Polyolefins

General aspects of polymers, properties and testing, processing, additives, and analysis are discussed in Plastics, General Survey; Plastics, Properties and Testing; Plastics, Processing; Plastics, Additives; and Plastics, Analysis, respectively. States of order are treated in Plastics, Properties and Testing. Fundamental aspects of polymerization reactions are treated in Polymerization Processes.

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1. Polyethylene

1.1. Introduction

Despite ethylene's simple structure, the field of polyethylene is a complex one with a very wide range of types and many different manufacturing processes. From a comparatively late start, polyethylene production has increased rapidly to make polyethylene the major tonnage plastics material worldwide (45×10^6 t capacity in

1995). In the 1920s research into the polymerization of unsaturated compounds such as vinyl chloride, vinyl acetate, and styrene led to industrial processes being introduced in the 1930s, but the use of the same techniques with ethylene did not lead to high polymers. The chance observation in 1933 by an ICI research team that traces of a waxy polymer were formed when ethylene and benzaldehyde were subjected to a temperature of 170 °C and a pressure of 190 MPa, led to the first patent in 1936 and small-scale produc-

tion in 1939. The polymers made in this way, by using free radical initiators, were partially crystalline, and measurement of the density of the product was quickly established as a means of determining the crystallinity. Due to the side reactions occurring at the high temperatures employed, the polymer chains were branched, and densities of $915 - 925\,kg/m^3$ were typically obtained. The densities of completely amorphous and completely crystalline polyethylene would be 880 and $1000\,kg/m^3$, respectively.

During the 1950s three research groups working independently discovered three different catalysts which allowed the production of essentially linear polyethylene at low pressure and temperature. These polymers had densities in the region of $960\,kg/m^3$, and became known as high-density polyethylenes (HDPE), in contrast to the polymers produced by the extensively commercialized high-pressure process, which were named low-density polyethylenes (LDPE). These discoveries laid the basis for the coordination catalysis of ethylene polymerization, which has continued to diversify. Of the three discoveries at Standard Oil (Indiana), Phillips Petroleum, and by KARL ZIEGLER at the Max-Planck-Institut für Kohlenforschung, the latter two have been extensively commercialized. More recently the observation that traces of water can dramatically increase the polymerization rate of certain Ziegler catalysts has led to major developments in soluble coordination catalysts and later their supported variants.

The coordination catalysts allowed for the first time the copolymerizaton of ethylene with other olefins such as butene, which by introducing side branches reduces the crystallinity and allows a low-density polyethylene to be produced at comparatively low pressures. Although Du Pont of Canada introduced such a process in 1960, worldwide the products remained a small-volume specialty until 1978 when Union Carbide announced their Unipol process and coined the name linear low-density polyethylene (LLDPE). In addition to developing a cheaper production process, Union Carbide introduced the concept of exploiting the different molecular structure of the linear product to make tougher film. Following this lead, LLDPE processes have been introduced by many other manufacturers.

The history of these discoveries is covered in [1–4, 20].

The three types of polyethylene outlined above account for the major part of polyethylene production (Table 1), but the picture is slightly confused since many plants have the capability of producing more than one type of product (so-called swing plants). Additionally, copolymers are made by both types of process. The free-radical process is used to produce copolymers of vinyl acetate, acrylates, methacrylates, and the corresponding acids, but chain transfer prevents the use of higher olefins because of the drastic reduction in molecular mass of the polymer. The coordination catalysts are able to copolymerize olefins, but are deactivated by more polar materials. Because of the complex interplay of the capabilities of modern plants, it is convenient to treat separately the products, the catalysts, and the processes.
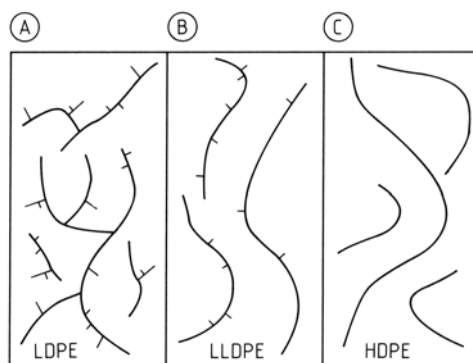
Figure 1. Schematic molecular structure
A) Low-density polyethylene; B) Linear low-density polyethylene; C) High-density polyethylene

1.2. Properties of Polyethylenes

1.2.1. Molecular Structure and Morphology

Figure 1 shows schematic structures for the three polyethylenes, with the main features exaggerated for emphasis. LDPE has a random long-branching structure, with branches on branches. The short branches are not uniform in length but are mainly four or two carbon atoms long. The ethyl branches probably occur in pairs [21], and there may be some clustering of other branches [22]. The molecular mass distribution (MMD) is moderately broad.

Table 1. Polyethylene production capacities in 10^3 t/a $*$ (1995)

	North America	Western Europe	Eastern Europe	Japan	Rest of World	Total
LDPE	3891	5783	1918	1444	4210	17 246
LLDPE	4422	1848	100	1059	3728	11 157
HDPE	6198	4008	873	1024	4715	16 891
Total PE	14 511	11 639	2891	3527	12 653	45 221

$*$ Data from Chem Systems, London.

LLDPE has branching of uniform length which is randomly distributed along a given chain, but there is a spread of average concentrations between chains, the highest concentrations of branches being generally in the shorter chains [23]. The catalysts used to minimize this effect generally also produce fairly narrow MMDs.
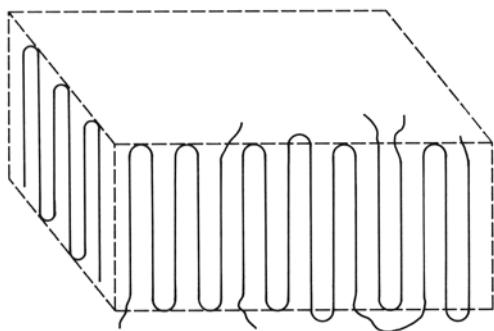
Figure 2. Folded-chain lamellar crystal of polyethylene

HDPE is essentially free of both long and short branching, although very small amounts may be deliberately incorporated to achieve specific product targets. The MMD depends on the catalyst type but is typically of medium width.

Polyethylene crystallizes in the form of platelets (lamellae) with a unit cell similar to that of low molecular mass paraffin waxes [24]. Due to chain folding, the molecular axes are oriented perpendicular to the longest dimension of the lamella and not parallel to it as might be expected (Fig. 2). The thickness of the lamellae is determined by the crystallization conditions and the concentration of branches and is typically in the range of $8 – 20$ nm. Thicker lamellae are associated with higher melting points and higher overall crystallinities. Slow cooling from the melt or annealing just below the melting point produces thicker lamellae. Where long molecules emerge from the lamella they may either loop back elsewhere into the same lamella or crystallize in one or more adjacent lamellae, thereby forming "tie molecules".

Thermodynamically the side branches are excluded from the crystalline region because their geometry is too different from that of the main chains to enter the crystalline lamellae. Therefore, the branches initiate chain folding, which results in thinner lamellae with the branches mainly situated on the chain folds on the surface of the lamellae. However, on rapid cooling these energetically preferred placements may not always occur, and some branches may become incorporated as crystal defects in the crystalline regions. Detailed measurements by solid-state NMR and Raman spectroscopy show that the categorization into crystalline and amorphous phases is too simplistic and a significant fraction of the polymer is present in the form of an "interfacial" fraction which has neither the freedom of motion of a liquid, nor the well-defined order of a crystal [25, 26]. A further result of a side branch is that having been prevented from folding directly into the same lamella, the polymer chain may form a tie molecule that links to one or more further lamellae.

Under moderately slow cooling conditions, crystallization may be nucleated at a comparatively small number of sites. Crystallization then propagates outwards from these centers until the surfaces of the growing spheres meet. The resulting spherulites show a characteristic banded structure under a polarizing optical microscope. The typical milkiness of polyethylene is due to light scattered by spherulites or other, less well defined aggregates of crystallites, rather than by the crystallites themselves, which are much smaller than the wavelength of light [27]. Ethylene copolymers may be transparent, although partially crystalline.

1.2.2. General Properties

LDPE and LLDPE are translucent whitish solids and are fairly flexible. In the form of films they have a limp feel and are transparent with only a slight milkiness. HDPE on the other hand is a white opaque solid that is more rigid and forms films which have a more turbid appearance and a crisp feel.

Polyethylene does not dissolve in any solvent at room temperature, but dissolves readily in aromatic and chlorinated hydrocarbons above its melting point. On cooling, the solutions tend to form gels which are difficult to filter. Although LDPE and LLDPE do not dissolve at room temperature, they may swell in certain solvents with a deterioration in mechanical strength. Manufacturers issue data sheets detailing the suitability of their products for use in contact with a wide range of materials. In addition to solvents, polyethylene is also susceptible to surface active agents which encourage the formation of cracks in stressed areas over prolonged periods of exposure. This phenomenon, known as environmental stress cracking (ESC), is believed to be due to lowering of the crack propagation energy [28]. In general, HDPE is the preferred polyethylene for liquid containers.

Some properties of typical LDPE, HDPE, and LLDPE are listed in Table 2. Polyethylenes are routinely characterized by their density and melt flow index (MFI). The MFI test was originally chosen for LDPE to give a measure of the melt characteristics under conditions related to its processing. It is carried out by applying a standard force to a piston and measuring the rate of extrusion (in g/10 min) of the polyethylene through a standard die (Fig. 3). Other standard conditions are sometimes used on the same equipment to extend the range of information and because higher loads are sometimes considered more appropriate for HDPE. The short parallel section of the standard die introduces errors which mean that the MFI cannot be accurately related to viscosity (it would be an inverse relationship). For LDPE and HDPE, the MFI increases disproportionately with the applied load. The ratio of the two MFIs gives a measure of the ease of flow at high shear and is sometimes known as the flow ratio. The die swell ratio can also be measured in the MFI test and gives a measure of the elastic memory of the melt. This parameter correlates usefully with extrusion processes, where a low value is desirable for tubular film, and a high value is necessary for extrusion coating.
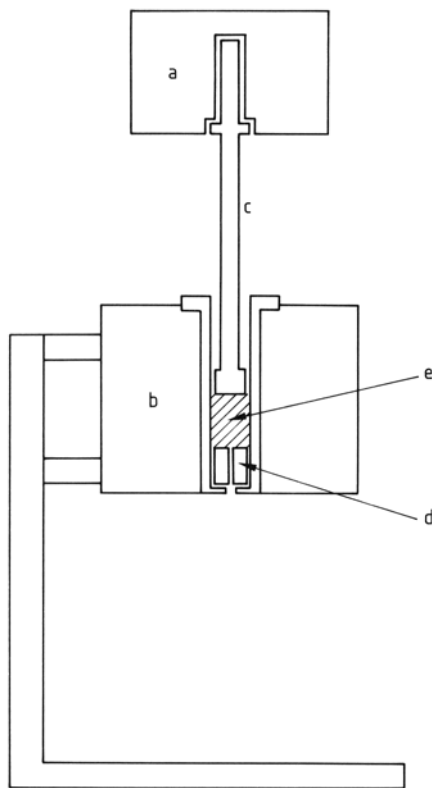
Figure 3. Melt flow index equipment
a) Interchangable piston loading weight; b) Electrically heated barrel; c) Piston; d) Die; e) Polyethylene melt

The behavior of polyethylene under shear is shown in Figure 4, which compares a LDPE and a LLDPE similar to those in Table 2. At sufficiently low shear rates the viscosity of all polyethylenes becomes Newtonian, i.e., independent of shear rate. Due to its narrow MMD the viscosity of the LLDPE is less shear dependent than that of the LDPE and has a higher viscosity under the higher shear conditions used in processing equipment.

As indicated above, the crystalline properties are affected by the rate of cooling from the melt and the subsequent thermal history. For the purposes of reproducibility it is usual to apply a standard annealing treatment to test samples, such as annealing at 100 °C for 5 min followed

Table 2. Properties of some typical polyethylenes (data from Repsol Quimica)

Property	LDPE	HDPE	LLDPE	Method	Standard
Polymer grade	Repsol PE077/A	Hoechst GD-4755	BP LL 0209		
Melt flow index (MFI), g/600 s	1.1	1.1	0.85	190 °C/2.16 kg	ASTM D1238
High load MFI, g/600 s	57.9	50.3	24.8	190 °C/21.6 kg	ASTM D1238
Die swell ratio (SR)	1.43	1.46	1.11		
Density, kg/m^3	924.3	961.0	922.0	slow annealed	ASTM D1505
Crystallinity, %	40	67	40	DSC	
Temperature of fusion (max.), °C	110	131	122	DSC	
Vicat softening point, °C	93	127	101	5 °C/h	ASTM D1525
Short branches **	23	1.2	26	IR	ASTM D2238
Comonomer		butene	butene	NMR	
Molecular mass*					
M_w	200 000	136 300	158 100	SEC	
M_n	44 200	18 400	35 800	SEC	
Tensile yield strength, MPa	12.4	26.5	10.3	50 mm/min	ASTM D638
Tensile rupture strength, MPa	12.0	21.1	25.3		
Elongation at rupture, %	653	906	811		
Modulus of elasticity, MPa	240	885	199	flexure	ASTM D790
Impact energy,					
unnotched, kJ/m^2	74	187	72		ASTM D256
notched, kJ/m^2	61	5	63		ASTM D256
Permittivity at 1 MHz	2.28				ASTM D1531
Loss tangent at 1 MHz	100×10^{-6}				ASTM D1531
Volume resistivity, $\Omega \cdot$ m	10^{16}				
Dielectric strength, kV/mm	20				

* Corrected for effects of long branching by on-line viscometry.
** Number of methyl groups per 1000 carbon atoms.
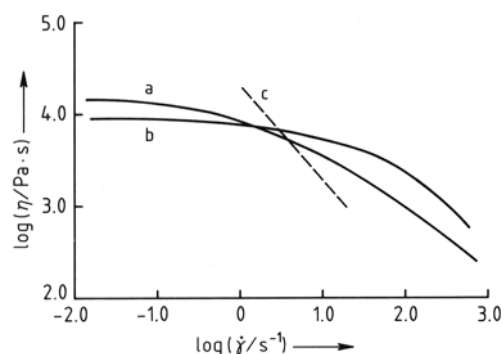
Figure 4. Dependence of viscosity η on shear rate $\dot{\gamma}$ for two polyethylenes
a) Low-density polyethylene; b) Linear low-density polyethylene; c) Apparent shear rate in melt flow index test
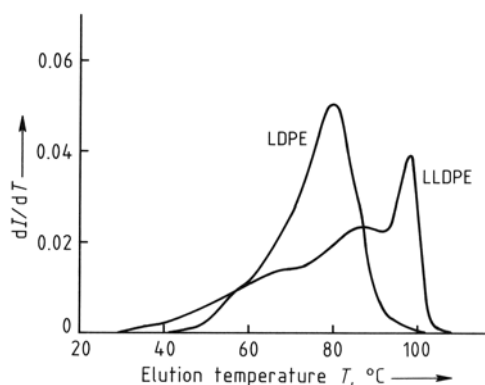
Figure 5. Temperature rise elution fractionation curves (I is the cumulative weight fraction)

by slow cooling to room temperature. The crystallinity correlates with the density, reflecting the average properties of the polymer, but the melting point and the softening points for LLDPE are higher than for LDPE due to the presence of some relatively sparsely branched species in the former type of polymer. In addition to the differential scanning calorimetry (DSC) technique

used to measure the fusion point, the relative heterogeneity of the LLDPEs is demonstrated even more clearly by temperature rise elution fractionation (TREF) [29, 30]. After depositing the sample by slow cooling from solution onto an inert support, elution is carried out over a programmed temperature range to measure the concentration of eluted polymer as a function of

elution temperature. Examples are shown in Figure 5. LLDPE produced with a single-site catalyst (see Section 1.3.2.3) shows a single sharp peak by this test.

The weight-average and number-average molecular masses determined by size exclusion chromatography (SEC, also known as gel permeation chromatography, GPC) are listed in Table 2, and Figure 6 shows their molecular mass distribution curves.
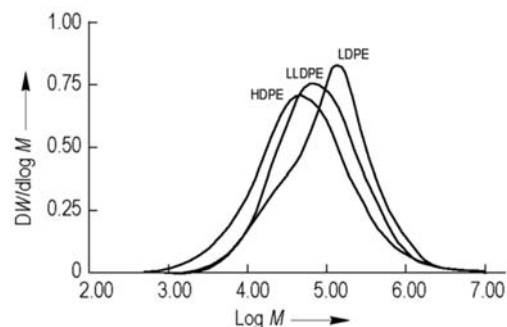
Figure 6. Molecular mass distribution curves for the polyethylenes of Table 2 (data from Repsol Quimica)
I is the cumulative weight fraction.

In the tensile test the yield strengths and the elastic moduli are as expected from the respective crystallinities. The higher rupture strength of the LLDPE relative to the LDPE is typical when the two polymers are chosen to have equal MFIs, but if the criterion were constant high-shear extrudability (e.g., the high load MFI) the tensile strengths would be very similar. The example chosen for the LLDPE is a butene copolymer. For higher performance applications longer chain olefins are used as comonomers [31]; e.g., octene (Du Pont, Dow), hexene (UCC, Exxon), 4-methylpentene (BP). These produce higher tensile strengths and impact energies, particularly in the form of film.

In common with other polymers, polyethylene is viscoelastic in the solid state. This means that the strain produced by applying a stress is time dependent, and in defining an elastic modulus it is important to specify the timescale of the measurement. Figure 7 shows the results of a measurement of strain versus time for a HDPE specimen at a constant tensile stress of 6.5 MPa [32]. The strain continues to increase approximately linearly with log t and after 4 d would

have reached almost four times the value measured after 10 s. Thus the effective Young's modulus after 4 d is only 25 % of the short-term value and after several years would be lower still. This creep behavior is particularly marked in the case of polyethylenes because the amorphous regions are relatively mobile at room temperature [33]. For design purposes the modulus must be estimated for the timescale and temperature expected for the application. A related problem in designing for long-term use is that a prolonged high stress may lead to crack formation and failure at a stress significantly below the conventionally measured yield stress [34].
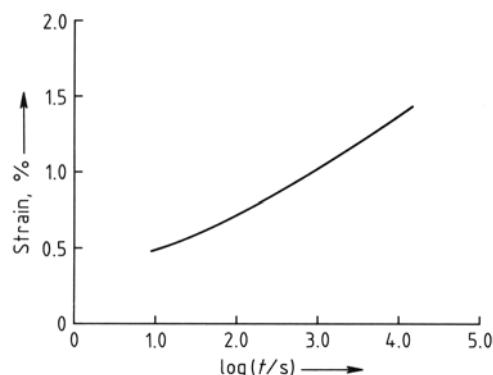
Figure 7. Tensile creep of HDPE (Rigidex 006-60) [32]

The extremely low loss tangent (power factor) makes LDPE ideally suitable as an insulator for high-frequency cables. Since pure polyethylene contains no polar groups, a very low power factor is expected, and most of the measured value is due to traces of oxidation, catalyst residues, antioxidant, etc. Because they contain Ziegler or Phillips catalyst residues, such low power factors are not generally achievable with HDPE or LLDPE.

Figure 8 shows the permeability of LDPE and ethylene–vinyl acetate copolymer (EVA) films to oxygen and water vapor. Although LDPE has a very useful role as a packaging material, the gas and water vapor permeabilities are not particularly low compared to other film forming materials (see → Films, Chap. 6.2.1.). Since permeation takes place in the mobile amorphous phase, the permeability of HDPE is appreciably lower.

Polyethylene is a high molecular mass hydrocarbon which can be considered as toxico-

logically inert, and indeed high-purity forms are used in medical prostheses. The suitability of a polyethylene for use in contact with food or in medical prostheses depends on its content of catalyst residues and principally on additives such as antioxidants. Acceptable limits on process residues and additives are normally controlled by national regulatory bodies, but in many cases they are based on the standards defined by the American Food and Drug Administration (FDA) or the German Bundesgesundheitsamt.
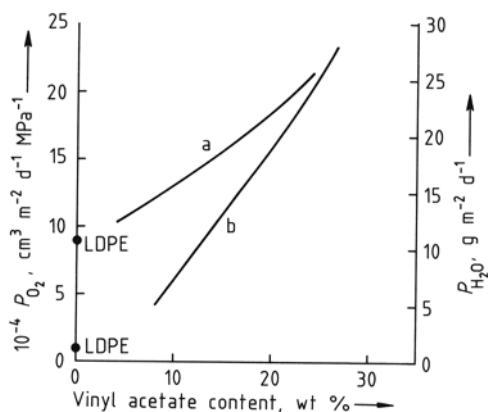
Figure 8. Permeability P of 0.025 mm films of LDPE and EVA at 23 °C (data are based on Exxon Escorene Ultra EVA copolymers [35])
a) Oxygen; b) Water vapor (50 % R.H.)

1.2.3. High Molecular Mass (Bimodal) Polyethylene (HMWPE)

This description is usually applied to HDPEs with MFIs in the range 0.01 – 0.1 by the normal test, although a higher load is usually used to characterize them. They are processable with some difficulty on conventional PE processing machinery, although some advantages can be gained by using equipment optimized for these grades. In general, they are not simply higher molecular mass versions of normal HDPE grades, but are specially designed broad-MMD polymers, often produced by using multiple reactors or combinations of catalysts [36]. The broad MMD, which may be bimodal, produces a highly shear dependent melt viscosity combined with good mechanical strength.

A particularly important type of bimodal polymer is produced by combining a high molecular mass component having a relatively high concentration of short branches with a low molecular mass component containing few or no branches. In this way the low molecular mass component crystallizes as folded chain lamellae and the high molecular mass component forms tie molecules which crystallize in several of the lamellae. This combination of branching and molecular mass is the reverse of what is usually observed in LLDPEs (see Sections 1.2.1 and 1.3.2.3), where the more higly branched components have low molecular masses. The desired bimodal distribution is achieved by careful process modifications using multiple reactors. The optimization of the tie molecules confers excellent resistance to long term crazing and crack growth [37], making the polymers particularly suitable for pipe and liquid containers.

1.2.4. Ultra High Molecular Mass Polyethylene (UHMWPE)

These polyethylenes were commercialized shortly after HDPE and have extremely high molecular mass ($3-6 \times 10^6$ according to ASTM D4020), but do not usually have a broad molecular mass distribution. The viscosity is too high to be measured by the MFI test, and they are usually characterized either by the relative solution viscosity in decalin at 135 °C, or by specially developed melt flow tests. The material is processed by techniques similar to those developed for PTFE, which involve fusing by sintering, rather than plastification to a true melt. UHMWPE has a remarkable combination of abrasion resistance, chemical inertness, low friction, toughness, and acceptability in contact with foodstuffs. Some properties are listed in Table 3. The density is only 940 kg/m^3, even though the polymer is unbranched, because the extremely high viscosity hinders the crystallization process.

1.2.5. Properties of Ethylene Copolymers

Table 4 lists the principal types of ethylene copolymers which are in commercial production. Of these the vinyl acetate copolymers are produced in the largest quantities. All the ester

Table 3. Properties of an ultra high molecular mass polyethylene (Hoechst GUR 412) [38]

Property	UHMWPE	Method	Standard
Molecular mass	4.5×10^6	viscometric	DIN 53 728
Reduced specific viscosity, cm^3/g	2300	0.05 % in decalin	
Density, kg/m^3	940		DIN 53 479
Crystalline melting range, $^\circ$C	135–138	polarizing microscope	
Tensile yield strength, MPa	22		DIN 53 455
Tensile rupture strength, MPa	44		
Elongation at rupture, %	> 350		
Impact energy, notched, kJ/m^2	210	double V-notch	DIN 53 453
Volume resistivity, $\Omega \cdot$ m	> 10^{13}		DIN 53 482

and acid copolymers are produced by the high-pressure free-radical process, but most of the plants in the rapidly expanding LLDPE sector have the capability to produce VLDPE copolymers with higher content of α-olefin and this is an area with a large potential for expansion.

The principal effect of copolymerization is to reduce the crystallinity. The effect is approximately the same for all comonomers on a molar basis, with the exception of propene which can be incorporated into the crystal lattice. At room temperature the amorphous regions of the copolymer (where the comonomer groups are concentrated) are mobile and the effect of introducing a comonomer is to progressively reduce the stiffness (Fig. 9). In addition to the branches due to the comonomer, the branches which occur under the high pressure synthesis conditions also contribute to the reduction in crystallinity. Below room temperature there are differences between ester copolymers due to the differences in the glass transition temperature T_g of the amorphous material. This follows the T_g of the ester homopolymer and results in EEA and EBA copolymers being flexible down to lower temperatures than EVA, with EMMA having the highest T_g. The VLDPEs produced by the LLDPE processes should have the best low-temperature properties, particularly in the case of narrow composition distribution polymers. Properties of three typical EVAs and a VLDPE [42] are listed in Table 5.

The methacrylic and acrylic acid copolymers are produced to provide enhanced adhesion, particularly in coextruded films or laminates. Not included in Table 4 are terpolymers in which acid monomers are used together with ester comonomers to improve adhesive properties.

The ionomers are produced by the partial neutralization of acidic copolymers containing 10 wt % of (meth)acrylic acid by sodium or zinc ions. The ionic salts and the unneutralized acid groups form strong interchain interactions, producing a form of thermally labile cross-linking in both the solid and the molten states [43, 44]. The T_g of the amorphous material in ionomers is slightly above room temperature, resulting in a stiffness similar to that of LDPE at room temperature. However, the stiffness of most ionomers decreases rapidly with increasing temperature above 40 $^\circ$C.
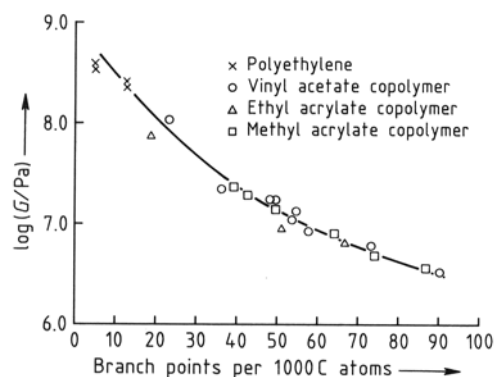
Figure 9. Dynamic modulus G (ca. 2 Hz) at 23°C as a function of total branch points

In polyketone (PK) and cycloolefin (COC) copolymers ethylene is present as a 50 mol % alternating copolymer [45]. The PK materials are believed to be made with a novel group VIII catalyst [46]. They are targeted at medium-stiffness applications and also have good barrier properties for hydrocarbons. The carbonyl group, however, makes the polymers susceptible to degradation by sunlight. The COC materials from Hoechst make use of the remarkable catalyst activity and copolymerization ability of the new single site catalysts [47] (Section 1.3.2.3)

Table 4. Principal types of ethylene copolymer

Comonomer	Abbreviation	Feature	Catalysis *
Vinyl acetate	EVA	flexibility	FR
Methyl acrylate	EMA	flexibility, thermal stability	FR
Ethyl acrylate	EEA	flexibility at low temperature, thermal stability	FR
Butyl acrylate	EBA	as for EEA	FR
Methyl methacrylate	EMMA	flexibility, thermal stability	FR
Butene	VLDPE	flexibility at low temperature, thermal stability	Z, SS
Hexene	VLDPE	as for butene copolymer	Z, SS
Octene	VLDPE	as for butene copolymer	Z, SS
Acrylic acid	EAA	adhesion	FR
Methacrylic acid	EMAA	adhesion	FR
Methacrylic acid $+ Na^+$ or Zn^{2+} (ionomer)		adhesion, toughness, stiffness	FR
Acrylic acid $+ Zn^{2+}$ (ionomer)		adhesion, toughness, stiffness	FR
Carbon monoxide	PK	polyketone, stiffness, high melting	**
Norbornene	COC	cycloolefin copolymer, transparency	SS

∗ FR = free radical, Z = Ziegler catalysis, SS = single-site catalyst. ∗∗ Novel group VIII metal catalyst.

Table 5. Properties of ethylene copolymers

Property	EVA (Repsol PA-501)	EVA (Repsol PA-538)	EVA (Repsol PA-440)	VLDPE (DSM TMX 1000) [a]	Condition	Standard
Vinyl acetate content, wt %	7.5	18	28			
Melt flow index, g/600 s	2	2	6	3	190 °C/2.16 kg	ASTM D1238
Density, kg/m³	926	937	950	902	rapid annealed	ASTM D1505
Vicat softening point, °C	83	64		66		
Tensile strength, MPa	16	16	11	11.5	50 mm/min	ASTM D638
Elongation at rupture, %	700	700	800		TMX 1000: 0.4 m/s	
Modulus of elasticity, MPa	156 [b]	47 [b]	24 [b]	95 [c]		
Permittivity at 1 MHz	2.46	2.70				ASTM D1531
Loss tangent at 1 MHz	0.014	0.035				ASTM D1531
Volume resistivity, $\Omega \cdot m$	2.0×10^{15}	2.5×10^{14}				
Dielectric strength, kV/mm	19	20				

[a] Octene copolymer.
[b] 0.2 % strain, 100 s.
[c] ASTM D790.

and the high transparency and low birefringence will allow its use in compact discs and transparent packaging.

1.3. Polymerization Chemistry

Heat of Reaction. The heat of polymerization of ethylene is 93.6 kJ/mol (3.34 kJ/g). Since the specific heat of ethylene is $2.08 \, J \, °C^{-1} \, g^{-1}$, the temperature rise in the gas phase is ca. 16 °C for each 1 % conversion to polymer. Heat removal is thus a key factor in a commercial polymerization process. Some processes (e.g., ICI autoclave, Unipol fluidized bed) employ only a limited conversion per pass, and the heat of reaction is absorbed by the cool reactants. The unreacted monomer is then cooled in the recycle stage. In other cases (e.g., UCC or BASF tubular and various slurry processes) more surface area or more residence time is provided, and heat is removed through the reactor walls.

1.3.1. Free-Radical Catalysis

1.3.1.1. Introduction

Free-radical catalysis is used exclusively in the high-pressure process, that is at pressures above 100 MPa. The reason for the use of such high pressures is a combination of historic, economic, and technical factors [39]. Because ethylene is gaseous above its critical temperature of 9 °C, a pressure of ca. 20 MPa would be necessary in any case to achieve a reasonable concentration of monomer. Employing pressures of ca. 200 MPa and temperatures above 160 °C enables the polyethylene produced to dissolve in the unreacted ethylene, and the high reaction rate makes the best use of the very expensive high-pressure equipment. 20 % conversion of the monomer is typically achieved in 40 s. A schematic phase diagram for an ethylene – polyethylene system is shown in Figure 10 [48]. For a more detailed account of the effect of molecular mass and MMD on the phase equilibria, see [49].
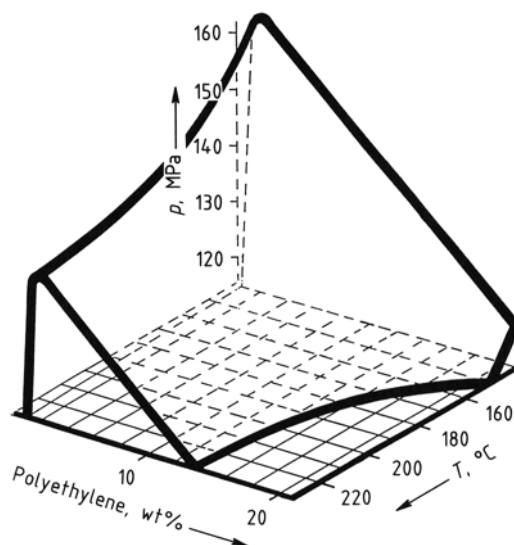
Figure 10. Schematic cloud point surface for ethylene – polyethylene [48]

The single-phase ethylene – polyethylene mixture allows the reaction to take place as a classical free-radical-initiated solution polymerization (→ Polymerization Processes). Some aspects which are particularly important for ethylene systems are as follows:

1) In addition to the effect of concentrating the gaseous monomer, the pressure also influences the reaction rate constants, as is also the case for liquid systems subjected to high pressures [50]. This is generally considered in terms of a volume of activation, analogous to the energy of activation. High pressure affects the configuration change necessary for the reactants to reach the transition state. The overall contribution of the effect of pressure on the rate constants over the pressure range 0 to 200 MPa is to increase the polymerization rate by a factor of ca. 12 [51].

2) The reaction temperatures employed are also high, an average of ca. 220 °C being typical. In parts of the reactor the temperature may be as low as 140 °C but in other parts may reach over 300 °C. These high temperatures also contribute to the high reaction rates, the activation energy being 32 kJ/mol.

3) The growing polymer chains are linear alkyl radicals and as such are very reactive not merely in the addition to double bonds, but also in abstracting hydrogen atoms from other molecules, thereby forming saturated alkyl chains and new radicals. The process is called chain transfer. Since these hydrogen atom abstraction reactions have higher activation energies than polymerization, they become increasingly important as the polymerization temperature rises. On the one hand they put stringent demands on the monomer purity to avoid traces of compounds which could give rise to chain transfer and thereby reduce the molecular mass, and on the other hand it is possible to use low concentrations of suitable materials (so-called chain-transfer agents or modifiers) to control the polymer molecular mass. Chain-transfer agents which have been used commercially include hydrogen, propane, propene, acetone, and methyl ethyl ketone. Chain transfer to some compounds with very active hydrogen atoms such as propene, and particularly the higher alkenes, can lead to radicals which are insufficiently reactive towards ethylene to reinitiate new chains rapidly, and reduced reaction rates result.

4) Chain transfer can also occur with the polyethylene chains themselves, either to the same growing chain (intramolecular) or

to other polyethylene chains (intermolecular transfer). These reactions create the characteristic structural features of LDPE which distinguish it from HDPE. As can be demonstrated with models, the most probable intramolecular chain-transfer reaction is to the carbon atom four carbons back down the chain, which produces butyl groups (Fig. 11 A). This so-called back-biting mechanism was first published by M. J. ROEDEL of Du Pont [52]. If, after the addition of one ethylene molecule to the newly formed secondary radical, a further back-bite occurs (Fig. 11 B), a pair of ethyl branches or a 2-ethylhexyl group is formed. A further possibility, shown in Figure 11 C, is that a back-bite occurs to a branch point, and the tertiary radical then decomposes into a new short radical, leaving a vinylidene group at the end of the polyethylene chain. This process is the principal chain-termination mechanism in LDPE, and concentrations of vinylidene groups approach one per number average molecule for LDPEs produced at high temperature. These three reactions account for the principal features observed in the infrared spectrum of LDPE, but to a lesser extent other intramolecular transfers also occur [9]. Since the activation energy for transfer is higher than for the polymerization reaction and the activation volume is smaller, branching and unsaturation increase with increasing polymerization temperature and decrease with increasing reaction pressure [53,54].

5) Intermolecular transfer leads to long branching and broadening of the molecular mass distribution. Since they have more hydrogen atoms available for chain transfer, the long chains tend to be the most highly branched, and there may be branches on the branches. Statistically each new radical produced by initiation or chain-transfer reactions has a range of probabilities of growing to various lengths before being terminated by one of these same chain-transfer or radical combination reactions. The probable length is the same whether the chain grows from a new initiating radical or a branch point. Thus branches are statistically the same length as the backbone itself and, taking into account statistical variations, the branches may in some cases be longer than the initial backbone. Since the long-branching reaction is a chain-transfer mechanism, the average chain length of an unbranched molecule or a branch is shorter than it would be in the absence of the long-branching reaction. The effects of temperature and pressure are similar to those for short branching, but additionally the amount of long branching is proportional to the concentration of dissolved polymer. In principle, this leads to a clear difference between plug flow (tubular) and continuous stirred-tank reactors (CSTRs, autoclaves). Theoretical analyses have been presented for autoclave [55–57] and tubular [58] reactors.

6) Initiation is very similar to that in many other free-radical polymerizations, but there are some limitations. Initiators are commonly referred to as "catalysts". In the sense that one mole of initiator will achieve the polymerization of several thousand moles of ethylene this is so, but the initiator is destroyed in the process and so the term is, strictly speaking, incorrect. Oxygen was used as initiator in the early commercial processes because of the ease of introducing it into the process. With the development of high-pressure pumps and new initiators, modern plants are able to maintain more precise control of temperature profiles by the injection of solutions of liquid catalysts. The mechanism by which oxygen forms free radicals is rather complicated, and at lower temperatures oxygen can act as an inhibitor [59]. In the autoclave process the use of oxygen has been largely superseded, but in the tubular reactor process it is still widely used, sometimes in combination with liquid initiators. The two overall limitations on initiators are that they should be readily soluble in alkanes and they should produce reactive radicals, ideally alkyl or alkoxy radicals. On the former count, all the aqueous systems and most azo compounds are excluded, and on the second count dibenzoyl peroxide is unsuitable. The initiators are selected for use on the basis of their half-lifes at the reaction temperature. Since the residence time in the reactor zone may be of the order of 20 s or less, to obtain good control of the reaction rate, an initiator half-life of about 1 s is required. For a tubular reactor the same initiator is active over a wider range of tem-

peratures, but its selection is equally critical. Typical initiators are listed in Table 6 [60].

7) The mechanism of kinetic chain termination is by combination of radicals. This further widens the MMD in long-branched systems when the rate of initiation-combination is high [57].

8) Although the conversion of ethylene to polyethylene is thermodynamically favorable, the decomposition into carbon and a mixture of methane and hydrogen is also highly exothermic:

$$C_2H_4 \longrightarrow C + CH_4 \quad \Delta H = 127 \text{ kJ/mol}$$

$$C_2H_4 \longrightarrow 2\,C + 2\,H_2 \quad \Delta H = 53 \text{ kJ/mol}.$$
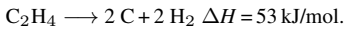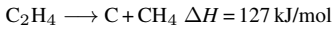
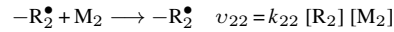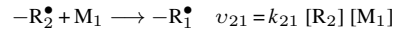For kinetic reasons these reactions are only important at the high temperature and pressures of the high-pressure process. In a confined system the large amount of heat released can raise the temperature, and hence the pressure, of the methane and hydrogen to potentially dangerous levels. The theoretical final temperature and pressure for a contained decomposition starting at 250 °C and 200 MPa are 1400 °C and 620 MPa. In practice much of the heat would be absorbed by the walls of the vessel or pipework. High-pressure plants are designed with relief valves or bursting disks to protect the equipment from overpressurization due to decomposition. Decompositions usually start as a runaway polymerization reaction, but then they can propagate as a slow flame front even into cold gas. Experimental decompositions usually show low propagation velocities of ca. 0.2 m/s [61], but under the more turbulent conditions of commercial plant operation, propagation can be more rapid.

1.3.1.2. Copolymerization

High-pressure ethylene copolymerization follows the classical free-radical copolymerization mechanism ($\rightarrow$ Polymerization Processes, Chap. 2.2.1.). One of the most important characteristics are the reactivity ratios r_1 and r_2. The rates v of the four growth reactions are

$$-R_1^\bullet + M_1 \longrightarrow -R_1^\bullet \quad v_{11} = k_{11}\,[R_1]\,[M_1]$$

$$-R_1^\bullet + M_2 \longrightarrow -R_2^\bullet \quad v_{12} = k_{12}\,[R_1]\,[M_2]$$

$$-R_2^\bullet + M_1 \longrightarrow -R_1^\bullet \quad v_{21} = k_{21}\,[R_2]\,[M_1]$$

$$-R_2^\bullet + M_2 \longrightarrow -R_2^\bullet \quad v_{22} = k_{22}\,[R_2]\,[M_2]$$
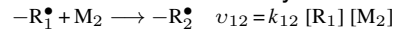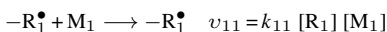
$$r_1 = k_{11}/k_{12} \quad r_2 = k_{22}/k_{21}$$

$-R_1^\bullet$ represents a growing radical where the last unit added is monomer 1 (ethylene for the purpose of this discussion).

Table 7. Copolymerization reactivity ratios and chain transfer [a]

Comonomer M_2	r_1 (rel. to ethylene)	r_1 (rel. to VA) [b]	Chain transfer [c]
Vinyl acetate (VA)	1.05		0.7
Methyl acrylate	0.13	0.1	0.4
Ethyl acrylate	0.08		3.3
Methyl methacrylate	0.06	0.015	2.2
Methacrylic acid	0.015	0.01	
Styrene	0.01	0.01	
Vinyl chloride	0.18	0.23	> 10
Propene	1.3		1.1
Butene	2.0	2.0	20
Isobutene	1.0		2.1
Hexene	1.4		> 20

[a] Reactivity ratios and chain transfer measured in a continuous reactor at 190 °C and 157 MPa, except for the olefins where the data are from a batch reactor at 140 °C and 196 MPa.
[b] Literature values from [40,41]. [c] d[log(MFI)]/d[M_2] in decades of MFI change per mol % in reaction mixture.

For low concentrations of monomer 2 it follows from the well-known copolymerization equation that:

$$1/r_1 = \frac{\text{concentration of monomer 2 in copolymer}}{\text{concentration of monomer 2 in reactor}}$$

The value of r_1 can thus give guidance on the effectiveness of incorporation of comonomer relative to the feed concentration. Some measured values are shown in Table 7. A more comprehensive compilation is given in [9]. Vinyl acetate has a reactivity ratio of almost exactly 1.0 which means that the copolymer has the same composition as the reactor feed. Acrylates on the other hand have r_1 much lower than 1 which means that the copolymer is much richer in acrylate than the reactant mixture. This has implications for the type of reactor. A continuous stirred-tank reactor (CSTR) operates with the comonomer concentrations in a dynamic equilibrium. To make a copolymer containing 20 wt % ethyl acrylate, the feed composition

Table 6. Peroxide initiators for the high-pressure process [60]

Peroxide	Formula	Temperature for half-life of 1 s, °C	Storage temperature, °C
Di-(2-ethylhexyl) per-oxydicarbonate	$\begin{array}{l} C_2H_5 \\ | \\ CH-CH_2-O-\overset{O}{\underset{\|\|}{C}}-O-O-\overset{O}{\underset{\|\|}{C}}-O-CH_2-CH \\ | \\ C_4H_9 \end{array}$ with C_2H_5 and C_4H_9 branches	130	< -15
tert-Butyl 2,2-dimethylperoxy-propanoate	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{O}{\underset{\|\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	154	< 0
Di-(3,5,5-trimethyl-hexanoyl) peroxide	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_2-\overset{O}{\underset{\|\|}{C}}-O-O-\overset{O}{\underset{\|\|}{C}}-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	173	-10 to 0
tert-Butyl 3,5,5-trimethyl-peroxyhexanoate	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{O}{\underset{\|\|}{C}}-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	211	$< +30$
Di-tert-butyl peroxide	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	244	$< +30$

Figure 11. Principal intramolecular chain-transfer reactions

would contain typically 4 % of ethyl acrylate, but the reactor and the stream leaving the reactor would contain only 1.6 %. In the case of a continuous plug flow reactor (CPFR), corresponding to a tubular reactor or a laboratory batch reactor, the corresponding figures would be 3.1 and 0.7 %. The copolymer would in this case be a continuous blend of compositions ranging from 38 % to 9 % produced as the comonomer was used up progressively along the reactor. A useful feature of r_1 for vinyl acetate being 1.0 (and r_2 is also 1.0) is that values of reactivity ratios reported in the literature for other monomers copolymerizing with vinyl acetate can be used to estimate the reactivity ratios for ethylene at high pressure [39]. This is illustrated in Table 7.

Comonomers also act as chain-transfer agents. Table 7 shows some practical measure-

ments of these effects on the MFI under standard conditions. Reference [9] tabulates the chain-transfer effects in terms of molecular mass reduction. Clearly a moderate chain-transfer activity can be tolerated more readily for a comonomer with a low r_1 since the concentration in the reactor will be lower. The chain-transfer activity of the higher α-olefins such as butene is very high, precluding their use in the free-radical process. The radicals produced by chain transfer are relatively stable and retard the reaction. Propene is less extreme in these effects and is sometimes used in the high-pressure process.

Copolymerization theory shows that if r_2 is greater than 1 (it usually approximates to $1/r_1$), then the overall reaction rate is reduced. In a continuous process this translates to an increased initiator demand which in extreme cases makes the process inoperable. As indicated above for homopolymers, a high initiation rate broadens the MMD. Thus acrylate and methacrylate copolymers require higher initiator injection rates and produce hazier films due to the wider MMD.

1.3.2. Coordination Catalysis

The three independent discoveries of low-pressure routes to linear polyethylene had one thing in common: they used catalysts containing transition metals. Despite their very different methods of preparation, there is general agreement that the basic mechanism of polymerization by these catalysts is the same. At some stage a σ-bonded alkyl group is formed. Ethylene is coordinated to the transition metal by a π-bond. This then facilitates the insertion of the ethylene molecule into the metal – alkyl bond producing a longer chain alkyl and a vacant coordination site.
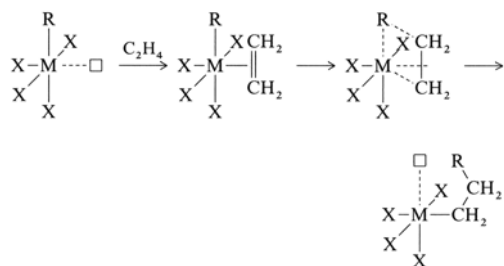
The direct insertion of ethylene into σ-bonded aluminum alkyls was discovered by ZIEGLER in 1950, but the reaction was slow and did not lead to high polymers. The prior coordination of ethylene is clearly crucial. The active species in commercial catalysts is complex, but there is a very large worldwide activity in investigating coordination catalysts, usually by way of model compounds [16, 17]. Commercial catalysts are virtually all heterogeneous solids (at least on a microscopic scale) and require careful attention to the particle shape and size in the development of the manufacturing process. A feature of modern coordination catalysts (except those used in solution processes) is that the catalyst particles grow by a process of replication [13]. This means that the overall shape of each particle is maintained as it grows by polymerization, and thus the distribution of polymer particle sizes is related to the distribution of catalyst particle sizes. For this type of growth to occur, the polymerization process must break down the catalyst particles into much smaller entities which remain held together by the polymer formed, sometimes in the form of fibrils (Fig. 12). Electron microscopy has shown, for one type of supported catalyst at least, that the growth occurs in the form of cylinders, in the growing end of which a catalyst fragment is embedded[62]. This type of growth explains why polymerization rate does not decrease as the overall particle size increases, since the monomer diffusion path remains short. The active catalyst fragments range in size from about 4 nm for $TiCl_3$ to 100 nm for oxide-supported catalysts.

By suitable technology, catalysts can be prepared so that replication leads to polymer particles with a spherical shape and a diameter of ca. 1 mm, suitable for direct use without a pelletization step. Examples of this are the Phillips Particle Form and UCC's Unipol processes based on silica-supported catalysts, and the Montedison Group's Spheripol catalyst based on $MgCl_2$. Outside the United States there is considerable resistance by fabricators to the direct use of polymer powder, and much of the product is pelletized.

Not being simple isolated molecules, the active catalyst sites are not all identical and their activities and the average chain lengths which they produce vary. Instead of a simple statisti-

Catalyst particle   Polymer particle

15 µm   400 µm
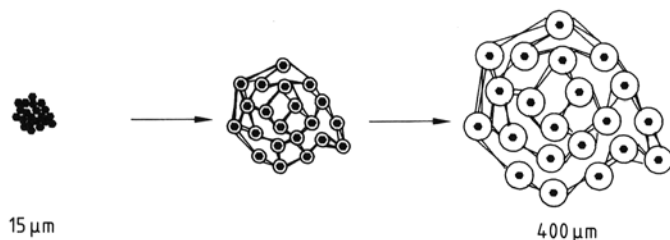
Figure 12. Catalyst particle growth by replication [13]

cal distribution of molecular mass, which would lead to a ratio of weight-average to number-average molecular mass of 2.0, appreciably broader MMDs are obtained (Fig. 13).
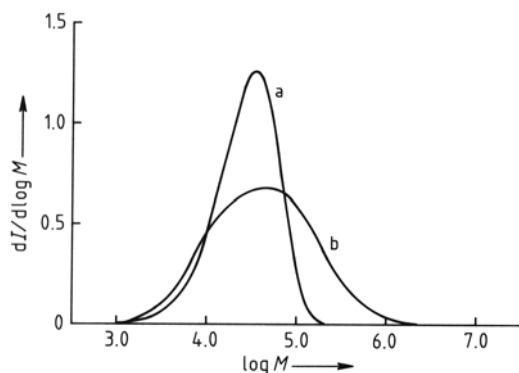
Figure 13. MMD curve of a Ziegler HDPE compared with simple statistical theory
a) Most probable distribution; b) Hostalen GD-4755

1.3.2.1. Phillips Catalysts

A typical Phillips catalyst is produced by impregnating silica particles with a solution of CrO_3 to give a chromium content of ca. 1 %. The powder is then calcined in a current of air with increasing temperature to a final value of ca. 800 °C. At this temperature all of the physically absorbed water and most of the surface hydroxyl groups are driven off [63] and the chromium is present as surface chromate. The formation of a surface silyl chromate is significant, because at the calcining temperature CrO_3 would decompose to lower valent oxides. This catalyst, which is now moisture sensitive, will polymerize ethylene, but with an induction period. During the

initial reaction with ethylene the catalyst's color changes from orange to blue. This is believed to be due to the reduction to Cr^{2+}. The reduction can also be brought about by treatment with carbon monoxide, and in this case the catalyst reacts immediately with ethylene without an induction period.
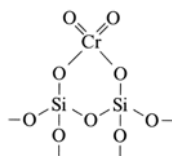
The selection and treatment of the support is fundamental to the process, and a plant may use catalysts made from a variety of supports to produce the whole range of products. The optimum silica is claimed to have a high percentage of pores with a pore diameter of 20–50 nm. A frequently used grade, Grace Davison 952, combines the required pore characteristics with a microspheroidal form. Where the spherical form is not necessary, other silicas are also used, made from crushed and graded silica gel with the required pore structure. The supports are normally supplied with the chromium already impregnated, leaving only the activation stage to be carried out at the polyethylene plant.

As a means of increasing the catalyst productivity and facilitating the production of lower molecular mass (higher MFI) polymers, treatment with titanium compounds is frequently used [64]. The resulting polymers have MFIs more suitable for many applications and also have somewhat broader MMDs. Molecular mass control is a problem with the Phillips process, since it is not possible to use a chain-transfer

agent such as hydrogen, which is oxidized to water by the chromate groups and acts as a catalyst poison. Molecular mass control is therefore effected mainly by the choice and treatment of the support. The use of titanium compounds is believed to result in the chromium atoms being bound to the support via titanate bonds [65]. A further parameter available for modifying the surface characteristics is treatment with fluorine compounds which convert surface hydroxyl groups to fluoride and reduce the surface area. To some extent the effect is similar to high temperature calcination [65,66].

Catalyst productivities are of the order of 5 kg PE per gram of catalyst [63] or higher, with a corresponding chromium content of 2 ppm or less. The percentage of chromium atoms which form active polymerization centers has been estimated as 12 % [67]. With a number-average chain length of the order of 1000 monomer units, each chromium atom thus produces about 1000 molecules. The chains are terminated by a β-hydrogen shift reaction:
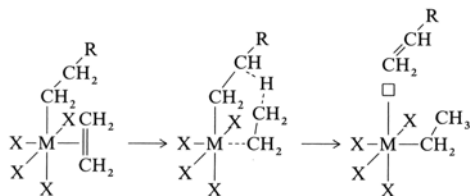
forming an unsaturated molecule and an ethyl ligand attached to the chromium atom [66].

The primary form of molecular mass (and hence MFI) control is by selection of a catalyst which favors the hydrogen shift reaction, but fine adjustments can be made by varying the reaction temperature, since a higher temperature favors the shift reaction.

There have been two developments of chromium catalysts by UCC which fall conceptually in the field of Phillips catalysts. CARRICK et al. reported that bis(triphenylsilyl) chromate, which is closely related to the proposed active site of a Phillips catalyst, polymerizes ethylene at high pressure [69]. When supported on silica it forms a very active catalyst for low-pressure polymerization [70]. The second type of catalyst is formed by the reaction of chromium compounds having π-bonded ligands with the

hydroxyl groups on silica [16,17,71,72]. Paricularly favored is dicyclopentadienyl chromium (chromacene). Unlike the Phillips catalyst it is believed that the chromium is attached to the support by only one bond, with one bond remaining to a cyclopentadienyl group. A very useful feature of these catalysts is their sensitivity to hydrogen, which allows a wide range of molecular masses to be produced. The MMD produced is fairly narrow, but not as narrow as that from some of UCC's Ziegler catalysts.

Somewhat similar to the Phillips catalyst is the Standard Oil (Indiana) catalyst which was the first of the coordination catalysts to be discovered [73]. It typically consists of MoO_3 supported on alumina or silica and calcined in air at high temperature. Unlike the Phillips catalyst it is necessary to reduce the precursor with hydrogen at elevated temperature before using in the polymerization reactor. Despite extensive development it has not been widely commercialized.

1.3.2.2. Ziegler Catalysts

The range of catalysts which function by the Ziegler mechanism is extremely broad and it would be impossible to cover all the variants here. However, those catalysts which meet the requirements of modern polyethylene processes are more restricted in number and tend to follow a common pattern. Some of the developments in Ziegler catalysts for polyethylene have arisen out of developments for polypropylene (see Section 2.1), but since ethylene has a higher reactivity and the extra parameter of stereoregularity does not have to be dealt with, the requirements of the polyethylene catalysts have generally been met more easily.

Early Ziegler catalysts for ethylene were based on β-$TiCl_3$, produced by reducing $TiCl_4$ with $AlEt_2Cl$ or $Al_2Et_3Cl_3$ at low temperature. As cocatalyst, $AlEt_3$ was used. The $TiCl_3$ produced in this way contains $\frac{1}{3}$ mole of cocrystallized $AlCl_3$. Although the catalyst productivities were much higher than for propene, it was necessary to extract the catalyst residues in order to reduce the quantities of Ti and Cl in the product to acceptable levels. Later, by the use of longer chain aluminum alkyls as cocatalyst and alkoxytitanium chlorides as transition metal compound [74,75], the catalyst productivity was

improved sufficiently to allow the costly residue removal stages to be eliminated.

Kinetic studies have shown [17,67] that only a small proportion of the titanium atoms in $TiCl_3$ catalysts form active centers (typically < 1 %). This is believed to be due to the fact that, even with the small polymerizing particles, only a small fraction of the titanium atoms are at the crystallite surface. In order to make a higher proportion of the titanium atoms available to form active centers, various developments were made to support the transition metal compound on a carrier. Early attempts to support $TiCl_4$ directly onto silica, alumina, or magnesia did not lead to a sufficient increase in productivity [74]. The first useful high-yield catalyst used Mg(OH)Cl as support [76]. Since then a variety of magnesium compounds have been used successfully as supports [17,74], but preeminent amongst these is $MgCl_2$ or reaction mixtures which can produce this compound, at least on the support surface. Most modern Ziegler processes seem to use catalysts which fall into this category. The massive increase in activity of $MgCl_2$ supported catalysts has been claimed to be due to an increase in the percentage of titanium atoms forming active centers (approaching 100 %) and not to a significant increase in reaction rate at the active center [16,67]. The $MgCl_2$ supported catalysts produce polyethylenes with narrower MMDs than unsupported catalysts [16] and a narrower distribution of composition in the case of LLDPEs. As with polypropylene, electron donors such as esters or THF may be employed to modify the characteristics of the $MgCl_2$ based catalysts [16], but are not invariably used in the case of polyethylene.

For some processes, particularly the fluidized-bed and loop reactors, the catalyst shape and size is very important, and procedures such as ball-milling and chemical reaction used to produce the basic catalysts do not lead to particle sizes and shapes suitable for direct use. Further processing is required to produce a defined particle size range. Spray-drying can be used to produce spherical paricles. UCC have filed patents on the use of the microspheroidal silicas used in the Phillips process for supporting $MgCl_2 - TiCl_4$ systems for their gas-phase process [77]. For solution processes, as small a particle size as possible is desirable, and this may be achieved either by the method of catalyst preparation [78] or by prepolymerization treatment with a higher olefin [79].

The molecular mass of polyethylene is normally controlled by the use of hydrogen. With Ziegler catalysts at $70-100\,°C$ this can require 20 mol % hydrogen in the gaseous phase of a slurry process or a gas-phase process. When other olefins are copolymerized with ethylene the concentration of hydrogen required is lower, due to chain transfer to the comonomer. At the high temperatures employed in the high-pressure process, the hydrogen concentrations used are much lower due to a relative acceleration of the rate of chain transfer to hydrogen and also a greater proportion of chain transfer by the β-shift reaction. Chain transfer to monomer or comonomer by the β-shift reaction results in unsaturation, primarily in the form of vinyl groups, but hydrogen chain transfer forms methyl-terminated chains.

1.3.2.3. Single-Site Catalysts (Metallocenes)

Typical Phillips or Ziegler catalysts do not follow classical polymerization kinetics and the resulting MMDs are substantially broader than the simple statistical case (see Section 1.3.2). For homopolymers this is probably an advantage and gives rise to the good processing characteristics of HDPE. In the case of copolymers this type of kinetic behavior leads to a broad distribution of composition, in which some chains have low comonomer concentrations and others high concentrations. For LLDPE there are advantages such as higher stiffness than LDPE of the same density, but disadvantages of higher extractable fractions and stickiness in the lower density versions. A catalyst which could produce a narrow composition distribution would overcome these disadvantages, and at the same time less of the expensive comonomer would be required for a given density reduction.

Catalysts which behave in a uniform manner to produce simple statistical distributions of molecular mass and composition have been known for many years, but they are low-yield systems and have not been commercialized for polyethylene [80]. Such catalysts, made from vanadium oxide trichloride [80] and bis(cyclopentadienyl)titanium dichloride [81], remain soluble in the presence of the cocatalyst.

In 1983 KAMINSKY described a catalyst which combined ideal MMD and composition distribution with high yield [82,83]. A basic form of the catalyst was bis(cyclopentadienyl)-dimethylzirconium with a massive excess of methyl aluminoxane $(CH_3-Al-O)_n$ as cocatalyst. Al/Zr ratios as high as 10 000 or more are typically employed. Since then there has been intensive development in academia and industry with the objectives of improving the thermal stability of such catalysts, reducing the concentration of cocatalyst, and, above all, making supported versions.

Because the original catalysts were bis(cyclopentadienyl) transition metal compounds, known as metallocenes, there is a tendency to refer to these as "metallocene catalysts", but a more general term is "single-site catalysts". Given that metallocenes had previously been investigated as catalysts with conventional alkylaluminum compounds as cocatalysts [84], it could be said that the key discovery was the use of methyl aluminoxane (MAO) as cocatalyst. The latter is made by controlled hydrolysis of trimethylaluminum and has a rather ill-defined structure. To avoid too rapid a reaction leading to aluminum hydroxide and unreacted trimethyl, SINN et al. initially used the water of crystallization of materials such as copper(II) sulfate pentahydrate as the source of water [85]. Later developments have led to physical methods for the controlled hydrolysis and the material is commercially available.

Since the transition metal components of the catalysts are stable entities with well-defined structures, investigators have been able to make systematic changes to the structure and achieve the sort of control over the polymerization process which had been hoped for in the early days of Ziegler catalysis. Principal achievements include stereospecific polymerization (see Chapter 2), higher reactivity towards other olefins and also towards other monomers not industrially polymerizable by Ziegler catalysis. It is generally accepted that the active catalytic species is a transition metal cation associated with an aluminoxane counteranion [19,20]. Some investigators believe that the function of the MAO is to act as a source of free trimethylaluminum and also to act as a receptor of the anion produced by the reaction between the catalyst and cocatalyst [86,87]. Polymerization proceeds more rapidly in aromatic solvents and even more rapidly in chlorinated aromatic solvents, and this supports the view that a higher dielectric constant aids the formation of an optimal ion pair [87] (see bottom of page).

Both metallocene dichlorides and dimethyl forms of the catalysts are frequently described, but MAO transforms the former into methyl-substituted species. Chemical changes have been generally directed to modifying the stereochemical environment of the active center and include changes such as replacing the cyclopentadienyl groups with indenyl or fluorenyl, alkyl substitution of the cyclopentadienyl rings, and linking two indenyl units to form a more rigid cage. Alkyl substituents can have a major effect on the catalyst activity [88]. Single-site catalysts have also been made which have only one cyclopentadienyl ligand [89]. Some general forms of single-site catalysts include:
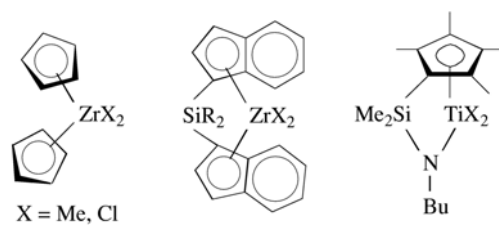
The active sites are tetrahedrally coordinated, in contrast to heterogeneous Ziegler catalysts which are octahedrally coordinated in a $TiCl_3$ or $MgCl_2$ crystal lattice. In principle the greater openness of the tetrahedral configuration allows more ready access to bulkier monomers than the octahedral structure, but the ligands themselves are generally rather large. The improved

$$\text{ZrMe}_2 + [\text{R}_3\text{NH}]^+\,[\text{B}(\text{C}_6\text{F}_5)_4]^- \longrightarrow \text{Zr}^+\,[\text{B}(\text{C}_6\text{F}_5)_4]^-$$
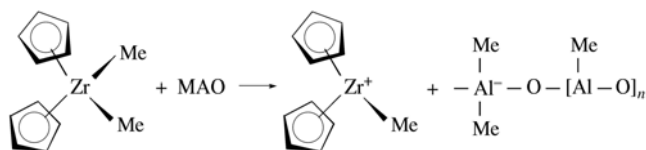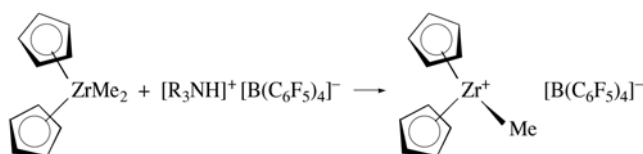
incorporation of monomers larger than ethylene is generally only achieved by bridged systems, in which the opening angle can be greater than the 109° of a regular tetrahedron. Dow refer to their catalysts as "constrained geometry" catalysts and specify that they reduce the bond angles of the coordinated ligands to less than 109°, so that a greater solid angle is available for the entry of monomers to the free coordination site [90].

Developments in cocatalysts have been directed to reducing the ratio of cocatalyst to transition metal and developing better defined chemical entities as cocatalysts. Montell have shown that highly active aluminoxanes can be formed from trialkylaluminum compounds other than the methyl derivative, and that in some cases they are even more active than MAO [91]. When made from higher molar mass aluminum alkyls, well-defined cocatalyst compounds such as tetraalkyldialuminoxanes can be isolated.

$$\text{R}\diagdown \text{Al} \diagup \text{O} \diagdown \text{Al} \diagup \text{R}$$
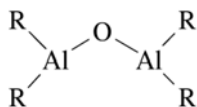
The large excess of MAO found to be necessary to obtain optimum activity in many studies on metallocene catalysts may be due in part to moderately high molar concentration of the cocatalyst needed to generate the active centers. When catalyst and cocatalyst are precontacted at high concentrations and then diluted for polymerization, Al/Zr ratios as low as 20 can be effective [92]. Apart from aluminum-based cocatalysts, boron compounds have been used and allow much lower cocatalyst/catalyst molar ratios to be achieved [93] (see top of page).

The general aspects of ethylene polymerization with metallocene catalysts are similar to those of Ziegler catalysis: molecular mass control can be effected by chain transfer to hydrogen; at higher temperatures chain transfer by the β-shift reaction produces vinyl groups; metal-

locene catalysts tend to be thermally labile and decompose to inactive species [87].

Industrially, the fact that the original metallocene catalysts were soluble meant that the immediate applications were in solution processes. Exxon took the view that the catalysts were short-lived and expensive and developed a high-pressure process to give a high catalyst yield [94,95]. Product targets were VLDPEs with a lower content of extractables and less tackiness. Dow, which operates a solution process for HDPE and LLDPE, has developed high-temperature catalysts for producing a range of homopolymers and copolymers. They claim improved processability for these products due to incorporation of long branches by copolymerization of vinyl end groups of polymer chains formed by β-scission [90]. The solution process favors end-group polymerization because the high temperature leads to formation of a high proportion of chain ends by β-scission; the polymer to monomer concentration ratio is high; and the catalyst is chosen to readily incorporate higher molecular mass olefin monomers. Other routes to improve the processability of the product include the use of mixed catalysts with different molar mass dependence on hydrogen concentration or temperature [96,97].

For use in fluidized bed or slurry phase reactors, a supported catalyst is required. This has been achieved by many companies by treating a silica having the required particle size with MAO and then with the metallocene catalyst. The characteristics of narrow MMD etc. are maintained. In 1996 most major manufacturers are developing single-site catalyzed PEs, but the amount actually being sold is a very small fraction of PE sales. However, the catalysts can be used in all the major PE processes now using Phillips and Ziegler catalysts, and a changeover to single-site catalysts could occur comparatively quickly, depending on the advantages and disadvantages the new products present to plastics fabricators and end-users.

1.3.2.4. Copolymerization

Copolymerization of ethylene and α-olefins is the basis of the large and expanding LLDPE market. As with the free radical case the important factors in addition to those of homopolymerization are the relative reactivities and chain transfer. Both Phillips and Ziegler catalysts copolymerize olefins, but the latter are more widely used because they can be more readily tailored to produce narrow distributions of composition and molecular mass. As has been noted in Section 1.3.2, polymerizations with typical coordination catalysts do not follow classical polymerization kinetics and hence the reactivity ratio concept is not strictly applicable. For completely soluble polymerization systems r_1 is very high and increases with the comonomer chain length (e.g., 29 for butene and 73 for octene, calculated from data in [41]). However, in the case of heterogeneous catalysts and heterogeneous polymerization systems, in particular, the apparent reactivity ratios are lower and may even decrease with increasing olefin chain length. This is presumably due to mass transfer and solubility effects in the growing particles. Chain transfer is enhanced in the presence of olefin comonomer, but this can be compensated by lowering the hydrogen concentration.

Literature articles have appeared on the copolymerization of ethylene with monomers such as styrene, butadiene, vinyl chloride, esters, and others but these have involved Ziegler catalyst variants with poor yields. For practical purposes the range of comonomers polymerizable by Ziegler catalysis is at present limited to olefins and nonconjugated diolefins. The advent of single-site catalysts with high intrinsic activity is removing some of these limitations.

1.4. Raw Materials

1.4.1. Ethylene

The first polyethylene plant built by ICI used ethylene produced by dehydration of ethanol. Modern ethylene production plants are based on the thermal cracking of hydrocarbon feedstocks at ca. 850 °C. Due to the availability of raw materials, the feedstock used predominantly in North America was originally ethane, with naphtha being used more commonly in Europe. The tendency now is for crackers to be designed to accept a wider range of feedstocks, so as to match the range of coproducts such as propene to the market requirements.

Modern plants produce ethylene with a quality which in many cases is suitable for polymerization with little or no further purification. In North America and Europe, producers supply ethylene to an agreed specification via a common ethylene grid, and polymerization plants take their supplies from these pipelines. In the case of sensitive catalyst systems such as the Phillips catalyst some further purification may be necessary to ensure that maximum impurity levels are not exceeded. Table 8 lists specifications for a polymerization-grade ethylene suitable for most processes. There are overall limits on inert materials such as ethane or nitrogen which, because of the efficient recycle system, could build up and dilute the process stream. The main impurities of importance to the free-radical process are oxygen and water. The former could cause inhibition of low-temperature initiators, or uncontrolled initiation of reaction at higher temperatures. At moderate concentrations (after concentration by the recycle) water can form ethylene hydrate [98] in the cooler parts of the high-pressure process, completely blocking the pipework. Some of the other specified compounds can produce problems of molecular mass control or inhibition in the free-radical process, but only at very much higher concentrations.

Table 8. Specifications for polymerization-grade ethylene $*$

C_2H_4	> 99.9 vol %
CH_4, C_2H_6, N_2	< 1000 vol ppm
Olefins + diolefins	< 10 vol ppm
Acetylene	< 2 vol ppm
H_2	< 5 vol ppm
CO	< 1 vol ppm
CO_2	< 1 vol ppm
O_2	< 5 vol ppm
Alcohols (as MeOH)	< 1 vol ppm
H_2O	< 2.5 vol ppm
Sulfur	< 1 vol ppm
Carbonyl sulfide	< 1 vol ppm

$*$ Data obtained from Repsol.

In the case of the Phillips and Ziegler processes, the materials included in the specifica-

tion act as catalyst poisons. Hydrogen is a poison only for the Phillips catalyst.

1.4.2. Comonomers

The vinyl acetate and acrylate esters used as comonomers in the free-radical process are normal commercial quality materials containing sufficient stabilizer to prevent homopolymerization in storage or during pumping, but not so much as to affect the copolymerization reaction. They must be freed of dissolved oxygen by nitrogen sparging.

The butene used in LLDPE is normally a purified refinery product, although in the United States material is available from the oligomerization of ethylene. As an alternative to buying butene with its associated transport problems, IFP have developed the Alphabutol process [99, 100] for dimerizing ethylene as a compact adjunct to a polymerization plant. There is also the possibility of using a polymerization catalyst capable of simultaneously dimerizing ethylene [101, 102].

The higher α-olefins such as hexene and octene used in LLDPE processes are ethylene oligomerization products. They must be freed of oxygen and water before use in the polymerization process. The 4-methylpentene used by BP is a propylene dimer made by an alkali metal catalyzed process.

1.4.3. Other Materials

The initiators and catalysts are described in Section 1.3.1. All the free radical initiators and many of the Ziegler and Phillips catalysts are manufactured by specialist suppliers. Some of the simpler Ziegler catalysts may be made on-site from basic chemicals such as $TiCl_4$, $MgCl_2$, etc. The aluminum alkyls are made by a very few international suppliers.

Initiator solvents and compressor lubricants for the free-radical process are carefully selected to be free of aromatic compounds, since much of the product may be used for food packaging.

1.5. Production Processes

Modern polyethylene production processes offer the possibility of a versatile range of products. High-pressure processes can produce LLDPE in addition to the normal range of LDPEs and ester copolymers. As well as HDPE some low-pressure plants can also produce LLDPE and VLDPE, and in many cases these compete for the same market as LDPE and the ester copolymers. A guide to the applicability of the various types of processes is given in Table 9.

Table 10 compares the capital and operating costs for various types of polyethylene plant. The comparison is on the basis of construction on a United States Gulf Coast site using the largest stream size currently (1996) available for licensing. The costings assume the production of pellets and this results in higher costs for the gas-phase and slurry plants than would be the case if 100 % sales of ex-reactor granules could be assumed. Some differences due to the economy of scale occur as a result of the available stream size. The production costs are dominated by the cost of ethylene, although some differences such as the extra cost of electrical energy can be noted. In the case of LLDPE these costings assume a unit cost for the butene equal to 1.05 times that of ethylene. In many other parts of the world the price of butene, including transport, is considerably higher. The unit price of higher olefins is generally appreciably higher than that of ethylene, from which they are derived by oligomerization.

1.5.1. High-Pressure Process

A flowsheet of the high-pressure polyethylene process is shown in Figure 14. The reactor may take one of two forms: a high-pressure autoclave or a jacketted tube, but otherwise the processes are similar. The reaction pressure is typically in the range 150 – 200 MPa for the autoclave process and 200 – 350 MPa for a tubular reactor. Such high pressures call for very specialized technology and many key features have remained proprietary information. The design of thick-walled cylinders requires a different type of analysis [103, 104] from that for lower pressure vessels, and fatigue is a major design consideration for pumps and compressors. A drawing of the second stage cylinder of a high-pressure ethylene compressor is shown in Figure 15,

Table 9. The technical applicability of processes for polyethylene manufacture *

	High-pressure autoclave	High-pressure tubular	Gas-phase fluidized bed	Slurry phase autoclave/loop	Solution autoclave
Installed capacity ** worldwide, 10^6 t/a	8.8	8.3	12.8	12.5	3.2
LDPE	+	+	−	−	−
EVA copolymers	+	+	−	−	−
Acrylate copolymers	+	+	−	−	−
HDPE	0	−	+	+	+
HMW HDPE	−	−	+	+	−
UHMPE	−	−	0	+	−
LLDPE	+	0	+	0	+
VLDPE	+	0	+	−	+

* + = suitable; 0 = technically feasible with some limitations; − = unsuitable or not possible. ** Capacity data (1995) obtained from Chem Systems, London.

Table 10. Production costs for polyethylene processes in $/t (1996 U.S. Gulf Coast prices) *

Product	LDPE		LLDPE		HDPE		
Process	Autoclave	Tubular	Fluid bed	Solution	Fluid bed	Ziegler	Phillips
Capacity, 10^3 t/a	117	200	225	200	200	200	200
Capital cost, 10^6 $	85	116	98	138	90	135	105
Monomer costs	447	443	450 **	452 **	449	456	445
Catalysts, chemicals	20	18	29	31	26	22	20
Electricity	31	33	15	9	15	16	16
Other utilities	5	2	5	17	5	10	11
Manpower	10	6	6	6	6	6	6
Maintenance	15	13	9	15	9	15	13
Overheads	35	29	22	31	22	26	29
Production costs	565	544	534	561	553	553	539
Depreciation	71	59	44	69	45	68	53
Total costs	636	603	578	630	577	620	592

* Data from Chem Systems, London. ** Includes cost of butene monomer at a unit price equal to 1.05 times that of ethylene; other locations or the use of other olefin comonomers could lead to a higher monomer cost.

which illustrates the massive construction necessary and the avoidance of cross-bores to improve fatigue resistance at the very highest pressures. Specialized forms of sealing joints in vessels and pipework have been developed which make use of the pressure itself to increase the sealing forces [105].

Referring to Figure 14, the fresh ethylene enters from the refinery at ca. 5 MPa, mixes with the low-pressure recycle and is compressed to 25 MPa. After mixing with the intermediate-pressure recycle, the pressure is raised in the secondary (or hyper) compressor to 150 – 350 MPa for feeding to the reactor. The pressure in the reactor is controlled automatically by a flow control valve at the reactor outlet. The reaction mixture then passes through a cooler to re-duce the polymer temperature to a value suitable for feeding the pelletizing extruder. The polyethylene is separated from the majority of the unreacted monomer in the intermediate separator at ca. 27 MPa. This pressure is chosen to give a compromise between separation efficiency and compression energy savings. The remaining monomer is removed in the low-pressure separator that feeds the pelletizing extruder. The extrudate is pelletized underwater by a die-face cutter, and the pellets are then dried and conveyed to temporary storage hoppers to await quality control clearance. Finally the pellets are transferred to silos for blending and storage, before off-loading to tankers or sacks.
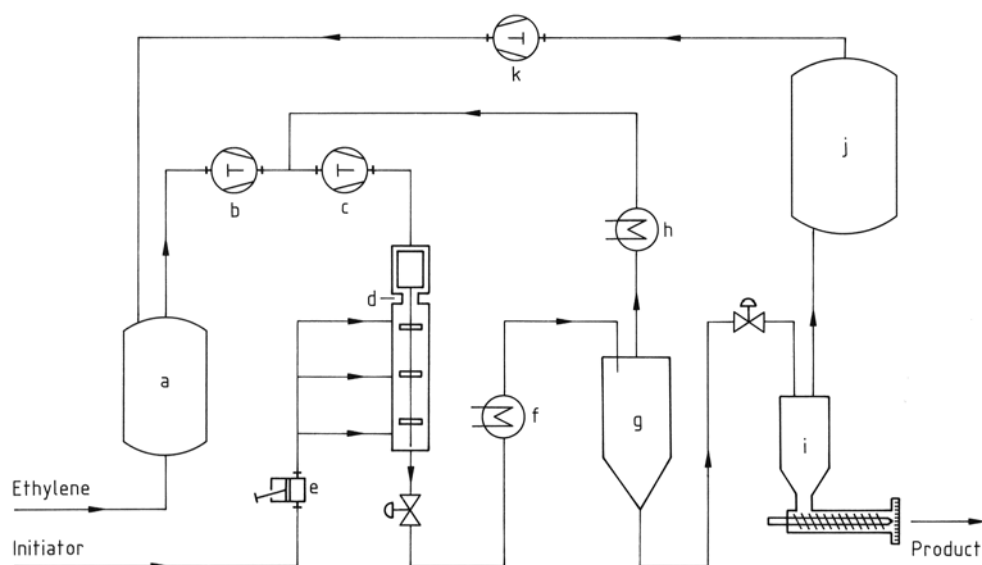
Figure 14. High-pressure autoclave process
a) Ethylene stock tank (5 MPa); b) Primary compressor; c) Secondary compressor (200 MPa); d) Autoclave reactor; e) Initiator pumps; f) Product cooler; g) Separator (25 MPa); h) Recycle cooler; i) Low-pressure separator and melt extruder; j) Low-pressure stock tank (0.2 MPa); k) Booster compressor
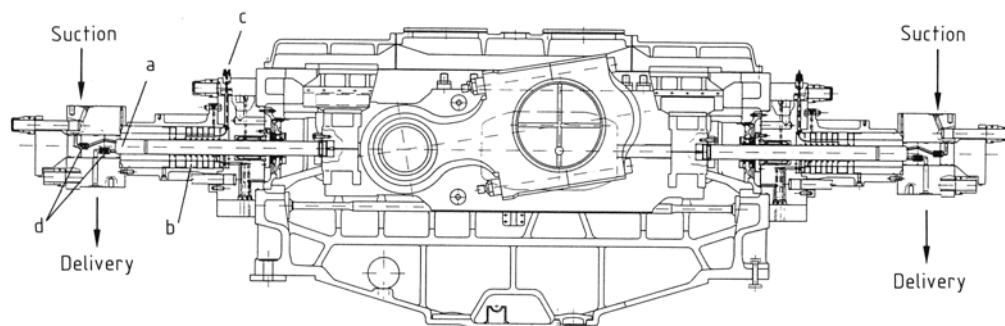
Figure 15. Second stage cylinder of a Nuovo Pignone compressor with 350 MPa maximum output pressure
a) Piston; b) Packings; c) Lubricant injection to packings; d) Valves

1.5.1.1. Autoclave Reactor

A typical autoclave design is shown in Figure 16. The autoclave volume is chosen to give an overall residence time of ca. $30-60$ s, with corresponding volumes in larger plants of ≥ 1 m^3. A novel feature is the internal stirrer motor. The Du Pont process uses an external motor. The elongated cylindrical form arises partly from the fabrication constraints of making a thick-walled forging, and partly from the requirements of the process for multiple zones. Cross-bores are provided along the length of the reactor for thermocouples, and monomer and initiator entries. Bursting disks or other relief devices are

mounted directly into the reactor walls to provide unrestricted passage for the reactor contents in the event of a pressure rise due to a decomposition.

The autoclave functions as an adiabatic continuous stirred-tank reactor (CSTR), with the heat of reaction being removed by the fresh ethylene entering the reactor. The conversion of monomer to polymer is thus related to the difference in temperature between the feed gas and the final reaction temperature. For practical purposes percentage conversion $= 0.075 \times \Delta T$. Most modern reactors have two or more zones with increasing temperatures. The reaction tem-

peratures are maintained constant by controlling the speeds of the pumps feeding initiators into the respective zones. The first zone is typically 180 °C and the final zone 290 °C. For adequate control the initiators must have decomposition half-lifes of ca. 1 s under the reaction conditions in the zone. Table 6 lists a range of commercial initiators used in both the autoclave and tubular processes.
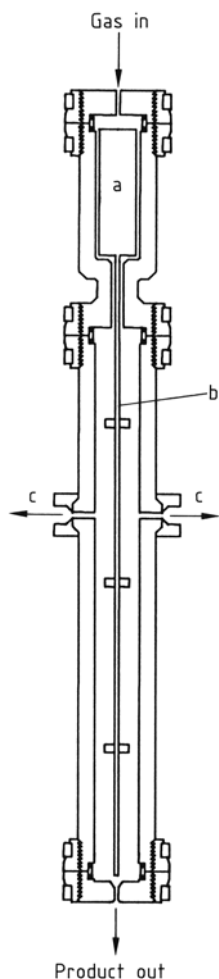
Figure 16. High-pressure autoclave reactor
a) Stirrer motor; b) Stirrer shaft; c) Bursting disk ports

1.5.1.2. Tubular Reactor

A tubular reactor typically consists of several hundred meters of jacketted high-pressure tub-ing arranged as a series of straight sections connected by 180° bends. Inner diameters of 25 – 75 mm have been quoted, but 60 mm or somewhat larger is probably typical of modern tubular reactors. A ratio of outer to inner diameters of about 2.5 is used to provide the necessary strength for the high pressures involved. At many of the pipe junctions thermocouples are introduced to follow the course of the reaction, and initiator and gas inlets or pressure relief devices may also be incorporated. Unlike the autoclave process, no after-cooler is required for the secondary compressor, but the first section of the tubular reactor must function as a preheater to raise the ethylene to a sufficiently high temperature for the reaction to start. This temperature depends on the initiator employed, ranging from 190 °C for oxygen to 140 °C for a peroxydicarbonate. The latter part of the reactor functions as a product cooler similar to that of the autoclave process.

A tubular reactor works in the plug flow regime with heat transfer to the jacket. Plug flow is achieved by the correct choice of pipe diameter relative to the flow rate [106] so as to give sufficient turbulence and good axial mixing. Although heat is transferred through the reactor wall, it is not generally possible to maintain isothermal conditions, and temperature peaks occur. Because of the temperature peaks, which may not occur at exactly constant position in the tube, automatic temperature control must be more sophisticated than in the autoclave process; i.e., it must be possible to calculate average temperatures for appropriate regions of the reactor. When oxygen is used as initiator, the temperature control acts on the rate of addition of oxygen in the lower pressure part of the system. When peroxide initiators are used, the speeds of the high-pressure pumps are controlled. Oxygen is still widely used in the tubular reactor process, either alone or in conjunction with peroxides. Because of its complex initiation mechanism, oxygen tends to give more gentle temperature peaks with less tendency for decomposition. In the case of reactors with multiple initiator injection, liquid initiators offer more flexibility, since they can be injected at points where there is no fresh ethylene injection (which would be required to carry in oxygen as initiator). Injection of initiator at various positions along the tube produces new temperature peaks, increas-

ing the overall conversion. By using these techniques higher conversions than in the autoclave reactor can be achieved, but at a higher cost in compression energy. Although conversions of up to 35 % (compared with 20 % for the autoclave) have been claimed, the maximum useful conversion depends on the product quality required, since quality deteriorates markedly with increasing conversion.

1.5.1.3. High-Pressure Copolymers

The high-pressure processes described are also suitable for the copolymerization of monomers such as vinyl acetate or acrylic esters. The autoclave process is generally preferred for its well-defined operating conditions and its ability to produce a useful conversion at a low maximum temperature. In the case of vinyl acetate the reactivities of the two monomers are virtually identical and so they are consumed at the same rate. This means that the reacting monomer mixture and the copolymer produced maintain a constant composition even in multizoned reactors, but the recycle system must handle high concentrations of vinyl acetate. The converse is the case for the acrylate esters. If a multizoned or a tubular reactor is used the composition varies in the different zones, but the recycle is nearly pure ethylene. The principal modifications to a high-pressure polyethylene plant to enable it to manufacture copolymers are:

1) Installation of liquid pumps, which usually pump the comonomer into the suction of the secondary compressor
2) In the case of vinyl acetate, it is necessary to collect the monomer which condenses in the low-pressure recycle system and purify it before returning it to the liquid pump
3) The system for removing final traces of monomer must be improved, because the comonomers are more soluble than ethylene and they have more offensive odors

Technically a copolymer plant could also copolymerize acrylic or methacrylic acid, but there are long-term corrosion problems. Major producers of these copolymers have constructed plants especially for their manufacture, using corrosion-resistant steels.

1.5.1.4. Linear Low-Density Polyethylene (LLDPE)

CdF Chimie converted high-pressure process equipment to use Ziegler catalysts to make HDPE. These plants were later used to copolymerize ethylene with butene and other comonomers to make LLDPE. The catalysts used are generally of the Ziegler type but have been specially developed for the high temperatures of the high-pressure process [107]. Several other manufacturers have modified existing high-pressure plants to enable them to make a rapid, but limited entry into the LLDPE market, but this route is not seen as suitable for a large new investment. The required modifications (generally similar to those for free-radical co-polymers together with some additional ones associated with the different type of catalyst) are as follows:

1) Purification columns to remove polar impurities from the ethylene and olefin comonomer.
2) Hydrogen injection for MFI control.
3) Compressor modifications to take account of the lower compressibility and poorer lubricating properties of the monomer mixture [108]. The concentrations of butene or other olefin of ca. 50 % are much higher than in the free-radical copolymer case.
4) Catalyst handling equipment to produce pumpable dispersions, and to maintain the catalyst under a nitrogen atmosphere.
5) A system for injecting a catalyst deactivator such as a suspension of calcium stearate [109], after the reactor and before the separator.
6) Usually some modifications to the pelletizing extruder to take account of the higher torque generated by LLDPE.

1.5.2. Suspension (Slurry) Process

The formation of polyethylene suspended in a hydrocarbon diluent was envisaged as a convenient form of production process from the earliest patenting by Ziegler [110]. This was reinforced by the fact that, for a given pressure, most Ziegler catalysts give their highest yields

at temperatures at which polyethylene is insoluble. The Phillips process on the other hand originated in the laboratory as a solution process that uses a fixed bed of catalyst [111] and was commercialized in 1956 as a solution process using a powdered catalyst which had to be removed by filtration. Laboratory developments led to the discovery of high-activity catalysts which fragment at temperatures below 105 °C to enable the low concentration of finely divided catalyst residues to be left in the product. Since 1961 all Phillips plants have been of this type using novel process technology to implement their Particle Form suspension process.

Many companies have built plants to make polyethylene by using Ziegler catalysts, but because the license was only for the use of the catalyst, there has been a diversity of process designs, even amongst the suspension processes. The Phillips process was licensed as a package and the plants themselves tended to be very similar. More recently the picture has become blurred as chromium-based catalysts have been used in fluidized-bed reactors and Ziegler catalysts are being employed in loop reactors. Early Ziegler plants included a catalyst residue removal stage which added considerably to the complexity and cost. Since the late 1960s it has been possible to eliminate this step. Other variations arise from the selection of the diluent. A high-boiling diluent generally requires more energy to remove the final traces from the polymer, and stripping with steam is frequently employed. Because of the low flash point, the use of a low-boiling diluent such as hexane requires more care in the design and operation of the plant, but this seems to be the preferred route for modern plants.

The suspension process has been used extensively for the production of HDPE, and in many cases these polymers incorporate a small amount of comonomer to increase the toughness or resistance to stress cracking. The use of higher concentrations of comonomer to produce LLDPE presents problems however, as a significant fraction of the product dissolves in the diluent. Because of the poorer solvent properties of isobutane, the Phillips process is best suited to making lower density materials. With the original Phillips catalysts the lower density limit was considered to be about 930 kg/m^3, but with more recent catalysts, particularly supported single-site catalysts, the limit is reduced to around 920 kg/m^3.

1.5.2.1. Autoclave Process

Figure 17 shows a flowsheet for a suspension (slurry) process based on various descriptions of the Hoechst process [8, 74, 112, 113]. The pressure employed is between 0.5 and 1.0 MPa, allowing the use of large reactors (ca. 100 m^3). The reaction temperature is 80 – 90 °C. The diluent is a low-boiling hydrocarbon such as hexane. The catalyst compounds and aluminum alkyl are slurried with diluent in the catalyst mixing vessel before being fed to the reactor at a rate sufficient to maintain the required polymerization rate. Only one main reactor is shown but, at least in the case of bimodal MMD high molecular mass polymers [114], two or more reactors in cascade may be used. The reaction mixture is then passed to a run-down reactor where the dissolved ethylene is consumed almost completely, avoiding the need for an ethylene recycle. The slurry concentration is an important parameter in the process. A high concentration allows higher outputs from a given reactor volume, but the heat transfer to the cooling jacket is worse and stirring becomes more difficult. The maximum usable slurry concentration depends on a number of factors, including solvent type, particle size and shape, but principally on the bulk density of the polymer particles. Slurry concentrations vary from 15 to 45 wt % [115], with many patents reporting values in the range 30 – 35 % in a heavy diluent.

The slurry from the run-down reactor then passes to a centrifuge to remove the bulk of the diluent, which is recycled directly to the reactor. This diluent contains aluminum alkyl and comonomer, if used, and the injection rates of these raw materials are adjusted to take into account the amounts reintroduced by the diluent recycle. The polymer is dried in a continuous fluidized-bed drier in a stream of hot nitrogen to remove residual diluent. Further quantities of diluent are condensed from the circulating nitrogen stream and recycled. Before extrusion into pellets, stabilizers are added to neutralize the catalyst residues, and other additives such as antioxidants may be added at this point.
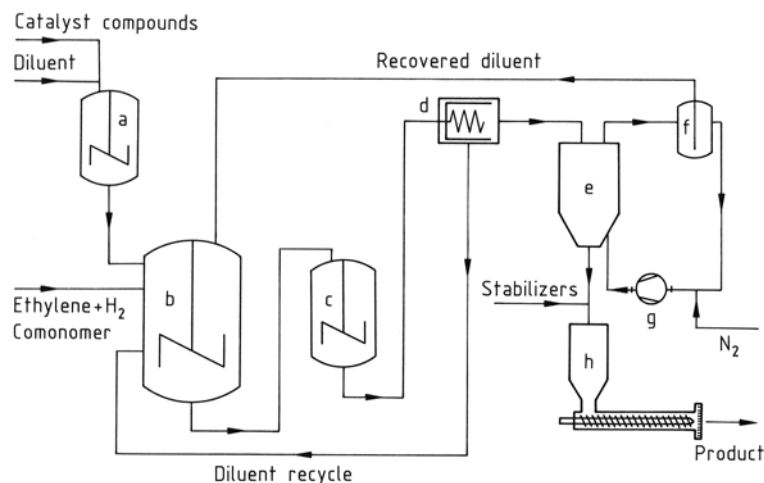
Figure 17. Hoechst suspension polymerization process
a) Catalyst preparation vessel; b) Polymerization reactor; c) Run-down reactor; d) Centrifuge; e) Fluidized-bed drier; f) Diluent condenser; g) Nitrogen circulator; h) Powder-fed extruder

The powder-fed extruder has a longer barrel than is the case for the high-pressure process because in addition to generating sufficient pressure for the pelletizing head, it must also melt the polymer powder. Although a single long barreled extruder is shown, new installations increasingly make use of a combination of a short extruder to melt the polymer followed by a gear pump to generate the pelletizing pressure. This combination has a lower energy requirement.

1.5.2.2. Loop Reactor Process

A simplified flowsheet for the Phillips Particle Form process is shown in Figure 18. The novel double loop reactor constructed from wide-bore jacketted pipe was developed by Phillips engineers to avoid deposits, which had been troublesome in a stirred autoclave [111, 116]. It also has a high surface-to-volume ratio, facilitating heat removal and allowing short residence times. The impeller forces the reaction mixture through the pipework in a turbulent regime with a velocity of 5 – 10 m/s. The reaction conditions of 100 °C and 3 – 4 MPa correspond to the needs of the chromium-based Phillips catalyst and the required productivity. The diluent used is isobutane which facilitates the subsequent flash separation and, being a poor solvent for polyethylene, permits higher operating temperatures than the higher alkanes. The catalyst is flushed into the reactor with diluent from the metering device at the base of the catalyst slurry tank. The polymer is taken off from a sedimentation leg which enables the slurry to be passed to the flash tank at a concentration of 55 – 65 % instead of the 30 – 35 % circulating in the loop reactor [111]. The isobutane diluent evaporates in the flash tank and is then condensed and recycled. Residual isobutane is removed in a nitrogen-flushed conveyor. Pelletization is carried out in a powder-fed extruder in a similar way to the Hoechst process.

1.5.3. Gas-Phase Process

Fluidized-bed processes for the production of HDPE were developed in the late 1960s by Union Carbide and somewhat later by Naftachemie (now BP). Although an innovative technology, the process did not offer clear economic advantages over the established slurry processes (see Table 10). A rapid increase in the building of fluidized-bed plants followed Union Carbide's announcement of their Unipol process for LLDPE in 1977. In this case the fluidized-bed process is competing with solution and high-pressure processes compared to which it has lower capital and operating costs, particularly if it can be assumed that customers are able to use ex-reactor granules directly (not assumed in Table 10). Many fluidized-bed units have been built
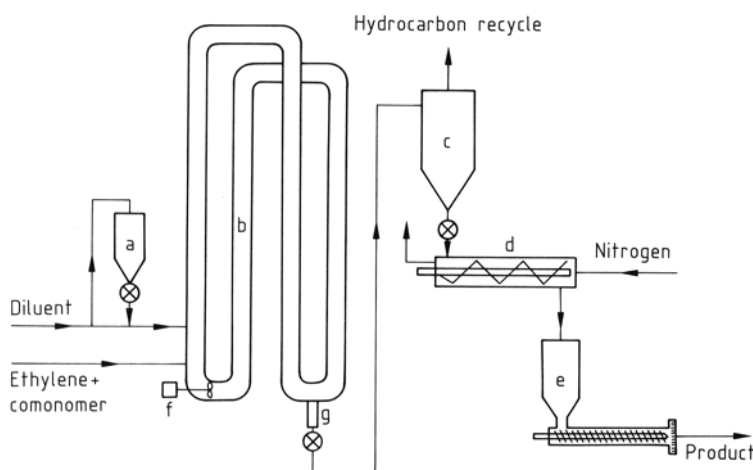
Figure 18. Flowsheet of the Phillips Particle Form process
a) Catalyst hopper and feed valve; b) Double loop reactor; c) Flash tank; d) Purge drier; e) Powder-fed extruder; f) Impeller; g) Sedimentation leg

as dual-purpose plants ("swing plants") with the ability to produce either LLDPE or HDPE according to demand. The fluidized-bed process can produce a very wide range of MFIs and densities since it is free of the viscosity constraints of the solution process and the solubility constraints of the slurry process. Ranges of < 0.01 to > 100 in MFI and densities from 890 to 970 kg/m^3 have been claimed [117, 118]. Originally the process used butene as the comonomer for LLDPEs, but later hexene was introduced for high-performance copolymers. BP uses 4-methylpentene for its high-performance LLDPEs.

Figure 19 shows a flowsheet for the Union Carbide fluidized-bed process [119]. The reactor has a characteristic shape with a cylindrical reaction section, and an expanded section in which the gas velocity is reduced to allow entrained particles to fall back into the bed. The bed diameter is ca. 4 m with a working height of 10 m and an overall height of the reaction unit of ca. 30 m. The gas enters the reactor through a distributor plate which provides an even distribution of gas and must also prevent powder falling through when the gas flow is stopped. The fluidized bed functions more or less as a continuous stirred-tank reactor in which mass transfer provides back mixing of material and heat throughout the reactor. There is a predominant upflow at the center and downflow at the walls. Reaction temperature is 80 – 100 °C, depending on the

density of the product being made, and the pressure is in the range of 0.7 – 2.0 MPa. Originally, lower pressures were used for butene and hexene to avoid condensation in the recycle cooler, but it is now claimed that condensation can be used to increase the output since the heat of vaporization of the liquid olefin absorbs more heat from the polymerizing particles [120]. The conversion per pass is ca. 2 % for HDPE, but higher when using an olefin comonomer in the condensing mode. The positioning of the catalyst feed point and the polymer offtake is important to minimize the loss of catalyst particles, which results in low conversion. A cyclone and/or filter prevent fine particles reaching the recycle cooler and compressor. The polymer is removed via a sequenced valve to a powder cyclone, from which residual monomers are recovered and recompressed. The main recycle compressor circulates gas at a high flow rate, but with a small pressure rise. Since the process operates close to the melting point of the polymer, accurate temperature control is necessary by regulating the rate of catalyst addition. If a runaway reaction is detected, a gas such as carbon dioxide can be injected to poison the catalyst.

The selection of the catalyst is critical for the success of the process. The catalyst particle grows by a process of replication to about 15 – 20 times its initial size. Not only does this affect the fluidization characteristics, but the polymerization rate and heat transfer must be con-
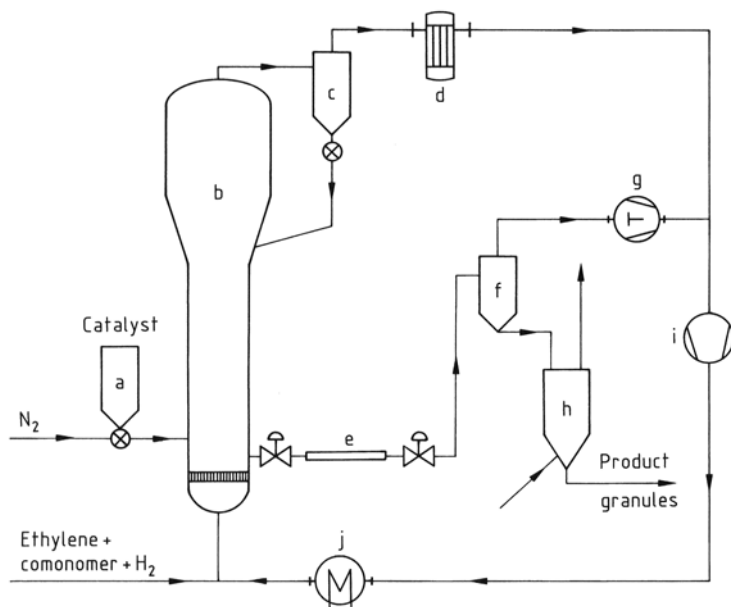
Figure 19. Fluidized-bed process
a) Catalyst hopper and feed valve; b) Fluidized-bed reactor; c) Cyclone; d) Filter; e) Polymer take-off system; f) Product recovery cyclone; g) Monomer recovery compressor; h) Purge hopper; i) Recycle compressor; j) Recycle gas cooler

trolled to prevent fusion of the particles or a thermal runaway reaction. Catalysts based on microspheroidal silica or $MgCl_2$ with a mean particle size of about 50 μm are claimed to be particularly suitable [77].

1.5.4. Solution Process

Solution processes have been developed by various companies including Du Pont, Dow, DSM, and Mitsui for the manufacture of LLDPE or HDPE/LLDPE on a swing basis. The advantages are that they readily handle a wide range of comonomer types and product densities and, depending on catalyst type, tend to produce narrow MMD products more readily. Like the high-pressure process (which is also a solution process) they are unable to handle high-viscosity products. The Du Pont and DSM processes are similar to the high-pressure process in that they function adiabatically with short residence times, whereas the Dow and Mitsui processes remove heat from the reaction mixture. Since the Du Pont process is available under license and more plants of this type have been constructed, this is the process included in the table of cost estimates (Table 10) and described below. The Du

Pont process has a catalyst residue removal stage and for this reason is probably not the most economic solution process.

Figure 20 shows a flowsheet of the Sclairtech process of Du Pont of Canada [121]. The ethylene is dissolved in a diluent such as cyclohexane and pumped to the reactor at ca. 10 MPa. The reaction step is adiabatic and the reaction temperature is in the range 200 – 300 °C. The feed contains ca. 25 wt % ethylene, of which 95 % is converted to poylethylene in the reactor. The residence time is ca. 2 min. The catalyst most frequently quoted in patents is a mixture of $VOCl_3$ and $TiCl_4$ activated by an aluminum alkyl. Although the catalyst components may be initially soluble, the active catalyst species appears to be heterogeneous [80]. The polyethylene solution leaving the reactor is treated with a deactivating agent and the mixture then passes through a bed of alumina where the deactivated catalyst residues are adsorbed. Two depressurization stages follow, similar to the high-pressure process, in which solvent and unreacted monomers are volatilized. After extrusion into pellets, further removal of solvent residues is achieved by passing a heated stream of gas through the bed of pellets.
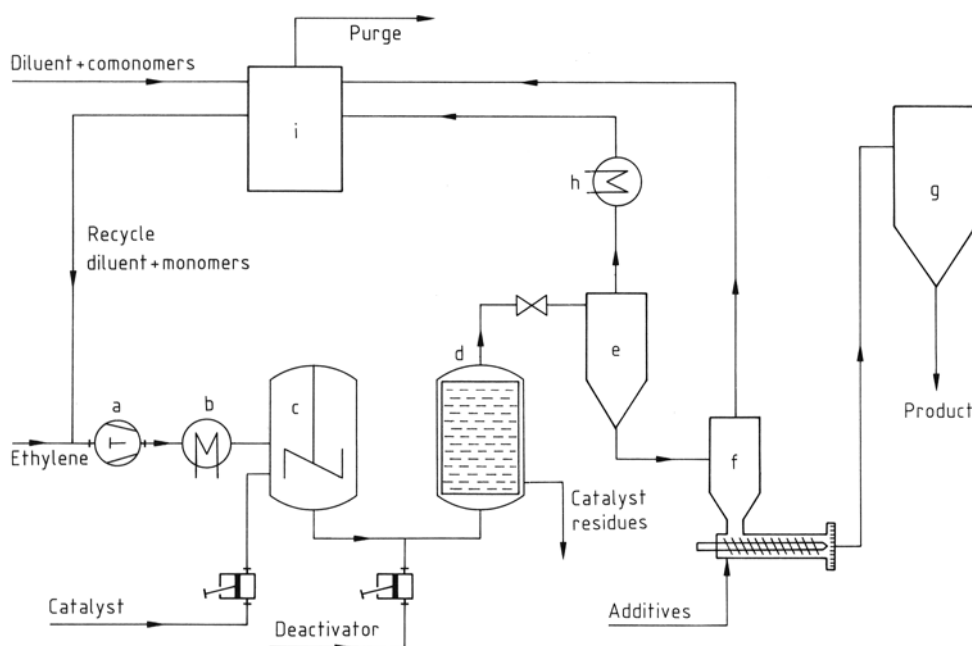
Figure 20. Solution polymerization process
a) Reactor feed pump; b) Temperature control; c) Reactor; d) Catalyst adsorber; e) First separator; f) Low-pressure separator and melt-fed extruder; g) Purged product hopper; h) Recycle cooler; i) Diluent and monomer purification unit

Table 11. Consumption by application∗, %

Market	HDPE	LDPE and LLDPE
Film	24	71
Blow molding	36	1
Injection molding	21	6
Extrusion coating		9
Pipe	10	2
Wire and cable insulation	1	4
Others	8	6

∗ Percentages based on data for Western Europe, Japan, and North America 1996 [122].

1.6. Uses

Table 11 shows an analysis by end-use of approximately half of the world market for polyethylenes. The pattern is very different for the two classes. LDPE (together with LLDPE which is sold into the same market) is used predominantly for films, not all of which is for packaging. Because of its greater rigidity and better creep properties, HDPE is used in more structural applications, and also has important applications in the packaging of aggressive liquids such as bleach, detergent, and hydrocarbons. The basic techniques of plastics fabrication are treated in → Plastics, Processing and so only the aspects particular to polyethylene are discussed here.

1.6.1. Film

LDPE retains its position as a preferred packaging material because of its limp feel, transparency, toughness, and the ability to rapidly take up the shape of the contents of the bag. Other materials such as thinner HDPE film or paper may in some cases be more economical, but are less acceptable to the customer. Most LDPE film is produced by the film blowing process (→ Films) but flat film extruded onto chilled rolls (→ Films) is also made, particularly in the United States. An LDPE for high-clarity film typically has a MFI of 2 and a density of 920 kg/m^3 and is extruded at 160 – 180 °C. The cast film process is usually used with higher density polyethylenes (930 – 935 kg/m^3), where the quenching on the chilled rolls enables good optical properties to be achieved with a higher film stiffness. The bubble diameter in the tubular film process may be up to 2 m for general purpose

packaging, and larger for heavy gauge industrial film. Originally, bags were made directly from tubular film by welding one end, but the tendency now is to make wide film on large machines and fabricate the bags by welding and cutting. Apart from packaging film and heavy duty sacks, increasing quantities of polyethylene are used for impermeable or stabilizing membranes in civil engineering construction.

Additives play a particularly important role in the production of LDPE film by the film blowing process. Without additives, the pressure of the windup rollers on the warm film forces the surfaces into such close contact that subsequently it may be virtually impossible to separate them. High-gloss films are the worst affected. This is overcome by adding an antiblocking agent such as very fine silica, which roughens the surface on a submicroscopic scale without significantly affecting the optical properties. To reduce the friction between the surfaces a slip agent such as oleamide or erucamide is added. Other additives may be added to achieve effects in the final product such as oxidation resistance, UV resistance, or antistatic properties.

A film extruder designed for LDPE requires extensive modifications to allow it to extrude LLDPE at comparable rates [123–125]. To avoid this investment and the lack of flexibility, many film manufacturers (particularly in Europe) use blends of LDPE and LLDPE. The equipment modifications required are:

1) The screw must have greater clearance between the flights and the barrel to avoid temperature buildup due to the higher shear viscosity. Ideally the screw should be shorter.
2) The die gap must be widened to reduce the shear rate and so avoid a type of surface defect, known as shark skin, to which narrow MMD polymers are prone. To some extent this problem can be avoided by incorporating additives based on fluoroelastomers (Du Pont, 3M) or silicones (UCC) [126–128].
3) The cooling ring must give more rapid quenching of the melt to avoid the development of excessive crystalline haze, and also to give more support to the bubble because of the lower tensile viscosity under the inflation conditions. Apart from this lack of inherent stability of the bubble, the low tensile viscosity is responsible for the major prod-

uct advantage of LLDPE, since high stresses do not occur when the melt is drawn down to thin film. LLDPE can be drawn down to much thinner film without the bubble tearing than can a LDPE with equivalent mechanical properties.

HDPE film is generally made on units specifically optimized for the high molecular mass grades normally used. To produce tough films a balanced orientation of the film is necessary, and a high ratio of die diameter to bubble diameter ("blow ratio") is used so as to balance the machine direction draw with a high transverse draw. A characteristic stalk-shaped bubble is used in which substantial machine-direction draw takes place before a rapid expansion occurs some distance above the die. Mechanical guides are needed to stabilize the bubble. HDPE film is opaque and is usually used in much thinner gauges than LDPE. It competes with LDPE in areas such as carrier bags and supermarket convenience bags.

1.6.2. Extrusion Coating

LDPE is used extensively for coating cardboard, paper, and aluminum for milk cartons etc., for which a very low level of impurities is required. Extrusion is carried out at ca. 300 °C through a wide-slit die. Polymers with a high die swell due to long branching perform best, since the tendency to expand on leaving the die opposes the "neck-in" tendency when the melt is drawn onto the substrate. A typical LDPE used for this application has a MFI of 4 and a density of 920 kg/m^3.

1.6.3. Blow Molding

HDPE is now the preferred material for blow-molded containers for liquids, combining adequate environmental stress crack resistance with higher rigidity than LDPE, and hence permitting lower bottle weights for a given duty. The major uses are in the domestic market for bleach, detergents, and milk. For this application a HDPE with a MFI of 0.2 and a density of 950 g/m^3 is suitable. Other uses include a variety of industrial containers and gasoline tanks. There is a trend to higher molecular mass and to broader MMD polymers, with bimodal MMDs achieved by using catalyst or reactor developments [129].

1.6.4. Injection Molding

Injection molding is used for a variety of products. Some, such as caps and lids are used in the packaging field. Other applications such as housewares, toys, and industrial containers are more durable. According to whether high flexibility is required or not, LDPE or HDPE may be used. Some LLDPEs with a narrow MMD are particularly well suited for this method of fabrication. MFIs range from 2 to > 40. A narrow MMD gives the best compromise between toughness, flow into the mold, and freedom from warpage in the finished product.

1.6.5. Pipe

The use of polyethylene for pipes is one of the few engineering applications, where the applied stresses are carefully assessed and a lifetime of at least 50 years is required. Polyethylene is used for water and natural gas local distribution systems and, unlike many other uses, there is a substantial stress applied continuously. The potential problem is thus long-term stress rupture, and this must be carefully assessed by extrapolation and accelerated testing. Large quantities of pipe made of a medium-density polyethylene designed to withstand a stress in the PE of 8 MPa have been laid, but advances in bimodal HDPE polymers now enable a 50-year lifetime at a design stress of 10 MPa to be met. The first polymers which met this specification (PE 100) were introduced by Solvay in their TUB 120 range, but now all major producers have similar polymers in their ranges [130, 36].

1.6.6. Wire and Cable Insulation

Because of its outstanding dielectric properties, the first application of polyethylene was the insulation of very high frequency and submarine telephone cables. These have continued to be made from LDPE, but uses have expanded into telephone and power cables. In the latter case cross-linking is increasingly used to enhance the properties and allow a higher current rating for a given size of cable.

1.6.7. Ethylene Copolymers

The processing techniques used for copolymers are generally the same as used for polyethylene homopolymers, but the range of applications is generally more diverse [12]. The property most generally exploited is the decreased rigidity to give more flexible film, moldings, and tubing than is possible with LDPE. Copolymers with high comonomer content are generally competitive with plasticized PVC and rubbers, with a low extractable additive content as an advantage. For flexibility down to the lowest temperatures acrylate copolymers are preferred over EVA copolymers. VLDPE copolymers, particularly those made by single-site catalysts, are increasingly being used in applications requiring flexibility combined with thermal stability and good low-temperature flexibility.

Ethylene copolymers are also used in blends, in the same way as rubbers, to confer increased toughness. Particular applications include blends with wax and with bitumen for paper coating and road surfacing, respectively. Copolymers are also used as constituents of hot melt adhesives.

1.6.8. Ultra High Modulus Polyethylene Fibers

Because of their low softening point polyethylene fibers have not been of interest for general purpose textile use, although substantial amounts are used for producing monofilament. In 1973 Capaccio and Ward showed that solid HDPE could be drawn at elevated temperatures to very high draw ratios to produce fibers with a tensile modulus of 70 GPa and a tensile strength of 1 GPa (Kevlar 149: 172 GPa and 3.4 GPa, respectively). Theoretical values for a perfect extended-chain crystal are 300 GPa and ca. 25 GPa, and thus these early results achieved a significant fraction of the maximum modulus possible. Further developments have been on parallel fronts: melt spinning followed by solid-state drawing, and gel spinning.

Melt spinning has been adopted commercially by Celanese, SNIA, and Mitsui. Gel spinning consists of forming a dilute solution in a heavy solvent and then extruding it so that gelled PE fibers are formed on cooling and can then be

drawn on conventional fiber-making equipment. The solvent has to be removed by evaporation or solvent extraction. The gel-spinning process is operated by Allied Signal and DSM. The melt-spinning process is limited to moderate molecular masses because of the polymer viscosity, but the gel-spinning process can use higher molecular mass PEs and achieves higher modulus and tensile strength (172 GPa and 3.0 GPa). Further advances may be expected on using PEs made with single-site catalysts. Since the production costs of the gel-spinning process are higher there seems to be a market for both types of product.

Limitations on the uses include the low softening temperature and creep. Creep can be reduced considerably by cross-linking [131]. For use in composites the fibers must exhibit good adhesion to epoxy resins, and this can be achieved by various methods, principally by plasma treatment [132]. PE fibers have poor compressive strength and so for composites they are usually used in combination with other reinforcing fibers such as glass or carbon. The principal market is probably in energy-absorption applications such as personal armour where the characteristics which are responsible for creep give rise to energy absorption superior to existing materials. Other applications which make use if its high modulus are in leading-edge sporting goods where it competes with carbon fiber, aramid etc. [132–134].

1.6.9. Joining Polyethylene

The most satisfactory method of joining PE is by welding but considerable experience is required to achieve satisfactory results. A widely used method uses a stream of hot gas (usually nitrogen to avoid oxidation) in a similar manner to gas welding of metals. The edges to be joined are chamfered to allow a bead of PE to be melted into the join. The heating causes changes in the annealed state of the PE adjacent to the join and it may become weaker than the original material, but this can be overcome by welding a reinforcing strip over the joint line [135].

Welding is used by the gas and water industries to join pipe in their distribution networks. The most satisfactory method is butt welding, in which the ends are machined true and then heated by a PTFE-insulated electrical heater.

The automated machine then removes the heater and presses the ends together at a predetermined force. The procedure produces a bead of PE on the inside and outside surfaces, and the external bead is machined flush with the pipe surface.

Because of its low surface energy PE cannot be joined in its natural state by any of the strong adhesives such as epoxy resins. Rubbery adhesives such as pressure-sensitive and hot-melt adhesives function satisfactorily, but the mechanical strength of the bonding material is not very high. By treatment of the surface it is possible to form a bond with epoxies. A recommended method is oxidation with chromic acid, after which the surfaces can be glued with epoxy resin [135]. A more recent development for bonding polyolefins is the use of an aliphatic amine primer that penetrates into the surface of the PE. When a cyanoacrylate adhesive is then applied, polymerization to form a bond occurs in the usual way [136].

1.7. Chemically Modified Polyethylenes

1.7.1. Cross-Linked Polyethylene

As noted in Section 1.3.1, polyethylene free radicals combine to form larger molecules, unlike materials such as polypropylene, which tends to degrade. This cross-linking reaction has been made use of in a number of ways to effectively increase the molecular mass with corresponding improvements in some properties. The principal commercial methods of cross-linking [137] are:

1) Free radicals can be generated by mixing in a peroxide such as dicumyl peroxide or di-*tert*-butyl peroxide in an extruder at as low a temperature as possible and then curing the extruded cable in an external heated zone [138]. This process uses ca. 2 % peroxide and the curing process must be carried out under pressure to avoid excessive formation of voids. Peroxide together with a blowing agent is used for making foamed sheeting or molded articles, particularly of EVA.

2) Polyethylene can be cross-linked by radiation either above or below the melting point, but commercially, products are cross-linked in the solid state after the basic fabrication

step. There are some differences in properties between peroxide and radiation cross-linked polyethylene due to the fact that in the solid state the cross-links occur in the existing amorphous regions, and the existing crystallinity is largely retained. Electron accelerators are used to provide the radiation in a readily controlled process [139]. Products include shrink tubing and sheeting, wire insulation, and water pipes.

3) Dow has developed a process (Sioplas-E) in which a peroxide is used to graft a vinylsilane to the polyethylene. The silane groups can then react together in the presence of moisture to form cross-links. A catalyst such as dibutyltin dilaurate is added to accelerate the cross-linking reaction. The process has the advantage that only a tenth of the amount of peroxide is required and the curing stage is simpler. However, since water must diffuse in from the surface, curing times become excessive for thick sections. The original process produced the graft polymer as a separate stage from the cable extrusion, but the Monosil process achieves the grafting in the cable extruder [140].

4) A further variant of silane cross-linking is the production of a silane copolymer by direct copolymerization of a vinylsilane in a high-pressure polyethylene reactor. This process developed by Mitsubishi for their Linklon-X polymers has been licensed to A. T. Plastics for their Aqualink process [141].

1.7.2. Chlorinated Polyethylene

Both LDPE and HDPE can be chlorinated to form what are in effect ethylene/vinyl chloride copolymers which are not accessible by direct polymerization. Chlorine contents of 34 – 44 wt % are reported [142]. By selection of the polyethylene and the chlorination conditions, products can be made with a range of processing viscosities and with the chlorination either randomly distributed or concentrated in segments, leaving some polyethylene crystallinity. The principal application is as a toughening agent for PVC, but there are other uses in the same general area as flexible materials such as EVA, but with the emphasis on outdoor weather resistance.

Du Pont manufacture a chlorosulfonated polyethylene (Hypalon) in which the sulfonyl groups are used in a propietary vulcanizing process. The materials are used as rubbers with good weathering properties.

1.7.3. Fluorinated Polyethylene

Fluorinated polyethylene is not produced as a bulk material, but surface treatment of articles with fluorine gas is used to produce a highly fluorinated surface layer. In this way the permeability of containers to a wide range of solvents can be reduced drastically. The treatment can be applied to finished articles, or fluorination can be carried out in-line by employing a dilute mixture of fluorine gas in nitrogen as the blow gas in the blow molding process [143]. Gasoline tanks are a major application, but the process is also used for containers for materials such as solvents and pesticides.

1.8. Environmental Aspects

1.8.1. Manufacture

Under normal operating conditions the impact on the environment of polyethylene production plants is minimal. There are some hydrocarbon emissions, particularly from those plants using solvents, but these are regulated by local legislation. In some cases hazardous materials such as the Phillips catalyst or aluminum alkyls are handled safely by attention to detail in the plant design and operation. The preparation of both peroxide initiators and Ziegler catalysts involves some extensive chemical operations with the attendant problems of waste disposal. All peroxide initiators are now made by specialist producers and there is also a tendency for this to be the case for Ziegler and Phillips catalysts.

The high-pressure autoclave process is protected against over-pressurization by bursting disks. When a disk bursts, the vessel contents, including carbonized polyethylene, are discharged quite safely to the atmosphere, but with the impression of an explosion. Thus, it is not feasible to site this type of plant as close to residential areas as would otherwise be possible.

1.8.2. Polymer Disposal and Recycling

At the time of writing (1997), much of the polyethylene produced is dumped into landfill within a few months of manufacture. This represents the fraction used in packaging. However, the use of disposable packaging is being increasingly called into question. In the 1970s and 1980s the concern was with the unsightliness of a material which was littering the environment, and did not degrade. Various schemes were developed to promote more rapid degradation based either on photosensitized oxidation [144] or biodegradation of blends with starch [145]. Some of these developments have reached commercialization, but now public opinion is moving towards the need to conserve plastics. Table 12 shows some of the options available to deal with the problem of disposable packaging.

Much emphasis centers on recycling, that is converting the polyethylene back into granules and then using it to produce more film etc. There is some oxidation during use and recovery, leading to some cross-linking and a slight deterioration in extrusion properties. It will be difficult therefore to match the original manufacturer's tightly controlled specification, particularly if the recovered material is of a variety of grades from different producers. There will also be a problem of suitability for use in contact with food, since the recovered material may contain a range of unknown organic and inorganic impurities. At present the intentions are to use recycled material in uncritical nonfood uses. However, a successful recycling program could outstrip such uses. Ideally recycling should be at the monomer level, but polyethylene does not readily decompose to form ethylene.

Processes have been developed which crack the plastics waste to a liquid hydrocarbon suitable for use as the feedstock to a conventional cracker, which effectively allows recycling via the monomer [146]. In the BP process plastics waste is fed to a fluidized bed reactor maintained at about 500 °C, and the liquid feedstock is recovered from the recirculating gas stream. Gaseous byproducts are used as fuel to maintain the temperature of the fluidized bed. This process has advantages over the hypothetical process of cracking PE to ethylene in that it tolerates the presence of other plastics materials, even PVC. The ever present problem of collection and transport is also eased in that the cracked feedstock could be produced in relatively small local units and transported in tankers to the refineries.

Another approach is to burn the polyethylene to recover electrical or thermal energy, thereby saving on fossil fuel which in most economies is still being used for this purpose.

2. Polypropylene

2.1. Historical Survey

In the 1950s KARL ZIEGLER discovered new catalysts which were to revolutionize the plastics industry. Before then, propene could not be polymerized to high molecular mass products with the catalysts then available, namely, free-radical, anionic and cationic systems. Even the most favorable of these yielded only liquids consisting of many isomers and greaselike materials unsuitable for making hard plastic products.

In 1953 KARL ZIEGLER, Professor at the Max-Planck-Institut für Kohlenforschung, demonstrated that ethylene could be polymerized to a high molecular mass crystalline polymer at moderate pressure and temperature. His group had for some years been using aluminum alkyls to convert ethylene into a range of oligomers having an even number of carbon atoms. Unexpectedly, almost total conversion to butenes occurred in one experiment. The cause was eventually traced to nickel-ion contamination in the autoclave. Tests with many other metallic compounds revealed that a combination of zirconium ion with aluminum alkyl converted ethylene to high molecular mass polymer. Further searching revealed that titanium ion was even more active in producing polyethylene (November 1953). Such combinations of transition metal compounds with an aluminum alkyl later became known as Ziegler – Natta Catalysts, thereby acknowledging the immense contribution of GIULIO NATTA to discovering and characterizing polypropylene (PP) and other α-olefin polymers in 1954.

NATTA, Professor and Director of the Milan Institute of Industrial Chemistry, was a consultant to Montecatini, to whom NATTA assigned his patents. The close collaboration between ZIEGLER and NATTA was acknowledged in 1963 by the joint award of a Nobel prize in Chemistry

Table 12. Polyethylene packaging disposal strategy

Disposal method	Advantages	Disadvantages
Incineration	avoids landfill	generates CO_2 without benefits
Incineration with energy recovery	displaces existing fossil fuel use	loss of fabrication costs
Biodegradation	removes unsightly refuse	doubts about completeness of degradation; generates CO_2 without benefits
Promoted degradation	removes unsightly refuse; lower labor costs for agricultural uses	degradation slow away from sunlight; generates CO_2 without benefits
Recycling via melt	makes use of scarce resource	some deterioration in quality
Recycling via monomer	top-quality product; processes mixed plastics	fairly large scale processing plant
Reuse	saves on fabrication costs	PE may not be the best material

for their outstanding contributions to polymer science. A fascinating account of ZIEGLER and NATTA's personal approach to these discoveries is provided by MCMILLAN [147].

Table 13. Global PP capacity (10^3 t/a) and its distribution

Country/region	End 1990	End 1994	Growth * 1990 – 1994, %
Western Europe	4530	5705	26
North America	4400	5440	24
Japan	1870	2656	42
Other Far East/Australia	2734	4090	50
Middle East/Africa	280	655	34
South America	450	1035	30
Eastern Europe	790	930	18
Total/average	15 054	20 511	36

* 7 % per annum growth for four years is 31 % total growth.

In the the United States, patents on crystalline polypropylene were awarded originally to NATTA et al. (on behalf of Montecatini), but were overturned later in favor of Phillips Petroleum Company. The immense legal procedings to establish inventor rights to crystalline polypropylene in the United States are outlined by HOGAN and BANKS [148], with more recent comments by PINO and MORETTI on this costly litigation [149]. Phillip's polymerization catalyst, consisting of chromium-ion promoted silica – alumina, has not been used in any commercial plant to manufacture crystalline polypropylene.

Notwithstanding the complexities and hazardous nature of these new coordinated catalysts, industrialists and academe alike were stimulated by ZIEGLER and NATTA's prompt and prolific disclosures concerning this new, high-melting polymer. Industrial-scale produc-

tion of PP started at Ferrara, Italy, in 1957 with a 6×10^3 t/a plant. By the end of 1994 global capacity had risen to 20.5×10^3 t/a (Table 13), spread over 35 countries [150]; today, new plants are expected to be capable of producing 200×10^3 t/a to achieve reasonable economies of scale.

There are several reasons for this phenomenal growth, which exceeds that of other bulk plastics [151] (Table 14). At first propene was readily available, almost at byproduct prices, from petrochemical cracker plants making ethylene. The polymer itself was suitable for a wide range of existing and new applications such as films, various fibers, large and small moldings from boat hulls to instrument parts. In addition, new manufacturing technologies based on $MgCl_2$ supported catalyst systems yielded both cost savings and improved products by eliminating atactic PP removal steps and then the deashing stage. Some 40 years on there are expectations that the new metallocene catalyts will extend these uses, even to the extent of challenging products such as polyamide, ABS, and flexible PVC for part of their market [152].

2.2. Polymer Structure

2.2.1. Molecular and Chain Structure

Polypropylene is a synthetic, high molecular mass linear addition polymer of propene. In 1954/5, NATTA et al. prepared sufficiently large amounts of PP to isolate and characterize various stereoisomers. This led to a new descriptive nomenclature still used today. Commercial interest lies primarily in highly crystalline PP, together with its further modifications through copolymerization.

In perfectly isotactic PP, each monomer unit in the chain is arranged in a regular head-to-tail assembly without any branching or 1,3 additions (Fig. 21 A). This is the result of template-type constraints by the heterogeneous stereospecific catalyst. In practice such perfection is hard to achieve. An occasional error (Fig. 21 B), averaging about $0.3 - 1.5$ per hundred chain links, occurs in some, but not equally in all chains. The multisite nature of solid catalysts is thought to be responsible for this behavior.

Table 14. Major polymer usage in Western Europe

Polymer	Consumption, 10^3 t/a			Growth rate, %	
	1974	1984	1994	'74/'84	'84/'94
LLDPE +LDPE	3080	4089	6015	33	47
HDPE	1035	1704	3570	65	110
PS	1118	1290	1908	15	48
PVC	3360	3825	5480	14	43
PP	680	1895	5178	179	173

Solvay and $MgCl_2$ supported systems reduce the extent of these errors, and with them the amount of noncrystalline (atactic) polymer. Still at the development stage, metallocene-based single-site catalysts (SSCs) also produce stereoregularity errors, but these seem to be distributed more uniformly along the chains, regardless of their length (Fig. 21 E). This contrasts with multisite catalysts (MSCs), for which misplacements vary in frequency and in number. The tendency here is for the high molecular mass fraction to contain fewer faults, while the short chains suffer from excessive disruptions, which lead to reduced crystallinity.

Until recently, syndiotactic PP (Fig. 21 C) was not commercially important because of unacceptable polymerization difficulties at low temperatures. Some metallocene catalysts overcome this problem to produce a regular sequence of racemic (r) propene placements yielding a crystalline polymer melting at $130\,^\circ C$. Mitsui Toatsu and Fina have entered into a joint venture to assess costs and customer reaction to syndiotactic PP.

Complete loss of steric regulation generates atactic polymer chains (Fig. 21 D), incapable of crystallizing. Hitherto this low molecular mass byproduct had only a few commercial outlets for adhesives. The position could change with the emergence of high molecular mass versions deliberately made with a metallocene-based catalyst, $[(Me_2SiFlu_2)ZrCl_2]$ (Flu = fluorenyl) [153].

All Ziegler–Natta commercial polymers have broad molecular mass distributions within the range $M_w/M_n = 5 - 10$ for ex-reactor material. Any reduction is achieved by peroxide-induced chain clipping in an extruder. Metallocene polymers have narrower distributions ($M_w/M_n = 2 - 4$) as a consequence of their single-site mechanism. This avoids the need for peroxide additives, which produce objectionable odor and volatile byproducts.

2.2.2. Crystallization and Morphology

Polypropylene's strength and versatility stem from a matrix of interlocking crystallites that allow formation of rigid and tough articles. Highly isotactic polymer, with its regular structure, forms a helical coil having three monomer units per turn. These coils stack together into thin lamellar crystallites which force the chains to fold several times as they emerge and reenter lamellae. Polyethylene behaves similarly (see Fig. 2)

While the equilibrium (i.e., thermodynamic) melting point is $188\,^\circ C$, at normal analysis heating rates the final melting point is ca. $160 - 170\,^\circ C$. Three crystalline forms are known (Table 15), of which the α-form is the most stable. Rapid quenching yields the β-form with a lower density and melting point of $150\,^\circ C$. Polymers of lower stereoregularity and random copolymers usually contain γ- crystallites in addition to the α-form.

Crystallization is complicated further by assembly of these lamellar crystals into larger structures, called spherulites. These have radial symmetry and can adopt five different forms (Table 16). While the size of the crystallites is in the region of $10 - 50$ nm, too small to scatter visible light ($400 - 600$ nm), spherulites are much larger ($10^3 - 10^5$ nm). The latter are responsible for the translucency of slowly cooled PP moldings. Rapid crystallization from the melt by fast cooling, adding nucleating agents, and reducing spherulite sizes by stretching a partially solidified melt all improve transparency.
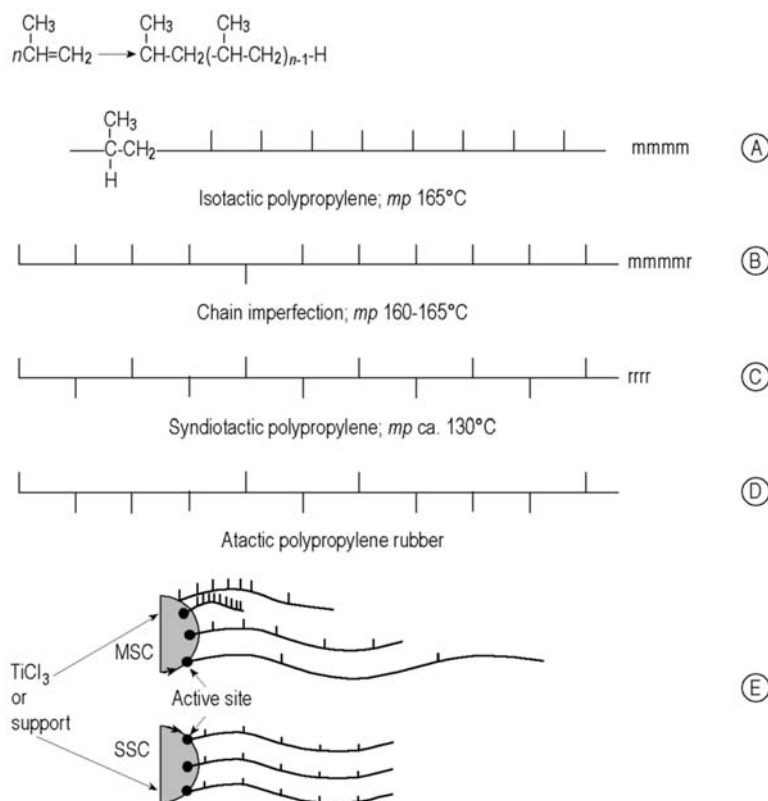
Figure 21. PP chain structures

Table 15. Crystal habits of PP [154–156]

Crystal form	System	Crystal density (20 °C), g/cm^3	Chains per unit cell	mp, °C *
Iso α	monoclinic	0.932 – 0.943	4	171
Iso β	pseudo hexagonal	0.922	9	150
Iso γ	triclinic	0.939	1	131
Smectic		0.916		
Amorphous		0.85		
Syndio	orthorhombic	0.93	2	138
			(4/1 helix)	

* The enthalpy of melting for 100 % crystalline isotactic PP is variously reported, due to different techniques. WUNDERLICH [154] gives 165 ± 18 J/g, BRANDRUP and IMMERGUT report 209 J/g [155], the ICI DSC standard is 185 J/g, and the Shell DSC standard is 188 J/g [157, p. 590].

Crystallization from a viscous melt is hindered by chain entanglements and by the need for helices to fold as they close-pack into lamellae. This, and the formation of nuclei might contribute to the low degree of crystallization even in highly stereoregular polymers. Typically, the onset of crystallization occurs at ca. 110 – 120 °C in DSC instruments. This point coincides with the cooling peak for polyethylene, whose pres-

ence would be masked in blends and in ethylene copolymers. Using the melting curve overcomes this analytical difficulty. Another aspect of tardy crystallization is the low level of crystallinity in fabricated items, even when highly stereoregular polymers are used. Commercial articles vary from 30 % crystallinity in rapidly quenched films to 50 – 60 % in moldings. Even purified and annealed samples of highly stereo-

regular PP rarely achieve more than 70 % crystallinity. Polypropylene is properly regarded as a semicrystalline polymer for these reasons.

Table 16. Spherulitic structures

Spherulite type	Crystal type	Features
I	α	positive birefringence, lost at $160-170°C$; epitaxial branching; always associated with type II
II	α	negative birefringence, lost at $160-170\,°C$; fibrillar crystals radiating from nucleus; most stable of all spherulites
III	β	strongly negative birefringence; associated with β-crystals and high shear in cooling; melts and reverts to type II at $145-150\,°C$
IV	β	special case of Type III, characterized by banded concentric rings
V	γ	rare variant formed under high pressure with γ-crystals

2.3. Raw Materials

2.3.1. Propene

Sensitive Ziegler – Natta catalysts require pure propene to ensure high polymerization rates and good yields of isotactic polymer, without wasteful byproducts. Harmful impurities can be grouped into two main categories which have different effects on the process. The most destructive contaminants are polar and highly unsaturated compounds which react directly with the catalyst systems, retarding polymerization and impairing stereospecificity. Examples include acetylenes, dienes, carbon monoxide and dioxide, carbonyl sulfide, water, alcohols, and ammonia. The second group contains materials which adversely influence the process, but not the chemistry, by raising the pressure during reaction due to an accumulation of inert substances. These further complicate the monomer recovery section and recycle streams. This group contains materials such as methane, ethane, propane, butane, and nitrogen.

Most manufacturers use polymer-grade propene as feedstock, which can be further refined by passing it through local guard columns containing alkali, molecular sieve, alumina, supported copper, etc. to guarantee consistently high purity [158, 159]. Typically, monomer conforming to the following specification, is ade-

quate for most plants, but certain sensitive supported catalysts require the lower levels listed for carbonyl sulfide, carbon monoxide, and oxygen (this quality is said to be suitable for metallocene catalysts) [160]:

Propene	99.5	wt % min.
Propadiene	5	vol ppm max.
Propyne	5	vol ppm max.
Butadienes	10	vol ppm max.
Oxygen	5–2	vol ppm max.
Carbon monoxide	3–0.3	vol ppm max.
Carbon dioxide	5	vol ppm max.
Carbonyl sulfide	0.5–0.03	vol ppm max.
Total sulfur	1	wt ppm max.
Water	5	wt ppm max.
Methanol	5	vol ppm max.
Ammonia	1	vol ppm max.
Ethane	500	vol ppm
Propane	0.5	wt %
Butane	500	vol ppm
$N_2 + CH_4$	300	vol ppm
Isobutene	50	vol ppm (estimated)
Hydrogen	10	vol ppm max.
Ethylene	50	vol ppm max.
1-Butene	50	vol ppm max.

Ethylene and 1-butene copolymerize with propene to marginally reduce the polymer softening point. Hydrogen is a powerful chain-transfer agent whose concentration must be accurately controlled in the reactor.

Propene is normally manufactured outside the PP plant. An important source of both ethylene and propene, in the approximate weight ratio of 2 : 1, is from steam cracking naphtha or gas oil at $700-950\,°C$, followed by fractionation. Refinery catalytic cracking of petroleum products yields $2-5\%$ of propene, which is isolated as a chemical grade containing $90-95\%$ of the monomer with much propane. This can be purified further to polymer-grade specification, but some PP plants which are able to handle the extra propane may bypass further refining or add a simplified hydrogenation unit to reduce dienes [161]. These possibilities arise at the milder end of the cracking range of $400-500\,°C$, which then generates lower amounts of harmful highly unsaturated products. There has been some interest in building propane dehydrogenation plants as a third source of pure propene [161, 162].

Some properties of propene relevant to polypropylene production are as follows:

Heat of polymerization	2514 kJ/kg
bp	$-47.7\,^\circ\text{C}$
Critical temperature	$92\,^\circ\text{C}$
Critical pressure	4.6 MPa
Vapor pressure at $20\,^\circ\text{C}$	0.98 MPa

2.3.2. Polymerization Diluents

Most early processes and some current plants use an inert hydrocarbon diluent in the reactor to help transfer propene to the solid catalyst and to convey reaction heat to the water-cooled jacket. Typically there is twice as much diluent in the reactor as polymer; thus, the purity demands on the diluent are as important as for the monomer. Refined petroleum fractions and synthetic hydrocarbons in the $C_6 - C_8$ range perform well, while solvents ranging from butane to dodecane are also used commercially. Polar impurities, such as alcohols, carbonyl compounds, water, and sulfur-containing compounds must be kept below $1 - 5$ ppm. The content of aromatics should be below $0.1 - 0.5$ vol %, depending on the catalyst employed. Here UV spectroscopy, supplemented with IR spectroscopy and refractive index measurement, is used to monitor quality. Regular checks must be made on recycled-diluent quality to prevent oxidized species and catalyst fragments accumulating unnoticed.

Polypropylene articles, such as films and containers, are widely used for food packaging and handling. In these cases the diluents and other additives must conform with the appropriate health regulations.

Since polymerizations carried out in the gas phase or in liquid propene only use small amounts of diluent as catalyst carriers, their purity requirements are less stringent.

2.3.3. Catalyst Preparation [163]

All current commercial manufacturing processes for highly isotactic PP use heterogeneous Ziegler–Natta catalyst systems. These two-component initiators consist of a solid transition-metal halide, usually $TiCl_3$, and an organoaluminum alkylating agent such as diethylaluminum chloride (DEAC). This system was the basis of PP plants until about 1980 when supported catalysts were commercialized.

An overview of the four development phases is given in Table 17.

2.3.3.1. $TiCl_3$-Based Catalysts

Of the four known crystalline forms of $TiCl_3$, three are purple (α, γ, δ) while the fourth is brown (β). The latter is not used in PP manufacture because of its poor stereospecificity. All the purple forms have a layer lattice consisting of closely packed chlorine atoms (Fig. 22) either hexagonal (α), cubic (γ), or intermediate between the two (δ). Preparative methods are critical to achieve good stereoregulation and high activity with these catalyst components.

Individual $TiCl_3$ layer

○ Chlorine
● Titanium
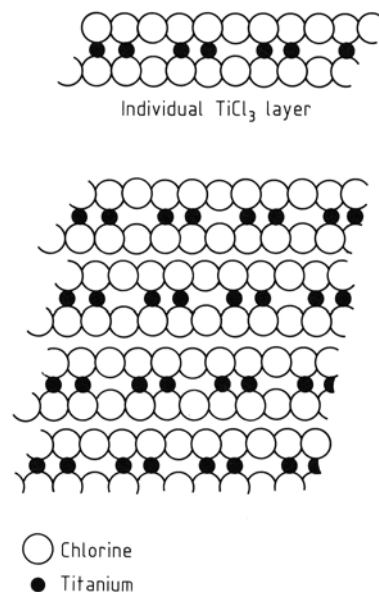
Figure 22. Layer lattice of α-$TiCl_3$ [165] (printed with permission of Harwood Academic Publishers)

Early work by the NATTA school used pure $TiCl_3$ made by hydrogen reduction of $TiCl_4$, followed by ball milling to give a high surface area.

$$TiCl_4 + 1/2\,H_2 \longrightarrow TiCl_3 + HCl$$
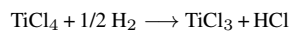
A more active form is made by reduction with aluminum powder, followed by ball milling.

$$3\,TiCl_4 + Al \longrightarrow 3\,TiCl_3 \cdot AlCl_3$$
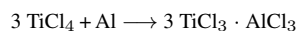
Much of the aluminum chloride is present as a true solid solution in crystalline δ-$TiCl_3$. This

Table 17. Catalyst development

System	Catalyst performance		Plant
	Activity, kg PP/g catalyst	I.I. *, wt %	process
1st Generation			
1957 – 1970	0.8 – 1.2	88 – 93	deash and remove
TiCl$_3$ · AlEt$_2$Cl			atactic
2nd Generation			
1970 – 1980	3 – 5	92 – 97	deash/deactivate,
TiCl$_3$ · AlEt$_2$Cl +			atactic usually remains
Lewis base (Solvay)			
3rd Generation			
1980 – 1990	5 – 20	≥ 98	no deash and
MgCl$_2$-supported TiCl$_4$ · AlEt$_3$			no atactic removal
4th Generation			
1995	ca. 20	?	no deash and
Metallocene/MAO systems			no atactic removal
			MMD ca. 2 – 4

*Isotactic index (% insoluble in boiling heptane).

catalyst has a larger surface area of $10 - 40 \, \text{m}^2/\text{g}$ and is commercially available from several companies. Nowadays, a Lewis base, such as an ester or ketone, may be introduced at the milling stage to increase stereospecificity.

Another important route dispenses with ball milling by reducing a hydrocarbon solution of TiCl$_4$ with an organoaluminum compound below room temperature. Di- and trialkylaluminum compounds are suitable. In this process the titanium trichloride precipitates in the brown, β form. Heating to $80 - 120\,^\circ\text{C}$ completes the reduction and transforms this solid to the required purple variety. Several hydrocarbon washes remove some of the aluminum compounds to leave an active, stereospecific catalyst. A useful aspect of this technique is that conditions can be selected to precipitate spherical catalyst particles. Subsequent propene polymerization then yields spherical polymer particles that exhibit good flow characteristics. This ability to replicate the shape of catalyst particles is quite general in Ziegler – Natta polymerization. Polymer forms throughout the agglomerate of small catalyst clusters, expanding the particle uniformly in all dimensions as polymerization continues.

Major refinements in alkyl-reduced TiCl$_3$ systems were made by Solvay [164–166] in their three-stage process, which gives a $4 - 5$-fold increase in activity:

1) Titanium tetrachloride solution is reduced with diethylaluminum chloride at $0\,^\circ\text{C}$

$$TiCl_4 + AlEt_2Cl \longrightarrow TiCl_3 \cdot x \, AlCl_3 \cdot z \, AlEtCl_2$$

where $x = 0.15$, $z = 0.20$

2) The brown β-TiCl$_3$ solid is treated with diisoamyl ether to dissolve out most of the aluminum compounds

3) The extracted solid is reacted with neat titanium tetrachloride at $65\,^\circ\text{C}$ to transform the β crystallites to the violet δ-form

The novelty lies in removing much of the aluminum residues at the β stage, without collapsing the particle, and then transforming to the stereoregulating δ-form while retaining a spongelike structure with a surface area of $150 \, \text{m}^2/\text{g}$ [164]. Analogous commercial products are available in Japan and the United States.

2.3.3.2. Supported Catalysts

The third-generation, supported titanium catalysts, are based on research by Montedison (now Montell) in Italy and Mitsui Petrochemical Industries (now Mitsui Sekka) in Japan. Collaboration and cross-licensing between these two companies avoided incipient interference claims. Starting around 1968 with finely milled magnesium chloride, which has a similar layer structure to violet TiCl$_3$, ways were discovered of depositing stereoregulating titanium compounds on the surface.

A particle-form supported catalyst may be prepared as follows [167]:

1) A spheroidal support is prepared by making a fine dispersion of molten ($125\,^\circ\text{C}$) magnesium chloride ethanolate complex in hot

kerosene containing sorbitan distearate as surfactant. The dispersion is quenched by pumping into kerosene at $-15\,°C$ to give particles with a diameter of $5-30\,\mu m$.

2) A slurry of the particles is added to neat $TiCl_4$ at $20\,°C$.

3) Diisobutyl phthalate (17 % v/w) is added and the mixture heated to $120\,°C$.

4) Decant, and heat with further $TiCl_4$ to $130\,°C$. Isolate by hot filtration and washing. The product contains 2.3 wt % Ti, 63 wt % Cl, 20 wt % Mg, and 9.9 wt % diisobutyl phthalate.

For the polymerization of propene, triethylaluminum is used as a cocatalyst, and phenyltriethoxysilane as an additional external Lewis base stereoregulator. Potential corrosion problems have been substantially reduced by using the chlorine-free triethylaluminum.

By ca.1980, commercial plants were achieving $20-30$ kg polymer per gram catalyst, and the isotactic index progressively improved from 88 to 99 %.

These catalysts form the basis of advanced technology plants in which deashing (removal of catalyst residues) and atactic polymer separation can be eliminated entirely [168]. It is estimated that by 1998 70 % of global plants will be operated with such "high mileage" technology. Coupled with this is the possibility of exploiting the good handling characteristics of the Spheripol coarse particle-form powders, thus dispensing with the need for expensive pelletizing plant. The segregation of added powdered stabilizers during storage and the problems of handling such mixtures are addressed, to some degree, by Montell's Valtec products, in which the additives are treated to provide a hard coating on the polymer. Some customers still prefer to handle traditional granules from an extruder.

2.3.3.3. Homogeneous Catalysts [163, 169, 170],

Metallocenes have been used for 30 years as model compounds for Ziegler – Natta reactions. They were quite unsuitable for commercial reactors because of their extremely low activity and poor stereocontrol. In the early 1980s, Sinn and Kaminsky serendipitously discovered that re-placing triethylaluminum with methylaluminoxane (MAO) enormously increased the polymerization rate of ethylene when combined with a substituted zirconocene dichloride. There were several other major hurdles to overcome before a suitable candidate was available for use in PP plant. Low stereospecificity succumbed to a more stereorigid metallocene, and the poor reactivity and polymerization temperature restrictions were solved by further molecular tailoring. Trials were conducted in 1996 on commercial-scale streams.

Metallocenes suitable for isotactic PP manufacture generally seem to be based on zirconocenes supported on inert solids to preserve particle size and shape. This makes them more compatible with the advanced process technologies of the major operators who refer to them as "drop-in catalysts". Sophisticated chemistry (Figure 23) is needed to prepare the base metallocenes, many of which have been made only in laboratory-scale equipment. An additional constraint is the heavy patenting, already amounting to some 900 applications since 1984. Hoechst, Exxon, Fina, Mitsui, and BASF together hold half of these.

The great versatility of single-site metallocenes has been demonstrated in trials that yielded improved and novel polymers. It remains to be seen how many of these desirable features can be incorporated in a single catalyst and how easily appropriate changes can be introduced at plant level. Some of these polymer properties are mentioned in Section 2.7.1 [169].

2.3.3.4. Aluminum Alkyl Cocatalysts.

Nowadays, aluminum alkyls are purchased from outside manufacturers. In the case of DEAC systems it is necessary to tailor the chlorine content to the type of $TiCl_3$ used. As the various alkyls interact rapidly, it is simple to adjust the composition by adding $AlEt_3$ or $AlEtCl_2$:

$$2\,AlEt_2Cl \rightleftharpoons AlEtCl_2 + AlEt_3$$

Triethylaluminum is made commercially from aluminum, ethylene, and hydrogen. Care should be taken to avoid the high levels of the hydride that are sometimes present. Trimethylaluminum is available from outside manufacturers, as is methyl aluminoxane (MAO). The latter is
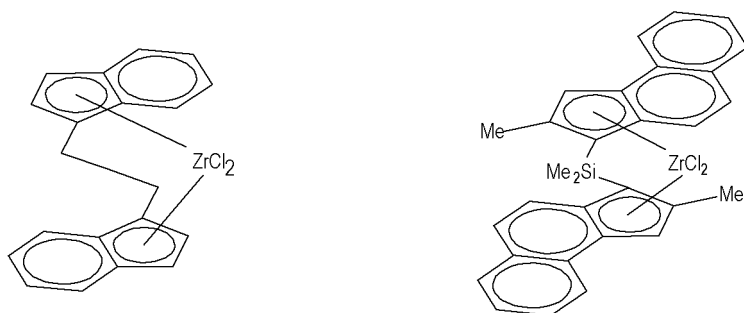
Figure 23. Hoechst (left) and BASF metallocenes

made by the controlled addition of water to the trialkyl with various techniques to moderate the potentially violent reaction. One method uses a salt hydrate, such as such as hydrated potassium aluminum sulfate (potassium alum). Various grades of MAO are available, possibly due to the different manufacturing methods and the polymeric nature of the product, which contains linear and cyclic short chains.

2.3.4. Hydrogen

Pure hydrogen is used at concentrations of 0.05 – 1 vol % based on propene to control molecular mass. Polar and highly unsaturated contaminants should be excluded, as usual.

$$Cat \diagdown\diagdown\diagdown + H_2 \longrightarrow Cat-H + H \diagdown\diagdown\diagdown$$

where $\diagdown\diagdown\diagdown$ = polymer chain.

2.4. Polymerization Mechanism

Many kinetic and theoretical models have been applied to Ziegler catalysts. Only a very small proportion ($<$ 1 %) of the titanium atoms in violet $TiCl_3$ are active for stereospecific polymerization. COSSEE proposed that an active site is generated at those surface titanium atoms which have one chloride vacancy and one exposed and weakly bound chloride anion, the remaining four chlorine atoms being firmly held in the lattice. These sites are located on the lateral faces of violet $TiCl_3$ crystals where the protruding chlorine is alkylated by aluminum alkyl (Fig. 24 A). An incoming propene molecule approaches this

active site (Fig. 24. B), whose immediate crystal geometry controls both the initial coordination and the configuration as the monomer inserts into the titanium – alkyl σ-bond (Fig. 24 C). Accordingly, this is a template type [171] polymerization controlled by the surface shape, and not by the previously inserted monomer unit. Atactic polymer is formed at more open surface sites having two vacancies or two weakly bonded chlorine atoms. While there are a number of alternative proposals [163, 172, 173] the essentials of the Cossee – Arlman model are widely accepted.

Since each active site on the crystal is unlikely to be unique, a distribution of imperfections is to be expected. Sometimes Ziegler – Natta catalysts are referred to now as multisite catalysts to emphasize this wide distribution of polymer chain lengths and stereoregularities.

In $MgCl_2$ supported titanium chloride systems, 10 – 20 % of the titanium is thought to be in the form of active sites, substantially more than in Solvay's improved catalyst, which contains ca. 0.8 – 2.7 % of the titanium in active form. Surface geometry still controls stereoregularity, but Lewis bases are much involved in this regulation [174].

In 1996 metallocene single-site catalysts have unique structures which secure precise control and definition of the active site. Consequently, a narrow molecular mass distribution and better control of chain irregularities, now including new types of chain defects, may be obtained with selected metallocenes/aluminoxanes. These catalysts can be used in solution, but manufacturers usually prefer them supported to secure better control of particle size and shape, together with freedom from reactor build-up [170]. Apparently certain
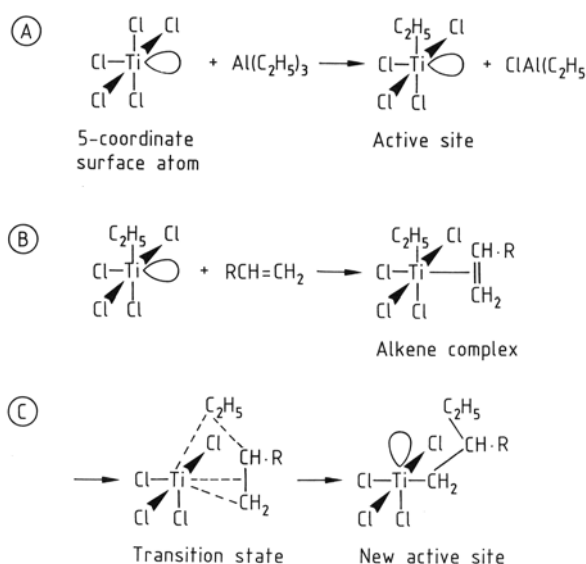
Figure 24. Cossee – Arlman model for polymerization site
A) Alkylation of lateral surface chlorine; B) Propene complex; C) Insertion into Ti – C$_2$H$_5$ σ-bond

supports can be used without spoiling catalyst or plant performance. Hence the name drop-in catalysts to emphasize the ease with which they can be introduced into existing plant. Their considerable potential and performance are being tested at the pilot-plant stage [175].

2.5. Industrial Processes

In the laboratory, it is a fairly simple matter to make a sample of PP from a given catalyst. All that is necessary is to suspend the solid transition metal compound in dry, inert-gas-blanketed, pure heptane containing aluminum alkyl cocatalyst and then bubble in propene gas at about 60 °C and atmospheric pressure. Polymer forms as a white solid permeating the catalyst particles which give an overall red-pink hue (with TiCl$_3$). Elevated pressures increase reaction rates according to a first order law.

Industrial manufacturing plants must incorporate many other stages to secure salable product: some of these complications are eliminated in modern high-technology plants by using advanced catalysts. Here the residual catalyst and atactic levels can be sufficiently low not to discolor polymer nor to generate odor and smoking. Although older plants still using the traditional process make high quality products, their higher cost base means that they are becoming increasingly uncompetitive, except in some highly specialized and low-tonnage applications. Some 70 % of global PP plants have installed new "High Mileage" processes .

The following sections describe one older slurry type of plant and four state-of-the-art advanced processes. From these it will be possible to visualize a number of hybrid alternatives to suit particular catalyst characteristics [178]. Copolymerization is dealt with separately for each system in Section 2.5.7, though for convenience the process flow sheets illustrating homopolymerization (Figs. 26, 27 and 29) include the bolt-on copolymer plant.

2.5.1. Suspension Homopolymerization (Early Diluent Processes)

Details of the individual steps shown in Figure 25 vary between manufacturers as regards process conditions and type of equipment.

Polymerization. For continuous systems, which have largely superseded batch polymerization, the mean residence time of catalyst in the reactor(s) is usually 1.3 – 3 h. Individual autoclaves started out as 10 – 30 m^3 vessels, but as stream capacities increased sizes up to 100 m^3
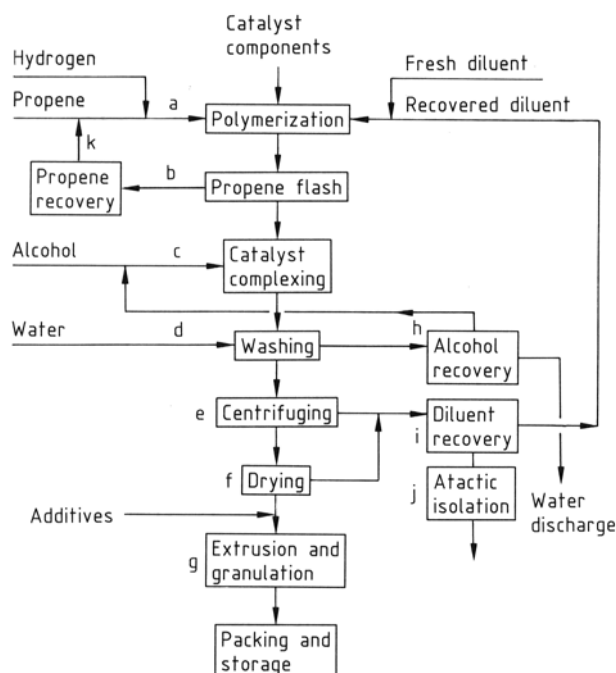
Figure 25. Schematic of early PP manufacturing process

have been installed. Another common practice involves linking reactors together in series or in parallel configurations. The maximum output rate of a reactor is determined by the heat removal system, which no longer relies simply on water-cooled polymerizer jackets. Internal and external cooling circuits provide the necessary extra cooling at these high rates ($> 0.3\,\mathrm{t\,h}^{-1}\,\mathrm{m}^{-3}$).

It is only necessary to meter catalyst into the first reactor of a cascade system, both because the activity decay is fairly small, and because it is not desirable on quality grounds to generate a second family of particles downstream. Propylene and hydrogen feeds to each reactor maintain the required pressure and gas compositions to secure the correct polymerization rate and molecular mass. Most of the reaction diluent is metered into the first vessel in the train, but some can be added further downstream to minimize fouling as the polymer concentration increases. Slurry viscosity increases rapidly during the latter stages of polymerization as the swollen polymer particles approach close packing. This point is strongly dependent on the size and shape of the catalyst particles. Seldom will the slurry con-

centration be allowed to exceed 42 wt % unless a very low density diluent is used.

As a rule, polymerization temperatures lie between 50 and 75 °C; the desirability of using a higher temperature being countered by decreased catalyst stereospecificity causing increased solubles and poorer properties. While reactor pressures of 0.5 – 1.0 MPa typified earlier plants, intensified processes expand this to 2 MPa.

Propene Flashing and Recovery. Two ways of removing and recovering unreacted propene, stages b and k in Figure 25, are practiced commercially. Most commonly, slurry from the last reactor discharges into a heated vessel at lower pressure to flash off propene vapor and other volatiles. After cooling and condensation, fractional distillation recovers pure propene as an overhead stream with a bottom discharge of propane and some diluent. In certain cases it is more economical to return the flashed propene to an adjacent plant for use there. The alternative scheme simply allows polymerization to continue without feeding any fresh propene to the latter part of the reaction train. Propene in solution is gradually converted into polymer as the

polymerization rate falls exponentially in the first-order reaction. This simple scheme entirely eliminates the recovery stage, but it does call for additional reactors working at low rates.

Catalyst Removal (Deashing). Catalyst removal, steps c and d in Figure 25, involves the extraction of highly polar particulate $TiCl_3$ from a hydrophobic polymer particle. Procedures differ appreciably, but the first step always converts titanium and aluminum residues into complexes or alkoxides that are soluble in the diluent, usually by heating to $60\,°C$ with $2-20\,\%$ of an alcohol, though acetylacetone has also been used. The choice of ethanol, propanol, or butanol is influenced by the diluent boiling point and subsequent recovery schemes.

Step d, Figure 25, shows a widely practised arrangement whereby water washing is used to transfer all these catalyst complexes into an aqueous phase, leaving behind a purified polymer slurry.

$$TiCl_3 \cdot (ROH)_4 + H_2O \longrightarrow Ti^{3+} + 3\,Cl^-$$
(in hydrocarbon)   (in aqueous soln.)
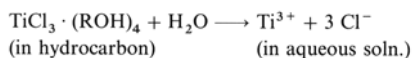
It is vital to work with either a strongly acidic or strongly alkaline complexing medium to repress hydrolysis and polycondensation, which impair the extraction efficiency. This technique normally yields polymer containing $10-30$ ppm of Ti, $10-40$ ppm of Al, and $20-40$ ppm of Cl residues. Very pure polymer can be made in an alternative form of step d. Here, the polymer is isolated by filtration, and is repeatedly washed by reslurrying in diluent/alcohol mixtures to remove all solubilized catalyst without introducing water. This process adds to the load on diluent and alcohol recovery, but PP quality improves.

Centrifuging. Centrifuging the deashed slurry (step e, Figure 25) removes most of the free diluent, but the wet cake can still hold up to 50 wt % (dry basis) of diluent containing dissolved atactic polymer. Depending on the grade of polymer being produced, it is sometimes beneficial to introduce a washing stage with diluent while centrifuging to reduce the amount of soluble polymer in the final product. Centrifuges can be of the filtering (basket) or decanting type according to the powder characteristics.

Drying. Drying the wet cake sometimes requires more than one stage, particularly in processes using high-boiling solvents. Steam distillation removes most of the diluent to leave an aqueous slurry from which the polymer is readily isolated by filtration. A conventional drier removes the small amount of water still adhering to the hydrophobic particles. More elaborate driers, operating under a nitrogen atmosphere, remove diluent directly in flash drying, fluidized beds, or hot surface contact type systems. Before the advent of high-technology systems (Section 2.5.4), some manufacturers had already improved catalyst stereospecificity such that the low level of atactic polymer in the diluent could be left in the product. In this case, the total slurry can be dried without previous centrifugation. This avoids all atactic polymer handling problems. All these drying stages must use nitrogen blankets throughout to minimize hazards with flammable hydrocarbons, as well as to protect the polymer.

Extrusion and Pelletizing. Powder leaving the driers at about $100-120\,°C$ can be fed directly to a pelletizing extruder, in which it is stabilized and converted into dense granules. As intermediate powder storage is often necessary, common practice introduces a cooling stage to $70-80\,°C$ to prevent adventitious oxidation when antioxidants are absent.

Diluent and Alcohol Recovery. An essential part of the schematic plant shown in Figure 25 is solvent and alcohol recovery, and atactic polymer separation (stages h–j). Diluent from the centrifuge contains soluble polymer and traces of alcohol. This mixture, together with liquid from the driers, is separated by multistage distillation. Pure diluent is then recycled to the polymerizers, while viscous atactic polymer separates out as a heavy end. Wiped film evaporators can be used to strip the last traces of diluent from highly viscous solutions.

Most of the alcohol is recovered from the first few water washes by fractional distillation (step h) followed by azeotrope splitting.

2.5.2. Bulk Polymerization in Liquid Propene

A special case of the slurry is to use liquid propene, with its poorer solvent power, instead of an inert diluent. Polymerization rates increase considerably with pressures around 3 – 4 MPa. Stirred autoclaves incorporating evaporative cooling, and loop reactors provide good heat-transfer rates. The chemistry parallels that described in Section 2.5.1, but the engineering demands are greater [178]. After polymerization, the catalyst is solubilized with polar complexing agents to permit extraction from the polymer by countercurrent washing with liquid propene. Hybrid plants are known which use liquid propene for polymerization, followed by flashing and resuspension in heptane for polymer deashing.

2.5.3. Solution Polymerization

In contradistinction to polyethylene manufacture, solution polymerization at high temperature is rarely practiced for isotactic PP. Special catalysts are necessary to minimize the customary reduction in stereospecificity above 100 °C, but the activity and stereoregularity still remains too low to dispense with catalyst extraction and removal of atactic PP. The original Eastman – Kodak process makes grades for some special markets, but there are no plans for further new plants along these lines. While polymerization at ca. 150 – 200 °C should permit some useful recovery of polymerization heat, overall costs are high for isotactic PP. It is reported [179] that the solution process is being used to make atactic PP, for which it seems more suited. Commercial plants dedicated to make only atactic PP have been announced by Himont (Canada), El Paso (Texas), and Huls (Germany).

2.5.4. Spheripol Process [180]

Figure 26 depicts a modern state-of-the-art plant based on Himont technology [180] for making homopolymer and impact copolymers (Section 2.5.7.2) with supported catalysts. The latter are sufficiently active not to require any catalyst

extraction, nor removal of atactic polymer because of the high stereospecificity. Homopolymerization takes place at ca. 70 °C and 4 MPa in liquid propene circulating round one or more loop reactors. A single axial flow agitator in each loop maintains high flow rates to ensure good heat transfer to the water-cooled jackets, whilst also preventing any polymer particles settling from the slurry [181]. Typically the PP concentration is ca. 40 wt %.

Continuously metered catalyst, triethylaluminum, and a Lewis base stereoregulator such as a dialkyldimethoxysilane are fed into the reactor to maintain polymerization and stereocontrol. The initial few seconds of polymerization with a new high-activity catalyst particle are quite critical to secure good performance. For this reason, some processes have a prepolymerization stage in which the catalyst components react at lower temperature and monomer concentration. This can be either a batch or continuous pretreatment which produces only small amounts of polymer (< 100 g/g) in the catalyst. This prepolymerized catalyst is then fed into the loop reactor as usual. Mean residence time in a single polymerizer is 1 – 2 h. Two loop reactors can be operated in series to narrow residence time distributions, modify the polymer, and increase output.

A continuous stream of polymer slurry discharges through a heated zone for the first stage of pressure let down in cyclone (b). For homopolymers, this connects directly to the secondary cyclone (d), bypassing the copolymerization unit (Section 2.5.7.2). Unreacted propene flashes off from the first cyclone and is condensed with cooling water and recycled to the reactor. A compressor is required for gas from cyclone (d). Polymer powder from the cyclone is fed into vessel (e) for deactivation with small amounts of steam and undisclosed additives. Residual moisture and volatiles are removed by a hot nitrogen purge in vessel (f) before conveying polymer to storage silos for conventional finishing as stabilized powder or extruded pellets.

Provided the expensive extrusion stage can be dispensed with by selling powder, then it is claimed that the capital cost of Himonts Spheripol process is only 50 % of the suspension process described in Section 2.5.1 [180].
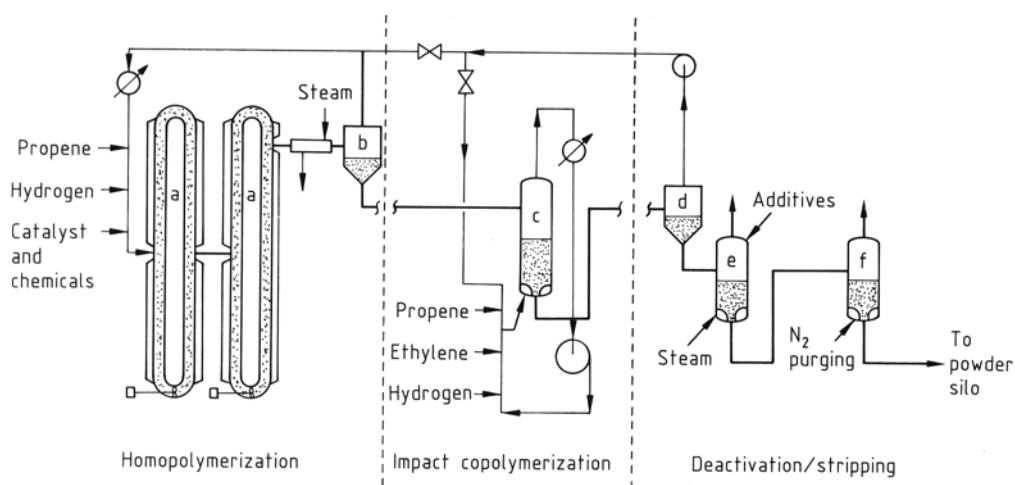
Figure 26. Spheripol process
a) Loop reactors; b) Primary cyclone; c) Copolymer fluidized bed; d) Secondary and copolymer cyclone; e) Deactivation; f) Purging

2.5.5. Hypol Process

Mitsui Petrochemical, co-inventor with Himont of the supported catalyst system, has developed an analogous cheap process using bulk polymerization with their own supported catalysts. It differs from the Spheripol system in that batch prepolymerization is used with washing. Two conventional stirred polymerizers are used in series, with heat removal by evaporative cooling of liquid propene in the reactors. Slurry is then discharged into a stirred, heated flash vessel, where propene is recovered from polymer, as in the Himont system.

2.5.6. Gas-Phase Processes

In gas-phase processes, gaseous propene is contacted with solid catalyst intimately dispersed in dry polymer powder. Industry uses two different methods of carrying out this reaction depending on the chosen method of heat removal. The Union Carbide/Shell process uses an adaptation of the Unipol polyethylene fluidized-bed system. BASF and Amoco use mechanically agitated dry powder beds with evaporative cooling in vertical and horizontal autoclaves, respectively.

BASF Novolen Process [182]. Figure 27 shows the BASF continuous process for making

homopolymers, impact copolymers, and random propylene – ethylene copolymers using high-activity, highly stereospecific catalysts. The reactor vessels, of 25, 50, or 75 m^3 capacity, are equipped with proprietary helical agitators, which give excellent agitation. Homopolymerization needs only the primary reactor, into which the catalyst components are fed. These must be very well dispersed in the powder bed to avoid build-up. The reaction conditions of 70 – 80 °C and 3 – 4 MPa ensure that the monomer phase is gaseous in the reactor. Low concentrations of hydrogen are used to control molecular mass over wide ranges. The temperature is controlled by removing gaseous propene from the reactor head space, condensing it with cooling water, and then recirculating it back into the reactor, where its evaporation provides the required cooling, as well as further aeration of the stirred powder bed. Each tonne of polymer made requires ca. 6 t of liquid propene to be evaporated as coolant.

Powder and associated gas discharge continuously from the primary reactor dip tube directly into a low-pressure cyclone (g). Propene carrier gas from this cyclone is recycled to the reactor after compression, liquifaction, and, sometimes, distillation. The powder then passes to a purge vessel where a deactivator quenches all residual catalyst activity, and nitrogen strips out traces of propene from the hot powder. From here powder is conveyed into silos for stabilization and
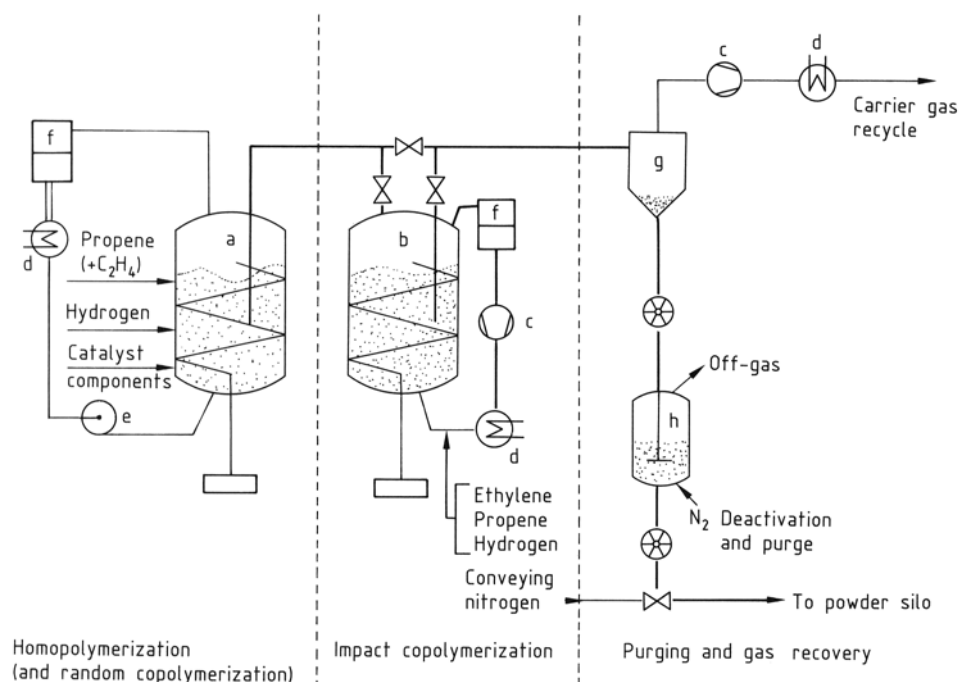
Figure 27. BASF gas-phase Novolen process
a) Primary reactor; b) Copolymerizer; c) Compressors; d) Condensers; e) Liquid pump; f) Filters; g) Primary cyclone; h) Deactivation/purge

extrusion into granules. BASF also offers a post-granulation steam-stripping package to remove any oligomers and oxidized residues from the granules for demanding applications.

BASF pioneered their gas-phase process with commercial production in 1969. The products made, Novolen 1300 series, were based on high molecular mass total work up polymers (i.e., containing atactic PP and catalyst residues) having reduced stereoregularity. Today, such grades still find niche markets, although they are vulnerable to competition from random copolymers. Production is to be phased out shortly.

BASF also uses their process with a cheaper second-generation catalyst $TiCl_3/AlEt_2Cl$, which then requires an additional dry-powder dechlorination stage.

Amoco – Chisso Stirred-Bed Process. Collaboration between Amoco and Chisso resulted in joint licensing arrangements from 1985. This process uses a horizontally stirred reactor, Figure 28, instead of the vertical helical agitator of the BASF process. Condensed recycled monomer sprayed into the top of the reactor provides cooling, while uncondensed monomer and hydrogen injected into the base maintain the gas composition. Figure 28 also includes a fluidized-bed deactivation system for use with second-generation, chlorine-rich catalysts. Amoco – Chisso claim that their reactor achieves some degree of plug flow, roughly equivalent to that of 2 – 3 fully back mixed reactors in series [183].

Unipol – Shell Fluidized-Bed Process [184]. The Unipol – Shell plants, commissioned in 1986, combine technologies from Union Carbide and Shell. Most conspicuous in this process, Figure 29, is the tall fluidized-bed reactor with its expanded upper section to reduce gas velocity and powder entrainment. Continuous feeds of catalyst components, comonomer, if any, hydrogen, and propene are thoroughly mixed in the dense-phase fluidized bed of powder. A large cooler in the gas recirculation loop removes all the reaction heat from the considerable gas flow. In this system the fluidized bed is said to behave as a fully back mixed reactor, without undue separation of coarse particles. No mechanical
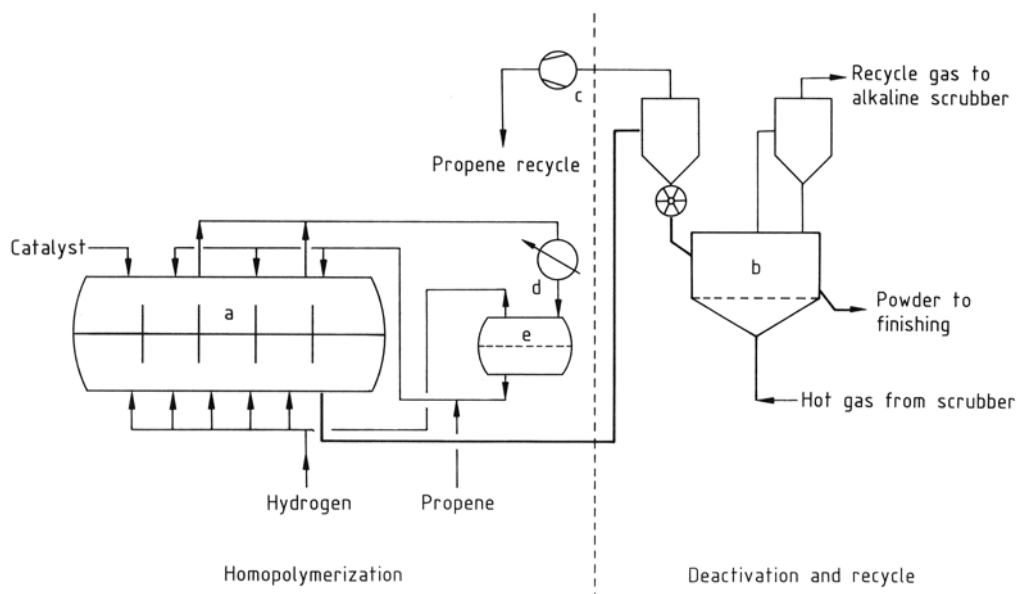
Figure 28. Amoco – Chisso gas-phase process
a) Horizontal reactor; b) Fluidized-bed deactivation; c) Compressor; d) Condenser; e) Hold/separator tank
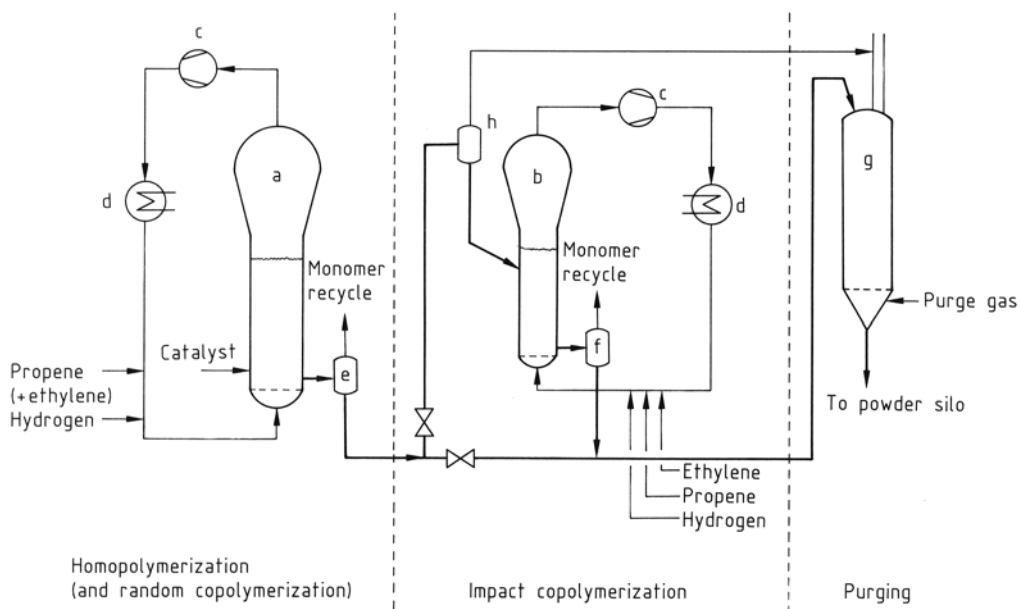
Figure 29. UCC/Shell – Unipol fluidized-bed process
a) Primary fluidized bed; b) Copolymer fluidized bed; c) Compressors; d) Coolers; e), f) Discharge cyclones; g) Purge

agitation is needed. Reaction conditions are reported as $< 88\,°C$ and $< 4\,MPa$.

Product powder and associated gas are discharged from just above the distributor plate by timed valves into a cyclone separator (e) and then directly to a purge vessel (g) to remove residual monomer. Neither catalyst removal nor atactic polymer extraction is necessary with the modern Shell catalysts used in the Unipol process.

2.5.7. Copolymerization

Copolymers of propene with other α-olefins account for ca. 30 % of all PP sales. There are two distinct classes of copolymer having different application areas. Random copolymers, obtained by copolymerizing mixtures of propene and other α-olefins have lower melting points and improved clarity. Impact (block) copolymers, made in a two-stage polymerization process, are high-impact-strength grades that contain dispersed propene – ethylene elastomers.

2.5.7.1. Random Copolymerization

Random copolymers are made in the same way as homopolymers, but a mixture of propene and the comonomer is used in place of pure propene. Usually, polymers containing 2 – 6 wt % of combined ethylene cover most applications. Sometimes the resulting copolymers are referred to as "statistical" because heterogeneous Ziegler catalysts rarely yield truly random copolymers [157] with mixed feeds of monomers. 1-Butene can also be used, especially as a termonomer along with ethylene. The higher α-olefins are more expensive and less reactive than propene and can complicate the monomer recycle stage. However, attractive product properties are stimulating manufacture [185, 186].

In the case of suspension polymerization, either in hydrocarbon diluent or in bulk, significant amounts of soluble byproducts add to handling difficulties due to viscosity increases at higher comonomer contents. Drying temperatures must be reduced because of the lower softening point and more cohesive nature of the particles.

Gas-phase systems, especially those having some degree of mechanical agitation, are less adversely affected, though maximum temperatures still need careful control.

Random copolymers often find use in food packaging (see Section 2.7.2), where the polymer must not contain high proportions of extractable material. Clarity improves and melting points fall as comonomer and solubles increase. A compromise is reached at about 3 wt % of ethylene. Changes to catalyst and polymerization techniques can raise this by securing a more uniform disruption of the isotactic sequences, which in turn encourages formation of the lower melting γ- crystallites [187].

2.5.7.2. Impact (Block) Copolymerization [188, 189]

Impact copolymerization is regarded as the lowest cost process for making toughened PP. It can be visualized as a method for producing an intimate blend of PP homopolymer with a toughening ethylene – propene elastomer. Approximately 10 – 20 wt % of this elastomer suffices for most applications, though the availability of products containing 30 – 40 wt % will expand their use.

The minimum requirement for block copolymerization is a two-stage process. In one stage homopolymer is prepared by any of the methods described in Sections 2.5.1, 2.5.2, 2.5.3, 2.5.4, 2.5.5, 2.5.6. The other stage uses a mixed monomer feed of ethylene and propene to produce a largely amorphous, elastomeric phase within the polymer particles. Many other more complex configurations have claimed to be advantageous for certain products, but two stages are generally adequate [188, 189].

Homopolymer, or a very low ethylene copolymer, is always made in the first reactor because the elastomer fragments catalyst particles in diluent systems and produces sticky products in gas-phase reactors. This first stage of reaction, using propene and hydrogen as molecular mass controller, is indistinguishable from conventional homopolymerization. In batch slurry systems, propene is metered into a reactor until the amount of polymer formed is 80 – 90 % of the intended final make. The remaining 10 – 20 % is made in the second stage as follows. Normally the propene concentration is allowed to fall, by continued polymerization, to a predetermined value before introducing ethylene, propene, and possibly hydrogen. No further catalyst is needed for the second stage, and the reaction temperature might be lowered to reduce the amount of soluble polymer diffusing out of the particles. The high reactivity of ethylene promotes rapid copolymerization in a more exothermic reaction. Venting and polymer isolation follow the procedure already described in Section 2.5.1, but filtration and atactic polymer separation are more difficult because of additional amounts of viscous soluble copolymer.

Gas-phase systems using modern catalysts avoid much of this difficulty. Figure 27 shows a typical BASF continuous process using two stirred reactors for making impact copolymers [182]. Active polymer and gas from the first reactor discharge directly into the copolymerizer, operated at $1-2$ MPa lower pressure and lower temperature. Normally, the propene/ethylene/hydrogen ratio is adjusted such that the rubbery copolymer made in this reactor contains $40-60$ wt % ethylene, depending on the particular grade. This gas composition is not readily condensed with cooling water alone, so a compression stage is added to liquify some of the recycled gas returned to the reactor base. Copolymer powder, with its associated carrier gas, discharges into the low-pressure cyclone separator (g), which passes this carrier gas to recompression for return to the copolymerizer. Residual monomer in the copolymer is removed in a combined purging and deactivation vessel (h) before conveying powder into silos for extrusion.

Analogous gas-phase techniques are used by other manufacturers. Amoco – Chisso (see Fig. 28) add a second horizontal stirred reactor when making impact copolymers, and El Paso also add a similar polymerizer after their bulk first stage. Unipol – Shell introduce a second, but smaller, fluidized bed (Fig. 29), operating at ca. 1.5 MPa, for their impact copolymers, thus taking advantage of enhanced copolymerization activity. Sumitomo's new process also uses two fluidized beds. Himont (Fig. 26) and Mitsui Petrochemical retain their normal bulk polymerization for the first, homopolymerization step, but use gas-phase copolymerization in a fluidized bed for producing impact copolymers. Such dry powder reactions overcome the problems arising from extraction of soluble copolymer species in liquid-based processes. At the same time, copolymer diffusion to the surface should be reduced by the lower degree of swelling in dry powder systems.

While copolymers containing 40 %, or more, of elastomer can be handled satisfactorily in plant processes, their cohesiveness calls for more care than with homopolymers. Himont patents suggest that their fluidized-bed technology recognizes this aspect. Overall, there is complete unanimity that a gas-phase copolymerization stage is preferred for this class of copolymer in modern plant.

2.5.8. Product Finishing

Considerable capital is involved in the finishing areas of all plants after the dry powder stage. The great majority of this powder is extruded with a variety of additives, pelletized, tested, and then stored in various packages for sale. Direct sale of suitably stabilized reactor powder circumvents some, but not all, of these costs.

Extrusion and Pelletization. Proprietary equipment from specialist manufacturers will always be used for high-throughput plants operating at $5-20$ t/h and 250 °C. In selecting extruders the following factors are relevant (in addition to costs): powder morphology, product MFI range, melt filtration needs, devolatalization, turn down ability (i.e., efficient operation at low rates), temperature control, mixing needs, and additive feeds. The types of extruder available include long, single-screw machines and two-stage systems in which powder is melted in a continuous high-speed mixer which discharges the melt into a short, pressure-generating extruder. Twin-screw machines with corotating and segmented screws are increasingly used for additional flexibility. Versatility and output can also be increased by installing a gear pump between the die plate and the discharge end of the screw in any of these systems.

Pelletization takes two forms. Extruded laces from the die plate are quenched in water to give rigid strands. High-speed cutters then chop the continuous strands into $2-5$ mm lengths to produce so-called lace-cut pellets. In the other system, high-speed knives rotate against the extruder die plate to cut off short lengths of the molten extrudate. Either the insulated die plate is immersed in water, or the molten pellets are instantly solidified by being flung into a water ring quench zone to prevent cohesion. These die face cut granules are increasingly common in large plants.

Salable Powder. Densification is avoided entirely for those outlets willing to use suitably stabilized powder. Spherical particles, up to ca. 0.3 mm diameter, have been available for many years, but in most applications pellets are preferred because of their better housekeeping

(spillages, dust, etc.), easier handling in standard systems, and absence of concern about possible dust explosions due to powder attrition. Emergence of coarse Spheripol powders from Himont, 1 – 5 mm diameter, should dispel some of these concerns provided adequate and nonseparating stabilization systems are established with mechanically robust coarse particles. This will entail some additional manufacturing costs, and perhaps more product constraints, but this expenditure should be less than that for capital and energy intensive extrusion and pelletization operations. Himont is constructing a PP plant in Brazil, due for completion in 1991, which is claimed to have no extrusion facilities. However, these have subsequently been installed.

Additive Incorporation. Extrusion provides an efficient and convenient way of incorporating antioxidants and other modifiers into polymers. Metered amounts are mixed with the main powder feed to the extruder and homogenized in the molten polymer. Good mixing is essential to prevent extrusion of unstabilized product at high temperature. Nitrogen blanketing is common practice. Highly specialized and low-tonnage formulations are either made on a separate plant having appropriately sized equipment, or the customer himself adds concentrates in the form of stabilizer master batches.

Liquid additives, such as some antistats, can be metered directly into the melt, given good subsequent homogenization in the extruder.

2.5.9. Additives

Stabilizers [190]. Like most hydrocarbons, PP must be protected against oxidation, particularly above 100 °C. The dominant reaction is chain scission by free-radical attack at the tertiary carbon atoms of the backbone. This generates hydroxyl and carbonyl groups, accompanied by yellow discoloration and brittleness. Incorporating radical scavengers considerably delays the onset of embrittlement and increase of the MFI. Antioxidants are always incorporated into PP before or during extrusion at manufacturing plants. Usually a peroxide decomposer, such as a phosphite, is introduced to improve melt stability, together with hindered phenols to confer long-term aging resistance. Typically,

the amount of each of these additives is 0.05 – 0.2 wt %, but in more aggressive environments the levels might rise to 0.5 %, with thiodipropionate esters as peroxide decomposers. The choice of stabilizer is influenced by the application, for example, interaction with spin finishes [191], resistance to extraction by hot water, and regulatory constraints.

Traces of copper or cobalt powerfully accelerate thermal oxidation, especially at sustained temperatures above 60 °C. In these cases a chelating agent such as a bishydrazone is added [192].

Continuous outdoor exposure also requires protection from the damaging effects of UV radiation. The severity of embrittlement increases at high temperature and with rainfall in some polypropylenes. Atmospheric pollution can deposit protective layers on the surface. Ultraviolet-absorbing compounds, such as alkoxybenzophenones and hydroxybenzotriazoles for thick sections, and hindered amine light stabilizers (HALS) for films, provide protection at contents of 0.1 – 1.0 wt % [193]. Screening with some fine pigments or carbon black is effective, but restrictive on appearance.

Gamma radiation, used for packaged food and sterilization of medical equipment, degrades PP, causing embrittlement. The effects can be mitigated by the careful choice of stabilizer.

Antistats. The familiar static charges and resulting dust deposits on many plastics can be overcome in PP by incorporating 0.2 – 1.0 wt % of polar additives. Suitable materials, such as polyether fatty amide and fatty amine condensates and glyceryl monostearate reduce the surface resistivity from $> 10^{13}$ to ca. $10^7 \Omega$. The mechanism involves slow diffusion of the additive to the surface where it picks up atmospheric moisture. Hence, time and humidity are important. At 50 % RH most of the recommended additives are satisfactory, but at 30 % RH the fatty amine derivatives are advantageous. A few days storage at room temperature is sufficient to develop the conducting surface layer.

Compositions containing moderate amounts of conductive carbon black are also effective, as are small amounts of polyacetylenes. The latter, and the incorporation of small amounts of fine metallic wire, are too expensive for PP applications.

Antacids. Most of the earlier PP formulations contained $0.05 - 0.2$ wt % of calcium stearate to prevent traces of acidic catalyst residues from corroding customers' equipment. It behaves as a mild slip agent and suppresses attack of HCl on certain antioxidants. Zinc, magnesium, and sodium stearates have also been used, and more recently synthetic hydrotalcite (a hydrated magnesium aluminum hydroxycarbonate). Lower levels of such additives are still widely used.

Slip and antiblock agents are mainly used in film production where high-speed handling requires a controlled reduction in frictional forces. $0.1 - 0.5$ wt % of oleamide, erucamide, glyceryl monostearate, etc., usually suffices. Fine, spherical particles of silica incorporated at the pelletization stage prevent layers of film adhering to each other during storage.

Crystallization Nucleants. Although pure PP has a final melting point of $176\,°C$, the melt supercools by $50 - 60\,°C$ before crystallization sets in at ca. $115\,°C$. Small amounts of certain additives [194] nucleate the melt, raising the crystallization temperature by $10 - 15\,°C$. Smaller spherulites result, sometimes having different structures. Advantages of nucleated grades include shorter injection molding cycles, higher moduli, greater transparency, and higher heat distortion temperatures. Suitable additives include dibenzylidene sorbitol and substituted variants, di-*tert*-butylbenzoate salts, sodium benzoate, finely divided talc, sodium diaryl phosphates, and some pthalocyanine pigments. These materials are somewhat selective in their effects, i.e., some are particularly good for transparency improvement, but less effective for modulus enhancement. Careful balancing of the overall additives recipe is also essential because both adverse and beneficial interactions occur between some of the components [195].

2.6. Compounding

Compounding includes incorporating mineral fillers, glass fibers, elastomers, flame retardants, pigments, and carbon black. It is a specialized operation dealing with relatively short run lengths in specified compounding extruders or mixers. For this reason, and for concern about cross contaminating unmodified PP grades, compounding plants usually operate separately from main PP production plants.

Substantial property enhancements enable polypropylene-based products to compete in quite demanding areas where unmodified PP would be inadequate (see Table 18). Examples include tough front and rear bumpers for cars, rigid coupled glass compositions for washing machine tubs, dense grades for outdoor garden furniture, and temperature-resistant compositions for car under hood applications. Long-fiber-reinforced PP secures further increases in toughness and stiffness over short-glass-fiber compounds [196]. Fibers with a minimum length of between 0.8 and 3 mm, depending on the coupling between matrix and fiber, are likely to be satisfactory. These form an interlocking skeletal structure which dissipates the impact energy over a large area of the molding.

The combination of lower production rates, specialized equipment, and dense additives mean that PP compounds are always more expensive than natural grades.

2.7. Properties

2.7.1. Homopolymer

Basic mechanical properties are largely influenced by molecular mass and molecular mass distribution (MMD), chain stereoregularity, and processing conditions, which introduce orientation, strain, etc. Various additive packages must be tailored to the application to achieve good and durable performance.

Molecular Mass. At low shear rates melt viscosities are proportional to the 3.4 power of the weight-average molecular mass. At the higher shear rates found with most processing equipment, the dependence is still greater than a power of 2 because much chain entanglement still exists. As a result of this sensitivity, and the direct relevance to processing, the melt flow index (MFI) is always used to describe the viscosity characteristics of each polymer grade. The dependence of melt viscosity on shear rate is also related to MMD as a result of the strong influence of very long chains. Hence MFI is often

Table 18. PP compounds – property enhancement

Property	Homopolymer	Impact copolymer	Compound	Composition
Toughness, kJ/m^2 (N Izod, 0 °C)	3.0	10.0	> 50	rubber + filler (car spoilers)
Modulus, GPa	1.5	1.0	7.6	coupled glass
	1.5	1.0	2.7	chalk loaded
Heat distortion temperature	105	90	160	coupled glass
(0.45 MPa), °C	105	90	130	talc filled (heater casings)

measured at two different shear rates to give some idea of MMD. Increasing importance is being attached to a more comprehensive rheological characterization [197, 198].

A typical, medium-flow polymer has an MFI (230 °C/2.16 kg) value of 3 dg/min, corresponding to a M_w of 460 000 and M_n of 54 000. The practical grade range of 0.3 – 50 MFI covers applications from sheet and pipe extrusion to high-speed fiber spinning.

Heterogeneous Ziegler – Natta catalysts yield broad MMD polymers having $M_\mathrm{w}/M_\mathrm{n}$ of 5 – 10, the lower values being associated with the more recent Solvay and supported catalysts. Very narrow MMDs are still made by preferentially cleaving long chains in an extruder, usually with the assistance of organic peroxides. Such grades, commonly referred to as controlled rheology (CR) polymers, reduce extrusion and molding orientation caused by high molecular mass species with their long relaxation times [199]. Note that reworked polymer is likely to have a higher MFI and a correspondingly narrower MMD than the starting material.

Stereoregularity. Very high stereoregularity is now achievable with modern catalysts, even without removing any soluble byproduct. In some applications processing is helped by a small lowering (detuning) of the isotactic index. This is readily achieved by minor changes to the polymerization recipe, and by introducing small amounts of copolymerized ethylene.

Metallocene-Based PP. An expanded range of products is iminent following the encouraging metallocene developments. Further pilot trials and customer assessment of processing, product, and economics is needed before precise definition is possible. The advantages already seen include higher extrusion rates for films and fibers, enhanced clarity, absence of oligomers, superior property balances, and the ability to control

further melting point reductions by copolymerization without significantly increasing the low level of xylene-soluble material.

Other Properties. Table 19 lists the properties of several polymers measured by standard procedures, with some copolymer data included for comparison. Care must be taken in translating these exact values to fabricated products because properties are dependent on built in stress and orientation. Increasing the molecular mass, i.e., lowering MFI, raises toughness somewhat, but the modulus and hardness decrease with the lower crystallinity.

Some general and electrical properties of polypropylene are as follows:

Density, kg/m^3
20 °C	905
200 °C	770
220 °C	760
240 °C	740
260 °C	710

Coefficient of linear expansion, K^{-1}
20 °C	1.1×10^{-4}
80 °C	1.7×10^{-4}

Specific heat, kJ kg^{-1} C^{-1}
20 °C	1.93
50 °C	2.04
100 °C	2.37
150 °C	4.0

Glass transition temperature T_g, °C
isotactic	−13 to 0
atactic	−18 to −5

Flammability
UL 94, 3 mm thick	UL 94 HB
ASTM D635, 3 mm	23 mm/min
FMVSS 302	
1 mm	43 mm/min
2 mm	38 mm/min
3 mm	20 mm/min

Table 19. Mechanical and thermal properties of PP Origin "Propathene" (with permission of ICI Chemicals & Polymers)

Property	Method	Temperature	Homopolymer				Impact copolymer		Random copolymer
			GSE 16	GWM 22	LYM42	LZM 55/52	GWM 101	GWM 213	LXF 301
Melt flow index (230 °C/2.16kg), g/10 min (dg/min)	ISO 1133		1.00	4.00	12.00	33.00	6.00	2.00	7.50
Tensile yield stress, MPa	ISO 527		33.50	34.50	34.50	34.00	27.00	23.50	25.00
Flex. modulus, GPa	ISO 178 (10mm/min)		1.45	1.50	1.50	1.55	1.15	1.00	0.85
Izod impact strength, kJ/m^2	ISO 180 (0.25 mm notch radius)	23 °C	4.50	4.50	4.00	3.00	9.50	no break	5.00
		0 °C	3.00	3.00	2.50	2.00	5.50	10.00	2.50
		−20 °C	2.00	2.00	2.00		3.50	7.50	
		−40 °C						5.00	
Instrumented drop weight impact strength, J	ICI method	23 °C					7.00	10.00	10.00
		0 °C					6.00	11.00	2.00
		−20 °C					6.00	11.00	
		−40 °C						9.50	
Embrittlement temperature, °C	ICI method		> 23	> 23	> 23	> 23	−20.00	−45.00	
Rockwell hardness	ISO 2039/2, ASTM D785 R scale		93.00	95.00	95.00	95.00	90.00	75.00	
Vicat softening temperature (10N force), °C	ISO 306A, BS 2782: 120A		154.00	154.00	154.00	154.00	147.00	143.00	135.00
Heat distortion temperature, °C	ISO 75/A & /B								
A − 1.8 MPa			65.00	65.00	65.00	68.00	60.00	50.00	46.00
B − 0.45 MPa			100.00	100.00	100.00	102.00	95.00	90.00	71.00

Thermal conductivity, W m^{-1} $°$C^{-1} 0.209	
Combustion heat, kJ/g	44.0
Autoignition temperature, $°$C	360
O$_2$ index (ASTM D28) at 600 $°$C	3.5
Relative permittivity at 1 kHz (IEC 250)	2.25
Volume resistivity, 1 min, $\Omega \cdot$ m (IEC 93)	$> 10^{15}$
Electrical strength (20 – 80 $°$C, 10 – 20 s, 3.2 mm, IEC 243)	> 12 kV/mm
Dissipation factor tan δ (IEC 250)	
50 Hz	0.00015
1 kHz	0.0002
1 MHz	0.00015

The final melting point of commercial PP lies in the range 160 – 170 $°$C, with purified polymer reaching 176 $°$C. However the safe upper working temperature limit should be 100 – 120 $°$C, depending on the stress, with short excursions up to 140 $°$C being permissible. This comfortably extends the upper operating range available with high-density polyethylene by ca. 20 $°$C, which has a similar room temperature modulus.

Favorable long-term creep characteristics under load permit useful increases in the stacking height of PP crates or other pelletized containers. The repose angle of PP moldings on wood or canvas, unpredictably 30 % higher than for HD polyethylene, is allegedly a useful stabilizing feature in mechanical conveyors.

The crystalline and nonpolar nature of PP confers good resistance to a wide range of aqueous and polar media, including emulsifier solutions with their strong stress cracking abilities. Powerful oxidizing agents and highly aromatic or chlorinated solvents are too aggressive for safe storage in PP containers.

The ease with which homopolymers can be drawn into high strength structures has been heavily exploited in the fiber and film industries (see Section 2.8.3).

2.7.2. Copolymers

Random Copolymers. Incorporating 2 – 7 wt % of ethylene into the main chain lowers the overall crystallinity, gives a broader softening range with reduced melting points (Figs. 30 A, 30 B), increases the fraction of soluble polymer, and improves transparency and surface gloss. These changes are dependent on the amount of comonomer and its distribution along the chain. Table 19 shows how the modulus decreases for a random copolymer containing ca. 3 wt % of combined ethylene.
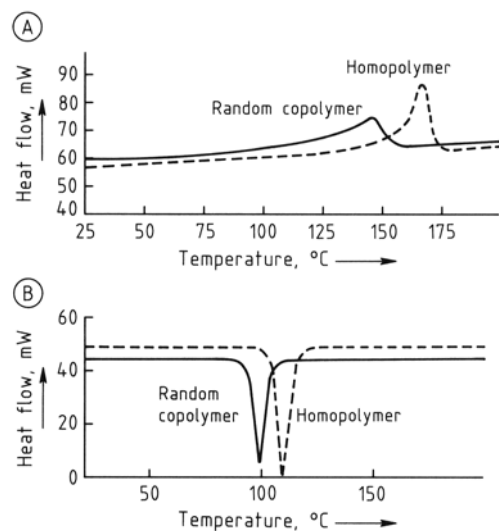
Figure 30. A) DSC heating endotherm; B) DSC cooling exotherm
Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

Several applications take advantage of the lower melting point to make thermoweldable film. Ideally, it would be useful to have a low melting range without undue increases in the proportion of xylene-soluble residues. This is claimed to be possible with butene copolymers, perhaps because the solubles are produced at semi-exposed catalyst sites more easily accesible to ethylene [186]. Some advantages are also claimed for propene – ethylene – butene terpolymers [180, 185]. Butene helps the development of low-melting γ-triclinic crystallites. Random copolymers are somewhat tougher than homopolymers, and do not exhibit the familiar stress-whitening behavior of the tougher copolymer impact grades.

Impact Copolymers. Section 2.5.7.2 describes block copolymerization systems for making high impact strength grades of PP. These are often referred to as block copolymers, toughened polypropylene, or more pedantically heterophasic copolymers [180].

Essentially, these products are best viewed as an intimate dispersion of elastomer in a PP matrix. The particulate rubber phase confers good toughness, while the homopolymer matrix is responsible for retaining good high-temperature performance and adequate stiffness. In this respect they are far superior to random copolymers, and become the first choice when impact strength and rigidity are called for. In extruded pellets or molded articles the rubbery copolymer phase is well distributed in the form of droplets 1 – 5 μm in diameter. Such a structure (Fig. 31) is produced during melting and recrystallization. Powder direct from the reactor has elastomer permeating throughout the particle in a more continuous form. Many of the complex interactions which control the stability of this phase structure and the resulting toughness, await further study [189].
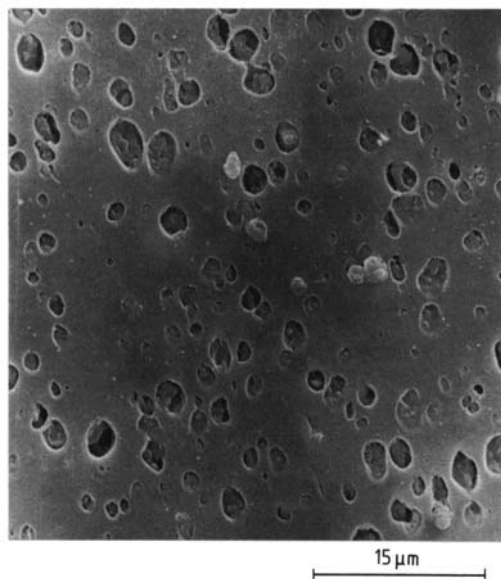
Figure 31. Electron micrograph of high impact copolymer molding after hexane surface wash

Toughness, stiffness, and softening points are given in Table 19 for two impact copolymers containing ca. 10 and 20 % of elastomer. Gas-phase polymerization systems are able to increase the rubber content to 40 %, but the products are not available in large commercial quantities at present. These impact copolymers naturally contain more soluble polymer than ho-

mopolymer, and this second phase reduces the translucency. Severe deformation causes some whitening or blushing [200] in the stressed regions, particularly in very high impact grades. In other respects the rules relating processing and properties to MFI, nucleation, controlled rheology, stabilization, etc., are the same as for homopolymer.

2.7.3. Elastomer Blends with Polypropylene

Originally, PP was toughened by blending with ca. 10 wt % of polyisobutylene (PIB) elastomer. In some situations the same technique is used today, with ethylene – propene rubber (EPR) or ethylene – propene – diene rubber (EPDM) replacing PIB.

As rubbers are incompatible with PP, considerable mechanical work is necessary to secure the vital fine dispersion of elastomer. Good blending also requires a reasonable viscosity match between the two components. Common practice is to use a two-stage process in which the elastomer is first compounded with PP to give a 50 – 70 wt % masterbatch of the rubber as free flowing granules. Such masterbatches can be purchased at extra cost. Good mixing devices are essential for the final compounding step with PP. Twin-screw extruders or high-speed mixing devices perform satisfactorily.

Well-prepared blends have physical property combinations only just short of those of directly polymerized impact copolymers. However, the latter are generally preferred on account of consistency and grade versatility. Elastomer blending is also part of the broad spectrum of compounds referred to in Section 2.6. Here they are used to uprate the toughness of homopolymer and impact copolymers in these complex formulations. Some manufacturers also introduce HD polyethylene, in addition to rubber, to secure further toughness improvements. In these cases, electron microscopy reveals that in well-dispersed systems the polyethylene is always located inside and towards the center of these rubber droplets. This encapsulation of PE makes it behave more like rubber towards the matrix, thereby increasing toughness at the expense of modulus in such ternary blends.

2.8. Uses

Polypropylene is readily processed in conventional equipment used for other thermoplastics. Injection molding, commonly using screw-type reciprocating machines, accounts for $40 – 50\%$ of all applications. Extrusion processes account for the remainder with domination by fiber and film.

A more detailed picture is obtained by analysing the North American 1996 sales data (in 10^3 t/a) listed in the following [202] :

Blow molding	
Containers	74
Others	5
Total blow molding	79
Extrusion	
Coatings	5
Fibers and filaments	1463
Film (up to 0.25 mm)	
Oriented	503
Unoriented	111
Pipe and conduit	
Sheet (over 0.25 mm)	110
Wire and cable	5
Others	43
Total extrusion	2240
Injection molding	
Appliances	139
Consumer products	565
Rigid packaging	523
Transportation	186
Others	131
Total injection molding	1544
Export	503
All others	1177
Total	5543

2.8.1. Injection Molding

An exceptionally wide range of injection-molded products stems from the rigidity, toughness, and chemical and temperature resistance of PP. Examples include automotive trim and ventilation components, bottle crates, industrial containers, washing machine tops and tubs, kitchenware, tool handles, domestic waste systems, and small boat hulls. Such a variety of articles requires careful grade selection according to the required impact strength of the product and the melt flow constraints of the processing equipment. An MFI ($230\,°C/2.16\,kg$) range of $2 – 20$ dg/min meets most needs. Increasing the MFI not only assists mold filling and reduces cycle times, but it helps manufacture of complex moldings having high flow ratio geometries (flow ratio is the ratio of longest path to the section thickness). The inevitable fall in impact strength at high MFI can be recouped, in some cases, by moving from homopolymer to impact copolymer grades.

While molding conditions vary with the size and complexity of the article, the following machine settings will cover most products [199]:

Melt temperature:	$230 – 275\,°C$
Injection pressure:	$55 – 100$ MPa
Mold temperature:	$40 – 80\,°C$, lower still for thin walled items

The low moisture absorption of PP largely dispenses with any need to dry granular feedstock. Neither do gaseous or carbonaceous decomposition products form in extruder dead spots. Instead, polymer remaining there becomes progressively more fluid through chain scission. Machine shot weight capacities normally refer to performance with polystyrene, i.e., the polystyrene yardstick figure. The lower melt density of PP (0.75 g/cm^3) lowers the machine's weight capacity by ca. 25% when molding PP. Plasticizing capacity is slightly greater than for polyethylene, but is lower than for amorphous polystyrene. Machine outputs with PP benefit from the ability to eject moldings at higher temperatures than with their lower softening counterparts.

Linear post-molding shrinkage of PP is $1 – 2\%$, of which 85% occurs within the first 24 h. Distortion in molded products reflects internal stress caused by nonuniform cooling and polymer orientation. The latter is especially pronounced in surface skins where the viscous melt stretches as it is pulled along by the advancing melt front adjacent to cool walls. Controlled rheology (CR) polymer, containing fewer of the orientation-prone long chains, reduces this type of warping [199].

An important practical aspect of PP concerns its ability to form strong integral hinges, such as in a lidded box, where the lid is permanently attached to the base by a thin web of polymer along the whole of one edge (Fig. 32). This web, about $0.25 – 0.6$ mm thick, can be produced directly in the molding process or by post forming operations. An initial flexing of the hinge while slightly warm induces the correct molecular orientation to permit repeated opening, even

at subzero temperatures. In the laboratory, such hinges have withstood 23×10^6 flexes without failure [203].
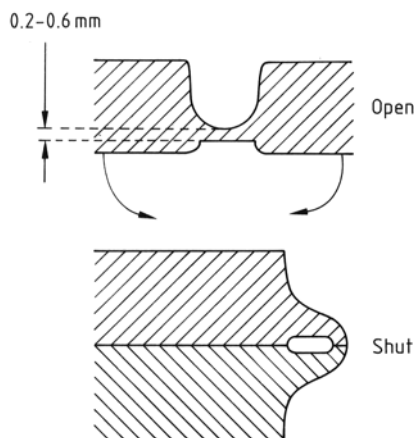

Figure 32. Integral hinge
Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

Various types of structural foamed moldings can be produced having a cellular core sandwiched between solid integral skins giving an overall density in the range $600-800 \, kg/m^3$ [204]. These lightweight, but rigid parts can vary in size from a paint brush handle to a sack pallet or car body panel. Foaming results from using a tumble-blended feedstock of granules and a chemical blowing agent. Alternatively, high-pressure nitrogen can be injected into the melt. Molding techniques are altered to achieve extremely rapid polymer injection rates into the mold. This prevents premature foaming before the solid skin forms. Foaming in the core arises by allowing the melt pressure to fall rather than maintain the customary pressure hold to keep the mold full.

Four alternative foam processes exist:

1) In the ICI sandwich molding process, different polymers are used for the skin and core by using two separate injection barrels. As the skin is unfoamed, high-quality surfaces result.
2) In the Varitherm Process (BASF, Krauss Maffei), improved surface finish is achieved by using a hot mold $(100-120 \, °C)$ followed by rapid cooling after a short shot of the melt (i.e., an injection of polymer insufficient to fill the mold).
3) In the counterpressure method the mold is pressurized prior to filling to prevent degassing at the melt front.
4) In hollow section molding (e.g., CINPRES) nitrogen is injected in a continuous stream into the mold at the same time as the polymer melt. Under appropriate conditions, hollow or ribbed moldings are produced when gas flows preferentially down thick, hot sections of the molding. This technique is of increasing interest.

2.8.2. Blow Molding

The extrusion blow molding process for PP copies that already well established for low- and high-density polyethylene. However, application to PP has been slow while suitably viscous and tough polymers were developed at attractive prices. At present, the important areas are smaller packaging containers which take advantage of good transparency, good form stability up to $140 \, °C$ for hot filling or sterilization, and greater freedom from environmental stress cracking with aggressive products. Brake fluid reservoirs exemplify this. Very large containers are dominated by high-density polyethylene.

Extrusion blow molding employs two linked processes [205] in which an extruded molten parison is transferred to a mold for inflation with low-pressure air at $0.4-1.0 \, MPa$. High molecular mass polymer, MFI $(230 \, °C/2.16 \, kg) \, 0.4-2.0 \, dg/min$, combined with low melt temperatures at the die of $200-210 \, °C$, provide a suitably stiff melt. If the melt stress in a heavy PP parison exceeds ca. $20 \, kPa$, then the resulting tension thinning will be troublesome as regards parison stability and uniform wall thickness.

Injection blow molding replaces the extruded parison with an injection-molded preform. Blowing takes place in a second mold which maintains the high-definition neck of the preform. This process eliminates scrap and makes it easier to produce wide mouth containers having improved dimensional accuracy and appearance.

Injection stretch blow molding is a further refinement which introduces a plunger stretching

stage to elongate a conditioned parison or preform just before the final blow (see → Plastics, Processing). Better mechanical properties and enhanced transparency stem from partial orientation. This technique is sometimes referred to as the melt phase process.

In stretch blow molding, the extruded or molded preform is carefully conditioned to just below the polymer melting point before stretching. Axial stretching of the preform with simultaneous or almost immediate blowing in the mold produces a very high quality container. Correctly carried out, this process secures increased rigidity and toughness, high transparancies, and reduced permeabilities as a direct result of significant amounts of orientation. The more complex technique increases capital and operating costs, but it is of growing interest [206] and is already being applied extensively to biaxially oriented PETP bottles.

Coextruded parisons can be used as precursors for blow molding when special barrier properties are required [207]. In particular, a central layer of ethylene vinyl alcohol copolymer (EVOH) to reduce oxygen diffusion, combined with moisture protective outer layers of propene – ethylene random copolymer, give containers suitable for storing oxygen-sensitive food products.

2.8.3. Fibers and Flat Yarns

Very large amounts of polypropylene homopolymers are used for fiber manufacture in Europe and the United States. These applications exploit the wide range of physical forms, including increasing amounts of versatile nonwoven fabrics [208–210]. Monoaxial orientation can be applied to conventional spinneret yarns, as with polyamides and polyesters, and to flat tapes made from extruded film. These differ in the following respects (Table 20).

Spinneret Type Yarns. Here melt is extruded through a die plate perforated by many small holes to generate individual thread lines. In the long spin process [211] (see → Fibers, 4. Synthetic Organic, Chap. 4.1.2.2.), which has integral spinning and finishing stages as well as out of line drawing options, there may be 50 – 250 holes per spinneret. An air cooling gap of 2 – 5 m

is needed between the die plate and the wind-up roll. Line speeds up to 1000 m/min at the spinning stage, increasing to 3000 m/min during solid drawing over hot rolls, call for complex and expensive haul off, drawing, and wind-up sections. Product may be packed off as continuous yarn, tow, or staple. Suitable polymers have MFI (230 °C/2.16 kg) in the range 12 – 25 dg/min, with narrower molecular mass distribution grades offering some advantage with such high rates of melt draw. These are high-throughput plants, best suited to long runs of a single grade of product.

Table 20. Polypropylene fiber processes

Process	Filament count, tex ∗	Product
Long spin	0.2 – 3.0	high-tenacity monofilament; drawing integral or separate; high output
BCF yarn	0.2 – 2.0	special case of long spin making only bulked continuous fiber
Spunbonded	0.2 – 2.0	venturi haul off; no 2nd stage draw. bonded mat output
Shortspin	0.2 – 40	compact unit; tow stretched and cut in line for staple
Melt blown	0.002 – 0.02	low orientation, very fine fiber; only bonded mat output
Fibrillated yarn	110 – 500	oriented slit film; fibrillated for baler twine, rope, etc.
Weaving tape	ca. 110	nonfibrillated slit film for carpet backing, sacks, etc.
Strapping tape	500 – 1000	thick, oriented tape as a steel alternative

∗ tex = weight in grams of 1000 m of yarn; equivalent cylindrical fiber diameter in $\mu m = 37 \sqrt{tex}$.

In a variation of this technique [212], the integrated spunbonded process (see → Fibers, 3. General Production Technology, Chap. 6.), yields a continuous bonded mat of partially oriented yarn as a consequence of some draw in the venturi type haul off operating at up to 5000 m/min. There is no further drawing as the fiber is collected as a mat on the take-off belt for conversion into nonwoven fabrics. These are used, for example, in geotextiles, furnishings, carpet backing, etc. The balance of drawdown rate and orientation in this process is influenced by the polymer molecular mass distribution.

Figure 33 depicts a compact shortspin process for staple production using a die containing ca. 40 000 holes. Cooling air jets freeze the melt within about 20 mm so that Godet haul off rolls can be placed only 1 m away from the die. Orientation is achieved by the in-line stretching of this tow in an air oven, followed by chopping in line to produce staple [207]. Broad molecular mass distribution polymers give the necessary melt strength, while MFI (230 °C/2.16 kg) requirements increase from 7 to 20 dg/min as the filaments become finer. These find use in geotextiles, carpet face fiber, and diaper cover stock applications. A useful feature of PP fabrics made from fine fibers is the ability of underwear garments to reduce claminess by transferring moisture away from the skin to an outer absorbent layer. Polypropylene based fabrics are also used for sports clothing and socks, but the low melting point of PP calls for special attention to the heat setting of the average domestic iron.
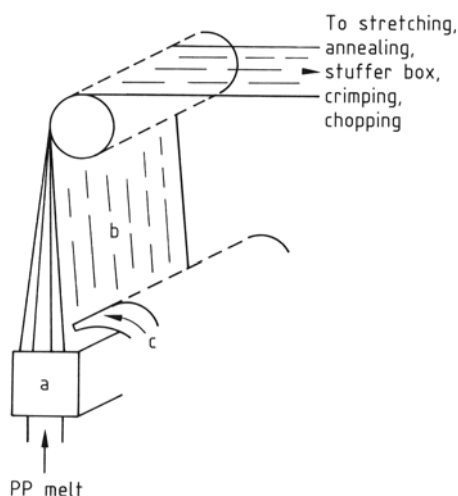
Figure 33. Shortspin process
a) Spinneret; b) Quenched fibers; c) Air-jet cooling Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

In the third production process (Fig. 34), air is blown through a very fluid polymer melt maintained at high temperature to assist chain scission in the spinning process itself [212,213]. Polymer MFI (230 °C/2.16 kg) at the nozzle can range from 35 to 300 dg/min or higher. The specially designed die, having a row of nozzles along its width, sprays a stream of short, low-orientation fibers onto a moving belt where they are bonded together and wound onto a roll. This process produces nonwoven fabrics which are of increasing importance for industrial wipes and surgical wrap, and for a variety of filtration applications, such as face masks made from bonded mats of very fine fibers.
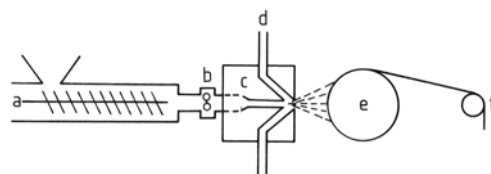
Figure 34. Melt blowing process
a) Extruder; b) Gear pump; c) Heated die; d) Hot air manifold; e) Collector; f) Take-off roll

Flat Yarns [214] (see also → Fibers, 4. Synthetic Organic, Chap. 4.2.). In this process (Fig. 35), extruded film is the basis of a cheap and different type of product to that achievable with filament-based yarns. Melt from a conventional slot die is rapidly quenched with cold water or water-cooled steel rolls to give low-crystallinity film, 50 – 250 µm thick. Razor blade type knives then slit this broad film into strips 5 – 20 mm wide, which are oriented in a hot air oven at 120 – 180 °C by drawing between Godet rolls at ratios in the range 5 : 1 to 10 : 1. Both film thickness and width diminish in this operation by approximately the square root of the draw ratio.

Fibrillated Tape (see also → Fibers, 4. Synthetic Organic, Chap. 4.2.). While flat yarns are quite strong in the direction of draw, they are very weak in the transverse direction. With normal homopolymer, simply twisting high-draw-ratio tape induces spontaneous fibrillation. A web of irregular fine fibers is formed as the film splits down its length. The resulting product resembles a coarse sisal twine, for which it is a good substitute. Such fibrillated yarns can be tailored to specific applications by controlling draw ratios, thickness, and polymer. Nowadays, pin fibrillation, in which a corotating spiked roll contacts the film just after slitting, offers more precise control over this step. The products are familiar as baler twine, string, and some ropes.
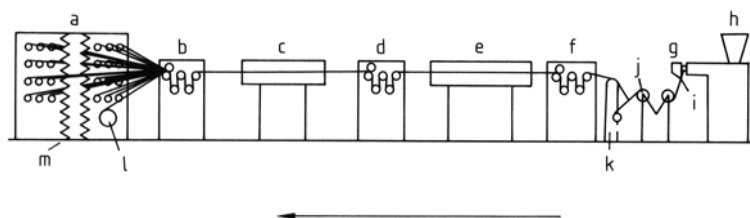
Figure 35. Flat tape/yarn production unit
a) Wind up frame; b) 3rd Godet stand; c) Hot air annealing oven; d) 2nd Godet stand; e) Hot air orientation oven; f) 1st Godet stand; g) Simple film costing unit; h) Extruder; i) Film die; j) Water- cooled chromium-plated rolls or water bath; k) Slitting unit; l) Starting drum; m) Individual precision flangeless bobbin wind up
Courtesy of the "Propathene" Business, ICI Chemicals & Polymers

Weaving Tapes. High strength tapes, without fibrillation, are made by controlling extrusion, orientation, and polymer type. Introduction of finely divided chalk, together with some polyethylene, usually as the chalk masterbatch, is particularly effective in reducing splitting. Impact copolymers are a more expensive, and rarely used, alternative to homopolymer for this application.

Both tapes and fibers contain residual stress from the extrusion and orientation processes. This results in linear shrinkages of up to 8 % immediately after manufacture, but after storage for a few days at room temperature the value falls to about 2.5 %. For those applications, such as weaving tapes for carpet backing, where zero shrinkage is often needed, a heat setting stage is essential. Out-of-line storage of the tapes on bobbins at 130 – 135 °C for several hours often suffices.

Thick, 0.3 – 0.9 mm, oriented tapes are established alternatives to steel bands in many strapping applications. They are generally made by the water quench process operating at draw ratios of 9 – 10. Thicker tapes are made from foil or individually extruded film tapes. High molecular mass, MFI (230 °C/2.16 kg) 0.4 – 2.0 dg/min, homopolymers and block copolymers with added chalk and polyethylene largely suppress fibrillation. A further precaution here is to emboss the finished tape with a diamond pattern. A useful aspect of PP strapping tapes is their higher elongation and elastic recovery which helps them to remain tight on packages prone to shrink or settle.

2.8.4. Film

Packaging film is an important outlet for PP, accounting for about one sixth of polymer sales in Europe, and rather more in Japan (see Section 2.6). By far the major proportion of this is biaxially oriented PP (BOPP), an established replacement for regenerated cellulose. Although the equipment needed for orientation is complex and expensive, it secures superior physical properties.

Good clarity in unoriented film is dependent on very rapid quenching of the melt to reduce spherulite size. The chill roll extrusion process (see → Films, Chap. 2.2.2.) for making 30 – 250 μm film extrudes a mobile, hot melt from a slot die onto water-cooled, highly polished steel rolls. Extrusion temperatures of 240 – 270 °C combined with an MFI (230 °C/2.16 kg) of about 7 dg/min minimize surface irregularities in the melt. Random copolymers containing 2 – 3 wt % of combined ethylene enhance toughness, clarity, and gloss, with some loss of modulus. These soft-feel transparent films are used as textile packages, bakery wraps, and document sleeves at thicker gauges.

Tubular quenched (TQ) film made in a downwardly extruded bubble (Fig. 36) uses some external water cooling which achieves reasonable clarity in film for packaging. In contrast, the less common tubular film from the air- cooled upwardly extruded bubble is more hazy, but finds use in the production of weaving tapes (Section 2.8.3). For most film applications, slip and antiblock additives are needed.
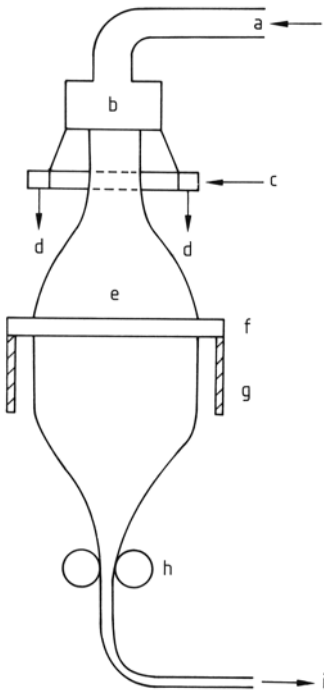
Figure 36. Tubular quenching process
a) Melt from extruder; b) Die; c) Air ring; d) Air flow;
e) Film; f) Water quench weir; g) Cooling skirt; h) Nip rolls;
i) Dewatering, slitting, wind up etc.

Biaxially oriented polypropylene (BOPP) film [215, 216], typically $12 - 40\,\mu\mathrm{m}$ thick, has excellent transparency, toughness, and stiffness, and is widely used in cigarette and biscuit packages, potato chip bags, and carton overwrap. Film modulus is three times that of the unoriented cast product. These complex film manufacturing plants are usually proprietary systems based either on a bubble process, or on a flat die (stenter) process. In the bubble process (Fig. 37), thick cast tube is reheated and then blown into a bubble with simultaneous stretching in the transverse and machine directions to produce a balanced film. The stenter process (see → Films, Chap. 2.3.2.) uses thick cast sheet which is reheated and conditioned for drawing. Longitudinal and lateral stretching are performed separately and can be adjusted to secure the required orientation balance. The typical area draw in these processes is $30 : 1$ to $50 : 1$.
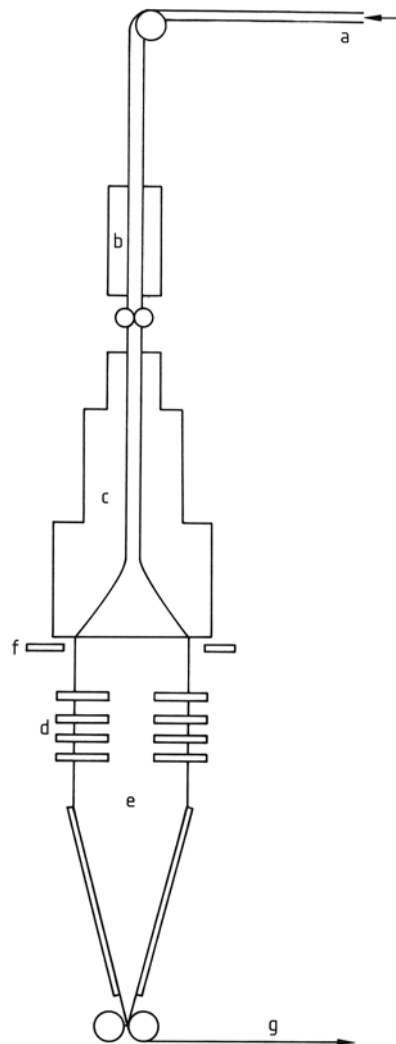
Figure 37. BOPP bubble process
a) Cast tube; b), c) Stretching heaters; d) Bubble guides;
f) Air ring; g) Wind up, slitting, etc.

It is impossible to heat seal such highly oriented material because unacceptable shrinkage then occurs. Low-melting surface coatings overcome the problem by reducing the sealing temperature to a level which the films can safely withstand. Suitable materials are vinylidene chloride copolymers, polyethylene, poly(1-butene), as well as butene, propene, and ethylene co- and terpolymers. Some of these may be applied as aqueous emulsions, but common practice is to coextrude the low-melting polymer as an outer layer of the cast tube or

sheet. After orientation, this layer can be less than 1 µm in thickness. These more compatible polyolefin coextruded coatings also simplify scrap recovery and recycling without fear of the coating instability inherent in halogenated polymers.

Polypropylene film, however made, is not receptive to printing inks and adhesives because of the low polarity. Mild surface oxidation by corona discharge treatment overcomes these problems.

2.8.5. Foil and Sheet

Slow heat transfer rates in sheet and thick foil call for extended cooling times at the extrusion stage. Foil, up to about 0.7 mm thick, can be made by the cast tube process (Section 2.8.4), but the more versatile three roll stack system (Fig. 38) is able to produce sheet with thicknesses of 0.3 – 15 mm. Use of additional and larger diameter rolls extends this range to 40 mm. Thicker sheets are made by compression molding of granules or large molded slabs, and by injection – compression molding. This can make 2 m square slabs with thicknesses up to 240 mm. High molecular mass homo- and copolymer, MFI (230 °C/2.16 kg) ca. 0.3 – 1.0 dg/min, provide higher dimensional stability in slow- cooling, thick-section melts whose temperature at the die exit is ca. 210 °C. Higher flow grades with MFI (230 °C/2.16 kg) of up to 5 dg/min may be used for thin foil, depending on the available equipment.
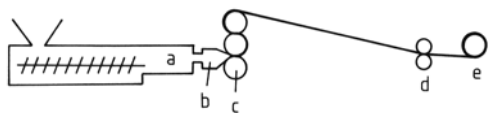
Figure 38. Three roll stack extrusion
a) Extruder; b) Slot die; c) Polishing stack; d) Nip rolls; e) Wind up

Commercial sheets, normally up to 2 m wide provide stock for fabricating into welded tanks for storing corrosive liquids. They are also used as linings for steel and concrete containers, for ducting construction, and as an inert construction stock for chemical plant. It is possible to bond woven glass or polyester fabric to the heated surface for subsequent further strength-

ening using traditional glass fiber lamination techniques. Punched sheets can be biaxially oriented to generate heavy duty meshlike structures for geotextiles [217].

Thick sheet, as made, has a nonuniform structure across its thickness as a result of considerable differences in cooling rate.

2.8.6. Extruded Pipe

Compared with polyethylene, tubing applications for PP are quite small. However there are several areas where PP's increased resistance to aggressive media and its better performance at elevated temperatures are advantageous.

Extrusion at ca. 225 °C is straightforward; a central torpedo is used to make the hollow pipe [218]. Homogeneous melts require an extruder having a length-to-diameter ratio of 25 : 1 and a compression ratio of 4 : 1 to reduce the risk of trapping air in the extrudate. Pipe up to 300 mm outside diameter is generally vacuum sized in a water bath: semi-molten pipe passes through a finely perforated steel tube having vacuum applied to its external surface. Larger pipes are made by pressure sizing where nitrogen or air is injected via a small capillary into the torpedo to expand the pipe to the sizing die form. Both homopolymers and impact copolymers are used in the MFI (230 °C/2.16 kg) range 0.3 to 2.0 dg/min, increasing to 4.0 for drinking straws and ballpoint pen tubing.

Copolymers, providing superior impact strength with some flexibility, find use in domestic waste systems. Homopolymers have higher resistance to stress. It is essential to have a heavy duty stabilization system which will withstand extraction for applications involving aggressive and hot environments, such as chemical plants and effluent pipes. Manufacturers offer guidance [218] on polymer selection and pipe design conforming to the various pressure classes in BS 4991, and to BS 52 254 and BS 5255 for domestic waste pipes and fittings. Creep data are available [218] for pressure pipes predicting performance for up to 50 years.

Pipe jointing uses all the common techniques, with the exception of solvent welding. Ring seals with rubber inserts allow some movement in domestic waste pipes. Also used are flanged joints,

hot plate butt welding, and socket fusion welding, the latter being optionally supplemented with hot-gas bead welding. Compression joints involving copper alloys should not be used at temperatures exceeding 60 °C because of reduced life expectancy.

2.9. Environmental Aspects

2.9.1. Recycling

The structure and properties of PP make it well suited to recycling operations. There is no fear about cross-linking, nor of complications with plasticizers or chlorine-rich species. Re-extruding PP usually lowers its molecular mass and narrows the molecular mass distribution, particularly in aged feedstock. This can be helpful in some applications that require enhanced flow. Adverse factors which must be assessed include some loss of strength from reprocessing/ageing, oxidation stability, discoloration, and contamination.

PP Manufacturers. Manufacturers usually produce small proportions of PP which do not meet their full quality requirements. Examples include deviations in MFI/MMD, antioxidant levels, copolymer characteristics, and gels. Provided these faults are within predetermined limits in the quality protocol, the material may be recycled in small proportions, sometimes with further corrective adjustments to the composition. This operation calls for additional work, and can reduce plant output by having to process the polymer twice. For this reason, and in those cases where recycle is not permitted or the deviations are too large, manufacturers either reclassify the product to a lower grade, or sell to an outside compounder for further reprocessing. This minimizes disturbances to continuous manufacturing processes.

A second source of much lower grade material, arises when manufacturing conditions are severely disturbed. This can be due to instrumental and human error, blockages, equipment failure, or extrusion disturbances. In these cases scrap can vary from substandard reactor powder to blocks of polymer from extruder dumps. External reprocessors convert such products into surprisingly useful materials by blending and recompounding. To them, the availability of essentially pure PP is the prime requirement.

Plastics Converters. Turning PP into moldings, pipe, film, etc., invariably involves some scrap production. Apart from substandard articles, there are sprues from moldings, edge trim from film and sheet, parison waste, and stamped sheet from thermoforming. These are recovered for recycling by the converter himself if the application allows, or more often by an outside compounder. In favorable situations involving long runs of a standard product, the converter segregates waste, grinds it, and then recycles it by blending small amounts with virgin feedstock when specifications permit. Occasionally there is an undemanding application which can accept large proportions of such regrind without difficulty. Storage and segregation problems are reduced when the converter simply collects his scrap together in the form of regrind for sale to a compounder.

The British Plastics Federation (BPF) estimates [219] that there are about 60 reprocessing companies in the United Kingdom handling at least 150 000 t/a of polymer. Forty three of these process an estimated 25 000 t/a of PP [220]. Only a few of these also process recovered scrap into molded products such as horticultural, highway, safety, and street furniture, which do not make excessive demands on polymer behavior. Included in the estimated figure are 15 000 t of recovered used battery cases and crates which can be converted into quite respectable compounds. Most reprocessors only handle single polymers, not mixtures. Their main supply sources are plastics converters and industrial or commercial establishments as suppliers of fairly well defined PP scrap [221].

Recycling PP After a Full Service Life. Nearly half the thermoplastics used in Europe are converted into packaging [222]. In the United Kingdom 13 % of this is based on PP, involving an estimated 142 000 t of polymer in 1988.

Polymers used in United Kingdom for packaging in 1988 (in 10^3 t) broke down as follows [222]:

Low-density polyethylene (LLDPE and LDPE)	510
High-density polyethylene	255
Polypropylene	142
Polystyrene	78
Poly(vinyl chloride)	68
Poly(ethylene terephthalate)	53
Expanded Polystyrene	21
Total	1127

Inevitably, much of this has only a short life before it ends up as waste in some form. Domestic waste contains $5-7$ wt % (up to 20 % by volume) of such products [220], very little of which is currently recovered. Public concern about the environment naturally includes highly visible plastic litter, which is made unduly prominent by its low density and durability. This is an additional factor accelerating legislation for recovery of all types of packaging, including glass, metal, paper, as well as plastic [223–225].

In the case of PP, notable success rests with recycling old plastic bottle crates and battery boxes in Western Europe and the United States. This is mainly attributable to the ease with which large amounts of a clean single polymer can be collected without cross contamination from other plastics. Cooksons Plastics [226] and others [227, 228] have expanded on lead recovery to retrieve PP battery cases themselves. A mechanised sorting system has to separate stones, metal, wood, string, ebonite paper, and residual acid. The Cookson process involves crushing, several stages of washing, flotation, and screening followed by drying and extrusion. The final products include good-quality PP capable of being used in automotive products and for certain types of battery cases. Success here rests in quality upgrading by adding elastomer to enhance toughness, stabilizers, and antacid incorporation to recoup oxidative stability, and molecular mass tailoring with peroxides for specific applications. Hoechst [229] plan to collect plastic waste from scrap cars, household appliance industries, and presorted packaging waste. The 5000 t/a plant near Cologne should be in operation by mid-1992. ICI studies on scrap recycling from used PP crates stress the need to incorporate additional stabilizer in weathered products, and to allow for some reduction in impact strength for seven-year-old crates.

Recovery and reuse of mixed plastics is more difficult. The real need is to develop applications and fabrication processes for such comingled polymers, which are essentially incompatible and contaminated. Generally, they will be channeled into some massive products, such as posts, construction boards, and other bulky structures where resistance to water and decay is more important than high inherent strength. Some 20 different European schemes aim to make recycled plastic components as wood and concrete replacements for agricultural applications [223, 230]. Comingled scrap can be upgraded by blending with other recycled polymers to assist processing.

2.9.2. Pyrolysis

PP can be cracked to liquid hydrocarbons by thermal pyrolysis at $400-550$ °C. In a process developed in Japan [231], zeolite catalysts enable this temperature to be reduced to $200-420$ °C by using a two-stage heating process. Other polyolefins, such as polyethylene and polystyrene, and some chlorinated plastics can also be pyrolyzed to liquid products. Process cost estimates are $ 235 per ton of plastic, which yields $0.5 \, m^3$ of gasoline, $0.5 \, m^3$ of kerosene, and diesel products. Plants are expected to be built in Taiwan and Korea in 1991.

2.9.3. Incineration

Municipal waste is normally disposed of in landfill sites, with incineration being the next most important method [232]. As suitable landfill sites become rarer and more expensive, pressure is exerted to reduce waste volume either by incineration or by scrap recovery.

Modern incineration technology, with energy recovery in the form of electricity generation, can take advantage of the high calorific value of thermoplastics. Municipal waste calorific values average 10 kJ/g, compared with $30-35$ kJ/g for coal. At 44 kJ/g, PP and other polyolefins have the same calorific value as fuel oil. Moreover, PP has an exceptionally low sulfur content, making it a very clean fuel with no apprehensions about toxic flue-gas emissions. These incineration plants are costly to build. Even after allowing for the sale of electricity, the net disposal cost in the United States is estimated at $40-70$ $/t of processed waste [224]. Special burners have been developed to handle atactic and isotactic

waste PP feedstock, but more profitable outlets are now available.

2.9.4. Environmental Interactions

Overall PP manufacture, like any other product, involves some interaction with the environment. Various essential inputs, such as raw materials and services need to be considered along with all the plant output streams.

Inputs. The principal input for PP is pure propene, with lesser amounts of ethylene for copolymer grades. Energy is required to manufacture these monomers from petroleum feedstocks, and still more is needed for conversion into polymer. At present, most of this power comes from burning fossil fuel which then discharges carbon dioxide and water vapor to the atmosphere. Table 21 compares the overall energy input needed to make various raw materials. This can be expressed either as the weight of oil to produce this energy, or in terms of joules per unit volume. Both values include energy for monomer production, but exclude the hydrocarbon content of the monomer, which is transformed into polymer without combustion. On a weight basis, polyolefin energy requirements are broadly similar to those of most alternative raw materials. On a more realistic volume basis, the strength and lightness of plastics gives energy savings. Usually this is enhanced further in the final article where, for example, thin and strong plastic bottles show savings over their thicker glass counterparts.

Table 21. U.K. energy requirements for the manufacture of natural and synthetic materials [232]

Material	Energy requirements	
	TOE ∗, overall conversion	kJ/cm^3
Aluminum	5.6	661
Tinplate	1.3	427
Copper billet	1.2	469
Glass bottles	0.5	46
Paper and board	1.4	50
Cellulose film	4.4	293
Low-density polyethylene	1.2	51
PP, old process, with extrusion	1.5	61
PP, new process, with extrusion	1.3	52

∗ TOE = tonnes of oil equivalent to the energy requirement for overall conversion.

Propene and ethylene monomers themselves are nontoxic asphyxiant gases whose flammable nature calls for the usual extensive precautions. Ignition by static electricity is possible with high-pressure leaks and accidental discharges.

Autoxidation of hot, unstabilised PP powder in storage silos containing air is another known cause of fire.

Effluents. Although catalyst components constitute only a very small proportion of plant materials, both their manufacture and disposal involve noxious substances. Titanium tetrachloride is used for all catalysts, sometimes in considerable excess for high-activity systems. Whereas expensive recycle and recovery stages may be installed as capacities increase, some remaining complexed residues will require disposal. Often, this involves hydrolysis with water to generate corrosive HCl and titanium dioxide suspensions. After neutralization with alkali, these slurries are either discharged as aqueous effluent or settled out and used in landfill. Some incineration is planned. Disposal facilities also need to be capable of receiving occasional faulty catalyst batches. Older plants still using catalyst extraction processes simply use aqueous slurry discharges, or dump concentrated residues from the base of stills.

Lower aluminum alkyls are pyrophoric, react violently with water, and are intensely aggressive towards exposed skin. Safe handling usually calls for full protective clothing. Disposal can be by burning to generate alumina, or quite often, by controlled hydrolysis with water after deactivation with alcohols. Some alkyl manufacturing plants will accept returned waste alkyls for disposal in their own dedicated facilities.

Atactic PP. Older plants needed to dispose up to 5 % of their output as low molecular mass atactic residues from solvent recovery streams. Landfill was a common outlet, with some incineration. Useful low- cost applications appeared in adhesives and roofing felt compositions, which now consume nearly all of the increasingly rare atactic PP byproduct.

Gaseous Effluent. Traditional flare stacks receive most of the voluntary and involuntary process gaseous discharges. Normally, these comprise small flows from distillation column

purges which can be dealt with by screened low level flares. These reduce the visual impact of flares which some people find objectionable, especially at night. Some nitrogen purges containing traces of hydrocarbons are discharged to the atmosphere. Scrubbing systems and carbon adsorption beds reduce hydrocarbon emissions, but only a few manufacturers use them because of the cost.

3. Poly(1-Butene)

3.1. Production

Introduction. Poly(1-butene) is a thermoplastic polymer produced by solution polymerization of 1-butene with a Ziegler – Natta catalyst system. Hüls developed a process during the 1960s and produced the polymer in a 12 000 t/a plant in the Federal Republic of Germany. Mobil started to develop a process in 1968 and, together with Witco, built a plant in Taft, Louisiana with a capacity of 30 000 t/a. Shell (USA) bought the plant in 1977 and is at present the only commercial producer.

The feedstock of pure 1-butene is supplied from the Shell Higher Olefins Plant in Geismar, Louisiana.

The poly(1-butene) plant produces grades specifically developed for pipe and speciality film applications.

Process. The commercial poly(1-butene) production process consists of seven primary unit operations: (1) polymerization, (2) deashing, (3) polymer/monomer separation, (4) monomer purification, (5) extrusion, (6) pellet blending, and (7) packaging (Fig. 39).

In the polymerization step the catalyst system is fed into the reactor with the purified 1-butene recycle stream. Hydrogen is added as a chain terminator to control the melt flow index of the polymer. Ethylene is fed to the reactor when producing random 1-butene – ethylene copolymers.

Polymerization catalyst residues must be removed from the product to preserve its long-term properties. In the deashing step, the poly(1-butene) is mixed with dilute caustic soda to dissolve and extract the catalyst components. The cleaned hydrocarbon – polymer phase and the catalyst-containing aqueous phase are then separated.

During the polymer/monomer separation step, unreacted 1-butene is separated from the poly(1-butene) for recycle to the reactor. Separation is carried out by heating the polymer solution under pressure then flashing off the monomer by rapidly reducing the pressure. The remaining molten polymer feeds the extrusion step, while the vaporized monomer flows to the monomer purification section of the process.

The monomer purification step accomplishes separation of impurities both heavier and lighter than 1-butene. Water is removed by azeotropic distillation. Fresh 1-butene is added to the process at this stage.

In the extrusion step further volatile hydrocarbons are removed, additives for color, product performance, processing, and stabilization are added, and the polymer is pelletized.

The pellets are pneumatically conveyed to the batch blending stage and then transferred to the packaging area. Pellets are typically sold in 450-kg boxes.

3.2. Properties

3.2.1. Structure and Physical Properties

The properties of a high-molecular material are essentially determined by the dimensions and structure of the molecular chain (fine structure) and by the thermomechanical history [233]. Since the fine structure of poly(1-butene) can be varied across a broad range by means of the polymerization process, a knowledge of this is essential for the spectrum of properties.

Molecular Structure. Polymerization with Ziegler – Natta catalysts produces both atactic and isotactic polymer. Atactic poly(1-butene) is virtually impossible to crystallize, while isotactic poly(1-butene) has a crystallinity of 40 – 55 % at normal cooling speeds.

The molecular chains in the crystal form helices. Depending on the crystallization conditions, poly(1-butene) forms 11_3, 3_1, or 10_3 helices, which differ in their helical dimensions [234–236] and give rise to different crystalline modifications (see below).

The isotactic content of poly(1-butene) is generally determined by the solubility in boiling
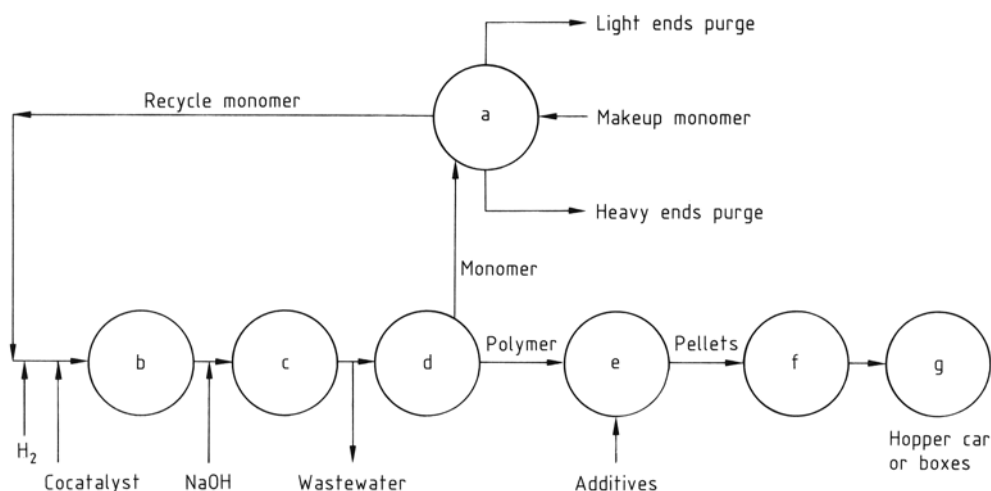
Figure 39. Flow sheet for the production of poly(1-butene)
a) Monomer purification; b) Polymerization; c) Deashing; d) Monomer/polymer separation; e) Extrusion and pelletizing; f) Blending and storage; g) Packaging

diethyl ether ("ether extract"), whereby it is assumed that only the atactic components are soluble. However, infrared spectroscopy and X-ray crystallography have shown that the atactic extract contains crystallizable components, mostly of low molecular mass. A quicker and more reliable method of determining the atactic content is by evaluating the infrared band in the region of 920 cm^{-1} [237]. This leads to the following definition of the atactic content Y_a:

$$Y_a = \frac{\bar{v} - 918\,\text{cm}^{-1}}{30\,\text{cm}^{-1}}$$

where $\bar{v}$ is the band position of the unknown sample in cm^{-1}.

The advantage of this method is that it is independent of the molecular mass and of the morphology of the sample.

Molecular Mass. The average molecular mass may be determined either by direct methods such as light scattering or osmometry, or by indirect methods such as determination of the intrinsic viscosity [238, 239]. The molecular mass is calculated from the viscosity number using the Mark – Houwink equation [239]. Mark – Houwink equations for isotactic poly(1-butene), which give virtually identical molecular masses are as follows:

$$[\eta]_{n-\text{nonane}} = 5.9 \times 10^{-5} \times M^{0.80}$$

$$[\eta]_{\text{dekalin},135°\text{C}} = 6.2 \times 10^{-5} \times M^{0.79}$$

These equations also apply to atactic poly(1-butene).

The molecular mass distribution can be determined easily by gel permeation chromatography in 1-chloronaphthalene as solvent. Industrial products have molecular nonuniformities $U = (M_w/M_n) - 1$ between 5 and 12 (M_w = weight-average value, M_n = number-average value).

Crystal Structure and Superstructure. Like most polymers isotactic poly(1-butene) can crystallize in various modifications. However, the polymorphism is more marked and of greater industrial significance in poly(1-butene) than in any other polymer. Four crystal forms of poly(1-butene) are known at present and are designated modification I, I′, II, and III [234, 240]. Characteristic physical data of these modifications are listed in Table 22.

Modifications I′ and III are formed on crystallization from solution. They are of no industrial importance. However, modifications II and I, which are obtained by crystallization from the melt, are industrially significant. All the crystal forms can be obtained from modification III in a single step [246], as shown in Figure 40. The transitions from one crystal form to another are monotropic. Modification I′ crystallizes preferentially from solution at lower temperatures [240], while at high temperature the

Table 22. Characteristic data for crystal modifications of poly(1-butene)

	Modification II (tetragonal)	Modification I (hexagonal)	Modification III (orthorhombic)	Modification I' (hexagonal)	Amorphous phase	Reference
Helix type	$11_3/40_{11}$	3_1	10_3	3_1		[235,240, 242]
Helix length per monomer unit, nm	0.187	0.217		0.217		
Helix cross section, nm^2	0.055	0.044				
Specific volume at 25 °C, cm^3/g	1.1364	1.0453			1.1579 1.16 for mod. II 1.14 for mod. I	[243] [243]
Specific coefficient of volume expansion, cm^3 g^{-1} K^{-1}	3.05×10^{-4}	3.13×10^{-4}			8.12×10^{-4}	[243]
Melting point, °C	ca. 125	ca. 140	93–98	100		[241, 244–246]
Heat of fusion, kJ/mol	ca. 3.1	ca. 6.7				[247–249]
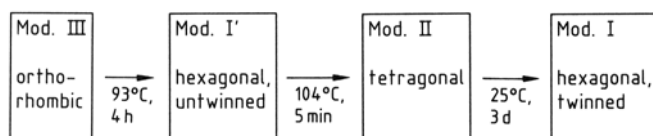
Figure 40. Monotropic interconversion of the four modifications of poly(1-butene)

orthorhombic modification III is produced [250, 251]. Modification III is also formed by precipitation, e.g., by addition of methanol to a benzene solution of poly(1-butene) [252]. Modifications I′ and III are also formed in solution or suspension polymerization [253].
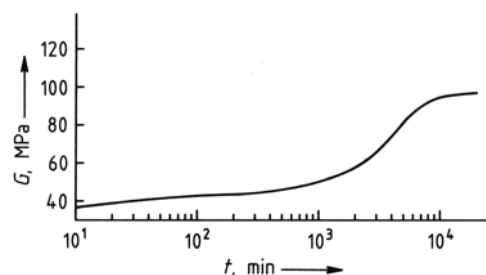
Figure 41. Time dependence of the shear modulus G of modification II of poly(1-butene)
Thermal history: 1 mm thick test bar cooled from the melt (160 °C) in air to the test temperature of 20 °C

The tetragonal modification II and the hexagonal form I are industrially important. As a melt cools, i.e., after most processing operations, form II crystallizes out first. This is thermodynamically unstable and in the absence of external mechanical stresses it changes monotropically into the stable hexagonal modification I after a period ranging from a few hours to several days,

depending on the temperature and thermal history [234]. The transformation from II to I is associated with a change in various physical properties, e.g., an increase in melting point, density, [243] and modulus (Fig. 41).
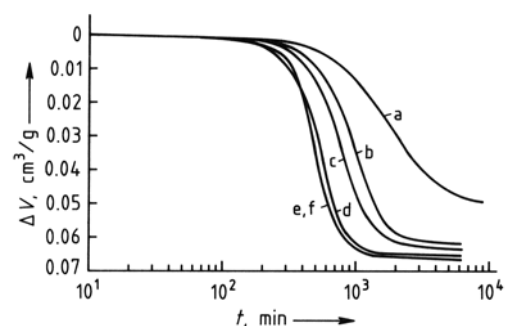
Figure 42. Time dependence of specific volume during transformation (II → I) of poly(1-butene) at 20 °C
a) Quenched; b) Crystallized for 200 min at 92 °C; c) Crystallized for 5700 min at 102 °C; d) Crystallized for 5600 min at 102 °C; e) Crystallized for 7500 min at 106 °C; f) Crystallized for 7200 min at 108 °C

These changes in properties are primarily due to the change in crystal modification. The degree of crystallization and the mean spherulite size remain virtually constant during the transition from II to I [243]. The crystallite size also remains unchanged [244]. This is a purely crys-

tal – crystal transformation without experimentally detectable melting of modification II crystals.

The rate of conversion, as indicated for example by the half-value time $t_{1/2}$ depends on the thermal history (Fig. 42) and on the temperature (Fig. 43).
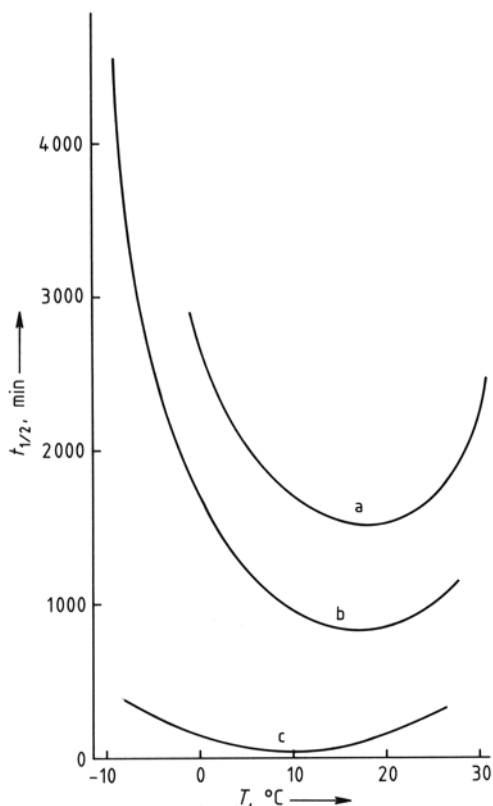
Figure 43. Temperature dependence of half-value time $t_{1/2}$ for the transition II → I
a) Pure poly(1-butene); b) Melt mixture of poly(1-butene) and polypropylene in the ratio of 1: 1; c) Poly(1-butene) with 30 % butyl stearate

Mechanical stresses may significantly increase the conversion rate [254, 255]. Figure 44 shows the influence of constant tensile stress on the conversion rate, monitored by IR spectroscopy. Whereas these measurements show a stress-free sample to have a half-value time of 5500 min, the half value for a sample under a tensile load of 4.4 MPa is only ca. 10 min. Internal stresses and orientations have a similar effect to external stresses. The conversion of II to I is also accelerated by hydrostatic pressure

[256]. The conversion rate can also be increased by certain additives, such as polypropylene or plasticizers (see Fig. 43) [240, 257, 258].
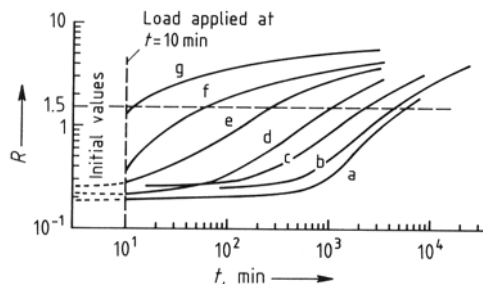
Figure 44. Poly(1-butene) conversion curves for modification II → I for various constant tensile stresses
R is the ratio of the IR extinction of modification I at $920\,cm^{-1}$ to the extinction of modification II at $920\,cm^{-1}$. The half-value time $t_{1/2}$ (II → I) is reached when R has a value of ca. 1.5
a) 0 MPa; b) 0.12 MPa; c) 1.48 MPa; d) 1.91 MPa; e) 2.55 MPa; f) 2.95 MPa; g) 4.23 MPa
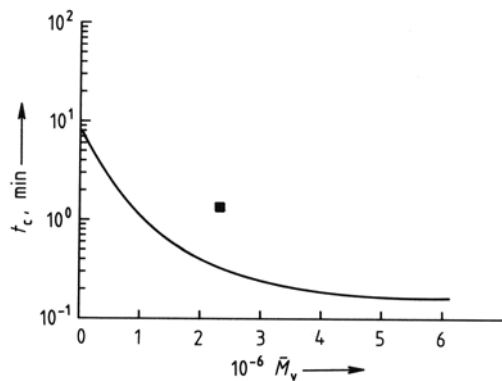
Figure 45. Crystallization time t_c of poly(1-butene) at 78 °C as a function of the viscosity-average molecular mass $\bar{M}_v$
Curve: measurements on fractions, ■ unfractionated product

The molecular mass and the molecular mass distribution have virtually no effect on the conversion rate. However, the molecular mass does have significant influence on the rate of crystallization of modification II (Fig. 45). The crystallite and spherulite sizes of all crystal modifications can be varied over a broad range by modifying the cooling and crystallization conditions of the melt [248, 259, 260]. Surprisingly, the mean crystallite size and size distribution are not increased by subsequent tempering [259, 260]. This may be a reason for the low time de-

pendence of certain mechanical properties (see page 74).

The four modifications are distinguished analytically and characterized quantitatively by a combination of X-ray, infrared, and differential thermal analysis [245–247, 261].

3.2.2. Application Properties

In normal processing operations, isotactic poly(1-butene) is heated to above its melting point. Therefore it is the unstable modification II which forms immediately after cooling, and is converted to the stable form I during storage or on application of mechanical stress. Since only the properties of form I are of interest from the point of view of applications, the statements below refer only to this modification.

In terms of density, melting point, and glass transition temperature, poly(1-butene) resembles polyethylene rather than polypropylene [262]. This similarity extends to cross-linked polyethylenes, although some of their properties naturally vary, depending on their cross-linking density [263]. Commercial material is around 40 % to 55 % crystalline. Since the crystallization rate is slow by comparison with polyethylene and polypropylene, superstructures which are of interest for applications can be obtained by the choice of cooling conditions [264]. Nucleators increase the rate of crystallization, leading in some conditions to a material that is somewhat more brittle at low temperature [264].

Mechanical Properties. Table 23 lists some mechanical properties of poly(1-butene), polyethylene, and polypropylene. According to the VDE hardness, poly(1-butene) is softer than polyethylene and polypropylene. However, the Shore hardness is virtually the same as for polyethylene. The surface gloss of components made from poly(1-butene) is similar to those made from polypropylene [265].

The rigidity of poly(1-butene) is relatively low. The flexural stress at conventional deflection and modulus of elasticity are lower than for polyethylene (Table 23).

The impact strength and notched impact strength are significantly higher than those of polypropylene. Above 0 °C the values are similar to those for high molecular mass polyeth-

ylene, but at lower temperature they are inferior [265]. Nevertheless the low-temperature strength, as characterized by the brittle point, is relatively good [254, 265].

The stress – strain behavior of modification I differs noticeably from that of other polyolefins. The differences are not only in the shape of the stress – strain curve, which for industrial material has virtually no maximum [265, 266], but also in the dependence on time and temperature [267]. Figure 46 shows the yield strength σ_{ys}, measured in an uniaxial tensile test as a function of the stretching time t_s. Whereas the yield strength of polyethylene and polypropylene declines sharply with increasing stretching time, the values for poly(1-butene) remain virtually constant above 0.1 s. The good creep resistance and resistance to stress cracking of poly (1-butene) pipes subject to internal pressure [262] is due to the low time dependence of the mechanical properties.
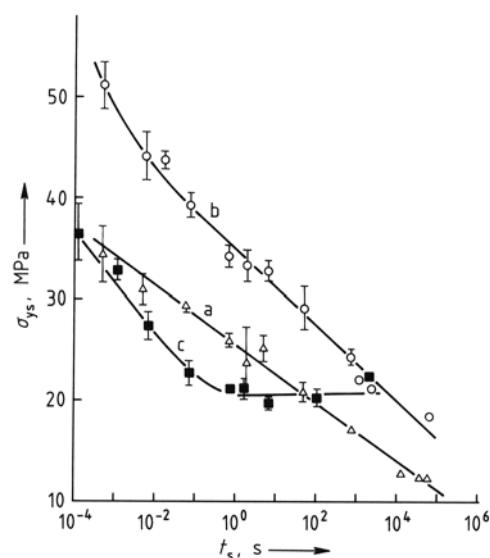
Figure 46. Yield strength σ_{ys}, measured in a tensile test at 22 °C, as a function of the stretching time t_s [266]
a) Polyethylene; b) Polypropylene; c) Poly(1-butene)

Since this low time dependence of the mechanical characteristics is maintained at higher temperatures, poly(1-butene) is particularly suitable for hot-water pressure pipes [263, 268]. Figure 47 shows the burst hoop stress performance of poly(1-butene) pipe under inter-

Table 23. Hardness, rigidity and strength of low-pressure polyolefins [265]

Property	Test method	Polyethylene	Polypropylene	Poly(1-butene)
VDE hardness (60 s), MPa	VDE 0302	44 – 64	61 – 80	25 – 45
Shore D hardness	DIN 53 505	62 – 69	70 – 75	60 – 68
Flexural stress at conventional deflection, MPa	DIN 53 542	26 – 43	34 – 50	15 – 25
Modulus of elasticity, MPa	[a]	900 – 1200	1000 – 1500	500 – 900
Impact strength	DIN 53 453	no break	no break	no break
Notched impact strength, kJ/m^2	DIN 53 453	5 to no break	3 – 15	20 to no break
Brittle point, °C	ASTM D 746-57T	below − 70	+ 20 to − 5	− 10 to − 30

[a] Measured in Hooke range by bending tests.

nal pressure according to ISO-SEM (DIS 9080) [269].
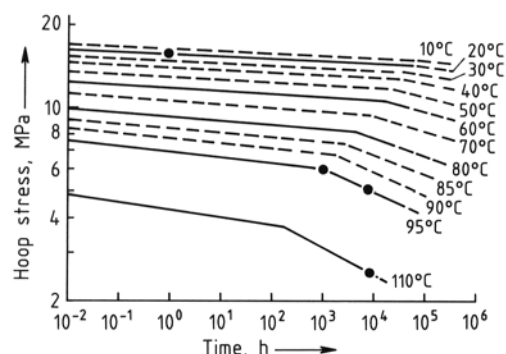
Figure 47. Burst hoop stress performance of poly(1-butene) pipes

As well as the outstanding resistance to stress cracking, the unusually good creep behavior is significant. The tendency to creep, i.e., to undergo plastic deformation below the yield point, is significantly lower than for other polyolefins, even at temperatures up to 100 °C [263, 265, 270]. This is also an essential requirement for the use of poly(1-butene) as a film material, particularly for the packaging sector [270].

Electrical Properties. The electrical behavior of poly(1-butene) does not differ significantly from that of polyethylene and polypropylene [265]. Apart from the usual quantities of stabilizers, it only contains residues of polymerization catalysts. Because of its good resistance to chemicals, outstanding resistance to stress cracking, and flexibility, poly(1-butene) is an important material for special applications in the cable and electrical industry.

Resistance to Chemicals and Gas Permeability. Because of its paraffinic structure, poly(1-butene) is resistant to most common chemicals such as acids, alkalies, salts, alcohols, and ketones. However, it swells or dissolves in hot aromatic and chlorinated hydrocarbons. It is less inert to aliphatic hydrocarbons than polyethylene and polypropylene and more prone to permeation [265, 271, 272]. A detailed table on the resistance of poly(1-butene) to chemicals is given in [270].

Permeability to gases and vapors, in particular water and oxygen, is comparable to that of polyethylene of similar crystallinity. Permeability to carbon dioxide, however, is higher [264].

3.3. Processing

Processing poly(1-butene) on conventional machines presents no problems. Because of its low crystallite melting point and particularly because of the rapid decrease in melt viscosity with increasing temperature, poly(1-butene) can be processed by extrusion (pipes, profiles, sheets), extrusion blow molding (hollow bodies), and injection molding (engineering products, sheathing for metals) [265]. Sheets made by extrusion or compression molding can be shaped hot or cold. A special feature is cold shaping of the relatively soft modification II. Articles shaped from this modification then become increasingly rigid as the conversion to modification I progresses.

3.4. Applications

Pipe. The major outlet for poly(1-butene) is in high-performance pipes, which exploit its creep resistance and long lifetime at elevated service temperatures, flexibility, light weight,

corrosion resistance, and its ability to be heat welded [263]. It competes in plumbing and radiator heating applications with copper, where progress is mainly limited by resistance to replacing traditional working practises. In the underfloor heating pipe market it competes with other plastics such as cross-linked polyethylene and polypropylene.

The advantage of poly(1-butene) over other polymers in both these applications is its better ability to retain its mechanical and performance properties at elevated temperature. For instance a comparison of tangent modulus, yield stress, ultimate stress, and elongation at break within and transverse to the extrusion direction of the pipes shows a more balanced performance for pipes made of poly(1-butene) [273]. In the last decade the long-term properties of poly(1-butene) pipes and their lifetime at temperatures up to $120\,°C$ have been studied [274] and the methodology for such long-term tests has been developed for various plastics [275–277].

Extrapolation methods give estimated lifetimes of 50 years at $70\,°C$ [273]. An evaluation of pipes based on polymers as well as traditional materials, such as copper, favored poly(1-butene) [278].

The problem of oxygen diffusion in plastic piping systems, which was given as one explanation of corrosion in metal radiators, tanks, and boilers in the past, has been resolved by the use of multilayer pipes containing an oxygen-barrier layer and the addition of inhibitors to the circulating hot water [278].
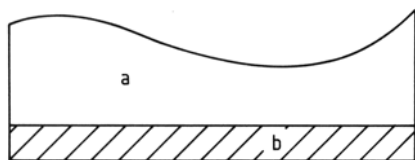
Figure 48. Cross section of a coextruded peel-seal layer on an LDPE substrate
a) LDPE substrate; b) Peel-seal blend LDPE in which incompatible poly(1-butene) particles are dispersed

Packaging. In the packaging sector, poly (1-butene) has become established in speciality film applications which require resistance to cooking temperatures, and in heat-seal layers for oriented polypropylene, which exploit the high compatibility of poly(1-butene) with polypropylene. The incompatibility of poly(1-butene) in blends with various polyethylenes and ethylene copolymers, such as low-density polyethylene, linear low-density polyethylene, high-density polyethylene and ethylene–vinyl acetate copolymers, forms the basis of peelable seals (see Fig. 48).

Peel-seal technology provides a robust pack, yet allows the consumer to open it easily without ripping or tearing. The key attributes of systems based on poly(1-butene) are the broad heat sealing range and the cohesive failure mechanism, which results in an aesthetically attractive package after opening. This is because cohesive failure propagates through the peel-seal layer itself due to the weaker intermolecular forces between the dissimilar materials, and results in clean uniform separation. Additional advantages are good clarity and a clean peel with no stringing [279, 280]. The more conventional system relies on delamination between layers as a result of adhesive failure and is also more difficult to control.

A correlation of peel-seal strength with blend composition and temperature is shown in Figure 49.
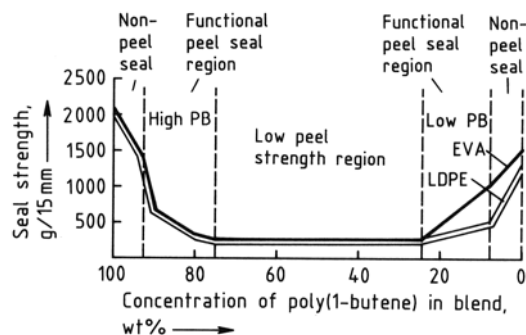
Figure 49. Dependence of peal-seal strength on blend composition

Manufacture of packaging film or sheet incorporating a poly(1-butene) peel-seal blend is possible by all the conventional processes such as film blowing or casting, sheet extrusion or coextrusion, extrusion or coextrusion coating, and lamination.

Poly(1-butene) peel seals are used in flexible packaging such as box liners for cereals, cake mixtures, and biscuits. In combination with more sophisticated barrier films, they are used

for processed meat and vegetable packs. They are also used for packaging medical products.

An important growth area for peelable seals is in lids for rigid or semirigid containers. These range from the relatively simple yogurt, milk, and cream pots to individual-portion containers for microwave meals.

Two features of poly(1-butene) peel seals are considered to be of particular importance to the development of the next generation of high-performance packages. The first is their resistance to high-temperature cooking or sterilization. Often referred to as "retortability", this is an increasingly important feature both in the food and nonfood sectors. Poly(1-butene) peel seals can be made heat resistant by formulation with higher-temperature-resistant materials such as polypropylene or high-density polyethylene.

The second important feature is a distinct whitening effect when the seals are opened because of the characteristic cohesive failure mechanism. This gives a clear indication that the package has been opened or tampered with.

4. Polyisobutylene

4.1. Introduction

Industrially important polyisobutylenes can be divided into five groups:

1) Di-, tri-, and tetraisobutenes
2) Low molecular mass polyisobutylenes with $\bar{M}_n = 330 – 1600$
3) Medium molecular mass polyisobutylenes with $\bar{M}_n = 20\,000 – 45\,000$
4) High molecular mass polyisobutylenes with $\bar{M}_n = 75\,000 – 600\,000$
5) Ultra high molecular mass polyisobutylenes with $\bar{M}_n > 760\,000$

History. In 1925 LEBEDEW was the first to prepare polyisobutylene [281, 282]. He obtained products of varying chain length: liquids of oily to honey-like consistency; sticky, doughy materials; or solid, rubber-like materials.

Relatively uniform low molecular mass polyisobutylenes were first obtained by the company de Bataafse [283] by polymerizing isobutene at + 10 to − 10 °C in the presence of metal halides.

High molecular mass polyisobutylenes were first prepared by OTTO and MÜLLER-CUNRADI by polymerizing isobutene below − 10 °C in presence of volatile inorganic halides [284].

Polymerization Mechanism. Even in the early studies, two important aspects of the polymerization of isobutene were recognized: (1) catalysis with initiators of the Friedel – Crafts type, and (2) the inverse dependence of the molecular mass on the temperature. Subsequent studies led to the first formulations of a reaction mechanism [285].

According to these ideas, which essentially remain valid today, the reaction consists of the following steps:

Initiation:

$$BF_3 + HX \longrightarrow H[BF_3X]$$

$$H[BF_3X] + \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}CH_2 \longrightarrow \left[CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]^+ [BF_3X]^-$$

Chain growth:

$$\left[CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]^+ + n\,CH_2{=}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}$$

$$\longrightarrow \left[CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\left[{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]_{n-1}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]^+$$

Chain termination:

$$R{-}\left[{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]^+ \longrightarrow R{-}CH{=}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} + H^+$$

$$\longrightarrow R{-}CH_2{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H^+$$
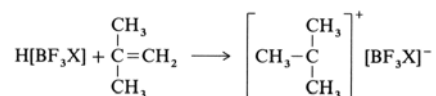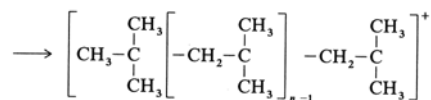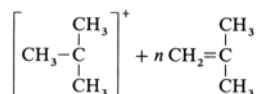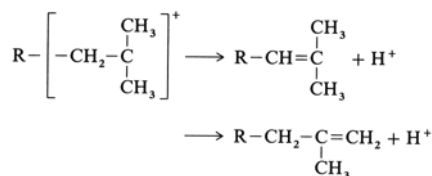
The initiator is a Lewis acid (BF_3, $AlCl_3$) in combination with a proton source, which is usually present as a trace impurity, e.g., water, hydrogen, fluoride, or hydrogen chloride.

The competition between the growth reaction and chain termination determines the chain length (i.e., the molecular mass). Since the activation energy of chain termination is higher,

increasing the polymerization temperature lowers the polymer chain length (ln $M \sim 1/T$).

Meanwhile [286], a series of studies have appeared which have revealed a considerably refined view of the course of the reaction; yet a comprehensive mechanism which is consistent with all experimental findings is still lacking. Other studies deal with new initiators (aluminum alkyls; inorganic initiators such as acid clays and molecular sieves; Ziegler catalysts; high-energy radiation as an initiator). However, none of these new catalyst systems are used industrially. Industrial processes for polyisobutylene production still use the conventional Friedel – Crafts catalysts, boron trifluoride and aluminum chloride.

4.2. Production

4.2.1. Isobutene as Raw Material

The production of isobutene is described in $\rightarrow$ Butenes, Chap. 4., $\rightarrow$ Butenes, Chap. 5.

The purity requirements for the isobutene differ according to the type of polyisobutylene produced.

For the production of low molecular mass polyisobutylenes, butadiene-free C_4 fractions can be used, which apart from isobutene contain *n*-butane, isobutane, and *n*-butenes; stricter requirements are set for the isobutene for high molecular mass and solid polyisobutylenes.

During isolation of isobutene from C_4 fractions, an isobutene must be obtained which is as free from *n*-butene as possible. Primarily the content of *cis*- and *trans*-2-butene must be minimized. Both are powerful polymerization poisons and chain terminators. On the other hand, 1-butene can be used as a regulator in the production of high molecular mass and solid polyisobutylenes.

4.2.2. Low Molecular Mass Polyisobutylenes

Figure 50 shows the layout of the Cosden Petroleum continuous process, which can be regarded as a kind of fluidized-bed process.

A liquefied refinery-gas mixture with $C_1 - C_5$ hydrocarbons and an isobutene content of 3 – 50 % is freed from pentenes in a preliminary distillation, enriched in isobutene in an absorption column, washed in a wash tower with ca. 20 % caustic soda solution to remove sulfur, cooled in a heat exchanger, dewatered in a water separator, dried in silica gel towers and, after further low-temperature cooling in a second heat exchanger, introduced into the lower part of the reaction vessel. The polymerization takes place here at temperatures between -43 and $+16\,°C$ and pressures of 0.1 – 0.35 MPa, so that the liquid phase is maintained. The catalyst used is a mushy suspension of finely divided (50 – 100 mesh) aluminum chloride in dry, liquid polyisobutylene, which is prepared in a mixing tank and supplied to the reaction vessel by a gear pump.

The quantity of aluminum chloride is about 10 – 20 % of the total hydrocarbons in the reaction mixture. The activity of the aluminum chloride is increased by adding 0.08 – 0.12 % hydrogen chloride (relative to aluminum chloride) as activator and accelerator. Water or chloroform have the same effect. The diameter of the reaction zone (A) and the feed rate of the catalyst slurry are so matched to each other that the aluminum chloride particles do not settle. Zone (B) of the reaction vessel, with a diameter two to six times that of zone (A), reduces the flow rate by a factor of about three to four, and functions as a calming zone. It merges into the settling zone (C), in which the aluminum chloride particles settle and are pumped off as a suspension through the offtake pipe which extends into zone (B). This catalyst slurry returns via a cooler into the reaction zone (A). Spent, aggregated catalyst is discharged at the bottom of the reaction zone.

A variant of the process uses separate vessels for polymerization and for catalyst settling.

From the settling zone flows a clear, light solution of liquid polyisobutylene in unreacted starting material. To improve the yield, the reaction mixture is pumped at least four times, but usually more than eight times, through the reaction zone (A). The clear polymer solution flows through the heat exchangers (g) and (d) to cool the isobutene and, after a water wash to remove acidic constituents, into a stripping column in which about one to two thirds of the inert, unreacted starting material is distilled off. After post-treatment of the concentrated polymer solution in a clay-filled tower, which may precede the stripping column, all volatile constituents of the starting material, especially unpolymerized
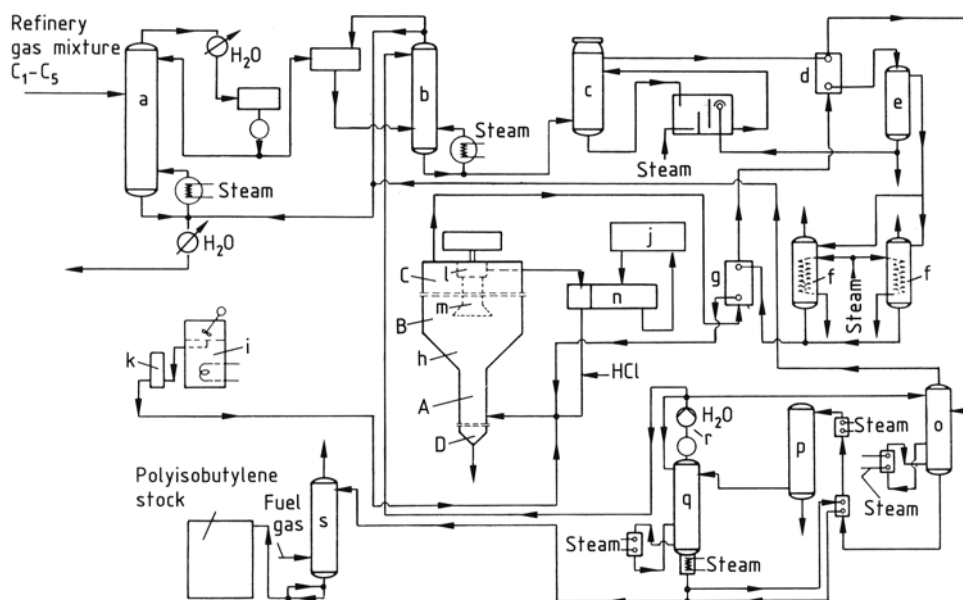
Figure 50. Cosden Petroleum process for producing low molecular mass polyisobutylene
a) Preliminary distillation; b) Absorption column; c) Caustic soda solution wash tower; d) Heat exchanger; e) Water separator; f) Silica gel towers; g) Heat exchanger; h) Reaction vessel; i) Mixing tank; j) Refrigeration unit; k) Gear pump; l) Pump; m) Offtake pipe; n) Cooler; o) Stripping column; p) Clay-filled tower; q) Distillation column; r) Water cooler; s) Pressure column; (For A to D, see text)

isobutene, are vaporized in a distillation column and returned via a water cooler into the absorption column. In a further column, the last traces of volatile constituents are distilled from the liquid polyisobutylene at atmospheric pressure.

Aside from this process of the Cosden Petroleum Corp., others have been developed. For a description of the BASF and Exxon processes, see [287, pp. 94–97], [288].

4.2.3. Medium Molecular Mass Polyisobutylenes

The basic principle of the Exxon process for producing medium molecular mass polyisobutylenes (Fig. 51) [289] resembles the process for low molecular mass polyisobutylenes. However, a purer isobutene is used as starting material and pentane or hexane is added as solvent. The polymerization temperature must be lower to obtain a higher molecular mass. A mixture prepared from fresh isobutene, recycled isobutene, and hexane with 30 % isobutene and 70 % hexane is brought via a heat exchanger and a cooler to the polymerization temperature of $-40\,°C$ and fed into the

reaction vessel. Simultaneously, a slurry of 5 % finely divided aluminum chloride in hexane at a temperature of below $-23\,°C$ flows into the reaction vessel.

The polymerization takes place with powerful stirring so that the aluminum chloride does not settle, and external cooling. The throughput is 378.5 L/h isobutene – hexane mixture and 0.454 kg/h $AlCl_3$. The resulting solution of polyisobutylene in hexane with suspended aluminum chloride is drawn off, and after it has passed through a heat exchanger an excess of dilute caustic soda solution is added to destroy the catalyst. After thorough mixing in a nozzle mixer, the mixture of polymer solution and dilute caustic soda solution runs into a settling tank, where it forms two layers. The lower layer, consisting of dilute caustic soda solution, aluminum hydroxide, and salts, is discarded. The upper layer, consisting of a solution of polymer in hexane and unreacted starting material, is fed into a degassing vessel, in which the lower boiling components, principally unreacted isobutene, are stripped off at 99 °C and 0.35 bar. n-Butenes if present are removed from the system to avoid poisoning the reaction. In a sec-
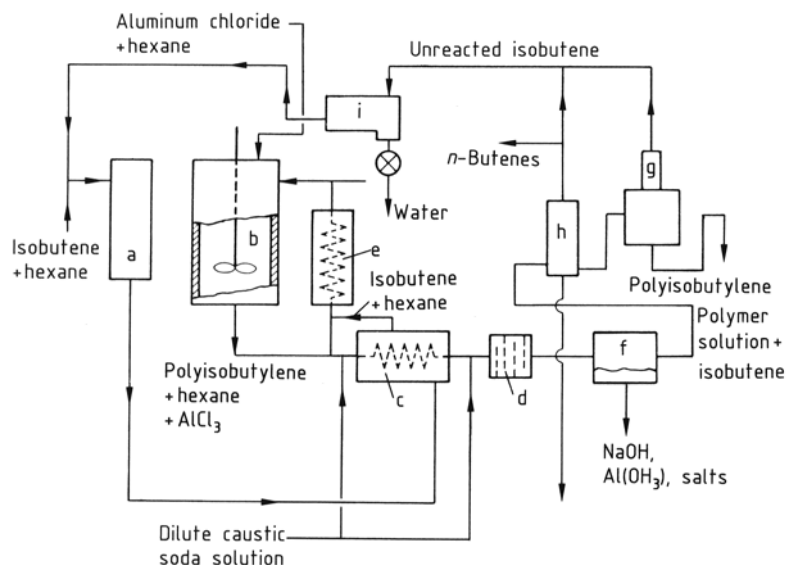
Figure 51. Exxon process for producing medium molecular mass polyisobutylenes
a) Mixing vessel; b) Reaction vessel; c) Heat exchanger; d) Nozzle mixer; e) Cooler; f) Settling tank; g) Degasser; h) Degassing vessel; i) Water separator

ond degasser, the last traces of volatile constituents are removed. The unreacted isobutene is condensed, dewatered in a water separator, and added as recycle isobutene to the starting mixture.

In its batch process for producing medium molecular mass polyisobutylenes, BASF makes use of the chain-terminating effect of diisobutene [287, pp. 88 – 91], [290].

Figure 52. BASF belt process for high molecular mass polyisobutylenes
a) Steel belt; b) Twin-screw machine; c) Cooling and compounding; d) Purification

In a conical reaction vessel with good thermal insulation, pure, dry liquid isobutene and pure, dry liquid ethylene as internal coolant are mixed in the ratio 1 : 2. The quantity of diisobutene added to the isobutene depends on the desired

molecular mass of the polyisobutylene. A sufficient quantity of gaseous boron trifluoride for the polymerization is then carefully introduced into the mixture. The mixture starts to boil, and the evaporating ethylene removes the heat of polymerization. The polyisobutylene remains behind in the reaction vessel in the form of a white foam. It is removed from the vessel and freed from all volatile constituents in a degassing machine.

4.2.4. High Molecular Mass Polyisobutylenes

BASF and Exxon have developed continuous processes for producing high molecular mass solid polyisobutylenes [287, pp. 97 – 104].

BASF Belt Process. In the belt process, the conical polymerization vessel of the BASF batch process described above is replaced by a continuous polymerization belt (Fig. 52) [291].

A gently inclined trough-shaped continuous steel belt, 16 – 18 m long and 50 cm wide, runs in a gastight housing over a drive roller and a tension roller. A mixture of pure, dry liquid ethylene and isobutene in the ratio 1 : 1 flows through a pipe onto one end of the steel belt. From a second pipe a solution of boron trifluoride in the same quantity of ethylene as is

mixed with the isobutene is added. The quantities of cocatalyst and chain-length regulator [287, pp. 82 – 91] depend on the desired molecular mass. The polymerization starts instantly. It continues at the boiling point of the liquid ethylene ($-103.7\,°C$) and in a short time is ended. The heat of polymerization is absorbed by the evaporation of ethylene. The vaporized ethylene is recycled via a purification and liquefaction system. The polyisobutylene is stripped from the steel belt with a scraper and degassed and homogenized in a twin-screw machine.

Exxon Process. Polyisobutylene is also produced by the process used for butyl rubber (see → Rubber, 3. Synthetic) [292].

4.3. Structure

The polymer obtained by cationic polymerization has the following structure:

$$\text{H}_3\text{C}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-\text{CH}_2-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-\text{CH}_2-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}- \cdots\cdots \text{CH}_2-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_2}{||}}{\text{C}}}$$

In the stretched state polyisobutylene gives a well-developed X-ray diffraction pattern which shows that 8 monomers with their 16 methyl groups are arranged in an almost regular helix around the principal axis, forming one translation period of the chain after 3 rotations [293].

It has been shown by IR spectroscopy that the principal end group is the methylene group [294].

4.4. Properties

The rubber-like polyisobutylenes, like all other polyisobutylenes, owe their physical and chemical properties to their paraffinic character. This results in a low glass transition temperature, low specific thermal conductivity, very low water vapor permeability, high dielectric strength, high resistivity, low dielectric constant, low dielectric loss factor, high ageing resistance, and rot resistance as well as an unusually wide-ranging

chemical resistance. The good solubility in hydrocarbons and chlorohydrocarbons and the insolubility in alcohols, esters, and ketones also result from the paraffinic nature of the polyisobutylenes.

At room temperature, polyisobutylenes are resistant to dilute and concentrated hydrochloric acid, sulfuric acid, phosphoric acid, chlorosulfonic acid, phenolsulfonic acid, naphthalenesulfonic acid, formic acid, acetic acid, ammonia, potassium hydroxide solution, caustic soda solution, as well as aqueous calcium hydroxide, aqueous hydrogensulfite, copper sulfate solution, potassium permanganate solution, hydrogen peroxide, chromic acid, and d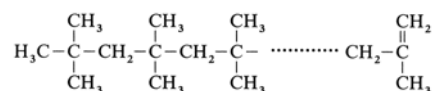ichromate solution. Above $80\,°C$, concentrated sulfuric acid causes carbonization and concentrated nitric acid causes decomposition.

Some properties of polyisobutylene that are independent of the degree of polymerization are as follows:

Density, g/cm^3	0.92
Volume coefficient of thermal expansion at $20\,°C$, K^{-1}	6.3×10^{-4}
Specific heat, kJ kg^{-1} K^{-1}	2.0
Glass transition temperature (DSC), $°C$	-60
Thermal conductivity, W K^{-1} m^{-1}	0.19
Refractive index n_{20}^{D}	1.51
Dielectric constant ε_r (50 Hz, $20\,°C$) DIN 53 483	2.2
Dielectric loss factor tan δ (50 Hz, $20\,°C$) DIN 53 483	$\leq 5\times10^{-4}$
Water vapor permeability, g m^{-1} h^{-1} mbar^{-1}	2.5×10^{-7}

Further properties are listed in Tables 24 and 25.

4.5. Uses and Processing

The low molecular mass polyisobutylenes are used as plasticizing components for modifying sealants. In addition, they are used for producing insulating oils.

After further functionalization with polar groups, the low molecular mass polyisobutylenes are used as dispersants in fuel and lubricant additives.

The medium molecular mass polyisobutylenes are chiefly used as raw materials for adhesives and sealants. Due to their very low

Table 24. Properties of polyisobutylenes dependent on degree of polymerization, exemplified by Oppanol B (BASF)

Oppanol	Viscosity, Pa · s		Intrinsic viscosity	Number-average molecular
	at 20 °C	at 100 °C	$[\eta]$, cm^3/g	mass $\bar{M}_n*$
Low molecular mass				
B 3	25	0.2 ± 0.02		820
Medium molecular mass				
B 10	5.0×10^4	2.2×10^2	27.5 – 31.2	24 000
B 12			34.0 – 39.1	30 000
B 15	5.0×10^5	3.0×10^3	45.9 – 51.6	40 000
High molecular mass				
B 50	1.5×10^8	8.0×10^5	113 – 143	120 000
B 80			178 – 236	180 000
B 100	3.6×10^8	6.7×10^7	241 – 294	250 000
B 120			295 – 361	300 000
B 150			416 – 479	425 000
B 200	1.5×10^{11}	1.0×10^9	551 – 661	600 000
Ultra high molecular mass				
B 246			> 770	> 760 000

$\bar{M}_n = {}^{0.94} \sqrt{\frac{[\eta] \cdot 10^3}{2.27}}.$

water-vapor permeability, permanently flexible sealants based on polyisobutylene – carbon black are important in the production of sealed double glazing units. Combinations of polyisobutylene with paraffin or wax are used for impregnating paper and board.

The breaking point of bitumen is lowered and its flexibility improved by addition of medium molecular mass polyisobutylene.

High molecular mass polyisobutylenes are used as blends with medium molecular mass grades for producing self-adhesive compounds, e.g., for adhesive plasters.

Because of their good tolerance by the skin, filled polyisobutylenes are used to produce sealing rings for colostomy bags.

Unstabilized polyisobutylenes are used in chewing gum bases.

Blending polyisobutylenes with paraffin oil and inorganic fillers gives permanently elastic sealants, which are usually marketed in extruded form as strip or round-profile string.

High molecular mass polyisobutylenes with high filler contents are used to produce sheets that are used for sealing buildings against groundwater and seeping water as well as for protection against corrosion and radiation. Conductive and magnetic polyisobutylene sheetings are also available.

Table 25. Behavior of Oppanol B100 and B200 towards solvents (weight increase by swelling in wt % at room temperature)

Storage time	3 1/2 days		30 days	
Oppanol type	100	200	100	200
Acetone	1.7	1.5	3.9	3.6
Alcohol	0.1	< 0.1	0.35	0.2
Benzene	400	400	500	500
Butyl acetate	34	24	34	37
Carbon tetrachloride			soluble	
Chlorobenzene			soluble	
Chloroform			soluble	
Cyclohexane			soluble	
Cyclohexanone	9	7.4	24	18
Dimethylformamide	0.6	0.6	2.1	1.7
Ether	200	100		
Ethyl acetate	18	12	21	20
Ethylene glycol	0.6	1.4	0.9	2.0
Gasoline			soluble	
Glycerol	0.6	0.6	1.0	1.6
Hydrogen sulfide			soluble	
Isobutanol	1	0.3	2.4	0.7
Isooctane			soluble	
Methanol	< 0.1	< 0.1	0.1	0.1
Methyl acetate	8	5	7.8	10
Methylene chloride	200	200	200	200
Mineral oil			soluble	
Nitrobenzene	3	2	5.4	4.5
Olive oil	4	1.5	4.2	3.1
Paraffin			soluble	
Paraffin oil			soluble	
Tetrahydrofuran			soluble	
Toluene			soluble	
Water	< 0.1	< 0.1	0.1	0.1
Xylene			soluble	

The cold impact resistance of polypropylene is improved by blending with polyisobutylene. The sensitivity of polyethylene to environmental

stress cracking is reduced by adding polyisobutylene.

Polyisobutylenes are compatible with natural and synthetic rubber and with reclaimed rubber.

Solutions of ultra high molecular mass polyisobutylenes ($\bar{M}_n > 760\,000$) in organic solvents even in low concentrations ($\ll 1\,\%$), have pronounced viscoelastic properties and distinctly increased extensional viscosity.

Polyisobutylene can be compounded on a roll mill or in an internal mixer. Compounding is carried out at $140 - 170\,°C$ to minimize thermal degradation of the polyisobutylene.

4.6. Commercial Products

BASF, Germany:	Oppanol B 3 (liquid); Oppanol B 10, B 12, B 15 (flexible resin-like, tacky); Oppanol B 50, B 80, B 100, B 120, B 150, B 200, B 246 (solid, rubber-like)
Exxon, United States:	Vistanex LM-MS, LM-MH (flexible resin-like, tacky); Vistanex MM L-80, MM L-100, MM L-120, MM L-140 (solid, rubber-like)

In addition, a range of low molecular mass polyisobutylenes are marketed.

4.7. Copolymers [295]

Isobutene – isoprene – divinylbenzene terpolymers are produced under conditions similar to those used for butyl rubber, with the addition of divinylbenzene. Unlike butyl rubber, they exhibit no cold flow.

Isobutene – styrene copolymers behave similarly to polyisobutylenes or butyl rubber.

The copolymers have no economic significance.

5. Poly(4-Methyl-1-Pentene)

As described for polypropylene in Chapter 2, Ziegler – Natta stereospecific catalysts discovered in 1954/1955 polymerize α-olefins to crystalline products. Foremost of these are polypropylene and, to a lesser extent, poly(1-butene), but higher α-olefins also yield crystalline products having helical chains in the crystallites [296–298]. Much laboratory work

on $C_5 - C_{18}$ olefins centers on polymerization mechanisms and the interesting crystallization behavior of homopolymers and copolymers, but only poly(4-methyl-1-pentene), PMP, based resins have reached commercial production status. Their excellent optical clarity combined with a high melting point, reasonable toughness, and general inertness has led to use in demanding applications where the much higher raw material cost is a secondary consideration. Operating temperatures for PMP in service can be as high as $200\,°C$ for short times, after which thermal oxidation is likely to start. For this reason and because of impact strength limitations, the potential advan-tages of even higher melting poly(α-olefins) cannot be realized in practice. Engineering resins such as polyimides, polysulfones, and polysulfides must be used for sustained high-temperature operations and extra toughness.

4-Methyl-1-pentene monomer can be polymerized with cationic and Ziegler – Natta catalysts. The former cause some isomerization and yield irregular chains, giving amorphous viscous liquids or rubber-like solid products of little commercial interest [299, 300].

In 1965 ICI made several grades of PMP, under the trade name TPX, in its semitechnical plant at Welwyn Garden City for distribution and in-depth evaluation [301]. Manufacture on its Wilton production site started in June 1968 on a 2000 t/a plant producing transparent and opaque grades. In 1973 the process was sold to Mitsui Petrochemical Industries, which became the sole manufacturer on its plant at Iwakuni-Ohtake works in Japan. Capacity was increased from 2000 t/a to 3000 t/a in 1982, and then to 6000 t/a in 1983. In 1989, Phillips 66 in Bartlesville, United States, started supplying development quantities from a 250 t/a pilot plant in the United States under the trade name Crystalor.

5.1. Raw Materials

5.1.1. Monomers

Several monomers are used in TPX production to overcome the deficiencies of haze and brittleness in pure homopolymers of 4-methyl-1-pentene. The restricted availability of these monomers in commercial quantities in the early

1960s proved troublesome for ICI's development program.

Polar and highly unsaturated contaminants retard polymerizations with Ziegler – Natta catalysts. Handling precautions must recognize flammability hazards and facile peroxidation of these liquid monomers on exposure to air. At high concentrations they exert a narcotic effect.

4-Methyl-1-pentene (4MP) is prepared by selectively dimerizing propene at ca. 150 °C and 10 MPa with supported alkali metals, particularly potassium. British Petroleum first established a commercial process in 1967, followed by further patents to Chevron and Idemitsu (Table 26). All these processes yield a liquid fraction containing ca. 80 % of 4MP. Separation of pure 4MP from the C_6 fraction requires superfractionation with a 100-plate column.

Apart from being the main feedstock for PMP manufacture, 4MP is now used as comonomer in certain grades of linear low-density polyethylene. However, 4MP is not traded commercially, and there is no quoted price. The name plate capacity of Mitsui Petrochemical Industries plant for 4MP is 13 000 t/a.

A typical analysis (wt %) of 4MP monomer used by ICI to make TPX is as follows:

4-Methyl-1-pentene	97.4
Lighter than C_6	0.1
cis-4-Methyl-2-pentene	0.9
trans-4-Methyl-2-pentene	1.5
1-Hexene	0.1

Some physical properties of 4MP [306, 307], relevant to its polymerization are:

bp, °C	53.86
mp, °C	− 153.64
Density at 20 °C, g/cm³	0.6637
Vapor pressure at 20 °C, kPa	29.47
Vapor pressure at 50 °C, kPa	89.34
Refractive index n_D^{20}	1.38267
Heat capacity of liquid at 25 °C, $J g^{-1} K^{-1}$	2.191
Heat of vaporization at *bp*, J/g	0.3221
Flash point, °C	− 7.0
Autoignition temperature, °C	300

Linear C_6 – C_{12} α-Olefins. Most commercial grades of PMP contain small amounts of higher α-olefins as comonomer to modify the main chain. Usually, the even carbon number olefins are made by oligomerizing ethylene with triethylaluminum or soluble nickel complexes.

Commercial quantities of these pure olefins up to C_{18} are priced at about £1/kg. Table 27 lists some of their physical properties, together with those of useful branched comonomers.

5.1.2. High-Melting Nucleating Polymers

It is reported [308, 309] that < 1 % of well dispersed high-melting polymers from branched α-olefins nucleate PMP crystallization to enhance transparency. Isotactic polymers of 3-methyl-1-butene, 3-methyl-1-pentene, and 4,4-dimethyl-1-pentene are preferred. These branched monomers are much more expensive than linear α-olefins because they arise only as minor byproducts from refining and cracking operations, or by special synthesis. For example, 3-methyl-1-butene can be prepared by dehydrating isoamyl alcohol. The same isospecific catalysts used to polymerize 4MP are also suitable for making these branched olefin polymers (see Section 5.2). Preferably these high-melting polymers are prepared as a stage of the PMP polymerization process, rather than as separate additives.

5.1.3. Catalysts

Most Ziegler – Natta catalysts suitable for polypropylene polymerize and copolymerize 4MP to give linear head-to-tail polymers. The reactivity of the higher α-olefins is appreciably lower than that of propene under comparable conditions. Copolymerization data compiled by KISSIN [310, 311] illustrate how branching and chain length impede reaction with titanium-based catalysts (Table 28). Steric hindrance by bulky groups in the 3-position, adjacent to the double bond, is particularly pronounced (3-methyl-1-butene and 3-methyl-1-pentene). 4-Methyl-1-pentene is several times less active than propene, as are all the higher linear α-olefins. Low overall reaction rates arise when some of the active sites on certain catalysts are inaccessible to bulky monomers [311].

It is necessary to use highly isospecific catalysts to achieve good yields of crystalline polymer without much atactic byproduct. Preferred systems use combinations of $TiCl_3$ with $Al(C_2H_5)_2Cl$ as activator [312], or possibly

Table 26. Dimerization of propene to 4-methyl-1-pentene [298]

Company	Process	Catalyst	Temperature, °C	Pressure, MPa	Yield *, % 4MP	Patent priority
British Petroleum [302]	rocking bed	K on graphite	160	11	85	12.12.62
British Petroleum [303]	fixed bed	Na on K_2CO_3	160	12	75	8.8.63
Chevron [304]	slurry	K on $MgSiO_3$	150	5	80	17.5.66
Idemitsu [305]	slurry	K/Cu/*tert*-amine	180	7	90	13.4.76

* In liquid fraction.

Table 27. Physical properties of some comonomers * [306]

Comonomer	*bp*, °C	*mp*, °C	Density at 20 °C, g/cm^3	*mp* of isotactic homopolymer, °C	
1-Pentene	29.96	− 165.22	0.6405	75 – 80	
3-Methyl-1-butene	20.05	− 168.49	0.6272	310	
1-Hexene	63.48	− 139.83	0.6732	amorphous at 20 °C	
3-Methyl-1-pentene	54.17	− 153.0	0.6674		> 350
4-Methyl-1-pentene	53.86	− 153.64	0.6637	235 – 250	
4,4-Dimethyl-1-pentene	72		0.6827		> 380
1-Octene	121.29	− 101.72	0.7149	34	
1-Decene	170.60	− 66.28	0.7408	45	
1-Dodecene	213.30	− 33.60	0.7583	60	

* Data for 4-methyl-1-pentene included for comparison.

the newer supported catalyst systems such as $TiCl_4 – MgCl_2 – Al(C_2H_5)_3$ with an appropriate Lewis base [313]. Catalysts made directly from $TiCl_4$ and organoaluminum compounds only yield 60 % of crystalline polymer, and even violet $TiCl_3$ activated with aluminum trialkyls produces some 20 % of solubles. These trialkylaluminum – titanium halide systems also cause some isomerization of 4MP, but this is completely avoided with $TiCl_3 – AlEt_2Cl$. The original ICI process used a coarse, preformed spherical $TiCl_3$ made by controlled reduction of $TiCl_4$ with alkyl aluminum chlorides. Experiments showed that it was important to secure a very mobile slurry to permit thorough catalyst extraction for the highest polymer transparency.

Table 28. Relative copolymerization activities r_2 of higher α-olefins relative to propene [310]

Monomer	r_2 *
Ethylene	8 – 20
Propene	1
1-Pentene	0.2 – 0.5
1-Hexene	0.2 – 0.4
1-Decene	0.1 – 0.3
1-Octadecene	0.1 – 0.15
3-Methyl-1-butene	0.02 – 0.06
3-Methyl-1-pentene	0.05
4-Methyl-1-pentene	0.15

* Ratio of propagation rates, $r_2 = k_2^2/k_2^1$.

5.2. Industrial Manufacture

Published information on the production of TPX is very limited apart from the disclosures of ICI. Details which follow relate to their early slurry process, but some improvements have been introduced by Mitsui Petrochemical Industries as their manufacturing capacity expanded from 2000 to 6000 t/a.

Semibatch polymerizations used a conventional water-jacketed stirred reactor containing inert aliphatic hydrocarbon diluent, $AlEt_2Cl$, and particle-form purple $TiCl_3$ catalyst. A nucleating polymer of a high-melting polyolefin can be formed on this catalyst either prior to its introduction into the reactor, or at the end of the main polymerization stage [301]. Overall reaction cycles are shortened when the catalyst is first subjected to prepolymerization as a concentrated slurry in a separate reactor to generate the high-melting polymer. This procedure yields a supply of treated catalyst ready for use in the main reactor without delays caused by the low-activity monomer. Sometimes this simple technique yields prepolymer which is poorly dispersed. The problem is reportedly overcome [309] by first polymerizing a small amount of 4MP on the catalyst before adding monomer

to generate nucleating polymer. An even simpler procedure apparently works: If a mixture of 4MP and the preferred monomer for nucleation is used for prepolymerization, 4MP is consumed first because of its higher reactivity, leaving the virtually pure second monomer free to polymerize on the expanded catalyst particles. Less than 1 % of this additive is needed.

Following the addition of (prepolymerized) catalyst to the main reactor, an initial charge of 4MP and comonomer establishes both the required composition and the polymerization rate, which is first order with respect to catalyst and monomer. As polymerization proceeds at ca. 60 °C, continuous injection of monomers maintains the reaction conditions until the prescribed amount of polymer has formed. This reaction lasts a few hours, during which small injections of hydrogen control molecular mass, as in polypropylene manufacture. Termination of monomer feeds, followed by a short run-down period ensures that most of the monomer is consumed before deashing starts.

All catalyst components are solubilized by adding a $C_3 - C_6$ alcohol to the slurry in a second heated vessel. Centrifuging, followed by several stages of washing with alcohol–diluent mixtures extracts catalyst residues and soluble polymer. Importantly, addition of water, used in some polypropylene deashing processes, results in lower transparency of molded articles. Ash levels below 0.01 %, and < 10 ppm of Al and Ti are readily achieved. All filtrates are recycled after separation by fractional distillation.

Conventional hot-nitrogen driers remove diluent from the centrifuged cake. After addition of stabilizers, the dry powder is densified at 270 – 300 °C in an extruder with a length/diameter ratio of about 30/1. Various grades differ in comonomer content, molecular mass, and additive formulation (e.g., reinforcement with glass fibers, mica, and mineral fillers).

A Mitsui patent [314] describes techniques for making broad MMD (co)polymers from 4MP using $MgCl_2$ supported catalysts in a two-stage polymerization system. This can be either conventional diluent-based slurry for each stage, or slurry for the first stage followed by a fluidized-bed reactor operating at 100 °C and 0.2 MPa absolute pressure.

In 1989, Phillips Petroleum commissioned a 250 t/a integrated pilot plant at Bartlesville, United States, making 4MP monomer to convert into PMP for evaluation and sale. This plant operates a slurry process using a conventional semibatch stirred reactor.

Patents to BASF [315,316] describe bulk polymerization of 4MP at 90 – 150 °C under inert gas pressures up to 2 MPa to increase the yield. Catalysts used were $TiCl_3 \cdot AlCl_3$/tributyl phosphine/$AlEt_2Cl$. Hot-heptane solubles of ca. 30 % were, however, high, and no process has yet been announced.

Institut Français du Petrole's intriguing isomerization – polymerization of potentially cheap 4-methyl-2-pentene to PMP, using $TiCl_3$, nickel acetylacetonate, and $AlEt_2Cl$, has not been commercialized [317,318].

5.3. Polymer Structure

5.3.1. Homopolymer

PMP polymer, made with highly isospecific catalysts, has the following regular head-to-tail structure in which all isobutyl groups lie on one side of the chain in a two dimensional Fischer projection.
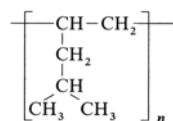
NMR spectroscopy, so useful in polypropylene and ethylene – propene copolymer characterization, is of limited use for higher poly (α-olefins) where overlapping resonances of the main-chain atoms and pendant groups severely impair resolution and interpretation [319]. Deductions concerning polymer stereoregularity largely rely on crystallinity related phenomena, such as X-ray and IR spectra, melting behavior, solvent fractionation, and various physical properties.

Stereoregular poly(α-olefin) chains pack together to form high-melting crystallites, which then assemble into a superstructure of radially symmetric spherulites during crystallization from a melt phase. In unbranched polyethylene, the chains adopt a zig-zag arrangement in the crystal. The methyl side group

in polypropylene forces the chain to adopt a helical configuration involving three monomer units per turn (3/1 helix). With still larger branches the helix unwinds to 4/1. In the case of PMP, the bulky isobutyl group is accommodated in a 7/2 helix with 3.5 monomer units in each turn, and four chains per unit cell of 28 monomer units. Unit cell parameters are $a = b = 1.86$ nm and c (chain axis) = 1.38 nm [320]. This gives an exceptionally low calculated crystal density of 0.822 ± 0.006 g/cm^3, largely because of the loose space packing of helices. At room temperature, the amorphous phase in this semicrystalline polymer has the higher density of 0.838 g/cm^3 [320, 321]. In a typical molding, the average polymer density of PMP is ca. 0.83 g/cm^3. Such a unique reversal of crystalline and amorphous polymer densities has some interesting implications for molding operations. At 60 °C, a common mold temperature, the densities of the two phases are judged to be equal, i.e., there would be no volume change for crystallization at this temperature.

Crystalline PMP finally melts at about 250 ± 5 °C (slow heating) and has a glass transition temperature T_g of 50–60 °C at 100 Hz [312] (18–30 °C by dilatometry [321]). Other transitions have been reported [322]: 130 °C (start of crystal disordering) and at −120 °C to −150 °C (relaxation of short chain segments). Crystallization from the melt does not require massive supercooling. Isothermal crystallization half time at 220 °C is 0.5 min, increasing to 480 min at 236 °C. As with polypropylene, PMP is properly viewed as a semicrystalline polymer, achieving a crystallinity of ca. 75 % in fully annealed samples, 40 % in quenched moldings, and 55–65 % in normally fabricated articles [323]. The only stable crystallite formed from polymer melts is tetragonal, but up to five polymorphs can be obtained by crystallization from solution [324].

5.3.2. Copolymers

Random copolymers of 4MP, with ca. 2–8 wt % of C_6–C_{12} linear α-olefins, are important commercially because of their good transparency and robust processing behavior.

All linear α-olefins copolymerize with 4MP to some degree. Products are complex, with a single copolymer preparation yielding chains with a wide range of compositions and degree of block structure. The more active comonomers, such as ethylene and propene, produce a dispersed phase of slightly modified PE or PP, even when only 5 mol % of the comonomer is fed [325]. The amount of this phase increases as more comonomer is used, thereby further reducing transparency through light scattering. 1-Hexene and a few other comonomers behave differently in that they are able to substitute for 4MP units in the crystal without significantly distorting or altering the crystal structure of PMP; nor do they generate a second dispersed phase [326]. In these cases, the physical properties still resemble those of PMP at low comonomer contents. Small decreases in crystallinity and melting point are measurable but they are less severe than with noncocrystallizing monomers. 1-Pentene copolymers also readily cocrystallize, causing some slight lattice contraction. Only small proportions of 1-butene can be accommodated within the lattice.

Increasing the monomer chain length to octene, decene, and above makes cocrystallization increasingly difficult. However, small amounts of 1-octene and 1-decene are accommodated within the lattice by expansion, but octadecene is far too large. The latter monomer severely reduces crystallinity and forces the copolymer into amorphous regions. The magnitude of these crystal changes is detailed in [326]. α-Axis spacing in cocrystallized copolymers can expand from 1.86 to 1.91 nm with octene, and shrink to 1.81 nm with 1-pentene copolymers.

Glass transition temperature is favorably reduced by 15–20 °C in 5 mol % 1-decene copolymers. This in itself is only sufficient to give a small toughness improvement because of the high T_g of PMP homopolymer. Copolymerization usually lowers the modulus.

5.4. Properties of PMP Products

5.4.1. Optical Properties

Crystalline PMP polymers exhibit unusually high optical transparency, both in terms of clarity (narrow-angle scatter) and haze (high-angle

scatter). Optical transmittancies of commercial resins are in the region of 90 – 95 %, compared with 88 – 92 % for polystyrene and 90 – 92 % for acrylics. Other, more familiar crystalline polyolefins, such as polyethylene and polypropylene, are at best translucent in thin sections. In these cases light is scattered from spherulitic assemblies of crystalline and amorphous regions that have different optical refractivities. Additionally, the crystallites themselves are anisotropic.

With spherulitic PMP, high transparency is favored by the similar densities of the crystalline and amorphous regions, and by the low optical anisotropy of helical chains in the spherulites. Providing polymers have been thoroughly deashed, homopolymer optical transmittances of 80 – 85 % can be realized in quenched, 3 mm thick moldings, and > 90 % in 1.5 mm thick samples. Plaques cooled more slowly develop considerable haze and lower transparency (20 %) as a result of increased interspherulitic voiding. These voids, about 1 µm in diameter, cluster round the boundaries of spherulites in the form of "shells" which are responsible for haze [327]. Quenched moldings have fewer microvoids because crystallization takes place at lower temperatures. This lowers the volume reduction on crystallization as the densities of amorphous and crystalline phases become more similar. At this lower temperature, the stronger melt is more able to resist shrinkage stresses without forming voids.

Copolymers of the type described in Section 5.3.2 have improved transparencies because of such reduced voiding. With these products the crystallization temperature is reduced by 10 – 30 °C, depending on composition, giving improved transparency in both quenched and slowly cooled moldings. With 11 wt % 1-octene copolymer, the transmittance increases to 91 % and 85 % in 3 mm thick quenched and slowly cooled moldings, respectively. This improvement with copolymers is useful, even with 5 wt % comonomer, because high transparency then becomes less dependent on maintaining very precise molding conditions. It is interesting to note that spherulite size is largely unaffected by copolymerization, or by quenching a molding [328], except in the thin surface skin.

The final, but major improvement to optical transparency comes from introducing properly dispersed nucleating agents into homo- or copolymers to reduce the size of spherulites from 50 µm to < 5 µm. In quenched, nucleated homopolymers optical transmission reaches 96 %, which only falls to about 88 % with slower cooling (Tables 29 and 30). Copolymers, already quite transparent when quenched, now achieve transmittancies around 96 % in slow-cooled moldings after nucleation (Table 30). The combination of nucleation, rapid cooling, and copolymerization virtually eliminates microvoiding in most moldings.

Table 29. Optical transmission of PMP homopolymer with poly(4,4-dimethyl-1-pentene) nucleant [309]

Spherulite size, µm			Transmission of
Max.	Mean	Min.	quenched moldings, %
100	50	< 1	69
15	10	< 1	86
< 1	< 1	< 1	96

Excellent light transmission in the near UV region makes PMP superior to glass and other transparent plastics in this respect, and inferior only to quartz (Figure 53).
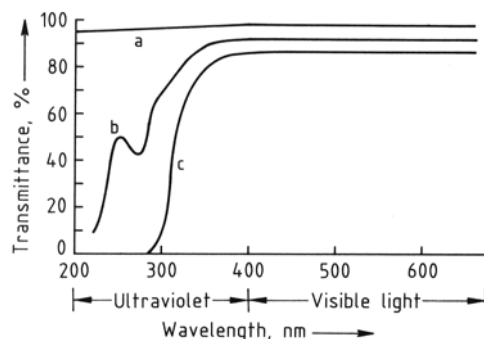
Figure 53. Light transmission [329]
a) Quartz; b) Poly(4-methyl-1-pentene); c) Glass

5.4.2. Stability and Chemical Resistance

The semicrystalline and saturated hydrocarbon nature of PMP confer excellent resistance to polar solvents and inorganic substances, and to strong aqueous solutions of most mineral acids, alkalies, and salts. Vulnerable tertiary C – H bonds make PMP unsuitable for use in highly oxidizing environments, such as chromic acid, concentrated nitric acid, and chlorine. It is permeable to some light hydrocarbons, aromatic

Table 30. Copolymer nucleation [a] with poly(3-methyl-1-pentene) [309]

Comonomer	Optical transmission, %			
	Quenched moldings		Slow-cooled moldings	
	No nucleant	Nucleated	No nucleant	Nucleated
1-Pentene [b], 2 wt %	84	97	40	94
1-Hexene [b], 2 wt %	84	97	40	94
1-Octene [b], 2 wt %	84	97	40	94
1-Decene [b], 2 wt %	84	97	40	94
None	84	95	20	88
1-Hexene, 2 wt %	84	97	40	94
1-Hexene, 5 wt %	87	98	72	96

[a] Nucleated samples all had mean spherulite diameters $< 2\,\mu m$, while unnucleated samples had mean spherulite diameters $> 25\,\mu m$.
[b] Optical transmission similar for all four comonomers.

liquids, and halogenated solvents, which cause swelling and some loss of strength. Repeated sterilization with superheated steam at $135\,°C$ over 60 cycles causes only minor reductions in mechanical properties [330]. Accordingly, PMP is especially suited to medical uses. None of the alternative transparent polymers (polystyrene, acrylics, polycarbonate, and polyester) can offer PMP's broad range of resistance at room and elevated ($60\,°C$) temperature. Resistance to detergent stress cracking, while better than other transparent polymers, is not quite up to the standard of the best bottle-blowing grades of polyethylene.

Above $100\,°C$, several aromatic and aliphatic solvents will effect complete dissolution. Stable gels containing $0.5 - 2\,mm$ diameter spherulites form on rapidly quenching cyclohexane solutions containing $150\,g/L$ of PMP [331]. Decalin at $135\,°C$ is suitable for conventional molecular mass measurements by viscometry according to the Mark–Houwink equation [332] $[\eta] = 1.94 \times 10^{-4} M_v^{0.81}$.

Thermal Degradation. Processing temperatures of ca. $300\,°C$ are necessary for the majority of PMP grades. Even under high vacuum these severe conditions promote degradation as evidenced by a marked decrease in molecular mass and gas evolution [333], principally isobutene (55 %) and propane (35 %). Carbon-carbon bond cleavage occurs in chain reactions in which hydrogen is abstracted from tertiary C–H bonds. The initial high rate seems to stem from a few weak links, possibly resulting from adventitious oxidation. Degradation subsequently continues at a lower rate. Suitable melt stabiliz-

ers incorporated by manufacturers severely retard much, but not all degradation.

Thermo-oxidation. Oxygen greatly accelerates the rate of chain scission over heat alone [334–336]. Precautions must be taken not only at high melt processing temperatures, but also in the solid state. Oxidation is accompanied by molecular mass reduction along with hydroxyl and carbonyl formation in the polymer, leading to yellow discoloration, brittleness, and odor at long exposures. Low molecular mass volatiles such as aldehydes, ketones, acids, water, and carbon dioxide form in chain reactions involving peroxidation of tertiary C–H bonds and radical-induced chain cleavage. The well-established faster oxidation of PMP compared to PP is attributed to the more rapid diffusion of oxygen in the open PMP structure. Studies indicate [335] that oxygen also attacks PMP crystallites, and not just the amorphous phase, as in PP.

Stabilizers derived from bulky hindered phenols and polyphenols, phosphites, and thioesters provide reasonable protection against deterioration during processing and in service at elevated temperature. The useful life with ca. $0.2 - 0.5\,\%$ of these additives increases from around one day at $200\,°C$ to seven years at $100\,°C$ [337]. Manufacturers advise on the most suitable polymer grade and further appropriate antioxidants for demanding applications.

Photo-oxidation. Photodegradation of PMP is basically similar to thermal oxidation, but UV light of wavelength $< 400\,nm$ seriously accelerates decomposition because chromophores, perhaps from impurities or oxygen charge-transfer complexes, assist oxidation by peroxide inter-

mediates. Chain decomposition then yields an array of oxidized products and lowers the molecular mass [338–340]. These reactions can be minimized by incorporating into the polymer specific stabilizers to deactivate excited chromophores, scavenge radicals, and reduce peroxides. Hindered amine light stabilizers (HALS), which behave as UV-stable antioxidants, and metal chelates are quite effective [340]. However, the latter can cause mild blue-green discoloration.

Enhanced oxygen diffusion in PMP is cited as a principal reason for its greater susceptability to photodecomposition than PP. Applications involving extended outdoor weathering need careful appraisal, even with UV-stabilized grades, unless there is heavy protection by pigment screening with carbon black, ferric oxide, rutile, etc. Light reaching earth is screened of wavelengths < 290 nm by the atmosphere.

Suitably formulated PMP is also able to withstand up to 50 kGy of high energy β- and γ-radiation, used for sterilization, without discoloration or embrittlement [341]. Irradiation at higher doses (3 MGy) causes cross-linking and generation of volatiles [342], whereas chain scission is the dominant reaction with PP except at high doses.

5.4.3. Mechanical Properties

PMP has mechanical properties reasonably similar to those of PP at 0 – 100 °C. This applies to flexural modulus, yield strength, and hardness, though the precise comparison is dependent on the chosen grade (Table 31). Copolymers are more flexible with lower yield strengths and softening points. Melting and crystallization curves of two commercial copolymer grades, provided by Mitsui Petrochemical Industries (Figs. 54 and 55) illustrate some differences. Figure 54 shows DSC (differential scanning calorimetry) exotherms and endotherms for a lightly copolymerized PMP. While the final melting is at 242 °C, with a peak melting rate at 233 °C, the onset of melting is clearly visible at 200 °C. The second copolymer (Figure 55) is much less crystalline (melting peak areas 28.2 and 37.2 J/g respectively), with a slightly lower final melting point of 231 °C and a peak at 226 °C. This reduction in crystallinity is responsible for lowering

modulus, heat deflection temperature, and surface hardness. A presumed lowering of the glass transition temperature accounts for the increased unnotched impact strength of MX004, although this is still inade-quate to raise notched impact strengths at room temperature.
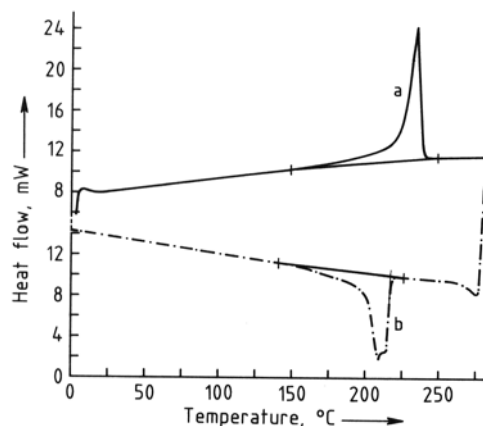
Figure 54. DSC traces for TPX, RT 8XB [343]
a) Melting endotherm; b) Crystallization exotherm

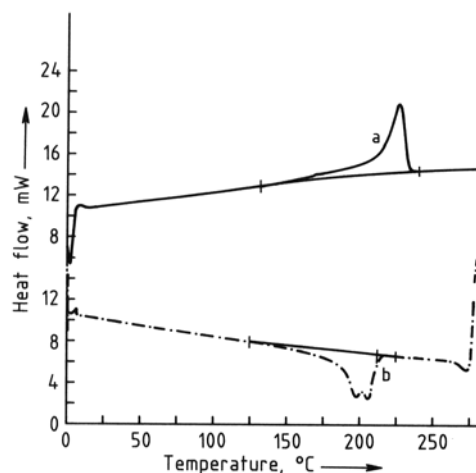**Figure 55.** DSC traces for TPX, MX004 (food grade) [343]
a) Melting endotherm; b) Crystallization exotherm

Carefully molded PMP articles are less brittle than transparent polystyrene and acrylics, and they are nearly as tough as polypropylene homopolymer. The latter usually fails with some yielding in unnotched Izod tests at room temperature, thereby giving high failure energies.

Table 31. Mechanical properties of PMP [a]

| Property | Method | Poly(4-methyl-1-pentene) | | | | | Polypropylene | |
| | | Crystalor | | TPX | | Crystalor, TPX | Propathene | |
		HBC-020 (homopolymer)	CBN-020 (copolymer)	RT18 (copolymer)	MX004 (copolymer)	30 % glass fiber filled	GWM 22 (homopolymer)	GWM 101 (copolymer)
Density (20 °C), g/cm³	ASTM D 1505	0.835	0.835	0.833	0.834	1.04	0.905	0.905
Melt flow index (MFI) at 260 °C, 5 kg, g/10 min	ASTM D 1238	20	20	26	26		4.0[b]	6.0[b]
Melting point, °C	Manufacturers	240	235	240	240	230 – 240	170	165 – 170
Vicat softening point, °C	ASTM D 1525	188	175	173	160		154	147
Heat deflection temperature, °C	ASTM D 648							
0.46 MPa load		90	85	90	85	227	100	95
1.80 MPa load		54	49		40	189	65	60
Tensile yield strength, MPa	ASTM D 638 5 mm/min	32.4	27.6	23.0	19.6	59 – 67	34.5	27
Flexural modulus, GPa	ASTM D 790	1.92	1.24	1.27	0.74	5.5 – 5.9	1.5	1.15
Izod unnotched impact strength, kJ/m²	ASTM D 256	12	19	15	49	22	60	tough
Charpy notched impact strength, kJ/m²	ASTM D 256	5	5	5	4	8	4.5	9.5
Hardness (Rockwell)	ASTM D 785	90	85	85	60	107	95	90

[a] Taken from manufacturer's literature of Phillips 66, Mitsui Petrochemical Industries, and ICI.
[b] Measured at 230 °C, 2.16 kg.

PMP's higher T_g causes failure in a brittle mode unless it is sufficiently modified by copolymerization. Above 150 °C, PMP has greater strength and form stability than PP and polycarbonate as a result of its high melting point. At 20 °C PMP creeps less in long-term tests than either polypropylene or high-density polyethylene.

Polymers filled with glass fiber and mineral additives are available from Mitsui, Phillips, and Schulman in Belgium. Composites with 30 % glass fiber are particularly useful due to their enhanced modulus and greater form stability at 200 – 250 °C. With 30 wt % glass fiber, room temperature modulus is triple that of PMP homopolymer, while the heat deflection temperature increases from 90 °C to 227 °C (Table 31).

Table 32. General properties of PMP products

	PMP	PP
Coefficient of linear expansion, K^{-1}	1.17×10^{-4}	1.1×10^{-4}
Thermal conductivity, $W m^{-1} K^{-1}$	0.168	0.209
Specific heat (20 °C), $J g^{-1} K^{-1}$	1.97	1.93
Heat of melting[a], J/g	143[b]	185
Burning rate, cm/min	2.54	2.3
Mold shrinkage, %	1.5–3.0	1–2
Refractive index, n_D^{20}	1.463–1.470	1.503
Volume resistivity, $\Omega \cdot cm$	$> 10^{16}$	$> 10^{16}$
Dielectric breakdown voltage, kV/mm	42–65	75
Permittivity at 100 Hz–1 MHz	2.1	2.25
Dielectric loss factor $\tan \delta$ (20 °C) 50 Hz 10^{-6}	60	150
1 kHz 10^{-6}	35–140	200
1 MHz 10^{-6}	25–50	150

[a] For 100 % crystalline polymer. [b] Mitsui value; for other measurements see [320, 323, 344].

5.4.4. Electrical Properties

The excellent electrical insulation properties of PMP (Table 32) are similar to those of PTFE and the best cable-grade polyethylene, whilst in the frequency range of 10 kHz to 20 MHz PMP is superior. Its permittivity (dielectric constant) is the smallest of all synthetic plastics, and it remains essentially constant over wide temperature and frequency ranges. A combination of low dielectric loss factor and good form stability at high temperature makes it very suitable for microwave oven applications. Due to its negligible moisture absorption, PMP preserves these electrical characteristics under adverse conditions.

5.4.5. Surface Properties and Permeability

PMP's surface tension of only 24 mN/m is the second lowest to PTFE (20 mN/m) [345]. This confers good stain resistance and excellent release properties towards other materials.

Confirmation of PMP's loose space packing is to be found in its high permeability towards gases (Table 33). Oxygen, nitrogen, and carbon dioxide diffuse some 25 times more rapidly through PMP film than through cast PP or HDPE films. Moisture vapor transmission is substantial, despite the low absorption of only 0.01 %, even after total immersion in water.

Table 33. Gas and water vapor permeability of 50 µm PMP film [346]

Permeability to	PMP	HDPE	PP
Oxygen, L m^{-2} d^{-1} atm^{-1}	40	1.1	1.6
Nitrogen, L m^{-2} d^{-1} atm^{-1}	9.5	0.3	0.36
Carbon dioxide, L m^{-2} d^{-1} atm^{-1}	120	4.6	6.5
Water vapor, g m^{-2} d^{-1} atm^{-1}	65	4.0	7.0

5.4.6. Rheology

PMP melts are strongly non-Newtonian. Their viscosity decreases rapidly at high shear rates and with increasing temperature (Fig. 56). These two effects produce particularly fluid melts under optimum processing conditions, and they call for some alteration to processing techniques compared to PP. In most cases friction heating alone in the extruder barrel is insufficient for uniform melting, and pressure generation also needs improving. Allowance should be made for low melt strength. There is a suggestion [323] of some melt order in view of the low entropy of fusion, 10.3 J K^{-1} mol^{-1}. The particularly rapid decline in viscosity with increasing temperature, around 280 °C, also has been linked with helical association in the melt [344, 347, 348].

5.5. Economic Aspects

The following list prices (in £/t) for polymerization grade materials and polymers prevailed in the fourth quarter of 1991:

Propene (Western Europe)	210
4-Methyl-1-pentene	Not traded
1-Hexene	1010
1-Octene	920
1-Decene	900
Polypropylene (Western Europe and United States)	360 – 450
PMP (grade and volume dependent)	2500 – 4300

The higher cost of PMP over PP reflects higher raw material prices without the economies of scale now realized for PP, as well as 10 years difference in experience.
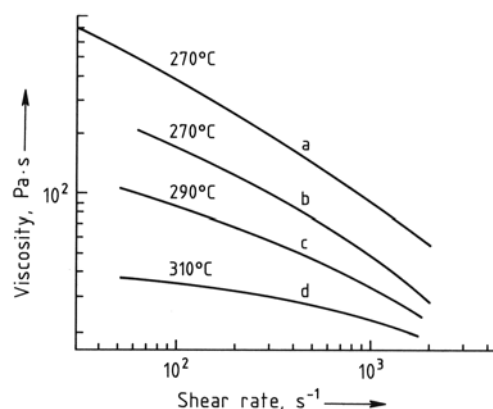

Figure 56. Viscosity curves [347]
a) Polypropylene (Propathene) MFI 4.0 (230 °C/2.16 kg);
b) – d) Poly(4-methyl-1-pentene), TPX, grade DX810, MFI 70 (260 °C/5.0 kg)

5.6. Fabrication and Applications

5.6.1. Fabrication

In principle, most of the normal fabrication techniques used for polyolefins can be used to make PMP articles, provided due recognition is given to its high melting point and low melt viscosity. Further changes to processing techniques have been introduced over the past five years to improve output rates and quality.

Injection Molding. While both piston and screw injection molding machines can be used, the ideal type employs a slow-compression screw with an L/D ratio of 20 – 24. The cylinder must be capable of being heated to 350 °C, with precise temperature control over the preferred operating range of 280 – 320 °C. Friction heating is inadequate, and can cause local decomposition. An alternative is to feed the machine with granules preheated to 130 °C. A valved nozzle prevents die drool between shots with very fluid melts. Injection pressures only need to be 50 and 25 MPa for the primary and secondary stages, with a relatively slow injection speed (< 50 % of the machine capacity) into a mold at 20 – 60 °C. Gas venting of molds is imperative to avoid burning from any volatile decomposition products formed at high melt temperatures.

Extrusion Blow Molding. The attraction of making high-quality transparent containers by blow molding PMP is tempered by poor melt strength and additional heating requirements. Some simple adjustments to secure accurate melt temperature control in the range 220 – 250 °C, the use of a parison controller and accumulator, and pressure generation with a barrier type torpedo are satisfactory for certain applications. Still higher quality and better production rates call for a number of additional alterations. These include continuous parison extrusion, modification of the pinch-off blades, a long L/D extruder, and mold vents. Manufacturers advise on the best conditions for their resins.

Injection stretch blow molding is the ideal method for making high-clarity containers having excellent physical properties due to biaxial orientation (see Section 2.8.2). A standard low-compression screw normally suffices, but improved heating to 200 °C is called for in the conditioning station before transfering to the final mold. Here, the blowing air must have a supply pressure of 3 MPa. Standard machines are easily modified to process PMP.

Extrusion. PMP can be used in most plastic extrusion processes for making film, fiber, sheet, pipe, and coatings for wire and paper. In all cases the extrusion stage should have ample barrel heating arrangements. Twin and single conventional full-flighted or three-stage screws used for PE or PP are suitable, provided that those generating excessive shear are avoided.

However, the throughput is reduced with PMP, and surging tends to occur when the screw speed is increased. A more suitable single screw has a double flight in the compression zone to separate melt and solid polymer before it is plasticized (Fig. 57). This secures stable operation without any throughput penalties.

The downstream equipment used for making sheet, film, tubes, and coatings is similar to that used for PP, but with appropriate temperature adjustments. Fine fibers can be made by the blown melt method or by the long spin process (see Section 2.8.3).

Difficult and Impractical Processes. Thermoforming, either by vacuum, pressure, or matched-mold processes is difficult, but possible, with PMP thin sheet. The need to use high temperatures, followed by a long cooling period gives a cycle time of approximately 1.5 min. However, attractive food trays for microwave ovens are being made from thin sheet by using low draw down ratios. Rotational molding and mechanical forming are unsuited to PMP. Small amounts of foamed moldings are marketed.

5.6.2. Applications

The sales pattern of PMP worldwide in 1991 is reported by Mitsui Petrochemical Industries (MPC) as follows [350]:

Release film and paper	22 %
Industrial	20 %
Medical and laboratory	13 %
Cookware	11 %
Electric	7 %
Packaging	6 %
Others	21 %

PMP film, manufactured by MPC under the trade name Opulent, is available in different thicknesses ($25-500\,\mu$m), with different flexibilities (modulus $0.7-1.6$ MPa), and with alternative surface finishes. Three-layer laminates with Kraft paper or low-softening polyolefins extend the range. These products find extensive use in applications requiring good release characteristics combined with high temperature resistance and chemical inertness. Important examples include release films in manufacturing electronic circuit boards, in curing advanced composites for aircraft parts, and in continuous

curing of rubber with heat or by UHF vulcanization. Inert mandrels made from flexible grades of PMP are used as supports during the manufacture and curing of reinforced high-pressure rubber hoses.

Good electrical properties and heat resistance meet specifications for use as covering for heat resistant wire, power, oil well, and communication cables. Glass-fiber-filled grades have sufficient shape retention after a few minutes at 260 °C to be used in dip soldering applications. Other industrial uses include replacement of stainless steel chemical treatment trays, sight glasses and floats, and a multitude of electrical insulators.

Labware and medical products were the first to take advantage of PMP. Transparency, convenience of sterilization with either γ-rays, ethylene oxide, dry heat, or steam autoclaves, and resistance to soiling are all relevant. Examples include blood test cells, medical instruments, tubing connectors, centrifuge cups, syringes and other measuring devices, urine collection tubes, and blood transfusion equipment. In the laboratory, PMP cages for small animals are easily cleaned and sterilized. Shatterproof transparent replacements for glass embrace most of the familiar items such as beakers, measuring cylinders and jugs, funnels, bottles, and Petri dishes.

Important outlets exist in food preparation where resistance to heat, oil, and steam is needed. Baking trays for bread, and thermoformed PMP-coated paper cartons for cooking foods, either in microwave or sometimes in gas-heated ovens, have superior releasability to aluminum foil containers. Application extend to coffee maker parts, popcorn popper covers, packages suitable for food retorting, microwave oven cookware, and service trays.

New areas under investigation include outlets for PMP fibers, such as nonwoven fabric, gas separation systems, and optical fibers.

5.7. Health and Environmental Aspects

PMP itself is regarded as inert and nontoxic, like polyethylene and polypropylene. Formulation systems for various grades are available to conform with food regulations in Japan, Germany, the United States, and the United Kingdom. Being a saturated hydrocarbon, PMP presents no
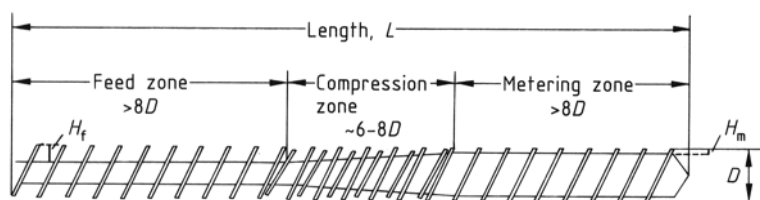
Figure 57. Screw for PMP [349]
$L/D \geq 28$; $CR = H_f/H_m = 2.5-3.0$; H_f = Depth of feed zone; H_m = Depth of metering zone

problems in disposal by complete combustion. Flammability is the same as for PP. In principle, PMP can be recycled for reuse in similar or lower-quality applications, but attention must be paid to molecular mass reduction as a consequence of high-temperature processing.

6. References

General References

1. *Golden Jubilee Conference, Polyethylenes 1933 – 1983,* Preprints, The Plastics and Rubber Institute, London 1983.
2. *Golden Jubilee Conference, Polyethylenes 1933 – 1983,* Plenary Papers, The Plastics and Rubber Institute, London 1983.
3. R. B. Seymour, T. Cheng (eds.): *History of Polyolefins,* Reidel Publ. Co., Dordrecht 1986.
4. F. M. McMillan: *The Chain Straighteners,* Macmillan, London 1981.
5. R. A. V. Raff, K. W. Doak: *Crystalline Olefin Polymers,* parts I and II, Interscience Publishing, London 1965.
6. A. Renfrew, P. Morgan (eds.): *Polythene,* 2nd ed., Iliffe, London 1960.
7. S. van der Ven: *Polypropylene and other Polyolefins,* Elsevier, Amsterdam 1990.
8. *Aufbereiten von Polyolefinen,* VDI-Verlag, Düsseldorf 1984.
9. P. Ehrlich, G. A. Mortimer: "Fundamentals of the Free Radical Polymerization of Ethylene," *Adv. Polym. Sci.* **7** (1970) 386 – 448.
10. Papers and Proceedings, *Polycon '84* LLDPE, Plastics and Rubber Institute, London 1984.
11. Conference Papers, *Polyethylene – The 1990s and Beyond*, Plastics and Rubber Institute, London 1992.
12. G. W. Gilby: "Ethylene-Vinyl Acetate Copolymers," in A. Whelan, K. S. Lee (eds.): *Developments in Rubber Technology-3,* Applied Science Publishers, Barking 1983, chap. 4.
13. J. Boor Jr.: *Ziegler-Natta Catalysis and Polymerization,* Academic Press, New York 1979.
14. W. Kaminsky, H. Sinn (eds.): *Transition Metals and Organometallics as Catalysts for Olefin Polymerization,* Springer Verlag, Berlin 1988.
15. R. P. Quirk (ed.): *Transition Metal Catalyzed Polymerizations,* Cambridge University Press, Cambridge 1988.
16. F. J. Karol, *Catal. Rev.-Sci. Eng.* **26** (1984) no. 3, 4, 557 – 595.
17. P. J. T. Tait: "Ziegler-Natta and Related Catalysts," in R. N. Haward (ed.): *Developments in Polymerization-2,* Applied Science Publishers, London 1979, chap. 3.
18. Papers presented at MetCon 96, Worldwide Metallocene Conference, Houston, TX, USA 1996.
19. A. D. Horton: "Metallocene Catalysis: Polymers by Design?", *Trends Polym. Sci.* **2** (1994) no. 5, 158 – 166.
20. M. Bochmann: Cationic Group 4 Metallocene Complexes and their Role in Polymerisation Catalysis: the Chemistry of Well-Defined Ziegler Catalysts. *Chem. Soc. Dalton Trans.,* **1994**, 255 – 270.

Specific References

21. W. L. Mattice, F. C. Stehling, *Macromolecules* **14** (1981) 1479.
22. see General Ref. [7].
23. F. M. Mirabella, E. A. Ford, *J. Polym. Sci. Polym. Phys. Ed.* **25** (1987) 777.
24. A. Keller, *Philos. Mag.* **2** (1957) 1171. *Prog. Phys.* **31** (1968) 623 See General Ref. [1], paper D1.
25. K. Bergmann, K. Nawotki, *Kolloid Z.* **219** (1967) 132.
26. S.-D. Clas, D. C. McFaddin, K. E. Russell, *J. Polym. Sci. Part B* **25** (1987) 1057.
27. R. S. Stein, R. Prud'homme, *J. Polym. Sci. Part B* **9** (1971) 595.
28. H. Schonhorn, H. L. Frisch, R. V. Albarino, *J. Polym. Sci. Polym. Phys. Ed.* **11** (1973) 1013.

29. L. Wild, T. Ryle, D. Knobeloch, *J. Polym. Sci. Polym. Phys. Ed.* **20** (1982) 441. G. Glöckner, *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **45** (1990) 1 (review).

30. M. Aroca Hervás, *Revista de Plásticos Modernos* (1996) no. 481, 61 – 68.

31. Du Pont, US 4 076 698, 1957 (A. W. Anderson, G. S. Stamatoff).

32. M. Philip, I. M. Ward, B. Parsons, *J. Mat. Sci.* **21** (1986) 879.

33. L. C. E. Struik, *Polymer* **28** (1987) 1521.

34. P. C. Powell: *Engineering with Polymers,* Chapman and Hall, London 1983, p. 130.

35. Exxon Chemicals, Escorene Ultra EVA Copolymers, company brochure, Kraainem, Belgium.

36. J. Scheirs, L. L. Böhm, J. C. Boot, P. S. Leevers, *Trends Polym. Sci.* **4** (1996) no. 12, 408 – 415.

37. Y-L. Huang, N. Brown, *J. Polym. Sci. Part B* **29** (1991) 129 – 137;

38. Hoechst, Hostalen GUR Ultra High Molecular Weight Polyethylene, company brochure, Frankfurt 1989.

39. K. S. Whiteley in General Ref. [1], paper B2.

40. L. J. Young in Brandrup and Immergut (eds.): *Polymer Handbook,* 2nd ed., Wiley, New York 1975, Section II, p. 105.

41. L. J. Young, *J. Polym. Sci.* **54** (1961) 411.

42. DSM, Teamex Octene based VLDPE, company brochure, Geleen, The Netherlands, 1990.

43. R. J. Statz in General Refs. [1], paper B5 and [3], chap. 11.

44. W. J. MacKnight, T. R. Earnest, *Macromol. Rev.* **16** (1981) 41.

45. P. Mapleston, *Modern Plastics International*, June 1996, 56 – 61.

46. Shell, US 4 808 699, 1987 (J. A. M. Van Broekhoven, M. J. Doyle).

47. Hoechst, US 5 610 253, 1995 (W. Hatke, F. Osan).

48. A. Gilchrist (ICI): unpublished work, 1965.

49. R. Spahl, G. Luft, *Ber. Bunsenges. Phys. Chem.* **86** (1982) 621. G. Jungermann, G. Luft, *Ber. Bunsenges. Phys. Chem.* **91** (1987) 541.

50. K. E. Weale: *Chemical Reactions at High Pressures,* Spon, London 1967.

51. P.-C. Lim, G. Luft, *Makromol. Chem.* **184** (1983) 849.

52. M. J. Roedel, *J. Am. Chem. Soc.* **75** (1953) 6110.

53. M. E. A. Cudby in General Ref. [1], paper D6.

54. G. Luft, R. Kämpf, H. Seidl, *Angew. Makromol. Chem.* **108** (1982) 203.

55. L. Nicolas, *J. Chim. Phys.* **55** (1958) 185.

56. H. Tobita, *J. Polym. Sci. Polym. Phys.* **33** (1995) 841 – 853.

57. R. A. Jackson, P. A. Small, K. S. Whiteley, *J. Polym. Sci. Polym. Chem. Ed.* **11** (1973) 1781.

58. P. Ehrlich et al., *A. I. Ch. E. Journal* **22** (1976) no. 3, 463.

59. Y. Tatsukami, T. Takahashi, H. Yoshioka, *Makromol. Chem.* **181** (1980) 1107.

60. Peroxid Chemie, Organic Peroxides P 3.2.1 (Half-Lifetimes), A 3.7.4 (Ethylene Polymerization I, II), company brochure, München.

61. W. W. Lawrence, S. E. Cook: Loss Prevention S.10, Chemical Engineering Progress Technical Manual, A.I.Ch.E. 1967.

62. D. G. H. Ballard et al., *Polymer* **15** (1974) 169.

63. M. P. McDaniel, M. B. Welch, *J. Catal.* **82** (1983) 98.

64. C. E. Marsden: Paper 4A3 in General Ref. [11].

65. M. P. McDaniel, M. B. Welch, M. J. Dreiling, *J. Catal.* **82** (1983) 118.

66. M. P. McDaniel, M. M. Johnson, *Macromolecules* **20** (1987) 773.

67. F. J. Karol in General Ref. [16], p. 573.

68. V. A. Zakharov, Yu. I. Yermakov, *Cat Rev.-Sci. Eng.* **19** (1979) no. 1, 67.

69. W. L. Carrick et al., *J. Polym. Sci.* A1, 10 (1972) 2609.

70. L. M. Baker, W. L. Carrick, *J. Org. Chem.* **35** (1970) 714.

71. F. J. Karol et al., *J. Polym. Sci.* A1, 10 (1972) 2621.

72. Union Carbide, NL 68 16149, 1968.

73. Standard Oil (Indiana), US 2 692 257, 1951 (A. Zletz).

74. B. Diedrich, *Appl. Polym. Symp.* **26** (1975) 1.

75. Hoechst, DE 1 595 666, 1966 (B. Diedrich, K. D. Keil).

76. Solvay, BE 650 679, 1963.

77. Union Carbide, US 4 293 673, 1979 (A. D. Hamer, F. J. Karol).

78. Stamicarbon, BE 751 315, 1969.

79. ICI, GB 1 253 046, 1968 (J. C. Greaves, W. G. Oakes).

80. Du Pont, GB 1 209 825, 1967.

81. G. Henrici-Olivé, S. Olivé, *Adv. Polym. Sci.* **15** (1974) 1 – 30.

82. J. Herwig, W. Kaminsky, *Polym. Bull.* **9** (1983) 464.

83. W. Kaminsky: Paper 5.1 in General Ref. [1].

84. For a review of earlier work, see General Ref. [20].

85. BASF, US 4 404 344, 1981 (H. W. Sinn, W. O. Kaminsky, H. C. Vollmer, R. O. H. H. Woldt)

86. L. Resconi, S. Bossi, L. Abis, *Macromolecules* **23** (1990) 4489 – 4491.

87. P. J. Tait, M. G. K. Monteiro, M. Yang, J. L. Richardson: "Some Recent Advances in Supported Metallocene Catalysts," in General Ref. [20].

88. M. Arndt, I Beulich, W. Kaminsky: "C1 Symmetric Metallocenes for Olefin Copolymerization: Catalytic Performance and Polymer Properties," in General Ref. [18].

89. Dow, US 5 064 802, 1990 (J. C. Stevens, D. R. Neithamer). Exxon, US 5 026 798, 1990 (J. A. M. Canich).

90. Dow, EP 416 815, 1990 (J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S. Lai).

91. M. Galimberti, T. Dall'Occo, F. Piemontesi, I. Camurati, G. Collina: "Metallocenes and Alumoxanes: Do they determine the Copolymer's Fingerprint," in General Ref. [18].

92. Exxon, US 4 752 597, 1987 (H. W. Turner).

93. Dow, US 5 064 802, 1990 (J. C. Stevens, D. R. Neithamer).

94. P. Mapleston, *Modern Plastics International* **21** (1991) no. 3, 63; **19** (1989) no. 11, 36.

95. N. Baron: "A New Polyolefin Product Family Based on EXPOL Catalyst Technology," paper presented at 2nd International Symposium on High Pressure Chemical Engineering, Erlangen 1990.

96. Exxon, US 4 530 914, 1983 (J. A. Ewen, H. C. Welborn).

97. Phillips, US 5 594 078, 1994 (M. B. Welch, R. L. Geerts, S. J. Palackal, T. M. Pettjohn).

98. G. A. M. Diepen, M. A. de Zeeuw in S. A. Miller (ed): *Ethylene and its Industrial Derivatives,* Ernest Benn, London 1969.

99. D. Commereuc et al., *Hydrocarbon Process.* **63** (1984) no. 11, 118.

100. A. Chauvel, Y. Chauvin, J. Gaillard, J. Leonhard: *LLDPE in Europe,* Preprints to Conference, Madrid 1986, Plastics and Rubber Institute.

101. ICI, GB 1 456 841, 1973 (R. R. Cooper, K. S. Whiteley).

102. Y. V. Kissin, D. L. Beach, *J. Polym. Sci., Polym. Chem. Ed.* **24** (1986) 1069.

103. W. R. D. Manning, S. Labrow: *High Pressure Engineering, Chemical and Process Engineering Series,* Leonard Hill, London 1971.

104. B. C. Crossland: "Philosophical Thoughts on Standards for High Pressure Systems," *ASME Conference on Pressure Vessels and Piping,* Chicago 1986.

105. K. E. Bett, B. C. Crossland, H. Ford, A. K. Gardner in General Ref. [1], paper B1.

106. Esso, Research and Engineering, DT 2 151 649, 1970 (K. L. O'Hara).

107. J. P. Machon in Ref. [15], p. 344.

108. Charbonnages de France, GB 2 141 491, 1983 (D. Grasset).

109. Charbonnages de France, US 4 105 609, 1978 (J. P. Machon, B. Levresse, P. Gloriod).

110. K. Ziegler, GB 799 392, 1953.

111. J. P. Hogan in General Ref. [1], paper B3.

112. *Hydrocarbon Process* **62** (1983) no. 11; **64** (1985) no. 11.

113. L. Böhm, *Chem.-Ing.-Tech.* **56** (1984) 674.

114. Hoechst, DE 1 720 611, 1967 (B. Diedrich, K. D. Keil).

115. *Ullmann,* 4th ed., **19** p. 185.

116. Phillips Petroleum, US 3 405 109, 1960 (R. G. Rohlfing).

117. R. B. Staub in General Ref. [1], paper 5.4.

118. R. B. Staub: *LLDPE in Europe,* Preprints to Conference, Madrid 1986, Plastics and Rubber Institute, paper 1.

119. Union Carbide, US 4 003 712, 1975 (A. R. Miller).

120. D. E. James in Ref. [116], paper 2. Union Carbide, US 4 543 399,1984(J. M. Jenkins et al.).

121. T. K. Moynihan in General Ref. [1], paper 5.3.1.

122. *Mod. Plast. Int.* **27** (1997) no. 1.

123. C. Krumm: *Polycon '84,* Papers and Proceedings, Plastics and Rubber Institute, London 1984, paper D.

124. Miller et al., *Plast. Eng.* **42** (1986) 37.

125. S. Bork, *Kunststoffe* **74** (1984) 474.

126. G. R. Chapman, D. E. Priester, R. D. Souffie: *RETEC Polyolefins V,* Houston 1987, Society of Plastics Engineers, Brookfield, Conn., p. 271.

127. D. F. Klein in Ref. [126], p. 285.

128. W. A. Fraser, W. B. Herdle in Ref. [126], p.301.

129. R. D. Leaversuch, *Modern Plastics International* **20** (1990) no. 9, 55.

130. J-M. Yernaux: Paper S3B in General Ref. [11].

131. D. W. Woods, I. M. Ward, *Plastics, Rubber and Composites Processing and Applications* **18** (1992) no. 4, 255 – 261.

132. A. B. Brennan: "Surface Modification of Polyethylene Fibres for Enhanced Performance in Composites," *Trends Polym. Sci.* **3** (1995) no. 1, 4 – 11.

133. I. M. Ward: "A Review of Recent Developments in the Processing and Properties of Oriented Polyethylene," *Plastics, Rubber and Composites Processing and Applications* **19** (1993) no. 1, .

134. D. C. Prevorsek: "Preparation, Structure, Properties and Applications of Gel-spun Ultrastrong Polyethylene Fibers," *Trends Polym. Sci.* **3** (1995) no. 1, 12–21.

135. Rigidex HDPE Technical Manual No. 22 (BP).

136. Loctite Data Sheets: Primer 770 and Adhesive 406.

137. B.-A. Sultan, M. Palmlöf in General Ref. [11], paper 4B/3

138. B. E. Roberts, S. Verne in General Ref. [1], paper C3.1.

139. B. J. Lyons in General Ref. [1], paper C3.2.

140. L. Panzer: *ANTEC '88,* Conference Proceedings Society of Plastics Engineers, Brookfield, Conn., p. 1421.

141. D. C. Eagles, *Wire Technology International* **18** (1990) no. 6, 15. Mitsubishi, US 4 413 066, 1981 (T. Isaka, M. Ishioka, T. Shimada, T. Inoue).

142. Hoechst, Hostapren Chlorinated Polyethylene, company brochure, Frankfurt 1986.

143. D. A. Buck, F. A. Milcetich, P. D. Marsh, K. J. Kallish: *ANTEC '86,* Conference Proceedings, Society of Plastics Engineers, p. 803. Air Products, US 3 862 242, 1972 (R. C. Terrell).

144. G. Scott in S. A. Barenberg, J. L. Brash, R. Narayan, A. E. Redpath (eds.): *Degradable Materials,* CRC Press, Boca Raton 1990, p. 143.

145. W. J. Maddever, P. D. Campbell in Ref. [144], p. 237.

146. I. Dent, S. Hardman: "Plastics Waste Recycling – an Alternative Approach," I.Chem.E. Environmental Protection Bulletin Issue 044, 1996.

147. F. M. McMillan: *The Chain Straighteners,* McMillan Press, London 1979.

148. J. P. Hogan, R. L. Banks in R. B. Seymour, Tai Cheng (eds.): *History of Polyolefins,* Reidel Publ. Co., Dordrecht 1986, p. 103.

149. P. Pino, G. Moretti: "The Impact of the Discovery of the Polymerization of α-Olefins on the Development of Stereospecific Polymerization of Vinyl-monomers," *Polymer* **28** (1987) 683.

150. D. J. B. Potter, The Manor, Goose Lane, Ilminster, Somerset TA19 9RU: Consultant for Polypropylene Producers and Their Technologies, page preceding p. 55, consultant's Fig. 4.16.

151. D. J. B. Potter, The Manor, Goose Lane, Ilminster, Somerset TA19 9RU: Consultant for Polypropylene Producers and Their Technologies, page following p. 30, consultant's Fig. 4.1.

152. E. Seiler, *Kunststoffe Plast. Eur.* 1995, no. 8, 31.

153. R. Silvestri, L. Resconi, A. Pelliconi, Metallocenes '95, 1st Int. Congr. Mettalocene Polym., Brussels, April 26–27, 1995, p. 209.

154. B. Wunderlich: *Macromolecular Physics,* **vol. 3,** Academic Press, New York 1980, p. 63.

155. J. Brandrupp, E. H. Immergut: *Polymer Handbook,* 3rd. ed., J. Wiley, New York 1989, V27.

156. A. Turner-Jones, *Makromol. Chem.* **75** (1964) 134–158.

157. S. van der Ven: *Polypropylene and other Polyolefins,* Elsevier, Amsterdam 1990, chap. 4.

158. A. W. Sloley, S. W. Golden, *Hydrocarbon Technol. Int. HTI Q.* **Spring 1995**, 111.

159. D. L. Smith, Am. Inst. Chem Eng., Summer Meeting, San Diego, Aug. 1990, Paper 34a.

160. H. Mark et al. (eds.): *Encyclopaedia of Polymer Science and Engineering,* **vol. 13,** J. Wiley, New York 1987, p. 472–473.

161. B. V. Vora, P. R. Pujado, N. D. Adams, C. A. LeMerle, *International Conference, Polypropylene – the Way Ahead,* Madrid, Nov. 9–10, 1989, Paper 1/1–1/5.

162. *Eur. Chem. News* **53** (1989) 18th Dec., 14.

163. B. L. Goodall in van der Ven (ed.): *Polypropylene and other Polyolefins,* Elsevier, Amsterdam 1990, chap. 1.

164. Solvay et Cie, US 4 210 738, 1980 (J. P. Hermans, P. Henriqulie); US 3 769 233, 1973 (J. P. Hermans, P. Henriqulie).

165. R. P. Nielson in R. P. Quirke (ed.): *Transition Metal Catalysed Polymerizations,* **vol. 4,** part A, Harwood Academic Publ., New York 1983, p. 61.

166. P. Fiasse, *International Conference, Polypropylene – the Way Ahead,* Madrid, Nov. 9–10, 1989, paper 4/1.

167. Mitsui Petrochem. Ind., AU 89462 82, 1981, Example 1 (N. Kashiwa, A. Toyota).

168. *Chem. Eng.* (1985) July 8, 22.

169. W. Biddel et al., Metallocenes '96, 2nd Int. Congr. Mettalocene Polym., Düsseldorf, March 6–7, 1996, Session 3.

170. F. Langhauser, D. Fischer, S. Seelert, Metallocenes '95, 1st Int. Congr. Mettalocene Polym., Brussels, April 26–27, 1995, p. 245.

171. H. V. Vendilla, G. Guerra, P. Corradini, *Eur. Polym. J.* **27** (1991) no. 1, 45 – 54.

172. G. Natta, I. Pasquon, *Adv. Catal.* **XI,** Academic Press, London 1959, pp. 1 – 66.

173. T. Keii, *Kinetics of Ziegler-Natta Polymerization,* Kodansha, Tokyo 1972.

174. U. Giannini, G. Giunchi, E. Albizzati, P. C. Barbe in M. Fontanille, G. Guyot (eds.): *Recent Advances in Mechanistic & Synthetic Aspects of Polymerization,* Series C, vol. 215, Reidel Publ. Co., Dordrecht 1987, pp. 473 – 484.

175. M.-J. Brekner, Metallocenes '96, 2nd Int. Congr. Mettalocene Polym., Düsseldorf, March 6 – 7, 1996, p. 155.

176. D. B. J. Potter, *Chem. Week* (1990) April, 22 – 25.

177. E. Johnson, *Chem. Eng.* **97** (1990) no. 5, 30 – 37.

178. N. F. Brockmeier in R. P. Quirk (ed.): *Transition Metal Catalysed Polymerization, Alkenes & Dienes,* **vol. 4,** part B, Harwood Academic Press, New York 1983, pp. 671 – 696.

179. T. C. Cheng in R. B. Seymour, T. Cheng (eds.): *History of Polyolefins,* Reidel Publ. Co., Dordrecht 1986, p. 119.

180. D. Del Duca: "Le Polypropylène," *Euretec'88',* Société Française des Ingénieurs Plasticiens, Paris, April 20 – 21, 1988, paper 5.

181. M. A. Ferrero, M. G. Chiovetta, *Polym. Plast. Technol. Eng.* **29** (1990) no. 3, 263 – 287.

182. K. D. Rumpler, J. F. R. Jaggard, R. A. Werner: "Le Polypropylène," *Euretec '88,* Société Française des Ingénieurs Plasticiens, Paris, April 20 – 21, 1988, paper 4.

183. N. Hattori, *Chem. Econ. Eng. Rev.* **18** (1986) no. 3, 21.

184. H. K. Ficker, G. L. Goeke, G. W. Powers, *Plast. Eng.* **43** (1987) no. 2, 29 – 32.

185. R. D. Leaversuch, *Mod. Plast.* **20** (1990) no. 10, 46 – 48.

186. H. K. Ficker, D. A. Walker, *International Conference, Polypropylene – the Way Ahead,* Madrid, Nov. 9 – 10, 1989, paper 5/4.

187. P. Galli, T. Simonazzi, P. C. Barbe, *Conv. Ital. Sci. Macromol. (Atti) 6th,* **1** (1983) 113 – 126.

188. T. G. Heggs in D. C. Allport, W. Janes (eds.): *Block Copolymers,* Applied Science, London 1973, chapt. 4, 8D.

189. S. van der Ven: *Polypropylene and other Polyolefins,* Elsevier, Amsterdam 1990, chap. 5, 6.

190. R. Gachter, H. Muller: *Plastics Additives Handbook,* Hanser Verlag, München 1985.

191. H. Hinksen, F. K. Meyer, *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 25.

192. T. J. Henman: *World Index of Polyolefin Stabilizers,* Kogan Page, London 1982.

193. W. Meyer, H. Zweifel: "Le Polypropylène," *Euretec '88,* Société Française des Ingénieurs Plasticiens (SFIP), Paris 1988, paper 20.

194. B. Wunderlich: *Macromolecular Physics,* **vol. 2,** Academic Press, New York 1976, p. 1.

195. K. T. Collington, *International Conference, Polypropylene – the Way Ahead,* Madrid, Nov. 9 – 10, 1989, paper 8/1.

196. A. Lucke, *Kunststoffe Plast. Eur.* **87** (1997) no. 3, 7 – 8.

197. R. C. Kowalski in R. B. Seymour, T. Cheng (eds.): *History of Polyolefins,* Reidel Publ. Co., Dordrecht 1986, p. 307.

198. G. R. Zeichner, C. W. Macosko, *Soc. Plast. Eng. 40th Ann. Tech. Conf., Eng. Props Struct. Div.,* San Francisco, May 1982, pp. 79 – 81.

199. ICI, Propathene Technical Data, P11/1 Injection Moulding, Middlesbrough, UK, 1989.

200. M. Kojima, *J. Macromol. Sci., Phys.* **B19** (1981) no. 3, 523 – 541.

201. *Mod. Plast.* **20** (1990) no. 1, 31, 39.

202. *Mod. Plast. Int.* **27**(1997) 65 – 68.

203. ICI, Propathene Technical Data, P12/1 Integral Hinges, Middlesbrough, UK.

204. ICI, Propathene Technical Data, P13/1 Structural Foam, Middlesbrough, UK.

205. ICI, Propathene Technical Data P14/1, Blow Moulding, Middlesbrough, UK.

206. R. D. Leaversuch, *Mod. Plast.* **20** (1990) no. 10, 46 – 48.

207. R. Mikielski: "Le Polypropylène," *Euretec '88,* Société Française des Ingénieurs Plasticiens (SFIP), Paris, April 4, 1988, paper 19.

208. J. Bonus: "Market Facts and Figures," *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham, Sept. 23 – 25, 1987, paper 2.

209. R. G. Mansfield: "Structure of Unsaturated Polypropylene Fiber Business," *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 3.

210. J. E. Ford: "Comparative Properties of Polypropylene and Other Man Made Fibers," *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 5.

211. M. Navone: "New Concepts and Development in Machinery and Process for Production of Polypropylene Fibers, *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 15.

212. N. D. Scott: "Polypropylene into Non Wovens," *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 38.

213. L. C. Wadsworth, A. O. Muschelewicz: "Effects of Resin and Process Variables on the Production of Ultrafine Melt Blown Polypropylene Fibers", *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 45.

214. ICI, Propathene Technical Data, P7/1, Tapes, Film Yarns, Fibers, Middlesbrough, UK, 1989.

215. P. Mapleston, *Mod. Plast.* **20** (1990) no. 6, 38.

216. N. Petiniot, A. Gemmi, M. Gillet, *Euretec 88,* Paris, April 21, 1988, paper 15.

217. K. F. Martin, J. Paul: "Manufacture and Civil Engineering Applications of High Strength Polypropylene Grids," *Fourth International Conference on Polypropylene Fibers and Textiles,* Nottingham 1987, paper 50.

218. ICI, Propathene Technical Data, P10/1, Pipework, Middlesbrough, UK, 1989.

219. Directory of UK Companies Involved in Recycling Plastics, 2nd ed., Brit. Plast. Federation, London 1989.

220. *Plastics & the Environment. Fact Sheet – Recycling,* Brit. Plast. Federation, London.

221. R. Armson, *Resources, Conservation and Recycling* **2** (1988) no. 1, 13 – 16.

222. T. W. Moffit: *Plastics Packaging – The Environmental Dimension,* Brit. Plast. Federation, London 1990.

223. *Eur. Plast. News* **15** (1988) no. 12, 25 – 31.

224. C. H. Kline, *Chem. Ind. (London)* 1989, July, 440.

225. C. H. Kline, *Chem. Ind. (London)* 1989, Aug., 483.

226. G. G. David, *Chem. Ind. (London)* 1989, Aug., 487.

227. Hüls: "Recycling Batteries," *Chem. Rundsch.* Nov. 10, 1989, p. 6.

228. British Plastics & Rubber: *Case Study by DTI (London) of Waste Minimisation at Chloride Battery Plant,* Feb. 1990, p. 15.

229. *Plast. Rubber Wkly,* Dec. 8, 1990, no. 1365, 2.

230. J. Maczko, *Plast. Eng.* **44** (1988) no. 6, 39.

231. *Chem. Eng. (N.Y.)* **97** (1990) no. 6, 15.

232. ICI, The Competiveness of LDPE, PP, PVC after the 1973 Oil Crisis, the ICI View, Welwyn Garden City, 1974.

233. B. Wunderlich: *Macromolecular Physics,* Academic Press, New York "Crystal Structure, Morphology, Defects,", vol. 1, 1973; "Crystal Nucleation, Growth, Annealing," vol. 2, 1976.

234. G. Natta, P. Corradini, I. W. Bassi, *Makromol. Chem.* **21** (1956) 240 – 244.

235. A. Turner Jones, *J. Polym. Sci. Part B* **1** (1963) 455 – 456; *Polymer* **7** (1966) 23 – 59.

236. S. W. Cornell, J. L. Koenig, *J. Polym. Sci. Part A-2* **7** (1969) 1965 – 1982.

237. I. T. Luongo, R. Salovey, *J. Polym. Sci. Part A-2* **4** (1966) 997 – 1008.

238. I. D. Rubin in H. Marowetz (ed.): *Polymer Monographs,* vol. 1, Gordon & Break Sci. Publ., New York 1968.

239. H. Tompa: *Polymer Solutions,* Butterworths, London 1956.

240. V. F. Holland, R. L. Miller, *J. Appl. Phys.* **35** (1964) 3241 – 3248.

241. G. Natta, *Angew. Chem.* **68** (1956) 393 – 403.

242. S. W. Cornell, I. L. Koenig, *J. Polym. Sci. Part A-2* **7** (1969) 1965 – 1982.

243. G. Videtto, A. I. Kovacs, *Kolloid Z. Z. Polym.* **220** (1967) 1 – 18.

244. W. Glenz, G. Goldbach, unpublished data from measurements made by Chemische Werke Hüls AG, Marl.

245. C. Geacintow, R. B. Milles, H. I. L. Schuurmans, *J. Polym. Sci. Part A-1* **4** (1966) 431 – 433.

246. G. Goldbach, G. Peistscher, *J. Polym. Sci. Part B* **6** (1968) 783 – 788.

247. F. Danusso, G. Gianotto, *Makromol. Chem.* **61** (1963) 139 – 156.

248. I. Powers, I. D. Hoffman, I. I. Weeks, F. A. Quinn, Jr., *J. Res. Natl. Bur. Stand. Sect. A* **69** (1965) 335 – 345.

249. H. Wilski, T. Grewer, *J. Polym. Sci. Part C* **6** (1964) 33 – 41.

250. Allied Chem. Corp., BE 652 381, 1965.

251. C. Geacintow, R. S. Schotland, R. B. Miles, *J. Polym. Sci. Part B* **1** (1963) 587 – 591; *J. Polym. Sci. Part C* **6** (1964) 197 – 207.

252. I. Boor, Jr., E. A. Youngman, *J. Polym. Sci.* **2** (1964) 903 – 907.

253. J. P. Rakus, C. D. Mason, *J. Polym. Sci. Part B* **4** (1966) 467 – 468.

254. G. Goldbach, *Angew. Makromol. Chem.* **29/30** (1973) 213 – 227.

255. G. Goldbach, *Angew. Makromol. Chem.* **39** (1974) 175 – 188.

256. C. D. Armeniades, E. Baer, *J. Makromol. Sci. Phys. B* **1** (1967) no. 2, 309 – 334.

257. I. D. Rubin, *J. Polym. Sci. Part A* **3** (1965) 3803 – 3813.

258. I. Boor, I. C. Mitchel, *J. Polym. Sci.* **62** (1962) 70 – 73.

259. J. Haase, R. Hosemann, S. Köhler, *Polymer* **19** (1978) 1358 – 1361.

260. J. Haase, S. Köhler, R. Hosemann, *Z. Naturforsch. A* **33** (1978) 1472 – 1483.

261. M. Goldstein, M. E. Seeley, H. A. Willis, V. J. I. Zichy, *Polymer* **19** (1978) 1118 – 1122.

262. J. Plenikowski, O. Umminger, *Kunststoffe* **55** (1965) 822 – 827.

263. M. L. Kasakevich, *Kunststoffe* **80** (1990) 54 – 57.

264. A. I. Foglia, *Appl. Polym. Symp.* **11** (1969) 1 – 18.

265. J. Plenikowski, *Kunststoffe* **55** (1965) 431 – 437.

266. I. P. Rakus, C. D. Mason, R. J. Schaffhauser, *J. Polym. Sci. Part B* **7** (1969) 591 – 595.

267. G. Goldbach, *Kunststoffe* **64** (1974) 475 – 481; *Angew. Makromol. Chem.* **74** (1978) 123 – 146.

268. W. Bollmann, *NDZ, Neue Deliwa-Z.* **9** (1972) 385 – 391.

269. Unpublished data from measurements made on behalf of Shell Research.

270. C. R. Lindgren, *Polym. Eng. Sci.* **10** (1970) 163 – 169.

271. J. Park et al., *J. Am. Water Works Assoc.,* Oct. 1991, 71 – 78.

272. J. Park et al., *J. Am. Water Works Assoc.,* Nov. 1991, 85 – 91.

273. M. Kasakevich et al., *Kunststoffe* **80** (1990) 1361 –1362.

274. M. Ifwarson, T. Traenker, *Kunststoffe* **79** (1989) 827 – 830.

275. M. Ifwarson, P. Eriksson, *Kunststoffe* **76** (1986) 245 – 248.

276. M. Ifwarson, *Kunststoffe* **79** (1989) 525 – 529.

277. M. Ifwarson, P. Eriksson, "40A: Experience from 12 Years Evaluation of Cross-Linked Polyethylene," report at *6th International Conference Plastic Pipes VI,* York 1985, p. 40A.1.

278. J. Schultze, M. Homann: *C₄ Hydrocarbons and Derivatives,* Springer-Verlag, Berlin 1989.

279. A. Wouters, D. Hopper: "Polybutylene Film for Non-retortable Applications," *Pira 5th International Packaging Conference,* London Oct. 3 – 4, 1990.

280. A. Wouters: "Polybutylene Film for Non-retortable Applications," *Packforst Seminar Scanplast '91,* Gothenburg, March 6, 1991. R. Lee: "High Performance Lidding Films from Polybutylene Blends," *Pira International Conference,* Birmingham, Nov. 22, 1990.

281. S. W. Lebedew, E. P. Filonenko, *Ber. Dtsch. Chem. Ges.* **58** (1925) 163 – 168.

282. S. W. Lebedew, G. G. Kobliansky, *Ber. Dtsch. Chem. Ges.* **63** (1930) 103 – 112.

283. De Bataafse, GB 358 068, 1930 (H. D. Elkington).

284. I. G. Farbenindustrie, DT 641-284, 1931 (M. Otto, M. Müller-Cunradi).

285. P. H. Plesch: *The Chemistry of Cationic Polymerization,* McMillan Publ., New York 1963.

286. J. P. Kennedy: *Cationic Polymerization of Olefins, A Critical Inventory,* Wiley-Interscience, New York 1975, pp. 86 – 137.

287. H. Güterbock: *Polyisobutylen and Isobutylen-Mischpolymerisate,* Springer Verlag, Berlin 1959.

288. Cosden Petroleum, US 2 957 930, 1956 (W. K. Jackson); BE 584 683, 1959 (W. K. Jackson); *Chem. Eng. N. Y.* **67** (1960) no. 16, 98 – 101.

289. Standard Oil Development Co., US 2 698 320, 1952 (A. R. Garabrant, H. G. Goering, H. G. Schneider). Esso Research and Engineering, US 2 849 433, 1953 (H. G. Schneider, H. G. Goering, V. F. Mistretta); US 8 42 533, 1955 (R. P. Cahn).

290. Standard Oil Dev., US 2 176 194, 1936 (L. A. Bannon). Jasco, US 2 296 399, 1939 (M. Otto, H. G. Schneider).

291. I. G. Farbenindustrie, DT 496 482, 1937 (M. Otto, H. Güterbock, A. Hellemanns).

292. Exxon Research and Eng. Comp., US 2 893 981, 1954 (J. L. Ernst, A. B. Small, L. W. McLean); US 2 856 394, 1954 (A. B. Small, J. L. Ernst).

293. H.-U. Lenne, *Kolloid Z.* **137** (1954) 65 – 70. A. M. Liquori, *Acta Crystallogr.* **8** (1955) 345 – 347.

294. J. F. Gross, K. W. Nelson, J. M. Slobodin, *Zh. Fiz. Khim.* **25** (1951) 504 – 512. M. S. C. Flett, O. H. Plesch, *J. Chem. Soc.* 1952, 3355 – 3358.

295. J. P. Kennedy, E. Marechal: *Carbocationic Polymerization,* Wiley Interscience, New York 1982.

296. G. Natta et al., *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **19** (1955) 397, 404. G. Natta, F. Danusso (eds.): *Stereoregular Polymers and Stereospecific Polymerization,* **vol. 1,** Pergamon Press, New York 1967, p. 86.

297. Van der Ven: *Polypropylene and other Polyolefins,* Elsevier, Amsterdam 1990, p. 525.

298. *Kirk-Othmer,* 3rd. ed., **16,** John Wiley pp. 470 ff.

299. P. D. Trifedi, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **17** (1976) 803 – 807.

300. J. P. Kennedy, J. E. Johnston, *Adv. Polym. Sci.* **19** (1975) 37.

301. *Kirk-Othmer,* 2nd ed., **suppl. vol.,** pp. 800 – 807.

302. Brit. Petroleum, GB 912 824, 1962 (J. K. Hamblin).

303. Brit. Petroleum, GB 933 253, 1963 (G. W. Alderson, J. K. Hamblin).

304. Chevron Res. Co., US 3 251 895, 1966 (J. B. Wilkes).

305. Idemitsu Petr. Co., US 3 950 450, 1976 (H. Hashimoto, S. Omiya).

306. ASTM DS4A, Physical Constants of Hydrocarbons $C_1 - C_{10}$, American Soc. for Testing and Materials, Philadelphia 1971, p. 44.

307. Y. V. Kissin, in J. I. Kroschwitz (ed.): Encyclopedia of Polymer Science Engineering, vol. 9, Wiley, New York 1987, pp. 707 – 718.

308. In [301], p. 799.

309. ICI, GB 1 085 914, 1967 (K. J. Clark).

310. Y. V. Kissin, *Isospecific Polymerization of Olefins with Heterogeneous Ziegler-Natta Catalysts,* Springer-Verlag, New York 1985, pp. 227, 237.

311. V. S. Steinbeck et al., *Eur. Polym. J.* **11** (1975) 457 –465.

312. K. J. Clark, R. P. Palmer, *The Chemistry of Polymerization Processes,* Monograph no. 20, Soc. of Chemical Industry, London 1966, pp. 82 – 103.

313. P. J. G. Tait, M. Ab Fid, A. E. Enenmo in R. B. Seymour, T. Cheng (eds.): *Advances in Polyolefins,* Plenum Press, New York 1987, p. 309.

314. Mitsui Petrochemical Industries, EP 0 253 625, 1986 (J. Yoshitake et al.)

315. BASF, GB 1 493 166, 1974 (H. Schick, H. Mueller-Tamm, N. Johann).

316. BASF, GB 1 489 312, 1974 (H. Schick et. al.).

317. Instit. Français du Petrole, FR 1 540 270, 1968 (Y. Chauvin, G. Lefebvre, M. Uchino).

318. Instit. Français du Petrole, FR 1 540 271, (Y. Chauvin, G. Lefebvre). See also [301], p. 794.

319. In [297], p. 529.

320. J. Brandrup, E. H. Immergut: *Polymer Handbook,* 3rd ed., John Wiley and Sons, New York 1989, V1/15.

321. J. H. Griffith, B. G. Ranby, *J. Polym. Sci.* **44** (1960) 369.

322. Y. Tanada, N. Kawasaki, K. Imada, M. Takayanagi, *Rep. Progr. Polym. Phys. Jpn* **9** (1966) 165 –168.

323. P. Zoller, H. W. Starkweather, G. A. Jones, *J. Polym. Sci. Polym. Phys. Ed.* **24** (1986) 1451.

324. G. Charlet, G. Delmas, J. H. Revol, R. St. J. Manley, *Polymer* **25** (1984) 1613 – 1619.

325. In [301], p. 795.

326. A. Turner-Jones, *Polymer* **6** (1965) 249 – 268.

327. In [312], p. 89.

328. In [312], p. 91.

329. Mitsui Petrochemical Industries, Technical Brochure, TPX, p. 6.

330. Mitsui Petrochemical Industries, TPX, no. 2312A, p. 8.

331. T. Tanigami, H. Suzuki, K. Yamamura, S. Matsuzawa, *Macromolecules* **18** (1985) 2595.

332. A. S. Hoffman, P. A. Frier, P. C. Condit, *J. Polym. Sci., Polym. Symp.* **4** (1963) 109.

333. L. Reginato, *Makromol. Chem.* **132** (1970) 113, 125.

334. N. C. Billingham, T. J. Walker, *J. Polym. Sci., Polym. Chem. Ed.* **13** (1975) 1209.

335. N. C. Billingham, P. Prentice, T. J. Walker, *J. Polym. Sci., Polym. Symp.* **57** (1976) 287 – 297.

336. F. Tudos, M. Iring, T. Kelen, in A. V. Patsis (ed.): *Advances in Stabilization and Controlled Degradation of Polymers,* **vol. 1,** Technomic Publ. Comp., Pennsylvania 1989, p. 86.

337. Mitsui Petrochemical Industries, TPX, General Brochure, p. 7.

338. R. Arnaud, J. Lacoste, J. Lemaire, *Makromol. Chem. Rapid Commun.* **6** (1985) 803.

339. R. Chandra et al., *Acta Polym.* **39** (1988) 265 – 267.

340. N. S. Allen, J. F. McKellar, *Br. Polym. J.* **9** (1977) 302 – 311.

341. ICI, early data on TPX, Welwyn Garden City.

342. N. S. Soboleva, S. S. Leshchenko, V. L. Karpov, *Vysokomol. Soedin, Ser. A* **25** (1983) 381. *Chem. Abstr.* (1983) 98 127069h.

343. Mitsui and ICI data, 1992.

344. G. Charlet, G. Delmas, *J. Polym. Sci. Part B, Polymer Phys.* **26** (1988) 1123.

345. Mitsui Petrochemicals Industries, TPX Document 2312A, p. 13.

346. Mitsui Petrochemicals Industries, TPX Film Brochure, p. 5.

347. Mitsui Petrochemicals Industries, TPX Document, TM-550, p. 6.

348. M. N. Matrosovich et al., *Vysokomol. Soedin, Ser.* **B 22** (1980) 357. H. Ohi, K. Furuya in I. I. Rubin (ed.): *Handbook of Plastics Materials and Technology,* Wiley Interscience, New

York 1990, pp. 375 – 383. G. C. Garland, L. M. Fodor in *Modern Plastics,* October 1991, p. 81. Mitsui Petrochemicals Industries and Phillips 66, Data sheets.

349. Mitsui Petrochemicals Industries, TPX Document TM-506, p. 3.
350. Mitsui Petrochemical Industries, personal communication.