

# Composition Dependence of Crystallized Lamellar Morphology Formed in Crystalline-Crystalline Diblock Copolymers

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## Introduction

We have investigated the morphology formed in double crystalline poly( $\epsilon$ -caprolactone)-*block*-polyethylene (PCL-*b*-PE) diblock copolymers with various compositions, and clarified the stability of the PE lamellar morphology against PCL crystallization as a function of the crystallinity of PE blocks  $\chi_{PE}$  in the whole systems.

## Experimental Section

**Samples** The molecular characteristics of PCL-*b*-PE used in this study are shown in Table 1. The volume fraction of PE blocks in PCL-*b*-PE changes from 0.86 to 0.25, which yields the variation of  $\chi_{PE}$  from 0.19 to 0.02, leading to a large change in the stability of the PE lamellar morphology against PCL crystallization.

**SR-SAXS Measurements** The static SR-SAXS experiment was performed at beam line BL-10C. The accumulation time was 300 sec for each measurement. The background scattering and Lorentz factor were taken into account, and finally the relative intensity was obtained as a function of wave number  $s$  ( $= (2/\lambda)\sin \theta, 2\theta$ : scattering angle and  $\lambda = 0.1488$  nm). The peak position

(or long period) and peak intensity were evaluated at each crystallization temperature  $T_c$  ( $15^\circ\text{C} < T_c < 90^\circ\text{C}$ ).

## Results and Discussion

Fig. 1 shows the SAXS curves for E49 at each temperature indicated. At  $130^\circ\text{C}$ , where both blocks are amorphous, a couple of scattering peaks are observed, indicating that regular microdomains are formed in the melt. By quenching the sample into low  $T_c$  (between  $15$  and  $45^\circ\text{C}$ ), PE blocks crystallize first to form the PE lamellar morphology and subsequently PCL blocks start to crystallize from this morphology. As a result, we have various SAXS curves, in which the scattering peak is moderately diffused and the peak position depends intimately on  $T_c$ .

Fig. 2 shows the long period  $L$  of resulting morphology plotted against  $T_c$  for selected PCL-*b*-PE copolymers.  $L$  changes complicatedly with changing  $T_c$  for E49 and E25;  $L$  at  $T_c < 30^\circ\text{C}$  is equal to that of the PE lamellar morphology (at  $T_c = 60 \sim 85^\circ\text{C}$ ) while it increases further with increasing  $T_c$  up to  $45^\circ\text{C}$ . This difference arises from the difference in the crystallization mechanism of PCL blocks at each temperature. The boundary temperature  $T_p$  between two different morphologies can be evaluated from Fig. 2 as a temperature where  $L$  deviates from that of the PE lamellar morphology. However,  $T_p$  is almost constant ( $\sim 33^\circ\text{C}$ ) for PCL-*b*-PE with  $\chi_{PE} < 0.10$  (E25 ~ E58), indicating that the PE lamellar morphology controls the crystallization of PCL blocks by an intermediate manner between glassy and rubbery confinements.

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Table 1 Molecular characteristics of PCL-*b*-PE used in this study.

	$M_n^a$	$M_w/M_n^b$	PCL:PE <sup>c</sup>	EB <sup>c</sup>	$T_{m,PCL}^d$	$T_{m,PE}^d$
E86	14,000	1.16	14:86 (vol.%)	-	50 ( $^\circ\text{C}$ )	103 ( $^\circ\text{C}$ )
E73	16,000	1.13	27:73	-	55	102
E58 (A1)	8,400	1.13	42:58	6 (mol%)	58	101
E49 (A3)	18,000	1.18	51:49	5	59	100
E36	13,000	1.16	64:36	7	59	97
E31 (A2)	11,000	1.09	69:31	6	59	99
E25	14,000	1.08	75:25	-	59	101

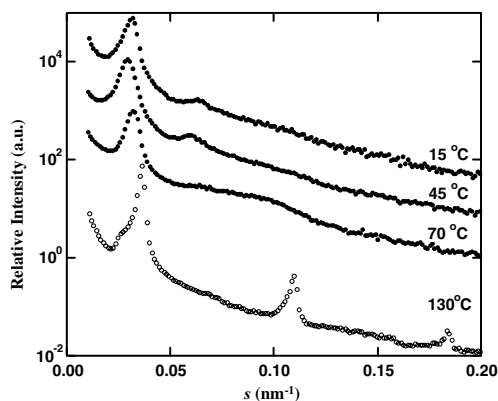


Fig. 1 SAXS intensities plotted against  $s$  for E49 at each temperature indicated. Open circles represent the scattering from the molten microdomain structure.

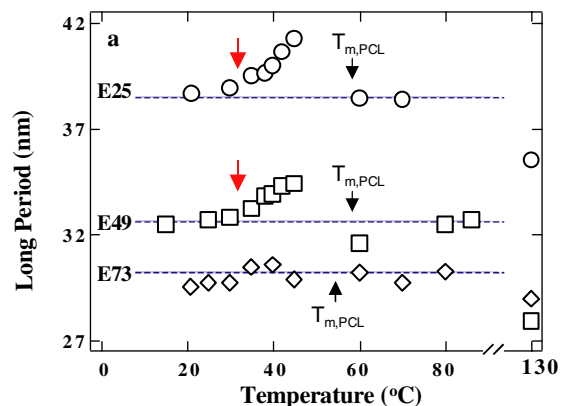


Fig. 2 The long period  $L$  plotted against  $T_c$  for E73, E49, and E25. The boundary temperature  $T_p$  between different morphologies is shown by a red arrow.