Solvent and Probe Diffusion in Aroclor Solutions of Polystyrene, Polybutadiene, and Polyisoprene

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ABSTRACT: Pulsed-field-gradient NMR has been used to measure the Aroclor 1248 solvent diffusion in solutions of polystyrene (PS), polybutadiene (PB), and polyisoprene (PI), at 28.5 and 63.5 °C. Six samples of PS ($M = 2.0 \times 10^3$, 5.5×10^3, 9.0×10^3, 2.04×10^4, 3.2×10^4, and 1.05×10^6), one of PB ($M = 1.44 \times 10^5$), and one of PI ($M = 1.35 \times 10^5$) were examined; in all cases the polydispersities were less than 1.1. Additional measurements of azobenzene diffusion in PS ($M = 1.79 \times 10^5$), PB, and PI/Aroclor 1248 solutions were made by forced Rayleigh scattering, at 25.0 °C. Polymer volume fractions, ϕ, ranged up to 0.2. Reduced diffusion coefficients, D/D_0, where D_0 corresponds to the diffusion coefficient in neat solvent, were equal for the two experiments within the data uncertainty. For PS solutions, D/D_0 was also independent of molecular weight. For PS solutions at 28.5 °C, the solvent diffusion decreased with increasing ϕ more rapidly than the decrease observed for a variety of other polymer/solvent systems. For PB solutions at the same temperature, D/D_0 increased with increasing ϕ, while for PI solutions, the mobility was essentially independent of ϕ. At the higher temperature the differences in D/D_0 behavior among the Aroclor solutions of all three polymers, and relative to data for other chemical systems, were substantially reduced. The composition dependence of the solution glass transition temperature was also determined for each of the three systems. The diffusion results correlate with the changing solution free volume, as both PB and PI have lower glass transition temperatures than the neat solvent. However, it is doubtful whether the data for all three systems can be described concurrently by using a free volume equation based on the model developed by Fujita. The results for solvent diffusion in PB and PI solutions do correspond closely to previously reported anomalous viscosity, viscoelasticity, and oscillatory flow birefringence properties for these systems. If the composition dependence of D/D_0 is viewed as an effective local friction, then chain dynamics measurements on these systems may require some reinterpretation. In particular, the postulate that anomalous high-frequency viscoelastic and flow birefringence properties, reported for these and other systems, reflects primarily the modification of bulk solvent properties by the presence of polymer chains is supported by the diffusion results reported here.

Introduction

The dynamics of conformational change for flexible and semiflexible chains in polymer liquids have long served as a sensitive test of molecular theory, as well as a powerful source of detailed characterization information. For example, measurements of the linear viscoelastic (VE) or oscillatory flow birefringence (OFB) properties of polymer solutions have provided uniquely detailed insights into the concentration and molecular weight dependence of homopolymer chain dynamics, the effects of chain stiffness, branching, and tacticity on the relaxation time spectrum, and the role of chemical structure on the dynamics of block copolymers.[1,2] Although considerable current emphasis is directed toward understanding the dynamics of concentrated solutions and melts, there are fundamental questions about the dynamics of isolated chains that remain unresolved. One such issue is the correct molecular interpretation of solution properties measured at high effective frequencies, where in general the experimental results are not in accordance with expectation. The significance of these discrepancies is at least 2-fold. On the one hand, it is both intrinsically interesting and potentially very informative to understand the nature of local chain motions, and how they depend on polymer and solvent molecular structure. On the other hand, until the observed behavior is fully understood, it is not possible to extract unambiguously the true chain dynamics contribution to the measured solution properties, even at very low frequencies.

Statistical mechanical theories of chain dynamics, such as the bead-spring model pioneered by Rouse[3] and Zimm,[4] are not designed to describe explicitly either the VE or OFB properties at higher frequencies where characteristic motions involving only a few monomer units dominate the measured response. Nevertheless, such theories do assume limiting high-frequency behavior for a single isolated chain, namely, that the solution properties should converge to the equivalent quantities for the solvent (at frequencies below those at which substantial solvent relaxation is observed). However, extensive VE measurements have revealed the existence of a high-frequency plateau in the in-phase component, η', of the dynamic viscosity, η^*, which has been designated η'_∞, and which differs from the bulk solvent viscosity, η_s.[5-20] Similarly, in OFB experiments the in-phase component, S', of the dynamic birefringence, S^*, exhibits a high-frequency plateau designated S'_∞ which differs from the assumed solvent contribution, S_s.[20-25] Various possible contributing factors, including chain stiffness or internal viscosity, possibly resulting from local constraints, have been considered as explanations for these observations, but as yet without complete success.[26-41] For example, although all three considerations lead directly to finite, positive values for the quantity $(\eta'_\infty - \eta_s)$, only the internal viscosity approach is of the correct order of magnitude; however, internal viscosity considerations do not predict a nonzero $(S'_\infty - S_s)$. Furthermore, *negative* values of $(\eta'_\infty - \eta_s)$ have been reported at low temperatures for the systems polybutadiene/Aroclor 1248 and polyisoprene/Aroclor 1248;[17,18] this observation is inconsistent with any explanation for η'_∞ which invokes an additional mechanism of energy dissipation.

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Table I

polymer	$10^{-4}M_w$	M_w/M_n	source
polystyrene	0.20	1.06	Pressure Chemical 61222
polystyrene	0.55	1.1	Goodyear CDS-S-10
polystyrene	0.90	1.06	Pressure Chemical 80314
polystyrene	2.04	1.06	Pressure Chemical 41220
polystyrene	3.2	1.06	Pressure Chemical 80317
polystyrene	17.9	1.06	N.B.S. 705
polystyrene	105	1.1	N.B.S. 1479
polybutadiene	14.4	1.07	L. J. Fetters RC-4
polyisoprene	13.5	1.04	Polymer Labs

Another possible contribution, the modification of the bulk solvent properties by the presence of dissolved polymer, has recently come under closer scrutiny. In effect, the addition of polymer means that η_s and S_s are no longer the appropriate quantities for the subtraction of the solvent contribution to the measured solution properties.[2,17,18,20,25,42,43] This has been illustrated extensively for the two diene/Aroclor systems mentioned above. For example, it was observed that addition of butadiene and isoprene oligomers to Aroclor 1248 resulted in solution viscosities and birefringence magnitudes below those of the neat solvent.[18,25,42] Furthermore, for higher molecular weight polybutadienes and polyisoprenes time–temperature superposition failed, unless empirical, modified solvent subtraction procedures were employed.[17,18,25] It is clear that in these particular systems, the addition of polymer is capable of modifying the properties of the solvent significantly. However, the exact nature of such modifications has yet to be identified. As these effects may well prove to be major contributions to the measured high-frequency response, it is important to consider other experimental methods by which the effects of added polymer on solvent properties may be investigated.

In this paper we report pulsed-field-gradient NMR measurements of the translational diffusion of Aroclor 1248 in dilute solutions of polystyrene, polybutadiene, and polyisoprene, as a function of polymer concentration, at two temperatures. In addition, forced Rayleigh scattering has been used to determine the diffusion behavior of a tracer molecule, azobenzene, in some of the same solutions. These results illustrate the qualitatively and quantitatively different effects the three polymers have on the properties of the solvent, effects which in some degree parallel the magnitudes and signs of the quantity $(\eta'_\infty - \eta_s)$ reported for the same systems. The results are discussed in terms of possible origins of the phenomena, including correlation with changes in solution free volume, and also in relation to the extraction of polymer chain dynamics contributions to measured solution properties. In particular, the results suggest that the observed values of $(\eta'_\infty - \eta_s)$ in these systems may be mostly due to the modification of the solvent by the polymer.

Experimental Section

Samples and Solutions. The molecular weights, polydispersities, and sources of the polymer samples employed are listed in Table I. All samples were used as received, except for the five lower molecular weight polystyrenes, which were purified by dissolving in benzene, filtering, and freeze-drying. The Aroclor 1248 (A1248) solvent, lot no. KM 502, is a chlorinated biphenyl product of the Monsanto Chemical Co. and was used after filtration. Azobenzene (Kodak Chemicals Co.) was filtered and recrystallized from ethanol before use. Solutions were prepared gravimetrically, with direct addition of solvent to polymer. Dissolution was assisted by stirring and gentle heating (<50 °C) for the polystyrene (PS) solutions. Both polyisoprene (PI) and polybutadiene (PB) are sensitive to degradation, and thus their solutions all contained antioxidant in trace amounts. Concentrations of all solutions in units of g/cm^3 or volume fraction were calculated assuming additivity of volumes and densities of 1.05, 0.985, 0.913, and 1.45 g/cm^3 for PS, PB, PI, and A1248, respectively. For solutions containing azobenzene, the dye concentration was less than or equal to 0.1% by weight.

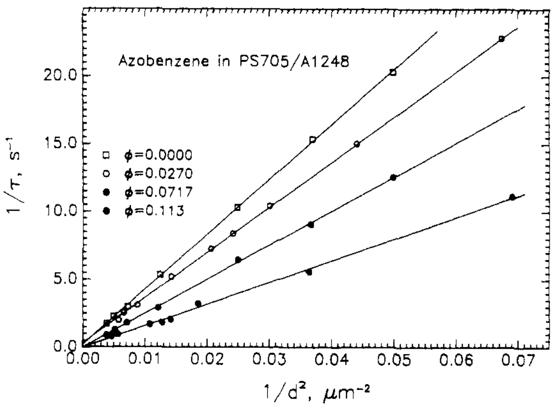

Figure 1. Measured decay rate versus inverse grating spacing squared, for azobenzene in PS/A1248 at three concentrations and in neat solvent at 25.0 °C.

Forced Rayleigh Scattering Measurements. The forced Rayleigh scattering (FRS) apparatus and measurement procedure have been described in detail previously.[43] Briefly, a chemical diffraction grating was created in the sample by exposure to intersecting beams from an Ar$^+$ laser emitting at 488 nm. The decay of the grating by mass diffusion of azobenzene was monitored by detecting the diffracted intensity of an attenuated HeNe laser beam at 633 nm. Each decay curve was represented by 1000 discrete points, obtained with 12-bit resolution at equal time intervals. Curves were analyzed by nonlinear regression to extract decay rates, as previously described.[43] For each solution, measurements were made at five or more grating spacings and diffusion coefficients extracted from the slopes of plots of decay rate versus inverse grating spacing squared and decay time versus grating spacing squared. In these solutions, mass diffusion is more rapid than the thermal reisomerization of the dye, and thus both plotting approaches yield equivalent results; the reported values represent the average of the two methods. An example of the former approach is shown in Figure 1, for azobenzene in PS/A1248 solutions at the indicated polymer volume fractions. Measurement temperatures were maintained at 25.00 ± 0.02 °C by using a sample cell holder with flow-through temperature control and a thermistor calibrated to within ±0.003 °C.

NMR Measurements. The NMR and pulsed-field-gradient spin-echo (PGSE) equipment and calibration procedures[44,45] and data collection and reduction methods[46-48] have been described in detail and were used here with various refinements. The spectrometer operated at 33 MHz and detected proton NMR. Temperature calibration and stability were better than 0.2 °C. Magnetic-field-gradient pulses of magnitude 126 or 340 G/cm and durations up to 16 ms were separated by a delay of typically 25 ms, in coordination with the radio-frequency (rf) pulse sequence, which was usually the principal echo two-pulse sequence (90°–180°–echo), occasionally supplemented by the three-pulse stimulated echo sequence. A steady gradient of magnitude 0.8 G/cm was also applied to narrow and stabilize the echo. These large gradient experiments were conducted at resonance without Fourier transformation but with digital data collection and screening, followed by signal averaging. Between 10 and 20 echo attenuation measurements were averaged for a given gradient duration; one diffusion measurement consisted of between 5 and 30 data points taken at constant gradient pulse magnitude, with varying pulse lengths. The reproducibility of the single-component diffusion measurements was approximately 2–3% while the accuracy (including the uncertainty in gradient calibration) was closer to 5%. The need to resolve two-component diffusivity spectra introduced additional minor uncertainties.

Since chemical shifts could not be resolved directly in these experiments, discrimination at resonance between species containing the same nuclide was based principally on differences in diffusion rates. Thus, the analysis software[47,48] was instructed to interpret the data in terms of a single diffusion rate for neat

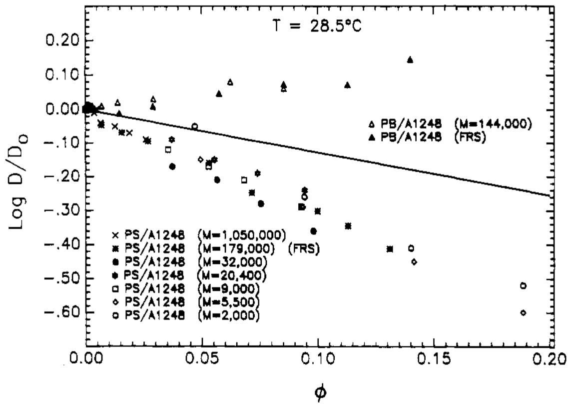

Figure 2. Reduced diffusion coefficient, D/D_0, versus polymer volume fraction, ϕ, for A1248 in PS and PB solutions at 28.5 °C measured by NMR. PS molecular weights are indicated on the plot. Values of D/D_0 for azobenzene, measured by FRS at 25.0 °C, are also included.

solvents and two diffusivities if a polymer echo contribution was significant (i.e., at concentrations greater than perhaps 0.5% against the background of the solvent echo). Significant polydispersity in either polymer or solvent results in a corresponding distribution of diffusion rates. The effect is visible in PGSE echo attenuation plots; information concerning the diffusivity distribution may be extracted via comparisons with analytical or numerical simulations.[49,50] In the solutions examined here, the effects of polymer polydispersity needed to be accounted for only at the highest concentrations. The A1248 solvent also displayed very modest polydispersity behavior in its diffusion spectrum. The diffusion coefficients cited in these cases correspond to molecules having a molecular weight in the vicinity of the number average of the distribution.[50] In this work only the solvent diffusivity results are discussed; the diffusivity of the low molecular weight polystyrenes in A1248 will be presented in a subsequent publication.

DSC Measurements. Thermal analyses of PS, PB, and PI/A1248 solutions were performed with either a Perkin-Elmer Series 7 Thermal Analysis System or a Mettler DSC 30 low-temperature cell, using a heating rate of 10 °C/min. Samples were approximately 20 mg in quantity and were contained in standard aluminum sample pans. The molecular weights employed were 1.79×10^5, 1.44×10^5, and 1.35×10^5 for PS, PB, and PI, respectively. Nominal values of the solution glass transition temperature, T_g, were obtained as the temperature at which the DSC trace was exactly midway between the tangents to the trace above and below the transition. For the purposes of this work, the relevant information is the polymer concentration dependence of the solution T_g, and thus it is assumed that the exact choice of T_g for a given solution is not critical as long as the choice is made consistently.

Viscosity Measurements. Solution viscosities for PB/A1248 were measured in a capillary viscometer at 25.00 ± 0.02 °C. The polymer molecular weight was 1.44×10^5 and the concentrations ranged up to 0.0343 g/cm^3. Flow times were always in excess of 100 s to eliminate the need for kinetic energy corrections.

Results

The effect of polymer volume fraction, ϕ, on the translational diffusion coefficient, D, of the A1248 solvent is illustrated in Figure 2, for one molecular weight of PB and six of PS, at 28.5 °C. The diffusion coefficients are plotted semilogarithmically in reduced form, D/D_0, where D_0 represents the value of D determined in neat A1248. Also included on this plot are the reduced diffusion coefficients for trace quantities of azobenzene in PS/A1248 and PB/A1248, determined by FRS at 25.0 °C, where D_0 now refers to the value measured for azobenzene in neat A1248 at 25.0 °C. The PB molecular weight in this case, 1.44×10^5, is the same as that used for the NMR measurements of solvent diffusion, while the PS sample has $M = 1.79 \times 10^5$.

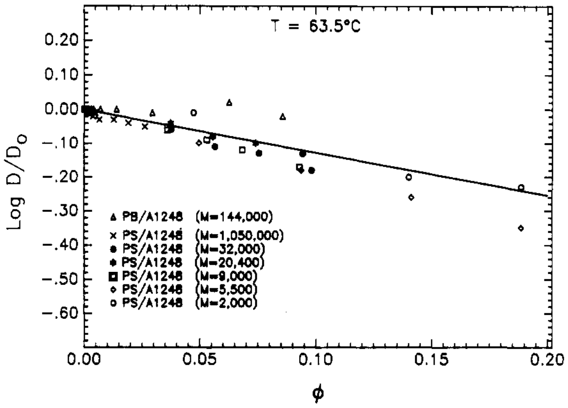

Figure 3. Reduced diffusion coefficient versus polymer volume fraction for A1248 in PS and PB solutions at 63.5 °C.

There are at least two unusual features evident in Figure 2. First, in the PB case, the solvent and probe mobilities are actually enhanced by the addition of polymer, in contrast to the reduction typically observed in polymer solutions. Second, although the addition of PS reduces the mobilities as expected, the reduction is more substantial than in the typical case. To illustrate this point, Figure 2 also includes a smooth curve, defined by

$$D/D_0 = (1 - \phi)/(1 + \phi)^2 \qquad (1)$$

This function has been shown to describe the polymer concentration dependence of solvent diffusion for a wide range of chemical systems and may thus be considered to represent some form of typical behavior.[51,52] (It should be noted that various other functional forms have also been considered, and eq 1 is by no means established as correct. Nevertheless, over the rather narrow concentration range considered here, the difference between the various forms is not substantial.) It is clear from Figure 2 that eq 1 describes neither the PS nor the PB solution behavior at this temperature. In both cases, the data are reasonably well described by straight lines, suggesting that D/D_0 depends exponentially on concentration. At the same time, over the range of ϕ considered here, eq 1 is also closely approximated by an exponential function. This exponential dependence may or may not have great physical significance but is very useful in representing the data for interpolation or comparison purposes, as will emerge in the subsequent discussion.

The azobenzene diffusion behavior is essentially indistinguishable from that of the solvent, which is quite reasonable considering the similarity in molecular size and shape between solvent and probe. However, the fact that two completely different experimental approaches yield the same result is strong evidence for the accuracy of both techniques. In the PS case the solvent diffusion behavior is independent of M over a very wide range, with the possible exception of the smallest polymer ($M = 2 \times 10^3$). This observation is also in accordance with both expectation and measurements on other systems.[51,53]

Figure 3 presents A1248 diffusion data in PS and PB solutions, at 63.5 °C. In this case, the qualitative effect of added polymer on D is the same as in Figure 2, but for both systems the data lie closer to the curve of eq 1. Thus, the polymer–solvent interactions reflected in the unusual behavior in Figure 2 are substantially reduced at this elevated temperature.

In Figure 4, the quantity D/D_0 is plotted semilogarithmically against ϕ for PI/A1248 solutions, both for azobenzene at 25.0 °C and for A1248 at 28.5 and 63.5 °C. In this instance, the FRS and NMR results at the lower temperatures are not in as close agreement as for the other

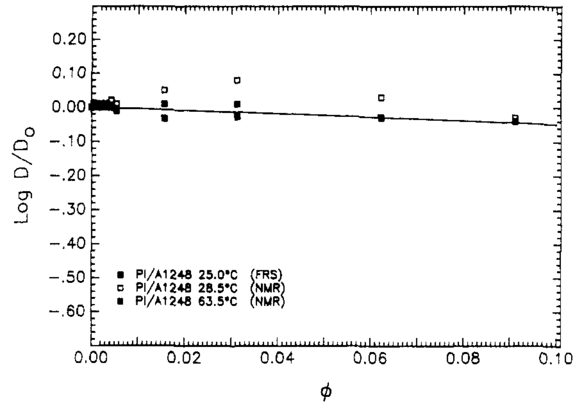

Figure 4. Reduced diffusion coefficient versus polymer volume fraction for A1248 in PI solutions at 28.5 and 63.5 °C. Data for azobenzene at 25.0 °C are also included.

Table II
Solvent Diffusion in Polystyrene/A1248 Solutions

M	ϕ	log $\hat{\zeta}_D$ (28.5 °C)	log $\hat{\zeta}_D$ (63.5 °C)
2.0×10^3	0.0471	0.05	0.01
	0.0943	0.26	0.14
	0.140	0.41	0.21
	0.189	0.52	0.24
5.5×10^3	0.0496	0.15	0.10
	0.0936	0.29	0.18
	0.141	0.45	0.26
	0.189	0.60	0.35
9.0×10^3	0.0357	0.12	0.06
	0.0530	0.17	0.09
	0.0683	0.21	0.12
	0.0930	0.29	0.17
2.04×10^4	0.0372	0.09	0.04
	0.0556	0.15	0.08
	0.0740	0.19	0.10
	0.0944	0.24	0.13
3.2×10^4	0.0374	0.17	0.07
	0.0565	0.21	0.12
	0.0755	0.28	0.14
	0.0981	0.36	0.19
1.05×10^6	0.000473	0.00	0.00
	0.000930	0.00	0.00
	0.00191	0.00	0.01
	0.00282	0.00	0.01
	0.00376	0.01	0.02
	0.00476	0.00	0.01
	0.00653	0.01	0.03
	0.0127	0.02	0.03
	0.0190	0.04	0.04
	0.0261	0.05	0.05
		$D_0 = 7.8 \times 10^{-8}$ cm^2/s	$D_0 = 7.8 \times 10^{-7}$ cm^2/s

Table III
Solvent Diffusion in Polybutadiene/A1248 and Polyisoprene/A1248 Solutions

polymer	ϕ	log $\hat{\zeta}_D$ (28.5 °C)	log $\hat{\zeta}_D$ (63.5 °C)
polybutadiene	0.000499	0.01	0.00
$M = 1.44 \times 10^5$	0.000999	0.00	0.01
	0.00197	-0.01	0.00
	0.00293	-0.01	0.00
	0.00405	0.00	0.00
	0.00703	-0.01	0.00
	0.0140	-0.02	0.00
	0.0293	-0.03	0.01
	0.0625	-0.08	-0.02
	0.0859	-0.06	0.02
polyisoprene	0.000542	-0.01	-0.01
$M = 1.35 \times 10^5$	0.00106	-0.01	0.00
	0.00217	-0.01	0.00
	0.00330	-0.01	0.00
	0.00432	-0.02	0.00
	0.00546	-0.01	0.01
	0.0157	-0.05	-0.01
	0.0313	-0.08	-0.01
	0.0623	-0.03	0.03
	0.0912	0.03	0.04

Table IV
Azobenzene Diffusion in A1248 Solutions

polymer	ϕ	log $\hat{\zeta}_D$ (25.0 °C)
polystyrene	0.0069	0.046
$M = 1.79 \times 10^5$	0.0157	0.069
	0.0270	0.095
	0.0533	0.16
	0.0717	0.25
	0.104	0.30
	0.113	0.35
	0.131	0.41
polybutadiene	0.0146	0.011
$M = 1.44 \times 10^5$	0.0291	-0.0087
	0.0576	-0.046
	0.0855	-0.073
	0.113	-0.072
	0.140	-0.15
polyisoprene	0.0157	0.032
$M = 1.35 \times 10^5$	0.0313	0.027
	0.0623	0.027
		$D_0 = 1.09 \times 10^{-7}$ cm^2/s

two polymers; this may reflect in part the particular difficulty of separating the solvent and polymer echoes in the NMR signal for the PI solutions. Nevertheless, in general the results for PI lie between those for PS and PB and also do not conform closely to eq 1. Furthermore, as in the case of PS and PB, the data at 63.5 °C lie closer to eq 1 than do the results at lower temperatures. All the data in Figures 2–4 are tabulated in Tables II–IV, in the form of a dimensionless friction function defined in eq 2.

Discussion

The results presented in Figures 2–4 have important implications for the study of polymer conformational dynamics and particularly in these chemical systems. The ensuing discussion is organized around three general issues: possible origins of the differences between the data and the behavior approximated by eq 1, the influence of these results on the interpretation of chain dynamics properties in these chemical systems, and the possible correspondence between these results and the observed high-frequency viscoelastic and flow birefringence properties. In order to facilitate the discussion, the results are presented in terms of a normalized, average solvent friction function, $\hat{\zeta}_D(\phi,T)$, defined by

$$\hat{\zeta}_D(\phi,T) \equiv D_0(T)/D(\phi,T) \qquad (2)$$

It is also helpful to define a concentration- and temperature-dependent effective average solvent or local viscosity, $\eta_e(\phi,T)$, as

$$\eta_e(\phi,T) \equiv \eta_s(T)\hat{\zeta}_D(\phi,T) \qquad (3)$$

It should be recognized that there is no reason to expect either $\hat{\zeta}_D$ or η_e to be spatially homogeneous, i.e., independent of distance from a polymer chain, but it is not possible to conclude anything about the degree of inhomogeneity from the data presented here.

Possible Origins of the Behavior of $\hat{\zeta}_D(\phi,T)$. All of the general features of the solvent and probe diffusion behavior illustrated in Figures 2–4 are at least qualitatively interpretable as the result of changing free volume. The three polymers PS, PB, and PI have glass transition temperatures, T_g, of approximately +100, -96, and -67 °C, respectively, while the neat solvent exhibits a T_g at -44 °C. Thus, addition of PS to A1248 should decrease the

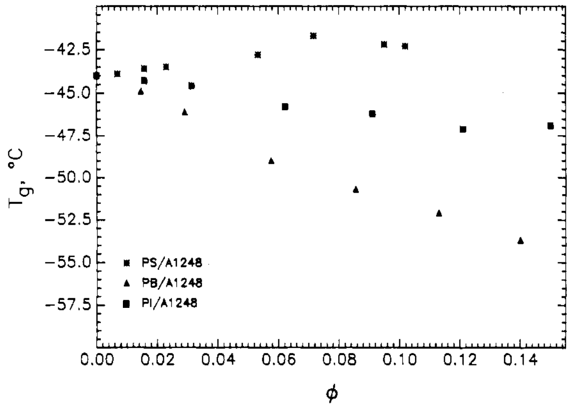

Figure 5. Solution glass transition temperature, T_g, versus polymer volume fraction, for A1248 solutions of PS, PB, and PI.

available free volume, while the addition of PB and PI should actually enhance the available free volume. This is consistent with the fact that D/D_0 lies below the line of eq 1 for PS/A1248 and above the same line for PB/A1248 and PI/A1248. Furthermore, the difference between eq 1 and the PB/A1248 data is greater than for PI/A1248 just as the difference between polymer and solvent T_g's is greater in the PB/A1248 case. Finally, as the solution temperature is raised from near room temperature to 63.5 °C, D/D_0 values for all three systems lie closer to the prediction of eq 1. In all cases, the rise in temperature takes the system further from its glass transition, thus decreasing the influence of limited free volume on the mobility of the various components.

Although it is apparent that $\hat{\zeta}_D(\phi,T)$ correlates qualitatively with the changes in free volume, it is not clear that these effects can be described quantitatively by the same argument. As a first step, $T_g(\phi)$ has been measured for all three systems; the results are presented in Figure 5. The results are reasonably represented as linear functions, given the limited concentration range employed, and the resulting slopes, γ, obtained by regression are +20.7, −71.0, and −21.9 °C cm^3/cm^3, for PS/A1248, PB/A1248, and PI/A1248, respectively. If extrapolated to $\phi = 1$, the corresponding intercepts would be −23.3, −115, and −65.9 °C for undiluted PS, PB, and PI, respectively. Thus, $T_g(\phi)$ must begin to curve upward very steeply for the PS/A1248 system at concentrations higher than those examined, for PB/A1248 solutions it would curve upward only mildly at higher concentrations, and for PI/A1248 it could remain essentially a straight line over the complete composition range. In these measurements, there was no evidence of two glass transitions, as has been reported for example in solutions of PS/tricresyl phosphate.[54]

A direct application of free volume ideas to small molecule diffusion is embodied in the treatment of Fujita.[55] The basic equation is

$$\ln [\hat{\zeta}_D(\phi_s,T)] = -B\beta\phi_s/[f_p^2 + f_p\beta\phi_s] \qquad (4)$$

where f_p is the fractional free volume of bulk polymer at the measurement temperature, ϕ_s is the solvent volume fraction, β relates to the change in solution free volume with addition of solvent, and B is a factor usually taken to be unity. From eq 4, plots of $[-1/\ln \hat{\zeta}_D]$ versus ϕ_s^{-1} and $[\phi_s/\ln \hat{\zeta}_D]$ versus ϕ_s should be linear, with respective slopes and intercepts yielding consistent values for f_p and β. However, this approach is primarily applicable to the high polymer concentration regime because it assumes that the solution free volume differs from f_p linearly with added solvent; nevertheless, numerous systems have been examined for which $\hat{\zeta}_D(\phi)$ is described by eq 4 over the complete composition range.[1,56,57] Starting with the assumption that the results in Figure 2 reflect changing solution free volume, it is possible to recast eq 4 in terms of the fractional free volume of the solvent, f_s, the polymer volume fraction, ϕ, and the coefficient β', here representing the change in solution free volume with ϕ

$$f_s(\phi,T) = f_s(0,T) + \beta'\phi \qquad (5)$$

Thus, β' is negative for PS/A1248 and positive for PB/A1248. The resulting analogue to eq 4 is

$$\ln [\hat{\zeta}_D(\phi,T)] = -B\beta'\phi/[f_s^2 + f_s\beta'\phi] \qquad (6)$$

The two plots ($[-1/\ln \hat{\zeta}_D]$ versus ϕ^{-1} and $[\phi/\ln \hat{\zeta}_D]$ versus ϕ) are not successful for the data here, due in some part to the limited range of, and uncertainty in, the $\ln \hat{\zeta}_D$ values; both features are accentuated in the reciprocal plotting format. Thus it is not possible in this manner to assess the ability of the free volume approach to describe the data quantitatively. However, an alternate, related approach can be adopted, which utilizes additional information for these chemical systems.

The temperature dependence of the solution fractional free volume may be expressed as

$$f(\phi,T) = f(\phi,T_g(\phi)) + \Delta\alpha_\phi[T - T_g(\phi)] \qquad (7)$$

where $\Delta\alpha_\phi$ is a composition-dependent thermal expansion coefficient for the solution. From the data in Figure 5, $T_g(\phi)$ follows

$$T_g(\phi) = T_g(0) + \gamma\phi \qquad (8)$$

If the assumption is made that, over the limited composition range employed, both $f(\phi,T_g(\phi))$ and $\Delta\alpha_\phi$ are independent of ϕ, then eq 7 reduces to

$$f(\phi,T) = f_s(T) - \gamma\Delta\alpha\phi \qquad (9)$$

The first assumption is tantamount to identifying $T_g(\phi)$ as an iso-fractional free volume state, which has some support in the literature.[1] The second assumption is supported by measurements of Merchak for PI/A1248 solutions, for which the thermal expansion is a very weak function of composition, and is approximately 7 × 10^{-4} °C^{-1}.[17] This predicts a dependence for $\ln \hat{\zeta}_D$ of

$$\ln \hat{\zeta}_D(\phi,T) = B\gamma\Delta\alpha\phi/[f_s^2(T) - f_s(T)\gamma\Delta\alpha\phi] \qquad (10)$$

The temperature dependence of η_s for A1248 reported by Merchak[17] is consistent with values for B and $f_s(T_g)$ of 1.2 and 0.025, respectively. Using these parameters and the data in Figure 5 for γ, eq 10 predicts (at 28.5 °C)

$$\log [D(\phi)/D_0] = -1.31\phi/[1 - 0.19\phi] \approx -1.3\phi \qquad (11)$$

for PS/A1248 and

$$\log [D(\phi)/D_0] = +4.48\phi/[1 + 0.65\phi] \approx +4.5\phi \qquad (12)$$

for PB/A1248. These may be compared with linear regression fits to the data in Figure 2, which yield dependencies for $\log [D(\phi)/D_0]$ of -3.05ϕ and $+0.86\phi$ for PS/A1248 and PB/A1248, respectively. Thus eq 11 and 12, which have the virtue of containing no adjustable parameters, substantially underestimate the concentration dependence of D for PS/A1248 but overestimate it for PB/A1248.

The failure of eq 11 and 12, as presented, to describe the observed behavior of $\hat{\zeta}_D(\phi,T)$ does not by itself eliminate the possibility of a successful free volume description. Introducing a composition dependence for $f_s(\phi,T_g(\phi))$, allowing B to differ between PS and PB and between diffusion and viscosity experiments, or invoking an otherwise more elaborate free volume model could all be expected to give better agreement. However, as discussed below and elsewhere,[58] there are substantial reasons why free volume considerations alone cannot describe changing solvent friction in these systems. For example, the free volume explanation ascribes a symmetry to the two cases PS/A1248 and PB/A1248 in the sense that the behavior in each has a common physical origin but differs merely in sign. As a consequence, any temperature dependence in a free-volume-dependent measurable property should be consistent between the two systems. As will be discussed subsequently, this is not, in fact, the case for these two systems. As an example, the high-frequency limiting viscosity, η'_∞, exhibits the same temperature dependence as η_s for PS/A1248 but does not for PB/A1248 or PI/A1248.[17,18] Furthermore, in the PS/A1248 case, the addition of polymer brings the system glass transition temperature closer to the typical measurement temperatures, which should serve to heighten the temperature dependence of any free-volume-based phenomenon, while in PB/A1248, the addition of PB moves the glass transition further away from the measurement temperature, and the sensitivity of free volume effects to temperature should decrease. These trends are opposite to those reported for the high-frequency viscosity. Furthermore, measurements of solvent relaxation in PS/A1248 and PB/A1248 have shown that the changes in effective solvent friction are clearly not consistent with a free volume interpretation.[58,59]

The Aroclor solvents fall into the class of "associating" or "structured" fluids, which have been studied extensively in the past by a variety of means. In particular, the remarkably strong temperature dependence of η_s presumably reflects substantial cooperativity in molecular motions. It has been postulated that such cooperativity is manifest in the formation of dynamic molecular clusters, whose average size is temperature-dependent.[60-62] In the cluster picture, therefore, it could be argued that the presence of PB (or, to a lesser extent, PI) acts to reduce the mean cluster size at a given temperature, while PS increases the same quantity; this possibility has been raised previously by Minnick and Schrag[25] and Man.[18] It is not possible to argue strongly either for or against this picture solely on the basis of the results presented here. However, the close correspondence between the FRS and NMR results in the PS solutions may not be completely consistent with a cluster model. During an NMR experiment, a given solvent molecule presumably spends time in clusters of varying dimensions, and the net mobility is an average over all cluster mobilities. However, in the FRS case the probe dye might not participate in clustering at all, or at least to a different extent than the solvent, yielding on the average a different net mobility. Of course, to some extent these differences might be canceled out in the ratio D/D_0.

Evidence for clusters presented elsewhere has centered largely on mechanical, ultrasonic, and dielectric relaxation properties, in which the breadth of the relaxation time distribution is the crucial parameter.[61,62] In the diffusion experiments the corresponding parameter is the breadth of the distribution of mobilities, which is harder to extract precisely, particularly in the NMR case where the polymer echo contributes to the net signal. Thus, it may be more appropriate to investigate this particular issue with a relaxation experiment. Recently, an extensive series of oscillatory electric birefringence (OEB) measurements of solvent relaxation in PS/A1248 and PB/A1248 solutions, as a function of concentration and temperature, has been undertaken.[59,63] Some particularly pertinent features of these preliminary results will be discussed in the later sections of this paper. It is also significant that Moore et al. have reported measurements of dynamic shear modulus for Aroclors and PS/Aroclor solutions at very high frequencies and concluded that there was no direct evidence for large clusters;[64] however these experiments were performed at a single frequency as a function of temperature and may not have been sensitive to small clusters.

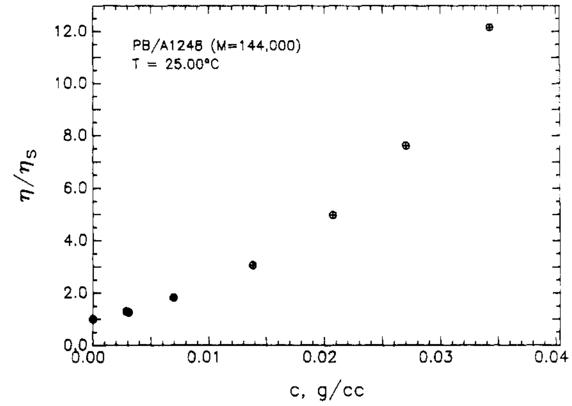

Figure 6. Relative viscosity, η/η_s, versus polymer concentration, for PB/A1248 at 25.0 °C ($M = 1.44 \times 10^5$).

Unusual properties of PB/A1248 and PI/A1248 solutions have already been noted and discussed elsewhere. For example, solutions of PB with $M = 3.4 \times 10^4$ or 6.0×10^4 in A1254 at 15 °C exhibited viscosities below that of the neat solvent.[42] Similarly, the low-frequency solution viscosities and flow birefringence magnitudes for butadiene and isoprene oligomers in A1248 and A1254 were well below the corresponding solvent values.[18,25] In addition, measurements of the OFB properties of higher M PB and PI in A1248 solutions did not exhibit time–temperature superposition, unless a modified procedure was employed for subtracting the solvent contribution from the measured solution properties.[18,25] This empirical procedure essentially involved replacing the bulk solvent values with those measured for oligomer solutions of equivalent monomer concentration. This approach has more recently been discussed in greater detail.[17] The origin of the observed behavior was not established, but it was postulated that the diene polymers might be particularly effective in breaking up solvent clusters, as discussed above. In general, the effects were seen to be independent of polymer molecular weight but dependent on temperature and concentration, thus supporting the interpretation of the effects as being due to a local polymer–solvent interaction.

The behavior of $\hat{\zeta}_D(\phi,T)$ in PB and PI solutions reported here is consistent with these earlier OFB and VE results. For example, the effective viscosity $\eta_e(\phi,T)$ defined in eq 3 can be compared to that obtained in butadiene and isoprene oligomer solutions. At a volume fraction of 0.141 and a temperature of 25.0 °C, a solution of PB ($M = 500$) in A1248 had a viscosity equal to 0.39 times the solvent value and a birefringence equal to 0.55 times the solvent value.[18] Interpolating the results in Figure 2, the effective viscosity experienced by a diffusing solvent or probe molecule at this volume fraction of PB is 0.78 times its value in neat solvent. Repeating the analysis for PI ($M = 1000$) at $\phi = 0.077$ and 25.0 °C, the corresponding factors are 0.86 for the solution viscosity, 0.96 for the birefringence, and 0.85 ± 0.1 for the diffusion measurement. These results do suggest, however, that the degree of modification of any solvent property by the addition of polymer will depend on the property in question.

One difference between the PB solutions studied here and those employed by Johnson[42] or Minnick and Schrag[25] is in the solution viscosity. In Figure 6, the relative viscosity of the PB/A1248 solutions is plotted as a function of PB volume fraction, over the range $0 \leq \phi \leq 0.035$. The behavior is quite normal, in the sense that the viscosity rises approximately exponentially with concentration, and a positive intrinsic viscosity could be obtained. The difference between these results and those of Johnson[42] may be due to the difference in solvent and temperature employed; A1254 has a glass transition at approximately −24 °C, and the measurement temperature was 15.0 °C. Thus, the earlier results were presumably obtained at temperatures much closer to the solution T_g. The difference between the viscosities in Figure 6 and those reported by Minnick and Schrag[25] and Man[18] is certainly due to the difference in polymer molecular weight; even in the absence of polymer–solvent interactions, the viscosity of an oligomer solution should not be expected to rise very steeply with concentration.

Polymer Chain Dynamics. The function $\hat{\zeta}_D(\phi,T)$, representing the effective local friction, controls the time scale of local molecular motions and thus influences the dynamics of the polymer chains. This is a familiar idea and is traditionally associated with the concept of the monomeric friction coefficient, as discussed by Ferry.[1] In general, any global chain property, such as the polymer diffusion coefficient, terminal relaxation time, or solution viscosity, is considered to be factorizable into the product of two functions. The first, dependent on M, concentration, degree of branching, etc., is that predicted by chain dynamics models, for example, the bead-spring model (BSM) for very dilute solutions, whereas the second, the local friction, depends on concentration and temperature and perhaps weakly on M. Furthermore, it has become standard practice to approximate the local friction function by the diffusion coefficient of a solvent or probe molecule, both in semidulute solutions and at very high polymer concentrations. In the latter case, the friction experienced by the small molecule has been very successful in reconciling the observed shifts in viscoelastic properties with diluent concentration,[1] while in semidilute solutions this approach has been applied primarily to the translational diffusion coefficient of polymer chains.[53,65] In this context it is interesting to note that von Meerwall et al.[53] have suggested that the concentration dependence of the friction experienced by the small molecule in semidilute solutions is, in fact, not equivalent to that inferred from viscoelastic measurements, the concentration dependence of the latter being noticeably greater.

For dilute solutions, and in general for polymer volume fractions up to approximately 0.10, it has usually been assumed that the change in local friction is insignificant, and thus no correction need be applied to the measured solution properties in order to extract the chain contribution. Clearly, for the systems considered here, this assumption is less justified. For example, at a polymer volume fraction of 0.10 and a temperature of 25.0 °C, the local friction has increased by a factor of 2 in PS/A1248 and decreased by a factor of 1.2 in PB/A1248. In comparison, for chemical systems in which D/D_0 follows eq 1 in the dilute regime, the local friction increases by a factor of approximately 1.3 over this range. As mentioned in the Introduction, the PS/A1248, PB/A1248, and PI/A1248 systems have been used extensively for VE and OFB measurements, and very recently the first polymer diffusion studies in these systems have been reported.[66] In some cases, therefore, it may be appropriate to reconsider the interpretation of parameters extracted from such measurements. This is illustrated below for the concentration dependence of the longest chain relaxation time, in the context of the BSM.

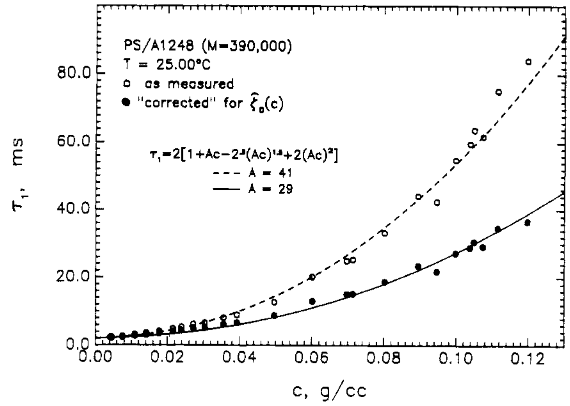

Figure 7. Longest relaxation time, τ_1, for PS ($M = 3.9 \times 10^5$) in A1248 at 25.0 °C, as measured by oscillatory flow birefringence[22,24] (open circles) and as corrected for changes in solvent friction (crossed circles). Theoretical curves correspond to the Muthukumar theory expression indicated on the plot.

In the BSM, each relaxation time τ_i is given by

$$\tau_i = \zeta_0 b^2/6kT\lambda_i \qquad (13)$$

where λ_i is the ith eigenvalue of the Lodge–Wu **B** matrix[67] (directly related to the Zimm **H·A** matrix[4]), b is the root-mean-square subchain length, and ζ_0 is the subchain friction coefficient. Although the BSM as presented by Rouse and Zimm applies strictly only to infinite dilution properties, the concentration dependence of τ_i has been calculated for dilute solutions by Muthukumar and Freed[68] and for more concentrated solutions by Muthukumar.[69] The resulting equations are respectively

$$\tau_i(c) = \tau_i(0)\{1 + Aci^{\kappa} + ...\} \qquad (14)$$

for the Muthukumar–Freed theory and

$$\tau_i(c) = \tau_i(0)\{1 + Aci^{\kappa} - 0.5[2Aci^{\kappa}]^{1.5} + 2[Aci^{\kappa}]^2\} \qquad (15)$$

for the Muthukumar case. Here A is a parameter directly related to the intrinsic viscosity, $[\eta]$, and κ varies from 0.5 to 0.8 with increasing solvent quality and is analogous to the Mark–Houwink exponent. Both expressions have been compared with extensive OFB measurements on PS/A1248 solutions;[22,24] eq 14 appears to work quite well in the range $0 < c[\eta] < 2$, while eq 15 holds up to about $c[\eta] = 5$. However, both expressions are designed to account for polymer–polymer interactions in terms of chain dynamics and thus ignore $\hat{\zeta}_D(c,T)$. (In the ensuing discussion, polymer concentrations are expressed in units of g/cm^3 rather than volume fraction to coincide with the previously published results.) Therefore, these or similar theories may be more appropriately compared to experimental dynamics information after the measured properties have been scaled by $\hat{\zeta}_D(c,T)$. For example, Figure 7 presents extensive measurements of the longest relaxation time, τ_1, for PS ($M = 3.9 \times 10^5$) in A1248, at 25.00 °C, as a function of concentration.[22,24] Both the original data and the scaled data, $\tau_1/\hat{\zeta}_D(c,T)$, are compared to eq 15; it can be seen that the agreement is excellent in both cases, but the values of A implied are significantly different, i.e., approximately 41 and 29 cm^3/g in the unscaled and scaled cases, respectively. (It has recently been pointed out that it is not strictly correct to factor out the monomeric friction from the expression in eq 15;[70] thus, the values of A cited are probably not completely appropriate.) The implication is that for PS/A1248 the form of the concentration dependence of chain dynamics is unaffected by $\hat{\zeta}_D(c,T)$, but the magnitude of the chain contribution is significantly overestimated if $\hat{\zeta}_D(c,T)$ is not considered. Thus, for PB/A1248 and to a lesser extent PI/A1248, the measured solution properties may actually underestimate the chain contribution to the concentration dependence.

High-Frequency Properties. The results in Figures 2–4 indicate that the local viscosity, defined by solvent diffusion measurements, can be markedly different in these solutions from the neat solvent value. Thus, it is appropriate to compare the function $\hat{\zeta}_D(c,T)$ with the behavior of the high-frequency limiting viscosity, η'_∞. Values of η'_∞ have been reported for a wide variety of systems, but most extensively for PS and PI in Aroclor solvents. For PS/A1248, the results can be summarized as follows: η'_∞ is independent of polymer molecular weight and chain architecture and exponentially dependent on concentration.[13,14] The temperature dependence follows that of η_s, and thus $\eta'_\infty(c,T)$ can be written

$$\eta'_\infty(c,T) = \eta_s(T)\exp\{[\eta'_\infty]c\} \qquad (16)$$

where the intrinsic value, $[\eta'_\infty]$, is defined by analogy with the intrinsic viscosity

$$[\eta'_\infty] = \lim_{c\to 0}\{(\eta'_\infty(c,T) - \eta_s(T))/\eta_s(T)c\} \qquad (17)$$

For PS/A1248 from −1.42 to 25.0 °C, $[\eta'_\infty]$ is approximately 14 ± 1 cm^3/g[13,19] while for PS/Aroclor 1232 at 25.0 °C a value of 12.1 cm^3/g has been reported.[19] Similar values for PS have also been determined in decalin,[19] α-chloronaphthalene,[19] and toluene.[9] In the case of PB/A1248 and PI/A1248, the less numerous results differ from those for PS/A1248 in two important respects: at certain temperatures, $[\eta'_\infty]$ is negative, and, as mentioned previously, the temperature dependence of η'_∞ does not follow that of η_s. For PB/A1248, values for $[\eta'_\infty]$ of -12 ± 1 cm^3/g at −4.0 °C[18] and $+8 \pm 2$ cm^3/g at 30 °C[16] have been determined, while for PI/A1248 $[\eta'_\infty]$ was found to be −4.3, −2.8, and −1.0 cm^3/g at −8.0, −4.0, and 0.0 °C, respectively, and estimated to be between +3 and +7 cm^3/g at 25.0 °C.[17]

The relevance of the diffusion data reported here to the determination of η'_∞ lies in the use of η_s in eq 17. As η_s in this equation is taken to represent the solvent contribution to the measured solution viscosity, it would be perhaps more appropriate to replace $\eta_s(T)$ with the effective solvent viscosity, $\eta_e(c,T)$, defined in eq 3. Furthermore, the data in Figures 2–4 indicate that $\hat{\zeta}_D(c,T)$ is reasonably well represented by an exponential function of concentration

$$\hat{\zeta}_D(c,T) = \exp\{[\eta_e]c\} \qquad (18)$$

where the quantity $[\eta_e]$ is defined by analogy to $[\eta'_\infty]$. For PS/A1248 between 25.0 and 28.5 °C, $[\eta_e] = 6.5$ cm^3/g, whereas for PB/A1248 it is approximately −2.2 cm^3/g at the same temperature. If η_e given by eq 3 is inserted into eq 16 in place of η_s, a new quantity would be obtained, $[\eta'_\infty]_e$, with a value for PS/A1248 reduced by almost 50% relative to $[\eta'_\infty]$. In the case of PB/A1248, the value for $[\eta'_\infty]_e$ would be 25% larger than the value of 8 cm^3/g for $[\eta'_\infty]$ cited by Cooke.[16] The PI/A1248 diffusion data are not sufficiently precise to determine a reliable value of $[\eta_e]$, but it would clearly be negative and smaller in magnitude than for PB/A1248 or PS/A1248. Thus, the estimate for $[\eta'_\infty]_e$ for PI/A1248 at 25.0 °C would be only slightly larger than $[\eta'_\infty]$.

The calculations outlined above suggest that in the case of PS/A1248, the modifications to the solvent properties as revealed by $\hat{\zeta}_D(c,T)$ account for a substantial fraction of the high-frequency limiting viscosity values. As the data reported here are restricted to higher temperatures, it is not possible to perform the calculation at lower temperatures such as −1.42 °C, for example. However, for this system, $[\eta'_\infty]$ is at most a weak function of temperature over this range. An implication of this observation is that $[\eta_e]$ should also be independent of temperature over this range, which could be verified by performing additional diffusion measurements at lower temperatures. Unfortunately, due to the large increase in η_s, the NMR experiment cannot be used to monitor A1248 diffusion reliably below about 10 °C. Thus it would be necessary to make the measurements via FRS and assume that the close correspondence between the two techniques would be maintained. In the case of PB or PI, the situation is different. Here, the strong temperature dependence of $[\eta'_\infty]$ suggests that $[\eta_e]$ might have a similarly strong dependence. This rests on the assumption that the value of $[\eta'_\infty]_e$ would not be strongly temperature dependent. However, any of the mechanisms for additional energy dissipation mentioned in the Introduction would certainly not lead to much of a temperature dependence for $[\eta'_\infty]$, and thus if the use of η_e for η_s takes account of the modification of solvent properties correctly this assumption may be reasonable.

It is important to emphasize that the use of diffusion data to arrive at $\eta_e(c,T)$ is but one possible method, and there is no a priori reason to suppose that all methods are equivalent or that this route is the most appropriate. For example, the diffusion measurement inherently averages over all local environments in the solution because the solvent molecules move many times their own dimensions during the course of the measurement. On the other hand, to the extent that η'_∞ reflects a chain contribution, it may be much more sensitive to local environments in the neighborhood of the polymer, where it is certainly conceivable that the polymer is more effective in modifying the solvent properties, and thus $\eta_e(c,T)$ deduced from solvent diffusion measurements may actually be an underestimate of the effect revealed by viscoelastic or birefringence measurements.

One other technique for examining the behavior of the solvent in the presence of polymer is OEB, as mentioned previously. In this case, mean reorientation times have been determined for A1248 in the presence of PS and PB as a function of temperature and concentration.[58,59] The results are qualitatively consistent with $\hat{\zeta}_D(c,T)$, in the sense that the solvent reorientation time increases with PS concentration but decreases with the addition of PB. Furthermore, values of $[\eta_e]$ inferred from these measurements were 13 ± 1 cm^3/g for PS/A1248, for PS concentrations up to 0.27 g/cm^3, and temperatures from 2.81 to −11.50 °C. However, for PB over the same concentration range, $[\eta_e]$ decreased monotonically from −8 cm^3/g at 2.81 °C to −18 cm^3/g at −17.3 °C. Thus, if this determination of $\eta_e(c,T)$ were used to correct the viscoelastic results, values of $[\eta'_\infty]_e$ would be reduced by an order of magnitude from $[\eta'_\infty]$, and to less than ±1–2 cm^3/g, for both PS/A1248 and PB/A1248 in this temperature range.

Summary

The translational diffusion of the A1248 solvent in dilute solutions of polystyrene, polybutadiene, or polyisoprene has been measured at 28.5 and 63.5 °C by pulsed-field-gradient NMR. Solution concentrations ranged up to 0.20 g/cm^3, and in the case of polystyrene, polymer molecular weights varied from 2.0×10^3 to 1.05×10^6. In addition, forced Rayleigh scattering measurements of azobenzene diffusion have been made in some of the same solutions, at 25.0 °C. With the possible exception of the polyisoprene solutions, measurements by NMR and forced Rayleigh scattering are equivalent, when the respective diffusion coefficients are normalized by the values in neat solvent. In the polystyrene solutions, the results are independent of polymer molecular weight over the range studied.

There are two unusual features present in the data. In the case of polystyrene solutions at 28.5 °C, the solvent mobility decreases with increasing polymer concentration significantly more rapidly than in numerous other polymer/solvent systems. In the case of polybutadiene, the solvent mobility increases with added polymer. Both of these observations are qualitatively consistent with changes in solution free volume, as revealed by the composition dependence of the solution glass transition temperature. However, consideration of the temperature dependence of viscoelastic, oscillatory flow birefringence, and oscillatory electric birefringence properties reported for these systems suggests strongly that, at least in the case of polybutadiene and polyisoprene, free volume changes are not sufficient to reconcile the observed behavior. Due to experimental constraints, extensive NMR measurements of the temperature dependence of diffusion in these solutions is not feasible. The concentration dependence of the normalized diffusion coefficient is found in all cases to be well represented by an exponential function. Following other authors, the reciprocal of this function is interpretable as the concentration dependence of an effective local friction or local viscosity. However, in the solutions considered here this function is noticeably different from that observed in other polymer/solvent systems. In the case of polystyrene/A1248 at 28.5 °C, for example, the local friction is approximately 50% greater than that observed in polystyrene/THF or polystyrene/toluene, at a polymer volume fraction of 0.1. Thus, a common assumption in polymer solution dynamics studies, that for polymer concentrations below about 10% changes in local friction are insignificant, is not as justifiable in these solutions. Since a large number of conformational dynamics experiments have been performed on these systems, some of the results may require some reinterpretation, particularly where the concentration dependence of a global chain property is concerned.

Of particular interest is the possible relevance of the effective local viscosity function determined by diffusion measurements to the extensive high-frequency viscoelastic properties reported in the literature. For polystyrene/A1248, use of the effective local viscosity in place of the bulk solvent value, when subtracting the solvent contribution from the measured solution viscosity, reduces the (as yet unexplained) intrinsic high frequency limiting plateau, $[\eta'_\infty]$, by a factor of 2. In the case of polybutadiene/A1248 and polyisoprene/A1248, negative values of $[\eta'_\infty]$ are also rationalizable in terms of the local viscosity properties revealed by diffusion measurements. Previous suggestions that the high-frequency behavior may reflect to a significant degree the modification of solvent properties by the presence of polymer are in general supported by the results presented here.

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Registry No. PS, 9003-53-6; PB, 9003-17-2; PI, 9003-31-0; Aroclor 1248, 12672-29-6; azobenzene, 103-33-3.

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Application of the Perturbation Molecular Orbital Method to Aromatic Oligomers and Conducting Polymers

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ABSTRACT: The perturbation molecular orbital (PMO) method has been used to calculate band gaps (E_g), ionization potentials (IP), and electron affinities (EA) of a number of electronically conducting aromatic hydrocarbon polymers. The polymers chosen were poly(*p*-phenylene) (**1**), poly(*p*-phenylenevinylene) (**2**), polyacene (**3**), poly(2,6-naphthylene) (**4**), poly(1,4-naphthylene) (**5**), and poly(perinaphthylene) (**6**). The results obtained were compared with those in the literature calculated by much more sophisticated and extensive methods and with experimental values where those were available. This method was also used to calculate E_g of a 126 carbon graphite fragment. The results show that the PMO method is quite simple, can be done rapidly, and is a very useful qualitative predictor of several electronic properties of conducting polymers. Further, it can readily distinguish those polymers predicted to have zero band gaps from those having larger ones.

Introduction

The field of conducting polymers has been the subject of major research for the past 15 years.[1,2] Organic, polymer, inorganic, and theoretical chemists have long been intrigued by the possibility of certain polymers behaving as "organic metals". It has only been recently that rational syntheses of these systems have been carried out and that theoretical chemists have attempted to calculate and predict the properties of these polymers.[3,4]

The properties of conducting polymers that one would like to accurately predict are band gaps (E_g), ionization potentials (IP), electron affinities (EA), and, less importantly, bandwidths (BW).[2] The band gap largely determines whether the polymer is intrinsically a metal, a semiconductor, or an insulator, with low band gaps required for "metal-like" behavior. For intrinsically semiconducting or insulating polymers, IP and EA are a measure of oxidizability and reducibility, respectively. Polymers that have low values of IP can be effectively doped with electron acceptors such as I_2 or AsF_5, while polymers with large values of EA can be effectively doped with electron donors such as alkali metals.[5,6] Bandwidths are a measure of electron delocalization in the polymer backbone with high values indicating high degrees of electron mobility.[7,8] However, intrachain mobility is, in general, not the limiting factor in determining the conductivity of a doped polymer but rather it is the interchain electron transfer.[9] Therefore, correlations between observed conductivities and theoretically calculated bandwidths are expected to be qualitative at best.[4]

Many techniques have been applied to the calculation of the electronic band structure of conjugated polymers. Ab initio calculations yield reliable valence band information but are not easily adapted to predict optical properties.[4,7] Also, high quality ab initio calculations require extensive computer time and are not practical for large multiatom repeat units of conjugated polymers. Semiempirical techniques such as CNDO (complete neglect of differential overlap)[10] and MNDO (modified neglect of differential overlap)[11] have been applied to conjugated polymers with some success. However, as with other semiempirical techniques, CNDO and MNDO depend heavily on parameters obtained from experimental data for small molecules and the extrapolation to polymer systems must be done with caution. A completely theoretical technique called the valence-effective Hamiltonian (VEH) technique has been successfully applied to conjugated polymers.[4,8,12,13] However, as with the above techniques, the molecular geometry must be known or readily calculated by using semiempirical techniques. Finally, a very interesting qualitative approach using perturbation theory, in which the effects of chemical substitution of atoms in conducting polymers can be estimated, has been developed by Lowe and co-workers.[14] For example, using the extended Hückel crystal orbital (EHCO) method,[15] qualitative predictions of band gaps can be performed when one C–H of poly(acetylene) is substituted by N, S, or C–F.

In this paper we discuss the use of perturbation molecular orbital (PMO) theory as a very simple alternative (paper and pencil) method to calculate E_g, IP, and EA of several conjugated hydrocarbon conducting polymers. The PMO method[16–18] is a well-established approach in dealing with chemical systems and is still used quite frequently.[19] Dewar and Dougherty (ref 16, pp. 405–7) have shown that the PMO method can successfully predict π–π^* transitions for several 1–6 ring-fused aromatic hydrocarbons, but to the best of our knowledge, the PMO method has not been applied to the study of polymeric systems.

The PMO Method

The success of the PMO method lies in the fact that it uses two odd alternant fragments A and B, each of which has a nonbonding molecular orbital (NBMO) which are, to a first approximation, degenerate. These fragments are then brought together, allowed to interact and finally to bond resulting in the formation of the new system AB (see Figure 1). There is then a first-order change in π energy

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