Altering the Self-Assembly of Poly(styrene-block-methyl methacrylate) by Introduction of Strongly Dissimilar Molecules at the Block Interface

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A triblock copolymer (triBCP) containing a short glycidyl methacrylate (GMA) middle block was chemically altered using the efficient thiol-epoxy ring-opening reaction. The resultant modified triBCPs showed significantly different self-assembly behavior from that of the parent triBCP. Analysis by SAXS and TEM showed that this technique can be used to modify the effective interaction parameter ($\chi_{eff}$) and the self-assembled morphology in the bulk. When modified with strongly interacting hydroxyl groups, $\chi_{eff}$ was found to have increased by a factor of 5. By introducing fluorinated liquid-crystalline molecules, the self-assembled morphology changed from purely lamellar to a complex mixture of lamellae and tetragonally packed cylinders with domain spacing of 20.4 nm and 14.6 nm respectively.

Keywords: Block copolymer, Self-assembly, Block copolymer lithography, Post-polymerization functionalization

1. Introduction

Block copolymer (BCP) lithography, whereby self-assembled patterns are used to pattern a substrate, has been receiving increased attention as a potential candidate for next-generation lithographic processes, particularly as feature sizes shrink well below 10 nm [1–7].

BCPs will spontaneously microphase separate to form domains rich in one block when the product of the interaction parameter ($\chi$) and the degree of polymerization ($N$) exceeds a minimum critical value, usually near 10.5 [8]. As the product $\chi N$ becomes much greater than 10.5, the feature size ($L_0$) generated during microphase separation scales on the order of $L_0 \sim \chi^{1/6} N^{2/3}$ [9]. Since $\chi$ is predetermined by the monomers used, it follows that one must decrease $N$ to decrease $L_0$ to the desired value for a given BCP, assuming $\chi$ remains large enough for $\chi N > 10.5$.

However, other constraints also limit the choice of monomers for BCP lithography. The microphase-separated structures must usually be oriented perpendicular to the substrate which necessitates a neutral interface at the substrate and free surface. As $\chi$ for a given pair of polymers increases, typically so too does the disparity in surface free energy of the two blocks, making it increasingly difficult to achieve perpendicular orientation [10,11].

Poly(styrene-block-methyl methacrylate) (PS-PMMA) has been widely studied because of the nearly equal surface energies of PS and PMMA, which, along with an appropriate neutralizing layer, makes perpendicular orientation relatively simple to achieve [12–15]. However, this diblock system has $\chi \approx 0.04$ which prevents $L_0$ from scaling below ~20-22 nm [16]. Despite this, some other BCP systems have been developed that can fulfill both the high-$\chi$ and perpendicular orientation requirements by using top-coats or solvent-vapor annealing [11,17,18]. However, these methods add complexity which is undesirable from a processing standpoint.

In this work, we propose a new method for altering the self-assembly behavior of a PS-PMMA BCP by introducing a short middle block which can be chemically tailored using a simple and efficient post-polymerization reaction (Scheme 1). By introducing different functional molecules at the interface, not only can we increase the effective $\chi$
by introducing strongly dissimilar molecules, we also demonstrate the ability change the self-assembled morphology by introduction of bulky liquid-crystalline molecules.

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, 1,1-diphenylethylene (DPE), glycidyl methacrylate (GMA), and methyl methacrylate (MMA) were purchased from Tokyo Chemical Industry. Styrene, GMA, and MMA were distilled over CaH₂ under reduced pressure. The purified styrene, GMA and MMA were further distilled over di-n-butylmagnesium, CaH₂, and trioctylaluminum respectively. All other reagents were reagent grade and purchased from Tokyo Chemical Industry or Sigma-Aldrich and used as received.

2.2. Synthesis of PS-b-PGMA-b-PMMA (SGM)

Polymerization was performed under an argon atmosphere. To a round bottom flask sealed with a stopcock and septum was added LiCl (34.7 mg, 0.819 mmol) and 40 ml of THF. The flask was then chilled to -78°C. sec-BuLi was added slowly until a faint yellow color persisted. The flask was then allowed to slowly warm to room temperature where it was kept until the solution became colorless. After returning the flask to -78°C, the calculated amount of sec-BuLi was added (0.110 mL, 0.114 mmol) followed immediately by styrene (1.40 mL, 12.2 mmol), changing the color to orange, and stirred for 30 minutes. DPE (0.100 mL, 0.566 mmol) was added, changing the color to dark red, and stirred for 30 minutes. Next, GMA (0.150 mL, 1.13 mmol) was added, causing the solution to become colorless, and stirred for 30 minutes. Finally, MMA (1.60 mL, 15.0 mmol) was added and stirred for 30 minutes before being terminated by the addition of degassed methanol. The product was precipitated into cold methanol, filtered, and dried under reduced pressure at 40 °C overnight to obtain PS-b-PGMA-b-PMMA as a white powder (2.52 g, 85% yield). The Mₙ and dispersity of the polymer were 20900 g mol⁻¹ and 1.15 respectively. ¹H NMR (400 MHz, chloroform-d, δ, ppm): 7.22-6.85 (br, m-, p-aromatic), 6.82-6.25 (br, o-aromatic), 4.28 (s, -(C=O)O-C₃H₂-), 3.78 (s, -(C=O)O-CH₂-), 3.59 (s, -(C=O)O-CH₃), 3.21 (s, -CH₂-CH(CH₃)-), 2.83 (s, -CH₂-CH(CH₃)-O-), 2.62 (s, -CH₂-CH(CH₃)-O-), 2.20-1.67 (br, -CH₂-CH-, -CH₂-C(CH₃)-), 1.54-1.22 (br, -CH₂-CH-), 1.05-0.75 (br, -CH₂-C(CH₃)-).

2.3. Thiol-epoxy reaction

A typical procedure for the post-polymerization functionalization of SGM is given. 1-Thioglycerol (7.7 mg, 71.4 mmol, 2 eq. per GMA unit) and SGM (149.2 mg, 7.1 mmol) are dissolved in 1 mL of THF. LiOH (0.05 M in water, 71 µL, 0.1 eq per GMA unit) is then added. The resulting solution is heated to 40 °C and stirred for 3 hours. The resultant polymer is precipitated in methanol a minimum of three times to remove excess 1-thioglycerol. The product was dried under reduced pressure at 40 °C overnight yield a white powder (112.6 mg, 75% yield).

2.3.1. Characterization of SGM modified with 1-thioglyceryl (SGM-gly)

¹H NMR (400 MHz, chloroform-d, δ, ppm): 7.22-6.85 (br, m-, p-aromatic), 6.82-6.25 (br, o-aromatic), 4.04 (m, -(C=O)O-CH₂-), 4.04 (m, -CH₂-CH(CH₃)-OH), 3.62 (m, -S-CH₂-CH-), 3.59 (s, -(C=O)O-CH₃), 3.48 (m, S-CH₂-CH(OH)-CH₂-OH), 2.73 (m, -CH₂-S-CH₂-), 2.20-1.67 (br, -CH₂-CH-, -CH₂-C(CH₃)-), 1.54-1.22 (br, -CH₂-CH-), 1.05-0.75 (br, -CH₂-C(CH₃)-).

Scheme 1. Post-functionalization of poly(styrene-b-glycidyl methacrylate-b-methyl methacrylate) by the thiol-epoxy reaction.
(br, -CH2-C(CH3)-).

2.3.2. Characterization of SGM modified with 1H,1H,2H,2H-Perfluorodecanethiol (SGM-fluoro)

\(^1\)H NMR (400 MHz, chloroform-d, \(\delta\), ppm):
7.22-6.85 (br, m- aromatic), 6.82-6.25 (br, \(\alpha\)-aromatic), 4.04 (m, -(C=O)O-CH\(_2\)), 4.04 (m, -CH2-CH(CH\(_2\))=O), 3.59 (s, -(C=O)O-CH\(_3\)), 2.81 (m, -CH(OH)-CH\(_2\)=S-), 2.71 (br -S-CH\(_2\)-CH\(_2\)-CF\(_2\)), 2.39 (br, -S-CH\(_2\)-CH\(_2\)-CF\(_2\)), 2.20-1.67 (br, -CH\(_2\)-CH\(_2\)-, -CH\(_2\)-C(CH\(_3\))-), 1.54-1.22 (br, -CH\(_2\)-CH\(_2\)-), 1.05-0.75 (br, -CH2-C(CH\(_3\))-).

2.4. Bulk film preparation

Bulk films were prepared by slow evaporation of a chloroform solution containing the polymer at 40 °C. The resultant film was dried under reduced pressure before being annealed at 180 °C for 24 h.

2.5. Measurements

The \(^1\)H nuclear magnetic resonance (NMR) spectra of the polymers were recorded on a JEOL 400 MHz NMR instrument using chloroform-d\(_1\) as a solvent. The number-average and weight-average molecular weights (\(M_n\) and \(M_w\)) were measured by size exclusion chromatography (SEC) using a Shodex GPC-101 system equipped with a refractive index detector and a LF-804 column (Showa Denko) with tetrahydrofuran (THF) as the eluent. SAXS measurements were carried out using a Bruker NanoSTAR (50 kV/50 mA) with a 2D-PSPC detector (detector distance of 1055 mm) to determine the morphology in the bulk. Transmission electron microscopy (TEM) (H-7650, Hitachi High Tech) was used to examine ultrathin slices produced by ultramicrotomy (Leica EM UC7) and stained by ruthenium tetroxide (RuO\(_4\)). Differential scanning calorimetry (DSC) measurements were carried out using an EXSTAR7000 series DSC7020 (Hitachi High Tech) by heating the prepared samples at a rate of 10 °C min\(^{-1}\). WAXS measurements were performed on a Bruker D8 Discover (40 kV/40 mA) with a 2-D Vantec 500 detector (detector distance of 210 mm).

3. Results and discussion

3.1. Synthesis and characterization of BCPs

For this study, a single batch of PS-b-PGMA-b-PMMA was synthesized by sequential anionic polymerization at -78 °C in THF in the presence of excess LiCl under an inert argon atmosphere [19–21]. This approach eliminated any potential batch-to-batch variation. The \(M_n\) and \(\bar{D}\) of the obtained polymer were obtained by SEC using THF as the eluent and calibrated with PS standards. The volume fraction of each block was calculated by \(^1\)H NMR (Fig. 1) and using densities of 1.05 g cm\(^{-3}\), 0.805 g cm\(^{-3}\), and 1.18 g cm\(^{-3}\) for PS, PGMA, and PMMA.

Fig. 1. NMR spectra of a) SGM, b) SGM-gly, and c) SGM-fluoro.
respectively [22]. The parent polymer was found to comprise 49 vol% Styrene, 7 vol% GMA, and 44 vol% MMA. The degree of polymerization of the middle GMA block was calculated to be 6.

SGM was functionalized by the base-catalyzed ring-opening reaction of the epoxy group using two different thiols to obtain chemically altered derivatives of the parent polymer [23–25]. The 1H NMR spectra of SGM-gly and SGM-fluoro (Fig. 1b,c) show the disappearance of the peaks attributed to the glycidyl group (4.28, 3.78, 3.21, 2.83, and 2.62) and the appearance of new peaks, particularly those near 2.8 adjacent to the thioether, indicating that the reactions proceeded successfully.

3.2. Bulk morphology

The microphase-separated morphology of the bulk films was analyzed by SAXS and TEM. The samples were prepared by slow evaporation from a dilute chloroform solution followed by annealing at 180 °C for 24 h, well above the glass-transition temperature (T_g) of each block to achieve thermal equilibrium. 2-D SAXS spectra were taken at room temperature and azimuthally integrated to obtain the 1-D scattering profiles (Fig. 2). The scattering intensity is plotted against the scattering vector (q = 4π sin(θ/2)/λ, where λ = 0.154 nm, and θ = scattering angle). The domain spacing (d-spacing) was calculated based on the location of the first-order scattering peak. The 3 samples used in this work were all found to have sharp first-order peaks with various higher-order peaks, indicating the formation of ordered structures.

We found that the addition of a very short chain of PGMA was enough to induce microphase separation in PS-PMMA with a domain-spacing of 18.9 nm (Fig. 2a) and higher order scattering peaks suggesting a lamellar morphology. For comparison, PS-b-PMMA synthesized using the same technique, with M_n = 19.8 kg mol^{-1}, is shown (Fig. 2d) and does not self-assemble [26]. The chemically altered triblock BCPs (triBCP) show a dramatic change in self-assembly behavior. The SAXS spectrum of SGM-Gly (Fig. 2b) shows a noticeable leftward shift of the primary peak indicating an increase in the domain spacing to 24.8 nm. Additionally, the appearance of integer-multiple higher-order peaks up to the 6th order suggests that the long-range order of the lamellae was much improved over the unmodified SGM. We believe this increase can be attributed to a large increase in \( \chi_{AB} \) and \( \chi_{BC} \) of the BCP because of the presence of three hydroxyl groups per GMA unit in the middle block [5,27].

On the other hand, the SAXS spectrum of SGM-fluoro (Fig. 2c) shows only a slight increase in the d-spacing, but instead shows a complex mixed morphology with peak ratios of q/q* = 1:2:3 and q/q'* = 1:√2:2:5:3. These peaks correspond to lamellar domains and tetragonally packed cylinders (P4mm space group) with 20.4 nm and 14.6 nm d-spacing respectively [28,29]. Additionally, the SAXS spectrum of SGM-fluoro shows a broad peak in the high angle region suggesting the presence of liquid crystal domains.

To confirm the presence of liquid crystalline domains, we further analyzed SGM-fluoro by DSC and WAXS. The DSC curve (Fig. 3a) exhibits a sharp endothermic peak around 350 K suggesting the presence of liquid-crystal domains. This is corroborated by the WAXS spectrum which shows a scattering peak at 3.4 nm (Fig. 3b). The calculated length of a single GMA-fluoro unit is 1.7 nm, suggesting that a smectic A phase was formed with the fluorinated side-chains fully-extended. The microphase-separated structures were also observed directly by TEM (Fig. 4). Areas of lamellae and tetragonally packed domains were both observed, confirming the morphology observed by SAXS.

3.3. Estimation of \( \chi_{\text{eff}} \) of SGM-gly

Though we were unable to directly estimate the
χ_eff of this BCP system using techniques like the random-phase approximation (RPA) because of the large molecular weight, we can estimate the relative increase in χ_eff by simple comparison of the SGM and SGM-gly d-spacing found by SAXS [30–32]. Since d ~ χ_eff/ΔN^2/3 and N has remained constant, the change in d can be attributed to an increase in χ_eff which can be calculated using equation 1. We found that by chemically altering the GMA block with 1-thioglycerol, χ_eff of the triBCP increased by a factor of 5.

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χ_{eff,PSM-gly} = \frac{d_{PSM-gly}χ_{eff,PSM}}{d_{PSM}}
\]  

Fig. 3. a) DSC spectrum and b) WAXS spectrum of SGM-fluoro with a schematic of the proposed structure.

4. Conclusion

In this work, we have proposed a new method of chemically tailoring a PS-PMMA triblock BCP by using the simple and efficient thiol-epoxy reaction to customize its self-assembly behavior. This approach is not limited to increasing the χ_eff, thereby decreasing the minimum d-spacing achievable by PS-PMMA; it can also be used to completely alter the self-assembled morphology. We envisage this approach being particularly useful at large scale where a single batch of PSGM can be synthesized and then simply modified to suit a given demand.

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