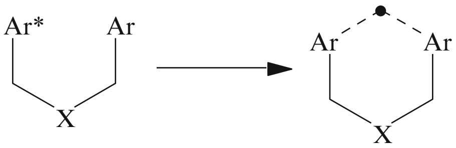
Chapter 9
Organic Reactions of Polymers

9.1 Reactivity of Macromolecules

In consideration of various chemical reactions of macromolecules, the reactivity of their functional groups must be compared to those of small molecules. The comparisons have stimulated many investigations and led to conclusions that functional groups exhibit equal reactivity in both large and small molecules, if the conditions are identical. These conclusions are supported by theoretical evidence [1, 2]. Specifically, they apply to the following situations [1]:

1. Reactions that take place in homogeneous fluid media with all reactants, intermediates, and end products fully soluble. These conditions exist from the start to the end of the reactions.
2. All elementary steps involve only individual functional groups. The other reacting species are small and mobile.
3. The steric factors in the low molecular weight compounds selected for comparison must be similar to those of the large molecules.

The above can be illustrated by a few examples. For instance, the rates of photochemical *cis–trans* isomerization of azobenzene residues on the backbones of flexible polymeric chains are analogous to those of small molecules [3]. Another example is the activation energy for *cis–trans* isomerization of azo-aromatic polymers. It is the same for low molecular weight analogs [4]. A third example is an experiment in comparing conformational transitions of some eximers in large and small molecules. A sandwich complex forms between an excited aromatic chromophore, *Ar,* and a similar chromophore in the ground state when irradiated with light of an appropriate wavelength. The conformation required by such an excimer can correspond to a prohibitive energy requirement for the unexcited molecule. All conformational transitions must take place during the lifetime of the excited state of the chromophore that is of the type [5]:



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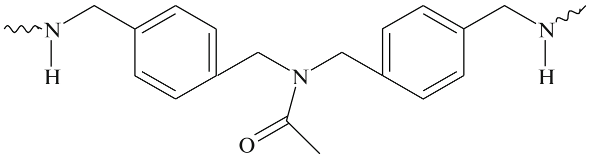
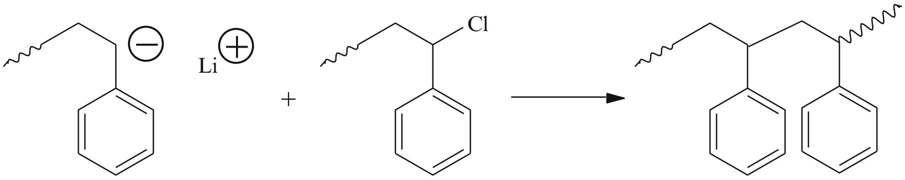
The ratio of the fluorescence intensity of an excimer and a normal molecule is a measure of the probability that the conformational transition takes place during the excited lifetime. A polyamide with only a small proportion of the following units was used for comparison:

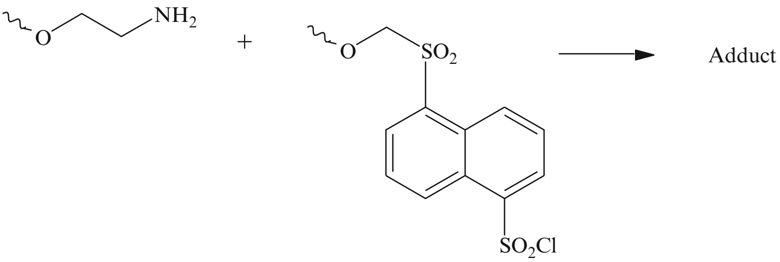


Emission spectra of dilute solutions of the above polyamide and its low molecular weight analog were measured over a range of temperatures. They showed that the activation energies of the conformational transitions required for excimer formations are essentially the same for both materials [5].

In addition, all bimolecular activation-controlled reactions are independent of the degree of polymerization [6]. Simple S_N2 reactions between reactive groups attached to chain ends of monodisperse macromolecules in a wide range of molecular weights are independent of the DP [7, 8] in the range of 20–2,000 [7]. This was shown on three different reactions. In the first one, the reactivities of chlorine-terminated low and high molecular weight polystyrenes towards polystyryllithium are equal in benzene and cyclohexane solvents:



In the second one, the reactivity of primary amine-terminated polyoxyethylenes with sulfonyl chloride-ended polyoxyethylenes in chloroform is also the same:



In the third one, chain length dependence of the propagation rates was measured in polymerizations of methyl methacrylate. In the range of DPs from 130 to 14,200, the propagation constant was shown to be independent of the chain length [8].

On the other hand, unequal reactivity was observed:

1. In bimolecular reactions that are diffusion-controlled.
2. When neighboring group participations become significant.
3. When the properties of the polymers in solution are altered by gelation.
4. When the tacticities of the polymers affect neighboring group interactions.
5. When heterogeneous conditions affect accessibility to the reactive sites.

There are special situations that can occur. For instance, electrostatic charges carried by the polymers may extend over long distances in solutions and may manifest themselves in reactions with charged reagents. Sometimes, chain flexibility or folding can cause functional groups to come together and interact, though they may be located well apart on the polymer backbone. Polymer solutions of this type are comparable to dispersions of individual droplets of concentrated solutions.

Some statements above may require additional clarification. An elaboration, therefore, follows.

9.1.1 Diffusion-Controlled Reactions

Reactions that are bimolecular can be affected by the viscosity of the medium [9]. The translational motions of flexible polymeric chains are accompanied by concomitant segmental rearrangements. Whether this applies to a particular reaction, however, is hard to tell. For instance, two dynamic processes affect reactions, like termination rates, in chain-growth polymerizations. If the termination processes are controlled by translational motion, the rates of the reactions might be expected to vary with the translational diffusion coefficients of the polymers. Termination reactions, however, are not controlled by diffusions of entire molecules, but only by segmental diffusions within the coiled chains [10]. The reactive ends assume positions where they are exposed to mutual interaction and are not affected by the viscosity of the medium.

9.1.2 Paired Group and Neighboring Group Effects

When *random*, *irreversible*, and *intramolecular* reactions occur on polymeric backbones with the functional groups adjacent to each other, they can be expected to react. There is, however, an upper limit to conversions. This upper limit is due to statistical probability that some functional groups are bound to become isolated. The limit for conversion was calculated to be 86.5% [11].

Theoretically, quantitative conversions should be possible with *reversible* reactions of paired functional groups on macromolecular backbones. The ability, however, of isolated reactive groups to find each other and then pair off depends either upon particularly high driving forces, or upon the time required to accomplish complete conversions [12]. For reactions initiated randomly, at different sites, the probability is high that two groups on the terminal units will eventually meet and react. Since the reactions are reversible, at least in theory, very high conversions are possible.

Neighboring group participation can usually be deduced from three types of evidence:

1. If the reactions occur more rapidly during the rate-determining step than can be expected from other considerations.
2. If the stereochemistry of the reactions suggests neighboring group involvement.
3. If molecular rearrangements occur and the groups remain bonded to reaction centers, but break away from the atoms to which they were originally attached on the substrates.

There are many examples in the literature that describe neighboring group effects in reactions of polymers. One example is hydrolysis of poly(*p*-nitrophenyl methacrylate-co-acrylic acid). The high reaction rate at a neutral pH is due to attacks by the carboxylic moieties upon the neighboring carbonyl carbons [13–15]. Decomposition rates of *t*-butyl acrylate-styrene copolymers [16] can serve as an another example. Experimental data show pronounced acceleration for all samples. This is interpreted in terms of both intra and intermolecular interactions of the esters and the carboxylic groups. It follows a suggestion of Cherkezyan and Litmanovich [16, 17] that the instantaneous reactivity of any group depends on its microenvironment. That includes (for reactions of polymer in molten condition) two nearest units on the same chain (internal neighbors) and two units belonging to two different chains (external neighbors).

Another example of the neighboring group effect is the behavior of polyacrylamides in hydrolyses. There are two distinct and successive rates [18]. After conversions of up to 40–50% are reached, the reactions slow down. This is due to accumulations of negative electrostatic charges on the polymeric backbones [18]. In alkaline media, the increasing negative charges along the chains exert electrostatic repulsions toward the hydroxyl ions. This results in rate decreases.

9.1.3 Effect of Molecular Size

An example is the effect of DP on the rates of alkaline hydrolyses of poly(vinyl acetate)s. Rapid increases in the rates can be seen [19] in large, but not in small molecules, as the reactions progress. Solvents that are good for the products, like acetone–water mixtures, are used in these reactions. These are, however, poor solvents for the staring materials with high DP. Low molecular weight molecules are more soluble. This means that, at the start of the reaction, the large molecules are coiled up and the reactive sites not readily available. As the reactions progress, the chains unravel and the sites became more accessible with accompanying increases in the reaction rates. Because the small molecules are more soluble, the reactive sites are accessible from the start of the reactions, and the rates are constant.

There are many report in the literature on the *effects of chain conformation* [19–25]. One example is radical bromination of poly(methyl styrene) [20] with *N*-bromosuccinimide-benzoyl peroxide or Br_2-K_2CO_3-light. ^{13}C NMR spectroscopy shows differences in reactivities of the methyl groups in the 3 and 4 positions on the benzene rings between isotactic and atactic polystyrenes [20].

The differences in reactivities in poly(vinyl alcohol)s between isotactic (*meso*) and syndiotactic (*dl*-diol) portions of the polymers and between *cis* and *trans* acetals [26–28] is another example. In extending this to model compounds, reactions of stereo isomers of pentane-2,4-diol and heptane-1,4,6-triol with formaldehyde take place much faster for the meso than for the *dl*-diol portions [26–28]. Even more important are the steric effects imposed by restricted rotations. For instance, quaternizations of chloromethylated polyether sulfones exhibit decreasing rates at high degrees of substitution. This can be attributed to restricted rotations of the polymeric chains, because this phenomenon is not observed with more flexible chloromethylated polystyrene under identical conditions [23, 24].

9.1.4 Effects of Changes in Solubility

Changes in solubility can occur during the courses of various reactions. Such changes are observed, for instance, during the chlorination of polyethylene in aromatic and chlorinated solvents [29]. There is an increase in the solubility until 30% conversion is reached. After that, solubility decreases and reaches a minimum at 50–60% chlorine content. Following that it increases again. This, however, is not typical of many reactions of polymers in solutions. More common is that the starting material is soluble, but not the product or the opposite is true. Higher conversions are, usually, expected when the polymers are solvated and the chains are fully extended. In such situations, the reagents have ready access to the reactive sites [29]. If the products are insoluble in the reaction medium and tend to precipitate as the reaction progresses, the sites become increasingly less accessible. This can result in low conversions and premature terminations. If the opposite is true and the product is more soluble than the starting material, homogeneous limited reactions can be controlled. When the starting material is incompatible with the product, mutual precipitation or coiling of the chains can take place. This can also result in limited reactions. In addition, only minor differences in the constitutions of two polymers can cause incompatibility. For instance, among methacrylate polymers, there are incompatibilities in benzene solutions that result from differences only in the amount of branching of the alkyl groups [29].

Problems with solvent incompatibility can sometimes be overcome by using mixtures of solvents. Those that are good for the starting materials can be combined with those that are good for the products. With careful experimentation, it may be possible to develop a mixture of solvents that will keep all components in solution [30]. In some instances, however, insolubility of the products might be an advantage. This is the case in alcoholysis reactions of poly(vinyl acetate), where the polymer precipitates during the reactions and in doing so absorbs the catalyst with it. The phenomenon permits complete alcoholysis, particularly with the higher molecular weight species that precipitate first.

Secondary reactions, like cross-linking and gelation, can result in precipitations from solution. The extent of the reactions, however, is not necessarily limited, because diffusions of low molecular weight species are still possible. Isolation of useful products, however, often becomes very difficult.

9.1.5 Effects of Crystallinity

Crystallinity can only affect reactivity when the reactions are carried out on polymers in the solid state and at heterogeneous conditions. The differences in accessibility to the reactive sites vary with the amount of crystallinity. Cellulose, for instance, is often reacted in the solid state and the degree of crystallinity is expressed in terms of reactivity to various reagents [31]. The progress of a reaction can sometimes be monitored by a loss of crystallinity. What is more significant, however, is that greater accessibility to amorphous regions results in reaction products with special properties. An example is heterogeneous and homogeneous chlorination of polyethylene. Two different products are obtained [32]. The material from heterogeneous chlorination is much less randomly substituted and remains crystalline up to a chlorine content of 55%. The products from the homogeneous reactions, on the other hand, are amorphous after 35% substitution.

9.1.6 Reactions That Favor Large Molecules

Hydrophobic interactions play important roles in many polymeric reactions. They are, for instance, significant in the hydrolyses of low molecular weight esters when catalyzed by polymeric sulfonic acid reagents, like poly(styrene sulfonic acid). In these reactions, the hydrogen ions are located close to the macromolecules [19]. The hydrolytic cations are located in the regions of the macromolecules and not in the bulk of the solution. The rates of the reactions are high. Low molecular weight catalysts, on the other hand, like HCl, have all the hydrogen ions distributed evenly throughout the reaction medium. As a result, the rates are lower. Adsorption of the ester groups to the polymeric sites is accompanied by an increase in the apparent rate constant, as compared to reactions with HCl.

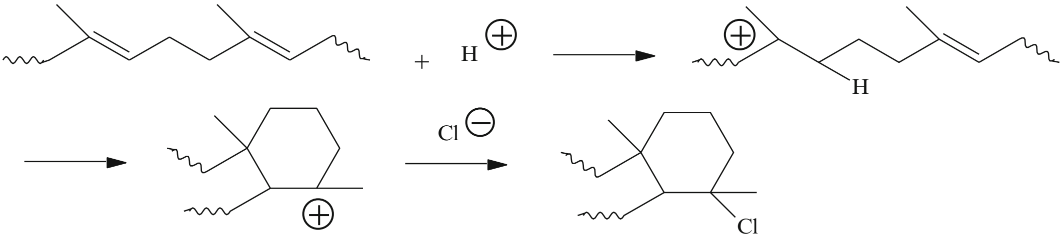
Examples are hydrolyses of methyl and butyl acetates [19]. Another example is formation of eximers and exiplexes in polyesters and methacrylate polymers that always favor large molecules over small ones [33]. Proton transfer reaction of poly(vinyl quinoline) [34] can serve as a third example. The emission, excitation, and absorption spectra of this polymer in a mixture of dioxane and water can be compared to that of 2-methylquinoline. The emissions coming from the protonated heterocyclic rings in the polymer occur sooner than from the low molecular weight compound [34].

9.2 Addition Reactions

Polymers with double bonds in the backbones or in the pendant groups can undergo numerous addition reactions. Some are discussed in this section.

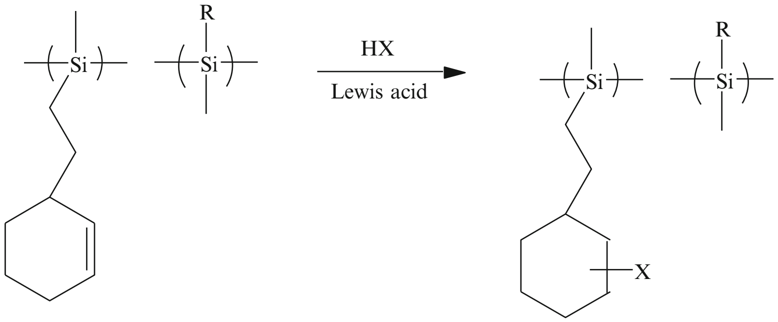
9.2.1 Halogenation

Hydro chlorination of natural rubber is often accompanied by cyclization [35, 36]:

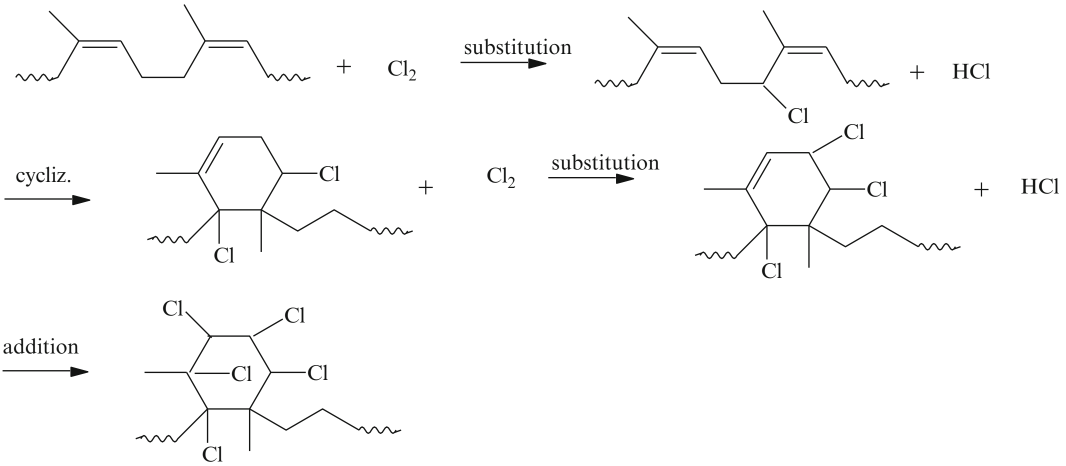


trans-1,4 and 1,2-Polybutadiene can be hydro halogenated under mild conditions with gaseous HCl [51]. The same is true of copolymers of butadiene with piperylene and also of isotactic *trans*-1,4-piperylene. The addition of HCl to the asymmetric double bond is *trans* for polypiperylene and occurs in a stereoselective way, judging from the ^{13}C NMR [51] spectra.

Polysilanes with alkene substituents add HCl and HBr in the presence of Lewis acids [58]. The products are the corresponding chlorine and bromine containing polymers with little degradation of the polysilane backbone:



Chlorinations of rubber, however, are fairly complex, because several reactions occur simultaneously. These appear to be: (1) additions to the double bond; (2) substitutions; (3) cyclizations; and (4) cross-linkings. As a result, the additions of halogens to the double bonds are only a minor portion of the overall reaction scheme [37, 38]. In CCl_4, the following steps are known to occur:

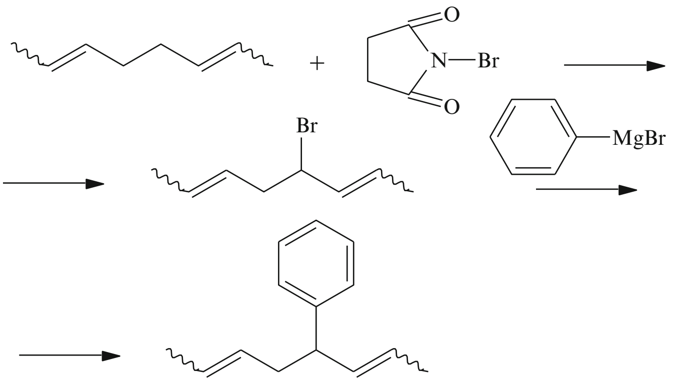


Halogenation reactions of unsaturated polymers follow two simultaneous paths, ionic and free radical. Ionic mechanisms give soluble products from chlorination reactions of polybutadiene [42]. The free-radical mechanisms, on the other hand, cause cross-linking, isomerization, and addition products. If the free-radical reactions are suppressed, soluble materials form. Natural rubber can be chlorinated in benzene, however, with addition of as much as 30% by weight of chlorine without cyclization [39, 40]. Also, chlorination of polyalkenamers both *cis* and *trans* yields soluble polymers. X-rays show that the products are partly crystalline [43, 44]. The crystalline segments obtained from 1,4-*trans* polyisoprene are diisotactic poly(erythro dichlorobutamer)s, while those obtained from the 1,4-*cis* isomer are diisotactic poly(threo 1,2-dichlorobutamer)s [45].

Additive type chlorination of natural rubber can also be carried out with phenyl iododichloride or with sulfuryl chloride [39, 40]. Traces of peroxides must be present to initiate the reactions. This suggests a free-radical mechanism. Some cyclization accompanies this reaction as well [40]. In CCl_4, for the first 25 chlorine atoms that add per each 100 isoprene units, 23 double bonds disappear and only a small quantity of HCl forms. Subsequent 105 chlorinations, however, cause a loss of only 53 double bonds.

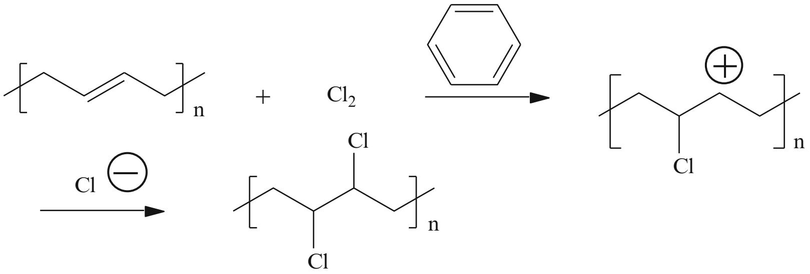
Rubber can be ***brominated*** at 30°C. If traces of alcohol are present, the reaction appears to go on entirely by addition [39, 40]. Without alcohol, substitutions take place rapidly and simultaneously with the additions to the double bonds [41]. Exomethylene groups and intramolecular cyclic structures form in the process. Slow additions of bromine to vinylidene double bonds result in formations of tri bromides, $–C_5H_7Br_3$. Also, ***cis*** and ***trans*** isomers of polyisoprene [41] brominate differently. Substitution reactions take place in brominations with *N*-bromosuccinimide. They are accompanied by cyclizations [39].

Brominations of polybutadienes with *N*-bromosuccinimide yield α-brominated polybutadienes [46, 47] that may also contain butane diylidene units. The products act as typical alkyl halides and can undergo Grignard-Wurz reactions:



The bromination reaction is accompanied by shifts of the double bonds that are coupled with the sites of substitution. Several different substituents can form. The polymers may contain pentane diylidene, hexane diylidene, and heptane diylidene units [46, 47].

By contrast, chlorination of polybutadiene in benzene is a straightforward addition reaction of the halogens to the double bonds [48, 49]:



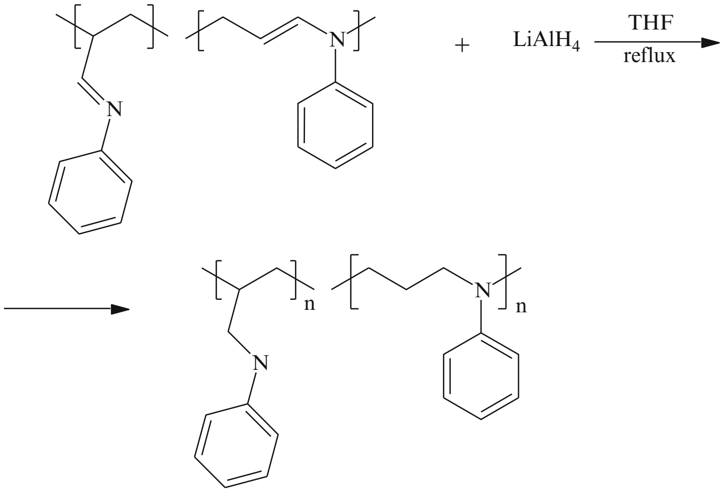
Very little HCl is liberated until all the double bonds are consumed. When CCl_4 is used in place of benzene, some substitutions occur during the latter stages of the reactions. If cross-linking occurs at the same time, the substitutions may not be extensive. The cross-linking reactions are believed to involve carbocationic intermediates.

Polybutadiene can be halogenated readily in tetrahydrofuran with iodine chloride or bromine [49]. The products are glassy polymers. These products dehalogenate in reactions with organolithium compounds, like *n*-butyllithium, *sec*-butyllithium, and polystyryllithium in tetrahydrofuran solution. Dehalogenation of poly(iodo-chlorinated butadiene) with *n*-butyllithium yields product with different *cis*/*trans* ratios. Also, this is accompanied by partial cross-linking. The reactions may involve [49] halogen-metal exchanges that are followed by intra- and intermolecular elimination of lithium halide. In brominations of polybutadienes, both couplings and eliminations take place. Both iodo-chlorinated and brominated polybutadienes form graft copolymers when reacted with polystyryllithium in tetrahydrofuran [50]. Gel formation, however, accompanies the grafting reaction.

9.2.2 Hydrogenation

Atactic 1,4-polybutadiene and syndiotactic 1,2-polybutadiene can be hydrogenated at 100°C and 50 bar pressure of hydrogen with a soluble catalyst $\{[(Ph)_3\text{-}P]_3RhCl\}$. Complete saturation of double bonds results [52]. Butadiene acrylonitrile copolymers can also be hydrogenated quantitatively with this rhodium catalyst under mild conditions [53]. The kinetics are consistent with a mechanism where the active Rh-catalyst interacts with the unsaturation at the polymer in the rate-determining step. The nitrile group, however, appears to also interact with the catalyst and inhibit the rates [53].

Hydrogenation of carbon-to-nitrogen double bonds in polymer backbones and in the pendant groups can be carried out with lithium borohydride [86]:

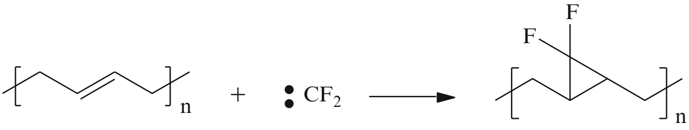


It was reported [485] that syndiotactic polystyrene can be hydrogenated over Ni/SiO_2 and Pd/$BaSO_4$ catalysts. The Ni catalyst yields complete hydrogenenation when low molecular weight polymer is used. Hydrogenation of high molecular weight polystyrene, however, is incomplete. On the other hand, the Pd catalyst yields completely hydrogenating material. The hydrogenated syndiotactic polystyrene is a crystalline material with good heat resistance [485].

9.2.3 Addition of Carbenes

Polyisoprenes and polybutadienes can also be modified by reactions with carbenes. Dichlorocarbene adds to natural rubber dissolved in chloroform in a phase transfer reaction with aqueous NaOH [54]. A phase transfer reagent must be used with the aqueous NaOH. Solid sodium hydroxide can be used without a phase transfer reagent. There is no evidence of *cis–trans* isomerization and the distribution of the substituents is random [54].

Difluorocarbene, generated under mild neutral conditions, adds to 1,4-*cis*- and 1,4-*trans*-polybutadienes to give materials containing cyclopropane groups [55]. The addition takes place randomly, to give atactic stereo sequence distributions [55]:

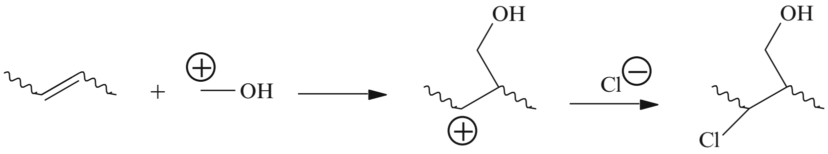


Fluorocarbene, formed from phenyl(fluoro,dichloromethyl)mercury by thermolysis in situ, also adds to 1,4 *cis*- and *trans*-polybutadienes. The carbene can add at various levels [57]. The addition is stereospecific and preserves the alkene geometry of the parent polybutadiene. Also, the addition is random, showing that the reactivity of the double bonds is independent of the sequence environment [57].

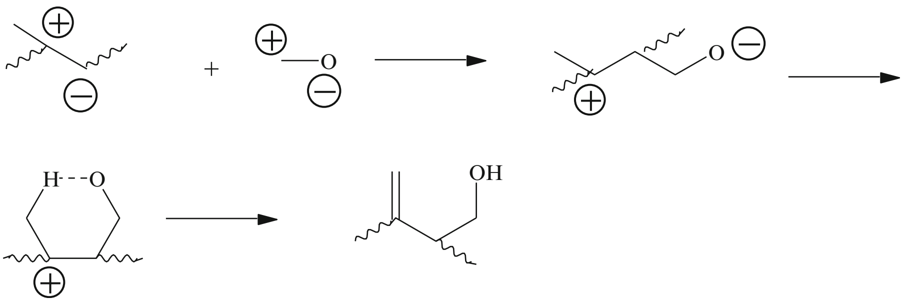
Dichlorocarbene, generated in situ from an organomercury precursor, phenyl(bromo, dichloromethyl)mercury (Seyferth reagent), adds to polybutadiene in a similar manner [56]. The reactions take place under homogeneous conditions. They can be carried out on 1% solutions of the polymer in benzene, using 10–20% mol excess of the reagent.

9.2.4 *Electrophilic Additions of Aldehydes*

These are additions to double bonds, like the *Prins reaction*, and they can be carried out on natural and synthetic rubbers [59, 60]. They take place rapidly in the presence of acid catalysts. Aqueous formaldehyde [61], or paraform in CCl_4 [62], can be used. The catalysts are inorganic acids or anhydrous Lewis acids, like boron trifluoride in acetic acid solution [63]:

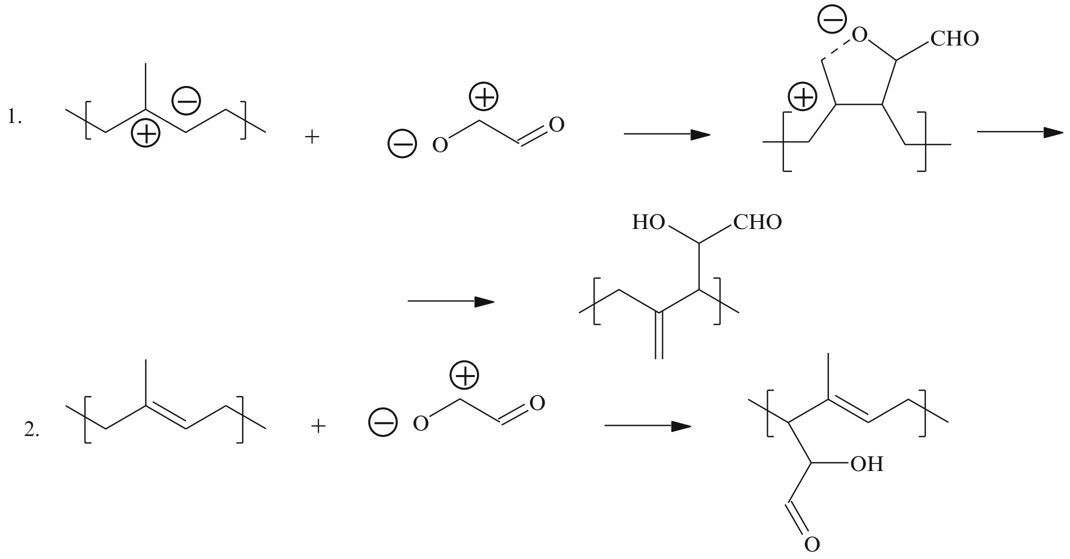


The reaction takes a different path in the absence of a catalyst [62]:



The products of the Prins reaction with rubbers are thermoplastic polymers that possess fair resistance to acids and bases. Free hydroxyl groups in the products are available for cross-linking with diisocyanates [64] or by other means. The Prins reaction can be carried out directly on rubber latexes [65]. It is also possible to just mill the rubber together with formaldehyde and then heat the resultant mixture in the presence of anhydrous metal chlorides [64] to get similar results [66].

Higher aldehydes also react with natural rubber [67]. The reaction works best with purified rubber. Additions take place without a catalyst at 180°C or in the presence of $AlCl_3$–NaCl at 120°C. These reactions can be carried out in the solid phase by milling the rubber with an aldehyde, like glyoxal [68]. Heating in a pressure vessel at above 175°C is required to complete the reaction. Infra-red spectra of the products from reactions in solution show presence of ether, carbonyl, and hydroxyl groups [69]. Two types of additions appear to take place [69]:



Products from reactions of rubber with glyoxal have a strong tendency to become spontaneously insoluble. This is probably due to a presence of residual aldehyde groups, because a treatment of the product with 2,4-dinitrophenyl-hydrazine eliminates spontaneous gelation.

Chloral adds to polyisoprene similarly. The reaction is catalyzed by Lewis acids [70]. Both $AlCl_3$ and BF_3 are efficient catalysts. Less cross-linking is encountered with aluminum chloride. Infra-red spectra of the products shows presence of hydroxyl groups, chlorine atoms, and vinylidene unsaturation [70].

9.2.5 Polar Additions

A number of polar additions to unsaturated polymers are known. These include Michael addition, hydroboration, 1,3-dipolar additions, ene reaction, the Ritter reaction, Diels–Alder additions, and others.

9.2.5.1 Michael Addition

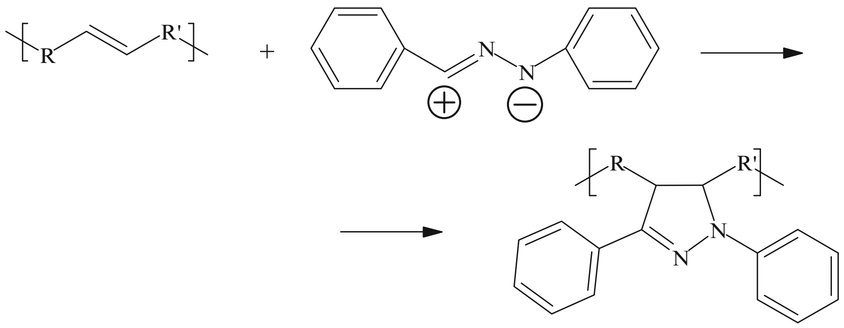
Among polar additions to unsaturated polymers are reactions of amines and ammonia with unsaturated polyesters in a form of a Michael condensation. Thus, for instance, additions to poly(1,6-hexanediol maleate) and poly(1,6-hexanediol fumarate) [71] show a difference in the reactivity of the two isomers. The maleate polyester reacts with ammonia to yield a cross-linked product at room temperature, when stoichiometric quantities or excess ammonia in alcohol is used. At the same reaction conditions, the fumarate isomer only adds a few percent of ammonia [71]. In a 1:1 mixture of chloroform and ethanol, however, approximately half of the fumarate double bonds react. Also, the maleate polyester reacts differently with piperidine or cyclohexylamine. In butyl alcohol at 60°C, the polymer initially isomerizes and precipitates. After the isomerization is complete and the temperature is raised to 80°C, the polymer redissolves. An exothermic reaction follows and Michael type adducts form [71].

9.2.5.2 Hydroboration

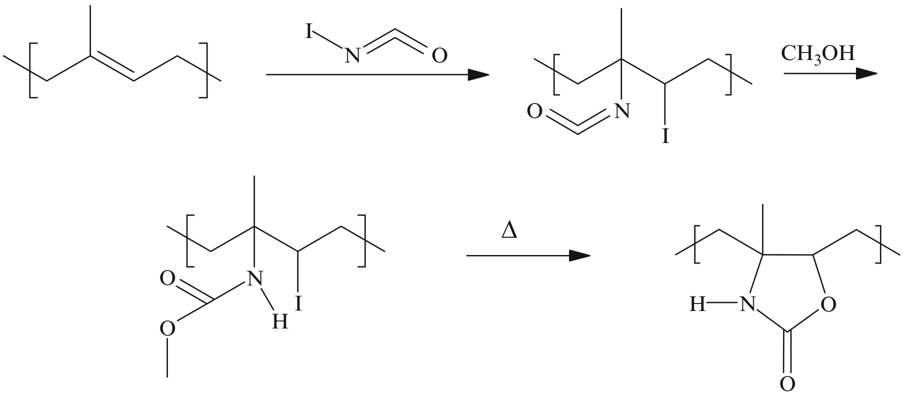
Polymers and copolymers of butadiene or isoprene with styrene can react with diborane [72]. A suitable solvent for this reaction is tetrahydrofuran. Subsequent hydrolyses result in introductions of hydroxyl groups into the polymer backbones. The reactions with diborane are very rapid. Some side reactions, however, also occur [72].

9.2.5.3 1,3-Dipolar Additions

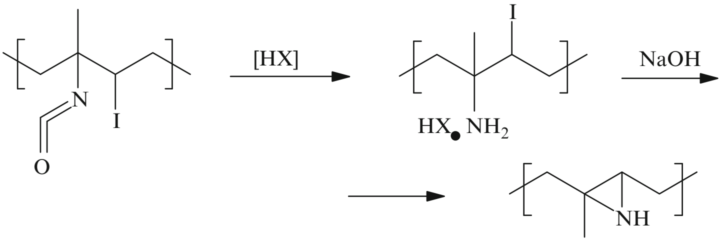
Cyclic structures form on polymer backbones through 1,3-dipolar additions to carbon to carbon or carbon to nitrogen double bonds [73]. Because many 1,3-dipoles are heteroatoms, such additions can lead to formations of five-membered heterocyclic rings. An example is addition of nitrilimine to an unsaturated polyesters [73]:



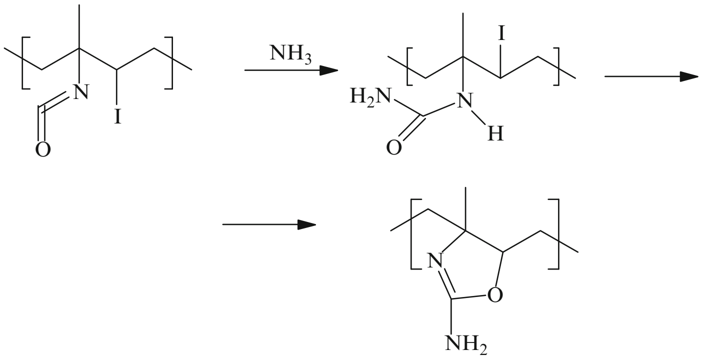
Also, iodine isocyanate adds to polyisoprene. The product can be converted to methyliodocarbamate or to iodourea derivatives [74]:



Iodine isocyanate additions result in approximately 40% yields. The products can undergo typical reactions of the isocyanate group [74], as for instance:

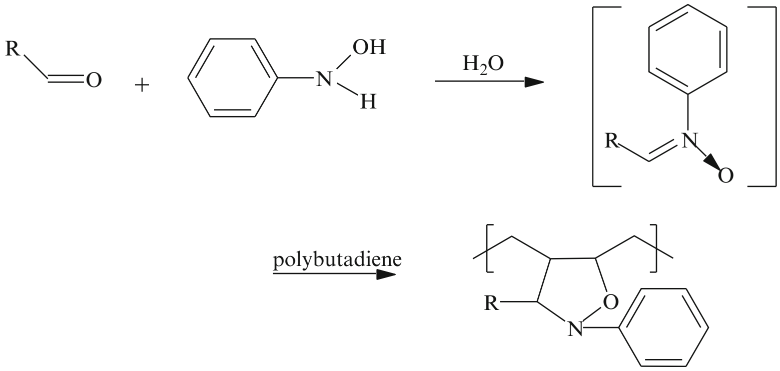


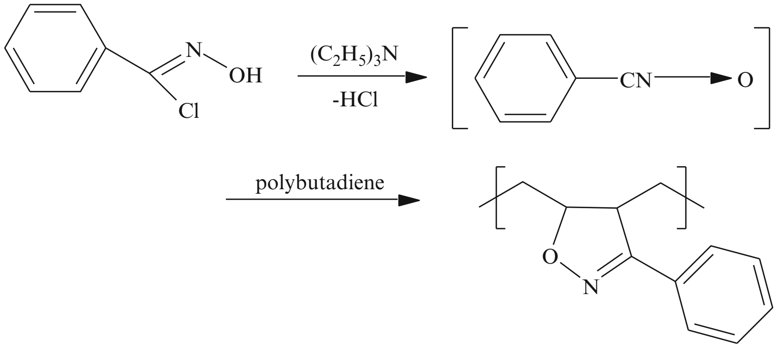
as well as:



where HX is a halogen acid. The products exhibit enhanced heat stability [74].

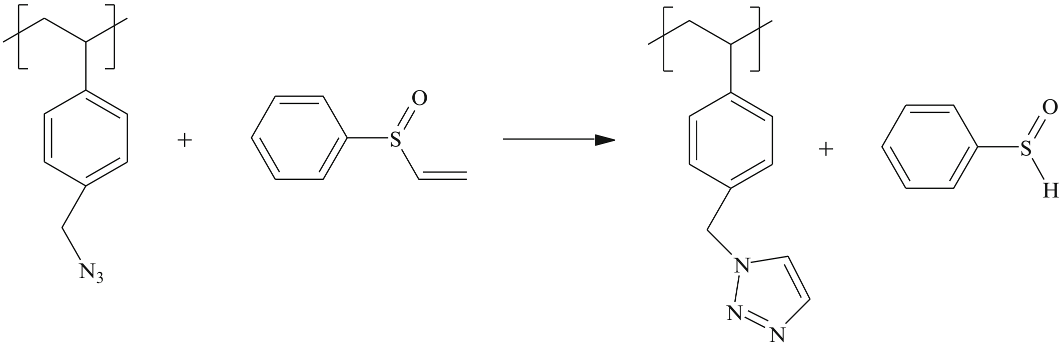
Dipolar cycloadditions take place when nitrones or nitrile oxides add to butadiene rubber. Some of the products contain isoxazolidine rings [75]:





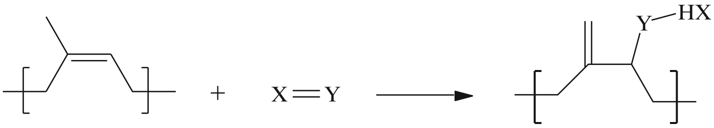
The above modification of butadiene rubber can be carried out to the extent of 3.1 mol.%. The product is higher in tensile modulus values and is greater in strength than the parent compound [75].

A final example is a 1,3 dipolar addition to pendant azide groups [87]. The reaction takes place with phenyl vinyl sulfoxide in dimethylformamide. Forty-eight hours at 110°C are required for the azide groups to become undetectable by infra-red spectroscopy. The product precipitates out with addition of ether [87]:

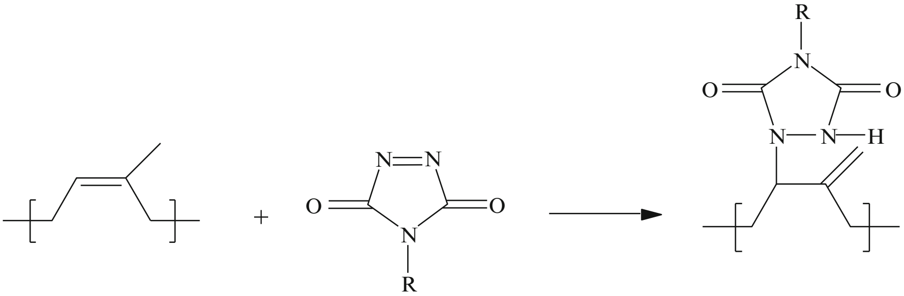


9.2.5.4 The Ene Reaction

The polymers of conjugated dienes can also be modified via the ene reactions [76], as for instance:

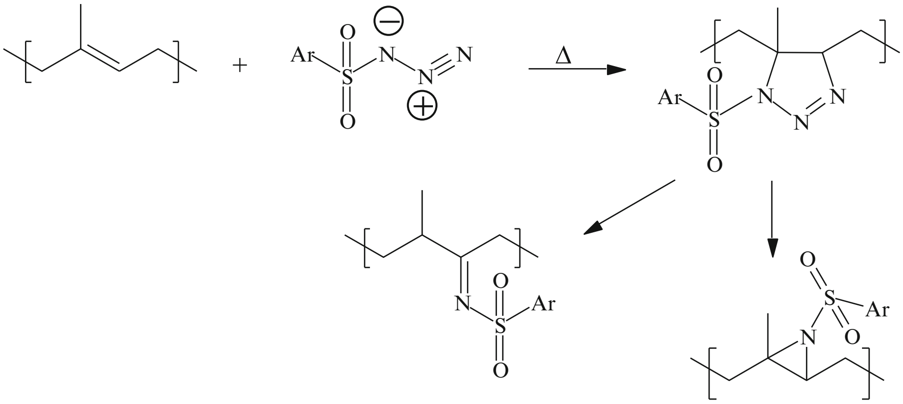


where, X=Y can be O=N–, –N=N–, >C=S, >C=O, or>C=C<. An example of this is an addition of triazolidones [76]:

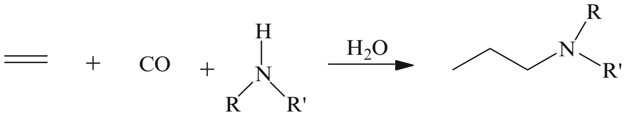


This results in formation of pendant urazole groups. The exact structure of the products, however, has not been fully established. The tensile strength of polymers improves considerably, but it is accompanied by a dramatic loss in molecular weight [76]. Nevertheless, ene reagents like C-nitroso and activated azo compounds are very efficient in adding to rubber. They add in a few minutes at temperatures between 100 and 140°C. In the case of the azo compound, the addition can be greater than 90%.

Substituted aryl sulfonyl azides decompose at elevated temperatures to nitrenes and add to natural rubber:

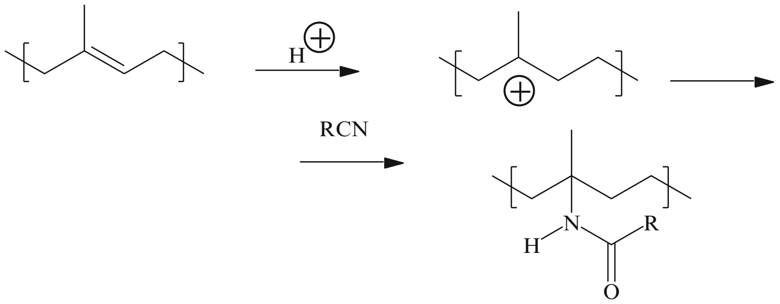


Novel types of polyamines and cationic polyelectrolytes form from polymers of conjugated dienes [77] in reactions with carbon monoxide, amines, and water at 150°C and 1,000–1,500 psi pressure. The reaction can be illustrated as follows [77]:



9.2.5.5 The Ritter Reaction

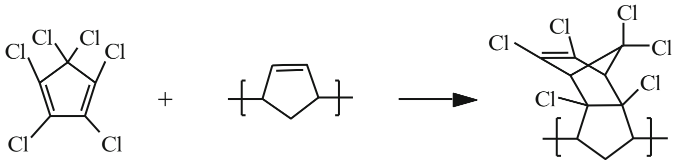
This reaction can be carried out on natural rubber and on synthetic polyisoprenes [78]:



The carbon cation, apparently, reacts with any nucleophile present. When the reaction is carried out in dichloroacetic acid, chlorine atoms can be detected in the product [78].

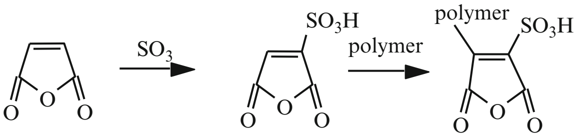
9.2.5.6 Diels–Alder Condensations

Crotonic acid esters of cellulose undergo addition reaction with cycloaliphatic amines, like morpholine or piperidine and with aliphatic primary amines [79]. Unsaturated polymers can also undergo Diels–Alder reactions. One example is a reaction of hexachlorocyclopentadiene with polycyclopentadiene [80]:



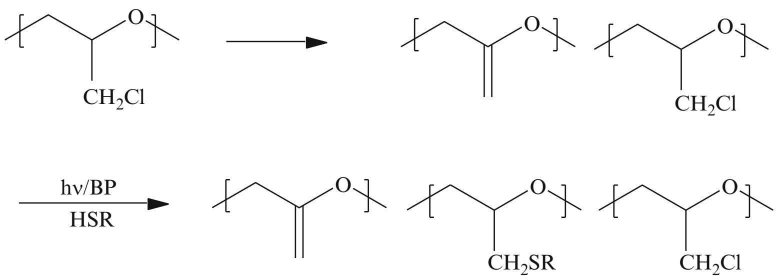
The addition takes place in an inert atmosphere at 140–150°C. Over 90 mol.% conversion is achieved in 6 h.

Diels–Alder condensations of fumaric and maleic acids polyesters with various dienes [81] can serve as another example. These reactions require 20 h at room temperature. Diels–Alder condensations can also be carried out on polymers of 1,3,5 hexatriene, 1,3,5-heptatriene, and 2,4,6-octatriene [82]. Sulfonate-substituted maleic anhydride adds to low functionality hydrocarbon elastomers, like EPDM, presumably via an Alder-ene type reaction [83]:



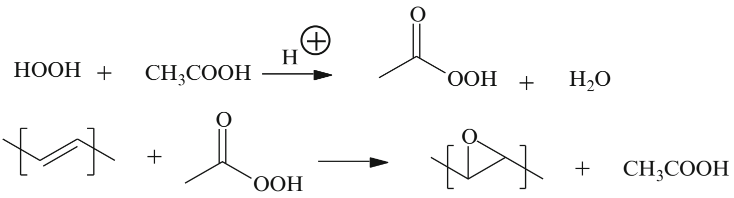
Thiols add to diene rubbers by a free-radical mechanism [84]. Thus, antioxidants, like 4-(mercaptoacetamido)-diphenylamine, add –SH groups to the double bonds of *cis*-polyisoprene and polybutadiene in the presence of free-radical initiators [84].

Thiol compounds also add photochemically to polymers containing double bonds. For instance, unsaturation can be introduced into polyepichlorohydrin by a partial elimination reaction. The product then reacts with mercaptans, aided by a photosensitizer (like benzophenone) and ultraviolet light [85]:

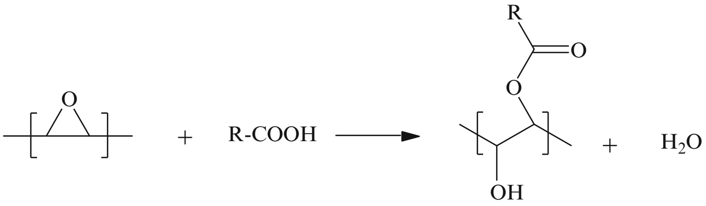


9.2.5.7 Epoxidation Reactions

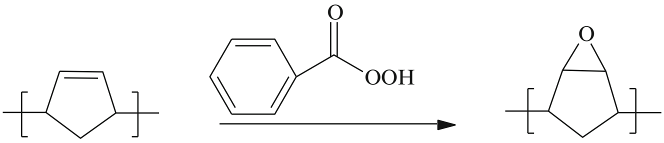
These addition reactions of unsaturated polymers, like liquid polybutadiene, developed into preparations of useful commercial materials [88–94]. Patent literature describes procedures that use hydrogen peroxide in the presence of organic acids or their heavy metal salts. Reaction conditions place a limitation on the molecular weights of the polymers, because it is easier to handle lower viscosity solutions. A modification of the procedures is to use peracetic acid in place of hydrogen peroxide [95–97]. The most efficient methods rely upon formations of organic peracids in situ with cationic exchange resins acting as catalysts [98]. This can be illustrated as follows:



The reaction is accompanied by formations of by-products:

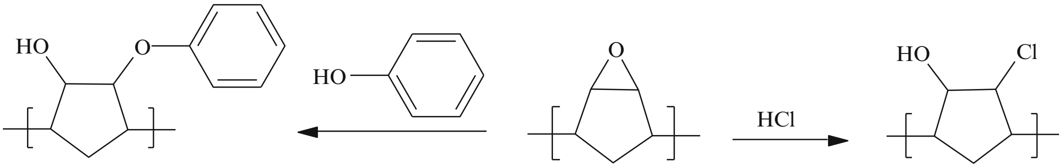


Polybutadienes that are high in 1,4-structures tend to epoxidize more readily and yield less viscous products [100, 101]. The epoxidation reaction can also be carried out on poly(1,4-cyclopentadiene) [99]:

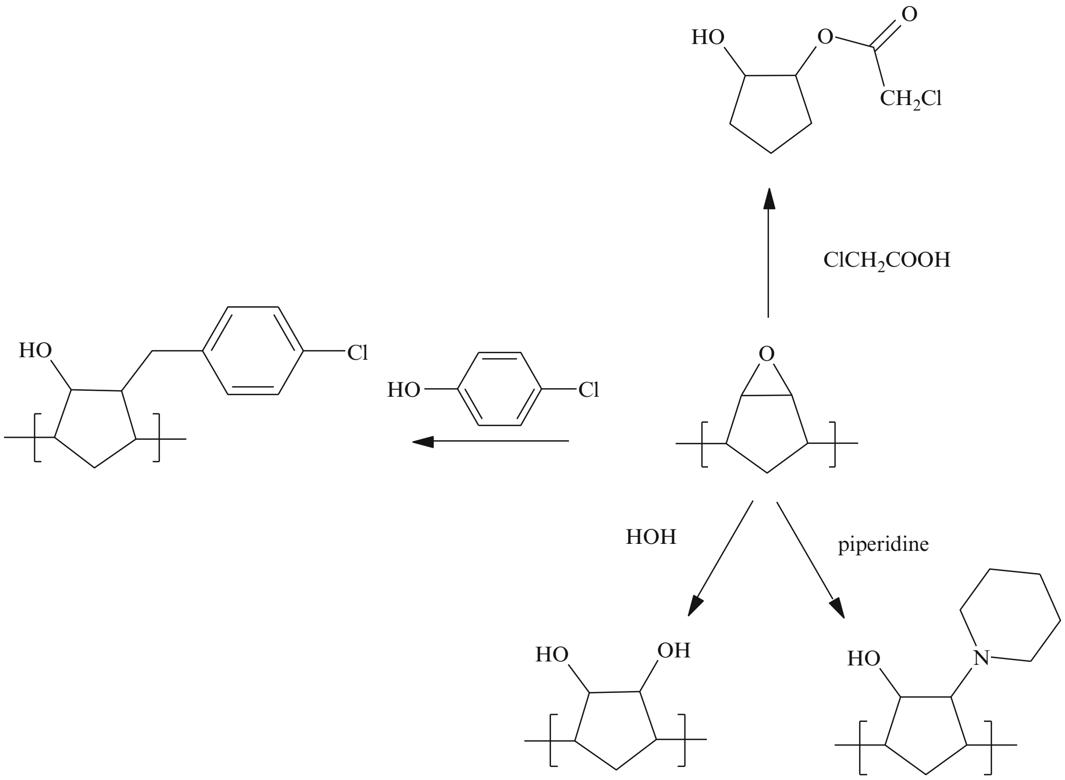


Perbenzoic acid is an effective reagent in chloroform and in methylene chloride solutions at 0–20°C. The conversions are high, yielding brittle materials soluble in many solvents. The products can be cast into transparent films [99].

Monoperphthalic and *p*-nitroperbenzoic acids are also efficient epoxidizing agents. They can, however, cause cross-linking, as is the case in epoxidation of polycyclopentadiene [99]. The products react like typical epoxy compounds [99]:



Some other reactions of the epoxy groups are [99]:

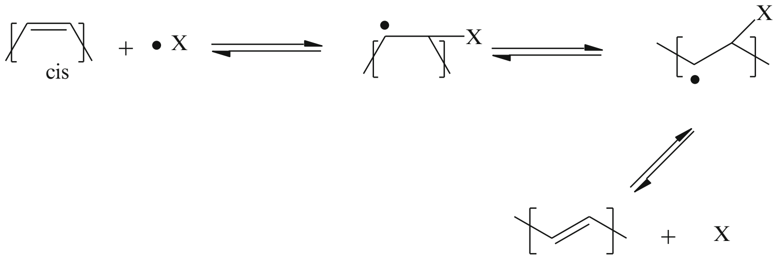


9.3 Rearrangement Reactions

There are different types of polymeric rearrangements. One of them is isomerizations of polymers with double bonds. Others can be intramolecular cyclizations in the polymeric backbone.

9.3.1 Isomerization Reactions

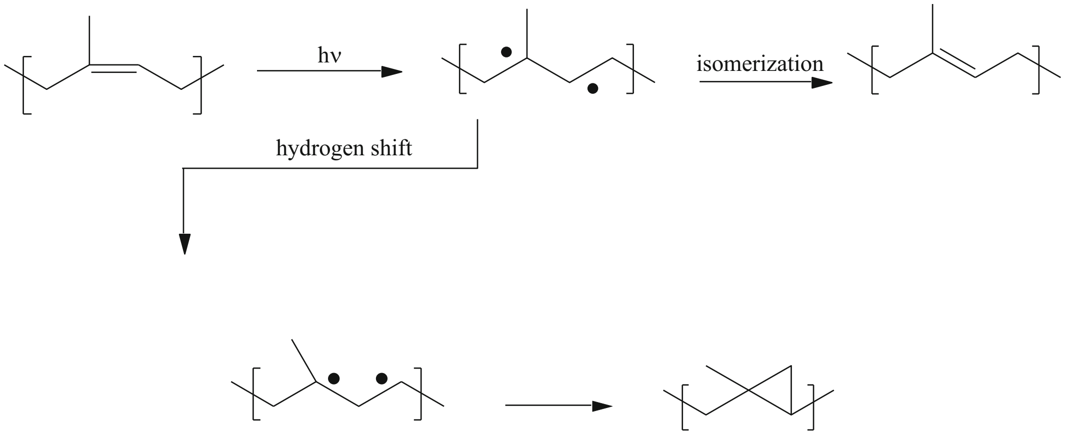
The isomerization of *cis*-polybutadiene can be carried out with the aid of ultraviolet light or with gamma radiation. When light is used, the free-radical reaction requires photoinitiators [102, 103]. The mechanism involves freely rotating transitory free-radicals on the polymer backbone. These form from additions of photoinitiator fragments to the double bonds. The adducts break up again, releasing the attached initiator fragments and reestablishing the double bonds. The new configurations are *trans* because they are more thermodynamically stable [102, 103]. This can be shown as follows:



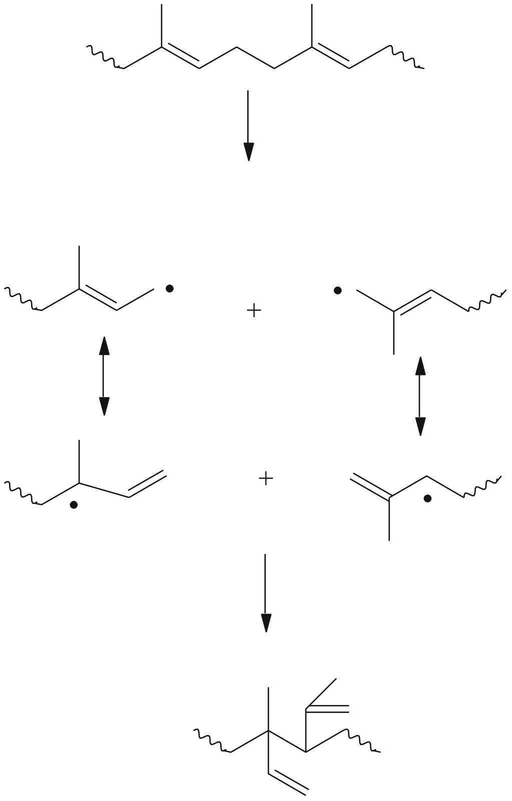
where, X• represents a free-radical fragment from a photoinitiator.

With gamma radiation, there is no need for any additives [104, 105]. Here, the mechanism of isomerization is believed to involve direct excitation of the π-electrons of the double bonds to antibonding orbitals where free and geometric interconversions are possible. In benzene solutions, energy transfers take place from excited benzene molecules to the polymer double bonds.

When 1,4-polyisoprene films are irradiated with light [122], *cis–trans* isomerizations occur. In the process, the quantities of 1,4-unsaturations decrease. Also, vinyl and vinylidene double bonds and cyclopropyl groups form. This can be illustrated as follows:



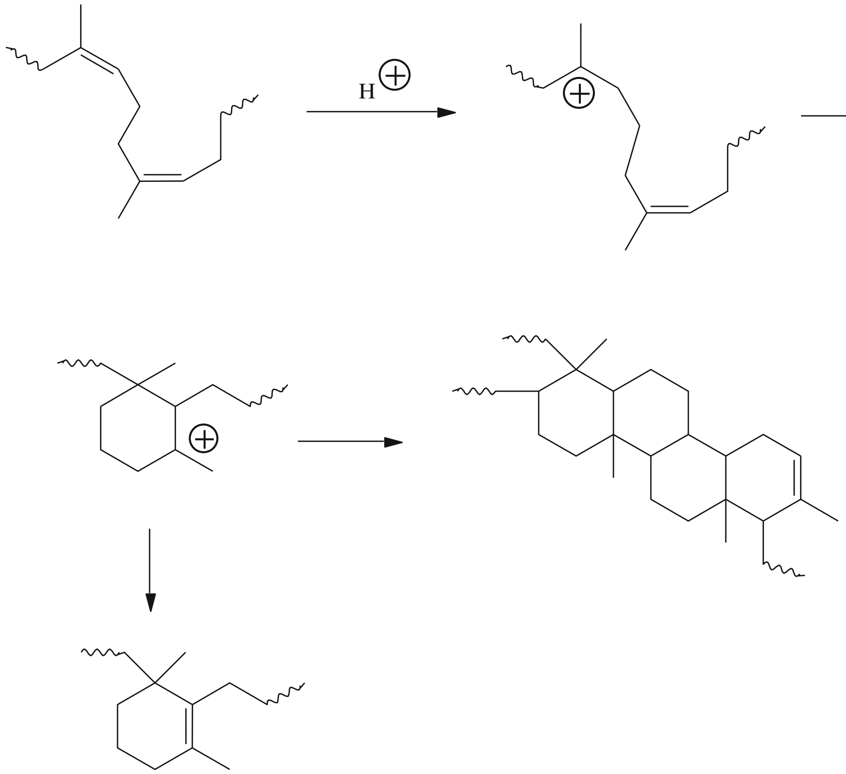
and



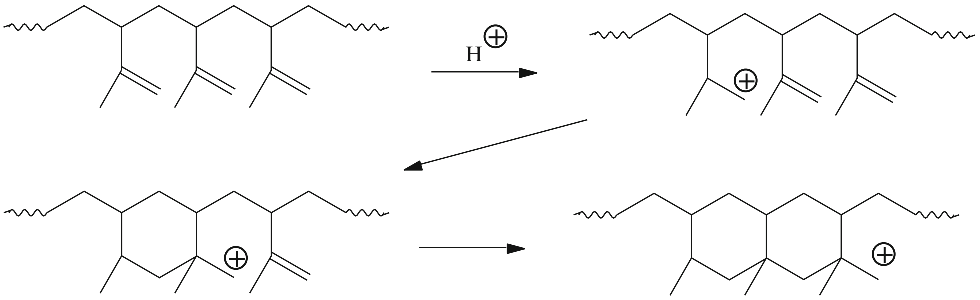
Polybutadiene can also isomerize *cis–trans* and lose unsaturation when irradiated in the solid state. This must be done in vacuum with ultraviolet light of 1,236 or 2,537 Å [106, 107]. Both free-radical and ionic mechanisms are suspected to operate simultaneously.

9.3.2 Cyclizations and Intramolecular Rearrangements

Cyclization reactions of natural rubber and other polymers from conjugated dienes have been known for a long time. The reactions occur in the presence of Lewis and strong protonic acids. They result in loss of elastomeric properties and some unsaturation. Carbon cations form in the intermediate step and subsequent formation of polycyclic structures [108, 109]:



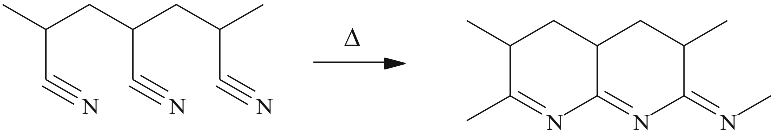
In a similar manner, polymers with pendant unsaturation undergo cyclization reactions in benzene in the presence of BF_3 or $POCl_3$, yielding ladder structures. The exact nature of the initiation process is not clear. Water may be needed for the initiation step [110, 111]:



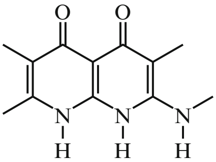
The reactions result in formations of six-membered monocyclic and fused polycyclic units. These reactions of carbon cations should also lead to molecular rearrangements, like 1,2 shifts of protons, resulting in formations of five-membered rings and spiro cyclopentane repeat units [111].

Cyclization reactions of polyisoprene can be catalyzed by $TiCl_4$ [112] and by sulfuric acid [113–115, 117]. The products appear similar in the infra-red spectra [110] with only a few minor differences. Also, there are only a small number of fused rings in the product.

Polyacrylonitrile converts to a red solid when heated above 200°C [116]. Only a small amount of volatile material is given off. Further heating of the red residue to about 350°C or higher converts it to a black brittle material. This black material has a ladder structure:

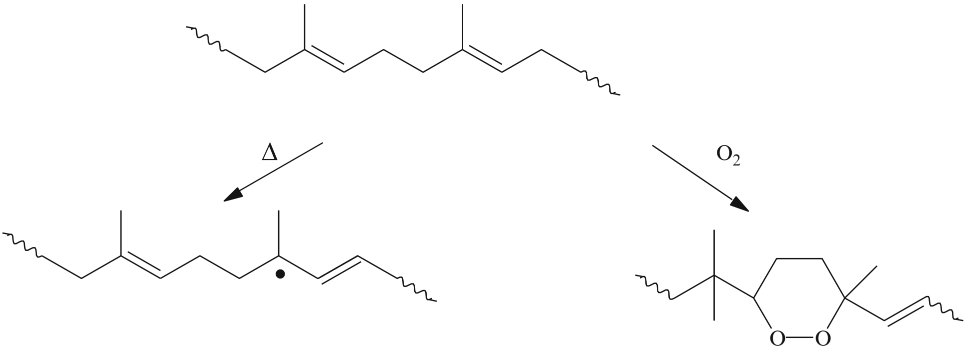


Heating of polyacrylonitrile in the presence of oxygen yields some quinone-type structures:

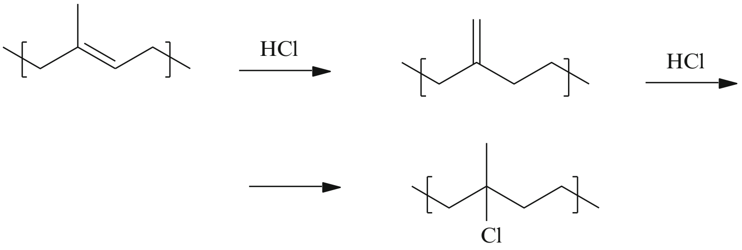


Further heating of the polymer, at very high temperatures, in excess of 2,000°C, results in formation of graphite-like structures [116]. All, or almost all nitrogen is lost, probably as HCN and N_2.

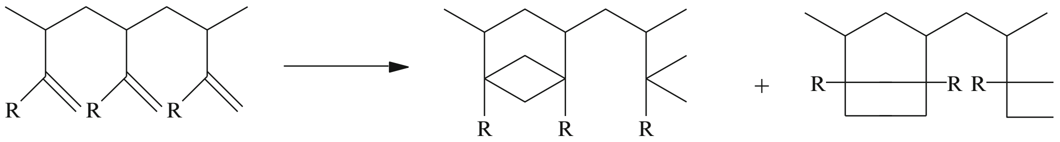
Migration of double bonds is a well-established phenomenon in polymers from conjugated dienes. It occurs, for instance, during vulcanization of rubber (discussed in a later section). It also occurs upon simply heating some polymers [117–119]. Thus, the double bonds shift in natural rubber when it is heated to temperatures of 150°C or above [120]:



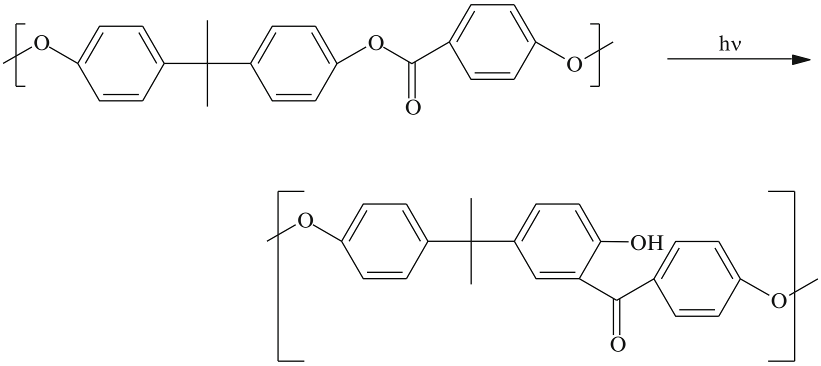
Hydro chlorination of rubber in solution causes a different kind of double bond shirt [121]:



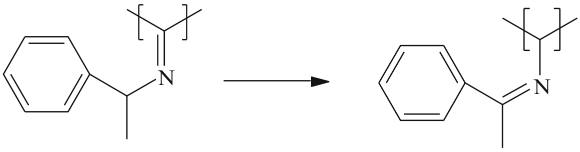
In polymers with pendant double bonds, facile cycloadditions occur upon heating [123–125]:



Many other polymeric structures can rearrange under proper conditions. For instance, poly(4,4′-diphenylpropane isophthalate) rearranges upon irradiation with UV light to a structure containing *o*-hydroxybenzophenones [126]:

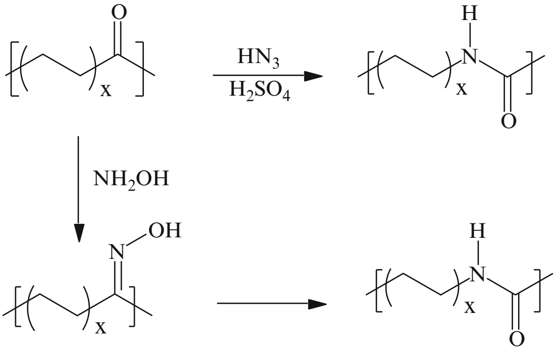


The mechanism is believed to be that of a photo-induced *Fries rearrangement*. It may be similar to one catalyzed by Lewis acids. Another example is a spontaneous rearrangement in the solid state of poly(α-phenylethylisonitrile) [128]:



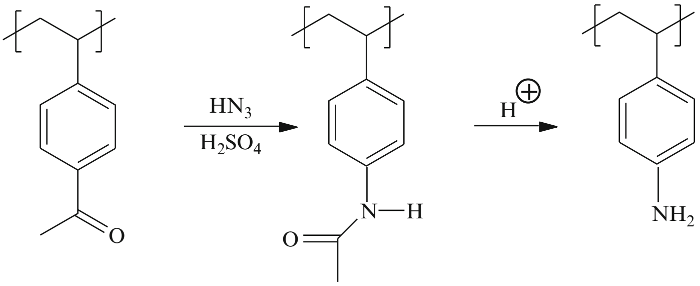
Based on studies of molecular models, it was concluded [128] that the substituents force progressive, one-handed twisting of the helix shape of the molecules. This occurs to such an extent that the vicinal imino double bonds are out of conjunction with each other. As a result, each benzylic hydrogen atom becomes localized over the electrons of the imino groups. It proceeds in a constant screw direction around the axis of the helix. Such steric confinement causes tautomeric rearrangements, as shown above, which results in some relaxation of the compression. An additional driving force is a gain in conjugation between the imino double bonds and the aromatic rings of each substituent.

Intramolecular rearrangements of polymers with ketone groups were subjects of several studies. The *Schmidt* and *Beckmann rearrangements* were carried out on copolymers of ethylene and carbon monoxide [129]:

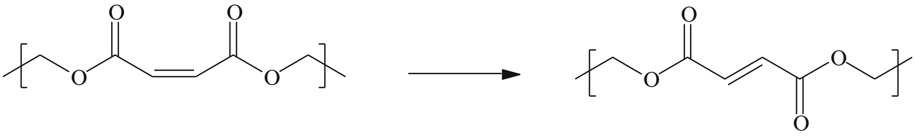


The starting materials were low and medium molecular weight copolymers. Infra-red spectra of the products from the Schmidt reaction show a high degree of conversion [129]. The yields of the oximes and subsequent Beckmann rearrangements are also high.

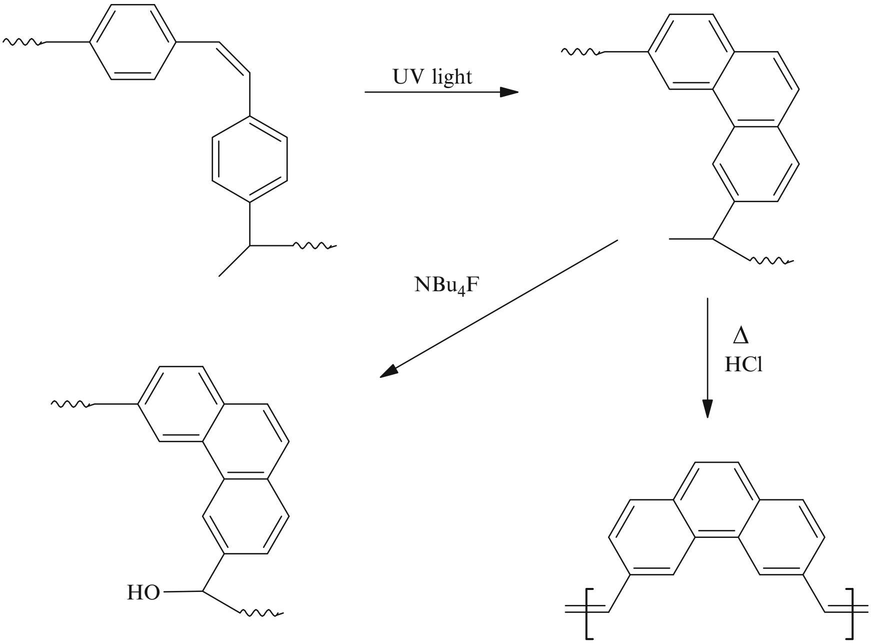
A Schmidt reaction on poly(*p*-acetyl styrene) yields a product containing acetyl amino styrene groups in high yields and the products are surprisingly pure [130]. The solvent is acetic acid and the converted material precipitates out as a sticky mass:



Another rearrangement reaction is isomerization of unsaturated polyesters upon heating. Thus, for instance, maleate polyesters rearrange to the fumarate analogs at elevated temperatures [131]:



It was reported that polymers with *cis*-stilbene moieties in the backbone can undergo photocylization that is almost quantitative [473]:



9.4 Substitution Reactions

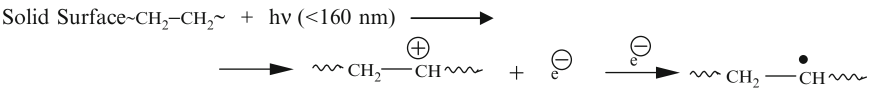
Many substitution reactions are carried out on polymers in order to replace atoms in the backbones or in the pendant groups with other atoms or groups of atoms. These reactions do not differ much from those of the small molecules.

9.4.1 Substitution Reactions of Saturated Polymeric Hydrocarbons

It is often desirable to replace hydrogens with halogens. *Fluorination of polyethylene* can be carried out in the dark by simply exposing the polymer, either in sheet or in powder form, to fluorine gas. The reaction is exothermic and it is best to dilute the gas with nitrogen 9:1 to allow a gradual introduction of the fluorine and avoid destruction of the polymer [132, 133]. In this manner, however, only the surface layers are fluorinated and the substitutions occur only a few molecular layers deep.

In surface fluorination with vacuum ultraviolet glow discharge plasma, the photon component of the plasma enhances the reactivity of the polymer surfaces toward fluorine gas [134]:

$$\text{Gas phase}: F_2 + h\nu(210\text{–}360\,\text{nm}) \rightarrow 2F^{\bullet}$$



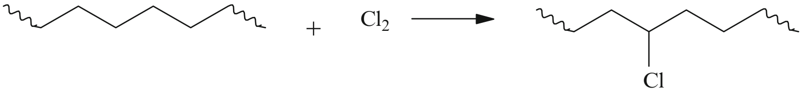
The surface free-radicals can also cause elimination of hydrogen radicals and formation of double bonds. Whether as free-radicals or through unsaturation, the units are now more reactive toward fluorine.

A film that is 3 mil thick can be completely fluorinated on a 100-mesh phosphor bronze gauze, if the reaction is allowed to proceed for several days [135]. Fluorination can also be carried out with mercuric or cupric fluorides in hydrofluoric acid. The reaction must be carried out at 110°C for 50 h. As much as 20% of fluorine can be introduced [136].

In direct fluorination of powdered high-density polyethylene with the gas, diluted with helium or nitrogen, the accompanying exotherm causes partial fusion. In addition, there is some destruction of the crystalline regions [137]. On the other hand, fluorination of single crystals of polyethylene can result in fluorine atoms being placed on the carbon skeleton without disruption of the crystal structure. The extent of cross-linking, however, is hard to assess [138]. The reaction has all the characteristics of free-radical mechanism [139]:

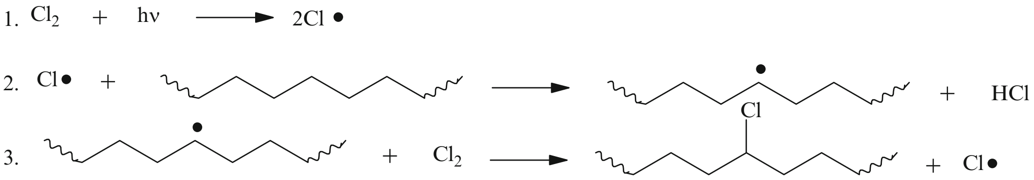
$$F_2 \rightarrow 2F^{\bullet}$$
$$\text{RH} + F^{\bullet} \rightarrow \text{R}^{\bullet} + \text{HF}$$
$$\text{R}^{\bullet} + F_2 \rightarrow \text{RF} + F^{\bullet}$$

Chlorinations of polyethylene can be carried out in the dark or in the presence of light. The two reactions, however, are different, though both take place by free-radical mechanism. When carried out in the dark at 100°C or higher, no catalyst is needed, probably because there are residual peroxides from oxidation of the starting material. Oxygen must be excluded because it inhibits the reaction and degrades the product [140]. The reaction is catalyzed by traces of $TiCl_4$ [141]. Such trace quantities can even be residual titanium halide from a Ziegler-Natta catalyst left over in the polymer from the polymerization reaction. When it is carried out at 50°C in chlorobenzene, –CHCl– groups form [142]:



This slows the chlorination of adjacent groups.

Trace amounts of oxygen catalyze chlorinations in the presence of visible light [140]. The same reaction in ultraviolet light is accompanied by cross-linking. The photochemical process can be illustrated as follows:



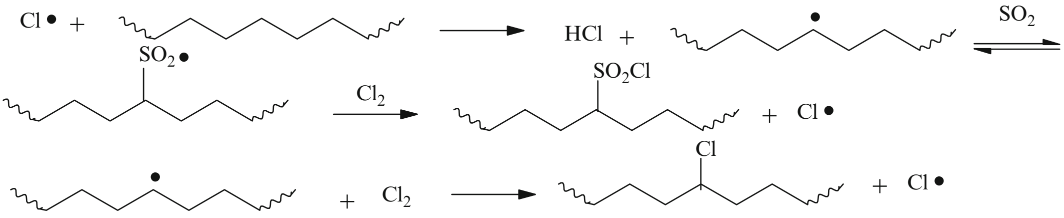
etc.

Chlorination of polyethylene can result in varying amounts of hydrogen atoms being replaced by chlorine. It is possible to form a product that contains 70% by weight of chlorine. The amount of chlorination affects the properties of the product. At low levels of substitution, the material still resembles the parent compound. When, however, the level of chlorine reaches 30–40%, the material becomes an elastomer. At levels exceeding 40%, the polymer stiffens again and becomes hard.

Commercial chlorinations of polyethylene are usually conducted on high-density ($D > 0.96$) linear polymers. The molecular weights of the starting materials vary. High molecular weight polymers form tough elastomers. Low molecular weight materials, however, allow easier processing of the products. The reactions are carried out in carbon tetrachloride, methylene dichloride, or chloroform at reflux temperatures of the solvents and at pressures above atmospheric to overcome poor solubility. The solubility improves with the degree of chlorination. Industrially, two different procedures are used. In the first one, the reactions are conducted at 95–130°C. When the chlorinations reach a level of about 15%, the polymers become soluble and the temperatures are lowered considerably [143]. In the second one, the reactions are conducted on polymers suspended in the solvent. When the chlorine content reaches 40% and the polymers become soluble, chlorinations are continued in solution. By continuing the reaction, a chlorine content of 60% can be reached. The products from the two processes differ. The first one yields a homogeneous product with the chlorine atoms distributed uniformly throughout the molecules. Chlorination in suspension, on the other hand, yields heterogeneous materials with only segments of the polymeric molecules chlorinated. Some commercial chlorinations are conducted in water suspensions. These reactions are carried out at 65°C until approximately 40% levels of chlorine are achieved. The temperatures are then raised to 75°C to drive the conversions further. In such procedures, agglomerations of the particles can be a problem. To overcome that, water is usually saturated with HCl or $CaCl_2$ [144]. Problems with agglomeration are also encountered during suspension chlorinations in solvents, like CCl_4. Infra-red spectra of chlorinated polyethylenes show presence of various forms of substitutions. There are –CHCl–CHCl– as well as –CCl_2– groups present in the materials [145, 146]. Surface photo chlorination of polyolefin films [146] considerably improves the barrier properties of the films to permeations of gases.

Chlorinations of polypropylene usually result in severe degradations of the polymer. When $TiCl_4$ is the chlorination catalyst, presumably, less degradation occurs [140]. Studies of *bromination of polypropylene* (atactic) show that when the reaction is carried out in the dark, in CCl_4 at 60°C, the substitution reactions proceed at the rate of 0.5%/h [147].

Chlorosulfonation or polyethylene is a commercial process. The reaction resembles chlorination in the step of hydrogen abstraction by chlorine radicals. It is catalyzed by pyridine [148–150] and can be pictured as follows [147]:



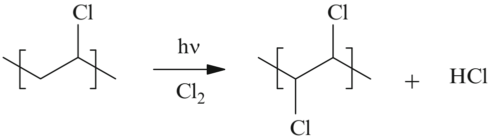
The amount of SO_2 vs. chlorine in the reaction mixture affects the resultant ratios of chlorosulfonation vs. chlorination of the polymer. These ratios and the amounts of conversion vary with the temperature [149].

Commercially produced chlorosulfonated polyethylene contains approximately 26–29% chlorine and 1.2–1.7% sulfur [151]. The material is an elastomer that remains flexible below −50°C. It is commonly cross-linked (vulcanized) through the sulfonyl chloride groups. Heating it, either as a solid or in solution, to 150°C results in loss of SO_2 and HCl. If the material is heated for 2 h at 175°C, all SO_2Cl groups are removed. In gamma radiation-induced chlorosulfonations and sulfoxidations of polyethylene powders [153] at room temperature, the ratios of SO_2Cl groups to Cl groups decrease with increases in radiation.

Polypropylene can be chlorosulfonated to the extent of containing 6% chlorine and 1.4% sulfur without embrittlement. The reaction can be done in CCl_4 at 55°C. There is apparently less degradation than in a direct chlorination reaction [148, 152].

9.4.2 Substitution Reactions of Halogen-Bearing Polymers

Procedures for commercial *chlorinations of poly(vinyl chloride)* vary. Low temperature chlorinations are done on aqueous dispersions of the polymers that are reacted with chlorine gas in the presence of swelling agents, like chloroform. These are light catalyzed reactions, usually carried out at about 50°C. They result in substitutions of methylene hydrogens [158, 159].



Some breakdown of the polymers accompanies the reactions in suspension [154]. Irregularity in the structures and the release of HCl significantly contribute to this. It appears that the degradations are initiated by HCl that is released as a result of the chlorination. In the process, double bonds form. Immediately upon their formation, they become saturated with chlorines.

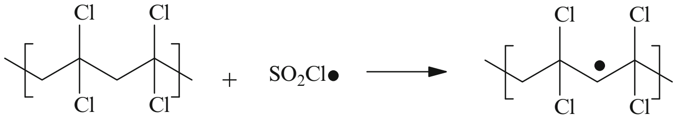
A study was conducted on solution chlorination of poly(vinyl chloride) in the presence of free radicals [155] generated from azobisisobutyronitrile. The reaction appears to proceed in two stages. The first one takes place until 60% of all the CH_2 groups have reacted. After that, in the second stage the original –CHCl groups are attacked. Some unreacted $–CH_2–$ groups, however, remain [155].

Photo chlorination can achieve 90% conversion [156, 157]. Typical commercially chlorinated poly (vinyl chloride), however, has a chlorine content of 66–67%. The material contains methylene groups and is in effect a copolymer of vinyl chloride and 1,2-dichloroethylene.

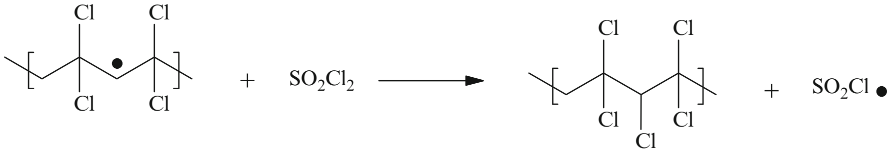
Chlorination raises the softening temperature of poly(vinyl chloride). The products exhibit poorer heat stability than the parent material and are higher in melt viscosity. High-temperature chlorinations in chlorinated solvents at 100°C result in extensive substitutions of the methylenic hydrogens as well. The reactions, however, are accompanied by extensive chain scissions. The products are soluble in solvents like acetone and methylene chloride and have low softening points, low impact strength, and poor color stability.

Chlorination of poly(vinylidene chloride) can be carried out with sulfuryl chloride using azobisisobutyronitrile [155]. The reaction appears to proceed in three steps:

1. Formation of SO_2Cl• free radicals by abstraction.
2. Formation of free radicals on the polymeric backbones:

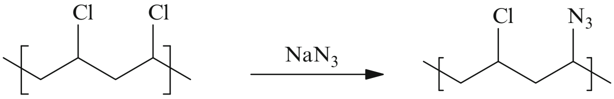


3. Transfer reactions of the active sites:

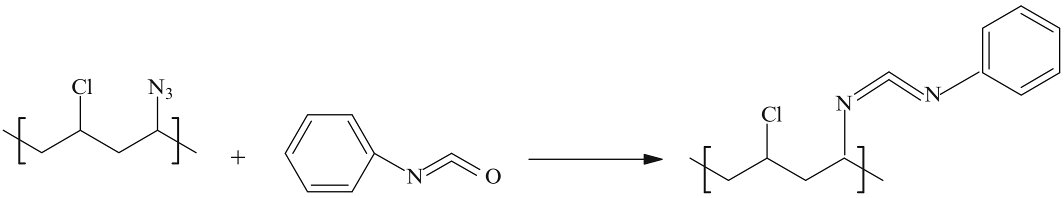


Chlorination of poly(vinyl fluoride) yields a product with 40–50% chlorine content [158]. *Fluorination* of poly(vinylidene fluoride) was reported [160]. When mixtures of fluorine and nitrogen gases are used, the reactions are limited by the amount of diffusion of fluorine into the polymer network. X-ray photoelectron spectroscopy shows presence of –CF_2–, –CHF–, and –CH_2– groups in the product [161].

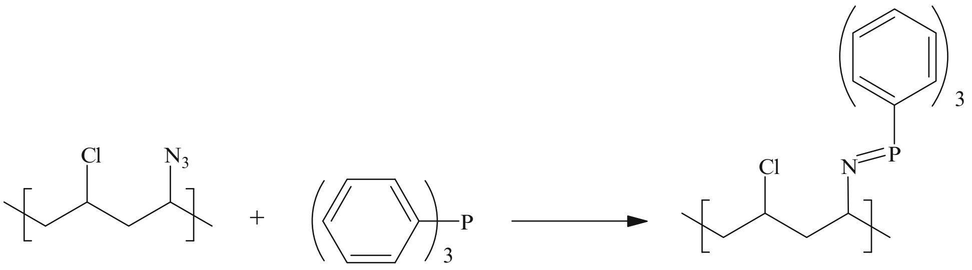
Many attempts at other modifications of poly(vinyl chloride) were reported in the literature. Often the reactions are based on expectations that the polymers will react like typical alkyl halides. Unfortunately, in place of nucleophilic substitutions, the polymers often undergo rapid and sequential eliminations of HCl along the chains. Nevertheless, many substitution reactions are still possible and can be successfully carried out. One example is a replacement of 43% of the chlorine atoms with azide groups [162]:



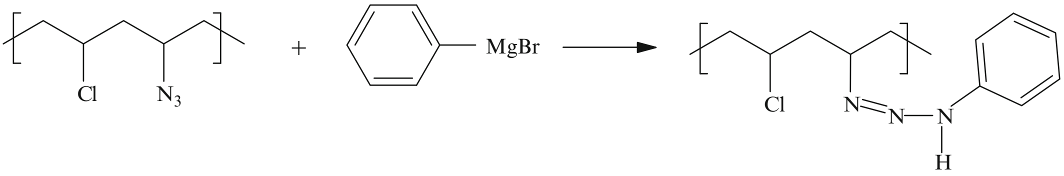
The reaction can be carried out at 60°C for 10 h and the polymer does not cross-link. It proceeds faster in DMF than in other solvents. Once substituted, the polymer becomes photosensitive and cross-links when irradiated with ultraviolet light. The presence of azide groups allows further modifications. One such modification is a reaction with an isocyanate [162]:

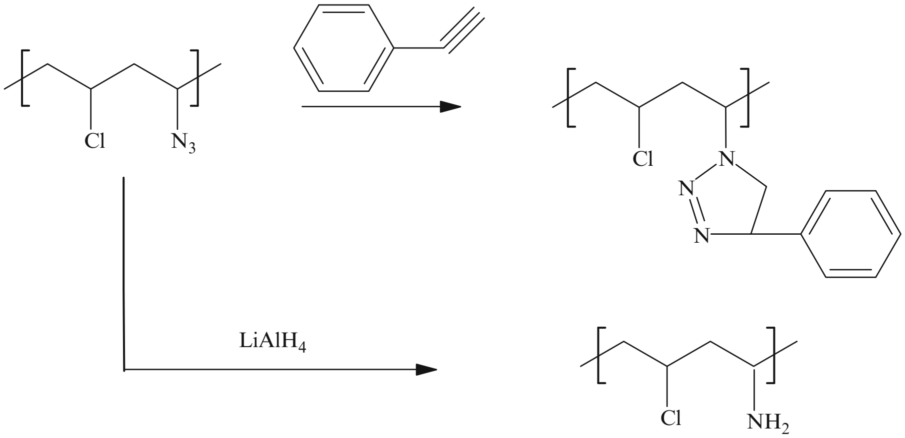


By a similar reaction, phosphinimine groups can be formed on the polymer backbone [162]:



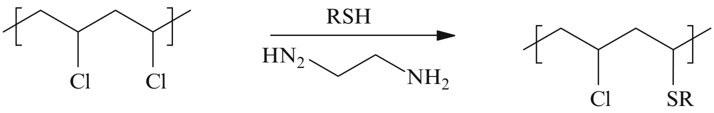
Some other modifications of the azide group containing polymers are [163, 164]:



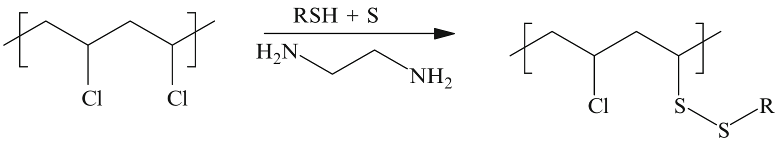


Note: The illustration of the reactions with $LiAlH_4$, as shown above, implies that all chloride atoms remain intact on the polymer backbones. It appears likely, however, that some of them might get removed and double bonds might form instead in the backbone.

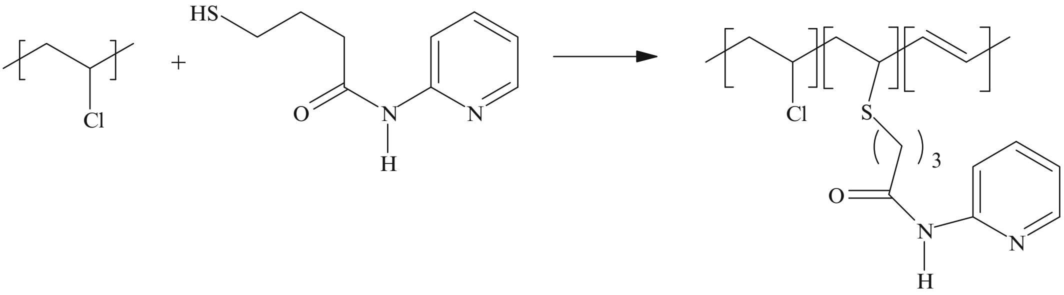
Poly(vinyl chloride) reacts with various thiols in ethylene diamine to produce monosulfide derivatives [165]:



When sulfur is added to the reaction mixture, disulfides form instead [165]:

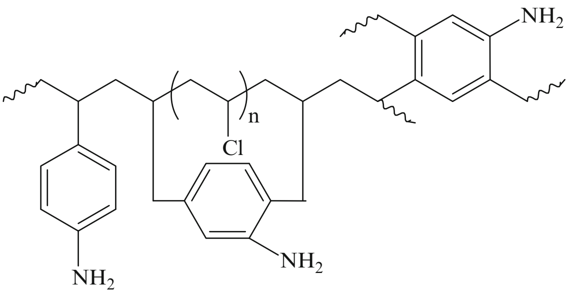


The thiolate ions can serve as strong nucleophiles and also as weak bases [166]. When poly(vinyl chloride) is suspended in water in the presence of swelling agents and phase transfer catalysts, it reacts with mercaptans, like 3-[*N*-(2-pyridyl)carbamoyl]-propylthiol:

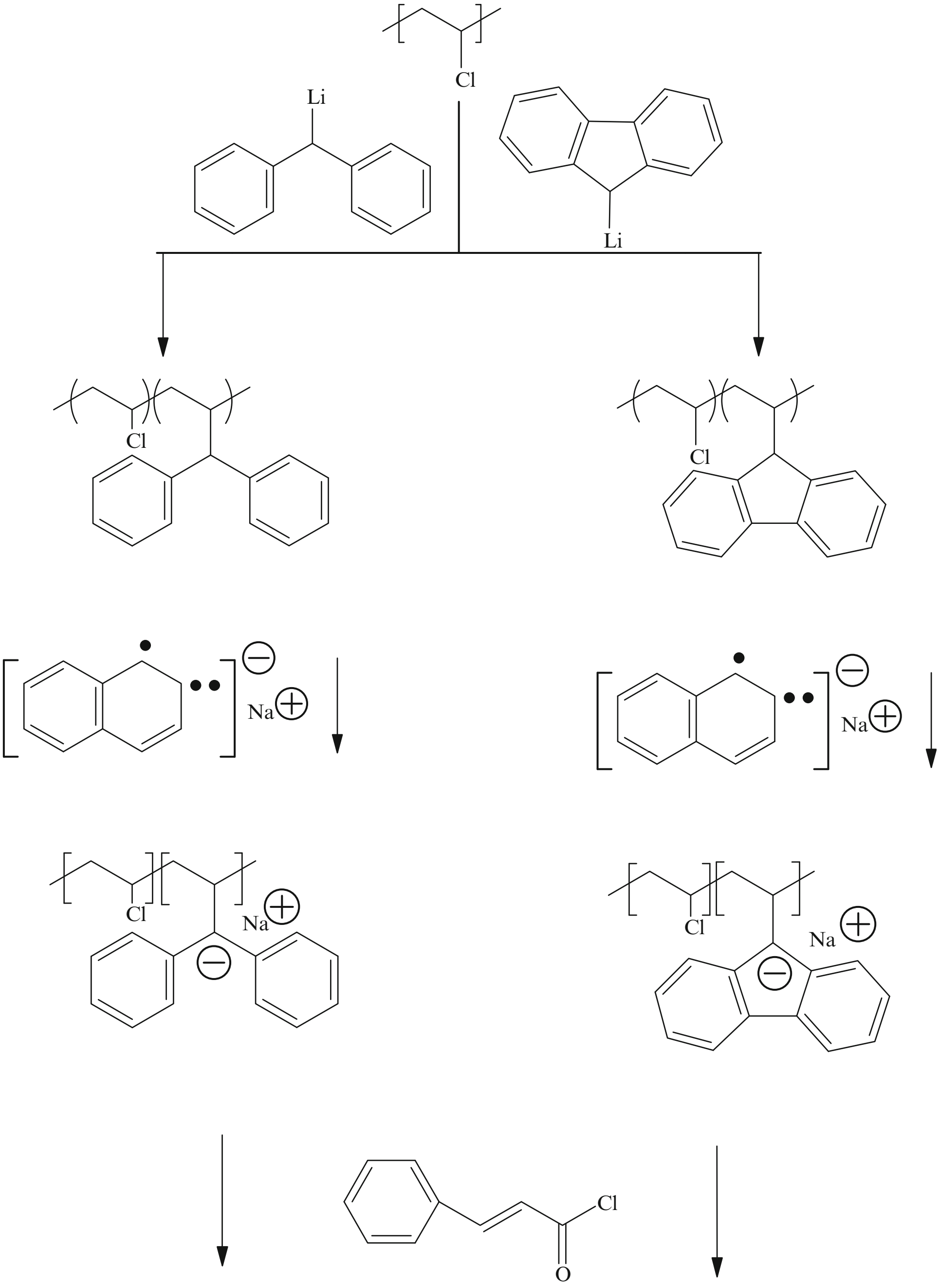


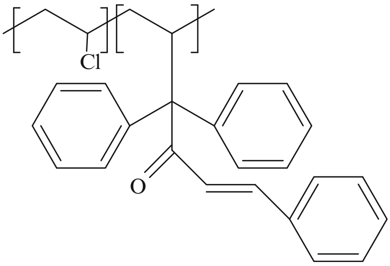
Acetoxylation of poly(vinyl chloride) can be carried out under homogeneous conditions [167]. Crown ethers, like 18-crown-6, solubilize potassium acetate in mixtures of benzene, tetrahydrofuran, and methyl alcohol to generate unsolvated, strongly nucleophilic "naked" acetate anions. These react readily with the polymer under mild conditions [167]. Substitutions of the chlorine atoms on the polymeric backbones by anionic species take place by S_N2 mechanism. The reactions can also proceed by S_N1 mechanism. That, however, requires formations of cationic centers on the backbones in the rate-determining step and substitutions are in competition with elimination reactions. It is conceivable that anionic species may (depending upon basicity) also facilitate elimination reactions without undergoing substitutions [167].

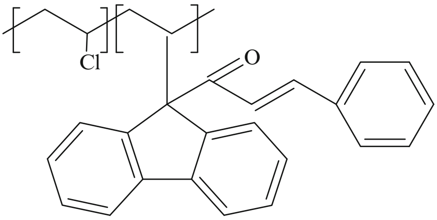
Reactions of poly(vinyl chloride) with aromatic amines, amino alcohols, or aliphatic amines in DMF solution result in both substitutions and in eliminations [168]. Reactions with aniline yield the following structure [168]:



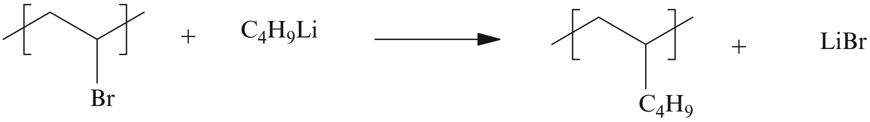
Carbanionic reaction sequences can be used to introduce various photosensitive groups [169]. The process consists of creating carbanionic centers on the backbone and then reacting them with various halogenated derivatives:



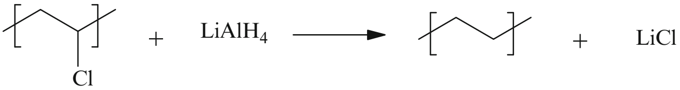




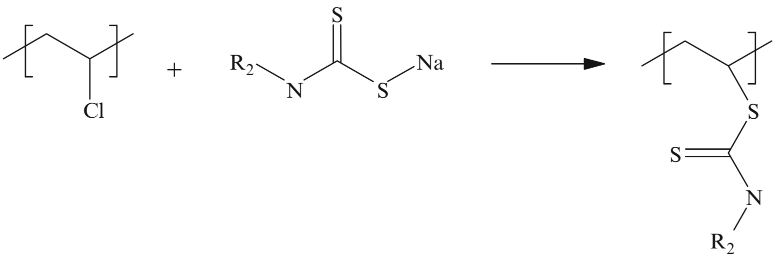
A redox cyclopentadienyl iron moiety can also be introduced into the poly(vinyl chloride) backbone by a similar technique [170]. Many other attempts were reported at replacing the halogens of poly(vinyl chloride), poly(vinyl bromide), and poly(vinyl iodide) with an alkali metal or with a hydrogen. For instance, in an effort to form poly(vinyl lithium), the polymers were reacted with organolithium compounds and with metallic lithium. The reactions with alkyllithium, however, resulted in substitutions by the alkyl groups, similarly to the reactions shown previously [171]:



Reactions with metallic lithium lead to formations of polyenes [171]. On the other hand, when poly(vinyl chloride) is reacted with metal hydrides, like lithium aluminum hydride in a mixture of tetrahydrofuran and decalin at 100°C, macroalkanes form [172]:



Replacement of the chlorine with *N*,*N*-dialkyl dithiocarbamate was reported to occur at 50–60°C in DMF solvent [173]:



The reaction is catalyzed with ethylene diamine [174].

9.4.3 Substitution Reactions of Polymers with Aromatic Rings

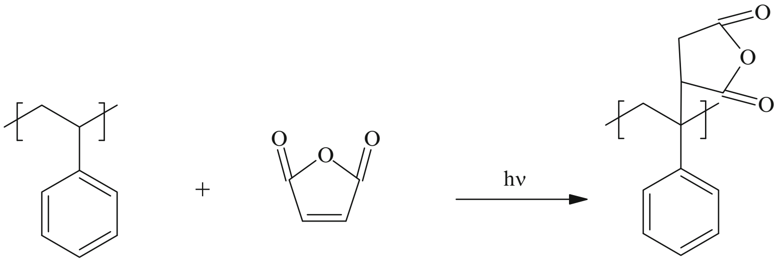
There are some interesting reports in the literature on reactions carried out on the backbones of polystyrenes. There are also many reports in the literature on aromatic substitution reactions of polystyrene. Only a few, however, are in industrial practice.

9.4.3.1 Reactions of Polystyrene

Photo chlorination of polystyrene involves replacement of hydrogens at the α and β positions [175, 176]. It was believed in the past that the chlorine atoms react preferentially at the α-position until the chlorine content of the product reaches 20% by weight. After that, it was thought that the chlorines are introduced into the other position. Later, however, this was contradicted [177]. In fact, when polystyrene is photo-chlorinated in carbon tetrachloride at low temperatures, like 13°C, it is substituted equally at both positions. At higher temperatures, like 78°C, substitutions at the β-position actually predominate [177].

Chlorinations of poly(*p*-methyl styrene) are somewhat more selective for the pendant methyl groups and result in di- and tri-substitutions at the *p*-methyl position. Only small amounts of chlorine are introduced into the polymer backbones [178]. Substitutions at the backbones, however, are possible with the use of SO_2Cl_2 as the chlorinating agent. In this case, half of the chlorines still replace the methyl hydrogens, but the other half replace hydrogens on the backbone.

Free radical additions of maleic anhydride to polystyrene backbones can be carried out with the help of either peroxides or ultraviolet light [164]. Approximately 2% of the anhydride can be introduced. If, however, the additions are carried out on α-brominated polystyrene, the anhydride content of the polymer can be raised to 15% [164]:



Note: the extra hydrogen shown above on the maleic anhydride moiety of the product presumably comes from chain transferring.

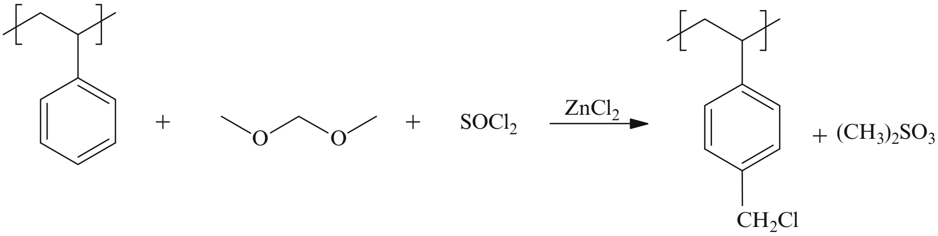
Bromination of polystyrene with *N*-bromosuccinimide and benzoyl peroxide in CCl_4 at room temperature can achieve a 61% conversion in 4 h. Considerable degradation, however, accompanies this reaction [180].

9.4.3.2 Chloromethylation Reactions

Chloromethylation reactions of the aromatic rings of polystyrene and styrene copolymers are being carried out extensively. Chlorodimethyl ether (a carcinogen) is a good solvent for these polymers. It is, therefore, commonly employed as the reagent [181, 182]. Laboratory preparations can be carried out in mixtures of carbon disulfide and ether, using zinc chloride as the catalyst. A 9-h reaction at room temperature yields 10% substitution [183]. The chloromethylation process [184] occurs in two steps. Benzyl methyl ether forms as an intermediate. Cross-linking reaction between the aromatic nuclei and the formed CH_2Cl group occurs as side reaction. There are strong indications that the chloromethylation takes place only at one position on the ring [185]. The same is true of bromomethylation [185].

Stannic chloride is a very effective catalyst for this Friedel-Craft reaction [186]. Iodomethylation can also be carried out in the same manner with similar results [179]. When the reactions are carried out on cross-linked styrene copolymers with chlorodimethyl ether and stannic chloride catalyst, they are accompanied by strong morphological changes [187]. If these reactions are carried out with low levels of chloromethylating agents or catalysts, they occur more or less homogeneously. Larger levels of either of them, however, result not only in greater levels of chloromethylation, but also in higher degrees of secondary cross-linkings and in uneven distributions of the chloromethyl groups [188].

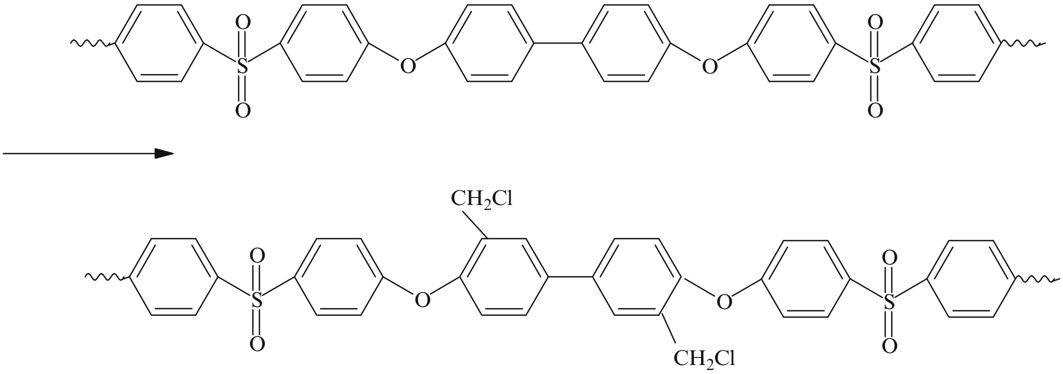
Another technique of chloromethylating polystyrene is to react it with methylal and thionyl chloride in the presence of zinc chloride [189]:



Chloromethyl-substituted polystyrenes can also be prepared from poly(*p*-methyl styrene)s by treating them with aqueous sodium hypochlorite in the presence of a phase transfer catalysts, like benzyltriethylammonium chloride [190]. The conversions of methyl to chloromethyl groups can be as high as 20% without any detectable morphological changes [187]. If these reactions are carried out with low levels of chloromethylating agents or catalysts, they occur more or less homogeneously. Larger levels of either of them, however, result not only in greater levels of chloromethylation, but also in higher degrees of secondary cross-linkings and in uneven distributions of the chloromethyl groups [188].

Another technique of chloromethylating polystyrene is to react it with methylal and thionyl chloride in the presence of zinc chloride [189].

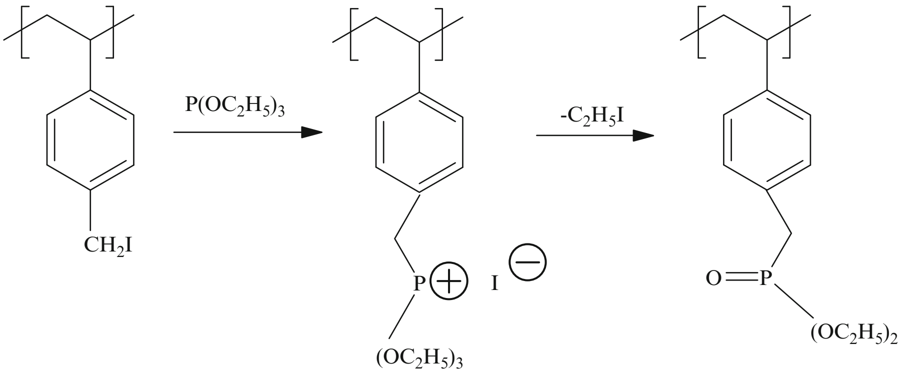
Techniques for chloromethylating polyarylether sulfones, polyphenylene oxide, phenolic resins, and model compounds were described recently [191]. When the subsequent products are converted to quaternary amines, there is a decrease in the quaternization rate with increase in degree of substitution. This may be due to steric effects imposed by restricted rotation of the polymeric chains [191]. This phenomenon was not observed in quaternization of poly(chloromethyl styrene). The chloromethylation reaction of a polysulfone with chloromethyl ether, catalyzed by stannic chloride, can be illustrated as follows:



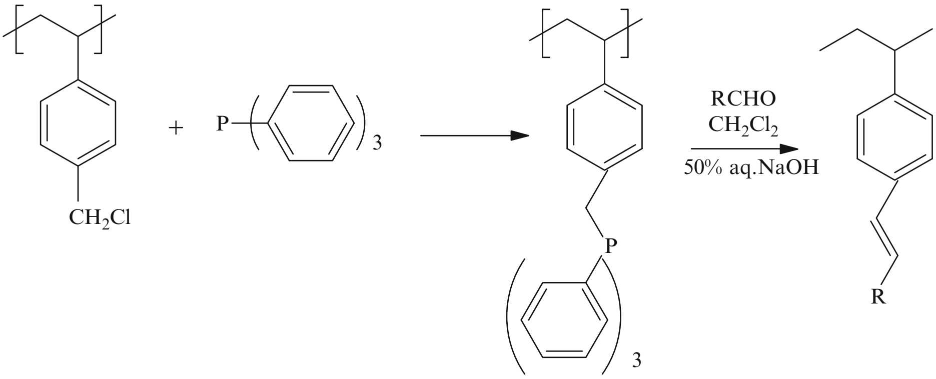
Vinyl benzyl chloride monomer is available commercially. It is possible, therefore, to simply prepare the chloromethylated polystyrene or copolymers from the monomer without the chloromethylation reactions.

9.4.3.3 Reactions of Halomethylated Polymers

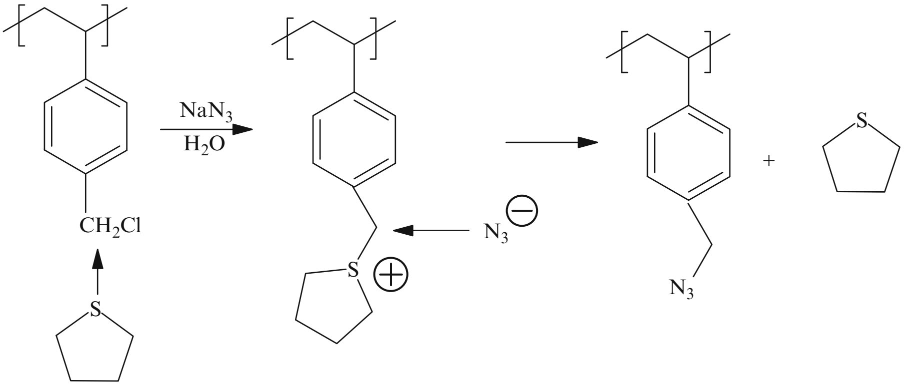
Many known reactions of the halomethyl groups on polymers are possible. One can, for instance, convert poly(chloromethyl styrene) to poly(hydroxymethyl styrene) [183]. Also, iodomethylated polystyrene can be treated with triethyl phosphite in order to carry out an *Arbuzov* reaction [192]:



Chloromethylated polystyrene can also be converted to a phosphonium salt for use in the *Wittig* reaction [193]:



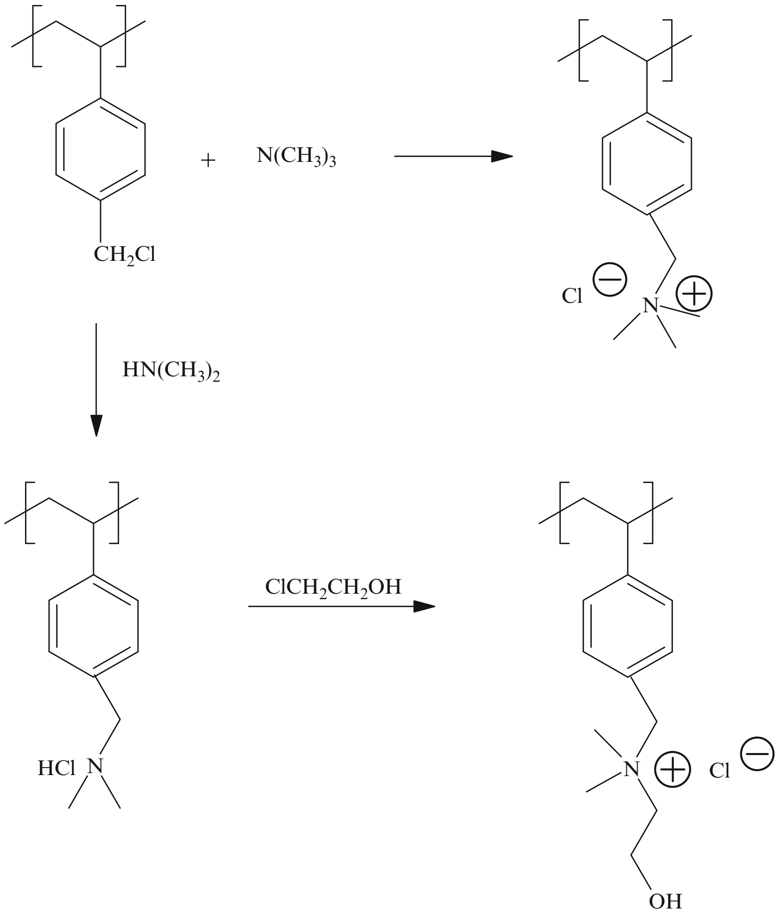
The product of a reaction of chloromethylated polystyrene and triphenylphosphine can also convert to nucleophiles [194]. In addition, use of a phase transfer catalyst converts soluble chloromethylated polystyrenes to phosphine oxides. Reactions with dioctylphosphine can serve as an example [195]. Sometimes phase transfer reactions are easier to carry out than conventional ones. This is the case with a Witting reaction. Both linear and cross-linked chloromethylated polystyrenes react smoothly with triphenylphosphine to give derivatives that react with various aldehydes [196, 197]. Phase transfer catalysts can also be used in carrying out nucleophilic substitutions with the aid of sulfides, like tetrahydrothiophine [198]:



When chloromethylated cross-linked polystyrene is reacted with potassium superoxide, the yield depends upon the type of solvent used. In dimethylsulfoxide, in the presence of 18-crown-6 ether, the conversion to hydroxymethyl groups is 45%. In benzene, however, it is only 25%. High conversions are obtained by catalyzing the reaction with tetrabutylammonium iodide in a mixture of solvents. This results in 85% conversions to hydroxymethyl groups, while the rest become iodide groups [199].

Quaternary salts are more effective than crown ethers in reactions with salts of oxygen-anions, such as carboxylate and phenolate [200]. On the other hand, lipophilic crown ethers, like dicyclohexyl-18-crown-6, exhibit higher catalytic activity than the quaternary salts in reactions with salts of the sulfur anions. Also, the catalytic activity of the phase transfer catalysts toward nitrogen anions is intermediate between that toward oxygen and that toward sulfur anions. Solid–liquid two-phase systems generally give higher degrees of conversion than do liquid–liquid systems. When, however, lipophilic phase transfer catalysts are used with lipophilic reagents, high degrees of substitutions are achieved in liquid–liquid two-phase systems [200].

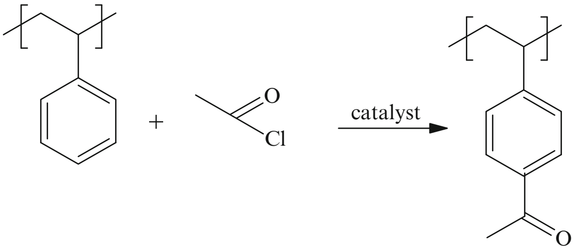
Conversion of chloromethylated styrene to anionic exchange resins is done commercially by amination reactions to form quaternary ammonium groups [201, 202]. This reaction can be illustrated as follows [203]:



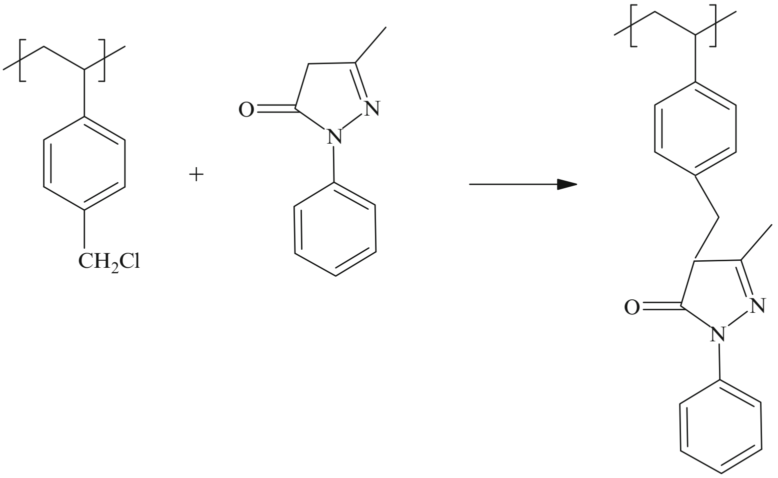
The kinetics of amination of chloromethylated polystyrene with monohydroxy dialkyl tertiary amines shows that the reactions proceed in two steps, at two different rates. The rate changes take place at conversions of 45–50% [205]. These rates are favorably influenced by increases in the dielectric constants of the solvents [204]. Two different rate constants also exist in reactions with 3-alkylaminopropionitrile.

9.4.3.4 Friedel-Craft Alkylation Reactions

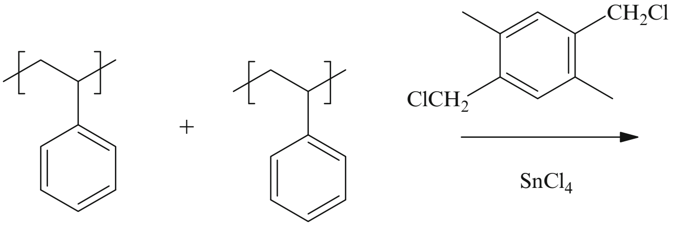
Friedel-Craft acylations of polystyrene can be carried out in CS_2 or in CCl_4 at reflux temperatures of the solvents. The yields are high [209]:

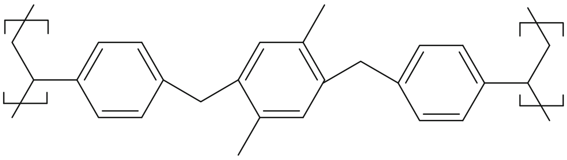


Chloromethylated copolymers of styrene with divinyl benzene undergo Friedel-Craft type reactions in condensations with 1-phenyl-3-methylpyrazolone or with 1-phenyl-2,3-dimethyl-pyrazolone-5 in the presence of either $ZnCl_2$, BF_3, or $SnCl_4$ [208]:



Polystyrene can also cross-link by a Friedel-Craft reaction [210]:





The above condensation takes place in dichloroethane, with stannic chloride catalyst at 50°C [210]. The maximum reaction rate varies with both, the initial concentration of 1,4-dimethyl-2,5-dichloromethylbenzene, shown above, and the initial concentration of $SnCl_4$. Cross-linked polystyrene particles, or beads also form by Friedel-Craft suspension cross-linking of polystyrene with 1,4-dichloromethyl-2,5 dimethyl-benzene [211]. The polymer is dissolved in nitrobenzene and a two-phase reaction occurs in 70% by weight of an aqueous suspension of $ZnCl_2$. Poly(vinyl alcohol) can be used as the suspending agent.

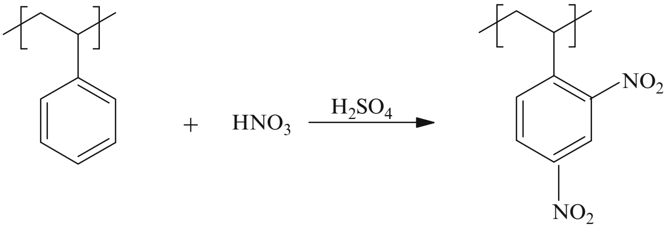
9.4.3.5 Sulfonation Reactions

Sulfonation reactions of polystyrene and its copolymers with divinyl benzene are carried out commercially to prepare ion exchange resins. Partial sulfonations of polystyrenes are achieved in the presence of ethers. When more than 50% of the aromatic rings are sulfonated, the polymers become water-soluble. At lesser amounts of sulfonation, 25–50%, the polymers are solvent-soluble [212, 213].

When polystyrene is sulfonated in chlorinated hydrocarbons with a complex of dioxane-SO_3, the polymer precipitates from solution at low concentrations [214, 215]. Complexes of ketones with SO_3 can also be used to sulfonate polystyrene in halogenated solvents [216]. The ratio of sulfonation is more favorable for poly(vinyl toluene) than it is for polystyrene at the same conditions [217]. Also, sulfur dioxide swells polystyrene. The polymer can be sulfonated in this medium with sulfur trioxide or with chlorosulfonic acid [218]. Polystyrene, sulfonated in CS_2 with aluminum chloride catalyst, is water-insoluble in a free acid form [219].

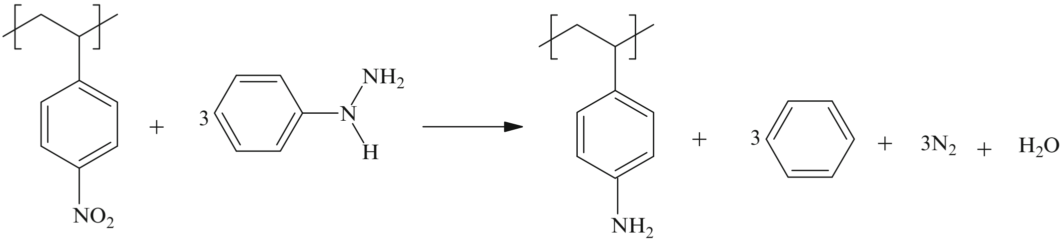
9.4.3.6 Nitration, Reduction, and Diazotization

Nitration of polystyrene was originally carried out a long time ago [220]. A nitrating mixture of nitric and sulfuric acids dissolves the polymer and a nitro derivative forms at 50°C within 3 h [221]:

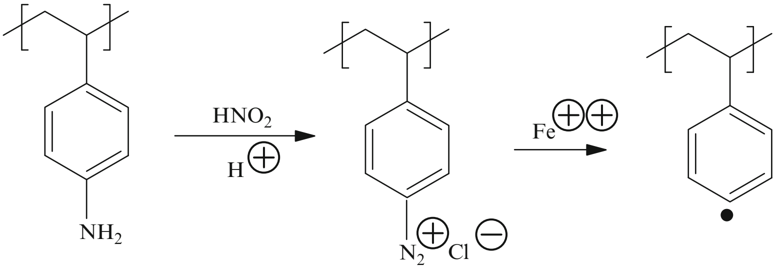


The reaction is accompanied by a loss of molecular weight. Nitration of isotactic polystyrene yields a more crystalline product (about 1.6 NO_2/ring) than the parent compound [222]. Here too, however, a loss in molecular weight accompanies the reaction [223]. Polystyrene can be nitrated under mild conditions using acetyl nitrate. The product contains approximately 0.6 nitro groups per each benzene ring [224].

The nitro groups of polynitrostyrene are reduced by phenyl hydrazine that acts as a hydrogen donor [225]:

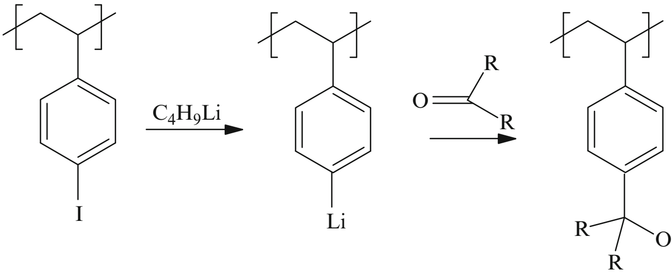


Polyaminostyrene can undergo typical reactions of aromatic amines, such as diazotization [226]. The diazonium salt decomposes with ferrous ions to yield polymeric free-radicals:

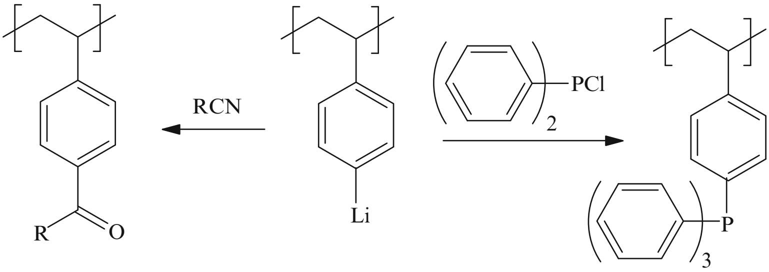


9.4.3.7 Metalation Reactions

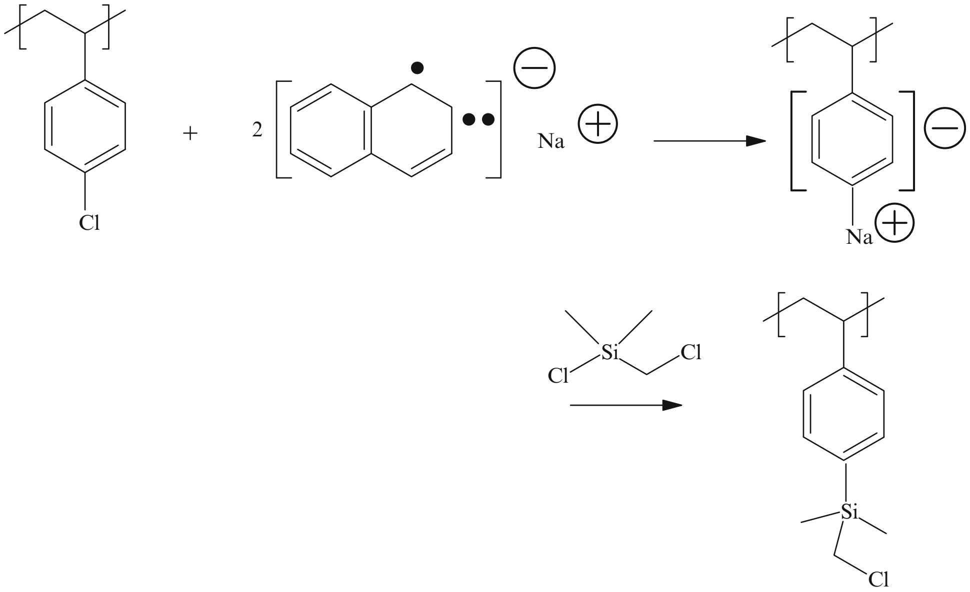
Functional polystyrene derivatives are starting materials for further reactions in many multistep syntheses. An example is a metalation of polystyrenes for use as intermediates [227]:



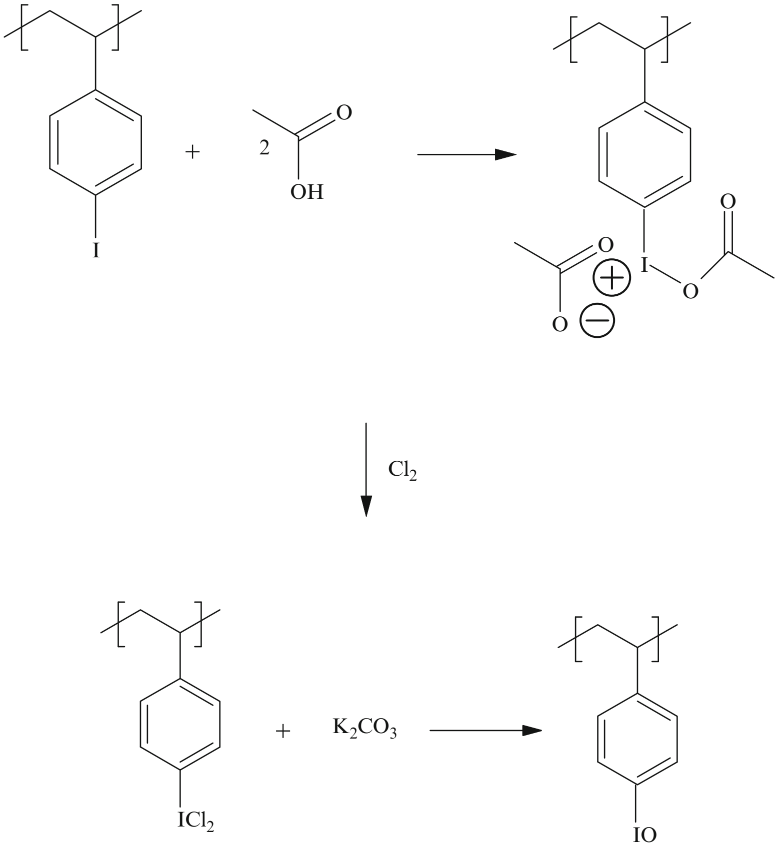
Some other reactions of lithiated polystyrene are [227]:



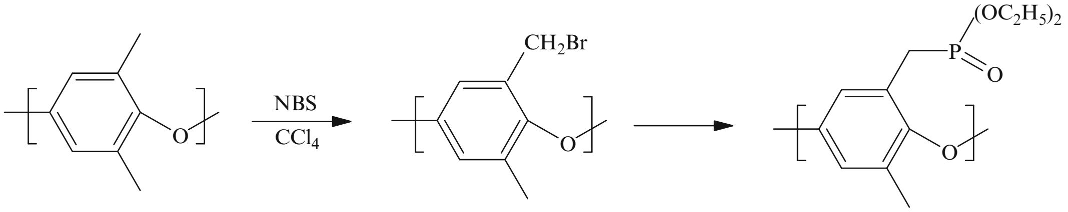
When polystyrenelithium is aminated by a reagent prepared from methoxyamine and methyllithium, two reaction mechanisms are possible. One may proceed via nitrene intermediates and the other one via electrophilic nitrenium ions [228]. Many other reactions of polystyrenelithium can be found in the literature [229–232]. Sodium metalated polystyrene reacts in a similar manner [228]:



Polyiodostyrene is a good starting material for many other reactions. Some of them are [233, 234]:



Poly(2,6-dimethyl-1,4-phenylene oxide) can be brominated with *N*-bromo-succinimide [235]. The product can also subsequently be used for further reactions [235], as, for instance, phosphorylation with triethyl phosphite:

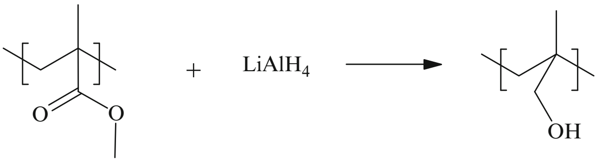


9.4.4 Reactions of Acrylic, Methacrylic, and Related Polymers

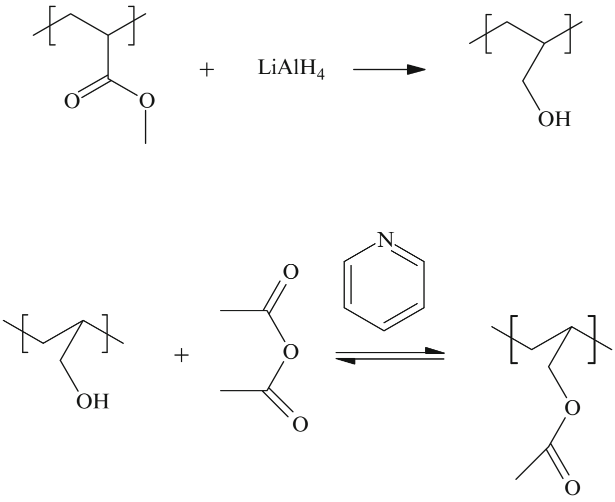
The functional groups of polymers from acrylic and methacrylic esters can undergo all the typical reactions of such groups. There are, therefore, numerous reports in the literature on such reactions.

9.4.4.1 Reduction of the Ester Groups

Perhaps the most reported reactions of these polymers are *reductions* of the functional groups. Among them is the reaction with lithium aluminum hydride to reduce the ester groups. The success, however, depends upon the reaction medium. Poly(methyl methacrylate) can be reduced to poly(methallyl alcohol) in ether solvents [236]:



The results, however, are inconclusive, because combustion analyses fail to match the theoretical composition for poly(methallyl alcohol). It is impossible to tell to what extent the reduction takes place [236]. Inconclusive results are also obtained in similar reductions of poly(methyl acrylate) in mixtures of tetrahydrofuran and benzene. The product of such reduction is acetylated with acetic anhydride in pyridine [237] as follows:

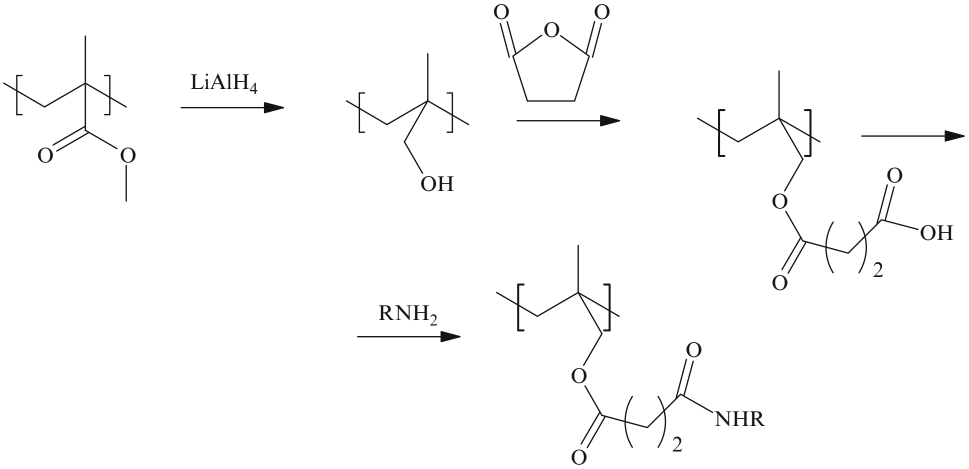


Hydrolysis in water of the product of acetylation, followed by treatment with hot *m*-cresol, and subsequent extraction with hydrochloric acid to remove the suspended inorganic matter [237], yields a material that is still only soluble in pyridine and *m*-cresol.

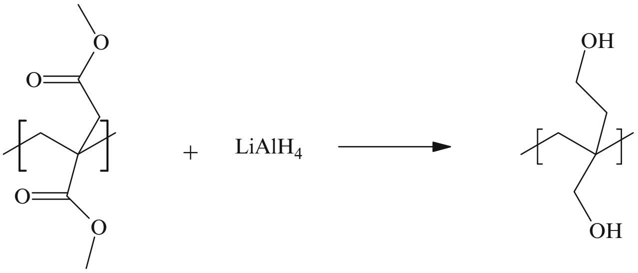
Somewhat similar results are obtained in reductions of high molecular weight poly(methyl acrylate) with lithium aluminum hydride [238] in tetrahydrofuran. The reaction yields a product that is only soluble in mixtures of hydrochloric acid with either methyl alcohol, dioxane, or tetrahydrofuran. The problem is apparently due to some residual aluminum that is hard to remove [239]. If, however, the reduction is carried out in a *N*-methylmorpholine solution, followed by addition of potassium tartrate, a pure product can be isolated [240]. *N*-methylmorpholine is a good solvent for reductions of various macromolecules with metal hydrides [236]. In addition, the solvent permits use of strong NaOH solutions to hydrolyze the addition complexes that form. Other polymers that can be reduced in it are those bearing nitrile, amide, imide, lactam, and oxime pendant groups. Reduction of polymethacrylonitrile, however, yields a product with only 70% of primary amine groups [241].

Complete reductions of pendant carbonyl groups with $LiAlH_4$ in solvents other than *N*-methylmorpholine, however, were reported. Thus, a copolymer of methyl vinyl ketone with styrene was fully reduced in tetrahydrofuran [242].

Reductions with metal hydrides are often preliminary steps for additional reactions. For instance, a product of $LiAlH_4$ reduction of syndiotactic poly(methyl methacrylate) can be reacted with succinic anhydride and then converted to an amide [243]:

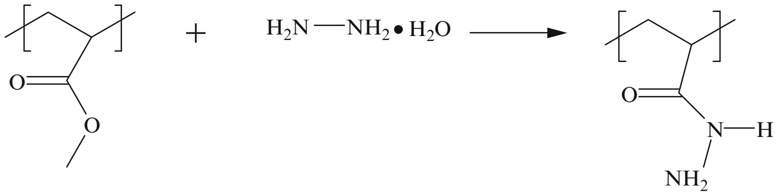


Substituted succinic anhydride can be used as well. When poly(dimethyl itaconate) is reduced with $LiAlH_4$ in THF, the product contains some ash, but 93% of the functional groups are reduced [239]:

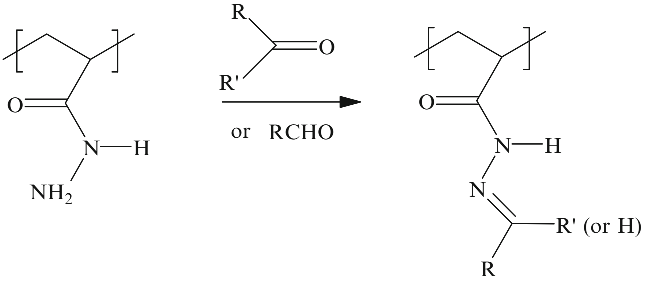


9.4.4.2 Nucleophilic and Electrophilic Substitutions

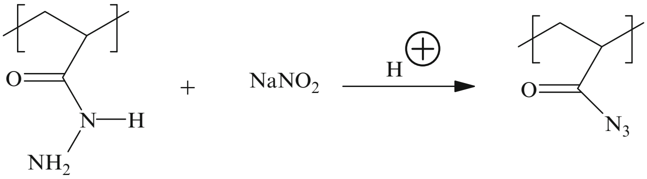
Many other conversions of functional groups of acrylic and methacrylic resins were reported. One of them is a conversion of methyl acrylate to a hydrazide by a direct reaction with hydrazine [244]:



The above reaction requires a 10:1 ratio of hydrazine to the ester groups. In the laboratory, it can be carried out on a steam bath over a period of 2–3 h. Approximately 60–80% of the ester groups convert [244]. The hydrazides can form various hydrazones through reactions with aldehydes and ketones:



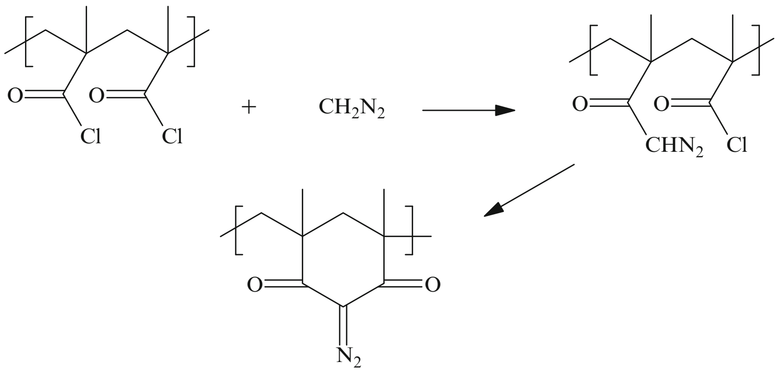
The hydrazide can also be converted to an azide [244]:



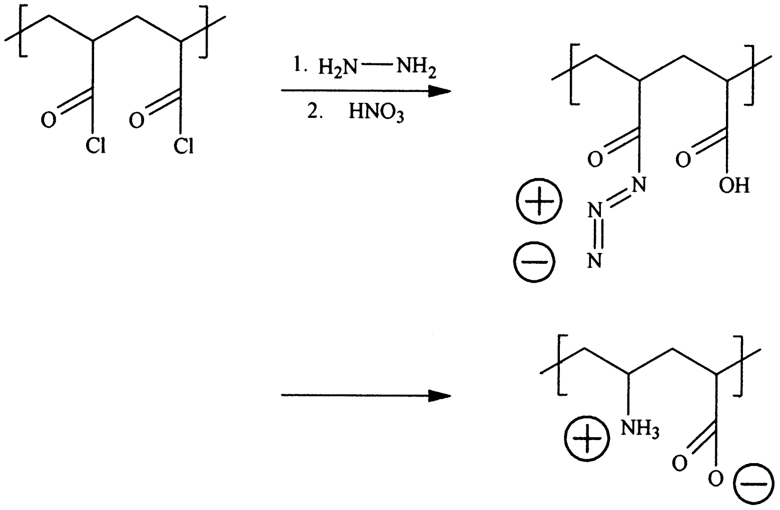
A *Hoffman reaction* of the azide yields a cross-linked polymer [244]. Syndiotactic poly(methyl methacrylate) converts to a hydrazide in a similar manner [245].

Nucleophilic substitution reactions can be carried out on poly(methyl methacrylate) with heterocyclic organolithium reagents [246]. The reactions are conducted in homogeneous solutions in tetrahydrofuran or in benzene combined with hexamethyl-phosphoramide. Copolymers will form with tautomeric keto-β-heterocyclic structures. Following heterocyclic reagents are useful [246]: 2-picolinyllithium, [(4,4-dimethyl-2-oxazole-2-yl)methyl]lithium, quinaldinyllithium, and [2-thiazole-2-yl-methyl]lithium.

In attempts to carry out *Arndt-Eister* reactions on poly(methacryloyl chloride), the polymer was reacted with diazomethane in various molar ratios and at different temperatures [247]. Initially, acid chloride groups do react with diazomethane as expected. The products, however, undergo subsequent reactions with neighboring acid chloride groups and form cyclic structures [247]:

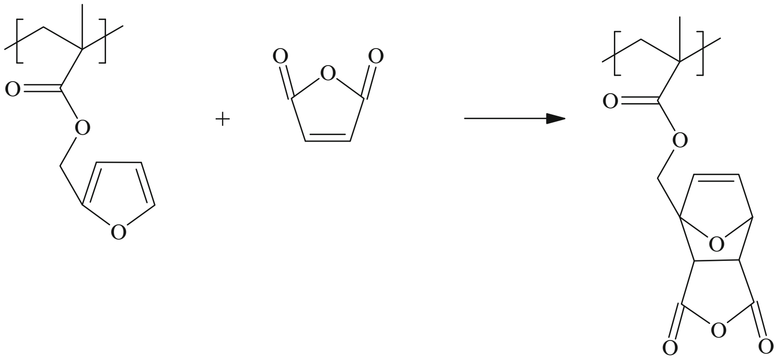


When *Curtius* and *Lossen* rearrangement reactions are attempted on poly(acryloyl chloride) [248], the products are fairly regular polyampholytes:



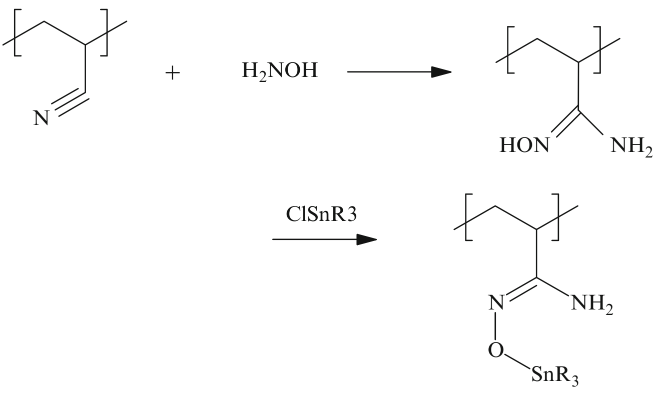
Somewhat similar results are obtained with a *Hoffman reaction* on polyacrylamide [279]. A *Schmidt reaction* on poly(acrylic acid) also yields mixed results [250]. When it is run in acetic acid, the intermolecular reactions appear to predominate over the intramolecular ones. Also, the products formed in acetic acid have higher nitrogen content that those formed in dioxane [250]. The NMR spectra show presence of some acid anhydride groups. This has an additional effect of lowering the yield.

Diels-Alder reactions can be carried out on poly(furfuryl methacrylate) with dienophiles like maleic anhydride or a maleimide [252]. Dilute solutions (10%) of the polymers in benzene can be used, requiring up to 30% molar excess of the dienophiles:



The additions take place at room temperature and the reactions take from 7 to 30 days [252] to complete.

Polyacrylonitrile reacts with hydroxylamine and the product can be metalated by elements from Group IV (Sn, Ge, and Si). This is a convenient route to formation of polymers with such pendant organometallic groups [253]:

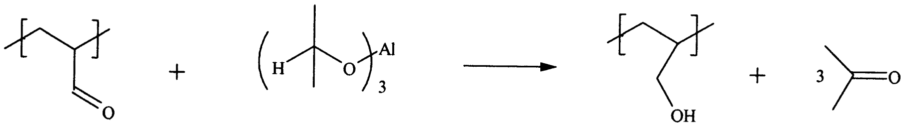


The yields are high when the reactions are carried out on dilute solutions of polyacrylonitrile in dimethylformamide at 75°C. The solutions must contain 1.5 mol each of hydroxylamine hydrochloride and sodium carbonate per mole of acrylonitrile groups [253].

A *Ritter* reaction can be carried out on atactic polyacrylonitrile with *N*-hydroxymethylamides of acetic, benzoic, and benzene-sulfonic acids [254]. When the same reactions are carried out with *N*-hydroxymethylimides of succinic or phthalic acids in tetramethylene sulfone, there is a stronger tendency toward cross-linking.

Copolymers of methacroyl chloride will undergo an *Arbuzov rearrangement* in reactions with triethyl phosphite in dimethylformamide, dioxane or benzene at 75°C [255]. The conversions are high, ranging between 96 and 98%.

The aldehyde groups of polyacrolein can be reduced by the *Meerwein-Ponndorf reaction*. There is a limit, however, to the amount of alcoholate that can be used and to the concentrations of free aldehyde groups in the starting material [256]. Also, ester condensations take place (*Tischenko* reaction) at the same time as the reductions occur [256].



9.4.5 Substitution Reactions of Poly(vinyl alcohol)

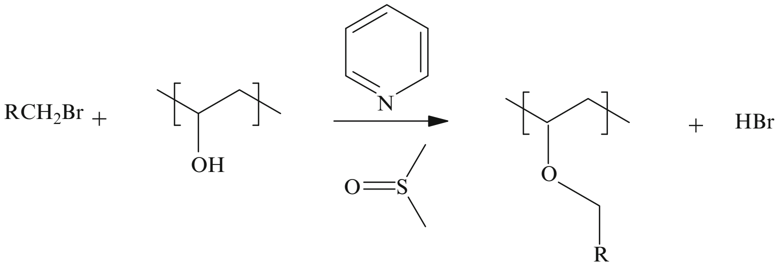
There are many practical uses for products from reactions of poly(vinyl alcohol). Among them are commercial preparations of poly(vinyl acetal)s formed through condensations with aldehydes. Two materials that are currently being marketed are poly(vinyl formal) and poly(vinyl butyral). The first one is formed from partially hydrolyzed poly(vinyl acetate) that is dissolved in aqueous acetic acid and excess formaldehyde. The mixture is heated, sulfuric acid is added, and the reaction is allowed to proceed at 70–90°C for 6 h. Sulfuric acid is then neutralized and the formal precipitates out.

Two different industrial processes are used for preparations of the butyral. In both of them, acetate free poly(vinyl alcohol) is used. In the first one, 10% solutions of the starting material are treated with butyraldehyde and sulfuric acid. The mixtures are heated to 90°C for 1½ h and the products precipitate. They are neutralized, washed, and dried. In the second one, poly(vinyl alcohol) is suspended in ethanol/ethyl acetate and butyraldehyde together with a strong mineral acid is added. The solutions are then neutralized. The butyrals separate out. They are neutralized and the resin are washed and dried.

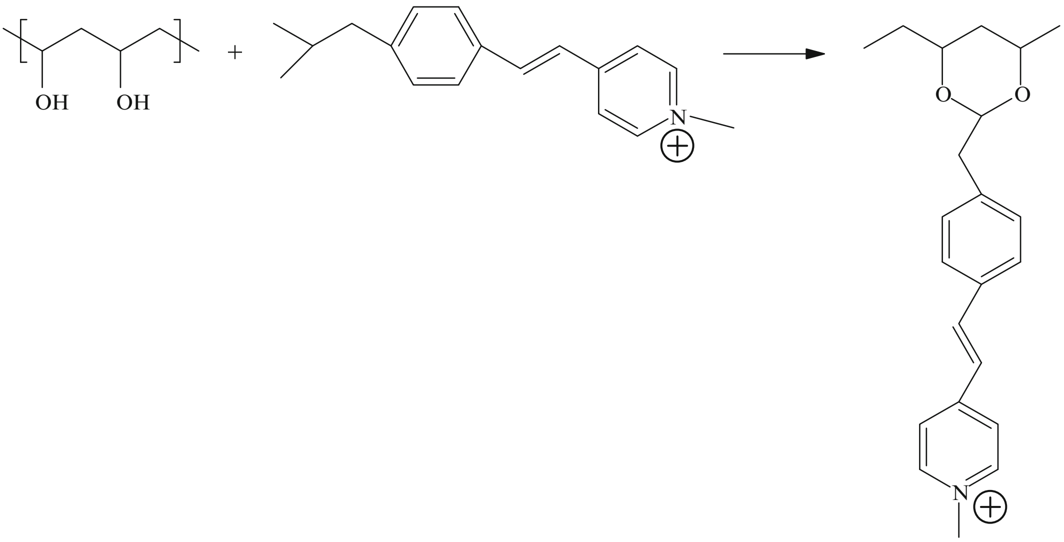
If poly(vinyl alcohol) films are reacted with formaldehyde in water containing salt and an acid catalyst (heterogeneous formalization), cross-linking occurs. The number of the cross-links increases with decreasing acid concentration and fixed amounts of formaldehyde and salt [257].

Direct reactions of poly(vinyl alcohol) with aldehydes in the *Kornblum reaction* result in formations of acetals that also contain residual hydroxyl group and often acetate groups. The acetate groups can be there from incomplete hydrolysis of the parent poly(vinyl acetate) that was used to form the poly(vinyl alcohol). Reactions of poly(vinyl alcohol) with ketones yield similar ketals. At present, no ketals are offered commercially.

Alkyl etherification of poly(vinyl alcohol) occurs when the polymer is combined with *n*-alkyl halides in dimethylsulfoxide combined with pyridine [258, 259]. It was suggested that the alkyl halides convert to aldehydes and acids and then act as intermediates in the dimethylsulfoxide-pyridine solution [258, 259]:



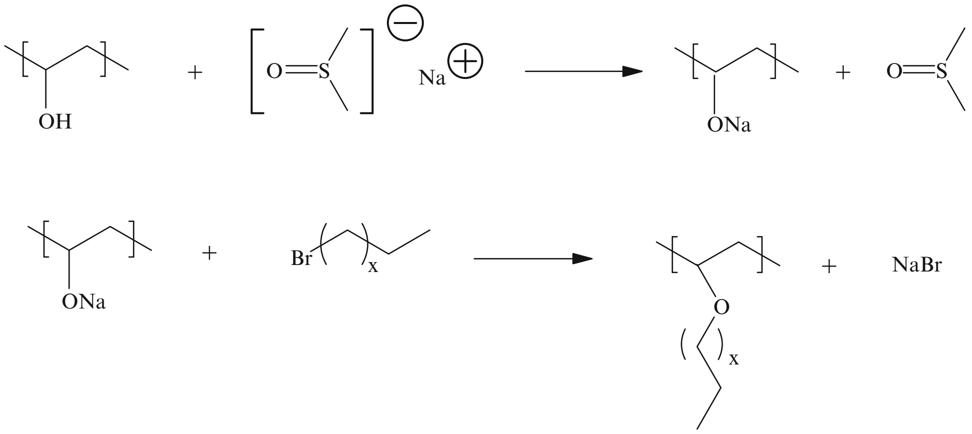
Many modifications of poly(vinyl alcohol) were carried out to form photosensitive materials. Thus, unsaturation was introduced into the pendant groups for photocross-linking. One example is a condensation with pyridinium and quinolinium salts [260]:



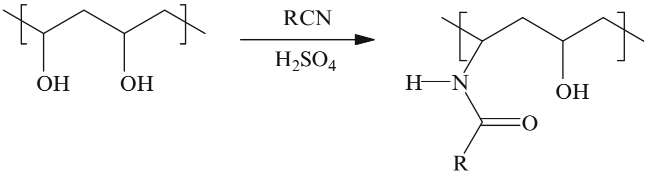
The material cyclodimerizes on exposure to light [261] (see Chap. 10 for additional discussion of this subject).

Schotten-Baumann esterifications of poly(vinyl alcohol) are used extensively in preparations of various derivatives. The reactions appear to proceed well when acid chlorides are employed in two-phase systems [262]. The polymers are dissolved in water and the solutions are blended in 1:1:1 equal volume with NaOH solutions and cyclohexanone. They are then mixed thoroughly with solutions of the acid chlorides in mixtures of cyclohexanone and toluene. The reaction mixture is stirred vigorously for about 90 min at −5 to 5°C to obtain the desired product.

Metalation of poly(vinyl alcohol) is used to form ether derivatives [263]:



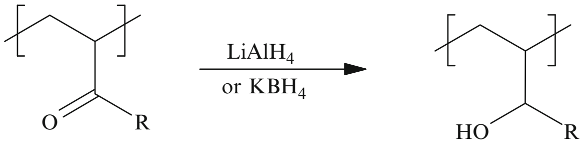
The *Ritter reaction* on poly(vinyl alcohol) yields soluble products. Only some of the hydroxyl groups, however, are converted to amide structures [264]:



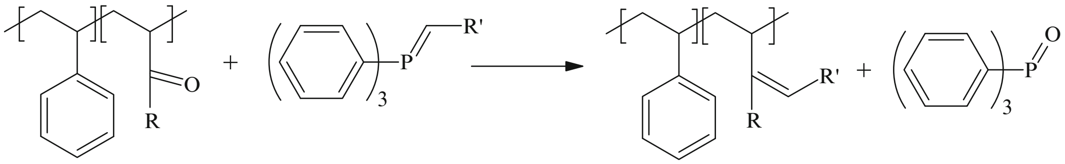
Also, it is possible that neighboring group interactions may lead to cyclizations and formations of 1,3-oxazines [264].

9.4.6 Miscellaneous Exchange Reactions

Many miscellaneous exchange reactions are reported in the literature. A few are presented here. One such reaction is reduction of pendant carbonyl groups of poly(vinyl methyl ketone) with metal hydrides [242, 265]:

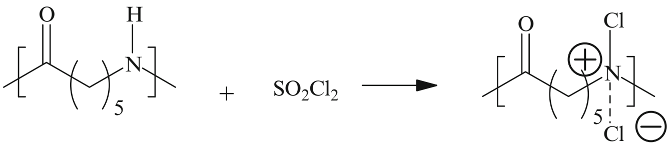


Another one is introduction of unsaturation into pendant groups by a Wittig reaction on pendant carbonyls [266]:

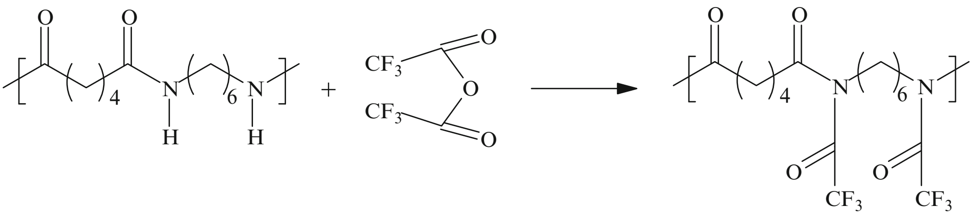


The same reaction can also be carried out on a copolymer of ethylene and carbon monoxide [266].

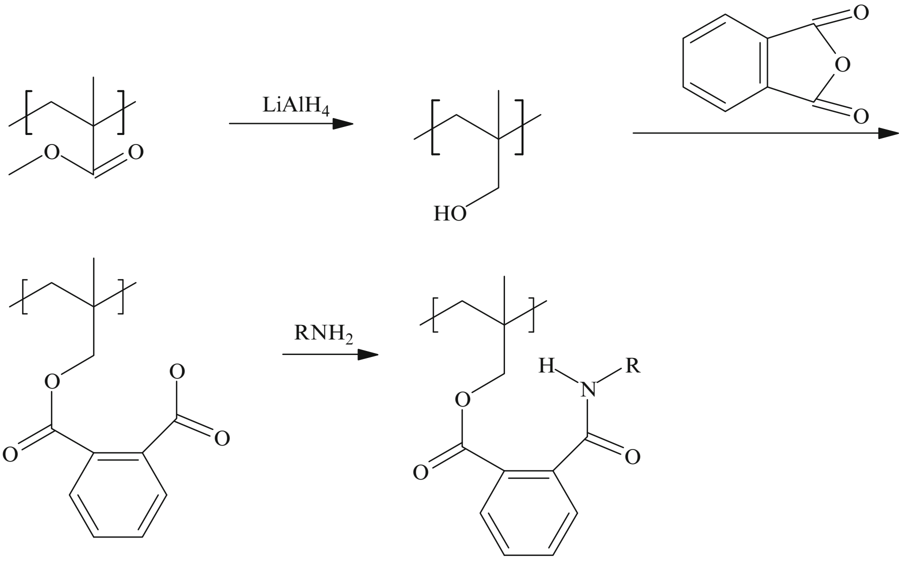
Polycaprolactam can be treated with either SO_2Cl_2, $POCl_3$, or PCl_5 at 70°C to introduce ionic chlorine groups [267]. The main product is poly(α,α-dichloro-caprolactam):



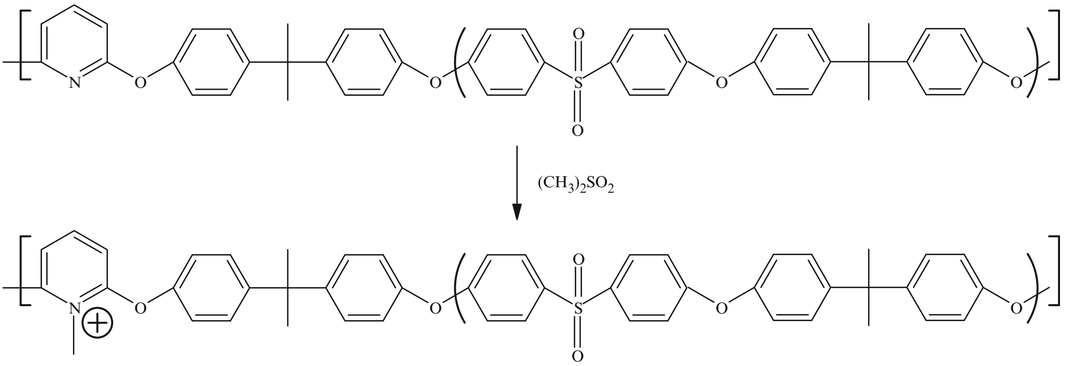
Also, when Nylon 6,6 is reacted with trifluoroacetic anhydride, trifluoroacetyl nylon forms [268]:



Syndiotactic poly(2-methallyl hydrogen phthalate) can be prepared and amidated according to the following scheme [269]:

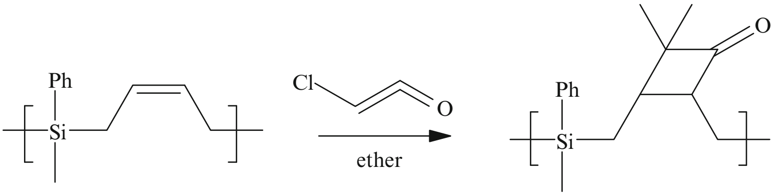


poly(pyridine ether sulfone)s in nitrobenzene [70]. The reaction can be illustrated as follows:



A 20% mol excess of the alkylating reagent is required and the reaction must be conducted for 6 h at 80°C.

Dichloroketene, generated by the ultrasound-promoted dechlorination reaction of thrichloroacetyl chloride with zinc, adds to the carbon–carbon double bonds of poly(methyl-1-phenyl-1-silane-*cis*-pent-3-ene) [271]. This can be illustrated as follows:

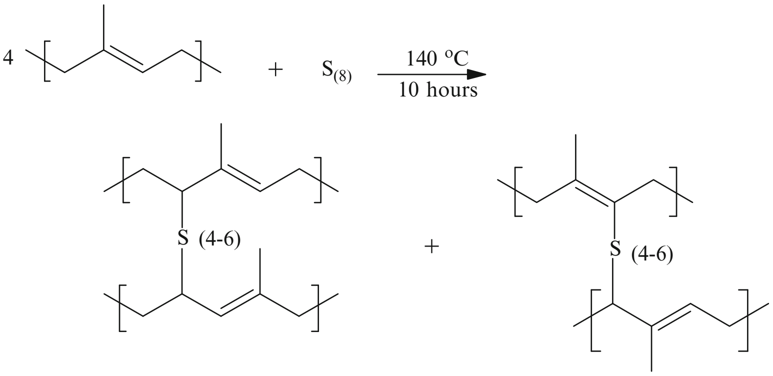


9.5 Cross-linking Reactions of Polymers

These reactions are quite numerous and have been utilized for a long time. They also include all thermosetting processes of polymers. Many are discussed in previous chapters.

9.5.1 Vulcanization of Elastomers

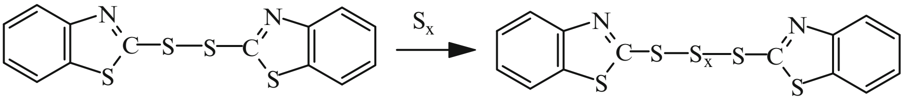
Cross-linking of natural rubber was discovered by Goodyear back in 1839. Sulfur, which was the original cross-linking agent, is still utilized today in many processes. Early studies demonstrated that the cross-links are mainly polysulfides:



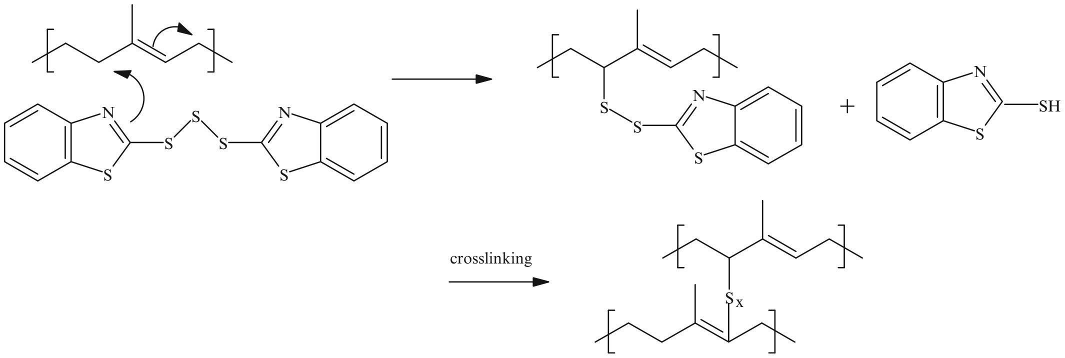
The reactions take place at all temperatures, but industrially they are carried out from 50 to 75°C and above. At lower temperatures, however, the process may take days to complete. At temperatures of 135–155°C, approximately 8% of sulfur (by weight of rubber) reacts [272]. Also, sulfur dissolves in unvulcanized rubber even at room temperature. The overall mechanism of the reaction is still being studied. Most evidence points to an ionic mechanism and a sulfonium ion intermediate [272]. It was shown [273] that a straightforward reaction of sulfur with rubber is insufficient. Somehow, between 40 and 100 atoms of sulfur must be combined in order to obtain one cross-link. Out of 40–100 atoms, only 6–10 are actually engaged in the formation of the cross-links. The rest of the atoms form cyclic sulfide units that become spread along the main chain [273].

To improve the efficiency of the vulcanization reaction, various accelerators were developed. Among them are zinc oxide combined with fatty acids, and/or amines. Zinc oxide forms zinc mercaptides like $(XS)_2ZnL_2$ where X is an electron withdrawing substituent and L is a ligand from a carboxyl or an amine group. The function of the ligand is to render the complex soluble. The mercaptide complexes are believed to react with additional sulfur to form zinc perthiomercaptides.

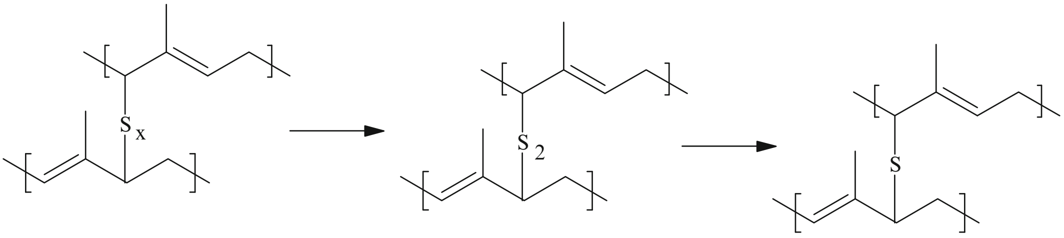
The accelerators that are most commonly used are derivatives of 2-mercaptobenzothiazole. They are very effective when used in combinations of metal oxides with fatty acids (referred to as *activators*). The favorite activators are zinc oxide combined with stearic acid. The combinations permit rapid vulcanizations that take minutes compared to hours when sulfur is used alone. In the process of vulcanization, 2,2′-dithiobisbenzthiazole forms initially and then reacts with sulfur to form polysulfides [273]:



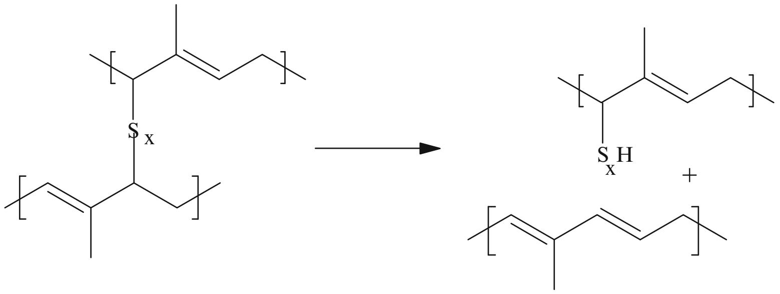
The products from reactions with sulfur in turn react with natural or synthetic rubber at any allylic hydrogen. This is a concerted reaction that results in formation of sulfur containing adducts of the polymers:



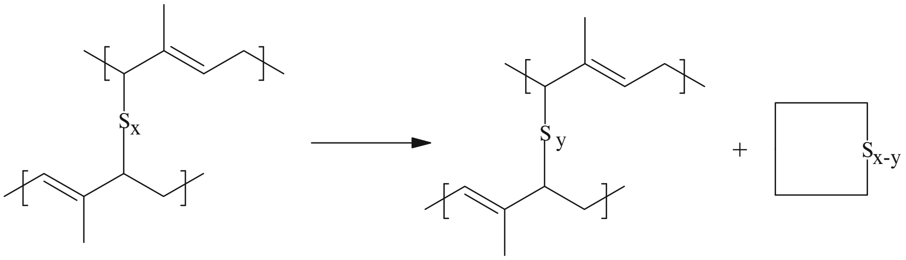
Once the cross-links are formed, further transformations take place. Some of them consist of reactions that shorten the polysulfide links:



Also, some cross-links are lost through elimination reactions:

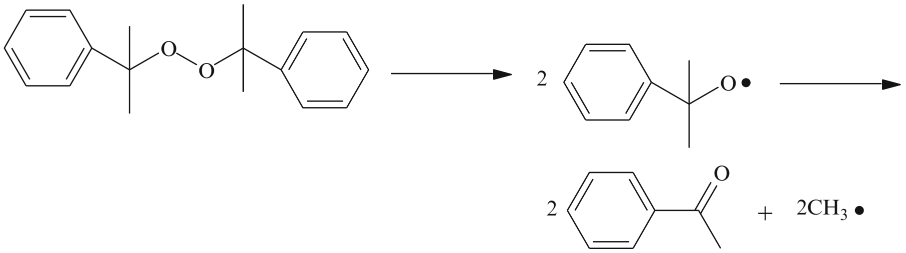


In addition, some cyclic sulfur compounds form in the process [273]:

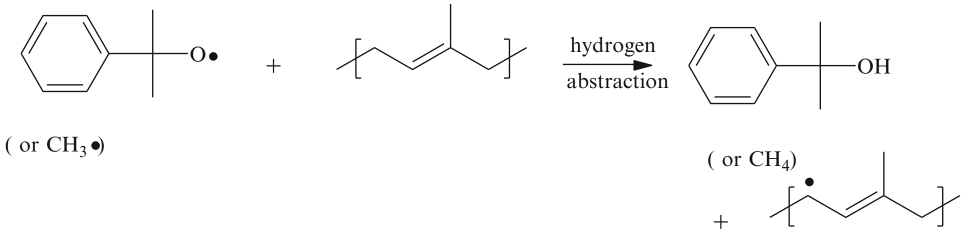


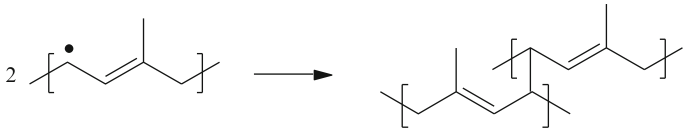
9.5.2 *Cross-linking of Polymers with the Aid of Peroxides*

The reaction can be utilized with many polymers such as polyolefins, polymers of dienes, and others. The reactions with natural rubber can be illustrated as

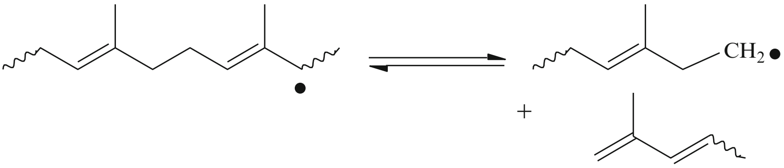


follows [274]:





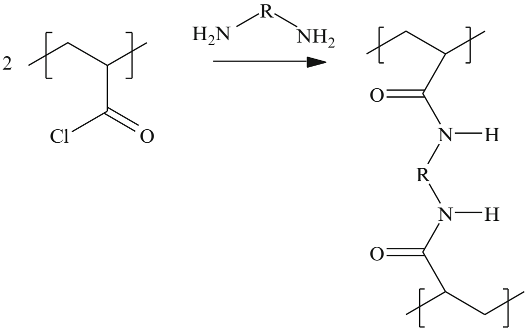
The extent of the cross-linking, as shown above, is not clear. It is known, however, that cleavage reactions that are followed by free-radical recombinations can take place [274]:



Polymeric chains bearing free radicals combine with each other to give branched structures. Additions of chains with freeradical to double bonds result in formations of cross-links [274].

9.5.3 Miscellaneous Cross-linking Reactions of Polymers

Many other miscellaneous cross-linkings of polymeric materials are reported in the literature. For instance, poly(acryloyl chloride) can be cross-linked with diamines [275]:



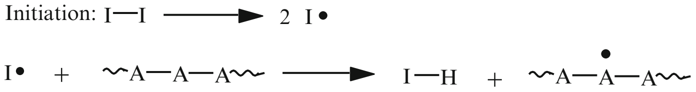
In a similar manner, polymers with pendant chlorosulfonate groups cross-link when reacted with diamines or with glycols [275].

9.6 Graft Copolymers

This is an important part of polymer syntheses that is used in many industrial processes. In 1967, Battaerd and Tregear [282] published a book on the subject that contains 1,000 references to journal publications and 1,200 references to patents. In addition, there are several monographs and many review papers [283]. The synthetic methods developed to date range from using free radical attacks on polymeric backbones to highly refined ionic reactions. There are examples where these ionic reactions attach the side-chains at well-designated locations.

9.6.1 Free-Radical Grafting by Chain-Transferring Process

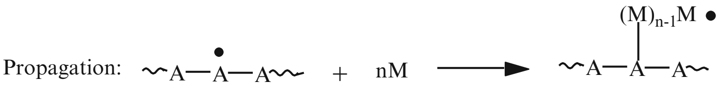
This technique is probably one of the simplest ways to form graft copolymers. It consists of carrying out free-radical polymerizations of monomers in the presence of polymers preformed from different monomers. A prerequisite for this synthesis is that the active sites must form on the polymeric backbones during the course of the reactions. Ideally, this occurs if the steps of initiations consist only of attacks by the initiating radicals on the backbones:



$$\text{Initiation: } I{-}I \longrightarrow 2\ I\bullet$$

$$I\bullet + \sim A{-}\overset{}{A}{-}A\sim \longrightarrow I{-}H + \sim A{-}\overset{\bullet}{A}{-}A\sim$$

Propagations then precede from the backbone sites:



$$\text{Propagation: } \sim A{-}\overset{\bullet}{A}{-}A\sim + nM \longrightarrow \sim A{-}\overset{(M)_{n-1}M\bullet}{\overset{|}{A}}{-}A\sim$$

Terminations can take place in many ways. Of course, termination by combination will lead to cross-linked insoluble polymers and that is undesirable. An ideal termination takes place by chain transferring to another site on a polymer backbone to initiate another chain growth.

The above, however, is an ideal picture. In reality, the efficiency of grafting by this technique depends upon the following:

1. Competitions between the different materials present in the reaction mixture, such as monomer, solvent, and polymer backbone for the radical species. This includes competition between chains growth and chain transferring to any other species present.
2. Competition between the terminating processes, such as disproportionation and chain transferring.

The conditions can vary considerably and it is possible to carry out the reactions in bulk, solution, or in emulsion. When the reaction take place in emulsion, the success depends greatly on experimental techniques. The rate of diffusion is a factor and anything that affects this rate must be considered. Because grafting efficiency depends upon chain transferring to the backbone, knowledge of the chain-transferring constants can help predict the outcome of the reactions. Sometimes, the information on the chain-transferring constants is not available from the literature. It may, however, be possible to obtain the information from reactions of low molecular weight compounds with similar structures [284–286]. One assumes equal reactivity toward attacking radicals. The validity of such an assumption was demonstrated on oligomers [281–283].

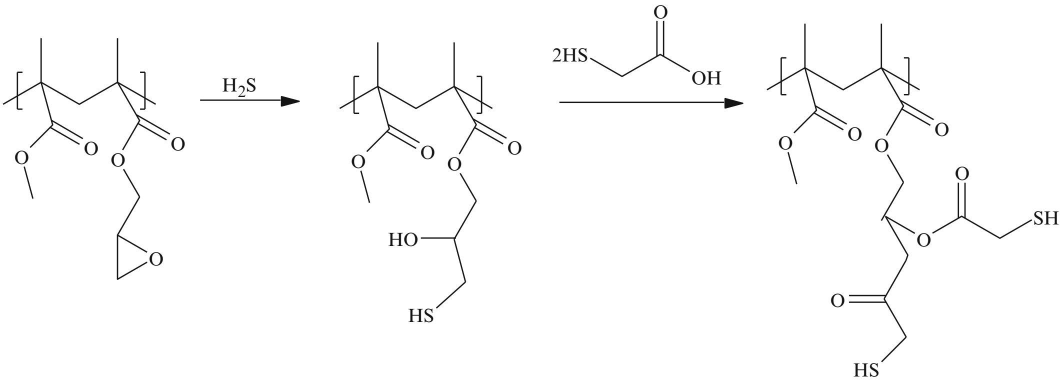
The reactivity of the initiating radicals toward the backbones can vary and this can also vary the efficiency of grafting. Benzoyl peroxide-initiated polymerizations of methyl methacrylate monomer, for instance, in the presence of polystyrene [284] yield appreciable quantities of graft copolymers. Very little graft copolymers, however, form when di-*t*-butyl peroxide initiates the same reactions. Azobisisobutyronitrile also fails to yield appreciable quantities of graft copolymers. This is due to very inefficient chain transferring to the polymer backbones by *t*-butoxy and isobutyronitrile radicals.

A better approach is work by Chung and coworkers [288] who grafted maleic anhydride to polypropylene with the use of Borane/O_2 initiator. This initiator is claimed to form in situ a monooxidized adduct (R–O* *O–BR_2). These adducts then carry out hydrogen abstractions from the polypropylene chains at ambient temperature. This results in formation of stable tertiary polymer radicals that react with maleic anhydride to form graft copolymers:

Not all chain transferring to the backbones results in formations of graft copolymers. An example is polymerization of vinyl acetate in the presence of poly(methyl methacrylate). No graft copolymers form and this is independent of the reactivity of the initiators [285]. In fact, grafts of poly(vinyl acetate) to poly(methyl methacrylate) and to polystyrene cannot be prepared by this technique [286].

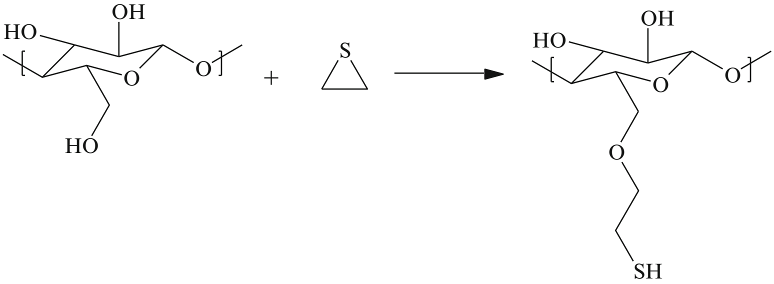
Grafting efficiency may increase with temperature [287]. This could be due to higher activation energy of the transfer reaction than that of the propagation reaction [288]. Meaningful effects of temperature, however, are not always observed. In grafting polystyrene to poly(butyl acrylate) in emulsion, for instance, there is no noticeable difference between 60 and 90°C by this technique [289].

The presence of sites with high transfer constants on the polymeric backbone enhances the efficiency of grafting. Such sites can be introduced deliberately. These can, for instance, be mercaptan groups [290] that can be formed by reacting H_2S with a polymer containing epoxy groups:



Free-radical polymerizations of acrylic and methacrylic esters in the presence of the above backbones result in high yield of graft copolymers [291, 292].

Another example is formation of mercaptan groups on cellulose in order to form graft copolymers [293]:



Pendant nitro groups are also effective in chain transfer grafting reactions. Thus, graft copolymers of polystyrene with cellulose acetate *p*-nitrobenzoate [294] and with poly(vinyl *p*-nitrobenzoate) [295] form readily. Nitro groups appear to be more effective in formations of graft copolymers by radical mechanism than are double bonds located as pendant groups [294].

9.6.2 Free-Radical Grafting Reactions to Polymers with Double Bonds

Carbon to carbon double bonds, either in the backbone or in the pendant groups, are potential sites for free-radical attacks. In addition to the double bonds, the hydrogen atoms on the neighboring carbons are allylic and potential sites for chain transferring. Because rubbers, natural and synthetic, possess such unsaturations, they are used extensively as backbones for various grafting reactions. Whether the reactivity of the initiating radical is important in determining grafting efficiency is not completely established. Graft copolymers of poly(methyl methacrylate) on gutta-percha, however, form in good yields when the initiator is benzoyl peroxide [296, 297]. Yet, when azobisisobutyronitrile is used, only a mixture of homopolymers forms. Work with ^{14}C-labeled initiators shows that the primary radicals react both by addition to the double bonds and by transfer to the methylene group [298].

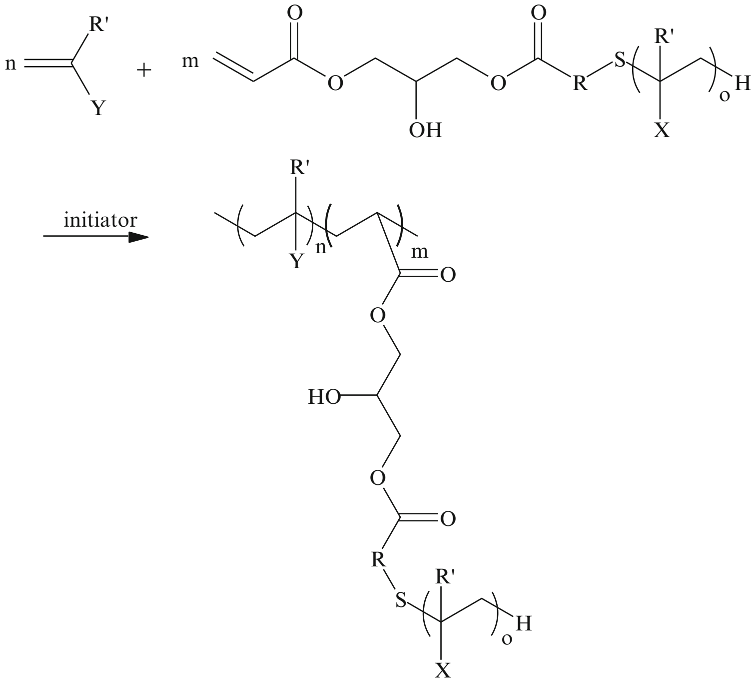
Grafting reactions to polybutadiene, however, proceed via chain transferring from the growing chain radical to the backbone [299]. Nevertheless, strong evidence also shows that the initiator radicals can interact directly with polymeric backbones [299, 300].

When graft copolymers of polystyrene to natural rubber form, the chain length of the attached branches equals to the chain lengths of the unattached polystyrene homopolymer that forms simultaneously [301]. This led to the following conclusions [303]:

1. As the concentration of rubber increases, the length of the grafted branches diminishes, while their number remains the same.
2. When the concentration of the initiator increases, the length of the branches diminishes, but the number of branches increases.
3. When the concentration of monomers increases, the length of the branches also increases, but their number diminishes.
4. When the polymerization time increases, the length of the branches remains the same, but their number increases.

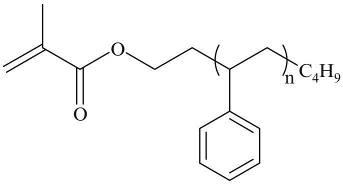
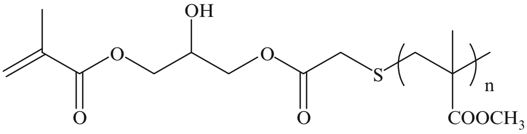
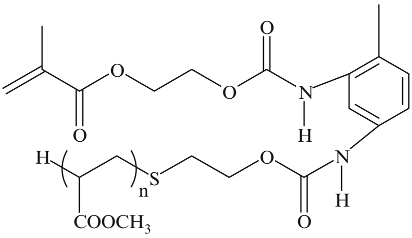
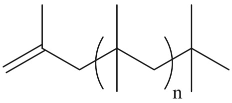
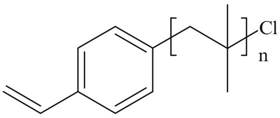
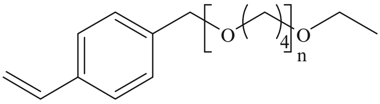
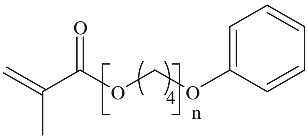
9.6.3 *Preparation of Graft Copolymers with the Aid of Macromonomers*

The chain-transferring methods for preparing graft copolymers suffer from the disadvantages of low efficiency and contamination by homopolymers. The efficiency in forming graft copolymers, however, increases with the use of *macromonomers*. A macromonomer is a macromolecular monomer, an oligomer, or a polymer with a polymerizable end group. When macromonomers are copolymerized with other monomers, comb-shaped polymers form [302, 303]. The copolymerizations can be free radical or ionic in mechanism. Some examples of macromonomers are presented in Table 9.1. A preparation of graft copolymers with the aid of macromonomers can be illustrated as follows [304]:



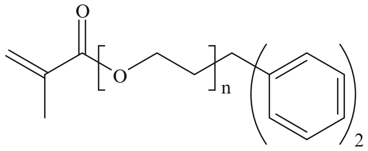
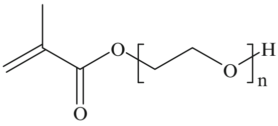
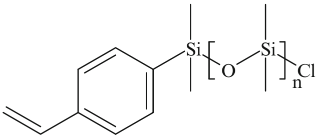
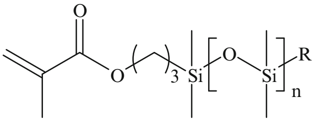
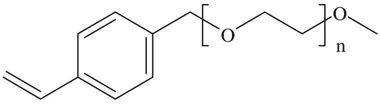
Many variations on the above technique are possible.

Table 9.1 Some macromonomers reported in the literature

Macromonomer	References
	[320]
	[321]
	[322]
	[323]
	[324]
	[325]
	[326]

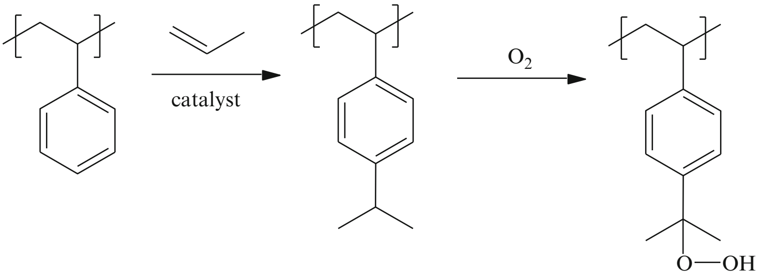
(continued)

Table 9.1 (continued)

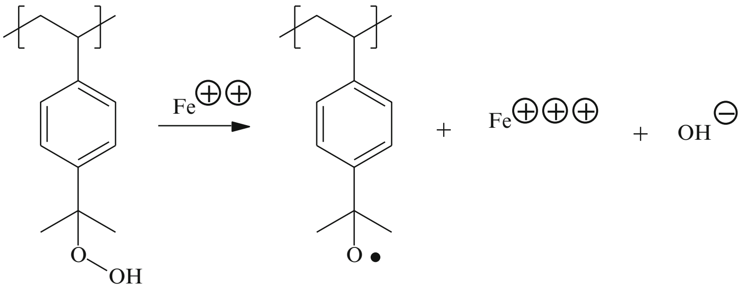
Macromonomer	References
	[327]
	[328]
	[329]
	[330]
	[331]

9.6.4 Initiations of Polymerizations from the Backbone of Polymers

High degrees of grafting by free-radical mechanism can be attained when polymerizations are initiated from the backbones of the polymer. One way this can be done is to form peroxides on the backbone structures. Decompositions of such peroxides can yield initiating radicals. Half of them will be attached to the backbones. An example is preparation of graft copolymers of polystyrene [305, 306]:



Thermal cleavage of the above peroxides leads to both macromolecules with free-radicals sites. Hydroxyl radicals also form and initiate formations of homopolymers. Decompositions of the peroxides by redox mechanisms, however, increase the yields of graft copolymers, but do not stop all formations of hydroxy radicals [303]:



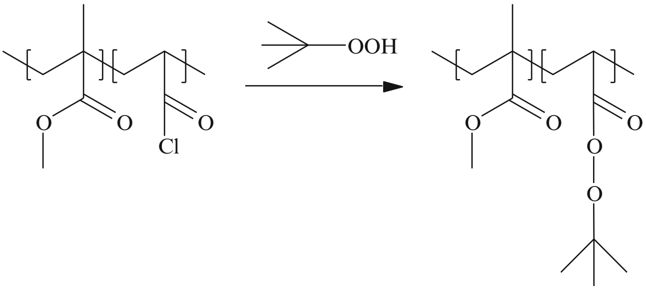
Some homopolymers still form [307].

Air oxidation of polypropylene can result in formation of hydroperoxide units at the sites of the tertiary hydrogens [383]. The polymer can also be oxidized when dissolved in cumene that contains some cumene hydroperoxide at 70–80°C. A product containing 0.8% oxygen by weight as a hydroperoxide [308] can be formed and can subsequently be reacted to form graft copolymers. Various monomers [309–311] can be used, such as vinyl acetate or 2-vinyl pyrrolidone.

Many other hydroperoxidations of polymers were reported in the literature. The materials are used in formations of graft copolymers. One example is hydroperoxidation of poly(ethylene terephthalate) and poly(ε-caproamide). The products yield graft copolymers with various acrylic and methacrylic esters and acrylic and methacrylic acids [312–314].

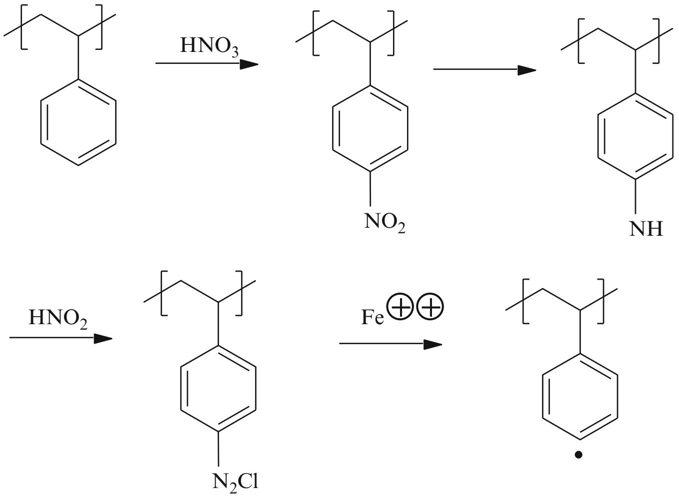
Ozone treatment of polymers can also cause hydroperoxidation of labile hydrogens. It can, however, also cause extensive degradation of the backbone polymers, because attacks by ozone on double bonds in the backbones convert them to unstable ozonides. Starch can be ozonized to form graft copolymers [315, 316]. The same is true of cellulose [317], poly(vinyl chloride) [318], and polyethylene [319]. Hydroperoxides form without noticeable degradation. This allows subsequent preparations of graft copolymers.

In a similar manner, it is possible to start with copolymers of acryloyl or methacryloyl chloride and react them with hydroperoxides [332]. This can be illustrated as follows:

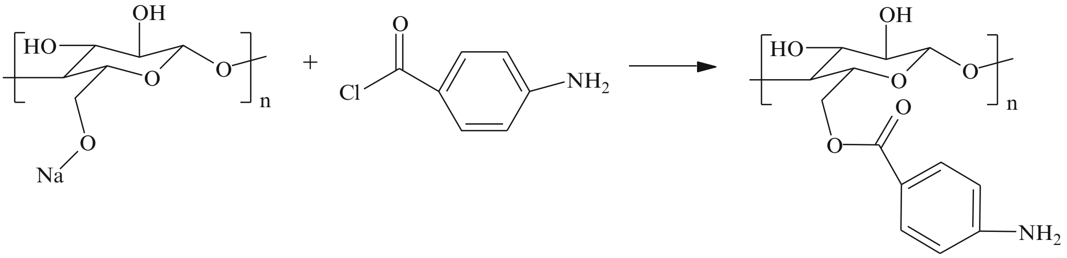


The decomposition of the pendant peroxide in the presence of vinyl monomers yields mixtures of graft copolymers and homopolymers.

Preparation and subsequent decomposition of polymers with diazonium salts can also be used to form graft-copolymers. An example is nitrated polystyrene, reduced to the amine derivative and then diazotized [333]. The decomposition of the diazonium salt results in formation of radicals:

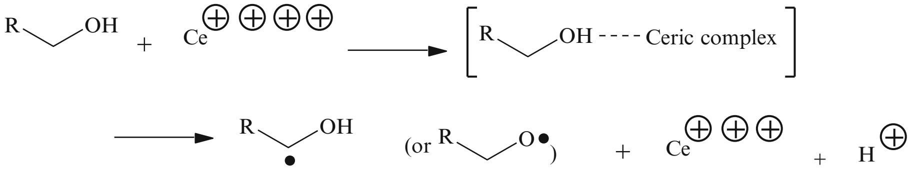


The radical sites are capable of initiating polymerizations of monomers. A similar approach can be taken with cellulose [334]. Mercerized cotton and sodium salt of carboxymethyl cellulose will react with *p*-aminophenacyl chloride:



The material can be converted to diazonium salts and then decomposed with ferrous ions in the presence of some vinyl monomers to form graft copolymers. Acrylonitrile forms graft copolymer readily without formation of any homopolymers. Styrene and vinyl acetate, however, do not. A modification of this technique is to conduct the diazotization reaction in the presence of emulsifiers [335]. The amounts of graft copolymers that form with acrylic and methacrylic monomers and *N*-vinylpyrrolidone depend upon the nature and pH of the emulsifiers, the reaction time, and the temperature.

Ceric ions form graft copolymers with various macromolecules by a redox mechanism. The reactions can be illustrated as follows:

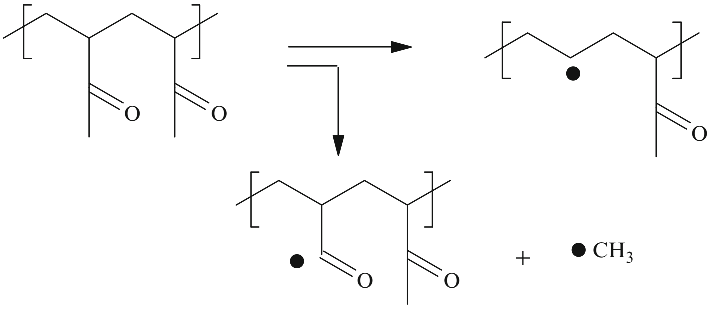


The almost exclusive formation of free radicals on the polymeric backbones results in formations of many products that are close to being free from homopolymers [346, 350]. The reactions are widely used in formations of graft copolymers of poly(vinyl alcohol) and particularly of cellulose and starch. The grafting reaction fails, however, when attempted on polysaccharides that lack free hydroxyl groups on the second and third carbons. This led to speculation [351] that the bond between these carbons cleaves. In the process, free radicals, presumably, form on the second carbons and aldehyde structures on the third carbons of the glucose units. This point of view, however, is not generally accepted. Instead, it was proposed that more likely positions for attacks by the ceric ions are at the C_1 carbons of the glucoses at the end of the polysaccharide chains [352]. This is supported by observation that oxidation of cellulose is an important prerequisite for the formation of graft copolymers [353].

Graft copolymerizations by redox mechanism can also take place with the aid of other ions. This includes grafting on cellulose backbones with ferrous ions and hydrogen peroxide [354]. Redox grafting reactions can also take place on nylon and on polyester. For instance, graft copolymers of methyl methacrylate on nylon 6 can be prepared with manganic, cobaltic, and ferric ions [355]. Another example is grafting poly(glycidyl methacrylate) on poly(ethylene terephthalate) fibers with the aid ferrous ion–hydrogen peroxide. The reaction depends on the concentration of the monomer, hydrogen peroxide, time, and temperature [356].

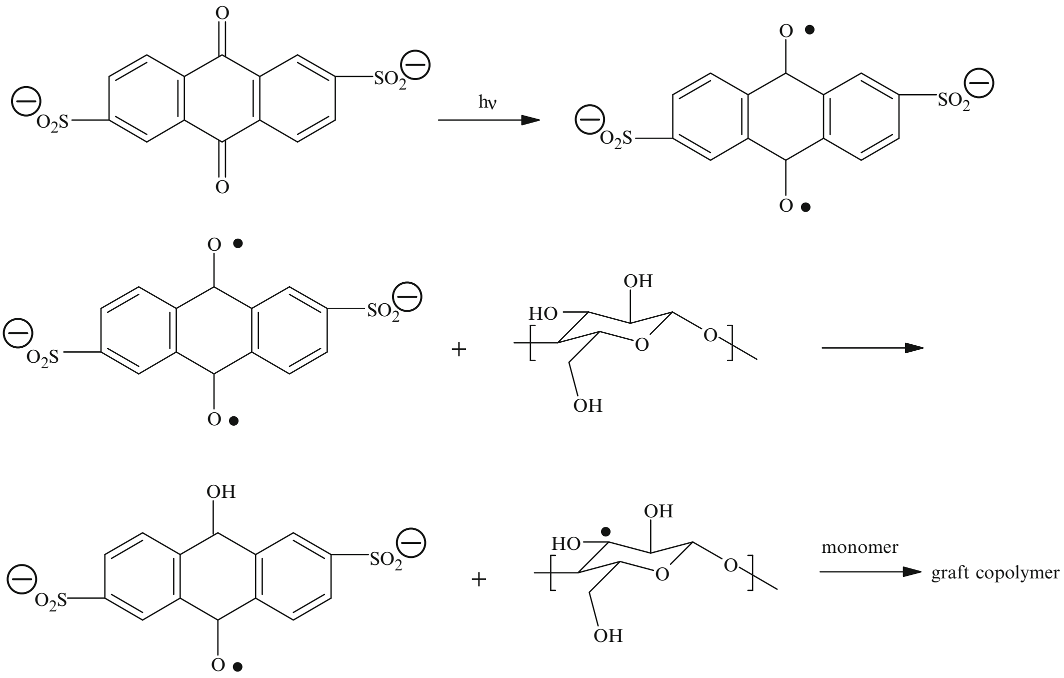
9.6.5 Photochemical Syntheses of Graft Copolymers

Photo labile groups on polymers can serve as sites for photoinitiated graft copolymerizations. For instance, when polymers and copolymers of vinyl ketone decompose in ultraviolet light in the presence of acrylonitrile, methyl methacrylate or vinyl acetate graft copolymers form [357]:



The free radicals that are unattached to the backbone polymers, like the methyl radical shown above, also initiate polymerizations and considerable amounts of homopolymers form as well.

In some instances, graft copolymers form as a result of chain transferring that takes place after photodecomposition of the photo labile materials. An example is formation of graft copolymers of polyacrylamide on natural rubber, poly(vinyl pyrrolidone), or dextrin with the aid of benzophenone and ultraviolet light [358]. The free radicals from photodecomposition of benzophenone react with the polymers by chain transferring. The growth of acrylamide is subsequently initiated from the polymer backbones. Photo tendering dyes can be used in this manner with cellulose [359]. Thus, anthraquinone dyes can be adsorbed to cellulose. Upon irradiation, proton abstractions take place, creating initiating radicals on the backbone polysaccharide:



It is believed that the above dye mono radicals disproportionate to hydroquinones and quinones. Transfer reactions to solvent lead to formations of homopolymers. This gives high yields of graft copolymers of methyl methacrylate with cellulose. The same is true of acrylonitrile [360]. On the other hand, only small quantities of graft copolymers form with styrene or vinyl acetate monomers [360].

It is also possible to form graft copolymers on the surface of fibers by coating them with photoinitiators, like benzophenone together with a monomer and then irradiating them with ultraviolet light [414]. Similar to the action of the anthraquinone dyes shown above, benzophenone in the excited triplet state mainly abstracts hydrogens and forms radicals on the surface [415].

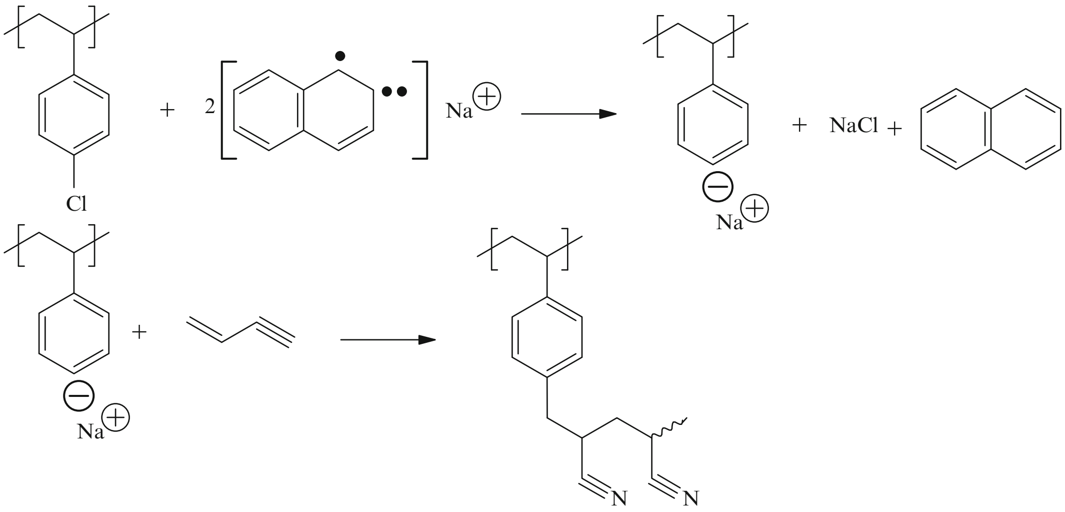
9.6.6 Graft Copolymer Formation with the Aid of High-Energy Radiation

High-energy radiation sources include gamma rays from radioactive elements, electron beams from accelerators, and gamma rays from nuclear reactors. The energy radiated by these sources is sufficiently high to rupturing covalent bonds. This results in formations of free radicals. Several different methods are used to form graft copolymers. One of them is ***irradiation in open air***. The free radicals that form scavenge oxygen and form peroxides and hydroperoxides on the polymeric chains. These are subsequently decomposed in the presence of monomers to form graft copolymers. When they are decomposed thermally [361], the hydroperoxides yield much greater quantities of homopolymers then do the peroxides. When, however, the decompositions are done at room temperature by redox mechanisms, formations of homopolymers are reduced [361, 362]. Another method is ***irradiation in vacuum***. This results in formations of trapped radicals on the polymer backbones. After irradiation, the polymers are heated in the absence of oxygen and in the presence of vinyl monomers. The best results are obtained when irradiations are done at low temperatures, below T_g of the polymers. High degree of crystallinity is also beneficial, because mobility of the chains results in loss of trapped radicals. When the monomers are added, however, heat must be applied, but this can result in loss of some of the radicals. The third method is ***mutual irradiation*** in an inert atmosphere of polymers and monomers together. The polymers are either swelled or dissolved by the monomers. The relative sensitivities of the two species, the monomer and the polymer to radiation, can be important factors in this third procedure. Efficiency of grafting depends upon formations of free radicals on the polymer backbones. If only a small number of free radicals form, the irradiations produce mainly homopolymers. Also, if the polymers tend to degrade from the irradiation, block copolymers form instead. Presence of solvents and chain-transferring agents tends to lower the amount of the grafting [363].

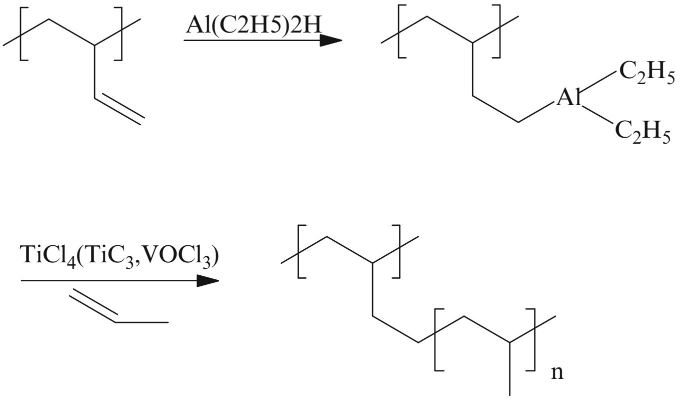
It was also shown [409] that energetic heavy ions can also produce graft copolymers. The results appear similar to those obtained by electron beams. Also, many papers reported use of plasma for surface modification of films. The process can result in formation of graft copolymers when it is accompanied by an introduction of a monomer or monomers. One such example is a use of argon plasma to graft polyacrylamide to polyaniline films [410]. The near ultraviolet light plasma induces the reaction. Other monomers that can be grafted by this reaction are 4-styrenesulfonic acid and acrylic acid [410].

9.6.7 Preparation of Graft Copolymers with Ionic Chain-Growth and Step-Growth Polymerization Reactions

Both anionic and cationic mechanisms can be used to form graft copolymers. A typical example of graft copolymer formation by anionic mechanism is grafting polyacrylonitrile to polystyrene [364]:

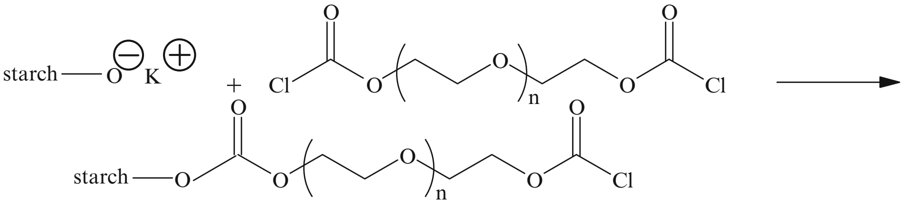


Another example of ionic graft copolymerization in a reaction carried out on pendant olefinic groups using Ziegler-Natta catalysts in a coordinated anionic type polymerization [365]. The procedure consists of two steps. In the first one, diethylaluminum hydride is added across the double bonds. The product is subsequently treated with a transition metal halide. This yields an active catalyst for polymerizations of α-olefins. By this method, polyethylene and polypropylene can be grafted to butadiene styrene copolymers. Propylene monomer polymerization results in formations of isotactic polymeric branches:



Another example is formation of graft copolymers of formaldehyde with starch, dextrin, and poly (vinyl alcohol) [366, 367]. This procedure is also carried out in two steps. Potassium naphthalene is first reacted with the backbone polymer in dimethylsulfoxide. The formaldehyde is then introduced in gaseous form to the alkoxide solution.

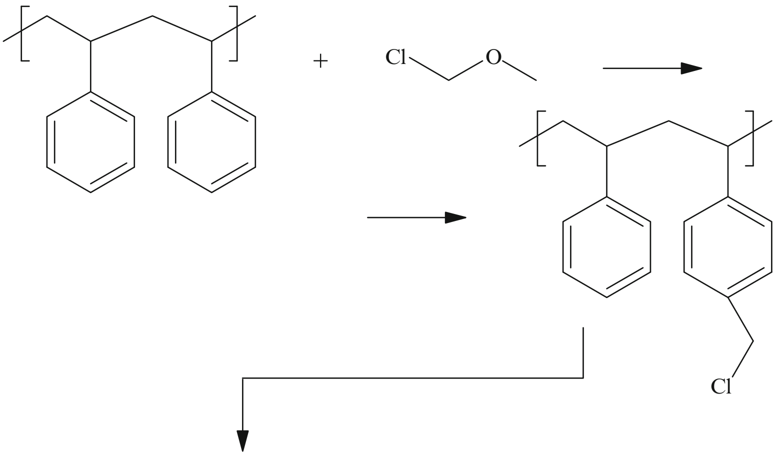
A similar reaction can be used to form graft copolymers of poly(ethylene oxide) on cellulose acetate [391]. Poly(ethylene oxide) can also be grafted to starch. For instance, a preformed polymer [392] terminated by chloroformate end groups can be used with potassium starch alkoxide:

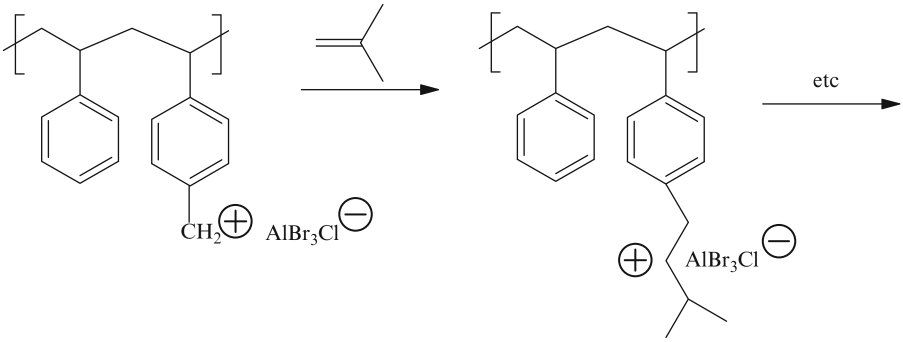


The products are water-soluble. The efficiency of the coupling process, however, decreases with an increase in the DP of poly(ethylene oxide).

Lithiated polystyrene reacts readily with halogen-bearing polymers like polychlorotrifluoroethylene [411]. This can be utilized in formation of graft copolymers. The reactions can be conducted in solutions as well as in preparations of surface grafts on films [411].

An example of a cationic grafting reaction is formation of graft copolymers of polyisobutylene on polystyrene backbones [393]. Polystyrene is chloromethylated and then reacted with aluminum bromide in carbon disulfide solution. This is followed by introduction of isobutylene:





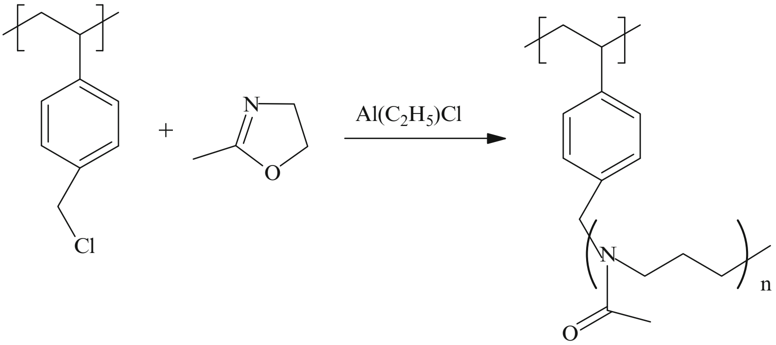
The above, however, yields only 5–18% of a graft copolymer, even at −60°C. It is possible that considerable amounts of cross-linking occur at the reaction conditions and may, perhaps, be the reason for the low yield [393].

Another example is grafting to cellulose. BF_3 can be adsorbed to the surface of the polymer. It then reacts with hydroxy groups and yields reactive sites for cationic polymerization of α-methyl styrene and isobutylene [402]. These reactions are carried out at −80°C.

Cationic graft copolymerizations of trioxane can be carried out with the help of reactive C–O–C links in a number of polymers, like poly(vinyl acetate), poly(ethylene terephthalate), and poly(vinyl butyral) [403]. Many graft copolymers can also be formed by ring opening polymerizations [404]. The reactions with active hydrogens on the pendant groups, like hydroxyl, carboxyl, amine, amide, thiol, and others, can initiate some ring opening polymerizations. An example is preparation of graft copolymers of ethylene oxide with styrene [405]. Copolymers of styrene with 1–2% of hydrolyzed vinyl acetate (vinyl alcohol after hydrolysis) can initiate polymerizations of ethylene oxide and graft copolymers form.

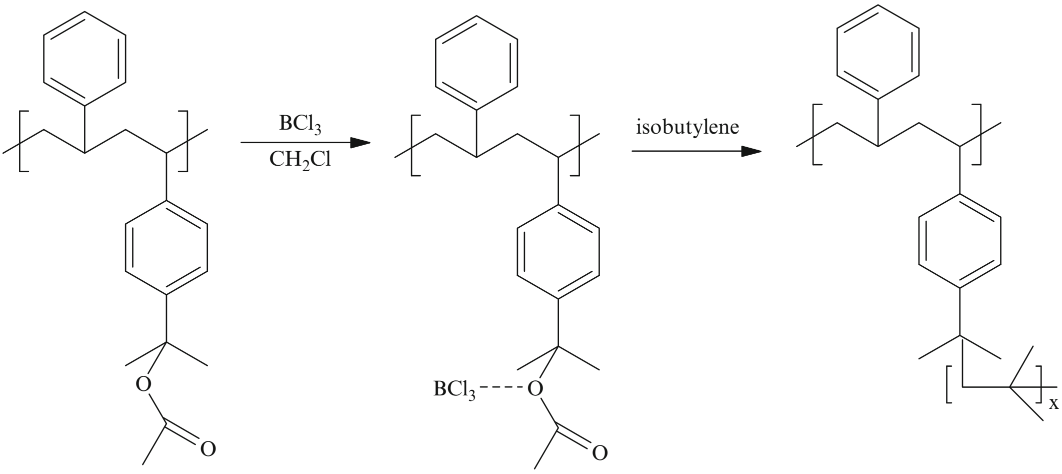
Recently, solutions of polysilanes were treated with controlled amounts of triflic acid (CF_3SO_2OH) in CH_2Cl_2 and afterwards with tetrahydrofuran. This yielded a graft copolymer of poly(tetramethylene oxide) on polysilane backbones [412].

An interesting series of papers were published by Kennedy and coworkers on use of alkylaluminum compounds as initiators of graft copolymerizations [366, 367]. Allylic chlorines form very active carbon cations in the presence of this initiator. This is also true of macromolecular carbon cation sources [402]. As a result, very high grafting efficiency is achieved in many different polymerizations using macromolecular cationogens and alkylaluminum compounds. In some instances, formation of graft copolymers is greater than 90%. The grafting reaction can be illustrated as follows [367].



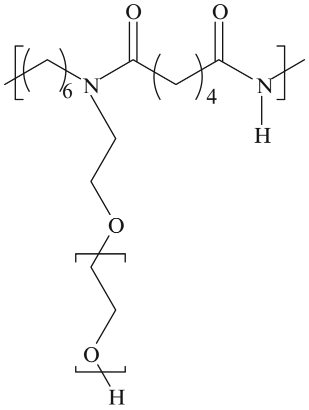
The temperatures of the reactions and the nature of the aluminum compounds are the most important synthetic variables [367].

On the other hand, many other graft copolymerizations by cationic mechanism suffer from low grafting efficiencies. They are also often accompanied by large formations of homopolymers. Use, however, of living cationic processes appears to overcome this drawback. An illustration of this can be another preparation of a graft copolymer of polyisobutylene on a polystyrene backbone [413]:



9.6.8 Miscellaneous Graft Copolymerizations

In a rather interesting reaction, ethylene oxide can be graft-copolymerized with nylon 6,6 [406]. Formation of the graft copolymer greatly enhances flexibility of the material, while the high melting point of the nylon is still maintained. Thus, nylon 6,6 that contains as much as 50% by weight of grafted poly(ethylene oxide) still melts at 221°C and has an apparent T_g below -40°C. It also maintains flexibility and other useful properties over a wide range of temperatures [406]:



An entirely different procedure can be used to form graft copolymers by a step-growth polymerization [347]. Formaldehyde is condensed with either phenol, *p*-cresol, or *p*-nonyl phenol and the resin is attached to either nylon 6, nylon 6,6, nylon 6,10, or nylon 11 backbones. Initially, the formaldehyde is prereacted with an excess of phenol in the presence of the nylon, but without any catalyst, at temperatures high enough to cause condensation. This is followed by addition of toluenesulfonic acid at lower temperatures. At that point, when free formaldehyde is no longer present in the reaction mixture to cause gelation, the novolac molecules attach themselves to the nylon backbones. The excess phenol is washed away, leaving pure graft copolymers [347].

Yagci and coworkers reported a special preparation of perfectly alternating poly(*p*-phenylene) amphilitic graft copolymers by combination of controlled free-radical polymerization and Suzuki coupling process [345].

9.7 Block Copolymers

These polymers consist of two or more strands of different polymers attached to each other. There does not appear to be any general stipulation to the minimum size of each block. There does appear to be, however, a general agreement that each sequence should be larger than just a few units. In describing a block copolymer, it is helpful if the following structural parameters are available to characterize the material:

1. Copolymer sequence distribution as well as the length and the number of blocks.
2. The chemical nature of the blocks.
3. The average molecular weight and the molecular weight distribution of the blocks and of the copolymer.

Block copolymers, particularly of the A—B—A type, can exhibit properties that are quite different from those of random copolymers and even from mixtures of homopolymers. The physical behavior of block copolymers is related to their solid state morphology. Phase separation occurs often in such copolymers. This can result in dispersed phases consisting of one block dispersed in a continuous matrix from a second block. Such dispersed phases can be hard domains, either crystalline or glassy, while the matrices are soft and rubber-like.

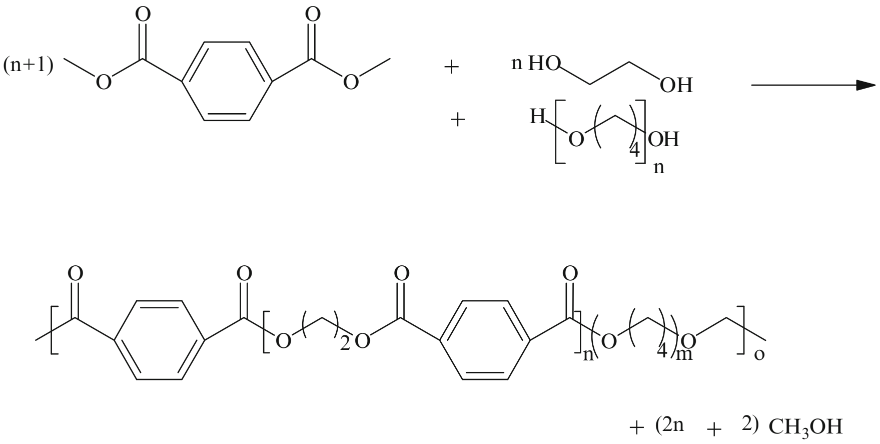
An interesting example of block copolymers is work by de Ruijter et al. [348], who prepared a series of block copolymers that contain rigid liquid crystal forming blocks of poly(*p*-phenylene terephthalamide) and flexible blocks of hexamethylene adipamide. The polymers have been prepared in a one-pot procedure by a low-temperature polycondensation reaction in *N*-methyl-2-pyrrolidone.

9.7.1 Block Copolyesters

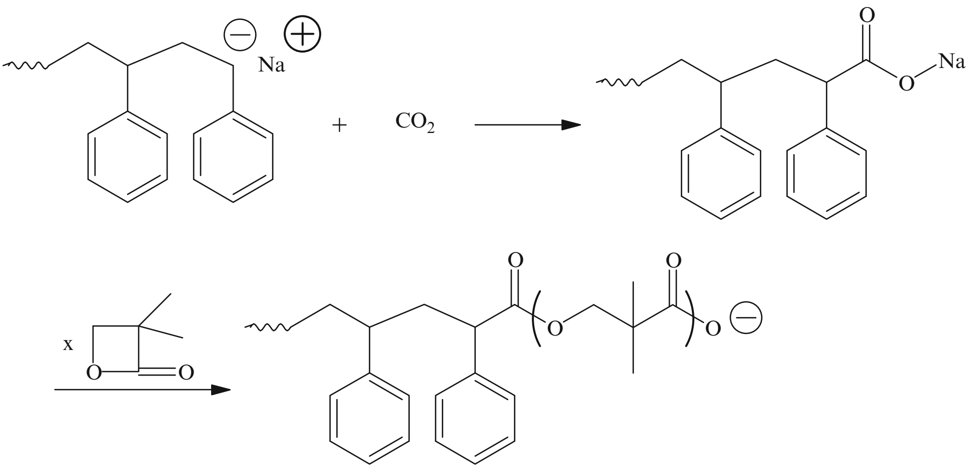
Two polyester homopolymers can react and form block copolymers in a molten state at temperatures high enough for ester interchange [414]. As the reaction mixtures are stirred and heated, the interchanges initially involve large segments. With time, however, smaller and smaller segments form as the transesterifications continue. To prevent eventual formation of random copolymers, the reactions should be limited in time.

Ester interchange can be retarded, particularly when esterification catalysts like zinc or calcium acetate are present by addition of phosphorous acid or triphenyl phosphite [415]. This improves the chances of forming block copolymers. The procedure can be applied to preparation of block copolymers of poly(ethylene terephthalate) with poly(ethylene maleate), poly(ethylene citraconate), and poly(ethylene itaconate) [416]. With ester interchange catalysts, like titanium alkoxides or their complexes, melt randomization may be inhibited by adding arsenic pentoxide that deactivates them [417].

Block copolyesters also form in reactions between hydroxy and acid chloride-terminated prepolymers [419]. This can take place in the melt or in solution in such solvents as chlorobenzene or *o*-dichlorobenzene [418]. For relatively inactive acid chlorides, like terephthaloyl chloride, high reaction temperatures are required. Phosgene also reacts with hydroxy-terminated polyesters to form block copolymers. The reactions must be carried out in inert solvents. Block copolyethers also form readily by ester interchange reactions with low molecular weight diesters [348]:



Acetates of tin, lead, manganese, antimony, and zinc as well as esters of orthotitanates catalyze the reactions [421]. Optimum temperatures for these reactions are between 230 and 260°C at 0.03–1 mm Hg pressure [421]. Block copolymers can also form by ring opening polymerizations of lactones, when carboxyl-terminated macromolecular initiators are used [422]:



9.7.2 Block Copolyamides

Simple melt blending reactions can also be applied to preparations of block copolyamides, similarly to the process for polyesters. With time, total equilibrium conditions also are gradually achieved in the melt [423]. Interfacial polycondensation is also useful in preparation of block copolymers. When mixed diacid chlorides and/or mixed diamines are reacted, the more active diacid chlorides and/or diamines react preferentially and blocks form. In addition, it is possible to carry out the growth of one of the segments first, to a fairly large size and follow it by addition of the other comonomers [424].

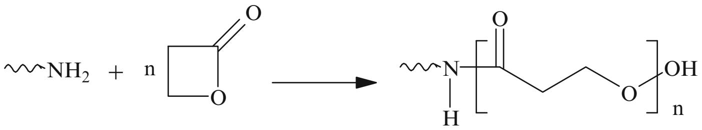
9.7.3 Polyurethane-Polyamide Block Copolymers

These block copolymers can be formed in many ways. One technique is to prereact a diamine with a diacid chloride. The polyamide that forms is then treated with bischloroformate to attach to polyurethane blocks [425]. The process can be reversed and the polyurethane can be formed first and then attached to polyamide blocks [425].

9.7.4 Polyamide-Polyester Block Copolymers

Block copolymers consisting of polyamide and polyester blocks can form through melt blending [426]. The reactions probably involve aminolyses of the terminal ester groups of the polyesters by the terminal amine groups of the polyamides. Ester interchange catalysts accelerate the reaction [427].

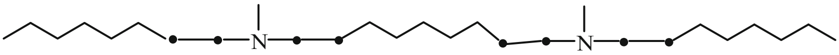
Block polyester-polyamides also form through initiation of ring opening polymerizations of lactones by the terminal amine groups of the polyamides [428]:



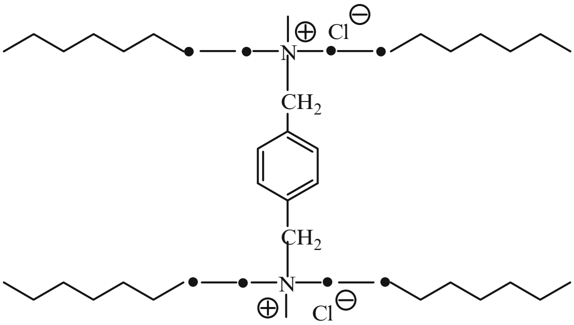
If the polyamide has terminal amine groups at both ends, then triblock copolymers form.

9.7.5 Polyurethane Ionomers

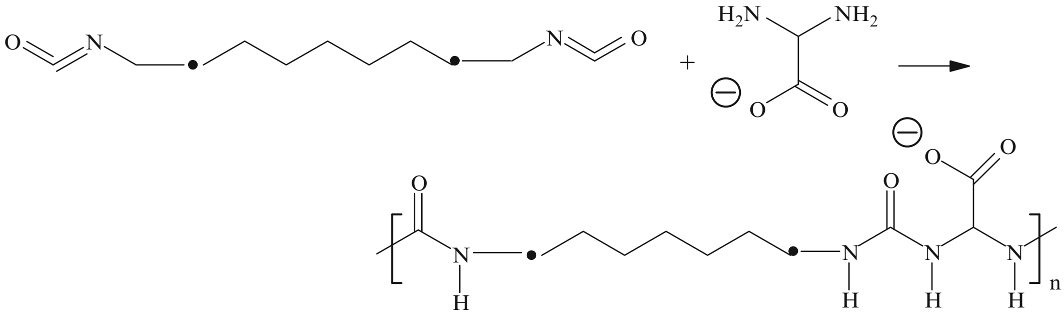
These materials were reviewed as a special class of block copolymers [433]. They are linear polyaddition products of diisocyanates containing nonrandom distributions of ionic centers. The preparations are similar to those of polyurethane elastomers that are described in Chap. 6. One example is a material prepared from high molecular weight polyester that is free from ionic centers and that is terminated by isocyanate groups at each end. The prepolymer is coupled with *N*-methylamino-2,2′-diethanol to form a segmented polymer:



Similar products form from isocyanate-terminated polyethers. This material can be cross-linked with difunctional quaternizing agents, such as 1,4-bis(chloromethyl) benzene [434]:



The products are cationic ionomers. Anionic ionomers form very similarly through coupling of chains with bifunctional anionic "chain lengtheners" [435]:



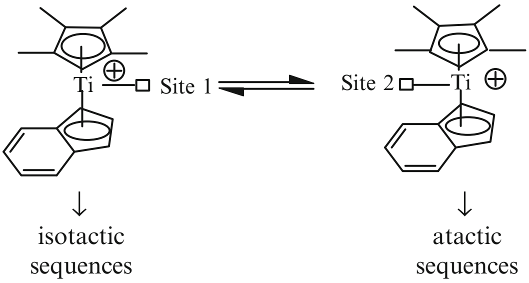
Because of interactions between the chains, the polyurethane ionomers are similar in properties to cross-linked elastomers. In solution, they are strongly associated.

9.7.6 Block Copolymers of Poly(α-Olefin)s

These block copolymers form readily when appropriate Ziegler-Natta catalysts are used [436]. This is discussed in Chaps. 4 and 6. In addition, there is a special technique for preparations of such block copolymers. At the outset of the reaction, only one monomer is used in the feed. A typical catalyst might be α-$TiCl_3/(C_2H_5)_3Al$. After the first monomer has been bubbled in for a short period, perhaps 5 min, the addition is stopped and the unreacted monomer removed by evacuation or by flushing. The second monomer is then introduced and may also be bubbled in for the same period. The addition of the second monomer may then be stopped, the second monomer evacuated, and the whole thing might be repeated. If equal length of each block is desired, the addition times of each monomer may be varied to adjust for different rates of polymerization [436].

Kuhlman and Klosin [436] reported forming multiblock copolymers of polyethylene and tuning block composition by catalyst selection. Chain shuttling, the fast exchange of growing polymer chains among catalyst centers mediated by a chain shuttling agent (CSA), has enabled the production of ethylene-based olefin block copolymers. Diethyl zinc was used as a chain shuffling agent. Thus, copolymerization of ethylene and α-olefin by certain catalyst pairs in the pretense of a CSA produces blocks that are alternately highly or lightly branched. Chain shutling polymerizations are bet conducted in continuous reactors.

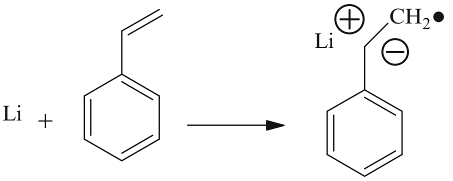
A catalyst system derived from titanocene complex and methyl-aluminoxane (see Chap. 5) has been used to polymerize propylene and, depending on polymerization conditions, produce a block copolymer of crystalline and amorphous, elastomeric polypropylene [440]:



In the above process, the formation of crystalline domains involves consecutive insertions from one of the lateral coordination sites of the catalyst so as to give rise to isotactic sequences, whereas consecutive insertions at the other site (2) give rise to atactic amorphous sequences. Interconversion between these two states must occur within the lifetime of a given polymer chain in order to generate a physically cross-linked network and is believed to occur via occasional isomerizations of the polymer chains (i.e., interconversion at the metal center). Preparation of an oscillating catalyst that yields an elastomeric polypropylene was also reported by others [441].

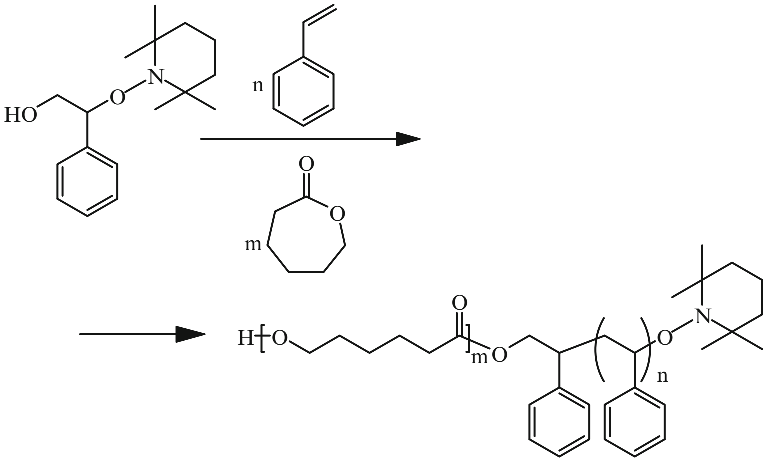
9.7.7 Simultaneous Use of Free Radical and Ionic Chain-Growth Polymerizations

This technique allows formation of many different types of block copolymers [437]. Lithium metal can be used to initiate polymerizations in solvents of varying polarity. Monomers, like styrene, α-methylstyrene, methyl methacrylate, butyl methacrylate, 2-vinylpyridine, 4-vinyl pyridine, acrylonitrile, and methyl acrylate, can be used. The mechanism of initiation depends upon formation of ion-radicals through reactions of lithium with the double bonds:



Propagation reactions proceed from both active sites, the radical and the carbanion. When two different monomers are present, free-radical propagation favors formation of copolymers, while propagation at the other end favors formation of homopolymers. There is a tendency, therefore, to form AB—B type block copolymers.

Several publications appeared recently that describe use of controlled/"living" radical polymerizations to form block copolymers. Thus, Jerome et al. [435] described formation of block copolymers by using an initiator capable of initiating simultaneously dual living polymerizations:



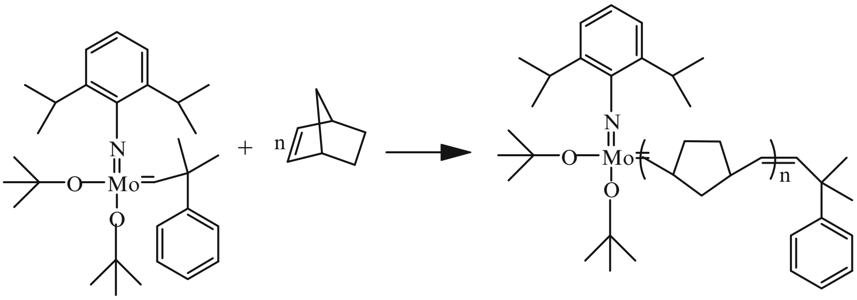
In a similar manner, Yoshida and Osagawa [436] synthesized poly(ε-caprolactone) with 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO) at one end by anionic polymerization of caprolactone using an aluminum tri(4-oxy-TEMPO) initiator. The TEMPO-supported polycaprolactone behaved as a polymeric counter radical for a controlled/"living" radical polymerization of styrene to form block copolymers [436].

Also, Kotani et al. [437] reported using controlled/"living" atom transfer radical polymerization (ATRP) to form block copolymers of ethyl and *n*-butyl methacrylates. A ternary initiating system that consists of carbon tetrachloride, tris(triphenyl-phosphine)ruthenium dichloride [$RuCl_2(PPh_3)_3$], and aluminum compounds produced ABA triblock copolymers [437].

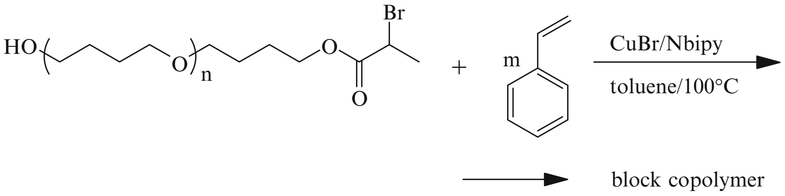
Huang and coworkers [437] reported preparation of a series of well-defined amphiphilic block copolymers containing conjugated poly(fluorene) (PF) block and coil like poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA). The block copolymers were synthesized through ATRP. The reactions were initiated by a 2-bromoisobutyrate end-capped macroinitiator using CuCl/ 1,1,4,7,10,10-hexamethyltriethylenetetramine as the catalyst.

Matron and Grubbs formed block copolymers by combining ring opening metathesis polymerization with ATRP [437]. Use was made of fast initiating ruthenium metathesis catalyst to form three different monotelechelic poly(oxa)norbornenes. The ends were functionized and ATRP polymerizations of styrene and *tert*-butyl acrylate followed.

Coca et al. [438] showed a general method of transforming living ring opening metathesis polymerization into controlled/"living" atom transfer polymerizations to form block copolymers. Ring opening polymerizations of norbornene or dicyclopentadiene were followed by Witting-like reactions with *p*-(bromomethyl)benzaldehyde to form efficient (ATP) macroninitiators for formation of block copolymers with styrene [478]:



Other cationic ring opening polymerizations can also be transformed to ATRP to yield block copolymers [439]. Thus, formation of block copolymers was initiated by poly(tetramethylene glycol) containing one bromopropionyl end group. These were used to form block copolymers by ATP polymerization of styrene, methyl methacrylate, and methyl acrylate.



9.7.8 Preparation of Block Copolymers by Homogeneous Ionic Copolymerization

Formation of block copolymers by this method depends upon the ability to form "living" chain ends. Among the anionic systems, the following polymerizations fit this requirement:

1. Polymerizations of nonpolar monomers with alkali metal-aromatic electron transfer initiators in ethers [398].
2. Polymerizations of nonpolar monomers with organolithium compounds in hydrocarbon solvents [399].
3. Acrylonitrile polymerizations in dimethyl formamide initiated by sodium triethylthioisopropoxyaluminate at −78°C [340].
4. Copolymerizations of hexafluoroacetone and cyclic oxides initiated by CsF [341].
5. Polymerization of alkyl isocyanates initiated by organoalkali species in hydrocarbons at −78°C [342].

Among the cationic "living" polymerizations that can be used for block copolymer formation are:

1. Polymerizations of isobutylene [361] and/or vinyl ethers [363] with appropriate catalysts. This includes formation of block copolymers from the two types of monomers [365].
2. Polymerizations of tetrahydrofuran with the aid of chlorobenzene diazonium hexafluorophosphate [343], triphenylmethyl hexachloroantimonate [344], or phosphorus pentafluoride [445].
3. Polymerization of *p*-methyl styrene, *N*-vinylcarbazole, and indene with appropriate catalysts.

The preparations by anionic mechanism of A—B—A type block copolymers of styrene and butadiene can be carried out with the styrene being polymerized first. Use of alkyl lithium initiators in hydrocarbon solvents is usually a good choice, if one seeks to form the greatest amount of *cis*-1,4 microstructure [346]. This is discussed in Chap. 4. It is more difficult, however, to form block copolymers from methyl methacrylate and styrene, because "living" methyl methacrylate polymers fail to initiate polymerizations of styrene [347]. The poly(methyl methacrylate) anions may not be sufficiently basic to initiate styrene polymerizations [345].

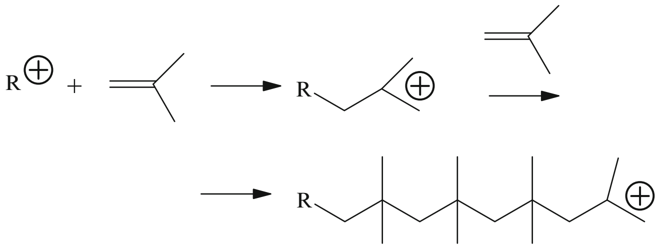
A "living" cationic polymerization of tetrahydrofuran, using BH_3 as the initiator in the presence of epichlorohydrin and 3,3-bis(chloromethyl)oxacyclo-butane [348], results in formation of block copolymers. Two types form. One is an A—B type. It consists of polytetrahydrofuran blocks attached to blocks of poly(3,3-bis(chloromethyl)oxacyclo-butane). The other one is an A—AB—B type [348].

The preparation of well-defined sequential copolymers by anionic mechanism has been explored and utilized commercially for some time now. Initially, the cationic methods received less attention until it was demonstrated by Kennedy [424] that a large variety of block copolymers can be formed. The key to Kennedy's early work is tight control over the polymerization reaction. The initiation and propagation events must be fundamentally similar, although not identical [424]:

Ion generation:

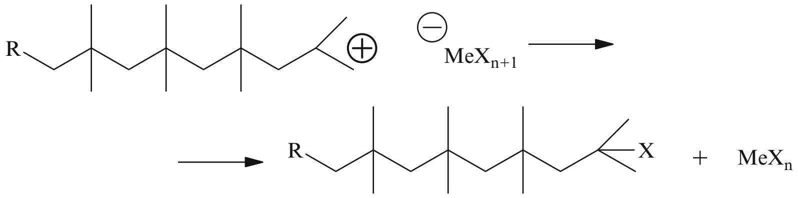
$$RX + MeX_n \rightleftharpoons R^{\oplus}MeX^{\ominus}_{n+1}$$

Cationization and propagation:



In this scheme, chain transfer to monomer must be absent and the termination is well defined.

Termination:



where X is a halogen, Me is a metal.

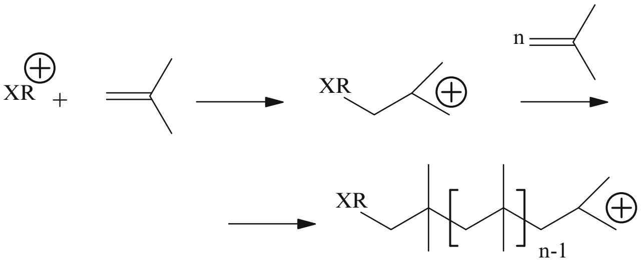
This allows formation of macromolecules with terminal halogens. They can be used to initiate new and different polymerizations.

Three methods were developed to overcome transfer to monomer [424]. These are: (1) use of *inifers*; (2) use of proton traps; and (3) establishing conditions under which the rate of termination is much faster than the rate of transfer to monomer. The first one, the inifer method, is particularly useful in formation of block copolymers. It allows preparation of *head* and *end* (α and ω) functionalized telechelic polymers. Bifunctional initiators and transfer agents (*inifers*) are used. The following illustrates the concept [424]:

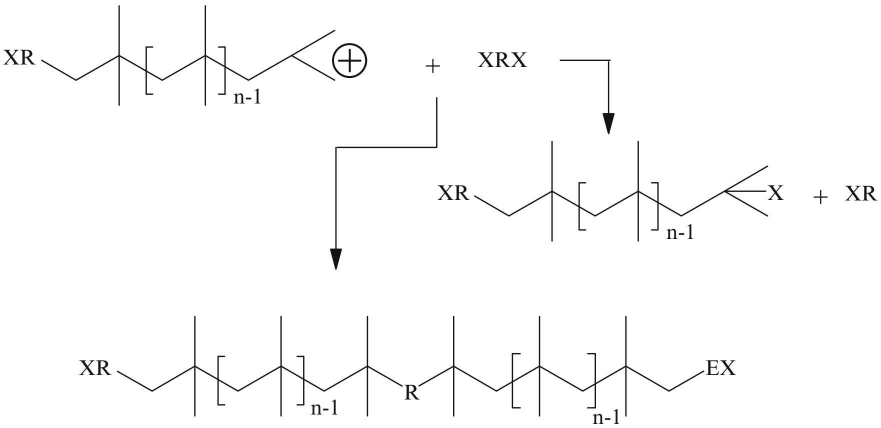
Ion generation:

$$XRX + MeX_n \rightleftharpoons XR^{\oplus} + MeX_{n+1}^{\ominus}$$

Cationization and propagation:



Chain transfer with inifers:



In the above scheme, the inifer, XRX, is usually an organic dihalide. If chain transferring to the inifer is faster than chain transferring to the monomer, the polymer end groups become exclusively terminated with halogens.

It is also possible to carry out "living" cationic polymerization of isobutylene, initiated by a difunctional initiator [435]. This results in a formation of bifunctional "living," segments of polyisobutylene that are soft and rubbery. Upon completions of the polymerization, another monomer, one that yields stiff segments and has a high T_g, like indene, is introduced into the living charge. Polymerization of the second monomer is initiated from both ends of the formed polyisobutylene. When the reaction is complete, the polymerization is quenched. Preparations of a variety of such triblock and star block polymers have been described [435].

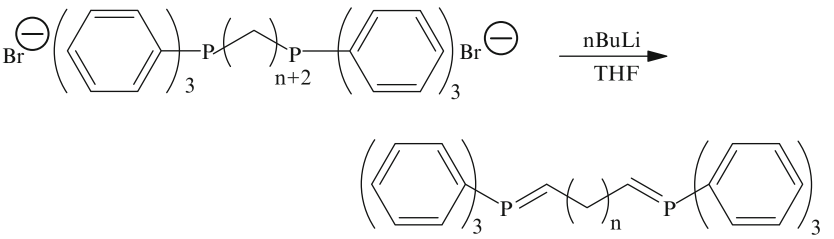
A technique was developed, by introducing cationic to anionic transformation [438]. A "living" carbocationic polymerization of isobutylene is carried out first. After it is complete, the ends of the chains are quantitatively transformed to polymerization-active anions. The additional blocks are then built by an anionic polymerization. A triblock polymer of poly(methyl methacrylate)-polyisobutylene-poly(methyl methacrylate) can thus be formed. The transformation takes several steps. In the first one, a compound like toluene is Friedel-Craft alkylated by α,ω-di-*tert*-chloropolyisobutylene. The ditolylpolyisobutylene, which forms, is lithiated in step two to form α,ω-dibenzyllithium polyisobutylene. It is then reacted with 1,1-diphenylethylene to give the corresponding dianion. After cooling to −78°C and dilution, methyl methacrylate monomer is introduced for the second polymerization [438] in step 3.

Formation of block copolymers from polymers with functional end groups has been used in many ways. In anionic polymerization, various technique were developed for terminating chain growth with reactive end groups. These end groups allow subsequent formations of many different block copolymers. One such active terminal group can be toluene diisocyanate [439]. The isocyanate group located ortho to the methyl group is considerably less reactive toward the lithium species due to steric hindrance [438]. The unreacted isocyanate group can be used for attachment of various polymers that are terminated by hydroxy, carboxy, or amine groups. Other functional compounds that can be used in such reactions are alkyl or aryl halides, succinic anhydride, *n*-bromophthalimide [448], and chlorosilanes [449].

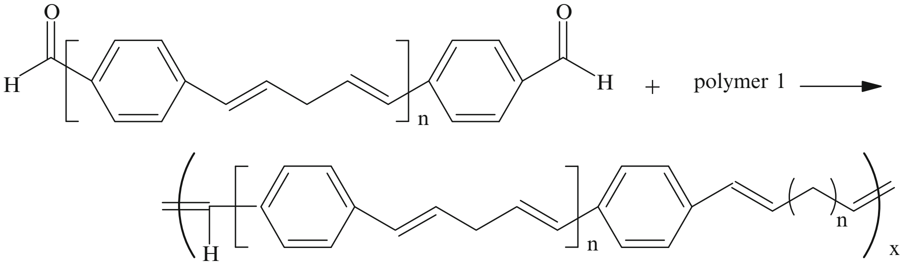
Because block copolymers can often offer properties that are unattainable with simple blends or random copolymers [364], many efforts were made to combine dissimilar materials, like hydrophilic with hydrophobic, or hard with soft segments, as was shown earlier. One paper [432] describes formation of block copolymers containing helical polyisocyanide and an elastomeric polybutadiene. Compound $[(\eta^3\text{-}C_3H_5)\text{-}Ni(OC(O)CF_3)]_2$ was used to carry out "living" polymerization of butadiene and then followed by polymerization of *tert*-butyl isocyanide to a helical polymer.

9.7.9 Special Reactions for Preparation of Block Copolymers

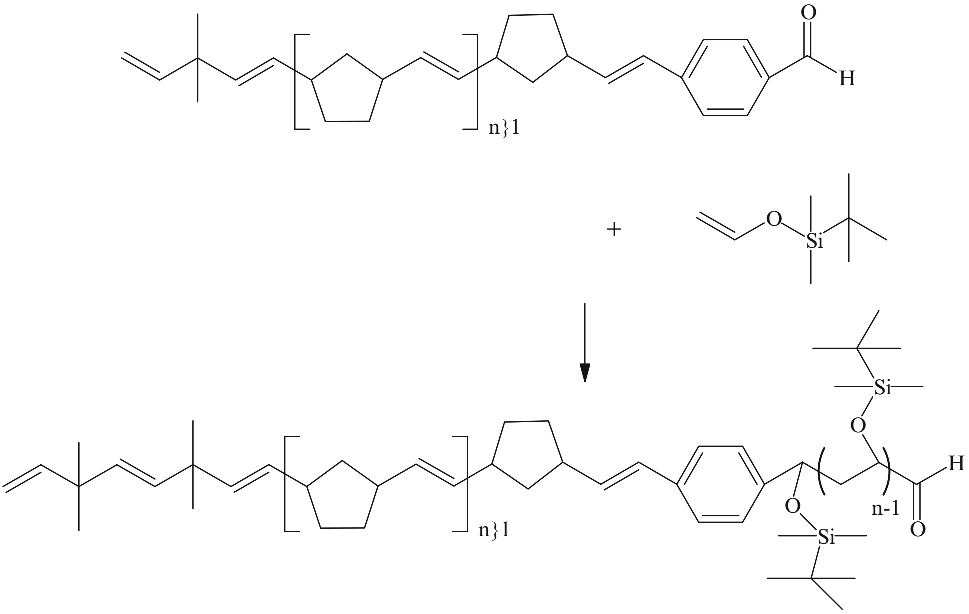
A special case is the use of the *Witting* reaction. Poly(*p*-phenylene pentadienylene) [415] is prepared by this reaction first. This is utilized in a preparation of a block copolymer [456] according to the following scheme:



polymer 1

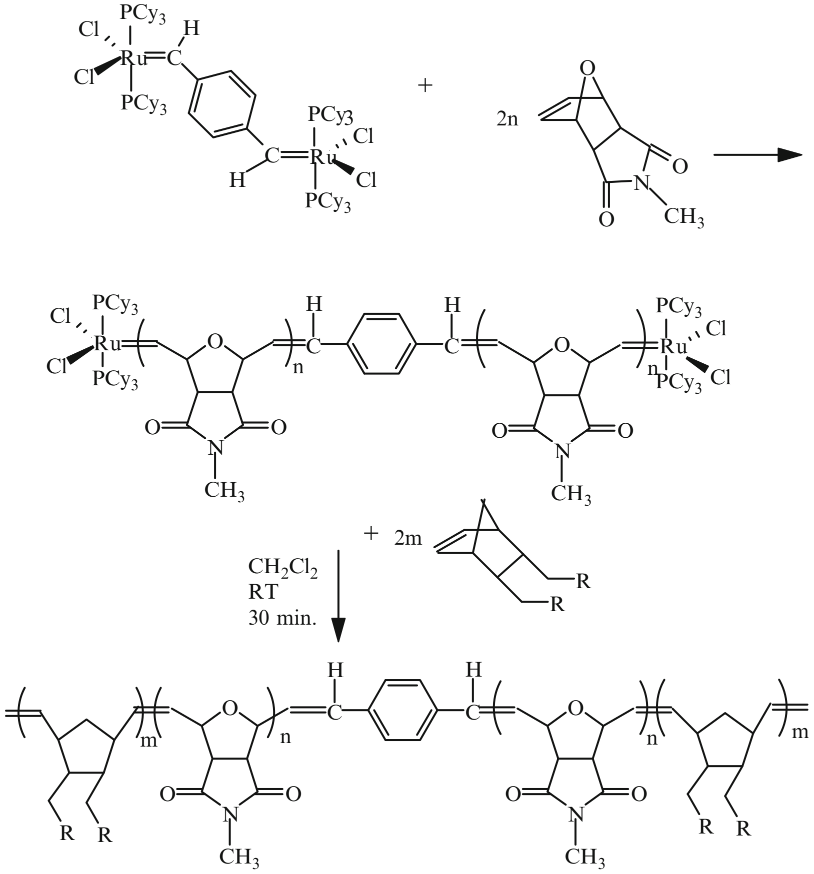


A preparation of block copolymers by “living” ring-opening olefin metathesis polymerization was reported [417]. Initially, norbornene or *exo*-dicyclopentadiene are polymerized by bis(η^5-cyclopentadienyl)titanacyl butane. The resulting living polymers are then reacted with terephthaldehyde to form polymers with terminal aldehyde groups. The aldehyde groups in turn initiate polymerizations of *t*-butyldimethylsilyl vinyl ether by aldol-group transfer polymerizations [418]. Following is an illustration of the process:

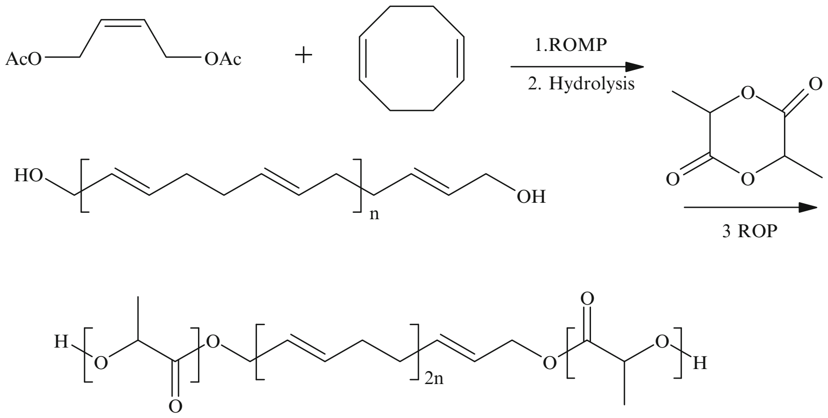


Subsequently, the terminal aldehyde group is reduced with $NaBH_4$ and the silyl groups cleaved off by treatment with tetrabutylammonium fluoride to produce a hydrophobic-hydrophilic A—B diblock copolymers.

Living metathesis type polymerization was also employed to form block copolymers from norbornene and its derivative with bimetallic ruthenium catalysts, $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4CH=)RuCl_2(PR_3)_2$ [434]. This can be illustrated as follows [434]:



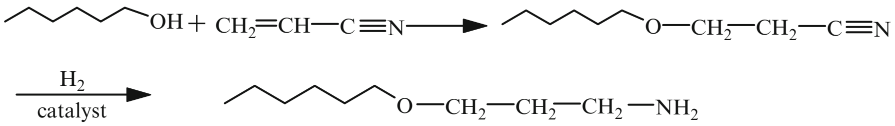
Pitet and Hillmyer [436] formed triblock copolymers from 1,5-cyclooctadiene and DL-Lactide by combining ring opening metathesis polymerization with cyclic ester ring opening polymerization.



Proto et al. [434] living isoselective coordination polymerization of styrene to form isoselective block copolymers. This was accomplished by sequential monomer addition.

9.7.10 Miscellaneous Block Copolymers

Polyamide-polyether block copolymers can be formed by a variety of techniques. One of them consists of initial preparation of amine-terminated polyethers. This can be done by reacting hydroxy-terminated polyethers with acrylonitrile and then reducing the nitrile groups to amines [429]:

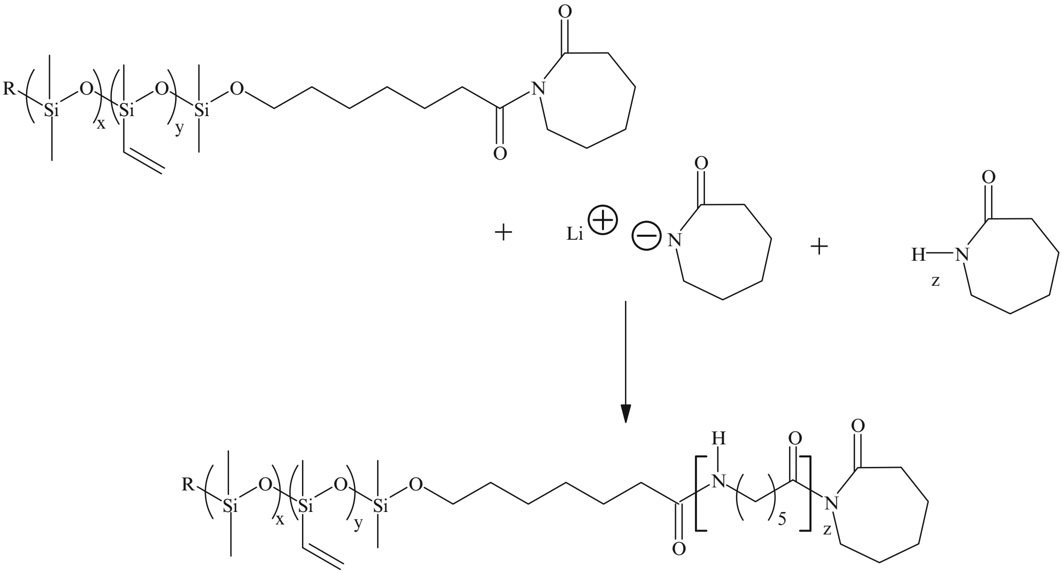


The products of the reduction condense with carboxylic acid-terminated polyamides to form block copolymers.

Another one is to form the polyethers with terminal chloride groups [430]. Hydroxy-group-terminated polyethers, for instance, can be converted to halogen-terminated polyethers. The products will react with ammonia and the amine-terminated polymer will react with carboxylic acid-terminated polyamides [430].

A British patent describes preparations of block copolymers in two steps. In the first one, two different salts of hexamethylene diamine are formed; one with carboxylic acid-terminated polyoxyethylene and the other one with adipic acid (nylon 6,6 salt). In the second step, the two salts are reacted in the melt. Caprolactam can be used in place of the second salt [431]. Also, a Japanese paper describes formations of block copolymers by reacting polyoxyethylene in melt condensation reactions with caprolactam in the presence of dicarboxylic acids [432].

Polyamide-6 (nylon 6) can form block copolymers with rubber [419] and with poly(dimethylsiloxane) [420]. In the latter case, the polysiloxane forms first by "living" polymerization and is terminated by an acylated caprolactam. The caprolactam portion of the molecule is then polymerized with the aid of lithium caprolactamate:



This diblock copolymer can be melt annealed at ca. 250°C. It exhibits superior mechanical properties to nylon 6 homopolymer [420].

9.7.11 Mechanochemical Techniques for Formation of Block Copolymers

These techniques rely upon high shear to cause bond scissions. Ruptured bonds result in formations of free radical and ionic species [413]. When this application of shear is done in the presence of monomers, block copolymers can form. This approach is exploited fairly extensively. Such cleavages of macromolecules can take place during cold mastication, milling, and extrusion of the polymers in the visco-elastic state. Both homolytic and heterolytic scissions are possible. The first one yields free radical and the second one ionic species. Heterolytic scissions require more energy, but should not be written off as completely unlikely [413]. Early work was done with natural rubber [413]. It swells when exposed to many monomers and forms a visco-elastic mass. When this swollen mass is subjected to shear and mechanical scission, the resultant radicals initiate polymerizations. The mastication reaction was shown to be accompanied by formation of homopolymers [413]. Later the technique was applied to many different polymers with many different monomers [414].

9.8 Processes in Polymer Degradation

There are many causes of degradation of polymers. The chief ones among them are heat, oxidation, light, ionic radiation, hydrolysis, and mechanical shear. The effect can be discoloration, loss of molecular weight, cross-linking, or cyclization. The loss of molecular weight can be so severe that the polymer is degraded to a mixture of monomers and oligomers. The other effects can be blackening or charring and loss of useful properties. On the other hand, mechanical shearing is often applied to some polymers like rubbers to deliberately reduce molecular weight for commercial processing. In the environment, synthetic polymers generally degrade due to man-made environmental pollutants in the atmosphere, like carbon monoxide, sulfur dioxide, nitrogen oxide, and oxidizing smog rich in ozone.

Molecular weight loss occurs through the breaking of primary valence bonds. Such chain scissions may occur at random points along the polymer backbone or they may take place at the terminal ends of the polymer where monomer units are released successively. This last effect can be compared to *unzipping*. The response of any particular polymeric material to specific causes of degradation depends upon the chemical structure.

This chapter presents the degradation processes in some typical commercial polymers. The materials selected were those that received major attention in the literature.

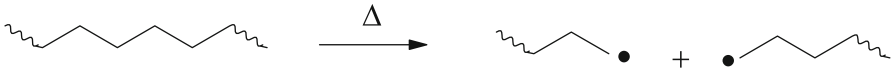
9.8.1 Thermal Degradation of Common Chain-Growth Polymers

Thermal degradation of polymers is conveniently studied by pyrolytic methods. The polymer literature contains many reports on such studies conducted at various temperatures in inert atmospheres, in air, or in vacuum. The volatile products are usually monitored with accompanying measurements of the weight loss per unit time. The reaction rates are thus measured by:

1. Loss of molecular weight as a function of temperature and the extent of degradation
2. The quantity and the composition of the volatile and nonvolatile products of degradation
3. The activation energy of the degradation process

A general scheme for thermal degradations of chain-growth polymers by free-radical reactions can be written as follows:

Random type chain scission:



Chain-end type scission:

In a thermal chain depolymerization, the degradation can also be random. Rupture occurs at various points along the chain. The products are various size fragments of the polymer, usually larger than individual monomers. Both reactions shown above can take place simultaneously in the same polymer chain or only one of them might take place exclusively. Also, chain depropagation may not necessarily be initiated from the terminal ends of the macromolecules, though such depolymerizations are more common. They may instead start from some points of imperfection in the chain structures. These imperfections might consist of incorporated initiator fragments, or peroxides, or ether links. They might have formed as a result of oxygen molecules being present during chain growths. Weak points in polymer backbones can also be at locations of some tertiary hydrogens. Each individual polymer will depolymerize at its own specific rate and the degradation products will be peculiar to the particular chemical structure of the polymer [446–452]. For instance, poly(methyl methacrylate) can be converted almost quantitatively back to the monomers. The depolymerization occurs from the terminal end in an unzipping fashion with the overall molecular weight decreasing slowly in proportion to the amount volatilized. Polyethylene, on the other hand, undergoes scission into longer olefin fragments. Very little monomer is released. At the same time, the molecular weight tends to decrease rapidly and only a small amount of volatilization takes place. The two polymers are good examples of extreme behavior of chain-growth polymers. Most of the chain-growth polymers, however, fall between the two. The depolymerization reaction of chain-growth polymers generally occurs by a free-radical mechanism and the reactions are similar. If depropagation is the major portion of the degradation process, then the molecular weight reduction is proportional to the quantity of the monomer that forms. If, on the other hand, chain transferring is the major portion of the degradation process, then there is rapid loss of molecular weight with little accompanying monomer accumulation and the reaction products are large segments of the chains. The rate of depolymerization exhibits a maximum.

When depropagation takes place at an elevated temperature, at a rate that is equal to the propagation in a free-radical polymerization, then the temperature of the reaction is a ceiling temperature (see Chap. 3). Termination can take place by disproportionation. Secondary reactions, however, may occur in the degradation process depending upon the chemical structure of the polymer. Such side reactions can, for instance, be successive eliminations of hydrochloric acid, as in poly(vinyl chrolide), or acetic acid as in poly(vinyl acetate).

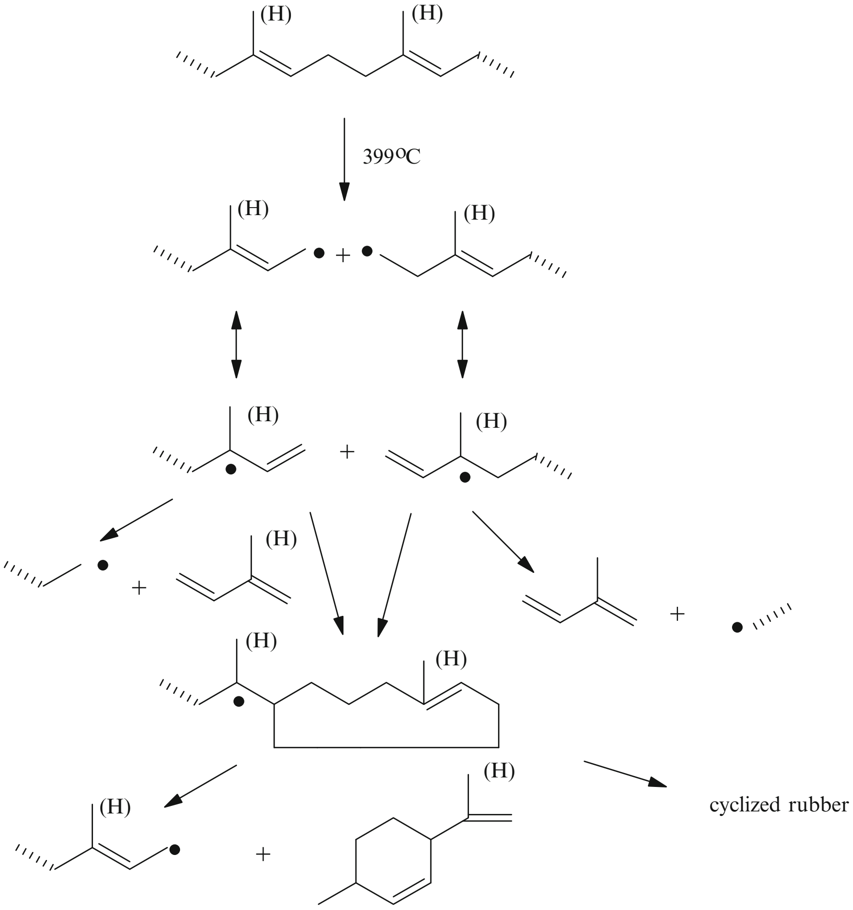
9.8.2 *Thermal Degradation of Polyolefins and of Polymers from Conjugated Dienes*

One early study of *thermal degradation of polyethylene* was carried out on low molecular weight polymers [453]. Later the work was repeated with high-density polyethylene [454]. The volatile products were identified by gas chromatography. The biggest portion of the volatiles was found to be propylene.

The remaining materials were methane, ethane, propane, and a number of unsaturated and saturated higher hydrocarbons. The quantity of ethylene increased slightly with an increase in the temperature of pyrolysis. Formation of propylene can occur in two ways. The first one is through intramolecular radical transfer to the second carbon, followed by a decomposition reaction. This, however, is not believed to contribute significantly to the quantity of propylene obtained, based on theoretical consideration [454]. The second one can occur as a result of scissions of C–C bonds located in the positions β to the terminal double bonds. Such double bonds probably form in large quantities during decomposition and this process is thought to be the main source of propylene [454]:

It was observed that *isotactic polypropylene decomposes* thermally by a mechanism that varies at different temperatures and conditions [455]. Thus, at 340°C the major volatile product is propane, while at 380°C it is *n*-pentane, and at 420°C it is propylene. The propane is believed to originate from some weak spot in the polymeric chain. Formation of *n*-pentane involves a radical abstraction and a six-membered ring formation in a backbiting process. Propylene may come from a free-radical depolymerization process or a cyclic six-membered ring formation involving a terminal double bond [455].

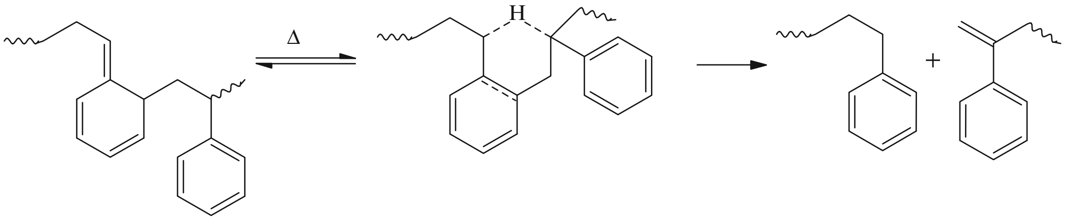
The thermal *degradation of diene polymers* was the subject of several studies [456, 457]. The scheme for polyisoprene and polybutadiene degradation was postulated in part by Golub and Garguila [458, 460]. It is based on infra-red spectra and NMR studies of the products:

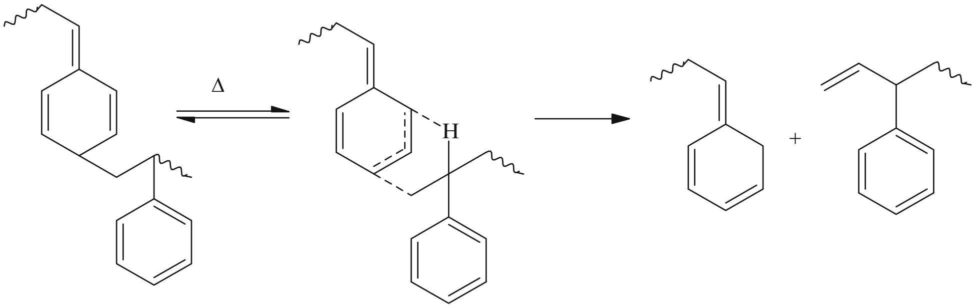


In addition, spectroscopic evidence shows that *cis–trans* isomerizations as well as cyclizations occur in the process of thermal degradation of 1,4-polyisoprene. It is interesting that the *cis–trans* isomerizations were observed at temperatures as low as 200°C [460].

9.8.3 Thermal Degradation of Polystyrene and Polystyrene-Like Polymers

Thermal *degradation of atactic polystyrene* results in formation of volatile products that contain as much as 42% of the monomer and small quantities of toluene, ethylbenzene, and methylstyrene. The rest of the volatile material is made up of dimers, trimers, and tetramers. No large fractions were isolated. This suggests that the main mechanism of decomposition is depropagation. The rate, however, exhibits a maximum and there is a rapid decline in molecular weight. This indicates scission of the chains. Some evidence was presented that rapid decrease in molecular weight is a result of scission of weak points in the polymer and is independent of the free-radical depropagation reaction [461–465]. Some of the weak spots are believed to be occasional “head-to-head” placement of monomers [19]. It was suggested that some weak spots may also be structures that form as a result of monomer additions to the aromatic ring during the chain growth (see Chap. 6) [466]. The following scheme of chain scission was, therefore, proposed [466]:





The identity of the weak spots, however, has not been established with certainty [467]. The evidence does indicate that the “weak points” are head-to-head bonds, branch points, or unsaturated structure [467].

The rate of conversion of polystyrene into volatiles was measured in numerous studies.

In contrast to polystyrene, poly(α-methyl styrene) yields in vacuum pyrolyses at temperatures between 200 and 500°C 95–100% monomer. By comparison, polystyrene only yields about 40.6% [457]. The difference can be attributed to the fact that hydrogen transfer is completely blocked from the sites of chain scission by the methyl groups in the α-positions [457]. As a result, the terminal free-radicals unzip into monomers and dimers.

Polystyrenes that are substituted on the benzene ring, like poly(vinyl toluene), behave similarly to polystyrene when pyrolyzed [457]. Also, poly(*m*-methylstyrene) at 350°C yields 44.4% monomer as compared to polystyrene that yields 40.6% monomer at these conditions. The rate, however, for polystyrene at this temperature is 0.24 mol.%/min, while for poly(*m*-methylstyrene) it is 0.9 [457].

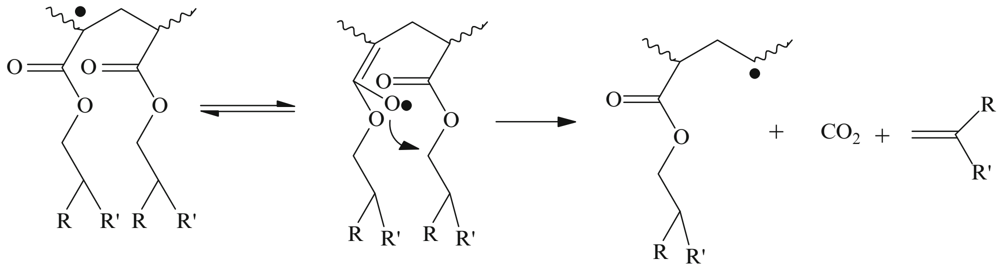
9.8.4 Thermal Degradation of Methacrylic and Acrylic Polymers

The thermal degradation of *polymers of acrylic* and *methacrylic alkyl esters* is a process of depolymerization to monomers at temperatures up to 250°C, provided that the alkyl group is small, less than butyl [468]. Poly(*t*-butyl methacrylate) yields quantitatively isobutene instead. It was shown that thermal depolymerization to monomers is probably common to all poly(methacrylate ester)s. As the size of the alkyl group increases, however, particularly within secondary or tertiary structures, there is increased tendency for the alkyl group to also decompose. This decomposition interferes with the depolymerization process

Thermal stability of poly(methyl methacrylate) appears to vary with the molecular weight. For instance, a sample of the polymer of molecular weight of 150,000 when heated in vacuum for 30 min at 318°C yields 74.3% volatiles. By comparison, a sample of this polymer of molecular weight of 5,100,000 when heated for 30 min at 319°C yielded only 35.2% volatiles [456].

The thermal stability of copolymers of long-chained diol dimethacrylates was investigated [583]. These copolymers included 1,4-butane-, 1,5-pentane-, 1,6-hexane-, 1,8-octane-, 1,10-decane-, or 1,12-dodecanediol dimethacrylates, respectively, as well as 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]propane and triethylene glycol dimethacrylate. The polymers were found to be thermally stable up to ≈250°C, as shown by the initial decomposition temperature and their degradation profiles.

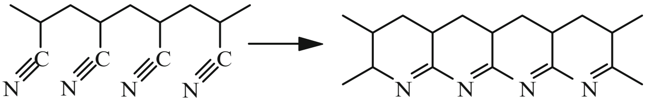
A quantitative investigation of the thermal degradation of poly(ethyl acrylate), poly(*n*-propyl acrylate), poly(isopropyl acrylate), poly(*n*-butyl acrylate), and poly(2-ethylhexyl acrylate) demonstrated that the principle volatile products are carbon dioxide, olefin, and alcohol corresponding to the alkyl group [469, 470]. The following mechanism of degradation was proposed [469, 470]:



More recently, another study was carried out on the thermal decomposition of homopolymers of ethyl methacrylate, *n*-butyl methacrylate, and 2-hydroxyethyl methacrylate as well as their copolymers [471]. The copolymers of hydroxyethyl methacrylate with ethyl methacrylate and butyl methacrylate were found to degrade by unzipping to yield the monomers similarly to poly(methyl methacrylate). In addition, there is competition between unzipping and cross-linking in binary copolymers of hydroxyethyl methacrylate with ethyl methacrylate and in *n*-butyl methacrylate.

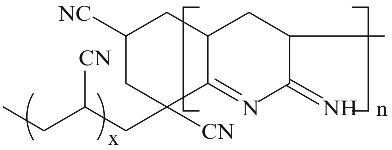
Thermal degradation of *nitrile polymers*, particularly acrylonitrile, was studied in detail [472–478]. It was shown that there can be two paths of degradation, depending upon the temperature (see also Chap. 8). One reaction takes place at a low temperature, between 100 and 200°C, and the other one occurs above 240°C. At the low temperature, the polymers develop dark color. There is, however, very little evolution of volatiles. At the high temperature, on the other hand, there are evolutions of volatiles and thermally stable residues develop.

The low temperature darkening process of polyacrylonitrile was shown to be intramolecular cyclization and polymerization of the cyanide groups [475, 476]. The overall reaction can be illustrated as follows:



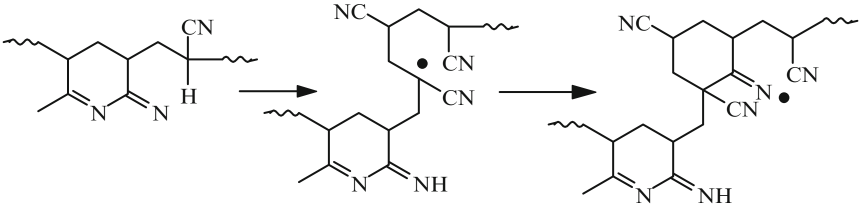
The above shown ladder structure is actually a vary idealized picture. Nevertheless, the formation of fused tetrahydropyridine rings was demonstrated by IR data [475, 476]. At the same time, there are many irregularities in the above shown structure. Also, it was demonstrated that the longer are the isotactic sequences in the polymeric structures, the longer are the sequences of ladder structures that form [479].

High temperature degradation of polyacrylonitrile leads to formation of oligomers. The general form of the oligomerized material can be shown as follows [480]:



where, $x = 0–2$ and $n = 0–5$.

The above structure occurs as a result of an initiation and termination process of cyclization at frequent intervals along the chain. The growth of the ladder structure, however, terminates due to hydrogen transfer. This process is associated with the atactic sequences in the polymer chain:



Polymethacrylonitirle develops color upon heating as a result of linking up of adjacent carbons and nitrogen atoms in intramolecular cyclization reactions similar to acrylonitrile.

This reaction is initiated primarily by impurities that are often present in the polymer both at the end of the chains and at various locations at the backbones. Due to this ring formation, the amount of monomer that can be obtained from the polymer at 200°C is approximately 50%. If, however, the polymer is prepared from highly purified monomer, the yield of monomer upon thermal degradation at 300°C is 100%. Also, a yellow color does not develop from such a polymer at temperatures of 120–220°C [457].

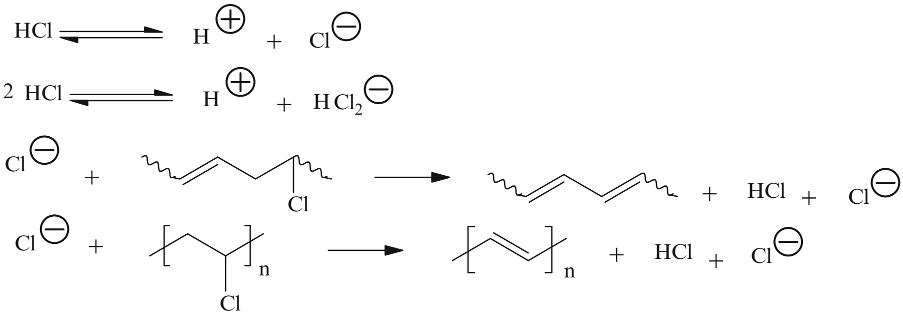
Poly(vinylidine cyanide) has the structure that would suggest formation of a double ladder polymer upon pyrolysis. It was shown, however, in an early study that this does not happen. Instead, the polymer mostly depolymerizes [481, 482].

9.8.5 Thermal Degradation of Chlorocarbon and Fluorocarbon Polymers

The thermal instability of *poly(vinyl chloride)* is a cause for concern commercially and has, therefore, stimulated extensive investigations. The overall process of degradation is complex and still not completely resolved. Some of the questions that remain are:

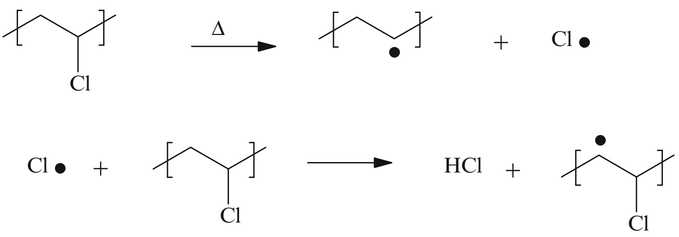
1. Is the overall process of degradation ionic or free radical in nature?
2. What is the exact mechanism of initiation?

It is easily observable that the degradation is accompanied by evolution of HCl and blackening of the polymer. Also, at elevated temperatures, poly(vinyl chloride) not only gives off hydrogen chloride, but this dehydrochlorination is also accompanied by rapid depolymerization [483]. The rate of decomposition decreases with increasing molecular weight and is highest in oxygen and lowest in helium atmosphere. It was claimed that HCl exerts no catalytic effect upon the rate of decomposition [483]. This contrasts with evidence that was presented earlier that HCl does accelerate thermal degradation [484]. The earlier evidence was obtained from autocatalytic decmposition of films. Based on that eveidence, it was hypothesized that the chloride ion acts as a base (supporting an ionic mechanism of decomposition) [484]:

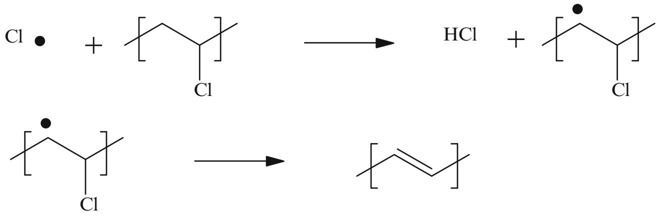


In a more recent study, HCl was also found to be essential for the initiation of the unzipping process, but may or may not be essential to the depolymerization reaction itself, once the process has been started [485]. The above shown ionic mechanism was disputed in a study where ESR signals were recorded during thermal decomposition of the polymer at elevated temperatures [486]. This strongly supports a free-radical mechanism. A free-radical mechanism was proposed earlier by Bamford and Feuton [487]. This mechanism illustrates the formation of hydrochloric acid and is based on rupture of carbon–chlorine bonds:

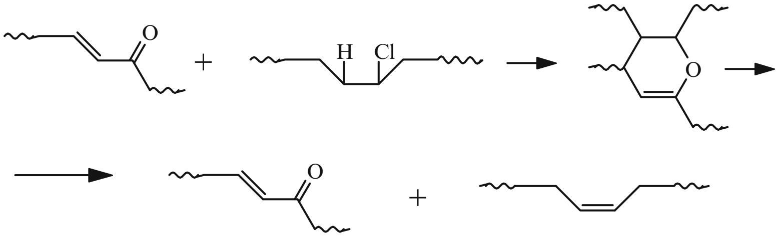
Initiation:



Propagation:

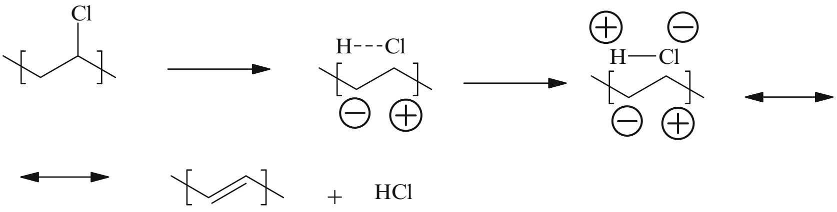


Subsequent interaction of macromolecular radicals leads to cross-linking. Many additional investigations demonstrated that thermal decompositions of vinyl polymers with pendant electronegative groups that we can designate as X, result, after elimination of HX and formation of macromolecular residues, with polyene structures [488]. In addition to that, at higher temperatures the polyene sequences that form rearrange into a large numbers of aromatic hydrocarbons [489–492]. Formation of polyenes is common to poly(vinyl chloride), poly(vinyl bromide), poly(vinyl alcohol), and poly (vinyl acetate) [493]. The polyene structures partly decompose at formation due to bond stress and molecular reorganization processes. The stresses result from formation of conjugated structures along the polymeric chains. When the chains fracture, the remaining portions of polyene sequences form aromatic compounds [47]. It was postulated that the process initially involves reactions of enone groups, which are present in poly(vinyl chloride) as anomalies, with chlorine units of a neighboring polymeric chains [494, 495]:



The first step is formation of a dihydropyran ring. This is followed by a retro-Diels-Alder splitting and leads to regeneration of the α,β-unsaturated ketone and to formation of a double bond in the poly (vinyl chloride) molecule. The double bond initiates a subsequent elimination of hydrogen chloride from that molecule [495].

An intramolecular initiation process that explains constant rate of dehydrochlorination was also proposed [496]:



It was pointed out that poly(vinyl chloride) is, in a sense, its own worst enemy, in that all the structural defects that are known to contribute appreciably to its thermal instability. They are formed in the polymer molecules during the process of polymerization by routes involving hydrogen abstraction from the polymer backbone [584].

Gupper et al. used micro Raman spectroscopy to study thermal degradation of poly(vinyl chloride) containing various additives [586]. They observed a linear increase in conjugated sequences in the process of dehydrochlorination.

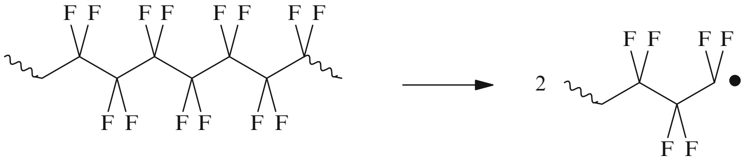
Carty and coworkers investigated thermal decomposition of chlorinated poly(vinyl chloride) [496]. The thermal decomposition of pure chlorinated poly(vinyl chloride) (without stabilizer or lubricant) was studied by dynamic thermogravimetric analysis at heating rates from 5 to 100°C/min in atmospheres of nitrogen, air, and oxygen. In each case, a two-step decomposition was observed, similar to that for poly(vinyl chloride) where dehydrochlorination is followed by pyrolysis/oxidation of the carbonaceous residue. The rate of dehydrochlorination was dependent on atmosphere, occurring slightly slower in nitrogen than in air, and slightly more quickly in oxygen than in air. The decomposition of the residual char was clearly dependent on the conditions that it formed in. Under dynamic conditions, chars formed at high heating rates appeared more resistant to oxidative degradation than those formed more slowly. However, when chars were formed by heating at different rates and then held at 500°C, the char formed at the slowest heating rate was the slowest to be oxidized. The uptake of oxygen by the char appears to be rate limiting. At low heating rates, char oxide is similar in both air and oxygen. As the heating rate is raised, the rate of mass loss of char in air becomes progressively closer to that in nitrogen until at 100°C/mm they are almost identical.

The rates of thermal decompositions of *poly(vinylidine chloride)s* were shown to depend upon the method by which the polymers were prepared [497]. Those that were formed from very pure monomers by mass polymerization are most stable. Polymers prepared by emulsion polymerization, on the other hand, degrade fastest. The mechanism of degradation of poly(vinylidine chloride) was proposed to be as follows [498–500]:

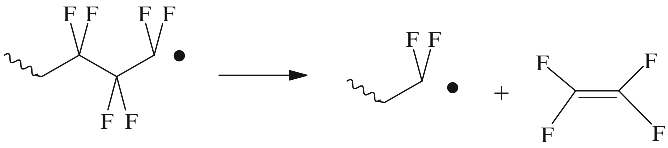
1. Hydrochloric acid is eliminated in a chain reaction.
2. Conjugated sequences condense to form cross-linked structures.

Some support for the above mechanism came from stepwise heating studies of poly(vinylidine chloride) [501].

Although *polytetrafluoroethylene* has the reputation for being quite stable thermally, it does degrade at elevated temperatures. The polymer upon pyrolysis yields almost 100% of monomer. The mechanism is believed to be free-radical unzipping of the chains until the entire chain is consumed. This can be illustrated as follows [457]. Initially, the chain ruptures:



this is followed by formation of monomers:

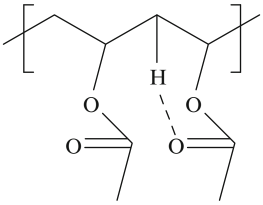


Polychlorotrifluoroethylene is less stable thermally than polytetrafluoro-ethylene. It yields as much as 86.0% volatiles in 30 h at 331.8°C [11]. These volatiles contain large amounts of monomer. A mechanism that resembles the postulated degradation mechanism of polytetrafluoroethylene was proposed [457].

Unlike polytetrafluoroethylene*, polyvinyl fluoride, poly(vinylidine fluoride),* and *polytrifluoroethylene* yield primarily on heating HF [457]. Among these three, poly(vinylidine fluoride) yields larger amounts of HF than do the other two polymers with an accompanying formation of double bonds.

9.8.6 *Thermal Degradation of Poly(Vinyl Acetate)*

Thermal decomposition of poly(vinyl acetate) results in a loss of acetic acid. The reaction is typical of thermal cleavages of esters. It is facilitated by formation of pseudo six-membered rings as a result of interactions between the β-hydrogens of the alcohol residues and the carboxylic groups:



When double bonds form, adjacent methylene groups become activated. The loss of acetic acid is the main product at temperatures up to 200–250°C. Beyond these temperatures, aromatic pyrolytic compounds form.

Studies of thermal degradation of copolymers of vinyl chloride with vinyl acetate showed that the copolymers are thermally less stable than the homopolymers [502, 503]. The ratio of hydrochloric acid to that of acetic acid that volatilize remains constant during the degradation. This indicates that neither is evolved preferentially, once the reaction begins [502, 503]. It is interesting to note that degradation studies of a copolymer of vinyl chloride and styrene also demonstrated that the copolymer is less stable than each of the homopolymers [504].

9.9 Thermal Degradation of Common Step-Growth Polymers

The thermal decomposition of step-growth polymers cannot take place by a chain reaction like that of chain-growth polymers. As a result, these materials degrade in a random fashion, rupturing at the weakest bonds first.

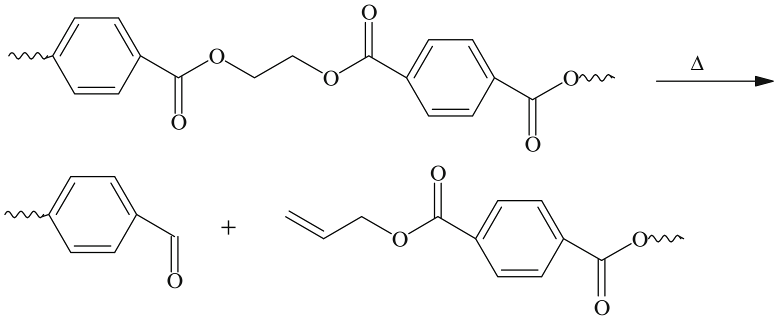
9.9.1 *Thermal Degradation of Polyoxides*

Polyoxymethylene depolymerizes into formaldehyde at 220°C. This was found to be a first-order reaction with the rate varying from 0.42 to 5.8%/min, depending upon conditions of polymer preparation and the molecular weight of the polymer [457].

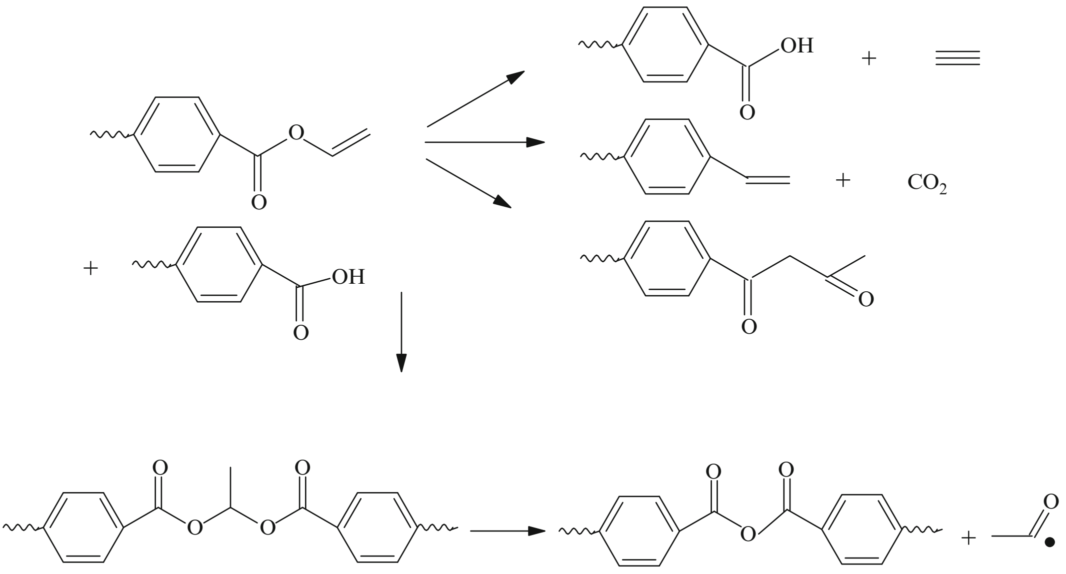
Poly(ethylene oxide) decomposes upon heating at lower temperatures than does polyethylene. Among the volatile products are found formaldehyde, ethanol, ethylene oxide, carbon dioxide, and water. *Poly(propylene oxide)* is also less heat stable than polypropylene. Isotactic poly(propylene oxide) is somewhat more stable than the atactic one.

9.9.2 Thermal Degradation of Polyesters

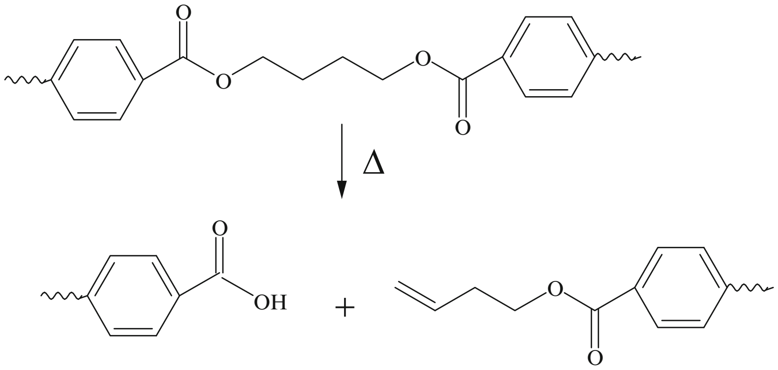
Poly(ethylene terephthalate) decomposes upon heating through a series of different reactions. These run either concurrently or consecutively. The result is a complex mixture of volatile and nonvolatile products. It was found that when poly(ethylene terephthalate) is maintained in molten condition under an inert atmosphere at 282–323°C, it slowly converts to a mixture of gaseous low molecular weight fragments [581]. The major products from pyrolysis of poly(ethylene terephthalate) are carbon dioxide, acetaldehyde and terephthalic acid. In addition, there can be detected trace amounts of anhydrides, benzoic acid, *p*-acetylbenzoic acid, acetophenone, vinyl benzoate, water, methane, ethylene, acetylene, and some ketones [505]. The following mechanism of degradation was postulated [505]:



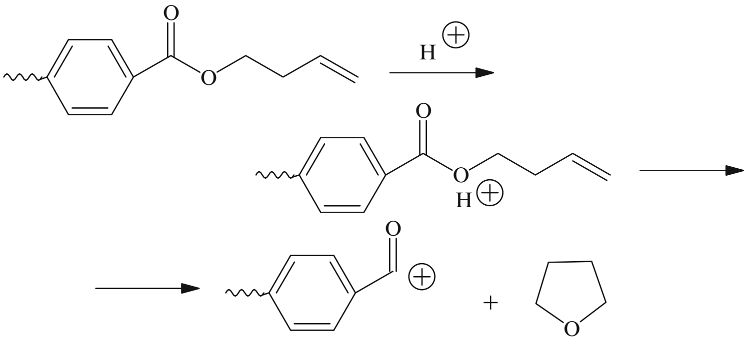
The vinyl end groups that form from cleavage of the ester groups decompose further in a number of ways:



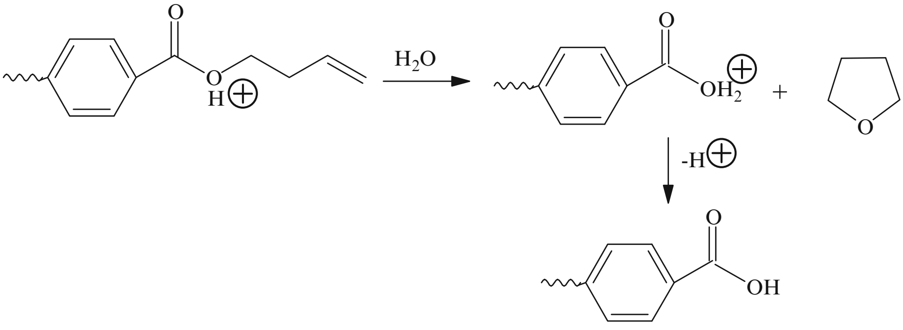
The thermal degradation of *poly(butylene terephthalate)* was examined with the aid of a laser microprobe and mass spectrometry [506]. A complex multistage decomposition mechanism was observed that involves two reaction paths. The initial degradation takes place by an ionic mechanism. This results in an evolution of tetrahydrofuran. This is followed by concerted ester pyrolyses reactions that involve intermediate cyclic transition states and result in formation of 1,3-butadiene. Simultaneous decarboxylations occur in both decomposition paths. The latter stages of decomposition are characterized by evolutions of carbon monoxide and various aromatic compounds, like toluene, benzoic acid, and terephthalic acid. The first step can be shown as follows [506]:



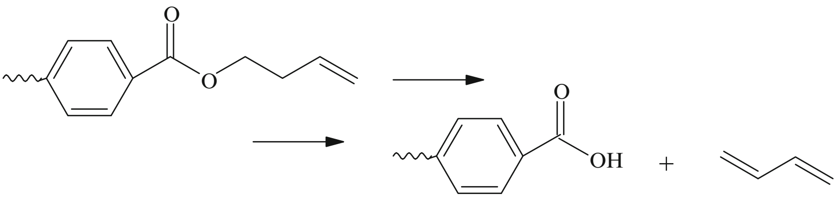
The subsequent decomposition, shown below, can actually take place at lower temperatures:



There are indications that there is moisture among the decomposition products. This may imply that acid hydrolysis plays a part in tetrahydrofuran formation:



At higher temperatures, the reaction path involves elimination of 1,3-butadiene [506, 507];



In oxidations of hydrocarbons, oxygen is believed to act as a diradical in the ground state. This would explain radical combination reactions:

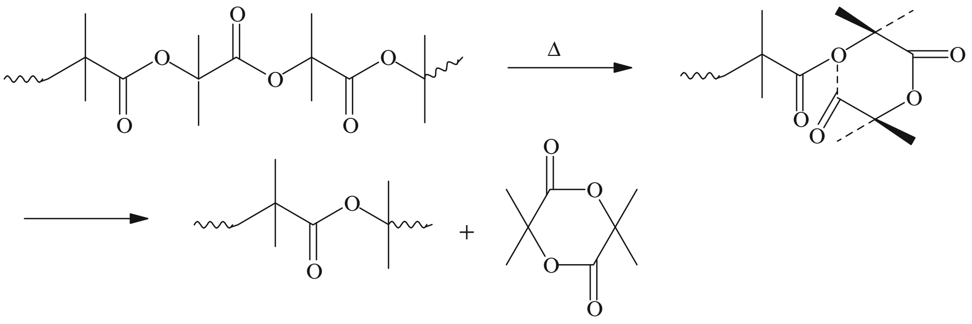
$$R\bullet + \bullet O{-}O\bullet \rightarrow R{-}O{-}O\bullet$$

and the subsequent hydrogen abstraction reaction:

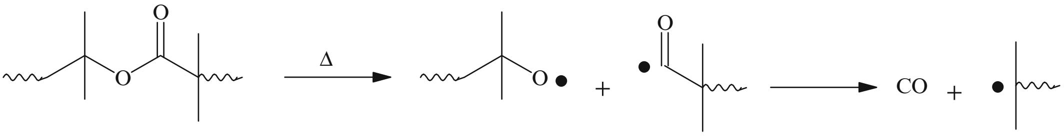
$$R - O{-}O\bullet + R'H \rightarrow RO - OH + R'\bullet$$

The rate of formation of the peroxy radical is much higher than is the rate of hydrogen abstraction [521]. The overall rate of oxidation of polymeric materials by atmospheric oxygen is strongly affected by light, heat, oxygen concentration, moisture, and the presence of traces of impurities. The impurities, however, can act as either catalysts or as inhibitors of oxidation.

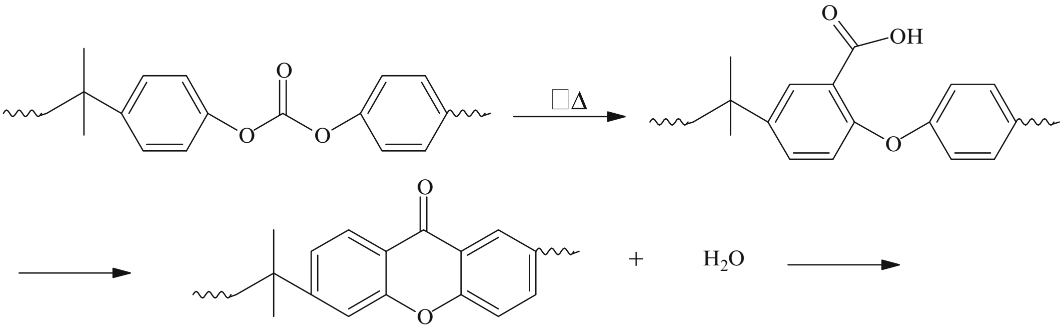
The degradation of *poly-α-esters* was studied on poly(isopropylidine carboxylate) [518] over a range of temperatures, from 200 to 800°C. Among the decomposition products were found tetramethyl glacolide, acetone carbon monoxide, and to a lesser extent methacrylic acid. The primary decomposition product appears to be tetramethylene glacolide that becomes an intermediate upon further pyrolysis:

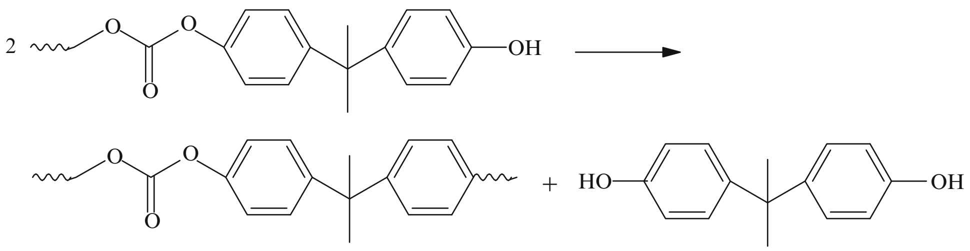


also:



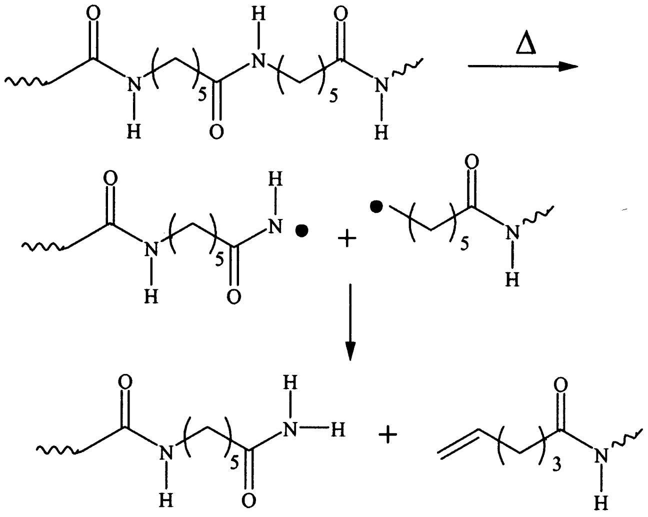
Decomposition of polycarbonates was studied on poly[2,2′-propane-bis-(4-phenyl) carbonate] [519]. It was concluded that a rearrangement mechanism is the main intermediate material in subsequent formation of carbon dioxide and volatile phenolic compounds [519]:



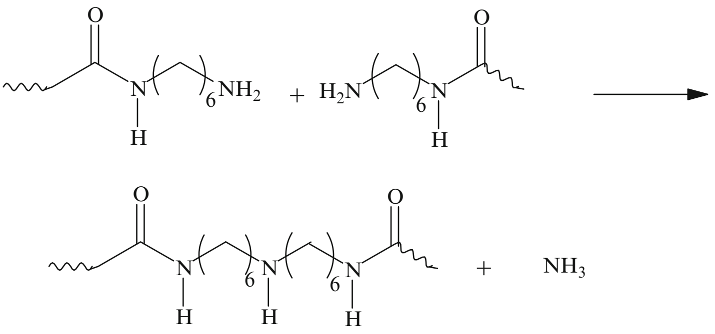


9.9.3 Thermal Degradation of Polyamides

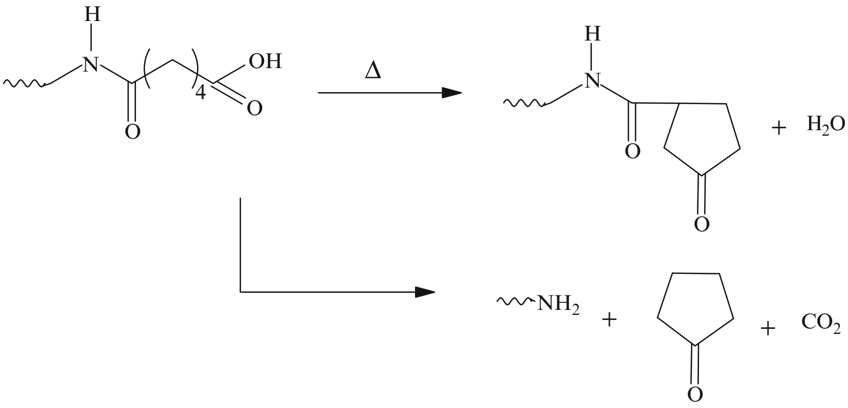
The thermal degradation of polyamides starts with free-radical cleavage of nitrogen–carbon bonds [520]. Degradation of *nylon 6* can be illustrated as follows:



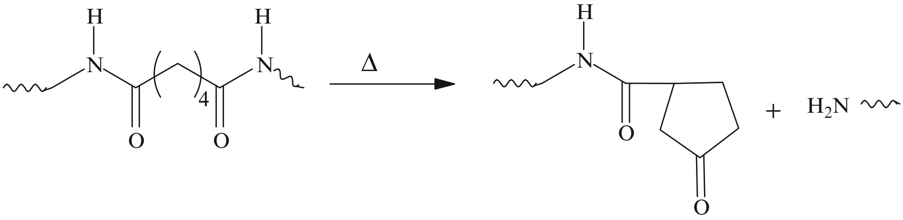
When nylon 6 is heated for 100 h at 305°C, half of the nitrogen escapes from the polymer and a small amount of carbon dioxide forms [457]. This was postulated by Kamerbeek et al. as being the result of reactions of two terminal amine groups [579]:



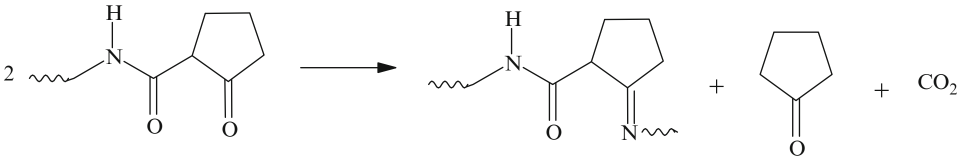
In decomposition of *nylon 6,6,* there is the additional tendency for ring closure by adipic acid [509]:



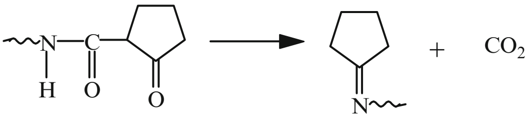
The cyclization reaction can also occur as follows [509]



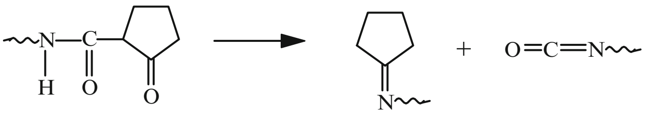
or, perhaps, as a bimolecular reaction [509]:



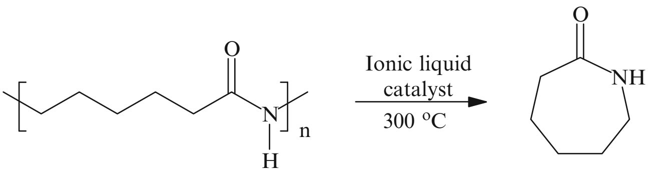
At higher temperatures, the carbamoyl ketone might convert to the Schiff base by a monomolecular process [509]:



The route to the Schiff base may also be through elimination of an isocyanate [509]:



Rather than thermal degradation of nylon 6, it is possible to depolymerize this polyamide. Kamimura and Yamamoto reported that it is possible to depolymerize this nylon back to caprolactam [510]:

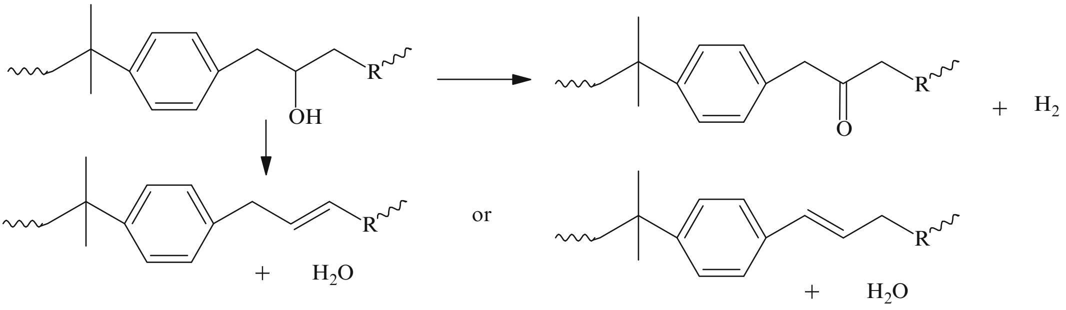


The best yield of caprolactam was 86% obtained with *N*-methyl, *N*-propyl piperidinium bis (trifluoromethyl-sufonyl)imide as the solvent and *N*,*N*-dimethylpyridine as the catalyst.

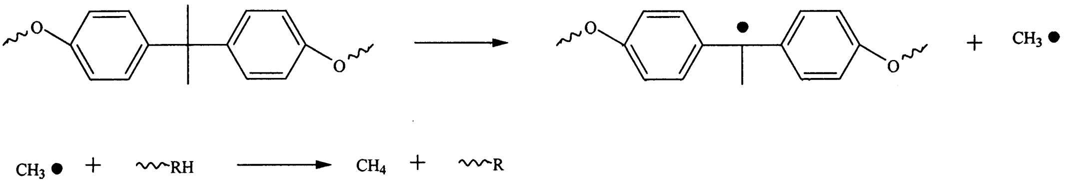
In the past, it was believed that at high temperatures nylons degrade at a faster rate at elevated humidity. This assumption, however, was shown to be erroneous by Bernstein et al. [457].

9.9.4 Thermal Degradation of Epoxy Resins

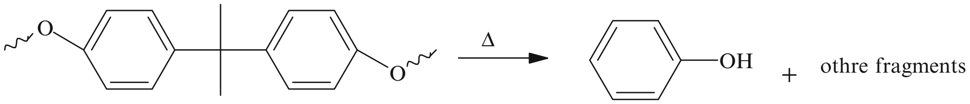
The thermal degradations of *Bisphenol A-based epoxy resins* cross-linked with diaminodiphenylmethane or with phthalic anhydride were studied with the aid of pyrolysis and radiochemical gas chromatography technique [511]. The products of degradation depend upon the temperature. At 400°C, the amine cross-linked resins yield hydrogen, methane, and water. The resins cross-linked with phthalic anhydride yield hydrogen, methane, carbon dioxide, and water. The number of degradation products increases with temperature. It was concluded that the most important nonscission reactions in these resins are competing with dehydration and dehydrogenation reactions [511]:



A nonscission reaction that yields methane is:

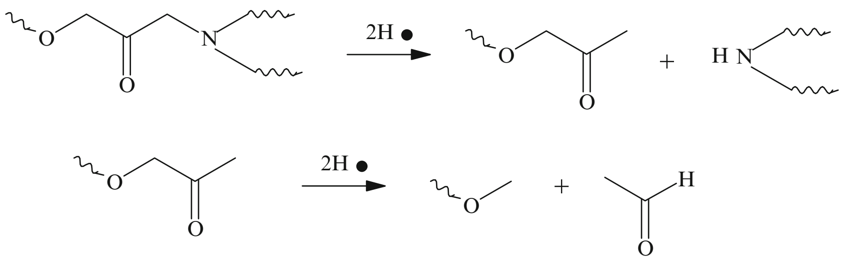


The scission reactions can take place at various weak spots. The breakdown of bisphenol A segments produces phenol [511]:

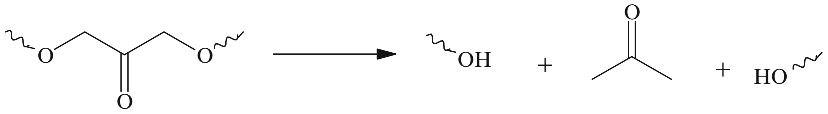


The main differences that were observed between amine-cured and anhydride-cured resins are [511]:

1. The amine cross-linked resin generated more water and hydrogen, because they contained more –CH_2–CHOH–CH_2– groups.
2. Scissions of anhydride-reacted resins tend to regenerate the anhydride and release CO and CO_2 in large quantities
3. The aliphatic segments of the amine cross-linked resins yield more acetaldehyde than acetone. The reverse is true of the anhydride-cured resins. This is thought to be due to preferential rupture of carbon–nitrogen bonds [511]:

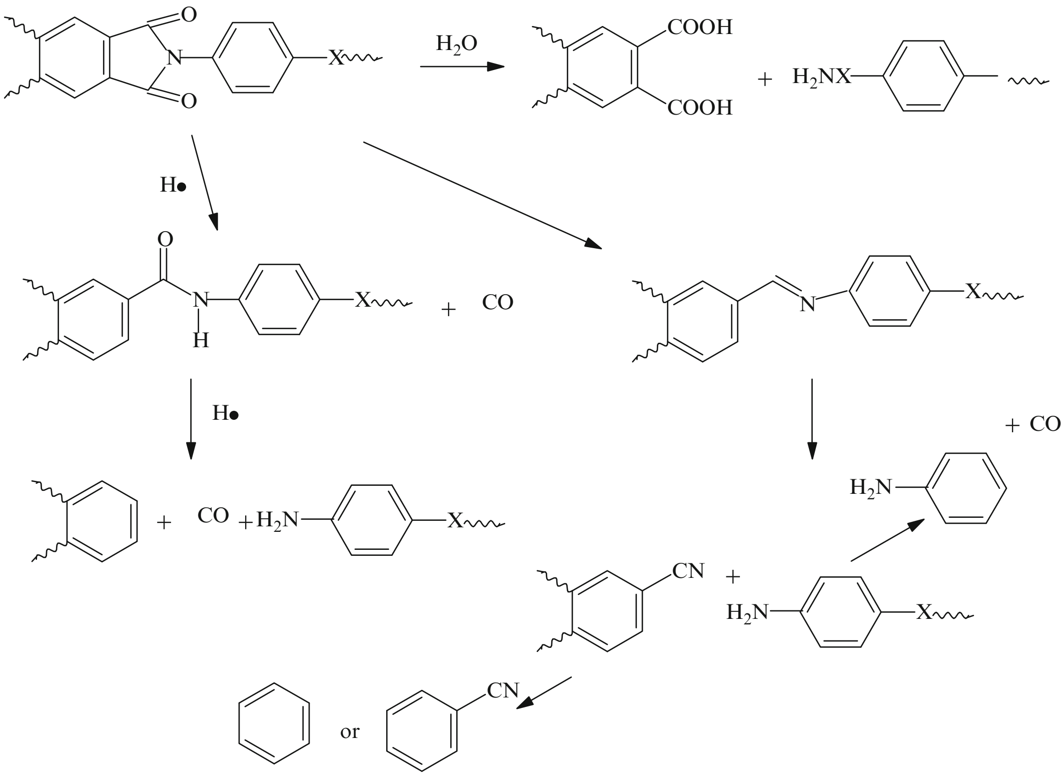


The anhydride-cured compositions may tend to break up symmetrically instead:



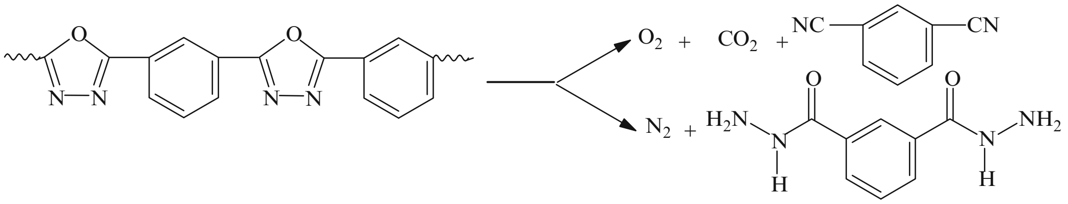
9.9.5 Thermal Degradation of Polyimides, Polyoxidiazoles, and Polyquinoxalines

The technique mentioned in the previous section of pyrolysis and radiochemical gas chromatography was also applied in a study to thermal degradation of *aromatic polyimides* [512]. Aromatic polyimides are more stable thermally than previously discussed polymers and require higher temperature for decomposition. Based on the experimental results, the following mechanism was proposed [512]. Initially, hydrogen radicals form. They come from various places of the polymer backbone during the pyrolytic decomposition. Also, decomposition of amic acid may yield water (see Chap. 6).

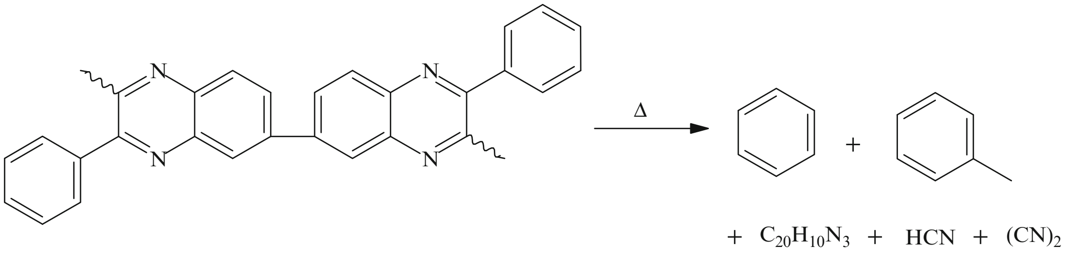


Another study of thermal degradation of aromatic polyimides led to similar conclusions [513]. At lower temperatures, the degradation of polyimides proceeds by a hydrolytic mechanism that is greatly influenced by presence of uncyclized units. At higher temperatures, the degradation is mainly by decarbonylation of the imide ring and breaking down of the polymer chain through “weak” bonds.

The thermal *degradation of polyoxidiazoles* was shown to proceed mainly through the heterocyclic rings that are apparently the weak spots [514, 515]:



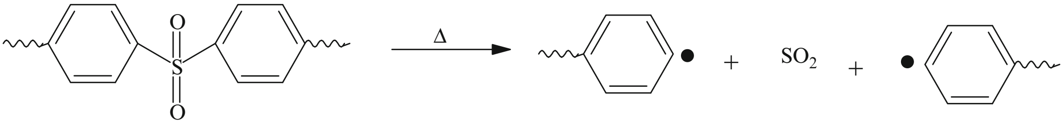
The process by which aromatic polyquinoxalines decompose is random. At 500–600°C, it involves the opening of the heterocyclic ring with loss of fragment [516]:



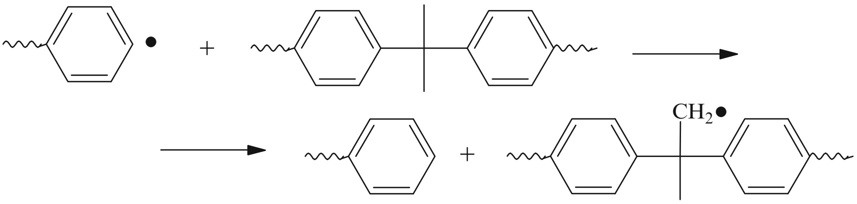
At still higher temperatures, between 640 and 690°C dehydrogenation of nitrogen residues takes place.

9.9.6 Thermal Degradation of Aromatic Polysulfones

In *aromatic polysulfones,* the weakest link was found to be the carbon–sulfur bond [517]. These polymers are processed at about 300°C. At that temperature, the thermodegradative processes as well as thermo-oxidative ones can occur. The rupture of the C–S bonds produces molecules of SO_2 and fragments of the polymer molecules with terminal phenyl radicals [517]:



The phenyl radicals then abstract hydrogens from the methyl groups that are present when the polysulfone is prepared from bisphenol A:



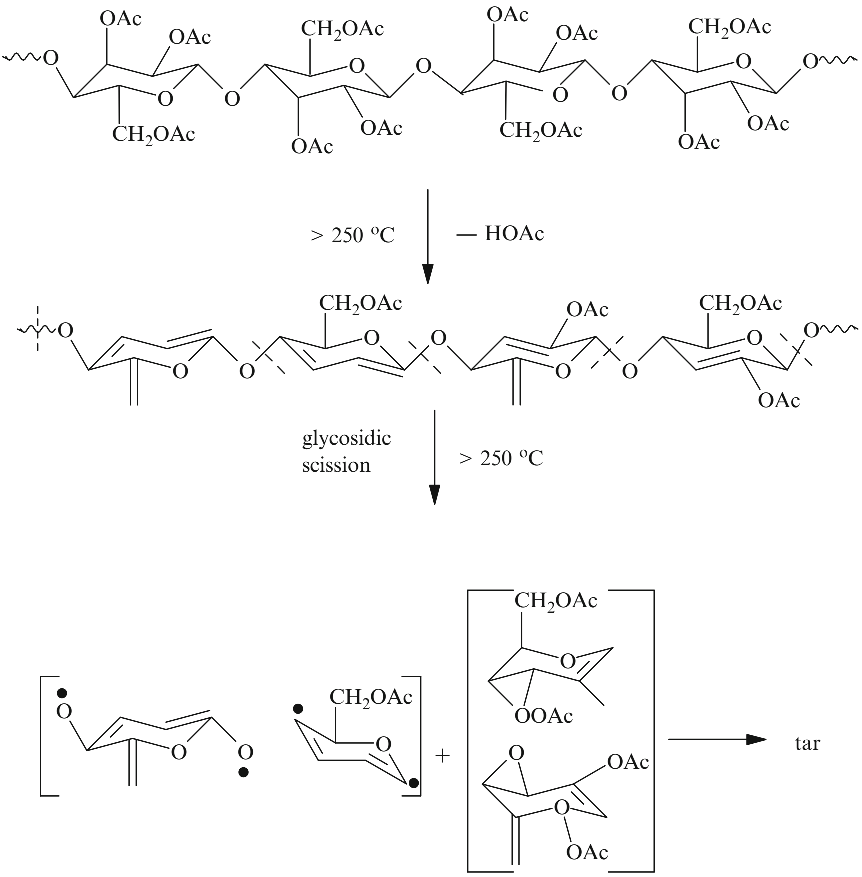
9.9.7 Thermal Degradation of Polyethers

The *aromatic polyethers* are subject to rupture at the ether link at around 300°C [518]. Products from such ruptures are somewhat similar to those obtainable from decomposition of the polysulfones, shown above.

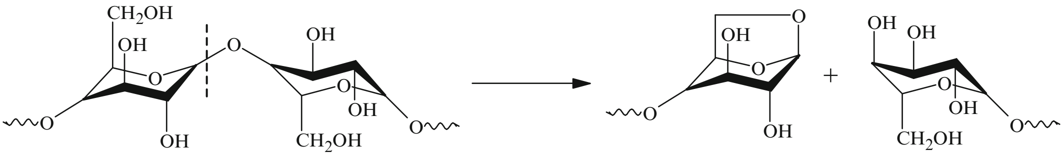
The thermal degradation of *polyoxymethylene* was found to be initiated at the chain ends. There appear to be three possible sites for initiation of homolytic bond cleavages [519]:

9.9.8 Thermal Degradation of Cellulosic Materials

The degradation of cellulose triacetate in vacuum was analyzed with the aid of chromatography, mass spectrometry, infra-red, and NMR spectroscopy [517]. The mechanism of degradation was proposed by Scotney to consist primarily of deacetylation in the polymer chain and scission of the chain at the 1,4 glycosidic linkage between the pyranose rings [517]. The type of products that are formed depends upon the degradation temperature. At temperatures above 250°C but below 350°C, unstable intermediates form. Continued heating results in loss of carbon monoxide, carbon dioxide, and acetic acid, and eventually end in formation of tar. Heating above 350°C causes condensation of radical intermediates, cross-linked aromatic, and hydroaromatic ring systems. This can be illustrated as follows:



The mechanism of thermal degradation of cellulose appears to include two reactions. The first reaction consists of dehydration and the second one of scission of C–O bonds in the chains between the rings or within the rings [457]. This can give rise to levoglucosan [457]:



9.9.9 *Hydrolytic Degradation of Polymers at Elevated Temperatures*

Hydrolytic degradation is only significant in polymers with chain links that can react with water, such as polyesters. A recent study reports on depolymerization of poly(ethylene terephthalate) during processing, if the material is not dried thoroughly, prior to melting [530]. The hydrolytic depolymerization of poly(ethylene terephthalate) was carried out in a stirred batch reactor at 235, 250, and 265°C above the polymer melting point and under autogenous pressure. The solid products were mainly composed of terephthalic acid. The liquid products were mainly composed of ethylene glycol and a small amount of its dimer. Moreover, an autocatalytic mechanism was detected. That indicates that some of the hydrolytic depolymerization of PET is catalyzed by the carboxylic acid groups produced during the reaction. The dependence of the rate constant on the reaction temperature was correlated by the Arrhenius equation [530].

9.9.10 Oxidative Degradation of Polymers

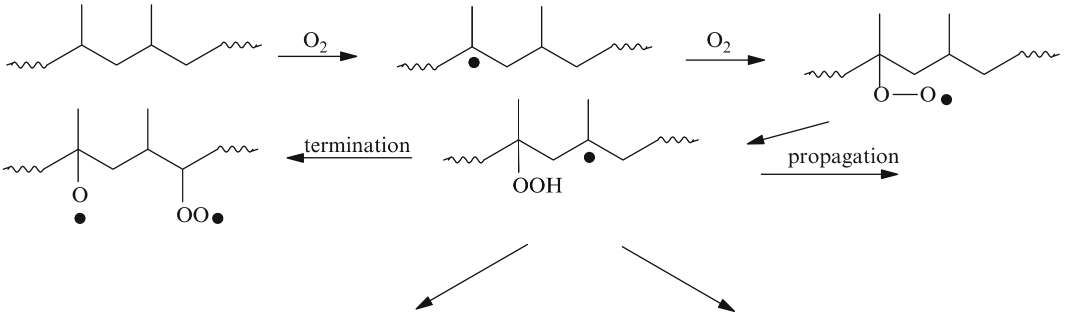
This section deals not only with oxidative reactions of polymers at room temperature, but also with thermo-oxidative degradation at elevated temperatures. Although this type of degradation resembles photo-oxidative degradation, for the purpose of maintaining clarity, the latter is discussed separately in the next section.

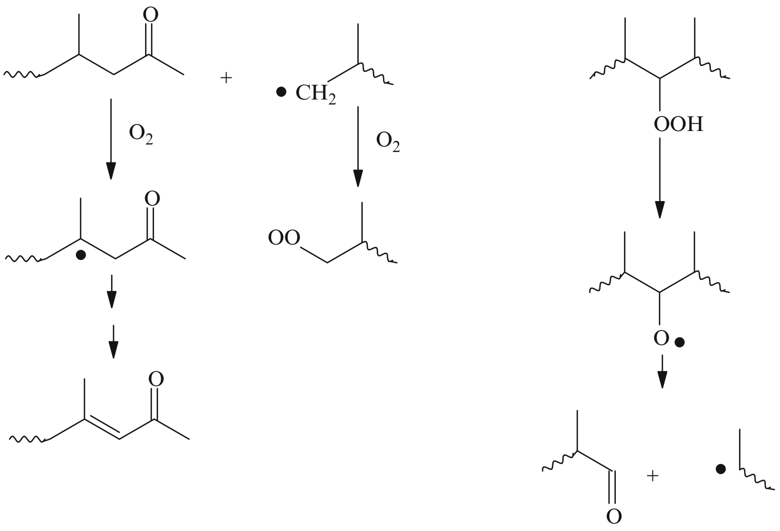
The simplest oxidative reactions occur in hydrocarbon polymers. This free-radical process generally follows the same path as the oxidation of low molecular weight compounds. The difference, however, is in the propagation of the reaction. In oxidation of low-molecular weight hydrocarbons, each step of chain propagation results in transfer of active center from on molecule to another. In polymers, however, the probability of such a transfer is low. Instead, the oxidation propagates along the polymer backbone [520].

9.9.11 Oxidation of Chain-Growth Polymers

Polymers that lack double bonds, like polyethylene, can be considered high molecular weight paraffin. They are slow to oxidize in the absence of UV light, much like the low molecular weight hydrocarbons. On the other hand, polymeric materials with double bonds oxidize rapidly. Nevertheless, polymers like polyethylene may oxidize rapidly as well when contaminated with metallic ions because such ions catalyze the decomposition of peroxides.

The chemical structure of the polyolefins determines their susceptibility to oxidative degradation. Linear polyethylene, in the absence of additives, is more resistant to oxidation that polypropylene that oxidizes rather readily due to the presence of labile tertiary hydrogens. It was demonstrated, for instance, that the molecular weigh of polypropylene sheets in a 138°C oven can drop from 250,000 to approximately 10,000 in 3 h [522]. The process of oxidation was shown to take place according to the following scheme [522]:



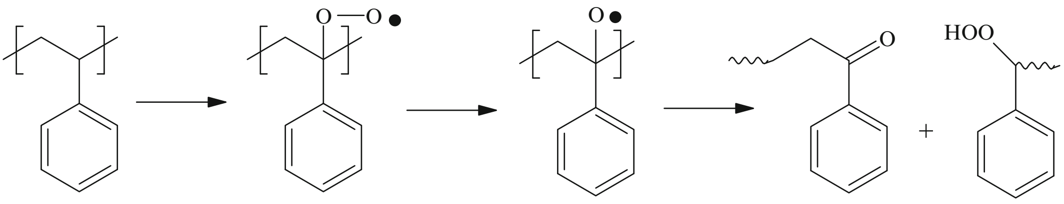


Further oxidative degradation of fragments leads to formation of a carboxylic acid, an ester, and a γ-lactone [522]. It was also found that the main oxidation products of polyethylene are an acid and a ketone. On the other hand, polypropylene yields upon oxidation approximately equal quantities of an acid, a ketone, an aldehyde, an ester, and a γ-lactone [522].

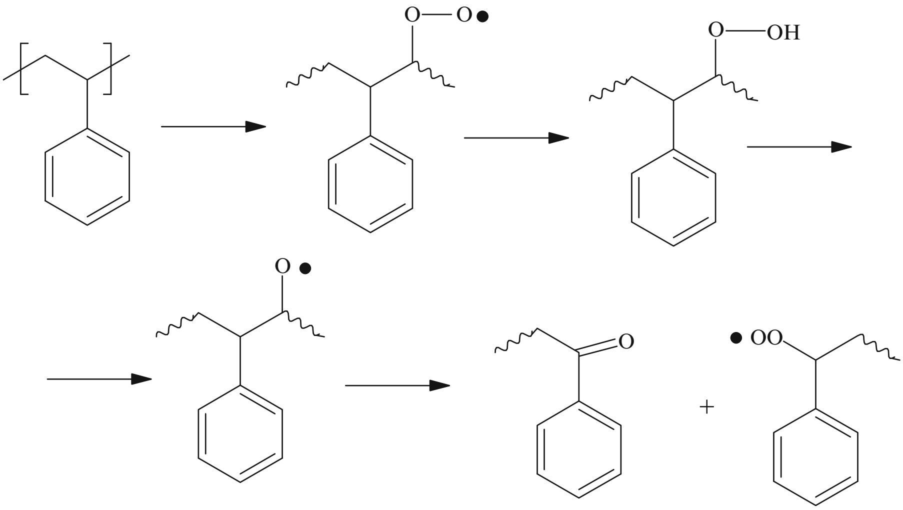
In order for a polymer molecule to be attacked by oxygen, it must come in contact with it. This means that oxygen must be able to permeate into the material. Otherwise, all the oxidation will occur only at the surface. It was shown that oxidation occurs more readily in amorphous regions of the polymers where permeation of oxygen is not hindered by the chains being packed tightly together in the crystallites. That is only true, of course, at temperatures below T_m of the polymer.

Among the chain-growth polymer, oxidation of *polystyrene* was investigated thoroughly. It was found that the rate of oxygen absorption and the number of chain scissions remain constant up to a high degree of reaction. There is no evidence of cross-linking under these circumstances [523]. During the degradation process, carbonyl groups accumulate in the polymer [524]. Among the degradation products were identified benzaldehyde [525] and a number of ketones [526].

The primary oxidation and chain scission process in polystyrene at room temperature is as follows [527]:

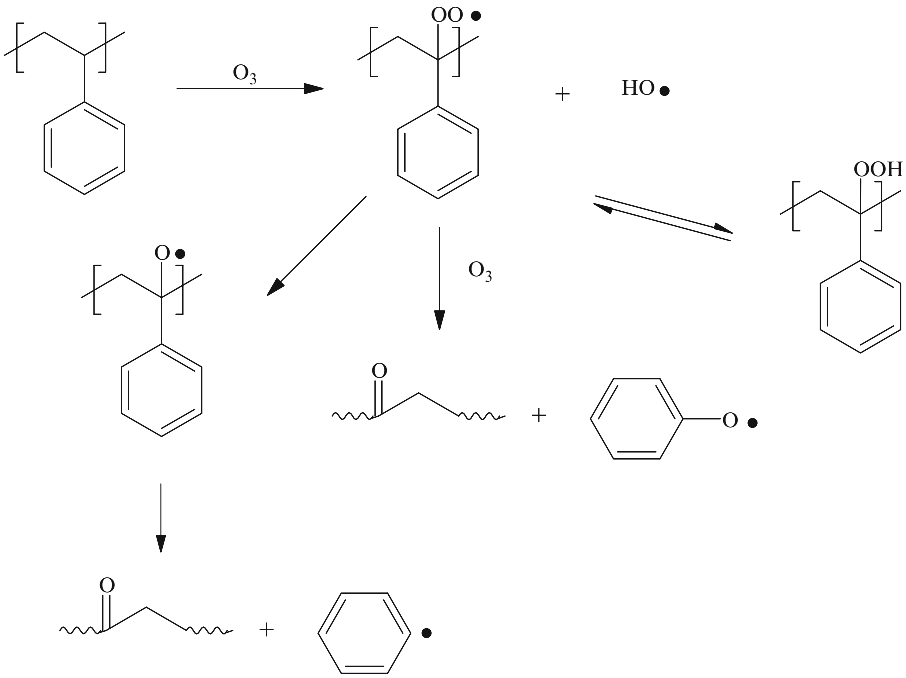


the reaction can also proceed in this manner:



Continuation of the process reduces the polymer to small fragments that include benzaldehyde and methyl phenyl ketone [527].

When solid polystyrene is subjected to an *ozone attack*, carbonyl, peroxide, and carboxylic acid groups form on the surface of the polymer [528]. The reaction rate is proportional to the concentration of the ozone and the surface of the sample. As a result of the ozone action, intramolecular cross-linking takes place. The reaction mechanism of the ozone attack on polystyrene can be shown as follows [528]:

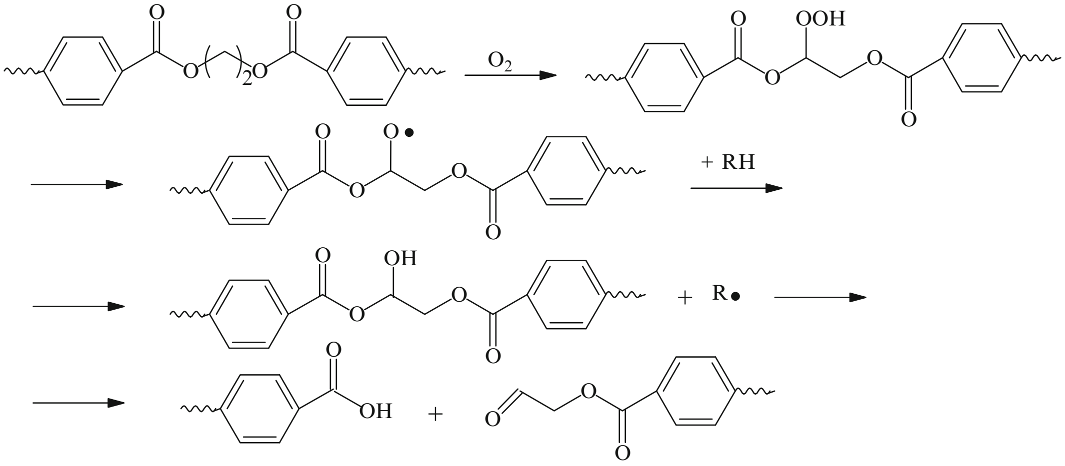


In *poly(vinyl toluene),* the initial oxidation steps consist of formations of radicals at the tertiary carbon atoms as they do in polystyrene. The radicals subsequently form peroxides that decompose into ketones and aldehydes.

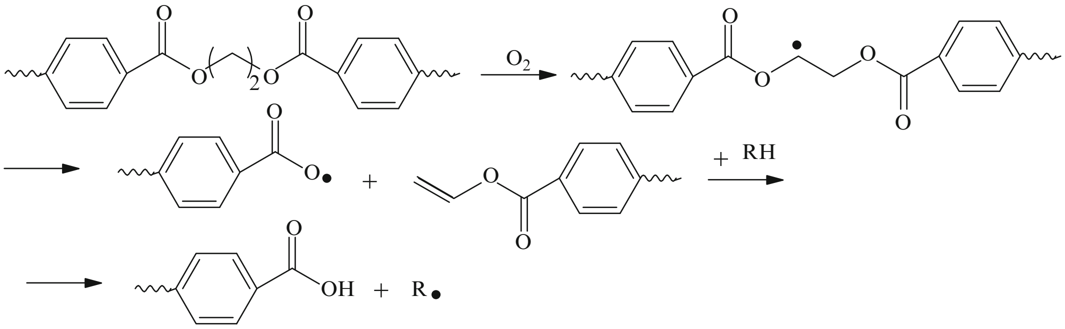
9.9.12 Oxidation of Step-Growth Polymers

Oxidation of step-growth polymers follows the paths that are similar to oxidation reactions of organic molecules. Thus, oxidation of poly(ethylene terephthalate) was shown to proceed as follows [529]:

Path1

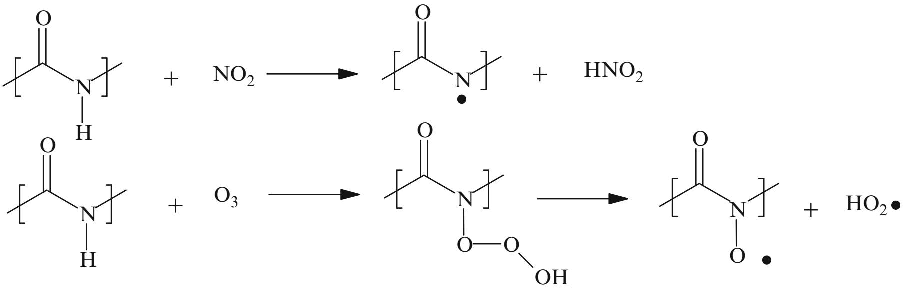


Path2



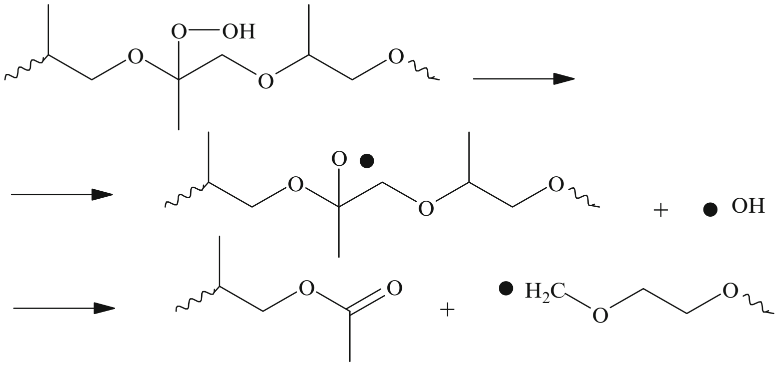
During thermal oxidation of *polyamides,* the *N*-vicinal methylene group is the preferred side of attack [531]. The reactivity depends, apparently, on the conformation of the amide group because an interaction takes place between the π-electronic system of the carbonamide group and its C–H bonds. In polycaprolactam, there exists a statistical distribution of both gauche and *trans*-conformations. The *N*-vicinal methylene groups in the *trans*-conformations to the amide groups are much more reactive than gauche [531].

When the oxidation of a polyamide occurs through an attack by NO_2 or ozone, then the amide groups themselves are subject to the attack [532]:

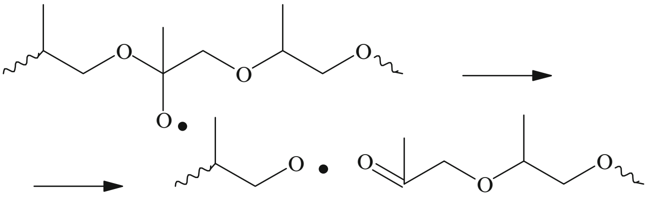


This appears to take place with hydrogen-bonded amide groups as well. The reaction, however, is inhibited by benzaldehyde or by benzoic acid. When the degradation does take place, it occurs at random [532].

Thermo-oxidative degradation of *polyoxyglycols* is reported to occur typically by a free-radical mechanism with the formation of hydroperoxides. The decomposition of the peroxides leads to formation of acids and carbonyl compounds [533]. A study of thermal oxidation of oligomers (molecular weight approximately 1,900) of polyoxypropylene glycols showed that at 70–120°C the end hydroxyl groups are not responsible for degradation and that chain ruptures occur through decomposition of the hydroperoxides [534]: Two types of cleavage are possible. One can take place through the carbon to carbon single bonds as follows:

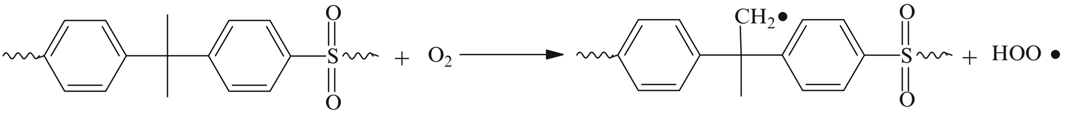


The other type of cleavage can occur through the oxygen–carbon bonds:



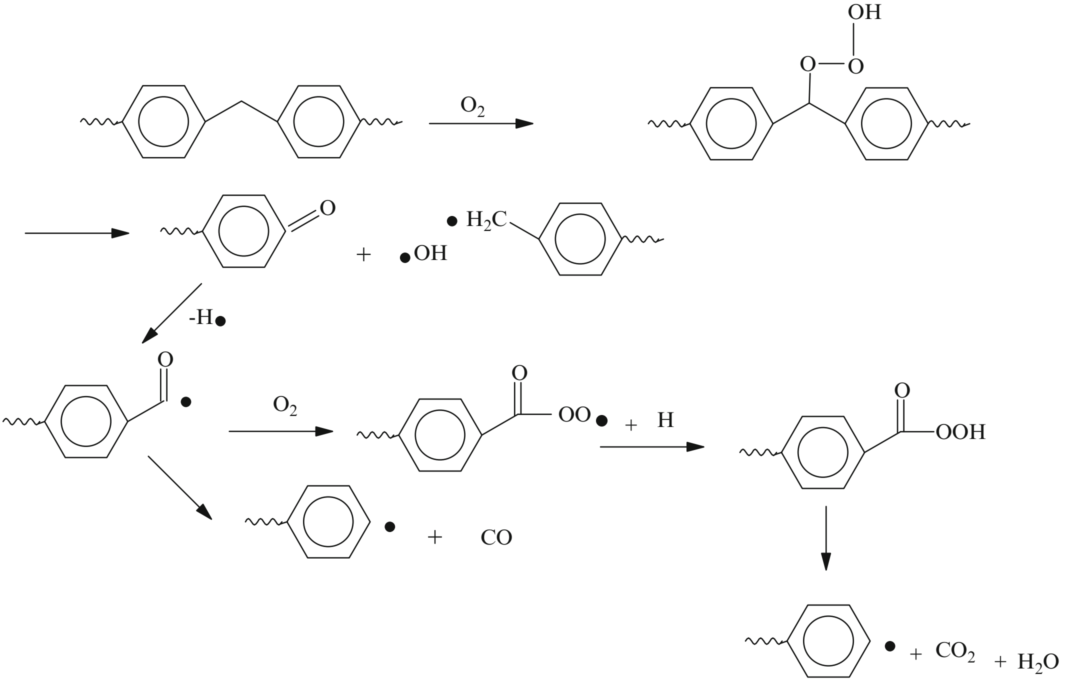
Both long and short molecular chains undergo degradation in an identical manner. The secondary radicals that form as a result of the decomposition of the alkoxy radical accelerate the oxidation process. It transforms into a chain process with an accompanying formation of various compounds. The products are alcohols, aldehydes, and ketones. The aldehydes are easily oxidized into peracids that degrade further into radicals.

Thermal–oxidative degradation of *polysulfones* was studied at 280°C [535]. The oxidation is a radical chain reaction with the initiation consisting of hydrogen abstraction from a methyl group:



The process then continues with formation of alkyl peroxide radicals, isomerization, breakdown, and formation of oxygen-containing compounds like aldehydes, and ketones.

In the oxidative pyrolysis of *poly-p-xylene,* the oxygen attacks methylene groups first to form hydroperoxides [536]. This is followed by chain cleavage:



9.9.13 Photo-Degradation of Macromolecules

The quantum energies associated with sunlight in the violet and near ultraviolet portions of the spectrum are of the magnitude sufficient to rupture chemical bonds present in most polymers [537]. The mechanism of photo-degradation, however, is more complex than would be visualized by the simple bond rupture, because photo-absorptions are complicated by various factors, including crystallinity that causes scattering of light. In addition, it was demonstrated that little light is absorbed above the wavelength of 2,800 Å. Yet, this wavelength represents the lower limit of sunlight reaching the earth. On the other hand, presence of impurities that can act as photosensitizes can markedly accelerate the degradation process.

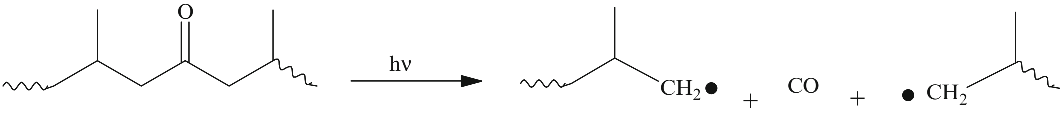
Polymers that are in current commercial use on a large scale fall roughly into three categories, depending upon their ability to withstand photo-degradation [538]:

1. Polymers that are resistant to sunlight attacks outdoors, like polyethylene and poly(methyl methacrylate).
2. Moderately stable polymers, like poly(ethylene terephthalate) and polycarbonate.
3. Polymers that are unstable in sunlight and require ultraviolet light stabilizer, like poly(vinyl chloride), polypropylene, nylons, rubbers, and cellulose.

In addition to structural instability of some polymer molecules in the ultraviolet light, degradation may also be accelerated by chromophores that can form from oxidation during preparation or processing. These compounds can act as excited donors and transfer the energy to the polymers that may act as acceptors. An intramolecular energy transfer may, actually, occur within the same polymer molecule. This can take place between an excited chromophore that is present in one segment of the chain and an acceptor at another segment. Also, chromophores, like carbonyl groups, can undergo Norrish Type I or a Norrish Type II reaction.

Several studies were carried out on *photolysis of polyethylene* [539, 540]. The primary process of photo-degradation, however, is still being elucidated. Direct irradiation of pure low-density polyethylene with ultraviolet light from a mercury lamp results in formation of free-radicals that were identified by ESR. They are alkyl radicals of the type: $\sim CH_2{-}CH_2^{\bullet}$ and $\sim CH_2{-}CH^{\bullet}{-}CH_2\sim$ [539, 540]. The true absorption bands of polyethylene, however, are located at wavelengths shorter than 200 nm. It is difficult, therefore, to accept that the radiation from the lamp caused chain scissions, because the output of the lamp is much longer in wavelength. It is suspected, therefore, that the degradation is a result of photo-oxidation. This is discussed in the next section.

A similar photo-degradation process is believed to take place in polypropylene [541]. The formation of free-radicals is ascribed to presence of oxidized molecules that form during processing. The oxidation products are carbonyl compounds and hydroperoxides [542]. The photolysis of the carbonyl derivatives is as follows [541]:



And the photolysis of chains carrying hydroperoxide group can be shown in this manner [541]:

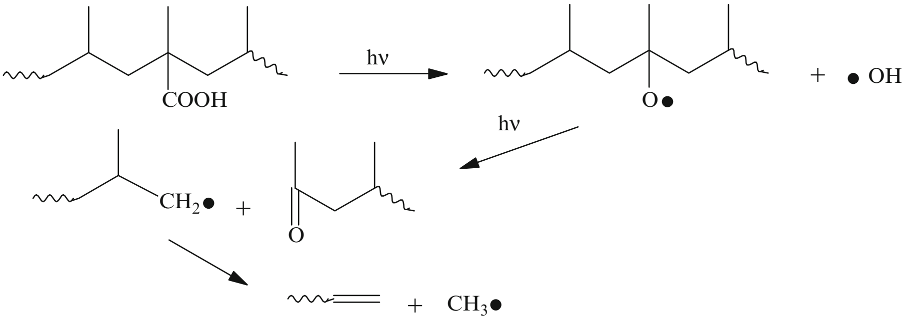
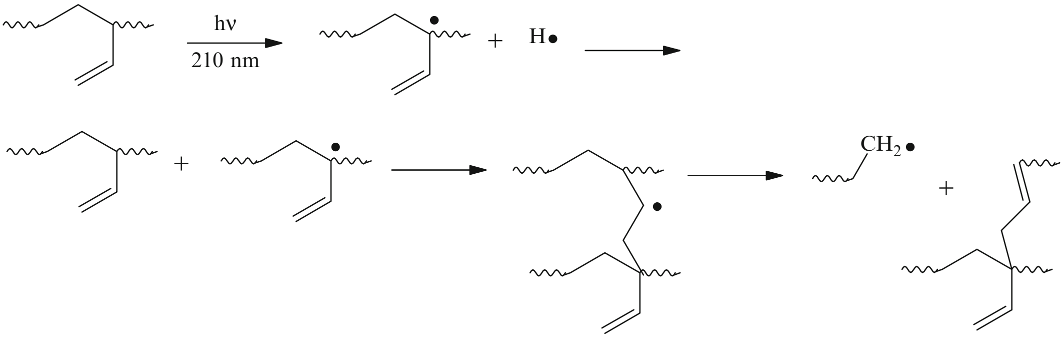
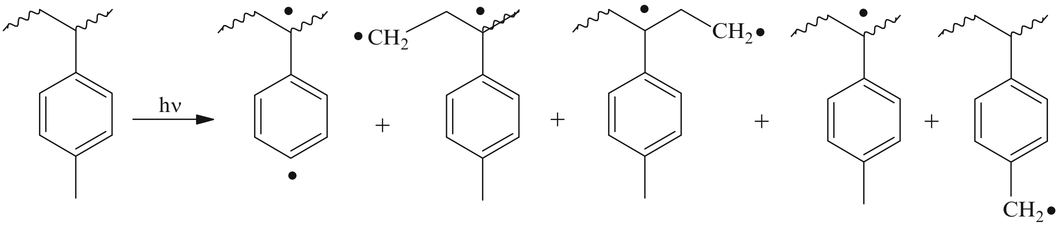


Photo-degradation of 1,2-polybutadiene was studied on a film [543]. Among the degradation products were found hydrogen, compounds with methyl groups, vinyl groups, and cross-linked material. The following mechanism of photo-initiation of the degradation reaction was proposed [543]:



The mechanism of photo-degradation of *poly(p-methylstyrene)* was studied by several investigators [544–547]. A gas evolution was observed during the irradiation with ultraviolet light. This gas contains hydrogen as its major portion and methane, ethane as the minor portions. There are also traces of styrene, *p*-methylstyrene, and toluene [101]. The gas evolution is accompanied by cross-linking. The start of the process is pictured as follows [547]:



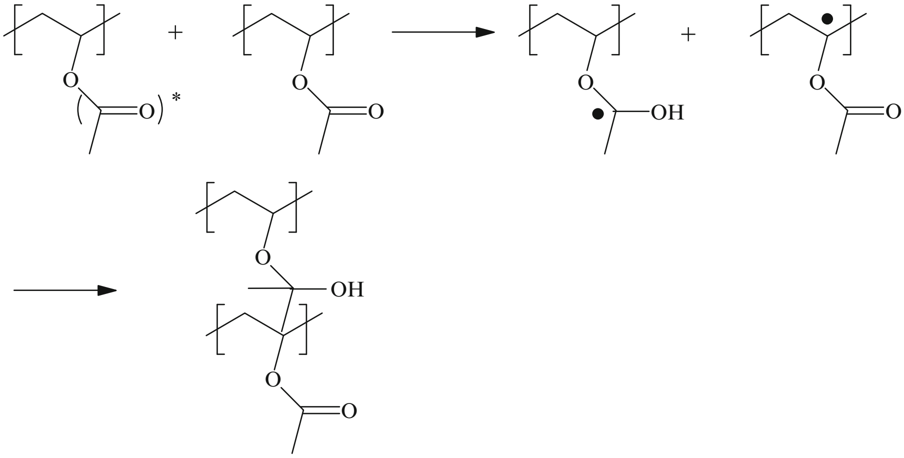
The products react to further yield hydrogen, cross-linked material, monomer, and cyclohexadiene.

Photolysis of *poly(p-isopropyl styrene)* with ultraviolet light of 254 nm in vacuum at 10^{-6} mbar and room temperature yields hydrogen as the main product and a small quantity of methane, ethane, and a trace of propane [548].

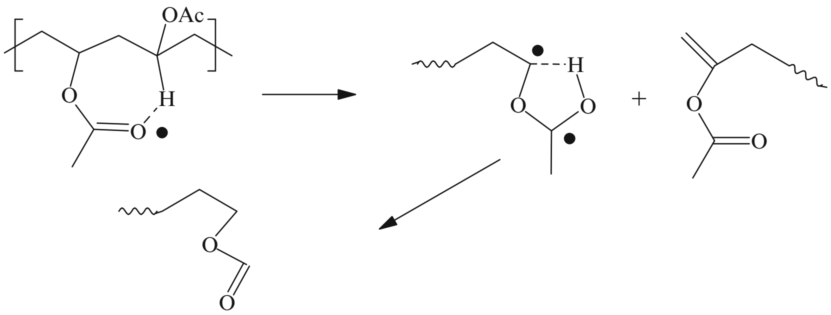
Poly(methyl methacrylate) depolymerizes at elevated temperature under the influence of ultraviolet light of 259.7 nm [549]. Irradiation of polyacrylonitrile, however, leads to chain scission at the acrylonitrile units. The difference between thermal and ultraviolet light degradation of polyacrylonitrile is principally in the different sites of initiation and the fact that the reaction occurs at 160°C in the presence of light and at 280°C in the darkness [550].

When a copolymer of methyl methacrylate and *n*-butyl acrylate is irradiated in vacuum at elevated temperature, like 165°C with light of 253.7 nm, the gaseous products are minor [551]. These are hydrogen, carbon monoxide, and methane. The liquid products are predominantly methyl methacrylate, *n*-butyl acrylate, *n*-butyl alcohol, and *n*-butyraldehyde. The degradation is explained by Grassie and coworkers [551] in terms of a radical process that is initiated by scission of pendant acrylate units. The propagation is actually a combination of depropagation of the chains and intra- and intermolecular chain transfer process. The relative importance of each phase of depropagation reaction depends upon the composition of the copolymer [551].

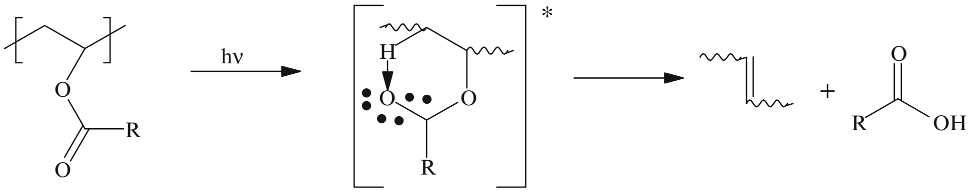
Poly(vinyl acetate) was shown to undergo simultaneous cross-linking and chain scission when irradiated in vacuum with ultraviolet light [552]. The following mechanism was proposed as the route to chain cleavage [552]:

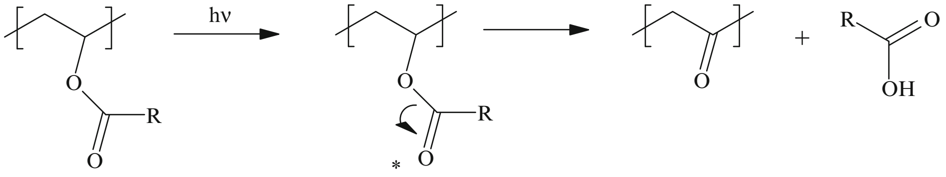


Also, intramolecular hydrogen abstraction is assumed to occur through a seven-membered ring transition state. This can provide a route to chain scission:

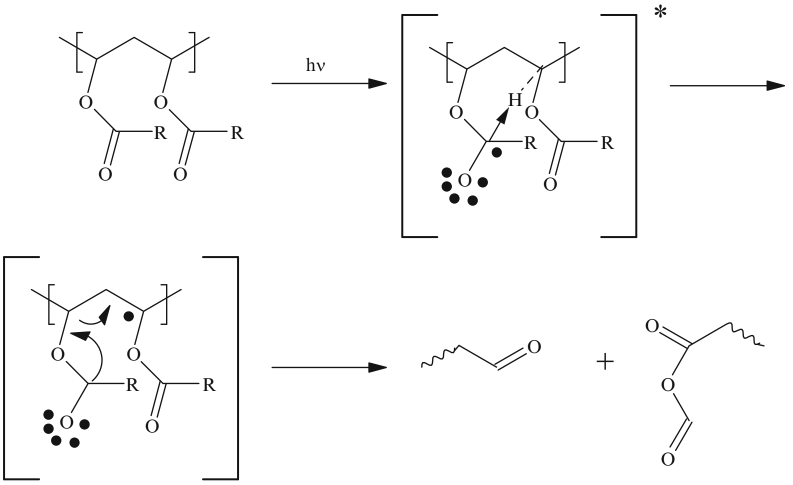


In subsequent studies of photo-degradation of poly(vinyl acetate) and poly(vinyl propionate) in vacuum, it was found that acids, aldehydes, and carbon dioxide were the principal products [553]. Two mechanisms, one involving hydrogen abstractions, were postulated. One of them takes place by abstraction by acyl radicals formed through Norrish Type I cleavages and the other by intramolecular hydrogen abstraction by excited carbonyl groups followed by fragmentation [553]:

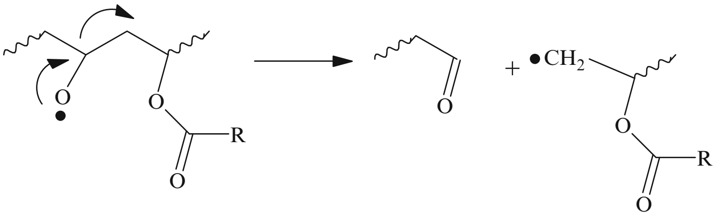


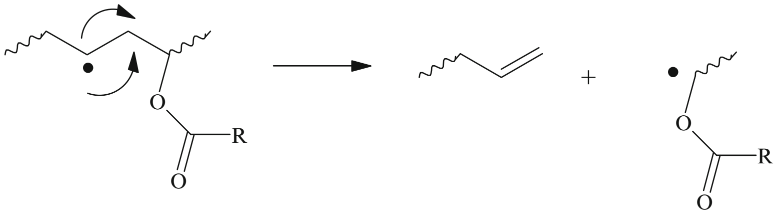


A second, perhaps more viable mechanism, was pictured for the production of aldehydes involving hydrogen abstraction as follows [553]:



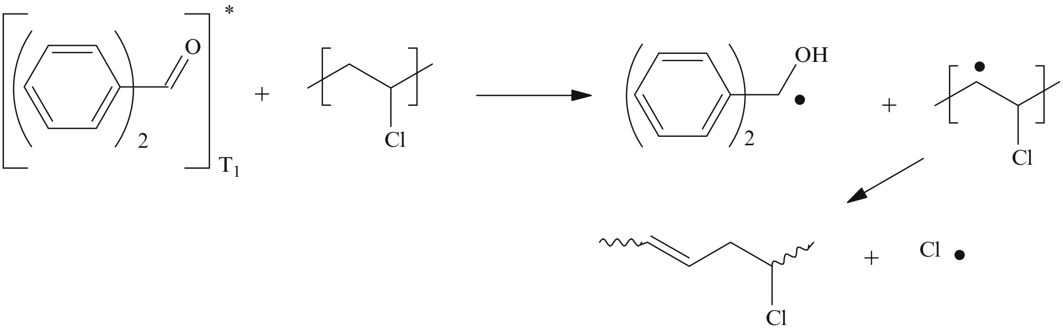
The main chain scissions are envisioned as involving fragmentation of the polymer alkoxy radicals that form [553]:





When cast *poly(vinyl chloride)* films are irradiated by ultraviolet light at various intensities and temperatures under a nitrogen atmosphere, dehydrochlorination reaction takes place [554]. This reaction occurs in two parts. During the first hour, the reaction is dependent on the intensity of light and the temperature, but after that it becomes independent of these two parameters.

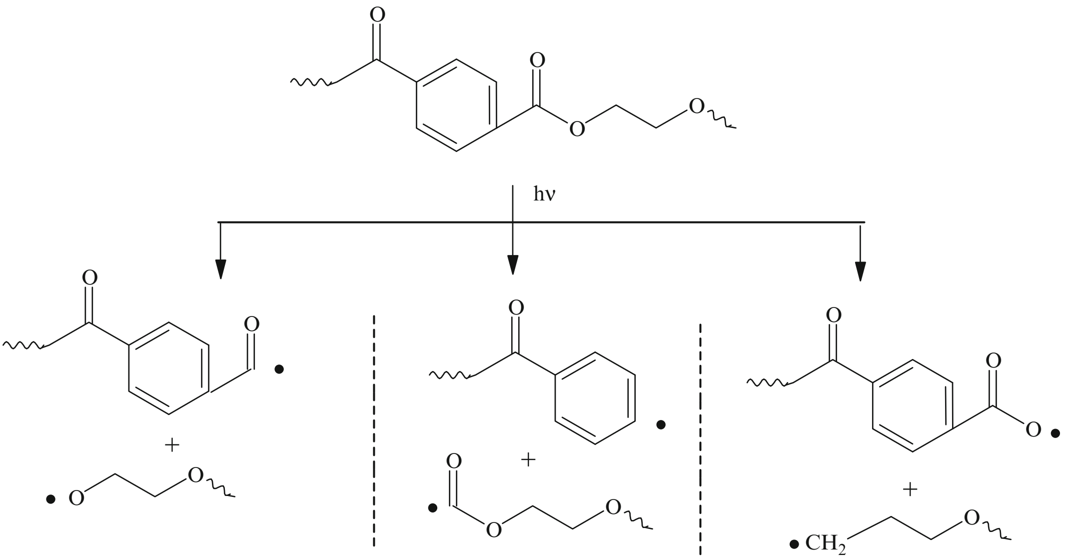
When poly(vinyl chloride) films are irradiated in the presence of benzophenone, the initiation is a result of hydrogen abstraction from the polymer by the excited triplet of the aromatic ketone [555]: This is followed by degradation that takes place by a chain mechanism:



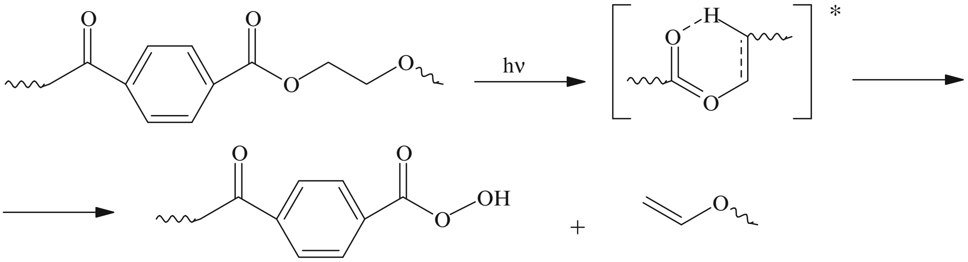
In the process, the chlorine radicals abstract hydrogens and form HCl. The quantum yield of hydrogen chloride from this reaction is $\Phi_{HCl} = 0.11$ [556]. This indicates that only 1 in every 100 photons that are absorbed causes the dehydrochlorination and is followed by formation of polyenes. It led to the conclusion that a photochemical process must take place between the polyene sequences and HCl [556, 557].

When *poly(phenyl vinyl ketone)* is irradiated by ultraviolet light of 365 nm, it degrades and exhibits a loss of molecular weight [558]. No benzaldehyde was found among the products. That excludes a Norrish Type I reaction and indicates that the polymer cleaves by a Norrish Type II mechanism [558].

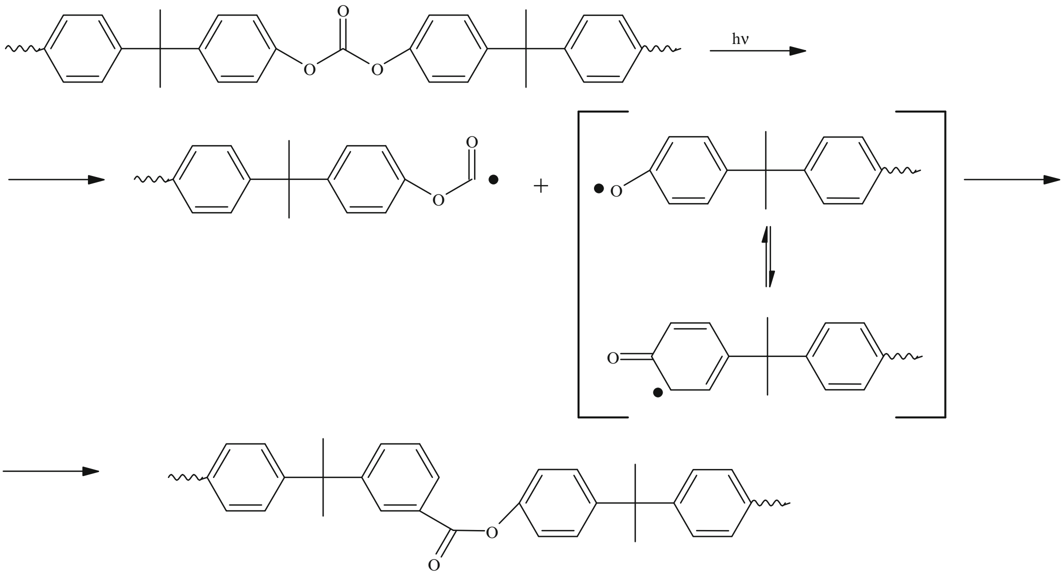
Day and Wiles have pictured the primary steps of photochemical decomposition of poly (ethylene terephthalate) as follows [559]:



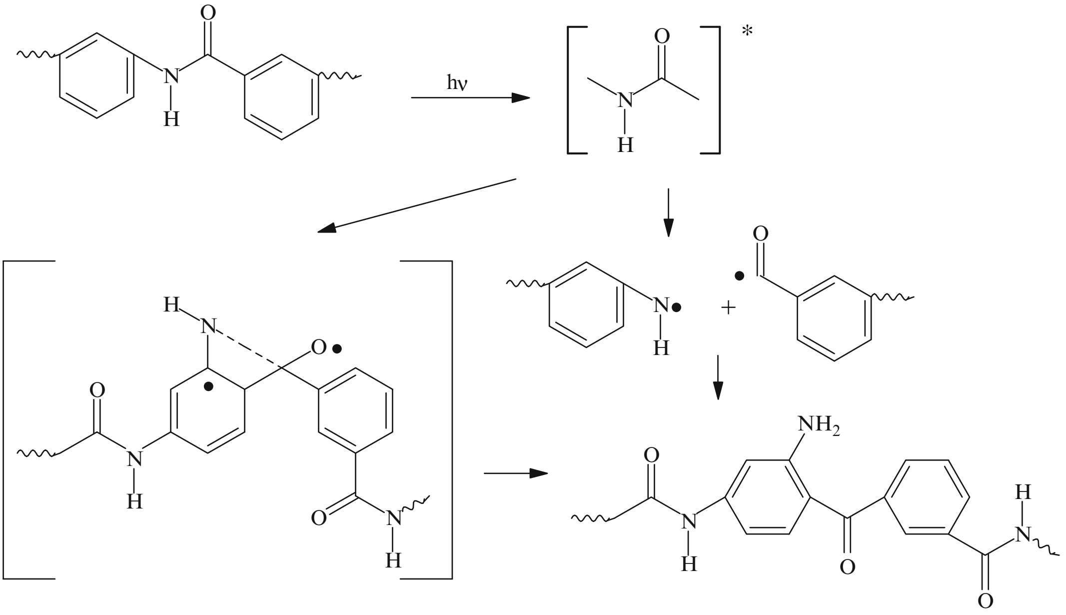
The mechanism of formation of carboxylic acid groups at the terminal ends of the degradation products was explained by a Norrish Type II reaction [559]:



In addition to the above, photo-Fries rearrangements occur in various aromatic polyester films upon ultraviolet light irradiation [560, 561]. Also, photo-Fries rearrangements are believed to occur in polycarbonate resins as well [562]. This can be illustrated as follows:



The same is true of aromatic polyamides where photo-Fries rearrangements are done according to the following mechanism [563]:



Photolytic decomposition of *polycarbonate* films was shown to produce products that are also consistent with the photo-Fries reaction. These are salicylic acid and bisphenol type species [580]. This is in agreement with earlier studies that showed that a variety of processes, including rearrangements (photo-Fries) and photo-oxidation, can occur when bisphenol A-based polycarbonate is photolyzed [581, 582].

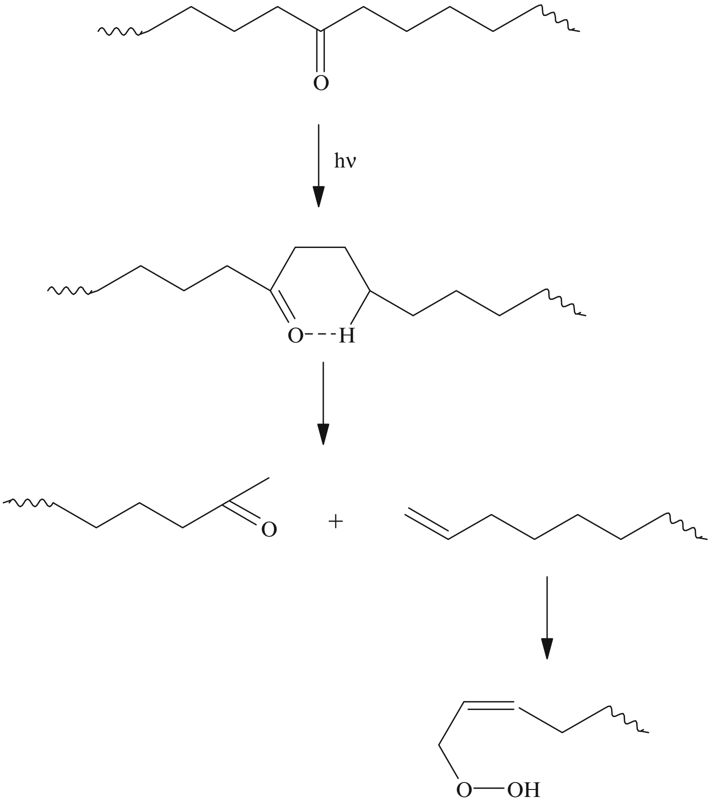
9.9.14 Photo-Oxidative Degradations of Polymers

Singlet oxygen, the lowest excited state of molecular oxygen, $^1\Delta_g$ O_2, is known to cause rapid degradation of polymers. Singlet oxygen forms by several processes, including one of two mechanisms: (1) through photosensitization by some impurity; (2) through energy transfer from an excited triplet state of a chromophore.

Polyolefins that are unprotected from weathering react very readily with oxygen in the presence of sunlight even at room temperature. This leads to loss of molecular weight and often embrittlement. The mechanism of *photo-oxidation of polyethylene* was demonstrated to involve carbonyl groups that developed in the polymer via oxidation during processing [564, 565]. These carbonyl groups act as chromophores and their triplet states ($n \to \pi^*$) are quenched by molecular oxygen in the ground triplet state. Electronically excited singlet oxygen molecules form as a result [564].

$$>C=O^3(n \to \pi^*) + O_2(^3\Sigma_g{}^-) \to C=O(S_0)+{}^1O_2$$

The Norrish Type II reaction then takes place with a cleavage of carbon to carbon bonds, formation of olefins and, subsequently, formation of hydroperoxides:



The hydroperoxides apparently have no photo inductive effect on the overall oxidation of polyethylene [566]. Photolysis of hydroperoxides, however, initiates new vinylidine oxidation.

It was shown that the kinetics of photo-oxidation of polyethylene is characterized by the superposition of two phenomena. The first corresponds to an exponential increase in the concentration of the carbonyl groups with time and is observed when the kinetics are controlled by the diffusion of oxygen. The second one is not controlled by diffusion, but corresponds to a linear increase of the carbonyl concentration with time and takes place in degraded samples. This is explained in terms of chain rupture in the amorphous regions of the polymer, allowing free access of oxygen [567].

Commercial *polypropylene* can photo-degrade rapidly. This is due to a presence of chromophore groups that form during polymerization. In addition, chromophores may also form through oxidation by singlet oxygen during extrusion in air. At temperatures of 250–300°C, light of 300 nm will initiate oxidation by atmospheric oxygen [568]. The hydroperoxide groups that form are not stable and decompose to alkoxy radicals to form ketones on the backbones and at the ends of the chains. These ketones in turn undergo Norrish Type I and Type II reactions when irradiated with ultraviolet light [568]:

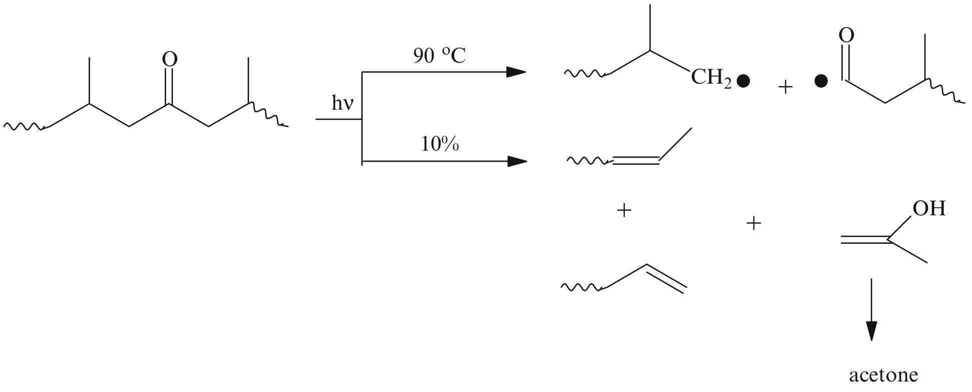


Photo-oxidation of *poly(vinyl chloride)* appears to be greatly enhanced by imperfections in the polymer structure that form during polymerization and processing. Formation of peroxide and carbonyl groups is very difficult to prevent. The initiation of photo-oxidation probably results from the free-radical that forms as these groups decompose upon irradiation [568]. In addition, double bonds that form from loss of HCl will sensitize formation of free radicals. These radicals are further oxidized and also promote cross-linking that results in gels.

Photo-oxidation of *cis-polybutadiene* was also shown to involve singlet oxygen [570]. Attacks by singlet oxygen on double bonds with formation of allylic hydroperoxides and shifts of these double bonds according to the *ene* reaction were confirmed by several other studies [571]. On the other hand, a study of model compounds for photo-oxidation of polyisoprene failed to show formation of endo peroxides by 1,4-cycloaddition [572].

Aromatic polyurethanes exhibit a strong tendency to yellow in sunlight. This may be accounted for by two mechanisms based on formation of different photoproducts. The first one was found to be a photo-Fries reaction caused by a short wave length light [572]. The second one, caused by longer wave length light, is formation of quinonoid structures [573]:

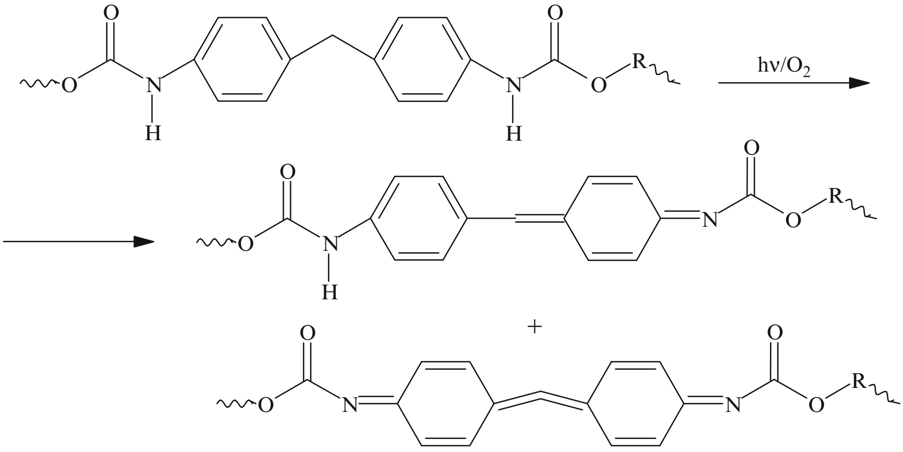
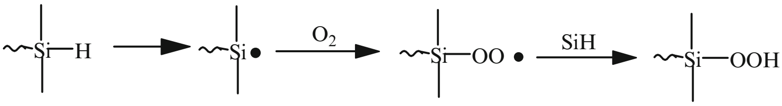


Photo-oxidation of Nylon 6 was also investigated [574]

The subject of *photo-oxidation of silicones* is seldom raised because these polymers are known for their stability to oxidation. Nevertheless, an investigation of photo-oxidative degradation of these materials showed that these materials can be affected by combined attacks of oxygen and ultraviolet irradiation [585]. The groups that are affected are the functional groups that are more fragile than the backbones. Thus, the silicon hydride group was found to be readily photo-oxidized, perhaps due to its low bond energy. The reaction can be illustrated as follows [585]:



The main process that occurs in silicones that contain vinyl groups is photo-scission. Also, the vinyl groups are photo-oxidized into silanols, carboxylic acids, and esters. Part of the silanols are condensed into high molecular weight silicones [585].

9.9.15 Degradation of Polymeric Materials by Ionizing Radiation

Ionizing radiation is not absorbed selectively like the ultraviolet. Instead, the absorption of gamma rays is a function of electron density in the path of the radiation. After a random ray strikes an atom, however, and energy transfer occurs, free-radicals may form and subsequent reactions, like oxidation and chain reactions, may proceed in the same manner as after UV light irradiation. In addition to creating free-radicals, ionizing radiation also gives rise to ions, electrons, and excited molecules in the medium. This is followed by reactions, like, chain scission, formation of unsaturation, and cross-linking that is accompanied by formation of volatile products.

Due to the high energy of ionizing radiation, if the irradiation dose is sufficiently high, all polymers will degrade to form low molecular weight fragments. The difference is in the rates of degradation and in the amounts of cross-linking.

Among vinyl polymers, those that tend to unzip and yield large quantities of monomers in thermal degradation are also likely to loose molecular weight rapidly upon irradiation. On the other hand, those vinyl polymers that yield low quantities of monomers during pyrolysis tend to cross-link instead. Also, it was observed that polymeric materials that exhibit high heats of polymerization during their formation tend to cross-link, while those that do not tend to degrade [575].

It was reported back in 1952 that *polyethylene* could be cross-linked by irradiation in a controlled manner [577]. The reaction is accompanied by evolution of considerable quantities of volatile gases that consist mainly of hydrogen. The portion of hydrogen that is released, however, is lower and the amount of volatile hydrocarbons is greater from polyethylene that is branched [578]. There appears to be an inverse relationship between the amount of branching and the quantity of hydrogen gas that is released [578].

Polypropylene was reported to cross-link under irradiation [579]. At the same time, there is a large evolution of gas. If the irradiation is carried out in air, there is marked degradation even at fairly low doses.

When polyisobutylene is irradiated, the molecular weight decreases rapidly until a viscous, low molecular weight liquid remains. At the same time, a mixture of hydrogen and methane (95% of total gas) is released [582].

Generally, aromatic structures are more stable to ionizing radiation than are the aliphatic ones. Accordingly, polystyrene is more resistant than polyethylene [575]. In addition, cross-linking predominates over chain scission.

The radiolysis of *poly(methyl methacrylate)* results in a rapid loss of molecular weight. This degradation increases with the intensity of the radiation [579]. The volatile products that form are hydrogen, carbon dioxide, carbon monoxide, methane, propane, and methyl methacrylate monomer. This varies with the temperature and the type of ionizing radiation that the polymer is exposed to.

Polytetrafluoroethylene is extremely sensitive to radiation and exhibits marked damage to its mechanical properties. It was shown that fluoride ions evolve from the polymer not only during irradiation, but also for long periods afterward [134]. The molecular weight of the polymer drops steadily with each dose. Many double bonds form in the polymer [580].

Review Questions

Section 9.1

1. What are the necessary conditions for a fair comparison of the reactivity of functional groups on macromolecules with those on small molecules.
2. When is unequal reactivity observed between large and small molecules?

3. Discuss the effect of diffusion-controlled reactions on reactivity of macromolecules.
4. Discuss how paired group and neighboring group effects influence random irreversible reactions.
5. Discuss reactions that favor large molecules.

Section 9.2

1. Explain, showing chemical equations, how hydrochlorination of natural rubber is often accompanied by cyclization.
2. Discuss chlorination of natural rubber. How can natural rubber and polybutadiene be brominated?
3. Discuss with the aid of chemical equations hydrogenation of 1,4-polybutadiene.
4. How can polyisoprene and polybutadiene be modified by additions of carbenes? Explain and discuss, showing the structures of the starting materials and the products.
5. Illustrate the Prins reactions of rubber with formaldehyde and with glyoxal. How can this reaction be carried out in the solid phase?
6. Discuss polar additions to unsaturated polymers. Give examples Include the *ene* reaction.
7. How can the Ritter reactions be carried out on isoprenes?
8. How can the Diels-Alder reactions are carried out with unsaturated polymers. Use chemical equations to illustrate.
9. Explain how polybutadiene and isoprene can be epoxidized, giving reagents and showing all by-products.

Section 9.3

1. Show how, and explain why, *cis*-polybutadiene rearranges to *trans* as a result of irradiation by gamma rays or ultraviolet light. Also, show what happens to polyisoprene when it is irradiated in the ultraviolet light.
2. Discuss with the aid of chemical equations the cyclization reactions of rubber.
3. How are polyacrylonitrile fibers converted to graphite-like fibers. Explain, showing all the steps in thermal cyclization of polyacrylonitrile.
4. Discuss migration of double bonds in polymers.
5. How does poly(4,4′-diphenylpropane isophthalate) rearrange upon irradiation with ultraviolet light?
6. Give examples of the Schmidt and Beckmann rearrangements.

Section 9.4

1. Discuss with the help of chemical equations the fluorination reactions of polyethylene.
2. Discuss chlorination of polyethylene and polypropylene.
3. How is chlorosulfonation of polyethylene carried out industrially. Explain and write the chemical equations for the reactions. How is the product used?

4. Discuss chlorination of poly(vinyl chloride).
5. Discuss chlorination of poly(vinylidine chloride) and poly(vinyl fluoride).
6. Describe the reactions of sodium azide with poly(vinyl chloride) and the subsequent reactions of the azide group. Use chemical equations.
7. Describe reactions of poly(vinyl chloride) with sulfur compounds.
8. What are the products of reactions of poly(vinyl chloride) with aniline? Show and explain.
9. Explain how carbanionic centers can be formed on the backbones of poly(vinyl chloride) molecules. Show what subsequent reactions can take place.
10. What happens when poly(vinyl chloride) is treated with organolithium compounds. Explain with the help of chemical equations.
11. Discuss photo chlorination of polystyrene.
12. Discuss chloromethylation reactions of polystyrene and its copolymers, showing all chemical reactions.
13. Discuss various reactions of chloromethylated polystyrene with the help of chemical equations.
14. Show examples of the Friedel-Craft reactions of polystyrene and chloromethylated polystyrene.
15. Discuss sulfonation of polystyrene.
16. Discuss nitration of polystyrene, reduction of nitropolystyrene, and the subsequent diazotization reaction.
17. Discuss matalation of polystyrene and subsequent reactions.
18. Discuss reduction reactions of the polymers of methacrylic and acrylic esters with metal hydrides. What solvents give optimum conditions?
19. Discuss nucleophilic substitution reactions of poly(methyl methacrylate); the Arndt-Eister reactions of poly(methacryloyl chloride) and the Curtius and Lossen rearrangements of poly (acryloyl chloride)
20. Show a Diels-Alder reaction of poly(furfuryl methacrylate) with maleic anhydride.
21. What are the industrial processes for preparation of poly(vinyl butyral)? Describe the process, showing all chemical reactions.
22. How can the Schotten-Baumann esterifications of poly(vinyl alcohol) are carried out? Explain.

Section 9.5

1. Discuss the vulcanization reactions of rubbers. Show all the chemical reactions.
2. Discuss ionizing radiation cross-linking of polymers.
3. Show the reaction of photocross-linking of poly(vinyl cinnamate) and explain the mechanism.
4. Show the reactions of photocross-linking of polymers bearing azide groups.
5. Draw examples of polymers with pendant benzoin and furoin groups.
6. Explain the mechanism of photocross-linking by $2\pi + 2\pi$ type dimerization. Give examples.
7. Discuss typical ultraviolet light-curable coating compositions by free radical and by cationic mechanisms.
8. Why are photoinitiators preferred to photosensitizers in UV-curable materials?
9. Discuss with the help of chemical equations the mechanism of photoreduction of aromatic ketone photoinitiators hydrogen donors and by electron donors.
10. Discuss photoinitiators for photocross-linking by cationic mechanisms, showing all reactions and products.
11. Discuss cross-linking reactions by electron beams.

Section 9.6

1. What is meant by microporous and macroreticular supports.
2. Discuss some applications of polymeric reagents. Show examples.
3. How are enzymes immobilized? Discuss, showing chemical reactions.
4. Discuss nonenzymatic catalysts.

Section 9.7

1. What is the mechanism of free-radical graft copolymer formation by chain-transferring technique. Explain by examples and discuss advantages and disadvantages.
2. Discuss free-radical grafting reactions to polymers with double bonds. Give examples and show reactions.
3. How can macromonomers be used to form graft copolymers? Give several examples.
4. How can polymerizations be initiated from the backbones of the polymers? Explain and give examples.
5. Discuss photochemical preparation of graft copolymers.
6. How is high-energy radiation used to form graft copolymers?
7. Discuss formations of graft copolymers by ionic chain-growth and step-growth polymerizations.

Section 9.8

1. Discuss advantages of block copolymers over polymer blends.
2. How can block copolyesters be formed? Explain with chemical equations.
3. How can block copolyamides be formed? Explain as in Question 2.
4. How can polyurethane-polyamide and polyamide-polyester block copolymers be formed? Explain and show chemical reactions.
5. What are polyurethane ionomers? How are they prepared?
6. Describe the technique for preparation of block copolymers of poly(α-olefins).
7. How do block copolymers form in simultaneous free radical and ionic chain-growth polymerizations? Explain and give examples.
8. Discuss formations of block copolymers by homogeneous ionic copolymerization.
9. How can block copolymers form by mechanochemical techniques?

Section 9.9

1. What is meant by polymer degradation and what are the various causes?

Section 9.10

1. What is the common technique for studying thermal degradation of polymers?
2. Explain the two thermal degradation processes in chain-growth polymers?

3. Describe the thermal degradation of polyolefins.
4. Describe the thermal degradation of polybutadienes.
5. What is the thermal degradation process in polystyrene and polystyrene-like polymers?
6. How do the methacrylic and acrylic esters degrade thermally?
7. What happens when polyacrylonitrile is heated? Describe
8. Discuss the thermal degradation of poly(vinyl chloride)
9. Discuss the thermal degradation of fluorocarbon polymers
10. Discuss the thermal degradation of poly(vinyl acetate)

Section 9.11

1. Can the step-growth polymers degrade in the same manner as the chain-growth polymers?
2. How do the polyoxides degrade thermally?
3. Discuss the thermal degradation of polyesters.
4. Discuss the thermal degradation of polyamides.
5. Discuss the thermal degradation of the epoxy resins
6. How do the polyimides and the polyquinoxalines degrade thermally?
7. Discuss the thermal degradation of polysulfones
8. How do cellulosic materials degrade thermally?

Section 9.12

1. How does hydrolytic degradation of polymers take place?

Section 9.13

1. Describe oxidative degradation in hydrocarbon polymers
2. Describe oxidative degradation of polystyrene
3. Describe oxidative degradation of poly(ethylene terephthalate)
4. How do the polyamides degrade oxidatively?

Section 9.14

1. What is meant by photo-degradation of polymers?
2. Describe photolysis of polyethylene.
3. Describe photo-degradation of polybutadiene and poly(*p*-methylstyrene)
4. How does poly(methyl methacrylate) degrade at elevated temperature under the influence of ultraviolet light?
5. Describe photo-degradation of poly(vinyl acetate) and poly(vinyl chloride)
6. What is the mechanism of photo-degradation of aromatic polyesters?

Section 9.15

1. What causes photo-oxidative degradation and how does it take place in polyolefins?
2. How does commercial polypropylene degrade photo-oxidatively?

Section 9.16

1. If you had to select polymeric materials for use near a nuclear reactor, what types of materials would you select? Explain.

References

1. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Chapt.II.
2. T. Alfrey Jr., *Chemical Reactions of Polymers*, (E.M. Fetters,ed)., Wiley-Interscience, New York, 1964, Capt. IA.
3. D.T.L. Chen and H. Morawetz, *Macromolecules*, **9**, 463 (1976)
4. S. Malkin and E. Fisher, *J. Phys. Chem*., **66**, 2482 (1962)
5. H. Morawetz, *J. Macromol. Sci.-Chem.,* **A13**, 311 (1979)
6. M. Kamachi, *Makromol. Chem., Suppl*., **14**, 17 (1985)
7. A. Okamoto, Y. Shimanuki, I, Mita, *Eur. Polym. J.,* **18**, 545 (1982); *ibid*, **19**, 341 (1983)
8. K.F. O'Driscoll and H.K. Mahabadi, *J. Polymer Sci., Chem. Ed.,* **11**, 869 (1976)
9. S. Benson and A.M. North, *J. Am. Chem. Soc.,* **84,** 935 (1962)
10. M. Kamachi, *Adv. Polym. Sci.,* **38**, 56 (1981)
11. P.J. Flory, *J. Am. Chem. Soc.*, **61**, 1518 (1939); T.H.K. Barron and E.A. Boucher, *Trans. Faraday Soc.,* **65** (12), 3301 (1969)
12. C.S. Marvel and C.L. Levesque, *J. Am. Chem. Soc*., **61**, 3234 (1939)
13. H. Morawetz and P.E. Zimmerling, *J. Phys. Chem.,* **58**, 753 (1954)
14. H. Morawetz and E. Gaetjens, *J. Polym. Sci*., **32**, 526 (1958)
15. P.E. Zimmerling, E.W. Westhead Jr., and H. Morawetz, *Biochem. Biophys. Acta,* **25**, 376 (1957)
16. V.O. Cherkezyan and A.D. Litmanovich, *Eur. Polym. J.,* **21**, 623 (1985)
17. A.D. Litmanovich, *Eur. Polym. J.,* **16**, 269 (1980)
18. S. Sawant and H. Morawetz, *Macromolecules*, **17**, 2427 (1984)
19. I. Sakurada, *Off. J. IUPAC,* **16** (2-3), 263 (1968)
20. D. Pini, R. Settambolo, A. Raffaelli, and P. Salvadori, *Macromolecules,* **20**, 58 (1987)
21. E. Gaetjens and H. Morawetz, *J. Am. Chem. Soc.,* **83**, 1738 (1961)
22. N. Plate, *Vysokomol. Soyed.,* **A10** (12), 2650 (1968)
23. W.H. Daly, *J. Macromol. Sci.-Chem.,* **A22**, 713 (1985)
24. A.R. Mathieson and J.V. McLaren, *J. Polymer Sci.,* **A,3**, 2555 (1965)
25. J.C. Layte and M. Mandel, *J. Polymer Sci.,* **A,2**, 1879 (1964)
26. F. Fleming and G.R. Marshal, *Tetrahedron Lett.,* 2403 (1970)
27. A. Patchornik and M.A. Kraus, *J. Am. Chem. Soc.,* **92**, 7587 (1970)
28. E.Bondi, M. Fidkin, and A. Patchornik, *Israel J. Chem.,* **6**, 22 (1968)
29. O. Fuchs, *Angew. Chem., Intern. Ed.,* **7** (5), 394 (1968)
30. M. Tsuda, *Makromol. Chem.,* **72**, 174 183 (1964)
31. D.M. Jones, *Adv. Carbohydrate Chem.,* **19**, 229 (1964)
32. E.M. Fetters, *Crystalline Olefin Polymers*, Part II, (R.A. Raff and K.W. Doaks, eds.), Interscience, New York, 1964
33. S. Tazuke, *Makromol. Chem., Suppl.,* **14**, 145 (1985)
34. M.R. Gomez-Anton, J.G. Rodriguez, and I.F. Pierola, *Macromolecules,* **19**, 2932 (1986)
35. A.D. Roberts, (ed.) *Natural Rubber Science and Technology,* Oxford University Press, New York, 1988
36. H. Staudinger and H. Staidinger, *J. Prakt. Chem.,* **162**, 148 (1943); *Rubber Chem. Technology,* **17**, 15 (1944)
37. C.S. Ramakrishnan, D. Raghunath, and J.B. Ponde, *Trans. Inst. Rubber Ind.,* **29**, 190 (1953); *ibid*., **30**, 129 (1954)
38. M. Troussier, *Rubber Chem. Technol.,* **29**, 302 (1956)
39. C.F. Broomfield, *J. Chem. Soc.,* **1944**, 114; *Rubber Chem. Technol.,* **17**, 759 (1944)

40. C.S. Ramakrishnan, D. Raghunath, and J.B. Ponde, *Trans. Instit. Rubber Ind.,* **30**, 129 (1954); *Rubber Chem. Technol.*, **28**, 598 (1955)
41. I.A.Tutorskii, L.V. Sokolova, and B.A. Dogadkin, *Vysokomol. soyed.,* **A13** (4), 952 (1971)
42. J. Royo, L. Gonzalez, L. Ibarra, and M. Barbero, *Makromol. Chem.,* **168**, 41 (1973)
43. G. Dall'Asta, P. Meneghini, and U. Gennaro, *Makromol. Chem,* **154**, 279 (1972)
44. G. Dall'Asta, P. Meneghini, I.W. Bassi, and U. Gennaro, *Makromol. Chem.,* **165**, 83 (1973)
45. I.W. Bassi and R. Scordamaglia, *Makromol Chem*., **166**, 283 (1973)
46. F. Stelzer, K. Hummel, C. Graimann, J. Hobisch, M.G. Martl, *Makromol. Chem.,* **188**, 1795 (1987)
47. K. Hummel, **J. Mol. Cat.**, **28**, 381 (1987); K. Hummel, *Pure Appl. Chem.,* **54**, 351 (1982)
48. Y.G. Garbachev, K.A. Garbatova, O.N. Belyatskaya, and V.E. Gul, *Vysokomol. Soed.,* **7**, 1645 (1965)
49. P.J. Canterino, *Ind. Eng. Chem.,* **49**, 712 (1957)
50. E. Ceausescu, R. Bordeianu, E. Buzdugan, I. Cerchez, P. Ghioca and R. Stancu, *J. Macromol. Sci. - Chem.,* **A22**, 803 (1985)
51. M. Bruzzone and A. Carbonaro, *J. Polymer Sci., Chem. Ed*., **23**, 139 (1985)
52. Y. Doi, A. Yano, K. Soga, and D.R. Burfield, *Macromolecules*, **19**, 2409 (1986)
53. N.A. Mohammadi and G.L. Rempel, *Macromolecules*, **20**, 2362 (1987)
54. H. Bradbury and M.C. Semale Perera, *Brit. Polymer J.,* **18**, 127 (1986); A. Konietzny and U. Bietham, *Angew. Makromol. Chem.,* **74**, 61 (1978)
55. S. Siddiqui and R.E. Cais, *Macromolecules*, **19**, 595 (1986)
56. S. Siddiqui and R.E. Cais, *Macromolecules*, **19**, 998 (1986)
57. R.E.Cais and S. Siddiqui, *Macromolecules,* **20**, 1004 (1987)
58. H. Stuger and R. West, *Macromolecules*, **18**, 2349 (1985)
59. H.J. Prins, *Chem. Weekblad,* **17**, 932 (1917); *ibid.,* **16**, 1510 (1919)
60. F. Kirchhoff, *Chem. Ztg.,* **47**, 513 (1923)
61. J. McGavack, U.S. Patent # 1,640,363 (Aug. 30, 1927)
62. D.F. Twiss and F.A. Jones, Brit. Patent # 348 303 (March 24, 1930)
63. D.F. Twiss and F.A. Jones, Brit. Patent # 523 734 (July 22, 1940)
64. G.H. Latham, U.S. Patent # 2,417,424 (March 18, 1947)
65. S. Hirano and R. Oda, *J. Soc. Chem. Ind. (Japan),* **47**, 833 (1944); from *Chem. Abstr.,* **42**, 7982 (1948)
66. D.F. Twiss and F.A. Jones, U.S. Patent # 1,915,808 (June 27, 1933)
67. C. Harris, *Ber.,* **37**, 2708 (1904)
68. C. Pinazzi and R. Pautrat, *Compt. Rend.,* **254**, 1997 (1962); from *Chem. Abstr.,* **56**, 15647 (1962)
69. C. Pinazzi and R. Pautrat, *Rev. Gen. Coutchuc*, **39**, 799 (1962)
70. C. Pinazzi, R. Pautrat, and R. Cheritat, *Compt. rend*., **256**, 2390, 2607 (1963)
71. S.K. Lee. *Am. Chem. Soc. Polymer Preprints*, **8**, 700 (1967)
72. Y. Minoura and H. Ikeda, *J. Appl. Polymer Sci.,* **15**, 2219 (1971)
73. G. Caraculacu and I. Zugravescu, *J. Polymer Sci., Polymer Letters*, **6**, 451 (1968)
74. C.G. Gubelein, *J. Macromol. Sci. - Chem.,* **A5**, 433 (1971)
75. K. Toda, Y. Numata, and T. Katsumura, *J. Appl. Polymer Sci.,* **15**, 2219 (1971)
76. K.W. Leong and G.B. Butler, *J. Macromol. Sci. - Chem*., **A14**,287 (1980); C,S,L. Baker and D. Bernard, *Am. Chem. Soc., Polymer Preprints*, **26** (2), 29 (1985)
77. D.A. Bansleben and F. Jachimowicz, *Am. Chem. Soc., Polymer Preprints,* **26** (1), 106 (1985)
78. M. Anavi and A. Zilkha, *Eu. Polymer J.,* **5**, 21 (1969)
79. J.W. Mench and B. Fulkerson, *Ind. and End. Chem.,* **7**, 2 (1968)
80. J.P. Kennedy and R.A. Smith *J. Polymer Sci., Chem. Ed.,* **18**, 1523 (1980)
81. B. Ivan, J.P. Kennedy and V.S.C. Chang, ***J.*** *Polymer Sci., Chem. Ed*.. **18**, 3177 (1980)
82. J.P. Kennedy, V.S.C. Chang, and W.P. Francik, *J. Polymer Sci., Chem. Ed.,* **20**, 2809 (1982)
83. W.A. Thaler, S.J. Brois, and F.W. Ferrara, *Macromolecules*, **20**, 254 (1987)
84. E. Ceausescu, S. Bittman, V. Fieroiu, E. Badea, E. Gruber, A. Ciupitoiu, and V. Apostol, *J. Macroml. Sci.-Chem.,* **A22** (5-7), 525 (1985)
85. T. Nishikubo, T. Shimokawa, and H. Arita, *Makromol. Chem*., **188**, 2105 (1987)
86. T. Katayama and H.K. Hill Jr., *Macromolecules*, **20**, 1451 (1987)
87. H.L. Cohen, *J. Polymer Sci., Chem. Ed.,* **22**, 2293 (1984)
88. G.J. Carlson, J.R. Skinner, C.W. Smith, and C.H. Wilcoxen Jr.,U.S. Patent # 2,870,171 (May 6, 1958)
89. C.W. Smith and G.P. Payne, U.S. Patent # 2,786,854 (March 26, 1957)
90. C.M. Gable, U.S. Patent # 2,870,171 (Jan 20, 1959)
91. W.C. Smith, *Rec. Trav. Chim.,* **29**, 686 (1930); from *Chem. Abstr.,* **24**, 4261 (1930)
92. F.P. Greenspan and R.E. Light Jr., U.S. Patent # 2,829,130 (April 1958)
93. S. Tocker, U.S. Patent # 3,043,818 (July 1962)

94. R.W. Rees, U.S. Patent # 3,050,507 (August 1962)
95. H. Lee and K. Neville, *Handbook of Epoxy Resins*, Mc Grow-Hill, New York, 1967
96. W.G. Potter, *Epoxy Resins*, Springer-Verlag, New York, 1970
97. C.A. May, (ed.) *Epoxy Resins: Chemistry and Technology*, 2nd. ed., Dekker, New York, 1988
98. A.F. Chadwick, D.O. Barlow, A.A. D'Adieco, and J.W. Wallace, *J. Am. Oil Chemists Soc*., **35**, 355 (1958)
99. K. Meyersen and J.Y.C. Wang, *J. Polymer Sci*., **A,5**, 725 (1967)
100. H.S. Makowski, M. Lynn, and D.H. Rotenberg, *J. Macromol. Sci.-Chem.,* **A4**, 1563 (1980)
101. D. Zuchowska, *Polymer*, **21**, 514 (1980)
102. M.A. Golub, *J. Am. Chem. Soc*., **80**, 1794 (1958)
103. M.A. Golub, *J. Am. Chem. Soc*., **81**, 54 (1959)
104. M.A. Golub, *J. Am. Chem. Soc*., **82**, 5093 (1960)
105. M.A. Golub, *J. Phys. Chem.,* **66**, 1202 (1962)
106. M.A. Golub and C.L. Stephens, *J. Polymer Sci.,* **C-6** (16), 765 (1967)
107. R.W. Lenz, K. Ohata, J. Funt, *J. Polymer Sci.-Chem. Ed.,* **11**, 2273 (1973)
108. M.A. Golub and J. Hiller, *Can. J. Chem.,* **41**, 937 (1963)
109. M.A. Golub and J. Hiller, *Tetrahedron Letters*, 2137 (1963)
110. R.J. Angelo, M.L. Wallach, and R.M. Ikeda, *Am. Chem. Soc. Polymer Preprints*, **8** (1), 221 (1967)
111. M.A. Golub and J. Heller, *J. Polymer Sci., Polymer Letters*, **4**, 469 (1966)
112. N.G. Gaylord, I. Kossler, M. Stolka, and J. Vodehnal, *J. Am. Chem. Soc.,* **85**, 641 (1963)
113. N.G. Gaylord, I. Kossler, M. Stolka, and J. Vodehnal, *J. Polymer Sci.,* **A-1,2**, 3969 (1964)
114. M. Stolka, J. Vodehnal, and I. Kossler, *J. Polymer Sci.,* **A-1,2**, 3987 (1964)
115. I. Kossler, J. Vodehnal, and M. Stolka, *J Polymer Sci.,* **A-1,3**, 2081 (1965)
116. P. Ehrburger and J.B. Donnet, *High Technology Rubbers*, Part A, (M. Lewin and J. Preston, eds.), Dekker, New York, 1985; G. Henrici-Olive' and S. Olive', *Adv. Polym. Sci.,* **51**, 1 (1983); E. Fitzer, *Angew. Chem., Intern. Ed*., **19**, 375 (1980)
117. E.M. Bevilacqua, *Rubber Chem. Technol.,* **30**, 667 (1957)
118. E.M. Bevilacqua, *J. Am. Chem. Soc.,* **79**, 2915 (1957)
119. E.M. Bevilacqua, *Science,* **126**, 396 (1957)
120. E.M. Bevilacqua, *J. Am. Chem. Soc.,* **81**, 5071 (1959)
121. G. Salmon and Chr. van der Schee, *J. Polymer Sci.,* **14**, 287 (1954)
122. M.A. Golub and C.L. Stephens, *J. Polymer Sci.,* **A-1,6**, 763 (1968)
123. M.A. Golub, *J. Polymer Sci., Polymer Letters,* **12**, 615 (1974); *ibid.,* **12**, 295 (1974)
124. M.A. Golub and J.L. Rosenberg, *J. Polymer Sci., Chem. Ed.,* **18**, 2548 (1980)
125. M.A. Golub, *J. Polymer Sci., Chem. Ed.,* **19**, 1073 (1981)
126. R.W. Lenz, K. Ohata, and J. Funt, *J. Polymer Sci., Chem. Ed.,***11**, 2273 (1973)
127. S.B. Maerov, *J. Polymer Sci.,* **A-1,3**, 487 (1963)
128. F. Millich and R. Sinclair, *Chem. and Eng. News*, p.30, (June 26, 1967)
129. R.H. Michel and W.A. Murphy, *J. Polymer Sci.,* **55**, 741 (1961)
130. S. van Paeschen, *Makromol. Chem.,* **63**, 123 (1963)
131. J.A. Banchette and J.D. Cotman Jr., *J. Org. Chem.,* **23**, 117 (1958)
132. H. Morawetz and B. Vogel, *J. Am. Chem. Soc.,* **91**, 563 (1969)
133. H. Morawetz and G. Gordimer, *J. Am. Chem. Soc*., **92**, 7532 (1970)
134. G.A. Gordon, R.E. Cohen, R.F.Baddour, *Macromolecules*, **18**, 98 (1985)
135. A.J. Rudge, Brit. Patent # 710,523 (June 16, 1954)
136. I. Vogt and W. Krings, German Patent # 1,086,891 (Aug. 11, 1960)
137. M. Okada and K. Makuuchi, *Kagyo Kagaku Zashi,* **73**, 1211 (1970) (from a private English translation)
138. H. Schonhorn, P.K. Gallagher, J.P. Luongo, F.J. Padden Jr., *Macromolecules*, **3**, 800 (1970)
139. W.T. Miller and A.L. Dittman, *J. Am. Chem. Soc.,* **78**, 2793 (1956)
140. J.R. Myles and P.J. Garner, U.S. Patent # 2,422,919 (June 24, 1947)
141. W.N. Baxter, U.S. Patent # 2,849,431 (Aug. 26, 1958)
142. L.B. Krentsel, A.D. Litmanovich, I.V. Patsukhova, and V.A. Agasandyan, *Vysokomol. soyed*., **A13**, 2489 (1971)
143. M. Goren, *Polim. Vehomerim Plast.,* #1, 8 (1971)
144. R.S. Taylor, U.S. Patent # 2,592,763 (April 20, 1952)
145. H.W. Thompson and P. Torkington, *Trns. Faraday Soc.,* **41**, 254 (1945)
146. K. Nambu, *J. Appl. Polymer Sci.,* **4**, 69 (1960)
147. T. Nakagawa and S. Yamada, *J. Appl. Polymer Sci.,* **16**, 1997 (1972)
148. G.D. Jones, *Chemical Reactions of Polymers*, (E.M. Fetters, ed.),Wiley- Interscience, New York, 1964
149. Brit. Patent # 811,848 (April 15, 1959); from *Chem. Abstr.,* **53**, 23100f (1951)
150. H. Noeske and O. Roeleau, U.S. Patent # 2, 889,259 (June 2, 1959)

151. A. McAlevy, U.S. Patent # 2,405,971 (August 20, 1946)
152. R.E. Brooks, E.D. Straom and A. McAlevy, *Rubber World*, **127**, 791 (1953)
153. G. Natta, G. Mazzanti, and M. Buzzoni, Ital. Patent # 563,508 (April 24, 1956)
154. K. Konishi, K. Yamaguchi, and M. Takahisha, *J. Appl. Polymer Sci.*, **15**, 257 (1971)
155. P. Bertican, J.J. Bejat, and G. Vallet, *J. Chim. Phys, Physicochim. Biol.,* **67**, 164 (1979)
156. R.T. Sikorski and E. Czerwinska, *Polymer,* **25**, 1371 (1984)
157. R.T. Sikorski and E. Czerwinska, *Eu. Polymer J.,* **22**, 179 (1986)
158. C. Decker, *J. Polymer Sci., Polymer Letters*, **25**, 5 (1987)
159. G. Svegliado and F.Z. Grandi, *J. Appl. Polymer Sci.,* **13**, 1113 (1969)
160. M. Kolinsky, D. Doskocilova, B. Schneider, and J. Stokr, *J. Polymer Sci.,* **A-1,9,** 791 (1971)
161. Backskai, L.P. Lindeman, and J.W. Adams. *J. Polymer Sci.,* **A-1,9**, 991 (1971)
162. G.G. Scherer, P. Pfluger, H. Braun, J. Klein, H. Weddecke, *Makromol. Chem., Rapid Commun.,* **5**, 611 (1984)
163. M. Takeishi and M. Okawara, J. Polymer Sci., Polymer Letters, **7**, 201 (1969)
164. M. Takeishi and M. Okawara, *J. Polymer Sci., Polymer Letters,* **8**, 829 (1970)
165. M. Okawara, T. Endo, and Y. Kurusu, *Progress of Polymer Sci., Japan*, (K. Imahori, ed.) Vol. 4, p. 105, 1972
166. K. Mori and Y. Nakamura, *J. Polymer Sci., Polymer Letters*, **9**, 547 (1971)
167. G. Levin, *Makromol Chem., Rapid Commun.,* **5**, 513 (1984)
168. M.K. Naqvi and P. Josph, *Polymer Communication*, **27**, 8 (1986)
169. Z. Wolkober and I. Varga, *J. Polymer Sci.*, **C** (16), 3059 (1967)
170. H. Calvayrac and J. Gole, *Bull. Soc. Chim. France*, **1986**, 1076
171. E. Roman, G. Valenzuela, L. Gargallo, D. Radic, *J. Polymer Sci.,* **21** 2057 (1983)
172. D. Braun and E. Seeling, *Makromol. Chem.,* **86**, 124 (1965)
173. W. Hahn and W. Muller, *Makroml. Chem.,* **16**, 71 (1955)
174. M. Okawara, *Am. Chem.Soc. Coatings and Plastics Chemistry Preprints*, **40**, 39 (1979)
175. Y. Nakamura, K. Mori, and M. Kaneda, *Nippon Kagaku Kaishi,* 1620 (1976); from ref. # 164.
176. R.K. Jenkings, N.R. Byrd, and J.L. Lister, *J. Appl. Polymer Sci.,* **12**, 2059 (1968)
177. R.A. Haldon and J.N. Hay, *J. Polymer Sci.,* **A-1,5**, 2295 (1967)
178. J.C. Bevington and L. Rotti, *Eu. Polym. J.,* **8**, 1105 (1972)
179. R. Tarascon, M. Hartney, M.J. Bowden, *Am. Chem. Soc. Polymer Preprints,* **25** (1), 289 (1984)
180. T. Saegusa and R. Oda, *Bull. Inst. Chem. Research Kyoto Univ.,***33,** 126 (1955); from *Chem. Abstr.,* **50**, 1357 (1956)
181. F. Helfferich, *Ion Exchange*, McGraw-Hill, N.Y., 1962; G.A. Olah and W.S. Tolgyesi, *Friedel-Craft and Related Reactions*, (G.A. Olah, ed.), Wiley-Interscience, New York, 1964; W.E. Wright, E.G. Topikar, and S.A. Svejda, *Macromolecules*, **24**, 5879 (1991)
182. G. Pozniak and W. Trochimszuk, *J. Appl. Polymer Sci.,* **27**, 1833 (1982)
183. C.H. Bamford and H. Linsay, *Polymer,* **14**, 330 (1973)
184. R. Hauptman, F. Wolf, and D. Warnecke, *Plaste Kaut.,* **18**, 330 (1971)
185. E.E. Ergojin, S.P. Rafikov, and B.A. Muhidtina, *Izv. Akad. Nauk Kaz. S.S.R.,* **19** (16), 49 (1969)
186. G.Z. Esipov, L.A. Derevyanki, V.P. Markidin, R.G. Rakhuba, and K.L. Poplavskii, *Vysokomol. soyed.,* **B12**, 274 (1970)
187. S. Belfer, R. Glozman, A. Deshe, and A. Warshawsky, *J. Appl. Polymer Sci.,* **25**, 2241 (1980)
188. S.R. Rafikov, G.N. Chelnokova, and G.M. Dzhilkibayeva, *Vysokomol. soyed.,* **B10**, 329 (1968)
189. L. Galeazzi, German Pat. # 2,455,946 (June 1975)
190. W.H. Daly, *J. Macromol. Sci., Chem.,* **A22**, 713 (1985)
191. S. Mohanraj and W.T. Ford, *Macromolecules,* **19**, 2470 (1986)
192. S.R. Rafikov, G.M. Dzhilkibayeva, G.N. Chelkova, and G.B. Shaltuper, *Vysokomol. soyed.,* **A12** (7) 1608 (1970)
193. P. Hodge and J. Waterhouse, *Polymer,* **22**, 1153 (1981)
194. M. Hassanein, A. Akelah, *Am. Chem. Soc. Polymer Preprints,* **26** (1), 88 (1985)
195. T.D. N'guyen, J.C. Gautier, and S. Boileau, *Am. Chem. Soc. Polymer Preprints,* **23**, 143 (1982)
196. P. Hodge, B.J. Hunt, E. Khoshdel, and J. Waterhouse, *Am. Chem. Soc. Polymer Preprints,* **23**, 147 (1982)
197. P. Hodge, B.J. Hunt, J. Waterhouse, and A. Wightman, *Polymer Communications*, **24**, 70 (1983)
198. M. Takeishi, N. Umeta, *Makromol. Chem., Rapid Commun.,* **3**, 875 (1982)
199. B.N. Kolarz, A. Rapak, *Makromol. Chem.,* **185**, 2511 (1984)
200. T. Iizawa, T. Nishikubo, Y. Masuda, M. Okawara, *Macromolecules*, **17**, 992 (1984)
201. G.D. Jones and S.J. Goetz, *J. Polymer Sci.,* **25**, 201 (1957)
202. G.D. Jones, *Ind. Eng. Chem.,* **44**, 2686 (1952)
203. F. Marinola and G. Naumann, *Angew. Makromolekulare Chem.,* **4/5**,185 (1968)
204. S. Dragan, I. Petrariu and M. Dima, *J. Polymer Sci., Chem. Ed.,* **10**, 3077 (1986)
205. S. Dragan, V. Barboiu, D. Csergo, I. Petrariu, M. Dima, *Makromol. Chem.,* **187**, (1986)

206. R.E. Kesting, *Synthetic Polymeric Membranes*, McGraw-Hill, New York, 1971
207. W.Chen, R. Mesrobian, and D. Ballantine, *J. Polymer Sci.,* **23**, 903 (1957)
208. G.V. Kharitonov and L.P. Belikova, *Vysokomol. soyed.,* **A11** (11), 2424 (1969)
209. W.O. Kenyon and G.P. Waugh, *J. Polymer Sci.,* **32**, 83 (1958); C,C, Unruh, *J. Appl. Polymer Sci.,* **2**, 358 (1959)
210. W.R. Bussing and N.A. Peppas, *Polymer*, **24**, 209 (1983)
211. D.G. Barar, K.P. Staller, and N.A. Peppas, *J. Polymer Sci., Chem. Ed.,* **21**, 1013 (1983)
212. R. Singer, A. Demagistri, and C. Miller, *Makromol. Chem.,* **18/19**, 139 (1956)
213. R. Singer and A. Demagistri, *J. Chim. Phys.,* **47**, 704 (1950)
214. M. Baer, U.S. Patent # 2,533,211 (Dec. 12, 1950)
215. R. Singer, U.S. Patent # 2,604, 456 (July 22, 1952)
216. B. Blaser, M. Rugenstein and T. Tischbirek, U.S. Patent # 2,764,576 (Sept. 25,1956)
217. H.H. Roth, *Ind. Eng. Chem*., **46**, 2435 (1954)
218. J. Eichhorn, U.S. Patent # 2,877,213 (Mar. 10, 1959)
219. C.F.H. Aleen and L.M. Minsk, U.S. Patent #2,735,841 (Feb. 21, 1956)
220. J. Blyth and A.W. Hofman, *Ann. Chem.,* **53**, 316 (1984)
221. H. Zenftman, *J. Chem. Soc.,* **1950**, 820
222. A.S. Matlack and D.S. Breslow, *J. Polymer Sci.,* **45**, 265 (1960)
223. J.A. Blanchette and J.D. Cotman Jr., *J. Org. Chem.,* **23**, 117 (1958)
224. F. Cramer, H. Helbig, H. Hettler, K.H. Scheit and H. Seliger, *Angew. Chem.,* **78**, 64 (1966); *ibid., Intern. Edit.,* **5**, 601 (1966)
225. B. Philipp, G. Reinisch, and G. Rafler, *Plaste und Kautschuk,* **3**, 190 (1972)
226. W.Kern, R.C. Schulz, and D. Braun, *Chemiker Ztg./Chem. Apparatur,* **84** (12), 385 (1960)
227. G. Greber and J. Toelle, *Makromol. Chem.,* **52**, 208 (1962)
228. R.P. Quirk and P.L. Chemg, *Macromolecules*, **19**, 1291 (1986)
229. D. Braun, *Makromol. Chem.,* **30**, 85 (1959)
230. D. Braun, *Makromol. Chem*., **33**, 181 (1959)
231. D. Braun, H. Daimond, and G. Becker, *Makromol. Chem.,* **62**, 183 (1963)
232. D. Braun, *Chimia,* **14**, 24 (1960)
233. Y. Yamada and M. Okawara, *Makromol. Chem.,* **152**, 153 (1972)
234. Y. Yamada and M. Okawara, *Makromol. Chem.,* **152**, 163 (1972)
235. K. Chander, R.C. Anand, I.K. Varma, *J. Macromol. Sci. - Chem.,* **A20**, 697 (1983)
236. J. Petit and B. Houel, *Comp. rend.,* **246**, 1427 (1958)
237. B. Houel, *Comp. rend.,* **246**, 2488 (1958)
238. R.C. Schulz, P. Elzer, and W. Kern, *Chimia*, **13**, 237 (1959)
239. C.S. Marvel and J.H. Shpherd, *J. Org. Chem.,* **24**, 599 (1961)
240. H.L. Cohen, D.G. Borden, and L.M. Minst, *J. Org. Chem.,* **26**, 1274 (1959)
241. W. Frey and E. Klesper, *Eur. Polym. J.,* **22**, 735 (1986)
242. H.L. Cohen and L.M. Minsk, *J. Org. Chem.,* **24**, 1404 (1959)
243. J.A. Banchette and J.D. Cotman, *J. Org. Chem.,* **23**, 1117 (1958)
244. W. Kern and R.C. Schulz, *Angew. Chem.,* **69**, 153 (1957)
245. R. Vartan-Boghossian, B. Dederichs, and E. Klesper, *Eur. Polym. J.,* **22**, 23 (1986)
246. R. Roussel, M.O. De Guerrero, J.C. Gallin, *Macromolecules*, **19**, 291 (1986)
247. S. Rondou, G. Smets, and M.C. De Wilde-Delvaux, *J. Polymer Sci.,* **24**, 261 (1957)
248. M. Vrancken and G. Smets, *J. Polymer Sci., 14,* 521 (1954)
249. M. Mullier and G. Smets, *J. Polymer Sci.,* **23**, 915 (1957)
250. A. Ravve, *J. Polymer Sci.,* **A-1,6**, 2889 (1968)
251. G. Van Paeschen, *Makromol. Chem.,* **63**, 123 (1963)
252. H. Boudevska, *Izv. Bulgar. Acad. of Sci.,* **3**, 303 (1970)
253. C.E. Carraher Jr., and L.S. Wang, *Makromol. Chem.,* **152**, 43 (1972)
254. V. Janout and P. Cafelin, *Makromol. Chem.,* **182**, 2989 (1981)
255. N.S. Bondareva and E.N. Rastovskii, *Zh. Prikl. Khim. (Leningrad),* **43** (1), 215 (1970)
256. I.V. Andreyeva, MM. Kotin, L.Ya. Modreskay, Ye.I. Pokrovskii, and G.V. Lyubimova, *Vysokomol. soyed.,* **A14** (7), 1565 (1972)
257. K. Ogasawara, N. Yamagami, and S. Matuzawa, *Angew. Makroml. Chem.,* **25**, 15 (1972)
258. K. Imai, T. Shiomi, T. Tsuchida, C. Watanabe, and S. Nishioka, *J. Polymer Sci.,* **A-1,21**, 305 (1983)
259. K. Imai, T. Shiomi, Y. Tezuka, M. Miya, *J. Polymer Sci., Chem. Ed.,* **22**, 841 (1984)
260. K. Ichimura, *J. Polymer Sci., Chem. Ed.,* **A-1,20**, 1411 (1982)
261. K. Ichimura and S. Watanabe, *J. Polymer Sci., Chem. Ed.,* **A-1,20**, 1419 (1982)
262. M. Tsuda, H. Tanaka, H. Tagami, F. Hori, *Makromol. Chem.,* **167**, 183 (1973)

263. P. Gramain and J. Le Moigue, *Eur. Polymer J.,* **8**, 703 (1972)
264. M. Anavi and A. Zilkha, *Eur. Polymer J.,* **5**, 21 (1969)
265. L. Merle-Aubry, Y. Merle, and E. Selegny, *Makromol. Chem.,* **172**, 115 (1973)
266. L.X. Mallavarapu and A. Ravve, *J. Polymer Sci.,* **A,3**, 593 (1965)
267. G. Reinisch and Dietrich, *Eur. Polymer J.,* **6**, 1269 (1970)
268. E.J. Gunster and R.S. Schulz, *Makromol. Chem.,* **180**, 1891 (1979)
269. J. Klein and E. Klesper, *Makromol. Chem., Rapid Commun.,* **5**, 701 (1984)
270. H.R. Kricheldorf, P. Jahnke, and N. Scharnag, *Macromolecules,* **25**, 1382 (1992)
271. H.S.J. Lee and W.P. Weber, *Macromolecules*, **24**, 4749 (1991)
272. H.L. Fisher, *Chemistry of Natural and Synthetic Rubber*, Reinhold, New York, 1957
273. P.W. Allen, D.Barnard, and B. Saville, *Chem. Brit.,* **6**, 382 (1970)
274. C.G. Moore and J. Scanlan, *J. Polymer Sci.,* **43**, 23 (1960)
275. N.G. Gaylord and F.S. Ang, *Chemical Reactions of Polymers*, (E.M. Fetters, ed.), Wiley-Interscience, New York, 1964
276. S.L. Regen. *J. Org. Chem.*, **1977**, *42*, 875
277. H. Komeili-Zadeh, H.J.-M. Don, and J. Metzger, *J. Organ. Chem.,* **43**, 156 (1978)
278. S. Colonna, R. Fornasier, and U. Pfeiffer, *J. Chem. Soc., Perkin Trans.,* **1**, 8 (1978)
279. E. Chiellini and R. Solaro, *J. Chem. Soc., Chem. Commun.,* **1977**, 231
280. A. Mastagli, A. Froch, and G. Durr, *C.R. Acad. Sci., Paris*, **235**, 1402 (1952)
281. E.C. Blossey, D.C. Neckers, C. Douglas, A.L. Thayer, and A.P. Schaap, *J. Am. Chem. Soc.,* **95**, 582 (1973)
282. H.A.J. Battaerd and G.W. Tregear, *Graft Copolymers,* Wiley-Interscience, New York, 1967
283. P. Dreyfus and R.P. Quirk, "Graft Copolymers", in *Encyclopedia of Polymer Science and Engineering,* Vol 7, 2nd. ed., (H.F. Mark, N.M. Bikales, C.G. Overberger, and G. Menges, eds.), Wiley-Interscience, New York, 1986
284. S. Basu, J.N. Sen, and S.R. Palit, *Proc. Roy. Soc. (London),* **A202**, 485 (1950);
285. R.A. Gregg and F.R. Mayo, *J. Am. Chem. Soc.,* **75**, 3530 (1953)
286. D. Lim and O. Wichterle, *J. Polymer Sci.,* **5**, 606 (1961)
287. M. Morton and I. Purma, *J. Am. Chem. Soc.,* **80**, 5596 (1958)
288. S. Okamura and K. Katagiri, *Makromol. Chem.,* **28**, 177 (1958); Z.M. Wang, H. Hong. and T.C. Chung, *Macromolecules*, **2005**, *38*, 8966
289. G.V. Schulz, G. Henrici, and S. Olive', *J. Polymer Sci.,* **17**, 45 (1955)
290. G. Smets, J. Roovers, and W. Van Humbeek, *J. Appl. Polymer Sci.,* **5**, 149 (1961)
291. G. Smets and M. Claesen, *J. Polymer Sci.,* **8**, 289 (1952)
292. R.A. Hays, *J. Polymer Sci.,* **11**, 531 (1953)
293. R.A. Gregg and F.R. Mayo, *J. Am. Chem. Soc.,* **75**, 3530 (1953)
294. A. Gsperowicz, M. Kolendowicz, and T. Skowronski, *Polymer*, **23**, 839 (1982)
295. M.S. Gluckman, M.J. Kampf, J.L. O'Brien, T.G. Fox, and R.K. Graham, *J. Polymer Sci.*, **37**, 411 (1959)
296. T.G. Fox, M.S. Guckman, F,B, Gornick, R.K. Graham, and G. Gratch, *J. Polymer Sci.,* **37**, 397 (1959)
297. D.K. Ray Chandhuri and J.J. Hermans, *J. Polymer Sci.,* **48**, 159 (1960)
298. S. Nakamura, E. Yoshikawa, and K. Matsuzaki, *J. Appl. Polymer Sci.,* **25**, 1833 (1988)
299. S. Nakamura, H. Sato, and K. Matsuzaki, *J. Polymer Sci., Polymer Letters*, **11**, 221 (1973)
300. P.W. Allen and F.M. Merrett, *J. Polymer Sci.,* **22**, 193 (1956)
301. P.W. Allen, G. Ayrey, C.G. Moore, and J. Scanlan, *J. Polymer Sci.,* **36**, 55 (1959)
302. R.J. Ceresa, (ed.) *Block and Graft Copolymers*, Wiley Interscience, New York, 1973
303. B.D. Gesner, *Rubber Chem. Technol.,* **38**, 655 (1965)
304. P.G. Ghosh and P.K. Sengupta, *J. Appl. Polymer Sci.,* **11**, 1603 (1967)
305. R.E. Wetton, J.D. Moore, and B.E. Fox, *Makromol. Chem.,***132**, 135 (1970)
306. L.V. Valentine and C.B. Chapman, *Ric. Sci. Suppl.,* **25**, 278 (1955)
307. G.N. Richards, *J. Appl. Polymer Sci.,* **5** (17), 553 (1961)
308. G.I. Simionescu and S. Dumitriu, *J. Polymer Sci.,* **C** (37), 187 (1972)
309. G. Mino and S. Kaizerman, *J. Polymer Sci.,* **31**, 242 (1958)
310. R.M. Livshits, V.P. Alachev, M.V. Prokofeva, and Z.A. Rogovin, *Vysokomol. soyed.,* **6** (4), 655 (1964)
311. Y. Iwakura, T. kurosaki, and Y. Imai, *J. Polymer Sci.,* **A-1, 3**, 1185 (1965); Y.Iwakura, Y. Imai, and K. Yagi, *J. Polymer Sci.,* **A-1, 6**, 801 (1968); *ibid.,* **A-1, 6**, 1625 (1968); Y. Imai, E. Masuhara, and Y. Iwakura, *J. Polymer Sci., Polymer Letters,* **8**, 75 (1970)
312. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polymer Sci.,* **A-1,6**, 1489 (1968)
313. A.A. Gulina, R.M. Livshits, and Z.A. Rogovin, *Vysokomol. soyed.,* **7** (9) 1693 (1965)
314. S. Lenka and P.L. Nayak, *J. Appl. Polymer Sci.,* **27**, 1959 (1962)
315. A. Hebeish, S. Shalaby, A. Waly, and A. Bayazeed, *J. Polymer Sci.,* **28**, 303 (1983)
316. J.E. Guillet and R.G.W. Norrish, **Nature**, **173**, 625 (1954); *Proc. Roy. Soc. (London),* **A 233**, 172 (1956)

317. G.C. Menon and S.L. Kapur, *J. Appl. Polymer Sci.,* **3**, 54 (1960)
318. N, Geacintov, V. Stannett, and E.W. Abrhamson, *Makromol. Chem.,* **36**, 52 (1959); A. Chapiro, *J. Polymer Sci.,* **29**, 321 (1958); *ibid*., **34**, 439 (1959)
319. G. Smets, W. De Winter, and G. Delzenne, *J. Polymer Sci.,* **55**, 767 (1961)
320. A. Chapiro, *J. Polymer Sci.,* **48**, 109 (1960)
321. Y. Hachihama, S. Takamura, *Technol. Report Osaka Univ.,* **11** (485) 431 (1961); from *Chem. Abstr.,* **57**, 6179 (1962)
322. A.J. Restaino and W.N. Reed, *J. Polymer Sci.,* **36**, 499 (1959)
323. A. Noshay and J.E. McGrath, *Block Copolymers*, Academic Press, New York, 1977
324. G. Gruber and G. Egle, *Makromol. Chem.,* **53**, 206 (1962)
325. G. Sasson and A. Zilkha, *Eur. Polymer J.,* **5**, 315 (1969)
326. R. Waak and M.A. Doran, *Polymer*, **2**, 365 (1961)
327. R. Milkovich, *Am. Chem. Soc. Polymer Preprints*, **21**, 40 (March 1980)
328. R. Milkovich and M.T. Chiang, U.S. Patent # 3,786,116 (1974)
329. M. W. Thompson and F.A. Waite, Brit. Patent # 1,096,912 (1967)
330. B.W. Jackson, U.S. Patent # 3,689,593 (1972)
331. J.P. Kennedy, V.S.P. Chang, R.A. Smith, and B. Ivan, *Polym. Bull.,* **1**, 575 (1978)
332. J.P. Kennedy, *Preprints, 5th Intern. Symposium on Cationic and Other Ionic Polymerizations,* **6**, (1980)
333. R. Asami, M. Takaki, K. Kita, and E. Asakura, *Plym. Bull.,* **3**, 83 (1980)
334. J.S. Vrgas, J.G. Zillox, P. Rempp, and E. Frauta, *Polymer Bull.,* **3**, 83 (1980)
335. P. Rempp, *Polymer Prepr. Jpn.,* **29**, 1397 (1980)
336. Y. Tanizaki, K. Minagawa, S. Takase, and K. Watanabe, Abstracts of the A.C.S.-C.S.J. Chemical Congress,INDE, 136 (1979)
337. G. Gerber and E. Reese, *Makromol. Chem.,* **55**, 96 (1962)
338. Y. Yamashita, *J. Appl. Polymer Sci., Applied Polymer Symposia*, **36**, 193 (1981)
339. R.B. Mesrobian and H. Mark, *Textile J.,* **23**, 294 (1953)
340. D.J. Metz and R.B. Mesrobian, . *J. Polymer Sci.,* **J16**, 345 (1955)
341. J.D. Matlack, S.N. Chinai, R.A. Guzzi, and D.W. Levi, *J. Polymer Sci.,* **49**, 533 (1961)
342. G. Natta, E. Beati, and F. Severini, *J. Polymer Sci.,* **34**, 685 (1959)
343. D. Makulova and D. Berek, *Sb. Prac. Chem. Fak. Sloven Vysokej. Skily Tech.,* **141**, (1961); from *Chem Abstr.,* **57**, 8729 (1962)
344. J.J. Wu, Z.A. Rogovin, and A.A. Konkin, *Khim Volokna,* **6**, 11 (1962); from *Chem. Abstr*., **58**, 11509 (1963)
345. E.L.Sahkulubey, Y.Y. Durmaz, A.L. Demirel, and Y. Yagci, *Macromolecules*, **2010**, *43*, 2732
346. A. Bar-Ilan and A. Zilkha, *Eur. Polymer J.,* **6**, 403 (1970)
347. A. Ravve and C.W. Fitko, *J. Polymer Sci.,* **A-1,4**, 2533 (1966)
348. C. de Ruijter, W. F. Jager, J. Groenewold, and S. J. Picken, *Macromolecules*, **2006**, *39*, 3824
349. Schollenberger, *Polymer Technology*, Interscience, New York, 1969
350. K.C. Gupta and K. Khandekar, *Am. Chem. Soc. Polymer Preprints*, **2005**, *46* (1), 654
351. G. Ezra and A. Zilkha, *J. Appl. Polymer Sci.,* **13**, 1493 (1969)
352. G. Kockelbergh and G. Smets, *J. Polymer Sci.,* **33**, 227 (1958)
353. K. Nakamura and S.K. Kuchi, *Bull. Chem. Soc. Japan,* **41**, 1977 (1968)
354. M. Tsuda, **J. Polymer Sci.**, **7**, 259 (1969);
355. H.G. Heine, H.J. Resenkranz, and H. Rudolph, *Angew. Chem., Int. Edit.Engl.,* **11**, 974 (1974);
356. C.J. Groeneboom, H.J. Hageman, T. Overeem, and A.J.M. Weber, *Makromol. Chem.,* **183**, 281 (1982)
357. J. Hutchison, M.C. Lambert, and A. Ledwith, *Polymer, 14*, 250 (1973)
358. A. Ledwith, *Pure and Appl. Chem.,* **49**, 431 (1977)
359. W.A. Pryor, *Free Radicals*, McGraw-Hill, New York, 1966
360. M.J. Gibian, *Tetrahedron Letters,* 5331 (1967)
361. G. Rausing and S. Sunner, *Tappi*, **45** (1), 203A (1962)
362. V. Jacks and W. Kern, *Makromol. Chem.,* **83**, 71 (1965)
363. P. Weiss, J. F. Gerecht, and I.J. Krems, *J. Polymer Sci.,* **35**, 343 (1959)
364. K. Ito, Y. Tomi, and S. Kawaguchi, *Macromolecules,* **25**, 1534 (1992)
365. S.G. Cohen, H.S. Haas, and H. Slotnick, *J. Polymer Sci.,* **11**, 913 (1953); H.S. Haas, S.G. Cohen, A.C. Oglesby, and E.R. Karlin, *J. Polymer Sci.,* **15**, 427 (1955); S.T. Rafikov, G.N. Chelnokova, I.V. Zhuraleva, and P.N. Gribkova, *J. Polymer Sci.,* **53**, 75 (1961)
366. J.P. Kennedy, ed., *J. Appl. Polymer Sci., Applied Polymer Symposia,* **30**, (1977); J.P. Kennedy, U.S. Patent # 3,349,065 (Oct. 24, 1967); J.P. Kennedy in *Polymer Chemistry of Synthetic Elastomers*, (J.P. Kennedy and E. Tornquist, ed.)Wiley-Interscience, New York, 1968; J.P. Kennedy and J.K. Gillham, *Adv. Polymer Sci.,* **10**, 1 (1972)
367. J.P. Kennedy and M. Nakao, *J. Appl. Polymer Sci., Appl. Polymer Symposia,* **30**, 73 (1977)

368. N.Betz, A. Le Moel, J.P. Duraud, and C. Darnez, *Macromolecules,* **25**, 213 (1992)
369. E.T. Kang, K.G. Neoh, K.L. Tan, Y. Uyama, N. Morikawa, and Y. Ikada, *Macromolecules*, **25**, 1959 (1992)
370. B.U. Kolb, P.A. Patton, and T.J. McCarthy, *Am. Chem. Soc., Polymer Preprints,* **28** (2), 248 (1987)
371. K Matyjaszewski, YGnanou, and L. Leibler, eds. '*Macromolecular Engineering*, Wiley, New York, **2007**
372. J. Hirkach, K. Ruehl, and K. Matyjaszewski, *Am. Chem. Soc., Polymer Preprints,* **29** (2), 112 (1988)
373. Y. Jiang and J.M.J. Frechet, *Am. Chem. Soc., Polymer Preprints,* **30** (1), 127 (1989)
374. J.F. Kenney, *Polymer Eng. and Sci*., **8** (3), 216 (1968); W.H.Charch and J.C. Shivers, *Textile Research J.,* **29**, 536 (1959)
375. Imperial Chemical Industries Ltd. Brit. Patent # 802,921 (Nov. 23, 1955)
376. A. Noshay and J.E. McGrath, *Block Copolymers: Overview and Critical Survey*, Academic Press, New York, 1977
377. D.H. Solomon, Chapter 1 in *Step Growth Poymerization*, (D.H. Solomon, ed.), Dekker, New York, 1972
378. J.A. Brydson, *Plastic Materials*, 4th ed., Butterworth Scientific, London 1982
379. General Electric Co., Brit. Patent # 984,522 (June 1, 1960)
380. Schollenberger, *Polymer Technology*. (P.F. Bruins, ed.) Interscience, New York, 1969
381. R. Ukielski and H. Wojcikiewicz, *Intern. Polymer Science and Technology,* **3** (11), T65 (1976); G.K. Hoexchele and W.K. Witsiepe, *Angew. Makromol. Chem.,* **29-30**, 267 (1973)
382. Y. Yamashita and T. Hane, *J. Polymer Sci., Polym. Chem. Ed.,***11**, 425 (1973); Y. Yamashita, Y. Murase, and K. Ito, *J. Polymer Sci., Polym. Chem. Ed.,* **11**, 435 (1973)
383. V.V. Korshak and T.M. Frunze, *Synthetic Hetero-Chain Polyamides*, S. Manson, Jerusalem. 1987
384. P.W. Morgan, *J. Polymer Sci.,* **C4**, 1075 (1964); D.J. Lyman and S.L. Yung, *J. Polymer Sci.,* **40**, 407 (1959)
385. D.J. Lyman and S.L. Yung, *J. Polymer Sci.,* **40**, 407 (1959)
386. V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, R.D. Fedorova, and G.Sh. Papara, *Vysokomol Soyed.,* **8** (12), 2155 (1966); V.V.Korshak, S.V.Vinogradova, M.M.Teplyakov, and A.D.Maksomov, *Izv. Vysok. Uchebn. Zaved Khim. i Khim. Technol.,* **10** (6), 688 (1967)
387. V.V. Korshak, S.V. Vinogradova, and M.M. Teplyakov, *Vysokomol. Soyed.,* **7** (8), 1406 (1965)
388. Y. Goto and S. Miwa, *Chem. High Polymers, Japan,* **25**, 595 (1968)
389. K.L. Mittal, *Polyamides: Syntheses, Characterizations and Applications*, Vols. 1 and 2, Plenum, New York, 1984
390. Imperial Chemical Industries, Brit. Patent # 807,666 (Jan 4, 1957)
391. Imperial Chemical Industries, Brit. Patent # 1,148,068 (Aug. 9, 1965)
392. M. Tsuruta, F. Kabayashi, and K. Matsuyata, *Kogyo Kagaku Zasshi*, **62**, 1084, 1087 (1959); from *Chem. Abstr.,* **57**, 13977 (1962)
393. D. Dieterich, W. Keberle, and H. Witt, *Angew. Chem., Intern. Ed.,* **9** (1), 40 (1970)
394. D. Dieterich. O. Bayer, J. Peter, and E. Muller, Ger. Patent # 1,156,977 (June 5, 1962)
395. D. Dieterich and O. Bayer, Brit. Patent # 1,078,202; W. Keberle and D. Dieterich, Brit. Patent # 1,078,688
396. C.A. Lukach and H.M. Spurlin, *Copolymerization*, (G.E. Ham, ed.), Interscience, New York, 1964; H.F. Mark and S.M. Atlas,*Petrol. Refiner*, **39**, 149 (1960); G. Natta, *J. Polymer Sci.,* **34**, 21, 531 (1959)
397. A.V. Tobolsky and K.F. O'Driscoll, DAS 1 114 323, June 24, 1959
398. M. Szwarc and J. Smid, *Progress in Reaction Kinetics*, Vol. II, p. 219, Pegamon Press, Oxford, 1964; M. Szwarc, *Nature*, **178**, 1168 (1956)
399. S. Bywater, *Fortsch-Hochpolym. Forsch.,* **4**, 66 (1965)
400. R. Chiang, J.H. Rhodes, and R.A. Evans, *J. Polymer Sci.,* **A-1,4**, 3089 (1966)
401. N.L. Madison, *Amer. Chem. Spc. Polymer Preprints,* **7**, 1099 (1966)
402. H.Yu, A.J. Bur, and L.J. Fetters, *J. Chem. Phys.,* **44**, 2568 (1966)
403. M.P. Dreyfuss and P. Dreyfuss, *Polymer*, **6**, 93 (1965)
404. C.E.H. Bawn, R.M. Bell, and A. Ledwith, *Polymer*, **6**, 95 (1965)
405. D. Sims, *Makromol. Chem*., **64**, 151 (1963)
406. S. Bywater, *Macromolecular Chemistry*, Buterworths, Longond, 1962; M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983
407. R.K. Graham, D.L. Dunkelburger, and W.E. Goode, *J. Am. Chem. Soc.,* **82**, 400 (1960)
408. T. Saegusa, S. Matsumoto, and Y. Hashimoto, *Macromolecules*, **3**, 377 (1970)
409. L.J. Fetters, *J. Polymer Sci.,* **C** (26), 1 (1969)
410. J.P. Kennedy, *Makromol. Chem., Suppl.,* **3**, 1 (1979)
411. R.J. Ceresa, *Block and Graft Copolymers*, Butterworths, Washington D.C., 1962
412. H. Staudinger, *Ber.*, **57**, 1203 (1924); *Kautchuk*, **5**, 128 (1929)
413. D.J. Angier and W.F. Watson*, J. Polymer Sci.,* **20**, 235 (1956)
414. R.J. Ceresa, *Polymer*, **1**, 477 (1960)
415. B. Gordon III and L.F. Hancock, *Am.Chem.Soc. Polymer Preprints,* **26** (1), 98 (1985)
416. P.J. Hans and B. Gordon III, *Am.Chem.Soc. Polymer Preprints*, **28** (2), 310 (1987)
417. W. Risse and R.H. Grubbs, *Am.Chem.Soc. Polymer Preprints*, **30**, 193 (1989)

418. D.Y. Sogah and O.W. Webster, *Macromolecules*, **19**, 1775 (1986)
419. D. Patit, R. Jerome, and Ph. Teyssie, *J. Polymer Sci., Polymer Chem. Ed.,* **17**, 2903 (1979); W.T. Allen and D.E. Eaves, *Angew. Makromol. Chem.,* **58/59**, 321 (1977); B.H. Wondraczek and J.P. Kennedy, *J. Polymer Sci., Polymer Chem. Ed.,* **20**, 173 (1982)
420. C.A. Veith and R.E. Cohen, *Am.Chem.Soc. Polymer Preprints,* **31** (1), 42 (1990)
421. J.P. Kennedy, B. Keszler, Y. Tsunogae, and S. Midha, *Am. Chem. Soc. Polymer Preprints*, **32** (1), 310 (1991)
422. T.J. Deming and B.M. Novak, *Macromolecules*, **24**, 5478 (1991)
423. T. Higashimura, S. Aoshima, and M. Sawamoto, *Makromol. Chem. Macromol Symp*., **13/14**, 457 (1988)
424. J.P Kennedy and J.L. Price, *Polym. Mater. Sci.,* **1991**, 64; J.P. Kennedy, J.L. Price, and K. Koshimura, *Macromolecules*, **24**, 6567 (1991)
425. T. Pernecker, J.P. Kennedy, and B. Ivan, *Macromolecules*, **25**, 1642 (1992)
426. M.G. Kanatzidis, *Chem. and Eng. News,* p. 38 (Dec. 3, 1990); L.Y. Chiang, P.M. Chaikin, D.O. Cowan,(eds.), *Advanced, Organic Solid State Materials*, *Mat. Res. Soc. Symp. Proc*., **173**, (1990); J.R. Reynolds, *Chemtech,* **18**, 440 (1988)
427. X.-F. Sun, S.B. Clough, S. Subrmanyam, A. Blumstein, and S.K. Tipathy, *Am. Chem. Soc. Polymer Preprints*, **33** (1), 576 (1992)
428. S. Subramanyam and A. Blumstein, *Macromolecules,* **24**, 2668 (1991)
429. R.D. McCullough and R.D. Lowe, *Am. Chem. Soc. Polymer Preprints*, **33** (1), 195 (1992)
430. W. Rutsch, G. Berner, R. Kirchmayr, R. Husler, G. Rist, and N. Buhler, *Organic Coatings-Science and Technology*, (G.D Parfitt and A.V. Patsis, eds.), Dekker, New York, Vol. 8, 1986
431. K. Dietliker, M. Rembold, G. Rist, W. Rutsch, and F. Sitek, Rad-Cure Europe 87**,** Proceedings of the 3rd Conference Association of Finishing Processes SME; Dearborn, MI, 1987
432. G. Rist, A. Borer, K. Dietliker, V. Desobry, J.P. Fouassier, and D. Ruhlmenn, *Macromolecules,* **25**, 4182 (1992)
433. B.J. Sun and G.C. Bazan, . *Am. Chem. Soc. Polymer Preprints,* **36** (1), 253 (1995)
434. M. Weck, P. Schwab, and R.H. Grubbs, *Macromolecules*, **29**, 1789 (1996); A. Proto, A. Avagliano, D. Saviello, R. Ricciardi and C. Capacchione, *Micrornolecules*, **2010**, *43* 5919
435. R. Jerome, J.L. Hedrick, and C.J. Hawker, *Angew. Chem, Int Ed. Engl.* **37**, 1274 (1998); C.J. Hawker, J.L. Hedrick, E.E. Malmstrom, M. Tollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules*, **31**, 213 (1998)
436. E. Yoshida and Y. Osagawa, *Macromolecules*, **31**, 1446 (1998); R.L.Kuhlman and J. Klosin, *Macromolecules*, **2010**, *45*, 7903; L.M. Pitet and M.A. Hillmyer, *Macromolecules*, **2009,** *42*, 3674
437. Y. Kotani, M. Kato, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **29**, 6979 (1996); S. Lu, Q.-L. Fan, S.-J. Chua, and W. Huang, *Macromolecules*, **2003**, *36*, 304; J.B. Matson and R.H. Grubbs, , *Macromolecules*, .**2008**, ASAP article10.1021/ma800980p
438. S. Coca, H.-j. Paik, and K. Matyjaszewski, *Macromolecules*, **30**, 6513 (1997)
439. A. Kajiwara and K. Matyjaszewski, *Macromolecules*, **31**, 3489 (1998)
440. W.J. Gauthier, J.F. Corrigan, N.J. Taylor, and S. Collins, *Macromolecules*, **28**, 3771 (1995)
441. R.W. Waymouth and G.W. Coates, *Science,* **267**, 222 (1995)
442. J.Vohlidal, J. Sedlacek, and M. Zigon, *Kovine, Zlitine, Tehnol.* **31**(6), 581 (1997); from *Chem. Abstr.***129**, 637 (1998)
443. Y. Misumi and T. Masuda, *Macromolecules,* **31**, 7572 (1998)
444. W. Liu, J. Kumar, S. Trypathy, K.J. Senecal, L. Samuelson, *J. Am. Chem. Soc.,* **121**, 71 (1999)
445. H. Nakatani, K.-H. Nitta, T. Uozumi, and K. Soga, *Polymer*, **40**, 1623 (1999)
446. L.A. Wall, S.L. Madorsky, D.W. Brown, S. Straus, and R. Simka, *J. Am. Chem. Soc*., **76,** 3430 (1954)
447. L.A. Wall and S. Straus, *J. Polymer Sci*., **1960**, *44*, 313
448. S. Madorsky, *J. Polymer Sci*., **1952**, *9*, 133
449. S. Madorsky, *J. Polymer Sci*., **1953**, *11*, 491
450. S. Madorsky, S. Straus, D. Thompson, and L. Williamson, *J. Polymer Sci*., **1949**, *4*, 639
451. S. Madorsky and S. Straus, *J. Polymer Sci*., **1959**, *36*, 183
452. S. Madorsky and S. Straus, *J. Res. Natn. Bur. St.,* **1948**, *40*, 417
453. W.G. Oaks and R.B. Richards, *J..Chem. Soc. (London),* **1949**, 2929
454. Y. Tsuchiya and K. Sumi, *J. Polymer Sci*., **1968**, *A-1,6,* 415
455. Chem. and Eng. News, p. 41, Sept. 28, 1964
456. S. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964
457. E.M. Bavilacqua, in *Thermal Stability of Polymers,* Vol. 1., R.T. Conley (ed.), Dekker, New York, 1970; R. Bernstein, D.R. Derzon, and K.T. Gillen, *Am. Chem. Soc. Polymer Preprints*, **2007**, *48*(1), 611
458. M.A. Golub and R.J. Gargiulo, *Polymer Letters,* **1972 ,** *10*, 41
459. M. Galin-Vacherot, *Eur. Polymer J*., **1971**, *7*, 1455
460. G.G. Cameron and N. Grassie, *Polymer,* **19961**, *2*, 367

461. H.H.G. Jellinek, *J. Polymer Sci.,* **1948**, *3*, 850
462. H.H.G. Jellinek, *J. Polymer Sci.,* **1949**, *4*, 1
463. H.H.G. Jellinek, *J. Polymer Sci.,* **1949**, *4*, 13
464. N. Grassie and W.W. Kerr, *Trans. Faraday Soc..*, **1959**, *66*, 1050
465. G.G. Cameron and N. Grassie, *Makromol. Chem.*, **1962**, *53*, 72
466. G.G. Cameron and G.P. Kerr, *Eur. Polymer J.*, **1970**, *6*, 423
467. J.W.C. Crawford, *J. Soc. Chem. Ind,*, **1949**, *68*, 201
468. N. Grassie and J.G. Speakman, *J. Polymer Sci.*, **1971**, *A-1,9*, 419
469. N. Grassie, J.G. Spaakman, and T.J. Davis, *J. Polymer Sci.*, **1971**, *A-1,9*, 931
470. .S. Choudhary and K. Lederer, *Eur. Polymer J.*, **1982**, *18*, 1021
471. W.J. Burlant and J.L. Parsons, *J. Polymer Sci.,* **1956,** *22*, 156
472. J. Schulz, H. Bayzer, W. Stubchen, and J. Schurz, *Makromol. Chem.* **1957**, *23*, 152; *ibid.,* **1959**, *29*, 156
473. S.L. Ma472orsky amd S. Strais. *J. Res. Natl. Bur. Std..* **1958**, *61*, 77
474. N. Grassie and J.N. Hay, *J. Polymer Sci.*, **1962**, *56*, 189
475. N. Grassie and J.N.Hay, *Makromol. Chem.*, **1963**, *64,* 82
476. J.N. Hay, *J. Polymer Sci.*, **1968**. *A-1,6*, 2127
477. N. Grassie and R. McGuchan, *Eur. Polymer. J.*, **1972**, *8*, 243
478. N.A. Kubasova, Din Suan Din, M.A. Heiderich, and M.V. Shishkina, *Vysokomol. soyed.***,** **1979**, *A13 (1)*, 162
479. N. Grassie and R. McGuchan, *Eur. Polymer. J.*, **1970**, *6*, 1277; *ibid.,***1971**, *7*, 1091; *ibid.,***1971**, *7*,1357
480. H. Gilbert, S.J. Averill, F.E. Miller, R.F. Schmidt, F.D. Stewart, and H.L. Trumbull, *J. Am. Chem. Soc.,* **1954**, *76*, 1074
481. N. Grassie and R. McGuchan, *Eur. Polymer. J.*, **1972**, *8*, 243
482. P. Bataille and B.T. Van, *J. Polymer Sci.*, **1972**, *A-1,10*, 1097
483. S. van der Ven and W.F. de Wit, *Angew. Makromol. Chem.*, **1969**, *8*, 143
484. J.D. Danforth, J. Spiegel, and J. Bloom, *J. Macromol. Sci. – Chem.,* **1982**, *A17* (7), 1107
485. S.A. Liebman, D.H. ahlstrom, E.J. Quinn, A.G. Geigley, and J.T. Melluskey, *J. Polymer Sci.*, **1971**, *A-1,9*, 1921 .
486. I. Mita in *Aspects of degradation and Stabilization of Polymers*, H.H. Jellinek (ed.), Elsevier, Amsterdam, 1978
487. H. Bamford and D.F. Feuton, *Polymer*, **1969**, *10*, 63
488. E.P.Chang and R.Salovey, *J. Polymer Sci., Chem. Ed.*, **1974**, *12*, 2927
489. D.O. Hummel, H.J. Dussel, and K. Rubenacker, *Makromol. Chem.,* **1971**, *145*, 267
490. R.M. Lum487. M.M. O'Mara, *J. Polymer Sci., Chem. Ed.*, **1970**, *A-1,8*, 1887 , *J. Polymer Sci., Chem. Ed.*, **1977**, *15*, 489
491. A. Ballistreri, S. Foti, G. montaudo, and E. Scamporrino, *J. Polymer Sci., Chem. Ed.*, **1980**, *18,* 1147
492. J. Svetly, R. Lucas, J. Michalcova, and M. Kolinsky, *Makromol. Chem.,Rapid Commun.*, **1980**, *1*, 247
493. J. Svetly, R. Lucas, S. Pokorny, and M. Kolinsky, *Makromol. Chem.,Rapid Commun.*, **1981**, *2*, 149
494. L. Valko, P. Simon, V.Kello *Makromol. Chem.*, **1982**, *183*, 3057
495. R.D. Bohme and R.A. Wessling, *J. Appl. Polymer Sci.,* **1972**, *16*, 1761
496. R.F. Boyer, *J. Phys. Coll. Chem.*, **1947**, *51*, 80; E. Elakesh, T.R. Hull, D. Price, P.Carty, *J. of Vinyl and Additive*, **2003**, *9*(3), 116
497. L.A. Matheson and R.F. Boyer, *Ind. Eng. Chem.*, **1942**, *44*, 867
498. C,B. Havens, *N.B.S. Cicrular # 525*, **1953**, 107
499. F.H. Winslow, W.O. Baker, and Y.A. Yager, *Proceeding of First and Second Carbon Conferences,* Univ. of Buffalo Press, 1956
500. N. Grassie, I.F. McLaren, and I.C. McNeill, *Eur. Polymer J.*, **1970**, *6*, 679
501. N. Grassie, I.F. McLaren, and I.C. McNeill, *Eur. Polymer J.*, **1970,** *6*, 865
502. R.A. Haldeon, *J. Polymer Sci.*, **1968**, *A-1,6*, 951
503. E.P. Goodings, *Soc. Chem. ind. (London), Monograph*, **1961**, *13*, 211
504. R.M. Lum, *J. Polymer Sci.*, **1979**, *17*, 203
505. V. Passalaqua, F. Pilati, V. Zamoni, B. Fortunato, and P. Manaresi, *Polymer*, **1976**, *17*, 1044
506. G.J. Sutton, B.J. Tighe, and m. Roberts, *J. Polymer Sci.,Chem. Ed.*, **1973**, *11*, 1079
507. A. Davis and J.H. Golden, *J. Chem. Soc., B, (London)*, **1968**, 45
508. F. Wiloth, *Makromol. Chem.* , **1971**, *144*, 283
509. D.P. Bishop and D.A. Smith, *J. Appl. Polymer Sci.*, **1970**, *14*, 205
510. A. Kamimura and S. Yamamoto, *Org. Lett.*, **2007**, *9*, 2533
511. Ye,P. Krasnov, V.P. Aksenova, S.N. Kharkov, and S.A. Baranova, *Vysokomol. soyed.*, **1970**, *A12* (4), 873
512. V.V. Rode. Ye.M. Bondarenko, V.V. Korshak, Ye.S. Krongauz, and A.L. Rusanov, *Dokl. ANSSSR,* **1966**, *171*, 355
513. V.V. Rode. Ye.M. Bondarenko, *Vysokomol. soyed.,***1967**,*A9*,(12), 218; W. Wrasidlo, *J. Polymer. Sci.,* **1970**, *A-1,8*, 1107
514. A. Scotney, *Eur. Polymer J.* **1972**, *8*, 175; *ibid.,* **1972**, *8*, 185
515. I.I. Levantovskaya, G.V. Dralyuk, O.A. Mochalova, I.A. Yurkova, M.s. Akutin, and B.V. Kovarkaya, *Vysokomol. soyed*, **1971**, *A13* (1), 8.

516. V.V. Kopylov and A.N. Pravednilkov, *Visokomol. Soyed.*, **1969**, *A11*, 849
517. N. Grassie and R.S. Roche, *Makromol Chem.* **1968**, *112*, 16.
518. Yu. Sclyapnikov, T.A. Bagaenskay, S.G. Kiryushkin, and T.V. Monakhova, *Eur. Polymer J.* **1979**, *15*, 737
519. .W.L. Hawkins and F.H. Winslow in *Chemical Reactions of Polymers*, E.M. Fetters (ed.), Interscience, NY.1964
520. J.H. Adams, *J. Polymer Sci.,* **1970**, *A-1,8*, 1077
521. V.M. Yurev, A.A. Pravednikov, and S.S. Medvedev, *Dokl.Akad. Nauk S.S.S.R.*, **1959**, *124*, 335
522. B.G. Achhammer, M.J. Reiney, and F.W. Reinhart, *J. Res.Nat. Bur. Standards*, **1951**, *47*, 116
523. B.G. Achhammer, M.J. Reiney, and F.W. Reinhart, *J. Polymer Sci.,* **1952**, *8*, 555
524. A. Votinova, P. Kobenko, and F. Marei, *Zh. fiz. Khim.,* **1952**, *16*, 106
525. C. Crouzet and J. Marchal, *J. Appl. Polymer Sci., Appl Symposia,* **1979**,*35*, 151
526. S.D. Rasumovskii, O.N. Karpukhin, A.A. Kefeli, T.V. Pokholok, and G.Ye. Zaikov, *Vysokomol. soyed.*, **1971**, *A13*, 782
527. L.X. Buxbaum, *Angew. Chem. Intern. Ed.*, **1968**, *7* , 182
528. K.,C.-Yu, W.,B.-Zu; C. W.-Hsun, *lnd. Eng. Chem. Res.* **1998,** 37(4), 1228
529. G. Valk, G. Heidemann, S. Dugal, and H. Krussmann, *Angew. Makromol. Chem.,* **1970,** *10*, 135
530. H.H.G. Jellinek and A.K. Chandhuri, *J. Polymer Sci.,* **1972**, *A-1,10*, 1773 *88. Synthetic Lubricants and Liquids*, R.S. Gunderson and A.V. Khart, (eds.), Chemistry publishing House, New York, 1965
531. P.A. Okunev and O.G. Tarakanov, *Vysokomol. soyed.* **1968**, *A10*, (1), 173
532. I.I.. Levantovskaya, G.V. Dralyuk, O.A. Mochalova, I.A. Yurkova, M.S. Akutin, and B.V.Kovarkaya, *Vysokomol. soyed.*, **1971**, *A13* (1), 8
533. H.H.G. Jellinek and S.H. Ronel, *J. Polymer Sci.*, **1971**, *A-1,9*, 2605
534. Fitton, .N. Howard, and G.R. Williamson, *Brit. Polymer J.*,**1970**, *2*, 217
535. B. Ranby and J.F. Rabek, *J. Appl. Polymer Sci., Appl. Symposia,* **1979**, *35*, 243
536. Y. Hama, K. Hosono, Y. Furui, and K. Shinohara, *J. Polymer Sci,* **1969**, *B7*, 839
537. T. Takeshita, K. Tsuji, and T. Keiki, *J. Polymer Sci.,* **1972**, *A-1,9*, 1411
538. K. Tsuji and T. Seiki, *J. Polymer Sci., Letters*, **1972**, *10*, 139
539. D.J. Carlson and D.M. Wiles, *Macromolecules,* **1969**, *2,* 587; 597
540. T. Kagiya and K. Takemoto, *J. Macromol. Sci.,* **1976**, *5*, 795
541. T. Takashita, K. Tsuji, and T. Keiki, *J. Polymer Sci.,***1972**, *A-1,10*, 2315
542. I.M. Rozman, *Izv. Akad. Nauk S.S.S.R.,***1958**, *22*, 60
543. G. Oldham, A.R. Ware, and S.A. Blackwell, *Nucl. Energy*, **1967**, *20*, 158
544. N.A. Weir, *J. Appl. Polymer Sci.,***1973**, *17*, 401
545. N.A. Weir and T.H. Milkie, *eur. Polymer J.*, **1980**, 141
546. N. Grassie and B.J.D. Torrance, *J. Polymer Sci.,* **1968**, *A-1,6*, 3303; 3315
547. N. Grassie and E. Farish, *Eur. Polymer J.*, **1967**, *3*, 627
548. N. Grassie and R.H. Jenkins, *Eur. Polymer J.*,**1973**, *9*, 697
549. C. David, M. Borsu, and G. Gleuskens, *Eur. Polymer J.*, **1970**, *6*, 959
550. K.J. Buchanan and W.J. McGill, *Eur. Polymer J.*, **1980**, *16*, 319
551. W.H. Gibb and J.R. MacCallum, *Eur. Polymer J.*, **1972**, *8*, 1223
552. E.D. Owens and R.J. Bailey, *J. Polymer Sci.,* **1972**, *A-1,10*, 113
553. C. Decker and M. balander, *Eur. Polymer J.*, **1982**, *18*, 1085
554. E.D. Owens and J.I. Williams, *J. Polymer Sci.,Chem. Ed.,* **1974**, *12,* 1933
555. C. David, W. Demarteau, and G. Gueskens, *Polymer*, **1967**, 497
556. M. Day and D.M. Wiles, *J. Polymer Sci.,Letters,* **1971**, *9*, 665
557. S.B. Maerov, *J. Polymer Sci.,***1965**, *A-1,3*, 487
558. S.M. Cohen, R.H. Young, and A.H. Markhart, *J. Polymer Sci.,* **1971**, *A-1,9,* 3263
559. J.F. Rabek, G. Ramme, G. Cauback, b. Ranby, and V.T. Kagiya, *Eur. Polymer J.,* **1979**, *15*, 339
560. D.J. Carlsson, R.D. Parnell, and D.M. Wiles, *J. Polymer Sci.,Letters,* **1973**, *11*, 149
561. O. Cicchetti, *Adv. Polymer Sci.,* **1970**, *7,* 70
562. M.L. Kaplan and P.O. Keller, *J. Polymer Sci.,Letters,* **1971**, *9*, 565
563. J.M. Ginhac, J.L Gardette, R. Arnaud, and J. Lemaire, *Makromol. Chem.*, **1981**, *182*, 1017
564. A. Huvet, J. Phillipe, and j. Verdu, *Eur. Polymer J.,***1978**, *14*, 709
565. B. Ranby and J.F. Rabek, *J. Appl. Polymer Sci., Appl. Symposia,* **1979**, *35*, 243
566. J.F. Rabek, G. Cauback, and B. Ranby, *J. Appl. Polymer Sci., Appl. Symposia,* **1979**, *35*, 299
567. M.L. Kaplan and P.G. Keller, *J. Polymer Sci.,* **1970**, *A-1,8*, 3163
568. J.F. Rabek, G. Ramme, G. Cauback, B. Ranby, and V.T. Kagiya, *Eur. Polymer J.,***1979**, *15*, 339
569. J. Chaineaux and C. Tanielian, *J. Appl. Polymer Sci., Appl. Symposia,* **1979**, *35*, 337
570. J.L. Gardette and J. Lemaire, *Makromol. Chem.,* **1982**, *183*, 2415

571. C.S. Schollenberger and F.d. Stewart, *Advances in Urethane Science and Technology*, K.C. Frisch and S.L. Reegen (eds.), Technology Publishing Co., inc. Westport, Conn., 1976
572. L. Reich and S.S. Stivala, *Elements of polymer Degradation,* McGraw-Hill Book Co., New York, 1971
573. A. Chapiro, *Irradiation of Polymers*, R.F. Gould (ed.), *Advances in Chemistry Series, # 66*, Am. Chem. Soc., Washington, D.C., 1967
574. S. Carroccio, C. Puglisi, and G. Montaudo, *Macromolecules*, **2003**, *36*, 7499
575. F. Harlen, W. Simpson, F.B. Waddington, J.D. Waldon, and A.C. Baskett, *J. Polymer Sci*., **1955**, *18*, 589
576. A.A. Miller, E.J. Lawton, and J.S. Balwit, *J. Polymer Sci*.,**1954,** *14*, 503
577. A Chapiro, *Radiation Chemistry of Poymeric Systems*, Interscience-Wiley, New York. 1962
578. E.P. Goodings, *Thermal Degradation of Polymers*, *Soc. Chem. Ind., Monogr.* **1961**, *No. 13*, 211
579. G. Kamerbeek, H. Kroes, and W. Grolle *Thermal Degradation of Polymers*, *Soc. Chem. Ind., Monogr.* **1961**, *No. 13*, 357
580. K**.** Pielichowski; D. Bogdal, J, Pielichowski, A. Boron, *Thermochim. Acta* **1997**, 307(2), 155
581. W.H. Starnes, Jr., H. Chung, B.J. Wojciechowski, D.E. Skillcorn, and G.M. Benedikt, *Am. Chem. Soc. Polymer Preprints,* **1993**,(2), *34*, 114
582. J. Lacoste and Y. Israeli, *Am. Chem. Soc. Polymer Preprints,* **1993**,(2), *34*, 127
583. C.R. Hoyle, I.B. Rufus, and H. Shah, *Am. Chem. Soc. Polymer Preprints,* **1993**,(2), *34*, 131
584. A. Rivaton, D. Sallet, J. Lemaire, *J. Polymer Degrad. Stab.* **1986**, *14*,1
585. A. Factor, W.V. Ligon, R.J. May, *Macromolecules,***1987**, *20*, 2461
586. A. Gupper, P. Wilhem, and M. Schiller, *Polymers and Polymer Composites*, **2003**, *11*(2), 123