

## Characteristic Melting Behavior Observed in Crystalline-Amorphous Diblock Copolymers. 2

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### Introduction

The heating process of crystalline-amorphous diblock copolymers was previously investigated using time-resolved synchrotron small-angle X-ray scattering (SR-SAXS), where the glass transition temperature of amorphous blocks  $T_g$  was nearly the same to the crystallizable temperature of crystalline blocks  $T_c$ . We found that the excess upturn scattering at low angles was transiently observed during melting of crystalline blocks, which depended significantly on the copolymer composition and the thermal history applied to the samples. In this study, we further analyzed the excess scattering appearing during heating, and tried to find the possible origin of the scattering.

### Experimental Section

**Samples** The crystalline-amorphous diblock copolymers used are a series of hydrogenated polynorbornene-*block*-hydrogenated poly(1,4-methano-1,4,4a,9a-tetrahydrofluorene) (hPNB-*b*-hPMTF) copolymers with various compositions. The total molecular weight of hPNB-*b*-hPMTF is in a range between 21,000 and 46,000, and the composition changes from 12 to 79 wt.% hPNB. When the hPNB block is the major component in hPNB-*b*-hPMTF,  $T_c$  of hPNB blocks ( $\sim 115^\circ\text{C}$ ) is nearly the same to  $T_g$  of hPMTF blocks ( $\sim 122^\circ\text{C}$ ). Therefore, we can expect that the morphology existing in the system before heating will be formed by a combined effect of

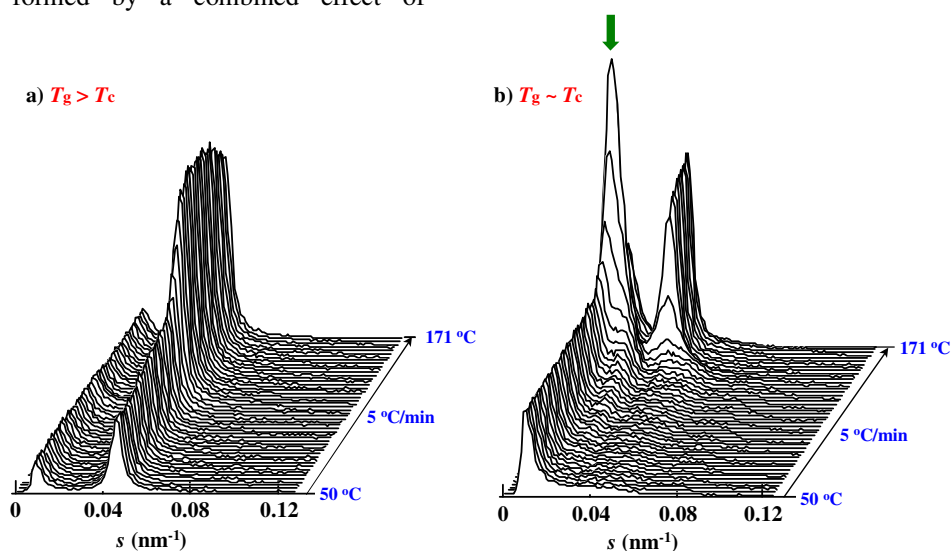
crystallization and glass transition.

**Measurements** The heating process was investigated using SR-SAXS, which was performed at beam line BL-10C. The background scattering was taken into account, and finally the relative intensity was obtained as a function of wave number  $s$  ( $= (2/\lambda)\sin \theta$ ,  $2\theta$ : scattering angle and  $\lambda = 0.1488$  nm).

### Results and Discussion

The excess X-ray scattering at low angles (green arrow in Figure 1) was transiently observed only for hPNB-*b*-hPMTF copolymers with  $T_g \sim T_c$  in the melting temperature range of hPNB blocks. In addition, the scattering intensity was significantly dependent on the crystallization time. We found from these results that the crystallized lamellar morphology, an alternating structure consisting of hPNB lamellar crystals and amorphous hPNB + hPMTF layers, was responsible for the emergence of this scattering. This is because the excess intensity was roughly proportional to the volume fraction of the crystallized lamellar morphology existing in the system. It is speculated that the scattering arises from the heterogeneous distribution of just melted hPNB regions (with slightly higher density) and originally amorphous hPNB regions (with normal density) existing within the crystallized lamellar morphology.

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**Figure 1.** Time-resolved SR-SAXS curves during heating at  $5^\circ\text{C}/\text{min}$  from  $50^\circ\text{C}$  into  $171^\circ\text{C}$  for hPNB-*b*-hPMTF with  $T_g > T_c$  (a) and  $T_g \sim T_c$  (b). The green arrow indicates the excess scattering appearing during melting of hPNB blocks.