Ellipsometry as a Probe of Crystallization Kinetics in Thin Diblock Copolymer Films

J. L. CARVALHO, M. V. MASSA, K. DALNOKI-VERESS

Department of Physics and Astronomy and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, L8S 4M1

ABSTRACT: We present results on the use of ellipsometry as a novel probe for the crystallization kinetics in thin films of a diblock copolymer. Ellipsometry makes use of the change in polarization induced upon the reflection of light from a film-covered substrate to enable the calculation of the refractive index and thickness of the film. The information obtained with these measurements can be compared with information from differential scanning calorimetry, with the additional advantages that small sample volumes and slow cooling rates can be employed and that expansion coefficients can be determined. By studying the temperature dependence of these quantities, we are able to measure the crystallization kinetics within very small volumes ($\sim 10^{-10}$ L) of a poly(butadiene-*b*-ethylene oxide) diblock copolymer. Through a comparison of two different poly(ethylene oxide) block lengths, we demonstrate a reduction in both the crystallization and melting temperatures as the domain volume is reduced. © 2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 3448–3452, 2006

Keywords: block copolymers; crystallization; nucleation

INTRODUCTION

Crystallization and interblock incompatibility in semicrystalline block copolymers drive self-organization, resulting in complex, ordered structures. In particular, when the crystal block is the minority component, crystallization may be restricted within nanoscale domains, and this allows for the study of crystal confinement. There are several recent reviews detailing progress as well as outstanding issues with semicrystalline block copolymers[1–3] and polymer crystallization in general.[4,5]

Confined crystallization in a semicrystalline–glassy block copolymer was first studied by Lotz and Kovacs[6] in an asymmetric poly(ethylene oxide-*b*-styrene) and later investigated by Robitaille and Prud'homme.[7] One of the main results was that large undercoolings were required to initiate crystallization, and this suggested that homogeneous nucleation (an intrinsic property of the material) was observed rather than heterogeneous nucleation (which is defect-driven). In general, when crystallization is confined to domains on a nanometer length scale, the kinetics are drastically different from those of bulk samples. Nucleation is thought to occur homogeneously because the number of domains is far greater than the number of defects, which usually serve as heterogeneous nucleation sites in bulk homopolymer systems.[8] The small size of the domains has two consequences: (1) the timescale for crystal growth is much smaller than that for nucleation, and (2) within a single sample, there is a large ensemble of isolated domains, each of which must crystallize by first forming a nucleus. This situation

Correspondence to: K. Dalnoki-Veress (E-mail: dalnoki@mcmaster.ca)

makes it possible to measure nucleation rates independently of the crystal growth. For systems in which the crystallization kinetics are driven by nucleation rather than crystal growth, the rate is proportional only to the number of domains yet to be crystallized, resulting in first-order kinetics.[2,6,8–10]

A deviation from first-order kinetics occurs when confinement is not strong enough to contain crystallization. Studies have shown that when the matrix is rubbery as opposed to glassy, crystallization can break out and destroy the phase-separated melt morphology.[2,11–14] However, if the blocks are strongly segregated, this may not be the case, and the phase-separated morphology can be preserved upon crystallization.[9] Chen et al.[10] found that they could increase confinement by blending poly(butadiene-*b*-ethylene oxide) (PB–PEO) with a low-molecular-weight polybutadiene (PB) homopolymer.

Previous studies of semicrystalline block copolymers have employed a range of techniques to probe the kinetics, with differential scanning calorimetry (DSC) being the most commonly used.[2,7,9,10,14–16] Atomic force microscopy (AFM) studies by Reiter et al.[8] have allowed for the direct visualization of nucleation within individual spherical domains of thin PB–PEO films. The use of AFM was particularly insightful because the random distribution of nucleated domains verified that crystallization was occurring in each sphere, independently of neighboring sites.

In this article, we employ ellipsometry to study crystallization in sphere-forming PB–PEO thin films. Ellipsometry measures changes in the polarization of elliptically polarized light upon reflection from a film-covered substrate to enable the calculation of the refractive index and thickness of the film.[17] In a nulling ellipsometer, light from a laser is passed through a quarter wave plate and a polarizer at an angle such that it is elliptically polarized before it reaches the sample but linearly polarized upon reflection. The light then passes through a second polarizer (called the analyzer), which is oriented such that all light is extinguished. The polarizer and analyzer angles can be inverted to calculate the film thickness and refractive index *if an isotropic film is assumed*. By monitoring the temperature dependence of these quantities, we can observe the densification associated with crystallization. To the best of our knowledge, the use of ellipsometry to characterize crystallization in polymer films is novel. Ellipsometry is a particularly useful probe for semicrystalline block copolymer systems. Through spin casting, it is straightforward to make thin films

that are suitably uniform for ellipsometry. The footprint of the laser beam on the sample is on the order of millimeters, whereas a typical spherical domain is on the nanometer length scale. Thus, in a single experiment, millions of domains are probed, each acting as a separate experiment in its ability to nucleate independently. Furthermore, the film can still be approximated as an isotropic medium because we are averaging over many domains almost 2 orders of magnitude smaller than the wavelength of the light used to probe them.

Here we extend our previous studies of crystallization in confinement, using ellipsometry to investigate nucleation in block copolymer systems. In our earlier work, we investigated how the nucleation rate scales with the domain size.[18] For the study presented here, we compare two diblocks that differ only in the length of the poly(ethylene oxide) (PEO) block. Given the uniformity of the domain sizes in the phase-separated block copolymers, this is an ideal system for a size comparison of nucleation kinetics.

EXPERIMENTAL

Thin films of poly(1,4-addition butadiene-*b*-ethylene oxide) were used for this study. All polymers were purchased from Polymer Source, Inc. (Dorval Quebec, Canada). Two polymers were compared that differed only in the length of the PEO chain. These were PB–PEO [number-average molecular weight of polybutadiene, $M_{n,PB}$ = 26 kg/mol, number-average molecular weight of poly(ethylene oxide), ($M_{n,PEO}$) = 6.8 kg/mol, and polydispersity index, M_w/M_n = 1.06] and PB–PEO ($M_{n,PB}$ = 26 kg/mol, $M_{n,PEO}$ = 4.5 kg/mol, M_w/M_n = 1.06). For these sphere-forming systems, the larger PEO block had a sphere radius (R) of 12.5 nm,[19] whereas the smaller block had R = 8.3 nm.[20] The PB–PEO diblocks were blended with the PB homopolymer (M_n = 1.1 kg/mol, M_w/M_n = 1.14, 1,4-addition) to inhibit domain coalescence upon crystallization.[19] The molecular weight of the PB homopolymer was much smaller than the PB block molecular weight to ensure wet-brush blends.[22] The PB–PEO/PB blends (20 wt % PB) were dissolved in toluene and spin-cast onto clean Si substrates that had been UV–ozone-treated to remove organic contaminants. The solution concentrations and spin speeds were varied to produce films with thicknesses greater than 60 nm but less than 170 nm.

After the preparation of the PB–PEO/PB films, the samples were annealed either in vacuum or in a dry nitrogen environment for at least 1 h at a temperature of 90 °C. This annealing temperature was above the melting temperature (T_m) for bulk PEO ($\approx$64 °C) and the glass-transition temperature (T_g) of 1,4-addition PB (< -40 °C)[23] but well below the order–disorder-transition temperature ($>$220 °C).[24] The resulting phase-separated morphology consisted of PEO minority spheres in a PB matrix, as verified by AFM. After annealing, the sample was transferred to the ellipsometer.

For our measurements, we used a custom-built, single-wavelength (632.8 nm), self-nulling ellipsometer. The temperature was controlled to 0.1 °C with a Linkam THMS 600 stage, and all experiments were conducted in a dry nitrogen atmosphere. The samples were annealed at 70 °C for a few minutes before being cooled to -30 °C, held there for 30 min, and then heated to 70 °C. In all experiments presented here, heating and cooling were carried out at 1 °C/min. The measured polarizer and analyzer null angles were inverted to the film-thickness and refractive-index values with the standard equations of ellipsometry.[17]

RESULTS AND DISCUSSION

The versatility of ellipsometry complements information gained through other techniques. This study shares some similarities with DSC measurement; however, ellipsometry allows for the study of thin films (volume $\sim 10^{-10}$ L). AFM has proven to be a very useful tool in thin-film studies,[8] although dynamic experiments are challenging. Typically, DSC requires fast heating and cooling rates ($\sim$10 °C/min). Ellipsometry is capable of both dynamic and isothermal experiments, which can serve to complement understanding gained through AFM and DSC. Furthermore, with ellipsometry, we have the ability to use quick temperature ramp rates ($\sim$50 °C/min) or rates as slow as one is willing to wait. The ability to carry out isothermal and dynamic experiments with very small volumes makes ellipsometry a versatile and complementary tool for the study of crystallization.

To study homogeneous nucleation in confined spherical domains of a phase-separated block copolymer, the melt morphology must be preserved upon crystallization. For our PB–PEO/PB films, T_g of the PB matrix is well below the crystallization temperatures (T_c's), which means that the PB matrix is in the rubbery state for the temperature range accessed. However, as Chen et al.[10] demonstrated, this diblock is strongly segregated, with confinement further strengthened by the presence of the PB homopolymer. Thus, crystallization is effectively confined within the spherical domains without breakout or domain coalescence occurring when T_c's are reached.

The results of a typical ellipsometry experiment are shown in Figure 1. We have measured the polarizer and analyzer angles that result in a null at the detector as a function of the temperature, and these have been converted into a measure of the thickness and index of refraction. The example shown in Figure 1 is the larger PEO block sample; however, although the quantitative features vary, the basic qualitative features of the thickness and index plots are the same for both block lengths.

A novel feature of using ellipsometry to study block copolymer crystallization is the ability to measure changes in a film's coefficient of volume expansion (α) due to crystal-related thermal transitions from plots of the film thickness versus the temperature [see Fig. 1(c)]. As the sample is cooled from 70 to -21 °C, we can observe that the PB melt matrix and the PEO supercooled melt contract at a constant rate [$\alpha = (7.3 \pm 0.2) \times 10^{-4}$ K^{-1}]. At -21 °C, the film suddenly undergoes a rapid contraction (over a range of approximately 5 °C) as the spheres begin to crystallize. The onset of crystallization is consistent with temperatures measured for nucleation within similarly sized spherical domains of PEO.[8] The rapid contraction at -21 °C is precisely what one should expect: as each domain crystallizes, it densifies, thus reducing the average thickness of the film. This densification is also reflected in the sudden increase in the refractive index over this temperature range. Throughout the experiments, the PB matrix remains in the melt state, so changes in the expansion coefficient are the result of a phase change in the PEO block. The PB–PEO expansion coefficient is consistent with what is observed for PB [$\alpha = (6.8 \pm 0.2) \times 10^{-4}$ K^{-1}] and PEO [$\alpha_{amorphous} = (7.3 \pm 0.2) \times 10^{-4}$ K^{-1}] homopolymers.[25] After crystallization is complete, we see the film contract with a smaller coefficient [$\alpha = (6.6 \pm 0.2) \times 10^{-4}$ K^{-1}], as reflected in the smaller slope in Figure 1(c) after nucleation in comparison with the slope before nucleation. Upon heating, the film expands with this new expansion coefficient until it reaches a temperature of approximately 50 °C. At this point, a rapid expansion can be seen as the crystal domains melt (over ca. 5 °C), with a corresponding decrease in the refractive index. Once all
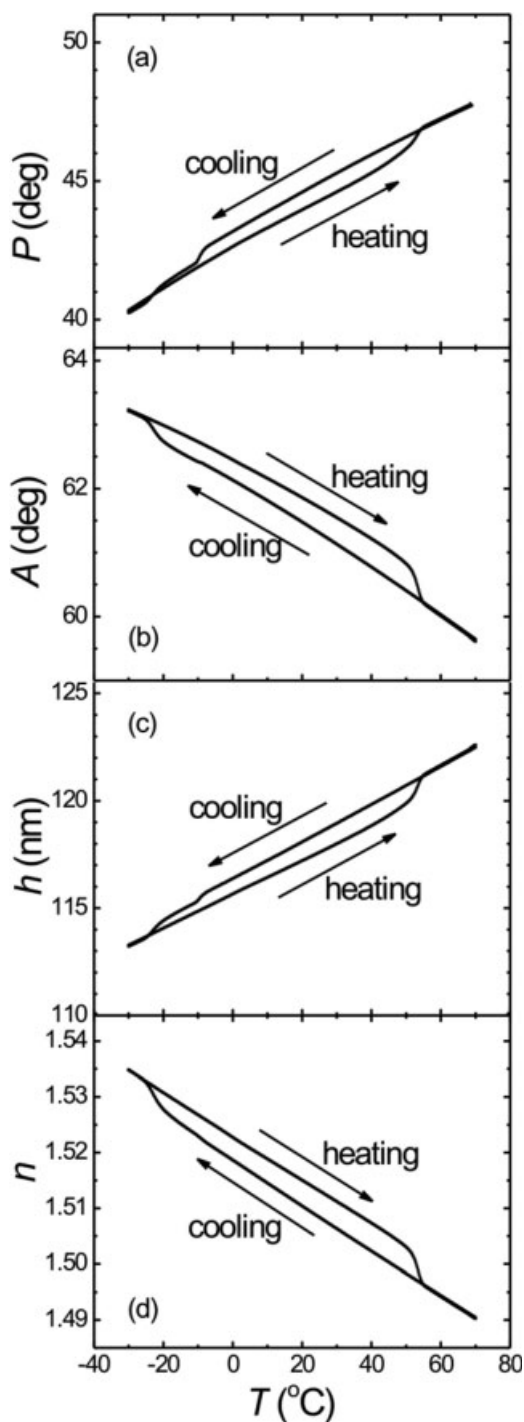
Figure 1. Results of a typical ellipsometry crystallization experiment: (a) the polarizer angle (P), (b) the analyzer angle (A), (c) the film thickness (h), and (d) the index of refraction (n) versus the temperature (T). The lack of scatter or drift in the data reflects the extreme sensitivity of the ellipsometry measurements. The linearity of the slopes in parts c and d, despite the curvature of the plots in parts a and b, indicates that treating the diblock as a uniform film is a good approximation.

the domains have melted, α returns to its initial value, as the material is completely amorphous again.

During cooling, a small deviation can be seen in the plots in Figure 1 around -10 °C. Subsequent experiments have shown that this deviation is neither an artifact nor related to crystallization, and this will be the subject of a future publication.

The large supercooling (≈ 80 °C) required to initiate crystallization is characteristic of homogeneous nucleation.[8,10] The transition occurs over a 5 °C range, which is expected because each domain must create its own nucleus, and this is a process that has been shown to occur stochastically.[8,28] In agreement with the findings of Röttele et al.,[15] we also have observed a wide temperature range (≈ 5 °C) over which melting occurs. This has been attributed to the fact that individual domains exist in various metastable states, having been formed under such large supercoolings. As a result, domains melt at different temperatures, depending on the extent of stability and reorganization within each individual domain.

In Figure 2, we plot T_c and T_m versus R for several films of the two PEO block lengths. We find
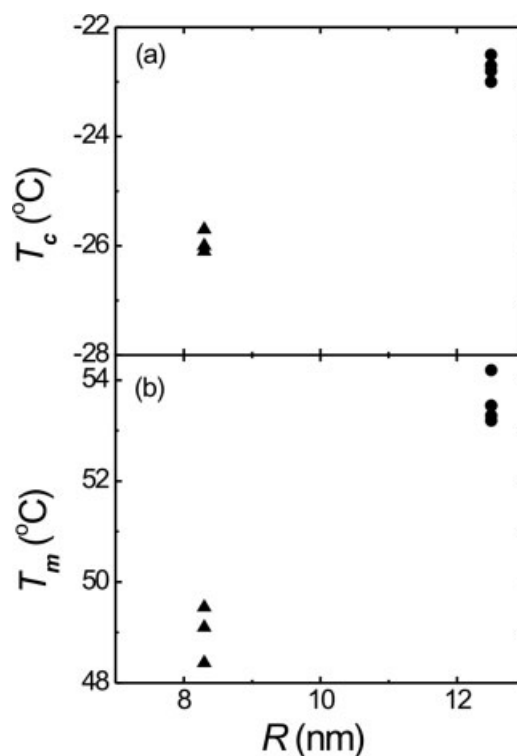
Figure 2. (a) T_c and (b) T_m versus R. The triangles represent the smaller PEO block length ($M_{n,PEO} = 4.5$ kg/mol), and the circles represent the larger PEO block length ($M_{n,PEO} = 6.8$ kg/mol).

that the longer block length samples ($R \approx 12.5$ nm) crystallize and melt at higher temperatures than the shorter PEO block samples ($R \approx 8.3$ nm). The change in T_c with R, shown in Figure 2(a), is consistent with our previous findings for larger volume droplets,[18] for which homogeneous nucleation was found to scale with the volume of the domain.

Generally, crystals that are nucleated at larger supercoolings experience faster growth rates than those that nucleate at higher temperatures. As a result, the crystals formed at the lower temperatures are less stable than their higher temperature counterparts and should melt at a lower temperature than more stable crystals. In Figure 2(b), we see a decrease in T_m with R (by ~ 1 °C/nm for the two samples presented), which is consistent with previous results in sphere-forming domains.[16] This is not surprising because the crystals within the smaller spheres are less stable than the larger domains.

CONCLUSIONS

Ellipsometry provides a novel probe for the study of crystallization kinetics in block copolymer systems and can offer valuable insight that complements other techniques currently being employed. We have demonstrated that ellipsometry is sensitive to the variations in crystallization and melting kinetics that occur with changing domain size in block copolymer films, even for very small sample volumes (10^{-10} L). For the experiments conducted in this study, we have been able to obtain expansion coefficients before and after crystallization. The ability to observe phase transitions through small changes in the density in thin films makes ellipsometry a versatile tool for the study of crystallization kinetics.

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