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Liquid Crystalline Block Copolymer Elastomers Comprising Main-Chain Liquid Crystal Polyesters Attached to Cross-Linked Amorphous Segments at Both Ends

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1 Introduction

Liquid crystal elastomers (LCEs) have attracted much attention because of the coupling between the backbone conformation and the LC orientational order can give rise to spontaneous and reversible elongation along the director axis on the isotropic–LC transition.[1] The main-chain LCEs with mesogenic moieties incorporated in the polymer backbone elongate larger than the side-chain LCEs due to the stronger coupling between the chain conformation and the ordering of the mesogens.[2–9] Such an anisotropic elongation is particularly pronounced for monodomain LCEs; however, the preparation of monodomain LCEs remains difficult because it requires polymer chains to be cross-linked in a macroscopically oriented state. Another puzzling phenomenon connected to the cross-linking LC polymers is the decreases in the isotropization temperature and enthalpy change.[7–11] A cross-linked main-chain smectic BB-5 polyester formed by the incorporation of 2 mol% of 1,3,5-benzene tricarboxylic acid exhibited the isotropization temperature (T_i) and enthalpy change (ΔH_i) of 182 °C and 2.8 kJ mol^{-1}, respectively, fairly lower than the corresponding values for the BB-5 homopolyester (i.e, T_i = 213 °C and ΔH_i = 5.9 kJ mol^{-1}).[9]

The difficulties in preparing monodomain LC elastomers may be avoided using rubber–nematic–rubber (RNR) triblock copolymers because, in this case, the cross-links are not included in the LC segment but rather in the rubber (R) segment. The R blocks segregate from the nematic (N) block to link the network of N segments. Although the nematic block is a main-chain nematic polymer in the model proposed by de Gennes,[12] the first RNR copolymer was prepared using a side-on nematic polyacrylate with a narrow molecular-weight distribution in order to form long-range-ordered lamellar microdomains.[13] The monodomain triblock copolymer was obtained using a magnetic-field orientation followed by a cross-linking in the R block induced by UV irradiation. The director of the N block was perpendicular to the lamellae, and the film contracted reversibly on the isotropization and elongated by a factor 1.23 on the liquid crystallization.

In this study, we investigated triblock B5Cin copolymers that comprise a main-chain smectic BB-5(3-Me) polyester where photo-cross-linkable poly(2-cinnamoyloxyethyl methacrylate) (PCEMA) blocks are connected at both ends (Chart 1). BB-5(3-Me) was synthesized by the polycondensation of 4,4′-biphenyl dicarboxylic acid and 3-methyl-1,5-pentanediol and forms a SmCA LC.[14–18] We use the main-chain smectic LC polymer as the middle block for the following two reasons. First, copolymers comprising smectic main-chain LC polyesters connected with polymethacrylates at both ends form long-range-ordered lamellar microdomains in a large range of compositions even though the LC segments have polydispersity indices as high as 2.[19–22] Second, the lamellae and LC director can be arranged perpendicular to the fiber axis (or the film drawing direction) and perpendicular to the lamellae, respectively. Such lamellae and LC orientations have been characteristically observed for the main-chain smectic triblock copolymers and are similar to the RNR copolymers.[12,13] In contrast, a main-chain nematic triblock copolymer formed lamellar microdomains, but both the lamellae and LC director were arranged parallel to the drawing direction.[23]

Similar to the smectic LC triblock copolymers, the B5Cin copolymers formed lamellar microdomains, in which the BB-5(3-Me) segments formed a SmCA LC arranging the LC director perpendicular to the lamellae. Melt drawing and successive annealing yielded monodomain films with the lamellar normal and the LC director lying along the film drawing direction. The PCEMA block lamellae were cross-linked by UV irradiation up to 20% conversion. Similar to monodomain LCEs, the UV-irradiated monodomain films contracted reversibly along the direction of the LC director on the LC isotropization. This film contraction coincided with the decrease in the lamellar spacing. The film elongated reversibly on the liquid crystallization by a factor ranging from 1.07 to 1.24, which is explained by the ratio of lamellar spacing in the LC phase to that in the isotropic phase.

Chart 1

2 Experiment

Materials. A B5Cin-235-41 copolymer was prepared using a BB-5(3-Me) polyester with number-average molecular weight ($M_{\mathrm{n,LC}}$) of 23500. The numbers of 235 and 41 in the code of the copolymer correspond to $M_{\mathrm{n,LC}}$ divided by 100 and the volume percentage (φ) of the PCEMA segment, respectively. The values of $M_{\mathrm{n,LC}}$ and M_{n} of amorphous PCEMA segment ($M_{\mathrm{n,am}}$) were determined by ^{1}H NMR spectroscopy. φ values were calculated from $M_{\mathrm{n,LC}}$, $M_{\mathrm{n,am}}$, and the densities of each segment (i.e., BB-5(3-Me): 1.23 g cm^{-3}, PCEMA: 1.23 g cm^{-3}). The polydispersity indices (PDIs) of the copolymers measured for the BB-5(3-Me) polyester and B5Cin-235-41 were 2.17 and 1.66 by size-exclusion chromatography (SEC).

The LC block of B5Cin235-41 exhibited the glass transition temperature (T_{g}) at 31°C, and the isotropization at 139 °C involving ΔH_{i} = 2.82 kJ mol^{-1} whereas that in the photo-cross-linked B5Cin235-41 exhibited T_{g} = 31 °C and T_{i} = 144 °C (ΔH_{i} = 2.47 kJ mol^{-1}). (cf. OH-terminated BB-5(3-Me)-235: T_{g} = 28 °C, T_{i} = 151 °C, and ΔH_{i} = 3.86 kJ mol^{-1})

Methods. Wide-angle and small-angle X-ray scattering patterns were measured using Cu Kα radiation with Bruker D8 DISCOVER and NanoSTAR-U, respectively, equipped with Vantec 500 and Vantec 2000 detectors, respectively. The synchrotron radiation (SR) small-angle X-ray scattering (SAXS) measurement was performed at the BL-10C and BL-6A beamlines 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 0.1488 nm. The temperature dependences of the strain for the B5Cin films were obtained using a Hitachi TMA7100. The elastomer in the film form with a thickness of 0.1 mm was cut into rectangular strips with lengths of 5 mm (in the elongation direction) and widths of 2 mm and clamped in the tensile testing machine. The sample was heated and cooled at a rate of 2 °C min^{-1} under a dry nitrogen atmosphere and the film length (L) was measured.

3 Results and Discussion

Morphology and Photo-Cross-Linking of B5Cin-235-41 Monodomain Films. The BB-5(3-Me) segment was segregated from the PCEMA segment to form a lamellar microdomain. Both the smectic LC and lamellar microdomain could be well oriented by drawing the copolymer melt at 160 °C into 100-μm-thick films and annealing the films for 12 h at 120 °C leading to the formation of the SmCA LC by the LC block. Figure 1 shows the typical wide-angle X-ray scattering (WAXS) and SAXS patterns measured for the B5Cin-235-41 film. The smectic layer reflections and scattering maxima ascribed to the stacked lamellae are observed along the film drawing direction in the WAXS and SAXS patterns, respectively, demonstrating that the smectic layers and microdomain lamellae stack along the film stretching direction. Thus, both the lamellae and smectic LC can be oriented macroscopically by first drawing the copolymer melt and then annealing at the LC temperature. Such lamellar and smectic LC orientations are a characteristic of ABA triblock copolymers with main-chain smectic LC polyesters as the middle blocks.[19–22] The lamellar spacing D and smectic layer spacing were 34.3 and 1.63 nm, respectively. These values were not altered for the photo-crosslinking of the amorphous segments by irradiating UV light (λ_{max} = 365 nm, 50 mW cm^{-2}) on each film face for 90 min. The value of the orientational order parameter, S, estimated from the azimuthal intensity distribution of the lamellar reflection was 0.86.[24]

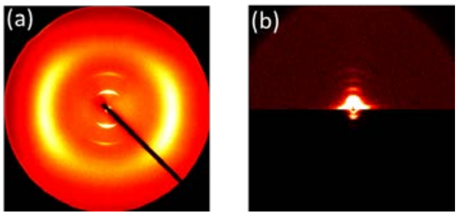

Fig. 1: (a) WAXS and (b) SAXS patterns for the B5Cin-235-41 film. The drawing direction is vertical.

Reversible Contraction of Photo-Cross-Linked B5Cin-235-41 Monodomain Films on the LC-to-Isotropic Transition. The reversible contraction along the film drawing direction on the LC–isotropic transition of the BB-5(3-Me) block is typical of the photo-cross-linked B5Cin copolymer films. Such reversible contraction was observed in the cross-linked copolymers although it has not been observed for the non-cross-linked copolymers. The temperature dependence of the film length (L) along the lamellar normal direction is shown in the upper part of Figure 2, where the ratio of the L to the L in the isotropic phase (L_{iso}) is plotted versus temperature. The measurements were performed by applying a stress of 1.5 kPa to the 100-μm-thick film sample, and the temperatures were scanned at a rate of 2 °C min^{-1}. It was found that the cross-linked film contracted upon heating to temperature beyond the T_{i} of the LC block. The shape change was fully reversible with a variation of 18%. The temperatures at which L/L_{iso} decreased and increased on heating and cooling, respectively, corresponded to the endothermic and exothermic peaks in the heating and cooling DSC thermograms, respectively, as shown in the lower part of Figure 2.

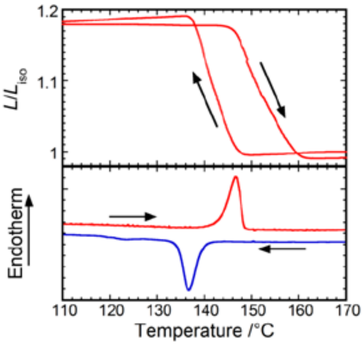

Fig. 2: Relative film lengths L/L_{iso} (upper) and DSC thermograms (lower) measured for the cross-linked

B5Cin-235-41 film during first cooling and then heating processes at a rate of 2 °C min^{-1}.

The spontaneous LC orientation can be attributed to the conservation of lamellar microdomain at $T > T_i$. SAXS patterns obtained for the heating of the film at 170 °C and the subsequent cooling to 120 °C include lamellar scattering maxima on the meridian showing that the lamellae stacking along the film drawing direction was conserved in the entire range of investigated temperatures. Although the lamellae were conserved, the spacing decreased at $T > T_i$. Figure 3a shows the SR-SAXS profiles measured for the cross-linked B5Cin-235-41 film on heating up to 170 °C followed by cooling at a rate of 2 °C min^{-1}. Here, the scattering intensities were obtained from the 2D scattering patterns by averaging the intensity over azimuthal sectors of 10° on each side of the film drawing direction and plotting against the scattering vector q. The as-UV irradiated film showed scattering maxima at q with ratios of 1:2:3:4:5 that were ascribed to lamellar microdomains stacking along the film drawing direction at a spacing (D) of 34.5 nm. The scattering intensity began to decrease at a temperature of 142 °C, and the scattering maxima attributed to lamellae at a smaller D (i.e., 26.7 nm) that began to appear at q with ratio of 1:2. Upon subsequent cooling, the scattering maxima ascribed to the original spacing recovered at 146 °C. Such a reversible decrease in D on the isotropization of the LC segment has been observed for similar ABA LC triblock copolymers and was explained by conformation changes in the LC block on the phase transition.[20,21]

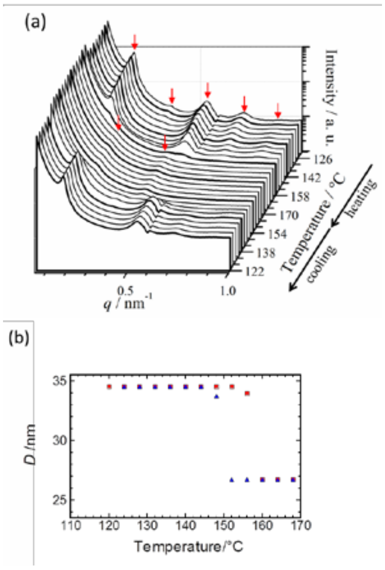

Fig. 3: (a) SR-SAXS profiles for the cross-linked B5Cin-235-41 film collected during heating and cooling at a rate of 2 °C min^{-1}. The arrows indicate the positions of scattering maxima. The profiles at an interval of 16 °C are shown by thick lines. (b) Temperature dependences of the lamellar spacing of the cross-linked B5Cin-235-41 film. The lamellar spacings collected through heating and cooling processes are shown with square and triangle marks, respectively.

The reversible contraction of the film length can be connected to the reversible decrease in D. In Figure 3b, D values measured by SR-SAXS for a cross-linked B5Cin-235-41 film upon heating or cooling at a rate of 2 °C min^{-1} were plotted versus the temperature. When the two sets of lamellae with different spacings appeared, the series of lamellae exhibiting the stronger scattering were selected. The lamellar spacing at $T < T_i$ was constant at D_{LC} = 34.5 nm and decreased to D_{iso} = 26.7 nm at $T > T_i$. The comparison of the temperature dependence of D with the temperature dependence of L/L_{iso} allows us to conclude that the film contraction coincides with the decrease in D. When the lamellae are tilted with respect to the film draw direction by an average angle of β, L_{LC}/L_{iso} is expected to correspond to the value of $\langle\cos\beta\rangle D_{LC}/D_{iso}$. $\langle\cos\beta\rangle$ can be calculated from the value of $S = [3\langle\cos^2\beta\rangle - 1]/2$ for the lamellae. For B5Cin-235-41, the value of L_{LC}/L_{iso} is 1.18, which fairly corresponds to the value of $\langle\cos\beta\rangle D_{LC}/D_{iso} = 0.95 \times 34.5/26.7 = 1.23$.

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