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Notes

Dynamic Behavior in Ternary Polymer Solutions. Concentration Dependence of Diffusion Coefficients

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Benmouna et al.[1] have developed a theory for dynamic light scattering from ternary mixtures of two homopolymers and a solvent, based on previous results for the elastic scattering from such systems. Using the random-phase approximation, their approach is to write down in matrix form the dynamic structure factor in terms of the intensity contributions from the individual species and the direct interactions between them. It is assumed that the Zimm type of hydrodynamic interactions are screened in the semidilute region and the hydrodynamic interactions between different molecules are not taken into account. Two examples were given: (A) two interacting polymers of the same size but having different contrast factors; (B) two monodisperse polymers differing in molecular weight but otherwise identical.

They were able to show that, in each case, two relaxation modes are obtained, and these were interpreted as the cooperative and interdiffusion modes, respectively (given in terms of the relaxation rates Γ_C and Γ_I). In contrast to the earlier reports of Phillies[5] and Pusey et al.,[6] Benmouna et al.[1a] give explicit expressions for the relaxation rates Γ_I and Γ_C as a function of the excluded-volume term: $2A_2M_wC$, where A_2 is the second virial coefficient and M the molecular weight. It should be noted that the theory as given is limited to interacting chains for which the second virial coefficient is nonzero, and therefore no provision was made for transport in Θ systems. Borsali[1d] has recently extended the discussion to include Θ systems.

It is of some relevance to compare the theoretical predictions for the relaxation rates with the results of experiments. We have recently[2] performed experiments dealing with case B, but employing only trace amounts of the one species (the "probe" chain) so that the interdiffusion coefficient approximately equals the self-diffusion coefficient of the probe. This point was confirmed in ref 2 where it is shown that, over the range of matrix concentration used, there is close agreement between the probe diffusion coefficients and the self-diffusion coefficients measured using pulsed-field-gradient NMR.

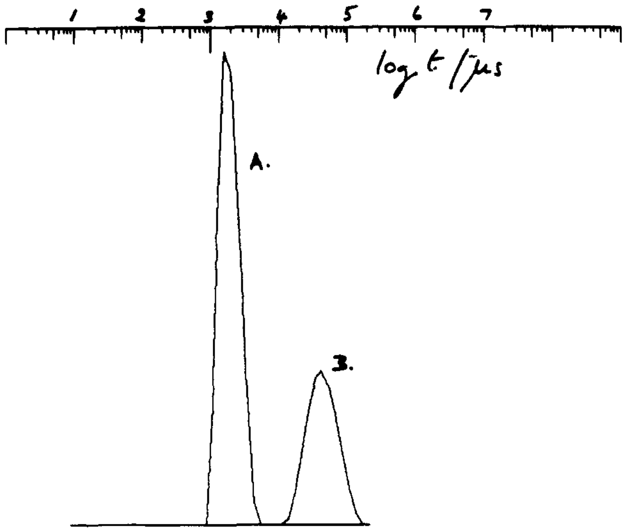

Figure 1. Decay time distributions for the ternary PIB system: for the PIB probe chain (B) ($M = 2.5 \times 10^5$) in a matrix (A) of PIB ($M = 4.9 \times 10^6$). Measurement angle 20°. Concentration of matrix 2×10^{-3} g·mL^{-1}.

Measurements were made on the two extremes: large probe chain in low molecular weight matrix and vice versa. In the present note, which complements the detailed paper,[2] we describe results on the previously examined polyisobutylene (PIB) system: A (PIB 4.9×10^6)/B (PIB 2.5×10^5)/chloroform. These two fractions have polydispersity indices $M_w/M_n \approx 1.2$. The following were used: (1) trace amount ($\approx$0.05%) of A in semidilute solutions of B; (2) trace amount of B in semidilute solutions of A.

These experiments became feasible due to two recent innovations:

(a) the development of a broad-band autocorrelator (ALV multibit, multi-τ instrument allowing 23 simultaneous sampling times and having 191 exponentially spaced channels);

(b) implementation of a new program (REPES(3)) for performing Laplace inversion to obtain the decay time dis-

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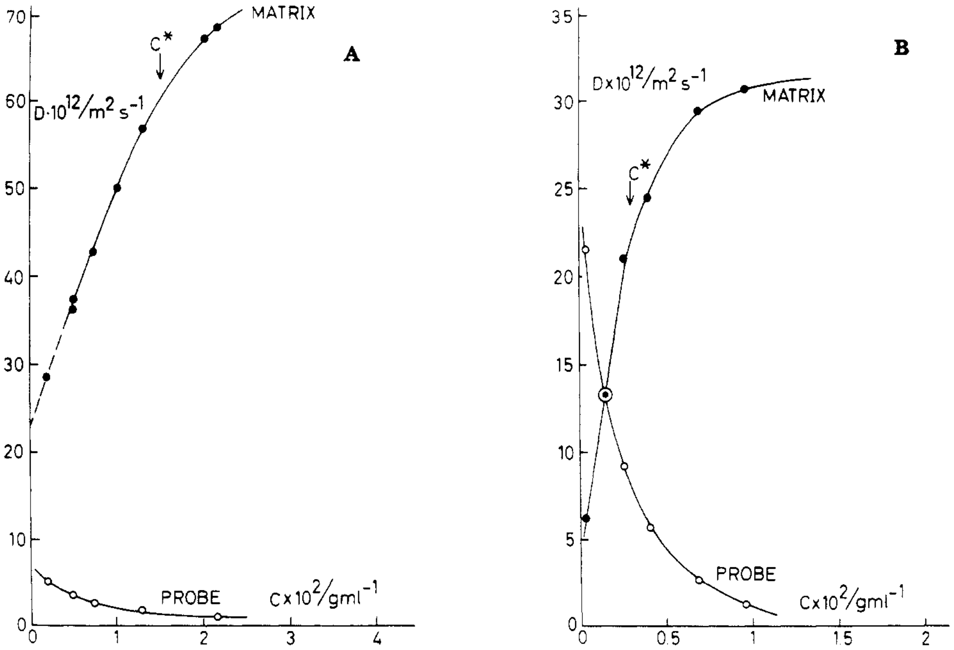

Figure 2. Experimental data: (A) probe ($M = 4.9 \times 10^6$) in matrix ($M = 2.5 \times 10^5$) where the diffusion coefficients have been obtained from the moments of the peaks in the decay time distributions; (B) probe ($M = 2.5 \times 10^5$) in matrix ($M = 4.9 \times 10^6$).

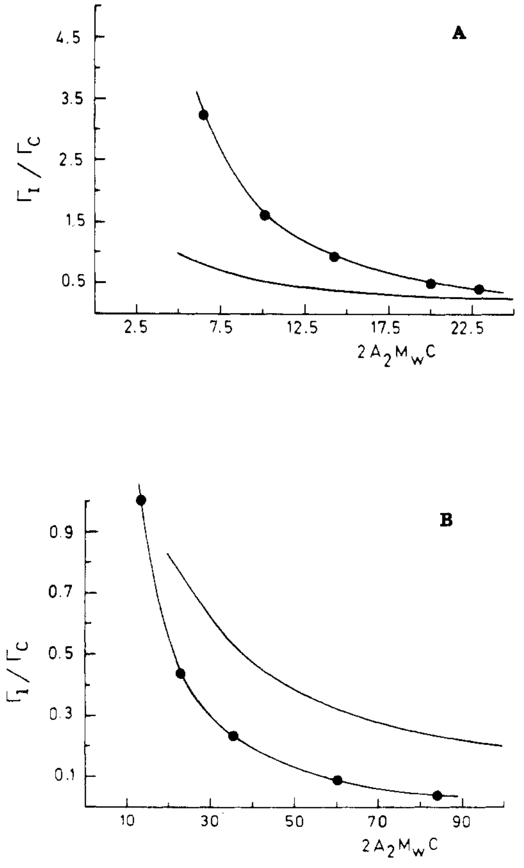

Figure 3. Ratio of relaxation rates (Γ_I/Γ_C) where the subscripts I and C refer to the interdiffusion and cooperative diffusion coefficients.[1] In the present measurements, a trace concentration of the probe chain is used and the interdiffusion coefficient may be approximated by the self-diffusion coefficient: full line, theory (ref 1a, eq 41 and 42); line with points, experimental data.

tribution. The algorithm differs from the usually employed CONTIN(4) program in that it directly minimizes the sum of the squared differences between the experimental and calculated $g^2(t)$ functions using nonlinear programming and the a priori chosen parameter "probability to reject"

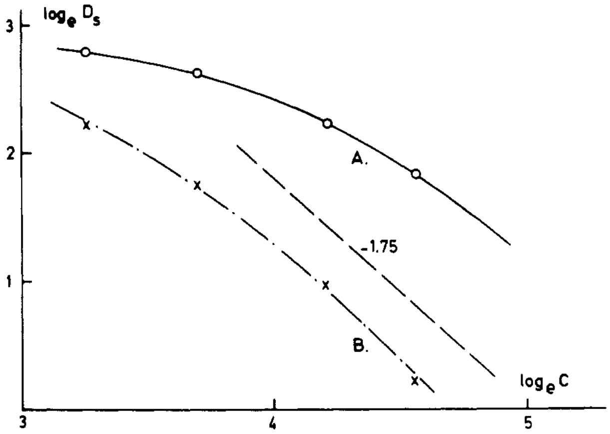

Figure 4. log–log plot of the self-diffusion coefficient for probe versus concentration of matrix taken from the data in Figure 2B. Curve A shows the values of D_s obtained from the ratio (Γ_I/Γ_C) using experimental values of Γ_C obtained in the binary matrix/solvent system. Curve B shows the experimental values of D_s obtained in the ternary system.

P (usually with $P = 0.5$). The moments of the peaks are given in the output, yielding the relative amplitude and frequency of each resolved component. The values of the relaxation rates could be evaluated with good precision even for very small relative amounts of one of the components of the ternary system. Typical decay time distributions are shown in Figure 1.

Primary data are shown in parts A and B of Figure 2. In these diagrams the matrix polymer displays a strong positive concentration dependence and the probe chain a negative concentration dependence as anticipated for the self-diffusion coefficient. It is important that the indicated intercept in each case coincides, within experimental error, with the value obtained by extrapolation to infinite dilution of dynamic light-scattering (DLS) data and also with the equivalent data from pulsed field gradient NMR measurements in the binary systems. In this way it was possible to unequivocally identify the two components determined from the decay time spectra. The separation of the two components has been discussed in more detail in ref 2. In order to eliminate the unknown quantity ζ (the monomeric friction coefficient), we have chosen to determine the ratio (Γ_I/Γ_C) as a function of the term $2A_2MC$ for the two extreme compositions. At each concentration the ratio (Γ_I/Γ_C) was calculated using eq 41 and 42 of ref 1a, and these data are plotted in parts A and B of Figure 3. Included in each figure are the theoretical ratios (lines without points) shown as a function of $v\phi N = 2A_2M_wC$. Here v is the excluded-volume parameter, ϕ the total segment concentration in the system, and N is the number of monomers per chain. A_2 values were obtained from static light-scattering measurements on the binary system: matrix polymer/solvent. The A_2 values in the ternary systems used here with trace amounts of the probe should differ insignificantly for present purposes from those in the binary system. Benmouna et al. point out that $A_2M_wC^* = 1$, and thus all the points shown refer to the semidilute range for the fast mode (the matrix component) using this definition of overlap. In the figures, however, we have used the usual definition of overlap: $C^* = 3M/4\pi R_g{}^3N_A$ (where R_g is the radius of gyration and N_A Avogadro's number), which is approximately equal to the inverse intrinsic viscosity. Above C^*, semiquantitative agreement is found between theory and experiment for the absolute values of the self-diffusion coefficients, which is encouraging since existing theories of self-diffusion give only the scaling result. For comparison with the latter, the concentration exponent for self-diffusion may be derived, for example, from the data in Figure 3. The concentration dependence (and intercept) corresponding to the high-concentration matrix component is well-defined from both these experiments together with data from the binary system. Using the experimental values of Γ_C in conjunction with the predicted ratio (Γ_I/Γ_C) gave the data shown in Figure 4. At a given concentration, the experimental values of D_s are substantially smaller than those predicted. Both the theory points (A) and experimental points (B) are best represented by smooth curves.

Scaling theory[7] predicts a concentration dependence indicated by the inserted line of slope −1.75. As has been shown before,[8-10] this slope has been found to describe experimental findings only over a limited range of concentration. The reptation model,[11] however, provides a less good agreement with experiment.

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Communications to the Editor

Elastic Anomaly near the Critical Point of Volume Phase Transition in Polymer Gels

Poly(*N*-isopropylacrylamide)/water gel (abbreviated as NIPA/water gel) is an ideal system for detailed studies of the volume phase transition (or gel–gel transition) of polymer gels. This gel, with a neutral network and with a pure solvent (water), undergoes a nearly critical phase transition as a function of temperature around $T_0 = 33.6$ °C.[1-3] There has already been a considerable amount of work on this phase transition, though some of the most fundamental properties related to the phase transition have not been studied. For example, no measurement of the elastic moduli has yet been reported.

Because the volume phase transition of gels is essentially a phase-separation phenomenon, it would be reasonable to identify the order parameter of this phase transition as the concentration difference between the two phases on the coexistence line[3] and the variable conjugate to the order parameter as the chemical potential. On the basis of the linear relation between the osmotic pressure of gels and the chemical potential of solvent, we may take the osmotic pressure, Π, as the intensive variable conjugate to the order parameter. Hence, a divergence of the osmotic compressibility or in other words a complete softening of the osmotic bulk modulus is expected at the critical point of the volume transition. The importance of the elastic measurement can hence be understood.

The light-scattering (photon correlation) spectroscopy has widely been used to study viscoelastic properties of gels.[4,5] The quantity measured by this technique, however, is not the elastic modulus itself but is $[K + (4/3)\mu]/f$, where K is the bulk modulus, μ the shear modulus, and f the friction coefficient between polymer and solvent. Thus, the light-scattering experiment alone can determine neither the absolute values nor the temperature dependence of the elastic moduli of gel network.

Static stress–strain measurements have also been made on various gels.[6] Such measurements have so far been made on gels far from the transition point using a compressional stress. A gel plate with a surface area on the order of centimeters squared is sandwiched between parallel glass plates, and a change in thickness of the gel due to compression was measured. Unfortunately, however, this method cannot be applied to NIPA/water gel in the close vicinity of the phase transition for the following reason. When a gel plate is compressed perpen-

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