Threshold Strain Value for Perpendicular Orientation in Dynamically Sheared Diblock Copolymers

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Received August 14, 1996
Revised Manuscript Received November 18, 1996

Introduction. It has been known for many years that lamellar diblock copolymer systems, when subjected to shear, tend to orient with their lamellar normals parallel to the shear gradient direction (parallel configuration).[1] In 1992, Koppi *et al*. reported that at temperatures near the order−disorder transition temperature (T_{ODT}), shear induces a new state into poly(ethylenepropylene)−poly(ethylethylene) (PEP−PEE) lamellae, with their normals parallel to the vorticity axis (perpendicular configuration).[2] This unexpected observation prompted a flurry of activity, both among experimentalists,[3−17] who examine the range of shear-orientation phenomena in lamellar block copolymers, and among theorists,[18−23] who try to describe the underlying physics. At this early stage in the development of the field, where so little firm understanding exists, many observations reported by different groups appear to be in contradiction. It is likely, however, that investigating the sources of these contradictions will reveal the key parameters that influence the shear orientation phenomena.

For example, for PEP−PEE, Koppi *et al.* reported parallel orientation at low shear frequencies and perpendicular orientation at higher ones. For poly(styrene-*b*-isoprene) (PS-*b*-PI), parallel orientation was reported at high and perpendicular orientation at lower frequencies.[3,4] Differences in behavior also occur with different chain lengths. Polymers long enough to be entangled show more complex behavior than that described above. In several such systems, the third principle orientation, with the lamellar unit normal parallel to the flow direction (the "transverse" orientation) has now been observed.[6,8,14] One report exists, however, where data seem to indicate the existence of this orientation also for a low molecular weight sample.[12]

One of our contributions to this area has been to show that the thermal history of the sample prior to shearing plays an important role.[15] This allowed us to discover, for unentangled PS-*b*-PI lamellar systems near T_{ODT}, that there are three orientation regimes: parallel at high, perpendicular at intermediate, and parallel again at very low shear frequencies.[7] These same three shear orientation regimes have now been found for PS−polybutadiene lamellae.[17] Without the prior thermal treatment, the parallel orientation at low shear is not uniformly created.

Here we present results which identify strain as the control parameter for these nonequilibrium phenomena.[24] We demonstrate that in the intermediate frequency regime a threshold strain value for the formation of the perpendicular orientation is observed that depends on frequency and temperature. Below this critical strain, parallel orientation is found. This allows us for the first time to construct an orientation diagram as a function of strain and frequency. While one can identify shear frequencies ω_d (separating the low and intermediate frequency regime) and ω_c (separating the intermediate and high frequency regime) at larger strain, at low strain values, parallel orientation is observed irrespective of frequency.

Table 1. Frequency and Temperature Dependence of Strain at the Flipping Point in the Intermediate Frequency Regime of Orientation II after 10 h of LAOS[a]

	% strain			
T (K)	2 rad/s	3 rad/s	10 rad/s	30 rad/s
409	46 ± 16	15 ± 10	11.5 ± 3.2	5.4 ± 1.1
398		16 ± 3		

[a] Note that, in order to compare the strain value of flipping at 398 K with those obtained at 409 K, the corresponding frequency has to be shifted according to the temperature dependence of the shift factor $a_T(T)$ (a factor of about 3.1). Thus, the strain value at the flipping point of about 16% at 398 K (for $\omega = 3$ rad/s) has to be compared with that of about 11.5% at 409 K (for $\omega = 10$ rad/s). As described in the text, this suggests that, with decreasing temperature away from T_{ODT}, the lower boundary between parallel and perpendicular orientation shifts toward higher strain.

Experimental Section. The lamellar PS-*b*-PI diblock copolymer studied (termed PS−PI-7 in our nomenclature) is the same characterized and used in earlier work.[15,16] The PS and PI block number-average molecular weights M_n are 9900 and 9100, respectively, and M_w/M_n of the block copolymer is 1.09. The T_g's for the PS and PI blocks as determined by DSC with a heating rate of 10 K/min are 341 and 213 K, respectively. T_{ODT} as determined by the temperature dependence of the storage modulus $G'(T)$[25,26] at $\omega = 3$ rad/s is 424 ± 1 K. In all samples 2,6-di-*tert*-butyl-4-methylphenol was used as an antioxidant.

Samples were pressed under vacuum at 340 K at 15 kN for about 30 min into disks with diameter of 13 mm and thickness of 1 mm. They were then annealed under vacuum at 358 K, i.e. roughly 20 K above the T_g of the PS blocks but far below T_{ODT}, for more than 24 h. A Rheometrics Mechanical spectrometer Model 800 (RMS-800) was used in the parallel plate geometry for the large amplitude oscillatory shear (LAOS) experiments on these sample disks. LAOS experiments were performed at 398 and 409 K using different frequencies within the intermediate frequency regime of the dynamic shear viscosity leading to perpendicular orientation as shown in earlier studies (see Table 1).[7,15,16] The amplitude at the rim of the sample disk was set between 30 and 150%, and shear flow was operating for 10 h.

SAXS experiments were performed on specimens cut from shear-oriented sheets. A Rigaku Rotaflex X-ray source at 0.154 nm (Cu Kα) was employed. A three-pinhole-collimator was used to generate a beam with diameter of 1 mm. Scattering patterns were recorded on a two-dimensional Siemens X-1000 Area Detector with a sample-to-detector distance of 130 cm. The experimental conditions for the SAXS measurements were the same for all diffractograms depicted. Typically six points along the radius $R = 6.5$ mm of the sample disks were investigated (c.f., inset Figure 1). This corresponds approximately to the resolution along the radius since the diameter of the X-ray beam is about 1 mm. Three scattering experiments were performed at each point corresponding to the three orthogonal directions with respect to the deformation geometry as illustrated in Figure 1.

Results and Discussion. For samples sheared under the experimental conditions described above, an

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S0024-9297(96)01234-X CCC: $14.00

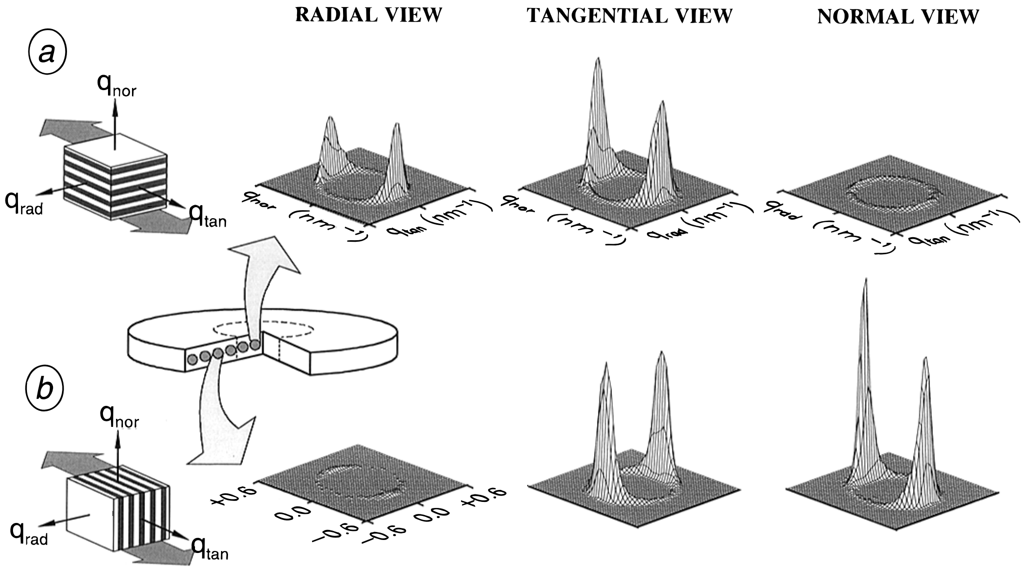

Figure 1. Two-dimensional SAXS results for the PS−PI-7 sample following large amplitude oscillatory shear for 10 h with a strain amplitude of 30% at the rim of the sample disk. The shearing conditions were $T = 409$ K and $\omega = 10$ rad/s. Results are presented for specimens cut at two different positions along the radius (r): (a) $r \approx 1$ mm, corresponding to approximately 4.6% strain; (b) $r \approx 4$ mm, corresponding to approximately 18.4% strain. For both positions diffractograms were measured along three orthogonal directions corresponding to the radial, tangential, and normal view, respectively. In the insets on the left-hand side, the resulting orientations are schematically depicted together with the used coordinate frame. A schematic drawing showing the positions along the radius of the sample disk, at which the displayed 2D-SAXS patterns have been measured, is also included. In addition, the position where roughly the flip of orientation from parallel to perpendicular occurs in the sample disk is indicated by a broken line (- - -).

interesting radial dependence with a flip of the lamellar orientation was observed. Two representative sets of 2D-SAXS patterns along the three orthogonal directions measured at different points along the radius are shown in Figure 1 for a sample sheared for 10 h at 409 K. The shear frequency was 10 rad/s and the amplitude at the rim of the sample disk was set to 30%. The 2D-SAXS patterns measured for the inner part of the sample disk show strong scattering peaks along $\mathbf{q}_{\mathrm{nor}}$ both in the $\mathbf{q}_{\mathrm{nor}}-\mathbf{q}_{\mathrm{tan}}$ and $\mathbf{q}_{\mathrm{nor}}-\mathbf{q}_{\mathrm{rad}}$ plane while the scattering in the $\mathbf{q}_{\mathrm{rad}}-\mathbf{q}_{\mathrm{tan}}$ plane is rather small (Figure 1a). As indicated in the schematic drawing on the left-hand side of Figure 1a, these are typical 2D-SAXS patterns of the morphology referred to as "parallel" orientation. The 2D-SAXS patterns measured at the outer part of the sample disk (Figure 1b) show strong scattering peaks along $\mathbf{q}_{\mathrm{rad}}$ both in the $\mathbf{q}_{\mathrm{nor}}-\mathbf{q}_{\mathrm{rad}}$ plane and the $\mathbf{q}_{\mathrm{rad}}-\mathbf{q}_{\mathrm{tan}}$ plane, while the scattering in the $\mathbf{q}_{\mathrm{nor}}-\mathbf{q}_{\mathrm{tan}}$ plane is rather small. This indicates that the normal unit of the lamellar microstructure is aligned preferentially in the radial direction ($\mathbf{q}_{\mathrm{rad}}$) of the sample disk, as indicated schematically on the left-hand side of Figure 1b. This morphology is the "perpendicular" orientation. From the SAXS results, the flipping point of orientation under the employed experimental conditions was at about 11% strain.

Results on the frequency dependence of the flipping point at 409 K are summarized in Table 1. When approaching the shear frequency ω_{d} around 1 rad/s at this temperature from above, a significant increase of strain at the flipping point is observed. From these results we conclude that in the intermediate frequency regime there is a frequency dependent threshold strain value for the formation of the perpendicular orientation. Below this critical strain, parallel orientation behavior is found. This observation has important consequences for the understanding of the orientation diagram of the lamellar microstructure of PS-*b*-PI diblock copolymers under large amplitude oscillatory shear. First, in all three frequency regimes, the parallel orientation can be obtained as the stable state. This is consistent with our observations in recent dual frequency experiments.[16] At intermediate frequencies, however, increasing the strain amplitude drives the system toward an instability. As expected from other nonequilibrium phenomena,[24] beyond this point new patterns can be formed which need not constitute the most stable state. In the present case this is the perpendicular orientation of the lamellae.

From these results for PS−PI-7 we propose an orientation diagram for the orientation behavior of lamellar PS-*b*-PI diblock copolymers of low molecular weight under large amplitude oscillatory shear flow in the vicinity of T_{ODT}. In Figure 2 strain amplitude (γ) is plotted versus shear frequency (ω). A third dimension, which needs further elaboration, is the temperature dimension. For simplicity, however, we will concentrate here only on the $\gamma-\omega$ plane. Previous work has shown[7,15] that, at temperatures close to T_{ODT}, for large strain amplitudes up to 100% there are three frequency regimes of orientation leading, with increasing frequency, to parallel, perpendicular, and parallel orientation, respectively. The characteristic frequencies separating the three regimes are ω_{d} at low frequency and ω_{c} at high frequency (see Figure 2). Whereas a number of groups have concentrated on the position and origin of ω_{c},[27] less attention has been paid to ω_{d}.[2,7,15,16] The molecular origin of this transition is much less well understood than that of ω_{c}, and more work is needed to clarify this point.

From the results presented here, we conclude that the vertical line corresponding to ω_{d} vanishes for low strain and an almost horizontal line has to be drawn instead. To understand what may occur at high strains in the vicinity of ω_{c}, we draw on the work of Gupta *et al.*[13] They recently reported that, in the intermediate frequency regime close to the critical frequency ω_{c}, a flip from perpendicular to parallel orientation occurs with in-

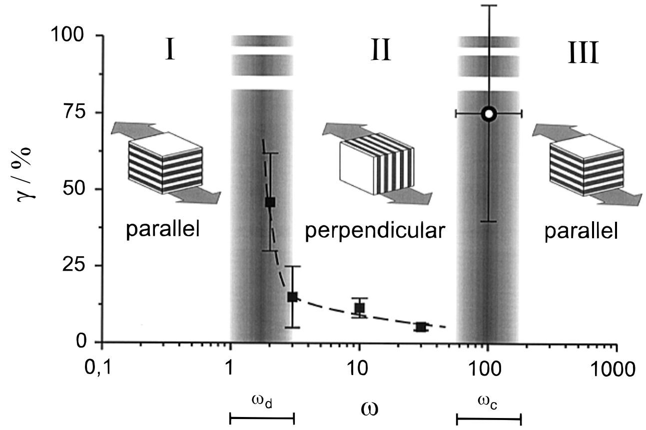

Figure 2. Proposed orientation diagram for the orientation behavior of lamellar PS-*b*-PI diblock copolymers under large amplitude oscillatory shear flow in the vicinity of T_{ODT} ($T < T_{ODT}$). It is based on results of the present and earlier studies (see refs 7, 15, and 16). A slice through the three-dimensional orientation diagram (including temperature as the third axis) for PS−PI-7 is depicted for $T = 409$ K. The frequencies ω_d and ω_c separate the three frequency regimes I, II, and III of orientation leading to parallel, perpendicular, and parallel orientation behavior, respectively, at larger strain values. The error bars for ω_d and ω_c along the frequency axis account for the experimental difficulties to determine precisely these quantities from the linear viscoelastic properties. Filled symbols indicate the positions of the flipping points of orientation from parallel at low strain to perpendicular at higher strain values (see Table 1). The dotted line through these data serves as a guide for the eye. The open symbol indicates an effort to map the flipping point from perpendicular at lower strain to parallel orientation at higher strain values observed by Gupta *et al.*[13] onto the region around ω_c.

creasing strain. These results suggest that, for large strain values, the vertical boundary separating the parallel regime (high frequency) from the perpendicular orientation (intermediate frequency) may also be inclined toward the low-frequency side. It should be emphasized, however, that, until backed by e.g. small angle X-ray or neutron scattering experiments, these findings should be taken as a guide for the design of future experiments, rather than the last word on morphology.

As the temperature is decreased away from T_{ODT}, i.e. along the third dimension of the orientation diagram, preliminary results suggest that the horizontal boundary between parallel and perpendicular orientations shifts toward higher strain (see Table 1). Ultimately, for very low temperatures, one possible scenario is that the region of perpendicular orientation shifts to inaccessibly high strain values. This evolution of the orientation diagram with temperature is consistent with the observation that, for the range of temperatures and strain values so far examined, the perpendicular orientation is not observed at very low temperatures. Further studies have to elucidate the exact evolution of the threshold strain with temperature, however, before final conclusions can be drawn. Experiments along these lines are now in progress in our laboratory.

Another important question concerns the sharpness of the boundaries. As we will show in a subsequent publication, for the case of the parallel plate geometry used in our experiments, the 2D-SAXS diffractograms exhibit peaks corresponding to parallel *and* perpendicularly aligned lamellae as the system crosses the threshold value with increasing strain.[28] Experiments using a homogeneous deformation geometry have to be performed, however, to settle this question since this effect could be due to the limited strain resolution in our measurements.

It should finally be mentioned that the flip of orientation from parallel to perpendicular as a function of strain, when viewed in the nonequilibrium phenomenon picture, is entirely consistent with the concepts developed in earlier studies to explain perpendicular alignment, i.e. selective layer melting and reorganization. These concepts are thereby further corroborated.

Acknowledgment. We thank T. Wagner and T. Volkmer for their help in preparing our samples and M. Bach for the help with the SAXS measurements. D.M. thanks Y. Zhang for introducing him to the different experimental techniques and for stimulating discussions. The authors are grateful to Prof. M. Winnik, Dr. T. Pakula, and Dr. H. Pleiner for carefully reading and advise for improving the manuscript. The authors are grateful to Prof. H. W. Spiess for his universal support. D.M. thanks the Max-Planck-Society and the C.N.R.S. for a stipend.

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MA961234Z