Dealy / Larson

Structure and Rheology of Molten Polymers
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From Structure to Flow Behavior and Back Again
Preface

Results of recently developed molecular models suggest the possibility of predicting the rheological behavior of a molten polymer when its molecular structure is well-known. Such models also provide the basis of methods for using rheological data to obtain information about the structure of a polymer whose structure is not known in detail. These models and relationships between structure and rheology are presented here from both phenomenological and molecular-theoretical points of view.

This book is intended to be useful to several types of reader. For those who have a basic knowledge of rheology but little experience with polymers, we have provided in the early chapters sufficient information about polymer physics and chemistry for an understanding of the later chapters. For readers who are currently active in polymer rheology and would like to know the state of the art with respect to quantitative relationships between molecular structure and rheology, the later chapters of the book provide this information. Thus, the book provides both an introduction to polymers and rheological concepts as well as an advanced treatment of potential interest both to polymer scientists and plastics engineers.

Until recent years, there existed major barriers to the development of quantitative relationships between the molecular structure of molten polymers and their rheological behavior. First, reaction systems capable of producing polymers on an industrial scale yielded materials with complex and imprecisely controlled structures. Second, the molecular weight distributions of linear polymers tended to be broad and somewhat irreproducible. And, finally, the branching structure of long-chain branched polymers, particularly low-density polyethylene, involves multidimensional distributions that can neither be predicted nor characterized with precision.

However, over the last ten years, advances in the areas of catalysis and molecular modeling have changed this situation dramatically. Using single-site catalysts, it is now possible to produce on an industrial scale polymers having structures that are much better defined and reproducible than those produced previously. Furthermore, new molecular models, particularly those based on the concept of a “molecule in a tube”, have been developed that can predict rheological behavior based on knowledge of molecular structure. While still requiring further work, particularly to deal with broad molecular weight distributions and complex branching structures, the new models show great promise for the quantitative prediction of flow behavior of polymers of commercial importance. The objective of this book is to present these important developments, along with the background necessary to understand them, and to provide industrial and academic researchers with the up-to-date knowledge and expertise required to use them effectively.

It is not feasible to mention here all the people who have helped us in various ways during the several years we spent writing this book, but we would like to mention the following who were helpful in particularly important ways: Ralph Colby, Stéphane Costeux, Richard Graham, Willem de Groot, Teresa Karjala, David Lohse, Guiseppe Marrucci, Hiroshi Watanabe, and Paula Wood-Adams. And we cannot fail to mention that the support of our tolerant families...
and the patient guidance of our Hanser editor, Dr. Christine Strohm, were essential to the completion of the project.

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1 Introduction

1.1 Melt Structure and its Effect on Rheology

Our subject is how molecular structure affects melt flow; we will not talk about solid state behavior at all. The science of how materials deform and flow under stress is called rheology. Rheology has been used as a semi-quantitative tool in polymer science and engineering for many years, for example for quality control, but quantitative relationships between structure and measurable properties have been elusive, particularly in the case of commercial polymers. However, catalyst systems have recently been developed that allow greatly improved control of the molecular structure of commercial polymers. This, together with major advances in the modeling of rheological behavior, has brought us much closer to a quantitative treatment of structure-rheology relationships for commercial polymer melts.

The relationship between the structure and the rheology of polymers is of practical interest for two reasons. First, rheological properties are both very sensitive to certain aspects of the structure and much simpler to use than analytical methods such as gel permeation chromatography and nuclear magnetic resonance. Second, it is the rheological properties that govern the flow behavior of polymers when they are processed in the molten state.

When we speak of the structure of a polymer, we mean the size and shape of the molecules and the distributions of these characteristics among the molecules. Thus, quantities of interest include the molecular weight and its distribution, tacticity (when the monomer has a pseudochiral center) and branching (types, lengths and their distributions). For linear homopolymers in which tacticity is not an issue, the molecular weight distribution contains complete information regarding structure. This is not a trivial special case, as it includes linear polyolefins that are used in many applications ranging from blow-molded milk bottles to molded polycarbonate compact disks. And already for such relatively simple materials, rheology provides a valuable tool for polymer characterization. Obviously, the determination of the structure of branched polymers is more difficult.

1.2 Overview of this Book

We treat here only systems in which most of the molecules are of a sufficient length to be in a highly entangled state. The basic idea of “entanglement” is that polymer molecules in a melt are embedded in a sea of other, very long molecules, and this greatly restricts their motions in response to an imposed deformation. Solutions of polymers in which the concentration and molecular weight are sufficient to generate a strong entanglement effect are also governed by the relationships discussed here and are mentioned specifically from time to time. Immiscible blends are not treated here, since their rheological behavior is strongly affected by interfacial
tension. For example, substantial recoil after deformation can occur even in immiscible mixtures of low-molecular weight liquids.

Most of the data shown are for polyolefins and vinyl polymers, because these are the materials that are most commonly met with in a highly entangled state. They can be easily polymerized at high molecular weights (that is, molecular weights above 100,000), and their entanglement molecular weights are sufficiently low that the products are highly entangled. In addition, polymers in these categories, particularly polyethylene, polypropylene and polystyrene are the world’s most important commercial polymers produced, and manufactured grades are generally very highly entangled. The “entanglement molecular weight” is discussed in Chapter 6, and some typical values for various polymer melts can be found in Table 7.1.

Chapter 2 defines quantitative measures of molecular structure and describes non-rheological methods for determining these, i.e. for characterizing the structure. The model of a freely-jointed chain provides the basis for relationships involving the mean-square end-to-end distance and the radius of gyration of a molecule. Equations describing molecular weight distributions are presented, and a branching factor is introduced to quantify the effect of long-chain branching on the radius of gyration. Methods for characterizing structure include the measurement of dilute solution viscosity and light scattering. To deal with polymers having heterogeneous structures, chromatography is used to separate a sample according to molecular size, and various sensors are used to determine the distributions of molecular weight and branching structure.

The characterization methods described in Chapter 2 are limited in what they can tell us about structure in the absence of any information about how a sample was made. Chapter 3 surveys the various types of reaction systems used in polymerization and describes the molecular structures that can be produced by each. Anionic and living free-radical polymerizations are used in the laboratory to prepare samples having ideal structures, while processes used in industry produce materials that more complex in structure. The commercial polymer with the most complex structure is low-density (highly branched) polyethylene. The development of single-site catalysts has led to the commercial production of polymers that, while they do not have the homogeneity of ideal samples, do have structures that are reproducible and simply described.

Chapter 4 introduces the subject of linear viscoelasticity for readers somewhat new to rheology and also defines a number of terms that are used in the remainder of the book. The relaxation spectrum is introduced as well as methods for its measurement. Also, time-temperature superposition and its applications are explained.

Chapter 5 is a fairly detailed discussion of the linear viscoelastic behavior of melts. The most used linear properties are the zero-shear viscosity and the storage and loss moduli, and the effects of molecular weight, molecular weight distribution, and branching on these properties are described. While the approach is primarily phenomenological, melt behavior is interpreted qualitatively in terms of the molecular models that are presented in mathematical detail in later chapters.

Chapter 6 treats mean-field theories of melt behavior. We begin with the Rouse model for molecules in dilute solution and its modification by Bueche to deal with unentangled melts. The longest Rouse relaxation time emerges from this treatment and plays an important role in all molecular models. The tube model is introduced, in which the basic relaxation
mechanisms involved in linear viscoelastic behavior are assumed to be “equilibration” among segments of the molecule within in a “tube” formed by surrounding molecules, and “reptation” out of this tube. The large difference between the time scales for these two processes explains the prominent plateau in the relaxation modulus of a monodisperse, entangled melt. In a polydisperse melt, short molecules cause the tube to become less restrictive of lateral motion during the reptation process, and this reduces or eliminates the flat plateau in the relaxation modulus. “Double reptation” is a semi-empirical method for dealing with this complication.

Chapter 7 describes the physics contained in the tube model in much more detail and presents alternative approaches to dealing with polydispersity.

In Chapter 8, methods for inferring the molecular weight distribution of a linear polymer are presented and compared. These range from semi-empirical methods based on measurement of the viscosity as a function of shear rate to sophisticated techniques based on the molecular models presented in Chapters 6 and 7.

Chapter 9 presents tube models for linear viscoelasticity in systems with long-chain branching. Reptation of the molecule as a whole is suppressed by branch points, and relaxation takes place primarily by primitive path fluctuation, a relatively slow process. An alternative to the tube picture, the “slip-link” approach, is examined in detail.

Chapter 10 deals with nonlinear viscoelasticity primarily from a phenomenological point of view. Nonlinear behavior supplements the structural information available from linear data, particularly in the case of long-chain branched polymers. Stress relaxation after a large step strain reveals a new feature that is described in terms of a “damping function” and is explained by tube models as the result of retraction following chain stretch. Non-zero normal stress differences are nonlinear phenomena that occur in all large, rapid shearing deformations. In order to explain the effect of shear rate on the viscosity, the concept of “convective constraint release” is introduced into the tube picture. Except in the step-strain test, shearing deformations do not generate significant chain stretch, but uniaxial (simple) extension does, and thereby displays interesting new phenomena such as “strain hardening,” which has been found to be particularly useful in the detection of long-chain branching.

Tube models capable of describing the essential features of nonlinear behavior are described in Chapter 11, which also introduces constitutive equations based on tube models. Such equations are of practical importance, as they aim to predict the way a melt behaves during industrial forming operations.

Chapter 12 briefly summarizes the book and lists the remaining challenges.

1.3 Applications of the Information Presented

The recent developments mentioned above open the door to the development of quantitative models relating molecular structure to rheological behavior. The two direct applications of these models are the prediction of rheological behavior when the molecular structure is well known and the determination of key aspects of molecular structure through rheological measurements. Going beyond the scope of the present book, the relationship between melt
structure and rheology is one link in a chain of relationships that starts from reaction conditions and ends in the way polymers behave in industrial melt forming operations. Making use of developments in the modeling of polymerization reactions and of melt forming operations, one can imagine a not very distant future in which it will be possible to do the following:

1. Predict the detailed structure of a polymer given the catalyst system and reaction conditions used to prepare it.
2. Given its structure, predict the rheological behavior of a polymer using molecular models.
3. Invert the above process by using rheology to determine polymer structure, or to confirm the predictions of structure that were made based on Step 1 above.
4. Using numerical flow simulations, predict the detailed behavior of a polymer during processing based on predicted rheological properties.

Each link in this chain of relationships is now nearing a state of development sufficient to make it possible to predict a priori the reaction conditions required to produce a polymer having a prescribed melt processing behavior. This book contributes little to step 1 of this chain, but focuses instead on step 2, and, to the extent currently possible, step 3. The book contributes also to step 4 by presenting some of the rheological constitutive equations that can be used in the simulation of flows and stresses in polymer processing operations.

### 1.4 Supplementary Sources of Information

Hundreds of reports of research results are cited in the book, but there are few books and major reviews that will prove of value to readers wishing to learn more about particular aspects of the topics discussed. The book by Ferry [1] continues to be a classic source in the area of polymer rheology, in spite of the fact that the third edition is now twenty-five years old. More recent, but less encyclopedic books on rheology include those of Macosko [2], Morrison [3], and Dealy and Wissbrun [4]. The structure and rheology of complex fluids is the subject of a monograph by Larson [5]. The phenomenology of polymer flow and continuum models are the domain of the book by Bird et al. [6], and constitutive equations of all types are treated in depth by Larson [7].

General texts on polymer physics include those of Sperling [8] and Painter and Coleman [9], and more advanced coverage is provided by Rubinstein and Colby [10] and by Graessley [11]. A second and closely related book by Graessley on polymer rheology has appeared very recently [12]. Polymer chemistry is covered, for example, by Stevens [13] and Allcock et al. [14]. The tube theory for melts was first presented in book form by Doi and Edwards [15], and an extensive review noting later developments was prepared by Watanabe [16].
References

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, \( \langle R^2 \rangle_0 \), i.e., the root-mean-square end-to-end vector of a molecule, \( \langle R^2 \rangle_0 \), 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.

\[
\langle R^2 \rangle_0 = b_f^2 N_f
\] (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].
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.

$$\langle R_g^2 \rangle_0 = \frac{1}{6} b_t^2 N_f = \frac{1}{6} \langle R^2 \rangle_0$$

where $b_t$ is the bond length.

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:

$$P(R) = \frac{3}{\pi N_f b_t^2} e^{-3 R^2 / 2 N_t b_t^2}$$

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.
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, \( C_\infty \), 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.

\[
C_\infty \equiv \frac{\langle R^2 \rangle_0}{n l^2} \quad (2.6)
\]

The infinity subscript indicates that this value applies when \( n \) is sufficiently large that the ratio is independent of \( n \). For polyethylene \( C_\infty \) 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.

\[
\langle R^2 \rangle_0 = C_\infty n l^2 = C_\infty j N l^2 = (C_\infty l^2 j/M_0) M \quad (2.7)
\]

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:

\[
\langle R^2 \rangle_g = (C_\infty l^2 j/6 M_0) M \quad (2.8)
\]

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, \( n \):

\[
\langle R^2 \rangle_0 = n b_n^2 \quad (2.9)
\]

so that \( b_n \) is defined by Eq. 2.10:

\[
b_n \equiv \sqrt{\langle R^2 \rangle_0 / n} \quad (2.10)
\]

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:

\[
b \equiv \sqrt{\langle R^2 \rangle_0 / N} = \sqrt{\langle R^2 \rangle_0 j / n} = l \sqrt{C_\infty j} = b_n \sqrt{j} \quad (2.11)
\]
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:

\[
L_p = \frac{\langle R^2 \rangle_0}{2L} \quad (2.12)
\]

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 \( b_K \),

\[
n_K b_K^2 = \langle R^2 \rangle_0 = C_{\infty} n l^2 \quad (2.13)
\]

and,

\[
R_{\max} = L = N_K b_K = K_{\text{geom}} n l \quad (2.14)
\]

Where \( K_{\text{geom}} \) 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:

\[
b_K \over l = \sqrt{C_{\infty} n \over N_k} = n K_{\text{geom}} \over N_k \quad (2.15)
\]

For polyethylene, using the values mentioned above, \( b_K/\ell \equiv 8 \), and \( N_k/n \equiv 1/10 \). 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:

\[
g \equiv \frac{\langle R_g^2 \rangle_B}{\langle R_g^2 \rangle_L} \quad (2.16)
\]

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:

$$g = \frac{3f - 2}{f^2} \quad (2.17)$$

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.

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

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

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

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:

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

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

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%.

$$g = \frac{3}{2} \left( \frac{\pi}{n} \right)^{1/2} - \frac{5}{2n} \quad (2.23)$$
Equation 2.21 is often used to interpret GPC data for branched commercial polymers, including LDPE, although this is not a randomly branched polymer. Equation 2.21 implies that the average number of branch points per 1000 carbon atoms $\lambda$, for molecules having $j$ backbone bonds per monomer unit, is as follows:

$$\lambda(M) = \frac{1000 M_0 n_w}{j M_n} \quad (2.24)$$

For $m$ randomly distributed branch points in each molecule of a sample that has been fractionated by molecular weight, i.e., that is monodisperse, Zimm and Stockmayer [8] showed that for larger values of $m$, average values of $g$ can be approximated by Eq. 2.25 for a functionality of 3 and by Eq. 2.26 for a functionality of 4.

$$g_3 = \left(1 + \frac{m/7}{\sqrt{\pi}} + \frac{4 m/9}{\pi}\right)^{-1/2} \quad (2.25)$$

$$g_4 = \left(1 + \frac{m/6}{\sqrt{\pi}} + \frac{4 m/3}{3\pi}\right)^{-1/2} \quad (2.26)$$

Here $m = \sum n w_n$ and $w_n$ is the fraction of chains having $n$ branch points. Hadjichristidis et al. [10] noted that the Zimm and Stockmayer model describes the sizes of lightly branched molecules but that the predicted sizes of more highly branched polymers are too low due to crowding of the branches.

Bonchev et al. [11] used graph theory to develop quantitative relationships between $g$ and several indices of branching complexity. The most important result of their work is that for a mono-disperse polymer with no rings, the unperturbed mean square radius of gyration is related very simply to two of these indices, the “Wiener number”, $W$, and the “Kirchhoff number”, $Kf$. For acyclic molecules, these two numbers are related by:

$$[W]_l = [Kf]_l / 2 = N_f^3 / 6 \quad (2.27a)$$

And for a branched acyclic system,

$$\left< R_g^2 \right>_B = \frac{b_f^2 W}{N_f^2} \quad (2.27b)$$

The value of $b$ depends on the detailed structure of the chain and is particularly sensitive to the length and flexibility of its bonds. From Eq. 2.2 we have:

$$\left< R_g^2 \right>_L = b_f^2 N_f / 6 \quad (2.28)$$

Equations 2.28 and 227 show that the branching ratio $g$ is given by Eq. 2.29.

$$g = \frac{6 W}{N_f^3} = \frac{W}{[W]_l} \quad (2.29)$$

Bonchev et al. [11] show how to calculate $g$ for many branched structures.
2.1.3 The Dilute Solution and the Theta State

Several important techniques for determining molecular size involve measurements in dilute solutions and the use of some Gaussian chain relationships. It is thus important to know when a molecule in a dilute solution can be modeled as a Gaussian chain. To answer this question, it is necessary to review the basic assumptions of the chain model that lead to the Gaussian size distribution. A key assumption is that of the phantom chain, which says that the chain is free to intersect itself and is thus free of long-range interactions between two portions of the molecule far from each other. But in fact only a fraction of all possible random-flight configurations are completely free of such interactions. As a result, in a neutral or good solvent the size of the molecule is significantly larger than that indicated by the phantom chain model. This volume effect manifests itself in values of molecular size parameters, such as \( \langle R^2 \rangle \), that are larger than those for an unperturbed, phantom chain, in this case \( \langle R^2 \rangle_0 \). This phenomenon was described by Flory [12] in terms of excluded volume, and modern treatments of this concept can be found in recent books [1, 13]. The main conclusion of these analyses for the purposes of the present book is that in a good solvent, \( \langle R^2 \rangle \) and \( \langle R_g^2 \rangle \) are larger than they would be for an unperturbed chain. One important effect of this phenomenon is in relating intrinsic viscosity to molecular weight, which is explained in Section 2.5. The complex problem of calculating the distribution of molecular sizes in a good solvent, where excluded volume must be taken into account, has been successfully approached by the use of Monte Carlo studies of the self-avoiding random walk (SAW) problem [14] and by renormalization group theories.

We have just observed that because of excluded volume the actual molecule tends to expand into more volume than does the unperturbed, Gaussian chain used to model it, but that is not the end of the story. In the words of Paul Flory [12, p. 34], this “long-range (or volume) effect depends not only on the volume of the chain unit itself but also on its interaction with the solvent”. This opens the door to the judicious selection of the solvent in order to manipulate the excluded volume. In a very poor solvent, segments along the chain will prefer to contact other chain segments rather than the solvent, and the chain will thus coil up on itself more tightly than it would without the solvent. This will cause it to occupy less volume than it would for a random-flight conformation. But as the power of the solvent is increased, the molecule will expand, and for certain combinations of solvent and temperature, the excluded volume can be effectively cancelled out, so that the possible conformations of the molecule have a Gaussian distribution. Such combinations are said to put the solution it its theta state, and at a given temperature, a solvent that produces this state is called a theta solvent. Thus, in the theta state, the energetic effect of self-attraction between segments of the molecule is exactly balanced by the entropic effect of expansion due to the excluded volume. A theta solvent turns out to be a relatively poor solvent, barely keeping a high-molecular weight polymer in solution.

It is often impractical to make measurements under theta conditions, and it is thus important to know how the use of a good solvent affects the size of a molecule. This effect has been sometimes described in terms of an expansion parameter \( \alpha \) defined by Eq. 2.30. (Doi and Edwards [5] call \( \alpha \) a “swelling coefficient”.)

\[
\langle R^2 \rangle = \alpha^2 \langle R^2 \rangle_0 = \alpha^2 N b^2
\]  

(2.30)
At one time, it was thought that this parameter depended only on the solvent and temperature for a given polymer. However, it was later realized that the scaling of the radius with molecular weight is not accounted for correctly by a constant value of $\alpha$ and that this parameter depends on the molecular weight. Experimental data indicate that the root-mean-square end-to-end vector is in fact proportional to $M^{0.6}$.

Flory [12] in developing what he called a “mean field theory” hypothesized that the size of a molecule in a good solvent is the result of a balance between repulsive, excluded volume interactions and elastic interactions that tend to shrink the molecule. This idea leads to the conclusion that:

$$\sqrt{\langle R^2 \rangle} \propto N^{3/5}$$  \hspace{1cm} (2.31)

While this result is in accord with observations, other predictions of the model are incorrect [5, p. 28].

A “two-parameter” model [15] predicts that $\alpha$ is a universal function of an excluded volume parameter, $z$, which is a dimensionless excluded volume, and the theory of Edwards and Singh [16] leads to the same conclusion. Their “self-consistent” model is based on the assumption of uniform expansion, i.e., that the expansion of the chain can be represented by an increase in the effective bond length. This affects the size of the molecule and thus the value of $\alpha$. Edwards and Singh developed the following explicit relationship between $\alpha$ and $z$ for large $N$:

$$\alpha^5 - \alpha^3 = \frac{4}{3} z$$  \hspace{1cm} (2.32)

They represent the expansion parameter $z$ in terms of the excluded volume $v$ as follows:

$$z \equiv \left( \frac{3}{2 \pi} \right)^{3/2} \frac{v \sqrt{N}}{b^3}$$  \hspace{1cm} (2.33)

For large $z$, this relationship implies that the root-mean-square end-to-end distance is proportional to $N^{3/5}$, which agrees with observations. As in the case of the Flory concept, implicit in this model is the assumption that the end-to-end distance in a good solvent is Gaussian. However, the Gaussian chain model for a polymer molecule is increasingly inaccurate as the solvent power increases. This is taken into account by a mean field theory that has been proposed to describe the excluded volume effect [17].

Baumann [18] proposed an empirical equation for calculating the unperturbed mean square radius of gyration, $\langle R_g^2 \rangle_0$, based on light scattering measurements made in a good solvent rather than a theta solvent:

$$\left( \frac{\langle R_g^2 \rangle}{M} \right)^{3/2} = \left( \frac{\langle R_g^2 \rangle}{M} \right)^{3/2} + B M^{1/2}$$  \hspace{1cm} (2.34)