the result may be that the rate of decay of segment orientation does not depend on the location of the segment on the polymer chain. This statement is inconsistent with the tube model for entangled polymers or with the Rouse model. Either of the theories tells that the rate of decay should be higher at the chain ends than at the central part of chain. If the theoretical results for the Rouse model[3] are used in place of eq 7, the deviation between the observed and theoretical values of $(\Delta n \sin 2\chi)/2$ becomes slightly larger than that shown in Figure 7.

The present polymer solution may not be a very well-entangled system to be quantitatively compared with entanglement theories. However, comments on earlier studies of entangled systems may be of some interest. The tube model theory has been successful in describing the nonlinear viscoelasticity of polymers.[18] Especially, the complicated data for the relaxation of shear stress and birefringence following double-step shear deformations were well explained in terms of the tube model theory.[19] The results were consistent with the assumption that the decay rate of anisotropic orientation of segments is larger at the chain ends than at the center of chain.[20] Lee and Wool observed that the orientation of the central block of a centrally deuterated triblock polystyrene in a matrix of polystyrene with a high molecular weight decayed more rapidly than the orientation of a fully deuterated polystyrene did.[21] Thus, we now have two inconsistent observations concerning the decay rate of segment orientation.

One possibility of compromise may be to find a defect of the calculation method of birefringence based on the addition of the segment polarizability. On the other hand, the method seems to give consistent descriptions of a variety of data for birefringence and segment polarizability.[1,2,16] The method was effective even in deriving the form birefringence in dilute polymer solutions provided that the effect of anisotropic distribution of segments was taken into account.[22] Thus, it may not be easy to find the defect of the theory for the origin of birefringence. It has been pointed out that a nematiclike interaction,[23,24] such as attractive coupling between neighboring segments, may lead to the results different from above-mentioned theoretical treatments.

In any case, the implication of the present observation seems important. Better understanding may be attained by additional experiments on block copolymers with a reversed structure, polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene, or with components of cosoluble polymers like polystyrene and poly(vinyl methyl ether).

Registry No. (Styrene)(methyl methacrylate) (block copolymer), 106911-77-7.

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Segmental Dynamics in Block Copolymers

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ABSTRACT: We have studied the segmental dynamics of a styrene/isoprene diblock copolymer in a melt of deuterated polyisoprene using quasi-elastic neutron scattering. The static structure factor of the block copolymer in the homogeneous melt state was measured by small-angle X-ray (SAXS) scattering. Static and dynamic data were interpreted in the RPA theory. The result is a good description of the observed SAXS profiles and their temperature dependence. The q dependence of the initial slope in the intermediate scattering law is also accounted for by the same theory. The segmental dynamics of the block copolymer are thus described on the basis of a Rouse model.

I. Introduction

Block copolymers are a class of materials of particular interest because of the specific interaction between their constituents. The interactions, in general, lead to special incompatibility effects, which in turn cause block copolymers to produce a variety of interesting morphologies. The dependence of morphology on molecular architecture and thermal history has been a subject of intensive study in recent years mainly because of the valuable technological applications.[1]

More recently, theoretical[2–4] and experimental[5,6] work has attempted to provide a microscopic understanding of

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Table I
Characterization of Polymers Used

	M_w	M_w/M_n	f
	Block Copolymers		
1. p-PI/d-PS	18 700	1.03	0.9
2. p-PI/d-PS	32 400	1.04	0.5
	Homopolymers		
3. d-PI	80 000	1.03	
4. p-PI	100 000	1.05	

the molecular interaction and the resulting microphase separation into different ordered structures (mesophases). The picture that emerges from these studies describes the polymer–polymer interaction in a mean-field theory known as the random-phase approximation (RPA).[2,7] Its primary predictions refer to the static correlations of fluctuations in the homogeneous block copolymer melt and their dependence on the strength of the segmental interaction. An important result is the determination of a specific wave vector $\mathbf{q}^*$ corresponding to those concentration fluctuations that dominate at the microphase separation temperature (mst). Experimental tests of this theory can be made with scattering experiments using X-rays or neutrons, and we will briefly discuss the underlying concepts together with new results in section III.

While structural properties have been considered from both theoretical and experimental viewpoints, the question of the segmental diffusion within a copolymer molecule in the homogeneous phase is still open. It is known that for linear flexible molecules in their melt the diffusive motion of segments within a polymer coil is well described by the Rouse model[8,9] as long as the relevant length and time scales of the experiment do not extend into the regime of entangled behavior. In section IV we therefore start from this simple situation of a labeled polymer molecule in its melt and replace it by a block copolymer. The dynamics of concentration fluctuations in such systems have been studied with quasi-elastic neutron scattering in order to reveal deviations from the standard Rouse model due to the interaction between segments on different blocks of the block copolymer.

II. Experimental Section

The samples used in this study were diblock copolymers of deuterated polystyrene (PS) and polyisoprene (PI) obtained from Polymer Laboratories Ltd., Shawbury, Great Britain, and a deuterated polyisoprene from PSS, Mainz, West Germany. A summary of the parameters characterizing these materials is given in Table I.

Section III presents SAXS data on block copolymer 1 whereas the quasi-elastic neutron scattering was done on blends of block copolymer 2 and the deuterated polyisoprene (polymer 3) and on polymer 4 in the same matrix 3.

The small-angle X-ray scattering (SAXS) data on our bulk block copolymers were obtained in slit collimation with a Kratky camera using either a position-sensitive detector or a scintillation counter in the usual step scanning mode. The samples were contained in a copper sample cell with acetate windows. This allowed precise temperature control with fluctuations smaller than 0.5 deg. All experiments were performed in an evacuated camera. Data were desmeared following Strobl's algorithm.[10]

For the quasi-elastic neutron scattering experiments, we employed the neutron spin echo (NSE) spectrometer IN11 at the ILL, Grenoble, France. This method[11] allows the direct determination of the normalized intermediate scattering law $S(q,t)/S(q,0)$ as a function of scattering vector q and correlation time t. The experimental study of internal polymer dynamics using quasi-elastic neutron scattering is generally limited to systems with high segmental mobility due to the finite resolution of the spectrometer. An important breakthrough was accomplished with the introduction of the neutron spin echo spectrometer.[11] Its effective energy resolution is of the order of 10^{-9} eV corresponding to a correlation time window from 10^{-9} to several 10^{-8} s. This appears to be a very convenient time range for the investigation of segmental polymer diffusion even in high-viscosity systems like the melt. However, only few polymers (such as PDMS) have proved flexible enough to be used in such experiments.

At a neutron wavelength $\lambda = 8.9$ Å it is possible to measure correlation times $0.3 \leq t$ <eq 18 ns and scattering wave vectors $0.05 \leq q$ (Å^{-1}) ≤ 0.15. In these experiments the samples were kept in aluminum containers with niobium foil windows under a helium atmosphere. Temperature control was again better than 0.5 K. The blends of protonated polyisoprene and the block copolymer 2 (see Table I) with deuterated polyisoprene were prepared by dissolving both components, evaporating the solvent, and then drying in a vacuum oven. Before the scattering experiments the blends were annealed for a minimum of 6 h at the temperature of measurement.

III. Static Structure of Concentration Fluctuations

In this section we deal with concentration fluctuations in the homogeneous phase of block copolymers. For the styrene/isoprene system the first SAXS data were reported by Mori.[5] The situation encountered in the homogeneous phase of block copolymers resembles the familiar homopolymer blend system in many respects. Due to the, in this case repulsive, interaction between segments of the different species, the driving force into the homogeneous state is of entropic nature. Lowering temperature shifts the balance to enhance the importance of interactions and thus leads to phase separation. In the case of blends, this is a macroscopic effect separating different polymer molecules whereas block copolymers are forced into a mesophase due to their molecular connectivity. Although the phase transition may be very different in nature, both systems in the homogeneous state produce concentration fluctuations, which reflect both the structure of the molecule and the strength of the interaction between segments.

The static structure factor $S(q) = S(q, t = 0)$ for these fluctuations is calculated in the random-phase approximation[2]

$$\frac{1}{S(q)} = \frac{S_{AA} + S_{BB} + 2S_{AB}}{S_{AA}S_{BB} - S_{AB}^2} - 2\chi_F \tag{1}$$

where S_{ij} denotes the Fourier transform of the density–density correlation function for the component i and j and χ_F is the usual Flory–Huggins parameter. In this general form eq 1 applies to bulk block copolymer systems as well as homopolymer mixtures[12] with appropriate S_{ij}. For example, one recovers the well-known expression for homopolymer blends from (1) using $S_{AB} = 0$. The case of block copolymer blends with either homopolymer A or B[4] is covered by eq 1. For a bulk block copolymer with sufficiently high block length, the correlation functions S_{ij} are expressed in terms of Debye functions

$$g(f, x) = \frac{2}{x^2}(fx + e^{-fx} - 1)$$
$$x = q^2R_g^2 \tag{2}$$

with R_g denoting the radius of gyration of the copolymer and $f = N_A/(N_A + N_B)$ being the number fraction of A segments. In our discussion f is taken as the fraction of polystyrene. Finally

$$S_{AA} = Ng(f, x)$$
$$S_{BB} = Ng(1 - f, x)$$
$$S_{AB} = \frac{N}{2}(g(1, x) - g(f, x) - g(1 - f, x)) \tag{3}$$

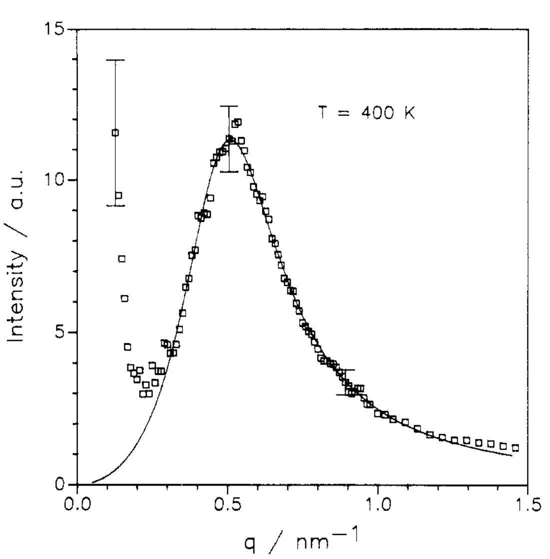

Figure 1. Typical SAXS curve on a bulk styrene/isoprene block copolymer (polymer 1 in Table I). The full line is a best fit of the RPA theory eq 3.

A direct observation of $S(q)$ is possible with scattering methods using X-rays or neutrons. The scattered intensity at scattering wave vector q is[13]

$$I \sim K^2 S(q)$$

The contrast factor K in the SAXS experiment is the difference in electron density of the two components A and B. For neutrons the electron density is to be replaced by the neutron scattering length density. When SAXS and SANS measurements are compared with eq 1–3, generally a good agreement is found between the experimental data and the calculated profiles as long as the temperature is not too close to the phase-separation temperature. Figure 1 shows our desmeared SAXS profile measured on sample 1 at 140 °C. The pronounced peak is a direct result of the block structure of the molecule and the corresponding correlation hole effect.[14] The peak exists even for block copolymers with a vanishing interaction between blocks as has been shown for copolymers of deuterated and protonated polystyrene.[15] This feature is, of course, incorporated in Leibler's theory. For the styrene/isoprene system, however, it turns out that a nonzero Flory–Huggins parameter is essential to obtain a good description of the measured SAXS profile.

An interesting feature observed in Figure 1 is the residual small angle scattering, which is not explained by the above theory. It may be due to polydispersity[16] or a residue of homopolymer in our sample (see section V).

In the temperature dependence of our scattering profiles (Figure 2), one observes a gain in peak height and a loss in width with decreasing temperature. This tendency expresses the fact that, with increasing significance of the interaction between different monomer species, those concentration fluctuations that lead to a separation of the respective copolymer blocks are thermodynamically preferred. The equivalent effect in the case of homopolymer mixtures leads to macroscopic phase separation and an increase of the intensity at $q = 0$.[17]

A quantitative fit of the SAXS data with eq 1–3 gives a radius of gyration of the copolymer—essentially from the peak position—and the product $\chi_F N$. The latter is found from peak height and width. Combining both parameters, one can calculate the interaction energy per segment χ_F/a^2 (a, segment length) without introducing an arbitrary reference volume. This quantity is independent of molecular weight and only dependent on the asymmetry of the block copolymer molecule (see section IV).

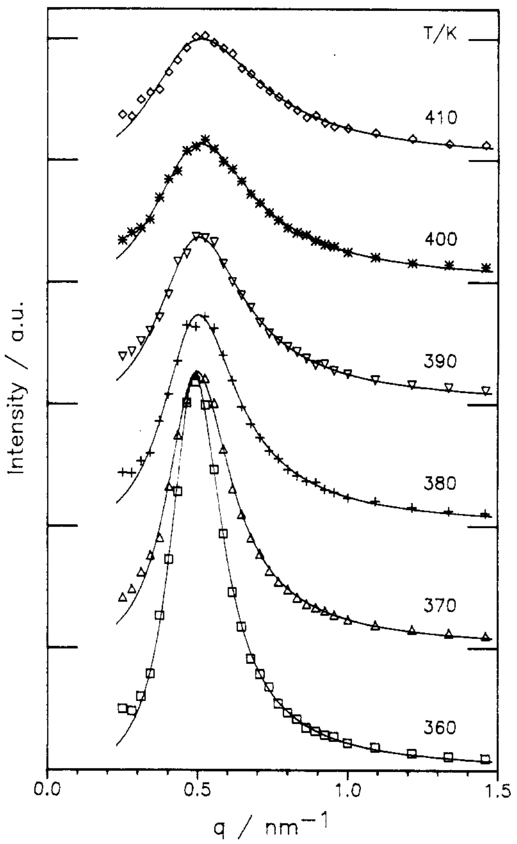

Figure 2. Temperature dependence of the SAXS intensity. The full lines represent fits of the RPA theory.

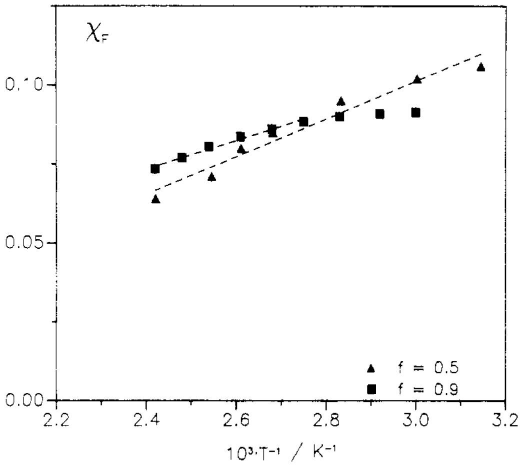

Figure 3. Flory–Huggins parameter χ for two isoprene/styrene block copolymers with styrene fractions $f = 0.9$ and $f = 0.5$.[5]

However, in order to compare our results with those of Mori,[5] we introduce a reference volume $\bar{v}$ in terms of the volumes per monomer of styrene and isoprene via

$$\bar{v} = (v_S v_I)^{1/2} \qquad N = \frac{v_S}{v_I} N_S + \frac{v_I}{v} N_I \tag{4}$$

and reduce the parameter $\chi_F N$ to χ_F with the assumption of (4). The number of monomers per chain N_S and N_I have to be taken from GPC measurements (see Table I).

The results of this procedure are displayed in Figure 3. We find good agreement between the values for χ_F from ref 5 and ours. Both sets of data refer to copolymers of very different architecture ($f = 0.9$ compared to $f = 0.5$ in ref 5). This is an indication for the correct representation of the real polymer with the mean-field parameters via eq 4.

A close inspection of Figure 3, however, reveals a clearly different temperature dependence of χ_F for both polymers in the regime of $\chi_F \approx A + B/T$ (A,B, constants). The deviations from a $1/T$ behavior at small T are supposed to be a result of the onset of the glass transition.[5]

For the radius of gyration as determined from the peak position we find a small shift to higher values with decreasing temperature. A more detailed discussion of the dependence of mean-field parameters deduced from static experiments on properties of the real polymer will be published elsewhere.

IV. Segmental Dynamics: Theory

The term "segmental dynamics" here refers to the Brownian motion of polymer segments as observed in the pair correlation function. Depending on length and time scale, various types of motion may be discriminated ranging from the so-called reptative behavior at sufficiently long times and correspondingly large diffusion distances to Rouse-type segmental diffusion at short times. The limiting characteristic length, the tube diameter D of the reptation model, defines the wave-vector range for the observation of reptative motion $q \leq q^* \simeq 1/D$. With D on the order of 30 Å we do therefore not expect to be in the regime of reptation with our experiment. Consequently, the scope of an adequate theory is set as an extension of the Rouse theory for a single chain in a heat bath. The coherent dynamic structure factor for this model was derived by de Gennes,[18] and in recent years it found experimental verification in NSE experiments on labeled polymer chains in the melt.[8,9]

It seems natural to combine the results of the RPA formalism with the dynamic properties of the Rouse model for a description of the dynamic structure factor of systems containing block copolymer molecules in the melt. This idea was used in a number of papers.[19,20] We can therefore restrict ourselves to a brief summary of the main points of the argument. Our aim is an explicit expression for the dynamic structure factor of a d-PS/p-PI block copolymer in a melt of d-PI.

The calculation of the full-shape function for the intermediate coherent scattering law is a formidable task and has only been accomplished for a few simple models.[18,22] In more complicated situations the methods of linear response theory at least permit the calculation of the initial slope[23]

$$\Omega(q) = -\lim_{t\to 0} \frac{\partial}{\partial t} \frac{S(q,t)}{S(q,0)} \tag{5}$$

Restricting attention to the initial slope alone amounts to a neglect of memory effects (cf. eq 8). A specific result for $\Omega(q)$ in the Rouse model is[18]

$$\Omega_R = \frac{1}{12}\frac{k_B T}{\zeta}a^2 q^4$$

$$\zeta/a^2\text{, segment friction coefficient} \tag{6}$$

In this case the initial slope is also the characteristic frequency of the shape function $\tilde{S}_R$ for $S_R(q,t)$, such that $S_R(q,t) = \tilde{S}(\Omega t)$. $\tilde{S}_R$ was given by de Gennes.[18]

The general result for a multicomponent system in the framework of the generalized Langevin equation theory is found to be[24]

$$\mathbf{\Omega} = k_B T \mathbf{V}\cdot\mathbf{S}^{-1} \tag{7}$$

$\mathbf{\Omega}$, $\mathbf{V}$, and $\mathbf{S}$ represent n by n matrices with n being the number of components in the system, in our case the number of monomer species. The structure factor matrix $\mathbf{S}_{ij}$ consists of the Fourier transform of the correlation functions for monomer species i and j and was given in eq 1 for the example of a copolymer melt. $\mathbf{V}_{ij}$ is the matrix of the generalized transport coefficients.[24] They may be expressed in terms of the monomer friction coefficient, and in the same example one has $V_{aa} = q^2/\zeta_a$.

Finally, the matrix of the collective frequencies $\mathbf{\Omega}_{ij}$ relates fluctuations in the density of component j with the time derivative of i. In Mori's projection operator formalism this relation is expressed as an integro-differential equation for the structure factor

$$\frac{\partial}{\partial t}\mathbf{S}(\mathbf{q},t) = -\mathbf{\Omega}\cdot\mathbf{S}(\mathbf{q},t) + \text{memory terms} \tag{8}$$

In a last step we need to incorporate the interaction between different monomer species into an expression for the measurable quantity Ω_{AA}. Combining RPA and standard procedures of linear response theory one arrives at[19]

$$\Omega_{AA} = \frac{1}{\mathbf{m}^T(\mathbf{\Omega}_o\mathbf{S}_o)^{-1}\mathbf{m}}(\mathbf{m}^T \boldsymbol{S}_o^{-1}\mathbf{m} - 2\chi_F)$$

$$\mathbf{m} = \begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{9}$$

The subscript o refers to properties of a system without interactions.

Inserting eq 1 into eq 9, one obtains the initial slope of the intermediate scattering law for a melt of block copolymer chains.[19] Here we are interested in the more general case of a system containing homopolymer A (subscript 2 in eq 9) and a volume fraction ϕ of copolymer A–B (subscript 1). The elements of the structure factor matrix $\mathbf{S}_o$ are correspondingly (cf. eq 1)

$$S_{AA} = \phi N_1(f, x_1) + (1-\phi)N_2 g(1, x_2)$$

$$S_{BB} = \phi N_1 g(1-f, x_1)$$

$$S_{AB} = \phi\frac{N_1}{2}(g(1,x_1) - g(f,x_1) - g(1-f,x_1)) \tag{10}$$

Assuming the dynamical properties of the noninteracting system to be described by the Rouse model, one finds for the frequency matrix $\mathbf{\Omega}_o$

$$\mathbf{\Omega}_o\mathbf{S}_o = \begin{bmatrix} \dfrac{\phi f}{\zeta_a} & 0 \\ 0 & [\phi(1-f) + (1-\phi)]\dfrac{1}{\zeta_b} \end{bmatrix} q^2 k_B T \tag{11}$$

Finally the quantity of interest is an approximate equation for Ω_{AA} in the regime of wave vectors $q \geq R_g^{-1}$. Inserting this condition into (9) we find

$$\Omega_{AA} \approx \Omega_{AA}{}^{\circ}\left\{1 - \frac{\chi_F}{a^2q^2}24(\phi^2 f(1-f) + \phi(1-\phi)(1-f))\right\} \tag{12}$$

Equation 12 clearly demonstrates the impact of a nonzero Flory–Huggins parameter on the relaxation frequency of the intermediate scattering law. Compared to the noninteracting system, relaxations are slowed down when the interaction is switched on. The absolute value of a decrease in Ω_{AA} is larger for small q, thus indicating an additional stabilization of long wavelength concentration fluctuations over the implicit q^4 dependence of Ω_{AA} on q in the Rouse model.

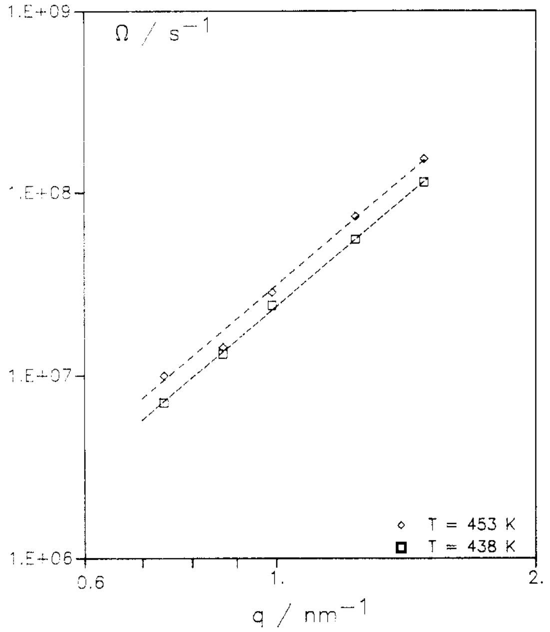

Figure 4. Logarithmic plot of the characteristic frequencies $\Omega(q)$ for p-PI chains in d-PI matrix. The broken lines correspond to a common fit of all measurements at one temperature with the Rouse model (see text).

In order to display the full q dependence of Ω_{AA} in the regime $q \geq R_g^{-1}$, we rewrite (12) introducing the effective friction coefficient ζ_0 instead of $\Omega_{AA}{}^0$:

$$\frac{\Omega_{AA}}{q^2} = \frac{k_B T}{12}\frac{a^2}{\zeta_0}q^2 - \frac{k_B T}{12}\frac{a^2}{\zeta_0}\frac{\chi_F}{a^2}24(\phi^2 f(1-f) + \phi(1-\phi)(1-f)) \quad (13)$$

ζ_0 may be expressed in terms of ζ_a and ζ_b using (11).

V. Discussion

For the investigation of segmental dynamics of block copolymers, we turned to the styrene/isoprene system because of the high mobility of the polyisoprene part. In order to discriminate the effects of block connectivity and segmental interaction from the normal linear-chain dynamics, it is necessary to study the diffusion of p-PI in a d-PI matrix and compare it with the p-PI/d-PS block copolymer in the same matrix. The scattering contrast in both cases is between the protonated PI and the matrix because deuterated PI and deuterated PS have nearly identical scattering length densities. The measured correlation function therefore is $S_{\rm II}(q, t)$.

The quasi-elastic scattering experiment (cf. section II) on the PI melt system was run at two different temperatures (438 and 453 K) and five scattering angles. The corresponding q values are all in the range $qR_g \gg 1$. We found the measured decay functions at each angle to be adequately described by the shape function of the Rouse model $\tilde{S}_R$ in accordance with earlier studies on PDMS.[8] Consequently, $\tilde{S}_R$ was used to extract the frequency $\Omega_{\rm II}(q)$ from the measured $S(q, t)$ in a least-squares fit. The results for $\Omega_{\rm II}$ are displayed in Figure 4 on a logarithmic scale. Obviously their dependence on the wave vector is correctly described by a power law $\Omega \approx q^4$, which is consistent with the assumption of a Rouse model. It is therefore tempting to use the full-time and wave vector dependence in $S_R(q, t)$ to describe all measurements at the different angles for one temperature with only a single parameter varied: the segmental friction coefficient ζ/a^2 (Table II). The result of this common fit procedure is included in Figure 4 as the straight line. The numerical values are tabulated in Table II.

Table II
Segment Friction Coefficients (Errors in Parentheses)

	$10^{-6}\zeta/a^2$, g cm^{-2} s^{-1}	
T, K	homopolymer	copolymer
438	2.1 (0.1)	2.6 (0.5)
453	1.68 (0.05)	2.1 (0.4)
473		1.1 (0.1)

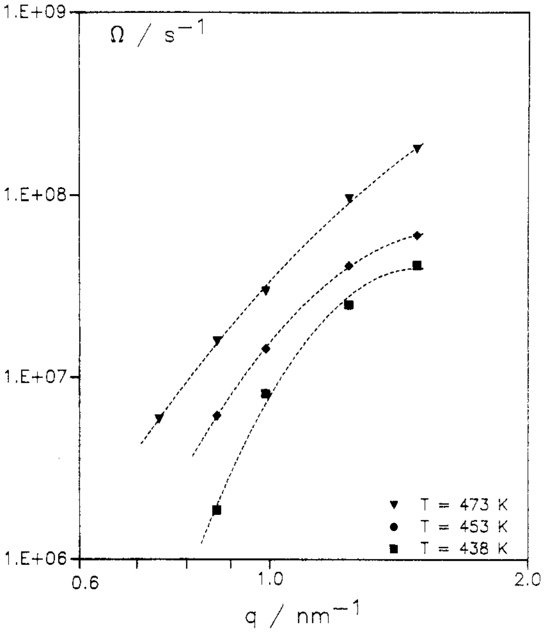

Figure 5. Logarithmic plot of the characteristic frequencies $\Omega(q)$ for the block copolymer (polymer in Table I) in a d-PI matrix. The broken lines are guide lines for the eye.

In summary, for the melt we find an overall correct description for the normalized intermediate scattering law in terms of the Rouse model. The underlying physical picture visualizes interactions between a specific polymer chain and its environment only as an averaged field represented by the segmental friction coefficient. This rather simple description appears to be adequate for dense polymer systems such as melts and motivates the application of the mean-field methods in section IV.

Sample 2 consisted of a blend of the same deuterated PI matrix with 7% of block copolymer. This concentration is well below the critical micelle concentration at the temperatures used.[25] A check of the static structure factor using SAXS showed the expected RPA profile (see eq 1 and 10) and no micelle scattering.[26] Measurements on this system are complicated by the comparatively low intensity as only one block of the copolymer contributes to the scattering. Careful correction of the measured polarization for matrix scattering is therefore important.

Spectra were taken at three temperatures (438, 453, and 473 K), and the extraction of $\Omega(q)$ from the decay functions followed the same procedure as for sample 1. The results are shown in Figure 5. No simple power law behavior is found for the dependence of Ω on wave vector. When the results found for the PI melt are compared with those of the block copolymer, it is further observed that Ω is considerably smaller at each q and the same temperatures for the latter.

The effect of connecting the p-PI block to the d-PS obviously leads to a slowing in the relaxation of internal fluctuations and to a modification of the mode structure. Both findings are predicted by the RPA expression (eq 12). A critical test for the validity of eq 13 is obtained from a

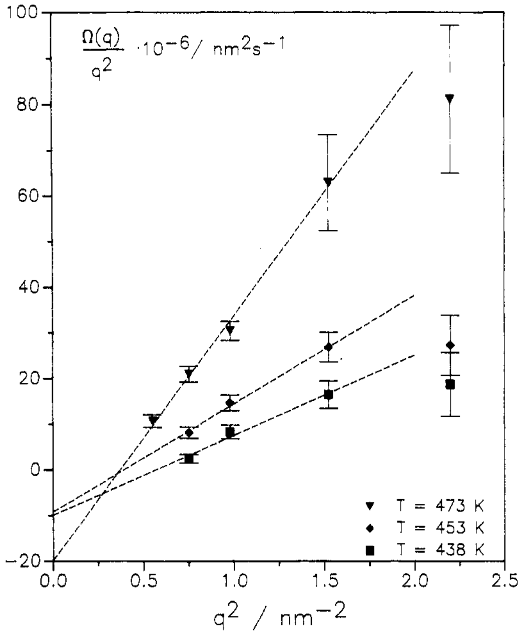

Figure 6. RPA plot following eq 13 of the frequencies Ω obtained for the block copolymer in a matrix of d-PI.

plot Ω/q^2 vs q^2, which is given as Figure 6. According to the RPA, one would expect to find a straight line with its slope and intercept defining the effective segmental friction coefficient and the interaction parameter.

Indeed, this behavior is clearly displayed by our data up to a wave vector $q \simeq 0.11$ Å^{-1}. Figure 6 allows a precise determination of the effective friction coefficient (see Table II). The interaction parameter χ_F/a^2, however, is only approximately obtained. Its values are lower than those found in the SAXS experiments on the bulk block copolymer. Unfortunately, our data do not allow a quantitative comparison. It can, however, be concluded from Figure 6 that χ_F/a^2 decreases with temperature as it is expected from the SAXS results.

The deviation of the points at largest q may be attributed to nonuniversal local modes that come into play in this regime.[27] They modify the Rouse mode structure and, in general, lead to weaker dependence of Ω on q. Using the concept of segmental diffusion,[28] one expects to find a plateau in Figure 6 for large q defining a segmental diffusion constant $D_s = k_B T/\zeta$. Combining D_s and the segment friction coefficient ζ/a^2, we arrive at an estimate for the segment length $a \cong 3.3$ nm.

VI. Conclusion

We have presented the first NSE measurements on block copolymer systems and thus demonstrated the feasibility of such experiments. Having confirmed the applicability of the Rouse model to the dynamics of a PI chain in a d-PI melt, we have described a theory for the copolymer (p-PI/d-PS) dynamics in the same matrix. This theory results from a combination of RPA and linear response theory and accounts fully for the experimentally determined initial slope of the intermediate scattering law. Its main benefit lies in a separation of the effects of segmental interaction from the mere modification of the friction coefficient. Whereas the latter takes into account the average environment of an individual segment, the interaction is found to slow down long wavelength fluctuations.

Using SAXS, we have measured the static structure factor of the bulk block copolymer styrene/isoprene. Its dependence on wave vector is found to be well described by the RPA. A comparison of the mean-field parameters from static and dynamic experiments is only qualitative.

The application of SAXS to the homogeneous phase of block copolymers shows a number of promising prospects. It opens the way to a detailed comparison between mean-field theory,[2] its numerical improvements,[29] and real polymer systems. Next to the static structure factor and its dependence on the geometry of the molecule and strength of the interaction, one should explore the phase transition at the microphase-separation temperature using the same technique. Experiments on this problem are currently in progress.

A second more practical result is the precise determination of a parameter for segmental interaction, which may then be used to predict thermodynamical properties of the coresopnding polymer pair in blends as well as for the block copolymers. The advantage of measurements on the copolymer system over the corresponding blend lies in the strength of the effect and the extension of the regime of homogeneity.

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Registry No. (I)(S) (block copolymer), 105729-79-1; PI, 9003-31-0; neutron, 12586-31-1.

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