Chapter 6
Common Chain-Growth Polymers

6.1 Polyethylene and Related Polymers

Polyethylene is produced commercially in very large quantities in many parts of the world. The monomer can be synthesized from various sources. Today, however, most of ethylene comes from petroleum by high temperature cracking of ethane or gasoline fractions. Other potential sources can probably be found, depending upon the availability of raw materials.

Two main types of polyethylene are manufactured commercially. These are low (0.92–0.93 g/cm^3) and high (0.94–0.97 g/cm^3) density polymers. The low-density material is branched while the high-density one is mostly linear and much more crystalline. The most important applications for the low-density polyethylene are in films, sheets, paper, wire and cable coatings, and injection molding. The high-density material finds use in blow molded objects and in injection molding.

6.1.1 Preparation of Polyethylene by a Free-Radical Mechanism

Up to the late 1960s, most low-density polyethylene was produced commercially by high-pressure free-radical polymerization. Much of this has now been replaced by preparation of copolymers of ethylene with α-olefins by coordination polymerization. These preparations are discussed further in this chapter. High-pressure polymerizations of ethylene, however, might still practiced in some places and it is, therefore, discussed here. The reaction requires a minimum pressure of 500 atm [1] to proceed. The branched products contain long and short branches as well as vinylidene groups. With an increase in pressure and temperature of polymerization, there is a decrease in the degree of branching and in the amount of vinylidene groups [2, 3].

Free-radical commercial polymerizations are conducted at 1,000–3,000 atm pressure and 80–300°C. The reaction has two peculiar characteristics: (1) a high exotherm and (2) a critical dependence on the monomer concentration. In addition, at these high pressures oxygen acts as an initiator. At 2,000 atm pressure and 165°C temperature, however, the maximum safe level of oxygen is 0.075% of ethylene gas in the reaction mixture. Any amount of oxygen beyond that level can cause explosive decompositions. History of polyethylene manufacture contains stories of workers being killed by explosions. Yet, the oxygen concentration in the monomer is directly proportional to the

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percent conversion of monomer to polymer, though inversely proportional to the polymer's molecular weight. This limits many industrial practices to conducting the reactions below 2,000 atm and below 200°C. These reactions were done, therefore, between 1,000 and 2,000 atm pressures. Small quantities of oxygen, limited to 0.2% of ethylene, are accurately metered in [4, 5]. The conversion per each pass in continuous reactors is usually low, about 15–20%.

There is an induction period that varies inversely with the oxygen concentration to the power of 0.23. During this period oxygen is consumed autocatalytically. This is not accompanied by any significant decrease in pressure. A high concentration of ethylene is necessary for a fast rate of chain growth, relative to the rate of termination. Also, high temperatures are required for practical rates of initiation.

If oxygen is completely excluded and the pressure is raised to between 3,500 and 7,750 atm, while using relatively low temperatures of 50–80°C, linear polyethylene forms [6]. The reactions take about 20 h. Various solvents can be used, like benzene, isooctane, methyl, or ethyl alcohols. Higher ethyl alcohol concentrations and low concentrations of the initiator result in higher molecular weights. The products range from 2,000 for wax-like polymers to 4,000,000 for nearly intractable materials. Favorite free-radical initiators for this reaction are benzoyl peroxide, azobisisobutyronitrile, di-*t*-butylperoxydicarbonate, di-*t*-butyl peroxide, and dodecanoyl peroxide. Above conditions differ, however, from typical commercial ones, because such high pressures and long reaction times are not practical.

The actual commercial conditions vary, depending upon location and individual technology of each company. Often, tubular and multiple-tray autoclaves are used [7]. Good reactor design must permit dissipation of the heat of polymerization (800–1,000 cal/g), with good control over other parameters of the reaction. Tubular reactors are judged as having an advantage over stirred autoclaves in offering greater surface-to-volume ratios and better control over residence time [7]. On the other hand, the stirred autoclaves offer a more uniform temperature distribution throughout the reactor.

The tubular reactors have been described as consisting of stainless steel tubes between 0.5 and 1 in. in internal and about 2 in. in the external diameters. The residence time in these tubes is from 3 to 5 min, and they can be equipped with pistons for pressure regulation. Pressure might also be controlled by flow pulses to the reactor [8]. For the oxygen-initiated reactions, the optimum conditions are [7] 0.03–0.1% oxygen at 190–210°C and 1,500 atm pressure. At this pressure, the density of ethylene is 0.46 g/cm^3. This compares favorably with the critical density of ethylene that is 0.22 g/cm^3. Once the polymerization is initiated, the liquid monomer acts as a solvent for the polymer. Impurities, such as acetylene or hydrogen cause chain transferring and must be carefully removed. In some processes, hindered phenols are added in small quantities (between 10 and 1,000 ppm). This has the effect of reducing long-chain branching and yields film grade resins with better clarity, lower haze, and a reduced amount of microgels. Also, diluents are used in some practices. Their main purpose is to act as heat-exchanging mediums, but they can also help remove the polymer from the reactor. Such diluents are water, benzene, and ethyl or methyl alcohols. Sometimes, chain transferring agents like carbon tetrachloride, ketones, aldehydes, or cyclohexane might also be added to control molecular weight. The finished product (polymer–monomer mixture) is conveyed to a separator where almost all of the unreacted ethylene is removed under high pressure (3,500–5,000 psi) and recycled. The polymer is extruded and palletized. Ethylene conversion per pass is a limiting factor on the economics. A tubular reactor is illustrated in Fig. 6.1.

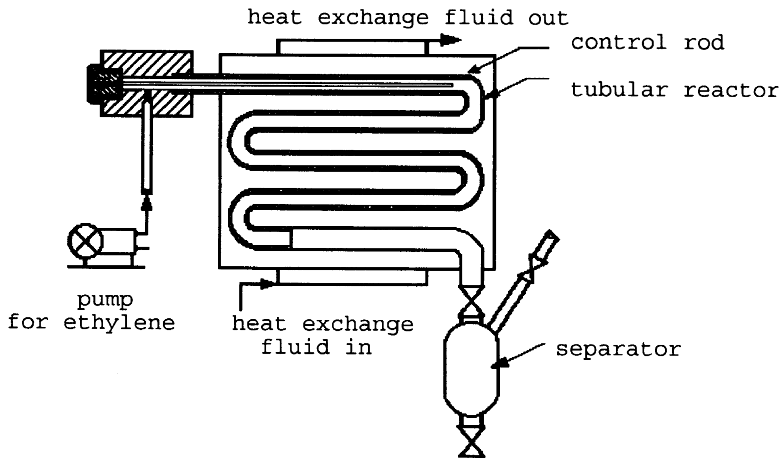
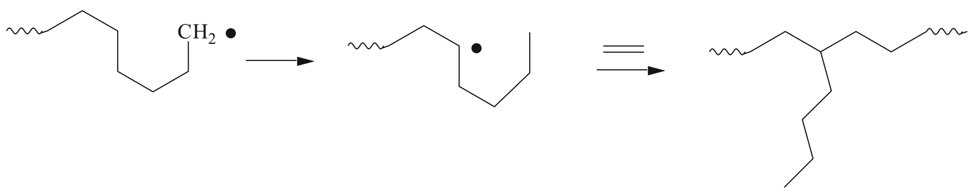
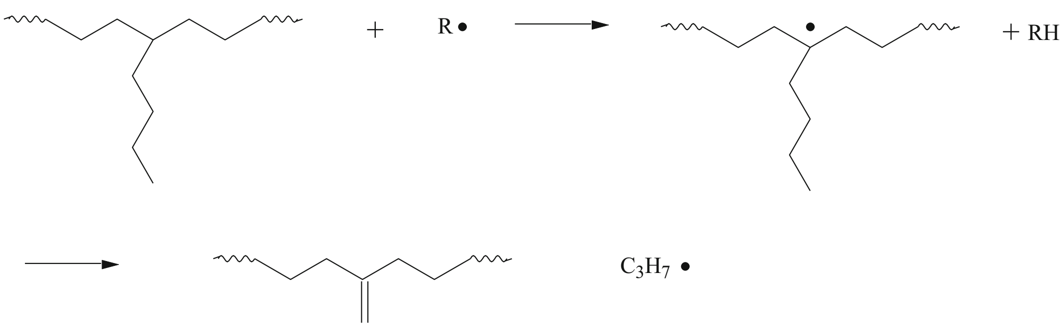


Fig. 6.1 Illustration of a tubular reactor

Polyethylene prepared in this way may have as many as 20–30 short branches per 10,000 carbon atoms in the chain [9] and one or two long-chain branches per molecule, due to "backbiting" [10] (explained in Chap. 3):



The reaction results in predominantly ethyl and butyl branches. The ratio of ethyl to butyl groups is roughly 2:1 [11, 12]. Chain transferring to the tertiary hydrogens at the location of the short branches causes elimination reactions and formation of vinylidene groups [13, 14]. This mechanism also accounts for formation of low molecular weight species.

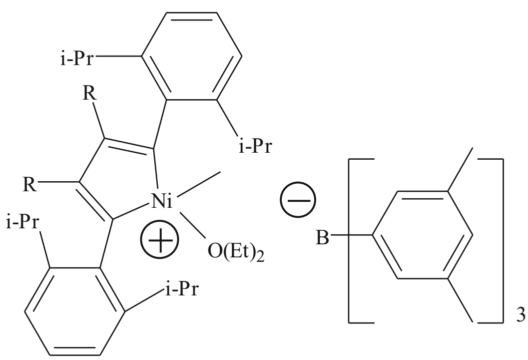


Commercial grades of low-density polyethylene vary widely in the number of short and long branches, average molecular weights, and molecular weight distributions. M_w/M_n is between 20 and 50 for commercial low-density materials. The short branches control the degree of crystallinity, stiffness, and polymer density. They also influence the flow properties of the molten material.

6.1.2 Preparation of Polyethylene by Coordination Mechanism

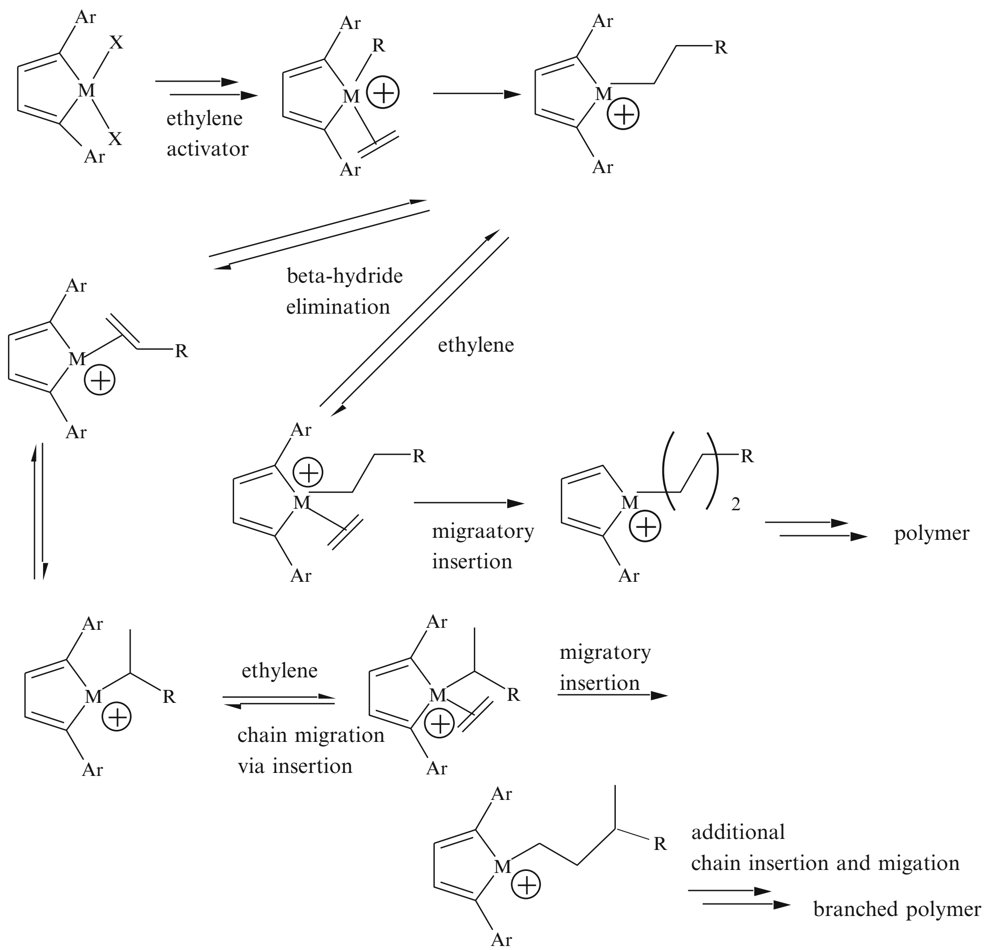
Low-density polyethylene can be prepared by coordination polymerization through copolymerization of ethylene with α-olefins. This is discussed in the section on copolymers of ethylene. Finding catalytic systems that would allow formation of amorphous, low-density polyethylene from the monomer alone by low-pressure polymerization, however, is an economically worthwhile goal. To this end, considerable research is being carried out to develop such catalytic systems. Particular attention is given to metallocenes and other single-site catalysts for olefin polymerization. Originally, the metallocene catalysts were typical metal complexes with two cyclopentadienyl or substituted cyclopentadienyl groups. Many variations were developed since. These materials are used in combination with methyl aluminoxane and have the potential of forming the polymers with high precision. Nevertheless, at this time it is probably still safe to say that low-density polyethylene is prepared by many but perhaps not by all of the processes and catalytic systems mentioned in this book. This is because the material is manufactured all over the world and different considerations govern the decisions on the processes and catalytic systems. The same is probably true of high-density polyethylene.

New catalysts based on palladium and nickel complexes with bulky α-diimine ligands were developed [17–19]. They can yield highly branched or moderately branched polymers of ethylene, as well as propylene and 1-hexene. The polyolefins produced by such catalysts can contain a considerable amount of branches along the backbone that are randomly distributed throughout the molecules. In these catalysts, the molecular weight-limiting β-hydrogen elimination process that is common to palladium and nickel catalysts has been suppressed through use of bulky α-diamine ligands [19]. This allows formation of high molecular weight polymers from ethylene and α-olefins. A nickel-based catalyst can be illustrated as follows:



It is claimed that the branching of polyethylene can be controlled to the extent that the product can even be more branched than conventional low-density polyethylene (1,2—300 branches/1,000 atoms) [18, 19]. The cationic Ni-diimine catalyst shown above (R = H, CH_3), with the methylaluminoxane analog, has been found to polymerize ethylene in toluene at room temperature at the rate of 110,000 kg/Ni/h. This is comparable to the metallocene rates. The Pd-based catalysts are less active than their Ni analogs [19].

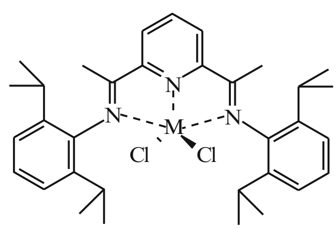
When nickel catalysts are used, the extent of branching is a function of the temperature, ethylene pressure, and catalyst structure. Branching increases as the temperature rises. At higher ethylene pressure less branching occurs. Brookhart et al. illustrate the mechanism of polymerization as follows [18]:



where X = CH_3, Br; M = Pd, Ni; R = $(CH_2CH_2)_nCH_3$; Ar = 2,6-dialkylphenyl.

A patent for the polymerization process of olefins (especially ethylene, α-olefins, cyclopentene, and some fluorinated olefins) describes the above catalytic systems [20]. The hindered diimines stabilize alkyl Ni(II) or Pd(II) with cationic complexes. After preparation, the complexes are reduced with methylaluminoxane and then activated with Lewis acids capable of forming non-coordinating counterions [20].

In addition, preparation of catalysts based on iron and cobalt [21] was also reported. These are complexes of bulky pyridine bis-imine ligands with iron or cobalt that are also activated by methylaluminoxane:

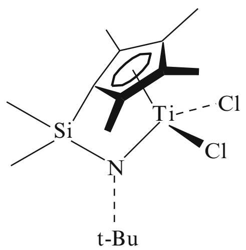


The iron-based catalysts are reported to be considerably more active than the cobalt analogs [21]. The yield of linear, narrow molecular weight distribution polyethylene per gram is reported to be very high [21].

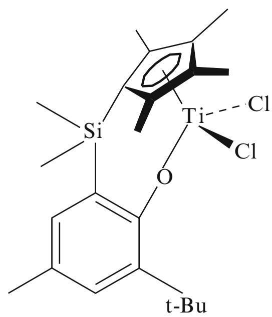
Baugh et al. [22] synthesized and characterized a series of nickel(II) and iron(II) complexes of the general formula [LMX_2] containing bidentate (for M = Ni) and tridentate (for M = Fe) heterocycle-imine ligands. Activation of these pre-catalysts with methyl aluminoxane yields active catalyst systems for the oligomerization/polymerization of ethylene. Compared to α-diimine nickel and bis (imino)pyridine iron catalysts, both metal systems provide only half of the steric protection and consequently the catalytic activities are significantly lower.

Lower activities were attributed to reduced stability of the active species under polymerization conditions. The lower molecular weights of their products were explained to be the result of increased hydrogen transfer rates. Variations within the heterocyclic components of the ligand showed that both steric and electronic factors influence polymerization behavior of such catalysts.

Hanaoka, Oda, and coworkers report [23] that single-site polymerization catalysts are of considerable interest industrially today, because they afford highly controllable polymerization performances based on precise design of catalyst architecture and their industrial applications. Among them, they point to constrained geometry catalyst and phenoxy-induced complex, they call phenics–Ti, that are used together with methyl aluminoxane



concentrated geometry catalyst-Ti



phenics-Ti

These are half-metallocene catalysts with an anionic armed-pendant that have now been well developed for industrial production of copolymers of ethylene with 1-olefins. Modification at the cyclopentadienyl ring system has been mainly tuned to finely control polymerization behaviors such as activity, molecular weight, and regiochemistry. In general, minimizing 2,1-insertion is essential to obtain high molecular weight polyolefins; otherwise, facile 6-elimination occurs, leading to termination of chain growth. Thus, the largely open coordination sites of half-metallocene catalyst systems possess an indispensable problem of irregularity in propagation. Through tuning bulkiness of substituents on the bridged-silicon unit of phenics–Ti, is claimed to have demonstrated that 2,1-insertion of propylene can also controlled by the bridging substituents to produce high molecular weight polypropylene [23].

Hong and coworkers [24] concluded that it is generally desirable to immobilize the single-site metallocene catalysts on a suitable carrier to obtain ideal product morphology. Ultrahigh molecular weight polyethylenes were successfully prepared by them through titanium complexes bearing phenoxy-imine chelate ligands

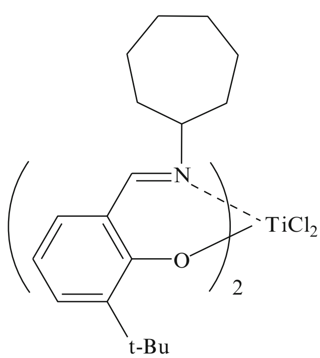


Table 6.1 Typical conditions for some preparation of high-density polyethylene

	Ziegler–Natta process	Cr_2O_3/support	MoO_3/support
Approx. temperature	75°C	140°C	234°C
Approx. pressure	60 psi	420 psi	1,000 psi
Usual state of the polymer in reaction mixture	Suspension	Suspension	Suspension

They demonstrated that the catalyst can be immobilized on silica. The product yields ultrahigh molecular weight polyethylene. Increased polymerization temperature resulted in higher activity, but lower molecular weight of polyethylene.

6.1.3 Commercial High-Density Polyethylene, Properties, and Manufacture

High-density polyethylene (0.94–0.97 g/cm^3) is produced commercially with two types of catalysts:

1. Ziegler–Natta type catalysts
2. Transition metal oxides on various supports

The two catalytic systems are used at different conditions. Both types have undergone evolution from earlier development. The original practices are summarized in Table 6.1.

The Ziegler process yields polyethylene as low as 0.94/cm^3 in density, but process modifications can result in products with a density of 0.965 g/cm^3. The transition metal oxide catalysts on support, on the other hand, yield products in the density range of 0.960–0.970 g/cm^3.

The original development by Ziegler led to what appears to be an almost endless number of patents for various coordination-type catalysts and processes. As described in Chap. 4, such catalysts have been vastly improved. Progress was made toward enhanced efficiency and selectivity. The amount of polymer produced per gram of the transition metal has been increased manyfold. In addition, new catalysts, based on zirconium compounds complexed with methyl aluminoxane oligomers (sometimes called Kominsky catalysts), were developed. They yield very high quantities of polyethylene per gram of the catalyst. For instance, a catalyst, bis(cyclopentadienyl)-zirconium dichloride combined with methylaluminoxane, is claimed to yield 5,000 kg of linear polyethylene per gram of zirconium per hour [14].

An important factor in the catalysts activity is the degree of oligomerization of the aluminoxane moiety. The catalytic effect is enhanced by increase in the number of alternating aluminum and oxygen atoms. These catalysts have long storage life and offer such high activity that they need not be removed from the product, because the amount present is negligible [14, 15]. This makes the work-up of the product simple.

The continuous solution processes are usually carried out between 120 and 160°C at 400–500 lb/in.^{2} pressure. The diluents may be cyclohexane or isooctane. In one zone reactors, the solid catalyst is evenly dispersed throughout the reactor. In the two zone reactors (specially constructed), the polymerizations are conducted with stirring in the lower zone where the catalysts are present in concentrations of 0.2–0.6% of the diluent. Purified ethylene is fed into the bottom portions of the reactors. The polymers that form are carried with small portions of the catalyst to the top and removed. To compensate for the loss, additional catalysts are added intermittently to the upper "quiescent" zones.

In suspension or slurry polymerizations, various suspending agents, like diesel oil, lower petroleum fractions, heptane, toluene, mineral oil, chlorobenzene, or others, are used. The polymerization temperatures are kept between 50 and 75°C at only slightly elevated pressures, like 25 lb/in.^{2}. If these are batch reactions, they last between 1 and 4 h. The slurry reactor is illustrated in Fig. 6.2.

Polymerizations catalyzed by transition metal oxides on support were described variously as employing solid/liquid suspensions, fixed beds, and solid/gas-phase operations. It appears, however, that the industrial practices are mainly confined to use of solid/liquid suspension processes. The polymerization is carried out at the surface of the catalyst suspended in a hydrocarbon diluent.

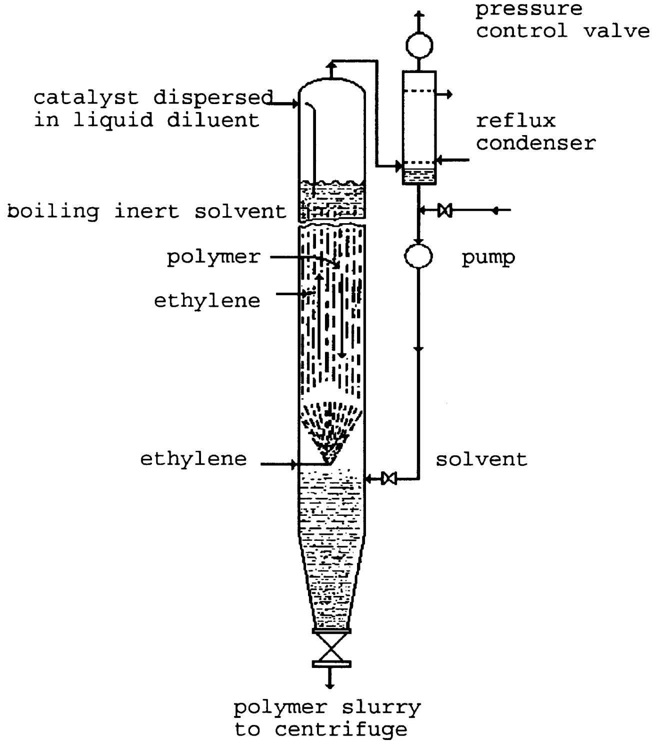


Fig. 6.2 Commercial flow reactor for slurry polymerization of ethylene with Ziegler–Natta catalysts as illustrated in a British patent # 826 523

In continuous slurry processes, the temperatures are kept between 90 and 100°C and pressures between 400 and 450 lb/in.^{2}. The catalyst concentrations range between 0.004 and 0.03% and typical diluents are *n*-pentane and *n*-hexane. Individual catalyst particles become imbedded in polymer granules as the reaction proceeds. The granules are removed as slurry containing 20–40% solids.

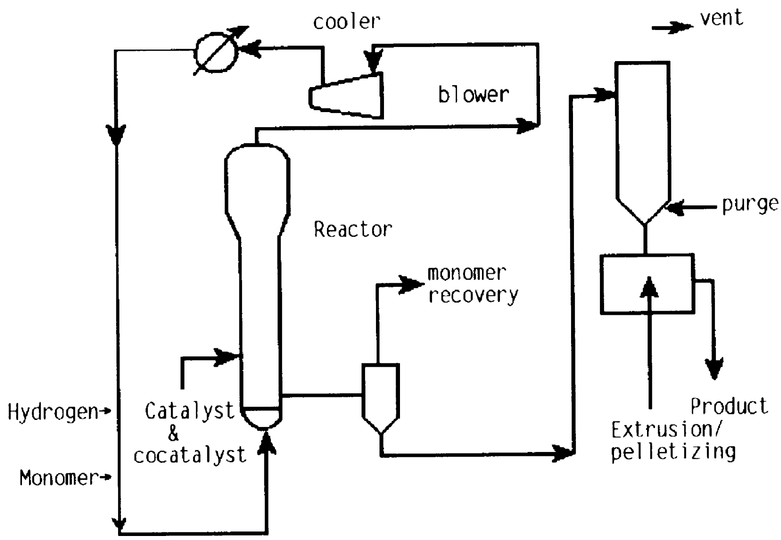
There are variations in the individual processes. In some procedures, the temperature is kept high enough to keep the polymer in solution. In others, it is kept deliberately low to maintain the polymer in slurry. The products are separated from the monomer that is recycled. They are cooled, precipitated (if in solution), and collected by filtration or centrifugation.

Various reactors were developed to handle different slurry polymerization processes. The slurry is maintained in suspension by ethylene gas. The gas rises to the top and maintains agitation while the polymer particles settle to the bottom where they are collected.

Several companies adopted loop reactors. These are arranged so that the flowing reactants and diluents continuously pass the entrance to a receiving zone. The heavier particles gravitate from the flowing into the receiving zone while the lighter diluents and reactants are recycled. To accommodate that, the settling area must be large enough for the heavy polymer particles to be collected and separated.

In addition to suspension, a gas-phase process was developed. No diluent is used in the polymerization step. Highly purified ethylene gas is combined continuously with a dry-powdery catalyst and then fed into a vertical fluidized bed reactor. The reaction is carried out at 270 psi and 85–100°C. The circulating ethylene gas fluidizes the bed of growing granular polymer and serves to remove the heat [15]. Formed polymer particles are removed intermittently from the lower sections of the vertical reactor. The product contains 5% monomer that is recovered and recycled. Control of polymer density is achieved by copolymerization with α-olefins. Molecular weights and molecular weight distributions are controlled by catalyst modifications, by varying operating conditions, and/or use of chain transferring agents [15], such as hydrogen [16]. This is illustrated in Fig. 6.3.

Fig. 6.3 Illustration of a gas-phase process (from Burdett, by permission of the American Chemical Society)



The reactors for the fluidized gas-phase process are simple in design. There are no mechanical agitators and they rely upon blowers to keep the bed fluidized and well mixed. Catalysts and cocatalysts are fed directly to the reactor [25].

Rieger and coworkers [26] investigated gas-phase polymerization of ethylene with supported α-diimine nickel catalysts. The reaction of 2,5 and 2,6 and 1,4 dithiane ligands with $Ni(acac)_2$ and trityl tetrakis(pentafluorophenyl)borate gave the corresponding Ni(II) complexes in high yields. These complexes were supported on silica without a chemical tether and were used as catalysts for ethylene polymerization reactions in the gas phase. Furthermore, ethylene was polymerized with the unsupported 2,5-complexes in homogeneous solution for comparison. The influence of the ligand structure, hydrogen, and temperature on the polymerization performance was investigated. The supported catalysts showed moderate to high activities and produced polyethylenes ranging from high-density polyethylene to linear low-density polyethylene, without further addition of a α-olefin comonomer.

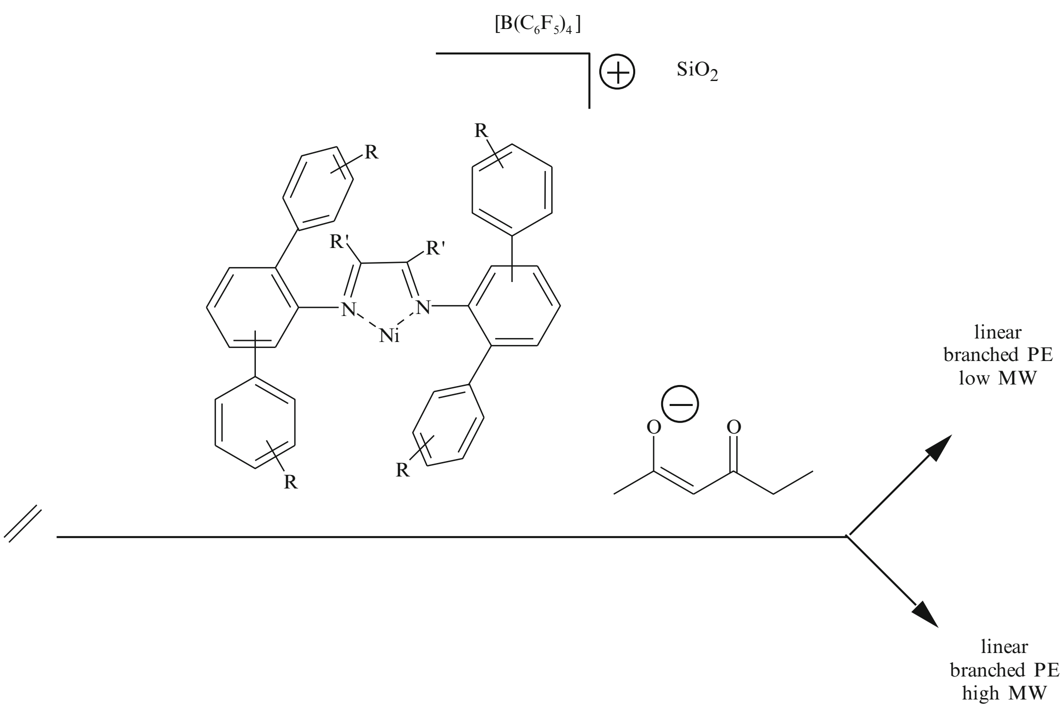


Table 6.2 Properties of commercial polyethylene

Properties	Free-radical polymerization	Ziegler–Natta type catalysts	Metal oxides on support
Density	0.92–0.93 g/cm^3	0.94 g/cm^3	0.95–0.96 g/cm^3
Melting point	108–110.7°C	129–131°C	136°C
% Amorphous	43.1	25.8	25.8
Structure	20–30 ethyl and butyl branches/1,000 carbons, a few long branches	Mainly linear 7 ethyl branches/ 1,000 carbons	Almost linear
Double bonds	0.6–2/1,000 carbons	0.1–1/1,000 carbons	Up to 3/1,000 carbons
Types of bonds	15% terminal vinyl 68% vinylidene 17% internal *trans* olefin	43% terminal 32% vinylidene 25% internal *trans* olefins	94% terminal 1% vinylidene 5% internal *trans* olefins

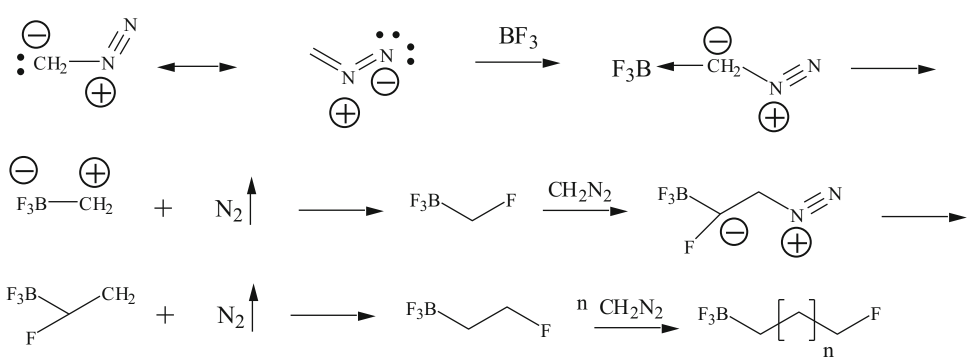
[a] From various sources in the literature

The weight average molecular weights of most commercial low- and high-density polyethylenes range between 5,000 and 300,000. Very low molecular weight polyethylene waxes and very high molecular weight materials are also available. The molecular weight distributions for high-density polyethylene vary between 4 and 15. The product generally has fewer than three branches per thousand carbon atoms [9].

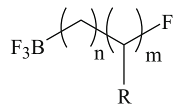
Table 6.2 summarizes the properties of various polyethylenes.

6.1.4 Materials Similar to Polyethylene

Materials that are quite similar to polyethylene can be obtained from other starting materials. The most prominent is formation of polymethylene and similar high molecular weight paraffin hydrocarbons from diazoalkanes. The reaction was originally carried out by Pechmann [27] when small quantities of a white flocculent powder formed in an ether solution of diazomethane. Bamberger and Tschirner [28] showed that this white powder is polymethylene –(–CH_2–)$_n$– that melts at 128°C. The synthesis was improved since by introduction of various catalysts. The reaction can yield highly crystalline polymers that melt at 136.5°C [29] with the molecular weight in millions [30]. Among the catalysts, boron compounds are very efficient [30]. Bawn et al. [31] postulated the mechanism of catalytic action. It consists of initial coordination of a monomer with the initiator, BF_3. This is followed by a loss of nitrogen and a shift of a fluorine atom from boron to carbon. The successive additions of molecules of diazoalkane follow a similar path with a shift of the chain fragment to the electron-deficient carbon:



The resulting macromolecules are still reactive toward additional diazoalkanes. The above step-growth polymerization reactions can also yield block copolymers:

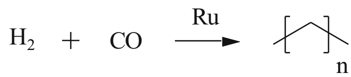


Formation of polymethylene by this reaction is not practical for commercial utilization.

Colloidal gold and fine copper powder also catalyze diazoalkane polymerizations. The reaction appears to precede by formation of alkylidine or carbene species that are bound to the surfaces of metals [31–33]. The initiations are completed by additions of diazoalkanes to the bound carbenes followed by liberation of nitrogen. Termination may take place by chain transfer, perhaps to a monomer, or to the solvent [31–33].

Many different diazoalkanes lend themselves to these polymerization reactions. Polypentylidine, polyhexylidine, polyheptilidine, and polyoctylidine form with a gold complex catalyst, $AuCl_3$-pyridine [34].

An entirely different route to preparation of macroparaffins is through a high-pressure reaction between hydrogen and carbon monoxide. Transition metals, like finely divided ruthenium, catalyze this reaction. At pressures of about 200 atm and temperatures below 140°C, polymethylene of molecular weight as high as 100,000 forms [35]:



6.2 Polypropylene

Propylene monomer, like ethylene, is obtained from petroleum sources. Free-radical polymerizations of propylene and other α-olefins are completely controlled by chain transferring [36]. They are, therefore, polymerized by coordination polymerization. At present, mainly isotactic polypropylene is being used in large commercial quantities. Also, there is some utilization of atactic polypropylene as well. Syndiotactic polypropylene, on the other hand, is still mainly a laboratory curiosity.

The polypropylene that was originally described by Natta contained less than 50% of isotactic fractions. The remainder was atactic material. Some stereoblocks composed of isotactic and atactic polypropylenes were also formed. This type of product forms when α-olefins are polymerized in inert hydrocarbons with catalysts prepared by reducing high valence metal compounds, like $TiCl_4$, with organometallic compounds like $Al(C_2H_5)$ prepared by reducing high valence metal compounds, like $TiCl_4$, with organometallic compounds like $Al(C_2H_5)_3$.

Later heterogeneous highly crystalline catalysts based on transition metals (valence 3 or less) like $TiCl_2$, $TiCl_3$, $ZrCl_3$, and VCl_3 were developed that yielded stereospecific polypropylene. The metal halides were combined with selected metal alkyls. Only those alkyls were picked that would not destroy the crystalline lattice of the transition metal salts in the process of the reaction. The resultant catalysts yielded crystalline polypropylenes with high fractions of the isotactic material. The products, however, also contained some low molecular weight fractions, some amorphous and stereoblock materials, that still required costly purification and separations to obtain relatively pure isotactic polypropylene. The atactic polymer is a wax-like substance that lacks toughness. Also, presence of amorphous materials, or very low molecular weight compounds, causes tackiness

Table 6.3 Polypropylenes prepared by Natta [37]

Transition metal halide	Metal alkyl halide	% Crystallinity
$TiCl_3$ (β)	$Al(C_2H_5)_3$	40–50
$TiCl_3$ (α, γ, or δ)	$Al(C_2H_5)_3$	96–98
$TiCl_3$ (α, γ, or δ)	$Al(C_2H_5)_2CI$	96–98
$TiCl_3$ (α, γ, or δ)	$Be(C_2H_5)_2$	94–96
$TiCl_3$ (α, γ, or δ)	$Mg(C_2H_5)_2$	78–85
$TiCl_3$ (α, γ, or δ)	$Zn(C_2H_5)_2$	30–40
VCl_3	$Al(C_2H_5)_3$	73
$TiCl_2$	$Al(C_2H_5)_3$	75

Table 6.4 Effect of addition of Lewis bases on the amount of crystalline fraction in polypropylene

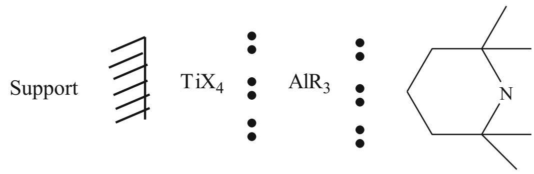
Transition metal halides	Aluminum alkyl	Lewis base	% Crystallinity
$TiCl_3$	$2Al(C_2H_5)Br_2$	Pyridine	>98.5
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N(C_2H_5)_3$	95
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$NH(C_2H_5)_2$	93
$TiCl_3$	$2Al(C_2H_5)Br_2$	$N^+(C_4H_9)_4I^-$	>99
$TiCl_3$	$2Al(C_2H_5)Cl_2$	$N^+(C_4H_9)_4Br^-$	96

[a] From Natta et al. [38]

and impedes processing. Table 6.3 lists some of the catalysts and the amounts of crystallinity in polymers that were reported by Natta et al. [37]. To avoid costly purification of isotactic polypropylene, three-component catalyst systems were developed. Some of the original ones appear to have been reported by Natta, himself, who found that addition of Lewis bases enhances the quantity of the crystalline material. Table 6.4 shows the effects of addition of Lewis bases on the amount of crystallinity, reported by Natta et al. [38].

Many other three-component systems were developed since [39–43]. Also, development of more active catalysts [44, 45] eliminates a need to remove them from the finished product [15]. The first improvement in catalyst productivity came from treating $TiCl_3$ (formed from $TiCl_4$ and $Al(C_2H_5)Cl_2$) with aliphatic ethers resulting in yields of 520 g of polymer for each gram of Ti [46]. Further improvement was achieved by supporting $TiCl_3$ on $MgCl_2$ or by producing a supported catalyst by reacting $TiCl_4$ with $Mg(OC_2H_5)$ or with other magnesium compounds. This raised the productivity to over 3,000 g of polymer for every gram of Ti [46]. The products, however, contained low percentages of the isotactic isomer (20–40%). Addition of a Lewis base like *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine in solid component and ethyl benzoate in solution raised the isotactic content to 93% with a productivity of 2,500 g of polymer per gram of Ti [41]. Claims are made today for much greater catalyst activity. It was reported, for instance, that catalyst efficiencies of 40 kg of polymer per 1 g of Ti can be achieved. Such yields require proper choice of catalysts and control over polymerization conditions. The isotactic fractions in the products are reported to range from 95 to 97% [47–49].

In a catalyst system $TiCl_3/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$, the high activity was initially attributed to higher propagation rates rather than to an increase in the concentration of the active sites [50]. The higher activity of these catalysts, however, was shown instead to be due to higher numbers of active centers and only slightly higher values of K_P [51]. Subsequent trends in modifications of supported Ziegler–Natta catalysts consisted of using sterically hindered amines [52–54]. For instance, 2,2,6,6-tetramethylpiperidine might be used together with different trialkylaluminum compounds as modifier-cocatalyst systems for the supported catalysts:

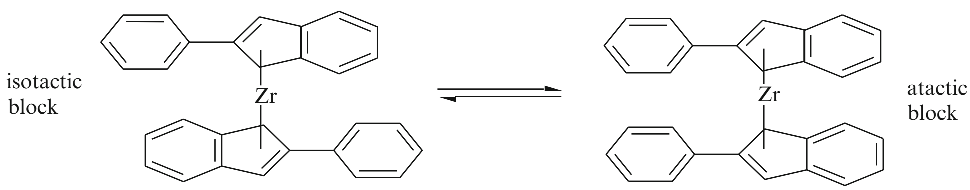


where X represents a halogen.

Other analogous amines, like 1,2,4-trimethylpiperazine and 2,3,4,5-tetraethylpiperidine, are also used in preparations of titanium halide catalysts supported on $MgCl_2$. The amine remains as a built-in modifier in the catalyst system [53].

Subsequent research efforts concentrated on soluble catalytic systems, like di-η^5-cyclopentadienyldiphenyltitanium and tetrabenzylzirconium complexed with methylaluminoxane, $(CH_3)_2Al$–[–O–$Al(CH_3)$–]$_n$–$Al(CH_3)_2$. Such catalysts, however, yield products that contain only about 85% isotactic polypropylene [55–61], and only if the reactions are conducted at low temperatures, −45°C or lower. A major breakthrough occurred when rigid chiral metallocene initiators were developed, like 1,1-ethylene-di-η^5-indenylzirconium dichloride, complexed with methylaluminoxane. In place of zirconium, titanium and hafnium analogs can also be used. These catalysts are highly isospecific [62–64] when used at low temperatures. The compounds are illustrated in Chap. 4. Typical catalysts consist of aluminum to transition metal ratios of 103 or 104:1. Many of them yield 98–99% isotactic fractions of the polymer. In addition, these are very active catalysts, yielding large quantities of polymer per gram of zirconium.

It was also reported that elastomeric polypropylenes can be formed from the monomer with the aid of some metallocene catalysts [62–64]. Because rigid, chiral metallocene catalysts produce isotactic polypropylene, while the achiral ones produce the atactic form, Waymouth and Coates [62] prepared a bridged metallocene catalyst with indenyl ligands that rotate about the metal–ligand bond axis. The rotation causes the catalyst to isomerize between chivalric and nonchiralic geometries:



Indenyl ligands, however, were found to rotate faster that the polymerization reaction. This prevents formation of stereoregular polymer blocks [62]. To overcome that, phenyl substituents were added to the ligands to slow down the rotation below the speed of monomer insertion, yet rotate faster than the time required for formation of the whole polymeric chain. The product, a catalytic system of bis(2-phenylindenyl)zirconium dichloride plus methylaluminoxane, was found to yield elastomeric block copolymers of isotactic and atactic polypropylene [62].

Vincenzo et al. [63] reported that ^{13}C NMR microstructural analysis of polypropylene samples produced with two representative "oscillating" metallocene catalysts was found to be largely different in steric hindrance. The original mechanistic proposal of an "oscillation" between the two enantiomorphous, a racemic-like (isotactic-selective) and a meso-like (non-stereoselective) conformation, according to them, cannot explain the observed polymer configuration.

They further feel that isotactic-stereoblock nature of the polymers obtained with this catalyst proves unambiguously that the active cation "oscillates" between the two enantiomorphous racemic-like conformations at an average frequency that, even at high propene concentration, is only slightly lower than that of monomer insertion. The less hindered catalyst gives instead a largely stereoirregular polypropylene, which is the logical consequence of a faster ligand rotation; however, depending on the use conditions (in particular, on the nature of the cocatalyst and the polarity of the solvent), the polymerization products may also contain appreciable amounts of a fairly isotactic fraction. The peculiar microstructure of this fraction, with isotactic blocks of the same relative configuration spanned by short atactic ones, rules out the possibility that the latter are due to an active species in meso-like conformation and point rather to a conformationally "locked" racemic-like species with restricted ring mobility. The hypothesis of a stereorigidity induced by the proximity to a counter anion, which would play the role of the inter-annular bridge in the racemic-bis(indenyl) ansa-metallocenes, was tested by computer modeling and found viable.

Preparation of elastomeric polypropylenes was also reported by Chien et al. [64]. Two metallocene catalysts of different stereospecificities were used. The isospecific catalyst precursors were either *rac*-ethylene bis-(1-η^5-indenyl)zirconium dichloride or *rac*-dimethylsilylene bis(1-η^5-indenyl)zirconium dichloride. The unspecific one was ethylene bis(9-η^5-fluorenyl)zirconium dichloride. The precursors were activated with triphenyl carbenium tetrakis(pentafluorophenyl)borate and triisobutylaluminum. The resultant catalysts exhibit very high activity, yielding products that range from tough plastomers to weak elastomers [64].

6.2.1 Manufacturing Techniques

The earliest commercial methods used slurry polymerizations with liquid hydrocarbon diluents, like hexane or heptane. These diluents carried the propylene and the catalyst. Small amounts of hydrogen were fed into the reaction mixtures to control molecular weights. The catalyst system consisted of a deep purple or violet-colored $TiCl_3$ reacted with diethyl aluminum chloride. The $TiCl_3$ was often prepared by reduction of $TiCl_4$ with an aluminum powder. These reactions were carried out in stirred autoclaves at temperatures below 90°C and at pressures sufficient to maintain a liquid phase. The concentration of propylene in the reaction mixtures ranged between 10 and 20%. The products formed in discrete particles and were removed at 20–40% concentrations of solids. Unreacted monomer was withdrawn from the product mixtures and reused. The catalysts were deactivated and dissolved out of the products with alcohol containing some HCl, or removed by steam extraction. This was followed by extraction of the amorphous fractions with hot liquid hydrocarbons.

Later bulk polymerization processes were developed where liquid propylene was either used as the only diluent in a loop reactor or permitted to boil out to remove the heat of reaction. The second was done in stirred vessels with vapor space at the top. More recently, gas-phase polymerizations of propylene were introduced. The technology is similar to the gas-phase technology in ethylene polymerizations [15] described in Sect. 6.1.

6.2.2 Syndiotactic Polypropylene

Isotactic polypropylene received most attention because it is commercially more desirable. Nevertheless, syndiotactic polypropylene, though less crystalline, has greater clarity, elasticity, and impact resistance. It melts, however, at lower temperature. This isomer was originally prepared with both, heterogeneous, titanium-based catalysts and soluble, vanadium-based ones. The heterogeneous catalysts gave very low yields of the syndiotactic fractions. In fact, original samples contained only a few percent of the desired material, almost an impurity. The yield of syndiotactic polypropylene increased with a decrease in polymerization temperature, but still remained low [65].

Highly syndiotactic polypropylene was prepared by Natta et al. [38] with homogeneous catalysts formed from VCl_4 or from vanadium tri-acetylacetonate, aluminum dialkyl halide, and anisole at −48 to −78°C.

Table 6.5 Comparison of isotactic and syndiotactic polypropylenes

				Typical	
Isomer	Crystal structure	Density at 25°C	MP (°C)	M_w	M_n
Isotactic	Monoclinic	0.92–0.43 g/cm^3	171–186	220–700 K	38–160 K
	Triclinic	0.943 g/cm^3			
	Hexagonal				
Syndiotactic	Orthorhombic	0.89–0.91 g/cm^3	138		

No isotactic fractions formed. This led to development of many effective soluble catalysts. The catalyst components and the conditions for their preparation are quite important in maintaining control over syndiotactic placement. For the most effective soluble catalyst the ratio of AIR_2X to the vanadium compound has to be maintained between 3 and 10 [66]. The organic portion of the organoaluminum compound can be either methyl, ethyl, isobutyl, neopentyl, phenyl, or methylstyryl [9, 67]. In addition to VCl_4 and to vanadium tri-acetylacetonate [66], various other vanadates can be used, like $[VO(OR)_xCl_{3-x}]$, where $x = 1, 2,$ or 3 [65]. The exact nature of the vanadium compound, however, is very important to the resultant steric arrangement of the product. For instance, VCl_4 combined with $Al(C_2H_5)_2F$ forms a heterogeneous catalyst that yields the isotactic isomer [65]. Vanadium tri-acetylacetonate, on the other hand, upon reacting with $Al(C_2H_5)_2F$ forms a soluble catalyst that yields the syndiotactic isomer [66]. Addition of certain electron donors increases the amount of syndiotactic placement. These are anisole, furan, diethyl ether, cycloheptanone, ethyl acetate, and thiophene [67]. The optimum results are obtained when an anisole to vanadium ratio is 1:1. Also, the highest amount of syndiotactic polymer is obtained when the soluble catalysts are prepared and used at low temperatures. Even at low temperatures, however, like −78°C, the amount of syndiotacticity that can be obtained with a specific catalyst decreases with time [65, 66, 68]. This indicates a deterioration of the syndiotactic placing sites. On the other hand, polymerization of propylene with soluble vanadium tri-acetylacetonate–$Al(C_2C_5)_2Cl$ system was reported to be a “living” type polymerization [69]. The product has a narrow molecular weight distribution ($M_w/M_n = 1.05$–1.20). A kinetic study indicates an absence of chain transferring and termination at temperatures below −65°C.

More recent catalysts for syndiotactic polypropylene are complexes, like *i*-propyl(cyclopentadienyl-1-fluorenyl)hafnium dichloride with methyl aluminoxane [70]. Another, similar catalyst is *i*-propyl(η^5-cyclopentadienyl-η^3-fluorenyl)zirconium dichloride with methyl aluminoxane. These catalysts yield polymers that are high in syndiotactic material (the zirconium-based compound yields 86% of racemic pentads) [70, 71]. Commercial production of syndiotactic polypropylene is in the early stages. What catalytic system is used, however, is not disclosed at this time. Some of the properties of the two isomers, isotactic and syndiotactic polypropylenes, are compared in Table 6.5.

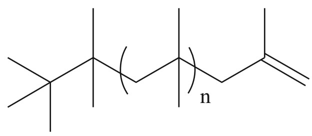
The molecular weights of syndiotactic polypropylenes can vary from a number average molecular weight of 25,000–60,000, depending upon reaction conditions [70]. Also, in isotactic polypropylene there is less than one double bond per 1,000 carbon atoms [72]. A typical $M_w/M_n = 5$–12.

6.3 Polyisobutylene

The original commercial methods for preparing high molecular weight polyisobutylene by cationic polymerization in good yields were reported in 1940. The reaction was carried out at −40 to −80°C in a diluent with BF_3 catalysis [72]. This developed into current commercial practices of polymerizing isobutylene at −80 to −100°C, using liquid ethylene or methyl chloride as a diluent [73, 74]. Even at these low temperatures the reaction is quite violent. Methods were developed, therefore, to dissipate the heat. In one of them, called "flash polymerization process" the catalyst (a Lewis acid, like BF_3 or $AlCl_3$, for instance) is added in solution to the cooled isobutylene solution. The polymerization takes place very rapidly and is complete in a few seconds with the heat of the reaction being removed by vaporization of the diluent. Such reactions, however, are very difficult to carry out in conventional batch reactors. Two types of procedures were, therefore, adopted [75]. The first one is built around a moving stainless steel belt contained inside a gas-tight reactor housing. Isobutylene and liquid ethylene from one source and a Lewis acid in ethylene solution (0.1–0.3% based on monomer) from another source are fed continuously onto the moving belt where they are mixed and moved. The movement of the belt is adjusted at such a speed that the polymerization is complete before the polymer arrives at the end of its travel, where it is removed with a scraper and further processed.

In the second process, the polymerization is carried out in multiple kneaders or mixers. These are arranged in a series of descending steps. Here the reaction mixture is carried from one kneader to another with the temperature being raised at each station and completed at the last one.

All commercially important polyisobutylenes are linear, head to tail polymers, with tertiary butyl groups at one end of the chains and vinylidene groups at the other:



The differences lie in molecular weights. They range from 2,000 to 20,000 for viscous liquids to between 100,000 and 400,000 for high molecular weight elastomers that resemble unmilled crepe rubber. The polymers degrade readily from thermal abuse. They can be stabilized effectively, however, by adding small quantities (0.1–1.0%) of such stabilizers as aromatic amines, phenols, or sulfur compounds. Polyisobutylenes are soluble in many hydrocarbons and are resistant to attacks by many chemicals.

Coordination polymerizations with Ziegler–Natta catalysts yield similar polymers that range from viscous liquids to rubbery solids. At 0°C, a catalyst with a 1:16 Ti to Al molar ratio yields a polymer with a molecular weight of 5,000–6,000 [76]. The molecular weight, however, is dependent upon the reaction time. This contrasts with polymerizations of ethylene, propylene, and 1-butene by such catalysts, where the molecular weights of the products are independent of the reaction time. In addition, there are some questions about the exact molecular structures of the products [76].

Bochmann and coworkers [77] carried out polymerizations of isobutylene and copolymerizations with isoprene using cationic zirconocene hydride complexes. The combination of $[Cp_2ZrH]$ with various trityl salts of weakly coordinating anions gives binuclear cationic hydrides $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+X^-$ which are powerful initiators for the polymerization of isobutene and its copolymerization with isoprene. The temperature dependence of M is indicative of a cationic mechanism. The highest molecular weights are obtained only under scrupulously dry conditions.

High molecular weight polyisobutylene has fair tensile strength but suffers from the disadvantage of considerable cold flow. A copolymer of isobutylene with some isoprene for cross-linking is, therefore, used as a commercial elastomer and called "butyl rubber." The isoprene is present in the copolymer in only minor proportions (1.4–4.5%). The uncross-linked material is very similar to polyisobutylene. Copolymers of isobutylene with other dienes are also called butyl rubbers. They can also be terpolymers, where the third component may be cyclopentadiene for improved ozone resistance.

The molecular weights of the copolymers vary inversely with the quantities of isoprene incorporated, the polymerization temperatures, and amount of impurities present during polymerization. Impurities like *n*-butene or water act as chain transferring agents [79].

To maintain uniform molecular weights, the conversions are usually kept from exceeding 60%.

6.4 Poly(α-olefin)s

Many α-olefins were polymerized by the Ziegler–Natta catalysts to yield high polymers and many such polymers were found to be stereospecific and crystalline. Polymerizations of α-olefins of the general structure of $CH_2 = CH - (CH_2)_x - R$, where x is 0–3 and R denotes CH_3, $CH–(CH_3)_2$, $C(CH_3)_3$, or C_6H_5, can be catalyzed by vanadium trichloride/triethyl aluminum [80]. The conversions are fairly high, though higher crystallinity can be obtained with titanium-based catalysts [81]. Addition of Lewis bases, such as $(C_4H_9)_2O$, $(C_4H_9)_3N$, or $(C_4H_9)_3P$, to the catalyst system further increases crystallinity [82].

6.4.1 Properties of Poly(α-olefin)s

Many poly(α-olefin)s reported in the literature are not used commercially for various reasons. Table 6.6 lists some of the olefins polymerized by the Ziegler–Natta catalysts [72, 83].

6.4.2 Poly(butene-1)

Isotactic poly(butene-1) is produced commercially with three-component coordination-type catalysts. It is manufactured by a continuous process with simultaneous additions to the reaction vessel of the monomer solution, a suspension of $TiCl_2–AlCl_3$, and a solution of diethyl aluminum chloride [84]. The effluent containing the suspension of the product is continually removed from the reactor. Molecular weight control is achieved through regulating the reaction temperature. The effluent contains approximately 5–8% of atactic polybutene that is dissolved in the liquid carrier. The suspended isotactic fractions (92–98%) are isolated after catalyst decomposition and removal. The product has a density of 0.92 g/cm^3 and melts at 124–130°C.

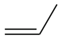
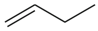
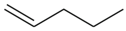
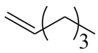
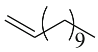
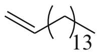
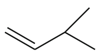
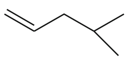
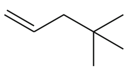
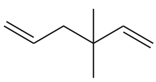
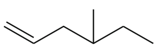
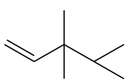
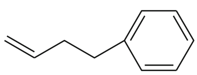
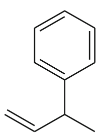
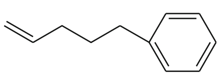
Isotactic polybutene crystallizes into three different forms. When it cools from the melt, it originally crystallizes into a metastable crystalline one. After several days, however, it transforms into a different form. Noticeable changes in melting point, density, flexural modulus, yield, and hardness accompany this transformation. The third crystalline form results from crystallization from solution. The polymer exhibits good impact and tear resistance. It is also resistant to environmental stress-cracking.

6.4.3 Poly(4-methyl pentene-1)

Another commercially produced polyolefin is isotactic poly(4-methyl pentene-1). The polymer carries a trade name of TPX. This material is known for high transparency, good electrical properties, and heat resistance. Poly(4-methyl pentene-1) has a density of 0.83 g/cm^3. This polyolefin exhibits poor load-bearing properties and is susceptible to UV degradation. It is also a poor barrier to moisture and gases and scratches readily. This limits its use in many applications.

Poly(4-methyl pentene) is produced by the same process and equipment as polypropylene. A post finishing de-ashing step, however, is required. In addition, aseptic conditions are maintained during manufacture to prevent contamination that may affect clarity.

Table 6.6 Properties of poly(α-olefin)s

Monomer	State	MP (°C)
	Crystalline	136
	Crystalline	165–168
	Crystalline	124–130
	Crystalline	75
	Rubber, amorphous	–
	Some crystallinity	45
	Crystallinity in pendant groups	70; 100
	Crystalline, hard	240–285
	Crystalline, hard	200–240
	Crystalline, hard	300–350
	Crystalline, hard	350
	Crystalline, hard	160
	Rubber, amorphous	–
	Crystalline, slightly rubbery	158
	Crystalline, intractable	360
	Rubber, amorphous	–

[a]From refs. [72, 83]

A number of similar polyolefins with pendant side groups are known. These include poly(3-methyl butene-1), poly(4,4-dimethyl pentene-1), and poly(vinyl cyclohexane). Due to their increased cohesive energy, ability to pack into tight structures, and the effect of increasing stiffness of the pendant groups, some of these polymers have a high melting point. This can be seen from Table 6.9. Many of these polymers, however, tend to undergo complex morphological changes on standing. This can result in fissures and planes of weakness in the structure.

6.5 Copolymers of Ethylene and Propylene

Many monomers have been copolymerized with ethylene by a variety of polymerization methods. When ethylene is copolymerized with other olefins, the resultant hydrocarbon polymers have reduced regularity and lower density, lower softening point, and lower brittle point.

Copolymers of ethylene and propylene are a commercially important family of materials. They vary from elastomers that can contain 80% ethylene and 20% propylene to polypropylene that is modified with small amounts of ethylene to improve impact resistance.

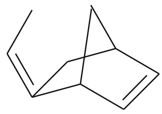
Metallocene catalysts can produce both random and alternating copolymers of ethylene and propylene [85]. At present there does not appear to be any commercial utilization of alternating copolymers. They were reported to form in polymerizations catalyzed by bridged fluorenyl catalysts [85].

6.5.1 Ethylene and Propylene Elastomers

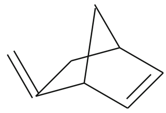
The commercial *ethylene-propylene rubbers* typically range in propylene content from 30 to 60%, depending upon intended use. Such copolymers are prepared with Ziegler–Natta type catalysts. Soluble catalysts and true solution processes are preferred. The common catalyst systems are based on VCl_4, $VOCl_3$, $V(Acac)_3$, $VO(OR)_3$, $VOCl(OR)_2$, $VOCl_2(OR)$, etc. with various organoaluminum derivatives. The products are predominantly amorphous. Polymerization reactions are usually carried out at 40°C in solvents like chlorobenzene or pentane. The resultant random copolymers are recovered by alcohol precipitation. Because these elastomers are almost completely saturated, cross-linking is difficult. A third monomer, a diene is, therefore, included in the preparation of these rubbers that carry the trade names EPTR or EPDM. Inclusion of third monomers presents some problems in copolymerization reactions. For instance, it is important to maintain constant feed mixtures of monomers to obtain constant compositions. Yet, two of the three monomers are gaseous and the third one is a liquid. Natta [86] developed a technique that depends upon maintaining violent agitation of the solvent while gaseous monomers were bubbled through the liquid phase. This was referred to as "semi-flow technique." The process allows the compositions of gaseous and liquid phases to be in equilibrium with each other and to be more or less constant [87]. Other techniques evolved since. All are designed to maintain constant polymerization mixtures.

The vanadium-based catalyst systems deteriorate with time and decrease in the number of catalytic centers as the polymerizations progress. The rate of decay is affected by conditions used for catalyst preparation, compositions of the catalysts, temperature, solvents, and Lewis bases. It is also affected by the type and concentration of the third monomer [88–90]. Additions of chlorinated compounds to the deactivated catalysts, however, help restore activity [91, 92]. Catalyst decay can also be overcome by continually feeding catalyst components into the polymerization medium [93].

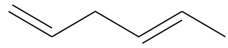
While third monomer can be a common diene, like isoprene, more often it is a bridged ring structure with at least one double bond in the ring. In typical terpolymer rubbers with 60–40 ratios of ethylene to propylene the diene components usually comprise about 3% of the total. Some specialty rubbers, however, may contain 10% of the diene or even more. Reaction conditions are always chosen to obtain 1,2 placement of the diene. Dienes in common use are ethylidine norbornene, methylene norbornene, 1,4-hexadiene, dicyclopentadiene, and cycloocatadiene:



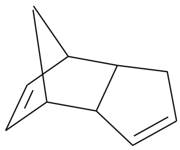
ethylidine norbornene



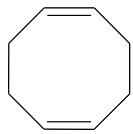
methyle norbornene



1,4-hexadiene

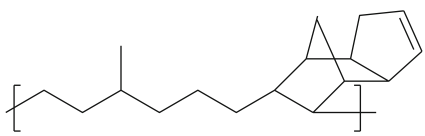


dicyclopentadiene



cyclooctadiene

In addition to the above, the patent literature describes many other dienes. An idealized picture of a segment of an uncross-linked gum stock might be shown as having the following structure:



6.5.2 Copolymers of Ethylene with α-Olefins and Ethylene with Carbon Monoxide

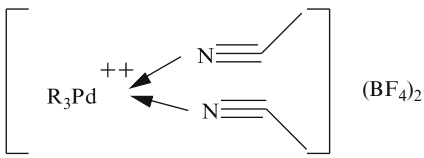
Many copolymers of ethylene with α-olefins are prepared commercially. Thus ethylene is copolymerized with butene-1, where a comonomer is included to lower the regularity and the density of the polymer. Many copolymers are prepared with transition metal oxide catalysts on support. The comonomer is usually present in approximately 5% quantities. This is sufficient to lower the crystallinity and to markedly improve the impact strength and resistance to environmental stress-cracking. Copolymers of ethylene with hexene-1, where the hexene-1 content is less than 5%, are also produced for the same reason.

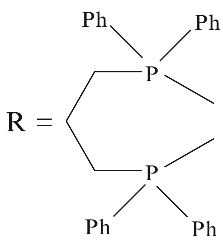
In most cases, the monomers that homopolymerize by Ziegler–Natta coordination catalysts also copolymerize by them [94]. In addition, some monomers that do not homopolymerize may still copolymerize to form alternating copolymers. Because the lifetime of a growing polymer molecule is relatively long (can be as long as several minutes), block copolymerization is possible through changes in the monomer feeds. Also, the nature of the transition metal compound influences the reactivity ratios of the monomers in copolymerizations. On the other hand, the nature of the organometallic compound has no such effect [95]. It also appears that changes in the reaction temperature between 0 and 75°C have no effect on the *r* values. Copolymers can be formed using either soluble or heterogeneous Ziegler–Natta. One problem encountered with the heterogeneous catalysts is the tendency by the formed polymers to coat the active sites. This forces the monomers to diffuse to the sites and may cause starvation of the more active monomer if both diffuse at equal rates.

Many different block copolymers of olefins, like ethylene with propylene and ethylene with butene-1, are manufactured. Use of the anionic coordination catalysts enables variations in the molecular structures of the products. It is possible to vary the length and stereoregularity of the blocks. This is accomplished by feeding alternately different monomers into the reactor. When it is necessary that the blocks consist of pure homopolymers, then after each addition the reaction is allowed to subside. If any residual monomer remains, it is removed [96]. This requires a long lifetime for the growing chains and an insignificant amount of termination. The stability of the anion depends upon the catalyst system. One technique for catalyst preparation is to form $TiCl_3$ by reducing $TiCl_4$ with diethyl aluminum chloride followed by careful washing of the product of reduction to remove the by-product $Al(C_2H_5)Cl$. Other reports describe using the α-form of $TiCl_3$ or heat treating it to form the β or γ-forms that yields more stereospecific products.

The transition metal oxide catalysts on support, such as the CrO_3/silica–alumina (Phillips) and MoO_3/Al_2O_3 (Standard Oil), are used to copolymerize minor quantities of α-olefins with ethylene. Such copolymerizations introduce short pendant groups into polymer backbones.

Ethylene and other olefins can also be copolymerized with carbon monoxide to form polymers of aliphatic ketones, using transition metal catalysts, like palladium(II) coupled with non-coordinating anions. There are numerous reports of such catalysts in the literature. One example is a compound composed of bidentate diarylphosphinopropane ligand and two acetonitrile molecules coordinating Pd^{2+} coupled with BF_3 counterions. This compound, bis(acetonitrile)palladium(II)-1,3-bis(diphenylphosphino)propane-(tetrafluoborate), can be illustrated as follows [97]:

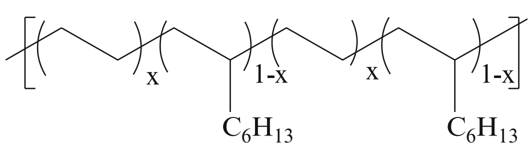




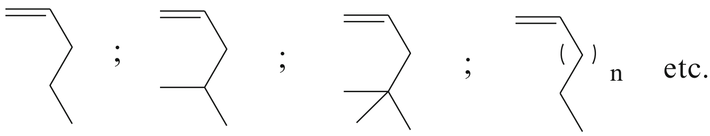
When the tetrafluoroborate is replaced with a perchlorate, the compound is a very active catalyst [97].

One copolymer of ethylene and carbon monoxide are available commercially. The material offered under the trade name of Carilon is actually a terpolymer, because it contains a small quantity of propylene. It is reported [98] that use of a palladium catalyst permits formation of perfectly alternating interpolymer.[08] The product is reported to be a tough, chemical resistant material.

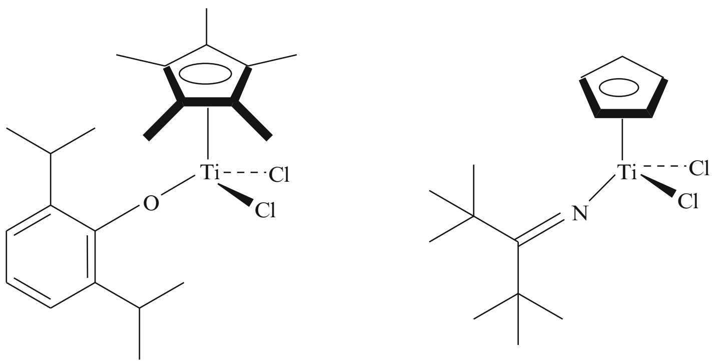
Hustad et al. [99] developed a technique to make polydisperse polyethylene diblock copolymers with 1-octene with a distribution of block lengths. When melted and compressed into films, the distinct polymeric segments self-assemble into layered patterns of semi-crystalline and hard and amorphous phases. Because each phase has a different refractive index, the block copolymer, shown below, can function as a photonic crystal and scatter visible light.



Nomura and coworkers [100] studied copolymerization of ethylene with various pentenes:



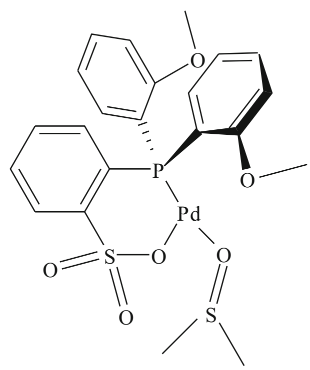
where $n = 8, 12$. The polymerizations were carried out with titanium catalysts illustrated below. Titanium compound were combined with methyl aluminoxane:



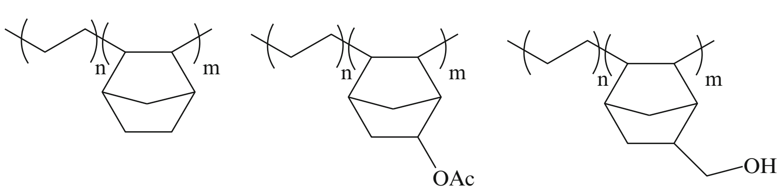
Their results show that the monomer reactivities are influenced not only by substituents on the olefins but also by the nature of the catalytically active species.

Derlin and Kaminsky [101] reported copolymerizations of ethylene and propylene with a sterically hindered monomer, 3-methyl-1-butene, using titanium and zirconium metallocenes with methyl aluminoxane cocatalyst.

Tritto and coworkers [102] reported that the complex [Pd(k^2-P,O-{2-(2-MeOC$_6$H$_4$)$_2$P}C$_6$H$_4$SO$_3$)Me(DMSO)] was investigated as a single-component catalyst for the copolymerization of ethylene with norbornene. The catalyst was illustrated as follows:

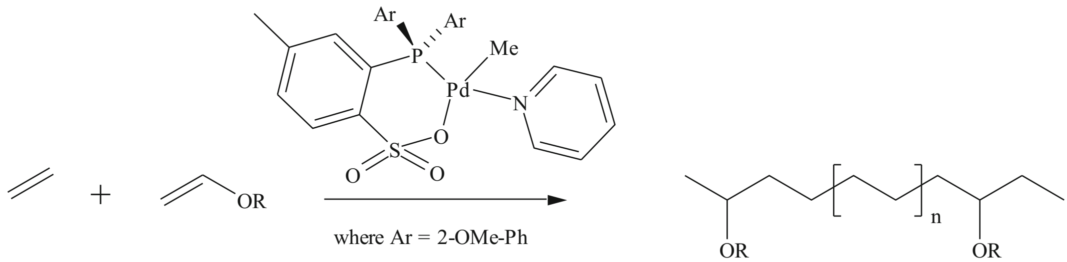


The copolymers were obtained in very good yields and molar masses were significantly higher than those of polyethylene. Three copolymers were formed:



Determination of microstructure and reactivity ratios revealed a strong inherent tendency to form alternating copolymers.

Jordan [103] described copolymerization of ethylene with vinyl ethers and with vinyl fluoride. The catalyst used was (*ortho*-phospheno-arenesulfonate)PdMe(pyridine). The reaction was illustrated as follows:



6.5.3 Copolymers of Propylene with Dienes

Although presently lacking industrial importance, alternating copolymers can be made from propylene and butadiene [104] and also from propylene and isoprene [105]. Copolymers of propylene and butadiene form with vanadium- or titanium-based catalysts combined with aluminum alkyls. The catalysts have to be prepared at very low temperature (−70°C). Also, it was found that a presence of halogen atoms in the catalyst is essential [75]. Carbonyl compounds, such as ketones, esters, and others, are very effective additives. A reaction mechanism based on alternating coordination of propylene and butadiene with the transition metal was proposed by Furukawa [104].

6.5.4 Copolymers of Ethylene with Vinyl Acetate

Various copolymers of ethylene with vinyl acetate are prepared by free-radical mechanism in emulsion polymerizations. Both reactivity ratios are close to 1.0 [106]. The degree of branching in these copolymers is strongly temperature-dependent [107]. These materials find wide use in such areas as paper coatings and adhesives. In addition, some are hydrolyzed to form copolymers of ethylene with vinyl alcohol. Such resins are available commercially in various ratios of polyethylene to poly(vinyl alcohol), can range from 30% poly(vinyl alcohol) to as high as 70%.

Vinyl acetate residues in ethylene–vinyl acetate copolymers reduce regularity of polyethylene. This reduces crystallinity in the polymer. Materials containing 45% vinyl acetate are elastomers and can be cross-linked with peroxides.

6.5.5 Ionomers

Another group of commercial copolymers of ethylene is those formed with acrylic and methacrylic acids, where ethylene is the major component. The copolymerizations are carried out under high pressures. These materials range in comonomer content from 3 to 20%. Typical values are 10%. A large proportion of the carboxylic acid groups (40–50%) are prereacted with metal ions like sodium or zinc. The copolymer salts are called ionomers with a trade name like Syrlin. The materials tend to behave similarly to cross-linked polymers at ambient temperature by being stiff and tough. Yet they can be processed at elevated temperatures, because aggregation of the ionic segments from different polymeric molecules is destroyed. The material becomes mobile but after cooling the aggregates reform. Ionomers exhibit good low temperature flexibility. They are tough, abrasion-resistant resins that adhere well to metal surfaces.

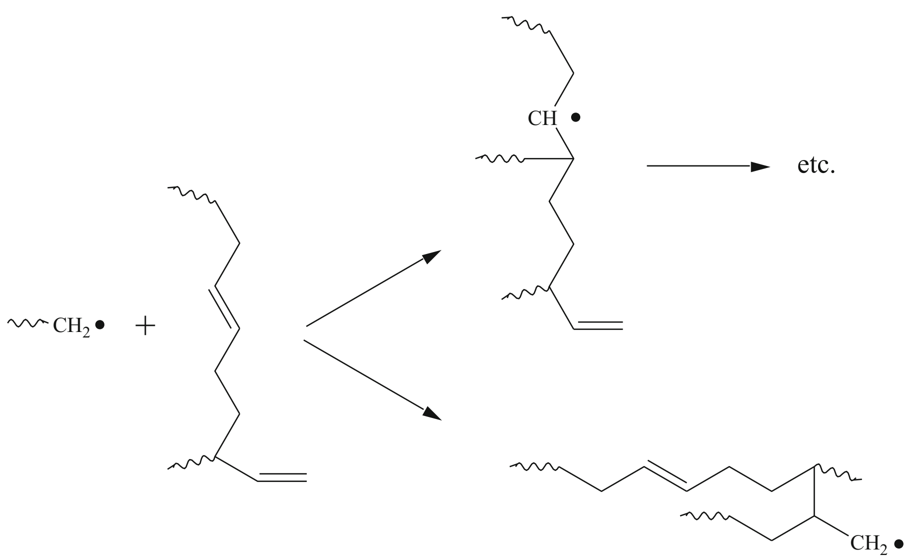
6.6 Homopolymers of Conjugated Dienes

Many different polymers of conjugated dienes are prepared commercially by a variety of processes, depending upon the need. They are formed by free-radical, ionic, and coordinated anionic polymerizations. In addition, various molecular weights homopolymers and copolymers, ranging from a few thousand for liquid polymers to high molecular weight ones for synthetic rubbers, are on the market.

6.6.1 Polybutadiene

1,3-Butadiene, the simplest of the conjugated dienes, is produced commercially by thermal cracking of petroleum fractions and catalytic dehydrogenation of butane and butene. Polymerization of butadiene can potentially lead to three poly(1,2-butadiene)s, atactic, isotactic, and syndiotactic and two *cis* and *trans* forms of poly(1,4-butadiene). This is discussed in Chaps. 3 and 4.

Free-radical polymerizations of 1,3-butadiene usually result in polymers with 78–82% of 1,4-type placement and 18–22% of 1,2-adducts. The ratio of 1,4 to 1,2 adducts is independent of the temperature of polymerization. Moreover, this ratio is obtained in polymerizations that are carried out in bulk and in emulsion. The ratio of *trans*-1,4 to *cis*-1,4 tends to decrease, however, as the temperature of the reaction decreases. Polybutadiene polymers formed by free-radical mechanism are branched because the residual unsaturations in the polymeric chains are subjects to free-radical attacks:



Should branching become excessive, infinite networks can form. The products become cross-linked, insoluble, and infusible. Such materials are called *popcorn* polymers. This phenomenon is more common in bulk polymerizations. The cross-linked polymers form nodules that occupy much more volume than the monomers from which they formed and often clog up the polymerization equipment, sometimes even rupturing it.

High molecular weight homopolymers of 1,3-butadiene formed by free-radical mechanism lack the type of elastomeric properties that are needed from commercial rubbers. Copolymers of butadiene, however, with styrene or acrylonitrile are more useful and are prepared on a large scale. This is discussed in another section.

6.6.1.1 Liquid Polybutadiene

Low molecular weight liquid homopolymers of 1,3 butadiene, also some liquid copolymers, find industrial uses in many applications. These materials can range in molecular weights from 500 to 5,000 depending upon the mode of polymerization. Liquid polybutadienes formed by cationic polymerizations are high *trans*-1,4 content. Such materials find applications in industrial coatings. They are usually prepared with Lewis acids in chlorinated solvents. When the reactions are catalyzed by $AlCl_3$ at −78°C, two types of polymers form [108]. One is soluble and the other is insoluble, depending upon the extent of conversion. $AlCl_3$, $AlBr_3$, and BF_3–Et_2O produce polymers with the same ratios of *trans*-1,4 to 1,2 adducts. These range from 4 to 5. Polymerizations carried out in ethylene chloride [108] catalyzed by $TiCl_4$ yield products with lower ratios of *trans*-1,4 to 1,2 adducts. The ratios of the two placements are affected by the solvents. They are also affected by additions of complexing agents, such as nitroethane and nitrobenzene [108]. The changes, however, are small.

Hydroxyl-terminated liquid polybutadienes are prepared for reactions with diisocyanates to form elastomeric polyurethanes (see Chap. 6). Such materials can be prepared by anionic polymerizations as "living" polymers and then quenched at the appropriate molecular weight. These polybutadienes can also be formed by free-radical mechanism. The microstructures of the two products differ, however, and this may affect the properties of the finished products. To form hydroxyl-terminated polymers by free-radical mechanism, the polymerization reactions may be initiated by hydroxyl radicals from hydrogen peroxide.

A new approach to preparation of hydroxyl-terminated liquid polybutadiene is to use a cyclic monomer, 1,5-cyclooctadiene, a ruthenium metathesis catalyst (see Chap. 5, Grubbs catalysts in section on metathesis ring opening polymerization) and an acetate functionalized chain transfer agent [109, 110]. The acetate-functionalized chain transfer agent is *cis*-2-butene-1,4-diacetate. The reaction can be carried out without a solvent and proceeds at 50°C over 6 h under an inert gas purge [111]. The acetate protecting groups provide compatibility with the ruthenium catalyst. Subsequent to polymerization the acetate groups can be converted to hydroxyl end groups with the aid of a base, like sodium methoxide.

Liquid polybutadienes that are high in 1,2 placement are also available commercially. These range from reactive polymers containing approximately 70% of vinyl groups to very reactive ones containing more than 90% of 1,2 units. The materials are formed by anionic polymerization with either sodium naphthalene, or with sodium dispersions, or with organolithium initiators in polar solvents. Carboxyl group terminated liquid polybutadienes are predominantly used as modifiers for epoxy resins (Chap. 7). They are formed by anionic mechanisms in solution with organolithium catalysts like diphenylethanedilithium, butanedilithium, isoprenelithium, or lithium methylnaphthalene complexes. Cyclohexane is the choice solvent. The reaction is quenched with carbon dioxide to introduce the terminal carboxyl groups.

Table 6.7 Microstructures of polybutadienes prepared with some coordination catalysts

	Microstructure (%)		
Catalyst	*Cis*-1,4	*Trans*-1,4	1,2
$TiI_4/Al(C_2H_5)_3$	95	2	3
$TiBr_4/Al(C_4H_9)_3$	88	3	9
β-$TiCl_3/Al(C_2H_5)_3$	80	12	8
$Ti(OC_4H_9)_4/Al(_2H_5)_3$	–	–	99–100
$Ti(OC_6H_5)_4/R_3Al$	90–100	–	–
(π-Cycloocatadiene)$_2$Ni,CF_3CO_2H	100	–	–
Bis(π-Crotyl NiCl)	92	–	–
Bis(π-Crotyl NiI)	–	94	–
$CoCl_2/Al(C_2H_5)_2Cl$	96–97	2.5	1–1.5
$CoCl_2/Al(C_2H_5)_3$	94	3	3
$CoCl_2/Al(C_2H_5)_3$/pyridine	90–97	–	–
Co-stearate/AlR_2Cl	98	1	1
VCl_3/AlR_3	–	99	1
$VOCl_3/Al(C_2H_5)_3$	–	97–9	2–3
$VCl_4/AlCl_3$	–	95	–
$Cr(C_6H_5CN)_6/Al(C_2H_5)_3$	100	–	–
$MoO_2(OR)_3/Al(C_2H_5)_3$	–	–	75

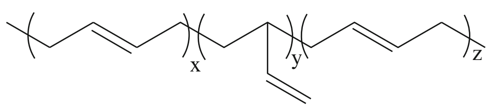
[a] From various sources in the literature

6.6.1.2 High Molecular Weight Polybutadiene

High molecular weight polybutadiene homopolymers are prepared commercially with anionic catalysts and with coordination ones. Polybutadiene formed with sodium dispersions was prepared industrially in the former USSR, and perhaps might still be produced in that area today. This sodium-catalyzed polybutadiene contains 65% of 1,2-adducts [112]. Many of the preparations by others, however, utilize either alkyllithium or Ziegler–Natta type catalysts prepared with titanium tetra iodide or preferably containing cobalt.

Because high molecular weight polybutadiene can be prepared by different catalytic systems, the choice of catalyst is usually governed by the desired microstructure of the product. Alfin catalysts yield very high molecular weight polymers with a large amount of *trans*-1,4 structures. Both the molecular weight and microstructure can be affected significantly, however, by variations in the Alfin catalyst components. These can be the alkyl groups of the organometallic compounds or alkoxide portions.

When butadiene is polymerized with lithium metal or with alkyllithium catalysts, inert solvents like hexane or heptane must be used to obtain high *cis*-1,4 placement (see Chap. 4). Based on ^{13}C NMR spectra, 1,4-polybutadiene formed with *n*-butyllithium consists of blocks of *cis*-1,4 units and *trans*-1,4 units that are separated by isolated vinyl structures [113]:

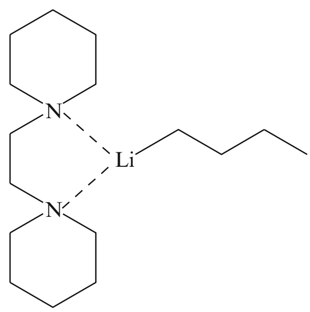


The quantity of such units in the above polybutadienes is approximately 48–58% *trans*-1,4, 33–45% *cis*-1,4, and 7–10% 1,2 units [112]. There is little effect of the reaction temperatures upon this composition. As described in Chap. 3, however, addition of Lewis bases has a profound effect. Reactions in tetrahydrofuran solvent result in 1,2 placement that can be as high as 87%.

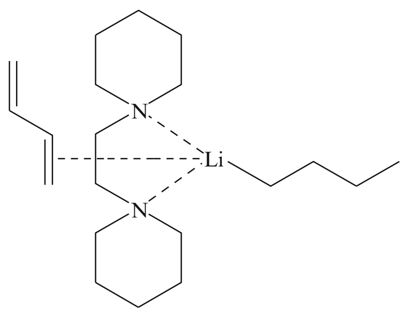
The microstructures of polybutadienes prepared with Ziegler–Natta catalysts vary with catalyst composition. It is possible to form polymers that are high either in 1,2 placement or in 1,4 units. The catalysts and the type of placement are summarized in Table 6.7.

Butadiene can be polymerized with chromium oxide catalyst on support to form solid homopolymers. The products, however, tend to coat the catalyst within a few hours after the start of the reaction and interfere with further polymerization. Polybutadiene can also be prepared in the presence of molybdenum catalyst promoted by calcium hydride. The product contains 80% of 1,4 units and 20% of 1,2 units. Of the 1,4 units, 62.5% are *cis* and 37.5% are *trans* [110].

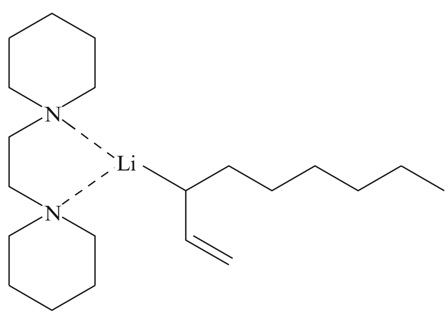
Cobalt oxide on silica–alumina in the presence of alkyl aluminum also yields high *cis*-1,4 structure polymers. An all 1,2 polybutadiene can be prepared with *n*-butyllithium modified with bis-piperidino ethane. The atactic polymer can be formed in hexane at −5 to +20°C temperature [111]. The 100% 1,2 placement was postulated to proceed according to the following scheme [111]. First a complex forms between the base and butyllithium:



The above complex reacts with butadiene to form a new complex:



This is followed by insertion of butadiene into the carbon–lithium bond:



Annunziata et al. [114] reported that Group 4 metals complexes bearing anilidomethylpyridine ligands were prepared by them. After activation by $AlBu_2H$ and methylalumoxane, the catalysts were tested in 1,3-butadiene and α-olefin polymerization. The zirconium complexes showed higher activity than the titanium analogous. Polymerization of ethylene resulted in all cases in the production of high molecular weight linear polyethylene. On the other hand, propylene polymerization tests provided substantially atactic polypropylene. 1,3-Butadiene polymerizations produced *cis*-1,4 polybutadiene. Use of zirconium complexes produced polymers with a content of *cis*-1,4 units higher than 99.9% were claimed.

6.6.2 Polyisoprene

Polyisoprenes occur in nature. They are also prepared synthetically. Most commercial processes try to duplicate the naturally occurring material.

6.6.2.1 Natural Polyisoprenes

Rubber hydrocarbon is the principle component of raw rubber. The subject is discussed in greater detail in Chap. 7. Natural rubber is 97% *cis*-1,4 polyisoprene. It is obtained by tapping the bark of rubber trees (*Hevea brasiliensis*) and collecting the exudates, a latex consisting of about 32–35% rubber. A similar material can also be found in the sap of many other plants and shrubs. The structure of natural rubber has been investigated over 100 years, but it was only after 1920, however, that the chemical structure was elucidated. It was shown to be a linear polymer consisting of head to tail links of isoprene units, 98% bonded 1,4.

6.6.2.2 Synthetic Polyisoprenes

In following natural rubber, the synthetic efforts are devoted to obtaining very high *cis*-1,4 polyisoprene and to forming a synthetic "natural" rubber. Two types of polymerizations yield products that approach this. One is through use of Ziegler–Natta type catalysts and the other through anionic polymerization with alkyllithium compounds in hydrocarbon solvents. One commercial process, for instance, uses reaction products of $TiCl_4$ with triisobutylaluminum at an Al/Ti ratio of 0.9–1.1 as the catalyst. Diphenyl ether or other Lewis bases are sometimes added as catalyst modifiers [113–116]. The process results in an approximately 95% *cis*-1,4 polyisoprene product. Typically, such reactions are carried out on continuous basis, usually in hexane and take 2–4 h. Polymerizations are often done in two reaction lines, each consisting of four kettles arranged in series. The heat of the reaction is partially absorbed by precooling the feed streams. The remaining heat is absorbed on cooled surfaces. When the stream exits, the conversion is about 80%. Addition of a shortstop solution stabilizes the product.

Alkyllithium-initiated polymerizations of isoprene yield polymers with 92–93% *cis*-1,4 content. One industrial process uses butyllithium in a continuous reaction in two lines each consisting of four reaction kettles. The heat of the reaction is removed by vaporization of the solvent and the monomer. The catalyst solution is added to the solvent stream just before it is intensively mixed with the isoprene monomer stream and fed to the first reactor. After the stream leaves each reactor, small quantities of methanol are injected between stages into the reaction mixture. This limits the molecular weight by stopping the reaction. Fresh butyllithium catalyst is added again at the next stage in the next reactor to initiate new polymer growth [117–119].

As is described in Chaps. 3 and 4, the monomer placement into the polyisoprene chain can occur potentially in nine different ways. These are the three tactic forms of the 1,2 adducts, two 1,4 adducts, *cis* and *trans*, and three tactic forms of 3,4-adducts. In addition, there is some possibility of head to head and tail to tail insertion, though the common addition is head to tail. Table 6.8 presents the various microstructures that can be obtained in polymerizations of isoprene with different catalysts.

Table 6.8 Polymerization products of isoprene

		Approximate			
Mode of polymerization	Solvent	% *Cis*-1,4	% *Trans*-1,4	% 1,2	% 3,4
Free radical	Emulsion in water	32	65	6	7
Cationic	–	37	51	4	9
	Chloroform (30°C)	–	90	4	6
Anionic					
Lithium	Pentane	94	0		6
Ethyllithium	Pentene	94	0		6
Butyllithium	Pentene	93	0		7
Sodium	Pentene	0	43	6	51
Ethylsodium	Pentene	6	42	7	45
Butylsodium	Pentane	4	35	7	54
Potassium	Pentane	0	52	8	40
Ethylpotassium	Pentane	24	39	6	31
Butylpotassium	Pentane	20	41	6	34
Rubidium	Pentane	5	47	8	39
Cesium	Pentene	4	51	8	37
Ethyllithium	Ethyl ether	6	29	5	60
Ethylsodium	Ethyl ether	0	14	10	76
Lithium	Ethyl ether	4	27	5–7	63–65
Alfin	Pentane	27	52	5	16
Coordination catalysis					
α-$TiCl_3/AlR_3$			91		
$VCl_3/Al(C_2H_5)_3$			99		
$TiCl_4/Al(C_2H_5)_3$		95–96			
Ti l_4/AlR_3 + amine		100	–		–
$CoCl_2/AlR_3$ + pyridine		96			
V(acetylacetonate)$_3/AlR_3$		90			
$Ti(OR)_4/Al(C_2H_5)_3$		95			

[a] From various sources in the literature

Cationic polymerizations of isoprene proceed more readily than those of butadiene, though both yield low molecular weight liquid polymers. $AlCl_3$ and stannic chloride can be used in chlorinated solvents at temperatures below 0°C. Without chlorinated solvents, however, polymerizations of isoprene require temperatures above 0°C. At high conversions, cationic polymerizations of isoprene result in formations of some cross-linked material [120]. The soluble portions of the polymers are high in *trans*-1,4 structures. Alfin catalysts yield polymers that are higher in *trans*-1,4 structures than free-radical emulsion polymerizations [121].

Chromium oxide catalysts on support polymerize isoprene-like butadiene to solid polymers. Here too, however, during the polymerization process, polymer particles cover the catalyst completely within a few hours from the start of the reaction and retard or stop further polymer formation. The polymerization conditions are the same as those used for butadiene. The reactions can be carried out over fixed bed catalysts containing 3% chromium oxide on SiO_2–Al_2O_3. Conditions are 88°C and 42 kg/cm^2 pressure with the charge containing 20% of isoprene and 80% isobutane [122]. The mixed molybdenum–alumina catalyst with calcium hydride also yields polyisoprene.

Lithium metal dispersions form polymers of isoprene that are high in *cis*-1,4 contents as shown in Table 6.8. These polymers form in hydrocarbon solvents. This is done industrially and the products are called Coral rubbers. They contain only a small percentage of 3,4-structures and no *trans*-1,4 or 1,2 units. The materials strongly resemble *Hevea* rubber.

Use of Ziegler–Natta catalysts, as seen from Table 6.8, can yield an almost all *cis*-1,4-polyisoprene or an almost all *trans*-1,4-polyisoprene. The microstructure depends upon the ratio of titanium to aluminum. Ratios of Ti:Al between 0.5:1 and 1.5:1 yield the *cis* isomer. A 1:1 ratio is the optimum. Ratios of Ti:Al between 1.5:1 and 3:1 yield the *trans* structures [123]. The titanium to aluminum ratios also affect the yields of the polymers as well as the microstructures. There also is an influence on the molecular weight of the product [124]. Variations in catalyst compositions, however, do not affect the relative amounts of 1,4 to 3,4 or to 1,2 placements. Only *cis* and *trans* arrangements are affected. In addition, the molecular weights of the polymers and the microstructures are relatively insensitive to the catalyst concentrations. The temperatures of the reactions, however, do affect the rates, the molecular weights, and the microstructures.

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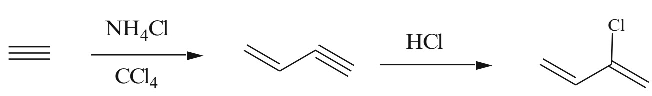
6.7 Methyl Rubber, Poly(2,3-dimethylbutadiene)

Early attempts at preparations of synthetic rubbers resulted in developments of elastomers from 2,3-dimethylbutadiene. The material, called “methyl rubber,” was claimed to yield better elastomeric properties than polybutadiene. Methyl rubber was produced in Germany during World War I where the monomer was prepared from acetone. The polymerizations were carried out by free-radical mechanism and anionically, using sodium metal dispersions for initiation. Later, it was demonstrated that 2,3-dimethyl polybutadiene can be polymerized to very high *cis*-1,4 polymer with Ziegler–Natta catalysts [125, 126].

6.8 Chloroprene Rubber, Poly(2-chloro-1,3-butadiene)

2-Chloro-1,3-butadiene (chloroprene) was originally synthesized in 1930. The material can polymerize spontaneously to an elastomer that has good resistance to oil and weathering. Commercial production of chloroprene rubber started in 1932. Since then, many types of polymers and copolymers were developed with the trivial generic name of *neoprene*.

The monomer can be prepared from acetylene:



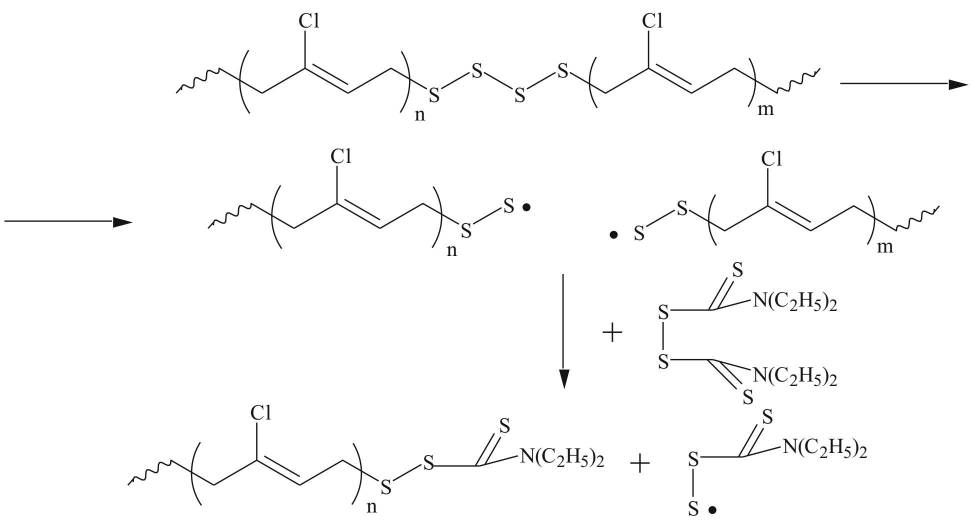
It can also be formed from butadiene.

Chloroprene is polymerized commercially by free-radical emulsion polymerization. The reaction is carried out at 40°C to a 90% conversion. A typical recipe for such an emulsion polymerization is as follows [127]:

Material	Parts
Water	150
Chloroprene	100
Rosin	4 (stabilizer)
NaOH	0.8 (stabilizer)
$K_2S_2O_8$	
Sulfur	
Methylene-bis-(Na-naphthalenesulfonic acid)	0.7

When the polymerization reaches 90% conversion, the reaction mixture is cooled to 20°C and tetraethylthiuram disulfide is added. This is done to prevent the pendant unsaturation in the polychloroprene backbones from cross-linking or forming branches. An unmodified polymer is difficult to process even at a 70% conversion. To overcome this, a sulfur–tetraethylthiuram modification is carried out.

When the product is treated with the thiuram, an exchange reaction takes place to yield a stable, thiuram-modified polymer of reduced molecular weight. It is believed that the reaction takes place through cleavage of the sulfur links, formed during polymerization in the presence of sulfur, and formation of free radicals [128]



After the reaction with tetraethylthiuram disulfide is completed, the latex is acidified with acetic acid, short of coagulation. The rubber is then recovered at a low temperature (about −15°C) in the form of sheets by deposition of the latex on cooled rotating drums [127, 128].

The polymer, formed by this technique, consists of about 85% of *trans*-1,4 units, 10% of *cis*-1,4 units, 1.5% of 1,2 units, and 1.0% of 3,4 units. The polymer is essentially linear with a molecular weight equal to approximately 100,000. The sulfur-modified polychloroprenes are sold under a trade name of Neoprene-G. An unmodified version prepared with mercaptan chain transferring agents (Neoprene W) is a polymer with a molecular weight of about 200,000 [128, 130].

Table 6.9 lists the structures of polychloroprenes that form by free-radical polymerization at different temperatures. Chloroprene polymerizes by cationic polymerization with the aid of Lewis acids in chlorinated solvents. When aluminum chloride is used in a mixture of ethyl chloride–methylene chloride solvent mixture at −80°C, the polymer has 50% 1,4 units [131, 132]. If it is polymerized with boron trifluoride, the product consists of a 50–70% 1,4-adducts. A very high *trans*-1,4 poly(2-chloro-1,3-butadiene) forms by X-ray radiation polymerization of large crystals of chloroprene at −130 to −180°C. It is 97.8% *trans*-1,4 [130]. Presumably the mechanism of polymerization is free radical.

Table 6.9 Structures of polychloroprenes formed by free-radical polymerization

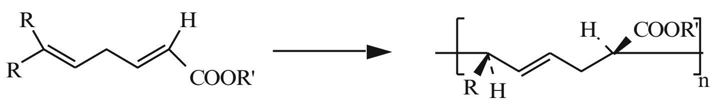
Polymerization temperature (°C)	% 1,4		% 1,2	% 3,4	References
	Cis	*Trans*			
−40	5	94	0.9	0.3	[112]
−20	6	91.5	0.7	0.5	[113]
−10	7	–	–	–	[112]
10	9	84	1.1	1.0	[112]
40	10	86, 81	1.6	1.0	[112]
40	13	88.9	0.9	0.3	[113]
100	13	71	2.4	2.4	[112]

[a] From refs. [127–132]

6.9 Special Polymers from Dienes

There are many reports in the literature of preparations of polymers from various other substituted dienes. Most have no commercial significance. Some are, however, interesting materials. An example is a polymer of 2-*t*-butyl-1,3-butadiene formed with $TiCl_4$ and either alkylaluminum or aluminum hydride catalysts [132]. The polymer is crystalline and melts at 106°C. It can be dissolved in common solvents. Based on X-ray data, the monomer placement is high *cis*-1,4.

Poly(carboxybutadiene)s also forms with coordination catalysts [133–135]:



where R = CH_3; R′ = CH_3, C_2H_5, C_4H_9, or C_6H_5.

X-ray crystallography [133–135] showed that the placement is *trans*-isotactic.

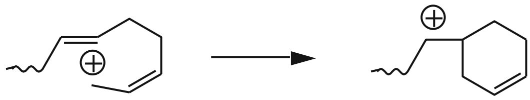
Based on the mode of packing of the chains in the crystalline regions and from the encumbrance of the side groups in relationship to the main chain, an *erythro* configuration can be assigned [134]. The polymers, therefore, are *trans-erythro*-isotactic.

Polymerization of 1,3-pentadiene can potentially result in five different insertions of the monomers. These are 1,4-*cis*, 1,4-*trans*, 1,2-*cis*, 1,2-*trans*, and 3,4. In addition, there are potentially 3-*cis*-1,4 and 3 *trans*-1,4 structures (isotactic, syndiotactic, and atactic). Formations of *trans*-1,4 isotactic, *cis*-1,4 isotactic, and *cis*-1,4 syndiotactic polymers are possible with Ziegler–Natta catalysts [136–138]. Amorphous polymers also form that are predominantly *cis*-1,4 or *trans*-1,4, but lack tactic order. Stereospecificity in poly(1,3-pentadiene) is strongly dependent upon the solvent used during the polymerization. Thus, *cis*-1,4 syndiotactic polymers form in aromatic solvents and *trans*-1,2 in aliphatic ones. The preparations require cobalt halide/aluminum alkyl dichloride(or dialkyl chloride) catalysts in combinations with Lewis bases. To form a *trans*-1,4 structure, a catalyst containing aluminum to titanium ratio close to 5 must be used [139].

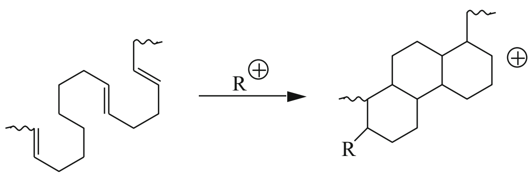
6.10 Cyclopolymerization of Conjugated Dienes

Conjugated dienes like isoprene, butadiene, and chloroprene cyclopolymerize with catalysts consisting of aluminum alkyls, like ethylaluminum dichloride, and titanium tetrachloride [141]. The ladder polymers that form contain fused cyclic structures. The products prepared in hexane are generally insoluble powders, while those prepared in aromatic solvents are soluble even when the molecular weights are high [142]. A high ratio of the transition metal halide to that of the aluminum alkyl must be used. Such a ratio might, conceivably, mean that the mechanism of polymerization is cationic. Also, conventional cationic initiators can be used to yield similar products. The cyclization occurs during propagation. Unsaturation in the products can vary from none to as high as 80%, depending upon the initiator used [142].

Different mechanisms were offered to explain the cyclization of 1,3 dienes [142, 143]. The cyclization might conceivably occur by a sequential process:



or, perhaps from attacks by the propagating carbon cation on *trans*-1,4 double bonds:



where R^+ can represent either a propagating carbon cation or an initiating species. The extensive cyclization may be a result of a sequential process [142, 143].

Cyclopolymerizations typically result in low conversions and dormant reaction mixtures. When additional monomer is added, the dormant mixtures reinitiate polymerizations that again proceed to some limited conversions. If the original dormant mixtures are allowed to stand for a long time the unreacted monomers are slowly consumed [142].

Polymerization of 2,3-dimethylbutadiene-1,3 with Ziegler–Natta catalysts consisting of $Al(i\text{-}C_4H_9)_3$–$TiCl_4$ yields *cis*-1,4-polydimethylbutadiene as described earlier. This, however, takes place when the aluminum alkyl is in excess. If, on the other hand, the ratio of Al to Ti is 1 or less, cyclic polymer forms instead. The product has reduced unsaturation and some *trans*-1,4 units in the chain [144]. A complex catalyst, consisting of $Al(i\text{-}C_4H_9)_3$–$CoCl_2$, yields polymers that are predominantly *cis*-1,4 with about 20% of 1,2 units. On the other hand, acid catalysts, like $Al(C_2H_5)Cl_2$, yield cyclic polymers [143, 144]. A polymer formed with the aid of X-ray radiation at low temperatures also contains cyclic units and some *trans*-1,4 [145]. Butadiene and isoprene also form this type of polymer at the same conditions [145].

6.11 Copolymers of Dienes

Several different elastomers, copolymers of butadiene, are produced commercially. The major ones are copolymers of butadiene with styrene and butadiene with acrylonitrile. Some terpolymers, where the third component is an unsaturated carboxylic acid, are also manufactured. Block copolymers of isoprene with styrene and butadiene with styrene are important commercial elastomers.

6.11.1 GR-S Rubber

Copolymerization of butadiene with styrene by free-radical mechanism has been explored very thoroughly [146]. The original efforts started during World War I in Germany. Subsequent work

Table 6.10 Typical recipes for preparation of butadiene–styrene rubbers by emulsion polymerization

	"Hot" process		"Cold" process	
Material	Parts	Purpose	Parts	Purpose
Butadiene	75	Comonomer	72	Comonomer
Styrene	25	Comonomer	28	Comonomer
Water	180	Carrier	180	Carrier
Fatty acid soap	5.0	Emulsifier	4.5	Emulsifier
n-Dodecyl mercaptan	0.5	Chain transferring agent	–	–
t-Dodecyl mercaptan	–	–	0.2	Chain transferring agent
Potassium persulfate	0.3	Initiator	–	–
Auxiliary surfactant	–	–	0.3	Stabilizer
Potassium chloride	–	–	0.3	Stabilizer
p-Menthane hydroperoxide	–	–	0.06	Initiator system
Ferrous sulfate	–	–	0.01	
Ethylenediamine tetraacetic acid sodium salt	–	–	0.05	
Sodiumformaldehyde sulfoxylate			0.05	

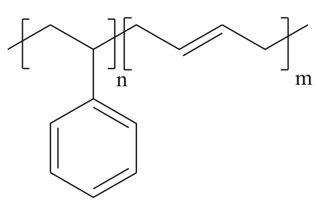
[a] From ref. [127] and other patent literature

during the 1930s was followed by a particularly strong impetus in the United States during World War II. This led to a development of GR-S rubber in the United States and Buna-S rubber in Germany. After World War II further refinements were introduced into the preparatory procedures and "cold" rubber was developed. Industrially, the copolymer is prepared by emulsion copolymerization of butadiene and styrene at low temperatures in a continuous process. A typical product is a random distribution copolymer, with the butadiene content ranging from 70 to 75%. The diene monomer placement is roughly 18% *cis*-1,4; 65% *trans*-1,4; and 17% 1,2. M_n of these copolymers is about 100,000.

A "redox" initiator is used in the cold process, but not in the "hot" one. Also, the "hot" process is carried out at about 50°C for 12 h to approximately 72% conversion. The "cold" process is also carried for 12 h, but at about 5°C to a 60% conversion. The two recipes for preparation of GR-S rubbers are shown in Table 6.10 for comparison of the "hot" and "cold" processes.

In both polymerizations, the unreacted monomer has to be removed. In the "hot" one the reaction is often quenched by addition of hydroquinone, and in the "cold" one by addition of *N*, *N*-diethyldithiocarbamate. After the monomers are steam stripped in both processes, an antioxidant like *N*-phenyl-2-naphthylamine is added. The latex is usually coagulated by addition of a sodium chloride–sulfuric acid solution. The "cold" process yields polymers with less branching than the "hot" one, slightly higher *trans* to *cis* ratios.

During the middle 1960s a series of butadiene–styrene and isoprene–styrene *block-copolymer-elastomers* were developed. These materials possess typical rubber-like properties at ambient temperatures, but act like thermoplastic resins at elevated ones. The copolymers vary from diblock structures of styrene and butadiene



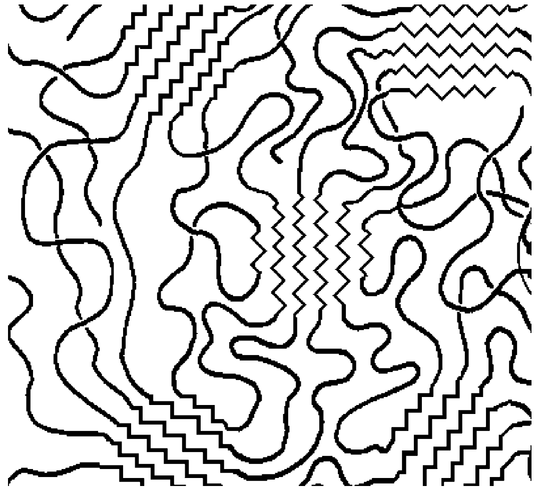
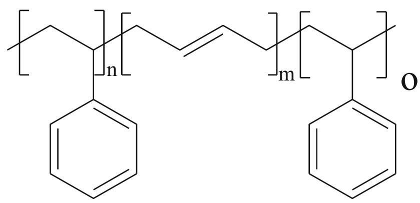


Fig. 6.4 Illustration of polystyrene and polybutadiene domains

to triblock ones, like styrene–butadiene–styrene:



A typical triblock copolymer may consist of about 150 styrene units at each end of the macromolecule and some 1,000 butadiene units in the center. The special physical properties of these block copolymers are due to inherent incompatibility of polystyrene with polybutadiene or polyisoprene blocks. Within the bulk material, there are separations and aggregations of the domains. The polystyrene domains are dispersed in continuous matrixes of the polydienes that are the major components. At ambient temperature, below the T_g of the polystyrene, these domains are rigid and immobilize the ends of the polydiene segments. In effect they serve both as filler particles and as cross-links. Above T_g of polystyrene, however, the domains are easily disrupted and the material can be processed as a thermoplastic polymer. The separation into domains is illustrated in Fig. 6.4.

These thermoplastic elastomers are prepared by anionic solution polymerization with organometallic catalysts. A typical example of such preparation is polymerization of a 75/25 mixture of butadiene/styrene in the presence of *sec*-butyllithium in a hydrocarbon–ether solvent blend. At these reaction conditions butadiene blocks form first and when all the butadiene is consumed, styrene blocks form. In other preparations, monomers are added sequentially, taking advantage of the "living" nature of these anionic polymerizations.

These block copolymers have very narrow molecular weight distributions. Also, the sizes of the blocks are restricted to narrow ranges to maintain optimum elastomeric properties.

6.11.2 GR-N Rubber

Butadiene–acrylonitrile rubbers are another group of useful synthetic elastomers. These copolymers were originally developed in Germany where they were found superior in oil resistance to the butadiene–styrene rubbers. Commercially, these materials are produced by free-radical emulsion polymerization very similarly to the butadiene–styrene copolymers. Similarly, "hot" and "cold" processes are employed. "Low," "medium," and "high" grades of solvent-resistant copolymers are formed, depending upon the amount of acrylonitrile in the copolymer that can range from 25 to 40%. The butadiene placement in these copolymers is approximately 77.5% *trans*-1,4, 12.5% *cis*-1,4, and 10% of 1,2-units. Also, the polymers formed by the "cold" process are less branched and have a narrower molecular weight distribution than those formed by the "hot" process.

An interesting alternating copolymer of butadiene and acrylonitrile was developed in Japan [147]. The copolymer is formed with coordination catalysts consisting of AlR_3, $AlCl_3$, and $VOCl_3$ in a suspension polymerization process. The product is more than 94% alternate and is reported to have very good mechanical properties and good oil resistance.

6.12 Polystyrene and Polystyrene-Like Polymers

Styrene is produced in the United States from benzene and ethylene by a Friedel–Craft reaction that is followed by dehydrogenation over alumina at 600°C. Polystyrene was first prepared in 1839, though the material was confused for an oxidation product of the styrene monomer [148]. Today polystyrene is produced in very large quantities and much is known about this material.

6.12.1 Preparation of Polystyrene by Free-Radical Mechanism

Styrene is one of those monomers that lends itself to polymerization by free-radical, cationic, anionic and coordination mechanisms. This is due to several reasons. One is resonance stabilization of the reactive polystyryl species in the transition state that lowers the activation energy of the propagation reaction. Another is the low polarity of the monomer. This facilitates attack by free-radicals, differently charged ions, and metal complexes. In addition, no side reactions that occur in ionic polymerizations of monomers with functional groups are possible. Styrene polymerizes in the dark by free-radical mechanism more slowly than it does in the presence of light [149]. Also, styrene formed in the dark is reported to have greater amount of syndiotactic placement [150]. The amount of branching in the polymer prepared by free-radical mechanism increases with temperature [136]. This also depends upon the initiator used [151].

The following information has evolved about the free-radical polymerization of styrene:

1. Styrene polymerizes thermally [151–155]. This is discussed in Chap. 3.
2. Oxygen retards polymerizations of styrene. At higher temperatures, however, the rate is accelerated due to peroxide formation [156].
3. The rate of styrene polymerizations in bulk is initially, at low conversions, first order with respect to monomer concentrations. In solution, however, it is a second order with respect to monomer [157].

Polystyrene that is manufactured by free-radical polymerization is atactic. Isotactic polystyrene formed with Ziegler–Natta catalysts was introduced commercially in the 1960s, but failed to gain acceptance. Syndiotactic polystyrene is now being produced commercially.

Industrially, free-radical styrene polymerizations are carried out in bulk, in emulsion, in solution, and in suspension. The clear plastic is generally prepared by mass polymerization. Because polystyrene is soluble in the monomer, mass polymerization, when carried out to completion, results in a tremendous increase in melt viscosity. To avoid this, when styrene is polymerized in bulk in an agitated kettle, the reaction is only carried out to 30–40% conversion. After that, the viscous syrup is transferred to another type of reactor for the completion of the reaction. According to one early

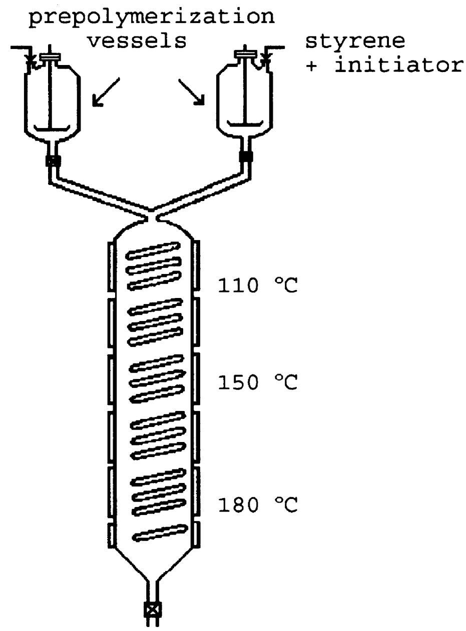


Fig. 6.5 Adiabatic tower for mass polymerization of styrene

German patent, polymerization is completed in a plate and frame filter press [157]. Water circulating through the press removes the heat of the reaction, and the solid polymer is formed inside the frames. This process is still used in some places [158].

Another approach is to use adiabatic towers. Styrene is first partially polymerized in two agitated reaction kettles at 80–100°C. The syrup solution of the polymer in the monomer is then fed continually into the towers from the top. The temperatures in the towers are gradually increased from 100–110°C at the top to 180–200°C at the bottom. By the time the material reaches the bottom, in about 3 h, the polymerization is 92–98% complete [159]. The unreacted monomer is removed and recycled. A modification of the process is to remove the monomer vapor at the top of the tower for reuse.

An improvement in the above procedure is the use of agitated towers [160]. To avoid channeling inside the towers and for better heat transfer, three towers are arranged in series. They are equipped with slow agitators and with grids of pipes for cooling and heating [160]. Polymeric melt is heated from 95 to 225°C to reduce viscosity and help heat transfer. A solvent like ethyl benzene may be added. A vacuum devolatalizer removes both monomer and solvent from the product (Fig. 6.5).

6.12.2 Polystyrene Prepared by Ionic Chain-Growth Polymerization

Much research was devoted to both cationic and anionic polymerizations. An investigation of cationic polymerization of styrene with $Al(C_2H_5)_2Cl/RCl$ (R = alkyl or aryl) catalyst/cocatalyst system was reported by Kennedy [161, 162]. The efficiency (polymerization initiation) is determined by the relative stability and/or concentration of the initiating carbocations that are provided by the cocatalyst RCl. *N*-butyl, isopropyl, and *sec*-butyl chlorides exhibit low cocatalytic efficiencies because of low tendency for ion formation. Triphenylmethyl chloride is also a poor cocatalyst because the triphenylmethyl ion that forms is more stable than the propagating styryl ion. Initiation of styrene polymerizations by carbocations is now well established [163].

Anionic polymerization of styrene with amyl sodium yields an isotactic polymer [164]. Polymerizations catalyzed by triphenylmethylpotassium also yield the same stereospecific polystyrene [165]. The same is true of organolithium compounds [166, 167].

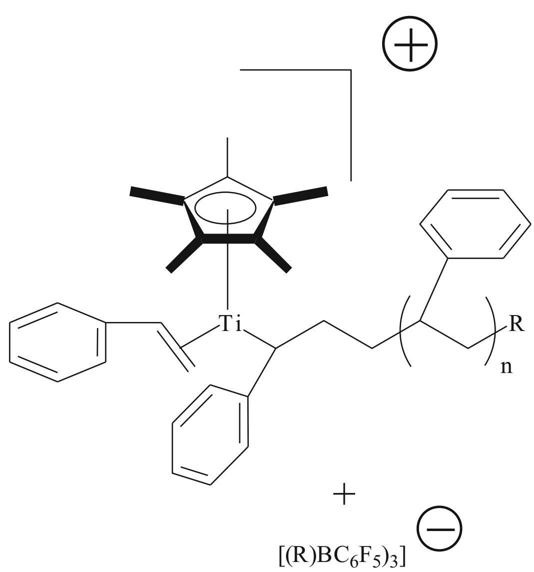
In butyllithium initiated polymerizations of styrene in benzene termination were claimed to occur by association between the propagating anions and the lithium counterions with another butyllithium molecule [168]. This was contradicted by claims that terminations result from association of two propagating chains [169]. Alfin catalysts polymerize styrene to yield stereospecific products [170].

Coordination catalysts based on aluminum alkyls and titanium halides yield isotactic polystyrene [171–174]. The polymer matches isotactic polystyrene formed with amylsodium. It is composed of head-to-tail sequences with the main chain fold being helical. There are three monomer units per each helical fold [171, 172]. The catalyst composition, however, has a strong bearing on the microstructure of the resultant polymer [175, 176].

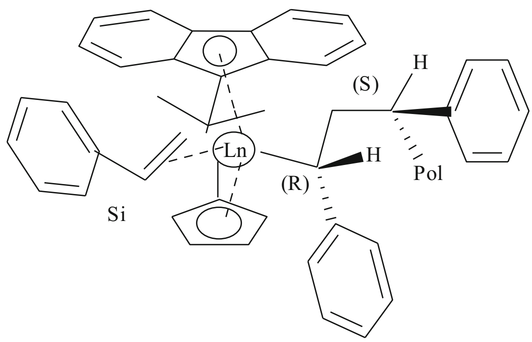
Ishihara et al. reported in 1986 that syndiotactic polystyrene can be prepared with the aid of organic or inorganic titanium compounds activated with methylaluminoxane [177]. There is much greater incentive to commercialize syndiotactic polystyrene than the isotactic one. This is because isotactic polystyrene crystallizes at a slow rate. That makes it impractical for many industrial applications. Syndiotactic polystyrene, on the other hand, crystallizes at a fast rate, has a melting point of 275°C, compared to 240°C for the isotactic one, and is suitable for use as a strong structural material.

Many catalysts were investigated for the preparation of syndiotactic polystyrene. High activity is claimed for half-sandwich titanocenes of the type $CpTiCl_3$, $IndTiCl_3$, and substituted $IndTiCl_3$ with methylaluminoxane as cocatalyst [178]. It was also reported that $BMe(C_6F_5)_3$ and other borates can be used as precursors instead of methyl-aluminoxane [178]. In addition, it was disclosed that fluorinated catalysts exhibit very high activities and produce polymers with higher molecular weight polymers [178].

The mechanism of polymerization was investigated by different groups. Grassi and Zambelli claim that the syndiotactic styrene polymerization proceeds through a secondary insertion of styrene into Ti–alkyl (or growing polymer chain) bond. In the half titanocene catalyst, the polymer chain appears to be η^6-coordinated to the metal of the active species [179]:



Maron and coworkers [180] reported that theoretical methods were used to investigate the syndiospecificity of the styrene polymerization catalyzed by single-site, single-component allyl ansa-lanthanidocenes:



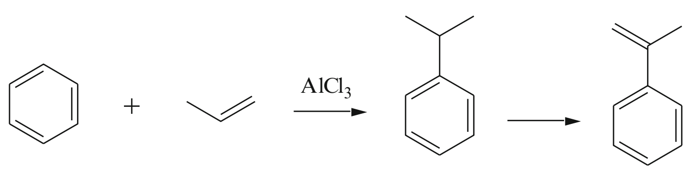
Two limiting chain end stereocontrol mechanisms were studied by them, namely, migratory insertion through a site epimerization and site stereoconfiguration independent of backside insertion on a "stationary" polymer chain. Four consecutive insertions of styrene were computed to reveal that (i) backside insertions are more favorable than, or at least as favorable as, frontside insertions. The formation of a syndiotactic polymer is controlled by the thermodynamics. Moreover, the odd (first and third) insertions are of 2,1-down-*si*-type and are kinetically favored over the 2,1-up-*re*-ones. This control is the conjunction of two effects: minimization of styrene–styrene and styrene (phenyl ring)–fluorenyl repulsions. The steric hindrance of the polymer chain induces a fourth insertion by an exocyclic coordination of the fluorenyl ligand that is compensated by the η^6 coordination of one of the phenyl ring in the growing chain.

Syndiotactic polystyrene is available commercially under the trade name of Questra. This material is produced with the aid of a metallocene catalyst and is sold in several grades [181].

There is a small interest in forming isotactic polystyrenes with vary narrow molecular weight distributions, because of some very limited practical applications, and from purely academic interests. Several preparations of virtually monodisperse polystyrenes of $M_w/M_n = 1.06$ by anionic polymerizations were developed. The materials are available commercially [181–186], small quantities for use as standards for GPC.

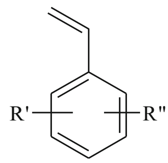
6.12.3 *Polymers from Substituted Styrenes*

Many derivatives of styrene can be readily synthesized. Some are commercially available. One of them is α-methyl styrene. It is formed from propylene and benzene by a process that is very similar to styrene preparation:

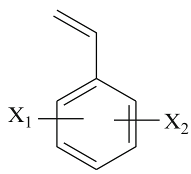


Due to the allylic nature of α-methyl styrene it cannot be polymerized by free-radical mechanism. It polymerizes readily, however, by an ionic one. Resins based on copolymers of α-methyl styrene are available commercially. Other styrene derivatives that can be obtained commercially are:

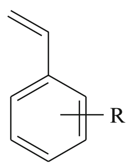
1. Alkyl or aryl substituted styrenes,



where R_1 and R_2 are alkyl or aryl groups.
2. Halogen derivatives,



where X_1 and X_2 = F, Cl, Br, or I.
3. Polar-substituted styrenes,

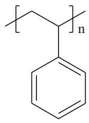
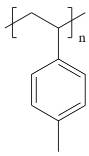
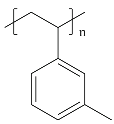
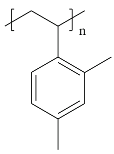
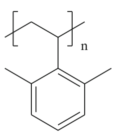
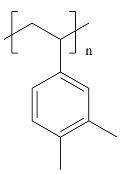
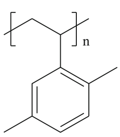
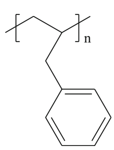
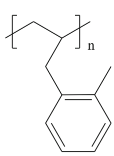


where R = CN, CHO, COOH, $OCOCH_3$, OH, OCH_3, NO_2, NH_2, and SO_3H.

Vinyl toluene polymerizes readily by free-radical mechanism at 100°C. The absolute rate at that temperature is greater than for styrene. The activation energy for vinyl toluene polymerization is 17–19 kcal per mole while that for styrene is 21 kcal mole. This monomer can also be polymerized by ionic and coordination mechanisms. Earlier attempts at polymerization of α-methyl styrene with Ziegler–Natta catalysts were not successful [187, 188]. Later, however, it was shown that polymerization does take place with $TiCl_4/Al(C_2H_5)_3$ at −78°C. The activity of the catalyst and the DP depend on the ratio of aluminum to titanium, the nature of the solvent, and on the aging of the catalyst [189]. The optimum ratio of the aluminum alkyl to titanium chloride is 1.0–1.2. Mixing and aging of the catalyst must be done below room temperature, and the valence of titanium must be maintained between 3 and 4 [189]. This led Sakurada to suggest that the reaction actually proceeds via a cationic rather than a coordinated anionic mechanism [189].

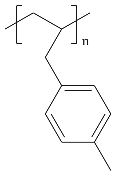
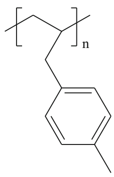
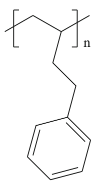
Various reports in the literature describe cationic polymerizations of α-methyl styrene with Lewis acids [190–192]. The products are mostly low molecular weight polymers, some containing unsaturation with pendant phenylindane groups. A high molecular weight polymer can be prepared from α-methyl styrene by cationic polymerization at −90 to −130°C with $AlCl_3$ in ethyl chloride or in carbon disulfide [193]. The product has a narrow molecular weight distribution. Some T_g and T_m values of polystyrene-like materials, including isotactic polystyrene, are presented in Table 6.11.

Table 6.11 Transition temperatures of poly(phenylene alkene)s

Polymer	T_g (°C)	References	T_m (°C)	References
	80	[178]	(i) 240; (s) 272	[178]
	73.81	[178]	Amorphous	[176]
	77	[178]	219	[176]
	92	[178]	310	[176]
	123	[178]	330	[176]
	91	[178]	240	[176]
	84	[177]	290	[176]
	60	[177]	207–208	[176]
	80	[177]	2	[177]

(continued)

Table 6.11 (continued)

Polymer	T_g (°C)	References	T_m (°C)	References
	34–40	[177]	180	[177]
	60–65	[177]	240	[177]
	10	[177]	162–168	[177]

[a] From refs. [196–198]

6.13 Copolymers of Styrene

Many copolymers of styrene are manufactured on a large commercial scale. Because styrene copolymerizes readily with many other monomers, it is possible to obtain a wide distribution of properties. Random copolymers form quite readily by free-radical mechanism [185, 194]. Some can also be formed by ionic mechanism. In addition, graft and block copolymers of styrene are also among commercially important materials.

Most comonomers differ from styrene in polarity and reactivity. A desired copolymer composition can be achieved, however, through utilization of copolymerization parameters based on kinetic data and on quantum-chemical considerations. This is done industrially in preparations of styrene–acrylonitrile, styrene–methyl methacrylate, and styrene–maleic anhydride copolymers of different compositions.

6.13.1 High-Impact Polystyrene

For many applications, the homopolymer of styrene is too brittle. To overcome that, many different approaches were originally tried. These included use of high molecular weight polymers, use of plasticizers, fillers (glass fiber, wood flour, etc.), deliberate orientation of the polymeric chains, copolymerization and addition of rubbery substances. Effect of plasticizers is too severe for practical use, and use of high molecular weight polymers exhibits only marginal improvement. Use of fillers, though beneficial, is mostly confined to United States. Orientation is limited to sheets and filaments, and copolymerization usually lowers the softening point too much.

Addition of rubbery materials, however, does improve the impact resistance of polystyrene. This is done, therefore, extensively. The most common rubbers used for this purpose are butadiene–styrene copolymers. Some butadiene homopolymers are also used but to a lesser extent. The high-impact polystyrene is presently prepared by dissolving the rubber in a styrene monomer and then polymerizing the styrene. This polymerization is either done in bulk or in suspension. The product contains styrene–butadiene rubber, styrene homopolymer, and a considerable portion of styrene-graft copolymer that forms when polystyrene radicals attack the rubber molecules. The product has very enhanced impact resistance.

Past practices, however, consisted simply in blending a mixture of polystyrene and rubber on a two-roll mill, or in a high shear internal mixer, or passing through an extruder. The impact strength of the product was only moderately better than that of the unmodified polymer. Another procedure was to blend polystyrene emulsion latex with a styrene–butadiene rubber emulsion latex and then to coagulate the two together. The product is also only marginally better in impact strength than styrene homopolymer. This practice, however, may still be in existence in some places.

In high-impact polystyrene, the rubber exists in discrete droplets, less than 50 μm in diameter. In effect the polymerization serves to form an oil in oil emulsion [199] where the polystyrene is in the continuous phase and the rubber is in a dispersed phase. The graft copolymer that forms serves to "emulsify" this heterogeneous polymer solution [200].

Commercial high-impact polystyrene usually contains 5–20% styrene–butadiene rubber. The particle size ranges from 1 to 10 μm. High-impact polystyrene may have as much as seven times the impact strength of polystyrene, but it has only half its tensile strength, lower hardness, and lower softening point.

6.13.2 ABS Resins

Styrene–acrylonitrile copolymers are produced commercially for use as structural plastics. The typical acrylonitrile content in such resins is between 20 and 30%. These materials have better solvent and oil resistance than polystyrene and a higher softening point. In addition, they exhibit better resistance to cracking and crazing and an enhanced impact strength. Although the acrylonitrile copolymers have enhanced properties over polystyrene, they are still inadequate for many applications. Acrylonitrile–butadiene–styrene polymers, known as ABS resins, were therefore developed.

Although ABS resins can potentially be produced in a variety of ways, there are only two main processes. In one of them acrylonitrile–styrene copolymer is blended with a butadiene–acrylonitrile rubber. In the other one, interpolymers are formed of polybutadiene with styrene and acrylonitrile.

In the first one, the two materials are blended on a rubber mill or in an internal mixer. Blending of the two materials can also be achieved by combining emulsion latexes of the two materials together and then coagulating the mixture. Peroxide must be added to the blends in order to achieve some - cross-linking of the elastomer to attain optimum properties. A wide range of blends are made by this technique with various properties [201]. Most common commercial blends of ABS resins may contain 70 parts of styrene–acrylonitrile copolymer (70/30) and 40 parts of butadiene–nitrile rubber (65/35).

In the second process, styrene and acrylonitrile are copolymerized in the presence of polybutadiene latex. The product is a mixture of butadiene homopolymer and a graft copolymer.

6.13.3 Copolymers of Styrene with Maleic Anhydride

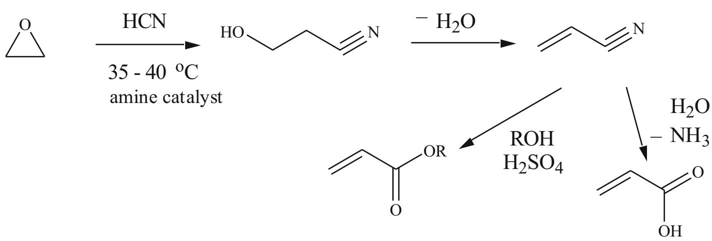
Many styrene–maleic anhydride copolymers are produced commercially for special uses. These are formed by free-radical copolymerization and many commercial grades are partially esterified. Molecular weights of such polymers may range from 1,500 to 50,000, depending upon the source. The melting points of these copolymers can vary from 110 to 220°C, depending upon molecular weight, degree of hydrolysis and esterification, and also the ratio of styrene to maleic anhydride.

Only a small percent of styrene copolymers reported in the literature achieved industrial importance. Some of the interesting copolymers of styrene that were reported but not utilized commercially are copolymers with various unsaturated nitriles. This includes vinylidene cyanide, fumaronitrile, malononitrile, methacrylonitrile, acrylonitrile, and cinnamonitrile [292]. Often, copolymerization of styrene with nitriles yields copolymers with higher heat distortion temperature, higher tensiles, better craze resistance, and higher percent elongation.

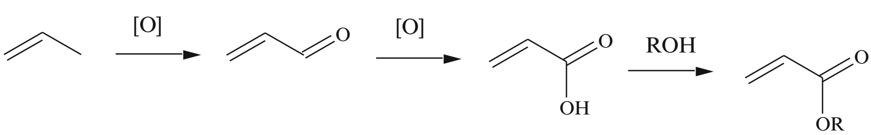
Styrene was also copolymerized with many acrylic and methacrylic esters. Products with better weathering properties often form. Copolymerization with some acrylates lowers the value of T_g [203].

6.14 Polymers of Acrylic and Methacrylic Esters

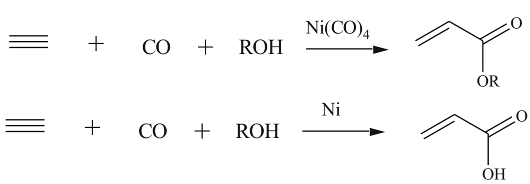
There are many synthetic procedures for preparing acrylic acid and its esters. One way, used early, is to make acrylic esters from ethylene oxide:



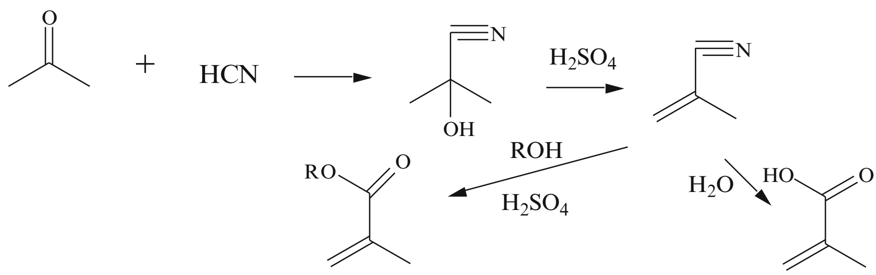
Another route is through oxidation of propylene over cobalt molybdenum catalyst at 400–500°C:



Many industrial preparations start with acetylene, carbon monoxide, and alcohol or water:



One route to α-methyl acrylic acid (or methacrylic acid) and its esters is by a cyanohydrin reaction of acetone:

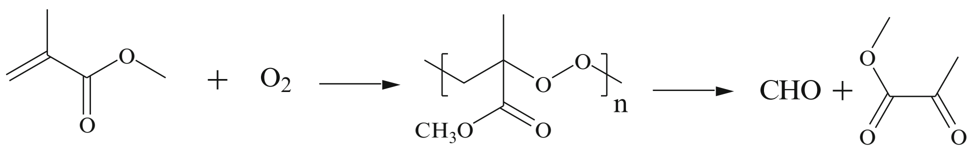


6.14.1 *Polymerizations of Acrylic and Methacrylic Esters*

Free-radical bulk polymerizations of acrylate esters exhibit rapid rate accelerations at low conversions. This often results in formation of some very high molecular weight polymer and some cross-linked material. The cross-linking is a result of chain transferring by abstractions of labile tertiary hydrogens from already formed "dead" polymeric chains [204]. Eventually, termination by combination of the branched radicals leads to cross-linked structures. Addition of chain transferring agents, like mercaptans (that reduces the length of the primary chains), helps prevent gel formation. There are no labile tertiary hydrogens in methacrylic esters. The growing methacrylate radicals are still capable of abstracting hydrogens from the α-methyl groups. Such abstractions, however, require more energy and are not an important problem in polymerizations of methacrylic esters [205]. Nevertheless, occasional formation of cross-linked poly(alkyl methacrylate)s does occur. This is due to chain transferring to the alcohol moiety [206, 210].

The termination reaction in free-radical polymerizations of the esters of acrylic and methacrylic acids takes place by recombination and by disproportionation [206, 207]. Methyl methacrylate polymerizations, however, terminate at 25°C predominantly by disproportionation [205].

Oxygen inhibits free-radical polymerization of α-methyl methacrylate [208]. The reaction with oxygen results in formation of low molecular weight polymeric peroxides that subsequently decompose to formaldehyde and methyl pyruvate [210]:



Oxygen is less effective in inhibiting polymerizations of acrylic esters. It reacts 400 times faster with the methacrylic radicals than with the acrylic ones. Nevertheless, even small quantities of oxygen affect polymerization rates of acrylic esters [216]. This includes photopolymerizations of gaseous ethyl acrylate that are affected by oxygen and by moisture [217].

Acrylic and methacrylic esters polymerize by free-radical mechanism to atactic polymers. The sizes of the alcohol portions of the esters determine the T_g values of the resultant polymers. They also determine the solubility of the resultant polymers in hydrocarbon solvents and in oils.

Solvents influence the rate of free-radical homopolymerization acrylic acid and its copolymerization with other monomers. Hydrogen bonding solvents slow down the reaction rates [219]. Due to electron withdrawing nature of the ester groups, acrylic and methacrylic ester polymerize by anionic but not by cationic mechanisms. Lithium alkyls are very effective initiators of α-methyl methacrylate polymerization yielding stereospecific polymers [213]. Isotactic poly(methyl methacrylate) forms in hydrocarbon solvents [214]. Block copolymers of isotactic and syndiotactic poly(methyl methacrylate) form in solvents of medium polarity. Syndiotactic polymers form in polar solvents, like ethylene glycol dimethyl ether, or pyridine. This solvent influence is related to Lewis basicity [215] in the following order:

$$\text{tetrahydrofuran} > \text{tetrahydropyran} > \text{dioxane} > \text{diethyl ether}$$

Furthermore, polymerizations in solvating media, like ethylene glycol dimethyl ether, tetrahydrofuran, or pyridine, using biphenylsodium or biphenyllithium yield virtually monodisperse syndiotactic poly(methyl methacrylate) [216].

The nature of the counterion in anionic polymerizations of methyl methacrylate in liquid ammonia with alkali metal amide or alkali earth metal amide catalysts is an important variable [217]. Lithium and calcium amides yield high molecular weight polymers, though the reactions tend to be slow. Sodium amide, on the other hand, yields rapid polymerizations but low molecular weight polymers. Polymers formed with sodium amide, however, have a narrower molecular weight distribution than those obtained with lithium and calcium amides. Calcium amide also yields high molecular weight polymers from ethyl acrylate and methyl methacrylate monomers in aromatic and aliphatic solvents at temperatures from −8 to 110°C. When, however, tetrahydrofuran or acetonitrile is used as solvents much lower molecular weight products form [218].

Products from anionic polymerizations of methyl methacrylate catalyzed by Grignard reagents (RMgX) vary with the nature of the R and X groups, the reaction temperature, and the nature of the solvent [219–221]. Secondary alkyl Grignard reagents give the highest yields and the fastest rates of the reactions. Isotacticity of the products increases with the temperature. When anion-radicals from alkali metal ketyls of benzophenone initiate polymerizations of methyl methacrylate, amorphous polymers form at temperatures from −78 to +65°C [222].

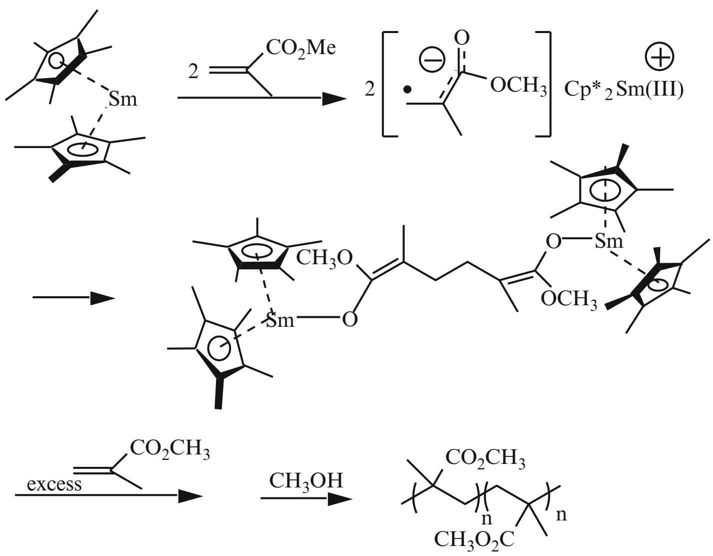
Sodium dispersions in hexane yield syndiotactic poly(methyl methacrylate) [223]. A 60–65% conversion is obtained over a 24-h period at a reaction temperature of 20–25°C. Lithium dispersions [224], butyllithium [203], and Grignard reagents [225, 226] yield crystalline isotactic poly(*t*-butyl acrylate). The reactions take place in bulk and in hydrocarbon solvents. Isotactic poly(isopropyl acrylate) forms with Grignard reagents [226, 227].

Coordination polymerizations of methyl methacrylate with diethyliron–bipyridyl complex in nonpolar solvents like benzene or toluene yield stereoblock polymers. In polar solvents, however, like dimethylformamide or acetonitrile, the products are rich in isotactic placement [229].

There are many reports in the literature on polymerizations of acrylic and methacrylic esters with Ziegler–Natta catalysts [230–233]. The molecular weights of the products, the microstructures, and rates of the polymerizations depend upon the metal alkyl and the transition metal salt used. The ratios of the catalyst components to each other are also important [234, 235].

In 1992 Yasuda et al. [236, 237] reported that organolanthanide complexes of the type $Cp^*{}_2Sm$-R (where Cp* is pentamethyl cyclopentadienyl, and R is either an alkyl, alkylaluminum or a hydride) initiate highly syndiotactic, living polymerizations of methacrylates. It was also reported that lanthanide complexes such as $Cp^*{}_2Yb(THF)_{1–3}$, $Cp^*{}_2Sm(THF)_2$, and $(indenyl)_2Yb(THF)_2$ can also initiate polymerizations of methylmethacrylate [238]. Although very low initiator efficiencies were observed, these were living polymerizations. The polymers that formed had the dispersity of 1.1 and were high in syndiotactic sequences.

Novak and Boffa, in studying lanthanide complexes, observed an unusual facile organometallic electron transfer process takes place that generates in situ bimetallic lanthanide(III) initiators for polymerizations of methacrylates [239]. They concluded that methyl methacrylate polymerizations initiated by the Cp^*_2Sm complexes occur through reductive dimerizations of methyl methacrylate molecules to form "bisinitiators" that consists of two samarium(III) enolates joined through their double bond terminally [239]. Their conclusion is based on the tendency of Cp^*_2Sm complexes to reductively couple unsaturated molecules:

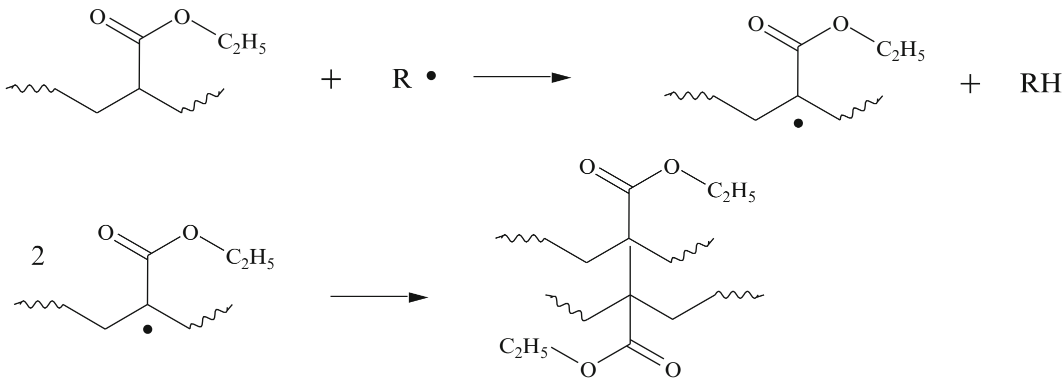


Montei and coworkers [240] reported that Nickel complexes [(X,O)NiR(PPh_3)] (X = N or P), designed for the polymerization of ethylene, are effective for home- and copolymerization of butyl acrylate, methyl methacrylate, and styrene. Their role as radical initiators was demonstrated from the calculation of the copolymerization reactivity ratios. It was shown that the efficiency of the radical initiation is improved by the addition of PPh_3 to the nickel complexes as well as by increasing the temperature. The dual role of nickel complex as radical initiators and catalysts was exploited to succeed in the copolymerization of ethylene with butyl acrylate and methyl methacrylate.

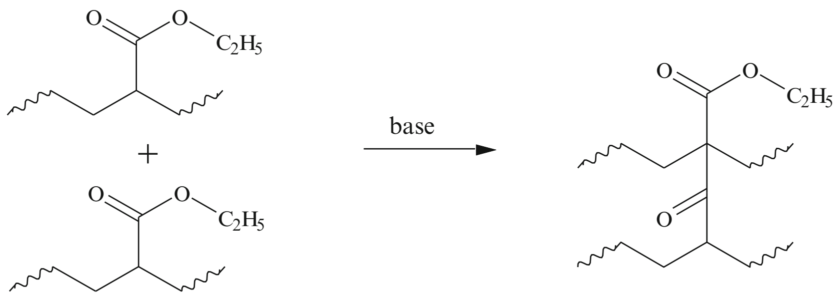
Multiblock copolymers containing sequences of both ethylene and polar monomers were thus prepared.

6.14.2 Acrylic Elastomers

Polymers of lower *n*-alkyl acrylates are used commercially to only a limited extent. Ethyl and butyl acrylates are, however, major components of ***acrylic elastomers***. The polymers are usually formed by free-radical emulsion polymerization. Because acrylate esters are sensitive to hydrolysis under basic conditions, the polymerizations are usually conducted at neutral or acidic pH. The acrylic rubbers, like other elastomers must be cross-linked or ***vulcanized*** to obtain optimum properties. Cross-linking can be accomplished by reactions with peroxides through abstractions of tertiary hydrogens with free radicals:



Another way to cross-link acrylic elastomers is through a Claisen condensation:



The above illustrated cross-linking reactions of homopolymers, however, form elastomers with poor aging properties. Commercial acrylic rubbers are, therefore, copolymers of ethyl or butyl acrylate with small quantities of comonomers that carry special functional groups for cross-linking. Such comonomers are 2-chloroethylvinyl ether or vinyl chloroacetate, used in small quantities (about 5%). These copolymers cross-link through reactions with polyamines.

6.14.3 Thermoplastic and Thermoset Acrylic Resins

Among methacrylic ester polymers, poly(methyl methacrylate) is the most important one industrially. Most of it is prepared by free-radical polymerizations of the monomer and a great deal of these polymerizations are carried out in bulk. Typical methods of preparation of clear sheets and rods consist of initial partial polymerizations in reaction kettles at about 90°C with peroxide initiators. This is done by heating and stirring for about 10 min to form syrups. The products are cooled to room

Table 6.12 Typical components of thermoset acrylic resins

Monomers that contribute rigidity	Flexibilizing monomers	Monomers used for cross-linking
Methyl methacrylate	Ethyl acrylate	Acrylic acid
Ethyl methacrylate	Isopropyl acrylate	Methacrylic acid
Styrene	Butyl acrylate	Hydroxyethyl acrylate
Vinyl toluene	*i*-Octyl acrylate	Hydroxypropyl acrylate
Acrylonitrile	Decyl acrylate	Glycidyl acrylate
Methacrylonitrile	Lauryl methacrylate	Glycidyl methacrylate
		Acrylamide
		Aminoethyl acrylate

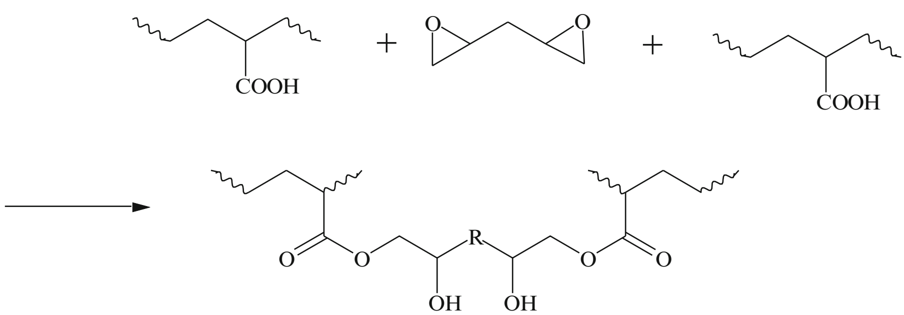
temperature and various additives may be added. The syrups are solutions of about 20% polymer dissolved in the monomer. They are poured into casting cells where the polymerizations are completed. The final polymers are high in molecular weight, about 1,000,000.

Poly(methyl methacrylate) intended for surface coatings is prepared by solution polymerization. The molecular weights of the polymers are about 90,000 and the reaction products that are 40–60% solutions are often used directly in coatings.

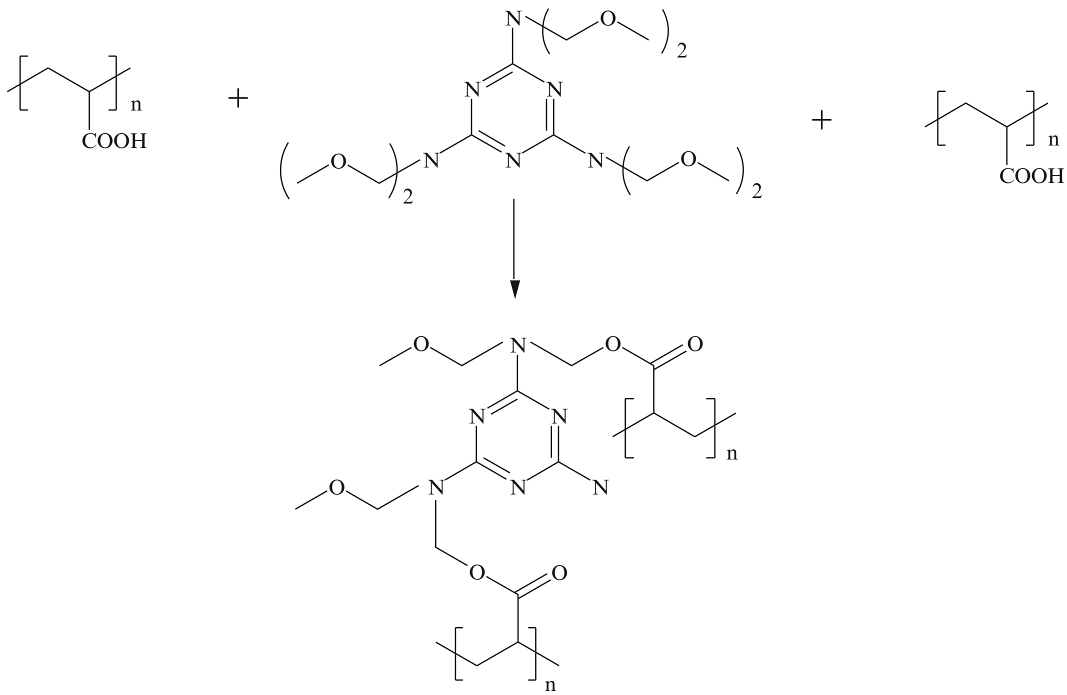
A certain amount of poly(methyl methacrylate) is also prepared by suspension polymerization. The molecular weights of these polymers are about 60,000 and they are used in injection molding and extrusion.

Thermosetting acrylic resins are used widely in surface coatings. Both acrylic and methacrylic esters are utilized and the term is applied to both of them. Often such resins are terpolymers or even tetra polymers where each monomer is chosen for a special function [214]. One is selected for rigidity, surface hardness, and scratch resistance; another for the ability to flexibilize the film, and the third one for cross-linking it. In addition, not all comonomers are necessarily acrylic or methacrylic esters or acids. For instance, among the monomers that may be chosen for rigidity may be methyl methacrylate. On the other hand, it may be styrene instead, or vinyl toluene, etc. The same is true of the other components. Table 6.12 illustrates some common components that can be found in thermoset acrylic resins.

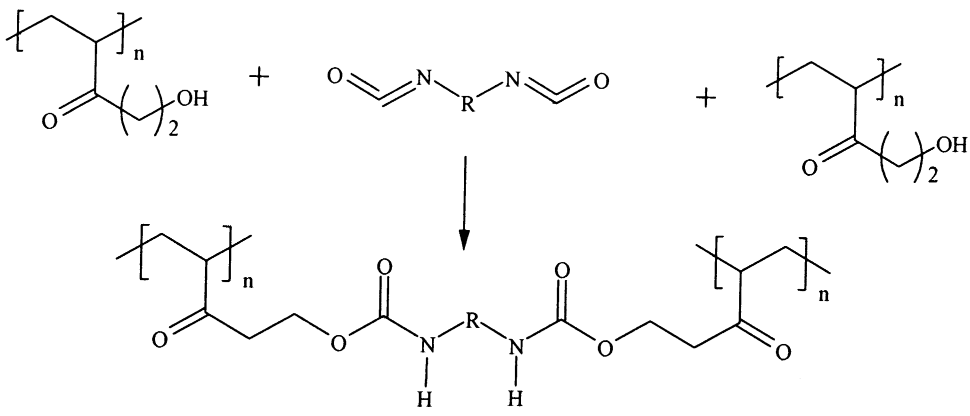
The choice of the cross-linking reaction may depend upon desired application. It may also simply depend upon price, or a particular company that manufactures the resin, or simply to overcome patent restrictions. Some common cross-linking reactions will be illustrated in the remaining portion of this section. If the functional groups are carboxylic acids in the copolymer or terpolymer, cross-linking can be accomplished by adding a diepoxide.



Other reactions can also cross-link resins with pendant carboxylic acid groups. For instance, one can add a melamine formaldehyde condensate:

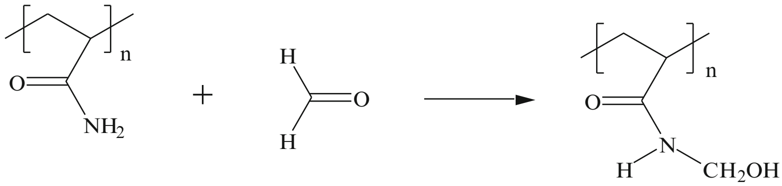


A diisocyanate, a phenolic, or a melamine–formaldehyde resin can be used as well. Resins with pendant hydroxyl groups can also be cross-linked by these materials. A diisocyanate is effective in forming urethane linkages:



When the pendant groups are epoxides, like glycidyl esters, cross-linking can be carried out with dianhydrides or with compounds containing two or more carboxylic acid groups [241]. Aminoplast resins (urea–formaldehyde or melamine–formaldehyde and similar ones) are also very effective [242].

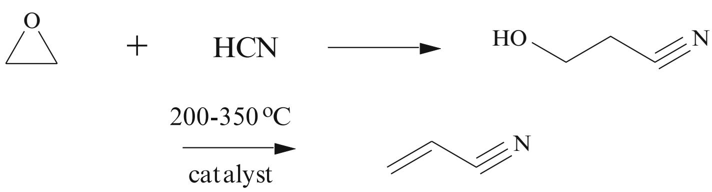
Pendant amide groups from terpolymers containing acrylamide can be reacted with formaldehyde to form methylol groups for cross-linking [243]:



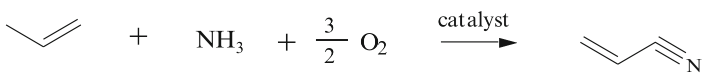
The product of the above reaction can be thermoset like any urea–formaldehyde resin (see Chaps. 7 and 9). Many cross-linking routes are described in the patent literature, because there are many different functional groups available.

6.15 Acrylonitrile and Methacrylonitrile Polymers

Polymers from acrylonitrile are used in synthetic fibers, in elastomers, and in plastic materials. The monomer can be formed by dehydration of ethylene cyanohydrin:

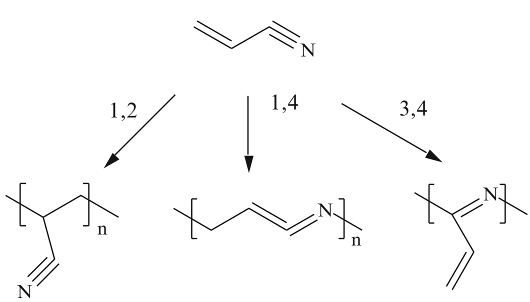


Other commercial processes exist, like condensation of acetylene with hydrogen cyanide, or ammoxidation of propylene:



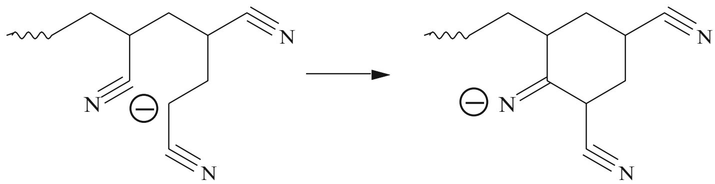
Acrylonitrile polymerizes readily by free-radical mechanism. Oxygen acts as a strong inhibitor. When the polymerization is carried out in bulk, the reaction is autocatalytic [242, 243]. In solvents, like dimethylformamide, however, the rate is proportional to the square root of the monomer concentration [242]. The homopolymer is insoluble in the monomer and in many solvents.

Acrylonitrile polymerizes also by anionic mechanism. There are many reports in the literature of polymerizations initiated by various bases. These are alkali metal alkoxides [246], butyllithium [247, 248], metal ketyls [249, 250], solutions of alkali metals in ethers [251, 252], sodium malonic esters [232], and others. The propagation reaction is quite sensitive to termination by proton donors. This requires use of aprotic solvents. The products, however, are often insoluble in such solvents. In addition, there is a tendency for the polymer to be yellow. This is due to some propagation taking place by 1,4 and by 3,4 insertion in addition to the 1,2 placement [253, 254]:



Another disadvantage of anionic polymerization of acrylonitrile is formation of cyanoethylate as a side reaction. It can be overcome, however, by running the reaction at low temperatures. An example is polymerizations initiated by KCN at −50°C in dimethylformamide [254], or by butyllithium in toluene at −78°C [255]. Both polymerizations yield white, high molecular weight products that are free from cyanoethylation.

It was suggested that the terminations in anionic polymerizations of acrylonitrile proceed by proton transfer from the monomer. This, however, depends upon catalyst concentrations [256, 257]. At low concentrations, the terminations can apparently occur by a cyclization reaction [257] instead:



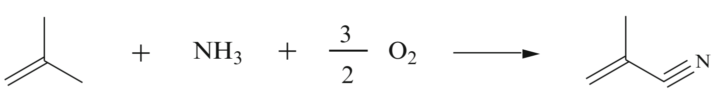
Industrially, polyacrylonitrile homopolymers and copolymers are prepared mainly by free-radical mechanism. The reactions are often conducted at low temperatures, in aqueous systems, either in emulsions or in suspensions, using redox initiation. Colorless, high molecular weight materials form. Bulk polymerizations are difficult to control on a large scale.

Over half the polymer that is prepared industrially is for use in textiles. Most of these are copolymers containing about 10% of a comonomer. The comonomers can be methyl methacrylate, vinyl acetate, or 2-vinylpyridine. The purpose of comonomers is to make the fibers more dyeable. Polymerizations in solution offer an advantage of direct fiber spinning.

Polyacrylonitrile copolymers are also used in barrier resins for packaging. One such resin contains at least 70% acrylonitrile and often methyl acrylate as the comonomer. The material has poor impact resistance and in one industrial process the copolymer is prepared in the presence of about 10% butadiene–acrylonitrile rubber by emulsion polymerization. The product contains some graft copolymer and some polymer blend. In another process the impact resistance of the copolymer is improved by biaxial orientation. The package, however, may have a tendency to shrink at elevated temperature, because the copolymer does not crystallize.

It is possible to form clear transparent polyacrylonitrile plastic shapes by a special bulk polymerization technique [258, 259]. The reaction is initiated with *p*-toluenesulfinic acid–hydrogen peroxide. Initially, heterogeneous polymerizations take place. They are followed by spontaneous transformations, at high conversion, to homogeneous, transparent polyacrylonitrile plastics [260]. A major condition for forming transparent solid polymer is continuous supply of monomer to fill the gaps formed by volume contraction during the polymerization process [261].

Methacrylonitrile, $CH_2{=}C(CH_3)CN$, can also be prepared by several routes. Some commercial processes are based on acetone cyanohydrin intermediate and others on dehydrogenation (or oxydehydrogenation) of isobutyronitrile. It is also prepared from isobutylene by ammoxidation:



Just like acrylonitrile, methacrylonitrile does not polymerize thermally but polymerizes readily in the presence of free-radical initiators. Unlike polyacrylonitrile, polymethacrylonitrile is soluble in some ketone solvents. Bulk polymerizations of methacrylonitrile have the disadvantage of long reaction time. The rate, however, accelerates with temperature. The polymer is soluble in the monomer at ambient conditions [262].

Emulsion polymerization of methacrylonitrile is a convenient way to form high molecular weight polymers. With proper choices of emulsifiers, the rates may be increased by increasing the numbers of particles in the latexes. At a constant rate of initiation, the degree of polymerization of methacrylonitrile increases rather than decreases as the rate of polymerization rises [263].

Methacrylonitrile polymerizes readily in inert solvents. The polymer, depending on the initiator and on reaction conditions, is either amorphous or crystalline. Polymerizations take place over a broad range of temperatures from ambient to −5°C, when initiated by Grignard reagents, triphenyl ethylsodium, or sodium in liquid ammonia [264]. The properties of these polymers are essentially the same as those of the polymers formed by free-radical mechanism.

The homopolymer, prepared by polymerization in liquid ammonia with sodium initiator at −77°C, is insoluble in acetone, but it is soluble in dimethylformamide [265]. When it is formed with lithium in liquid ammonia, at −75°C, the molecular weight of the product increases with monomer concentration and decreases with initiator concentration. If, however, potassium initiates the reaction rather than lithium, the molecular weight is independent of the monomer concentration [266, 267]. Polymethacrylonitrile prepared with *n*-butyllithium in toluene or in dioxane is crystalline and insoluble in solvents like acetone [268]. When polymerized in petroleum ether with *n*-butyllithium, methacrylonitrile forms a living polymer [269]. Highly crystalline polymethacrylonitrile can also be prepared with beryllium and magnesium alkyls in toluene over a wide range of temperatures.

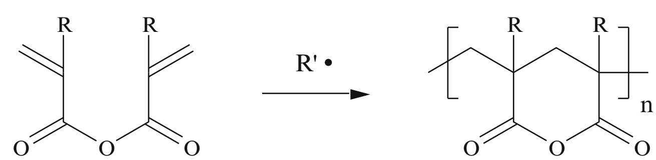
6.16 Polyacrylamide, Poly(acrylic acid), and Poly(methacrylic acid)

Commercially, acrylamide is formed from acrylonitrile by reaction with water. Similarly, the preferred commercial route to methacrylamide is through methacrylonitrile. Acrylamide polymerizes by free-radical mechanism [270]. Water is the common solvent for acrylamide and methacrylamide polymerizations because the polymers precipitate out from organic solvents.

Crystalline polyacrylamide forms with metal alkyls in hydrocarbon solvents by anionic mechanism [271]. The product is insoluble in water and in dimethylformamide.

Both acrylic and methacrylic acids can be converted to anhydrides and acid chlorides. The acids polymerize in aqueous systems by free-radical mechanism. Polymerizations of these monomers in nonpolar solvents like benzene result in precipitations of the products.

Polymerizations of anhydrides proceed by inter- and intramolecular propagations [272]:



where R = H, CH_3.

The above shown cyclopolymerizations produce soluble polymers rather than gels.

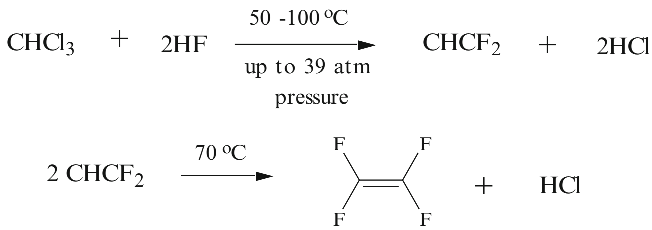
The *acid chlorides* of both acrylic and methacrylic acids polymerize by free-radical mechanism in dry aromatic and aliphatic solvents. Molecular weights of the products, however, are low, usually under 10,000 [273, 274]. Polyacrylic and polymethacrylic acids are used industrially as thickeners in cosmetics, as flocculating agents, and when copolymerized with divinyl benzene in ion-exchange resins.

6.17 Halogen-Bearing Polymers

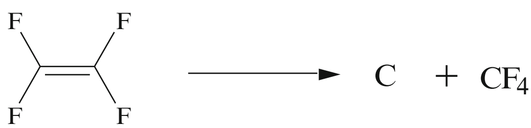
The volume of commercial fluorine-containing polymers is not large when compared with other polymers like, for instance, poly(vinyl chloride). Fluoropolymers, however, are required in many important applications. The main monomers are tetrafluoroethylene, trifluorochloroethylene, vinyl fluoride, vinylidine fluoride, and hexafluoropropylene.

6.17.1 Polytetrafluoroethylene

This monomer can be prepared from chloroform [275]:



Tetrafluoroethylene boils at $-76.3°C$. It is not the only product from the above pyrolytic reaction of difluorochloromethane. Other fluorine by-products form as well and the monomer must be isolated. The monomer polymerizes in water at moderate pressures by free-radical mechanism. Various initiators appear effective [276]. Redox initiation is preferred. The polymerization reaction is strongly exothermic, and water helps dissipate the high heat of the reaction. A runaway, uncontrolled polymerization can lead to explosive decomposition of the monomer to carbon and carbon tetrafluoride [277]:



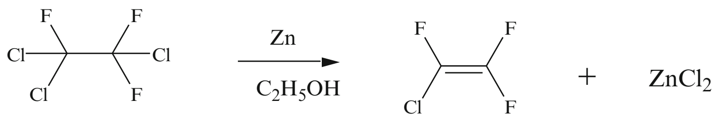
Polytetrafluoroethylene is linear and highly crystalline [278]. Absence of terminal $CF_2 = CF$-- groups shows that few, if any, polymerization terminations occur by disproportionation but probably all take place by combination [279]. The molecular weights of commercially available polymers range from 39,000 to 9,000,000. Polytetrafluoroethylene is inert to many chemical attacks and is only swollen by fluorocarbon oils at temperatures above 300°C. The T_m of this polymer is 327°C and the T_g is below $-100°C$.

The physical properties of polytetrafluoroethylene depend upon crystallinity and on the molecular weight of the polymer. Two crystalline forms are known. In both cases the chains assume helical arrangements to fit into the crystalloids. One such arrangement has 15 CF_2 groups per turn and the other has 13.

Polytetrafluoroethylene does not flow even above its melting point. This is attributed to restricted rotation around the C–C bonds and to high molecular weights. The stiffness of the solid polymer is also attributed to restricted rotation. The polymer exhibits high thermal stability and retains its physical properties over a wide range of temperatures. The loss of strength occurs at about the crystalline melting point. It is possible to use the material for long periods at 300°C without any significant loss of its strength.

6.17.2 Polychlorotrifluoroethylene

The monomer can be prepared by dechlorination of trichlorotrifluoroethane with zinc dust and ethanol.

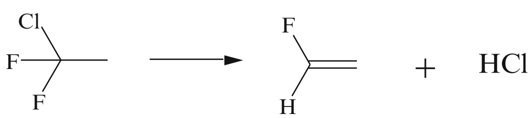


It is a toxic gas that boils at −26.8°C. Polymerization of chlorotrifluoroethylene is usually carried out commercially by free-radical suspension polymerization. Reaction temperatures are kept between 0 and 40°C to obtain a high molecular weight product. A redox initiation based on reactions of persulfate, bisulfite, and ferrous ions is often used. Commercial polymers range in molecular weights from 50,000 to 500,000.

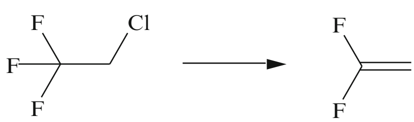
Polychlorotrifluoroethylene exhibits greater strength, hardness, and creep resistance than does polytetrafluoroethylene. Due to the presence of chlorine atoms in the chains, however, packing cannot be as tight as in polytetrafluoroethylene, and it melts at a lower temperature. The melting point is 214°C. The degree of crystallinity varies from 30 to 85%, depending upon the thermal history of the polymer. Polytrifluorochloroethylene is soluble in certain chloro fluoro compounds above 100°C. It flows above its melting point. The chemical resistance of this material is good, but inferior to polytetrafluoroethylene.

6.17.3 Poly(vinylidine fluoride)

The monomer can be prepared by dehydrochlorination of 1,1,1-chlorodifluoroethane:



or by dechlorination of 1,2-dichloro-1,1-difluoroethane [280]:



Vinylidine fluoride boils at −84°C. The monomer is polymerized in aqueous systems under pressure. Details of the process, however, are kept as trade secrets. Two different molecular weight materials are available commercially, 300,000 and 6,000,000. Poly(vinylidine fluoride) is crystalline and melts at 171°C. The material exhibits fair resistance to solvents and chemicals, but is inferior to polytetrafluoroethylene and to polytrifluorochloroethylene.

6.17.4 Poly(vinyl fluoride)

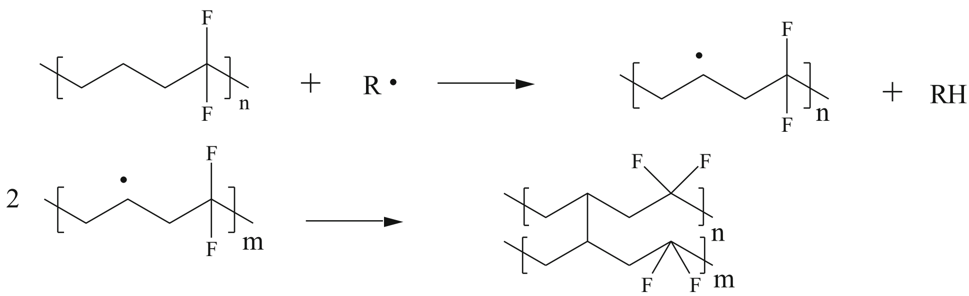
Vinyl fluoride monomer can be prepared by addition of HF to acetylene. The monomer is a gas at room temperature and boils at −72.2°C. Commercially, vinyl fluoride is polymerized in aqueous medium using either redox initiation or one from thermal decomposition of peroxides. Pressures of up to 1,000 atm may be used. Radicals generated at temperatures between 50 and 100°C yield very high molecular weight polymers.

Poly(vinyl fluoride) is moderately crystalline. The crystal melting point, T_m, is approximately 200°C. The high molecular weight polymers dissolve in dimethylformamide and in tetramethyl urea at temperatures above 100°C. The polymer is very resistant to hydrolytic attack. It does, however, loose HF at elevated temperatures.

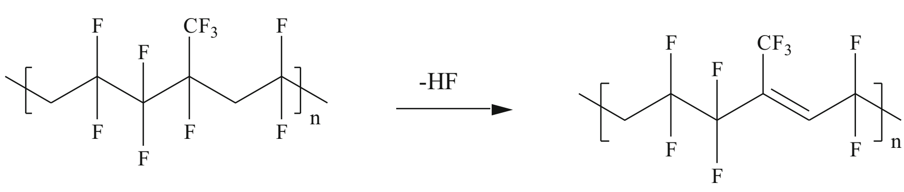
6.17.5 *Copolymers of Fluoroolefins*

Mary different copolymers of fluoroolefins are possible and were reported in the literature. Commercial use of fluoroolefin copolymers, however, is restricted mainly to elastomers. Such materials offer superior solvent resistance and good thermal stability.

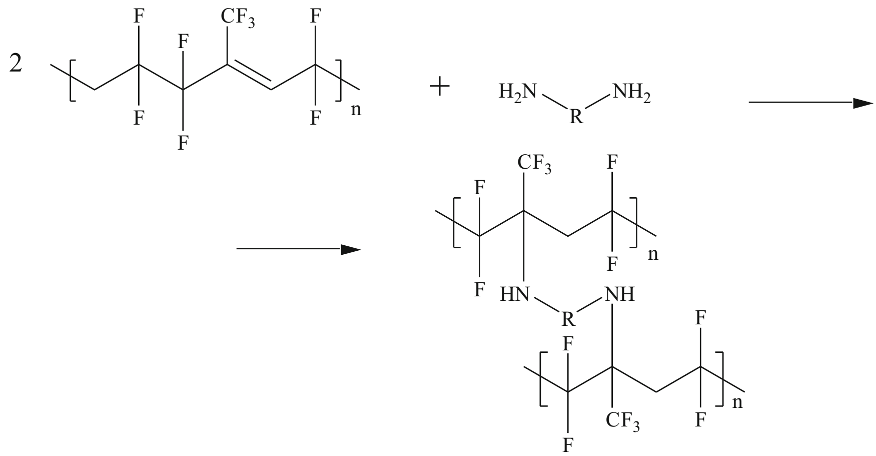
The elastomers that are most important industrially are vinylidine fluoride–chlorotrifluoroethylene [260] and vinylidine fluoride–hexafluoropropylene copolymers [282]. These copolymers are amorphous due to irregularities in their structures and can range in properties from resinous to elastomeric, depending upon composition [283]. Those that contain 50–70 mole percent of vinylidine fluoride are elastomers. The T_g ranges from 0 to −15°C, also depending upon vinylidine fluoride content [284]. They may be cross-linked with various peroxides, polyamines [284], or ionizing radiation. The cross-linking reactions by peroxides take place through hydrogen abstraction by primary radicals:



Copolymers of vinylidine fluoride with hexafluoropropylene are prepared in aqueous dispersions using persulfate initiators. Hexafluoropropylene does not homopolymerize but it does copolymerize. This means that its content in the copolymer cannot exceed 50%. Preferred compositions appear to contain about 80% of vinylidine fluoride. The cross-linking reactions with diamines are not completely understood. It is believed that the reaction takes place in two steps [285, 286]. In the first one, a dehydrofluorination occurs:



The above elimination is catalyzed by basic materials. These may be in the form of MgO, which is often included in the reaction medium. In the second step the amine groups add across the double bonds:

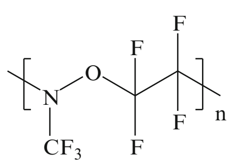


Free diamines, used for cross-linking, are too reactive and can cause premature gelation. It is common practice, therefore, to add these diamine compounds in the form of carbamates, like ethylenediamine carbamate or hexamethylene diamine carbamate. The above fluoro elastomers exhibit good resistance to chemicals and maintain useful properties from −50 to +300°C.

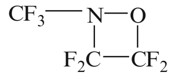
Copolymers of tetrafluoroethylene with hexafluoropropylene are truly thermoplastic polyperfluor-oolefins that can be fabricated by common techniques. Such copolymers soften at about 285°C and have a continuous use temperature of −260 to +205°C. Their properties are similar to, though somewhat inferior to, polytetrafluoroethylene.

6.17.6 Miscellaneous Fluorine Containing Chain-Growth Polymers

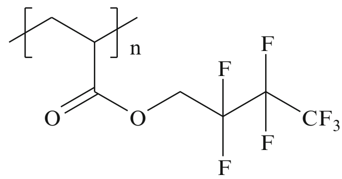
One of the miscellaneous fluoroolefin polymers is a copolymer of trifluoronitrosomethane and tetrafluoroethylene [287], an elastomer:



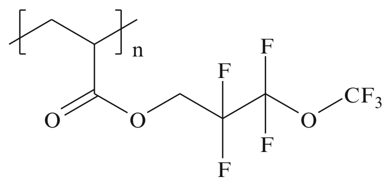
It can be formed by suspension polymerization. One procedure is to carry out the reaction in an aqueous solution of lithium bromide at −25°C with magnesium carbonate as the suspending agent. No initiator is added and the reaction takes about 20 h. Because the reaction in inhibited by hydroquinone and accelerated by ultra-violet light, it is believed to take place by a free-radical mechanism. Whether it is chain-growth polymerization, however, is not certain. A 1:1 copolymer is always formed regardless of the composition of the monomer feed, and the copolymerization takes place only at low temperatures. At elevated temperatures, however, cyclic oxazetidines form instead:



Two polyfluoroacrylates are manufactured on a small commercial scale for some special uses in jet engines. These are poly(1,1-dihyroperfluorobutyl acrylate):

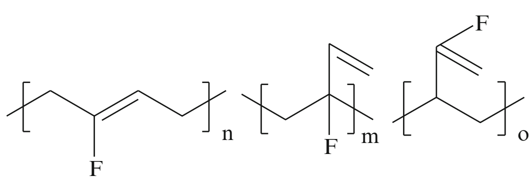


and poly(3-perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate):



The polymers are prepared by emulsion polymerization with persulfate initiators.

Although many other fluorine containing polymers were described in the literature, it is not possible to describe all of them here. They are not utilized commercially on a large scale. A few, however, will be mentioned as examples. One of them is polyfluoroprene [288]:

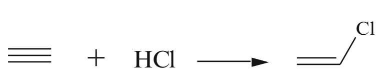


The polymer is formed by free-radical mechanism, in an emulsion polymerization using redox initiation. All three possible placements of the monomer occur [267].

Polyfluorostyrenes are described in many publications. A β-fluorostyrene can be formed by cationic mechanism [289]. The material softens at 240–260°C. An α,β,β-trifluorostyrene can be polymerized by free-radical mechanism to yield an amorphous polymer that softens at 240°C [290]. Ring-substituted styrenes apparently polymerize similarly to styrene. Isotactic poly(*o*-fluorostyrene) melts at 265°C. It forms by polymerization with Ziegler–Natta catalysts [291]. The *meta* analog, however, polymerized under the same conditions yields an amorphous material [291].

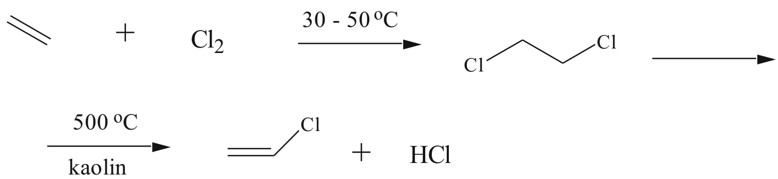
6.17.7 Poly(vinyl chloride)

Poly(vinyl chloride) is used in industry on a very large scale in many applications, such as rigid plastics, plastisols, and surface coatings. The monomer, vinyl chloride, can be prepared from acetylene:



The reaction is exothermic and requires cooling to maintain the temperature between 100 and 108°C.

The monomer can also be prepared from ethylene:



The reaction of dehydrochlorination is carried out at elevated pressure of about 3 atm.

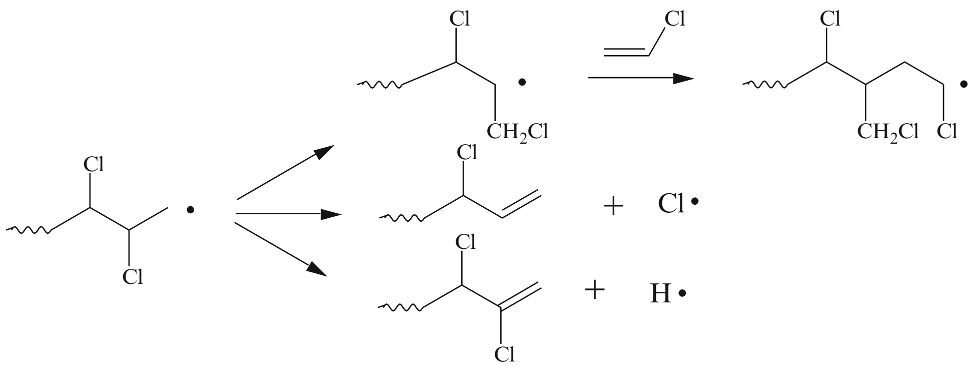
Free-radical polymerization of vinyl chloride was studied extensively. For reactions that are carried out in bulk the following observations were made [292]:

1. The polymer is insoluble in the monomer and precipitates out during the polymerization.
2. The polymerization rate accelerates from the start of the reaction. Vinyl chloride is a relatively unreactive monomer. The main sites of initiation occur in the continuous monomer phase.
3. The molecular weight of the product does not depend upon conversion nor does it depend upon the concentration of the initiator.
4. The molecular weight of the polymer increases as the temperature of the polymerization decreases. The maximum for this relationship, however, is at 30°C.

There is autoacceleration in bulk polymerization rate of vinyl chloride [293]. It was suggested by Schindler and Breitenbach [294] that the acceleration is due to trapped radicals that are present in the precipitated polymer swollen by monomer molecules. This influences the rate of the termination that decreases progressively with the extent of the reaction, while the propagation rate remains constant. The autocatalytic effect in vinyl chloride bulk polymerizations, however, depends on the type of initiator used [295]. Thus, when 2, 2′-azobisisobutyronitrile initiates the polymerization, the autocatalytic effect can be observed up to 80% of conversion. Yet, when benzoyl peroxide initiates the reaction, it only occurs up to 20–30% of conversion.

When vinyl chloride is polymerized in solution, there is no autoacceleration. Also, a major feature of vinyl chloride free-radical polymerization is chain transferring to monomer [296]. This is supported by experimental evidence [297, 298]. In addition, the growing radical chains can terminate by chain transferring to "dead" polymer molecules. The propagations then proceed from the polymer backbone [297]. Such new growth radicals, however, are probably short lived as they are destroyed by transfer to monomer [299].

The ^{13}C NMR spectroscopy of poly(vinyl chloride), which was reduced with tributyltin hydride, showed that the original polymer contained a number of short four-carbon branches [300]. This, however, may not be typical of all poly(vinyl chloride) polymers formed by free-radical polymerization. It conflicts with other evidence from ^{13}C NMR spectroscopy that chloromethyl groups are the principal short chain branches in poly(vinyl chloride) [301, 302]. The pendant chloromethyl groups were found to occur with a frequency of 2–3/1,000 carbons. The formation of these branches, as seen by Bovey and coworkers, depends upon head to head additions of monomers during the polymer formation. Such additions are followed by 1,2 chlorine shifts with subsequent propagations [301, 302]. Evidence from still other studies also shows that some head to head placement occurs in the growth reaction [303]. It was suggested that this may be not only an essential step in formation of branches but also one leading to formation of unsaturation at the chain ends [303, 304]:



Poly(vinyl chloride) prepared with boron alkyl catalysts at low temperatures possesses higher amounts of syndiotactic placement and is essentially free from branches [305–307].

Many attempts were made to polymerize vinyl chloride by ionic mechanisms using different organometallic compounds, some in combinations with metal salts [308–312]. Attempts were also made to polymerize vinyl chloride with Ziegler–Natta catalysts complexed with Lewis bases. To date, however, it has not been established unequivocally that vinyl chloride does polymerize by ionic mechanism. Use of the above catalysts did yield polymers with higher crystallinity. These reactions, however, were carried out at low temperatures where greater amount of syndiotactic placement occurs by the free-radical mechanism [313]. Vinyl chloride was also polymerized by $AlCl(C_2H_5)O_2H_5 + VO(C_3H_7O_2)$ without Lewis bases [312]. Here too, however, the evidence indicates a free-radical mechanism.

On the other hand, butyllithium–aluminum alkyl-initiated polymerizations of vinyl chloride are unaffected by free-radical inhibitors [313]. Also the molecular weights of the resultant polymers are unaffected by additions of CCl_4 that acts as a chain transferring agent in free-radical polymerizations. This suggests an ionic mechanism of chain growth. Furthermore, the reactivity ratios in copolymerization reactions by this catalytic system differ from those in typical free-radical polymerizations [313]. An anionic mechanism was also postulated for polymerization of vinyl chloride with *t*-butylmagnesium in tetrahydrofuran [314].

Commercially, by far the biggest amount of poly(vinyl chloride) homopolymer is produced by suspension polymerization and to a lesser extent by emulsion and bulk polymerization. Very little polymer is formed by solution polymerization.

One process for bulk polymerization of vinyl chloride was developed in France where the initiator and monomer are heated at 60°C for approximately 12 h inside a rotating drum containing stainless steel balls. Typical initiators for this reaction are benzoyl peroxide or azobisisobutyronitrile. The speed of rotation of the drum controls the particle size of the final product. The process is also carried out in a two-reactor arrangement. In the first one approximately 10% of the monomer is converted. The material is then transferred to the second reactor where the polymerization is continued until it reaches 75–80% conversion. Special ribbon blenders are present in the second reactor. Control of the operation in the second reactor is quite critical [315].

Industrial suspension polymerizations of vinyl chloride are often carried out in large batch reactors or stirred jacketed autoclaves. Continuous reactors, however, have been introduced in several manufacturing facilities [315]. Typical recipes call for 100 parts of vinyl chloride for 180 parts of water, a suspending agent, like maleic acid–vinyl acetate copolymer, a chain transferring agent, and a monomer soluble initiator. The reaction may be carried out at 100 $lb/in.^2$ pressure and 50°C for approximately 15 h. As the monomer is consumed the pressure drops. The reaction is stopped at an internal pressure of about 10 lb/in.^{2} and remaining monomer (about 10%) is drawn off and recycled. The product is discharged.

Emulsion polymerizations of vinyl chloride are usually conducted with redox initiation. Such reactions are rapid and can be carried out at 20°C in 1–2 h with a high degree of conversion. Commercial poly(vinyl chloride)s range in molecular weights from 40,000 to 80,000. The polymers are mostly amorphous with small amounts of crystallinity, about 5%. The crystalline areas are syndiotactic [317, 318].

Poly(vinyl chloride) is soluble at room temperature in oxygen-containing solvents, such as ketones, esters, ethers, and others. It is also soluble in chlorinated solvents. The polymer, however, is not soluble in aliphatic and aromatic hydrocarbons. It is unaffected by acid and alkali solutions but has poor heat and light stability. Poly(vinyl chloride) degrades at temperatures of 70°C or higher or when exposed to sun light, unless it is stabilized. Heating changes the material from colorless to yellow, orange, brown, and finally black. Many compounds tend to stabilize poly(vinyl chloride). The more important ones include lead compounds, like dibasic lead phthalate and lead carbonate. Also effective are metal salts, like barium, calcium, and zinc octoates, stearates, and laurates. Organotin compounds, like dibutyl tin maleate or laurate, also belong to that list. Epoxidized drying oils are effective heat stabilizers, particularly in coatings based on poly(vinyl chloride). Some coating materials may also include aminoplast resins, like benzoguanamine–formaldehyde condensate.

The process of degradation is complex. It involves loss of hydrochloric acid. The reactions are free radical in nature, though some ionic reactions appear to take place as well. The process of dehydrochlorination results in formations of long sequences of conjugated double bonds. It is commonly believed that formation of conjugated polyenes, which are chromophores, is responsible for the darkening of poly(vinyl chloride). In addition, the polymer degrades faster in open air than it does in an inert atmosphere. This shows that oxidation contributes to the degradation process. All effective stabilizers are hydrochloric acid scavengers. This feature alone, however, can probably not account for the stabilization process. There must be some interaction between the stabilizers and the polymers. Such interaction might vary, depending upon a particular stabilizer.

6.17.7.1 Copolymers of Vinyl Chloride

A very common copolymer of vinyl chloride is vinyl acetate. Copolymerization with vinyl acetate improves stability and molding characteristics. The copolymers are also used as fibers and as coatings. Copolymers intended for use in moldings are usually prepared by suspension polymerization. Those intended for coating purposes are prepared by solution, emulsion, and suspension polymerizations. The copolymers used in molding typically contain about 10% of poly(vinyl acetate). Copolymers that are prepared for coating purposes can contain from 10 to 17% of poly(vinyl acetate). For coatings, a third comonomer may be included in some resins. This third component may, for instance, be maleic anhydride, in small quantities, like 1%, to improve adhesion to surfaces.

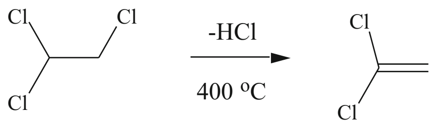
Copolymers of vinyl chloride with vinylidine chloride are similar in properties to copolymers with vinyl acetate. They contain from 5 to 12% of poly(vinylidine chloride) and are intended for use in stabilized calendaring.

Copolymers containing 60% vinyl chloride and 40% acrylonitrile are used in fibers. The fibers are spun from acetone solution. They are nonflammable and have good chemical resistance.

6.17.8 Poly(vinylidine chloride)

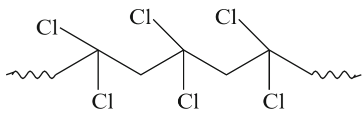
Vinylidine chloride homopolymers form readily by free-radical polymerization, but lack sufficient thermal stability for commercial use. Copolymers, however, with small amounts of comonomers find many applications.

The monomer, vinylidine chloride, can be prepared by dehydrochlorination of 1,1,2-trichloroethylene:



It is a colorless liquid that boils at 32°C. Also, it is rather hard to handle as it polymerizes on standing. This takes place upon exposure to air, water, or light. Storage under an inert atmosphere does not completely prevent polymer formation.

Poly(vinylidine chloride) can be formed in bulk, solution, suspension, and emulsion polymerization processes. The products are highly crystalline with regular structures and a melting point of 220°C. The structure can be illustrated as follows:



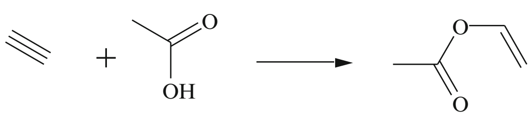
This regularity in structure is probably due to little chain transferring to the polymer backbone during polymerization. Such regularity of structure allows close packing of the chains and, as a result, there are no effective solvents for the polymer at room temperature.

Copolymerization of vinylidine chloride with vinyl chloride reduces the regularity of the structure. It increases flexibility and allows processing the polymer at reasonable temperatures. Due to extensive crystallization, however, that is still present in 85:15 copolymers of vinylidine chloride with vinyl chloride, they melt at 170°C. The copolymerization reactions proceed at slower rates than do homopolymerizations of either one of the monomers alone. Higher initiator levels and temperatures are, therefore, used. The molecular weights of the products range from 20,000 to 50,000. These materials are good barriers for gases and moisture. This makes them very useful in films for food packaging. Such films are formed by extrusion and biaxial orientation. The main application, however, is in filaments. These are prepared by extrusion and drawing. The tensile strength of the unoriented material is 10,000 lb/in.^{2} and the oriented one 30,000 lb/in.^{2}.

Vinylidine chloride is also copolymerized with acrylonitrile. This copolymer is used mainly as a barrier coating for paper, polyethylene, and cellophane. It has the advantage of being heat sealable.

6.18 Poly(vinyl acetate)

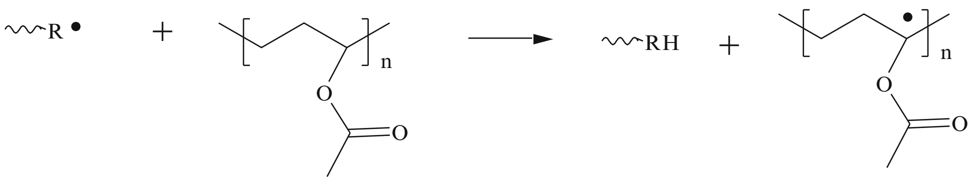
Vinyl acetate monomer can be prepared by reacting acetylene with acetic acid:



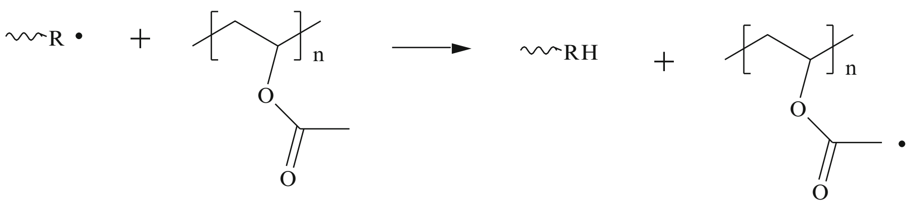
The reaction can be carried out in a liquid or in a vapor phase. A liquid phase reaction requires 75–80°C temperatures and a mercuric sulfate catalyst. The acetylene gas is bubbled through glacial acetic acid and acetic anhydride. Vapor phase reactions are carried out at 210–250°C.

Typical catalysts are cadmium acetate or zinc acetate. There are other routes to vinyl acetate as well, based on ethylene.

Commercially, poly(vinyl acetate) is formed in bulk, solution, emulsion, and suspension polymerizations by free-radical mechanism. In such polymerizations, chain transferring to the polymer may be as high as 30%. The transfer can be to a polymer backbone through abstraction of a tertiary hydrogen:



It can also take place to the methyl proton of the acetate group:



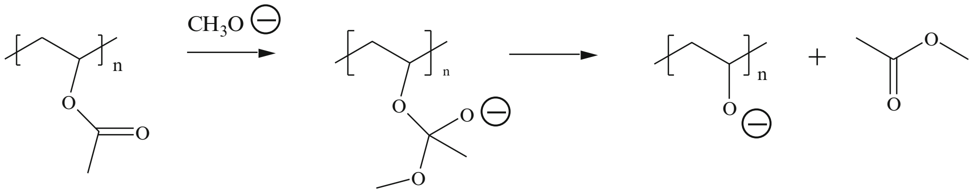
The polymer has a head to tail structure and is highly branched. It is quite brittle and exhibits cold flow. This makes it useless as a structural plastic. It is, however, quite useful as a coating material and as an adhesive for wood. The polymer is soluble in a wide range of solvents and swells and softens upon prolonged immersion in water. At higher temperatures or at extended exposures to temperatures above 70°C, the material loses acetic acid.

A number of copolymers are known where vinyl acetate is the major component. In coatings, vinyl acetate is often used in copolymers with alkyl acrylates (line 2-ethylhexyl acrylate) or with esters of maleic or fumaric acids. Such copolymers typically contain 50–20% by weight of the comonomer and are usually formed by emulsion polymerization in batch processes. They are used extensively as vehicles for emulsion paints.

Shaver and coworkers [319] investigated the mechanism of bis(imino)pyridine ligand framework for transition metal systems-mediated polymerization of vinyl acetate. Initiation using azobisisobutyronitrile at 120°C results in excellent control over poly(vinyl acetate) molecular weights and polymer dispersities. The reaction yields vanadium-terminated polymer chains which can be readily converted to both proton-terminated poly(vinyl acetate) or poly(vinyl alcohol). Irreversible halogen transfer from the parent complex to a radical derived from azobisisobutyronitrile generates the active species.

6.19 Poly(vinyl alcohol) and Poly(vinyl acetal)s

Vinyl alcohol monomer does not exist because its keto tautomer is much more stable. Poly(vinyl alcohol) can be prepared from either poly(vinyl esters) or from poly(vinyl ethers). Commercially, however, it is prepared exclusively from poly(vinyl acetate). The preferred procedure is through a transesterification reaction using methyl or ethyl alcohols. Alkaline catalysts yield rapid alcoholyses. A typical reaction employs about 1% of sodium methoxide and can be carried to completion in 1 h at 60°C. The product is contaminated with sodium acetate that must be removed. The reaction of transesterification can be illustrated as follows:



The branches of poly(vinyl acetate) that form during polymerization as a result of chain transferring to the acetate groups cleave during transesterification. As a result, poly(vinyl alcohol) is lower in molecular weight than its parent material.

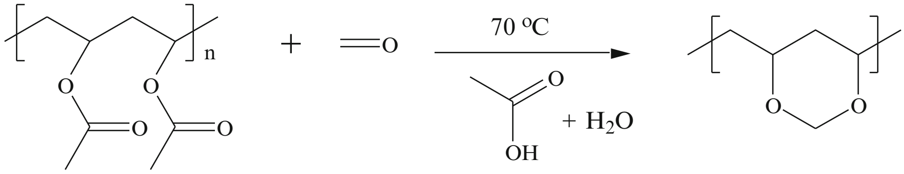
Poly(vinyl alcohol) is very high in head to tail structures, based on NMR data. It shows the presence of only a small amount of adjacent hydroxyl groups. The polymer prepared from amorphous poly(vinyl acetate) is crystalline, because the relatively small size of the hydroxyl groups permits the chains to line-up into crystalline domains. Synthesis of isotactic poly(vinyl alcohol) was reported from isotactic poly(vinyl ethers), like poly(benzyl vinyl ether), poly(*t*-butyl vinyl ether), poly (trimethylsilyl vinyl ether), and some divinyl compounds.

Poly(vinyl alcohol) is water soluble. The hydroxyl groups attached to the polymer backbone, however, exert a significant effect on the solubility. When the ester groups of poly(vinyl acetate) are cleaved to a hydroxyl content of 87–89%, the polymer is soluble in cold water. Further cleavage of the ester groups results in a reduction of the solubility and the products require heating of the water to 85°C to dissolve. This is due to strong hydrogen bonding that also causes unplasticized poly(vinyl alcohol) to decompose below its flow temperature. On the other hand, due to hydrogen bonding the polymer is very tough.

Poly(vinyl acetals) are prepared by reacting poly(vinyl alcohol) with aldehydes. Reactions of poly (vinyl alcohol) with ketones yield ketals. These are not used commercially.

Not all hydroxyl groups participate in formations of acetals and some become isolated. A typical poly(vinyl acetal) contains acetal groups, residual hydroxyl groups, and residual acetate groups from incomplete transesterification of the parent polymer.

Poly(vinyl acetal)s can be formed directly from poly(vinyl acetate) and this is actually done commercially in preparations of poly(vinyl formal). A typical reaction is carried out in the presence of acetic acid, formalin, and sulfuric acid catalyst at 70°C:



Poly(vinyl butyral), on the other hand, is prepared from poly(vinyl alcohol) and butyraldehyde. Sulfuric acid is used as the catalyst. Commercially only poly(vinyl formal) and poly(vinyl butyral) are utilized on a large scale in coating materials.

Review Questions

Section 6.1

1. What are the two types of polyethylene that are currently manufactured commercially?
2. Describe the chemical structure of low-density polyethylene produced by free-radical mechanism and show by chemical equations how all the groups that are present form. How can low-density polyethylene be prepared by ionic mechanism?
3. Describe conditions and procedure for commercial preparation of polyethylene by free-radical mechanism, the role of oxygen, and the problems associated with oxygen.
4. Describe a tubular reactor for preparation of polyethylene.
5. What are the industrial conditions for preparations of high-density polyethylene. Describe the continuous solution process, the slurry process, and the gas-phase process.
6. Show with chemical reactions how polymethylene forms from diazomethane.

Section 6.2

1. Discuss high activity catalysts for the manufacturing of isotactic polypropylene, heterogeneous and homogeneous.
2. What are the current techniques for polypropylene manufacture?
3. How can syndiotactic polypropylene be prepared and what are its properties?

Section 6.3

1. Describe the two industrial processes for manufacturing polybutylene.

Section 6.4

1. Draw the chemical structure of isotactic poly(butene-1). How is it prepared and used?
2. What is TPX, how is it prepared, and what are its properties?

Section 6.5

1. Discuss copolymers of ethylene with propylene. How are they prepared? What catalysts are used in the preparations? How are ethylene–propylene rubbers cross-linked?
2. What are the copolymers of ethylene with higher α-olefins and why are they prepared and how?
3. Discuss the copolymers of ethylene with vinyl acetate? How are they prepared and used?
4. What are ionomers? Describe each type. How are they used?
5. Describe the catalysts used in preparations of aliphatic ketones by copolymerization of ethylene with carbon monoxide.

Section 6.6

1. Discuss polybutadiene homopolymers. How are they prepared? What are their uses?
2. What are popcorn polymers? What causes their formation?
3. Discuss liquid polybutadienes. How are they prepared and used?
4. How are high molecular weight polybutadienes prepared and used?
5. Discuss polyisoprenes. What is natural rubber? Where does it come from? What are synthetic polyisoprenes? How are they prepared?

Section 6.7

1. What is methyl rubber?

Section 6.8

1. What is chloroprene rubber? How is it made and used?

Section 6.9

1. What are poly(carboxybutadiene)s?

Section 6.10

1. Discuss cyclopolymerization of conjugated dienes.

Section 6.11

1. What is SBR rubber? Explain and describe preparation and properties.
2. What are block copolymer elastomers? How are they prepared and what gives them their unique properties?
3. What is GR-N rubber? Explain and describe preparation and properties.

Section 6.12

1. How are atactic and syndiotactic polystyrenes prepared commercially? Describe and explain.
2. What polymers of substituted styrenes are available commercially? How are they prepared?

Section 6.13

1. What is high-impact polystyrene and how is it prepared?
2. Discuss ABS resins. How are they prepared?

Section 6.14

1. Discuss the chemistry of free-radical polymerization of acrylic and methacrylic esters.
2. What are acrylic elastomers and how are they vulcanized?
3. How is poly(methyl methacrylate) prepared commercially, such as Plexiglas in the form of sheets and rods? Is poly(methyl methacrylate) prepared in any other way, how? For what applications?
4. Describe the thermosetting acrylic resins used in industrial coatings. How are they prepared? How are they cross-linked?

Section 6.15

1. Discuss industrial polymers and copolymers of acrylonitrile and methacrylonitrile. How are they prepared and used?

Section 6.16

1. Describe preparation and uses of polyacrylamide, poly(acrylic acid), and polymethacrylic acid.

Section 6.17

1. How is polytetrafluoroethylene prepared, and what are its properties and uses?
2. Discuss the chemistry of polychlorotrifluoroethylene, poly(vinylidine fluoride), and poly(vinyl fluoride).
3. What common copolymers of fluoroolefins are used commercially?
4. Discuss the chemistry of poly(vinyl chloride) and poly(vinylidine chloride).
5. Discuss the important commercial copolymers of vinyl chloride. What are their main uses?
6. Discuss the chemistry of poly(vinylidine chloride).

Section 6.18

1. Discuss preparation, properties, and uses of poly(vinyl acetate).

Section 6.19

1. How is poly(vinyl alcohol) prepared, used, and converted to poly(vinyl acetal)s?

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