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Rheology and Shear-Induced Alignment of Lamellar Diblock and Triblock Copolymers

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ABSTRACT: The linear viscoelastic behavior of diblock and triblock copolymers of styrene and isoprene was studied in the lamellar phase both before and after alignment by large-amplitude oscillatory shear. The orientation of the lamellae, as determined by X-ray scattering, is controlled by the temperature and frequency of alignment. For triblocks, a high degree of alignment with the lamellar normal perpendicular to both the flow and shear gradient directions (perpendicular alignment) can be achieved, so that nearly terminal rheological behavior is observed at low frequencies. The diblock never aligns to this extent. Unlike the diblock, we were unable to align the triblock with the lamellae parallel to the shearing surfaces, presumably because triblocks can form bridges across lamellar domains and so hinder the sliding of lamellae past each other. The diblock lamellae have no bridges and can achieve parallel orientation at low temperatures and high alignment frequencies. This contrasts with the poly(ethylene–propylene)–poly(ethylethylene) (PEP–PEE) system, in which parallel alignment is only seen at low frequencies and low temperatures.[1]

Introduction

Block copolymers have received considerable experimental and theoretical interest in recent years.[3] Researchers have looked at the phase behavior[4–9] and rheological properties[1,2,10–30] of block copolymers as well as their mixtures with homopolymer blends.[31–34] The interesting properties of many of these materials have led to their widespread use as compatibilizers, surfactants, adhesives, and thermoplastic elastomers.[35]

Recently, there have been many studies of the relationship between the rheology and structure of diblock copolymers in the lamellar phase.[1,2,10,11,15–18,20,21,26,28–30] Some studies have shown that strains as small as 1% are outside the range of linear viscoelasticity for microphase-separated diblock copolymer lamellae and that strains of around 5% or greater may be used to align the lamellae. This alignment procedure lowers G'' and especially G' as determined by linear viscoelastic measurements before and after the alignment.

In the styrene–isoprene (SI) diblock system, Patel and co-workers[18] find that at low shearing frequencies and high temperatures, the lamellae tend to line up with the normal to the S–I interface perpendicular to both the flow and velocity gradient directions (perpendicular alignment). At higher frequencies and lower temperatures near the glass transition for the styrene block, the lamellae are parallel to the shearing plates (parallel alignment). A similar result has been reported by Gupta and co-workers.[26] Zhang and co-workers[30] report similar results, although they also find parallel alignment at high temperatures and low alignment frequency.

In contrast, Koppi and co-workers[1] find perpendicular alignment only at high frequencies and high temperatures and parallel alignment at other conditions for poly(ethylene–propylene)–poly(ethylethylene) (PEP–PEE) diblock copolymers.

One possible explanation for the difference in the results of the two groups may be the drastically different temperature dependences of the rheological properties of the blocks in the two studies. For SI, the polystyrene block is not far above its glass transition, so at a given frequency it has a higher modulus and its viscoelastic properties change much more rapidly with temperature than those of the polyisoprene block. At high frequencies and low temperatures, the length scales probed are the size of the lamellar spacing and smaller. Under these conditions, the overall stress in a shearing deformation should be lower if the lamellae orient in such a way that more of the strain can be taken up by the "soft" polyisoprene block than by the "hard" polystyrene block. The parallel orientation is the one that most readily permits the strain to be localized in this way. Thus, the large amplitude of the shear may allow the lamellae to adjust their orientation such that they arrive at their lowest stress state, which at high frequencies and low temperatures is parallel alignment. The PEP and PEE blocks of the PEP–PEE block copolymers, although differing significantly in entanglement molecular weights, are both far above their respective glass transitions, so their rheological properties are similar and have similar temperature dependences. The two blocks may therefore lack sufficient rheological contrast to realign in the parallel orientation at the temperatures studied for this system.

Although diblock lamellar rheology has received considerable attention, much less attention has been given to the rheological behavior of triblock copolymers in the lamellar phase.[14] Previous rheological studies of triblock copolymers have mainly focused on cylindrical domains.[22–25] We expect different mechanisms for alignment of triblock lamellae, since the central block is constrained at both ends. At equilibrium, two possible gross conformations of the central isoprene block are possible in the lamellar phase.[36] The block may bridge two styrene layers, or may form a loop, so that

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Table 1. Properties of the Block Copolymers

type	wt % styrene	T_{ODT} (°C)	M_n	M_w/M_n	sequence PS	sequence PI	sequence PS
SI	50.9	130 ± 1	19 900	1.025	10 100	9 700	
SIS	51.6	152 ± 1	39 300	1.020	10 100	19 000	10 100

both styrene blocks enter the same layer. Because of the presence of bridges, we expect that the mechanism of orientational selection under shear for triblocks will differ significantly from that of diblocks. Modifications in entanglements caused by the isoprene loops may also prove to be important in distinguishing triblock and diblock orientational dynamics. In the present paper, we attempt to shed light on these issues by reporting on a rheological and X-ray scattering investigation of model diblock and triblock copolymers of styrene and isoprene.

Experimental Section

Materials. Diblock and triblock copolymers of styrene and isoprene were obtained from Dexco. Properties of the polymers are given in Table 1. These polymers contain 1000 ppm of Irganox 565 as an antioxidant. To mold a sample disk, approximately 1.1 g of the polymer was cut into pieces and placed in a mold 29 mm in diameter and 1.5 mm thick. A plate containing the sample was inserted between sheets of a fluorinated polymer followed by metal plates 1.5 mm thick. The plates and polymer were placed in a hot press maintained at 120 °C. The metal plates were maintained in contact with the heated platens of the hot press. No extra pressure was applied for 5 min. Normal pressure was then applied and the polymer was allowed to flow to fill the mold for the next 15 min. The plates were then removed from the hot press and cooled with compressed air. When the plates cooled to roughly 50 °C, the sample disk was removed from the molds with a razor blade. This procedure was usually adequate for making bubble-free samples of SI diblocks. For triblocks, however, bubbles were more difficult to remove. If the first try failed to produce bubble-free samples, more polymer was added and the heating and pressing procedure repeated until samples with few bubbles resulted.

Rheology. Each molded sample was placed between 25 mm diameter parallel plates that were brought together in the heated oven of a Rheometrics mechanical spectrometer (RMS-800) until the sample thickness was reduced to about 1.35 mm. The oven was then opened and the excess polymer removed with a razor blade. The sample was then heated above the order–disorder transition (ODT) (to 140 °C for diblocks and 160 °C for triblocks) and allowed to remain at that temperature for 10–30 min. During this time, enough normal force was maintained on the plates for the polymer to conform to the plate diameter. Then various rheological studies were performed as described below.

Ordered, but unoriented, lamellar samples were obtained by cooling a sample from above the order–disorder transition temperature (T_{ODT}) to the desired temperature below the ODT, where it was equilibrated for about 30 min. The plate separation during the cooling was adjusted to minimize the magnitude of the normal force on the sample, since large normal forces may induce some flow leading to unknown alignment conditions.

Dynamic strain sweeps were performed on unoriented lamellar samples at frequencies of 1, 10, and 100 rad/s to determine the linear viscoelastic regime for the sample at the desired temperature. Strain sweeps were performed for all three frequencies after ordered samples were prepared as described above. The strain sweeps show that the linear viscoelastic region extends to between 1 and 2% for SI and to between 2 and 4% for SIS.

Dynamic frequency sweeps from 100 rad/s down to 0.1 rad/s were performed on unaligned samples with either a 1% (SI) or 2% (SIS) strain. The dynamic data were very reproducible from one sample to the next, which shows that little alignment is induced during quenches from above to below the ODT or that the induced alignment is always the same.

We have applied time–temperature superposition to our dynamic frequency sweep data, even though its use is not strictly correct for our system. There are different friction factors for the two types of polymers, each of which has a different temperature dependence. Also, the composition of the two microphase-separated blocks changes with temperature, the microphases being more highly segregated the further T is below T_{ODT}. However, many authors have shown that time–temperature superposition can be achieved over a limited range of temperatures for certain lamellar block copolymer systems.[2,7,10,11,18,20] Time-temperature superposition seems to be achievable in our system as well, and so we have decided to use it in what follows.

Two methods were used to determine T_{ODT}. The first method was to perform dynamic temperature sweeps with temperatures decreasing or increasing at a rate of 0.1 °C/min. Strain amplitudes of either 1 or 5% at a frequency of 10 rad/s were applied to the sample during cooling or heating. According to well-documented procedures[2,20] the order–disorder transition (ODT) can be identified by a sharp drop in the elastic modulus (G') on heating or a sharp rise in G' on cooling.

A second method for determining T_{ODT} is to plot G' versus G'' as done for SI in Figure 6 and as discussed by Han and co-workers.[12,13] For a given polymer microstructure, data at different temperatures should fit on a single curve. The presence of two curves indicates an ODT in the case of block copolymers, and the temperature where data shift from one curve to the other is T_{ODT}. Data sets that lie between the two curves are assumed to be in a temperature region where "fluctuation effects" are present. The temperature range in which fluctuation effects are significant thus encompasses temperatures where data fall between the two main curves.

Alignment of each sample was achieved by a large-amplitude oscillatory shear at some desired frequency and strain amplitude for a given time, as specified in the Results section. Alignment was followed by a small-amplitude dynamic frequency sweep. In many cases, this was the final rheological experiment before the sample was removed from the plates as described below. In some experiments, however, the sample was aligned further or the temperature was changed, as described in the Results section.

Detailed linear viscoelastic measurements were carried out at various temperatures on an SI sample aligned in the perpendicular orientation. Perpendicular alignment was produced at 120 °C at a frequency of 1 rad/s with 100% strain for 5 h. After the alignment, frequency sweeps were performed with 1% strain at various temperatures. We were unable to obtain good parallel alignment (X-ray patterns showed only a small bias toward parallel alignment) using the conditions of Patel and co-workers, so we did not look closely at the linear viscoelastic response for this orientation.[15,18]

Only perpendicular alignment was observed in the SIS sample. Detailed studies were performed on a sample in this orientation, prepared by aligning it at 140 °C at a frequency of 1 rad/s with 100% strain amplitude for 10 h. After the alignment step, frequency sweeps were carried out with 2% strain at various temperatures.

After all rheological tests were performed, the sample was cooled over a 5–10 min period to 50 °C while remaining between the parallel plates. Care was taken during the cooling to minimize normal forces on the sample by adjustment of the rheometer gap. The sample was then removed and stored for X-ray scattering.

X-ray Scattering. Philips and Enraf X-ray generators using Cu Kα (1.54 Å) were used to study the orientation of lamellae in the block copolymers. Samples were taped to a holder where the X-rays enter an evacuated chamber through a 1 mm diameter pinhole. The X-ray beam (30 mA and 30 kV for the Philips and 40 mA and 45 kV for the Enraf) was passed through the sample for 1 h (or 30 min for the Enraf) onto X-ray film located 30 cm away from the sample.

Three orientations were studied. We designate x as the flow direction, y as the velocity gradient direction, and z as the vorticity direction, as shown in Figure 1. When studying

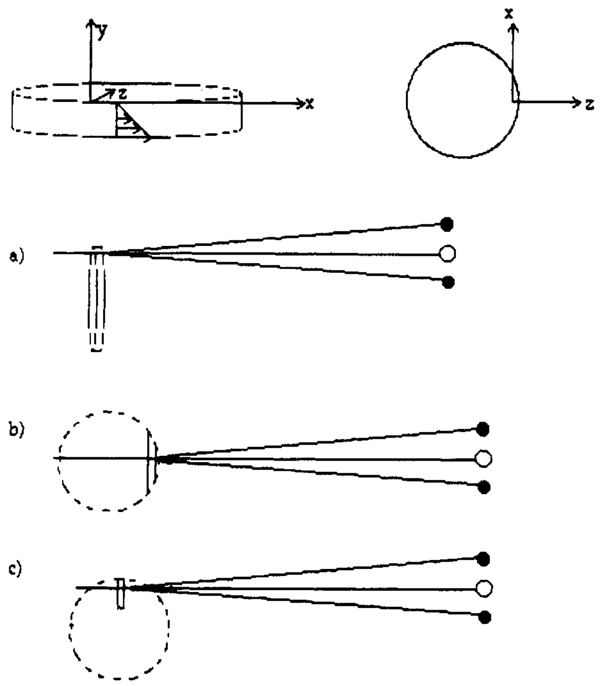

Figure 1. Orientations of SI and SIS samples observed using X-ray scattering. (a) Perpendicular alignment may be observed when the sample is oriented with respect to the X-ray beam as shown in (a) or (c); parallel alignment may be observed in orientations (b) or (c).

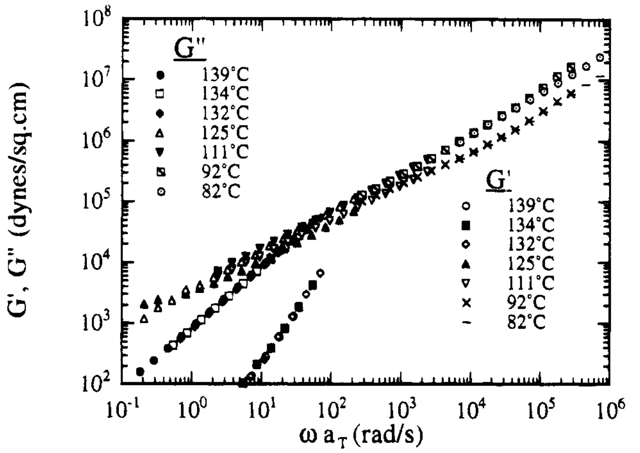

Figure 2. Dynamic moduli of unaligned SI shifted to a reference temperature of $T = T_{\mathrm{ODT}} = 130$ °C.

orientation normal to the y direction, we passed the X-ray beam through the uncut sample disk about 1 mm radially inward from the edge as shown in Figure 1a. Diffraction peaks with the sample oriented this way indicate perpendicular alignment of the lamellae. To study orientation normal to the z direction, a 1 mm slice was made near the edge of the disk and X-rays were passed through the slice as shown in Figure 1b. Diffraction peaks with the sample oriented this way indicate parallel alignment of the lamellae. A strip 1 mm thick in the flow direction was cut in order to study the x direction. Figure 1c shows how X-rays pass through the sample in this case. Diffraction peaks indicate either parallel or perpendicular alignment, depending on their orientation.

Results and Discussion

Linear Viscoelastic Measurements before Alignment. Figure 2 is a master curve of rheological data for unaligned SI shifted to a reference temperature of 130 °C. The data below the ODT are shifted horizontally to superpose the high-frequency data. For frequency sweeps at temperatures greater than 130 °C, the frequencies at which the data might be expected to superpose are above the experimental limit of 100 rad/s; hence for these temperatures, shifting is based on WLF parameters determined for SI below the ODT. The WLF parameters for unaligned SI are given in Table 2.

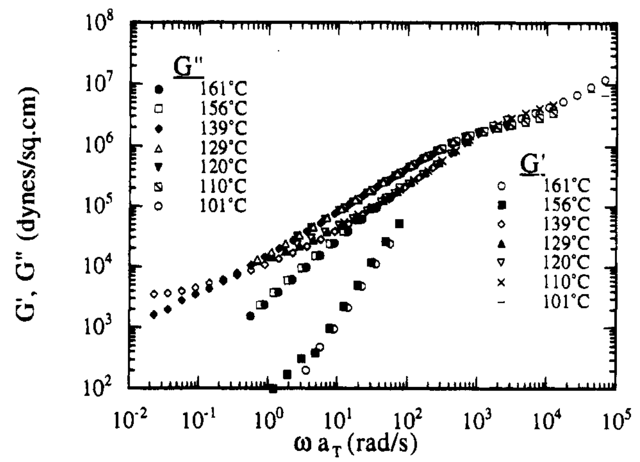

Figure 3. Dynamic moduli of unaligned SIS shifted to a reference temperature of $T = T_{\mathrm{ODT}} = 152$ °C.

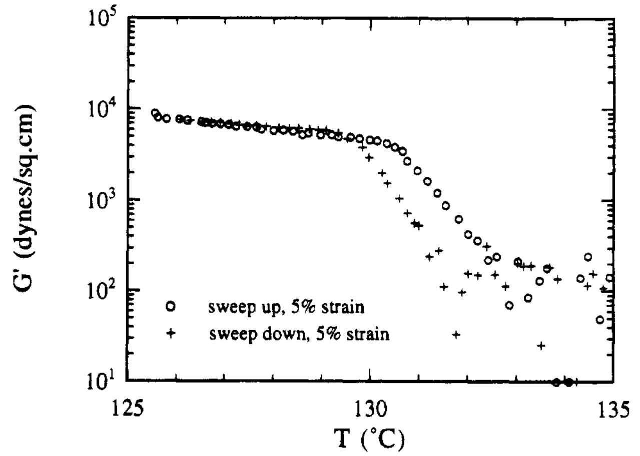

Figure 4. Elastic modulus G' of SI as a function of temperature during increasing and decreasing temperature sweeps with ramp rates of 0.1 °C/min., a frequency of 10 rad/s, and a 5% strain amplitude.

Table 2. WLF Parameters for SI and SIS

$$\log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + T - T_0} + c_3$$

sample	c_1^0	c_2^0	T_0 (°C)	c_3
unaligned SI	9.79	93.2	101	2.305
unaligned SIS	6.36	63.4	101	2.829
perpendicular SI	4.44	64.8	120	0.594
perpendicular SIS	4.54	111.0	140	0.443

Figure 3 is a master curve of rheological data for unaligned SIS shifted to a reference temperature of 152 °C. Data for temperatures above the ODT are shifted using the WLF parameters for unaligned SIS given in Table 2.

Determination of T_{ODT}. Figure 4 shows the elastic modulus for SI for increasing and decreasing temperature sweeps for a ramp rate of 0.1 °C/min, a frequency of 10 rad/s, and a 5% strain amplitude. The location of the ODT is independent of strain amplitude within experimental error for strains of 1 and 5%. From these results, we find that T_{ODT} for this SI diblock copolymer is between 129 and 132 °C. Figure 5 shows G' for SIS

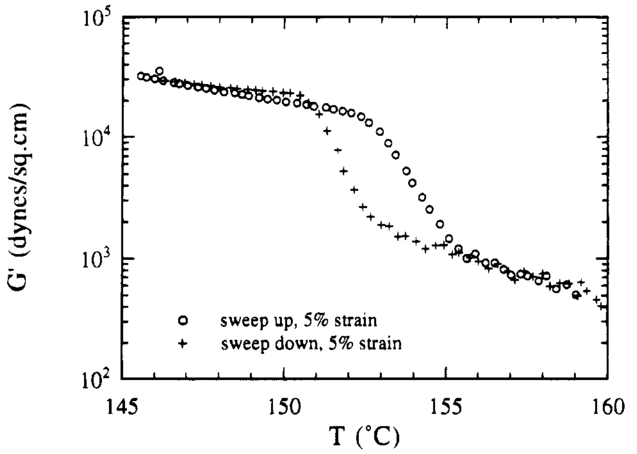

Figure 5. The elastic modulus G' of SIS as a function of temperature during increasing and decreasing temperature sweeps with ramp rates of 0.1 °C/min., a frequency of 10 rad/s, and a 5% strain amplitude.

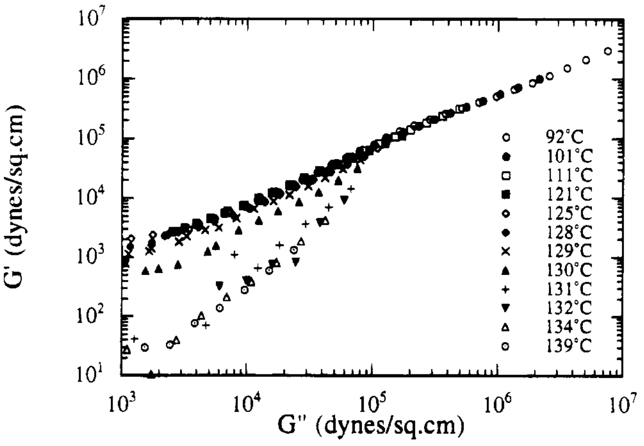

Figure 6. G' versus G'' for unaligned SI.

for increasing and decreasing temperature sweeps for ramp rates of 0.1 °C/min, a frequency of 10 rad/s, and a 5% strain amplitude. From these results, we find that T_{ODT} for this SIS triblock copolymer is between 151 and 153 °C. Note the hysteresis of about 2 °C for heating and cooling for both SI and SIS. The disordering process is much faster than the ordering process, so supercooling is likely at this temperature ramp rate. Superheating is less likely, so the heating curves give a better estimate of the thermodynamic T_{ODT}.

We plot G' versus G'' for SI in Figure 6. This plot shows two distinct low-frequency branches; from the jump from one branch to the other, we infer that T_{ODT} is between 128 and 132 °C, in agreement with our result for T_{ODT} using the temperature sweep method. The range of temperatures over which a $G'-G''$ curve lies between the two distinct branches is a measure of the temperature range over which compositional fluctuation effects are rheologically significant. With this criterion, we find that the range of fluctuation effects for SI is less than 4 °C, which is similar to the range of less than 3 °C found by Gehlsen and Bates for a symmetric diblock of polystyrene and polyisoprene with a molecular weight of 18 000.[10] We plot G' versus G'' for SIS in Figure 7 and find that T_{ODT} is between 150 and 153 °C, in agreement with our temperature sweep method. The range of fluctuation effects for SIS is less than 3 °C.

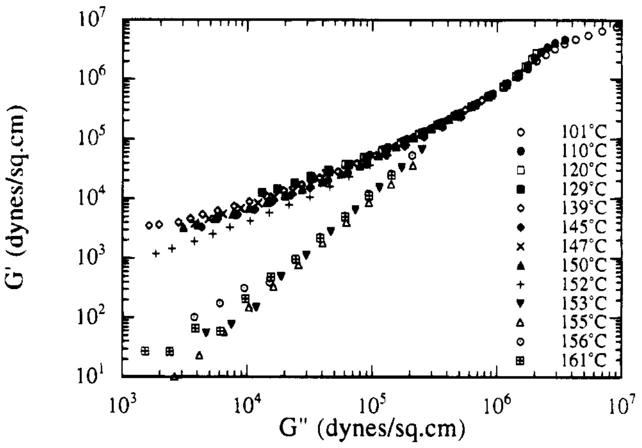

Figure 7. G' versus G'' for unaligned SIS.

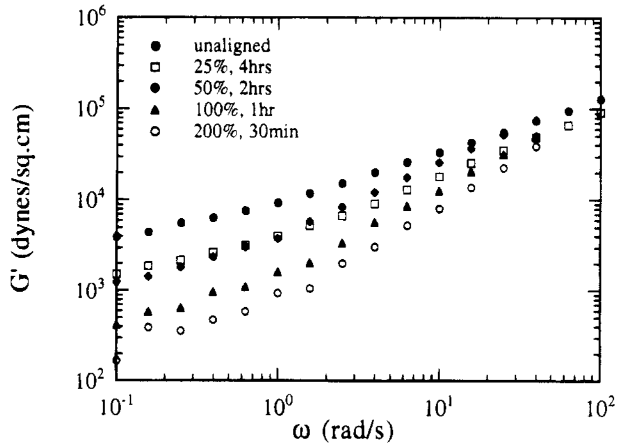

Figure 8. Elastic moduli of SI showing the effect of strain amplitude on alignment at 120 °C, a frequency of 1 rad/s, and 3600 total strain units.

Table 3. SI Alignment

	0.1 rad/s	1 rad/s	10 rad/s
123 °C	⊥	⊥	⊥
113 °C	⊥	⊥	∥ > ⊥[a]
103 °C			∥
93 °C		∥	∥

[a] The sample shows evidence of both parallel and perpendicular alignment, with parellel alignment being the more pronounced.

Shear Alignment of SI. Table 3 summarizes the type of alignment (parallel or perpendicular) obtained by aligning SI samples at frequencies of 0.1, 1, and 10 rad/s at 123, 113, 103, and 93 °C. The strain amplitude was 50%. As in the study of Patel et al.,[18] we observe that parallel orientation occurs at high frequency and low temperature and perpendicular alignment occurs at low frequency and high temperature.

In order to obtain samples with the best possible perpendicular alignment, we investigate rheologically the effects of strain amplitude, frequency, and time on alignment. We have chosen to concentrate on G' in the studies below. Similar trends occur with G'', but they are less pronounced.

Figure 8 shows G' for unaligned SI and for SI aligned at various strain amplitudes at a frequency ω of 1 rad/s for 3600 total strain units at 120 °C. The time t during which the aligning flow is imposed is varied with the strain amplitude γ_0 so that the total strain $\gamma_0\omega t$ is held constant at 3600. These results show more effective alignment for increasing strain amplitude at fixed total strain units.

For our studies of the effects of frequency and alignment time on alignment, we choose a strain amplitude of 100%. This is because larger strains at high frequen-

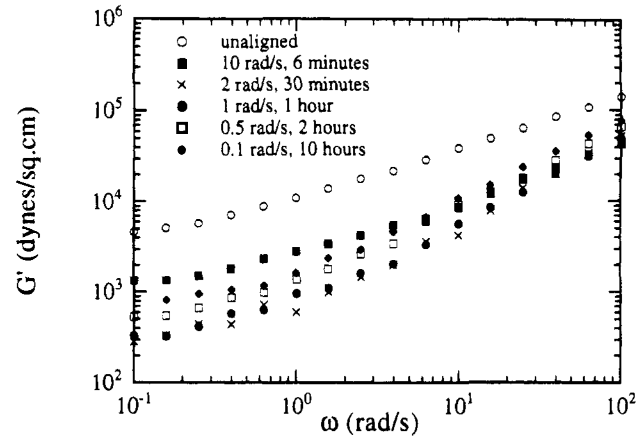

Figure 9. Elastic moduli of SI showing the effect of frequency on alignment at 120 °C, 100% strain amplitude, and 3600 total strain units.

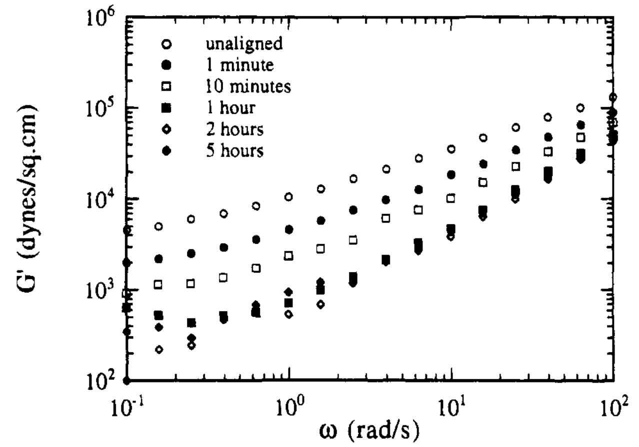

Figure 10. Elastic moduli of SI showing the effect of shearing time on alignment at 120 °C, 100% strain amplitude, and a frequency of 1 rad/s.

cies may lead to the polymer flowing out from between the plates. Figure 9 shows G' for unaligned SI and for SI aligned at various frequencies for a strain amplitude of 100% for 3600 total strain units at 120 °C. We find that the best alignment (lowest elastic modulus under these conditions) occurs for frequencies of 1 and 2 rad/s. Another important feature of Figure 9 is the lower slope of G' for the alignment at 10 rad/s. This is due to parallel alignment at these conditions; the other alignment conditions in Figure 9 produce perpendicular alignment. Changing the strain amplitude from 50 to 100% at $\omega = 10$ rad/s changes the alignment direction from perpendicular to parallel. A similar change in alignment direction with increased strain amplitude was recently reported by Gupta et al.[26]

Figure 10 shows G' for the SI sample aligned at 120 °C with $\omega = 1$ rad/s and 100% strain amplitude for various alignment times. We see that improvement in alignment for these conditions, as determined by the linear viscoelastic G', ceases after about 1 h. Even though no further rheological changes occur, terminal behavior is not obtained at these conditions, suggesting a residual population of textural defects. Using simultaneous measurements of the dynamic modulus and birefingence, Gupta et al.[26] have shown that continued improvement in alignment occurs during large-amplitude oscillatory shearing, even after changes in the moduli have ceased. Thus a cessation of change in the moduli may leave the sample's alignment far from complete.

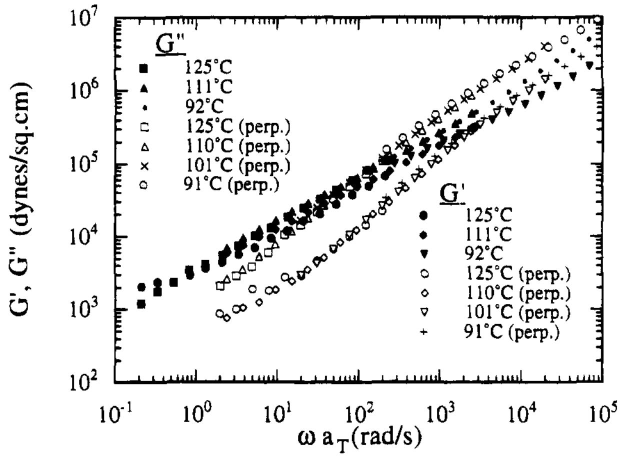

Figure 11. Dynamic moduli of unaligned SI (filled symbols) and SI in the perpendicular orientation (open symbols) shifted to a reference temperature of 130 °C. The shift factors for unaligned and perpendicular SI lamellae are given in Table 2.

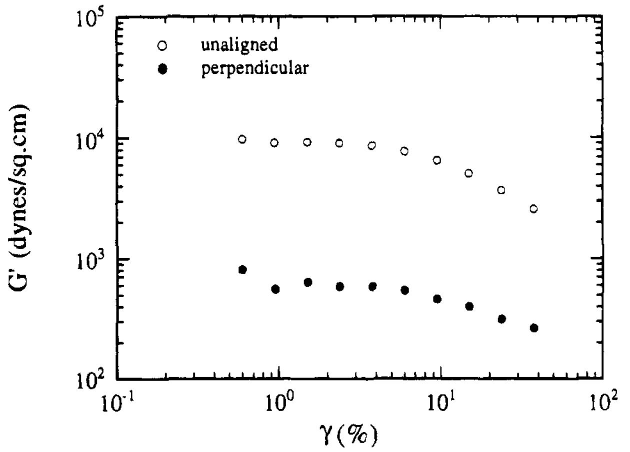

Figure 12. Strain sweeps for SI at 120 °C and 1 rad/s before and after alignment.

Figure 11 compares G' and G'' for frequency sweeps of unaligned diblock samples (filled symbols) with those for a well-aligned (as detailed in the Experimental Section) perpendicular sample (open symbols). The data were shifted to a reference temperature of 130 °C using WLF parameters for unaligned and perpendicular SI given in Table 2. The perpendicular sample appears more nearly terminal than the unaligned sample, though it is still far from terminal. It should also be noted that both G' and G'' are higher for the perpendicular sample at high frequencies than for the unaligned sample.

We previously alluded to the small linear viscoelastic regime for diblocks. Figure 12 shows strain sweeps at a frequency of 1 rad/s before and after the SI sample was well aligned in the perpendicular orientation. The limiting strain for obtaining linear viscoelastic behavior seems to stay about the same when the sample is aligned. Similar results were found for data at different frequencies and temperatures.

Shear Alignment of SIS Triblocks. We aligned SIS samples at frequencies of 0.1, 1, and 10 rad/s at 140, 130, 120, 110, and 100 °C. The strain amplitudes were 50% except at low temperatures and high frequencies, where a 50% strain overloads the transducer. In those cases, 25% amplitudes were used, as noted in Table 4. All of these samples showed the perpendicular orientation. No parallel alignment was observed.

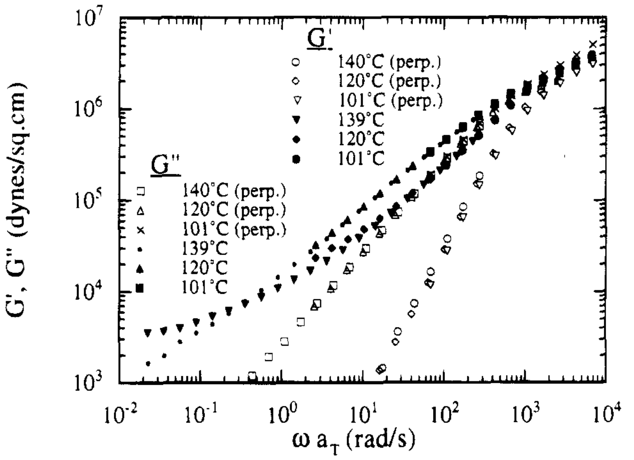

Figure 13. Dynamic moduli of unaligned SIS (filled symbols) and SIS aligned in the perpendicular orientation (open symbols) shifted to a reference temperature of 152 °C. The shift factors for unaligned and perpendicular SIS lamellae are given in Table 2.

Table 4. SIS Alignment

	0.1 rad/s	1 rad/s	10 rad/s
140 °C	$\perp$	$\perp$	$\perp$
130 °C	$\perp$	$\perp$	$\perp$
120 °C	$\perp$	$\perp$	$\perp$
110 °C	$\perp$	$\perp$	$\perp^a$
100 °C	$\perp$		

[a] 25% strain amplitude.

For SIS, we again investigate the effects of strain amplitude, frequency, and time on the rheologically determined degree of alignment. We choose a temperature of 140 °C since our preliminary studies gave sharper X-ray scattering patterns at this temperature. We once again find that with increasing strain amplitude, for a fixed total strain, the alignment improves, as indicated by reduced magnitudes of the moduli, G' and G''. We also find that the best alignment at 100% strain occurs for a frequency of around 0.5 rad/s. To be consistent with our SI studies, we choose a frequency of 1 rad/s and 100% strain amplitude for our studies of the effect of time on alignment. We find that improvement in alignment at these conditions, as determined rheologically, ceases after about 5 h.

Figure 13 shows G' and G'' for well-aligned SIS (as detailed in the Experimental Section) and unaligned SIS shifted to a reference temperature of 152 °C using WLF parameters for perpendicular and unaligned SIS given in Table 2. We note that the aligned SIS displays nearly terminal behavior.

Figure 14 shows strain sweeps at a frequency of 1 rad/s before and after the SIS sample was well aligned at 1 rad/s with 100% strain at 140 °C. The linear viscoelastic region for the aligned SIS clearly extends out to higher strains than for unaligned SIS.

Comparison of Results for SI and SIS. Note in Table 1 that the molecular weight of SIS is almost exactly twice that of SI; thus the SIS sample can be envisioned as two SI polymers tethered together at the isoprene ends.

The experimental value of T_{ODT} for SIS is around 152 °C, which is 22 °C higher than the T_{ODT} of SI. This is not unexpected, since a triblock made by tethering together two diblocks is predicted theoretically to have a somewhat higher T_{ODT} than the diblock. We apply the mean field predictions of Leibler for χN at the ODT for diblocks[4] and of Mayes and Olvera de la Cruz for triblocks,[5] where χ is the Flory χ parameter and N is an average degree of polymerization (defined below). These theories predict $\chi N = 10.5$ at T_{ODT} for SI and $\chi N = 18.1$ at T_{ODT} for SIS. We use an expression for the interaction parameter χ from Mori and co-workers[6] given by

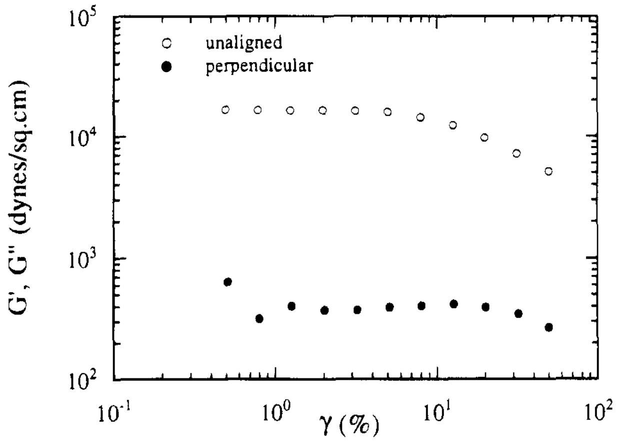

Figure 14. Strain sweeps for SIS at 140 °C and 1 rad/s before and after alignment.

$$\chi = -0.0937 + 66/T \tag{1}$$

Our value of N is given by[13]

$$N = \frac{M_{\mathrm{w,PS}}v_{\mathrm{PS}} + M_{\mathrm{w,PI}}v_{\mathrm{PI}}}{[(M_{\mathrm{S}}v_{\mathrm{PS}})(M_{\mathrm{I}}v_{\mathrm{PI}})]^{1/2}} \tag{2}$$

where the specific volumes of the homopolymers, v_{PI} and v_{PS}, are functions of temperature as given by eqs 3 and 4,[13]

$$v_{\mathrm{PS}} = 0.9199 + 5.098 \times 10^{-4}(T - 273) + 2.354 \times 10^{-7}(T - 273)^2 + \frac{32.46 + 0.1017(T - 273)}{M_{\mathrm{w,PS}}} \tag{3}$$

$$v_{\mathrm{PI}} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2 \tag{4}$$

$M_{\mathrm{w,PS}}$ and $M_{\mathrm{w,PI}}$ are the weight-averaged molecular weights of polystyrene and polyisoprene, and M_{S} and M_{I} are the molecular weights of the styrene and isoprene monomers. Using these mean field theories, we predict $T_{\mathrm{ODT}} = 205$ °C for SI and $T_{\mathrm{ODT}} = 226$ °C for SIS. The predicted difference of the T_{ODT}'s of 21 °C is very close to our experimentally determined difference of 22 °C.

The predicted T_{ODT}'s for both the diblock and the triblock are higher than the experimental values, presumably due to our neglect of fluctuation effects. To test this idea, we apply the fluctuation theory of Barrat and Fredrickson,[9] which takes into account the clustering of like monomers in the melt. This clustering reduces the interaction energy below the value predicted for random mixing and thus lowers the predicted T_{ODT}. Using the above expressions for the specific polymer volumes and statistical segment lengths of 6.8 Å for polystyrene[37] and 6.6 Å for polyisoprene,[38] we obtain a theoretical T_{ODT} of 162 °C for SI, which is considerably closer to the experimental value than is the mean field prediction. Presumably the remaining discrepancy between theory and experiment is a result of correlation effects at shorter length scales than those accounted for in the theory or is due to an inaccuracy in the theory at low N.

The temperature range of fluctuation effects observed rheologically is less than 4 °C for SI and 3 °C for SIS. This is much smaller than the range of around 40 °C for fluctuations in PEP–PEE systems.[2] The temperature range is presumably smaller because $d\chi/dT$ is more than 10 times larger for SI than for PEP–PEE.

Unaligned SI becomes nonlinear at strains larger than 1 or 2%, whereas unaligned SIS can be strained to 2–4% before demonstrating a nonlinear response. After alignment, there may be little change in the range of linear viscoelasticity for SI, which depends somewhat on the frequency and temperature. For SIS, alignment definitely increases the breadth of the linear viscoelastic region up to around 20% or higher.

In SI, we observe either parallel or perpendicular alignment depending on the alignment conditions. This is consistent with the work of other groups studying the SI system.[18] For SIS, however, we only see the perpendicular type of orientation. This can be explained by noting that for diblocks with parallel alignment, the lamellae can easily slide past each other when they are sheared. For triblocks, however, there is a resistance to sliding in the parallel orientation because of bridging of adjacent polystyrene layers by the polyisoprene blocks. Therefore, it is perhaps not surprising that the parallel alignment is not observed in the triblock.

For the SIS, perpendicular alignment results in nearly terminal behavior. In contrast, the "best" perpendicular alignment we can achieve (as detailed in the Experimental Section) for the diblock results in storage and loss moduli with slopes similar to each other and slightly less than 1. This, and the greater range of linear viscoelasticity for the aligned triblock compared to the aligned diblock, suggest better alignment for SIS than for SI. This conclusion is confirmed by X-ray scattering, which shows secondary peaks for SIS in the well-aligned and several other aligned samples, but never for SI. We expect that the lower molecular weight of the SI sample, as well as its obvious lack of bridging chain conformations, contributes to its poorer alignment behavior.

Conclusions

We have studied the rheological properties of unaligned and aligned diblock and triblock copolymers of styrene and isoprene. We have found both parallel and perpendicular alignment in the diblock copolymer, depending on the frequency and temperature of the alignment procedure, but only perpendicular alignment in the triblock. For SI, perpendicular alignment is favored in the diblock at low alignment frequencies and high temperatures, and parallel alignment occurs at lower temperatures and high frequencies. For triblocks, a high degree of perpendicular alignment can be achieved, so that nearly terminal rheological behavior is observed. The diblock never achieves such a high degree of perpendicular alignment. The quantitative interpretation of these results awaits the development of molecular-based rheological models for block copolymers.

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