Morphology Transitions of Linear A1B1A2B2 Tetrablock Copolymers at Symmetric Overall Volume Fraction

Seonghyeon Ahn and Jin Kon Kim*

National Creative Research Initiative Center for Smart Block Copolymers, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Republic of Korea

Bin Zhao, Chao Duan, and Weihua Li*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

Supporting Information

ABSTRACT: We investigated morphology transitions of linear tetrablock copolymers of polystyrene-block-polyisoprene-block-polyisoprene-block-polyisoprene (S1I1S2I2) by varying volume fraction of PI block ($f_{PI}$), while maintaining the symmetric volume fraction of total PS blocks and PI blocks ($f_{PS1+PS2}/f_{PI1+PI2}$). An interesting sequence of morphology transitions was observed as $f_{PS1}$ was increased: lamellae (L) $\rightarrow$ asymmetric lamellae (al) $\rightarrow$ hexagonally packed PI-cylinders (CPI) $\rightarrow$ double gyroid with PI-network domains (GPI) $\rightarrow$ short-period lamellae (SL). The domain spacing of SL was nearly half that of L, while al had asymmetric lamellar width of PS and PI microdomains. It is particularly interesting that cylindrical and gyroid morphologies were observed in linear block copolymers with symmetric overall volume fraction at intermediate segregation. The experimentally observed morphologies are in good agreement with the predicted equilibrium phases by self-consistent field theory (SCFT).

1. INTRODUCTION

Block copolymers have been extensively investigated because of their various nanostructures, depending on volume fraction, degree of polymerization ($N$), and the Flory–Huggins interaction parameter ($\chi$). For the phase diagram of a simple diblock copolymer, one of the controlling parameters is the volume fraction of one block. For example, hexagonally packed cylindrical microdomains have been found for AB diblock copolymers with volume fractions of one block ($f_A$) having 0.2–0.35, while lamellar microdomains were observed at $f_A$ having 0.35–0.5. However, binary blends of two block copolymers (AB)$_1$ and (AB)$_2$ where $f_A$ in (AB)$_1$ is different from that in (AB)$_2$ showed unconventional microdomains not attained for neat AB diblock copolymer. For example, Hashimoto and co-workers showed that binary blends of two lamellar forming polystyrene-block-polyisoprene copolymers (PS-b-PI) with different molecular weights exhibited hexagonally packed cylinders, although the volume fraction of PS ($f_{PS}$) in one PS-b-PI was 0.53, while that in the other PS-b-PI was 0.55. Sakurai and co-workers reported that binary blends of two cylinder-forming PS-b-PI with different $f_{PS}$ ($f_{PS}$ in one PS-b-PI was 0.65, while that of the other PS-b-PI was 0.26) showed gyroid microdomains when the overall volume fraction of PS block in the blend was 0.6. In addition, binary blends of AB and AC diblock copolymers where B and C blocks were capable of hydrogen bonding showed unconventional microdomains that could not be obtained by neat block copolymers of AB or AC. We obtained highly asymmetric lamellar structure by blending asymmetric polystyrene-block-poly(2-vinylpyridine) copolymer (as-PS-b-2PVP) and asymmetric polystyrene-block-poly(4-hydroxy styrene) copolymer (as-PS-b-PHS), even though both neat as-PS-b-2PVP and as-PS-b-PHS were body-centered cubic (BCC) spherical microdomains, where the hydrogen bond was expected between P2VP and PHS. Also, hexagonally packed cylindrical microdomains were obtained when a higher molecular weight of lamellar forming PS-b-P2VP was blended with a lower molecular weight of lamellar forming PS-b-PHS, where the volume fraction of total PS block in the blend was the same as that of P2VP + PHS blocks.

Among many microstructures, cylindrical and gyroid structures have received great attention due to potential applications to nanoporous and advanced optical materials. Wide ranges of the channel width in the gyroid structures would be needed to design a new optical material such as metamaterial because bandgap and effective plasma wavelength are easily adjusted by the channel size of gyroid structure. However, gyroid structures are usually observed at a narrow range of volume fraction of A block ($\sim$0.35) in AB diblock copolymer. Also, to facilitate the flux in nanoporous

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In this study, we verified experimentally the re-entrant phase behavior of linear A1B1A2B2 tetradiblock copolymers by changing the asymmetry of B blocks. For this, we synthesized, via anionic polymerization, S1I1S2I2 with various volume fractions (or chain lengths) of PI1 and PI2 blocks while keeping symmetric overall volume fraction of PS and PI blocks. We found, via small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM), that microdomains of S1I1S2I2 at a given fPS = 0.4 were changed from lamellae with symmetric width (L), to lamellae with asymmetric width (aL), to hexagonally packed cylinders with PI chains (CPI), then double gyroids with PI network domain (GPI), and finally short-period lamellae with symmetric width (sL), with increasing the chain length of PI block. The microdomain transitions are well consistent with those predicted by SCFT. CPI and GPI observed at a total volume fraction of PS blocks ~0.5 in linear A1B1A2B2 tetradiblock copolymers are very interesting because cylinder microdomain is expected for the volume fraction of A block (fA) having 0.2–0.35 (or 0.65–0.8) and gyroids for fA ~ 0.35 (or 0.65) in AB diblock and ABA linear triblock copolymers.

2. EXPERIMENTAL SECTION

Materials. S1I1S2I2 tetradiblock copolymers with various volume fractions of each block were synthesized by sequential anionic polymerization of styrene, isoprene, styrene, and isoprene in tetrahydrofuran (THF) at −78 °C under a purified argon atmosphere with benzyl potassium initiator. Styrene was polymerized for 4 h. At each step, we obtained aliquots by a syringe before addition of the next monomer.

Determined by SEC based on PS standard. *Calculated by 1H NMR with known density at room temperature (ρPS: 0.926; ρPI: 1.05). **τPS = (NPI1/ (NPI1 + NPS)) = (fPS1/(fPS1 + fPS2)). *SISI24/SISI40 was prepared by blending 35/65 (w/w) SISI24/SISI40. Mn, fPStotal, fPS2fPI2fPStotal and τPS of the blend sample were calculated by average value of neat samples. L = lamellae, aL = asymmetric lamellae width of PS and PI microdomains, CPI = hexagonally packed PI-cylinder, GPI = double gyroid with PI-network domains, sL = short period lamellae.
temperature (RT). For the complete removal of THF, samples were under vacuum for 24 h. Then, samples were thermally annealed at 240 °C for 2 h under high vacuum and quenched at RT. To fine-tune $\tau_{PI}$ between 0.24 and 0.40, we blended SISI24 and SISI40 (35/65 w/w) having $\tau_{PI} = 0.34$.

**Small-Angle X-ray Scattering (SAXS).** SAXS profiles $I(q) \propto q^\alpha$ vs $q \big(= (4\pi/\lambda) \sin \theta \big)$, where $q$ is the scattering vector and $2\theta$ is the scattering angle] were obtained at the in-vacuum Undulator 20 beamline (4C SAXS II) of the Pohang Accelerator Laboratory (PAL) Korea. The wavelength and beam size were 0.675 Å and 0.2 (beamline (4C SAXS II) of the Pohang Accelerator Laboratory (PAL) having $\tau_{PI}$ relative to $q^* (0.142$ nm$^{-1}$ corresponding to $D = 47$ nm), it was different from that of SISI0. First, the domain spacing slightly decreased compared with that of SISI0. Second, the strong scattering peaks at $2q^*$ and $4q^*$ imply that the lamellar widths of PS and PI microdomains in SISI17 should be unequal. From the paracrystalline model fitting to SAXS profile (Figure S3), the predicted volume fraction of PS was 0.59. This is consistent with the observed lamellar width ratio of PS to PI microdomains (about 3:2) from TEM image (inset of Figure 2b). At $\tau_{PI} = 0.24$—0.30, the scattering peaks at positions of $1:3:2$ relative to $q^*$ (0.200 nm$^{-1}$ for SISI24; 0.199 nm$^{-1}$ for SISI30) were observed. Thus, SISI24 and SISI30 showed hexagonally packed cylindrical morphologies. The domain spacing $D$ (or the cylinder-to-cylinder distance) was measured as 31 nm (or 36 nm) for the two samples. Well-ordered hexagonal packed cylinders were clearly seen in TEM images (Figure 2c,d) of SISI24 and SISI30. The volume fraction of the cylindrical cores from TEM image was estimated as almost 0.5. At $\tau_{PI} \sim 0.34$, the SAXS profile showed scattering peaks at positions of $\sqrt{6} : \sqrt{8} : \sqrt{14} : \sqrt{16} : \sqrt{18} : \sqrt{20} : \sqrt{22}$ relative to $q^*$ (0.274 nm$^{-1}$), corresponding to double gyroid. Figure 2e shows the [110] projection of the double gyroid. The double gyroid morphology of SISI34 was further confirmed by birefringence

**Transmission Electron Microscopy (TEM).** The samples were ultrasonicated using a Leica Ultracut Microtome (EM UC6 Leica Ltd.) at room temperature with a thickness of 40 nm. Then they were stained by exposure to OsO$_4$ vapor for 24 h at room temperature. The PI microdomains look dark in TEM images. The micrographs were taken at room temperature with bright-field TEM (S-7600 Hitachi Ltd.) at 80 kV.

3. RESULTS AND DISCUSSION

All samples showed unimodal and narrow molecular distribution (PDI < 1.15), as shown in SEC traces (Figure S1). Also, there was no peak corresponding to SIS triblock (or SI diblock and S homopolymer) due to using anionic polymerization. Thus, we successfully synthesized SISI0, SISI17, SISI24, SISI30, SISI40, and SISI60 with various $\tau_{PI}$ with a given $\tau_{PS} = 0.34$.

**Figures 1 and 2** give SAXS profiles and TEM images of all samples. At $\tau_{PS} = 0.17$ of SISI17, although the SAXS profile shows scattering peaks at positions of $1:2:3:4:5$ relative to $q^*$ (0.111 nm$^{-1}$), the lamellar domain spacing ($D = 2\pi/q^*$) obtained from SAXS profile was 57 nm. Very weak peaks at $2q^*$ and $4q^*$ indicate that SISI0 has symmetric lamellar width of PS and PI microdomains. This is consistent with the inset of TEM image in Figure 2a. At $\tau_{PS} = 0.17$ of SISI17, although the SAXS profile also shows scattering peaks at positions of $1:2:3:4:5$ relative to $q^*$ (0.111 nm$^{-1}$), it was different from that of SISI0. First, the domain spacing slightly decreased compared with that of SISI0. Second, the strong scattering peaks at $2q^*$ and $4q^*$ imply that the lamellar widths of PS and PI microdomains in SISI17 should be unequal. From the paracrystalline model fitting to SAXS profile (Figure S3), the predicted volume fraction of PS was 0.59. This is consistent with the observed lamellar width ratio of PS to PI microdomains (about 3:2) from TEM image (inset of Figure 2b). At $\tau_{PS} = 0.24$—0.30, the scattering peaks at positions of $1:3:2$ relative to $q^*$ (0.200 nm$^{-1}$ for SISI24; 0.199 nm$^{-1}$ for SISI30) were observed. Thus, SISI24 and SISI30 showed hexagonally packed cylindrical morphologies. The domain spacing $D$ (or the cylinder-to-cylinder distance) was measured as 31 nm (or 36 nm) for the two samples. Well-ordered hexagonal packed cylinders were clearly seen in TEM images (Figure 2c,d) of SISI24 and SISI30. The volume fraction of the cylindrical cores from TEM image was estimated as almost 0.5. At $\tau_{PS} \sim 0.34$, the SAXS profile showed scattering peaks at positions of $\sqrt{6} : \sqrt{8} : \sqrt{14} : \sqrt{16} : \sqrt{18} : \sqrt{20} : \sqrt{22}$ relative to $q^*$ (0.274 nm$^{-1}$), corresponding to double gyroid. Figure 2e shows the [110] projection of the double gyroid. The double gyroid morphology of SISI34 was further confirmed by birefringence
measurement because only SISI34 among all samples did not show any birefringence (Figure S4). When $\tau_{PI}$ was further increased, the scattering peaks became similar to those of SISI0, suggesting that the morphology was transformed back to symmetric lamellae. $D$ of SISI40 and SISI60 was measured as 19 and 23 nm, respectively, which is nearly half of that of SISI0.

In summary, by increasing $\tau_{PI}$ the morphology of S1I1S2I2 transferred from symmetric lamellae (L) to asymmetric lamellae (aL) to double gyroid with PI network (GPI) and finally to short-period symmetric lamellae (sL).

**Table 2. Free Energy per Chain of Various Ordered Mirodomains of S1I1S2I2 Samples Calculated by SCFT**

<table>
<thead>
<tr>
<th>sample</th>
<th>L or aL</th>
<th>C_{PI}</th>
<th>G_{PI}</th>
<th>sL</th>
</tr>
</thead>
<tbody>
<tr>
<td>SISI0</td>
<td>6.119</td>
<td>8.557</td>
<td>8.558</td>
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</tr>
<tr>
<td>SISI17</td>
<td>8.536</td>
<td>10.022</td>
<td>10.046</td>
<td></td>
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<td>SISI24</td>
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<td>11.184</td>
<td>11.192</td>
<td>11.263</td>
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<tr>
<td>SISI30</td>
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<td>11.192</td>
<td>11.263</td>
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<tr>
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<tr>
<td>SISI60</td>
<td>10.428</td>
<td>10.284</td>
<td>10.104</td>
<td></td>
</tr>
</tbody>
</table>

"The free energy was calculated by the pseudospectral method of SCFT using the parameters provided in Table S1 of the Supporting Information. The free energy data of the equilibrium morphology of each sample are shown in bold font.

predicted by SCFT are $L$, aL, C_{PI}, C_{PS}, G_{PI}, sL, and sL for SISI0, SISI17, SISI24, SISI30, SISI34, SISI40, and SISI60, respectively, which are in good agreement with the experimental observations. Density color map and one-dimensional density distribution for each sample calculated by SCFT are given in Figure S5.

Figure 3 gives D-spacing change of S1I1S2I2 with $\tau_{PI}$ at a given $\tau_{PS} = 0.4$, normalized by D-spacing of SI diblock copolymer ($\tau_{PS} = 0$). Since the total molecular weight ($M$) of all S1I1S2I2 samples was not the same, we additionally normalized $D$ by $N^{2/3}$ because of different total molecular weight of the samples. Whether the relationship of $D$ by $N^{2/3}$ holds for tetrablock copolymers, we obtained the dependence of $D$ on $N$ at fixed $\tau$ by the SCFT. As shown in Figure S6, $D$ of the different morphologies formed in the tetrablock copolymers with various values of $\tau$ exhibits a very good scaling relationship as $D \sim N^{2/3}$.

The explanation of the change of $D$ with $\tau_{PI}$ is as follows. As the symmetric lamellae transformed to asymmetric lamellae, the

D-spacing decreased slightly. This is because some PI blocks form looping configuration, causing to decrease the D-spacing. However, the portion of looping PI blocks is small, leading to a mild change in the D-spacing. When lamellar microdomains changed to C_{PI} the D-spacing rapidly decreased. This is attributed to the fact that many PI blocks migrate from the PS microdomain into the PI microdomain to overcome enthalpy penalty. In this situation, the portion of looping PI blocks increased rapidly, resulting in a sudden drop of the D-spacing.

When $\tau_{PI}$ is slightly increased, most of the short PI blocks prefer to being dangled in the PS microdomain instead of aggregating with the long PI blocks. With $\tau_{PI}$ increasing, a decreased portion of PI blocks swells the PS microdomain. Obviously, varying a portion of PI blocks swelling PS microdomain leads to a change of the volume of PS microdomain or PI microdomain, i.e., the effective volume fraction of PS and PI microdomains ($f_{PS}^{eff} > 0.5$ or $f_{PI}^{eff} < 0.5$) differing from the total volume fraction of S1I1S2I2 diblock copolymer (e.g., $f_{PS} = f_{PI} = 0.5$). The swollen PS microdomain becomes larger than the PI microdomain, leading to asymmetric lamellae (aL) (Figure 4b). Then, the domain spacing is slightly decreased, consistent with the experimental result given in Figure 3. With SISI17 sample, $\tau_{PI} = 0.17$, the width ratio between PS and PI microdomains was measured about 3:2, i.e., $f_{PS}^{eff} \approx 0.4$ To Predict $f_{PI}^{eff}$ depending on $\tau_{PI}$ we performed SCFT calculation, and the result is given in Figure 4f. From Figure 4f, the predicted $f_{PI}^{eff} = 0.43$ at $\tau_{PI} = 0.17$, close to the TEM image (Figure 2b). To confirm the compatibility between PS block and PI block in SISI17 sample, we performed differential scanning calorimetry (DSC) measurement. In SISI17, the glass transition temperature ($T_g$) of the PI block is the same as SISI0, but $T_g$ of the PS block ($T_g = 96^\circ C$) is definitely lower than that ($104^\circ C$) of SISI0, even though

Figure 3. Change of D-spacing for S1I1S2I2 with $\tau_{PI}$ at a given $\tau_{PS} = 0.4$, normalized by D-spacing of SI diblock copolymer ($\tau_{PS} = 0$): (■) lamellae, (◇) asymmetric lamellae, (▲) cylinders, (○) gyroids, and (□) short-period lamellae.

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they have similar molecular weights (Figure S7). This indicates that some of PI chains are dissolved into the PS microdomain.

When \( \tau_{PI} \) is further increased, the lamellar morphology transformed to the cylindrical morphology (Figure 4c). Surprisingly, an increase of \( f^a_{PI} \) is accompanied by the transition to CPI which is induced by the change of the chain configurations in response to the change of interfacial geometry. As the PI1 block becomes long, the interfacial energy between PI1/PS blocks becomes dominant over entropy, thus driving PI blocks to migrate from the PS microdomain into the PI microdomain. The PI1 blocks joining PI microdomains have to form loop configurations, causing an energy penalty. The energy penalty is relieved in curved interfacial geometries, thereby benefiting the formation of the CPI morphologies compared with the lamellar morphology.

After passing the transition from \( aL \) to CPI, increasing \( \tau_{PI} \) increases \( f^a_{PI} \) because longer PI1 blocks are more separated from PS blocks and are mixed with PI2 blocks. The increased \( f^a_{PI} \) leads to GPI morphology from CPI morphology (Figure 4d). Because the entropy penalty for the formation of loop configuration of the PI1 blocks in GPI is smaller than that in LAM, GPI becomes stable microdomains even at nearly symmetric effective volume fraction \( (0.45 < f^{eq}_{eff} < 0.46) \).

When the PI1 block is long enough \( (\tau_{PI} > 0.34) \), most PI1 blocks are separated from PS blocks and are mixed with PI2 blocks, which increased the effective volume fraction of the PS microdomain. Thus, the morphology changed from lamellar to asymmetric lamellar, cylinder, double gyroid, and finally to short-period lamellar (half-domain size). The experimental results were consistent with the results of SCFT. The morphology mainly depended on the length of the PI1 block. When the PI1 block was short, some of the PI1 blocks would stay inside the PS microdomain instead of joining the PI2 blocks, which increased the effective volume fraction of the PS microdomain.

4. CONCLUSION

A series of linear S1I1S2I2 tetrablock copolymers with symmetric volume fraction of PS/PI blocks were synthesized by sequential anionic polymerization, and their self-assembly behavior was studied by SAXS and TEM. With increasing the asymmetry of the PI1 block, the morphology changed from lamellar to asymmetric lamellar, cylinder, double gyroid, and finally to short-period lamellar (half-domain size). The experimental results were consistent with the results of SCFT. The morphology mainly depended on the length of the PI1 block. When the PI1 block was short, some of the PI1 blocks would stay inside the PS microdomain instead of joining the PI2 blocks, which increased the effective volume fraction of the PS microdomain. Thus, the morphology changed from lamellar to asymmetric lamellae. When the PI1 block was further increased, the interfacial energy between PI1/PS blocks became dominant over entropy. In this situation, the PI1 blocks joining PI microdomains have to form loop configurations, causing an energy penalty. This energy penalty was relieved in curved interfacial geometries, resulting in cylindrical microdomains and double gyroid. However, when the PI1 block was long enough, PI1 and PS2 blocks tend to form both loop and bridge configurations to maximize the configurational entropy, causing re-entry of lamellae. An important conclusion from our study is that double gyroid and cylindrical microdomains could be formed in near linear block copolymers with symmetric overall volume fraction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00567.

SEC chromatogram, \(^1^H\) NMR spectra, fitting data of SAXS profile with a variable lamellar thickness structure model, birefringence data, parameters of the experimental samples used in the calculations of SCFT, density color maps and one-dimensional density distribution.
calculated by SCFT, domain spacing calculations of SCFT as a function of $\chi N$, DSC curves (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail jkkim@postech.ac.kr (J.K.K.).
*E-mail weihuali@fudan.edu.cn (W.L.).

ORCID

Jin Kon Kim: 0000-0002-3872-2004
Weihua Li: 0000-0002-5133-0267

Notes

The authors declare no competing financial interest.

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