Oscillatory Flow Birefringence of Low Molecular Weight Polystyrene Solutions. High Frequency Behavior

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ABSTRACT: The oscillatory flow birefringence properties characterized by the magnitude S_m and relative phase angle θ_s of the complex mechano-optic coefficient S^* of solutions containing 0.113 g/cm^3 of polystyrene with narrow-distribution weight average molecular weight of 10^4 have been measured over a frequency range from 10^1 to 2×10^3 Hz at several temperatures. The solvents were three chlorinated biphenyls, Aroclors 1232, 1248, and 1254. Measurement temperatures ranged from +35 to −19° corresponding to solvent viscosities from approximately 3 to in excess of 10^5 P. A new thin fluid layer oscillatory flow birefringence apparatus has been used to obtain the birefringence properties to higher effective frequencies than were attainable previously. The data are analyzed in terms of the Peterlin modification of the bead-spring theory which incorporates internal viscosity. For frequencies such that θ_s is between −180 and −250°, the agreement between theory and experiment is remarkably good; however, at higher frequencies θ_s changes rapidly, exceeding the −270° limit associated with the theory. This deviation appears to be caused by another high-frequency relaxation process which has an intrinsic optical polarizability of opposite sign to that for long-range conformational changes in polystyrene. Such a sign change is known to occur in the equilibrium stress optical coefficient for undiluted polystyrene; below the glass transition temperature T_g it is positive, above it is negative. Studies of equilibrium orientation birefringence in undiluted polystyrene above and below T_g indicate that only very local rearrangements can occur in the glassy state. From the steady state data it is unclear whether the effects observed are due only to phenyl group motions, or represent very local backbone configurational rearrangements as well. The new oscillatory flow birefringence apparatus appears to be capable of studying motions in moderately dilute solutions on a sufficiently local scale to help clarify the characteristics of rearrangements of importance in the glassy state.

Extensive studies of the frequency dependence of oscillatory flow birefringence (OFB) and dynamic viscoelastic properties of polystyrenes dissolved in high viscosity solvents have provided considerable insight into the dynamics of conformational change in macromolecular solutions.[2,9] Both experiments have provided data extending to sufficiently high effective frequencies to detect the influence of chemical structure on relatively short-range configurational rearrangements.[3,6] The data obtained from both experiments were found to correspond to the predictions of the modified bead-spring theory of Peterlin over the then accessible frequency range.[3,6,10–12] At even higher measurement frequencies, motions more local than those treated by such theories will become dominant. Such motions, which may resemble those characteristic of the glassy state, may be at least partially responsible for the high-frequency limiting viscosity η_∞' that has been measured for solutions containing polystyrene and poly(α-methylstyrene).[6] Earlier OFB measurements indicated that a high-frequency relaxation mechanism might exist, with a relaxation time corresponding to frequencies somewhat higher than were accessible experimentally.[13] Such localized motions could account for the distinctly lower values of η_∞' obtained by Moore for polystyrene in dibutyl phthalate at very high frequencies (23 to 100 MHz).[14]

An improved OFB apparatus has been constructed that is capable of further exploration of this high-frequency regime. Examples of initial studies on moderately dilute solutions of a low molecular weight polystyrene are presented here.

Experimental Section

Materials. A narrow-distribution polystyrene with $\bar{M}_w$ = 10,000, $\bar{M}_w/\bar{M}_n$ < 1.06 (manufacturer's data; Pressure Chemical Co., batch No. 8B), was selected for the initial studies with the new instrument since measurements for low molecular weight solutions are more difficult to obtain and represent a more stringent test of apparatus capabilities. Three solutions were prepared with the chlorinated biphenyl solvents Aroclors 1232 (lot AK7), 1248 (lot KM502), and 1254 (lot KM626) from Monsanto Chemical Co. These solvents were selected for their large dependence of viscosity on temperature and the close match between their indices of refraction and that of solid polystyrene as shown in Figure 1. Solutions were made up by weight, with moderate heating (60°). After approximately 3 weeks of initial solvation the solutions were stirred very gently once a day. The total solvation time was 6 weeks for the Aroclor 1232 and 10 weeks for the Aroclor 1254 solutions. All three solution concentrations were identical, 0.113 g/cm^3 (assuming additivity of volumes), to match the concentration of a solution of polystyrene of comparable molecular weight in Aroclor 1248 studied previously[2b,3] in the original apparatus of Thurston and Schrag.[2a,15,16]

Method. A new thin fluid layer OFB apparatus has been used in conjunction with a PAR Model 129A two-phase/vector lock-in amplifier to obtain measurements over a frequency range from 10 Hz to approximately 3000 Hz. The new apparatus differs considerably from the original;[15,16] it incorporates gaps on either side of a moving glass driving surface for improved lateral motional stability, a combination electromagnetic and mechanical cantilever spring and suspension system to eliminate suspension resonances below 3000 Hz, more intense, stable, and geometrically controlled illumination, increased drive train stiffness so that larger solution viscosities can be tolerated, and a much lower transducer moving mass. The measurement technique is essentially the same as that described previously.[16] A 5770 Å first-order interference filter and super pressure mercury arc lamp provided the semimonochromatic illumination for all of the measurements reported here. Various gap widths ranging from 0.008 to 0.080 in. have been utilized to keep the shear wavelength to gap width ratio greater than 30 to 1 for all measurements to avoid errors in the assumed velocity gradient profile[17] while maintaining minimal mechanical loading conditions.[16] The absence of loading problems was assured by solvent measurements at sufficiently low temperatures to duplicate or exceed solution loading. The new instrument and a computerized online data acquisition and processing system nearing completion will be described in more detail in a future article.[18] All solution temperatures were determined by thermistors mounted in the reflector block as in the original apparatus;[15,16] the thermistors were calibrated against a standard platinum resistance thermometer recently calibrated at NBS.

Results

Data are reported as the magnitude S_m and phase angle θ_s of the complex mechano-optic coefficient S^* (phasor notation) defined as

$$S^* = S_m \exp(i\theta_s) \equiv -(\Delta n^*/g^*)$$

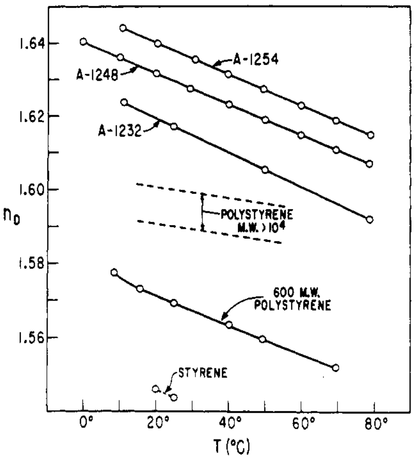

Figure 1. Temperature dependence of the static index of refraction at 5893 Å for Aroclors 1232, 1248, and 1254, undiluted polystyrene ($M > 10^4$) below T_g,[26] undiluted ($M = 600$) polystyrene above T_g, and styrene.[26]

where Δn, the real part of Δn^*, is the difference in indices of refraction n_1 and n_2 in principal directions 1 and 2 and g, the real part of g^*, is the sinusoidally time varying shear rate as defined previously.[2a,15,16] Unfortunately, the Aroclor solvents are weakly birefringent; for the measurement frequencies and temperatures utilized, $\theta_s = 0°$ and no frequency dependence of S_m was detectable for the solvents. In order to obtain the polymer contribution from the measured solution birefringence the usual correction procedure of Sadron[19] was followed; this assumes that the solution polarizability tensor is given by the sum of the solute and solvent tensors.[16,20] For the low gradient measurement conditions utilized in OFB the extinction angle for solution or solvent remains at 45° during the cycle of motion, leading to a particularly simple correction procedure.[2a]

Data were obtained for all three solutions at approximately 20 frequencies f ranging from 10 to 2000 Hz at various temperatures. The solution measurement temperatures were as follows: 35.7, 24.5, 20.1, and 17.7° in Aroclor 1254; 24.5, 15.9, 7.7, 2.8, and −1.4° in Aroclor 1248; and −13.1 and −19.0° in Aroclor 1232. Time–temperature superposition was utilized to obtain reduced variable plots of log (S_m/a_T) and θ_s vs. log fa_T; resultant plots for the Aroclor 1248 and 1254 solutions are shown in Figures 2 and 3 (circles). The superposition of data from different temperatures is excellent. The data below $fa_T = 10^5$ in Aroclor 1248 agree closely with the earlier results.[3] The Aroclor 1232 solution results were more limited in extent and are not shown because solvent crystallization reduced the accessible temperature range and the accuracy of the −19° data; however, the same theoretical curves fit these data as the others. The shift factors a_T were obtained from the temperature dependence of the steady flow birefringence[16] except for the lowest temperature for the 1254 and 1248 solutions where the information was unavailable and empirical shifts were utilized. Note that in both curves the phase angle changes by considerably more than 90°; the onset of this behavior was seen in previous OFB studies.[13] Relatively minor instrumental problems limited the accuracy of the lowest temperature data at the highest measurement frequencies; measurements corresponding to values of fa_T 20 to 100 times larger than shown should be attainable after minor apparatus modifications. Estimated measurement error bars for θ_s are shown in each figure for the two highest frequencies of measurement; estimated relative uncertainties for the remainder of the data are ±1% for S_m and ±2° for θ_s.

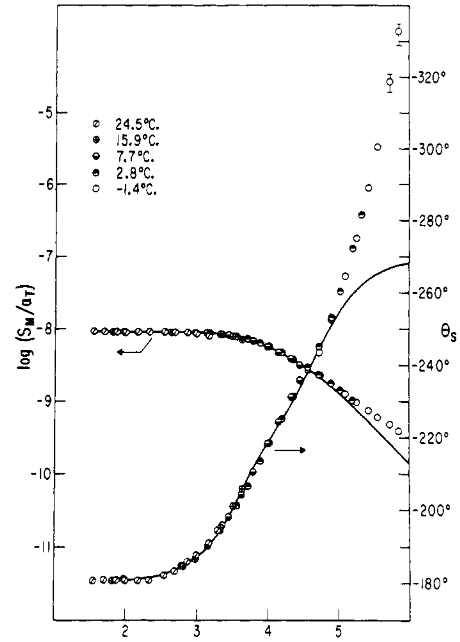

Figure 2. S_m/a_T (seconds) and θ_s (degrees) for $\bar{M}_w = 10{,}000$ polystyrene in Aroclor 1248, $c = 0.113$ g/cm³, plotted logarithmically against frequency reduced to 24.5°, from data at the five temperatures indicated (optical wavelength: 5770 Å). Curves from Peterlin theory for $N = 7$, $h^* = 0.125$, $\phi/f = 1.9$.

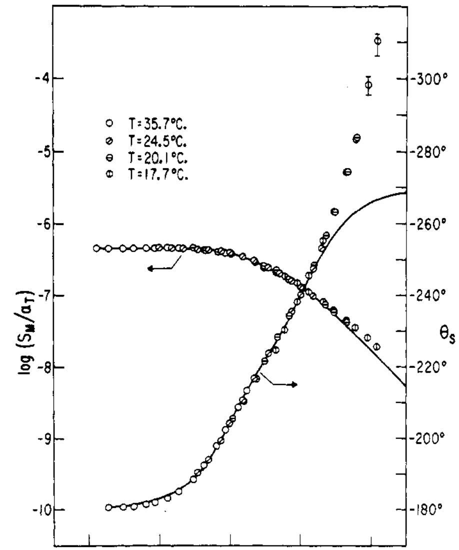

Figure 3. S_m/a_T and θ_s for $\bar{M}_w = 10{,}000$ polystyrene in Aroclor 1254, c = 0.113 g/cm³, plotted logarithmically against frequency reduced to 24.5°, from data at the four temperatures indicated (optical wavelength: 5770 Å). Curves from Peterlin theory for $N = 7$, $h^* = 0.125$, $\phi/f = 1.9$.

Discussion

Previous studies have indicated that the Peterlin theory[10,12] is remarkably successful in describing OFB and dynamic viscoelasticity for solutions of polystyrene in Aroclors over a wide range of molecular weights.[3,5,6] Both experiments yielded essentially the same values for the theoretical parameters N, the number of normal modes of motion for the bead-spring model of the molecule (proportional to molecular weight), h^*, the hydrodynamic interaction parameter, and ϕ/f, where ϕ is the internal viscosity coefficient and f is the friction coefficient assigned to a bead.[10–12] The initial comparisons of theoretical predictions and data utilized theoretical curves obtained with approximate eigenvalues;[12] more recently Thurston and Morrison[21] and Lodge and Wu[22] have shown that the use of exact eigenvalues leads to appreciably different values for N, h^*, and possibly ϕ/f, particularly at low molecular weight. Figures 2 and 3 also show theoretical curves (solid lines) for OFB from the Peterlin theory (exact eigenvalue calculation) for $N = 7$, $h^* = 0.125$, and $\phi/f = 1.9$. The horizontal positioning of the curve is arbitrary since the data are for a finite solution concentration. The agreement between experiment and theory is remarkably good for frequencies such that θ_s lies between −180 and −250°. Essentially the same curves are obtained from the approximate computations with $N = 10$, $h^* = 0.3$, and $\phi/f = 2.0$.[3] Thus the value of P/N (P is the degree of polymerization of the sample) which has been reported from comparisons based on inexact eigenvalues will be reduced, reflecting a lesser degree of molecular flexibility.[3,5,6] (P/N has been found to be sensitive to specific chemical structure.[6])

Measurements made at a single molecular weight cannot be used to obtain precise values of the theoretical parameters. This is particularly so for low molecular weights; N, h^*, and ϕ/f interact under these conditions to such an extent that the same theoretical curve can be generated for an appreciable range of parameter values. Since high molecular weight OFB analyses were not available, the values of h^* and ϕ/f used in calculations for Figures 2 and 3 were based on existing viscoelasticity data;[23] for this reason the values listed should be regarded as being approximate only. The fact that data for all three solutions fit the same theoretical curve indicates that the solvent power for all three solvents is essentially identical as expected. Strictly speaking, the application of an infinite dilution theory to finite concentration measurements is not appropriate; investigations of concentration effects on viscoelasticity data have shown that the initial influence of concentration is to reduce the apparent h^* value and to increase the longest relaxation time τ_1.[6] Future measurements of OFB will be extrapolated to infinite dilution when possible to provide better quantitative evidence for comparison with theory.

The most important aspect of the work reported here is the behavior at very high effective frequency where S_m and θ_s deviate significantly from theoretical predictions. Deviation from theory would not in itself be surprising, since the bead-spring model incorporates the Gaussian subchain concept; all motions within the subchain are explicitly ignored although it is believed that the additional energy dissipation from the internal viscosity included in the Peterlin theory may treat some aspects of these local motions.[24] The surprising result is the nature of the deviation; that is, that θ_s exceeds −270°, changing rapidly with frequency. Local chain backbone motions would exhibit negative optical anisotropy just as the longer range motions do,[20,25] provided the phenyl rings remain effectively normal to the backbone during the configurational rearrangements. Such contributions would cause the experiment to deviate from the theory (assuming that N does in fact indicate the number of Gaussian subchains for a molecule; if not, deviations might not be apparent) but would only alter the approach of θ_s to −270°.

Apparently, in order for θ_s to exceed this limit, some positive optical anisotropy must become significant. There are three possible sources of such a positive contribution: the solvent, form birefringence, and phenyl group motions relatively independent of backbone conformation changes. If the solvent correction procedure is inappropriate it would lead to improper phase angles since the intrinsic anisotropy of the Aroclors is positive. However, these corrections are small, less than 10° in phase at $\theta_s = -280°$. Thus even if the correction were increased by 50% the anomaly would still remain. Form birefringence also contributes an anisotropy that is of positive sign.[20,25] However, in steady flow, the form contribution becomes very small at low molecular weights; it is not clear how this effect enters into the OFB experiment, but it may be a very small contribution at high frequencies. In any event, Figure 1 shows the temperature dependence of the static indices of refraction at a wavelength of 5893 Å (sodium D line) for the Aroclors as determined in our laboratories with an Abbe refractometer. The OFB measurements were made on solutions utilizing all three solvents, partially to determine if different form birefringence effects might be detectable based on the curves of Figure 1. Unfortunately, the indices of refraction for all three are essentially identical at the requisite OFB measurement temperatures, so no concrete evidence on the form effect was obtained. Also shown are literature values[26] for undiluted polystyrene (below the glass transition temperature T_g) with molecular weight above 10^4, our data for undiluted 600 molecular weight polystyrene (Pressure Chemical Co., batch No. 16A) above T_g, and literature values for styrene.[26] Based on these data, it would appear that the solvent and solute indices do not differ by more than 0.05 at any of the OFB measurement temperatures; since in steady flow solution measurements the form birefringence effect shows a parabolic dependence on this difference, and is essentially undetectable for differences less than 0.1, it seems reasonable to assume that form birefringence is not responsible for the phase angle anomaly observed.

There is considerable evidence from birefringence studies of undiluted polymers to support the phenyl group motion hypothesis. The stress-optical coefficient (SOC) for polystyrene is small and positive below T_g, large and negative above T_g.[27,28] Further, as T_g is approached from below, the SOC decreases as relatively local chain motions apparently become more likely, resulting in larger and larger negative contributions that offset the positive birefringence associated with the phenyl group motions.[27] Alternatively, one might postulate that below T_g, as the temperature is reduced, the phenyl group on the average orients more and more completely with the strain direction, as evidenced by the increase in a positive sense of the SOC. Whatever chain motions are occurring in the glassy state must be quite local as is shown by careful orientation birefringence studies.[28,29] Similar SOC sign changes have been observed in other polymeric systems such as poly(vinyl chloride)[30] and poly(styrenedivinylbenzene).[31] Interestingly, the incorporation of the methyl group in poly(α-methylstyrene) inhibits the SOC sign change at T_g;[32] apparently the phenyl group is relatively immobile and normal to the backbone in this styrene derivative.

Based on the SOC studies of undiluted polystyrene we believe that the anomalous high-frequency values of θ_s for dilute solutions are due to some type of phenyl group wagging motions that tend to orient the group in the principal strain direction to a significant extent; rotations about the C–Ph bond would not produce sign changes unless the rotation angles are large. Such rotations are calculated to be relatively unlikely in both polystyrene and poly(α-methylstyrene).[33] These motions may or may not result from local configurational rearrangements of the chain; even if such local backbone changes occur, the phenyl group motions may mask their contributions. High-frequency OFB studies of poly(α-methylstyrene) should resolve this question under moderately dilute solution conditions for which theoretical analysis may be feasible; if indeed the phenyl motions are independent of local rearrangements in polystyrene, the data obtained for the methyl derivative might provide a better test of the high-frequency limitations of the Peterlin theory than the polystyrene studies since the chain backbone motions should then be detectable. Such information might provide considerable insight into configurational dynamics on spatial scales of importance in the glassy state. A future paper will report on more extensive studies of the high-frequency regime for both polystyrene and poly(α-methylstyrene).

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Dynamics of Block-Copolymer Molecules in Dilute Solution

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ABSTRACT: A theory for the dynamics of block-copolymer molecules in dilute solution has been developed by modifying the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. The eigenvalue equation encountered in the theory has been solved numerically by extending the method of Lodge and Wu. The applications of the theory have been illustrated with calculations for the viscoelastic properties of poly(styrene-*b*-methyl methacrylate) solutions and poly(styrene-*b*-*cis*-1,4-isoprene) solutions. It is found that, for some block copolymers in solution, the calculated values of the viscoelastic properties deviate significantly from the values for the parent homopolymers toward the values predicted by the free-draining case.

I. Introduction

The conformation of block-copolymer molecules in dilute solution still remains ambiguous. There are two conformations often discussed as plausible: one in which dissimilar segments are interpenetrating, and one in which the segregation of unlike segments occurs. Although there have been a large number of measurements[1] on the solution properties of block copolymers, the experimentalists have not been able to argue conclusively in favor of one of the plausible conformations. Considerable uncertainties are introduced in the conclusions obtained from viscometry, because these conclusions are invariably arrived at by extending, with the use of some additive rules, theories and procedures developed strictly for homopolymer solutions. In this work, a step toward the removal of these uncertainties has been made by generalizing the bead-spring model theory of Zimm[2] to make the generalized theory applicable to the viscoelasticity of block-copolymer solutions. The eigenvalue equation encountered in the Zimm theory[2] has been solved numerically by Lodge and Wu[3] and by Thurston.[4] We have numerically solved the eigenvalue problem from the present theory by extending the method of Lodge and Wu.[3] Our theory in the present form is strictly useful only to block-copolymer solutions in which the excluded-volume effect is negligible. However, if our theory is further modified to take into account the excluded-volume effect, we can use the theory thus obtained to determine whether the viscoelastic properties of block-copolymer molecules in non-Θ solvents can be interpreted without invoking the segregated conformation.

Work of a similar nature but in the free-draining limit is being communicated by Shen and Hansen,[5] by Stockmayer and Kennedy,[6] and by Wang and DiMarzio.[7]

II. Formulation of the Problem

We derive in this section the equation of motion of a block-copolymer molecule in dilute solution under the con-