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Pattern Formation in Ultrathin Films of a Novel Dimethylsiloxane–Acrylate Triblock Copolymer

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Received July 3, 2003

Revised Manuscript Received August 14, 2003

Introduction

The molecular structure and thermodynamics of polymer surfaces and solid interface differ from the corresponding bulk properties. This difference leads to a notable change in phase behavior and a lowering of the glass transition temperature (T_g) on moving from the bulk to the interfacial region.¹ Numerous studies have investigated surface pattern formation in block copolymer films² on account of its importance in the design of highly functionalized surfaces. These studies have shown that surface pattern formation in block copolymer thin films is strongly influenced by the film thickness, film properties, and the characteristics of the substrate. However, many questions remain unsolved on the surface pattern formation in polymer thin film. In the present study, we systematically investigated the surface pattern formation of a novel triblock copolymer with highly repulsive blocks: poly(*tert*-butyl acrylate)-*b*-poly(dimethylsiloxane)-*b*-poly(*tert*-butyl acrylate) (PtBA-*b*-PDMS-*b*-PtBA). Highly repulsive interactions between chain segments of PDMS and PtBA blocks can give a high selectivity to the substrate/polymer and air/polymer interfaces. The distinctive behavior of the triblock copolymer system developed in the present study is due to the difference between the T_g of the matrix PtBA block in the bulk and that in the thin film; the T_g of this block in the bulk is slightly above room temperature (RT), whereas it is expected to be slightly below RT in thin films due to the low interaction interface between PtBA block and PDMS block. Thus, if the PtBA block is the continuous phase in the thin film, chain segments of the triblock copolymer should be able to rearrange over time at RT, thereby changing the surface pattern.

In the present study we examined the dependence of surface patterning on the thickness (t) of the thin film in two different thickness regimes: $t < 2R_g$ and $t > 2R_g$, where R_g is the unperturbed radius of gyration of the triblock copolymer. In thin films with $t > 2R_g$, T_g was lower than in the bulk, and despite the high order–disorder transition temperature (T_{ODT}) of these systems, the film displayed a hierarchical surface pattern due to the destabilization caused by the decrease in T_g . In ultrathin films with $t < 2R_g$ (two-dimensional films), the film was stable, and a chemically heterogeneous pattern without dewetting was formed in films of thickness $t < R_g$.

Experimental Section

PtBA-*b*-PDMS-*b*-PtBA triblock copolymer was prepared by atom transfer radical polymerization of PDMS macroinitiator

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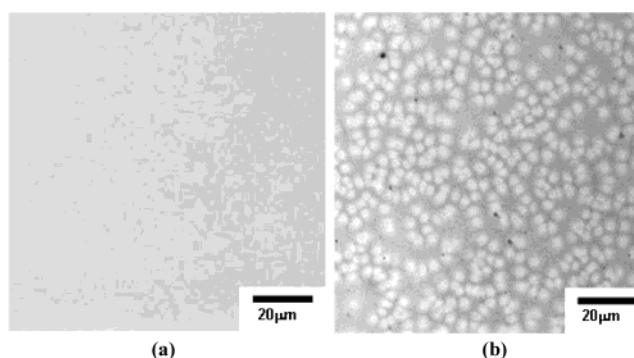


Figure 1. Optical micrographs in reflection mode for PtBA-*b*-PDMS-*b*-PtBA triblock copolymer thin film with $t = 45$ nm: (a) as-cast film; (b) films at RT after 7 days.

and *tert*-butyl acrylate at 100 °C using a CuCl/di(*n*-nonyl)-bipyridine system.³ The composition (70:30 w/w PtBA/PDMS) and molecular weight characteristics ($M_n = 56$ kg/mol; 20K:16K:20K and $M_w/M_n = 1.16$) were determined by means of ¹H NMR spectroscopy and size-exclusion chromatography, respectively. The lower (PDMS) T_g is -120 °C, and the upper (PtBA) T_g is 37 °C. By small-angle X-ray scattering measurement, it was confirmed that the bulk structure is a hexagonally packed cylindrical phase and that the microdomain spacing (L_0) is 26 nm. The unperturbed radius of gyration (R_g) of the present triblock copolymer calculated from the reference equation⁴ is ca. 7 nm. Thin films with thicknesses between 2 and 200 nm were prepared by spin-coating from THF solution onto cleaned Si(100) wafers. Silicon wafers were etched in H₂-SO₄/H₂O₂ solution prior to polymer deposition. Film thickness and the T_g of thin film were measured by ellipsometry (J.A. Woolam Co. VASE), and pattern images were acquired by atomic force microscopy (AFM) (Nanoscope IIIa, Digital Instrument) and optical microscopy (Zeiss).

Results and Discussion

Film Thickness $> 2R_g$. Figure 1 shows optical micrographs recorded in reflection mode of the PtBA-*b*-PDMS-*b*-PtBA triblock copolymer thin film ($t = 45$ nm). In the case of the as-cast film, no surface pattern is observed. However, the surface pattern becomes clear over time, with a spinodal or impinged rims pattern appearing at RT after ca. 7 days, despite the fact that the bulk T_g (37 °C) of the PtBA block is above ambient temperature.

Films with thicknesses in the range $30 \text{ nm} < t < 60$ nm formed an impinged rims structure at RT after ca. 7 days, as shown in Figure 1b. This macroscopic pattern did not change even after annealing at 70 °C for 24 h (Figure 2b). Another hierarchical pattern, namely a spinodal pattern, was observed in this triblock copolymer when the initial film thickness was in the range $14 \text{ nm} (=2R_g) < t < 30$ nm. Immediately after spin-coating (i.e., for the as-cast film), no surface pattern was observed. However, a spinodal pattern evolved at RT after ca. 7 days (Figure 2a, inset A). This pattern became fully developed after annealing at 70 °C for 24 h. The evolution of the surface pattern is attributed to an enhancement of the mobility of chain segments as a result of the matrix PtBA block in the thin film ($18 \text{ nm} < t < 80 \text{ nm}$) having a T_g that is lower than the bulk value. These results constitute a distinct evidence that the T_g of the PtBA block (matrix polymer) in thin films is lower than that in the bulk. We also confirmed that

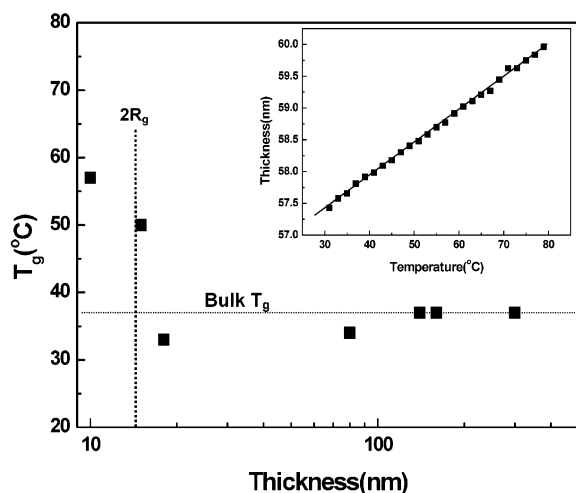


Figure 2. Thickness dependence of the glass transition temperature for PtBA-*b*-PDMS-*b*-PtBA triblock copolymer thin film. Inset plot is the ellipsometric thickness with increasing temperature for 58 nm thin film, in which the T_g could not be determined because the T_g of this film is lower than RT.

T_g of a thin film, $18 \text{ nm} < t < 80 \text{ nm}$, is lower than that of a 169 nm thick film by the ellipsometry measurement (Figure 2) even though the PtBA chain segment can interact with a polar substrate. Our result is very similar to the T_g of a symmetric polystyrene-*b*-poly(methyl methacrylate) diblock copolymer,^{1b} in which the surface T_g is much lower than that for its bulk sample. In our system, also, the reorganization of the randomly

oriented microphase structure of block copolymer can be attained below the bulk T_g of PtBA, proceeding with micro- and macrophase separation. Moreover, the microstructure of a thin film of asymmetric diblock copolymers is extremely sensitive to the film thickness and surface-polymer interaction.^{2f} In our case, as shown in Figure 2, the T_g of thin films, $t < 2R_g$, is higher than the bulk T_g since the carbonyl group in PtBA chain segments can interact with a polar substrate. Although PtBA having carbonyl group can interact with a polar substrate, there is an interfacial layer affected by the substrate. In our case, the interfacial layer thickness might be comparable with $2R_g$ because the surface pattern in ultrathin film ($t < 2R_g$) was not changed at room temperature.

Additionally, a PDMS microdomain structure was observed after annealing at 70 °C for 24 h, as shown in parts a (inset B) and b (inset) of Figure 3. This morphology could be obtained by the "hard tapping" method because the top layer is fully covered with a rubbery PDMS, which has a very low surface energy. The appearance of this microdomain structure implies that for thin films of thickness $t > 2R_g$ the T_{ODT} of the triblock copolymer thin film is above RT, and these patterns were formed without dewetting.

The surface morphology of PDMS-containing block copolymers has been examined in various recent studies.⁵ Those studies showed that the PDMS segments are the most apt to segregate in the free surface region, and this segregation behavior is dependent on the chain architecture of the block copolymer. Green and co-

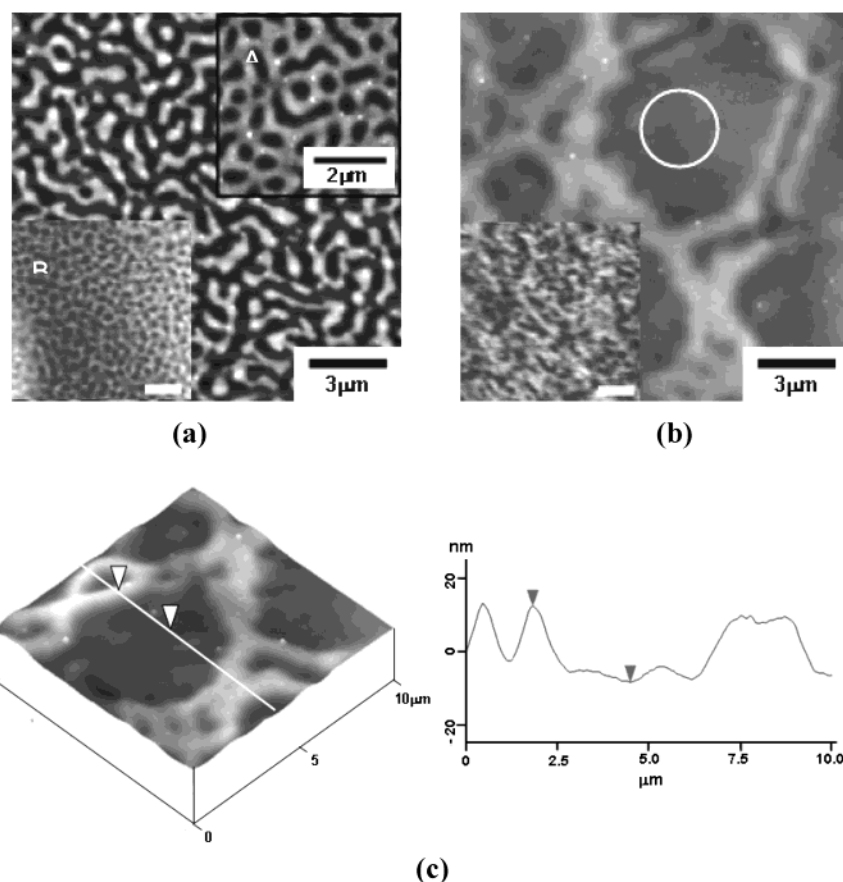


Figure 3. AFM images showing the structural evolution of (a) spinodal and (b) impinged rims pattern. Insets A and B in (a) are an evolution image at RT after ca. 7 days and a high-magnification image of the dark part in (a), respectively. Inset in (b) is a high-magnification image of the circular region in (b). (c) 3D AFM topographic image of 45 nm thin film and the height profile corresponding to the line in Figure 2c. The initial thickness of (a) and (b) is 20 and 45 nm respectively.

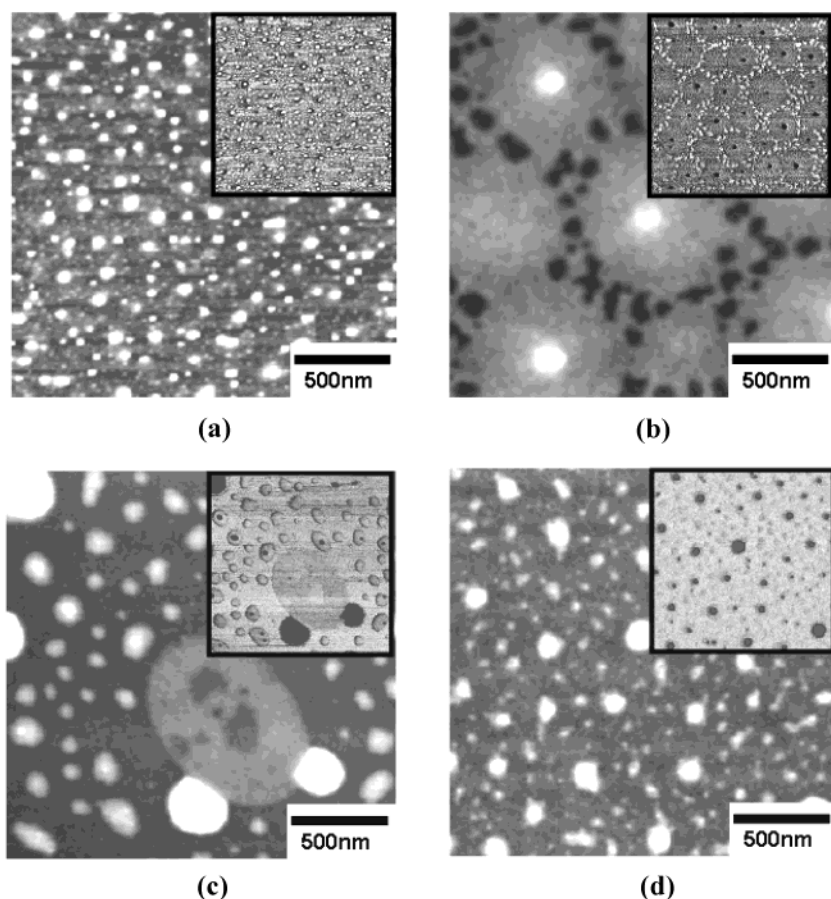


Figure 4. AFM images after annealing at 70 °C for 24 h. Images of as-cast films do not differ from that after annealing. Initial thickness: (a) 12, (b) 6.5, (c) 3, and (d) 2 nm. Inset images are phase images.

workers⁶ reported that spinodal and rims structures similar to those found in the present study can form in thin films of a PS-*b*-PMMA diblock copolymer above the T_{ODT} . In addition, Spontak and co-workers⁷ observed multiscale dewetting in low molecular weight styrene-isoprene diblock copolymer thin films at RT, which they attributed to the depression of the upper T_g and T_{ODT} . The major difference between the present triblock copolymer and other systems is that for our system, even though the T_{ODT} is far above RT, a spinodal-like and impinged rims pattern without dewetting is observed at RT after ca. 7 days. In fact, the rims structure observed in our system, which is generated without dewetting, is remarkably different from that which has been generally documented for systems that dewet by a nucleation and growth mechanism. Both Green⁶ and Spontak⁷ found that the dewetted region is a dense "brush" structure due to the surface-induced ordering of block copolymer. Although the pattern in Figure 1b is very similar to a typical dewetting region, however, in our system the inner region of the rim structure is not flat from the height profile as shown in Figure 3c, and there is no dense "brush" region; instead, a microdomain structure of block copolymer as can be seen in Figure 3b. It is tempting to speculate about this behavior that there is an interfacial layer ($< 2R_g$) being affected by the substrate, resulting in formation of the dewetting-like rims structure. Moreover, this behavior might be associated with the interplay between the highly repulsive interactions between chain segments and the high selectivity of the chain segments to the air or substrate interface.

Film Thickness $< 2R_g$ (Two-Dimensional Ultrathin Film). The lamellae of symmetric diblock copolymers at $T < T_{ODT}$ typically orient parallel to the plane of the substrate because one component of the A-B diblock exhibits a preferential affinity for the substrate.⁸ When a block copolymer thin film is confined to two dimensions and one of the block segments interacts preferentially with the substrate, chemically heterogeneous surface patterns may form due to lateral phase separation of the block copolymer;⁹ such behavior has been observed in symmetric polystyrene-*b*-poly(2-vinylpyridine),^{9a} polystyrene-*b*-poly(*p*-methylstyrene),^{9b} and ABC triblock copolymer.^{9c} In a study of ultrathin films of polystyrene-*b*-poly(2-vinylpyridine), Möller et al.^{9a} found that nanomosaic surface patterns can be generated by the strong interaction of poly(2-vinylpyridine) with a polar substrate.

In our system with $t < 2R_g$, the film was stable at RT and no distinct change in surface morphology was observed even after annealing at 70 °C for 24 h, in contrast to films of thickness $t > 2R_g$. In a film of thickness 12 nm ($R_g < t < 2R_g$), only a dropletlike surface pattern was observed (Figure 4a). Similar dropletlike discrete mounds have been observed previously in other thin films such as poly(styrene-*b*-isoprene) block copolymer thin films,⁷ although in our system the droplets are larger and show a distribution of sizes. We found that the top layer of the 12 nm thick film was mostly covered with PDMS, as determined from the observation that the contact angle of water on this film was similar to that of the thick film (ca. 110°), which corresponds to the characteristic contact angle of water on PDMS

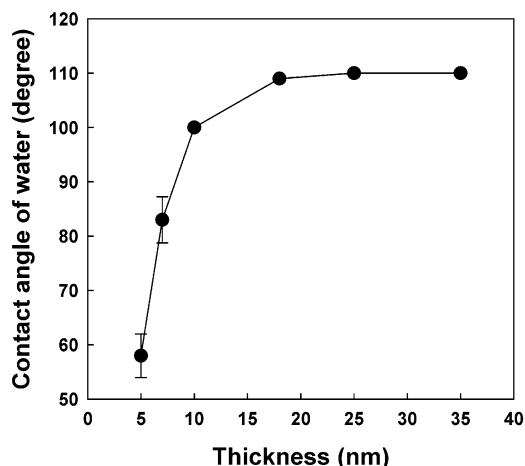


Figure 5. Contact angle of water of triblock copolymer thin films having different thickness annealed at 70 °C for 24 h.

(Figure 5). However, when t was below R_g ($t < 7$ nm), a microscale islandlike and dropletlike surface pattern without dewetting were formed. In particular, it is noticeable that an interconnected island structure was generated in the 6 nm ultrathin film (Figure 4b). On further decrease of the thickness to 3 nm, isolated islands were observed (Figure 4c), and only droplets were observed at $t = 2$ nm (Figure 4d). The substrate was fully covered by block copolymer even in a 2 nm ultrathin film. These results might be attributed to the good affinity of PtBA for the silicon substrate and the large repulsive force between PtBA and PDMS. By measuring the contact angle of water on the film surfaces (Figure 5), we confirmed that the surface patterns of thin films of thickness $t < R_g$ have a different phase (a chemically heterogeneous pattern) on the top layer in comparison to films of thickness $t > R_g$. From the phase images (inset in Figure 4a,c) in the AFM images of ultrathin films ($t = 12$ and 3 nm), we speculate that the islandlike phase is a lamellar phase that forms as a result of surface-induced ordering of the triblock block copolymer and that the dropletlike phase is a PDMS-rich region because PDMS blocks tend to be located at the air/polymer interface due to the very low surface energy of the PDMS block.

Conclusion

We systematically examined the effect of film thickness on surface pattern in ultrathin films of an asymmetric ABA triblock copolymer in which the A block interacts preferentially with the polar substrate and the interaction between the A and B blocks is highly repulsive.

In thin films ($t > 2R_g$) of the PtBA-*b*-PDMS-*b*-PtBA triblock copolymer, surprisingly, impinged rims structures without dewetting were observed below T_{ODT} at RT. The formation of these structures was attributed to the depression of T_g of PtBA block, and the interplay

between the highly repulsive interactions between chain segments and the high selectivity of the chain segments to the air or substrate interface. This result provides a distinct evidence that the T_g of the polymer thin film is lower than that of the bulk due to the low interaction interface between PtBA block and PDMS block. However, films of thickness $t < 2R_g$ were stable at RT because the chain segments of the PtBA block interacts and is confined with a substrate. Films in the range $R_g < t < 2R_g$ formed a chemically homogeneous droplet morphology. For $t < R_g$, island patterns (both interconnected and isolated) and dropletlike patterns (chemically heterogeneous patterns) were observed without dewetting.

Acknowledgment. This work was supported by the Korea Research Foundation Grant KRF-2002-005-D00008.

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