Side-Chain Fluorination Effects on Morphological Behavior of PS-b-PtBMA: Disorder to Order Structures

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Side-chain fluorination effects on morphological behavior of symmetric polystyrene-b-poly(tert-butyl methacrylate) (PS-b-PtBMA) was investigated using small angle X-ray scattering, where the tBMA units were partially modified into 2,2,2-trifluoroethyl methacrylate (TFEMA) and methacrylic anhydride (MAA) units to form PS-b-P(tBMA-r-TFEMA-r-MAA)s. Above 50% fluorination from 7.8 kg/mol PS-b-PtBMA, a lamellar structure was identified over the entire temperature range up to 240 °C. However, a 36% fluorination product exhibited the morphological transition from cylindrical to gyroid structures further to disordered state with increasing temperature. This abnormal phase stability was attributed presumably to a transient increase in conformational asymmetry that creates spontaneous interfacial curvatures between the two blocks.

Keywords: Block copolymer, Fluorination, High-χ, Lamellae, Cylinder, Gyroid

1. Introduction

Block copolymer (BCP) self-assembly has offered the platform for soft material nanotechnology due to their well-defined nanoscopic arrays and patterns with a typical feature size from 10 to 50 nm [1-4]. To take a leading nanotechnology for the industrial application, scaling down the feature size has gained great attention for ordering and microdomain orientation of the small size BCPs. Recently, the feature size of diblock copolymers has remarkably dropped down below 10 nm using the new-generation high-χ BCPs, where χ denotes the Flory-Huggins interaction parameter between the two blocks [5-8]. Since an inter-lamellar spacing (L₀) in the strong segregation regime has a relationship by L₀ ~ N²/₃χ¹/₆, where N is the total number of segments, such an increase in χ of BCPs promotes the miniaturization of feature sizes (or reduction in N) to satisfy the critical value χN >> 10.5 in a symmetric ordering of lamellar structure [9-11].

To enlarge the χ, Lodge, Hillmyer, and coworker introduced fluorine substitution using polystyrene-b-polyisoprene (PS-b-PI), in which the fluorine addition reaction in isoprene units increases χ between the two components [12]. Similarly reported by Rzayev, Russell, and coworkers using poly(solketal methacrylate)-b-PS, the partial substitution of solketal methacrylate into glycerol-including units intrinsically increases χ due to high incompatibility of hydrophilic hydroxyl (HO) units against the disparate PS block [13]. A direct synthesis of fluorine-containing BCPs was designed by Hayakawa and coworkers to gain high incompatibility with PS or Si-containing blocks [14, 15]. The strong incompatibility, compared to a precursor BCP, can be also accessed by an ionic incorporation into the selective blocks due to an increase in χ between the two components [16].

Meanwhile, the partial substitutions or selective coordinations readily alter the volumetric ratio between the two components, leading to the morphological transitions that cross the phase boundaries. Understanding the phase transitions during selective reaction of BCPs is of importance to figure out the pathway for desired morphologies of self-assembled nanostructures. Several reports have demonstrated the phase transitions using tert-butyl (meth)acrylate units that are capable to transform into acrylic acid or anhydride units upon...
heating (the so-called thermal deprotection) [17]. This chemical transformation is accompanied by a volumetric change of the BCPs by intra- and intermolecular cross-links, resulting in regularly organized nanostructures through morphological transition in topological trench patterns [18]. However, an additional aspect of the change in statistical segment length during side-chain modification has been overlooked, although the phase stability can be influenced by conformational asymmetry effect (or chain rigidity contrast) that that creates interfacial curvatures between the two blocks [19].

In this study, we controlled the partial substitution of tert-butyl methacrylates (tBMAs) using a symmetric PS-b-PtBMA, where the side-chains of tBMA units were partially modified into 2,2,2-trifluoroethyl methacrylate (TFEMA) and methacrylic anhydride (MAA) units. We studied temperature dependence of morphologies such as lamellar, cylinder, and gyroid, which were obtained from the various degrees of chemical transformation.

### 2. Experimental

A symmetric PS-b-PtBMA was synthesized by living anionic polymerization of styrene and tBMA monomers in tetrahydrofuran (THF) at -78 °C under purified argon using sec-butyllithium (1.4 M, Aldrich) as an initiator. The number-average molecular weight ($M_n$) of a PS-b-PtBMA and dispersity ($D = M_w/M_n$) were characterized by size-exclusion chromatography (SEC) using the PS standard samples. PS volume fraction ($f_{ps}$) was determined by $^1$H nuclear magnetic resonance ($^1$H NMR) spectroscopy based on the mass densities of 1.05 and 1.022 g/cm$^3$ for PS and PtBMA, respectively.

A series of partially substituted BCPs (as listed in Table 1), PS-b-P(tBMA-r-TFEMA-r-MAA)s, were prepared from a PS-b-PtBMA through transesterification with 2,2,2-trifluoroethanol (99+% Alfa Aesar) in tBMA units. Excess amount of degassed fluoro-alcohol and polyphosphoric acid (115% H$_3$PO$_4$ basis, Aldrich) were mixed at room temperature for 4 h. A BCP solution in toluene (98%, Junsei) was further added to the mixture under argon environment, followed by refluxing at 130 °C with different reaction times. The products were repeatedly precipitated in the water saturated with sodium hydrogen carbonate (99+%, Junsei) to rinse residual 2,2,2-trifluoroethanol and polyphosphoric acid. Finally, each sample was dried below 60 °C under vacuum for 48 h [6].

| Sample code | $M_n$ (g/mole) | $D$ ($M_w/M_n$) | $f_{ps}$ | Fluorination (%)$^b$ ($\text{PtBMA} \rightarrow \text{PTFEMA}$) |
|-------------|----------------|----------------|----------|---------------------------------|
| PS-b-PtBMA  | -              | 7800           | 1.12     | 0.495                           |
| PS-b-P(tBMA-r-TFEMA-r-MAA)36 | SBFA36 | 8000           | 1.12     | 0.510                           | 35.6           |
| PS-b-P(tBMA-r-TFEMA-r-MAA)50 | SBFA50 | 8100           | 1.12     | 0.517                           | 49.8           |
| PS-b-P(tBMA-r-TFEMA-r-MAA)76 | SBFA76 | 8300           | 1.12     | 0.529                           | 76.3           |

$^a$PS volume fraction and $^b$fluorination from PtBMA to PTFEMA were calculated by $^1$H NMR in CD$_2$Cl$_2$ solution, where the mass densities for the corresponding block are 1.05, 1.022, and 1.45 g/cm$^3$ for PS, PtBMA, and PTFEMA, respectively.
3. Results and discussion

Figure 1a shows the FT-IR spectra of PS-b-PtBMA and side-chain modified samples, where the S\textsubscript{t}BFA\(x\)x denotes partially fluorinated BCPs with \(\times\%\) conversion to TFEMA. Each conversion of S\textsubscript{t}BFAs was calculated by 1\text{H}-NMR results based on methylene units of TFEMA substituted at expense of \text{tert}-butyl units [6]. FT-IR spectrum of PS-b-PtBMA displays the characteristic absorption bands including C=O stretching of ester, phenyl ring stretching, CH\(_3\) bending of \text{tert}-butyl unit, and C-O stretching of ester, corresponding to 1724, 1601/1493/1454, 1393/1367, and 1140 cm\(^{-1}\), respectively.

With partial substitution into S\textsubscript{t}BFAs, most of characteristic absorption bands from tBMA units weaken, and additional absorption bands of C-F stretching and bending of CF\(_3\) occur at 1285 and 660 cm\(^{-1}\) (denoted as the red dotted lines), respectively. The shifts in two absorption bands of C=O stretching to 1805 and 1755 cm\(^{-1}\) (denoted as the green dotted lines) indicate the generation of MAA and TFEMA at expense of tBMA, while an absorption band of C-O stretching at 1022 cm\(^{-1}\) (denoted as the blue dotted line) arises only from MAA. Hence, we analogize the possible chemical structure of S\textsubscript{t}BFA, as described in Fig. 1b displaying a PS-b-P(tBMA-r-TFEMA-r-MAA).

Figure 2 shows the SAXS intensity profiles of PS-b-PtBMA and S\textsubscript{t}BFAs, which were measured at room temperature. The scattering vector \(q = (4\pi / \lambda) \sin \theta\), where \(\lambda\) and \(2\theta\) are wavelength and scattering angle of the incident beam, respectively. No characteristic peak is observed in PS-b-PtBMA due to a disordered state as well as its low electron density contrast between the two blocks. With partial substitution, the S\textsubscript{t}BFA36 exhibits a sharp primary peak (at \(q^*\)) along with higher-order peaks at \(q / q^* = 1:2:7:3\), corresponding to a hexagonally packed cylindrical structure. The 36\% partial substitution into PTFEMA produces a random block consisting of tBMA-r-TFEMA-r-MAA, and it sufficiently increases the segregation strength to develop microphase separation into a cylindrical structure against the PS block. As a possible result, the cylindrical morphology is attributed to a transient increase in conformational asymmetry that creates spontaneous interfacial curvatures between the two blocks [19] in addition to the volumetric shrinkage in the random block.

However, the S\textsubscript{t}BFA50 displays a sharp primary peak along with higher-order peaks at \(q / q^* = 1:2:7:3\),
corresponding to an asymmetric-like lamellar structure, as also observed in StBFA76. Notably, the smallest lamella-spacing ($L_0 = 10.1$ nm evaluated by $L_0 = 2\pi/q^*$) was identified in StBFA76, which is smaller than that ($L_0 = 11.2$ nm) of StBFA50. Considering a consistent lamellar morphology between the two StBFAs, larger lamellae ($L_0 = 11.2$ nm) of StBFA50 indicates that the $\chi$ (or incompatibility against the PS block) between the two components of StBFA50 is larger than that of StBFA76.

Temperature dependent SAXS intensity profiles of StBFA50 and StBFA76 are shown in Fig. 3, which were measured at a heating rate of 0.7 °C/min. The intensity profiles of both StBFAs display only the characteristic peak ratios of $q/q^* = 1:2:3$ over the entire temperature range up to 240 °C. A lamellar morphology of StBFA50 annealed at 130 °C was confirmed by a TEM image, as displayed in the inset, where the PS block (as the darker phase) was selectively stained with RuO$_4$ to enhance the phase contrast. According to the relationship of $L_0 \sim N^{2/3}\chi^{1/6}$ in the strong segregation regime [10], a gradual decrease in $L_0$ with increasing temperature represents an order-to-disorder transition (ODT) type behavior as the $\chi$ between the two components decreases with temperature.

![Fig. 3. Temperature dependent SAXS intensity profiles of StBFA50 and StBFA76. The intensity profiles are vertically shifted by a factor of $10^3$ for clarity. An inset TEM image displays a lamellar morphology of StBFA50.](image)

Figure 4 shows the SAXS intensity profiles of StBFA36, which were measured at a heating rate of 0.7 °C/min. From room temperature (25 °C) to 165 °C, the intensity profiles exhibit the peak ratios of $q/q^* = 1:2:3:7:3$, indicating a consistent cylindrical structure. Especially at 170 °C, an additional peak of $1.15q^*$ (at $q = 0.677$) appears at expense of the other higher-order peaks, and the intensities of $q^*$ and $1.15q^*$ increase as temperature increases to 190 °C, corresponding to $\{121\}$ and $\{220\}$ planes of a gyroid structure, respectively [20]. Unfortunately, we failed to measure TEM images for StBFA36 because the sample was too rubbery to handle at room temperature. With further increasing temperature above 200 °C, a diffuse maximum indicates a disordered state as the $\chi$ between the two components decreases. Accordingly, the temperature dependence of StBFA36 reveals the morphological transition from cylindrical to gyroid structures, and further to a disordered state.

![Fig. 4. Temperature dependent SAXS intensity profiles of StBFA36. The intensity profiles are vertically shifted by a factor of $10^3$ for clarity.](image)
To figure out the transitions in S\textsubscript{tBFA36}, the TGA was measured at the same heating rate (0.7 °C/min) under nitrogen flow, as shown in Fig. 5. For comparison, the TGA of PS-b-P\textsubscript{tBMA} was measured as well, representing a significant weight loss (23%) during heating due to the thermal deprotection (or anhydride linkage formation) from 170 to 220 °C. Since all of weight losses arising from the deprotection of remaining tert-butyl units are associated with forming anhydride linkages, the low weight loss (5.2%) of S\textsubscript{tBFA36} to a disordered state is negligibly smaller than that of PS-b-P\textsubscript{tBMA}. However, the anhydride linkages seem to be strongly rigid to enhance the bicontinuous curvatures in a gyroid structure upon heating. Therefore, we presume that the morphological transition from cylindrical to gyroid structures is caused by an increase in conformational asymmetry that shifts the phase diagram, because the random block (consisting of tBMA-r-TFEMA-r-MAA) become rigid (or translationally hindered) in contrast with the flexible PS block, rather than the volumetric shrinkage in the random block.

Meanwhile, a disordered state at higher temperature (above 200 °C) is attributed to a decrease in $\chi$ between the two components of StBFA36.

4. Conclusion
In summary, the side-chain fluorination effects on morphological behavior was studied by controlling the partial substitution using a symmetric 7.8 kg/mol PS-b-PtBMA, where the tBMA units were partially modified into TFEMA and MAA units during transesterification to form PS-b-P(tBMA-r-TFEMA-r-MAA). A lamellar structure was observed for above 50% fluorination products (StBFA50 and StBFA76) over the entire temperature range, while demonstrating the smallest $L_0 = 10.1$ nm of StBFA76. Judging from a larger lamellae ($L_0 = 11.2$ nm) of StBFA50, the $\chi$ between the two components of StBFA50 is larger than that of StBFA76. Particularly, a 36% fluorination product (StBFA36) revealed the morphological transition from cylindrical to gyroid structures further to disordered state with increasing temperature. We speculated a transient increase in conformational asymmetry that creates spontaneous interfacial curvatures between the two blocks to shift the phase diagram, rather than the volumetric shrinkage in the random block of P(tBMA-r-TFEMA-r-MAA).

Author contributions
$^*$S. J. and S. P. contributed equally.

Acknowledgements
This work was supported by the NRF grants (2017R1A2A2A05001048, 2017R1A4A1014569) funded by the Ministry of Science, ICT & Future Planning (MSIP), Korea.

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