

1.1 POLYETHYLENE (PE)

1.1.1 Introduction

Polyethylenes are olefin polymers manufactured in the largest tonnage of all the thermoplastic materials. They are produced by the addition polymerization of ethylene to give the basic structure $-(\text{CH}_2-\text{CH}_2)_n-$. Based on the constitutional repeating unit in the structure, the name of polymethylene is recommended by the IUPAC Commission on Macromolecular Nomenclature for this family of polymers. This name has already been used before for the strictly linear polymer obtained from diazomethane $-(\text{CH}_2)_n-$. In common use, the term ‘polyethylene’ is still attributed to the polymers obtained by the polymerization of ethylene and will be used in this text.

Several well established families of polyethylenes can now be found on the market, each having a different structure and very different behaviors, performances and applications:

- low density polyethylene (LDPE) $0.915\text{--}0.935 \text{ g/cm}^3$
- high density polyethylene (HDPE) $0.941\text{--}0.967 \text{ g/cm}^3$
- linear low density polyethylene (LLDPE) $0.910\text{--}0.925 \text{ g/cm}^3$
- very low density polyethylene (VLDPE) $0.880\text{--}0.912 \text{ g/cm}^3$
- high and ultrahigh molecular weight polyethylene, 200 000–500 000 for HMWPE and 3 000 000 for UHMWPE, respectively.

Other categories of PE polymers are crosslinked PE, chlorosulfonated PE and the copolymers of ethylene.

In 1994 the global demand for polyethylenes of all types was of the order of 37 million metric tons per year [1] of which 8.2 million metric tons was produced in the US alone [2]. LDPE and HDPE each account for 40.5% in the global production and LLDPE for 19% [1].

The sources of ethylene and of other olefins are petroleum and natural gas [3]. Petroleum is first separated by distillation into broad fractions which are

subsequently 'cracked' by heating (thermal cracking or pyrolysis). High yields of olefins are obtained and they are further separated into individual products by fractional distillation. Natural gas, the second major source of ethylene, contains methane (60–99%) and C_{2–5} paraffins which are converted to olefins by thermal cracking. Carbon monoxide, acetylene, oxygen, moisture and other impurities contained in raw ethylene must be carefully removed as they affect the polymerization process and the properties of the PE.

The first commercial production of PE started in 1939 at Imperial Chemical Industries Ltd in the UK and was based on the high pressure polymerization of ethylene experimented by Fawcet and Gibson. It was found that the new material had excellent electrical insulation properties; the first application was as underwater cable insulator and it also greatly aided in the development of radar. The needs of World War II significantly accelerated research and further developments in the field of PE [4].

In 1955, a plant using the Ziegler catalyst polymerization process began production at Farbwerte Hoechst AG Germany, almost simultaneously with Phillips Petroleum Co. (1957) and Standard Oil Co. (1961) of Indiana, both in the USA. These three processes were all based on the catalytic polymerization of ethylene in solution or in slurry at low pressures. The prepared PEs had higher densities and were more linear in structure than those produced under high pressure. They became known as high density polyethylene (HDPE) and the older material as low density polyethylene (LDPE).

In 1968, Union Carbide Corp. of USA developed a new low pressure polymerization process producing HDPE in the gas phase that required no solvents. This process led to the next major stage of development, the advent in 1977 of low density polyethylene produced by a low pressure, gas phase process and known as linear low density polyethylene (LLDPE). The production was less expensive and had lower energy demands than the conventional high pressure process [5].

The last twenty years have been marked by a huge research effort and accumulation of scientific knowledge on catalyst systems and by new developments of super high activity Ziegler catalysts and especially of the new class of metallocene catalysts. They have brought about not only improved efficiencies of the polymerization processes, but the manufacture of a new generation of tailor-made PE with an unprecedented control of MW, MWD and of comonomer incorporation [6,7]. In 1989, Exxon Chemical unveiled the so called Exxpol technology. They produced a wide range of PE grades with densities from 0.865 to 0.935 g/cm³ by solution polymerization of ethylene with 'single site catalysts', a new class of catalysts of the metallocene family [7]. At present, resins prepared with single site catalysts are produced on a precommercial scale and around 20 companies are examining the possibility of using metallocene catalysts for the production of polyolefins.

Many application areas were found for PEs such as electrical insulators, packaging films, different domestic goods, toys, and in chemical plants. Each particular application requires the best resin choice which implies the knowledge of the fundamental properties of the polymers such as the melt index, the density, the MW, the polydispersity (MWD) and the degree of branching [8].

1.1.2 Low density polyethylene (LDPE)

LDPE is prepared by a typical free radical polymerization process at high temperatures and extremely high pressures. Azoisobutyronitrile (AIBN), benzoyl peroxide (BP) or oxygen (10–100 ppm) are free radical initiators commonly used. The free radical polymerization of ethylene has a critical dependence on the monomer concentration: growing polymer radical have a very limited life to react with the monomer and high monomer concentrations are necessary to obtain high MW polymer. To meet this requirement, the process is operated at very high pressures in the range of 150–350 MPa (1500–3000 atmospheres) in order to maintain the necessary concentration of monomer and to control the reaction rate [9]. The temperature is in the range 80–300°C, the lower the temperature (with active initiators only) the higher the MW.

Under these conditions, ethylene is above its critical pressure and temperature (of 9.7°C) and is in the gas phase. The polymerization is highly exothermic, the heat of polymerization of ethylene in the gas phase is 92–96 kJ/mol (3.35 kJ/g) and the temperature would rise by about 12–13°C for each 1% of polymerized ethylene (the specific heat of ethylene at these conditions is 2.5–2.8 J/g·°C). If the reaction temperature becomes too high, exothermic decomposition reactions of ethylene (142 kJ/mol) may occur leading to a mixture of methane, hydrogen and carbon and to increasing explosive pressure. Very efficient temperature control must be maintained to prevent runaway reaction. High cooling surface/volume ratio reactors are used as well as different inert liquid diluents such as benzene or water to dilute the reaction heat. For the same reason the initiators are sometimes dissolved in a solvent and are injected in the reactor at different points that minimize high local concentrations of the initiator in the reactor [10].

The process is operated continuously and two main types of reactor are in use, namely, a narrow bore tubular reactor and a stirred autoclave. The tubular reactor has obvious advantages at high pressures. Because there is no mechanical agitation, a plug flow through the tube is produced by continuously pumping the ethylene into the tube and by releasing the product periodically from the other end [11]. This helps to eliminate the buildup of polymer on the walls.

In a typical process, 10–30% monomer is converted per cycle to polymer. The obtained polymer is dissolved in ethylene and the whole resembles

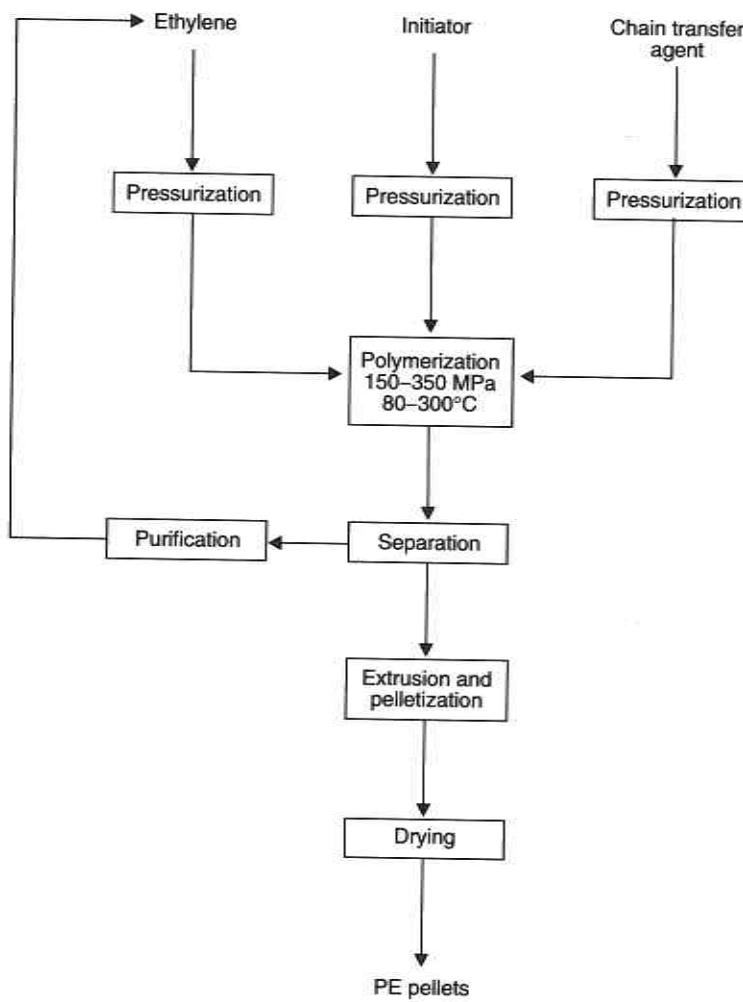


Figure 1.1 Continuous high pressure polymerization of ethylene.

conventional bulk polymerization. The molten polymer is separated from unreacted ethylene and from diluent by releasing the pressure, and then is extruded into a ribbon and granulated. Unreacted ethylene is purified and recycled.

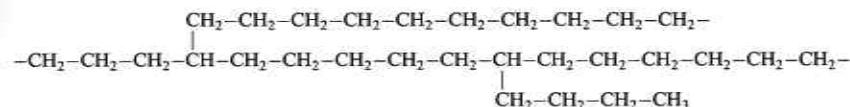
A flow chart of the high pressure continuous polymerization of ethylene is presented in Figure 1.1.

Under the vigorous conditions of high temperature and pressure, side reactions occur leading to chain branching that determines the properties of LDPE. Both short and long branches are formed [12]. The presence of 20–30 short chain branches per 1000 carbon atoms in the main chain was

evidenced by ^{13}C NMR, FTIR and pyrolysis–hydrogenation gas chromatography (PyHGC) [13–16]. They are mainly butyl branches, but also ethyl, methyl and amyl. Using size exclusion chromatography (SEC) and temperature-rising elution chromatography (TREF) combined with the methods mentioned above, it was found that the lower MW species have more short chain branches [12]. The level of short chain branching can be modified by the adjustment of pressure and temperature.

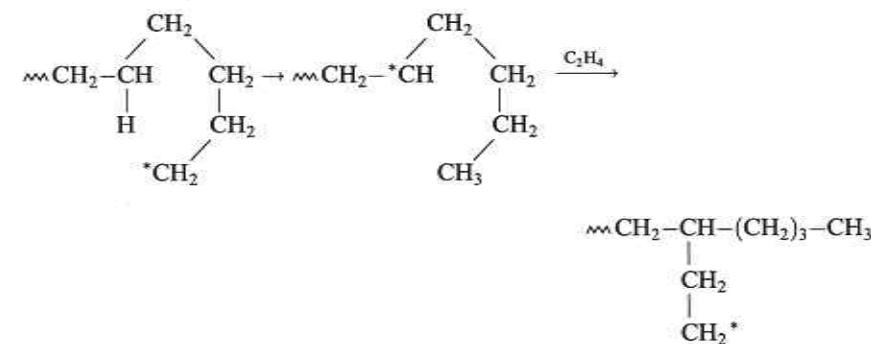
As for the long branches, there are on the average about three branches per 1000 carbon atoms and they have a range of lengths with an upper limit approaching the length of the main polymer chain. Long branches have been evidenced by combining SEC fractionation of the polymer with subsequent solution viscosity, light scattering and sedimentation measurements [17] and more recently with low angle laser light scattering [18] and ^{13}C NMR measurements [16]. The distribution of long chain branches with the MW depends strongly on the polymerization conditions [12].

The microstructure of LDPE may be represented as:



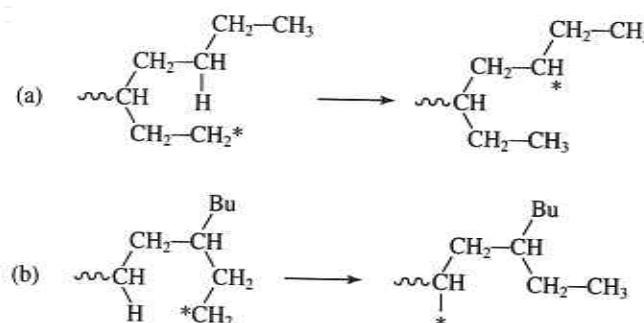
See also Figure 1.5.

The formation of branches is due to chain transfer reactions that occur both by intramolecular and intermolecular mechanisms [19]. Short chain branches are formed during the propagation stage by a 'backbiting' intramolecular mechanism. The end of the chain coiled backward extracts a hydrogen radical from a carbon atom in the chain, a six-membered ring transition state being favored. This results in butyl short branches. The propagation of the chain is thus transferred to the carbon atom from which the hydrogen was removed and the polymerization can continue in the normal way:

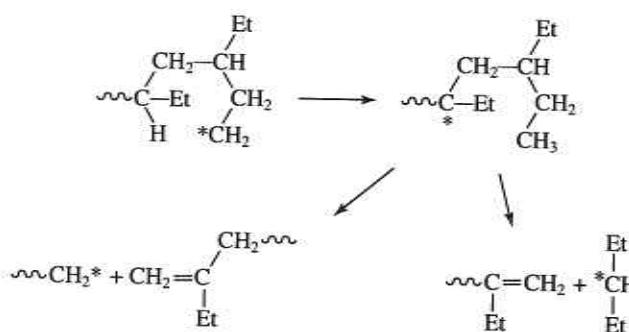


A second backbiting may occur either to (a) the butyl (Bu) group leading to ethyl (Et) side branches or (b) again to the main chain resulting in more

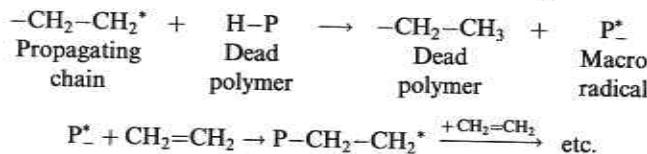
branched side chains:



A third backbiting is also possible with the formation of a tertiary radical which could depolymerize by β -scission. This generates vinylidene groups which have been observed and found to provide about 50% unsaturation in LDPE, the rest being about evenly divided by vinyl and in-chains double bonds (there may be up to about three double bonds per 1000 carbon atoms).



Long chain branches are formed through intermolecular transfer which arises when a growing chain extracts a hydrogen radical from a dead polymer molecule on which the propagation will continue leading to a long branch:



On a number-average basis, a typical low density polyethylene may contain one long branch for 50 short branches. The distribution of long branches is very uneven, most of the branches are concentrated on a few very large molecules, while many molecules contain no long branches.

Chain transfer agents such as light paraffins, propylene or hydrogen are frequently employed to adjust the MW to the desired values as they terminate

propagating polymeric chains and start other chains by an intermolecular chain transfer mechanism.

The characteristics of LDPE, such as branching and its distribution, MW and MWD, may be varied over a wide range by changing the conditions of the process (temperature, pressure) and the nature, the composition and the amount of initiator and of chain transfer agent.

Proprietary mathematical models have been developed for the operation of reactors used for the production of LDPE. They are very complex and serve to optimize the processes for desired types of PE.

A major trend in the high pressure technologies is their continued decline in favor of low pressure, gas phase processes. This is primarily due to the high operating costs and lack of product flexibility [6].

1.1.3 High density polyethylene (HDPE)

HDPE is produced by three basic types of process. They are all catalytic processes run at relatively low pressures. The details on methods of preparing the catalysts are closely guarded secrets.

In some of these processes a solvent is employed but, at the process temperature, the resultant polymer is not soluble so that a slurry of granular PE is formed. The slurry-type processes are the most important ones for the production of HDPEs. On the other hand, in the true solution processes, a higher temperature is employed permitting a complete dissolution of the PE in the solvent. The third type is a gas-solid process in which the powder of solid PE that forms is suspended in the gaseous ethylene.

HDPE can be broadly divided into two categories: high MW bimodal/broad MWD polymers used mainly for blow molding and pipe, and low MW grades with narrow MWD used for injection and rotomolding [6].

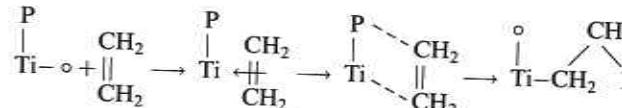
(a) Ziegler process

In the Ziegler process, the polymerization proceeds by a coordination mechanism which involves a catalyst–monomer coordination complex that controls the way in which the monomer approaches the growing chain.

The coordination catalyst is a complex formed by the interaction of (a) a compound of a transition metal in Groups IV–VIII of the Periodic Table (the catalyst) with (b) an organometallic compound of Groups I–III metals (the cocatalyst). The ligands in the catalyst compounds can be halide, oxyhalide, alkoxy, acetylacetonyl and phenyl. The metals in the catalyst are commonly titanium, vanadium, chromium, molybdenum, hafnium or zirconium. The cocatalysts are hydrides, alkyls or aryls of metals such as aluminum, lithium, zinc, tin, cadmium, beryllium or magnesium. One of the most common Ziegler–Natta catalysts is the complex $\text{TiCl}_4-\text{AlR}_3$ where R = alkyl.

Designing the chemical composition and the morphology of the heterogeneous catalyst particles is of paramount importance for both the polymerization efficiency and the polymer properties. New generations of super high activity catalysts have been prepared as result of the scientific understanding of their complex structure and intimate role in the polymerization. These catalysts are based on $MgCl_2$ -supported titanium compounds in combination with trialkyl aluminum cocatalyst and, in some cases, with an electron donor [20,21]. The $MgCl_2$ support maximizes the number of active sites on the catalyst surface. Catalysts based on a single transition metal are used for polymers with narrow MWD, while those based on two or more transition metals lead to polymers with bimodal/broad MWD which are easier to process; each metal forms polymers of average MW that differ from each other by more than one order of magnitude [22].

Of the various mechanisms that have been proposed, the two that are generally accepted are the so called monometallic and bimetallic mechanisms, the former being favored in heterogeneous processes [23]. In both mechanisms, the monomer is pictured as being incorporated into the polymer by an insertion reaction between the transition metal atom and the terminal carbon of the coordinated polymer chain:



where P = polymer chain; o = vacant coordination site.

A very large number of patents claim different ways of catalyst preparation. Basically, the catalyst may be prepared in two general ways both conducted in an inert atmosphere (since oxygen and water reduce its effectiveness): (a) *in situ* by feeding the components separately and directly into the main reactor as solutions in diluents (heptane, toluene) or (b) by preparing the catalytic complex separately and then adding the resulting slurry to the reactor.

Loop reactors and autoclave reactors are both used for slurry processes. Polymerization is conducted continuously by introducing into the reactor a liquid hydrocarbon diluent, the catalyst and the ethylene. The pressures are slightly above atmospheric, 0.2–0.4 MPa (2–4 atmospheres) and the temperatures are 50–75°C. In these conditions, the polymer is insoluble and forms a slurry which progressively thickens as the reaction proceeds and is continuously removed from the reactor.

Each catalyst particle forms one polymer particle. During the growth of polymer particles, the catalyst particle disintegrates and the fragments become dispersed throughout the whole polymer particle. With less efficient catalyst systems, the decomposition of the catalyst is very important particularly where the polymer is intended for use in electrical insulation. The catalyst is destroyed by the action of an alcohol (methanol, ethanol or isopropanol) and then extracted by alcoholic hydrochloric acid. By using

extremely active catalysts, so little catalyst residue is in the polymer that the onerous step of removing the catalyst is no longer necessary. As an example, a typical $TiCl_4$ – AlR_3 catalyst yields about 20–200 g of PE per gram of catalyst per hour per atmosphere of ethylene, whereas as much as 22–25 kg PE per gram may be produced using $MgCl_2$ -supported catalysts [7,23]. Values as low as 2–4 ppm of titanium have been reported in some PEs [10]. The polymer is finally separated by centrifugation and then dried, extruded and granulated.

Another improvement in the economics of the polymerization process brought about by the new $MgCl_2$ -supported catalysts is the possibility to eliminate the pelletizing step in the manufacture of the polymer. The polymer particle morphology depends on catalyst particle morphology, namely its shape, size, porosity, texture of particles and homogeneous distribution of active centers both in the core and on the surface layer (replication phenomenon). Tightly tailoring catalyst morphology makes it possible to control the morphology of the polymer particle in size, shape and bulk density, and thus avoids the pelletizing step [20].

The MW of the polymer may be controlled by the polymerization temperature, by the ratio Al–Ti in the catalyst or by using chain transfer agents. Hydrogen is the most commonly used chain transfer agent. A new multistep technology based on successive different hydrogen concentrations is used in order to broaden the MWD and thus to improve the processability of certain PE grades.

Ziegler HDPEs have densities of about 0.945 g/cm³ and branching of the order of five to seven ethyl groups per 1000 carbon atoms. Butyl and other branches seem to be absent.

A typical flow chart of the process is presented in Figure 1.2.

(b) Phillips process

This process is based on the use of a heterogeneous catalyst consisting of transition metal compounds (chromium oxides). A finely divided support of silica or silica–alumina (75–90% silica) is impregnated with an aqueous solution of a chromium compound and heated at 400–800°C. The resulting catalyst contains 5% chromium oxides, mainly CrO_3 . Very pure reactants must be employed as a number of impurities such as oxygen, nitrogen, acetylene and chlorine are catalyst poisons.

Two main variations of this process are known: the process may be conducted in solution or in a slurry depending on the temperature. The reaction temperature is highly important for controlling the MW of the PE. In the solution process, reactors are operated at 130–160°C, which is above the melting point of the PE and which makes the polymer more soluble. The solvent is a liquid hydrocarbon such as cyclohexane which dissolves the PE as it is formed and also serves as a heat transfer agent. In the slurry variant

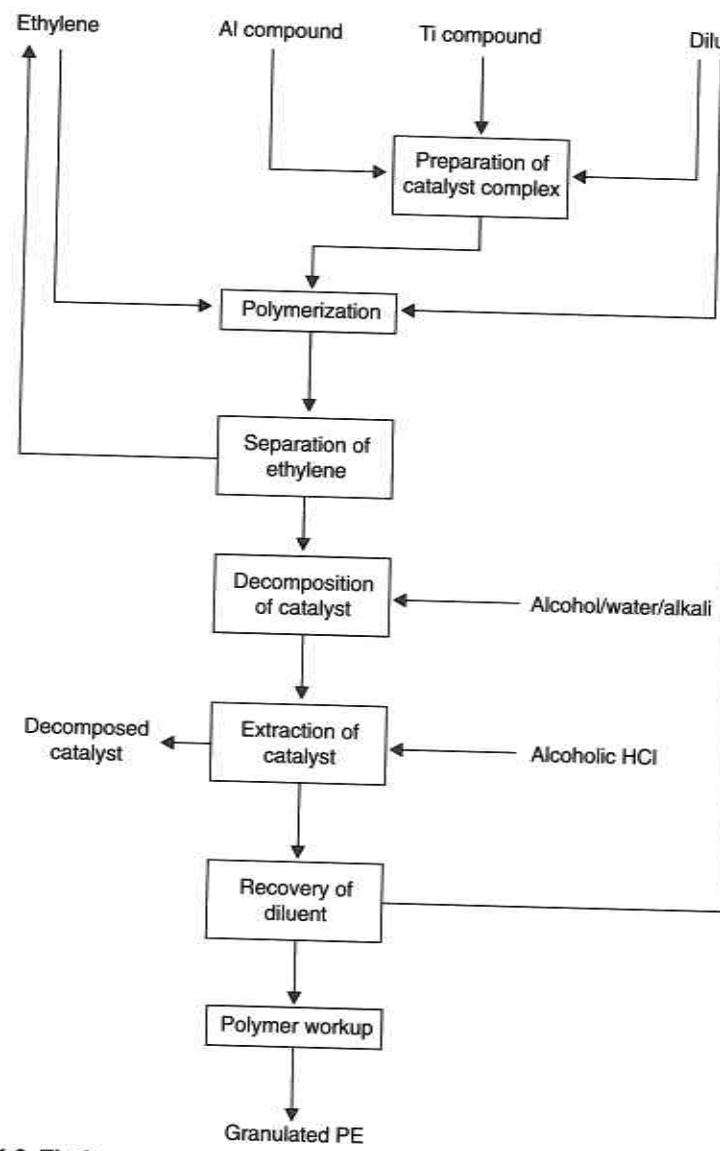


Figure 1.2 Ziegler process for ethylene polymerization.

of the process, temperatures are 90–100°C, which is below the crystalline T_m of the PE and so its solubility in the diluent is low.

Pressures are generally 1.4–3.5 MPa (14–35 atmospheres) which are between those used in high pressure and in Ziegler processes.

After reaction, the mixture is continuously withdrawn from the reactor into a gas–liquid separator where the unreacted ethylene is flashed off.

From the hot solution the catalyst is removed by filtration and the polymer is separated from the solvent either by flashing off the solvent or by precipitating the polymer by cooling. In the slurry process, after flashing off the ethylene, the polymer is separated by centrifugation.

In the slurry process, the granules of PE are each formed around individual catalyst particles which remain in the polymer. To reduce the level of contamination of the polymer, the polymerization is conducted to high conversion rates [10]. Higher MW polymers are prepared by the slurry method.

HDPEs prepared by this process have the highest density (about 0.96 g/cm³) of any commercial PE and are almost completely linear with up to three methyl groups per 1000 carbon atoms and no ethyl or butyl groups detected.

The flow chart of the Phillips process is presented in Figure 1.3.

(c) Standard Oil Company (Indiana) process

Many similarities are found between the Phillips and Standard Oil processes. The Standard Oil process is conducted preferably in solution in the presence of a metal oxide catalyst at 200–300°C and 4–10 MPa (40–100 atmospheres). The catalyst may be molybdenum trioxide, titanium dioxide or zirconium dioxide in combination with sodium or calcium hydrides as promoters and supported on alumina [24]. The catalyst must be activated before use by reducing it with hydrogen or with a metal hydride (in the Phillips process, the catalyst is activated by the ethylene itself). A hydrocarbon solvent is used as the reaction medium, serving both to dissolve the polymer and to remove the heat of reaction. The same marked effect of the temperature on the MW of the PE as in the Phillips process is evident.

Polymerization mechanisms by metal oxides are not well understood. The polyethylenes obtained have densities of about 0.96 g/cm³.

(d) Union Carbide gas phase process

HDPE is produced by a gas phase process developed at Union Carbide and known as Unipol process [25,26]. Ethylene serves at the same time as fluidizing gas and as reactant. No solvent is employed and hence there are no solvent recovery costs, the consumption of energy is lower and the process is simpler to operate.

The reaction is carried out at 75–100°C and 0.7–2 MPa (7–20 atmospheres). The Unipol technology employs highly effective transition metal catalysts of the Phillips-type (chromium oxide) or Ziegler-type (mostly titanium). Phillips catalysts consist of bis-tri-phenylsilyl chromate or of chromocene, $(C_5H_5)_2Cr$, on dehydrated silica support. The granules of PE

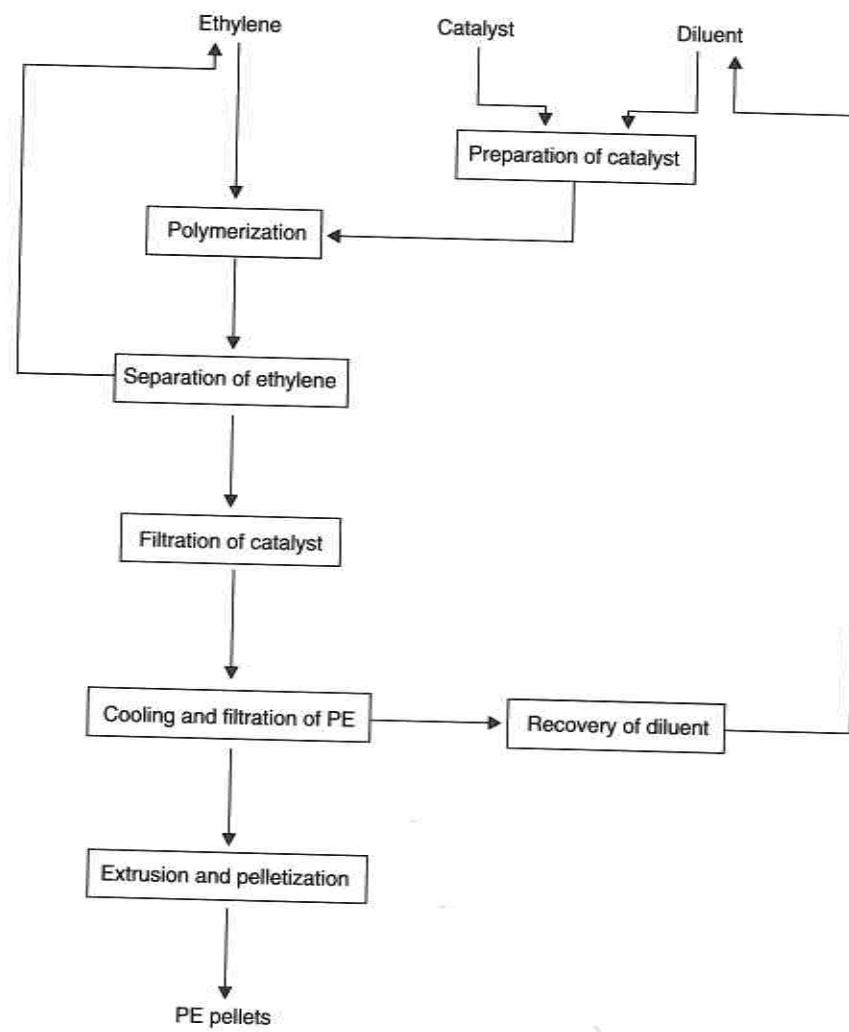


Figure 1.3 Phillips process for ethylene polymerization.

formed on the catalyst particles are in fluidized bed. Only about 2% of ethylene is polymerized at each pass and large flows are to be recycled but the overall conversion of ethylene is 97% [10].

PEs produced by this process have densities of 0.94–0.96 g/cm³. They can be obtained with any desired MW and MWD using hydrogen as the MW regulator and multistep process technology where bimodal or broad MWD are required.

Since only small amounts of very effective catalysts are used in the process, the PE is not separated from the catalyst.

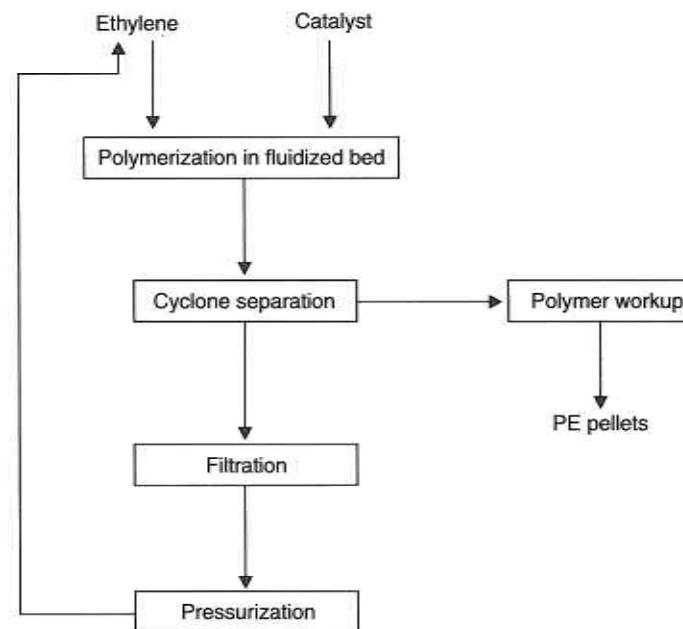


Figure 1.4 Gas phase process for ethylene polymerization.

Additional treatment for PE is used in conjunction with the main reactor. It consists of the incorporation of slip, antiblock and antioxidant additives into the granular particles of PE and thus the need for pelletizing is eliminated [10].

The flow chart of the gas phase process for the production of HDPE is presented in Figure 1.4.

Of all the methods for manufacturing PEs, the gas phase process is overwhelmingly preferred and still in expansion, due to its low cost and product flexibility (or ‘swing’ capacity) [6].

(e) Metallocene-based process

The newest type of catalysts for the polymerization of olefins has variously been termed Kaminsky-type, single-site, constrained-geometry or metallocene catalysts. The novelty of these soluble catalyst systems is that they allow a very precise control of the uniformity of chain length, degree of branching and stereoregularity leading to tailor-made polymers with predictable properties. In copolymerization processes, these catalysts show the capability of a rigorous control of the incorporation of comonomers into the polymer.

Metallocenes are extremely efficient catalyst systems, allowing yields in excess of one ton of polymer per gram of catalyst per hour [7]. Efficiencies as high as 25 tons of PE per gram have been reported [27].

Hundreds of published papers and patents describe an extremely large number of metallocene complexes in the polymerization of olefins but their detailed presentation is beyond the frame of this book. Various methodologies have been utilized to synthesize metallocenes with well defined electronic and steric structures [28].

In principle, a metallocene derivative has the formula L_2MX_2 , where M is a Group IV transition metal such as titanium, zirconium or hafnium; X may be a halogen or an alkyl, phenyl, benzyl or a trimethylsilyl group; and L is a ligand associated to the metal atom by π -bonds. The ligands may be the cyclopentadienyl (Cp), the indenyl (Ind) or the fluorenyl (Flu) anions. The ligands may be unsubstituted (I) or may bring one or several substituents (II). The ligands may be independent of each other in non-stereorigid metallocenes (I and II) or may be linked by an ethylene or isopropylene bridge in stereorigid metallocenes (III). Some examples are given below:



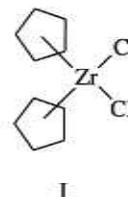
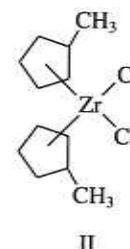
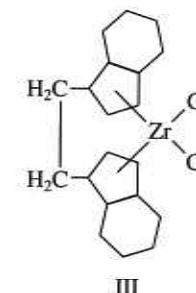
Cyclopentadienyl (Cp)



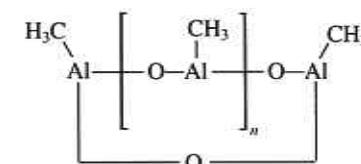
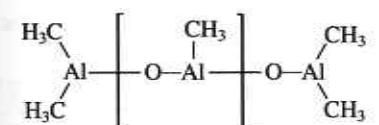
Indenyl (Ind)



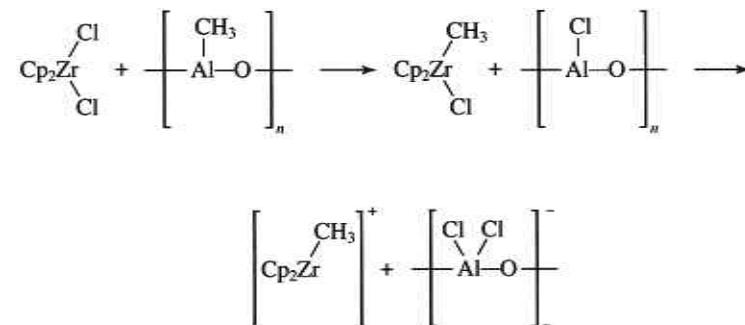
Fluorenyl (Flu)

Bis(cyclopentadienyl)
zirconocene dichloride
 Cp_2ZrCl_2 Bis(methylcyclopentadienyl)
zirconocene dichloride
 $(MeCp)_2ZrCl_2$ Ethylene bis(indenyl)
zirconocene dichloride
 $Et(Ind)_2ZrCl_2$

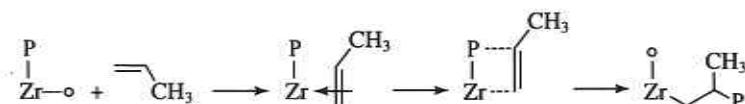
Two categories of metallocene complexes have been used, bicomponent systems and single component systems. Besides the metallocene, the bicomponent complexes contain an alumoxane compound as cocatalyst. There are some uncertainties concerning the structure and the role of the alumoxane despite the numerous physicochemical measurements. Methyl alumoxane ($AlMeO)_n$ contains alternating aluminum and oxygen atoms and it is considered to be an oligomeric chain or ring compound whose molecules are associated in supramolecular aggregates [29]:



The alumoxane acts as a soluble carrier-activator producing and stabilizing metallocene cations $[Cp_2ZrCH_3]^+$ that are actual active species [30,31]



During the polymerization, the monomer is coordinated with the highly electrophilic and coordinatively unsaturated cationic complex followed by the insertion of the monomer into the metal-carbon bond that occurs through a four-center transition state. The polymer chain migrates and a vacant coordination site is reformed at the site originally occupied by the polymer chain [32]:



where P = polymer; o = vacant coordination site.

In metallocene catalyzed olefin polymerization, the termination of the polymer chain may occur through chain transfer to aluminum, to monomer or to hydrogen or to β -H or β -methyl eliminations depending on the conditions [28].

A judicious balance of electronic and steric effects is necessary for designing metallocenes of high productivity and strict control on the MW and MWD. The productivity in the homopolymerization of ethylene decreases by changing the metal in the order $Zr > Ti > Hf$. In the metallocene Cp_2ZrR_2 the nature of the sigma ligand, R, increases the productivity and the MW in the order $R = Me < Ph < CH_2Ph < CH_2SiMe_3$ [33]. Mono-substituted cyclopentadienyl ligands with electron donating groups enhance the productivity whereas polysubstituted and steric crowded cyclopentadienyls lower the productivity. Monomodal or bimodal MWD = 5.5–10

have been obtained by changing the composition of the metallocene complex [28].

Factors such as the composition of the cocatalyst, i.e. the ratio methyl-aluminum/alumoxane as well as the ratio catalyst/cocatalyst, influence the productivity, the MW and the evolution of the rate of polymerization in time (kinetic profile). A minimum ratio Al/Zr of 3000 represents a threshold value for the activity of the catalyst [34].

An optimum temperature for maximum productivity has been found for each metallocene system. The yield of PE increases between 0 and 40°C but higher MWs are obtained at lower temperatures. Temperatures between 40 and 60°C lead to bimodal distributions. Hydrogen is used as a MW regulator. Toluene has been found to be the best solvent for maximum catalytic activity of the metallocene.

Supported metallocenes are under study in order to control polymer morphology better [28]. They require several-fold less alumoxane cocatalyst compared to unsupported metallocenes. The silica and MgCl₂ support help to adsorb Cp₂MR⁺ active species and thus to prevent their precocious deactivation [35].

The second category of metallocenes are the single-component systems which are ionic complexes with the general formula [Cp₂MR]⁺[B(C₆F₅)₄]⁻. They polymerize olefins without the utilization of alumoxane cocatalyst. The active species is the metallocene cation [Cp₂MR]⁺ which is stabilized by the use of counteranions such as tetraphenylborate, B(C₆H₅)₄⁻ or fluorinated tetraphenylborate, B(C₆F₅)₄⁻. The MW, MWD and yield of PE depend on the nature of the ligands, metals and counterions in the ionic metallocene complex as well as on the solvent polarity and temperature. The polymerization productivity increases in the following order: [(Ind)₂TiMe]⁺ > [Cp₂TiMe]⁺ > [Cp₂ZrMe]⁺ [36]. The optimum temperature is between -20°C and 15°C.

The exploitation of metallocenes is on a precommercial scale due to their prohibitive cost but it is fully expected that within a few years they will begin to be applied to the lower-price, larger-volume commodity markets [7]. Metallocene systems have been devised that are compatible with all existing polyolefin manufacturing technologies, and in most cases, they could be used in existing units to replace catalyst systems [7].

1.1.4 Linear low and very low density polyethylenes (LLDPE and VLDPE)

Different grades of PE are the linear LLDPEs which do not have long branches. Their density is kept in the low range (0.880–0.925 g/cm³) by the deliberate introduction of a controlled amount of short branches of the desired length [37]. The word 'linear' refers to the absence of long branches. The molecules of LDPE, HDPE and LLDPE are represented schematically in Figure 1.5.

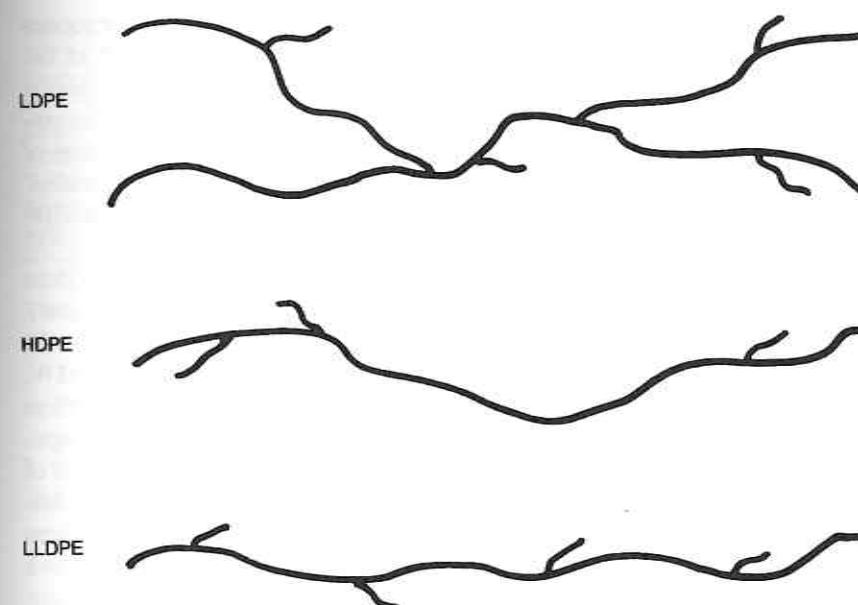


Figure 1.5 Schematic representation of the structures of various polyethylenes.

In fact, LLDPEs are copolymers of ethylene and another 1-olefin, such as 1-butylene, 1-hexene, 4-methyl-1-pentene or 1-octene. New generations of 'super strength' grades have been prepared most recently using higher olefin comonomers [1,6]. The length and position of the side chains are controlled by the comonomers used and by the catalyst system. Both the comonomer type and the polymerization conditions affect the properties of the copolymer.

The distribution of comonomers may be statistical or irregular (blocks). Statistical copolymers have lower density and crystallinity than the block copolymers.

LLDPE is produced basically by two types of low pressure processes, the gas phase and the solution processes [38]. Both the processes have been adapted from HDPE and many companies have swing capacities.

The gas phase fluidized bed process, initially developed at Union Carbide for the production of HDPE, has been modified for the production of LLDPE [39]. The reactor is operated at 80–100°C and 2.1 MPa (21 atmospheres) in the presence of a titanium-containing catalyst. It is now possible to obtain a complete array of LLDPE by the gas phase polymerization process.

Du Pont, Canada, was the first company to produce LLDPE. They have used a solution process at 150–300°C, 3–5 MPa (30–50 atmospheres) and a Ziegler-type catalyst [37].

DSC and TREF studies on LLDPE manufactured by different processes (gas, slurry, bulk and solution) have shown a bimodal distribution of the MW and a heterogeneous distribution of side branches [12]. The explanation is based on the existence of two groups of active sites in Ti-based heterogeneous Ziegler catalysts that produce different copolymerization rates of comonomers. In order to obtain a proper distribution of the side branches, the developed catalysts have to provide controlled rates of the copolymerization of comonomers.

Limited studies have been conducted on the copolymerization of ethylene with 1-butylene, 1-hexene and 4-methyl-1-pentene using metallocene-alumoxane catalyst systems [28]. The composition of the catalyst, the temperature and the concentration of comonomers determine the MW, MWD and the reactivity ratios. The reactivity ratios product ($r_1 r_2$) of less than 1 suggests an alternating sequence for the insertion of the monomers.

VLDPE ranges in density from 0.880 and 0.912 g/cm³. Their low degree of crystallinity imparts outstanding low temperature impact properties, flexibility and increased permeability to gases. These characteristics made them suitable materials for geomembranes, agricultural film, packaging for fresh produce and impact modifiers.

1.1.5 High and ultrahigh molecular weight polyethylenes

High molecular weight (HMW-HDPE) and ultrahigh molecular weight (UHMW-PE) polyethylenes are both HDPE with MW in the range 300 000–500 000 and 3–6 million respectively [40].

HMW-HDPE is produced by processes similar to those used for HDPE. The commercial process is based on a modified Ziegler catalyst system and the polymer is produced in the form of fine powder. The higher MW of these resins requires a broader polydispersity for acceptable processing characteristics. Typically these resins have bimodal MWD, the very high MW fractions impart strength and toughness while the low MW fractions facilitate extrusion [6].

UHMW-PE has essentially no flow above melting point due to its exceptionally high MW. Fabrication techniques are similar to that of metalworking, more intricate parts being machined from the solid resin.

UHMW-PE have a unique combination of physical and chemical properties such as exceptional impact strength at cryogenic temperatures, outstanding stress-crack resistance and the highest slurry-abrasion resistance of any thermoplastic. It therefore finds application in machine parts for service under severe conditions such as ore handling and food processing.

UHMW-PE is used to produce extended chain fibers (ECPE), the highest modulus and highest strength fibers ever made [41]. This enables PE to enter the field of specialized, high performance materials. The polymer is dissolved in a suitable solvent where the chains are disentangled and become extended.

Table 1.1 Comparison of some tensile properties of high performance fibers

Property	ECPE	Aramid	Glass	Carbon
Density (g/cm ³)	0.97	1.44	2.49	1.86
Tensile strength (MPa)	3000	2760	4590	2590
Tensile modulus (GPa)	172	131	90	393
Specific strength (cm × 10 ⁶)	31.5	19.8	18.8	13.7
Specific modulus (cm × 10 ⁶)	1813	927	355	2160

Then the solution is spun on conventional melt spinning equipment. The fibers are subsequently dried and postdrawn. The fibers acquire a specific structure in which all the macromolecules have fully extended chains oriented in the direction of the fiber so that the fiber is similar to a bundle of rods. The degree of crystalline orientation of the fibers is 95–99%.

Tensile properties of ECPE fibers are similar to other high performance fibers; however, because the density of PE is approximately two-thirds that of high modulus aramid fibers and half that of high modulus carbon fiber, ECPEs possess the highest ever obtained specific strength and specific moduli as can be seen from Table 1.1 [41].

1.1.6 Properties of polyethylenes

(a) Mechanical and thermal properties

There are available many hundreds of grades of PE which differ in their properties in one way or another. The main structural factors that determine PE properties are the degree of short and of long chain branching, the average MW and the polydispersity.

One of the most important characteristics that determines in the highest degree the properties and the behavior of different grades of PE is their branching. As has been mentioned in preceding sections, the number and the length of branches are controlled by the type and parameters of the polymerization process (temperature, pressure, type and amount of catalyst or initiator and of transfer agent, etc.). Branches prevent the polymer chains from packing together regularly and closely and have a predominant effect on the density of PE. The highest density for this family of polymers is about 0.98 g/cm³ and is reached by the strictly linear polymer – the polymethylene – obtained from diazomethane and which is a useful reference. The density can be considered a first indication of the degree of branching – the lower the density the higher the degree of branching [37]. The effect of density on some general properties of PE is illustrated in Figure 1.6.

The presence of branches interferes with the ability of the polymer to crystallize. The degree of crystallinity of LDPE is usually of the order of 55–70% compared with that of HDPE which is 75–90%. The crystalline

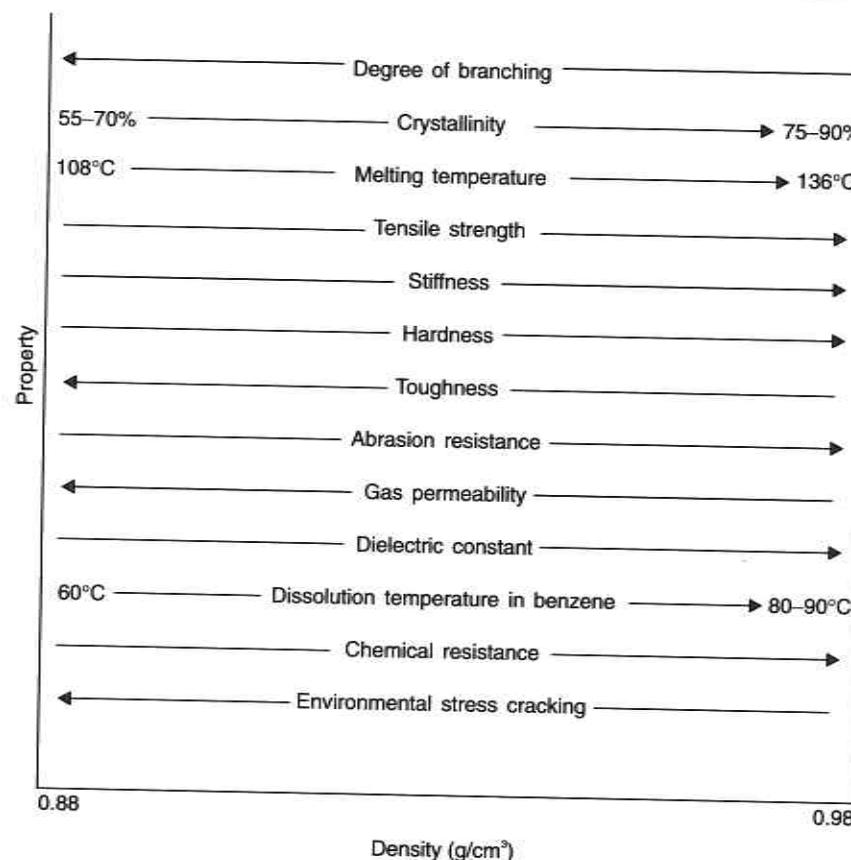


Figure 1.6 Effect of density on polyethylene properties.

T_m for PEs ranges from 108 to 132°C depending on the degree of crystallinity. Such low melting points are characteristic for structures with flexible C–C bonds and without strong intermolecular forces. T_g , which is associated with the motion of longer segments in amorphous matter, is reported in the literature as ranging between –60 and +130°C, the most likely value being considered –20°C [19].

The specific heat (C_p) of PE is higher than for most thermoplastics and strongly depends on the temperature. Values of 2.3 J/g are specific at room temperature and 2.9 J/g at 120–140°C for LDPE. This is an important feature for the processing of polyethylene.

Other properties depending on crystallinity, such as stiffness, hardness, tear strength, yield point, Young's modulus in tension and chemical resistance, increase with increasing degree of crystallinity (HDPE) whereas permeability to liquids and gases, flexibility and toughness decrease under the same conditions.

Since PE is crystalline non-polar hydrocarbon polymer it has no solvents at room temperature and dissolution takes place only on heating in solvents of similar solubility parameter (hydrocarbons and halogenated hydrocarbons). The higher the degree of crystallinity, the higher the dissolution temperature. LDPE dissolves at 60°C compared to 80–90°C for high density, more crystalline polymers.

The effect of branching also depends on the size of side chain branches. While short branches have a predominant influence on the degree of crystallinity and therefore on the density of the polymer, long branches affect more pronouncedly the polydispersity. The side chains may be as long as the main chain and like it may have a wide distribution of lengths. The higher the MW of the resulting polymer the wider the MWD, as chain transfer reactions may occur as well on side chains. Such a polymer may be made up of short chains grafted onto short chains, long chains onto long chains and a vast range of intermediate cases.

The ratio of weight- to number-average molecular weight (MWD) varies from 1.9 (for polymethylene) to 100; values of 20–50 are considered typical. High density polymers have MWD values of 4–15 [37]. The very high values of MWD for LDPEs are, in part, the result of long chain branching and sometimes it is not clear if an effect on the properties is due to branching or to MWD. It is generally considered, however, that when the other structural factors are constant, a narrower MWD leads to an increase in impact strength, tensile strength, toughness, softening point and resistance to environmental stress cracking.

Long chain branches also affect the flow properties. Long branched molecules are more compact and tend to entangle less with other molecules resulting in lower solution and melt viscosities as compared with unbranched polymers.

Another factor that influences the properties of the melt, as well as those properties that involve large deformations, is the weight-average MW. Ultimate tensile strength, tear strength, low temperature toughness, softening temperature, impact strength and environmental stress cracking increase as the MW increases; on the contrary, the fluidity of the melt and the coefficient of friction (film) decrease.

For technological purposes, the MW is characterized by the melt flow index (MFI) that is the weight in grams extruded under a standard load in a standard plastometer at 190°C in 10 minutes [42]. The higher is the MFI, the lower is the MW. However, MFI has to be considered carefully as the viscosity of the melt is strongly affected by the presence of long chain branches as has already been mentioned.

The influence of the density on some properties of different grades of PEs is illustrated in Table 1.2 [10,11,19,38,40].

The electrical insulating properties of PEs are excellent. The dielectric constant increases linearly with increasing density. As it is a non-polar material,

Table 1.2 Some properties of different grades of polyethylene

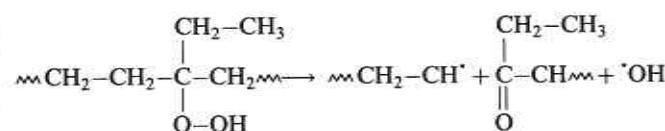
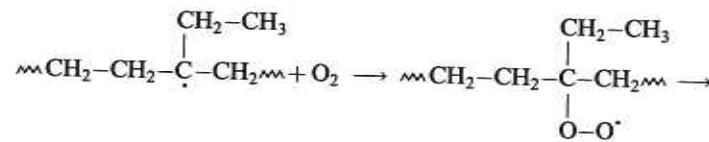
<i>Property</i>	<i>LLDPE</i>	<i>LDPE</i>	<i>HDPE</i>	<i>UHMW-PE</i>	<i>Poly-methylene</i>
Density (g/cm ³)	0.910–0.925	0.915–0.935	0.941–0.967	0.93	0.98
Melting temperature (°C)	125	106–112	130–133	132	136
Tensile strength (MPa)	14–21	6.9–17.2	18–30	20–41	34.5
Elongation at break (%)	200–1200	100–700	100–1000	300	500
Flexural modulus (MPa)	248–365	415–795	689–1654	—	—
Izod impact strength (J/m)	—	0.67–21	27–160	no break	—
Hardness (Shore D)	41–53	45–60	60–70	—	—

the dielectric constant and the power factor are almost independent of temperature and frequency. The presence of impurities such as metallic catalyst fragments or carbonyl groups formed by the oxidation of the PE has an adverse influence on the power factor.

(b) *Degradation*

PE has a chemical resistance similar to that of paraffins. Non-oxidizing acids, alkalis and aqueous solutions do not attack PE. On the contrary, PE is sensitive to oxidation that occurs on exposure to strong oxidizing agents (concentrated nitric acid, hydrogen peroxide or potassium permanganate), or even in air under ultraviolet light as well as at elevated temperatures during processing or service life. Resistance to oxidation increases with increasing density because a less branched polymer has a diminished permeability to gases and a smaller number of tertiary carbon atoms in the molecule (which constitute sensitive points of attack). Traces of metals (catalysts) enhance the oxidation process.

The oxidation proceeds by a free radical mechanism through the formation of hydroperoxides which decompose to new free radicals and the reaction is autocatalytic. Two kinds of reactions take place on oxidation.
 (a) The scission of polymer chains that leads to a deterioration of the mechanical properties as a result of the reduction of the MW.



(b) At higher levels of oxidation, combination reactions between existing radicals result in crosslinking of polymer chains and the formation of brittle products.

As a result of oxidation, there is a serious deterioration of the power factor and of electrical properties. The incorporation of antioxidants in PE is necessary for electrical insulation applications in order to reduce this effect.

Exposed under a certain stress or strain to some liquids such as alcohols, sulfonated alcohols, liquid hydrocarbons, esters, ketones, metallic soaps, silicone fluids, greases and oils, PE undergoes a fracture in a much shorter time than in the absence of this environment. This phenomenon is known as 'environmental stress cracking'. Some stress may remain in the material as a result of processing or may be due to distortion during use. The resistance to environmental stress cracking may be much improved by good processing conditions and good design of specific products.

(c) Additives and processing

PE is often used without the addition of any additive, but different types of additives may be incorporated into the polymer in order to impart various properties [43]. For long-term applications, especially as an electrical insulator, PE is blended with antioxidants which provide protection against oxidative degradation. Hindered phenols in small amounts (up to 0.1%) are used almost exclusively as chain breaking antioxidants. They block the hydroperoxide radicals formed by oxidation and thus interrupt the propagation of the oxidative process: the new aromatic radicals formed from phenols are too stable and are unable to propagate the oxidative chain.

Reinforcing fillers such as carbon black or still better silane and titanate coupling agents are used sometimes with PE. Pigments have to be chosen with special care to ensure that they do not catalyze the oxidation and do not bring about the rise of the power factor. Common pigments are compounds of cobalt, cadmium, manganese, iron or chromium.

As PE burns readily, halogenated compounds and antimony trioxide are used as flame retarders. Among other additives, antistatic agents of glycol alkyl ester type are widely used to reduce dust attraction. Antiblocking agents, such as fine silicas, are used to prevent the high cohesion between the layers of LDPE films and, in addition, slip agents are added in order to reduce the friction between film layers [19].

The addition of 10–40% starch to LDPE results in a biodegradable material used for carrier bags and for mulching of some crops. Starch decomposes in moist soils in one to five years and the remaining PE framework breaks up and is absorbed in the soil [44].

Products with a dielectric constant of about 1.45, useful as dielectric materials, can be obtained from cellular PE. Blowing agents such as 4,4-oxy-bis-benzenesulfonohydrazide and azocarbonamide are incorporated into the polymer, they decompose on extrusion and the evolved gas gives rise to a cellular extrudate.

PEs are processed almost exclusively by melt processing techniques. Extrusion, blow molding and injection molding are widely used with low, intermediate and high density polyethylenes. Mold shrinkage is 1.5–5.0% with LDPE and 2.5–6.0% with HDPE, the rather high values being due to the crystallization of the material.

There are basically two processes of making PE film, the tubular process and the flat film process. In the tubular process, used in larger proportion, a thin tube is extruded in a vertical upward direction and the tube is inflated into a bubble by blowing air through the die head. The bubble is cooled, flattened and wound up. In the flat film process, the film is extruded from a slit die either into a water bath or onto chilled rolls.

Coating with polyethylene is done by fluidized bed powder coating, by spraying, or by powder molding and powder rotational molding.

1.1.7 Applications

The widespread use of PE is due to its excellent electrical insulation properties and chemical resistance, easy processability and low cost.

A general overview of PE applications according to density and melt index is illustrated in Figure 1.7 [6]. The major applications of PEs (LDPE, LLDPE and HDPE) have been as film for general packaging (bags, sacks, food wrapping) and building and agricultural industries. HDPE film has also been used in a net-like form (or pseudofiber) [19].

PE (especially HDPE) is an important injection molding material for a wide range of products including toys, electrical fittings, seals, chemical plants, containers, cases, crates, housewares and many other applications. Specialized uses include the disposable syringes for medical purposes [19].

HDPE has been widely used for blow molding of bottles for milk and other foodstuffs, household chemicals and drug packaging. Squeeze bottles are made from LDPE.

Other areas for PE applications have been domestic water and gas piping, and agricultural piping [45]. PE has also been used as filament for ropes, fishing nets and fabrics.

Based on its excellent electrical insulation properties, PE has been extensively used in cable and wire covering (undersea cables) and air-borne

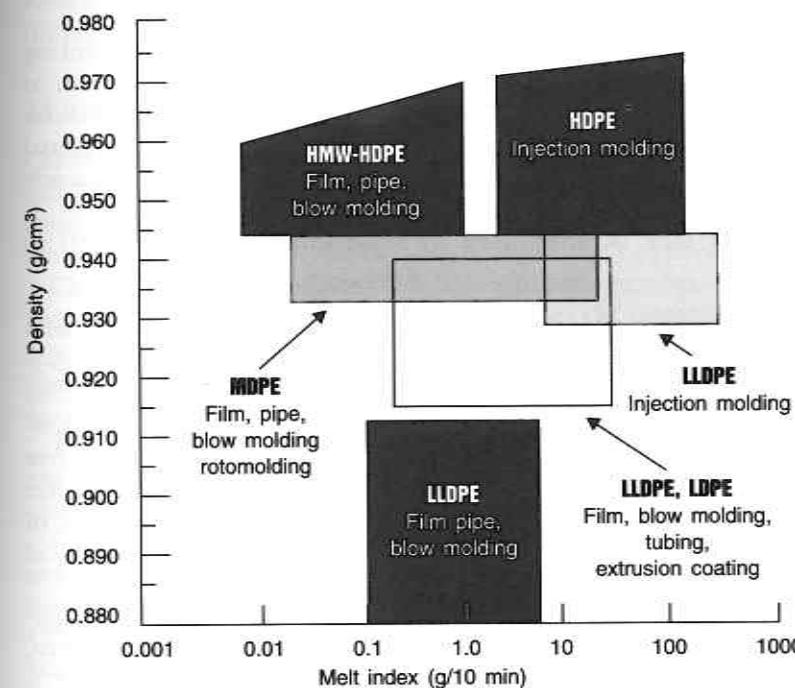


Figure 1.7 Polyethylene applications [6]. (Reprinted by special permission of McGraw-Hill, Inc., from *Modern Plastic Encyclopedia*, Vol. 71 (12), 1994. Copyright McGraw-Hill, Inc., New York, NY 10020.)

radar. Cellular PE with a very low dielectric constant (1.45) is used as insulator for television downlead aerials.

Synthetic wood pulp with cellulose-like morphology (fibriles) made from HDPE are used as battery separators and teabags [46].

Low MW oxidized PE (in the range of MW = 1000) is a wax-like product, water and chemical resistant. It constitutes an anticorrosion additive in lubricating wax formulations [47].

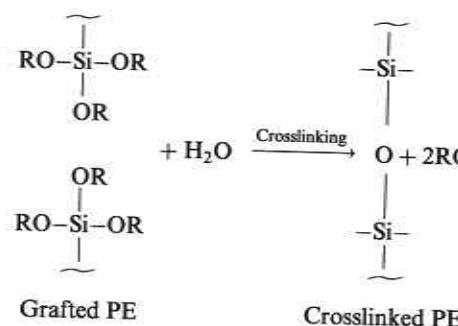
With the arrival on the market in 1985 of the ECPE fibers made from UHMW-PE, PE entered the specialized high performance composite industry. ECPE fibers are available in roving, fabric, continuous mat and chopped fiber. They have been used with a wide variety of resin systems imposed by the end-use application. Among the resin matrix are epoxies, polyesters, silicones, urethanes and polyethylene. For higher level of adhesion, specific surface treatments such as corona discharge or plasma treatments are applied to fibers [41]. They are used as reinforcing material for ballistic armor, radar protective domes, aerospace impact shields, sail cloth, marine ropes, sports equipment and concrete reinforcement [41,45].

1.1.8 Crosslinked polyethylene

A thermosetting PE has been obtained by a controlled process of crosslinking (vulcanization) [19]. The material has enhanced stability of the form at elevated temperatures, can withstand prolonged aging at 105°C or short-term exposures at 230°C and has a better resistance to environmental stress cracking. Crystallization is reduced by crosslinking and consequently modulus and hardness are lower.

Polyethylene may be crosslinked by three different processes [48] as follows.

1. Peroxide crosslinking is done by the incorporation of a peroxide with higher decomposition temperature such as dicumyl peroxide or di-*t*-butyl peroxide. The peroxides have to withstand temperatures during compounding and shaping operations and decompose only in a post-processing curing reaction at higher temperatures. The peroxide free radicals abstract hydrogen from the polymer leading to polymeric free radicals which combine to a network structure. The incorporation of carbon black into the PE before vulcanization improves the mechanical properties of the material.
2. Radiation crosslinking (X-rays, γ -rays or fast electrons) is done commercially on thin sections such as films. Small quantities of hydrogen, methane, ethane and propane are formed during irradiation and it seems that they result from the short side chains of the PE. Some insaturation is introduced in the PE by irradiation.
3. The third way for crosslinking is done by grafting onto the PE chain of trialkoxyvinylsilane compounds. The obtained trialkoxysilane PE is typically extruded onto a wire which is then treated with low pressure steam. The alkoxy groups hydrolyze with condensation leading to siloxane crosslinks:



Crosslinked PE has found application for insulating electrical power cables (which are subjected to elevated temperatures), transformers, motors and generators. Crosslinked cellular PEs, produced particularly in Japan,

have been used for carpeting in the automotive industry (sound deadening), for pipe insulation and as flotation media.

1.1.9 Chlorinated and chlorosulfonated polyethylenes

Chlorinated polyethylene (CPE) is produced commercially from both LDPE and HDPE. CPE has significant advantages compared to parent PE, such as an increased flexibility and toughness, ignition resistance, better filler acceptance and excellent compatibility with a large variety of polymers [49].

Chlorination may be effected in solution, in aqueous suspension or in fluid bed at temperatures in the range of 45–75°C in the presence of peroxides. Secondary hydrogen atoms are substituted by chlorine atoms that are distributed unevenly and are concentrated in certain regions of the macromolecules resulting in a block CPE.

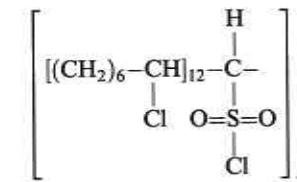
The properties of CPE depend on the properties of the starting material and on the amount and distribution of introduced chlorine. The end products can be thermoplastics or elastomers.

CPE with 25–30% Cl by weight is a thermoplastic material used as an impact modifier additive for rigid PVC and styrenic polymers leading to composite materials with improved impact strength for piping and sheathing. CPE with 36–48% Cl are elastomers that do not contain chain unsaturation and have improved oil, heat and aging resistance. CPE elastomers can perform continuously at 150°C and intermittently at 162°C, they retain their flexibility at –40°C and are used for cable sheathing and different technical goods [49]. Above 50% chlorine, the material becomes stiff.

CPEs have good resistance to most acids, bases, ozone, oil and fuel, and to many solvents.

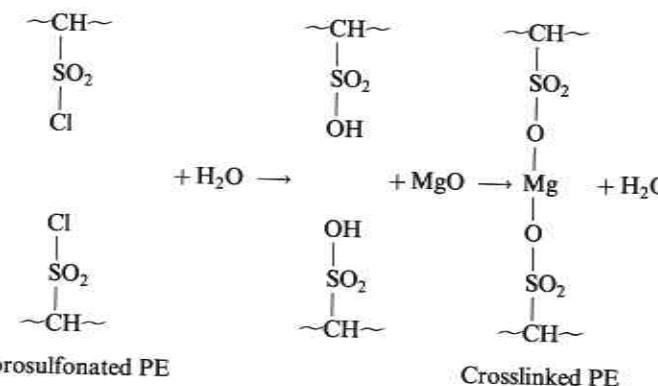
CPE elastomers are used for high performance applications such as wire jacketing, industrial and automotive hoses, tank linings and others.

When the chlorination of PE is conducted in the presence of sulfur dioxide, both chloride and sulfonyl chloride groups are introduced into the polymer, their ratio depending on the conditions of the process. Common commercial polymers contain about 1.5% sulfur and 30% chlorine, i.e. that some 25–42% of the monomer units are chlorinated. The polymer may be represented as follows:



The sulfonyl chloride groups serve to subsequently vulcanize the material. The vulcanization is effected in the presence of metal oxides (litharge, MgO)

and of water and results in a crosslinked structure:



The chlorosulfonated PE is a rubber with good resistance to oxidizing agents, such as oxygen and ozone, and excellent mechanical properties at elevated temperatures. It is used as a cable coating for special applications.

In the building industry, chlorosulfonated PE has been used as a rubber and sealant and also where resistance to weathering, corrosion or abrasion is required, e.g. flooring, lining for chemical plants, roofing, etc. [45].

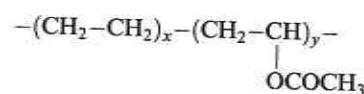
1.1.10 Ethylene copolymers

Ethylene is copolymerized with different olefinic or non-olefinic comonomers, in order to obtain more flexible and tougher materials, by the reduction of the degree of crystallinity and by the introduction of some polarity. Ethylene copolymers with higher olefins such as 1-butylene, 1-hexene and 1-octene have already been discussed as they are known as LLDPE. The copolymers with propylene will be discussed further.

In this section are presented the copolymers of ethylene with non-olefinic comonomers such as vinyl acetate, methyl and ethyl acrylates, acrylic and methacrylic acids. All these copolymers are prepared by free radical, high pressure polymerization technologies.

(a) Ethylene-vinyl acetate copolymers (EVAc)

EVAc is a random copolymer with the general formula:



The content of vinyl acetate varies between 5 and 50% and controls the crystallinity and the flexibility of the material. EVAc copolymers have improved clarity, low temperature flexibility, adhesion and stress cracking resistance but are more permeable to oxygen and vapors.

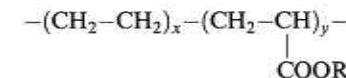
Depending on the composition and the MW of EVAc copolymers, they may have a low softening point and are used as wax additives or may be rubbery materials resembling LDPE in appearance. EVAc copolymers have good compatibility with bitumen and these mixtures are used for roof sheeting with improved properties [45].

EVAc copolymers with 5% VAc are used for film applications in packaging; with 10% VAc for extrusion and injection molding of flexible tubing and hose, footwear components, gaskets and squeeze bulbs; with 20% VAc they enter into hot-melt-adhesive formulations [48].

By the hydrolysis of the acetate moiety in EVAc, the copolymer ethylene-vinyl alcohol is prepared. This copolymer has excellent gas barrier properties associated with high moisture absorption. It has found use in multilayer film for food packaging.

(b) Ethylene-methyl acrylate (EMA) and ethylene-ethyl acrylate (EEA) copolymers

They are copolymers containing up to 20% acrylic comonomer [50] and may be represented as:



where R = CH₃ or C₂H₅

Compared to EVAc copolymers, they have better thermal and abrasion resistance but lower clarity and toughness. They are used for extrusion and injection molding of different items.

(c) Ethylene-acrylic acid (EAA) and ethylene-methacrylic acid (EMAA)

They may be represented as:

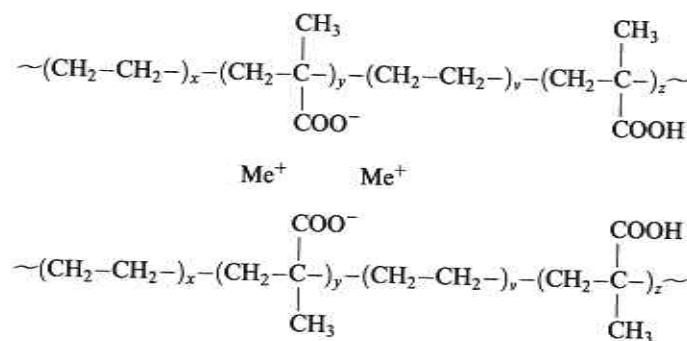


These copolymers exhibit very good adhesion to different substrates and particularly to metals due to their increased polarity compared to PE. Their current usage is as adhesive layers between aluminum foil and plastic films for applications such as toothpaste tubes.

(d) Ethylene-methacrylic acid ionomers

The term 'ionomer' refers to any copolymer of 1-olefins containing acid groups (carboxylic or sulfonic) but only ethylene-methacrylic acid ionomers have achieved significant commercial production.

They are produced by the high pressure copolymerization of ethylene with 1–10% methacrylic acid followed by partial neutralization of the carboxylic groups with a metal cation (sodium, magnesium, zinc). They may be represented as:



An ionic crosslink is formed which is stable at ambient temperature, but which reversibly breaks down on heating. The ionomers behave like thermosets at room temperature, but like thermoplastics on heating and they can be melt-processed by usual techniques.

The structure of ionomers consists of three molecularly interconnected different phases: an amorphous hydrocarbon phase, a fringed micellar crystal

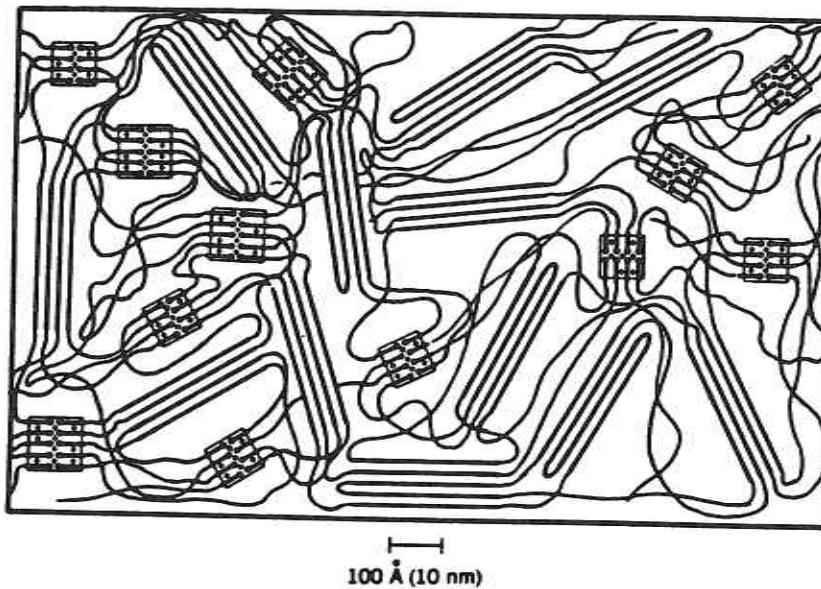


Figure 1.8 Schematic structure of ionomers [52]. (Reprinted by permission of J. Wiley & Sons, Inc., from *Handbook of Plastic Materials and Technology* by L.I. Rubin (ed.), 1990. Copyright J. Wiley & Sons, Inc.)

of PE and a layered ionic cluster [51]. Figure 1.8 represents a schematic structure of a ionomer [52].

Compared with LDPE, the ionomers have higher toughness, tensile strength and modulus, greater clarity and better abrasion and oil resistance. Recently, glass fiber ionomer composites have been introduced that have superior low temperature properties (at -29°C) and higher modulus (1034–2241 MPa) than unreinforced ionomers (172–345 MPa).

The ionomers are used as film and sheet with excellent optical properties and heat sealability for various food packaging. Injection moldings are used in footwear and ski boots. Ionomers' cut-through resistance and toughness make them superior materials for golf ball covers.

(e) Ethylene–carbon monoxide copolymers

Alternating copolymers are prepared by gas phase catalyzed copolymerization of ethylene and carbon monoxide [53]. The copolymers contain ketone groups in the main chain which absorb light that makes them photodegradable materials by chain scission [54]. They are used as packaging and sheeting film.

1.2 POLYPROPYLENE (PP)

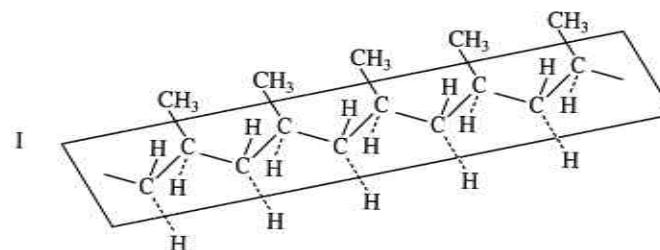
1.2.1 Introduction

PP is a major volume thermoplastic material ranked third in the production of plastics, after PE and PVC. Due to its cost effectiveness, versatility, overall competitiveness and excellent environmental aspects, PP is the fastest growing commodity plastic. Advanced polymerization processes in conjunction with highly developed compounding techniques make it possible to target PP for engineering applications. The world production volume was about 19 million tons in 1995, including 4.7 million tons in the US alone [55].

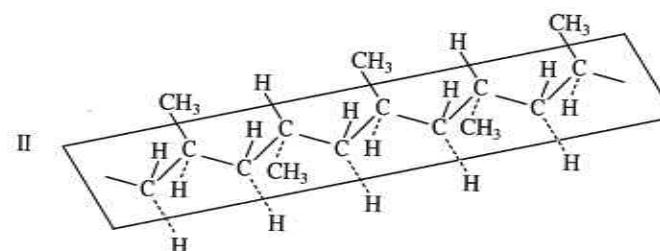
PP is produced by the stereospecific addition polymerization of propylene. The common name of the polymer is polypropylene, which corresponds fairly well with the name recommended by IUPAC where the repeating propylene unit is in brackets.

Commercial production of PP started in 1957 at Montecatini, Italy, at Hercules, USA, and at Farbewerke Hoechst AG, Germany, and was the result of the discovery of heterogeneous stereospecific catalysts by Ziegler in Germany that effected the polymerization of ethylene in 1953. Using these catalysts, Natta in Italy obtained in 1954 crystalline polymers of propylene. Earlier efforts to polymerize propylene had only resulted in amorphous polymers without any use at that time. Natta classified the three geometric forms adopted by the polymer chain of PP as follows.

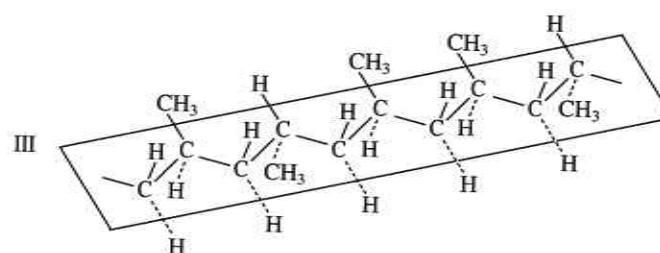
I. Isotactic; all methyl groups are situated on the same side of the chain.



II. Syndiotactic; methyl groups are on alternating sides.



III. Atactic; methyl groups are situated at random.



Isotactic and syndiotactic PPs are crystalline, whereas atactic polymer is amorphous.

As for ethylene, the raw materials for propylene are petroleum and natural gas from which the C₃ fraction is obtained after cracking and fractional distillation. Impurities such as water and methylacetylene must be carefully removed and the purity of propylene brought up to 99.7% [56].

Three different categories of PP materials are produced commercially: homopolymers, copolymers and blends.

1.2.2 Polymerization

The polymerization of propylene is effected in the presence of Ziegler-type catalysts which are composed of the reaction products of titanium trichloride

with aluminum compounds such as aluminum triethyl or tributyl or aluminum diethyl monochloride. These compounds form a 10% slurry in a diluent such as naphtha. The preparation of the catalyst for propylene polymerization is the most important step in the overall process. The composition of the catalyst as well as the shape and size of its particles are determinant for the properties of the polymer [57,58]. A good catalyst should produce high yield of polymer per part of catalyst, with a high content of isotactic PP, and with controlled MW and morphology. MWD are generally broader when insoluble catalysts are used and much narrower with soluble catalysts [59]. Hydrogen is used for MW control.

The different technologies that are used for the polymerization of propylene using Ziegler-type catalysts are (a) the slurry processes including the bulk process, (b) the solution process and (c) the gas phase process.

(a) The slurry processes

The oldest and the major processes are the slurry processes [60]. The polymerization resembles the Ziegler process described for PE. It may be carried out either in stirred batch reactors or in continuous loop reactors. The suspending liquid (C₄–C₆ paraffins), the catalyst and the propylene are metered separately into the reactor and the polymerization is conducted at 50–80°C and 0.5–3.0 MPa (5–30 atmospheres). The required isotactic polymer develops around the catalyst particles and forms a slurry since it is insoluble in the diluent. Some atactic amorphous polymer that is also formed is largely soluble in the diluent. The addition of the monomer is continued until the slurry reaches 30–60% solids. At this point the reaction mixture is transferred to a flash tank for the removal and recycling of unreacted monomer. The catalyst is then solubilized and deactivated by the addition of an acidified alcohol. The slurry is centrifuged for the separation of the crystalline isotactic polymer from the diluent which contains the soluble atactic polymer and the solubilized catalyst. The polymer is washed and dried. The flow chart of the slurry process is presented in Figure 1.9.

The newer, high activity and high stereospecificity magnesium-supported catalyst systems provide high enough yields of polymer per unit of catalyst so that the removal of the catalyst becomes unnecessary. Thus, 40 kilograms of PP are produced with today's catalysts compared to only 4 kg/g produced in the 1970s [61]. The ratio of isotactic/atactic PP is also improved and the separation of atactic polymer is no more required [60]. With some catalysts, polypropylene may be produced as dense spherical granules so that a pelletizing operation is avoided [62,63].

A variant of the slurry polymerization technology is the bulk process in which liquid monomer serves both as reactant and as suspending liquid for the resulting PP [56]. Temperature and pressure are adjusted to 45–80°C

POLYOLEFINS

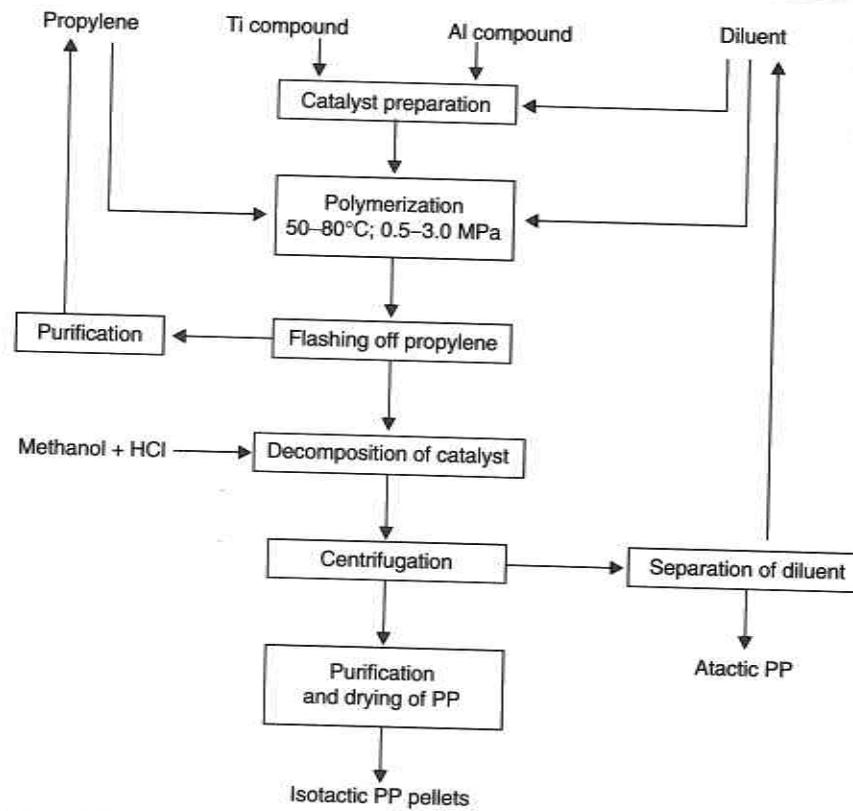


Figure 1.9 Polymerization of propylene by the slurry process.

and 1.7–3.5 MPa, respectively, in order to maintain the propylene in the liquid phase. PP results as a slurry in liquid monomer and is continuously withdrawn from the reactor when the slurry reaches 30–50% solids. In the flash chamber the unreacted monomer is eliminated and the polymer forms a powder that is subsequently dried and pelletized with stabilizers.

The slurry processes, which have been dominating the field for a long time, are increasingly giving way to superior gas phase technologies and to a combination of bulk and gas phase techniques [55].

(b) The solution process

In solution processes that are more expensive and hence used only for specialty products, higher temperatures (160–250°C) and pressures (2.7–8.0 MPa) are employed in order to dissolve the native polymer in the liquid monomer. PP produced in this process has higher impact strength and lower brittleness temperatures than conventional PP.

POLYPROPYLENE

(c) The gas phase process

The gas phase fluidized bed process introduced by Union Carbide for the production of LLDPE has been adapted for the polymerization of propylene to homopolymers or block copolymers [64,65]. The plants are equipped with swing capacities for the transition from PE to PP and back to PE [66]. Fluidization is maintained by the high rate of gaseous monomer recycle. The reactor has two zones: the reaction zone at the bottom where the catalyst and the growing polymer particles are fluidized by the gas stream of monomer and the disengagement zone at the top where the unreacted monomer and the solid particles separate. The gas is recycled while the polymer particles fall down and are continuously withdrawn. The polymer may be obtained in granular form with spherical morphology which eliminates any pelletizing operation [55]. The flow chart of the fluidized bed process is presented in Figure 1.10.

Compared to conventional PP, the property spectrum of the new PP types makes it possible to rate them as advanced materials designed for engineering applications. The technologies of the preparation of highly active catalysts and the state-of-the-art polymerization processes are highly proprietary and little information on any details can be found in the literature.

Totally new metallocene-based catalyst systems are entering the PP manufacturing technology. The general description of metallocene catalysts is given in Section 1.1.3(e). Such factors as the temperature, the transition metal (Ti, Zr, Hf), the ratio alumoxane/metallocene, the substitution in

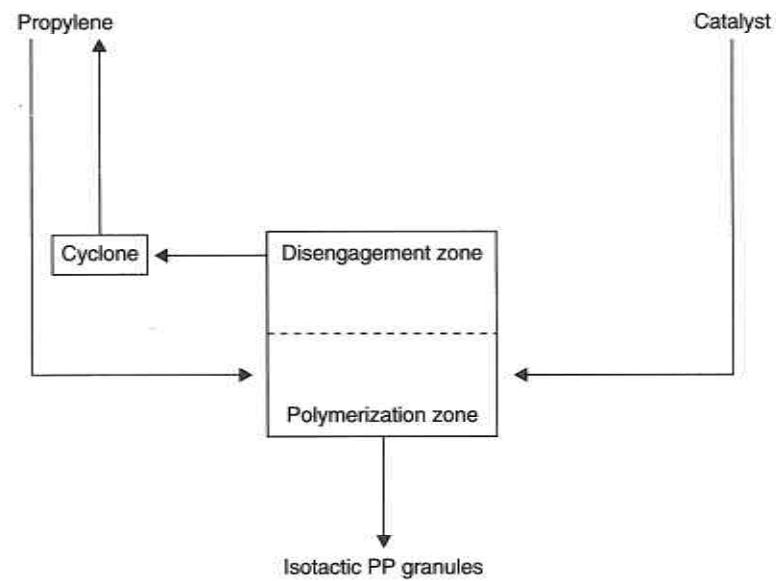
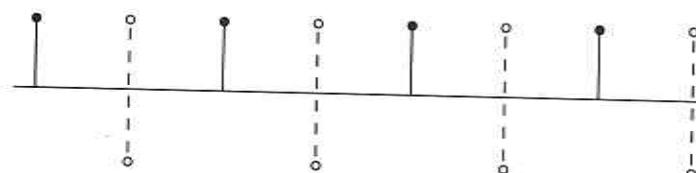


Figure 1.10 Gas phase fluidized bed polymerization of propylene.

the ligands (position, number and type of substituents) directly control the catalytic activity, the average MW, the MWD, the degree of tacticity, the sequence distribution and the microstructure of PP [28].

Stereoregulation in the polymerization of propylene is one of the most important capabilities of metallocenes. The possibility of steric design of the π -ligands (cyclopentadienyl, indenyl and fluorenyl) allows the synthesis of metallocenes with different symmetries, each giving rise to different stereo-regulated PPs. Four types of PP can be produced [28]: isotactic, syndiotactic, atactic and hemiisotactic. In hemiisotactic structures every other methyl group is in isotactic placement and the remaining methyls are placed at random [28]:



where • = isotactic placement; ○ = random placement.

The stereoregularity of the PP is controlled in two different ways: (a) by the chirality of the catalyst which governs the insertion of the monomer into the metal–carbon bond (enantiomorphic site control) and (b) in the case of achiral metallocenes, the tacticity is controlled by the configuration (chirality) of the last inserted monomer unit (chain end control) [28]. The tacticity of the PP is mostly affected by the symmetry of the metallocene [68].

Spherical megaparticles of PP are formed with metallocene systems that are quite different as compared with the particles obtained with conventional Ziegler catalysts [28].

Supported metallocenes on silica or $MgCl_2$ have also been studied.

Cationic metallocenes give productivities that are six times higher than metallocene/alumoxane systems and the stereospecificity is higher at low temperatures (96.3% isotactic PP at $-55^\circ C$) [69].

1.2.3 Properties

The tacticity of PP plays a major role in determining its properties. The isotactic PP has the most regular structure with the carbon chains arranged into right-hand and left-hand helices. Each turn of the helix is formed by three monomer units. The methyl groups are on the outside of the helix. These regular helices can pack closely together to form crystalline regions. Commercial polymers are 75–98% isotactic and may contain some atactic and syndiotactic forms as separate macromolecules or as blocks. Stereoblock chains may also be present in which right-hand and left-hand blocks alternate. When the inversion of these blocks is not frequent the polymers

behave like isotactic structures. The greater the amount of isotactic structure, the higher the degree of crystallinity.

PP is a crystalline polymer and the rate and manner in which the crystals have been formed from the melt influence the crystalline structure. This in turn largely determines both physical properties and processing characteristics of the polymer. Nucleation agents (crystalline organic acids or metal salts) are added in amounts below 0.1% to provide additional crystallization sites and the formation of smaller and more numerous polymer crystals. This controlled morphology of the polymer, referred to as ‘high crystallinity PP’, results in higher bulk properties of the material, namely the softening point, the stiffness, the tensile strength, the modulus and the hardness [56].

The melting temperature, T_m , of isotactic PP is $176^\circ C$, some $40^\circ C$ higher than that of HDPE and this fact makes possible steam sterilization of many PP articles. Strain-free articles retain their shape even at 135 – $140^\circ C$. The glass transition temperature, T_g , of PP is situated at about $0^\circ C$ and below this temperature the impact strength drops down and the polymer becomes brittle. A way to improve this behavior is by block copolymerization with ethylene that will be discussed later.

Some properties of PP are:

density (g/cm^3) = 0.903;
tensile strength (MPa) = 35.5;
tensile modulus (MPa) = 1380;
flexural modulus (MPa) = 1690.

The non-polar nature of PP provides the material with excellent electrical properties similar to those of HDPE. Chemical resistance to most chemicals and solvents is exceptionally high. The polymer is insoluble at room temperature and dissolves in hydrocarbons and chlorinated hydrocarbons only above $80^\circ C$. Unlike PE, PP does not suffer environmental stress cracking [70].

PP differs from PE by the presence of methyl side branches and of relatively labile tertiary hydrogen atoms at every second carbon atom on the backbone. This makes the polymer more susceptible to oxidation by oxidizing agents and by air at elevated temperatures. Antioxidants must be used in all commercial compounds. The general practice is to incorporate small quantities of stabilizers even before the drying operation or before a long-term storage. Additional stabilizers are blended with the polymer during pelletizing [56]. The general antioxidants are hindered phenols, hydroperoxide decomposers or various phosphites and they are synergistic. For special applications more specific stabilizers are added.

Unlike PE which may be crosslinked by high radiation, by heating with peroxides or by chlorosulfonation, PP is degraded to lower MW products by similar treatments.

PP is produced in a large variety of melt flow index (MFI) from 0.3 to 800 g/10 min [55]. Weight-average MW of commercial polymers is in the range 220 000–700 000 and MWD is 5.6–11.9. Both MW and MWD are dependent on many factors such as the polymerization process, the temperature, the pressure, the concentration of the monomer, the composition of the catalyst system, and the addition of hydrogen as chain transfer agent. A common practice to narrow the MWD is a post-reaction treatment usually with peroxides that also produces some chain scission. The products are known as ‘controlled rheology grades’ (CR) and they manifest a better balance of physical properties and processing characteristics [70].

The specific heat of PP is lower than that of PE allowing an increase in the plasticizing capacity of the injection molding machines compared to PE.

The higher the degree of induced crystallinity by the processing conditions the higher will be the molding shrinkage of the material. The reduction of the shrinkage can be realized by coupling a higher temperature of the melt with a lower temperature of the mold.

Besides antioxidants, other additives have been used with PP. Different mineral fillers such as talc, calcium carbonate or glass fibers confer an improved range of properties [56]. For example, 25% by weight of glass fibers leads to a fourfold increase of the tensile strength and to an eightfold increase of the rigidity of PP at 100°C. Rubbers, especially ethylene-propylene rubbers taken in amounts of up to 50% by weight, have been used as fillers in order to improve the impact strength of PP. Pigments, flame retarders, carbon black and ultraviolet absorbers have been used for specific applications. Foaming agents contribute to improve the ratio stiffness/weight and to eliminate the shrinkage [71].

Processing methods such as injection molding, blow molding, fiber extrusion and film manufacture (tubular bubble process or flat process) are the general processing techniques used with PP. The bulk of the film is used in biaxially oriented form which provides higher strength and better barrier properties.

1.2.4 Polypropylene copolymers, rubbers and blends

Besides homopolymers, PP materials are produced as copolymers and as blends.

PP copolymers account for 30% of PP products. The minor, second monomer is ethylene taken in 5–30% in order to improve impact properties especially at lower temperatures. Both random and block copolymers are produced.

(a) Random copolymers

Random copolymers contain 2–5% ethylene which is mixed with propylene in the reactor. The copolymerization processes are basically the same as those

described for the homopolymers. Random copolymers have lower strength and crystallinity but higher clarity and improved impact strength than homopolymers.

(b) Ethylene-propylene rubbers (EPRs or EPMS)

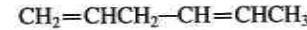
Ethylene-propylene rubbers are a special type of random copolymers. They are completely amorphous and are obtained when the propylene content varies from 30–60 mol%. They are prepared by Ziegler solution polymerization techniques using soluble catalysts such as vanadium oxychloride and aluminum trihexyl mixtures. In order to develop good physical properties, these linear copolymers have to be vulcanized. The vulcanization may be done in two ways. For ethylene-propylene copolymers without unsaturated groups, only peroxide vulcanization is possible which occurs by the abstraction of hydrogen atoms from the chain followed by the combination of resulting macroradicals.

(c) Ethylene-propylene-diene terpolymers (EPDMs)

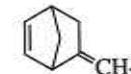
EPDMs are important commercial rubbers. They are prepared by the introduction of a small amount (no more than 1.2%) of a non-conjugated diene as the third comonomer, besides ethylene and propylene. The diene unit provides the necessary amount of unsaturation, usually 2–15 double bonds/1000 carbon atoms. These diene units allow the terpolymer to be crosslinked to a vulcanized rubber network. The diene comonomers commonly used for EPDM rubbers are:



Dicyclopentadiene



1,4-Hexadiene



5-Methylene-2-norbornene



5-Ethylidene-2-norbornene

One of the double bonds copolymerizes with ethylene and propylene entering the main chain, while the other remains like a pendant unsaturation. The vulcanization is subsequently done using common sulfur vulcanizing systems from the rubber industry.

EPDM rubbers have low polarity, good mechanical strength, ozone resistance, abrasion resistance, weatherability and thermal stability. EPDMs are widely used as roofing materials in the building industry [45].

(d) Block copolymers

Block copolymers of different types are produced by means of two or more reaction steps using slurry, bulk or gas phase polymerization techniques. The selection of the preferred process is based on both the desired properties of the copolymer and the operating costs.

Numerous combinations and modifications have been used for the multi-step operation. In the first reaction zone, only homopolymers of propylene are formed. They are then transferred to the second reactor where ethylene is fed in and it polymerizes to form the second block. The order of block formation may also be reversed.

(e) Polyallomers

A special type of block copolymers are the polyallomers which contain 5–15% ethylene. They are highly crystalline materials that combine the most valuable properties of both crystalline PP and HDPE. Their impact strength is three to four times that of PP and they withstand temperatures from –40 to 149°C. Strength properties of polyallomer film in the transverse direction are three to four times higher than those of PP or PE films [72].

(f) Reactor-made blends

Reactor-made blends may be prepared by the homopolymerization of propylene in the first reactor, followed by random copolymerization to a rubbery copolymer in the second reactor into which ethylene and propylene are fed. During this step, propylene homopolymer and the random ethylene-propylene copolymer form an intimately mixed blend. The common blends are prepared with less than 50% of the rubbery copolymer.

(g) Polyolefin thermoplastic elastomers

Polyolefin thermoplastic elastomers are blends of PP with up to 65% ethylene-propylene rubber. Thermoplastic elastomers are a class of specialty elastomers that behave as vulcanized elastomers at room temperature but can be processed as thermoplastics by extrusion and injection molding. These characteristics are obtained with linear macromolecules that are linked together by physical crosslinks resulting in physical network structures. Polyolefin thermoplastic elastomers represent about 23% of the global volume of thermoplastic elastomers, which also include polyester, polyurethane and styrene thermoplastic elastomers [73]. In the case of polyester and of polyurethane the physical crosslinks have a polar nature. In polyolefin thermoplastic elastomers that are non-polar, the physical crosslinks have another nature. It is supposed that the PP homopolymer in the

blend co-crystallizes with propylene short blocks of ethylene-propylene rubber and the resultant microcrystalline regions act as virtual crosslinks at room temperature. At higher temperatures, these microcrystalline regions reach their softening temperature and disappear so that the blend behaves like a thermoplastic.

These elastomers are low cost, general use rubbers with excellent resistance to ozone, oxygen and polar solvents and with good mechanical properties. Their main use is in the automotive field.

1.2.5 Applications

Around 30% of PP and its related copolymers is used as fibers and filaments produced by extrusion. Excellent wear and resistance to staining associated with low cost have led to uses in woven and non-woven form for carpeting in indoor and outdoor constructions, for clothing, inner liners, drapes, tea bags, wall coverings, furniture and automotive upholstery, and for ropes and netting [56].

Coatings for wire, piping or ducts, sheeting and film are also produced by extrusion.

Another large market for PP and for its copolymers is as film (both oriented and cast) for packaging of food and tobacco products and for textile goods.

Injection molded objects represent about 30% of PP applications. These are toys, laboratory and medical supplies, housewares, closures, appliances, luggage, automotive and truck battery cases, washing machines, agitators, pump housings, different parts in dishwashers, refrigerators and freezers.

In addition to its light weight, PP provides outstanding resistance to creep, high temperature rigidity, impact strength and resistance to corrosion. Disposable syringes and other medical applications are based on the possibility of applying sterilization either by autoclaving or by radiation [56].

Ethylene-propylene rubbers have found applications in the building industry for outside uses as sheeting and roofing [45]. Elastomer modified blends are widely used as bumpers, radiator grilles, fascia panels and protective strips in the car industry as well as weather strips for windscreens.

Atactic PP, which was an unwanted by-product for many years, is now specially produced for some applications. The material, which is intermediate between a wax and a rubber, is compatible with mineral fillers and bitumens. It has found use for roofing materials, as asphalt additive, for the formulation of sealing and adhesive compounds and for paper laminating [45].

Syndiotactic PP, which is not yet commercially available, has lower T_m , better impact resistance and more clarity than isotactic PP.

An obvious advantage of PP is its ease of recycling; this is especially important in many of the packaging and automotive applications [55].

1.3 POLYISOBUTYLENE (PIB)

In the 1980s, the USA's yearly consumption of this elastomer was 125 000 tons, compared with 150 000 tons in Western Europe and 30 000 tons in Japan.

The monomer isobutylene is obtained from petroleum sources through the following procedures: thermal and catalytic cracking of various petroleum and natural gas fractions, catalytic dehydrogenation of isobutane, depolymerization of di-isobutylene and alcohol dehydration.

Isobutylene is used in the petroleum industry for the synthesis of high octane number gasoline by alkylation, as an additive (polyisobutylene with low MW) for mineral oils, and in the synthetic elastomer industry.

Isobutylene polymerization occurs through a cationic mechanism at extremely low temperature (i.e. below -100°C) due to the low energy of activation [74]. Estimation of the activity of different acidic catalysts is evaluated based on the reaction rate, conversions and the MW of the obtained elastomer. The activity of Friedel–Crafts catalysts used for isobutylene polymerization decreases from BF_3 to SnCl_4 according to the following series: $\text{BF}_3 > \text{AlBr}_3 > \text{AlCl}_3 > \text{TiCl}_4 > \text{SnCl}_4$.

In the production of synthetic oils based on polyisobutylene production, a butane–butylene fraction, which contains 17–30% isobutylene, is used. For this application, polymerization is catalyzed by AlCl_3 and the polyisobutylene obtained has a low MW in the range 10 000–12 000. For the synthesis of a high MW polymer (above 100 000) a pure monomer is needed.

Isobutylene polymerization with BF_3 is one of the fastest known reactions in organic chemistry; even at very low temperatures, the reaction takes place violently, almost explosively. In some measure, the reaction rate can be regulated by adding diluents.

According to the modern conceptions, Friedel–Crafts catalysts form with alkenes complex molecular combinations able to activate polymerization reactions. Isobutylene is considered by J.P. Kennedy [75] as an ideal cationic monomer. It is an extremely reactive species under all kinds of acidic conditions and it is one of the few cationic monomers, indeed one of the few monomers, that can be readily polymerized from the lowest oligomer, through medium MWs up to the highest polymers with MWs in the millions.

Immediately after catalyst introduction (i.e. AlCl_3 in methyl chloride at -78°C) tens or hundreds of thousands of monomer molecules are mobilized, and polymer chains of MWs in the millions are formed within a fraction of a second.

One of the commercial procedures used to produce high MW polyisobutylene uses BF_3 as a catalyst diluted with ethylene. Liquid isobutylene and ethylene in a 1:1 ratio are sprayed on a cold, moving, stainless-steel trough. Polymerization is almost instantaneous and the considerable heat of polymerization is removed by the partial evaporation of the internal

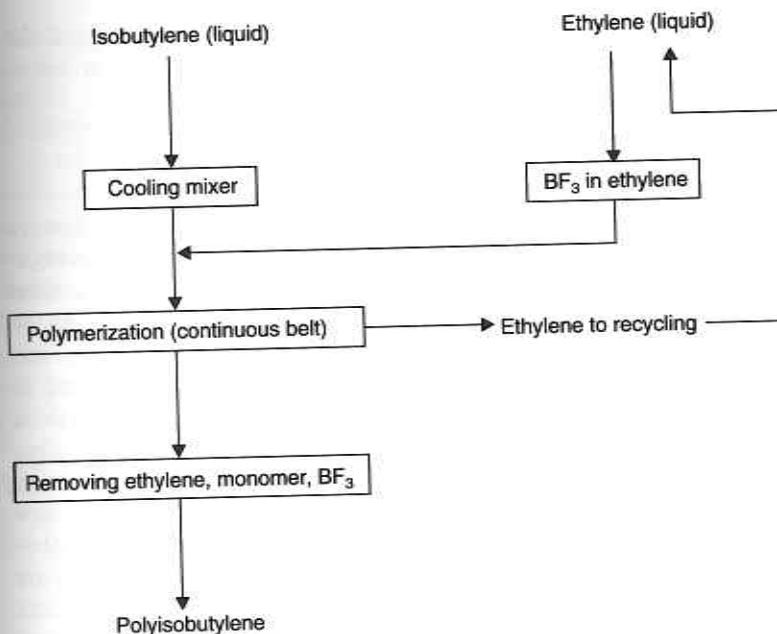


Figure 1.11 Solution polymerization of isobutylene.

coolant ethylene. The whole apparatus is enclosed to avoid loss of gases. The thick polyisobutylene layer transported by the moving belt is scraped off, and falls on steam heated compacting rolls to remove from the polymer BF_3 , unreacted isobutylene, and entrapped ethylene. This process is shown in Figure 1.11.

Other variants use methyl chloride as the diluent, and AlCl_3 as the catalyst in a polymerization at -100°C . It is known that the energy of cationic polymerizations is lower than 15 kcal/mol, and even negative in some cases. The high polymerization rate, e.g. that observed for isobutylene in methyl chloride with AlCl_3 co-initiated with ethyl chloride, cannot be reduced by lowering the temperature to -180°C [74]. Isobutylene forms copolymers with conjugated dienes [76]. Also known is the graft copolymer (poly vinyl chloride-g-isobutylene) [77].

(a) Properties

Polyisobutylene has good low and high temperature properties; maximum continuous service temperature is $+65^{\circ}\text{C}$ and minimum continuous service temperature is -50°C . It is tacky and has a very low T_g (-70°C). It has good aging resistance, excellent sunlight resistance, resistance to chemical agents and very good electrical insulating properties [78]. Measurements of complex shear modulus and complex shear compliance of relatively high

MW over a high range of frequencies show clearly the glassy region, the viscoelastic region, the rubbery and flow regions, characteristic for amorphous polymers [79].

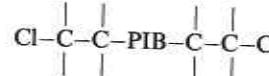
(b) Applications

Lower MW polymers are viscous liquids, but the more important polymers with medium MW (1×10^5 – 4×10^5) are highly extensible, tough, rubber-like products. These medium MW products are used in unvulcanized adhesive rubber compositions, in caulking and sealing compositions, to plasticize, tackify and impermeabilize polyethylene (for melt coating and heat sealing applications), as an additive to asphalts and waxes, and in vulcanizable rubber mixes and as a chewing gum base [45,80]. For these applications, the polymer is compounded with a wide variety of other materials, i.e. talc, calcium carbonate, asbestos, clays, etc. A large amount of PIB is used in blends with waxes because it improves wax low temperature brittleness and flaking, scuff resistance, tensile strength, flexibility, heat-sealing, strength and barrier characteristics. Wax-PIB blends are used in the paper industry to reduce water vapor transmission. Tank lining is an important application of PIB and its mixtures, especially with polyethylene. PIB-asphalt blends are useful in roofings, ditch and reservoir linings, and in general where moisture barrier characteristics are necessary [81]. The use as an additive for oils is related to PIB change in shape with increasing temperature. Since lubricating oil is not able to dissolve this polymer, its macromolecules will exist as coils when mixed at room temperature with the oil. As temperature increases the macromolecular chain tends to uncoil and the oil becomes a good solvent under these circumstances. This effect tends to counteract the decrease in the oil viscosity with the increasing temperature [80].

1.3.1 Butyl rubber

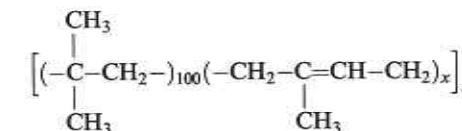
There is an abundance of information in the patent literature on the copolymerization of isobutylene with other monomers. The most important comonomers for isobutylene copolymerization are aromatic olefins like styrene and dienes, for example, isoprene.

Styrene and preferably α -methylstyrene were used as the second monomer in the two-stage synthesis of isobutylene-containing polymers. In this way, α -chloro-poly(isobutylene-block-styrene) was synthesized from the asymmetric prepolymer, but it was contaminated by homopolymers, the amount of which was dependent on the experimental conditions [82].



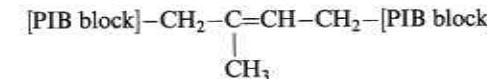
Among the different copolymers discussed in technical literature, only one product, an isobutylene-isoprene copolymer known as butyl rubber, has gained industrial importance. Its annual consumption in the USA is c. 150 000 tons.

In this isobutylene and isoprene copolymer, the latter is present in relatively small amounts, usually 0.6–3 mol% necessary to provide the unsaturation required for vulcanization. This unsaturation is only 0.6–3% of that of natural rubber, and many of the properties of butyl rubber are dependent on its very low unsaturation. This copolymer has the following microstructure:



where x varies from 0.6 to 3.0 and n from 350 to 1000.

Isoprene units are bonded almost exclusively as 1,4 units; the amount of 1,2 and 3,4 units is less than 1% of the unsaturated groups.



Butyl rubber is produced by copolymerizing isobutylene with small amounts of isoprene, using AlCl_3 catalyst in methyl chloride solution at c. -100°C . Although the catalytic system is not essentially stereospecific, the isobutylene units bond head-to-tail, and the copolymer chains contain a very regular structure, owing to the symmetrical nature of isobutylene.

The process is continuous and the copolymerization reaction is cooled by circulating liquid ethylene in the mantle of the reactor. The cooled mixture of comonomers and solvent has a 27–30% amount of comonomers. The slurry resulting from copolymerization contains 15–20% copolymer and 10–12% unreacted comonomers. Copolymerization is controlled through the catalyst feeding rate; it is a very fast reaction, and at the mixing of reaction medium with catalyst solution, each drop is covered with a copolymer thin film and further comonomer molecules diffuse in the already formed polymer-monomer particle.

Due to the copolymer low thermal conductivity, temperature in the polymer-monomer particles is higher than the reaction medium temperature, a fact which favors the formation of a low MW copolymer. This is the reason why thorough attention has to be given to a fast, fine and homogeneous distribution of the catalyst solution in reaction mass.

For an acceptable conversion (70%) the reaction mass has to be circulated in the copolymerization reactor for 90–120 minutes [83].

Copolymerization development can be monitored by observing the change of the amount of isobutylene in the slurry, or by observing the ethylene vapor

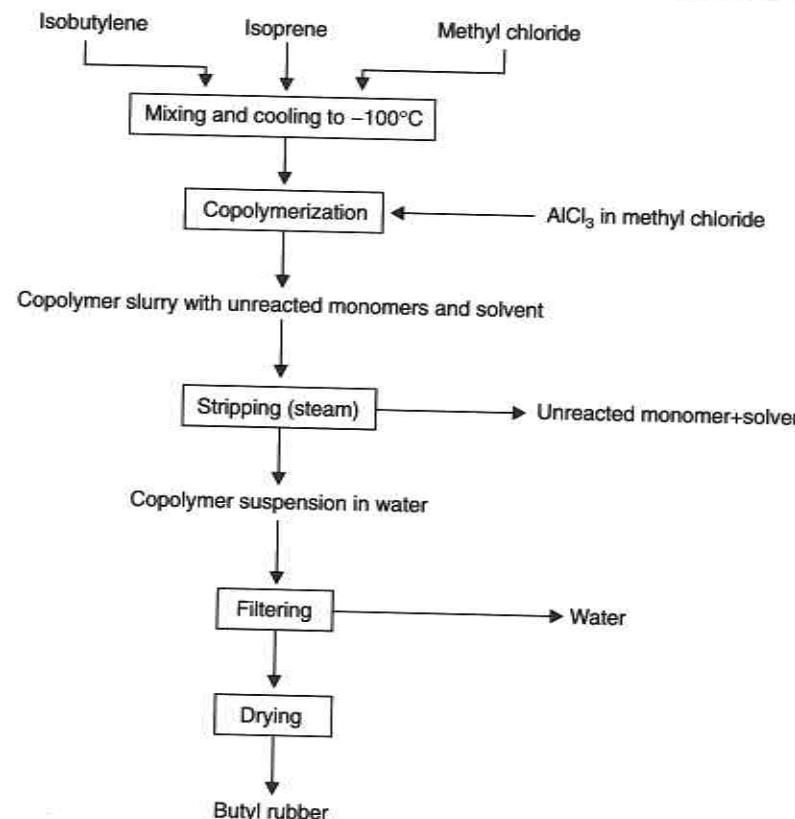


Figure 1.12 Butyl rubber synthesis.

pressure (ethylene which is circulating for the cooling of the system). The technical literature describes continuous plants for the synthesis of butyl elastomer, some of which have only one copolymerization reactor and some of which have several. The scheme for butyl rubber synthesis is shown in Figure 1.12.

During stripping, an antioxidant and zinc stearate are introduced. The antioxidant will prevent breakdown of the polymer in the subsequent operations. The stearate is added to prevent the agglomeration, or sticking together, of the wet crumb [84].

A solution process, developed in the former USSR, uses a C₅–C₇ hydrocarbon as the solvent and aluminum alkyl halide as the catalyst. The copolymerization is conducted in scraped surface reactors at -90° to -50°C. Producing the elastomer in solution avoids the use of methyl chloride and there is an advantage when butyl rubber has to be transformed in halogenated rubber [85].

Standard grades of butyl rubber have various mole per cent unsaturation. Butyl rubber is shipped in uncured condition and contains 1 part (by wt) of zinc stearate and 0.5 part (by wt) of an antioxidant. It is tacky and has a tendency to flow under its own weight and to adhere to storage racks. It does not require mastication before being compounded.

(a) Properties

Different types of butyl rubber have MWs in the range 40 000 to 85 000 and a density c. 0.91 g/cm³.

The principal drawback of this copolymer is its low elasticity at the ambient temperature. Compared with natural rubber, its gas permeability is 10–30 times lower. Maximum continuous service temperature is 100°C [78].

Due to low unsaturation, vulcanization of butyl rubber needs a longer time and higher temperature than other synthetic rubbers. Butyl rubber is free from branching provided that the degree of unsaturation is low. As the unsaturation is increased to 5%, cure rates are faster and the vulcanizates have better thermostability and higher modulus but lower ozone resistance [86]. In the case of sulfur vulcanization, the correct choice of the accelerator is very important. Vulcanization introduces a chemical crosslink approximately every 250 carbon atoms, producing a molecular network. The vulcanization can be done with phenolic resins instead of sulfur [85].

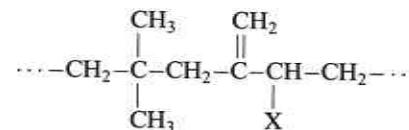
Butyl rubber belongs to the crystallizable rubbers group. It possesses a good adhesion, is stable to oxygen action, to that of oxidants, to most inorganic acids, alkali, salts and oxygenated organic compounds like alcohols, esters, ketones, animal and vegetable oils, and has a good weatherability.

The combination of low absorption properties with a good ozone stability and with good electrical indices, opens great possibilities of using butyl rubber as an electrical insulator. Carbon black is a very useful ingredient and is recommended for this kind of rubber; for reinforcement in this case, the ratio 1:1 is used.

Butyl rubber can be processed on conventional equipment and compounded besides carbon black with conventional mineral fillers, plasticizers, mineral oils and processing aids. It is usually cured in the temperature range of 148–200°C, but fast curing formulations give satisfactory vulcanizates at temperatures as low as 100°C.

A commercially important butyl rubber derivative is chlorinated butyl rubber, known also as chlorobutyl. It is a high MW isobutylene-isoprene copolymer containing reactive (allylic) chlorine atoms. It is superior to butyl rubber since it has a faster rate of vulcanization and enhanced compatibility with many other elastomers. Both brominated and chlorinated butyl rubbers are available on the market [86]. Their structure, determined by

NMR, is



where X stands for bromine or chlorine.

Halogenated butyls are vulcanized by the same agents as butyl rubber, as well as by zinc oxide, diamines, peroxides and dithiols [85,86].

One of the drawbacks of butyl rubber is its poor adhesive properties to metals and to other rubbers. This is largely due to the lack of polar groups in the microstructure of this copolymer; halogenation remedies this deficiency [45].

G. Balasz *et al.* [87] reported on a DSC study which shows that butyl rubber is very sensitive to light but more stable to thermo-oxidation or to ozone attack.

(b) Applications

Due to its very low permeability to gases, butyl rubber is used extensively for inner tubes, and in the form of chlorobutyl rubber, in tubeless tires. The service life of inner tubes made of butyl rubber is 10–18% longer than that of those made of natural rubber.

Its stability to steam and relatively high temperature permits the use of butyl rubber in the production of diaphragms and conveyer belts for hot materials.

Excellent chemical stability determines its use for tanks and pumps for very aggressive liquids, lining, for the manufacturing of textiles impermeable to yperite gas, various gas masks, various impermeable textiles, rubber coated pelerine, pneumatic boats, windproof and waterproof clothing, belts, pipes, steam and firefighting hoses, gaskets, adhesives, sealants, and caulks. Most butyl caulking compounds cure by solvent release. Some compositions are based on cured rubber solvated by mineral spirits. Some more solvent may be used to incorporate more filler into the compound [82]. Butyl rubber also proved suitable as a high quality roofing membrane [88].

Chlorobutyl rubber is widely used in applications where resistance to pollutants, barrier properties, speed and versatility of curing, ability to blend and covulcanize with other rubbers, and where high heat resistant vulcanizates are required.

Butyl rubber sealants can be obtained using butyl crude rubber, which can be dissolved in an appropriate organic solvent to give a solvent based butyl sealant. Non-shrinking caulking compounds can be obtained by using low MW polyisobutylene oils to soften the butyl rubber.

As shown in Table 1.3, the formulation of such a sealant is complex because of the numerous additives necessary for its compounding. In the

Table 1.3 Butyl rubber based caulking compound [89]. (Reprinted by permission of J. Wiley & Sons Inc. from *Construction Sealants and Adhesives* by J.R. Panek and J.P. Cook, 1984. Copyright © J. Wiley & Sons)

Ingredient	% by weight
Polyisobutylene	2.5
Butyl rubber, 50% solution in mineral spirits	20.5
Talc powder	30
Calcium carbonate filler	20
TiO ₂ pigment	3
Adhesion resin	4
Polybutylene	10
Plasticizer	2
Thixotropic agents	2
Drying catalysts	0.05
Mineral spirits	6
Total solids content	84

formulation, butyl rubber is used for structure but polyisobutylene and an adhesive resin are used for tack. The trace driers are used to give a tack-free surface and slowly cure. The total butyl composition is approximately 22%, but the total solvent is 16%, which could result in approximately 30% volume shrinkage. Most butyl caulking compounds cure by solvent release. Some compositions are based on crude rubber solvated by mineral spirits. Some more solvent may be used to incorporate more filler into the compound [89].

Besides adhesives and sealants, butyl rubber is used for weather seals and gaskets in buildings. Butyls require some joint cleaning, but extensive surface preparation is not required. Laitance and loose concrete should be removed from the faces of the concrete joints, but priming is unnecessary. Metal surfaces may be wiped with an oil-free cloth wet with solvent to remove contaminants. Wood surfaces and glass should be wiped clean. Butyl caulks work best in relatively non-moving joints. They are used on the mating surface of heating and air-conditioning ducts and for sealing openings where pipes and ducts pass through roofs and partitions. Butyl caulks can be used below grade on masonry joints. They may be used in lap joints of sheet siding, metal roofs, glazing, wooden doors and windows, and protective sidings. Butyls adhere to aluminum, steel and vinyl siding. Some advantages and disadvantages of butyl caulks are presented in Table 1.4.

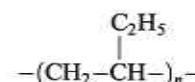
1.4 POLY(1-BUTYLENE)

Another polyolefinic thermoplastic material is poly(1-butylene) prepared by the stereospecific polymerization of 1-butylene in the presence of

Table 1.4 Advantages and disadvantages of butyl caulk [92]. (Reprinted by permission of J. Wiley & Sons Inc. from *Construction Sealants and Adhesives* by J.R. Panek and J.P. Cook, 1984. Copyright © J. Wiley & Sons)

<i>Advantages</i>	<i>Disadvantages</i>
1. Reasonable cost	1. Very slow cure
2. Availability	2. High shrinkage
3. Good flexibility	3. High compression set
4. Good adhesion to most substances	4. Limited to joints with $\pm 7.5\%$ joint movement
5. One-component	5. Not recommended for expansion joints
6. Little surface preparation	
7. Good water resistance	
8. Good color stability	
9. Four colors available	
10. Only material for capping neoprene gaskets	

Ziegler–Natta catalytic system [90.91]



The polymerization of 1-butylene was also effected using metallocene-alumoxane catalysts [28].

Commercial products have high MW, in the range 700 000–3 000 000 and are 98–99.5% isotactic. The polymer can exhibit three crystalline forms [92]. The first form is obtained by crystallization from the melt, has $T_m = 124^\circ\text{C}$ and the density 0.89 g/cm^3 . This form is unstable and after several days changes to a stable form with $T_m = 135^\circ\text{C}$ and the density 0.95 g/cm^3 . The hardness, the stiffness and the yield strength all increase. This characteristic has to be considered and the polymer must be aged for a week after processing. The third crystalline form is obtained by crystallization from solution.

Polybutylene exhibits the general properties of a polyolefin. Its outstanding property is a very high creep resistance that was advantageously used for the manufacture of pipes having a much reduced wall thickness as compared to PE and PP pipes. The main use of polybutylene is for pipes for cold and hot water plumbing as well as for the transportation of abrasive and corrosive materials in mining, chemical and power generation industries [93].

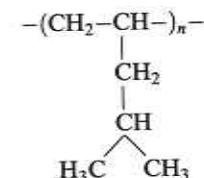
Film applications include food packaging and industrial sheeting as abrasion resistant liner.

Atactic polybutylene is used for roof coverings and sealing compounds [45].

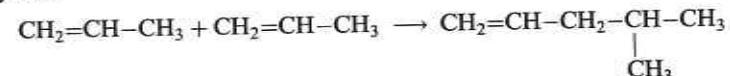
1.5 POLY(4-METHYL-1-PENTENE) (PMP)

PMP is a high performance specialty plastic without being a high volume material. The production volume is 6000 tons per year but the demand for PMP has grown steadily at a rate of 20% per year [45]. First produced by ICI Ltd of Britain in 1965, it is now manufactured and marketed solely by Mitsui Petrochemical Industries.

The repeating unit in PMP is:



The monomer, 4-methyl-1-pentene, is obtained by the dimerization of propylene:



The polymerization of the monomer is effected in a hydrocarbon diluent at 30–60°C and atmospheric pressure in the presence of a Ziegler–Natta catalyst composed of titanium trichloride and diethyl aluminum chloride. At the end of the polymerization the catalyst residues are washed out with an alcohol and the polymer is dried and compounded with antioxidants and other additives.

Experimental studies have been conducted on the polymerization of 4-methyl-1-pentene with metallocene-alumoxane catalyst systems [28].

The commercial polymer is isotactic and about 40% crystalline. In the crystalline part the molecules are arranged in a helix with seven monomer units per two turns of the helix. Crystalline and amorphous zones have similar refractive indices and similar densities and this accounts for the outstanding high degree of transparency of the material. The white light transmission is 90%. Some properties of PMP are in Table 1.5.

Table 1.5 Some characteristics of PMP

<i>Property</i>	<i>Value</i>
Density (g/cm ³)	0.834
Melting temperature (°C)	240
Glass transition temperature (°C)	50–60
Tensile strength (MPa)	195
Tensile modulus (MPa)	800
Flexural modulus (MPa)	750

PMP has the lowest density of any available plastics material. The bulky side chains contribute to the stiffening of the chains resulting in high T_m and T_g . The high permeability to gases is due to the same structural factor. PMP is capable of separating nitrogen and oxygen due to the great difference in the permeability of the two gases [94].

The presence of relatively labile tertiary hydrogen atoms on the chain makes the material more sensitive to oxidation especially at high processing temperatures and in working conditions at elevated temperatures. Hence compounding requires the use of efficient antioxidant systems.

The applications of PMP take advantage of the high transparency and heat resistance of the material, which can be used at up to 150°C. It can be bonded to metals and other materials through its own shrinkage without the use of adhesives. Medical and laboratory sterilizable equipment such as syringes, blood test cells, animal cages as well as cosmetic containers account for one third of PMP uses. Other applications are for heat resistant houseware such as microwave trays, coffee maker parts, nursery bottles and many others.

In the industrial area, PMP has been used as material for resin molds designed for manufacturing thermosetting plastics such as polyurethanes, epoxies, phenolics, melamine and urea resins as well as for molding contact lenses. It is also used for covering heat resistant wire, power cables, fuse covers, lighting fixtures, optical memory and optical fibers.

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