Stacked Layer to Gyroid Structures in Partially Fluorinated PS-\textit{b}-PtBMA Copolymer Films

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Partial fluorination of polystyrene-\textit{b}\text{-}\textit{poly}(\textit{tert}-butyl methacrylate) (PS-\textit{b}-PtBMA) copolymer was carried out to form PS-\textit{b}-P(\textit{r}BMA-\textit{r}TFEMA-\textit{r}MAA), where TFEMA and MAA denote 2,2,2-trifluoroethyl methacrylate and methacrylic anhydride units, respectively. Phase transitions of a partially (40\%) fluorinated copolymer were investigated both in bulk and film using X-ray scattering techniques. The bulk transition pathways showed lamellae to hexagonally perforated layer (HPL) to gyroid (GYR) as temperature increases, although the volumetric ratio between the two blocks is still close to symmetric composition. Meanwhile in copolymer film, the interfacial interactions at air surface altered temperature-increasing transition pathways including HPL to hexagonally modulated layer (HML). However, the suppressed GYR was recovered in isothermal condition of HML at 240 °C, while remaining the same HPL in isothermal condition at 140 °C, indicating that a HML is less stable in thick films.

Keywords: Block copolymer, Fluorination, Phase transition, HPL, HML, Gyroid

1. Introduction

Significant attention has been dedicated to block copolymer (BCP) self-assembly owing to the spontaneous nanoscale structures from microphase-separation. Well-organized nanostructures with periodicity ($L_0$) in tens of nanometers such as lamellae, cylinder, sphere, and the complex phases have shown high potential to the next generation technology [1-3]. A periodic nanostructure induced by chemical incompatibility between two blocks can be dictated by segregation power $\chi N$ with the volumetric composition ($f$), where $\chi$ and $N$ are the Flory-Huggins interaction parameter between the two blocks and total degree of polymerization, respectively. Accordingly, an increase in $\chi$ is required to meet the demand for reducing feature size at a given $N$, which are applicable to nanoscopic technologies such as nanoporous membranes, nanostructured networks, and nanolithography [4-8].

Many researchers have devoted an intensive effort in search of possible combination of block segments by designing new type of chemical components. Above all, it has been believed that an increase in chemical incompatibility (or an increase in $\chi$) between the two blocks opens up the route possible to sub-10 nm nanostructures. Representatively, fluorine-containing BCP exhibited a dramatic increase in $\chi$ to readily approach to less than 10 nm [9].

On the other hand, newly designed BCP self-assembly sometimes involves morphological transitions during thermal or solvent vapor annealing processes. A side-chain modification of BCP structure or selective incorporation of small molecules into one block was occasionally accompanied by these transitions, because of an increase in volumetric difference of the components [10-12]. The morphological variation can be also promoted by the difference in chain rigidity between the two blocks, because the conformational asymmetry favors interfacial curvatures [13,14]. Therefore, a comprehensive
understanding on the structural and compositional factors affecting the morphological transitions of BCPs is recognized as important.

Previously we reported the morphological behavior by side-chain fluorination using polystyrene-\(b\)-poly(\textit{tert}-butyl methacrylate) PS-\(b\)-PtBMA [15]. Partial introduction of fluorine units to \(b\)BMA effectively increases \(\chi\) to form small lamellae of \(L_0 = 10.1\) nm. However, the formation of anhydride linkages brings an increase in conformational asymmetry, favoring interfacial curvatures toward hexagonally packed cylinder (HEX) and gyroid (GYR). Particularly in BCP films, it is noted that the interfacial interactions at the bottom substrate and/or air surface affect phase behavior and microdomain orientation [16-18].

For a subsequent study, we set a partial fluorination of \(b\)BMAs to be 40% using a symmetric PS-\(b\)-PtBMA copolymer, namely PS-\(b\)-P(\textit{tert}-BMA-r-TFEMA-r-MAA), where TFEMA and MAA denote 2,2,2-trifluoroethyl methacrylate and methacrylic anhydride units, respectively. Small angle X-ray scattering (SAXS) and grazing incidence SAXS (GISAXS) were used to trace phase transitions of the bulk and film BCP self-assembly, respectively. As temperature increases, distinct transition pathways of a partially (40%) fluorinated copolymer were identified between the bulk and film BCP self-assembly. Apart from a stable HPL film, the GYR was recovered from isothermal condition of hexagonally modulated layer (HML) at high temperature.

2. Experimental

A symmetric (\(f_{PS} = 0.490\)) 9.5 kg/mol PS-\(b\)-PtBMA was synthesized and modified into PS-\(b\)-P(\textit{tert}-BMA-r-TFEMA-r-MAA), where transesterification occurs in \(b\)BMA units using 2,2,2-trifluoroethanol. A partially fluorinated copolymer of PS-\(b\)-PrBFA40 was set to denote 40% conversion from \(b\)BMA to TFEMA.

For morphological analysis, the bulk sample was compressed in a 1 mm thick sample holder at 120 °C, and thermally treated at the same temperature under vacuum condition prior to the SAXS measurements. The temperature was controlled at a heating rate of 0.7 °C/min from 30 to 240 °C under nitrogen flow. 400 nm thick PS-\(b\)-PrBFA40 films were prepared by spin-coating onto a standard Si wafer (with 2 nm native oxide layer). Film thicknesses were measured by a spectroscopic ellipsometry (SE MG-1000, Nano-view Co.) at an incidence angle of 70° using a light source of deuterium–tungsten lamp (Hamamatsu Photonics) having photon energy of 1.45–5.00 eV. The same heating rate (0.7 °C/min) was applied to GISAXS measurements under nitrogen flow.

For isothermal experiments, the BCP films were quenched in liquid nitrogen immediately after being thermally annealed at 140 °C or 240 °C for 12 h and 24 h under vacuum. The SAXS and GISAXS experiments were conducted at 4C and 9A beamlines, respectively, in Pohang Accelerator Laboratory (PAL), Korea. A 2D detector (SX 165, Rayonic) was used to record the scattered intensities in a sample-to-detector distance of 2 or 2.5 m and the exposure time of 1 ~ 10 s. Especially for GISAXS, an incidence angle (\(\alpha_i\)) was set as 0.150° above the critical angle (0.109°) of the BCP films to trace the surface and entire film structures.

3. Results and discussion

Figure 1a shows a synthetic scheme of PS-\(b\)-PrBFA40, in which the \(b\)BMA units (side chains) were partially modified to form TFEMA and MAA units. Figures 1b and 1c display \(^1\)H-NMR spectra of (b) a mother PS-\(b\)-PrBMA and (c) PS-\(b\)-PrBFA40.

Fig. 1. (a) Synthetic scheme of PS-\(b\)-PrBFA40 and \(^1\)H-NMR data of (b) a mother PS-\(b\)-PrBMA and (c) PS-\(b\)-PrBFA40.
estimated to be 9.8 kg/mol with no consideration of minor MAA units, and the conversion from tBMA to TFEMA was calculated to be 40%. Based on the mass density of each block: 1.05, 1.02, and 1.45 g/cm$^3$ for PS, PrBMA, and PTFEMA, respectively, $f_{PS}$ of both PS-b-PrBMA and PS-PrBFA40 turned out to be 0.490 and 0.507, respectively, indicating still close to symmetric composition between the two blocks.

Figure 2 shows temperature dependent SAXS intensity profiles of PS-PrBFA40 which were collected at heating rate of 0.7 °C/min. The intensity profiles were vertically shifted for clarity. (b) Corresponding fwhm, $I^{-1}(q^*)$, and (c) $d$-spacing with increasing temperature.

As temperature increases to 195 °C, however, higher-order peaks of HPL weaken and the additional peak assigned by the red arrow arises at 1.15$q^*$ due to the coexistence with GYR. Further increasing temperature to 240 °C, the multiple peaks are assigned by $q/q^* = 0.92 : 1.00 : 1.08 : 1.59 : 1.79 : 1.88 : 2.00$, as denoted by red arrows, corresponding to (113), (105), and (006) planes of an ABC stacked hexagonally perforated layer (HPL) phase, respectively [19].

The scattering parameters are plotted as a function of $1/T$ to discern phase transitions during heating of PS-PrBFA40, as displayed in Figs. 2b and 2c. The drops of $I^{-1}(q^*)$ and fwhm are seen at 160 and 200 °C, as denoted by dashed lines, corresponding to LAM to (HPL+GYR) and (HPL+GYR) to GYR transitions, respectively. The weak variation in $d$-spacing is presumably attributed to the epitaxial growth during transitions [21]. Moreover, the overall decrease in $d$-spacing indicates that $\chi$ between the PS and PrBFA blocks decreases with increasing temperature, as a typical order-to-disorder transition (ODT) type.

Consequently, the bulk PS-PrBFA40 undergoes phase transitions of LAM-(HPL+GYR)-GYR by
the decrease in $\chi$ with temperature, even though the volumetric ratio between the two blocks is still close to symmetric composition. Notably, the second random block of PrBFA becomes more rigid than the flexible PS block because additional anhydride linkages are formed among segments as temperature increases [15]. For this reason, we presume that the phase transition from LAM to GYR is due to an increase in conformational asymmetry that favors interfacial curvatures with increasing temperature, not to an increase in volumetric asymmetry.

To comprehend BCP morphologies confined in film geometry, Fig. 3 shows 2D GISAXS patterns of PS-PrBFA40 films, which were selected at the target temperatures during heating at a heating rate of 0.7 °C/min. The planes of each structure are assigned based on the reflected peaks. The sequential phase transitions of bulk and film are displayed on the bottom for comparison. Higher temperatures of 180 and 240 °C (Figs. 3c and 3d), the GISAXS patterns exhibit the characteristic peaks of a modulated layer with (01) and (10) planes, corresponding to a HML with C2mm space group. It should be pointed out that the HML turned out to be a stable structure, especially in thinner films than 10 $L_0$ since the interfacial interactions suppress the development of perforated channels [17]. However, our observation of HML is unusual in such a thick ($33L_0$) film, and there is no indication of GYR in film geometry during heating process.

The dissimilar pathways between the bulk and film BCP self-assembly are attributed to the interfacial interactions, as the PrBFA block is more favorable with air surface due to lower surface energy of fluorine units. The sequential phase transitions of the bulk and films are displayed on the bottom of Fig. 3 for comparison.

Figure 4 shows isothermal results of PS-PrBFA40 films, which were annealed at constant temperatures of 140 and 240 °C for long times (12 and 24 h). The 2D GISAXS patterns (Figs. 4a and 4b) coincide with an ABC stacking HPL with increasing annealing time in isothermal condition at 140 °C, which is also identified in the bulk sample. Another isothermal condition at
240 °C for 12 h (Fig. 4c) reveals a consistent HML with that similarly observed during heating experiment.

Surprisingly, longer annealing time of 24 h with the same temperature at 240 °C (Fig. 4d) produces a well-developed GYR with (121) and (220) planes. From the absence of HML and generation of GYR for longer annealing time at 240 °C, we infer that a HML is less stable in such a thick film like 33L0, which is consistent with prior result [17]. The interfacial interactions at air surface seem to alter temperature-increasing transition pathways including HPL to HML. Nevertheless, the GYR eventually recovers from a transient HML, indicating a long-time equilibrium morphology.

4. Conclusion
We have studied transition behaviors on a partially (40%) fluorinated PS-b-PtBMA, namely PS-b-P(bBMA-r-TFEMA-r-MAA) using X-ray scattering techniques. An increase in conformational asymmetry by the second random block leads to the phase transitions of LAM-(HPL+GYR)-GYR with increasing temperature, although the volumetric ratio between the two blocks is still close to symmetric composition.

Unlike the bulk transition pathways, the thick films present dissimilar pathways of HPL-HML during heating process, which is attributed to the preferential interfacial interactions at air surface with the PtBFA block. Such interactions and slow kinetics suppress the formation of GYR in film geometry. However, the suppressed GYR recovers in isothermal condition of HML at 240 °C for longer annealing time (24 h), while remaining the same HPL in isothermal condition at 140 °C.

As a matter of fact, a stable HML was reported in polystyrene-b-poly(2-vinylpyridine) films ≤ 10L0 even above the ODT temperature of the bulk, which is attributed to the suppressed compositional fluctuations by the enhanced substrate interactions [17]. In such a thick (33L0) PS-PtBFA40 film, our isothermal results support that a less stable HML morphology transits into GYR.

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