

## ETHYLENE POLYMERS, LLDPE

### Introduction

Linear low density polyethylene (LLDPE) was first commercialized in the late 1970s by Union Carbide and Dow Chemical. Since that first introduction, LLDPE has seen the fastest growth rate in usage of the three major polyethylene families—low density polyethylene (LDPE), LLDPE, and high density polyethylene (HDPE)—and now comprises approximately 25% of the annual production of polyethylene around the world, approaching 13 million metric tons. Conventional LLDPE differs from LDPE by having a narrower molecular weight distribution and by not containing long-chain branching. LLDPE is made by the copolymerization of ethylene and  $\alpha$ -olefins. Significant research and development efforts were conducted throughout the 1980s to tailor LLDPE properties by controlling molecular weight distribution and comonomer distribution. In the early 1990s, the LLDPE industry was revitalized with the introduction of several new product families, including novel single-site-catalyzed very low density polyethylenes (VLDPE) called plastomers (Exxon, 1991, and Dow, 1993), super-hexene LLDPE (Mobil, 1993), and metallocene-catalyzed LLDPE(mLLDPE) for commodity applications (Exxon, 1995) (see SINGLE-SITE CATALYSTS). Work continues by resin companies around the world on new classes of LLDPE for a variety of applications.

### Molecular Structure and Properties

**Comonomer Type and Content.** Although practically any  $\alpha$ -olefin from C<sub>3</sub> to C<sub>20</sub> can be used as comonomer for LLDPE, the four most commonly used are 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Approximately 40% of

**Table 1. Comonomer Content and Density Ranges for Commercial LLDPE Resins**

Family	Common name	Comonomer, mol%	Crystallinity, %	Density, g/cm <sup>3</sup>
Medium density	MDPE	1–2	55–45	0.940–0.926
Low density	LLDPE	2.5–3.5	45–30	0.925–0.915
Very low/ultra low density	VLDPE/ULDPE	>4	<30	<0.915
Very low density (single-site catalyzed)	Plastomer	≤25	0–30	≤0.912

LLDPE made uses 1-hexene as comonomer, approximately 35% uses 1-butene, and approximately 25% uses 1-octene. Only a small fraction is made using 4-methyl-1-pentene. Hexene and butene copolymers are more prevalent because they are less expensive than octene and because they are commonly used in the gas-phase process, which accounts for most of the global LLDPE production. For LLDPE, density is strongly controlled by comonomer content. Conventional LLDPE basically covers the density range of 0.915–0.940. Within that density range, and also lower density ranges, there are common product family subsets. Table 1 shows comonomer content and subsequent density ranges for commercial LLDPE.

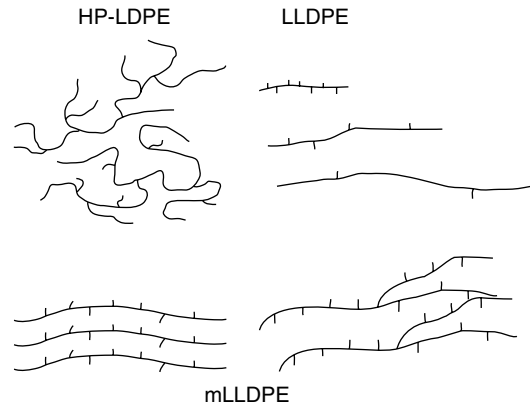
**Chain Structure.** LLDPE comprises linear molecules of ethylene and  $\alpha$ -olefins and can be generally represented by the formula  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-(\text{C}_{n-2}\text{H}_{2(n-2)+1})$ , where  $n$  is the number of carbon atoms in the  $\alpha$ -olefin. In LLDPE above 0.915 g/cm<sup>3</sup> density, most of the branching due to comonomer is randomly distributed along the polymer backbone, although there may be some adjacent comonomer units. Single-site-catalyzed resins have comonomer much more uniformly distributed along the polymer backbone than do conventional LLDPE resins. A conventional gas-phase hexene copolymer LLDPE at 0.918 g/cm<sup>3</sup> density has approximately 18 branches per thousand carbon atoms while a single-site-catalyzed gas-phase hexene copolymer LLDPE at the same density has 11–12 branches per thousand carbon atoms. In the single-site-catalyzed resins, the hexene is more randomly distributed along the backbone, shortening the average backbone sequence length for crystallization, and therefore less comonomer is needed to achieve the same density.

Most LLDPE chains have at least one methyl ( $-\text{CH}_3$ ) group at one chain end. Other chain ends can be a methyl group from termination from chain transfer, or a vinyl group ( $\text{CH}_2=\text{CH}=\text{}$ ) or vinylidene group ( $\text{CH}_2=\text{C}-$ ) from termination from  $\beta$ -hydride transfer (1).

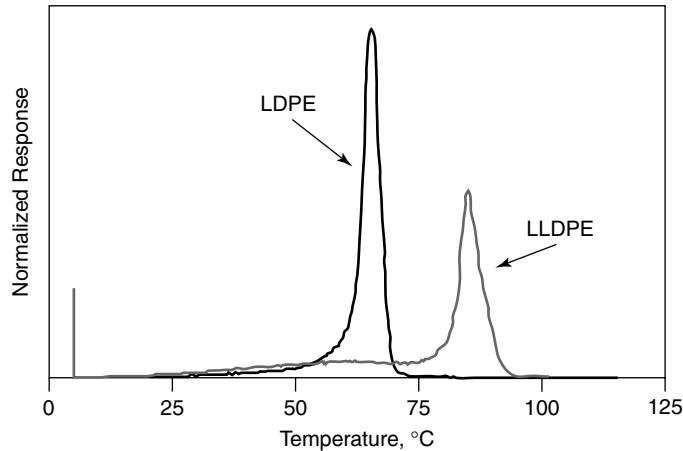
Generally speaking, LLDPE resins do not contain long-chain branching. However, certain families of plastomers may contain more than 0.01 long-chain branches per thousand carbons (2).

**Composition.** A representative schematic of the structural differences between LDPE, LLDPE, and single-site-catalyzed LLDPE is given in Figure 1.

LDPE contains a mixture of long-chain branching and short-chain branching. LLDPE contains only short-chain branching, but that branching is not uniformly distributed through the molecular weight. LLDPE made using Ziegler–Natta catalysts tends to have more comonomer in the lower molecular weight fraction and less in the high molecular weight fraction (3,4). A temperature rising elution



**Fig. 1.** Structural differences between LDPE, LLDPE, and single-site-catalyzed LLDPE.

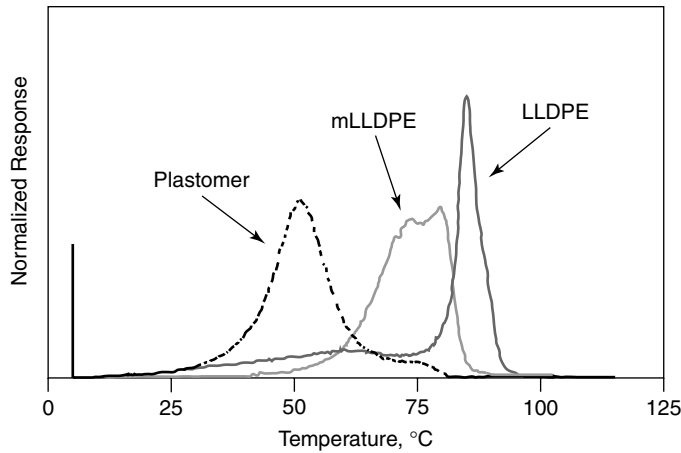


**Fig. 2.** LDPE and LLDPE TREF comparison.

fractionation (TREF) plot for LDPE at  $0.919 \text{ g/cm}^3$  and LLDPE at  $0.918 \text{ g/cm}^3$  is shown in Figure 2.

As you can see, the peak elution temperature for the LDPE is much lower and the peak is much narrower than that for the LLDPE. This indicates that the LLDPE is more compositionally heterogeneous than the LDPE.

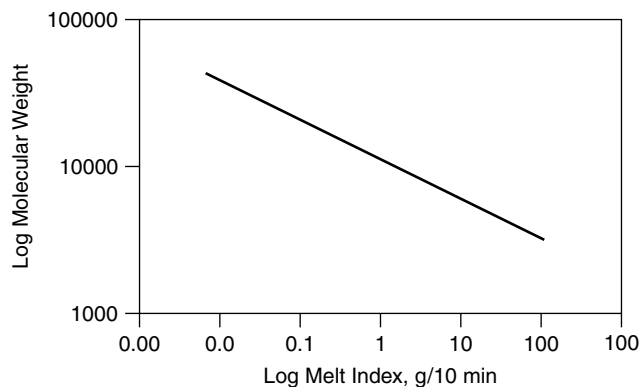
The first commercially available single-site-catalyzed polyethylenes were very low density resins called plastomers (5,6), which had high levels of comonomer and were very homogeneous. Later, commercial commodity grade mLLDPEs were not quite as homogeneous as the plastomers, but were still more homogeneous than LLDPE (7–9). Figure 3 shows a TREF plot of an LLDPE at  $0.918 \text{ g/cm}^3$  density and an mLLDPE at  $0.917 \text{ g/cm}^3$  density, both produced in the gas phase. Also included is a plastomer at  $0.900 \text{ g/cm}^3$  density produced in a slurry reactor.



**Fig. 3.** TREF profiles for LLDPE, mLLDPE, and plastomer.

A polymer that has branching more uniformly distributed along the polymer backbone will have shorter sequence lengths for polymer crystallization. Shorter sequence lengths result in thinner crystals that dissolve and elute at lower temperatures than thicker crystals. The mLLDPE has a lower peak elution temperature than LLDPE at the same density, indicating that mLLDPE is more compositionally homogeneous. The plastomer has a peak elution temperature of approximately 50°C and a very narrow peak indicating that the resin is very compositionally homogeneous.

**Molecular Weight.** Commercially available LLDPE resins can have weight-average molecular weights from less than 20,000 to over 200,000. *Melt index*, a measure of polymer flow through a specified die for a given time, is often used as an estimator of polymer molecular weight and is inversely proportional to weight-average molecular weight. An approximate correlation of weight-average molecular weight and melt index for LLDPE is shown in Figure 4.



**Fig. 4.** Molecular weight/melt index correlation for LLDPE.

**Table 2. Melt Index and Molecular Weight Data for LDPE and Several LLDPEs**

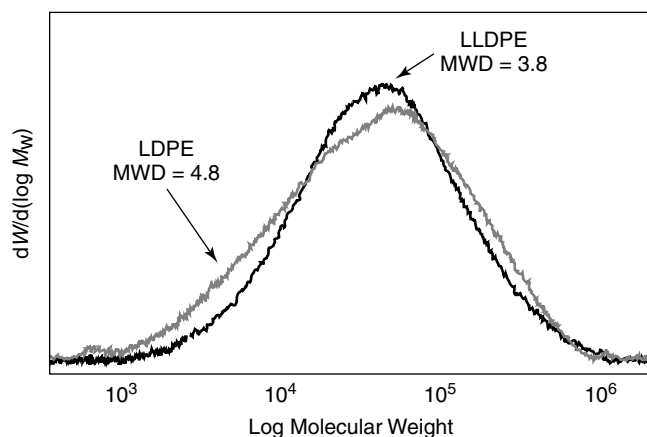
Property	HP-LDPE	Gas-phase LLDPE	Gas-phase mLLDPE	Plastomer	
				Slurry	Solution
Melt index $I_2$ , g/10 min	1.0	1.0	1.0	1.1	1.0
MIR $I_{21}/I_2$	60	33	17	21	31
$M_n$ , g/mol	22,000	28,000	44,000	46,000	40,000
$M_w$ , g/mol	104,000	107,000	102,000	99,000	82,000
PDI, $M_w/M_n$	4.7	3.8	2.3	2.2	2.1

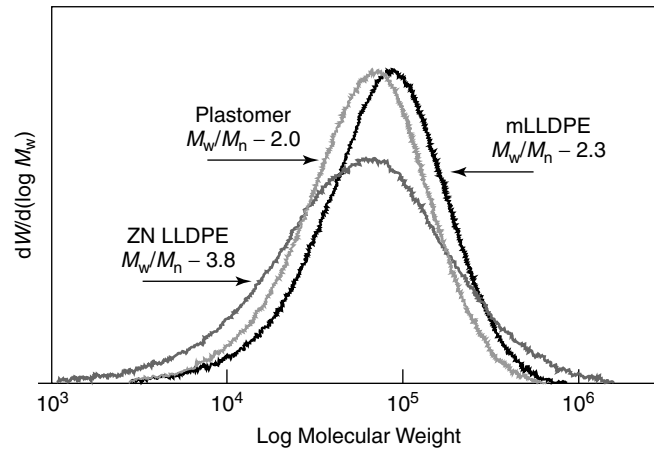
Over the range shown, the relationship between molecular weight and melt index is linear but will not be completely linear over a broader range. Commercially available film grade LLDPE resins can range from 0.2 g/10 min to over 5 g/10 min melt index. Injection-molding grades vary in melt index from approximately 10 g/10 min to greater than 125 g/10 min. Table 2 shows measured molecular weights and melt-flow properties for several LDPEs and plastomers at nominal 1 g/10 min melt index.

Molecular weight distribution plots for the resins in Table 2 are given in Figures 5 and 6.

Depending on the standards used for calibration of the molecular weight fractionation technique, LLDPE has a molecular weight polydispersity index (PDI,  $M_w/M_n$ ) between 3 and 4.5 with melt index ratios (MIR,  $I_{21}/I_2$ ) of 20–35. LDPE has PDI usually greater than 5 and contains long-chain branching. Therefore, although the LDPE and LLDPE resins shown have similar weight-average molecular weights and melt indices, their MIR ( $I_{21}/I_2$ ) values are significantly different. The higher MIR for LDPE indicates greater sensitivity to shear caused by the broader PDI and long-chain branching.

The single-site-catalyzed mLLDPE and slurry plastomers have much narrower molecular weight distributions and therefore have much lower MIR values

**Fig. 5.** Molecular weight distribution plots for LDPE and LLDPE.



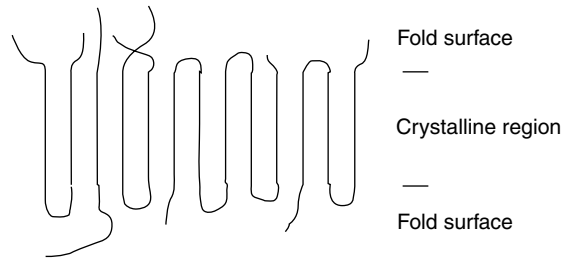
**Fig. 6.** Molecular weight distribution plots for LLDPE, mLLDPE, and a plastomer.

than LLDPE. The plastomer produced in solution phase has trace levels of long-chain branching that make it more sensitive to shear, giving it a higher MIR than the linear plastomer. A narrower PDI for the single-site-catalyzed resins means a smaller low molecular weight fraction commonly called hexane extractables, which can be a limiting factor for LLDPE use in food contact applications.

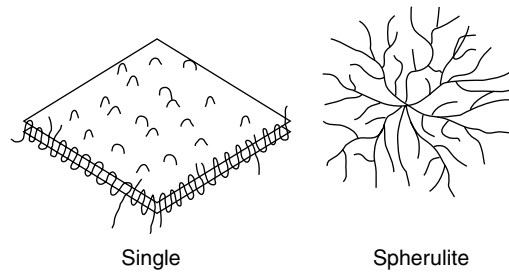
There is a relatively small volume of LLDPE resins made using chrome-based catalysts that have much broader PDI, 10 and higher, and MIR values of 70 and higher. Chrome-based LLDPEs are mostly used in wire and cable coatings, blow molding, and some film applications.

**Chemical Properties.** LLDPE is a saturated hydrocarbon and is generally unreactive. The most reactive parts of the polymer molecule are tertiary carbons at short-chain branch points and double bonds at chain ends. LLDPE is stable in alcohols, alkaline solutions, and saline solutions. It is not attacked by weak organic or inorganic acids. Reactions with concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , >70%) at elevated temperatures can result in the formation of sulfo-compounds. LLDPE can be nitrated with concentrated nitric acid ( $\text{HNO}_3$ ). Fuming nitric acid is also used in analytical techniques to etch away amorphous polyethylene. At room temperature, LLDPE is not soluble in low molecular weight solvent although very low molecular weight and very low density fractions may be extracted. At higher temperatures, LLDPE can be dissolved in certain aromatic, aliphatic, and halogenated hydrocarbons including xylenes, tetralin, decalin, and chlorobenzenes.

**Physical Properties.** All polyethylene above  $0.86 \text{ g/cm}^3$  density is semicrystalline. The basic crystalline structure for most commercial LLDPE is chain-folded lamellae (Fig. 7). The body of the crystal consists of polymer backbone segments, and the surfaces are a collection of chain folds, loose cilia, and tie chains (chains incorporated into more than one crystal). When crystallized isothermally, it has been found that 95% of the lamellae in a given sample are within 5% of the same thickness (10). There is some debate over the mechanism of chain folding and of the subsequent fold loops. The most likely model includes adjacent reentry, loose adjacent reentry, and nonadjacent reentry. Short-chain branch length



**Fig. 7.** Schematic of chain-folded lamellar structure.

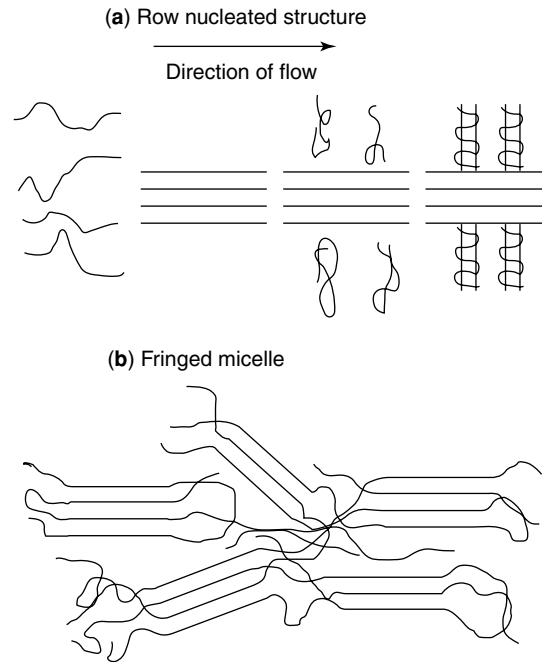


**Fig. 8.** Single crystal and spherulitic structures.

plays an important role in determining backbone flexibility for chain folding and subsequently fold loop size. Longer short-chain branches sterically hinder chain folding and therefore cause longer fold loops and increased numbers of tie chains. It has been found that a minimum sequence length of 14 carbons is needed for ready incorporation into a crystal lattice (11). The most stable crystalline form for polyethylene is orthorhombic with unit cell dimensions of  $a = 7.42 \text{ \AA}$ ,  $b = 4.94 \text{ \AA}$ , and  $c = 2.55 \text{ \AA}$ . Research has shown that the chain axis is inclined at an angle of  $30\text{--}45^\circ$  to the crystal surface (12,13).

From very dilute solution ( $\leq 0.1\%$  weight or volume) single, lozenge-shaped crystals are formed (Fig. 8). They have similar relative dimensions as a sheet of paper, Angstroms thick and microns in lateral dimensions. Cooled from an unstressed melt, LLDPE forms spherulitic structures, also shown in Figure 8. Spherulites form from a defect or nucleation site and are essentially ribbon-like lamellae radiating out from a central point. They begin as sheaf-like structures and grow into spherical shapes. Regions between lamellae are amorphous chain segments and tie chains (14,15). The tie chain density between lamellae plays a dominant role in determining mechanical properties.

It is now widely accepted that LLDPE will form row nucleated, a.k.a. “shish-kebob”, structures when crystallized in a melt subjected to a deviatoric stress, such as film extrusion (16–21). As given in Figure 9, a core of linear higher density polymer forms in the direction of stress (machine direction in film applications), and lamellae grow radially. Space between lamellae is filled with amorphous chain segments and tie chains. Some plastomers below  $0.89 \text{ g/cm}^3$  density will form a fringed micellar morphology because of the very short backbone sequence length between branch points (22,23).



**Fig. 9.** (a) Row nucleated and (b) fringed micelle structures.

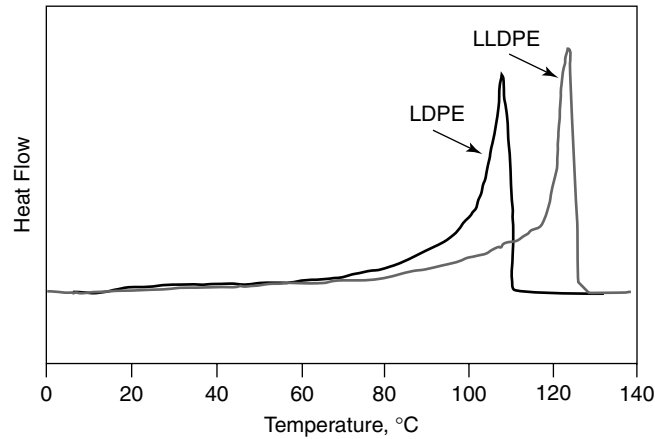
Polymer crystals are rarely perfect and can include chain ends, voids, and at times short-chain branches. As it is generally concluded that the ethyl branch from butene comonomers can be incorporated into the crystal lattice (24–28), this may explain why longer comonomers give LLDPEs with improved properties. Hexene and octene comonomers are more likely to produce large fold loops or tie chains that improve toughness. Quick quenching from the melt also provides less perfect crystals and may allow longer branches to be included in the crystal lattice (29).

As mentioned earlier, LLDPE has a heterogeneous composition and a higher density fraction with minimal branching. Because of this higher density fraction and its thicker crystals, the maximum melting peak in the relatively broad melting range of LLDPE usually falls between 122 and 128°C and is somewhat independent of comonomer-type. Even nonuniform VLDPE resins can have a melting point above 120°C. LDPE has thinner crystalline lamellae than LLDPE and therefore has a lower melting point as shown in the differential scanning calorimetry (dsc) profiles in Figure 10. Homopolymer LDPE usually has a melting point between 105 and 115°C.

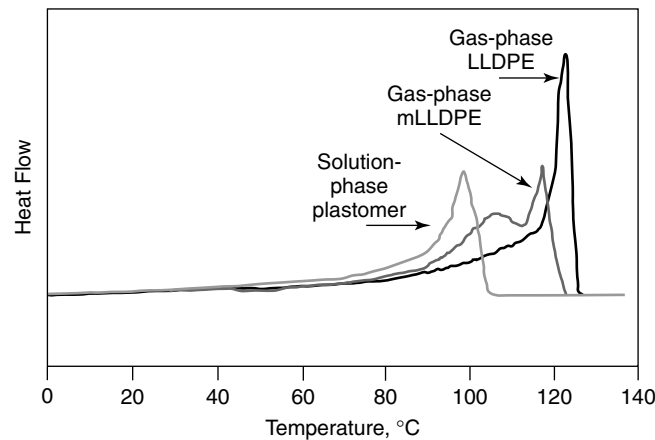
Because of its lower melting point, LDPE has been preferred over LLDPE for many heat-sealing applications. mLLDPE and plastomers are more compositionally homogeneous than LLDPE. Shorter backbone sequence lengths for crystallization results in thinner crystalline lamellae and therefore lower melting points (Fig. 11).

mLLDPE produced in the gas phase and several produced in the slurry phase have peak melting points of 115–118°C. Plastomers have peak melting





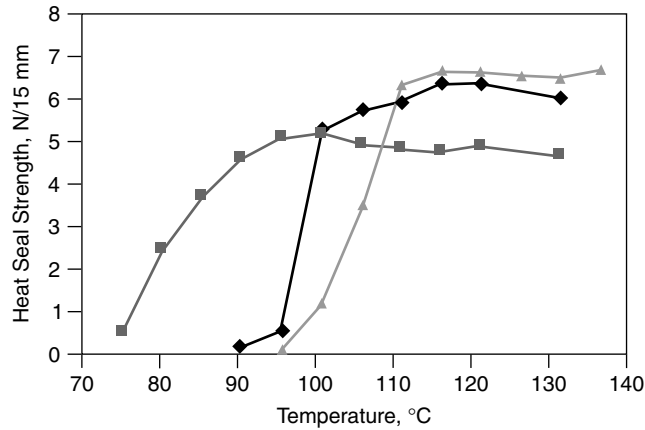
**Fig. 10.** The dsc melting profiles for LDPE and LLDPE.



**Fig. 11.** The dsc melting profiles for LLDPE, mLLDPE, and a plastomer.

temperatures below 100°C. Lower melting points make single-site-catalyzed LLDPEs ideal for use as heat seal layers in many applications. Figure 12 shows heat seal strengths for LLDPE and mLLDPE, both at 0.917 g/cm<sup>3</sup> density, and a 0.900 g/cm<sup>3</sup> density plastomer produced in a high pressure reactor. All have nominal 1 g/10 min melt index. The single-site-catalyzed resins have lower seal initiation temperatures and generally have higher hot tack strengths, which allows for shorter dwell time and faster line speeds.

As with all polymers that are at least partially amorphous, polyethylene has a glass-transition temperature  $T_g$  where the transition from brittle solid to viscoelastic material occurs. There is still disagreement as to the actual  $T_g$  for polyethylene and researchers have proposed different temperatures of  $-30 \pm$



**Fig. 12.** Heat seal strength comparison for LLDPE, mLLDPE, and plastomer. To convert N/15 mm to ppi, divide by 2.625.  $-\Delta$  LLDPE-;  $-\diamond$  mLLDPE-;  $-\blacksquare$  Plastomer-.

15°C (30,31),  $-80 \pm 10^\circ\text{C}$  (32), and  $-128 \pm 5^\circ\text{C}$  (33,34). Above the melting point, polyethylene is a viscous liquid.

Polyethylene has a dielectric constant of 2.3 at 1 kHz which makes it suitable for use as wire and cable housing.

## Mechanical Properties

**Effects of Density.** Decreasing the  $\alpha$ -olefin comonomer content increases the amount of crystallinity in LLDPE. Increasing the amount of crystallinity increases the density of the polymer and has a significant effect on polymer properties. As crystallinity increases, LLDPE becomes stiffer and in general, less tough. Table 3 shows the effect of increasing density in LLDPE blown films.

Only a seemingly small increase in density,  $0.005 \text{ g/cm}^3$ , can dramatically alter mechanical properties. Dart impact and puncture resistance are significantly reduced while tensile yield and modulus increase. For resins produced using the same catalyst and process, more crystallinity means more, larger light-scattering bodies in the film and a rougher film surface causing film haze to increase and surface gloss to decrease. At the relatively low strain rates used to test film tensile properties, density alone does not significantly affect ultimate properties such as tensile strength or elongation at break.

**Effects of Comonomer and Compositional Uniformity.** Table 4 shows blown film mechanical properties for an LDPE, two gas-phase LLDPEs, and one gas-phase mLLDPE, all at the same nominal melt index and density.

The first two resin columns show general film property differences between LDPE and LLDPE. LLDPE has higher tensile strength than LDPE. Modulus is higher in LLDPE resins allowing for downgauging without sacrificing stiffness. LDPE films have higher machine direction (MD) tear at low blow-up ratios (BUR) while LLDPE films have higher machine direction tear at higher BUR. Transverse

**Table 3. Effects of Resin Density on Blown Film<sup>a</sup> Properties<sup>b</sup>**

Property	ASTM test method	Gas-phase LLDPE	Gas-phase LLDPE
Melt index $I_2$ , g/10 min	D1238	0.80	0.80
Density, g/cm <sup>3</sup>	D792	0.921	0.926
Film thickness, $\mu\text{m}$		38	38
Dart impact $F_{50}$ , g	D1709	240	210
Puncture resistance, J/mm <sup>c</sup>		100	50
1% secant modulus, MPa <sup>d</sup>			
MD	D882	180	210
TD	882	200	250
Tensile yield strength, MPa <sup>d</sup>			
MD	D882	10	13
TD	D882	10	14
Haze, %	D1003	10	18
Gloss, 45°	D2457	60	39

<sup>a</sup>Blown film with BUR = 2.5.<sup>b</sup>Ref. 35.<sup>c</sup>To convert J/mm to ft-lbf/in., multiply by  $53.38 \times 10^3$ .<sup>d</sup>To convert MPa to psi, multiply by 145.**Table 4. Blown Film<sup>a</sup> Mechanical Properties for LDPE, LLDPE, and mLLDPE**

Property	ASTM Test method	ASTM Test			
		LDPE	C <sub>4</sub> LLDPE	C <sub>6</sub> LLDPE	C <sub>6</sub> mLLDPE
Melt index $I_2$ , g/10 min	D1238	1.0	1.0	1.0	1.0
Density, g/cm <sup>3</sup>		0.919	0.918	0.917	0.917
Gauge, $\mu\text{m}$		25	25	20	20
Tensile strength, MPa <sup>b</sup>					
MD	D882	39	46	55	66
TD	D882	26	37	42	59
1% Secant modulus, MPa <sup>b</sup>					
MD	D882	200	201	207	173
TD	D882	220	234	228	175
Elmendorf tear, g					
MD	D1922	170	140	255	185
TD	D1922	55	400	580	280
Dart impact, g		80	100	160	>1000
Haze, %	D1003	8	12	15	12
Gloss, 45°	D2457		50	51	47

<sup>a</sup>Films made at 1.8-kg/cm die circumference/h [10 lb/(hr-in.)] output rate, 2.5:1 BUR. 1.5-mm (60-mil) die gap used for LLDPE and mLLDPE, 0.76-mm (30-mil) die gap used for LDPE.<sup>b</sup>To convert MPa to psi, multiply by 145.

direction (TD) tear is significantly higher in LLDPE. LLDPE has better dart impact strength than LDPE, although 0.25 g/10 min melt index LDPE will have dart impact strength approximately equal to 1 g/10 min melt index butene copolymer LLDPE. In general, LDPE has better optical properties, lower haze, and higher gloss than LLDPE. LLDPE, blended with a small amount of LDPE, 5–25 wt%, has dramatically improved optical properties. Improved mechanical properties in LLDPE are often related to microstructure, ie, increased tie chain density (36,37),

although there has been some work to suggest LLDPE contains a dispersed soft phase that leads to improved impact and fracture properties (38).

In general, as side-chain branch length increases from methyl to ethyl to butyl ( $C_3$  to  $C_4$  to  $C_6$  comonomer), mechanical properties improve. While comparisons between butene and hexene copolymer LLDPEs are relatively straightforward, it is difficult to compare them with the effects of octene comonomer on properties. Butene and hexene copolymers are usually made in the gas phase while octene copolymers are usually made in solution phase. Differences in polymerization medium and catalyst can create subtle, yet significant, differences in molecular weight distribution and compositional homogeneity that make it difficult to sort out the effects of comonomer alone on mechanical properties. Generally speaking, there is little difference in mechanical properties in films made from hexene and octene copolymer LLDPEs. When produced in the same process, hexene and octene copolymer LLDPEs have nearly equivalent mechanical properties that are significantly better than those for butene copolymer LLDPE (39).

Butene copolymer LLDPE has the poorest balance of mechanical properties of the commercially available resins. Replacing even a small amount of butene comonomer with a longer  $\alpha$ -olefin can improve toughness properties (40). A butene copolymer LLDPE and hexene copolymer LLDPE, both made in the gas phase, are compared in Table 4. Even at thinner gauge, the hexene copolymer LLDPE has improved tensile, tear, and impact properties relative to the butene copolymer LLDPE.

Also included in Table 4 is a gas-phase process hexene copolymer mLLDPE. The mLLDPE has a narrow molecular weight distribution and is more compositionally homogeneous compared to a conventional LLDPE. A narrower molecular weight distribution gives improved tensile properties but lower tear resistance. Greater compositional uniformity produces smaller crystals resulting in lower tensile modulus, significantly improved impact strength, and lower film haze.

Properties for blown films made from two different plastomers are shown in Table 5. The plastomer made in the high pressure process has better overall toughness and optical properties than the plastomer made in the solution process.

#### **Effects of Molecular Weight and Molecular Weight Distribution.**

Molecular weight has the largest effect on tensile properties. Table 6 shows that for resins of equal density, higher molecular weight (lower melt index) translates into higher tensile strength. There is no major effect on yield strength or MD tear resistance, but TD tear resistance and dart impact strength are improved.

Effects of molecular weight distribution in mLLDPE have been discussed previously. Subtle changes in molecular weight distribution can also have a significant effect on LLDPE properties. Super-hexene LLDPE resins produced in the gas phase have slightly narrower molecular weight distributions, 3.5 compared to approximately 4 for conventional LLDPE, and slightly improved compositional homogeneity. The combination of molecular weight distribution and composition can lead to dart impact strengths improved over 250% and MD tear resistance improved over 30% compared to conventional LLDPE of similar melt index and density (42,43).

LLDPE resins with broad molecular weight distributions made using chrome-based catalysts find application in blown films and some molding applications (44). Because of broader molecular weight distribution, they tend to be more

**Table 5. Plastomer Blown Film Properties**

Property	ASTM test method	Plastomer	
		Solution	High pressure
Melt index $I_2$ , g/10 min	D1238	1.0	1.2
MFR $I_{21}/I_2$		30	15
Density, g/cm <sup>3</sup>		0.902	0.900
Comonomer		Octene	Hexene
Film thickness, $\mu\text{m}$		32	32
Tensile strength, MPa <sup>a</sup>			
MD	D882	77	81
TD	D882	62	77
1% Secant modulus MPa <sup>a</sup>			
MD	D882	73	79
TD	D882	81	83
Elmendorf tear, g			
MD	D1922	170	190
TD	D1922	470	300
Dart impact, g	D1709	1100	>1600
Haze, %	D1003	2.6	1.1

<sup>a</sup>To convert MPa to psi, multiply by 145.

**Table 6. Effects of Molecular Weight on Cast Film<sup>a</sup> Properties<sup>b</sup>**

Property	ASTM test method	C <sub>6</sub> LLDPE	C <sub>6</sub> LLDPE	C <sub>6</sub> LLDPE
Melt index $I_2$ , g/10, min	D1238	2.0	2.35	3.2
Density, g/cm <sup>3</sup>		0.917	0.917	0.917
Tensile strength @ break, MPa <sup>c</sup>				
MD	D882	69	67	61
TD	D882	37	34	34
Tensile strength at @ yield, MPa <sup>c</sup>				
MD	D882	8.3	7.4	7.9
TD	D882	7.6	7.6	7.6
Elmendorf tear, g				
MD	D1902	160	200	180
TD	D1902	920	840	770
Dart impact $F_{50}$ , g		90	85	75

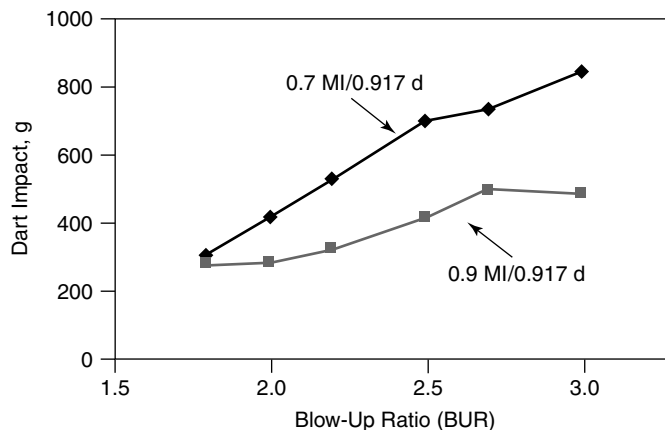
<sup>a</sup>Film made on 90-mm (3.5-in.) extruder at 230-m/min (750-ft/min) take-off speed, 274–300°C melt temperatures.

<sup>b</sup>Ref. 41.

<sup>c</sup>To convert MPa to psi, multiply by 145.

sensitive to orientation and therefore have less balanced properties compared to a conventional Ziegler–Natta-catalyzed LLDPE. The broad molecular weight distribution is a benefit in blow molding for having higher melt strength (for less sag) and higher environmental stress-crack resistance (ESCR) than LLDPE of similar molecular weight.

**Effects of Orientation.** Molecular orientation plays a significant role in determining physical performance of a finished article. In particular, film properties can be affected by processing conditions and their subsequent effects on



**Fig. 13.** Effects of blown film orientation on two LLDPEs.

molecular orientation. In general, polyethylene blown and cast films have predominant molecular orientation in the MD (41). LDPE films usually have more MD orientation than LLDPE films because of greater strain hardening behavior. Blow-up ratio (BUR) is a blown film process parameter used to control orientation. As BUR increases, molecular orientation in the MD is decreased and LLDPE blown film mechanical properties become more balanced. Impact strength is especially affected by changes in orientation. Figure 13 shows the effect of increasing BUR. In this example, output rate is held constant, BUR is increased, and line speed is reduced to maintain constant film gauge.

### Catalysts for LLDPE Production

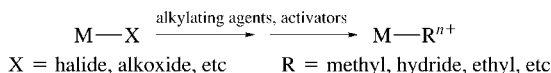
Central to the discovery and development of LLDPE has been transition-metal catalysis. However, because a given catalyst may be most useful for a different class of polyethylene or several classes, the following discussion will at times touch on other topics such as high density polyethylene (HDPE) or even polypropylene. Emphasis will be given to commercialized systems.

Almost two decades after ICI's commercialization of free-radical-polymerized LDPE in the 1930s, transition-metal catalysts proved capable to produce unbranched "linear low" density polyethylene (LLDPE) and linear "high density" polyethylene (HDPE), which had significantly different properties. Remarkably, the discovery occurred nearly simultaneously in three different research groups, using three different catalyst systems. First was Standard of Indiana's reduced molybdate on alumina catalyst in 1951 (46) followed by Phillips with chromium oxide on silica ("chromox") catalysts (47) and Ziegler's titanium chloride/alkylaluminum halide systems (48) in 1953. Only the second two were widely commercialized. This linear polyethylene is tougher than its predecessor and gave rise to entirely new markets, which are now larger globally than any other polymer. All these systems were characterized by low ethylene pressures (hundreds

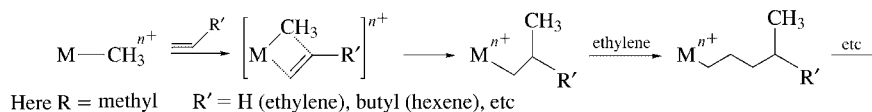
of psi vs tens of thousands for HPLDPE), broadened molecular weight distributions, the absence or strong reduction of the long-chain branches characteristic of high pressure polyethylene, and the ability to incorporate  $\alpha$ -olefins including the production of polypropylene.

The following decades saw generations of refinements to the Ziegler system, the advent of vanadium catalysts, some "single-sited," mainly for the production of ethylene-propylene-diene-modified "rubber" copolymers (EPDM), the discovery of organochromium catalysts for HDPE, and the introduction of slurry loop and gas-phase heterogeneous process technology. In the early 1980s, the field was again revolutionized by Kaminsky's discovery of the methylalumoxane (MAO) activator that led to single-site behavior and phenomenal activities for metallocene catalysts. Others, particularly Exxon and Fina, soon showed that variation of the metallocene structure leads to variation in and exquisite control of catalyst-polymer properties. While MAO has an undetermined polymeric structure, it was shown that discrete "noncoordinating" anions which could stabilize metallocene cations produced equally active catalysts. Bercaw's linked cyclopentadienylamide ligands were shown by Dow ("constrained geometry catalysts") and Exxon to give high activity when bound to titanium (see as given later). While these two catalyst systems, metallocene and "constrained geometry," long seemed unique in giving defined, single-site polyethylene, the 1990s have given rise to numerous nonmetallocene catalyst systems, some of which may be commercially viable in LLDPE applications. The uniting feature of these metal-catalyzed systems is the hypothesis that a metal-carbon bond is formed into which olefins can repeatedly insert, creating polymers by a chain-growth mechanism.

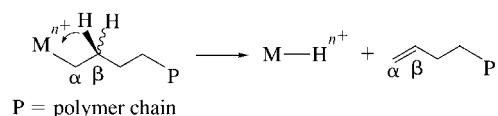
**Mechanism of Metal-Catalyzed Polymerization.** While the detailed mechanism of chain propagation may vary from system to system, most if not all are now believed to proceed by the Cossee-Arlman (49) mechanism in which an olefin monomer undergoes a concerted insertion into a metal-polymer chain bond via a 4-center transition state. Several fundamental steps describe the process. Initiation/Activation occurs when a metal center is transformed so that it is bonded to a group via carbon. A metal-carbon bond capable of inserting an olefin is created at the (usually cationic) metal center:



Propagation occurs when olefins insert into the metal-carbon bond, extending the chain. In the following the Cossee-Arlman transition state is shown:



Spontaneous termination of the chain occurs when a hydrogen on the beta carbon of the chain migrates to the metal creating a metal hydride, which can reinitiate, and a chain with an unsaturated end.

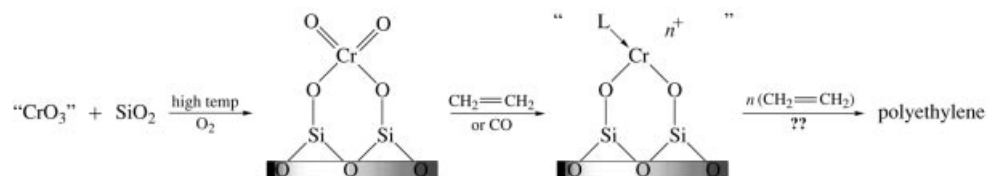


Chain transfer can occur to hydrogen, aluminum alkyls, or possibly even monomers, ending chain growth and initiating a new chain. Deactivation occurs by reaction with poisons or thermal decomposition of the catalyst center.

**Standard of Indiana Catalyst.** The first “low pressure” polyethylene catalyst invented (46), the Standard of Indiana catalyst system, saw relatively little commercial practice. Their 1951 patent discloses reduced molybdenum oxide or cobalt molybdate on alumina for ethylene polymerization, preferably in aromatic solvents. Later, work concerning the use of promoters was also disclosed.

**Phillips Chromox Catalyst.** Impregnation of chromium oxide into porous, amorphous silica–alumina followed by calcination in dry air at 400–800°C produces a precatalyst that presumably is reduced by ethylene during an induction period to form an active polymerization catalyst (47). Other supports such as silica, alumina, and titanium-modified silicas can be used and together with physical factors such as calcination temperature will control polymer properties such as molecular weight. The precatalyst can be reduced by CO to an active state. The percent of metal sites active for polymerization, their oxidation state, and their structure are the subject of debate. These so-called chromox catalysts are highly active and have been licensed extensively by Phillips for use in a slurry loop process (Fig. 14). While most commonly used to make HDPE, they can incorporate  $\alpha$ -olefins to make LLDPE. The molecular weight distributions of the polymers are very broad with PDI > 10. The catalysts are very sensitive to air, moisture, and polar impurities.

**Ziegler Catalysts.** For his work in the discovery of a new class of highly active catalysts for polymerization of ethylene, propylene, and dienes, Karl Ziegler shared the 1963 Nobel Prize in Chemistry with Giulio Natta whose contributions were predominantly related to polypropylene. Today, these catalysts together with the Phillips catalyst are responsible for the majority of the world’s polyethylene production. Loosely defined, Ziegler catalysts are polyethylene catalysts derived from transition-metal halides and main group metal alkyls (46,50–53). In modern



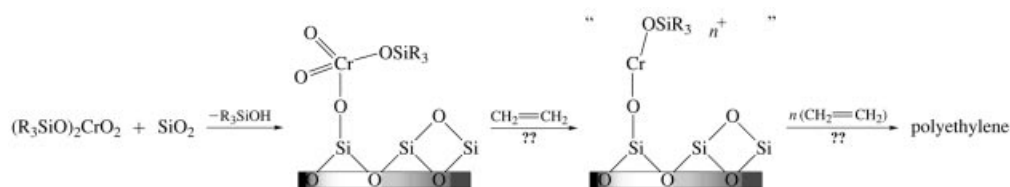
**Fig. 14.** Phillips’ chromox catalyst. (Here “??” indicates that the actual mechanisms are as yet unknown.)



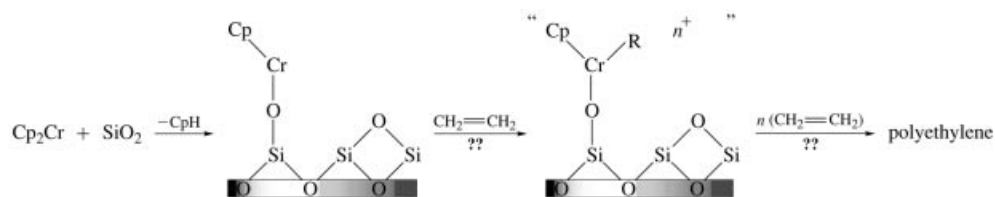
usage this generally means titanium (and sometimes vanadium) chlorides with aluminum alkyls or alkylchlorides. Numerous large research and commercialization efforts have progressed titanium-based systems through five or six generations, particularly for isospecific propylene polymerization. Most early systems used titanium halides with aluminum metal or aluminum alkylhalides to produce some form of crystalline  $\text{TiCl}_3$ , usually the alpha form, often with Al in the lattice. The Ti centers could be in +3, +4, and even +2 oxidation states. Aluminum alkyl cocatalyst was required for activity. In the next generation, large increases in activity were achieved by dispersing the titanium centers over crystalline  $\text{MgCl}_2$ , and this is now standard commercial practice. Modifiers, internal donors, external donors, and cocatalysts have been used to produce smaller  $\text{MgCl}_2$  crystals, higher surface areas, poison undesired sites, control oxidation states, enhance activity, and otherwise change the catalyst performance. Silica or other porous supports are usually used to introduce the catalyst into heterogeneous processes. As with most heterogeneous systems (eg, organochrome and chromox catalysts) there are multiple active sites which may only be a fraction of the total metal centers. The exact structure and number of active sites is usually a topic of debate because of the problem of extremely active catalysts: they must be used in extremely low concentration and usually cannot be detected directly at "real world" conditions. Multiple sites lead to polyethylene chains with varying structures from chain to chain, though the typical molecular weight PDIs of 3.5–6 for Ziegler catalysts are still much narrower than the chromox catalysts. Some producers (eg, Dow and Nova) use these catalysts in solution, but most of the LLDPE volume comes from supported catalysts because of their use in the heterogeneous gas-phase processes extensively licensed by Union Carbide and British Petroleum. These catalysts are substantially less sensitive to air and moisture than chromium-based systems. Polyethylene molecular weight can be reduced by the addition of  $\text{H}_2$ , and  $\alpha$ -olefin comonomers are copolymerized in order to lower the polymer's density.

**Organochrome Catalysts.** Like the Phillips chromox catalysts, the organochromium catalysts introduced by Union Carbide in the 1970s required an oxide support. Both disilyl chromates,  $(\text{R}_3\text{SiO})_2\text{CrO}_2$  (Fig. 15), and chromocenes,  $(\text{C}_5\text{H}_5)_2\text{Cr}$  (Fig. 16), are believed to bond to an oxo functionality on the support ultimately leading to  $\text{Cr}^{2+}$  species. How these form the active species and its nature remain unproven. These catalysts have been licensed extensively in slurry-phase and gas-phase processes, but only for HDPE production because of negligible comonomer incorporation ability. Molecular weight distributions are broad, and hydrogen lowers molecular weight by chain transfer. These systems are very sensitive to impurities as with the Phillips catalyst.

**Metallocene Catalysts.** Although some commercial solution catalysts (eg, vanadium halide/alkyl aluminum EPDM systems) exhibited single-site behavior (eg, PDI = 2) earlier, metallocenes ushered in well-understood, finely tunable single-site polymerization capability on a far broader scale. Metallocenes are molecular transition-metal compounds containing the flat cyclopentadienyl ring bound "side-on" to the metal center. Shortly after their discovery in the 1950s, it was known that metallocenes could polymerize or oligomerize olefins in the presence of aluminum alkyl cocatalysts. By the 1970s, it had been found that small amounts of water increased the system's activity (48,54,55). Around this time, it was shown that unactivated, neutral Group 3 metallocenes could



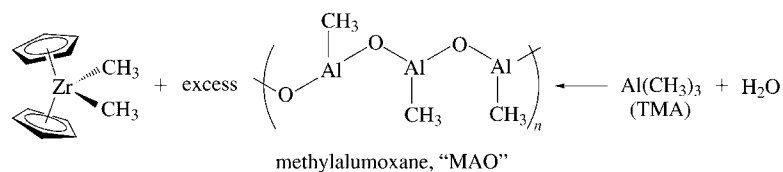
**Fig. 15.** Disilyl chromate catalyst. (Here “??” indicates that the actual mechanisms are as yet unknown.)



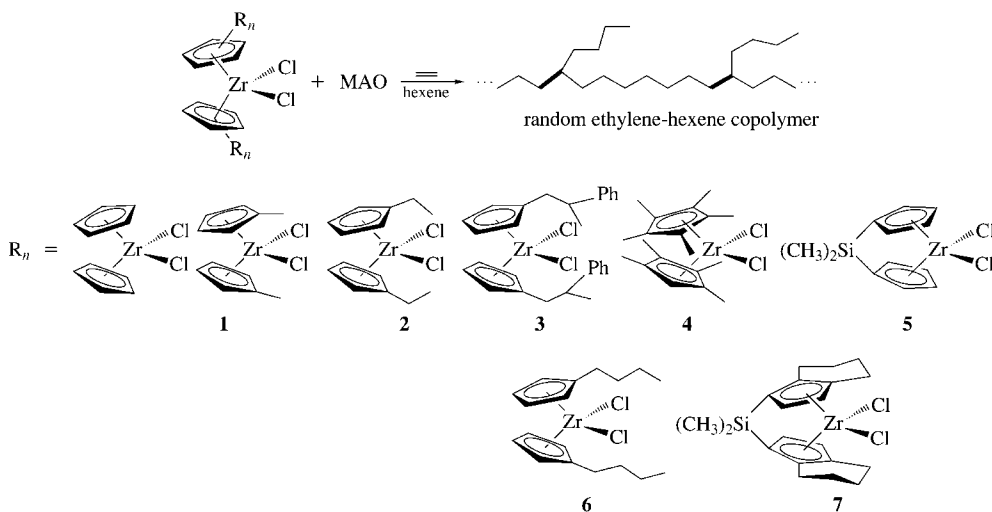
**Fig. 16.** Chromocene catalyst. (Here “??” indicates that the actual mechanisms are as yet unknown.)

polymerize olefins to high molecular weight with narrow molecular weight distributions (56,57). Despite these many works demonstrating most of the major characteristics of the current state-of-the-art polymerization catalysts, the critical breakthrough came in the activator.

**MAO—The Kaminsky Activator and Single-Site Catalysis.** In 1976, Kaminsky, Sinn, and co-workers discovered that water-treated trimethylaluminum activates metallocenes orders of magnitude better than previous systems (48,54,55,58). This finding has revolutionized this field of ethylene and  $\alpha$ -olefin polymerization, laying the foundation upon which all further advances were built. The key activator, known as methylalumoxane (MAO), is generally formed by the reaction of less than one water with one  $\text{Al}(\text{CH}_3)_3$  to create polymeric structures  $(\text{CH}_3\text{AlO})_n(\text{Al}(\text{CH}_3)_3)_n$  thought to contain chains, rings, three-dimensional cage structures, and unreacted trimethylaluminum (TMA). Typically formed in toluene, the original MAO has a tendency to form gels.



Versions incorporating, eg isobutyl groups (MMAO), have differing properties such as hydrocarbon solubility and less gelation. The optimal activator will vary from system to system. Despite the multisited structure of MAO, many MAO-activated metallocenes give polymers with narrow molecular weight distributions ( $\text{PDI} = 2.0$ ) and narrow comonomer distributions, behavior characteristic of only a

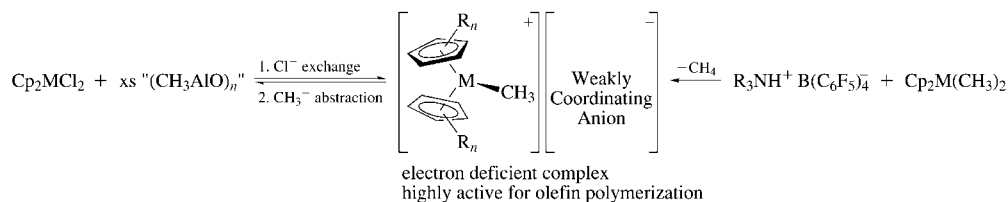


**Fig. 17.** Substituted metallocene catalysts. The identity of  $R_n$  controls polymer molecular weight and density, which in turn controls polymer properties.  $R_n = H$  or see other examples. (1), (2), (3), (4), (5) from the patent (59). Many further derivatives were later disclosed, notably, (6) and (7).

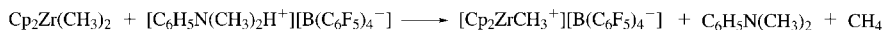
single active structure. The contrast with multi-sited Ziegler and chrome systems lead to the use of single-site catalysis to describe these systems.

**Metallocene Commercialization—The Significance of Substitution.** The parent metallocenes used by Kaminsky and co-workers are rarely used commercially, so it is fair to say that the breakthrough was not completed until the recognition that subtle variations in the metallocene molecular structure dramatically change the catalyst performance and polymer characteristics (Fig. 17). Welborn and Ewen of Exxon lead in this discovery, leading to base patent coverage in the field (59). Patents and articles on metallocene derivatives now number into the thousands. Ewen as well as Brintzinger and Kaminsky, Spaeleck and co-workers at Hoechst, Weymouth (60,61), and many others advanced the mechanistic insights into these systems by studying tacticity control in polypropylene.

**Noncoordinating Anions—Alternative, Discrete Activators.** Elucidation of the nature of the active species in MAO/metallocene catalyst systems was the subject of intensive research efforts with contributions coming from many laboratories. It would be artificial to attribute credit to any one group for solving the mystery, but it was the discoveries by Jordan (62) and by Turner and Hlatky of Exxon (63) that most clearly established the current view. They demonstrated that metallocene cations possessing stable, noncoordinating anions (NCAs) such as tetraarylborates were extremely active for olefin polymerization and were single-sited in nature (Fig. 18). This strongly implied that MAO functions by abstracting an anionic ligand from a neutral metallocene to form a metallocene cation and an MAO anion. Indeed, it was shown that a neutral aryl borate could abstract a methyl group to form a metallocenium—anion pair with high activity (64). Because of the known structure of these activators vis a vis MAO, these are often referred to as discrete activators. These activators are commercially viable,



**An exemplary discreet ionic activator**



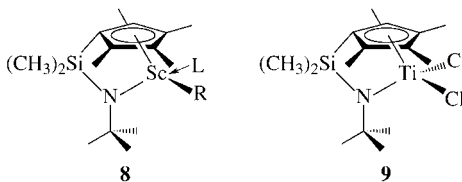
**An exemplary discreet neutral activator**



**Fig. 18.** Noncoordinating ionic catalysts.

often yielding greater activity than MAO with the cost advantage that large molar excesses are not needed as with MAO. Conversely, such systems are often very sensitive to impurities, whereas excess MAO acts as an impurity scavenger.

**The CPsiNR Ligand for Constrained Geometry Catalysts.** Biscyclopentadienylmetal complexes were not the only single-site catalysts for olefin polymerization. Monocyclopentadienyl complexes often showed activity, but generally were not competitive catalysts except when linked to a bulky amido group. Thus, Bercaw's Group 3 metal system CpSiNR ligand (**8**) was placed on titanium (**9**) by workers at Dow (65) and Exxon (66) and was found to produce very active catalysts with attractive features. The open structure leads to very good comonomer incorporation and has high molecular weight capability. Both companies filed patents in the U.S. and World offices within days of each other resulting in interferences and court actions over catalyst, activator, and polymer, which were recently settled after more than a decade. Dow proceeded with commercialization of the system dubbing them constrained geometry catalysts because of the bridge between the cyclopentadienyl and amide ligands.



**Commercialization of Single-Site Catalysts.** In commercial practice, mono and biscyclopentadienyl (mono Cp bis Cp) catalysts show sensitivity to oxygen, water, and polar functionality more comparable to that of chrome catalysts. Depending on catalyst molecular structure, molecular weight capability and comonomer incorporation level vary over a tremendous range beyond the capabilities of other commercial catalysts. Comonomer incorporation is usually more facile and more evenly distributed throughout the chain than in the older conventional systems in addition to less chain-to-chain molecular weight and comonomer

variation. Bis Cp catalysts are very sensitive to chain termination by H<sub>2</sub>, while mono Cp amide (constrained geometry) catalysts are more like titanium Ziegler systems in this regard. The systems are supported on silica when used in slurry-phase or gas-phase processes, and both MAO and NCA activation are practiced. Although the major components of these catalysts—metal complex, MAO, discrete activators—are inherently more expensive than conventional catalyst raw materials, volume manufacture and high activity have reduced costs to acceptable levels when combined with premiums commanded by the polymer products.

Though not well known, the commercial use of metallocenes for polymerization began in 1985 with Uniroyal's sale of "Trilene" low molecular weight polyethylene products. Exxon began production of metallocene VLDPE in a high temperature and pressure unit in 1991 under the EXACT trade name. These metallocene polymers are characterized by very narrow molecular weight and comonomer distributions, which lead to high strength and uniformity. Several years later, Dow introduced constrained-geometry-catalyst-produced polymers using a high temperature solution process to make VLDPE and LLDPE. These polymers generally emphasized easier processability relative to the bis metallocenes. Then in 1994, Exxon launched commercial metallocene products from the low pressure, low temperature, very large-scale UNIPOL<sup>TM</sup> gas-phase process. Metallocene polypropylene was introduced by Exxon and Hoechst the following year, and 1996 saw the sale by Exxon of metallocene polymers produced in slurry loop reactors. With the DuPont/Dow solution process to produce EPDM polymers, all major processes and polyethylene/polypropylene polymer types were being produced by single-site catalysts. While many commercialization announcements have been made up to 2000, relatively few producers beyond those mentioned earlier have initiated full commercial production. However, strong demand, production of specialty products like cyclic copolymers, the recent sale of single-site catalyst licenses, and the announcement of new nonmetallocene single-site catalysts suggest that these new technologies are finally coming into their own after more than a decade of development.

**Other Ligand-Based or Single-Site Catalysts.** The term single site is misleading because the polymers of these systems, including metallocenes, sometimes have broad molecular weight distributions indicative of multiple catalyst sites. Some prefer the term ligand-based catalysts to denote that the catalysts come from discrete molecular precursors (of exactly defined ligand sets) even though in the active system the metal complex may have been partially converted to multiple new species. The mono Cp and bis Cp complexes long seemed unique as commercially useful ligand-based catalysts, but that picture is changing. As metallocene catalysts have risen in profile during the 1990s, and MAO and discrete activators have become widely available enough, nonmetallocene ligand-based catalysts have been discovered to warrant reviews (67,68). Figure 19 depicts exemplary nonmetallocene systems, several of which may be near commercialization. Noteworthy are the nickel- and palladium-based "Versipol" catalysts of DuPont and the University of North Carolina that make hyperbranched polymers (69,70). Also, pyridyl bisimine ligand-based iron catalysts have been disclosed (71–73) and may be used in the near future for HDPE production. Nova has recently announced forthcoming products from ligand-based systems. With Stephan's titanium bisphosphamine systems for example, they

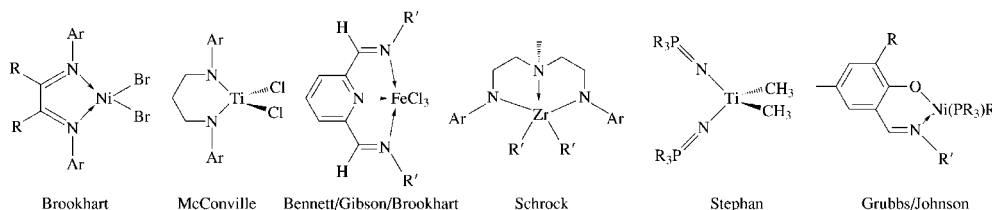


Fig. 19. Other ligand-based single-site catalysts.

collaboratively disclose performance comparable to the constrained geometry catalysts of Dow and Exxon under commercial reaction conditions (74). Given the current state of the technology, it seems very likely that advances in conventional, metallocene, and nonmetallocene catalyst systems will continue to drive LLDPE product and process performance to new levels for decades to come.

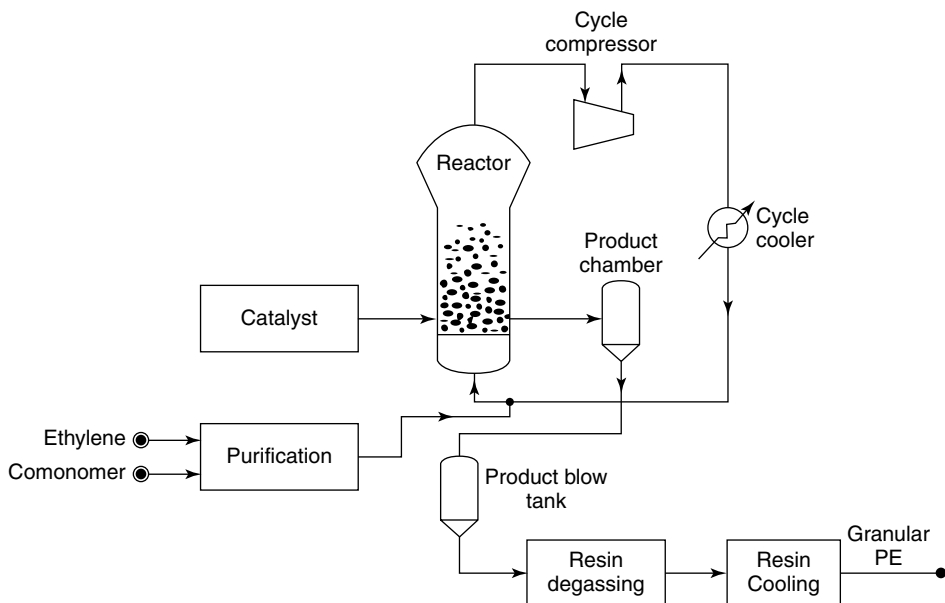
### Low Pressure Manufacturing Processes and Capacities

**Gas-Phase Process.** The gas-phase process is considered to be the most versatile low pressure process for producing polyethylene because it can make the broadest product portfolio in terms of molecular weight and density. It had been used since the 1960s to make HDPE and in 1977, Union Carbide built the first gas-phase plant for LLDPE production. Subsequently, British Petroleum and Himont developed alternative gas-phase processes for producing LLDPE. As a result of its versatility, it is the most widely licensed technology worldwide for linear low density production. A simplified schematic of the Union Carbide Unipol process is shown in Figure 20.

In this process, purified ethylene and comonomer are continuously fed into a fluidized bed reactor. Catalyst in dry form is added directly into the bed. The gas recycle stream serves several purposes—fluidizes the polymer particles, provides polymerization raw materials, and removes heat of polymerization. Reactor temperatures are usually below 100°C to prevent resin stickiness and pressures are approximately 2 MPa (300 psi).

The gas stream fed to the bottom of the reactor is the only source of cooling for reactor temperature control. Reactor temperature is a function of polymerization rate. At one time, output rates were limited to prevent high reactor temperatures and resin stickiness. To increase cooling capacity of the gas stream and therefore increase production rates, the recycle stream can be cooled below reactant dew point forming a liquid–gas mixture that is returned to the reactor, which operates above the dew point of the recycle stream. Evaporation of liquids in the recycle stream absorbs heat from the reactor allowing for greater production rates (75). This is commonly referred to as “running in condensed mode.” Nonreactive hydrocarbons such as *n*-hexane or isopentane in quantities up to approximately 30 wt% of the recycle stream can also be used as condensing agents allowing for production rates near twice design reactor capacity (76).

Residence time for polymer in the reactor can be several hours. This is one disadvantage to the gas-phase process as grade changes can take hours to



**Fig. 20.** Schematic of UNIPOL gas-phase polymerization process.

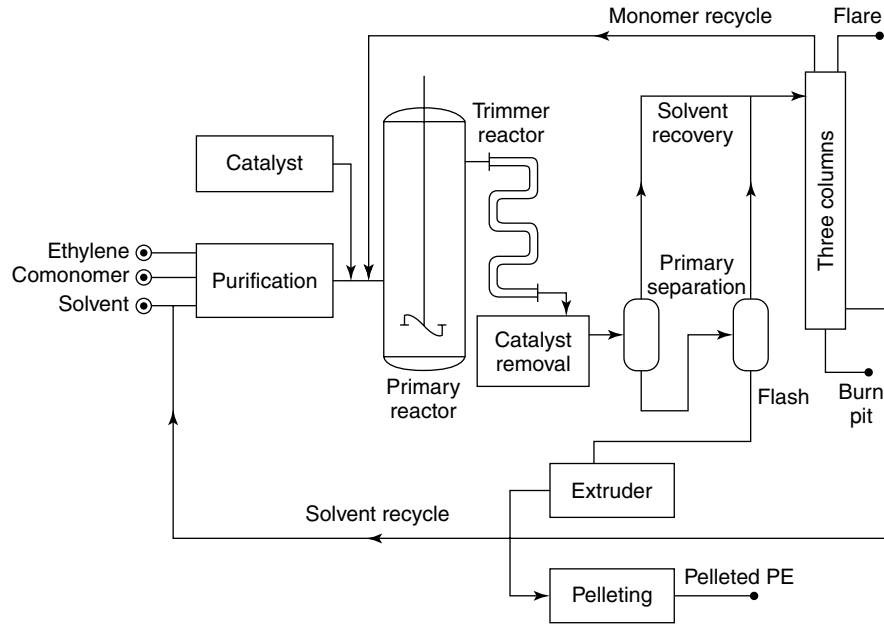
complete. Granular polyethylene is periodically removed from the reactor and sent via pressurized lines to a purge bin where residual catalyst is neutralized and residual monomers are removed. Resin is then conveyed to a pelleting process.

**Solution Process.** The solution-phase process is also very versatile. Because of short residence times in the reactor, product changes can be made in less than an hour at commercial production rates. A schematic of a solution-phase polymerization process is shown in Figure 21.

Ethylene and comonomer are purified and dissolved in a solvent. An activated catalyst is added to that solution, which is then fed to a stirred reactor. The temperature of the feed stream controls reactor temperature, which is a major determinant of polymer molecular weight. Reactor temperatures are usually 170–250°C with pressures of 4–14 MPa (500–2000 psi). The solution is then fed to a secondary, trimmer reactor where further polymerization takes place. Chelating agents are injected into the solution to neutralize active catalyst. A high pressure flash vessel is used to remove monomer and about 90% of the solvent. A secondary devolatilization step is required to completely remove solvent. Granular polymer is then conveyed for pelletization.

Two limiting factors in solution-phase polymerization are cost of operation and polymer molecular weight. Solvent recovery steps are very energy intensive and add to production costs. Also, the production of high molecular weight resins is limited because of the very high viscosity of the resultant solution. Advantages include short reactor residence time that allows for very quick product transitions (77).

**Slurry Process.** While the slurry polymerization process is more often associated with production of HDPE, improved catalyst technology has allowed



**Fig. 21.** Schematic of solution-phase polymerization process.

the production of LLDPE and mLLDPE resins. In the slurry process, monomer is dissolved in a diluent in which the polymer product is insoluble. Polymerization occurs below the melting point of the polymer product that forms as suspended particles. An example schematic of a slurry-phase polymerization process is shown in Figure 22.

Ethylene and comonomer are purified, then dried and fed with recycled diluent with a catalyst slurry to a double loop continuous reactor. Polymer forms as discrete particles on catalyst grains and is allowed to settle briefly at the bottom of settling legs to increase concentration from about 40% in main loop to 50–60% in the product discharge (77). Reactor temperatures are usually 70–110°C and reactor pressures are between 3 and 5 MPa (450 and 720 psi). Diluent and residual monomers are flashed off for recycle and polymer is conveyed for pelletization. Production of low density polymers was not practicable due to solubility of low density/low molecular weight polymer molecules in the diluent, but the use of chromox catalysts that produce broad molecular weight LLDPE and metallocene catalysts that produce mLLDPE have broadened the product portfolio for slurry-phase polymerization.

In order to more finely control polymer molecular architecture in LLDPE, much research and development effort has been spent on developing staged reactor technology. There are currently commercial systems in staged gas phase (Union Carbide) (78,79), staged slurry/gas phase (Borealis) (80), and staged solution phase (Nova) (81). Each of these processes allows for control of molecular weight distribution and location of comonomer, ie in high molecular weight or low molecular weight fractions.



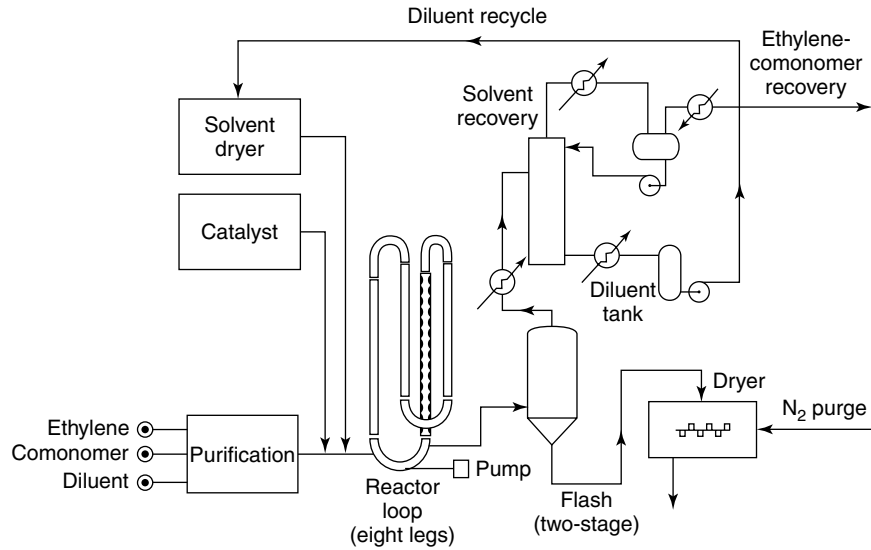


Fig. 22. Schematic of slurry-phase polymerization process.

## Processing of LLDPE

**Rheology.** Every process used to convert LLDPE into a finished product involves melting. Therefore, polymer viscosity is a very important resin parameter that must be considered when selecting a resin for use. LLDPE melts in the normal processing range of 150–300°C exhibit non-Newtonian (shear thinning) behavior as their apparent viscosity is reduced when melt-flow speed is increased (82–85). Figure 23 shows a plot of dynamic melt viscosity for LDPE, gas-phase

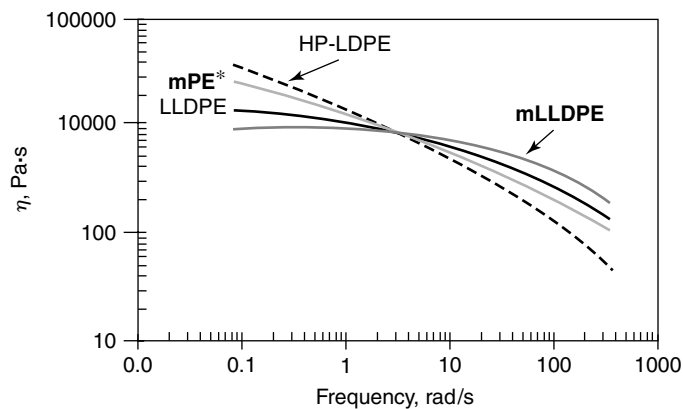
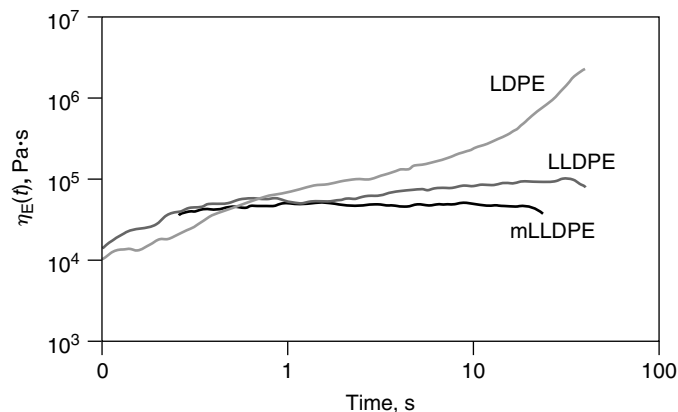


Fig. 23. Melt viscosity data for LDPE, LLDPE, and mLLDPE all normalized to 1 g/10 min melt index. Also shown is new type of easy-processing metallocene-catalyzed polyethylene, mPE\*. To convert Pa·s to P, multiply by 10.

LLDPE and gas-phase mLLDPE, all normalized to 1 g/10 min melt index. At very low shear rates, LDPE has the highest viscosity, caused by a broad molecular weight distribution and long-chain branching. LLDPE has a broader molecular weight distribution than mLLDPE and therefore has higher viscosity at very low shear rates. As you approach the shear rates commonly associated with extrusion, 100–1000 rad/s, those trends are reversed. The broad molecular weight distribution and long-chain branching seen in LDPE cause it to have a greater response to shear. As a result of increased shear thinning relative to LLDPE and mLLDPE, the melt viscosity of LDPE at higher shear rates is significantly lower than that of the linear resins. The LLDPE resin has lower shear viscosity than the mLLDPE because of its broader molecular weight distribution. Higher viscosities will translate to higher extrusion pressures, higher temperatures, and greater energy consumption.

Because melt viscosities for LLDPE and mLLDPE are so much greater than that for LDPE at the higher shear rates experienced during extrusion, market penetration has been limited in some applications and geographical areas where LDPE processing equipment dominates. Several resin companies are working to develop metallocene-catalyzed resins that are compositionally homogeneous but have slightly broader molecular weight distributions or trace levels of long-chain branching. This gives the resins improved mechanical properties relative to LLDPE, but with lower viscosities and easier extrudability (86–88). An example of this type of resin is shown in Figure 23. A relatively new type of metallocene-catalyzed polyethylene, here noted as mPE\*, is shown to have higher melt viscosity than LLDPE at very low shear rates because of a slightly broader molecular weight distribution and trace levels of long-chain branching. Because of its broader molecular weight distribution and long-chain branching, it demonstrates greater shear thinning behavior than LLDPE allowing for use in older equipment designed for LDPE extrusion.

Figure 24 shows extensional viscometry results for 1 g/10 min melt index LDPE, LLDPE, and mLLDPE. LDPE, with its broader molecular weight



**Fig. 24.** Extensional rheology data for LDPE, LLDPE, and mLLDPE. To convert Pa·s to P, multiply by 10.

distribution and long-chain branching, shows appreciable strain hardening behavior relative to the linear resins. LLDPE has greater extensional viscosity than mLLDPE because of broader molecular weight distribution. Lower extensional viscosity translates to poorer bubble stability in the blown film process, but lack of strain hardening allows linear resins to be drawn down to thinner gauges than LDPE of equivalent melt index.

**Film Extrusion.** Approximately 77% of the LLDPE produced globally is processed into film. The most common techniques for producing film are blown film extrusion and cast film extrusion. Both involve extrusion prior to film forming.

In the extrusion process, resin pellets are gravity fed into a heated barrel. Pellets are conveyed down the barrel by a screw that first compacts and then melts the pellets through shear-induced heat. The last section of the screw, also known as the metering section, ensures a homogeneous melt and uniform output. Because of its narrower molecular weight distribution and higher shear viscosity, LLDPE extrudes differently than LDPE. At equivalent melt index, LLDPE is expected to have higher extrusion pressures and temperatures than LDPE. At equivalent temperatures and pressure, LLDPE has better pumping characteristics than LDPE, ie pounds per hour per screw rpm (89). Higher resin viscosity for LLDPE means greater power consumption than LDPE.

To compensate for extrusion differences between LDPE and LLDPE extrusion, screw designs have changed. LLDPE screws have lower compression ratios (channel depth in feed section/channel depth in metering section). Barrier screws, which have additional flights to separate the melt pool from solids bed during melting, were developed to accommodate the different melting behaviors of LLDPE. Extrusion temperatures for LLDPE range from 180 to 300°C with pressures ranging from 15 to over 40 MPa. LLDPE resins, and especially mLLDPE resins, often incorporate fluoropolymer processing aids, such as Dynamar™ products from Dyneon. Fluoropolymer processing aids coat the barrel to reduce shear and therefore pressures and temperatures, and also coat die lips to eliminate melt fracture and die lip buildup. Metallocene-catalyzed resins can be extruded on any line used by LLDPE with the understanding that there may be higher extrusion temperatures and pressures as a result of narrower molecular weight distributions in the mLLDPE compared with conventional LLDPE (90).

In blown film extrusion, molten resin is forced through an annular die. Commercial-scale diameters range from 15 to 120 cm. There are four main components to a blown film die—mandrels, inner lip, outer lip, and body. The mandrel and body distribute polymer flow around the die. Most commercial mandrels have several spirals to more uniformly distribute melt flow and minimize gauge variation (91). Die lips define the die gap. Commercial die gaps for LLDPE blown film extrusion range from 1.5 to 2.5 mm compared to die gaps for LDPE processing, which range from 0.5 to 1.0 mm. Wider die gaps are needed to eliminate melt fracture in LLDPE caused by higher viscosity. After exiting the die, the molten tube of polymer is generally pulled upward by a set of nip rolls, although in some cases it is pulled horizontally or downward. As film thickness is reduced, the tube expands because of internal bubble pressure and forms a tube of larger diameter. The ratio of final bubble diameter to initial die diameter is the BUR. Blow-up

ratios in commercial processes range from 1.5 to over 4 and are largely determined by product end use. Film cooling is aided by air rings that supply air flow around the molten tube. Because of lower extensional viscosity, LLDPE can be drawn to thinner gauges than LDPE but is more prone to bubble instabilities. Dual-lip air rings that provide Venturi-type air flows around the bubble are used to stabilize the bubble in addition to providing cooling. The tubes are drawn down to final film thicknesses of 0.007–0.25 mm. Maximum line speeds approach 240 m/min. Film rolls up to 4 m in diameter are collected on cardboard cores. Many lines have in-line converting for producing articles such as trash bags as the film is being produced.

Cast film extrusion involves extruding molten polymer through a flat die, usually with a coat-hanger design. Commercial die widths can range from 150 to over 600 cm. Die gaps for LLDPE film extrusion are 0.5–0.8 mm. The molten sheet of film is usually extruded downward, but in some cases is extruded horizontally. Within inches after exiting the die, the film is deposited onto a rotating chilled or heated roller. The roller can be polished smooth, have a matte finish, or be embossed with a repeating pattern. Film edges are usually trimmed, chopped, and refeed into the system as flaky material called “fluff” or “regrind.” Film gauges range from 0.007 to 0.125 mm. Film rolls up to 4 m in diameter are collected on cardboard cores. Cast film processes can be run at much higher rates (over 600 m/min) than blown film processes.

**Injection Molding.** LLDPE is processed by injection molding to produce complex shapes from children’s toys to household containers. Polymer pellets are fed to a single-screw extruder and melted at approximately 160–240°C temperatures. The polymer melt is injected into a mold at 35–130 MPa. Higher viscosity resins, ie, higher molecular weight or narrower molecular weight distribution, will require higher pressures. Molds are usually made in two halves, one fixed and one movable. When the mold halves are together, at least one machined cavity will be formed into which molten resin is injected. Cooler mold temperatures decrease cycle time and increase toughness, but can increase molded-in stress. Higher mold temperatures produce high surface gloss. Filling times for very small molds range from 0.2 to 0.8 s and for larger, more complex molds from 3 to 6 s. After the mold is filled, it is held under pressure then cooled rapidly. Cycle time depends on polymer viscosity, density, and part requirements. LLDPE injection-molding cycle times range from 10 to 30 s (92). Plastomers can be injection molded on equipment designed for flexible polyvinyl chloride with only minor adjustments in processing conditions—colder dies, faster injection speeds, and hot runners (93).

**Blow Molding.** Bottles and drum liners are common LLDPE blow-molded articles. In the blow-molding process, a thick-walled tube of film called a parison is extruded vertically downward. The parison will have the correct dimensions, weight, and position relative to the mold to produce the finished product. After the parison is extruded, two mold halves with a machined cavity will close around it sealing the bottom of the tube, and the parison is then inflated by pressurized air. Air pressure is usually low, between 0.3 and 0.7 MPa. The molten resin takes the shape of the mold and is cooled to the solid state. The pressurized air is released, the mold is opened, and the part is ejected. Two areas of concern are polymer swell and melt strength. Swell is caused by shrinkage in the process direction

from elastic recovery of the melt. Melt strength of the polymer must be sufficient to support the weight of the extruded parison and prevent excessive “sag,” which occurs when the parison reaches some critical length and its weight causes an abrupt increase in speed. Both parameters can be controlled by process conditions and selection of polymer molecular weight (94,95).

**Rotational Molding.** Rotational molding is used to produce a variety of polymer parts from small to large and from simple to complex. Instead of resin pellets, finely granulated polymer powders are used. Rotational molds are filled with the exact weight of the part to be formed. They are then heated and simultaneously rotated in two perpendicular planes. Tumbling powder sticks to the heated mold and forms a uniform coating on the interior mold surface. Rotation speeds should be relatively low to prevent strong centrifugal forces that can cause uneven thicknesses. After heating, rotation continues and the mold is cooled. The part is removed after the cooling step (96,97). The impact strength of the product is strongly dependent on the internal air temperature of the mold. Lower internal temperatures lead to inadequate sintering of articles, increased void content, and poor crystalline microstructure (98).

**Extrusion.** Additional extrusion applications of LLDPE include pipe, tubing, sheet, and insulated wire. Pipe and tubing are extruded through annular dies similar to blown film dies. Small diameter products, less than 10 mm, are considered to be tubing while larger diameter products are referred to as pipes (99). Sheet is produced on flat dies and is usually classified as having thickness greater than 0.254 mm. Wire coatings are made by passing a conductor through the hollow center of an annular die and coating with molten polyethylene.

## Economic Aspects

LLDPE is made in every continent except Antarctica. It currently makes up approximately 25% of all polyethylene demand and has the greatest growth rate of the major product families (100) as Table 7 shows.

Usage of metallocene-catalyzed resins is predicted to grow at over 24% from 2000 to 2005 as manufacturing processes become more robust, more companies begin to produce these resins, and resin pricing becomes more competitive with commodity grades (100). Consumption in 2005 is expected to be near 3000 kton.

Table 8 shows global allocated LLDPE production capacities by country and process (101). It must be noted that capacity determination is difficult as

**Table 7. Predicted Annual Growth Rates for Polyethylene<sup>a</sup>**

Resin	Average annual growth rate, %		
	1996–2000	2000–2005	2005–2010
Polyethylene	5.5	6.0	4.7
LDPE	1.5	1.3	–0.2
LLDPE	9.4	9.3	7.3
HDPE	5.2	6.2	5.2

<sup>a</sup>Ref. 100.

Table 8. Global Allocated LLDPE Capacity, 10<sup>3</sup>t<sup>a</sup>

Country	Gas	Solution	Slurry	Other	Total
North America					
United States	3214	1018		75	4307
Canada	769	711			1480
Latin America					
Argentina	98	21			119
Brazil	425	100			525
Venezuela		120			120
Europe					
Finland	70				70
France	420			120	540
Germany	278	166			444
Italy	200	180			380
Netherlands	120	396			516
Russia	150				150
Spain		198		99	297
Sweden	253				253
United Kingdom	100				100
Africa					
Egypt	50				50
Libya	40				40
Nigeria		160			160
South Africa	115				115
Middle East					
Iran	60				60
Kuwait	325				325
Saudi Arabia	1160				1160
Asia & Pacific					
Australia	105				105
China	683	110		77	869
India	200	286			485
Indonesia	478				478
Japan	393	120	160	383	1046
Malaysia	209				209
Pakistan		15			15
Philippines	90				90
Singapore	120				120
South Korea	468	214			682
Taiwan	180				180
Thailand	70	261			331
<i>Totals</i>	<i>10,829</i>	<i>4062</i>	<i>160</i>	<i>754</i>	<i>15,805</i>

<sup>a</sup>Ref. 101.

many processes can be used to make LLDPE and HDPE. The values shown indicate capacity used solely for LLDPE and mLLDPE production. Total LLDPE–HDPE swing capacity is approximately  $25.3 \times 10^3$  kton (101). The countries with the largest LLDPE capacity are the United States, Saudi Arabia, and Japan. In the United States, LLDPE is produced by Chevron, Dow, Eastman,

Equistar, ExxonMobil, Huntsman, Montell, Phillips, Union Carbide, and Westlake. Commercial mLLDPE is available from Dow, ExxonMobil, and Phillips. Globally, it is estimated that there are eleven commercial suppliers of metallocene-catalyzed polyethylene (102).

Ethylene is produced primarily from “cracking” ethane or naphtha. Regions such as the Middle East, Western Canada, and Malaysia have cost advantages over other regions because of plentiful supply of ethane and low alternative values. Countries such as Japan and Korea have much higher ethylene production costs because of poorer plant economics (smaller scale) and expensive naphtha feedstock (82). U.S. pricing for ethylene in mid-2000 is approximately \$0.55–0.60/kg.  $\alpha$ -Olefins are commonly produced by distillation of hydrocarbons, ethylene oligomerization, catalytic dehydrogenation of alkanes, and wax cracking. Mid-2000 U.S. pricing for butene is approximately \$0.57–0.66/kg and pricing for hexene and higher is approximately \$1.25–1.35/kg (103).

Raw materials comprise the greatest fraction of the cost to produce LLDPE. Raw materials include ethylene,  $\alpha$ -olefin, hydrogen, catalyst, and additives. Depending on geographical region, raw materials (at cash cost) are approximately 60–75% of total production costs (100). Utilities, including power, cooling water, steam, and fuel, are approximately 5–15% of total LLDPE production costs. Overhead makes up the balance and includes physical structures, staffing, and shipping. Actual costs can vary significantly by reactor technology, environmental costs, and product mix. Frequent product or catalyst changes can significantly increase production costs by reducing the amount of prime material available for sale.

LLDPE pricing will vary according to comonomer, application, and sales volume. As of the middle of the year 2000, U.S. pricing for butene copolymer LLDPE ranged from \$0.79 to \$0.84 per kilogram for film grade resins. Hexene copolymer LLDPE film resins are \$0.06–0.09/kg higher, octene copolymer LLDPE film resins are \$0.08–0.11/kg higher, and metallocene-catalyzed volume film grades are \$0.08–0.13/kg higher. Pricing is nearly equivalent for general-purpose injection-molding grades and as much as 10% higher for lid grades. Rotomolding powders can be 50–100% greater than butene copolymer LLDPE film grades. Pricing for plastomers ranges from approximately \$1.40 to over \$2.00 per kilogram.

## Shipment and Specification

In the United States, bulk resin can be delivered by rail in hopper cars in quantities of 70–100 t. Smaller bulk quantities of 15–20 t can be delivered by hopper truck. Very small quantities and samples are usually delivered in large cardboard boxes called gaylords that contain 450–650 kg of resin. Globally, much resin is packaged in 25-kg sacks.

Polyethylene is categorized by physical property for specification into groups, classes, and grades as described in ASTM D4976-98. Group 1 resins are branched and Group 2 resins are linear. Class defines density and is divided as Class 1, low density resins, from 0.910 to 0.925 g/cm<sup>3</sup>, Class 2, medium density resins, from 0.926 to 0.940 g/cm<sup>3</sup>, Class 3, high density resins, 0.941 to 0.960 g/cm<sup>3</sup>, and

Class 4, high density resins,  $0.961 \text{ g/cm}^3$  and above. Polymer melt-flow rate at  $190^\circ\text{C}$  using 2.16-kg weight is specified by grade. Grade 1 is a melt-flow rate of greater than 25 g/10 min, Grade 2 is greater than 10–25 g/10 min, Grade 3 is greater than 1–10 g/10 min, Grade 4 is greater than 0.4–1 g/10 min, and Grade 5 is 0.4 g/10 min or less. There are also specifications for electrical requirements, flammability requirements, weatherability requirements, and mechanical properties such as tensile strength, flexural modulus, and crack resistance, but these are not widely used in most commercial LLDPE applications.

Wire and cable resins are also categorized for color by class according to ASTM D1248-98. Class A contains no pigments, Class B contains white or black pigment, Class C contains not less than 2% carbon black, Class D is uv-resistant with colored pigment.

## Analytical and Test Methods

**Molecular Weight and Distribution/Rheological Properties.** Methods of measuring number-average molecular weight ( $M_n$ ) include ebulliometry (freezing point depression or melting point elevation), membrane osmometry, and vapor-phase osmometry. Weight-average molecular weight ( $M_w$ ) can be quantified by light scattering and ultracentrifugation [ $M$ ]. Both number-average and weight-average molecular weight and therefore polydispersity of LLDPE ( $M_w/M_n$ ) can be measured simultaneously by high temperature gel permeation chromatography (gpc) using *o*-dichlorobenzene or 1,2,4-trichlorobenzene as solvents, ASTM D6474-99. In this method, a dilute polymer solution is passed over a porous inert material. Low molecular weight species follow a tortuous path through the system allowing the high molecular weight materials to elute first. Viscosity methods are also employed to measure molecular weight, ASTM D1601-99 and D2857-95.

Other methods for solvent fractionation are by precipitation method where a ratio of solvent and nonsolvent is incrementally adjusted from solvent-rich to nonsolvent-rich. In this technique, the higher molecular weight fractions will be precipitated first. A reverse technique is solvent gradient elution where a liquid mixture of increasing solvent power is used to remove the lowest molecular weight materials first (10).

Molten polymer flow through a specific die is often used as a quick estimation of polymer molecular weight. Such a measurement is called melt index. Melt index (also called melt-flow rate by some resin producers) for LLDPE is commonly measured according to ASTM D1238-99 using the 190/2.16 method ( $190^\circ\text{C}$  and 2.16-kg load). Notation is shown as  $I_2$  and this number is inversely proportional to molecular weight as long as the polydispersities of the resins compared are the same and there is no long-chain branching. A measure of polydispersity, or molecular weight distribution, can be obtained by measuring melt flow at higher stresses, 190/10 ( $I_{10}$ ) or 190/21.6 ( $I_{21}$ ). Ratios of the different rates,  $I_{21}/I_2$  (known as melt index ratio, MIR) and  $I_{10}/I_2$ , correlate very well with  $M_w/M_n$  for linear polymers.



**Density.** LLDPE density is commonly measured using a flotation method in a density gradient column as described in ASTM D1505-98. In this technique, a glass column is filled with a liquid that provides a density gradient from top (lower density) to bottom (higher density) which is marked using calibrated glass beads. The most common liquid used for LLDPE is an isopropanol–water mixture that provides for a density range of 0.79–1.00 g/cm<sup>3</sup>. Specimens are dropped into the column and their final resting place is then extrapolated into a resin density. One of the most important aspects of this test is sample preparation, which is done by slow cooling compression molded plaques (ASTM D1928-96). It is very important that the specimen be free of voids and have a thermal history that is consistent with prior samples for accurate comparison.

Polymer density can also be determined using ultrasonic techniques (ASTM D4883-99), and specific gravity (ASTM D792-98).

**Structure and Composition.** Knowing LLDPE comonomer content and distribution is an important part of predicting polymer properties. Carbon-13 nuclear magnetic resonance (nmr) is commonly employed to identify comonomer type, quantity incorporated, and distribution along the polymer backbone. ASTM D5017-96 provides for standard test method for this analysis. Branching can also be detected by infrared (ir) methods. The method described in ASTM D2238-92 (1999) quantifies methyl group absorption at 1378 cm<sup>-1</sup>. Infrared analysis is also used to determine vinyl and trans unsaturation in polyethylene (ASTM D6248-98) and vinylidene unsaturation (ASTM D3124-98).

Amount of crystallinity in LLDPE can be quantified using x-ray diffraction (xrd), ir, dsc, and density. The xrd methods usually involve subtracting the amorphous contribution from the x-ray diffraction pattern. ir uses ratios of absorptions from crystalline and amorphous components. dsc uses enthalpy of fusion  $\Delta H_f$  for a sample compared to the equilibrium heat of fusion  $\Delta H_f^\circ$  which for polyethylene is between 276 and 301 J/g. Percent crystallinity is given as  $X = (\Delta H_f / \Delta H_f^\circ) \times 100\%$ . An ASTM standard is given in D3417-99. Density measurements can also give percent crystallinity values  $X$  by using  $1/\text{density} = X/d_{cr} + (1-X)/d_{am}$ , where  $d_{cr}$  is usually accepted as 1.00 g/cm<sup>3</sup> and  $d_{am}$  is 0.852–0.862 g/cm<sup>3</sup>.

**Compositional Uniformity.** Temperature rising elution fractionation is the preferred technique for measuring compositional uniformity in LLDPE and metallocene-catalyzed resins (104–110). In a typical TREF experiment, a small portion of polymer is dissolved in a heated solvent such as 1,2,4-trichlorobenzene. An inert support is added to the solution that is then cooled at a prescribed rate, eg 1.5°C/h. Polymer fractionation occurs when chains with little to no comonomer crystallize from solution at temperatures higher than those chains that contain more comonomer. After cooling, the inert support is placed in a column and a progressively heated solvent is then passed over the solvent to wash away the crystallized polymer. In this heating step, the lower density fractions, ie those with more comonomer, are eluted at lower temperatures than higher density fractions with little comonomer. Concentration of the elute is detected using an ir detector and is plotted as a function of temperature (Figs. 2 and 3). Crystallization from solution can be affected by both comonomer content and molecular weight. A light-scattering detector can be used in conjunction with the ir detector to measure molecular weight of the eluted fractions. While very informative, the process is very time and labor consuming.

Thermal methods using dsc have been developed to give somewhat the same qualitative information as TREF, but without solvent and in a less labor-intensive manner (111,112). The dsc melting profiles can be used to approximate comonomer content and distribution.

Low molecular weight, low density fractions may migrate to whatever comes into contact with the LLDPE. For food-contact applications, these materials are called hexane extractables. FDA procedure 21 CFR177.1520 calls for immersing a sample in *n*-hexane at 50°C for 2 h and measuring weight loss in the sample. For food contact during cooking, hexane extractables levels need to be below 2.6 wt% and for general noncooking contact hexane extractables levels need to be below 5.5 wt%.

**Mechanical Properties of LLDPE.** There are literally hundreds of test specifications written for LLDPE mechanical properties testing for all sorts of end-use applications. Since more than 60% of LLDPE consumed is used in film applications, common methods for film testing will be discussed here.

Tensile properties of thin (<1.0 mm) LLDPE films are determined using ASTM D882-97. Strips of film are pulled at controlled strain rates while load cells measure the forces required. Initial strain rates for properties such as ultimate tensile strength and elongation are usually 10 mm/(mm·min) while tensile modulus is tested at 0.1 mm/(mm·min.) ASTM D638-99 is used for thicker sheeting and molded samples from 1.0- to 14-mm thickness.

Tear properties can be determined in a variety of ways. The most common tear test is the Elmendorf test (ASTM D1922-94a). In this test, a weighted pendulum propagates a tear in a specimen. The energy lost by the pendulum while propagating the tear is related to tear strength. In another tear propagation test (ASTM D1938-94), otherwise known as a trouser-leg tear test, a tensile tester is used to propagate a tear through a specimen that resembles a pair of trousers. ASTM D1004-94a is a test method that uses a tensile tester to measure the force to initiate a tear in film. The energy required to both initiate and propagate a tear is determined using ASTM D2582-93.

Impact properties are very important in many film applications. ASTM D1709-98 is the most common technique used to determine impact resistance because of test simplicity and low equipment costs. In this test, a weighted dart with a smooth hemispherical head is dropped from a prescribed height onto a circular diaphragm of film. If the sample does not break, weight is added to the dart. If the sample breaks, weight is removed. At least 10 breaks and 10 failures are recorded to give a good statistical average. Another dart impact test, D4272-99, determines the total energy impact of a film by measuring kinetic energy loss of a dart that passes through the film.

Optical properties are important in many packaging applications. Specular gloss is a measure of the shiny appearance of films. In this test, a beam of light is reflected off of a film surface at a specified angle. It is measured using ASTM D2457-97 at three angles, 20° for high gloss films, 45° for intermediate and low gloss films, and 60° for intermediate gloss films. Film haze is a measure of film clarity. In this test (ASTM D1003-97), the wide-angle light scattering properties of a film are quantified as a percentage of light diffused.

## Health and Safety

Resin manufacturers usually provide health and safety information through Material Safety Data Sheets (MSDS) that discuss resin handling and storage, toxicity, combustibility, disposal, labeling, and FDA status.

LLDPE resins are relatively inert and do not constitute hazards for skin contact and ingestion with normal handling (113,114).

Polyethylene is flammable and may give off toxic gases during combustion. Fires may be extinguished with water, carbon dioxide, or dry chemical units. Respiratory and eye protection is required for fire fighters.

Polyethylene may be disposed of by landfill or incineration. In landfill, polyethylene will not degrade unless exposed to sunlight. It is not expected to evolve gases or leechates to pollute water sources.

Most polyethylene is acceptable for use in food contact applications. In some cases of plastomers, resins containing as much as 50% comonomer are acceptable (115). FDA compliance is based mainly on levels of migratable low molecular weight, low density olefins called hexane extractables and various additive levels. A letter of compliance or other certification should be received from the appropriate resin supplier before actual use.

## LLDPE Applications

Annual global production of LLDPE is approximately 13.6 million tons. Of that amount, approximately 77% is used in film applications (100). With that proportion, it is not surprising that much of the research and development that is conducted at resin suppliers is on the film market. LLDPE is supplanting LDPE in many film applications because of its improved strength properties, downgauging potential, and cost.

**Film Applications.** Over 3.4 billion kilograms of LLDPE were consumed in North America for film applications. Trash bags, including retail and institutional markets, is the largest North American market for LLDPE film (over 0.64 billion kilograms). Compared to LDPE, LLDPE offers better puncture resistance, tear resistance, impact, and tensile properties along with the ability to downgauge. LLDPE has better tear resistance balance and puncture resistance than HDPE. The consumer retail trash bag market has two major market thrusts: (1) bags with high dart impact and tear strengths but relatively low modulus and (2) bags with high stiffness but minimal impact and tear resistance. A significant portion of the retail market consists of blown coextrusion capabilities to meet these challenging requirements. LLDPE melt index range for this market is approximately 0.5–1 g/10 min and density range is 0.917–0.928 g/cm<sup>3</sup>. mLLDPE resins tend to be used as layers in coextrusions or as blend components to improve the properties of less expensive resins.

Pallet wrap stretch film is the second largest North American market for LLDPE film. It consumes over 0.545 billion kilograms of LLDPE annually. Pallet wrap stretch film is used to unitize loads to prevent shifting during shipping. It is also used as a protective film and as a tamper indicator. Film

properties required for pallet wrap stretch film include high elongations, high tensile strength, high holding force, puncture resistance, tear resistance, and high cling. Stretch films must have adequate cling so that they will adhere to themselves after application to prevent unwinding and loss of holding force. The most widely used process is cast coextrusion with three, five, and seven layers now common. Approximately 40% of the stretch film capacity is produced via blown film monolayer and coextrusion. The stretch film market has two main product areas: (1) machine film and (2) handheld film. Machine film is applied by an automated unit that prestretches the film from 150 to over 300% and then applies the film under tension to a load which sits on a turntable. Handheld film is applied manually by a worker walking around a load and is usually stretched less than 200%. Common LLDPE melt indices in this market range from 1 to 4 g/10 min and most resins have a density of 0.917 or 0.918 g/cm<sup>3</sup>. mLLDPE has made a significant market penetration in stretch film by offering improved puncture resistance and greater holding force. Blends of LLDPE and mLLDPE are used to optimize properties and reduce costs (116,117). Plastomers are being used as cling layers for consistent cling without the use of additives such as polyisobutylene.

The third largest LLDPE film application in North America is industrial liners, greater than 250 million kilograms per year. Industrial liners are used inside cans, drums, cardboard boxes and the like to prevent spillage, contamination, moisture, and ease of container reuse. Important film attributes are puncture resistance, tear strength, and tensile strength. Common LLDPE melt indices are 0.5–2 g/10 min with densities of 0.917–0.930 g/cm<sup>3</sup>. mLLDPE finds little application here because of higher raw material costs.

Other areas where mLLDPE is making an impact are heavy-duty shipping sacks, food packaging (especially fresh produce packaging) (117–120), and breathable films for personal care use, eg diaper backsheet. Plastomers find application as modifiers in LLDPE and ULDPE to improve impact strength, low temperature toughness, and sealability (121).

ULDPE and VLDPE resins find application in low temperature applications, such as ice bags, where lower density offers greater toughness. They are also used as sealing layers, replacing low density copolymers such as vinyl acetate, and as blend components to improve toughness.

LDPE is still the preferred resin for extrusion coating. Because of the narrow molecular weight distribution of LLDPE (and also of metallocene-catalyzed polyethylenes), the resins are more difficult to extrude and have greater “neck-in” than LDPE.

**Injection Molding.** Injection molding is the second largest product area for LLDPE consuming approximately 8% of the global LLDPE produced. Injection-molded articles include trash cans, pails, food containers, lids, and closures. LLDPE has mechanical properties advantages over LDPE in environmental stress crack resistance, reduced warpage and shrinkage, and low temperature toughness (122). LLDPE is preferred for use over polypropylene in low temperature applications. An example of LLDPE improved properties is given in Table 9 comparing a butene copolymer LLDPE and LDPE of similar melt index and density.

Metallocene-catalyzed resins have not yet had a substantial impact on the marketplace. Primary advantages for metallocene-catalyzed resins compared to

**Table 9. Comparison of LLDPE and LDPE Injection Molding Resins<sup>a</sup>**

Property	ASTM test method	LLDPE	LDPE
Melt index $I_2$ , g/10 min	D1238	32	37.5
Density, g/cm <sup>3</sup>	D1505	0.925	0.923
Tensile strength @ yield, MPa <sup>b</sup>	D638	13.4	12.8
Tensile strength @ break, MPa <sup>b</sup>	D638	9.3	9.0
2% Secant modulus, MPa <sup>b</sup>	D790	366	186
Hardness, Shore D	D2240	55	41
Low temperature brittleness $F_{50}$ , °C	D746	< -76	-25

<sup>a</sup>Ref. 123.<sup>b</sup>To convert MPa to psi, multiply by 145.**Table 10. Comparison of LLDPE and HDPE Rotational Molding Resins<sup>a</sup>**

Property	ASTM test method	LLDPE		HDPE
		Gas phase	Solution	
Melt index $I_2$ , g/10 min	D1238	5.0	5.0	5.0
Density, g/cm <sup>3</sup>	D1505	0.935	0.937	0.945
Flexural modulus, MPa <sup>b</sup>	D790	601	520	931
Tensile strength @ yield <sup>b</sup>	D638	17	14	21
ESCR $F_{50}$ , h	D746	>1000	400	30

<sup>a</sup>Refs. (123) and (126).<sup>b</sup>To convert MPa to psi, multiply by 145.**Table 11. Comparison of LDPE, LLDPE, and HDPE Blow Molding Resins<sup>a</sup>**

Property	ASTM test method	LLDPE	LDPE	HDPE
Melt index $I_2$ , g/10 min	D1238	0.75	0.25	0.35
Density, g/cm <sup>3</sup>	D1505	0.934	0.918	0.954
Flexural modulus, MPa <sup>b</sup>	D790	578	234	1228
Low temperature Brittleness $F_{50}$ , °C	D746	< -76	< -76	< -76
ESCR, h	D1693	>1000	NM <sup>c</sup>	50

<sup>a</sup>Ref. 123.<sup>b</sup>To convert MPa to psi, multiply by 145.<sup>c</sup>NM = not measured.

conventional Ziegler–Natta-catalyzed LLDPE are improved impact strength, less brittleness at higher melt indices, and less odor and taste transfer. Plastomers are seeing some use as a replacement for poly(vinyl chloride) in injection-molded articles (124). Plastomers are also used as impact modifiers in molded polypropylene automotive parts (125).

**Rotational Molding and Blow Molding.** Rotational molding accounts for approximately 5% of LLDPE consumption and blow molding accounts for approximately 0.5%. Rotational-molded articles include storage tanks, shipping containers, recreational equipment, and outdoor furniture. LLDPE has higher impact

resistance and stress-crack resistance than LDPE and HDPE. Table 10 lists two LLDPE resins compared to an HDPE sample. Metallocene-catalyzed resins are finding application in rotational molding primarily because of reduced cycle times, reduced energy consumption, a wider processing window (127), and greater impact strength than conventional LLDPE. Improved flexibility and stress-crack resistance make LLDPE ideal for some blow-molded bottle applications. Table 11 details the improved escr compared to HDPE.

**Wire and Cable Insulation.** LLDPE use in wire and cable insulation makes up approximately 1% of LLDPE consumption. Cable insulation requires flexibility, toughness, abrasion resistance, low brittleness temperature, and good dielectric properties. LLDPE offers a better balance of flexibility and toughness than LDPE or HDPE. LLDPE-coated wire and cable is used in numerous low and medium voltage applications. Metallocene-catalyzed resins are finding use in wire and cable jacketing because of improved abrasion resistance, flexibility, and low temperature toughness (125,128).

**Pipe and Tubing.** Extrusion of pipe and tubing accounts for a very small fraction of LLDPE consumption. LLDPE offers higher burst strength, environmental stress crack resistance, and higher heat-distortion temperature than LDPE. Plastomer grades have been used to replace plasticized polyvinyl chloride in medical tubing applications (129).

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D. M. SIMPSON  
G. A. VAUGHAN  
Exxon Mobil Chemical Company