Macromolecules **1982,** *15,* 1376–1384

sites. It is therefore important to always use fresh film for these measurements. The quenching data reported previously[13] and the polarization ratios given in Table II may be used to calculate the number of "hops" required for a quenching encounter at a given probability, as well as the dependence of residual polarization of fluorescence on the number of hops taken by the migrating excitation prior to trapping.

The excimer formed in stretched films is found to have the same lifetime as that in annealed films, although the excimer fluorescence maximum is found to be considerably red shifted.[13] This is an unexpected result and our inclination is to postulate that the same excimer is formed (in other words, the distance between the chromophores is the same) in both cases, while the monomer emission is attenuated in stretched films relative to annealed films.[13] Analysis of the residual error of lifetime fits in fluid solution (Table I) shows that monomer emission may persist up to 335 nm in fluid solution. Fluorescence is found to be depolarized independent of the orientation of the exciting beam relative to the stretching direction. Formation of excimeric configurations or their population by the migrating excitation thus appears to be unaffected by orientation. Excimers may therefore be used as in situ probes for mechanical deformaton and fracture in quenched as well as annealed polymers.

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References and Notes

(1) For Part 8, see: Liang, R. H.; Tsay, F. D.; Gupta, A. *Macromolecules* **1982**, *15*, 974.

(2) Holden, D. A.; Guillet, J. E. "Developments in Polymer Photochemistry"; Allen, N. S., Ed.; Applied Science Publishers: England, 1980; Vol. 1, p 1–68.

(3) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289. Ng, D.; Guillet, J. E. *Ibid.* **1981**, *14*, 405.

(4) Hoyle, C. E.; Nemzek, T. L.; Mar, A.; Guillet, J. E. *Macromolecules* **1978**, *11*, 429.

(5) Hoyle, C. E.; Guillet, J. E. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 185. Holden, D. A.; Wang, P. Y. K.; Guillet, J. E. *Macromolecules* **1980**, *13*, 295.

(6) Gupta, A.; Liang, R.; Moacanin, J.; Kliger, D.; Goldbeck, R.; Horowitz, J.; Miskowski, V. M. *Eur. Polym. J.* **1981**, *17*, 485.

(7) Tagawa, S.; Washio, M.; Tabata, Y. *Chem. Phys. Lett.* **1979**, *68*, 276.

(8) Johnson, G. E. *Macromolecules* **1980**, *13*, 145.

(9) David, C.; Baeyens-Volant, D.; Geuskens, G. *Eur. Polym. J.* **1976**, *12*, 71.

(10) Coulter, D. R.; Liang, R. H.; Di Stefano, S.; Moacanin, J.; Gupta, A. *Chem. Phys. Lett.* **1982**, *87*, 594.

(11) MacCallum, J. R., *Eur. Polym. J.* **1981**, *17*, 209.

(12) Ghiggino, K. P.; Wright, R. D.; Phillips, D. *J. Polym. Sci. Polym. Phys. Ed.* **1978**, *16*, 1499. *Eur. Polym. J.* **1978**, *14*, 567.

(13) Gupta, M. C.; Gupta, A., submitted for publication.

(14) Fox, R. B. Pure *Appl. Chem.* **1973**, *30*, 87.

(15) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.

(16) MacCallum, J. R.; Rudkin, L. *Nature* (*London*) **1977**, *266*, 338.

(17) Klöppfer, W. *Eur. Polym. J.* **1975**, *11*, 203.

(18) Geuskens, G.; Baeyens-Volant, D.; Delaunois, G.; Lu-Vinh, G.; Piret, W.; David, C. *Eur. Polym. J.* **1978**, *14*, 291, 299.

(19) Hirayama, F.; Basile, L. J.; Kikuchi, C. *Mol. Cryst.* **1968**, *4*, 83.

(20) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40.

(21) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* **1962**, *37*, 2413.

(22) North, H. M.; Soutar, I. *J. Chem. Soc., Faraday, Trans. 1* **1978**, *68*, 1101.

(23) For a discussion of other previous work on excimer kinetics in PS, see: "Organic Molecular Photophysics"; Birks, J. B., Ed. Wiley: London, 1973; Vol. 1, pp 380–386.

(24) Millar, D. P.; Shah, R.; Zewail, A. H. *Chem. Phys. Lett.* **1979**, *66*, 435.

Initial Concentration Dependence of the Oscillatory Flow Birefringence Properties of Polystyrene and Poly(α-methylstyrene) Solutions

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ABSTRACT: The concentration dependence of the oscillatory flow birefringence (OFB) properties of narrow-distribution linear polystyrene ($\bar{M}_w = 390\,000$) or poly(α-methylstyrene) ($\bar{M}_w = 400\,000$ and $5\,000\,000$) Aroclor solutions has been obtained for concentrations in the range $c[\eta] \lesssim 3$. These data are compared with the predictions of the Muthukumar and Freed treatment of the concentration dependence of bead–spring model relaxation times, the Wang–Zimm theory, and the infinite dilution bead–spring model (hydrodynamic interaction varied to duplicate the apparent transition from nearly non-free-draining to free-draining behavior with increasing concentration). The data obtained show that the relaxation time spectrum is affected markedly by concentration. The longest relaxation time is affected most and appears to exhibit a nearly exponential dependence on concentration for the solutions examined; the shortest relaxation times are almost unaffected. The Muthukumar and Freed predictions provide the best OFB frequency dependence curve shapes and absolute positions on the frequency axis and predict the observed frequency dependence for a surprisingly large range in concentration. At the highest concentrations the OFB properties show behavior indicative of enhanced separation of the longest relaxation times due to the onset of significant entanglement effects.

Introduction

There have been several studies of the frequency dependence of the oscillatory flow birefringence (OFB) and linear viscoelastic (VE) properties of linear, monodisperse polymers in solutions sufficiently dilute to permit extrapolation to infinite dilution.[1–9] Bead–spring model[10–12] predictions (isolated-molecule theories) have been shown to be in very good agreement with the infinite dilution properties at low frequencies when exact eigenvalues are employed. The infinite dilution results exhibit behavior

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that is between free draining ("Rouse limit", negligible hydrodynamic interaction) and non-free draining ("Zimm limit", dominant hydrodynamic interaction), but is generally closer to the non-free-draining case. For dilute solutions, the relaxation times of the bead–spring model are expected to exhibit some concentration dependence while the corresponding relaxation strengths are usually assumed to be concentration independent.[9] Johnson and co-workers have shown experimentally that the intermolecular interactions occurring in dilute solutions affect relaxation times significantly, and the longest relaxation time more than the others.[1] For concentrations in the so-called semi-dilute regime, the presence of interpenetrating neighboring chains tends to reduce intramolecular hydrodynamic interaction, and behavior more closely resembling the theoretical free-draining prediction of isolated-molecule theories is observed.[9] Attempts have been made to duplicate the observed apparent transition from nearly non-free-draining to free-draining behavior employing the same isolated-molecule treatments by varying the hydrodynamic interaction parameter h^* introduced by Thurston and Peterlin;[9,12] h^* is decreased with increasing concentration. The theoretical predictions generated in this way are qualitatively rather similar to the observed concentration dependence but arbitrary shifts in the time scales and magnitudes of the measured quantities are required, and the curve shape agreement obtained between experimental finite concentration results and the dilute solution theory predictions is good only at low frequencies.[9] Recently, an explicit equation for the initial concentration dependence of the bead–spring model relaxation times has been obtained by Muthukumar and Freed.[13] This paper compares the predictions of the Muthukumar and Freed approach with extensive OFB measurements for solutions of polystyrene (PS) and poly(α-methylstyrene) (PMS) for concentrations in the range $c[\eta] \lesssim 3$. In addition, the data are compared to the (isolated molecule) Zimm theory with variable (concentration dependent) h^* and to an empirical exponential equation suggested by the experimental results for the concentration dependence of the longest relaxation time. These comparisons assume that relaxation strengths are independent of concentration for the solutions studied. OFB measurements on two more concentrated and presumably entangled solutions ($c[\eta] \simeq 12$ and 23) are also presented; these data have been converted to "derived" viscoelastic properties by use of the OFB–VE interrelations of the bead–spring model theories.[11,12,14]

Experimental Section

Materials. The studies reported here have been carried out with three narrow-distribution ($\bar{M}_w/\bar{M}_n < 1.10$), atactic polymer samples: polystyrene 3B, with $\bar{M}_w = 390\,000$ (manufacturer's data; Pressure Chemical Co.), and two poly(α-methylstyrene) samples with $\bar{M}_w = 400\,000$ and $\bar{M}_w = 5\,000\,000$, generously provided by Professor L. J. Fetters of the University of Akron. These three samples will be referred to as PS-3B, PMS-5, and PMS-10, respectively. All solutions were prepared in the chlorinated biphenyl solvent Aroclor 1248, lot KM 502 (Monsanto Chemical Co.). This solvent was selected for its large dependence of viscosity on temperature[9] and the close match of its index of refraction with that of PS and PMS.[15] All solutions were made up by weight; the concentrations were converted to g/cm^3 assuming additivity of volumes (assumed densities are 1.452, 1.060, and 1.080 g/cm^3 for Aroclor 1248, PS, and PMS, respectively). The initial solution of PS-3B (0.0713 g/cm^3) was prepared by direct addition of polymer to solvent. Solvation was assisted by moderate heating (<60 °C) and occasional gentle stirring; total solvation time was about 6 weeks. The initial poly(α-methylstyrene) solutions (0.105 g/cm^3 for PMS-5, 0.0411 g/cm^3 for PMS-10) were prepared by first dissolving the polymer in analytical reagent grade benzene, which was subsequently stripped out in vacuo after the addition of Aroclor 1248. All other solutions were prepared by direct dilution and were subjected to low heating (<40 °C) and occasional gentle stirring for at least 2 weeks prior to use.

Method. The second-generation thin fluid layer OFB apparatus and the measurement techniques have been described previously.[6,15,16] This transducer has been interfaced to a second-generation computerized data acquisition and processing system that increases the effective frequency range of the apparatus and improves its sensitivity; this system is also described elsewhere.[17,18] All data reported here were obtained at an optical wavelength of 5770 Å. Solution temperatures were controlled to within ±0.01 °C and were determined by means of thermistors calibrated against an NBS calibrated standard platinum resistance thermometer. The Aroclor solvent is itself weakly birefringent when subjected to a shearing deformation; thus the total birefringence observed for a given polymer solution has contributions from both the polymer and solvent constituents. The polymer contribution is obtained by correcting the measured values for the solvent contribution based on the assumption of simple additivity of the polarizability tensors for the various constituents (procedure of Sadron).[19–21] Thus the tensor sum of the polarizability contributions of the volume fractions of pure solvent and polymer is assumed to correspond to the solution properties. For the low shear rate conditions employed in the thin fluid layer OFB instrument, the principal polarizability directions remain at ±45° with respect to the streamline direction throughout the sinusoidally time-varying cycle of deformation, which leads to a particularly simple vector subtraction correction procedure, which is detailed elsewhere.[6,20]

Results and Discussion

The OFB data are reported in terms of the frequency dependence of the magnitude S_M and phase angle θ_s of the complex mechanooptic coefficient S^* defined as (phasor notation)

$$S^* = S_M \exp(i\theta_s) = S' + iS'' \equiv -\Delta n^*/\dot{\gamma}^* \qquad (1)$$

where Δn, the real part of Δn^*, is the difference between indices of refraction n_1 and n_2 corresponding to principal directions 1 and 2, and $\dot{\gamma}$, the real part of $\dot{\gamma}^*$, is the sinusoidally time-varying shear rate as defined previously.[6,16,22] The quantities S_M and θ_s are reported rather than the real and imaginary components S' and S'' since θ_s is by far the most sensitive function of the four and the OFB experiment is sufficiently precise to be able to utilize this sensitivity. Measurements obtained at four temperatures (25.00, 15.88, 2.81 and −1.42 °C) for each solution were reduced to the 25.00 °C reference temperature, resulting in reduced variable plots of log (S_M/a_T) and θ_s vs. log fa_T, where f is the frequency in hertz and a_T is the time–temperature superposition factor.[6,9,15] For the highest concentration solutions of each sample, measurements were also obtained at 45.00 °C. The a_T factors were obtained from the low-frequency, frequency-independent S_M values where possible;[16] for the low-temperature results (2.81 and −1.42 °C) empirical shifts were utilized. The superpositions thus obtained are excellent. Scatter in measured values of S_M and θ_s before superposition are estimated to be ±0.3% and ±0.3°, respectively, throughout the working frequency range, except for the lowest concentrations and highest frequencies, where the solvent correction becomes large.

The general character of the concentration dependence of the OFB properties is illustrated in Figure 1. The finite concentration results for four solutions of PS-3B and five solutions of PMS-5 are displayed in Figures 1A,B, respectively; the individual data points have been replaced by smooth curves for clarity, and these curves have been overlayed directly. The location on the reduced frequency axis of the initial departure of θ_s from the −180° low-frequency limit is governed by the longest relaxation time τ_1.

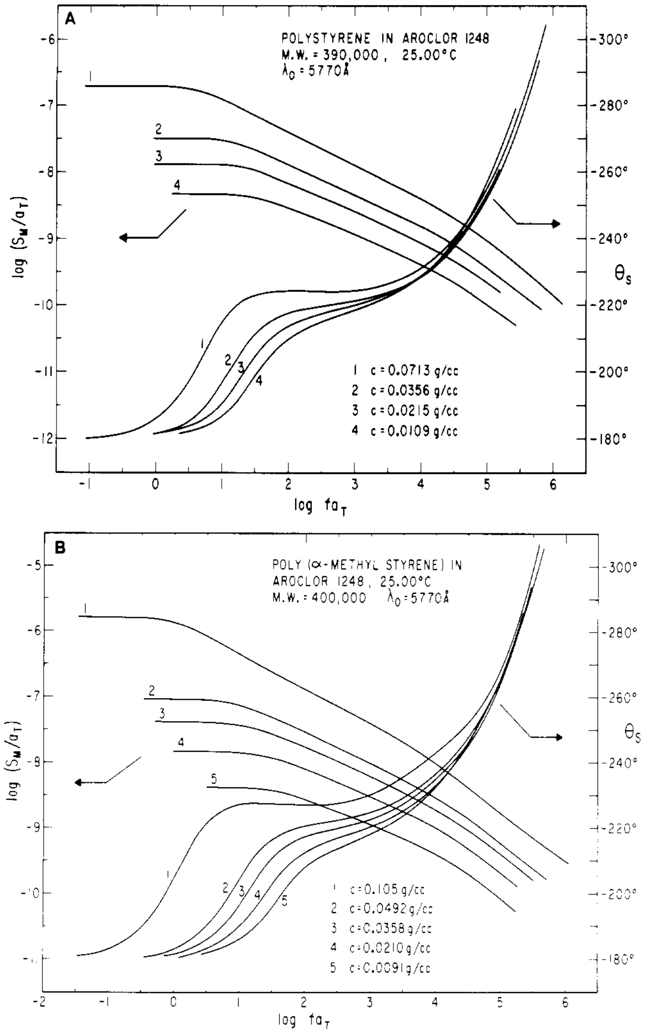

Figure 1. Plots of log (S_M/a_T) and θ_s vs. log fa_T at various concentrations for (A) 390000 MW PS and (B) 400000 MW PMS in Aroclor 1248, reduced to 25.00 °C.

Thus for PMS-5, τ_1 increases by a factor of ≈ 100 as the concentration is increased by a factor of ≈ 11; for PS-3B, τ_1 increases by a factor of ≈ 10 as the concentration is increased sevenfold. At high reduced frequencies (log $fa_T \gtrsim 5$), however, θ_s becomes essentially independent of concentration. In terms of the concentration dependence of the bead–spring model relaxation times $\{\tau_p\}$ these results suggest that the effect of concentration is mode dependent; with increasing mode number p (p increasing corresponds to τ_p decreasing) the effect of concentration is decreased. Thus τ_1 has a strong concentration dependence whereas τ_N (the shortest relaxation time) is almost concentration independent. For frequencies above log $fa_T \approx 5$, θ_s exceeds the −270° limit given by simple chain dynamics theories for all three polymer samples. This anomalous behavior has been reported previously for polystyrenes in Aroclor 1248;[6,15,17,18] it will also be the principal subject of a subsequent article.[23]

Comparisons of very dilute and infinite dilution linear viscoelastic properties and OFB results with the theoretical (isolated molecule) bead–spring model predictions indicate that in this concentration regime the observed properties tend to correspond more closely to the theoretical non-free-draining (dominant hydrodynamic interaction) predictions although the behavior is generally intermediate between the free-draining and non-free-draining limits; the appropriate value of the theoretical hydrodynamic interaction parameter required to fit experimental results is a function of the goodness of the solvent.[9] At higher concentrations the observed properties correspond more closely to the theoretical (isolated molecule) predictions for free-draining conditions. This has been interpreted in terms of a decrease in the strength of the intramolecular hydrodynamic interaction as concentration is increased due to partial screening by portions of other interpenetrating polymer chains.[9] Thus, although the bead–spring theories generally invoked strictly apply only at infinite dilution, the concentration-induced transition from non-free-draining to free-draining behavior may be approximately modeled by these theories by varying the hydrodynamic interaction parameter h^* ($h^* = \zeta/[(12\pi^3)^{1/2}b\eta_s]$, where ζ is the bead friction coefficient, b is the root-mean-square separation of adjacent beads, and η_s is the solvent viscosity). However, such finite concentration fits should be considered as approximate, empirically useful comparisons of theory and experiment since there are several aspects of the observed properties that are not predicted correctly, such as the concentration dependence of τ_1, τ_N, or the magnitude of the OFB or VE properties; in particular, these theories[10–12] do not treat the interactions between adjacent molecules that become important as concentration is increased. Infinite dilution VE properties (many different polymers) and OFB properties (PS-3B and PMS-5 in Aroclor 1248) have been compared with bead–spring model predictions; in general, excellent quantitative agreement has been obtained for VE properties at low frequencies such that $fa_T \lesssim 4.5$.[8,9,14] The values of the two theoretical parameters N and h^* (N is the number of springs or Gaussian subchains representing the polymer molecule; N is proportional to molecular weight) used to fit the OFB data were 75 and 0.15 for PS-3B and 50 and 0.175 for PMS-5.[8,14] The values of h^* of 0.175 and 0.15 for PMS-5 and PS-3B suggest that Aroclor 1248 is a moderately good solvent for PMS and a slightly better solvent for PS or that the friction constant for a subchain is somewhat greater for PMS than for PS, in agreement with the previous results for a range of molecular weights.[9,14,24] It should be noted that most of the comparisons of infinite dilution properties and bead–spring model predictions cited above have employed theoretical calculations in which Gaussian chain statistics are assumed although the data has been obtained for either Θ solvent or moderately good solvent conditions; fits have been obtained for different solvent conditions by varying h^* as required.[3,9] Thus a zero excluded volume form of the theory has been employed regardless of solvent power; strictly speaking, for either Θ or good solvent conditions, and particularly the latter, the influence of non-Gaussian chain statistics on interbead separations should be taken into account as has been done in approximate form assuming a uniform expansion by Tschoegl.[25] However, when exact eigenvalue calculations for good solvent conditions are carried out for the **H·A** matrix as modified by Tschoegl[25] or Thurston and Peterlin,[12] the effect of the non-Gaussian character of the assumed coil expansion on the VE or OFB properties is predicted to be small and similar to the effects produced by quite small changes in h^* for the longer relaxation times which are affected most by concentration. Much larger changes in h^* are required to fit good solvent data, indicating that the effect of the non-Gaussian character of the chain statistics is relatively small, usually negligible, in comparison to the major effects reflected by changes in h^*. The magnitude of the changes caused by the inclusion of this type of non-Gaussian statistics for typical coil expansions in moderately good solvents is close to the experimental scatter for low-frequency VE data; the higher precision of the OFB experiment may make the inclusion

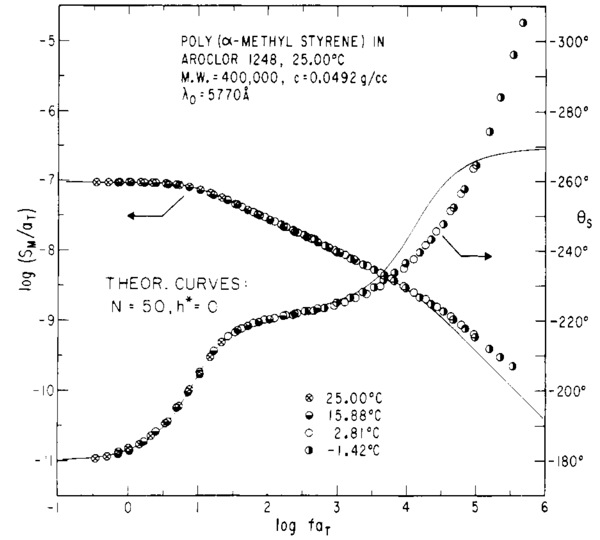

Figure 2. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0492 g/cm^3 solution of 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C. Curves: Zimm theory for $N = 50$, $h^* = 0$.

of this refinement of the bead-spring model appropriate in very good solvents, but the differences are again small. Thus for the studies reported here, which concentrate on the low-frequency end of the relaxation spectrum, the theoretical curves employed have been generated neglecting non-Gaussian effects; this also reduces the number of required theoretical fitting parameters from three to two. A subsequent paper will examine the influence of non-Gaussian statistics for OFB and VE properties predictions.[26]

Figure 2 presents OFB data for PMS-5 in Aroclor 1248 at a relatively high concentration, 0.0492 g/cm^3, corresponding to $c[\eta] \approx 5.4$; thus this solution falls in the semidilute regime. The theoretical bead-spring model curves shown in this figure (and Figures 4-14) were calculated from[22]

$$S^* = \pm(q'N_Ac/Mb^2)\sum_{p=1}^{N}\tau_p/(1 + i\omega\tau_p) \qquad (2)$$

where $\tau_p = b^2\zeta/(6kT\lambda_p)$ is the relaxation time of the pth mode, q' is an optical factor, N_A is Avogadro's number, c is polymer concentration, M is polymer molecular weight, ω is the radian driving frequency, and λ_p are the exact eigenvalues of the Zimm **H·A** (or Lodge-Wu **B**) matrix.[27-29] N has been maintained at a value of 50 in agreement with the infinite dilution results for PMS, while h^* has been taken as zero to correspond to the free-draining (Rouse) limit. At low frequencies (log $fa_T \lesssim 2.5$) the birefringence does exhibit Rouse-like curve shapes, apparently due to the increased spacings of the longer relaxation times at this concentration, which are mimicked by the infinite dilution theory by setting $h^* \simeq 0$. However, the overall width of the relaxation spectrum governed by the ratio τ_1/τ_N does not correspond to that predicted by the theory.

The finite concentration data for PMS-5 and PS-3B with concentrations in the range $0 < c[\eta] \lesssim 5$ may be compared with the (isolated molecule) bead-spring model predictions by using values of h^* between 0.175 and 0 for PMS-5 and between 0.15 and 0 for PS-3B. The results of such comparisons are qualitatively the same as is suggested by Figure 2: as concentration increases, h^* must be decreased to generate theoretical curves that match the curve shapes of measured properties at low frequencies (regions where increases in longer relaxation time spacings with decreasing h^* appear to be consistent with the data), but the overall breadth of the relaxation spectrum as determined experimentally becomes progressively larger than the theoretical predictions. Further, the theoretical shortest relaxation time τ_N actually decreases as h^* is decreased; thus to obtain fits such as are shown in Figure 2 one must employ large, arbitrary shifts along the frequency axis. Additional similar arbitrary vertical shifts are required to match the measured birefringence magnitude curves (log (S_M/a_T)).

A recent treatment by Muthukumar and Freed[13] has produced an explicit equation for the initial concentration dependence of the bead-spring model relaxation times by considering the effect of intermolecular hydrodynamic interaction (in the quasi-static limit) as described by the Freed-Edwards theory.[30,31] The Muthukumar and Freed expression for the concentration dependence of the pth relaxation time is

$$\tau_p = \tau_p^0(1 + Acp^{-\kappa} + \ldots) \qquad (3)$$

where τ_p^0 is the infinite dilution value for the pth relaxation time, A is a positive constant, and κ is a positive exponent with a value of 0.5 in Θ solvent and 0.65-0.80 in good solvents. The range of applicability for this expression was expected to be restricted to concentrations for which $c[\eta] \lesssim 1$ since the expansion is only evaluated to first order; it is also restricted to frequencies sufficiently low that quasi-static hydrodynamics are adequate. In addition, the theory does not attempt to describe the high-frequency phase angle anomaly. Qualitatively, eq 3 predicts the type of behavior illustrated in Figure 1: the longest relaxation time is affected most by concentration, and each successive (shorter) relaxation time is progressively less dependent on concentration.

In order to compare predictions based on eq 2 and eq 3 with experimental results, values of N, h^*, A, and κ are required. N and h^* are determined by comparison of the bead-spring model theory (Zimm theory) predictions and infinite dilution properties as discussed above.[8,9] Since Aroclor 1248 is a moderately good solvent for PS and PMS,[24] a value of κ of 0.65 has been arbitrarily selected; however, the resulting theoretical curves are not sensitive to small changes in κ, so its value is relatively unimportant. (This is not unexpected in view of the insensitivity of OFB and VE predictions to deviations from Gaussian chain statistics mentioned previously.) The value of A has been determined from the low-concentration limiting slope of a plot of τ_1 vs. c; from eq 2, A is given by

$$A = \frac{1}{\tau_1^0}\left(\frac{\mathrm{d}\tau_1}{\mathrm{d}c}\right)\bigg|_{c\to 0} \qquad (4)$$

The quantity A is determined to be 42 ± 0.5 cm^3/g for PMS-5 and 41 ± 0.5 cm^3/g for PS-3B. Figure 3 presents values of τ_1 plotted against c, determined from the finite concentration data using both Zimm theory curves with variable h^* and Muthukumar and Freed theory curves.[14] The smooth curve drawn through the τ_1 data is an exponential given by $\tau_1 = \tau_1^0 \exp(Ac)$, with $A = 42$ cm^3/g as determined for PMS-5 and $\tau_1^0 = 1.97$ ms as an average for the two molecules. The Muthukumar and Freed theory predicts a linear initial concentration dependence for τ_1, but over most of the range shown in Figure 3 ($0 < c[\eta] < 5$), τ_1 appears to exhibit a nearly exponential dependence on concentration. Estimates of the coil overlap concentration c^* for these two molecules fall in the range 0.01-0.02 g/cm^3;[8] evidently τ_1 does not exhibit a significant change in concentration dependence in the transition from dilute to semidilute conditions for these molecular weights.

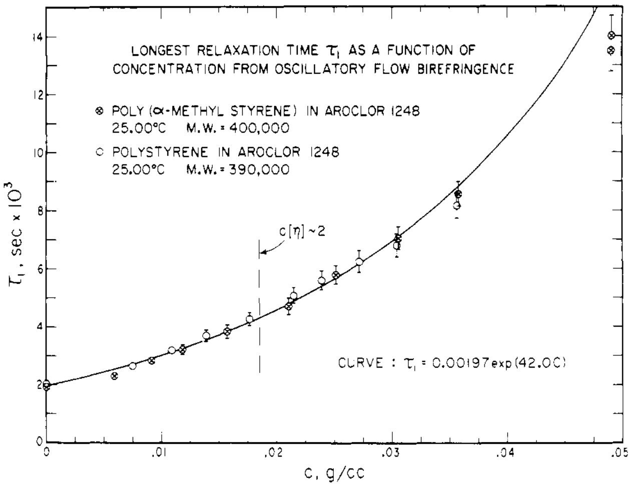

Figure 3. Plot of τ_1 vs. c for 390 000 MW PS and 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C.

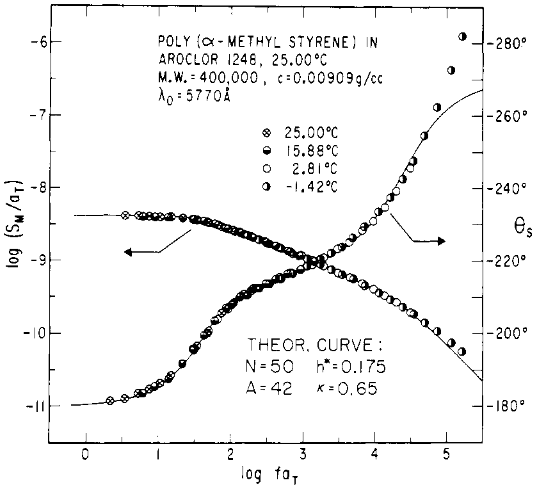

Figure 4. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.00909 g/cm^3 solution of 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: Muthukumar and Freed (M–F) theory for $N = 50$, $h^* = 0.175$, $A = 42$, $\kappa = 0.65$.

It should be noted that Dill has reported τ_1 measurements at low concentrations for T2 DNA solutions in Θ solvents that appear to be linear in c for $0 < c[\eta] < 1.7$;[33] Figure 3 might suggest a similar trend if one were to ignore the $\tau_1{}^0$ values obtained from the infinite dilution properties curves together with τ_1 data for $c > 0.02$ g/cm^3. Alternatively, the data might suggest that τ_1 is essentially concentration independent at very low concentrations, where the probability of binary interactions is negligibly small. Thus the τ_1 vs. c plot could be nearly horizontal at very low c, followed by a linear region of larger slope—similar to the Muthukumar and Freed prediction—at somehwat higher concentrations. There is some suggestion of this type of behavior in Figure 3, but detailed studies at very low concentrations are needed before any conclusions can be drawn. Since the utility of the original form of the Muthukumar and Freed predictions is being examined here, this possibility is not considered further.

Figures 4–7 present the finite concentration data for four solutions of PMS-5 and the appropriate Muthukumar and Freed theory curves generated using the parameter values discussed above. Similarly, Figures 8–12 present data for five concentrations of PS-3B. Figures 4–6 and 8–11 demonstrate that the agreement in curve shape between theory and experiment is generally excellent for $c[\eta] \lesssim 1.7$ for frequencies below the apparent onset of the high-frequency phase angle anomaly (log $fa_T \approx 4.7$). Figures 7 and 12 show that the agreement is still good at slightly higher concen-

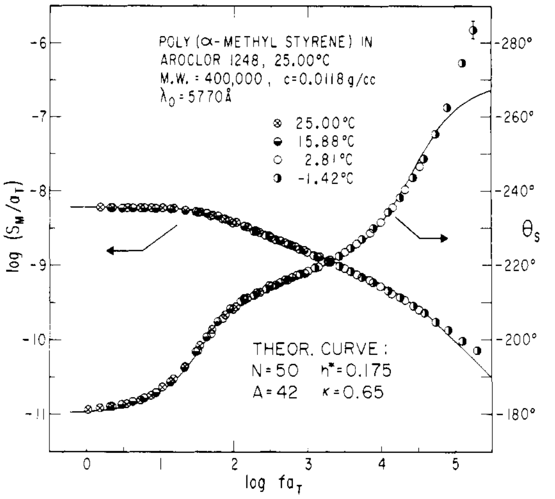

Figure 5. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0118 g/cm^3 solution of 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M–F theory.

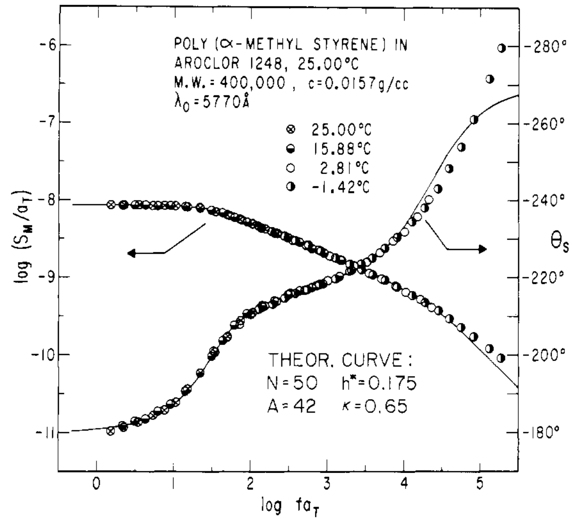

Figure 6. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0157 g/cm^3 solution of 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M–F theory.

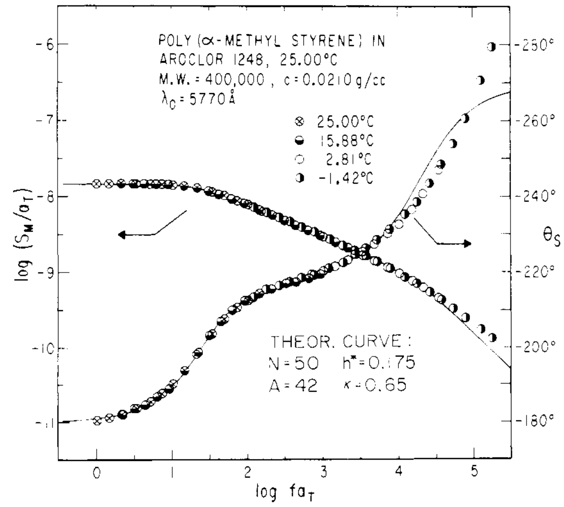

Figure 7. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0210 g/cm^3 solution of 400 000 MW PMS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M–F theory.

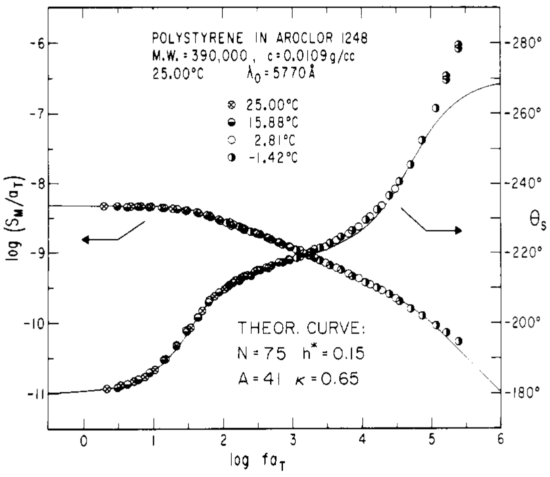

Figure 8. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0109 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M-F theory for $N = 75$, $h^* = 0.15$, $A = 41$, $\kappa = 0.65$.

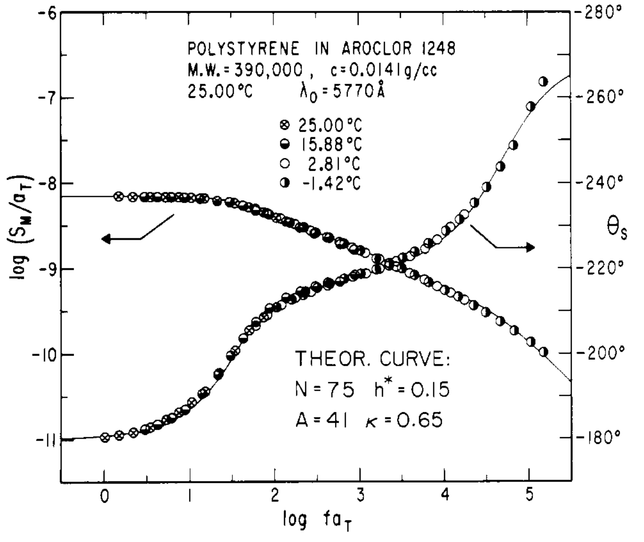

Figure 9. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0141 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M-F theory.

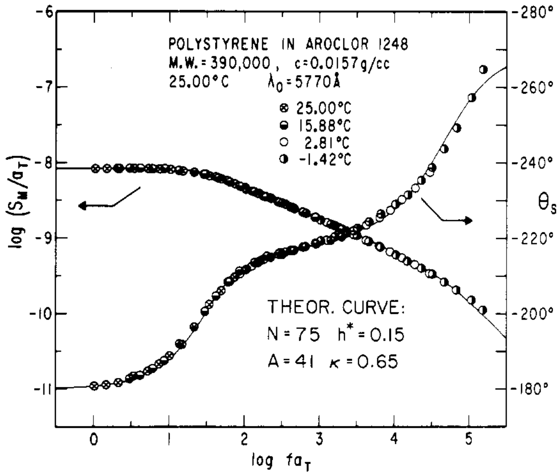

Figure 10. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0157 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M-F theory.

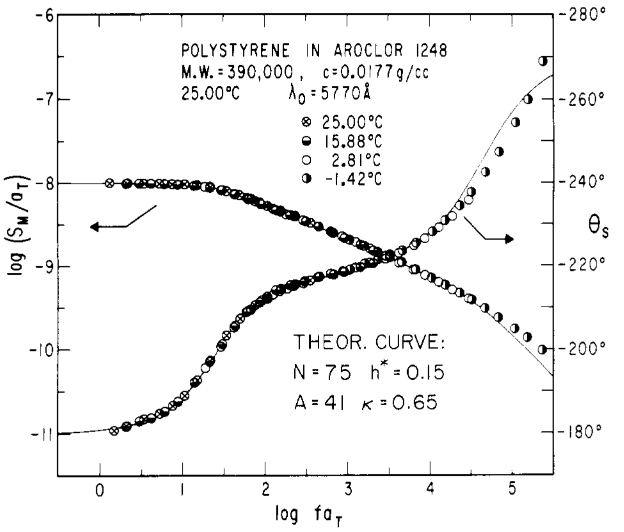

Figure 11. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0177 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M-F theory.

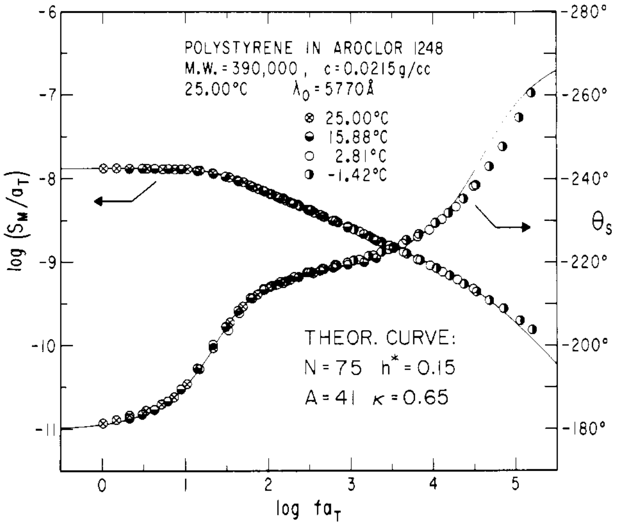

Figure 12. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0215 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: M-F theory.

trations, although the θ_s results as plotted display a noticeable deviation from theoretical predictions above log $fa_T \approx 4$. This deviation should not be interpreted as a theoretical failure to predict the concentration dependence of the shorter relaxation times correctly; in fact, the predicted shift for τ_N is quite close to what is observed experimentally. Rather it is due to the underestimation of the change in τ_1 with concentration. The theoretical curves have been shifted slightly along the frequency axis so that the low-frequency predictions coincide with the low-frequency data, thus forcing the deviation to appear at high frequency; this has been done since the major changes with concentration are observed at low frequencies, and this format provides a clearer visualization of the appropriateness of the theoretically predicted relaxation time spacing changes with concentration. The longer relaxation time spacings are predicted very well by the theory even at concentrations for which $c[\eta] \gtrsim 1.7$ although the ratio τ_1/τ_N is not. Figure 13 presents data for slightly higher solution concentrations for both PS-3B and PMS-5. Here the predictions of both the infinite dilution bead–spring model with variable h^* and the Muthukumar and Freed theory are compared with the experimental results. For both theoretical approaches the spacings of the longer relaxation times are in good agreement with the data; however, in the Muthukumar and Freed case the agreement extends approximately one decade higher in fre-

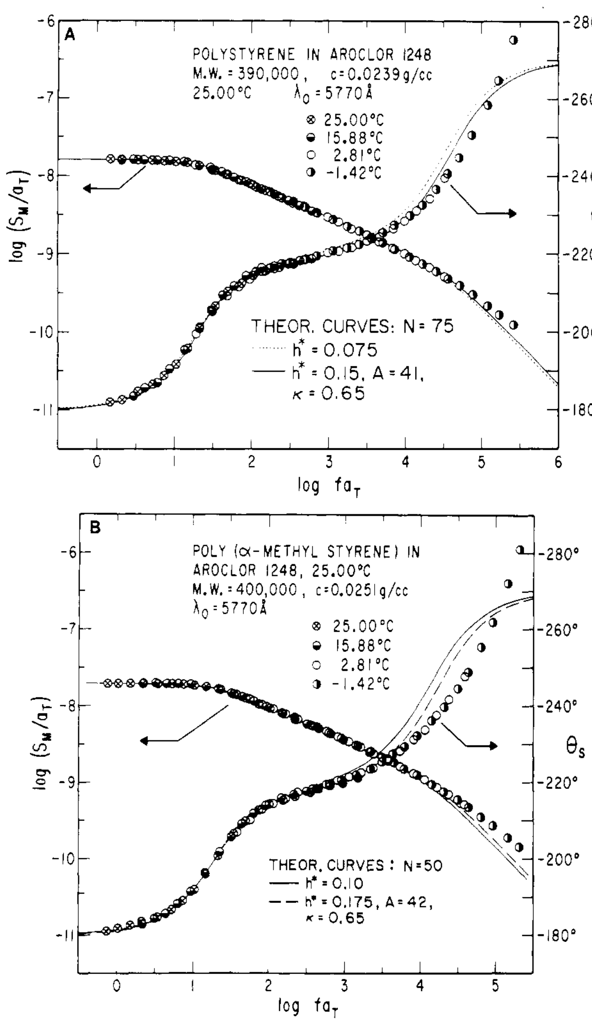

Figure 13. Plots of log (S_M/a_T) and θ_s vs. log fa_T for (A) 0.0239 g/cm^3 solution of 390 000 MW PS and (B) 0.0251 g/cm^3 solution of 400 000 MW PMS, both in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: (A) Zimm theory for $N = 75$, $h^* = 0.075$ (dotted lines), M–F theory (solid lines); (B) Zimm theory for $N = 50$, $h^* = 0.10$ (solid lines), M–F theory (dashed lines).

quency. Also, the absolute positioning predicted for the theoretical curves is much closer to being correct for the Muthukumar and Freed treatment.

The apparent exponential dependence of τ_1 on concentration displayed in Figure 3, of S_M/c at all experimentally accessible frequencies for several linear PS or PMS/Aroclor solutions, and of steady flow viscosity measurements (η_{sp}/c) for a variety of linear homopolymer/solvent systems over a wide range of concentration suggests the possibility that all relaxation times might have an exponential concentration dependence in this concentration regime.[8] By analogy with eq 3 the following empirical equation has also been considered:

$$\tau_p = \tau_p{}^0 \exp(Acp^{-\kappa}) \qquad (5)$$

As concentration approaches zero, the Muthukumar and Freed expression is recovered. Figure 14 displays the experimental results for PS-3B at a higher concentration, $c[\eta] \approx 2.7$, and the OFB predictions based on eq 2 and 5. In the region $1.3 \lesssim \log fa_T \lesssim 2.2$ the calculated θ_s is markedly different from the experimental results, suggesting that the ratio τ_1/τ_2 in particular, and the longer relaxation time spacings in general, are being overestimated. However, the overall width of the relaxation time spectrum as determined by eq 5 is in excellent agreement with the experimental results.

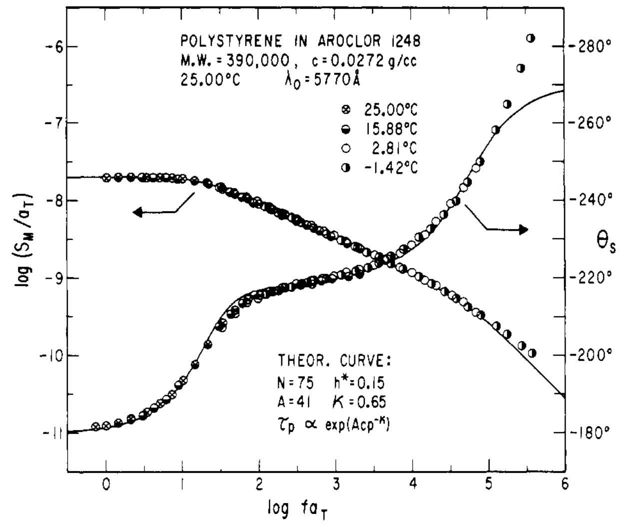

Figure 14. Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0272 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C. Theoretical curves: empirical exponential concentration dependence of relaxation times specified by eq 5 for $N = 75$, $h^* = 0.15$, $A = 41$, and $\kappa = 0.65$.

Another theoretical approach to treating the concentration dependence of the bead–spring model relaxation times is that of Wang and Zimm.[34] In this treatment the equilibrium preaveraged Oseen tensor is replaced by an explicitly concentration-dependent analogue, developed from the equations of Debye and Bueche[35] and Brinkman[36,37] for flow through a porous medium. Each off-diagonal element of the Zimm **H·A** matrix or the Lodge–Wu **B** matrix is modified by a term involving a parameter ϕ_0, which depends on concentration to the 0.5 power. Comparison of exact eigenvalue calculations with the experimental results of Figures 4–14 suggest that though the Wang and Zimm results are intermediate between the (infinite dilution) theoretical non-free-draining and free-draining limits, the character of the transition is not in quantitative agreement with the data.[14] This may be attributed in large measure to the predicted square root concentration dependence, which yields the physically unreasonable result that the concentration dependence is strongest as c approaches zero. Alternatively, by varying the value of the quantity ($\phi_0/c^{1/2}$) as a function of concentration (as in the original paper) theoretical fits to the data may be obtained that are almost as good as those shown in Figures 4–12, but the validity of this procedure is doubtful. Questions about certain approximations and simplifying assumptions incorporated in the Wang and Zimm approach have been raised, and modifications suggested;[38] in its present form, it is not successful in describing the observed concentration dependence of the OFB results.

The solutions considered heretofore fall into either the dilute or semidilute regimes but are not sufficiently concentrated for entanglement effects to be significant.[9,39] Measurements on two other solutions at substantially higher concentrations provide preliminary information about the effects of intermolecular entanglements on OFB properties. Figure 15A displays the OFB results for a solution of PMS-5 for which $c[\eta] \approx 12$. The general character of the data is similar to that at lower concentrations, as can be seen in Figure 1; the high-frequency phase angle anomaly is still present. However, at frequencies such that $1.0 \lesssim \log fa_T \lesssim 2.5$, the phase angle decreases with increasing frequency. This suggests that the longest relaxation time τ_1 is becoming separated from the remainder of the spectrum. Figure 15B displays the

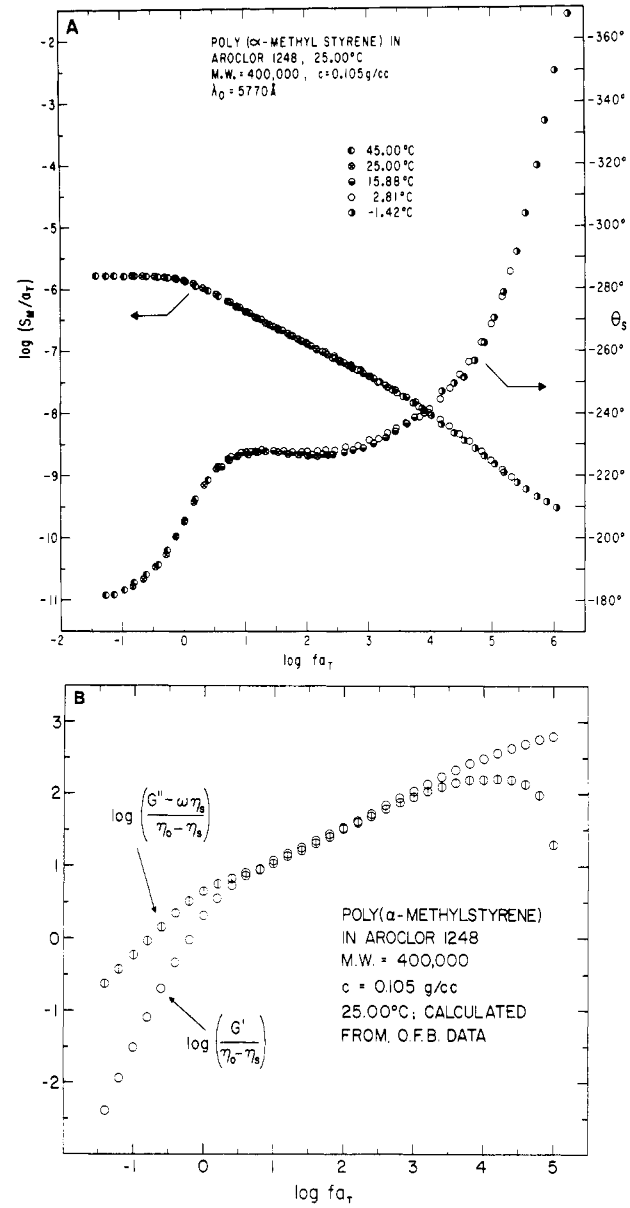

Figure 15. (A) Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.105 g/cm^3 solution of 400000 MW PS in Aroclor 1248, reduced to 25.00 °C. (B) Plots of log $[(G''-\omega\eta_s)/(\eta_0-\eta_s)]$ and log $[G'/(\eta_0-\eta_s)]$ vs. log fa_T (same solution) calculated from the OFB data via bead-spring model relations (eq 6a,b).

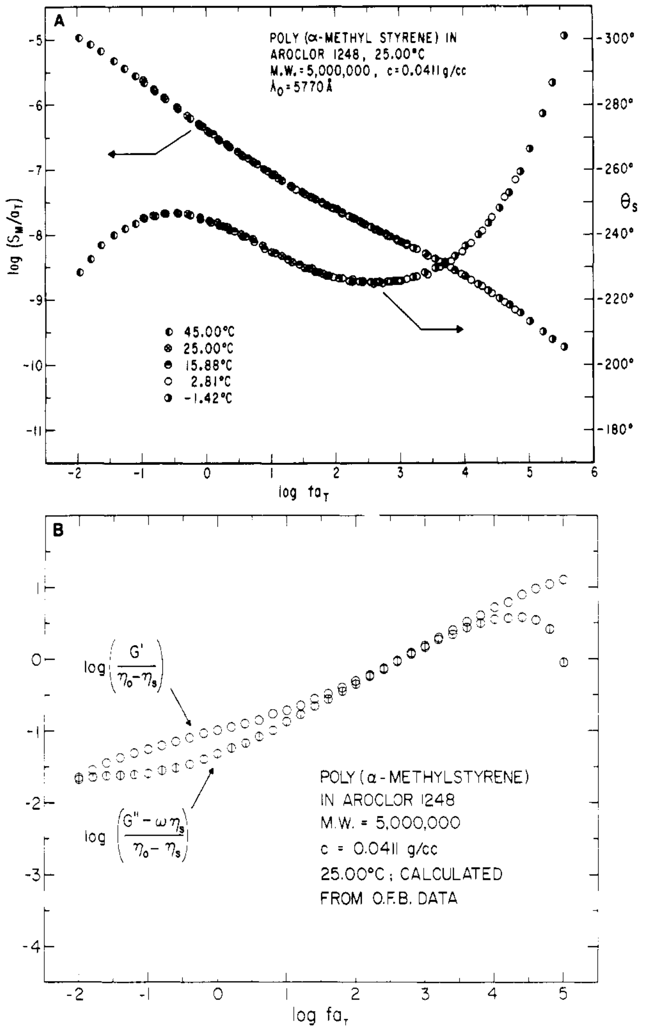

Figure 16. (A) Plots of log (S_M/a_T) and θ_s vs. log fa_T for 0.0411 g/cm^3 solution of 5000000 MW PMS in Aroclor 1248, reduced to 25.00 °C. (B) Plots of log $[(G''-\omega\eta_s)/(\eta_0-\eta_s)]$ and log $[G'/(\eta_0-\eta_s)]$ vs. log fa_T (same solution) calculated from the OFB data via bead-spring model relations (eq 6a,b).

"derived" VE properties for this solution in terms of the polymer contributions to the storage (G') and loss ($G''-\omega\eta_s$) components of the complex shear modulus G^*. These quantities have not been measured directly, but have been calculated from the birefringence results according to the (isolated molecule) bead-spring model relations

$$G'/\{\omega(\eta_0-\eta_s)\} = (S_M/S_{M0})/(1+\cot^2\theta_s)^{1/2} \qquad (6a)$$

$$(G''-\omega\eta_s)/\{\omega(\eta_0-\eta_s)\} = (S_M/S_{M0})/(1+\tan^2\theta_s)^{1/2} \qquad (6b)$$

where S_{M0} is the low-frequency, steady flow limit value of S_M, ω is the angular frequency, η_0 is the solution steady flow viscosity, and η_s is the solvent viscosity.[14,16] This transformation is strictly appropriate only for very dilute solutions and the lower frequency region where the simple bead-spring model can describe observed infinite dilution behavior. However, extensive steady flow, low shear rate measurements for a variety of polymer/solvent systems have shown that $S_{M0}/(\eta_0-\eta_s)$ is concentration independent into the semidilute solution regime, suggesting that the interrelation specified by eq 6a,b holds for the concentration regime considered here.[21,40] The Muthukumar and Freed treatment suggests the same conclusion since the concentration-modified relaxation times specify the motional dynamics of the model which are reflected by both the OFB and VE properties. The applicability of eq 6a,b at low frequencies has been demonstrated for a PS/Aroclor solution (MW = 390000; c = 0.011 g/cm^3) for which both VE and OFB data have been obtained.[14] Nevertheless, this transformation will fail at high frequency; for example, the high-frequency phase angle anomaly in the OFB would correspond to negative values of $G''-\omega\eta_s$ for frequencies above log $fa_T \approx 5$ if these relations were valid. In addition, the high-frequency slope of +1 for plots of log $(G''-\omega\eta_s)$ vs. log f observed experimentally for polystyrene and poly(α-methylstyrene) solutions, which has been attributed to an additional high-frequency loss mechanism, is not generated by this conversion procedure.[9,41] For frequencies below log $fa_T \approx 1.5$ the derived behavior is qualitatively similar to that observed experimentally for moderately concentrated solutions of polystyrene. In particular, the fact that G' exceeds $G''-\omega\eta_s$ in Figure 15B is in agreement with previous experimental observations for a 267000 MW PS in Aroclor 1232 for which $c[\eta] \approx 10$.[42] This "crossover" ($G' > G''-\omega\eta_s$) is typical of undiluted polymers, where it corresponds to the plateau zone of viscoelastic behavior which is attributed to entanglement coupling.[9]

Figure 16A presents the measured OFB properties and Figure 16B the derived viscoelastic behavior for a PMS-10 solution (MW $\approx$ 5 000 000); here $c[\eta] > 20$. The birefringence data extend over 7.5 decades of effective frequency, illustrating the wide range of polymer motions that may be probed by this experiment; time–temperature superposition is excellent over this entire range. The high-frequency phase angle anomaly is present and appears at the same frequencies as for the PMS-5 solutions. At low frequencies, the steady flow limiting values for S_M and θ_s are not attainable due to extinction angle modulation problems,[14] but the data indicate that the longest relaxation time for this solution is 2–3 orders of magnitude larger than for the PMS-5 solution in Figure 15. In addition, the slight decrease in θ_s with increasing frequency observed in Figure 15A has developed into a very broad peak in Figure 16A, suggesting a substantial increase in separation between τ_1 and τ_2. This peak results in a substantial crossover in the viscoelastic properties (Figure 16B) which extends over 3 decades of frequency.

Summary

The OFB results reported here show that the relaxation time spectrum is affected markedly by concentration. The longest relaxation time is affected most and appears to exhibit a nearly exponential dependence on concentration for the solutions examined; the shortest relaxation times are almost unchanged. The Muthukumar and Freed expression for the concentration dependence of the relaxation times of the bead–spring model provides better OFB frequency dependence curve shapes and absolute positions on the frequency axis than the Wang–Zimm theory or the infinite dilution bead–spring model employing variable h^* to imitate concentration effects. In addition, the Muthukumar and Freed equation appears to predict the OFB frequency dependence correctly for a surprisingly large range in concentration; comparison of the OFB data and theoretical predictions also indicates that for these solutions the assumption of concentration-independent relaxation strengths is reasonable. These results suggest that for a polymer/solvent system for which N, h^*, A, and κ are known, finite concentration OFB or VE data—which is much more readily obtainable than infinite dilution properties—can be analyzed to obtain chain dynamics information corresponding to isolated molecule conditions and thus may more readily provide additional practical characterization information such as the nature and extent of small degrees of long-chain branching. These possibilities are currently being explored in this laboratory.

The maximum in the OFB θ_s curve in the $\omega\tau_1 \simeq 1$ regime that is evident at the higher concentrations appears to be caused by enhanced separation of the longest relaxation times due to the onset of significant entanglement effects. Such effects are observed at concentrations well beyond the range considered in the Muthukumar and Freed treatment. The VE properties derived from the OFB data exhibit the "crossover" behavior that is strongly suggestive of the plateau zone seen in concentrated solutions and undiluted polymers.[42] Thus the OFB experiment may provide a sensitive means for exploring the dynamics of entangled systems.

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References and Notes

(1) Johnson, R. M.; Schrag, J. L.; Ferry, J. D. *Polym. J.* **1970**, *1*, 742.
(2) Osaki, K.; Mitsuda, Y.; Johnson, R. M.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *5*, 17.
(3) Osaki, K.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *5*, 155.
(4) Warren, T. C.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1973**, *6*, 467.
(5) Rosser, R. W.; Nemoto, N.; Schrag, J. L.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1031.
(6) Miller, J. W. Ph.D. Thesis, University of Wisconsin, 1979.
(7) Rosser, R. W.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1978**, *11*, 1060.
(8) Lodge, T. P.; Miller, J. W.; Schrag, J. L. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(9) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(10) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(11) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(12) Thurston, G. B.; Peterlin, A. *J. Chem. Phys.* **1967**, *46*, 4881.
(13) Muthukumar, M.; Freed, K. F. *Macromolecules* **1978**, *11*, 843.
(14) Lodge, T. P. Ph.D. Thesis, University of Wisconsin, 1980.
(15) Miller, J. W.; Schrag, J. L. *Macromolecules* **1975**, *8*, 361.
(16) Schrag, J. L. Ph.D. Thesis, Oklahoma State University, 1967.
(17) Soli, A. L. Ph.D. Thesis, University of Wisconsin, 1978.
(18) Soli, A. L.; Schrag, J. L. *Macromolecules* **1979**, *12*, 1159.
(19) Sadron, C. *J. Phys. Radium* **1936**, *9*, 381.
(20) Minnick, M. G.; Schrag, J. L. *Macromolecules* **1980**, *13*, 1690.
(21) Janeschitz-Kriegl, H. *Adv. Polym. Sci.* **1969**, *6*, 170.
(22) Thurston, G. B.; Schrag, J. L. *J. Chem. Phys.* **1966**, *45*, 3373.
(23) Lodge, T. P.; Schrag, J. L. *Macromolecules*, in preparation.
(24) Frederick, J. E.; Tschoegl, N. W.; Ferry, J. D. *J. Phys. Chem.* **1964**, *68*, 1974.
(25) Tschoegl, N. W. *J. Chem. Phys.* **1964**, *40*, 473.
(26) Sammler, R. M.; Schrag, J. L., in preparation.
(27) Thurston, G. B.; Morrison, J. D. *Polymer* **1969**, *10*, 421.
(28) Lodge, A. S.; Wu, Y. MRC Technical Summary Report No. 1250; Mathematics Research Center, University of Wisconsin: Madison, WI, 1972.
(29) Lodge, A. S.; Wu, Y. Rheology Research Center Reports No. 16 and No. 19; University of Wisconsin: Madison, WI, 1972.
(30) Edwards, S. F.; Freed, K. F. *J. Chem. Phys.* **1974**, *61*, 1189.
(31) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(32) Brandrup, J.; Immergut, E. H., "Polymer Handbook", 2nd ed.; Wiley: New York, 1975.
(33) Dill, K. A. *Macromolecules* **1980**, *13*, 620.
(34) Wang, F. W.; Zimm, B. H. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1619, 1639.
(35) Debye, P.; Bueche, A. M. *J. Chem. Phys.* **1948**, *16*, 573.
(36) Brinkman, H. C. *Proc. Ned. Akad. Wet.* **1947**, *50*, 618.
(37) Brinkman, H. C. *App. Sci. Res.* **1947**, *41*, 27.
(38) Johnson, N. L.; Bird, R. B.; Dotson, P. J. Rheology Research Center Report No. 66; University of Wisconsin: Madison, WI, 1980.
(39) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press, Ithaca, N.Y., 1979.
(40) Tsvetkov, V. N. *Polym. Rev.* **1964**, *6*, Chapter XIV.
(41) Brueggeman, B. G.; Minnick, M. G.; Schrag, J. L. *Macromolecules* **1978**, *11*, 119.
(42) Holmes, L. A.; Kusamizu, S.; Osaki, K.; Ferry, J. D. *J. Polym. Sci., Part A-2* **1971**, *9*, 2009.