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Molecular Weight and Concentration Dependences of the Terminal Relaxation Time and Viscosity of Entangled Polymer Solutions†

R. W. Rendell* and K. L. Ngai

Naval Research Laboratory, Washington, D.C. 20375-5000

G. B. McKenna

National Bureau of Standards, Gaithersburg, Maryland 20899. *Received February 5, 1987*

ABSTRACT: A new model is presented for entangled polymer solutions which accounts for the observed molecular weight and concentration dependences of the zero-shear viscosity η_0 and the terminal relaxation time τ_d. Our development, based upon the coupling model of relaxation, quantitatively describes how relaxation of a primitive mode is modified by coupling through entanglements to its environment. The primitive mode is represented by a Rouse chain of Gaussian submolecules, each of root mean square length σ equal to the entanglement distance and each characterized by an entanglement friction coefficient f_0. By extending the analyses developed previously for polymer melts, the model predicts that $\eta_0 \propto f^* M^{2/(1-n)} \phi^{\gamma} [\phi^{\alpha(1-\nu)}]^{2/(1-n)}$ where ϕ is the polymer volume fraction. Here n is the coupling parameter describing the terminal relaxation and γ, α, and ν are given by $G_N{}^0 \propto \phi^{\gamma}$, $M_e \propto \phi^{-\alpha}$, and $\sigma \propto \phi^{-\nu\alpha}$. Numerical examples are shown to agree with experiment; e.g., for $n = 0.41$, $\gamma = 2$, $\alpha = 1$, $\nu = 0.6$, $\eta_0 \propto f^* M^{3.4} \phi^{3.4}$. Comparison of the present results is also made to the reptation and scaling theory predictions.

I. Introduction

An understanding of the dynamics of the polymer chain in entangled systems includes not only a description of how the viscoelastic behavior in the terminal zone depends upon molecular weight but also how it depends upon the polymer concentration in entangled solutions. From experimental data, the picture which emerges[1-5] for the entangled polymer system is that the viscosity can be factored into a temperature- and concentration-dependent friction factor $\zeta(T,\phi)$ and a molecular weight dependent structural (topology) factor $g(M,\phi)$. The structure factor follows a power law dependence in both molecular weight, M, and concentration (volume fraction, ϕ), i.e.,

$$\eta_0 = \zeta(T,\phi) g(M,\phi) \propto \zeta(T,\phi) M^x \phi^y \tag{1}$$

The exponents x and y are generally reported to be approximately the same and have values between 3.4 and 3.7. The temperature and concentration dependencies of the friction factor are often considered[1] to be due to free volume changes and data are normally represented in an "isorelative (or fractional) free volume" state. This allows the dependence of ζ on $\zeta(T,\phi) = \zeta(T - T_g)$ to be separated from the topological effects due to M and ϕ. While x and y appear to be approximately the same for small molecule solvents ($x \approx 3.4$, $y \approx 3.4$), there have been recent reports[6] which indicate that in certain systems, for which the solvent molecular weight is near the polymer entanglement molecular weight, $y \cong 3.0$.

Furthermore, the plateau modulus, $G_N{}^0$, of the polymer system, while being independent of the molecular weight, is reported as scaling with the concentration as

$$G_N{}^0 \propto \phi^{\gamma} \tag{2}$$

where γ is reported to be approximately[7-10] 2.0–2.3. On the other hand, the terminal relaxation time, τ_d, is reported[9,11] to scale as

$$\tau_d \ \alpha \ \zeta(T,\phi) M^x \phi^z \tag{3}$$

where x is approximately 3.4–3.7, and now the value of z is approximately 1.4.

In this paper we present a new model for entangled polymer systems which accounts for the observed molecular weight and concentration dependences of η_0 and τ_d in entangled polymer systems. Our development is based upon a recently developed coupling model of relaxation.[12,13] The model describes how relaxation of a primitive mode is modified by coupling to its environment. In the application to entangled polymer systems, the primitive mode is approximately represented by a Rouse chain. The Rouse chain is coupled to its environment through entanglements. The coupling model allows such effects to be incorporated

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quantitatively. By extending the analyses developed previously[14-18] for polymer melts, the model predicts that

$$\eta_0 \propto f^* M^{3.4} \phi^y, \qquad y = 3.4\text{–}3.7 \tag{4}$$

$$\tau_d \propto f^* M^{3.4} \phi^z, \qquad z = 1.4\text{–}1.7 \tag{5}$$

where f^* is an entanglement friction factor. This is in reasonable agreement with observed behavior. The particular value of y or z depends on the values of the exponents γ, α, and ν (see eq 18–20).

The model is developed in the following sections. We also compare our results with the various predictions made by the reptation and scaling theories for the molecular weight and concentration dependences of η_0 and τ_d. An expression for the concentration dependence of the self-diffusion coefficient has not yet been developed within the context of the coupling model. For completeness, however, the melt prediction developed previously and the appropriate reptation and scaling theory predictions for the self-diffusion coefficient will also be presented.

II. The Coupling Model

a. General Considerations. The coupling model[12,13,15] addresses the problem of how the relaxation of a single "primitive" relaxation mode is modified by coupling to its complex surroundings. It predicts that the cooperative effects due to such coupling can be incorporated quantitatively by the use of a relaxation rate that is explicitly time dependent. The coupling model has previously been reviewed and discussed in applications to several problems of polymer physics.[13-21] In this section we merely state the physical concepts involved and the predictions which follow. Then we summarize our previous applications to polymer melts. In the next section we extend the model and apply it to entangled solutions.

The coupling of the primitive relaxation mechanism to its environment slows down the primitive relaxation rate W_0 at times longer than a characteristic time $t_c \equiv \omega_c^{-1}$ and causes the relaxation rate to become time dependent. The effective relaxation rate $W(t)$ is W_0 for $\omega_c t < 1$ and $W_0(\omega_c t)^{-n}$ for $\omega_c t > 1$, where n (satisfying the condition $0 \leq n < 1$), is a measure of the degree of slowing down. The relaxation function $c(t)$ then obeys the rate equation

$$\mathrm{d}c/\mathrm{d}t = -W(t)c \tag{6}$$

where

$$\begin{aligned} W(t) &= W_0 \qquad \omega_c t < 1 \\ &= W_0(\omega_c t)^{-n} \qquad \omega_c t > 1 \end{aligned} \tag{7}$$

Solution of eq 6 and 7 leads to three predictions for the normalized relaxation function $\phi(t) \equiv c(t)/c(0)$ that are interrelated. They are

$$\phi(t) = \exp(-t/\tau_0) \qquad \omega_c t < 1 \tag{8}$$

$$\phi(t) = \exp(-t/\tau^*)^{1-n} \qquad \omega_c t > 1 \tag{9}$$

and

$$\tau^* = [(1-n)\hat{\omega}_c^{\,n}\tau_0]^{1/(1-n)} \tag{10}$$

where $\tau_0 = W_0^{-1}$ and $\hat{\omega}_c$ is related to ω_c by factors of order unity. Equation 9 is a special form of the well-known fractional exponential or Kohlrausch decay law.[13] The physical significance of τ^* (the apparent relaxation time) is discussed subsequently.

We have been able to derive the time-dependent rate equation (7) in several different ways.[12,13,22] Only for very special simple systems does the rate have a constant value W_0 for all times. More typically, we find that the rate is modified by the explicitly time-dependent factor $(\omega_c t)^{-n}$ at times longer than ω_c^{-1}. This is consistent with the results of general derivations of rate equations from the equations of motion discussed in the classic relaxation papers of van Hove, Prigogine, Zwanzig, and others.[23] It is known that relaxation rates are generally time dependent. However, explicit evaluations of $W(t)$ have been carried out by previous workers only for special simple systems where $W(t)$ reduces to a constant W_0 for all time. The implications of using a time-dependent rate and the specific form which $W(t)$ takes for systems of interest had not been previously investigated.

In the past decade, it has become widely known that Hamiltonian systems typically have very rich dynamics, and they exhibit chaotic behavior and other signatures of complexity.[24,25] This was not widely appreciated when the relaxation papers of van Hove, Prigogine, and others were written. Such phenomena will modify the dynamics of relaxation, and these effects were incorporated into the coupling model calculations. For a large class of systems, an explicitly time-dependent rate of the specific form of eq 7 was found.[12,13,22] This slowed-down time-dependent rate reflects the effects of cooperativity present in the system. The form of eq 7 is insensitive to many of the details of the system, but the specific values and properties of the parameters n, ω_c, and τ_0 are system dependent. For polymers we have found $\omega_c \cong 10^9\text{–}10^{10}$ s^{-1} typically.[20] The dynamical mechanism giving rise to eq 7 is quite general, and we have found that it is also present in realistic glasses and polymers. The predictions given by eq 8–10 follow as a direct consequence of the time-dependent rate equation (7). At present, the use of the time-dependent rate equation (7) is the only way known to obtain eq 8–10. We have previously demonstrated that eq 8–10 are quantitatively obeyed by experimental data on small molecule glasses, entangled polymer chains in the melt, and many other physical systems where cooperativity affects the dynamics.[13,15]

The parameters n, ω_c, and τ_0 appear in several different places in eq 8–10, and the properties of these equations thus become interrelated. This immediately implies several rather striking correlations for the experimental data. For instance, n appears in both eq 9 and 10. In eq 9, n governs the time dependence of the decay of the relaxation function or, equivalently, the shape of the frequency-dependent loss curve. In eq 10, n modifies the primitive τ_0, which becomes the effective relaxation time τ^*. Therefore, eq 9 and 10 imply a correlation between the shape of the relaxation spectrum and the relationship between the primitive relaxation time τ_0 and the effective (measured) one, τ^*. We have previously demonstrated that these equations quantitatively describe a great deal of experimental data.[12-20]

b. Entangled Polymer Melts. Of particular relevance to this paper, the coupling model has been found to successfully describe the viscoelastic behavior of polymer melts in the terminal zone. By assuming that the polymer chain is a primitive Rouse chain which is "coupled" to its environment (presumably through entanglements) the model successfully predicts[14,15] the molecular weight dependence of the zero-shear viscosity ($\eta_0 \propto M^{3.4}$) and relates it to the product of the plateau modulus and the steady-state recoverable compliance ($G_N^0 J_e^0 \cong 2.5$). In addition, the model accounts for the observed differences in activation energies for self-diffusion and zero-shear viscosity of Arrhenius melts in a natural way.[17] In what follows, we summarize the equations of the coupling model as applied to polymer melts. Polymer solutions require a more precise discussion of the Gaussian submolecules which appear in the primitive Rouse mode, and this is described in the following section.

In the case of melts, eq 9 and 10 are found to be relevant in the entanglement regime. The Rouse modes[11,26] of relaxation of each chain before consideration of coupling have primitive relaxation times τ_{0i} given by the familiar expression

$$\tau_{0i} = \frac{M^2}{i^2}\left(\frac{a^2\zeta_0}{6\pi^2 M_0^2 k_B T}\right) \tag{11}$$

where $i = 1, 2, \ldots$

The relaxation mechanism given by eq 11 is now acted upon by the entanglement coupling and each primitive τ_{0i} is shifted to its effective τ^*_i as described by eq 10. M is the molecular weight, M_0 is the monomer molecular weight, a is the characteristic length of the subunit, and ζ_0 is the monomeric friction coefficient at the appropriate distance from the glass temperature. In the development for entangled solutions in the next section we propose that the appropriate friction factor for entangled systems is not the monomeric friction coefficient but an entanglement friction coefficient to be described subsequently. This distinction is not important for the molecular weight and temperature dependences of melts.

In the terminal zone, the dominant contribution to the viscoelastic behavior comes from the terminal Rouse mode, τ_{01}. Then the effective relaxation time for polymer melts is from eq 10 and 11

$$\tau^*_1 \propto \zeta^*\left(\frac{M}{M_0}a\right)^{2/(1-n)} \tag{12}$$

where $\zeta^* \equiv \zeta_0^{1/(1-n)}$, and we have ignored constant prefactors.

The coupling model predicts from eq 9 that the contribution of the terminal Rouse time to the relaxation modulus $G(t)$ is

$$G(t) = G_N^0 \exp[-(t/\tau^*_1)]^{1-n} \tag{13}$$

where G_N^0 is the plateau modulus. The zero-shear viscosity is given as

$$\eta_0 = \int_0^\infty dt\, G(t) = G_N^0\tau^*_1\Gamma\left(\frac{1}{1-n}\right)\Big/(1-n) \tag{14}$$

where Γ denotes the Γ function. It has been previously shown[14,15] that the terminal relaxation of monodisperse linear entangled melts is well described by eq 13 for n in the range 0.4–0.45. For $n = 0.41$, eq 12 and 14 give immediately $\eta_0 \propto M^{2/(1-n)} = M^{3.4}$. In addition, the activation energy E^*_a of Arrhenius melts, $\zeta^* \propto \exp(E^*_a/RT)$, was shown[16] to be quantitatively related to the activation energy E_a of rotational isomerism barriers, $\zeta_0 \propto \exp(E_a/RT)$, using the same value of n. From $\zeta^* \propto \zeta_0^{1/(1-n)}$, it follows that $E^*_a = E_a/(1-n)$, and this relation has been verified. The model also successfully accounts[17] in a natural way not only for the M^{-2} dependence of the self-diffusion coefficient but also for observed differences in activation energies between the self-diffusion coefficients and zero-shear viscosities of Arrhenius melts by allowing the coupling of the chain to its environment in diffusion to be different than for flow.

For the case of entangled solutions, the problem is more subtle. The dependence on concentration comes from several different sources. This requires a more precise description of the primitive Rouse mode than was necessary for the melts. In particular, the physical meaning of the Rouse submolecule length and friction factor must be carefully examined.

III. Coupling Model Analysis of Entangled Solutions

For the polymer melt, the primitive mode relevant to the coupling model was given by the Rouse description of the chain. However, bead-spring models such as that of Rouse are useful precisely because they circumvent the complications associated with describing the local motions of the chains. The large-scale chain motions are largely independent of such local details, and thus the flexible polymer molecule can be represented as a chain of N Gaussian submolecules, each of root-mean square length σ and comprised of q monomer units. Each submolecule is characterized by a friction coefficient f_0 associated with the bead which has been related to the monomeric friction coefficient ζ_0 by $f_0 = q\zeta_0$. The quantities q, σ, and N are arbitrary as long as q is large enough for the Gaussian approximation to be valid for the subchains and N is large enough for the frictional sites to be distributed uniformly over the chain contour. The Rouse relaxation times are often written in terms of monomeric units[11] as in eq 11 since $\sigma^2N^2f_0 = a^2(M/M_0)^2\zeta_0$.

However, when the Rouse bead-spring model is used as the primitive mode in the coupling model, careful attention must be paid to the meaning of these quantities due to the coupling of the primitive mode with its surroundings. In particular, for entangled polymer melts and solutions, the coupling of each chain is through the entanglement points, and these are separated on the average by a root mean square entanglement distance l_e. Thus the coupling introduces a new length scale into the problem, and it is natural to identify the root mean square length σ of the primitive Rouse submolecules with l_e. The choice $\sigma = l_e$ is dictated by the physical interpretation of the coupling model in which a Rouse chain couples to its surroundings by entanglements. The quantity q is then the average number of monomers between entanglement points per chain, and N is the average number of entanglement points. The friction coefficient f_0 is therefore the resistance encountered by each submolecule junction (bead). We, therefore, write specifically the Rouse relaxation times in terms of these parameters as

$$\tau_{0i} = \frac{M^2}{i^2}\left(\frac{\sigma^2 f_0}{6\pi^2 M_e^2 k_B T}\right) \tag{15}$$

where $i = 1, 2, \ldots$ and $M_e = M/N$ is the average molecular weight between entanglements.

For polymer melts no distinction can be made using eq 11 or eq 15 for the primitive relaxation time. However, the development of eq 15 is important and has physical consequences for our understanding of the concentration dependences of the properties of entangled solutions which result upon using eq 15 as the primitive relaxation mode in the coupling model. The reason is that the experimental data are generally described as the product of a friction factor $\zeta(T,\phi)$ and a structure factor $g(M,\phi)$ as in eq 1. As mentioned in section I, this form is obtained by a standard operation in which the free volume (temperature and concentration) dependence of ζ is separated from the topological dependences on M and ϕ. For the response of low molecular weight polymers and for local motions in higher molecular weight polymers, it is often assumed that ζ in eq 1 can be identified with ζ_0, the monomeric friction coefficient. However, for large-scale motions of high molecular weight polymers, there is no basis for this assumption. The coupling model, on the other hand, provides a guide for the identification of ζ in eq 1. From eq 10 and 15, the coupling model predicts that the effective relaxation time for entangled polymers in the terminal zone is

$$\tau^*_1 \propto f^*\left(\frac{M}{M_e}\sigma\right)^{2/(1-n)} \qquad (16)$$

where $f^* \equiv f_0^{1/(1-n)}$ is the effective entanglement friction coefficient and again we have ignored constant prefactors. And the corresponding zero-shear viscosity is

$$\eta_0 \propto G_N^0\tau^*_1 \propto f^*G_N^0\left(\frac{M}{M_e}\sigma\right)^{2/(1-n)} \qquad (17)$$

The use of the coupling model makes possible the identification of ζ in eq 1 with the effective entanglement friction factor f^*. As we will now see, eq 17 correctly predicts the concentration dependences of the structural factor $g(M,\phi)$ in the viscosity given the concentration dependences of M_e, σ, and G_N^0.

In eq 17 there are several terms which depend upon concentration, ϕ. In addition to the free volume effect on the friction coefficient f^*, there are also concentration dependences due to topological changes in the plateau modulus G_N^0, the molecular weight between entanglements M_e, and the root mean square distance between entanglements σ. The concentration dependence of each of these parameters is not given by the coupling model. Rather, these dependences can be obtained from experiment or from models of the topology of the entangled solution which are already available in the literature. The results are generally expressed as power law relations:[7-11]

$$M_e \propto \phi^{-\alpha} \qquad (18)$$

$$\sigma \propto \phi^{-\nu\alpha} \qquad (19)$$

$$G_N^0 \propto \phi^{\gamma} \qquad (20)$$

Here we briefly outline some arguments commonly used for the values of the exponents in expressions 18–20.

First we recall that the plateau modulus can be related to the entanglement density through classical rubber elasticity theory by[11]

$$G_N^0 \propto \phi/M_e \qquad (21)$$

which implies that $\gamma = 1 + \alpha$ in eq 2. From topological arguments that the entanglement density is related to the density of binary contacts[7] between chains, it has been argued that M_e should vary as the inverse of concentration, ϕ^{-1}, thus leading to the result that $\alpha = 1$ and correspondingly $\gamma = 2$. This is essentially a mean field argument. Since σ is the root mean square distance between entanglements, it should vary as the entanglement molecular weight to a power, ν, which depends upon the chain configuration. From classical arguments $\nu = 0.5$ in Θ-solvent conditions and from a variety of theoretical arguments $\nu \cong 0.6$ in so-called good solvent conditions where excluded volume effects are important.[27] In particular, the mean field analysis of Flory[28] predicts $\nu = 3/(d + 2)$ where d is the spatial dimension. For $d = 3$, this yields $\nu = 0.6$ for the excluded-volume exponent. Values close to this are also found from numerical studies. Refinements of mean field theory have suggested the relation $\gamma = \nu d/(\nu d - 1)$ for good solvents in the semidilute region.[29,30] For $d = 3$ and $\nu = 0.6$, this predicts $\gamma = 2.25$ and correspondingly $\alpha = \gamma - 1 = 1.25$. However, experimental results suggest a value of γ in the range $2.0 < \gamma < 2.3$ independent of solvent quality,[8] in contradiction to such a relation between γ and ν.

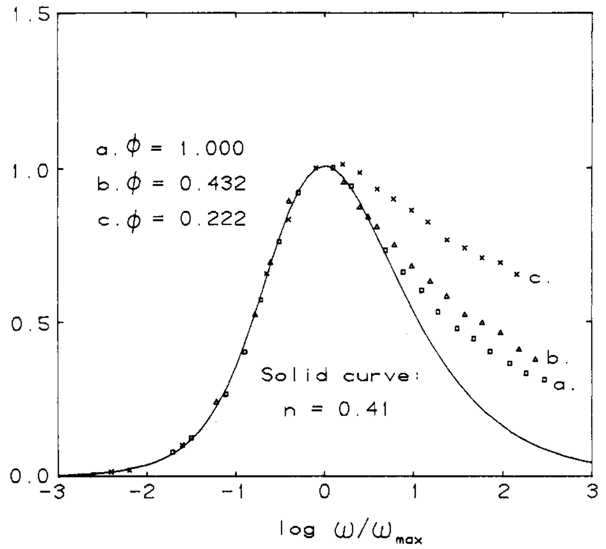

Figure 1. Reduced loss moduli data for polybutadiene solutions for the indicated volume fractions ϕ at 25 °C. The terminal dispersion is unaffected by ϕ and is well fit on the basis of a fractional exponential, eq 13, with $n = 0.41$ (solid curve). Data replotted from ref 8.

Instead of adopting one of these theoretical approaches for the values of γ, α, and ν, we will examine the coupling model for a range of values of these exponents which is within the experimentally observed limits. With these values of the exponents in expressions 18–20, the coupling model can be used to determine the concentration dependences of the terminal relaxation time and the zero-shear viscosities of entangled polymer solutions. From expressions 16, 18, and 19:

$$\tau^*_1 \propto f^*M^{2/(1-n)}[\phi^{\alpha(1-\nu)}]^{2/(1-n)} \qquad (22)$$

and from expressions 17 and 18–20:

$$\eta_0 \propto f^*M^{2/(1-n)}\phi^{\gamma}[\phi^{\alpha(1-\nu)}]^{2/(1-n)} \qquad (23)$$

These are the coupling model predictions for the molecular weight and concentration dependences of entangled solutions. Note that it has the same factorized form as eq 1. The exponent $2/(1 - n)$ describes the effects of cooperativity of the coupled chains. The cooperativity simultaneously modifies the molecular weight dependence and part of the concentration dependence of the primitive Rouse mode.

Since we know the approximate values of α, ν, and γ, eq 22 and 23 can be tested if the value of n can be determined. As discussed earlier for polymer melts, n can be independently determined by fitting the Kohlrausch decay law, eq 13, to the terminal dispersion of entangled solutions. This is illustrated in Figure 1 where we have replotted data from Raju et al.[8] of monodisperse polybutadiene solutions at different concentrations. As can be seen, the shape of the terminal dispersion (low frequency) is unaffected by ϕ and the value of n is similar to that for the undiluted case, i.e., $n \cong 0.4$–0.43. For $n = 0.41$ we evaluate eq 22 and 23 for a range of exponent values.

For good solvent conditions, $\nu = 0.6$,

$$\tau^*_1 \propto f^*M^{3.4}\phi^{1.4} \qquad \alpha = 1, \quad \gamma = 2.0 \qquad (24a)$$

$$\eta_0 \propto f^*M^{3.4}\phi^{3.4} \qquad (24b)$$

$$\tau^*_1 \propto f^*M^{3.4}\phi^{1.6} \qquad \alpha = 1.2, \quad \gamma = 2.2 \qquad (24c)$$

$$\eta_0 \propto f^*M^{3.4}\phi^{3.8} \qquad (24d)$$

For Θ-solvent conditions, $\nu = 0.5$,

$$\tau^*_1 \propto f^* M^{3.4} \phi^{1.7} \qquad \alpha = 1, \quad \gamma = 2.0 \tag{25a}$$

$$\eta_0 \propto f^* M^{3.4} \phi^{3.7} \tag{25b}$$

$$\tau^*_1 \propto f^* M^{3.4} \phi^{2.0} \qquad \alpha = 1.2, \quad \gamma = 2.2 \tag{25c}$$

$$\eta_0 \propto f^* M^{3.4} \phi^{4.2} \tag{25d}$$

These results are within reasonable agreement with what is observed experimentally.[2-9] An interesting point to note from these results is that much of the concentration dependence of the viscosity comes from the large dependence of the plateau modulus on concentration, and the change with concentration of the terminal relaxation time contributes much less. Thus, the model shows that the generally accepted procedure of writing the viscosity as a product of concentration and molecular weight to the same exponent, $\eta_0 \propto (M\phi)^x$, works only because the exponents x and y in eq 1 happen to be approximately equal.

IV. Comparison with Reptation and Scaling Predictions

It is useful to compare the coupling model predictions and results, eq 22–25, with the results from other approaches. We will discuss both the predictions of the Doi-Edwards model[31-33] based on the reptation mechanism of de Gennes and the predictions of de Gennes based on scaling concepts.[27,34,35] It will be important to emphasize that the scaling approach is separate and unrelated to the Doi–Edwards model, although this has been frequently confused in the literature. Both the reptation and scaling approaches make predictions only about the topological effects and, unlike the coupling model, neither discuss the friction coefficient. We will emphasize the predictions for the molecular weight and concentration dependences of the viscosity and terminal time, but for completeness we will also present results for the self-diffusion coefficient.

The general coupling model predictions, eq 16 and 17, had contributions to the concentration dependences from f^*, M_e, $G_N{}^0$, and σ. Similarly, the expressions obtained by Doi and Edwards contain a number of concentration-dependent quantities. Their predictions for the terminal time τ_d and zero-shear viscosity are[31]

$$\tau_d \propto M^2/Da^2 \tag{26}$$

$$\eta_0 \propto G_N{}^0 \tau_d \propto G_N{}^0 M^2/Da^2 \tag{27}$$

Here D is the curvilinear diffusion coefficient for the motion of the chain along its contour, $G_N{}^0$ is the plateau modulus, and a is the tube diameter which has been related to the distance between entanglements. Doi and Edwards do not discuss the friction coefficient. The molecular weight and concentration dependences of the former quantities are

$$D \propto \phi^{-\beta}/M \tag{28}$$

$$G_N{}^0 \propto \phi^{\gamma} \tag{29}$$

$$a \propto \phi^{-\nu\alpha} \tag{30}$$

Here we have changed the notation of ref 31 so that γ, ν, and α have the same meanings as described previously. Doi and Edwards considered only the case where $\nu = 0.5$. Little information is available concerning the value of β. However, Doi and Edwards argue that $\beta = 0$ in semidilute solutions. Using these dependences in eq 28, we find

$$\eta_0 \propto M^3 \phi^{2\nu\alpha+\gamma+\beta} \tag{31}$$

From the range of experimental values for γ and the value $\beta = 0$, we evaluate the reptation results for η_0 and τ_d. For good solvent conditions, $\nu = 0.6$,

$$\tau_d \propto M^3 \phi^{1.2} \qquad \alpha = 1, \quad \gamma = 2.0 \tag{32a}$$

$$\eta_0 \propto M^3 \phi^{3.2} \tag{32b}$$

$$\tau_d \propto M^3 \phi^{1.4} \qquad \alpha = 1.2, \quad \gamma = 2.2 \tag{32c}$$

$$\eta_0 \propto M^3 \phi^{3.6} \tag{32d}$$

For Θ-solvent conditions, $\nu = 0.5$,

$$\tau_d \propto M^3 \phi^{1.0} \qquad \alpha = 1, \quad \gamma = 2.0 \tag{33a}$$

$$\eta_0 \propto M^3 \phi^{3.0} \tag{33b}$$

$$\tau_d \propto M^3 \phi^{1.2} \qquad \alpha = 1.2, \quad \gamma = 2.2 \tag{33c}$$

$$\eta_0 \propto M^3 \phi^{3.4} \tag{33d}$$

It is well-known that the molecular weight dependence of τ_d and η_0 predicted by the Doi–Edwards model is incorrect.[9] The predicted concentration dependences are closer to the experimental values than the molecular weight dependence. The concentration dependence would change somewhat if β were nonzero, although there is presently no independent information concerning the value of β. There have also been several different recent proposals to modify the Doi–Edwards model to correct its deficiencies. Additional mechanisms such as tube leakage and constraint release have been introduced in addition to the reptation mechanism.[9,37] The effects of these modifications on the concentration dependences of τ_d and η_0 are not treated here.

The use of scaling laws have been discussed most often for the self-diffusion coefficient. However, de Gennes has also applied scaling directly to the viscosity.[34] The scaling approach makes the hypothesis that the structure factor g in eq 1 scales with concentration as $(\phi/\phi^*)^x$ where ϕ^* is the critical concentration required to produce molecular overlap and interpenetration. Then

$$\eta_0 \propto (\phi/\phi^*)^x \tag{34}$$

where the exponent is to be determined. The overlap concentration ϕ^* depends on molecular weight as

$$\phi^* \cong M/R_F{}^3 \propto M^{1-3\nu} \tag{35}$$

where the radius R_F of an isolated coil in the presence of excluded volume effects is described by $R_F \propto M^{\nu}$. Using eq 34 in eq 35, we find

$$\eta_0 \propto M^{x(3\nu-1)} \phi^x \tag{36}$$

or with $p \equiv x(3\nu-1)$

$$\eta_0 \propto M^p \phi^{p/(3\nu-1)} \tag{37}$$

Therefore the exponent for the concentration dependence can be predicted given the exponent p for the molecular weight dependence and the exponent ν. The scaling arguments make no discussion of the friction coefficient and make predictions only about the topological effects. From experimental data, $p \cong 3.4$. Then we find from eq 37

$$\eta_0 \propto M^{3.4} \phi^{6.8}, \qquad \nu = 0.5 \tag{38}$$

for a Θ solvent and

$$\eta_0 \propto M^{3.4} \phi^{4.25}, \qquad \nu = 0.6 \tag{39}$$

for a good solvent.

These results for the concentration dependence of η_0 are in very poor agreement with experimental data. Therefore the scaling hypothesis fails when applied to the zero-shear

Table I
Concentration and Molecular Weight Dependencies as Predicted by the Coupling, Reptation, and Scaling Models

model	zero-shear viscosity, η_0	self-diffusion coefficient, D_s	example
coupling[a]			
$M_e \propto \phi^{-\alpha}$, $\sigma \propto \phi^{-\nu\alpha}$	$\eta_0 \propto G_N{}^0 \tau^*{}_\eta$	$D_s \propto \langle R^2 \rangle / \tau^*{}_D \propto M/\tau^*{}_D$	$\eta_0 \propto f^*{}_\eta M^{3.4} \phi^{3.4}$ ($\nu = 0.6$), $\eta_0 \propto f^*{}_\eta M^{3.4} \phi^{3.7}$ ($\nu = 0.5$); $n_\eta = 0.41$, $\alpha = 1$, $\gamma = 2.0$
$G_N{}^0 \propto \phi^\gamma$	$\tau^*{}_\eta \propto f^*{}_\eta M^{2/(1-n_\eta)} [\phi^{\alpha(1-\nu)}]^{2/(1-n_\eta)}$	$\tau^*{}_D \propto f^*{}_D M^{2/(1-n_D)}$	
$G(t) \cong G_N{}^0 \exp[-(t/\tau^*{}_\eta)^{1-n_\eta}]$	$\eta_0 \propto f^*{}_\eta M^{2/(1-n_\eta)} \phi^\gamma [\phi^{\alpha(1-\nu)}]^{2/(1-n_\eta)}$	$D_s \propto f^*{}_D{}^{-1} M^{1-[2/(1-n_D)]}$	$D_s \propto f^*{}_D{}^{-1} M^{-2}$, $n_D = {}^1/_3$ (concn dependence not yet calcd)
reptation[b]			
$D \propto \phi^{-\beta} M^{-1}$, $a \propto \phi^{-\nu\alpha}$	$\eta_0 \propto G_N{}^0 \tau_d$	$D_s \propto a^2 D/M$	$\eta_0 \propto M^3 \phi^{3.2}$, $\eta_0 \propto M^3 \phi^3$
$G_N{}^0 \propto \phi^\gamma$	$\tau_d \propto M^2/Da^2 \propto M^3 \phi^{2\nu\alpha+\beta}$	$D_s \propto M^{-2} \phi^{-2\nu\alpha-\beta}$	$D_s \propto M^{-2} \phi^{-1.2}$ ($\nu = 0.6$), $D_\alpha \propto M^{-2} \phi^{-1}$ ($\nu = 0.5$)
	$\eta_0 \propto M^3 \phi^{2\nu\alpha+\gamma+\beta}$		$\beta = 0$, $\alpha = 1$, $\gamma = 2.0$
scaling[c,d]	$\eta_0 = \eta_{00} (\phi/\phi^*)^x$	$D_s = D_s{}^0 (\phi/\phi^*)^y$	$\eta_0 \propto M^{3.4} \phi^{4.25}$ ($\nu = 0.6$), $\eta_0 \propto M^{3.4} \phi^{6.8}$ ($\nu = 0.5$)
	$\phi^* \propto M^{1-3\nu}$	$\phi^* \propto M^{1-3\nu}$, $D_s{}^0 \propto M^{-\nu}$	$D_s \propto M^{-2} \phi^{-1.75}$ ($\nu = 0.6$), $D_s \propto M^{-2} \phi^{-3}$ ($\nu = 0.5$);
	$\eta_0 \propto M^p \phi^{p/(3\nu-1)}$	$D_s \propto M^{-q} \phi^{(\nu-q)/(3\nu-1)}$	$p = 3.4$, $q = 2.0$

[a] This work and ref 13–17. [b] References 31–33, 39, 40. [c] References 34–36, 41. [d] Assume scaling form; obtained concentration exponents from molecular weight exponents p and q; note, p and q can be taken from experiment or *any* viable model.

viscosity. It is more widely known that scaling is more successful when applied to the self-diffusion coefficient D_s, at least over a limited range of concentration.[34,36,38] The scaling result for D_s is

$$D_s \propto M^{-q} \phi^{(\nu-q)/(3\nu-1)} \tag{40}$$

Again the exponent for the concentration dependencies can be predicted given the exponent q for the molecular weight dependence and the exponent ν. From experimental data, $q \cong 2.0$. Then we find from eq 40

$$D_s \propto M^{-2} \phi^{-3}, \qquad \nu = 0.5 \tag{41}$$

for a Θ solvent and

$$D_s \propto M^{-2} \phi^{-1.75}, \qquad \nu = 0.6 \tag{42}$$

for a good solvent. It has not been adequately explained why scaling appears to work for self-diffusion but fails for the viscosity.

If an independent theory were available which correctly predicted the molecular weight dependence of D_s, this could also be used to provide the value of q. For instance, the coupling model[17] and the reptation model both give $q = 2$ and either of these models could be used in conjunction with the scaling hypothesis to obtain eq 41 and 42. However, the scaling hypothesis is separate and independent of these models. This point is frequently misunderstood in the literature. Several workers have associated the success of scaling for self-diffusion with the reptation model.[29,34-36] But the value of $q = 2$ can be provided by any model that predicts $D_s \propto M^{-2}$ or it can be taken from experiment. Scaling is independent of reptation. The Doi–Edwards model by itself makes prediction for both the molecular weight and concentration dependencies of the self-diffusion coefficient. The expression for the self-diffusion coefficient in the Doi–Edwards model[31] is

$$D_s \propto Da^2/M \tag{43}$$

or in terms of the dependences in eq 28–30

$$D_s \propto M^{-2} \phi^{-2\nu\alpha-\beta} \tag{44}$$

For $\beta = 0$ and using the values $\nu = 0.5$ and $\alpha = 1$, we find

$$D_s \propto M^{-2} \phi^{-1.0} \tag{45}$$

and the values $\nu = 0.6$ and $\alpha = 1$ give

$$D_s \propto M^{-2} \phi^{-1.2}$$

This result differs from the scaling result and is in poor agreement with experiment. This failure of the reptation model has prompted the use of reptation in conjunction with scaling to describe the concentration dependence. However, since scaling and reptation predict different concentration dependencies, such a procedure is inconsistent. It remains to be determined how the more recent modified versions of reptation will alter these concentration dependencies.

The coupling model has been shown to be a consistent approach that correctly predicts both the molecular weight and concentration dependencies for the zero-shear viscosity and terminal relaxation time of monodisperse entangled solutions. Motions of a Rouse chain with submolecules on the order of the entanglement length are modified by coupling to entanglements. The values of the molecular weight and concentration exponents are related to the shape of the terminal relaxation spectrum, as measured by n, and to the concentration dependences of the plateau modulus, entanglement length, and entanglement molecular weight. The viscosity appears in a factorized form as in eq 1, and the friction coefficient ζ is now identified with the effective entanglement friction factor f^*.

We have previously shown that the same coupling model correctly predicts the molecular weight and temperature dependences for the viscosity and self-diffusion coefficient of polymer melts.[14-17] In particular, the coupling model is the only approach that explains the differences in activation energies for viscosity and self-diffusion in Arrhenius melts.[17] The molecular weight and temperature dependences of the self-diffusion coefficient from the coupling model are

$$D_s \propto f^*{}_D{}^{-1} M^{1-[2/(1-n_D)]} \tag{46}$$

where $f^*{}_D(T) \propto f_0{}^{1/(1-n_D)}$ and in general the self-diffusion coupling parameter n_D may differ from the viscosity coupling parameter n discussed earlier. Predictions of the concentration dependences for the self-diffusion coefficient requires that a complete expression for D_s be derived within the coupling model. This is a more involved calculation than for the viscosity, and it has not yet been carried out. For convenience, we summarize many of the predictions and results for the coupling, reptation, and scaling theories in Table I.

V. Summary and Conclusions

A model of entangled polymer solutions and melts has been presented which gives results for the molecular weight and concentration dependencies of the terminal relaxation time and zero-shear viscosity. The results agree well with the experimentally observed behavior of real polymer systems, i.e., $\tau_d \propto M^{3.4}\phi^z$, $\eta_0 \propto M^{3.4}\phi^y$ with $z = 1.4$–1.7 and $y = 3.4$–3.7.

The model is based upon the coupling model for relaxation in complex systems in which a single (primitive) relaxation mechanism is slowed down due to environmental coupling and thereafter follows a nonexponential decay law. Upon assuming that the primitive relaxation mechanism for entangled polymers is defined by the Rouse model, but slowed due to entanglement coupling, several results become apparent. First, there is a natural separation of the viscosity functions into a friction factor multiplied by the molecular weight to some power, x, and the concentration to a different power, y. The exponents x and y are shown to be similar but due to different topological contributions. The M^2 dependence of viscosity in the Rouse model is naturally scaled to a $M^{3.4}$ power through the coupling parameter, n. However, the concentration dependence arises from a dependence of the plateau modulus on changing concentration multiplied by the terminal relaxation time which is modified by the coupling parameter.

The physics of the model suggests that for both melts and solutions the friction factor of interest in the terminal region is an entanglement friction factor rather than the monomeric friction factor that is normally used. Furthermore, the behavior of entangled polymer systems is represented here by a Rouse-like model in which the Rouse Gaussian subunit is the chain between entanglement points. The full implications for polymer chain dynamics have not yet been completely explored.

Registry No. Polybutadiene, 9003-17-2.

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(39) Reference 31, eq 2.1, 2.6, and 4.12. Notation has been adjusted to conform with ours.
(40) Reference 33, eq 5.9–5.11. Notation has been adjusted to conform with ours.
(41) Reference 35, eq IV.3–V.3. Notation has been adjusted to conform with ours.