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) 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 phase to yield extended-chain lamellar crystals [1]. This extended-chain crystallization via the Col mesophase has been observed at ambient pressure for poly(vinylidene fluoride-co-trifluoroethylene) (PVDF/TFE) [2]. The Col 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-t-g links; this translation disorder can be introduced by chemical aperiodicity, as in PVDF/TFE.

We examined the effects of chemical aperiodicity on layer order and lamellar morphology using liquid crystal PB-8/12-x copolyesters [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.

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 [5] and as observed by small-angle neutron scattering [6]. Smectic LCs having liquid-like packing of mesogens can include chain folding at thermodynamic equilibrium [7]. In contrast, the SmI phase, which is still present at small-angle neutron scattering, can include chain foldings at thermodynamic equilibrium [8]. In the SmI phase, the formation of extended chain lamellae is more likely because 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 order. 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.

REFERENCES

BEAMLINES
BL-6A and BL-10C

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