

Double Ordered Layers within Microphase-separated Lamellar Structure of Double Liquid Crystalline Side-chain Type Block Copolymer

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A new hierarchical nanostructure was created by self-assembly of a double liquid crystalline side-chain type block copolymer. The block copolymer was successfully prepared via a nitroxide-mediated living free radical polymerization and formed double ordered layers within a phase-separated lamellar structure of the cast film.

As the size of advanced technology devices such as electronic, optic, and magnetic devices or biosensors is scaled down, suitable new organic and polymeric materials with precisely controlled structures must be developed for these requirements. Block copolymers (BCPs) are great candidates for these materials because they can spontaneously self-assemble with periodic nanostructures, of which the size and morphology can be easily controlled by the molecular weight and composition of copolymers.¹ In a variety of BCPs, side-chain type BCPs have advantages for use in these devices because the functionality and physical properties based on the nanostructures can be tuned by altering the side-chain moieties of the polymer.² Furthermore, by introducing liquid crystalline or crystalline molecules as the side-chain into the blocks, the formation of higher order hierarchical structures can be created over multiple length scales.³⁻⁶ Although numerous side-chain type BCPs with a single side-chain substituted block have been prepared, little attention has been paid to synthesize BCPs with different liquid crystalline side-chains on each polymer block.⁷ Double liquid crystalline side-chain substituted BCPs (DLC-BCPs) can form unique hierarchical periodic nanostructures, in which different liquid crystalline layers are generated within the microphase-separated nanostructures. Materials incorporating two or more different functional groups can display not only their own properties independently but also new properties by combining the different functionalities for a cooperative effect. Herein, we report the synthesis of novel liquid crystalline diblock copolymers incorporating different side-chains in each block via a nitroxide-mediated living free radical polymerization (NMP) and characterization of their hierarchical periodic nanostructures by small- and wide-angle X-ray scattering (SAXS and WAXS).

To create the desired DLC-BCPs, two kinds of liquid crystalline styrenic monomers **M1** and **M2** shown in Figure 1 were designed and synthesized.⁸ The liquid crystalline structures are composed of typical biphenyl mesogenic groups and alkyl spacers. The principal difference of **M1** and **M2** was the order of mesogens and spacers from the styrene units in the primary monomer structures, which was expected to induce microphase-separation to produce the desired DLC-BCPs. The chemi-

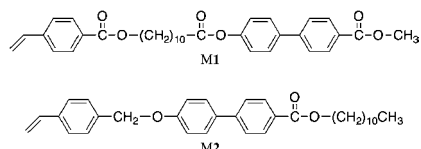
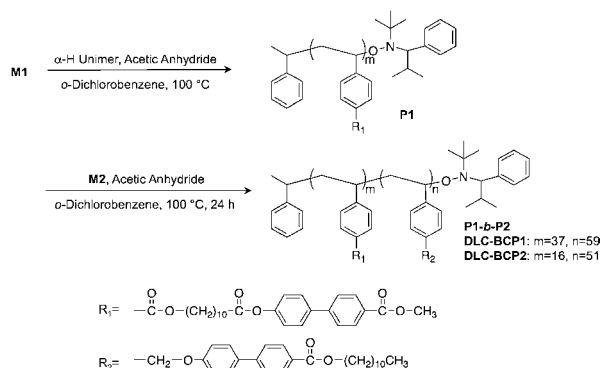


Figure 1. Chemical structures of liquid crystalline styrenic monomers, **M1** and **M2**.

cal structures of **M1** and **M2** were characterized by ¹H, ¹³C NMR, IR spectroscopy and elemental analysis, and all of the data showed the desired monomers were obtained without a side product.

In order to prepare the BCPs with well-controlled molecular weight and polydispersity, we applied a nitroxide-mediated living free radical polymerization (NMP) to polymerize the monomers obtained using 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (α -H Unimer) as the initiator.⁹ The homopolymerization of **M1** was carried out in the presence of the α -H Unimer, acetic anhydride as an accelerator, and *o*-dichlorobenzene at 100 °C for 24 h under reduced pressure. The product was purified by reprecipitation into a large amount of methanol. Size exclusion chromatography (SEC) indicated a low polydispersity index (PDI) of 1.08 and a number-average molecular weight M_n of 20800 (versus polystyrene standard in tetrahydrofuran). The polymer obtained **P1** was used as the macroinitiator to prepare the target DLC-BCPs **P1-b-P2** as shown in Scheme 1. The polymerization of **M2** was conducted in the presence of **P1** under similar conditions to the homopolymerization of **M1**. IR, ¹H and ¹³C NMR spectroscopy and SEC chromatogram showed that the desired BCP was obtained with M_n of 48800 and a low PDI of 1.10 (DLC-BCP1).



Scheme 1. Synthesis of DLC-BCPs via a nitroxide-mediated living free radical polymerization.

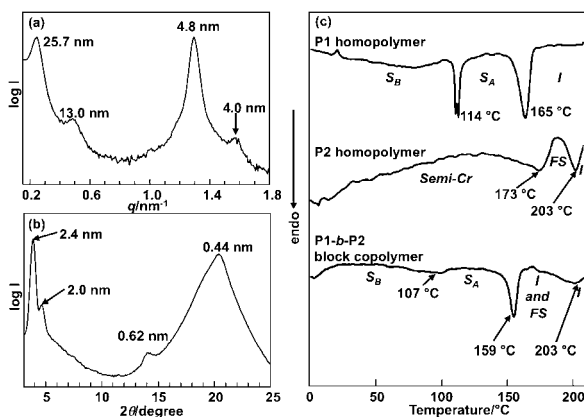


Figure 2. Characterization of DLC-BCP1: (a) SAXS and (b) WAXS profiles and (c) DSC curves of homopolymers P1, P2, and block copolymer P1-*b*-P2 (S_B : smectic B, S_A : smectic A, I: isotropic, FS: fluid smectic, Semi-Cr: semicrystal).

Additional DLC-BCPs with different molecular weights were also successfully prepared (DLC-BCP2 (P1-*b*-P2), M_n of 33400, PDI of 1.11 and DLC-BCP3 (P2-*b*-P1), M_n of 56900, PDI of 1.20).⁸

The formation of phase-separated hierarchical nanostructures in DLC-BCP1 was confirmed by small-angle and wide-angle X-ray scattering (SAXS and WAXS) profiles from a cast film prepared from a 5 wt % solution of the polymer in chloroform on a glass plate and then annealed for 3 h at 185 °C. The two diffractions observed in the smallest q region in the SAXS pattern (Figure 2a) are attributed to the lamellar structure composed of stacked P1 and P2 domains with a periodic length of 25.7 nm. The other two diffractions with spacings of 4.8 and 4.0 nm are attributed to the smectic structures within P2 and P1 domains, respectively, because these diffraction peaks can be observed for the P2 and P1 homopolymers. The WAXS pattern (Figure 2b) includes the second-order reflections of the smectic or semi-crystalline structures in each domain and a broad outer diffraction with a spacing of 0.44 nm characteristic to liquid crystalline-like spacing of the mesogenic moieties within the layers.

The DSC thermogram of DLC-BCP1 includes three endothermic peaks, suggesting that the BCP forms thermotropic liquid crystals (Figure 2c). The homopolymers P1 (M_n 16800 and PDI 1.08) and P2 (M_n 19800 and PDI 1.09) also show endothermic peaks at 114 and 165 °C and at 173 and 203 °C, respectively, in the DSC thermograms. These peak temperatures are comparable to or somewhat higher than the temperatures observed in the BCP, indicating that each segment phase segregates into discrete domains. Polarized optical microscopy (POM) and WAXS patterns show that P1 forms smectic B (S_B), smectic A (S_A) and isotropic phases in order of increasing temperature. While P1 does not form a crystalline phase, P2 does form a semicrystal (Semi-Cr) indicated in the WAXS pattern from the sharp and diffuse diffraction peaks around $2\theta = 20^\circ$ as well as a sharp reflection with a spacing of 4.8 nm. With increasing temperature, P2 shows fluidity and the WAXS pattern includes sharp and diffuse reflections characteristic to a fluid smectic mesophase (FS) such as S_A . The transition from FS to the isotropic liquid (I) phase was not fully observed because thermal decomposition begins around 210 °C. The three endothermic peaks observed for DLC-BCP1

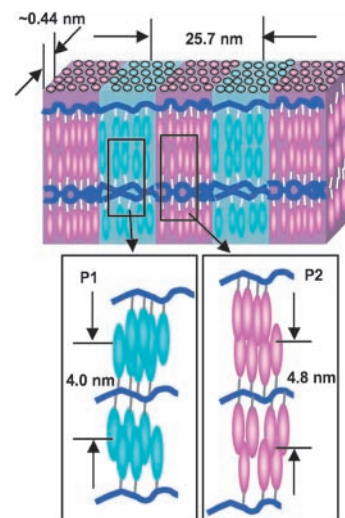


Figure 3. Schematic representation of the hierarchical ordered nanostructure composed of double ordered layers within the microphase-separated lamellar structure for DLC-BCP1.

are thus attributed to the phase transitions taking place in each segment. The peaks at 107 and 159 °C correspond to S_B - S_A and S_A -I transitions respectively, in the P1 segment. The isotropization in the P2 segment appears as an endothermic peak at 203 °C. The melting of the Semi-Cr in P2 has not been found possibly because of low crystallinity.

The experimental results presented above indicate the formation of hierarchical ordered nanostructure consisting of semi-crystalline and smectic layers within a microphase-separated lamellar structure in the cast film (Figure 3).

We have reported the synthesis of new double liquid crystalline side-chain substituted BCPs and their self-assembly to yield hierarchical nanostructures. The DLC-BCPs formed double ordered structures within a microphase-separated lamellar nanostructure. These materials can be further designed and tuned through the choice of the side-chains to offer very promising properties for advanced optical, electronic, and biosensors applications.

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