

1

Introduction to Polymers of Ethylene

1.1 Genesis of Polyethylene

Modern polyethylene has its origins in work by chemists at Imperial Chemical Industries beginning in 1933 (1). Eric Fawcett and Reginald Gibson were trying to condense ethylene with benzaldehyde at very high pressure and temperature (142 MPa* and 170 °C). They obtained a small amount of a residue that they concluded was polyethylene, but attempts to repeat the experiment minus benzaldehyde resulted in explosions. In late 1935, ICI chemist Michael Perrin succeeded in preparing a larger amount of polyethylene. Serendipitously, Perrin used ethylene containing traces of oxygen. Either oxygen itself or peroxides formed *in situ* initiated free radical polymerization of ethylene. In 1939, ICI began commercial production of high pressure polyethylene ("HPPE") now known as low density polyethylene (LDPE), and the product was used to insulate radar cable during World War II.

Work of other researchers portended the discovery of polyethylene. For example, in 1898, Hans von Pechman produced a composition he called "polymethylene" by decomposition of diazomethane. "Polymethylene" was also produced by other

* Please see glossary for definition of abbreviations, acronyms and terms.

chemistries, including the Fischer-Tropsch reaction. Most of these polymers had low molecular weights. In 1930, Marvel and Friedrich produced a low molecular weight polyethylene using lithium alkyls, but did not follow-up on this finding. Descriptions of early work on polyethylene have been provided by McMillan (1), Kiefer (2) and Seymour (3, 4).

Other noteworthy milestones in the evolution of industrial polyethylene include the following:

- In the early 1950s, transition metal catalysts that produce linear polyethylene were independently discovered by Hogan and Banks in the US and Ziegler in Germany.
- Gas phase processes, LLDPE and supported catalysts emerged in the late 1960s and 1970s.
- Kaminsky, Sinn and coworkers discovered in the late 1970s that an enormous increase in activity with metallocene single-site catalysts is realized when methylaluminumoxane (discussed in Chapter 6) is used as cocatalyst.
- In the 1990s, polyethylenes produced with metallocene single site catalysts were commercialized and non-metallocene single-site catalysts were discovered by Brookhart and coworkers.

A timeline of notable 20th century polyethylene developments is provided in Figure 1.1.

This chapter introduces basic features of polyethylene, a product that touches everyday life in countless ways. However, polyethylene is not monolithic. The various types, their nomenclatures, and how they differ will be discussed. Key characteristics and classification methods will be briefly surveyed. An overview of transition metal catalysts has been included in this introductory chapter (see section 1.5) because these are the most important types of catalysts currently used in the manufacture of polyethylene. Additional details on transition metal catalysts will be addressed in subsequent chapters.

This chapter may be skipped by readers having an understanding of fundamental properties and nomenclatures of industrial polyethylene and a basic understanding of catalysts.

1.2 Basic Description of Polyethylene

Ethylene ($\text{CH}_2=\text{CH}_2$), the simplest olefin, may be polymerized (eq 1.1) through the action of initiators and catalysts. Initiators are most commonly

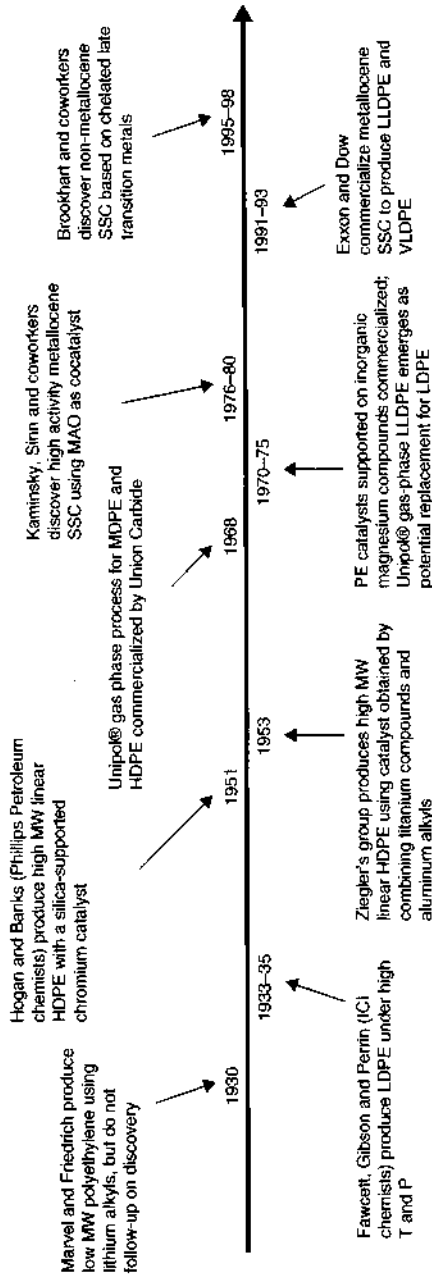
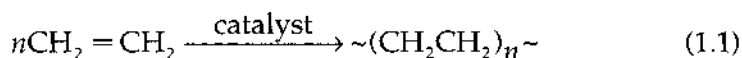


Figure 1.1 20th century milestones in polyethylene.

organic peroxides and are effective because they generate free radicals which polymerize ethylene via a chain reaction. Transition metal catalysts (primarily Ziegler-Natta and Phillips) are also widely employed in industry but produce polyethylene with different properties and by different mechanisms. Single-site catalysts also involve transition metal catalysts, but the quantity of polyethylene produced with single site catalysts at this writing is small (<4%). Initiators, transition metal catalysts and cocatalysts are discussed in Chapters 2–6.

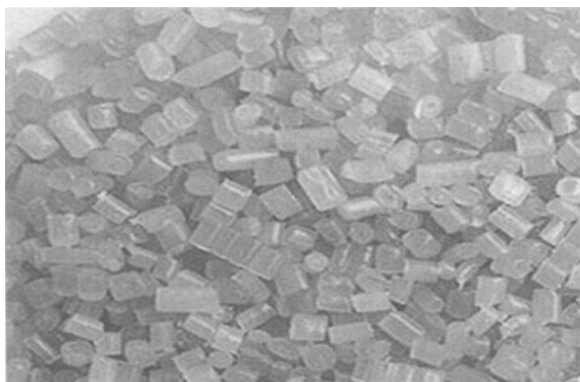
Conditions for polymerization vary widely and polyethylene compositions, as noted above, also differ substantially in structure and properties. In eq 1.1, subscript n is termed the degree of polymerization (DP) and is greater than 1000 for most of the commercially available grades of polyethylene.



The polymer produced in eq 1.1 is known as polyethylene and, less commonly, as polymethylene, polyethene or polythene. (In the late 1960s, “polythene” became part of popular culture when the Beatles released “Polythene Pam.”) Polyethylene is the IUPAC recommended name for homopolymer. As we shall see, however, many important ethylene-containing polymers are copolymers. Nomenclatures for various types of polyethylene are addressed in section 1.3. Though some have suggested that its name implies the presence of unsaturated carbon atoms, there are in fact few C=C bonds in polyethylene, usually less than 2 per thousand carbon atoms and these occur primarily as vinyl or vinylidene end groups.

Polyethylene is the least costly of the major synthetic polymers. It has excellent chemical resistance and can be processed in a variety of ways (blown film, pipe extrusion, blow molding, injection molding, etc.) into myriad shapes and devices. Fabrication methods will be briefly discussed in Chapter 8.

As removed from industrial-scale reactors under ambient conditions, polyethylene is typically a white powdery or granular solid. In most cases, the raw polymer is then melted and selected additives are introduced. (Additives are essential to improve stability and enhance properties of polyethylene. See Chapter 8.) The product is shaped into translucent pellets and supplied in this form to processors. Pelletization increases resin bulk density resulting in more efficient packing and lower shipping costs. It also lowers the possibility of dust explosions while handling.



Raw polyethylene resin is melted and shaped into pellets. This increases bulk density, improves handling characteristics and reduces shipping costs. Pellet size is typically ~3 mm (or ~0.1 in).

Polyethylene is a thermoplastic material. That is, it can be melted and shaped into a form which can then be subsequently remelted and shaped (recycled) into other forms. Polyethylene does not typically have a sharp melting point (T_m), but rather a melting range owing to differences in molecular weight, crystallinity (or amorphous content), chain branching, etc. Nevertheless, "melting points" between about 120 and 140 °C are cited in the literature. Because polyethylene is usually processed above 190 °C, where it is completely amorphous, melting ranges are less important than flow characteristics of the molten polymer. Molten polyethylene is a viscous fluid and is an example of what are termed "non-Newtonian fluids," that is, flow is not directly proportional to pressure applied (see section 8.3 of Chapter 8).

Polymerization of ethylene illustrated in eq 1.1 may be terminated by several pathways leading to different end groups. The type of end group depends upon several factors, such as polymerization conditions, catalyst and chain transfer agents used. Since end groups are primarily simple alkyl groups, polyethylene may be regarded as a mixture of high molecular weight alkanes.

Chain branching in low density versions of polyethylene is common. Extent and length of branching stem primarily from the mechanism of polymerization and incorporation of comonomers. Branching is classified as long chain branching (LCB) or short chain branching (SCB). By convention, SCB implies branches of 6 or fewer carbon atoms. LDPE contains extensive LCB and branches can contain hundreds of carbon atoms. Branches on branches are also common in LDPE.

This increases amorphous content and contributes to LDPE attributes, such as film clarity and ease of processing. As branching increases, density decreases. In LLDPE, incorporation of relatively large quantities of alpha olefin comonomers results in abundant SCB and lowering of density.

Ethylene may be copolymerized with a range of other vinylic compounds, such as 1-butene, 1-octene and vinyl acetate (VA). These are termed comonomers and are incorporated into the growing polymer. Comonomers that contain oxygenated groupings such as vinyl acetate are often referred to as "polar comonomers." Comonomer contents range from 0 to ~1 wt% for HDPE up to ~40 wt% for some grades of ethylene-vinyl acetate copolymer.

The range of suitable comonomers depends upon the nature of the catalyst or initiator. For example, Ziegler-Natta catalysts are poisoned by polar comonomers. Hence, commercial copolymers of ethylene and vinyl acetate are currently produced only with free radical initiators. However, some single site catalysts are tolerant of polar comonomers (see section 6.2.1).

When ethylene is copolymerized with substantial amounts (>25%) of propylene an elastomeric copolymer is produced, commonly known as ethylene-propylene rubber (EPR) or ethylene-propylene monomer (EPM) rubber. When a diene, such as dicyclopentadiene, is also included, a terpolymer known as ethylene-propylene-diene monomer (EPDM) rubber is obtained. EPR and EPDM are produced with single site and Ziegler-Natta catalysts and are important in the automotive and construction industries. However, EPR and EPDM are produced in much smaller quantities relative to polyethylene. Elastomers display vastly different properties than other versions of industrial polyethylene and are considered outside the purview of this text. EPR and EPDM will not be discussed further.

In copolymerizations of ethylene and α -olefins using Ziegler-Natta catalysts, ethylene is always the more reactive olefin. This causes compositional heterogeneity in the resultant copolymer. Composition distribution (CD) is the term applied to the uniformity (or lack thereof) of comonomer incorporation. For example, studies have shown that lower molecular weight fractions of LLDPE produced with Ziegler-Natta catalysts contain higher amounts of short chain branching, indicating nonuniform composition distribution. However, CD is highly uniform for ethylene copolymers made with single site catalysts.

Many grades of polyethylene are used in food packaging, e.g., blow molded bottles for milk and blown film for wrapping meat and poultry. In the EU, the USA and other developed countries, the resin must satisfy governmental regulations for food contact. In the USA, the resin (including additives; see Chapter 8)

must be compliant with FDA requirements for food contact, such as extractables and oxygen transmission rates. Catalyst residues are quite low in modern polyethylene and are considered to be part of the basic resin. Accordingly, catalyst residues are not subject to FDA regulations.

Polyethylene is available in a dizzying array of compositions, with different molecular weights, various comonomers, different microstructures, etc., predicated by selection of catalyst, polymerization conditions and other process options. Since 1933 when less than a gram was obtained unexpectedly from a laboratory experiment gone awry, polyethylene has grown to become the largest volume synthetically produced polymer, used today in megaton quantities in innumerable consumer applications. Recent analyses indicate global polyethylene production of about 77 million metric tons (~169 billion pounds) in 2008 (5).

1.3 Types and Nomenclature of Polyethylenes

Industrial polyethylenes are commonly classified and named using acronyms that incorporate resin density or molecular weight. IUPAC names are not typically used. In a few cases, copolymers are named using abbreviations for the comonomer employed. Nomenclature typically used for industrial polyethylenes will be discussed in this section. (Molecular weight will be discussed in section 1.4.)

Density is measured using density gradient columns and hydrostatic (displacement) methods. Density is directly related to crystalline content and in fact can be used to estimate % crystallinity in polyethylene.

The Society of the Plastics Industry (SPI), an industry trade association founded in 1937, identifies three main categories of polyethylene based on density:

- Low density: 0.910–0.925 g/cm³
- Medium density: 0.926–0.940 g/cm³
- High density: 0.941–0.965 g/cm³

The American Society for Testing and Materials (ASTM) has also defined various types of polyethylene. An ASTM publication entitled “Standard Terminology Relating to Plastics” (ASTM D 883-00) provides the following classifications based upon density:

- high density polyethylene (HDPE): >0.941 g/cm³
- linear medium density polyethylene (LMDPE): 0.926–0.940 g/cm³

- medium density polyethylene (MDPE): 0.926–0.940 g/cm³
- linear low density polyethylene (LLDPE): 0.919–0.925 g/cm³
- low density polyethylene (LDPE) 0.910–0.925 g/cm³

While useful as starting points, SPI and ASTM classifications are not sufficient to describe the wide range of polyethylenes available in the industry. Classifications have been further subdivided to convey additional information, such as molecular weight or comonomer employed. Further, manufacturers use their own nomenclature and trade names. Clearly, the names used for various polyethylenes are somewhat arbitrary and subjective. The reader should not rigidly construe classifications and may encounter other nomenclatures. An overview of various classifications of polyethylene in common use in industry is provided below:

- *Very Low Density Polyethylene*: VLDPE, also called ultra low density polyethylene (ULDPE) by some manufacturers, is produced primarily with Ziegler-Natta catalysts using α -olefin comonomers. Density ranges from about 0.885 to 0.915 g/cm³. Selected grades of VLDPE produced with single site catalysts are known as polyolefin plastomers (POP) and polyolefin elastomers (POE) because products display both thermoplastic and elastomeric properties. Densities of POP fall in the VLDPE range, but densities of POE are in the range 0.855 to 0.885 g/cm³. Manufacturers have registered trademarks for POE and POP, such as Affinity[®], Engage[®] and Exact[®]. A major application is in food packaging.
- *Low Density Polyethylene*: LDPE, the primeval polyethylene, is produced only by free radical polymerization of ethylene initiated by organic peroxides or other reagents that readily decompose into free radicals. Density is typically 0.915–0.930 g/cm³. LDPE is the most easily processed of major types of polyethylene and is often blended with linear low density polyethylene and high density polyethylene to improve processability. LDPE is highly branched and contains relatively high amorphous content which results in outstanding clarity in film for food packaging, a major application.
- *Copolymers of Ethylene with Polar Comonomers*:
 - *Ethylene-Vinyl Acetate Copolymer*: EVA is by far the most common copolymer of ethylene produced with a polar comonomer. EVA is produced by copolymerization of ethylene and vinyl acetate using free radical initiators, but cannot be produced with Ziegler-Natta or supported chromium catalysts. Vinyl acetate content ranges from about 8% to as high as 40%. Density is dependent upon amount of vinyl acetate incorporated, but is typically 0.93–0.96 g/cm³. When conducted under proper conditions (very high T), comonomer incorporation is random, resulting in uniform composition distribution. EVA contains high amorphous content which

results in outstanding clarity in film applications. EVA resins exhibit lower melting points than low density polyethylene and linear low density polyethylene and are useful for heat seal applications.

- *Ethylene-Vinyl Alcohol Copolymer*: EVOH is the name given to the specialty resin produced by alkaline hydrolysis of ethylene-vinyl acetate copolymer. It may be viewed as the product of copolymerization of ethylene with the hypothetical comonomer "vinyl alcohol." However, it is important to recognize that copolymerization of ethylene with vinyl alcohol is not possible. Vinyl alcohol exists in minute amounts (0.00006%) as the enol form in the keto-enol tautomerism of acetaldehyde (6). Density of EVOH is typically higher (0.96–1.20 g/cm³) than other types of polyethylene because of the high "vinyl alcohol" content. EVOH has excellent oxygen-barrier properties. A key application is laminated films for food packaging.
- *Ethylene-Acrylic Acid (EAA) and Ethylene-Methacrylic Acid (EMA) Copolymers*: EAA and EMA are produced by free radical copolymerization of ethylene with acrylic acid and methacrylic acid, respectively. An acrylate termonomer is incorporated in some grades to lower the glass transition temperature and to improve toughness. Like ethylene-vinyl acetate copolymer, EMA and EAA cannot be produced with Ziegler-Natta or supported chromium catalysts. Density is dependent upon amount of polar comonomer incorporated, but is typically 0.94–0.96 g/cm³. EAA and EMA copolymers have excellent adhesion to metals such as aluminum and are used in metal laminates. EAA and EMA are also used as precursors to ionomers. Ionomers are produced by reaction of a large portion (~90%) of the carboxylic acid moieties with metal bases, most often NaOH and Zn(OH)₂. Ionomers are rubbery solids at ambient temperatures, but become thermoplastic at higher temperatures. Though ionomers have low crystallinity, they exhibit excellent tensile strength and adhesion properties and form very tough films. A well known application for ionomers is their use as covers for durable (non-cut) golf balls. "Potassium ionomers" have recently been commercialized and are promoted for the antistatic properties they impart to blends (7).
- *Linear Low Density Polyethylene*: LLDPE is produced by copolymerization of ethylene with α -olefins using Ziegler-Natta, supported chromium or single site catalysts. LLDPE cannot be produced by free radical polymerization. Density is typically 0.915–0.930 g/cm³. Butene-1, hexene-1 and octene-1 are the most common comonomers, resulting in LLDPE with short chain branches of ethyl, *n*-butyl and *n*-hexyl groups, respectively. The quantity of comonomer incorporated varies depending upon the target resin. Typically, comonomer content is between about 2% and 4% (molar). Density decreases as greater amounts of comonomer are incorporated into the copolymer. (Figure 1.2 shows ethylene/ α olefin copolymer densities as a function of comonomer content.) LLDPE has improved mechanical properties relative

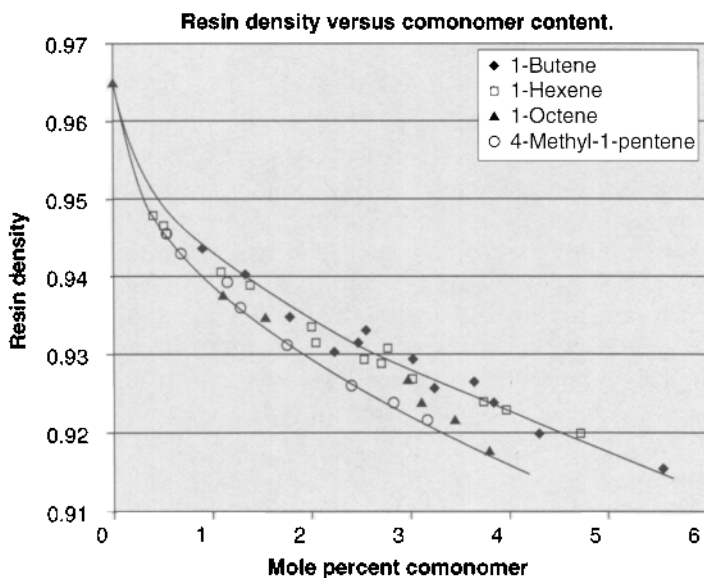


Figure 1.2 Density of LLDPE versus comonomer content (Reproduced with permission from *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., 6th edition, 2006).

to low density polyethylene and is used in blown and cast film applications, such as food and retail packaging. However, because it has lower amorphous content and heterogeneous composition distribution, LLDPE produces film that is not as clear as low density polyethylene made with free radical initiators.

- *Medium Density High Density Polyethylene:* MDPE (or MDHDPE) is produced by copolymerization of ethylene with α -olefins using Ziegler-Natta, supported chromium or single site catalysts. MDPE cannot be produced by free radical polymerization. MDPE has a linear structure similar to LLDPE, but comonomer content is lower. Density is typically 0.93–0.94 g/cm³. MDPE is used in geomembrane and pipe applications.
- *High Density Polyethylene:* HDPE is produced by polymerization of ethylene using Ziegler-Natta or supported chromium (“Phillips”) catalysts. HDPE cannot be produced by free radical polymerization. Density is typically 0.94–0.97 g/cm³. Small amounts (<1%) of α -olefin comonomers are used in many of the commodity grades to introduce low concentrations of short chain branching, primarily to enhance processability but also to improve toughness and environmental stress crack resistance. HDPE has high modulus, yield and tensile properties relative to LLDPE and MDPE. However, because it has higher crystallinity, HDPE cannot match the clarity of LDPE or LLDPE film. HDPE is

widely used in extruded pipe for potable water and gas distribution. Another important application is in blow molded packaging for household and industrial chemicals (HIC), such as bottles for bleach, shampoo, detergent, etc.

- *High Molecular Weight High Density Polyethylene:* HMW-HDPE (or HMWPE) is produced with Ziegler-Natta and supported chromium catalysts. HMW-HDPE cannot be produced by free radical polymerization. Molecular weight ranges from about 200,000 to 500,000 amu. Typically, density is in the range 0.94–0.96 g/cm³. HMW-HDPE grades are typically produced in a dual reactor configuration which results in bimodal molecular weight distribution with comonomer incorporated in the high molecular weight fractions. Key applications are pipe, grocery sacks and automotive fuel tanks.
- *Ultrahigh Molecular Weight Polyethylene:* UHMWPE is produced with Ziegler-Natta catalysts. Comonomers are not usually employed. Molecular weight ranges from about 3,000,000 to 7,000,000 amu. UHMWPE has a surprisingly low density (~0.94 g/cm³), most likely owing to crystalline defects and lamellar effects caused by the enormously long polymer chains. UHMWPE exhibits excellent impact strength and abrasion-resistance. Though difficult to process on standard equipment, UHMWPE may be compression-molded into prosthetic devices, such as artificial hips, or gel spun into very tough fibers used in bullet-proof vests worn by law enforcement personnel. UHMWPE is also used to make porous battery separator films.
- *Cyclic Olefin Copolymers:* COC are amorphous resins produced by copolymerization of ethylene with cyclic olefins, such as norbornene (8). COC are specialty resins with excellent optical properties and are produced with single site catalysts, but cannot be produced with conventional Ziegler-Natta catalysts. Relative to major types of polyethylene, COC are produced in very small quantities (<5 kT/y). On a molar basis, COC typically contain 40–70% ethylene. However, because of the relatively high molecular weight of comonomer, this amount corresponds to only 15–35% ethylene on a weight basis. For most commercial grades, density is 1.02–1.08 g/cm³. Key applications are in blister packaging for pharmaceuticals and anti-glare polarizing film (9).
- *Cross-linked Polyethylene:* XLPE (also PEX) is produced by cross linking polyethylene (mostly HDPE and MDPE) using free radicals generated by peroxides, ultraviolet or electron beam irradiation. A more intricate process involves grafting a vinylsilane compound, such as vinyltrimethoxysilane, onto polyethylene chains using free radicals. Subsequent moisture curing links adjacent chains through siloxide groupings. XLPE exhibits excellent environmental stress crack resistance (ESCR) and low creep. Used in piping for residential plumbing systems.

As previously noted, names given in the classifications above are those commonly used in the polyethylene industry, and these will be used throughout

this text. IUPAC nomenclature is usually more complex. For example, IUPAC naming of a copolymer depends upon whether it is statistical, random, alternating, block, etc. If unspecified or unknown, the copolymer is named with the infix "co" included in its name. In the case of LLDPE made with ethylene and 1-butene, the IUPAC name would be poly(ethylene-co-1-butene). See Table 1.1 for additional examples of IUPAC names for common ethylene-containing polymers.

Microstructures of polyethylene depend upon type of catalyst, polymerization conditions, comonomers used, etc. Polyethylene and copolymers produced by free radical polymerization (LDPE, EVA, EAA, etc.) contain both short chain and long chain branching and higher amorphous content relative to LLDPE and HDPE. LLDPE and VLDPE contain extensive short chain branching owing to incorporation of α -olefin comonomers. HDPE contains little short chain branching because comonomers are used in low quantities, if at all. HDPE produced with Ziegler-Natta catalysts contains essentially no long chain branching. However, HDPE from Phillips catalysts contains very small amounts of long chain branching (10). Schematic representations of microstructures of several types of polyethylene are given in Figures 1.3–1.7. Short chain and long chain branching may be determined analytically by several techniques, for example, infrared (IR)

Table 1.1 IUPAC names of selected polymers and copolymers of ethylene.

| Polymer Acronym | Comonomer | IUPAC Name |
|-----------------|--------------------|-------------------------------------|
| LDPE | none | polyethylene |
| VLDPE | butene-1 | poly(ethylene-co-butene-1) |
| LLDPE | butene-1 | poly(ethylene-co-butene-1) |
| LLDPE | hexene-1 | poly(ethylene-co-hexene-1) |
| LLDPE | octene-1 | poly(ethylene-co-octene-1) |
| LLDPE | 4-methyl-pentene-1 | poly(ethylene-co-4-methylpentene-1) |
| EVA | vinyl acetate | poly(ethylene-co-vinyl acetate) |
| EMA | methacrylic acid | poly(ethylene-co-methacrylic acid) |
| EVOH | vinyl alcohol* | poly(ethylene-co-vinyl alcohol) |
| HDPE | none** | polyethylene |
| COC | norbornene | poly(ethylene-co-norbornene) |

* Hypothetical comonomer (see section 1.3)

** Small amount of α -olefin incorporated to improve polymer properties

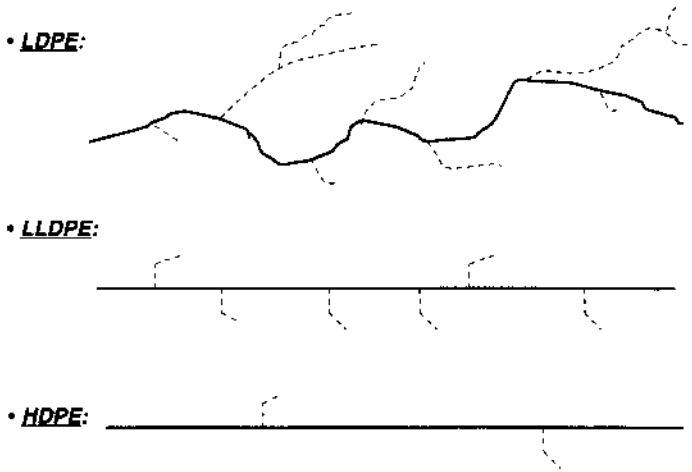


Figure 1.3 Schematic of microstructure of major types of polyethylene, where solid lines signify the “backbone” of the polymer and dashed lines represent SCB and LCB.

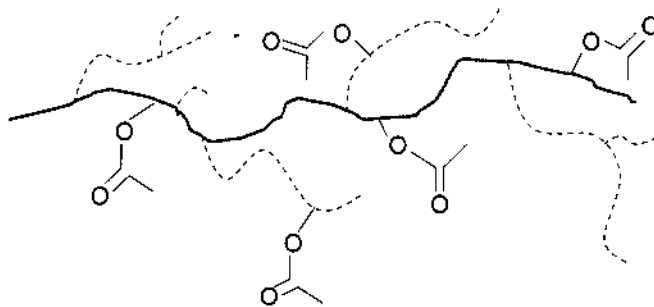


Figure 1.4 Schematic of microstructure of ethylene-vinyl acetate copolymer, where the solid line represents the “backbone” of the polymer and dashed lines signify SCB and LCB. Incorporation of VA results in pendant acetoxy groups.

and nuclear magnetic resonance (NMR, both proton and carbon-13) spectroscopy and temperature rising elution fractionation (TREF).

Table 1.2 provides a summary of commonly used classifications in the polyethylene industry. A brief note is warranted here to conclude the survey of polyethylene classifications and nomenclature. In the early 1990s, several types of polyethylene manufactured with metallocene catalysts (a type of single site catalyst, see Chapter 6) were introduced to the market. To differentiate polyethylene produced with metallocenes from polyethylene manufactured using older conventional catalysts, metallocene grades are sometimes abbreviated mVLDPE, mLLDPE, etc.

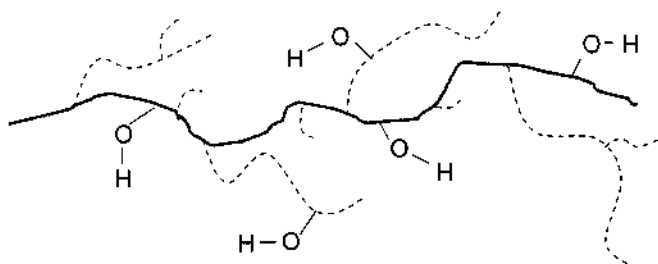


Figure 1.5 Schematic of microstructure of ethylene-“vinyl alcohol” copolymer, where the solid line signifies the “backbone” of the polymer and dashed lines represent SCB and LCB. Incorporation of VA results in pendant acetoxy groups which are subsequently hydrolyzed to $-OH$ groups.

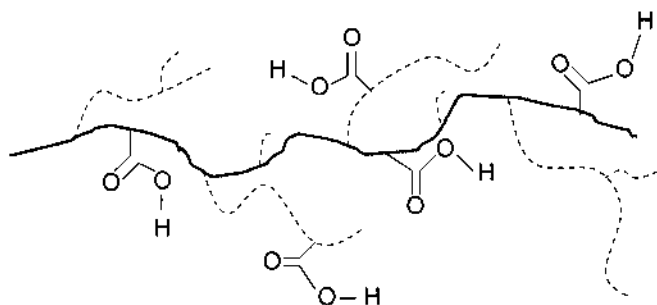


Figure 1.6 Schematic of microstructure of EAA, where the solid line represents the “backbone” of the polymer and dashed lines signify SCB and LCB. Incorporation of AA results in pendant carboxylic acid groups. EMA microstructure is similar, but includes a geminal methyl group.

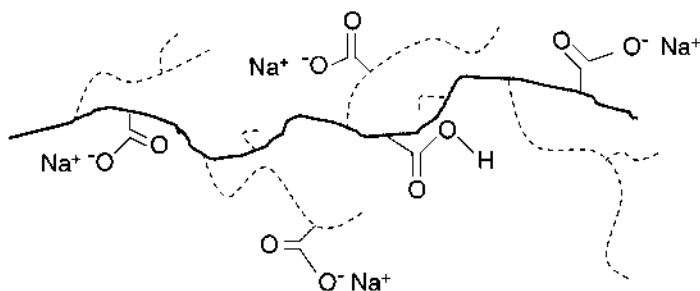


Figure 1.7 Schematic of microstructure of EAA ionomer, where the solid line signifies the “backbone” of the polymer and dashed lines represent SCB and LCB. Incorporation of AA results in pendant carboxylic acid groups which are $\sim 90\%$ converted to salts by reaction with a Bronsted base, such as $NaOH$. The microstructure of ionomer from EMA is similar, but includes a geminal methyl group.

Table 1.2 Classifications of selected polyethylenes.

| Polymer | Approximate Density Range (g/cm ³) | Typical Comonomer(s) | Catalysts (or Initiators) Used in Production |
|----------------------|--|--------------------------------|--|
| VLDPE ^a | 0.88–0.91 | α -olefins | ZN, SSC |
| LDPE | 0.91–0.93 | none | Organic Peroxides |
| EVA | 0.93–0.97 | vinyl acetate | Organic Peroxides |
| EAA/EMA ^b | 0.94–0.96 | AA, MA | Organic Peroxides |
| EVOH ^c | 0.96–1.20 | vinyl acetate | Organic Peroxides |
| LLDPE | 0.91–0.93 | α -olefins | ZN, supported Cr, SSC |
| MDPE | 0.93–0.95 | α -olefins | ZN, supported Cr |
| HDPE ^d | 0.95–0.97 | α -olefins ^e | ZN, supported Cr |
| UHMWPE | 0.93–0.95 | none | ZN |
| COC | 1.02–1.08 | norbornene | SSC |

^a Also known as ULDPE

^b Precursors for production of ionomers

^c Produced by saponification of EVA

^d Includes XLPE

^e Small amount of α -olefins often used to improve polymer properties

1.4 Molecular Weight of Polyethylenes

In addition to density, polyethylene manufacturers routinely supply data that correlate with molecular weight and molecular weight distribution. A measurement called the melt index (MI), also known as melt flow index (MFI), is determined by the weight of polyethylene extruded over 10 minutes at 190 °C through a standard die using a piston load of 2.16 kg. Reported in g/10min or dg/min, melt index is measured using an instrument called an extrusion plastometer according to ASTM D 1238-04c Condition 190/2.16, where the latter numbers refer to the temperature and the load in kg on the piston of the plastometer, respectively. Melt index is sometimes written “ I_2 ” and is inversely proportional to molecular weight, *i.e.*, MI increases as molecular weight decreases. With the possible exception of density, melt index is the most widely cited property of industrial polyethylene.



Melt index of polyethylene may be measured on an instrument called an extrusion plastometer. (Photo courtesy of Tinius Olsen.)

Another value is also measured on the plastometer at 190 °C, but under a load of 21.6 kg (ASTM D 1238-04c Condition 190/21.6). This is called the high load melt index (HLMI) and is also reported in g/10 min or dg/min. HLMI is often used for polyethylenes that have very high molecular weights. Because it may be difficult to measure the small amount of extrudate from the standard conditions for what are called “fractional” MI products (typically resins that have MIs <1), HLMI may be a more accurate measure of molten flow.

Dividing HLMI by MI affords the melt index ratio (MIR), a dimensionless number which gives an indication of breadth of molecular weight distribution. As MIR increases, MWD broadens.

$$\text{MIR} = \text{HLMI} \div \text{MI} \quad (1.2)$$

In ASTM D 1238-04c, a term called the flow rate ratio (FRR) for polyethylene is defined as flow rate at Condition 190/10 divided by flow rate at Condition 190/2.16, abbreviated “ I_{10}/I_2 ”. Like MIR, the flow rate ratio is dimensionless and conveys information on molecular weight distribution.

The term “melt flow rate” (MFR) is sometimes applied (erroneously) to polyethylene. ASTM suggests “melt flow rate” be applied to other thermoplastics and

"melt index" be reserved for polyethylene (see note 27 on p 10 of ASTM D 1238-04c). Melt flow rate is also determined under ASTM D 1238-04c, but different conditions are used in most instances. For example, MFR of polypropylene is determined at 230 °C and 2.16 kg.

MI and MIR measurements are inexpensive, relatively easy to conduct and are indicative of molecular weight and molecular weight distribution. Actual molecular weights may be determined using a variety of analytical methods, including gel permeation chromatography (GPC), viscometry, light scattering and colligative property measurements. (GPC is also called size exclusion chromatography or SEC.) However, these methods require more complex, sophisticated instruments, are more costly and difficult to perform and do not lend themselves to routine quality control procedures.

The number average molecular weight (\overline{M}_n) is calculated from the expression:

$$\overline{M}_n = \Sigma M_x N_x / \Sigma N_x \quad (1.3)$$

where M_x is the molecular weight of the x^{th} component and N_x is the number of moles of the x^{th} component. Weight average molecular weight (\overline{M}_w) is calculated using the second order equation:

$$\overline{M}_w = \Sigma M_x^2 N_x / \Sigma M_x N_x \quad (1.4)$$

The third order equation provides the "z-average molecular weight" and is calculated from the expression:

$$\overline{M}_z = \Sigma M_x^3 N_x / \Sigma M_x^2 N_x \quad (1.5)$$

Higher order molecular weight averages may also be calculated, but are less important than \overline{M}_w , \overline{M}_n , and \overline{M}_z . For polydisperse polymers, such as polyethylene, the following relationship holds:

$$\overline{M}_z > \overline{M}_w > \overline{M}_n \quad (1.6)$$

The ratio $\overline{M}_w/\overline{M}_n$ is called the polydispersity index (also known as heterogeneity index and dispersity index) and is an indication of the broadness of molecular weight distribution. As polydispersity index increases, MWD broadens. If the polymer were a single macromolecule, the polydispersity would be 1.0 and the polymer would be said to be monodisperse.

For polyethylene produced with transition metal catalysts, molecular weight distribution is dictated largely by the catalyst employed. Polydispersities typically range from 2-3 for polyethylene made with single site catalysts, 4-6 for polymer produced with Ziegler-Natta catalysts and 8-20 for polyethylene made with supported chromium catalysts. These differences are illustrated

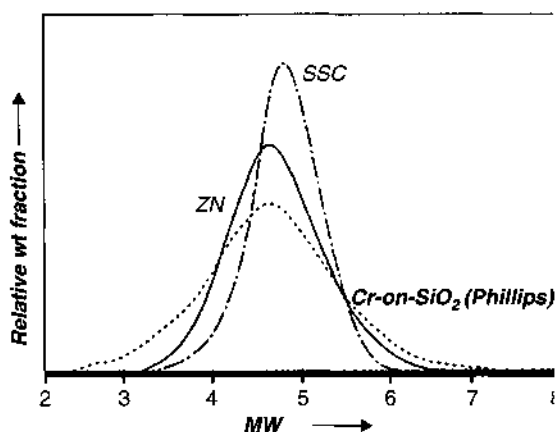


Figure 1.8 MWD of polyethylene from transition metal catalysts. (Reprinted with permission of John Wiley & Sons, Inc., *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., 6th edition, 2006).

schematically in Figure 1.8. Polyethylene with molecular weight distributions illustrated in Figure 1.8 are said to be unimodal.

In certain applications, such as blow molding, polyethylene with broad molecular weight distribution provides a better balance of properties. Higher molecular weight fractions impart mechanical strength while lower molecular weight fractions improve flow properties and make the polymer easier to process. The combination of good mechanicals and easier processing may also be realized if a resin with a bimodal molecular weight distribution can be produced.

Bimodal molecular weight distribution may be achieved by several techniques. The simplest method is post-reactor blending of polyethylene with different melt indices. Two other methods involve in-reactor production of polyethylene. One approach involves use of mixed catalyst systems that polymerize ethylene in different ways to produce polyethylene with different molecular weights. The latter requires that the catalysts are compatible. Another technique employs use of reactors in series operated under different conditions (see section 7.6 in Chapter 7). Figure 1.9 illustrates polyethylene with a bimodal molecular weight distribution produced with a single site catalyst system in a Unipol[®] gas-phase process.

Direct comparisons between melt index and molecular weight of polyethylene should be made with caution. Such comparisons are only appropriate when the polymers have similar histories (made using the same catalyst, by the same process, at near identical densities, etc.). An example of the relationship between melt index and molecular weight for a series of LLDPEs with similar histories is

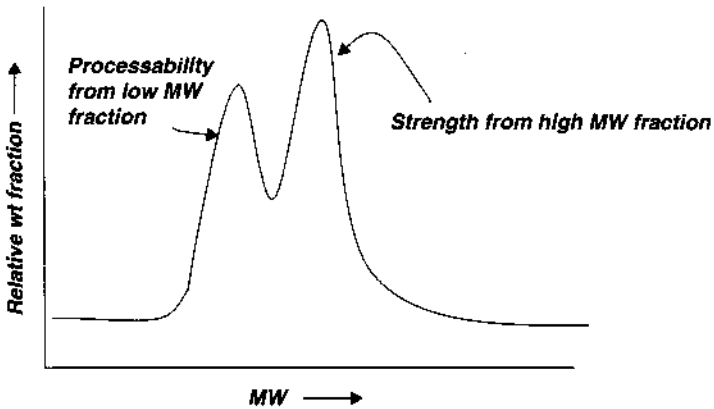


Figure 1.9 Bimodal MWD polyethylene produced with SSC in Unipol® gas phase process; P. J. Ferenz, 2nd Asian Petrochemicals Technology Conference, May 7–8, 2002, Seoul, Korea.

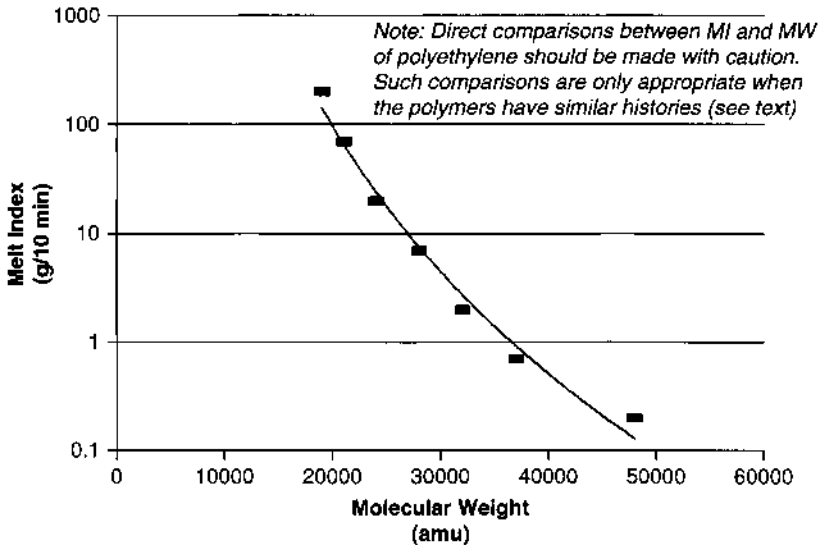


Figure 1.10 Molecular weight and melt index of LLDPE ($d = 0.920$ g/cc; data from H. Boenig, *Polyolefins: Structure and Properties*, Elsevier, p 80, 1966).

shown in Figure 1.10. While a valuable measurement, melt index provides little information regarding the shear sensitivity of the molten resin. Deformation under stress (“rheology,” see section 8.3) of the resin is important to the performance of the polymer in its applications and requires additional testing.

1.5 Transition Metal Catalysts for Ethylene Polymerization

As previously mentioned, in addition to free radical initiation, ethylene may be polymerized by use of transition metal catalysts. To place the importance of these catalysts in proper perspective, one must recognize that transition metal catalysts were used to produce about 73% of the global industrial output of polyethylenes in 2008 or about 56 million tons (124 billion pounds).

In this section, we will introduce key characteristics of transition metal catalysts. Conditions used for polymerization with transition metal catalysts are much less severe than those needed for free radical processes. Transition metal catalysts used in production of polyethylene include Ziegler-Natta, supported chromium and single site catalysts, all to be discussed in more detail in subsequent chapters. The vast majority of these catalysts are produced using compounds of transition metals from Groups 4–6 of the Periodic Table. Ziegler-Natta catalysts (Chapter 3) are typically derived from inorganic titanium compounds. The most well-known and widely used supported chromium catalysts are the so-called “Phillips catalysts” (Chapter 5) but there are other industrially important chromium catalysts. Chromium catalysts must be supported on refractory oxides, most often silica, to be effective. Most commercial single-site catalysts (Chapter 6) involve Zr, Hf or Ti, but single site catalysts based on late transition metals, especially Pd, Fe and Ni, began to emerge in the mid-1990s.

All transition metal catalysts must fulfill several key criteria:

- Activity must be high enough to insure economic viability and that catalyst residues are sufficiently low in the final polymer to obviate post-reactor treatment. As a rule of thumb, this requires that catalyst activity exceed 150,000 lb of polyethylene per lb of transition metal.
- The catalyst must be capable of providing a range of polymer molecular weights:
 - For Ziegler-Natta and single-site catalysts, molecular weight is controlled primarily by use of hydrogen as chain transfer agent. Catalyst reactivity with hydrogen to control polymer molecular weight is called its “hydrogen response.”
 - In general, the capability of supported chromium catalysts to produce polyethylene of high melt index (low molecular weight) is limited. The hydrogen response of most chromium catalysts is low. Polymer molecular weight may be controlled by chemical modification of the basic chromium catalyst and judicious choice of polymerization temperature and ethylene concentration.
- Control of polydispersity. Though each type of catalyst provides polyethylene with a characteristic range of molecular weight distributions, measures

can be taken to expand the range of achievable polydispersities. In general, polyethylene with broad molecular weight distribution provides a good balance of ease of processing while retaining desirable mechanical properties (modulus, toughness, etc.).

- If a copolymer such as VLDPE or LLDPE is the target resin, satisfactory comonomer incorporation must be achieved. This is manifested by the amount of comonomer incorporated (evidenced by density) and the distribution of comonomer in the polymer (evidenced by composition distribution). In general, supported chromium oxide catalysts incorporate comonomer more easily than Ziegler-Natta catalysts.
- Must have proper rate of polymerization, *i.e.*, its "kinetic profile" must fit the process selected. Representative types of kinetic profiles are shown in Figure 1.11.

Additional details will be provided in subsequent chapters on the composition and functioning of transition metal catalysts.

Transition metal catalysts are crucial to the production of polyethylene. Indeed, it would not be practical to produce linear versions of polyethylene without these catalysts. It is difficult to imagine a world without products made from these versatile polymers in our homes, vehicles and workplaces. Ziegler-Natta and supported chromium catalysts will continue to be the dominant catalysts for LLDPE and HDPE for the foreseeable future. However, as single-site catalyst

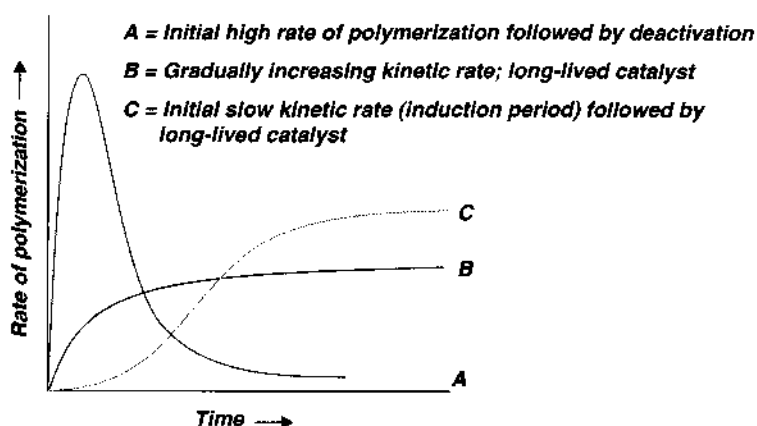


Figure 1.11 Rates of polymerization with transition metal catalysts may be quite different because of accessibility of active centers, presence of poisons, mechanism of activation, etc. Kinetic profile must be accommodated by process conditions (see Chapter 7).

Table 1.3 Principal characteristics of transition metal-containing catalysts for polyethylene production.

| | Ziegler-Natta | Metal Oxide Supported | Single-site |
|---------------------------------------|--------------------------------------|--|-----------------------|
| Commonly used transition metals: | Mostly Ti; small amount of V | Mostly Cr; small amount of Mo | Primarily Zr and Ti |
| Catalyst supports: | MgCl ₂ , SiO ₂ | SiO ₂ , SiO ₂ -Al ₂ O ₃ , Al ₂ O ₃ , AlPO ₄ | usually not supported |
| Typical cocatalyst(s): | TEAL | None for 1 st generation Phillips | MAO, MMAO and boranes |
| Primary commercial polymers produced: | LLDPE, VLDPE, HDPE | HDPE, LLDPE | LLDPE, VLDPE |
| Typical polydispersity range: | 4–6 | 8–20 | 2–3 |

technologies mature, they will increase in importance and complement Ziegler-Natta and chromium catalysts in manufacture of polyethylene. A summary of characteristics of the various transition metal catalysts is provided in Table 1.3.

References

1. FM McMillan, *The Chain Straighteners*, MacMillan Publishing Company, London (1979).
2. DM Kiefer, *Today's Chemist at Work*, June 1997, p 51.
3. RB Seymour and T Cheng, *History of Polyolefins*, D. Reidel Publishing Co., Dordrecht, Holland, 1985.
4. RB Seymour, *Advances in Polyolefins*, Plenum Press, New York, 3 (1985).
5. C. Lee and B. Singh, Chemical Marketing Resources, Webster, TX, personal communication, June, 2009.
6. MB Smith and J March, *March's Advanced Organic Chemistry*, John Wiley & Sons, New York, 5th ed., p 74 (2001).
7. B Morris, *International Conference on Polyolefins*, Society of Plastics Engineers, Houston, TX, February 25–28, 2007.
8. RD Jester, *International Conference on Polyolefins*, Society of Plastics Engineers, Houston, TX, February 25–28, 2007.
9. Anon., APEL® *Cyclo Olefin Copolymer* Product Sheet, Mitsui Chemicals Americas, Inc., 2007.
10. MP McDaniel, *Handbook of Heterogeneous Catalysis*, 1st ed, 1997, G Ertl, H. Knozinger and J. Weitkamp, (editors), VCH Verlagsgesellschaft, Weinheim, Vol 5, 2400.