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Crystallization Process of a Strongly Segregated Double Crystalline Diblock Copolymer with Close Melting Temperatures

Hiroshi IKEDA, Yasumasa FUKAGAWA, and Shuichi NOJIMA*
Department of Organic and Polymeric Materials, Graduate School of Science and Engineering,
Tokyo Institute of Technology, H-125, 2-12-1 Ookayama, Meguro-ku Tokyo 152-8552, Japan

Introduction

Morphology formation in crystalline-crystalline diblock copolymers is extremely complicated due to the interplay between two kinds of crystallization starting from the molten microdomain structure. The relative position of melting temperatures of two crystalline blocks is an important factor to control the crystallization process. In this study, we have investigated the non-isothermal crystallization process of a crystalline-crystalline diblock copolymer with close melting temperatures, poly(β-propiolactone)-*block*-low density polyethylene (PPL-*b*-PE). PPL-*b*-PE is strongly segregated in the melt, so that the crystallization of both blocks is effectively confined within the microdomain structure.

Experimental Section

Sample The total molecular weight of PPL-*b*-PE is 13,300 and the volume fraction of PPL blocks is 0.52. The melting temperature of PPL blocks is *ca.* 80 °C and that of PE blocks *ca.* 100 °C, so that we can expect coincident crystallization during cooling PPL-*b*-PE at constant rates.

Measurements The crystallization process during cooling from the melt at constant rates (1 °C/min ~ 10 °C/min) was investigated using differential scanning calorimetry (DSC), synchrotron small-angle X-ray scattering (SR-SAXS), and Fourier transform infrared spectroscopy (FTIR). SR-SAXS experiment was performed at beam line BL-10C in KEK-PF. The background scattering was taken into account, and finally the relative intensity was obtained as a function of wave number s (= $(2/\lambda)\sin\theta$, 2θ: scattering angle and $\lambda = 0.1488$ nm).

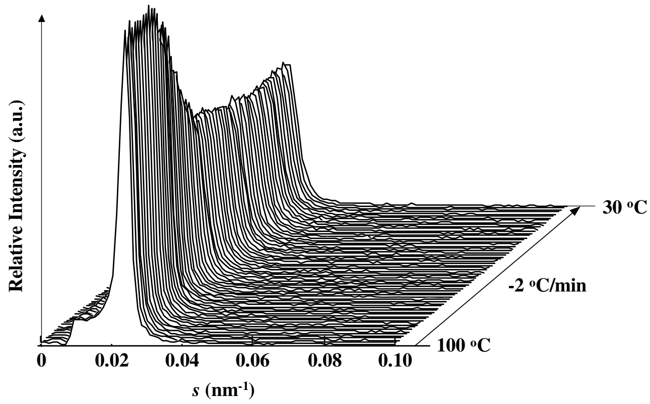

Figure 1 Time-resolved SR-SAXS curves of PPL-*b*-PE during cooling at –2 °C/min from 100 °C into 30 °C.

Results and Discussion

Figure 1 shows the time-resolved SR-SAXS curve during cooling at –2 °C/min. At 100 °C, the primary scattering peak arises from the molten lamellar microdomain structure. The intensity decreases significantly in the crystallization temperature range of PE blocks. However, the angular position of this peak does not change at all during cooling, indicating that PPL and PE blocks crystallize within each lamellar microdomain without any morphological transformation. That is, the lamellar microdomain is effectively confines the crystallization of both blocks. This fact is also verified using static SR-SAXS measurements at each temperature and also transmission electron microscope.

The time evolution of the crystallinity for each block was mainly evaluated from FTIR measurements. Figure 2 shows the time (or temperature) dependence of PE and PPL crystallinity (χ_{PE} and χ_{PPL}) when PPL-*b*-PE is cooled from the melt at –1 °C/min. Both χ_{PE} and χ_{PPL} show the complicated change during cooling. That is, the crystallization of PE blocks starts at t ~ 1150 s (~ 98 °C) and χ_{PE} increases steadily with increasing t. The PPL blocks, on the other hand, start to crystallize at t ~ 2400 s (~ 76 °C), where χ_{PE} is still increasing, and hence we can observe a coincident crystallization process after $t > 2400$ s (or $T < 76$ °C). Figure 2 clearly indicates that two crystallization processes interact intimately with each other during the coincident crystallization process of both the blocks.

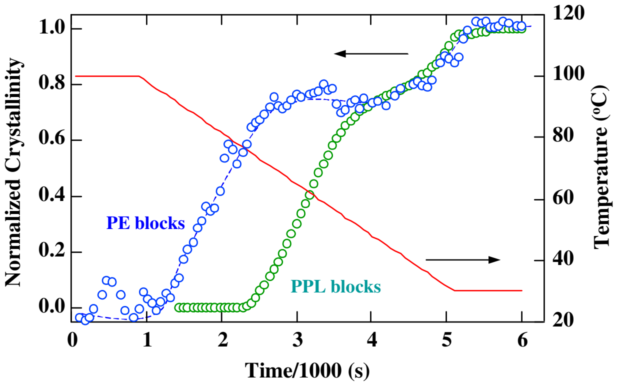

Figure 2 Normalized crystallinity of PPL blocks (green) and PE blocks (blue) plotted against time during cooling at –1 °C/min from 100 °C into 30 °C.

* snojima@polymer.titech.ac.jp