POLYETHYLENE, LINEAR LOW DENSITY

1. Introduction

The common commercial name of all resins derived from ethylene is polyethylene (PE) resins. Chemical industry manufactures a variety of PE resins. A large part of them are semicrystalline ethylene–α-olefin copolymers containing a small fraction of an α-olefin. These copolymers are produced in catalytic polymerization reactions and have densities lower than that of ethylene homopolymers. The latter are called high density polyethylene (HDPE) resins; their density is 0.95–0.96 g/cm^3 (see the article "POLYETHYLENE, HIGH DENSITY"). Ethylene–α-olefin copolymers are usually defined as "linear ethylene copolymers" to distinguish them from ethylene polymers containing long branches, which are produced in radical polymerization reactions at a high pressure (see the article "POLYETHYLENE, LOW DENSITY").

Density and crystallinity of ethylene–α-olefin copolymers mostly depend on their composition. The commonly used commercial classification is given in Table 1 according to ASTM D 1248-48.

The last group of the PE resins, very low density polyethylene (VLDPE), is usually further subdivided into PE plastomers, which are resins with low crystallinity, 10–20%, and densities in a 0.915–0.900-g/cm^3 range; and completely amorphous PE elastomers with densities as low as 0.86 g/cm^3.

Commercial production of PE resins in catalytic polymerization reactions started in 1968 in the United States by Phillips Petroleum Company. Over time, these resins, including linear low density polyethylene (LLDPE), became large-volume commodity products. Their combined worldwide production in 2005 reached $\sim 15 \cdot 10^6$ ton/year, which corresponds to ~55% market share of all low density PE resins, the rest being LDPE resins (1). By 2010, the combined LLDPE production is expected to reach $\sim 35–40 \times 10^6$ ton/year. Compositionally uniform LLDPE resins, ethylene–α-olefin copolymers produced with metallocene catalysts, were first introduced by Exxon Chemical Company in 1995. The combined production volume of these resins by several companies in 2005 will exceed 7×10^6 ton/year (1).

A large variety of commodity and specialty resins described by the term LLDPE resins differ in several respects:

1. Type of α-olefin. Four α-olefins are used in industry to manufacture LLDPE and VLDPE resins: 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Copolymers containing 1-butene account for ~40% of all LLDPE resins manufactured worldwide, 1-hexene copolymers for 35%, 1-octene copolymers for ~20%. The type of α-olefin exerts a significant influence on the copolymer properties. Ethylene–1-butene copolymers exhibit somewhat inferior mechanical properties compared to ethylene copolymers with other α-olefins; as a consequence, the share of 1-butene-based resins slowly decreases while the shares of ethylene copolymers with higher α-olefins increase. In addition to α-olefins, ethylene can be copolymerized with cycloolefins such as cyclooctene, dicyclopentadiene, and norbornene. These

materials are called “cycloolefin copolymers” (COC resins). Their properties are described in the article “POLYMERS OF HIGHTER OLEFINS”.

2. Content of α-olefin in copolymer (in engineer’s terminology, the branching degree). It varies in a broad range, from 1 to 2 mol% in MDPE resins to ~20 mol% in PE elastomers. The respective branching numbers are from 4–8 to ~80 CH_3 groups/1000 carbon atoms.
3. Compositional uniformity of ethylene–α-olefin copolymers (in engineer’s terminology, branching uniformity of PE resins). This term describes differences in copolymer compositions between different macromolecules in a given copolymer. Two classes of LLDPE resins are produced. The latest class of ethylene–α-olefin copolymers, introduced in 1990–1995, has a uniform compositional distribution (uniform branching distribution). All copolymer molecules in such a resin have approximately the same composition. In contrast, most commercially manufactured LLDPE resins have a pronounced nonuniform compositional distribution. For example, such a resin with an average content of an α-olefin of 3.0 mol%, is in fact a mixture of macromolecules with the α-olefin content ranging from < 0.3 mol% in the high molecular weight fraction of the resin to > 20 mol% in the fraction with the lowest molecular weight. The LLDPE resins with uniform and nonuniform compositional distributions differ significantly in their physical and mechanical properties.
4. Crystallinity and density. These two parameters, which are closely related, mostly depend on the amount of α-olefin in the copolymer, as shown in Table 1. In addition, both density and crystallinity of ethylene–α-olefin copolymers are significantly influenced by their compositional uniformity, as shown in Table 2. A uniformly branched LLDPE resin of a given density always contains a lower amount of an α-olefin than a nonuniformly branched resin of the same density.
5. Molecular weight. The range of molecular weights of commercial LLDPE resins is relatively narrow, usually from 50,000 to 200,000. The industry-accepted parameter that relates to the resin molecular weight is its melt index (see the definition in the Analytical section). The melt index is a rheologic parameter whose logarithm, in broad terms, is inversely proportional to molecular weight. A typical melt index range for LLDPE resins is from 0.1 to 5.0 g/10 min most often 0.7–1.3 g/10 min but can reach > 30 g/10 min for some resin applications (2-5).
6. Molecular weight distribution. In polymer science, the width of a molecular weight distribution (MWD) is usually represented by the ratio of the weight-average and the number-average molecular weights, M_w/M_n. In industry, the MWD is often represented by the value of the melt flow ratio (MFR). As defined in Analytical section, MFR is the ratio of two melt indexes measured at two melt pressures that differ by a factor of 10. Most commodity-grade LLDPE resins have a narrow MWD, with the M_w/M_n ratios of 2.5–4.5 and with MFR values in a 20–35 range. However, LLDPE resins produced with chromium oxide-based catalysts have a very broad MWD, with the M_w/M_n ratios of 10–35 and MFR values in a range of 80–200.

2. Molecular Structure and Chemical Properties

2.1. Chain Structure. The LLDPE resins are copolymers of ethylene and α-olefins with low α-olefin contents. Molecular chains of LLDPE resins contain monomer units derived both from ethylene, $-CH_2-CH_2-$, and from an α-olefin, $-CH_2-CHR-$, where R is C_2H_5 in ethylene–1-butene copolymers, n-C_4H_9 in ethylene–1-hexene copolymers, $-CH_2-CH(CH_3)_2$ in ethylene–4-methyl-1-pentene copolymers, and n-C_6H_{13} in ethylene–1-octene copolymers. In a typical copolymer molecule containing 2–4 mol% of an α-olefin, most of the α-olefin units stand alone in a copolymer chain and most ethylene units form long sequences (blocks). Usually one of the chain ends in an LLDPE molecule is the methyl group; the other chain end is either the methyl group or a double bond, the vinyl group, $CH_2{=}CH-$, or the vinylidene group, $CH_2{=}C<$.

As a rule, LLDPE resins do not contain long-chain branches. However, some ethylene–α-olefin copolymers produced with metallocene catalysts can contain up to ~0.002 long-chain branches/100 ethylene units (6,7). These branches are formed in auto-copolymerization reactions of ethylene with copolymer molecules containing vinyl double bonds on their ends (6,8).

2.2. Compositional Uniformity. The LLDPE resins produced with different catalysts vary greatly in their compositional uniformity. The fastest way to estimate the branching distribution of an LLDPE resin is to measure its melting point. By definition, if a copolymer has a uniform compositional distribution, all its molecules have approximately the same composition. Melting points of such copolymers show a noticeable dependence on their composition: they decrease from ~135°C for the ethylene homopolymer to ~120°C for a copolymer containing 1.5–2 mol% of α-olefin and to ~110°C for a copolymer containing 3.5 mol% of α-olefin. On the other hand, a copolymer with a nonuniform compositional distribution is a mixture containing copolymer molecules with a broad range of compositions, from practically linear macromolecules with very low α-olefin contents to copolymer macromolecules with quite high α-olefin contents. Melting of such mixtures is dominated by their fractions with the lowest α-olefin content, which are highly crystalline. As a result, the melting points of LLDPE resins with the nonuniform branching distribution are not very sensitive to the copolymer composition and usually are in a 125–128°C range (6). Figure 1 compares melting curves of two copolymers with the same average compositions, but with a different degree of compositional uniformity.

The fraction of a nonuniformly branched resin with the highest α-olefin content has a low molecular weight and is soluble in saturated hydrocarbons, even at room temperature. This fraction is called the “extractable” fraction. An excessive amount of the extractable material in an LLDPE resin can be detrimental to some of its end-use properties, especially in food packaging.

2.3. Chemical Properties and Reactivity. An LLDPE resin is a saturated branched hydrocarbon. The most reactive parts of LLDPE molecules are tertiary CH bonds in its branches. These resins do not react with inorganic and organic acids, but form sulfo compounds in concentrated solutions of H_2SO_4 (>70%) at elevated temperatures and are nitrated with concentrated HNO_3. Linear low density polyethylene is stable to alkaline and salt solutions.

At room temperature, these resins are not soluble in any known solvent, except for their extractable fractions, but the resins can be dissolved $> 80-100°C$ in many aromatic, aliphatic, and halogenized hydrocarbons such as xylenes, tetralin, decalin, and chlorobenzenes. This resin is very poorly permeable to water and inorganic gases and only slightly better permeable to organic compounds, both liquids and gases.

Thermal, Thermooxidative, and Photooxidative Degradation. Linear low density polyethylene is relatively stable to heat. Its thermal degradation starts at temperatures $> 250°C$ and results in a gradual decrease of molecular weight and the formation of double bonds in polymer chains. At temperatures $> 450°C$, LLDPE is pyrolyzed with the formation of isoalkanes and olefins.

Thermooxidation of LLDPE starts at temperatures $> 150°C$. This reaction produces hydroxyl and carboxyl groups in polymer molecules as well as low molecular weight compounds: water, aldehydes, ketones, and alcohols. The oxidation reactions can occur during LLDPE pelletization and processing. To protect molten resins from oxygen attack during these operations, antioxidants (radical inhibitors) are used, such as naphthylamines or phenylenediamines, substituted phenols, quinones, and alkylphosphites (6,9). Antioxidants are added to LLDPE resins in a 0.1–0.5 wt% concentration. Inhibitors based on hindered phenols are preferred. Photooxidative degradation of LLDPE at an ambient temperature under sunlight is also a radical oxidation reaction. It causes a change in color and a drastic deterioration of mechanical and dielectric properties of LLDPE articles. Photooxidation can be arrested by the use of light stabilizers. They protect the resins by absorbing ultraviolet (uv) radiation and terminating radical chain reactions. A large number of antioxidants and uv stabilizers is manufactured by the chemical industry: American Cyanamid, BASF, Ciba–Geigy, Eastman Chemical, Elf Atochem, Enichem, General Electric, Hoechst–Celanese, Sandoz, Uniroyal.

3. Physical Properties

3.1. Crystallinity. Linear low density polyethylene is a semi-crystalline plastic. Its chains contain long blocks of ethylene units that crystallize in the same fashion as HDPE. The degree of LLDPE crystallinity depends primarily on α-olefin content in a copolymer, it is usually $< 40-45\%$, see Table 1. The principal crystalline form of LLDPE is orthorhombic, the same as in HDPE. The cell parameters of linear PE are $a = 0.740$ nm, $b = 0.493$ nm, c (the direction of polymer chains) $= 0.2534$ nm. Introduction of branching into PE molecules expands the cell slightly: a increases to 0.77 nm and b to $\sim$0.50 nm.

Linear low density polyethylene rapidly crystallizes from the melt with the formation of spherulites, small spherical objects 1–5 μm in diameter visible under the microscope. The elementary structural blocks in spherulites are lamellae, small flat crystallites formed by folded linear segments in LLDPE chains. Lamellae are interconnected by polymer chains that pass from one lamella to another. These chains, called tie molecules, hold together neighboring lamellae and provide mechanical integrity and strength of spherulites. Numerous tie molecules also connect adjacent spherulites. Crystalline lamellae within spherulites and between spherulites give LLDPE articles necessary rigidity, whereas large amorphous regions between lamellae, which constitute $> 60\%$ of the spherulite volume, provide flexibility. The presence of α-olefin monomer units in LLDPE molecules inhibits uniform folding of polyethylene chains during crystallization. The effect of this hindrance is twofold: It decreases the lamella thickness and increases the number of interlamellar tie molecules.

The size of the lamellae for a copolymer of a given composition strongly depends on the degree of compositional uniformity. If an LLDPE resin is compositionally uniform, all its macromolecules crystallize equally poorly due to chain branching. They form very thin lamellae. Such materials have low rigidity (low tensile modulus) and are very flexible. On the other hand, if an LLDPE resin is compositionally nonuniform, its least-branched components form thicker lamellae while more highly branched fractions of the resin remain amorphous and fill the voids between the lamellae. Articles made from such resins are more rigid.

3.2. Thermal Properties. The projected equilibrium melting point of completely linear PE is 146–147°C and its actual highest melting point is ~138°C. In the case of ethylene–α-olefin copolymers with a uniform compositional distribution, the melting point strongly decreases with an increase of the α-olefin content in a copolymer and a decrease of its density; see Figure 2. Melting points of most commercially significant uniformly branched LLDPE resins are in a 115–120°C range and, for VLDPE resins, in an 80–110°C range. On the other hand, the melting points of compositionally nonuniform LLDPE products are not very sensitive to the average copolymer composition and usually range from 125 to 128°C. The brittle point of LLDPE is very low, from -100 to -140°C.

3.3. Electrical and Optical Properties. Linear low density polyethylene is a saturated aliphatic hydrocarbon. Consequently, it does not conduct electricity and is widely used for wire and cable insulation. Optical properties of LLDPE resins strongly depend on the degree of their branching uniformity. The resins with a uniform branching distribution make highly transparent film with low haze, 3–4%. The film manufactured from compositionally nonuniform copolymers is much more opaque due to the presence of large crystalline lamellae consisting of nearly unbranched PE chains; its haze is >10–15%.

3.4. Mechanical Properties. Mechanical characteristics of ethylene copolymers are a function of the following structural characteristics:

Content of α-Olefin. An increase in an α-olefin content results in a decrease of crystallinity and density and is accompanied by a significant reduction of the polymer mechanical modulus (stiffness). This effect is especially strong for LLDPE resins with uniform branching distribution, as an example of ethylene–1-octene copolymers demonstrates (6):

1-octene content, mol%	0.4	3.3	~18
density, g/cm^3	0.94	0.910	0.856
modulus, MPa	~500	~100	1.3

The same effect exists in the case of LLDPE resins with the nonuniform branching distribution, although such resins are more rigid overall. For example, the modulus of ethylene–1-butene copolymers with a nonuniform compositional distribution decrease as (6,10):

1-butene content, mol%	0	3.0	8.0
crystallinity, %	~60	~40	~25
density, g/cm^3	0.96	0.92	0.89
modulus, MPa	~1500	~240	~60

An increase in the α-olefin content also results in a decrease of the tensile strength and a small increase of the elongation at the breaking point. These two dependencies are not as pronounced as that for the modulus.

Type of α-Olefin. When the resins of the same density and crystallinity are compared, ethylene–1-butene copolymers show somewhat inferior mechanical properties compared to ethylene copolymers with higher α-olefins. These differences are most clearly manifested when one compares the properties of a thin film made of LLDPE. Table 3 gives the principal mechanical properties of eight film samples manufactured from three types of LLDPE, ethylene copolymers with 1-butene, 1 hexene, and 1-octene, all with a nonuniform compositional distribution. Tensile properties of all the resins are quite similar and show the above-described trends with density. However, the measure of film strength commonly used in industry, the dart impact strength of a film, gives a different picture. The dart impact measurement is equivalent to a tensile test at a very high stretching speed, as described in the Analytical section. The average dart impact strength of a 25-μm blown film made from ethylene–1-butene copolymers is 80–90 g, whereas the same parameter for blown film from common ethylene–1-hexene copolymers is 130–180 g and reaches 400–600 g in the case of ethylene–1-octene copolymers of the same density (2-5,10). The second commonly used technical measure of LLDPE properties, the tear strength of film shows the same trend, as shown in Table 3: ethylene–1-butene copolymers are inferior to ethylene–1-hexene and ethylene–1-octene copolymers.

Branching Uniformity (Compositional Uniformity). A comparison of uniformly and nonuniformly branched ethylene–1-hexene LLDPE resins of the same density (Table 4) shows that the uniformly branched resins are less rigid and have somewhat lower tensile properties, but exhibit a superior dart impact strength. The differences in the tensile properties become even more pronounced in the case of VLDPE resins (Table 5): the modulus of uniformly branched ethylene–1-octene copolymers with density of ~0.91 g/cm^3 is reduced by a factor of 2 compared to that of nonuniformly branched resins, a significant advantage for many applications of VLDPE resins. Uniformly branched resins are also much more elastic: Their strain recovery is nearly complete (10).

Molecular Weight and Molecular Weight Distribution. As a rule, an increase of the molecular weight of an ethylene–α-olefin copolymer (corresponding to a decrease of its melt index) results in significant improvement of its mechanical properties, in particular, the dart impact strength. Most LLDPE resins used for the film manufacture have a relatively narrow MWD: their M_w/M_n values are ~4.0 and their MFR values are in a 28–30 range. However, the MWD width can be reduced even further through a selection of special catalysts and fine tuning of polymerization processes. When the M_w/M_n value is decreased to 3.5 and the MFR value to 25–27, it results in an additional significant improvement in the film properties: the dart impact strength increases 2.5 times and the tear strength improves by >25% (11).

The LLDPE resins with a very broad MWD also can have superior mechanical strength. This occurs when the copolymers have a significant fraction of macromolecules with very high molecular weights. These molecules, called tie molecules, serve as links between polymer crystallites and strengthen LLDPE spherulites. Such LLDPE resins with densities of 0.925–0.900 g/cm^3 and melt indexes ranging from 0.05 to 0.35 are produced with chromium-based catalysts (6,12). The MFR values of these resins are in an 80–200 range. Due to higher molecular weights of the resins, the film manufactured from them also has high dart impact strength.

Orientation. Orientation has a significant beneficial effect on mechanical properties of LLDPE, especially in the case of LLDPE film. During film manufacture, a bubble of molten polymer exits a circular die with a narrow gap and immediately expands yielding to the pressure of air charged inside the bubble. The degree of expansion is usually given as a blow-up ratio, the ratio of the film bubble diameter to the die diameter. Film expansion induces significant orientation of polymer molecules in the plane of the film and improves its mechanical properties, as the following data for ethylene–1-hexene copolymer with the 0.917-g/cm^3 density and the 0.9 melt index demonstrate (11).

blow-up ratio	1.8	2.0	2.2	2.5
dart impact strength, g	170	178	220	280

Both techniques for the manufacture of LLDPE film, blowing and casting, produce nonuniform orientation in the film. As a result, mechanical properties of blown and cast LLDPE and VLDPE film are different in two directions, the direction of film manufacture (the machine direction) and perpendicular to it (the transverse direction), as shown in Tables 3-5.

4. Catalysts for LLDPE Production

The LLDPE resins are produced in industry with three classes of catalysts (6,13-15): titanium-based Ziegler catalysts, Phillips catalysts based on chromium oxides, and several types of metallocene-based catalysts.

4.1. Ziegler Catalysts. These catalyst systems account for the greatest share of LLDPE resins manufactured by industry, $> 75\%$. The catalysts consist of two components. The first component contains, as its active ingredient, a derivative of a transition metal, usually titanium, and the second component is an organoaluminum compound such as triethylaluminum (6,13-15). The molar [Al]/[Ti] ratio in these catalysts is usually held in a 50–500 range. Most commercially important catalysts are heterogeneous, and a large number of them are supported. The most important supports are $MgCl_2$, Mg(OH)Cl, silica, alumina, and MgO (6,16,17). Titanium compounds used for the manufacture of these catalysts are usually $TiCl_4$ or $Ti(OR)_4$. Catalysts with the highest activity contain a combination of titanium chlorides and $MgCl_2$. Titanium compounds are deposited into the support pores or they are anchored to the active groups, such as OH, on the support surface. Examples of supported catalysts include $TiCl_3$ on the surface of $MgCl_2$ or coprecipitated complexes of Ti chlorides and $MgCl_2$ within pores of inert carrier particles (6,18).

Typical heterogeneous Ziegler catalysts operate at temperatures in a 70–100°C range and at pressures of 0.3–2 MPa (50–300 psi). The polymerization reactions are carried out in an inert liquid medium, eg, isobutane, hexane, cyclohexane, or in the gas phase. Molecular weights of LLDPE resins are controlled by using hydrogen as a chain-transfer agent.

A necessary prerequisite for any catalyst for the LLDPE synthesis is its efficiency in copolymerizing α-olefins with ethylene. Ethylene has the highest reactivity among all olefins in catalytic polymerization reactions. As a consequence, a relatively high α-olefin concentration in a polymerization reactor is usually required to produce copolymers containing merely 3–4 mol% of α-olefin units. Reactivities of α-olefins in copolymerization with ethylene depend on two factors, the size of the alkyl group R attached to the double bond, $CH_2{=}CH{-}R$, and the type of the catalyst (6,19). Figure 3 shows the dependence of the relative reactivities of linear α-olefins in copolymerization with ethylene on the length of their alkyl groups (6). Only linear olefins with the smallest alkyl groups, 1-butene, 1-hexene, and 1-octene, can be relatively easily copolymerized with ethylene under commercial conditions.

All solid Ziegler catalysts contain mixtures of active centers of different types and produce compositionally nonuniform ethylene–α-olefin copolymers. Some of the active centers in these catalysts exhibit very low copolymerization ability and produce nearly linear PE while other centers incorporate α-olefins into copolymer chains quite efficiently and produce copolymer molecules with high α-olefin contents. The presence of several types of active centers in the catalysts also accounts for a relatively broad MWD of the copolymers. Subtle manipulation of relative fractions of various active centers in a catalyst can result in a significant improvement in mechanical properties of the copolymers. Table 4 gives one example of such an effect (11) when a relatively small change in the composition of a catalyst system produced a resin with a narrower MWD and with superior film properties. In another case, a specially designed catalyst system produced LLDPE resins with a pronounced high molecular weight component in their MWD (20). These resins also have noticeably improved mechanical properties.

4.2. Dual Ziegler Catalysts. The use of a particular α-olefin in commercial LLDPE manufacture is dictated by two variables: the desired resin properties and the cost and availability of an α-olefin. A special type of Ziegler catalysts, dual catalysts, allow the manufacture of ethylene–1-butene LLDPE resins from a single monomer source, ethylene (21). These catalyst systems contain two separate catalyst species, one for ethylene dimerization into 1-butene, usually a combination of $Ti(OR)_4$ and $Al(C_2H_5)_3$, and another for copolymerization of ethylene and the generated 1-butene.

4.3. Chromium Oxide-Based Catalysts. Phillips Petroleum Company originally developed chromium oxide-based catalysts for the manufacture of HDPE resins. Later, these catalysts were modified for ethylene–α-olefin copolymerization reactions (6,12). The catalysts use a mixed silica–titania support containing from 2 to 20 wt% of Ti. After deposition of chromium species onto the support, the catalyst is first oxidized by an oxygen–air mixture and then reduced at increased temperatures with carbon monoxide. The catalyst systems used for ethylene copolymerization consist of solid catalysts and cocatalysts, trialkylboron or trialkylaluminum compounds. Ethylene–α-olefin copolymers produced with these catalysts have broad molecular weight distributions characterized by M_w/M_n ratios in a 12–35 range and MFR values from 80 to 200.

4.4. Metallocene Catalysts. In 2004, ~ 15% of LLDPE in the United States was manufactured using metallocene catalysts; this fraction is expected to increase to ~25% by 2010. Several types of metallocene catalysts are presently used in industry (Fig. 4). The first type is called Kaminsky metallocene catalysts, the original metallocene catalyst systems. They contain two components, a bis(metallocene) complex of zirconium, titanium, or hafnium with two cyclopentadienyl rings, and methylaluminoxane (MAO) (6,14) Fig. 4a; The MAO is an oligomeric organoaluminum compound; it has the formula $[-O-Al(CH_3)-]_n$ with $n = 4-20$. Methylaluminoxane is manufactured by hydrolysis of trimethylaluminum (6,14,22). A large number of metallocene complexes can be used in Kaminsky catalysts. Their rings contain various alkyl substituents, both linear and cyclic, and the two rings can be linked together by bridging groups, see Figure 4a. Catalysts based on zirconocene complexes are preferred due to their exceptionally high activity in ethylene polymerization reactions and relatively high stability under polymerization conditions. The Kaminsky catalysts operate at the [Al]/[Zr] ratios of at least 100, but preferably > 1000. These catalysts are very sensitive to the presence of hydrogen, which greatly reduces molecular weights of polymers.

Most Kaminsky catalysts contain only one type of active center; they are often called single-site catalysts. They produce ethylene–α-olefin copolymers with a uniform compositional distribution and a quite narrow MDW which, at limit, is characterized by the M_w/M_n ratio of ~2.0 and the MFR value of ~15. These features of the catalysts determined their first applications: synthesis of uniformly branched VLDPE resins and completely amorphous PE elastomers. Presently, these catalysts are competing with Ziegler catalysts in the manufacture of commodity LLDPE products. Kaminsky catalysts also copolymerize ethylene with cyclic olefins such as cyclopentene, norbornene, etc. These copolymers are also compositionally uniform. Their properties are presented in the article "POLYMERS OF HIGHER OLEFINS".

The second class includes ionic metallocene catalysts containing cations derived from bis(metallocene) complexes of zirconium or titanium and anions of perfluorinated boronaromatic compounds (6,23). The simplest representative of such catalysts is an ion pair shown in Figure 4b (24). These catalysts do not need any organoaluminum compounds; however, monomers of high purity are required to prevent catalyst poisoning. These catalysts operate in a very broad range of temperatures, from −70 to +100°C. The ethylene copolymers they produce also have high compositional uniformity.

The third class of metallocene catalysts is called constrained-geometry catalysts (6,25-27). These catalyst systems contain monocyclopentadienyl derivatives of titanium or zirconium. One of the carbon atoms in the cyclopentadienyl ring and the metal atom are additionally linked by a bridge. The complexes are converted to polymerization catalysts by reacting them with MAO or by forming ionic complexes with noncoordinative anions such as $[B(C_6F_5)_4]^-$ and $[B(C_6F_5)_3CH_3]^-$ shown in Figure 4c (25-27). Constrained geometry catalysts contain only one type of active center and produce compositionally uniform ethylene−α-olefin copolymers (6,7). The catalysts operate at temperatures up to 160−180°C. They have two important distinctions:

1. The catalysts have a very high ability to copolymerize linear α-olefins with ethylene. Consequently, when these catalysts are used in solution-type polymerization reactions, they also copolymerize ethylene with polymer molecules containing vinyl double bonds at their ends. This autocopolymerization reaction produces LLDPE molecules with long-chain branches that account for many beneficial processing properties of the resins (6,8,25,26).
2. Constrained geometry catalysts can copolymerize ethylene with styrene and sterically hindered olefins (27).

The fourth type of metallocene-based catalysts uses complexes of a transition metal, usually titanium, containing one cyclopentadienyl ligand and some other ligands, such as a phosphinimine ($-N{=}PR_3$) or $-O-SiR_3$ (28,29). These complexes are also activated with MAO or with boron compounds. They are successfully used in commercial ethylene−1-octene copolymerization reactions at increased temperatures. The catalysts produce compositionally uniform copolymers and, depending on cocatalyst, resins with either narrow or broad MWD.

4.5. Catalysts Based on Other Complexes of Transition Metals. The latest addition to the family of ethylene polymerization catalysts is a group of organometallic complexes of various transition metals. These complexes are usually activated with the same cocatalysts as the metallocene complexes, predominantly with MAO. A variety of ligands in the complexes were tested (30). Depending on the nature of the ligand and the transition metal, these catalysts can be either single- or multisite catalysts. Most of these catalyst systems are still in the area of academic research. However, the first examples of the use of these catalysts for the synthesis of compositionally uniform LLDPE resins in solution and gas-phase processes have been published already (31).

5. Polymerization Processes

The technologies suitable for the LLDPE manufacture include gas-phase fluidized-bed polymerization, polymerization in solution, polymerization in a polymer melt under very high ethylene pressure, and slurry polymerization. Most catalysts are fine tuned for a particular processes. The significance of various technologies is reflected in the following numbers:

Process	Fraction of U.S. production in 2001–2002, %
gas phase	~70
solution	~23
slurry	~7

5.1. Gas-Phase Polymerization Processes. The first gas-phase, fluidized-bed process for the production of LLDPE was built by Union Carbide Company in 1977. Presently, two technologies compete worldwide, the Unipol process licensed by Univation Company, ~70% of the market; and the Innovene process licensed by British Petroleum Company, ~20% of the market. The gas-phase processes are economical, flexible, and afford the use of a large variety of supported catalysts. The first LLDPE products manufactured with gas-phase technology were ethylene–1-butene copolymers. 1-Butene was selected for two reasons: (1) because it was the least expensive comonomer that afforded the synthesis of LLDPE resins with mechanical properties superior to those LDPE, and (2) because it had a low dew point and did not condense in a gas-phase reactor. These resins are presently the staple of the large-volume commodity LLDPE market. Most gas-phase LLDPE producers later modified the technology and introduced a series of more advanced resins, called high strength LLDPE, which were required for high performance markets. These products utilize higher α-olefins: 1-hexene and 4-methyl-1-pentene. All these resins are manufactured with Ziegler catalysts and have a pronounced nonuniform branching distribution. Properties of two grades of LLDPE film resins produced in gas-phase processes, 1-butene- and 1-hexene-containing copolymers, are compared in Table 3. Impact strength, tear strength, and puncture energy of film produced from 1-hexene-derived LLDPE resins are substantially higher than those of 1-butene copolymers.

The gas-phase processes are suitable for the production of HDPE, LLDPE, and VLDPE resins (6,32,33). The diagram of the Unipol process is shown in Figure 5 (34). The reactor is a cylindrical tower with a height up to 25 m and with a length/diameter ratio of ~7. It usually operates at pressures of 1.5–2.5 MPa (220–360 psi) and temperatures from 70 to 90–95°C. The reactor is filled with a bed of dry polymer particles vigorously agitated by a high velocity gas stream, a mixture of ethylene, an α-olefin, nitrogen, and hydrogen, which is used for the molecular weight control. The gas stream enters the reactor through a perforated distribution plate at the reactor bottom. Rapid circulation serves two purposes, fluidization of the particle bed and the removal of heat of polymerization. The unreacted gas stream enters an expanded disengagement zone at the top of the reactor, separates from the entrained polymer particles, and then is compressed, cooled, and recycled. In some cases, the gas mixture can be cooled below its dew point. Such a gas stream carries fine droplets of liquid α-olefin into the reactor where they rapidly evaporate (32). Operation in the condensing mode increases the heat-removing capacity of the circulating stream.

A solid catalyst in a form of small spherical particles is continuously fed into the reactor above the distribution plate, either as a powder or slurry in a high boiling mineral oil. A solution of a cocatalyst, usually triethylaluminum, is charged to the bottom of the reactor. Catalyst particles remain in the reactor, on average, for 2.5–3 h. The particles gradually increase in size due to polymerization reaction; they can grow to an average size of 400–700 μm, but retain their spherical shape. Granular resin is continuously removed from the reactor and transferred into a series of vessels where it is stripped of ethylene and the α-olefin and then pelletized.

Fluidized-bed reactors are highly versatile with respect to the type of a polymerization catalyst they can accommodate. Most of the catalysts currently used for LLDPE production are supported heterogeneous Ziegler catalysts. The gas-phase process can also accommodate supported metallocene catalysts that produce compositionally uniform LLDPE resins (6,35,36).

Basell Company has developed a similar gas-phase polymerization technology that combines two different reactor types, a small slurry prereactor followed by one or two gas-phase fluidized-bed reactors (37). This process utilizes a special Ziegler catalyst that produces LLDPE resins in a form of large dense spherical particles, up to 4–5 mm in diameter, which do not require postproduction pelletization. Commercial production of these resins, called Spherilene LLDPE, began in 1993.

5.2. Solution Polymerization Processes.

Two types of solution polymerization technologies are used for LLDPE synthesis. The first processes utilize hydrocarbon solvents while the processes of the second type are carried out in mixtures of supercritical ethylene and molten PE as a polymerization medium. Original solution processes were introduced for the low pressure manufacture of PE resins in the late 1950s. Subsequent improvements of these processes gradually made them economically competitive with later more advanced technologies. In the early 1990s, solution processes acquired a new importance due to two factors:

1. Many heterogeneous multicenter Ziegler catalysts produce superior LLDPE resins with a better branching uniformity if the catalyst residence time in a reactor is short. Solution processes usually operate at residence times of the order of 5–10 min and are well suited to take advantage of this catalyst behavior.
2. Solution processes, both in hydrocarbon solvents and in the polymer melt, are inherently suitable to accommodate soluble metallocene catalysts (6,28,29). For this reason, these processes were the first to employ metallocene catalysts for LLDPE and VLDPE manufacture.

Commercial solution processes are practiced by Dow Chemical Company in low pressure reactors and by Nova Chemicals LP in medium pressure reactors, based on DuPont Sclair technology (33). The PE becomes soluble in saturated C_6–C_{10} hydrocarbons > 120–130°C. The original DuPont process scheme (Fig. 6) uses cyclohexane as a solvent (33) while the Dow solution process uses a mixture of saturated C_8–C_{10} hydrocarbons (6,7,38). In the Dow process, ethylene and hydrogen are combined in a single stream and introduced into a liquid mixture containing the solvent and a comonomer, 1-octene. In the solution processes, the solvent–monomer stream is continuously fed into the reactor; catalyst components are also premixed and continuously injected into the reactor. Copolymerization reactions are carried out in the temperature range of 130–200°C at reactor pressures of 3–20 MPa (430–3000 psi) and at the 8–10% ethylene content in the reactor. After 5–10 min, the product stream leaves the reactor and is discharged into a vessel where the molten polymer is separated from unreacted monomers, hydrogen, and the solvent, after which the resin is pelletized (7,28,29). Three properties of LLDPE resins are controlled independently: the molecular weight, the copolymer composition, and, in the case of metallocene catalysts, the degree of long-chain branching. The following parameters are used to control the process: the temperature, the pressure, monomer and polymer concentrations, the residence time, and the catalyst concentration. Dow Chemical Company manufactures two types of LLDPE products with this process. The first type, called Dowlex resins, are ethylene–1-octene resins with a nonuniform branching distribution produced with Ziegler catalysts, and the second type of resins, called Affinity resins, are uniformly branched VLDPE ethylene–1-octene resins produced with metallocene constrained-geometry catalysts.

Due to short residence times and the presence of streams of dissolved polymers, the solution processes are very flexible. One option is combining polymer solutions exiting from two different reactors into a single batch. For example, solutions of compositionally uniform and nonuniform copolymers of similar molecular weights can be mixed to produce resins with greatly improved combinations of end-use properties. Another option, developed by Nova Chemicals LP and called Advanced SclairTech is a dual-reactor system that affords synthesis of two polymer fractions under different reaction conditions or with two different catalysts, one metallocene and the second one a Ziegler catalyst (39). Several LLDPE resins currently on the market, such as Elite resins manufactured by Dow Chemical Company and Surpass LLDPE resins manufactured by Nova Chemicals use this processes to produce ethylene–1-octene copolymers with different degrees of branching uniformity.

The second type of the solution polymerization concept uses mixtures of supercritical ethylene and molten PE as the medium for ethylene polymerization. Some reactors previously used for free-radical ethylene polymerization in supercritical ethylene at high pressure (see the article on low density polyethylene) were converted for the catalytic synthesis of LLDPE. Both stirred and tubular autoclaves operating at 30–200 MPa (4,500–30,000 psi) and 170–350°C are used. Residence times in these reactors are very short, from 1 to 5 min. Three types of catalysts are used in these processes. The first type includes pseudohomogeneous Ziegler catalysts. In this case, all catalyst components are introduced into a reactor as liquids or solutions, but they form solid catalysts when combined in the reactor. Examples of such catalysts include $TiCl_4$ or its mixtures with $VOCl_3$ and a trialkylaluminum compound (38). The second type of catalyst is a solid Ziegler catalyst. Both classes of the catalysts produce compositionally nonuniform LLDPE resins.

5.3. Slurry (Suspension) Polymerization Processes.

The slurry polymerization technology is the oldest PE production process. Although many Ziegler catalysts, supported chromium oxide, and metallocene catalysts have been described in the patent literature for LLDPE slurry processes, this technology is not broadly practiced. The main obstacle is significant swelling of copolymer particles in hydrocarbon solvents that occurs at high temperatures due to a high content of the amorphous phase in LLDPE resins. The swelling can severely limit the accessible range of resin densities and production rates. The degree of swelling depends on a solvent. If relatively heavy solvents, such as hexane or cyclohexane, are used, the swelling limits the resins to the MDPE range with density of ~0.930 g/cm^3, whereas very light solvents expand this range to ~0.925–0.923 g/cm^3 (7,38,40). In addition, when compositionally nonuniform LLDPE resins are produced in heavy solvents at increased temperatures, their components with the highest α-olefin content dissolve in the solvents and are physically removed from the resins.

Chevron Phillips Chemical Company uses a very efficient slurry process, which is suitable for the production of both HDPE and LLDPE (Fig. 7). The reactor is built as a large folded loop containing long vertical runs of pipe from 0.5 to 1 m in diameter connected by short horizontal stretches of pipe. The reactor is filled with a light solvent, usually isobutane, circulating through the loop at a high speed. A mixed stream containing ethylene and an α-olefin combined with a recycled diluent, and catalyst slurry are fed into the reactor. 1-Butene, 1-hexene, 1-octene, or 4-methyl-1-pentene can be used as α-olefins in this process. Specially formulated chromium oxide-based catalysts are used to produce LLDPE resins with broad MWD characterized by MFR values in an 80–200 range (6,12). The reactors operate at a pressure of up to 3 MPa (~440 psi) and at temperatures in a 60–75°C range. The temperature is the crucial operating variable and must be closely controlled to avoid copolymer swelling. The concentration of polymer particles in the slurry is maintained at 20–25 wt% and also should be carefully controlled to prevent particle agglomeration. After a residence time from 1.5 to 3 h, the resin settles briefly in settling legs at the bottom of the loop and is discharged into a flash tank. The separated solvent and monomers enter the solvent-recovery system for purification and recycling.

6. LLDPE Processing

6.1. Rheology of LLDPE.

All LLDPE processing technologies involve resin melting. Viscosities of typical LLDPE melts are between 5 and 70 kPa s. The main factor that affects melt viscosity is the molecular weight of a resin. Viscosity of LLDPE melt also strongly depends on temperature. This dependence is described by the Arrhenius equation with the activation energy of 29–32 kJ/mol (7–7.5 kcal/mol) (41).

The processing range of LLDPE resins is from 140 to 250°C. The melts are non-Newtonian liquids: Their effective viscosity is significantly reduced when the melt flow speed is increased (42). This phenomenon is called shear thinning; it plays a very important role in the resin processing. The resins with expressed shear-thinning capability have greatly decreased viscosities at a high speed melt flow typical for industrial processing conditions, and hence call for a reduced energy demand. The shear-thinning ability is mostly affected by the MWD width of a resin: Compositionally nonuniform copolymers with MFR values in the 28–30 range reduce their viscosity 6–8 times at high processing speeds while most compositionally uniform resins with narrow MWD prepared with metallocene catalysts have a nearly constant melt viscosity (8). This deficiency of metallocene-derived LLDPE and VLDPE resins has been overcome through the use of specially designed metallocene catalysts and modification of solution processes (6,7,25,29). The LLDPE resins produced with some metallocene catalysts have long-chain branching. It significantly increases the melt flow ratios and enhances shear-thinning capability of the molten resins. As a result, such resins have processability of LDPE, but the strength and toughness of LLDPE (7,8). The LLDPE resins produced with chromium oxide-based catalysts have very broad MWD, with the MFR values in an 80–200 range. Their shear-thinning ability is very high, and their melt viscosity at high processing rates is reduced up to 100 times. This allows processing of copolymers with quite high molecular weights under standard conditions.

6.2. Main Processing Methods. Linear low density polyethylene is easily processed by most conventional techniques due to its low melting point and high chemical stability. The principal processing techniques are described in detail in Refs. 42–45.

Film Manufacture. Most of the LLDPE resins produced worldwide are made into thin films, either melt blown or cast from the melt. Blown film is produced by extrusion of an LLDPE melt through a circular die with a large diameter, up to 100–120 cm, and a narrow gap, usually <1 mm (42,46). The extruded thin-walled tube of molten polymer is rapidly cooled and stretched in two directions: It is mechanically pulled in a vertical direction and simultaneously expands in diameter due to internal air pressure in the melt bubble. Typically, the ratio of the diameter of the expanded film tube to the diameter of the circular die, called the blow-up ratio, is between 1.51 and 41, allowing formation of a continuous film trunk up to 4 m in diameter. The film, usually 0.007–0.125 mm thick, is air cooled and rolled.

The LLDPE cast film is manufactured by depositing polymer melt on a rotating heated drum with a highly polished surface. Mechanical properties of several blown and cast films are given in Tables 3,4. Compositionally uniform LLDPE resins produced with metallocene catalysts can be easily processed into film using standard equipment. The VLDPE resins with density in a 0.915–0.910-g/cm^3 range can also be converted to film (see Table 5).

Injection Molding. Injection molding technique is used for the manufacture of LLDPE articles of complex shapes. An injection-molding machine consists of two units: an extruder and a clamp unit (a mold). The mold consists of two steel platens: fixed and movable. Together, they form a cavity into which the resin melt is injected. The molds usually accommodate up to 50 or more articles formed in a single shot. The LLDPE pellets are fed into a single-screw extruder, where they are melted and the melt is injected into the mold through a nozzle at 200–260°C and 70–140 MPa (~10,000–20,000 psi) (42-44). After the mold is filled with the melt, it is held under pressure for a short period of time and then cooled and opened. The duration of the molding cycle depends on melt viscosity and the rate of polymer crystallization. Liquid low density polyethylene crystallizes rapidly; therefore, molding cycles are short, typically from 10 to 30 s.

Blow Molding. Bottles and simple containers are manufactured in large quantities by the blow molding technique (42,45). In this processing method, a thick-walled tube of LLDPE melt is extruded downward through a circular die and embraced by a split metal mold. The bottom part of the mold pinches and closes the tube of the molten resin, and then the closed bubble is blown by air pressure to conform to the internal surface of the mold. To prevent sagging of the free-hanging tube of molten polymer under its own weight during the manufacturing cycle, LLDPE resins with high molecular weights and high melt viscosities are used in this method.

Rotational Molding. Large containers and some toys are manufactured with a specialized technique called rotational molding (42). A rotational molding machine contains several large metal molds, which can be rotated in two perpendicular planes. A load of fine LLDPE particles is introduced into each mold, and the mold assembly is transferred into an oven. Inside the oven, heated molds rotate at speeds ranging from 10 to 40 rpm. The polymer powder melts and is uniformly distributed on the internal surface of each mold. After the article is formed, the mold assembly is removed from the oven, cooled, and the plastic articles are removed.

Extrusion. Extrusion processes include resin pelletization after LLDPE synthesis, manufacture of thick film, sheet, pipe, tubing, and insulated wire (42). Extrusion is carried out at temperatures of ~150°C and at 40–50-MPa (5800–7300-psi) pressure. The production line consists of a mono- or twin-screw extruder, a cooling and shaping device, a pulling device, usually a roller, and a cutter. Pipes and tubing (with a diameter < 1 cm) are produced by extruding LLDPE melt through a circular die. The molten tube enters a vacuum calibrator where it is pressed by air against sizing rings and cooled. The extrusion rate and the drawdown ratio (the ratio of the cross-sectional area of the die opening to the tube wall) are adjusted by using mechanical pulling devices. Modified extruders are also used to coat rolls of wire and cable with LLDPE skin.

7. Economic Aspects

Most LLDPE grades are commodity plastics manufactured in large quantities worldwide. The following numbers represent the dynamics of LLDPE production:

year	1983	1990	1995	2005
10^6 ton/year	1.46	4.74	7.76	~15

Table 6 gives the list of countries with LLDPE plants and swing PE plants that are capable of producing both HDPE and LLDPE, as well as LLDPE production volumes of some U.S. companies. Five companies produce the largest volume of VLDPE and LLDPE resins in North America: Dow Chemical Company (~40% of the market), ExxonMobil Chemical Company (~20%), Nova Chemicals (~15%), Equistar Chemicals LP (~8%) and Chevron Phillips Chemical Company (~6%). Most LLDPE-producing companies manufacture resins both with nonuniform and uniform branching distribution. Chevron Phillips Petroleum Company produces special grades of LLDPE resins with broad MWD under the trade name "Low Density Linear Polyethylene" or LDLPE.

In the case of commodity-grade LLDPE resins, the total production costs are dominated by the cost of raw materials, primarily ethylene and the comonomer, especially in the case of more expensive 1-hexene and 1-octene, as well as hydrogen, a diluent, a catalyst, and additives. The combined cost of two monomers usually amounts to ~ 75–80% of the total production costs. Other expenses include utilities costs (power, cooling water, steam, and fuel, ~5%); operating costs (maintenance); and overhead expenses. Investment volumes and operating costs for manufacturing LLDPE depend on the operating policy and marketing strategy of a particular company. The manufacturing cost is influenced by such factors as a product mix, marketing strategy, plant layout and design, quality control, environmental requirements and safety, inventory, etc. As a rule, the most capital-intensive processes are the solution processes, mostly due to high capital investment for machinery operating at high pressures, expenses for solvent and α-olefin recovery, purification, and recycling. Gas-phase processes require the lowest capital investment.

Different grades of commodity LLDPE containing different α-olefins and intended for different applications command different prices. The end-of-2004 list prices for large-volume grades of ethylene–1-butene LLDPE resins in the United States ranged from $1.45 to 1.50/kg for film resins and from $1.40 to 1.42/kg for injection-molding resins; they were 15–20 cents higher for ethylene–1-hexene resins and 25–30 higher for ethylene–1-octene resins. The most expensive are rotomolding LLDPE resins, $1.85–2.00/kg. The price of uniformly branched VLDPE resins produced with metallocene catalysts is ~$1.60–1.75/kg, depending on grade.

Large quantities of pelletized LLDPE are shipped by rail in hopper cars with a capacity of 80–100 ton. Smaller amounts are shipped in corrugated cardboard boxes 1.0 × 1.15 × 0.90 m containing 450–500 kg of resin.

8. Specifications, Standards, and Quality Control

The ASTM D 1248-84 classification, reapproved in 1989, is based on the two most easily measured properties of LLDPE: density and the melt index. Density determines the type of a resin and the melt index determines its category. The PE resins with a nominal density of 0.926–0.940 g/cm^3 belong to Type II (medium density) resins, those with a density in a 0.915–0.925 g/cm^3 range belong to Type I (low density) resins, and those with a density $<$ 0.915 g/cm^3 belong to Type 0 (very low density) resins. The five categories of PE are specified according to their melt index measured according to ASTM D 1238-84 (1989):

category	1	2	3	4	5
melt index, g/10 min	>25	10–25	1–10	0.4–1.0	< 0.4

Class specifies other characteristics, predominantly resin's color. The three classes of PE are designated as A, B, and C. They specify color and amounts and types of antioxidants and other additives. Class A covers naturally colored PE, Class B includes white- and black-colored polymer, and Class C covers weather-resistant black polymer containing > 2% carbon black.

9. Analytical and Test Methods

9.1. Structure and Composition. Commonly evaluated structural parameters of LLDPE include the type of an α-olefin used in copolymerization, the content of the olefin in the resin, the type and the degree of unsaturation, the degree of oxidation, and resin crystallinity. The type and content of an α-olefin is measured by (Nmr) and infrared spectroscopic (ir) methods (6,47,48). The ASTM method (ASTM D 2238-92) employs ir techniques for the estimation of the total methyl group content in the resins. Infrared spectroscopic methods also identify such features as unsaturation (ASTM D 3124-72, reapproved in 1988) and the carbonyl groups. A number of physical methods are used to measure LLDPE crystallinity: X-ray diffraction, ir, differential scanning calorimetry (DSC), and the density measurement. The DSC measurements also give the melting point and the heat of fusion.

Density. Density of LLDPE is measured by flotation in density-gradient columns according to ASTM Method D 1505-85 reapproved in 1990. The most often used liquid system is 2-propanol–water providing a 0.79–1.00-g/cm^3 density range. The technique is simple, but requires a long time, >50 h, for a precise measurement. The correlation between density (d) and crystallinity (CR) is given by $1/d \approx \mathrm{CR}/d_{\mathrm{cr}}+(1-\mathrm{CR})/d_{\mathrm{am}}$, where the density of the crystalline phase, d_{cr}, is 1.00 g/cm^3 and the density of the amorphous phase, d_{am}, is 0.852–0.862 g/cm^3. Ultrasonic and solid-state Nmr methods were developed for the crystallinity and density measurement of LLDPE resins, both in pelletized and granular forms.

Compositional Uniformity. The degree of compositional uniformity is measured experimentally with two techniques: the temperature-rising elution fractionation method, analytical Tref (49,50) and the crystallization fractionation method, Crystaf (51). A small amount of a resin is dissolved in an aromatic solvent at 120–130°C, and then the polymer is very slowly precipitated from solution by decreasing temperature. The Crystaf technique measures the fraction of the copolymer remaining in solution as a function of decreasing temperature. With the Tref technique, the precipitated polymer is then slowly redissolved in a fresh solvent flowing through the chamber with the residue, and the concentration of the dissolved polymer as a function of increasing temperature is measured. Both methods provide the data on the relative amounts of molecules of different compositions in a given LLDPE resin (49-51). The degree of compositional uniformity also can be measured on a semiquantitative level with the differential scanning calorimetry method (Fig. 1). Copolymers with a uniform compositional distribution have relatively low melting points, usually from 95 to 120°C, depending on copolymer composition, as shown in Figure 2, whereas copolymers with a nonuniform distribution have the melting point in a relatively narrow range, 125–128°C (6).

The nonuniformly branched resins contain a significant fraction of a highly branched, low molecular weight polymer component, which is soluble in light hydrocarbons. The content of this fraction, called the extractable fraction, is measured according to the FDA analysis procedure CFR177.1520. A piece of LLDPE film is immersed in hexane at 50°C for 2 h, then the solvent is evaporated and the extractable fraction is calculated as the weight ratio of the dry residue and the original film sample.

Molecular Weight and Rheologic Properties. Molecular weight and MWD of LLDPE resins are measured by a high temperature gel-permeation chromatographic (GPC) method or by a viscosimetric method (ASTM D 1601-86, reapproved in 1991, and D 2857-87). The GPC technique simultaneously determines the number- and weight-average molecular weights, M_n and M_w, and provides detailed information on MWD of LLDPE.

Standard ASTM procedures to measure rheologic, dielectric, and mechanical properties are the same as for HDPE, see the article "POLYETHYLENE, HIGH DENSITY". The measure of PE viscosity widely used in industry is the melt index, which is designated as MI or I_2, and is measured in apparatuses called Melt Index Tester. The parameter I_2 is defined as the amount of a polymer melt flowing at 190°C for 10 min through an 8-mm long capillary die with a 0.58-mm diameter under a load of 2.16 kg. The I_2 values for most LLDPE resins range from ~5 to 0.1 g/10 min. The logarithm of the MI value is inversely related to melt viscosity.

The molecular weight distribution of LLDPE resins is usually characterized in industry by the ratios of melt indexes measured in the same apparatus using different loads, 2.16, 10.16, and 21.6 kg. The commonly used ratios are I_{21}/I_2 (it is called the melt flow ratio, MFR) and I_{10}/I_2. Both these ratios approximately correlate with the $M_\mathrm{w}/M_\mathrm{n}$ ratio. For example, the dependence between $M_\mathrm{w}/M_\mathrm{n}$ and I_{21}/I_2 values for LLDPE resins with a nonuniform branching distribution is $M_\mathrm{w}/M_\mathrm{n} \sim 0.24\times(I_{21}/I_2)\text{-}2.4$ (6). The melt index ratios are also sensitive to the presence of long-chain branching in LLDPE resins produced in some solution processes: The I_{10}/I_2 values for such resins increase from 5–6 to 8–12 (7,8).

Mechanical Properties of LLDPE Film. Film accounts for the largest volume of LLDPE consumption. Several tests were developed specifically to evaluate film performance. Two such parameters are usually reported. One, the dart impact strength, is based on ASTM D 4272-90, Method A. It determines the overall strength of film and is evaluated by dropping a dart with a round tip 38.1 mm in diameter from a height of 66 cm on a piece of stretched LLDPE film 12.7 cm in diameter. The average weight of the dart sufficient to break through the film in

50% of the drop tests gives its dart impact strength. This value varies from ~80–100 g for film of poor quality to > 800 g for high grade film.

The second parameter, the tear strength, describes film resistance to tear propagation. It is measured with an apparatus called Elmendorf Tear Tester (ASTM D 1922-89). Tear strength is determined as the weight of a loaded pendulum that tears a notched piece of film. Two values are usually measured for each film sample. One determines tear propagation in the machine direction of the film, usually the lower value, and the second one in the transverse direction: see Tables 3-5. Both these film strength tests are essentially high speed tensile tests developed to evaluate properties that are important under conditions of the film's many uses.

9.2. Chemical Properties. Liquid low density polyethylene is chemically stable. Very few analyses and tests related to its chemical properties are carried out routinely. Resistance to thermal stress cracking is determined by exposing film wrapped on a metal mandrel to 100°C hot air for 48, 96, and 168 h, according to ASTM D 2951-71 reapproved in 1988.

10. Health and Safety Factors

The LLDPE by itself does not present any health-related hazard due to its chemical inertness and low toxicity. Film, containers, and container lids made from LLDPE are widely used in food and drug packaging. Some LLDPE grades produced with unsupported metallocene catalysts have especially high purity due to a very high catalyst productivity and a resulting very low contamination level of the resins with a catalyst residue. The FDA approved the use of the film manufactured from these resins for food contact and for various medical applications (52). If LLDPE articles contain fillers, processing aids, and colorants, their health factors should be judged separately.

However, LLDPE can present a certain health hazard when it burns because smoke, fumes, and toxic decomposition products could be formed in the process. Exposure to burning LLDPE can cause irritation of the skin, eyes, and mucous membranes of the nose and throat due to the presence of acrolein and formaldehyde. Toxicity of LLDPE pyrolysis products depends on temperature, the heating rate and the sample size (53).

Liquid low density polyethylene can be disposed of by landfill or incineration. In landfill, the material is completely inert, degrades very slowly, does not produce gases, and does not leach any pollutants into ground water. When incinerated in commercial or municipal installations, LLDPE produces a large amount of heat, the same as heating fuel, and should constitute < 10% of the total trash.

11. Uses

Ethylene-based polymers and copolymers have a broad range of applications due to their attractive mechanical properties and low cost. Table 7gives an overview of applications for all PE resins and the significance of LLDPE and VLDPE resins in this area.

11.1. Film. Film is the largest application for LLDPE resins, $> 55\%$ in the United States in 2005. His film has a high tensile strength and puncture resistance. The toughness and low temperature properties of the LLDPE film exceed those of conventional LDPE. The LLDPE resins exhibit relatively low strain hardening in the molten state and lower extensional viscosity and these factors allow the manufacture of LLDPE film at high rates with little risk of bubble breaks.

The trash-bag market exceeds 700,000 ton/year; it is the largest single market for LLDPE film. Typical LLDPE film properties are shown in Table 3. Ethylene−1-butene copolymers, which are the cheapest, have a lower film strength compared to those of the high strength ethylene−1-hexene and ethylene−1-octene copolymers. Bags for merchandise packaging manufactured from thin LLDPE film have excellent tensile strength, puncture resistance, and seal strength at thin gauges. This application includes bags on a roll, such as garment bags, laundry and dry cleaning bags, and ice bags. In the last case, LLDPE film has replaced low melt-index vinyl acetate copolymers.

Several LLDPE and VLDPE films are competing for a special film market, elastic stretch film for packaging. The principal requirements for stretch film are a relatively low modulus for easy stretching, high strength, high elongation, and a good puncture resistance (2-5). Both blown and die-cast film can be used for this application, see Tables 3,5. The stretch film can be produced from blends, by the coextrusion method, or as a single-layer LLDPE film. The resins based on ethylene−1-hexene and ethylene−1-octene copolymers are particularly suited for these purposes.

A significant volume of LLDPE film is used to manufacture large-size packaging for food and textiles as well as for nonpackaging applications such as industrial sheeting and agricultural mulch film. Another area for LLDPE film is grocery sacks. The LLDPE bags are thinner than LDPE bags; their thickness can be reduced down to $\sim 25\ \mu m$, which makes them price competitive with paper. The bags are easily reused, take up less space, and are moisture resistant.

Several VLDPE grades, especially compositionally uniform resins produced with metallocene catalysts, are used for the manufacture of very clear LLDPE film: see Table 5. These resins are also used as cast and blown layers for lamination and heavy-duty film, as well as in multilayer coextruded film. Compositionally uniform LLDPE resins have high toughness, high clarity and purity, and a very low level of extractable material. These features qualify the resins as replacement for ionomers and ethylene−vinyl acetate copolymers with high vinyl acetate content. High clarity is necessary in numerous packaging applications. For example, clarity and low oxygen- and CO_2-barrier properties of metallocene-derived LLDPE resins make their film especially attractive for packaging poultry, frozen foods, and vegetables (54). The same properties make these resins and their blends with HDPE suitable for producing film for blood bags, surgical disposable bags, and medical gowns (55).

Blending with LLDPE is practiced to upgrade the properties and improve the processing of conventional LDPE. For example, addition of 25% of ethylene−1-butene LLDPE resin with an I_2 value of 0.5 g/10 min to a conventional

LDPE resin increases the dart impact strength of 75 μm film from 490 to 560 g, the puncture strength from 41 to 49 J/mm, and the tear strength from 43 to 63 N/mm. Compositionally uniform VLDPE resins are used in blends with HDPE, commodity LLDPE, and polypropylene (55).

An important prerequisite for the use of LLDPE and VLDPE in many packaging applications is their sealability. Compositionally uniform resins are especially attractive for such use because their melting and softening points are 15–20°C lower than those of commodity LLDPE resins as shown in Figure 1 and Table 5.

11.2. Injection Molded Products. Injection molded products is the second largest market for LLDPE, it accounted for ~7% of its consumption in 2005. Over one-half of the LLDPE consumed in injection-molding applications is used for housewares. The LLDPE housewares are stiffer and more resistant to impact and distortion at elevated temperatures than those made of LDPE, and their low temperature impact strength is superior to that of polypropylene. Lids for glass and HDPE jars and containers made from LLDPE have excellent gloss and low warpage. Garbage cans and industrial containers made of LLDPE exhibit exceptional toughness and withstand rough treatment. A low brittleness point of LLDPE allows them to perform well at low temperatures. Table 8 compares mechanical properties of two resins, ethylene–1-butene LLDPE and high pressure LDPE, which was used for this purpose in the past. High mechanical characteristics the LLDPE resin afford articles with a better impact strength and stress-cracking resistance. Injection molding applications for compositionally uniform PE plastomers include clear lids for household containers, flexible parts for small appliances and disposable oxygen facemasks (56).

11.3. Blow-Molded and Rotationally Molded Articles. This market is relatively small for LLDPE resins, ~1%. The most important distinguishing feature of LLDPE resins formulated for the blow molding application, compared to similar HDPE resins, is their superior environmental stress-cracking resistance and lower gas permeability. This feature opened new bottle markets where these properties are important. Blow-molded drum liners made from LLDPE also meet industry standards for low temperature toughness and environmental stress-cracking resistance. Rotational molding of LLDPE resins capitalizes on higher impact strength and an increased stress-cracking resistance of LLDPE compared to LDPE and HDPE resins. Due to these properties, LLDPE competes against more expensive products such as cross-linked and rubber-modified PE. A large variety of molded articles with a complex configuration are manufactured from LLDPE resins. They include toys, large and very large square-edged containers, and tanks for agriculture and water treatment.

11.4. Pipe and Tubing. The same qualities that make LLDPE attractive for blow-molding applications play a crucial role in using LLDPE for the pipe manufacture, which accounts for ~1% of the LLDPE market. These pipes provide necessary flexibility, high burst strength, high environmental stress-cracking resistance, and higher heat-distortion temperature than LDPE and some HDPE grades. The LLDPE tubing is used for drip piping, swimming-pool tubing, household hoses, etc. Compositionally uniform LLDPE and VLDPE resins started replacing plasticized polyvinyl chloride (PVC) in some specialty markets such as medical tubing applications due to their high purity, transparency, and flexibility (54).

11.5. Wire and Cable Insulation. Liquid low density polyethylene is widely used for wire and cable coating in the electrical and telephone industry, the market accounting for 2–3% of the LLDPE production. The coating combines such attractive properties as flexibility, strength, a low brittleness temperature, high resistance to abrasion, and excellent dielectric properties typical for all PE resins. Compositionally uniform VLDPE resins with a narrow MWD produced with metallocene catalysts are especially suitable for this purpose (57). The LLDPE-coated wire is widely used in overhead medium and low voltage power distribution, in underground power cable insulation, in data–communication networks, automotive, and appliance wire. A significant volume of LLDPE is also used in such electrical applications as jacketing, molded accessory panels, shields for semiconductors, etc (54).

11.6. Fibers. Several grades of MDPE resins with density of 0.930 – 0.950 g/cm^3 and a low molecular weight, with I_2 values in a 15–30 g/10 min range, are suitable for the production of PE fibers and nonwoven materials. They are used for the manufacture of medical single-use covers, sheets, drapes, gowns, and other hygienic products. Due to their relatively low melting points, these MDPE resins can be also used for bicomponent fibers and melt-blown interlayers.

11.7. Other Uses. Other uses for LLDPE include rotomolding, manufacture of thick sheet, and extrusion coating, as well as compounding with other polyolefin resins.

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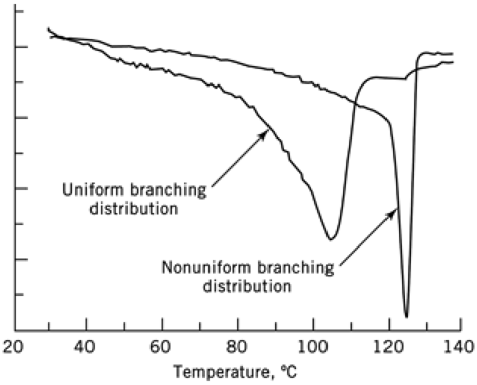

Fig. 1. Differential scanning caloumnetry (DSC) melting curves of two copolymers of the same average composition but with different degrees of compositional uniformity.

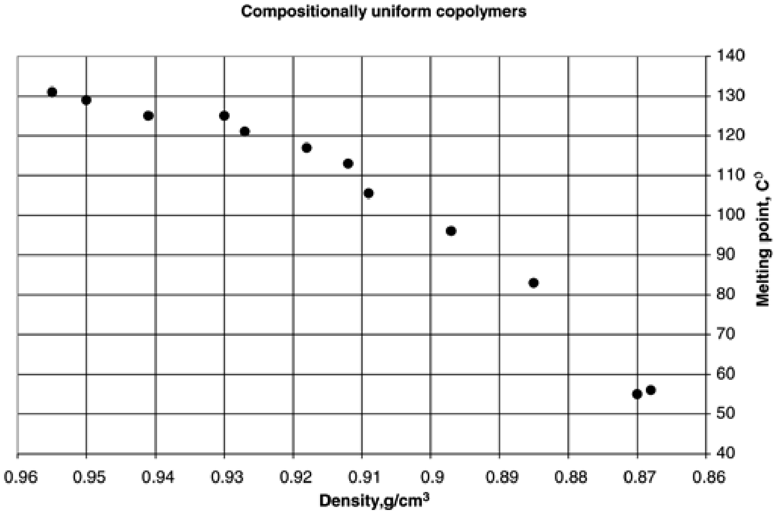

Fig. 2. Melting points of ethylene–α-olefin copolymers with uniform branching distribution as a function of their density (data from Refs. 2 and 3).

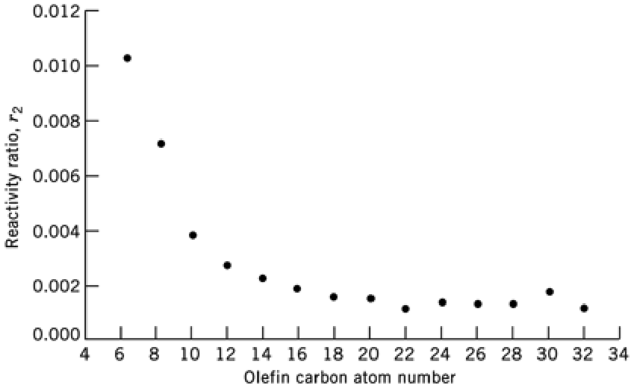

Fig. 3. Copolymerization of ethylene and linear α-olefins. Dependence of reactivity of linear α-olefins on their carbon atom number.

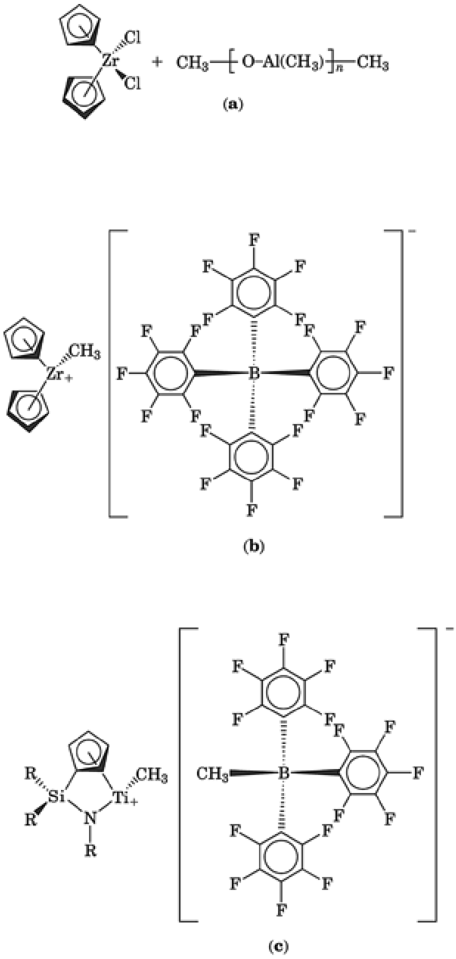

Fig. 4. Metallocene catalyst systems for LLDPE synthesis. (a) Kaminsky metallocene catalyst; (b) Ionic catalyst; (c) Constrained-geometry catalysts.

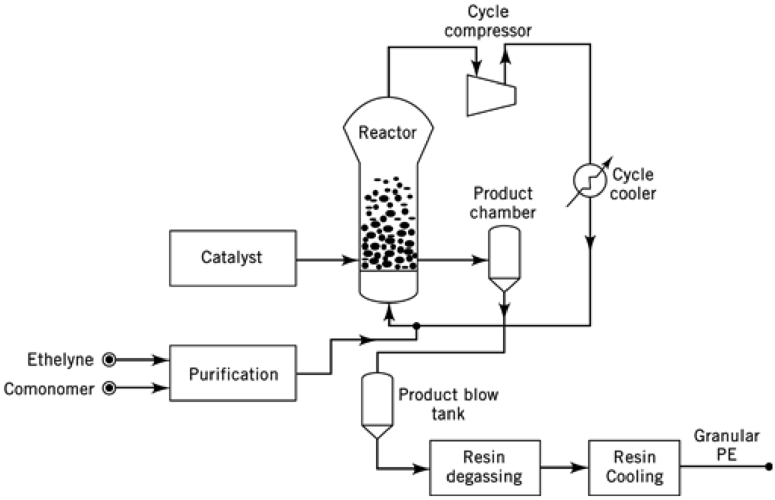

Fig. 5. Gas-phase fluidized-bed process (Univation Company).

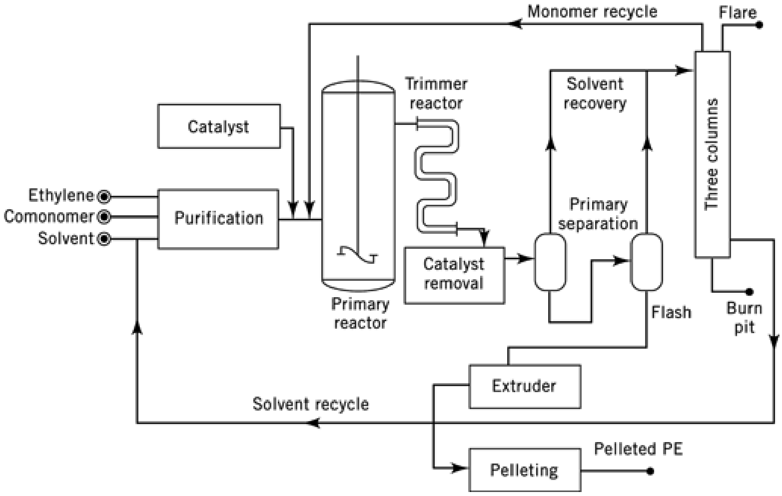

Fig. 6. Solution process (Nova Chemicals Company).

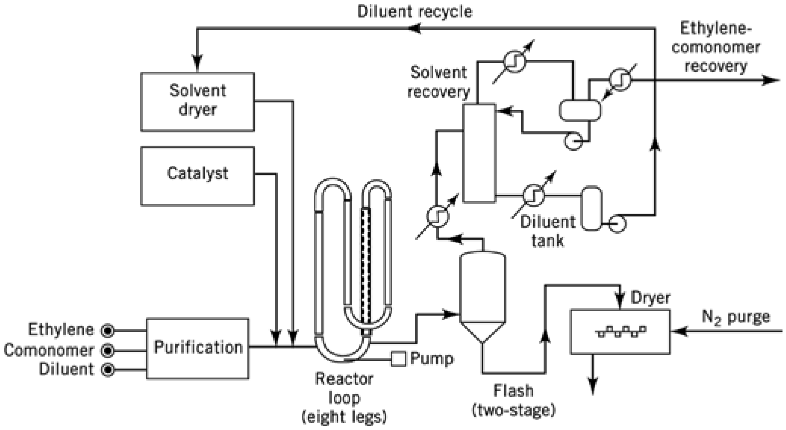

Fig. 7. Slurry process (Chevron Phillips Company).

Table 1. **Commercial Classification of Ethylene–α-Olefin Copolymers**

Resin	Name	α-Olefin content, mol%	Crystallinity, %	Density, g/cm^3
PE of medium density	MDPE	1–2	55–45	0.940–0.926
linear PE of low density	LLDPE	2.5–3.5	45–30	0.925–0.915
PE of very low density	VLDPE	>4	<25	<0.915

Table 2. **Density of LLDPE Resins with Different α-Olefin Contents**

α-Olefin (1-hexene) content:	2.0 mol%	3.0 mol%	4.0 mol%
density (g/cm^3)			
uniformly branched LLDPE	0.920–0.918	0.912–0.908	<0.900
nonuniformly branched LLDPE	0.930–0.927	0.922–0.920	0.915–0.912

Table 3. **Physical Properties of a Commercial LLDPE Film from Resins with Nonuniform Compositional Distribution**[a]

Copolymer of ethylene and	1-butene			1-hexene			1-Octene	
Resin parameters								
density, g/cm^3	0.918	0.922	0.918	0.918	0.917	0.917	0.917	0.917
melt index, g/10 min	1.0	0.8	2.0	1.0	1.0	2.0	0.85	2.3
type of film	blown[b]	blown[b]	cast[b]	blown[c]	blown[b]	cast[b]	blown[c]	cast[c]
Film property (adjusted to film thickness of 25 μm):								
Mechanical properties								
Yield strength, MPa								
machine direction	12	18	15	16	10	10	11	11
transverse direction	13	20	16	15	11	9	13	10
Tensile strength, MPa								
machine direction	38	102	70	61	55	80	41	60
transverse direction	31	52	36	48	45	51	32	34
Elongation at break, %								
machine direction	670	430	450	580	640	440	420	460
transverse direction	790	790	850	800	760	840	610	650
Modulus, MPa								
machine direction	155	393	138	204	190	138	186	
transverse direction	178	483	162	233	225	150	194	
Film properties								
dart impact strength, g	100	82	88	130	175	100	592	248
Tear strength, g								
machine direction	142			296	340	288		402
transverse direction	400			674	670	938		604
Optical properties								
Haze, %	14	32	1.6	12	13		9	0.4
Gloss, 45°	46	25	92	50	50		65	95

[a] Refs. 2,3,6,10.

[b] ExxonMobil Chemical Company.

[c] Dow Chemical Company.

Table 4. **Physical Properties of Commercial LLDPE Blown Film from Ethylene–1-Hexene Resins with Uniform and Nonuniform Compositional Distribution**[a,b,c]

	Standard resin	"Superstrength" resin[c]	Standard resin
Resin parameters			
compositional distribution	nonuniform	nonuniform	uniform
density g/cm^3	0.917	0.917	0.918
melt index, g/10 min	1.0	1.0	1.25
Film property (adjusted to film thickness 25 μm):			
Mechanical properties			
yield strength, MPa			
machine direction	10	10	9
transverse direction	11	10	9
tensile strength, MPa			
machine direction	55	60	67
transverse direction	45	40	62
elongation at break, %			
machine direction	640	560	560
transverse direction	760	650	650
modulus, MPa			
machine direction	190	193	166
transverse direction	225	207	172
Film properties			
dart impact strength, g	175	480	905
tear strength, g			
machine direction	340	430	304
transverse direction	670	750	400
Optical properties			
haze, %	13	17	
gloss, 45°	50	38	

[a] Refs. 2,6.

[b] ExxonMobil Chemical Company.

[c] Ref. 11.

Table 5. **Physical Properties of Commercial VLDPE Resins with Uniform and Nonuniform Compositional Distribution**[a]

α-Olefin comonomer	1-Butene[c]		1-Hexene[b]	1-Octene[c]		
Resin parameters						
compositional distribution	nonuniform		uniform	nonuniform	uniform	
density, g/cm^3	0.906	0.890	0.912	0.912	0.909	0.870
melt index, g/10 min	0.85	1.3	1.0	1.0	1.0	1.0
T_m, °C	119	114		123	105.5	55
Mechanical Properties						
tensile strength, MPa	24	6	69	64-60	23/20	14
elongation at break, %	800	625	470/620	465/490	620/ 580	1115
modulus, MPa		30	185	~135	60	7.5
hardness, Shore A		77				74
Film Properties (adjusted to film thickness 25 μm)			800	760	400	
dart impact strength, g						
tear strength, g						
machine direction			250	410		
transverse direction			490	660		
Optical Properties						
haze, %			8	8		

[a] Refs. 2–5.

[b] ExxonMobil Chemical Company.

[c] Dow Chemical Company.

Table 6. **Combined Worldwide Production Capacities for LLDPE in 2002**

Country	Company	Capacity, 10^3 ton/year
North America United States		
Total, LLDPE only		6800
	Basell	54
	Chevron Phillips	400
	Dow Chemical	2775
	Eastman Chemical	182
	Equistar	535
	ExxonMobil Chemical	1600
	Formosa Plastics	184
	Huntsman	100
	Nova Chemicals	880
	Westlake Polymers	100
Swing capacity (HDPE+LLDPE); ∼60% allocated to LLDPE		
Canada		3000
Central and South America		
Argentina		120
Brazil		425
Venezuela		160
Europe		
Austria		100
Czech Republic		120
Finland		250
France		1060
Germany		1270
Great Britain		485
Italy		640
Netherlands		450
Spain		465
Sweden		460
Asia and Pacific Region		
Australia		90
China		1350
India		300
Indonesia		240
Iran		100
Japan		765
Kuwait		600
Malaysia		175
Philippines		70
Saudi Arabia		2730
Singapore		300
South Korea		600
Taiwan		210
Thailand		260
Africa		
Egypt		35
South Africa		105
Other countries		45

Table 7. **Applications of Different PE Resins**

End use	HDPE	LLDPE	VLDPE	LDPE
film for packaging				
food, produce	●	●	●	
garment		●		
stretch film		●	●	
shrink film				●
garbage	●	●		
grocery sacks	●	●		
heavy duty sacks				●
extrusion coating		●		●
agricultural film		●	●	●
wire and cable		●	●	
adhesives			●	●
injection molding	●	●		
blow molding	●	●		
rotational molding	●	●		

Table 8. **Compaison of Injection-Molding Grades of LLDPE and LDPE**[a]

Property	Property	Resin	
		LLDPE	LDPE
melt index, g/10 min		0	40
density, g/cm^3		0.926	0.924
modulus, MPa		350	210
tensile strength, MPa		12.7	9.3
impact strength at 20°C, J		32.5	4.1
stress-cracking resistance at 23°C, h		70	<0.2

[a] Ref. 10.