Paper

Investigation of Microphase Separation of PS-PPrMA Diblock Copolymer Films by Time-of-Flight Secondary Ion Mass Spectrometry

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The microphase separation of diblock copolymers has been investigated by many different research groups for many years, because of the increasing use of diblock copolymers as compatibilizers, dispersants, impact modifiers, nanocarriers, and templates. In this presentation, surface characterization methods were utilized to study the surface morphology and composition produced after annealing thin polymer films. We report on the characterization of the morphology from symmetric diblock copolymers of polystyrene-b-poly(n-propyl methacrylate)(PS-PPrMA), where PS block was perdeuterated, using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). TOF-SIMS depth profiling was obtained for the lamellar morphology of deuterated PS-PPrMA which is found to orient parallel to the surface of the substrate. This preferential orientation resulted in a periodic variation in the composition of each block that continued through the entire copolymer film. Annealing studies on dPS-PPrMA thin films with different thickness on the silicon substrates were performed to investigate the lower disorder-to-order transition (LDOT) properties of diblock copolymers.

1. Introduction

The phase behaviour in polymer mixtures and block copolymers has been studied extensively, both theoretically and experimentally.[1-4] On heating, the translational entropy increases, and usually segmental interactions decrease, therefore a transition from a phase-separated to a phase-mixed state is expected.[5,6] This order-to-disorder transition(ODT) for block copolymers is accompanied by a small volume change on mixing that can be either positive or negative. More recently, block copolymers have been shown to undergo a transition from the phase-mixed to phase-separated state[7,8], namely a lower disorder-to-order transition(LDOT) for block copolymers. LDOT block copolymers can offer new types of sensor materials with high-temperature or pressure sensitivity.

Extensive studies have been performed for diblock copolymers using small-angle x-ray scattering(SAXS), transmission electron microscopy(TEM), optical microscopy, x-ray photoelectron spectroscopy(XPS), and atomic force microscopy(AFM).[9-13] Ryu et al. have reported the unusual phase behavior of symmetric diblock copolymers of polystyrene and poly(n-pentylmetacrylate) over a narrow range of molecular weight.[9] At higher temperature, P(S-b-nPMA) was found to undergo an additional transition from the ordered to the disordered state. Cho and co-workers have investigated phase coherence behavior in thin films of a diblock copolymer that exhibits microphase separation upon heating in the bulk by approximation theory and neutron reflectivity measurements [10]. Ade and co-workers have studied PS-PMMA blend films, using NEXAFS microscopy and SFM, which after annealing revealed PS droplets within a rim of PMMA in a PMMA-rich matrix [11]. Kailas et al. have used different techniques such as XPS, AFM, and SIMS to study the surface behavior of a two-phase polymer mixture depending on the chemical structure, the interaction, and processing conditions [12].

Here, we report TOF-SIMS results for direct chemical identification and depth profiling of the thin films of symmetric, diblock polystyrene/poly(n-propyl methacrylate) copolymers(PS-PPrMA), where the PS block was deuterated. Annealing studies on dPS-PPrMA thin films with different thickness on the silicon substrate were performed to investigate the LCOT properties of diblock copolymers.

2. Experimental

2.1 Materials

Deuterated polystyrene-block-poly(n-propyl methacrylate)(dPS-PPrMA) with symmetric composition was synthesized by the sequential, anionic polymerization of deuterated styrene and n-propyl methacrylate in tetrahydrofuran at -78°C in the presence of LiCl under purified Ar using sec-BuLi as an initiator[10,14]. Prior to spin-coating, the silicon wafers (5 mm thick, 100 mm in diameter) were sonicated in toluene, acetone, and methanol. A series of the diblock copolymers ca. 700 Å, 2100 Å and 6100 Å thick were prepared by spin casting from toluene solutions onto a silicon substrate (2000 rpm for 60 s). The film thicknesses were controlled to be ca. 700 Å, 2100 Å, and 6100 Å by varying the polymer mass fraction in toluene solutions. Film thickness measurements were made using FE-SEM cross-section image (HITACHI S-4100).

2.2 TOF-SIMS

Positive and negative ion TOF-SIMS analyses were carried out on an ION-TOF GmbH (Münster, Germany). TOF-SIMS 5 system equipped with a Bi liquid metal ion gun (LMIG) and Cs^+ primary ion beam sources. Bi^+ primary ions were selected for data acquisition. TOF-SIMS depth profiles were obtained in the dual-beam mode. In this mode, two different primary ion guns were used: one for collecting spectra and one for sputtering. The analysis source was a pulsed 25-keV Bi^+ beam, which bombarded the surface at an incident angle of 45° to the surface normal. The target current was maintained at 1 pA pulsed current with a raster size of 100 μm x 100 μm. A cycle time of 100 μs was employed for mass data acquisition. A low-energy electron flood gun was used for charge compensation of thick polymer films. Cs^+ ion source was employed as the sputter gun. A 3 keV or 10 keV Cs^+ ion source bombarded the surface at an incident angle of 45° to the surface normal. The target current was maintained at a 32 nA or 43 nA continuous current throughout the sputter process, with a rastered area of 300 μm x 300 μm.

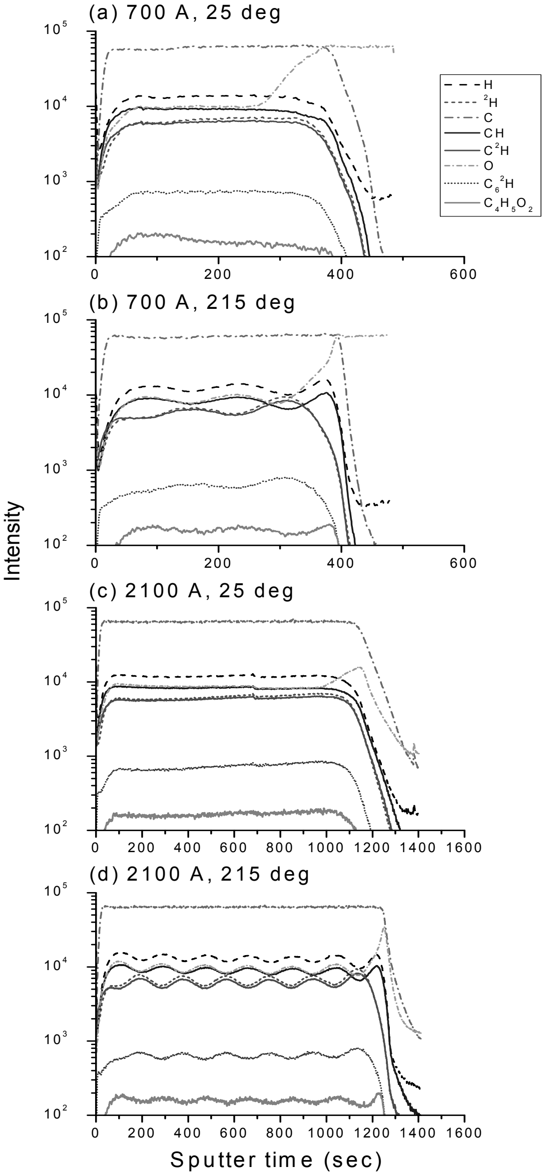

Fig.1. Depth profiles of dPS-PPrMA films before and after annealing: (a) 700Å at 25°C, (b) 700Å at 215°C (c) 2100Å at 25°C (d) 2100Å at 215°C.

3. Results and Discussion

To characterize dPS-PPrMA, the negative ion TOF-SIMS mass spectrum was acquired at the air/surface of the copolymers. The negative ion mass spectra of dPS-PPrMA were acquired with a Bi^+ primary ion beam under static SIMS conditions from a spin-coated copolymer film exposed to room temperature. The negative ion TOF-SIMS spectra for dPS-PPrMA showed specific fragment ion peaks from both deuterated PS blocks like $^2H^-$ (m/z 2.014), C^2H^- (m/z 14.014), and $C_6{}^2H^-$ (m/z 74.014) and PPrMA blocks like O^-,

OH^-, $C_3H_3O^-$ (m/z 55.020), and $C_4H_5O_2^-$ (m/z 85.034). The mass spectra of dPS-PPrMA copolymer surface stored at the room temperature shows the characteristic peaks from both the PS and PPrMA components of the copolymer.

Fig. 1(a) and (c) shows typical TOF-SIMS depth profiles obtained from dPS-PPrMA copolymer films (~700 Å and ~2100 Å) spun cast onto Si and preannealed for 5 h in vacuum at 90°C. In the case of dPS-PPrMA, the characteristic secondary ion intensities that were monitored include H^-(m/z 1.008), $^2H^-$ (m/z 2.014), C^-(m/z 12.000), CH^-(m/z 13.008), C^2H^-(m/z 14.014), and O^-(m/z 15.995). The H^-, $^2H^-$, C^-, and related secondary ion counts obtained as the ion beam penetrated into the copolymer were observed to remain constant as a function of the sputtering time or depth from the copolymer surface. This indicates that the diblock copolymer morphology is randomly oriented with respect to the film surface.

A different dPS-PPrMA copolymer film was annealed at 215°C for 4 h in a vacuum. The results of the TOF-SIMS depth profiles on these copolymers are shown in Fig. 1(b) and (d). The TOF-SIMS characteristics of the copolymer surface are similar to those shown in Fig. 1(a) and (c) for the specimen at the room temperature. As the ion beam penetrates into the copolymer pronounced oscillations in the H^- and CH^- peaks arising from the PPrMA and in the $^2H^-$ and C^2H^- peaks from the dPS are clearly shown in Fig. 1(b) and (d). The carbon peak remains invariant throughout the sputtering of the copolymer film. These results clearly indicate that increasing the temperature produces a strong orientation of the lamellar copolymer microdomains parallel to the film surface. Rapid orientation of the microdomains where a strong oscillation persisted throughout the entire film thickness was found to occur for the samples with thicknesses of approximately 700Å and 2100Å. Fig.1 also shows that the molecular ions attributed to the PPrMA, $C_4H_5O_2^-$ and to the dPS, $C_6{}^2H^-$, possess depth profile shapes similar to those observed with H^- and $^2H^-$ depth profiles, respectively, despite the fact that $C_4H_5O_2^-$ oscillation is not clear.

Fig. 2 shows the two-dimensional reconstructed TOF-SIMS images of hydrogen, deuterium and silicon secondary ion intensity obtained in the course of sputter depth profiling of the dPS-PPrMA copolymer sample annealed for 4 h at 215 °C.

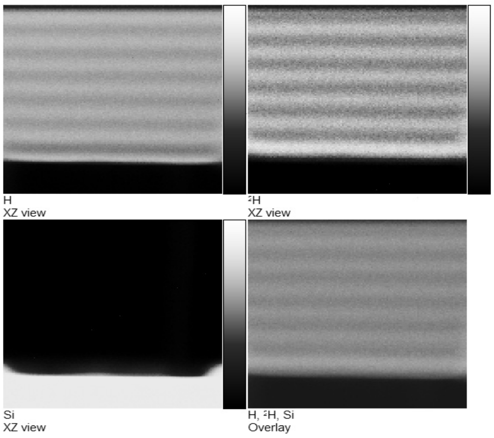

Fig. 2. 2-D TOF-SIMS images of H, ^{2}H, Si and overlay of dPS-PPrMA after annealing at 215°C.

The images show the presence of a higher hydrogen concentration on the surface and substrate interface. The two-dimensional reconstructed images of the deuterium signal also show clearly the microdomains parallel to the film surface.

A thicker dPS-PPrMA diblock copolymer was cast onto the silicon substrate to determine if the film thickness was significant. The TOF-SIMS depth profiles by the Cs^+ sputter ion beam for the H^-, $^2H^-$, C^-, CH^-, C^2H^- and O^- of the copolymer film prior to annealing are shown in Fig. 3(a). As shown with the thinner copolymer films, the H^-, $^2H^-$, C^-, CH^-, and C^2H^- peaks are constant throughout the entire film. After annealing at 215°C for 4 h under a vacuum dramatic results were obtained as shown in Fig. 3(b). Even for this thick film, significant oscillations of the H^-, $^2H^-$, CH^-, and C^2H^- peaks are observed while the C^- peak is constant throughout the sputtering of the film. These results are consistent with the previous small-angle X-ray scattering result [10]. In the phase coherence of the block copolymer, a period of 381 Å was obtained from a small-angle X-ray scattering measurement. This refers to the nanoscale separation of the PS and PPrMA blocks with a periodicity of 381Å. The total film thickness on the silicon substrates is given as nL, where n is the number of periods and L is the period spacing. Thus, for a thinner film, n=6 and a thickness of 2,286 Å would be expected, which is comparable to a value of nearly 2100 Å as measured via FE-SEM image. Fig. 3(b) also shows that the periodic lamellar morphology is strongly oriented parallel to the film surface and that the ordering persists over seventeen periods, corresponding to a film thickness of 6,477 Å. The

FE-SEM images show a similar thickness of 6100 Å. The amount of cast copolymer may differ from the quantity required for the exact number “n” for a fully lamellar condition. This explains why the measured thicknesses only roughly correspond to the calculated values. During the structuring of the films, the last layer remains incomplete with either islands protruding at the surface of layer n-1 or holes in the surface of layer n. This effect was studied by Kailas et al. with a combination of AFM and SIMS measurements [12]. These oscillatory results show that a slight difference in the surface tension between the two components in a block copolymer is sufficient to produce a strong orientation of the microdomains parallel to the surface of the substrate that propagates through the entire film thickness.

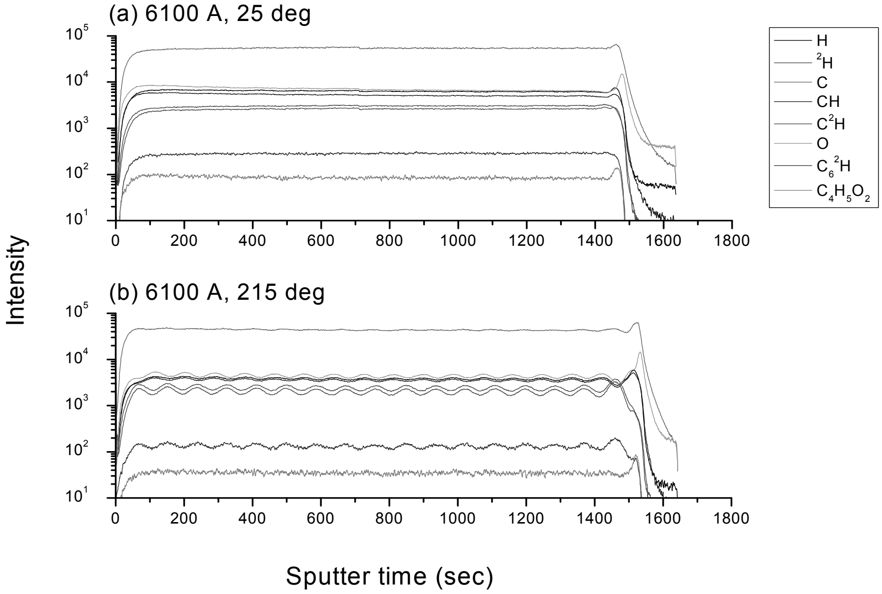

Fig.3. Depth profiles of 6100 Å thick dPS-PPrMA films (a) before and (b) after annealing.

4. Conclusions

It was shown by TOF-SIMS that the lamellar microdomain morphology of deuterated PS-PPrMA symmetric diblock copolymers orients parallel to the surface of a silicon substrate. In TOF-SIMS depth profiles, dPS-PPrMA exhibited microphase separation upon heating. Solution casting copolymer film was randomly oriented with respect to the surface before annealing. A depth profile with a Cs^+ primary ion beam exhibited strong orientation of the copolymer microdomains parallel to the surface after annealing at 215°C for 4 h. The PPrMA layer inside the film occurred at the copolymer/silicon interface and propagated from this interfaces throughout the film. This alternative orientation was also found in films with ca. 6100 Å thickness. Their depth profiles shows consistently regular alternative pattern with the same period because the size of the lamellar structure is determined by the total number of monomers in the copolymer chain. And TOF-SIMS depth profiles are in good agreement with the NR results. The ability to obtain depth profiles of microdomain separated dPS-PPrMA, made possible in this case by the Cs^+ sputter sources, will be of great importance to understanding and applications of the block copolymers.

5. References

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