Macromolecules 1986, *19*, 1754-1760

Effects of Polydispersity on the Linear Viscoelastic Properties of Entangled Polymers. 2. Comparison of Viscosity and Recoverable Compliance with Tube Model Predictions

William W. Graessley*[1] **and Mark J. Struglinski**[2]

Chemical Engineering Department, Northwestern University, Evanston, Illinois 60201.

Received February 21, 1986

ABSTRACT: We present here some comparisons between the values of zero-shear viscosity η_0 and recoverable compiance $J_e°$ measured for binary mixtures of nearly monodisperse linear polybutadiene and calculated with a theory based on the tube model. Reptation is assumed to be the primary motion, but allowance is made for tube renewal through the release of constraints that confine the chains. Fluctuation effects are also included, although in a rather simplified fashion and mainly as a device to force agreement with $\eta_0(M)$ for the pure components. The results for viscosity are quite satisfactory. Good agreement for the mixtures is obtained with a choice for the constraint release parameter that is consistent with independent estimates from tracer diffusion and relaxation studies. Agreement with J_e^0 is less satisfactory although the general trends and magnitudes are reproduced fairly well.

Introduction

Recently we reported some experimental results on viscoelasticity in binary mixtures of linear chains.[3] The components were nearly monodisperse polybutadienes ($\bar{M}_w/\bar{M}_n < 1.1$) with molecular weights well above the entanglement threshold. We commented upon the general character and compositional dependence of the relaxation spectra and then offered some molecular interpretations based on reptation theory and the tube model. We also compared the compositional dependence of zero-shear viscosity η_0 and recoverable shear compliance $J_e°$ with the predictions of several rheological mixing rules. The rules were selected from proposals in the literature on the basis of simplicity and absence of adjustable parameters. The results were generally disappointing and especially so for rules that had been motivated by molecular arguments.

In this paper we use the same η_0 and $J_e°$ data to examine a molecular theory based on reptation which also takes into account the effects of finite constraint lifetime (tube renewal) and length fluctuations of the primitive path. A preliminary account of the theory and results was reported elsewhere.[4]

Theoretical Background

Monodisperse Polymers. Our interest here is the terminal region of linear viscoelastic response. We will develop theoretical expressions for the shear stress relaxation modulus $G(t)$ and use the general equations of linear viscoelasticity to calculate viscosity and recoverable compliance[5]

$$\eta_0 = \int_0^\infty G(t)\,dt \tag{1}$$

$$J_e° = \int_0^\infty tG(t)\,dt/\eta_0^2 \tag{2}$$

The primary motion for relaxation of linear polymers is assumed to be reptation, i.e., the diffusion of random coil chains along their primitive paths through a highly entangled environment of other chains.[6-8] Accordingly, if the constraints that define the paths have lifetimes that are long enough, and if fluctuations of the path length are small enough, the chains move by reptation alone. The stress relaxation modulus of monodisperse polymers for this case[8,9] is

$$G(t) = G_N°F(t) \tag{3}$$

in which $G_N°$ is the plateau modulus and

$$F(t) = \frac{8}{\pi^2}\sum_{\substack{\text{odd}\\ p}}\frac{1}{p^2}\exp(-p^2t/\tau_d) \tag{4}$$

is a reduced relaxation function ($F(0) = 1$). The plateau modulus and the disengagement time τ_d are given by the Doi–Edwards tube model

$$G_N° = (4/5)nNkT \tag{5}$$

$$\tau_d = L^2/\pi^2D^* \tag{6}$$

where n is the number density of chains, k is the Boltzmann constant, T is the temperature, D^* is the diffusion coefficient of the chains along their paths ($D^* = kT/\zeta$, where ζ is the molecular friction coefficient), and L and N are respectively the average length and number of steps in the path. The latter two quantities are related to $\langle R^2\rangle$, the mean-square end-to-end distance of the chains

$$L = \langle R^2\rangle/a \tag{7}$$

$$N = \langle R^2\rangle/a^2 \tag{8}$$

where a is the step length of the path, a function of the polymer species and concentration but independent of chain length. With eq 1 and 2

$$\eta_0 = (\pi^2/12)G_N°\tau_d \tag{9}$$

$$J_e° = (6/5)(G_N°)^{-1} \tag{10}$$

In an entangled liquid the constraints that define the tube for each chain are supplied by neighboring chains that are also reptating. The lifetime of each constraint is of the order of the disengagement time of the chain that provides it.[10] The tube can move locally with each constraint release event, so the primitive path of the chain executes a Rouse-like motion. If the reptation of a chain and its tube-renewal motion are independent, the stress relaxation modulus can be written as[9]

$$G(t) = G_N°F(t)R(t) \tag{11}$$

where $R(t)$ is the reduced relaxation function associated with tube renewal ($R(0) = 1$).

An expression for $R(t)$ has been worked out[9] by assuming that the path motion can be represented by the Orwoll–Stockmayer "bond-flip" model[11]

$$R(t) = \frac{1}{N}\sum_{j=1}^{\infty}\exp[-\lambda_j t/2\tau_w] \tag{12}$$

$$\lambda_j(N) = \left[2\sin\frac{\pi j}{2(N+1)}\right]^2 \tag{13}$$

0024-9297/86/2219-1754$01.50/0

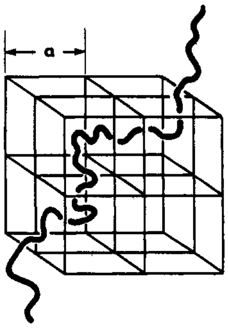

Figure 1. Representation of the constraints that surround each chain by a regular lattice.

Table I
Viscosity and Recoverable Compliance for Monodisperse Linear Polymers according to the Doi-Edwards Tube Model Modified by Constraint Release

z	$\eta_0/\tau_d G_N{}^\circ$	$J_e{}^\circ G_N{}^\circ$
0	0.822	1.20
1	0.448	1.41
2	0.318	1.75
3	0.244	2.15
4	0.196	2.60
6	0.134	3.68
10	0.071	6.76

The waiting time τ_w governs the time scale of renewal. An expression for τ_w was obtained by considering the surroundings to be a lattice of chains in which some universal number z of independent strands constrain the location of each juncture of successive primitive path steps (Figure 1). A local jump opportunity occurs each time one of these constraints is released by reptation of the chain supplying it. Thus[9]

$$\tau_w(z) = \int_0^\infty [F(t)]^z \, dt \tag{14}$$

With eq 4

$$\tau_w(z) = \Lambda(z)\tau_d \tag{15}$$

where, approximately[9]

$$\Lambda(z) = \frac{1}{z}\left(\frac{\pi^2}{12}\right)^z \tag{16}$$

In the context of the model, the strength of renewal contributions is governed by the choice of z, which we call the constraint release parameter. Values of $\eta_0/G_N{}^\circ\tau_d$ and $J_e{}^\circ G_N{}^\circ$ calculated with eq 11–14 for various z are given in Table I. (The tabulation in ref 9 contains some errors.) Diffusion studies,[12] relaxation of unattached chains in a network,[9,13] and relaxation of long chains dilutely dispersed in a short chain matrix[14] are all consistent with a choice for z of roughly 3. The value of $J_e{}^\circ G_N{}^\circ \sim 2.0$–$2.5$ found for nearly monodisperse polymers of many species also agrees with the prediction for $z \sim 3$ (Table I).

Pure reptation predicts $\eta_0 \propto M^3$, contrary to the experimental observation, $\eta_0 \propto M^{3.4}$, and although constraint release lowers the predicted values of viscosity it does not alter the exponent, at least in the model considered here.[9] Doi has proposed the the departure is caused by thermal fluctuations of the primitive path length.[15] He argues that, while pure reptation may be the dominant relaxation mechanism, a fraction of path steps of order $N^{-1/2}$ will have already been abandoned by fluctuations in times of order τ_d. As a result, chains with N steps will relax at long times like chains with $N(1 - \nu N^{-1/2})$ steps undergoing pure reptation. He obtains

$$\tau_d = (\tau_d)_0(1 - \nu N^{1/2})^2 \tag{17}$$

$$\eta_0 = (\eta_0)_0(1 - \nu N^{1/2})^3 \tag{18}$$

and, with $\nu = 1.47$ estimated as the lower bound, he shows that η_0 vs. M from eq 18 closely resembles $\eta_0 \propto M^{3.4}$ in some region of the typical experimental range, $10 < N < 100$, and then gradually reverts to M^3 dependence at still larger N. There is some question about that proposal because the magnitude of η_0 and $J_e{}^\circ$ in the detailed equations[15] do not go over to the Doi–Edwards (pure reptation) limits as $N \rightarrow \infty$. It also introduces a weak chain length dependence in $J_e{}^\circ$ and $G_N{}^\circ$, such that

$$J_e{}^\circ G_N{}^\circ = (J_e{}^\circ G_N{}^\circ)_0(1 - \nu N^{-1/2})^{-1} \tag{19}$$

which is not observed. On the other hand, the predicted variations of $J_e{}^\circ$ and $G_N{}^\circ$ with chain length are small and might be difficult to observe in a series of samples, especially since $G_N{}^\circ$ is difficult to measure in an unambiguous fashion unless the chains are very long and $J_e{}^\circ$ is so sensitive to sample polydispersity.[5]

Binary Mixtures of Chain Lengths. The pure reptation model is easily generalized to mixtures because the constraints are permanent and all chains relax independently. Thus for two components, short (S) and long (L) chains with weight (or volume) fractions ϕ_S and ϕ_L and with $N_S, N_L \gg 1$, the relaxation modulus for pure reptation is

$$G(t) = G_N{}^\circ[\phi_S F_S(t) + \phi_L F_L(t)] \tag{20}$$

where $F_S(t)$ and $F_L(t)$ are given by eq 4, using $(\tau_d)_S$ and $(\tau_d)_L$ respectively. Tube renewal can also be included, at least in a formal sense

$$G(t) = G_N{}^\circ[\phi_S F_S(t) R_S(t) + \phi_L F_L(t) R_L(t)] \tag{21}$$

Expressions for $R_S(t)$ and $R_L(t)$ can be established with the strand lattice model[4,9] (Figure 1). The fractions of S and L path steps are ϕ_S and ϕ_L, so, of the z strands that effectively define any junctures of steps, an average ϕ_S are supplied by short chains and ϕ_L by long chains. However, if all junctures have z constraints, any particular juncture will have m from short chains ($m = 0, 1, ..., z$) and $z - m$ from long chains. If the selection statistics are random, the fraction of junctures with m constraints supplied by short chains and $z - m$ by long chains is given by the binomial distribution

$$P_m = \frac{z!}{m!(z-m)!}\phi_S{}^m \phi_L{}^{z-m} \tag{22}$$

and the mean waiting time for first release is

$$\tau_m = \int_0^\infty F_S{}^m(t) F_L{}^{z-m}(t) \, dt \tag{23}$$

If we now assume that a mean waiting time can be used to describe the Rouse-like motions of all paths and that the mean is given accurately enough by the average of τ_m, then

$$\tau_w = \sum_{m=0}^{z} P_m \tau_m \tag{24}$$

Substitution of eq 22 and 23 and summation over m gives

$$\tau_w = \int_0^\infty [\phi_S F_S(t) + \phi_L F_L(t)]^z \, dt \tag{25}$$

which is equivalent to the result given as eq A-5 in ref 4. The stress relaxation modulus for binary mixtures is then obtained from eq 21 with $R_S(t)$ and $R_L(t)$ given by eq 12 and 13 for N_S and N_L, respectively, and with τ_w for each given by eq 25. The effect of this is to make the local

Table II
Molecular and Rheological Properties of Component Polybutadienes

sample	M	η_0,[a] P	$J_e°$, cm^2/dyn	$J_e°G_N°$	N[b]
41L	40700	$1.3_5 \times 10^4$	1.8×10^{-7}	1.9	$27._5$
98L	97500	3.1×10^5	2.0	2.5	66
174L	174000	$2.9_5 \times 10^6$	1.8	2.2	118
435L	435000	4.8×10^7	2.1	2.6	294

[a] Values at 25 °C. [b] Calculated from M with eq 28 and M_e = 1850.[3]

hopping rate the same for the paths of all chains but governed by a communal waiting time τ_w that depends on mixture composition. The paths of long chains relax more quickly and short chains more slowly than in the respective pure component liquids.

Expressions for viscosity and recoverable compliance can now be obtained with eq 1 and 2, using the procedure given in Appendix V of ref 9

$$\eta_0 = \frac{8}{\pi^2}G_N° \sum_{\substack{\text{odd}\\ p}} [\phi_S\tau_S(p^2 + r_S)^{-1/2} + \phi_L\tau_L(p^2 + r_L)^{-1/2}]/p^3 \tag{26}$$

$$J_e° = \frac{8}{\pi^2}\frac{G_N°}{\eta_0^2} \sum_{\substack{\text{odd}\\ p}} [\phi_S\tau_S^2(2p^2 + r_S) \times (p^2 + r_S)^{-3/2} + \phi_L\tau_L^2(2p^2 + r_L)(p^2 + r_L)^{-3/2}]/p^5 \tag{27}$$

where $r_S = 2\tau_S/\tau_w$ and $r_L = 2\tau_L/\tau_w$, τ_S and τ_L are the disengagement times (eq 6) for S and L chains, respectively, and the continuous representation of spectra for $R_L(t)$ is justified ($N_S^3 \gg N_L$; see Appendix). Equations 26 and 27 revert to the pure reptation expressions for binary mixtures when $z = 0$ ($\tau_w = \infty$), as given in ref 3. They also revert to the expressions in ref 9 for monodisperse polymers with reptation and renewal when $\phi_S = 1$, $\phi_L = 1$, or $\tau_S = \tau_L$. To compare with data, the compositional dependences will be expressed in reduced form, i.e., as $\eta_0/(\eta_0)_S$ and $J_e°/(J_e°)_S$ vs. ϕ_L, where $(\eta_0)_S$ and $(J_e°)_S$ are monodisperse component values.

Both pure reptation and reptation–renewal yield $\eta_0 \propto M^3$ for the monodisperse components. To force agreement with the $\eta_0 \propto M^{3.4}$ requirement at $\phi_L = 1$, one can simply take $\tau_L/\tau_S = (M_L/M_S)^{3.4}$ or $(\eta_0)_L/(\eta_0)_S$ instead of $(M_L/M_S)^3$. Alternatively, the deficiency at $\phi_L = 1$ can be softened by including the effect of path length fluctuations,[15] where ν is established by fitting the pure component η_0 vs. M data to eq 18. Finally, N_S and N_L can be calculated from eq 5, which gives

$$N = (5/4)(M/M_e) \tag{28}$$

where $M_e \equiv \rho RT/G_N° = nkTM/G_N°$ is the conventional definition of entanglement molecular weight for melts,[5] ρ being the melt density and R the gas constant.

Other methods for handling tube renewal have been proposed;[16–18] we have not included any comparisons with alternative models here.

Experimental Data

The values of η_0 and $J_e°$ used to test the predictions were obtained from measurements of complex modulus $G^*(\omega)$ at low frequencies and are given in the earlier paper.[3] Data at 25 °C are given there for four series of undiluted mixtures made with nearly monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$) linear polybutadienes (~8% vinyl content) of molecular weights 40.7 × 10^3, 97.5 × 10^3, 174 × 10^3, and 435 × 10^3. The entanglement molecular weight for the species is $M_e = 1.85 \times 10^3$,[3] so all components are well entangled.

Table III
Mixtures Used To Compare Theory and Experiment

series	M_s	M_L	M_L/M_S
41L/435L	40700	435000	10.7
98L/435L	97500	435000	4.5
174L/435L	174000	435000	2.5
41L/174L	40700	174000	4.3

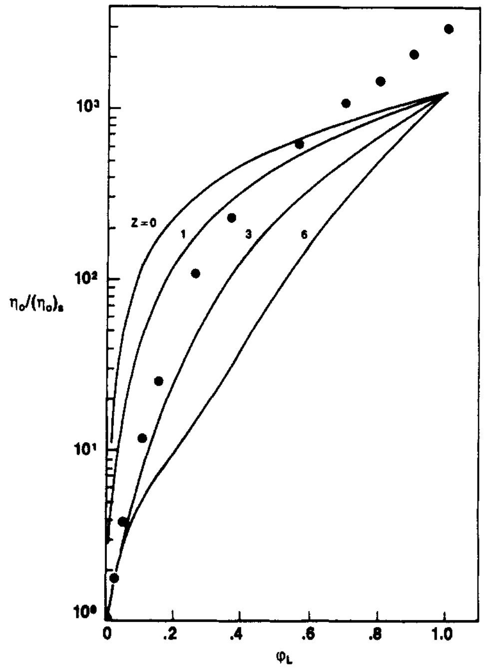

Figure 2. Reduced viscosity vs. volume fraction of the long chain component for combined reptation–renewal. The filled circles denote experimental data for the 41L/435L polybutadiene series.[3] The curves were calculated from eq 25 and 26 for the values of z indicated.

Values of η_0 and $J_e°$ for the individual components are listed in Table II. The viscosity data obey

$$\eta_0 = 3.63 \times 10^{-12}M^{3.41} \quad \text{(P)} \tag{29}$$

over this range. An analysis of the component η_0 results with eq 18 suggests $\nu = 3$ for Doi's model.[19] Values of $J_e°$ are nearly the same for all components. The value for the component of lowest molecular weight, 41L, is slightly smaller than the average, contrary to expectations based on the fluctuations model (eq 19 with $\nu = 3$). The characteristics of the mixtures, representing M_L/M_S values from 2.5 to 10.7, are given in Table III.

Results

Figure 2 compares the viscosity data for the 41L/435L series with the reptation–renewal model (eq 26) for several values of the constraint release parameter z. Similar results are found for the other series. Reptation alone (z = 0) predicts a much too strong dependence on small amounts of the long chain component, as also noted earlier.[3] The rise near $\phi_L = 0$ is more gradual when renewal is included, and $z \sim 3$ gives rather good agreement with the data in that region. However, the M^3 dependence of τ_d forces the prediction of η_0 to fall below the experiment at larger ϕ_L. As discussed above, this fundamental deficiency of the pure reptation model is not remedied by including renewal effects in the manner presented here.

Experimental viscosities for all four series are compared with predictions of the reptation–renewal–fluctuations (ν = 3) model in Figures 3–6. The composition variable used here is the weight-average molecular weight of the mixture, $\bar{M}_w = \phi_SM_S + \phi_LM_L$, since the data in that form are found

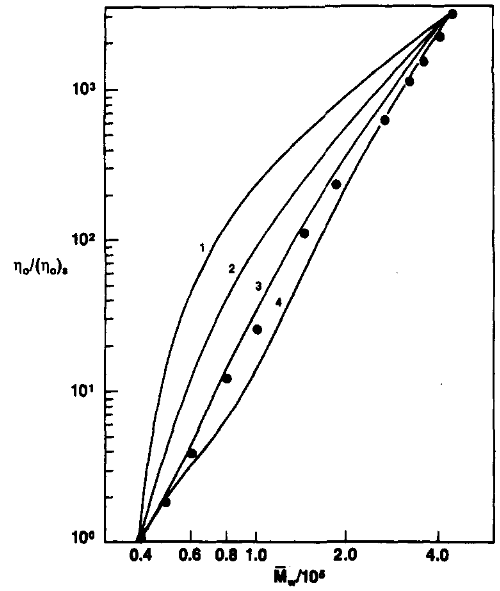

Figure 3. Reduced viscosity vs. weight-average molecular weight for combined reptation–renewal–fluctuations ($\nu = 3$). The filled circles denote experimental data for the 41L/435L polybutadiene series.[3] The curves were calculated from eq 17, 25, and 26 for the values of z indicated.

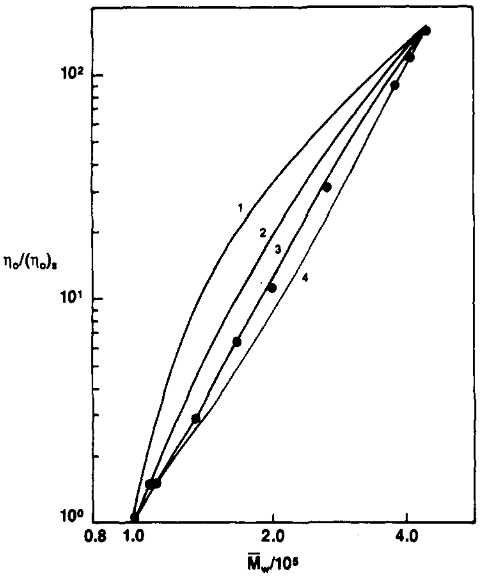

Figure 4. Reduced viscosity vs. weight-average molecular weight for combined reptation–renewal–fluctuation ($\nu = 3$) for the 98L/435L polybutadiene series. See the caption to Figure 3.

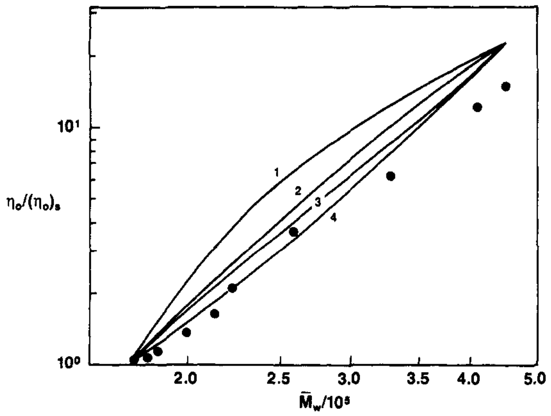

Figure 5. Reduced viscosity vs. weight-average molecular weight for combined reptation–renewal–flucturations ($\nu = 3$) for the 174L/435L polybutadiene series. See the caption to Figure 3.

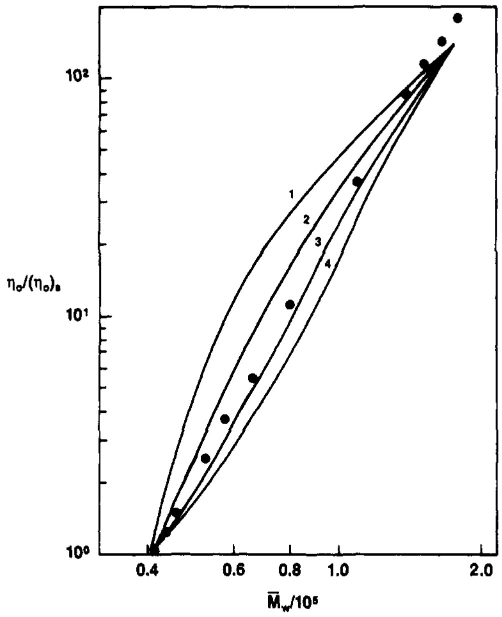

Figure 6. Reduced viscosity vs. weight-average molecular weight for combined reptation–renewal–fluctuations ($\nu = 3$) for the 41L/174L polybutadiene series. See the caption to Figure 3.

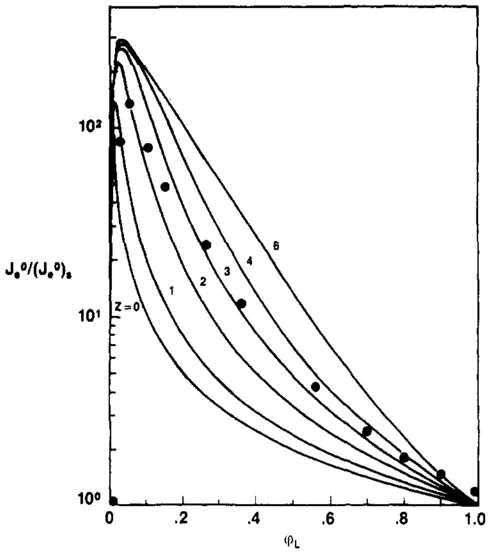

Figure 7. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal. The filled circles denote experimental data for the 41L/435L polybutadiene series.[3] The curves were calculated from eq 25–27 for the values of z indicated.

to closely approximate a pure power law:[3] $\eta_0 \propto \bar{M}_w^{3.41}$. Agreement near $\phi_L = 1$ is improved although not exact; η_0 for the pure 174L component differs slightly from the curve for $\nu = 3$, and departures near $\phi_L = 1$ are found for the two mixtures that contain that component (Figure 4 and Figure 6). When allowance is made for that effect, however, the calculations with z = 3–4 accommodate the data rather well. The resulting curve is sigmoidal rather than a power law, but the departures are not very large. We have also calculated results for reptation–renewal alone but using $\tau_L/\tau_S = (\eta_0)_L/(\eta_0)_S$ and $(M_L/M_S)^{3.41}$ to force agreement at $\phi_L = 1$. The results do not change in any significant way: the compositional dependence of viscosity for all mixtures is given fairly well with values of z in the range 3–4.

Experimental values of recoverable compliance are compared with predictions of the reptation-renewal model (eq 27) in Figures 7–10. Qualitatively, the mixtures exhibit

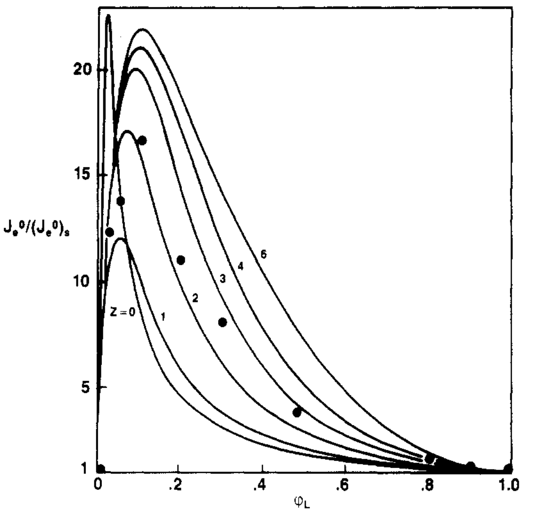

Figure 8. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal in the 98L/435L polybutadiene series. See the caption to Figure 7.

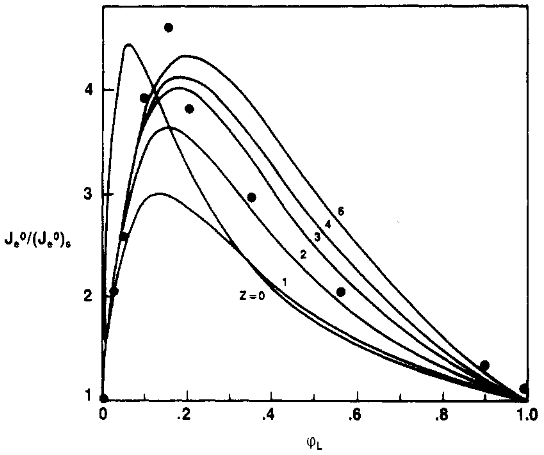

Figure 9. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal in the 174L/435L polybutadiene series. See the caption to Figure 7.

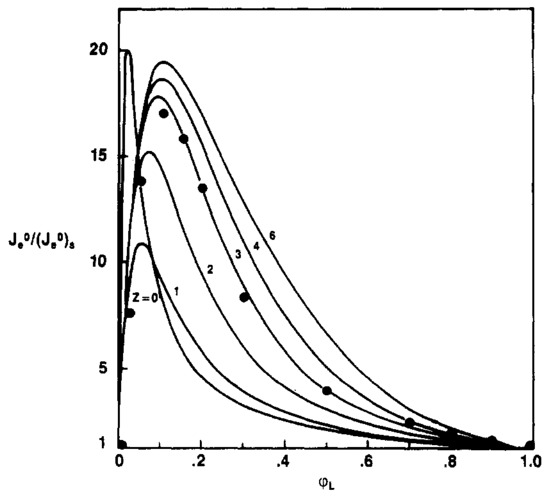

Figure 10. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal in the 41L/174L polybutadiene series. See the caption to Figure 7.

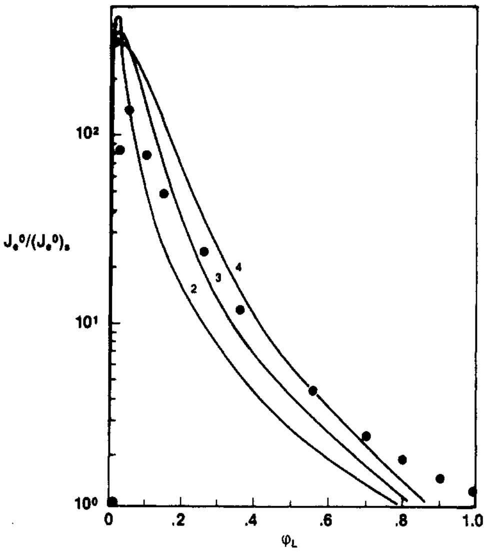

Figure 11. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal–fluctuations ($\nu = 3$). The filled circles denote experimental data for the 41L/435L polybutadiene series.[3] The curves were calculated from eq 17 and 25–27 for the values of z indicated.

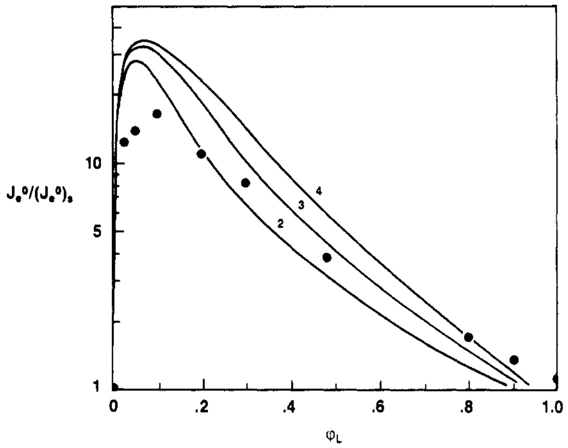

Figure 12. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal–fluctuations ($\nu = 3$) in the 98L/435L polybutadiene series. See the caption to Figure 11.

the well-known maximum in J_e° at low ϕ_L, $(J_e^\circ)_{max}$ at $(\phi_L)_{max}$, with the magnitudes of $(J_e^\circ)_{max}$ increasing and $(\phi_L)_{max}$ decreasing as M_L/M_S increases.[3] As noted previously, pure reptation ($z = 0$) locates the maximum at unreasonably small values of ϕ_L and seriously underestimates J_e° at larger ϕ_L.[3] Inclusion of constraint release ($z > 0$) tends to alleviate both deficiencies, and the general trends for all four series are predicted reasonably well by $z \sim 3$.

There is some tendency of the theory to predict values of $(J_e^\circ)_{max}$ that are larger than observed as M_L/M_S increases, but that region of small ϕ_L and large M_L/M_S is also the most difficult experimentally, with errors which are likely to produce values of J_e° that are too small. Some departures near $\phi_L = 1$ are caused by the small differences in J_e° among pure component samples. The reptation–renewal theory requires all pure component values to be the same, and we could not think of a reasonable way to allow for such variations.

Agreement in J_e° is less satisfactory for the reptation–renewal–fluctuations model. The results for $\nu = 3$ are shown in Figures 11–14. The trends are not as well represented even for the optimum choice of z, and no single choice of z fits all mixtures equally well. Thus, $z \sim 3$–4 seems best for the 41L/435L series (Figure 11, $M_L/M_S = 10.7$), $z \sim 2$ for the 98L/435L series (Figure 12, $M_L/M_S = 4.5$) and 174L/435L series (Figure 13, $M_L/M_S = 2.5$), and $z \sim 3$ for the 41L/174L series (Figure 14, $M_L/M_S = 4.3$). This may be caused, in part at least, by the fluctuation contribution that predicts J_e° to be larger for the 41L

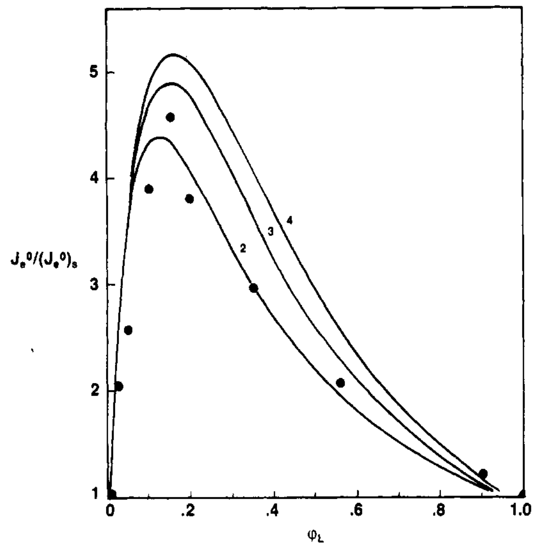

Figure 13. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal–fluctuations ($\nu = 3$) in the 174L/435L polybutadiene series. See the caption to Figure 11.

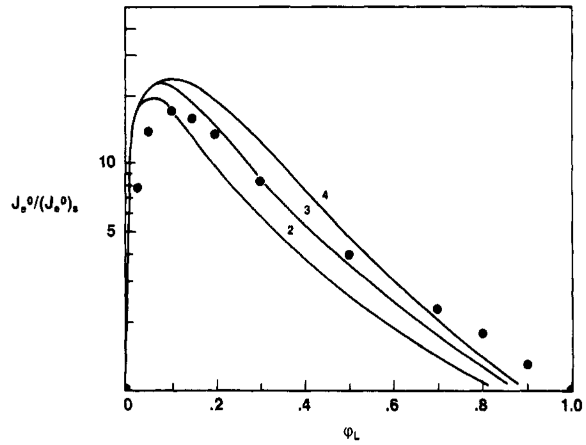

Figure 14. Reduced recoverable compliance vs. volume fraction of the long chain component for reptation–renewal–fluctuations ($\nu = 3$) in the 41L/174L polybutadiene series. See the caption to Figure 11.

component, whereas the opposite is observed experimentally. Thus, the calculated $J_e{}^\circ/(J_e{}^\circ)_S$ values are less than unity near $\phi_L = 1$, and the departure is especially large when 41L is the short component (Figures 11 and 14). Imposing $\tau_L/\tau_S = (M_L/M_S)^{3.41}$ in eq 28 in place of fluctuations again makes all pure component values of $J_e{}^\circ$ the same but does not change the situation for the mixtures appreciably. Agreement near $\phi_L = 1$ is certainly improved, but, if anything, the departures in general may be slightly exaggerated, as shown by results for data for the 41L/174L series in Figure 15.

Discussion

The comparisons above demonstrate that reptation and tube-renewal processes, the latter embodied in a simple model for constraint release, can provide a reasonable account for η_0 and $J_e{}^\circ$ in highly entangled mixtures. The compositional dependence of η_0, with τ_L/τ_S adjusted from $(M_L/M_S)^3$ to $(M_L/M_S)^{3.41}$, is in excellent agreement for all four series of mixtures when the constraint release parameter $z = 3$ is used. The results for $J_e{}^\circ$ are less satisfactory, since the same model requires slightly different values of z (2–4) to achieve best fits with data for different series, and even then the best fits are far from perfect. Nevertheless, the general trends seem well represented, and the differences from experiment, where a single value of $z = 3$ is used, are less pronounced than those found for many empirical mixing rules.[3] It is at least somewhat reassuring to find that the range of z required is consistent with estimates based on a diversity of other experiments.[12-14] Tests of other models to handle tube renewal are under way,[18] and an examination of the predictions by the present model for complete relaxation functions, such as the dynamic modulus, is planned.

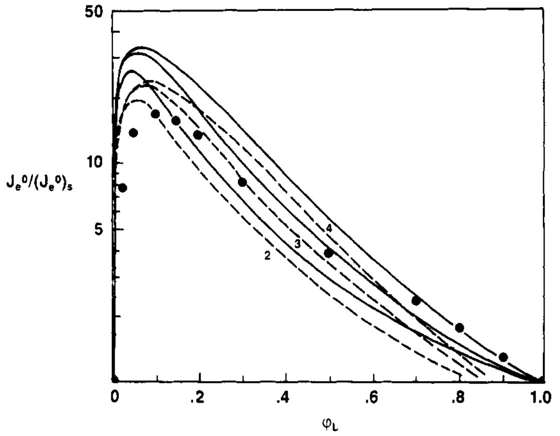

Figure 15. Reduced recoverable compliance vs. volume fraction of the long chain component for the 41L/174L polybutadiene series. The data and dashed curves are those shown in Figure 14. The solid curves were calculated from eq 25–27 with $\tau_L/\tau_S = (M_L/M_S)^{3.41}$.

Finally, for completeness we present here the equations for relaxation modulus in the terminal region for highly entangled polymer liquids of arbitrary molecular weight distribution

$$G(t) = G_N{}^\circ \int_0^\infty W(N)F(N,t)R(N,t)\,\mathrm{d}N \qquad (30)$$

$$\tau_w = \int_0^\infty \left[\int_0^\infty W(N)F(N,t)\,\mathrm{d}N\right]^z \mathrm{d}t \qquad (31)$$

where $W(N)\,\mathrm{d}N$ is the fractional weight of the polymer from chains with path steps in the range N to $N + \mathrm{d}N$ and $F(N,t)$ and $R(N,t)$ are the reduced relaxation functions. The equations are easily obtained generalizations of eq 21 and 25 for binary mixtures.

Acknowledgment. This work was supported by the National Science Foundation (Grant CPE 80-00030). Criticisms of this work by D. S. Pearson and E. Helfand and discussions with them and M. Rubenstein about alternative renewal models are acknowledged with gratitude.

Appendix. Relaxation Spectrum of $R(t)$ in Binary Mixtures

In Appendix V of ref 9, an expression for the relaxation function and corresponding expressions for η_0 and $J_e{}^\circ$ were obtained for monodisperse polymers using the reptation–renewal model. There only the fastest modes of $R(t)$ contributed. Since the relaxation times are closely spaced in that region, the summation index j was treated as a continuous variable, and summation was replaced in integration (see eq 12 and 13 of the present paper). That approximation is not necessarily valid for the L chains in a mixture. We examine here the most extreme case of L chains that are dispersed in S chains alone.

The longest tube-renewal relaxation time for L chains is given by the Rouse formula

$$(\tau_{\mathrm{Ren}})_L \sim N_L{}^2(\tau_d)_S \qquad \text{(A-1)}$$

since the local hopping time here ($\phi_L = 0$) is roughly $(\tau_d)_S$

if z is not too large. If the reptation time for L chains is small enough, the contributions of the slowest renewal modes, where the relaxation times are widely spaced, will be negligible. The criterion for validity of the continuous representation is therefore

$$(\tau_d)_L \ll N_L^2(\tau_d)_S \qquad \text{(A-2)}$$

If $(\tau_d)_L$ is independent of mixture composition, then $(\tau_d)_L/(\tau_d)_S = N_L^3/N_S^3$, and the criterion becomes

$$N_S^3 \gg N_L \qquad \text{(A-3)}$$

as reported in the text. This is precisely equivalent to $M_S^3 \gg M_L M_e^2$, the criterion for case I relaxation behavior in mixtures,[3] i.e., where the relaxation time of L chains is independent of mixture composition. All mixtures in the present study satisfy that criterion,[3] so the continuous approximation for $R(t)$ should be quite acceptable here.

Registry No. Polybutadiene, 9003-17-2.

References and Notes

(1) Current address: Corporate Research Laboratories, Exxon Research and Engineering Co., Annandale, NJ 08801.
(2) Current address: Paramins Technology Division, Exxon Chemical Co., Linden, NJ 07036.
(3) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630.
(4) Graessley, W. W. *Faraday Soc. Symp.* **1983**, *18*, 7.
(5) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(6) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(7) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(8) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(9) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(10) Klein, J. *Macromolecules* **1978**, *11*, 852.
(11) Orwoll, R. A.; Stockmayer, W. *Adv. Chem. Phys.* **1969**, *15*, 305.
(12) Green, P. F.; Mills, P. J.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(13) Kan, H.-C.; Ferry, J. D.; Fetters, L. J. *Macromolecules* **1980**, *13*, 1571.
(14) Montfort, J. P.; Marin, G.; Monge, Ph. *Macromolecules* **1984**, *17*, 1551.
(15) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265.
(16) Marrucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 159.
(17) Viovy, J. L., unpublished manuscript.
(18) Helfand, E.; Rubenstein, M., unpublished manuscript.
(19) Struglinski, M. J.; Doctoral Thesis, Chemical Engineering Department, Northwestern University, Evanston, IL, 1984.

Scaling Relations for Aqueous Polyelectrolyte Salt Solutions. 4. Electric Birefringence Decay as a Function of Molar Mass and Concentration

Sybren S. Wijmenga, Frans van der Touw, and Michel Mandel*

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands.

Received October 9, 1985

ABSTRACT: The electric birefringence decay of aqueous sodium poly(styrenesulfonate)–0.01 M NaCl solutions with various polyelectrolyte molar mass and concentrations has been studied after the application of rectangular electric field pulses. All decay curves could be represented by a superposition of at least three exponential functions. The longest relaxation time τ_1 (or the mean relaxation time $\bar{\tau}$ to which it is proportional) exhibits a different concentration dependence in the dilute and in the semidilute regime. In the former it is nearly concentration independent and may be related to the rotational motion of isolated polyelectrolyte chains, yielding values for the mean-square radius of gyration in good agreement with theoretical predictions based on a wormlike chain approach to polyelectrolytes. In the semidilute regime, τ_1 and $\bar{\tau}$ considerably increase with increasing concentration but remain molar mass dependent. The reduced values $(\bar{\tau}/\tau_d)$, where τ_d refers to the value in the dilute regime, are found to scale like $(C/C^*)^\beta$ after due correction for the concentration dependence of the ionic strength and to be independent of molar mass, C^* being the critical concentration and $\beta = 0.60$. This can be understood if the renewal time of the chain is expressed by using a "blob" model for the macromolecule, as should apply if the semidilute solutions form transient networks, and is assumed to depend on the numbers of blobs to the power $\nu = (4\beta + 9)/5 = 2.3$.

Introduction

Electric birefringence is observed when a linearly polarized light beam, traveling through an otherwise isotropic system in a direction perpendicular to that of an externally applied field, becomes elliptically polarized due to the induced anisotropy of the refractive index. This Kerr effect is a nonlinear electric field effect and is generally attributed to the orientation of the molecules under the action of the electric field. It thus can be understood in terms of the optical polarizability tensor of the molecules and an orientational function arising from the interaction of the molecules with the electric field. The latter may involve, in a first approximation, permanent dipole moments as well as induced dipole moments. As long as a constant field maintains the polarization of the system, the electric birefringence will tend to a stationary value. Both this stationary value of the birefringence and its time dependence are determined by the orientational mechanism responsible for the induced anisotropy. Only in the case of solutions of simple molecules and in the approximation of negligible intermolecular interactions has it been possible to derive mathematical expressions for the time dependence and the stationary value of the birefringence after switching on the electric field.[1] For more complicated molecules and, in particular, for macromolecules with a large number of internal degress of freedom, the situation is much more complicated unless simplifying models are used.[2] In the case of solutions containing charged macromolecules the situation is even more complex because nonconventional polarization phenomena involving perturbation of the small ion distribution by the electric field have probably to be taken into account.

In general the situation is easier to analyze for the opposite case where the electric birefringence spontaneously

0024-9297/86/2219-1760$01.50/0 © 1986 American Chemical Society