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Well-Ordered Lamellar Microdomains of ABA Triblock Copolymers Containing a Main-Chain Liquid Crystalline Polyester as the Middle Segment

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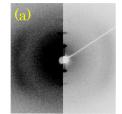
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Liquid crystal (LC) block copolymers composed of LC and isotropic blocks are interesting because the LC orientation owing to an external field can induce macroscopic orientation of the microdomans.[1,2] In addition, microdomain morphology itself can be influenced by liquid crystallinity. Upon the transition from isotropic to nematic phases in the LC segments, the amorphous segments changed their shape from spherical into cylindrical in order to avoid LC director distortion.[3–5] Smectic LC block copolymers formed a lamellar morphology at unusually low LC compositions. In some smectic LC block copolymers, lamellar spacing increased with decreasing temperature in the LC temperature region corresponding to change in the LC segment configuration from a random coil to a more extended configuration in the lamellar normal direction. In most of these copolymers, LC mesogens lie parallel to the microdomain interface. Such homogeneous anchoring of the mesogens on the interface is attributed to the chemical structure of LC segments in block copolymers. The LC segments are the side-chain type and have mesogens in the side chains. Such a comb-shaped LC segment tends to stretch the backbone perpendicular to the interface, so the mesogens in the side chain are parallel to the interface. If mesogenic moieties are embedded in the chain backbone as in the case of the main-chain LC polymers (MCLCPs), the mesogens as well as chain backbone will lie perpendicular to the interface to produce other types of coupling between the microdomain and LC.

In this paper, we report on an LC block copolymer having a main-chain LC polyester segment.[6–11] The block copolymer was an ABA triblock consisting of poly(methyl methacrylate) (PMMA) or poly(ethyl methacrylate) (PEMA) as amorphous end blocks (A) and MCLCP of BB-5(3-Me) as the LC central block (B).

 $R = CH_3$ or CH_2CH_3

Though the LC block was synthesized by melt condensation and has a molecular weight distribution as large as 2, these two types of segments were segregated from each other to form lamellae that showed a clear small-angle X-ray scattering (SAXS) profile. Combining the wide-angle X-ray diffraction (WAXD) pattern and the SAXS profile demonstrated that the BB-5(3-Me) segment adopted the most extended conformation and lay perpendicular to the lamellae to form smectic layers parallel to the lamellae (Figure 1). Thus, the mesogens established homeotropic alignment on the microdomain boundary. The LC lamellar thickness is much smaller than the contour chain length of the BB-5(3-Me) segment (52 nm), suggesting that the LC segment is folded to be accommodated in the LC lamella. We examine the effects of the molecular weight of the amorphous segment on the microdomain morphology of the LC triblock copolymers. A series of the LC block copolymer was prepared using an identical BB-5(3-Me) with a molecular weight of 10,000. The molecular weight of the amorphous segment attached to the LC segment ranges from 2,300 to 10,000. All copolymers formed well-ordered lamellar microdomains with the smectic layers lying parallel to the lamellae.



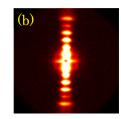


Fig. 1 (a) WAXD and (b) SAXS patterns of the fiber sample of 39E. The fiber sample was spun from the isotropic melt at 160 °C and annealed at 120 °C of the LC phase for 12 h. The fiber axis lies in the vertical direction.

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