Macromolecules 1991, *24*, 6546-6548

Effect of an Electric Field on Block Copolymer Microstructure

Introduction. External forces such as those induced by flow[1-5] and surfaces[6-8] have been shown to cause alignment of block copolymer microstructure. In this paper, we report the alignment of lamellar microstructure by an electric field. Electrostatic alignment of microstructure could be used to tailor anisotropic properties in block copolymer materials. In addition, electrostatic interactions with block copolymer composition fluctuations and microstructure can be exploited to study the behavior of block copolymers near the order-disorder transition (ODT). This will be the subject of a future report.

Electrostatic Interaction with Composition Variations. If an electrostatic field is applied to a dielectric material, the free energy contains an electrostatic contribution[9]

$$\mathcal{F} = \mathcal{F}_0 - \frac{1}{8\pi}\int_V \epsilon(\mathbf{r})\,|\mathbf{E}(\mathbf{r})|^2\,\mathrm{d}^3\mathbf{r} \qquad (1)$$

where $\mathcal{F}$ is the free energy, $\mathcal{F}_0$ the free energy in the absence of an electric field, $\epsilon(\mathbf{r})$ the local dielectric constant, and $\mathbf{E}(\mathbf{r})$ the electric field. Different composition patterns within a block copolymer material, and the associated spatially varying local dielectric constant, produce different patterns in the electric field. The consequence is a composition-pattern-dependent electrostatic contribution to the free energy. Certain orientations of the composition pattern are thus thermodynamically favored over others.

The ability to induce macroscopic anisotropy in block copolymer microstructure with an electric field depends not only on the field strength but also on the size of ordered regions being acted upon by the field. For example, consider the situation where block copolymer material in the high-temperature, disordered phase is held between flat, parallel electrodes used to create an electric field. In the disordered phase there are time-varying composition fluctuations but no stationary composition pattern. The copolymer is slowly cooled, and the ordered phase first appears as a nucleation center, which is described as a stationary plane wave composition pattern within a sphere of radius R, as depicted in Figure 1. This scenario, developed by Fredrickson and Binder,[10] is based upon the theory of microphase separation of Leibler[11] as extended by Fredrickson and Helfand[12] to include fluctuation effects.

The electrostatic contribution to the free energy associated with the plane wave pattern within the ordered region contains an anisotropic term of the form[13]

$$\frac{1}{48}|\mathbf{E}_0|^2 R^3 a^2 \left(\frac{\beta^2}{\epsilon^{(0)}}\right)(\hat{\mathbf{e}}_z\cdot\hat{\mathbf{e}}_k)^2 \qquad (2)$$

where a is the amplitude of the plane wave pattern, $\epsilon^{(0)}$ is the dielectric constant in the absence of fluctuations, and β is the rate of change of the dielectric constant with composition: $\beta = \mathrm{d}\epsilon/\mathrm{d}\phi$, where ϕ is the local volume fraction of one of the copolymer components. Equation 2 is zero when the wave vector, $\mathbf{k}$, is orthogonal to $\mathbf{E}_0$ and a maximum when $\mathbf{k}$ is parallel to $\mathbf{E}_0$. Note that this energy is proportional to the volume of the ordered region. If the applied field is sufficiently large and ordered regions are of sufficient size that this term is at least comparable to thermal energy, then the ordered regions and resultant microstructure will be aligned so that the composition pattern wave vectors have a significant tendency to be orthogonal to the applied field. For a lamellar microstructure (the case studied here) this is the set of orientations for which the lamellar planes contain the electric field vector. For a cylindrical microstructure, the minimum energy orientation would place the cylindrical axes parallel to the field. By symmetry, there would be no anisotropy in the electrostatic energy associated with spherical or bicontinuous double-diamond microstructures.

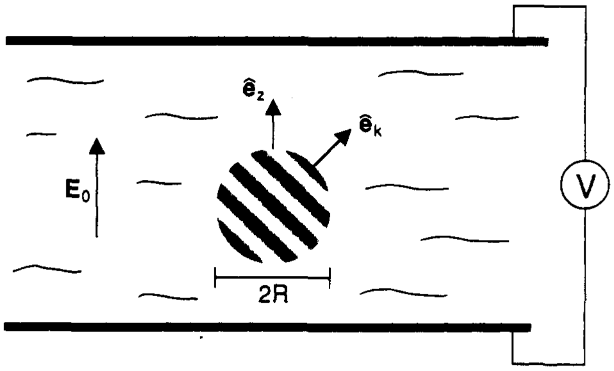

Figure 1. Schematic of the nucleation of an ordered phase in a disordered block copolymer phase in a uniform applied electric field $\mathbf{E}_0$. $\hat{\mathbf{e}}_z$ and $\hat{\mathbf{e}}_k$ are unit vectors in the direction of the applied field and the composition pattern wave vector, respectively. R is the nucleation center radius. The light and dark bands within the nucleation center represent a plane wave composition variation pattern with wave vector $\mathbf{k}$. The size of the nucleation center is greatly exaggerated. The wavy lines represent a background of disordered material (containing other nuclei far removed).

It should be mentioned that Le Meur and co-workers[14] found that dilute (6-9 wt %) solutions of a symmetric polystyrene-polyisoprene diblock copolymer (MW ~ 1 400 000) in toluene and styrene exhibited anisotropic diffraction of UV light after application of an electric field. The diffracting element had a repeat distance of about 360 nm. Also, interesting new morphological structures have been shown to arise in poly(ethylene oxide)/polystyrene polymer *blends* undergoing phase separation in an electric field.[15] The coupling between an electric field and the compositional variations in polymer blends is similar to the coupling of the field with block copolymer microstructure—in each case, the electric field couples to space charges created by the electric field and variations in the local dielectric constant. A difference between the subject of this paper and the work with polymer blend morphology in electric fields is that for block copolymers the morphological structures are given predominantly by thermodynamics, while in blends the reported morphologies are determined by kinetics.

Experimental Section. Synthesis and Characterization. The polystyrene-poly(methyl methacrylate) diblock copolymer was synthesized anionically. Its molecular weight average was 37 000 (polydispersity index, 1.07), as determined by size-exclusion chromatography using polystyrene standards. The composition was determined to be 53 vol % polystyrene by ^{1}H NMR. The ODT temperature was determined by dynamic mechanical spectroscopy to occur at 251 ± 1 °C.[16]

Poling Experiment. The poling apparatus is shown in Figure 2. Heated nitrogen gas flows through the poling apparatus. A rectangular reservoir between the two electrodes is filled with PS-PMMA block copolymer between 180 and 200 °C. A platinum resistance temperature detector, bolted to the lower electrode, has an accuracy of ±2 °C and a precision of 0.2 °C. The temperature of the poling apparatus was calibrated against

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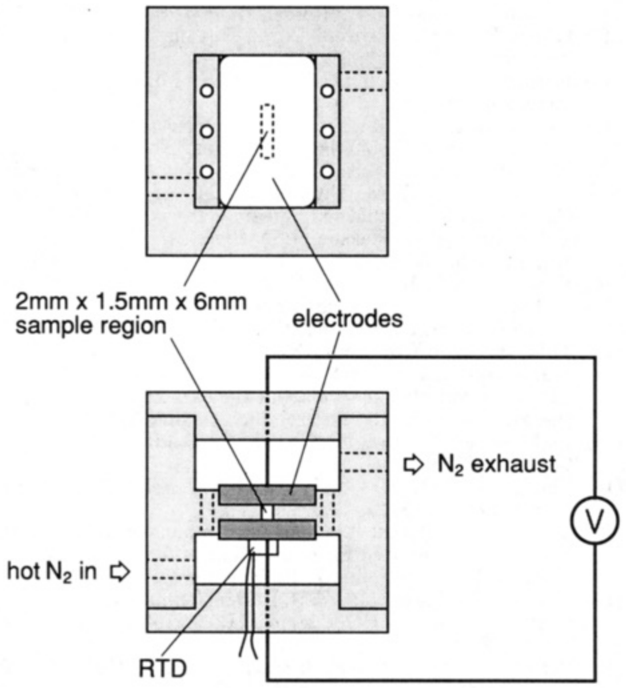

Figure 2. Top (upper) and side (lower) cross-sectional views of the poling apparatus.

the Rheometrics dynamic mechanical spectrometer used to measure the ODT temperature.

The temperature was raised either 14 or 30 °C above the ODT, held within a few degrees of that temperature for about 10 min, and then slowly cooled (4 °C/min). A voltage of 3.53 kV was applied across the two electrodes (producing an electric field of 17.7 kV/cm) once the upper set point temperature was reached and was maintained throughout cooling down to below the glass transition (at 120 °C). A control experiment was run before each poling experiment, where the same procedure was followed, but no voltage was applied.

SAXS. Small-angle X-ray scattering (SAXS) was done at room temperature using Cu Kα radiation with pinhole collimation and a Rigaku vacuum camera. The anode voltage was 25 kV, and the anode current was 10 mA.

Results. After each control experiment or poling operation, samples were removed for analysis by SAXS at ambient temperature. Typical SAXS patterns are shown in Figure 3. Samples were oriented in the SAXS apparatus so that the direction of the applied electric field (indicated by the arrow in Figure 3) was orthogonal to the direction of the X-ray beam. The scattered ring position corresponds to a repeat distance of 23 ± 1 nm; this agrees with the calculated 22-nm lamellar period, based upon the theory of Helfand and Wasserman.[17,18] Parts a and b of Figure 3 show the results of thermal cycles in the absence of an electric field. After cooling from 281 °C, the material exhibits no preferred orientation of its lamellae, as expected. After cooling from 265 °C, some anisotropy is present. This anisotropy was repeatedly observed and typically resulted in SAXS intensity maxima within ±45° of the vertical. It is apparently induced by the flow involved in filling the poling apparatus. (We can rule out the possibility that surfaces induce this alignment because microstructure aligned in a different direction by the electric field persists even after heating to 265 °C in the absence of a field. Also, all anisotropy is eliminated by heating samples to 281 °C.) The persistence of anisotropy even after heating above the ODT is a direct consequence of metastability inherent in the first-order character of the phase transition, as discussed below.

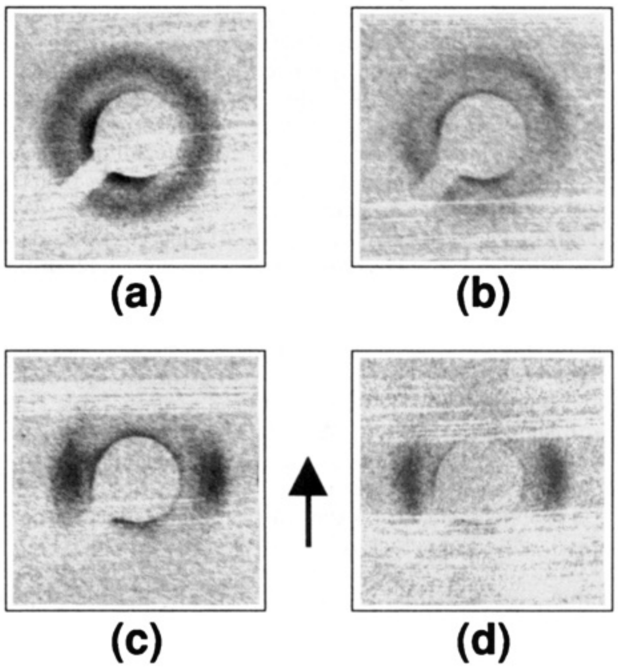

Figure 3. SAXS patterns from block copolymer samples after cooling from (a) 265 °C and (b) 281 °C in the absence of an electric field. c and d are of the same samples, respectively, but after a second identical thermal cycle where a 17.7 kV/cm electric field was applied during cooling. The arrow indicates the direction of the applied field during poling in c and d.

Poled samples exhibit strong anisotropy as shown in parts c and d of Figure 3. In both cases, most of the scattering intensity lies within 20° of the horizontal, indicating that lamellar surfaces are strongly oriented *orthogonal* to the electrode surfaces. This is the orientation of minimum electrostatic free energy. The fact that this anisotropy was not present before poling (compare with Figure 3a,b) is persuasive evidence that the microstructure was aligned by the electric field.

Discussion. The SAXS results clearly show that macroscopic alignment of microstructure in a symmetric diblock copolymer can be induced by application of an electric field while cooling through the ODT. Based upon eq 2, the nucleation centers would need at least a 150-nm radius to be significantly aligned against thermal randomization. The theory of Fredrickson and Binder predicts that nucleation centers as small as 45 nm are stable (a size somewhat smaller than required for quantitative applicability of the theory). Thus it seems likely that a nucleation center grows and then reorients by rotation of the ordered region as a whole once its radius reaches about 150 nm. Based upon the viscosity of the disordered phase and field strength, the time scale for reorientation is estimated to be on the order of minutes. (The time scale for ordering of the block copolymer used in this study has not been measured. Rosedale and Bates[19] found this time scale to be tens of minutes for a symmetric polyalkene diblock copolymer at 4 °C supercooling, although the ODT temperature and molecular weight of that copolymer were very different from those for the block copolymer used in this study.) Another possibility is that nucleation centers coalesce to form a polydomain structure with no macroscopic orientation. Subsequent alignment would occur by movement of "grain boundaries" such that regions of favorable orientation grow at the expense of neighboring regions.

Supercooling of the ordering transition has been studied in a symmetric polydiene diblock copolymer by means of rheology.[19,20] However, to our knowledge, the presence of superheated metastable structures in diblock copolymers has not been previously reported. Such structures could perhaps be destroyed by flow and thus may not be observed in rheological studies (this is suggested by the fact that these structures can be altered significantly by the comparatively weak influence of an electric field, as we have shown). The persistence of macroscopic alignment even after heating the material 14 °C above the ODT, as shown by SAXS, indicates the presence of metastable structures that persist at least as long as the time of superheating, about 10–15 min. Using the theory of Fredrickson and Binder,[10] we predict that metastable states will become unstable at 260 °C. However, this theory is not expected to make quantitative predictions for copolymers with the low degree of polymerization used in this study. The observation that metastable structures could be reoriented or selectively destroyed by an electric field was unexpected. The mechanism by which this occurs is under consideration and will be the subject of a future report.

Acknowledgment. We thank Glenn Fredrickson for helpful discussions and Arman Ashraf for assistance in synthesis and characterization of materials.

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Karl Amundson,* Eugene Helfand, Don D. Davis,
Xina Quan, and Sanjay S. Patel

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Steven D. Smith

The Procter and Gamble Company
Cincinnati, Ohio 45239

Received May 23, 1991
Revised Manuscript Received August 21, 1991

Registry No. PS–PMMA (block copolymer), 106911-77-7.