

Colligative properties include Cryoscopy, ebulliometry, osmometry, Ultra centrifuge method sedimentation velocity method, sedimentation equilibrium method viscosity measurement, end group analysis light scattering method and membrane osmometry. The latter property is considered here, since it is the most important of the group as far as synthetic polymers are concerned. The use of colligative properties of solution in the determination of the molecular weight of various compounds has been one of the simplest methods. Since colligative properties of solutions depend only on the number of molecules of solute in them, this method is especially used for determining the molar masses of complex molecules, proteins, macromolecules, polymers.

7.1 Osmometry

A measure of any of the colligative properties involves counting solute (polymer) molecules in a given amount of solvent. The most common technique for polymers is membrane osmometry. The technique is based on the use of a semipermeable membrane through which solvent molecules freely pass, but through which the large polymer molecules are unable to pass.

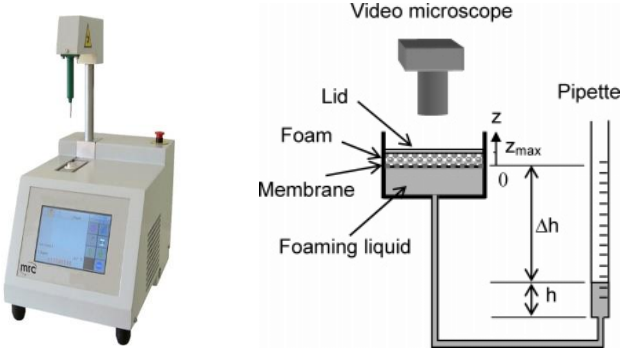


Figure 7.1schematic view of membrane osmometer

Existing membranes only approximate ideal semi permeability, the chief

limitation being the passage of low-molecular-weight chains through the membrane. There is a thermodynamic drive toward dilution of the polymer-containing solution with a net flow of solvent toward the cell containing the polymer. This results in an increase in liquid in that cell causing a rise in the liquid level in the corresponding measuring tube. This rise in liquid level is opposed and balanced by a hydrostatic pressure resulting in a difference in the liquid levels of the two measuring tubes. The difference is directly related to the osmotic pressure of the polymer-containing solution. Thus, solvent molecules pass through the semipermeable membrane reaching a static equilibrium. Since osmotic pressure is dependent on the number of particles present, the measurement of this osmotic pressure can be used to determine the **Mn** of the dissolved polymer. The difference in height **(Δh)** of the liquids in the columns is converted to osmotic pressure (π) by multiplying the gravity (g) and the density of the solution **(ρ)**

$$\boldsymbol{\pi = \Delta h \rho\, g}$$

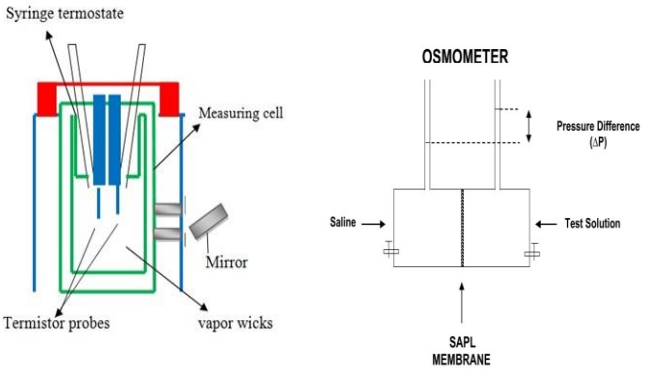


Figure 7.2 structure of osmometer

7.1.1Automated osmometers

In the old static osmometers, it might take weeks to months for equilibrium to become established allowing excessive passage of polymer chains through the membrane. Today, automated osmometers allow molecular weight measurements to occur in minutes with a minimal of passage of polymer chains through the membrane. The relationship between molecular weight

and osmotic pressure is given in the following van't Hoff equation

$$\pi = RTC/ Mn BC^2$$

Thus, the reciprocal of Mn is the intercept when data for π/RTC versus Care extrapolated to zero concentration. The value for B would be zero at the theta temperature. Since this slope increases as the solvency increases, it is advantageous to use a dilute solution consisting of a polymer and a poor solvent to minimize extrapolation errors.

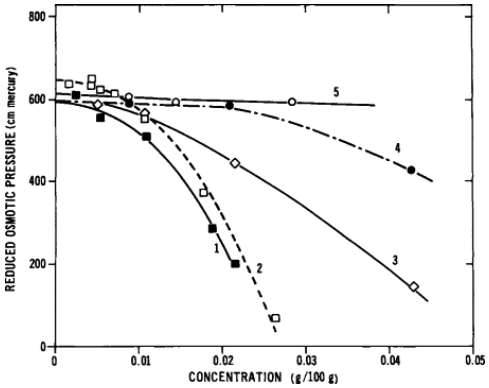


Figure 7.3 graph between concentration and reduced pressure

7.1.2 Vapor phase osmometry technique

In the vapor phase osmometry technique, drops of solvent and solution are placed in an insulated chamber in proximity to thermistor probes. Since the solvent molecules evaporate more rapidly from the solvent than from the polymer solution, a temperature difference results that is related to the molarity of the polymer (M) can be determined if the heat of vaporization per gram of solvent (λ) is known using the following relationship

$$DT = RT^2 M / \lambda 100$$

7.2End-group analysis

End groups are an important aspect of polymer synthesis and characterization. In polymer chemistry, they are functional groups that are at the very ends of a macromolecule or oligomer (IUPAC). In polymer synthesis, like condensation polymerization and free-radical types of polymerization, end-groups are commonly used and can be analyzed by

nuclear magnetic resonance (NMR) to determine the average length of the polymer. Other methods for characterization of polymers where end-groups are used are mass spectrometry and vibrational spectrometry, like infrared and Raman spectroscopy. These groups are important for the analysis of polymers and for grafting to and from a polymer chain to create a new copolymer. One example of an end group is in the polymer poly(ethylene glycol) diacrylate where the end-groups are circled.

End group analysis is the most important absolute method of obtaining number-average molar mass values for polymers of the step-growth polymerization type. A great number of methods are available which primarily differ in the detection of the end group concerned.In cases where the end groups are known and their concentration can be determined, knowledge of their abundance allows a determination of Mn. The sensitivity of this method decreases and the chain length becomes greater. Some end groups can be determined using spectroscopic techniques and other through titration.

Because of the importance of end groups, there have been many analytical techniques developed for the identification of the groups. The three main methods for analyzing the identity of the end group are by NMR, mass spectrometry (MS) or vibrational spectroscopy (IR or Raman). Each technique has its advantages and disadvantages.

7.2.1 NMR spectroscopy

The advantage of NMR for end groups is that it allows for not only the identification of the end group units, but also allows for the quantification of the number-average length of the polymer. End-group analysis with NMR requires that the polymer be soluble in organic or aqueous solvents. Additionally, the signal on the end-group must be visible as a distinct spectral frequency, i.e. it must not overlap with other signals. As molecular weight increases, the width of the spectral peaks also increase. As a result of this, methods which rely on resolution of the end-group signal are mostly used for polymers of low molecular weight (roughly less than 20,000 g/mol number-average molecular weight). By using the information obtained from the integration of a 1H NMR spectrum, the degree of polymerization (Xn) can be calculated. With knowledge of the identity of the end groups/repeat unit and the number of protons contained on each, the Xn

can then be calculated. For this example above, once the 1H NMR has been integrated and the values have been normalized to 1, the degree of polymerization is calculated by simply dividing the normalized value for the repeat unit by the number of protons continued in the repeat unit. For this case, Xn = n = 100/2, and therefore Xn = 50, or there are 50 repeat units in this monomer.

7.2.2 Mass spectrometry

Mass spectrometry (MS) is helpful for the determination of the molecular weight of the polymer, structure of the polymer, etc. Although chemists utilize many kinds of MS, the two that are used most typically are matrix-assisted laser desorption ionization/time of flight **(MALDI-TOF)** and electrospray ionization-mass spectroscopy **(ESI-MS).**One of the biggest disadvantages of this technique is that much like NMR spectroscopy the polymers have to be soluble in some organic solvent. An advantage of using MALDI is that it provides the simpler data to interpret for end group identification compared with **ESI**, but a disadvantage is that the ionization can be rather hard and as a result some end groups do not remain intact for analysis. Because of the harsh ionization in MALDI, one of the biggest advantages of using ESI is for its "softer" ionization methods. The disadvantage of using **ESI** is that the data obtained can be very complex due to the mechanism of the ionization and thus can be difficult to interpret.

7.2.3 Vibrational spectroscopy

The vibrational spectroscopy methods used to analyze the end groups of a polymer are infrared (IR) and Raman spectroscopy. These methods are useful in fact that the polymers do not need to be soluble in a solvent and spectra can be obtained simply from solid material. A disadvantage of the technique is that only qualitative data is typically obtained on the identification end groups.

7.2.4 End group removal

Controlled radical polymerization, namely reversible addition−fragmentation chain-transfer polymerization **(RAFT)**,is a common method for the polymerization of acrylates, methacrylate's and acrylamides. Usually, a thiocarbonate is used in combination with an effective initiator for RAFT. The thiocarbonate moiety can be functionalized at the R-group for

end group analysis. The end group is a result of the propagation of chain-transfer agents during the free-radical polymerization process. The end groups can subsequently be modified by the reaction of the thiocarbony compounds with nucleophiles and ionic reducing agents.

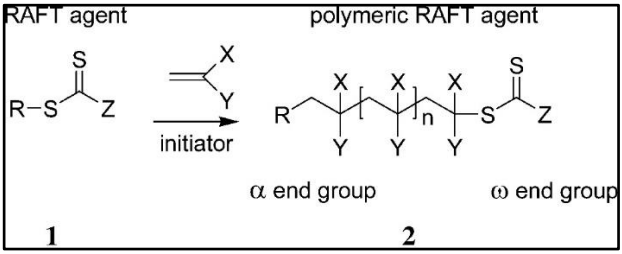


Figure 7.4 thiocarbonyl thio end group analysis

The method for removal of thiocarbonyl containing end groups includes reacting the polymers containing the end-groups with excess of radicals which add to the reactive C=S bond of the end group forming an intermediate radical . The remaining radical on the polymer chain can be hydrogenated by what is referred to as a trapping group and terminate; this results in a polymer that is free of the end groups at the **α** and **ω** positions.

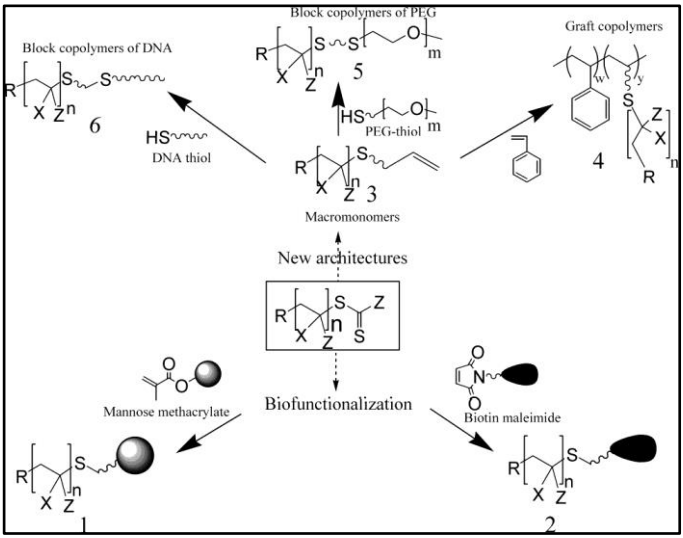


Figure 7.5 modification of RAFT polymer by thiole ene reaction

7.2.5 Thermolysis

Another method of end group removal for the thiocarbonyl containing end-groups of RAFT polymers is the addition of heat to the polymer; this is referred to as thermolysis. One method of monitoring thermolysis of RAFT polymers is by thermogravietric analysis resulting in a weight-loss of the end group. An advantage of this technique is that no additional chemicals are required to remove the end group; however, it is required that the polymer be thermally stable to high temperature and therefore may not be effective for some polymers. Depending on the polymers sensitivity to ultraviolet radiation (UV) it has been reported in recent years that decomposition of end-groups can be effective, but preliminary data suggest that decomposition by UV leads to a change in the distribution of molecular weights of the polymer.

7.2.6 Surface modification using RAFT

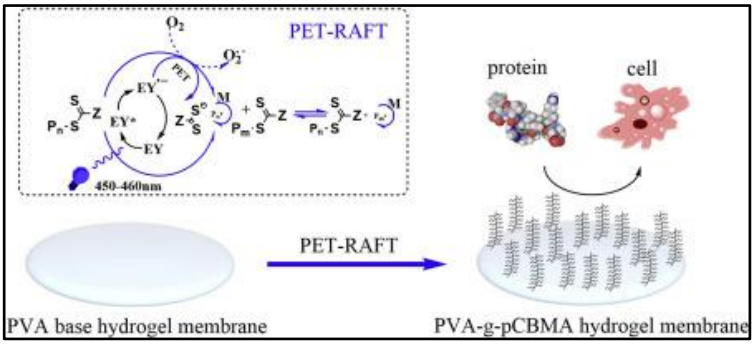


Figure 7.6 surface modification reaction by PET-RAFT on hydrogel surface

Surface modification has gained a lot of interest in recent years for a variety of applications. An example of the application of free radical polymerizations to forming new architectures is through RAFT polymerizations which result in dithioester end groups. These dithioesters can be reduced to the thiol which can be immobilized on a metal surface; this is important for applications in electronics, sensing and catalysis. The schematic below demonstrates the immobilization of copolymers onto a gold surface as reported for poly(sodium 4-styrenesulfonate) by the McCormick group at the University of Southern Mississippi.

7.3Light-scattering photometry

The illumination of dust particles is an illustration of light scattering, not of reflection. Reflection is the deviation of incident light through one particular angle such that the angle of incidence is equal to the angle of reflection. Scattering is the radiation of light in all direction. Thus, in observing the moonbeam, the dust particle directs a beam toward you regardless of your angle in relation to the scattering particle. The energy scattered per second (scattered flux) is related to the size and shape of the scattering particle and to the scattering angle. Scattering of light is all about us—the fact that the sky above us appears blue, the clouds white, and the sunset is shades of reds and oranges is a consequence of preferential scattering of light from air molecules, water droplets, and dust particles. This scattered light caries messages about the scattering objects. The measurement of light scattering is the most widely used technique for the determination of Mw. This technique is based on the optical heterogeneity of polymer solutions and was developed by Nobel Laureate Peter Debye in 1944. Today, modern instruments utilize lasers as the radiation source because they provide a monochromatic, intense, and well-defined light source. Depending upon the size of the scattering object, the intensity of light can be essentially the same or vary greatly with respect to the direction of the oncoming radiation. For small particles the light is scattered equally independent of the angle the observer is to the incoming light. For larger particles, the intensity of scattered light varies with respect to the angle of the observer to the incoming light. For small molecules at low concentrations, this scattering is described in terms of the Rayleigh ratio. In 1871, Rayleigh showed that induced oscillatory dipoles were developed when light passed through gases and that the amount (intensity) of scattered light (τ) was inversely proportional to the fourth power of the wavelength of light. These oscillations reradiate the light energy–producing turbidity, that is, the Tyndall effect. Other sources of energy, such as x-rays or laser beams, may be used in place of visible light sources.

For light-scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I_0, as it passes through a polymer sample. Where τ is the measure of the decrease of the incident beam intensity per unit length of a given solution and is called the turbidity of the solution.

$$I/ I_0 = e^{-\tau}$$

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solution and of the solvent (n_0), to the molecular weight of the polymerMw , and to the inverse fourth power of the wavelength of light used (λ).

$$Hc / \tau = 1/Mw\ P_0(1+2Bc +Cc^2 +.....)$$

The incident light sends out a scattering envelope that has four equal quadrants for small particles. The ratio of scattering at 45° compared with that for 135° is called the dissymmetry factor or dissymmetry ratio Z. The reduced dissymmetry factor Z0 is the intercept of the plot of Z as a function of concentration extrapolated to zero concentration.

7.3.1 Dissymmetrical method

The intercept of the extrapolated line is the reciprocal of Mw and the slope contains the viral constant B. Z0 is directly related to the particle scattering factor, and both are related to both the size and shape of the scattering particle. The molecular weight for dilute polymer solutions is typically found using one of two techniques. The first technique is called the dissymmetrical method or approach because it utilizes the determination of Z0 as a function of the particle scattering factor as a function of polymer shape. Mw is determined from the intercept through substitution of the determined particle scattering factor. The weakness in this approach is the necessity of having to assume a shape for the polymer in a particular solution. For small Z0 values, choosing an incorrect polymer shape results in a small error, but for larger Z0 values, the error becomes significant.

7.3.2Multiple detectors method

The second approach uses multiple detectors allowing a double extrapolation to zero concentration and zero angle with the data forming what is called a Zimm plot. The extrapolation to zero angle corrects for finite particle size effects. The radius of gyration, related to polymer shape and size, can also be determined from this plot. The second extrapolation to zero concentration corrects for concentration factors. The intercepts of both plots are equal to 1/Mw. The Zimm plot approach does not require knowing or having to assume a particular shape for the polymer in solution. Related to the Zimm plot is the Debye plot. In the Zimm approach, different concentrations of the

polymer solution are used. In the Debye approach, one low concentration sample is used with 1/Mw plotted against sin2(θ/2), essentially one-half of the Zimm plot. Low-angle laser light-scattering photometry **(LALLS)** and multiangle low-angle laser lightscattering photometry **(MALS)** take advantage.

7.3.3Automated systems

A number of automated systems exist with varying capabilities. Some internally carry out dilutions and refractive index measurements allowing molecular weight to be directly determined without additional sample treatment. The correct determination of dn/dc is very important since any error in its determination is magnified because it appears as the squared value in the expression relating light scattering and molecular weight. Low-angle and multiangle light-scattering photometers are available that allow not only the determination of Mw but also additional values under appropriate conditions. These systems may also allow the determination of molecular conformation matching the radius and molecular weight to graphs showing the change in the root-mean-square radius of gyration and molecular weight for different shaped molecules. One of the most important advances in polymer molecular weight determination is the coupling of SEC and light-scattering photometry, specifically LALLS or MALS.

In LALLS or MALS usual operational configuration, it does not itself allow the calculation of an absolute molecular weight but relies on calibration with polymers of known molecular weight. By coupling HPLC and light-scattering photometry, the molecular weight of each fraction can be determined giving an MWD and various molecular weight values (Mw, Mz, and Mn). The LALLS or MALS detector measures τ-related values, a differential refractive index detector is used to measure concentration, and the SEC supplies samples containing fractionated polymer solutions allowing both molecular weight and MWD to be determined. Further, polymer shape can be determined. This combination represents the most powerful, based on ease of operation, variety of samples readily used, cost, means to determine polymer size, shape, and MWD available today.

7.3.4Dynamic light scattering

This is similar in principle to typical light scattering. When several particles

are hit by oncoming laser light, a spotted pattern appears, the spots originating from the interference between the scattered light from each particle giving a collection of dark (from destructive interference) and light (from constructive interference) spots. This pattern of spots varies with time because of the Brownian motion of the individual scattering particles. The rate of change in the pattern of spots is dependent on a number of features including particle size. The larger the particle, the slower the Brownian motion and consequently the slower the change in the pattern. Measurement of these intensity fluctuations with time allows the calculation of the translational diffusion constant of the scattering particles. The technique for making these Computer Waste mini-DAWN with QELS (DLS) inside UV detector.

Three-dimensional plot of scattering intensity as a function of scattering angle and elution volume for a broad molecular weight distribution polystyrene sample measurements is given several names including dynamic light scattering (DLS) emphasizing the fact that it is the difference in the scattered light with time that is being measured, photon correlation spectroscopy with the name emphasizing the particular mathematical technique employed to analyze the light-scattering data, and quasielastic light scattering with name emphasizing the fact that no energy is lost in the collision between the particle and the light photon. The effect of subtle particle changes as a function of temperature, sample preparation, time, solvent, and other changes can be measured using DLS. Such changes can then be related to performance variations eventually interrelating structure shape and biological/physical property.

7.3.5 Light scattering photometry

Another variation that is useful employing coupled light scattering is referred to as a triple detection set. The set consists of three detectors: a light-scattering detector, a differential refractometer detector, and a capillary differential viscometer. It functions in concert with a GPC and light-scattering source. The GPC separates the polymer mixture into molecular weight fractions. According to the Einstein equation, the intrinsic viscosity times the molecular weight is equal to the hydrodynamic volume or size of polymers in solution. Thus, the molecular weight is determined using lightscattering photometry, viscometry gives the intrinsic viscosity, and the

equation is solved for size. Generally, light-scattering photometry has a limit to determining molecular size with the lower limit being about 10 nm. The addition of the viscometer allows molecular sizes to be determined for oligomeric materials to about 1 nm. The assembly allows an independent measure of size and molecular weight as well as additional conformational and aggregation information including small conformational changes.

7.4 Ultracentrifugation

There are two kinds of ultracentrifuges, the preparative and the analytical ultracentrifuge. Both classes of instruments find important uses in molecular biology, biochemistry, and polymer science. The kinetic energy of solvent molecules is greater than the sedimentation force of gravity, polymer molecules remain suspended in solution. However, this gravitational field, which permits Brownian motion, may be overcome by increasing this force by use of high response to selected detectors as a function of retention volume.

Figure 7.7 Ultracentrifuge matchine

Both Mw and Mz may be determined by subjecting dilute polymer solutions to high centrifugal forces. Solvents with densities and indices of refraction different from the polymers are chosen to ensure polymer motion and optical detection of this motion. In sedimentation velocity experiments, the ultracentrifuge is operated at extremely high rotational speeds up to over 70,000 rpm in order to transport the denser polymer molecules through the less dense solvent to the cell bottom or to the top if the density of the solvent

is greater than the density of the polymer. The boundary movement during ultracentrifugation can be followed using optical measurement to monitor the sharp change in refractive index (n) between the solvent and solution. The sedimentation velocity determination is dynamic and can be completed in a short period of time. The sedimentation equilibrium method gives quantitative results, but longer time is required for centrifugation at relatively low velocities to establish equilibrium between sedimentation and diffusion. As shown in the following equation, the weight-average molecular weight Mw is directly proportional to the temperature T and the In of the ratio of concentration c2/c1 at distances r1 and r2 from the center of rotation and the point of observation in the cell and inversely proportional to the buoyancy factor, the square of the angular velocity of rotation and the difference between the squares of the distances r1 and r2.

$$M = \frac{2RT \ln c2/c1}{(1- Vp)\, \omega 2\, (r2^2 - r1^2)}$$

7.5 Viscometry

Viscosity is a measure of the resistance to flow of a material, mixture, or solution. Here, we will consider the viscosity of solutions containing small, generally 1 g/100 cm3 (or 1 g/100 mL; called 1% solutions) and less, amounts of polymer. The study of such dilute polymer solutions allows a determination of a relative molecular weight. The molecular weight is referred to as "relative" since viscosity measurements have not been directly related, through rigorous mathematical relationships, to a specific molecular weight. By comparison, measurements made using lightscattering photometry and some of the other methods covered before are relatable to specific molecular weight values, and these techniques are said to give us absolute molecular weights. The relationship between the force f necessary to move a plane of area A relative to another plane a distance d from the initial plane. This factor is called the coefficient of shear viscosity or simply viscosity. The inverse of viscosity is given the name "**fluidicity**." As a material's resistance to flow increases, its viscosity increases.

It is important to note the wide variety of viscosities of materials from gases such as air to viscoelastic solids as glass. In polymer science, viscosity is not usually directly measured, but rather relative viscosity is obtained by

measuring the flow rate of one material relative to that of a second material. Viscosity is one of the most widely used methods for the characterization of polymer molecular weight because it provides the easiest and most rapid means of obtaining molecular weight–related data that requires minimal instrumentation.

7.5.1Mark–Houwink equation

A most obvious characteristic of polymer solutions is their high viscosity, even when the amount of added polymer is small. This is because polymers reside in several flow planes acting to resist the flow of one plane relative to another flow plane. The ratio of the viscosity of a polymer solution to that of the solvent is called the "relative viscosity (ηr)." This value minus 1 is called the "specific viscosity (ηsp)," and the reduced viscosity (ηred) or viscosity number is obtained by dividing ηsp by the polymer concentration c, that is, **ηsp/c**. The intrinsic viscosity, or LVN, is obtained by extrapolating ηsp/c to zero polymer concentration showed that the intrinsic viscosity of a solution [η] or LVN is related to the molecular weight of the polymer. The present form of this relationship was developed by Mark– Houwink, in which the proportionality constant **K** is characteristic of the polymer and solvent and the exponential "a" is a function of the shape of the polymer in a solution. For theta solvents, the value of "a" is 0.5. This value, which is actually a measure of the interaction of the solvent and polymer, increases as the coil expands and the value is between 1.8 and 2.0 for rigid polymer chains extended to their full contour length and 0 for spheres. When a is 1.0, the Mark–Houwink equation becomes the Staudinger viscosity equation.

Viscosity is unable to give absolute molecular weight values and must be calibrated, that is, values of a and K are determined using polymer samples where their molecular weights have been determined using some absolute molecular weight method such as light-scattering photometry. It is customary in determining the and K values to make a plot of log LVN versus log M, that is a straight line relationship where the slope is a and intercept K. In reality, a is determined from the slope but K is determined by simply selecting a known **LVN-M** couple and using the determined a value to calculate the K value

LVN = AeE/RT

However, if the original temperature is below the theta temperature, the viscosity will increase when the mixture of polymer and solvent is heated to a temperature slightly above the theta temperature. The viscometer is placed in a constant temperature bath and the time taken for a polymer solution to flow through a set space in the viscometer measured

[η] = AeE/RT

While the description of viscosity is complex, the relative viscosity is directly related to the flowthrough times using the same viscometer, where t and t0 are the flow times for the polymer solution and solvent.

Table 7.1Viscosities of Selected Common Materials Substance General viscosity (MPas)

Air	0.00001
Water	0.001
Polymer latexes/paints	0.01
PVC plastisols	0.1
Glycerol	10.0
Polymer resins and “pancake” syrups	100.0
Liquid polyurethanes	1,000.0
Polymer “melts”	10,000.0
Pitch	100,000,000.0
Glass 1,000,000,000,000,000,000,000.0	

Problem

Determine the molecular weight of a polystyrene sample which has an a value of 0.60, a K value of 1.6×10^{-4} dL/g, and a limiting viscosity number or intrinsic viscosity of 0.04 dL/g. The molecular weight can be found by the relationship:

[η] = KMa

Log [η] = a log M + log K

Log M =log[η] -log K]/a = [log (0.04)- log ($1.6 – 10^{-4}$]/0.060

M = 1 × 104

7.5.2 Melted polymer viscosities measurement

The viscosity of melted polymers is important when resins are transferred and in polymer processing when determining the correct conditions to have a specific flow rate for injection processing and in determining the optimum conditions to get the necessary dimensions of extruded shapes. Fillers, plasticizers, temperature, solvents, and molecular weight are just some of the variables that influence the viscosity of polymer melts. Here, we will look at the dependence of melt viscosity on polymer molecular weight. Polymer melts have viscosities on the order of 10,000 MPas (1 centipoise is equal to 0.001 Pas/s). For largely linear polymers, such as linear polystyrene, where there are not present particularly bulky side chains, the viscosity or flow is mainly dependent on the chain length. In most polymers the melt viscosity–chain length relationship has two distinct regions where the region division occurs when the chain length reaches some length called the "**critical entanglement chain length(Z)"** where intermolecular entanglement occurs. This intermolecular entanglement causes the individual chains in the melt to act as being much more massive because of the entanglement. Thus, the resistance to flow is a combination of the friction and entanglement between chains as they slide past one another. Below the critical entanglement length, where only the friction part is important, the melt viscosity, η, is related to the weight-average molecular weight . And above the critical chain length, where both the friction and entanglement are important, the relationship is

$$\mathbf{h = K\ Mh}$$

where **Kl** is a constant for the precritical entanglement chain length Kh is for the situation above Z and where both K values are temperature dependent The first power dependence is due to the simple increase in molecular weight as chain length increases, but the 3.4 power relationship is due to a complex relationship between chain movement as related to entanglement and diffusion and chain length. The critical chain length often corresponds to the onset of strength-related properties and is often considered the lower end for useful mechanical properties. The Z value for polymers varies but is

generally between about 200 and 1000 units in length. For instance, the Z value for polystyrene is about 700; for polyisobutylene about 600; for poly(decamethylene sebacate) about 300; for poly(methyl methacrylate) about 200; and for poly(dimethyl siloxane) about 1000. A number of techniques have been developed to measure melt viscosity.

7.5.3 Rotational viscometers

Rotational viscometers are of varied structures. The Couette cup and bob viscometer consists of a stationary inner cylinder, the bob, and an outer cylinder, cup that is rotated. Shear stress is measured in terms of the required torque needed to achieve a fixed rotation rate for a specific radius differential between the radius of the bob and cup.

7.5.4 Brookfield viscometer

The Brookfield viscometer is a bob and cup viscometer.

7.5.5 Mooney viscometer

The Mooney viscometer, often used in the rubber industry, measures the torque needed to revolve a rotor at a specified rate. In the cone and plate assemblies, the melt is sheared between a flat plate and a broad cone whose apex contacts the plate containing the melt.

Table 7.2 Viscosity Measuring Techniques and Their Usual Range

Capillary pipette	0.01–1000
Falling sphere	1–100,000
Parallel plate	10,000–109
Falling coaxial cylinder	100,000–1011
Stress relaxation	1000–1010
Rotating cylinder	1–1012
Tensile creep	100,000—greater than 10^{12}

7.6 Cryoscopy

Cryoscopy method was formally introduced in the 1880's when François-

Marie Raoult published how solutes depressed the freezing points of various solvents such as benzene, water, and formic acid. He concluded from his experimentation “if one molecule of a substance can be dissolved in one-hundred molecules of any given solvent then the solvent temperature is lowered by a specific temperature increment”. Based on Raoul’s research, Ernst Otto Beckmann invented the Beckmann thermometer and the associated freezing - point apparatus, which was a significant improvement in measuring freezing - point depression values for a pure solvent. The simplicity, ease, and accuracy of this apparatus has allowed it to remain as a current standard with few modifications for molecular weight

7.6.1 Freezing Point Depression

Freezing point depression is a colligative property in which the freezing temperature of a pure solvent decreases in proportion to the number of solute molecules dissolved in the solvent. The known mass of the added solute and the freezing point of the pure solvent information permit an accurate calculation of the molecular weight of the solute.ΔT_f is the change in the initial and final temperature of the pure solvent, K_f is the freezing point depression constant for the pure solvent, and m (moles solute/kg solvent) is the *molality* of the solution.

$\Delta Tf=Kfm$

$\Delta Tf=Kfm$

For an ionic solution the dissociation particles must be accounted for with the number of solute particles per formula unit

$\Delta Tf=Kfmi$ $\Delta Tf=Kfmi$

7.6.2 Cryoscopic Apparatus

For cryoscopy, the apparatus to measure freezing point depression of a pure solvent may be representative of the Beckmann apparatus. The apparatus consists of a test tube containing the solute dissolved in a pure solvent, stir bar or magnetic wire and closed with a rubber stopper encasing a mercury thermometer. The test tube component is immersed in an ice-water bath in a beaker.

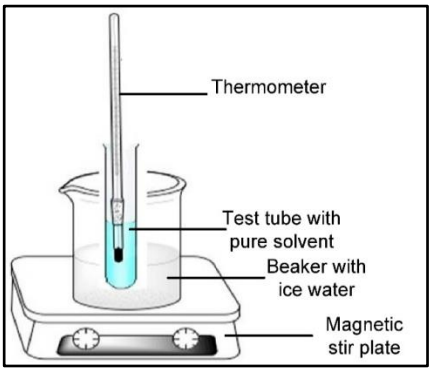


Figure 7.8 apparatus of cryoscopy

7.6.3 Sample and Solvent Selection

The cryoscopic method may be used for a wide range of samples with various degrees of polarity. The solute and solvent selection should follow the premise of like dissolved like or in terms of Raoult's principle of the dissolution of one molecule of solute in one-hundred molecules of a solvent. The most common solvents such as benzene are generally selected because it is unreactive, volatile, and miscible with many compounds

Mw=Kf/ΔTf

7.6.4Molecular Weight of Polymers

Knowledge of the molecular weight of polymers is very important because the physical properties of macromolecules are affected by their molecular weight. For example, the interrelation between molecular weight and strength for a typical polymer. Dependence of mechanical strength on polymer

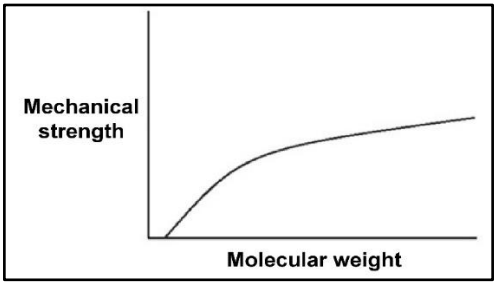


Figure 7.9Graph between molecular weight and mechanical strength

The melting point of polymers are also slightly depend on their molecular weight. Relationship between molecular weight and melting temperatures of polyethylene shown in graph .Most linear polyethylene have melting temperatures near 140 °C. The approach to the theoretical asymptote, that is a line whose distance to a given curve tends to zero, indicative that a theoretical polyethylene of infinite molecular weight (i.e., M = ∞) would have a melting point of 145 °C.

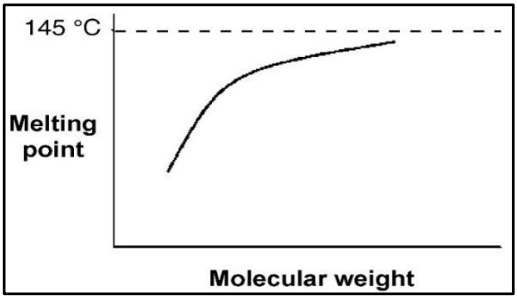


Figure 7.10 The molecular weight-melting temperature relationship for the alkane.

There are several ways to calculate molecular weight of polymers like number average of molecular weight, weight average of molecular weight, Z-average molecular weight, viscosity average molecular weight, and distribution of molecular weight.

7.6.5 Molecular Weight Calculations

- **Number average of molecular weight (M_n)**

Number average of molecular weight is measured to determine number of particles. Number average of molecular weight is the total weight of polymer

$$M_n = \frac{\sum M_i N_i}{\sum N_i}, \quad M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i},$$

Example

Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 40.000 g/mol and 15 moles of polymer

molecules having molecular weight of 30.000 g/mol.

$$\text{Total weight} = (5 \text{ mol} \times 40.00 \text{ g/mol}) + (15 \text{ mole} \times 30.00 \text{ g/mol}) = 650{,}000 \text{ g}$$

$$\text{Total number} = 5 \text{ mol} + 15 \text{ mol} = 20 \text{ mol}$$

$$M_n = \frac{650{,}000 \text{ g}}{20 \text{ mol}} = 325{,}000 \text{ g/mol}$$

7.7 Ebulliometry

Ebulliometry, one of the classical methods for determining molecular weights, has undergone great improvement in recent years. The requirements of a successful ebulliometric system are thermal stability, temperature and concentration equilibrium, and temperature sensing.

7.7.1Ebulliometric System

The system consists of a simple ebulliometer, a temperature sensing element, and an electrical recording device. The ebulliometer is essentially the same as that described by Glover and Stanley . It consists of a platinum immersion heater, a vapor lift pump of the Cottrell type, and a recycle arrangement patterned.

Temperature sensing is an important part of ebulliometry. In the work being described, thermopiles are used. They are very stable in operation and change little, if any, with age. One advantage is the leveling effect of the multiple temperature sensing points of the thermopile on rapid temperature fluctuations caused by uneven boiling or pumping.

Thermistors have been used, with equal success, for temperature sensing by many workers. Also, devices such as the quartz crystal thermometer might be adapted to this application. Finally, the signal from the thermopile is amplified and is recorded on a strip chart recorder. Thermal stability is obtained with a vapor jacket. This jacket normally contains the solvent to be used in the determination and is covered with aluminum foil which serves as a light shield as well as a thermal barrier. The jacket is connected directly to the ebulliometer to prevent pressure differences, and the system is vented to ambient pressure through a surge tank. Operation of the system has been simplified to permit routine determinations by a laboratory technician with no active supervision. After fresh solvent is added, the output of the

thermopile ("zero line") for the solvent recorded. Further, a decreasing heat input program is followed to eliminate the effects of foaming and superheating. Normally three or four weighed portions of the sample are added successively, and the elevation in boiling temperature is recorded for each portion.

$$\left(\frac{\Delta T_b}{C}\right)_{C=0} = \frac{RT^2}{\rho \Delta H_v \overline{M}_n} + A_2 C$$

The molecular weight is obtained from these data by the limiting slopes calculation.About 8000 determinations involving a range of solvents and solutes have been made with the system as described.

$$M_n = \frac{K_b c}{\Delta T_b}$$

The most recent and perhaps most interesting development in this respect is the use of hexafluoro-2-propanol (HFIP) as an ebulliometric solvent for the study of polyesters and polyamides. Precision of these measurements varies with molecular weight level, solvent, and to some extent, solute. With a series of polyglycols. For polyethyleneprecision does vary with molecular weight and is obviously influenced by other factors, such as homogeneity and purity of the sample.

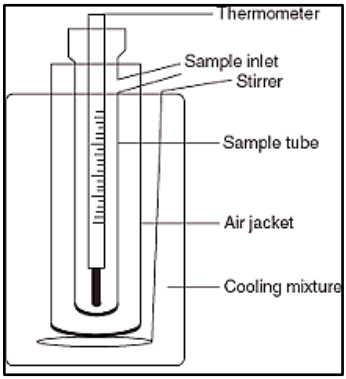


Figure 7.12 structure of ebullometer

The Cottrell-type pump presents an additional variable. With it the rate and

the heat input to the boiling solution cannot be varied independently. For this reason, the possibility of superheating cannot be rigorously eliminated. To overcome superheating, a no-dead-space mechanical pump constructed, and installed in an experimental ebulliometer.

7.8 Sedimentation velocity

Sedimentation velocity (SV) experiments take place in an ultracentrifuge, usually starting with a spatially uniform initial equilibrium of dissolved particles in a solution volume that forms a cylinder segment from a "meniscus" air/water interface closest to the axis of rotation to a "bottom" radius, which is by the highest radius of the solution column defined by the sample The solution is placed in a rotor and subjected to centrifugal field, which is typically constant but may be modulated with time. In a basic SV configuration, experiments are conducted such that the start of the centrifugation will place the system far from its centrifugal equilibrium, essentially allowing one to visualize the free fall of the ensemble. Sedimentation velocity (SV-AUC) is an analytical ultracentrifugation method that measures the rate at which molecules move in response to centrifugal force generated in a centrifuge. This sedimentation rate provides information about both the molecular mass and the shape of molecules.Analytical ultracentrifugation (AUC) is a versatile and powerful method for the quantitative analysis of macromolecules in solution. AUC has broad applications for the study of biomacromolecules in a wide range of solvents and over a wide range of solute concentrations. Three optical systems are available for the analytical ultracentrifuge (absorbance, interference and fluorescence) that permit precise and selective observation of sedimentation in real time. In particular, the fluorescence system provides a new way to extend the scope of AUC to probe the behavior of biological molecules in complex mixtures and at high solute concentrations. In sedimentation velocity, the movement ofsolutes in high centrifugal fields is interpreted using hydrodynamic theory to define the size, shape and interactions of macromolecules. Sedimentation equilibrium is a thermodynamic method where equilibrium concentration gradients at lower centrifugal fields are analyzed to define molecule mass, assembly stoichiometry, association constants and solution nonideality. Using specialized sample cells and modern analysis software, researchers can use sedimentation velocity to determine the homogeneity of a sample and define

whether it undergoes concentration-dependent association reactions. Subsequently, more thorough model-dependent analysis of velocity and equilibrium experiments can provide a detailed picture of the nature of the species present in solution and their interactions.Mass will redistribute in a gravitational field until the gravitational potential energy exactly balances the chemical potential energy at each radial position. If we monitor the rate at which boundaries of molecules move during this redistribution, then we are conducting a sedimentation velocity experiment. If we determine the concentration distribution after equilibrium is reached, then we are conducting an equilibrium sedimentation **experiment.**We can understand a sedimentation velocity experiment by considering the forces acting on a molecule during a sedimentation velocity experiment. The force on a particle due to the gravitational field is just $M_p\omega^2 r$, where M_p is the mass of the particle, ω is the rotor speed in radians per second ($\omega = 2\pi \bullet rpm/60$), and r is the distance from the center of the rotor. A counterforce will be exerted on the particle by the mass of solvent, M_s, displaced as the particle sediments, $M_s\omega^2 r$. The net force is $(M_p - M_s)\omega^2 r$. The mass of solvent displaced is just the M_p times partial specific volume of the particle, $\bar{v}$ (cm^3/g), times the density of the solvent, ρ (g/cm^3). So the effective, or buoyant mass of the particle is

$$\mathbf{M_b = M_p(1 - \bar{v}\,\rho).}$$

7.8.1 Sedimentation coefficient

The last force to consider is the frictional force developed by the motion of the particle through the solvent, which given by fv, where f is the frictional coefficient and v is the velocity. Balancing these forces we obtain the following relationship

$$\mathbf{S = v\omega 2r = Mbf}$$

7.8.2 Stokes-Einstein

Which is also definition of the sedimentation coefficient, s, as the ratio of the velocity to the centrifugal field. In terms of molecular parameters, indicates that s is proportional to the buoyant molar mass, M_b, and inversely proportional to the frictional coefficient, f. Diffusion causes the sedimenting boundary to spread with time. Hence by monitoring the motion and shape of a boundary it is possible to determine both the sedimentation coefficient and

the translation diffusion coefficient, D. From the Stokes-Einstein relationship, we know that

$D = RT/N_af$

7.8.3 Svedberg equation

Where R is the gas constant (erg/mole °K), T the absolute temperature and N_a is Avogadro's number. By taking the ratio S/D, the frictional contribution to these parameters is removed and the result is proportional to the buoyant molar mass, M_b, through the Svedberg equation

$SD=MbRT$

7.9 Sedimentation equilibrium

Sedimentation equilibrium (analytical ultracentrifugation) is one of the most inherently suitable methods for the determination of average molecular weights and molecular weight distributions of polymers, because of its absolute basis (no conformation assumptions) and inherent fractionation ability (without the need for columns or membranes and associated assumptions over inertness). With modern instrumentation it is also possible to run up to 21 samples simultaneously in a single run. Its application has been severely hampered because of difficulties in terms of baseline determination (incorporating estimation of the concentration at the air/solution meniscus) and complexity of the analysis procedures.

7.9.1 SEDFIT

We describe a new method for baseline determination based on a smart-smoothing principle and built into the highly popular platform SEDFIT for the analysis of the sedimentation behavior of natural and synthetic polymer materials. The SEDFIT-MSTAR procedure – which takes only a few minutes to perform - is tested with four synthetic data sets (including a significantly non-ideal system) a naturally occurring protein (human IgG1) and two naturally occurring carbohydrate polymers (pullulan and λ–carrageenan) in terms of

(i) weight average molecular weight for the whole distribution of species in the sample

(ii) the variation in "point" average molecular weight with local concentration in the ultracentrifuge cell and

(iii) molecular weight distribution.The molecular weight (Da) or equivalently the 'molar mass' (g/mol) is one of the most important parameters defining a polymer, although it is not trivial to measure, particularly for polydisperse systems.

7.9.2Sedimentation equilibrium

(SE) in the analytical ultracentrifuge is a well-established method for obtaining the molecular weights of polymers. It has an absolute basis (not requiring calibration standards or markers, or assumptions over conformation) and has an inherent fractionation ability, without the need for columns or membranes and associated assumptions over inertness. It is also not hampered by contamination through large supramolecular particles. With the use of multi-hole rotors and multi-channel cells, it is now possible to run up to 21 samples simultaneously in a single run. One drawback which has held back its wide application is that the procedures for data capture and analysis previously available have not made the method the easiest to apply. For studies on proteins and other molecules with well-defined molecular weights the last two decades has seen the development of powerful software procedures for the analysis of optical records from sedimentation equilibrium, taking advantage of on-line scanning of uv/visible optical records (absorption/ fluorescence) or the on-line capture using a charge-coupled device (CCD) camera of the higher precision data yielded in the form of fringe displacements by the Rayleigh interferometric system. A characteristic feature of the analysis of protein interactions by SE is the direct fit of the measured signal profiles with a few discrete terms of Boltzmann exponentials, each corresponding to a different species of free protein or protein complex, and often linked in their amplitude by mass action law for reversibly interacting system.

7.9.3 SEDPHAT

As recently reviewed, advanced strategies for SE analysis, such as implemented in the multi-method analysis platform SEDPHAT, include the global fitting of many SE signal profiles acquired at different loading concentrations, different rotor speeds, and different data acquisition with models that create constraints through implicit mass conservation and different interaction models, yielding binding affinities and

stoichiometries.The analysis of polymers with a quasi-continuous distribution of molecular weight – or suspensions of mixtures with a diverse distribution of molecular weight – poses different problems. In contrast to the quasi-discrete problem of protein interactions, where often the buoyant molar mass values and therefore the exponents of the Boltzmann terms for each species are known a priori, here the buoyant molecular weights are unknown and their averages and their entire distribution is estimated from the evaluation of the exponential SE profiles.

7.9.4 *M** function

A different approach was therefore introduced involving an operational point average molecular weight known as the *M** function: this approach offered a significant advantage over conventional methods which involved concentration extrapolation to the cell base, since the *M** function is a less sensitive function of radial position, permitting a more accurate evaluation of the (apparent) weight average molecular weight $M_{w,app}$ for the macromolecular components in the solution. When applied to the analysis of multiple sedimentation equilibrium data sets from the same sample acquired at multiple rotor speeds, the combination of *M** with *c*(*M*) can be particularly powerful, especially if mass conservation and ideal sedimentation can be assumed. In this case, the global *c*(*M*) fit can serve to provide a single consistent interpretation of multiple individual *M** transforms, which otherwise may be difficult to mutually reconcile and potentially result in different extrapolations and cell-average molecular weight estimates. It is now fair to say that estimation of M_w is also routine using the application of SEDFIT-MSTAR to sedimentation equilibrium data for polymer solutions of wide ranging polydispersity's and non-idealities.The big advantage of sedimentation equilibrium, SE, is that it removes all hydrodynamic effects, so that purely thermodynamic analysis is possible. The requirements for sample purity and homogeneity are much stricter for SE measurements that for velocity experiments. In the latter case, the boundaries associated with each species separate during the sedimentation run so that it is possibly to isolate contaminants from the species of interest. In contrast, different species are incompletely fractionated in an SE gradient. Furthermore, as shown below, fitting SE concentration gradients requires deconvolution of multiple exponential functions, which is a challenging mathematical operation that becomes increasingly difficult with larger numbers of species.

CHAPTER 8

Amorphous and crystalline state of polymers

8.0 Polymer crystals

Prior to 1920, not only leading scientists stated that macromolecules were nonexistent, but they also believed, if they did exist, they could not exist as crystals. However, in the early 1920s, Haworth used x-ray diffraction techniques to show that elongated cellulose was a crystalline polymer consisting of repeat units of cellobiose. In 1925, Katz in jest placed a stretched natural rubber band in an x-ray spectrometer and to his surprise observed an interference pattern typical of a crystalline substance. This phenomenon may be shown qualitatively by the development of opacity when a rubber band is stretched and by the abnormal stiffening and whitening of unvulcanized rubber when it is stored for several days at 0°C. The opacity noted in stretched rubber and cold rubber is the result of the formation of crystallites.

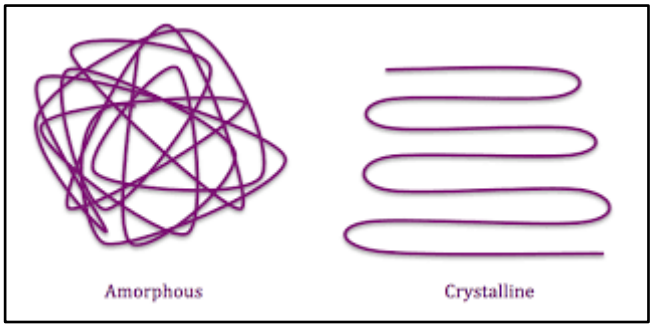


Figure 8.1Difference in structure of crystalline and amorphous polymer

The latter were first explained by a fringed micelle model that is now found not consistent with much of the current experimental findings. Amorphous polymers with irregular bulky groups are seldom crystallizable, and unless special techniques are used, even ordered polymers are seldom 100% crystalline. The combination of amorphous and crystalline structures varies with the structure of the polymer and the precise conditions that have been imposed on the material.

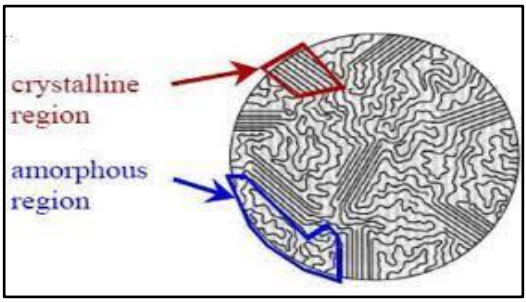


Figure 8.2 Amorphous and crystalline regions

8.1 Spherulite

For instance, rapid cooling of an amorphous polymer sample often decreases the amount of crystallinity because there is not sufficient time to allow the long chains to organize themselves into more ordered structures before they become frozen in place. The reason linear ordered polymers fail to be almost totally crystalline is largely kinetic, resulting from an inability of the long chains to totally disentangle and perfectly align themselves during the time the polymer chain is cooling and mobile. Mixtures of amorphous and mini-crystalline structures or regions may consist of somewhat random chains containing some chains that are parallel to one another forming short-range mini-crystalline regions. Crystalline regions may be formed from large range ordered platelet like structures, including polymer single crystals, or they may form even larger organizations such as spherulite.

Table 3.1 Types of polymers and their uses

	POLYMER	USE
HIGHLY CRYSTALLINE	Polytetrafluoroethylene	Electrical insulation, Teflon
	Polypropylene	Insulating films, cable wrap, capacitor dielectric
	Kevlar	Protective apparel, friction products
CRYSTALLINE	Nylon 6,6	Textile fibers, jacket over primary wire insulation
	Polyethylene terephthalate	Electrical insulation, Mylar
	Polyethylene	Extruded dielectric in wires and cables
IMPERFECTLY CRYSTALLINE	Polyvinyl chloride	Electrical insulation, PVC, pressure-sensitive tapes
	Acrylonitrile	Orlon, Acrilan
HIGHLY CROSSLINKED	Alkyd resin	Molding compound
	Phenol-formaldehyde resin	Bakelite, lacquers
	Epoxy resin	Embedment of electrical components, GIS spacers
AMORPHOUS	Polystyrene	Wire and cable insulation, packaging
	Polyvinyl acetate	Adhesives, Emulsion paints
	Polymethyl methacrylate	Lucite, Plexiglas
	Polycarbonate	Compact discs, housings for power tools
	Polyisoprene	Elastomers, tires, baby bottle nipples

Short- and longer-range ordered structures can act as physical cross-links. In

general, linear polymers form a variety of single crystals when crystallized from dilute solutions. For instance, highly linear PE can form diamond-shaped single crystals with a thickness on the order of 11–14 nm when crystallized from dilute solution. The surface consists of "**hairpin turned**" methylene units. The polymer chain axes are perpendicular to the large flat crystal faces. A single polymer chain with 1000 ethylene (2000 methylene) units might undergo on the order of 50 of these hairpin turns on the top surface and another 50 turns on the bottom face with about 20 ethylene units between the two surfaces.

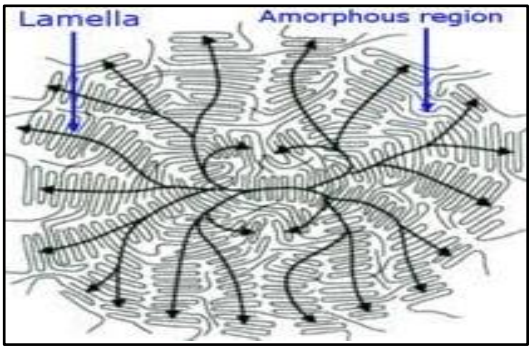


Figure 8.3 Lamella and amorphous regions

8.2 Hedrites

2D representation of a modified micelle model of the crystallineamorphous structure of polymers represent structure of a spherulite from the bulk.Many polymers form more complex single crystals when crystallized from dilute solution including hollow pyramids that often collapse on drying. As the polymer concentration increases, other structures occur, including twins, spirals, and multilayer dendritic structures with the main structure being spherulites. When polymer solids are produced from their melts, the most common structures are these spherulites that can be seen by the naked eye and viewed as Maltese cross-like structures with polarized light and crossed Nicol prisms under a microscope. For linear PE, the initial structure formed is a single crystal with folded chain lamellae. These quickly lead to the formation of sheaflike structures called **axialites** or **hedrites**.

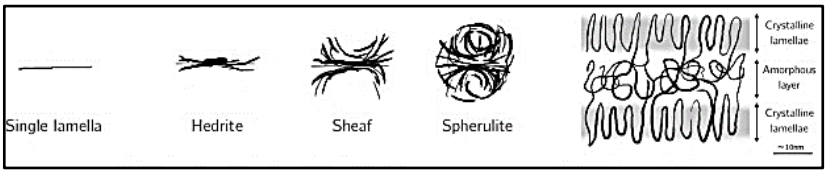


Figure 8.4 formation of spherulite in thin film

8.3 Lamellae

As growth proceeds, the lamellae develop on either side of a central reference point. The lamellae continue to fan out, occupying increasing volume sections through the formation of additional lamellae at appropriate branch points. The result is the formation of spherulites. While the lamellar structures present in spherulites are similar to those present in polymer single crystals, the folding of chains in spherulites is less organized. Further, the structures that exist between these lamellar structures are generally occupied by amorphous structures including a tactic chain segments, low-molecular-weight chains, and impurities.

8.4 Crystalline platelets

The individual spherulite lamellae are bound together by "tie" molecules that are present in more than one spherulite. Sometimes these tie segments form intercrystalline links, which are threadlike structures, which are important in developing the characteristic good toughness found in semicrystalline polymers. They act to tie together the entire assembly of spherulites into a more or less coherent "package." Depending upon the particular conditions of crystallization, a number of secondary and tertiary structures can be formed. In most cases, crystalline polymers attempt to form crystalline platelets. Under little or no externally applied stress, these platelets organize themselves in spherulites. They start by a nucleating process and begin to radiate outward from the central nucleating site. Amorphous chain segments get trapped between the forming crystalline platelet combinations giving a kind of a fuzzy or frayed exterior. Either these platelets are generally planar, or they can be helical or twisted. The platelets continue to grow until they butt up against other spherulites.

8.5 Fibrils

Under externally applied stress, including simple melt flow, the tertiary

structure can approach a shish kebab arrangement where there are planes of platelets separated by areas where there exist both crystalline and amorphous regions. These shish kebab structures often organize into quaternary structures consisting of bundles of shish kebab single-strand filaments forming fibrils. Under more rapid flow conditions, the shish kebab itself becomes distorted .Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements and more complete model of two sets of three lamellar chain-folded platelets. This theme of amorphous flexibility and crystalline strength (and brittleness) is a central idea in polymer structure–property relationships. It must be remembered that the secondary structure of both the amorphous and crystalline regions typically tends toward a helical arrangement of the backbone for most polymers but not PE that forms a crank-shaft structure because of the lack of steric restraints (i.e., lack of pendent groups off the backbone). The kind, amount, and distribution of polymer chain order/disorder (crystalline/amorphous) is driven by the processing (including pre- and post-) conditions and thus it is possible to vary the polymer properties through a knowledge of and ability to control the molecular-level structures.

8.6 Thermoforming

The crystalline regions may be disrupted by processing techniques such as thermoforming and extrusion of plastics and drawing of fibers. In the last process, which is descriptive of the others, the crystallites are ordered in the direction of the stress, the filament shrinks in diameter, and heat is evolved and reabsorbed as a result of additional orientation and crystallization. In addition to crystallization of the backbone of polymers, crystallization may also occur in regularly spaced bulky groups even when an amorphous structure is maintained in the backbone. In general, the pendant group must contain at least 10 carbon atoms in order for this side chain crystallization to occur.

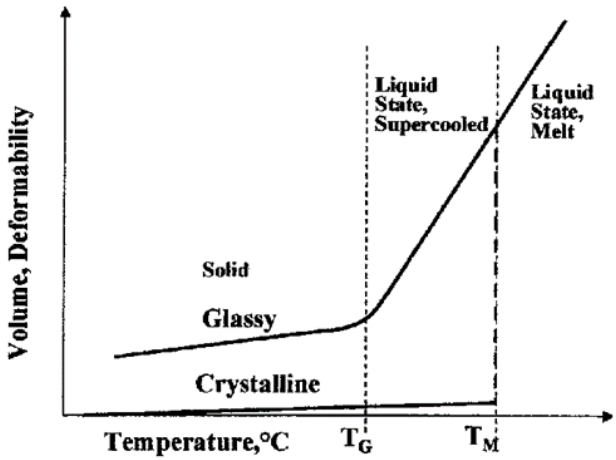


Figure 8.5 graphical representation of glassy and crystalline polymer

Ordered polymers with small pendant groups crystallize more readily than those with bulky groups. While polymeric hydrocarbons have been used as illustrations for simplicity, it is important to note that the principles discussed apply to all polymers, organic as well as inorganic, and natural as well as synthetic, and to elastomers, plastics, and fibers.

8.7 Crystalline and amorphous combinations

Most polymers consist of a combination of crystalline and amorphous regions. Even within polymer crystals such as spherulites, the regions between the ordered folded crystalline lamellae are less ordered, approximating amorphous regions. This combination of crystalline and amorphous regions is important for the formation of materials that have both good strength (contributed largely by the crystalline regions) and some flexibility or "softness" (derived from the amorphous portions). Note the cavities within the amorphous regions with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of the crystalline regions are referred to as being crystalline, and they are less flexible and stronger and offer better stability to nature and attack by acids and bases, oils, etc. Also as noted before, amorphous regions give the material flexibility while the crystalline regions give the material strength. Thus, many materials contain

both crystalline and amorphous regions giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

8.8 Space filled model

This model of PE contains a mixture of amorphous and crystalline regions. Note the cavities within the amorphous regions with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of the crystalline regions are referred to as being crystalline, and they are less flexible and stronger and offer better stability to nature and attack by acids and bases, oils, etc. Also as noted before, amorphous regions give the material flexibility while the crystalline regions give the material strength. Thus, many materials contain both crystalline and amorphous regions giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

8.9 Polymer structure–propertyrelationships

Throughout the text we will relate polymer structure to the properties of the polymer. Polymer properties are related not only to the chemical nature of the polymer but also to such factors as extent and distribution of crystallinity, distribution of polymer chain lengths, and nature and amount of additives, such as fillers, reinforcing agents, and plasticizers, to mention a few. These factors influence essentially all the polymeric properties to some extent including hardness, flammability, weather ability, chemical stability, biological response, comfort, flex life, moisture retention, appearance, dye ability, softening point, and electrical properties. Materials must be varied to perform the many tasks required of them in today's society. Often they must perform them repeatedly and in a special manner.

We get an ideal of what materials can do by looking at some of the behavior of giant molecules in our body. While a plastic hinge must be able to work thousands of times, the human heart, a complex muscle largely composed of protein polymers. Elastomers are high polymers possessing chemical and/or physical cross-links. For industrial application, the use temperatures must be above **Tg** (to allow for ready chain mobility), and its normal state

(unextended) must be amorphous. The restoring force, after elongation, is largely due to entropy. On release of the applied force, the chains tend to return to a more random state. Gross, actual mobility of chains must be low. The cohesive energy forces between chains should be low permitting rapid, easy expansion. In its extended state, a chain should exhibit a high tensile strength, whereas at low extensions, it should have a low tensile strength. Cross-linked vinyl polymers often meet the desired property requirements.

8.10 Crystalline and amorphous combinations

Most polymers consist of a combination of crystalline and amorphous regions. Even within polymer crystals such as spherulites, the regions between the ordered folded crystalline lamellae are less ordered, approximating amorphous regions. This combination of crystalline and amorphous regions is important for the formation of materials that have both good strength (contributed largely by the crystalline regions) and some flexibility or "softness" (derived from the amorphous portions). Note the cavities within the amorphous regions with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of the crystalline regions are referred to as being crystalline, and they are less flexible and stronger and offer better stability to nature and attack by acids and bases, oils, etc. Also as noted before, amorphous regions give the material flexibility while the crystalline regions give the material strength. Thus, many materials contain both crystalline and amorphous regions giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

CHAPTER 9

Glass transition temperature

9.0 Glass transition and melt transition

The change in the physical state of a solid from solid to liquid is known as melting. The heat supplied dissolves the crystal lattice with the temperature of the material remaining constant during the entire melting process. So, there is a defined melting temperature.The reversal of this first order phase, the transition from the amorphous-liquid state of the melt to the crystalline state, is called crystallization. It is a kinetically controlled process and depends primarily on nucleation. Therefore, the crystallization temperature is always below the thermodynamically controlled melting temperature.

9.1 Glass transition

Non-crystalline materials such as polymers, on the other hand, have a glass transition. This is where completely or partially amorphous polymers change from a highly viscous or rubber-elastic, flexible state to a glass-like or hard-elastic, brittle state. To characterize the glass transition, the glass transition temperature Tg expresses the point at which half of the change in the specific heat capacity is reached. It is also called the glass transition temperature or softening temperature.

The thermal glass transition is observed when a melt which cannot crystallize is supercooled. The so-called cooperative molecular movements, such as rearrangements of main chain segments, side chain rotations, and end group rotations, then “freeze.” This results in sudden changes in mechanical and thermodynamic properties such as modulus of elasticity, specific heat capacity, and the coefficient of thermal expansion. The cooling rate has a decisive influence on the glass transition temperature. If the melt is cooled down quickly, the glass transition temperature is higher. With an infinitely slow cooling, there is no glass transition, since no amorphous partial areas result. Many common plastics are partially crystalline: they therefore have a glass transition temperature below which the amorphous phase freezes. At the same time, they also have a melting temperature at which the crystalline area dissolves.

9.2 Classification

Polymers can be classified based on their glass transition.Since every plastic has a specific glass transition, this is an important parameter for characterizing the material. Therefore, the determination of the glass transition temperature is often used in thermal analysis, in order to make such statements as the dimensional stability of a polymer under the action of heat. For example, elastomers are only used in the rubber-elastic range, i.e. above the glass transition temperature. In contrast, amorphous thermoplastics are only used below Tg.

9.3 Factors affecting glass transition

Since the glass transition depends on the type of plastic and its manufacture, information on changes in the material can be obtained by determining the Tg. Among other things, the following relationships exist:

Chemical structure: the more flexible the main chain, the lower the Tg

Molar mass: the Tg increases as molar mass increases

Molecular orientation: e.g. Tg increases in foils

Crosslinking:the Tg increases as the degree of crosslinking increases

Plasticizers: the Tg decreases as the plasticizer content increases.

The glass transition temperature also provides information on the physical aging of plastics, which occurs as an enthalpy relaxation peak in **DSC** measurements. Polymer mixtures can also be characterized using Tg. If the polymers are immiscible, the individual components appear phase-separated so that they exist side-by-side and several glass transitions can be measured. A comparison with the pure components can provide information about the proportions and quality of the mixing process.

Small molecules such as water can exist in three phases—solid, liquid, and gas. Polymers do not boil so this phase is missing for polymers so they do not exist in the gaseous state. But polymers undergo other transitions besides melting. The most important of these is called the “glass transition,”Before we turn to the glass transition, it is important to note that polymers may undergo many other transitions. About 20 transitions have been reported for PE. Polystyrene undergoes several transitions that have been identified. About −230°C, the movement, often described as wagging or oscillation, of

the phenyl groups begins. At about −140°C, movement of four-carbon groups in the polystyrene backbone begins. By 50°C, torsional vibration of the phenyl groups begins. At about 100°C, long-range chain movement begins corresponding to the reported Tg value for polystyrene.It is important to remember that while small molecules have a precise temperature associated with its transitions.

9.4 Glass transition temperature

Thus heating/cooling rate affects the temperatures required to effect the changes. Polymers generally undergo several major thermal transitions. At low temperatures, most polymers are brittle and glassy since there is not sufficient energy present to encourage even local or segmental chain movement. As the temperature is increased, at some temperature there is sufficient energy available to allow some chain mobility. For a polymer containing both amorphous and crystalline portions or is only amorphous, the onset of this segmental chain mobility for the amorphous segments is called the "glass transition temperature," Tg. Because there is unoccupied volume in the amorphous polymer structure, some segmental chain movement occurs. This segmental chain movement is sometimes likened to a snake or worm slithering "in place" within the grass.

The Tg is then the temperature when the snake or worm begins to wiggle. The localized chain movement causes a further increase in unoccupied volume and larger segments are able to move eventually allowing the snake further movement in the grass. As the temperature is increased, there is sufficient temperature to overcome the forces present in the crystalline portion of the polymer allowing a breaking up of the crystalline portion. This temperature is often referred to as the "**crystalline transition temperature**," Tc. This temperature is generally directly related to the "melt transition temperature," Tm or melting point. Finally, as the temperature continues to rise, there is sufficient energy available to overcome the primary bonds holding the polymer together and the polymer decomposes at the "**decomposition temperature**," Td. The Tg and Tm are described further later. The flexibility of amorphous polymers is reduced drastically when they are cooled below the "**glass transition temperature**" (Tg). At temperatures below Tg, there is no ready segmental motion and any dimensional changes in the polymer chain are mainly the result of temporary distortions of the

primary covalent bonds. Below the Tg, the chains are "frozen" into place and the material acts as a brittle solid or glass, hence the name "**glassy state**." Amorphous plastics perform best below Tg but elastomers must be used above the brittle point, Tg, or they will act as a glass and be brittle and break when bent. The importance of a material being above its Tg to offer some flexibility was demonstrated by the space shuttle Challenger disaster where the cool temperature at the launch pad resulted in the "O" ring not being flexible so that fuel escaped resulting in the subsequent explosion.

9.5 Thermal coefficient of energy

The major reasons why amorphous polymers go from a solid glassy state to a more flexible plastic state are the presence of sufficient energy and unoccupied volume. The energy is supplied by heating the sample allowing the polymer sufficient energy for chain segments to become separated and begin movement, which in turn creates free or unoccupied volume that allows the chain segments to slip past one another resulting in the material being more flexible. In order for the chains to begin moving, the secondary forces that hold the chains together must be overcome. As movement begins additional unoccupied volume is created, and this expansion within a complex maze of intertwining chains creates additional free volume. A measure of this expansion is the "**thermal coefficient of expansion**." The temperature range where the available free volume and energy necessary to overcome segmental chain interactions is available is called the "glass transition temperature," Tg.

9.6 Kauzmann's paradox

Entropy difference between crystal and undercooled melt**.** As a liquid is super cooled, the difference in entropy between the liquid and solid phase decreases. By extrapolating the heat capacity of the super cooled liquid below its glass transition temperature, it is possible to calculate the temperature at which the difference in entropies becomes zero. This temperature has been named the Kauzmann temperature.

9.7 Measurement of glass transition temperature/ DSC and TGA

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information

about physical phenomena, such as phase transitions, absorption, adsorption and desorption; as well as chemical phenomena including chemisorption's, thermal decomposition, and solid-gas reactions Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.Simultaneous Thermal Analyzer can be used to determine simultaneous changes of mass (TG) and caloric reactions (DSC) of a sample in the temperature range from –150°C up to 2400°C. The unique characteristics of this product are highest precision, highest resolution and long term drift stability.

The **STA** Series was especially developed to meet the challenging demands of the high temperature as well as low temperature applications. To cover this broad range, several specifically designed furnace types are available.

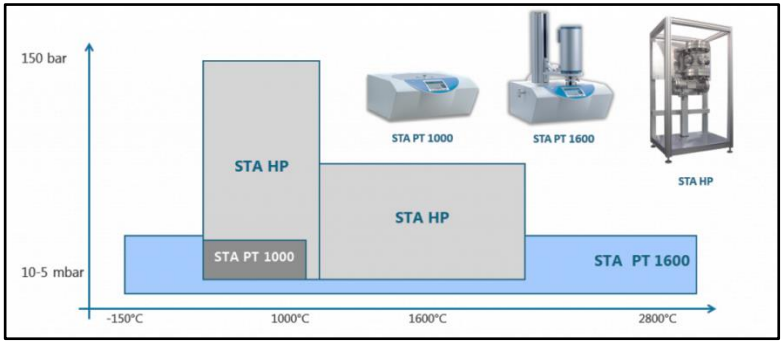


Figure 9.1 STA series show different temp furnace setup

Furthermore MS (Mass Spectrometer) and FTIR Spectrometer couplings can be added to receive unique additional information. Due to its superior performance, user friendliness and modularity.

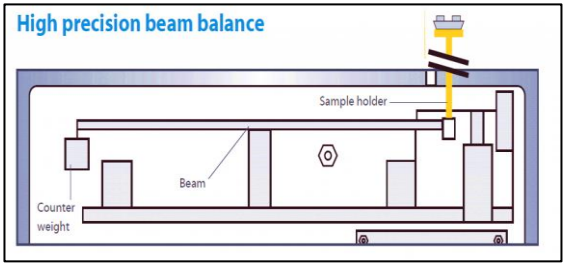


Figure 9.2functioning of high precision beam balance

Different microbalances are specifically designed to accomplish thermal analysis tasks in the best possible way. Providing ultra-light weight design to follow fast weight changes and symmetric construction for ultra-low drift long term measurements.

9.8 Thermal method of STA

Simultaneous **TGA-DSC** measures both heat flow (green curve) and weight changes (orange curve) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results.The complimentary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss .

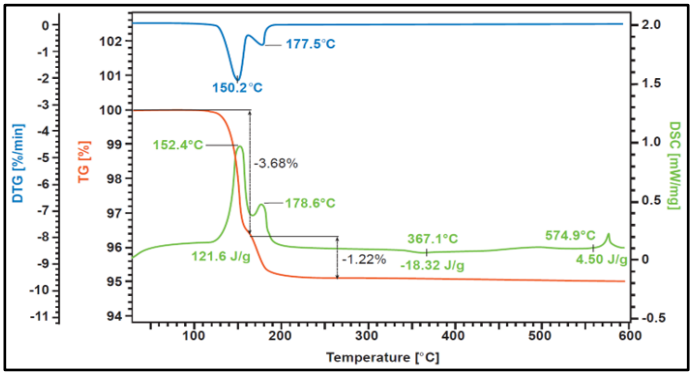


Figure 9.3The graph gives an impression about the information obtained by a STA (TG-DSC) measurement.

9.9 Measurable properties

Some measureable properties are listed below

Table 4.1mass change and rate controlled mass lose properties

Mass change as % and mg	Rate controlled mass loss
Evaluation of mass loss	Residue mass evaluation
Compositional analysis	Enthalpy
Endo- / Exothermic reactions	Phase transformation
Melting point	Glass point
Crystallinity	Thermal stability
Oxidation stability	

9.10 Time–temperature superposition

Temperature dependence of elastic relaxation modulus of a viscoelastic material. Here t is the time, G is the modulus, and $T_0 < T_1 < T_2$.

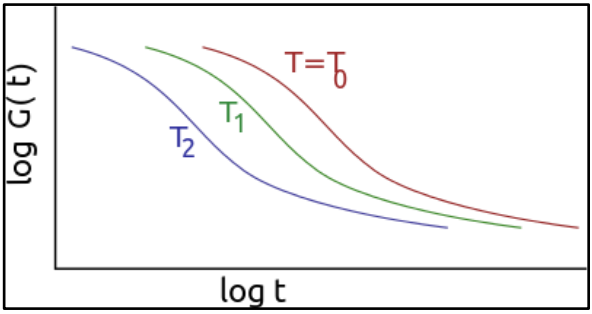


Figure 9.4 temperature dependence of viscoelastic material

Temperature dependence of elastic modulus of a viscoelastic material under periodic excitation. The frequency is ω, G' is the elastic modulus, and $T_0 < T_1 < T_2$.

The **time–temperature superposition** principle is a concept in polymer physics and in the physics of glass-forming liquids. This superposition principle is used to determine temperature-dependent mechanical properties of linear viscoelastic materials from known properties at a reference temperature. The elastic moduli of typical amorphous polymers increase with loading rate but decrease when the temperature is increased. Curves of the instantaneous modulus as a function of time do not change shape as the temperature is changed but appear only to shift left or right. This implies that a master curve at a given temperature can be used as the reference to predict curves at various temperatures by applying a shift operation. The time-temperature superposition principle of linear viscoelasticity is based on the above observation.

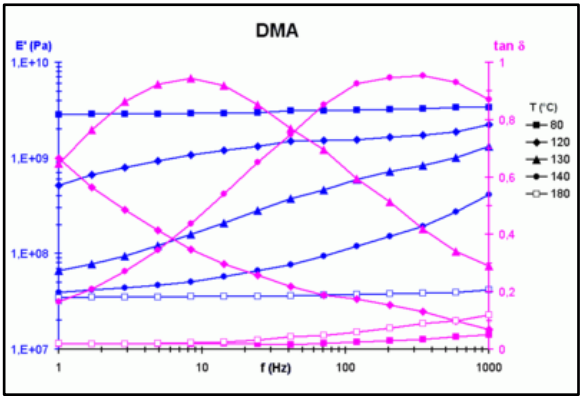


Figure 9.5 Time temperature superposition

Moduli measured using a dynamic viscoelastic modulus analyzer. The plots show the variation of elastic modulus $E'(f, T)$ and the loss factor, $\tan \delta(f, T)$, where δ is the phase angle as a function of frequency f and temperature T.

9.11 Applications

The application of the principle typically involves the following steps:

- experimental determination of frequency-dependent curves of

isothermal viscoelastic mechanical properties at several temperatures and for a small range of frequencies

- computation of a translation factor to correlate these properties for the temperature and frequency range
- experimental determination of a master curve showing the effect of frequency for a wide range of frequencies
- Application of the translation factor to determine temperature-dependent moduli over the whole range of frequencies in the master curve.

9.12 Transition factor

The translation factor is often computed using an empirical relation first established by Williams-Landel-Ferry or WLF model. An alternative model suggested by Arrhenius is also used. The WLF model is related to macroscopic motion of the bulk material, while the Arrhenius model considers local motion of polymer chains.

Some materials, polymers in particular, show a strong dependence of viscoelastic properties on the temperature at which they are measured. If you plot the elastic modulus of a non-crystallizing crosslinked polymer against the temperature at which you measured it, you will get a curve which can be divided up into distinct regions of physical behavior. At very low temperatures, the polymer will behave like a glass and exhibit a high modulus. As you increase the temperature, the polymer will undergo a transition from a hard "glassy" state to a soft "rubbery" state in which the modulus can be several orders of magnitude lower than it was in the glassy state. The transition from glassy to rubbery behavior is continuous and the transition zone is often referred to as the leathery zone. The onset temperature of the transition zone, moving from glassy to rubbery, is known as the glass transition temperature, or T_g.

Modulus measurements are made by stretching or compressing a sample at a prescribed rate of deformation. For polymers, changing the rate of deformation will cause the curve described above to be shifted along the temperature axis. Increasing the rate of deformation will shift the curve to higher temperatures so that the transition from a glassy to a rubbery state will

happen at higher.Time–temperature superposition is a procedure that has become important in the field of polymers to observe the dependence upon temperature on the change of viscosity of a polymeric fluid. Rheology or viscosity can often be a strong indicator of the molecular structure and molecular mobility. Time–temperature superposition avoids the inefficiency of measuring a polymer's behavior over long periods of time at a specified temperature by utilizing the fact that at higher temperatures and shorter time the polymer will behave the same, provided there are no phase transitions.

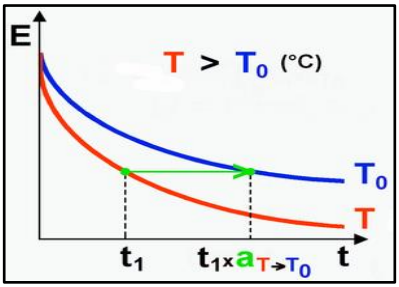


Figure 9.6 graphical representation of energy with time

Schematic of the evolution of the instantaneous modulus ***E(t,T)*** in a static relaxation test. t is the time and T is the temperature. Consider the relaxation modulus **E** at two temperatures T and T_0 such that $T > T_0$. At constant strain, the stress relaxes faster at the higher temperature. The principle of time-temperature superposition states that the change in temperature from T to T_0 is equivalent to multiplying the time scale by a constant factor $\boldsymbol{a_T}$ which is only a function of the two temperatures T and T_0.

$$E(t,T) = E(\frac{t}{a_T}, T_0)\,.$$

The quantity a_T is called the horizontal translation factor or the shift factor and has the properties.

$$\begin{aligned} T < T_0 \quad &\Longrightarrow \quad a_T < 1 \\ T > T_0 \quad &\Longrightarrow \quad a_T > 1 \\ T = T_0 \quad &\Longrightarrow \quad a_T = 1\,. \end{aligned}$$

For the superposition principle to apply, the sample must be homogeneous, isotropic and amorphous. The material must be linear viscoelastic under the deformations of interest, i.e., the deformation must be expressed as a linear

function of the stress by applying very small strains.

9.13Plasticizers

9.13.1 Definition

A plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and glass transition temperature (Tg) of a plastic. Thus, the utility of cellulose nitrate (CN) produced by Schonbein, was limited until Parkes added castor oil to CN and Hyatt added camphor to plasticize CN. Another plasticizer, tricresyl phosphate (TCP), was used to replace part of the camphor and reduce the flammability. Waldo Semon patented the use of tricresyl phosphate as a plasticizer for poly(vinyl chloride) . This was later replaced by the less toxic di-2-ethylhexyl phthalate (DOP), which is now the most widely used plasticizer. The annual worldwide production of plasticizers is 3.2 million tons. In fact, plasticizers are major components of a number of polymer-containing products. For instance, the adhesive in automobile safety glass is typically composed mainly of poly(vinyl butyral) and about 30% plasticizer. The effect of plasticizers may be explained by the lubricity, gel, and free volume theories.

9.13.2 Characteristics

Plasticizers should be relatively nonvolatile, non-mobile, inert, inexpensive, nontoxic, and compatible with the system to be plasticized.

9.13.3 Classification according to flexibility

Flexibilizing of polymers can be achieved through internal and external plasticization.

- **Internal plasticizers**

Internal plasticizerscan be produced through copolymerization giving a more flexible polymer backbone or by grafting another polymer onto a given polymer backbone. Thus, poly(vinyl chloride-co-vinyl acetate) is internally plasticized because of the increased flexibility brought about by the change in structure of the polymer chain. The presence of bulky groups on the polymer chain increases segmental motion and placement of such groups through grafting acts as an internal plasticizer. However, linear groups with more than 10 carbon atoms reduce flexibility because of side-chain

crystallization when the groups are regularly spaced. Internal plastization achieves its end goal at least in part through discouraging association between polymer chains.

- **External plasticizers**

External plasticization is achieved through incorporation of a plasticizing agent into a polymer through mixing and/or heating.

9.13.4 Classification according to compatibility

They can be divided based on their solvating power and compatibility.

- **Primary plasticizers** are used as either the sole plasticizer or the major plasticizer with the effect of being compatible with some solvating nature.
- **Secondary plasticizers** are materials that are generally blended with a primary plasticizer to improve some performance, such as flame resistance and mildew resistance, or to reduce cost. The division between primary and secondary plasticizers is at times arbitrary. Here we will deal with primary plasticizers.

For instance, the adhesive in automobile safety glass is typically composed mainly of poly(vinyl butyral) and about 30% plasticizer. The effect of plasticizers may be explained by the lubricity, gel, and free volume theories.

9.13.4 Gel theory

The gel theory, which is applicable to amorphous polymers, assumes that a polymer such as PVC has many intermolecular attractions that are weakened by the presence of a plasticizer such as DOP. It is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at Tg. Performance plasticizers offer added performance over general purpose plasticizers generally with added cost.

9.13.6 Permanent plasticizers

Performance plasticizers include fast solvating materials such as butyl benzyl phthalate and dihexyl phthalate; low-temperature plasticizers such as di-n-undecyl phthalate and di-2-ethylhexyl adipate; and so-called “permanent plasticizers” such as tri-2-ethylhexyl trimellitate, triisononyl trimellitate, and diisodecyl phthalate. Specialty plasticizers include materials that provide

important properties such as reduced migration, improved stress–strain behavior, flame resistance, and increased stabilization.

9.13.5 Chemical composition

The three main chemical groups of plasticizers are phthalate esters, trimellitate esters, and adipate esters. In all three cases, performance is varied through the introduction of different alcohols into the final plasticizer product. There is a balance between compatibility and migration. Generally the larger the ester grouping the less the migration up to a point where compatibility becomes a problem and where compatibility now becomes the limiting factor. The most used phthalate ester is di-2-ethylhexyl phthalate, DOP, made from the reaction of 2-ethyl hexanol with phthalic anhydride. Phthalic acid esters, such as DOP, may be extracted from blood stored in plasticized PVC blood bags and tubing. These aromatic esters are also distilled from PVC upholstery in closed automobiles in hot weather. These problems have been solved by using oligomeric polyesters as no migrating plasticizers, instead of DOP.

9.13.6 Applications

External plasticizers are not permanent. Plasticizer molecules associate with one another eventually creating "preferred" migration routes to the material's surface where the plasticizer is rubbed or washed away. The preferential association of plasticizer molecules also leaves certain sites less flexible and creates variations in material stress–strain and expansion/contraction behavior. Plasticizers also extend the lower temperature range for use of materials since they both discourage polymer chain associative behavior and encourage segmental flexibility increasing the rotational freedom effectively decreasing the materials typical Tg. Volume-wise, about 90% of plasticizers are used with PVC and PVC containing polymer systems. Water is a widely utilized plasticizer in nature, permitting flexibility of much of the human body as well as the "bendability" of flowers, leaves, tree branches, and so on. Fats and many proteins also act as plasticizers in animals. Plasticizer containment still remains a major problem, particularly for periods of extended use. For instance, most plastic floor tiles become brittle with extended use, mainly due to the leaching out of plasticizer. This is being overcome through many routes including surface treatment of polymer product surfaces affecting less porous surface features and use of branched

polymers which can act as plasticizers to themselves. Being polymers themselves, the highly branched polymers are slow to leach because of physical entanglements within the total polymer matrix.

CHAPTER 10

Electrical properties
10.0 Dialectical properties

The term "**dielectric behavior**" usually refers to the variation of these properties within materials as a function of frequency, composition, voltage, pressure, and temperature. The dielectric behavior of materials is often studied by employing charging or polarization currents. Since polarization currents depend on the applied voltage and the dimensions of the condenser, it is customary to eliminate this dependence by dividing the charge Q by the voltage V to obtain a parameter C, called the capacitance (capacity)

C = Q /V

10.1 Polarizabilities

The polarizability is the electric dipole moment per unit volume induced by an applied field or unit effective intensity. The molar polarizability is a measure of the polarizability per molar volume; thus it is related to the polarizability of the individual molecules or polymer repeat unit. Conductivity is a measure of the number of ions per unit volume and their average velocity in the direction of a unit applied field. Polarizability is a measure of the number of bound charged particles per cubic unit and their average displacement in the direction of the applied field.

10.2 Conductive polymers

Intrinsically conducting polymers (**ICPs)** are polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their process ability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoform able. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesisand by advanced dispersion techniques.

10.3 Background

Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colorless but the oxidized forms were deep blue.The first highly-conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens.

10.4 Types

Linear-backbone "polymer blacks" (polyacetylene, polypyrrole, polyindole and polyaniline) and their copolymers are the main class of conductive polymers. Poly (p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

Table 10.1presents some organic conductive polymers according to their composition.

Main chain contain	No heteroatom	Heteroatoms present	
		Nitrogen-containing	Sulfur-containing
Aromatic cycles	• *Poly(fluorene)s* • *polyphenylenes* • *polypyrenes* • *polyazulenes* • *polynaphthalenes*	The N is in the aromatic cycle: • poly(pyrrole)s (PPY) • *polycarbazoles* • *polyindoles* • *polyazepines* The N is outside the aromatic cycle: • polyanilines (PANI)	The S is in the aromatic cycle: • poly(thiophene)s (PT) • poly(3,4-ethylenedioxythiophene) (PEDOT) The S is outside the aromatic cycle: • poly(p-phenylene sulfide) (PPS)
Double bonds	Poly(acetylene) (PAC)		
Aromatic cycles and double bonds	• Poly(p-phenylene vinylene) (PPV)		

10.5 Synthesis

Conductive polymers are prepared by many methods. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions go dehydrogenation:

$$\mathbf{n\ H–[X]–H \rightarrow H–[X]_n–H + 2(n–1)\ H^+ + 2(n–1)\ e^-}$$

The low solubility of most polymers presents challenges. Some researchers add solubilizing functional groups to some or all monomers to increase solubility. These include polyaniline nanofibers and PSS. In many cases, the molecular weights of conductive polymers are lower than conventional polymers such as polyethylene. However, in some cases, the molecular weight need not be high to achieve the desired properties.There are two main methods used to synthesize conductive polymers, chemical synthesis and electro (co)polymerization.

10.6 Chemical synthesis

The chemical synthesis means connecting carbon-carbon bond of monomers by placing the simple monomers under various condition, such as heating, pressing, light exposure and catalyst. The advantage is high yield. However, there are many impurities plausible in the end product.

10.7 Electro co polymerization

The electro (co)polymerization means inserting three electrodes (reference electrode, counter electrode and working electrode) into solution including reactors or monomers. By applying voltage to electrodes, redox reaction to synthesize polymer is promoted. Electro (co)polymerization can also be divided into Cyclic Voltammetry and Potentiostatic method by applying cyclic voltage and constant voltage. The advantage of Electro (co)polymerization are the high purity of products. But the method can only synthesize a few products at a time.

10.8 Molecular basis of electrical conductivity

The conductivity of such polymers is the result of several processes. For example, in traditional polymers such as polyethylene, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the

material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a molecule wide delocalized set of orbitals. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped ox datively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction of silicon atoms are replaced by electron-rich, *e.g.*, phosphorus, or electron-poor, *e.g.*, boron, atoms to create n-type and p-type semiconductors, respectively.

10.9 Doping conductive polymers

Although typically "**doping**" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be self-doped. Undoped conjugated polymers are semiconductors or insulators. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 KS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 KS/cm. Although the pi-electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is

diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "**switching**" analogous to that seen in inorganic amorphous semiconductors.

It is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains, however this could not be confirmed for polyaniline and was only recently confirmed for **PEDOT**, which are largely amorphous.

10.10Properties and applications

a. Conductive polymers show promise in antistatic materials and they have been incorporated into commercial displays and batteries.
b. They are also promising in organic solar cells, printed electronic circuits, organic light-emittingdiodes, actuators, electrochromism, supercapacitors, chem ical sensors, chemical sensor arrays, and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide.
c. Another use is for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft.
d. Conducting polymers are rapidly gaining attraction in new applications with increasingly process able materials with better electrical and physical properties and lower costs. The new nano-structured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability.
e. Research reports showed that nanostructured conducting polymers in the form of nanofibers and Nano sponges, showed significantly improved capacitance values as compared to their non-nanostructured counterparts.
f. With the availability of stable and reproducible dispersions, **PEDOT** and polyaniline have gained some large-scale applications. While **PEDOT** (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of **PEDOT:PSS** dispersions (PSS=polystyrene sulfonic acid)

g. Polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solder ability.
h. Polyindole is also starting to gain attention for various applications due to its high redox activity, thermal stability, and slow degradation properties than competitor's polyaniline and polypyrrole.

10.11 Electroluminescence

Electroluminescence is light emission stimulated by electric current. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

10.12 Barriers to applications

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their process ability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. The poor process ability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis. Experimental and theoretical thermodynamically evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

10.13 Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference **(EMI)** and electrostatic discharge **(ESD)** protection have led to

both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. As of 2001, there remains to be discovered an organic polymer that is intrinsically electrically conducting. Recently, researchers from **IMDEA** Nanoscience Institute reported experimental demonstration of the rational engineering of 1D polymers that are located near the quantum phase transition from the topologically trivial to non-trivial class, thus featuring a narrow bandgap.

CHAPTER 11

Polymer solution and blends

11.0 Polymer visco-elasticity

A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties. Polymer blends can be broadly divided into three categories:

1. **immiscible polymer blends** (heterogeneous polymer blends)

   This is by far the most populous group. If the blend is made of two polymers, two glass transition temperatures will be observed.

2. **compatible polymer blends**

   Immiscible polymer blend that exhibits macroscopically uniform physical properties. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the component polymers.

3. **miscible polymer blends** (homogeneous polymer blend)

   Polymer blend that is a single-phase structure. In this case, one glass transition temperature will be observed.

The use of the term polymer alloy for a polymer blend is discouraged, as the former term includes multiphase copolymers but excludes incompatible polymer blends.

11.1 Examples

Examples of miscible polymer blends:

- homopolymer/homopolymer:
  - polyphenylene oxide (PPO) and polystyrene (PS).
  - polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)
  - poly(methyl methacrylate) (PMMA) and polyvinylidene fluoride (PVDF)
- Homopolymer/copolymer:

- polypropylene (PP) and EPDM
- polycarbonate (PC) and acrylonitrile butadiene styrene (ABS): Bay blend, Pulse, Anjablend

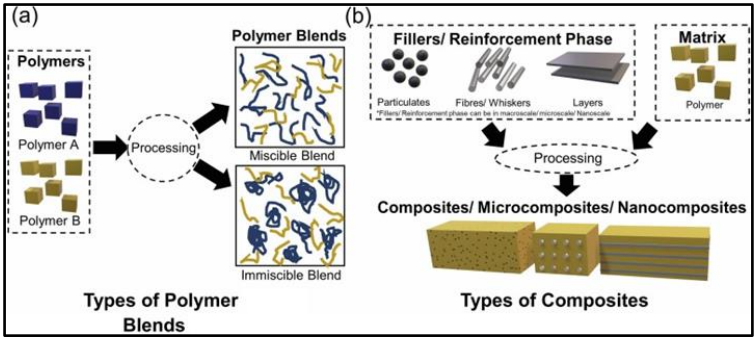


Figure 11.1 Types of polymer blends

11.2 Uses of polymer blends

Unique applications recently proposed for polymer blends include immobilization of enzymes, perm selective membranes, reverse osmosis membranes, selective ion-exchange systems, and medical applications using polyelectrolyte complexes. Polymer blends can be used as thermoplastic elastomer

11.3 Polymer solutions

Polymersolutions are solutions containing dissolved polymers. These may be liquid solutions (e.g. in aqueous solution), or solid solutions (e.g. a substance which has been plasticized).The introduction into the polymer of small amounts of a solvent (plasticizer) reduces the temperature of glass transition, the yield temperature, and the viscosity of a melt. An understanding of the thermodynamics of a polymer solution is critical to prediction of its behavior in manufacturing processes ,for example, its shrinkage or expansion in injection molding processes, or whether pigments and solvents will mix evenly with a polymer in the manufacture of paints and coatings. A recent theory on the viscosity of polymer solutions gives a physical explanation for various well-known empirical relations and numerical values including the Huggins constant, but reveals also novel simple concentration and molar mass dependence.

11.4 Applications

Polymer solutions are used in producing fibers, films, glues, lacquers, paints, and other items made of polymer materials. Thin layers of polymer solution can be used to produce light-emitting devices. Guar polymer solution gels can be used in hydraulic fracturing ("**fracking**")

Figure 11.2 application of polymers

11.5 Viscoelasticity of polymers

In materials science viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like water, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain when stretched and immediately return to their original state once the stress is removed.

Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscosity is the result of the diffusion of atoms or molecules inside an amorphous material iscoelastic materials are those which exhibit both viscous and elastic characterists. Viscoelasticity is also known as an elasticity, which is present in systems when undergoing deformation. Viscous materials, like honey, polymer melt etc., resist shear flow (shear flow is in a solid body, the gradient of a shear stress force through the body) and strain, i.e. the deformation of materials caused by stress, is linearly with time when a stress is applied. Shear stress is a stress state where the stress is parallel or tangencial to a face of the material, as opposed to normal stress when the stress is perpendicular to the face.

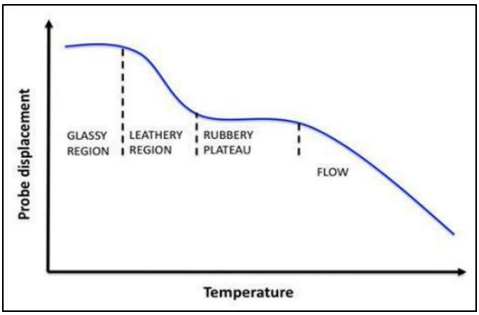


Figure 11.3 Temperature and probe displacement curve

Example is when a plastic beaker struck, emits a dull note of short duration, which is quite different from the ringing note emitted by a bell or a crystal wine glass. This property of high mechanical damping is another manifestation of viscoelasticity. It is a property that is frequently of value. In plastic structures subject to forced oscillation, mechanical vibrations at the natural frequencies of the structure do not easily build up due to the high damping capacity of the plastic. According to McCrum a good example of this is the application of plastic materials in sailing craft, particularly in hull construction. Vibration of the hull stimulated by elements are rapidly damped.

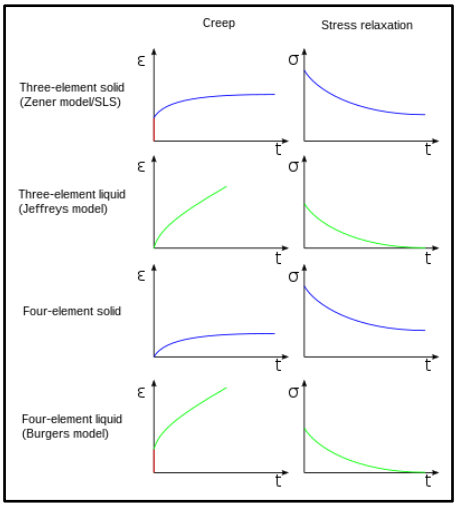


Figure 11.4Comparison of three and four models**11.6 Classical theories**

Classical theories of elasticity and viscosity of a body assume steady state stress, strain and strain rate. Therefore, the time it takes to reach equilibrium conditions is not considered. Observers over one hundreds of years ago found that most materials failed to reach equilibrium in an observable time period. Moreover, the constant coefficients of viscosity and elasticity were dependent on pre-treatments and loading history. Such effects, which were not accounted for the classical theories were called "**elastic after-effects**".

These were more pronounced in some materials such a food dough, wet clays, pitch and un vulcanized rubbers. In particular, slow deformation rates made the material act like a liquid and high deformation rates made the same material act like a elastic solid. Eventually, researchers accepted the idea that all materials behave in a viscous or elastic manner that depends on how quickly or slowly they were deformed. This behavior led to a new term: viscoelasticity.

In other words, the mechanical properties of materials, primarily polymers, are time-dependent and perfectly elastic deformation and perfectly viscous flow are idealizations that are approximately reached in some limited conditions. Viscoelasticity is, then, the study of the response of polymers (or other materials) which exhibit some of the features of both elastic and viscous behavior. Elastic materials deform instantaneously when a load is applied, and "remember" their original configuration, returning there instantaneously when the load is removed. In solids, the relaxation of the structure at the molecular level is extremely low and, therefore, their response is essentially elastic. On the other hand, viscous materials do not show such characteristics, but instead exhibit a time-dependent behavior. While under a constant stress, a viscous body strains at a constant rate, and when this load is removed, the material has "**forgotten**" its original configuration. In ordinary liquids, molecular reorganization occurs very rapidly and structural memory at the molecular level is very short. The response is essentially viscous unless the frequency of the testing experiment is very high. Viscoelastic materials exhibit certain characteristics of these two behaviors as manifested in time-dependent behavior, a "**fading memory**", partial recovery, energy dissipation, etc. Such behavior may be linear (stress and strain are proportional) or nonlinear.

Polymers are the most important viscoelastic systems. Above glass transition temperature, the response of these materials to a mechanical perturbation field involves several types of molecular motions. For instance, the rearrangement of flexible chains may be very fast on the length scale of a repeated unit. These movements imply some type of cooperativity in the conformational transitions that produce them. Cooperativity occurs even as the relaxation propagates along the chains, involving a growing number of segments of the backbone as time passes. At very long times, disentanglements of the chains takes place, and the longest relaxation time associated with this process shows a strong dependence on both the molecular weight and the molecular architecture of the system. The disentanglement process governs the flow of the system. In consequence of the complexity of the molecular responses, polymer chains exhibit a wide distribution of relaxation time that extend over several decades in the time or frequency domain.

1. Superposition principles

There are two superposition principles that are important in the theory of Viscoelasticity. The first of these is the Boltzmann superposition principle which describes the response of a material to different loading histories. This principle suggests that small changes in stress are equal to small changes in modulus multiplied by the strain. This means that the modulus is independent of the amount of material that deforms. Therefore, each loading step makes independent contribution to total loading history and the total final deformation is the sum of each contribution. The second one is the time-temperature superposition principle that establishes the correspondence between time and temperature. It has been used for a long time. Viscoelastic curves made at different temperatures are found to be superposable by horizontal shifts along a logarithmic time scale to give a unique curve covering a very large range of times or frequencies.

2-Non-linear viscoelastic response

If the Boltzmann superposition principle holds, the strain is directly proportional to the stress at any given time and, similarly, the stress at any particular time is directly proportional to the strain depending upon which of these two magnitudes are the stimulus and the corresponding

response. These assumptions are generally true for small stresses or strains, but the principle is not exact. If large loads are applied in creep measurements or large strains in stress relaxation ones, as can occur in practical structural applications, non-linear effects come into play.

11.7 Structural parameters affecting the viscoelastic response

There are several accountable inherent parameters that condition the viscoelastic behavior of polymeric materials. The primary ones are the following:

a) chemical structure
b) molecular architecture
c) molecular weight and crosslinking
d) copolymers and blends
e) effect of plasticizers
f) molecular orientation
g) fillers and fibers

11.8 Types of experiments

The analysis of the viscoelastic response is basically carried out by four different types of tests.

a) creep
b) stress relaxation
c) stress-strain experiments
d) dynamic mechanical measurements

11.9 Creep

Creep and stress relaxation tests measure the dimensional stability of a polymer, and because the tests can be of long duration, such tests are of great practical importance. Creep measurements, especially, are of interest to engineers in any application where the polymer must sustain loads for long periods. Creep and stress relaxation measurements are also of major importance to anyone interested in the theory of or molecular origins of viscoelasticity.

CHAPTER 12

Stress relaxation

12.0 Stress relaxation phenomenon

In materials science, stress relaxation is the observed decrease in stress in response to strain generated in the structure. This is primarily due to keeping the structure in a strained condition for some finite interval of time and hence causing some amount of plastic strain. This should not be confused with creep, which is a constant state of stress with an increasing amount of strain.

Since relaxation relieves the state of stress, it has the effect of also relieving the equipment reactions. Thus, relaxation has the same effect as cold springing, except it occurs over a longer period of time. The amount of relaxation which takes place is a function of time, temperature and stress level, thus the actual effect it has on the system is not precisely known, but can be bounded. Stress relaxation describes how polymers relieve stress under constant strain. Because they are viscoelastic, polymers behave in a nonlinear, non-hookean fashion. This nonlinearity is described by stress relaxation.

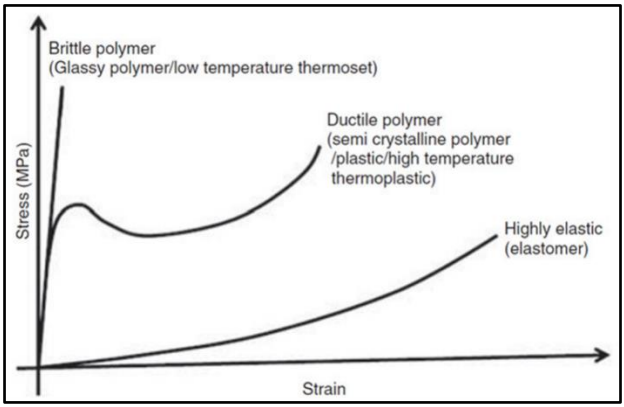


Figure 12.1 Stress relaxation process to identify brittle, ductile and elastic polymer

Viscoelastic materials have the properties of both viscous and elastic materials and can be modeled by combining elements that represent these characteristics. One viscoelastic model, called the Maxwell model predicts

behavior akin to a spring (elastic element) being in series with a dashpot (viscous element), while the Voigt model places these elements in parallel. Although the Maxwell model is good at predicting stress relaxation, it is fairly poor at predicting creep. On the other hand, the Voigt model is good at predicting creep but rather poor at predicting stress relaxation

In stress relaxation tests, the specimen is quickly deformed a given amount and the stress required to hold the deformation constant is measured as a function of time. Stress relaxation experiments are very important for a theoretical understanding of viscoelastic materials. However, such tests have not been as popular as creep measurements with experimentalists. There are probably at least two reasons for stress relaxation experiments, specially on rigid materials, are more difficult to make than creep tests .

12.1 Stress-strain experiments

This type of test measures the response (strain) of a sample subjected to a force that varies with time at constant rate. It is widely used, resulting a very important practical measurement. However, the relationship of this test to use applications is not as clear as is generally assumed. Because of the viscoelastic nature of polymers with their sensitivity to many factors, the stress-strain test is, at best, only a rough guide to how a polymer will behave in a finished object. To give the engineer or designer a complete and realistic information, tests at many temperatures, rates of testing and other conditions are required. Consequently, it needs much time and material. The shape of stress-strain curves is used to define brittle and ductile behavior. Since the mechanical properties of polymers depend on both temperature and observation time, the shape of the stress-strain curves deeply changes with the strain rate and temperature .This behavior is characteristic of amorphous and semicrystalline polymers well below the glass transition temperature, Tg. These materials fails at low strains (usually lower than 10 %) leading to a brittle fracture. The most ductile polymers undergo necking and cold drawing failing at higher strains (around 250-400 %). Semicrystalline polymers are typical examples that display this behavior at temperatures intermediate between glass transition and melting. The curves depicted in Figure 10c are characteristic of elastomers or amorphous

polymers above their Tg,showing an elastomeric behavior reaching very high deformations before breaking. The deformation takes places homogeneously in these materials or at these temperatures.shows a stress-strain curve corresponding to a tensile test for ductile polymers. Nominal stress (load divided by initial cross-sectional area of the strip) is plotted against strain. It has been observed for many years that some thermoplastics can be deformed at room temperature as a result of cold drawing. This is a remarkable phenomenon, in which the plastic deformation is concentrated in a small region of the specimen. The behavior at low strains is homogeneous and the stress rises steadily with increasing strain. Therefore, the relationship between these two magnitudes is linear since this region is that where Hooke's law is obeyed and the polymer might recovers the original shape if the stress is removed (linear elastic or viscoelastic behavior, i.e., instantaneously or temporally delayed).

12.2 Yield point

At B the sample thins to a smaller cross-section at some point with the formation of the neck. A maximum point is reached, that is called yield point, and characterized by its two coordinates: yield strain and yield stress **(εY,σY)**. In general, the yield point indicates the beginning of the plastic deformation. Further extension occurs by the movement of this neck through the specimen as it progressively thins from its initial state to the final drawn state. A decrease of the nominal stress is observed at strains higher than **εY** until the value corresponding to point C. In the region CD, the material is deformed without any apparent change of the nominal stress, giving rise to the phenomenon called cold drawing.

12.3 Strain hardening

Starting from point D, stress begins again to considerably go up indicating that the material becomes rigid. This process is labeled as strain hardening. After that, fracture of the material occurs at point X. Information about three important mechanical parameters can be obtained from this type of test: stiffness, strength and toughness.The mechanical strength is related to the highest stress that material can bear before its breaking. Its value is usually given by the breaking stress. The concept of toughness

might be defined in several ways, one of which is in terms of the area under the stress-strain curve. It is, therefore, an indication of the energy that a material can store before its rupture.

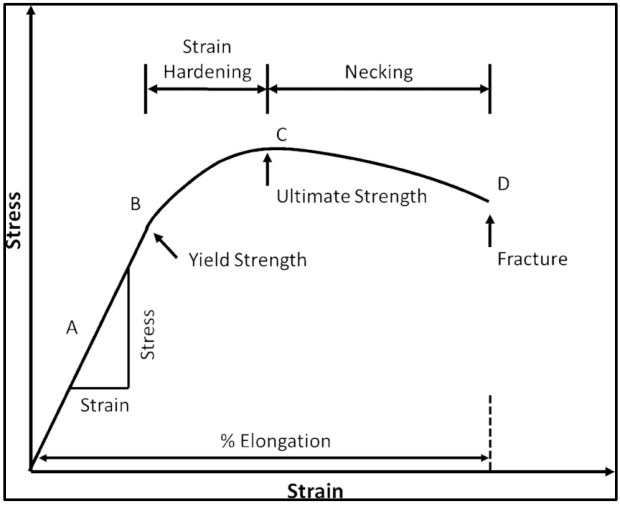


Figure 12.2 Curve graph to explain stiffness , strength and strain hardning

12.4 Factors effecting the stress relaxation

The following non-material parameters all affect stress relaxation in polymers

a) Magnitude of initial loading
b) Speed of loading
c) Temperature (isothermal vs non-isothermal conditions)
d) Loading medium
e) Friction and wear
f) Long-term storage
g) Creep
h) Viscoelasticity
i) Standard Linear Solid Model
j) Burgers material
k) Maxwell material
l) Kelvin–Voigt material

CHAPTER 13

Mechanics and Rheology of polymers

13.0 Mechanical model of polymer behavior(Newtonian equation and Hook's law)

13.1 Mechanical properties

The mechanical properties of polymers are one of the features that distinguishes them from small molecules. The mechanical properties of a polymer involve its behavior under stress. These properties tell a polymer scientist or engineer many of the things he or she needs to know when considering how a polymer can be used.

- How strong is the polymer? How much can you stretch it before it breaks?
- How stiff is it? How much does it bend when you push on it?
- Is it brittle? Does it break easily if you hit it hard?
- Is it hard or soft?
- Does it hold up well under repeated stress?

13.2 Stress and Strain

Stress: It is the resistance offered by the body to any deformation. Mathematically, it can be expressed as the restoring force per unit area.

Stress = Restoring Force /Area

= F / A

Strain: Deformation per unit length in the direction of deformation is known as strain.

Strain = Change in length / original length

= ΔL / L

13.3 Plasticity

It is the belongings of material by which material does not regain its original dimension after the removal of deforming forces. This material goes in inelastic strain. In this case, permanent deformation occurs.

13.4 Elasticity

Elasticity is the property by virtue of which a material deformed under the influence of load but after the removal of the deforming load the object tends

to recover its original dimension. If the body completely regains its original shape and size, then it is called a perfectly elastic body.

13.5 Ductility

It is the property of material, which permits material to be drawn out longitudinally to a reduced cross-sectional area, because of the application of tensile force. It also can be defined as the property of material, which permits a material to be drawn out in the form of wire.

13.6 Brittleness

It implies that material cannot be drawn out in the form of wire. The failure takes place without any significant deformation

The characterization of mechanical properties in polymers typically refers to a measure of the strength, elasticity, viscoelasticity, and anisotropy of a polymeric material. The mechanical properties of a polymer are strongly dependent upon the Van der Waals interactions of the polymer chains, and the ability of the chains to elongate and align in the direction of the applied force. Other phenomena, such as the propensity of polymers to form crazes can impact the mechanical properties. Typically, polymeric materials are characterized as elastomers, plastics, or rigid polymers depending on their mechanical properties.

The tensile strength, yield strength, and Young's modulus are measures of strength and elasticity, and are of particular interest for describing the stress-strain properties of polymeric materials. These properties can be measured through tensile testing. For crystalline or semicrystalline polymers, anisotropy plays a large role in the mechanical properties of the polymer. The crystallinity of the polymer can be measured through differential scanning calorimetry. For amorphous and semicrystalline polymers, as stress is applied, the polymer chains are able to disentangle and align. If the stress is applied in the direction of chain alignment, the polymer chains will exhibit a higher yield stress and strength, as the covalent bonds connecting the backbone of the polymer absorb the stress. However, if the stress is applied normal to the direction of chain alignment, the Van der Waals interactions between chains will primarily be responsible for the mechanical properties and thus, the yield stress will decrease. This would be observable in a stress strain graph found through tensile testing. Sample preparation, including chain orientation within the sample, for tensile tests therefore can play a large role in the observed mechanical properties.

13.7Charpy tests

The fracture properties of crystalline and semicrystalline polymers can be evaluated with charpy impact testing. Charpy tests, which can also be used with alloy systems, are performed by creating a notch in the sample, and then using a pendulum to fracture the sample at the notch. The pendulum's motion can be used to extrapolate the energy absorbed by the sample to fracture it. Charpy tests can also be used to evaluate the strain rate on the fracture, as measured with changes in the pendulum mass. Typically, only brittle and somewhat ductile polymers are evaluated with charpy tests. In addition to the fracture energy, the type of break can be visually evaluated, as in whether the break was a total fracture of the sample or whether the sample experienced fracture in only part of the sample, and severely deformed section are still connected. Elastomers are typically not evaluated with charpy tests due to their high yield strain inhibiting the charpy test results.

13.8 Tensile Strength

The tensile strength is the stress needed to break a sample. It is expressed in Pascals or psi (pounds per square inch).

1 MPa = 145 psi

The tensile strength is an important property for polymers that are going to be stretched. Fibers, for instance, must have good tensile strength.

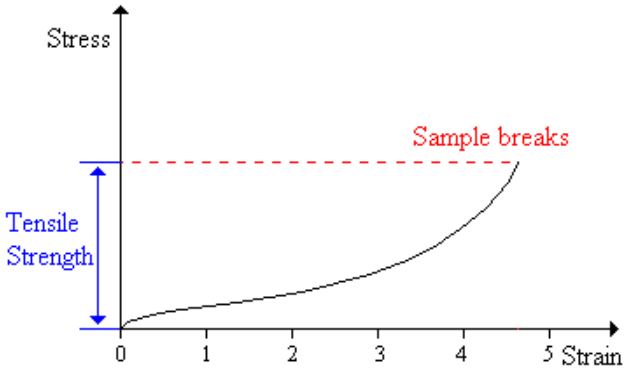


Figure 13.1 stress and strain curve to show tensile strength

13.9 % Elongation to Break

The elongation-to-break is the strain on a sample when it breaks - this usually is expressed as a percent. The elongation-to-break sometimes is called the **ultimate elongation**. Fibers have a low elongation-to-break and elastomers have a high elongation-to-break.

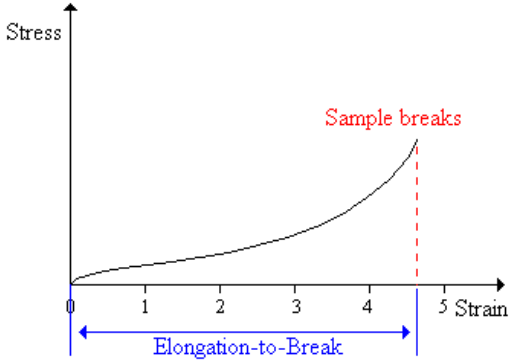


Figure 13.2 Stress and strain curves to show elongation

13.10 Young's Modulus

Young's modulus is the ratio of stress to strain. It also is called the modulus of elasticity or the tensile modulus. Young's modulus is the slope of a stress-strain curve. Stress-strain curves often are not straight-line plots, indicating that the modulus is changing with the amount of strain. In this case the initial slope usually is used as the modulus, as is illustrated in the diagram at the right.

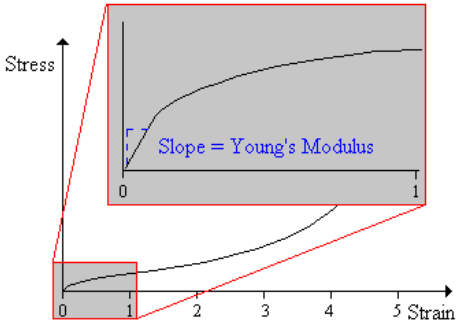


Figure 13.3 stress and strain curve to show young modulus

Rigid materials, such as metals, have a high Young's modulus. In general, fibers have high Young's modulus values, elastomers have low values, and plastics lie somewhere in between.

13.11Toughness

The toughness of a material is the area under a stress-strain curve. The stress is proportional to the tensile force on the material and the strain is proportional to its length. The area under the curve then is proportional to the integral of the force over the distance the polymer stretches before breaking.

Area$\propto\int$F(L)dL

This integral is the work (energy) required to break the sample. The toughness is a measure of the energy a sample can absorb before it breaks.

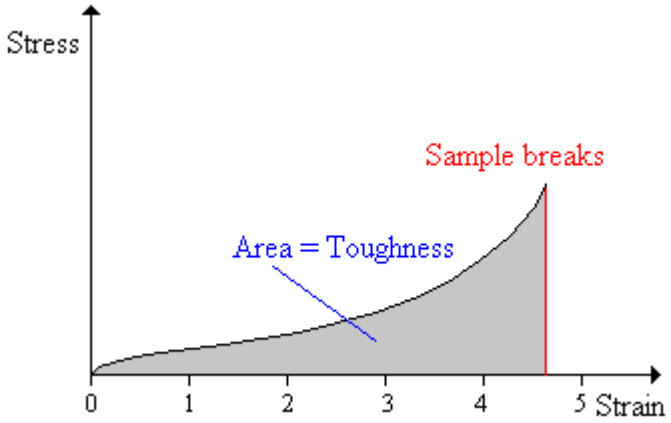


Figure 13.4 stress and strain curve to show sample breaks

There is a difference between toughness and strength, as is illustrated in the three plots below.

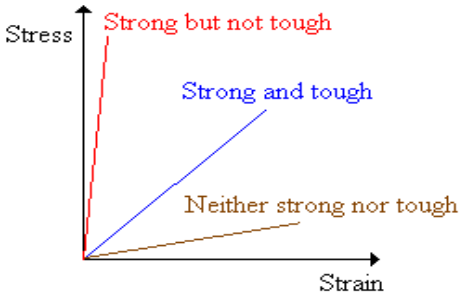


Figure 13.5 graphical representation of toughness and strength

A material that is strong but not tough is said to be brittle. Brittle substances are strong, but cannot deform very much. Polystyrene **(PS)** is brittle, for example. High impact polystyrene (HIPS), a blend of polystyrene and polybutadiene (a rubbery polymer above its glass transition temperature) is said to be rubber-toughened.

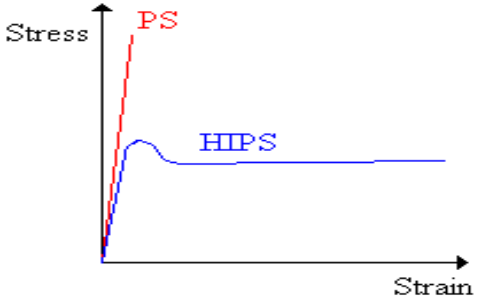


Figure 13.6 polystyrene and high impact polystyrene stress and strain curve

13.12 Fundamentals of rheology

The branch of science related to the study of deformation and flow of materials was given the name "rheology" by Bingham, whom some have called the father of modern rheology. The prefix rheo is derived from the Greek term rheos, meaning current or flow. The study of rheology includes two vastly different branches of mechanics called fluid and solid mechanics. The polymer scientist is usually concerned with viscoelastic materials that act as both solids and liquids. The elastic component is dominant in solids; hence, their mechanical properties may be described by Hooke's law, which

states that the applied stress **(s)** is proportional to the resultant strain **(γ)** but is independent of the rate of this strain

S= (dγ/dt)

Eγ Stress is equal to the force per unit area, and strain or elongation is the extension per unit length. For an isotopic solid, that is, one having the same properties regardless of direction, the strain is defined by Poisson's ratio, **V = γw/γl** , which is the change in thickness (**γw; lateral contraction**) compared to the change in length **(γl).** When there is no volume change, as when an elastomer is stretched, Poisson's ratio is 0.5.

13.12.1 Hooks laws and Newtonian equation validation

The viscous component is dominant in liquids; hence, their flow properties may be described by Newton's law. Where η is the viscosity, which states that the applied stress s is proportional to the rate of strain **dγ/dt**, but is independent of the strain γ or applied velocity gradient.Both Hooke's and Newton's laws are valid for small changes in strain or rate of strain, and both are useful in studying the effect of stress on viscoelastic materials.

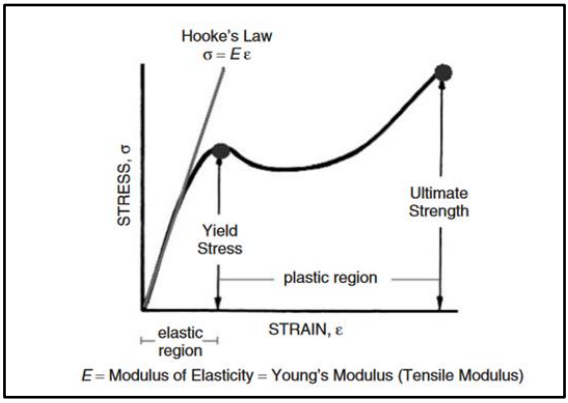


Figure 13.7 stress and strain curve to show hooks' law

The initial elongation of a stressed polymer below **Tg** is reversible elongation due to a stretching of covalent bonds and distortion of the bond angles. Some of the very early stages of elongation by disentanglement of chains may also be reversible. However, the rate of flow, which is related to slower disentanglement and slippage of polymer chains past one another, is

irreversible and increases (and **η** decreases) as the temperature increases in accordance with the following form of the Arrhenius equation , in which E is the activation energy for viscous flow:

$$\eta = Ae^{E/RT}$$

It is convenient to use a simple weightless Hookean, or ideal, elastic spring with a modulus G and a simple Newtonian (fluid) dashpot or shock absorber having a liquid with a viscosity of η as models to demonstrate the deformation of an elastic solid and an ideal liquid, respectively. In general terms, the Hookean spring represents bond flexing, while the Newtonian dashpot represents chain and local segmental movement. It is customary to attempt to relate stress–strain behavior to combinations of dashpots and springs as indicators of the relative importance of bond flexing and segmental movement. Again, in general terms, below their **Tg** polymers can be modeled as having a behavior where the spring portion is more important. Above their Tg where segmental mobility occurs, the dashpot portion is more important. The relative importance of these two modeling parts, the spring and the dashpot, is also dependent on the rate at which an experiment is carried out.

Relations between thestructureandpropertiesof polymer-based materials, thereby bridging the fields ofpolymer chemistryandpolymer engineering. To achievethis goal, so far, we have studied the structure and dynamics of single chains andthe thermodynamics of multichain systems in the preceding chapters; with that, wehave erected three fundamental pillars of that foresaid bridge. Now, the construction of the actual bridge will be the goal of the forthcoming chapter. This will helpus to rationally and quantitatively understand why many of the polymeric materialsthat we encounter in our everyday lives behave the way they do. Our prime focuswill be on those properties of polymers that have made greatest impact on our livesin the past decades, which is theirmechanicalproperties. Hence, we will first dealwith a fundamental introduction to the field ofrheology The term rheology derives from the Greek wordsrheos, meaning“flow”,andlogos, meaning understanding”. The name reminds of a famous aphorism voiced bythe Greek philosopher Simplicus, who had stated that,“everything flows”.As such, rheology is the study of the flow of matter, and therefore the branch of

physics that deals with the deformation and flow of materials, both solids and liquids. Elementary cases of mechanical response. Two elementary extreme cases can be distinguished from one another in view of amaterial's mechanical properties: it can behave either as anelastic solid, like arubber band, or as aviscous fluid, like water or syrup.In the first case of an ideal elastic solid, the energy introduced into the materialthrough exertion of an external force,f, which can also be expressed in a normalizedform as astress,σ=f/A(withAbeing the cross-sectional area of the material specimen onto which the force acts), is stored elastically.

When polymers are subjected to stress, they undergo microscopic and macroscopic deformations by conformational changes (i.e. smaller and larger-scale molecular rearrangements) and by viscoelastic flow. To analyze the viscoelastic response in creep and relaxation experiments, both elastomeric and plastic materials are often modeled by combinations of spring and dashpot elements. The spring behaves exactly like a metal spring, stretching instantaneously under stress and holding the load, whereas the plunger immersed in the dashpot filled with a Newtonian liquid moves at a rate proportional to the stress. On removing the stress, there is no recovery. The ideal spring obeys Hooke's law ***(σ = E · ε)*** and the liquid in the dashpot obeys Newton's law of viscosity:

$$\sigma = \eta \cdot d\varepsilon / dt.$$

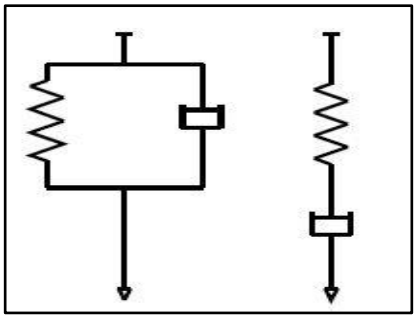


Figure 13.8 newton law of viscosity experiment

Phase changes, phase transitions, refer to changes of state. Most low-molecular-weight materials exist as solids, liquids, and gases. The transitions that separate these states are melting (or freezing) and boiling (or condensing). By contrast, polymers do not vaporize "intact" to a gas, nor do they boil. The state of a polymer, that is, its physical response character, depends on the time allotted for interaction and the temperature as well as the molecular organization (crystalline, amorphous mix). The term "relaxation" refers to the time required for the response to a change in pressure, temperature, or other applied parameter. The term "dispersion" refers to the absorption or emission of energy at a transition. In practice, the terms relaxation and dispersion are often used interchangeably. An experiment that can be used in the classroom involves the comparison between the bounce of a superball and a ball bearing. Drop both from the same height and notice which rebounds the greatest. The ball bearing is typically some metal such as steel and the impact of the drop causes some of the iron atoms to come closer to one another. The rebound is the result of enthalpy forces as the iron atoms pushed back to their original shape.

13.12.2 Stress–strain curve

Rigid PVC is representative of hard and strong polymers. These polymers have a high modulus of elasticity and high yield strength. The curve for hard and tough polymers, such as ABS copolymers, shows moderate elongation prior to the yield point followed by non-recoverable elongation. In general, the behavior of all classes of polymer behavior is Hookean prior to the yield point. The reversible recoverable elongation prior to the yield point, called the elastic range, is primarily the result of bending and stretching of covalent bonds in the polymer backbone. This useful portion of the stress–strain curve may also include some recoverable uncoiling of polymer chains. Irreversible slippage of polymer chains is the predominant mechanism after the yield point. Since these properties are time dependent, the soft and weak polymers may resemble the hard and strong polymers if the stress is rapidly applied and vice versa. These properties are also temperature dependent. Hence, the properties of soft and tough polymers may resemble hard and brittle when temperature is decreased.

GLOSSERY

Bakelite: A polymer produced by the condensation of phenol and formaldehyde.

biopolymer: A naturally occurring polymer, such as protein.

buna: Copolymer of butadiene and styrene or acrylonitrile.

butyl rubber: A copolymer of isobutylene and isoprene.

cellulose: A naturally occurring carbohydrate polymer consisting of repeating glucose units.

cellulose acetate: The ester of cellulose and acetic acid.

cellulose nitrate: The product obtained by the reaction of nitric acid and sulfuric acid with

cellulose; erroneously called nitrocellulose. The product is classified as primary,

secondary, or tertiary according to how many groups in each repeating anhydroglucose unit in cellulose are nitrated.

cis: A geometric isomer with both groups on the same side of the ethylenic double bond.

collodion: A solution of cellulose nitrate in an equimolar mixture of ethanol and ethyl ether.

colloid: An aggregate 109 to 107 m long; an aggregate of smaller particles.

coumarone-indene resins: Polymers produced by the polymerization of distillation residues.

covalent bond: Chemical bonds formed by the sharing of electrons of the bonded atoms

such as the carbon atoms in graphite or diamonds.

cross-links: Covalent bonds between two or more linear polymeric chains.

crystallites: Aggregates of polymers in crystalline form.

C-stage: A crosslinked resole resin.
denaturation: The change in properties of a protein resulting from the application of heat or the addition of a foreign agent, such as ethanol.

ebonite: Hard rubber; highly crosslinked natural rubber (NR).

elastomer: A rubber.

filament: The individual extrudate emerging from the holes in a spinneret.

functionality: The number of reactive groups in a molecule.

Galalith: A plastic produced by molding casein.

glyptal: A polyester produced by the condensation of glycerol and phthalic anhydride.

hydrogen bonds: Very strong forces resulting from the attraction of hydrogen atoms in one molecule with an oxygen or nitrogen atom in another molecule. These forces may also be present as intramolecular forces in macromolecules.

intermolecular forces: Secondary valence forces between molecules.

intramolecular forces: Secondary valence forces within a molecule.

linear: A continuous chain, such as HDPE.

natural rubber, or NR (Hevea brasiliensis): Polyisoprene obtained from rubber plants.

novolac: A thermoplastic phenol-formaldehyde resin prepared by the condensation of phenol and a small amount of formaldehyde on the acid side. Novolacs may be advanced to thermoset by heating with formaldehyde, which is usually obtained by the thermal decomposition of hexamethylenetetramine.

NR: Natural rubber.

nylon-66 (or nylon-6,6): A polyamide produced by the condensation of adipic acid

[HOOC(CH2)4COOH] and hexamethylenediamine [H2N(CH2)6NH2].

oligomer: A very low molecular weight polymer in which the number of repeating units (n) equals 2 to 10 (oligos is the Greek term for few).

plasticizer: An additive that reduces intermolecular forces in polymers.

polymer: A giant molecule (or macromolecule) made up of multiple repeating units, such as polyethylene, in which at least 1000 ethylene units (MCH2CH2M) are joined

together by covalent bonds. The word is derived from the Greek words meaning many parts.

polymer age: An age when the use of polymers is emphasized, as in the twentieth century.

protein: A polymer made up of many amino acid repeating units, i.e., a polyamide.

Raoult's law: A law that states that colligative properties of solutions, such as osmotic pressure and changes in vapor pressure, are related to the number of solute molecules present.

rayon: Regenerated cellulose in the form of filaments.

resole: A condensation product produced by the reaction of phenol and formaldehyde

under alkaline conditions.

shellac: A resin secreted by small coccid insects.

spinneret: Small holes through which a solution or molten polymer is extruded in order to form filaments for fibers.

tanning: Crosslinking of proteins by the reaction with crosslinking agents such as tannic acid.

thermoplastic: A linear polymer that may be softened by heat and cooled in a reversible physical process.

thermoset plastic: A network polymer usually obtained by crosslinking a linear polymer.

Thiokol: A polyethylene sulfide elastomer.

amorphous: Noncrystalline polymer or noncrystalline areas in a polymer.

anti form: Trans (t) or low-energy conformer.

aramides: Aromatic nylons.

Arrhenius equation: An equation showing the exponential effect of temperature on a process.

atactic: A polymer in which there is a random arrangement of pendant groups on each side of the chain, as in atactic PP:

Avrami equation: An equation used to describe the crystallization rate.

backbone: The principal chain in a polymer molecule.

biaxially oriented film: A strong film prepared by stretching the film in two directions at right angles to each other. This strong film will shrink to its original dimensions when heated.

branched polymer: A polymer having extensions of the polymer chain attached to the

polymer backbone, such as LDPE. Polymers having pendant groups, such as the methyl groups in polypropylene, are not considered to be branched polymers.

bulky groups: Large pendant groups on a polymer chain.

cellulose: A polymer in which cellobiose is the repeating unit.

chiral center: An asymmetric center such as a carbon atom with four different groups.

cold drawing: The stretching of a fiber or fibers to obtain products with high tensile strength.

configurations: Related chemical structures produced by the breaking and making of primary valence bonds.

conformations: Various shapes of polymers resulting from the rotation of single bonds in the polymer chain.

conformer: A shape produced by a change in the conformation of a polymer.

contour length: The fully extended length of a polymer chain, equal to the product of the length of each repeating unit (1) times the number of units, or mers (n), i.e., nl is the full contour length.

critical chain length (z): The minimum chain length required for entanglement of the polymer chains.

crosslinked density: A measure of the relative degree of crosslinking in a network polymer.

crystalline polymer: A polymer with ordered structure that has been allowed to disentangle and form crystals such as HDPE. Thus, isotactic polypropylene, cellulose, and stretched rubber are crystalline polymers.

crystallites: Regions of crystallinity.

differential scanning calorimetry (DSC): An instrumental thermal analytical technique in which the difference in the amount of heat absorbed by a polymer sample and a standard is measured by the power consumed as the temperature is increased.

differential thermal analysis (DTA): A thermal instrumental analytical technique in whichthe rate of absorption of heat by a polymer is compared with that of a standard suchas glass or alumina.

dilatometry: A technique in which changes in specific volume are measured.

dipole-dipole interactions: Moderate secondary valence forces between polar groups in different molecules or in different locations in the same molecule.

dispersion forces: Same as London forces.

DNA: Deoxyribonucleic acid.

DP: Degree of polymerization or the number of repeating units (mers) in a polymer chain.

DP: Average degree of polymerization in a polydisperse polymer.

end-to-end distance (r): The shortest distance between chain ends in a polymer.

endothermic: A process in which energy is absorbed.

eutactic: An isotactic or syndiotactic polymer.

excluded volume: The volume that must be disregarded because only one atom of a chain may occupy any specific space at any specified time.

fiber: A polymer with strong intermolecular hydrogen bonding.

flexibilizing groups: Those groups in the polymer backbone that increase the segmental motion of polymers, e.g., oxygen atoms or multiple methylene groups.

fringed micelle model: An outmoded model showing amorphous and crystalline domains in a polymer.

gauche forms (g): Conformers in which the methylene groups in the polymer chain are apart relative to rotation about a C–C bond.

glass transition temperature (Tg): A characteristic temperature at which glassy amorphous polymers become flexible or rubber-like because of the onset of segmental motion.

glassy state: Hard, brittle state.

gutta percha: naturally occurring trans isomer of polyisoprene.

head-to-tail configuration: The normal sequence of mers in which the pendant groups are regularly spaced like the methyl groups in polypropylene, i.e., high-density polyethylene (HDPE): Formerly called low-pressure polyethylene, a linear polymer produced by the polymerization of ethylene in the presence of Ziegler-Natta or Phillips catalysts.

hydrogen bonding: Strong secondary valence forces between a hydrogen atom in one molecule and an oxygen, nitrogen, or fluorine atom in another molecule. These forces may also exist between hydrogen atoms in one location and oxygen, nitrogen, or fluorine atoms in another location in the same molecule. Intermolecular hydrogenbonds are responsible for the high strength of fibers. Helices are the result of intramolecular hydrogen bonds.

intermolecular forces: Secondary valence, or van der Waals, forces between different molecules.

isotactic: A polymer in which the pendant groups are all on the same side of the polymer backbone.

lamellar: Plate-like in shape

linear polymer: A polymer like HDPE that consists of a linear chain without chain-extending branches.

London forces: Weak transitory dispersion forces resulting from induced dipole-induced dipole interaction.

low-density polyethylene (LDPE): Formerly called high-pressure polyethylene, a branched polymer produced by the free radical-initiated polymerization of ethylene at high pressure.

Maltese cross: A cross with arms like arrowheads pointing inward.

melting point (Tm): The first-order transition when the solid and liquid phases are in equilibrium.

mer: The repeating unit in a polymer chain.

methylene: —CH2—.

modulus: The ratio of stress to strain, as of strength to elongation, which is a measure of stiffness of a polymer.

monodisperse: A polymer made up of molecules of one specific molecular weight, such as a protein.

n: Symbol for the number of mers (repeating units) in a polymer.

nanometer (nm): 109 m.

nylon: A synthetic polyamide.

pendant groups: Groups attached to the main polymer chain or backbone, like the methyl groups in polypropylene.

pentane interference: The interference with free motion caused by the overlap of the hydrogen atoms on the terminal carbon atoms in pentane.

polydisperse: A polymer consisting of molecules of many different molecular weights,such as commercial HDPE.

r: Symbol for end-to-end distance.

radius of gyration (S): The root-mean-square distance of a chain end to a polymer's center of gravity.

random flight technique: A statistical approach used to measure the shortest distance between the start and finish of a random flight.

RNA: Ribonucleic acid.

S: The radius of gyration.

side chain crystallization: Crystallization related to that of regularly spaced long pendant groups.

single polymer crystals: A lamellar structure consisting of folded chains of a linear polymer, such as polyethylene.

spherulites: Aggregates of polymer crystallites.

stiffening groups: Those groups in the polymer backbone that decrease the segmental motion of polymers, e.g., phenylene, amide, carbonyl, and sulfonyl groups.

switchboard model: A model resembling a switchboard used to depict crystalline and amorphous domains in a polymer.

syndiotactic: A polymer in which the pendant groups are arranged alternately on each side of the polymer backbone, as in syndiotactic PP:

Bingham plastic: A plastic that does not flow until the external stress exceeds a critical threshold value (S0).

Brownian motion: movement or large particles in a liquid as a result of bombardment by smaller molecules. This phenomenon was named after the botanist Robert Brown, who observed it in 1827.

buoyancy factor: (1 V) or 1 the specific volume density of a polymer. This

term, used in ultracentrifugal experiments, determines the direction of polymer transport under the effect of centrifugal forces in the cell.

CED: Cohesive energy density.

chromatography: Separation technique based on use of a medium that shows selective absorption.

Clausius-Clapeyron equation: For small changes in pressure, the unintegrated expression dT/dp = RT2

/Lp may be used where L is the molar heat of vaporization

colligative properties: Properties of a solution that are dependent on the number of solute molecules present and are usually related to the effect of these molecules on vapor pressure lowering.

cloud point: The temperature at which a polymer starts to precipitate when the temperature is lowered.

cohesive energy density (CED): The heat of vaporization per unit volume

commercial polymer range: A molecular weight range high enough to have good physical properties but not too high for economical processing.

critical molecular weight: The threshold value of molecular weight required for chain entanglement.

cryometry: Measurement of Mn from freezing point depression.

d: The width of the baseline of idealized peaks in a gel permeation chromatogram.

delta : Symbol for solubility parameter.

e: Symbol for base of Napierian logarithms (e = 2.718).

E: Energy of activation.

electrophoresis: A form of chromatography that uses an electric field to separate molecules. end group analysis: The determination of molecular weight by counting of end groups.

f: Symbol for frictional coefficient in ultracentrifugal experiments.

Flory-Huggins theory A theory used to predict the equilibrium behavior between liquid phases containing an amorphous polymer.

fractional precipitation: Fractionation of polydisperse systems by adding small amounts of a nonsolvent to a solution of the polymer and separating the precipitate.

fractionation of polymers: Separation of a polydisperse polymer into fractions of similar molecular weights.

gel permeation chromatography: A type of liquid-solid elution chromatography which automatically separates solutions of polydisperse polymers into fractions by means of the sieving action of a swollen crosslinked polymeric gel. Also called size exclusion chromatography.