Breathing and Composition Pattern Relaxation in "Homogeneous" Diblock Copolymers

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The relaxation mechanism of diblock copolymers above the order-to-disorder transition has been identified. We present the first experimental evidence of the existence of both a local internal breathing relaxation process and a diffusive pattern relaxation mode measured on the same sample for a series of diblock copolymers by applying photon correlation spectroscopy in the polarized geometry. The relaxation characteristics of both modes are modeled in terms of recent theories, with the necessity for a complete theory becoming evident.

Diblock copolymers are macromolecules composed of two covalently bonded sequences, or blocks, of chemically distinct repeat units. The extensive literature [1] on diblock copolymers A-B deals mainly with their complex phase behavior and morphological characteristics, which are determined by the overall degree of polymerization, N, the composition of A, f, and the Flory-Huggins interaction parameter, χ. For $\chi N \ll 10$, the copolymers exist in a spatially homogeneous or disordered state [2]. As χN is increased to be $O(10)$, local composition fluctuations are developed on a scale proportional to the polymer size [3,4]. These equilibrium composition field configurations have been viewed as a superposition of isotropic composition plane waves with wave vectors having random directions and phases and a preferred [3] or not [4] magnitude, q^*, which create a "pattern" that fluctuates in time with a cooperative correlation length ξ. The fluctuations lead to a weak first-order order-to-disorder transition (ODT) towards a microphase with long-range order in its composition. Strong unambiguous evidence of significant composition fluctuations at temperatures well above ODT has been recently reported. Small angle neutron scattering and rheological measurements [5] revealed characteristics that quantitatively agree with the fluctuation theory predictions and established that the pattern resembles the transient morphologies encountered during the final stages of spinodal decomposition. Dielectric relaxation spectroscopy [6–8] and depolarized dynamic light scattering [7,8] (photon correlation spectroscopy—PCS) produced clear evidence of the existence of two distinctly different segmental orientation times in "homogeneous" diblock copolymer melts, which proves the existence of two different local environments in diblocks, i.e., strong composition fluctuations even far above the ODT. The root-mean-square amplitude of the composition fluctuations estimated from the local segmental orientation times compares favorably [8] with the amplitude predicted by theory [3].

Relatively less effort has been devoted to the dynamical

properties of block copolymer melts, with the understanding of the mechanism of their relaxation still missing. Rheological investigations [5] showed evidence of critical slowing down near the ODT, with theory [9] qualitatively capturing the relative fluctuation contributions to the shear and normal stress coefficients. The random phase approximation method [10] and the Edwards Hamiltonian approach [11] have been used to derive the intermediate scattering functions and their relaxation characteristics in bulk homogeneous diblock copolymers; the mean-field fluctuation-free calculations predict a single relaxation process that is attributed to the relative motion of the two polymer blocks (internal or breathing mode). The relaxation rate of this mode is predicted to be independent of the scattering vector q for low q's. Very recently PCS in the polarized geometry revealed [8] a new relaxation mode in "homogeneous" diblocks. This mode is of diffusive nature (q^2-dependent relaxation rate) and was attributed to the relaxation of the composition fluctuation induced pattern. Investigations on the dynamics of diblock copolymer solutions, on the other hand, lead to the observation of various modes of relaxation [12,13] without a concensus regarding the underlying dynamics.

In this Letter, we present the first experimental evidence of the existence of both the q-independent internal breathing relaxation process and the diffusive q^2-dependent pattern relaxation mode measured on the same sample by applying PCs in the polarized geometry on a series of diblock copolymers with different N's and f's, thus identifying the mechanism of relaxation of diblock copolymer melts above the ODT. The relaxation characteristics of both modes may be consistently modeled using bulk copolymer viscosities and friction coefficients deduced from interdiffusion data on the corresponding mixtures.

Four poly(dimethyl siloxane-b-methyl ethyl siloxane), P(DMS-b-MES), diblock copolymers with different N's and f's were anionically synthesized and characterized, as will be described elsewhere [14], and their characteris-

TABLE I. Sample molecular characteristics and relaxation behavior at 80 °C.

Sample	N[a]	Weight % (PDMS)	M_w/M_n	$D_{s,exp}$ (cm^2/s)	$\Gamma_{f,exp}$ (s^{-1})	ξ (Å)	τ_0 (s)	$D_{s,calc}$ (cm^2/s)	$\Gamma_{f,calc}$ (s^{-1})
I	1110	49	1.04	4.0×10^{-10}	3900	127	3.5×10^{-10}	1.2×10^{-11}	7150
II	790	30	1.05	6.0×10^{-10}	4700	47	4.4×10^{-10}	5.8×10^{-11}	19410
III	530	43	1.04	2.3×10^{-9}	30000	41	3.7×10^{-10}	1.5×10^{-10}	66200
IV	241	46	1.08	3.6×10^{-8}	$\cdots$	23	3.6×10^{-10}	7.2×10^{-9}	1.7×10^6

[a]Based on PMES segmental volume.

tics are given in Table I. Gel permeation chromatographic results showed no evidence of precursor homopolymer contamination in the samples used. The samples display homogeneous behavior for the temperatures used in this work and their ODT determined rheologically are about 25 °C for sample I and ≤ -20 °C for the others. The similarity of the chemical structure of the two repeat units leads to small interaction parameter values ($\chi = -2.0\times10^{-3}+4.07/T$, by cloud-point measurements in blends [15] with T the absolute temperature, based on PMES segmental volume) and allows the investigation of high molecular weight (MW) diblock copolymers in the disordered state. In addition, the very low glass transition temperatures, T_g, of the respective homopolymers (ca. -130 °C) lead to similar segmental mobilities over the whole temperature range of the experiments.

The intermediate normalized structure factor of composition fluctuations, $S_n(q,t)$, is related to the autocorrelation function, $G_{VV}(q,t)$, of the intensity of the polarized scattered light by $S_n(q,t) = \{[G_{VV}(q,t)-1]/f^*\}^{1/2}$ under homodyne conditions. $q = (4\pi n_0/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector at scattering angle θ, with n_0 the refractive index of the medium, and λ the wavelength of the incident radiation in vacuum. f^* is an instrumental factor calculated by means of a standard
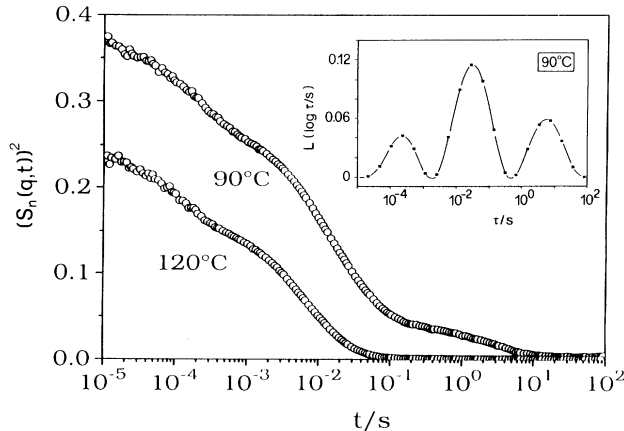

FIG. 1. The square of the normalized dynamic structure factor for sample I at $q = 2.5\times10^5$ cm^{-1} for different temperatures. The inverse Laplace transform of the correlation function at 90 °C is shown in the inset.

polystyrene/CCl$_4$ solution. $G_{VV}(q,t)$ is measured using an ALV-5000 full digital correlator over the time range 10^{-6}–10^3 s with both the incident laser beam ($\lambda =488$ or 647 nm, single mode intensity 150 mW) and the scattered beam polarized perpendicular (V) to the scattering plane.

Figure 1 shows the square of the $S_n(q,t)$ for sample I. Three relaxation processes are seen to contribute to the time correlation functions. $S_n(q,t)$'s were then analyzed by performing the inverse Laplace transformation (ILT) of the data without assumption of the shape of the distribution function $L(\ln\tau)$ but assuming a superposition of exponentials; $S_n(q,t) = \int_{-\infty}^{\infty}L(\ln\tau)e^{-t/\tau}d(\ln\tau)$. This determines a continuous spectrum of relaxation times like the one shown in the inset of Fig. 1. The sufficient separation of the three processes facilitates the analysis of their relaxation characteristics as a function of q, shown in Fig. 2. The very slow process that contributes significantly to $G_{VV}(q,t)$ at low angles and modifies the scattered intensity is attributed to "cluster" formation (called "slow density fluctuations"), also found in molecular and macromolecular glass formers [16], and signifies diffusion of moieties on the scale of 2000 Å; at higher T, this slow process loses amplitude significantly. Its presence affects the ILT values of the amplitudes of the two other modes but not their characteristic times because of the more than 2 orders of magnitude separation of the characteristic times. The fast process exhibits a q-independent relaxation rate, Γ_f, and a normalized amplitude, α_f, that depends on q^2, whereas the slower process has a q^2-dependent relaxation rate, Γ_s, and an almost constant normalized amplitude, α_s, as expected for scattering of moieties with $q\xi < 1$. Therefore, the slower process is diffusive, with an apparent diffusion coefficient D_s (Table I), whereas the fast process is a localized process. Sample IV, however, that has a significantly lower MW, showed only the diffusive process and the very slow clusters, similar to the low MW diblock investigated earlier [8]. This is due to the N dependence of the amplitude and the relaxation rate of the fast process, as will be discussed later. Figure 3 shows the N dependence of D_s and Γ_f at 80 °C.

The q^2-dependent relaxation process has only very recently been documented [8] on a homogeneous poly(styrene-b-methyl phenyl siloxane) diblock and was attributed to the relaxation of the equilibrium composition
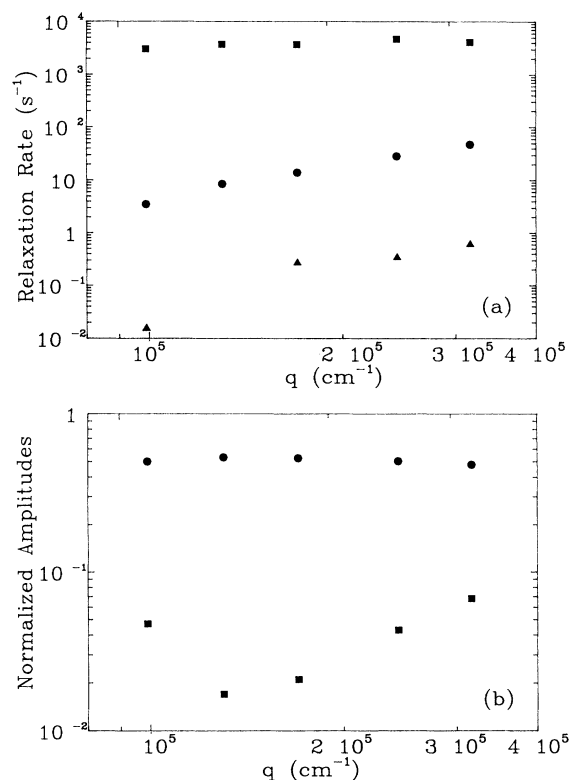
FIG. 2. Relaxation rates (a) and normalized amplitudes (b) of the three processes as a function of q for sample II at 80 °C. The amplitudes are normalized to constant clusters amplitude, to take into account the complications on the ILT amplitude arising by the presence of the very slow process. ■: breathing mode; ●: diffusive mode; ▲: clusters.
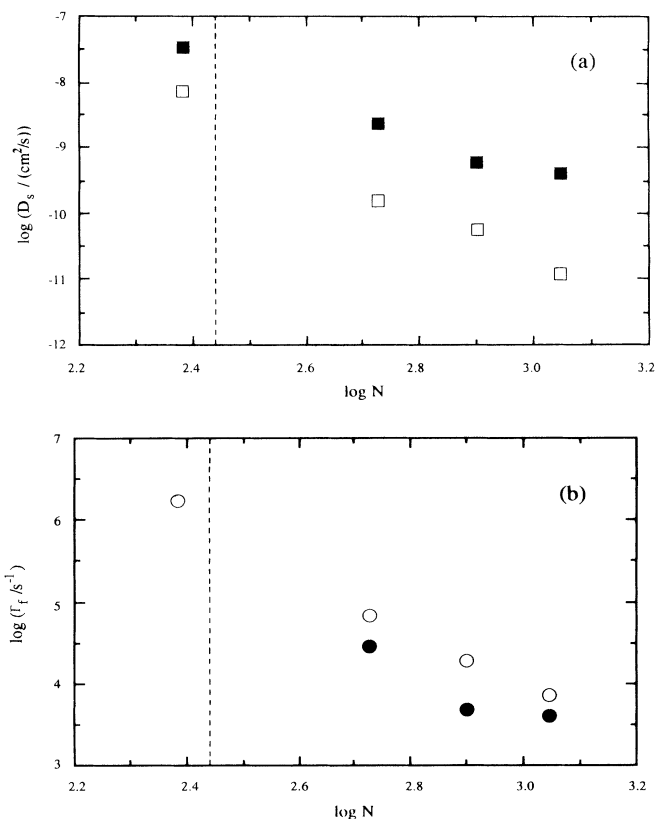

FIG. 3. Molecular weight dependence of (a) the diffusion coefficient D_s, and (b) the breathing relaxation rate Γ_f at 80 °C. ■,●: experimental data; □,○: calculated values (see text). Dashed line denotes N_c.

field configurations (pattern) by a diffusive mechanism. The presence of substantial polarized light scattering from composition fluctuations is justified by the finite difference in scattering amplitude because of the existence of the two environments with root-mean-squared fluctuation amplitude of about [3,8] 0.3, and the finite value of the structure factor $S(q)$ even at the low q's of light scattering arising from polydispersity [8,17]. Its relaxation rate was modeled by assuming a Stokes-Einstein formula $(D_s = k_B T/6\pi\eta\xi)$ for the diffusion of moieties of size [3] ξ in an environment with viscosity η and an average local friction coefficient dominated by the slow component (k_B is Boltzmann's constant, and T the temperature). The fluctuation theory [3] leads to cooperative concentration correlation lengths, ξ, given in Table I for 80 °C, and composition fluctuation amplitudes of about 0.2. For the highest N, sample I, theory [3] predicts the ODT at 11 °C that, given the uncertainty in χ, compares well with the experimental 25 °C. Zero shear viscosities for the diblocks I–III were determined rheologically [14] as $\eta = \lim_{\omega \to 0} G''(\omega)/\omega$ where $G''(\omega)$ is the loss modulus at frequency ω, which at low frequencies showed a ω^1

dependence for the disordered diblocks [6]. For the low MW sample IV, viscosity was estimated using Rouse dynamics [18] with friction coefficient, ζ, discussed below. The calculated diffusion coefficients are shown in Table I and Fig. 3. A systematic deviation is observed with the theoretical values being 1 to 2 orders of magnitude lower than the experimental ones, the deviation being larger for sample I, which is much closer to the ODT. A possible explanation, provided that the Stokes-Einstein relation applies, may be that the macroscopic bulk viscosity used in the calculation overestimates significantly the local effective viscosity felt by the copolymer "blobs."

The q-independent relaxation process has been predicted by the mean field theory (absence of fluctuations) and was attributed to the relative motion of the two blocks. Theory [10,11] predicted the existence of a single process in homogeneous diblock copolymer metals, and, in the Rouse regime and for the low q's of light scattering, provided expressions for a q-independent relaxation rate and a q^2-dependent amplitude. This mode has been experimentally observed in diblock copolymer solutions [12] together with the cooperative diffusion of the diblock

chains. Extension of this to cover the reptation regime is accomplished by modifying the mobility term by a factor [19] a^2/Nb^2, where a is the diameter of the tube in the reptation model which is related to the number of segments between entanglements, N_e, by [18] $a^2 = \frac{4}{5}N_e b^2$, with b the statistical segment length. The relaxation rate of the process is then $\Gamma_f = 24 N_e f(1-f)q^2 R_G^2/5\tau_0 N^2 \times S(q)$, where $S(q)$ is the static structure factor [2–4], R_G is the radius of gyration of the diblock, and the average local time is $\tau_0 = \zeta b^2/k_B T$. Because of the very low T_g of both components, the local segmental times cannot be determined by PCS, as was done for other systems [7,8]. An alternative approach is to estimate ζ from interdiffusion measurements in unentangled binary PDMS/PMES mixtures [20] far above the macrophase separation by PCS. The estimated segmental times are shown in Table I. The characteristic number of segments for reptation, N_c, has been obtained by viscosity measurements [20] on the two homopolymers to be 275 for both. The number of segments between entanglements, N_e, is then [21] $N_c/2.2 = 125$. Both the values and the N dependence of the calculated relaxation rates compare reasonably well with the experimental ones (Table I and Fig. 3) for the symmetric diblocks, whereas there is some deviation for sample II.

The scattering amplitude of the process, a_f^*, is predicted to be equal to the total $S(q)$ of homogeneous diblocks. In the low q limit, $S(q)$ shows an almost q^2 dependence and, therefore, the data agree with the q dependence of both the rate and the amplitude of the process, where the amplitude is predicted to scale with N^2. Quantitative comparison of the magnitudes of the scattering amplitudes is subject to large experimental uncertainties, since a major part of the dynamic structure factor relaxes with the diffusive mode with an experimental normalized amplitude that is about 1 order of magnitude larger than the one for the breathing process. Therefore, only about a tenth of the dynamic structure factor contributes to this mode. Besides, the theory for the internal mode applies only in the mean field picture in the absence of composition fluctuations. A different approach is required in order to predict both the relaxation of the composition field configurations together with the internal relaxation process in the Hartree fluctuation approximation. The q-independent relaxation mode is not observed for the lowest MW diblock (sample IV) due to its low amplitude ($a_f^* \sim N^2$), similarly to the low molecular weight diblock investigated before [8]. In addition, the predicted Γ_f is too fast to be measured by PCS.

These results elucidate the relaxational behavior of block copolymer melts above the ODT. There are two different mechanisms of relaxation: a local (q independent) process attributed to the relative motion of the two blocks, and a diffusive (q^2 dependent) process attributed to the motion of the composition fluctuations induced pattern.

In conclusion, we have identified the mechanisms of

relaxation in homogeneous diblocks by presenting the first experimental evidence for a q-independent internal breathing relaxation process, predicted by mean-field theory, together with a q^2-dependent diffusive compositional pattern relaxation process. Both the relaxation rates and the amplitudes of the two processes were compared with theoretical predictions employing the latest theories in the field. A necessity for a complete theory to describe the relaxations in diblock copolymer above the ODT is clearly evident.

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