

Polymer Modification

I. INTRODUCTION

In [Chapter 2](#), we discussed the various polymerization mechanisms. In principle, with the large number of monomers available, a virtually endless number of polymers can be obtained by various polymerization reactions. Quite frequently, a given monomer is converted into the corresponding homopolymer. However, in order to meet increasingly stringent and specific end-use requirements, novel polymeric materials have also been developed through modification of existing polymers. Development of tailor-made materials by polymer modification is usually less costly and can be achieved more readily than through synthesis of new polymers.

For a polymer to be useful, it must be able to function properly in a given application. The performance of a polymer is determined primarily by the composition and structure of the polymer molecule. These control the physical, chemical, and other characteristics of the polymer material. Therefore modification of the composition of the structural units represents one of the main approaches to the modification of polymer behavior. In addition to the chemical nature and composition of the structural units that constitute the polymer backbone, molecular architecture also contributes to the ultimate properties of polymeric products. Thus polymer modification can be accomplished by employing one or more of the following techniques:

- Copolymerization of more than one monomer
- Control of molecular architecture
- Postpolymerization polymer reactions involving functional/reactive groups introduced deliberately into the polymer main chain or side groups

The above property modification techniques are associated with the control of the chemical, composition, and structural nature of the polymer, which is effected largely during the polymerization process. However, few polymers are used technologically in their chemically pure form. Virtually all commercially available polymeric materials are a combination of one or more polymeric systems with various additives designed, with due consideration to cost factors, to produce an optimum property and/or process profile for specific applications. Modification of polymers through the use of chemical additives and reinforcements through alloying and blending procedures and by composite formation is discussed in [Chapter 9](#). In this chapter, we restrict our discussion to polymer modification techniques associated with chemical phenomena brought about either during or after polymerization.

II. COPOLYMERIZATION

Macromolecular design and architecture through copolymerization of monomers has led to a number of commercially important polymers. Copolymer composition can be varied over wide limits, resulting in a wide range of property/process performance. A copolymer may be composed of comparable amounts of the constituent monomers. The properties of the resulting copolymer will be substantially different from those of the parent homopolymers. On the other hand, the copolymer may contain only a very small amount of one of the monomers. In this case, the gross physical characteristics of the copolymer probably approximate those of the homopolymer of the major constituent, while the minor constituent confers specific chemical properties on the copolymer. We now illustrate these principles by discussing some examples.

A. STYRENE–BUTADIENE COPOLYMERS

Polybutadiene is an elastomeric material with good elastic properties and outstanding toughness and resilience. However, it has relatively poor resistance to oils, solvents, oxidation, and abrasion. Polystyrene, on the other hand, is relatively chemically inert and is quite resistant to alkalis, halide acids, and

oxidizing and reducing agents. It is also very easy to process. But then, polystyrene is quite brittle with a low heat-deflection temperature (82 to 88°C). Styrene and butadiene copolymers provide a good illustration of the considerable latitude in the variation of polymer properties that can be achieved by a careful manipulation of the composition of the copolymer and the distribution of these components. Styrene and butadiene can be copolymerized to produce either random, graft, or block copolymers. Styrene–butadiene random copolymer exhibits a homogeneous single phase and has properties intermediate to those of the parent homopolymer. On the other hand, block or graft copolymers of styrene and butadiene form heterogeneous multiphase systems whose properties are not simply characteristic of each homopolymer, but are dictated by the multiphase character of the copolymer.

Most of the defects of polybutadiene homopolymer can be overcome by the incorporation of 28% styrene into the copolymer. This is due essentially to the great rigidity and other beneficial properties of the styrene molecule. The enhanced properties of SBR and its ease of processability makes SBR the preferred material over natural rubber in such applications as belting, hose, and molded goods and in vulcanized sheet and flooring. Rubber shoe soles are made almost exclusively from SBR. Copolymers containing about 25% styrene are also useful adhesives, especially in the form of aqueous dispersion or in solution. If the ratio of styrene to butadiene is in the range 60:40 and higher, the copolymer is nontacky and is used in hot-melt adhesives and latex paints. For example, emulsion copolymers composed of 74% styrene and 25% butadiene (by weight) find wide applications in paints. In those applications, the hardness of polystyrene is partially retained, but its brittleness is modified by the presence of butadiene.

1. Styrene–Butadiene Rubber (SBR) (Random Copolymer)

SBR is produced by the free-radical polymerization of styrene and butadiene, and, as such, the resulting copolymer is necessarily random. Also, the structure is irregular. Consequently, SBR is not crystallizable. Butadiene can undergo either 1,2 or 1,4 polymerization. The structure of the resulting SBR copolymer is shown in Figure 5.1.

Commercial SBR is produced by either emulsion or solution copolymerization of butadiene and styrene. Emulsion copolymerization is either a cold (41°F) or hot (122°F) process. The copolymers from the hot and cold processes have principal differences in molecular weight, molecular weight distribution, and microstructure, as shown in Table 5.1. The solution copolymerization process for the production of

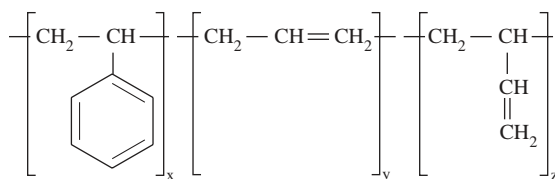


Figure 5.1 Structure of styrene–butadiene rubbers.

Table 5.1 Property Differences between Hot and Cold SBR

Property	Hot	Cold
Molecular weight		
Viscosity average, \overline{M}_v	150–400,000	280,000
Weight average, \overline{M}_w	250–450,000	500,000
Number average, \overline{M}_n	30–100,000	110–260,000
Microstructure (%)		
1,4 (<i>cis</i>)	15	18
1,4 (<i>trans</i>)	58	69
1,2 (vinyl)	27	23

From Strichartzuk, P.T. and Wright, D.E., *Handbook of Adhesives*, 2nd ed., Skeist, I., Ed., Van Nostrand Reinhold, New York, 1977. With permission.

SBR involves the use of alkyllithium catalysts. Solution SBR generally has a higher molecular weight, narrower molecular weight distribution, and higher *cis*-diene content than emulsion SBR.

Example 5.1: Generally, hot SBR is better suited to adhesive formulation than cold SBR. Explain.

Solution: From Table 5.1, hot SBR has a lower molecular weight and a broader molecular weight distribution than cold SBR. The lower molecular weight fraction provides “quick stick,” while the higher molecular weight fraction provides shear strength. On the other hand, narrow molecular weight distribution and higher *trans*-structure of cold SBR make it less adaptable to adhesives.

Example 5.2: Explain the following observations:

- Tire treads made from solution SBR are superior to those from emulsion SBR.
- The ozone resistance of SBR is superior to that of natural rubber, but when cracks start in SBR they grow much more rapidly.

Solution:

- Solution SBR has a higher molecular weight, narrower molecular weight distribution, and higher *cis*-1,4-polybutadiene content than emulsion SBR. These qualities reduce tread wear and enhance crack resistance of the tire.
- The presence of styrene in SBR reduces the amount of unsaturation relative to natural rubber. Consequently, the ozone resistance of SBR is higher than that of natural rubber. Natural rubber has a *cis*-1,4 configuration, which makes it a tough material resistant to crack growth. SBR is mainly *trans*-1,4, which is less impact resistant.

2. Styrene–Butadiene Block Copolymers

Styrene–butadiene block copolymers belong to a new class of polymers called thermoplastic elastomers (TPE). Products made from these polymers have properties similar to those of vulcanized rubbers, but they are made from equipment used for fabricating thermoplastic polymers. Vulcanization is a slow and energy-intensive thermosetting process. In contrast, the processing of thermoplastic elastomers is rapid and involves cooling the melt into a rubberlike solid. In addition, like true thermoplastics, scrap from TPE can be recycled.

Styrene–butadiene block copolymer belongs to the A-B-A type thermoplastic elastomer. The principal structure of this type of polymer involves the thermoplastic rubber molecules terminated by the hard, glassy end blocks. The A and B copolymer block segments are incompatible and, consequently, separate spontaneously into two phases. Thus in the solid state, the styrene–butadiene (S-B-S) thermoplastic elastomer has two phases: a continuous polybutadiene rubber phase and the dispersed glassy domains of polystyrene. The styrene plastic end blocks, called domains, act as cross-links locking the rubber phase in place.

In commercial thermoplastic S-B-S rubber, the end-block phase is present in a smaller proportion with a styrene-to-butadiene (end-block-to-midblock) ratio in the range 15:85 to 40:60 on weight basis. The useful temperature range of S-B-S copolymer lies between the T_g of polybutadiene and polystyrene. Below the T_g of polybutadiene, the elastomeric midblocks become hard and brittle. Above the T_g of polystyrene, the domains soften and cease to act as cross-links for the soft midblocks. Between the T_g of both homopolymers, however, the hard styrene domains prevent the flow of the soft elastomeric butadiene midsegments through a network similar to vulcanized rubber. Therefore, within normal use temperature, S-B-S block copolymer retains the thermoplasticity of styrene blocks and the toughness and resilience of the elastomer units.

B. ETHYLENE COPOLYMERS

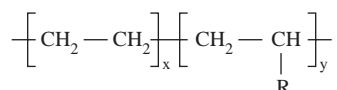
Low-density polyethylene (LDPE) is produced under high pressures and temperatures. It finds applications in film and sheeting uses and in injection-molded products such as insulated wires and cables. Its physical properties are dictated by three structural variables: density, molecular weight, and molecular weight distribution. As density increases, barrier properties, hardness, abrasion, heat, and chemical resistance, strength, and surface gloss increase. On the other hand, decreasing density results in enhanced

Table 5.2 *Some Ethylene Copolymers*

R	Copolymer
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{Me} \end{array}$	Ethylene–methyl acrylate (EMA)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{Et} \end{array}$	Ethylene–ethyl acrylate (EEA)
$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{C}-\text{Me} \end{array}$	Ethylene–vinyl acetate (EVAc)

toughness, stress-crack resistance, clarity, flexibility, and elongation and in reduced creep and mold shrinkage. Melt index (MI) is a measure of molecular weight; it decreases with increasing molecular weight. Increasing MI improves clarity, surface gloss, and mold shrinkage. Decreasing MI leads to improved creep and heat resistance, toughness, melt strength, and stress-cracking. Narrower molecular weight distribution gives better impact strength, but reduced resin processability. A broader molecular weight distribution is more shear sensitive and, consequently, leads to shear viscosity at high shear rates and is thus easier to process.

By copolymerizing ethylene with polar α -olefins, it is possible to produce a variety of materials ranging from rubbery to low melting products — suitable for hot-melt adhesives — to those that demonstrate unusual toughness and flexibility. This class of copolymers can be represented by the general formula



where R is a polar group shown in Table 5.2. The introduction of comonomers with a polar pendant group, R, produces a highly branched random copolymer but with increased interchain interaction. Thus, relative to the homopolymer, these copolymers have enhanced flexibility, toughness, stress-cracking resistance, oil and grease resistance, clarity, and weatherability. Some of these are illustrated for EVAc in Table 5.3. EEA, for example, also has the flexibility of plasticized vinyl without the thermal instability and plasticizer migration problems associated with PVC. In general, the range of properties of the copolymer can be varied by varying the proportion and molecular weight of the comonomer.

C. ACRYLONITRILE-BUTADIENE-STYRENE (ABS)

ABS is the generic name of a family of engineering thermoplastics produced by a combination of three monomers: acrylonitrile, butadiene, and styrene. The overall property balance of the terpolymer is a

Table 5.3 *Properties of Rotational-Molding Polyethylene Resins*

Property	EVAc Copolymer	LDPE
Melt index, g/10 min	1.5	1.5
Density, g/cm ³	0.933	0.925
Tensile strength, psi	1600	1450
Elongation, %	500	450
Flexural modulus, psi	50,000	35,000
Environmental stress-crack resistance, h	50	20
Tensile impact strength, ft-lb/in. ²	32	25
Dart impact strength at -20°F, ft-lb	32	20

From Wake, W.C., *Adhesion and the Formulation of Adhesives*, Applied Science Publishers, London, 1976.

result of the contribution of the unique characteristics of each monomer. Polymer chemical resistance and heat and aging stability depend on acrylonitrile, while its toughness, impact resistance, and property retention at low temperature are developed through butadiene. Copolymer rigidity, glossy surface appearance, and ease of processability are contributions from styrene. The terpolymer properties are controlled by manipulation of the ratio and distribution of the three components.

ABS resins consist essentially of two phases: a rubbery phase dispersed in a continuous glassy matrix of styrene–acrylonitrile copolymer (SAN) through a boundary layer of SAN graft. The dispersed rubbery phase is rubber polymerized from butadiene. Styrene and acrylonitrile are graft-polymerized to the rubber thus forming the boundary layer between the dispersed rubber phase and the continuous glassy matrix. Increased molecular weight of SAN improves product strength and ease of processability, while the concentration, size, and distribution of the rubber particles influence product toughness and impact strength. By a careful variation of the parameters controlling the phases, a family of ABS with a broad range of properties has been developed.

D. CONDENSATION POLYMERS

A large number of commercially important condensation polymers are employed as homopolymers. These include those polymers that depend on crystallinity for their major applications, such as nylons and fiber-forming polyesters, and the bulk of such important thermosetting materials like phenolics and urea–formaldehyde resins. In many applications, condensation polymers are used as copolymers. For example, fast-setting phenolic adhesives are resorcinol-modified, while melamine has sometimes been incorporated into the urea–formaldehyde resin structure to enhance its stability. Copolyesters find application in a fairly broad spectrum of end uses.

The diverse end-use pattern of copolyesters derives from the rather broad structural modifications that are in general possible with condensation polymers. Addition polymers consist of a chain of carbon atoms on their backbones. Modification of these polymers is limited essentially to the manipulation of the pendant group. On the other hand, for condensation polymers, in addition to the modification of the pendant structure, there is the benefit of the additional possible structural alteration of the backbone. In the case of polyesters and copolyesters a variety of monomers offers this possibility: aromatic, alicyclic, and unsaturated diols and dibasic acids. As discussed in [Chapter 4](#), the presence of aromatic or alicyclic rings on the chain backbone enhances chain stiffness, while the presence of oxygen facilitates chain rotation and consequently increases chain flexibility. Also, by a suitable choice of monomers, the spacing between the polar ester groups and hence the cohesive energy density can be controlled. The numerous and varied applications of copolyesters are a consequence of the literally infinite combinations of dibasic acids and diols that are possible. Some of these applications include surface coatings, polyurethane polyester–polyether thermoplastic elastomers, laminating resins, and thermosetting molding compounds.

Most polymers that function properly at ambient temperature quite frequently have limited performance at sustained elevated temperatures. This invariably limits the utility of polymeric materials. The low thermal stability is generally due to decreased crystallinity and/or thermal decomposition. Polymer chemists have, through some ingenious ways, synthesized polymer — such as aromatic polyimides and the so-called ladder polymers — specifically designed for high-temperature applications. However, it has also been possible to modify polymers to improve their thermal stability and hence extend their range of utility. A few examples of condensation polymers illustrate this point.

1. Acetal Copolymer

The elemental composition of the backbone of a polymer determines its thermal stability. Most olefin polymers with carbon–carbon backbone degrade thermally by random chain scission. They are usually difficult to stabilize thermally through copolymerization. On the other hand, heterochain addition polymers degrade thermally by depolymerization or successive unzipping of monomers. If a comonomer is incorporated into the polymer backbone to interrupt the unzipping action, improved thermal stability of the polymer can be achieved. This principle is illustrated by the thermal stabilization of acetal polymers. Acetal homopolymer or polyoxymethylene is a formaldehyde polymer that is characterized by a good balance of physical, mechanical, chemical, and electrical properties. However, the polymer has hemiacetal hydroxy end groups that render the polymer thermally unstable. One way of stabilizing the homopolymer is by the use of appropriate additives. Another approach is to transform the unstable end groups into stable end groups by “end capping” through acetylation or methylation. The polymer reaction is carried

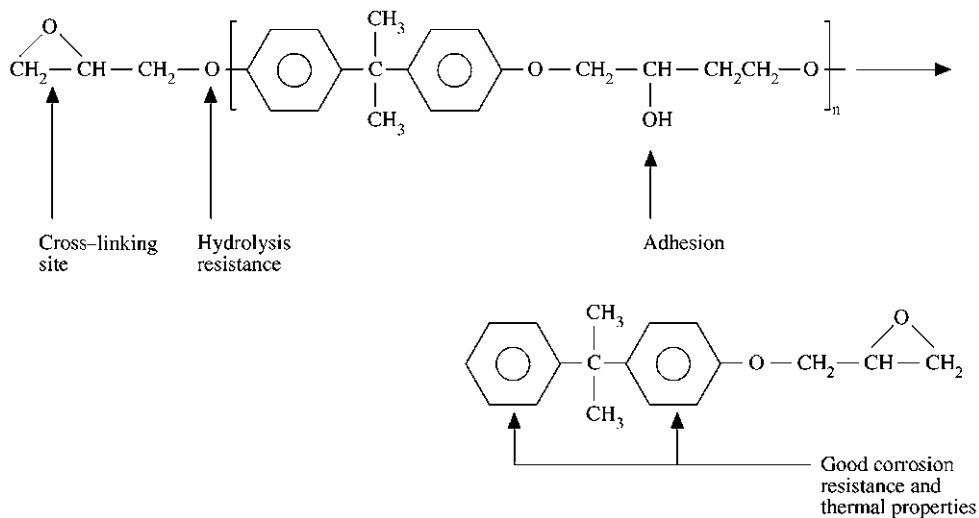
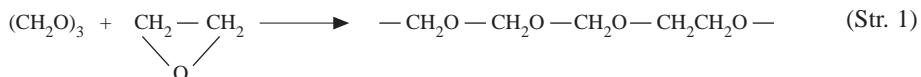


Figure 5.2 Diglycidyl ether of bisphenol A (DGEBA).

out in the solid state to produce a polymer that is sufficiently thermally stable to be fabricated by melt processing.

In contrast to acetal homopolymer, acetal copolymers have built-in heat stabilization. They are prepared by copolymerization of trioxane with small amounts of comonomer, usually cyclic ethers like ethylene oxide or 1,3-dioxolane.



This results in the random distribution of C–C bonds in the polymer chain. The depolymerization of ethylene oxide units is much more difficult than that of oxymethylene units. Thus copolymerization confers thermal stability on the acetal copolymer. The copolymer exhibits good property retention when exposed to hot air at temperatures up to 220°F or water as hot as 180°F for long periods of time. For intermittent use, higher temperatures can be tolerated.

2. Epoxies

Epoxies are polymer materials characterized by the presence of reactive terminal epoxide groups. A frequently used epoxy resin is diglycidyl ether of bisphenol A (DGEBA) (Figure 5.2). Epoxy resins, because of their versatility, are used in a variety of applications in protective coatings, adhesives, laminates, and reinforced plastics and in electrical and electronic devices. Epoxy resins, however, exhibit lower heat resistance than phenolics due to the lower aromatic units in their structures. A combination of the desirable characteristics of phenolics and epoxies is obtained in epoxy–novolak, which is a type of multifunctional epoxy resin based on the modification of epoxy resin with novolak phenolics (Figure 5.3). In this system, the phenolic component confers thermal stability, while the epoxide group provides sites for cross-linking. The strength–temperature profiles for three unmodified epoxies are shown in Figure 5.4A. It can be observed that none of these adhesives shows any appreciable strength retention beyond 100°C. However, the phenolic-modified epoxy adhesive system exhibits good strength retention even up to 300°C (Figure 5.4B).

3. Urea–Formaldehyde (UF) Resins

Another example of the improvement of properties of condensation polymers through copolymerization is illustrated by recent work with urea–formaldehyde (UF) resins.^{3,4} The preponderance of wood adhesive

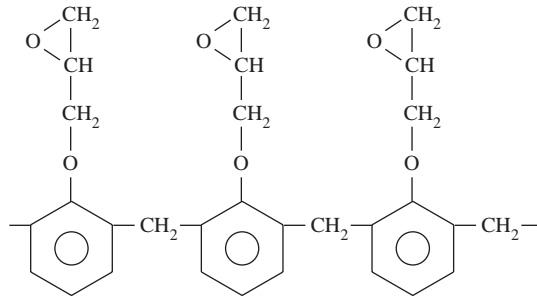


Figure 5.3 Structure of novolak-modified epoxy resin.

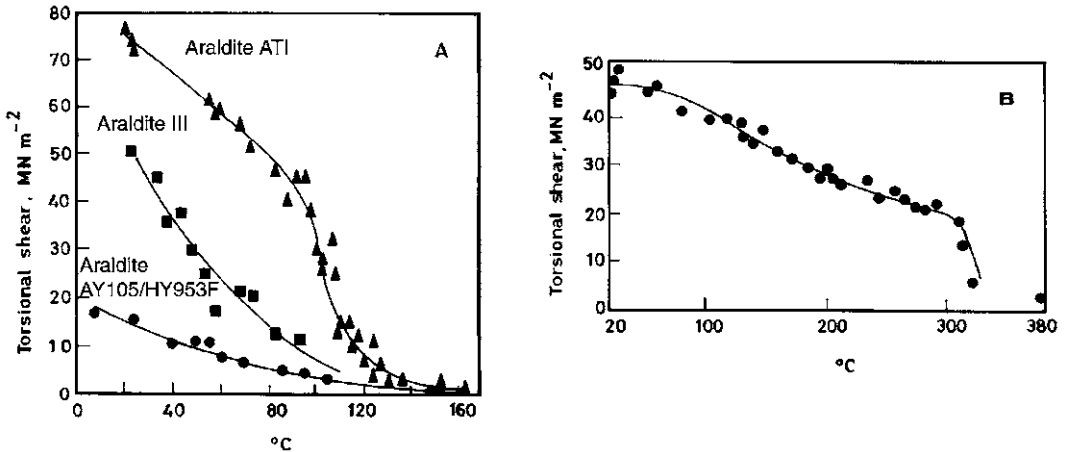


Figure 5.4 Comparison of temperature dependence of adhesive strength. (A) Three Araldite epoxy adhesives; (B) Epoxy-phenolic copolymer. (From Wake, W.C., *Adhesion and the Formulation of Adhesives*, Applied Science Publishers, London, 1976.)

bonding is done with urea-formaldehyde and phenol-formaldehyde (PF) adhesives. Compared to PF resins, bonding with UF resins is cheaper and can be carried out under a wider variety of conditions. However, PF-bonded wood products can be employed in outdoor structural applications, while the poor stability of UF-bonded wood products limits their use to interior, nonstructural applications. Evidence of these limitations includes strength losses of UF-bonded solid wood joints, irreversible swelling of UF-bonded composite panels, and formaldehyde release. Two bond degradation processes viewed currently as responsible for the poor durability of UF are hydrolytic scission and stress rupture. Some of the molecular structural factors that contribute to these processes are (1) low and nonuniform distribution of cross-links in cured UF resins, which lead to extreme sensitivity to small losses in cross-link density arising from hydrolytic scission or stress rupture, and (2) the brittleness of the cured resin due partly to the inherent rotational stiffness of urea molecules leading to inability to respond reversibly to stresses arising from cure shrinkage and moisture-related wood swelling and shrinking. To minimize these defects, urea derivatives of flexible di- and trifunctional amines were incorporated into UF resin structure through copolymerization. Figure 5.5 shows the improved response to cyclic wet-dry stress of joints bonded with a modified UF resin compared with joints bonded with unmodified resin. The amine modifier employed in this case was the urea derivative of propylene oxide-based triamine with the structure shown in Figure 5.6.

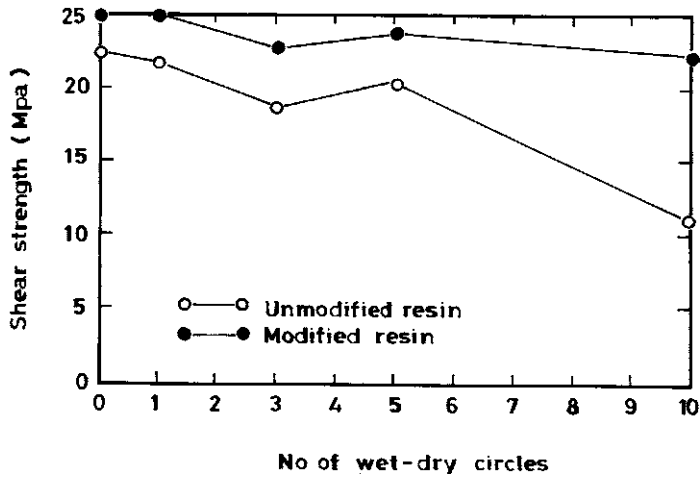


Figure 5.5 Enhanced soak-dry stress resistance of solid wood joints bonded with UF-resin modified with the urea derivative of a flexible propylene oxide-based triamine.

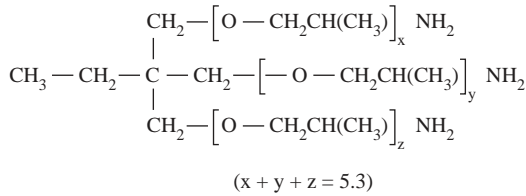


Figure 5.6 Structure of propylene oxide-based triamine modifier.

Example 5.3: Internal stresses are developed as a result of shrinkage during adhesive cure. These stresses can be determined by measuring the deflection of an aluminum strip coated on one side with a thin film of the adhesive (Figure E5.3). The maximum in the curve for the unmodified resin was found to coincide with the fragmentation of the adhesive film. Explain the observed deflections under ambient cure of two such aluminum strips coated, respectively, with a modified and an unmodified UF resin. The modifier is the urea derivative of propylene oxide-based triamine shown in Figure 5.6.

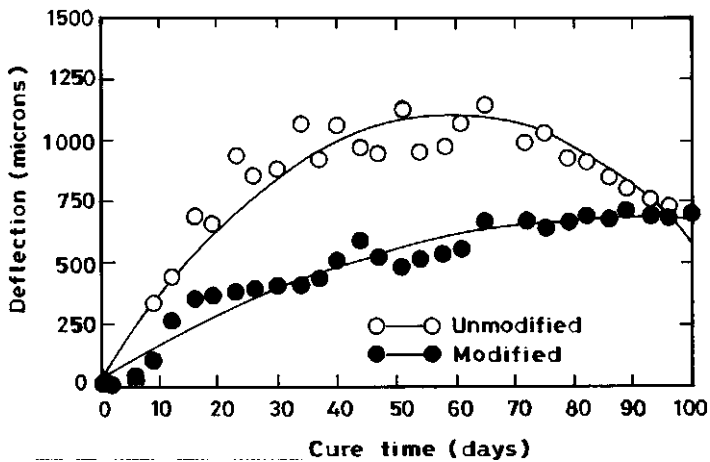


Figure E5.3 Relative internal stresses generated during cure by unmodified and modified UF adhesives.

Solution: As a result of the intrinsic rotational stiffness of the urea molecule, UF resins develop a considerable amount of internal stresses during cure. These stresses are seen to build up with time under ambient cure. However, for the unmodified resin after 60 days of ambient cure, the magnitude of the stresses resulted in a breakup of the resin. This relieved the internal stress, and consequently the deflection of the aluminum strip began to decline. On the other hand, with the modified resin, the flexibility of the modifying agent incorporated into the resin cure. Thus the aluminum strip coated with the modified resin structure provides an internal mechanism for relieving some of the stresses generated during resin cure. The modified resin showed much smaller deflection for the same duration of cure. Apparently even after 100 days of ambient cure, the internal stress generated in the modified resin had not reached a level where it became greater than the cohesive strength of the cured resin.

III. POSTPOLYMERIZATION REACTIONS

As indicated earlier, another powerful tool for upgrading polymer properties is the postpolymerization reaction of preformed polymers. These reactions may occur on reactive sites dispersed in the polymer main chain. Such reactions include chain extensions, cross-linking, and graft and block copolymer formation. The reactions may also occur on reactive sites attached directly or via other groups/chains to the polymer backbone. Reactions of this type are halogenation, sulfonation, hydrolysis, epoxidation, surface, and other miscellaneous reactions of polymers. In both cases these types of reactions transform existing polymers into those with new and/or improved properties.

A. REACTIONS OF POLYSACCHARIDES

Even though the treatment of polysaccharide chemistry falls outside the scope of this volume, reactions of the polysaccharide cellulose provide an excellent illustration of how the modification of a polymer, in this case a natural polymer, can transform an otherwise intractable material into one that can be readily fabricated.

1. Cellulose Derivatives

Cellulose is a polysaccharide — a natural polymer composed of glucosidic rings linked through oxygen bridges (Figure 5.7). The repeating unit has three hydroxyl groups and an acetal linkage. The cyclic nature of the repeating units results in stiff molecules. In addition, the β -(1 \rightarrow 4) links between the anhydro-D-glucose units confer linearity on cellulose molecules. These factors coupled with the strong hydrogen-bond formation through the hydroxyl groups make cellulose a highly crystalline polymer. As a result of the extremely high interchain bonding between cellulose molecules, cellulose is insoluble and infusible. It burns rather than melts. To make cellulose processable it is necessary to reduce its melting point below its decomposition temperature. This is achieved by derivatization, which essentially breaks down the intrinsic hydrogen bonding while also interfering with the crystalline nature of the polymer.

In the preparation of cellulose derivatives a controlled degree of substitution of the three hydroxyls is necessary. Complete reaction of the three hydroxyls is generally not desirable. In addition, the fine structure of cellulose dictates both the course of reaction and the properties of the end products. When reacting with cellulose, reagents normally attack the most accessible (noncrystalline) regions first. Therefore, if the reaction is stopped prematurely, the reacted groups will be concentrated in certain regions rather than distributed randomly within the cellulose structure. For example, 30% acetylated cellulose prepared by direct acetylation has different properties from that prepared by 70% hydrolysis of the acetyl groups in cellulose triacetate.

The most important cellulose derivatives are cellulose esters and ethers. Cellulose esters are prepared by the reaction of an activated cellulose with the corresponding carboxylic acid, acid anhydride, or acid halide. Esterification is taken to completion (triester) and then hydrolyzed back to the desired free hydroxyl content. Viscosity is controlled by holding the reaction at the acid stage until the molecular weight has been reduced to the desired level. For plastics, a relatively high molecular weight is desirable, while for applications as adhesives, lacquer, and hot melts, a much lower molecular weight is more suitable.

The history of the development of polymers is intimately tied to cellulose nitrate, also referred to as nitrocellulose. This inorganic cellulose ester is obtained by reacting cellulose with a mixture of nitric acid and sulfuric acid for about 30 min.

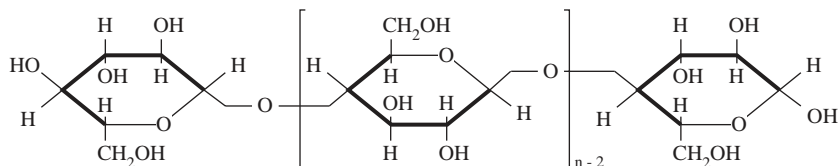
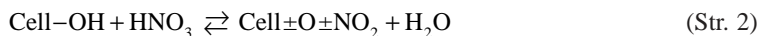
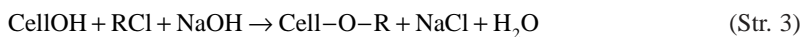


Figure 5.7 Structure of cellulose.



Some degradation accompanies the nitration process. Products with different nitrate contents are obtained. Fully nitrated products have a nitrogen content of about 14.8%. The properties and applications of the nitrated material depend on its degree of nitration; plastics and lacquer-grade material contain 10.5 to 12% nitrogen, which corresponds to the dinitrate roughly. Products with nitrogen content greater than 12.5% are used for explosives.

Cellulose ethers like methyl cellulose are prepared by reacting sodium cellulose (obtained by the action of aqueous sodium hydroxide on cellulose) with the corresponding alkyl halide.



The ether content and the viscosity of the product are controlled by controlling the reaction conditions. In some cases, cellulose ethers are made by reacting sodium cellulose with ethylene or propylene oxide to yield the corresponding hydroxyalkyl ether. Such hydroxy-terminated cellulose ethers are of considerable interest.

Ethyl cellulose is the most important of the cellulose ethers. Commercial ethyl cellulose, which has about 2.4 to 2.5 ethoxy groups per glucose residue is a molding material that is heat stable and has low flammability and high impact strength. It is flexible and tough even at low temperatures; it has a relatively high water absorption, which is, however, lower than that of cellulose acetate.

2. Starch and Dextrins

Like cellulose, starch is also a polysaccharide that on complete hydrolysis yields glucose units. However, there are two significant differences between starch and cellulose. Unlike those in cellulose, the anhydro-D-glucose units in starch are linked through α -(1 \rightarrow 4) glycosidic bonds. Also, in contrast to the completely linear structure of cellulose molecules, the structure of starch is a mixture of linear amylose molecules and branched amylopectin chains. Granular starch has no adhesive use. Therefore for adhesive and most applications, starch must be dispersed in solution by cooking in water until the granules swell and rupture. Such aqueous dispersions of starch are extremely viscous. In order to reduce the viscosity of such starch dispersions, starch must be modified through processes that involve partial depolymerization and/or rearrangement of molecules. To effect this conversion, starch must be subjected to hydrolytic, oxidative, or thermal processes, which yield three classes of products: acid-converted (thin boiling) starches; oxidized starches; and dextrins.

Conversion processes cause weakening and/or solubilization of starch granules, resulting in products that are more readily dispersible and of lower viscosities. Thin boiling starches are produced by reactions of granular starch with warm mineral acids such as HCl or H₂SO₄. Oxidized starches are made by the reaction of starch with sodium hypochlorite. These reactions introduce carbonyl and carboxyl groups and cleave the glycosidic linkages. Dextrins are degradation products of starch produced by heating starch in the presence or absence of hydrolytic agents. Depending on the conditions of conversion, three types of dextrins are produced: white dextrins, yellow (canary) dextrins, and British gums. The conversion mechanism is complex, but is thought to involve hydrolytic breakdown of starch molecules into smaller fragments followed by their rearrangement/repolymerization into a branched polymer structure (Figure 5.8).

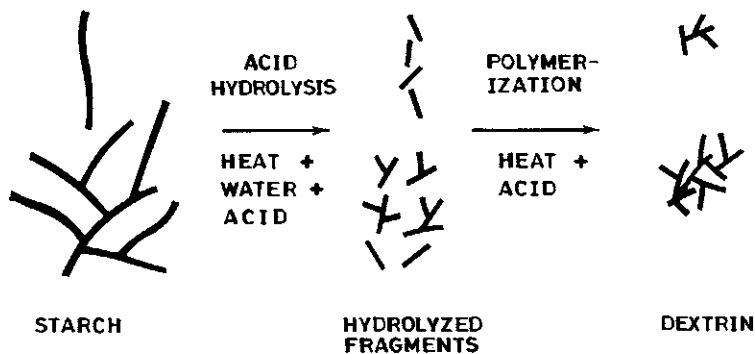


Figure 5.8 Hydrolysis and repolymerization during dextrination of starch. (From Jarowenko, W., *Handbook of Adhesives*, 2nd ed., Skeist, I., Ed., Van Nostrand Reinhold, New York, 1977. With permission.)

Example 5.4: Explain the following observations:

- Cellulose acetate-molded and extruded articles are used extensively where extreme moisture resistance is not required. On the other hand, plastic sheets and films made from cellulose propionate, cellulose butyrate, or cellulose-acetate-butylate are hydrophobic.
- Products from cellulose ethers with the same degree of substitution as cellulose ester have similar properties but are more resistant to hydrolysis.

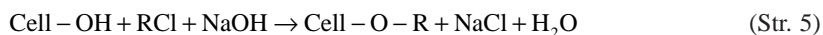
Solution:

- Cellulose acetate is an ester formed by the reaction of acetic acid with the polyhydric alcohol cellulose. Esterification reactions are typically equilibrium reactions.



In the presence of water (moisture) the reverse reaction can occur and is indeed favored at ordinary conditions for organic acids. Consequently, cellulose esters from organic acids like acetic acid and higher homolog are prepared only by the removal of water as it is formed. The resulting product is moisture sensitive, the degree of which decreases with the progressive hydrocarbon nature of R. Therefore while cellulose acetate (R = -CH₃) is susceptible to hydrolysis, cellulose propionate (R = -CH₂-CH₂-CH₃) and cellulose butyrate [R = -(CH₂)₃-CH₃] are hydrophobic.

- The formation of cellulose ethers, unlike that of cellulose esters, is not reversible. Cellulose ethers are therefore less sensitive to hydrolysis than cellulose esters.



B. CROSS-LINKING

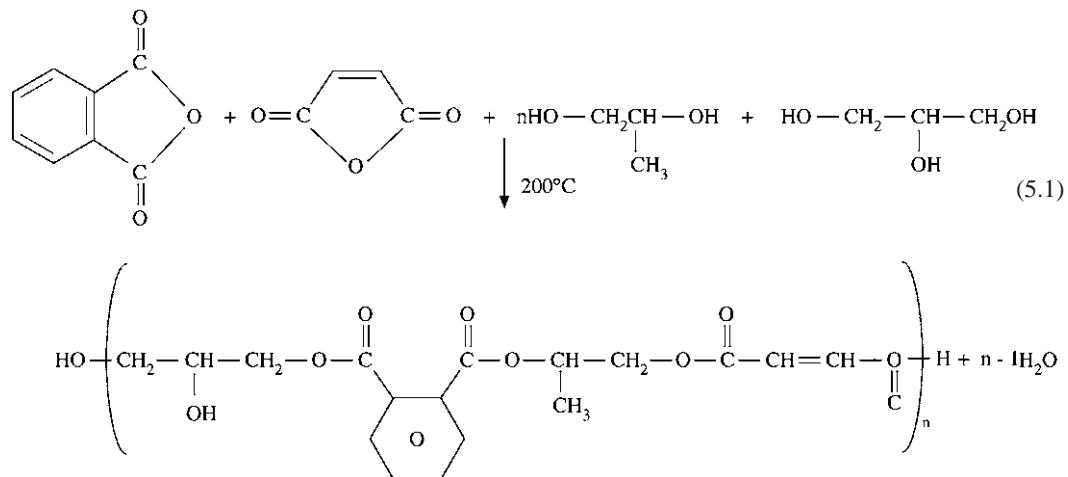
In [Chapter 2](#) we indicated that the formation of a polymer requires that the functionality of the reacting monomer(s) must be at least 2. Where the functionality of one of the monomers is greater than 2, then a cross-linked polymer is formed. Thermosets like phenol-formaldehyde, urea-formaldehyde, and epoxy resins develop their characteristic properties through cross-linking. In this section our discussion is confined to those polymeric systems designed with latent cross-linkability that under appropriate conditions can be activated to produce a polymer with desirable properties.

1. Unsaturated Polyesters

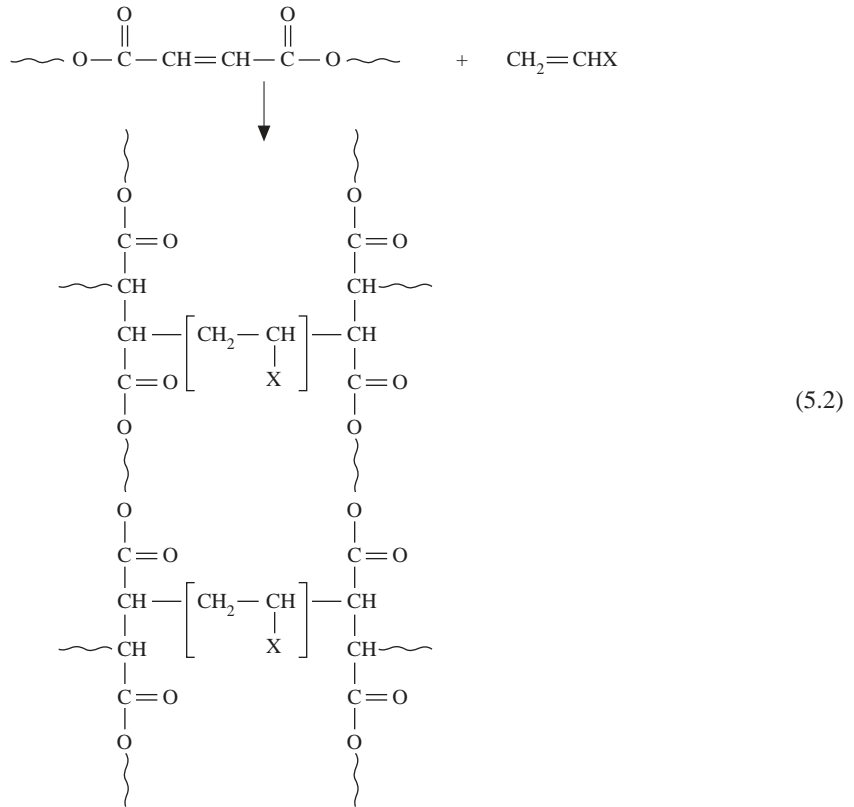
Unsaturated polyesters represent an excellent illustration of a polymeric system with a latent ability to cross-link. Unsaturated polyesters are, as the name implies, unsaturated polyester prepolymers mixed with

cross-linking monomers and catalysts. The resulting mixture is normally a viscous liquid that can be poured, sprayed, or shaped into the desired form and then transformed into a thermosetting solid by cross-linking.

The unsaturated polyester prepolymers are obtained from the condensation of polyhydric alcohols and dibasic acids. The dibasic acid consists of one or more saturated acid and/or unsaturated acid. The saturated acid may be phthalic anhydride, adipic acid, or isophthalic acid, while the unsaturated acid is usually maleic anhydride or fumaric acid. The polyhydric alcohols in common use include glycol (such as ethylene glycol, propylene glycol, diethylene glycol), glycerol, sorbitol, and pentaerythritol (Equation 5.1).

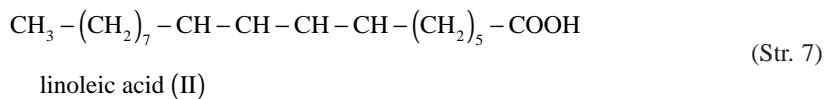
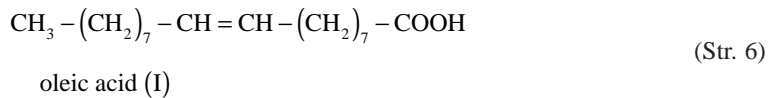


The reactive monomer responsible for the cross-linking reaction is normally styrene, vinyl toluene, methyl methacrylate, or diallyl phthalate. The unsaturated polyester prepolymers are, by themselves, relatively stable at ambient temperatures. When they are added to the cross-linking monomers, however, the blend is extremely unstable. To prevent premature gelation and to control the cross-linking process, inhibitors like hydroquinone are added to the blend. The cross-linking process is usually initiated by an organic peroxide added by the end user. The peroxide may be activated by heat. For room-temperature cure, accelerators and activators such as cobalt salts are also added. The cross-linking reaction can be represented as follows (Equation 5.2):



Alkyd resins constitute a special class of unsaturated polyesters. They are used predominantly as surface coatings (organic paints) and, to a limited extent, as molding compounds. Unlike the related polyester molding compounds (used in the manufacture of automotive parts like distributor caps, ignition coil towers, and similar electrical parts, the cross-linking monomer in alkyd molding compounds is nonvolatile, e.g., allyl phthalate. The organic peroxide catalyst decomposes on the application of heat and initiates cross-linking yielding on infusible, insoluble solids.

Alkyd resins used as surface coatings are usually modified by the addition of fatty acids derived from mineral and vegetable oils. Those modified with unsaturated acids such as oleic acid (I) or linoleic acid (II) are the air-drying type cured through oxidation by atmospheric oxygen. Those types of surface coatings that dry through chemical reactions are known as varnishes. Others that dry through solvent evaporation are referred to as lacquers.



Example 5.5: An unsaturated polyester based entirely on maleic anhydride as the dibasic acid, when cross-linked with styrene, forms a hard and rigid polymer. However, that based on maleic anhydride mixed with some phthalic anhydride forms a less rigid polymer. Explain.

Solution: As we shall see in [Chapter 8](#), the copolymerization of maleic anhydride and styrene shows a strong tendency toward alternation ($r_1 r_2 = 0.06$). Consequently, a maleic anhydride-based unsaturated polyester cross-linked with styrene forms a large number of short cross-links, resulting in a rigid polymer. With the addition of phthalic anhydride, the tendency toward alternation is reduced due to the occasional intervention of phthalic anhydride. The reduction of cross-link density results in a less rigid polymer.

2. Vulcanization

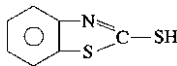
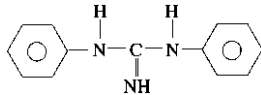
Elastomers such as 1,4-diene polymers — polychloroprene, polybutadiene, and polyisoprene — and copolymers — butadiene–acrylonitrile and butadiene–styrene — must possess the capability of undergoing large deformations under stress and the essential property of rapid and complete recovery from such deformations on the removal of the imposed stress. This means, in molecular terms, that the long-range movements of the polymer molecules must be restrained at the same time that high local segmental mobility is permitted. To acquire this property, an elastomer needs to be lightly cross-linked. The process by which such a network of cross-links is introduced into an elastomer is called vulcanization. It transforms an elastomer from a weak thermoplastic mass without useful properties into a strong, elastic, tough rubber. Vulcanization decreases the flow of an elastomer and increases its tensile strength and modulus, but preserves its extensibility. Vulcanization, discovered by Goodyear in 1939, achieved by heating the elastomer solely with sulfur is a slow and inefficient process. It can be speeded up considerably and the sulfur waste reduced substantially by the addition of small amounts of organic and inorganic compounds known as accelerators. Many accelerators themselves require the presence of activators or promoters to function optimally. Some accelerators used include sulfur-containing compounds and a few nonsulfur-containing compounds, as shown in [Table 5.4](#).

Activators are normally metallic oxides such as zinc oxide. They function best in the presence of soap such as metallic salt of stearic acid. The use of accelerators and activators has increased the efficiency of cross-linking in some cases to less than two sulfur atoms per cross-link.

a. Rubbers³³

The early synthetic rubbers were diene polymers such as polybutadiene. Diene elastomers possess a considerable degree of unsaturation, some of which provide the sites required for the light amount of cross-linking structurally necessary for elastomeric properties. The residual double bonds make diene elastomers vulnerable to oxidative and ozone attack. To overcome this problem, saturated elastomers like butyl rubber and ethylene–propylene rubber (EPR) were developed. These rubbers were, unfortunately, not readily vulcanized by conventional means. To enhance cure, it was therefore necessary to

Table 5.4 Some Accelerators Used in Vulcanization.

Accelerator	Structure
2-mercaptobenzothiazole	
Tetramethylthioureasulfide	$(\text{CH}_3)_2\text{N}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}-\text{S}-\overset{\text{S}}{\parallel}{\text{C}}-\text{N}-(\text{CH}_3)_2$
Diphenylguanidine	
Zinc butyl xanthate	$(\text{C}_4\text{H}_9\text{O}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S})_2 \text{Zn}^{2+}$

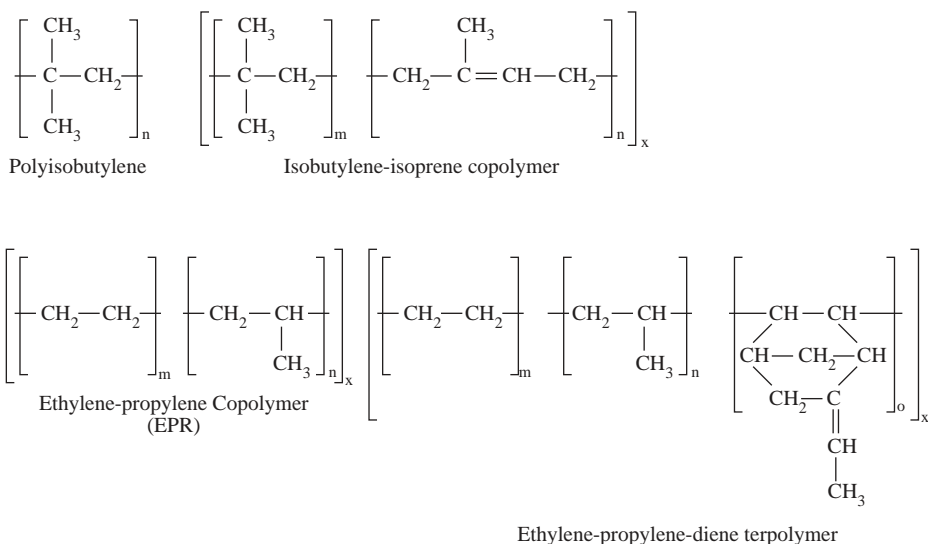
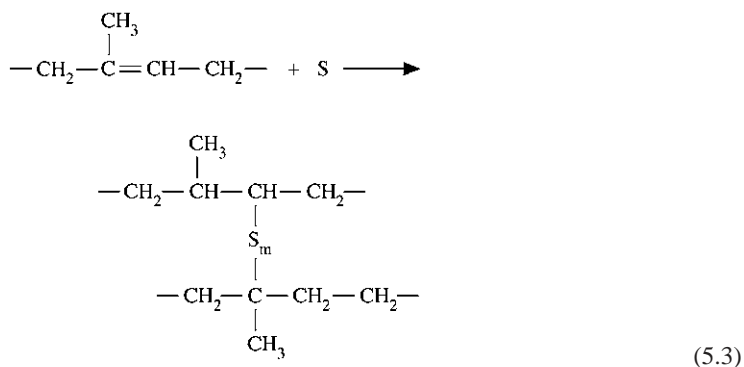


Figure 5.9 Creation of vulcanization sites for butyl and ethylene-propylene rubbers through copolymerization.

incorporate some unsaturation into the structure of these polymers through copolymerization of unsaturated monomers. The usual monomers for butyl rubber and EPR are shown in Figure 5.9.

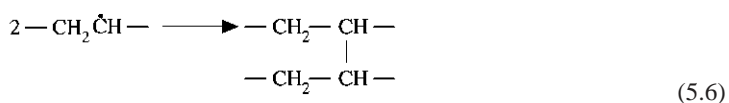
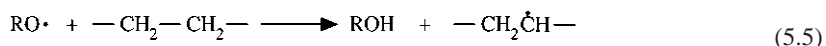
The comonomer shown for EPR is dicyclopentadiene. Other comonomers are ethylidene norbornene (obtained from the reaction of butadiene with cyclopentadiene) and 1,4-hexadiene. Each of the diene copolymers with ethylene and propylene produces different characteristics in the final elastomer. Dicyclopentadiene yields a branched polymer with slow cure rates because of the low reactivity of the second double bond. With ethylidene norbornene, both linear and branched polymers can be produced and sulfur vulcanization is improved. The polymer resulting from the incorporation of 1,4-hexadiene into EPR possesses good processing characteristics and heat resistance. Since EPR is considered saturated, it usually requires peroxide cure, while EPDM polymers are cured normally by conventional sulfur vulcanization. The type of cure is dictated by the polymer and the expected processing technique (extrusion, calendaring, molding, etc.). The commercial cross-linking of diene polymers is carried out almost exclusively by heating with sulfur (Equation 5.3).



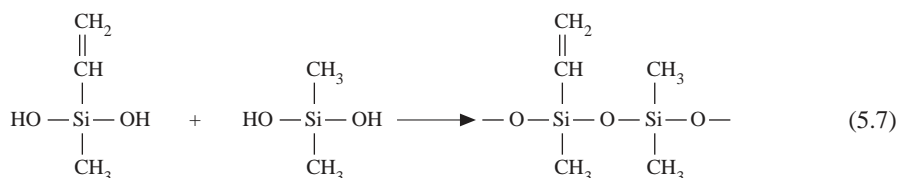
b. Polyolefins and Polysiloxanes

While the first vulcanization involved heating the elastomer with sulfur, it has since been recognized that neither heat nor sulfur is imperative for the vulcanization process. Vulcanization or cure can be effected by nonsulfur-containing compounds, including peroxides, nitro compounds, quinones, or azo compounds. Polyethylene, ethylene-propylene copolymers, and polysiloxanes are cross-linked by compounding them

with a peroxide and heating them. The process involves the formation of polymer radicals followed by the coupling of these radicals (Equations 5.4–5.6).



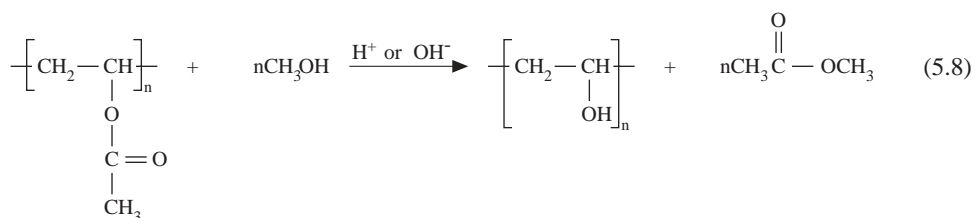
The efficiency of this process is usually less than one cross-link per peroxide molecule decomposed. To increase the cross-linking efficiency, small amounts of unsaturation are introduced into the polymer structure. We have already discussed EPDM polymers, which are essentially diene monomers copolymerized with ethylene–propylene (EPR) polymers. For polysiloxanes, copolymerization of small amounts of vinyl–methylsilanol greatly enhances cross-linkability (Equation 5.7). The unsaturation introduced into an otherwise saturated structure provides additional sites for cross-linking through chain reaction.



C. HYDROLYSIS¹¹

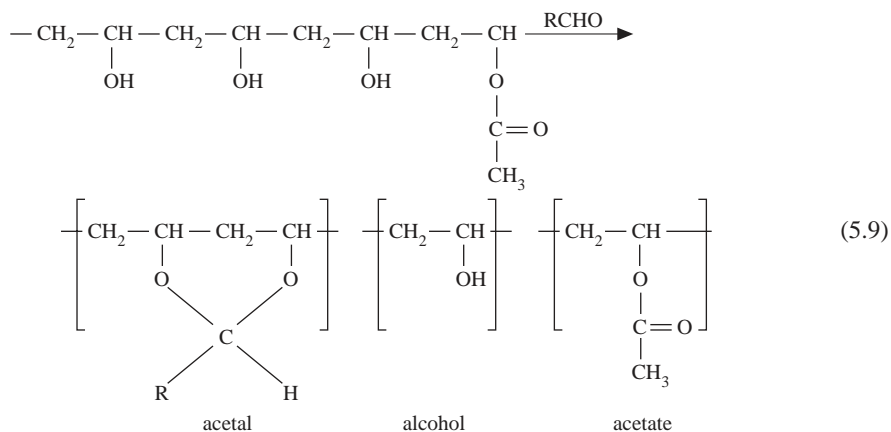
A primary use of poly(vinyl acetate) is in the production of water-based emulsion paints in addition to its wide use in emulsion-type and hot-melt adhesives. It is also used in the production of poly(vinyl alcohol) and poly(vinyl acetal) polymers, which cannot be prepared directly since their monomers are unknown.

Poly(vinyl alcohol) (PVA) is prepared by the hydrolysis (or more correctly alcoholysis) of poly(vinyl acetate) with methanol or ethanol. The reaction is catalyzed by both bases and acids, but base catalysis is normally employed because it is faster and free of side reactions (Equation 5.8).



Because of its water solubility, poly(vinyl alcohol) is used as a thickening agent for various emulsion and suspension systems. With its high hydroxyl content, PVA is used widely as water-soluble adhesive with excellent binding capacity for cellulosic materials like paper.

Partially hydrolyzed poly(vinyl acetate) contains both hydroxyl and acetate groups. When the OH groups in partially hydrolyzed poly(vinyl acetate) are condensed with aldehydes, acetal units are formed. The resulting polymer contains acetal, hydroxyl, and acetate groups and is known as the poly(vinylacetals) (Equation 5.9).



The reaction of butyraldehyde or formaldehyde results in poly(vinyl butyral) or poly(vinyl formal), respectively. The most important of the poly(vinylacetals) is by far poly(vinyl butyral). The residual OH groups in poly(vinyl acetal) can condense with methylol groups in PF, MF, and UF resins. For example, poly(vinyl formal) cured with phenolic resins was first used as a structural adhesive for metals. Poly(vinyl butyral) finds important application as the interlayer in laminated automotive and aircraft safety glass. Laminated glass, also made from poly(vinyl butyral), is used in buildings for controlled transmission of light and heat through reduction of glare, heat loss, and UV, thus providing aesthetic appeal. In these applications, the residual hydroxyl groups provide the needed strength and adhesion to glass.

D. BLOCK AND GRAFT COPOLYMER FORMATION^{6,7}

Block and graft copolymer formation involves the reaction of a previously formed homopolymer or copolymer with fresh monomers. Consequently, normal methods of polymerization can be utilized. For vinyl monomers two general methods are employed: (1) the polymerization of a monomer in the presence of a polymer by the initiation of growth through chain transfer; and polymerization of a monomer in the presence of a polymer containing reactive sites. The first procedure necessarily leads to the formation of graft copolymers. In the second case, block copolymers are formed from polymers with terminal active sites while graft copolymerization occurs on active sites located on the polymer backbone or pendant groups. In both of these methods, the polymerization of a monomer in the presence of a polymer results in a mixture of products: (1) the initial homopolymer that did not participate in the reaction; (2) the homopolymer of the fresh monomer; (3) the cross-linked parent homopolymer through graft polymerization or the branched block copolymer; and (4) the desired copolymer. The composition of the product mixture will depend on the nature of the polymer, monomer, and initiator. For example, the polymerization of methyl methacrylate in the presence of polystyrene yields appreciable amounts of graft copolymer with benzoyl peroxide as the initiator. However, if AIBN is the initiator, the amount of graft copolymer formed is considerably smaller. In contrast, the polymerization of vinyl acetate in the presence of poly(methyl methacrylate) yields appreciable amounts of the graft copolymer irrespective of the nature of the initiator. In any case, while it is possible in principle to obtain a pure product by employing general separation processes, this is often problematic for industrial purposes.

1. Block Copolymerization^{8,9}

The preparation of block copolymers requires the presence of terminal reactive groups. A variety of techniques have been used to achieve this. We briefly discuss a few of them.

Block copolymers of butyl acrylate-styrene and acrylonitrile-styrene have been prepared by irradiating butyl acrylate or acrylonitrile containing a photosensitive initiator (e.g., 1-azo-bis.1-cyanocyclohexane) with an intensive UV radiation. This creates a radical-rich monomer that when mixed with styrene yields the appropriate block copolymer.

In situ block polymer formation is obtained by using a mixture of water-soluble and oil-soluble monomers. An example involves dissolution of acrylic acid or methacrylic acid in water followed by

Table 5.5 Various Block Copolymers Prepared by Mechanical Rupture of Polymer Chains in Presence of Monomer

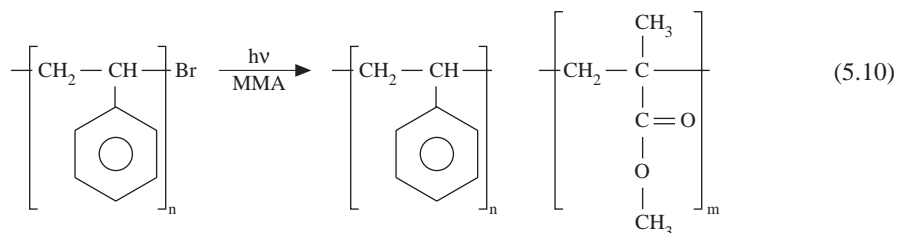
Polymer Unit	Monomer
Acrylamide	Acrylonitrile
Isobutylene	Acrylonitrile
	Styrene
	Vinylidene chloride
Methyl acrylate	Vinyl chloride
	Vinylidene chloride
Methacrylonitrile	Acrylonitrile
Methacrylonitrile- <i>co</i> -vinyl chloride	Methyl methacrylate
Methyl methacrylate	Methacrylonitrile
	Styrene
	Vinylidene chloride
Methyl methacrylate- <i>co</i> -methacrylonitrile	Styrene
Styrene	Methyl methacrylate
	Vinylidene chloride
Vinyl acetate	Vinyl chloride
Vinyl chloride	Methyl vinyl ketone

From Fetters, E.M., Ed., *Chemical Reactions of Polymers*, Interscience, New York, 1964. With permission.

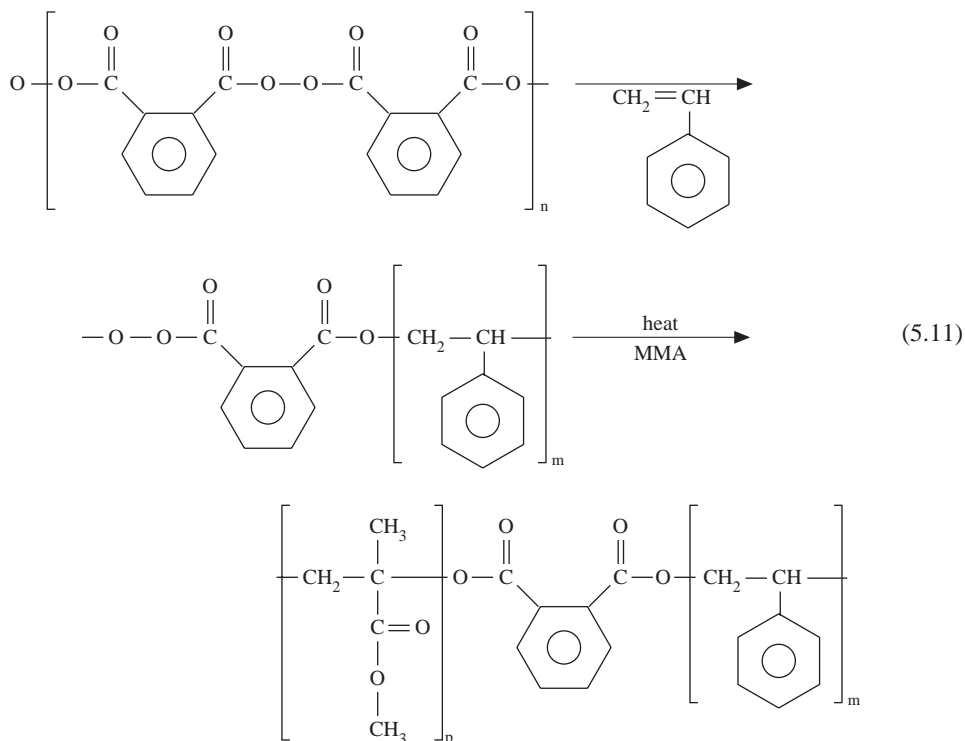
styrene emulsification in the water. With persulfate initiator, polymerization of acid occurs in the aqueous phase until the growing chains diffuse into the micelle containing styrene monomer, whereupon styrene chain growth ensues resulting in the formation of acrylic/methacrylic acid–styrene block copolymer.

When a polymer chain is ruptured mechanically, terminal-free radicals can be generated, and these can be utilized to initiate block copolymerization. Under an inert atmosphere, block copolymers can be produced by cold milling, or mastication of two different polymers or of a polymer in the presence of a second monomer. This generally results in the formation of graft copolymers in addition to the block copolymers since radicals can be located in nonterminal positions by chain transfer. However, predominant yield of block copolymers is obtained by milling monomer-swollen polymers. The success of this technique depends on the physical state of the polymer. Generation of radical is favored if the polymer exists at or near the glassy state; otherwise, polymer flow rather than bond rupture will occur. Table 5.5 shows some block copolymers prepared by this technique.

When polymer chains are terminated by labile end groups, block polymers can be produced by irradiation. An example is the irradiation of terminal-brominated styrene dissolved in methyl methacrylate to yield styrene–methyl methacrylate block copolymer (Equation 5.10).



A common technique of preparing block copolymers is the introduction of peroxide groups into the polymer backbone or as stable end groups. The polymers are then mixed with fresh monomer, and the peroxide groups are decomposed under appropriate conditions to yield block copolymers. For example, polymeric phthaloyl peroxide was polymerized to a limited extent with styrene. The resulting polymer was mixed with methyl methacrylate. On decomposition, the internal and terminal peroxide groups formed radicals that initiated the polymerization of methyl methacrylate, as shown below in Equation 5.11.



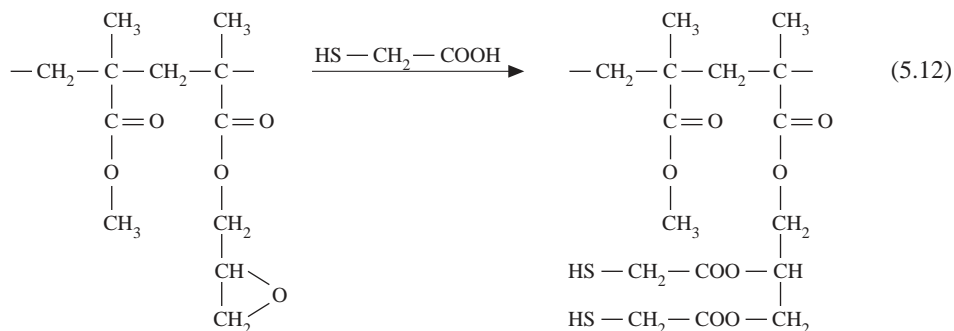
2. Graft Copolymerization⁸

There are essentially three approaches to the preparation of graft copolymers via free radical mechanism:

1. Chain transfer to a saturated or unsaturated polymer
2. Activation by photochemical or radiative methods
3. Introduction and subsequent activation of peroxide and hydroperoxide groups

Graft copolymer formation by chain transfer requires three components: a polymerizable monomer, a polymer, and an initiator. By definition, the initiator serves to create active sites either on the polymer or on the monomer. The amount of initiator added to a polymerization system is generally low. Therefore, if this is the sole source for the initiation of radical sites on the backbone of the polymer by way of chain transfer, only a relatively few branches will be produced. Consequently, to achieve a reasonable amount of grafting, the polymer itself must be capable of generating radicals through hydrogen abstraction and hence promote chain transfer. As we shall see in [Chapter 8](#), the relative reactivity ratios dictate that for copolymerization to occur the nature of the monomer must be such that it can react with the polymer radical. This means that not all monomers can be grafted onto a polymer backbone, and, by the same argument, not all polymers can react with a given monomer. For example, whereas vinyl acetate can be grafted onto poly(vinyl chloride) or polyacrylonitrile, hardly any grafting occurs in the case of vinyl acetate or vinyl chloride and polystyrene; styrene or vinyl chloride and poly(vinyl acetate); or styrene and poly(vinyl chloride).

Sites that are susceptible to chain transfer may be introduced into the polymer structure during synthesis or as a postreaction. An example of the latter case involves the introduction of a reactive mercaptan group by the reaction of thioglycolic acid or hydrogen sulfide with a copolymer of methyl methacrylate and glycidyl methacrylate (Equation 5.12).



Monomers such as styrene, acrylate, and methacrylate have been grafted onto this polymer, with a relatively high yield of pure graft copolymer. A commercially important graft copolymer resulting from transfer to unsaturated polymer is impact polystyrene, which is butadiene grafted to polystyrene. The nature of the transfer process in this case results in a copolymer with the rubber (polybutadiene) graft existing as a dispersed phase within a styrene matrix. Such a copolymer morphological structure reduces the brittleness of polystyrene, and this enhances its impact resistance.

Active sites can be generated on a polymer to initiate graft copolymerization by ultraviolet light and high-energy irradiation. The process may involve (1) simultaneous irradiation of polymer in contact with monomer; (2) irradiation of polymer predipped in the monomer; (3) pre-irradiation of the polymer in the absence of air (O₂) followed by exposure to the monomer; and (4) pre-irradiation of the polymer in air to form peroxide and subsequent decomposition in the presence of the monomer. The first two techniques are known as mutual irradiation, as distinct from pre-irradiation.

Photolytic activation of polymer growth is based on the ability of certain functional groups to absorb radiation. This generally involves polymers with pendant halogen atoms or carbonyl groups, which are highly susceptible to activation by UV radiation. When sufficient energy is absorbed, bond scission occurs resulting in the generation of radicals. Monomers such as acrylonitrile, methyl methacrylate, and vinyl acetate have been grafted onto poly(vinyl methyl ketone) by this technique. Other examples include grafting of styrene and methyl methacrylate on brominated styrene. Mutual irradiation with UV in the presence of a photosensitizer has also been used to graft methyl methacrylate and acrylamide to natural rubber.

Generation of active sites for radical graft copolymerization using X-rays or γ -rays is less selective. In this case, hydrogen cleavage and carbon-carbon bond scission occur resulting in homopolymerization of the vinyl monomer, cross-linking in addition to the grafting reaction. Table 5.6 shows some graft copolymers produced by natural irradiation with high-energy radiation and the properties of the resulting graft copolymer.

Unstable compounds such as peroxides and hydroperoxides are usual initiators for vinyl polymerization reactions. These groups can be introduced into a solid polymer by pre-irradiation in the presence of air or oxygen. Thermal decomposition of these groups in the presence of monomer yields graft copolymers. Some examples include grafting of acrylonitrile, styrene, and methyl methacrylate to polyethylene and polypropylene.

Table 5.6 *Properties of Graft Copolymers Produced by Mutual Irradiation of Monomer*

Polymer	Monomer	Property Changes
Polyethylene	Acrylonitrile	Increased solvent resistance and softening temperature; excellent adhesion to polar materials
	Vinyl chloride	Retention of superior electrical properties while increasing softening point to 215°C
	Acrylate methacrylate	Following hydrolysis, surface becomes permanently conductive; prevention of accumulation of static charges; good adhesion to materials like cellulose, glass, and metals
	Styrene	Increased melt viscosity
Polytetrafluoroethylene	Styrene	Enhanced adhesion, enhanced elimination of plastic flow, and increased ultimate strength
Polychlorotrifluoroethylene		

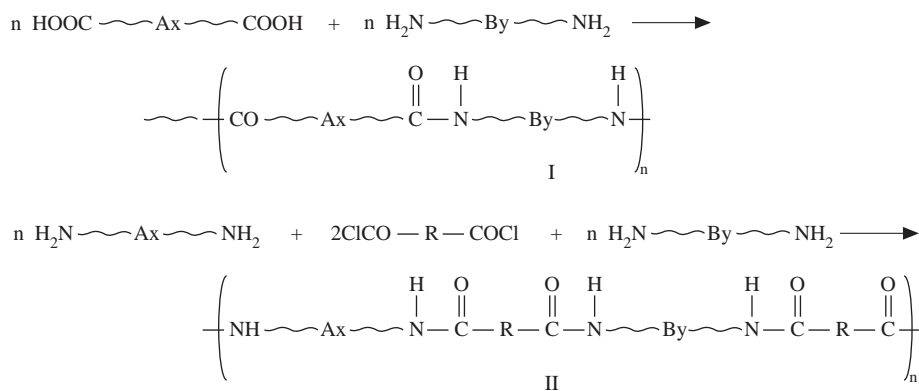


Figure 5.10 Formation of block copolymers from condensation polymers: (I) from two prepolymers with mutually reactive terminal end groups; (II) by the use of a coupling agent.

So far, our discussion has been restricted to chain block and graft copolymerization. This is largely because the practical utility of copolymerization is more elaborate in chain polymerization than step polymerization. Also, in step copolymerization, block copolymers are generally preferred to the other types of copolymers. Therefore only block step-polymerization copolymers are discussed here and only in a very limited scope to illustrate the principles involved in their preparation.

Block copolymers have been prepared from condensation polymers by coupling low-molecular-weight homopolymer with appropriate reactive end groups. These prepolymers may possess terminal end groups that are different but mutually reactive. If, however, the two polymer blocks have the same or similar terminal groups, a bifunctional coupling agent capable of reacting with such groups is employed to prepare the block copolymers. Step-polymerization block copolymer can also be prepared via interchange reactions. Figure 5.10 illustrates these general principles.

There are a variety of commercially important condensation block copolymers. For example, alkyd-amine resins are cross-linked block copolymers resulting from the reaction of hydroxyl and carboxyl groups on alkyd resins with the methylol groups of urea- or melamine-(amine)-formaldehyde resins. Epoxy resins contain secondary hydroxy and terminal epoxy groups that are capable of reacting with other functionalities to produce block copolymers. Reaction with the amine groups (primary and secondary) in polyamide yields block copolymers ranging from rubbery and resilient to hard, tough, and shock-resistant solids. Epoxy resins can also react with polysulfide liquid polymers to give products varying in property from brittle to highly flexible. Formaldehyde resins (phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde) react with epoxy resins to yield block copolymers used in coatings and adhesives.

E. SURFACE MODIFICATION¹⁰

Surface reactions of polymers, in strict terms, should include polymer interactions with its environment, referred to as aging or weathering. The discussion here, however, focuses on the deliberate chemical modifications of surface properties. Surface reactions, by definition, do not include bulk homogeneous reactions of polymers, but refer to those confined to the surface and those that generally do not significantly alter the physical properties of the substrate. Surface reactions have been used commercially to improve feel, washability, dye retention, antistatic properties, and abrasion resistance of fibers and to enhance printability, solvent resistance, adhesion, and permeability to liquids and vapors of films. Surface modification of polymers can be effected by three general procedures: interpolymerization by energy irradiation or chemical means and by conventional chemical reactions of polymers. Interpolymerization, as has been discussed, results in the formation of graft or block copolymers. The chemical treatment of

polymers, including such reactions as oxidation, halogenation, and other standard chemical reactions, are briefly reviewed.

Surface oxidation reactions have been carried out on a number of polymers, particularly polyethylene. Surface oxidation techniques include the use of corona discharge, ozone, hydrogen peroxide, nitrous acid, alkaline hypochloride, UV irradiation, oxidizing flame, and chromic acid. The reactions lead initially to the formation of hydroperoxides, which catalyze the formation of aldehydes and ketones and, finally, acids and esters. Surface oxidation treatment has been used to increase the printability of polyethylene and poly(ethylene terephthalate) and to improve the adhesion of polyethylene and polypropylene to polar polymers and that of polytetrafluoroethylene to pressure-sensitive tapes. Surface-oxidized polyethylene, when coated with a thin film of vinylidene chloride, acrylonitrile, and acrylic acid terpolymers becomes impermeable to oxygen and more resistant to grease, oil, abrasion, and high temperatures. The greasy feel of polyethylene has also been removed by surface oxidation.

Alkali and acid treatments have also been used to modify surface properties of polymers: sulfonated polyethylene films treated first with ethylenediamine and then with a terpolymer of vinylidene chloride, acrylonitrile, and acrylic acid exhibited better clarity and scuff resistance and reduced permeability. Permanently amber-colored polyethylene containers suitable for storing light-sensitive compounds have been produced by treating fluorosulfonated polyethylene with alkali. Poly(ethylene terephthalate) dipped into trichloroacetic/chromic acid mixture has improved adhesion to polyethylene and nylons. Antifogging lenses have been prepared by exposing polystyrene films to sulfonating conditions. Acid and alkali surface treatments have also been used to produce desired properties in polymethylmethacrylates, polyacrylonitrile, styrene-butadiene resins, polyisobutylene, and natural rubber. Surface halogenation of the diene polymers natural rubber and polyisobutylene resulted in increased adhesion to polar surfaces.

Treatment of a large number of thermoplastics with alkyl or alkenyl halosilanes has yielded materials with improved heat, stain, and scratch resistance. The use of silane coupling agents in a number of systems is particularly instructive. These systems include glass- or carbon-fiber-reinforced composites, phenolic-bonded sand, grinding wheel composites of aluminum oxide, metal-filled resins for the tool and die industry, etc. In fiber-reinforced composites where the interfacial area between the matrix resin and fiber reinforcement is very high, adequate fiber-matrix adhesion is necessary for the efficient transfer of the applied stress across the fiber-matrix interface required for the production of high-performance composite systems.¹¹ Silane coupling agents are characterized by terminal groups specifically designed to effect chemical linkage between matrix resin and the fiber reinforcement. A typical example is γ -aminopropyltriethoxy silane, $(\text{C}_2\text{H}_5\text{O})_3\text{-Si-(CH}_2)_3\text{-NH}_2$, with terminal amino and ethoxy groups. When the glass fiber is treated with the silane coupling agent, the ethoxy groups are hydrolyzed to form the silanol group, $-\text{Si-(OH)}_3$, which then condenses with the silanols on the glass fiber to form $-\text{Si-O-Si-}$ covalent bonds. On incorporation of the silane-treated glass fibers into the matrix resin, the unreacted terminal amino groups react with the epoxy matrix resin. Consequently, the silane coupling agent forms a molecular bridge between the matrix resin and the fiber reinforcement (Figure 5.11). A number of

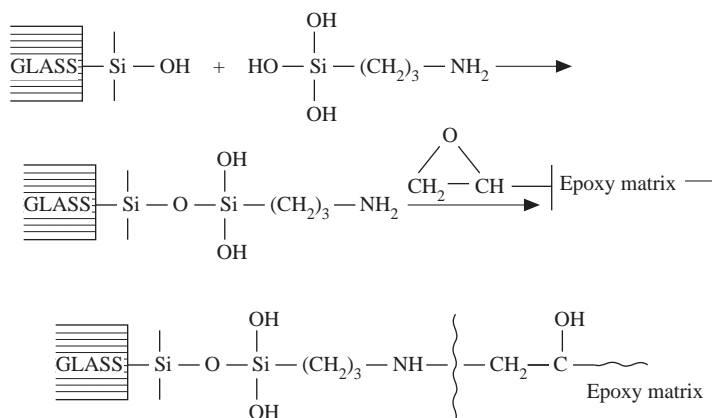
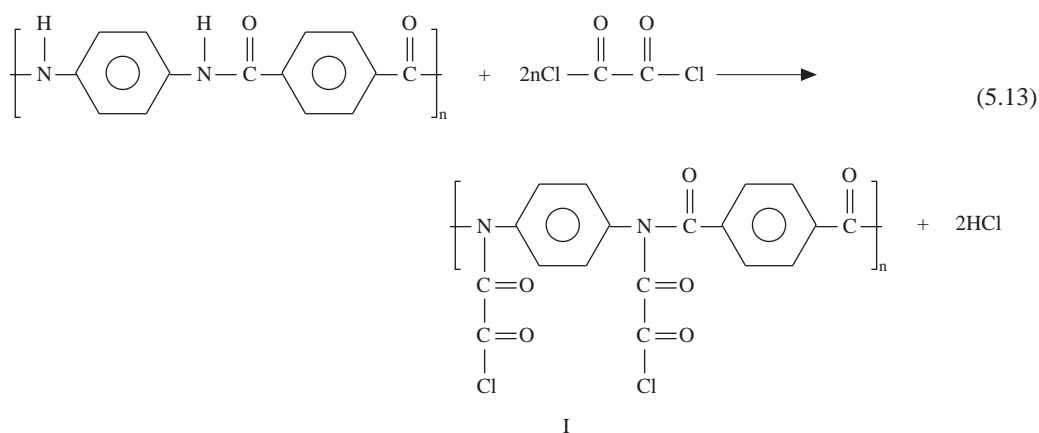


Figure 5.11 Chemical linkage between matrix resin and glass-fiber reinforcement through a silane coupling agent.

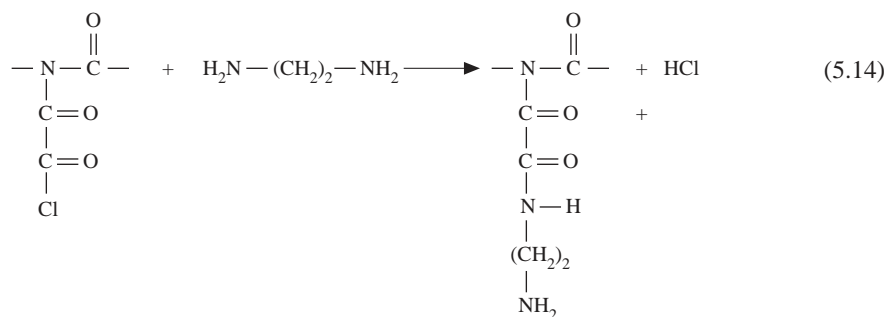
silane coupling agents are available with reactive groups such as amine, epoxy, or vinyl, which can react with epoxy, polyester, and other matrix resins during polymer cure. The resulting polymer materials exhibit improved mechanical properties and durability.

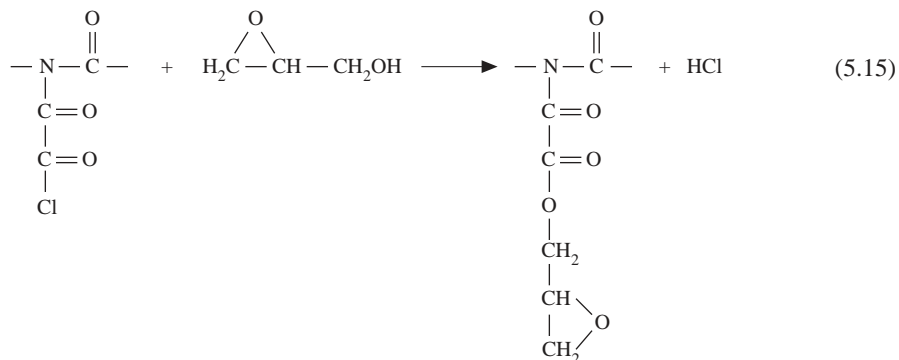
Another illustration of the use of surface modification in the production of improved composite systems is the surface modification of aramid fibers.¹² Poly(*p*-phenylene terephthalamide) (PPTA) (aramid) fibers have excellent mechanical properties and good thermal stability. These properties combined with their low density make aramid fibers prime candidates for reinforcement in high-performance, lightweight composite materials. However, the usefulness and effectiveness of these fibers in such composite systems depend on the adhesion between the fiber reinforcement and matrix resin. Unfortunately, the adhesion between PPTA fibers and most matrices is poor because the chemical inertness and smooth surface quality of fibers preclude chemical bonding and mechanical anchorage. One of the ways of overcoming this problem involves chemical modification of the surface of the fibers by introducing functional groups capable of reacting with the matrix resin.

The surface treatment procedure consists of two stages. In the first step, PPTA fibers are treated with sulfolane/oxalychloride to produce an intermediate (I) in Equation 5.13.



This highly reactive intermediate can react with a number of compounds to introduce different functionalities on the fiber surface. The resulting functional groups, in the case of reaction with ethylenediamine and glycidol, are shown in Equations 5.14 and 5.15, respectively.





The introduction of these functionalities on the surface of the aramid fiber resulted in substantial improvement in the fiber–epoxy resin matrix adhesion (about 70%) without a noticeable change in the tensile strength of the fibers. This suggests first that these were possibly covalent and/or hydrogen bonds formed between the fibers and the epoxy resin and that the modification was confined to the surface of the fibers.

Other miscellaneous reactions of polymer have been used to modify the properties of polymers. Polytetrafluoroethylene and polytrifluoroethylene are extremely inert polymers. However, when films of these polymers are treated with solutions of Li, Na, Ca, Ba, or Mg in liquid ammonia, they can be bonded with conventional adhesives to metals and other materials and can be used as backing for pressure-sensitive adhesive tapes. The bonds between active hydrogen-containing polymers, such as natural rubber, and diisocyanate have been enhanced by treatment of the polymer with aliphatic diazo compounds. The weathering properties of poly(vinyl fluoride) have been increased quite considerably by reacting the surface of the polymer with a mixture of diisocyanate and a benzoyl compound, thus resulting in a UV-absorbing surface. Poly(ethylene terephthalate) (PET) fabrics have been freed of the objectionable static charge by reacting PET with 2% NaOH or by reduction with aluminum hydride and subsequently treating with various diisocyanate–polyglycol reaction products.

IV. FUNCTIONAL POLYMERS

There is an ever increasing demand for polymers for specific end-use properties such as enhanced resistance to fire or environmental attack or, in some cases, enhanced degradability. Development of new polymeric materials to meet this challenge has involved the use of a multidisciplinary approach involving chemistry, physics, and engineering. Every decade since the middle of 20th century seems to have witnessed an additional dimension in the thrust of development research in polymer science: the 1950s saw serious advances in polymer chemistry, the 1960s in polymer physics, the 1970s in polymer engineering, and the 1980s in functional polymers.¹³ We are currently witnessing the emergence of high-performance polymeric materials such as alloys and blends and advanced composites (so-called polymer abc) being developed through the application of polymer physics and engineering. In this discussion, we focus attention on functional polymers.

Functional polymers may be considered in broad terms as those polymers whose efficiency and characteristics are based on a functional group. A specific functional group is usually carefully designed and located at a proper place on the polymer chain. The functional groups may be dispersed along the polymer main chain (including chain ends) or attached to the main chain either directly or via spacer groups. The main objective of the introduction of special functional groups into the polymer backbone or side chains is to give the polymers special features. Functional groups are, therefore, typically chemical units that are chemically reactive, biologically active, electroactive, mesogenic (liquid crystals), photoactive, and, more commonly, ionic, polar, or optically active.¹³ There are two general techniques used for the preparation of functional monomers:¹⁴

- Polymerization or copolymerization of functional monomers
- Chemical modification of preformed polymers

The use of functional monomers permits ready control of the content and sometimes the distribution of units along the polymer chain; this procedure gives more latitude concerning the physical properties of the final product. On the other hand, chemical modification of an existing polymer, when possible, enables the choice of molecular weight and the dispersity of the polymer. It also allows the synthesis of polymers inaccessible by direct route.¹⁵

Cross-linking, vulcanization, and grafting are some of the polymer reactions that take place on functional or reactive groups located in the polymer main chain. We have already discussed some of these reactions in the preceding sections. We now discuss other examples of modification of polymers based on reactive monomers, oligomers, or polymers.

A. POLYURETHANES

As we shall see in [Chapter 15](#), polyurethane is a polymer of choice for a wide variety of biomedical applications. Polyurethane is used extensively in the construction of devices such as vascular prostheses, membranes, catheters, plastic surgery, heart valves, and artificial organs. Polyurethanes are also used in drug delivery systems such as the sustained and controlled delivery of pharmaceutical agents, for example, caffeine and prostaglandin.³⁴

The major reason for the successful application of polyurethanes as biomaterials is their biocompatibility and formulation versatility. The properties of polyurethanes can be controlled over a wide range by a careful choice of the initial reactants, their ratio, and reaction conditions. Polyurethane elastomers that are of particular interest in medical technology provide a good illustration of the use of functional oligomers/polymers with terminal reactive groups. Bifunctional end-terminated oligomers or low-molecular-weight polymers are made by capping polyols — or polyols of polyether, polyester, or polyalkene — with either aromatic or aliphatic diisocyanate. Typical diisocyanates and polyols used in the synthesis of these polyurethane intermediates are shown in [Tables 5.7](#) and [5.8](#), respectively. The isocyanate-terminated oligomers (prepolymers or telechelic polymers) are then coupled by reacting with low-molecular-weight diol or diamine chain extenders. A number of aliphatic and aromatic diols and diamines used as chain extenders or cross-linking agents in this synthesis are shown in [Table 5.8](#). This two-step polymerization process (Equations 5.16–5.18), which is usually carried out in solution, results in polyurethane elastomers with good physical characteristics.

Polyurethane elastomers are thermoplastic copolymers of $(AB)_n$ type consisting of an alternating block of relatively long, flexible “soft segment” and another block of highly polar, rather stiff chains or “hard segment.” The soft segment is derived from a hydroxyl-terminated aliphatic polyester, polyether, or polyalkene (MW 500 to 5000), while the hard segment is formed from the reaction of diisocyanates with low-molecular-weight diol or diamine chain extenders. The unique physical and mechanical properties of polyurethane elastomers are determined by their two-phase domain structure. These properties can be regulated by exploiting the structural variations possible in R, R', and R". Therefore, the ultimate properties of polyurethane-based materials can be controlled largely by the proper choice of the starting monomers used in their synthesis. For example, caprolactone and/or polycarbonate-based polyesterurethanes are more stable to hydrolysis than those based on polyethylene adipate or oxalate.^{17,18} Polyetherurethanes exhibit better hydrolytic stability than polyesterurethanes. For hydrophobic urethane elastomers, propylene oxide is used alone or mixed with a small amount of ethylene oxide. Elastomers with high resistance to light and thermal and hydrolytic degradation are prepared from hydroxy-terminated homo- and copolymers of butadiene and isobutylene, copolymers of butadiene and styrene,^{19–21} or aliphatic diisocyanates.²² Polyurethanes produced with aromatic chain extenders are generally stiffer than those prepared with aliphatic extenders.

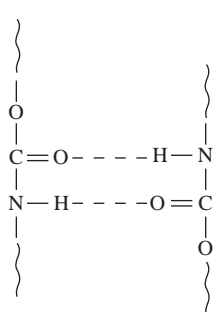
Typical medical-grade polyurethanes that have been developed and used successfully in various extracorporeal and intracorporeal devices include Biomer (Ethicon Inc.); Cardiothane 51 (Kronton Inc.); and Pellethane (Upjohn/Dow Chemical). For example, resistance to tear and fatigue, as exemplified by adequate modulus and strength, is essential for polymers to be used in reconstructive surgery of soft tissue and cardiovascular surgery. Cardiothane is a block copolymer consisting of 90% poly(dimethylsiloxane) ([Figure 5.13](#)).¹⁶ It has been used as intra-aortic balloons, catheters, artificial hearts, and blood tubings. This polymer, with its reactive (cross-linkable) acetoxy groups, combines the good mechanical characteristics of polyurethane with the surface properties of silicone. It further illustrates how the introduction of reactive groups in the polymer backbone can be used to produce a polymer with specific end-use properties.

The chemical and/or biological modification of polyurethane surfaces, such as grafting of hydrogels like acrylamide or poly(hydroxyethyl methacrylate) enhances blood compatibility. Biocompatibility and blood compatibility can be improved by treating the polymer surface with a solution of albumin or gelatin followed by cross-linking with gluteraldehyde or formaldehyde.²³

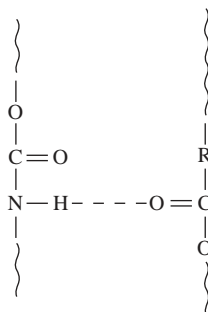
Example 5.6: The tendency for hard segment–soft segment phase separation in urethane copolymers increases in the order: polybutadiene and/or polyisoprene soft segment >> polyether soft segment > polyester soft segment. Explain.

Solution: Polyurethane elastomers are segmented copolymers composed of alternating soft and hard blocks. Hydrogen bonding in polyurethanes occurs between the NH hydrogens in the hard segment and the carbonyl oxygens in the hard segment or between the carbonyl and ether oxygens in the soft segment (Table E5.6).

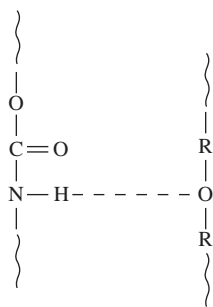
Table E5.6 Possible Hydrogen Bonding in Polyurethane



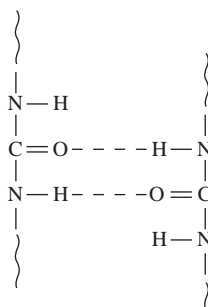
Urethane-Urethane



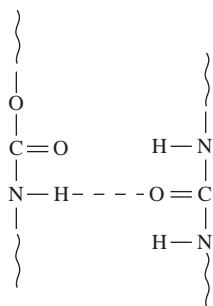
Urethane-Ester



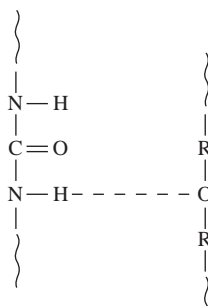
Urethane-Ether



Urea-Urea

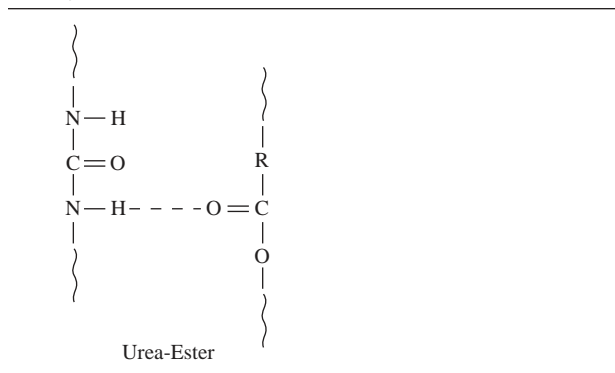


Urethane-Urea



Urea-Ether

Table E5.6 (continued) *Possible Hydrogen Bonding in Polyurethane*



The degree of microphase separation, therefore, depends on the relative magnitudes of intra- and interphase H-bonding. The strength and degree of hard segment–soft segment H-bonding are greater for the carbonyl group than the ether oxygen due to its relative polarities. Consequently, hard segment–soft segment compatibility is higher with polyester soft segment than polyether soft segment. With polybutadiene and/or polyisoprene soft segments, the potential for hard segment–soft segment H-bonding is nonexistent; only van der Waals forces operate between the two phases. Consequently, the tendency for phase separation is pronounced.

B. POLYMER-BOUND STABILIZERS^{13,24}

Traditionally, stabilizers for polymers such as antioxidants, ultraviolet stabilizers, and flame retardants are low-molecular-weight compounds. However, several problems are associated with the use of these stabilizers. These include their loss from the finished product by evaporation or leaching during fabrication. Also, compatibility at higher levels of incorporation of the stabilizers may be problematic. Another problem is the potential danger of toxicity. Low-molecular-weight chlorine, bromine, or phosphorous compounds commonly used as flame retardants, as well as phenolic derivatives that are frequently employed as antioxidants or ultraviolet stabilizers, are potentially toxic. Oligomeric or, possibly, polymer-bound stabilizers have the potential for eliminating these problems. These are prepared by synthesizing suitable functional monomers followed by homo- and/or copolymerization.

1. Antioxidants

2,6-ditertiarybutyl-1,4-vinyl phenol or 4-isopropenyl phenol polymerizes readily with isoprene, butadiene, styrene, and methyl methacrylate (Equation 5.19).

The resulting copolymers are good antioxidants for their parent polymers at copolymer compositions of only 10 to 15 mol% of polymerizable antioxidant.

2. Flame Retardants

Flame retardants are usually halogen-containing materials. 2,4,6-Tribromophenyl, pentabromophenyl, and 2,3-dibromopropyl derivatives of acrylate and methacrylate esters can be readily polymerized or copolymerized with styrene, methyl methacrylate, and acrylonitrile to produce polymers with improved flame retardancy (Equation 5.20).

Table 5.7 Typical Polyols Used in Syntheses of Polyurethane Elastomers

Polyols	
$\text{HO} - (\text{CH}_2\text{CH}_2 - \text{O} -)_n \text{H}$	Polyethylene oxide (PEO)
$\text{HO} - (\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{O} -)_n \text{H}$	Polytetramethylene oxide (PTMO)
$\text{HO} - (\text{CH}_2\overset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{O} -)_n \text{H}$	Polypropylene oxide (PPO)
$\text{HO} - [\text{C} - (\text{CH}_3)_2 - \text{CH}_2]_n - \text{OH}$	Polyisobutylene (PIB)
$\text{HO} - [(\text{CH}_2)_4 - \text{O} - \text{OC}(\text{CH}_2)\text{CO} - \text{O} -]_n \text{H}$	Polyethylene adipate (PEA)
$\text{HO} - [(\text{CH}_2)_3 - \text{CO} - \text{O} -]_n \text{H}$	Polycapropactone (PCL)
$\text{HO} - (\text{CH}_2)_4 - [\text{Si}(\text{CH}_3)_2 - \text{O} -]_n - \text{Si}(\text{CH}_3)_4 - \text{OH}$	Polydimethylsiloxane, hydroxybutyl terminate (PDMS)-OH
$\text{HO} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2\underset{\text{CH} = \text{CH}_2}{\underset{ }{\text{CH}}} = \text{CH} - \text{CH}_2 - \text{OH}$	Polybutadiene (PBD)

From Gogolewski, S., *Colloid Polym. Sci.*, 267, 757, 1989. With permission.

Table 5.8 Typical Chain Extenders Used in Syntheses of Polyurethane Elastomers

Chain Extenders	
$\text{HO} - (\text{CH}_2)_4 - \text{OH}$	1,4-Butanediol (BD)
$\text{HO} - (\text{CH}_2)_6 - \text{OH}$	Hexanediol (HD)
$\text{HO} - (\text{CH}_2)_2 - \text{OH}$	Ethylene diol (ED)
$\text{HO} - (\text{CH}_2)_2 - \text{O} - (\text{CH}_2)_2 - \text{OH}$	Diethylene diol (DED)
$\text{H}_2\text{N} - (\text{CH}_2)_2 - \text{NH}_2$	Ethylenediamine (EDA)
$\text{H}_2\text{N} - \text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{NH}_2$	Propylenediamine (PDA)

From Gogolewski, S., *Colloid Polym. Sci.*, 267, 757, 1989. With permission.

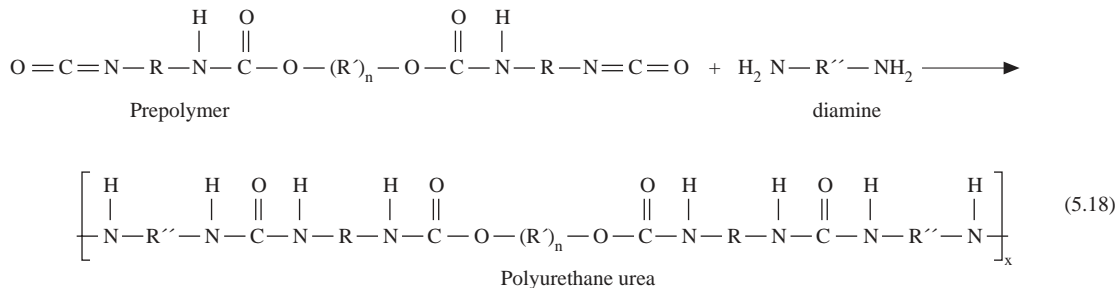
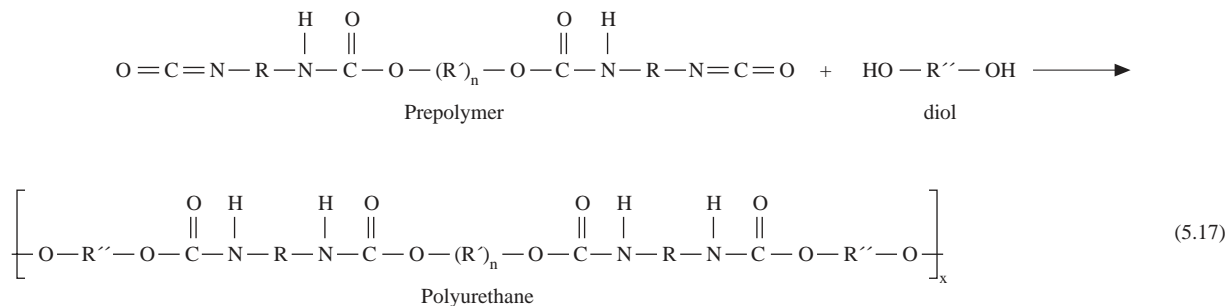
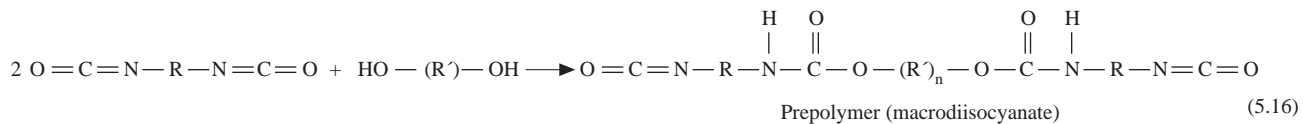


Figure 5.12 Equations representing the two-step process for producing polyurethane copolymers.

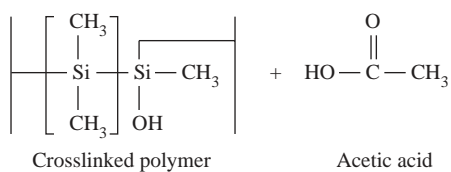
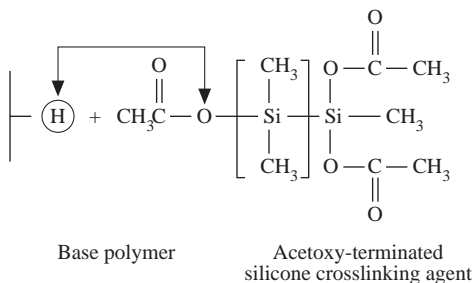
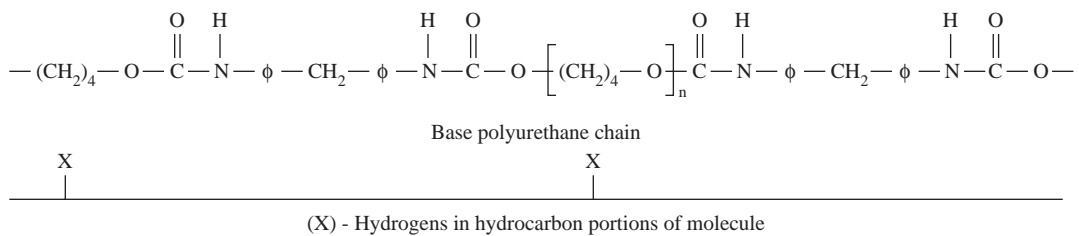
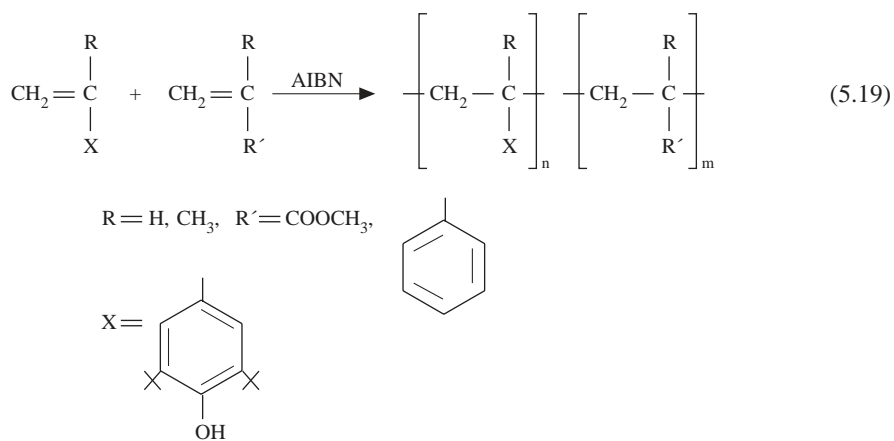
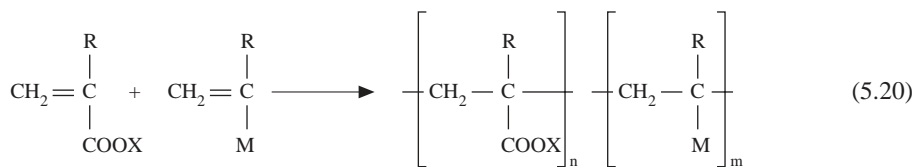


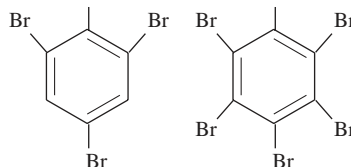
Figure 5.13 Structure of Cardiothane. (From Gogolewski, S., *Colloid Polym. Sci.*, 267, 757, 1989. With permission.)





R = H, CH₃

X = —CH₂CH₂Br — CH₂Br,



M = —COOCH₃, —CN;

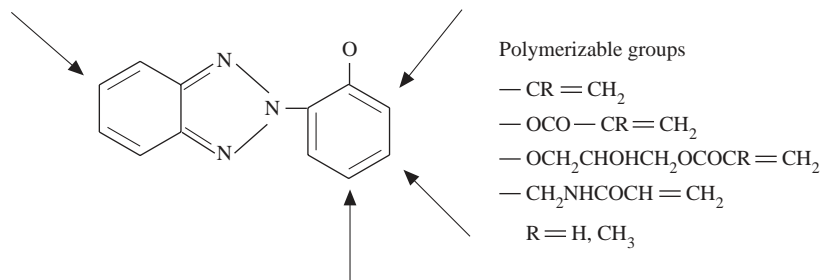
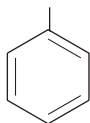
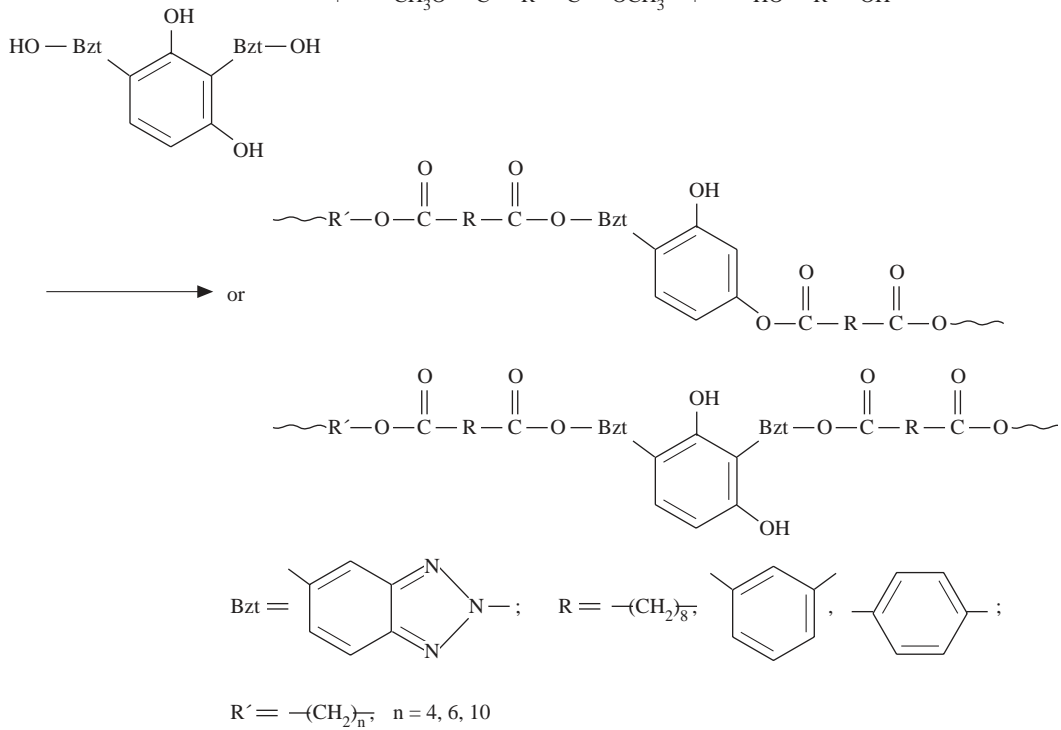
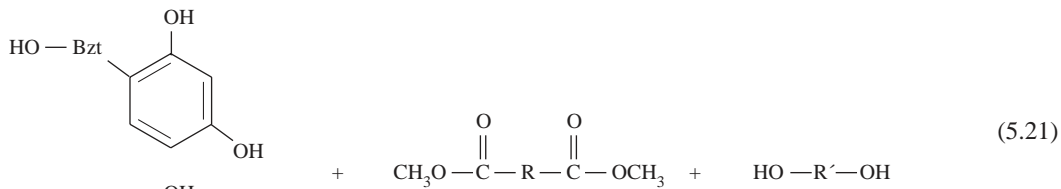


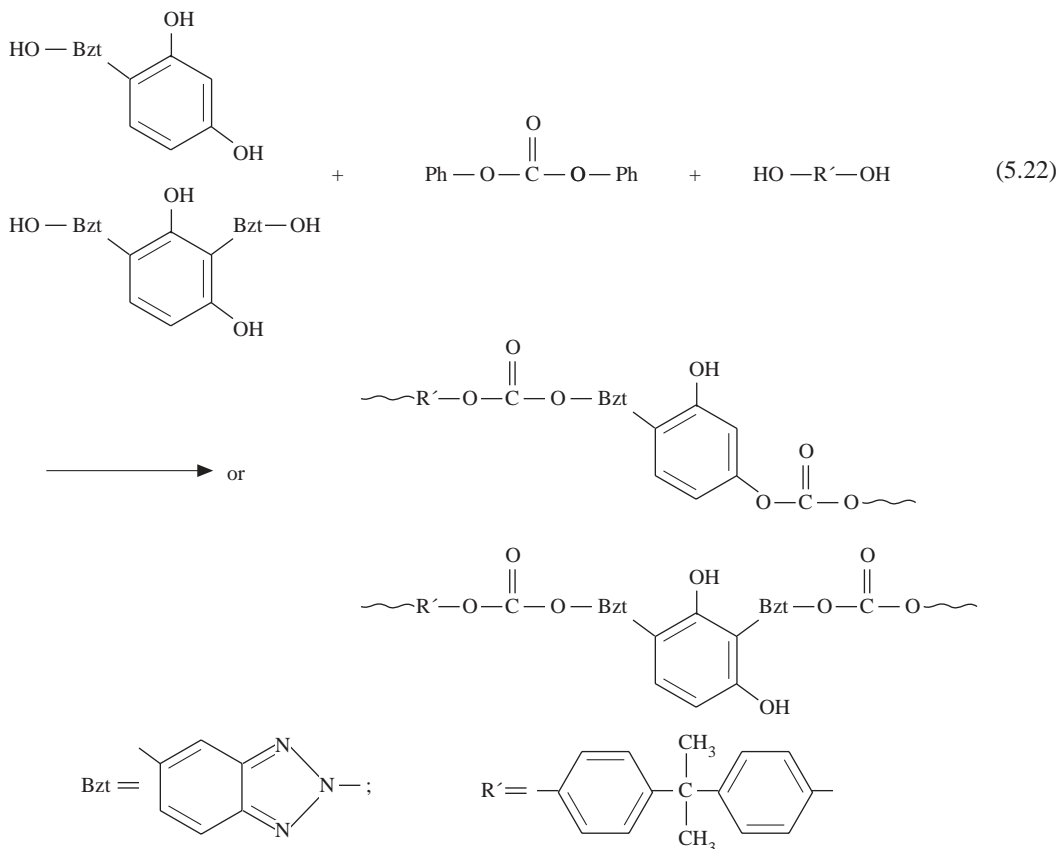
Figure 5.14 Polymerizable 2(2-hydroxyphenyl) 2H-benzotriazole derivatives.

Incorporation of only about 5% of these copolymers in polystyrene increased the limited oxygen index by 30%.¹³ This is substantially lower than the 10 to 12% of the usual flame retardant materials required to protect polystyrene and similar polymers from being highly inflammable.

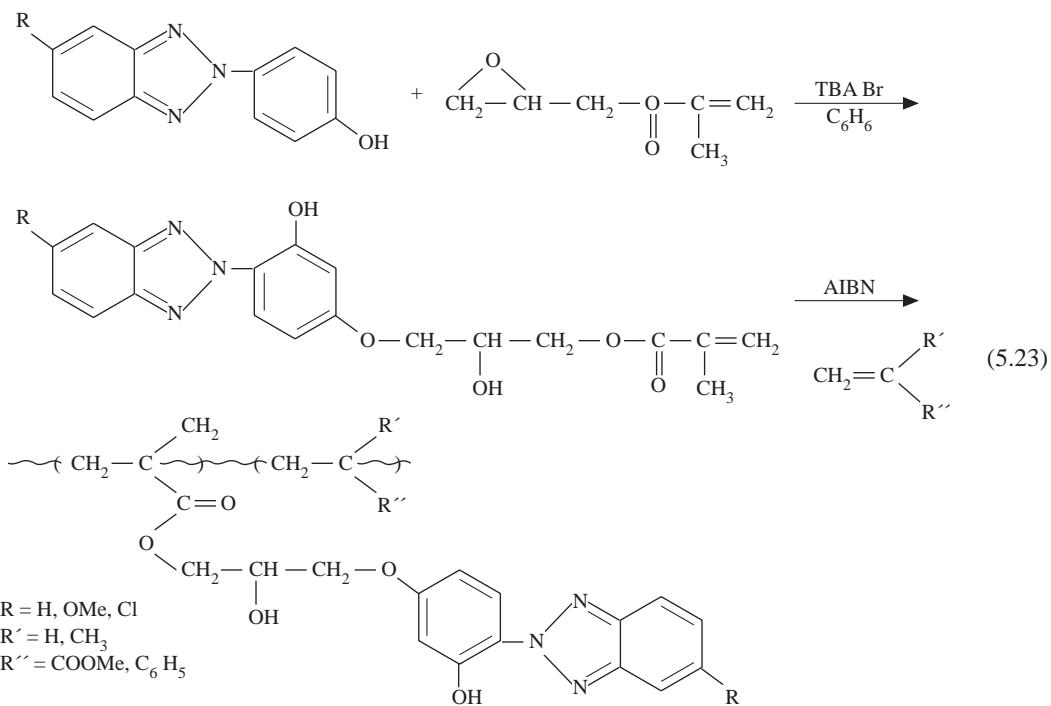
3. Ultraviolet Stabilizers

Upon exposure of polymeric materials to sunlight, ultraviolet stabilizers tend to evaporate from their surfaces where, incidentally, the stabilizing action is particularly required. 2(2-Hydroxyphenyl) 2H-benzotriazole derivatives (Figure 5.14) have been recognized to be the most effective compounds for protecting polymeric materials from ultraviolet and photodegradation. Small quantities (a few percentage points) of photostabilizers have been introduced into polyesters, polycarbonates, and polyamide using hydroxy-, acetoxy-, carboxyl-, and carbomethoxy-derivatives of this compound. These polymer-bound stabilizers are substantially more effective than the lower molecular weight UV stabilizers. The modified polyester has been synthesized directly. For example, poly(ethylene sebacate) was made from dimethyl sebacate and ethylene glycol with 1 to 3% of ethylene glycol replaced by 2(2,4-dihydroxyphenyl) 2H-benzotriazole (Equation 5.21). Similarly, ultraviolet-stabilized polycarbonate was made using bisphenol A and diphenyl carbonate (Equation 5.22).

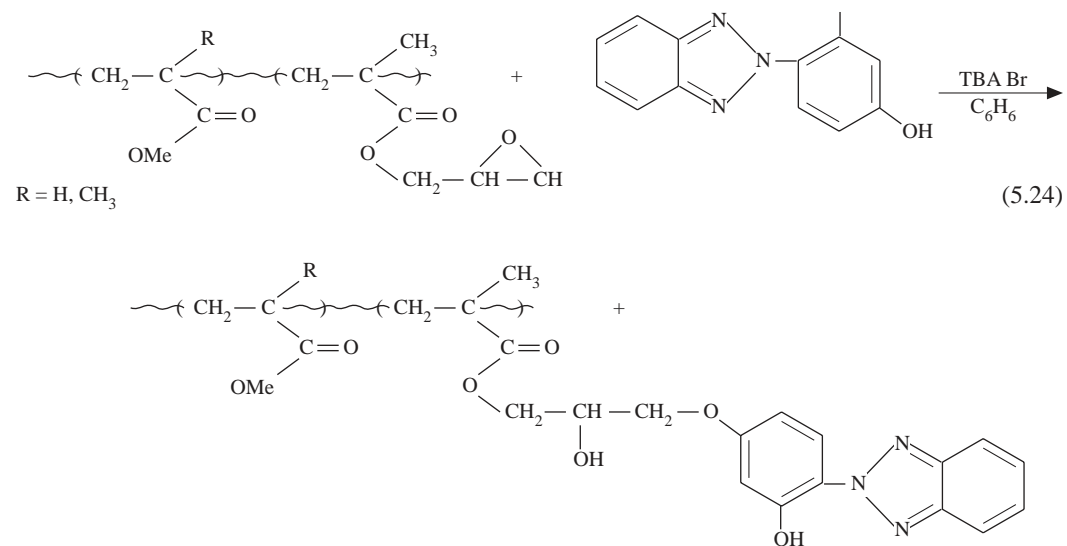




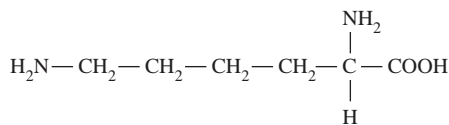
The discussion so far involves cases of functional polymers where the reactive/functional groups are attached directly to the backbone. The reactivity of a functional group directly attached to the polymer backbone depends on the proximity, flexibility, and polarity of the polymer main chain. The interference from the polymer main chain can be eliminated, or at least reduced, through functional groups attached as side groups or through the use of spacer groups inserted between the reactive groups and the polymer main chain. For example, in addition to the techniques discussed above, the ultraviolet stabilizer (2-(2-hydroxyphenyl) 2H-benzotriazole can be incorporated in the polymer structure using functional monomers or polymers with reactive side groups: the ring-opening reaction of the oxirane ring of glycidyl methacrylate followed by copolymerization with methyl methacrylate produces UV-stabilized PMMA (Equation 5.23).¹³



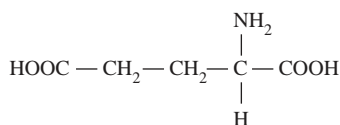
PMMA containing a small amount of glycidyl methacrylate units, when allowed to react with tetraalkyl ammonium salts, will undergo ring-opening reaction with 2(2,4-dihydroxyphenyl) 2H-benzotriazole (Equation 5.21).



Natural polymers very frequently link functional groups via spacer groups. For example, the amino acids lysine and glutamic acid have some of their functional groups linked by spacer groups (Figure 5.15). In synthetic polymer, spacer groups might be stiff groups like the phenyl group in *p*-substituted polystyrenes used in ion-exchange resins or, as is usually the case, flexible groups such as methylene or fluorocarbon groups. Fluorocarbon ether groups have been used successfully to separate sulfonate or



Lysine



Glutamic acid

Figure 5.15 Spacer groups in amino acids.

carboxylate groups from the polytetrafluoroethylene main chain to produce fluorocarbon polymer membrane of unusual properties.²⁴ Polymers have also been synthesized with spacer groups that have polyethylene, polyoxyethylene, and even the much stiffer polymethacrylate backbone. Polymethacrylates have been particularly useful as polymers with functional groups that can be separated effectively from the polymer main chain. Polymers and copolymers based on hydroxyethyl methacrylate or glycidyl methacrylate, for example, have been used in biomedical applications.

C. POLYMERS IN DRUG ADMINISTRATION^{28,30}

The medical field is no longer imaginable without synthetic polymers. They are used both as implant and surgical materials and as drugs or carriers for drugs. Drugs are hardly ever administered to patients in an unformulated state. Polymers have long been employed as excipient for adjusting the consistency and release properties of simple solid, cream, and liquid formulations. Polymers that have typically been used in drug delivery include various cellulose derivatives, polyacrylates, poly(vinyl pyrrolidone), polyoxyethylene, poly(vinyl alcohol), and poly(vinyl acetate). Poly(vinyl pyrrolidone), poly(2-hydroxypropyl methacrylamide), and polyoxazoline are examples of synthetic polymers that have been used as plasma expanders.²⁸ We discuss a few examples to illustrate the use of functional polymers in drug administration.

The traditional approach in pharmaceutical research is to focus effort on the discovery of new compounds with biological activity that can be used in the treatment of diseases. The main problem associated with this approach is that the drug may be distributed to a variety of sites in the body where it may be inactive, harmful, and/or toxic. Both the therapeutic and harmful/toxic effects of drugs depend on their concentrations at the various sites in the body.²⁸ There is normally an optimal therapeutic range within which the therapeutic effects of the drug outweigh its harmful effects. Outside this range, the drug may either be inactive or its harmful effects may predominate (Figure 5.16).

Two distinct approaches are currently used to improve drug action through its mode of delivery. These are controlled drug release and site-directed or targeted drug delivery.

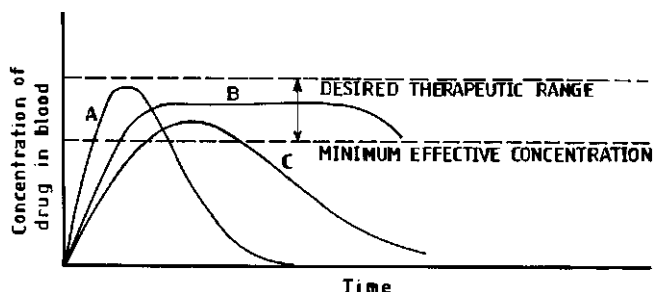


Figure 5.16 A schematic plot of different drug administration routes. (A) Single dose preparation; (B) sustained release preparation; (C) prolonged release preparation.

1. Controlled Drug Release

Most drugs are low-molecular-weight compounds, which when administered conventionally are often rapidly excreted from the body. Intermittent doses result in a sawtooth pattern of the drug in circulation due to the rise and fall of the concentration of the drug. Consequently, large and repeated doses are required to sustain a therapeutic effect. The aim of controlled drug release, therefore, is to eliminate or at least reduce the danger of overdose, with risk of side effects or subtherapeutic blood levels, by producing and maintaining an optimal therapeutic concentration of the drug in the body. Most controlled-release delivery systems rely on a polymer to regulate the flow of the therapeutic agent out of the device. A number of techniques are used to achieve this objective, including encapsulation, dispersion in hydrophobic vehicles or porous polymers, binding of the drug to macromolecules, and formation of drug-carrier complexes. We illustrate a couple of these techniques.

a. Tablets with Prolonged and Sustained Drug Release²⁹

The overall release profile of a drug can be controlled by the physical shape of the device or by the chemical nature of the polymer matrix. Tablets with a sustained and prolonged delivery have been prepared using polymers and terpolymers based on acrylic and methacrylic acids as coatings for some dosage forms. The behavior of these polymeric materials in the various parts of the gastrointestinal tract varies depending on the chemical structure and molar mass and on the ratio of basic, acidic, and hydrophobic groups. Thus the location and rate of release of the active substance can be controlled.

Figure 5.17 shows a typical cationic copolymer. It is basic, swells in the pH range of 5 to 8 but is soluble at pH 2.5. The anionic polymers Eudragit L, S (Figure 5.18) are based on methacrylic acid and methacrylic acid methyl ester. They are resistant to gastric juice, but soluble in the small intestine and insoluble and impermeable to water below pH 6 to 7 range. They consequently provide full protection against gastric acid and ensure drug release in the small intestine.

Another variation of these acrylic copolymers are acrylic terpolymers based on methacrylic acid with a small amount of quaternary ammonium group. These terpolymers are water insoluble in the entire physiologic field. They, however, swell and are permeable to water and drugs. Their permeability is independent of pH and can be controlled by appropriate structural modification. The polymeric films behave essentially as semipermeable membranes with a domain microstructure: the predominant hydrophobic parts of the macromolecule cause insolubility in water, while the hydrophobic quaternary groups permit the passage of water and drug molecules.

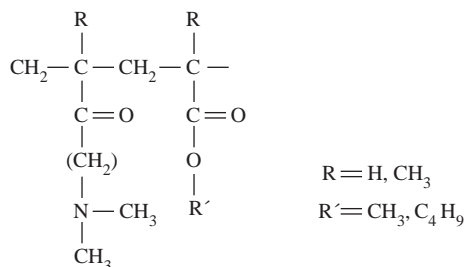


Figure 5.17 Eudragit E-cationic polymer. (From Kalal, J., *Makromol. Chem. Macromol. Symp.*, 12, 259, 1987.)

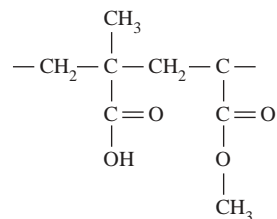
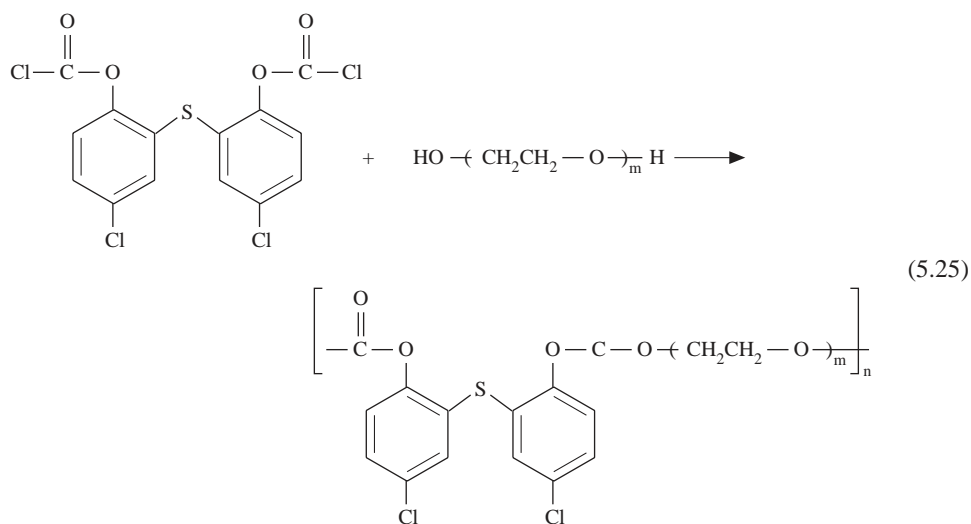


Figure 5.18 Eudragit anionic polymers: (L) $-\text{COOH}/-\text{OCH}_3 = 1/1$; (S) $-\text{COOH}/-\text{OCH}_3 = 1/2$. (From Kalal, J., *Makromol. Chem. Macromol. Symp.*, 12, 259, 1987.)

b. Degradable Polymers³

Polymers with functionalities in the main chain very often have aromatic groups that consequently cause the polymers to become infusible, intractable, and nonfabricable.^{30,31} For example, the copolycarbonates or bithionol and glycols where the glycol units are small are essentially intractable. However, by using an appropriate spacer group, the hydrophilicity of the polymer can be modulated. This is achieved by using bithionol — an antibacterial agent — and a bisphenol as a comonomer in an alternating copolycarbonate with a poly(ethylene oxide) glycol with a DP of at least 10 (Equation 5.24). The resulting polycarbonate has useful physical characteristics. In addition, it is degradable under physiologic conditions for controlled release of the bactericide bithionol and of the carbon dioxide and poly(ethylene oxide) glycol.



Polycarbonate of bithionol with poly(ethyleneoxide) glycol as spacer group

2. Site-Directed (Targeted) Drug Delivery

The basic principle in site-directed or targeted drug delivery is that the carrier will recognize the disease-related target or biochemical site of action, interact with it, and concentrate delivery of the drug at the site. The drug is thus rendered inactive elsewhere in the body. The polymer in targeted drug delivery systems acts merely as a carrier with no intrinsic pharmacologic activity or therapeutic effect. In other words, the macromolecule is chemically modified with molecules of the drug and other moieties to overcome some undesirable characteristics of the drug, but can be transformed by a chemical or enzymatic process to release the pharmacologically active drug at the appropriate time or location (Figure 5.19). To satisfy this requirement the macromolecule must be designed to accommodate features that may even be in conflict. Some of these features are²⁸

- It must provide overall solubility to the targeting system, and after the drug release the carrier itself must be both water soluble and capable of being totally excreted by the body after the required period of time.
- It may need to contain groups available for the chemical attachment of drugs via biodegradable linkages.
- It must contain structural features necessary for interaction specifically with the discrete features of the biosystem.
- It is expected to prevent nonspecific interactions between the components of the biological system and polymer targeting system.

In general, the properties of a biosystem and a synthetic polymer as well as the nature of the biological medium dictate the degree and type of interaction between a biostructure and a polymer. The biocompatibility of synthetic polymers depends on their chemical nature, physical state, and macroscopic form, which can be modified by functionalization of the polymer skeleton. Many biopolymers, such as proteins and nucleic acids, are natural polyelectrolytes. Similarly, the outer cell membrane of living cells has charged groups. The biological medium is an electrolyte with an aqueous phase. Therefore, electrostatic

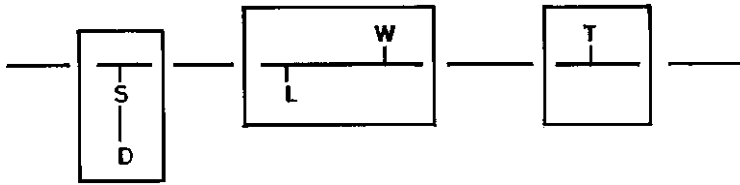


Figure 5.19 Generalized structure of soluble polymeric drug carriers: (D) drug; (S) spacer group; (L) and (W) groups that determine the solubility of macromolecule in nonaqueous and aqueous environment, respectively; (T) a group specifically recognized by an organ/tissue/cell of the body. (From Petrak, K., *Br. Polym. J.*, 22, 213, 1990. With permission.)

forces play a dominant role in the reversible interaction of biopolymer with synthetic polymers, while covalent bonding serves the irreversible immobilization of biostructures.³²

Most polymer carriers per se do not possess the ability to recognize the target site. Consequently, biological macromolecules such as polysaccharides, antibodies, and toxin fragments are introduced into the polymer carrier as the directional component and to ensure the required selectivity. The functional groups of the polymer are usually modified or activated to effect coupling of the biomolecule (Table 5.9).

Sometimes spacer groups are used to increase the distance between the polymer carrier and the biostructure so as to reduce interference from the polymer main chain and maintain proper functional properties. While there are currently no efficient site-directed drug delivery systems available for practical clinical applications, the feasibility of the general concept has been amply demonstrated. Examples are prodrugs based on *N*-(2-hydroxypropyl)-methacrylamide copolymers containing oligopeptide side chains terminating in an anticancer drug, Adriamycin (Figure 5.20). The bond between the drug and the carrier is stable in the bloodstream, but is cleared intracellularly on exposure to appropriate enzymes.²⁹

Table 5.9 Chemical Modification of Synthetic Polymers for Covalent Linkage of Biomacromolecules and Affine Ligands

Functional Group of the Polymer	Chemical Modification (activation) of the Polymer	Binding Group of the Biomacromolecule and Ligand
-OH	Cyanogen bromide	-NH ₂
	Triazines	-NH ₂
	Periodate oxidation	-NH ₂
	Benzoquinones	-NH ₂
	Epoxides	-NH ₂ , -COOH, -OH, -SH
	Silanization	-NH ₂ , -COOH, -C ₆ H ₅ -R
	Carboxylating reagents	-NH ₂
-COOH, -NH ₂ Carbodiimides	-NH ₂ , -COOH	
	Acylation	-NH ₂ , -COOH
	Active esters	-NH ₂ , -COOH
-CHO		-NH ₂
-C ₆ H ₄ -R	Diazotation reagents	-C ₆ H ₄ -R, histidine, tryptophan
-SH	Thiol-disulfide exchange	-SH

From Kalal, J., *Makromol. Chem. Macromol. Symp.*, 12, 259, 1987.

V. PROBLEMS

5.1. When two homopolymers with the same melt index are blended together by the addition of a compatibilizing agent, the resulting blend has a higher melt index. Explain.

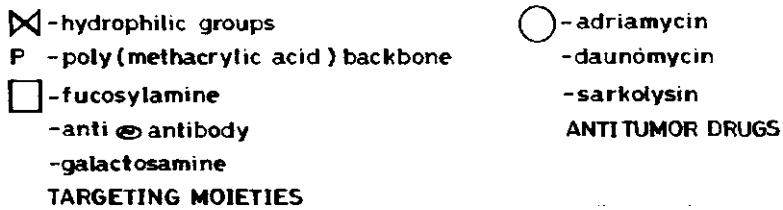
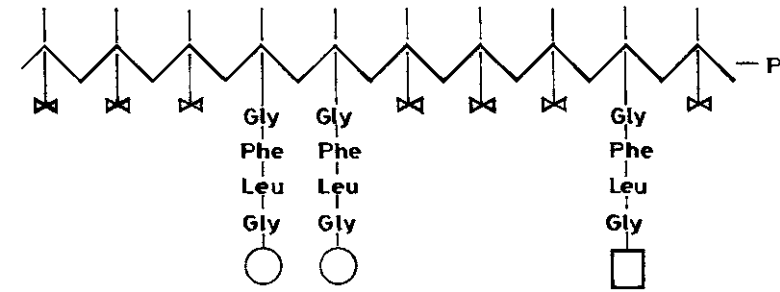


Figure 5.20 Schematic diagram of *N*-(2-hydroxypropyl)-methacrylamide copolymers containing oligopeptide side chains terminating in anticancer drugs or targeting moieties. (From Kalal, J., *Makromol. Chem. Macromol. Symp.*, 12, 259, 1987.)

5.2. Dextrins are degradative products of starch obtained by heating starch in the presence or absence of hydrolytic agents. Typical conditions for the white and yellow (canary) dextrins are shown in the following table.

Manufacturing Condition	White Dextrins	Canary Dextrins
Usual catalyst	HCl	HCl
Temperature, °C	79–121	149–190
Time, h	3–7	6–20

Envelope front seal adhesives are made from solutions of dextrins in water. They require high solid contents, usually 60 to 70%. Which of the two dextrin types (white or yellow) would be more suitable as adhesives for envelope seals?

5.3. Indicate how you would increase:

- The moisture resistance of nylon 6
- The toughness and crack resistance of polyethylene (HDPE)
- Impact resistance of polystyrene

5.4. Explain the observed trends in the data for the melt index and the peel strength to aluminum of polyethylene (PE) and ethylene–acrylic acid copolymer (EAA) shown in the following table.

Polymer	Acrylic acid (mol%)	Melt Index (g)	Peel Strength (lb/in.)
PE	0	1.5	<1
EAA	4.6	83	56
EAA	6.0	58	81
EAA	8.2	52	100

5.5. Nitrile rubbers possess outstanding oil-resistant properties. Explain the following variation in properties of nitrile rubber.

Acrylonitrile Content in Copolymer (%)	Properties of Nitrile Rubber
2–5	Rubbery with poor oil resistance
15	Rubbery with fair oil resistance
25	Rubbery with medium oil resistance
35–40	Leathery with high oil resistance
50–60	Tough, leathery plastic with high resistance to aromatics

5.6. Suggest a possible method to effect the following changes through copolymerization. Briefly explain the basis of your suggestion.

i. Increase:

(a) the rigidity of $\left[\text{O} - (\text{CH}_2)_{20} - \text{CO} \right]_n$ (Str. 11)

(b) the chemical resistance of $\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_n$ (Str. 12)

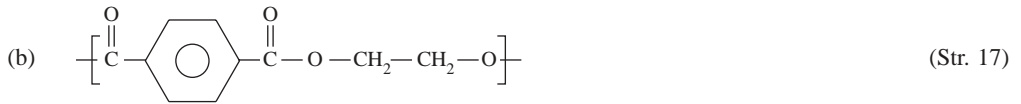
(c) the flexibility of $\left[\text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} - \text{C}_6\text{H}_4 - \text{N} \begin{array}{c} \text{H} \\ | \end{array} \right]_n$ (Str. 13)

(d) adhesion to polar substrates of $\left[\text{CH}_2 - \text{CH}_2 \right]_n$ (Str. 14)

(e) the temperature resistance of $\left[\text{N} \begin{array}{c} \text{H} \\ | \end{array} - (\text{CH}_2)_6 - \text{N} \begin{array}{c} \text{H} \\ | \end{array} - \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} - (\text{CH}_2) - \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \right]_n$ (Str. 15)

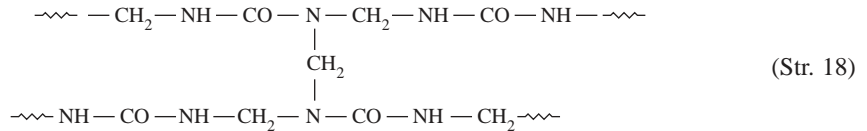
ii. Obtain cross-linked polymers from:

(a) $\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_n$ (Str. 16)

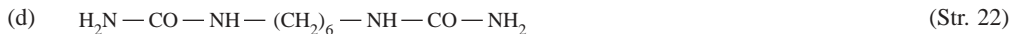
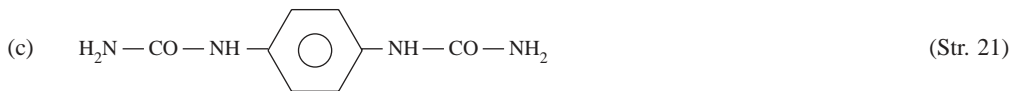
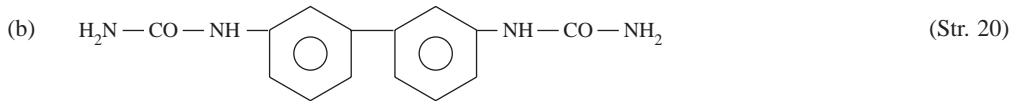
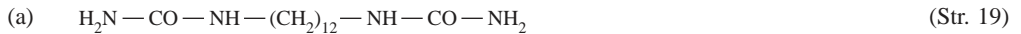


5.7. An unsaturated polyester based on maleic anhydride is to be used in an application requiring good creep resistance. Which of the available unsaturated monomers (methyl methacrylate or vinyl acetate) would you choose for curing the polyester? Explain your choice.

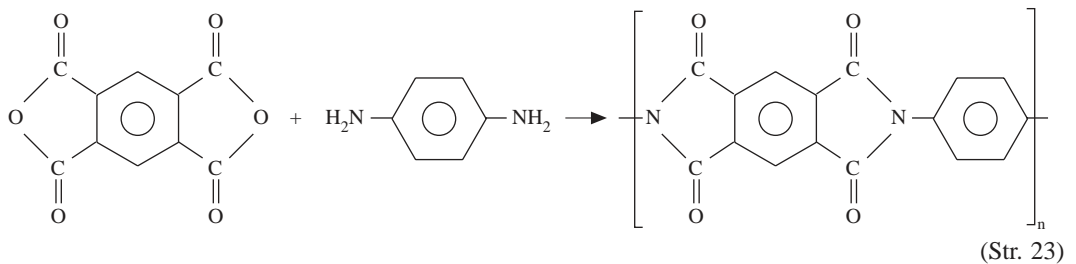
5.8. The nature of cross-linked urea-formaldehyde (UF) resins is thought to be



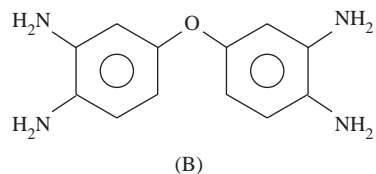
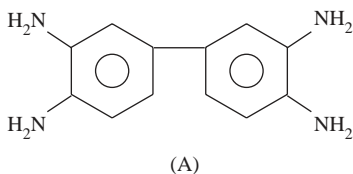
Films from cured UF resins are very brittle. Arrange the following components in their increasing ability to reduce the brittleness of UF films through copolymerization with urea and formaldehyde.



5.9. Polyimides are formed by the reaction:



Polyimides are insoluble, infusible polymers that cannot be used as adhesives. Which of the following two compounds would you copolymerize with the starting monomers to produce a useful adhesive? Comment on the temperature resistance of the resulting adhesive.



(Str. 24)

- 5.10. How much sulfur, in parts per hundred resin (phr), would be required to vulcanize polybutadiene rubber of molecular weight 5400 assuming:
- Disulfide cross-links
 - Decasulfide cross-links
- 5.11. UF resins are susceptible to hydrolytic degradation. Rank the following monomers in order of the expected increase in the hydrolytic stability of UF resins modified by the incorporation of these monomers through copolymerization of their urea derivatives. Explain the basis of your ranking order.

Monomer	Structure
1. Hexamethylenediamine	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$
2. Trimethylene oxidediamine	$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{NH}_2$
3. Dodecanediamine	$\text{H}_2\text{N}-(\text{CH}_2)_{12}-\text{NH}_2$

- 5.12. The stiffness of the polymer backbone chain has been found to be responsible for the minimum length of spacer groups required to make the reactivity of the functional group free from the interference of the polymer main chain. For poly(ethylene oxide) three to four methylene groups are required, whereas spacer groups of one or two methylene are necessary for polyethylene. Explain this observation.

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