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Viscometric Properties of Block Polymers near a Critical Point

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ABSTRACT: The three viscometric coefficients for the disordered phase of a diblock copolymer melt near its critical point are calculated from a dynamical mean field theory. The zero-shear-rate limits of these coefficients are respectively the steady shear viscosity η, the first normal stress coefficient Ψ_1, and the second normal stress coefficient Ψ_2. We find that all three coefficients are singular as the critical point is approached, scaling respectively as $a^{-3/2}$, $a^{-5/2}$, and $a^{-5/2}$, where $a = 2(\chi N)_s - 2\chi N$ is a measure of the temperature difference from criticality. χ is the usual Flory interaction parameter, χ_s is its value on the classical (Leibler) spinodal, and N is the total number of statistical segments on each block copolymer chain. While the critical contributions to η and Ψ_1 are positive in sign and are predictable from previous results for the dynamic shear modulus of diblocks, Ψ_2 is an independent measurable that is found to be negative and of the same order of magnitude as Ψ_1. These results provide a basis for the quantitative interpretation of mechanical or optical experiments on near-critical block copolymers under flow.

I. Introduction

In an earlier paper[1] (part I), the contributions of critical fluctuations to the dynamic shear modulus and the steady shear viscosity of the disordered phase of diblock copolymer melts were calculated by a mean field approach. We found that near the critical point and at sufficiently low frequencies, the critical contributions to these viscoelastic functions swamp the ordinary contributions from reptation or Rouse modes of relaxation. The critical contributions become singular as $a = 2(\chi N)_s - 2\chi N$ approaches zero. Here, the Flory interaction parameter is denoted χ, N is the number of statistical segments per chain, and $(\chi N)_s$ is the value of χN on the spinodal curve predicted by Leibler.[2] The most strongly singular function is $G'(\omega)$, the storage modulus, which scales like $\omega^2 a^{-5/2}$ at low frequency. It was found that the loss modulus, $G''(\omega)$, shows a weaker singularity, scaling at low frequency as $G''(\omega) \sim \omega a^{-3/2}$. The storage and loss moduli[3] are the contributions respectively in phase and 90° out of phase with a low-amplitude oscillatory shear strain. The zero-shear viscosity, i.e., the steady shear viscosity at asymptotically small shear rates, was found to scale as $a^{-3/2}$.

These singularities are much stronger than those predicted by mean field theories for mixtures of small molecules[4,5] or for homopolymer blends near a critical point. While such systems exhibit the critical behavior of the Ising universality class, diblock copolymer melts are describable by a coarse-grained Hamiltonian that belongs to the Brazovskii universality class.[2,18,22,23] Systems in the latter class have the property that the disordered phase becomes unstable at the spinodal temperature with respect to composition fluctuations with *nonzero* wavevectors. These unstable modes lie within a particular surface in reciprocal space. For example, at equilibrium, Leibler[2] predicted that the scattering function of diblocks will diverge on the spinodal for all wavevectors of magnitude k^*, roughly one over the radius of gyration of a molecule. Under homogeneous flows, whose velocity gradient tensor is characterized by having at least one eigenvalue that is zero or pure imaginary (such as simple shear flow), the mean field theory developed in ref 6 predicts that diblocks retain a finite band of unstable nonzero wavevectors. In contrast, mixtures of small molecules or homopolymer blends become unstable at the classical spinodal only to composition fluctuations with *zero* wavevector. This difference has a profound effect on the structure of the respective dynamical mean field theories and leads to the prediction of stronger viscoelastic singularities for the diblock copolymer case.

Because of their strong singular character, the critical contributions to rheological properties should be much easier to observe in block polymers than in conventional binary mixtures. Indeed, critical contributions to $G'(\omega)$ and $G''(\omega)$ may have been observed in the experiments of Bates[7] with blocks of 1,2- and 1,4-polybutadiene. Although a quantitative comparison of his measurements with the theory is not possible,[1,8] Bates found $G'(\omega)$ to be more sensitive to the distance from the critical point than $G''(\omega)$, in agreement with the predicted scaling. We hope that the theory developed in part I and extended in the present work will stimulate further experiments.

In this paper, we calculate the critical contributions to the low shear rate *viscometric coefficients*; these are obtained from the components of the stress tensor in a *viscometric flow*. A viscometric flow is a homogeneous simple shear flow or a flow that is a homogeneous simple shear flow in a suitably rotating frame. For all viscometric flows, a frame of reference can be chosen so that the velocity gradient tensor, **E** is

$$\mathbf{E} = \begin{bmatrix} 0 & \dot\gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad (1)$$

where $\dot\gamma$ is the shear rate. The viscometric coefficients in this frame are the shear viscosity $\eta \equiv \sigma_{12}/\dot\gamma$, the first normal stress coefficient $\Psi_1 \equiv (\sigma_{11} - \sigma_{22})/\dot\gamma^2$, and the second normal stress coefficient $\Psi_2 \equiv (\sigma_{22} - \sigma_{33})/\dot\gamma^2$, where σ_{ij} is the ij component of the stress tensor. Only *differences* in normal stress components can be measured because the stress tensor for an incompressible fluid is only determined to within an isotropic term. (This isotropic term is related to the pressure, which in experiments is controlled by the boundary conditions.) The normal stresses are even functions of shear rate and in a low shear rate expansion have leading order terms that are quadratic in $\dot\gamma$. In contrast, the shear stress is linear in $\dot\gamma$ at low shear rates. Hence, the viscometric coefficients, η, Ψ_1, and Ψ_2, approach constant values in the limit of vanishingly small shear rates.

II. Mean Field Dynamics

The basic premise in the formulation of our theory is that sufficiently close to the critical point, the low-frequency dynamics of block copolymer melts are dominated by the slow relaxation of an order parameter field $\psi(\boldsymbol{x})$. For a diblock copolymer the order parameter[2] is frequently assumed to be related to the density field for segments of component A by the expression, $\psi(\boldsymbol{x}) \equiv \rho_A(\boldsymbol{x})/\rho - f$, where $\rho_A(\boldsymbol{x})$ is the local density of A segments at point $\boldsymbol{x}$, ρ is the overall (A plus B) segment density, and f is the fraction of type A segments on each chain. The dynamic shear modulus in part I and the viscometric coefficients in the

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present paper are calculated from a Fokker–Planck equation that describes the time evolution of $P[\psi]$, the distribution function of order parameter fluctuations. This equation can be written[6]

$$\frac{\partial}{\partial t} P[\psi,t] = \int_{\mathbf{k}} \frac{\delta}{\delta\psi_{\mathbf{k}}} \left\{ k^2\lambda(k)\left[\frac{\delta}{\delta\psi_{-\mathbf{k}}} + \beta\frac{\delta H}{\delta\psi_{-\mathbf{k}}}\right] - \boldsymbol{k}\cdot\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}\psi_{\mathbf{k}}\right\} P[\psi,t] \tag{2}$$

where $\psi_{\mathbf{k}} = \int \mathrm{d}\boldsymbol{x}\, e^{i\mathbf{k}\cdot\mathbf{x}}\psi(\boldsymbol{x})$ is the Fourier component of $\psi(\boldsymbol{x})$ with wavevector $\boldsymbol{k}$, $\beta = 1/k_{\mathrm{B}}T$, and we have adopted the shorthand $\int_{\mathbf{k}} \equiv \int \mathrm{d}\boldsymbol{k}/(2\pi)^3$. The magnitude of $\boldsymbol{k}$ is denoted k, and all lengths and reciprocal wavevectors are expressed in units of $\rho^{-1/3}$. In eq 2 $H = H[\psi]$ is an effective Hamiltonian,[18] which describes the energy penalty associated with a spatial fluctuation in component density. The first term in the braces of eq 2 describes the thermodynamic force that drives $P[\psi,t]$ to relax toward its equilibrium distribution, while the second term describes convection of the order parameter by the average velocity field $\nu(\boldsymbol{x}) = \mathbf{E}\cdot\boldsymbol{x}$. The quantity $\lambda(k)$ is a phenomenological Onsager coefficient.

We adopt a mean-field, quadratic approximation for the Hamiltonian[1,6,9,18]

$$\beta H[\psi] = \frac{1}{2}\int_{\mathbf{k}} S_0^{-1}(k)\psi_{\mathbf{k}}\psi_{-\mathbf{k}} \tag{3}$$

where $S_0^{-1}(k)$ is the reciprocal of the equilibrium static structure factor ($S_0(k) = \langle\psi_{\mathbf{k}}\psi_{-\mathbf{k}}\rangle_{\mathrm{eq}}$). The static structure factor (scattering function) has been computed in the random phase approximation for diblock copolymers by Leibler.[2] Leibler's result is

$$NS_0^{-1}(k) = F(k^2R^2,f) - 2\chi N \tag{4}$$

where R is the radius of gyration of a molecule,

$$F(x,f) \equiv \frac{g(1,x)}{g(f,x)g(1-f,x) - \frac{1}{4}[g(1,x) - g(f,x) - g(1-f,x)]^2} \tag{5}$$

and

$$g(f,x) \equiv 2x^{-2}[fx + \exp(-fx) - 1] \tag{6}$$

The viscometric coefficients near the critical point are dominated by the behavior of $S_0(k)$ near its sharply peaked maximum at a wavevector k^*. To extract the most singular contributions to these coefficients, we use the following approximation for Leibler's structure factor:[1,18,19]

$$NS_0^{-1}(k) = F(x,f) - 2\chi N \approx \frac{[x^* - x]^2}{2f(1-f)x} + a \tag{7}$$

where $x = (Rk)^2$, and $x^* \equiv (Rk^*)^2$ is given by

$$x^* = \left[\frac{3}{f(1-f)}\right]^{1/2} \tag{8}$$

In eq 7, $a = 2(\chi N)_{\mathrm{s}} - 2\chi N$, where $(\chi N)_{\mathrm{s}}$ is defined as the spinodal value of χN obtained by Leibler.[2] [$(\chi N)_{\mathrm{s}} = 10.5$ in the case of a symmetric melt with $f = {}^1/_2$.] The above approximation for the equilibrium structure factor preserves the limiting behavior of eq 4 at both large and small k and its accuracy for intermediate wavevectors was verified in ref 18 and 19.

In the present calculations, we make use of an expression derived by Binder[9] for the transport coefficient $\lambda(k)$ that appears in eq 2

$$\lambda(k) = \frac{1}{2}NR^2\tau^{-1}g(1,x) \tag{9}$$

where the terminal relaxation time of the block copolymer melt far from the critical point (in the disordered phase)[21] is denoted τ. Equation 9 was employed in earlier calculations of the low-frequency dynamics of diblocks.[1,6] It was originally derived, however, for noninteracting ($\chi = 0$) homopolymer mixtures by Binder[9] and is numerically very similar to an expression given by Pincus.[20] Arguments can be given for its applicability to the present case of diblock copolymers.[6,21] It turns out, however, that the detailed wavevector dependence of λ has no effect on the scaling exponents of the viscometric coefficients or the dynamic moduli at low frequency. In contrast, the prefactors in the scaling relations derived below do depend on the choice of $\lambda(k)$.

The above equations define the evolution of the distribution of order parameter fluctuations for an arbitrary deformation history. In the present paper we are concerned only with the steady-state distribution in the presence of a weak shearing flow ($\dot\gamma\tau \ll 1$). The general steady-state solution of eq 2 for flows of arbitrary strength has been considered in ref 6.

In part I we derived the shear stress of a near-critical diblock melt from the distribution function, $P[\psi]$, using a simple virtual work argument. Other investigators[10] have derived the complete stress tensor, σ_{ij}, from related arguments. For an incompressible material the stress tensor is

$$\sigma_{ij} = \frac{1}{2}\int_{\mathbf{k}} \left\langle \left(k_i \frac{\partial}{\partial k_j}\psi_{\mathbf{k}} + k_j\frac{\partial}{\partial k_i}\psi_{\mathbf{k}}\right)\frac{\delta H}{\delta\psi_{-\mathbf{k}}}\right\rangle \tag{10}$$

to within an isotropic term. Here the angular brackets denote an average over the steady-state distribution function, $P_{\mathrm{ss}}[\psi]$. For the quadratic Hamiltonian, eq 3, this leads to

$$\sigma_{ij} = -k_{\mathrm{B}}T\int_{\boldsymbol{k}} k_ik_jS(\boldsymbol{k})\frac{\partial}{\partial k^2}S_0^{-1}(k) \tag{11}$$

where $S(\boldsymbol{k}) = \langle\psi_{\mathbf{k}}\psi_{-\mathbf{k}}\rangle$ is the steady-state (nonequilibrium) structure factor. As discussed in part I, the wavevector integral in eq 11 should be cut off at large k for the case of high strain rates. For the low-shear-rate results reported here, however, the cutoff is unnecessary.

III. Viscometric Coefficients

To compute η, Ψ_1, and Ψ_2 to lowest order in $\dot\gamma$, we follow the procedure in ref 6 and expand $S(\boldsymbol{k})$ in a perturbation series in $\dot\gamma$,

$$S(\boldsymbol{k}) = S_0 + S_1 + S_2 + \ldots \tag{12}$$

where S_i is ith order in $\dot\gamma$ and $S_0 = S_0(k)$ is the equilibrium structure factor given in eq 7. The first-order term S_1 is sufficient to compute η, but the second-order term is required for the leading contributions to Ψ_1 and Ψ_2. Explicit expressions for the S_i, obtained from eq 2, are

$$S_1 = \frac{-2DR^2k_xk_y\,\partial F/\partial x}{xg\Omega^3} \tag{13}$$

$$S_2 = -2D^2R^2k_x^{\,2}\left\{\frac{\partial F/\partial x}{x^2g^2\Omega^4} + \frac{2k_y^{\,2}R^2}{xg\Omega}\frac{\partial}{\partial x}\left[\frac{\partial F/\partial x}{xg\Omega^3}\right]\right\} \tag{14}$$

where

$$\Omega \equiv NS_0^{-1}(k) = F(x,f) - 2\chi N \tag{15}$$

and $g \equiv g(1,x)$ are given by eq 6 and 7. $D \equiv \dot\gamma\tau$ is the "Deborah number", a dimensionless shear rate expressed in units of the terminal relaxation time, τ. When the above expansion for $S(\mathbf{k})$ is inserted into the equation for the stress tensor, one obtains the leading order (in $\dot{\gamma}$) contributions to η, Ψ_1, and Ψ_2. The most singular parts of these viscometric coefficients are found to be

$$\eta = \left(\frac{2}{3}\right)^{1/2} \frac{k_{\mathrm{B}}T\tau[x^*]^2}{120\pi R^3 g(1,x^*) a^{3/2}} \tag{16}$$

$$\Psi_1 = \left(\frac{2}{3}\right)^{1/2} \frac{k_{\mathrm{B}}T\tau^2 x^*}{120\pi R^3 g^2(1,x^*) a^{5/2}} \tag{17}$$

$$\Psi_2 = \left(\frac{2}{3}\right)^{1/2} \frac{k_{\mathrm{B}}T\tau^2 x^*}{3360\pi R^3 g^2(1,x^*) a^{5/2}} \left[12\left(\frac{x}{g(1,x)} \times \frac{\partial g(1,x)}{\partial x} \right)_{x=x^*} - 11 \right] \tag{18}$$

These results for the shear viscosity and the first normal stress coefficient at low shear rates could have been predicted from the linear viscoelastic functions $G'(\omega)$ and $G''(\omega)$ at low frequency;[3] namely $\eta = \lim_{\omega\to0} G''(\omega)/\omega$ and $\Psi_1 = \lim_{\omega\to0} 2G'(\omega)/\omega^2$. Equations 16 and 17 are consistent with the expressions for $G'(\omega)$ and $G''(\omega)$ obtained in part I.[25] The second normal stress coefficient, however, is not predictable from the complex modulus. Because $\partial g/\partial x|_{x^*} < 0$, the sign of Ψ_2 is *negative*, in agreement with what is typically found in noncritical polymer solutions or melts.[3,11] It is also of interest to note that Ψ_2 exhibits the same $a^{-5/2}$ temperature dependence as Ψ_1. For the case of a symmetric copolymer with $f = {}^1/_2$, $xg^{-1}\,\partial g/\partial x|_{x^*}$ is found from eq 6 and 8 to be approximately −0.655. The ratio $|\Psi_2|/|\Psi_1|$ then follows from eq 17 and 18 and is found to be 0.68. Hence, our theory predicts that near the critical point the second normal stress coefficient should be only slightly smaller in magnitude than Ψ_1.

This sharply contrasts with noncritical polymer solutions or melts,[11] where Ψ_2/Ψ_1 has been found to lie in the range −0.05 to −0.20; i.e., Ψ_2 is considerably smaller in magnitude than Ψ_1 for noncritical polymeric fluids. Thus, measurements of Ψ_2 in the low shear rate regime for near-critical diblock polymers should provide a sensitive test of the theory. The value of Ψ_2 deduced from the theory is influenced by three contributions: the *curvature* of the equilibrium scattering function near its peak, the *asymmetry* of $S_0(k)$ at the peak, and the k dependence of the Onsager coefficient. Only the first of these, the curvature of $S_0(k)$, affects the magnitudes of Ψ_1 and η, although they do depend on the value of $\lambda(k)$ at $k = k^*$. Measurements of η, Ψ_1, and Ψ_2 for near-critical diblock melts could provide useful information regarding the applicability of Binder's expression for the Onsager coefficient to copolymer systems.

The steady-state rheological properties of diblocks in any sufficiently slow homogeneous flow can be obtained from the three viscometric coefficients computed here. The stress tensor, σ, to second order in the velocity gradient for an arbitrary flow is[17]

$$\sigma = 2\eta\mathbf{D} - \Psi_1\overset{\circ}{\mathbf{D}} + (2\Psi_1 + 4\Psi_2)\mathbf{D}^2 \tag{19}$$

where

$$\overset{\circ}{\mathbf{D}} \equiv \dot{\mathbf{D}} - \boldsymbol{w}^T\!\cdot\mathbf{D} - \mathbf{D}\cdot\boldsymbol{w}$$

Here

$$\mathbf{D} \equiv {}^1\!/_2(\mathbf{E} + \mathbf{E}^T)$$

is the symmetric part of the velocity gradient tensor, and

$$\boldsymbol{w} \equiv {}^1\!/_2(\mathbf{E} - \mathbf{E}^T)$$

is the antisymmetric part. $\dot{\mathbf{D}}$, the substantial time derivative of $\mathbf{D}$, is zero in homogeneous steady extensional flows, i.e., steady flows free of vorticity. Note that when $-\Psi_2/\Psi_1 > {}^1/_2$, as was predicted to be the case for symmetric diblock melts sufficiently near the critical point, the coefficient of $\mathbf{D}^2$ is *negative*. This means that the first deviation from constancy in the uniaxial extensional viscosity will be a *decrease* in the viscosity with increasing deformation rate. This prediction also contrasts with the behavior of typical noncritical polymeric fluids.

The above mean field results for the scaling behavior of the viscometric coefficients of diblock copolymers are expected to be applicable to experiments in the disordered phase close to the critical point. Furthermore, because such systems are expected to exhibit singular *form* birefringence and dichroism,[24,26] both optical and mechanical experiments could be used to test the theory.

Although dynamical mean field theories for mixtures of small molecules are known to break down near the critical point,[12] corresponding theories for homopolymer mixtures are believed to be good, except extremely close (within $1/N$) to the critical point.[9,13–16] The accuracy of mean field theory for the kinetics of block copolymers is not yet known. However, we have recently studied corrections to mean field theory for the *equilibrium* properties of diblock melts.[23] It was found that Leibler's prediction of a second-order transition for symmetric diblocks at $\chi N = 10.5$ is correct only for infinite molecular weight. For experimentally realizable systems with finite N, a first-order transition at[23] $(\chi N)_t = 10.5 + 41.0N^{-1/3}$ was found in place of the continuous transition. Although systems exhibiting first-order transitions have no true critical singularities, the present mean field results likely have some range of validity for large N. In such a case the transition is near second order, so it is probable that the scaling laws discussed above will be observed in the vicinity of the phase transition, except at temperatures very near $(\chi N)_t$. At such temperatures the divergences predicted for the viscometric coefficients and dynamic moduli will be cut off. It is hoped that experiments to test the ideas presented here will shed some light on these issues.

References and Notes

(1) Fredrickson, G. H.; Larson, R. G. *J. Chem. Phys.* **1987**, *86*, 1553.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(3) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(4) Sallavanti, R.; Fixman, M. *J. Chem. Phys.* **1968**, *48*, 5326.
(5) Yamada, T.; Kawasaki, K. *Prog. Theor. Phys.* **1967**, *38*, 1031.
(6) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 5306.
(7) Bates, F. S. *Macromolecules* **1984**, *17*, 2607.
(8) A quantitative comparison of the theory with the experiments of Bates is not possible because of some uncertainty in the location of the critical point for the experimental system. Bates, F. S., private communication.
(9) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(10) Wegner, F. J. In *Phase Transitions and Critical Phenomena*; Domb, C., Green, M. S., Eds.; Academic: New York, 1976; Vol. 6.
(11) Tanner, R. I. *Engineering Rheology*; Oxford: New York, 1985.
(12) Hohenberg, P. C.; Halperin, B. I. *Rev. Mod. Phys.* **1977**, *49*, 435.
(13) de Gennes, P. G. *Scaling Concepts in Polymer Physics*: Cornell University Press: Ithaca, NY, 1979.
(14) de Gennes, P. G. *J. Phys. Lett.* (*Paris*) **1977**, *38* , L-441.
(15) Joanny, J. F. *J. Phys. A* **1978**, *11*, L-117.
(16) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 3556.
(17) Larson, R. G. *Rheologica Acta* **1985**, *24*, 443.
(18) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(19) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1986**, *19*, 2501.
(20) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.
(21) In ref 1 and 6 explicit expressions were given for the composition dependence of τ that follows from the homopolymer theories. These expressions should not be taken seriously;

instead τ should be determined from dynamical measurements on the appropriate diblock melt in the disordered phase far from the critical point.
(22) Brazovskii, S. A. *Sov. Phys. JETP (Engl. Transl.)* **1975**, *41*, 85.
(23) Fredrickson, G. H.; Helfand, E. H. *J. Phys. Chem.*, in press.
(24) Onuki, A.; Doi, M. *J. Chem. Phys.* **1986**, *85*, 1190.
(25) Equation 4.15 of ref 1 is in error by a factor of 2. The correct result is 2 times the expression for $G'(\omega)$ given in that equation.
(26) Fredrickson, G. H. submitted for publication in *Macromolecules*.

Dynamics of Polymers in Polydisperse Melts

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ABSTRACT: The dynamical behavior of a mixture of two narrow molecular weight distribution homopolymers is analyzed on the basis of the concepts of reptation and constraint release. We propose that constraint release causes not only tube renewal (the relaxation of the tube) but also tube dilation (the enlargement of the effective tube diameter). A general scheme of accounting for these effects is given. As an example, the rheological properties of the mixture are analyzed in the entire parameter space, which consists of the molecular weights of each component and the mixing ratio. It is shown that even though the molecular weight dependence of the longest relaxation time is reptation-like the shape of the relaxation modulus can be Rouse-like.

1. Introduction

In a melt of polymers of high molecular weight, it is now well established that molecular motion is dominated by reptation, the slithering motion of a polymer through a tubelike region formed by surrounding polymers.[2,3] For polymer melts of narrow molecular weight distribution, the diameter of the tube is an intrinsic property of the polymer and is characterized by the entanglement molecular weight M_e. In this case, the tube can be assumed, in the first approximation, to be fixed during the characteristic time of reptation.

The fixed-tube assumption becomes invalid if the system has a broad molecular weight distribution. Consider for example a system having a bimodal distribution of molecular weight, i.e., a mixture of short (S) and long (L) polymers. If the molecular weight of the short polymers M_S is close to that of the long polymers, M_L, the fixed-tube assumption will be valid. However, as M_S decreases, the constraints imposed by the short polymers must become weaker, and in the extreme case of M_S being comparable to that of monomers, the constraints that are due to the short polymers become effectively null. A natural question is how such weakening of the tube takes place when the molecular weight M_S and the volume fraction ϕ_S of the short polymers are varied. The purpose of this paper is to give a qualitative answer to that question.

In the limiting case of a dilute blend ($\phi_L = 1 - \phi_S \rightarrow 0$), theories for the problem have been presented in the context of the diffusion of a polymer in a matrix,[4,5] and the results have been confirmed by experiments using forward recoil spectroscopy.[6,7] On the other hand, the case of finite concentration, which is particularly important for rheological properties, has not been investigated in detail.

Experimentally, considerable work has been done to find "blending laws" for rheological properties.[8-10] Although success has been achieved in some individual studies, the blending laws are empirical and do not seem to have general validity. This is not surprising considering that many parameters are involved in the problem: even in the simplest case of a bimodal distribution there are already three independent parameters M_L, M_S, and ϕ_L, which leads to a rather complex analysis. In general polydisperse melts, there is no guarantee that the system can be characterized by a few kinds of average molecular weight. In this paper, we do not attempt to give a general blending law. Rather we offer some theoretical guidelines for this complex problem by examining the bimodal distribution case in detail.

According to the pure reptation model, the relaxation modulus $G(t)$ of a blend of two monodisperse samples obeys the linear additivity law[11]

$$G(t) = \phi_L G_L(t) + \phi_S G_S(t) \tag{1.1}$$

where $G_L(t)$ and $G_S(t)$ are the relaxation moduli of the pure components. This simple relation, however, is inconsistent with many experiments.[9,10,12-15] Amendment of the theory has been made,[16-19] but so far the understanding has been limited to the special cases in the parameter space spanned by (M_L, M_S, ϕ_L).

In this paper we shall discuss the behavior of a polymer blend in the entire parameter space. We shall divide the space into regimes and discuss their characteristic features. Such a delineation will be useful to interpret experimental data and to plan further experiments.

The basic proposal of this paper is that the tube diameter of long chains can change when short chains are added. We shall call this effect tube dilation. (Tube dilation should not be confused with the concept proposed recently by Marrucci[20] and Viovy,[21] who argued that even in monodisperse systems the tube diameter increases as the stress relaxes. We do not take this view. In our theory, tube dilation takes place only for polymer blends, not in monodisperse systems.)

The idea that the tube in blends may dilate has been suggested by several authors.[12,19,22] However, no systematic theory has been given to estimate the effect. In this paper we shall propose a general method of estimating tube dilation and its effect on diffusion and rheological properties. Although the method can be applied to a general polydisperse system, we shall focus our attention to a

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