

Supporting Information

Chemically Directed Self-Assembly of Perpendicularly Aligned Cylinders by Liquid Crystalline Block Copolymer.

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1. Synthesis of PMA(Az)₂₄-OH.¹

Hydroxy terminated PMA(Az), PMA(Az)₂₄-OH, was newly synthesized by atom transfer radical polymerization (ATRP). Firstly, ethylene glycol (1.1 g, 18 mmol) was treated with sodium hydride (60 mg, 18 mmol) under tetrahydrofuran (THF) (35 ml) to convert mono-sodium derivatives directly. Mono-sodium ethylene glycol (Na-O-CH₂-CH₂-OH) was then treated with t-butyldimethylchlorosilane (TBDMSiCl) (2.7 g, 18 mmol) to protect sodium modified end as described in somewhere (crude product 3.1 g).¹ The reaction mixture (0.64 g) was purified by the silica gel column with the eluent of hexane and ethylacetate with the ratio of 10:1. The obtained powder was esterified by drop wise addition of 2-Bromo-2-methylpropionyl bromide (2.9 ml, 21 mmol) in THF solution (6 ml) in ice bath. For the complete esterification, the reaction mixture was stirred for overnight at room temperature. After the reaction, the solution was filtrated, dried and the chloroform solution (0.20 l) was then washed subsequently with 1M HCl (0.12 l), saturated NaHCO₃ (0.20 ml) and distilled water and the chloroform solution was dried over MgSO₄, solvent was evaporated and dried in vacuum to obtained 3.9 g of initiator (2-bromo, 2-methyl propanic acid, 2-[[[(1, 1-dimethylethyl) dimethylsilyl]oxy] ethyl ester). The TBDMS substituent of the initiator was then exchanged with hydroxyl group of acetic acid (0.21 ml, 3.7 mmol) at room temperature. Finally the

initiator (2.9×10^{-5} mol) subjected to ATRP was mixed with (11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate) (2.0×10^{-3} mol) as monomer, copper chloride(I) (8.6×10^{-5} mol) and HMTETA (8.6×10^{-5} mol) in anisole under argon atmosphere in the glove box and stirred at 80 °C for 12 h. The solution was passed through a neutral Al_2O_3 column with chloroform as eluent to remove the catalyst and the unreacted monomer was separated by the repeated washing with hot hexane and finally the polymer solution was precipitated in hexane from chloroform. Yellow polymer was collected by filtration and dried under vacuum. Yield was 1.2 g (29 % based on the macroinitiator). The conversion of the monomer was calculated to be 82 % ($M_n(\text{GPC}) = 12\,000$, $M_w/M_n = 1.2$). ^1H NMR analysis of the synthesized PMA(Az)-OH gave its polymerization degree of 24. Peak assignments were carried out by ^1H NMR shown in Figure. S1. Inset is chemical structure of PMA(Az)₂₄-OH polymer as a polymer brush.

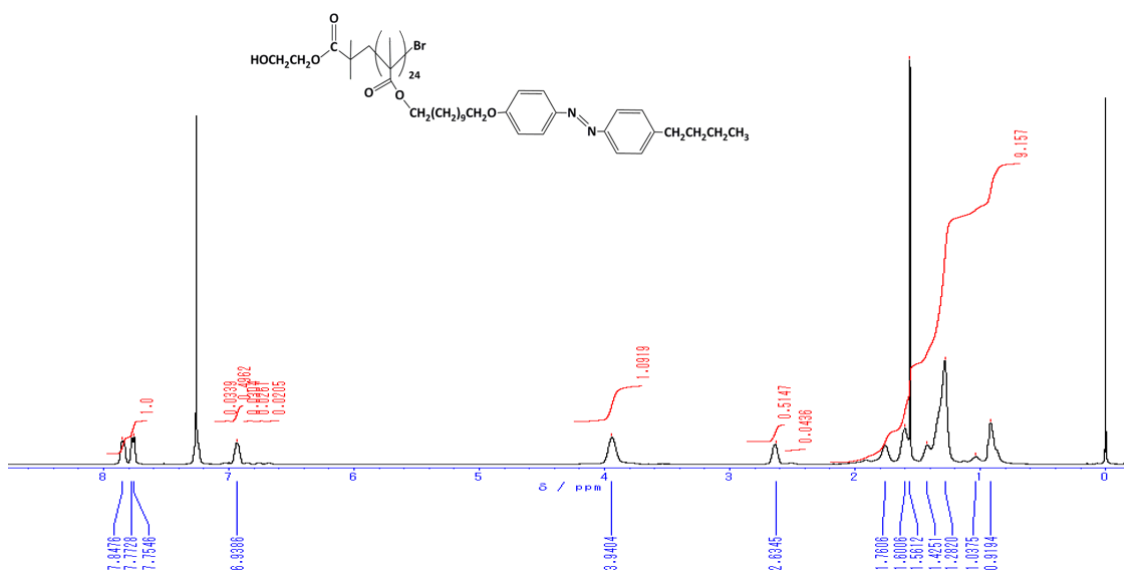


Fig. S1 ^1H NMR of synthesized PMA(Az) brush and inset is the chemical structure of synthesized PMA(Az) $_{24}$ -OH.

2. Preparation of liquid crystalline block copolymer PEO₁₁₄-*b*-PMA(Az)₂₄.^{2,3}

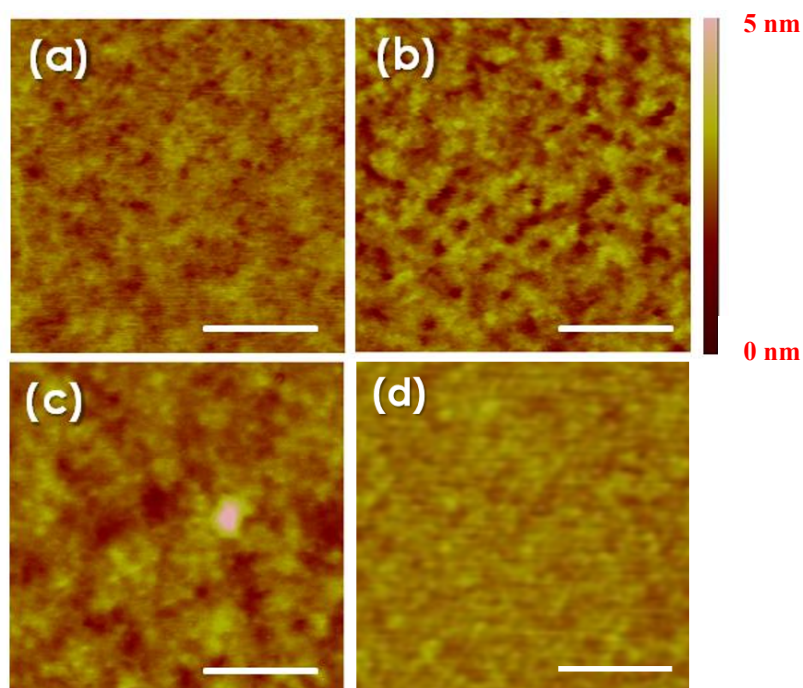
PEO₁₁₄-*b*-PMA(Az)₂₄ was synthesized via ATRP of 11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate as the monomer from α -methoxy-poly(ethylene oxide)- ω -(2-bromo-2-methylpropionate) as the macroinitiator by using copper chloride(I) (Kanto Chem. Co., Japan) and 1,1,4,7,10,10-hexamethylenetetramine (HMTETA, Aldrich) as catalyst in anisole according to our previous report.² A mixture of copper chloride(I) (0.12 g, 1.2 mmol) and HMTETA (0.28 mg, 1.2 mmol) in anisole solution (50 mL) was added to anisole solution containing α -methoxy-poly(ethyleneoxide)- ω -(2-bromo-2-methylpropionate) (2.0 g, 0.4 mmol) and 11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate (4.9 g, 10 mmol), and then the mixture was stirred at 80 °C for 12 h. The solution was passed through a neutral Al₂O₃ column with chloroform as eluent to remove the catalyst. After the solvent was removed under reduced pressure, the residue was taken for ¹H NMR measurement. The conversion of the monomer was 71%. The residue was reprecipitated twice with hot hexane to remove the remaining monomer, and then the residual solid was dissolved in a minimum amount of chloroform, followed by re-precipitation in methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 3.5 g (50% based on the macroinitiator). The degree of polymerization and molecular weight were evaluated by

^1H NMR and gel permeation chromatography (GPC). M_n (GPC) = 17 400, $M_w/M_n = 1.1$.

^1H NMR analysis of synthesized block copolymers gave $\text{PEO}_{114}\text{-}b\text{-PMA(Az)}_{24}$ of polymerization degree, and 16 808 of the molecular weight M_n (NMR).³

3. Observation of PMA(Az) brush layer on Si wafer by AFM.

Nanostructure of PMA(Az) polymer brush layer was captured by AFM using Dimension Icon, Veeco. Typical tapping mode AFM height images of PMA(Az)-OH layer on the Si wafer are presented in Figures S1 (a) ~ (c). Figure S1 (a) is the image of the PMA(Az)-OH layer after thermal annealing at 170 °C for 48 hour, Figure S1 (b) is that after removal of un-reacted PMA(Az)-OH chains by rinsing with toluene, and Figure S1 (c) is that after thermal annealing at 140 °C for 2 hour. Figure S1 (d) shows



bare Si wafer surface as a reference.

Fig. S2 Tapping mode AFM height images of PMA(Az) brush layer (a) before and (b) after rinsing substrate with toluene, (c) after annealing at 140 °C for 2 hours. AFM image of bare Si wafer is presented in (d) as for a reference. Scale bars insetted in the images indicate 100 nm. Full Z-height scale (vertical scale) of the images is 5 nm (Z-scale is shown by a color bar shown beside image (b)).

4. Voronoi analysis for the PEO cylindrical microdomains on the chemically patterned substrates and without patterned substrates.

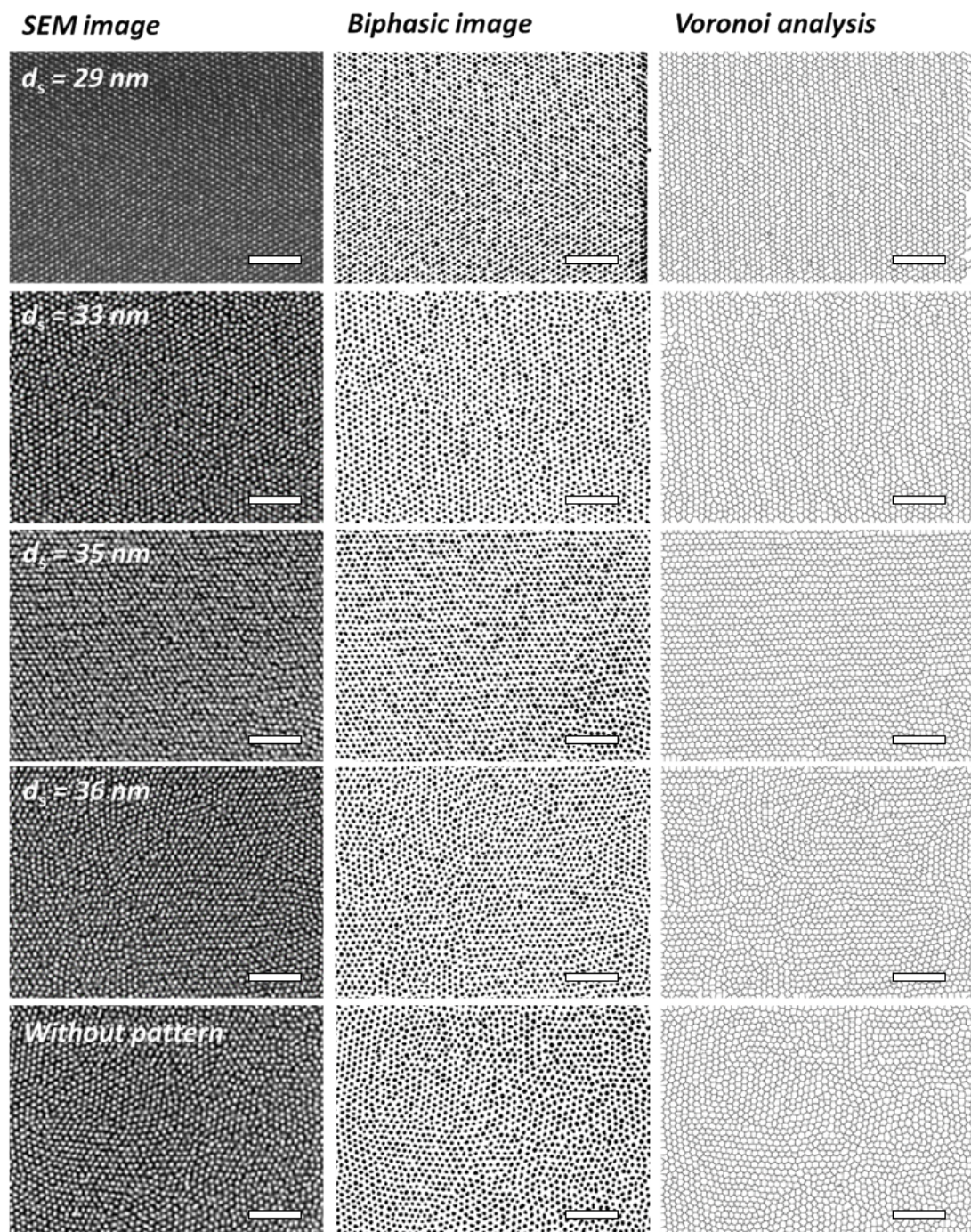


Fig. S3 SEM images (left column), binary images (middle column), and their voronoi images (right column) for the PEO cylindrical microdomains on the chemically patterned templates varying from $d_s = 29\text{ nm}$ to 36 nm and without chemical pattern template. All scale bars reveal 200 nm .

Table S1. Summary of the PEO cylindrical microdomains defects analyzed by voronoi method on the different chemically patterned templates and without chemically patterned template.

<i>Templates / d_s</i>	<i>n (= d_s/d_0)</i>	<i>Defects /pixel</i>
<i>29 nm</i>	<i>1.7</i>	<i>5</i>
<i>33 nm</i>	<i>1.9</i>	<i>31</i>
<i>35 nm</i>	<i>2</i>	<i>3</i>
<i>36 nm</i>	<i>2.1</i>	<i>49</i>
<i>without template</i>		<i>51</i>

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