Effect of the Disorder-to-Order Transition in Diblock Copolymers on the Segmental Dynamics: A Study Using Depolarized Photon Correlation Spectroscopy

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ABSTRACT: Depolarized light scattering has been applied to study the anisotropy fluctuations in a series of polystyrene/polyisoprene diblock copolymers. This method is selective for the dynamics of the polystyrene block. The molecular weights of the block copolymers (10500–20800) were chosen such that the microphase separation transition (MST) occurs at temperatures which are experimentally accessible with photon correlation spectroscopy. Small-angle X-ray scattering (SAXS) was used to identify the disordered regime, the fluctuation-controlled transition regime, and the ordered state. The relaxation time spectrum in the disordered state is similar to that of bulk polystyrene. Concentration fluctuations increasingly broaden the spectrum and lead to a bimodal shape. Close to the MST the spectrum becomes dominated by a slow, nearly single exponential contribution. Comparison with the SAXS results suggests that this splitting of the relaxation time spectrum can be related to chain stretching.

I. Introduction

Block copolymers are known to possess a disordered state with their different blocks interpenetrating in just the same way as homopolymers in the melt. Their chain conformation is believed to be ideal; i.e., the distance distribution of chain segments within a molecule is Gaussian. This state of ideal disorder is only attained if there is no repulsive interaction between the different constituents of the block copolymer. In general, one needs high temperatures and comparatively low molecular weight to make the entropy of mixing the dominating part in the free energy of the system. With lowering temperature the mostly repulsive interaction between the blocks of the polymer will gain importance and finally lead to a demixing on the length scale of the blocks and to the formation of an ordered mesophase. This is called the microphase separation transition (MST). Although the existence of both disordered and ordered states of block copolymers had been demonstrated long ago, there are only a few examples of the direct observation of the MST in a temperature-driven experiment.[1,2]

Major properties of the MST may be described in a mean field theory, the random phase approximation (RPA).[3] An extension of the RPA to describe the dynamic structure factor was demonstrated to apply to neutron scattering experiments probing the segmental dynamics of diblock copolymers in a homopolymer melt.[4] However, the theory neglects fluctuations in the local composition, which were subsequently shown to play an important role for the MST.[1,5] They give rise to a transition regime which is characterized by partial demixing on the scale of the block radius in the absence of long-range order.

The degree of mixing immediately influences the segmental dynamics of the block copolymer as the mobility of a chain segment is directly related to the free volume of its environment. Demixing of segments may therefore be monitored as a change of the segmental mobility of the polymer chain. However, this information will only be clear if the segmental mobility of the constituents of the block copolymer differ significantly. This will be the case if the corresponding homopolymers exhibit widely different glass transition temperatures.

A further complication may arise from the superposition of the signal obtained from the different blocks of the copolymers.

In the present work we have applied depolarized photon correlation spectroscopy (PCS) to investigate the segmental dynamics in polystyrene/*cis*-1,4-polyisoprene diblock copolymers. The glass transition temperatures of polystyrene (T_g^{PS} = 377 K) and polyisoprene (T_g^{PI} = 204 K) differ greatly. A strong dependence of the segmental mobility on the degree of order will therefore be expected. Furthermore, the use of depolarized scattering makes the experiment selective for the segmental dynamics of the polystyrene block. Our results are in this sense complementary to previous work on the same polymers using dielectric spectroscopy.[6] There the observed quantity was the dynamics of the polyisoprene block. A further difference lies in the length scale of observation. Whereas the dielectric experiment measured the relaxation in the autocorrelation of the end-to-end vector of the polyisoprene block, we show in section IV that the relevant scale in the present experiment is the segment length.

To relate the segmental dynamics observed in PCS to the structural properties of the diblock copolymer, it is essential to determine the transition temperatures and the effective interaction parameter from small-angle X-ray scattering (SAXS). We present PCS measurements on three block copolymers in a temperature regime that extends from the disordered into the ordered regime. The impact of concentration fluctuations on the observed relaxation functions is discussed, and the results are compared to information obtained from dynamic mechanical[2] and dielectric experiments.[6]

In a preliminary account of these measurements[7] we had emphasized the existence of two well-separated relaxations even in the disordered state. This finding has been supported by similar PCS measurements on very short diblock copolymers[8] and diblock copolymers with highly compatible blocks.[9] Our aim here is to follow these relaxations across the MST and to determine the temperature dependence of their amplitudes and their relaxation time spectrum.

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Table I. Characterization of the Polymers Used

sample	f^a	M_w	M_w/M_n
	Block Copolymers		
B1	0.44	15700	1.04
B2	0.50	10500	1.04
B4	0.77	20800	1.06
	Homopolymers		
H1	1.0	22800	1.06
H2	1.0	48600	1.05

[a] Volume fraction of polystyrene.

II. Experiment

A. Samples. We report results on three polystyrene/*cis*-1,4-polyisoprene diblock copolymers—B1, B2, and B4—that differ in molecular weight and composition. The polymers were anionically synthesized using standard techniques. The polymerization was carried out in cyclohexane using *sec*-butyllithium as initiator. The monomers were sequentially added to the solvent, starting with styrene. A sample of the styrene block was taken before addition of the isoprene monomer. The molecular weight of this block and of the block copolymer was determined using gel permeation chromatography with polystyrene as a standard. The molecular weights were also measured by osmometry.

Further characterization of the samples involved ^{13}C NMR for the microstructure of the isoprene block. The trans content was thus found to be about 15%; ^{1}H NMR gave the volume fraction f of polystyrene.

In differential scanning calorimetry (DSC) all block copolymers show the glass transition of the polyisoprene domain. For B1 and B2 it is $T_g^{\mathrm{Is}} = 216$ K; for the asymmetric B4 $T_g^{\mathrm{Is}} = 231$ K. Only sample B1 displays a clear second glass transition at $T_g^{\mathrm{St}} = 335$ K, indicating the formation of well-defined polystyrene domains. Details of the DSC measurements have been reported separately.[10]

Two homopolymers of polystyrene were used in the PCS experiments as a reference measurement. H1 was purchased from PSS, Mainz, and H2 was synthesized in the same way as the block copolymers.

All data are collected in Table I.

B. PCS Measurement and Data Evaluation. The PCS experiments were performed using a commercial goniometer equipped with a photon correlator (ALV 3000). The light source was an Ar ion laser (Coherent, Model Innova 90-3) operating at a wavelength $\lambda = 488$ nm. The accessible scattering angle (2θ) interval was from 30 up to 150°, resulting in scattering vectors in a sample of refractive index n of $10 \leq q = 4\pi n/\lambda \sin(\theta)$ [μm^{-1}] ≤ 37.

The beam was polarized perpendicular to the scattering plane using the combination of a quarter-wave plate and a Glan-Thomson polarizer. A second polarizer in front of the photomultiplier was set parallel to the scattering plane to detect depolarized (vh) scattering. The correlator operated in the "multiple τ" mode, and it was thus possible to register the intensity autocorrelation function over 8 decades in time from 10^{-5} up to 10^3 s on a logarithmic scale.

Great care was taken to produce dust-free samples for the light scattering experiments. All glassware was prepared in dust-free conditions by cleaning it in a jet of distilled acetone using an apparatus described in ref 11. All manipulations were carried out in a dust-free flow cabinet. The polymer was dissolved in dioxane, and the solution was pressed through a 0.2-μm Millipore filter. The solvent was subsequently removed by freeze-drying. Finally, the sample was transferred into a cylindrical cuvette and dried further in an evacuated oven at 370 K. The cuvette was then sealed with a Teflon lid.

The cuvette was immersed in silicone oil. The bath liquid was index matched to the cuvette. Temperature variation was accomplished by heating of the bath, and temperature stability was better than 0.1 K.

III. Data Analysis

The desired quantity in a PCS experiment is the normalized autocorrelation function of the scattered electric field $E_s(q,t)$ at wave vector q

$$g_1(q,t) = \frac{\langle E_s(q,0)\, E_s(q,t)\rangle}{\langle E_s(q,0)\, E_s(q,0)\rangle} \tag{1}$$

where t is the correlation time.

The brackets in eq 1 denote an average over the time of duration of the measurement. In a homodyne experiment g_1 is in general related to the experimentally determined intensity autocorrelation function g_2 via the Siegert relation.[12] The situation encountered in dense polymer systems, however, is more complex. Besides a fluctuating component I_f of the scattered intensity, there is an additional ultraslow mode which in our experiment at low temperatures appears as a constant intensity I_c. The general procedure for data evaluation in such a nonergodic situation is discussed in ref 13. For the present situation the relation between g_1 and g_2 is found as[14]

$$g_2(q,t) = 1 + f\alpha^2 |g_1(q,t)|^2 + 2f\alpha(1-\alpha)\mathcal{R}\{g_1(q,t)\} \tag{2}$$

where α is the fraction of the fluctuating intensity

$$\alpha = \frac{\langle I_f\rangle}{\langle I_f\rangle + \langle I_c\rangle} \tag{3}$$

The experimental determination of α is based on the limit $t \rightarrow 0$ in eq 2: $g_2(q,t\rightarrow 0) = 1 - f\alpha^2 + 2f\alpha$. α differs significantly from 1 only for polymer B4, which is due to the high volume fraction of polystyrene and the consequently high glass transition temperature for the disordered state of this polymer.

The influence of the finite coherence area on the detector needs to be taken into account. It leads to a decrease of the observed fluctuating signal and is described by the factor f in eq 2.[12] f is determined from a measurement of the correlation function of a dilute solution of polystyrene in dioxane and will be used in the following to derive $g_1(q,t)$ from the intensity autocorrelation function via eq 2.

Equation 2 may be interpreted as an interpolation between the homodyne case ($\alpha \rightarrow 1$) and the heterodyne case ($\alpha \ll 1$). The latter situation is realized in the presence of a local oscillator, which in our case is the nondecaying part of the scattering function.

To arrive at a quantitative description of the measured field correlation function $g_1(q,t)$, we use two approaches which differ in the mathematical technique applied. The first method is to fit g_1 in a nonlinear least squares procedure to a Kohlrausch–Williams–Watts (KWW) function:

$$g_1(q,t) \rightarrow A_q e^{-(t/\tau_q^{\mathrm{KWW}})^\beta} \tag{4}$$

The resulting parameters then are the amplitude A_q of the relaxation, the relaxation time τ_q^{KWW}, and the line shape parameter β describing the width of the relaxation time spectrum. The case $\beta = 1$ corresponds to a single (Debye type) relaxation whereas the spectrum width increases considerably with decreasing β. An important

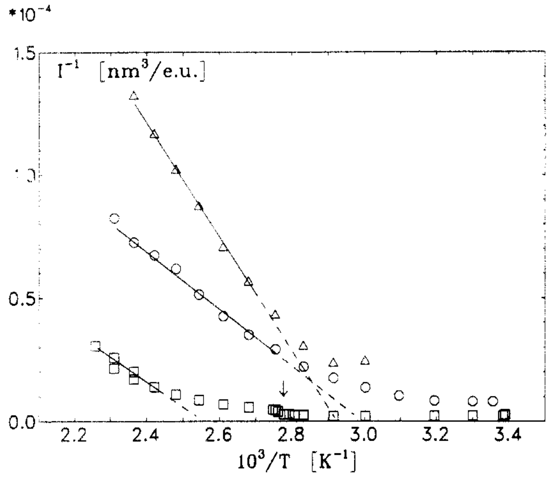

Figure 1. Inverse SAXS intensity at the peak maximum q^* for the diblock copolymers (B1, □; B2, ○; B4, △). T_s is obtained as an extrapolation of the linear relation at high T. The arrow indicates the temperature T_{MST} for sample B1 at which formation of long-range order occurs.

quantity is the mean relaxation time $\langle \tau_q \rangle$ which is obtained as[15]

$$\langle \tau_q \rangle = \frac{\tau_q^{\text{KWW}}}{\beta} \Gamma\left(\frac{1}{\beta}\right) \qquad (5)$$

where $\Gamma(x)$ is the Gamma function.

An alternative approach to an interpretation of g_1 is the solution of the integral equation which defines the relaxation time spectrum $h_q(\log \tau)$:

$$g_1(q,t) \rightarrow \int_{-\infty}^{\infty} h_q(\log \tau) e^{-t/\tau} \, d(\log \tau) \qquad (6)$$

The problem of inverting eq 6 to obtain $h_q(\log \tau)$ from a finite set of values $\{g_1(q,t_i)\}_i$ that carry experimental errors has no unique solution. In the following we use the method of Provencher[16] as implemented in the program CONTIN, which is optimized to produce a smooth curve with a minimum number of peaks in $h_q(\log \tau)$.

IV. Results and Discussion

A. Structure of Concentration Fluctuations. It is well known that the disordered state of diblock copolymers is characterized by concentration fluctuations on a local scale in the absence of long-range order. In this section we will report the results of an application of SAXS on our diblock copolymers. The aim is to determine their phase transition temperature T_{MST} and to characterize the state of local order in the temperature range of the PCS measurements.

The dominant contribution to the concentration fluctuations is at wavevector q^*, which is of the order of the reciprocal radius of gyration of the polymer.[3] The amplitude and the correlation length of these fluctuations increase when the temperature is lowered and ideally diverge at the transition temperature T_{MST}. For our samples q^* is of the order of 0.4 nm^{-1} and is therefore well within the range of observation in SAXS. Details of these investigations may be found elsewhere.[2,6,17]

SAXS directly measures the concentration fluctuations in a diblock copolymer. The scattered intensity $I(q)$ at scattering vector q is related to the correlation of concentration fluctuations $S(q)$

$$I(q) = VKS(q) \qquad (7)$$

where V denotes the volume of a polymer chain and K is the scattering contrast factor given as the square of the electron density difference between isoprene and styrene.

Table II. Characteristic Temperatures and the Position q^* of the Maximum in $S(q)$ (in the Disordered State) Obtained in SAXS

sample	T_s/K	T_t/K	T_{MST}/K	q^*/nm^{-1}
B1	390	395	362	0.46
B2	336	342		0.53
B4	342	353		0.52

The results are in qualitative agreement with RPA theory[3] for sufficiently high temperature. A broad peak is observed at position q^*. Its intensity and width may be used to obtain the effective Flory-Huggins parameter χ_{eff} if the polydispersity of the polymer is taken into account.[17] However, the values for $\chi_{\text{eff}}(T)$ thus obtained still depend on the composition f and on the extent of composition fluctuations.[5] They therefore allow at best a qualitative estimate of the phase behavior for a given diblock copolymer.

The quantity of interest is the amplitude of concentration fluctuations at q^*, the wavevector at which the phase transition occurs. According to eq 7 this is directly measured by the X-ray intensity at q^*. Figure 1 displays the temperature dependence of $I(q^*)$ in a representation which is based on the RPA result

$$I(q^*)^{-1} \propto \frac{1}{T_s} - \frac{1}{T} \qquad (8)$$

The spinodal temperature T_s is derived from this plot as the extrapolation $I(q^*)^{-1} \rightarrow 0$ of the linear dependence of $I(q^*)^{-1}$ on T^{-1} at high temperatures. The values are given in Table II together with q^* in the high-temperature regime. T_s is the transition temperature of a hypothetical mean field system. It characterizes the extent of concentration fluctuations in the disordered state. Figure 1 shows clearly the deviation of the data points from the straight line already about 15 deg above T_s. The main reason for this is concentration fluctuations which lead to a modification of eq 8[5,17] and avoid the divergence of $I(q^*)$ at T_s. For the present discussion we only note that T_s is well determined from the SAXS experiments. The fluctuation-controlled transition regime is characterized by the temperature T_t below which RPA theory and eq 8 are no longer valid. The values for T_s and T_t are given in Table II.

A further remark concerns the position q^* of the maximum intensity in the X-ray profile. Whereas RPA theory assumes this wavevector to be independent of temperature, the experiments show a shift of q^* to smaller values with lowering temperature.[17,18] This shift is shown for our polymers in Figure 2. It is accompanied by an increase of the segment length as derived from the Kratky regime in the SAXS profile.[17] The increase of concentration fluctuations in the vicinity of the disorder-to-order transition leads to a stretching of the polymer coil by about 15% over its ideal (Gaussian) value. This finding is in agreement with the results of recent computer simulations.[19,20]

Finally, we point out that sample B1 displays a strong discontinuity in the temperature dependence of the intensity $I(q^*)$ at T = 362 K.[2] It is reproducibly observed in heating and cooling runs. This sudden jump of intensity reflects the building up of long-range order in the system. Sample B1 thus constitutes the first example of a polystyrene/polyisoprene diblock copolymer that allows the study of the disorder-to-order transition in a temperature-driven experiment.

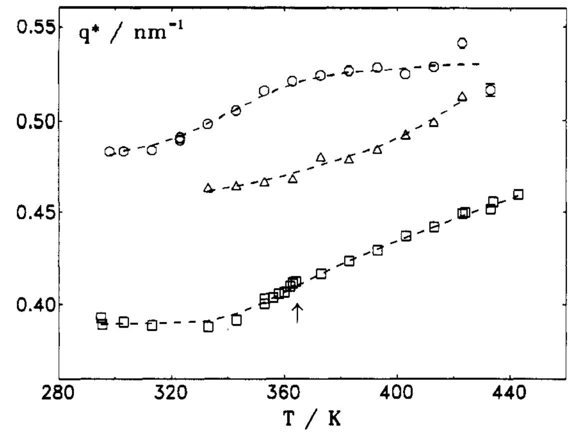

Figure 2. Shift of peak position q^* in the SAXS profiles as a result of chain stretching (B1, □; B2, ○; B4, △). Chain stretching occurs smoothly in the transition regime. At T_{MST} (sample B1) one finds an additional discontinuous jump (see arrow).

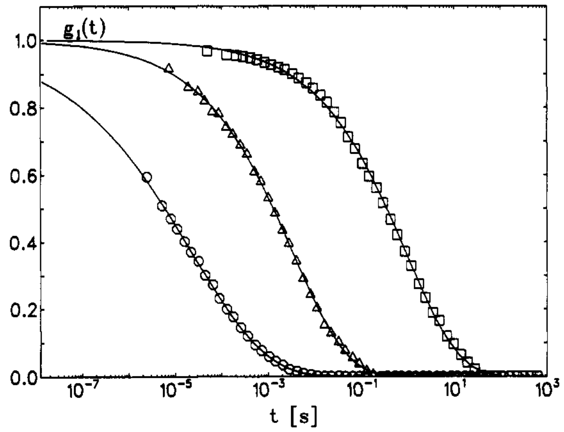

Figure 3. Depolarized PCS data for bulk polystyrene at three temperatures (□, $T = 373$ K; △, $T = 388$ K; ○, $T = 402$ K). The drawn curves are fits of the KWW function.

B. Segmental Dynamics. We now turn to the main part of the discussion which concerns the segmental dynamics of diblock copolymers. We will first present depolarized PCS measurements on bulk polystyrene and relate them to the underlying molecular dynamics. Subsequently, we discuss corresponding results on our diblock copolymers in the disordered state, the transition regime, and the ordered lamellar phase.

It was mentioned in the Introduction that the depolarized scattering is mainly caused by the polystyrene block of the block copolymer. Depolarized scattering from bulk polyisoprene gives rise to a fast mode with a relaxation time $\tau = 10^{-6}$ s at $T = 310$ K. We recover this mode also in our block copolymers B1 and B2 at the lowest temperatures. In all other cases it lies outside the time window of the correlator.

There have been several reports on the depolarized light scattering of bulk polystyrene.[14,21] In general, the observed field correlation function $g_1(q,t)$ is not a simple exponential. It is well described by the stretched exponential form of eq 4 with an exponent $\beta \approx 0.4$. A typical example of g_1 obtained on the homopolymer sample H2 just above its glass transition is given in Figure 3. The drawn curve is a fit of the KWW law (eq 4). It is important to use eq 2 for the calculation of g_1 from the intensity autocorrelation function g_2 because of the presence of an excess intensity giving rise to an ultraslow mode in the relaxation curve. This phenomenon is not unique to block copolymers and is discussed elsewhere.[22,23] g_1 does not depend on the scattering vector q. The molecular motion producing the observed anisotropy fluctuation is therefore a local process.

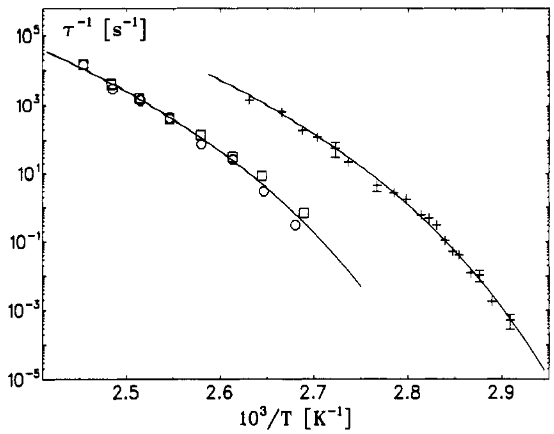

Figure 4. Temperature dependence of the mean relaxation time $\langle\tau\rangle$ for bulk polystyrene (H1, ○; H2, □) and for block copolymer B4 (+). The drawn curves are fits of eq 9 for H1 and H2 and eq 13 for B4.

The shape of the correlation function as described by the line shape parameter β is nearly independent of temperature. β decreases slightly to 0.3 when the temperature is raised above 390 K. However, the mean relaxation time $\langle\tau\rangle$ (cf. eq 5) varies strongly with T as shown in Figure 4. Its temperature dependence conforms well with the WLF equation

$$\log \frac{\langle\tau_g\rangle}{\langle\tau\rangle} = \frac{C_1(T-T_g)}{C_2+T-T_g} \tag{9}$$

with parameters $C_1 = 11.9$ and $C_2 = 59$ K and a glass transition temperature $T_g = 374$ K. $\langle\tau_g\rangle$ is the relaxation time at the glass transition temperature T_g. The anisotropy fluctuations in bulk polystyrene couple to the glass transition.

Microscopically, the field correlation function $g_1(q,t)$ in depolarized scattering may be expressed in terms of the molecular polarizability tensor α. Let y and z be the direction of the polarization for the polarizer and the analyzer, respectively. The incident light propagates along the x axis. Then for $q \rightarrow 0$[24,25]

$$g_1(q,t) = \frac{\langle\alpha_{yz}(0)\ \alpha_{yz}(t)\rangle}{\langle\alpha_{yz}(0)\ \alpha_{yz}(0)\rangle} \tag{10}$$

Nonentangled macromolecules in the melt are known to perform diffusional motion which is well described by the Rouse model.[26] Assuming the polymer chain to consist of cylindrical segments with an optical anisotropy described by the polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ parallel and perpendicular to their symmetry axis, one arrives at[24,25]

$$\langle\alpha_{yz}(0)\ \alpha_{yz}(t)\rangle = \left(\frac{\alpha_\parallel - \alpha_\perp}{3}\right)^2 \sum_l e^{-t/\tau_l} \tag{11}$$

The spectrum of relaxation times $\{\tau_l\}$ is the Rouse spectrum of the polymer chain. In the case of an ideally flexible chain it may be expressed in terms of the segment length a, the segmental friction coefficient ζ, and the number of segments N as[27]

$$\tau_l^{-1} = 2\frac{3k_BT}{\zeta a^2}4\sin^2\frac{l\pi}{2(N+1)} \tag{12}$$

The quantity $3k_BT/a^2$ plays the role of a spring constant which lets the deformed random coil relax into its equilibrium configuration.

The unweighted sum of exponentials in eq 11 does not quantitatively describe the experimentally determined correlation function. In particular, the assumption of cylindrical symmetry of the freely jointed chain segments neglects the pronounced asymmetry of the polystyrene monomeric unit. Interchain correlations are also not taken into account. Equations 11 and 12 therefore cannot apply to short correlation times which will contain bond rotations. The model explains only qualitatively the observed stretched form of g_1 in terms of a relaxation time spectrum of the polymer chain. It is, however, possible to use this formalism and study the effect of chain stiffness on the relaxation time spectrum.[25] We will return to this point later.

Block copolymer B4 is expected to be rather similar to bulk polystyrene with regard to its segmental diffusion. From the SAXS results it is known that this sample is in a disordered state without significant contribution of concentration fluctuations above 350 K. The PCS experiments cover a temperature regime from 340 up to 380 K. It is necessary to employ eq 2 to arrive at the field correlation function. The decay of g_1 is indeed described by an exponent $\beta = 0.3$, which is very close to the one found in bulk polystyrene. However, the temperature dependence of the mean relaxation time $\langle\tau\rangle$ is modified (see Figure 4). Due to the nearly homogeneous mixing between the polystyrene and polyisoprene blocks, the mobility of the polystyrene segments is enhanced. In the formalism of free volume theory one can calculate the free volume available for reorientation of a polystyrene segment in the mixture by an averaging of the corresponding free volumes available in a polystyrene and a polyisoprene environment, respectively. This calculation is outlined in ref 6. One arrives at an expression for renormalized WLF parameters $\tilde{C}_1$, $\tilde{C}_2$, and $\tilde{T}_g$ in terms of the known parameters for polystyrene and polyisoprene

$$\tilde{C}_1^{-1} = \Phi(C_1^{St})^{-1} + (1-\Phi)(C_1^{Is})^{-1}$$

$$\tilde{C}_2^{-1} = \tilde{C}_1[\Phi(C_1^{St}C_2^{St})^{-1} + (1-\Phi)(C_1^{Is}C_2^{Is})^{-1}]$$

$$\tilde{T}_g = \tilde{C}_1\tilde{C}_2[\Phi T_g^{St}(C_1^{St}C_2^{St})^{-1} + (1-\Phi)T_g^{Is}(C_1^{Is}C_2^{Is})^{-1}] \qquad (13)$$

where Φ is the volume fraction of polystyrene averaged over the volume of a polystyrene chain. The curve drawn through the data points of block copolymer B4 in Figure 4 is calculated using $\Phi = 0.79$, which is very close to the bulk volume fraction $f = 0.77$ for this system. For polyisoprene we use $C_1^{Is} = 16.8$, $C_2^{Is} = 53.6$ K, and $T_g = 204$ K.[6] This finding is in accordance with the assumption of a homogeneous mixture of the polystyrene and polyisoprene segments.

The situation looks different for a diblock copolymer in the transition regime. Figure 5a displays the field correlation function g_1 for the symmetric diblock B1 just below T_s (at $T = 373$ K). The curve is clearly not described by a single stretched exponential. It consists of two well-separated relaxations with very different relaxation time distributions. Whereas the fast component shows an exponent $\beta \approx 0.2$, the slow component is characterized by $\beta \approx 0.9$; i.e., it is nearly single exponential. We emphasize that this component is not identical with the "ultraslow mode" that has been identified in various polymer systems[22] and other glass-forming liquids.[23] The latter is additionally present in our system at low temperatures, as has been mentioned before, and has been accounted for by the application of eq 2 to derive the field correlation function g_1.

g_1 in the transition regime is also independent of the scattering vector q as was shown for the disordered state above. We demonstrate this in Figure 5b, which shows the average relaxation times $\langle\tau\rangle$ (see eq 5) for both the slow and the fast mode measured at scattering angles between 30 and 150°.

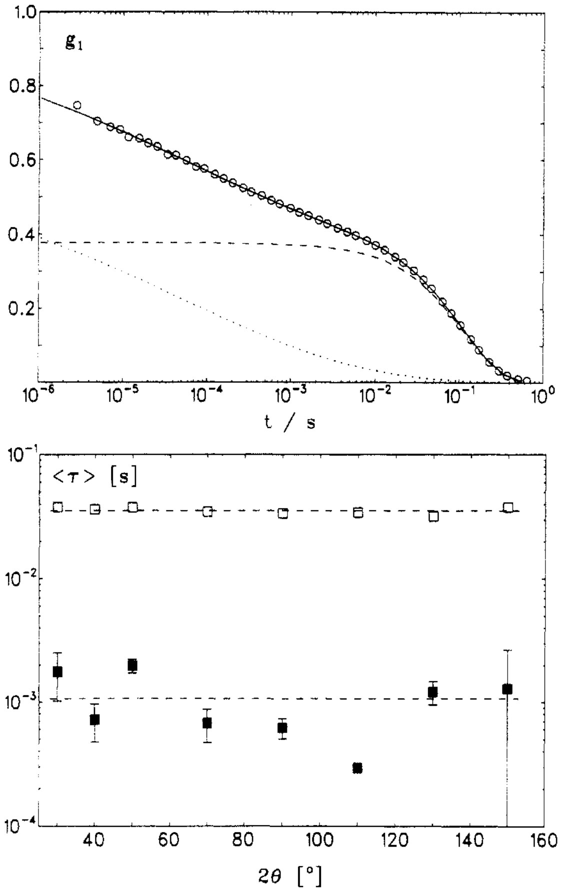

Figure 5. (a, Top) Field correlation function g_1 for block copolymer B1 at $T = 365$ K and its decomposition into two relaxation curves of the KWW type. (b, Bottom) Angular dependence of g_1 for block copolymer B1 at $T = 368$ K. The slow (□) and the fast (■) relaxation times $\langle\tau\rangle$ are independent of the scattering angle 2θ.

We now return to the temperature dependence of the relaxation time spectrum. Its form changes only gradually with temperature. However, its time scale shifts strongly with T. To compare the relaxation time spectra in the disordered and in the transition regime we therefore make use of the rather wide spread of T_s in our three samples.

In Figure 6 we show the relaxation time spectra $h_q(\log \tau)$ for the three diblock copolymers at temperatures above and below T_s. The spectra were calculated using the inversion procedure described in section IIB. It is clearly seen that the disordered state (sample B4, Figure 6a) exhibits a broad relaxation time spectrum with a shoulder on the fast side. This separation of time scales is enhanced when going to the symmetric diblocks B2 and B1 (Figure 6b,c). They are both in their transition regime at the temperatures of the PCS experiment. Coming closer to the MST obviously leads to an increasing bimodality of the relaxation time spectrum.

To arrive at a description of the relaxation behavior, we model g_1 as a sum of two KWW functions with drastically different line shape parameters β. Whereas the fast relaxation is described by $\beta_{fast} \approx 0.2$, which indicates an even broader relaxation time spectrum than the one found in pure polystyrene, the slow relaxation is close to single exponential (β_{slow}). The quality of these fits is demonstrated in Figure 5a. β_{fast} was kept fixed at high temperatures to avoid ambiguity in the fit procedure. The

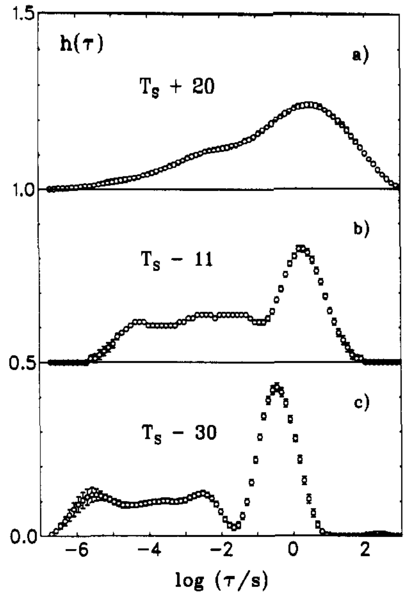

Figure 6. Relaxation time spectra of the diblock copolymers calculated from g_1 according to eq 6: (a) sample B4 at $T = 362$ K in its disordered state; (b) sample B2 at $T = 325$ K at the beginning of the transition regime; (c) sample B1 at $T = 360$ K in the transition regime. h_q is seen to broaden increasingly when approaching the transition temperature. It acquires a bimodal structure, the slow mode being nearly single exponential.

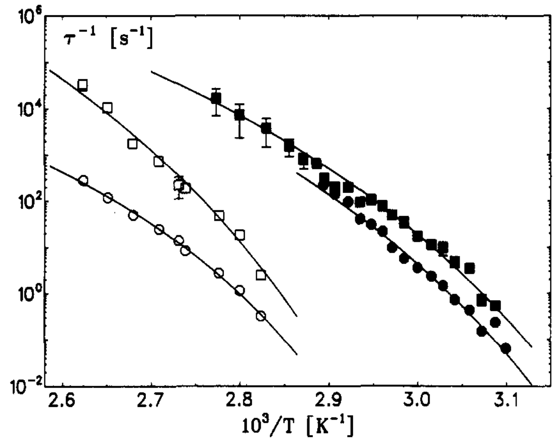

Figure 7. Temperature dependence for the slow (○) and the fast (□) component for block copolymers B1 (open symbols) and B2 (filled symbols). The drawn lines correspond to a fit of eq 13, resulting in $\Phi_{slow} = 0.77$, and $\Phi_{fast} = 0.70$ for B1 and $\Phi_{slow} = 0.56$ and $\Phi_{fast} = 0.54$ for B2.

resulting mean relaxation times show different temperature dependences. With lowering temperature the relaxation regimes move further apart.

Figure 7 displays these results for the slow and fast components of both diblocks B1 and B2. Above T_t for sample B2, i.e., in the homogeneous state, only one component could be determined. They are all well described by the free volume mixing concept of eq 13. The local compositions Φ obtained from applying this concept are quoted in the figure caption. They suggest the existence of two types of environment for the polystyrene segments. The slow, long-wavelength part of the relaxation time spectrum is controlled by a larger effective segmental friction coefficient than the local modes. The system is no longer homogeneous but it consists of domains that are enriched with polystyrene or depleted. This local ordering in the transition regime has also been found in dielectric experiments.[2] The ordering is stronger for B1 than for B2 for a given temperature, which is due to the higher molecular weight of B1.

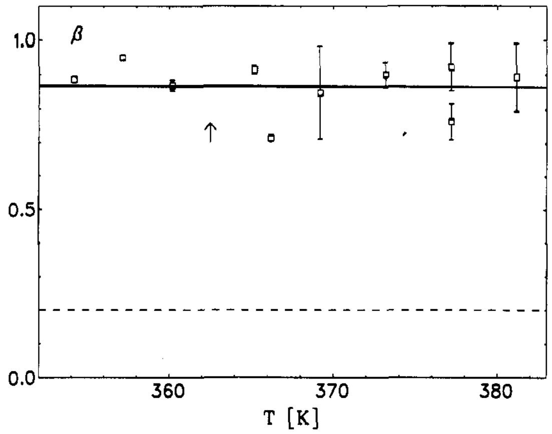

Figure 8. Line shape parameters β_{slow} (●) and β_{fast} (broken line) for block copolymer B1 in the temperature regime ranging from ordered state into the transition regime. The arrow marks T_{MST}. No discontinuity is found at T_{MST}.

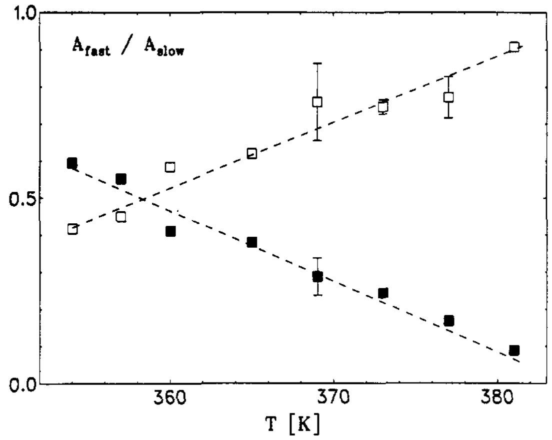

Figure 9. Relative amplitudes A_{fast} (■) and A_{slow} (□) for both relaxations in block copolymer B2. At T_{MST} both components are of equal strength. The slow mode vanishes near the end of the transition regime.

Finally, we examine the influence of the long-range ordering which occurs at $T_{MST} = 362$ K for sample B1 as was shown in section IVA. Opposed to the discontinuous changes observed in the static structure factor, there are only gradual temperature dependences observed in the relaxation time spectrum for anisotropy fluctuations. Figure 8 displays the exponent β for the slow and fast relaxations in diblock B1 in the full temperature regime from the ordered state into the transition regime. There is no change in both parameters at T_{MST}. The formation of long-range order obviously does not change the average environment of the polystyrene segments.

This finding supports conclusions drawn from measurements of the dynamic shear modulus on the same sample.[2] Relaxations referring to wavelengths larger than the radius of gyration of the polymer there were found to be strongly influenced by the building up of long-range order. On a short, segmental scale, however, no change of the mechanical relaxation time spectrum could be observed.

There is, however, a gradual increase of the relative intensity of the slow relaxation with lowering temperature. This exchange of relaxation strength is shown in Figure 9. It levels off at T_{MST}, where both relaxations are of equal strength. The slow mode merges completely into the rest of the relaxation time spectrum at T_t, the onset of the homogeneously disordered state.

Comparing Figure 9 and the chain stretching shown in Figure 2, one is led to relate the broadening of the relaxation time spectrum to the stretching of the block copolymer chain. This dependence has been studied in detail by Pecora and Moro.[25] They consider a Rouse chain which is subjected to an additional potential opposing bending fluctuations. The introduction of this stiffness has two effects: it increases the size of the chain and at the same time it modifies the relaxation time spectrum. Fast, short-wavelength modes afford a large amount of bending, and their weight is consequently reduced in this model with respect to the spectrum of an unrestricted Gaussian chain (cf. eq 11). Already for a moderately stretched chain (10% of the chain segments oriented in the direction of the first segment) they obtain a ratio $A_{\mathrm{slow}}/A_{\mathrm{fast}}$ of 0.36, in qualitative accordance with our observation.

V. Conclusions

The disordered state in diblock copolymers is not fully homogeneous. Concentration fluctuations show up in static experiments as well as in measurements probing the segmental dynamics of the polymer. SAXS can be used to define a transition regime which is not described by the mean field theory of the disordered state.

The anisotropy fluctuations caused by the dynamics of the polystyrene block in polystyrene/polyisoprene block copolymers show a complex relaxation time spectrum. Its shape becomes bimodal in the vicinity of the MST. This form is understood as a consequence of chain stretching, which is also observed in SAXS measurements. It enhances the strength of the long-wavelength modes of the chain over the rest of the relaxation time spectrum. The heterogeneity of the system leads to a different temperature dependence for the friction coefficients governing the slow, long-wavelength mode and the fast, local relaxations, respectively.

The MST is observed as a discontinuous transition leading to the formation of the long-range order of lamellae alternatingly being rich in polystyrene or polyisoprene. This phase transition has no direct impact on the segmental dynamics of the polystyrene block as seen in the PCS experiment. The formation of the lamellae affords local demixing and stretching of the polymer coil, and both processes are seen in the relaxation time spectrum. However, they occur gradually in the transition regime preceding the MST.

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