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Shear Orientation and Rheology of a Lamellar Polystyrene−Polyisoprene Block Copolymer

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ABSTRACT: A low molecular weight, slightly entangled polystyrene−polyisoprene (PS−PI) diblock copolymer is quenched from the disordered to a locally ordered but macroscopically disordered lamellar state and then subjected to large-amplitude oscillatory shearing to induce a macroscopically aligned state. Substantial alignment is achieved, as shown by X-ray scattering; at high frequency and/or low temperature, the lamellae orient parallel to the shearing surfaces with their normal parallel to the velocity gradient, while at low frequency and/or high temperature, the normal to the lamellae orient perpendicular to both the shearing surfaces and the velocity gradient. These same two alignment directions were discovered earlier by Koppi et al. in shear-aligned polyolefin−polyolefin diblock copolymers, but in PS−PI the alignment directions depend differently on temperature and frequency than in the polymers of Koppi et al. In our PS−PI, the alignment direction at each temperature and frequency is that which has the lower value of the complex modulus G^*; and the crossover from parallel to perpendicular alignment in our PS−PI sample occurs at a fixed value of the reduced frequency $a_T\omega$, where a_T is the shift factor used to superimpose the linear moduli. The linear viscoelastic properties of the two different aligned states and their shift factors suggest that the parallel orientation is favored at high frequency for PS−PI because of the large contrast in the viscoelastic properties between the styrene and isoprene blocks.

I. Introduction

It has been known since the work of Keller et al.[1] and Hadziioannou et al.[2,3] that large deformations can orient cylindrical and lamellar microdomains of locally ordered block copolymers. For lamellar domains, Hadziioannou et al. showed that *large-amplitude oscillatory shearing* orients lamellar microdomains parallel to the shearing surfaces, so that the normal to the lamellae is in the direction of the shearing gradient. More recently, Koppi et al.[4] showed for a polyolefin−polyolefin diblock copolymer, namely poly(ethylene−propylene)−poly(ethylene) or PEP−PEE, that a second lamellar orientation could also be achieved, in which the normal to the lamellae lies in the *vorticity direction*, that is, perpendicular to both the flow direction and the gradient direction. Following Koppi et al., we shall refer to this latter orientation as the "perpendicular orientation", and the former as the "parallel orientation". The direction chosen by the PEP−PEE lamellae depends on the frequency of the large-amplitude oscillation, as well as the temperature at which the oscillation is performed. For the PEP−PEE diblock copolymer, at low temperatures far below the order−disorder transition temperature T_{ODT}, the parallel orientation is chosen. At high temperatures just below T_{ODT}, the parallel orientation is chosen at low frequencies and the perpendicular orientation is chosen at high frequencies. Thus there is evidently more than one alignment mechanism for these materials.

Recently, we reported shear-alignment results for a low molecular weight polystyrene−polyisoprene diblock copolymer, PS−PI, in which the molecular weight of the polystyrene block is 12 500 and of the polyisoprene block is 9500. This material was synthesized by Yao et al.[5] and has an ordering transition to the lamellar state at 152 °C.[7] At a low temperature of 98 °C, both X-ray scattering and transmission electron microscopy show that nonlinear oscillatory shearing, with strain amplitudes as low as 5%, align the lamellae in the parallel orientation.[6] At higher temperatures, nearer T_{ODT}, strains as low as 5% are not effective in aligning the lamellae, but higher strains of 100%, at a frequency $\omega = 10\ \mathrm{s}^{-1}$, induce alignment in the perpendicular orientation.[7,8] These results are consistent with the pattern of alignment found by Koppi et al. but cover only a limited range of conditions. Here we shall determine the alignment direction induced by shearing over a wider range of conditions: temperatures ranging from 98 to 145 °C, and oscillation frequencies from 0.01 to 10 s^{-1}, all at a strain amplitude of 100%, which is the same amplitude used by Koppi et al.

II. Experimental Section

We determine the direction of alignment by quenching the aligned sample to room temperature and subjecting it to X-ray scattering; the X-ray setup is described elsewhere.[6] As reported below, we find that over this wide range of alignment conditions, the alignment directions of PS−PI lamellae follow a pattern different from that found by Koppi et al.[4] for their polyolefin−polyolefin diblock copolymer. Both before and after alignment by large-amplitude oscillatory shearing, the viscoelastic properties of PS−PI are probed using small-amplitude shearing, over a range of frequencies with a small strain amplitude of 10% for samples above T_{ODT} and 1% for samples below T_{ODT}. These small probe amplitudes are low enough to lie within, or almost within, the linear range and are too small to induce alignment for the samples below T_{ODT}. Both the

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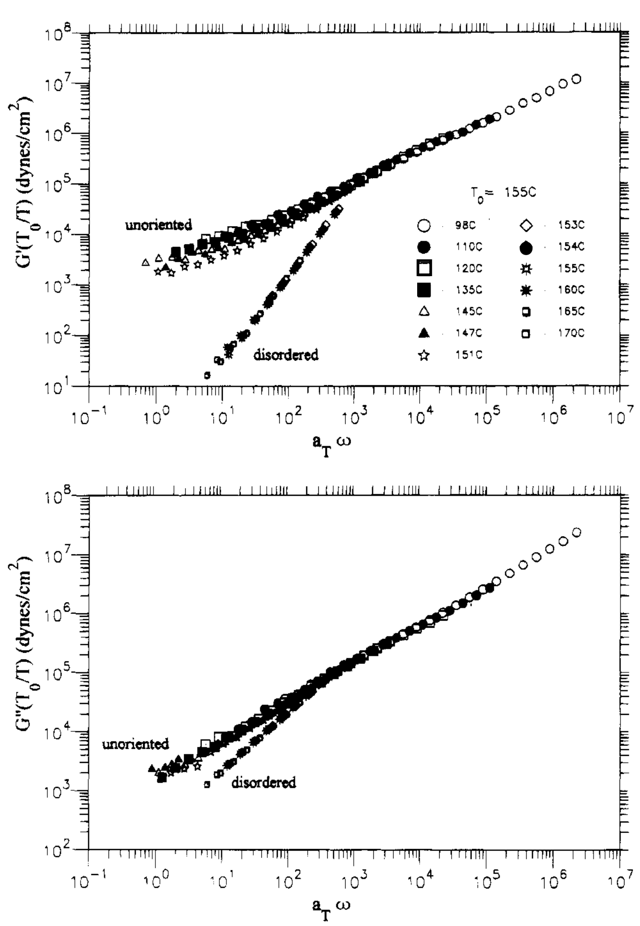

Figure 1. Master curves of G' and G'' versus reduced frequency at 10% strain for disordered PS–PI samples at temperatures above T_{ODT} = 152 °C and at 1% strain for ordered, but unaligned, samples at temperatures below T_{ODT}. All curves are shifted to the reference temperature of T_0 = 155 °C.

Oscillatory strain amplitude γ = 100% T_{ODT} = 152°C

	0.01 s^{-1}	0.1 s^{-1}	1.0 s^{-1}	10.0 s^{-1}
145°C	↑	↑	↑	↑
135°C		↑	↑	↑
120°C		↑	↑	⇨
110°C		↑	⇨	⇨
98°C		⇨	⇨	⇨

Figure 2. Orientation "map" showing the direction of orientation induced by large-amplitude shearing for each temperature and frequency of oscillation. The up arrows denote perpendicular alignment, while the horizontal arrows denote parallel alignment.

large-amplitude and the small-amplitude oscillations are carried out using a Rheometrics System 4 rheometer, using 25 mm diameter coaxial disks, with a gap between them of about 1.0 mm.

III. Results

Figure 1 shows G' and G'' at 10% strain on samples above T_{ODT} and at 1% strain on samples quenched to temperatures below T_{ODT}, without alignment by large-amplitude shearing. The data have been shifted along the frequency and modulus axes using conventional time–temperature shifting, so that the G'' data at high frequency superpose. The shift factors that produced superposition of the G'' data at high frequencies also superpose the available high-frequency G' data, although for the highest temperatures the frequencies at which the two branches of the G' curve merge are above the frequency range of the instrument ($\omega \leq 500$ s^{-1}). For the G'' data, the reduced frequency at which the two branches merge is somewhat lower than for G', and superposition of all data sets at high frequency is achieved. This method of time–temperature shifting, whereby superposition of the high-frequency data is achieved, is the same as that used by Koppi et al.[4] As was found by those authors and others,[9–13] above T_{ODT} both G' and G'' show classical terminal behavior at low frequency, wherein the scaling $G' \propto \omega^2$ and $G'' \propto \omega$ is obeyed. For our low molecular weight sample, above T_{ODT} the longest relaxation time is very short, and the terminal region encompasses almost the entire frequency range of the instrument. Below T_{ODT}, both terminal scaling and time–temperature superposition fail at frequencies less than a critical reduced frequency, ω_c, with $a_T\omega_c \approx 1000$ s^{-1} at the reference temperature of 155 °C, presumably because of the presence of the locally ordered domains. Thus at reduced frequencies below $a_T\omega_c$, there are contributions to the modulus from deformation of the microdomain pattern (i.e., of the interfaces between polystyrene and polyisoprene domains), while above $a_T\omega_c$, the modulus is dominated by molecular relaxations of the bulk polyisoprene and polystyrene material within each of the microdomains.

After the quenched samples were probed with small-amplitude oscillations, the samples were aligned by oscillations at 100% strain, usually for 1000 min or 16.7 h. There were two exceptions to this: The sample at 98 °C and ω = 10 s^{-1} was sheared for only 3 h, because of disruptions that were becoming evident at the sample's edge. And the sample sheared at ω = 0.01 s^{-1} was sheared for 1 week, so that, for all samples, a minimum of about 900 cycles of strain were imposed to achieve alignment. After alignment, the samples were probed by small amplitude oscillatory shearing, then quenched to room temperature, and subjected to X-ray scattering. With one exception, well-defined Bragg spots were obtained, indicating a high degree of either perpendicular or parallel orientation; typical scattering patterns are shown elsewhere.[6,7] In the exceptional case of ω = 0.01 s^{-1}, the Bragg spots were accompanied by a diffuse scattering ring, indicating rather weak alignment in this low-frequency case. The directions of lamellar alignment, determined by X-ray scattering, are compiled in Figure 2, for each frequency and temperature at which the sample was sheared at large amplitude. Notice that for PS–PI, the parallel alignment is induced at high frequency or low temperature, while perpendicular alignment is produced at low frequency or high temperature.

Next we studied the linear viscoelastic properties of the aligned PS–PI diblocks. A sample with parallel alignment was prepared by subjecting a quenched sample at 98 °C to large amplitude oscillatory shearing at a frequency of 1.0 s^{-1}, producing parallel alignment, as shown in Figure 2. Then the linear moduli at 1% strain were measured at 98 °C. Next, the frequency and temperature dependences of the viscoelastic moduli of this parallel-aligned sample were measured by subjecting it to small-amplitude shearing at a wide range of frequencies and temperatures, but always at a small strain of 1%, so that the direction of alignment would not be altered. When the temperature of an aligned sample in the rheometer was changed, care was taken

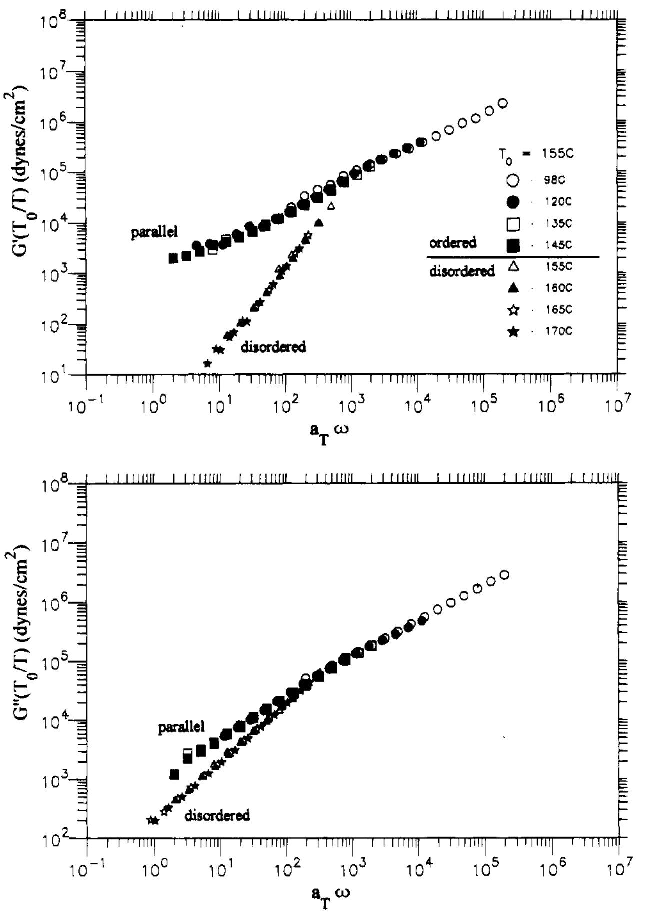

Figure 3. Master curves of G' and G'' versus reduced frequency at 1% strain for PS–PI for samples oriented in the parallel alignment condition and for disordered samples above T_{ODT}.

to adjust the gap of the sample to keep the normal stress close to zero as the sample expanded or contracted during heating or cooling. This was done to minimize buckling or other distortions to which a lamellar morphology is prone when it is compressed or dilated. After this set of tests, the linear moduli were remeasured at 98 °C and were found not to have been changed by the temperature history or by small-amplitude tests at the various temperatures. A similar suite of tests was carried out on a quenched sample aligned in the perpendicular orientation by large-amplitude oscillatory shearing at 145 °C and $\omega = 10\ \mathrm{s}^{-1}$.

Figures 3 and 4 show the storage and loss moduli G' and G'' for each of these samples as functions of ω and temperature, where these data have been shifted to achieve superposition of the high-frequency values of the storage and loss moduli. For reference, Figures 3 and 4 also contain the storage and loss moduli for the high-temperature disordered state. The shift factors required to produce superposition for the aligned and the unaligned samples are listed in Table 1 and plotted in Figure 5, along with the shift factors for bulk polystyrene and polyisoprene.[14] Note in Figures 3 and 4 that *the parallel and perpendicular samples have different moduli.* Figure 6 compares the complex modulus G^*, where $(G^*)^2 = (G')^2 + (G'')^2$, for parallel, perpendicular, and unoriented samples at temperatures of 98, 120, and 135 °C. At the lowest temperature, the sample with parallel alignment has the lowest complex modulus, while at the highest temperature, the one with perpendicular orientation has the lower modulus, except at frequencies above $10^2\ \mathrm{s}^{-1}$. At the intermediate temperature, 120 °C, the complex modulus of the perpendicular sample is lower than that of the parallel sample at low frequencies, while the reverse is true at high frequencies. Comparing these results with the frequency and temperature dependence of the alignment direction in Figure 2, we find that *the alignment direction is that which produces the lowest value of the complex modulus G^*.* It is surprising, and perhaps partially fortuitous, that there is such a good correlation between alignment direction and the magnitude of the linear complex modulus. Because the alignment occurs at high strain amplitude, where the stresses are strongly affected by nonlinearities, one would not necessarily expect such a strong correlation of the alignment direction with the small-amplitude linear modulus. We note that the magnitudes of the storage and loss moduli, like the complex modulus, also correlate with the alignment direction, although the correlation is less perfect for the storage modulus (which is the smaller of the two).

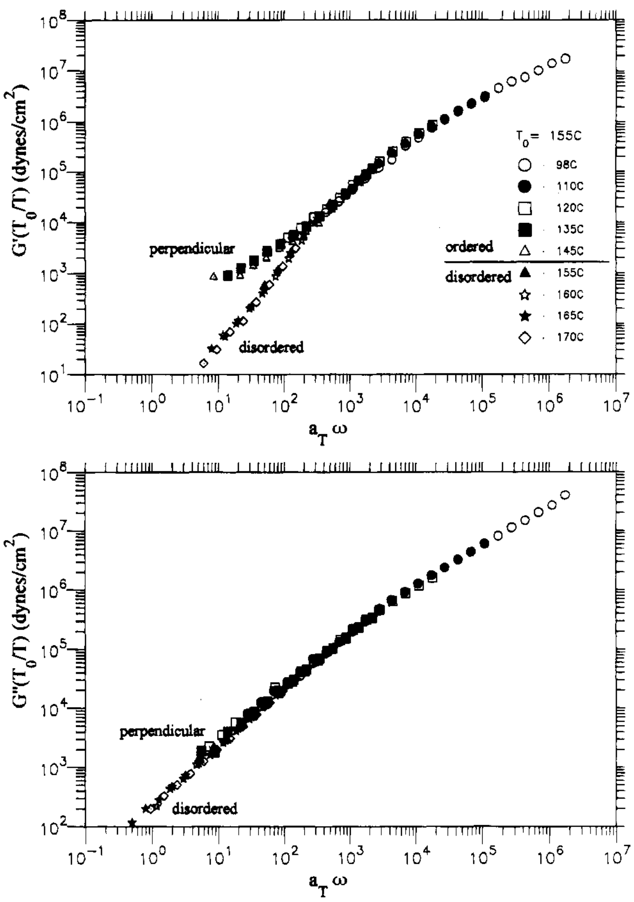

Figure 4. Master curves of G' and G'' versus reduced frequency at 1% strain for PS–PI for samples oriented in the perpendicular alignment condition and for disordered samples above T_{ODT}.

Table 1. Shift Factors a_T for PS–PI for Various Orientations

temp (°C)	disordered	unaligned	perpendicular	parallel
170	0.31			
165	0.42			
160	0.63			
155	1.00			
145		2.2	1.7	1.6
135		6.3	4.4	4.0
120		45	36	23
110		225	220	unavail
98		4500	3500	400

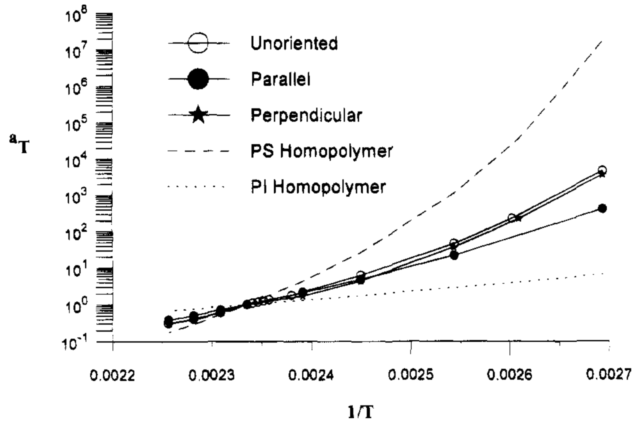

Figure 5. Shift factor a_T versus inverse temperature $1/T$ for PS−PI in the parallel, perpendicular, and unaligned orientations, compared to the shift factors for homopolymer polystyrene and polyisoprene.

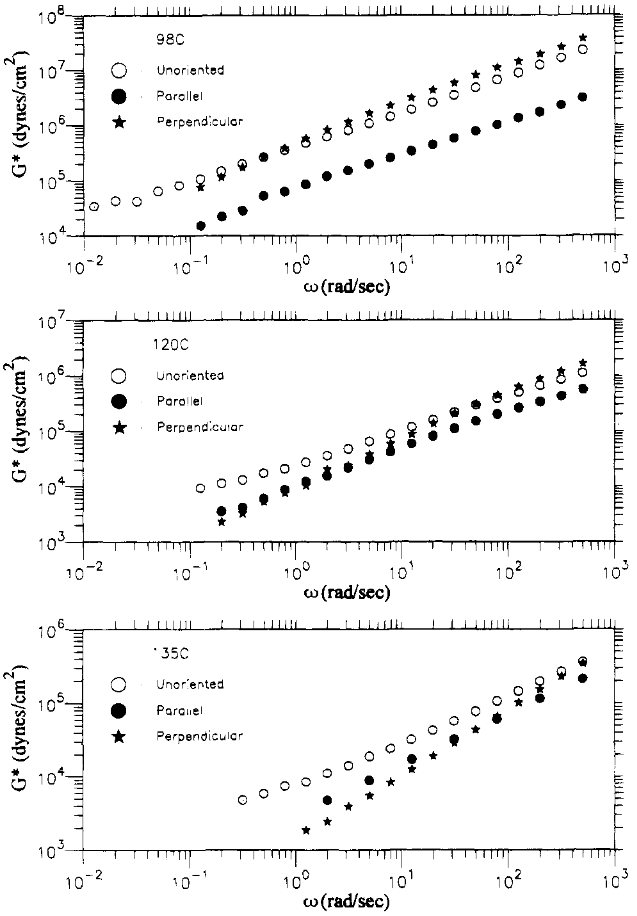

Figure 6. G^* versus frequency at three different temperatures for PS−PI in the parallel, perpendicular, and unaligned orientations.

Our results are summarized in Figure 7, which shows the master curves of G^* for three states: disordered isotropic, parallel aligned, and perpendicular aligned. Each curve has been time−temperature shifted using the shift factors *appropriate to that state.* Also shown on Figure 7 are the alignment directions produced by large-amplitude oscillatory shearing at the various temperatures and frequencies tabulated in Figure 2, where the alignment frequencies have been shifted using the shift factors of the unaligned state. The shift factors of the unaligned state are used to shift the aligning frequencies because the sample is in the unaligned state when it initially begins to align. The qualitative appearance of Figure 7, and the conclusions we draw from it, are not especially sensitive to this choice of shift factors.

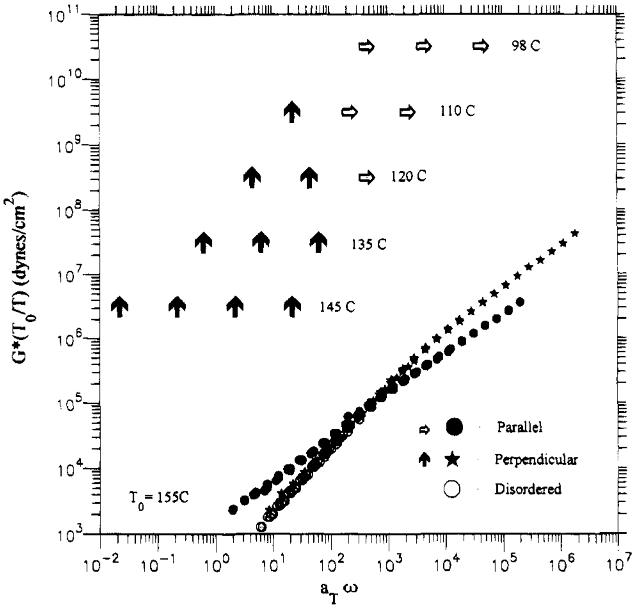

Figure 7. Master curves of G^* versus reduced frequency at 1% strain for PS−PI for samples in the parallel, perpendicular, and unaligned orientations. The shift factors for each curve are thos plotted in Figure 5 and tabulated in Table 1. Included on the plot are arrows to denote the alignment conditions achieved using large-amplitude oscillatory shearing at each temperature and frequency; the location of each arrow on the frequency axis is the alignment frequency shifted using the shift factor of the unaligned state.

Note, in Figure 7, that the transition from perpendicular to parallel alignment occurs at roughly the same reduced frequency, $a_T\omega_{\perp-\parallel} \approx 10^2$ s^{-1}, for all temperatures. Thus *the transition frequency at which perpendicular gives way to parallel alignment seems to follow the same time−temperature shift factor as that governing the moduli.* Note also that $a_T\omega_{\perp-\parallel}$ is equal to $a_T\omega_c$, the reduced frequency at which the high-temperature disorder branch of the complex modulus joins the low-temperature ordered branch, and that this reduced frequency is, in turn, equal to the reduced frequency at which the moduli for samples with parallel and perpendicular orientation intersect.

Finally, a couple of experiments were done to see if the alignment direction could be reversed without reheating the sample into the disordered state. A sample quenched to 120 °C was aligned in the perpendicular orientation for 16 h by large-amplitude straining at a frequency of 0.1 s^{-1}. It was then subjected to shearing at this same temperature, but at a frequency of 10 s^{-1} for 16 h. This frequency, which is high enough that an initially unaligned sample would align in the parallel direction (see Figure 2), flipped the alignment from perpendicular to parallel. However, this same sample, now in the parallel orientation, could not be driven back to the perpendicular orientation, even by 16 h of shearing at the low frequency $\omega = 0.1$ s^{-1}. These limited experiments there indicate for PS−PI *the parallel orientation might be the more stable of the two.* The opposite was found by Koppi et al. for PEP−PEE block copolymers; a sample in the parallel orientation could be driven to a perpendicular orientation by increasing alignment frequency, but at decreased frequency, the reverse transition back to parallel alignment did not occur.

IV. Discussion

We find, for a PS−PI block copolymer, the same two alignment directions as were reported by Koppi et al.[4] for their PEP−PEE sample. As in their study, we find that lower temperature tends to favor the parallel alignment. However, in other respects our results differ from those for PEP−PEE. In our experiments, perpendicular alignment is found at low frequencies, while in the experiments of Koppi et al., perpendicular alignment is only found at their highest frequencies.

An important difference between our material and theirs, that might account for this difference, is that our PS−PI diblock is composed of blocks with dissimilar mechanical properties. Our experimental temperature range is not far from the glass transition of the polystyrene block, which we measure to be around 78 °C for our polystyrene block.[6] The polyisoprene block, on the other hand, has a glass transition of around −70 °C, much below the experimental temperature range. As a result, the shear modulus of the polystyrene material at the temperatures and frequencies studied here, is expected to be much higher than that of the polyisoprene. Hence, in a microseparated sample, at frequencies high enough to probe molecular relaxation—that is at reduced frequencies above $a_T\omega_c$—the polystyrene domains offer a much greater resistance to deformation than do the polyisoprene domains.

When a microseparated sample with a large difference in modulus from one domain to the next is subjected to a shearing deformation, the shearing strain will not necessarily be uniformly distributed throughout the sample. In samples with lamellae in the parallel orientation, the strain is expected to concentrate in the softer polyisoprene layers; in the limit of perfectly stiff, perfectly aligned polystyrene blocks, only the polyisoprene layers would deform. However, in a sample with perfect perpendicular alignment, lamellae of polystyrene bridge the gap between the shearing surfaces, and the polystyrene cannot escape bearing its share of the deformation. Hence, at frequencies high enough that the stress is dominated by the bulk properties of the polystyrene and polyisoprene, the parallel orientation should be favored, because in it the polystyrene layers could avoid bearing their full share of the strain, and the overall stress would be lower. For the PEP−PEE material of Koppi et al., both blocks are polyolefins which are expected to have similar mechanical properties, especially at the temperature of the alignment, which is far above the glass transition temperatures of either polyolefin block. Thus, parallel alignment at high frequencies would not necessarily be expected for PEP−PEE.

The idea that a *mechanical contrast* between domains influences the alignment direction is consistent with our observations that for PS−PI, the high-frequency moduli of the parallel and perpendicular samples are not the same and do not have the same shift factors. For the PEP−PEE samples, with much less mechanical contrast, the moduli for parallel and perpendicular orientations at high frequencies, above ω_c, are equal and have the same shift factors.[4,11,15] This is consistent with our explanation that there is a large viscoelastic contrast between blocks in the PS−PI system, and very little in the PEP−PEE system. For PS−PI, the samples with parallel alignment have a lower high-frequency modulus and lower shift factor than those with perpendicular alignment. At each temperature the shift factor of the parallel samples is closer to that of pure polyisoprene than is the shift factor of the perpendicular samples; see Figure 5. The lower high-frequency modulus G^* and lower shift factor of the samples with parallel orientation can be explained if in the parallel orientation the more rigid polystyrene block bears a smaller share of the deformation than it does in the perpendicular orientation. If our explanation for the occurrence of parallel alignment at high frequencies in PS−PI is correct, one would expect that the reduced crossover frequency, $a_T\omega_{\perp-\parallel}$, should be roughly equal to $a_T\omega_c$, the frequency above which the moduli of the material in the blocks dominates the stress. As shown in Figure 7, $a_T\omega_{\perp-\parallel}$ is almost equal to $a_T\omega_c$.

Of course, close to the ODT, the viscoelastic contrast diminishes because of thermodynamically driven mixing of the blocks. But for the low molecular weight PS−PI, the transition between the disordered and the lamellar state seems to be a rather strong one, as judged by the jump in modulus G' at the transition and the lack of anomalous "fluctuation" contributions; see Figure 1. Thus, even just below the ODT, the microphase separation in PS−PI might be strong enough to give a large mechanical contrast between the blocks. For PEP−PEE, on the other hand, not only are the two blocks more similar rheologically, but also they are of higher molecular weight, and hence the degree of microseparation just below the ODT is likely to be smaller than in PS−PI;[16] therefore, whatever viscoelastic contrast exists in this system is significantly attenuated near T_{ODT}.

While these observations support the idea that the parallel orientation is favored at high frequency in the PS−PI diblock but not in the polyolefin−polyolefin diblocks because of the dissimilarity of the moduli of the two blocks in the former, Koppi et al. have suggested that the perpendicular alignment might be favored because it is the only alignment direction in which the interfaces between the blocks have no tendency to rotate in a shearing flow. At high temperatures near T_{ODT}, wavelike fluctuations in the lamellar pattern are expected, which produce portions of the interface that are imperfectly aligned; in the parallel alignment condition, misaligned portions of interface will be rotated by the shearing flow, thereby increasing the misalignment and producing stress. Another related possibility is suggested by recent computer simulations[17] showing that near T_{ODT} thermal fluctuations produce "bridges" of material "A" that connect two neighboring layers of "A" across a layer of "B". In the parallel orientation, such bridges would prevent lamellae from sliding easily past each other and could lead to large stresses during large-amplitude oscillatory shear. Such stresses, produced by the coupling "wavelike" or "bridge" fluctuations to the shearing flow, might disfavor the parallel orientation. Such a mechanism might be operative in both the PS−PI and PEP−PEE systems.

However, in the experiments of Koppi et al. with PEP−PEE, at high temperatures near T_{ODT}, a transition is observed from perpendicular to parallel alignment as the frequency is decreased. This transition occurs when the reduced frequency ω/ω_x drops below about $(1-5) \times 10^{-2}$, where ω_x is the frequency at which the G' and G'' curves cross. Such a transition from perpendicular to parallel alignment as the shear rate decreases was recently predicted by Fredrickson.[18] We observed no such transition in our diblock PS–PI, even though the lowest reduced frequency ω/ω_x probed in our study is around 10^{-5}, three decades lower than the reduced frequency at which Koppi et al. observed the transition. In the PS–PI, $a_T\omega_x \approx 10^3$ can be estimated by a short extrapolation of the G' and G'' data above T_{ODT}. Thus, it would appear that the transition is completely absent in our sample of PS–PI.

We note, however, that during final editing of this manuscript, our attention was called to a recent independent submission to *Macromolecules* by Zhang et al.,[19] showing not only high-frequency parallel alignment and intermediate-frequency perpendicular alignment, as reported here, but also a regime of low-frequency parallel alignment. Although the frequency ω_x was not accessed in the work of Zhang et al., by extrapolation it would appear that the regime of low-frequency parallel alignment occurs at $\omega/\omega_x \approx 10^{-5}-10^{-3}$, which is a regime covered by our experiments. The source of the discrepancy between these findings and ours is unknown, but it might be related to the differences in the values of T_{ODT}, namely 131 °C in the work of Zhang et al. and 152 °C in ours.

In any event, comparing our findings (and those of Zhang et al.) on PS–PI with the work of Koppi et al. on PEP–PEE, one must conclude that the alignment processes occurring in lamellar block copolymers are not the same in all block copolymers. Some of these differences can be explained by variations in viscoelastic contrast, and other differences will probably only be explained after further results are available for other diblock lamellar polymers, one with differing ratios of moduli of the two blocks, and differing degrees of influence of compositional fluctuations. Finally, we note that a study by Gupta et al.[20] of the kinetics of parallel and perpendicular alignment in PS–PI has recently been submitted to *Macromolecules*.

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