Highly Ordered Methacrylate Block Copolymers Containing Liquid Crystal Side Chains

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Block copolymers composed of cinnamate or biphenyl liquid crystal and fluorinated side chain blocks were synthesized by RAFT polymerization. The block copolymers (BCPs) showed sharp phase separation benefit from the chemistry incompatibility of the fluorinated and the liquid crystal blocks. Both cinnamate and cyano-biphenyl liquid crystal containing BCPs formed highly ordered nanostructures with domain-spacing ranged from 15.6 nm to 12.4 nm. UV exposure could alter the cinnamate containing domain morphology via partially dimerization.

Keywords: Block copolymer, Directed self-assembly, Cinnamate side chain, Cyano-biphenyl side chain, Sub-7 nm

1. Introduction

In order to achieve smaller feature size at lower cost in microelectronics manufacture, directed self-assembly has been developed for next generation technology [1,2]. Majority of the researches focused on PS-b-PMMA type copolymers [3-5], while block copolymers (BCPs) with liquid crystal [6-9] were also explored. However, less attention paid on the photo-chemical cross-linking of the BCPs, despite the research [6,10] of the photo-isomerization of azobenzene mesogen influenced the alignment of block-copolymer.

In 1954, Eastman Kodak issued the patent on polyvinyl cinnamate as a negative tone photoresist [11]. Cinnamate and its derivatives, as the first generation of lithographic material applied on integrated circuit manufacture, which was the milestone of electronics industry. The double bond in cinnamate is reactive by photodimerization under ultraviolet light. The difference in solubility or the high contrast between the exposed and unexposed areas, make it possible as photoresist material. Cyano-biphenyl monomer liquid crystals have wide applications in optical display devices due to their good optical stability, dielectric properties and moderate phase transition temperature range.

Our group previously synthesized several BCPs with similar fluorinated first block, and various second block [12,13]. Last year, we reported primary results of the synthesis of methacrylate BCPs containing cyano-biphenyl liquid crystal (LC) side chain [14]. Due to the chemistry incompatibility of fluorinated and LC blocks, these materials exhibited good phase-separation to form sub-5 nm nano-structures after quick thermal annealing at moderate temperature even under 100 °C.

In this study, we designed and synthesized methacrylate BCPs containing cinnamate or cyano-biphenyl liquid crystal side chain and the fluorinated one via RAFT polymerization. Both LC containing BCPs formed very fine domains after thermal annealing at 160 °C (above LC isotropic temperature), both displaying as small as 12.4 nm domain spacing or 6.2 nm feature domain size, which could be applied for sub-7 nm patterning technology. After 365 nm UV exposure, some dimerization occurred in cinnamate units, which lightly cross-linked the BCPs.

2. Experimental

2.1. Synthesis of monomers, block copolymers and the characterization (Scheme 1)

The cinnamate monomer and biphenyl monomer were synthesized as follows. Firstly, p-hydroxy cinnamic acid methyl ester or cyano-biphenol
reacted with bromohexnaol, followed by the reaction with methacryl chloride to produce the monomers. Column chromatography and recrystallization were employed to purify the monomers. Block copolymers were synthesized by RAFT polymerization in hexafluoro-isopropanol (HFIP) at 65 °C. Reaction time was 12 hours for the fluorinated block and 24 hours for the cinnamate or biphenyl block. All polymers were precipitated in methanol and then dried in vacuum at room temperature.

Scheme 1. Synthetic route of PF-b-PCNA and PF-b-PCB block copolymers.

Molecular weight and PDI were measured by gel permeation chromatography measurements, carried out on Agilent 1260. \(^1\)H nuclear magnetic resonance (\(^1\)H-NMR) was acquired on a 400 MHz AVANCE III spectrometer. Since the fluorinated chain has poor solubility in most organic solvents, trifluoroacetic acid (\(d\)-TFA) was used as deuterated solvent. Resulted BCPs were soluble in \(d\)-CDCl\(_3\) and the mole ratio of the two blocks was calculated by \(^1\)H-NMR.

SAXS characterization was conducted at room temperature. BCPs were dissolved in dichloromethane (DCM) and drop-coated on silicon wafer. After the solvent completely evaporated, thermal annealing process was conducted on a hot plate at 160 °C for 1 hour in air, followed by the immediately chilled by liquid nitrogen to freeze the phase-separated structures. And then the samples were scratched into powder for SAXS (Xenocs, Xeuss 2.0) measurement at room temperature.

2.2. UV exposure of the cinnamate BCP (Scheme 2)
Samples were exposed to 365 nm ultraviolet light from 25 W UV lamp at room temperature.

The BCP sample was dissolved in DCM and drop-coated on silicon wafer. Irradiation was performed for various times, followed by SAXS measurement after 1 h thermal annealing at 160 °C.

3. Results and discussion
3.1. LC BCPs synthesis and characterization

In the design of the polymer structure, we adopted the classic decoupling method in liquid crystalline molecules [15]. A flexible spacer, \(n\)-hexyl, was introduced between the main chain and the mesogen. In this way, the movement of main chains and the alignment effect of the side chains can be balanced.

RAFT polymerization is a convenient and effective method to build specific polymer structures. Purified monomers had good reactivity in this condition.

Molecular weight of first fluorinated block was determined by \(^1\)H-NMR spectra through the integration ratio between methylene hydrogen and RAFT-CTA end group aromatic hydrogen, while the ratio between first and second block was determined by peak a over peak b in Fig. 1. All GPC curves of resulted BCPs showed singular symmetrical peaks indicating the successful synthesis of the target BCPs.

Fig. 1. \(^1\)H-NMR spectra of block copolymer in CDCl\(_3\), (a) PF-b-PCB block copolymer, (b) PF-b-PCNA before and (c) after 365 nm UV irradiation.
3.2. Domain spacing determined by SAXS

A series BCPs were obtained by varying the length of cinnamate block \( N \) from 4.6 to 10.6, which resulted in domain spacing ranged from 15.6 nm to 12.4 nm (Table 1 and Fig. 2a). The sharp peaks and \( q/q_0 \) ratio between primary, second and third peak confirmed the formation of lamella morphology. When the cinnamate block was shortened to 2, less ordered structure was observed with no second and higher scattering peaks.

Table 1. Characterization of block copolymers.

| Sample         | \( M^{(a)} \) | \( N^{(a)} \) | \( M_n^{(b)} \) (kg/mol) | PDI  
|----------------|--------------|--------------|--------------------------|------
| P1 PF\(_{15}\)-b-PCNA\(_{11}\) | 15           | 10.6         | 10.9                     | 1.32 |
| P2 PF\(_{15}\)-b-PCNA\(_{9}\) | 15           | 8.5          | 10.1                     | 1.27 |
| P3 PF\(_{15}\)-b-PCNA\(_{5}\) | 15           | 4.6          | 8.8                      | 1.20 |
| P4 PF\(_{15}\)-b-PCNA\(_{3}\) | 15           | 2.3          | 8.0                      | 1.16 |
| P5 PF\(_{11}\)-b-PCB\(_{28}\) | 11           | 27.5         | 15.3                     | 1.14 |
| P6 PF\(_{11}\)-b-PCB\(_{16}\) | 11           | 15.8         | 11.1                     | 1.08 |
| P7 PF\(_{11}\)-b-PCB\(_{8}\) | 11           | 6.2          | 7.6                      | 1.15 |

(a) Degree of polymerization of fluorinated block \( M \) and cinnamate/biphenyl block \( N \), calculated by \(^1\)H-NMR; (b) Molecular weight was calculated by \(^1\)H-NMR spectra. (c) Polydispersity index (PDI) was measured by GPC using a PS standard at 35 °C.

PF\(_{11}\)-b-PCB\(_{28}\) (P5) and PF\(_{11}\)-b-PCB\(_{16}\) (P6) formed hexagonal morphology, with liquid crystal matrix and enclosed fluorinate cylindrical domains. When the length of LC block increased, the \( d \)-spacings decrease from 15.4 to 12.8 nm. Further decreased the \( N \) of LC block, second and higher scattering peaks disappeared, indicating less ordered structures (Fig. 2b).

The cinnamate photo-dimerization reaction has been used in the negative tone photoresist technology. We thus examined whether the dimerization could happen in the BCPs after UV exposure. Although \(^1\)H-NMR spectra displayed small new peaks (p, q, r) corresponding to the dimer structure after 30 min UV exposure, the majority of the monomer peak at aromatic region (peak c, d in Figs. 1b and 1c) remained unchanged, which demonstrated partially dimerization occurred in the BCP solution.

SAXS (Fig. 3) was then employed to examine the phase-separated domain change in PF\(_{15}\)-b-PCNA\(_{11}\) (P1) after the UV exposure 30 min: domain spacing calculated by primary peak was reduced slightly from 15.6 nm to 15.1 nm with the second diffraction peak disappeared, indicating a less ordered BCP after dimerization cross-linking.

![Fig. 2. SAXS profiles of (a) PF-b-PCNA and (b) PF-b-PCB after 1 h annealing at 160 °C above LC isotropic temperature.](image)

![Fig. 3. SAXS profiles of PF\(_{15}\)-b-PCNA\(_{11}\) (P1) before and after UV irradiation for 30 minutes. Samples were pre-annealed at 160 °C for 1 hour.](image)

4. Conclusion

In this study, we designed and synthesized a cinnamate and cyano-biphenyl liquid crystalline monomers to produce block copolymers by RAFT polymerization from the similar fluorinated macro-initiator. Driven by the chemistry incompatibility between fluorinated block and the liquid crystal block, highly ordered nanostructures with \( d \)-spacing ranged from 15.6 nm to 12.4 nm were obtained after 1 h annealing at 160 °C above LC isotropic temperature. UV exposure could alter the cinnamate containing BCP’s domain morphology via partially dimerization.
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