Dynamics of Composition Fluctuations in Diblock Copolymer Solutions Far from and Near to the Ordering Transition

T. Jian, S. H. Anastasiadis,*,† A. N. Semenov,‡ and G. Fytas

Foundation for Research and Technology—Hellas, Institute of Electronic Structure and Laser, P.O. Box 1527, 711 10 Heraklion Crete, Greece

K. Adachi and T. Kotaka

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan

Received March 8, 1994; Revised Manuscript Received May 23, 1994®

ABSTRACT: Dynamic light scattering in the polarized geometry has been used to investigate the dynamics of composition fluctuations in solutions of two poly(styrene-*block*-1,4-isoprene) diblock copolymers in a nonselective, good solvent both far from and near to the ordering transition. Four different relaxation mechanisms were identified. One relaxation relates to the cooperative diffusion of copolymer chains, and it behaves similarly to that in semidilute homopolymer solutions. As concentration increases, two additional relaxations gain in amplitude: the wavevector-independent internal or breathing mode, predicted by theory, with amplitude increasing with scattering angle, and the recently established for copolymer melts diffusive relaxation; the relaxation times of both processes increase with copolymer concentration. In addition, another very slow process is evident at low scattering angles and is related to the long-range density fluctuations. A theoretical analysis is presented that predicts the existence and the behavior of the first three relaxations. The new diffusive relaxation is attributed to the composition polydispersity of the diblocks; its intensity is proportional to the degree of polydispersity; its rate is governed by the self-diffusion of the copolymer chains; both its intensity and its relaxation time increase with the copolymer concentration, in contrast to the behavior of the cooperative diffusion.

I. Introduction

Diblock copolymer solutions have long been used to investigate the rich variety and diversity of phase morphologies and the resulting phase transitions in diblock copolymers.[1] For good solvents, the unfavorable interactions between the blocks are diluted by the solvent, and, therefore, the microphase transitions are more easily accessed even for high molecular weight copolymers. The effect of nonselective good solvents on the phase transitions in diblock copolymers has been investigated both experimentally[2] and theoretically.[3-6]

The dynamics of diblock copolymer melts and solutions, and the influence of the disorder-to-order transition (ODT) on the dynamics have only recently attracted the increasing interest of polymer scientists.[7] Theory attempted to derive the intermediate scattering function and its relaxation characteristics for diblock copolymers both in bulk[8,9] and in semidilute solutions[9-11] in the disordered state, as well as to investigate the rheological behavior of disordered diblock copolymers melts.[12] Experimentally, rheological investigations probed the substantial fluctuation enhancement of the shear viscosity and first normal stress coefficients in the pretransitional disordered state near the ODT,[13] with theory only qualitatively capturing the pertinent features. On the other hand, neutron spin-echo,[14] dynamic light scattering in the polarized[10,15-22] and depolarized[22-25] geometry, dielectric relaxation spectroscopy,[23,26-28] forced Rayleigh scattering,[29-31] and forward recoil spectroscopy[32] were utilized to identify the mechanisms of relaxation and diffusion in both disordered and ordered diblock copolymers in the bulk and in solutions in nonselective solvents. In the Background section, we will discuss the experimental and theoretical investigations that have recently appeared on diblock copolymer solution dynamics.

In this paper, we present a polarized dynamic light scattering investigation of the dynamics of composition fluctuations in semidilute solutions of two high molecular weight poly(styrene-*block*-1,4-isoprene) diblock copolymers in a nonselective, good solvent (toluene), in the disordered state, near the ODT, and in the ordered state. This work differs significantly from recent works in the field[17,19] in both the observation and the interpretation of the modes of relaxation in the disordered and ordered diblock copolymer solutions. Four different relaxations were found to contribute to the polarized intensity autocorrelation function in the disordered state: the cooperative diffusion of the physical network formed by the diblock copolymer chains; the internal structural mode predicted by theory with wavevector- (q) independent relaxation rate and a q^2-dependent amplitude; the diffusive relaxation, recently established for copolymer melts, with q^2-dependent rate and q-independent intensity; and a very slow process more pronounced at low scattering angles, that is related to "long-range density fluctuations" or "cluster" relaxation. Both the intensity and the relaxation times of the second and third processes increase with copolymer concentration, in contrast to the behavior for the cooperative diffusion. A theoretical analysis is presented that predicts the existence and the behavior of the first three relaxations, i.e., the cooperative diffusion, the internal relaxation, and the new diffusive process. The intensity of the new process is proportional to the degree of composition polydispersity of the diblocks, while its relaxation rate is governed by the self-diffusion of the copolymer chains. The disorder-to-order transition is accompanied by a significant increase in the polarized light scattering intensity, without affecting significantly the diffusion dynamics. This is attributed to a change in the mechanism of relaxation in the microstructured solution;

* Author to whom correspondence should be addressed.
† Also at Physics Department, University of Crete, 711 10 Heraklion Crete, Greece.
‡ Permanent Address: Physics Department, Moscow State University, 117234 Moscow, Russia.
® Abstract published in *Advance ACS Abstracts*, July 15, 1994.

0024-9297/94/2227-4762$04.50/0

it is still under investigation, and is not discussed here any further.

This article is arranged as follows: in the Background section, the experimental and theoretical investigations on block copolymer dynamics will be reviewed. Following the Experimental Section, the results of the polarized dynamic light scattering investigations are presented in section IV. In section V, the new theoretical approach is presented, and the predictions of the theory are discussed in relation to our experimental data in section VI. Finally, the concluding remarks constitute section VII.

II. Background

The early approach when investigating the phase behavior of diblock copolymer solutions was to adopt the "dilution" or "pseudobinary" approximation,[2] which states that the phase diagram of a solution of a diblock copolymer in a nonselective solvent and its radiation scattering may be obtained by the corresponding melt phase diagram by replacing the Flory–Huggins interaction parameter, χ ($\chi = \chi_S + \chi_H/T$, with $\chi_H > 0$, χ_S constants, and T the absolute temperature), the radius of gyration, R_g [$R_G = (N/6)^{1/2}b$, with N as the overall number of segments, and b the statistical segment length], and the scattering power, $(\alpha - \beta)^2$, by $\phi\chi$, R_G in solution, and $\phi(\alpha - \beta)^2$, respectively, where ϕ is the volume fraction of the polymer in the solution. For the important semidulute regime,[5,6] the blob model assumes that the copolymer chain in a good solvent consists of $N^* \cong N\phi^{1.30}$ blobs with blob correlation length $\xi \propto b\phi^{-0.77}$ that interact with a blob–blob interaction parameter $\chi^* \propto \chi\phi^{0.17}$. The phase diagram is obtained from that in the bulk when N^*, χ^*, and ξ are substituted instead of N, χ, and b. For high concentrations and/or low temperatures (high χ) a long-range coherent periodic microstructure has been obtained[2] with characteristic dimensions in agreement with mean-field strong-segregation theories of copolymer solutions;[4] for low concentration and/or high temperature homogeneous solutions have been observed[2] with the structure factor, $S(q)$, showing the characteristic correlation hole maximum[33] at a wavevector $q^* = O(R_G)$ independent of both ϕ and T and a magnitude increasing with increasing ϕ and/or decreasing temperature, similarly to the behavior of $S(q)$ of homogeneous diblock copolymer melts.

The equilibrium phase morphology of a bulk diblock copolymer is determined by N, the overall volume fraction of segments of one type, f, and the interaction parameter χ; due to both enthalpic and entropic contributions, it is the product χN that dictates the morphology for a certain f. For $\chi N \ll 10$, the copolymers exist in a spatially homogeneous or disordered state.[33] As χN is increased to be $O(10)$, local composition fluctuations are developed that lead to an ODT toward a microphase with long-range periodic order in its composition,[34] with the morphological symmetry for $\chi N \gg 10$ determined by the volume fraction f. Seven types of ordered phase symmetries have been identified as a function of f: two types of body-centered-cubic spherical, two hexagonally-packed cylindrical, two types of an ordered-bicontinuous-double-diamond, and a lamellar morphology.

The dynamics of composition fluctuations in disordered diblock copolymers has been investigated using the random phase approximation method[8,10,11] and the Edwards Hamiltonian approach[9] in order to derive the intermediate scattering functions in bulk[8-10] and in solution.[9-11] The spirit of this approach is to express the total intensity scattered by various species in the interacting system in terms of scattered intensity by the individual molecules. For homogeneous diblock copolymer solutions in nonselective, good solvents, this mean-field fluctuation-free approach predicts two modes of relaxation in diblock copolymer solutions above the overlap concentration,[35] c^*. The first one is the cooperative mode of the physical network formed by the entangled macromolecules, which is identical to the relaxation that is observed in semidilute homopolymer solutions. The second one is an internal relaxation process which reflects the relative motion of one block with respect to the other; the main feature of this structural mode is that its rate is virtually independent of the scattering vector, q, for the low q's of light scattering. This is the only relaxation process predicted by the mean-field theory for diblock copolymer melts[8,9] and is the only mode one should observe in diblock copolymer solutions in the zero average contrast condition.[11] The internal structural mode has been experimentally observed in diblock copolymer solutions above c^* by neutron spin–echo[14] and dynamic light scattering[15] and very recently in the bulk by dynamic light scattering,[21] whereas the cooperative diffusion mode in solution has also been observed by quasi-elastic light scattering.[10,15,16,18,19]

However, two more relaxation processes have been observed in disordered diblock copolymers in bulk[20-22] or in solution.[6-19] One is a diffusive relaxation process[17,19-22] (q^2-dependent relaxation rate). In the bulk,[20,21a,22] its diffusion coefficient shows the same temperature dependence with the self-diffusion coefficient of the higher friction homopolymer, and it has been attributed either to the relaxation of the composition fluctuations induced "pattern" via a diffusive mechanism[20,21a] or, alternatively, to the self-diffusion of the copolymer chains, which is observable by light scattering because of the intrinsic composition polydispersity of the diblocks.[36,21b] In solution,[17,19] it was interpreted as corresponding to the translational diffusion coefficient of the individual block copolymer chains, due to the similarity of both the magnitude and concentration dependence of its diffusion coefficient to the tracer diffusion coefficient of homopolymer in the same block copolymer solutions measured by forced Rayleigh scattering[17,29] and the fact that it was "only 1.8 times faster than the self-diffusion coefficient" measured by pulsed-field-gradient nuclear magnetic resonance[17] (NMR). The other process[16,17,20-22] is a very slow process that shows a q^2 to q^3 dependence[17,21] and a relaxation rate decreasing strongly with copolymer concentration in solution. This should be attributed to "cluster" formation by the copolymer molecules,[16,20-22,37] called "long-range density fluctuations",[37] with estimated length scale of about 1000–2000 Å, also found in molecular and macromolecular glass formers[37] and not to be related to composition fluctuations in the incipient microdomains or grains in the block copolymer solutions, as referred to before.

Summarizing these studies on diblock copolymer solutions dynamics, one is allowed to say that no conclusive picture has emerged with regard to the presence and the origin of the different relaxations. Our main aim is to identify the mechanisms of relaxation of composition fluctuations in semidilute diblock copolymer solutions in the disordered state and near the ODT by combining the experimental investigations for the wavevector and concentration dependencies of the relaxational characteristics with a theoretical approach which predicts the existence and the behavior of the various relaxations observed.

III. Experimental Section

Materials. Two poly(styrene-*block*-1,4-isoprene), SI, diblock copolymer samples were synthesized by anionic

Table 1. Sample Characteristics

species	MW_{PS}	MW_{PI}	M_w/M_n	w_{PS}[a]	N[b]	f_{PS}[c]	κ_0	SSL[d]
SI(43–86)	43000	86000	1.06	0.333	1570	0.306	$9.4\cdot10^{-3}$	cylinders
SI(76–67)	76000	67000	1.06	0.530	1696	0.500	0.015	lamellae
PS(100)	95000	-	1.04	1.000	913	1.000		-

[a] Polystyrene weight fraction. [b] Based on average segmental volume. [c] Polystyrene volume fraction. [d] Strong segregation limit equilibrium ordered morphology.[1,2,32]

polymerization using a high-vacuum technique. The details of the synthesis and characterization have been described earlier.[24,27] First, a small fraction of a prescribed amount of isoprene (I) monomer was reacted in *n*-heptane with *sec*-butyllithium for 20 min at 60 °C (a seeding reaction). Then, the remaining monomer was introduced and allowed to polymerize at room temperature for 48 h to obtain the precursor polyisoprenyl anions. Under these conditions, narrow molecular weight distribution *cis*-polyisoproenes (PI) were obtained with high cis content. Most of the solvent, *n*-heptane, was then replaced by benzene via vacuum distillation, and a prescribed amount of styrene (S) monomer was introduced and allowed to react with the living macroanions. After 48 h of reaction at room temperature, the resulting SI anions were terminated with methanol to recover the block copolymer. The product was precipitated in methanol, dissolved in benzene again, freeze-dried and stored in vacuo until use. The characteristics of the samples are shown in Table 1. The synthetic procedure produced a polyisoprene (PI) sequence with cis:trans:vinyl ≈ 75:20:5. A polystyrene standard (our code, PS100) was purchased from Polymer Standards Services with the characteristics in Table 1 and used as received. A relatively low concentration (<5% by weight) copolymer solution in HPLC grade toluene solvent was initially prepared and filtered through a 0.22-μm Millipore filter directly into a dust-free light scattering cell (12.5 mm). During the measurements, the cell was closed air-tight to avoid evaporation of toluene. The concentration was checked before and after each measurement by weighting the solution. The concentration was then gradually increased by slow evaporation of a small amount of solvent, and the resulting solutions were weighed.

Photon Correlation Spectroscopy (PCS). The autocorrelation function of the polarized light scattering intensity, $G_{VV}(q,t) = \langle I_{VV}(q,t)\, I_{VV}(q,0)\rangle / \langle |I_{VV}(q,0)|^2\rangle$, with $I_{VV}(q,0)$ as the mean light scattering intensity, was measured at different scattering angles, θ, using an ALV spectrophotometer and an ALV-5000 full digital correlator over the time range 10^{-7}–10^3 s. Both the incident beam from an Adlas diode pumped Nd-YAG laser, with wavelength $\lambda = 532$ nm and single mode intensity 160 mW, and the scattering beam were polarized perpendicular (V) to the scattering plane. $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector, with n the refractive index of the medium. In quasi-elastic light scattering under homodyne conditions, $G_{VV}(q,t)$ is related to the desired normalized field correlation function, $g(q,t)$, by

$$G_{VV}(q,t) = [1 + f^*|ag(q,t)|^2] \qquad (1)$$

where f^* is an experimental factor calculated by means of a standard, and a is the fraction of $\langle |I_{VV}(q,0)|\rangle$ with decay times slower than about 10^{-7} s.

The experimental correlation functions, $g(q,t)$, are often represented by the Kohlrausch–Williams–Watts function, $g(q,t) = \exp[-(t/\tau)^\beta]$, where τ and $\beta(\leq 1)$ are respectively the relaxation time and shape parameter. $\beta = 1$ corresponds to single exponential relaxational modes usually observed for diffusive processes. For multiple relaxation processes, the experimental correlation functions may be analyzed by performing the inverse Laplace transform (ILT) of $g(q,t)$, without assumption of the shape of the distribution function $L(\ln\tau)$ but assumping a superposition of exponentials:

$$ag(q,t) = \int_{-\infty}^{\infty} L(\ln\tau)\exp(-t/\tau)\, d(\ln\tau) \qquad (2)$$

This determines a continuous spectrum of relaxation times $L(\ln\tau)$; the average times obtained from $L(\ln\tau)$ are used to determine the characteristic relaxation times.

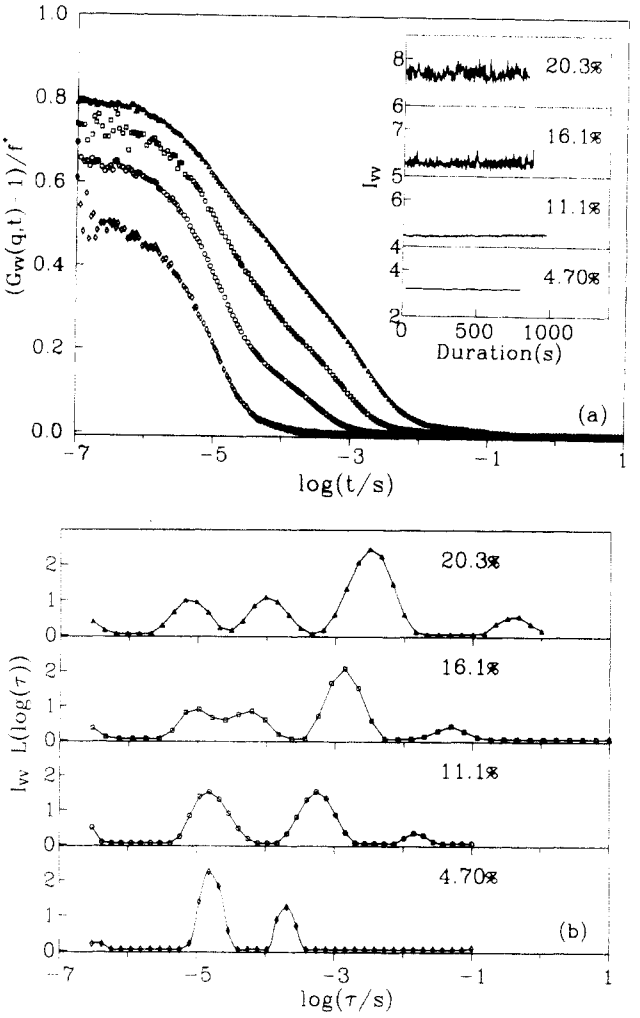

Figure 1. (a) Polarized intensity net autocorrelation function at $\theta = 90°$ scattering angle for 4.7 (◇), 11.1 (○), 16.1 (□), and 20.3 wt % (△) disordered SI(76–67)/toluene solutions at 23 °C. The polarized light scattering intensity traces normalized to the intensity of toluene are shown in the inset. (b) Distribution of relaxation times obtained from the inverse Laplace transform of the experimental correlation functions of part a multiplied by the total polarized intensities normalized to the intensity of toluene.

IV. Results

The net polarized intensity autocorrelation function, $[G_{VV}(q,t) - 1]/f^*$, for a series of SI(76-67) diblock copolymer solutions in toluene at 23 °C for $\theta = 90°$ are shown in Figure 1a, with the traces of the polarized light scattering intensities depicted in the inset; the intensities were normalized to the mean polarized scattering intensity of toluene. Note that, due to the high quality of the samples used for the light scattering experiments, we are able to present unnormalized experimental correlation functions

that decay to the theoretical base line where the low time intercept is related to the part of the scattering intensity that relaxes with relaxation rates faster than about 10^{-7} s, and not normalized correlation functions.

The form of the $G_{VV}(q,t)$ in Figure 1a indicates that multiple relaxation processes contribute to the experimental polarized correlation functions; therefore, their analyses require the ILT procedure. The ILT of the correlation functions are shown in Figure 1b for various concentrations, where for comparison reasons the distributions $L(\log \tau)$ are multiplied by I_{VV}, the total polarized intensity normalized to that of toluene. Four processes are seen to contribute to the experimental correlation function and are clearly observed especially for the higher concentrations; for the low concentrations the two faster relaxations merge due to their different concentration dependencies to be discussed later. The three faster relaxations will be discussed in detail later in relation to their wavevector and concentration dependencies. The very slow process, however, will not be extensively discussed; it exhibits a close to q^2-dependent relaxation rate and an amplitude that strongly depends on q, increasing with decreasing scattering angle, which signifies scattering by large moieties. This relaxation process, which is attributed to the relaxation of the "clusters" formed by the copolymer molecules, has been also observed in diblock copolymer melts[20-22] and in semidilute diblock copolymer solutions,[16,17] is a common characteristic of both molecular and macromolecular glass formers[37] arising from "long range density fluctuations", and has been the subject of extensive research,[38] with the understanding of its origin still unknown. The q-dependent amplitude and rate signify scattering moieties with a size on the scale of about 1000–2000 Å.

The three faster relaxations of Figure 1b show a different concentration and, as will be shown later, wavevector dependencies of both the dynamics and the associated scattering intensities; these differences will facilitate the assignment of the three modes of concentration fluctuations. It is worth mentioning here that the short time intercept of the correlation functions is less than 1. This means that a significant part ($1 - \sqrt{0.50} = 29\%$ for 4.7 wt % at $\theta = 90°$) of the polarized intensity relaxes with time constants outside the time window of PCS, i.e., faster than ca. 10^{-7} s. The missing relaxations, attributed to much faster density and optical anisotropy fluctuations, amount to 21% for the 11.1 wt % solution, to 16% for the 16.1 wt %, and to 11% for the 20.3 wt % solution.

Figure 2a shows the intensity autocorrelation functions for the 20.3 wt % SI(76-67) solution at 23 °C and various scattering angles with the intensity traces shown in the inset, whereas the ILT of the experimental correlation functions are shown in Figure 2b. From now on, we concentrate on the three faster processes of Figure 1b, and neglect the "long-range slow density fluctuations" scattering. The $L(\log \tau)$ of the experimental distributions in Figure 2b reveal significant differences between the wavevector dependencies of the three relaxations. The relaxation times of the fast and slow processes apparently depend on the scattering angle, whereas the rate of the intermediate process does not. In contrast, the amplitude of the intermediate process increases with increasing scattering angle, whereas those for the other processes are more or less constant. Similar behavior is observed at different concentrations as well.

Figure 3a,b shows the wavevector dependence of the relaxation rates, Γ, and the dynamic intensities, αI_{VV}, associated with the three processes, where α is the

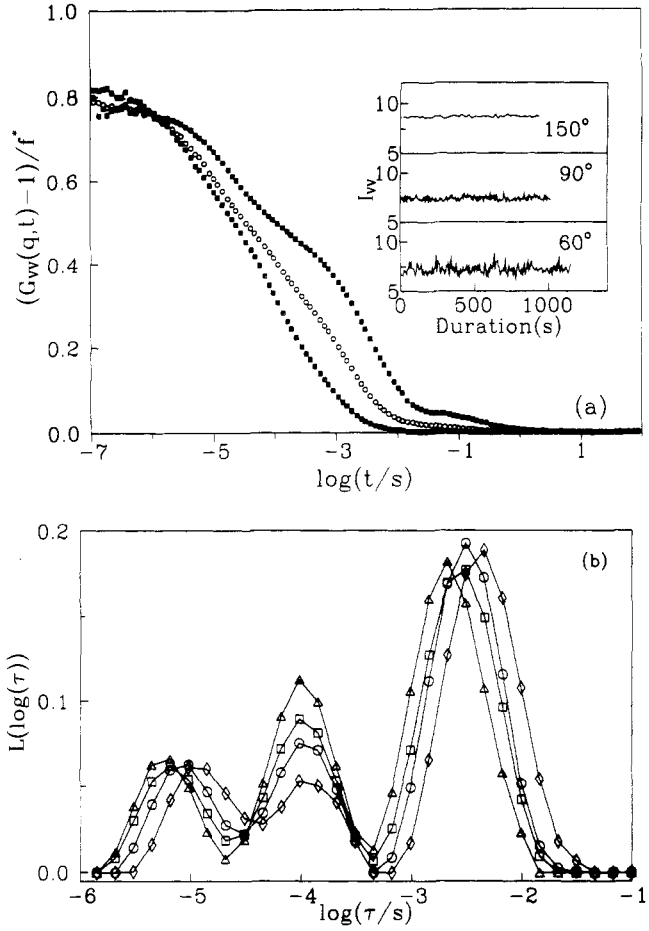

Figure 2. (a) Polarized intensity autocorrelation function for a disordered SI(76–67)/toluene solution (20.3 wt %) at 23 °C for three scattering angles 150° (▨), 90° (○), and 60° (■). The polarized light scattering intensity traces are shown in the inset. (b) Distribution of relaxation times obtained from the inverse Laplace transform of the experimental correlation functions at 75° (◇), 90° (○), 101° (□), and 120° (△) scattering angles.

amplitude of the process and I_{VV} the mean polarized light scattering intensity normalized to that of toluene. The fast process exhibits a q^2-dependent relaxation rate and a q-independent intensity. This relaxation is attributed, as will be discussed later, to the cooperative motion[35,39] of the physical network formed by the copolymer molecules, similarly to the cooperative motion in homopolymer solutions above the overlap concentration[35,39,40] $c^* = 3M_w/(4\pi R_G^3 N_{AV})$, with N_{AV} being Avogadro's number. The R_G of SI(76-67) in toluene is estimated from the R_G of polystyrene (M_w = 640 000) in toluene[16] according to an $N^{0.6}$ dependence[35,40] as R_G = 163 Å. Therefore, c^* = 0.012 g/cm^3 or 1.4 wt %, and the solutions we are discussing are in the semidilute regime. The insensitivity of the intensity on the variation of q signifies scattering by moieties with characteristic size ξ, such that $q\xi \ll 1$. The intermediate process shows a q-independent relaxation rate and a q^2-dependent intensity, thus signifying an internal structural mode. This will be identified with the internal or breathing mode predicted by theory[8-11] and recently documented for diblock copolymer melts[21] and solutions.[8] It is related to the relative motion of one block with respect to the other and is what should have been the interdiffusion mode in the case of two homopolymers. The third process exhibits a q^2-dependent relaxation rate and a q-independent intensity, similar to the cooperative diffusion mode, and is of the same origin as the diffusive relaxation recently observed in diblock copolymer melts[20,21,36] This has been attributed before to the

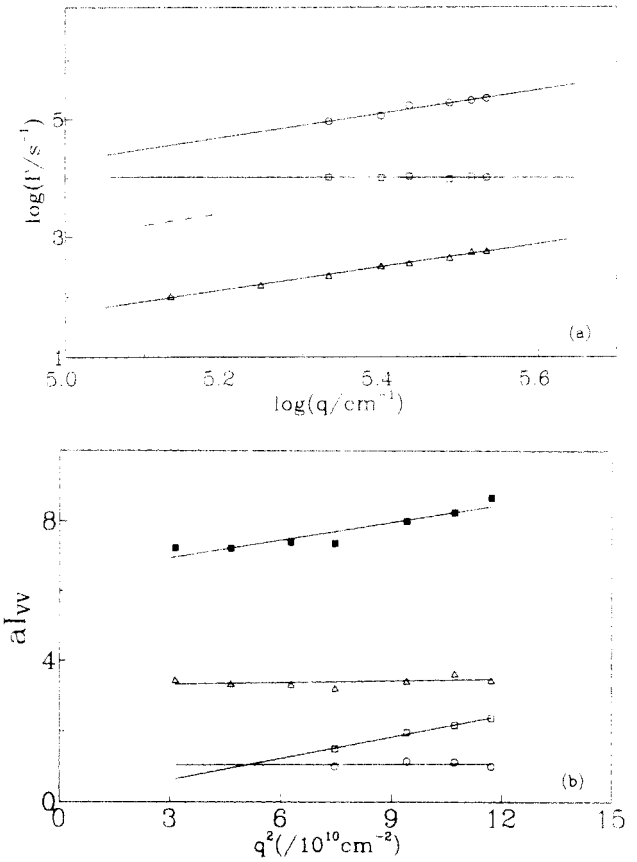

Figure 3. Wavevector, q, dependence of (a) the relaxation rates, Γ, and (b) of the dynamic intensities, αI_{VV}, associated with the three modes in Figures 1 and 2 for the 20.3 wt % SI(76-67)/toluene solution at 23 °C: (○) cooperative diffusion, (□) internal breathing process, (△) "polydispersity" mode. In part b, ■ denotes the total scattering intensity. All the intensities are normalized to that of toluene. The dashed line in part a indicates slope 2 for a diffusive process.

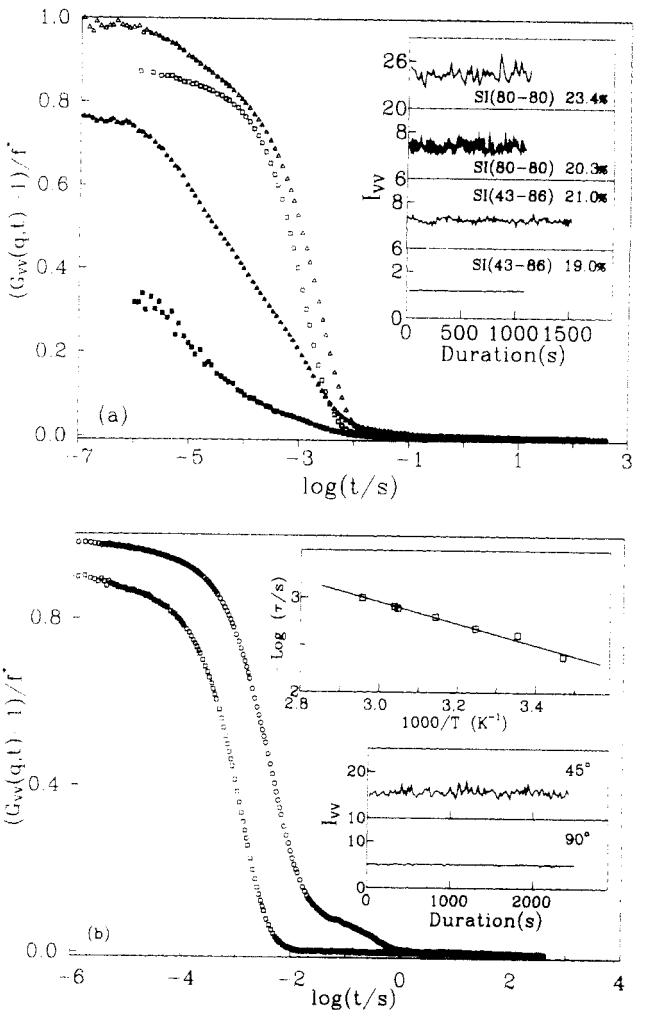

Figure 4. (a) Polarized intensity net autocorrelation function at $\theta = 90°$ for 19 wt % (■) and 21 wt % (□) SI(43-86)/toluene solutions at 25 °C and for 20.3 wt % (▲) and 23.4 wt % (△) SI(76-67)/toluene at 23 °C. The polarized light scattering intensity traces are shown in the inset. (b) Polarized intensity autocorrelation function for the ordered 21 wt % SI(43-86)/toluene solution at 25 °C for $\theta = 45°$ (○) and $\theta = 90°$ (□) recorded simultaneously. The polarized light scattering intensity traces normalized to the intensity of toluene for both angles and the temperature dependence of the domain or polydispersity diffusion coefficient for the 21 wt % solution are shown in the inset.

relaxation of the composition fluctuation induced "pattern"[20,21a] or, alternatively, to be related to a modification[36,21b] of the self-diffusion of the copolymer chains observable because of the intrinsic composition polydispersity of the diblocks. In section V we will present a theoretical approach that predicts the existence of this "polydispersity" mode and its behavior with wavevector and concentration.

The behavior of the total scattering intensity in Figure 3b reflects the increased scattering intensity for the internal relaxation with increasing q. Note that any presence of aggregates/micelles in the solution would have caused an excess scattering at low wavevectors due to their size. A recent report[18] on poly(styrene-*block*-methylmethacrylate) diblock copolymer solution in toluene near c^* ($0.2c^*$–$1.4c^*$) attributes a slower relaxation to possible aggregate formation. Comparison of Figure 1 of ref 18 to our Figure 1b, however, indicates that their slow process might actually be a combination of our intermediate q-independent and our third diffusive process; aggregates would exhibit much more pronounced intensity[41] than the one shown in their Figure 1.[18]

Figure 4a shows the net polarized intensity correlation function for two SI(43-86) diblock copolymer solutions in toluene at 25 °C, $\theta = 90°$ and for concentrations 19 and 21 wt % and two SI(76-67) solutions at 23 °C, $\theta = 90°$ for concentrations of 20.3 and 23.4 wt %, with the traces of the normalized polarized light scattering intensities depicted in the inset. A dramatic change in both the amplitude of the polarized scattering intensity autocorrelation function and the total polarized intensity (inset) is observed for the SI(43-86) solution between 19 and 21 wt %; the change in the amplitude of G_{VV} is not so dramatic for the SI(76-67) solutions. The changes are attributed to the solutions undergoing a disorder-to-order transition in this concentration range, as will become evident in the next paragraph.[24]

The experimental correlation functions for the 21 wt % SI(43-86) solution at 25 °C and for two scattering angles are shown in Figure 4b, with the polarized light scattering intensity traces normalized to the intensity of toluene for both angles shown in the inset. The faster relaxation processes that were clearly observed for lower concentrations (Figures 1 and 2) and now only marginally visible probably because of their low amplitude compared to the amplitude of the process that now dominates the time correlation function. Note that this is not the "long-range density fluctuations", that are also observed (Figure 4b) at lower angles with similar characteristics as before. This relaxation mode shows a q^2-dependent relaxation rate and q-dependent intensity (Figure 4b) and should be discussed in terms of a "domain" relaxation mechanism observed and discussed before for ordered diblock copolymers.[20]

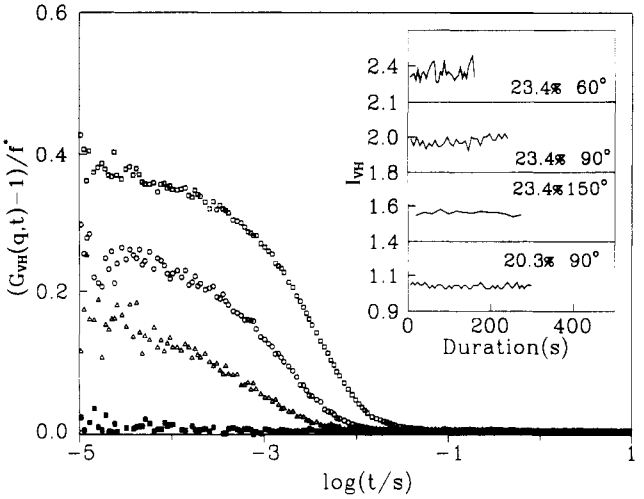

Figure 5. Depolarized intensity autocorrelation function for a disordered SI(76–67)/toluene solution (20.3 wt % at $\theta = 90°$, ■) and for an ordered solution (23.4 wt %) at 25 °C for $\theta = 60°$ (□), 90° (○), and 150° (△). The depolarized light scattering intensity traces for a disordered (20.3 wt %) solution at 90° and for the ordered solution at the three angles are shown in the inset.

Besides the "domain" relaxation, the correlation functions for the SI(76-67) indicate the presence of the intermediate internal relaxation and the cooperative diffusion even for the 23.4 wt % solution. The fact that the latter two relaxations are more evident for the SI(76-67) will become clear in section V below, where it is shown that the amplitude of the internal mode scales with $N^2f^2(1-f)^2$ and that for the cooperative diffusion with $(\bar{n}^2 - n_s^2)^2$, where $\bar{n}$ is the average refractive index of the copolymer and n_s of the solvent. The significant increase in the polarized light scattering intensities between 19 and 21 wt % for SI(43-86) and 20.3 and 23.4 wt % for SI(76-67), shown in the inset of Figure 3a, should also be emphasized. The scattering intensities, to be discussed in connection with Figure 7 below for the SI(76-67), change moderately for lower concentrations (see for example the inset of Figure 1a), whereas they show a significant increase in the concentration regime of Figure 4.

Depolarized light scattering investigations[24] on the SI-(43-96) diblock copolymer solutions have unequivocally shown that at this concentration regime the solution undergoes a disorder-to-order transition to a multicrystalline morphology of coherently ordered cylinders. The ordering was evident by the appearance of a new relaxation process in the depolarized intensity autocorrelation function that was accompanied by a significant increase in the depolarized intensity. The scattering was due to the establishment of significant form anisotropy due to grains of coherently ordered cylinders in the ordered state with correlation length of $O(\mu m)$. Figure 5 shows the net depolarized intensity autocorrelation, $(G_{VH}(q,t) - 1)/f^*$, for two SI(76-67) diblock copolymer solutions at 23 °C with concentrations of 20.3 ($\theta = 90°$) and 23.4 wt % (various scattering angles). The flat, featureless correlation function at 20.3 wt % (as well as at all lower concentrations) corresponds to the disordered state, whereas the relaxation process that appears in the window for the 23.4 wt % solution is accompanied again by a significant increase in the depolarized intensity, shown in the inset. The mode behaves similarly to that observed for SI(43-86)[24], i.e., shows a q^2-dependent relaxation rate in the ordered state and disappears with increasing temperature. This verifies that the SI(76-67) solution undergoes a disordered-to-ordered transition between 20.3 and 23.4 wt %. This information is useful when discussing the change in the

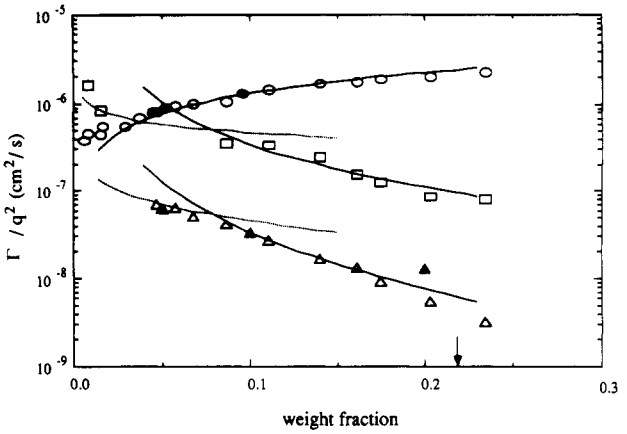

Figure 6. Relaxation rates obtained from the inverse Laplace transform of the correlation functions for SI(76–67)/toluene solutions at 23 °C as a function of concentration (weight percent): (○) cooperative diffusion, (△) "polydispersity" diffusive mode, (□) internal breathing mode (in this case the rate is divided by the wavevector at 90° scattering angle), (●) cooperative diffusion for the PS100/toluene solution, (▲) self-diffusion coefficient for a polystyrene of equal molecular weight with that of the diblock in toluene interpolated from data in reference 42. The three solid lines show the predicted concentration dependence for the three modes in the entanglement regime, whereas the dotted lines are the predictions for the Rouse regime. A multiplication constant is used as an adjustable parameter. The arrow denotes the region of the ODT.

behavior of the polarized intensity in this concentration regime and in the ordered state. The featureless VH correlation functions and low depolarized intensities for concentrations lower than 20.3 wt % prove the absence of any aggregation of the copolymer molecules in the solution.

The relaxation rates for the three processes, obtained from the ILT of the experimental correlation functions at various scattering angles, are shown in Figure 6 for SI-(76-67) at 23 °C as a function of copolymer concentration in the disordered state. For the faster and the slower processes, that both show a q^2 dependence of the relaxation rate, Γ, the ordinate of the figure corresponds to the respective diffusion coefficients, whereas for the intermediate q-independent structural mode the ordinate is calculated at 90° scattering angle. Please note (see also Figure 3a), that for both the fast and slow modes, the Γ vs q^2 line goes through zero; i.e., the modes are purely diffusive.

The diffusion coefficients of the fastest relaxation process observed in the diblock copolymer solutions are very close to the cooperative diffusion coefficients measured by us on the PS100/toluene solutions (shown in Figure 6) and the literature data[40] in polystyrene/toluene solutions, and they increase with increasing copolymer concentration. This verifies the assignment of the fastest relaxation process to the cooperative diffusion coefficient of the network of diblock copolymer chains. For high molecular weights, the cooperative diffusion coefficient is independent of the molecular weight[39,40] and, apparently, independent of the chemical nature of the two blocks. The least squares fit of the experimental cooperative diffusion coefficient data for both diblock copolymer solutions leads to $D_c \propto w^{0.7}$, with w being the weight fraction and the exponent 0.7 being in very good agreement with the theoretically predicted 0.77 dependence of the cooperative diffusion coefficient on polymer concentration[39,40] and with data on polystyrene/toluene solutions.[40]

The diffusion coefficient for the new slower mode, however, shows a different dependence on concentration;

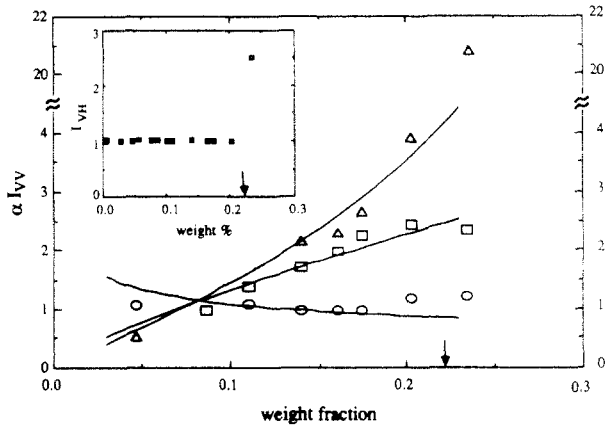

Figure 7. Mean polarized light scattering intensities associated with the different relaxation processes in SI(76–67)/toluene solution at θ = 150° scattering angle, normalized to the mean polarized intensity of toluene, for different concentrations at 23 °C: (○) cooperative diffusion, (□) internal breathing mode, (△) "polydispersity" mode. The three solid lines show the predicted concentration dependence for the three modes. A multiplication constant is used as an adjustable parameter. The inset shows the mean depolarized light scattering intensity for SI(76–67)/toluene solutions at θ = 90°, normalized to the mean depolarized intensity of toluene, for different concentrations at 23 °C (■). The arrows denote the region of the ODT.

it decreases with increasing concentration, in contrast to that for the cooperative diffusion mode; i.e., a different mechanism governs this relaxation than the cooperative mode.[39,40] The diffusion coefficient for the respective process in the case of diblock copolymer melts showed a temperature dependence similar to the temperature dependence of the diblock copolymer shear viscosity[20] and of the self-diffusion of the copolymer chains measured by pulsed-field gradient NMR.[21b] Actually, there is a quantitative agreement with the bulk self-diffusion data measured by pulsed-field gradient NMR.[21b] For the solutions in this paper, a very good agreement is also found between the measured diffusion coefficients and the self-diffusion coefficients of polystyrene with total molecular weight equal to that of the diblock estimated from interpolation of literature data[42] also shown in Figure 6; the agreement is much better for lower concentrations, i.e., far from the ordering transition. The dependence on concentration will be discussed later in connection with the theoretical model that will be presented in section V.

The relaxation time of the intermediate process exhibits a concentration dependence similar to that for the new diffusive mode; i.e., it decreases with increasing copolymer volume fraction with a least squares fit showing a $\Gamma \propto w^{-1.72}$ dependence. Theory suggests that the internal mode is governed by the normal mode of relaxation of the diblock in the solution (see also section V) the relaxation time of which increases with polymer concentration.

Figure 7 shows the mean normalized polarized light scattering intensity associated with the three processes, αI_{VV}, as a function of copolymer concentration for SI(76-67) at 23 °C and for θ = 150° scattering angle. The amplitudes of the processes were obtained from the area under the peak of the ILT, and the intensities are normalized to that of toluene. In the disordered state, the intensities of the two diffusive processes are independent of the wavevector q (Figure 3b above), and, therefore, the values in Figure 7 are independent of the scattering angle, whereas the intensity of the internal mode depends on q^2 (Figure 3b), and its value at θ = 150° is shown in Figure 7.

The intensity associated with the faster mode decreases slightly with increasing copolymer concentration, in agreement with the behavior expected[39,40] and found[40] for the cooperative diffusion. Actually, the expected dependence (see also eq 24 in section V) is[39,40] $I_{coop} \propto \phi^{-0.30}$. In contrast to the behavior for the cooperative diffusion mode, the intensities of both the intermediate internal mode and of the new slow diffusive process increase with copolymer concentration (see also eqs 30 and 33 in section V); this will be thoroughly discussed in sections V and VI below.

A dramatic increase is observed, however, in the mean polarized light scattering intensity when either the SI(43-86) copolymer concentration changes from 19 to 21 wt % or the SI(76-67) concentration changes from 20.3 to 23.4 wt % (upper part of the y-axis in Figure 7). This concentration regime is related to the ODT of the copolymer solutions as discussed earlier in relation to ref 24 and Figure 5 above. The formation of coherently-ordered grains of either long cylinders for SI(43-86) or lamellae for SI(76-67) in the ordered state, with coherence length of $O(\mu m)$, gives rise to large form anisotropy in the microstructured solution and a significant increase in the depolarized intensity (inset of Figure 7); the appearance and disappearance of the relaxation mode in depolarized scattering with concentration and/or temperature is consistent with the solution crossing over from the disordered to the ordered state. Therefore, the significant increase in the polarized intensity should be related to the ODT and to a change in the mechanism of the diffusive relaxation in the microstructured solution.

The development of the grains of cylinders for SI(43-86) or lamellae for SI(76-67) with coherence lengths of the $O(\mu m)$ may lead to concentration fluctuations coherent over large distances that produce the significant increase in the light scattering intensity at these low q's. The diffusive relaxation observed for the ordered 21 wt % solution of SI(43-86) in Figure 4a,b, is, therefore, termed "domain diffusion", similarly to the relaxation observed in ordered cylindrical diblock copolymers in the bulk.[20] The "domain diffusion" coefficient in the bulk exhibited the temperature dependence of the self-diffusion of the pure homopolymer that, as one block, formed the matrix, whereas the glass transition temperature of the component forming the cylinders had no effect on the diffusion coefficient.[20] The relaxation was pictured as dominated by the fast translational diffusion of the cylinders along their axes in the environment of the matrix. It is interesting to note, however, that although the polarized intensity shows a very abrupt increase at the concentration regime of the ODT, the measured dynamics of the slower diffusive mode do not change significantly, as evidenced in Figure 6 for SI(76-67). Moreover, based on depolarized measurements,[24] the 21 wt % SI(43-86) solution transforms back to the disordered state at about 35 °C whereas the respective diffusion coefficient shows an apparent insensitivity to the temperature of the ODT as indicated by the Arrhenius plot in the inset of Figure 4b. Although equilibration for the solutions in the disordered state is fairly fast, the development and dissolution of the long-range ordered morphology is much slower; both the polarized and depolarized light intensities continuously increased with time for both systems in the ordered state. The behavior in the ordered state is currently under investigation and is not discussed any further in the present paper.

In the sections below, we present a theoretical formulation for the relaxation of composition fluctuations in disordered diblock copolymer solutions. In section V, we

predict the existence and the behavior with concentration of all three modes discussed above including the newly established slower diffusive relaxation. The theoretical predictions are compared with our experimental data in section VI.

V. Theoretical Approach

V.1. Preliminary Considerations. Polarized dynamic light scattering provides important information on the dynamics of concentration and/or density fluctuations in multiconstituent polymeric systems.[43] The intermediate scanning intensity, $I(q,t)$, is related to the correlation function of the polarizability density:[43]

$$I(q,t) \propto \langle \delta\alpha_q(t)\, \delta\alpha_{-q}(0)\rangle \tag{3}$$

where $\delta\alpha_q(t)$ is the Fourier image of the polarizability density at time t and q is the scattering wavevector.

Let us consider a melt of AB diblock copolymer chains each consisting of $N = N_A + N_B$ links. Scattering here is mainly due to composition fluctuations (the system is assumed nearly incompressible), and eq 3 reduces to

$$I(q,t) \propto (n_A^2 - n_B^2)^2 S(q,t) \tag{4}$$

where n_A, n_B are the refractive indices of pure components (A and B), and $S(q,t)$ is the dynamic structure factor of composition fluctuations,

$$S(q,t) = \langle \delta\phi_q(t)\, \delta\phi_{-q}(0)\rangle \tag{5}$$

$\delta\phi_q(t$ is the Fourier image of the composition fluctuations, $\delta\phi(r,t) = \phi(r,t) - f$, with $\phi(r,t)$ being the local volume fraction of the A-component, and f the nominal volume fraction.

The static correlation function of the composition fluctuations for a monodisperse diblock copolymer melt in a disordered state ($\chi < \chi_s$) has been predicted by Leibler:[33]

$$S(q,0) = \frac{Nv}{F(u) - 2\chi N} \tag{6}$$

where

$$F(u) = \frac{g(u) f^{-2}(1-f)^{-2}}{g(fu)\, g((1-f)u) - h(fu)\, h((1-f)u)} \tag{7}$$

Here $f = N_A/N$ is the composition of copolymer chain, $u \equiv q^2R_G^2$; $R_G = (Nb^2/6)^{1/2}$, the radius of gyration of the copolymer chain; b is the statistical segment length, assumed equal for both components; χ is the Flory–Huggins interaction parameter; and v is the average volume per link. $g(u) = 2u^{-2}(u - 1 + e^{-u})$ is the Debye function, and $h(u) = u^{-1}(1 - e^{-u})$. Note the $S(q,0) \to 0$ as $q \to 0$, i.e., the long-range composition fluctuations in monodisperse copolymer melts are suppressed. The situation is quite different in a polydisperse system.[44,45] In this case $S(q,0) \to$ constant as $q \to 0$, where the constant depends on the degree of polydispersity.[45]

V.2. Dynamic Scattering from Diblock Copolymer Melts. 1. Internal Chain Relaxation. In light scattering experiments, the wavelength corresponding to the scattering vector q, i.e., $l = 2\pi/q$ is usually much larger than the characteristic coil size, and $u \equiv q^2R_G^2 \ll 1$. In a monodisperse melt, a composition fluctuation can be created only by "polarization" of copolymer chains, i.e. by shifting of the centers of mass of, say, A blocks relative to the centers of mass of the corresponding B blocks.[46] The corresponding relaxation process, which was originally called the "breathing" mode,[21] has been predicted within the framework of the dynamic random phase approximation[8] or the Edwards Hamiltonian approach[9]. For $u \ll 1$, the results can be represented in a simple way:

$$I_{int}(q,t) = I_{int} \exp(-t/\tau_{int}) \tag{8}$$

where the static intensity of the internal or breathing mode is

$$I_{int} \cong (n_A^2 - n_B^2)^2 \frac{2}{3} N v f^2 (1-f)^2 q^2 R_G^2 \tag{9}$$

and the time, τ_{int}, is essentially the longest time of conformational relaxation of the copolymer chains. In the limit of $u \ll 1$, the thermodynamic effects are not important.[8,9] Therefore, for low molecular weights in the Rouse regime, τ_{int} is the Rouse time:

$$\tau_{int} = \tau_R = \tau_0 N^2 \tag{10a}$$

where $\tau_0 \cong (3\pi^2)^{-1} b^2/D_0$ is the characteristic microscopic time for one link, and D_0 is the mobility of a link, related to the friction coefficient. In the entanglement regime, the reptation time should be used

$$\tau_{int} = 5N/(4N_e)\tau_R = 5\tau_0 N^3/(4N_e) \tag{10b}$$

with N_e being the number of segments between entanglements.[37] In the above equations, higher order terms in the expansions in u are neglected for $u \ll 1$.

2. "Polydispersity" Mode. Now let us consider a polydisperse diblock copolymer melt and assume that the degree of polydispersity, $\delta \equiv N_w/N_n - 1$, is small. For low q's, i.e., for $qR_G \ll 1$, polydispersity can significantly enhance composition fluctuations; a fluctuation can now be created not only by "polarization" of the copolymer chains but also by an exchange between "rich in A" and "rich in B" block copolymer chains. The corresponding relaxation is essentially due to mutual diffusion of the macromolecules.

The dynamic correlation function for the polydisperse case is obtained using the general approach that has been outlined before.[36,47-49] First we introduce the generalized susceptilibity of the system, $\kappa(q,t)$ to an external filed, U_{ext}, acting on A-links

$$\langle \delta\phi_q(t)\rangle = \int_0^\infty \kappa(q,t)\, U_{ext}(q,t-\tau)\, d\tau \tag{11}$$

where $\delta\phi(t)$ is the composition fluctuation induced by the field. The susceptibility is related to the correlation function by[50]

$$\kappa(q,t) = \frac{\partial S(q,t)}{\partial t}, \quad t > 0 \tag{12}$$

We make now use the general relation between the Laplace image of the function $\kappa(q,t)$,

$$\kappa(q,p) = \int_0^\infty \kappa(q,t) \exp(-pt)\, dt \tag{13}$$

and the generalized susceptibilities of an ideal system of block copolymer chains without any interaction between the polymer links

$$\frac{1}{\kappa(q,p)} = \frac{\langle\kappa_{AA}\rangle + \langle\kappa_{BB}\rangle + \langle\kappa_{AB}\rangle}{\langle\kappa_{AA}\rangle\langle\kappa_{BB}\rangle - \langle\kappa_{AB}\rangle^2} - 2\chi \tag{14}$$

Here $\langle \kappa_{ij} \rangle = \langle \kappa_{ij}(q,p) \rangle$ are the ideal susceptibilities averaged over the molecular distribution of blocks, $\rho(N_A,N_B)$

$$\langle \kappa_{ij} \rangle = \int \kappa_{ij}^{N_A,N_B} \rho(N_A,N_B)\, dN_A\, dN_B \tag{15}$$

where $\kappa_{ij}^{N_A,N_B}$ is the ideal susceptibility of a monodisperse system with a specified numbers of links, N_A and N_B, in the two blocks, and $\rho(N_A,N_B)$ is the number density of copolymer chains with N_A and N_B links with $\int \rho(N_A,N_B)\, dN_A\, dN_B = 1$. The ideal susceptibilities are related to the correlation functions of the ideal system with relations similar to eq 12. Finally, the correlation functions of an ideal system may be calculated using standard procedures.[33,47]

Following this approach, one may predict simultaneously the internal mode, which is nearly not affected by a small polydispersity and thus its characteristics are given by eqs 8–10, and a new "polydispersity" mode.[36] The latter is characterized by

$$I_{poly}(q,t) = I_{poly}(q) \exp(-q^2 D_{poly} t) \tag{16}$$

where the intensity of the "polydispersity" mode and the corresponding diffusion constant are

$$I_{poly}(q) = (n_A^2 - n_B^2)^2 \frac{\kappa_o N v}{1 - 2\chi N \kappa_o} \tag{17}$$

$$D_{poly} = D_s(N)(1 - 2\chi N \kappa_o) \tag{18}$$

Here, $D_s(N) \cong D_o/N$ is the self-diffusion constant of the N-link chains in the Rouse regime or $D_s(N) \cong 4D_o N_e/(15N^2)$ in the entangled regime, and

$$\kappa_o = \frac{\langle N_A^2 \rangle \langle N_B^2 \rangle - \langle N_A N_B \rangle^2}{N^2 \langle (N_A + N_B)^2 \rangle} \tag{19}$$

is a measure of the polydispersity, where $N = \langle N_A + N_B \rangle$. Note that κ_o is sensitive to the composition polydispersity only; for a system of copolymer chains with the same composition, κ_o is equal to zero even if the distribution of total molecular weight is broad.

Assuming independent molecular weight distributions of A and B blocks, i.e., $\rho(N_A,N_B) = \rho(N_A)\rho(N_B)$, one gets

$$\kappa_o \cong 2\delta \frac{f^2(1-f)^2}{f^2 + (1-f)^2} \tag{20}$$

Comparing eq 11 and eqs 19 and 22, one may predict that the "polydispersity" mode dominates over the internal one when

$$\delta > \frac{q^2 N b^2}{36} \tag{21}$$

Note that this condition is normally fulfilled for light scattering wavevectors.

A preliminary version of the above approach for symmetric diblocks has been presented before,[36a] whereas the theory has already been applied in order to quantitatively explain the data for a series of high molecular weight poly(dimethylsiloxane-*block*-methylethylsiloxane) diblock copolymer melts.[21b] The comparison for high molecular weights was facilitated by using the above expressions for τ_{int} (eq 10b) and $D_s(N)$ (eq 18) in the entanglement regime.

V.3. Dynamic Scattering from Semidilute Diblock Copolymer Solutions. Let us consider now the dynamic light scattering from a disordered semidilute diblock copolymer solution in a nonselective, good solvent. There are two main differences in the scattering behavior of this system compared to the melt case: (i) an additional cooperative diffusion mode will appear, and (ii) the parameters of the internal and the "polydispersity" mode should be renormalized by the presence of the solvent, assumed to be equally good for both components.

1. Cooperative Diffusion. The cooperative diffusion mode here is quite similar to that for homopolymer solutions;[35,39] it corresponds to a concerted motion of the network of polymer chains relative to the solvent. The intensity of the mode depends on the contrast between the solvent and the block copolymer, and is proportional to the number of links per "blob"[35,39], g,

$$I_{coop} \propto (\bar{n}^2 - n_s^2)^2 \phi g \propto (\bar{n}^2 - n_s^2)^2 \phi^{\alpha_1} \tag{22a}$$

since $g \sim \phi^{-1/(3\nu-1)}$. $\phi = \phi_o$ is the mean volume fraction of the diblock copolymer in the solution, n_s is the refractive index of the solvent, $\bar{n}$ is the mean refractive index of the copolymer chains, $\bar{n}^2 = f n_A^2 + (1-f) n_B^2$, and

$$\alpha_1 = \frac{3\nu - 2}{3\nu - 1} \cong -0.30 \tag{22b}$$

is the corresponding concentration exponent, where $\nu \cong 0.59$ is the Flory exponent in good solvents. The corresponding relaxation time is governed by the cooperative diffusion constant,

$$D_{coop} \cong \frac{k_B T}{6\pi \eta_s \xi} \sim \frac{k_B T}{\eta_s b} \phi^{\alpha_2} \tag{23a}$$

where $\xi \sim b g^{\nu}$ is the correlation length of the solution, η_s is the solvent viscosity, and

$$\alpha_2 = \frac{\nu}{3\nu - 1} \cong 0.77 \tag{23b}$$

2. "Polydispersity" Mode. As for the "polydispersity" mode, the following renormalizations will account for the presence of solvent[5,6,35,39]

$$v \to \phi g v; \quad N \to N^* = N/g; \quad \chi \to \chi^* = \chi g^z \tag{24}$$

The last renormalization takes into account that the mean number of contacts between neighboring blobs in a good solvent is of order of g^z. The exponent z has been calculated using ϵ-expansion:[51]

$$z = 2 - \nu(d + \theta_2) \cong -\frac{\epsilon}{4}\left(1 - \frac{15\epsilon}{32}\right) \tag{25}$$

i.e., $z \cong -0.13$ for $\epsilon \equiv 4 - d = 1$, and d is the dimensionality. More recent calculations using a Pade approximation[52] for the series in the right-hand-side of eq 25 found $z \cong -0.17$ for $\epsilon = 1$, whereas a Pade–Borel resummation of the 3rd-order ϵ-expansion resulted in $z \cong -0.225 \pm 0.005$. Thus, using this last value for z,

$$\chi^* N^* \propto \chi N \phi^{(1-z)/(3\nu-1)} \cong \chi N \phi^{1.59} \tag{26}$$

Therefore, the following characteristics of the "polydispersity" mode in a block copolymer solution are obtained

$$I_{poly} = (n_A^2 - n_B^2)^2 \frac{\kappa_o N v \phi}{1 - 2\chi N \kappa_o \phi^{1.59}} \tag{27}$$

and

$$D_{poly} = D_s(N,\phi)(1 - 2\chi N\kappa_o\phi^{1.59}) \quad (28a)$$

The self-diffusion coefficient in semidilute solutions depends on concentration and in the Rouse regime is[35,39]

$$D_s(N,f) \cong \frac{k_BT}{\eta_s\xi}\frac{g}{N} \sim \frac{k_BT}{\eta_s b}\frac{\phi^{-(1-\nu)/(3\nu-1)}}{N} \sim \frac{\phi^{-0.53}}{N} \quad (28b)$$

or in the entanglement regime[35,39]

$$D_s(N,\phi) \cong \frac{k_BT}{\eta_s\xi}\left[\frac{g}{N}\right]^2 \sim \frac{k_BT}{\eta_s b}\frac{\phi^{-(2-\nu)/(3\nu-1)}}{N^2} \sim \frac{\phi^{-1.83}}{N^2} \quad (28c)$$

and $\nu = 0.59$ for good solvents. Note that the intensity of the "polydisperse" mode should be larger than that for the cooperative mode if

$$\delta > \frac{g}{N} \sim \frac{1}{N}\phi^{-1/(3\nu-1)} \cong \frac{\phi^{-1.3}}{N} \quad (29)$$

i.e., if the volume fraction of the solution is high enough, $\phi \gtrsim (\delta N)^{-0.77}$.

3. Internal Chain Relaxation. The internal relaxation mode for semidilute diblock copolymer solutions in neutral solvents has been calculated before[9-11] in the framework of the dynamic random phase approximation. In the nomenclature used in this paper and using the general approach outlined above, the relaxational characteristics of the internal breathing mode for $u \ll 1$ are

$$I_{int} \cong (n_A^2 - n_B^2)^2\frac{1}{9}\phi^{\nu/(3\nu-1)}vf^2(1-f)^2N^2b^2q^2 = (n_A^2 - n_B^2)^2\frac{1}{9}\phi^{0.77}vf^2(1-f)^2N^2b^2q^2 \quad (30)$$

and in the Rouse regime[35]

$$\tau_{int} \cong \tau_{blob}\left[\frac{N}{g}\right]^2 \sim \frac{\eta_s b^3}{k_BT}N^2\phi^{(2-3\nu)/(3\nu-1)} = \tau_o N^2\phi^{0.30} \quad (31a)$$

whereas in the entanglement regime[35]

$$\tau_{int} \cong \tau_{blob}\left[\frac{N}{g}\right]^3 \sim \frac{\eta_s b^3}{k_BT}N^3\phi^{3(1-\nu)/(3\nu-1)} = \tau_o N^3\phi^{1.60} \quad (31b)$$

where the value of $\nu = 0.59$ for good solvents has been used. τ_{blob} is the local jump time of the blob, $\tau_{blob} = \eta_s\xi^3/(k_BT)$, and $\tau_o = \eta_s b^3/(k_BT)$. Higher order terms in $u \equiv q^2R_G^2$ are again neglected for $u \ll 1$.

The differences in the behavior of the three different relaxation processes should be pointed out here. The cooperative diffusion behaves quantitatively similar to that in semidilute homopolymer solutions, i.e., q^2-dependent relaxation rate, q-independent intensity, and both intensity and relaxation time decreasing with increasing copolymer concentration. The "polydispersity" mode exhibits a diffusive behavior (q^2-dependent rate and q-independent intensity), whereas the internal mode assumes a q-independent rate and a q^2-dependent intensity. As the concentration increases, both the intensities and the relaxation times of both the "polydispersity" and the internal mode increase, in contrast to the behavior of the cooperative diffusion mode. Moreover, the intensity of the internal mode shows a N^2 dependence on molecular weight whereas that for the cooperative diffusion is independent of N and the one for the polydispersity mode exhibits the N dependence of eq 27.

VI. Discussion

The theoretical formulation presented in Section V above for the relaxation of composition fluctuations in diblock copolymer melts has been discussed in relation to experimental data in a recent article[21b] for a series of high molecular weight poly(dimethylsiloxane-*block*-ethylmethylsiloxane) homogeneous diblock copolymer melts. It was found that the q-independent internal relaxation decay rate varies with N^{-3} (eq 10b) whereas the diffusion coefficient of the polydispersity process[21] agrees well with the self-diffusion of the copolymer chains either measured by pulsed-field gradient NMR or derived by shear viscosity data, in agreement with the theoretical predictions (eq 18). Moreover, the data agree very well with the theoretical predictions for the wavevector and molecular weight dependence of both the internal and the polydispersity modes.

Below we discuss and compare the theoretical predictions with the experimental data for the SI(76-67) diblock copolymer solutions in toluene. The mean volume composition of the copolymer is $f_{PS} = 0.500$; the degree of polydispersity of total molecular weight of polymer chains is estimated as $\delta = M_w/M_n - 1 \cong 0.06$ (Table 1). The measure of polydispersity κ_o is estimated from the total molecular weight polydispersity according to eq 20 and is listed in Table 1. In order to proceed with quantitative comparison, the value of the effective χ parameter, χ^*, in the semidilute solution is need. As we are not aware of any direct measurements of this parameter, we will use the following indirect way to determine it based on the location of ODT observed in the solution. The experimental evidence strongly suggests that the system undergoes a microphase separation transition (ODT) between 20.3 and 23.4 wt %, i.e., at $\phi_{ODT} \cong 0.21$. On the other hand, the mean-field theory[5,33] predicts the ODT at

$$(\chi^*N^*)_{ODT} = X(f) \cong 10.5 \quad (32)$$

where the universal function $X(f)$ has been originally predicted by Leibler.[33] Using eq 26 one gets

$$\chi^*N^* = \chi N\phi^{1.59} = X(f)(\phi/\phi_{ODT})^{1.59} \cong 10.5(\phi/\phi_{ODT})^{1.59} \quad (33)$$

Therefore, the theoretical predictions to be compared with the experimental data for the polydispersity diffusive mode may be expressed by substituting eq 33 in eq 27

$$I_{poly} \propto \frac{\kappa_o N\phi}{1 - 2X(f)\,\kappa_o(\phi/\phi_{ODT})^{1.59}} \quad (34)$$

and in eqs 28a and 28b (Rouse regime)

$$D_{poly} \propto \frac{\phi^{-0.53}}{N}[1 - 2X(f)\,\kappa_o(\phi/\phi_{ODT})^{1.59}] \quad (35a)$$

or in eq 28c (entangled regime)

$$D_{poly} \propto \frac{\phi^{-1.83}}{N^2}[1 - 2X(f)\,\kappa_o(\phi/\phi_{ODT})^{1.59}] \quad (35b)$$

The predictions for the internal breathing relaxation and the cooperative diffusion remain as in eqs 30-31 and 22-23, respectively. It should be noted that eqs 35b and 31b are valid for the entanglement regime, whereas eqs 35a

and 31a should be applied in the Rouse regime. It is known that the critical molecular weight for entanglements is a function of the solution concentration;[39] therefore, although the molecular weight of the SI(76–67) is higher than the critical molecular weight for entanglements, M_c, it might be more appropriate to use the equations for the Rouse regime (eqs 35a and 31a) for the lowest concentrations ($\phi < \phi_e = N_e/N$) in the present experiments.

The theoretical predictions for both the relaxation rates and the scattering intensities are compared with the data for their concentration dependence in Figures 6 and 7. The theoretical curves are shifted vertically using adjustable multiplication factors to account for the various numerical constants in the theoretical expressions. Theory is found to predict the correct concentration dependence for both the intensities and the relaxation times of all three processes. At low concentrations the predictions for the diffusion coefficient of the polydispersity mode and for the relaxation rate of the internal process using eqs 35b and 31b in the entanglement regime overestimate the concentration dependence; this can be overcome if eqs 35a and 31a are used to account for the Rouse regime.

Quantitatively, the prediction of eq 28a, i.e., that the diffusion coefficient for the polydispersity mode is controlled by the self-diffusion coefficient of the copolymer chains, is verified by the close proximity of the data for the slow diffusive mode with the estimated[42] self-diffusion data for a polystyrene of equal molecular weight, shown also in Figure 6. This is due to both the low κ_0 values for the diblock. The agreement is much better when the comparison is made far from the ODT (small $\chi N\kappa_0\phi^{1.59}$), whereas D_{poly} is smaller than D_s at higher concentrations near the ODT. According to eqs 18, 28, and 35, a slowing down of the diffusion coefficient D_{poly} is predicted for high values of $\chi N\kappa_0$ for melts and $\chi N\kappa_0\phi^{1.59}$ for solutions; this is currently under investigation by mixing two diblock copolymers with different compositions (f) but the same total number of segments (N).[54]

One should also compare the theoretical predictions for the wavevector dependence of the various processes. The q dependence of both the intensity and the relaxation rate of the cooperative diffusion process (eqs 22 and 23) is well-established and is not discussed further. The approach presented here is in agreement with previous calculations[9–11] for the relaxation of composition fluctuations for monodisperse diblocks in that the internal process should exhibit a q-independent relaxation rate (eq 31a or 31b) and a q^2-dependent amplitude (eq 30); both predictions are in good agreement with the data (Figure 3a,b). Our new contribution is the prediction and experimental documentation of the existence of a new diffusive process (q^2-dependent relaxation rate, eq 28), called the polydispersity mode, which is attributed to additional composition fluctuations due to the inherent composition polydispersity of the diblocks. The intensity of this mode is a measure of the degree of polydispersity (eqs 27 and 20) and is independent of the wavevector (eq 27), in agreement with scattering due to moieties of size less than the measurement wavelength ($1/q$). The diffusion coefficient of the process is related to the self-diffusion of the diblocks in the solution. The predictions for the wavevector dependence of this process is in agreement with the data, as shown in Figure 3a,b, whereas the concentration dependence was discussed before.

VII. Concluding Remarks

The dynamics of composition fluctuations in solutions of diblock copolymers in a non-selective, good solvent were investigated using polarized dynamic light scattering. Three different relaxations were found to contribute to the polarized intensity autocorrelation function besides the long-range (slow) density fluctuations. The three relaxations are identified as follows: one is the cooperative diffusion of the physical network formed by the entangled diblock copolymer chains, which is identical to the cooperative diffusion in semidilute homopolymer solutions. Its diffusion coefficient increases with concentration as $\phi^{0.77}$ whereas its intensity decreases as $\phi^{-0.30}$. The second is the copolymer specific structural internal process predicted by theory with wavevector-independent relaxation rate and a q^2-dependent amplitude for light scattering q's. Its intensity increases with concentration and its rate decreases with ϕ. The third relaxation is a diffusive relaxation, recently established for copolymer melts, with a q^2-dependent rate and q-independent amplitude. Its intensity increases with the copolymer concentration whereas its diffusion coefficient decreases with concentration. A theoretical approach is presented which predicts the existence and the dependence of the three processes on the wavevector and the concentration. The new diffusive relaxation is predictive to originate from the relaxation of the additional composition fluctuations due to the composition polydispersity of the diblocks. Its intensity is predicted to be proportional to the degree of polydispersity, while its relaxation rate is governed by the self-diffusion of the copolymer chains. The diffusive character of the process and the concentration dependence of the diffusion constant are in quantitative agreement with the dynamic light scattering data.

It should also be noted that the predictions for the intensity and dynamics of the polydispersity mode depend on the degree of composition polydispersity of the diblock; this dependence is more crucial for high values of χN (eqs 27, 28, 34, and 35). It is the degree of compositional polydispersity that is important; however, its degree is estimated indirectly (eq 20) using the value for the polydispersity of the total molecular weight and the assumption of nearly independent distributions of A and B blocks. Moreover, the theory described above is based on the mean-field approximation similar to that used by Leibler,[33] which does not take into account fluctuation corrections.[12] These corrections, however, are not likely to modify noticeably the behavior of the polydisperse mode even in the vicinity of ODT.

The disorder-to-order transition is found to be accompanied by a significant increase in the polarized light scattering intensity, without affecting significantly the diffusion dynamics. This is attributed to a change in the mechanism of relaxation from the chain diffusion in the disordered state to the relaxation of the ordered morphology in the microstructured solution. One may consider that the additional scattering due to the polycrystalline (domain) structure of the ordered system might explain the behavior of the "domain" mode near ODT and in the ordered state. We comment, however, that a mode due to scattering from grains (or grain boundaries) must be characterized by rather specific properties: its intensity should increase with time since the grains grow gradually (in agreement with the observed behavior); the characteristic time of the "grain" mode should be very large, larger than that predicted for the polydisperse mode in the disordered state by a factor of $\sqrt{N} \gtrsim 30$; the "grain" mode is not expected to be diffusive; it should be characterized by a wide distribution of relaxation times. Thus, it is not likely that the "domain" mode is due to grain structure. Therefore, the understanding of both the

dynamics and the scattering intensity in the ordered state is still missing and is under investigation.

Acknowledgment. A.N.S. acknowledge the hospitality and financial support of the Foundation for Research and Technology—Hellas. S.H.A. would like to acknowledge that part of this research was sponsored by NATO's Scientific Affairs Division in the framework of the Science for Stability Programme and by the Greek General Secretariat of Research and Technology. G.F. acknowledges the financial support of the Alexander von Humboldt Foundation (Grant No. FOKOOP USS 1685).

References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525. Bates, F. S. *Science* **1991**, *251*, 898. Legge, N. R., Holden, G., Schroeder, H. E., Eds. *Thermoplastic Elastomers*; Hamser: Vienna, 1987.
(2) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093. Shibayama, M.; Hashimoto, T.; Hasegawa, H.; Kawai, H. *Macromolecules* **1983**, *16*, 1427. Hashimoto, T.; Kowasaka, K.; Shibayama, M.; Kawai, H. *Macromolecules* **1986**, *19*, 754. Hashimoto, T.; Mori, K. *Macromolecules* **1990**, *23*, 5347.
(3) Benmouna, M.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227. Benoit, H.; Wu, W.; Benmouna, M.; Mozer, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(4) Hong, K. M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083. Onuki, A.; Hashimoto, T. *Macromolecules* **1989**, *22*, 879.
(5) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1989**, *22*, 1238.
(6) Olvera de la Cruz, M. *J. Chem. Phys.* **1989**, *90*, 1995.
(7) Fytas, G.; Anastasiadis, S. H. In *Disorder Effects on Relaxation Processes*; Richert, R., Blumen, A., Eds.; Springer Verlag: Berlin, 1994.
(8) Akcasu, A. Z.; Benmouna, M.; Benoit, H. *Polymer* **1986**, *27*, 1935. Akcasu, A. Z.; Tombakoglu, M. *Macromolecules* **1990**, *23*, 607. Akcasu, A. Z. *Macromolecules* **1991**, *24*, 2109.
(9) Borsali, R.; Vilgis, T. A. *J. Chem. Phys.* **1990**, *93*, 3610.
(10) Borsali, R.; Fischer, E. W.; Benmouna, M. *Phys. Rev. A* **1991**, *43*, 5732.
(11) Benmouna, M.; Benoit, H.; Borsali, R.; Duval, M. *Macromolecules* **1987**, *20*, 2620.
(12) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1988**, *89*, 5890.
(13) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.
(14) Borsali, R.; Benoit, H.; Legrand, J.-F.; Duval, M.; Picot, C.; Benmouna, M.; Farago, B. *Macromolecules* **1989**, *22*, 4119. Duval, M.; Picot, C.; Benoit, H.; Borsali, R.; Benmouna, M.; Lartigue, C. *Macromolecules* **1991**, *24*, 3185.
(15) Duval, M.; Haida, H.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1991**, *24*, 6867.
(16) Haida, H.; Lingelser, J. P.; Gallot, Y.; Duval, M. *Die Makromol. Chem.* **1991**, *192*, 2701.
(17) Balsara, N. P.; Stepanek, P.; Lodge, T. P.; Tirrell, M. *Macromolecules* **1991**, *24*, 6227.
(18) Konak, C.; Vlcek, P.; Bansil, R. *Macromolecules* **1993**, *26*, 3717.
(19) Tsunashima, Y.; Kawamata, Y. *Macromolecules* **1994**, *27*, 1799.
(20) Vogt, S.; Jian, T.; Anastasiadis, S. H.; Fytas, G.; Fischer, E. W. *Macromolecules* **1993**, *26*, 3357.
(21) (a) Anastasiadis, S. H.; Fytas, G.; Vogt, S.; Fischer, E. W. *Phys. Rev. Lett.* **1993**, *70*, 2415. (b) Vogt, S.; Anastasiadis, S. H.; Fytas, G.; Fischer, E. W. *Macromolecules*, in press.
(22) Anastasiadis, S. H.; Fytas, G.; Vogt, S.; Gerharz, B.; Fischer, E. W. *Europhys. Lett.* **1993**, *22*, 619.
(23) Rizos, A. K.; Fytas, G.; Roovers, J. E. L. *J. Chem. Phys.* **1992**, *97*, 6925. Alig, I.; Kremer, F.; Fytas, G.; Roovers, J. E. L. *Macromolecules* **1992**, *25*, 5277.
(24) Jian, T.; Anastasiadis, S. H.; Fytas, G.; Adachi, K.; Kotaka, T. *Macromolecules* **1993**, *26*, 4706.
(25) Jian, T.; Semenov, A. N.; Anastasiadis, S. H.; Fytas, G.; Feh, F.-J.; Chu, B.; Vogt, S.; Wang, F.; Roovers, J. E. L. *J. Chem. Phys.* **1994**, *100*, 3286.
(26) Quan, X.; Johnson, G. E.; Anderson, E. W.; Bates, F. S. *Macromolecules* **1989**, *22*, 2451.
(27) Yao, M.-L.; Watanabe, H.; Adachi, K.; Kotaka, T. *Macromolecules* **1992**, *25*, 1699. Yao, M.-L.; Watanabe, H.; Adachi, K.; Kotaka, T. *Macromolecules* **1991**, *24*, 2955.
(28) Karatasos, K.; Anastasiadis, S. H.; Semenov, A. N.; Fytas, G.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 3543.
(29) Balsara, N. P.; Eastman, C. E.; Foster, M. D.; Lodge, T. P.; Tirrell, M. *Makromol. Chem., Macromol. Symp.* **1991**, *45*, 213.
(30) Ehlich, D.; Takenaka, M.; Hashimoto, T. *Macromolecules* **1993**, *26*, 189, 492.
(31) Dalvi, M. C.; Lodge, T. P. *Macromolecules* **1993**, *26*, 859.
(32) Shull, K. R.; Kramer, E. J.; Bates, F. S.; Rosedale, J. H. *Macromolecules* **1991**, *24*, 1383.
(33) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(34) Helfand, E.; Wasserman, Z. R. In *Development of Block Copolymers I*; Goodman, I., Ed.; Applied Science: London, 1982.
(35) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(36) (a) Fytas, G.; Anastasiadis, S. H.; Semenov, A. N. *Makromol. Chem., Macromol. Symp.* **1994**, *79*, 117. (b) Semenov, A. N.; Fytas, G.; Anastasiadis, S. H. *Polymer Prepr.* **1994**, *35*(1), 618.
(37) Gerharz, B.; Meier, G.; Fischer, E. W. *J. Chem. Phys.* **1990**, *92*, 7110.
(38) Fischer, E. W. *Physica A* **1994**, in press.
(39) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Science Publishers: Oxford, 1986.
(40) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum Press: New York, 1985.
(41) Schillén, K.; Brown, W.; Konak, C. *Macromolecules* **1993**, *26*, 3611.
(42) Léger, L.; Hervet, H.; Rondolez, F. *Macromolecules* **1981**, *14*, 1732.
(43) *Dynamic Light Scattering. The Method and Some Applications*; Brown, W., Ed.; Oxford Clarendon Press: Oxford, 1993. *Dynamic Light Scattering. Applications of Photon Correlation Spectroscopy*; Pecora, R., Ed.; Plenum Press: New York, 1985. Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley-Interscience: New York, 1976.
(44) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.
(45) Hong, K. M.; Noolandi, J. *Polym. Commun.* **1984**, *25*, 265. Burger, C.; Ruland, W.; Semenov, A. N. *Macromolecules* **1990**, *23*, 3339.
(46) Pakula, T. *Makromol. Chem., Theory Simul.* **1993**, *2*, 239.
(47) Erukhimovich, I. Ya.; Semenov, A. N. *Zh. Eksp. Teor. Fiz.* **1986**, *63*, 259 [*Sov. Phys. JETP* **1986**, *63*, 149].
(48) Semenov, A. N.; Erukhimovich, I. Ya. *Vysokomol. Soed. A* **1986**, *28*, 2031 [*Polym. Sci. USSR* **1986**, *28*, 2253].
(49) Brochard, F.; de Gennes, P. G. *Physica A* **1993**, *118*, 289.
(50) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*, 3rd ed.; Pergamon Press: Oxford, 1980; Part 1.
(51) de Cloizeaux, J. *J. Phys. Fr.* **1980**, *41*, 223.
(52) Joanny, J.-F.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.
(53) Schaefer, L.; Kappeler, Ch. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 1853. Kosmas, M. *J. Phys. Lett.* **1984**, *45*, L889. Broseta, D.; Leibler, L.; Joanny, J.-F. *Macromolecules* **1987**, *20*, 1935.
(54) Jian, T.; Fytas, G.; Anastasiadis, S. H.; Vilesov, A. D. *Polym. Mater. Sci. Eng.* **1994**, *71*.