John M. Dealy
Ronald G. Larson

Structure and Rheology of Molten Polymers

From Structure to Flow Behavior and Back Again

Sample Chapter 2:
Structure of Polymers

2   Structure of Polymers

This chapter introduces concepts and models that are used in subsequent chapters of this book. A much more thorough treatment of polymer structure can be found in the monograph of Graessley [1].

2.1   Molecular Size

2.1.1   The Freely-Jointed Chain

If we know the molecular weight of a linear polymer, it is easy to calculate the stretched-out length of a molecule. However, this dimension is very much larger than the size of a coiled-up molecule in a solution or melt. And it is essential to our purposes to establish a quantitative measure of the size of such a coil. Due to Brownian motion, a polymer molecule is constantly exploring a very large number of possible conformations due to its great length and flexibility. A detailed analysis of all these conformations would be an enormous undertaking, but if we are interested only in certain average quantities, such an analysis is not necessary. In fact, it is possible to derive some useful expressions by analyzing a freely-jointed chain rather than the actual molecule. Of course the segments of the molecule that consist of atoms and chemical bonds do not constitute a freely-jointed chain because of limitations on bond angles and orientations, but on a scale that is somewhat larger than that of a chemical bond but still much smaller than that of the stretched-out molecule, there is sufficient flexibility that the molecule does, indeed, act like a freely-jointed chain.

In addition to the assumption of a freely-jointed chain, in the following discussion, we will ignore restrictions on molecular conformation due to the inability of two segments of a molecule to occupy the same space. A chain for which this is allowed is called a *phantom* or *ghost* chain. Finally, we will assume that the chain is not stretched very much. To summarize, in the following development for the freely-jointed chain we will make use of three assumptions: 1) the molecule is very long; 2) it is a phantom chain; and 3) the chain is not extended by flow or external forces. Assumptions two and three imply that the molecule is in an *unperturbed* state, *i.e.*, that it is free of the effects of external forces resulting from flow or solvation. These assumptions are applicable to a molten polymer and to a very dilute solution when the combination of solvent and temperature is such that the conformation of the polymer molecules is unaffected by polymer-polymer or polymer-solvent interactions, *i.e.*, such that the solution is in its *theta state*. The theory of the freely-jointed chain is described only in general terms in the following section, and a more detailed discussion can be found, for example, in the text of Boyd and Phillips [2].

2.1.2   The Gaussian Size Distribution

In order to calculate the coil size of a freely-jointed, phantom chain, we start with the assumptions noted above and consider a chain consisting of N_f freely-jointed segments of length b_f. Since there are no restrictions on the orientation of one segment with respect to its neighbors, the position of one end of the chain relative to the other is given by a three-dimensional random-walk calculation, also called a random-flight calculation. Such calculations can be used to determine the average end-to-end distance, *i.e.*, the root-mean-square end-to-end vector of a molecule, $\sqrt{\langle R^2 \rangle_0}$, where the subscript indicates that this average applies to the unperturbed molecule (equivalent to a dilute solution in the theta state defined in Section 2.1.3) or to a melt. For a vinyl polymer with a degree of polymerization of 1000, the root-mean-square end-to-end distance is about 22 nm.

Figure 2.1 shows a freely-jointed chain superposed on the molecule that it represents. By Brownian motion, a molecule will move through a broad sampling of all its possible configurations in any significant period of time. Assuming that each configuration is equally probable, random flight calculations show that when N_f is large, the mean-square end-to-end distance is given by Eq. 2.1.

$$\langle R^2 \rangle_0 = b_f^2 \, N_f \tag{2.1}$$
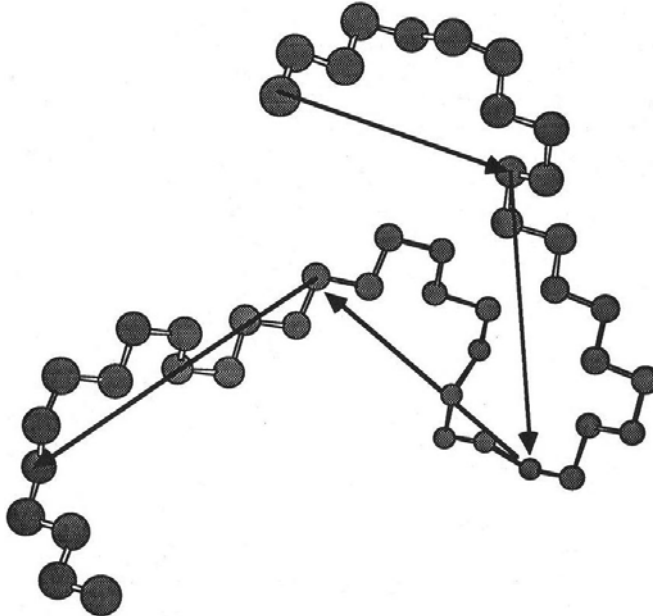
Figure 2.1   Segment of a polyethylene molecule with vectors showing a freely-jointed chain that can be used to simulate its behavior. In the chain shown there is about 1 segment for every ten bonds, and each segment is about eight times as long as a PE bond. From Boyd and Phillips [2].

Values of this parameter for several polymers are tabulated in Appendix A. The *radius of gyration* R_g of a molecule is the root-mean-square distance of mass elements of the chain from its center of gravity. (It is also the radius of a body having the same angular momentum and mass as the molecule but whose mass is concentrated at the radius, R_g.) Averaged over all possible conformations of the freely-jointed chain, the mean-square radius of gyration is given by Eq. 2.2.

$$\langle R_g^2 \rangle_0 = \frac{1}{6} b_f^2\, N_f = \frac{1}{6} \langle R^2 \rangle_0 \tag{2.2}$$

It is also possible to calculate the distribution of end-to end vectors for a random walk, and while the result is rather complex, it is very closely approximated by Eq. 2.3:

$$P(R) = \left[\frac{3}{3\,\pi\,N_f\,b_f^2} \right]^{3/2} e^{-3\,R^2\,/\,2\,N_f\,b_f^2} \tag{2.3}$$

where $P(R)\mathrm{d}R$ is the fraction of all possible random flights having end-to-end radii between R and $R+\mathrm{d}R$. The function defined in Eq. 2.3 is called a Gaussian distribution, and a molecule in which the end-to-end distance follows this distribution is often called a Gaussian chain or a random coil. We note that this probability density only approaches zero at very large values of R, while in reality the maximum extension of the chain is limited to a finite value. This reminds us that the Gaussian (freely-jointed) chain model is not valid for a highly extended molecule. Note that the mean-square end-to-end distance has no meaning for a branched molecule, while the mean-square radius of gyration is still a meaningful measure of size.

We can now use the Gaussian distribution to recalculate the mean-square end-to-end distance:

$$\langle R^2 \rangle_0 = \int R^2\, P(R)\, \mathrm{d}R = N_f\, b_f^2 \tag{2.4}$$

Thus, the approximate distribution function of Eq. 2.3 leads to the correct mean-square value.

The useful results that arise directly from the freely-jointed chain model of a polymer molecule are the relationship between the average size parameters, $\langle R^2 \rangle_0$ and $\langle R_g^2 \rangle_0$, and the Gaussian distribution. Now we want to relate the average size parameters to those describing the chemical bonds making up the backbone of the actual molecule and thus to its molecular weight. At the level of the carbon-carbon bonds, the chain is not freely-jointed, as the relative motions of the bonds are limited by the bond angle and rotational energy potentials. One manifestation of this is that the fully-extended length or *contour length* of the molecule is less than $n\,l$, where n is the number of backbone bonds, and l is the bond length.

$$L = \text{Extended (Contour) Length} = K_{geom}\, n\, l \tag{2.5}$$

where K_{geom} is the sine of one half the bond angle, which for polyethylene is 109.47°, so that K_{geom} is equal to 0.816. Another manifestation of the limitations on motions in the actual molecule is that the mean-square end-to-end distance $\langle R^2 \rangle_0$, which is equal to $N_f\, b_f^2$ for the

freely-jointed model chain, is considerably greater than $n\,l^2$. The ratio of $\langle R^2 \rangle_0$ to $n\,l^2$ is thus a measure of the flexibility of the chain. This quantity, the *characteristic ratio*, C_∞, can be calculated from the chain valence angles and the distribution of bond rotational energy states, and it is a constant for a given polymer.

$$C_\infty \equiv \frac{\langle R^2 \rangle_0}{n\,l^2} \tag{2.6}$$

The infinity subscript indicates that this value applies when n is sufficiently large that the ratio is independent of n. For polyethylene C_∞ is equal to 6.8, while for polystyrene, a stiffer molecule, it is 9.85 [3]. Values for several other polymers are tabulated in Appendix A.

We will let N be the *degree of polymerization*, which is M/M_0, where M is the molecular weight of the polymer, and M_0 is the monomer molecular weight. The number of bonds in the backbone, n, is then $j\,N$, where j is the number of bonds per monomer unit. For vinyl polymers $j = 2$. Using these symbols, the mean-square end-to-end distance can be written in terms of the molecular weight as shown by Eq. 2.7.

$$\langle R^2 \rangle_0 = C_\infty\,n\,l^2 = C_\infty\,j\,N\,l^2 = (C_\infty\,l^2\,j/M_0)\,M \tag{2.7}$$

This shows that $\langle R^2 \rangle_0$ is proportional to the molecular weight and that $\langle R^2 \rangle_0/M$ is thus a constant for a given polymer. Combined with Eq. 2.2 it shows that the unperturbed mean-square radius of gyration is also proportional to the molecular weight:

$$\langle R_g^2 \rangle_0 = (C_\infty\,l^2\,j/6\,M_0)\,M \tag{2.8}$$

Several additional characteristic lengths will also be used in this book. One is the *effective random-walk step*, b_n, which is defined by use of Eq. 2.1, with the number of freely-jointed segments set equal to the actual number of backbone bonds, n:

$$\langle R^2 \rangle_0 = n\,b_n^2 \tag{2.9}$$

so that b_n is defined by Eq. 2.10:

$$b_n \equiv \sqrt{\langle R^2 \rangle_0 /n} \tag{2.10}$$

Thus, b_n is the bond length of a hypothetical, freely-jointed molecule of n segments that has the same value of $\langle R^2 \rangle_0$ as the actual molecule.

Another length closely related to b_n is the structural length introduced by Ferry [4, p. 185]. This is the *statistical segment length* for which we will use the symbol b (Ferry uses the symbol a). This is defined in a similar manner as b_n, but with n replaced by N, the degree of polymerization:

$$b \equiv \sqrt{\langle R^2 \rangle_0 /N} = \sqrt{\langle R^2 \rangle_0\,j/n} = l\sqrt{C_\infty j} = b_n \sqrt{j} \tag{2.11}$$

where j is the number of backbone atoms per monomer unit. Note that when the monomer is an alkene with a single double bond or a vinyl monomer, $j = 2$, and $b = b_n \sqrt{2}$.

The *persistence length*, L_p, is the distance along the molecule at which the orientation of one segment loses its correlation with the orientation of another. In other words, a bond located a distance L_p from a second bond experiences negligible effect on its orientation due to the second bond. Quantitatively it is defined as the average projection of the end-to-end vector of an infinitely long chain in the direction of the first segment. Doi and Edwards [5, p. 317] show that for a Gaussian chain, this length is related to $\langle R^2 \rangle_0$ and the contour length L as follows:

$$L_p = \frac{\langle R^2 \rangle_0}{2L} \tag{2.12}$$

Yet another length parameter that will be useful is the Kuhn length, b_K. Kuhn [6] imagined an *equivalent* freely-jointed chain that has the same extended length L as the actual molecule. Thus, if the equivalent chain has N_K segments of length b_K,

$$n_K b_K^2 = \langle R^2 \rangle_0 = C_\infty n l^2 \tag{2.13}$$

and,

$$R_{max} = L = N_K b_K = K_{geom} n l \tag{2.14}$$

Where K_{geom} is a constant for a given chain structure, as explained below Eq. 2.5. In the remainder of the book, R_{max} will be referred to simply as L.

Thus the Kuhn length is given by:

$$\frac{b_K}{l} = \sqrt{\frac{C_\infty n}{N_k}} = \frac{n K_{geom}}{N_k} \tag{2.15}$$

For polyethylene, using the values mentioned above, $b_K/l \cong 8$, and $N_K/n \cong 1/10$. We also note that the persistence length L_p is just one half the Kuhn length.

The above discussion of molecular size applies to linear molecules. The picture is considerably more complicated for branched molecules. One measure of the effect of branching on the size of a molecule is the *branching factor g*, which reflects the effect of branching on the mean square radius of gyration for a given molecular weight:

$$g \equiv \frac{\langle R_g^2 \rangle_B}{\langle R_g^2 \rangle_L} \tag{2.16}$$

The radii of gyration in this equation refer to a molecule in solution in its unperturbed state, and as we will see shortly, they also apply to molecules in the melt.

To relate g to parameters describing the branching level, information about the type of branching present is required. Such information can be developed from knowledge of the polymerization process. (Note that $\langle R^2 \rangle$ has no meaning for a branched polymer.) Small [7] lists sources of formulas giving g for a number of well-defined branching structures, and we present a few examples here.

For star molecules with f arms of equal length, Zimm and Stockmayer [8] showed that g is given by:

$$g = \frac{3f - 2}{f^2} \tag{2.17}$$

For randomly-branched molecules of uniform molecular weight, each with n branch points having a functionality of f, Zimm and Stockmayer [8] made several simplifying assumptions to arrive at the expressions for $g_f(n)$ shown below as Eqs. 2.18 to 2.20 for one, two and three branch points per molecule (n) respectively.

$$g_f(1) = \frac{6f}{(f+1)(f+2)} \tag{2.18}$$

$$g_f(2) = \frac{3(5f^2 - 6f + 2)}{f(4f^2 - 1)} \tag{2.19}$$

$$g_f(3) = \frac{3(13f^2 - 20f + 8)}{f(9f^2 - 9f + 2)} \tag{2.20}$$

For heterogeneous polymers with larger, uniform numbers of randomly distributed branch points per molecule with a random distribution of branch lengths, they derived Eqs. 2.21 and 2.22 for tri- and tetra-functional branch points, respectively:

$$\langle g_3 \rangle_w = \frac{6}{n_w} \left(\frac{1}{2} \left(\frac{2 + n_w}{n_w} \right)^{1/2} \ln\left[\frac{(2 + n_w)^{1/2} + n_w^{1/2}}{(2 + n_w)^{1/2} - n_w^{1/2}} \right] - 1 \right) \tag{2.21}$$

$$\langle g_4 \rangle_w = \frac{1}{n_w} \ln(1 + n_w) \tag{2.22}$$

In these equations, n_w is the weight average number of branch points per molecule. Lecacheux et al. [9] reported that for n greater than 5, the following approximation is accurate to within 3%.

$$g = \frac{3}{2} \left(\frac{\pi}{n} \right)^{1/2} - \frac{5}{2n} \tag{2.23}$$