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Self-diffusion coefficient studies in polystyrene/polystyrene/toluene solutions: Dynamic light scattering and fluorescence recovery after photobleaching experiments

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Abstract :

The dynamical behavior of a polystyrene(M_{w1})/polystyrene(M_{w2})/toluene ternary mixture has been investigated by Dynamic Light Scattering (DLS) and Fluorescence Recovery After Photobleaching (FRAP). The experiments were made at several total polymer concentrations C_T from dilute to semi-dilute range of concentration. In FRAP experiments, the dynamic of such a system is characterized by the existence of one relaxation mode identified to the self-diffusion coefficient D_s of the labelled polymer. This mode has been compared to the corresponding extracted D_s value from the two relaxation modes observed in DLS. The comparison between the results shows that in the semi-dilute range of concentration the agreement is good between both D_s values. As the concentration decreases, the agreement becomes less and less satisfactory, showing the limitation of the theory used to extract D_s from DLS measurements to the semi-dilute regime.

Introduction

The study of the dynamical relaxation characterizing mixtures of polymers in solution has been a subject of particular interest in the last few years. In previous papers, it has been shown theoretically [1-6] and experimentally [7-10] that the dynamic behavior of ternary systems consisting of two monodisperse polymers in a good solvent is characterized by two relaxation modes, i.e. the eigenvalues of the first cumulant matrix. Under particular conditions, these two dynamical processes can be interpreted as follows. The first can be viewed as the total polymer concentration fluctuations with respect to the solvent and referred as the cooperative mode. It depends on the excluded-volume parameter and increases with the total polymer concentration. The second depicts the composition fluctuations between the polymers and is recognized as the interdiffusive mode. It has been shown [1] that the two relaxation modes detected by Dynamic Light Scattering (DLS) rigorously correspond to the cooperative and interdiffusive mode exclusively in the case of a symmetrical system where the components have the same dimensions and thermodynamic properties, equal composition, and where the polymer chains differ from each other only by their chemical natures. In the case of a non-symmetrical system, the immediate consequence of the loss of symmetry is the fact that the relaxation modes cannot be strictly identified as cooperative and interdiffusive modes. Nevertheless for bimodal mixtures where the two polymers have the same chemical nature but differ in molecular weight Benmouna et al. [12] have shown numerically that the two relaxation modes are quantitatively identical to the cooperative and the interdiffusive modes in a concentration range corresponding to the semi-dilute regime, even though the mixture is not symmetrical. Our goal is to show that the coefficient which appears in the expressions of the diffusion coefficient characterizing the two modes observed by DLS in ternary mixture (interdiffusive and cooperative modes respectively) and described in the theory of Benoit and Bennmouna, is the self diffusion coefficient that one can measure in a Fluorescence Recovery After Photobleaching (FRAP) experiment. For this purpose we compare the value of the self-diffusion coefficient D_s measured using FRAP to that deduced from the DLS experiments on the same system. This kind of work have been done successfully by Giebel et al. [11] on a Poly(dimethylsiloxane)/Poly(methyl methacrylate)/Chloroform symmetrical mixture and by Brown et al [10,13] on a PIB (poly-iso-butylene)/PIB/chloroform system using pulsed field NMR to measure directly the self diffusion coefficient. Comparison of the results provided by same techniques than us on a ternary solution of polymer has been recently done [14], zero average contrast condition (ZAC) was used for extracting the interdiffusion mode from DLS experiments. This mode was identified as the single chain diffusion coefficient at small composition of the probed polymer. The system investigated (F-dextran in PVP/water) was not ideal, polymers studied were rather polydisperse and incompatible, water does not fulfill ZAC condition (average refractive index of the two polymers matches exactly the refractive index of the solvent). The agreement between values obtained by both techniques was not complete especially for the lowest concentrations.

We consider here a bimodal mixture in toluene, composed of two monodisperse polystyrenes (PS), with different molecular weights in order to use well characterized polymers and to avoid incompatibility problems. The model we have used for the interpretation of the relaxation modes in ternary mixtures has been developed by Akcasu, Benmouna and Benoit [3, 12] using the random phase approximation. For convenience it is useful to recall some relations that are of interest for this work. In any ternary mixtures of two polymers in a solvent, the total dynamic structure factor $S_T(q,t)$ is defined by :

$$S_T(q,t) = S_{11}(q,t) + S_{22}(q,t) + S_{12}(q,t) + S_{21}(q,t) \tag{1}$$

And $S_I(q,t)$ depicts the intermediate scattering function

$$S_I(q,t) = \frac{S_{11}(q,t)}{x^2} + \frac{S_{22}(q,t)}{(1-x)^2} - \frac{S_{12}(q,t) + S_{21}(q,t)}{x(1-x)} \tag{2}$$

The initial decay of these scattering functions is governed by the total or cooperative relaxation frequency Γ_T and by the intermediate or interdiffusive relaxation frequency Γ_I respectively. A solution containing two polymers with different molecular weight but otherwise identical, is characterized by one refractive index increment and one friction coefficient. We shall suppose, for sake of simplicity, that it is also characterized by one excluded volume parameter. Therefore, we have

$$\chi = 0 \quad ; \quad u_{11} = u_{22} = u_{12} \quad \xi_1 = \xi_2 = \xi$$

$$y = \frac{N_2}{N_1} \neq 1 \quad ; \quad x = \phi_1/\phi \quad ; \quad \phi = \phi_1 + \phi_2$$

Where u_{ij} are the elements of the interaction matrix u. N_i, Φ_i, and ξ_i are the degrees of polymerization, the volume fraction and the monomeric friction coefficient of species i respectively. x is the fraction of polymer 1 in the solute and Φ is the total polymer volume fraction ($\Phi = C_T/\rho$ where C_T is the total polymer concentration and ρ is the polymer density). In semi-dilute solutions hydrodynamic interactions are screened and the dynamic motion of polymer chains can be described by the Rouse model. The calculations performed by Benmouna et al. [12] lead to the following expressions

$$\frac{\Gamma_T}{q^2 D_{s1}} = \frac{N_1 \phi}{S_T} = \frac{1}{xP_1(q) + (1-x) y P_2(q)} + u\phi N_1 \tag{3}$$

$$\frac{\Gamma_I}{q^2 D_{s1}} = \frac{N_1 \phi}{x(1-x) S_I(q)} \tag{4}$$

where

$$S_T(q) = \frac{\phi\left[xN_1 P_1(q) + (1-x) N_2 P_2(q)\right]}{1 + u\phi\left[xN_1 P_1(q) + (1-x) N_2 P_2(q)\right]} \tag{5}$$

$$S_I(q) = \frac{\left\{ \phi N_1 P_1(q)\left[1 + u(1-x)\phi N_2 P_2(q)\right] \big/ x + \phi N_2 P_2(q)\left[1 + ux\phi N_1 P_1(q)\right] \big/ (1-x) + 2u\phi^2 N_1 N_2 P_1(q) P_2(q) \right\}}{\left[1 + u\phi\left[xN_1 P_1(q) + (1-x) N_2 P_2(q)\right]\right]} \tag{6}$$

and $P_1(q)$, $P_2(q)$ are the form factors of polymer 1 and 2 respectively.

According to Benmouna et al.[12], if the two relaxation modes observed by DLS in $S_T(q,t) = A\exp(-\Gamma_T t) + B\exp(-\Gamma_I t)$ can be interpreted as the cooperative and the interdiffusive mode, this allows us, from these equations, to extract the diffusion coefficient of a single chain in the Rouse limit : $D_{s1} = \frac{kT}{N_1 \xi}$ Comparing these values to the self-diffusion coefficient of the labelled chains measured by FRAP is a good means of verifying experimentally the validity of this assumption.

Experimental Section

Materials and sample preparation

Polystyrene samples were prepared by anionic polymerization under inert atmosphere according to a process described elsewhere [15]. The characteristics of these polymers are given in Table 1. The weight-average molecular weights M_w, the radii of gyration R_g, and the second virial coefficients A_2 of these samples were determined by static light scattering measurements in toluene, the overlap concentration C* is calculated according to the expression $A_2 M_w C^* = 1$.

Table I : Properties of polymer samples

Sample	M_w (g.mol^{-1})	$I = M_w/M_n$	Rg (Å)	A_2 (10^{-4} mol.cm^3.g^{-2})	C* (10^{-2} g.cm^{-3})
PS178	26000	1.01	50	7.6	5.1
PSS52	610000	1.17	350	3.9	0.42

Polystyrene samples (PSS52) were labelled statistically at the phenyl groups by chloromethylation with chloromethyl methyl ether in dichloromethylene solution using zinc chloride as the catalyst and subsequent reaction with the cesium salt of fluorescein in DMF solution. Varying temperature, time and the concentration of catalyst and chloromethyl ether allows us an easily controlled chloromethylation [16] and therefore an accurate labeling. In our studies the polystyrene labeling was typically one fluorescein molecule per 2000 PS monomers units. The labelled PS samples were stable over a period of more than three weeks and we have checked that labelled PS has the same dynamical properties than unlabelled PS. The polydispersity index of these samples determined from the M_w distribution curves was less than 1.35. All the measurements were done at a small composition of PS labelled with fluorescein, $X_f < 1\%$.

Equipment and data analysis.

The dynamic light scattering measurements were performed using a home-built apparatus. The optical and mechanical parts of the apparatus have been described elsewhere [17]. The scattered light of a vertically polarized 488 nm argon laser (Spectra Physics 2020) was measured at a scattering angle of 20°. The full homodyne correlation function of the scattered intensity defined on 192 channels was obtained by using the ALV-3000 (ALV-Langen,FRG) autocorrelator in its multi-τ mode. In this mode the correlation function cover 7 decades in delay times going from 1 μs to 63 s. The experimental intermediate scattering function S(q,t), related to the measured homodyne intensity autocorrelation function $G^{(2)}(q,t)$ by the Siegert relation [18], was analyzed using the constrained regularization method (CONTIN) developed by Provencher [19]. The base line of the scattering function was allowed to float in the fitting procedure, and any measurement with a base line different from zero (less than 10% of the total number of measurements was rejected). An example of the distribution function calculated by the CONTIN method is shown in Figure 1.

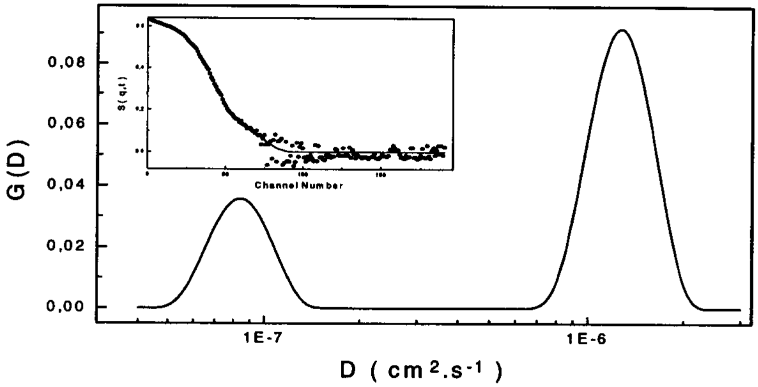

Figure 1 : Diffusion coefficient distribution obtained from CONTIN analysis for the ternary mixture PSS52/PS178/toluene at the total polymer concentration $C_T = 5.03\times10^{-2}$ g.cm^{-3} (composition of PSS52 x= 17%, scattering angle 20°). The inset represent the dynamic structure factor, the solid line is the result of the fit according to CONTIN.

The diffusion of fluorescein labeled PS was measured by a fringe pattern fluorescence bleaching technique similar to the one described by Davoust et al. [20]. The light beam of an etalon-stabilized monomode Ar laser (1W at λ = 488 nm) was split and the two beams crossed in the cell providing illumination in a deep interference fringe pattern. The fringe spacing $i=2\pi/q$ set by the crossing angle ϕ, $q = (4\pi/\lambda)\sin(\phi/2)$, ranged from 3 to 60 µm, defining the diffusion distance. Fluorescence bleaching of the labelled polymers in the illuminated fringes was obtained by producing a 1-s full-intensity bleach pulse by means of Pockels's cell between nearly crossed polarizers. The experimental signal vanished because of diffusion of molecules between bleached and unbleached fringes. The decay of the amplitude of the fringe pattern of concentration of fluorescent molecules after photobleaching was detected by modulation of the illuminating fringe position using a piezoelectrically modulated mirror and lock-in detection of the emerging fluorescence. Nonpreaveraged data were fitted with an exponential decay $\exp(-t/\tau)$. The characteristic time τ of the exponential decay is related to the self diffusion coefficient of the molecules by $\tau = \frac{1}{D_s q^2}$. Figure 2 shows a typical experimental signal of the monoexponential decay of the fluorescein labeled PS.

We have checked for two concentrations (one in the dilute regime and one in the semidilute) that τ is linear with q^{-2}. For the other concentrations, we performed the measurements at only one q vector value and average over 10 measurements on the same sample. The error bar is roughly 10 %.

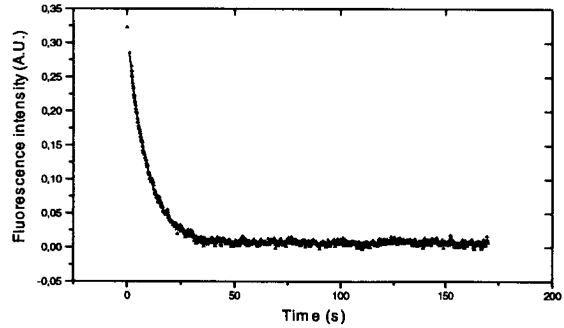

Figure 2 : Typical fluorescence intensity function measured using FRAP for the ternary mixture PSS52/PS178/toluene at the total polymer concentration $C_T = 5.03\times10^{-2}$ g.cm^{-3}, (composition of PSS52 x= 17%, and q = 1409cm^{-1}). The triangles represent the experimental data and the solid line the monoexponential fit.

Results and discussion

The experiments were performed at the temperature t=(25.0±0.1)°C at different total polymer concentrations from the dilute to the semi-dilute regime $2.6\times10^{-3} < C_T(\mathrm{g.cm^{-3}}) < 5.72\times10^{-2}$, at a composition of 83% PS178 and 17% PSS52. Composition of the mixture was chosen in a way to obtain well defined diffusion modes, this means amplitudes of the same order of height and distinct relaxation times. The dynamic light scattering functions were measured at a scattering angle of 20°. As mentioned above, the relaxation rates of the two modes obtained by the DLS experiment on the ternary polymer solution provide information on the self-diffusion coefficient D_s of the PSS52, if we assume that the relaxation modes observed correspond to the cooperative and the interdiffusive modes. In Figure 3 we have plotted the self-diffusion coefficient of the labelled PSS52 in the ternary mixture directly measured by FRAP as a function of the total polymer concentration C_T. The same figure also shows, for comparison, the values of the self-diffusion coefficient of the PSS52 deduced from the DLS experiment and from equations (3,4). These data are also listed in Table 2.

Table II : Values of the diffusion coefficients $D_{C,I}$ measured by DLS and of the self diffusion coefficient D_{SF} measured by FRAP as function of total polymer concentration C_T. D_{SDLS} are calculated values from equations (3,4).

C_T (10^{-2} g.cm^{-3})	D_C (10^{-6} cm^2.s^{-1})	D_I (10^{-7} cm^2.s^{-1})	D_{SDLS} (10^{-8} cm^2.s^{-1})	D_{SFRAP} (10^{-8} cm^2.s^{-1})
5.72	1.20±0.03	1.06±0.2	2.9±0.5	2.8±0.3
5.03	1.15±0.04	1.15±0.3	3.4±0.8	3.1±0.4
4.43	1.13±0.02	1.27±0.04	3.9±0.3	4.5±0.6
3.90	1.10±0.05	1.48±0.2	5.1±0.8	4.9±0.7
3.30	1.00±0.03	1.25±0.03	4.1±0.4	6.4±0.7
2.77	1.18±0.08	1.88±0.2	7.5±0.9	7.0±0.7
2.26	1.02±0.04	1.63±0.1	6.5±0.8	8.9±0.9
1.69	1.02±0.04	1.66±0.2	6.7±0.7	9.6±0.9
1.16	0.85±0.08	1.54±0.2	7.0±0.9	10±1
0.58	1.02±0.06	1.72±0.07	7.2±0.9	10±1
0.26				11±2

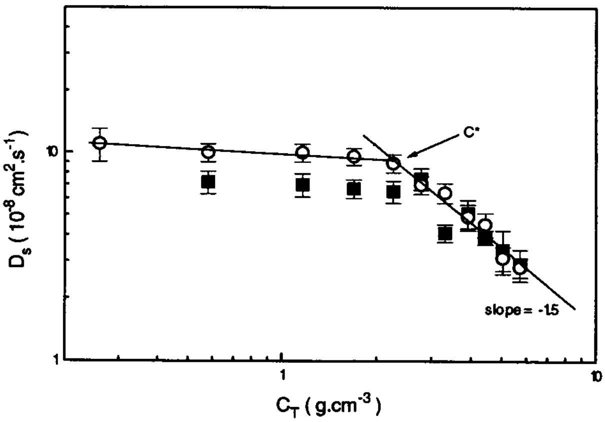

Figure 3 : Variation of the self diffusion coefficient D_s measured in the ternary polymer mixture PS178/PSS52/toluene as function of the total polymer concentration C_T : DLS (■), FRAP (O). Lines are guides to the eyes.

The results show that D_s decreases with the concentration, which is qualitatively in agreement with earlier DLS experiments. Both curves are similar in their shapes and two different regions seem to be described. The crossover between these two regions experimentally determined on the curves around the concentration $C_T \approx 2.3\times10^{-2}$ g.cm^{-3} is in good agreement with the overlap concentration of the mixture ($C^*_m = 1.8\times10^{-2}$ g.cm^{-3}), assuming this value can be estimated by the following relation :

$$\frac{1}{C_m^*} = \frac{x}{C_1^*} + \frac{1-x}{C_2^*} \qquad (7)$$

where x is the composition of polymer PSS52 in the mixture, C_1* and C_2* are the overlap concentrations of polymer PSS52 and PS178 respectively.

Relation (7) is deduced from the intrinsic viscosity of the mixture $[\eta_m] = x[\eta_1] + (1\text{-}x)[\eta_2]$, where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosity of polymer PSS52 and PS178 respectively, and considering the overlap concentrations equal to the inverse intrinsic viscosity. At higher concentration D_s decreases rapidly with the concentration and the measured slope is approximately -1.5, near the -1.75 exponent predicted by the reptation model [21] and experimentally observed [22]. The difference between these exponents is not surprising since the concentration range is too restricted to reach the possible limiting slope of -1.75.

Within experimental error, a satisfactory agreement between both D_s FRAP and DLS is reached in the semi-dilute regime. As the concentration is decreased in the dilute regime this agreement fails, this is to some extend comforting since the model is rather valid above C*. One of the major contributions to this discrepancy in the dilute regime is probably the hydrodynamics interactions which are not taken in account in the model used to extract the self-diffusion coefficient from the DLS relaxation modes. Indeed in this regime the assumption that the mobilities can be described by the Rouse approximation is no more valid. In this way one of the most important correction which should be introduced in the model would be the variation of the ratio $D_{s1}/D_{s2} \sim (N_2/N_1)^{\nu}$ where $\nu=3/5$ in the good solvent limit instead of $D_{s1}/D_{s2} \sim (N_2/N_1)$. These effects are less important compare to previous work [14]. Nevertheless, for higher concentration where hydrodynamics interactions are screened the agreement between both D_s seems to indicate that the assumption of Benmouna et al. which identified the relaxation modes as the cooperative and interdiffusive mode for a non-symmetrical ternary mixture is valuable. This agreement is better than in the previous work [14] where the investigated system (PVP/dextran/water) was less suited.

Conclusion

We have investigated the dynamic behavior of a ternary mixture in the case where the two polymers have the same chemical nature but differ in molecular weight using fluorescence recovery after photobleaching experiments and values extracted from dynamic light scattering. The values obtained from both techniques have been compared. The agreement is found satisfactory in the semi-dilute regime and follows the numerical results from Benmouna et al [12] confirming that the relaxation frequencies observed by DLS can be interpreted as the cooperative and the interdiffusive modes for ternary mixtures of two identical polymers having widely different dimensions and composition different from 1/2. However, as the concentration decreases, this agreement become unsatisfactory, showing importance of hydrodynamic interactions and limitation of the interpretation done here to the semi-dilute range of concentrations.

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