Synthesis and Thin-film Self-assembly of Cylinder-Forming High-χ Block Copolymers

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1. Introduction

Directed self-assembly (DSA) is one of the most promising candidates for resolution enhancement for advanced lithography node [1]. While PS-b-PMMA is the most widely used BCP, poly(styrene-b-poly(methyl methacrylate) (PS-b-PMMA). In this work, two PC-containing BCPs, poly(styrene-b-trimethylene carbonate (PS-b-PTMC) and poly(styrene-b-methyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (PS-b-PMTC-Me) were synthesized using ring opening polymerization (ROP) of the cyclic carbonyl monomers from hydroxy-functional polystyrene (PS-OH) with diazabicyclo[5.4.0]undec-7-ene (DBU) as the base catalyst. Resulting BCPs were purified by fractionating in methanol:acetonitrile (MeOH:MeCN) solvent mixture to afford clean BCPs that are needed for thin-film applications. Thin-film morphologies and the orientation of the purified BCPs were determined using atomic force microscopy (AFM) analysis by coating the BCP solution on neutral underlayer modified substrates followed by short thermal annealing. It was observed that while the PS-b-PTMC domains oriented parallel to the surface, the PS-b-PMTC-Me BCP domains oriented perpendicular to the surface at similar thermal annealing temperatures without the use of topcoat or additives.

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crystallized three times from toluene followed by drying under vacuum for two days to remove any residual toluene. The monomer was stored in a desiccator when it was not used for polymerization. Hydroxyl-end functional polystyrene (PS-OH, Mn = 6600, PDI = 1.05) and AZEMBLY™ NLD-303 (PMMA brush solution) was obtained as a gift from EMD Performance Materials Corp. Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Sigma-Aldrich and was distilled over calcium hydride under vacuum prior to using. Anhydrous dichloromethane (DCM) was received from Sigma-Aldrich and was used as received.

Gel permeation chromatography was performed using THF as an eluent and calibrated with polystyrene standards. Morphology of the BCP thin films was characterized by atomic force microscopy (AFM) on Digital Instruments 3100 under ambient conditions. Pitch of block copolymer features were derived from FFT image processing of AFM images.

2.2 Synthesis of 5-Methyl-5-methoxycarbonyl-1,3-dioxan-2-one (MTC-Me) monomer.

2,2-Bis(hydroxymethyl)propionic acid (20.0 g, 0.149 mol) and 300 mL of methanol were added 500 ml round bottom flask equipped with a magnetic stir bar and an overhead condenser. To this mixture, a few drops of concentrated sulfuric acid were added and the reaction was stirred under reflux for 72 hours. At this point, the reaction was cooled to room temperature and methanol was removed under vacuum. The crude product was distilled under high vacuum to obtain the pure methyl 2,2-bis-(hydroxymethyl)propionate. Next, to a two liter round bottom flask equipped with a magnetic stir bar, purified methyl 2,2-bis-(hydroxymethyl)propionate (20.0 g, 0.135 mol) and anhydrous THF (1.35 L, 1 molar w.r.t. to the diol) were taken. The reaction was stirred under nitrogen blanket and was cooled to 0 °C over 20 minutes. Ethyl chloroformate (32.2 g, 0.297 mol) was added to the cold reaction mixture while continued stirring. Finally, triethylamine (34.15 g, 0.337 mmol) was added dropwise to the reaction mixture. The reaction was stirred for 18 hours while slowly warming it up to room temperature. After 18 hours, the reaction was stopped and filtered to remove the salt. THF was evaporated under vacuum and the crude product was dissolved in approximately 200 mL of ethyl ether. This mixture was cooled to -20 °C to crystallized the 5-methyl-5-methoxycarbonyl-1,3-dioxan-2-one (MTC-Me) monomer. Ethyl ether was decanted and the MeCAR monomer was further crystallized three times to remove any ring opened diol or oligomeric impurities. To the purified monomer, approximately 5 ml of toluene was added and mixture was placed under high vacuum to remove any residual moisture. Finally the monomer was stored in a desiccator until it was used for polymerization. Yield 12.0 g, ~ 51%. \(^1\)H NMR (CDCl\(_3\), ppm) δ: 1.34 –1.38 (3H, C-CH\(_3\)), 3.80–3.82 (3H, O-CH\(_3\)), 4.18–4.22, 4.66– 4.72 (4H, O-CH\(_2\)-O-).

2.3. Representative synthesis of polystyrene-<i>b</i>-polytrimethylene carbonate (PS-<i>b</i>-PTMC) block copolymer

Hydroxy-terminated polystyrene macrorinitiator (PS-OH, 0.15 g, 0.028 mmol, Mn = 6600, PDI = 1.05), TMC (0.192 g, 1.88 mmol) and DCM (1.90 mL) were added to an oven-dried 4 mL glass vial equipped with a magnetic stir bar. The reaction mixture was stirred until the PS-OH macroinitiator and TMC were completely dissolved in DCM, upon which ring opening polymerization catalyst DBU (17.5 mg, 0.113 mmol) was added. The reaction mixture was stirred at room temperature for 17 hours in a N\(_2\) glove box. The reaction was stopped by adding DCM (1 mL), TEA (0.1 mL, 0.388 mmol) and acetyl chloride (0.02 mL, 0.28 mmol). The reaction was further stirred for two hours at room temperature. The block copolymer was isolated by precipitating the reaction mixture in methanol. The product was collected in a frit funnel by removing methanol under vacuum. The resulting solids were redissolved in THF to form a 20 wt% solution and reprecipitated in methanol. The solid was collected in a frit funnel and dried under vacuum at 40 °C for two hours to obtain the PS-b-PTMC block copolymer. The crude PS-b-PTMC obtained above was further purified to remove any homopolymer of TMC. The resulting BCP had Mn (GPC) = 14,400, PDI = 1.05. The PS block had Mn = 6600 and a degree of polymerization (DP) = 63. The PTMC block had Mn = 3200 (by 1H NMR) and DP = 31. The volume fraction of PTMC block, \(V_{f_{PTMC}}\) of the purified PS-<i>b</i>-PTMC was ~0.27.

2.4. Synthesis of TMC-functional random graft copolymer underlayer for PS-<i>b</i>-PTMC cylinder BCP

Styrene (Sty, 14.4 g, 138.0 mmol), hydroxy ethyl methacrylate (HEMA, 1.0 g, 7.68 mmol), glycidyl methacrylate (GMA, 1.09 g, 7.66 mmol), THF (50
g), and azobisisobutyronitrile (AIBN, 0.757 g, 4.61 mmol, 3 mol% based on total moles of vinyl monomers) were combined in a 250 mL round bottom flask (RBF) equipped with a magnetic stir-bar and an overhead condenser. The reaction mixture was stirred at 70°C for 18 hours and was stopped by cooling the reaction to room temperature. The resulting polymer was isolated by two precipitations in MeOH, and was dried under vacuum at 50°C for 24 hours. Mn = 6200, Mw = 8700, PDI = 1.40. The product Sty:HEMA:GMA x:y:z mole ratio was calculated by 13C inverse gated NMR as x:y:z = 88:6:6 (mole ratio). Based on the Mn and the product monomer mole ratio, the degree of polymerization (DP) ratio of the repeat units was calculated to be x': y': z' = 50.5: 3.5: 3.5 (Sty:HEMA:GMA, respectively).

Next, trimethylene carbonate (TMC, 0.060 g, 0.588 mmol) and dichloromethane (DCM, 0.2 g) were added to an oven dried 4 ml glass vial equipped with a magnetic stir bar. The reaction mixture was stirred until the macroinitiator and TMC were completely dissolved in DCM, upon which 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, ~10 mg) was added. The reaction mixture was stirred until the macroinitiator and TMC were completely dissolved in DCM, upon which 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, ~10 mg) was added. The reaction mixture was stirred at room temperature (rt) for 1 hour in a glove box. The reaction was stopped by bringing the reaction vial out of the glove box and by adding DCM (0.5ml), triethylamine (TEA, 0.27 g, 2.72 mmol) and acetyl chloride (~60 mg, 0.764 mmol). The reaction was further stirred for two hours at room temperature. The resulting polymer was isolated by precipitating the reaction mixture in methanol. The product was collected in a frit funnel and dried under vacuum at 40°C for two hours to obtain random graft copolymer G1-1, where the Sty:TMC mole ratio x':y'a' =73:27 was determined by 1H NMR.

2.5. Fabrication of underlayer and BCP coated substrates

The following general procedure was used to prepare a thin film underlayer on a silicon wafer. A solution was prepared by dissolving the random graft copolymer (95 parts by weight) and p nitrobenzylsulphonic acid triflate salt (p-NBT, 5 parts by weight) in propylene glycol monomethyl ether acetate (PGMEA, 10,000 parts by weight) to form a 1.0 wt% solution based on total dry solids. p-NBT is a thermal acid generator and was added to promote the grafting and partial crosslinking of a thin film of the random graft copolymer on the silicon wafer substrate when baked (annealed). The solutions were passed through a 0.2 mm polytetrafluoroethylene (PTFE) filter prior to spin coating the solution on a silicon wafer at 2000 rpm spin rate. After forming the thin film, the coated wafer was baked at 190°C for 3 minutes and cooled to room temperature. The initial baked thin film (underlayer) had a thickness of 20 nm, measured with a Nanospec Reflectometer. The underlayer was then given a solvent rinse by casting PGMEA on top of the coated wafer, letting the solvent puddle for 30 seconds, and spin drying the treated wafer at 2000 rpm for 30 seconds. The rinse was intended to remove any excess random graft copolymer that was not crosslinked or grafted to the wafer surface. The final film thickness of the underlayer was 10 nm after the solvent rinse.

3. Results and Discussion

3.1. Block Copolymer Synthesis

To enable sub-10 nm half-pitch resolution for future patterning applications, polycarbonate-based BCP platform was developed by ring opening polymerization (ROP) of cyclic carbonyl monomers from hydroxyl-functional polystyrene macroinitiator using DBU as the base catalyst [13, 14]. Two BCPs were synthesized and used in this work – PS-b-PTMC (6.6k-b-3.2k, PDI = 1.05, VfPTMC ~ 0.27) and PS-b-PMTC-Me (12.5k-b-5.6k, PDI = 1.03, VfPMTC-Me ~ 0.27) (Figure 1).

3.2. Thin-film self-assembly of BCPs

Thin film self-assembly of the cylinder-forming BCPs were studied by spin coating a 1.2 wt.% BCP solution in PGMEA on neutral...
underlayer modified substrates followed by thermal annealing at 170 °C for 5 minutes. The neutral underlayer for PS-b-PTMC BCP had about 73% styrene and PS-b-PMTC BCP had 40% styrene and 60% methyl methacrylate.

Figure 2 shows the AFM images of the two BCPs on neutral underlayer modified substrate.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{afm_images.png}
\caption{AFM height images of PS-b-PTMC and PS-b-PMTC-Me on neutral ULs, a. PS-b-PTMC, showing parallel cylinders and b. PS-b-PMTC-Me, showing perpendicular cylinders when annealed at 170 °C for 5 minutes.}
\end{figure}

4. Conclusion

In conclusion, we have synthesized two cylinder-forming high-χ BCPs based on PC platform. These BCPs have potential for use in advanced patterning applications for sub-20 nm feature sizes.

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References