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Oscillatory Flow Birefringence Properties of Polymer Solutions at High Effective Frequencies

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ABSTRACT: The oscillatory flow birefringence (OFB) properties of a variety of polymer/solvent systems are considered, with particular emphasis on the phase angle behavior (relative phasing of the birefringence with respect to the shear rate) at high effective frequencies. For polymers with large, optically anisotropic side groups and negative polarizability anisotropy, the birefringence is observed to change sign at high frequency, in contrast to the prediction of straightforward chain dynamics treatments such as the bead–spring model. The systems for which this anomaly is reported include polystyrenes with molecular weights ranging from 2100 to 44 000 000 (both linear and branched), three poly(α-methylstyrenes), and one poly(4-vinylbiphenyl) sample in the viscous solvents Aroclor 1248, Aroclor 1254, and tricresyl phosphate. For these solutions the high effective frequency phase angle behavior is essentially independent of concentration and molecular weight over the rather wide ranges covered; on the other hand, the time scale on which the anomaly is detected is proportional to solvent viscosity and is sensitive to the detailed side-group structure, though not to the overall chain topology. Initial measurements on an additional poly(α-methylstyrene) sample did not display the anomalous sign change, but remeasurement after 5 years revealed OFB properties consistent with those on all other poly(α-methylstyrene) and polystyrene solutions measured. This apparently extremely slow approach to full solvation is attributed to microcrystallinity, which may be eliminated by reprecipitation and freeze-drying. In addition, preliminary OFB results are presented for a tetrachlorinated polycarbonate of bisphenol A in Aroclor 1248; this polymer has no significant optically anisotropic side group, and no evidence of a sign change in the birefringence is observed. Possible sources of a positive birefringence which could account for the observed anomalous behavior are considered. These include internal field effects ("form birefringence"), uncertainty in the solvent birefringence contribution correction procedure, various kinds of polymer–solvent interactions, and quasi-backbone-independent orientation of side groups in the flow field. Only a side-group orientation process or a substantial modification of solvent properties upon the addition of polymer appears to be consistent with the observed behavior.

Extensive studies of the oscillatory flow birefringence (OFB) properties of polymer solutions have provided considerable insight into the dynamics of conformational change in both the dilute and the semidilute regimes.[1-9] As with the complementary linear viscoelastic (VE) experiment, the use of viscous Aroclor solvents and time–temperature superposition extends the experimentally accessible frequency range to as many as 7 decades, thus providing information about polymer dynamics ranging from the slowest modes of the entire chain down to rearrangements involving a small number of monomer units. The OFB measurement technique is sufficiently sensitive and precise to permit extrapolation of low-concentration data to infinite dilution and versatile enough to provide useful information for solutes ranging in molecular weight from a few hundred to at least five million. The infinite dilution results have been found to be in quantitative agreement with the bead–spring model predictions (isolated-molecule theories evaluated with exact eigenvalues for finite N and intermediate degrees of hydrodynamic interaction) at low and intermediate frequencies; the initial concentration dependence ($c[\eta] \leq 1.5$) of the relaxation time spacing also appears to be in quantitative agreement with the Muthukumar and Freed predictions[9,10] over a similar frequency range. As with the VE results, deviations from simple bead–spring model predictions have been observed at high effective frequencies for both infinite dilution and finite concentration results, deviations which are themselves sensitive to the detailed molecular structure. That there are deviations from the theories is not surprising per se, inasmuch as the bead–spring model incorporates the Gaussian subchain concept; all motions within the subchain (which may contain as many as 50 monomers for polystyrene in Aroclor 1248[8]) are explicitly ignored. In the VE experiment these deviations may be indicative of an additional loss mechanism(s), resulting in a high-frequency limiting viscosity designated as η_∞'.[11-14] For the OFB case, the results suggest the presence of either an anomalous high-frequency relaxation process(es) which contributes a birefringence term of opposite sign to that of the lower frequency motions or a substantial change in the solvent contribution to the OFB due to the presence of polymer. The existence of this anomaly was first reported for a polystyrene of molecular weight 10 000 in both Aroclor 1248 and Aroclor 1254.[5] The experimental evidence seemed to suggest that motions intimately involving the side groups were the most probable cause of the observed behavior. Such motions, which may have some relation to local motions in the glassy state, could also represent a contribution to η_∞'. In this paper we report OFB results for a variety of polymer solutions and discuss the implications of the new experimental data in terms of possible causes for the anomaly.

Experimental Section

Materials. Two narrow-distribution atactic linear polystyrenes were obtained from Pressure Chemical Co. with the following manufacturer specifications: batch 3b, $M = 390\,000$, $M_w/M_n < 1.06$; batch 8b, $M = 10\,000$, $M_w/M_n < 1.10$. An additional polystyrene sample S-102 was obtained from Dow Chemical Co., courtesy of Dr. H. W. McCormick. Its nominal molecular weight is 82 000, but subsequent analysis yielded the following composition: $M_w = 75\,000$, 94% by weight, $M_w = 150\,000$, 2.5%, $M_w = 250\,000$, 3%, and $M_w = 500\,000$, 0.6% (analysis assumed linear chains).[15,16] Poly(α-methylstyrene) PMS-5 was provided by Dr. L. J. Fetters of the University of Akron; $M = 400\,000$ and $M_w/M_n < 1.10$. Poly(α-methylstyrene) BB9 was synthesized by Dr. Y. Tsunashima of the Institute for Chemical Research, Kyoto University; $M = 355\,000$ and $M_w/M_n < 1.06$. A tetrachlorinated polycarbonate of bisphenol A, $\mathrm{Cl_4BPAPC}$, was provided by Dr. D. J. Massa of Eastman Kodak Co.; complete characterization information is not yet available, but preliminary GPC results suggest that the molecular weight distribution is rather broad and

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centered in the region from 50 000 to 150 000.[17]

Solutions were prepared in the chlorinated biphenyl solvents Aroclor 1248, lot KM502, and Aroclor 1254, lot KM626 (Monsanto Chemical Co.) and in tricresyl phosphate (TCP) (tri-*m*-tolyl phosphate, Eastman Kodak Co.). All initial solutions of polystyrene were made up by weight by direct addition of solvent to polymer; dissolution was assisted by moderate heating and gentle stirring, as previously described.[5,8,9] Concentrations were converted to g/cm^3 assuming additivity of volumes and density values of 1.452, 1.536, and 1.167 for Aroclor 1248, Aroclor 1254, and TCP, respectively. Subsequent dilutions were made by direct addition of solvent to solution and assisted by gentle heating (<40 °C) and stirring for a period of at least 2 weeks. The TCP solvent was subjected to sustained heating at 80 °C for a period of 1 week prior to use to remove any volatile low molecular weight species, as suggested by Riande and coworkers.[18] The Cl_4BPAPC sample was initially dissolved in reagent grade chloroform which was stripped out in vacuo after the addition of Aroclor 1248. PMS-5 was similarly initially dissolved in reagent grade benzene as previously described.[8,9]

The dissolution of PMS-BB9 deserves special comment. A portion of this sample, henceforth designated as PMS-BB9A, was reprecipitated and freeze-dried by Dr. K. Osaki prior to use. This portion was subsequently dissolved in Aroclor 1248 by direct addition of solvent; dissolution was complete in 2–4 weeks, as with a typical polystyrene sample. A different portion, henceforth designated as PMS-BB9B, was not reprecipitated; direct dissolution of this sample in Aroclor 1248 proceeded prohibitively slowly.[19] As a consequence, this sample was initially dissolved in reagent grade benzene, as with PMS-5. The OFB results from these two distinct PMS-BB9 samples in Aroclor solution were markedly different, as will be discussed in the main body of the paper.

Method. The OFB measurements were made by using the thin fluid layer instrument as previously described.[16,19,20] With the exception of some solutions of PMS-BB9B and PS-8b, for which a PAR Model 129A two-phase/vector lock-in amplifier was employed, all data were obtained with a second-generation computerized data acquisition and processing system (DAPS II) as previously described.[6,21] Data were typically obtained at about 20 frequencies between about 0.5 and 2000 Hz for each measurement temperature and combined to form master curves via time–temperature superposition. Data were reduced to a reference temperature of 25.00 °C; values of the shift factor a_T were obtained from the low-frequency limiting values of the magnitude of the birefringence whenever possible; otherwise empirical shift factors were utilized. The solution temperature was controlled to within ±0.02 °C by use of thermistors calibrated against a platinum resistance thermometer calibrated at NBS. Shear rates were generally in the range from 1 to 100 s^{-1} and in all cases were sufficiently small that the extinction angle χ remained at 45° throughout the cycle of deformation. All data were obtained at an optical wavelength of 577 nm.

Results

In general, the measured OFB properties reflect contributions from both polymer and solvent. The polymer contribution, which is typically the larger, is extracted from the measured properties assuming additivity of the polarizability tensors for polymer and solvent (see Discussion); the resulting polymer OFB is reported in terms of the frequency dependence of the magnitude S_M and relative phase angle θ_S of the quantity S^*, defined as (phasor notation)

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

where Δn, the real part of Δn^*, is the polymer contribution to the sinusoidally time-varying difference in indices of refraction n_1 and n_2 along principal directions 1 and 2, and $\dot{\gamma}$, the real part of $\dot{\gamma}^*$, is the sinusoidally time-varying shear rate.[1,19,20] Although S' and S'' are directly analogous to the commonly reported viscoelastic quantities η' and η'' (or G'' and G'), the quantity θ_S is by far the most sensitive of the four (S_M, θ_S, S', and S'') to changes in molecular properties, and it is thus more instructive to display the OFB results in terms of S_M and θ_S. This option is only useful when the data have the precision typical of the OFB results: ±0.3% for S_M and ±0.3° for θ_S throughout most of the accessible frequency range.

The bead–spring model expression for S^* as a function of angular frequency may be written as[1,19,20,22,23]

$$S^* = \left(\frac{N_a c}{M}\right)\left(\frac{4\pi}{45}\right)\frac{(n_s^2 + 2)^2}{n_s}(\alpha_1 - \alpha_2)\sum_{p=1}^{N}\frac{\tau_p}{1 + i\omega\tau_p} \qquad (2)$$

where N_a is Avogadro's number, M the molecular weight, c the concentration, n_s the solvent index of refraction, τ_p the relaxation time of the pth normal mode, and $\alpha_1 - \alpha_2$ the polarizability anisotropy of a Kuhn segment, as determined by the method of Kuhn and Grun.[24,25] This result also assumes that the principal axes of the solution index of refraction tensor remain at ±45° to the flow direction throughout the cycle of deformation. The choice of sign on the right-hand side of eq 2 is dictated by the coordinate system selected; in this laboratory it is chosen to be positive. The quantity $\alpha_1 - \alpha_2$ is related but not equal to the monomer polarizability anisotropy $\alpha_\parallel - \alpha_\perp$. However, they do have the same sign: positive for polymers such as polyethylene, polybutadiene, polyisoprene, and poly(dimethylsiloxane) and negative for polystyrene, poly(α-methylstyrene), poly(4-vinylbiphenyl), and poly(methylphenylsiloxane).[8,17,26,27] From eq 2 it can be seen that when $\omega\tau_1 \ll 1$ ("steady flow" limit) the phase angle θ_S will approach 0° if $\alpha_1 - \alpha_2 > 0$ and −180° if $\alpha_1 - \alpha_2 < 0$. Similarly, at high frequencies ($\omega\tau_N \gg 1$) the theory predicts that θ_S will tend to −90° or −270°, respectively. The behavior of θ_S between these two extremes will be governed by the structure of the relaxation spectrum itself, but as long as the relaxation processes yield birefringence contributions of the same sign, θ_S will remain in the appropriate quadrant (e.g., $-180° < \theta_S < -270°$ for polystyrene). Although the preceding discussion is based on the predictions of the bead–spring model, it is important to note that the conclusion regarding the range of θ_S is unchanged by modifications to the bead–spring model which affect only the relaxation spectrum. In particular, consideration of such questions as initial concentration dependence, intermediate degrees of hydrodynamic interaction, preaveraged or nonpreaveraged Oseen tensor, coil expansion, and inclusion of internal viscosity terms[28–30] will not alter the limiting values of θ_S. In fact, any general chain dynamics theory which does not consider inertial terms or build in birefringence contributions of opposite sign will yield the same limiting behavior for θ_S.

The OFB results obtained for a relatively high concentration (0.0713 g/cm^3) solution of PS-3b in Aroclor 1248 are shown in Figure 1. Even though this solution ($c[\eta] \simeq 7$) falls in the semidilute regime, the data are in qualitative agreement with the infinite dilution bead–spring model predictions at frequencies below log $(fa_T) \simeq 4.5$, where a_T is the time–temperature superposition shift factor and f is the driving frequency in hertz.[8] Note that the results obtained at four different temperatures extend over 7 decades of reduced frequency and that the superposition appears to be excellent throughout this range. The particular feature of interest here is the fact that at frequencies for which log $(fa_T) \geq 5$ the phase angle θ_S exceeds the theoretical limit of −270° and continues to increase rapidly with increasing frequency. This anomaly was first reported for solutions of PS-8b in Aroclor 1248 and Aroclor 1254[5] and subsequently for PS-3b and PMS-5 in Aroclor 1248, for a series of dilute and semidilute solutions.[9] It

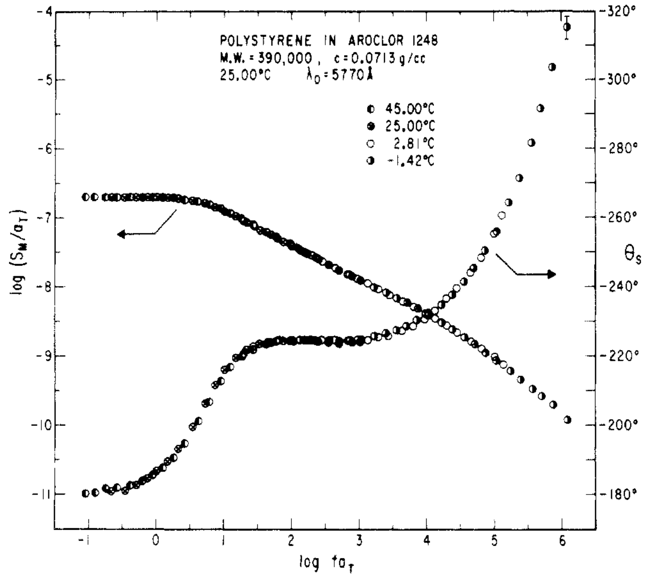

Figure 1. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 0.0713 g/cm^3 solution of 390 000 MW PS in Aroclor 1248, reduced to 25.00 °C.

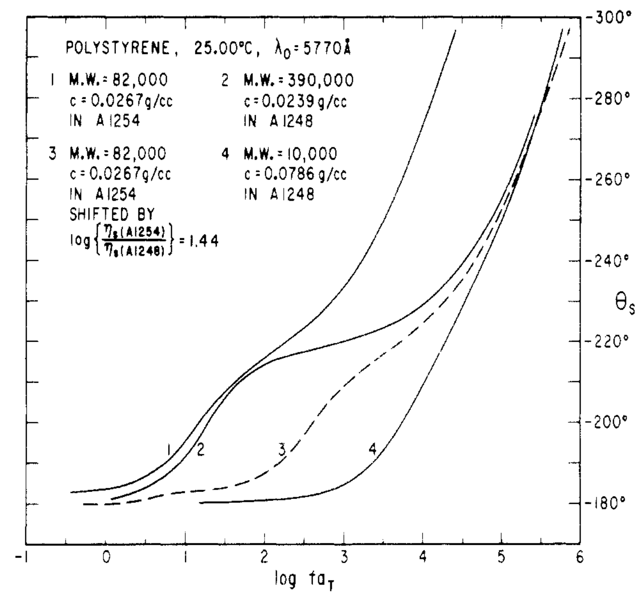

Figure 2. Plots of θ_S vs. log (fa_T) (actual data replaced by smooth curves for clarity): curve 1, 82 000 MW PS in Aroclor 1254, 0.0267 g/cm^3; curve 2, 390 000 MW PS in Aroclor 1248, 0.0239 g/cm^3; curve 3, identical with curve 1, but shifted along frequency axis by ratio of solvent viscosities; curve 4, 10 000 MW PS in Aroclor 1248, 0.0786 g/cm^3.

has also been observed for polystyrenes of molecular weight 2100, 37 000, 82 000, 110 000, and 44 000 000, for a series of star-branched polystyrenes, for a poly(α-methylstyrene) of molecular weight 5 000 000, and for solutions of poly(4-vinylbiphenyl) in Aroclor solvents.[6,8,9,17] In this frequency range the OFB experiment is apparently probing rather local motions in the polymer solution (log (fa_T) $\simeq$ 5 in Aroclor 1248 at 25 °C corresponds to a time scale of 10–100 ns in a solvent with a viscosity similar to that of benzene, assuming τ_p proportional to solvent viscosity); however, even very local motions of the polymer molecule should reflect the same negative polarizability anisotropy as long as the backbone segments tend to orient along the principal axes of the stress tensor. Thus in order for θ_S to exceed the theoretical limit either some relaxation process(es) involving positive birefringence must become significant or the solvent contribution is not being treated correctly. Before discussing either of these possibilities, we present other pertinent experimental results that serve to further characterize the nature of the anomaly.

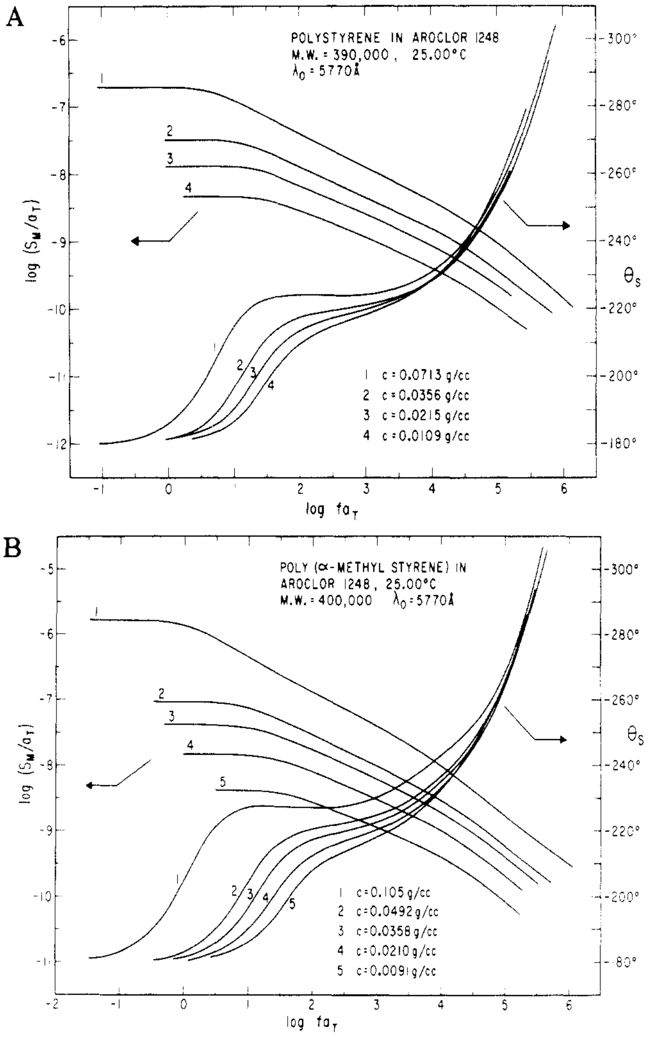

Figure 3. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) (actual data replaced by smooth curves for clarity): (A) 390 000 MW PS, 0.0109, 0.0215, 0.0356, and 0.0713 g/cm^3, in Aroclor 1248, reduced to 25.00 °C; (B) 400 000 MW PMS, 0.0091, 0.0210, 0.0358, 0.0492, and 0.105 g/cm^3, in Aroclor 1248, reduced to 25.00 °C.

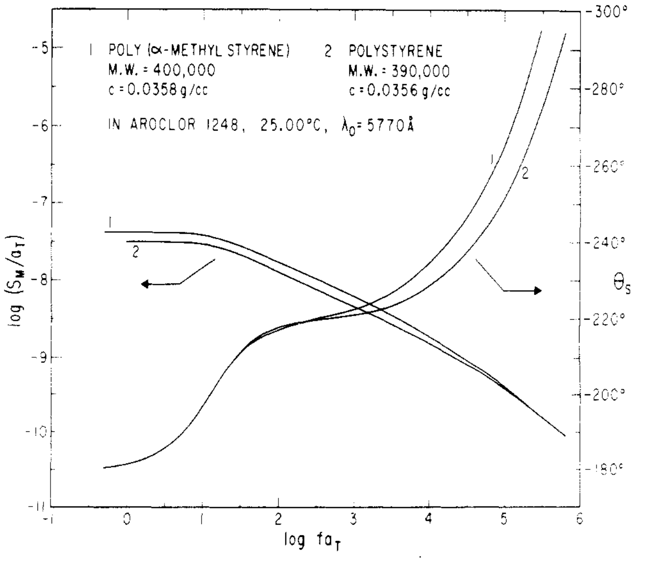

Figure 4. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) (actual data replaced by smooth curves for clarity): curves 1, 400 000 MW PMS, 0.0358 g/cm^3; curves 2, 390 000 MW PS, 0.0356 g/cm^3; in Aroclor 1248, reduced to 25.00°C.

Figures 2–4 illustrate some general features of the high-frequency behavior of polystyrene and poly(α-methylstyrene) solutions; the actual data are represented by smooth curves for the sake of clarity. In Figure 2 the phase angle behaviors for three different molecular weight polystyrenes are compared. Curves 2 and 4 are for PS-3b and PS-8b in Aroclor 1248, with $c = 0.0239$ and 0.0786 g/cm^3, respectively. Curves 1 and 3 are for polystyrene S-102 in Aroclor 1254, $c = 0.0267$ g/cm^3; curve 3 is identical with curve 1 except that it has been shifted along the frequency axis by the ratio of the viscosity of Aroclor 1254 to that of Aroclor 1248 at 25.0 °C. Above log $(fa_T) \simeq 5$ the phase angle behavior becomes (within the increased uncertainty) independent of molecular weight, which is to be expected if the relaxation process(es) involved corresponds to local motion(s). At these higher frequencies the uncertainty in θ_S may increase significantly, as indicated by the error bars in Figures 1, 6, and 7. This is due to at least three factors: approaching the edge of the working frequency range of the TFL transducer, the decrease in S_M at higher frequencies, and the fact that the solvent contribution to the measured birefringence becomes comparable to that from the polymer.

The fact that curve 3 coincides with the other two in this region suggests that the relaxation time(s) associated with the relevant local motions is proportional to the solvent viscosity, as is the case for the bead–spring model relaxation times. As an interesting footnote, the low-frequency portion of curve 3 exhibits a small but distinct peak located near log $(fa_T) \simeq 0.8$; this is ascribed to the small quanity of high molecular weight species present in the sample as discussed in the Experimental Section. This serves to illustrate the sensitivity of the OFB technique to small amounts of polydispersity; by comparison, this polydispersity was not detected in viscoelastic measurements on the same solution.[31]

Figure 3, here reproduced from ref 9, demonstrates the concentration dependence of the OFB properties for dilute and semidilute solutions of PS-3b and PMS-5. (For both molecules the coil overlap concentration c^* is estimated to be between 0.01 and 0.02 g/cm^3.) In both cases the high-frequency phase angle behavior is essentially independent of concentration, as expected for very local motions in these concentration regimes. (The values of θ_S for PMS-5, $c = 0.105$ g/cm^3, may be up to 5° high in the range $3 \leq \log (fa_T) \leq 4.5$; this is due to significant deformations of transducer components at very high solution viscosities). In the high-frequency region the magnitude of the birefringence is expected to be directly proportional to the concentration of monomer units in solution; as reported previously, log (S_M/ca_T) does become independent of concentration for log $(fa_T) > 5$.[8]

In Figure 4 the OFB results from one solution each of PS-3b and PMS-5 are compared to each other directly. The degrees of polymerization and the concentrations are almost identical, and thus the long-range motions should be very similar; this is indeed the case. (The difference between the two low-frequency limiting values of S_M may be attributed to the difference in $\alpha_1 - \alpha_2$ for the two polymers). However, at high frequencies the two phase angle curves are distinct, and this difference is significant beyond the increased uncertainty in the data referred to earlier. If local motions are causing the anomaly, the time scale over which their contribution becomes significant depends on the details of the chemical structure. Thus, for the dynamically "stiffer" poly(α-methylstyrene) molecule,[8] such local motions would dominate the observed response at longer times. It is interesting to note that the phase angle curves diverge around log $(fa_T) \simeq 3$, corresponding to a time scale of 1–10 μs in a solvent such as benzene. Evidently the conformational dynamics as reflected in the OFB results show a sensitivity to monomer structure at relatively long times; the potential of OFB as a powerful characterization technique needs to be explored further.

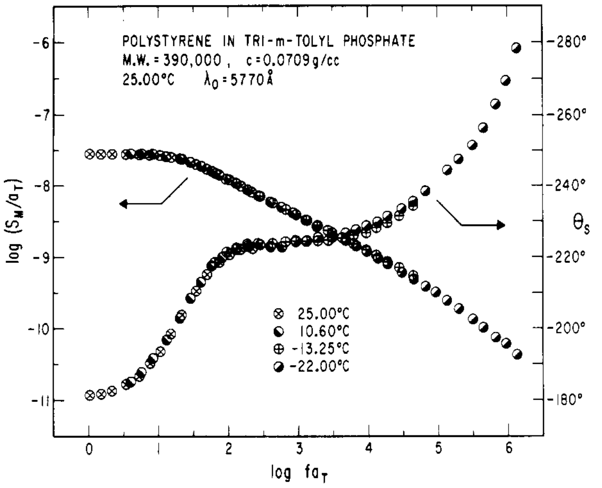

Figure 5. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 0.0708 g/cm^3 solution of 390 000 MW PS in TCP, reduced to 25.00 °C.

Figure 5 presents the OFB results for PS-3b in tri-*m*-tolyl phosphate (TCP), $c = 0.0709$ g/cm^3. These are the first OFB data from this laboratory that utilize time–temperature superposition in a non-Aroclor solvent. TCP was selected as a potential replacement for the Aroclor series on the basis of its strong dependence of viscosity on temperature and its close match of index of refraction with that of polystyrene. In addition, TCP has been used successfully for viscoelastic measurements on polystyrenes over a wide range of concentration and temperature.[18] The TCP solvent is itself weakly birefringent, and the same correction procedure employed with the Aroclor solvents has been used. The concentration of the solution measured here is closely matched to that of the Aroclor 1248 solution of the same polymer in Figure 1. The frequency dependence of both S_M and θ_S is essentially identical for the two solutions; in particular, the use of a non-Aroclor solvent has not eliminated the high-frequency phase angle anomaly. Due to the difference in solvent viscosities at the 25.00 °C reference temperature, the θ_S curves in Figures 1 and 5 are displaced relative to one another along the frequency axis; similarly, the log (S_M/a_T) curves are displaced relative to each other along both horizontal and vertical axes. However, even after this shift has been taken into account, the magnitude of the polymer birefringence is higher in Aroclor 1248 by a factor of $\simeq$1.6. In light of eq 1 this indicates that the subchain polarizability anisotropy is a function of solvent, as has been reported by several workers.[26,27,32–34]

Representative examples of the remarkable OFB results obtained on different solutions of PMS-BB9 referred to in the Experimental Section are presented in Figures 6 and 7. Figure 6A presents the data for the initial solution of PMS-BB9B (unreprecipitated sample) in Aroclor 1248, while the results for a subsequent dilution (3 months later) of this solution are shown in Figure 6B. Figure 7A also presents OFB results obtained on this dilution, but these particular data were obtained some 5 years later. Finally, Figure 7B presents OFB data obtained on the initial solution of PMS-BB9A (reprecipitated sample).

The high-frequency phase angle behavior in Figure 6A is unlike that observed for any other poly(α-methylstyrene)

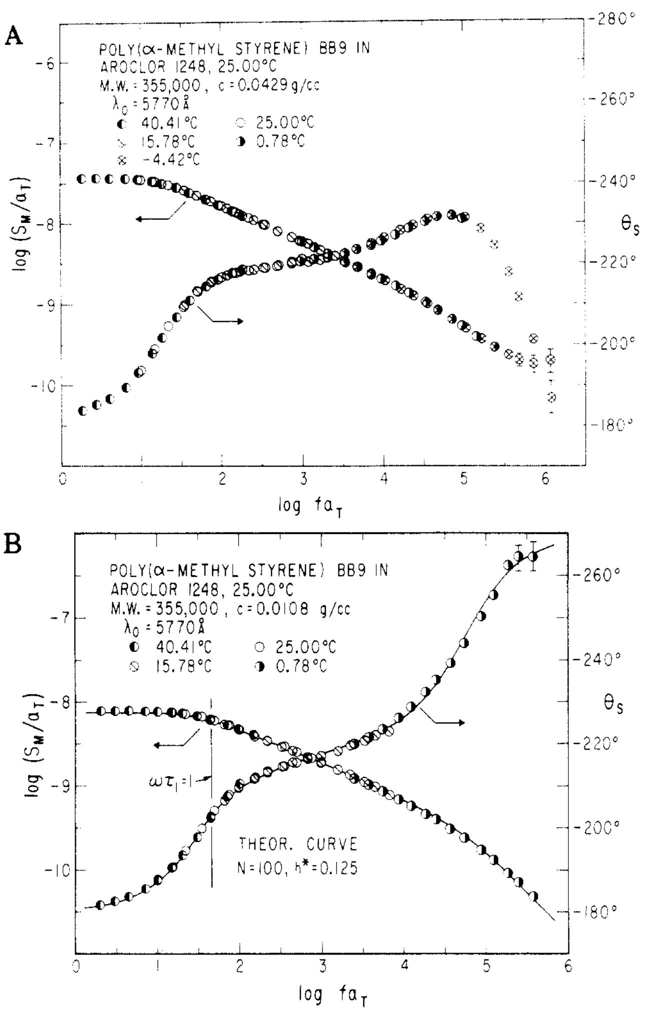

Figure 6. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 355 000 MW PMS-BB9B (unreprecipitated sample) in Aroclor 1248, reduced to 25.00 °C: (A) 0.0429 g/cm^3; (B) 0.0108 g/cm^3. Theoretical curves: Zimm theory for N = 100, h^* = 0.125.

or polystyrene sample. Not only does θ_S not exceed −270° but it decreases sharply and returns toward −180°. In Figure 6B, θ_S also does not exceed −270°, but in this case it appears to approach the theoretical high-frequency limit; these data have been compared with bead–spring theory curves for N (the number of subchains) and h^* (the hydrodynamic interaction parameter) of 100 and 0.125, respectively. However, although this fit appears to be very good throughout the accessible frequency range, the value of N = 100 contrasts sharply with that of 50 obtained for the infinite dilution results for PMS-5. Even though Figure 6B represents finite concentration data, the values of N ought to be comparable.[9] In addition, attempts to extrapolate S_M/c and θ_S to infinite dilution for these two solutions of PMS-BB9B and other intermediate concentrations failed, as neither quantity varied monotonically with concentration, even at the lowest frequencies.[19] Thus the phenomenon that gives rise to the drop in θ_S at high frequencies in Figure 6A is apparently affecting the S_M values throughout the entire frequency range.

This solution of PMS-BB9B (0.0108 g/cm^3) was remeasured some 5 years later; these results are shown in Figure 7A. The high-frequency values of θ_S now exceed −270° just as with all other poly(α-methylstyrene) and polystyrene samples measured to date. In addition, the low-frequency limiting magnitude of the birefringence has decreased by a factor of 2. These data have been fitted with the Muthukumar and Freed (MF) theory for the initial concentration dependence of the bead–spring model relaxation times. The values of the four parameters N, h^*, A, and κ were selected entirely on the basis of the infinite dilution and finite concentration results for PMS-5.[8,9] The MF theory expression for the initial concentration dependence ($c[\eta] < 1$) of the pth relaxation time is[10]

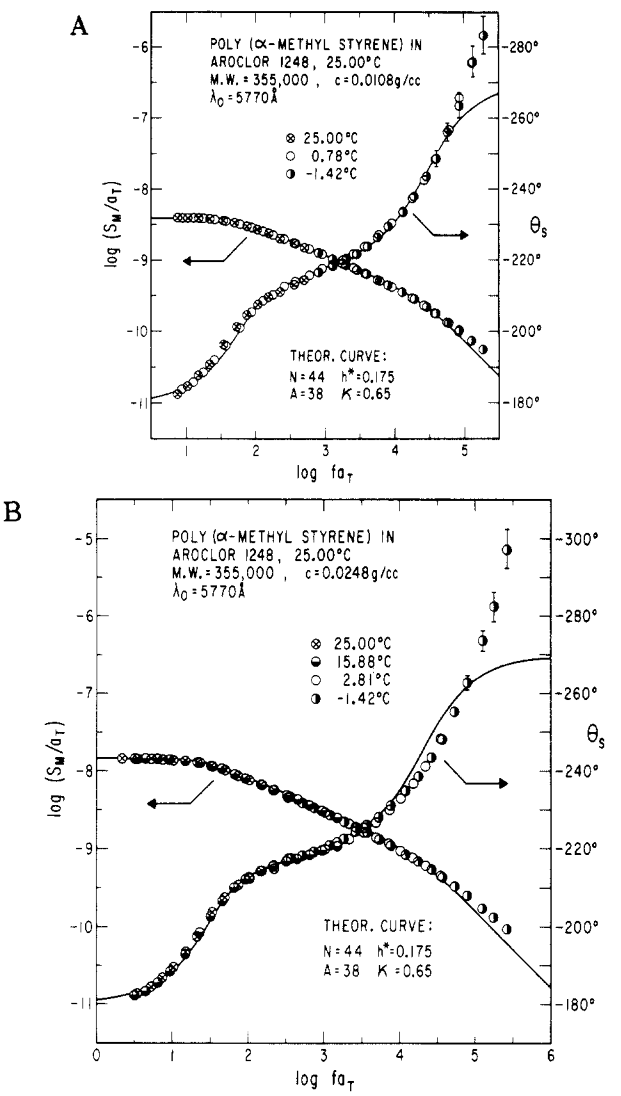

Figure 7. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 355 000 MW PMS in Aroclor 1248, reduced to 25.00 °C: (A) PMS-BB9B (unreprecipitated sample), 0.0108 g/cm^3 (same solution as in Figure 6B, remeasured 5 years later); (B) PMS-BB9A (reprecipitated sample), 0.0248 g/cm^3. Theoretical curves: Muthukumar and Freed theory, N = 44, h^* = 0.175, A = 38, and κ = 0.65.

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

where $\tau_p^{\,0}$ is the infinite dilution relaxation time for the pth normal mode, A is a positive constant related to the Huggins coefficient, and κ is an exponent that varies between 0.5 in a Θ solvent and 0.8 in a good solvent. The agreement between theory and experiment is excellent for log $(fa_T) \leq 5$; in particular, the value of N = 44 results in a reasonable fit and is in sharp contrast to the value of N = 100 employed in Figure 6B.

The solution of PMS-BB9A (reprecipitated sample), recently prepared by direct addition of solvent to polymer as described in the Experimental Section, yielded the results displayed in Figure 7B. The phase angle again clearly exceeds −270° at high frequencies. In addition, these data have also been compared with the MF theory predictions with the same parameter values as in Figure 7A. Even though this concentration ($c[\eta] \simeq 2.5$) is too high to fall in the domain of validity of eq 3, the agreement is very

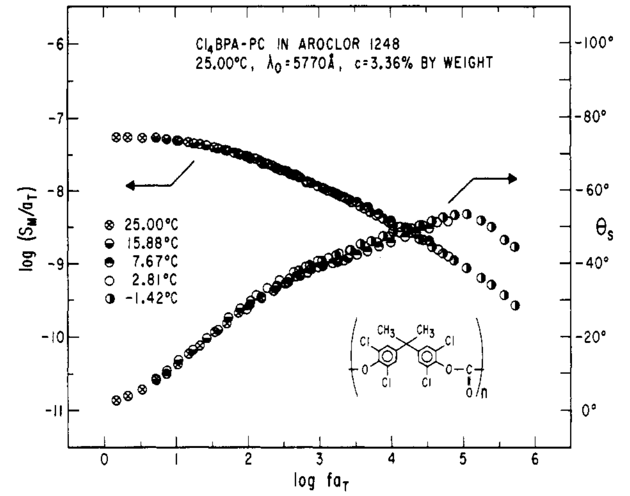

Figure 8. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for Cl_4BPAPC in Aroclor 1248, 3.36% by weight, reduced to 25.00 °C.

good even up to the onset of the high-frequency phase angle anomaly.

In light of the fact that the data in Figure 7 form a consistent picture with the other OFB results on poly(α-methylstyrene) and polystyrene solutions, it is reasonable to assume that it is the data in Figure 6 that reflect an unexplained phenomenon. This new anomaly appears to be time dependent, as evidenced by the results in Figure 7A; thus the difference in phase angle behavior between parts A and B of Figure 6 may be due more to the passage of time than to the difference in concentration, as originally supposed.[19] In addition, this anomaly is apparently intimately associated with the solubility properties of the sample. One possible explanation for this behavior is that the PMS-BB9B sample possessed a significant degree of local ordering. This order could be eliminated either by reprecipitation followed by freeze-drying, as with PMS-BB9A, or by allowing sufficient time to reach an equilibrium, fully solvated state in Aroclor solution. It is worth noting that the cause of the observed behavior is apparently not very sensitive to solution temperature over a short (i.e., days) time scale; there is no evidence of a breakdown in time-temperature superposition in Figure 6. Whatever the explanation for the observed behavior, these results again suggest that the OFB technique is a sensitive probe of changes in the local chemical or physical structure.

Figure 8 presents preliminary OFB results for a tetrachlorinated polycarbonate of bisphenol A, Cl_4BPAPC, dissolved in Aroclor 1248. This particular molecule was selected for study because it has no strongly optically anisotropic side group; it is felt that the high-frequency phase angle results for other samples are intimately connected with side-group structure and/or mobility. In addition, local motions in polycarbonates in general are of considerable interest in attempting to understand the mechanical properties of the glassy state.[35-38] Several features of these data are worthy of note. First, the phase angle does not exceed -90° in the accessible frequency range, and clearly $\alpha_1 - \alpha_2$ is positive, as expected.[39] The time-temperature superposition is not as successful as with the polystyrene/Aroclor system; the reason for this is as yet unidentified but may reflect differences in solvent power. The broad molecular weight distribution indicated by the GPC analysis is evident in both the smoothly varying log (S_M/a_T) curve and the relatively featureless approach of θ_S to 0° for log (fa_T) $\leq$ 3. The decrease in θ_S at frequencies above log (fa_T) $\simeq$ 5 is possibly reminiscent of the behavior observed with solutions of PMS-BB9B. As in that case, the possibility of incomplete solvation needs to be considered. However, the θ_S decrease could also result from some additional positive birefringence contribution. The values of θ_S in the intermediate and higher frequency regions suggest that this polymer may be considerably more flexible than either polystyrene or poly(α-methylstyrene). These several questions must await a more detailed study of the OFB properties of polycarbonate systems.

Discussion

The anomalous high-frequency phase angle behavior observed for polystyrene and poly(α-methylstyrene) solutions is apparently the result of a birefringence contribution of positive sign becoming dominant. Several possible sources of a positive birefringence may be identified. These include (1) effects of the internal electromagnetic field (form birefringence), (2) contributions from the bulk solvent, (3) polymer-solvent interactions which serve to orient solvent molecules, and (4) quasi-backbone-independent motions of the polymer side groups. Each of these possibilities will be considered in terms of the experimental results presented above.

Form Birefringence. The internal field effect, or form birefringence, has been the object of considerable attention, both theoretical and experimental.[26,34,40-44] Tsvetkov has treated this contribution in terms of a macroform effect, due to the nonspherical distribution of polymer segments in a coil and the optical interaction between distant segments, and a microform effect between neighboring segments.[26] Fortelny, however, points out that this division may not be rigorously justifiable.[44] Nevertheless, all of the various attempts to treat form birefringence theoretically yield the result that the effect will be positive in sign and proportional to the square of the difference between the polymer and solvent indices of refraction $n_p - n_s$. For steady flow birefringence, such effects have been negligible for $n_p - n_s \leq 0.1$; for all of the systems considered here which display the high-frequency anomaly, $n_p - n_s \leq 0.05$. In addition, low-frequency OFB measurements have been made in a variety of solvents, with $n_p - n_s$ ranging from -0.02 to +0.15;[45] no significant form effects were evident. For flexible chains, the macroform effect has been shown to be at least 5 times as great as the microform effect; the macroform effect is also predicted to increase with molecular weight and decrease with increasing concentration. In view of the independence of the anomaly with respect to molecular weight and concentration, and especially the closely matched indices of refraction, it is reasonable to discount the form effect as a significant contributor to the observed behavior.

Bulk Solvent Contribution. The Aroclor solvents and TCP display a weak positive birefringence in a shear flow. For all the results reported here the measured solution birefringence has been corrected to extract the polymer contribution according to the relation[7]

$$S_M \exp(i\theta_S) = (S_M)_{\text{tot}} \exp(i(\theta_S)_{\text{tot}}) - \nu S_{MS} \exp(i\theta_{SS}) \quad (4)$$

where $(S_M)_{\text{tot}}$ and $(\theta_S)_{\text{tot}}$ are the measured values, S_{MS} and θ_{SS} the values for the pure solvent, and ν is the volume fraction of solvent in the solution. This subtraction procedure is derived from that of Sadron;[46] it is made particularly simple in this instance by the collinearity of the principal axes of the solvent and solution polarizability tensors, and by the fact that the incident light beam propagates along one of these axes. For the frequencies and temperatures employed in these studies both S_{MS} and θ_{SS} are frequency independent; for Aroclor 1248, θ_{SS} = 0°

at all temperatures and $S_{MS} = 5.4 \times 10^{-10}$, 1.7×10^{-9}, 2.2×10^{-8}, and 6.7×10^{-8} s at T = 25.00, 15.88, 2.81, and −1.42 °C, respectively. Thus νS_{MS} can be as large or even larger than S_M at high frequencies. However, the experimental results as a whole strongly suggest that the uncertainty in νS_{MS} is at most a minor contributor to the observed behavior. First, whereas S_M and $(S_M)_{tot}$ vary roughly linearly with concentration in the high-frequency regime, νS_{MS} remains virtually constant for dilute solutions. From Figure 3 it can be seen, however, that the high-frequency phase angle behavior is independent of concentration over a decade range in concentration. For example, for PMS-5 at $\log (fa_T) = 5$ the θ_S curves are indistinguishable within experimental uncertainty, whereas the ratio $S_M/\nu S_{MS}$ varies from $\simeq 3$ to $\simeq 0.1$. Second, an error in the value of νS_{MS} of 1% will contribute an error on the order of 1° to θ_S in the region $5 \leq \log (fa_T) \leq 6$. Data have been reported for a polystyrene (M = 37 000) in Aroclor 1248 for which θ_S exceeded −360°;[17] thus the value of νS_{MS} would have to be at least 100% too low in order to account for the anomaly; the estimated uncertainty in νS_{MS} is less than 2%. Third, if uncertainty in νS_{MS} is indeed the cause, the error must be virtually identical for Aroclor 1248, Aroclor 1254, and TCP, which seems unlikely.

The solvent correction procedure outlined above assumes that solvent properties are not modified by the introduction of polymer. It is possible, perhaps likely, that the solvent properties are modified. However, if the high-frequency OFB anomaly is due solely to an improper accounting of the solvent contribution in eq 4, the solvent term would need to be increased by a factor of up to 3 for the polystyrene/Aroclor solutions studied. Thus substantial modification of solvent properties must occur if this is the only factor giving rise to the high-frequency OFB anomaly.

Polymer–Solvent Interactions. The known dependence of $\alpha_1 - \alpha_2$ on solvent indicates clearly that the optical properties of polymer solutions are quite sensitive to polymer–solvent interactions. For convenience sake, such interactions may be classified as either long range or short range. In the former case, the presence of the polymer molecules modifies the properties of the solvent beyond the immediate vicinity of the chain. For solvents such as the Aroclors and TCP, whose extremely strong temperature dependence of viscosity implies a significant ordering, this represents a real possibility as noted above. For the polyisoprene/Aroclor and polybutadiene/Aroclor systems, such long-range interactions have been observed; these interactions manifested themselves in a reduction of both solvent viscosity and solvent birefringence upon the addition of small quantities of polymer.[7] This led in the first case to the determination of negative intrinsic viscosities and in the second case to a failure of time–temperature superposition at high frequencies, unless a modified solvent correction procedure was employed. However, for the polystyrene/Aroclor and poly(α-methylstyrene)/Aroclor systems, no similar direct evidence of such interactions has been observed. In addition, in the polyisoprene and polybutadiene cases, the solvent birefringence was reduced, not enhanced, by the presence of polymer, and in a strongly concentration-dependent manner. Neither of these observations is consistent with what would be required to produce the observed high-frequency behavior of polystyrene and poly(α-methylstyrene)/Aroclor solutions.

Short-range polymer–solvent interactions have been implicated in the solvent dependence of $\alpha_1 - \alpha_2$. The contribution of these interactions to the observed birefringence may be subdivided into two mechanisms—the anisotropic distribution or orientation of solvent molecules in the neighborhood of the chain that tend to follow chain motions, and modification of the conformational energetics within the polymer subchain. In the former case, this means that the flow orientation of the polymer will lead to a modified birefringence which appears to be the chain contribution; the dependence on solvent of $\alpha_1 - \alpha_2$ for polyisoprene has been interpreted in this fashion.[27] The important characteristic is the geometrical asymmetry of the solvent molecules;[47] for isotropic solvent molecules $\alpha_1 - \alpha_2$ becomes solvent independent. However, for polystyrene no clear correlation between $\alpha_1 - \alpha_2$ and solvent asymmetry was found; the variation of $\alpha_1 - \alpha_2$ was tentatively ascribed to the other mechanism, namely, enhanced motional freedom of the side groups in different solvents.[48]

For the case of polystyrene/Aroclor 1248 and polystyrene/TCP such an alignment of solvent molecules with the chain backbone could be postulated. However, since only the effective $\alpha_1 - \alpha_2$ would be altered, the observed character of the frequency dependence (polymer contribution) would remain unchanged. As indicated earlier, the value of $\alpha_1 - \alpha_2$ for polystyrene is markedly different in Aroclor 1248 and TCP, yet the frequency dependence of the polymer dynamics as revealed by OFB is identical. Therefore, while the detailed behavior of the solvent molecules in the neighborhood of the chain is probably crucial in determining the dynamics on a very local scale, it is not at all clear how this may reasonably be invoked as the explanation for the observed OFB results.

Side-Group Motions. As postulated previously,[5] the observed high-frequency behavior could be caused by side-group motions in which the optically dominant moieties (the phenyl rings for polystyrene and poly(α-methylstyrene)) are able to orient to some degree with the flow, rather than remaining effectively normal to an orienting backbone. Such motions would most likely be cooperative in nature, involving several adjacent side groups. In particular, simple, small rotations of individual side groups about the bond connecting the ring to the chain would not be sufficient to generate a positive birefringence; large (≥30°) rotations are calculated to be rather unlikely for polystyrene and poly(α-methylstyrene).[49]

Mechanisms involving side-group mobility have been invoked to account for the birefringence behavior of bulk amorphous samples. For example, the stress-optical coefficient (SOC) of polystyrene is large and negative above T_g but small and positive in the glassy state;[50,51] as long-range chain motions are effectively frozen out below T_g, only local motions contribute significantly to the birefringence. Similar SOC sign changes have been observed in other polymer systems such as poly(vinyl chloride)[52] and poly(styrene-*co*-divinylbenzene).[53] However, this sign change was not observed for poly(α-methylstyrene).[33] Apparently the incorporation of the methyl group inhibits the local motions responsible for the sign change in the glassy state, whereas in the solution results presented here (with the exception of the initial PMS-BB9B results) the high-frequency sign change is still present. Relative motional freedom of side groups has also been implicated in the observed solvent dependence of $\alpha_1 - \alpha_2$ for polystyrene,[48] as mentioned previously.

Peterlin has shown that the assumption of free orientation of side groups can lead to a sign change in the high-frequency birefringence.[55] Similarly, the OFB results for PS-3b have been simulated in model calculations by the addition of a single relaxation process with a positive birefringence to the bead–spring model spectrum.[19] Although it is possible to mimic the observed behavior in this fashion, the experimental results do not extend to sufficiently high-frequency to enable meaningful estimation of the motional time scale of the additional process. A prototype high-frequency OFB apparatus has been developed in this laboratory;[45] in the future it may be possible to extend the accessible frequency range by several decades. Such an apparatus would also obviate the need to make measurements in the viscous Aroclor and TCP solvents; thus it would be possible to investigate polymer–solvent interactions directly. Even though time–temperature superposition is currently employed to obtain the widest possible frequency range, the high-frequency phase angle results are in no way dependent on the assumed validity of the superposition. Because θ_S involves the ratio S''/S', actual θ_S values are absolute and are not altered when the reduction to any reference temperature is performed; rather, only the time scale is affected as the θ_S curves are shifted horizontally along the frequency axis.

It is interesting to speculate on the nature of the relationship between the observed high-frequency OFB results and the more extensively studied high-frequency VE behavior. At these high frequencies, the measured values of $G'' - \omega\eta_S$ do not approach the limiting behavior predicted by the bead–spring model but maintain a first power dependence on ω. This has been ascribed to the presence of an extra dissipation mechanism(s) resulting in a frequency-independent contribution designated as η_∞'.[11-14] These two departures from theoretical predictions (OFB and VE) occur at similar frequencies and have been observed for identical systems; the magnitude of η_∞' depends on the side-group structure.[13] It is possible to predict a finite value for η_∞' using a variety of theoretical approaches. These include the inclusion of the chain stiffness,[55,56] the addition of an internal viscosity term,[14,29,30,58-60] and consideration of energy transfer from global to local modes.[61] None of these has been successful to date in quantitatively predicting the observed OFB and VE results, however. In addition, a successful description of η_∞' need not be relevant to the OFB results; the VE experiment senses energy loss and storage, whereas the OFB experiment reflects bond orientation and molecular polarizability. On the other hand, Freed and Adler have recently shown that a high-frequency limiting viscosity can also be obtained by including correlated motions of neighboring side groups.[62] This raises the distinct possibility that any relaxation mechanism responsible for the OFB anomaly could be a contributor to the observed VE behavior.

Conclusions

Anomalous high-frequency behavior in the OFB phase angle θ_S has been observed for a variety of polystyrene and poly(α-methylstyrene) solutions. This anomaly, previously reported for solutions of 10 000 MW polystyrene, indicates the existence of an unexpected birefringence contribution of positive sign, which may be due to local motions of the polymer molecule that intimately involve the mobility of the side groups, or to a substantial modification of solvent properties due to the presence of polymer. The observed behavior is essentially independent of molecular weight and concentration over the ranges studied and also independent of solvent for Aroclor 1248, Aroclor 1254, and TCP. However, the time scale at which the anomaly appears is proportional to solvent viscosity and depends on the local chemical structure; for the dynamically stiffer poly(α-methylstyrene) it appears at lower frequencies than for polystyrene.

Initial measurements on another poly(α-methylstyrene) sample PMS-BB9B did not display a sign change; however, measurements performed on the same solutions after a period of about 5 years and on fresh solutions of a reprecipitated sample PMS-BB9A did show the anomaly. In addition, these subsequent measurements were in excellent agreement with the predictions of the Muthukumar and Freed theory at low and intermediate frequencies; all parameter values were selected on the basis of previous results on a different poly(α-methylstyrene) sample. The cause of the unusual initial results for PMS-BB9B is tentatively assumed to involve microcrystallinity.

Four possible sources of a positive birefringence contribution were identified: form birefringence (internal field effects), uncertainty in the solvent contribution to the observed birefringence, polymer–solvent interactions leading to a modified solvent contribution, and relatively local motions in which the side groups are able to orient to some degree with the flow, quasi-independently of the chain backbone. Form birefringence is probably not a significant factor, primarily because of the close match of solvent and polymer indices of refraction, but also due to the observed independence of the anomaly with respect to molecular weight and concentration. Similarly, it is unlikely that a simple error in the solvent contribution correction procedure is responsible for the anomaly; this conclusion is reached on the basis of the magnitude of the error required to account for the observed results and the concentration and solvent independence of the high-frequency behavior.

No direct evidence for long-range polymer–solvent interactions of the type reported for polyisoprene and polybutadiene in Aroclor has been observed for the polystyrene and poly(α-methylstyrene)/Aroclor systems. Short-range polymer–solvent interactions have been invoked to account for the solvent dependence of the polymer segment polarizability anisotropy $\alpha_1 - \alpha_2$; no specific mechanisms have been identified but significant orientation of solvent molecules in the neighborhood of the chain could account for a modified $\alpha_1 - \alpha_2$. However, $\alpha_1 - \alpha_2$ is markedly different for polystyrene in Aroclor 1248 and TCP, whereas the high-frequency behavior is identical.

On the basis of the results presented here and the discussion above we believe that the observed anomaly reflects either local motions that involve some net orientation of side groups with the flow or a substantial modification of solvent properties due to the presence of a polymer. Such motions would be most probably cooperative in nature, involving several neighboring pendant groups, and could be similar to those which occur in the glassy state, which have been used to explain the sign change in the stress-optical coefficient that has been observed near T_g for several bulk polymers.

Resolution of these various issues will require extensive measurements on a variety of polymer–solvent systems and would be greatly facilitated by the availability of high-frequency OFB and VE apparatuses. Until high-frequency OFB and VE results can be given a quantitative, molecular interpretation it will be difficult to extract chain dynamics information unambiguously in any frequency regime, particularly for lower molecular weight polymers. On the other hand, the sensitivity of the OFB experiment to changes in molecular dynamics over the entire frequency range, and the high-frequency regime in particular, makes it a potentially powerful technique for obtaining unique conformational dynamics and polymer characterization information.

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Registry No. Polystyrene (homopolymer), 9003-53-6; poly(α-methylstyrene) (homopolymer), 25014-31-7; tetrachlorobisphenol A polycarbonate (SRU), 26913-25-7; (carbonic acid)·(tetrachlorobisphenol A) (copolymer), 26814-08-4.

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Influence of Pendant Chains on the Loss Modulus of Model Networks

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ABSTRACT: The progress of the loss component of the shear modulus, G'', of a model silicone network has been studied during the cross-linking reaction. It has been observed that G'' increases steadily after the gel point until a maximum value is reached. Then G'' decreases up to a final definite value when the reaction is completed. By a recursive technique, the evolution of the molecular structure of the network with the extent of the reaction was calculated and associated with G'', leading to the conclusion that pendant chains contribute significantly to the loss modulus of an amorphous rubbery material.

Introduction

The study of model rubber networks has been developed extensively during the last years in order to investigate the influence of several structural characteristics on the mechanical properties of these materials. Most of the past research has been focused on the quantitative verification of the theory of rubber elasticity. Several of these studies have been done with poly(dimethylsiloxane) networks[1-8] including some of our own work in which we have looked to the evolution ot the elastic modulus with the extent of the cross-linking reaction.

While working with this chemical system, we have observed that the loss modulus increases steadily after the gel point until a maximum value is reached at a certain extent of reaction. Then G'' decreases up to the completion of the curing process. The same kind of behavior has been observed with networks of different chemical structure like urethanes[9] and epoxies.[10]

In this work we look for a molecular justification of this behavior, studying several silicone networks and simultaneously calculating the evolution of the molecular structure by means of a recursive approach originally proposed by Macosko and Miller.[11,12]

Experimental Section

The model silicone network system that was used for this work

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