

Characteristic Melting Behavior of Crystalline-Crystalline Diblock Copolymers. 2

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Introduction

We have investigated the melting behavior of double crystalline diblock copolymers, poly(ϵ -caprolactone)-*block*-polyethylene (PCL-*b*-PE), where the starting morphology depended significantly on the crystallization temperature T_c and therefore we expect T_c -dependent melting behavior during heating. We try to explain the characteristic melting behavior of PCL-*b*-PE mainly observed by time-resolved synchrotron small-angle X-ray scattering (SR-SAXS) from the viewpoint of the unique morphology formed in PCL-*b*-PE.

Experimental Section

Samples The samples are double crystalline PCL-*b*-PE diblock copolymers with various molecular characteristics. The melting temperature of PCL blocks is *ca.* 56 °C and that of PE blocks is *ca.* 96 °C, so that the PCL block melts first during heating to reproduce the PE lamellar morphology (*i.e.*, an alternating structure consisting of thin PE crystals and amorphous layers) followed by the melting of PE blocks at a high temperature range (~ 100 °C).

SR-SAXS Measurements The SR-SAXS experiment was performed at beam line BL-10C. The thermal history applied is shown in Fig. 1, where the sample was annealed at the temperature T_a between the melting temperatures of both blocks, and morphological change was pursued by SR-SAXS. The background scattering and Lorentz factor were taken into account, and finally the relative intensity was obtained as a function of wave number s ($= (2/\lambda)\sin \theta$, 2θ scattering angle and $\lambda = 0.1488$ nm). The peak position (or long period (LP)) was evaluated as a function of annealing time t_a .

Results and Discussion

Fig. 2-(a) shows the plot of LP against t_a for PCL-*b*-PE first crystallized at $T_c = 45$ °C (open circle) and 0 °C

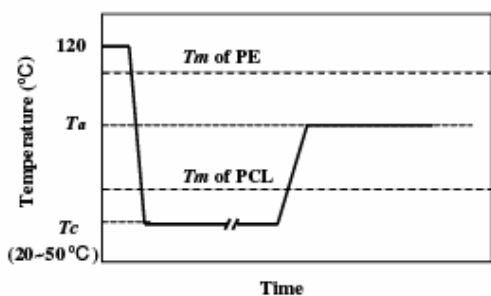


Fig. 1 Thermal history applied to the sample. The time-resolved SR-SAXS measurement was carried out during annealing at T_a as a function of t_a .

(closed circle) and subsequently moved to 70 °C, where t_a dependence of LP is extremely different between two cases; LP for PCL-*b*-PE crystallized at 0 °C does not change at all during annealing, while that crystallized at 45 °C decreases considerably at the early stage of annealing and after that it keeps constant. The decrease of LP at the early stage of annealing suggests the transformation of the morphology formed at 45 °C into a new morphology favorable for PCL-*b*-PE at 70 °C.

The final LP is plotted against T_a for PCL-*b*-PE crystallized at 45 °C (blue circle) and 0 °C (blue square), where the change in LP during heating is also plotted (open symbols). LP finally obtained after annealing at T_a coincides moderately with that observed during heating for PCL-*b*-PE crystallized both at high and low T_c , indicating that the morphology appearing during heating is not unstable but at least meta-stable depending on each temperature.

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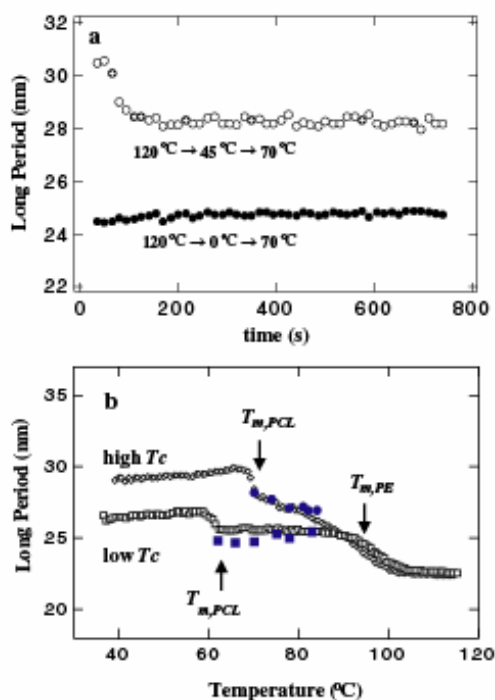


Fig. 2 (a) LP plotted against t_a at 70 °C for PCL-*b*-PE crystallized at 45 °C (open circle) and 0 °C (closed circle). (b) Final LP plotted against T_a for PCL-*b*-PE crystallized at high temperature (45 °C, blue circle) and low temperature (0 °C, blue square). Open symbols represent the temperature dependence of LP during heating at 3 °C/min.