

Crystal Orientation of Poly(ϵ -caprolactone) Homopolymers Confined in Cylindrical Nanodomains. 2. Analysis of Experimental Results

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Introduction

We have reported the results of crystal orientation for homopolymers and block chains both confined within identical cylindrical nanodomains [1]. In this report, we analyze the experimental results and try to elucidate the difference in crystal orientation between both chains as a function of crystallization temperature T_c .

Experimental Section

Sample The copolymer used in this study is poly(ϵ -caprolactone)-*block*-polystyrene (PCL-*b*-PS) with a photocleavable *o*-nitrobenzyl group between PCL and PS blocks. The sample was subjected to the rotational shear at 120 °C to orient the nanocylinders. Subsequently, UV with 200 mW in intensity and wavelength longer than 300 nm was irradiated to the sample to cleave the *o*-nitrobenzyl group, and eventually we obtained PCL homopolymers confined in oriented nanocylinders.

Measurements The morphology formed was measured using 1D synchrotron small-angle X-ray scattering (SR-SAXS) and 2D conventional SAXS. The orientation of PCL crystals was investigated using 2D wide-angle X-ray diffraction (2D-WAXD). The SR-SAXS experiment was performed at beam line BL-10C in KEK-PF.

Analysis of data The WAXD intensity at selected diffraction angles was plotted as a function of azimuthal angle ϕ after subtracting the background scattering to evaluate the degree of PCL crystal orientation f . We evaluated ϕ from the second-order moment of the orientation distribution function using the (100) diffraction profile.

Results and Discussion

We found two clear diffractions in every WAXD pattern in addition to the amorphous halo arising from the amorphous components. They corresponded to the (110) diffraction at $2\theta = 21.41^\circ$ and the (200) diffraction at $2\theta = 23.76^\circ$. When we plotted the (110) diffraction intensity against ϕ we found four distinct peaks at off-axis regions, the positions of which were almost independent of T_c . When we plotted the (200) diffraction intensity we had two

diffuse peaks centered at $\phi = 0^\circ$ and 180° . If we assume that the *b* axis of the unit cell for PCL crystals is oriented parallel to the long axis of nanocylinders, we can satisfactorily explain these results.

We calculated f as a function of T_c both for PCL blocks and PCL homopolymers, and the results are shown in Figure 1. Though f is small and similar for both cases at lower T_c ($-60^\circ\text{C} \leq T_c \leq -54^\circ\text{C}$), it increases remarkably with increasing T_c for PCL homopolymers, indicating that crystal orientation is considerably improved at higher T_c . On the other hand, f increases slightly for PCL blocks, suggesting T_c does not seriously affect the crystallization process and crystal orientation of PCL blocks. The T_c dependence of f for PCL blocks and PCL homopolymers can be successfully explained by considering the crystal growth mechanism as well as the tethering effect of block chains. Figure 2 illustrates the difference in crystal orientation between PCL homopolymers crystallized at higher temperatures ($\sim -40^\circ\text{C}$) and lower temperatures ($\sim -60^\circ\text{C}$).

[1] *PF Activity Report 2008*, **26**, 139 (2009).

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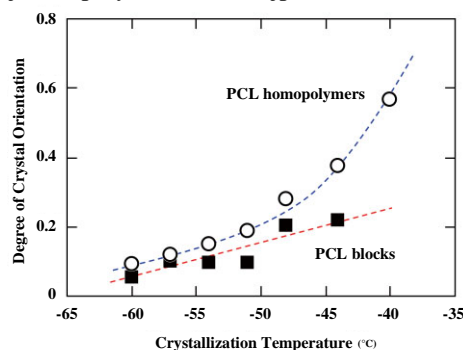


Fig. 1. Degree of crystal orientation plotted against crystallization temperature for PCL blocks and PCL homopolymers.

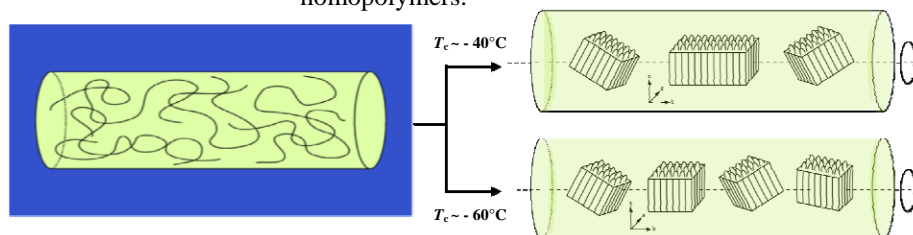


Fig. 2. Schematic illustration showing the difference in crystal orientation between PCL homopolymers crystallized at -40°C (upper) and -60°C (lower).