Macromolecules **1982,** *15,* 1329-1332

Newtonian Viscosity of Semidilute Solutions of Polystyrene in Tetrahydrofuran

Alex M. Jamieson* and David Telford

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106. Received January 15, 1982

ABSTRACT: Newtonian solution viscosities of linear atactic polystyrenes of narrow molecular weight distributions in tetrahydrofuran at 30 °C were measured at concentrations encompassing the dilute and semidilute regimes. These data were interpreted according to recent dynamical theory, based on the reptation model, combined with chain statistical scaling laws. An independent empirical evaluation of the appropriate scaling behavior was made based on dynamic light scattering results described elsewhere.

Introduction

Superposition relationships for the concentration and molecular weight dependence of the Newtonian viscosity of polymer solutions have been explored for many years.[1-7] Such efforts have the practical and fundamental goals of establishing a relationship between the static (structural) properties and the dynamic (transport) behavior of the solutions. Most recently, molecular dynamic models, based on reptation in a "tube" formed from entanglement constraints,[3-7] have been successfully compared with experimental data in a few cases.

We focus on two theoretical results. First, as shown by Klein,[5] the reptation model leads to a scaling relation for the concentration, C_e, at which onset of reptation begins and at which the entanglement transition in the Newtonian viscosity of the solution is anticipated:[5]

$$\log M = \log \left[\frac{3(2^{1/2})\pi M_0}{A} \right] - \nu \log C_e \qquad (1)$$

M_0 is the monomer molecular weight and coefficient A is given by[5]

$$A = 0.83^2 j(\bar{V})\nu / C_\infty$$

where j is the number of backbone units per monomer, $\bar{V}$ is the monomer partial specific volume, and C_∞ is the characteristic ratio. It is noted that eq 1 implies an equivalent relation for the concentration dependence of the critical molecular weight, M_c, for the entanglement transition. The scaling coefficient ν is thus determined by the concentration dependence of the molecular weight of the chain length between entanglement, M_e, or, more precisely, by the concentration dependence of the dynamic screening length, ξ_h. The usual procedure is to identify ξ_h with the static screening length ξ, whose properties have been described by Daoud and Jannink[8] and Schaefer et al.[9] We will use the analysis of Schaefer et al.,[9] which generalizes the earlier work[8] to include chain rigidity. This theory[9] predicts a number of crossovers in the dependence of ξ on molecular weight $N = M/M_0$, number density $\rho = N_A C/M$, temperature $\tau = (T - \Theta)/\Theta$, where Θ is the theta temperature, and persistence length b. Table I summarizes the results of Schaefer et al.[9] With regard to eq 1, the following are noted: in regime II, $\xi \sim c^{-0.75} \sim M_e^{0.6}$ (thus $M_e \sim c^{-1.25}$ and $\nu = 1.25$); in regime III, $\xi \sim c^{-0.5} \sim M_e^{0.5}$ ($M_e \sim c^{-1}$ and $\nu = 1.0$); in regime IV, $\xi \sim c^{-1.0} \sim M_e^{0.5}$ ($M_e \sim c^{-2.0}$ and $\nu = 2.0$); in regime V, $\xi \sim c^0 \sim M_e^{0.5}$ ($M_e \sim c^0$ and $\nu = 0$).

The second dynamical result of interest here is that derived by Doi[6] and Pearson et al.[7] for the dependence of zero-shear viscosity on c, M, and M_e:

$$\eta = G T_d \qquad (2)$$

where G is the elastic modulus

$$G = ckT/M_e \qquad (3)$$

Table I[a]
Concentration, Molecular Weight, and Temperature Dependence of the Radius of Gyration (R_g) and Correlation Range (ξ)

regime	boundaries	R_g^2	ξ
I, dilute Θ	$\rho < \rho^* = 1/R_g^3$	N	
I, dilute good	$\rho < \rho^* = 1/R_g^3$	$N^{6/5}\tau^{2/5}$	
II, semidilute good	$\rho^* < \rho < \tilde{\rho} = \tau/b^3$	$N\rho^{-1/4}\tau^{1/4}$	$\rho^{-3/4}\tau^{-1/4}$
III, semidilute marginal	$\tilde{\rho} < \rho < \rho^+ = \tau$	N	$\rho^{-1/2}\tau^{-1/2}$
IV, semidilute Θ	$\rho^+ < \rho < \rho_\Theta = n^{-1/2}$	N	ρ^{-1}
V, concentrated	$\rho > \rho_\Theta$	N	ρ^0

[a] Predictions based on theoretical arguments presented by Schafer et al.[9]

and T_d is the time for a polymer chain to reptate free of its "tube". Doi[6] derived an expression for T_d that incorporates the "tube" lifetime. The result is given in terms T_d^∞, the relaxation time for infinitely large M:

$$T = T_d^\infty f(M/M_e) \qquad (4)$$

where

$$f(M/M_e) = \left[\left(1 - \left(\frac{M_e}{M} \right)^{1/2} \right)^3 + \frac{1}{5} \left(\frac{M_e}{M} \right)^{3/2} \right] \qquad (5)$$

and

$$T_d^\infty \sim \frac{\eta_s}{kT} \left(\frac{M}{M_e} \right)^3 \xi^3 \qquad (6)$$

where η_s is the solvent viscosity.

Equations 2-6 lead to an expression for the viscosity of the form

$$\eta/\eta_s \sim \xi^3 \left(\frac{M}{M_e} \right)^3 \frac{c}{M_e} f(M/M_e) \qquad (7)$$

and, as described by Doi,[6] eq 7 can be represented, to a high degree of approximation, by the power law expression

$$\eta/\eta_s \sim \frac{c\xi^3}{M_e} (M/M_e)^{3.4} \qquad (8)$$

Now, consideration of the statistical scaling relations presented in Table I leads to the following results:

Regime II

$$\xi \sim R_g(c^*/c)^{0.75} \qquad (9a)$$

$$M_e \sim M(c^*/c)^{1.25} \qquad (9b)$$

Regime III

$$\xi \sim R_g(c^*/\tilde{c})^{0.75}(\tilde{c}/c)^{0.5} \qquad (10a)$$

$$M_e \sim M(c^*/\tilde{c})^{1.25}(\tilde{c}/c)^{1.0} \qquad (10b)$$

0024-9297/82/2215-1329$01.25/0 © 1982 American Chemical Society

Regime IV

$$\xi \sim R_g(c^*/\tilde{c})^{0.75}(\tilde{c}/c^+)^{0.5}(c^+/c)^{1.0} \tag{11a}$$

$$M_e \sim M(c^*/\tilde{c})^{1.25}(\tilde{c}/c^+)^{1.0}(c^+/c)^{2.0} \tag{11b}$$

Regime V

$$\xi \sim R_g(c^*/\tilde{c})^{0.75}(\tilde{c}/c^+)^{0.5}(c^+/c_\Theta)^{1.0} \tag{12a}$$

$$M_e \sim M(c^*/\tilde{c})^{1.25}(\tilde{c}/c^+)^{1.0}(c^+/c_\Theta)^{2.0} \tag{12b}$$

By applying these statistical laws to eq 8, we obtain the following scaling relations for the viscosity:

Regime II

$$\frac{\eta}{\eta_s} \sim \left(\frac{c}{c^*}\right)^{4.25} \sim c^{4.25}M^{3.4} \tag{13}$$

Regime III

$$\frac{\eta}{\eta_s} \sim \frac{c^{3.9}\tilde{c}^{0.35}}{c^{*4.25}} \sim c^{3.9}\tilde{c}^{0.35}M^{3.4} \tag{14}$$

Regime IV

$$\frac{\eta}{\eta_s} \sim \frac{c^{6.8}\tilde{c}^{0.35}}{c^{*4.25}(c^+)^{2.9}} \sim \frac{(c^2M)^{3.4}\tilde{c}^{0.35}}{(c^+)^{2.9}} \tag{15}$$

Regime V

$$\frac{\eta}{\eta_s} \sim \frac{c\tilde{c}^{0.35}{c_\Theta}^{5.8}}{c^{*4.25}(c^+)^{2.9}} \tag{16}$$

This latter result (eq 16) may, however, be erroneous, since regime V can be influenced by proximity to the glass transition of the system, and the onset of the glass transition is known to dramatically modify the viscometric properties. Equation 14 corresponds to the result derived by Pearson et al.[7]

Experimental Methods

Photon Correlation Spectroscopy. The instrumentation and analytical procedures for these studies have been well described elsewhere.[10-12] All concentrated solutions were prepared by slow controlled evaporation of optically clean dilute solutions in dust-tight containers.[10-12] For the purposes of this paper we present data for the first moment $\bar{\Gamma}$ (initial decay slope) of the correlation functions. This time constant reflects the fastest motion of the polymer chains and is therefore numerically related to the dynamical screening length.[13,14] In fact, we may approximately write[13,14]

$$\bar{\Gamma}/2\kappa^2 = D^{\text{app}} = kT/6\pi\eta_s\xi_h^{\text{app}} \tag{17}$$

where κ is the scattering vector.[10-12]

Newtonian Viscometry. Viscosity measurements were made in a series of Cannon-Ubbelohde viscometers with different capillary diameters. A temperature of 30 °C was chosen to enable comparison with earlier PCS results.[10-12] Four linear polystyrene standards were examined (Table II).

Results

In Figure 1B, we compare the concentration dependence of D^{app} determined from $\bar{\Gamma}$ using eq 17 for a series of polystyrene standards above c^*. These data are compared with Figure 1A, the temperature–concentration diagram for polystyrene in THF at 25 °C. The latter was constructed by Schaefer et al.[9] from the molecular weight scaling behavior of the limiting translational diffusion coefficient D_{t0} vs. M, using the blob model of Akcasu and Han.[15] If we assume that this diagram is, within experimental error, also applicable at T = 30 °C, from comparison of (A) and (B) of Figure 1, it is deduced that $\tau \approx 0.2$.

Table II
Polystyrene Standards

standard	$M_w \times 10^{-5}$ [a]	M_w/M_n
PS39	3.9 ± 0.15	<1.1
PS60	6.0 ± 0.20	<1.1
PS180	18.0 ± 1.5	<1.1
PS780	78.0 ± 2.5 [b]	<1.2

[a] Weight-average molecular weight determined by light scattering. [b] Determined from an average of nine light scattering measurements at angles 2.2° < θ < 4.2° on six concentrations in the range $0.1 < c < 1.0$ mg/mL in toluene as solvent, using the Chromatix photometer.

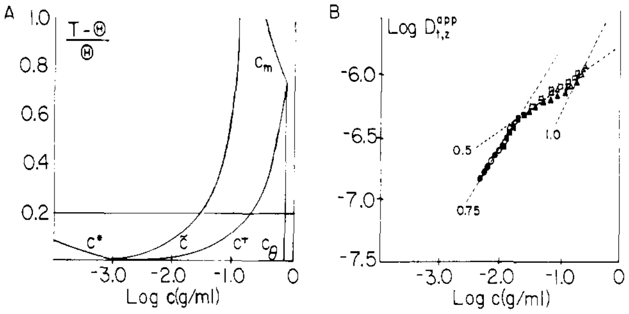

Figure 1. (A) Temperature–concentration diagram for chain statistics in polystyrene–tetrahydrofuran solutions at 25 °C, from Schaefer et al.[9] (B) Concentration dependence of apparent z-average translational diffusion coefficient of polystyrene in tetrahydrofuran at 30 °C. Dashed lines are drawn to indicate crossover in concentration scaling laws.

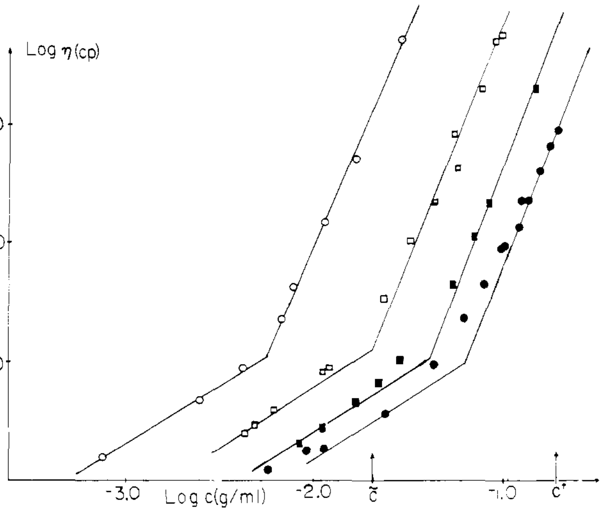

Figure 2. Newtonian viscosities of polystyrene in tetrahydrofuran at 30 °C plotted logarithmically vs. log (concentration): (○) PS780; (□) PS180; (■) PS60; (●) PS39. Also indicated by arrows are crossover concentrations $\tilde{c}$ and c^+ deduced from Figure 1B.

In Figure 1B, we show lines corresponding to $\xi_h \sim c^{-0.75}$, $\xi_h \sim c^{-0.5}$, and $\xi_h \sim c^{-1.0}$, corresponding to regimes II, III, and IV. The apparent molecular weight dependence of ξ_h in regimes III and IV has been discussed elsewhere[12] and is believed to reflect the fact that ξ_h^{app} cannot be precisely identified with ξ_h at these concentrations for PS18 and PS39, the two samples of lowest molecular weight, because of the finite entanglement lifetime.[12,16] However, for the sample with M = 600 000, we determined $\xi_h \sim c^{-0.5}$ to a high degree of accuracy in regime III. Evidence for the existence of regime IV is less impressive, but it is the behavior of regimes II and III that is particularly relevant for our subsequent discussion of viscometric data. Finally,

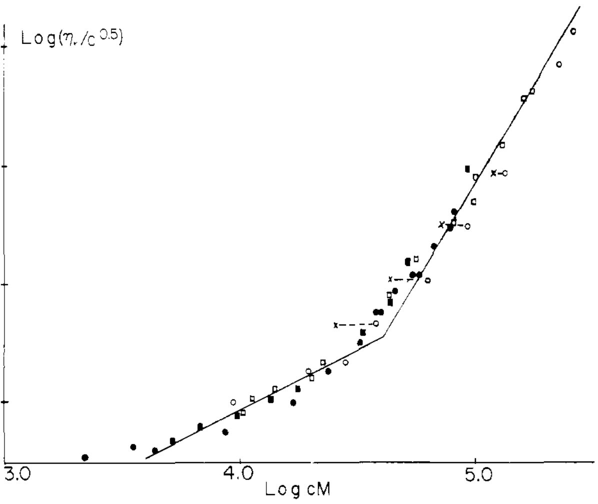

Figure 3. Plot of log $(\eta_r/c^{0.5})$ vs. log (cM) for polystyrene in tetrahydrofuran at 30 °C: (○, □, ■, ●) same as for Figure 2; (×) data transposed by $(c/\tilde{c})^{0.35}$, $\tilde{c} = 0.018$ g/mL. Solid lines have slopes 1.5 and 3.4, respectively.

we remark that our results are consistent with those of Schaefer et al.,[9] measured at $T = 20$ °C.

Viscosity Data. In Figure 2, viscosity values measured in the Newtonian region are shown for four polystyrene standards in THF at 30 °C. Lines are drawn to indicate approximate regions of asymptotic logarithmic behavior. These lines have a slope of ~1.0 in the "dilute" region and ~4.0 in the "entangled" region.

Discussion

The light scattering results presented in Figure 1 support the conclusion of Schaefer et al.[9] that, over large domains of the temperature–concentration plane, mean field theory is appropriate when polymers are rigid on the scale of a few monomers. In Figure 2, we show with arrows the crossover concentrations $\tilde{c}$ and c^+, which separate regimes II from III, III from IV, and IV from V, respectively. Evidently, the asymptotic high-concentration data for the three lower molecular weight samples PS39, PS60, and PS180 fall in regime III, while the corresponding results for the sample PS780 are in regime II.

On the basis of Figures 1 and 2, therefore, we select eq 14 to attempt a superposition of the viscometric results. This is shown in Figure 3. As anticipated, from the above discussion, viscosity values for the three low molecular weight values superpose well. However, data for PS780 that are in regime II lie systematically below the latter. From a comparison of eq 13 and 14, it is deduced that a superposition of the PS780 results on the others can be achieved, in principle, by a shift of $(c/\tilde{c})^{0.35}$ on the abscissa axis. This is also shown in Figure 3, and it can be seen that a reasonable correspondence can be achieved in this manner for the PS780 data in the asymptotic high molecular weight regime.

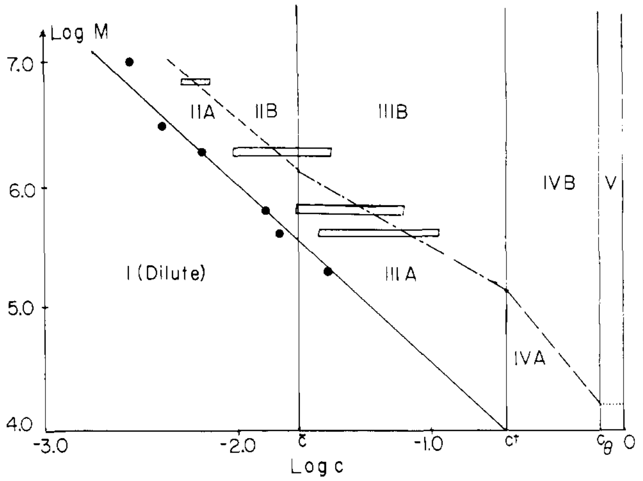

Figure 4. Molecular weight–concentration diagram for viscoelastic properties of polystyrene in tetrahydrofuran at 30 °C. Lines drawn are described in text. The solid circles refer to experimental values for the overlap concentration c^* deduced by dynamic light scattering.[11] Horizontal bars indicate entanglement crossover region in Newtonian viscosities shown in Figure 2. Roman numerals refer to statistical regimes defined in Table I. Concentration domains where chains are entangled but not so closely as to produce reptation are labeled A. Reptation behavior is implied in domains labeled B.

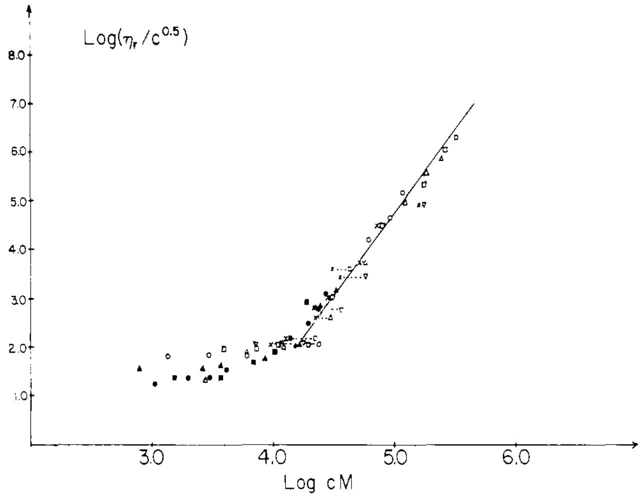

Figure 5. Plot of log $(\eta_r/c^{0.5})$ vs. log (cM) for polyisobutylene in toluene at (□) $M_w = 7.27 \times 10^6$, (△) $M_w = 3.55 \times 10^6$, (○) $M_w = 2.5 \times 10^6$, (▽) $M_w = 1.25 \times 10^6$, (▲) $M_w = 3.78 \times 10^5$, (●) $M_w = 1.39 \times 10^5$, and (■) $M_w = 4.06 \times 10^4$; (×) points transposed by $(c/\tilde{c})^{0.35}$, $\tilde{c} = 0.03$ g/mL. Solid line has slope 3.4.

In Figure 4, we show a version of the concentration–molecular weight diagram for the viscoelastic properties of polystyrene in tetrahydrofuran at 30 °C, following the recent suggestions of Graessley[17] and based on eq 8–12. The dotted line is drawn for regime V, based on the eq 1 of Klein with $\nu = 0$, using for polystyrene[5] $A = 0.078$. Orientation lines (— — —), (— - —), and (- - -) are drawn to represent crossover to eq 11b, 10b, and 9b, respectively, at the experimental crossovers in dynamical scaling deduced from Figure 1A. The latter are denoted as vertical solid lines. The solid line is drawn to denote the overlap concentration $c^* = M/N_A R_g^3$ and corresponds to eq 6 of ref 11. The solid circles are experimental values corresponding to the initial deviation of the diffusion coefficient from the linear dilute solution regime.[10-12] The horizontal bars are used to denote the concentration ranges spanning the point at which, based on Figure 2, initial departure from the asymptotic dilute regime of viscosity behavior to that at which initial onset of the asymptotic high-concentration regime of viscosity begins.

In summary, the PCS and Newtonian viscosity data for polystyrene in THF both appear to be consistent, within experimental error, with the theoretical results derived from the reptation model, coupled with appropriate statistical scaling of the chain entanglement screening length. It is of interest to note that Klein[18] pointed out to us that the viscometric data reported by Schurz and Hochberger[19] for polyisobutylene in cyclohexane show clear evidence for a crossover from regime II to regime III behavior in the correlation of log M to log C_e (eq 1). In Figure 5, we have plotted their results according to the mean field result eq 14. Data that appear to lie in regime II are then shifted, according to eq 13, by $(c/\bar{c})^{0.35}$, with $\bar{c} = 0.03$ g/mL. Again, a statistically better superposition of these results is achieved by the theory.

Finally, it is of interest to compare the viscometric–superposition results in eq 13–15 with the earlier superposition theories. As pointed out by Doi,[6] the function $(M/M_e)^3 f(M/M_e)$ implicit in eq 13–15 behaves rather closely as $(M/M_e)^{3.4}$ for $10 < M/M_e < 100$. Utilization of this result leads in eq 13–15 in each case to a result of the form

$$\eta \sim c^{\epsilon_1} M^{\epsilon_2} \tag{18}$$

with ϵ^2 always equal to 3.4. With regard to ϵ_1, from eq 13, we obtain $\epsilon_1 = 4.25$, from eq 14, $\epsilon_1 = 3.9$, and from eq 15, $\epsilon_1 = 6.8$. These results are consistent with the superposition theories[1,2] referred to earlier. In particular, we consider the approach of Simha and co-workers,[1] who propose a relation of the form

$$\eta_{sp}/c[\eta] = f(c\gamma^{-1}) \tag{19}$$

where $\gamma = K_1 M^{-a_1}$. Equation 19 leads to a scaling relation for ϕ_e of the form

$$(M_e/M)^{a_1} = \phi_e \tag{20}$$

Equation 20 is equivalent to eq 1 or eq 9b with the identification $\nu \equiv 1/a_1$. Comparison of eq 19 with eq 18 in the asymptotic high-concentration region indicates[20]

$$\epsilon_1 a_1 = \epsilon_2 + (a - a_1) \tag{21}$$

where a is the Mark–Houwink–Sakurada exponent. For Θ conditions, $a = a_1 = 0.5$ and eq 21 indicates $\epsilon_1 = 6.8$, with $\epsilon_2 = 3.4$. This is consistent with regime IV behavior. It is interesting, moreover, that the statistical scaling laws lead to a numerically similar result in both regimes II and III, viz., $\epsilon_1 = 3.9$ and $\epsilon_1 = 4.25$, respectively, indicating that a successful superposition can be achieved with an essentially constant a_1 over this part of the temperature–molecular weight–concentration plane. However, for the portion spanning regimes III and IV, substantial concentration dependence of a_1 is anticipated. This behavior is indeed observed in solutions of short chains in good solvents.[21] However, it is also likely[2,21] that in such systems the glass transition will influence the rheological behavior.

The above analysis, based on the reptation model, is also consistent with the superposition theory of Berry and Fox,[2] who write

$$\eta = F(x)\xi(T) \tag{22}$$

where $\xi(T)$ is a temperature-dependent frictional coefficient, and

$$F(x) = (N_A/6)x(x/x_c)^a$$

where

$$x = \langle S^2\rangle_0 \phi_2 / v_2 m_0$$

$\langle S^2\rangle_0$ is the unperturbed radius of gyration, ϕ_2 is the solute volume fraction, M_0 is the monomer molecular weight, and

$$a = 2.4 \qquad x > x_c$$

$$a = 0 \qquad x < x_c$$

In particular, the observation[2] that the crossover value x_c is a constant for many polymers implies a scaling relation of the form of eq 1 with $\nu = 1.0$ and therefore that the transitions occur for these systems in the mean field regime III.

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grant CPE-8017821. We also thank Professor M. E. McDonnell, Department of Physics, West Virginia University, for small-angle light scattering measurements on polystyrene standard PS780.

References and Notes

(1) Utracki, L. A.; Simha, R. *Rheol. Acta* **1973**, *12*, 455.
(2) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(3) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(4) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(5) Klein, J. *Macromolecules* **1978**, *11*, 852.
(6) Doi, M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 100.
(7) Pearson, D. S.; Mera, A.; Rochefort, W. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 102.
(8) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.
(9) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(10) Yu, T. L.; Reihanian, H.; Southwick, J. G.; Jamieson, A. M. *J. Macromol. Sci., Phys.* **1980**, *B18*, 777.
(11) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 695.
(12) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980**, *13*, 1590.
(13) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(14) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(15) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(16) Reihanian, H.; Jamieson, A. M. *Macromolecules* **1979**, *12*, 684.
(17) Graessley, W. *Polymer* **1980**, *21*, 258.
(18) Klein, J. Cambridge University, U.K., personal communication.
(19) Schurz, J.; Hochberger, H. *Makromol. Chem.* **1966**, *96*, 141.
(20) Utracki, L.; Simha, R. *J. Polym. Sci., Part A-2* **1967**, *5*, 853.
(21) Utracki, L.; Simha, R. *J. Rheol.* **1981**, *25*, 329.