

1 Chemistry and structure of reactive polymers

The purpose of this chapter is to provide the background principles from polymer physics and chemistry which are essential to understanding the role which chemorheology plays in guiding the design and production of novel thermoplastic polymers as well as the complex changes which occur during processing. The focus is on high-molar-mass synthetic polymers and their modification through chemical reaction and blending, as well as degradation reactions. While some consideration is given to the chemistry of multifunctional systems, Chapter 2 focuses on the physical changes and time–temperature-transformation properties of network polymers and thermosets that are formed by reactions during processing.

The attention paid to the polymer solid state is minimized in favour of the melt and in this chapter the static properties of the polymer are considered, i.e. properties in the absence of an external stress as is required for a consideration of the rheological properties. This is addressed in detail in Chapter 3. The treatment of the melt as the basic system for processing introduces a simplification both in the physics and in the chemistry of the system. In the treatment of melts, the polymer chain experiences a mean field of other nearby chains. This is not the situation in dilute or semi-dilute solutions, where density fluctuations in expanded chains must be addressed. In a similar way the chemical reactions which occur on processing in the melt may be treated through a set of homogeneous reactions, unlike the highly heterogeneous and diffusion-controlled chemical reactions in the solid state.

Where detailed analyses of statistical mechanics and stochastic processes assist in the understanding of the underlying principles, reference is made to appropriate treatises, since the purpose here is to connect the chemistry with the processing physics and engineering of the system for a practical outcome rather than provide a rigorous discourse.

1.1 The physical structure of polymers

The theory of polymers has been developed from the concept of linear chains consisting of a single repeat unit, but it must be recognized that there are many different architectures that we will be discussing, viz. linear copolymers, cyclic polymers, branched polymers, rigid-rod polymers, spherical dendrimers, hyperbranched polymers, crosslinked networks etc., all of which have important chemorheological properties. Initially we will consider the theory for linear homopolymers (i.e. only a single repeat unit) in solution and the melt. This will then be extended to determine the factors controlling the formation of the polymer solid state.

The starting point for an analysis of the structure of linear polymers is the C–C backbone of an extended hydrocarbon chain, the simplest member of which is polyethylene. The

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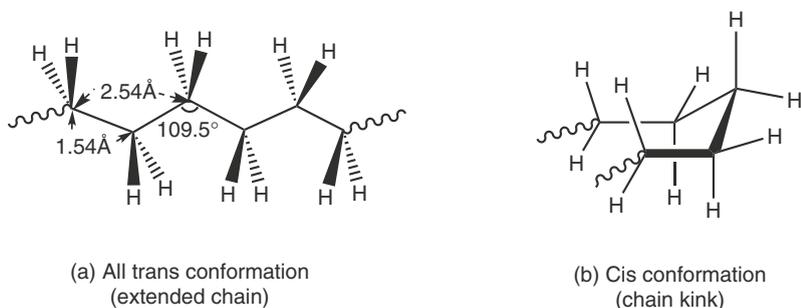


Figure 1.1. The carbon–carbon backbone of a polyethylene chain in its extended planar (all-*trans*) conformation (a) and its kinked, out-of-plane (*cis*) conformation (b).

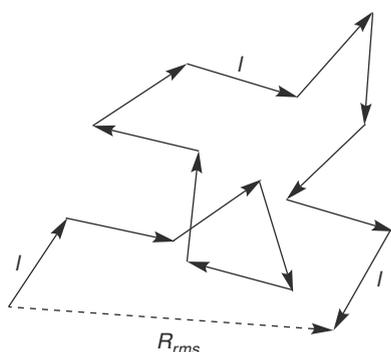


Figure 1.2. A schematic diagram of a freely jointed polymer chain with n segments of length l (in this case $n = 14$) showing the end-to-end distance, R_{rms} .

sp^3 -hybridized tetravalent site of carbon that defines the angles and distances between the atoms along the backbone is shown in Figure 1.1 in

- (a) an all-*trans* conformation with a planar C–C backbone and
- (b) with the introduction of a *cis* conformation (as occurs in a cyclic six-membered hydrocarbon, cyclohexane), which allows the chain to kink out of the plane and change direction.

In the following we will initially consider the simpler concept of a freely jointed chain in which none of these constraints are present.

1.1.1 Linear polymers as freely jointed chains

The concept of polymer chains consisting of a freely jointed backbone which could occupy space as a random coil dated from 1933 when Kuhn defined a polymer chain as having n links of length l and the properties defined by a random flight in three-dimensions (Strobl, 1996). This is shown schematically in Figure 1.2.

This gave the coil the following properties: root mean separation of ends

$$R_{rms} = n^{1/2}l \quad (1.1)$$

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and radius of gyration

$$R_g = (n/6)^{1/2}l. \quad (1.2)$$

Thus,

$$R_{\text{rms}}^2 = 6R_g^2. \quad (1.3)$$

From mechanics, the radius of gyration, R_g , is the average value of the first moment of all segments of the chain with respect to the centre of mass of the chain. If the chain is fully extended with no constraints regarding bond angles, i.e. a fully jointed chain as defined by Kuhn, then the maximum value of R_{rms} becomes

$$R_{\text{max}} = nl. \quad (1.4)$$

The ratio ($R_{\text{rms}}^2/R_{\text{max}}$) is a measure of the stiffness of the chain and is termed the Kuhn length. Thus, if there is a hypothetical freely jointed polyethylene that has 1000 carbon atoms separated by 1.54 Å then $R_{\text{max}} = 1540$ Å, $R_{\text{rms}} = 49$ Å and $R_g = 20$ Å.

The limitations of the random-flight model when applied to real polymer chains arise from

- the fixed bond angles
- steric interactions, which restrict the angles of rotation about the backbone.

This is apparent for polyethylene as shown in Figure 1.1. The restriction from a freely jointed chain to one with an angle of 109.5° between links increases R_{rms}^2 by a factor of two (namely the value of $(1 - \cos \theta)/(1 + \cos \theta)$). Other effects that must be taken into account are the restricted conformations of the chain due to hindered internal rotation and the excluded-volume effect, both of which may be theoretically analysed (Strobl, 1996). The excluded-volume effect was recognized by Kuhn as the limitation of real chains that the segments have a finite volume and also that each segment cannot occupy the same position in space as another segment. This effect increases with the number of segments in the chain as the power 1.2, again increasing the value of R_{rms} (Doi and Edwards, 1986).

When all of these effects are taken into account, a characteristic ratio C may be introduced as a measure of the expansion of the actual end-to-end distance of the polymer chain, R_0 , from that calculated from a Kuhn model:

$$C = R_0^2/(nl^2). \quad (1.5)$$

Experimental values of this parameter are given in Table 1.1 and it may be seen that the actual end-to-end distance of a polyethylene molecule with 1000 carbon atoms (degree of polymerization DP of 500) is 126 Å from Equation (1.5) (i.e. $C^{1/2}n^{1/2}l$) rather than 49 Å from the Kuhn model, Equation (1.1). Data for several polymers in addition to polyethylene are given, including a rigid-rod aromatic nylon polymer, poly(*p*-phenylene terephthalamide) (Kevlar®), as well as the aliphatic nylon polymer poly(hexamethylene adipamide) (nylon-6,6).

Comparison of the values of C for the polymers with a flexible C–C or Si–O–Si backbone (as occurs in siloxane polymers) of about 6–10 with the value for the rigid-rod polymer of 125 demonstrates the fundamental difference in the solution properties of the latter polymer which has a highly extended conformation characteristic of liquid-crystal polymers. Equation (1.5) also shows that for a real chain the value of R_0 would be expected to increase as the half power of the number of repeat units, i.e. the degree of polymerization, $DP^{1/2}$.

Table 1.1. Experimental values of the characteristic ratio, C , for Equation (1.5)

Polymer	Characteristic ratio, C
Poly(ethylene)	6.7
Poly(styrene)	10.2
Poly(hexamethylene adipamide), Nylon-6,6	5.9
Poly(<i>p</i> -phenylene terephthalamide), Kevlar [®]	125

Conditions for observing the unperturbed chain

The data shown in Table 1.1 were experimentally determined from solutions under θ -temperature conditions. This involves measuring the properties when a solution has the characteristic properties which allow the polymer chain to approach ideality most closely. When a polymer chain is in solution the coil will expand due to polymer–solvent interactions and an expansion coefficient, α , is defined so that the actual mean square end-to-end distance $[R_{\text{rms}}]_{\text{act}}$ becomes

$$[R_{\text{rms}}]_{\text{act}} = \alpha R_0. \quad (1.6)$$

The magnitude of α depends on the forces of interaction between the solvent and the polymer chain. Thus, if the polymer is polar, when it dissolves in a polar ‘good’ solvent, it will expand and α is large. The converse is true for ‘poor’ (eg. non-polar) solvents and the chain will contract to lower than the unperturbed dimensions and, in the limit, the polymer may precipitate from solution. When a combination of solvent and temperature is found that is neither ‘good’ nor ‘poor’, i.e. $\alpha = 1$, then the chain–solvent and polymer–polymer interactions balance and R_0 is the unperturbed dimension of the chain. For a particular solvent, the temperature at which this occurs is the θ -temperature.

An interesting calculation is that of the volume occupied by the segments themselves compared with the total volume that the chain occupies. The diameter of a sphere within which the chain spends 95% of the time is about $5R_0$. Since the chain segments occupy only about 0.02% of this volume, the remaining space must be occupied by other chains of different molecules both when the polymer is under θ -conditions and in the presence of solvent molecules when it is expanded. Thus, except in very dilute solutions, polymer molecules interpenetrate one another’s domains so that intermolecular forces between chains are significant.

Polymer chains in the melt

Polymer chains, in the melt, behave as if they are in the θ -condition, so the dimensions are those in the unperturbed state. This argument was put forward by Flory on energetic grounds and has been confirmed by neutron scattering (Strobl, 1996). The consideration begins with an analysis of the excluded-volume forces on an ideal chain. These arise from non-uniform density distributions in the system of an ideal chain in solution as shown in Figure 1.3.

This shows the way that the local monomer concentration, c_m , varies from the centre of the chain ($x = 0$) to either end. The excluded-volume forces on the chain create a potential energy ψ_m sensed by each repeat unit, which depends on c_m and on a volume parameter v_c that controls their magnitude:

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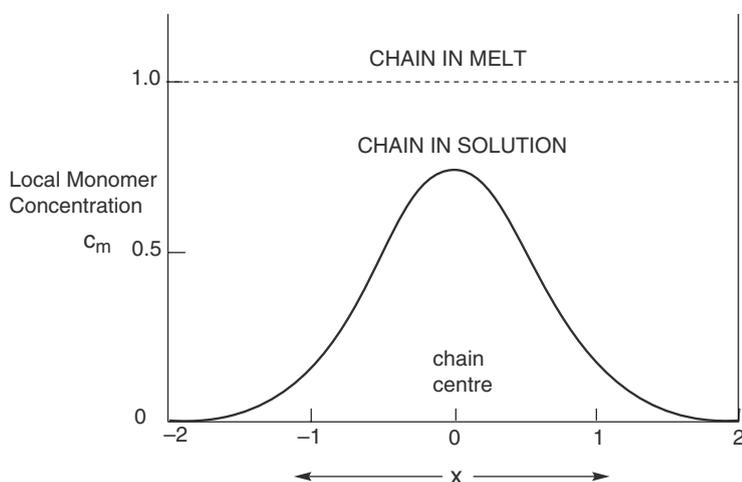


Figure 1.3. Comparison of the change in local monomer concentration with distance from the chain centre for a random chain in solution and in the melt. Adapted from Strobl (1996).

$$\psi_m = v_e c_m kT. \quad (1.7)$$

This produces a net force for all non-uniform density distributions so that for the bell-shaped distribution in Figure 1.3 there will be a net force of expansion of the chain. When the melt is considered, every chain is surrounded by a chain of the same type, so the concentration c_m is constant in all directions (the dotted line in Figure 1.3). No distinction is drawn between repeat units on the same or different chains. (As noted above, there will be interpenetration of chains in all but dilute solutions.) The result is that there is no gradient in potential and there are no forces of expansion. In effect, the polymer chain in the melt behaves as if the forces of expansion due to excluded volume were screened from each chain and the dimensions are those for the unperturbed chain.

This result may, by a similar argument, be extended to the interpenetration of chains as random coils in the amorphous solid state. These results will be of importance when the rheological properties of the melt through to the developing solid are considered in Chapters 2 and 3.

1.1.2 Conformations of linear hydrocarbon polymers

Figure 1.1 showed the planar zigzag (a) and the kinked chain (b) as two possible ways of viewing the chain of polyethylene. The conformation that the chain will adopt will be controlled by the energy of the possible conformers subject to the steric and energetic constraints dictated by the structure. The main feature of transforming from the stretched chain (a) to the coil through structures such as the *cis* conformation (b) depends on the rotation about the C–C backbone. The remaining degrees of translational and vibrational freedom will affect only the centre of mass and the bond angles and bond lengths, not the molecular architecture.

The possible rotational conformations possible for the chain can be envisioned by focussing on a sequence of four carbon atoms as shown in Figure 1.4(a).

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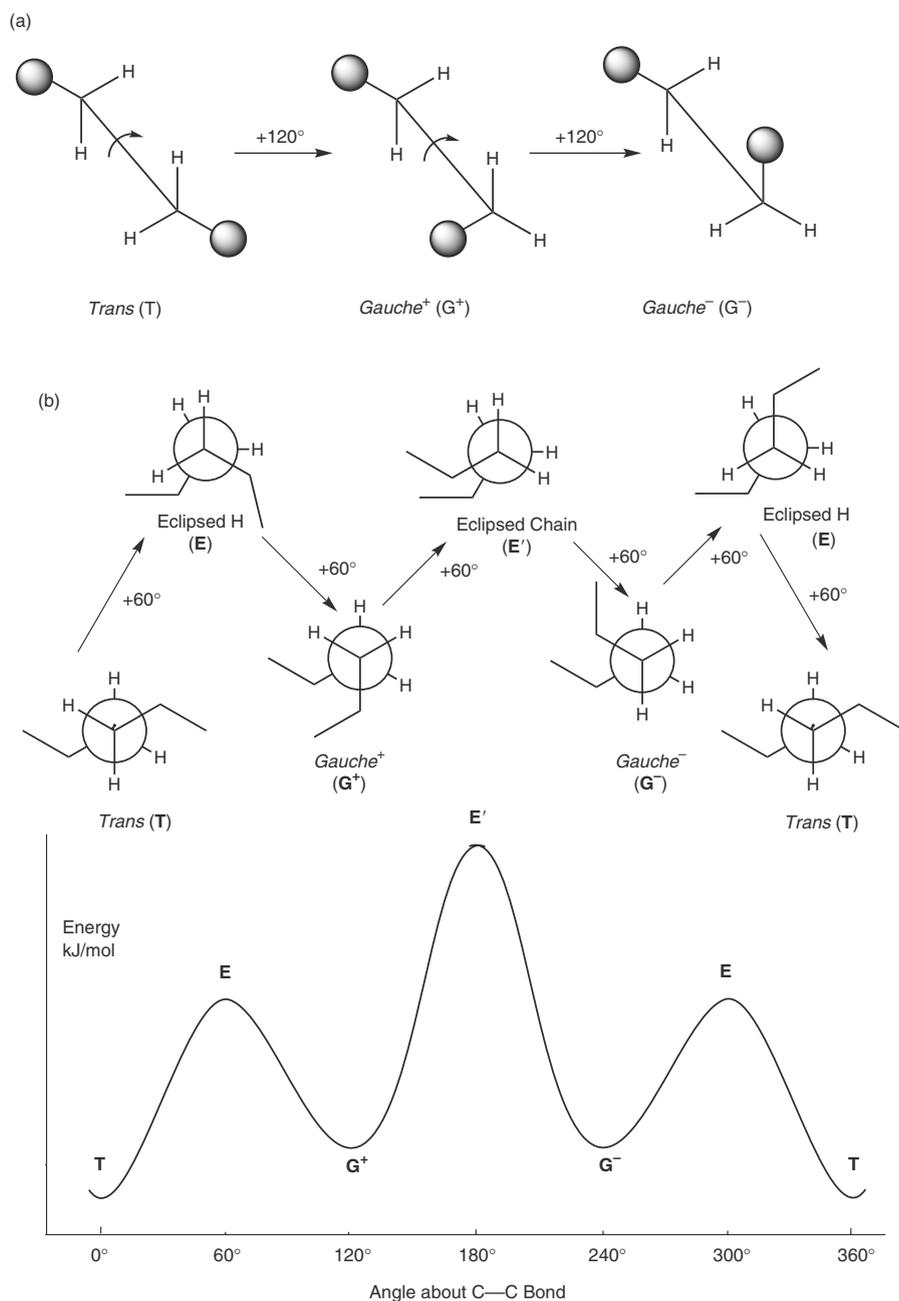


Figure 1.4. (a) Conformations adopted by a segment of a polymer chain by successive rotation about a C—C bond. The balls represent the carbon atoms from the continuing chain (initially in an all-*trans* extended-chain conformation). (b) Changes in conformational energy on successive rotation of an all-*trans* extended-chain conformation by 60° about a C—C axis.

This shows the successive rotation by 120° about the central C—C bond of the adjacent methylene group. Initially all carbon bonds lie in a plane and then after each rotation a hydrogen atom lies in the initial plane. A detailed analysis may be made of the rotational

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isomeric states of model compounds progressively from ethane, butane and pentane to determine the energy states of the conformers and, from the Boltzmann distribution, their populations (Boyd and Phillips, 1993).

The depiction of the conformers is facilitated by a simple schematic approach in which the atoms in Figure 1.4(a) are viewed along the central C–C bond initially in the *trans* (T) conformation and then rotation of the groups clockwise by 60° occurs in succession about this axis (Figure 1.4(b)). Analysis of these conformations identifies the energy maxima (eclipsed, E, conformations) and the energy minima (*trans* and *gauche* conformations) separated by up to 21 and 18 kJ/mol, respectively, as shown in the energy profile in Figure 1.4(b).

For polyethylene, the actual bond rotation from the *trans* (T) position to the other stable conformers (the *gauche* positions, G⁺ and G[−], respectively) is slightly less than 120° due to unsymmetrical repulsions (Flory *et al.*, 1982). There are situations in which the repulsion due to steric crowding results in further deviations. For example, the sequence TG⁺G[−] will produce a structure with a sharp fold where the steric repulsion between methylene groups no longer allows an energy minimum. This is accommodated by a change in the angle of rotation giving an angle closer to that for the *trans* position (the so-called pentane effect) (Boyd and Phillips, 1993, Strobl, 1996).

When other groups are introduced into the polymer chain, such as oxygen in poly(oxy methylene) [−CH₂−O−]_n, the most stable conformation is no longer the all-*trans* chain but the all-*gauche* conformation G⁺G⁺G⁺, etc. This means that the chain is no longer planar but instead is helical. The stability of the *gauche* conformation over *trans* is linked in part to the electrostatic interactions due to the polar oxygen atom in the chain (Boyd and Phillips, 1993). These conformations translate to the most stable structure expected at low temperatures. However, the low energy barriers between isomeric states mean that in the melt a large number of conformations is possible, as indicated in the previous section where the melt is seen to reproduce the properties of an ensemble of ideal random interpenetrating coils.

Asymmetric centres and tacticity

The structures considered above have been concerned with the behaviour of the backbone of the polymer. On proceeding from polyethylene to the next member in the series of olefin polymers, polypropylene, [−CH₂−CH(CH₃)−]_n, an asymmetric centre has been introduced into the backbone, in this case the carbon bearing the methyl group. An asymmetric centre is one where it is possible to recognize two isomeric forms that are mirror images and not superimposable. These are often described as optical isomers and the terms *d* and *l* are introduced for *dextro* (right-) and *laevo* (left-) handed forms. For small molecules these isomers may be resolved optically since they will rotate the plane of polarization in opposite directions.

For macromolecules it is useful to consider the structure of the polymer resulting from monomer sequences that contain the asymmetric centre. Figure 1.5 shows the two possibilities for the addition of the repeat unit as sequences of *d* units or *l* units to give meso (*m*) diads (*dd* or *ll*) when adjacent groups have the same configuration or racemic (*r*) diads (*dl* or *ld*) when they are opposite. If these sequences are repeated for a significant portion of the chain then we can define the tacticity of the polymer as being principally

isotactic if they are . . . mmmmmmmmm . . .

syndiotactic if they are . . . rrrrrrrrrrrrr . . .

atactic if they are random . . . mrmrmmrmmr . . .

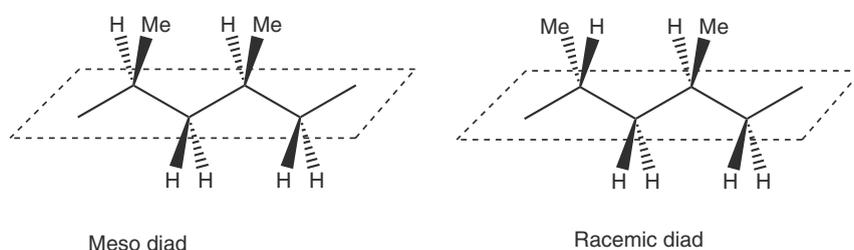


Figure 1.5. A schematic diagram illustrating meso (m) and racemic (r) diads.

As will be discussed later, special synthetic techniques are required to achieve isotactic and syndiotactic structures, and polypropylene, the example above, achieved commercial success only through the discovery of stereoregular polymerization to achieve the isotactic structure. The measurement of the degree of tacticity of a polymer is achieved through ^{13}C NMR studies of the polymer in solution (Koenig, 1999).

Isotactic polypropylene will adopt a conformation very different from the extended chain of polyethylene. In the early part of Section 1.1.2 it was noted that the minimum-energy conformations were considered to be attained by rotation about the C–C backbone and this introduced the possibility of *gauche* conformers as alternative energy minima. This can now be performed on the meso dyad in isotactic polypropylene by considering rotations about the two C–C bonds that will minimize the interactions between the pendant methyl groups. The starting point in this analysis is the nine near *trans* and *gauche* conformers since these define the local minima in energy of the backbone in the absence of the methyl groups. Introduction of the steric repulsion by the methyl groups in a TT conformation (Figure 1.5) suggests that this is not going to be a likely conformation and the conformers which are able to minimize the repulsion due to methyl groups in a meso dyad are limited to TG^- and G^+T . Just as a helix was generated when *gauche* conformers were accessible minima in poly(oxymethylene), so too we have two possible helices if the chain consists of m-dyads as in isotactic polypropylene. For TG^- it will be right-handed and for G^+T it will be left-handed. This helix will have three repeat units in one turn of the helix, i.e. a 3/1 helix, and this is the form which crystallizes.

In syndiotactic polypropylene, the methyl groups are well separated and the TT form is favoured, but there are other energy minima among the *gauche* conformations and $\text{TT}/\text{G}^+\text{G}^+$ and $\text{TT}/\text{G}^-\text{G}^-$ sequences can generate left- and right-handed helices, respectively, where the repulsions are minimized (Boyd and Phillips, 1993). The chains may crystallize both in the TT and in the TTG^+G^+ form, so syndiotactic polypropylene is polymorphic.

1.1.3 Molar mass and molar-mass distribution

The length of the polymer chain or the degree of polymerization, DP, will have a major effect on the properties of the polymer since this will control the extent to which the polymer chain may entangle. The changes in this degree of polymerization that may occur on processing, resulting in either an increase (crosslinking) or a decrease (degradation) in DP, will have a profound effect on the properties both of the melt (e.g. viscosity) and of the resulting solid polymer (strength and stiffness). A formal definition of DP and thus the **molar mass** (or, less rigorously speaking, **molecular weight**) of a polymer is required in order to investigate the effect on properties as well as the changes on processing.

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The addition polymerization reactions, discussed later in Section 1.2, result in the growth of polymer chains that consist of chemically identical repeat units arising from addition reactions of the original monomer, terminated by groups that will be chemically different from the repeat unit due to the chemistry of the reaction, the starting materials (e.g. initiators, catalyst residues), which may be attached to the chain, and impurities. Since these are generally only a very small fraction of the total polymer mass, the effect of the chemistry of the end groups can be ignored to a first approximation, although their quantitative analysis provides a method for estimating the number average molar mass as discussed below. Particular ‘defects’ such as chain branching, must be taken into account when the molar mass–property relationships are developed since the chain is no longer linear.

The mass of the linear polymer chain is thus related directly to the number of monomer units incorporated into the chain (DP) and will be $M_0 \times \text{DP}$, where M_0 (g/mol) is the molar mass of the monomeric repeat unit. Thus, if all chains grew to exactly the same DP, then $M_0 \times \text{DP}$, would be the molar mass of the polymer. If the end groups on the chain can be readily and uniquely analysed, then an average molar mass, M_n , or number-average molecular weight (as discussed in the next section) can be immediately determined since, if there are a mol/g of end group A and b mol/g of end group B then

$$M_n = 2/(a + b) \text{ g/mol.} \quad (1.8)$$

The conformation, end-to-end distance and radius of gyration of the polymer would be described by the simple considerations in Section 1.1.1. In the real polymer, the length of the polymer chain is controlled by the statistics of the chemical process of polymerization, so the distribution of chain lengths will depend on the reaction chemistry and conditions. The distribution is **discontinuous** since the simple linear chain can increase only in integral values of the molar mass of the repeat unit, M_0 . The chain mass also includes that of the end groups M_e , so the first peak appears at $M_0 + M_e$, and then increments by $\text{DP} \times M_0$ as shown in Figure 1.6(a). When the molar mass is low, as in oligomers, the individual polymer chains may be separated by chromatographic or mass-spectroscopic techniques and a distribution such as that shown in Figure 1.6(a) is obtained. For the large molar masses encountered in vinyl polymers ($>10^5$ g/mol) the increment in molar mass for each increase in DP is small and the end-group mass is negligible compared with the total mass of the chain. The distribution then appears to be continuous and sophisticated analytical methods such as MALDI-MS are required to resolve the individual chains (Scamporrino and Vitalini, 1999).

Size-exclusion chromatography (SEC) has become the technique of choice in measuring the molar-mass distributions of polymers that are soluble in easily handled solvents (Dawkins, 1989). The technique as widely practised is not an absolute method and a typical SEC system must be calibrated using chemically identical polymers of known molar mass with a narrow distribution unless a combined detector system (viscosity, light scattering and refractive index) is employed.

The effect of the chemical reactions during polymer synthesis on the molar-mass distribution is discussed in Section 1.2, but prior to this it is important to consider the various averages and the possible distributions of molar mass that may be encountered. It is then possible to examine the experimental methods available for measuring the distributions and the averages which are of value for rationalizing dependence of properties on the length of the polymer chain.

Molar-mass distributions and averages

The definitions of molar mass and its distribution follow the nomenclature recommended by the International Union of Pure and Applied Chemistry (IUPAC) (Jenkins, 1999).

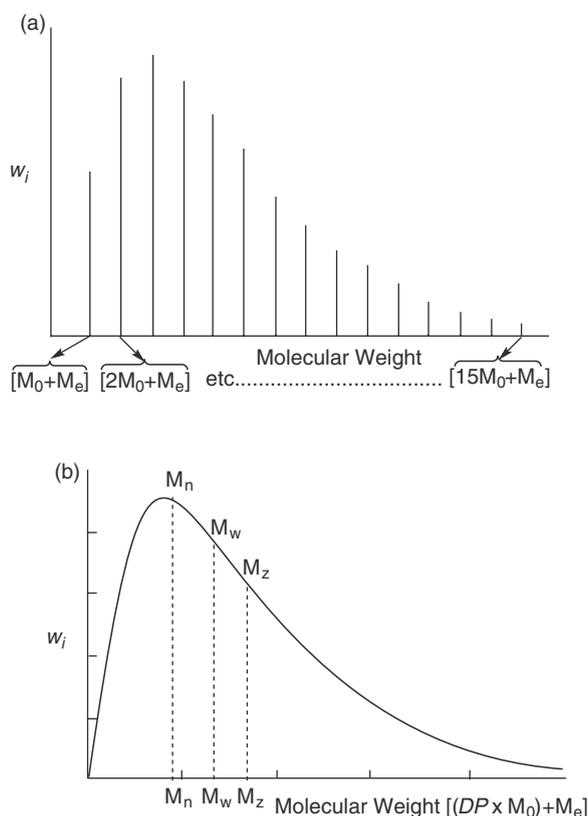


Figure 1.6. Illustration of the discontinuous distribution of polymer chain lengths (a) and the apparently continuous distribution and molar-mass averages (b) from a polymerization; w_i is the weight fraction of each chain length.

The simple averages that are used for property–molar-mass relations of importance in chemorheology as used in this book are the following:

(a) the **number average**, M_n :

$$M_n = 1 / \sum_i (w_i / M_i) = \sum_i N_i M_i / \sum_i N_i, \quad (1.9)$$

where w_i is the weight fraction of species i (i.e. $\sum_i w_i = 1$) and N_i is the number of molecules with molar mass M_i ;

(b) the **weight average**, M_w :

$$M_w = \sum_i w_i M_i = \sum_i N_i M_i^2 / \sum_i N_i M_i; \quad (1.10)$$

(c) the **z average**, M_z :

$$M_z = \sum_i w_i M_i^2 / \sum_i w_i M_i = \sum_i N_i M_i^3 / \sum_i N_i M_i^2. \quad (1.11)$$

Thus, when considering what these different averages describe regarding the actual molar-mass distribution, it is useful to consider the continuous distribution as shown in Figure 1.6(b).