Synthesis of Semicrystalline/Fluorinated Side-Chain Crystalline Block Copolymers and Their Bulk and Thin Film Nanoordering

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ABSTRACT: Semicrystalline/fluorinated side-chain crystalline block copolymers, dinonylphenyl end-capped poly(ethylene glycol)-block-poly[(fluorinated methyl methacrylate) (DNPEPEO-b-PFMAs), were synthesized by ATRP of 3,3,4,4,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate using a surfactant poly(ethylene glycol) dinonylphenyl ether as precursor. Bulk and thin film morphologies in the block copolymers of DNPEPEO-b-PFMAs were investigated by DSC, WAXS, SAXS, TEM, AFM, and GISAXS. The block copolymers show microphase separated and ordered structures. In the bulk, a cylindrical morphology with PEO cylinders confined in PFMA matrix was confirmed by SAXS and TEM. WAXS studied on the copolymers bulk revealed semicrystalline PEO cylinders and PFMA matrix with the fluorinated side chain organized in bilayers. In thin films of DNPEPEO-b-PFMAs on PDMS modified silicon substrates, well ordered hexagonally packed arrays with PEO cylindrical microdomains normal to the substrate were observed. This fluorinated block polymer with strong unfavorable interaction between two blocks and subsequently hierarchical self-assembly could be a promising material for nanolithography applications.

INTRODUCTION

Block copolymers (BCPs) have attracted significant attentions as templates for the fabrication of nanostructured materials, such as in nanolithography,1 optical material,2 and templates for storage devices.3 The self-assembly of BCPs leads to various nanostructures, like spheres, gyroids, cylinders and lamellae depending on the volume fractions of each block and the chain architectures of the BCPs.4 BCP lithography, a “bottom-up” strategy, allows exquisite control over the size and arrangement of the features.

Several BCPs, such as polystyrene-block-poly(methyl methacrylate)(PS-b-PMMAs),5 poly(ethylene oxide)-block-polystyrene(PEO-b-PS),6 poly(ethylene oxide)-block-poly-(methyl methacrylate)-block-polystyrene(PEO-b-PMMAs-b-PS),7 polyisoprene-block-poly lactide (PI-b-PLA),8 polystyrene-block-poly(4-vinylpyridine)(PS-b-P4VP)9 were reported with successfully controlled orientation of microstructures in their thin films. A small but significant number of defects remain in these polymers thin films, which is undesirable for nanolithographic applications. The defect population is related to the Flory–Huggins interaction parameter, χ, which describes the driving force for microphase separation in BCPs. BCPs with larger χ have a stronger driving force to reduce the defect population, and are therefore more desirable to achieve long-range ordering.10 Meanwhile, BCPs with larger χ will enable smaller feature sizes, hence increase domain density since high-χ BCPs have high degree of chemical repulsion between the blocks and enable the usage of small molecular weight.11,12

Fluorinated BCPs are reported to have large χ. The χ of polystyrene-block-polybutadiene increases significantly from about 0.05 at 0 mol % C6F13H modifications to about 0.75 at 80 mol % C6F13H modification.13 The χ of segmented block copolymer consisting of polysulfone and semifluorinated aromatic polyester segments is 13.68.14 The large χ facilitates the formation of long-range ordered structures.

Side-chain crystalline diblock copolymers (SC-BCPs) are a special class of soft matter with various potential applications in the field of nanotechnology.15 For side-chain crystalline diblock copolymers, their microstructure is formed under the influence of two driving forces: side-chain crystalline ordering and the microphase separation.16 The crystalline ordering of side-chain and the microphase separation of the two blocks lead SC-BCPs to organize on different length scales, which can be exploited to tailor material properties.17 Compared to nonfluorinated SC-BCPs, fluorinated SC-BCPs (FSC-BCPs) exhibit a more pronounced ability to organize due to their intrinsic low surface energy.18 In thin film diblock copolymer poly(methyl methacrylate) (PMMA)-block-poly(1H,1H,2H,2H-perfluorodecylacrylate) (PF8H2A) forms cylindrical PMMA domains.
The copper catalyst was removed with a neutral alumina column. The dinonylphenyl ether (Igepal DM-970, Adlrich) (DNPEPEO, μPMDETA (16 DNPEPEOBr (0.32 g, 0.083 mmol), CuBr (0.012 g, 0.083 mmol), PMDETA (16 μL, 0.083 mmol), FMA (0.64 g, 1.2 mmol), and dry THF (5 mL) were added to a Schlenk tube and subjected to three freeze–pump–thaw cycles. The reaction was heated for 20 h at 90 °C. The copper catalyst was removed with a neutral alumina column. The product was obtained in yield of about 49% by precipitation from hexane. (Mn,GPC = 18706 g/mol, Mw/Mn = 1.12).

**EXPERIMENTAL SECTION**

Materials. All commercially obtained solvents and reagents were used without further purification except as noted below. Poly(ethylene glycol) dinonylphenyl ether (Igepal DM-970, Aldrich) (DNPEPEO, Mw, Ms = 3896 g/mol, Mw,NMR = 5630 g/mol, Mw,GPC = 7900 g/mol, Mn/Mw = 1.05) was washed with hexane, filtered and dried in a vacuum oven. Then, it was dissolved in anhydrous toluene and purified by azotropic distillation before use. 3,4,4,5,6,6,7,7,8,8,9,9,10,10-Octadecafluorocyclooctane (RM) and trifluorotoluene (80 v%) were used as received. Poly(dimethylsiloxane), hydroxyl terminated (PDMS-OH) and trifluorotoluene (80 v%). Poly(ethylene glycol) dibutyl ether (Igepal DC-630, Aldrich) (DNPEPEO-PFMA) were synthesized by one step ATRP based on poly(ethylene glycol) dinonylphenyl ether. The bulk and thin film morphologies of DNPEPEO-PFMA were studied using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXS), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), atomic force microscopy (AFM), and grazing-incidence small-angle X-ray scattering (GISAXS) techniques. The introducing of fluorinated blocks drives the microphase separation and forms ordered structures. By thermal annealing on poly-(dimethylsiloxane)(PDMS) modified silicon substrates, well-ordered nanostructures were obtained in the thin films with semicrystalline PEO cylinders and layered PFMA matrix. To the best of our knowledge, this is the first report about the controlled long-range ordering of FSC-BCPs thin films. The templates from the self-assembly of those FSC-BCPs could be useful scaffolds for nanolithography applications.

### Table 1. Molecular Weight, Compositions, and Thermal Analysis of the DNPEPEO-b-PFMAs and their Precursors

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Mw,NMR (g/mol)</th>
<th>Mw,NMR (g/mol)</th>
<th>Mw,GPC (g/mol)</th>
<th>fDMA (%)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Tn (°C)</th>
<th>Tc (°C)</th>
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</thead>
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<tr>
<td>DNPEPEO75</td>
<td>3615</td>
<td>7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>DNPEPEO75-PFMA55</td>
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<td>8100</td>
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<tr>
<td>DNPEPEO75-PFMA55</td>
<td>18 706</td>
<td>10 194</td>
<td>10 900</td>
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<td>39.1</td>
<td>-24.3</td>
<td></td>
</tr>
<tr>
<td>DNPEPEO75-PFMA55</td>
<td>22 962</td>
<td>11 258</td>
<td>11 200</td>
<td>78.6</td>
<td>-33.3</td>
<td>37.8</td>
<td>-41.7</td>
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</tr>
<tr>
<td>DNPEPEO75-PFMA55</td>
<td>24 026</td>
<td>10 560</td>
<td>11 100</td>
<td>79.5</td>
<td>-36.3</td>
<td>40.1</td>
<td>n.d.</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated from 1H NMR measurement in mixture of CDCl3 (20 v%) and trifluorotoluene (80 v%). 4Determined by 1H NMR in mixture of CDCl3 (20 v%) and trifluorotoluene (80 v%). 4Determined by 1H NMR in mixture of CDCl3 (20 v%) and trifluorotoluene (80 v%). 4Determined by GPC. 5Volume fraction of PFMA block (density of the PFMA block is 1.605 g/mL and PEO block is 1.1 g/mL). Not detected by DSC.

**Preparation of the Diblock Copolymer DNPEPEO-b-PFMA.** DNPEPEOBr (0.32 g, 0.083 mmol), CuBr (0.012 g, 0.083 mmol), PMDETA (16 μL, 0.083 mmol), FMA (0.64 g, 1.2 mmol), and dry THF (5 mL) were added to a Schlenk tube and subjected to three freeze–pump–thaw cycles. The reaction was heated for 20 h at 90 °C. The copper catalyst was removed with a neutral alumina column. The product was obtained in yield of about 49% by precipitation from hexane. (Mw,GPC = 18706 g/mol, Mw,NMR = 18706 g/mol, Mw/Mn = 1.12).

**Characterization.** 1H NMR and 19F NMR spectra were taken on a Bruker DPX-300 NMR spectrometer in chloroform-d and dimethyl sulfoxide-d, Molecular weight and polydispersity (D) of DNPEPEO-PFMA were measured by GPC in THF at 40 °C with a flow rate of 1 mL/min on systems equipped with two-column sets (from Polymer Laboratories) and refractive index detectors (K-2301). Polyisoprene standards were used for molecular weight calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF–MS) was performed on a Bruker Omniflex spectrometer equipped with a 337 nm nitrogen laser. 2, 5-dihydroxybenzoic acid (DHB) was used as the matrix and sodium iodide (NaI) as the salt. Thermal behavior was analyzed by differential scanning calorimetry (DSC) using a TA Instruments Q200 at a scanning rate of ±10 °C/min under a flow of argon. Glass transition temperatures (Tg) were determined as the midpoint of the transition process, and the exothermic and the endothermic maximum temperatures were taken as the crystallization temperatures (Tc) and the melting temperatures (Tm), respectively.

**Thin Film Preparation.** The DNPEPEO-b-PFMAs BCPs were spin-coated from trifluorotoluene solutions on to silicon substrates and PDMS-modified silicon substrates, respectively, and subsequent annealing at 130 °C under vacuum for 18 h (Tm and Tn of PEO and PFMA blocks are shown in Table 1). PDMS brushes were anchored to the silicon substrates by spin coating a thin film of PDMS–OH and subsequent react at 130 °C under vacuum for 18 h. The unreacted materials were washed away by heptane. The thickness of the PDMS buffer layer is roughly estimated to be several nanometers.

**Atomic Force Microscopy (AFM).** AFM images were obtained in both the height and phase-contrast mode using a Digital Instruments Dimension 3000 scanning force microscope in the tapping mode.

**Transmission Electron Microscopy (TEM).** To observe the microstructures by TEM, the samples were first thermally annealed for 16h at 120 °C in vacuum (Tm and Tn of PEO and PFMA blocks are shown in Table 1). Ultrathin sections with thicknesses of 50–70 nm were obtained by cryo-microtomy (Leica Ultracut) using a diamond knife at -70 °C to ensure that no alteration of the morphology took place during cutting. To enhance contrast, the TEM samples were exposed to the vapor of 0.5 wt % RuO4 aqueous solution for 20 min before measurement. The ether bonds in the ethylene glycol block were selectively stained by RuO4 and appeared dark in the TEM images. Bright field TEM measurements were performed with a JEOL 200CX electron microscope operated at an accelerating voltage of 200 kV.

**Wide and Small-Angle X-ray Scattering (WAXS and SAXS).** SAXS and WAXS were performed using an in-house setup from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000). It uses a 3 W microsource (Bede) with a 30 μm2 spot size matched to a Maxilux optical system (Osmic) leading to a low-divergence beam of monochromatic CuKα radiation (wavelength λ=0.1542 nm). After passing beam-defining and guard pinholes, the divergent beam of monochromatic CuKα radiation (wavelength λ=0.1542 nm). After passing beam-defining and guard pinholes, the
SAXS intensity is collected by a two-dimensional gas-filled wire detector at a distance of about 1500 mm from the sample. A beamstop of 4 mm in diameter has a photodiode in its center which allows the monitor of the direct beam intensity. The sample was pressed in an aluminum washer between two Kapton films. Samples were heated to desired temperatures and kept at equilibrium for about half an hour before each measurement. WAXS was performed using an image plate positioned in the sample chamber at a distance of 139 mm from the sample. The image plate (maximum resolution 50 μm) has a hole in its center allowing simultaneous SAXS and WAXS measurements. The actual scattering angles are calibrated using the silver behenate standards.

Grazing-Incidence Small Angle X-ray Scattering (GISAXS). GISAXS measurements were performed on beamline 7.3.3 at the Advanced Light Source at the Berkeley National Laboratory. An X-ray beam impinged onto the sample at a grazing angle slightly above or below the critical angle of the polymer film (δc = 0.16°) but below the critical angle of the silicon substrates (δc = 0.28°). The wavelength of X-rays used was 1.240 Å, and the scattered intensity was detected by using a two-dimensional charge-coupled device (CCD) camera with image sizes of 2304 × 2304 pixels.

RESULTS AND DISCUSSION

Poly(ethylene glycol) Dinonylphenyl Ether (DNPEPEO) and the Macroinitiator. The general synthetic procedure of the block copolymer dinonylphenyl end-capped poly(ethylene glycol)-block-polyfluorinated methyl methacrylate) (DNPEPEO-b-PFMA) is shown in Scheme 1. The starting material, Igepal DM-970, is a commercially available nonionic macromolecular surfactant with a hydrophilic−lipophilic balance (HLB) value of 19.0. The main component of the surfactant is poly(ethylene glycol) dinonylphenyl ether (DNPEPEO) with a minor component of poly(ethylene glycol) nonylphenyl ether (NPEPEO). Figure 1a shows 1H NMR spectrum of Igepal DM-970. The absence of a benzyl proton resonance indicates that dinonyl group is nonlinear and the complicated resonances at δ 6.8−7.4 ppm demonstrate that there are structural isomers in Igepal DM-970. On the basis of the integration of the −CH2−O−C6H4 protons at δ 4.1 ppm and the methylene protons in PEO block at δ 3.7 ppm, the molecular weight (Mn,NMR) of Igepal DM-970 was calculated to be 3630 g/mol and the calculated number of PEO repeat units is 75. To further confirm the molecular weight and the end group of Igepal DM-970, MALDI−TOF−MS analysis was applied. As shown in Figure 2, the Mn,MS value (molecular weight for the peak maximum) for Igepal DM-970 is 3897 g/mol, which agrees well with the Mn,NMR. By enlarging the MS spectrum, two peak series were observed and each peak series has a peak difference of 44 amu (CH2CH2O). In addition, a difference between two adjacent peaks from different series is 6 amu. This difference is due to two different end groups in Igepal DM-970, the dinonylphenyl group and the nonylphenyl group, respectively. The formula of DNPEPEO molecular
weight \( M_{n,NPEPEO} \) and NPEPO molecular weight \( M_{n,NPEPEO} \) can be described as eq 1 and eq 2, respectively.

\[
M_{n,NPEPEO} = 220 + (44) \times n
\]  

(1)

\[
M_{n,DNPEPEO} = 346 + (44) \times m
\]  

(2)

Here \( n \) and \( m \) are the numbers of PEO repeating units for NPEPEO and DNPEPEO, respectively. When \( n \) is equal to the sum of \( m \) and 3, the difference between \( M_{n,DNPEPEO} \) and \( M_{n,NPEPEO} \) is just 6. In addition, the GPC result shows that Igepal DM-970 has number-average molecular weight of 7900 g/mol (Table 1) with a very narrow polydispersity of 1.05. Since DNPEPEO is the major component in Igepal DM-970, in the following part we named the starting materials as DNPEPEO.

Synthesis of DNPEPEOBr macroinitiator was a simple esterification reaction between the hydroxyl end groups in DNPEPEO and 2-bromoisobutyryl bromide. To promote complete conversion, excess 2-bromoisobutyryl bromide was used. The \(^1\)H NMR spectrum of DNPEPEOBr is shown in Figure 1b. The integration of the \(-C(CH_3)_2Br\) resonance and the methylene protons of PEO indicates that the conversion is around 96%. As shown in Figure S1, Supporting Information, the GPC curve of DNPEPEOBr was parallel shifted to a slightly higher molecular weight than that of the DNPEPEO starting material.

**Synthesis of the DNPEPEO-b-PFMA Block Copolymers.** Fluorinated polymers are the most studied triphilic polymers due to the mutually orthogonal solubility of hydrophilic, hydrophobic and fluorophilic blocks.\(^{19}\) Here, the triphilic-like fluorinated block polymer DNPEPEO-b-PFMA (hydrophilic/fluorophilic blocks with oleophilic tail) were synthesized via ATRP of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl methacrylate (FMA) in THF using
DNPEPEOBr as the macroinitiator. Parts a and b of Figure 3 show the $^1$H NMR spectra of FMA monomer and block copolymer DNPEPEO-$b$-PFMA, respectively. All of the characteristic peaks of the FMA and DNPEPEO-$b$-PFMA were labeled. According to the integration of the methylene protons in the PEO block at $\delta$ 3.7 ppm and the $-\text{CH}_2\text{CF}_2-$ protons of the PFMA block at $\delta$ 2.5 ppm (Figure 3b), the $M_{n,NMR}$ of DNPEPEO-$b$-PFMA was calculated and listed in Table 1. $^{19}$F NMR spectra of FMA and DNPEPEO-$b$-PFMA are shown in Figure 3, parts c and d, respectively. For FMA monomer, six different fluorine resonances originate from the eight groups of fluorine on the aliphatic fluorocarbon chain, while for DNPEPEO-$b$-PFMA polymer, all these resonances broaden and resonances c, d, e, f, and g overlap with each other.

The molecular weight of DNPEPEO-$b$-PFMA was also determined by GPC. Two peaks, one of which is positive and the other is negative, were observed (Supporting Information, Figure S2). The molecular weight and polydispersity from the positive peak are listed in Table 1. The negative peak at the short elution time area is probably due to the micelles of triphilic-like DNPEPEO-$b$-PFMA forming in the GPC solvent THF and its lower refractive index than GPC solvent THF.

Figure 5. SAXS traces for DNPEPEO-$b$-PFMAs polymers after thermal annealing at 150 °C: (a) DNPEPEO$_{75}$-$b$-PFMA$_{28}$; (b) DNPEPEO$_{75}$-$b$-PFMA$_{36}$; (c) DNPEPEO$_{75}$-$b$-PFMA$_{38}$.

Figure 6. SAXS traces for DNPEPEO$_{75}$-$b$-PFMA$_{38}$ at different temperatures: (a) room temperature; (b) 65 °C; (c) 95 °C; (c) 120 °C. The sample was thermally annealed at 120 °C for 15 h before SAXS experiment.
otoluene (1v:4v) was used in H NMR experiments. As appeared darker due to selective staining by RuO4). The integration of the DNPEPEO-

Information). Table 1 summarized the molecular weight of PFMA, because CDCl3 is a selective solvent like THF (GPC Information, the DNPEPEO-

Copolymers. As shown in Table 1 and Figure S4, Supporting Information, the DNPEPEO-b-PFMA block crystallize at around 75–79 °C and melt at 82–85 °C, and the main chain of the PEO block crystallize at around −30 to −36 °C and melt at 37–40 °C. The PEO block shows about 70 °C supercooling phenomenon. This is probably due to the dispersion of the PEO block into a large number of spatially isolated microdomains (which was observed and will be discussed in the following sections). There were no heterogeneities present in these microdomains and therefore they were forced to nucleate at lower temperatures in a probably more homogeneous manner. Homogeneous nucleation exhibits a much higher degree of supercooling than heterogeneous nucleation.21

Wide-angle X-ray diffraction at different temperatures was used to investigate the crystalline structures of DNPEPEO75-b-

PFMA28, respectively, which is consistent with the SAXS data. TEM images of DNPEPEO75-b-PFMA28, DNPEPEO75-b-PFMA36, and DNPEPEO75-b-PFMA38 respectively, which increases with the increasing of the PFMA block content.

Thermal morphology of the DNPEPEO-b-PFMA thin films was investigated by SAXS experiments (Figure 6). The sample was thermally annealed at 120 °C for 18h. Figure 8 shows the AFM phase images for DNPEPEO75-b-PFMA38 thin films after thermal annealing at 130 °C for 18h on silicon substrate (left), and on PDMS modified silicon substrate (right).

Figure 7. TEM images of DNPEPEO-b-PFMA$. The blend appears darker due to selective staining by RuO4.

Figure 8. AFM phase images for DNPEPEO75-b-PFMA$38$ thin films after thermal annealing at 130 °C for 18h on silicon substrate (left), and on PDMS modified silicon substrate (right).

This results remind us that the $M_{n,NMR}$ of DNPEPEO-b-PFMA in CDCl3 is not genuine molecular weight of DNPEPEO-b-

PFMA, because CDCl3 is a selective solvent like THF (GPC solvent) for DNPEPEO-b-PFMA, where DNPEPEO-b-PFMA can also self-assemble to form micelles with PFMA as the core and DNPEPEO as the corona, which results in the deviation of the $M_{n,NMR}$. So, the mixed solvent of CDCl3 and trifluorotoluene (1v:4v) was used in H1 NMR experiments. As expected, the integration of the $\text{O}^{-}\text{CH}_2\text{CH}_2\text{CF}_2$ protons in the PFMA block in the mixture solvent is almost three times larger than that in pure CDCl3 (Figure S3, Supporting Information). Table 1 summarized the molecular weight of DNPEPEO-b-PFMA and volume fraction of PFMA block calculated from their molecular weight in the mixed solvent. And cylindrical morphologies are expected on the basis of their volume fractions.20

Bulk Morphology of the DNPEPEO-b-PFMA$. As shown in Table 1 and Figure S4, Supporting Information, the DNPEPEO-b-PFMA blocks are semicrystalline/fluorinated side-chain crystalline block copolymers. The perfluoroalkyl side chains of PFMA block crystallize at about 20–65 °C and melt at 85–120 °C, which agreed well with the X-ray diffraction patterns of PEO homopolymer.22 The intensities of the reflections of PFMA block at $q = 2.0$ and $12.5$ nm$^{-1}$ decreased with increasing temperature. The peaks at $q = 13.6$ and $16.5$ nm$^{-1}$, which have been reported to be the (120) reflection of PEO, an overlap of (032), (132), and (212) reflections of PEO, respectively, disappeared when the temperature increased from 20 to 65 °C and 100 °C, respectively.

The bulk morphologies for each sample were investigated by SAXS as shown in Figure 5. DNPEPEO-b-PFMA$\_26$ exhibited hexagonal morphologies, as evidenced by the higher order reflections at $q/q^* \text{ values of } 1, 3/2, 4/2, 7/2, g/2$, where $q^*$ is the scattering vector of the first-order reflection. High order peaks in SAXS patterns are not very clear, which suggests the level copolymer bulk ordering is not high. This may be improved by further increasing the unfavorable interaction with larger blocks. The domain spacings ($d$) by $d = 2\pi/q^*$ are $16.8, 17.6$, and $20.3$ nm for DNPEPEO75-b-PFMA26, DNPEPEO75-b-PFMA36, and DNPEPEO75-b-PFMA38, respectively, which increases with the increasing of the PFMA block content.

We also investigated morphologies of DNPEPEO75-b-

PFMA$\_26$ at different temperatures by SAXS experiments (Figure 6). The sample was thermally annealed at 120 °C for 16hours before measurement. The hexagonal morphology persists at all measured temperatures, even at 120 °C, where both blocks are amorphous.

TEM images of DNPEPEO-b-PFMA$\_s$ (Figure 7) show cylindrical morphology with PEO cylinders confined in a PFMA matrix. Clear grain boundaries were observed with PEO cylinders parallel to the z-axis and aligned horizontally. The center-to-center distance between adjacent two cylinders, the long period, is determined to be around $16, 17$, and $21$ nm for DNPEPEO75-b-PFMA26, DNPEPEO75-b-PFMA36, and DNPEPEO75-b-PFMA38, respectively, which is consistent with the SAXS data.

Thin Film Morphology of the DNPEPEO-b-PFMA$\_s$ Block Copolymers. To investigate the thin film behavior of the samples, solutions were first spin-coated onto silicon substrates with a native oxide layer or PDMS brushes, respectively. The film thickness was controlled to be around 1 $\text{L}_0$ (natural period of block copolymer). The films were thermally annealed at 130 °C for 18h. Figure 8 shows the AFM
phase images of the DNPEPEO\textsubscript{75-b-PFMA\textsubscript{38}} thin films on both substrates. For thin film prepared on silicon substrate with a native oxide layer, cylindrical domains oriented normal to the silicon substrate can be seen, although good lateral order was not achieved. At certain area, “worm-like” structures were also observed which suggested some cylinders were aligned parallel to the silicon substrate. This mixed structure may be resulted from the strong interaction between the PEO block and the native oxide surface, and the low surface energy of the fluorinated block which would like to segregate on the film−air interface. While on the PDMS modified silicon substrate, well ordered hexagonally packed arrays were observed everywhere with increased grain sizes. The improvement of lateral ordering on the PDMS modified substrates (Figure 8, right) might be attributed to the nonfavorable interactions of both blocks with the PDMS brushes. The low surface energy of PDMS surface reduces the interfacial interactions between the PEO block and the substrate surface, resulting in a low energy barrier for DNPEPEO\textsubscript{75-b-PFMA\textsubscript{38}} to self-organize on the surface. The \(d\) spacing was determined 20.5 nm which is consistent with the SAXS data.

The thermally annealed thin film on PDMS modified silicon substrates was further investigated by grazing-incidence small-angle X-ray scattering (GISAXS). Since AFM only gives the real-space surface image of a small area of the thin films, while GISAXS averages over a much larger area and can be used to probe the structure through the entire thickness of the film. \textsuperscript{6b,24}

Parts a and b of Figure 9 show two GISAXS patterns, where the incident angles were below and above the critical angle of the polymer film and the horizontal line cut of 2D images in parts a and b of Figure 9 were plotted in parts c and d of Figure 9, respectively. The sharp Bragg rods (vertical streaks) in both GISAXS patterns correspond to the reflections from a 2D lattice of cylinders of finite length oriented normal to the film surface. From the scattering vector of the primary reflection, the \(d\) spacing was calculated to be 21 nm, which is consistent with the bulk SAXS observations.

Meanwhile, GISAXS measurement of the DNPEPEO\textsubscript{75-b-PFMA\textsubscript{38}} thin film on silicon substrate with a native oxide layer

Figure 9. GISAXS patterns of DNPEPEO\textsubscript{75-b-PFMA\textsubscript{38}} thin film on PDMS modified silicon substrate: (a) incident angle of 0.14\(^\circ\); (b) incident angle of 0.20\(^\circ\); (c, d) intensity scans along \(q_x\) of GISAXS patterns shown in parts a and b, respectively.
was performed. As shown in Figure 10, there are no scattering peaks and no lateral ordering, which indicates the disordered or very poorly ordered structure of DNPEPEO75-b-PFMAs thin film on silicon substrate with a native oxide layer.

**CONCLUSIONS**

A novel semicrystalline/fluorinated side-chain crystalline block copolymer DNPEPEO-b-PFMA with a long oleophilic alkyl end group has been synthesized in one step ATRP from a commercially available nonionic surfactant and characterized in detail. Bulk and thin film orderings of DNPEPEO-b-PFMAs were investigated in detail. The results show that DNPEPEO-b-PFMAs clearly exhibit hexagonal morphologies in the bulk, which are very stable regardless of the copolymers being in the semicrystalline or amorphous state. Besides the cylindrical nanostructure with PEO cylinders embedded in a PFMA matrix, both minor and major blocks have subordering structures: the PEO cylinders are semicrystalline while the PFMA block macromolecules form bilayer structures with a spacing of 3.2 nm and the perfluoroalkyl side chains arrange within the layers with a spacing of \( d = 0.5 \) nm. In thin films, interfacial interactions between the block copolymer and the surface of the silicon substrate were tuned by anchoring a layer of PDMS. On silicon substrate with a native oxide layer, disordered cylindrical microdomains were observed, while on PDMS modified silicon substrate, well ordered PEO cylinders oriented perpendicular to the substrate were obtained. The fluorinated BCPs with strong unfavorable interaction between two blocks may open up opportunities to be used as scaffolds for nanolithographic applications. Further control over the size and defect of domains is a subject for our future studies.

**ASSOCIATED CONTENT**

Supporting Information

GPC traces of DNPEPEO, macroinitiator DNPEPEOBr, DNPEPEO-b-PFMAs and DNPEPEO, \( ^1H \) NMR spectra of DNPEPEO75-b-PFMAs in CDCl$_3$ and in the mixture solvent of CDCl$_3$ and trifluorotoluene, and DSC traces of DNPEPEO-b-PFMAs. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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