

MORPHOLOGICAL CHARACTERIZATION OF SYMMETRIC DIBLOCK COPOLYMERS VIA NOVEL COMBINATORIAL METHODS

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Introduction

The development and application of combinatorial methods and techniques to pharmaceutical drug discovery has revolutionized the process of bringing new drugs to market.¹ Similarly, application of combinatorial principles to materials science is expected to greatly influence the future direction of research, as is already being witnessed for catalyst studies.² One area of materials research where these principles are just now beginning to be applied is the characterization of polymer physical properties. Towards this goal we have developed a technique to create polymer thin films with a controlled, continuous gradient in film thickness. As a demonstration of the utility of this technique, we have revisited the well-studied phenomena of the morphology of symmetric diblock copolymer thin films.

Symmetric diblock copolymers are defined as block copolymers where the two polymers are nearly equal in molecular weight. Previous studies³⁻¹⁰ have shown that in annealed thin films of these materials surface energetics induces formation of lamellae parallel to the substrate surface having a thickness L ¹¹ equal to the bulk equilibrium lamellae spacing. When one block segregates to both the substrate and air interface the film thickness is given by nL , while $(n + \frac{1}{2})L$ describes the film thickness when one block segregates to the substrate and the other to the air. In the case where the film thickness deviates from these integer thicknesses, the excess material forms incomplete layers with islands or holes of height L . The percentage coverage of the incomplete layer depends on the fraction t/L where t is the film thickness above the last integer layer height. This dependence is utilized to demonstrate the efficacy of combinatorial methods applied to polymer characterization by creating thin films of symmetric polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) copolymer having continuous gradients in thickness. The morphology and incomplete layer formation is characterized by atomic force microscopy.

Experimental

Library Creation. PS-*b*-PMMA diblock copolymer (M_n ¹² = 51 kg/mol, M_w/M_n = 1.06) was purchased from Polymer Source Inc. and used as received. Thickness gradients were prepared on Si wafers (10 cm diameter, Polishing Corporation of America¹³) which were "piranha-etched" to form a native SiO₂ surface layer. The cleaned wafer was placed on a robotic stage under computer control and secured. A 3 cm wide knife-edge angled approximately 5° was placed 0.3 mm above the surface and 50 μL of solution (mass fraction (2 to 5) % PS-*b*-PMMA in toluene) placed under it. The stage was then directed to move with constant acceleration to spread the solution. Solvent evaporation was achieved in seconds after spreading and a thin film with thickness proportional to the velocity produced. Control of initial thickness and slope is achieved by modifying the solution concentration and stage acceleration. Resultant films are (20 to 35) mm in length and have nominal thickness variations of 40 nm, although greater and lesser variations are possible. The film thickness is characterized by 0.5 mm diameter spot-ellipsometry (with standard uncertainty ± 1 nm at 500 nm film

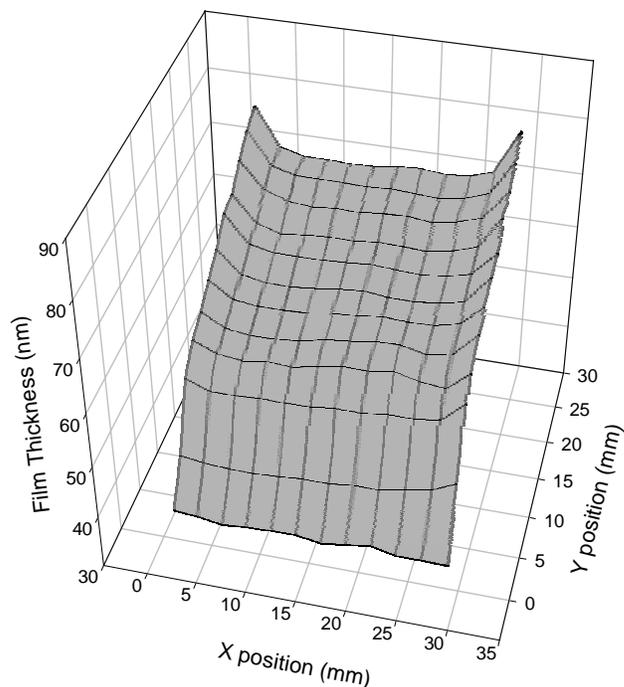


Figure 1. Film thickness of a PS-*b*-PMMA copolymer film with a continuous thickness gradient. Thickness is measured by automated spot ellipsometry on a 2.5 mm grid.

thickness) connected to a robotic stage such that measurements are automated on a grid (generally (2 to 3) mm spacing). Figure 1 contains a plot of the film thickness from a typical gradient as determined by ellipsometry. This sample is 30 mm wide and 30 mm long with a thickness range of (35 to 75) nm and measurements were acquired with a 2.5 mm grid spacing. A similar technique was used to produce thickness gradients for studying thin film dewetting.¹⁴

Copolymer Analysis. For the diblock copolymer experiment, three to four thickness gradients possessing overlapping thickness ranges were placed on a Si wafer. The wafer was subsequently annealed at 170 °C for up to 30 h under vacuum to allow reorganization of the thin films. This method of sample preparation allowed for a greater range of thickness variation as well as duplication of the results. In addition, since all the samples are on one wafer, potential differences in processing conditions are eliminated. After annealing, the surface morphology is characterized by atomic force microscopy (AFM).

Results and Discussion

Previous research⁷ has shown that when PS-*b*-PMMA is placed on a SiO₂ surface the PMMA segregates to the substrate interface while the PS segregates to the air interface. This results in an equilibrium film thickness of $(n + \frac{1}{2})L$ for this system. For the polymer molecular mass utilized here, L is calculated⁴ to be 28 nm meaning layer formation will be observed beginning at approximately 42 nm. Based on this calculation thin films have been prepared ranging in thickness from (35 to 110) nm, roughly corresponding to $1.25L$ to $4L$. After annealing the sample the expected morphological dependence on film thickness is observed as illustrated in Figure 2. Here AFM micrographs obtained from the sample annealed at 170 °C for 6 h at initial film thickness a) (72 ± 1) nm, b) (77 ± 1) nm, c) (83 ± 1) nm, d) (90 ± 1) nm, e) (94 ± 1) nm and f) (101 ± 1) nm are displayed. This thickness range roughly corresponds to $2.5L - 3.5L$.

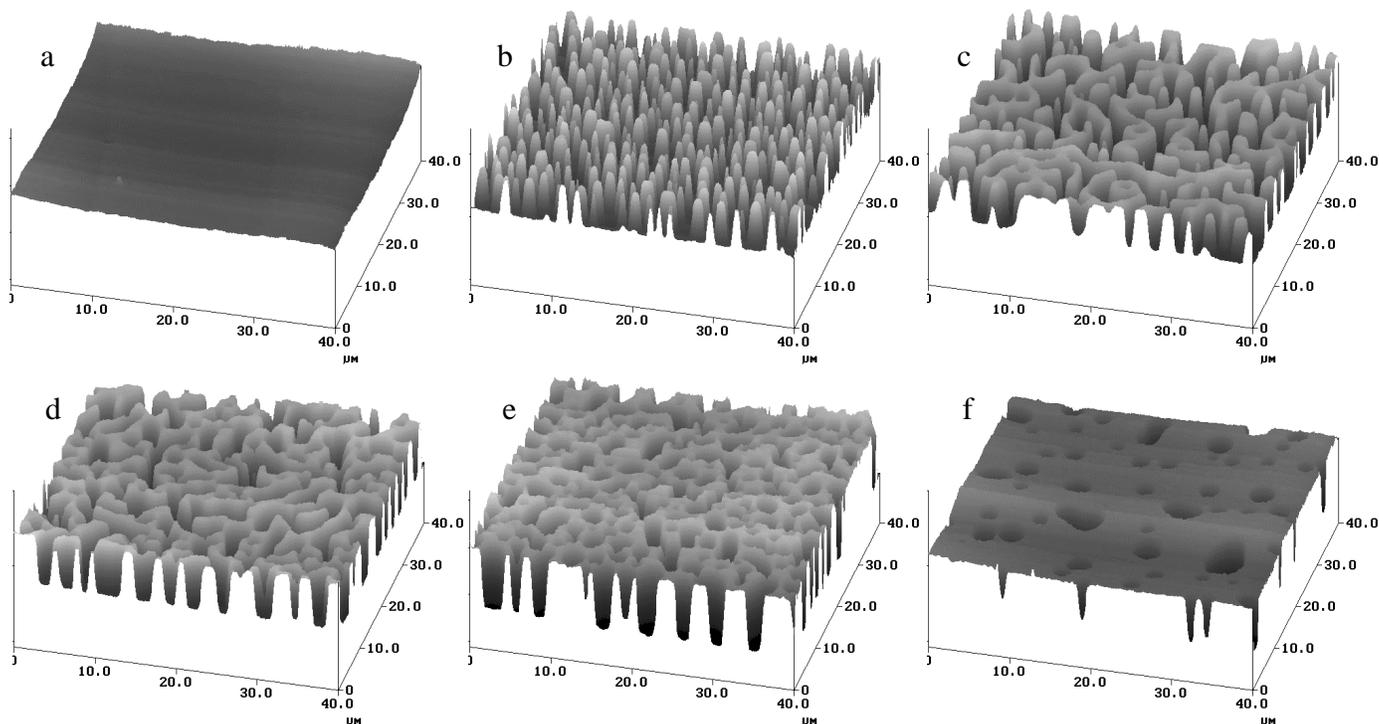


Figure 2. AFM micrographs obtained from a PS-*b*-PMMA film annealed 170 °C for 6 h at initial film thickness of a) (72 ± 1) nm, b) (77 ± 1) nm, c) (83 ± 1) nm, d) (90 ± 1) nm, e) (94 ± 1) nm and f) (101 ± 1) nm. These micrographs demonstrate the formation of the block copolymer lamella and how it evolves with changing film thickness. All micrographs were obtained from one film gradient.

for this molecular mass. Figure 2a shows a nearly smooth surface with little height differentiation indicating that an integer layer of thickness corresponding to $2.5L$ is achieved. When the film thickness is increased to 77 nm (Fig. 2b) the excess material forms islands of the next layer (third) on the underlying layer (second).

As the film thickness further increases (Fig. 2c) the islands join together and form a semi-continuous morphology very reminiscent of blend spinodal decomposition morphology. This morphology eventually undergoes a “phase inversion” where the growing third layer becomes continuous with holes down to the second layer interspersed within (Fig. 2d). These holes become less dense (Fig. 2e and f) as the thickness nears the next integer layer ($3.5L$) and eventually a smooth surface is recovered without holes or islands (not shown). The morphological evolution described above is also observed for film thickness above and below the range discussed. In addition, intermediate morphologies that occur between the thicknesses shown are present due to the continuous nature of the thin films and are easily observed.

Conclusions

In this study a new methodology for characterization of polymer thin films via continuous, multi-state libraries has been developed. Polymer thin films with a continuous, controlled gradient in thickness have been realized. These libraries have been utilized to readdress the morphology of symmetric diblock copolymers with a significant increase in the phase space explored and decrease in overall experimental time. No deviation from previously observed behavior is found, confirming the utility and accuracy of this experimental approach. These results indicate that continuous gradient combinatorial methods can successfully be applied to polymer physical property characterization.

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- (12) According to ISO 31-8, the term “molecular weight” has been replaced by “relative molecular mass”, M_r . The number average molecular mass is given by M_n .
- (13) Certain equipment and instruments or materials are identified in the paper to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.
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