The Role of Liquid Crystalline Side Chains for Long-range Ordering in the Block Copolymer Thin Films

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In this study, side chain liquid crystalline (SCLC) fluorinated functionalities capable of controlling the orientation of the block copolymer (BCP) domains in thin film were successfully demonstrated. By introducing 1H,1H,2H,2H-perfluorodecanethiol onto a precursor polymer to obtain a novel BCP with a C8F17-containing LC side chain, BCP domains in 6.3-36.3 nm scale were obtained. For the studied symmetric SCLC diblock copolymers, a morphology transition from lamellae to cylinder was observed with reduced molecular weight ($M_n$). A co-existed 3.6 nm periodicity from lamellar smectic phase of SCLC was also verified in all synthesized BCPs of varied $M_n$ by comprehensive characterizations of small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Atomic force microscopy (AFM) of the thin films revealed the formation of fingerprint patterns with increased correlation length when the domain spacing of the BCP is closer to the periodicity of the smectic structures, which are supported by the quantitative analysis on AFM images.

Keywords: Diblock copolymer, Sub-5 nm self-assembly, Liquid crystalline side chain, Correlation length, Fluorine

1. Introduction

The ability to self-assemble into 1-100 nm scale regular patterns gives block copolymers (BCPs) great potential in various industrial applications. Especially, perpendicularly-oriented lamellae with sub-10 nm feature sizes can be applied to next-generation lithography for semiconductor manufacturing. However, numerous issues including increasing the strength of segregation ($\chi_{eff}$), lowering the defectivity of the nanostructures, and inducing perpendicular orientation on thin films, need to be addressed simultaneously before any practical applications [1,2]. Although previous studies have achieved the formation of sub-10 nm lamellae on thin films, additional processing such as the use of solvent vapor annealing [3-7] or a top-coat [8-14] can complicate and add to the cost of manufacturing. By designing a novel BCP with advanced functionalities, a BCP can be tailored to fulfill the requirements of such lithographic applications with relative ease [15,16]. Previously, we introduced a trifluoroethyl-containing functionality to the glycidyl moieties of a polystyrene-block-poly(glycidyl methacrylate) (PS-b-PGMA) precursor polymer to obtain polystyrene-block-poly[2-hydroxy-3-(2,2,2-trifluoroethylsulfanyl)-propyl methacrylate] (PS-b-PHFMA) [17]. Since the trifluoroethyl functionality is incompatible with the polar (PGMA) and non-polar (PS) segments, PS-b-PHFMA was capable of forming 9.6 nm lamellae in the bulk. Additionally, the relatively hydrophobic trifluoroethyl moieties counteracted the hydrophilic PGMA moieties, balancing the surface free energies (SFE) of the two segments in PS-b-PHFMA and facilitating the formation of perpendicular lamellae on thin films. However, as the interfacial confinement can heavily influence the self-assembly of BCPs, sub-10 nm structures could not form on the PS-b-PHFMA thin films.

Besides balancing the SFE of a BCP segment, side chain liquid crystalline (SCLC) functionalities have also been shown to be capable of controlling the orientation of the BCP domains [18-22]. In the
thermal annealing process, the formation of the self-assembled periodic nano-structures will be synergistically influenced by the interplay of liquid crystal (LC) ordering and segregation between blocks. Verploegen and coworkers [23] systematically controlled the percent covalent attachment of a smectic LC side chain onto the vinyl functionalities of poly(styrene)-block-poly(methylvinyl siloxane) (PS-b-PMVS). Due to the drastically different SFEs of PS and PMVS, PS-b-PMVS typically forms parallel structures on thin films, and with low LC content, the LC mesophase does not affect domain orientation. However, at high LC content, perpendicular structures could be achieved despite the disparate SFEs. This was attributed to the tendency for homogenous or parallel alignment of the LC moieties, which possessed less conformational freedoms compared to the polymeric backbone, driving the hierarchical BCP nanostructures to orient normal to the substrate. Therefore, the introduction of LC functionalities onto the side chains of BCPs is a promising method for developing a novel BCP that can simultaneously fulfill the requirements for next-generation BCP lithography applications.

In this study, we demonstrated the formation of perpendicularly-oriented lamellar/parallel-oriented cylindrical thin films with a minimized 6 nm half-pitch size and long range ordering by introducing 1H,1H,2H,2H-perfluorodecanethiol onto a precursor polymer to obtain a novel BCP with a C$_8$F$_{17}$-containing LC side chain (PS-b-P8FMA). Small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) analyses of the bulk revealed the formation of hierarchical structures in which lamellae/cylinder with domain spacings ($d_{\text{spacing}}$) of 6.3 to 36.3 nm and smectic structures with 3.6 nm periodicities have co-assembled. Atomic force microscopy (AFM) of the thin films revealed the formation of fingerprint patterns with increased correlation length when the $d_{\text{spacing}}$ is closer to the periodicity of the smectic structures.

2. Experimental

2.1. Materials

Sec-butyllithium (sec-BuLi, Kanto) was used as received. Lithium chloride (LiCl, Kanto) was dried in a vacuum oven overnight before use. Styrene and glycidyl methacrylate (GMA) (Tokyo Chemical Industry) were distilled over di-n-butylmagnesium (MgBu$_2$) or CaH$_2$ and subsequently degassed under Ar. Diphenylethene (DPE) was distilled over n-butyl lithium and subsequently degassed under Ar. Other reagents and solvents were used as received.

2.2. Methods

The $^1$H NMR spectra were recorded with a 400 MHz instrument (JNM-ECS400, JEOL, Japan) using chloroform-$d$ as the solvent. The number average molecular weights ($M_n$) and polydispersity ($M_w/M_n$) were determined by size exclusion chromatography (SEC; GPC-101, Showa-Denko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene. The glass and LC phase transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan) and calibrated with polystyrene.
Finally, 3 mL of degassed methanol (MeOH) was added to the Schlenk flask to yield proton-terminated PS-b-PGMA. The polymer was precipitated into MeOH and filtered. The product was dried under reduced pressure at 40 °C overnight to yield PS-b-PGMA as a white powder (1.80 g, 90% yield). The $M_n$ and dispersity ($D = M_w/M_n$) of the product determined by SEC were 27200 g mol$^{-1}$ and 1.15, respectively. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$, ppm): 0.98 (s, $\alpha$-CH$_3$, PGMA), 1.14 (s, $\alpha$-CH$_3$, PGMA), 1.29-1.80 (br, backbone, -CH$_2$-CH-, PS), 1.84-2.30 (br, backbone, -CH$_2$-CH-, PS, br, backbone, -CH$_2$-(CH$_3$)$_2$-, PGMA), 2.70 (s, -CH$_2$-CH(CH$_2$)-O-, PGMA), 2.82 (s, -CH$_2$CH(CH$_2$)-O-, PGMA), 3.28 (s, -CH$_2$CH(CH$_2$)-O-, PGMA), 3.84 (s, -(C=O)O-CH$_2$-, PGMA), 4.37 (s, -(C=O)O-CH$_2$-, PGMA), 6.39-6.85 (m, o-aromatic, PS), 6.91-7.42 (m, m-, p-aromatic, PS).

2.4. Synthesis of PS-b-P8FMA through the post-functionalization of PS-b-PGMA with 1H,1H,2H,2H-Perfluorodecanethiol

A 10 mL glass tube was charged with PS-b-PGMA and THF (20 mole equiv. per GMA unit) and immersed in an ice-water bath. 1 wt% lithium hydroxide (LiOH) aqueous solution (LiOH 0.05 mole equiv. per GMA unit) and 1H,1H,2H,2H-perfluorodecanethiol (1.5 mole equiv. per GMA unit) were added to the tube. After stirring for 20 min at room temperature, the reactor was set to 30 °C and stirred for 3 h. The crude solution was precipitated from hexane and methanol. The product was dried under a reduced pressure to yield a white powder (0.78 g, 65% yield). The $M_n$ and dispersity ($D = M_w/M_n$) of the product determined by SEC were 40800 g mol$^{-1}$ and 1.21, respectively. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$, ppm): 0.98 (s, $\alpha$-CH$_3$, P8FMA), 1.12 (s, $\alpha$-CH$_3$, P8FMA), 1.26-1.74 (br, backbone, -CH$_2$-CH-, PS), 1.82-2.30 (br, backbone, -CH$_2$-CH-, PS, br, backbone, -CH$_2$-(CH$_3$)$_2$-, P8FMA), 2.30-2.45 (t, -(C=O)O-CH$_2$-, P8FMA), 2.60-2.76 (t, -(S)-CH$_2$-CH$_2$-CF$_2$-, P8FMA), 2.76-2.87 (d, -(CH(OH))CH$_2$-S-, P8FMA), 3.82-4.17 (d, -(C=O)O-CH$_2$-, P8FMA) (m, -CH(OH)-, P8FMA), 6.39-6.82 (m, o-aromatic, PS), 6.92-7.32 (m, m-, p-aromatic, PS).

Fig. 1. $^1$H NMR spectra of (A) PS-b-PGMA and (B) corresponding chemically modified PS-b-P8FMA (SF11).

2.5. Bulk sample preparation

The bulk samples used to investigate the bulk morphologies and $d$ spacing of the microphase-separated structures were prepared by slowly evaporating a dilute BCP THF solution filtered through a 0.25 μm pore size PTFE membrane syringe filter at 30 °C. The as-prepared samples were dried under a reduced pressure before annealing at 150 °C for 24 h.

2.6. Thin film preparation

Bare silicon wafers were treated with a mixture of H$_2$O$_2$ (30%) and H$_2$SO$_4$ (70%) (v/v) (piranha solution) at 80 °C for 40 min. The wafers were rinsed with water repeatedly and dried in a stream of nitrogen. Bottom surface layers (BSL) were prepared by spin coating a 1.0 wt% poly(2,2,2-trifluoroethyl methacrylate)-random-poly(methyl methacrylate)-random-poly(methacrylic acid) (PTFEMA-r-PMMA-r-PMAA) solution in propylene glycol monomethyl ether acetate (PGMEA) solution at
3000 rpm and 30 s onto the cleaned silicon wafers, followed by crosslinking at 200 °C for 5 min. The substrates were sonicated in toluene to remove any random copolymers that were not attached to the substrate. Furthermore, 1.0 wt% solutions of the BCPs in toluene were spin-coated at 3000 rpm for 30 s onto the surface-modified silicon substrates to obtain thin films with ca. 1.4 \( L_0 \) thicknesses (1.0 \( L_0 \) denotes one periodic length of self-assembled nanostructure). The thin films were annealed at 150 °C for 24 h under ambient conditions. An oxygen plasma etching was conducted for a certain time (40 sccm, 20 W, 20 Pa) to selectively remove the methylacrylate-based block.

3. Results and discussion

3.1. Synthesis and characterization of the BCPs

A series of PS-\( b \)-PGMA precursor polymers were successfully synthesized via the sequential anionic polymerization of styrene and GMA using sec-BuLi, excess LiCl, and DPE in THF at -78 °C under an Ar atmosphere (Scheme 1). Based on \( ^1 \)H NMR and SEC analyses, the synthesized BCPs were found to have number-average molecular weights ranging from 27 to 2 kg mol\(^{-1} \) and narrow dispersities.

The precursor PS-\( b \)-PGMAs were then functionalized with 1H,1H,2H,2H-perfluorodecanethiol in THF with LiOH as the catalyst at 30 °C for 3 h to yield the targeted PS-\( b \)-P8FMAs. Following the post-functionalization reaction, the \( M_n \) of the BCPs increased while dispersities remained narrow (Table 1). Additionally, as the characteristic \( ^1 \)H NMR signals corresponding to the glycidyl moieties in PS-\( b \)-PGMA (a, a’, b, c, and c’ at 2.70, 2.82, 3.28, 3.84, and 4.37 ppm, respectively) (Fig. 1A) had disappeared in the \( ^1 \)H NMR spectra of the PS-\( b \)-P8FMAs, only to be replaced with signals at 4.03, 2.82, 2.72, and 2.39 ppm (Fig. 1B), the post-functionalization of the PS-\( b \)-PGMAs had proceeded to completion to successfully yield a series of PS-\( b \)-P8FMAs with well-defined primary structures and a wide range of molecular weights.

3.2. Morphologies in the bulk

The bulk morphologies of the synthesized PS-\( b \)-P8FMAs were then analyzed by SAXS using synchrotron radiation and TEM. Thermal analysis based on DSC measurements between 25 and 250 °C also suggested that all investigated PS-\( b \)-P8FMAs of varied \( M_n \) exhibited LC phase, which is consistent with the representative POM results of SF7. The detected \( T_{iso} \) was proportional to \( M_n \) of P8FMA blocks. As the LC transition in kinetics was dependent on the number of LC side chain within one polymer chain, the transition from ordered to isotropic phase could be achieved under a reduced temperature. The \( T_{iso} \) of all PS-\( b \)-P8FMAs, except SF3 which had only three LC side chains, are well-above 150 °C annealing temperatures. Herein, the LC ordering of side chain will be co-existed with block segregation in thermal annealing process. The two-dimensional SAXS profiles were azimuthally integrated to generate one-dimensional scattering profiles and analyzed using the equation:

\[
q = \frac{4\pi \sin(\theta/2)}{\lambda}
\]

(1)

where \( \theta \) and \( \lambda \) are the scattering angle and wavelength, respectively. The domain spacings were subsequently determined using the equation:

\[
d = 2\pi/q^*
\]

(2)

where \( q^* \) is the position of the first-order scattering peak in the SAXS profile. The domain spacings (\( d_{spacing} \)) were estimated from the position of first-order scattering peak in the SAXS profile. The morphologies in the bulk were determined by SAXS and TEM. The \( \chi \) parameter was estimated being 0.223 at 150 °C based on random-phase approximation (RPA) method.

| Label | \( M_n \) (kg mol\(^{-1} \)) | \( D \) | \( w_{PS} \) | \( f_{PS} \) | \( d_{spacing} \) (nm) | Morphology | \( \chi \) (150 °C) |
|-------|-----------------|-------|--------|---------|-----------------|------------|---------|
| SF41  | 40.8            | 1.21  | 0.45   | 0.57    | 36.3            | Lamella    | 98.7    |
| SF20  | 19.9            | 1.12  | 0.43   | 0.55    | 21.6            | Mixed      | 46.7    |
| SF11  | 11.1            | 1.16  | 0.45   | 0.57    | 13.7            | Cylinder   | 26.4    |
| SF7   | 7.5             | 1.15  | 0.38   | 0.50    | 11.5            | Cylinder   | 16.7    |
| SF3   | 3.2             | 1.18  | 0.47   | 0.59    | 6.3 (8.0)       | Cylinder   | 7.7     |

\( a \) The labels SF refer to PS-\( b \)-P8FMAs, while the number in the right refers to the number-average molecular weight (\( M_n \)) of the polymer. \( b \) \( M_n \) and dispersities (\( D \)) were obtained by SEC using THF as the eluent based on PS standards. \( c \) PS weight fractions (\( w_{PS} \)) of PS-\( b \)-PGMA were calculated via \( ^1 \)H NMR and PS weight fractions (\( w_{PS} \)) of PS-\( b \)-P8FMA were further estimated from SEC based on constant \( M_n \) of PS block. \( d \) The volume fractions (\( f_{PS} \)) were calculated via \( ^1 \)H NMR based on the densities of 1.05 g cm\(^{-3} \) for PS and 1.73 g cm\(^{-3} \) for P8FMA. \( e \) The domain spacings (\( d_{spacing} \)) were estimated from the position of first-order scattering peak in the SAXS profile. \( f \) The morphologies in the bulk were determined by SAXS and TEM. \( \chi \) parameter was estimated being 0.223 at 150 °C based on random-phase approximation (RPA) method.
Fig. 2. SAXS profiles of the PS-b-P8FMA bulk samples following thermal annealing and TEM images of PS-b-P8FMA (A: SF41, B: SF20, C: SF11, D: SF7, E: SF3). The dark regions correspond to the P8FMA block owing to heavy RuO₄ staining on hydroxyl groups. The bottom left inset displays the Fourier-transform pattern of the real-space image and the periodic length was also indicated based on the pattern. The estimated $d_{\text{spacing}}$ from TEM is highly consistent with $d_{\text{spacing}}$ extracted from SAXS.

For SF41 of the highest $M_n$, the scattering peak resulting from micro-phase separation was labeled with upside-down black triangles at the integer ratios to the first-order peaks, suggesting the formation of well-ordered lamellar architecture. In contrast, a mixed morphology consisted of lamellar and cylindrical domains in SF20 sample was revealed by the insignificant scattering peak at $\sqrt{3}q^*$, which is the characteristic evidence of minor hexagonally packed cylindrical morphology. As $M_n$ of the studied PS-b-P8FMAs was further scaled down, more obvious cylindrical morphologies were revealed by the featured $\sqrt{3}q^*$, $\sqrt{7}q^*$ and even $\sqrt{12}q^*$ scattering peak. The broad peak in response to disordered morphology with 8.0 nm $d_{\text{spacing}}$ next to the primary scattering peaks in SF3 was merely caused by the driving force from block segregation. As the temperature is further cooled down into side chain LC phase regime, a morphology transition to hexagonally packed cylinder of 6.1 nm $d_{\text{spacing}}$ was suggested by the appearance of characteristic scattering peaks in higher $q$ region. Based on TEM characterization results (Fig. 2), hexagonally packed cylindrical domains of long-range ordering were observed for SF7 and SF3 of lowest $M_n$. In contrast, minor cylindrical domains ($d_{\text{spacing}}=27.3$ nm) mixed with major lamellar domains ($d_{\text{spacing}}=17.0$ nm) were typically observed in SF20 of higher $M_n$, which is highly consistent with the SAXS analysis. According to the flexible coil-coil model in Leibler’s theory, amorphous symmetric BCPs were predicted to form lamellar structure. However, the studied side chain liquid crystalline (SCLC) block copolymers were recently predicted to exhibit cylindrical morphology [24,25] even at symmetric block volume fraction, which are consistent with the discoveries in this study. Remarkably, the peaks labeled with upside-down blue triangles were attributed to the featured periodicity from LC side chain, which were further verified by the WAXD of bulk samples as shown in Fig. 3(c). The observed lamellar structure with 3.6 nm spacing was assigned to smectic phase of LC side chain [26], which is consistent with the thermal analysis results. The possible LC side chain conformation was also depicted based on the estimation on monomer molecular size using MM2 energy-minimization based on Chem 3D 16.0 (Fig. 3(e)). The estimated side chain length (1.8 nm) was equal to half of LC periodic length (3.6 nm). Therefore, a single LC periodic length was composed of a pair of mesogens with end-to-end
3.3. Nanostructure in thin films

In AFM images (Fig. 4), fingerprinted patterns with removal of P8FMAs domain were observed. The periodic lengths ($L_0$) of formed patterns were highly correlated with those characterized in bulk samples. The high correlation between the domain dimension in bulk and thin film was reasonably thought caused by stereo-regularity.

Fig. 4. AFM phase images of the thin films prepared from (a) SF41, (b) SF20, (c) SF11, and (d) SF7 after oxygen plasma etching. The inset presents the color mapping of each image, which indicates the domain orientation angle by distinctive colors.

Fig. 5. Autocorrelation intensity plot and the estimated correlation length $\xi$ based on AFM images obtained from (a) SF41, (b) SF20, (c) SF11, and (d) SF7. The averaged periodic lengths ($L_0$) of formed patterns were also given in the textbox.
by the introduced LC side chain. As entropy plays a more important role on the self-assembly in thin film compared to that in bulk, the intrinsic LC ordering from long fluorine-containing moieties could confine the entropy change of polymer chain [27] and thus minimize the interface effects. When the molecular weight is scaled down with a reduced value of $\chi N$, the driving force of micro-phase separation is also minimized. Meanwhile, the driving force for LC ordering is not significantly changed by reduced $M_n$ [28], as evidenced by the similar characteristic peaks indicating LC smectic phase in WAXD measurements. Therefore, the LC ordering from side chain begins to dominate the formation of nano-structure. As shown in quantitative analysis on AFM images (Fig. 5) based on the methodology in literature [29], a significantly increased correlation length ($\xi$) from 31.8 to 154.4 nm was suggested despite the reduced domain size, as LC ordering was capable of forming regularly elongated stripe and nearly defect-free morphology [22]. SF7 thin film sample with the most enhanced contributor from LC ordering reveals a $\xi$ of 12.2 times of periodic length ($L_0$), which is surprisingly 24.3 times of single line width (half-pitch).

4. Conclusion

In this study, a BCP molecular design capable of forming long-ranged ordered striations in thin film via facile introduction of fluorinated LC side chain was demonstrated. The SAXS and TEM analyses of the PS-b-P8FMA revealed a gradual morphology transition from ordered lamellae to hexagonally packed cylinder with a minimum $d_{\text{spacing}}$ of 6.3 nm in bulk. A co-existed smectic phase of LC side chain in 3.6 nm scale was also suggested by using WAXD, DSC and POM. In thin film studies, a high correlation in BCP domain scale of bulk and thin film states was revealed and the correlation length was increased under reduced $M_n$, which is caused by the enhanced role of LC ordering in the interplay between entropy-driven LC side chain ordering and block segregation in annealing process. Based on the thin film results, PS-b-P8FMA has proven to be a highly competitive candidate for sub-5 nm next-generation BCP lithography resist.

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