Macromolecules **1986**, *19*, 393–399

The significant weighting of the base-line term in the present analysis, which includes a very slow relaxation, further complicates data interpretation for Θ systems. Estimation of an apparent relaxation rate shows that this slowest component(s) is of the magnitude of the disentanglement time T_R. Some aspects suggest that it may reflect the separation and rearrangement of entanglement zones.

A salient difference is noted here in comparison with the behavior in good solvent systems[14] where there is a smooth increase in the number density of segments of progressively shorter length as interpenetration proceeds. In a Θ solution of large molecules the coils may entangle in a more complex manner and lead to very slow structural rearrangements. Measurements are needed at higher concentrations, but the asymptotic semidilute region is experimentally difficult to gain access to for high molecular weight samples. The structural relaxation referred to above seems to be the limiting factor in applying the QELS technique to such systems. Developments in multi-τ correlators provide optimism for future studies of this feature.

Acknowledgment. I am grateful to M. Adam and M. Delsanti and to P. Štěpánek, K. Zimmermann, and C. Konak for making available preprints of their articles prior to publication.

Registry No. PS (homopolymer), 9003-53-6.

References and Notes

(1) Brochard, F.; de Gennes, P. G. *Macromolecules* **1977**, *10*, 1157.
(2) Brochard, F.; *J. Phys.* (*Les Ulis, Fr.*) **1983**, *44*, 39.
(3) (a) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587, 594. (b) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: London, 1979.
(4) Hecht, A.-M.; Bohidar, H. B.; Geissler, E. *J. Phys. Lett.* **1984**, *45*, L121.
(5) (a) Chu, B.; Nose, T. *Macromolecules* **1980**, *13*, 122. (b) Chu, B.; Nose, T. *Macromolecules* **1979**, *12*, 590. (c) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 599.
(6) Adam, M.; Delsanti, M. *J. Phys.* (*Les Ulis, Fr.*) **1980**, *41*, 721.
(7) Adam, M.; Delsanti, M. *J. Phys. Lett.* **1984**, *45*, L279.
(8) Amis, E. J.; Han, C. C.; Matsushita, Y. *Polymer* **1984**, *25*, 651.
(9) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636.
(10) Munch, J.-P.; Hild, G.; Candau, S. J. *Molecules* **1983**, *16*, 71.
(11) Zimmerman, K.; Štěpánek, P.; Proceedings of the 27th Microsymposium on Macromolecules, Prague, 1984.
(12) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379.
(13) Johnsen, R. M.; Proceedings of the 27th Microsymposium on Macromolecules, Prague, 1984.
(14) Brown, W. *Macromolecules* **1985**, *18*, 1713.
(15) Kubota, K.; Abbey, K. M.; Chu, B. *Macromolecules* **1983**, *16*, 137.
(16) Brown, W. *Polymer* **1984**, *25*, 680.
(17) Roots, J.; Nyström, B. *Macromolecules* **1980**, *13*, 1595.
(18) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(19) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 668.
(20) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(21) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.
(22) Štěpánek, P.; Zimmermann, K.; Konak, C. *Polym. Bull.* (*Berlin*), submitted.
(23) Carlfors, J.; Rymden, R.; Nyström, B. *Polym. Commun.* **1983**, *24*, 263.
(24) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(25) Cotton, J. P.; Nierlich, M.; Boué, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.

Effect of Tube Renewal on the Viscoelastic Properties of Concentrated Solutions of Polymers

J. P. Montfort,* G. Marin, and Ph. Monge

Université de Pau et des Pays de l'Adour, Laboratoire de Physique des Matériaux Industriels, Institut Universitaire de Recherche Scientifique, 64000 Pau, France.

Received June 26, 1985

ABSTRACT: The viscoelastic properties of binary blends of polystyrene fractions have been studied in the terminal region of relaxation. Since one of the components is entangled ($M > M_c$), these blends are in fact concentrated polystyrene solutions, the low molecular weight component acting as a solvent. The effect of molecular weight on the so-called "monomeric" friction factor ζ_0 has been quantified. An improvement of the reptation model is proposed, taking into account the "tube renewal" mechanism. Reasonable agreement was found with experimental data relative to the viscoelastic parameters of the entangled component (i.e., steady-state recoverable compliance $J_e°$, terminal relaxation time τ_0, and zero-shear viscosity η_0). The main results are that $J_e°$ varies with the high molecular weight polymer volume fraction ϕ as ϕ^{-2} and that τ_0 and η_0 exhibit values far from a pure reptation behavior for $\phi M/M_e < 30$–50; the reptation regime is however achieved at higher entanglement density.

Introduction

Many studies[1-6] have been performed on the viscoelastic properties of concentrated polymer solutions. The diluents used are good solvents, Θ solvents, or even commercial oils. Some data were presented for solutions in which the solvent was a low molecular weight polymer of the same species as the entangled polymer.[4,5] The concentration dependences of the plateau modulus $G_N°$ and steady-state recoverable compliance $J_e°$ generally follow power laws: $G_N° \propto \phi^a$ and $J_e° \propto \phi^{-a}$, with $2.0 < a < 2.3$ (ϕ is the volume fraction of polymer). But the viscosity data vary strongly according to the authors, from ϕ^3 to ϕ^6 and even higher exponent values. The main reason for these discrepancies in exponent values for the concentration dependence of viscosity is the "correction" or "noncorrection" of the viscosity through the friction factor ζ_0. Empirical[7] and theoretical[8,9] models indeed provide

$$\eta_0 \propto \phi \zeta_0 M_e (M/M_e)^b \tag{1}$$

where the average spacing between entanglements, M_e, depends on polymer concentration as ϕ^{-1}. So, the exponent b can be calculated from the variation of η_0/ζ_0 vs. ϕM.

The friction factor ζ_0 depends on temperature, concentration, and diluent nature. Its temperature dependence is the same as that of the viscosity η_0 and is represented by the WLF equation. The parameters of the WLF

0024-9297/86/2219-0393$01.50/0 © 1986 American Chemical Society

equation depend on concentration and nature of diluent, mainly the characteristic temperature T_∞ at which the viscosity would become infinite. But even when all the above effects are taken into account, results differ: for example, data on poly(vinyl acetate) in good solvents[3] agree with relation 1, giving $b = 3.4$, but other data on polybutadiene in oils[5] lead to a law $\eta_0/\zeta_0 \propto \phi^4 M^{3.4}$. Then it is difficult to test the models if all the effects are not mastered.

For these reasons, we have studied concentrated solutions of an entangled polymer (polystyrene) in a low molecular weight polymer of the same species. The nature of the solvent–polymer interaction is therefore the same as the polymer–polymer interactions. The chain dimensions are unperturbed and the friction factor variations with temperature and concentration are well-known, starting from the viscoelastic behavior of the pure components. First, we present an extension of the Doi–Edwards model, including reptation and tube renewal, which gives the concentration dependence of the terminal viscoelastic parameters: recoverable compliance $J_e°$, zero-shear viscosity η_0, and average relaxation time τ_0. Then experimental data are compared with the theoretical analysis.

Reptation and Tube Renewal

The Doi–Edwards theory[9] on the dynamics of polymer chains in the melt and in concentrated solutions is based on the concept of a sliding motion of every chain in a fixed tube. Any chain is represented by N_0 segments of length b. In concentrated solutions, its dimensions are assumed to be unperturbed, the mean square end-to-end distance remaining equal to N_0b.[2] The topological constraints are represented by entanglement points separated by N_e segments of length a. The set of constraints acting on any chain constitutes a tube with $N = N_0/N_e$ elements and a total length $L = Na$. The primitive chain, which is the center line of the tube in which the real chain is trapped, has the same mean square end-to-end distance. Then $N_0b^2 = Na^2$ implies

$$N_e = a^2/b^2 \qquad L = N_0(b^2/a) \tag{2}$$

The "diameter" of the tube, a, corresponds to a correlation length and is assumed to vary with the concentration, represented by the volume fraction of polymer ϕ, according to

$$a \propto \phi^{-\alpha} \tag{3}$$

The Brownian motion of a chain trapped in its tube is characterized by a curvilinear diffusion coefficient, D_c, related to the monomeric friction factor ζ_0 by $D_c = kT/N_0\zeta_0$ and the disengagement time is $\tau_d = L^2/\pi^2 D_c$.

D_c, and thus ζ_0, may depend on concentration. It is assumed that

$$D_c \propto N_0^{-1}\phi^{-\beta} \tag{4}$$

Then

$$\tau_d \propto N_0^3\phi^{2\alpha+\beta} \tag{5}$$

The rheological constitutive equation, based on this model, gives the parameters η_0 and $J_e°$ of the terminal relaxation as

$$\eta_0 = \frac{\pi^2}{20}\nu NkT\tau_d \propto N_0^3\phi^{4\alpha+\beta+1} \tag{6}$$

$$J_e° = \frac{2}{\nu NkT} \propto \phi^{-2\alpha-1} \tag{7}$$

for ν (number concentration) $\propto \phi N_0^{-1}$.

The product $\eta_0 J_e°$ represents an average terminal relaxation time τ_w[10] and the above expressions show that $\tau_w \simeq \tau_d$. Experimentally, we have shown[11] that, for polymers not strongly entangled, the terminal relaxation included reptation and tube renewal. This mechanism, due to a release of constraints constituting the tube, has been modeled by Klein[12] and Graessley[13] and characterized by a relaxation time τ_m such that

$$\tau_m \propto N^2\tau_d \propto N_0^5\phi^{6\alpha+\beta} \tag{8}$$

It seems that there is a discrepancy between the theories of tube renewal and experimental data; we have found $\tau_m \propto N^2(\tau_d/N_0)$ with $\tau_d \propto N_0^{3.4}$. If we assume that the two processes are uncorrelated and the concentration dependence is satisfied (relation 5), the resulting relaxation τ is given by

$$1/\tau = 1/\tau_d + 1/\tau_m$$

or

$$\tau^{-1} = \tau_{d0}^{-1}\phi^{-2\alpha-\beta} + \tau_{m0}^{-1}\phi^{-6\alpha-\beta} \tag{9}$$

the subscript zero corresponding to the pure component.

We derive from the above relation the concentration dependence of η_0 and $J_e°$ as

$$\eta_0 \propto \nu N\tau \propto \frac{\phi^{2\alpha+1}}{\tau_{d0}^{-1}\phi^{-2\alpha-\beta} + \tau_{m0}^{-1}\phi^{-6\alpha-\beta}} \tag{10}$$

and

$$J_e° \propto 1/\nu N \propto \phi^{-2\alpha-1} \tag{11}$$

Let us point out that the concentration dependence of the steady-state shear compliance $J_e°$ is the same as for pure reptation but the zero-shear viscosity η_0 does not follow a power law when tube renewal occurs on the same time scale as reptation. This situation is achieved when ϕ tends toward $\phi_c = 2N_e/N_0$, the concentration below which the chains are unentangled.

Experimental Section

Sample Preparation and Experimental Technique. These have been detailed in a previous paper.[11] The samples were dissolved in benzene, freeze-dried in liquid nitrogen, and then vacuum molded in the shape of the experimental cell. The dynamic shear measurements were performed with an Instron 3250 rheometer, shearing the samples between cone and plate. The complex shear modulus $G^*(\omega)$ was obtained in a range of 4–6 decades in frequency, using time–temperature superposition. The shift factor $a = \tau(T)/\tau(T_0)$ is found equal to the ratio of viscosity $\eta_0(T)/\eta_0(T_0)$ because of the weak variations of $T_0\rho_0/T\rho$ in a range of temperatures T such that $1.2 < T/T_g < 2$.

Monomeric Friction Coefficient. Theories indicate that viscosity η_0 is proportional to the friction coefficient ζ_0, so the shift factor a_T can be written as $\zeta_0(T)/\zeta_0(T_0)$. For glass-forming polymers, the mobility at any temperature depends primarily on the fractional free volume f, which depends on the chain length. For fractions, assuming a linear expansion of the specific volume, we get

$$f(M,T) = \alpha_f(T - T_\infty(M)) \tag{12}$$

where T_∞ is a WLF parameter. Then the temperature dependence is given by

$$\log \zeta_0(M,T) = \log \zeta_0(M,T_0) + \frac{B}{2.303}\left[\frac{1}{f(M,T)} - \frac{1}{f(M,T_0)}\right] \tag{13}$$

or

$$\log a_T = \frac{B}{2.303\alpha_f}\,\frac{1}{T - T_\infty(M)} - C(M,T_0) \tag{14}$$

Table I
Molecular and Rheological Properties of Linear Polystyrenes at $T - T_\infty$ = 110.4 °C

sample	M_w	P	T_∞, °C	τ_0, s	η_0, P	$J_e°$, cm²/dyn
F002	2000	1.05	7	1.3×10^{-5}	5.4×10^{2}	1.6×10^{-8}
F004	4000	1.05	26.6	6×10^{-5}	1.26×10^{3}	3.2×10^{-8}
F008	8500	1.05	39.0	3.8×10^{-4}	2.6×10^{3}	9.55×10^{-8}
F018	17500	1.05	44.0	2.6×10^{-3}	8.7×10^{3}	1.95×10^{-7}
F04	35000	1.06	48.0	2×10^{-2}	3.2×10^{4}	4.0×10^{-7}
F11	110000	1.05	48.6	8.3×10^{-1}	8.7×10^{5}	1.25×10^{-6}
F20	200000	1.06	49.6	5×10^{0}	6.0×10^{6}	1.38×10^{-6}
F39	390000	1.10		4×10^{1}	4.4×10^{7}	1.58×10^{-6}
F90	900000	1.12		1.0×10^{3}	6.9×10^{8}	2.09×10^{-6}

This indicates that a superposition of curves representing the variations of η_0 vs. the temperature T for each sample can be achieved if B/α_f is a constant. The equation of the master curve, with a reference mass M_0, gives the values of the parameters B/α_f and $T_\infty(M_0)$. We can derive the T_∞ value for all the samples from the horizontal shift factor.

On the other hand, it has been shown that the fractional free volume f depends on chain length as

$$f(M,T) = f(M) + A/M \qquad (15)$$

Then relations 12 and 15 give

$$T_\infty(M) = T_{\infty\infty} - (A/\alpha_f)/M \qquad (16)$$

So we obtain all the coefficients describing the variations of the monomeric friction factor ζ_0 for pure fractions of polystyrene.

For broad molecular weight distribution samples, a law for T_∞ has been postulated. Fox and Flory[14] have shown that the specific volume of a polymer is a linear function of $1/M_n$—which is proportional to the number of chain ends—and proposed that the free volume should follow the same relation. A good confirmation was obtained by Ninomiya, Ferry, and Oyanagi[15] for poly(vinyl acetate) fractions and their blends. Thus, we may use relation 16 for blends of polystyrene, replacing M and M_n. The concentration dependence for ζ_0 can be derived from the variations of A and α_f.

Viscoelastic Parameters. In the time scale where entangled chains may relax, corresponding to $\omega\tau \sim 1$, the low molecular weight component in such binary blends acts as a viscous solvent ($\omega\tau_s \ll 1$).

Thus we can define the terminal viscoelastic parameters of the entangled polymer relaxation by

zero-shear viscosity $\qquad \eta_0' = \eta_0 - \eta_s \qquad (17)$

steady-state compliance $\qquad J_e'° = J_e°\left(\dfrac{\eta_0}{\eta_0 - \eta_s}\right)^2 \qquad (18)$

relaxation time $\qquad \tau = \eta_0' J_e'° \qquad (19)$

where η_0 and $J_e°$ are measured quantities for the blend and η_s is the solvent viscosity.

η_0 and η_s can be derived as the intercept with the real axis of the relaxation domain relative to the entangled chains in the complex diagram η'' vs. η' (see, for example, Figure 5). On the other hand, the high dispersion of the relaxation time values calculated from the data (η_0, η_s, and $J_e°$) does not allow us to test efficiently eq 9. It seemed more reasonable to use an average relaxation time τ_0,[11] defined as the reciprocal of the frequency at the maximum of η''. We have shown that this relaxation time τ_0 is intermediate between the τ_n and τ_w average times defined by Graessley.[10] Thus the experimental concentration dependence of these parameters η_0', $J_e'°$, and τ_0 will be compared with theoretical calculations (relations 10, 11, and 9).

Results and Discussion

Fractions. In Table I, we have reported the structural and viscoelastic parameters for fractions of linear polystyrenes. Samples F002, F008, and F018 have been used as a solvent for entangled samples F11 and F90. Their relaxation times are far from those of F11 and F90, confirming the fact that the low molecular weight components act as a viscous solvent in a range of frequencies such as $\omega\tau_0 \sim 1$ for entangled samples.

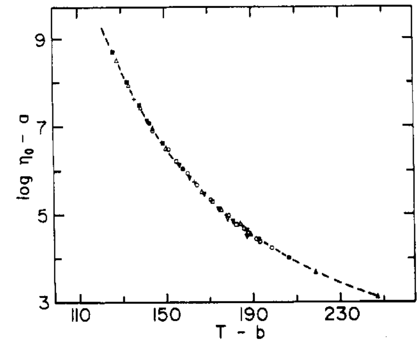


Figure 1. Master curve of the zero-shear viscosity η_0 vs. temperature for fractions of polystyrene: (□) F002; (△) F004; (+) F008; (▼) F018; (○) F04; (×) F11; (●) F20; (□) F39; (▲) F90.

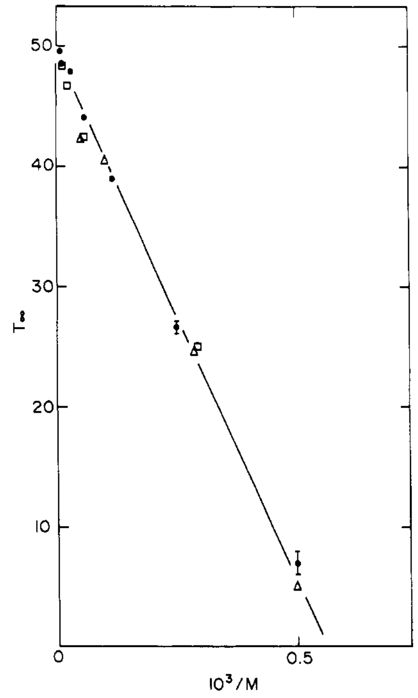


Figure 2. Characteristic temperature T_∞ as a function of the inverse of the molecular weight for narrow-distribution samples: (○) our results; (□) ref 16; (▽) ref 17.

Measurements of viscosity η_0 for all the fractions at various temperature lead to a master curve (Figure 1) by horizontal and vertical shifts. We derive a value for α_f/B = 6.17×10^{-4} K^{-1} and $T_\infty(M_0)$ = 48.6 °C for M_0 = 110000. From the horizontal shift factor b, we obtain the values of $T_\infty(M)$ for each sample (Table I). The variations as a function of M are in agreement with eq 16:

$$T_\infty(M) = 49.6 - 8.8 \times 10^4/M \text{ °C} \qquad (20)$$

as shown in Figure 2. Assuming B = 1, we can derive A = 54.3 g from eq 16. Then the isomobility state of fractions

Table II
Molecular Characteristics of Blends Included in This Study[a]

blend	N_0	N_{0s}	N_0/N_{0s}^2	ϕ_c
F11-F002	1060	19	2.87	0.34
F11-F018	1060	168	0.04	0.34
F90-F008	8650	82	1.30	0.04

[a] N_0 is the number of monomers per molecule.

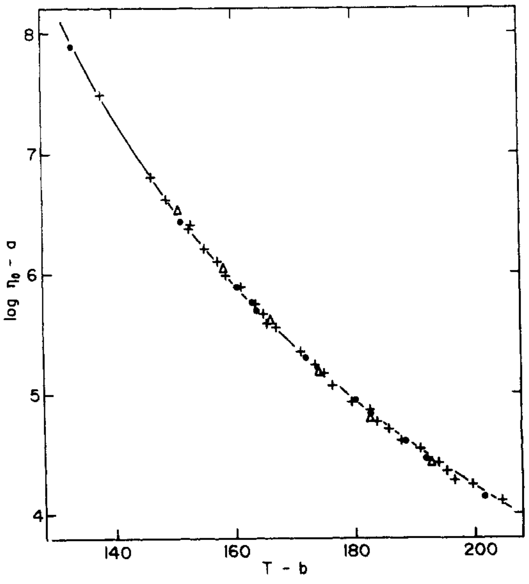


Figure 3. Data of viscosity η_0 for concentrated solutions of polystyrene vs. temperature: (●) F11/F002; (▲) F11/F018; (+) F90/F008; (—) master curve of pure fractions.

($\zeta_0(T_1,M_1) = \zeta_0(T_2,M_2)$ corresponds to $T_1 - T_\infty(M_1) = T_2 - T_\infty(M_2)$) can be characterized by relation 20.

Concentrated Solutions. Mixtures of two samples of the same polymer allow one to maintain a constant concentration of monomers, neglecting the density difference, over a large range of volume fraction ϕ. The N_0, high-polymer part remains entangled up to $\phi_c = N_c/N_0$, where $N_c \sim 2N_e$ represents the onset of the entangled regime for fractions. The chain topology is unperturbed if, theoretically, the Flory conditions are fulfilled, namely, $N_0/N_{0s}^2 < 1$,[18] this value being only an order of magnitude. Experimental conditions are summarized in Table II.

(a) Concentration Dependence for the Friction Factor ζ. In the case of a distribution of molecular weights, it is assumed that the critical temperature T_∞ varies with the number-average molecular weight M_n. $T_\infty(M_n)$ was calculated from 20, inducing the horizontal shift factor b for the thermal variations of viscosity η_0. Figure 3 shows that, for all solutions studied, the experimental points are well located on the fraction master curve. The friction factor ζ_0 is affected only by the molecular weight distribution. No concentration dependence may be seen; i.e., $\beta = 0$ in relation 4. This conclusion is not surprising, the solvent being of the same species as the entangled polymer. The polymer–solvent segmental interactions are unchanged, compared with interactions within the pure polymer. Keeping $T - T_\infty(M_n)$ constant means working at the same value of the friction coefficient ζ_0, taking into account the effect of the molecular weight distribution. All the data presented below are given at $T - T_\infty = 110.4$ °C, corresponding to $T = 160$ °C in the limit of high molecular weights.

(b) Concentration Dependence for the Viscoelastic Parameters. The zero-shear viscosity η_0 and steady-state compliance $J_e{}^\circ$ are classically derived from the curves of $G''(\omega)$ and $G'(\omega)$. Figure 4 shows the master curves obtained for the F90–F008 solutions and the pure components. Their terminal relaxation domains are well separated. In the case of the solutions, the relaxation domain observed at the lowest frequencies is due to the entangled chains. The representation of the complex viscosity (Figure 5) shows the extent of this area and allows one to

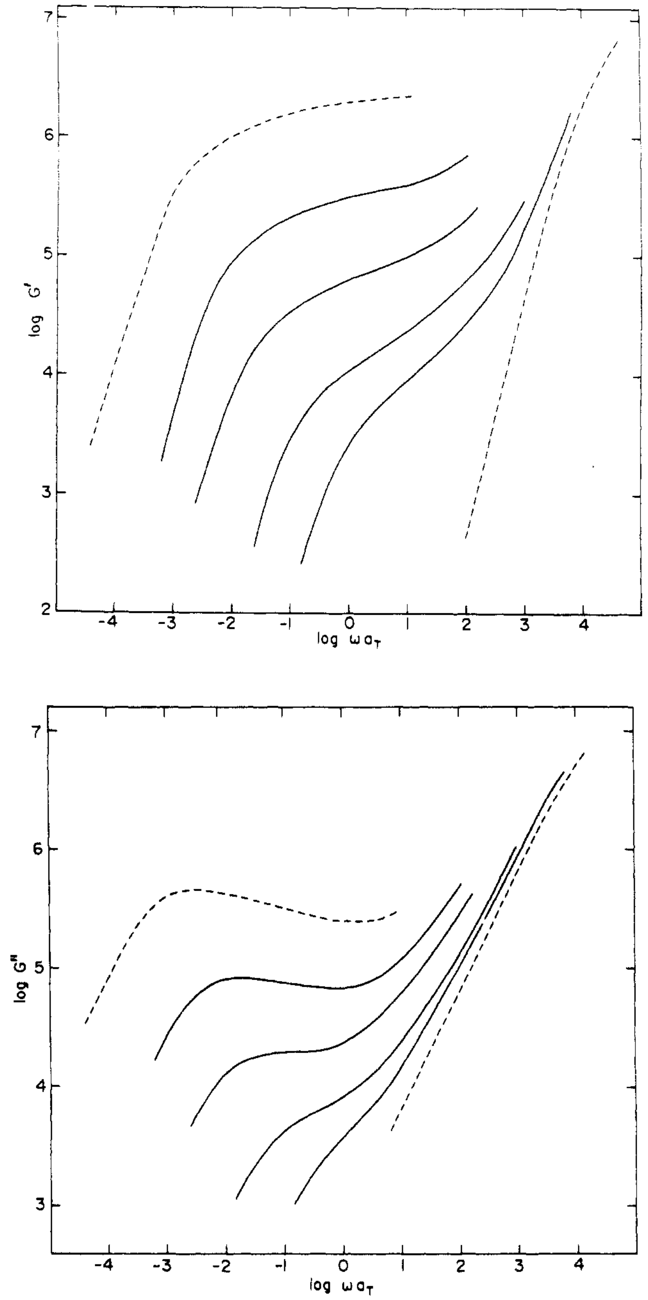


Figure 4. Master curve of $G'(\omega)$ and $G''(\omega)$ at 160 °C for pure fractions F90 and F008 (dotted lines) and for binary blends (full lines): from left to right, ϕ = 0.40, 0.20, 0.10, and 0.05.

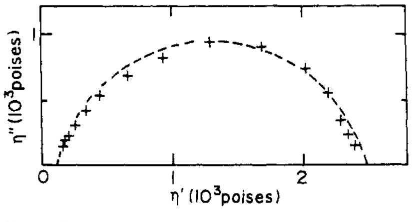


Figure 5. Complex viscosity $\eta^*(\omega)$ for a F11–F002 blend at T = 160 °C (ϕ = 0.40). The intersections with the real axis give η_s and η_0.

Table III
Data of the F90–F008 Blends at $T - T_\infty$ = 110.4 °C[a]

ϕ	T_∞, °C	τ_0, s	$\eta_0 - \eta_s$, P	$J_e'^\circ$, cm²/dyn
0.05	39.8	4×10^0	2.3×10^4	4×10^{-4}
0.10	40.3	2.09×10^1	2×10^5	1.4×10^{-4}
0.20	41.3	9.3×10^1	3×10^6	5×10^{-5}
0.40	43.4	2.7×10^2	4×10^7	8×10^{-6}
1	49.5	1.0×10^3	6.9×10^8	2.09×10^{-6}

[a] T_∞ was calculated from relation 20 with $M = M_n$. $J_e'^\circ$ was calculated from relation 18.

Table IV
Data of F11 Sample Solutions at $T - T_\infty$ = 110.4 °C[a]

ϕ	T_∞, °C	τ_0, s	$\eta_0 - \eta_s$, P	$J_e'^\circ$, cm²/dyn
		F11–F002 Blend		
0.40	22.9	1.26×10^{-1}	3×10^4	6.6×10^{-6}
0.60	31.1	3.1×10^{-1}	1.3×10^5	2.9×10^{-6}
0.80	40	5×10^{-1}	3.2×10^5	1.8×10^{-6}
0.90	44.5	6.5×10^{-1}	5.5×10^5	1.4×10^{-6}
1	48.8	8.3×10^{-1}	8.7×10^5	1.25×10^{-6}
		F11–F018 Blend		
0.70	47.5	4.2×10^{-1}	3×10^5	2.2×10^{-6}

[a] T_∞ was calculated from relation 20 with $M = M_n$. $J_e'^\circ$ was calculated from relation 18.

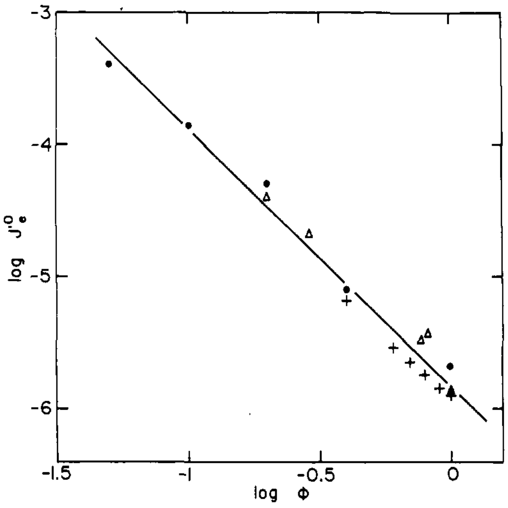


Figure 6. Variations of the reduced recoverable compliance $J_e'^\circ$ vs. concentration: (●) F90; (+) F11; (Δ) ref 4 (M = 592 000, M_s = 20 000).

calculate $\eta_0 - \eta_s$ and τ_0. It can be noticed that, in almost all the solutions, η_s is negligible. When it is measurable, its value is comparable with the viscosity of the pure solvent for the same value of $T - T_\infty$. The data for the three solutions studied are presented in Tables III and IV. Figure 6 shows that the recoverable compliance obeys the relation

$$J_e'^0 = 1.5 \times 10^{-6}\phi^{-1.95}\ \mathrm{cm^2\ dyn^{-1}} \qquad (21)$$

leading to a value of exponent α near 0.5 in eq 11. Then the average relaxation time τ_0 (relation 9) is given by

$$\tau_0^{-1} = \tau_{d0}^{-1}\phi^{-1} + \tau_{m0}^{-1}\phi^{-3} \qquad (22)$$

with $\tau_{d0} = 2.3 \times 10^{-17}M^{3.3}$ and $\tau_{m0} = 1.4 \times 10^{-21}M^{4.2}$ at T = 160 °C.[11]

Figures 7 and 8 show good agreement with experimental data and, above all, that pure reptation cannot explain these results. The dotted straight lines correspond to $\tau_0 \propto \phi$ (relation 5) and the curves are obtained from relation 22. The influence of tube renewal is well emphasized in such solutions which are slightly entangled. The pure F11 sample is itself weakly entangled ($M/M_e \sim 6$) and tube renewal is the dominant relaxation mechanism for its solutions (Figure 7). In this figure, it can be noticed that the relaxation time, τ_0, does not depend on nature of the solvent (F002 and F018). This time is then a characteristic time for the relaxation of the entangled chains.

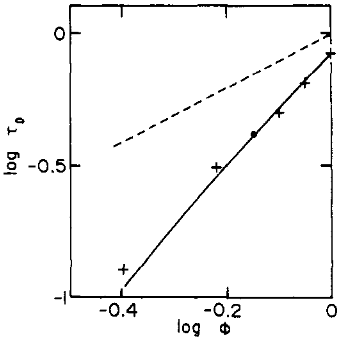


Figure 7. Terminal relaxation time τ_0 for the F11 sample as a function of the volume fraction, ϕ, at $T - T_\infty$ = 110.4 °C. The dotted line represents a pure reptation regime; the full curve represents the combined effects of reptation and tube renewal (relation 22).

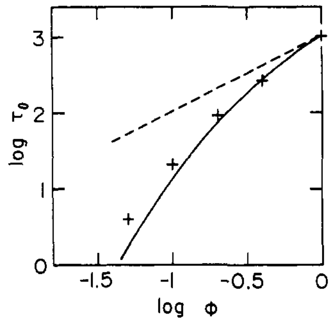


Figure 8. Terminal relaxation time τ_0 for the F90 sample as a function of the volume fraction, ϕ, at $T - T_\infty$ = 110.4 °C. The meaning of the curves is the same as in Figure 7.

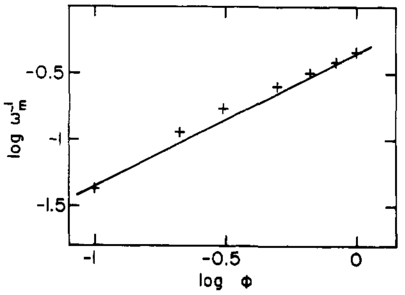


Figure 9. An average relaxation time as a function of the concentration for strongly entangled HPB solution (ref 6). The straight line represents the reptation theory: $\tau_0 \propto \phi^1$.

For the F90 solutions (Figure 8), the pure F90 sample is itself strongly entangled ($M/M_e \sim 50$) and its behavior comes closer to that of pure reptation. But when ϕ decreases to ϕ_c, tube renewal becomes dominant from $\phi \sim 0.1$. Then we can assume that the reptation theory should be adequate only for high values of $\phi M/M_e$. A confirmation of this assumption is given in Figure 9. Dynamic measurements of solutions of hydrogenated linear polybutadiene in low molecular weight linear polyethylene have been performed by Raju et al.[6] The HPB 350/Bareco 1000 solutions lie within the range $30 < \phi M/M_e < 300$. These authors have measured the frequency ω_m at the maximum of the loss modulus $G''(\omega)$ curve. The reciprocal of ω_m is a measure of an average terminal relaxation time ($\tau_0 = \omega_m^{-1}$ in the Maxwell model) and its variations, for strongly en-

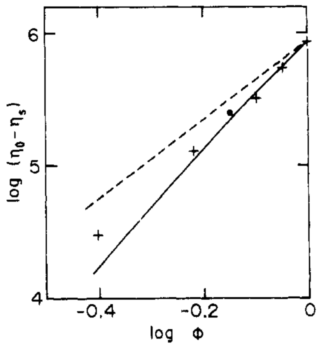


Figure 10. Viscosity of the F11 sample as a function of the concentration at $T - T_\infty = 110.4$ °C. The curve corresponds to relation 23, the dotted line to reptation theory.

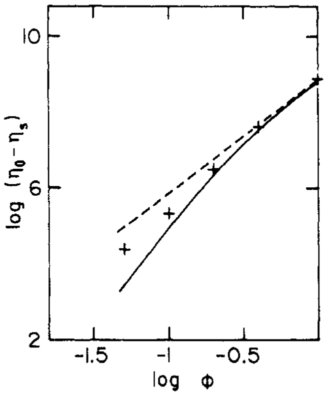


Figure 11. Viscosity of the F90 sample as a function of the concentration at $T - T_\infty = 110.4$ °C. The curve corresponds to relation 23, the dotted line to reptation theory.

tangled solutions, follow a law $\omega_m^{-1} \propto \phi$ in agreement with the reptation theory.

The zero-shear viscosity $\eta_0 - \eta_s$ is given by relation 10 or

$$\eta_0 - \eta_s = \eta_{00}\frac{\tau_0}{\tau_{00}}\phi^2 \qquad (23)$$

with η_{00} and τ_{00} relative to the pure polymer.

For the highest concentrations, the experimental data follow the above law (Figures 10 and 11) but, when ϕ tends to ϕ_c, the agreement is worse. This can be related to the fact that the tube renewal model omits all the fluctuations of entanglement concentration. These experimental conditions correspond indeed to the crossover region between the entangled and unentangled regimes, located at $\phi \sim \phi_c$. Then the tube concept is less appropriate; the polymer has an individual chain behavior. The dotted lines in Figures 10 and 11 show that, as for relaxation times, pure reptation is not satisfactory ($\eta_0 - \eta_s \propto \phi^3$). If one would use a power law, for the F11 sample, one gets $\eta_0 - \eta_s \propto \phi^{3.58}$ and for the F90 sample $\eta_0 - \eta_s \propto \phi^{3.50}$, in agreement with the empirical law $\eta_0 - \eta_s \propto (\phi M)^b$.[7]

Other viscosity data obtained from creep and recovery measurements on blends of polystyrene by Orbon and Plazek,[4] confirm that tube renewal cannot be neglected for $M/M_e < 30$ (Figure 12). In this molecular weight range, the same empirical law applies well. But at higher entanglement densities, as in the case of hydrogenated linear polybutadiene solutions mentioned above, data agree very well with the reptation theory; i.e., $(\eta_0/\zeta_0) \propto \phi^3$ in the range $62 < \phi M/M_e < 300$, as can be seen in Figure 13. It is important to point out that, for fractions of hydrogenated linear polybutadienes with the same microstructure, the molecular weight dependence for viscosity is described by

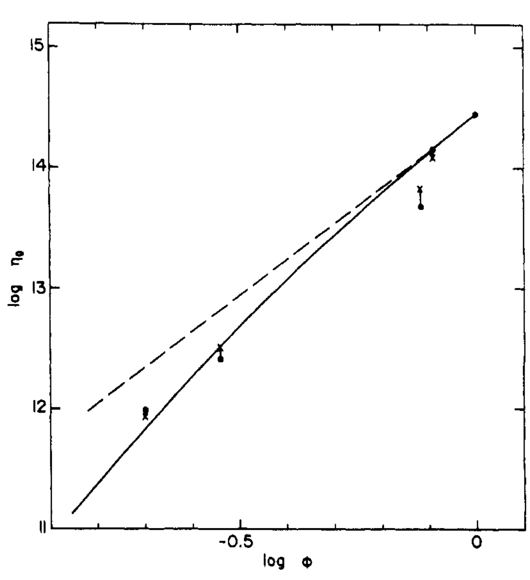


Figure 12. Viscosity of entangled polystyrene (M = 590 000) as a function of the concentration at $T - T_\infty = 56.2$ °C (ref 4): (O) data corrected by effects of impurity; (X) data uncorrected. The curves have the same meaning as in Figures 10 and 11.

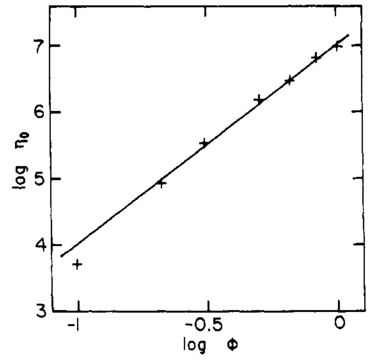


Figure 13. Viscosity η_0 as a function of the concentration for strongly entangled HPB solutions (ref 6). The straight line represents the reptation model: $\eta_0 \propto \phi^3$.

$\eta_0/\zeta_0 \propto M^{3.6}$ for $67 < M/M_e < 300$.[19] Accordingly, the viscosity of concentrated solutions of linear HPB highly entangled should be expressable by the form

$$\eta_0/\zeta_0 \propto \phi^3 M^{3.6}$$

Graessley and Raju[20] noticed the "weaker than expected" concentration dependence in relation to a form $\eta_0/\zeta_0 \propto (\phi M)^{3.6}$ but offered no explanation.

All these results indicate that the reptation model describes correctly the concentration dependence of the terminal relaxation times and zero-shear viscosities, if we include the tube renewal effects. However, this model (reptation plus tube renewal) fails in describing the molecular weight dependence and this had been shown previously.[11] Thus, it seems to us that the empirical law $\eta_0/\zeta_0 \propto (\phi M)^b$ observed for $\phi M < 30$–50 is fortuitous or, at least, the same exponent b for the two parameters does not have the same origin. Further analysis is needed to understand this double aspect of the dynamics of macromolecules: the influence of chain length and entanglement density.

Conclusion

Our analysis gives a reasonable picture of the concentration effect on the terminal viscoelastic parameters (zero-shear viscosity, limiting compliance, and relaxation time) in the case of concentrated solutions of linear entangled polymers. The reptation model has been improved by taking into account the motion of the surrounding chains. The experimental data give $J_e^\circ \propto \phi^{-2}$ for the concentration dependence of the limiting compliance: that means that the average spacing between entanglements N_e varies as ϕ^{-1}, in agreement with the reptation model with or without tube renewal effects. Our model explains reasonably the variations of the terminal relaxation time, its value being clearly influenced by tube renewal when the entanglement density is weak, i.e., $\phi M/M_e$ lower than about 30–50. In the same range of concentrations, our model predicts correctly the empirical law for zero-shear viscosity: $\eta_0/\zeta_0 \propto \phi^{3.4-3.5}$. But for strongly entangled solutions ($\phi M/M_e > 60-50$), the reptation is dominant and data of the literature show that, in this case $\tau_0/\zeta_0 \propto \phi^1$ and $\eta_0/\zeta_0 \propto \phi^3$. Within the same range, the molecular weight dependence remains $\eta_0/\zeta_0 \propto M^{3.4-3.6}$, confirming that tube renewal is not an explanation for the discrepancy between experiment and theory as far as the molecular weight dependence is concerned.

References and Notes

(1) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1980; Chapter 17, p 486.
(2) Isono, Y.; Fujimoto, T.; Takeno, N.; Kjiura, H.; Nagasawa, M. *Macromolecules* **1978**, *5*, 888.
(3) Berry, C. G.; Nakayasu, H.; Fox, T. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1825.
(4) Orbon, S. J.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1871.
(5) Marin, G.; Menezes, E. V.; Raju, V. R.; Graessley, W. W. *Rheol. Acta* **1980**, *19*, 462.
(6) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W. *Macromolecules* **1981**, *14*, 1668.
(7) Berry, C. G.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(8) Graessley, W. W. *J. Chem. Phys.* **1971**, *54*, 5143.
(9) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1818.
(10) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(11) Montfort, J. P.; Marin, G.; Monge, Ph. *Macromolecules* **1984**, *17*, 1551.
(12) Klein, J. *Macromolecules* **1978**, *11*, 852; *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 105.
(13) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(14) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(15) Ninomiya, K.; Ferry, J. D.; Oyanagi, Y. *J. Phys. Chem.* **1963**, *67*, 2297.
(16) Plazek, D. J.; O'Rourke, V. M. *J. Polym. Sci., Part A* **1971**, *9*, 209.
(17) Gray, R. W.; Harrison, G.; Lamb, J. *Proc. R. Soc. London, Ser. A* **1977**, *356*, 77.
(18) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(19) Raju, V. R.; Rachapudy, H.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1223.
(20) Graessley, W. W.; Raju, V. R. *J. Polym. Sci., Polym. Symp.* **1984**, *No. 71*, 77.

Chain Statistics of Poly(diacetylenes) in Solution

G. Allegra and S. Brückner*

Dipartimento di Chimica del Politecnico, 20133 Milano, Italy

M. Schmidt and G. Wegner

Max-Planck Institut für Polymerforschung, D-6500 Mainz, West Germany.

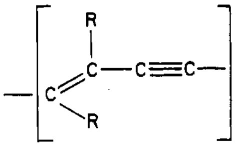
Received May 21, 1985

ABSTRACT: Light-scattering results from dissolved poly(diacetylene) chains (Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* 1984, *17*, 837) may be quite satisfactorily interpreted on the basis of a single rotational isomer undergoing twisting and bending fluctuations, their amplitude being directly derived from IR force constants. The usual rotation-matrix algorithm is adopted. Randomly introducing a $^1/_6$ fraction of ±90° rotations around the triple bonds of the structure $-(\mathrm{CR{=}CR{-}C{\equiv}C}-)_N$ to account for the specifically observed conjugation length, the mean-square chain size shrinks by less than 7% (the persistence length decreases from 190 to 177 Å); inaccuracy in the force constant adopted for twisting around the C=C bond and perhaps excluded-volume effects may account for the difference. It is shown that both models are very well represented by an ideal wormlike chain with the proper persistence length. No significant amount of either the cis conformation of the double bonds or the cumulene structure $=(\mathrm{CR{-}CR{=}C{=}C}=)_N$ is compatible with observation, in that they would cause a drastic reduction of the chain size.

Introduction

As first shown by Wegner in 1960,[1] poly(diacetylenes) (PDA) may be synthesized as macroscopic single crystals by solid-state polymerization.[2-7] X-ray analysis indicates that the structure is close to a regular sequence of double and triple bonds separated by single bonds, as shown in Figure 1a.[8,9] Although additional evidence from spectroscopic investigations confirms this structure to be the most important, it suggests that the resonance structure reported in Figure 1b may also play some role, thus stabilizing chain planarity.[10] More recently, it has been shown[11] (henceforth quoted as paper 1) that suitably substituted PDA's may be dissolved in appropriate solvents, thus opening the way to a vast field of physicochemical studies. In particular, in paper 1 extensive investigations were reported on PTS-12 and P3BCMU (see Table I) dissolved in $CHCl_3$, CH_2Cl_2, and dimethylformamide. Amid a series of interesting results, it was shown that both polymers (i) display features analogous to those of the wormlike (Porod–Kratky) chain model, the persistence length l_{pers} being in the range 150–200 Å for PTS-12, and (ii) may be described as consisting of seg-

Table I
Two Examples of Soluble Poly(diacetylenes) of General Structure



	R
PTS-12	$(CH_2)_4OSO_2C_6H_4CH_3$
P3BCMU	$(CH_2)_3OCONHCH_2CO_2\text{-}n\text{-}C_4H_9$

0024-9297/86/2219-0399$01.50/0