Orientation Flip of Lamellar Polystyrene−Polyisoprene Diblock Copolymers under Extrusion

Heike Leist,[†] Kalman Geiger,[‡] and Ulrich Wiesner*[,†]

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany, Institut für Kunststofftechnologie (IKT), Universität Stuttgart, Böblinger Strasse 70, D-70199 Stuttgart, Germany

Received September 30, 1998
Revised Manuscript Received December 16, 1998

Introduction. The effect of shear flow on complex fluids[1−3] has attracted increasing interest in recent years. Among these materials block copolymers have proven to be particularly interesting due to the variety of microstructures they exhibit.[4] Under shear flow the microstructure can be macroscopically aligned leading to highly anisotropic materials. In 1970 Keller et al. performed the first flow induced orientation experiments on a hexagonal triblock copolymer.[5] In the following years numerous studies have elucidated the effects of large amplitude oscillatory shear (LAOS) and steady shear flow on various block copolymer phases and a number of reviews are now available.[6−9] As an example the orientation behavior of lamellar poly(styrene-*block*-isoprene) diblock copolymer melts (PS-*b*-PI) under LAOS is now well-known phenomenologically although the underlying orientational mechanisms are not yet fully understood.[9−13] Different states of orientation have been observed through a careful choice of the shear parameters (see Figure 1a). In the following we will focus on what is referred to as the "parallel" and "perpendicular" orientations, i.e., with the layer normal along the velocity gradient direction and the vorticity direction, respectively.[14]

It is difficult to envision a technical application of block copolymer materials oriented by LAOS, however, since shearing times are typically on the order of hours. In the present communication we, therefore, want to investigate the orientation of lamellar block copolymers by means of extrusion. This would bridge the gap between long orientation experiments on a laboratory scale and technically relevant fast extrusion processes. The two flow conditions are schematically depicted in Figure 1b: the drag flow in an oscillatory shear experiment and the pressure gradient flow in an extrusion. We show that under extrusion conditions rapid macroscopic parallel and, after annealing, perpendicular orientations of the lamellae can indeed be obtained which may open an avenue to applications.

Experimental Section. The diblock copolymer termed PS-*b*-PI 21 has been synthesized via conventional anionic polymerization techniques. The dispersity is 1.06 and PS and PI block molecular weights are 9200 and 8800, respectively. The glass transition temperatures, T_g, for PS and PI are 337 and 213 K, respectively. For the rheological characterization, a Rheometrics mechanical spectrometer model RMS 800 was used. The rheologically determined order−disorder transition temperature (T_{ODT}) is 388 K.[15] For the extrusion experiments a miniaturized high-pressure capillary rheometer with a rectangular slit die (gap $h = 0.1$ mm, width $b = 3$ mm, length $l = 9.3$ mm, entrance angle of ~60°, and diameter of the melt reservoir $d = 5$ mm) was used at different apparent shear rates and different temperatures. The apparent shear rates, $\dot{\gamma}_{app}$, (eq 1), and the shear stresses, τ (eq 2), were determined by means of the flow rate, $\dot{V}$, and pressure gradient, Δp, in the slit, respectively

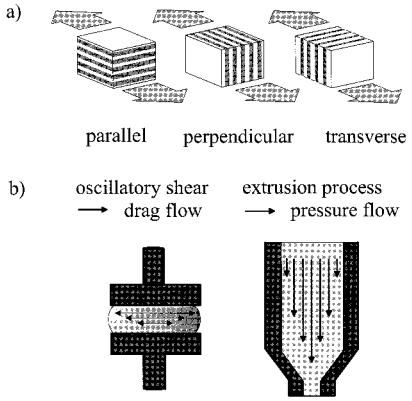

Figure 1. (a) Three states of macroscopic lamellar orientation observed under LAOS. (b) Schematic comparison of drag flow in oscillatory shear experiments and pressure flow in extrusion processes.

$$\dot{\gamma}_{app} = \frac{6\dot{V}}{bh^2} \tag{1}$$

$$\tau = \frac{h}{2}\frac{\Delta p}{\Delta x} \tag{2}$$

where Δx is the distance between points where the pressure is measured. The pressure gradient was determined by using two pressure transducers placed at the positions $\Delta x_1 = 3.1$ mm and $\Delta x_2 = 6.2$ mm from the slit die entrance section. The entrance pressure drop was determined as the difference of the measured pressure (by using a third pressure transducer) in the melt reservoir and of the extrapolated pressure exactly at the die entrance section (calculated from the linear pressure profile along the slit die). Since only two pressure transducers were used along the slit, the exit pressure (and subsequent estimation of the first normal stress difference) was not determined. The apparent viscosity, η_{app}, is calculated using the following equation:

$$\eta_{app} = \frac{\tau}{\dot{\gamma}_{app}} \tag{3}$$

More details, about the miniaturized high-pressure capillary rheometer, will be published elsewhere.[16] The extruded strands are quenched to room temperature by the surrounding air. For the two-dimensional small-angle X-ray scattering (2D-SAXS) experiments, a Rigaku Rotaflex X-ray source and a 2D Siemens area detector were employed. For experimental details the reader is referred to ref 17. Diffractograms obtained from samples after different extrusion and annealing experiments were independently normalized. The spatial period of the lamellar microstructure of PS-*b*-PI 21 determined from SAXS is 15 nm. Birefringence measurements were

[†] Max-Planck-Institut für Polymerforschung.
[‡] Universität Stuttgart.

10.1021/ma981544c CCC: $18.00
Published on Web 02/02/1999

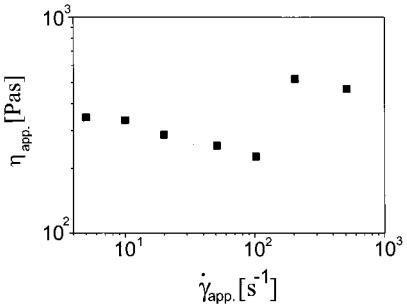

Figure 2. Apparent viscosity η_{app} as a function of apparent shear rate $\dot{\gamma}_{app}$ at 373 K as determined from measurements with a miniaturized high-pressure capillary rheometer.

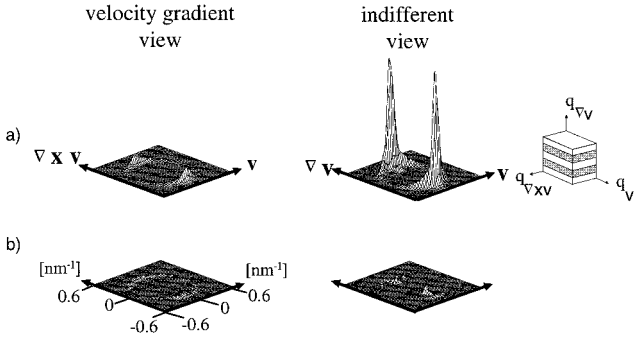

Figure 3. 2D-SAXS results for PS-*b*-PI 21 following extrusion in the low and high apparent shear rate regimes. Samples were extruded at 373 K with an apparent shear rate of (a) $\dot{\gamma}_{app}$ = 100 s^{-1} and (b) $\dot{\gamma}_{app}$ = 500 s^{-1}, i.e., above and below the jump in the apparent viscosity curve. In the schematic drawing on the right-hand side of part a, the resulting lamellar orientation together with the coordinate frame is schematically depicted.

performed with a Zeiss polarization microscope under crossed polarizers.

Results and Discussion. To characterize the flow behavior of PS-*b*-PI 21 the dependence of the apparent shear viscosity η_{app} on the apparent shear rate $\dot{\gamma}_{app}$ was investigated at different temperatures above T_g(PS) and below T_{ODT}. For the sake of simplicity Figure 2 only displays the viscosity curve measured at 373 K since the features of the flow behavior were similar for all temperatures investigated in the interval 363−383 K. The apparent viscosity first decreases with increasing apparent shear rate ("low apparent shear rate regime I") according to non-Newtonian flow behavior (shear thinning). By further increasing $\dot{\gamma}_{app}$ the shape of the viscosity curve changes drastically. For 100 $s^{-1} < \dot{\gamma}_{app} < 200$ s^{-1}, the viscosity displays a jump to higher values. Beyond this discontinuity η_{app} decreases again with increasing $\dot{\gamma}_{app}$ ("high apparent shear rate regime II"). Since homopolymers only show shear thinning, the observed viscosity jump must be related to morphological changes. To check this, 2D-SAXS measurements were performed on samples extruded with shear rates falling in the two regimes. Scattering patterns were taken with the beam along two orthogonal directions of space with respect to the sample geometry (Figure 3). Since the polymer strands extruded at different shear rates in the vicinity of the viscosity jump exhibited qualitatively similar behavior within one regime, only the results of one typical experiment for each regime are discussed. The resulting morphologies, as revealed by 2D-SAXS measurements, are shown in Figure 3. The upper row (a) depicts the scattering patterns for an extrusion experiment performed at 100 s^{-1}, falling in regime I. This sample shows strong scattering peaks

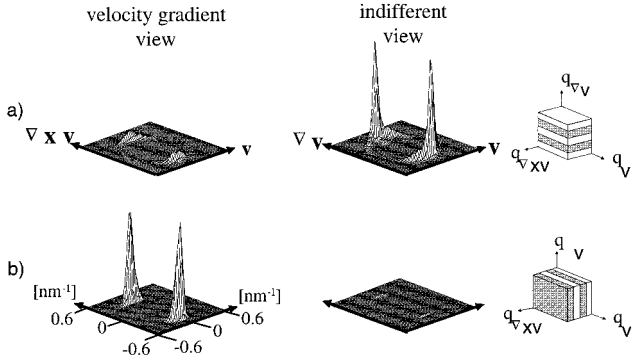

Figure 4. 2D-SAXS results obtained from the same samples as in (a) Figure 3a and (b) Figure 3b after annealing for 5 min at 363 K. The insets on the right-hand side depict the resulting lamellar orientations together with the coordinate frame.

along $q_{\nabla v}$ in the $q_{\nabla v} - q_v$ plane (indifferent view) while the scattering intensity in the $q_{\nabla xv} - q_v$ plane (velocity gradient view) is rather low. This indicates a parallel orientation of the lamellae (see right-hand side of Figure 3a). The lower row (b) shows diffractograms obtained from a sample extruded in regime II at 500 s^{-1}. No sharp reflexes, either in the $q_{\nabla v} - q_v$ plane or in the $q_{\nabla xv} - q_v$ plane, are observed, and the overall scattering of the sample is rather weak. From these data, it can be concluded that no macroscopic lamellar orientation is induced under extrusion conditions in regime II. Furthermore the lack of intensity implies a partial destruction of the lamellar microstructure. These results clearly demonstrate that the morphology of the polymer is strongly modified by the extrusion process.

It is interesting to note that in the indifferent view for both cases a and b there are narrow streaks of low intensity along the velocity gradient direction. Whereas we never observed this phenomenon[9] under LAOS, we frequently reproduced it in the extrusion experiments. Although the nature of these streaks is unknown to us they must be related to small amounts of large scale structures forming under extrusion since they extend to the low q-range.

We have shown that annealing has a significant effect on the lamellae orientation.[17] In a second set of experiments the extruded PS-*b*-PI plugs were therefore annealed after extrusion at a fixed temperature of 363 K and the course of the birefringence was followed simultaneously. The sample extruded in regime I showed no significant change in birefringence. In contrast, a strong increase of birefringence within the first 2 min followed by an asymptotic approach to a constant value after 5 min was observed for the plug extruded in regime II (data not shown). In subsequent 2D-SAXS experiments (see Figure 4) no significant annealing induced changes in the diffractograms could be observed for the polymer strand extruded in regime I (compare Figures 3a and 4a). This is consistent with the constant value of the birefringence during annealing. In contrast the 2D-SAXS diffractograms of the annealed polymer plugs extruded in regime II show dramatic differences to the nonannealed ones (compare Figures 3b and 4b). Now, sharp scattering peaks occur along $q_{\nabla xv}$ in the $q_{\nabla xv} - q_v$ plane, whereas almost no scattering can be observed in the $q_{\nabla v} - q_v$ plane. The analysis of the data reveals a perpendicular orientation of the lamellae (see right-hand side of Figure 4b). This is consistent with interpretation of the final levels of birefringence. After annealing values between 1.2 × 10^{-3} and 1.4 × 10^{-3}

are observed which are close to the theoretically suggested value of 1.6×10^{-3} for a perfectly aligned perpendicular sample.[18]

We also calculated values for the order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, for the distribution of the unit vectors of the lamellae normals according to ref 19, as well as the full width at half-maximum, fwhm, of the scattering peaks. No differences in the order parameters were found for the annealed and nonannealed sample (Figures 3a and 4a) extruded in regime I. The order parameters were determined to be $\langle P_2 \rangle = 0.42$ and $\langle P_4 \rangle = 0.14$. These values correspond to those frequently obtained for parallel orientation in LAOS experiments. The order parameters for the annealed sample in Figure 4b extruded in regime II (perpendicular orientation) were calculated to be $\langle P_2 \rangle = 0.69$ and $\langle P_4 \rangle = 0.49$, which are quite high for a shear oriented sample. The fwhm of the different scattering peaks was estimated to be 15° for all orientations. The lower $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for the parallel orientation compared to the perpendicular case can be attributed to a small amount of weakly oriented lamellae leading to a tail in the scattering peaks (compare patterns in parts a and b of Figure 4). On the other hand, the small value of the fwhm shows that most of the lamellae are highly oriented.

The discontinuity in the apparent viscosity leading to a destruction of the lamellar microstructure in regime II with perpendicular orientation after subsequent annealing signifies a transition to an orientation regime with no analogue in the LAOS experiments. Although difficult to compare, in this regime shear rates expressed as a frequency[14] ω are expected to be 2 orders of magnitude larger than the characteristic frequency, ω_c', at which under LAOS (100% shear amplitude) the crossover from the perpendicular regime to the high frequency parallel regime occurs. This is supported by the observation that in regime I the third principle orientation direction of the lamellae, the transverse orientation, can be obtained[16] which in LAOS experiments occurs roughly above $10\omega_c'$ for unentangled diblock copolymers.[10]

In regime II we are thus dealing with shear rates (or frequencies) as well as amplitudes which are much higher than those typically probed in LAOS experiments. At such high shear rates, local relaxation modes correlated with the glass transition of PS are dominant. In the present communication we want to speculate about a possible orientation mechanism in this regime. As discussed elsewhere[9,10,20] at shear rates (or frequencies) higher than the inverse of the single chain relaxation time, block copolymer chains start to orient along the flow direction, leading to an intermediate transverse orientation on the way to the final parallel state under LAOS. At very high shear rates, as the microstructure is increasingly destroyed, this chain orientation is expected to become unstable. However, one possible stable chain orientation under these conditions is the one along the vorticity axis. This would correspond to the "log-rolling" process predicted for nematic liquid crystals by Larson and Öttinger in 1991[21] and recently observed by Romo-Uribe and Windle.[22,23] After subsequent annealing for a duration of several minutes, during which the orientational correlations have no time to relax,[24] the lamellar microstructure is reformed and a perpendicular orientation is observed.

In conclusion we demonstrated that the lamellar microstructure of a PS-*b*-PI diblock copolymer can be oriented macroscopically under extrusion within seconds, leading to a highly anisotropic material. As in the case of LAOS experiments, both states of orientation, i.e., the parallel and the perpendicular orientation, can be obtained. This is achieved at temperatures close to both T_g and T_{ODT} under extrusion by changing the apparent shear rate and subsequent annealing. More experimental as well as theoretical studies are now needed to understand the nature of the apparent viscosity curve and the underlying orientation mechanisms.

Acknowledgment. We thank Prof. H. W. Spiess, MPI für Polymerforschung Mainz, for his support and Prof. H. C. Öttinger, ETH Zürich; Prof. M. H. Wagner, IKT Stuttgart; and Prof. Y. Yang, Fudan University, Shanghai, China, for fruitful discussions.

References and Notes

(1) Garrido, L. *Complex Fluids*; Springer: Berlin and Heidelberg, Germany, 1993.
(2) Onuki, A.; Kawasaki, K. *Dynamics and Patterns in Complex Fluids*; Springer: Berlin and Heidelberg, Germany, 1990.
(3) Safran, S. A.; Clark, N. A. *Physics of Complex and Supermolecular Fluids*, John Wiley & Sons: New York, 1987.
(4) Bates, F. S. *Science* **1991**, *251*, 898.
(5) Keller, A.; Pedemonte, E.; Willmouth, F. M. *Nature* **1970**, *255*, 538.
(6) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501.
(7) Honecker, C. C.; Thomas, E. L. *Chem. Mater.* **1996**, *8*, 1702.
(8) Colby, R. H. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 454.
(9) Wiesner, U. *Macromol. Chem. Phys.* **1997**, *198*, 3319.
(10) Chen, Z. R.; Kornfield, J. A.; Smith, S. S.; Grothaus, J. T.; Satowski, M. M. *Science* **1997,** *277*, 1248.
(11) Okamoto, S.; Saijo, K.; Hashimoto, T. *Macromolecules* **1994**, *27*, 3753.
(12) Pinheiro, B. S.; Winey, K. I. *Macromolecules* **1998**, *31*, 4447.
(13) Wang, H.; Kesani, P. K.; Balsara, N. P.; Hammouda, B. *Macromolecules* **1997**, *30*, 982.
(14) Koppi, K. A.; Tirrell, M.; Bates, F. S.; Almdal, K.; Colby, R. H. *J. Phys. 2, Fr.* **1992**, 1941.
(15) Bates, F. S. *Macromolecules* **1984,** *17*, 2607.
(16) Leist, H.; Geiger, K.; Wiesner, U. Manuscript in preparation.
(17) Zhang, Y.; Wiesner, U.; Yang, Y.; Pakula, T.; Spiess, H. W. *Macromolecules* **1996**, *29*, 5427.
(18) Lodge, T. P.; Fredrickson, G. H. *Macromolecules* **1992**, *25*, 5643.
(19) Ehlich, D.; Takenaka, M.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 189. Strictly speaking calculation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ is only valid for uniaxial symmetry, which is broken in the case of strong flow. In the present SAXS experiments the lamellar orientation, rather than a molecular property, is probed; therefore the concept of a direction of average orientation remains useful.
(20) Zhang, Y.; Wiesner, U. *J. Chem. Phys.* **1995**, *103*, 4784.
(21) Larson, R. G.; Öttinger, H. C. *Macromolecules* **1991**, *24*, 6270.
(22) Romo-Uribe, A.; Windle, A. H. *Macromolecules* **1993**, *26*, 7100.
(23) Romo-Uribe, A.; Windle, A. H. *Macromolecules* **1996**, *29*, 6246.
(24) Pakula, T. *J. Macromol. Sci.—Phys.* **1998**, *B37*, 181.

MA981544C