

THE EFFECTS OF STEADY SHEAR ON THE ORDER AND ORIENTATION OF A DIBLOCK COPOLYMER MELT USING IN-SITU SMALL-ANGLE NEUTRON SCATTERING

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Abstract

To understand the effects of processing on polymer melts requires experimental techniques that show the orientation of materials during processing. Small-angle neutron scattering (SANS) has been recently adapted to allow for examination of polymeric materials during shear. This work will highlight the benefits of combining shear and scattering techniques to study morphology, ordering and orientation of a polystyrene-polybutadiene diblock copolymer melt under steady shear flow. The order-disorder transition temperature (T_{ODT}) is unchanged at low shear rates but increases by $\Delta T_{ODT} \approx \dot{\gamma}^{1.35}$ at high shear rates. An analysis of the degree of orientation using order parameter calculations shows that maximum ordering occurs within 30 minutes of shear and better alignment is obtained at low shear rates. A large relative increase in the order parameter (up to 600 %) is seen upon cessation of the shear flow.

Introduction

Materials with ordered states on microscopic length scales that involve phase transitions are of interest to many scientists and engineers. The increasing demands of technology are continually calling for smaller structures with improved characteristics and performance. Liquid crystalline polymers (LCP's) and displays (LCD's) are examples of the recent advances in the study of ordered structures on intermediate (mesoscopic) length scales. Another fascinating class of materials that inherently form ordered structures on small scales (10 - 20 nm) are block copolymers. Block copolymers have been commercially exploited in the last 35 years as thermoplastic elastomers, used in the production of pressure-sensitive adhesives, high-performance automobile parts and impact-resistant plastics, to name a few. Ordered phases are primarily of interest to research engineers and scientists who try to develop, understand, and control the ordering and alignment processes of microscopic block-copolymer domains. Control of the microphase separation and ordering of biphasic block copolymer melts could allow use and control of the small structures as membranes, electrical devices or unidirectional flow devices that can be turned on and off with the phase-transition process.

The focus of this paper is on ordering and alignment of a diblock copolymer in response to shear. In particular, the work describes the *in-situ* small-angle neutron scattering (SANS) of a (deuterated)polystyrene-polybutadiene (dPS-PB) diblock copolymer exhibiting cylindrical microdomains when microphase separated. The effect of shear on the order-disorder transition temperature and the alignment of ordered domains using an order-parameter analysis of the SANS during and after shear are presented.

Background

Block copolymers undergo a transition (termed the order-disorder transition, ODT) from microphase-separated, ordered structures to a homogenous single phase with temperature. When microphase-separated, the polymer block chains gather into ordered domains in response to repulsive interactions between blocks. These domains form structures commonly seen in crystals and metals such as spheres on a cubic lattice, cylinders on a hexagonal lattice and alternating lamellae. The strength of the repulsion between the polymers (χ), the length of the polymer chains (degree of polymerization N), and the relative amounts of the A and B polymers (volume fraction, ϕ) are known to be the three main factors controlling the thermodynamics of microphase separation in block copolymers.

Phase behavior of block copolymers under static conditions as a function of the system characteristics (N , χ , ϕ) and temperature has been extensively investigated [1]. In addition, work has been done to study the influence of shear on block copolymer systems in efforts to align the microdomains and induce long-range order [2]. Researchers have found that shear can enhance the degree of microdomain alignment in block copolymers and that it may also effect the order-disorder and order-order transitions in block copolymers. Both the phase behavior and degree of microdomain alignment in the flow direction are important when relating block copolymers to industrial uses where shear forces are inevitable.

Neutron scattering is used to reveal phase and order information of block copolymers under various conditions of shear and temperature. The length scale of microphase-separated domains in block copolymers is on the order of tens of nanometers which is much larger than the periodic domains seen in small-molecule crystals and metals. Scattering spectra are reported by the intensity of scattering as a function of wavevector:

$$q = 4\pi/\lambda \sin \theta/2 \quad (1)$$

which is specifically related to distances in real-space. Since this relation between the scattering distance q , and the real-space distance is inversely proportional, large structures require small values of q to capture the scattering. The value of q is determined by the wavelength and scattering angle of the incident neutron beam, and therefore small angles and small q are used when large structures are probed and is referred to as small-angle neutron scattering (SANS).

The scattering image from a block copolymer takes on different forms in the homogeneous and microphase-separated states. The intensity of scattering from the homogeneous block copolymer exhibits an isotropic scattering ring called the correlation-hole effect, described originally by de Gennes [3] and experimentally observed by Bates [4,5]. Correlation hole scattering is caused by density fluctuations in the material which occur on the same length scale as the radius of gyration, R , of the polymer components. A low intensity isotropic ring from the correlation-hole effect is the only significant scattering feature observed when the melt is in the disordered state.

In the microphase-separated state, the intensity of scattering is a convolution of the single structure particle form factor and the lattice structure of the ordered domains. Information on microdomain alignment is obtained from lattice scattering which is a result of the interparticle interference from the regular, periodic spacings of the microdomains. Constructive interference occurs at specific points due to the regular lattice structure with maxima of constructive interference located at positions corresponding to different lattice plane spacings of the microstructure. The incident neutron beam, at a wavelength, λ , provides scattering related to the distance between planes (analogous to crystalline plane spacing), d , and the scattering angle, θ by Bragg's law as represented schematically in Figure 1.

$$n\lambda = 2d\sin(\theta/2) \quad (2)$$

Assuming elastic scattering dominates [6], the wavelength ($2\pi/\lambda$) of the incoming incident beam vector remains unchanged and only the direction changes. Using the definition of q (Equation 1) and substituting in λ from equation 2, we arrive at the following:

$$2\pi/q_{max} = d \quad (3)$$

where n has been set to unity for first-order scattering. This important relation tells us how the locations of the maxima in scattering (q_{max}) from ordered structures which satisfy the Bragg conditions can be directly related to various interplanar distances in the material, therefore providing information on the spacings of the microdomain lattice and the size of the microdomains in question.

Using this knowledge about correlation hole and lattice scattering, we can determine when the block copolymer melt is homogeneous and the orientation of lattice planes when microphase separated. Using *in-situ* SANS and shear allows for imaging of the morphology in block copolymers while transitions occur and morphologies develop.

Experimental

A diblock copolymer of (deuterated) polystyrene-polybutadiene with a total molecular mass of 27,500 g/mol (7,400 g/mol dPS and 20,100 g/mol PB) was prepared by Dr. Jimmy Mays of the University of Alabama. This material, in the microphase-separated state, forms cylinders on a hexagonal lattice consisting of polystyrene in a matrix of polybutadiene.

SANS experiments were performed at the NIST Center for Neutron Research in Gaithersburg, MD. A couette shearing device was used for the steady shear experiments which has been adapted for simultaneous use with neutron scattering. The through view is oriented with the neutron beam parallel to the shear gradient, y , direction, and the tangential view is configured with the incoming neutron beam along the shear-gradient direction as shown in Figure 2.

Order parameter analysis was performed on the SANS experimental data taken in the through view to give information on the degree of alignment of cylinders in the shear direction (relative to cylinders directed in other positions). An order parameter (ψ) of 1 indicates complete orientation of the cylinder planes (and therefore the cylinders) in the direction of shear using the following equation: [7]

$$\psi = \frac{1}{2} [3\langle \cos^2 \phi \rangle - 1] \quad (4)$$

The term $\langle \cos^2 \phi \rangle$ represents the mean-square of the angle between the rod axis and the flow direction axis as defined by:

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (5)$$

As the angle, ϕ , between the flow direction and the cylinder planes goes to zero (corresponding to the azimuthal angles of 90° and 180°), the cosine portion of Equation 5 dominates, and ψ goes to unity. Conversely,

as the angle between the flow direction and the cylinders becomes 90° (perpendicular to one another), the sine contribution dominates, and ψ becomes -0.5 .

There is one serious limitation to the order-parameter analysis. Since the scattering of lattice planes is dependent upon the satisfaction of Bragg conditions, the number of scattering sites (lattice planes which contribute to the scattering image) is not constant throughout all the experiments. Therefore, comparison of the order-parameter between experiments is restricted by a relative standard uncertainty of 7.5 %

Results

The order-disorder transition temperature, T_{ODT} , determined by the rheological tests indicate a zero-shear ODT temperature of $103^\circ\text{C} \pm 1^\circ\text{C}$. This is confirmed by the fact that no peaks are observed in the scattering pattern from SANS above 103°C during low shear conditions. Interestingly, there appears to be no change in the ordering temperature at moderate shear rates of 0.17 , 0.34 and 1.70 s^{-1} . As the shear rate is increased further, the transition between no-peak observed (disordered) and one-peak observed (ordered) occurs at slightly higher temperatures, falling between 103°C and 104°C at 3.4 s^{-1} , between 104°C and 107°C at 6.8 s^{-1} and above 107°C at 17 s^{-1} . This transition is marked by a line indicating the shear rate required to induce ordering at temperatures which show disorder under zero-shear conditions in Figure 3. It clearly shows that for the diblock material used in this research, the ODT shows no dependence on shear at rates up to 1.70 s^{-1} ($\Delta T_{\text{ODT}} \approx \dot{\gamma}^0$). Above this region, the T_{ODT} becomes strongly dependent on shear rate to the power of 1.35 ($\Delta T_{\text{ODT}} \approx \dot{\gamma}^{1.35}$).

The order parameter is used as a method to monitor the percentage of lattice planes that are guided along the flow direction. From the example in Figure 4, it is immediately apparent that the maximum ordering of 110 planes in the shear planes occurs within 30 min of the onset of shear. After such time, the material response shows little or no dependence on the time of shear and therefore does not exhibit strain-dependence after the maximum degree of alignment has been reached. It appears that at temperatures farther from the ODT, maximum alignment is achieved. This can be explained by the idea that the thermal effects very near the ODT temperature allow more freedom for the polymer chains to exhibit amorphous behavior, showing a more isotropic nature as the ODT transition is approached. This is characteristic of the fluctuation effects discussed in the theory of mean-field behavior.

The behavior after cessation of shear of the styrene-butadiene diblock material is perhaps the most remarkable observation of this study. Order-parameter calculations

show the alignment of 110 planes in the shear plane can display a relative increase of 600 % after cessation of shear. Monitoring the progression of the order parameter for shear rates of 3.4 s^{-1} , at 99°C the order parameter increases 30 % immediately after cessation of shear and maintains that degree of alignment through 70 min after cessation of shear. Similarly, at 100°C , the order parameter jumps by 40 % after shearing has stopped. After a 2°C temperature increment to 102°C , the initial order parameter is low and shows a small increase after shear stops. Interestingly, the alignment continues to grow over the next 60 min and then starts to level off, giving a total relative increase from the end of shear to the 70 min after shear of 600 %. A separate run under the same experimental conditions is shown in Figure 4 where shearing had been performed for 90 min total followed by 90 min of cessation data. The initial degree of alignment remains approximately the same at an order parameter of 0.05 and the cessation behavior increases a little more quickly, reaching a constant increase within 10 min. This indicates that the cessation behavior does depend on the length of time sheared. In this case, the longer shear time produces a lower alignment after cessation (although it is still a 300 % increase). These reported increases far exceed the 7.5 % relative standard uncertainty associated with a change in lattice scattering sites.

An isothermal comparison of runs taken at increasing shear rates is also shown in Figure 4. Similar to the behavior during shear, the experiments with the lowest shear-rates produce the highest order-parameter after cessation as well. The largest overall change in the order parameter, however, is seen at an intermediate shear rate of 1.7 s^{-1} where the order parameter increases with time after shear stops to give a relative final order-parameter increase of 560 % from the value during shear. The jump in order parameter after cessation of higher shear rates is less dramatic than for the lower shears mentioned above. This indicates that high shear rates somehow prohibit the after-shear alignment process.

An increase in planar alignment in the direction of flow like the one seen in the present study has not yet been reported. Most *in-situ* shear studies, however, have reported only limited results on the material behavior after shear. An increase in the order parameter after shear has been reported in liquid crystalline solutions [8] and for liquid-crystalline suspensions of cellulose microfibrils [9]. Orts et al. reported that long cellulose microfibrils show an increase in alignment after shear flow has ceased and show an initial change in the order parameter from 0.86 to 0.91. This alignment slowly decays as the time after shear progresses which is in contrast to the present study which maintains a much larger increase in alignment after shear for the entire time that cessation data were collected.

The magnitude of such a relative increase (up to 600 % as shown in Figure 3) is fascinating but may be simple

to explain. We assume that the cylinders arrange in their preferred lowest energy state after shear. Considering the high shear rates applied to the material, the shearing stresses will fracture the cylinder and/or the matrix of cylinders and cause more randomness with shear than alignment. This will be apparent in the block copolymer as defects in the material and/or a different shear morphology resulting from the applied stresses. After the shear is stopped, the system returns to the lowest energy state, as evidenced by the increase in order parameter.

Conclusions

Combined shear and neutron scattering experiments have been used to identify phase behavior and microdomain alignment in a polystyrene-polybutadiene diblock copolymer. Shear has been shown to increase the temperature of the order-disorder transition at high shear rates by $\Delta T_{ODT} \approx \dot{\gamma}^{1.35}$. Using an order-parameter calculation, we have shown that a significant increase in the alignment of lattice planes in the shear direction occurs after the cessation of shear. The alignment of lattice planes along the flow direction occurs within the first ten minutes of shear and stabilizes at that point, displaying a strong dependence only at the onset of shear. Once the shearing has been turned off, the order parameter consistently increases, in some cases up to 600 % of the parameter obtained during shear. The overall increase in alignment appears to be most favorable in the low shear-rate regime and might be attributed to a mixing of shear planes at high shear rates that cannot be recovered. To the best of our knowledge, this is the first report of an increasing degree of alignment in a block-copolymer melt after shear has stopped.

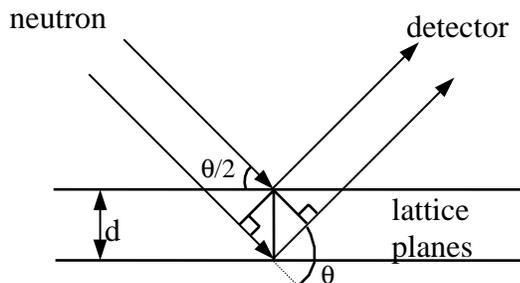


Figure 1: Schematic of the picture relating Bragg's law to scattering from lattice planes as a function of the interlattice distance, d , and the scattering angle, θ .

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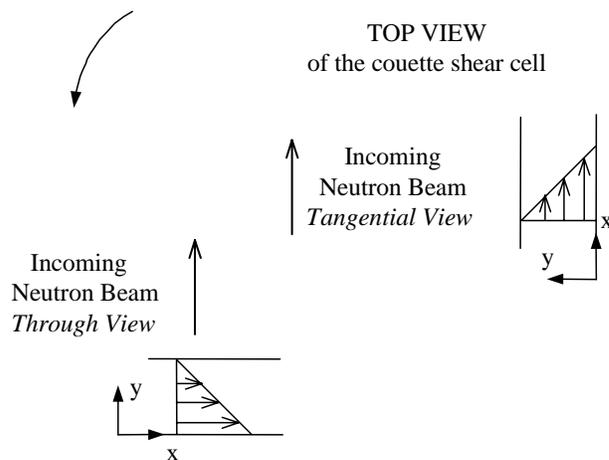


Figure 2: Schematic of the simple shear flow in two positions on the couette geometry used for small-angle neutron scattering.

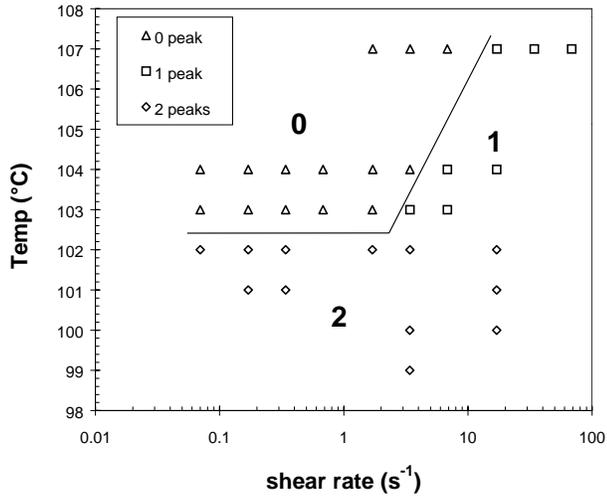


Figure 3: The number of observed peaks from scattering as a function of temperature and shear rate. The solid line shows the change from order to disorder with shear.

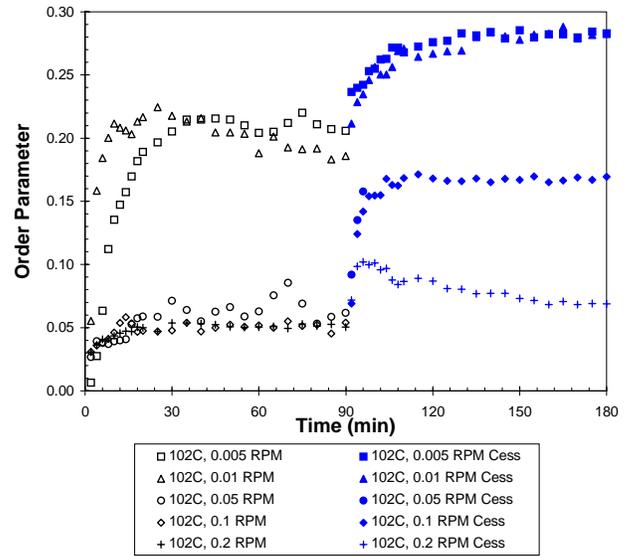


Figure 4: Order-parameter calculations performed on intensity at the first peak (q^*) at 102 °C and 0.17 s⁻¹, 0.34 s⁻¹, 1.7 s⁻¹, 3.41 s⁻¹ and 6.82 s⁻¹.