Materials Science

15A/2007G100

Fddd phase boundary of polystyrene-*block*-polyisoprene diblock copolymer melts in polystyrene-rich region

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Introduction

Recently, we found the *Fddd* structure has been found to exists as an equilibrium structure of polystyrene-*block*-polyisoprene (SI) diblock copolymer for the first time in addition to lamellae (L), gyroid (G), hexagonally packed cylinder (C), and sphere in the body-centered lattice (S)[1-3]. We observed the *Fddd* structure exists between lamella and gyroid phases and lamella-*Fddd*-gyroid-disorder transition occurs according to the increase in temperature. We found that the stable region of *Fddd* phase is limited within $0.629 \leq f_{PI} \leq 0.649$ and $25.59 < \chi N < 29.78$, where f_{PI}, χ, and, N are, respectively, volume fraction of PI in SI diblock copolymer, the Flory-Huggins interaction parameter between two polymers, and polymerization index of the diblock copolymer. In our previous studies described above, we focused on *Fddd* phase in PI rich region or $f_{PI}>0.5$. It is anticipated that *Fddd* phase exists in polystyrene (PS) rich region or $f_{PI}<0.5$. In this study, we, thus, synthesized eight SI diblock copolymers with various compositions in PS rich region and investigated their phase behavior by small-angle X-ray scattering (SAXS) to determine the *Fddd* phase boundary in PS rich region.

Experimental section

Eight SI diblock copolymer samples having $f_{PI} \leq 0.5$ were synthesized via living anionic polymerization at 50˚C in benzene under an argon environment using sec-BuLi as an initiator. Synchrotron SAXS experiments were performed at BL-15A in KEK to examine the phase behavior of samples. At BL-15A, the X-ray wavelength and the sample-to-detector distance were, respectively, 1.54Å and 2000mm. Imaging plates were used as the detector. Prior to SAXS experiment, cast films were annealed in the 3mm SAXS holder at 230˚C corresponding to disorder state, for 30 min followed by annealing at 120˚C for 1 day under vacuum and quenched to RT. Most of SAXS profiles were measured after keeping the sample at each temperature for at least 30 min. The obtained data was corrected for air scattering.

Results and discussion

Figure 1 shows the temperature dependence of SAXS profiles of I4 (f_{PI}=0.389) during heating procedure. The scattered intensity I(q) in arbitrary unit is plotted as a function of wave number q ($q = (4\pi/\lambda)\sin(\theta/2)$; θ is scattering angle and λ is wavelength). At 230˚C, a single broad peak is observed, reflecting that I4 is in its disordered state. At 145 and 150˚C, we found that the peaks in the SAXS profiles appeared at q with integer multiples of q_m, where q_m is q at the first order peak. This indicates that I4 has the lamella phase at 145 and 150˚C. At 155 and 160˚C, we could observe the several peaks at q/q_m =1, and 1.22, indicating that *Fddd* is formed at these temperatures. While we observed *Fddd* structure in I4, there is no *Fddd* phase in the other samples. The other samples shows L-disorder transition or L-G-disorder transition. The χN region of the *Fddd* phase in PS-rich region is shifted to lower χN than that in polyisoprene (PI) rich region. The asymmetry of the *Fddd* phase between both rich regions agrees with the phase diagram calculated with self-consistent field theory including the effects of conformational asymmetry by Matsen, indicating that the conformational asymmetry causes the asymmetry of the *Fddd* phase in the phase diagram of SI diblock copolymer.

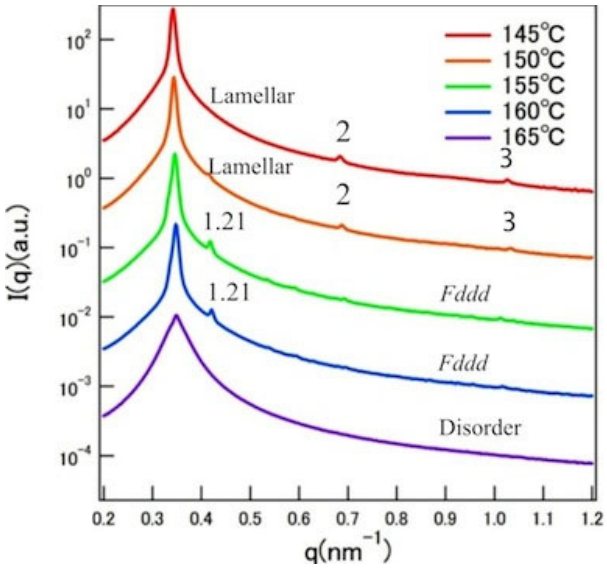

Figure 1 Change in SAXS profiles with temperature for I4.

References

[1] M.Takenaka et al., Macromolecules 40, 4399 (2007).
[2] M.I.Kim et al., Macromolecules 41, 7667 (2008).
[3] M.I.Kim et al., Macromolecules 42, 5266 (2009).
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