Extended Chain Lamellae in Polymer Smectic Liquid Crystals

The LC structure and morphology were examined for the series of liquid crystal (LC) PB-8/12 copolyesters consisting of 4,4'-biphenol, sebacic acid, and tetradecanedioic acid. The copolyesters formed smectic I (SmI) LCs; however, the smectic layer order decreased due to the dissimilarity of the comonomer lengths while the hexagonal order in the lateral packing of the chains was sustained. The SmI LCs consisted of 100-nm-thick lamellae stacked along the polymer chain direction. The lamellar thicknesses are comparable to or greater than the chain contour lengths, indicating the formation of extended chain lamellae.

Although flexible polymers usually form meta-stable folded-chain lamellar crystals at the highest growth rate from the isotropic melt, they can crystallize into extended conformations through the hexagonal columnar (Col$_h$) mesophase. While polyethylene (PE) crystallizes directly from the isotropic melt at ambient pressure to yield folded-chain lamellae with thicknesses of approximately 10 nm, at pressures above 4 kbar and at small supercooling temperatures, PE crystallizes from the Col$_h$ phase to yield extended-chain lamellar crystals [1]. This extended-chain crystallization via the Col$_h$ mesophase has been observed at ambient pressure for poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF/TrFE)) [2]. The Col$_h$ phases in simple polymers such as PE are induced by breaking the translation order along the chain axis due to conformational defects such as g+tg– kinks; this translation disorder can be introduced by chemical aperiodicity, as in P(VDF/TrFE).

We examined the effects of chemical aperiodicity on layer order and lamellar morphology using liquid crystal PB-8/12-*x* copolymers [3]. *x* is the molar fraction of the PB-8 unit in units of percent. The PB-8 and PB-12 homopolymers formed hexatic smectic I (SmI) liquid crystals; their morphologies are characterized by lamellae that consist of the SmI and isotropic liquid phases and that stack along the chain axis [4]. The copolymer SmI phases have lower layer orders than the homopolymer phases, while preserving the hexagonal lateral packing of the mesogens.
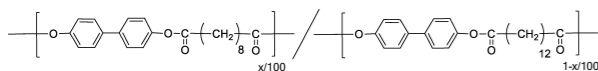
Figure 1A shows small-angle X-ray scattering (SAXS) profiles measured for the PB-8 and PB-12 polyesters and the PB-8/12-*x* copolyesters. Here, the sample was cooled from the isotropic liquid phase to room temperature at a rate of 10 °C min^{-1}; the temperature was then increased to a liquid crystalline temperature just moments before X-ray irradiation. To prevent any changes in morphology, such as lamellar thickening, the SAXS data were obtained using 5 min synchrotron radiation (SR) X-ray illumination. The copolymers displayed first-order scattering peaks at a smaller *q* than the homopolymers, although the first-order peak was not observed for PB-8/12-50 because of its larger lamellar spacing (d_0); this indicates that the d_0 values of the copolymers are remarkably larger than those of the homopolymers. The thicknesses of the lamellae of smectic LC and isotropic liquid phases (d_{LC} and d_{am}) as well as the d_0 values were estimated by comparing the observed intensities with scattering profiles numerically calculated using paracrystal theory [5]. The d_{LC} values of the PB-8/12-50 and PB-8/12-75 copolymers are 100 nm, comparable to the chain contour length (L) calculated from the degree of polymerization and the length of repeat unit assuming the all-trans conformation, while the PB-8 and PB-12 homopolymers formed chain-folded lamellae with d_{LC} values of 30 and 50 nm, respectively, which are less than half as long as the L values. **Figure 1B** shows the lamellar stacks observed by scanning electron microscopy (SEM) of the PB-8/12-50 copolymers. SEM images of the surfaces display the LC lamellae as either protrusions or grooves. Assuming that edge-on lamellae appear at the smallest spacing, the values of lamellar thickness are comparable to those estimated by SAXS.
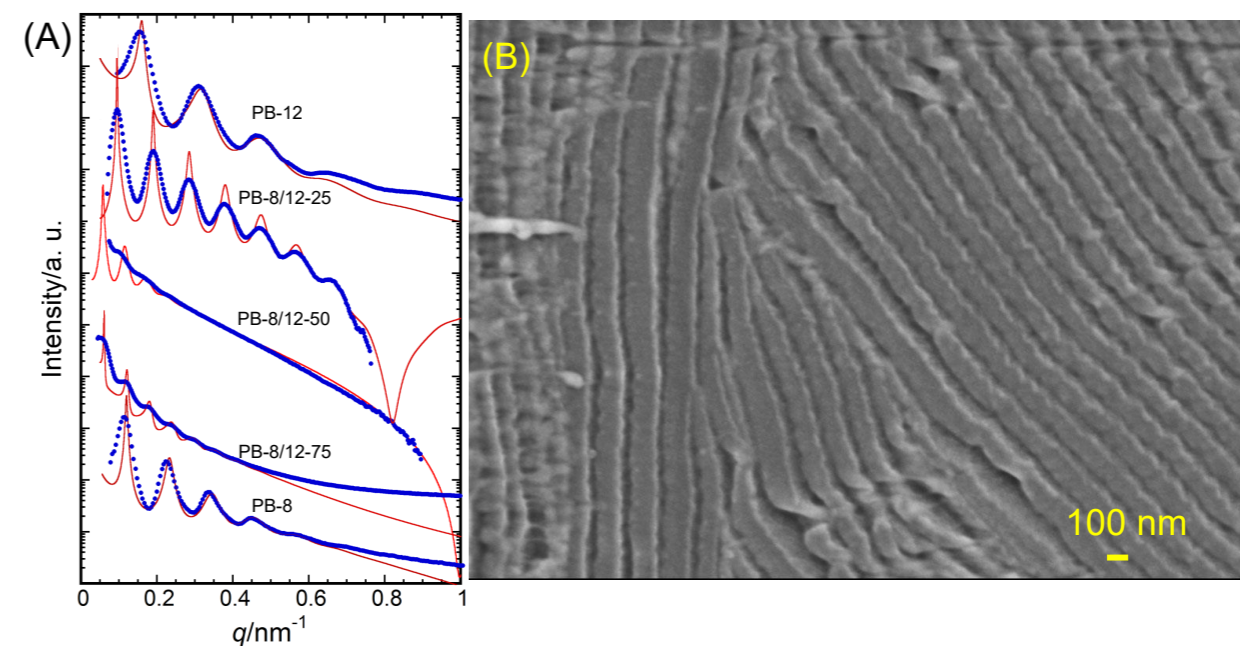

Figure 1: **(A)** SR-SAXS intensity profiles (dots) for PB-8/12 copolymers. The samples were initially prepared by cooling the isotropic melts at a rate of 10 °C min^{-1} and then heating to LC temperatures. The solid curves indicate the calculated intensities based on paracrystal theory. **(B)** Lamellar stack in PB-8/12-50 copolymer cooled from the isotropic liquid phase at a rate of 10 °C min^{-1}. Scale bar: 100 nm.

The formation of extended chain lamellae requires a hexagonal order in the lateral chains as well as a lowered positional order along the chain axis. The main-chain LC polymers in the nematic LCs having no positional order along the chain axis are extended owing to the orientational order of the mesogens incorporated in the backbone and lose the conformational entropy; however, they include chain foldings at thermodynamic equilibrium to recover the entropy loss, as pointed out theoretically [6] and as observed by small-angle neutron scattering [7]. Smectic LCs having liquid-like packing of mesogens can include chain folding at thermodynamic equilibrium [8]. In contrast, the SmI phase arranges the lateral mesogens in a short-range two-dimensional hexagonal positional order. The SmI phases of PB-*n* polyesters exhibited SAXS maxima that are ascribed to stacked chain-folded lamellae; the spacing increased with annealing in the SmI phase, suggesting that the SmI LCs tend to eliminate chain folding by chain-sliding diffusion. The rate of chain-sliding diffusion can be increased by decreasing the smectic layer orders. Thus in the PB-8/12 copolymer SmI phases with lowered layer orders, polymer chains can extend rapidly and thus assemble to form extended chain lamellae. The extended-chain PB-*n* polyester exhibits a greater thermal conductivity than PB-10 polyesters whose thermal conductivity has been reported to be 1.2 W m^{-1} K^{-1}, six times higher than that of commodity plastics [9].

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BEAMLINES
BL-6A and BL-10C

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