Relaxation Dynamics in Bimodal Polystyrene Melts: A Fourier-Transform Infrared Dichroism and Small-Angle Neutron Scattering Study

C. Hayes,[†] L. Bokobza,[†] F. Boué,[‡] E. Mendes,*,[†] and L. Monnerie[†]

ESPCI-PCSM, Laboratoire Associé au CNRS, URA 278, 10, rue Vauquelin,
75231 Paris Cedex 05, France, and Laboratoire Léon Brillouin-CEA-Saclay,
91191 Gif-sur-Yvette Cedex, France

Received January 5, 1996[⊗]

ABSTRACT: Polymer chain orientational relaxation has been studied in bimodal polystyrene melts composed of long hydrogenated chains and 20 wt % short deuterated chains. Thin polymer films were uniaxially stretched above the glass transition temperature, relaxed, and then quenched after different relaxation times. The chain orientation in the deformed samples was analyzed on different length scales using two different techniques—Fourier-transform infrared dichroism (FTIRD) and small-angle neutron scattering (SANS). The local orientational relaxation of the long matrix chains, as well as that of the short deuterated chains, is measured using FTIRD. It is shown that the relaxation of the long chains ($M_w \sim 2 \times 10^6$) is not affected by the presence of the short chains, for the particular weight fraction of short chains (20%), and for the two different short chain masses used: $M_w \sim 27\,000$ and $M_w \sim 188\,000$. The SANS isointensity patterns are elliptical in shape for short relaxation times but take the form of lozenges when the terminal/Rouse time of the short chains is approached. For relaxation times of the order of (or longer) than the terminal/Rouse time of the short chains, that is, in the relaxation time range where a residual short chain orientation is measured, isointensity curves in the form of butterflies are observed. For the sample containing small chains of $M_w \sim 27\,000$, a new isointensity curve is observed at relaxation times of the order of the Rouse time. This isointensity curve has the form of a "4-leaved shamrock". A qualitative interpretation is given in terms of the stochastic process governing chain relaxation.

1. Introduction

In order to study chain relaxation processes in uniaxially deformed bimodal polystyrene melts, samples of different deformation histories have been examined using two different techniques: Fourier-transform infrared dichroism (FTIRD) and small-angle neutron scattering (SANS).

Infrared dichroism spectroscopy provides information on the orientation of polymer chains on a monomeric scale. The second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle$, can be measured by this technique. Such a distribution function describes the average orientation of chain segments.[1]

In the case of polymer melts consisting entirely of monodisperse chains, the time evolution of $\langle P_2(\cos\theta)\rangle$ following a rapid uniaxial deformation reflects the average orientational relaxation of all the identical polymer chains present in the sample. For entangled melts, the Rouse theory[2] of molecular dynamics can account for experimental results on a short time scale, while a modified reptation theory can describe the experimental results in semiquantitative terms, up to the terminal time.[3]

In the case of highly asymmetric bimodal melts, wherein one of the species is deuterated, it is possible to follow the orientational relaxation of each component simultaneously using FTIRD. For the longer chains, it was, for example, demonstrated in a previous study that the orientation is not strongly affected by the presence of 15 wt % shorter chains, with a molecular weight of the order of the molecular weight between entanglements.[4] The present paper actually focuses on the relaxation dynamics of the shorter chains. Two characteristic relaxation time ranges have already been well-defined. At short times, weakly entangled chains relax as described by the Rouse model. At long relaxation times a residual orientation has been detected and was attributed to orientational coupling with the longer matrix chains.[4]

Unlike FTIRD which provides a measure of the average local chain orientation, the SANS technique probes scales which are far greater than the monomeric unit. The length scale range accessible by SANS measurements varies from tens to hundreds of angstroms depending on the wavelength of the neutrons and the spectrometer configuration. In the case of a mixture of deuterated and non-deuterated chains of identical molecular weight distributions, the average conformation of the individual chains may be determined.[5]

SANS experiments have previously been performed on uniaxially elongated unimodal melts.[6] In this case, the scattered intensity has been analyzed to follow chain conformational relaxation as a function of time. It has been shown that Rouse and reptation dynamics apply at least qualitatively.

In the case of the bimodal melts, where one species is labeled, the SANS signal contains information about both intra- and interchain correlations. In an initial time range, shortly after deformation, it has been shown that bimodal melts present a random mixing behavior: all chains are highly oriented.[7] The corresponding SANS isointensity curves are elliptical in shape, with major axes perpendicular to the elongation direction (data recorded on a bi-dimensional detector). As the system relaxes, the elliptical patterns should theoreti-

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* To whom correspondence should be addressed, at his present address: Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, URA 851, 4, Rue Blaise Pascal, Université Louis Pasteur, 67070 Strasbourg Cedex, France.

[†] ESPCI-PCSM, Laboratoire Associé au CNRS.

[‡] Laboratoire Léon Brillouin-CEA-Saclay.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

S0024-9297(96)00015-0 CCC: $12.00

cally transform at longer relaxation times to circles, corresponding to a return to an isotropic configuration. However, a very different behavior has been observed for intermediate and long relaxation times. In fact, at intermediate times, the isointensity patterns have been shown to take the shape of diamonds ("lozenges"), while for long relaxation times, eight-shaped curves with a principal axis parallel to the stretching direction have been observed.[7] The latter patterns, otherwise known as "butterfly patterns", were also observed in the SANS signal from uniaxially deformed permanently cross-linked polymers containing short un-cross-linked deuterated chains.[8] It was later demonstrated that such patterns arise from interchain correlations.[9]

Butterfly patterns were also observed for elongated gels swollen in a good solvent.[10] In this case, they were attributed to the presence of frozen-in quasi-static heterogeneities, which separate upon elongation. However, as regards the small-angle neutron scattering spectra of high molecular weight melts, often referred to as temporarily cross-linked systems, the overall situation is less clear, and no theory has yet satisfactorily accounted for the observation of the "non-classical" isointensity patterns (lozenge and butterfly).

In this paper, chain orientational relaxation in two different bimodal polystyrene melts is analyzed and discussed. Both systems consist of a mixture of long hydrogenated chains and short deuterated chains. The molecular weight of the long chains is approximately 2 × 10^6, and that of the short chains is either 27 000 or 188 000. The weight fraction of the short deuterated chains in each case is 20 wt %. In order to successfully couple the FTIRD and SANS techniques, the same samples were used for both measurements.

2. Experimental Section

Sample Preparation. Films were prepared by solution casting 0.06 g/mL solutions of polystyrene in benzene. After evaporation of the solvent, the films were cut in 2-cm-wide strips and annealed for 72 h at 30 °C above the glass transition temperature, T_g. The glass transition temperature of the annealed polymer films was determined by differential thermal analysis with a heating rate of 10 °C/min. All polymer films and mixtures had the same T_g (103 °C). The high molecular weight polystyrene (PSH2000, $M_w = 1\,921\,000$, $M_w/M_n = 1.26$) was purchased from Pressure Chemical, and the deuterated samples (PSD27, Mw = 27 000, $M_w/M_n = 1.03$, and PSD188, $M_w = 188\,000$, $M_w/M_n = 1.03$) were purchased from Polymer Laboratories. The sample code number represents the molecular weight in units of 1000. The short chain concentration is 20 wt %.

The thin polymer films (16 × 40 × 0.07 mm) were stretched at constant strain rate (0.115 s^{-1}) at temperatures above the glass transition temperature. Then, at a draw ratio $\lambda = 4$ ($\lambda = L/L_0$, where L is the final and L_0 the initial sample length), the samples were maintained under constant elongation and temperature for a time t_R, called the relaxation time, and then quenched rapidly to room temperature. The stretching device and the actual procedure are described in ref 11. The same samples, in quenched film form, were used for both the FTIRD and SANS measurements. In the latter measurements, in order to obtain the larger thickness necessary for good statistics in a reasonable time, the deformed films (160 mm long) were cut in pieces 1.5 cm long and superposed. The final thickness was approximately 0.4 mm.

The temperature of deformation and the relaxation time were varied in order to study the chains in various relaxation states. The time temperature superposition principle was used to construct a master relaxation curve at a given reference temperature:

$$\log a_{T/T_0} = \frac{-C_1^0(T - T_0)}{C_2^0 + T - T_0} \tag{1}$$

where $a_{T/T_0} = t_R(T)/t_R(T_0)$ and C_1 and C_2 are the WLF coefficients for polystyrene at the temperature T_0. The WLF parameters, $C_1 = 10$ and $C_2 = 65$ $\deg^{-1}$, corresponding to T_0 = 115 °C, were determined from rheological measurements.[12]

Infrared Dichroism Measurements. The infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer equipped with a SPECAC gold wire-grid polarizer. The samples rather than the polarizer were rotated in order to measure the absorption in the directions parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the stretching direction. The average segmental orientation of the defomed polymer chains was determined using the relation

$$\langle P_2(\cos\theta)\rangle = {}^1/_2(3\langle\cos^2\theta\rangle - 1) = [(R - 1)/(R + 2)][2/(3\cos^2\alpha - 1)] \tag{2}$$

where θ is the angle between the local chain axis and the stretching direction, $R = A_{\parallel}/A_{\perp}$ is the dichroic ratio, and α is the angle between the dipole moment vector of the vibration considered and the local chain axis. The orientation of the PSH2000 chains was measured using the 906 cm^{-1} band associated with the out-of-plane vibration of the benzene ring, ν_{17b},[13] while the 2273 cm^{-1} band, characterized as described in ref 14, was used to probe the deuterated chain orientation.

Small-Angle Neutron Scattering. The SANS experiments were carried out at the PAXY spectrometer at Laboratoire Léon Brillouin, Saclay, France. The bi-dimensionnel detector (128 × 128 square (0.25 cm^2) cells) was placed at 3.2 m from the sample, and the incident wavelength was $\lambda = 10$ Å. The detector was normalized using the incoherent scattering from water, and the appropriate incoherent scattering background was calculated using the incoherent absolute scattering levels from a completely deuterated and a completely hydrogenated sample, that were measured separately.

In order to avoid eventual misinterpretation of the results due to the superposition of pieces of the deformed films, certain samples for the SANS measurements were dismounted and thinner samples, consisting of only two or three superposed pieces of film, were analyzed separately. In each case the same isointensity curves as for the thicker samples were recorded.

3. Results

3.1. Infrared Dichroism Measurements.

The average local molecular orientation, $\langle P_2(\cos\theta)\rangle$, of the long chains and the short chains is compared in Figure 1 for the two different bimodal mixtures. The molecular weight of the long chains is identical for both mixtures (PSH2000). The orientation of the short chains (guest chains) is strongly molecular weight dependent. The longer of these guest chains (PSD188, $M_w = 188\,000$) presents a local orientation which is equivalent at short times to that of the matrix chains. On the contrary, the orientation of the PSD27 chains ($M_w = 27\,000$) is much lower than that of the long chains at short times and decreases more rapidly.

The local orientational relaxation master curves may be crudely divided into two time regions. It is seen in Figure 1 that in a first time domain the orientation of the short chains decreases rapidly; in a second time domain the orientation varies more slowly. The first time region may be characterized by the Rouse time, τ_{Rouse}, of the PSD27 chains or the retraction time, τ_B, of the PSD188 chains. These characteristic times are indicated in the figures. At 115 °C, the Rouse time of the PSD27 chains is roughly 35 s ($\log t \approx 1.2$) while the retraction time of the PSD188 chains is roughly 3700 s

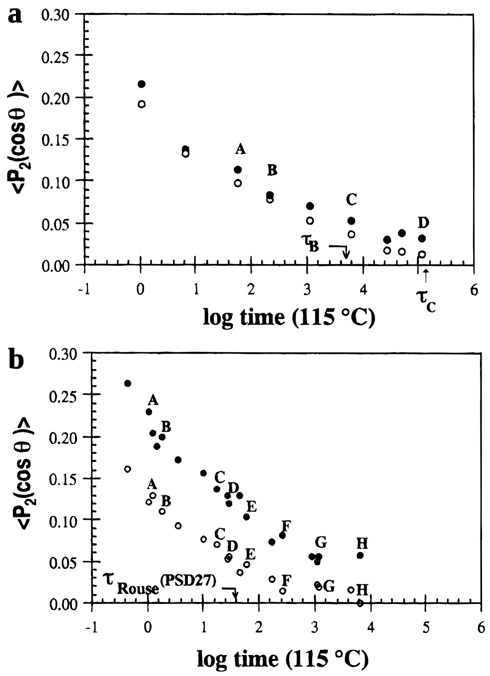

Figure 1. Average local orientation, ⟨$P_2(\cos\theta)$⟩, as a function of the relaxation time (logarithmic scale) at 115 °C for both long chains (PSH2000) (●) and short deuterated chains (○) in mixtures (a) PSH2000/PSD188 and (b) PSH2000/PSD27. The letters correspond to the samples studied by small-angle neutron scattering. The characteristic relaxation times ($\tau_{\rm Rouse}$, τ_B, and τ_C) of the short chains are also indicated in the figures.

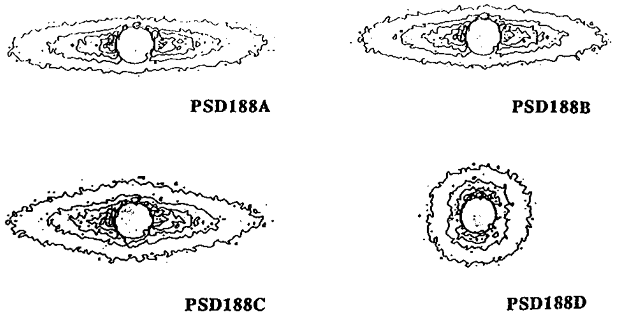

Figure 2. SANS isointensity curves for the mixture PSH2000/PSD188 at different relaxation times.

(log $t \approx 3.6$). The reptation or terminal time, τ_C, of the PSD188 chains at 115 °C is estimated at 100 000 s (log $t = 5$).

The orientational relaxation of the long chains is the same in both bimodal systems studied. It was previously shown to be identical to that of the pure PS2000 relaxation.[15]

3.2. Small-Angle Neutron Scattering. 3.2.1. Isointensity Patterns. Samples in different states of orientational relaxation are analyzed by both infrared dichroism and small-angle neutron scattering techniques, and they are indicated by a letter (A, B, C, etc.) in Figure 1. The isointensity patterns corresponding to these samples are shown in Figures 2 and 3 for the mixtures PS2000/PSD188 and PS2000/PSD27, respectively. The isointensity pattern corresponding to a given sample in Figure 1, panels a and b, is indicated by the same letter in Figures 2 and 3.

Consider the isointensity patterns A to D of mixture PSH2000/PSD188 (Figure 2). The isointensity pattern is elliptical in shape with a major axis perpendicular to the stretching direction for samples PSD188A and PSD188B. These samples (1.8 〈 log t_R (115 °C) < 2.4) present a relatively high local orientation (Figure 1a). Such patterns arise from chain orientation along the stretching axis (direction). With increasing relaxation times, the ellipse contracts to acquire a "lozenge" shape (PSD188C). For relaxation times of the order of the reptation time, τ_C(PSD188), the isointensity contours are almost circular at large q values (outer contours) but eight-shaped at smaller q values (inner contours). The major axis of these so-called butterfly patterns is parallel to the stretching direction.

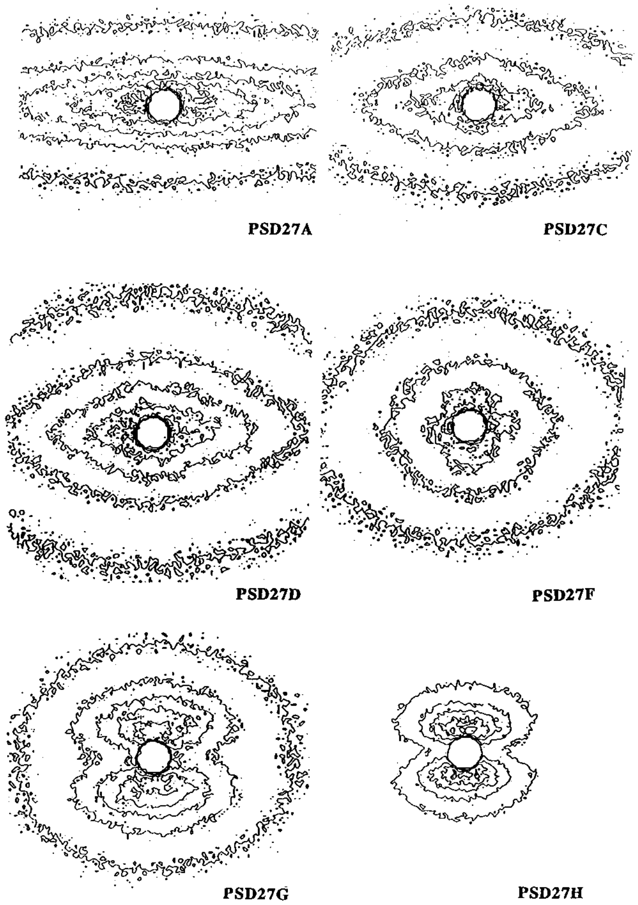

Figure 3. SANS isointensity curves for the mixture PSH2000/PSD27 at different relaxation times.

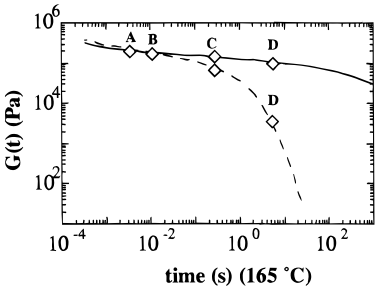

Figure 4. Stress relaxation modulus as a function of time at 165 °C for PSH2000 (full line) and PS188 (dashed line). The letters A–D correspond to the relaxation times, calculated at 165 °C using the time temperature superposition principle, of samples PSD188A–D indicated in Figure 1a.

Figure 4 shows the stress relaxation modulus as a function of time (logarithmic scale) for a reference temperature of 165 °C for PSH2000 and PSH188. Indicated in this figure are the relaxation times of samples PSD188A–D calculated at 165 °C using the WLF equation. For sample PSD188D, for example, while the PSH2000 chains are still in mechanical equilibrium (the modulus presents a plateau), the

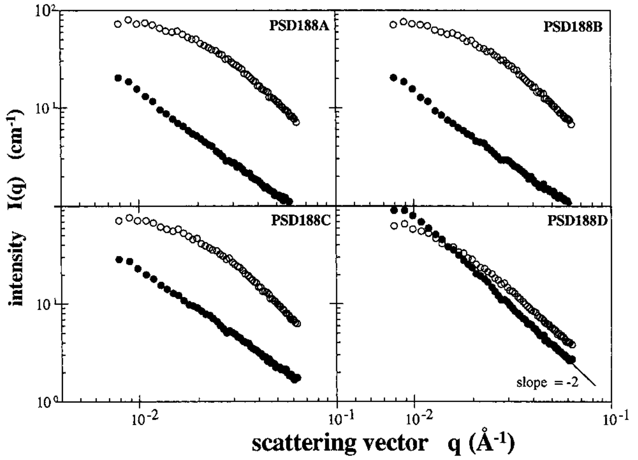

Figure 5. Absolute scattering intensities in the parallel (●) and perpendicular (○) directions for samples PSD188A, PSD188B, PSD188C, and PSD188D.

PSH188 chains are already in the terminal zone (the modulus decreases rapidly with time).

For mixture PSH2000/PSD27 the evolution of the isointensity patterns with increasing relaxation times follows the same trend as for the previous mixture (Figure 3). Elliptical curves are observed for short relaxation times (PSD27A and PSD27B), lozenge-shaped curves are observed for intermediate times (PSD27C), and well-defined butterfly patterns (PSD27G and PSD27H) are recorded when the relaxation time is greater than the Rouse time, τ_{Rouse}, of the deuterated PSD27 chains. A novel isointensity pattern (PSD27F) is observed intermediate between the lozenge and butterfly patterns. The inner contours of this pattern are in the shape of a “cross” or a “four-leaved shamrock”.

3.2.2. Analysis of the Absolute Scattered Intensity in Parallel and Perpendicular Directions.

The scattered intensities, in parallel and in perpendicular directions, are compared in Figure 5 for samples PSD188A-D. With increasing relaxation times, the difference between the orthogonal anisotropic intensities decreases. In the first three figures (PSD188A, B, and C), $I(q)$ parallel is always less than $I(q)$ perpendicular. The fourth figure (PSD188D) presents a crossover point at small q values: $I(q)$ parallel is greater than $I(q)$ perpendicular. This low-angle overscattering corresponds to larger values than the zero q limit of the intrachain scattering (molecular weight) and is the signature of the butterfly pattern. The slope of $I(q)$ parallel as a function of q at large q values is -2. This value suggests that in the large q range (small distances), the chain segments present a Gaussian distribution and are therefore relaxed.

In Figure 6, panels a and b, the same scattering spectra are replotted, comparing respectively $I(q)$ perpendicular and $I(q)$ parallel for the different samples. While the intensity of the neutrons scattered in the direction perpendicular to the stretching direction varies slightly between samples A, B, C, and D, the parallel scattered intensity increases significantly over the entire q domain studied with increasing relaxation times. Thus the butterfly patterns are associated moreso with an increase in the intensity of the neutrons scattered in the parallel direction than with a decrease in the perpendicular intensity.

The SANS spectra relative to mixture PSH2000/PSD27 are shown in Figure 7. On plotting together parallel and transverse intensities, the same general

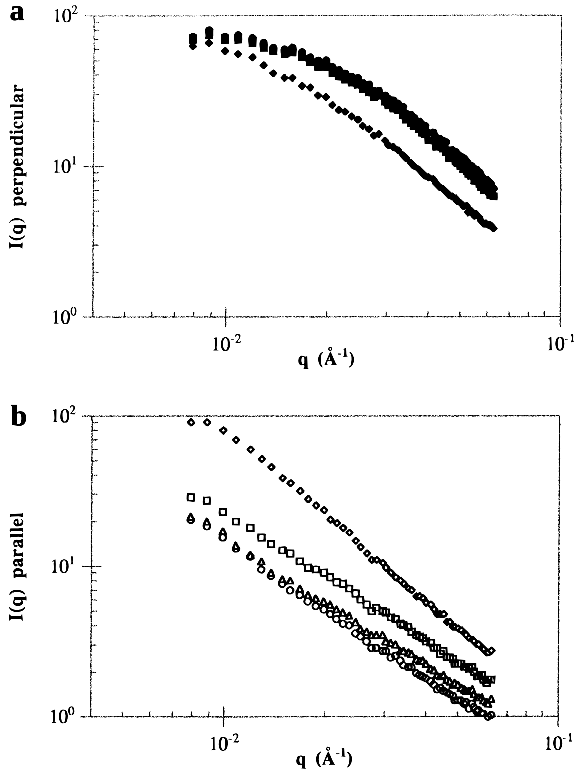

Figure 6. Absolute scattering intensities in the perpendicular (a) and parallel (b) directions for samples PSD188A (circles), PSD188B (triangles), PSD188C (squares), and PSD188D (diamonds).

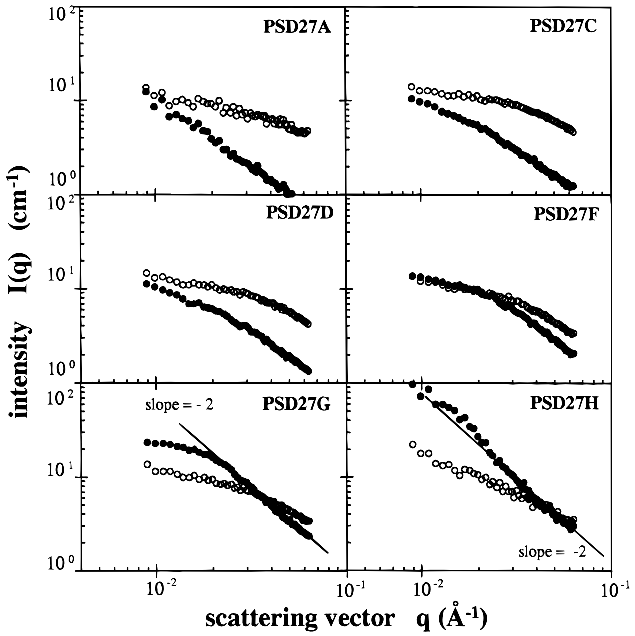

Figure 7. Absolute scattering intensities in the parallel (●) and perpendicular (○) directions for samples PSD27A, PSD27C, PSD27D, PSD27F, PSD27G, and PSD27H.

trend is observed: with increasing relaxation times, the parallel intensity increases and for long relaxation times is greater than the perpendicular intensity for large q values. We notice however two particularities. First, data corresponding to the “shamrock” pattern are almost superimposed for the two directions. Second, the parallel and perpendicular intensities corresponding to well-defined butterflies show a much stronger difference at small angles, but superimpose at large q. The slope of the parallel signal is stronger than -2, in an

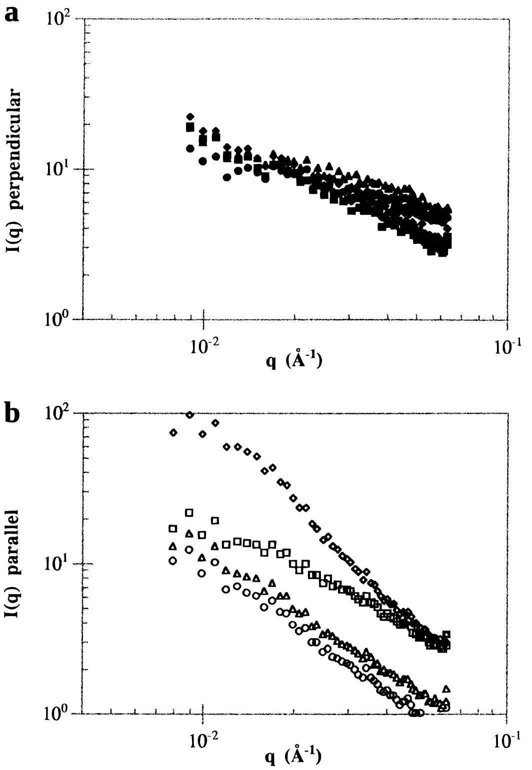

Figure 8. Absolute scattering intensities in the perpendicular (a) and parallel (b) directions for samples PSD27A (circles), PSD27B (triangles), PSD27E (squares), and PSD27H (diamonds).

"intermediate" range of q values for sample PSD27F.[16] However, at large q, the slope -2 is recovered, which implies that, for long relaxation times, the behavior of the short chain is almost Gaussian at short scales. This curve (PSD27F) starts to "saturate" at very small angles, and a correlation length associated with it is of the order of $\xi \sim 100$ Å.

Panels a and b, Figure 8, show respectively the absoulte intensity of the neutrons scattered in the perpendicular direction and in the parallel direction for four representative samples of the mixture PSH2000/PSD27. Despite the dispersion of the points due to the weak signal, the perpendicular signal at large q seems to decrease slightly with time. For the parallel direction, most striking is the final evolution of the intensity as already observed in Figure 7.

4. Discussion

As mentioned above, the local orientational relaxation of the long matrix chains (PSH2000) is unaffected by the presence of a small percentage of short deuterated chains. Even when the molecular weight of the short chains is of the order of M_e, the entanglement molecular weight ($M_e \sim 18\,000$ for polystyrene, therefore a molecular weight of 27 000 corresponds to less than one entanglement per chain), the orientational efficiency of the long chains is unaltered. The influence of short chains of different molecular weights and different concentrations on the relaxation behavior of the long chains is discussed in ref 12 and will be the subject for further publication.

The short chains, which are less oriented at short times, since they are less entangled, present a residual orientation at long relaxation times. A similar phenomenon has already been observed for un-cross-linked chains dissolved in uniaxially elongated PDMS rubbers by Deloche and Dubault using NMR techniques.[17] The same effect was also recently found in asymmetric blends of the same polymer (PS).[18] Such a residual relaxation has been attributed to an orientational coupling mechanism: the short chains acquire a certain small-scale orientation from the surrounding long chain matrix. This coupling originates in short-range interactions between partially aligned chain segments.

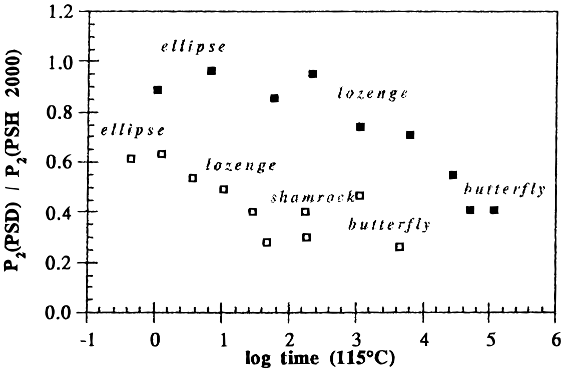

Figure 9. Ratio of the average local orientation, $\langle P_2(\cos\theta)\rangle$, of the short deuterated chains, PSD27 (white squares) and PSD188 (black squares), to that of the long chains PSH2000 in the mixtures PSH2000/PSD27 and PSH2000/PSD188 as a function of time at 115 °C.

Figure 9 shows the ratio of the orientation, $\langle P_2(\cos\theta)\rangle$, of the short chains to that of the long chains as a function of the experimental relaxation time. The shapes of the SANS isointensity curves corresponding to a given relaxation time are also indicated in the figure. Although it has been previously suggested that the butterfly patterns arise due to phase separation because of local orientational differences, the magnitude of the $\langle P_2(\cos\theta)\rangle$ ratio does not suggest that this is the case. As Figure 9 and also Figures 2 and 3 indicate, the experimental relaxation time must be of the order of, or greater than, the Rouse or retraction time of the short chains, in order to observe nonclassical scattering curves. Such effects start with the appearance of lozenge curves at these characteristic times, and then, for longer times, butterfly patterns are observed. Therefore, the butterfly patterns seem to be governed by the diffusion of short chains. Also, the appearence of such patterns does not appear to be due to local constraint release, that is, matrix tube destruction, since the local orientational relaxation of the long chains is almost not affected by the presence of the small ones.

The above picture suggests that small chains diffuse and increase interchain correlations. The question is, where do they diffuse? One possible interpretation is to make an analogy with the case of swollen gels. It has been suggested[19] that the butterfly patterns observed for polymer melts originate in the random distribution of entanglements in space. Consequently, because of the randomness of the distribution of entanglements in space, zones which are richer than average in entanglements would be harder to deform. This would be responsible for the formation of soft and hard zones even in the melt. During the relaxation, short chains would tend to diffuse to the regions which are poorer in entanglements, and the interchain correlation would be responsible for the butterfly patterns.

Consider now the isointensity patterns observed for experimental relaxation times of the order of τ_{Rouse}, that is, the lozenge and shamrock patterns. Earlier studies established[20] that the lozenge-shaped patterns may be produced for ternary systems of long and short deuterated chains in a very long chain matrix at times corresponding to the butterfly of the short deuterated chains and the ellipse of the long deuterated chains. It was suggested that the lozenges are a combination of an ellipse and a butterfly and that such patterns arise from a bimodal distribution of free chains. In that case, the long deuterated chains are still oriented while the short deuterated chains are relaxed, with interchain spatial correlations giving rise to butterflies. These previous studies also indicated that the lozenge–butterfly transition is very rapid, and is accompanied equally by an important increase in the intensity in the parallel direction. The observation of the shamrock patterns above helps the corroboration of this fact. Despite the fact that in the present case no bimodal distribution is used for the short chains, one could interpret this as follows. Since relaxation phenomenon of the free chains is stochastic, when the relaxation time approaches the terminal time of the short chains, part of the chains will be completely relaxed while others will be nearly, but not completely relaxed. The completely relaxed chains, having enough time to diffuse, would "prefer" to diffuse to soft zones, poorer in entanglements. This would lead to an increase in the intensity at small angles in the parallel direction, because of the correlations between soft zones. The other chains, still partially aligned along the elongation direction, would produce a signal in the form of an ellipse. The combination of these intra- and interchain correlations could explain the SANS spectra in the parallel and perpendicular directions corresponding to the shamrock and lozenge patterns observed here and in the case of the ternary melts recalled above. In this case, the shamrock pattern could only be observed in a very narrow time window, as seems to be the case here.

5. Conclusion

The present study couples two different techniques which provide information about local (FTIRD) and large-scale (SANS) orientational chain relaxation in uniaxially deformed bimodal polymer melts. SANS isointensity curves evolve from ellipses at short relaxation times to butterflies for relaxation times greater than the terminal or Rouse time of the short chains. Since we could not detect any variation of the kinetics of the long chain relaxation on a local scale due to the presence of the short chains, it is suggested that the appearance of butterfly patterns is related to short chain diffusion rather than to matrix (tube) release due to the short chains. Lozenge patterns for relaxation times of the order of the Rouse time (or the retraction time) of the short chains were also observed as well as a new isointensity curve having the shape of a 4-leaved shamrock. The latter curve was observed in a narrow relaxation time window, and it appears just after the observation of the lozenge-type curve, and just prior to the observation of butterfly patterns. The shamrock and lozenge patterns were interpreted as a consequence of having in the system, at a relaxation time of the order of τ_{Rouse}, some chains already relaxed and displaced due to diffusion while others are still more oriented and relaxing. The former give rise to an interchain signal which leads to a increase in the scattered neutron intensity in the direction parallel to the stretching direction while the latter give rise to elliptical patterns aligned perpendicular to the stretching direction. "Lozenges" and "shamrocks" can be a consequence of the combination of these two different signals. For longer relaxation times only butterfly patterns are observed, and it is suggested that they are a consequence of an inhomogeneous distribution of entanglements among the matrix chains.

Acknowledgment. The authors (E.M. and F.B.) would like to thank C. Picot and J. Bastide for interesting discussions and suggestions.

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MA960015A