Lamellar microdomains formed by ABA triblock copolymers consisting of a main-chain nematic polyester B-block and polystyrene A-blocks

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1 Introduction

Liquid crystalline block copolymers (LCBCPs) consisting of liquid crystalline (LC) segments have attracted considerable attention because the self-assembled structures of the LC segment are easily oriented using an external field. A magnetic field can align amorphous microcylinders as well as the LC director of the matrix along the field direction. The microdomain orientation is induced by the LC orientation via mesogenic units anchoring parallel to the microdomain interface. Such an LC anchoring is readily explained for the side-chain type of LC polymer segments typically adopted in LCBCPs. The mesogens arrange their long axis parallel to the interface because they are connected at the end to the segment's backbone that stretches perpendicularly to the interface via the most extended spacers.

We previously reported on LCBCPs using the main-chain-type LC polymers as an LC segment [1,2]. The LCBCPs were ABA triblock copolymers comprising an LC polyester as the B block connected at both ends to poly(methacrylate) (PMA) A blocks. Although the LC polyesters had molecular weight distribution with a polydispersity index as large as 2, the BCP with the B block of a smectic (Sm) LC BB-5(3-Me) polyester formed a well-defined lamellar microdomain structure to display scattering maxima up to the seventh order in the small-angle X-ray scattering (SAXS) pattern. The LC lamellar microdomain consisted of an Sm LC with the LC director perpendicular to the lamellar interface. Such an LC orientation was reasonable for main-chain LC segments incorporating mesogens within the backbone and agreed with the tendency of BCP segments extended perpendicularly to the microdomain interface. However, LC segments with contour lengths longer than the lamellar thickness must be folded several times to be accommodated in the lamellar microdomains. When the stem length of the folded LC segment was comparable to the persistence length, the LC segment could not increase the number of foldings. Therefore, the segment was inclined with respect to the lamellae to increase the interface area [2].

An ABA BCP composed of the B block of a main-chain nematic HBA10THQ LC polyester connected to the A segments of poly(styrene) (PS) formed a lamellar structure at a PS volume fraction of 0.45 [3]. Although the LC segment was segregated from PS to form lamellae, the nematic director was parallel to the lamellae, indicating that the LC segment was elongated along the lamellar boundary. This LC segment orientation was not expected from the tendency of the BCP segments to elongate away from the microdomain interface but could be a feature of a flexible main-chain LC polymer with longer spacers. HBA10THQ has a longer spacer of decane methylene connecting two consecutive mesogens in the backbone than BB-5(3-Me), which has a spacer backbone that consists of five carbon atoms.

In this study [4], we synthesized a series of ABA triblock T5PS-φ copolymers using a main-chain nematic LC HBA5THQ polyester with a pentamethylene spacer.
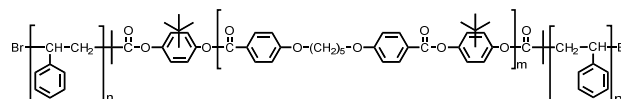
HBA5THQ with a number average molecular weight (M_n) of 22 k was connected to the PS segments, with M_n ranging from 3 k to 12 k. The LCBCPs at the PS volume fraction (φ) ranging from 13% to 38% formed lamellar microdomains. The LCBCP with $\varphi > 34\%$ formed flat lamellae, with the nematic director parallel to the lamellae. As φ decreased, the flat lamellae became zigzag at $\varphi = 29\%$, and the zigzag lamellae ran perpendicularly to the nematic director at $\varphi = 13\%$. In this report, we focus on the lamellar microdomain morphology of T5PS-φ.

2 Experiment

The T5PS-φ copolymers were prepared by the atom transfer radical polymerization of styrene at 110 °C using anisole and α,ω-di-2-bromoisobutyryl-terminated HBA5THQ as a solvent and a macroinitiator, respectively [3]. The degree of polymerization (DP) and the number average molecular weights ($M_{n,LC}$ and $M_{n,am}$) of the central LCP and amorphous groups were estimated by ^{1}H-NMR spectra. The PS volume fraction (φ) was estimated on the basis of the densities. The polydispersity indices (PDIs) of the copolymers were obtained by size exclusion chromatography (SEC) (Table 1).

Table 1. Characterization of Polymers

Sample	φ/%	$M_{n,LC}$ /g mol^{-1}	$M_{n,am}$ /g mol^{-1}	PDI
T5PS-13	12.8	22100	2900	2.16
T5PS-29	28.9	22100	7900	1.75
T5PS-34	34.4	22100	10200	1.88
T5PS-38	38.0	22100	12000	1.86

Small-angle X-ray scattering (SAXS) patterns were recorded using a Bruker AXS Nano-STAR-U instrument. Synchrotron radiation (SR) SAXS measurements were performed at the BL-6A beam line in Photon Factory (Tsukuba, Japan) equipped with a Dectris PILATUS 300K-W detector with a camera length of approximately 2 m. The X-ray wavelength was 0.15 nm. The scattering intensity was corrected by the transmission and subtraction of background scattering and plotted against the scattering vector $q = (4\pi \sin \theta)/\lambda$.

3 Results and Discussion

The LC segment formed a nematic LC as did the HBA5THQ homopolyester [5]. All the fibrous copolymers aligned the nematic director along the fiber axis to display the similar wide-angle scattering pattern. However, the corresponding SAXS patterns exhibited different azimuthal directions of the maxima among the copolymers. All the copolymers displayed scattering maxima at scattering vectors (q) with integer ratios, demonstrating that the T5PS-φ copolymers formed lamellar microdomains. However, the normal direction with respect to the nematic director orientation was dependent on φ. T5PS-38 and T5PS-34 displayed SAXS maxima concentrated on the equator perpendicular to the fiber axis (Fig. 1a and b). The SAXS pattern did not change as φ was decreased to 34%. However, T5PS-29 exhibited scattering maxima azimuthally extended above and below the equator (Fig. 1c), suggesting that the lamellae adopted a zigzag conformation. In addition, when φ was reduced to 13%, the scattering maxima spot appeared at a larger azimuth from the equator (Fig. 1d). Such a SAXS maximum in the quadrant could be ascribed to the lamellae running in a zigzag perpendicular to the fiber with the addition of transmitted electron microscopy. These results demonstrate that T5PS-φ changed the lamellar orientation with respect to the LC director orientation.
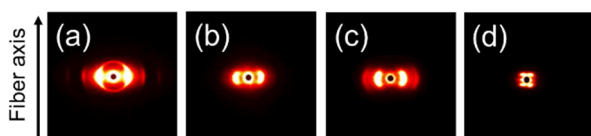

Fig. 1: SAXS patterns of fibrous T5PS-38 (a), T5PS-34 (b), T5PS-29 (c), and T5PS-13 (d) samples. The fiber axis is vertical.

T5PS-38 formed lamellae parallel to the fiber axis so that the nematic director was parallel to the lamellar boundary. In the LC lamellae, the LC segments should be elongated along the nematic director. Fig. 2a depicts a plausible conformation of the LC segment accommodated in an LC block lamella. An LC segment with the contour length of 102 nm primarily stretches along the nematic direction but folds to meander through a 13-nm-thick LC lamella and bridges the PS lamellae. In the amorphous block, the PS segment could extend along the boundary because both segments must occupy the same interface area to form a flat lamellar boundary.

This lamellar structure was affected by the nematic order in the LC block. The SR-SAXS profiles of T5PS-38 were measured during heating and cooling at a rate of 2 °C min^{-1} as they crossed the LC–isotropic liquid transition temperature (T_i = 182 °C) of the LC segment (Fig. 2b). The profiles include the first- and second-order scattering maxima, indicating that the lamellar morphology was conserved during the heating/cooling cycle. The first-order maximum at $q = 0.3$ nm^{-1} shifted toward a smaller $q = 2.5$ nm^{-1} as the temperature increased from 180 to 200 °C and then returned to its original position with a subsequent temperature decrease. The estimated d_0 from the first-order scattering maximum was plotted against the temperature (Fig. 2c). The lamellar spacing increased the isotropization of the LC segment reversibly from 24.2 to 28.5 nm. A similar reversible increase in d_0 was observed for homologous copolymers with different LC spacer lengths.[3]
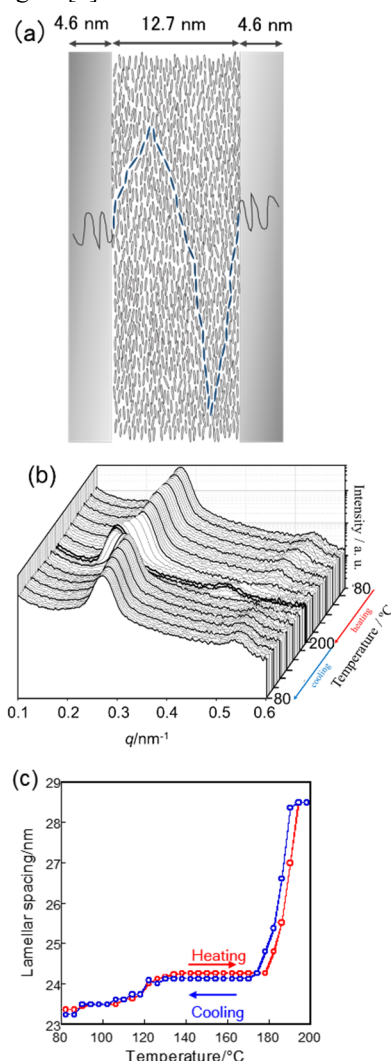

Fig. 2: (a) Schematic of lamellar microdomains in T5PS-38. (b) Sets of SR-SAXS profiles of the non-oriented T5PS-38 copolymer recorded during heating and cooling at a rate of 2.0 °C min^{-1}. (c) Lamellar spacing determined by the SAXS profiles against temperature.

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