Dielectric Normal Mode Spectroscopy in the Ordered and Disordered States of Diblock Copolymers

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ABSTRACT: The microphase separation transition (MST) in a series of diblock copolymers of polystyrene/*cis*-1,4-isoprene of low molecular weight (10500–20800) and various compositions is studied using small-angle X-ray scattering (SAXS) and dielectric spectroscopy. The full regime from the ordered to the disordered state is investigated. The combination of both methods makes it possible to relate dynamical to structural properties. SAXS identifies a broad transition regime which is characterized by strong concentration fluctuations in the absence of long-range order. The polymers are shown to go through their MST at experimentally accessible temperatures. Dielectric spectroscopy of the polyisoprene normal mode in the diblock copolymers is compared to the homopolymer case. It is used to study the temperature dependence of the effective composition in the volume of the polyisoprene block. The ordered state consists of well-separated polyisoprene regimes. However, the relaxation time spectrum is considerably broadened with respect to the homopolymer case due to the coupling to polystyrene. The order-to-disorder transition does not lead to a homogeneous mixing of both blocks. The full temperature dependence of the normal mode relaxation time is described in a free volume model.

I. Introduction

Diblock copolymers are known to exist in a disordered or in an ordered, microphase-separated state. The latter has attracted a lot of attention from both scientific and theoretical points of view mainly because of the large variety of possible morphologies and their interesting properties.[1] The disordered phase on the other hand has only been studied intensively in recent years. This may be caused by the problem of attaining the disordered state for high molecular weight polymers. The entropy of mixing in this case is negligibly small, and most pairs of monomers energetically favor the separated, ordered state. If is therefore often necessary to use comparatively short chains in order to study the disordered state of diblock copolymers.

Several experiments have been devoted to the study of the structure of concentration fluctuations using mainly scattering methods.[2] An important result is the characterization of the microphase separation transition (MST) as a fluctuation driven disorder-to-order transition[3] which is of first order even in the case of diblocks with symmetric composition. This is in contradiction to the widely accepted mean field theory or random phase approximation (RPA).[4] Experimental evidence for this discrepancy is based on the temperature dependence of the structure factor for concentration fluctuations and on the deviation of the single-chain conformation from the Gaussian coil in the vicinity of the MST.[5,6] The direct, temperature-driven disorder-to-order transition has been observed very recently[7] for a nearly symmetric diblock of polystyrene/polyisoprene. The transition temperature was found to be clearly lower than the extrapolated spinodal temperature in accordance with the assumption of concentration fluctuations contributing to the free energy of the disordered state.

Very few papers have so far been devoted to a study of the segmental dynamics in diblock copolymers. Quasielastic neutron scattering was used to investigate the dynamics of a polystyrene/polyisoprene diblock copolymer in a matrix of polyisoprene.[8] It was concluded that the segmental dynamics were well described in a Rouse mode concept by the extension of the RPA to the dynamic structure factor. Quasielastic light scattering in the homogeneous phase of diblock copolymers[9] and in both the homogeneous and the ordered phases[10] revealed considerable broadening of the relaxation time spectrum compared to the polystyrene melt. This broadening was attributed to a heterogeneity of the system due to concentration fluctuations.

In the present paper we will describe the use of dielectric spectroscopy for the investigation of the segmental dynamics in the disordered as well as the ordered state of diblock copolymers. Polyisoprene was shown to have an in-chain component of the electric dipole moment.[11] The relaxation of the end-to-end vector therefore shows up in the spectrum of the dielectric function $\epsilon^*(\omega)$ as a clearly discernible relaxation mode. We will characterize this so-called *normal mode* process for short-chain homopolymers and diblocks of polystyrene/polyisoprene. Its relation to the properties of the diblock in particular to its phase state will be discussed. This method allows the selective study of the polyisoprene block dynamics: the electric dipole acts as an intrinsic label. Combining these results with a detailed characterization of the phase state of our samples using small-angle X-ray scattering (SAXS), it is possible to directly relate the polyisoprene block dynamics to the average composition on the scale of the block.

II. Experimental Section

A. Samples. The four diblock copolymers of polystyrene/poly(*cis*-1,4-isoprene) were anionically synthesized using standard techniques. The polymerization was carried out in cyclohexane using *sec*-butyllithium as an 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 was determined using gel permeation chromatography.

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 of polystyrene, *f*. All data are collected in Table I.

The homopolymers of polyisoprene were purchased from PSS, Mainz, Germany. For further purification they were dissolved and freeze dried from dioxane.

B. Dielectric Measurements. The capacitor used in the dielectric experiments consisted of two circular gold-plated copper

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Table I
Characterization of the Polymers Used

sample	f	M_w	M_w/M_n
	Block Copolymers		
B1	0.44	15 700	1.04
B2	0.50	10 500	1.04
B3	0.20	14 300	1.03
B4	0.77	20 800	1.06
	Polyisoprene Homopolymers		
H1		3 900	
H2		8 200	
H3		15 500	

plates. They were separated by a polyimide spacer ring to define a fixed sample thickness of 125 μm. The filled capacitor was placed in a nitrogen-flooded container which allowed temperature variation between 200 and 400 K. Temperature stability was better than 0.5 K, and the sample temperature was directly measured at the capacitor.

The dielectric measurements were carried out with a Schlumberger 1260 impedance analyzer. In order to cover a wide frequency range of $10^{-1} \leq \nu/\text{Hz} \leq 10^6$ at a loss angle $\tan \delta \approx 10^{-3}$, the impedance analyzer was fitted with an impedance transformer (Chelsea Dielectric Interface, Pugh Dielectric Instrumentation, Worcester, England) which allows the alternating measurement of a sample capacitor and a similar reference capacitor. This reference technique minimizes phase errors and improves the performance of the system at low frequencies and low losses.

The whole setup operates under microcomputer control and allows automatic data collection for various temperatures and frequencies.

C. Small-Angle X-ray Scattering. The SAXS experiments were performed in an evacuated Kratky camera with the conventional slit collimation. The samples were contained in brass sample holders with acetate windows. Temperature stability was better than 0.5 K. The data were collected with a scintillation counter in a step scanning mode and transferred to a minicomputer. Standard data treatment involves subtraction of background and calculation of the desmeared intensity for ease of comparison with other scattering techniques.

The radiation used was monochromatic Cu Kα with a wavelength λ = 0.154 nm. In an accessible scattering angle interval of $0.15° \leq 2\theta \leq 4.2°$ one covers a range of scattering vectors $q = (4\pi/\lambda) \sin \theta$ between 0.1 and 3 nm^{-1}.

III. Results and Discussion

A. Small-Angle X-ray Scattering of the Block Copolymers. SAXS provides detailed information on the static structure of concentration fluctuations in a two-component system. The measured intensity is directly related to the Fourier transform of the correlation function of concentration fluctuations. In the disordered state of a block copolymer the scattered intensity at scattering vector q is given as

$$I(q) = (\eta_{\text{Is}} - \eta_{\text{St}})^2 V S(q) \qquad (1)$$

The η_i are the electron densities of polystyrene and polyisoprene, respectively. V denotes the volume of a block copolymer chain. $S(q)$ then is the structure factor as given, e.g., by Leibler[4] within the RPA. $S(q)$ may be computed for samples with polydispersity and compared to measured intensity profiles in a least-squares fit. Details of this procedure are given elsewhere.[6] In general good agreement between the RPA structure factor and the experiment is reported for the disordered phase of diblock copolymers.[2] However, there are clear deviations observed in approaching the separation temperature[6,12] which are related to a stretching of the polymer coil. This deviation from Gaussian conformation is also observed in numerical studies. It violates a basic assumption of the RPA. A theory which takes this effect into account is not available at present.

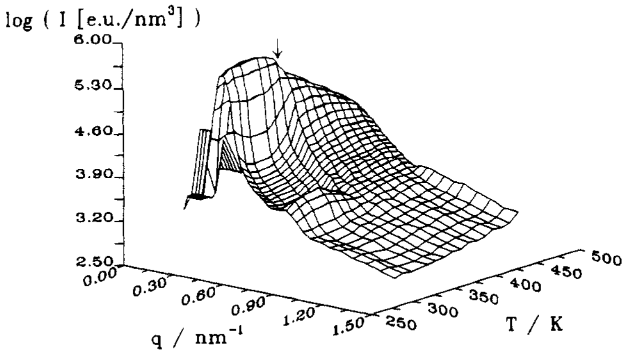

Figure 1. Temperature dependence of the SAXS structure factor for sample B1. The MST is identified as the discontinuous step in the intensity of the main peak and the appearance of a second-order reflection at the same temperature (see arrow).

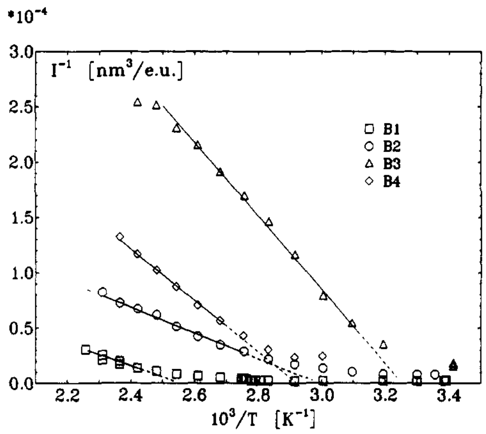

Figure 2. Intensity of the main peak in the SAXS structure factor for the diblock copolymers. The extrapolation of the linear regime defines the temperature T_s (see text).

An experimental result for the temperature dependence of the SAXS pattern of a diblock copolymer is given in Figure 1 for sample B1. At high temperatures one observes a broad peak which is related to the block structure of the polymer. It is located at $q^* \approx 1/R_g$ and may be used to determine the segmental interaction parameter χ and the apparent radius of gyration R_g^{app} of the polymer.[6] In the present context we are mainly interested in a characterization of the phase state of the sample and the microphase separation temperature T_{MST}. This information is contained in the temperature dependence of the SAXS intensity at the peak position q^*. Figure 2 presents the results for the four diblock copolymers used in this study. At high temperature one observes a linear regime in the dependence of $S(q^*)$ on T^{-1}. From RPA theory one expects

$$S(q^*) \propto \frac{1}{T_s} - \frac{1}{T} \qquad (2)$$

defining a spinodal temperature T_s.

T_s must be considered a parameter describing the concentration fluctuations in the system at high temperatures. It is not to be confused with the actual phase transition temperature T_{MST}. Sample 1 provides the unique example of a clearly observed microphase separation transition in a temperature-driven experiment.[7] Whereas T_s is extrapolated from the high-temperature regime to be about 390 K, we find $T_{\text{MST}} = 362 \pm 2$ K from the discontinuity in the peak intensity $S(q^*)$ and the appearance of a second-order peak at the same temperature (see Figure 1). The block copolymer remains in the disordered state even for temperatures $T < T_s$ because of the possibility to lower its free energy through the formation of strong concentration fluctuations. Samples

2–4 behave similar as may be seen in Figure 2. However, no discontinuity in $S(q^*)$ vs T^{-1} is observed. For these samples the microphase separation temperature T_{MST} is below the glass transition of the polystyrene block. As a consequence the formation of long-range order is stopped by the glass transition.[12]

In summary the SAXS measurements characterize the disordered phase of the diblock copolymers with a temperature T_s which is given in Table II. They provide evidence for the existence of strong concentration fluctuations. For sample 1 the phase transition temperature T_{MST} is observed in the formation of long-range order.

B. Dielectric Spectroscopy of Polyisoprene Homopolymers. Details of the dielectric spectroscopy of polyisoprene have been given in the literature.[11,13] In the present section we will therefore only recall some important results and present new data on polyisoprenes of very low molecular weight (samples H1, H2, and H3) close to the glass transition temperature.

Quite generally the relation between the frequency-dependent dielectric permittivity $\epsilon^*(\omega)$ and the dynamics of the dipoles $\vec{\mu}_i$ in a sample is given as[14]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \mathcal{L}(-\dot{\Phi}(t)) \tag{3}$$

In the following we refer to the difference $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ as the relaxation strength. ϵ_s and ϵ_∞ are the permittivities at low and high frequencies, respectively. $\mathcal{L}$ symbolizes the Laplace transform and $\Phi(t)$ is the dipole correlation function

$$\Phi(t) = \frac{\langle \vec{\mu}_{\mathrm{Ch}}(0)\cdot\vec{\mu}_{\mathrm{Ch}}(t)\rangle}{\langle \vec{\mu}_{\mathrm{Ch}}(0)\cdot\vec{\mu}_{\mathrm{Ch}}(0)\rangle} \tag{4}$$

As long as there are no correlations between different chains, $\vec{\mu}_{\mathrm{Ch}}$ involves the summation of all monomeric dipoles in one chain. We neglect the influence of the internal field in the present discussion.

For a polyisoprene monomer the electric dipole $\vec{\mu}$ consists of an in-chain component $\vec{\mu}_\parallel$ and a perpendicular component $\vec{\mu}_\perp$. Assuming both components to be noncorrelated, one arrives at

$$\Phi(t) = \Phi_\perp + \Phi_\parallel$$

$$\Phi_\perp = \alpha_\perp \sum_{j,l} \langle \vec{\mu}_\perp(0)^j \cdot \vec{\mu}(t)^l \rangle \tag{5}$$

$$\Phi_\parallel = \alpha_\parallel \sum_{j,l} \langle \vec{\mu}_\parallel(0)^j \cdot \vec{\mu}_\parallel(t)^l \rangle$$

The summation in eq 5 extends over the monomers of a polyisoprene chain. $\alpha_\perp$ and $\alpha_\parallel$ are suitable normalization constants. $\Phi_\perp$ and $\Phi_\parallel$ translate into components $\epsilon_\perp$ and $\epsilon_\parallel$ of the dielectric permittivity via eq 3. As long as the time scales for the relaxation of both dipole components are well separated, the frequency-dependent dielectric permittivity $\epsilon^*(\omega)$ will show two relaxations.

Table II
WLF Parameters for the Normal and Segmental Modes of Polyisoprene and for the Segmental Mode in the Block Copolymers[a]

	normal mode			segmental mode		
sample	C_1	C_2	$\log \nu_0$	C_1	C_2	$\log \nu_0$
H1	13.1	57.9	−3.70	13.1	41.5	−1.60
H2	14.3	51.7	−5.90	15.5	43.0	−2.96
H3	15.1	38.6	−8.26	17.1	57.2	−2.30
B1				18.5	65.6	−2.87
B2				17.6	25.8	−7.30
B3				16.8	40.3	−3.67
B4[b]	14.1	21.6	−6.24			

[a] The parameters refer to the glass transition temperature T_g = 204 K. [b] The reference temperature for sample B4 was chosen to be T_s = 342 K.

It is immediately seen from eq 5 that the summation of in-chain dipoles results in a vector parallel to the end-to-end vector $\vec{r}_e$ of the polyisoprene chain.

$$\sum_{j,l} \langle \vec{\mu}_\parallel(0)^j \cdot \vec{\mu}_\parallel(t)^l \rangle = \tilde{\mu}^2 \langle \vec{r}_e(0)\cdot\vec{r}_e(t)\rangle \tag{6}$$

$\tilde{\mu}^2$ is the mean squared electric dipole moment per squared length

$$\tilde{\mu}^2 = \langle \vec{\mu}^2 \rangle / \langle \vec{r}_e^{\,2} \rangle$$

Through eq 6 the relaxation mode $\epsilon_\parallel$ is expressed in terms of the dynamics of the end-to-end vector of the polymer chain and $\epsilon_\parallel$ is consequently called the *normal mode*. The detailed relaxation time spectrum may be calculated from models for the underlying chain dynamics, but this is not the topic of our discussion.

Another interesting feature of the normal mode is the dependence of its relaxation strength $\Delta\epsilon_\parallel$ on the chain length. Writing Onsager's relation for this mode, one obtains

$$\Delta\epsilon_\parallel = \frac{\rho_{\mathrm{P}}}{\epsilon_0 3kT} \tilde{\mu}^2 r_e^{\,2} \tag{7}$$

ρ_{P} is the number density of polymer chains per volume and ϵ_0 the permittivity of free space. For Gaussian chains and constant mass density, $\Delta\epsilon_\parallel$ should be independent of molecular weight according to eq 7. Deviations from the Gaussian conformation, however, will show up in $\Delta\epsilon_\parallel$.

Turning to the perpendicular dipole component $\vec{\mu}_\perp$, it is reasonable to assume correlations of dipoles on different monomers to decay rapidly with distance along the chain contour. The elementary process of relaxation therefore is the motion of segments, and this mode is consequently termed *segmental mode*. The relation equivalent to eq 7 for the normal mode now reads

$$\Delta\epsilon_\perp = \frac{\rho_{\mathrm{S}}}{\epsilon_0 3kT} \mu_\perp^{\,2} \tag{8}$$

ρ_{S} now is the monomer number density.

Figure 3 displays the experimental result of the loss part $\epsilon''(\omega)$ of the dielectric permittivity for the example of sample H2. The normal and the segmental mode are clearly discernible. The normal mode is characterized by its strong temperature dependence. Both spectra are phenomenologically well described by the Havriliak-Negami function

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (\iota\omega\tau)^\alpha)^\gamma} \tag{9}$$

The case $\alpha = \gamma = 1$ (Debye function) corresponds to a simple exponential decay of $\Phi(t)$ (see eq 3). $\alpha = 1$ and $\gamma < 1$ is known as the Cole Davidson function. In general the parameter $\gamma < 1$ leads to an asymmetric broadening

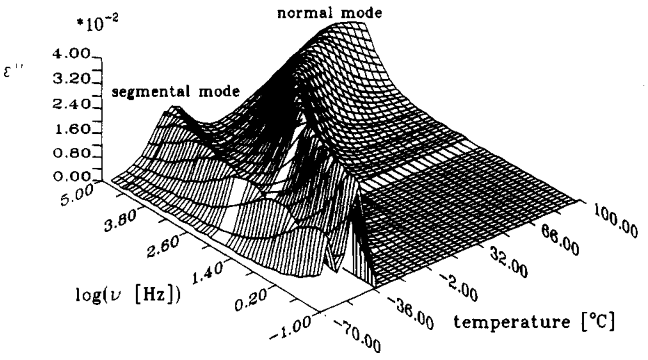

Figure 3. Loss part $\epsilon''(\omega)$ of the complex dielectric permittivity for the homopolymer H2.

of $\epsilon''(\omega)$ if plotted on a logarithmic ω axis. $\alpha < 1$ results in a symmetric broadening.

The segmental mode of polyisoprene homopolymers turns out to be significantly broadened with respect to the Debye function. It is characterized by $0.5 \leq \alpha_S \leq 0.7$ and $\gamma \simeq 0.5$. From the relaxation strength of the segmental mode the mean squared transverse dipole moment per monomer $\langle \mu_\perp{}^2 \rangle$ is obtained as $\langle \mu_\perp{}^2 \rangle^{1/2} = 0.19 \pm 0.02$ D in accordance with the results of ref 11.

For temperatures between the glass transition and about 20 K above, the form of the segmental mode spectrum becomes even more asymmetric ($\gamma \leq 0.50$). Detailed calculations within a rotational isomeric state model have been performed that aim at an explanation of these features.[15]

For the normal mode spectrum we obtain a good description using $\alpha = 1$ and $\gamma \simeq 0.5$. This is in agreement with a Rouse-type spectrum of relaxation times[16] which generates an asymmetric $\epsilon_\parallel''(\omega)$. We do not find a satisfactory description of the experimental $\epsilon_\parallel''(\omega)$ within the Rouse model which is commonly accepted as a good representation for the relaxation time spectrum of a polymer chain in an unentangled melt. It should, however, be noted that the dielectric normal mode is essentially equivalent to a sum of the first three contributing Rouse modes (numbers 1, 3, and 5)[16] whereas the quasielastic neutron scattering experiments test a much higher mode number depending on the scattering vector used.[8] As in the case of the segmental mode we find an increase in the broadening of the normal mode with lowering temperature such that $\gamma \simeq 0.35$ at 250 K.

For the above defined parallel dipole moment $\tilde{\mu}_\parallel{}^2$ of polyisoprene one arrives at $\tilde{\mu}_\parallel{}^2 = 0.20 \pm 0.03$ D^2/nm^2. This figure compares well with the dipole moment per segment μ_l given by ref 11. Using their $l = 0.42$ nm, one obtains $\mu_l = (\tilde{\mu}_\parallel{}^2 l^2)^{1/2} = 0.19 \pm 0.03$ D.

The full temperature dependence of the spectra is contained in a master plot of sample H1 in Figure 4. The spectra have been shifted horizontally on a logarithmic frequency axis. Vertically a factor T/T_{ref} was applied (cf. eq 7). T_{ref} was chosen to be 250 K. The glass transition for the polyisoprenes was determined with DSC to be $T_g = 204$ K. The data in Figure 4 cover a temperature range of $210 \leq T/\mathrm{K} \leq 320$. For $T \geq 220$ K the spectra obviously superimpose on a master curve because the variations of the Havriliak-Negami parameter γ discussed above are hardly visible on the scale of the figure. Normal and segmental modes are consequently governed by the same friction coefficient $\zeta(T)$ which carries their full temperature dependence. Close to T_g, however, this concept appears to break down (see Figure 4). The difference in length scales between the end-to-end vector and the segment decouples the temperature dependence of both relaxations. There have been speculations that relate such a length scale dependence to the cooperative nature of the glass transition.[17] A continuation of our measurements to lower frequencies could help to test these ideas as there are two length scales available in the polyisoprene system on which relaxational dynamics may be studied.

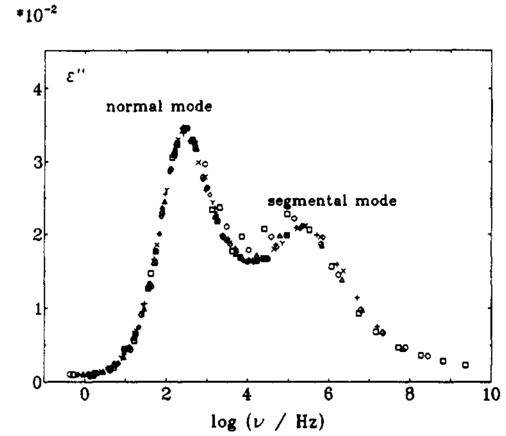

Figure 4. Master plot of ϵ'' for sample H1 (see text).

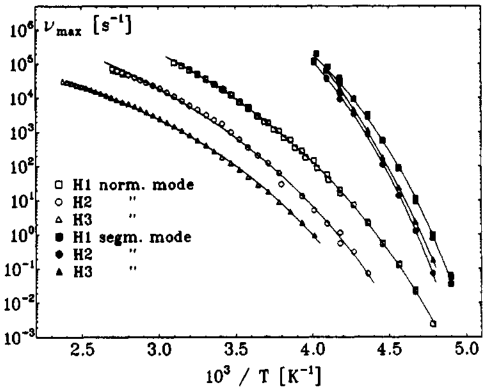

Figure 5. Temperature dependence of the normal mode and the segmental mode for the homopolymers H1, H2, and H3. The drawn curves are fits of the WLF eq 10.

About 20 K above T_g both normal and segmental modes display a temperature dependence which is in accordance with the WLF description

$$\log \nu_{\max} = \log \nu_0 + \frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{10}$$

$\nu_{\max} = \omega_{\max}/2\pi$ is the position of the maximum in $\epsilon''(\omega)$, and $\log \nu_0$, C_1, and C_2 are the WLF parameters. We use the glass transition temperature $T_g = 204$ K as the reference temperature. Figure 5 displays the experimental results together with a fit of eq 10 in an Arrhenius diagram. The description of the data by the WLF theory is satisfactory, and the resulting parameters are given in Table II for both the segmental and the normal mode processes.

Whereas there is essentially no difference in the segmental mode for the three polymers, one observes a strong molecular weight dependence for the normal mode in accordance with the Rouse model prediction[16]

$$\tau_n = N^2 \frac{4}{\pi^2} \tau_0 \tag{11}$$

τ_0 is a segmental relaxation time which is related to the segmental friction coefficient ζ and the segment length l via

$$\tau_0 = \zeta l^2 / 12kT \tag{12}$$

From eqs 11 and 12 it is evident that τ_n depends on the scale invariant quantity ζ/l^2 and the radius of gyration R_g.

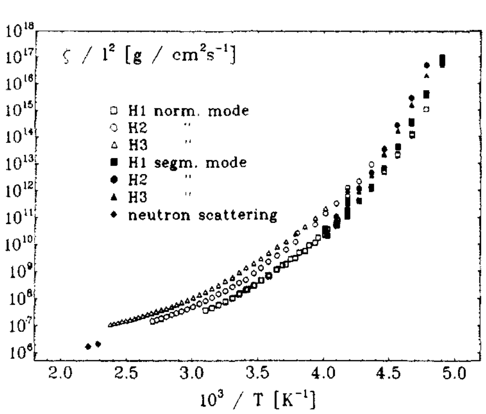

Figure 6. The segmental friction coefficient for polyisoprene obtained from the normal mode and segmental mode measurements and from quasielastic neutron scattering.

Calculating the coil dimension with the help of the statistical segment length $l = 0.63$ nm,[18] one obtains a satisfactory agreement between ζ/l^2 as obtained from quasielastic neutron scattering and the dielectric normal mode. This comparison is made in Figure 6. The plot of the segmental friction coefficient versus temperature is particularly sensitive to deviations from the N^2 dependence of τ_n in eq 11. The remaining molecular weight dependence may be attributed to the extra free volume created by chain ends.

The relaxation time τ_s of the perpendicular dipole $\mu_\perp$ is of course not identical with the elementary time τ_0 of the Rouse model. It will, however, be of the same order of magnitude as the elementary step of motion in the Rouse model, and the segmental motion refers to the diffusion of the same chain segment. We therefore use eq 12 to calculate the segmental friction coefficient from the segmental mode relaxation time. These data fit indeed very well with the normal mode results and lead to a temperature dependence of the segmental friction coefficient for polyisoprene which covers 11 orders of magnitude.

C. Dielectric Spectroscopy of Diblock Copolymers. It was shown in section A that for our diblock copolymers the disordered as well as the ordered state is within the accessible temperature range for the dielectric measurements. Using both the segmental and the normal mode processes it should therefore be possible to investigate the effective friction factor on two different length scales. In addition to the dielectric relaxation of the polyisoprene block, the spectra of the block copolymers also show a weak contribution from polystyrene. It only appears in a small temperature interval above the glass transition of the polystyrene domains and will not be considered in the following.

Due to the finite frequency window of the dielectric spectroscopy the segmental mode for samples B1 through B3 was only observed for temperatures below the ordering transition. For the asymmetric, styrene-rich sample B4 the segmental mode could not be detected. In this low-temperature range there was no difference between the segmental mode of the homopolymers and that of the block copolymers as is seen from a comparison of Figures 5 and 7. The average environment of an isoprene segment in the ordered state is the same as in bulk polystyrene. On local scale the ordering leads to a complete separation of styrene and isoprene monomers. The effect of the transition zone between both species does not show up significantly. This observation is in accordance with DSC measurements which show nearly no difference between the glass transition temperatures of neat polyisoprene and the isoprene phase in diblocks of polystyrene/polyisoprene.[12]

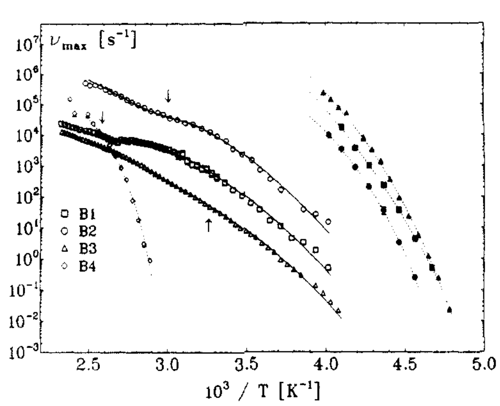

Figure 7. Temperature dependence of the normal mode (open symbols) and the segmental mode (filled symbols) for the diblock copolymers. The arrows indicate T_s as determined from SAXS for B1, B2, and B3. The data for the normal mode of B2 have been shifted upward by 1.5 decades for clarity of presentation. The unusual curvature of the curves for samples B1 and B2 around their separation temperature shows the sensitivity of the normal mode for the local composition. The drawn curves are calculated with eq 17. The dotted lines correspond to a fit of the WLF equation (eq 10).

The situation is different for the temperature dependence of the normal mode process. The frequency ω_{max} of its maximum in $\epsilon''(\epsilon)$ may be followed through the microphase separation transition. Figure 7 shows the temperature variation of $\nu_{max} = \omega_{max}/2\pi$ in an Arrhenius representation. Also marked in the plots are the spinodal temperatures T_s for the diblocks as obtained from the SAXS measurements.

The graphs make evident that the dielectric normal mode in the diblock copolymers differs markedly from the simple WLF behavior which was found in the case of the homopolymers. Only at low temperatures, in the ordered state, the temperature dependence of the normal mode is identical with that of bulk polyisoprene. Heating above T_{mst}, however, leads to a drastic change: the increase of mobility with temperature is suddenly slowed due to the mixing of polystyrene segments into the volume of the polyisoprene block. This effect is particularly clearly displayed by both symmetric diblocks (samples B1 and B2) which display a dip in Figure 7 around their phase transition temperature. The effect is hardly visible for the isoprene-rich sample B3.

Sample B4 shows no normal mode process below T_s. The rather small block of polyisoprene (cf. Table I) is obviously not able to develop a separate domain because the microphase separation is stopped by the glass transition of the polystyrene domains.[12] Above the transition temperature the dielectric spectrum displays a clear relaxation which is the normal mode process of the polyisoprene block in the polystyrene-rich surrounding.

A quantitative description for the unusual temperature dependence of the normal mode process may be obtained in the framework of free volume theory. Relaxation processes in the diblock copolymers are governed by the presence of a distribution of concentration fluctuations. In general the effective composition depends on the length scale on which a relaxation takes place. For the dielectric normal mode this is the end-to-end vector of the polyisoprene block. Its relaxation time spectrum may quite generally be calculated on the basis of the Rouse model,[19] taking into account the composition f of the block copolymers and the segmental friction coefficients of its constituents. This concept has been successfully applied

Table III
T_{MST} and T_s As Extrapolated from the SAXS Structure Factors and Parameters Describing the Local Composition $\Phi(T)$ According to Equation 18[a]

sample	T_0/K	ΔT/K	Φ_∞	$\log \nu_0$	T_s/K	T_{MST}/K
B1	365 (1)	32 (1)	0.16 (0.03)	−8.21 (0.03)	390 (5)	362 (2)
B2	330 (1)	20 (1)	0.08 (0.02)	−8.06 (0.02)	336 (12)	
B3	310[b]	56 (3)	0.07 (0.01)	−9.00 (0.02)	310 (5)	
B4					342 (11)	

[a] The WLF parameters used in eq 17 are $C_1 = 16.8$, $C_2 = 53.6$ K, and $T_g = 204$ K for polyisoprene and $C_1 = 13.5$, $C_2 = 49$ K, and $T_g = 370$ K for polystyrene. The numbers in parentheses are error estimates. [b] $T_0 = T_s$ was used as a fixed parameter.

to the interpretation of the composition and molecular weight dependence of polybutadiene/polyisoprene block copolymers in their disordered state.[20] The repulsive interaction between different blocks in this system is very small, and the assumption of a homogeneously mixed state with only one common friction coefficient for both blocks is therefore justified.

However, for polystyrene/polyisoprene the situation is different. Our data refer mainly to the ordered state and extend into the disordered regime, which is still characterized by local ordering as was shown in section III.A. We therefore assume the mode spectrum of the polyisoprene block to be essentially identical to that of a polyisoprene chain of the same length with one end fixed to a nearly immobile polystyrene block. Imposing this boundary condition, one obtains a modified longest relaxation time τ_{fix} of the block as compared to τ_{free} of the free chain[21]

$$\tau_{fix} = 4\tau_{free} \tag{13}$$

For nonentangled chains, eq 11 gives the molecular weight dependence of τ_{free} and one arrives at the interesting conclusion that the τ_{fix} of a chain with one end fixed should be the same as the τ_{free} of a free chain with twice the molecular weight. Two pairs of our samples, B1/H3 and B2/H2, are therefore equivalent (see Table I). Comparing Figures 5 and 7, one finds that the ν_{max} values of these pairs indeed coincide at low temperatures. We conclude that in the ordered state of the diblock copolymers the normal mode relaxation of the polyisoprene block is that of a polyisoprene chain in its own melt with one end fixed to the nearly immobile polystyrene block.

In the following the temperature dependence of the maximum frequency ν_{max} is described as a variation of the effective composition Φ. Within the volume of this block, one has a fraction Φ of styrene segments. Φ varies with temperature and should tend to zero in the ordered phase. In the ideally disordered phase one expects $\Phi \rightarrow f$.

In the present discussion the averaged effective concentration Φ is the only parameter of the distribution of concentration fluctuations that will be considered. Higher moments are contained in the detailed form of $\epsilon^*(\omega)$. It is indeed found that $\epsilon''(\omega)$ in the diblock copolymers is broadened with respect to the homopolymers. The parameter α of the Havriliak-Negami function (see eq 9) differs significantly from 1 and is 0.35 in the ordered state. Such a broadening is qualitatively understood as a consequence of the fixing of one end of the polyisoprene block in the polystyrene domain.[21] The influence of a possible change in the coupling between both blocks with temperature on the position of ν_{max} is small and will be neglected.

Following Fujita,[22] we assume the free volume ν_f involved in the relaxation of the polyisoprene end-to-end vector to be a linear combination of the known free volumes for polystyrene and polyisoprene

$$\nu_f(T) = \Phi\nu_f^{St}(T) + (1-\Phi)\nu_f^{Is}(T) \tag{14}$$

Within WLF theory the temperature dependence of ν_f is expressed in terms of the glass transition temperature T_g, an expansion factor $\Delta\alpha$, and a reference volume $\bar{\nu}_m$ as

$$\nu_f = \nu_f(T_g) + \Delta\alpha\bar{\nu}_m(T - T_g) \tag{15}$$

Equation 15 leads to the WLF eq 10 by inserting it into $\tau_g/\tau = \exp(-\nu^*/\nu_f)$, where ν^* is an activation volume. The experimental parameters C_1 and C_2 are then given as[23]

$$C_1 = \frac{1}{2.303}\frac{\nu^*}{\nu_f(T_g)}$$

$$C_2 = \frac{\nu_f(T_g)}{\Delta\alpha\bar{\nu}_m} \tag{16}$$

Inserting the mixing concept eqs 14 into 15, one arrives again at a WLF-type equation with new parameters $\tilde{C}_i$ and $\tilde{T}_g$ expressed in terms of those characterizing the free volume of polystyrene and polyisoprene:

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

$$\tilde{C}_2^{-1} = \tilde{C}_1[\Phi(C_1^{St}C_2^{St})^{-1} + (1-\Phi)(C_1^{Is}C_2^{Is})^{-1}] \tag{17}$$

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

Finally one needs to specify the temperature dependence of the distribution of concentration fluctuations and therefore of the average concentration Φ. We choose a phenomenological tanh law:

$$\Phi(T) = \frac{\Phi_\infty}{2}\left[1 + \tanh\frac{T - T_0}{\Delta T}\right] \tag{18}$$

Equation 18 describes a variation of the composition Φ from 0 at low T to Φ_∞ at high T. The smooth step is located at T_0 and has a width ΔT.

Inserting eq 18 into eq 17, one arrives at a description of the temperature dependence of the normal mode maximum frequency using only Φ_∞, T_0, ΔT, and $\log \nu_0$ as variable quantities. The WLF parameters for polyisoprene and polystyrene are taken from ref 23, and their values are given in Table III. The quality of the fits thus obtained may be judged from the drawn curves included in Figure 7. The parameters used in these calculations are compiled in Table III.

It is interesting to note that the volume fraction Φ_∞ in no case reaches its limiting value f. Even in the disordered state the system contains concentration fluctuations on the scale of the diameter of the polyisoprene block. The system changes from the ordered to the disordered state in a temperature interval of typically 30 K. This interval is characterized by long-living concentration fluctuations

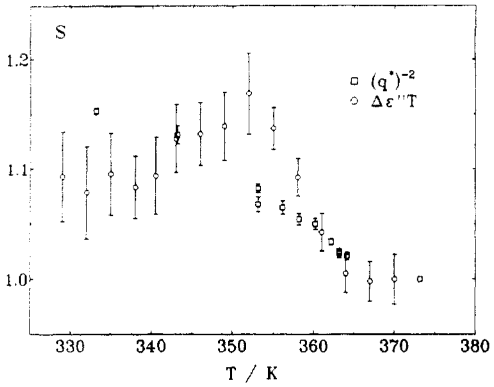

Figure 8. Stretching of the polymer coil during the microphase separation observed in the position of the main peak of the SAXS structure factor q^* as well as the relaxation strength $\Delta\epsilon''$ of the normal mode. S is a reduced quantity (see text).

in the absence of long-range order, as was found in the SAXS measurements. This is clear evidence for the mixed character of the phase transition: although of first order, it is accompanied by strong fluctuations.

A further comparison of the SAXS results and the dielectric measurements is given in Figure 8 for the example of sample B1. It was mentioned before that deviations from Gaussian coil conformation caused by a stretching of the molecule at the disorder-to-order transition lead to an increase of the relaxation strength $\epsilon_{\parallel}$ (see eq 7). A stretching factor S may be calculated as the reduced quantity $\Delta\epsilon_{\parallel}(T)\cdot T/\Delta\epsilon_{\parallel}(T_{\mathrm{ref}})\cdot T_{\mathrm{ref}}$. It can also be obtained as the position of the maximum in the SAXS profiles $(q^*(T_{\mathrm{ref}})/q^*(T))^2$ because both quantities should be proportional to the squared end-to-end distance of the polyisoprene block. Both quantities are compared in Figure 8. T_{ref} is chosen as 373 K. The dielectric relaxation as well as the scattering experiment indicate an increase of r_e^2 of about 10% during the ordering transition.

IV. Conclusion

The dielectric normal mode process of polyisoprene has been used to study the distribution of concentration fluctuations in diblock copolymers. The method determines the relaxation time of the end-to-end vector of the polyisoprene block and therefore possesses an intrinsic length scale on which concentration fluctuations become effective. Their impact on the relaxation time is described with the help of the free volume concept. The existence of the segmental mode may be used to study fluctuations on a shorter scale.

In order to uniquely relate the experimental results of the dielectric experiments to the distribution of concentration fluctuations in the diblock copolymer, it turned out to be essential to measure their static structure factor with SAXS. These measurements determine the disordered and the ordered regimes of the system and indicate the existence of a transition regime which is characterized by strong, long-lived concentration fluctuations in the absence of long-range order.

The dielectric normal mode process was shown to exist in all temperature regimes. An exception is the low-temperature phase of an asymmetric diblock with a polyisoprene block of only 70 units: in this case the transition zone between the glassy polystyrene and the polyisoprene seems to contain such a large portion of the polyisoprene block that no normal mode could be observed in the ordered state.

In the other cases the dielectric normal mode displayed a temperature dependence which was clearly different from a simple WLF law. The strong change in the distribution of concentration fluctuations on the length scale of the polyisoprene block can be characterized as a mixing of polystyrene segments into the volume of a polyisoprene block. This process occurs in a temperature interval of about 30 K and does not lead to a completely homogeneous mixing. The temperature of mixing is close to the T_s obtained from SAXS measurements.

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