# Polyethylene

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## 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 ($45 \times 10^6$ 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 production 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/m³ were typically obtained. The densities of completely amorphous and

**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.

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.

## 2. Properties of Polyethylenes

### 2.1. Molecular Structure and Morphology

Figure 1 shows schematic structures for the three polyethylenes, with the main features exaggerated
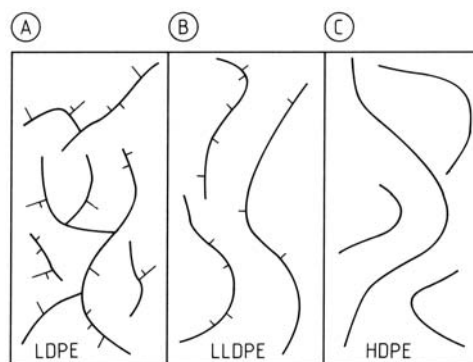


**Figure 1.** Schematic molecular structure
A) Low-density polyethylene; B) Linear low-density polyethylene; C) High-density polyethylene

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.

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.

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.

## 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



**Figure 2.** Folded-chain lamellar crystal of polyethylene

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.

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

**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 | $100 \times 10^{-6}$ | | | | ASTM D1531 |
| Volume resistivity, $\Omega \cdot$ m | $10^{16}$ | | | | |
| Dielectric strength, kV/mm | 20 | | | | |

[*] Corrected for effects of long branching by on-line viscometry.
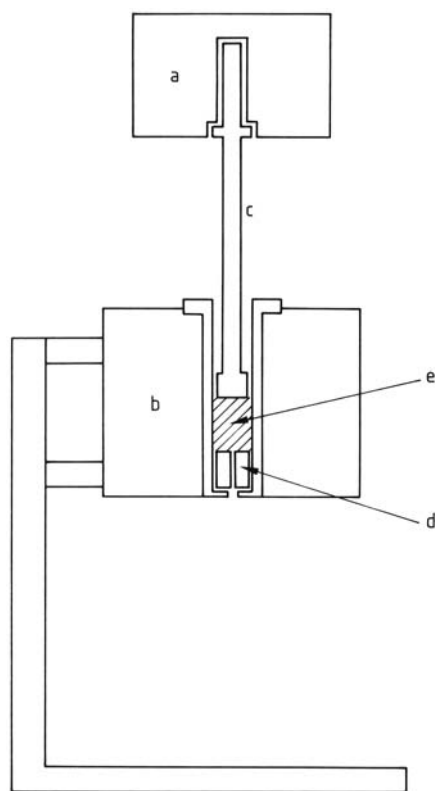[**] Number of methyl groups per 1000 carbon atoms.

**Figure 3.** Melt flow index equipment
a) Interchangable piston loading weight; b) Electrically heated barrel; c) Piston; d) Die; e) Polyethylene melt

higher shear conditions used in processing equipment.

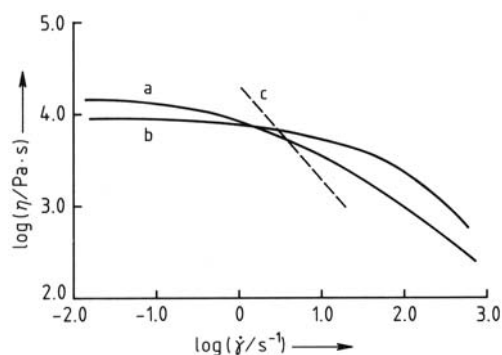As indicated above, the crystalline properties are affected by the rate of cooling from the melt and the subsequent thermal history. For the purposes of reproducibility it is usual to apply a standard annealing treatment to test samples, such as annealing at 100 °C for 5 min followed by slow cooling 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 3.3.3) 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.

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,



**Figure 4.** Dependence of viscosity $\eta$ 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
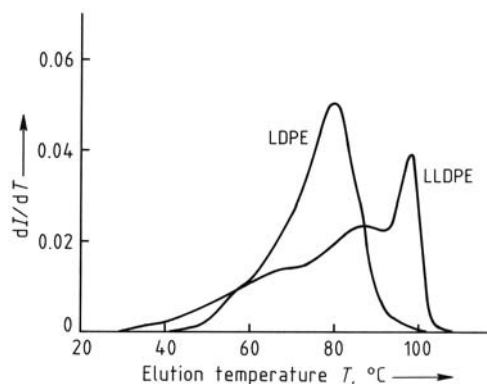


**Figure 5.** Temperature rise elution fractionation curves ($I$ is the cumulative weight fraction)
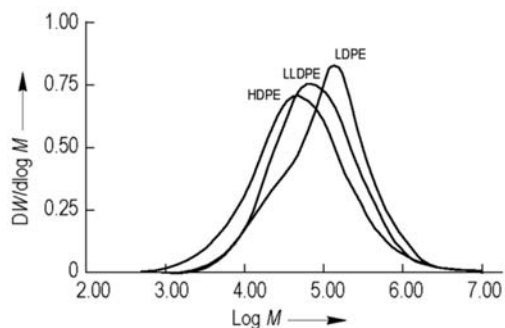
**Figure 6.** Molecular mass distribution curves for the polyethylenes of Table 2 (data from Repsol Quimica)
*I* is the cumulative weight fraction

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
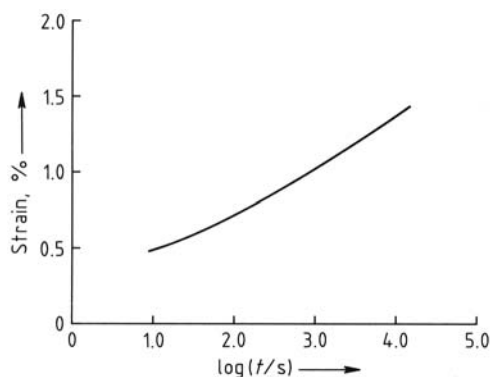
after 10 s. Thus the effective Young's modulus after 4 d is only 25 % of the short-term value and after several years would be lower still. This creep behavior is particularly marked in the case of polyethylenes because the amorphous regions are relatively mobile at room temperature [33]. For design 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].

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). Since permeation takes place in the mobile amorphous phase, the permeability of HDPE is appreciably lower.



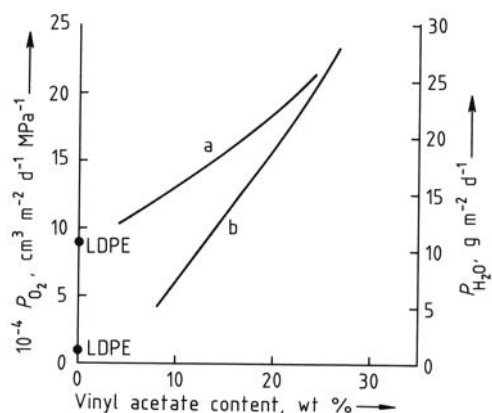**Figure 7.** Tensile creep of HDPE (Rigidex 006–60) [32]



**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.)

Polyethylene is a high molecular mass hydrocarbon which can be considered as toxicologically 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.

## 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 2.1 and 3.3.3), 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.

## 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.

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

| Property | UHMWPE | Method | Standard |
| --- | --- | --- | --- |
| Molecular mass | $4.5 \times 10^6$ | 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, °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 |

## 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 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 $\alpha$-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,
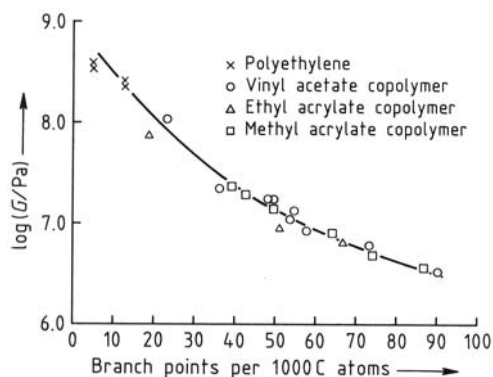


**Figure 9.** Dynamic modulus $G$ (ca. 2 Hz) at 23°C as a function of total branch points

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

**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/m$^3$ | 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, Ω · m | $2.0 \times 10^{15}$ | $2.5 \times 10^{14}$ | | | | |
| Dielectric strength, kV/mm | 19 | 20 | | | | |

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

stiffness similar to that of LDPE at room temperature. However, the stiffness of most ionomers decreases rapidly with increasing temperature above 40 °C. The polyketone (PK) and cycloolefin (COC) copolymers are both recent developments in which 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 3.3.3) and the high transparency and low birefringence will allow its use in compact discs and transparent packaging.

# 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.

## 3.2. Free-Radical Catalysis

### 3.2.1. 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].

The single-phase ethylene – polyethylene mixture allows the reaction to take place as a classical free-radical-initiated solution polymerization (→ Polymerization Processes, 2. Modeling of Processes and Reactors). Some aspects which are particularly important for ethylene systems are as follows:
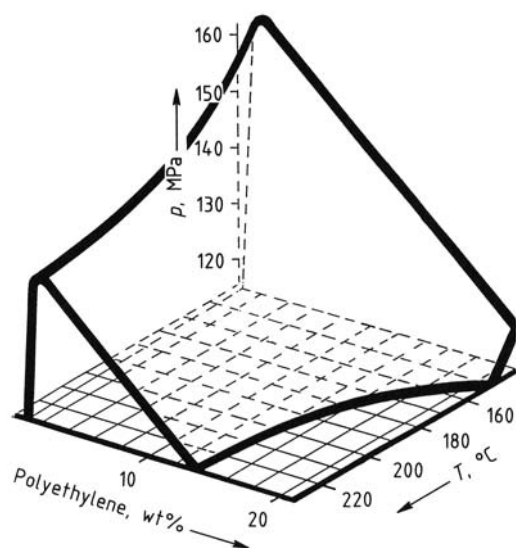
**Figure 10.** Schematic cloud point surface for ethylene – polyethylene [48]

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
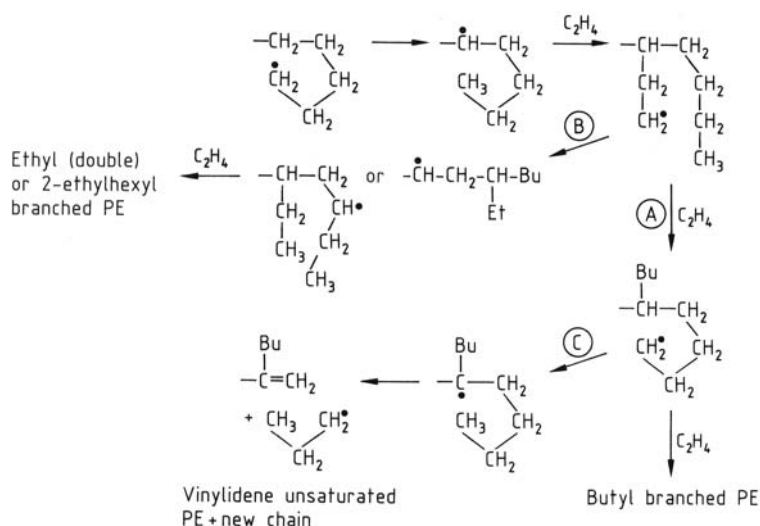
**Figure 11.** Principal intramolecular chain-transfer reactions

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

**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 | $C_2H_5$<br>$\mid$<br>$CH-CH_2-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-CH_2-CH$<br>$\mid$                                 $\mid$<br>$C_4H_9$                                 $C_4H_9$ | 130 | $< -15$ |
| *tert*-Butyl 2,2-dimethylperoxy-propanoate | $\quad\quad CH_3 \quad\quad O \;\; CH_3$<br>$\quad\quad\mid\quad\quad\quad\parallel\;\;\mid$<br>$CH_3-C-O-O-C-C-CH_3$<br>$\quad\quad\mid\quad\quad\quad\quad\;\;\mid$<br>$\quad\quad CH_3\quad\quad\quad\;\; CH_3$ | 154 | $< 0$ |
| Di-(3,5,5-trimethyl-hexanoyl) peroxide | $\quad\; CH_3\quad\; CH_3\quad\; O\quad\quad O\quad\; CH_3\quad\; CH_3$<br>$\quad\;\mid\quad\quad\;\mid\quad\quad\;\parallel\quad\quad\parallel\quad\;\mid\quad\quad\;\mid$<br>$CH_3-C-CH_2-CH-CH_2-C-O-O-C-CH_2-CH-CH_2-C-CH_3$<br>$\quad\;\mid\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\mid$<br>$\quad\; CH_3\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$ | 173 | $-10$ to $0$ |
| *tert*-Butyl 3,5,5-trimethyl-peroxyhexanoate | $\quad\; CH_3\quad\quad O\quad\quad CH_3\quad\; CH_3$<br>$\quad\;\mid\quad\quad\;\parallel\quad\quad\;\mid\quad\quad\;\mid$<br>$CH_3-C-O-O-C-CH_2-CH-CH_2-C-CH_3$<br>$\quad\;\mid\qquad\qquad\qquad\qquad\qquad\mid$<br>$\quad\; CH_3\qquad\qquad\qquad\qquad CH_3$ | 211 | $< +30$ |
| Di-*tert*-butyl peroxide | $\quad\; CH_3\quad\quad CH_3$<br>$\quad\;\mid\quad\quad\quad\;\mid$<br>$CH_3-C-O-O-C-CH_3$<br>$\quad\;\mid\quad\quad\quad\;\mid$<br>$\quad\; CH_3\quad\quad CH_3$ | 244 | $< +30$ |

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 temperatures, 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 inititation-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:

$$C_2H_4 \rightarrow C + CH_4 \;\; \Delta H = 127\,kJ/mol$$

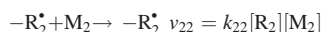$$C_2H_4 \rightarrow 2\,C + 2\,H_2 \;\; \Delta H = 53\,kJ/mol.$$
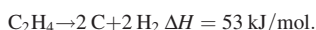
For kinetic reasons these reactions are only important at the high temperature and pressures of the high-pressure process. In a confined sys-tem the large amount of heat released can raise the temperature, and hence the pressure, of the methane and hydrogen to potentially dangerous levels. The theoretical 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.

### 3.2.2. Copolymerization

High-pressure ethylene copolymerization follows the classical free-radical copolymerization mechanism ($\rightarrow$ Polymerization Processes, 2. Modeling of Processes and Reactors). One of the most important characteristics are the

reactivity ratios $r_1$ and $r_2$. The rates $\upsilon$ of the four growth reactions are

$$-R_1^\bullet + M_1 \rightarrow -R_1^\bullet \quad \upsilon_{11} = k_{11}[R_1][M_1]$$

$$-R_1^\bullet + M_2 \rightarrow -R_2^\bullet \quad \upsilon_{12} = k_{12}[R_1][M_2]$$

$$-R_2^\bullet + M_1 \rightarrow -R_1^\bullet \quad \upsilon_{21} = k_{21}[R_2][M_1]$$

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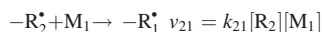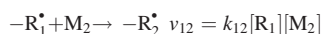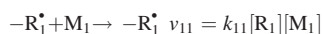
$$r_1 = k_{11}/k_{12} \quad r_2 = k_{22}/k_{21}$$

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

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 im-

plications 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 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 measurements 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.

**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.

## 3.3. Coordination Catalysis

The three independent discoveries of low-pressure routes to linear polyethylene had one thing

Catalyst particle

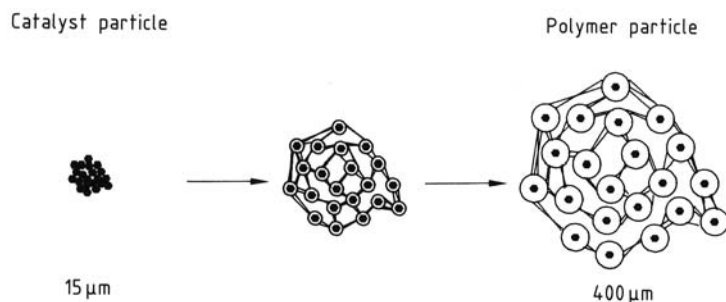Polymer particle



15 µm

400 µm

**Figure 12.** Catalyst particle growth by replication [13]

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.
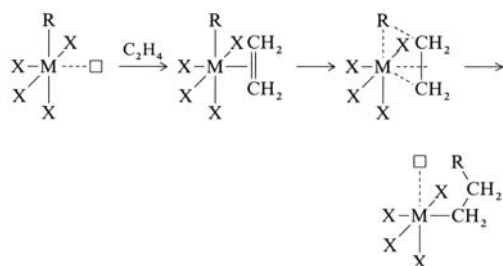


The direct insertion of ethylene into σ-bonded aluminum alkyls was discovered by ZIEGLER in 1950, but the reaction was slow and did not lead to high polymers. The prior coordination of ethylene is clearly crucial. The active species in commercial catalysts is complex, but there is a very large worldwide 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 parti-

cle 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 statistical 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).
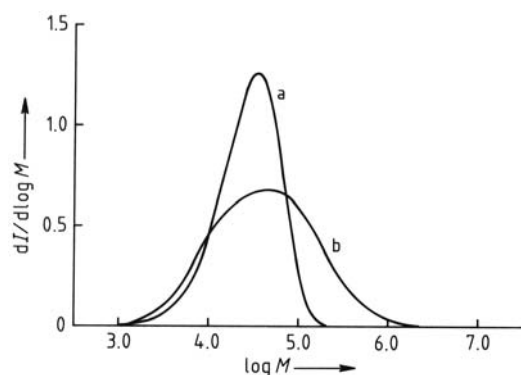
**Figure 13.** MMD curve of a Ziegler HDPE compared with simple statistical theory
a) Most probable distribution; b) Hostalen GD-4755

### 3.3.1. 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
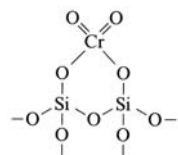


is significant, because at the calcining temperature $CrO_3$ would decompose to lower valent oxides. This catalyst, which is now moisture sensitive, will polymerize ethylene, but with an induction period. During the initial reaction with ethylene the catalyst's color changes from orange to blue. This 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:
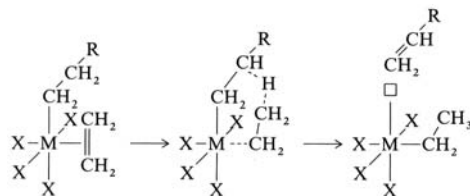


forming an unsaturated molecule and an ethyl ligand attached to the chromium atom [66].

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]. Pariculary 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.

### 3.3.2. 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 → Polypropylene, Chap. 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 $1/3$ 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 particles. 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 $70 – 100\ ^{\circ}$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.

### 3.3.3. 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 3.3). 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 recent developments 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 → Polypropylene), 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 formula below)
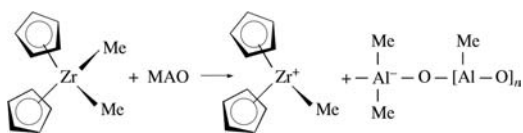


Both metallocene dichlorides and dimethyl forms of the catalysts are frequently described, but MAO transforms the former into methyl-substituted species. Chemical changes have been generally directed to modifying the stereochemical environment of the active center and include changes such as replacing 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:
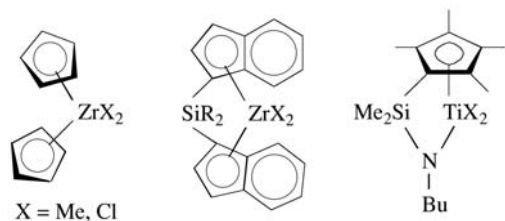


The active sites are tetrahedrally coordinated, in contrast to heterogeneous Ziegler catalysts which are octahedrally coordinated in a $TiCl_3$ or $MgCl_2$ crystal lattice. In principle the greater openness of the tetrahedral configuration allows more ready access to bulkier monomers than the octahedral structure, but the ligands themselves are generally rather large. The improved 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.
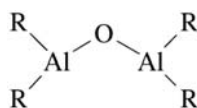


The large excess of MAO found to be necessary to obtain optimum activity in many studies on metallocene catalysts may be due in part to moderately high molar concentration of the cocatalyst needed to generate the active centers. When catalyst and cocatalyst are precontacted at high concentrations and 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 formula above)
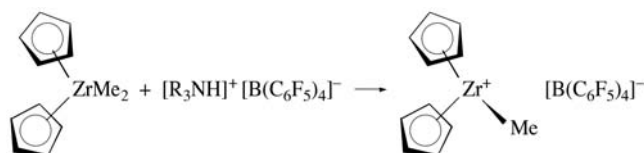
The general aspects of ethylene polymerization with metallocene catalysts are similar to those of Ziegler catalysis: molecular mass control can be effected by chain transfer to hydrogen; at higher temperatures chain transfer by the β-shift reaction produces vinyl groups; metallocene catalysts tend to 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.

### 3.3.4. 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 3.3, 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.

# 4. Raw Materials

## 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.

In the case of the Phillips and Ziegler processes, the materials included in the specification act as catalyst poisons. Hydrogen is a poison only for the Phillips catalyst.

## 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.

## 4.3. Other Materials

The initiators and catalysts are described in Section 3.2. 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

**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.

to be free of aromatic compounds, since much of the product may be used for food packaging.

## 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

**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.

than that of ethylene, from which they are derived by oligomerization.

## 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, 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
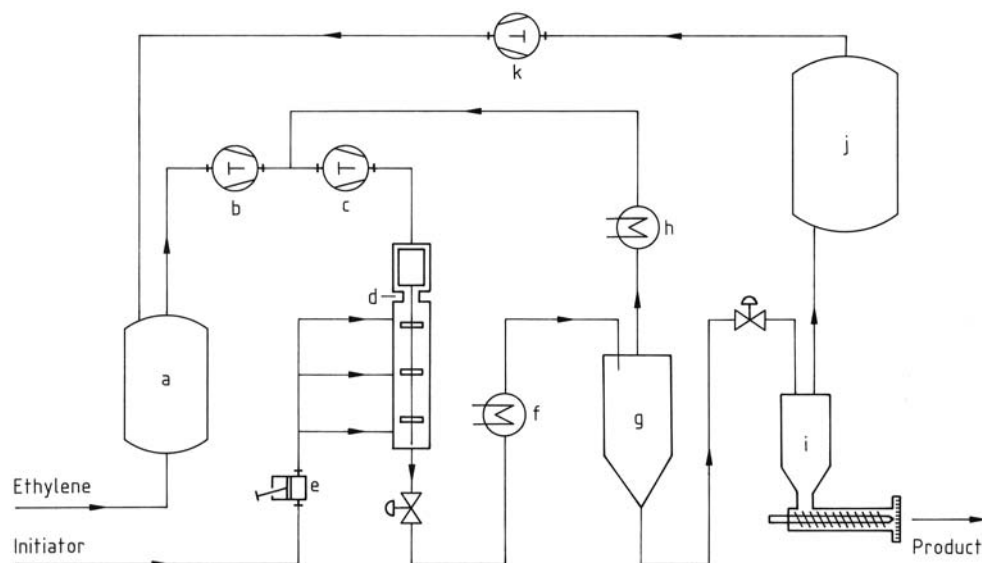
**Figure 14.** High-pressure autoclave process
a) Ethylene stock tank (5 MPa); b) Primary compressor; c) Secondary compressor (200 MPa); d) Autoclave reactor; e) Initiator pumps; f) Product cooler; g) Separator (25 MPa); h) Recycle cooler; i) Low-pressure separator and melt extruder; j) Low-pressure 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

pipework have been developed which make use of the pressure itself to increase the sealing forces [105].

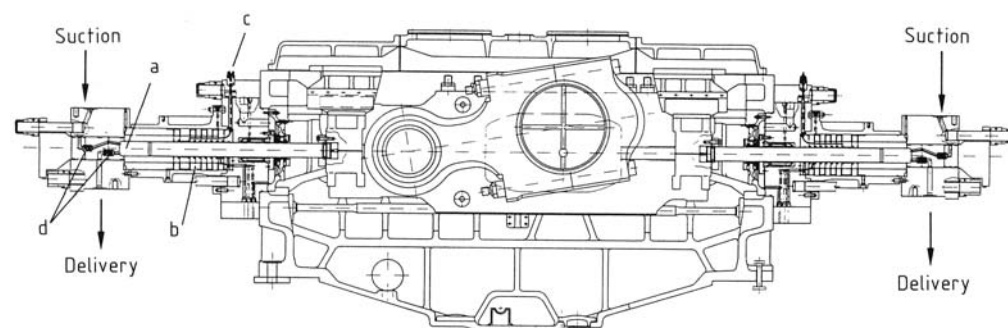Referring to Figure 14, the fresh ethylene enters from the refinery at ca. 5 MPa, mixes with the low-pressure recycle and is compressed to 25 MPa. After mixing with the intermediate-pressure recycle, the pressure is raised in the secondary (or hyper) compressor to 150 – 350 MPa for feeding to the reactor. 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 reduce 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.

### 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 $\geq 1$ 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
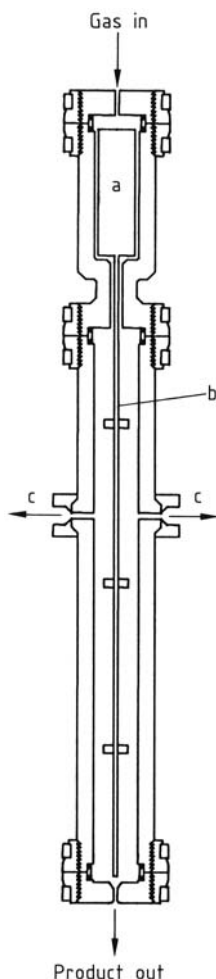


**Figure 16.** High-pressure autoclave reactor
a) Stirrer motor; b) Stirrer shaft; c) Bursting disk ports

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 temperatures 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.

## 5.1.2. Tubular Reactor

A tubular reactor typically consists of several hundred meters of jacketted high-pressure tubing 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 re-quired to carry in oxygen as initiator). Injection of initiator at various positions along the tube produces new temperature peaks, increasing 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.

## 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.

### 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.

### 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/m³.

### 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 m³). 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.

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.
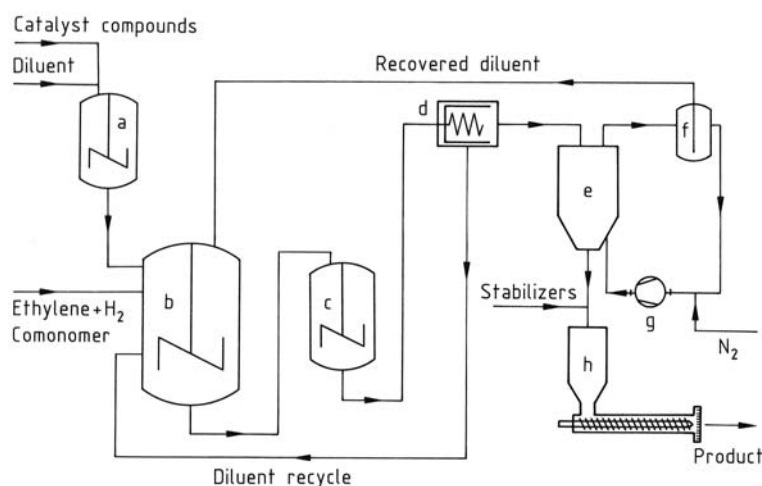


**Figure 17.** Hoechst suspension polymerization process
a) Catalyst preparation vessel; b) Polymerization reactor; c) Run-down reactor; d) Centrifuge; e) Fluidized-bed drier;
f) Diluent condenser; g) Nitrogen circulator; h) Powder-fed extruder

## 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.

## 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 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.
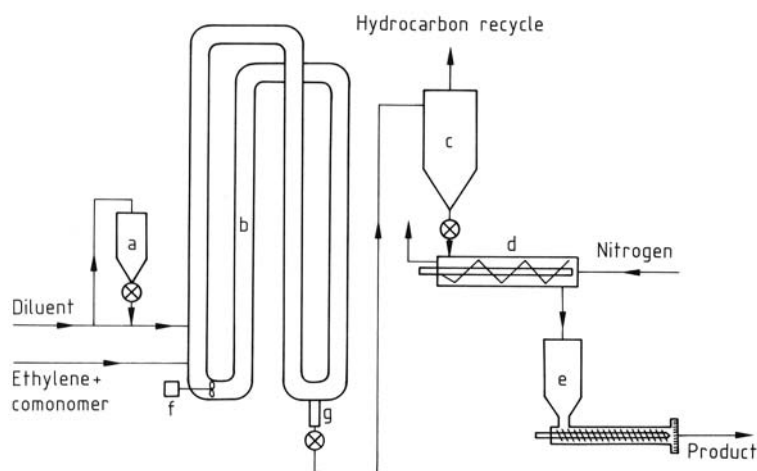


**Figure 18.** Flowsheet of the Phillips Particle Form process
a) Catalyst hopper and feed valve; b) Double loop reactor; c) Flash tank; d) Purge drier; e) Powder-fed extruder; f) Impeller; g) Sedimentation leg
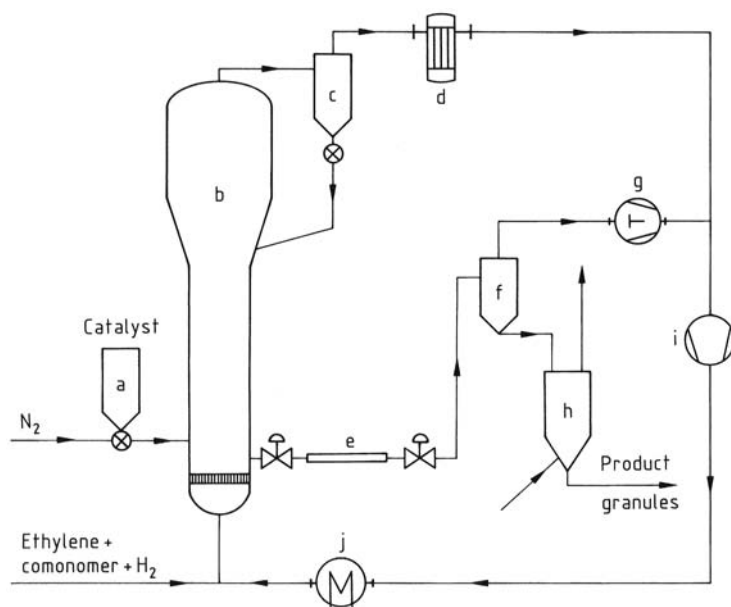
**Figure 19.** Fluidized-bed process
a) Catalyst hopper and feed valve; b) Fluidized-bed reactor; c) Cyclone; d) Filter; e) Polymer take-off system; f) Product recovery cyclone; g) Monomer recovery compressor; h) Purge hopper; i) Recycle compressor; j) Recycle gas cooler

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 controlled to prevent fusion of the particles or a thermal runaway reaction. Catalysts based on microspheroidal silica or $MgCl_2$ with a mean
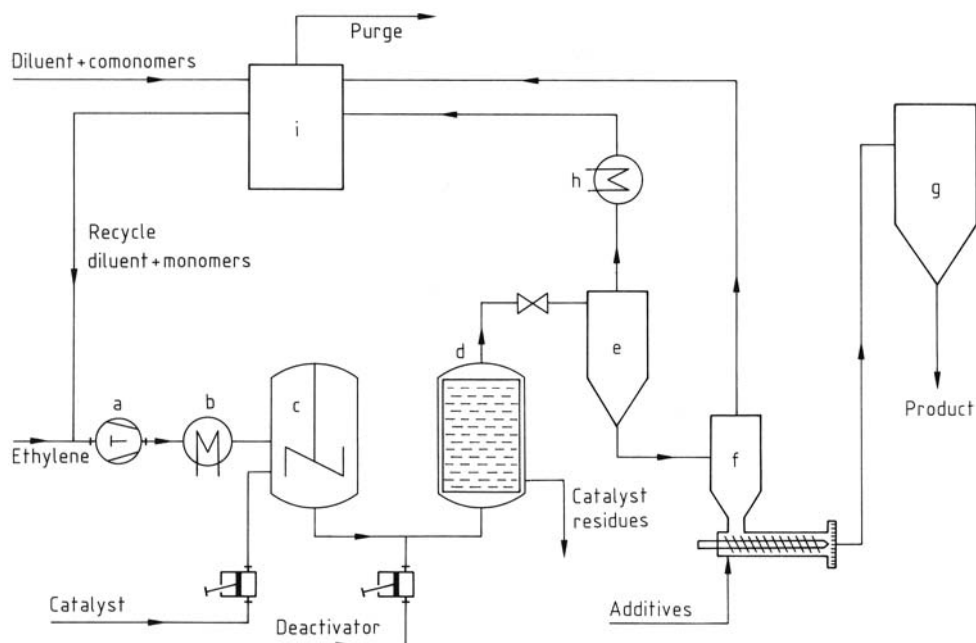
**Figure 20.** Solution polymerization process
a) Reactor feed pump; b) Temperature control; c) Reactor; d) Catalyst adsorber; e) First separator; f) Low-pressure separator and melt-fed extruder; g) Purged product hopper; h) Recycle cooler; i) Diluent and monomer purification unit

particle size of about 50 μm are claimed to be particularly suitable [77].

## 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.

**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].

## 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, 1. Processing of Thermoplastics and so only the aspects particular to polyethylene are discussed here.

### 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 product 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.

## 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$^3$.

## 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].

## 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.

## 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 recent 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].

## 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.

## 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.

## 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. [133, 134, 132].

## 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 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].

# 7. Chemically Modified Polyethylenes

## 7.1. Cross-Linked Polyethylene

As noted in Section 3.2, 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].

## 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.

## 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.

# 8. Environmental Aspects

## 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.

## 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

**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 |

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 non-food 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.

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