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Crystallization and Melting Behavior of Poly(ϵ -caprolactone) Under Physical Confinement

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*We studied the crystallization behavior of poly(ϵ -caprolactone) (PCL) in a physically confined system, the self-assembly of poly(ϵ -caprolactone)/polystyrene-*b*-poly(ethylene-propylene) (PCL/PS-PEP) blends, using simultaneous small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD). The glassy PS-rich phases effectively confined the PCL crystallization due to the localization behavior of PCL. Contrary to a typical microphase-separated morphology of semi-crystalline copolymers (i.e. a chemically confined system), the physically confined system for the crystallization of PCL provides a representative system for understanding crystallization behavior under spatial confinement. With effective confinement, the crystalline chains of PCL appeared in a random orientation at low crystallization temperatures but in a parallel orientation at high crystallization temperatures.*

Crystallization behavior under nanoscale confinement has drawn attention due to the necessity of having a basic understanding of crystallization in order to develop nanotechnology applications. In particular, the crystallization behavior of semi-crystalline block copolymers, in which at least one of the constituted blocks is crystallizable, has been thoroughly studied as illustrated in **Figure 1a** (namely, a chemical confinement). By contrast, the unique morphology with a crystallizable PCL component localized between the lamellar microdomains of PS-PEP gives rise to a specific crystallization environment in which the crystallization is carried out in a nanometer-scale confined environment without the restraint of a chemical connection (**Figure 1b**, a physical confinement). This unique morphology, a crystallizable PCL component localized favorably within PS-rich constituted lamellar in a PS-PEP block copolymer, has been obtained via melt-mixing in a MiniMax mixer. Shear (velocity), vorticity, and velocity gradient directions are labeled *x*, *y*, and *z*, respectively. Two-dimensional SAXS patterns along the *x*, *y*, and *z* directions indicate that microphase-separated microdomains can be oriented after melt-mixing, as illustrated in **Figure 2** for PCL11/PS-PEP blends (the M_w of PCL11 is 11000g/mol). Up to four orders of lamellar scattering peaks ($q/q^* = 1 : 2 : 3 : 4$) can be identified when the incident x-ray beams are along *x* and *y*, as shown in **Figures 2a and 2b**. By contrast, we found no significant scattering peak along the *z* direction in the two-dimensional SAXS pattern (**Figure 2c**). These two-dimensional SAXS results indicate that microphase-separated lamellae of PCL11/PS-PEP are aligned parallel to the *x-y* plane (i.e. the shear plane). Moreover, the oriented microphase-separated lamellar microstructure was preserved after PCL crystallization so that the PCL is completely confined in the PS-PEP lamellar layer.

For PCL crystallization at low crystallization temperatures (for instance, at $T_c = -20^\circ\text{C}$), the two-dimensional WAXD patterns exhibit a typical ring pattern in all directions, suggesting that PCL crystals appear randomly oriented under confinement. However, a specific orientation of the PCL crystals can be identified when the shear-aligned samples are crystallized at high crystallization temperatures (for instance, 40°C). Two-dimensional WAXD patterns along the *x* and *y* directions are practically identical, and exhibit oriented features (**Figures 2d**



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and 2e). Only an isotropic ring pattern along the z direction was observed (Figure 2f). On the basis of the orthorhombic lattice structure of PCL crystals with a unit cell of $a=0.749$ nm, $b=0.498$ nm, $c=1.703$ nm, and $\alpha = \beta = \gamma = 90^\circ$, the corresponding reflections were identified as $\{110\}$ and $\{200\}$. The azimuthal profiles (Figure 3a) were obtained from the two-dimensional WAXD pattern (Figure 2d). The intense $\{110\}$ diffraction peaks are separated into four diffraction arcs and appear at $\Phi=56^\circ$, 124° , 236° , and 304° , and two $\{200\}$ reflections appear at $\Phi=0^\circ$, 180° , respectively. According to the azimuthal results, the diffraction pattern is illustrated in Figure 3b. The fiber-pattern-like diffractions suggest a parallel-type orientation with PCL crystalline chains parallel to the microphase-separated lamellae (i.e. the x and y directions). Figure 3c shows the molecular disposition of crystalline PCL chains, and indicates their parallel orientation at high crystallization temperatures in a physically confined environment. The crystalline orientation is strongly dependent upon the crystallization temperature under physical confinement. As a result, the orientation of the PCL crystalline chain localized between the PS-PEP layers can be thoroughly understood by two-dimensional SAXS and WAXD techniques at a synchrotron light source.

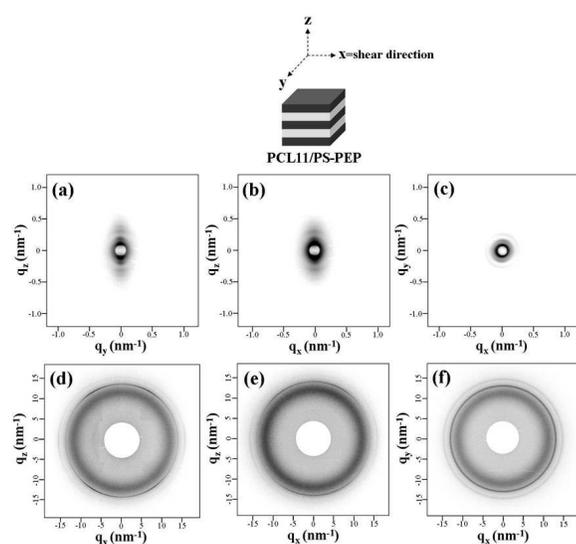


Figure 2. Simultaneous SAXS and WAXD patterns of orientated PCL11/PS-PEP samples isothermally crystallized at 40°C from ordered melt at 100°C . 2D SAXS (top row) and 2D WAXD (bottom row) obtained (a,d) along the x-direction, (b,c) along the y-direction, and (c,f) along the z-direction.

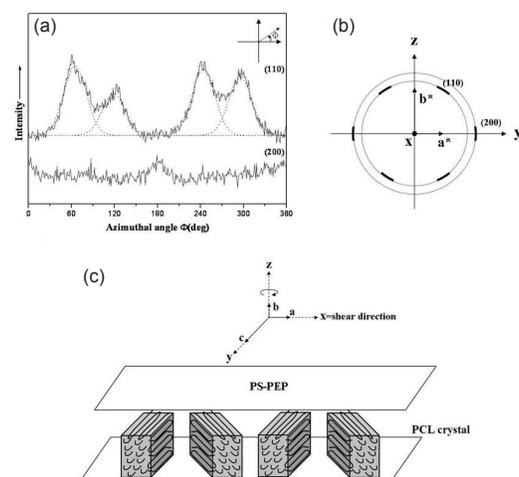


Figure 3. (a) Azimuthal scanning profiles of the $\{110\}$ and $\{200\}$ reflections of the WAXD patterns in Figure 2d for the PCL11/PS-PEP blends isothermally crystallized at 40°C . (b) Schematic diagram of the WAXD pattern with indexed reflections. (c) Schematic diagram of the microstructure of orientated PCL11/PS-PEP samples isothermally crystallized at 40°C from ordered melt at 100°C . The crystallization of PCL is confined between the preformed lamellar PS layers, and the a and c axes of the PCL crystals are preferentially parallel and perpendicular to the axes of the PS lamellar normal, respectively.

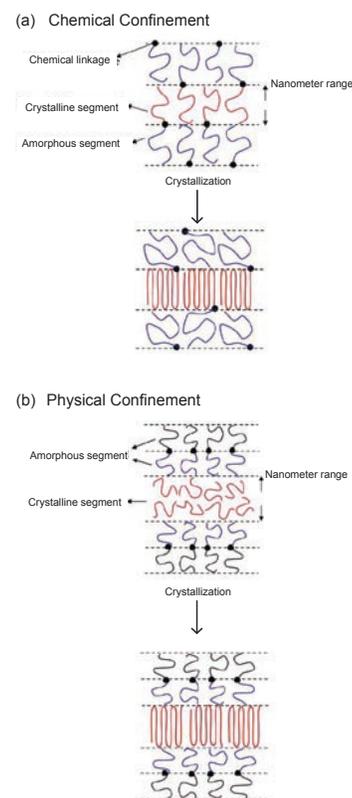


Figure 1. Schematic pictures of (a) chemical confinement and (b) physical confinement.