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phenol, 118-79-6; 2,4,6-tribromoresorcinol, 2437-49-2; benzyl bromide, 100-39-0.

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(23) This yield is much less than the theoretically expected value. This is due to the dissolution of the polymer in water. Moreover, it was also observed that the polyacrylamide sample used contained about 18% water (by thermogravimetric analysis). The hygroscopic nature of the polyacrylamide does not permit complete removal of the water under the present conditions.
(24) GPC analyses were performed with DMSO as the mobile phase on a Waters GPC instrument with a μBondagel E linear column, R401 RI detector, and U6K injector.
(25) Microanalyses were done at Regional Sophisticated Instrumentation Centre, Lucknow.

Notes

Comparison of Diffusion Coefficients in Ternary Polymer Solutions Measured by Dynamic Light Scattering and Forced Rayleigh Scattering

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Several dynamic light scattering (DLS) studies of ternary solutions (polymer A/polymer B/solvent) have recently been reported.[1–14] By selecting a solvent isorefractive with polymer B and employing sufficiently small concentrations of (chemically distinct) polymer A, the resulting autocorrelation functions are reasonably interpreted as reflecting the dynamics of the A chains. Furthermore, the measurements have generally been restricted to the range $qR < 1$, and thus the measured diffusion coefficients have (with one exception[2]) been identified with the translational diffusion of A. This technique has been demonstrated as an effective means to investigate two areas of great current interest: diffusion mechanisms in semidilute and concentrated solutions and thermodynamics of multicomponent systems. Nevertheless, there are several reasons for caution in this identification of the measured diffusion coefficient as the tracer or pure center-of-mass translational diffusion of component A. These include (i) the concentration of A is necessarily nonvanishing in order to effect the measurements, (ii) the refractive index increment for component B in the solvent may not be exactly zero, (iii) the inevitable molecular weight polydispersity of the A chains has a substantial influence on the correlation function as the matrix concentration increases, even for nearly monodisperse samples,[7] and (iv) the DLS properties for semidilute binary solutions are as yet incompletely understood, as illustrated both by the variety in number of modes reported and in their differing assignment to dynamical processes.[15–20]

We have previously reported extensive DLS measurements on the system polystyrene (PS)/poly(vinyl methyl ether) (PVME)/*o*-fluorotoluene (oFT) and have interpreted the results consistently as reflecting the translational diffusion coefficients of the PS chains, for linear,[3,6,7,9] 3-arm star,[8] and 12-arm star[10] diffusants. Furthermore, in all cases the observed decay rate distribution was unimodal, although the breadth of the distribution was a strong function of matrix concentration. Hanley et al. have shown that in principle the distribution should be bimodal when either the matrix isorefractivity condition or the vanishing probe concentration condition is not met.[21] The failure to observe bimodality is strong but not conclusive evidence that both of these conditions are satisfied for this chemical system; for example, the two modes might overlap to an extent that prohibits their resolution, while contaminating the extracted mean decay rates. In this work we report further measurements of PS diffusion in PVME solutions, by both DLS and forced Rayleigh scattering (FRS), as a function of matrix concentration. In addition, at fixed PVME concentrations the DLS measurements have been repeated as a function of PS concentration. Two important questions are thus addressed directly: (i) Is the diffusion coefficient measured by DLS identical with that obtained by FRS and thus correctly identified as the translational diffusion coefficient? (ii) Is it necessary to correct for the error arising from the finite PS concentrations employed in the DLS measurements?

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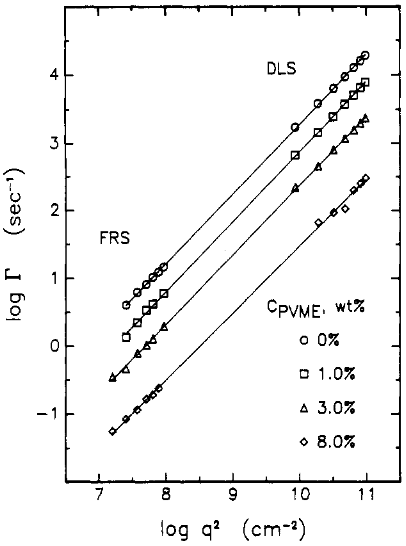

Figure 1. Measured decay rate Γ versus squared scattering vector, plotted logarithmically, for PS ($M = 3.0 \times 10^5$) in oFT solutions of PVME ($M = 6.0 \times 10^4$), by both forced Rayleigh scattering and dynamic light scattering.

Table I
Measured Diffusion Coefficients

FRS		DLS	
c_{PVME}[a]	D[b]	c_{PVME}	D
0	1.70×10^{-7}	0	1.96×10^{-7}
0.997	6.86×10^{-8}	0.992	8.04×10^{-8}
2.88	2.08×10^{-8}	2.99	2.45×10^{-8}
7.96	2.94×10^{-9}	7.95	3.10×10^{-9}

[a] Concentrations expressed as weight percent. [b] Diffusion coefficient in units of cm²/s.

Experimental Section

Two narrow-distribution PS samples ($M_w = 1.05 \times 10^6$, from the N.B.S., and $M_w = 3.0 \times 10^5$ from Pressure Chemical Co.) and two unfractionated PVME samples ($M_w = 6.0 \times 10^4$, from Polysciences, and $M_w = 2.4 \times 10^5$, especially prepared[22]) were used. Dye labeling of the 3.0×10^5 PS was achieved by random aminomethylation of the PS followed by reaction with [(dimethylamino)phenyl]azobenzoic acid (Kodak Chemicals), as previously described;[23] the labeling ratio was approximately 1/300 monomers. Solution preparation, data acquisition, and subsequent analysis were all as previously described.[8-10,24]

Results and Discussion

Diffusion coefficients were measured by both FRS and DLS for the 3.0×10^5 PS, in pure oFT and in PVME/oFT solutions with matrix concentrations, c_{PVME}, of 1.0, 3.0, and 8.0 wt %. The FRS experiments were conducted by using the dye-labeled polymer, with $c_{PS} = 0.5$ mg/mL, while the DLS study used the unlabeled precursor at the same concentration. The results are plotted logarithmically in Figure 1, as measured decay rate Γ versus squared scattering vector. For the DLS experiment, Γ refers to the initial rate of decay of the scattered electric field autocorrelation function, while in the FRS case it is the decay rate of the intensity diffracted from a transient chemical grating. In both instances, Γ equals q^2D, where q is the scattering wavevector. It is apparent that the two experiments yield D values which are essentially equivalent; the actual values are listed in Table I. In particular, the regression lines in Figure 1 all have slopes of 1.0, confirming the expected q^2 dependence.

Examination of the D values in Table I reveals that they are not quite identical for the two experiments, differing by 15% in pure solvent and 5% at $c_{PVME} = 8.0\%$. The DLS values are consistently higher. The difference is within experimental error; although the relative precision in D is typically 1–3% for DLS and 5–10% for FRS, uncertainty in the absolute accuracy of either technique is undoubtedly greater. The presence of the dye labels has no noticeable effect; DLS measurements on both labeled and unlabeled polymers in pure solvent agreed to within 5%. It is possible that the different distance scales in the two experiments may influence the results. For DLS, q^{-1} is in the range 30–100 nm, while for FRS the grating spacing was 1–2.5 μm. A reasonable estimate for the coil radius for this PS in pure oFT is 20–25 nm,[25] and thus the DLS results may not represent the true "long time" diffusion coefficients. Another possible contribution, the difference between the mutual diffusion measured by DLS and the tracer diffusion measured by FRS, is shown below to be insignificant. These possibilities notwithstanding, the agreement between the two experiments is sufficiently close to establish firmly that the DLS experiment measures the translational diffusion coefficient of the PS component in these ternary solutions.

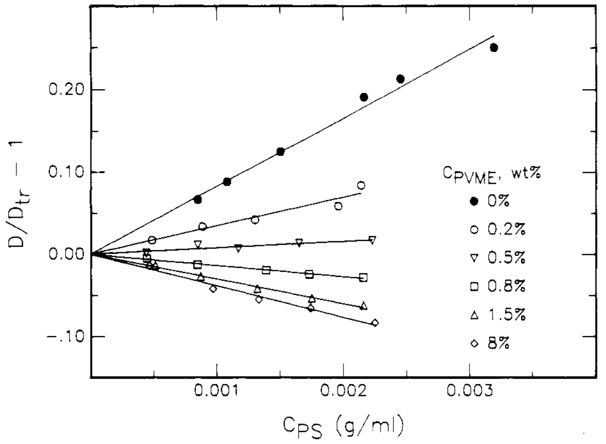

Figure 2. Reduced diffusion coefficients, $[(D_{measd}/D_{tr}) - 1]$, as a function of c_{PS}, for PS ($M = 1.05 \times 10^6$) in PVME/oFT solutions with $c_{PVME} = 0, 0.2, 0.5, 0.8, 1.5$, and 8 wt %, measured by dynamic light scattering.

In the DLS experiment the effect of finite c_{PS} may be accounted for by the expression

$$D_{measd} = D_{tr}\{1 + k_D c_{PS} + ...\} \quad (1)$$

where D_{measd} is extracted from plots of Γ versus q^2 and where D_{tr} should be compared to the value obtained via FRS. In our previous ternary solution work, all reported diffusion coefficients were D_{measd}, not D_{tr}, because the latter would be prohibitively time-consuming to obtain. The assumption was thus made that the difference was small; i.e., $k_D c_{PS} \leq 0.05$. Given the low values of c_{PS} typically employed, and the range of k_D reported for dilute binary solutions,[26,27] this assumption was reasonable. However, in order to assess the validity of this assumption quantitatively, we obtained values of k_D from D_{measd} as a function of c_{PS} for the 1.05×10^6 PS sample, at fixed values of c_{PVME}. These measurements were made with the 2.4×10^5 PVME, at PVME concentrations of 0, 0.2, 0.5, 0.8, 1.5, and 8.0%. The extrapolations are illustrated in Figure 2, where $[(D_{measd}/D_{tr}) - 1]$ is plotted against c_{PS} for the various PVME concentrations. In all cases the extrapolations are linear, and it is interesting to note that initially k_D decreases rapidly with increasing c_{PVME}, before becoming negative and essentially independent of c_{PVME}. This is qualitatively what would be expected in dilute solution if the solvent quality were systematically decreased from good to near-Θ conditions. In the context of this paper, the main conclusion from these results is that the magnitude of k_D in ternary solutions is less than or equal to that in pure solvent, and no substantial error is incurred by equating D_{measd} and D_{tr}. Specifically, for the 3.0×10^5 PS used in the DLS/FRS comparison, k_D is approximately 40 mL/g in pure oFT, and the product k_Dc_{PS} was at most 0.02. These results also justify, a posteriori, the use of the assumption $D_{measd} \approx D_{tr}$ in our previous work.[3,6-10]

A remarkable feature of these data is that the transition from good to apparently θ-like quality occurs at very low PVME concentrations; the onset of semidilute conditions is expected to occur at $c_{PVME} = 1.3\%$. Conversely, when the matrix concentration is semidilute, k_D is at most a weak function of c_{PVME}. In contrast, in binary PS solutions, the decrease from good solvent to θ solvent conformation with increasing concentration occurs over the semidilute region.[28-30] This observation of decreasing solvent quality is mirrored in the dependence of R_g (from static light scattering[25]) and R_h (from D_{tr} corrected for solution viscosity) on c_{PVME}, both of which decrease significantly in the same concentration range. This behavior contradicts an assumption invoked in current theories for the thermodynamic properties of ternary polymer solutions[31] and will be reported on in more detail in a future publication.[32] This PS coil contraction with increasing c_{PVME} was also inferred previously from the low c_{PVME} behavior of D_{measd}, for both linear and star PS.[9,10] The conclusions from the results presented here may be summarized as follows. 1. Within the accuracy of the experiments, both FRS and DLS yield equivalent values for D, confirming the identification of D measured by DLS as the translational diffusion of the PS component. 2. The finite PS concentrations used for DLS measurements lead to negligible differences between D_{measd} and D_{tr}. 3. The dependence of k_D on c_{PVME} is quite interesting and is under further investigation. Although these results justify a posteriori the interpretation of our previous results, the universality of these conclusions has not been established. In other words, it would be desirable to perform similar measurements for other ternary systems.

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Investigation of Ion Binding Properties of Synthetic Polyelectrolytes Using a Terbium(III) Probe: Elucidation of the Number of Coordinated Water Molecules on Metal Polyelectrolyte Complexes[1]

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Introduction

The extremely low activity coefficients of counterions in polyelectrolyte solutions are attributed to two types of association of counterions to polyions. One type of binding is referred to as "diffuse" or "ion atmosphere binding", where the counterions are located in the area of the polyelectrolyte domain due to the large electrostatic forces and have some mobility. Another type of binding is "site binding", where the counterions are attracted to specific sites of the polyions through the formation of the complex.[2] Evidence for site binding has been accumulated from studies of dialysis equilibrium,[3] dilatometric measurements,[4,5] UV spectroscopy,[6,7] and potentiometric titrations of synthetic polyelectrolytes.[8] The ion binding can be characterized quantitatively by phenomena which are directly related to the release of water molecules coordinated to the cations. Since the hydration shell is compressed by electrostriction, this release leads to an increase in volume[4,5] and characteristic decrease in refractive index.[9]

The fluorescence properties of lanthanide ions in aqueous solution are known to be strongly influenced by their immediate coordinative environment.[10,11] The fluorescence intensity of the ions is normally quite weak in aqueous solution since the coordinated water molecules serve as efficient quenchers of the emission.[12] Recently, we have observed that the fluorescence intensities and excitation spectra of Tb(III) are greatly enhanced upon binding of this ion to either polyacrylate[13] or to polysaccharides such as carboxymethylcellulose or heparin.[14]

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