

Characteristic melting behavior of crystalline-crystalline diblock copolymers

Shuichi NOJIMA*, Toshimitsu KIJII, and Michiaki AKABA

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, H-125, Ookayama 2-12-1, Meguro-ku 152-8552, Tokyo Japan

Introduction

We have recently investigated the crystallization behavior and resulting morphology of double crystalline diblock copolymers, poly(ϵ -caprolactone)-*block*-polyethylene (PCL-*b*-PE), where the crystallization of PCL blocks started from a solid lamellar morphology formed in advance by the crystallization of PE blocks (PE lamellar morphology) [1,2]. It was found that the resulting morphology was significantly dependent on the crystallization temperature of PCL blocks T_c ; the PCL blocks crystallized within the PE lamellar morphology at low T_c (< 40 °C), while at high T_c (> 40 °C) the crystallization of PCL blocks destroyed the existing PE lamellar morphology to result in a new lamellar morphology mainly consisting of PCL lamellae and amorphous layers (PCL lamellar morphology). In this study, we pursue the melting behaviour of PCL blocks and subsequent reorganization process of the PE lamellar morphology at a constant heating rate for PCL-*b*-PE crystallized at various temperatures.

Experimental Section

Samples The samples used in this study are two PCL-*b*-PE copolymers. The molecular characteristics are shown in Table 1. It is known from our previous studies that the final morphology at room temperature is absolutely determined by T_c ; the PE lamellar morphology is preserved and hence PCL blocks crystallize within this morphology at low T_c while the PCL lamellar morphology develops and eventually PE crystals are fragmentarily dispersed at high T_c .

SAXS measurements The melting behavior of PCL blocks was observed by time-resolved small-angle X-ray scattering with synchrotron radiation (SR-SAXS). The experiment was performed at PF beamline BL-10C. The melting process was pursued with an accumulation time of 10 sec by heating the sample from room temperature at a constant rate ($= 3$ °C/min) until the PE blocks melted completely.

Table 1. Molecular characteristics of polymers used in this study.

	M_n^a	M_w/M_n^b	PCL:PE ^c	EB (mol%) ^c	$T_{m,PCL}^d$	$T_{m,PE}^d$
A2	11,000	1.09	69:31 (vol%)	6 (mol%)	55 (°C)	97 (°C)
A3	18,000	1.18	51:49	5	56	95

^a Determined by membrane osmometry

^b Determined by GPC

^c Determined by ¹H-NMR

^d Determined by DSC for the samples crystallized at room temperature

Results and Discussion

The SR-SAXS curves change extensively during heating from room temperature up to 120 °C, which also depend significantly on the thermal history (or T_c) applied to the sample. Fig. 1 shows the result for the temperature dependence of the spacing evaluated from the angular position of SR-SAXS peak for A2 crystallized at 23 °C (low T_c) and 48 °C (high T_c). The samples crystallized at $T_c > 40$ °C and those at $T_c < 40$ °C showed the similar results with those at $T_c = 48$ °C and 23 °C, respectively. We can see from Fig. 1 that (1) the melting temperature of PCL blocks $T_{m,PCL}$ is considerably different between two cases, (2) the spacing of A2 crystallized at low T_c is almost constant after the melting of PCL blocks while that crystallized at high T_c decreases gradually with increasing temperature, and (3) the melting temperature of PE blocks $T_{m,PE}$ is almost equal for two cases.

Fig. 1, together with other results, clearly indicates that the morphological change during heating for A2 with high T_c is distinctly different from that with low T_c . That is, the reorganization of the PE lamellar morphology, which was previously destroyed by the crystallization of PCL blocks, occurs after the melting of PCL blocks for A2 crystallized at high T_c while the morphological reorganization does not take place for A2 crystallized at low T_c because the PE lamellar morphology has not been destroyed by the crystallization of PCL blocks.

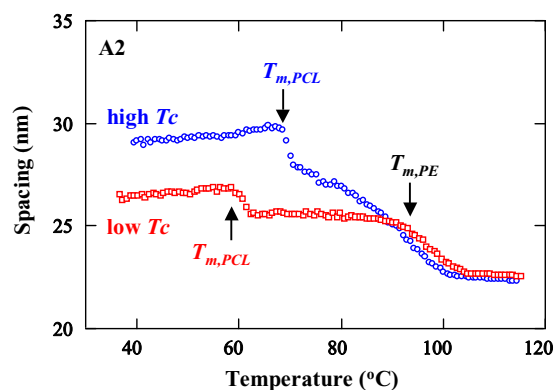


Fig. 1 Change in spacing during heating at a rate of 3 °C/min for A2 crystallized at high T_c ($= 48$ °C) and low T_c ($= 23$ °C).

References

- [1] S. Nojima *et al.*, *Polymer*, 45, 7317-7324 (2004).
 [2] S. Nojima *et al.*, *Polymer*, 46, xxxx-xxxx (2005).

* snojima@polymer.titech.ac.jp