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# Polymer Chemistry

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# 5 Molecular Characterization of Polymers

## 5.1 Introduction

Polymers differ from most chemicals in that they do not consist of identical molecules. All polymers comprise a distribution of molecules that share certain chemical characteristics, but may vary widely in terms of their lengths and precise compositions. Polymer scientists typically describe polymers in terms of their average molecular characteristics or some readily measurable value that represents the average composition of the ensemble of molecules. Thus, we commonly describe the lengths of polymers in terms of one or more averages that reflect moments of their overall molecular weight distribution. Similarly, we describe chemical composition in terms of the average comonomer content, which does not completely describe the distribution of comonomers within a given chain. Other commonly measured values that are related to polymer composition include melt flow rate, density, and melting temperature.

In order to take advantage of a polymer's properties we do not need to know its precise chemical composition, i.e., the exact chain length, number, and location of branches and comonomers, etc. in every molecule. Under most circumstances it is sufficient for a polymer engineer to know and understand the significance of a relatively small number of key characteristics, such as average molecular weight, molecular weight distribution, average chemical composition, branching type and concentration, crosslinking density, and average tacticity. Not all of these characteristics are applicable to all polymers, so an engineer may need to compare only three or four key variables in order to select an appropriate polymer grade for a given application. Often it is not necessary to know the absolute value of a given molecular characteristic, providing that there is some readily measurable physical property that can be directly correlated to the characteristic in question. For instance, the stiffness of an injected molded polyethylene item is directly related to its density, which can be accurately and quickly measured.

Polymers exhibit various degrees of complexity. At the simplest level are linear homopolymers, which are made from a single type of monomer that is polymerized to form unbranched chains with a statistical distribution of chain lengths. Complexity increases as comonomers are introduced, either at random intervals along the chain, or as blocks of various lengths. Chain branching adds another level of complexity, as does crosslinking. Even linear homopolymers can be made more complex if steric centers are present, which can lead to different types and degrees of tacticity.

## 5.2 Molecular Weight

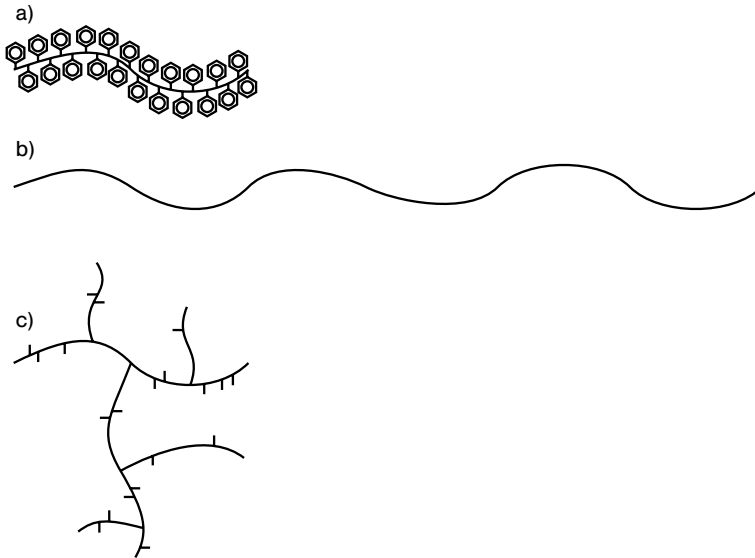
The average molecular weight and molecular weight distribution of a polymer are extremely important because these characteristics, in combination with chemical composition, largely control a polymer's melt flow characteristics. Other intrinsic properties that are directly influenced by molecular weight include tensile strength, extensibility, and toughness. Molecular weight distribution also strongly influences molecular orientation, which in turn affects many other physical properties, including elastic modulus, tensile strength, tear strength, coefficient of friction, extensibility, refractive index, melting temperature, and solvent resistance. Oriented polymers exhibit anisotropy; that is, their measured properties depend on the direction of testing. We commonly see this in packaging films. As everyone has doubtless experienced, it is easier to tear open a snack package in one direction than another. In this case, the tear propagates much more readily in a direction parallel to the chain orientation than in does in the perpendicular direction.

### 5.2.1 Molecular Weight versus Molecular Length and Molecular Volume

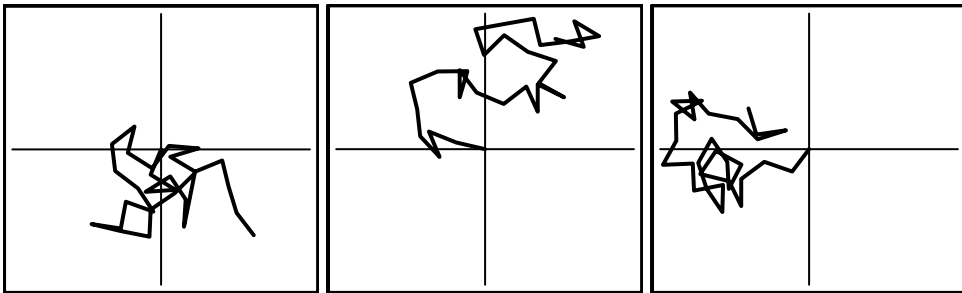
Many polymer properties are related to the size of the constituent molecules. In order to understand these properties it is important that we make clear the relationship between molecular weight, molecular length, and molecular volume. Molecular weight is not a unique descriptor of a polymer molecule. For instance, molecules of polystyrene and high density polyethylene may share the same molecular weight, but polyethylene will have a much longer chain, as illustrated schematically in Fig. 5.1 a) and b). In the absence of long chain branching, the high density polyethylene molecule contains approximately 3.7 times as many backbone carbon atoms as the polystyrene. The difference reflects the ratio between the molecular weights of the styrene and ethylene monomers, of 104 and 28 g/mole respectively.

Chain branching also plays a significant role in producing a more compact molecule as illustrated schematically in Fig. 5.1 b) and c), in which high density and low density polyethylene are compared. Both the molecules contain the same number of carbon and hydrogen atoms, but the low density polyethylene incorporates significant numbers of short and long chain branches. The presence of branches (particularly long chain branches) results in a much more compact molecule than that of a linear molecule of similar molecular weight.

When polymer chains are allowed to reach a fully relaxed state, they adopt a configuration known as a "three-dimensional random walk". This concept was introduced in Chapter 1 to help us visualize a polymer's configuration (see Fig. 1.15). The random angular configurations adopted by the bonds in the backbone of the molecule define the random walk. The volume encompassed by a molecule's random walk depends on its molecular weight, monomer type(s), short and long chain branching, chain flexibility, temperature, and the solvating power of the surrounding medium. Other factors remaining constant, the volume encompassed by a polymer molecule in a random walk configuration increases as molecular weight increases, chain flexibility decreases, branching decreases, and temperature decreases. (The inverse



**Figure 5.1** Schematic representation of relative chain lengths of molecules of:  
a) polystyrene,  
b) high density polyethylene, and  
c) low density polyethylene, sharing the same molecular weight  
(for simplicity, the carbon and hydrogen atoms are not shown)



**Figure 5.2** Planar random walks for chains comprising 30 freely jointed segments

relationship between temperature and volume may seem to be counterintuitive, but is readily explained in terms of chain flexibility. Higher temperatures enhance molecular motion, which increases chain flexibility and thus reduces the molecular volume.) Random walk configurations vary widely from molecule to molecule; in fact, no two are alike. Figure 5.2 illustrates this point for random walks comprising 30 freely jointed segments. Each of the three configurations shown is distinctly different from the other two.

The three-dimensional random walk of an isolated polymer molecule encompasses a very large fraction of volume that is not occupied by the polymer. In practice, polymer molecules are not found in isolation and the random walks of numerous chains overlap each other. Overlap between polymer molecules results in entanglements between neighboring chains. The degree of entanglement becomes more complex as molecular weight increases. Entanglements between molecules play an important role in determining polymer properties in both the molten and solid states.

### 5.2.2 Molecular Weight Distribution

Polymer scientists normally represent molecular weight distribution as a plot of fractional mass versus the logarithm of molecular weight. Figure 1.14 shows a generalized example of such a plot. These plots, while being accurate representations of a polymer's molecular weight distribution, do not provide a ready means for comparing the molecular weight of polymers. As a more practical method, we commonly resort to the use of a few key numerical values that reflect one or more moments of the molecular weight distribution. These average values are increasingly weighted to the longer chains of the distribution.

We calculate the number average molecular weight ( $M_n$ ) from Eq. 5.1.

$$M_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{\sum W_i}{\sum N_i} \quad (5.1)$$

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  $i$

Similarly, we calculate the weight average molecular weight ( $M_w$ ),  $z$  average molecular weight ( $M_z$ ), and  $z + 1$  average molecular weight ( $M_{z+1}$ ) from Eqs. 5.2, 5.3, and 5.4, respectively.

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{\sum M_i W_i}{\sum W_i} \quad (5.2)$$

$$M_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i} = \frac{\sum M_i^2 W_i}{\sum M_i W_i} \quad (5.3)$$

$$M_{z+1} = \frac{\sum M_i^4 N_i}{\sum M_i^3 N_i} = \frac{\sum M_i^3 W_i}{\sum M_i^2 W_i} \quad (5.4)$$

Each of the molecular weight averages is sensitive to a different portion of the overall molecular weight distribution. The shorter chains in a distribution have the greatest effect on the number

average molecular weight. The central portion of the distribution has the largest effect on the weight average molecular weight. The  $z$  and  $z + 1$  averages are increasingly sensitive to the higher molecular chains, particularly any high molecular weight tails that may be present in the distribution.

It may seem redundant to employ several different molecular weight averages, but each one has its use, reflecting different aspects of a polymer's molecular structure. Thus, the viscosity of a molten polymer at low shear rates is directly related to the weight average molecular weight, whereas the flow rate at higher shear rates is more sensitive to the  $z$  average molecular weight.

In order to summarize the breadth of a molecular weight distribution we commonly refer to the ratio of two of the molecular weight averages, such as  $M_w/M_n$ ,  $M_z/M_w$ , or  $M_z/M_n$ . Generally, the larger the ratio, the broader the molecular weight distribution. For example, we frequently refer to molecular weight ratios when comparing the flow properties of different polymers. Thus, a polymer with a larger  $M_z/M_n$  ratio would be expected to have a lower viscosity at high shear rates than a polymer with a similar weight average molecular weight but a smaller  $M_z/M_n$  ratio.

We need to be careful when referring to a polymer by a single molecular weight average without reference to its actual molecular weight distribution. Figure 5.3 illustrates this point, showing four very different molecular weight distributions. Each of these polymers shares a common weight average molecular weight, but their other averages vary widely.

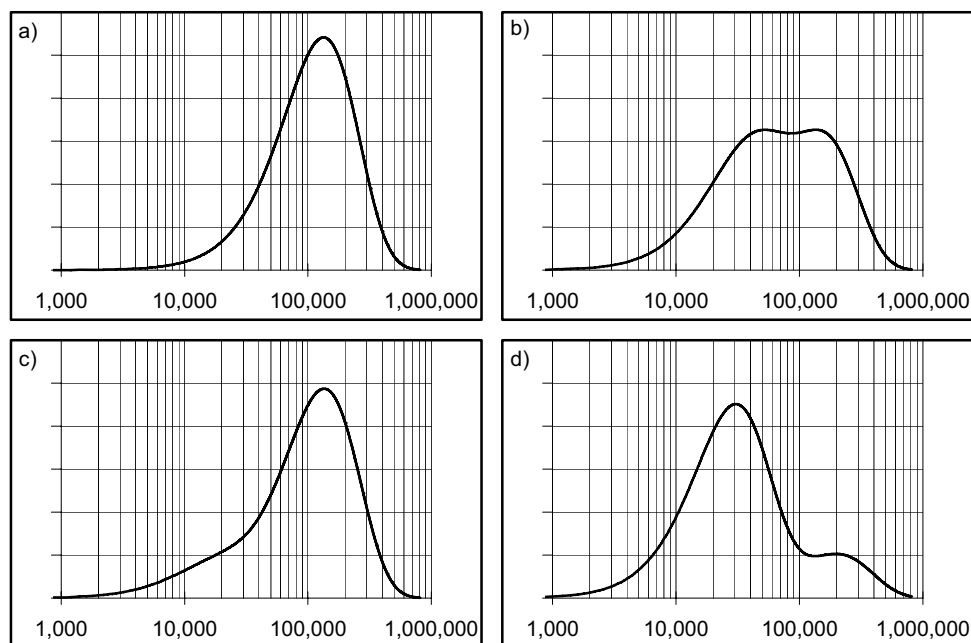
The molecular weight distribution in Fig. 5.3 a) exhibits a “most probable molecular weight distribution”, which is characteristic of polymers produced by metallocene catalysts. This distribution contains relatively few molecules with either extremely high or low molecular weights. Products made with this type of distribution are relatively difficult to process in the molten state, exhibit modest orientation, and have good impact resistance.

Resins with a bimodal molecular weight distribution, as illustrated in Fig. 5.3 b), are more readily processed than those with a most probable molecular weight distribution, but are more likely to be oriented in the solid state and have a somewhat reduced impact resistance.

Resins with a significant low molecular weight tail, as shown in Fig. 5.3 c), exhibit similar melt flow characteristics to the most probable molecular weight distribution, but may be more flexible in the solid state due to the plasticizing effect of the shorter chains.

Resins that have a high molecular weight tail, as illustrated in Fig. 5.3 d), often display good melt processing characteristics. The long chains take longer to relax than the shorter ones and are responsible for the high orientation often associated with these products. Thin films made from such resins are likely to display a high degree of anisotropy; they may be readily torn parallel with the preferential chain orientation, but show good tear resistance in the perpendicular direction.

In practice, product developers often blend two or more resins together in order to obtain a product that has the required melt flow and solid-state characteristics. Thus, we frequently combine metallocene catalyzed linear low density polyethylene, having a most probable molecular weight distribution, with low density polyethylene, having a broad molecular weight distribution. The linear low density polyethylene provides good impact resistance, while the low density polyethylene improves melt flow characteristics.



	a)	b)	c)	d)
	MPMWD	Bimodal	Low Tail	High Tail
$M_n$	67,000	51,400	61,700	31,200
$M_w$	133,800	133,800	133,700	133,500
$M_z$	200,600	218,400	202,600	277,400
$M_{z+1}$	267,500	297,600	270,400	394,900
$M_w / M_n$	2.0	2.6	2.2	4.3
$M_z / M_w$	1.5	1.6	1.5	2.1
$M_z / M_n$	3.0	4.3	3.3	8.9

**Figure 5.3** Examples of various molecular weight distributions sharing the same weight average molecular weight

### 5.2.3 Molecular Weight Determination

We can measure a polymer's molecular weight by one of two general methods. In the first, we fractionate the polymer to generate a plot of fractional mass versus molecular weight. The most commonly used method of this type is size exclusion chromatography. The second family of molecular weight determination methods yields a single value that represents a complex function of the overall molecular weight distribution. This category includes light scattering, viscometry, and melt flow rate measurements.

### 5.2.3.1 Size Exclusion Chromatography

Size exclusion chromatography (which is also known as gel permeation chromatography) is based on the premise that a polymer molecule in solution adopts a random coil configuration, which encompasses a volume (known as its hydrodynamic volume) that is proportional to its molecular weight. We fractionate polymers according to their hydrodynamic volumes to generate a molecular weight distribution plot.

Figure 5.4 illustrates the principles of size exclusion chromatography. The first step is to inject a dilute polymer solution into a column packed with crosslinked polymer microspheres, the surfaces of which are honeycombed with pores of various sizes. The more pores that a polymer molecule can enter, the longer it takes to elute from the column. Thus, the largest molecules, which can only enter the largest pores, elute first. Smaller molecules can enter a larger fraction of the pores and thus their passage through the column is retarded. We record the concentration of the polymer solution exiting the column as a function of time. The molecular weight of each fraction is calculated from a calibration curve that relates molecular weight to elution time. We can then plot the molecular weight distribution based on the mass and molecular weight of each fraction. Finally, we calculate the various molecular averages and their ratios. Naturally, all the calculations and graphing is carried out by computer.

Long chain branches complicate the measurement of molecular weight. This is because the hydrodynamic volume of a molecule is not simply related to its molecular weight. For a given molecular weight, branched molecules have smaller hydrodynamic volumes than linear ones. In order to correct for this complication, we employ two or more detectors to analyze the solution as it elutes from the column. One of the detectors (typically a refractive index detector) measures the polymer concentration in the eluent, while the other (normally a light scattering or viscometric detector) measures the hydrodynamic volume of the eluting polymer molecules. The variance between the observed relationship between the two detectors and a theoretical value for linear molecules provides a measure of the branching. The greater the variance, the more branched are the polymer molecules.

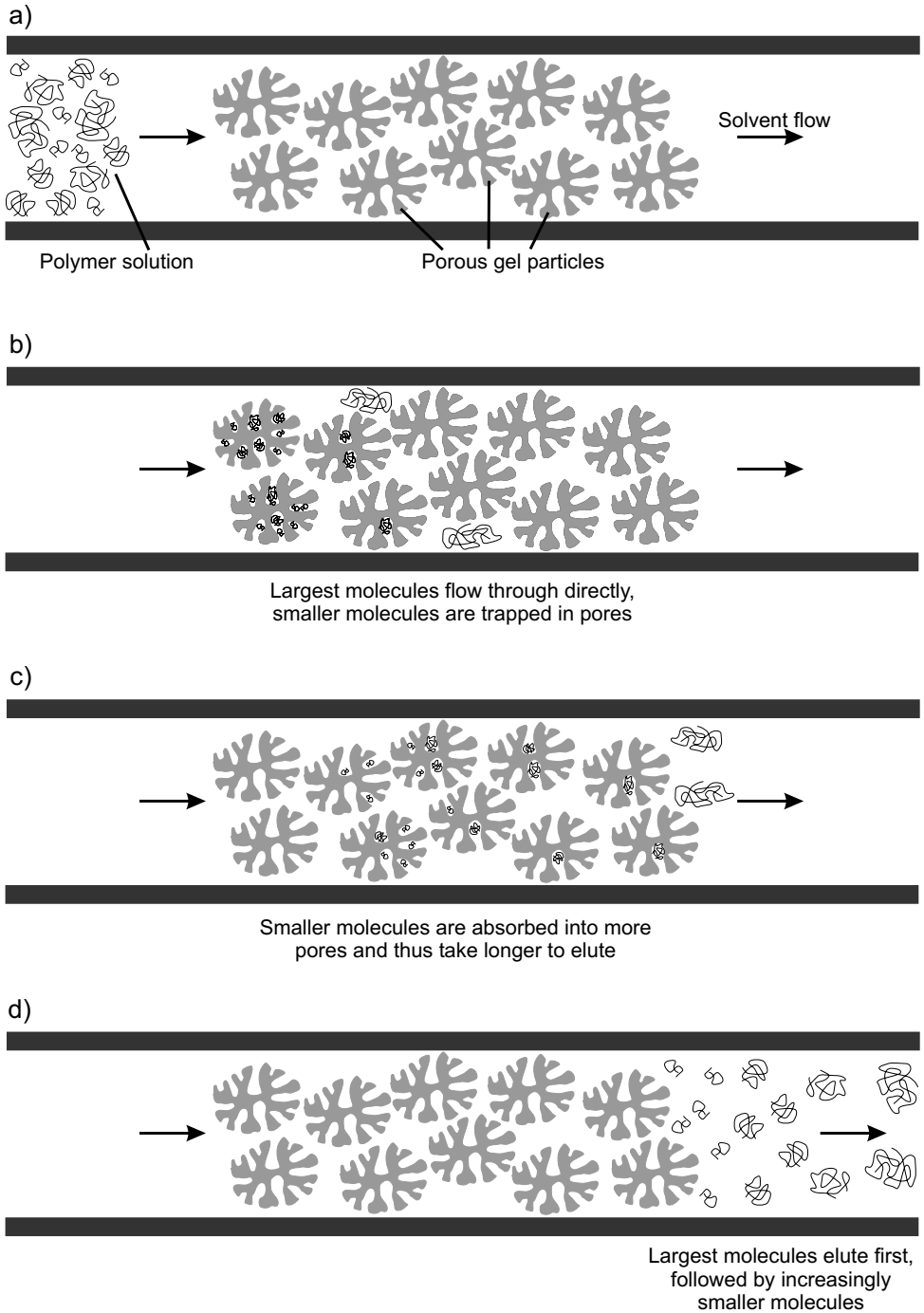
### 5.2.3.2 Intrinsic Viscosity

The viscosity of a dilute solution of polymer depends on the molecular weight of the polymer. This gives us a simple method for measuring molecular weight based on viscosity, which is readily measured.

To perform this analysis, we first prepare a dilute solution of polymer with an accurately known concentration. We then inject an aliquot of this solution into a viscometer that is maintained at a precisely controlled temperature, typically well above room temperature. We calculate the solution's viscosity from the time that it takes a given volume of the solution to flow through a capillary. Replicate measurements are made for several different concentrations, from which the viscosity at infinite dilution is obtained by extrapolation. We calculate the "viscosity average molecular weight" from the Mark-Houwink-Sakurada equation (Eq. 5.5).

$$[\eta] = K M_v^\alpha \quad (5.5)$$





**Figure 5.4** Principle of size exclusion chromatography

where:

$[\eta]$  = viscosity at infinite dilution

$K$  and  $\alpha$  = Mark-Houwink constants (which reflect polymer/solvent interactions)

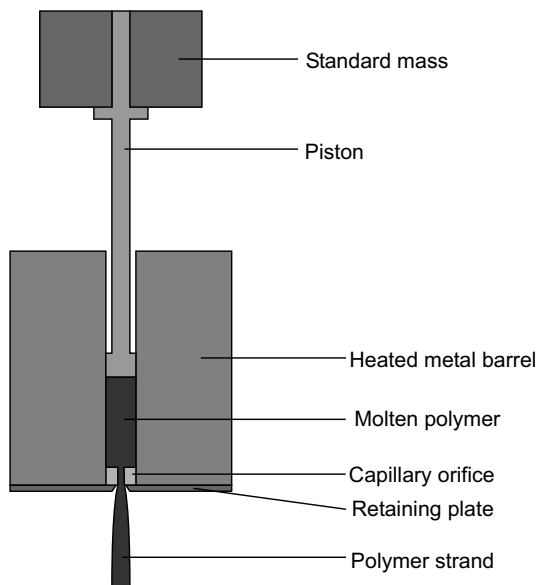
$M_v$  = viscosity average molecular weight

The viscosity average molecular weight typically falls somewhere between  $M_n$  and  $M_w$ .

### 5.2.3.3 Melt Flow Rate

The rate at which a molten polymer flows through a capillary under standard conditions is known as its “melt flow rate” (MFR). The melt flow rate of a polymer is inversely related to its molecular weight. Theoretically, a melt flow rate can be converted to a molecular weight, but this is rarely done in practice. Polymer engineers commonly refer to melt flow rates when comparing material specifications and make comparisons directly based on these values.

The melt flow rate of a polymer is the weight of polymer in grams that extrudes from a standard capillary die under a standard load, at a standard temperature, over a ten minute period. The term “melt index” is used exclusively for polyethylene; melt flow rate is the preferred term for all other polymers. We measure melt flow rates using a piece of equipment called a “melt indexer”. The capillary dimensions, testing temperature, and load are specified for a given polymer by the National Institute for Standards and Testing.



**Figure 5.5** Schematic illustration of a melt indexer

Figure 5.5 shows a schematic diagram of a melt indexer (which is also sometimes referred to as an extrusion plastometer). To determine the melt flow rate of a polymer resin, we place a suitable mass of it into the barrel, which is pre-heated to a standard temperature appropriate to the polymer. We then place a weighted piston on top of the sample. After allowing the polymer to reach the temperature of the barrel we allow it to extrude from the capillary orifice. The melt flow rate is the mass of polymer in grams that extrudes in ten minutes.

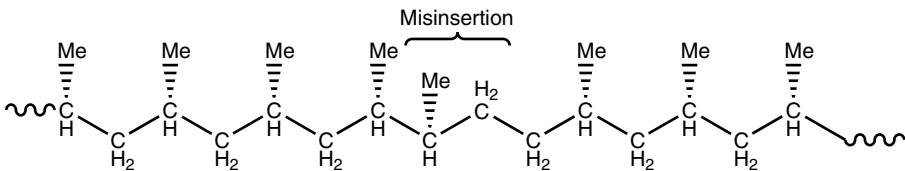
### 5.3 Homopolymer Chemical Composition

Homopolymers can exhibit two types of chemical variation along their lengths. Regiodefects occur when asymmetric monomers are incorporated into the polymer in some combination of “head-to-tail”, “head-to-head” and “tail-to-tail” configurations. Homopolymers display tacticity when their monomer residues contain a steric center that is incorporated into the backbone. Stereodeflects occur when a regular sequence of tacticity is interrupted by a steric center with the opposite configuration from one or both of its neighbors. Certain polymers, notably polypropylene, can exhibit both regiodefects and stereodeflects

#### 5.3.1 Regiodefects

Regiodefects occur in addition polymers when a monomer is added to the growing chain in a configuration that is reversed relative to those around it. Figure 5.6 shows an example of a misinsertion in a polypropylene chain. “Head-to-tail” polymerization is followed by a misinserted monomer that introduces a “head-to-head” and “tail-to-tail” configuration, followed by a return to head-to-tail polymerization. Condensation polymers typically do not contain regiodefects, because the polymerization process inevitably results in a head-to-tail configuration.

Regiodefects are less readily incorporated into crystallites than defect-free chain sequences. In semicrystalline polymers, increasing levels of misinsertion result in reduced crystallinity. This can affect numerous physical properties, resulting in reduced modulus, lower heat distortion temperature, and decreased tensile strength.



**Figure 5.6** Regiodefect in a polypropylene chain

## 5.3.2 Tacticity

Polymers that incorporate steric centers into their backbones can display various types of tacticity. The three principal types of tacticity are isotactic, syndiotactic, and atactic, as illustrated in Fig. 1.8 for polypropylene. Other polymers that display tacticity include polystyrene and poly  $\alpha$ -olefins.

When adjacent monomers in a backbone share the same stereoconfiguration, the placement is known as a meso diad. When adjacent monomers have opposing stereoconfigurations, the placement is known as a racemic diad. Thus, a purely isotactic polymer comprises all meso placements, and a syndiotactic polymer consists of all racemic placements.

In practice, the monomers comprising a polymer are never arranged in a purely isotactic or syndiotactic fashion. All stereoregular polymers contain some misinsertions. The polymerization catalyst and polymerization conditions control the level of stereoregularity.

### 5.3.2.1 Isotacticity

In isotactic polymers the configuration of the steric centers on the backbone is identical. The net result is that all side groups are positioned on the same side of the chain, as illustrated schematically in Fig. 1.8 a).

The presence of all the side groups on the same side of the polymer chain has a significant effect on chain configuration. The side groups tend to interfere with each other, impeding free rotation of the backbone bonds and rendering certain configurations energetically unfavorable. The chain configuration shown in Fig. 1.8 a), in which the backbone carbon atoms are arranged to form a planar zig-zag, is unstable. As drawn, the pendant methyl groups would sterically interfere with their nearest neighbors. In practice, the closest that an isotactic chain can come to a linear configuration is a helix with the pendant groups extending outwards from the principal chain axis. The larger the pendant group, the greater the number of monomers per turn of the helix. Thus, isotactic polypropylene, with its small methyl side group, forms a helix with three monomers per turn, while poly-1-butene, which has an ethyl side group, adopts a helix with four monomers per turn. Due to their regular nature, isotactic polymers will crystallize from the molten state when thermodynamic conditions are favorable.

Stereodefects are the result of one or more racemic diads interrupting a sequence of meso diads. Figure 5.7 illustrates the two principal types of stereodefekt. In Fig. 5.7 a), a single racemic placement results in the subsequent methyl groups being placed on the opposite side of the chain from those of the preceding sequence. In Fig 5.7 b), a pair of racemic placements interrupts the meso sequence. In this case, both the meso sequences have their methyl groups on the same side of the chains.

Stereodefects reduce the overall regularity of an isotactic polymer chain and hinder its ability to crystallize. As the concentration of defects increases, the degree of crystallinity falls, resulting in reduced density, reduced melting temperatures, lower heat distortion temperatures, reduced modulus, and reduced yield stress.