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Polymer–Solvent Interaction Effects in Oscillatory Flow Birefringence Studies of Polybutadienes and Polyisoprenes in Aroclor Solvents

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ABSTRACT: Oscillatory flow birefringence measurements for solutions of 500 and 150 000 MW polybutadienes (PB) and 1000 and 57 000 MW polyisoprenes (PI) in high-viscosity Aroclors (1248 and 1254) are reported. These data show substantial reductions in the solvent birefringence contributions to the total solution value when small amounts of polymer are present, suggesting that polymer–solvent interactions occurring in these systems somehow modify the solvent–solvent interactions responsible for the unusually large and strongly temperature-dependent viscosity of Aroclors. Similar large reductions in the effective solvent viscosity are detected. These Aroclor solvent modifications due to the presence of PB or PI are strong functions of temperature and concentration but appear to be independent of polymer molecular weight and are insensitive to moderate variations in microstructure. When the normal correction procedure for determination of the polymer contribution to the observed total birefringence is applied to these data, time–temperature superposition appears to be invalid and both PB and PI seem to be dynamically "stiffer" than polystyrenes in Aroclors, for example. However, if modified solvent birefringences deduced from the oligomer-containing solutions are employed, time–temperature superpositions are obtained and the dynamic "stiffness" of PB and PI appears to be substantially less than for polystyrenes. These polymer–solvent interactions for these systems clearly influence both oscillatory flow birefringence and viscoelastic properties, and hence configurational dynamics interpretations obtained from such measurements for these solutions; polystyrenes, poly(α-methylstyrenes), and several poly(2-substituted methyl methacrylates) in Aroclors have not shown any evidence of similar interaction effects.

Extensive studies of the frequency dependence of oscillatory flow birefringence (OFB) and dynamic viscoelastic (VE) properties of polymer solutions have provided considerable insight into the dynamics of conformational change in these systems.[1–14] By employing Aroclors (chlorinated biphenyls) as solvents, both experiments have provided data apparently extending over sufficiently wide effective frequency ranges (as much as 7 decades) to detect the influence of motions ranging from the slowest overall chain rearrangements (low frequency) to very short-range configurational changes and side-group motions (high frequency).[4,12–14] The instrumentation employed for the studies noted above typically has a maximum working frequency of the order of 10^4 Hz or less.[4,15,16] The high-frequency/local-motion information has been obtained with these apparatuses by employing time–temperature superposition; the large temperature dependence of the viscosity of the Aroclor solvents, together with their relatively high viscosities, has been essential to shift the time scales of the various configurational rearrangements down to instrumentally accessible frequencies.[15,17] Thus the solvent requirements for such studies are almost unique to such materials as the Aroclors or tricresyl phosphate;[18] the large temperature dependence of viscosity for these materials suggests significant solvent–solvent interaction, perhaps leading to the formation of small solvent clusters which exhibit temperature-dependent dimensions. For OFB measurements, the Aroclors exhibit one undesirable feature in that they are weakly birefringent when undergoing a shearing deformation, so that the total birefringence observed for a given polymer solution has contributions from both the polymer and solvent constituents. The temperature dependence of the birefringence and viscosity for a given Aroclor is almost identical.[19]

The polymer contribution to the OFB data is obtained by correcting the measured values for the solvent contribution. The procedure generally utilized is based on the assumption of simple additivity of the polarizability tensors for the various constituents.[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; i.e., the net solution polarizability is essentially unaffected by long-range interactions between polymer and solvent. For the low velocity gradient conditions employed in the thin fluid layer OFB instrument, the principal directions of the polarizability tensors for both solution and solvent remain at 45° with respect to the streamline direction throughout the cycle of deformation,[1,19] which leads to the particularly simple vector subtraction correction procedure described below. This approach gives results for dilute solutions of polystyrene, poly(α-methylstyrene), and poly(2-substituted methyl acrylates) that are consistent with theoretical predictions[22–24] as well as measured viscoelastic properties except at high effective frequencies or extremely low degrees of polymerization.[3,4,7,14]

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The situation changes markedly, however, when polybutadiene (PB) or polyisoprene (PI) is dissolved in Aroclors. For example, the viscosity (at 15 °C) of moderately dilute solutions containing 34 000 or 60 000 MW PB in Aroclor 1254 is substantially less than that of the pure solvent, which leads to an apparent negative intrinsic viscosity when extrapolated in the usual manner; [25] the glass transition temperatures of both components are below −20 °C.[15,26] Similarly, OFB measurements obtained at various temperatures for moderately dilute solutions of 57 000 MW PI and 150 000 MW PB dissolved in Aroclor 1248 did not exhibit time–temperature superposition and seemed to suggest a peculiar overall frequency dependence with a surprising similarity to that obtained at high effective frequencies for polystyrene/Aroclor solutions[27] although other measurements indicate that polystyrene is a stiffer molecule than either PB or PI.[28,29] These earlier observations suggest that there may be some type of interaction between PB (or PI) and Aroclors that results in a reduction in the solvent contributions to both solution viscosity and birefringence. This paper reports on further OFB investigations into the nature of this interaction, which have included studies of low molecular weight oligomers of PB and PI in Aroclors as well as additional measurements on solutions containing higher molecular weight samples. The solutions containing oligomers exhibit a birefringence effectively due to the Aroclor only, so that the substantial influence of the PB or PI on the birefringence of this solvent can be readily monitored. The results of the oligomer birefringence studies appear to correspond closely to what was observed by Johnson for the VE properties of higher molecular weight PB in Aroclor 1254,[25] suggesting that the interactions involved are insensitive to molecular weight. When the polymer-modified solvent birefringence from the oligomer studies is employed to evaluate the polymer contribution to the OFB properties for the higher molecular weight solutions, one obtains good time–temperature superposition and overall frequency response curves indicative of highly flexible molecules.

Experimental Section

Materials. This investigation of the OFB properties of Aroclor-based solutions of PB and PI was carried out for the following samples: 500 MW polybutadiene (approximately 50% trans, 30% cis, and 20% vinyl), sample no. CDS-B-1 from Goodyear, for which $\bar{M}_w/\bar{M}_n \leq 1.7$; 1000 MW polyisoprene (approximately 95% 1,4 addition, 5% 3,4 addition), sample no. CDS-I-1 from Goodyear, for which $\bar{M}_w/\bar{M}_n \leq 2$; 57 000 MW (±10%) polyisoprene (approximately 70% cis, 30% trans) synthesized by Dr. J. Hinkley in the laboratories of Professor H. Yu of this department; and 150 000 MW polybutadiene (approximately 40% cis, 53% trans, and 7% vinyl), sample no. 45454 from Phillips Petroleum, for which $\bar{M}_n = 150000$ and $\bar{M}_w/\bar{M}_n \leq 1.14$. The above characterization information is that specified by each manufacturer. Other relevant physical properties[15,29] are the refractive index (1.51–1.52 for both polymers at 25 °C) and the densities (0.985 and 0.913 g/mL for polybutadiene and polyisoprene, respectively). The chlorinated biphenyl solvents Aroclor 1248 (lot KM502; ρ = 1.45 g/mL, η = 2.16 P at 25.0 °C; n = 1.630 at 5893 Å, T = 25 °C)[4] and Aroclor 1254 (lot KM626; ρ = 1.54 g/mL, η = 91 P at 25.0 °C; n = 1.638 at 5893 Å, T = 25 °C) were obtained from Monsanto Chemical Co.; both exhibit glass transition temperatures below −24 °C.[26] Solutions of the highest concentration were made up by weight and successively diluted to obtain the lower concentrations. Since the low molecular weight PB and PI are liquids at 20 °C, solutions of these samples were prepared by combining and gently stirring appropriate amounts of solvent and polymer at room temperature. The higher molecular weight, highest concentration solutions were subjected to an undisturbed initial solvation period of about 1 week in an oven at 40 °C, after which time they were stirred very gently once a day over a period of about 1 week. Solution concentrations have been calculated by assuming additivity of volumes. It should be noted that most of the samples are rather polydisperse. If one is studying polymer conformational dynamics per se via OFB or VE studies, sharp distribution samples are necessary. Here, however, the emphasis is on the substantial changes in measured properties caused by polymer–solvent effects rather than motional dynamics information, so sample polydispersity is unimportant.

Method. The OFB measurements were obtained with the thin fluid layer (TFL) OFB instrument[30,31] and a second-generation computerized data acquisition and processing system.[5,27] The usable frequency range of this combination is 0.01–2500 Hz; the velocity gradient (shear rate) magnitudes typically range from 1 to 150 s^{-1}, depending on solution viscoelasticity, gap width, and oscillation frequency. In all cases the shear rate was kept sufficiently small that the principal directions (extinction angle) of the solution polarizability tensor remain at 45° to the streamline direction throughout the cycle of deformation. Various gap widths were employed, ranging from about 0.005 to 0.10 cm, to keep the shear wavelength to gap width ratio greater than 30:1 to avoid significant errors in the assumed shear rate.[31] A first-order 5770-Å interference filter and superpressure mercury arc provided the semimonochromatic illumination. All temperatures were determined to ±0.02 °C by a thermistor calibrated against a standard platinum resistance thermometer calibrated at NBS.

Results

The birefringence data described herein are reported in terms of the magnitude S_M and relative phase angle θ_S of the complex mechano-optic coefficient S^* defined as

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

where Δn, the real part of Δn^*, is the difference in indices of refraction n_1 and n_2 for principal directions 1 and 2, and $\dot{\gamma}$, the real part of $\dot{\gamma}^*$, is the sinusoidally time-varying shear rate, as defined previously.[30-33] θ_S specifies the phasing of Δn with respect to $\dot{\gamma}$. Additional subscripting is utilized herein to distinguish between the various birefringence contributions; $(S_M)_{TOT}$ and $(\theta_S)_{TOT}$, S_{MS} and θ_{SS}, S_M and θ_S, and S_{MS}' and θ_{SS} denote, respectively, the total (or measured) solution birefringence properties, the pure solvent properties, the polymer contribution to the measured properties, and the solvent properties when PB or PI is present. For the low gradient conditions employed here, the normal solvent birefringence correction procedure utilized to obtain the polymer contribution from the measured solution birefringence reduces to a simple vectorial subtraction in the complex plane as follows:

$$S_M \exp(i\theta_S) = (S_M)_{TOT} \exp[i(\theta_S)_{TOT}] - \nu S_{MS} \exp(i\theta_{SS}) \qquad (2)$$

where ν is the volume fraction of solvent.

For the frequencies and temperatures employed in this study the Aroclor solvent properties are frequency independent (S_{MS} is constant, $\theta_{SS} = 0°$ so that $\exp(i\theta_{SS}) = 1$).[4,19-21] However, for cases where substantial interactions exist between polymer and solvent, a modified solvent correction S_{MS}', θ_{SS}' must be used corresponding to the solvent birefringence contribution appropriate for the given solution conditions. Here again S_{MS}' is constant and $\theta_{SS}' = 0°$, but no volume fraction correction is required so the polymer birefringence contribution is specified by

$$S_M \exp(i\theta_S) = (S_M)_{TOT} \exp[i(\theta_S)_{TOT}] - S_{MS}' \qquad (3)$$

Note that correction procedures (2) and (3) both assume simple additivity of the polarizability tensors for polymer and solvent. Typical measurement precisions for the high molecular weight solutions give rise to uncertainties in $(S_M)_{TOT}$ and $(\theta_S)_{TOT}$ of ±2% and ±0.5°, respectively. For the weakly birefringent solutions of low molecular weight PB at 25.00 °C the relative standard deviation of several

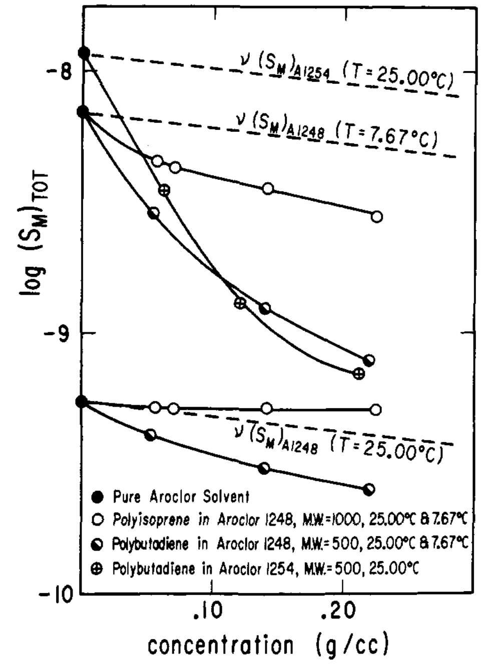

Figure 1. Plots of log $(S_M)_{TOT}$ vs. concentration for 500 MW polybutadiene in Aroclors 1248 (25.00 and 7.67 °C) and 1254 (25.00 °C) and 1000 MW polyisoprene in Aroclor 1248 (25.00 and 7.67 °C). Dashed lines are plots of log (νS_{MS}) vs. concentration (see text) for Aroclors 1248 and 1254 at the same temperature.

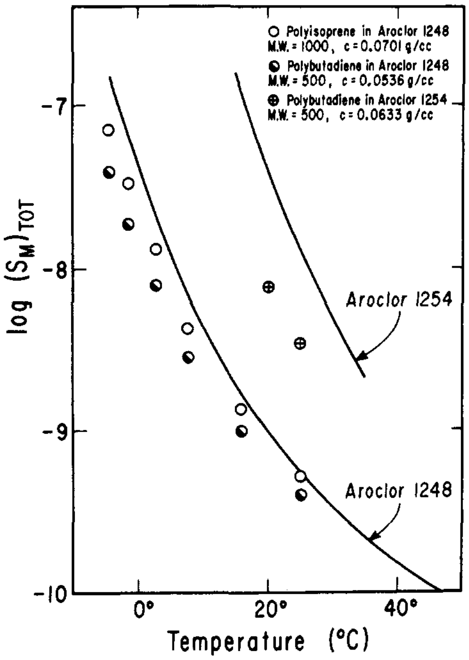

Figure 2. Plots of log $(S_M)_{TOT}$ vs. temperature for solutions of 500 MW polybutadiene in Aroclors 1248 and 1254 and 1000 MW polyisoprene in Aroclor 1248 as specified in the figure. Solid lines are log S_{MS} values for Aroclors 1248 and 1254.

measurements was less than ±10%; phase angle measurement uncertainties were generally no larger than ±0.5° unless otherwise specified in the figures.

Solutions containing the PI and PB oligomers in the Aroclor solvents are expected to give very small (less than 5% at the highest concentrations) positive contributions ($\theta_S = 0°$) to the observed solution birefringence for concentrations up to 25% by weight since the segmental polarizability anisotropy of PI or PB is a factor of 4 or 5 less than that of polystyrene (PS) and 600 MW PS has been found to contribute less than 20% of the measured solution birefringence at a 20% weight concentration in Aroclor 1248.[30,34,35] Thus the measured birefringence should essentially reflect solvent properties and should be frequency independent. If the oligomers should give rise to a detectable contribution, the magnitude of the observed birefringence would increase with increasing low molecular weight PB or PI concentration. For the oligomer-containing solutions, if the solvent properties are not influenced by a solvent–polymer interaction, the solution birefringence at a given shear rate would be approximately equal to or somewhat greater than the volume fraction of solvent times the birefringence that would be observed for pure solvent only. However, substantially different behavior is observed, as shown in Figures 1 and 2. Figure 1 demonstrates the dependence of the frequency-independent solution birefringence data on the concentration of the PB and PI oligomers in Aroclor 1248 at 7.67 and 25.00 °C and for the PB oligomer in Aroclor 1254 at 25.00 °C. The dashed lines in the figure indicate the expected behavior in the absence of polymer–solvent interaction; a substantially larger initial decrease in solvent birefringence is evident, followed by a continued decrease, except for the 25.00 °C PI/Aroclor 1248 data. Figure 2 illustrates the temperature dependence of the birefringence for the two Aroclors and for three oligomeric solutions as specified in the figure; note that the solution concentrations are not high in terms of the measurements shown in Figure 1. Figure 2 illustrates that as temperature decreases, the deviation (a decrease) of the solution birefringence increases relative to those for the pure solvents. Thus both figures suggest a substantial temperature- and concentration-dependent interaction between either PI or PB and Aroclors which substantially reduces the solvent birefringence. Note that Figure 1 suggests that there is essentially no significant contribution from the oligomers themselves at these concentrations since the birefringence is a monotonically decreasing function of concentration, with the possible exception of the data for PI in Aroclor 1248 at 25.00 °C for which a slight polymer contribution may be indicated. Interestingly, the character of the concentration dependence shown in Figure 1 is quite similar to that displayed by the VE data of Johnson for 34 000 and 60 000 MW PB in Aroclor 1254,[25] suggesting that the solvent modification taking place may be rather insensitive to molecular weight and modest changes in microstructure.

If one evaluates the polymer contribution to the solvent birefringence in the normal way (specified by eq 2) for the higher molecular weight PB and PI samples, one obtains the frequency-dependent values, reduced to a reference temperature of 25.00 °C, shown in Figures 3–5. These plots clearly demonstrate the apparent failure of time–temperature superposition, and the apparent frequency dependence of θ_S at high frequencies suggests that PB and PI are dynamically "stiffer" (correspond to small values of N when fitted to the Zimm theory, for example) than polystyrenes in the same solvent.[3,12–14,30] These results, together with the observations from the oligomer studies, strongly suggest that the simple volume fraction solvent correction procedure of eq 2 is not valid. Since these oligomer studies together with Johnson's results suggest a solvent–polymer interaction that may be independent of molecular weight and modest variations in microstructure, solvent birefringences obtained from the low molecular weight studies for temperatures and polymer concentrations identical with those employed for the higher molecular weight polymer solutions have been employed as modified solvent correction values S_{MS}' as shown in eq 3. The results of this modified solvent correction, reduced

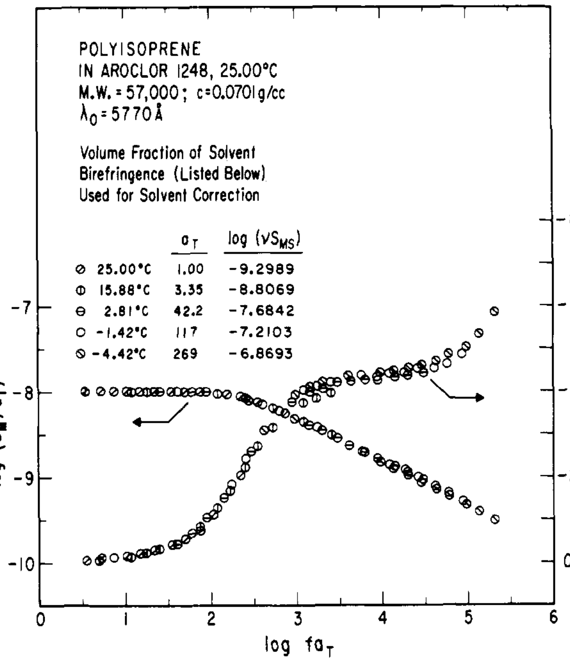

Figure 3. Plots of log (S_M/a_T) and θ_S vs. log of the reduced frequency fa_T for 57 000 MW polyisoprene in Aroclor 1248 as specified in the figure. Standard solvent correction procedure has been employed (eq 2). Values of the time–temperature shift factor a_T and log (νS_{MS}) are shown for each measurement temperature.

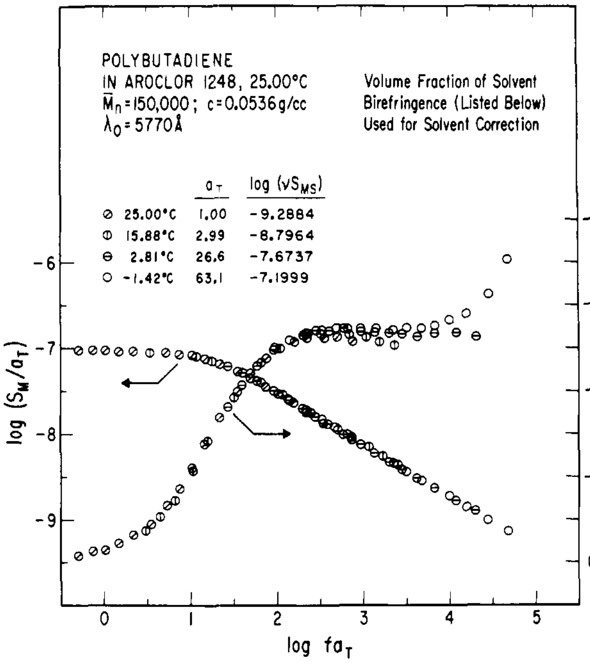

Figure 4. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 150 000 MW polybutadiene in Aroclor 1248 as specified in the figure. Standard solvent correction procedure has been employed.

to 25.00 °C, are shown in Figures 6–8; the dashed lines in the figures indicate the general trends of the data when the original solvent volume fraction correction procedure employed in Figures 3–5 was employed. The frequency-dependent polymer birefringence properties obtained when the modified solvent correction values are used exhibit satisfactory time–temperature superposition and a substantially different frequency dependence of θ_S at higher frequencies. It is interesting to note that the modified data plots for the higher concentrations of the 57 000 MW PI and 150 000 MW PB ($c[\eta]$ = 4.8 and 11.2, respectively)

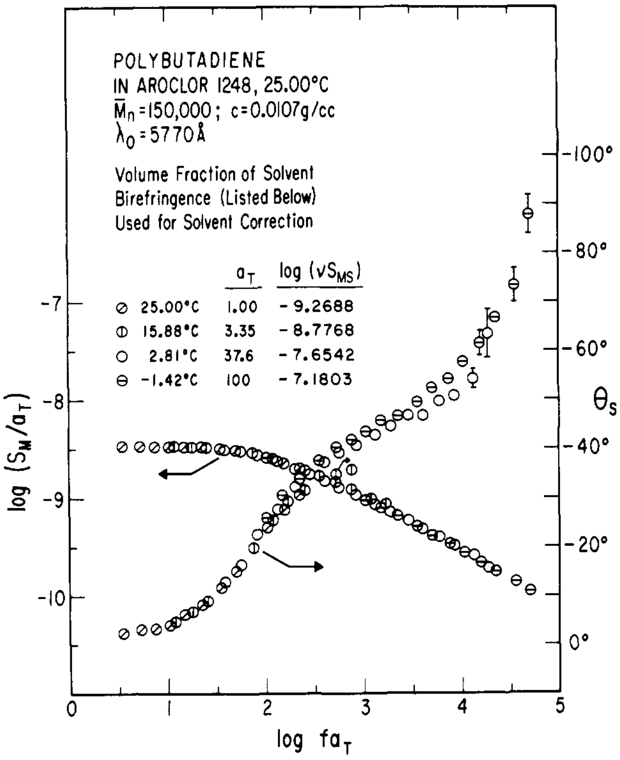

Figure 5. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 150 000 MW polybutadiene in Aroclor 1248 as specified in the figure. Standard solvent correction procedure has been employed.

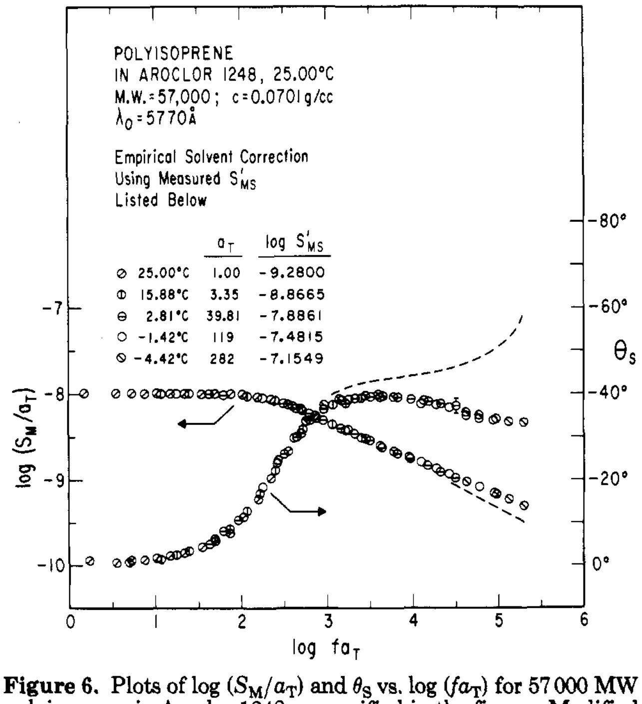

Figure 6. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 57 000 MW polyisoprene in Aroclor 1248 as specified in the figure. Modified solvent correction procedure has been employed (values of S_{MS}' are shown in the figure). Dashed curves, normal solvent correction procedure.

exhibit a peak in θ_S at low frequencies of the type that is commonly observed as one approaches the entanglement regime. As usual, when the solution concentration is reduced as shown for the 150 000 MW PB in Figure 8 ($c[\eta] \approx 2.2$, i.e., somewhat above the onset of coil overlap), this peak disappears and the data can be fitted by Zimm theory[19,22,24] curves as shown by the solid lines in the figure which were generated for N (number of normal modes of motion available to the bead–spring model of the polymer)

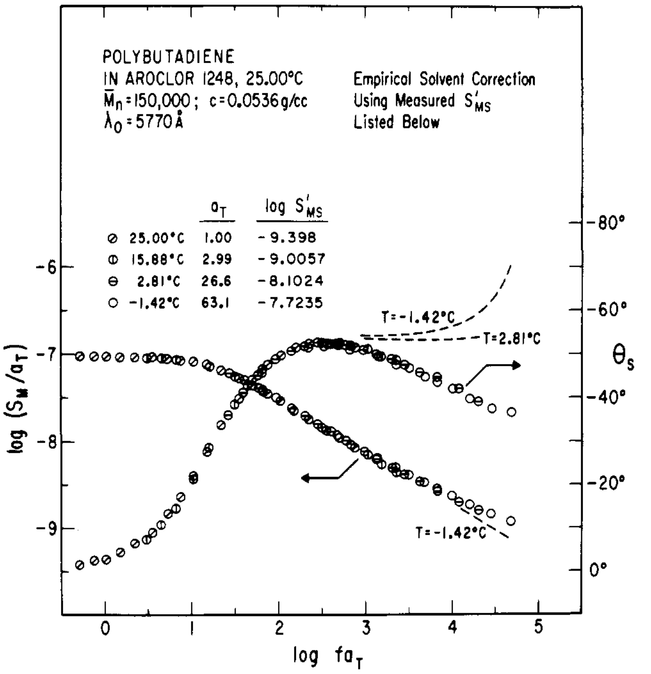

Figure 7. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 150 000 MW polybutadiene in Aroclor 1248 as specified in the figure. Modified solvent correction procedure has been employed. Dashed curves, normal solvent correction procedure.

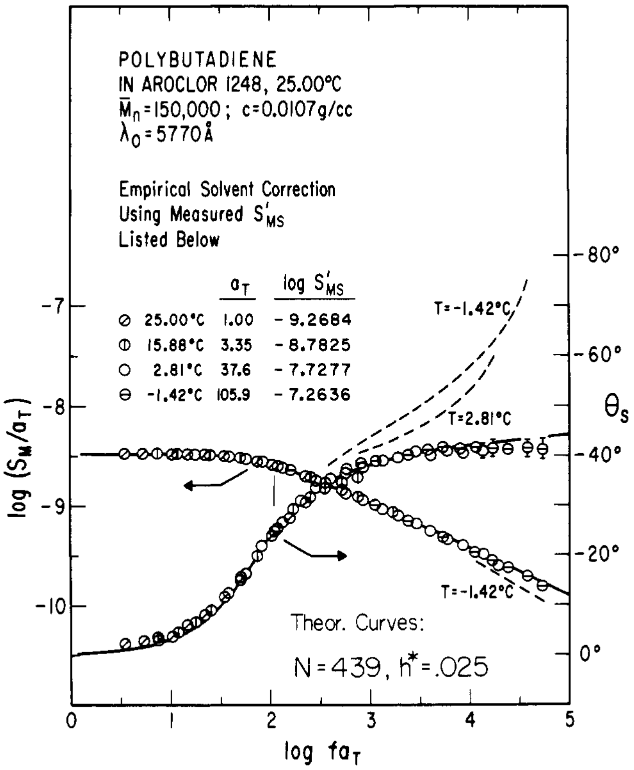

Figure 8. Plots of log (S_M/a_T) and θ_S vs. log (fa_T) for 150 000 MW polybutadiene in Aroclor 1248 as specified in the figure. Modified solvent correction procedure has been employed. Dashed curves, normal solvent correction procedure.

equal to 439 and h^* (hydrodynamic interaction parameter) = 0.025, close to the free-draining limit as expected for solution concentrations in the coil-overlap regime.[15,16] The positioning of the theoretical curve on the data shown in the figure corresponds to a value for the longest relaxation time τ_1 of 1.5 ms.

The substantially altered θ_S curves of Figures 6–8 indicate much less dynamic "stiffness" for these molecules than was suggested by Figures 3–5. In fact, PB and PI properties obtained via the modified solvent correction procedure indicate that these molecules are dynamically much more flexible than polystyrene, for example, as would be expected from steady-state stress optical coefficient studies of Gent and Kuan[34] or the [η] studies of Mark.[37] The N value used for the theoretical curves shown in Figure 8 is clearly too small; computer limitations dictated the maximum matrix size (439 × 439) for which exact eigenvalues could be obtained. An appropriate N would be substantially greater than 439 indicating that the ratio P/N, where P is the degree of polymerization, is more than 7 times larger for polystyrene than for PB,[14,30,36] and the ratio of the number of carbon–carbon bonds per Gaussian subchain (Zimm theory) to N is at least 3–4 times larger for polystyrene. These results, as well as the good time–temperature reductions obtained, give credence to the properties obtained with the modified solvent correction procedure. Note that internal electric field effects ("form birefringence") are assumed to be unimportant in the above analysis since the difference in indices of refraction between polymers and solvents is approximately 0.13 or less; Tsvetkov[35] found that form birefringence effects were negligible in steady flow birefringence measurements for dilute polymer solutions when the index difference was 0.1 or less, and Janeschitz-Kriegl[21] demonstrated that form effects become less significant as polymer concentration increases. In addition, OFB studies of polymer solutions with concentrations similar to those reported here have shown no detectable form effects for index differences as large as 0.15.[38]

Discussion

On the basis of the above, the interactions between PB or PI and the Aroclors appear to be concentration and temperature dependent, but at least relatively independent of molecular weight and modest differences in microstructure, suggesting that this interaction is relatively local. The magnitude of this effect is surprising, especially at the lower temperatures. For example, at −1.4 °C the solution birefringence of 0.0536 g/cm^3 of 500 MW PB in Aroclor 1248 is about a factor of 3 lower than the pure solvent birefringence. If the reduction in the solvent contribution to the solution birefringence is due to local interactions between solvent molecules and the polymer chain as indicated by the apparent molecular weight independence of this interaction, it is difficult to see how the presence of such a small amount of polymer (see Figure 1) could bring about more than a minor change in solvent birefringence. Apparently the polymer–solvent interaction disrupts a solvent–solvent interaction that involves several solvent molecules which perhaps form "clusters" and thus decreases the solvent birefringence and viscosity. Such a mechanism seems to be consistent with the observed concentration and temperature effects for these solutions as well as the temperature dependence of the birefringence and viscosity for pure Aroclors in which the cluster size might be greater at lower temperatures. It is not clear, however, why these effects should be greater for PB than for PI or why this effect is not observed for polystyrene, poly(α-methylstyrene) or poly(2-substituted methyl methacrylates).[22-24] There are differences in the accessibility to the solvent of the chain backbone, of course, due to the methyl side group for PI and the phenyl ring structures in polystyrene or poly(α-methylstyrene), but it seems unlikely that such local effects could influence a much larger volume of solvent molecules.

Approximate viscosity measurements for the PB and PI solutions obtained simultaneously with the OFB measurements indicate that the reduction in the solution birefringence properties corresponds to the observed reduction in the solution viscosity. However, VE and OFB measurements of the same PI or PB solutions in Aroclors are needed to quantitatively establish that the observed properties arise only from the influence of PB or PI on the flow properties of the Aroclors and not from some optical effect. It would also be very desirable to substantially extend the frequency range of these measurements to see whether long- and short-range motions are affected differently. However, the limited frequency range of the TFL instrument used here will not provide such data, particularly if additional studies in other solvents (typically with lower viscosities) are to be carried out; a prototype version of a new instrument capable of performing OFB measurements over a wider frequency range (1–100 kHz) is currently being evaluated in this laboratory.[38]

Evidence for polymer–solvent interactions that appear to be different in nature has been reported by other investigators.[21,34,39,40] For example, stress-optical coefficients (SOC) are found to depend on solvent species when various solvents are used in polymer solutions or to swell networks. In the absence of polymer–solvent interactions these SOC measurements would be expected to be solvent independent except for internal electric field contributions ("form effects");[21,34] the SOC anomalies reported do not appear to correlate with the difference between the indices of refraction of polymer and solvent and thus do not appear to be due to internal field effects but may arise from the way in which the polymer–solvent interaction affects the local configurations—and possibly the motional dynamics—of the polymer.[34,39]

Polymer–solvent interactions of the type demonstrated here for PB or PI in Aroclors clearly influence substantially both OFB and VE properties, and hence the conformational dynamics interpretations obtained from such measurements. It is not clear how many polymer/solvent systems might exhibit similar but perhaps much weaker effects, or what mechanisms are responsible, but proper interpretations of these experiments may require a better understanding of these interactions. Additional examples in which these solvent modifications give rise to anomalies have been noted; in particular, Aroclor solutions containing block copolymers which have PB or PI as one block show surprising OFB properties at least partially due to different solvent properties in the various spatial regimes containing a predominance of each particular component.[27,41]

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