

# Crystal Orientation of Poly( $\epsilon$ -caprolactone) Blocks Confined in Crystallized Lamellar Morphology of Poly( $\epsilon$ -caprolactone)-*block*-Polyethylene Copolymers.

## 2. Analysis of Experimental Results

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### Introduction

We have reported the experimental results for crystal orientation of poly( $\epsilon$ -caprolactone) (PCL) blocks spatially confined in the solid lamellar morphology formed by the crystallization of polyethylene (PE) blocks (PE lamellar morphology) in PCL-*b*-PE copolymers. In this report, we analyze the experimental results, and crystal orientation of PCL blocks was derived as a function of crystallization temperature  $T_c$  and confinement size  $d_{PCL}$ .

### Analysis Method

**Crystal Orientation of PCL Blocks** The two-dimensional wide-angle X-ray diffraction (2D-WAXD) patterns were first decomposed into those from PE crystals and PCL crystals, and the (110) and (200) diffraction intensities from PCL crystals were plotted as a function of azimuthal angle  $\phi$ . The orientation of PCL crystals confined in the PE lamellar morphology was evaluated from this plot.

**Degree of Crystal Orientation** The degree of crystal orientation  $f$  for PCL blocks was calculated by,

$$f = (k^{-1} \langle \cos^2 \phi \rangle - 1) / (k^{-1} - 1) \quad (1)$$

where  $k$  represents  $\langle \cos^2 \phi \rangle$  at random orientation (usually  $k = 1/3$ ), and  $\langle \cos^2 \phi \rangle$  can be calculated from the  $\phi$  dependence of the (110) diffraction intensity arising from PCL crystals.

### Results and Discussion

The 2D-WAXD pattern changed significantly with changing  $T_c$  when  $d_{PCL} = 8.8$  nm (CL33). That is, when  $45^\circ \text{C} \geq T_c \geq 25^\circ \text{C}$  we had four distinct peaks at off-axis regions, the positions of which were almost independent of  $T_c$ . These results mean that the  $c$  axis of PCL crystals is perpendicular to the lamellar surface normal. On the other hand, the (110) diffraction curve at  $20^\circ \text{C} \geq T_c \geq 0^\circ \text{C}$

was almost isotropic, suggesting that orientation of PCL crystals is random. When  $d_{PCL} = 10.7$  nm (CL38), 11.7 nm (CL46), and 16.5 nm (CL51), we found two distinct diffraction peaks at  $\phi = 90^\circ$  and  $270^\circ$  at every  $T_c$ , indicating that the  $c$  axis of PCL crystals is parallel to the lamellar surface normal irrespective of  $T_c$ .

The  $T_c$  dependence of  $f$  calculated from eq. (1) is plotted in Fig. 1 for PCL-*b*-PE with various  $d_{PCL}$ . We find that when  $16.5 \text{ nm} \geq d_{PCL} \geq 10.7 \text{ nm}$   $f$  is constant irrespective of  $T_c$ , while it depends significantly on  $T_c$  when  $d_{PCL} = 8.8$  nm. The orientation of PCL crystals is schematically shown in Fig. 2 at various  $T_c$  and  $d_{PCL}$ . From these results we can conclude that the PE lamellar morphology plays a similar role to glassy microdomains regarding spatial confinement against subsequent PCL crystallization.

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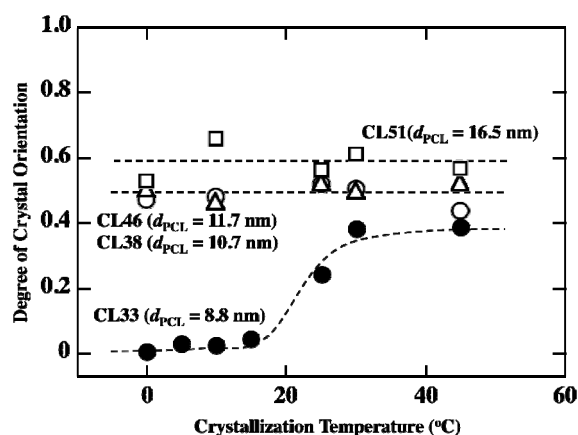


Fig. 1. Degree of PCL crystal orientation plotted against  $T_c$  for PCL-*b*-PE with various  $d_{PCL}$ .

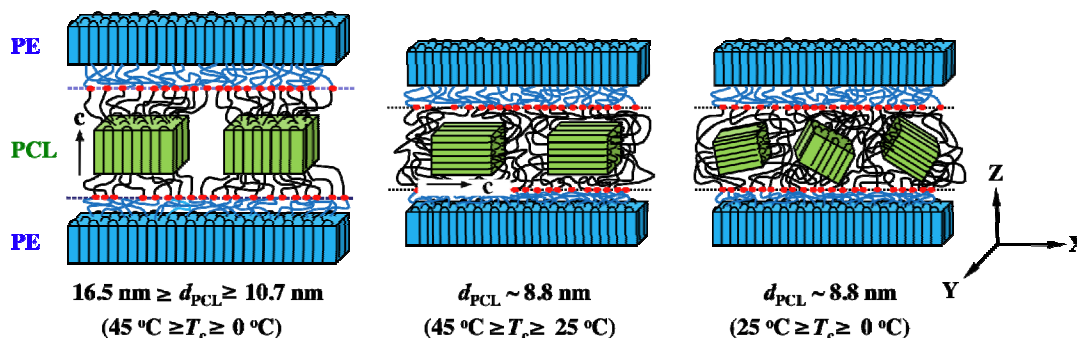


Fig. 2. Schematic illustration showing the orientation of PCL crystals spatially confined within the PE lamellar morphology at different  $d_{PCL}$  and  $T_c$ .