particular, simplified example, let us consider the important case that the time scale of interest is large compared with τ_0, so that the integral in eq 1 may be replaced by $\tau_0\dot{x}'_1(q,t)$ and the final differential equation equivalent to (10) is of the second order only. The solution is

$$x_A(t) = \frac{1}{(b^2 + c^2\tau_0^2)^{1/2}} \int_{-\infty}^{t} \left\{ X_A(\tau) \cos\left[\frac{t-\tau}{T_1} - \gamma_1\right] \oplus iX_B(\tau) \sin\left[\frac{t-\tau}{T_1} - \gamma_1\right] \right\} e^{-(t-\tau)/\tau_1}\, d\tau \quad (13)$$

where

$$\tau_1 = (b^2 + c^2\tau_0^2)/ab; \qquad T_1 = (b^2 + c^2\tau_0^2)/ac\tau_0; \qquad \gamma_1 = \arctan(c\tau_0/b) \quad (14)$$

Needless to say, all the above results are fully equivalent to a superposition of the normal modes propagating along opposite directions, as obtained in I. It should be pointed out that the arbitrary (circled) signs left in eq 8 and 11 (or (13)) do not entail any ambiguity; in fact, a typical quantity relevant to physical measurement is the average $\langle x_A(t) \cdot x^*_A(t')\rangle$, which is given by the same expression whether the circled signs are as given above or they are *both* changed, as they could be. In analogy with the previous picture,[1,2] eq 11 and 13 imply a relaxation mechanism through damped oscillations, which in turn is strictly associated with the strain propagation along the chain.

In conclusion, the $2N$ normal-mode equations of the previous description, represented by the N equations (1) plus the N associated ones with $1 \rightarrow 2$, $\oplus \rightarrow \ominus$, are now replaced by the N equations (10). The classical physical picture with N normal modes for N chain atoms is thus recovered. In view of eq 5, $x_A(t)$ is the authentic normal-mode amplitude and may be conveniently labeled as $x'(q,t)$. The new equations are symmetrical and no sign ambiguity is left.

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Communications to the Editor

Self-Diffusion of Polymers in Concentrated Ternary Solutions by Dynamic Light Scattering

The mechanism of molecular transport in entangled polymer systems is a problem of fundamental interest. The concept of reptation and the related process of tube renewal lead to specific predictions for the molecular weight and concentration dependence of the self-diffusion coefficient D_S for polymers in the melt and in solutions of sufficiently high concentration.[1-5] Several experimental techniques have been used to investigate these predictions, including IR microdensitometry,[6,7] pulsed field gradient nuclear magnetic resonance (PFGNMR),[8-11] forced Rayleigh scattering (FRS),[12,13] and dynamic light scattering.[14,15] It is the purpose of this communication to present preliminary data which indicate that self-diffusion behavior in entangled solutions may also be investigated by dynamic light scattering from ternary systems.

The ternary system selected for this study was polystyrene/poly(vinyl methyl ether)/*o*-fluorotoluene. Under suitable conditions polystyrene (PS) and poly(vinyl methyl ether) (PVME) form a compatible pair,[16,17] and thus it is possible that small amounts of PS dissolved in concentrated PVME solutions will display dynamical behavior equivalent to that for PS in concentrated binary solutions. The solvent, *o*-fluorotoluene (*o*-FT), was chosen to match the refractive index of PVME very closely ($\partial n/\partial c$ for PVME/*o*-FT is 0.0016 at 25 °C[22]); thus the observed dynamic scattering may be attributed solely to the PS component. Static and dynamic scattering results from the ternary system PS/PVME/toluene have been reported elsewhere.[18] However, the refractive indices for toluene (1.495) and PVME (1.467)[19] are sufficiently different that it may not be feasible to extract the PS contribution directly when the PVME concentration greatly exceeds that of PS. Dynamic scattering has also been investigated from the PS/PMMA/toluene system.[20]

Table I
Composition of Solutions

concn, g/cm³		concn, g/cm³	
PS	total	PS	total
PS705			
0.0140	0.0380	0.0114	0.167
0.0128	0.0610	0.0117	0.292
0.0128	0.116	0.0125	0.389
PS1479			
0.0034	0.0202	0.0048	0.171
0.0048	0.0312	0.0044	0.300
0.0048	0.0507	0.0043	0.403
0.0034	0.0936		

Experimental Section. Two monodisperse PS samples were used, with molecular weights 179 000 (NBS 705) and 1 050 000 (NBS 1479). The PVME was obtained from Polysciences, Inc.; it is polydisperse and has a molecular weight of 5×10^4, as determined by light scattering measurements in methyl ethyl ketone. The *o*-FT was obtained from Aldrich and used without further purification. The ternary solutions were prepared gravimetrically by combining appropriate quantities of binary PS/*o*-FT and PVME/*o*-FT solutions. Concentrations were converted to g/cm³ assuming additivity of volumes and densities of 1.05, 1.02, and 1.00 for PS, PVME, and o-FT respectively. The ternary solutions were allowed to mix thoroughly over the course of 2 weeks, assisted by gentle agitation. Prior to use, the solutions were filtered directly into clean scattering cells through Millipore filters (0.22 μm for PS705 solutions and 0.45 μm for PS1479), and the cells were subsequently sealed. The compositions of the solutions are listed in Table I. The PS concentrations were designed to provide ample scattered intensity, while remaining below the overlap concentration (i.e., $c_{PS} \leq c^*_{PS}$). In the future, it will be appropriate to vary the PS con-

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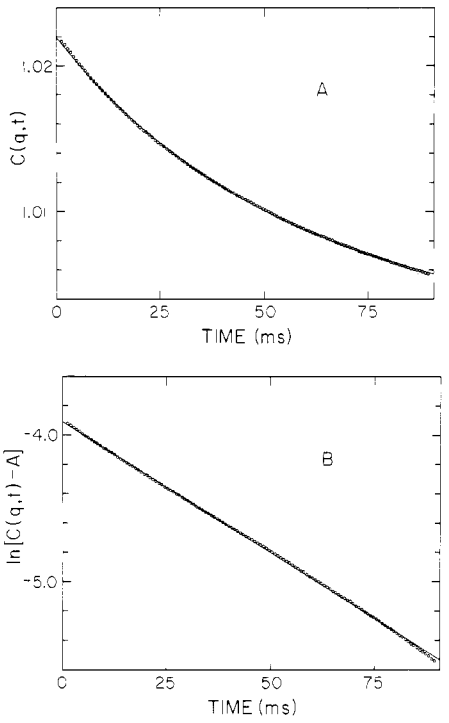

Figure 1. Experimental correlation function for PS1479 in 0.171 g/cm^3 total polymer, as (A) $C(q,t)$ and (B) ln $[C(q,t) - A]$ vs. time, at a scattering angle of 30° and a delay time of 0.7 ms. Smooth curves are for single-exponential fit according to eq 1.

centration at fixed PVME concentrations and thus obtain diffusion coefficients for PS at "infinite dilution". The PVME concentrations were chosen to cover a range extending from the dilute to the concentrated regime. The PVME is not of particularly high molecular weight, and the relevant quantity M/M_e (where M_e is the entanglement molecular weight[21]) is as yet undetermined; thus it is not clear if the PS molecules may be assumed to be topologically constrained. Preliminary rheological characterization indicates that M_e may be quite large for PVME (i.e., ≥20 000).[22]

Data were obtained at room temperature with a spectrometer as previously described.[23] Vertically polarized incident radiation at 488 nm was scattered and detected at several angles in the range from 30° to 90°; correlation was performed with a 128-channel multibit correlator (Malvern 7025). Delay times (sample times) were chosen to provide a reasonable portion of a single-exponential decay and ranged from 4 μs to 3 ms. All data were analyzed by using a three-parameter model

$$C(q,t) = A + Be^{-2\Gamma t} \quad (1)$$

where $C(q,t)$ is the experimental correlation function and q is the scattering vector $[q = (4\pi/\lambda) \sin(\theta/2)]$. Diffusion coefficients were extracted as Γ/q^2 and interpreted as D_S for the PS component. In general, the single-exponential fit to the data was excellent. Figure 1 presents the data and fitting curves for the solution of PS1479 in 0.171 g/cm^3 total polymer, both as $C(q,t)$ vs. t and as ln $[C(q,t) - A]$ vs. t. In this case the delay time was 0.7 ms, the scattering angle was 30°, and the fit obtained was one of rather poor quality relative to the typical case for the entire set. It is evident in this example, though not in all cases, that the observed scattering function is not a pure single exponential; this issue will be addressed in a future report. However, the results obtained in this manner should be adequate for the purposes of this communication. Some

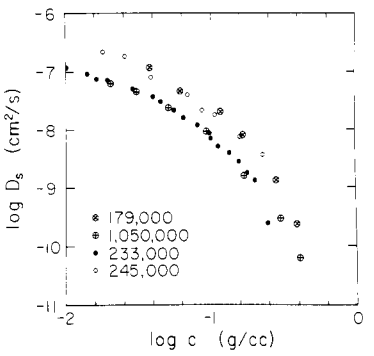

Figure 2. Self-diffusion of polystyrene in ternary solutions as a function of total polymer concentration. Data are also included for PS (M = 233 000 in CCl_4)[9] by pulsed field gradient NMR and PS (M = 245 000 in benzene)[13] by forced Rayleigh scattering.

question exists as to whether scattering from concentrated solutions should be treated as heterodyne or homodyne.[14] In this study all data were interpreted as homodyne for the sake of consistency, but the essential features of the results are, of course, unaffected in either case.

Results and Discussion. Figure 2 presents the D_S data for PS as a function of total polymer concentration. For comparison purposes, the graph also includes D_S data obtained for PS in good solvents obtained by PFGNMR (M = 233 000 in CCl_4)[9] and FRS (M = 245 000 in benzene).[13] The primary observation to be made is that the D_S values obtained by scattering from ternary solutions are in excellent qualitative agreement with those from other methods. In particular, the similarity in both concentration dependence and order of magnitude of D_S should be emphasized.

It should be noted that the remarkably close agreement between the magnitude of D_S for the FRS data and for PS705, and also for the PGFNMR data and for PS1479, is not especially significant. The absolute value of D_S will in general depend on properties of the polymer/solvent system in addition to the concentration, molecular weight, and solvent quality. D_S values for PS1479 are considerably larger than would be expected for purely reptative motion ($D_S \sim M^{-2}$), on the basis of the results for the other three samples. However, in light of the relatively low molecular weight of the matrix polymer, it is unlikely that reptation is the primary mechanism of transport for PS1479 in these solutions. As pointed out by Klein,[5] for the diffusion of linear polymers of molecular weight M in a matrix of molecular weight P, tube renewal should be the dominant process when $M \gg P^2/P_e$. Under those circumstances, or if P is so low that the matrix is effectively a viscous Θ solvent, the expected dependence would be $D_S \sim M^{-0.5}$.

Conclusion. In summary, the technique of dynamic light scattering from ternary systems appears to offer an excellent method for investigating dynamics in concentrated solutions. Its advantages include instrumental simplicity, use of unlabeled polymers, and the possibility of investigating both reptation and tube renewal regimes by varying M and P over wide ranges. This last point is also of particular interest for determining the transport properties of branched polymers in entangled systems. In addition, by judicious selection of ternary systems and experimental conditions it should be possible to shed considerable light on dynamics and thermodynamics of polymer blends on the molecular level. An extensive examination of D_S as a function of c, M, P, and solvent/polymer system for both linear and branched polymers is currently in progress.

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Registry No. PS, 9003-53-6; PVME, 9003-09-2; *o*-FT, 95-52-3.

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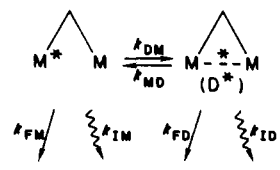
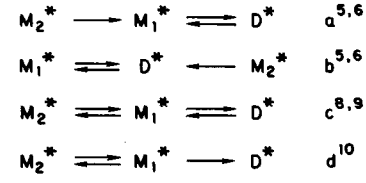
An Explanation of the Existence of Three Decay Constants in a Singlet Monomer–Excimer System

Recently, many reports concerning intramolecular excimer formation in polymer systems have been published, as nanosecond or picosecond time-resolved transient techniques have been developed. In particular, it has become of major interest lately that the conventional kinetic scheme of Birks[1,2] and Klöpffer[3,4] may not be applicable to some polymer systems. Although there should be only two decay constants in a monomer–excimer fluorecence system, the decay curves of some polymers have been found to be fit better by a linear combination of three exponentials. These results were reported for copolymers of 1-vinylnaphthalene (1VN) and methyl methacrylate (MMA),[5] copolymers of acenaphthylene and MMA,[6] P1VN, P2VN, and poly(1-naphthyl methacrylate) (PNMA)[7] by Phillips et al., PNMA[8] and dicarbazolylpropane (DCzP)[9] by Guillet et al., P2VN,[10,11] bis(2-naphthylethyl) ether,[10] and bis(1-naphtylmethyl) ether[12] by De Schryver et al., and P1VN by Gupta et al.[13] If there are three decay constants in these systems, there is a need to examine photophysically the kinetics of intramolecular excimer formation, because the existence of three decay constants corresponds to the existence of three excited states.

Scheme I



Scheme II



The conventional model used to describe the kinetics of excimer formation is shown in Scheme I, which was obtained by Birks for an intermolecular excimer system and then uncritically applied to the intramolecular excimer system. In Scheme I, k_{FM} and k_{FD} are the rate constants for the radiative deactivation of monomer and excimer state, respectively, k_{IM} and k_{ID} are those for the nonradiative deactivation, and k_{DM} and k_{MD} are those for excimer formation and dissociation. According to Scheme I, the response function of each fluorescence after pulse excitation is as follows: if [D*] is zero at $t = 0$

$$I_M(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$

$$I_D(t) = A_3\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}$$

$$\lambda_2 > \lambda_1 > 0$$

Phillips et al.,[5,6] Guillet et al.,[8,9] and De Schryver et al.[10] recognized the need for appropriate kinetics and proposed new models, which are summarized in Scheme II. M_1 and M_2 represent the different conformers. The excimer can be formed only from the M_1 conformer by internal rotation (Scheme IIa,c,d), while Scheme IIb proposes that excimer also can be formed from the M_2 conformer by long-range interaction. The existence of a conformer that cannot form an excimer also was proposed by Goldenberg et al.[14]

However, the discrete two-state model does not seem to be the most appropriate for explaining this problem, because more than two conformers exist in various proportions (e.g., in *meso*-2,4-di(2-naphthyl)pentane, the fractions of tg^-, g^+t, and tt conformers are 0.49, 0.49, and 0.02[15]).

We think that these experimental data should be divided into three groups corresponding to a dimer model, a homopolymer, and a copolymer. The inherent complexity of polymer systems (namely, the existence of several configurations and many conformations, the distribution of polymer molecular weight, and photophysical processes such as energy migration and excimer formation between nonadjacent chromophores) makes it very difficult to elucidate this problem. The values of the time constants of oligomers are particularly dependent on the degree of polymerization. For instance, the lifetime of a monomer singlet is ca. 3 ns in the dimer, while it is only 1 ns in the octamer of oligostyrenes.[16] Accordingly, the decay curves may be multicomponent when the sequence length of chromophores in copolymers is in the oligomer region and has some complicated distribution. Therefore, if we consider this problem of three decay constants in relation to conformation, the dimer model is most suitable for exact examination.

We think that two explanations are possible for the case where three decay constants exist in a monomer–excimer

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