Synthesis of Liquid Crystalline Block Copolymers 
Self-assembled into Sub-5 nm Microdomains

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The directed self-assembly (DSA) of block copolymers (BCPs) is a potentially feasible option for next-generation lithography, due to its potential high resolution and low cost. The smallest domain spacing of conventional BCPs such as polystyrene-b-poly(methacrylate) (PS-b-PMMA) are larger than 10 nm, which limits their application in sub-10 nm lithography when compared with EUVL technology. BCPs with high $\chi$ value could further reduce the domain spacing to achieve higher resolution. In this work, we synthesized a series of BCPs with biphenyl-typed liquid crystalline (LC) block and fluorine-containing block. With strongly segregated repulsion between isotropic coil and anisotropic LC blocks, the new BCPs yielded highly ordered nanostructures with lamellar and hexagonal morphologies. The smallest feature size was 4.8 nm, showing great potential for sub-5 nm patterning technology.

Keywords: Block copolymer, Directed self-assembly, Liquid crystalline, Sub-5 nm

1. Introduction

Following the Moore’s Law, feature size scaling down has been imperative and challenging in manufacturing ultrahigh-density devices for semiconductor industry. Advanced lithographic technologies like extreme ultraviolet (EUV) lithography have been explored to tackle this dilemma [1,2]. Block copolymers (BCPs), with superior ability to self-assemble into highly ordered nanostructures, also demonstrate great potential in application for next-generation lithography [3-5]. To achieve sub-10 nm, BCPs with high-$\chi$ (Flory–Huggins interaction parameter) value gained more attention from researchers [6,7]. Recently, several BCP systems with domain sizes ranged from 3 to 5 nm have been reported [8-10].

Liquid crystalline (LC) BCPs usually have mobile mesogenic groups in one of blocks [11]. Due to the coexistence of LC mesogens and microphase separation, there is a hierarchical nanostructure in LC BCPs [12]. More importantly, the introduction of LC blocks can enhance the immiscibility between isotropic block and anisotropic segment, thus bringing about strongly segregated repulsion and yielding well-defined nanostructures [12,13].

More recently, we have reported a series of fluorine-containing BCPs, which can self-assemble into sub-5 nm nanostructures [14,15]. These perfluoroalkyl BCPs could form fine microdomains in much shorter time and at much lower temperature (1 min at 80 °C) compared with conventional high-$\chi$ BCPs (>1 h, > 160 °C), indicating the fluorinated block played a key role to trigger the fast self-assembly process.

Via replacing the polystyrene (PS) block with a LC methacrylate block, we expect the resulted perfluoroalkyl LC BCPs could also form sub-5 nm microdomains after fast thermal annealing. Therefore, in this study, a series of novel BCPs including both biphenyl-typed LC blocks and fluorine-containing blocks were synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization. With variation of the block compositions, different kinds of phase-separated morphologies could be observed. The smallest domain spacing calculated from small angle X-ray scattering (SAXS) measurement was 9.6 nm, indicating potential application as sub-5 nm DSA
materials. The following characterizations are related to the LC BCP which has the smallest feature size (Fig. 1).

![Fig. 1. Nanostructures formed by LC BCPs.](image)

### 2. Experimental

#### 2.1. Synthesis and characterization

In this study, a series of LC BCPs with relatively narrow polydispersity (PDI) (< 1.14) were synthesized by RAFT polymerization. All the monomers, initiators and materials for LC monomer were purchased from Energy Chemical and J&K. All the solvents like THF and methanol were obtained from Titan. PMMA-typed fluorine-containing monomer was purified by passing through a neutral alumina column to remove stabilizer, and the LC monomer was synthesized according to the method reported before [16]. Azobisisobutyronitrile (AIBN) was used after recrystallization from ethanol. Other chemicals were used as received without other purifications.

We synthesized these LC BCPs following the standard process [15], in which three circles of freezing-pumping-thawing were needed to remove the air thoroughly. After polymerization at 75 °C for 10 h and 85 °C for 12 h, the LC BCPs could be obtained successfully. The polymers were purified via dissolution and precipitation, which was repeated three times to remove the residual monomer absolutely.

1H nuclear magnetic resonance (1H NMR) spectrums in CDCl3 were recorded on a Bruker spectrometer (400 MHz). The number-average molecular weight ($M_n$) and the PDI of polymers were determined by the gel permeation chromatography (GPC) instrument with THF as an eluent. Thermal behaviors of polymers were studied by a TA Instruments Q2000 differential scanning calorimeter (DSC). The LC textures of polymers were characterized by a Leica optical polarizing microscope DM2500P. The diffraction patterns of powder polymer samples were recorded in SAXS equipped with monochromatized X-ray ($\lambda = 1.54 \text{ Å}$). The morphologies of spin-coated thin polymer films were investigated via a Zeiss Ultra 55 field emission scanning electron microscope (FESEM).

#### 2.2. Preparation of bulk samples and thin film

Solution of these LC BCPs in THF was dropped onto washed silicon wafer. After THF evaporated fully, the samples were thermally annealed at related temperatures. The morphologies of these annealed bulk samples were investigated by SAXS at room temperature.

0.5 wt% solution of these LC BCPs was prepared using THF, and then spun coating onto cleared silicon wafer. After annealing onto a hot plate at 160 °C for 12 h, the nanostructures of the samples were investigated by SEM.

### 3. Results and discussion

#### 3.1. Thermal and LC properties of LC BCP

Thermal properties of LC BCPs were investigated via DSC. The glass transition temperature ($T_g$), mesophase transition temperature ($T_{lc}$) and LC-isotropic transition temperature ($T_{iso}$) are shown in Fig. 2. Taking the second heating scan as an example, the DSC curve had three thermal signals, among which the endothermic peaks at the vicinity of 62 °C, 107 °C, and 128 °C were assigned to the $T_g$, $T_{lc}$, and $T_{iso}$, respectively. Due to small molecular weight of this polymer, the LC BCP had only one $T_g$, rather than two $T_g$ designated to different blocks.

![Fig. 2. The DSC curve of LC BCP with the smallest $M_n$, and each thermal scan was at a rate of 10 °C /min.](image)

Liquid crystal textures were characterized by polarized optical microscope (POM) equipped with a precise heating stage (Fig. 3). When cooling from the isotropic phase, the schlieren texture appeared, suggesting a nematic phase was formed in this temperature range.
3.2. SAXS results of LC BCPs

Varied phase-separated domain sizes and morphologies could be obtained through varying molar ratio of two blocks. The feature domain spacing, $d$, was calculated by $d = 2\pi/q^*$, in which $q^*$ is determined by the position of principal scattering peak. The SAXS intensity profile of LC BCP with lowest $M_n$ showed a sharp primary and secondary peak with $q/q^*$ position ratios of 1:2, indicating a lamellar morphology. The feature size measured from $q^*$ was 9.6 nm, indicating the width of each micro domain was sub-5 nm.

The self-assembly behaviors of this LC BCP as the temperature increased were examined. After thermal annealing at 60 °C, 100 °C, and then 160 °C for 5 min, the LC BCP showed highly ordered structures, where the domain spacing changed from 8.9 nm, 9.7 nm to 9.6 nm (Fig. 4a). The plot of the domain sizes against the temperatures was shown in Fig. 4c. Under $T_{lc}$, the lamellar domain spacing was around 8.8 nm. At $T_{lc}$, the lamellar domain spacing increased to a larger size, and then this LC BCP conserved the dimension and the lamellar morphology even being heated above $T_{iso}$. Compared with PS-typed BCPs, which replaced the LC block with PS block, the domain spacing (11.3 nm) and morphology kept unchanged after annealing at different temperatures (Fig. 5b). A possible reason is that the change of temperature affected the alignment of LC mesogens, thus leading to the overall variation of domain spacing.

3.3. SEM images of LC BCPs

Besides lamellar morphology, a hexagonal one was also obtained. In order to improve the contrast of image, the LC BCP thin film samples for SEM measurement were under plasma etch with CF$_4$ for 40 s at 75 mTorr, and RF power is 10 W. After thermal annealing on the silicon substrate, the in-plane cylinders of hexagonal LC BCP were observed via SEM (Fig. 5). The domain spacing observed in SEM was 14 nm, which is consistent with SAXS results (13 nm).

4. Conclusion

In this study, we designed and synthesized a series of BCPs composed of biphenyl-typed LC methacrylate blocks and fluorine-containing methacrylate blocks via RAFT polymerization. It was demonstrated that the LC-containing BCPs were successfully obtained through $^1$H NMR, GPC, SAXS, SEM, DSC, and POM analysis. After thermal annealing, the LC BCPs with various compositions self-assembled into lamellar and hexagonal morphologies. It was observed that the domain size of LC BCPs were successfully obtained.
through $^1$H NMR, GPC, SAXS, SEM, DSC, and POM analysis. After thermal annealing, the LC BCPs with various compositions self-assembled into lamellar and hexagonal morphologies. It was observed that the domain size of LC BCP obtained after thermal annealing below $T_{lc}$ was smaller than those around or above $T_{lc}$, although they all formed highly ordered lamellar morphologies. The smallest domain size of LC BCPs was 4.8 nm. Via incorporation of fluorine-containing block and LC block, nanostructures with sizes ranging from 5 nm to 15 nm could be constructed, which can not only be used as DSA materials, but also have potential for various functional nanomaterials.

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