# POLYETHYLENE, HIGH DENSITY

## 1. Introduction

Polyethylene (PE) is the most widely used plastic throughout the world, and high density polyethylene (HDPE) is the most widely used type of polyethylene. High density polyethylene has generally been taken to mean the product of ethylene polymerization having density greater than ~0.935 (or 0.94). It includes both ethylene homopolymers and copolymers of ethylene and alpha-olefins, such as 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene. Other types of PE include low density PE (LDPE) made through a free radical process, and linear low density PE (LLDPE).

An analysis of the amount of commercial usage of the world's major plastic types is shown in Table 1. In terms of amount used, polyethylene dominates the other major types. Table 2 lists the worldwide usage of the various types of polyethylene. In comparison to the other major types of PE, HDPE is by far the most widely used. The HDPE consumption worldwide accounted for ~58.7 billion lb / year in 2004, or almost one-half of the total U.S. production of all PE types. Figure 1 shows how the usage of HDPE in the United States has developed historically since its invention in 1951.

## 2. History of Polyethylene

**2.1. Early Work.** The history of HDPE (and polyolefins in general) actually began in the 1890s with the synthesis of "polymethylene" from the decomposition of diazomethane. Between 1897 and 1938 numerous reports of such polymers appear in the literature (1–6). Catalysts such as unglazed china, amorphous boron, and boric acid esters were used for the decomposition. The empirical formula of such products was found to be $CH_2$. Later, reproductions of the work of Werle (6) and Bamberger and Techirner (3) established that the polymethylene thus obtained was a high molecular weight linear polymer having a melting point of 134–137°C, and a density of 0.964–0.970 $g/cm^3$ (7). Thus it can be stated that, although no commercial use was initially made of it, HDPE was discovered long before the well-known LDPE was introduced (8,9).

In another early approach, Pichler (10) and Pichler and Buffleb (11) describe in 1938–1940 the preparation of high molecular weight (Mn = 23,000) polymers from the hydrogenation of carbon monoxide over ruthenium and cobalt catalysts. The reported melting point of 132–134°C and density of 0.980 $g/cm^3$ indicate again that linear, HDPE was obtained.

**2.2. Free-Radical Process.** The first commercial polyethylene was developed by Imperial Chemical Industries from 1932 to 1938 using a free-radical process (12). Ethylene was polymerized at high pressure (142 MPa or 1400 atm) and at ~180°C. It was discovered by accident that oxygen impurity could serve as the initiator. An ICI British patent filed in 1936 (13) disclosed pressures of ~50–300 MPa (500–3000 atm), temperatures of 100–300°C, the necessity of removing heat to control temperature, and the necessity of controlling the oxygen content of the ethylene used.

The PE produced at this time had a melting point of 115°C and a density of 0.91–0.92 g/cm$^3$. In 1940, Fox and Martin (14) found by infrared (ir) analysis that there were more methyl groups in the polymer than could be accounted for by the end groups of a linear chain. Thus, the importance of chain branching was recognized, and subsequent studies of branching led to a better understanding of its effect on mechanical properties and polymer morphology. This material is called LDPE and is still in high commercial demand today. Further work on the free-radical process extended the pressure. Larcher and Pease (15) disclosed polyethylene with densities of 0.95–0.97, melting points $>$ 127°C, and branching of $<$1 side chain / 200 carbon atoms.

**2.3. Transition Metal Catalysts.** Today's "low pressure" catalytic processes, from which HDPE now comes, were discovered in the early 1950s. The term "low pressure" refers to operating pressures of generally 1.4–6.9 MPa (200–1000 psig), in contrast to the ICI free-radical process. Patent applications were filed in 1951 by Zietz (16) of Standard Oil of Indiana, by Hogan and Banks (17) of Phillips Petroleum in early 1953, and by Ziegler and co-workers (18) in late 1953.

The Standard Oil patent (16) describes a supported reduced molybdenum oxide or cobalt molybdate on alumina, with the ethylene preferably contacting the catalyst in an aromatic solvent to affect the polymerization. Operating temperatures of from 100 to 270°C were disclosed and the molecular weight could be varied from very high to greases.

At about the same time, Hogan and Banks at Phillips Petroleum Co., discovered that supported chromium oxide catalysts would also polymerize ethylene at low pressures to produce high molecular weight polymers. Reaction temperatures were in the range of 60–190°C (17). Polymer characteristics, particular molecular weight and molecular weight distribution, could be varied by reactor temperature, pressure, and activation temperature of the catalyst.

Shortly thereafter, in 1953, Karl Ziegler in Germany discovered yet another transition metal catalyst capable of polymerizing ethylene at low pressure (18). Ziegler's approach used a transitional metal halide, or other complex, activated by an aluminum alkyl cocatalyst. Transition metal compounds of groups 4–6 (Ti preferred) were claimed.

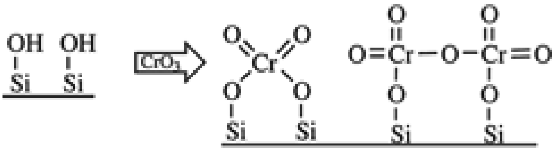
Although the Standard Oil discovery came first, its importance was not recognized until the Phillips process had been developed. Therefore, commercialization was slow (19,20). Three plants were eventually built between 1961 and 1971, but the process had poor economics and was soon scrapped. In contrast, the Phillips and Ziegler discoveries were both commercialized rapidly and still exist today in more advanced forms. At Phillips, the first plants were brought on stream in 1955 and 1956. However, Phillips management concluded that no one manufacturer could develop the full market potential of the Phillips HDPE, and therefore decided to license the process. By 1956, nine companies in seven countries became licensees (21–24). Ziegler also began to license his patent, following the discovery that good activity could be obtained by use of titanium halides in combination with aluminum alkyls. However, the patent included only catalyst knowledge, and each licensee had to develop a process. The first Ziegler plant was brought on stream in late 1956 by Hoechst. A second one was built in 1957 by Hercules. By 1960, U.S. production of HDPE via the

Phillips process had reached > 200 million lb annually, while 70 million lb came from the Ziegler process.

Today, HDPE is still made almost entirely through chromium or Ziegler systems. The two systems produce different types of polymer, which is useful for different applications. The Phillips catalyst generally produces broader molecular weight distributions than that of typical Ziegler catalysts. Metallocene and other "single site" catalysts, usually based on zirconium or titanium, are also gaining in importance, but to date their share of the overall HDPE market amounts to less than ~1%.

## 3. Catalysts Used for HDPE Production

**3.1. Chromium Catalysts.** The Phillips chromium catalyst, which perhaps account for about one-half of the total HDPE production, is usually made by impregnating a chromium compound onto a porous, high surface area oxide carrier, such as silica, and then calcining it in dry air at 500–900°C (25). This latter activation step converts the chromium into a hexavalent surface chromate, or perhaps dichromate, ester. Because each Cr atom is individually attached to the surface, the support is not inert, but exerts a strong influence on the polymerization behavior of the site.



The first step in the development of polymerization activity occurs when these hexavalent surface species are then reduced by ethylene in the reactor to a lower valent active precursor, probably $Cr^{2+}$ (25–28). Because $Cr^{6+}$ is tetrahedrally coordinated, and the reduced species can be octahedral, the resultant expansion of the coordination sphere creates a high level of coordinative unsaturation, which plays a role in the polymerization mechanism. Thus the reduced species chemisorbs olefin readily. However, this same trait makes the catalyst very sensitive to small levels of polar impurities in the feed streams, such as alcohols, water, amines, etc (29,30). Commercial catalysts usually contain 1.0 wt% Cr, but only a small fraction of this, perhaps 10–20% or even less, is actually active for polymerization (25,27,30).

The second step in the development of polymerization activity is an alkylation reaction, in which the first chain begins growing on the reduced chromium species. Exactly how this reaction occurs has been unclear. Several possibilities have been suggested over the years, but no clear answer has yet been established (25,31–35). Recent studies suggest that initial adsorption of olefin on $Cr^{2+}$ sites may cause an oxidation to an alkylated $Cr^{4+}$ as the active polymerization species (34,35). These two initial steps, reduction followed by alkylation, cause the catalyst to display an induction time. That is, the onset of polymerization occurs gradually after a delay that can last from a few minutes to > 1h depending on reaction conditions (25,27).

Alternatively, the reduction step can also be accomplished before the catalyst contacts ethylene in the reactor, by exposure to carbon monoxide at 350°C (25,27). In this case, the reduced species has definitely been identified as $Cr^{2+}$ (28,36–40). This catalyst behaves much like its $Cr^{6+}$/silica parent when introduced into the reactor, producing similar polymer at similar activity in most cases. However, the onset of polymerization often occurs more rapidly when the catalyst is prereduced, since the reduction step is omitted (25,27).

Once the polymerization reaction has developed, a decay in activity can also sometimes be observed, due to a chemical instability of the active species. Thus the kinetic profile of the polymerization reaction can be defined as a series of three consecutive reactions: (*1*) reduction, (*2*) alkylation, and (*3*) decay. Each step in the series has its own dependency on ethylene concentration, temperature, and catalyst composition. Figure 2 shows some typical kinetic profiles that are often obtained, and that can be produced by varying the individual rate constants of the three steps (41).

Metal alkyl cocatalysts, such as alkyl boron, aluminum, zinc, lithium, etc, can also be added to the reactor as a way of enhancing the activity of the catalyst. Such agents act by accelerating the reduction step, by alkylating the chromium, or by scavenging minor amounts of poisons, such as water and oxygen. These agents are sometimes used commercially for specific resin types, although they are not essential and in most cases are not used (41,42).

In another, less common, variation of the catalyst, lower valent organochromium compounds can be deposited onto an already calcined support to produce very active catalysts (43–51). These compounds react with surface hydroxyls to become attached to the support, often losing one or more ligand. Examples include bis(arene) $Cr^0$, allyl $Cr^{2+}$ and $Cr^{3+}$, beta stabilized alkyls of $Cr^{2+}$ and $Cr^{4+}$, and bis(cyclopentadienyl) $Cr^{2+}$. The latter example has been used commercially to a great extent. Such catalysts often develop activity more rapidly than the chromium oxide catalysts, being already reduced and in some cases already alkylated. The remaining organic ligands can also change the polymer obtained in certain ways.

The most common support used commercially is silica and silica-titania. However, silica-alumina, alumina, and aluminophosphates can also be used (52,53). Adding titania to the recipe enhances activity and broadens the molecular weight distribution, not because the titanium itself is active, but because it influences the chromium (54). It is believed that some chromium sites become attached to the titania, which then indirectly influences the polymerization reaction through electronic effects. Likewise, adding alumina, magnesia, boria, and other oxides have unique effects. Aluminum phosphate is particularly interesting in that it is isoelectronic and isostructural with silica, but of course the surface chemistry is quite different, containing such diverse groups as P−OH, P=O, and Al−OH (41,52,53,55). Thus, changing the support can be a way of varying polymer characteristics.

**3.2. Ziegler Catalysts.** Titanium chloride-based Ziegler catalysts are also widely used throughout the HDPE industry. These catalysts generally produce a narrower molecular weight distribution than obtained from chromium oxide catalysts. Figure 2 shows this typical distinction. Because of this, the Ziegler catalysts are often used for different applications compared to chromium oxide.

Whereas chromium oxide species may vary considerably in their local environment, due to the heterogeneous nature of an amorphous oxide carrier, Ziegler species are often thought to be more uniform, occupying certain places in a microcrystalline environment (56–58). Frequently, donor compounds, such as ethers, esters, and silane alkoxides, are added to neutralize or modify certain undesirable sites (59).

The early commercial Ziegler catalysts were based on titanium(III) chloride, often ball milled or otherwise treated, to provide higher surface area. In ~1968, Hoechst introduced the so-called "high activity" Ziegler catalysts, in which the titanium was dispersed in a magnesium chloride lattice, into which it fits nicely (60–62). In this way the polymer yield per titanium atom was increased by 10-fold or more.

The transition metal compound, usually a titanium(III) or (IV) chloride, is transformed into the active catalytic species upon reaction with an aluminum alkyl cocatalyst. During this reaction, the active metal becomes alkylated, and ethylene insertion occurs into the metal–alkyl bond. Often the active site is considered to be a bridging complex between the transition metal and the alkyl aluminum compound, in which one or two ligands are shared between the two metals.

In some cases, broadening has been achieved by using vanadium, zirconium, or other metal halides in the recipe, either alone or in combination with titanium (63–65). In other cases, broadening has been achieved by providing two distinctly different chemical environments for the titanium (66), or in the process by passing the Ziegler catalyst through two or more reaction zones (67).

**3.3. Metallocenes and Other "Single-Site" Catalysts.** One type of Ziegler catalyst, based on cyclopentadienyl titanium or zirconium halides, which provided only marginal activity using aluminum alkyls as cocatalysts, received an extreme enhancement in activity in the mid-1970s with the discovery of methyl aluminoxane (MAO) cocatalyst (68,69). Unlike traditional aluminum alkyl cocatalysts, MAO is more acidic, and therefore more capable of activating (sometimes called "ionizing") the transitional metal compound (57,70–73). This activation is sometimes expressed in a formal way as follows:

$$\mathrm{Cp_2ZrCl_2} + \mathrm{CH_3Al}{=\!=} \longrightarrow \mathrm{Cp_2ZrCH_3Cl} \longrightarrow \mathrm{Cp_2ZrCH_3(+)\,MAO-Cl(-)}$$

where Cp = cyclopentadienyl.

Since that time other "ionizing" agents have also been developed that are capable of activating these metallocene and other single-site compounds (74–77).

Metallocene catalysts differ from the traditional catalysts in that the site is derived from a singular molecular species with defined ligands, unlike the heterogeneous character of chromium or Ziegler species. This accounts for the ultranarrow molecular weight distribution of the polymer obtained (see Fig. 3), which approaches the theoretical limit of the ratio of the weight average MW to the number average MW (Mw/Mn) = 2 expected from a single type of site. Although usually described as "single-site" catalysts, it is nevertheless clear on closer inspection that many of these catalysts do not entirely fit the description, because the ionization agent is still part of the active site. The partial hydrolysis product of trimethylaluminum, MAO, is also sometimes capable of providing a complex and varied site environment.

Metallocene catalysts are at present still entering the PE market in certain specialty applications, accounting for perhaps $< 1\%$ of all HDPE sales. However, the greater degree of control offered by metallocenes, and the ability to combine different metallocenes into one catalyst, offers the ability for the first time to truly tailor polymer architecture. Thus, it seems likely that future advancements in metallocene chemistry will have a profound impact on the HDPE market.

Within the past 5 years, other types of new organo transitional metal compounds have also been reported that can be activated by ionizing agents like MAO (78–80). Some of these compounds, such as Brookhart's nickel diimine complex, offer the possibility of producing highly branched ethylene homopolymers polymers that have never before been possible before from low pressure systems. To date, no commercial PE polymers are made from these systems, but like metallocenes they offer intriguing possibilities for the future.

## 4. Polymerization Mechanism and Reactor Control

**4.1. MW and MW Distribution.** Once an active site has been formed, through reduction and alkylation of chromium oxide species, and once polymerization has been initiated, two reactions occur simultaneously and competitively: propagation and termination (or chain transfer). As illustrated in Fig. 4, these catalysts are not "living" systems, in which the polymer chain grows indefinitely. Rather, the length of the chain formed is determined by the rate of propagation relative to the rate of termination. On average in a commercial process, the lifetime of a chain on an active site is typically a small fraction of a second, say 0.1 s or less. Since the lifetime of the catalyst in the reactor is usually 1–2 h, this means that each site produces many chains before being discharged from the reactor.

For active chromium species on the Phillips catalyst, the rates of propagation and termination are thought to be characteristic of the local geometry and ligand field surrounding each site on the heterogeneous silica surface. Thus different sites tend to produce polymers of different average MW, and the overall MW distribution of the polymer reflects the site heterogeneity of the catalyst. This connection allows the molecular weight distribution to be controlled by varying the composition and heat history of the catalyst.

The Schultz-Flory distribution has usually been considered as the simplest model for representing molecular weight distribution expected from a single polymerization site (81). It assumes that each site is identical, and that the probability of termination is not dependent on the length of the growing chain. Thus if the probability of propagation is considered to be p, and of termination to be (1 - p), then the probability of producing a chain $n$ units long would simply be $F(n) = \mathrm{p}^n(1\text{-p})$. This distribution produces a breadth of MW distribution, or polydispersity (weight average/number average), of 2.0. In reality, typical chromium catalysts produce much broader MW distributions, with polydispersity values of 4–100. This is taken as an indication of multiple site environments on these catalysts. Indeed, this is also evident by the fact that the MW changes (increases) as the activity develops with time. Those sites that come on stream first produce the lowest MW. Some metallocene and other "single-site" catalysts, however, do approach the narrow theoretical Schultz-Flory distribution of 2.0.

The propagation step, usually first order in ethylene concentration (82), is thought to occur through the insertion of coordinated ethylene into the metal–alkyl bond (56–58). Termination, or chain transfer, can occur through several different mechanisms. Two of the most common reactions are shown in Fig. 3 as beta-H elimination (*1*) to monomer and (*2*) to the metal. Both reactions leave a vinyl group on one end of the chain and a methyl on the other. In the former case, the transfer step is dependent on ethylene concentration, while in the latter case it is not. On many Ziegler and metallocene catalysts, the primary transfer mechanism is to monomer, so that the molecular weight is unrelated to ethylene concentration (since both propagation and transfer are first order in ethylene). However, on chromium oxide catalysts transfer to metal also becomes significant and this fact is used to control product molecular weight during commercial manufacture. When ethylene concentration in the reactor is increased, the molecular weight also increases (25).

Hydrogen can also be added to the reactor to control molecular weight for most catalyst systems. When deuterium is used in place of hydrogen, the prominent chain end-group $-CH_2D$ is observed (27). Metallocene and Ziegler catalysts are more sensitive to hydrogen than most chromium oxide systems. In the latter case, adding hydrogen to the reactor also tends to narrow the MW distribution, because the high MW producing sites seem to be most sensitive. Metal alkyls can also sometimes terminate chains through alkyl exchange. Aluminum, zinc, and boron alkyls have been reported to do this for some catalyst systems. For chromium oxide catalysts, there are indications that boron alkyls are particularly potent and the process may even be catalytic (83). Again some sites seem to be more affected than others, which can be used to produce special polymer effects (84).

**4.2. Fracturing.** On silica supported catalysts, such as the Phillips chromium oxide system and some Ziegler catalysts, the active sites are attached to the internal surface of pore walls. Within a minute or so after polymerization begins, these pores become clogged with polymer. At this point, the silica particle begins to fracture into perhaps a billion smaller fragments due to the internal pressure created by polymer generation (25,85,86). This fracturing process only occurs on certain high porosity (and thus friable) silicas that are specially prepared for use as polymerization catalyst supports. Otherwise, fracturing does not take place and the catalyst has little or no activity. These fragments, which may be as small as 0.1 μ, then become engulfed in polymer, and unless the polymer is made in a solution process, these subparticles are loosely held together by entwined polymer into a larger polymer particle, which replicates the shape of the original catalyst particle. Each pound of catalyst produces some 2000–10,000 lb of polymer (or more) before being discharged from the reactor. Thus each catalyst particle thus produces a polymer particle of about the same shape, but many thousands of times its own mass. The catalyst is left in the polymer as a harmless minor impurity.

## 5. Polymer Structure

**5.1. General Structure.** Commercial HDPE is a predominantly linear polymer with the chemical composition roughly of polymethylene, $(CH_2)_n$. Its name reflects the principal method of production: ethylene polymerization by transition metal catalysts. At least one end group of each chain contains a methyl group, and depending on the method of manufacture, the other end group is also a methyl, or a vinyl group. Some general properties are shown in Table 3.

The weight average MW of typical commercial HDPE grades can vary from 20,000 to $> 3,000,000$, depending on the application. The molecular weight distribution of commercial HDPE polymers can range from very narrow, for metallocene derived polymers, to very broad, for grades made from chromium oxide catalysts. A convenient measure of the MW breadth is the polydispersity, or the Mw/Mn. Experimentally, the Mw distribution is measured by gel permeation chromatography.

**5.2. Short-Chain Branching.** Although described as "high density", commercial HDPE can actually vary in density from 0.975 down to 0.935. The HDPE contains a crystalline phase and an amorphous phase, and the measured density directly reflects the percentage of each. Typical homopolymer is normally $\sim$70% crystalline and has a density of 0.960–0.965. Higher densities can be achieved by low molecular weight and slow cooling.

Crystallinity is disrupted, and density therefore is lowered, if branching is added to the otherwise linear polymer backbone. This is typically accomplished by copolymerizing alpha olefins in small amounts with the ethylene. 1-Butene, 1-hexene, 1-octene, and 4-methyl-1-pentene are the comonomers most commonly used commercially, producing, respectively, ethyl, butyl, hexyl, and isobutyl branches. On a weight basis, comonomer is usually added in an amount $< 5\%$ of the total composition. Figure 5 shows the relationship between density and comonomer content.

**5.3. Rheology and Long-Chain Branching.** Molten HDPE is a non-Newtonian fluid at temperatures of 140–200°C. Its effective viscosity is reduced sharply, up to several thousand times, when the melt flow speed is increased. The viscosity of the polymer is also a function of its molecular weight. Non-Newtonian behavior of the melt at low shear rates allows correlation of melt viscosity with molecular weight. The reason for this behavior is thought to be disentanglement of polymer coils at high shear rate and their partial orientation in the flow direction.

By convention, the most convenient and generally accepted of melt viscosity is the "melt index", which is the amount of polymer flowing through a standard capillary viscometer at 190°C under a 2.16-kg load for 10 min. (87). The melt index is inversely connected with MW.

In addition to the so-called short-chain branches (ethyl, butyl, hexyl, etc from copolymerization of alpha olefins), many HDPE grades also contain a very small amount (perhaps $< 1$ branch / 10,000 carbons) of "long-chain branches". These branches are defined as being long enough to affect the rheology of the polymer, ie, longer than $\sim$130 carbons, the critical entanglement length (88).

The viscosity of HDPE melt is strongly temperature dependent and can be described by an exponential dependence similar to the Arrhenius equation. The activation energy of the viscous flow of HDPE melt is usually 25–30 kJ/mol, but it increases with increasing long-chain branching (LCB) up to 40 kJ/mol, or even higher. This is one main method of determining the extent of long-chain branching in a particular resin. Another method is to compare the measured (extrapolated) zero-shear viscosity to a value expected from a linear polymer of the same molecular weight.

Although long-chain branching occurs very infrequently in commercial HDPE, it has a profound effect when it does occur on the polymer flow behavior. Control of long-chain branching is therefore critical in the manufacture of HDPE grades because it affects the suitability of the resin for film, blow molding, sheet, injection molding, and many other applications. Some applications require the presence of LCB, while in other applications it is a detriment (89,90).

Long-chain branching in HDPE grades is thought to have its origin in the copolymerization of vinyl end groups (91).Upon termination of a chain, chromium oxide catalysts typically leave one vinyl group on one end of that chain, which can then be copolymerized by a neighboring site into another growing chain, as shown in Fig. 6 (25,92). This fact would explain why most Ziegler resins, which contain few vinyl end groups, also exhibit little LCB. Since polymer chains are frozen out of solution almost instantaneously as they are formed (except in solution polymerization) reincorporation of vinyl end groups might occur on a neighboring (rather than the parent) site (91). This could explain why the degree of LCB can be controlled on a chromium oxide catalyst, by varying the chromium–chromium separation distance (ie, the chromium loading). Figure 7 shows how the shear response of the polymer, which reflects the degree of LCB, is affected by chromium loading on the catalyst.

Other origins of LCB have also been identified. It has been observed that at the typically high molecular weight used in extrusion grade resins, LCB content is highly dependent on the pore structure of the catalyst, even when the chromium site density is held constant (91). When the primary particles of the silica are well fused or coalesced into a firm structure, such as by sintering or alkaline aging, high levels of LCB are seen in the resin. The exact reason for this behavior is unknown. It is not exactly clear how a long polymer chain of say 50,000 Å forms inside a 100-Å catalyst pore. Presumably the chains are prevented from folding in the usual way, until they have somehow exited the pore. Perhaps this unnatural state increases the chain reactivity. Thus the more fused silica structure may fragment into larger and more robust fragments, which can then affect polymerization to yield higher amounts of LCB. Whatever the explanation, chromium catalysts offer many unique ways of subtle control of LCB.

More recently, very high levels of LCB have also been observed from HDPE samples made from certain metallocene catalysts (93,94). Reincorporation of vinyl end groups is again a possible method of origin. However, if true, it is hard to explain why some metallocenes are so much more potent than others at creating LCB. Direct activation of polymer C–H bonds by some catalysts has also been proposed as avenue to the formation of LCB (95). And most recently still another mechanism of LCB formation has also been considered although not proven. It is suggested that on some catalysts two alkyl chains may simultaneously grow from one site through a bridging aluminum. If true, one chain terminated through beta-H elimination could be easily incorporated into the other on the same site as LCB (96).

**5.4. Morphology.** The only stable local-chain conformation of HDPE at low temperature is the flat zigzag chain configuration with C–C bond length of 1.54Å, and C–C–C bond angle of 112° (97). This local chain conformation also prevails in the melt and solution. The principal crystalline form of linear PE is orthorhombic, like the linear paraffins, with theoretical density of 1.00 g/cm$^3$. A second crystalline form is pseudomonoclinic with theoretical density of 0.965 g/cm$^3$. The former is typical of most articles made of HDPE, while the latter forms during low temperature stretching and orientation of films, and is thus sometimes present in HDPE film. It is stable only $< 50°C$; annealing at 80–100°C restores the orthorhombic form.

The principal morphological units of PE crystallizing under typical conditions from the melt are spherulites, very small anisotropic spheres ($\sim$1–5 μ) visible under high magnification with polarizers (Fig. 7). The spherulites form as a result of a complex crystallization process of macromolecules. Their structural subunits are "rays", thin rodlike fibrils spreading in all directions from the center to the periphery and frequently branching, thus filling the spherulite body. The fibrils consist of lamellae (crystallites). Spherulites are characteristic only where HDPE crystallized slowly from the melt. In rapid crystallization intertwined lamellae or rod-like structures are formed (98). During crystallization, polymer chains fold many times. When HDPE is crystallized from solution, this folding is tight, but when crystallized from the melt, the chain packing organization is much looser (99).

The HDPE crystallizes very rapidly. Articles such as films, filaments, pipes, and injection-molded articles, exhibit some degree of molecular and crystal orientation. This orientation develops either spontaneously during melt flow and crystallization, or is introduced deliberately by stretching. The degree of orientation can be measured by X-ray, polarization spectroscopy, acoustical methods, or birefringence.

When films or filaments are stretched uniaxially below the melting point, the c axis of the crystals is always oriented parallel to the stretching direction, as is typical for all semicrystalline polymers. The degree of orientation increases with the stretching ratio and can approach 100% (100). A similar orientation is developed during the crystallization of a strongly oriented PE melt, such as during capillary melt flow or solid-state extrusion. Under these conditions, both crystalline and amorphous phases are nearly perfectly oriented in the flow direction (101). When a polymer melt is slightly stretched at the outset of crystallization, a condition typical in the production of blow-molded parts, the resulting solid films exhibit a significant orientation of the *a* axis of the crystal in the machine direction (102) (Fig. 8).

## 6. Polymer Properties

**6.1. Mechanical Properties.** Polyethylene properties can be made to vary over a wide range, by controlling the molecular weight, the MW distribution, the degree of branching, the type and placement of branching, the end-group moieties, the extent of LCB, and by adding certain fillers, flow enhancers, etc. It is no surprise then that hundreds of different grades of HDPE exist for as many different applications, each of which require widely different properties. Such important final end-use properties include the stiffness of the polymer, the gloss, or clarity, the impact, puncture or tear resistance, chemical resistance, electrical insulation properties, molding characteristics, and tensile properties, to name only a few. Thus the discussion below provides only the briefest mention of this area. Table 3 lists some of the most important polymer properties for three typical commercial HDPE grades.

Measurements of highly crystallized HDPE samples give melting points of 133–138°C. The melting point is a function of both molecular weight and of branch content. In linear PE, the decrease in MW from ∼1,000,000 to 40,000 is accompanied by a decrease in melting point from 137 to 128°C. The change in melting point with branch content is shown in Fig. 9.

HDPE is a very good insulator and is therefore widely used for wire and cable encapsulation. Polymer density and MW affect electrical properties very little. HDPE is only slightly permeable to organic compounds, both in liquid and gas phases. Permeability to water and inorganic gases is also low.

Forced elongation of an HDPE sample into a film or rod is accompanied by structural and mechanical changes (Fig. 10). At low deformations (∼0.5% of sample length), spherulites elongate elastically. Further strain results in a partial break of bridges between crystallites in lamellae, slippage of the lamellae in rays constituting spherulites, ray splitting, and other irreversible mechanical changes. These processes can be regarded as a succession of partial “meltings” of the morphological features of HDPE under mechanical stress.

At some point, called the yield point, these transformations accumulate, causing a significant change in sample appearance. A “neck” develops, an area consisting of highly oriented bundles of polymer molecules. With further elongation, the initial morphological structures (spherulites, rays) are disassembled and the growth of the oriented polymer area continues. The primary mechanism of this transformation is slippage of lamellae with respect to one another and crystallite reorientation. This process develops in the boundary layer between the unchanged part of the sample and the neck, and continues in the neck, causing further strain. As a result, the sample elongates at nearly constant stress until all material in the samples becomes highly oriented. Subsequently, the oriented structure adsorbs additional small strain at increased stress and finally beaks. This ultimate stress is defined as the tensile strength.

Molecular weight has a large effect on this behavior. Low molecular weight HDPE is brittle and breaks at low strain (∼10%) without neck development. In the range of 80,000–1,200,000, typical for commercial HDPE, the neck always develops. The yield point of such polymers is nearly constant. However, increasing molecular weight is accompanied by decreasing elongation at the breakpoint, from ∼1200–1500 to 200–300% and by significant increase in tensile strength, from ∼35–40 to ∼60 MPa. Finally, HDPE with MW $>$ 1,500,000 does not develop a neck but elongates by 200–400%. Tensile strength of such polymers is very high, ∼60–70 MPa.

Molecular weight also significantly affects impact strength. Low molecular weight samples are brittle, but with increasing MW, impact–stress resistance can become very high.

An increase in branching reduces crystallinity and is accompanied by significant modification of mechanical characteristics. An increase in branching is accompanied by an increase in elongation at breakpoint and a significant drop in tensile strength.

It is generally accepted that the mechanical strength of a polymer sample is determined by the number of intercrystallite links, ie, polymer chains anchored in adjacent crystallites and binding them (Fig. 11). These links are the weakest elements of the polymer structure. Special developments in processing allow a significant increase in the number of the intercrystallite links. The technology employed is either low temperature ($\sim$100°C) extrusion of solid HDPE at high pressure ($\sim$200–300 MPa) or continuous casting of film from a dilute solution. Such films are highly stretched (up to 40 times), usually transparent, and almost perfectly oriented in both phases. They exhibit ultrahigh modulus (up to 100 GPa) and very high tensile strength of $\sim$500–600 MPa.

One type of PE that has an increased number of intercrystallite links, and thus improved physical properties, is called “bimodal” polymer. These polymer grades are usually made of two components: a low MW homopolymer blended with a high MW branched copolymer. In this combination, having branches on the longest chains selectively places these chains in the amorphous phase, which thus increases the probability that they will function as intercrystallite links. Much of polyethylene research today is aimed at producing more efficient methods of manufacturing such bimodal polymers.

Another important property that is influenced by MW, by branching, and by intercrystallite links, is load-bearing ability or resistance to creep. This property is of particular importance in applications in which the applied stress is continuous or frequent and represents an appreciable (though not necessarily large) fraction of the tensile strength. Even though the tensile strength of linear polyethylene decreases considerably as density is decreased, the load-bearing ability of the polymer is greatly improved at densities decreasing from 0.960 to 0.950 g/cm$^3$. Not only is time to failure increased greatly, but also deformation is decreased.

**6.2. Chemical Resistance.** Linear PE is predominantly saturated linear hydrocarbon and thus in general it exhibits low chemical reactivity. High crystallinity and low permeability to most chemicals reduce the reactivity of solid HDPE even further. HDPE is stable to alkaline solutions, solutions of salts, including oxidizing agents such as $KMnO_4$ and $K_2Cr_2O_7$. It does not react with organic acids, HCl, or HF. Concentrated $HNO_3$ ($\sim$50%) does nitrate the polymer, even at room temperature.

HDPE is not soluble in any known solvent at room temperature, although several solvents (ie, xylenes) have a swelling effect. However, certain binary solution mixtures including $CS_2$ dissolve HDPE at as low as 30–40°C. Above 80°C, HDPE dissolves in many aliphatic and aromatic hydrocarbons and their halogen-substituted derivatives. Solvents most frequently used include xylenes, tetralin, decalin, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,4-trimethylbenzene. These solvents are employed for the determination of molecular weights from solution viscosity data of by gel permeation chromatography.

An important measure of chemical resistance, which is often used in household and industrial containers, is environmental stress crack resistance (ESCR). Many variations of the test are known and used, such as ASTM D1693, Conditions A and B. In these tests, the plastic part, a molded bar, or a bottle, or tube, etc, is placed under a standardized stress usually at elevated temperature, and exposed to a surface active agent. For example, one test uses 10% surfactant in aqueous solution at 60°C. The time needed for the sample to break is then recorded. The surfactant is thought to aid in the relaxation and disentanglement of chains.

**6.3. Degradation.** HDPE is relatively stable to heat due to the high bond energy of the single C−C bond. However, above ~290−300°C chemical processes in an inert medium begin to result in breakage and cross-linking of chains. This reaction is similar to thermocracking of linear hydrocarbons. Near 500°C in an inert atmosphere, HDPE is rapidly pyrolized to a mixture of low molecular weight alkanes, alkenes, and dienes.

Oxygen is quite aggressive toward the C−H bonds of these macromolecules at the usual melt processing temperatures (200−300°C). This type of degradation is also a combination of radical reactions, resulting in a reduction of molecular weight, formation of oxygen-containing groups such as −OH, −C=O, and low MW by-products like water, aldehydes, ketones, etc. The initiation of oxidation can be enhanced by transition metal impurities in the polymer from catalyst residues. For this reason, it is important to achieve high activity from the catalyst, leaving only a few ppm of transition metal in the polymer. The conditions of commercial pelletization and molding favor thermooxidative degradation, and therefore oxygen preferably excluded if possible. Protection is also nearly always afforded by the addition of an antioxidant package as well, which can include hindered phenols, phosphites, and other specialized agents added in the concentration of 0.01−1.0%.

Exposure of the molded HDPE articles to sunlight and air also attacks the polymer over time, especially at wavelengths < 400 nm. Photooxidation resembles thermooxidation in that it is a complex chain of radical transformations. Such exterior "aging" of the polymer results in development of surface cracks, brittleness, changes in color, and a deterioration of mechanical and dielectrical properties. Photooxidation degradation is prevented by addition of small amounts of light stabilizers, such as 2−4% carbon black or, for colorless articles, esters of salicylic acid, derivatives of benzotriazole, benzophone, and others in the 0.1−0.5% range.

Chemical reactions of HDPE not involving oxidation include fluorination, chlorination, and sulfonation. Sometimes molded articles, such as fuel tanks, are given such a surface treatment to increase diffusional resistance.

## 7. Manufacturing Processes

Many diverse commercial technologies exist for the manufacture of HDPE, developed by many different companies worldwide. However, they can be divided into three fundamental types: (*1*) solution processes, (*2*) slurry processes, and (*3*) gas-phase processes. In recent years, hybrids and combinations of these three basic forms have also been widely used.

**7.1. Solution Processes.** The earliest commercial HDPE plants used a solution process in which the polymer dissolves in a hydrocarbon solvent as it is formed. Cylcohexane was commonly used as solvent at 120–150°C. Initially, catalyst productivity was low, but the solution process allowed a filtration or centrifugation step in which catalyst residue could be removed. Later, as catalyst productivity improved, this step could be omitted in some processes. Low molecular weight polymers are made more easily in the solution process because of the lower solution viscosity. Although most of the earlier solution processes have been shut down due to poor economics, more recent improved designs, such as those developed by DuPont, Dow, and others, are still in production today and considered competitive (102–108).

For example, the DuPont process is reported to operate at a temperature in excess of 150°C and a pressure of ~80 bar. Residence time in the reactor is short, on the order of 5–10 min and polymer concentration relatively high, up to 35 % for low molecular weight grades. The sensible heat of the reaction mixture is employed to flash concentrate the solution from which the product is recovered in a devolatilizing extruder. Terminating agents and stabilizers are added in the extruder. Vapor from the flash step is condensed, cooled, and returned to the reactor. Residual hydrocarbon is removed in the extrusion step and purified for recycle to the polymerization.

The advantages of this process are a relatively small reactor and short residence times, which allows fast transition between grades and easy control of some polymer properties. Because of the higher reactor temperature, higher alpha olefins can be more easily used in the solution process than in other processes, and thus ethylene 1-octene copolymers are common from this technology. The longer side chains derived from 1-octene (vs. 1-hexene or 1-butene) are thought to improve some resin properties. The solution process is also easily adaptable to multiple reactor schemes in order to tailor the molecular weight distribution.

Further development of the solution polymerization concept has led to molten polyethylene as a medium for ethylene polymerization. Installations typically used for free-radical ethylene polymerization at high pressure are converted to accommodate catalytic ethylene polymerization. Stirred autoclaves operating at 30–200 MPa and 170–350°C are convenient (109,110). Residence time can be very short, for example $< 1$ min.

**7.2. Slurry Processes.** If the hydrocarbon liquid described above is deliberately chosen to be a bad solvent for polyethylene, and the temperature is lowered so that the polymer does not swell or melt in the hydrocarbon, the resultant process is called “slurry” technology because the polymer is produced as a suspended powder. In slurry systems, the hydrocarbon “nonsolvent” is called the diluent. Two major types of slurry systems are widely used throughout the worldwide HDPE industry: (*1*) light hydrocarbon loop reactor processes, and (*2*) heavier hydrocarbon stirred tank reactor processes.

Phillips Petroleum Co. originally developed the loop slurry process in the late 1950s for its chromium oxide catalyst, and Phillips has continued to develop the loop technology up to the present on an ever larger scale. The preferred diluent is isobutane, which was chosen to allow maximum reactor temperature without polymer swelling. This was necessary because the early chromium catalysts tended to produce lower melt index polymer (higher MW) than optimum for the new extrusion market. Higher reaction temperatures yield a higher melt index polymer. Initially, many hydrocarbon diluents were tested, and the degree of polymer swelling caused by each diluent was found to be related to the ratio of $CH_3$ to total carbons in the hydrocarbon (111). Thus, eg, pentane was inferior to isopentane, and neopentane, which has the highest $CH_3/C$ ratio of any hydrocarbon, permitted the highest reactor temperature without swelling. However, isobutane, which permits a top reactor temperature of 113°C, was considered as a close second and more economical.

The choice of light diluents and high reactor temperatures also means relatively higher operating pressures. Thus a pipe-loop reactor was considered a convenient way to accommodate operating pressures of up to 5.5 MPa (800 psig). The reactor is equipped with an impeller that drives a concentrated slurry of polymer and isobutane rapidly around the jacketed loop at 5–12 m/s. Today's loop reactors can run at 50% solids by weight, typically in the temperature range of 80–110°C. Residence time is 0.5–1.5 h and conversion is high (95–98%) (103).

The initial development of a slurry process for Ziegler- based catalysts did not face the same problems as scientists at Phillips. Since Ziegler catalysts are much more sensitive to hydrogen, MW control does not rely on precise control high reactor temperatures, as it did for the chromium oxide based loop slurry process. Therefore, lower reactor temperatures and heavier hydrocarbons were possible, and there was no need to go beyond a stirred tank. Hoechst developed the first such process, but Montedison, Mitsui, Solvay, and others have also developed similar processes.

In the Hoechst process, eg, hexane is used as the diluent (112,113). Hexane, ethylene, alpha-olefin, catalyst components, and hydrogen are continuously fed into a stirred reactor for polymerization. The slurry is then transferred into a smaller reactor for postpolymerization, after which the total charge is separated by a centrifuge into a liquid stream, which is returned to the initial reactor, and solid polymer. The wet polymer is steam-stripped from the solvent, dried and pelletized. The stripped hexane is purified and recycled. Although stirred tanks are most common, loops can also be used in this fashion. In some schemes, a portion of the recycle diluent from the centrifuge is returned to the reactor, and a portion is fed to recycle purification for wax removal. This step removes some of the lowest molecular weight polymer, which dissolves in the diluent.

**7.3. Gas-Phase Processes.** Unlike solution or slurry processes, the original gas-phase polymerization processes employed no hydrocarbon diluent. Union Carbide introduced the first gas-phase technology in 1968, and other firms soon developed the approach still further, such as Naphtachimie, British Petroleum, BASF, and Amoco (114–118). In this technology, solid catalysts are used for ethylene polymerization of its copolymerization with light comonomers in the gas phase. The system is agitated by mechanical devices, such as horizontal paddles or screws, but more often by a gas stream of ethylene, which fluidizes the PE particle bed.

A typical fluidized-bed reactor has a length/diameter ratio of ∼7 and a disengagement zone at the top. Uniform fluidization is achieved by ethylene flow through a distribution plate at the reactor bottom, and rapid circulation is needed to remove heat. Conversion is ∼2%/pass. Unreacted ethylene enters the disengagement zone, separates from the entrained polymer particles, is filtered, cooled, compressed, and recycled. A catalyst is continuously fed to the reactor without diluent, and polymer particles are continuously removed from the bed through a system of valves. Reactor temperatures of 70−100°C are common, with pressure of 1.4−3.5 MPa (200−500 psig).

Polymerization of ethylene is quite exothermic ($3.4 \times 10^6$ J/kg) and since the heat capacity of gas is much lower than that of liquid, removal of the heat of polymerization can be problematic compared to solution and slurry processes. This was usually accomplished by lowering the activity of gas-phase catalysts by say 50−75% to reduce the rate of local heat generated. To compensate, the residence time was then extended to several hours. As a result of these differences, gas-phase processes tend to have a much larger polymer inventory in the reactor. The gas-phase approach is also more rigid in its catalyst requirements. The kinetic profile of a catalyst for a gas-phase process should have a steady activity lasting 2−3 h. The particle size for consistent fluidization is also important, and smaller particles are preferred for heat removal.

The fluidized-bed gas-phase process offers some advantages and disadvantages compared to the slurry processes. Since there is no diluent, it makes low density resins well, without swelling. The lack of diluent also simplifies the operations and equipment to some degree. On the other hand, transitions are extremely slow and there is usually a large inventory, which can greatly increase the off-specification rate during transitions. Gas-phase units are sometimes also more sensitive to poisons in the feedstocks, and more sensitive to fouling. Once a reactor has "logged" cleanup can be longer and more difficult for a gas-phase reactor.

In recent years the fluidized-bed processes have been improved through the addition of liquid hydrocarbons into the polymer bed (119,120). These evaporate, adsorbing heat from the bed more effectively than gas alone, and then are condensed in the recycle stream and reused. The result of this "condensed" or "super-condensed mode" approach is increased production rates from the same reactor, or greater tolerance for higher activity catalysts. Of course, it reverses some of the benefits of pure gas phase, since it is a step back toward hydrocarbon diluent. Nevertheless, this innovation has greatly improved operations and production of the gas-phase process, instilling new life into the technology.

**7.4. Bimodal Reactor Technology.** In a modification of the original stirred tank slurry process, Hoechst, Nissan, Mitsui etc developed cascade reactor systems to make bimodal resins with improved properties (67,121,122). Under these processes, multiple reactors are aligned in series, parallel, or a combination of series and parallel, so that a Ziegler catalyst is exposed to more than one set of reaction conditions during its lifetime. In this way, low MW homopolymer can be produced in combination with high MW copolymer, the so-called "bimodal" resin combination. This technique was originally developed to counteract the limitation of Ziegler catalysts, which unaided, tend to make a narrow MW distribution that is not useful for many extrusion applications. However, this type of broadening also allows the branching to be selectively placed into the high MW portion of the distribution.

In later years, other reactor arrangements have also been developed to produce bimodal resins. Other variations include combining two loops in series (Solvay, Fina, etc), two gas-phase reactors in series (Union Carbide), and loop–gas phase (Borealis).

Multiple reactor processes have some advantages and disadvantages over single reactor arrangements of similar capacity. They produce some unusual resins that (at the time of this writing) cannot be exactly duplicated by any other means, such as high MW film or pipe resins. However, they are also more complicated and more expensive to build and run, and they are much less flexible in what can be made. Many HDPE researchers believe that new single-site catalyst advances that will eventually make bimodal reactor technology obsolete.

## 8. Health and Safety Factors

High density polyethylene is generally inert and lacking any toxicity, which accounts for its widespread use in food packaging. It is also used in prosthetic devices, in surgery, hip or knee joint replacements, etc.

High density polyethylene can present some health hazard during its combustion, pyrolysis, or during thermocutting, when smoke, fumes, or toxic decomposition products can be formed. Irritation of the skin, eyes, and mucous membranes of the nose and throat are possible. In some cases this irritation has been traced to traces of acrolein or formaldehyde from thermo-oxidative decomposition. However, other large-scale fire testing of foamed PE under actual conditions did not reveal significant acrolein formation and demonstrated that PE presents no worse hazard than cellulosic materials. Still other studies indicate that maximum evolution of irritants occurs from smoldering combustion at 300–400°C.

## 9. Commercial Applications

The low melting point and high chemical stability of HDPE facilitate its processing by many conventional techniques. Some of the most common applications include, injection molding, blow molding, blown and cast film, pipe and tubing, wire and cable coating, thermoformed sheet, spinning, etc. Table 4 indicates the approximate current breakdown in the United States by end use.

**9.1. Injection Molding.** In this technique, molten HDPE is injected into a metal mold at 200–260°C and 70–140-MPa pressure. The mold is then cooled and opened and the solid article, which is now in the shape of the mold, is removed. Usually, resins with a narrow molecular weight distribution are preferred for injection molding applications, because broader distributions are more likely to leave orientations frozen into the articles upon cooling due to the slower relaxation time. Such frozen orientations can lead to warpage of the article upon cooling. For this reason, most injection molding resins are prepared from Ziegler catalysts. Because of the narrow MW distribution, which tends to resist flow at high shear, and because of the need to completely fill sometimes intricate molds, injection molding resins generally have lower average molecular weights than are needed for other applications. Injection molding resins generally include the melt index range of 1–80. A wide diversity of articles are made from injection molded HDPE including cups, pails, toys, housewares, auditorium seats and chairs, crates, food containers, etc.

**9.2. Blow Molding.** Blow molded articles account for the largest single use of HDPE. The technique is used for rapid processing of large quantities of articles of relatively simple configuration, such as bottles, drums, tanks, and simple containers. A molten tube of HDPE, called a parison, is extruded from a die and then enclosed by a doubly split metal mold (Fig. 12). The parison is blown by air pressure to conform to the internal configuration of the mold into the formed article, much as glass is blown into bottles. When the melt leaves the die, it swells and the parison diameter increases, especially with HDPE of high MW and at high extrusion rates.

In the initial phase of blow molding, the molten tube is extruded at high pressure and rate through a small die gap and the tube thus formed is free-hanging in the mold. Thus, low viscosity at high shear is preferred to enhance extrusion, but to resist sagging in the mold, high zero-shear viscosity is preferred. Thus combination is achieved by using broader MW distribution resins of relatively high MW (melt index 0.1–0.5), often having elevated levels of LCB. Chromium catalysts are ideal for producing blow molding resins.

Another important characteristic of blow molding resins is the degree of “parison swell” and “die swell”. The former is the extent to which the molten tube tends to flare out during the extrusion step. An excessively high degree of flare can cause the tube to extend beyond the mold cavity while too little flare can sometimes cause incomplete filling of the mold structure. Die swell is a measure of how much the tube wall expands as it exits the die under high pressure. The die gap must be adjusted to take die swell into account in order to produce the desired wall thickness. Molders prefer to set this parameter midway and not have to readjust it from one resin lot to another. The degree of swell in these resins is highly influenced by the degree of long-chain branching in the resin. A certain minimum level of LCB is required for most resins. This is another reason that chromium oxide catalysts lend themselves well to blow molding applications. LCB content can be adjusted easily by varying chromium loading, activation temperature, or cocatalyst level (91).

Blow molding is widely used to form bottles for food packaging, detergents, oil, and other household materials, industrial drums, fuel tanks for automobiles, toys, and a wide assortment of other articles.

**9.3. Blown Film.** The impermeability, stiffness, and higher softening temperature of HPDE make it useful for certain film applications. A continuous roll of blown film is produced by extrusion of HDPE melt through a die with a circular slit of ~0.6–1.5 mm; the diameter of the ring can typically be as large as 80–100 cm. The extruded thin-walled tube rises vertically and is filled with air, thus expanding the tube to a certain size. Often, the ratio of the tube diameter to the die diameter is ~4:1, allowing for the formation of a film trunk up to 4 m in diameter. The film, 0.007–0.125 mm thick, is air-cooled and rolled.

Bags can be made from the rolled hollow film tube, or it can be split into one continuous sheet for wrapping and other uses. In coextrusion, two different types of plastic are simultaneously extruded through a single die with two concentric circular slits, giving a layered film. This can be done to achieve special physical properties or permeability resistance.

Chromium-based catalysts can be used quite widely for production of HDPE film grades, but some of the best HDPE films, in terms of mechanical properties and extrusion rates, are bimodal resins made from Ziegler catalysts passing through two or more reaction zones. Most recently, metallocene resins have been used to produce extremely high clarity resins, despite the high density. Applications of HDPE films include food packaging, grocery and merchant bags, and drum liners Fig. 13.

The thickest blown film made from HDPE, sometimes called sheeting, ranges in gauge from 0.5 to 3.0 mm and is used in geomembranes. Geomembrane blowing operations typically produce a sheet 6.9 m wide (22.5 ft), with the bubble rising eight stories into the air, weighing 2.5 tons. Geomembrane sheeting is used to protect the environment by lining pits and covering landfills. For example, sewage ponds and spillover sumps near oil and chemical storage tank areas are first lined with geomembrane to prevent seepage into the groundwater. Reservoirs to hold drinking water are also lined with geomembrane in some regions to prevent loss. Leaching pads used in mining operations, irrigation canals, evaporation ponds, and industrial waste lagoons are other applications of geomembrane. In this type of service, toughness is extremely valued to avoid penetration by rocks, tree roots, etc. Thus, high molecular weight and a significant amount of branching are preferred in the polymer. The blowing operation favors resins with high melt strength, which is imparted by high levels of long-chain branching. Chromium catalysts are best for this type of blown film.

**9.4. Thermoforming.** Thermoforming is a process in which the resin is extruded into flat sheets of perhaps 2–13 mm after which that sheet is softened by heat and then stamped or pulled by vacuum into a large mold. Thermoformed sheet is widely used for trays, pans, for lining the beds of pickup trucks or other vehicles, for flooring and a wide variety of other articles. Thermoforming resins typically require stiffness, toughness, and good melt strength, all of which are achieved from chromium oxide catalysts at 0.05–0.2 melt index.

**9.5. Pipe and Tubing.** Pipes (diameter $> 1$ cm) and tubing (diameter $<$ 1 cm) are produced by passing HDPE melt through a die with a circular channel, forming a thick tube. Immediately after leaving the die, the molten tube enters a vacuum calibrator, where it is forced against sizing rings and cooled. Extrusion and drawdown (ratio of the cross-sectional area of the die opening to the tube wall) are adjusted with the help of mechanical pulling devices. For pipe manufacture, die openings are large, resistance to polymer flow is low, and drawdown does not exceed 1.1. Pipes with diameter $\sim$1.5 m are made commercially.

HDPE pipe is used in low pressure applications for transporting potable water, gas, acids, liquid hydrocarbons, oils, salt water, and other chemicals and solvents. Long-term load bearing, or “creep”, tests are essential to determine the life of polyethylene pipe under pressure. This pipe withstands pressures in short-term burst tests that are several times greater than long-term burst pressures because of the creep phenomenon. Broad MW distribution resins, as obtained from chromium oxide catalysts, are ideal for most pipe applications. The introduction of superior, bimodal type, pipe resins in recent years has extended HDPE pipe applications.

**9.6. Wire and Cable Insulation.** Excellent electrical properties and moisture resistance make linear polyethylene ideal for wire and cable coatings. Use include power, communications, and control applications. Continuous coatings can be extruded directly onto wire at high speed, followed by cooling in a bath. The lubricity and high abrasion resistance of the coating aid in conduit installations. Copolymers of 0.935–0.945 g/cm$^3$ density and $\sim$1 melt index are commonly used because of the good balance of toughness, ESCR, and extrudability. Polymers of medium-to-broad molecular weight distribution are preferred because of high coating speeds and good surface finish. Addition of $\sim$2.5% small particle carbon black greatly increases weather resistance.

**9.7. Filament.** In the production of monofilament, extruded strands are quenched, reheated, and then pulled to draw ratios of 10:1. The tensile strength of finished filament is 345–690 MPa due to the high degree of orientation. Cord and rope are used in sporting goods and utility purposes. Larger polyethylene rope is used in marine applications where it has a clear advantage over nylon, since HDPE floats and does not adsorb water. Ribbon yarn, made from split film, finds applications in carpet backing, some fabrics, bags, and in binding of multiwire cable together. A large market for these products is especially found in Asia and South America. Owing to its chemical inertness, linear PE is used for monofilament gauze for tissue reinforcement in surgery. Ziegler resins are particularly well suited to these applications, although chromium oxide derived resins are also common.

**9.8. Rotomolding.** Larger items, such as tote boxes, fuel tanks, and water storage tanks are often made by a rotational molding operation. Usually, HDPE powder or pellets are introduced into a mold cavity, which is then heated and rotated evenly. As the polymer melts, it coats the inside surface of the mold uniformly. The mold is then cooled while still under rotation to prevent sagging or other imperfections. Sometimes organic peroxide is added so that upon heating the plastic, a cross-linking reaction takes place in which the MW and viscosity of the plastic dramatically increases. The mold is then separated and the article removed. Tanks up to 10,000 gal are made in this way. Rotomolding applications require good flow under zero-shear conditions. Narrow molecular weight distribution resins, as provided by Ziegler or metallocene catalysts, are preferred for rotomolding applications.

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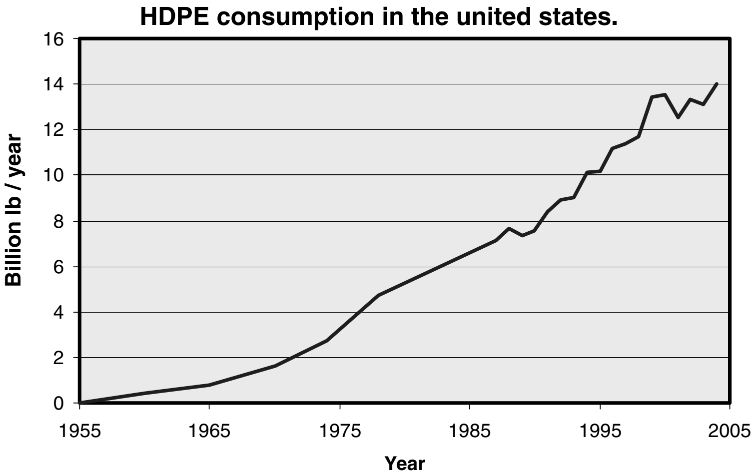

**Fig. 1.** HDPE consumption in the United States.

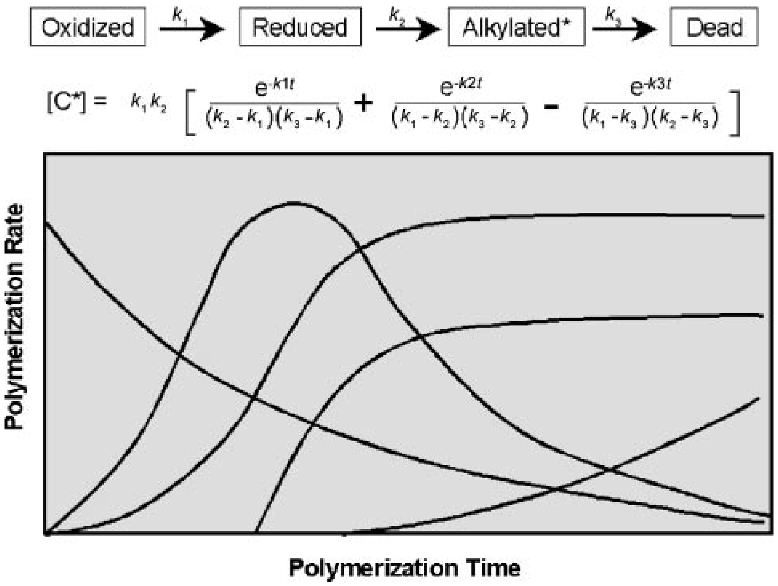

**Fig. 2.** Kinetic profiles of Cr based catalysts.

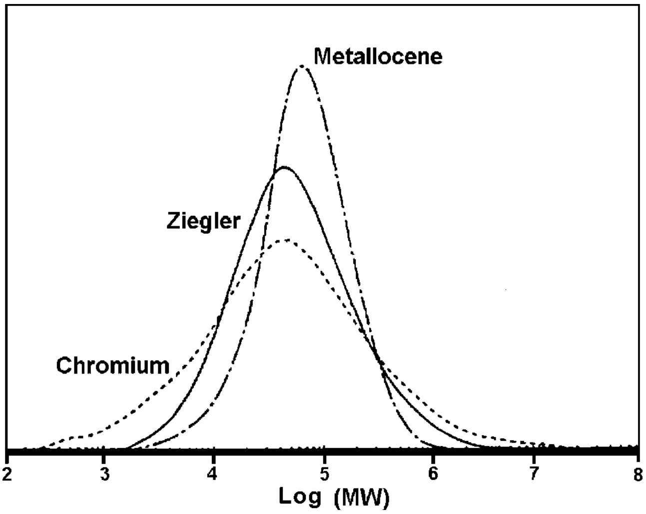

**Fig. 3.** Molecular weight (MW) distribution (GPC curves) of resins derived from metallocene, Ziegler, and chromium oxide-based catalysts.

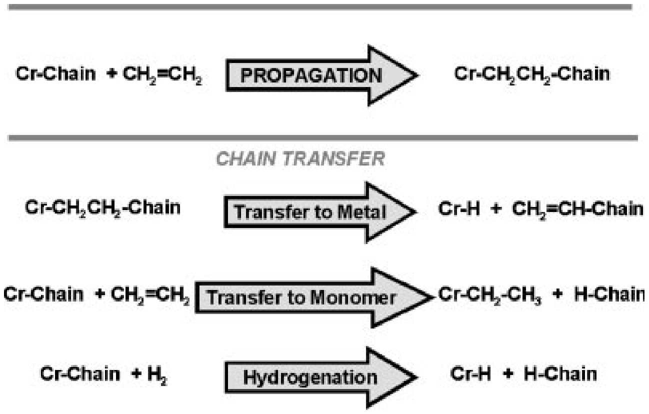

**Fig. 4.** Steps of polymerization.

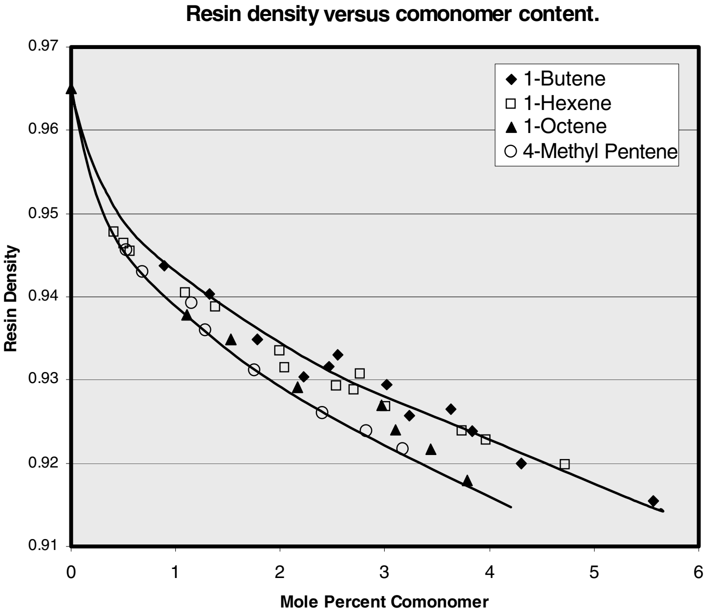

**Fig. 5.** Resin density versus comonomer content.

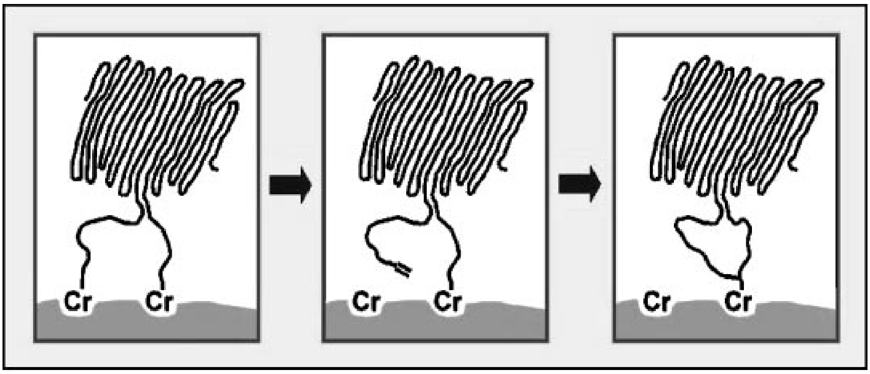

**Fig. 6.** Long-chain branch formation through reincorporation of vinyl end groups.

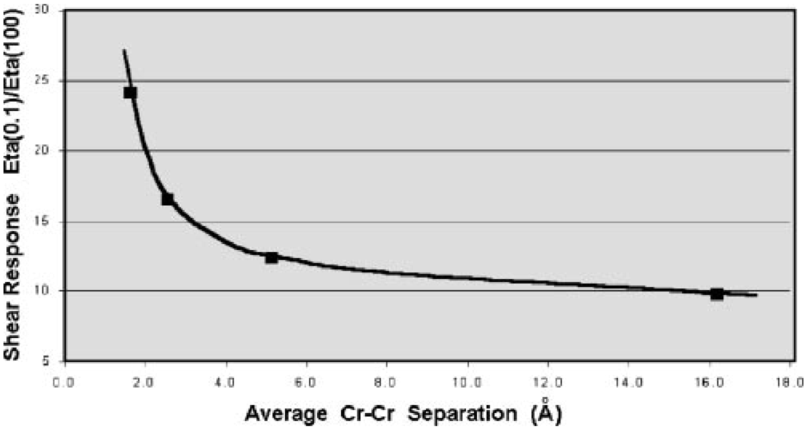

**Fig. 7.** Dependence of LCB (as measured by shear response) on chromium loading.

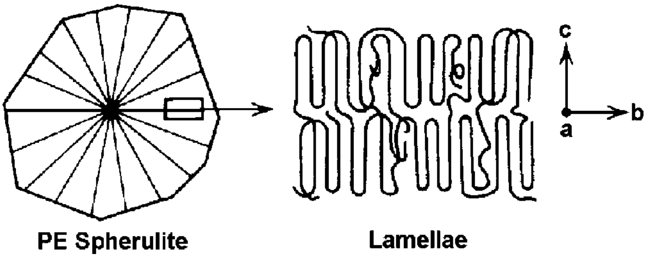

**Fig. 8.** Structure of HDPE spherulite.

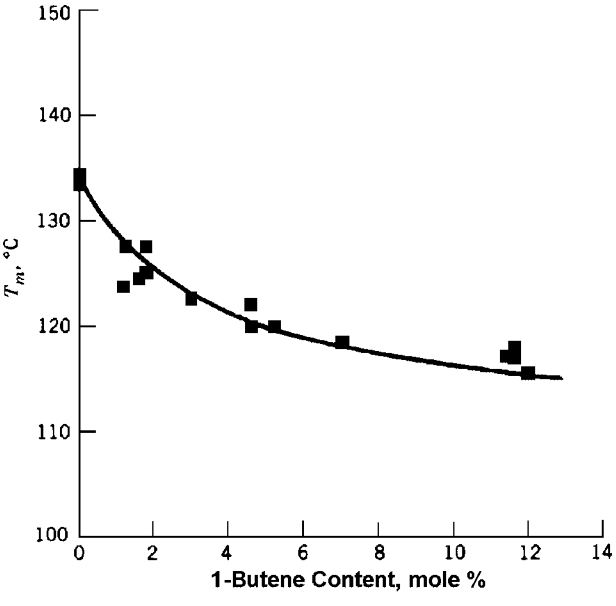

**Fig. 9.** Melting point of HDPE as a function of 1-butene content.

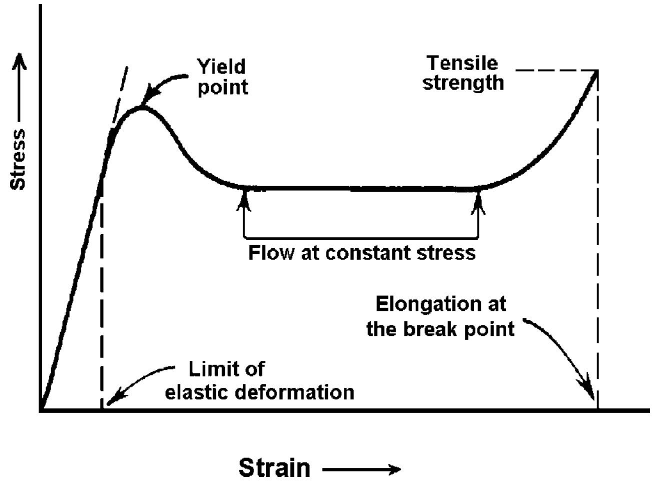

**Fig. 10.** Idealized stress–strain curve for HDPE.

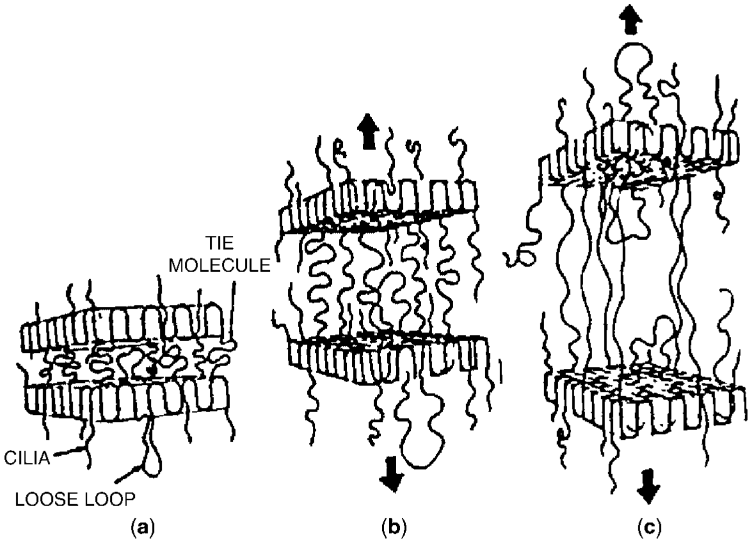

**Fig. 11.** Role of intercrystallite links in resin failure.

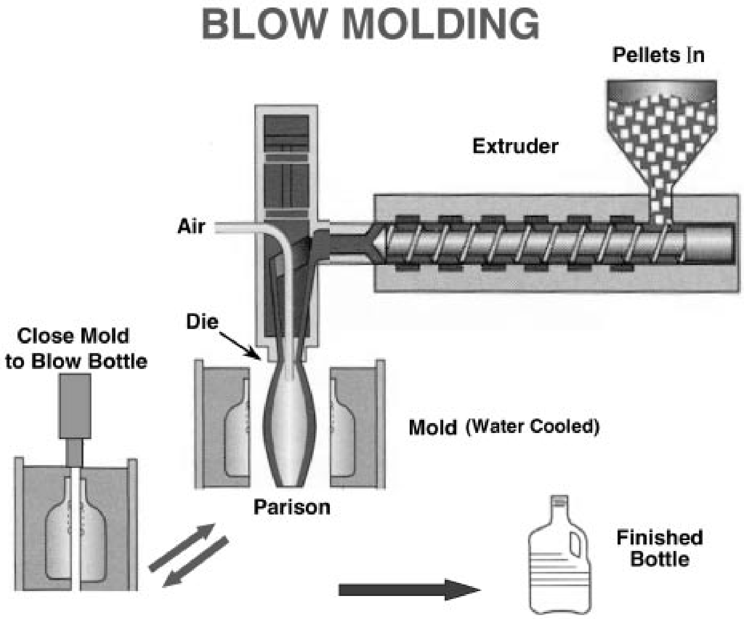

**Fig. 12.** The HDPE blow-molding processing steps: (**a**) extrusion of parison, mold is open; (**b**) mold is closed; (**c**) air is blown into parison; and (**d**) mold is opened for removal of article.

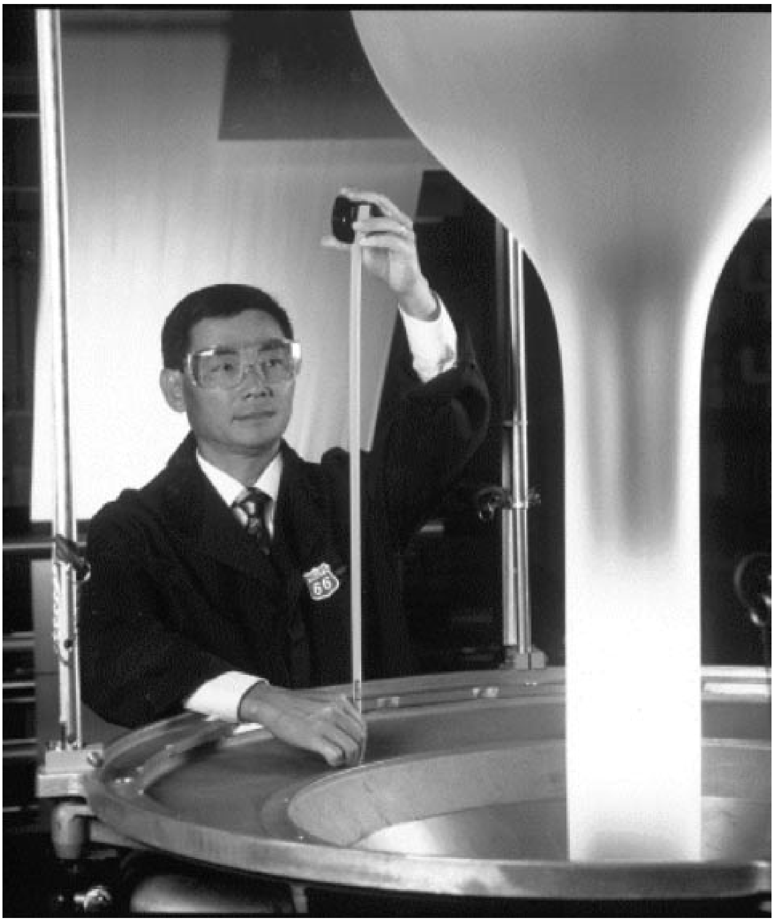

**Fig. 13.** HDPE film blowing.

Table 1. **Worldwide Usage in 2004 of Most Common Thermoplastics**[a]

| Polymer type | Share of world usage, % |
|---|---|
| polyethylene (LDPE, EVA, LLDPE, and HDPE) | 39 |
| polypropylene | 24 |
| PVC | 19 |
| polystyrene | 7 |
| ABS | 4 |
| PET | 7 |
| *total* | *100* |

[a] Data from CMAI.

Table 2. **Polyolefins Worldwide Usage in 2004**[a]

| Polymers | Billion pounds consumed | Percent of all plastics consumed, % | Percent of total PE consumption, % |
|---|---|---|---|
| total polyethylene | 134.6 | 62 | 100 |
| LDPE (and EVA) | 38.0 | 17 | 28 |
| LLDPE | 38.0 | 17 | 28 |
| HDPE | 58.7 | 27 | |
| *Total polypropylene* | *82.8* | *38* | *44* |
| *Total plastics* | *217.5* | *100* | |

[a] Data from CMAI.

Table 3. **Properties of Three Typical Commercial HDPE Grades**[a]

| | | Resin grade | | |
|---|---|---|---|---|
| Property | Test | Injection molding | Blow molding | Film |
| ***Physical*** | | | | |
| melt index (2.16 kg) | ASTM D1238 | 33.59 | 0.36 | 0.31 |
| high load melt index (21.6 kg) | ASTM D1238 | high | 34.14 | 23.22 |
| density, $g/cm^3$ | ASTM D1505 | 0.9678 | 0.9557 | 0.939 |
| refractive index, $n_D{}^{25}$ | | 1.54 | 1.53 | 1.51 |
| MW (weight average) | GPC | 13,900 | 17,800 | 13,600 |
| MW (number average) | GPC | 48,400 | 143,000 | 177,000 |
| polydispersity (Mw/Mn) | GPC | 3.5 | 8.0 | 13.1 |
| weight percent hexene | $C^{13}$ nmr | 0.00 | 0.60 | 3.50 |
| ***Mechanical*** | | | | |
| Yield point, MPa | ASTM D638 | 31.0 | 27.8 | 19.1 |
| tensile strength, mPa | ASTM D638 | 31.0 | 23.4 | 29.5 |
| tensile impact, $kJ/m^2$ | ASTM D638 | 9.0 | 56.8 | 143.6 |
| elongation, % | | | | |
| at yield point | ASTM D638 | 8.2 | 10.1 | 13 |
| at break point | ASTM D638 | 8.2 | 669 | 745 |
| notched impact strength, $kJ/m^2$ | ASTM D256-84a | 0.90 | 17.3 | no break |
| flexural modulus, MPa | ASTM D790-95a. | 1894 | 1375 | 822 |
| brinell hardness, MPa | | 60–70 | 50–60 | 35–50 |
| shore D hardness | ASTM D2240 | 67 | 62 | 51 |
| environmental stress crack resistance | | | | |
| condition A (hrs) | ASTM D1693 | 0 | 49 | >1000 |
| condition B (hrs) | ASTM D1693 | 0 | 29 | >1000 |
| condition C (hrs) | ASTM D1693 | 0 | 0 | >1000 |
| ***Thermal*** | | | | |
| melting point, °C | | 136 | 133.5 | 127 |
| brittleness temp. °C | ASTM D746 | | −140 to −70 | |
| heat resistance temp, °C | | ~122 | ~120 | ~117 |
| vicat softening point, °C | ASTM D1525 | 126 | 133 | |
| specific heat capacity, kJ/(kgK) | | 1.67–1.88 | 1.88 – 2.09 | |
| thermal conductivity, W/(mK) | | 0.46–0.52 | 0.42 – 0.44 | |
| temp coefficient of linear expansion | | | $(1 - 1.5) \times 10^{-4}$ | |
| temp coefficient of volume expansion | | | $(2–3) \times 10^{-4}$ | |
| heat of combustion, kJ/g | | | 46.0 | |
| ***Electrical*** | | | | |
| dielectric constant at 1MHz | | 2.3–2.4 | 2.2–2.4 | 2.0–2.3 |
| dielectric loss angle, 1kHz–1MHz | | | $(2–4) \times 10^{-4}$ | |
| volume resistivity | | | $10^{17}–10^{18}$ | |
| surface resistivity | | | $10^{15}$ | |
| dielectric strength, Kv/mm | | | 45–55 | |

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[a] Data was provided by D.R. Register from Phillips Petroleum Co. Polymer testing laboratory.

Table 4. **U.S. Usage of HDPE by Application**[a]

| Market | Billion pounds annually | Percent market share, % |
|---|---|---|
| extrusion | | |
| film (up to 12 mils) | 2.33 | 15.6 |
| sheet (over 12 mils) | 0.77 | 5.1 |
| pipe and conduit, corrugated | 0.66 | 4.3 |
| pipe and conduit, noncorrugated | 1.28 | 8.5 |
| other extruded products | 0.47 | 3.1 |
| rotomolding | 0.15 | 1.0 |
| injection molding | 2.37 | 15.7 |
| blow molding | 4.90 | 32.5 |
| resellers and compounders | 1.87 | 12.4 |
| all other uses | 0.27 | 1.8 |
| *Total* | *15.06* | *100.0* |

[a] Reflecting usage from the first quarter, 2000. Data from Digest of Polymer Developments, Series I, Number 95, STR Publishing, Enfield, Connecticut, May, 2000.