Intermediate Wavelength Composition Fluctuations in Diblock Copolymers: Modification of the Diffusive Mode near the Ordering Transition

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ABSTRACT: The relaxation of composition fluctuations of diblock copolymers in the intermediate wavevector range $0.08 < q/q^* < 0.61$ is investigated by photon correlation spectroscopy, thus bridging the $q/q^* \ll 1$ and $q/q^* \sim 1$ regimes (q^* is the wavevector of the most probable composition fluctuations). Although away from the ordering transition (ODT) the modes of relaxation follow the behavior established for $q/q^* \ll 1$, the enhanced thermodynamic interactions by approaching the ODT lead to a modification of the intensity characteristics of the polydispersity (slower) mode, which now increases with increasing q and shows a concentration dependence stronger than ϕ^1. The diffusive character of this process, however, is not affected, and it still reflects the self-diffusion of the chains. The characteristics of the internal mode remain unchanged. The findings can be accounted for by a theory recently developed for the dynamic structure factor of polydisperse entangled diblocks.

I. Introduction

Block copolymers are interesting polymeric materials with respect to both their morphology and properties.[1] An important characteristic of their structure is that, due to the thermodynamic incompatibility between the two covalently bonded sequences of different monomers A and B, they undergo a disorder-to-order transition[2] (ODT) from a homogeneous state toward one with spatially periodic order. The dynamic structure factor, $S(q,t) = \langle \delta\phi_{\mathrm{A}}(q,0)\, \delta\phi_{\mathrm{A}}(-q,t)\rangle$, describes their static[2] and dynamic[3] behavior, where $\delta\phi_{\mathrm{A}}(q,t)$ is the Fourier transform of the composition fluctuations $\delta\phi_{\mathrm{A}}(r,t)$ at position r and time t and q is the wavevector. Their most probable composition fluctuations are of finite size,[2] leading to a maximum of the static structure factor, $S(q)$, at a wavevector $q^* \propto R_{\mathrm{g}}^{-1}$, where R_{g} is the chain radius of gyration.

Composition fluctuations in disordered diblock copolymers relax via the “internal” copolymer mode[4,5] and the “polydispersity” diffusive process,[6] which have been studied in detail in the low wavevector regime ($qR_{\mathrm{g}} \ll 1$) using photon correlation spectroscopy either in the melt[7,8] or in solution in a neutral good solvent.[6,9,10] For $qR_{\mathrm{g}} \ll 1$, the relaxation time of the former is controlled by the longest relaxation time of the chains while its intensity in semidilute solution is $I_{\mathrm{int}} \propto \phi^{0.77}q^2$. For the latter, $I_{\mathrm{poly}} \propto \kappa_0\phi q^0$, with κ_0 the variance of composition polydispersity, while its diffusion coefficient $D \cong D_{\mathrm{s}}(N,\phi)$, where D_{s} is the chain self-diffusion coefficient, which is a function of the number of segments N and polymer volume fraction ϕ. The effect of thermodynamics in this regime is negligible.

On the other hand, the regime $0.3 < qR_{\mathrm{g}} < 3.4$ (or, equivalently, $0.2 < q/q^* < 2.1$) has been recently investigated[11,12] utilizing semidilute solutions of three ultrahigh molecular weight almost symmetric diblocks exhibiting a q^* within the wavevector range of photon correlation spectroscopy. A main mode of relaxation of composition fluctuations[12] was resolved with characteristics apparently resembling a mixed “internal” and “polydispersity” mode. Its intensity approaches a constant value while its rate $\Gamma(q) \propto q^2$ for $qR_{\mathrm{g}} \ll 1$, whereas it shows a minimum in its effective diffusion coefficient $D(q) = \Gamma(q)/q^2$ and a maximum in its intensity for $q \sim q^*$. Therefore, it exhibits the thermodynamic slowing down, originally anticipated for the internal mode of monodisperse diblocks.[4,5] As the ODT was approached, this slowing down became dramatically pronounced, mirroring the significant increase of the intensity. A theory was developed for the calculation of $S(q,t)$ of entangled polydisperse diblocks within the reptation model. $S(q,t)$ was expressed as a superposition of relaxation modes with the two slower ones dominating. Their relative intensities depend on the wavevector, the proximity to the ODT, and the composition polydispersity of the diblocks. The modes are significantly affected by the polydispersity even away from the transition whereas there is a strong coupling as the ODT is approached, leading to an interplay of their characteristics; this hinders their assignment as “internal” and “polydispersity” over the whole qR_{g} range. The slower mode, which is the one that exhibits the influence of thermodynamic interactions around q^* (increase of the intensity and slowing down of the dynamics) and has a finite intercept in both its intensity and effective diffusion coefficient, favorably compares with the experimental data of the dominant mode.[13] Asymmetric high molecular weight diblocks[14] with extra fractionation

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Table 1. Molecular Characteristics of SM Diblocks[16]

	M_w	M_w/M_n	w_{PS}^a	N^b	f_{PS}^c	κ_0^d	ϕ_{ODT}^e
SM600-39	640 000	1.06	0.391	6221	0.41	0.014	0.132
SM600-75	600 000	1.05	0.756	6027	0.77	0.005	0.200

[a] Polystyrene weight fraction. [b] Based on average segmental volume. [c] Polystyrene volume fraction. [d] Variance of composition polydispersity (ref 6) as $\kappa_0 \cong 2(M_w/M_n - 1)f^2(1 - f)^2[f^2 + (1 - f)^2]^{-1}$ with f the copolymer composition (e.g., f_{PS}). [e] Estimated from the theory[21] for polydisperse diblocks as $\chi N \phi_{ODT}^{1.59} = (\chi^* N)_s$ using $\chi = 0.041$ from ref 20.

have revealed the bimodal shape of $S(q,t)$ for $q/q^* \approx O(1)$ far away from the ordering transition.

The main objective of the present paper is to investigate the $S(q,t)$ for intermediate wavevectors as a function of the distance from the ODT. Two polystyrene-*block*-poly(methyl methacrylate), SM, diblock copolymers with molecular weights $M_w \sim 600\,000$ are being used in semidilute solutions in toluene in order to probe the $0.13 < qR_g < 0.99$ ($0.08 < q/q^* < 0.61$) range. This will bridge the low $qR_g \ll 1$ regime, where there are two well-accepted relaxation modes, with that around q^*, where the slower mode dominates, in a continuing effort to construct piece by piece the dynamic structure factor for disordered diblocks over the whole qR_g range. For the present qR_g's and for concentrations away from the ordering transition, the polydispersity and the internal modes exhibit the well-known behavior for low qR_g's. However, as the concentration increases toward the ODT, it is the polydispersity mode that is modified: its intensity increases with increasing wavevector and shows a concentration dependence stronger than ϕ^1. Its dynamics remains diffusive and is still controlled by the self-diffusion of the chains, as verified by independent measurements of the self-diffusivity by pulsed-field-gradient nuclear magnetic resonance (PFG-NMR). The characteristics of the internal mode are apparently not affected by the proximity to the ODT in this wavevector range. The data are analyzed within a theory developed for polydisperse diblocks, and a good agreement is observed.

A second objective of the present paper is to resolve an apparent confusion in the literature, which resulted from contradictory assignments of the relaxation modes in solutions of very similar copolymers.[15−17] The aim of those early investigations was to probe the internal mode (which was the only one predicted at the time[4,5]), but the lack of knowledge regarding the existence and characteristics of the polydispersity process made the mode assignment inconclusive. The present paper clearly identifies the relaxation modes and proves that the SM system can be also accounted along the same lines with the other systems investigated.

This article is arranged as follows: Following the Experimental Section, the results and the discussion are shown in section III. Finally, the conclusions constitute section IV.

II. Experimental Section

Materials. Polystyrene-*block*-poly(methyl methacrylate) diblock copolymers, SM, were synthesized by anionic polymerization under an inert atmosphere. The polystyrene blocks were polymerized first in THF at low temperature (−70 °C) using (phenyl−isopropyl)potassium as initiator, followed by the addition of methyl methacrylate monomers. The characteristics of the samples were measured with size exclusion chromatography, low-angle laser light scattering, and viscometry and are shown in Table 1. More details about the synthesis have been reported elsewhere.[16] The two copolymers possess similar molecular weights, but different compositions and were studied in concentrations that cover the semidilute homogeneous regime. The solvent used was toluene, which is considered to be almost equally good for both blocks.

Photon Correlation Spectroscopy (PCS). The autocorrelation function of the polarized light scattering intensity $G_{VV}(q,t) = \langle I(q,t)\ I(q,0)\rangle / \langle I(q,0)\rangle^2$ 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; $I(q,0)$ is the mean scattered intensity. Generally both the incident and the scattered beam were polarized perpendicular (VV geometry) to the scattering plane. The horizontal polarization of the scattered beam (VH geometry) was also used for every concentration; the flat depolarized correlation function together with the low VH scattered intensity verified that the solutions were in the disordered state.[6] An Adlas diode-pumped Nd:YAG laser was used as the light source with wavelength $\lambda = 532$ nm and single mode intensity 100 mW. The magnitude of the scattering wavevector is $q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the refractive index of the medium, resulting in an accessible q range of $3.7 \times 10^{-3} \le q \le 3.4 \times 10^{-2}$ nm^{-1}.

Under homodyne conditions, $G_{VV}(q,t)$ is related to the desired scattered field autocorrelation function $C(q,t)$ by $C(q,t) = \{[G_{VV}(q,t) - 1]/f^*\}^{1/2}$, where f^* is an experimental factor calculated by means of a standard. The experimental correlation functions $C(q,t)$ are analyzed by performing the inverse Laplace transform (ILT) using the routine CONTIN assuming a superposition of exponentials for the distribution of relaxation times $L(\ln \tau)$, i.e., $C(q,t) = \int_{-\infty}^{\infty} L(\ln \tau) \exp[-t/\tau]\ d(\ln \tau)$. All the measurements were performed at 20 °C.

Pulsed-Field-Gradient Nuclear Magnetic Resonance (PFG-NMR). PFG-NMR is a stimulated echo measurement using the proton spin as a probe (deuterated toluene is used as a solvent) if two magnetic field gradients with amplitude $\mathbf{g}$ and width δ are applied as pulses separated by the diffusion time t. The spin echo attenuation provides the incoherent structure factor[18] $S_{inc}(q,t) = \langle \sum_j \exp(i\mathbf{q}[\mathbf{r}_j(t) - \mathbf{r}_j(0)])\rangle / N$, where $\mathbf{r}_j(t)$ is the position of monomer j at time t. Experiments were performed for $0.013 \le t \le 0.503$ s and for generalized wavevectors, $\mathbf{q} = \gamma \mathbf{g} \delta$, $1.2 \times 10^{-4} \le q \le 1.2 \times 10^{-2}$ nm^{-1}, where γ is the gyromagnetic ratio of the proton. $S_{inc}(q,t)$ is normalized to $S_{inc}(q{=}0,t)$ at zero $\mathbf{g}$. All the measurements were performed at 20 °C. The normalized incoherent structure factor, $S_{inc}(q,t)$, exhibits a single-exponential decay vs q^2 for all diffusion times measured and an excellent superposition when plotted vs q^2t. Therefore, the data correspond to Fickian diffusion, with a self-diffusion coefficient $D_s \propto t^0$, determined from analysis of the data according to $S_{inc}(q,t) = \exp(-D_s q^2 t)$.

III. Results and Discussion

Figure 1 shows the net polarized intensity autocorrelation function for a 10.9 wt % SM600-75 solution in toluene for different scattering angles. Three different relaxation processes exist (the distribution of relaxation times for $\theta = 90°$ is given in inset a) with different dependencies of their intensities (inset b) and relaxation times (inset c) on the scattering wavevector, which are the three well-known modes in the low qR_g regime. The fast process is the cooperative diffusion ($I_{coop} \propto q^0$, $\Gamma_{coop} = D_{coop}q^2$), and the intermediate is the internal mode ($I_{int} \propto q^2$, $\Gamma_{int} \propto q^0$), whereas the slower one is the polydispersity mode ($I_{poly} \propto q^0$, $\Gamma_{poly} = D_{poly}q^2 \cong D_s q^2$), with D_{coop} the cooperative diffusion coefficient and D_s the chain self-diffusivity. Therefore, even in the present wavevector range, the behavior at this concentration away from the transition is identical to that for $qR_g \ll 1$. Assuming that the interaction parameter in semidilute solutions can be renormalized[19] as $\chi^* = \chi\phi^{(1-z)/(3\nu-1)}$, where $z = -0.225$, $\nu = 0.59$ is the Flory exponent in a good solvent, and χ is the bulk interaction parameter ($\chi = 0.041$ for SM[20]), the concentration of Figure 1

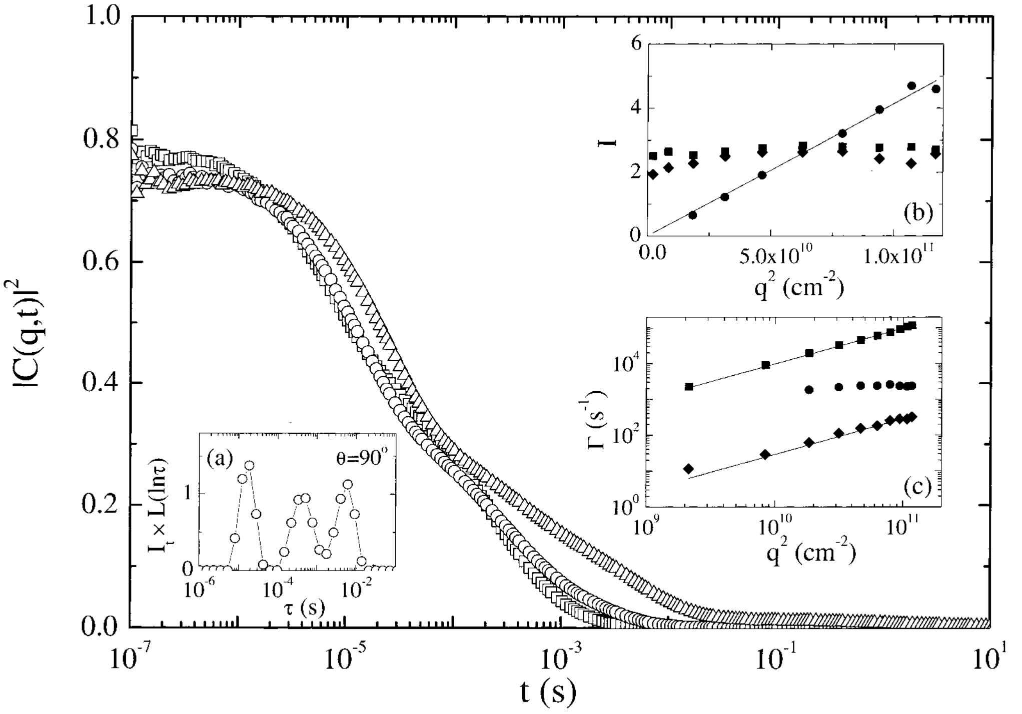

Figure 1. Intensity correlation functions for a 10.9 wt % SM600-75/toluene solution at three different scattering angles $\theta = 150°$ (□), 90° (○), and 60° (△). Inset a: distribution of relaxation times, $L(\ln \tau)$, at $\theta = 90°$ multiplied by the total scattered intensity normalized to that of toluene, I_t. Insets b and c: intensities and the relaxation rates, respectively, of the cooperative diffusion (■), the internal mode (●), and the polydispersity diffusion (◆). The lines represent the q^2 dependence.

corresponds to an incompatibility degree $\chi^*N \approx 5.1$, whereas the value at the spinodal can be estimated as $(\chi^*N)_s = 19.1$ using the theory for polydisperse diblocks.[21] The reduced distance from the ODT is, then, $\epsilon_r \equiv [(\chi^*N)_s - \chi^*N]/(\chi^*N)_s = 0.73$. (Note that this quantity was symbolized as ϵ in ref 12.) A behavior similar to that of Figure 1 is consistently observed for all the lower concentrations of SM600-75 (i.e., for $\epsilon_r > 0.73$) as well as for SM600-39 (with $(\chi^*N)_s = 10.2$) for concentrations up to 9.1 wt %, i.e., for $\epsilon_r > 0.62$. Therefore, it is concluded that in the case of solutions that are far away from the ODT, even for $qR_g \rightarrow 1$, the behavior is identical to the one predicted and observed for the $qR_g \ll 1$ regime provided that the polydispersity degree is not very high. It is mentioned that the concentrations discussed above already cover the concentration range that was studied before (from c^* to $8c^*$, with c^* the overlap concentration),[15-17] resolving the apparent controversy concerning the identification of the relaxation processes in SM diblocks up to $qR_g \sim 1$ far from the ODT. The cooperative diffusion is always the faster and the polydispersity self-diffusion mode is the slower process, while the intermediate is the internal copolymer mode. Additionally, there is no formation of aggregates.

This situation is modified, however, as the concentration is increased further toward the ODT. Field correlation functions of a 12.9 wt % SM600-39/toluene solution ($\chi^*N \approx 6.96$, $\epsilon_r = 0.32$) are shown in Figure 2 for three different scattering angles, with the q dependencies of the intensities and the relaxation rates of the modes shown in insets b and c. Three relaxation processes are still present (inset a). The intensities of the cooperative and of the internal modes depend on q^0 and q^2, respectively, similar to the lower concentrations. However, the intensity of the polydispersity mode, which was q-independent at lower concentrations, now exhibits a pronounced increase with increasing wavevector. At the same time, the relaxation rates of all three processes follow the dependencies of Figure 1. This is even more important for the polydispersity mode, which is still diffusive despite the q dependence of its intensity.

The effect of the proximity to the ODT on the intensities of the two main modes for the two diblocks is shown in Figure 3 for different concentrations. The intensity of the internal mode (Figure 3b) exhibits a q^2 dependence for all concentrations whereas it conforms (within the error) to the predicted $\phi^{0.77}$ scaling even close to the ODT. On the other hand, the initially q-independent intensity of the slower polydispersity mode, I_{poly} (Figure 3a), gains intensity at high wavevectors with increasing concentration, i.e., as the system approaches the ODT. The increase at high wavevectors leads to stronger concentration dependence as well; i.e., the intensity is proportional to ϕ only for the lower wavevectors whereas it shows a stronger dependence for higher ones, i.e., as q increases toward the critical wavevector q^*. (For the specific copolymers q^* is larger than the highest q available in light scattering.) Once more it is emphasized that, in the $qR_g \ll 1$ limit, the intensity of the polydispersity mode is always q-independent and proportional to ϕ even close to the ODT;[6-9,22,23] i.e., the increased thermodynamic interactions modify the behavior of the polydispersity mode in the intermediate qR_g range. This modification in the behavior is first observed for experimental reduced distances from the ODT between 0.48 and 0.62 for SM600-39 and between 0.61 and 0.73 for SM600-75.

Despite the peculiar behavior of the intensity of the polydispersity mode, the q dependence of its dynamics as well as of the dynamics of the other processes is not affected as shown in Figure 2. However, it is important to quantitatively verify whether the polydispersity diffusion is still determined by the copolymer self-diffusivity. Thus, the self-diffusion coefficients, D_s, were

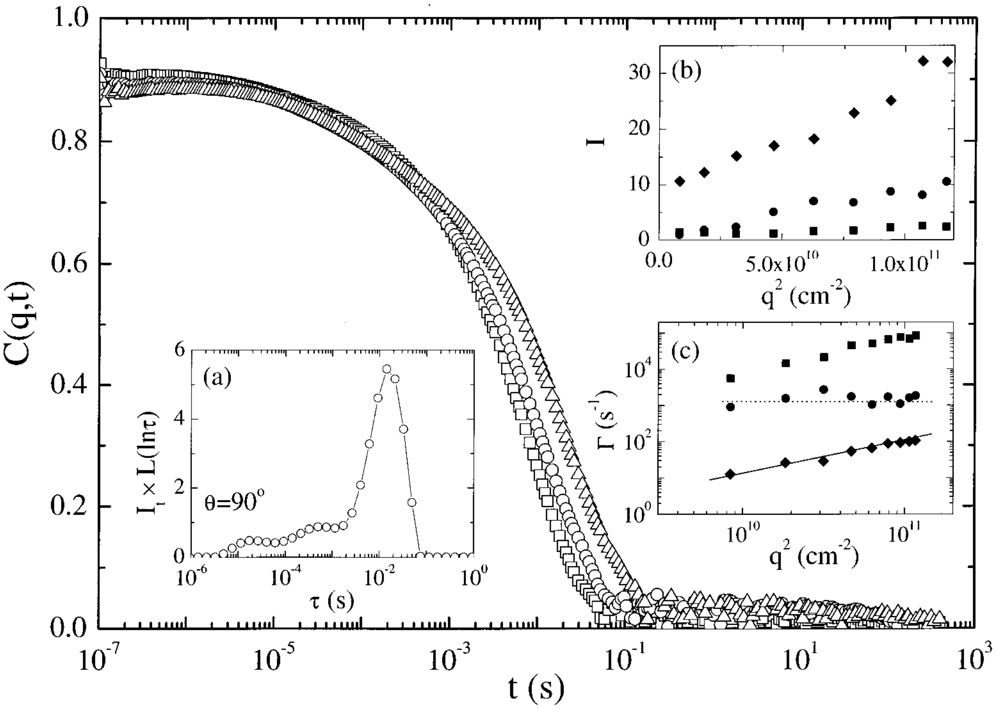

Figure 2. Field correlation functions for a 12.9 wt % SM600-39/toluene solution at three different scattering angles $\theta = 150°$ (□), 90° (○), and 60° (△). Inset a: distribution of relaxation times, $L(\ln \tau)$, at $\theta = 90°$ multiplied by the total scattered intensity normalized to that of toluene, I_t. Insets b and c: intensities and the relaxation rates, respectively, of the cooperative diffusion (■), the internal mode (●), and the polydispersity diffusion (◆). The solid and dotted lines represent the q^2 and q^0 dependencies of the rates of the polydispersity and the internal mode, respectively.

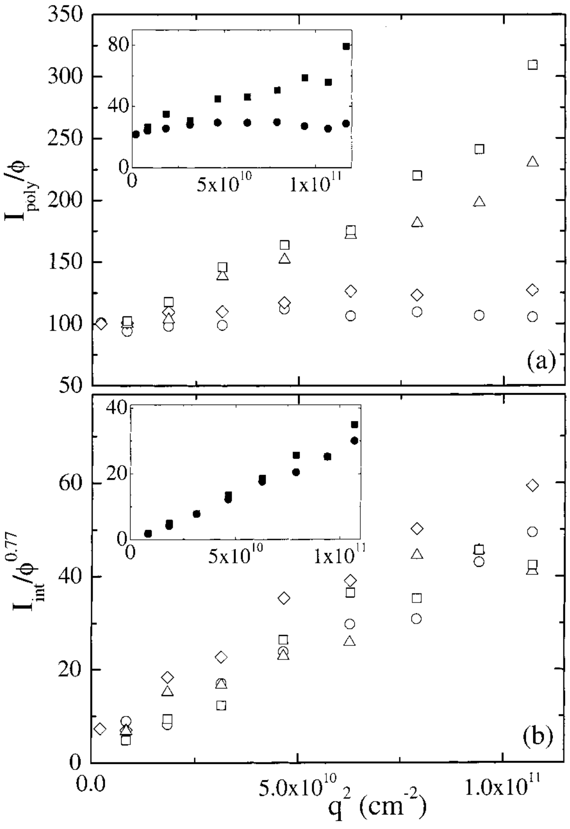

Figure 3. Wavevector dependence of (a) I_{poly}/ϕ and (b) $I_{\mathrm{int}}/\phi^{0.77}$ for the SM600-39/toluene solutions at 6.95 (○), 9.15 (◇), 11.0 (△), and 12.9 wt % (□). In the insets, the respective plots for SM600-75/toluene at 10.94 (●) and 15.0 wt % (■).

measured by PFG-NMR for concentrations covering the homogeneous as well as the weakly ordered state and are shown in Figure 4.

Figure 4 and its inset show the results for the dynamics of both diblocks vs concentration. As expected, D_{coop} increases whereas $\Gamma_{\mathrm{int}}/q^2$, D_{poly}, and D_{s} decrease with increasing ϕ.[24] An important observation is that there is still a perfect superposition of the values of D_{poly} and D_{s}, which means that, despite the change in the behavior of I_{poly}, this process (in the present q/q^* range) continues to reflect the self-diffusion of the chains. Moreover, the relaxation time of the internal mode is very close to the inverse of the longest relaxation time measured by rheology for one concentration, showing that it indeed reflects the longest relaxation time of the chains, in agreement with previous studies.[14]

An attempt is now made to analyze the experimental data with the appropriate theoretical model,[12] which predicts the relaxation of the dynamic structure factor $S(q,t)$ for symmetric diblock copolymers assuming reptation dynamics and taking into account the polydispersity. For entangled homogeneous diblocks, $S(q,t)$ is expressed as a superposition of relaxation processes

$$S(q,t) = \sum_k I_k(q) \exp[-\Gamma_k(q)t] \tag{1}$$

with $I_k(q)$ and $\Gamma_k(q)$ the intensity and the relaxation rate of the kth mode, which are evaluated by

$$1/\kappa(q, -\Gamma_k) = 0 \quad \text{and} \quad I_k = \frac{1}{\Gamma_k}\mathrm{Res}_{p=-\Gamma_k}[\kappa(q,p)] \tag{2}$$

$\kappa(q,p)$ is the Laplace transform of the generalized susceptibility of the system which is related to $S(q,t)$ via the fluctuation–dissipation theorem,[26] where Res means the residue of a pole singularity. (In the above equation, $I_k = I_k(q)$ and $\Gamma_k = \Gamma_k(q)$.) $\kappa(q,p)$ has been analytically calculated for polydisperse diblock copolymers in the framework of random phase approximation

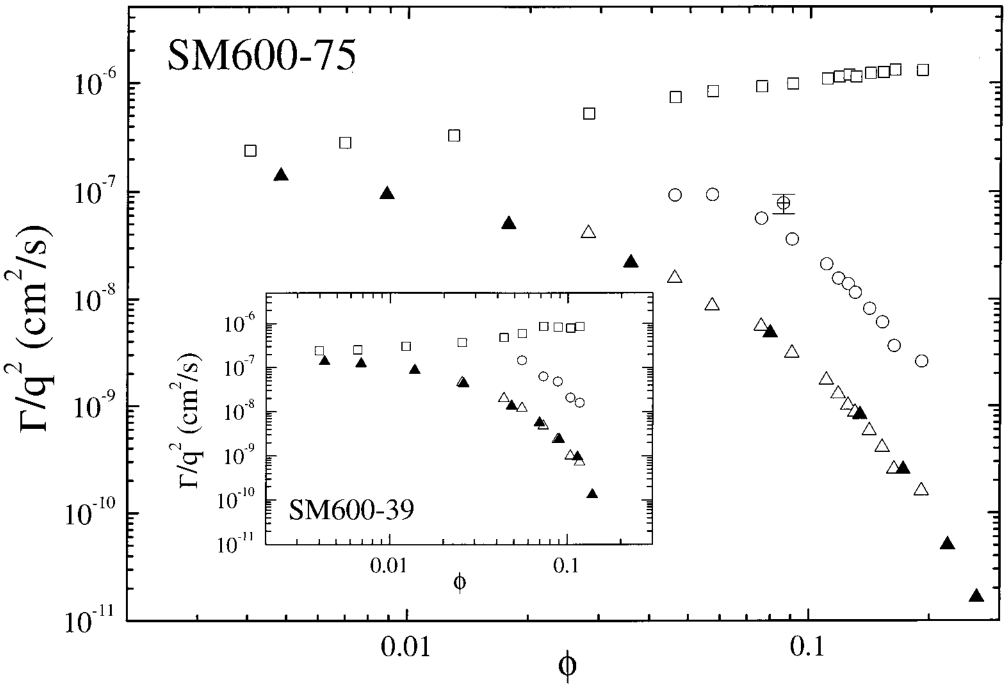

Figure 4. Concentration dependence of the effective diffusion coefficients Γ/q^2 for the relaxation processes of SM600-75/toluene and SM600-39/toluene (inset): (□) cooperative diffusion, (○) internal mode, and (△) polydispersity mode. (▲) Self-diffusion coefficients measured by PFG-NMR. (⊕) The inverse of the longest relaxation time from rheological measurements (dynamic frequency sweeps in the linear viscoelastic regime). The relaxation rate of the internal mode as well as the inverse of the longest relaxation time has been divided by q^2 at $\theta = 90°$. The errors bars are smaller than the size of the points.

(eqs 8b and 16 of ref 12); however, those expressions are not reproduced herein due to their length. According to this theory, the two slower relaxation modes are the most important since almost all the scattering intensity relaxes via them. Their relative intensities, however, depend on the composition polydispersity of the diblock copolymers, the wavevector, and the distance from the ordering transition. It is predicted that, in the general case and for reasonable composition polydispersities, the two processes are coupled over the whole qR_g regime except for $qR_g \rightarrow 0$; only in that limit the two relaxation processes can be really identified as the known internal and polydispersity modes. Additionally, it is the slowest process that is mostly affected by both the thermodynamic interactions (strong increase of the intensity and a pronounced slowing down of the dynamics near q^*) and the polydispersity (constant intensity and diffusion coefficient for $qR_g \rightarrow 0$).

The theory was explicitly developed for symmetric systems. However, one can attempt a quantitative comparison with the data for the SM600-39, with composition $f_{PS} = 0.41$. The result is shown in Figure 5 for a 12.9 wt % SM600-39/toluene solution ($\phi = 0.104$) where the theoretical curves are compared to the experimental data for the intensities and relaxation rates of the internal and polydispersity modes. A quite good agreement between the experimental data and the theoretical curves for $\epsilon_r = 0.25$ is observed. All the curves have been generated using as adjustable parameters the interaction parameter $\chi^* = 0.0012$, the radius of gyration $R_g = 28.6$ nm (which compares favorably to that estimated from dilute solution data or from the melt within the blob model), and proportionality constants for both the intensities and relaxation rates. (The one for the latter should be inversely proportional to the disentanglement time, τ_d.) For the polydispersity index, the value $M_w/M_n = 1.08$ was used, which is slightly higher than the one that came out from the

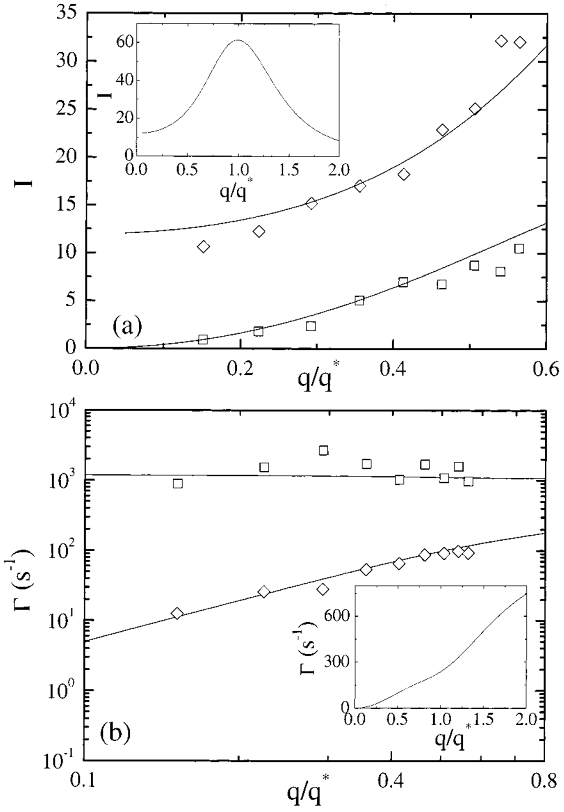

Figure 5. Intensities (a) and relaxation rates (b) of the internal (□) and the polydispersity (◇) modes as a function of the reduced wavevector q/q^* for a 12.9 wt % SM600-39/toluene solution. The lines are the corresponding fits according to eqs 1 and 2 for $k = 0$ and $k = 1$. In the insets the theoretical prediction for the intensity and the relaxation rate of the slower mode are shown for the whole wavevector range.

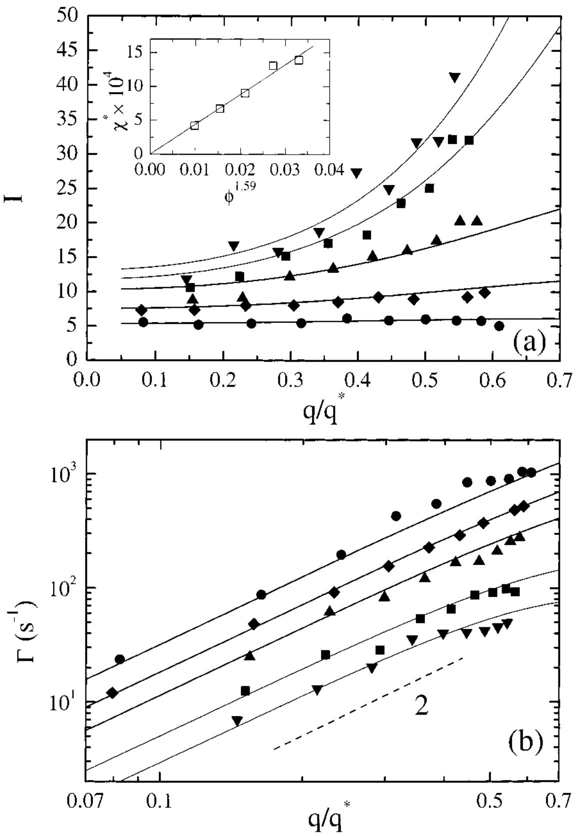

Figure 6. Intensities (a) and relaxation rates (b) of the polydispersity mode as a function of the reduced wavevector q/q^* for (●) 6.95, (◆) 9.15, (▲) 11.0, (■) 12.9, and (▼) 14.5 wt % SM600-39/toluene solutions. The solid lines are the theoretical fits according to eqs 1 and 2 for $k = 0$ whereas the dashed line indicates the q^2 dependence. The inset shows the dependence on concentration of the renormalized interaction parameter χ^* used in the fits.

characterization of the diblock. In the two insets the theoretical curves for the intensity and the relaxation rate of the slower mode are shown for a larger wavevector range. For this concentration, there is only a very weak slowing down of the dynamics near q^* although the mode exhibits a peak in its intensity. Note that, much closer to the ODT, the slowing down at q^* mirrors the sharp increase of the intensity due to the enhanced thermodynamic interactions.[12] Note that the fit of the theory to experimental data is much more robust when q^* is in the experimental window, which is not the case for the present systems.[27] The comparisons for the intensities and relaxation rates of the polydispersity mode are shown in Figure 6 for different concentrations of SM600-39 covering the range from far from the ordering transition (with a q-independent intensity) up to close to ODT, where a significant increase is observed. The good agreement discussed in Figure 5 is observed for all the concentrations investigated. The theory can capture the increase of the intensity as well as predict the dynamics, which, for this wavevector range, remains always almost diffusive. (For the highest concentration in Figure 6b, the theoretical curve shows deviation from q^2 for the higher q's.)

Although the concentration range covered is very small in order to deduce a ϕ dependence of the adjustable parameters, it is mentioned that the proportionality coefficient used to multiply the theoretical intensity curves is constant (reflecting only the optical setup and the refractive index contrast), and the estimated R_g decreases slowly with ϕ (as expected), whereas τ_d shows a dependence stronger than the $\phi^{1.6}$ predicted for entangled chains (as observed earlier as well[12]). The estimated χ^* (inset of Figure 6a) shows a linear dependence on $\phi^{1.59}$ (as predicted for semidilute solutions), which results in $\chi = 0.044$, close to the value $\chi = 0.041$ given in the literature.[20] It is noted that the concentrations shown in Figure 6 are not "too close" to the ODT (they correspond to reduced distances from the ODT $\epsilon_r > 0.096$), for which deviations from the expected behavior are not observed; it was shown before (Figure 12 of ref 12) that the estimated parameters (χ^*, R_g, and t^* or τ_d) deviate significantly from the behavior expected within the blob picture for concentrations much closer to the ODT, where fluctuation corrections[19] should become important (for the copolymer in Figure 12 of ref 12, for $\phi^{1.59} > 0.002$, which corresponds to $\epsilon_r \leq 0.037$). Therefore, the theory can capture the main features of the observed behavior, i.e., the modification of the relaxation modes of composition fluctuations in disordered diblocks in the present range of wavevectors and thermodynamic interactions, despite its inherent assumptions (RPA, reptation dynamics, blob picture); these are expected to only influence the estimated values of the fitting parameters.

Finally, it should be mentioned that for the highest concentrations a fourth relaxation process is observed with relaxation rate between those of the cooperative diffusion and the internal mode (not shown). All the modes starting from the fastest are the cooperative diffusion, an intermediate process, the internal mode, and the polydispersity diffusion. This intermediate process has a q^2-dependent intensity and a q-independent relaxation rate. These characteristics resemble the ones predicted for the Rouse mode, which has been observed in high molecular weight[11-13] entangled copolymers and was attributed to curvilinear chain fluctuations within their reptation tube. The intensity and relaxation rate of the Rouse mode, for low qR_g's, depend on the wavevector as $I_R \propto q^2 R_g^2$ and $\Gamma_R \propto q^0$. These expressions agree with the observed dependencies for the intermediate process, whereas no conclusion can be drawn for the ϕ dependence, since this process is observed only for the highest concentrations.

It is stressed that the terminology "internal mode" and "polydispersity mode" has been used in this work to describe the main processes of relaxation of composition fluctuations, although it has been shown[12] that this identification is valid only in the very low qR_g regime and far way from the ordering transition or for very low polydispersities. Outside these limits there is a coupling between the modes as is also evident in the present study.

IV. Concluding Remarks

Photon correlation spectroscopy and pulsed-field-gradient NMR have been used to identify the modes of relaxation of composition fluctuations in diblock copolymer solutions in the intermediate $0.13 < qR_g < 0.99$ regime. The purpose was to experimentally bridge the range between the previously studied $qR_g \ll 1$ and $q \sim q^*$ regimes and to clear the apparent confusion in the early literature on SM solutions. The three relaxation modes—cooperative diffusion, internal mode, and polydispersity diffusion—identified for $qR_g \ll 1$ were verified in this range as well. Their characteristics at low concentrations away from the ODT are identical to those for $qR_g \ll 1$. However, by approaching the ordering transition, it is the characteristics of the intensity of the so-called polydispersity diffusive mode (both its q and ϕ dependencies) which are modified, although its dynamics is still determined by the chain self-diffusivity. Comparison of the experimental results with a theory that predicts the decay of the dynamic structure factor $S(q,t)$ taking into account the composition polydispersity of the diblocks gives qualitative and quantitative agreement.

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(23) Data on a series of lower molecular weight polystyrene-*block*-poly(methyl methacrylate) diblocks,[22] i.e. for $qR_g \ll 1$, confirm that the polydispersity mode exhibits a $q^0\phi^1$ dependence even very near the ODT.

(24) All the effective diffusion coefficients for the three relaxation processes attain similar values for the two diblocks. For D_{coop} this is due to the very similar c/c^* range whereas for the others it is due to both the similar molecular weights as well as to the very similar entanglement characteristics of the two constituents.[22,25]

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(27) For the present systems, the critical wavevector q^* lies outside the experimental range of PCS. To overcome this, complementary measurements were performed using small-angle X-ray scattering for SM600-75/toluene, covering the $qR_g > 2.5$ regime ($q > 0.09$ nm^{-1}). The X-ray data can be spliced together with the PCS data of the total intensity of composition fluctuations and analyzed using the theoretical expressions for the static structure factor.[21] For a 18.2 wt % SM600-75/toluene solution, the fit gave $\chi^* = 0.0025$ and $R_g = 26.8$ nm.

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