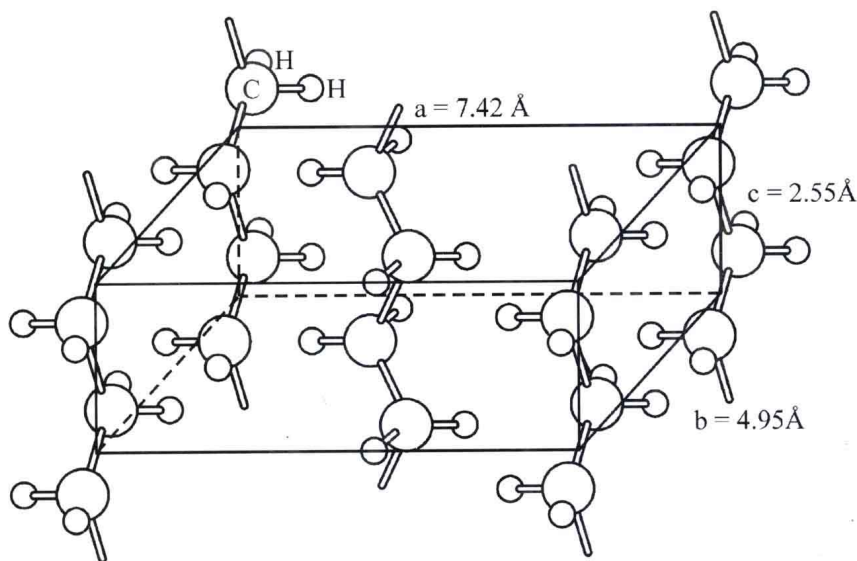


# HANDBOOK OF POLYETHYLENE

**Structures, Properties,  
and Applications**



**Andrew J. Peacock**

# **HANDBOOK OF POLYETHYLENE**

**Structures, Properties, and Applications**

**ANDREW J. PEACOCK**

*Exxon Chemical Company  
Baytown, Texas*



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# Preface

The aim of this book is to provide a comprehensive introduction to the field of polyethylene in all its aspects as it applies to production, properties, and applications. Specifically, it correlates molecular structure with morphological features and thus with properties and end-use applications. Starting from a molecular description of the principal variants of polyethylene, it constructs a unified picture of polyethylene's melt structure and solid-state morphology and explains how this relates to processing variables and end-use applications.

An introductory chapter acquaints the reader with the field of polyethylene and provides an outline of polyethylene's molecular structure, morphology, properties, markets, and uses. Subsequently, the body of the book enlarges upon these themes. A chapter devoted to the history of polyethylene describes the development of the field from 1933 to the present day. Market development is explained in terms of the innovations that permitted molecular tailoring and expansion into new applications. Current catalysis and production processes are surveyed to explain the formation of the molecular features that distinguish the different types of polyethylene. The relationship between molecular structure and end-use properties begins with an examination of polyethylene's semicrystalline morphology and how this is formed from the molten state during crystallization. A complete range of physical attributes is discussed, encompassing solid-state mechanical, chemical, thermal, optical, and electrical characteristics and melt rheological properties. Methods of characterizing molecular characteristics and physical properties are described in the context of end-use applications. Chemical degradation, oxidation, and stabilization are described, as well as the deliberate chemical modification of surfaces. The molecular processes active during deformation are described in order to explain the properties of oriented structures, including high-modulus fibers and billets. The commercial processing techniques used to convert raw polyethylene to products are discussed, with emphasis on properties and end-use applications. The markets of polyethylene are broken down by use and molecular type. Finally, emerging trends in polyethylene production and usage are described to indicate the future trends of the industry.

The intended audience of this book includes chemists, engineers, physicists, and supervisory personnel who wish to expand their knowledge of the field of polyethylene. It would also serve as an introduction for graduate students or others considering a career in polymers. In order to reach as wide an audience as possible, no prior knowledge of the field of polymers is assumed. All relevant terms and background are explained prior to detailed discussion.

This book could not have been written without the help, cooperation, and encouragement of many people. I am indebted to various colleagues who read parts or all of the manuscript during its preparation, and who offered many critical and useful observations. Professor Leo Mandelkern was most helpful with the chapters dealing with morphology, crystallization, and properties. Gary Brown reviewed several chapters and offered suggestions, especially with regard to microscopic analysis. In particular I must express my utmost gratitude to Dr. Ferdinand Stehling, a retired colleague, who spent much time and energy reviewing the entire work during its preparation. Ferd's insight and encouragement were invaluable and added immeasurably to the quality of the book as a whole. Last, but not least, I must thank my wife, Shavon, who for more than half of our married life has had to tolerate my spending evenings and weekends closeted with books, papers, and a computer.

*Andrew J. Peacock*



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# 1

## Introduction

### I. THE ESSENCE OF POLYETHYLENE

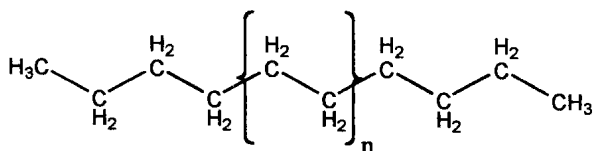
#### A. Molecular Structure

In its simplest form a polyethylene molecule consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon; chain ends are terminated by methyl groups. This structure is shown schematically in Figure 1.

Chemically pure polyethylene resins consist of alkanes with the formula  $C_{2n}H_{4n+2}$ , where  $n$  is the degree of polymerization, i.e., the number of ethylene monomers polymerized to form the chain. Unlike conventional organic materials, polyethylene does not consist of identical molecules. Polyethylene resins comprise chains with a range of backbone lengths. Typically the degree of polymerization is well in excess of 100 and can be as high as 250,000 or more, equating to molecular weights varying from 1400 to more than 3,500,000. Low molecular weight polyethylenes (oligomers) with a degree of polymerization between 8 and 100 are waxy solids that do not possess the properties generally associated with a plastic. When the degree of polymerization is less than 8, alkanes are gases or liquids at ordinary temperatures and pressures. Polyethylene molecules can be branched to various degrees and contain small amounts of unsaturation.

#### 1. Variations on a Theme

Many types of polyethylene exist, all having essentially the same backbone of covalently linked carbon atoms with pendant hydrogens; variations arise chiefly from branches that modify the nature of the material. There are many types of branches, ranging from simple alkyl groups to acid and ester functionalities. To a lesser extent, variations arise from defects in the polymer backbone; these consist principally of vinyl groups, which are often associated with chain ends. In the solid state, branches and other defects in the regular chain structure limit a sample's crystallinity level. Chains that have few defects have a higher degree of



**Figure 1** Chemical structure of pure polyethylene.

crystallinity than those that have many. As the packing of crystalline regions is better than that of noncrystalline regions, the overall density of a polyethylene resin will increase as the degree of crystallinity rises. Generally, the higher the concentration of branches, the lower the density of the solid. The principal classes of polyethylene are illustrated schematically in Figure 2.

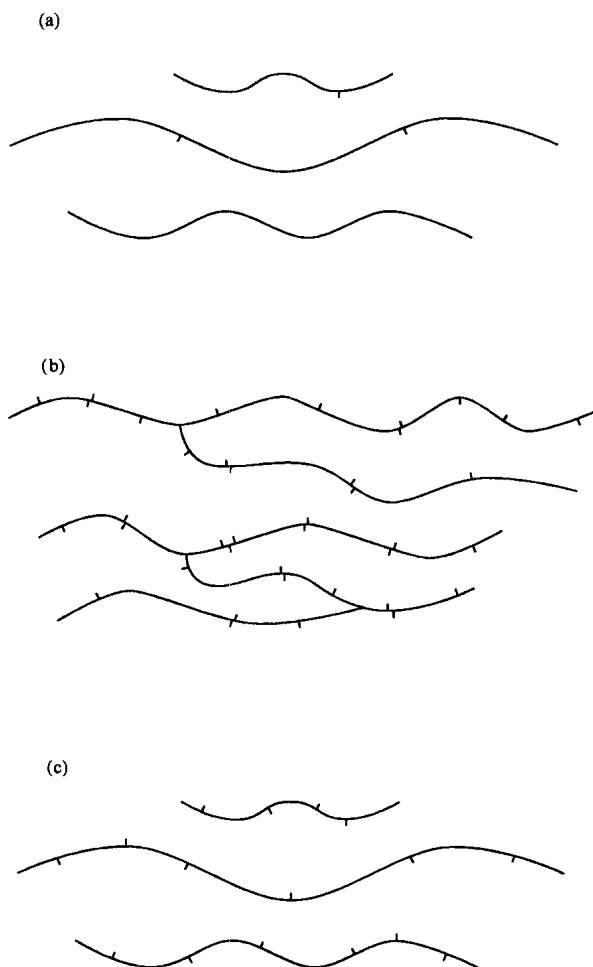
*a. High Density Polyethylene.* High density polyethylene (HDPE) is chemically the closest in structure to pure polyethylene. It consists primarily of unbranched molecules with very few flaws to mar its linearity. The general form of high density polyethylene is shown in Figure 2a. With an extremely low level of defects to hinder organization, a high degree of crystallinity can be achieved, resulting in resins that have a high density (relative to other types of polyethylene). Some resins of this type are copolymerized with a very small concentration of 1-alkenes in order to reduce the crystallinity level slightly. High density polyethylene resins typically have densities falling in the range of approximately 0.94–0.97 g/cm<sup>3</sup>. Due to its very low level of branching, high density polyethylene is sometimes referred to as linear polyethylene (LPE).

*b. Low Density Polyethylene.* Low density polyethylene (LDPE) is so named because such polymers contain substantial concentrations of branches that hinder the crystallization process, resulting in relatively low densities. The branches primarily consist of ethyl and butyl groups together with some long-chain branches. A simplified representation of the structure of low density polyethylene is shown in Figure 2b. Due to the nature of the high pressure polymerization process by which low density polyethylene is produced, the ethyl and butyl branches are frequently clustered together, separated by lengthy runs of unbranched backbone. Long-chain branches occur at random intervals along the length of the main chain. The long-chain branches can themselves in turn be branched. The mechanisms involved in the production of branches are discussed in Chapter 3. The numerous branches characteristic of low density polyethylene molecules inhibit their ability to crystallize, reducing resin density relative to high density polyethylene. Low density polyethylene resins typically have densities falling in the range of approximately 0.90–0.94 g/cm<sup>3</sup>.

*c. Linear Low Density Polyethylene.* Linear low density polyethylene (LLDPE) resins consist of molecules with linear polyethylene backbones to which are attached short alkyl groups at random intervals. These materials are produced by the copolymerization of ethylene with 1-alkenes. The general structure of linear low density polyethylene resins is shown schematically in Figure 2c. The branches most commonly encountered are ethyl, butyl, or hexyl groups but can be a variety of other alkyl groups, both linear and branched. A typical average separation of branches along the main chain is 25–100 carbon atoms. Linear low density polyethylene resins may also contain small levels of long-chain branching, but there is not the same degree of branching complexity as is found in low density polyethylene. Chemically these resins can be thought of as a compromise between linear polyethylene and low density polyethylene, hence the name. The branches hinder crystallization to some extent, reducing density relative to high density polyethylene. The result is a density range of approximately 0.90–0.94 g/cm<sup>3</sup>.

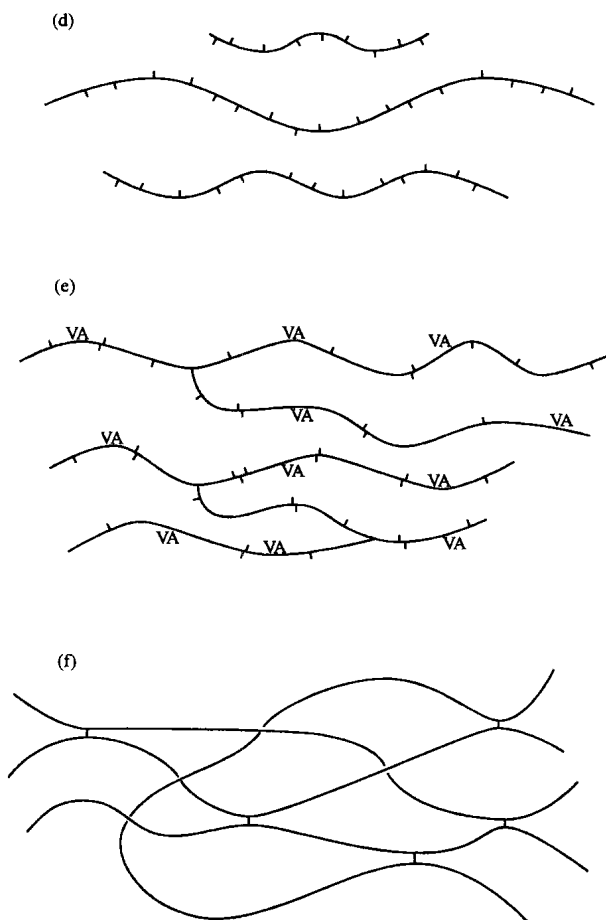
*d. Very Low Density Polyethylene.* Very low density polyethylene (VLDPE)—also known as ultralow density polyethylene (ULDPE)—is a specialized form of linear low density polyethylene that has a much higher concentration of short-chain branches. The general structure of very low density polyethylene is shown in Figure 2d. A typical separation of branches would fall in the range of 7–25 backbone carbon atoms. The high level of branching inhibits crystallization very effectively, resulting in a material that is predominantly noncrystalline. The high levels of disorder are reflected in the very low densities, which fall in the range of 0.86–0.90 g/cm<sup>3</sup>.

*e. Ethylene-Vinyl Ester Copolymers.* By far the most commonly encountered ethylene-vinyl ester copolymer is ethylene-vinyl acetate (EVA). These copolymers are made by the same high pressure process as low density polyethylene and therefore contain both short- and long-chain branches in addition to acetate groups. The general structure of ethylene-vinyl acetate resins is shown schematically in Figure 2e (in which “VA” indicates an acetate group). The acetate groups interact with one another via dispersive forces, tending to cluster. The inclusion of polar groups endows such copolymers with greater chemical reactivity than high density, low density, or linear low density polyethylene. The acetate branches hinder crystallization in proportion to their incorporation level; at low levels these copolymers have physical properties similar to those of low density polyethylene, but at high levels of incorporation they are elastomeric. Due to the incorporation of oxygen, ethylene-vinyl acetate copolymers exhibit higher densities at a given crystallinity level than polyethylene resins comprising only carbon and hydrogen.



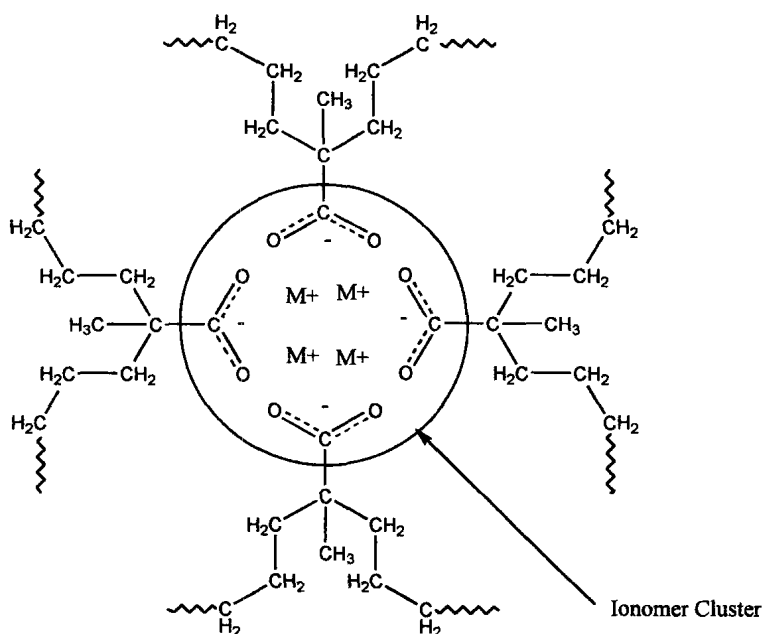
**Figure 2** Schematic representations of the different classes of polyethylene. (a) High density polyethylene; (b) low density polyethylene; (c) linear low density polyethylene; (d) very low density polyethylene; (e) ethylene-vinyl acetate copolymer; (f) cross-linked polyethylene.

*f. Ionomers.* Ionomers are copolymers of ethylene and acrylic acids that have been neutralized (wholly or partially) to form metal salts. The copolymerization of these molecules takes place under conditions similar to those under which low density polyethylene is made; thus, in addition to polar groups, ionomers contain all the branches normally associated with low density polyethylene. The



neutralized acid functionalities from adjacent chains interact with the associated metal cations to form clusters that bind neighboring chains together. A two-dimensional representation of an ionomer cluster is shown in Figure 3. The complex branching structure of ionomers and the existence of polar clusters drastically reduce their ability to crystallize. Despite their low levels of crystallinity, the density of ionomers is normally the highest of all polyethylenes due to the relatively high atomic weight of the oxygen and metal atoms in the ionic clusters.

*g. Cross-Linked Polyethylene.* Cross-linked polyethylene (XLPE) consists of polyethylene that has been chemically modified to covalently link adjacent chains. A schematic representation of cross-linked polyethylene is shown



**Figure 3** Schematic representation of an ionomer cluster.

in Figure 2f. Cross-links may comprise either direct carbon–carbon bonds or bridging species such as siloxanes. Cross-links occur at random intervals along chains; the concentration can vary widely, from an average of only one per several thousand carbon atoms to one per few dozen carbon atoms. The effect of cross-linking is to create a gel-like network of interconnected chains. The network is essentially insoluble, although it can be swollen by various organic solvents. This is in direct contrast to the non-cross-linked varieties of polyethylene that are soluble in appropriate solvents at high temperature. Cross-links greatly hinder crystallization, limiting the free movement of chains required to organize into crystallites. Thus the density of a cross-linked polyethylene is lower than that of the polyethylene resin on which it is based.

## B. Molecular Composition

Polyethylene resins consist of molecules that exhibit a distribution of molecular lengths and branching characteristics. The characteristics of a polyethylene resin could be uniquely described if each of its component molecules were defined

in terms of its exact backbone length and the type and placement of each branch. This cannot be achieved, because separative techniques are not adequate to divide any resin into its myriad constituent molecules, nor could the molecules be characterized with sufficient precision even if homogeneous fractions could be obtained. In practice one must settle for determining various average characteristics that are representative of the molecular weight and branching distribution.

The size of a polyethylene molecule is normally described in terms of its molecular weight. All polyethylene resins consist of a mixture of molecules with a range of molecular weights. The average molecular weight and the distribution of chain lengths comprising a polyethylene resin profoundly affect its properties. The molecular weights of molecules found in commercial resins may range from a few hundred up to 10 million.

## 1. Molecular Weight Distribution

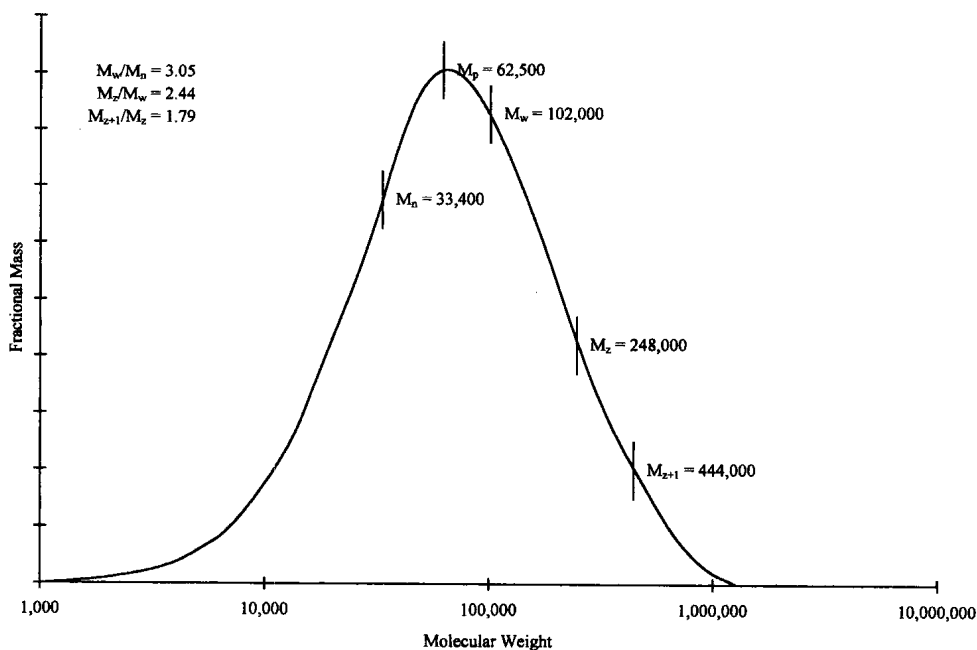
The distribution of molecular sizes within a polyethylene resin can be described in terms of various molecular weight averages. The molecular weight averages are calculated as the moments of the distribution of molecular masses. The molecular weight distribution (MWD) of a polyethylene resin is normally plotted on a semilogarithmic scale, with the molecular weight on the abscissa and the fractional mass on the ordinate. Such a plot (derived from size elution chromatography) is shown in Figure 4, indicating various molecular weight averages. The molecular weight distribution may be (and often is) simplistically defined in terms of the ratio of two of the molecular weight averages. The breadth and shape of the molecular weight distribution curve can vary greatly; distribution plots can exhibit multiple peaks, shoulders, and tails. Molecular weight characteristics have a profound effect on the physical properties of polyethylene resins, affecting such properties as viscosity, environmental stress cracking, and impact strength. The relationship between properties and molecular weight distribution is discussed in Chapter 5.

*a. Number-Average Molecular Weight.* The number-average molecular weight ( $\bar{M}_n$ ) of a polyethylene resin is defined in terms of the number of molecules and molecular weight of the chains making up a series of fractions that account for the molecular weight distribution. Thus, a molecular weight distribution plot is divided into 50 or more fractions, the characteristics of which are used to calculate the number-average molecular weight.

The number-average molecular weight is calculated according to

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{\sum W_i}{\sum N_i}$$





**Figure 4** Typical molecular weight distribution plot of polyethylene.

where:

$M_i$  = molecular weight of chains in fraction  $i$

$N_i$  = number of chains in fraction  $i$

$W_i$  = weight of chains in fraction  $i$

The number-average molecular weight is a function of all the molecular weight species present, but it is most sensitive to the lower molecular weight fractions, which generally contain the largest numbers of molecules. Thus a low molecular weight tail will reduce the number-average molecular weight to a much greater extent than a high molecular weight tail will increase it.

*b. Weight-Average Molecular Weight.* The weight-average molecular weight ( $\bar{M}_w$ ) is calculated from the same parameters used to calculate the number-average molecular weight, but a greater emphasis is placed on the higher molecular weight species.

The weight average molecular weight is calculated according to

$$\bar{M}_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{\sum M_i W_i}{\sum W_i}$$