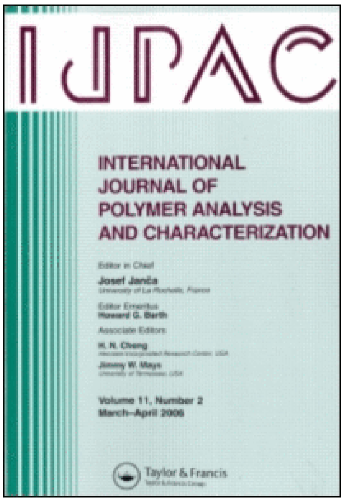

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Three-Dimensional Analysis of Dynamic Light Scattering Data: Application to Self-Organized Polymer Solutions

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Abstract: Semi-dilute solutions of diblock copolymers in selective partially miscible solvent mixtures have been studied by dynamic light scattering and pulsed-field gradient NMR. Several dynamic modes have been identified as cooperative diffusion, polymer self-diffusion, and cluster diffusion. Their temperature dependences changed dramatically at a certain temperature, below which solutions underwent self-organization. Interpretation of the complex behavior of the dynamic processes observed has been made. The importance of a 3-D representation of the distributions of relaxation times is demonstrated.

Keywords: Block copolymers; Cooperative diffusion; Dynamic light scattering; Polymer self-diffusion; Pulsed-field gradient NMR; Semidilute solutions

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INTRODUCTION

Dynamic light scattering (DLS) has, in the past two decades, become a very important tool for polymer characterization. DLS was originally used mainly for the determination of diffusion coefficients and hydrodynamic radii of polymer molecules.[1] Later, the continuing advance of lasers and sophisticated correlators made the investigation of dynamics of more complicated polymer systems possible. Typically, semi-dilute polymer solutions must have been described by multimode correlation functions, with several dynamic modes, ascribed to cooperative diffusion of the transient polymer network,[2] heterogeneity mode[3] related to polymer self-diffusion (in the case of copolymers), entanglement mode,[4] and diffusion of polymer clusters.[5] The existence of such modes has been supported by theory or other experimental methods.[6,7] In our recent work, we have also revealed the presence of dynamic processes corresponding to thermal diffusion and self-diffusion of solvent molecules.[8]

Our ongoing systematic study of semi-dilute solutions of block copolymers in demixing binary selective solvents[9] shows even more complicated behavior. A typical example of such a system is a diblock copolymer, e.g., polystyrene-*b*-polyisoprene (PS-*b*-PI) or polystyrene-*b*-poly(ethylene-*co*-propylene) (PS-PEP), in a mixture of dimethylformamide (DMF) and cyclohexane (CX) or methylcyclohexane (MCX). DMF is a thermodynamically good solvent for PS and a precipitant for PI or PEP; CX and MCX are theta solvents for PS at 34.4°C and 70.5°C, respectively. Both solvent mixtures are virtually isorefractive and have coexistence curves with critical points at 32.7 vol.% of DMF and 51.4°C for CX/DMF, and 36.3 vol.% of DMF and 49.7°C for MCX/DMF. Above the coexistence curve, the copolymers behave as if they were dissolved in any other single good solvent. Below the coexistence curve, the copolymers solutions do not separate macroscopically. Instead, the system is macroscopically homogeneous and solvents are microphase-segregated to DMF-rich and CX-rich domains, separated by interfaces covered with diblock copolymers. Our recent small-angle neutron scattering (SANS) and ultra-small-angle neutron scattering studies show that the low-temperature ordered phases have in all the cases examined hexagonal or cubic building blocks on a scale of tens to hundreds of nm, and they form large grains on the scale of microns.[10]

In the present article, we show a complex behavior of various dynamic processes in block copolymer semi-dilute solutions in such partially miscible solvent mixtures. We point out the possibilities of characterization of polymer dynamics by up-to-date dynamic light scattering techniques and demonstrate the importance of a graphic presentation of DLS results. We also speculate qualitatively on the nature of some dynamic phenomena not observed or studied so far.

EXPERIMENTAL SECTION

Materials

The polymers used are diblock copolymers polystyrene-*b*-poly(ethylene-*co*-propylene), commercial products of the Shell company (Shellvis®) labeled as SV-50 with molecular weight $M_w = 96.000$ and styrene weight fraction $f_S = 0.43$, and SV-40 with $M_w = 200.000$ and $f_S = 0.25$. The solvents, dimethylformamide (DMF), cyclohexane (CX), and methylcyclohexane (MCX) of p.a. grade, were purchased from Aldrich and used as received.

Dynamic Light Scattering

The dynamic light scattering (DLS) instrument consists of an ALV CGE photogoniometer equipped with a Uniphase 22 mW HeNe laser, an ALV6010 correlator, and a pair of avalanche photodiodes operated in a pseudo-cross-correlation mode using an optical fiber splitter. The instrument is described in more detail elsewhere.[8] All measurements were made at a 90° angle.

The measured intensity correlation function $g^2(t)$ was analyzed using the program REPES performing the inverse Laplace transformation (ILT) according to

$$g^2(t) = 1 + \beta\left[\int A(\tau)\exp(-t/\tau)d\tau\right]^2 = 1 + \beta\left[\sum_{i=1}^{n} A_i \exp(-t/\tau_i)\right]^2 \qquad (1)$$

and yielding the distribution of relaxation times $A(\tau)$, which in the numerical calculations is represented by the set of amplitudes A_i corresponding to the relaxation times τ_i. In graphs with logarithmic scale on the relaxation time axis, the distributions are shown in the equal area representation[11] $\tau A(\tau)$ versus $log(\tau)$. The relaxation time τ is related to the diffusion coefficient D by the relation $D = (1/\tau q^2)$, where q is the scattering vector.

Pulsed-Field Gradient NMR

Self-diffusion pulsed-field gradient nuclear magnetic resonance (PFG NMR) experiments were measured at 16–44°C with an upgraded Bruker Avance DPX300 spectrometer using a *z*-gradient inverse-detection diffusion probe connected to a BGU2 gradient unit. A Tanner pulsed-gradient stimulated echo sequence was used with the field-gradient incremented in the range 0–650 G/cm. The lengths of the gradient pulses δ as well as the diffusion delay time Δ were held constant, 1 ms and 60 ms, respectively. The signal intensity decay was fitted to the exponential dependence on the square of gradient magnitude g:

$$I(g)/I(0) = \exp[-\gamma^2 D_{S,NMR} \delta^2 (\Delta - \delta/3) g^2] \tag{2}$$

where γ is the gyromagnetic ratio of protons and $D_{S,NMR}$ is the fitted self-diffusion coefficient. In some cases the monoexponential function in Equation (2) did not describe accurately the measured data, and an adaptation of Equation (2) to a double-exponential process was used instead.

RESULTS AND DISCUSSION

Considering first a not very complicated case of semi-dilute solutions of a diblock copolymer dissolved in a single solvent that is thermodynamically good for both blocks; we recall first the dynamic processes identified in such a system earlier. In a typical solution, e.g., a solution of SV-50 in CX at a concentration of 5%, the fastest mode 1 related to polymer chains is the cooperative diffusion (with relaxation time $\tau = 4.4\,\mu$s), the next slower mode 2 corresponds to polymer self-diffusion ($\tau = 2.8$ ms), and the slowest mode 3 represents the diffusion of clusters ($\tau = 58.6$ ms) (Figure 1). When the temperature of the system is varied, the changes

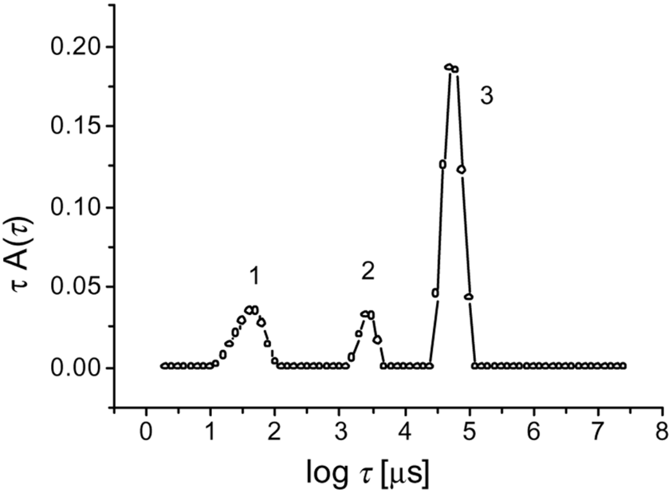

Figure 1. Distribution of relaxation times of a 5 wt% solution of SV-40 in CX at 25°C.

of relaxation times are the same for all three modes and are simply given by changes in the viscosity of the solvent (not shown here).

The distributions of relaxation times on a similar system where the solvent is a mixture of 96% CX and 4% DMF are more complicated, and a different number of modes is observed when the temperature is varied. Three modes are observed at high temperatures, four modes in the temperature range from 25° to 18°C, and three modes below 18°C. In order to understand the dynamic behavior of the system, we performed a temperature scan of DLS measurements, accumulating a total of about 50 correlation curves at various temperatures. All correlation functions were analyzed individually, but with such a large number of distributions exhibiting a variable number of dynamic processes for different temperatures, it was not possible to grasp the complex dynamic behavior of the system.

A reasonable way to visualize and describe such a complex behavior is to use a three-dimensional (3-D) representation of the distributions of relaxation times. For the generation of the 3-D image, we used the program Matlab R2006b (The Mathworks, Inc., USA). The input to this program is one rectangular matrix *data*[*m*, *n*] of n rows with m elements and two vectors *time*[*m*] and *temp*[*n*]. Each row of *data*[*m*, *n*] represents the amplitudes of a distribution function $A(\tau)$. The vector *time*[*m*] contains the grid points $i = 1 \ldots n$ used in the inverse Laplace transformation (ILT) in Equation (1). For all the correlation curves, the ILT must be performed with the same grid points. The vector *temp*[*n*] contains the temperatures of the individual measurements. With these input variables, Matlab then generates a 3-D view of the data using the command *surf*.

An example of such an image is shown in Figure 2, describing in more detail the results for the solution of SV-40 in the mixed solvent of 96% CX and 4% DMF at a concentration of 4%. The dynamic properties of the system are now easily understandable. The system obviously has a characteristic temperature T^* of approximately 27°C. Above this temperature the system behaves as a polymer in good solvent where the three dynamic processes 1, 2, 3 mentioned above are visible. Below T^*, the solution becomes self-organized as we have shown previously by SANS experiments,[9] and a new mode appears in Figure 2 as a result of a split of the heterogeneity mode 2 into modes 2a and 2b. We have performed PFG NMR experiments on the same solution. Above T^*, the data can be described by a single self-diffusion process, representing the center of mass motion of block copolymer chains in the semi-dilute solution. To allow comparison with light scattering, the values of $D_{S,NMR}$ obtained from Equation (2) were converted into relaxation times τ, shown as open dots in Figure 2. Below T^*, two processes are needed to describe the PFG NMR results, as shown in Figure 2.

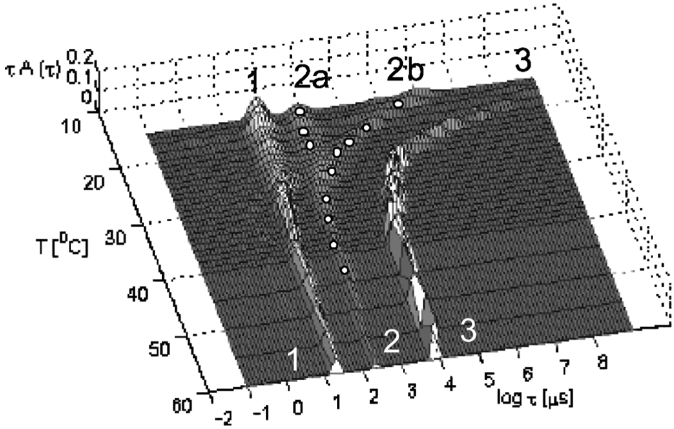

Figure 2. Three-dimensional representation of temperature dependence of the distributions of relaxation times $\tau A(\tau)$ vs. $log(\tau)$, for a 4 wt% solution of SV-40 in a mixed solvent 96% CX and 4% DMF. Open circles represent PFG NMR data. For identification of modes see text.

Modes 2, 2a, and 2b thus correspond to a self-diffusion process. The temperature dependence of the faster self-diffusion process (mode 2a) follows that of mode 1 (the cooperative diffusion) both above and below T^* and is governed only by the changes in local viscosity as a function of temperature. Mode 2a therefore corresponds to polymer self-diffusion in the self-organized solution below T^*. By comparison with PFG NMR results, mode 2b is also a self-diffusion process. Its dynamics, however, closely follows that of mode 3, the cluster diffusion that remarkably slows down by four orders of magnitude over a temperature interval of about 10° below T^*. Mode 2b thus corresponds to diffusion of larger objects, the dynamics of which is governed by the increase of macroscopic viscosity due to microscopic self-organization of the solution below T^*. The appearance of an ordering in the vicinity of T^* is not a phase transition but a gradual process, as we have shown by SANS experiments.[9] We propose that mode 2b represents diffusion of micelle-like particles of the block copolymer that coexist with a loose copolymer network in such a way that the solution is in the transition region below T^* structurally heterogeneous, as the long-range order is progressively being built on cooling. At temperatures below approximately 18°C the cluster diffusion is no longer visible, and the SANS results show that under such conditions the long-range order is already fully built.

The progressive buildup of order at temperatures below T^* is a gradual process; on the other hand, the behavior of the cooperative mode and its slowing down on cooling from high temperature towards T^* can be identified with the approach to a critical point[12] with the expectation that the correlation length ξ of fluctuations corresponding to the cooperative diffusion will be described by a power law $\xi \approx \varepsilon^{-\nu}$, where ν is a critical exponent and $\varepsilon = (T - T_c)/T_c$ is the reduced temperature, with T_c being the critical temperature. The correlation length ξ has been calculated from the values of the cooperative diffusion coefficient using the Stokes-Einstein equation $D = kT/6\pi\eta\xi$, where k is the Boltzmann constant, T is absolute temperature, and η is the viscosity of the solvent, which for the present mixture has been taken from literature data.[13] Figure 3 shows a detail of the critical region in the 3-D diagram for a similar 5 wt% solution of SV-50 in a mixture of 92 vol.% MCX and 8 vol.% DMF where the order in the solution appears at higher temperatures. Relaxation times of mode 1 have been extracted from the data and converted to correlation length ξ as described.

Figure 4(a) shows a typical dependence of ξ on temperature, from which we can estimate with good precision the critical temperature of 49.0°C. Figure 4(b) shows a logarithmic plot of the dependence of the correlation length ξ on reduced temperature ε. The fact that the data follow a linear dependence indicates that they are well described by the theoretical equation in the form of a power law. The slope of the straight line corresponds to the exponent $\nu = 0.25$. This value is remarkably different from that predicted and observed in the critical region of a binary mixture of neat solvents, $\nu = 0.63$ (Ising type of critical behavior) as well as from that observed in a critical mixture of a single polymer with one

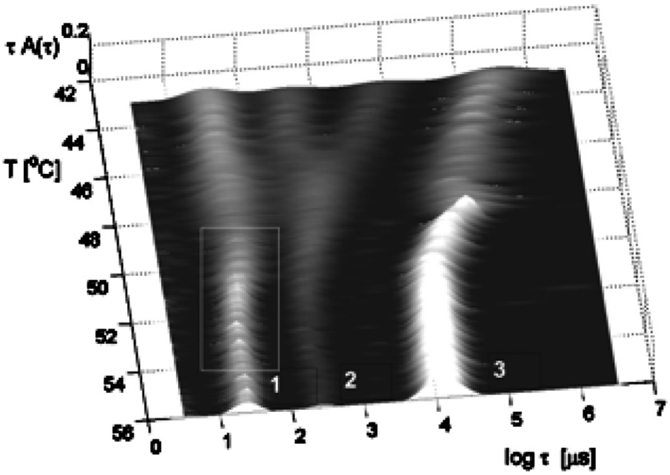

Figure 3. Detail of the distributions of relaxation times in the vicinity of T^*, for a 5 wt% solution of SV-50 in a mixed solvent 92% MCX and 8% DMF. For identification of modes see text.

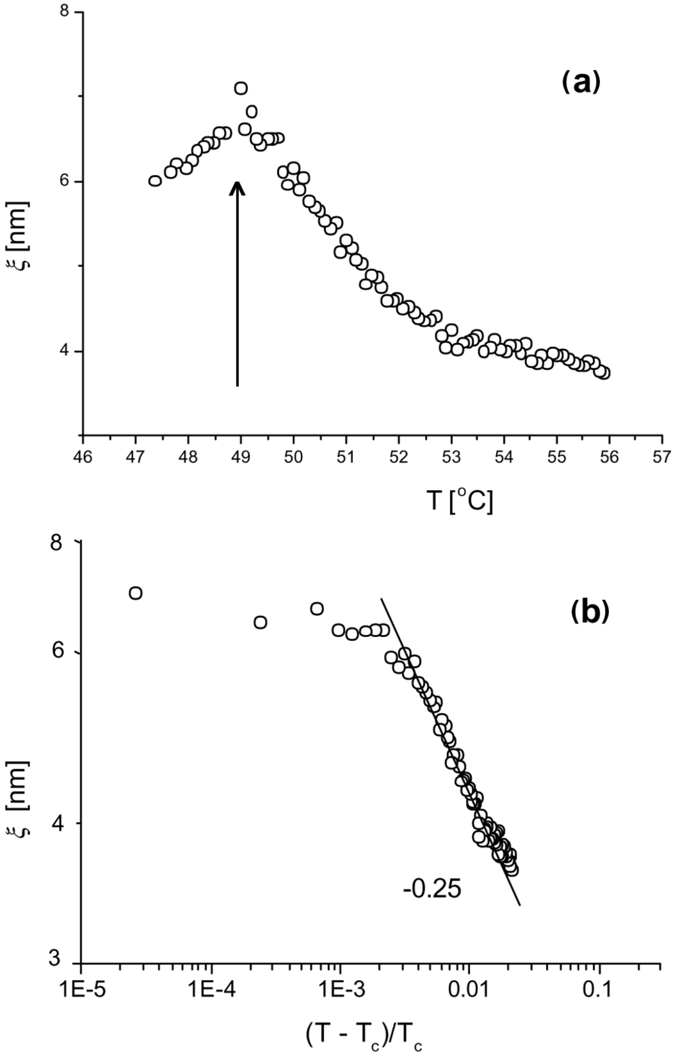

Figure 4. (a) Dependence of correlation length ξ on temperature T in the vicinity of the critical temperature T_c (shown by arrow); (b) dependence of ξ on the reduced temperature.

solvent, e.g., polystyrene in cyclohexane, where $\nu = 0.5$ was predicted and observed (mean-field type of critical behavior).[12] In fact the value 0.25 of the critical exponent ν corresponds to the theoretical value for mean-field *tricritical* conditions.[14] This situation could occur in the present system if certain conditions were met: the critical temperature of the binary mixture CX/DMF would coincide with the critical temperature of the binary mixture PS/MCX, and the concentration of the polymer and composition of the solvent are close to their critical values. In ternary polymer solvent mixtures selective sorption always plays an important role, as we have demonstrated earlier,[9] leading to changes in local composition of the solvent and to substantial modifications of the coexistence curve and shifts in critical temperatures and compositions. For this reason we are unable to verify quantitatively the two assumptions mentioned above. Nevertheless, we see that the simultaneous microphase separation of the solvents and the microphase separation of the copolymer blocks that are more and more swollen by the solvent components leads to the appearance of a self-organized phase with very small polymer content.

CONCLUSION

We have shown that very complicated dynamics of complex polymer solutions (and other systems) can be better figured out using a 3-D representation of distributions of relaxation times obtained from dynamic light scattering correlation curves by the inverse Laplace transformation. The 3-D representation helps in identifying the character of the dynamic processes observed. The block copolymer self-diffusion process in semidilute solutions on partially miscible solvents splits into two components below a certain temperature, where the faster process corresponds to the motion of polymer chains and the slower to the motion of micelle-like particles. In the temperature behavior of the cooperative diffusion a critical temperature can be identified above which the temperature dependence of the correlation length ξ derived from the cooperative diffusion coefficient has some properties of tricritical behavior.

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