Relaxation Processes in Semidilute Solutions of Polymers in Liquid Crystal Solvents

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We investigate the relaxation phenomena in a polymer (polystyrene)/liquid crystal (4-cyano-4′-n-octyl-biphenyl) system, in its homogeneous isotropic phase near the isotropic—nematic, isotropic—smectic, and isotropic—smectic coexistence curve, using both polarized and depolarized photon correlation spectroscopy (PCS). We study this system for different polystyrene molecular weights (4750, 12 500, and 65 000 g/mol), different compositions (50, 40, 30, and 10% polystyrene (PS) by weight), and different temperatures close to phase boundaries. First of all, we determine the phase diagrams of this system for the different molecular weights. The shape of the phase diagrams strongly depends on the molecular weight. However, in all cases, at low temperatures, these systems separate into an almost pure liquid crystalline (LC) phase and polystyrene-rich phase. PCS measurements show that the relaxation processes in the homogeneous phase are not affected by the proximity of the nematic or smectic, boundaries (even at a temperature of 0.1 °C above the phase separation in two phases). In polarized PCS experiments, we always see three relaxation processes well separated in time: one, very fast, with a relaxation time of the order of $10^{-3}$ s; a second one with a relaxation time within the range $10^{-2}$–$10^{-3}$ s; and a last one, very slow, with a relaxation time of the order of 1 s. Both the fast and slow modes are independent of the wave vector magnitude, while the intermediate relaxation process is diffusive. In depolarized PCS experiments, the intermediate mode disappears and only the fast and slow relaxation processes remain, and they are independent of the magnitude of the wave vector. The diffusive mode is the classical diffusive mode, which is associated with the diffusion of polymer chains in all polymer solutions. The fast mode is due to the rotational diffusion of 4-cyano-4′-n-octyl-biphenyl (8CB) molecules close to polystyrene chains (transient network). Finally, we assign the slowest mode to reorientational processes of small aggregates of PS chains that are not dissolved in 8CB.

I. Introduction

Interest in mixtures of low-molecular-weight liquid crystal molecules and polymers is becoming increasingly important because of the technological applications that these mixtures have in the production of high-modulus fibers, in nonlinear optics, and in the design of electro-optical devices.1 Polymer/liquid crystalline (LC) blends raise also interesting fundamental questions.2,3 These systems exhibit a wide variety of equilibrium phases as a function of temperature and concentration: a homogeneous isotropic phase and several biphasic solutions in which a nematic, cholesteric, or smectic phase is in equilibrium with polymer domains. Experimental4–7 and theoretical8–12 studies of mixtures of flexible polymers with nematogen molecules show that the phase diagram depends on the molecular weight of the polymer and on the strength of nematic interactions.16 Recently, the phase behaviors in binary mixtures of liquid crystal molecules and flexible polymers have been analyzed by combining the Flory–Huggins theory for isotropic mixing and the Maier–Saupe theory for anisotropic ordering.18,19 Though the study of the phase behavior of such mixtures, as well as their equilibrium properties, is the subject of active research, the dynamics of these systems, especially in the homogeneous isotropic phase, has been little investigated so far. To our knowledge, just a few studies have been carried out concerning the dynamics of relaxation processes in homogeneous phases of liquid crystal molecule/polymer mixtures.20–23 Therefore, the purpose of this paper is to provide experimental measurements of the dynamics of these mixtures in their homogeneous isotropic phases. Such an investigation is interesting from several points of view. The study of the relaxation processes provides valuable information on the equilibrium properties of these mixtures in their homogeneous isotropic phases. Especially, for such a binary system, are there any pretransitional effects as temperature approaches that at which the mixture undergoes a phase separation? Finally, one can question the effects of polymer chains on the relaxation processes of liquid crystal molecules in their isotropic state.

This study is carried out by the means of both polarized and depolarized photon correlation spectroscopy (PCS) on mixtures of 4-cyano-4′-n-octyl-biphenyl and polystyrene, with 4-cyano-4′-n-octyl-biphenyl, also called 8CB, being the mesogenic molecules and polystyrene (PS) being the polymer. We investigate 4-cyano-4′-n-octyl-biphenyl/polystyrene mixtures made up of polystyrene of different molecular weights: $M_w = 4750$, 12 500, and 65 000 g/mol. The phase diagrams in the temper-
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II. Systems and Samples

(a) Experimental Systems. 4-Cyano-4′-n-octyl-biphenyl (8CB)/polystyrene (PS) mixtures are prepared according to the following procedure. First of all, for a desired composition, the proper amounts of 8CB and PS are dissolved in toluene. After full homogenization of all of the compounds, the obtained solution is filtrated through a 0.20 μm PTFE (polytetrafluoroethylene) Rotilabo filter to remove dusts. Then, toluene is removed by leaving the solution under vacuum at T ~ 80 °C for several hours (typically 12 h).

The 8CB used is synthesized by the Institute of Chemistry, Military University of Technology, Warsaw, Poland, and is used without further purification. In its pure state, we observe that 8CB is an isotropic liquid for temperatures above T = 40.8 ± 0.05 °C, smectic below T = 33.8 ± 0.05 °C, and nematic in between. The full length of the 8CB molecule is around 2.1 nm, and its molecular weight is 290 g/mol. The viscosity of 8CB changes with temperature and can be modeled according to the Vogel–Tamman–Fulcher equation, the parameters of which were measured by Jadzyn et al.24 According to this latter reference, the viscosity of 8CB as a function of temperature follows the relation \( \eta_{8CB}(T) = 0.1458 \exp(3.3003/191.902/(T - 191.902)) \) Pa s.

The polystyrene of three different molecular weights (65 000, 12 500, and 4750 g/mol) is bought from Fluka Chemical Co. and also used without further purification. These polymers are monodisperse; their mass polydispersity, which is characterized by the ratio \( M_w/M_n \) (\( M_w \) is the average molecular weight), is, respectively equal to 1.02, 1.02, and 1.08 for 65 000, 12 500, and 4750 g/mol PS. Note that whatever the molecular weight used in the temperature range studied pure PS forms a glass.

The molecular weight of PS monomer is 104.5 g/mol which gives a polymerization index, \( N \), equal to 622, 120, and 46 for PS with a molecular weight of 65 000, 12 500, and 4750 g/mol, respectively. Here, we make the assumption that PS chains in 8CB solvent are in theta solvent (i.e., the value of the Flory–Huggins parameter, \( \chi_{8CB} \), is equal to \( 1/2 \)). Thus, in this framework, we can estimate the size of the radius of gyration, \( R_g \), of PS chains that is given by \( R_g \approx a\sqrt{N} \), where \( a \) is the “monomer size”, which according to many references is of the order of 3.5 Å. Therefore, \( R_g \) is expected to be around 8, 3.8, and 2.3 nm for PS 65 000, 12 500, and 4750, respectively.

(b) Samples for Experiments. First of all, it should be noted that, for all kinds of investigations we performed, 8CB/PS mixtures were always set in flat borosilicate glass capillaries from VitroCom Inc., with a cross section of \( 0.2 \) mm \( ^2 \) (i.e., inner thickness of \( h = 200 \) μm). To introduce the mixtures into the capillaries, the mixtures were first heated in their homogenous isotropic phase and then vacuumed into the capillaries with a pump.

The phase diagrams of 8CB/PS mixtures as a function of temperature and PS weight fraction, for molecular weights of both 4750 and 65 000 g/mol, are determined by means of static light scattering and optical microscopy experiments. For both systems, eight mixtures with different compositions (i.e., different 8CB/PS ratios) are prepared to investigate these phase diagrams accurately.

Relaxation processes are studied with the help of photon correlation spectroscopy (PCS), also called quasi-elastic light scattering (QELS). Measurements are carried out on seven different mixtures. Three mixtures are made up of 8CB and PS 4750 and have a PS composition, in weight fraction, equal to 50, 30, and 10%, respectively. Three mixtures are made up of 8CB and PS 65 000 with a PS composition, in weight fraction,
equal to 40, 30, and 10%, respectively. The last mixture is made up of 8CB and PS 12 500 and has a PS composition, in weight fraction, equal to 30%. (The mixture density is close to 1 g/cm$^3$, so 10, 30, 40, and 50% PS by weight correspond to 0.1, 0.3, 0.4, and 0.5 g/cm$^3$, respectively.) Every mixture is homogeneous and isotropic above a given temperature (which depends both on PS molecular weight and its composition), and then, below this temperature, the system separates into two phases (Figure 1). For 10 and 30% PS 4750, the homogeneous mixtures separate into nematic + isotropic phases; for 50% PS 4750, the homogeneous mixture separates into smectic + isotropic phases; and for 40, 30, and 10% PS 65 000 and 30% PS 12 500, the homogeneous mixtures separate into isotropic + isotropic phases. For each mixture, the temperature of phase separation is accurately determined and QELS measurements are performed as a function of temperature in the homogeneous phase, from several degrees down to 0.1 °C above the temperature of phase separation. For mixtures with 10 and 30% PS 4750, we expect the PS concentration to be below the overlap concentration, $c^*$, and therefore to be in the dilute regime, while the sample with 50% PS should be slightly above $c^*$. On the other hand, for all mixtures made of PS 12 500 and PS 65 000, we expect the PS concentration to always be higher than the overlap concentration, $c^*$, and therefore to be in the semidilute regime.

III. Experimental Procedures

(a) Phase Diagram Investigation. The temperature-versus-composition phase diagrams of 8CB/PS mixtures for PS molecular weights of 4750 and 65 000 g/mol are investigated by means of static light scattering and optical microscopy experiments. Static light scattering experiments at small angles are monitored with the help of a homemade apparatus, which has already been described elsewhere. Samples are illuminated with a He–Ne laser operating at 632.8 nm with a power of a few milliwatts, temperature is controlled with a homemade heating/cooling stage, and the scattered light at small angles is detected on a linear array of 512 photodiodes. The measurements start at a temperature above the temperature of phase separation, that is, with the mixtures in the homogeneous isotropic phase. The temperature is slowly decreased, and as soon as the phase separation occurs, one observes a strong increase in the scattered intensity. Both the intensity magnitude amount and the angle distribution of the scattered light intensity stop evolving when the separation process is completed. Optical microscopy experiments are performed using a Nikon ECLIPSE E 400 optical polarizing microscope equipped with a Nikon DVM 1200 digital camera and a LINKAM THMS 600 heating/cooling stage with a 0.1° temperature control. Here again, the measurements start at a temperature above the temperature of phase separation with the mixtures in the homogeneous isotropic phase; then, in the microscope, the samples appear uniform. The temperature is slowly decreased, and as soon as the phase separation starts, one sees the appearance of PS droplets in the samples. Once the phase separation is achieved, analysis of the texture of the continuous phase between crossed polarizers indicates the state of the 8CB-rich phase (isotropic, nematic, or smectic).

(b) Photon Correlation Spectroscopy Experiments. Setup. The relaxation processes of these mixtures in their homogeneous phase are studied as a function of PS molecular weight, concentration, and temperature with the help of photon correlation spectroscopy (PCS), also called quasi-elastic light scattering (QELS). These experiments are carried out using a Coherent Innova 305 ionized argon laser light source, operated at $\lambda = 514$ nm, the beam of which is linearly polarized vertically just before the sample. The scattered light is collected with a photon-counting PMT (photomultiplier tube) set on a goniometer. The angle $\theta$ between the incident beam and the direction of the photomultiplier can be changed between 10 and 150°. To analyze the polarization state of the scattered light, a polarizer set in either the vertical (V) or horizontal (H) position is placed just in front of the detector. With this polarizer set in the vertical position, we perform polarized measurements (VV configuration), and with the polarizer set in the horizontal position, we perform depolarized measurements (VH configuration). The typical power of the laser for the polarized measurements is 0.4 W. In the case of depolarized measurements, the typical power of the laser is 0.75 W. Finally, to allow the measurement of the time autocorrelation function of the scattered intensity, the measured photocurrent is processed using a PC-controlled 256-channel 4700-Malvern correlator, which is able to work either in a linear mode or in a logarithmic mode with sample times as fast as 0.1 $\mu$s. All of the measurements are performed using the logarithmic mode; this allows probing relaxation frequencies over more than six decades, typically in the range $10^{-0.1}$ s$^{-1}$.

The sample held in the capillary is mounted in a capillary holder, with the width of the capillary parallel to the incident laser beam direction (i.e., the normal to the flat side of the capillary perpendicular to the incoming beam) and set at the center of a temperature-regulated vat containing an index-matching liquid (decahydronaphthalene), the refractive index of which is $n_t = 1.48$. The internal temperature of the vat is monitored within $\pm 0.05$ °C by means of a PC-controlled water bath. Working with the width of the capillaries parallel to the incoming laser beam direction, the experimental setup allows valuable measurements between 40 and 135°. The index of refraction of PS is $n_{PS} = 1.589$, and that in the isotropic phase is $n_{PS} = 1.566$. Therefore, in our experiments, the modulus $q$ of the scattering wave vector $\mathbf{q}$ that is given by the relation $q = \sqrt{2\pi n_t \sigma}$, with $\sigma$ being the wavelength and $n_t$ being the sample refractive index, varies in the range $1 \times 10^2$ to $3.7 \times 10^5$ m$^{-1}$.

Principle. The principle of PCS measurements can be summarized as follows. Quasi-elastic light scattering experiments, with homodyne detection, give access to the time autocorrelation function of the scattered light intensity, namely, $(I(q,0) I(q,\tau))$, where $q$ is the scattering wave vector. This function is built, using a correlator device, from the fluctuations of the scattered light intensity measured by a detector. The scattered light intensity arises from fluctuations in the local dielectric tensor of the sample, $\delta e(r,t)$. We have

$$\langle (I(q,0) I(q,\tau)) \rangle = N \langle [\delta e(q,0) \delta e(q,\tau)]^2 \rangle + N^2 \langle [\delta e(q,0)]^2 \rangle \langle [\delta e(q,\tau)]^2 \rangle \rangle \quad (1)$$

where $\delta e(q,\tau)$ is the spatial Fourier transform of $\delta e(r,t)$ and $N$ is the number of coherence area on the detector surface (i.e., the number of speckle spots). The coherence loss of the scattered intensity is given by the first term of the right-hand side of eq 1. Assuming that the fluctuations in the local dielectric tensor have Gaussian statistics, we simply have

$$|C(q,\tau)|^2 = \langle [\delta e(q,0) \delta e(q,\tau)]^2 \rangle = \sum_i A_i \exp(-\Omega_i \tau) \rangle \quad (2)$$

Each exponentially decaying function of time, $A_i \exp(-\Omega_i \tau)$, corresponds to one of the relaxation processes of the sample.
associated with the fluctuations in the local dielectric tensor. The frequency characterizing the time decay of the function is the characteristic frequency of the given relaxation process. Both density and temperature fluctuations relax too quickly to be observed in this kind of experiment; therefore, only concentration fluctuations and translational and reorientational diffusion of “molecules” are measured.

In this paper, both polarized and depolarized quasi-elastic light scattering experiments are presented, since, in the systems we investigate, further information on the physical origin of the observed relaxation processes can be obtained through analysis of the polarization state of the scattered light. Polarized light scattering experiments provide information about the scattered light, which has a polarization state parallel to that of the incoming beam. In that case, QELS experiments probe the relaxation of fluctuations of all quantities that are related to the local dielectric tensor (i.e., concentration and optical anisotropy). On the other hand, depolarized light scattering experiments analyze the scattered light, which has a polarization state perpendicular to that of the incoming beam. In that case, measurements are sensitive to the anisotropic part of the local dielectric tensor, and therefore, QELS experiments only probe the relaxation of fluctuations of quantities that are related to this anisotropic part, namely, optical anisotropy fluctuations.27

IV. Results

(a) 8CB/PS Phase Diagrams. Parts a and b of Figure 1 present the equilibrium phase diagrams, temperature versus 8CB weight fraction, of 8CB/PS mixtures for PS with a molecular weight of 4750 and 65 000 g/mol, respectively. The phase diagrams are very different.

For mixtures with PS 4750 (Figure 1a), the phase diagram shows three distinct regions: isotropic (I), nematic + isotropic (N + I), and smectic + isotropic (Sm + I). In the upper region of the phase diagram, a single phase is observed where 8CB and PS form a homogeneous isotropic solution (I); PS chains are dissolved in 8CB solvent. Increasing the polymer concentration allows stabilization of this homogeneous isotropic phase to lower temperatures (i.e., the liquid crystalline phases are destroyed upon an increase of the polymer concentration). For compositions with a 8CB weight fraction larger than 50% (i.e., PS weight fraction ≤0.55), one observes the first transition line, which has an “asymmetric bell” shape, between the homogeneous isotropic phase and a biphasic region in which a rich 8CB phase in the isotropic state and drops of PS are at equilibrium. Increasing the polymer concentration between 0 and 10% destabilizes the homogeneous isotropic phase, whereas increasing the polymer concentration above 10% allows stabilization of this homogeneous isotropic phase to lower temperatures. The temperature of the (I)-to-(I + I) phase separation is always lower than that of the isotropic-to-nematic phase transition in pure 8CB.

(b) PCS Results. In both the VV and VH configurations, the observed value of the signal-to-noise ratio, namely, \( \langle |0(\Delta t)|^2 \rangle / \langle |0(0)|^2 \rangle \), is always in the range 1.1–1.5. This indicates that the dynamic part of the scattered signal is important compared to its static part and, hence, that the signal corresponds to homodyne detection.

Polarized Scattering Experiments (VV Configuration). All autocorrelation functions of the scattered intensity that are measured in the VV configuration have the same features. We always clearly observe three separated relaxation processes with very different relaxation times, as can be seen in Figure 2. Therefore, we analyze the autocorrelation functions with a test function which is the square of a sum of three exponential

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The phase diagram for 8CB/PS mixtures with \( M_w = 65 000 \) g/mol (Figure 1b) indicates an upper critical solution temperature shape and is asymmetric. The critical point is located at 85% 8CB by weight and a temperature of \( T_c = 62 \) °C. This phase diagram exhibits three phase transition lines, and four different regions are clearly identified in this diagram: the homogeneous isotropic (I), isotropic + isotropic (I + I), nematic + isotropic (N + I), and smectic + isotropic (Sm + I) phases. Here again, in the upper region of the phase diagram, a single phase is observed where 8CB and PS form a homogeneous isotropic solution (I); PS chains are dissolved in 8CB solvent. For compositions with a 8CB weight fraction larger than 45% (i.e., PS weight fraction ≤0.55), one observes the first transition line, which has an “asymmetric bell” shape, between the homogeneous isotropic phase and a biphasic region in which a rich 8CB phase in the isotropic state and drops of PS are at equilibrium. Increasing the polymer concentration between 0 and 10% destabilizes the homogeneous isotropic phase, whereas increasing the polymer concentration above 10% allows stabilization of this homogeneous isotropic phase to lower temperatures. The temperature of the (I)-to-(I + I) phase separation is always lower than that of the isotropic-to-nematic phase transition in pure 8CB.
separated relaxation processes with very different relaxation times. The magnitude. Contrary to the two other magnitudes, the largest one, within the range 40–16256 J. Phys. Chem. B, Vol. 109, No. 34, 2005.

\[ |C(t)|^2 = (A_F^{VV} \exp(-\Omega_F^{VV} t) + A_1^{VV} \exp(-\Omega_1^{VV} t) + A_S^{VV} \exp(-\Omega_S^{VV} t))^2 \] 

where \( A_F^{VV}, A_1^{VV}, \) and \( A_S^{VV} \) are the respective magnitudes of these three modes and \( \Omega_F^{VV}, \Omega_1^{VV}, \) and \( \Omega_S^{VV} \) are their frequencies. All measured autocorrelation functions fit very well to eq 3, which gives access to the magnitude and frequency of each mode. For all mixtures and temperatures, whatever the investigated wave vector \( \mathbf{q} \), several measurements of the autocorrelation function are carried out (typically 3–4) and the three characteristic frequencies that are associated to this given wave vector are taken as the average over the different measured frequencies.

(i) The characteristic features of the slow mode (\( \lambda_S^{VV} \) and \( \Omega_S^{VV} \)) are the following. First of all, its magnitude is always the largest one, within the range 40–75% of the total signal magnitude. Contrary to the two other magnitudes \( A_F^{VV} \) and \( A_1^{VV} \), \( A_S^{VV} \) increases as the magnitude of the wave vector decreases and seems to increase upon a decrease in temperature. Furthermore, \( A_S^{VV} \) seems to increase with PS concentration but seems to be independent of the molecular weight.

(ii) For the intermediate mode (\( A_1^{VV} \) and \( \Omega_1^{VV} \)), one observes that its magnitude seems to be independent of temperature and does not vary with the magnitude of the wave vector. Moreover, \( A_1^{VV} \) increases with both concentration and molecular weight. For every mixture and temperature, whatever the wave vector \( \mathbf{q} \), the discrepancy between the different measured frequencies is rather large (can be up to 20%); hence, it is difficult to obtain accurate values of \( \Omega_1^{VV} \). The main reason for this is that precise measurement of such low frequencies requires noise-free autocorrelation functions at long times that are very difficult to obtain because the acquisition time (i.e., the measurement duration) that is necessary to obtain good statistics at long times is very long (a few minutes). During that period, many events can occur (dusts in the index-matching liquid passing through the incoming laser beam, small fluctuations of the incoming laser beam intensity, electrical noises, etc.) that pollute the autocorrelation functions at long times, which hinders precise measurement of \( \Omega_1^{VV} \). Nevertheless, despite the lack of accuracy, it can be observed that \( \Omega_S^{VV} \) is independent of the wave vector magnitude (Figure 3) and increases with temperature (Figure 4), which seems to be reasonable, as the sample viscosity decreases upon an increase in temperature. \( \Omega_2^{VV} \) is about 1 order of magnitude higher for mixtures with 10% PS 4750 and 10% PS 65 000 than for the other mixtures for which this frequency seems to be constant whatever the molecular weight and concentration.

(iii) For the fast mode (\( A_2^{VV} \) and \( \Omega_2^{VV} \)), the magnitude seems to be independent of temperature and wave vector magnitude but decreases as the concentration and/or molecular weight increases; for the mixture with 10% PS 4750, \( A_F^{VV} \) is about one-third of the total signal magnitude, whereas it is just 3% of the total signal magnitude for the mixture with 40% PS 65 000. For PS 4750, we observe that \( A_2^{VV} \) is always larger than \( A_1^{VV} \), while \( A_S^{VV} \) is always smaller than \( A_1^{VV} \) for PS 65 000. For every mixture and temperature, whatever the wave vector \( \mathbf{q} \), the discrepancy between the different measured frequencies is rather
Figure 5. Characteristic frequency of the intermediate mode versus \( q^2 \) observed in the mixture with 30% PS 12 500 at various temperatures \((T = 55, 52, 50, 48, 46, 45, 44, 43, 42.5, \) and \(42.1 \, ^\circ C)\). We observe that this mode is always diffusive \((\omega \propto q^2)\), and from the slope of the straight line, we obtain the cooperative diffusion coefficient according to the formula \( \omega = D_c q^2 \).

Figure 6. Characteristic frequency of the fast mode as a function of the square of the wave vector: \((\bullet)\) \( \Omega_V^V \) (VV configuration); \((\odot)\) \( \Omega_F^V \) (VH configuration), for the mixture with 40% PS 65 000 at \( T = 64 \, ^\circ C \). The line corresponds to the average value of \( \Omega_F \).

Figure 7. Average value of the characteristic frequency of the fast mode, \( \Omega_F \), as a function of the inverse of temperature, for the different investigated mixtures: \((\bullet)\) 40% PS 65 000; \((\Delta)\) 30% PS 65 000; \((\triangledown)\) 10% PS 65 000; \((\ast)\) 30% PS 12 500; \((\odot)\) 50% PS 4750; \((\triangle)\) 30% PS 4750; \((\triangledown)\) 10% PS 4750. The lines correspond to the fits of \( \Omega_F \) to Arrhenius law.

Figure 8. Measured \( |C(q,t)|^2 \) in the depolarized (VH) configuration (i.e., \( |C^V(q,t)|^2 \)): \((\bullet)\) measurement taken at \( \theta = 90^\circ \) on the mixture with 10% PS 65 000 \((T = 68 \, ^\circ C)\); \((\odot)\) measurement taken at \( \theta = 90^\circ \) on the mixture with 50% PS 4750 \((T = 42 \, ^\circ C)\). We clearly observe two separated relaxation processes with very different relaxation times. The lines correspond to the fits of \( |C(q,t)|^2 \) to eq 4. \( |C^V(q,t)|^2 \) is obtained from the measured autocorrelation function as follows:

\[ |C(q,t)|^2 = (\langle I(q,t) \rangle - \langle I(q,\infty) \rangle) \langle I(q,\infty) \rangle \langle I(q,t) \rangle. \]

Figure 9. Measured \( |C(q,t)|^2 \) in the polarized (VV) configuration on pure 8CB measurement taken at \( \theta = 90^\circ \) and at \( T = 55 \, ^\circ C \). The line corresponds to the fit of \( |C(q,t)|^2 \) to the square of a sum of two exponential decaying functions of time (eq 4).

an increase in temperature). \( \Omega_F^V \) decreases as \( M_w \) increases, and it can be seen that, for PS 4750, \( \Omega_F \) decreases as the PS concentration increases, while, for PS 65 000, \( \Omega_F^V \) seems to be the same for all concentrations.
where $A$, the autocorrelation functions with a test function which is the
we clearly observe two separated relaxation processes with very
measured in the VH configuration have the same features. Here,
and slow modes (Figures 3 and 6). Furthermore,
A as those that are measured in the VV configuration for the fast
modes are independent of $A$.

Depolarized Scattering Experiments (VH Configuration). All
autocorrelation functions of the scattered intensity that are
measured in the VH configuration have the same features. Here,
we clearly observe two separated relaxation processes with very
different relaxation times, as can be seen in Figure 8. We analyze the
autocorrelation functions with a test function which is the
square of a sum of two exponential decaying functions of time,
that is,

$$
|C^{VH}(q,t)|^2 = (A_{1}^{VH} \exp(-\Omega_{1}^{VH} t) + A_{2}^{VH} \exp(-\Omega_{2}^{VH} t))^2
$$

where $A_{1}^{VH}$ and $A_{2}^{VH}$ are the respective magnitudes of these two
modes and $\Omega_{1}^{VH}$ and $\Omega_{2}^{VH}$ are their frequencies. All measured
autocorrelation functions fit very well to eq 4, which gives access to the magnitude and the frequency of both modes. These
two modes are independent of $q$ and have similar frequencies
as those that are measured in the VV configuration for the fast and slow modes (Figures 3 and 6). Furthermore, $A_{1}^{VH}$ and $A_{2}^{VH}$
behave the same way as $A_{1}^{VV}$ and $A_{2}^{VV}$, respectively. Therefore, we can conclude that the fast and slow modes, which are
observed in the VV configuration, are preserved in the VH configuration, whereas the intermediate mode disappears.

Thus, to summarize our results, we observe three modes in
the VH configuration and two in the VV configuration. In the
VV configuration, two modes are independent of $q$, while the
third one is diffusive. In the VH configuration, we only observe the
two modes that are independent of $q$, with the diffusive
to the scattered signal cannot be ignored. To the best of our knowledge, a theory describing the dynamic light scattering by dispersions of polymer chains in a solvent made up of “large” anisotropic molecules does not exist. The first
and simplest approach to describe this is to separate the contribution arising from polymer chains from that of the
anisotropic solvent, that is, assuming that there is no coupling
between the relaxation processes of polymer chains and those of
the solvent. Therefore, one can write

$$
\delta \epsilon(\vec{r}, t) = \delta \epsilon_{\text{pol}}(\vec{r}, t) + \delta \epsilon_{8CB}(\vec{r}, t)
$$

where $\delta \epsilon_{\text{pol}}(\vec{r}, t)$ is the “polymer” contribution to the fluctuations of $\epsilon$ and $\delta \epsilon_{8CB}(\vec{r}, t)$ is the contribution coming from the molecules of the solvent. In the simplest framework, the polymer contribution originates from two different processes: one depending on the polymer concentration that is related to the diffusion of polymer chains through the solution and a second one that is
due to intermolecular motions, that is, fluctuations of the
orientation of the Kuhn segments (or Rouse). The solvent
contribution arises from both the translational diffusion through the
solution and the reorientational motion of 8CB molecules.

Polymer Contribution. First of all, we briefly present the basic
theory for dynamic light scattering by polymer/isotropic solvent
solutions with $qR_{g} \ll 1$. In the so-called dilute regime, in which
polymer chains do not overlap (concentration below $c^*$), the
solutions can be considered as a dispersion of particles in a
solvent (i.e., similar to a colloidal solution). Then, theory predicts a
diffusive relaxation mode due to the translational diffusion
of polymer chains that can be observed only in the VV configuration. 

The characteristic relaxation time of this mode is simply given by $\tau_{d} = (Dq^2)^{-1}$, where $D$ is the translational
diffusion coefficient of a single polymer chain. This diffusion
coefficient is given by $D = f(c)k_{B}T/6\pi\eta_{s}R_{g}$, with $\eta_{s}$ being the
solvent viscosity, $R_{g}$ the radius of gyration, and $f(c)$ a function of polymer concentration that accounts for the interactions
between the polymer chains: $f(c) \approx (1 + [k'_{D} - 1]/c - k_{D}c^2)$, where $k_{D}^* is the dynamic virial coefficient for polymer solvent (i.e., similar to a colloidal solution). Then, theory predicts a
diffusive relaxation mode due to the translational diffusion
of polymer chains that can be observed only in the VV configuration.

A second mode of relaxation also exists that can give a
depolarized contribution and which arises from orientation
fluctuations of Kuhn segments due to conformation fluctuations of the polymer chains $27,28$ (Kuhn segments are rodlike objects, optically anisotropic). For $qR_{g} \ll 1$, this latter mode is
independent of the magnitude of the wave vector and its
characteristic relaxation time is given by the terminal Rouse
time for dilute solutions, $\tau_{\text{Rouse}}$. In theta solvent, this time
is given by the Rouse–Zimm model and is equal to $\tau_{\text{Rouse}} = \tau_{0}^{\text{Rouse}}(1 + \alpha c)$, with $\tau_{0}^{\text{Rouse}} \approx 0.325\eta_{s}R_{g}^2/k_{B}T^{1.3}$
and $\alpha$ being a constant depending on the excluded volume effect
and $R_{g}$. In all cases, $\tau_{\text{Rouse}}$ is much shorter than $\tau_{d}$; in our case, for the
mixtures with PS 4750, according to simple estimations, we
expect $\tau_{\text{Rouse}}$ to be of the order of $10^{-6}$–$10^{-3}$ s, while $\tau_{d}$ should
be within the range $10^{-3}$–$10^{-2}$ s. Therefore, for dilute solutions,
in the VV configuration, the polymer contribution should give
two relaxation modes well separated in time: a fast mode
independent of $q$ and a much slower diffusive mode, with the fast
relaxation mode remaining in the VH configuration.

$$
C_{\text{pol}}^{VH}(q,t) = B_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}})
$$

and

$$
C_{\text{pol}}^{VH}(q,t) = B_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}})
$$

V. Discussion

(a) Theoretical Concepts for Dynamic Light Scattering
by 8CB/PS Mixtures. QELS experiments performed on pure
8CB at 55 °C show two relaxation processes in the VH configuration (Figure 9). The fast mode is $q$ independent and has a characteristic frequency of the order of $(7-6) \times 10^5$ s$^{-1}$, while the slow mode is diffusive, with a diffusion coefficient
equal to $(4.6 \pm 0.5) \times 10^{-11}$ m$^2$ s$^{-1}$. Moreover, we observe that the magnitude of the fast mode is larger than that of the slow mode. In the VH configuration, only the fast mode remains.

Therefore, contrary to dynamic light scattering by polymer chains in a solvent made up of “small” isotropic molecules (such as water or toluene, for example), in our case, the solvent
Usually, $\kappa_{\text{Rouse}}$ and $R_{\text{Rouse}}$ are very weak, and therefore, often, the “Rouse” mode is not observable experimentally.

In the semidilute regime (concentration above $c^*$), polymer chains overlap and form a transient network that gives these systems viscoelastic properties. Taking into account the viscoelastic characteristics of these systems, theoretical models predict two modes for the relaxation of fluctuations of concentration $\delta\phi(q,t)$:

$$\langle \delta\phi(q,0) \delta\phi(q,t) \rangle = A_1 \exp(-t/\tau_1) + A_s \exp(-t/\tau_s)$$

where $\tau_1$ and $\tau_s$ are the fast and slow relaxation times, respectively. There are two characteristic regimes: the liquid regime and the gel regime, both of which are related to the “viscoelastic” time of the system, that is, the terminal time of the reptation process, $\tau_{\text{rep}}$. If $\tau_{\text{rep}}$ is shorter than the “diffusion” time, that is, the classical relaxation time of fluctuations of concentration in binary mixtures, $\tau_c$, then the system is in the liquid regime. (Preliminary rheological experiments we performed show that in our mixtures $\tau_{\text{rep}}$ is always shorter than $10^{-4}$ s, while QELS results show relaxation times that are always longer than $10^{-3}$ s; therefore, in our experiments, we only probe the liquid regime.) In that case, according to the models, the fast mode has a magnitude of $A_1$ that vanishes while its characteristic relaxation time $\tau_1$ is independent of the magnitude of the wave vector $q$ and is equal to $\tau_{\text{rep}}$. The slow mode, on the other hand, is a diffusive mode, the characteristic time of which is monitored by the osmotic compressibility of the solution. This is the classical diffusive mode, which is associated with the relaxation of fluctuations of concentration in binary mixtures (i.e., cooperative diffusion of polymer chains). Thus, $\tau_c^{-1} = \tau_1^{-1} = D_\xi/\chi_c$ where $D_\xi$ is the cooperative diffusion coefficient of fluctuations of concentration. According to the hydrodynamic theory of binary fluids, it is given by $D_\xi \propto \xi^2/\eta \chi$ where $\chi$ is the osmotic compressibility of the mixture and $\xi$ the correlation length of concentration fluctuations. As we assume that the polymer is in theta solvent, $D_\xi$ can be rewritten as a function of polymer concentration as follows: $D_\xi \propto \eta_a^2 \eta / \chi$. Therefore, in QELS experiments, in the VV configuration, one expects to observe a single diffusive relaxation mode arising from the cooperative diffusion of polymer chains. Furthermore, as in dilute solutions, a mode also exists which arises from orientation fluctuations of Kuhn segments and that gives a depolarized contribution. This latter mode is independent of the magnitude of the wave vector, and its characteristic time is given by the terminal Rouse time for semidilute solutions, $\tau_{\text{Rouse}}$, which is given by $\xi^2 \eta_a^2 / \eta \chi$. As $\xi^2 \sim \kappa^2 / \eta \chi$, we expect $\tau_{\text{Rouse}}$ to decrease with concentration: $\tau_{\text{Rouse}} \propto \eta / \eta_a$. Moreover, $\tau_{\text{Rouse}}$ is always shorter than $\tau_{\text{rep}}$; thus, we have $\tau_s \gg \tau_{\text{Rouse}}$. Hence, for semidilute solutions, in the VV configuration, the polymer contribution should give two relaxation modes well separated in time, a fast mode independent of $q$ and a diffusive slow mode, and in the VH configuration, only the fast relaxation mode remains:

$$C_{\text{pol}}^{\text{VV}}(q,t) = A_1 \exp(-t/\tau_1) + A_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}})$$

and

$$C_{\text{pol}}^{\text{VH}}(q,t) = B_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}})$$

Usually, $A_{\text{Rouse}}$ and $B_{\text{Rouse}}$ are weak and the Rouse mode is not observable experimentally.

$8CB$ Contribution. We believe that the diffusive mode arises from the translational diffusion of $8CB$ molecules through the solution. Indeed, our experimental measurement is in good agreement with what is expected for the translational diffusion coefficient of $8CB$ molecules. The translational diffusion coefficient of $8CB$ molecules can be estimated using the following formula: $D_{8CB}^T = k_B T \ln(L/d) / \eta_{8CB}$, where $\eta_{8CB}$ being the $8CB$ viscosity and $L$ and $d$ being the length and diameter of $8CB$ molecules, respectively. For $55^\circ$C, we find $D \approx 2.6 \times 10^{-11}$ m$^2$ s$^{-1}$ (in the temperature range we probe, we expect $D_{8CB}^T$ to be within the range $1.5 \times 10^{-11}$ to $6 \times 10^{-11}$ m$^2$ s$^{-1}$). Moreover, the diffusion coefficient of fluorescence probes (molecules smaller than $8CB$) in $8CB$ was measured and found to be of the order of $(1-2) \times 10^{-11}$ m$^2$ s$^{-1}$, again in good agreement with our data.

According to its features, the fast mode is likely to be due to reorientations of the $8CB$ molecules. Nevertheless, this mode does not correspond to the reorientational dynamics of $8CB$ molecules in the isotropic phase. Far from the isotropic-to-nematic phase transition, the characteristic time for the reorientational dynamics of $8CB$ molecules is found, using NMR or dielectric relaxation measurements, to be of the order of $10^{-9}$ s, again much shorter than what we observe. However, $8CB$ molecules are known to form transient bichromes, that is, “pseudonematic domains”, even far from the isotropic-to-nematic phase transition and the reorientational dynamics of these domains is much slower than that of single molecules (typically 3 orders of magnitude slower). We believe that the fast mode originates from the reorientation of pseudonematic domains. Hence, the contribution of $8CB$ molecules can be written as:

$$C_{8CB}^{\text{VV}}(q,t) = B_{8CB} \exp(-D_{8CB}^T q^2 t) + \xi_{8CB}^V \exp(-6D_{8CB}^R q^2 t)$$

and

$$C_{8CB}^{\text{VH}}(q,t) = S_{8CB} \exp(-6D_{8CB}^R q^2 t)$$

with $\xi_{8CB}^V \gg B_{8CB}$ and $D_{8CB}^R \gg D_{8CB}^T$ ($D_{8CB}^R$ is the rotational diffusion coefficient of the pseudonematic domains).

$8CB$/PS Mixtures. Therefore, in this simple framework, assuming that $B_{8CB}$ is much weaker than the magnitudes of the other modes, for $8CB$/PS mixtures, in the VH configuration, we expect to measure an autocorrelation function that is the sum of three modes: two fast modes independent of the magnitude of the wave vector, one originating from reorientational motions of $8CB$ bunches and the other from orientation fluctuations of Kuhn segments, and one diffusive mode, much slower than the two others, which is due to the diffusion of polymer chains. Depending on the polymer concentration, we should have

(dilute solutions)

$$C_V^{\text{VV}}(q,t) = A_d \exp(-t/\tau_d) + A_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}})$$

$A_d \exp(-t/\tau_{\text{Rouse}}) + \xi_{8CB}^V \exp(-6D_{8CB}^R q^2 t)$

and

$$C_V^{\text{VH}}(q,t) = A_d \exp(-t/\tau_d) + \xi_{8CB}^V \exp(-6D_{8CB}^R q^2 t)$$

In the VH configuration, the measured autocorrelation function should be bimodal, only with the relaxation modes that are due to reorientational motions:

(dilute solutions)

$$C_V^{\text{VV}}(q,t) = B_{\text{Rouse}} \exp(-t/\tau_{\text{Rouse}}) \exp(-t/\tau_{\text{Rouse}})$$

$$S_{8CB} \exp(-6D_{8CB}^R q^2 t)$$
(semidilute solutions) \[ C^{\text{VH}}(q,t) = B_{\text{Rouse}}^{\text{vd}} \exp(-t/\tau_{\text{Rouse}}^{\text{vd}}) + \]
\[ \eta_{\text{8CB}}^{\text{VH}} \exp(-6D_{\text{8CB}}^{\text{pol}} t) \] (11)

(b) Comparison with Experimental Results. In the VV configuration, three modes are observed, two modes independent of \( q \) and one diffusive, while, in the VH configuration, the diffusive mode disappears and only both modes independent of \( q \) remain. Furthermore, one of the \( q \) independent modes has a characteristic time which is much longer than those of the diffusive mode. This result is quite puzzling, and at first sight, the simple considerations we present above do not describe our results well.

Long Relaxation Time. This mode is independent of the wave vector magnitude and is observed both in the VV and VH configurations; thus, we conclude that it is due to reorientational motions of objects. The magnitude of this mode is large and increases as the magnitude of the wave vector decreases, and moreover, its relaxation frequency is slow; these features suggest that this mode is due to the reorientation of large objects (much larger than PS chains and 8CB molecules). However, these objects must be smaller than a few microns, since we do not see them in optical microscopy. Using the hydrodynamic theory of Tirado and García de la Torre for dilute solutions of rodlike aggregates, the rotational diffusion coefficient is given by
\[ D_{R} \approx \frac{3k_{B}T}{\pi \eta_{m} L} \left[ \ln \left( \frac{L_{d}}{d} \right) - 0.662 + 0.917 \frac{d}{L_{d}} \right] \] (12)
where \( \eta_{m} \) is the mixture viscosity (as these objects are assumed to be large, we must use the mixture viscosity and not the 8CB viscosity) and \( L \) and \( d \) are the length and diameter of these objects, respectively. Estimating the mixture viscosity as a function of concentration and molecular weight and assuming that the axial ratio, \( L/d \), is equal to 10, we find \( L \) in the range 300–900 nm; while using \( L/d = 2 \), we obtain \( L \) in the range 150–500 nm. Thus, such low frequencies can give anisotropic objects smaller than 1 \( \mu \)m. Therefore, this mode is due to reorientational processes of “impurities,” the size of which is of the order of a few hundred nanometers.

The behaviors of both the relaxation frequency and magnitude of this mode with concentration and molecular weight (Figure 7) suggest that this mode depends on the way the mixtures were prepared. Thus, these impurities could be dusts, with the samples being polluted with dusts when the capillaries are filled up. However, this mode is not observed in demixed mixtures; this feature makes us believe that this slow mode might be due to reorientational motions of nondissolved particles of PS (solid particles still in the glass state) in the mixtures.

Diffusive Mode: Concentration Effects. The diffusive mode is easy to assign; this is the classical diffusive mode, which is associated with the diffusion of polymer chains in all polymer solutions. Analysis of this mode allows the measurement of \( D \) in the dilute regime or \( D_{c} \) in the semidilute regime. In Figure 10, we display the values of the product \( \eta_{\text{8CB}}D_{\text{pol}}^{\text{diff}} \) (i.e., \( \eta_{\text{8CB}}D_{c} \) or \( \eta_{\text{8CB}}D_{c} \)) versus the inverse of temperature, for all the measured values of \( D_{c} \). The multiplication of the diffusion coefficient \( D_{c} \) by \( \eta_{\text{8CB}} \) takes into account the variation of the solvent viscosity with temperature. First of all, one notices that \( \eta_{\text{8CB}}D_{c}^{\text{pol}} \) increases as the temperature increases. For all mixtures, the dependence of \( \eta_{\text{8CB}}D_{c}^{\text{pol}} \) with temperature exhibits Arrhenius behavior: \( \eta_{\text{8CB}}D_{c}^{\text{pol}} = A \exp(-E_{D}/RT) \), where \( E_{D} \) is an energy of activation. The different activation energies determined from the Arrhenius plots are listed in Table 1. \( E_{D} \) depends on the PS molecular weight (it increases with \( M_{w}, E_{D}(M_{w}) \approx \ln(M_{w}) \) but does not seem to vary much with polymer concentration.

For mixtures made up of PS 65 000, we are in the semidilute regime; thus, \( D_{\text{pol}}^{\text{diff}} \) is equal to \( D_{c} \). One observes that the value of \( D_{c} \) increases with polymer concentration (Figures 10 and 11). This result is in agreement with what is usually observed for polymer solutions in the semidilute regime; the increase of \( D_{c} \) with concentration results from the fact that the restoring force for the concentration fluctuations (i.e., the osmotic pressure) is larger at higher concentrations. However, whatever the temperature, one can see (Figure 11) that \( D_{c} \) does not increase linearly with concentration. Rather, the variation of \( D_{c} \) with concentration is described by a polynomial function of \( c \) (like in colloids). This suggests that PS chains in 8CB are not in theta solvent and they are not in good solvent either; then, \( D_{c} \) should increase with concentration as \( \exp(\theta c) \), which is not the case (see the inset of Figure 11). The observed increase in \( D_{c} \) with concentration is below that expected for polymer in theta or good solvent; therefore, our results suggest that the value of the Flory–Huggins parameter, \( \chi_{\text{8CB}} \), is much likely to be larger than \( 1/2 \); that is, PS chains in 8CB are rather in (weak) poor solvent. Furthermore, we assume that the decrease of \( \eta_{\text{8CB}}D_{c} \) upon a decrease in temperature originates from an increase in the attractive interactions between the polymer chains. This latter assumption is compatible with the approach of a phase separation.

For mixtures made up of PS 4750, samples with 10 and 30% PS are in the dilute regime and that with 50% is just above \( c^{*} \); thus, \( D_{\text{pol}}^{\text{diff}} \) is equal to \( D_{c} \). The decrease of \( \eta_{\text{8CB}}D_{c} \) as the temperature decreases can originate from an increase of the radius of gyration and/or a decrease in \( f(c) \) that could be due to an increase in the attractive interactions between the polymer

<table>
<thead>
<tr>
<th>PS Mw</th>
<th>PS conc (in % by weight)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4750</td>
<td>10</td>
<td>40.6 ± 5.4</td>
</tr>
<tr>
<td>4750</td>
<td>30</td>
<td>50.4 ± 5.9</td>
</tr>
<tr>
<td>4750</td>
<td>50</td>
<td>39.3 ± 5.5</td>
</tr>
<tr>
<td>12 500</td>
<td>30</td>
<td>78.5 ± 6.8</td>
</tr>
<tr>
<td>65 000</td>
<td>10</td>
<td>95.9 ± 8.1</td>
</tr>
<tr>
<td>65 000</td>
<td>30</td>
<td>97.5 ± 7.8</td>
</tr>
<tr>
<td>65 000</td>
<td>40</td>
<td>105.5 ± 8.5</td>
</tr>
</tbody>
</table>

Figure 11. Values of the cooperative diffusion coefficient, \( D_{c} \), as a function of PS concentration, for the mixtures made up of PS 65 000, at different temperatures: (○) \( T = 62 ^{\circ} C \); (○) \( T = 64 ^{\circ} C \); (●) \( T = 66 ^{\circ} C \); (△) \( T = 68 ^{\circ} C \); (◆) \( T = 70 ^{\circ} C \); (◇) \( T = 72 ^{\circ} C \). Inset: \( D_{c} \) vs PS concentration in log–log plot; the dashed line corresponds to \( \exp(\theta c) \). The values of \( D_{c} \) displayed here are calculated using the Arrhenius law with the parameters obtained from the fits of the experimental results.

TABLE 1: Activation Energy Determined from the Temperature Dependence of the Product \( \eta_{\text{8CB}}D_{\text{pol}}^{\text{diff}} \) for the Different 8CB/PS Mixtures (Arrhenius Plot, e.g., Figure 10)
chains. Furthermore, we observe that $D$ decreases as the polymer concentration increases (Figures 10 and 12). Here again, this result is in agreement with what is usually observed for polymer solutions in the dilute regime. With the increase in concentration, the friction between the polymer chains increases, leading to a decrease of $D$. One can see that the variation of $D$ with the concentration is all the more important that temperature is higher (Figure 12). Such behavior is not compatible with an increase in the radius of gyration upon a decrease in temperature. In that case, friction between the polymer chains should be larger and thus the values of $D$ should decrease more as the concentration increases. Hence, one can imagine that the attractive interaction between the polymer chains increases as the temperature decreases, which is in agreement with the conclusions made for PS 65 000.

Furthermore, one can also notice that $D_c$ depends on the molecular weight (Figure 10). This feature supports the idea that PS chains in 8CB solvent are rather in poor solvent (in good and theta solvent, $D_c$ is independent of $M_w$). One can imagine that the attractive interactions, which exist between PS chains in 8CB, are an explanation for the presence of PS aggregates in the 8CB/PS mixtures.

**Short Relaxation Time.** According to the features of this mode, we can conclude that it is due to the reorientational motion of small objects that can be either 8CB or Kuhn segments. The characteristic frequency of this mode is at least 1 order of magnitude lower than what we measure in pure 8CB. However, for Kuhn segments, we expect the magnitude of this mode to increase with polymer concentration and we observe the opposite. In the dilute regime, its characteristic frequency should decrease as the concentration increases, while it should increase with concentration in the semidilute regime. We observe that $\Omega_R$ decreases as the PS concentration increases. These features are not compatible with a signal arising from the reorientational motion of Kuhn segments. It has already been seen that the presence of PS chains slows the reorientation process of anisotropic molecules such as dioctyl phthalate (DOP) by several orders of magnitude. Hence, we can imagine that PS chains slow the reorientation of 8CB as well and make $D_{8CB}^R$ decrease as the concentration, or molecular weight, increases in the 8CB/PS mixtures. Therefore, we assign this fast mode to the rotational diffusion of 8CB. We believe that we cannot observe the Rouse mode because its magnitude is too weak. Furthermore, one can notice that the dependence of $\Omega_F$ with temperature exhibits Arrhenius behavior (Figure 7), which seems the same for all mixtures, with an energy of activation equal to $24.3 \pm 1.65$ kJ/mol.

This result shows that the reorientational motion of 8CB molecules is strongly affected by the presence of polymer chains; its characteristic time is indeed increased by at least 1 order of magnitude. Several phenomena are well-known for slowing down the reorientational process of liquid crystal molecules in the isotropic state: first of all, the approach of the isotropic-to-nematic transition, confinement, and partial ordering by a solid substrate. For example, a NMR study of LC molecules in a polymerized solid matrix showed that polymer solid interfaces weakly orient LC molecules at their surface (the nematic order parameter is small, $S \sim 0.1$). Nevertheless, this weak order strongly affects the LC molecule dynamics, leading to an increase of the reorientational time by at least 4 orders of magnitude, even far away from the isotropic-to-nematic transition. In our experiments, there is no evidence of any effect of the approach of the isotropic-to-nematic transition. Thus, the increase of the reorientational relaxation time of 8CB that is observed in our experiments could originate from a partial ordering of 8CB molecules by polymer chains. Even if the polymer chains do not form a solid substrate, they might order 8CB molecules. However, one can think to another explanation for this decrease that would be the increase in the viscosity that 8CB bunches experience during their reorientational motions due to the presence of PS chains (in the mixtures we investigate, the mean distance between polymer chains, within the range $4-10$ nm, is of the order of magnitude of the 8CB molecule length). This “local” effective viscosity can be estimated using the relation $D_{8CB}^R \approx 3k_B T \ln(L/d_h)/4\pi\eta_{local}L^2$. The value of $\eta_{local}$ found within the range 1–2 Pa·s, increase with concentration and molecular weight, but they do not correspond to the macroscopic viscosity of the mixtures. (According to the preliminary rheological experiments we performed, $\eta_{local}$ is too high for mixtures with PS 4750 and too low for mixtures with PS 65 000.)

**VI. Summary**

With the help of both polarized and depolarized photon correlation spectroscopy, we have investigated the relaxation processes of 8CB/PS mixtures in their homogeneous isotropic phase, as a function of temperature, approaching the phase separation. Whatever the experimental conditions, temperature, composition, and molecular weight, we have always observed the same features. In polarized PCS experiments, we always see three relaxation processes well separated in time: one, very fast, with a relaxation time of the order of $10^{-5}$ s; a second one with a relaxation time within the range $10^{-2}-10^{-3}$ s; and a last one, very slow, with a relaxation time of the order of 1 s. Both the fast and slow modes are independent of the wave vector magnitude, while the intermediate relaxation process is diffusive. In depolarized PCS experiments, the intermediate mode disappears and only the fast and slow relaxation processes remain, and they are independent of the magnitude of the wave vector.

(i) The diffusive mode is the classical diffusive mode, which is associated with the diffusion of polymer chains in all polymer solutions. From its analysis, we can obtain information on the thermodynamics of these mixtures. We conclude that PS chains in 8CB are rather in poor solvent, with the solvent quality getting worse and worse with decreasing temperature.

(ii) We assign the fast mode to the rotational diffusion of 8CB molecules. Our results show that the reorientational motion...
of 8CB molecules is strongly affected by the presence of polymer chains (the rotational diffusion coefficient of 8CB molecules is reduced by at least 1 order of magnitude). This increase of the reorientational relaxation time of 8CB could originate from a partial ordering of 8CB molecules by polymer chains even if they do not form a solid substrate.

(iii) We do not observe any influence of the proximity of the phase boundaries on the diffusion coefficient of PS in 8CB solvent. The relaxation processes in these mixtures are not affected by the approach of phase separations (isotropic + isotropic, nematic + isotropic, or smectic + isotropic). Therefore, we believe that the phase separation processes in these mixtures are driven by the polymer—polymer interactions and not by ordering of the 8CB molecules.

(iv) Finally, the slow mode could be an artifact (the samples being polluted with dusts when the capillaries are filled up) or, more likely, due to reorientational processes of nondissolved particles of PS (solid particles in the glass state) in the mixtures (PS chains might not dissolve well in 8CB during the mixing of the biphasic solution into a homogeneous isotropic phase because of the bad solvent quality).

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References and Notes

References and Notes


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