Crystallization of Poly(styrene)-b-syndiotactic Poly(propylene) Block Copolymers from Confinement to Breakout

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Various crystalline textures have been identified in a crystallizable block copolymer system, poly(styrene)-b-syndiotactic poly(propylene) (PS-sPP), having glass transition temperature of PS ($T_{g,PS}$) located in the midst of the sPP crystallization window. Confined morphology for crystallization of sPP was observed while the crystallization temperature of sPP ($T_{c,sPP}$) was less than $T_{g,PS}$. A further increase in $T_{c,sPP}$ could lead to a breakout in nanostructure. This study revealed the T_g effect on crystallization-induced morphological changes of block copolymers from confinement to breakout.

All samples were first annealed at 180 ^oC (i.e., above the melting temperature of sPP) to eliminate the thermal history, and then rapidly cooled to a preset temperature for crystallization study. An interesting morphological evolution was observed in this study, depending on the experimental temperature with respect to $T_{c,sPP}$ and $T_{g,PS}$. When $T_{c,sPP}<T_{g,PS}$ (i.e., hard confinement), microphase-separated lamellar morphology was found to persist after crystallization, as indicated in Figure 1a. However, templated crystallization was observed when $T_{c,sPP}$ approaches $T_{g,PS}$ (Figure 1b), where "rogue" crystals can be seen. It appears that the reduced restraint in crystallizable sPP blocks at the connected junctions of the incompatible microdomains probably increases the mobility of the entire block copolymer chain, resulting in a change of lamellar morphology driven by the crystallization process. Consequently, the breakout of nanostructure occurred when $T_{c,sPP}>T_{g,PS}$ as illustrated in Figure 1c.

Figures 2 and 3 indicate the plot of one dimensional SAXS profiles in real-time heating experiments and the plots of I_m^{-1} and σ_q^2 versus 1/T for PS-sPP, respectively. As expected, both I_m^{-1} and σ_q^2 have similar temperature dependence. A sharp discontinuous change of I_m^{-1} and σ_q^2 appeared once temperature reached 265 ^oC; suggesting the occurrence of order-disorder transition at around 265 ^oC. The scattering results from q at 0.65 nm^{-1} was determined as the sPP crystalline lamellae whereas the broaden peak disappeared at temperature above the melting of sPP.

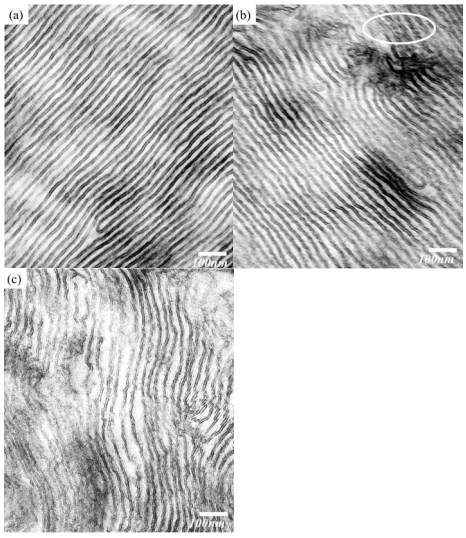

Figure 1. TEM micrographs of PS-sPP isothermally crystallized at (a) room temperature; (b) 65^oC for 10 min; (c) 100^oC for 75 min. White oval highlights the "rogue" crystals which run between microdomains.

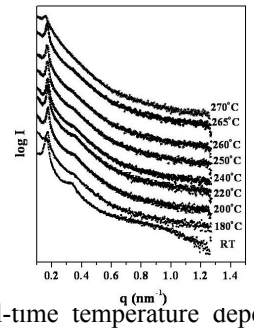

Figure 2. Real-time temperature dependence of SAXS profiles for the PS-sPP in the heating process at various temperatures.

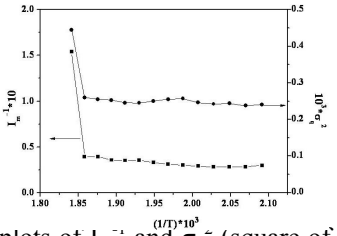

Figure 3. the plots of I_m^{-1} and σ_q^2 (square of the the half-width at half-maximun of the first-order SAXS maximum) versus 1/T for the PS-sPP.

* *Macromolecular Rapid Communications; **2005**;* **26(2); 107-111**