

Synthesis and solution-state assembly or bulk state  
thiol-ene crosslinking of pyrrolidinone- and  
alkene-functionalized amphiphilic block  
fluorocopolymers: From functional nanoparticles to  
anti-fouling coatings

*Jun Ma,<sup>A</sup> Jeremy W. Bartels,<sup>A</sup> Zhou Li,<sup>A</sup> Ke Zhang,<sup>A</sup> Chong Cheng,<sup>B</sup> and Karen L. Wooley<sup>A,C</sup>*

<sup>A</sup>Department of Chemistry, Washington University, Saint Louis, MO 63130

<sup>B</sup>Department of Chemical and Biological Engineering, the State University of New York at Buffalo, Buffalo, NY 14260

<sup>C</sup>Departments of Chemistry and Chemical Engineering, Texas A&M University, College Station, TX 77842

**Experimental section**

**Materials and Equipment.** All chemicals and reagents were purchased from Aldrich Chemical Co. and used as received. The chain transfer agent S-1-dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic

acid)trithiocarbonate (DDMAT) was prepared using the published procedure.<sup>1</sup> The bifunctional fluoro-containing monomer 4-(3'-buten-1'-oxy)-2,3,5,6-tetrafluorostyrene (**3**) was prepared in our previous work.<sup>2</sup> A F300S UV system (Fusion UV Systems, Inc) was used for the irradiation of samples.<sup>3</sup> The UV system consists of a P300MT power supply and an I300MB irradiator with an H bulb (13 mm, 300 W/inch) which emits UV light in a range from 200-600 nm with peaks at 265, 315, 405, 435, 545 and 575 nm.

**Characterization Methods.** <sup>1</sup>H NMR spectra were recorded at 300 MHz on solutions in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or acetone-*d*<sub>6</sub> on a Varian Mercury 300 spectrometer, with the solvent proton signal as standard. <sup>13</sup>C NMR spectra were recorded at 75 MHz on at Varian Mercury 300 spectrometer with the solvent carbon signal as standard. <sup>19</sup>F NMR spectra were recorded at 282.2 MHz on a Varian Mercury 300 spectrometer with external CFCl<sub>3</sub> as standard. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR system as thin films on NaCl disks and were analyzed using FT-IR Spectrum v2.00 software (Perkin-Elmer Corp., Beaconsfield, Bucks, England).

Gel permeation chromatography (GPC) was conducted on a either a tetrahydrofuran (THF) based GPC system or a *N,N*-dimethylformamide (DMF) based GPC system. The THF-based Waters 1515 HPLC (Waters Chromatography, Inc.), equipped with a Waters 2414 differential refractometer and a three-column series PL gel 5 μm Mixed C, 500 Å, and 10<sup>4</sup> Å, 300×7.5 mm columns (Polymer Laboratories, Inc.). The system was equilibrated at 35 °C in THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (*ca.* 3 mg/mL), and an injection volume of 200 μL was used. Data collection and analysis were performed, respectively, with Precision Acquire software and Discovery 32 software (Precision Detectors, Inc.). Molecular weight and molecular weight distributions were determined, based on calibration of the GPC system with polystyrene standards. The DMF-based Waters HPLC was equipped with an isocratic pump model 1515, a differential refractometer model 2414 and a two-column set of Styragel HR 4 and HR 4E 5 μm DMF 7.8 x 300 mm columns. The system was equilibrated at

70 °C in pre-filtered dimethylformamide (DMF) containing 0.05 M LiBr, which served as polymer solvent and eluent (flow rate set to 1.00 mL/min). Polymer solutions were prepared at concentration ca. 3 mg/mL and an injection volume of 200 µL was used. Data collection and analysis was performed with Empower Pro software. The system was calibrated with polystyrene standards.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851<sup>°</sup> instrument (Mettler-Toledo, Inc.) measuring the total mass loss on approximately 6 mg samples from 25 to 550 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min. Glass transition temperature ( $T_g$ ) determinations were measured by differential scanning calorimetry (DSC) on a DSC822<sup>°</sup> instrument (Mettler-Toledo, Inc.) in a temperature range of 0 to 200 °C with a heating rate of 10 °C/min under nitrogen. For both TGA and DSC, data were acquired and analyzed with STAR<sup>°</sup> software (Mettler-Toledo, Inc.). The  $T_g$  values were taken at the midpoint of the inflection tangent upon the third heating scans.

Hydrodynamic diameters ( $D_h$ ) and size distributions for the block copolymer assemblies in aqueous solutions were determined by dynamic light scattering (DLS). The DLS instrumentation consisted of a Brookhaven Instruments Limited (Worcestershire, U.K.) system, including a model BI-200SM goniometer, a model BI-9000AT digital correlator, a model EMI-9865 photomultiplier, and a model 95-2 Ar ion laser (Lexel, Corp.; Farmindale, NY) operated at 514.5 nm. Measurements were made at  $20 \pm 1$  °C. Prior to analysis, solutions were filtered through a 0.45 µm Millex®-GV PVDF membrane filter (Millipore Corp., Medford, MA) to remove dust particles. Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 ratio spaced channels, and initial delay of 5 µs, a final delay of 100 ms, and a duration of 8 minutes. A photomultiplier aperture of 400 µm was used, and the incident laser intensity was adjusted to obtain a photon counting of ca. 200 kcps. Only measurements in which the measured and calculated baselines of the intensity autocorrelation function agreed to within 0.1 % were used to calculate particle size. The calculations of the particle size distributions and distribution averages were performed with the ISDA software package (Brookhaven Instruments Company), which employed single-exponential fitting, cumulants analysis, non-negatively

constrained least-squares (NNLS) and CONTIN particle size distribution analysis routines. The determination was made in an average of 10 runs.

Contact angles were measured as static contact angles using the sessile drop technique<sup>4</sup> with a TanteC CAM micro-contact-angle meter and the half-angle measuring method. Films were prepared by drop-casting a THF solution of the corresponding polymer onto a glass microscope slide and dried in ambient condition. Contact angles ( $\theta_{\text{water}}$ ) of 18 M $\Omega$ •cm nanopure water were measured on the films by placing a 2  $\mu$ L drop on the surface. Each of the reported values is an average of six of such measurements on different regions of the same sample.

TEM experiments were performed on a Hitachi H-7500 transmission electron microscope operating at an accelerating voltage of 80 kV. TEM samples were prepared by applying a drop of micelle solutions (about 4  $\mu$ L) directly onto a carbon-coated copper TEM grid (pre-wetted by ethanol twice). After 5 mins, the excess solution was wicked away by a piece of filter paper. Then, a droplet of 1 wt% phosphotungstic acid solution (about 4  $\mu$ L) was deposited onto the dried samples. After 1 min, the excess stain solution was wicked away by a piece of filter paper. The sample was then allowed to dry under ambient conditions. The height measurements ( $H_{\text{av}}$ ) and distributions for the micelles were determined by tapping-mode atomic force microscopy (AFM) under ambient conditions in air. The AFM instrumentation consisted of a Nanoscope III BioScope system (Digital Instruments, Veeco Metrology Group; Santa Barbara, CA) and standard silicon tips (type, OTESPA-70; L = 160  $\mu$ m; normal spring constant, 50 N m<sup>-1</sup>; resonance frequency, 246 – 282 kHz). Samples for AFM imaging were prepared by spin-casting *ca.* 2.0  $\mu$ L of the sample solution onto a freshly cleaved mica plate (Ruby clear mica, New York Mica Co.) and allowed to dry in air.

**Synthesis of 4-(pyrrolidin-2'-one)-2,3,5,6-tetrafluorostyrene (1):** 2-Pyrrolidinone (6.02 g, 70.7 mmol) was diluted with 150 mL of DMF, and deprotonated by addition of NaH (1.74 g, 72.0 mmol) over 20 min at 0 °C. After H<sub>2</sub> was released completely, PFS (13.7 g, 71.0 mmol) in 50 mL of DMF was added in over 10 min. The reaction mixture was heated at 45 °C overnight and cooled down to room

temperature. 200 mL of saturated aqueous  $\text{NH}_4\text{Cl}$  solution was added slowly, and the organic products were extracted into diethyl ether (100 mL $\times$ 2), which was then washed with water (80 mL) and brine (80 mL), followed by dried over  $\text{MgSO}_4$  and filtered to afford the crude product. Recrystallization of the crude product from in acetone/hexane (v/v = 1/9) yielded **1** (10.9 g, 59%) as colorless crystals. mp 69-70 °C.  $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ : 3050-2800, 2645, 1883, 1708, 1644, 1581, 1503, 1484, 1466, 1433, 1410, 1379, 1325, 1310, 1292, 1256, 1227, 1205, 1166, 1113, 1078, 1068, 1021, 996, 968, 951, 854, 791, 758, 739, 709, 679, 638, 578.  $\delta_{\text{H}}$  (300 MHz, acetone- $d_6$ , 2.05 ppm): 2.30 (p,  $J=7.5$  Hz, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 2.50 (t,  $J=7.5$  Hz, 2H,  $-\text{CH}_2\text{C}(=\text{O})-$ ), 3.84 (t,  $J=7.5$  Hz, 2H,  $>\text{NCH}_2-$ ), 5.80 (d,  $J=12.0$  Hz, 1H, *cis*  $\text{CHH}=\text{CHAr}$ ), 6.10 (d,  $J=18.0$  Hz, 1H, *trans*  $\text{CHH}=\text{CHAr}$ ), 6.73 ppm (dd,  $J=12.0$  and 18.0 Hz, 1H,  $\text{CH}_2=\text{CHAr}$ ).  $\delta_{\text{C}}$  (75 MHz, Acetone- $d_6$ , 29.5 ppm): 18.3, 30.7, 42.3, 47.9, 68.2, 72.5, 113.7, 126.4, 127.8, 128.0, 136.5, 144.8, 174.2.  $\delta_{\text{F}}$  (282.2 MHz, Acetone- $d_6$ ): -160.1 (m, 2F, *meta*-F), -156.9 ppm (m, 2F, *ortho*-F).  $m/z$  (ESI)  $[\text{M}+\text{H}]^+$  260.0693 ( $\text{C}_{16}\text{H}_{14}\text{OF}_4$  requires 260.0695).

**Synthesis of 4-(2'-(pyrrolidin-2''-one)-ethoxy)-2,3,5,6-tetrafluorostyrene (2):**  
1-(2'-Hydroxyethyl)-pyrrolidin-2-one (7.40 g, 57.2 mmol) was diluted with 150 mL of DMF and deprotonated by addition of NaH (1.52 g, 62.9 mmol) over 20 min at 0 °C. After  $\text{H}_2$  was released completely, PFS (10.0 g, 51.5 mmol) in 50 mL of DMF was added in over 10 min. The reaction mixture was heated at 45 °C overnight and cooled down to room temperature. 200 mL of 1N HCl was added slowly to quench the reaction, and the organic products were extracted into diethyl ether (100 mL $\times$ 2), which was then washed with water (80 mL $\times$ 3) and brine (80 mL), followed by dried over  $\text{MgSO}_4$ . Further purification was performed by silica gel chromatography using  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  (v/v = 1/9) as eluent to yield **2** (11.1 g, 71%) as a viscous oil.  $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ : 3050-2820, 2646, 2572, 1863, 1681, 1649, 1580, 1504, 1463, 1428, 1387, 1365, 1327, 1310, 1288, 1227, 1205, 1152, 1121, 1081, 1021, 992, 969, 935, 840, 783, 757, 738, 711, 653, 611, 582.  $\delta_{\text{H}}$  (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 5.30 ppm): 1.89 (p,  $J=7.5$  Hz, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 2.20 (t,  $J=8.1$  Hz, 2H,  $-\text{CH}_2\text{C}(=\text{O})-$ ), 3.43 (t,  $J=7.5$  Hz, 2H,  $-\text{CH}_2\text{CH}_2\text{N}<$ ), 3.47 (t,  $J=5.2$  Hz, 2H,  $-\text{OCH}_2\text{CH}_2\text{N}<$ ), 4.19 (t,  $J=5.2$  Hz, 2H,  $-\text{OCH}_2-$ ), 5.45 (d,  $J=12.0$  Hz, 1H, *cis*  $\text{CHH}=\text{CHAr}$ ), 5.77 (d,  $J=18.0$  Hz, 1H, *trans*  $\text{CHH}=\text{CHAr}$ ), 6.39 (dd,  $J=12.0$  and

18.0 Hz, 1H, CH<sub>2</sub>=CHAr).  $\delta_C$  (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 52.5 ppm): 22.6, 35.2, 47.1, 53.0, 77.3, 115.5, 126.2, 126.6, 140.6, 144.2, 147.4, 148.1, 151.3, 181.1.  $\delta_F$  (282.2 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -156.4(m, 2F, *meta*-F), -143.1 (m, 2F, *ortho*-F).  $m/z$  (ESI) [M+H]<sup>+</sup> 304.0957 (C<sub>16</sub>H<sub>14</sub>OF<sub>4</sub> requires 304.0955).

**Synthesis of poly(1), 4:** A 10mL Schlenk flask fitted with a stir bar and covered with a rubber septum was charged with **1** (2.590 g, 10.0 mmol), DDMAT (45.5 mg, 0.125 mmol), 2,2'-azobis(isobutyronitrile) (AIBN, 1.6 mg, 1.0×10<sup>-2</sup> mmol), 2-butanone (1.30 mL) and DMF (0.70 mL) as the co-solvents. After five freeze–pump–thaw cycles, the flask was backfilled with N<sub>2</sub>, sealed and placed into a 68 °C oil bath to allow for polymerization. During polymerization, small aliquots (0.1 mL) of polymerization solution were withdrawn with syringe and were analyzed by <sup>1</sup>H NMR spectroscopy for the determination of monomer conversions based on the remaining vinylic proton resonances of **1** at 5.80, 6.10, and 6.73 ppm compared with methylene protons (>NCH<sub>2</sub>-) at 3.55-3.90 ppm. Finally, the polymerization was quenched, by being allowed to cool to room temperature, and then opening of the flask to air and dilution of the reaction mixture by addition of acetone, at a polymerization time of 12 h, with an estimated conversion of **1** of 78%. The polymer solution was precipitated three times into 400 mL of diethyl ether. The product was collected and dried *in vacuo* at room temperature to afford **3** as a pale yellow powder. Yield: 1.42 g (70 % based on the final conversion of monomer).  $M_n^{\text{NMR}} = 16700 \text{ g mol}^{-1}$ ,  $M_n^{\text{GPC}} \text{ (THF)} = 10700 \text{ g mol}^{-1}$ , PDI = 1.09.  $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ : 3020-2850, 1722, 1716, 1682, 1651, 1538, 1504, 1494, 1461, 1418, 1384, 1311, 1252, 1228, 1202, 1166, 1130, 1099, 1075, 955, 895, 850, 788, 734, 698, 668, 640, 538.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, 7.27 ppm): 0.83 (br, -CH<sub>3</sub> of RAFT agent), 1.20 (br, alkyl protons of RAFT agent), 1.40-3.00 (br, protons of polymer backbone, >NCH<sub>2</sub>CH<sub>2</sub> and >CH<sub>2</sub>C(=O)), 3.27 (br, -SCH<sub>2</sub>- of RAFT agent), 3.70 (br, >NCH<sub>2</sub>).  $\delta_C$  (75 MHz, CDCl<sub>3</sub>, 77.2 ppm): 19.7, 30.3, 32.8, 34.6, 36.0-39.5, 49.1, 77.4, 117.0-119.2, 139.5, 141.6, 142.2, 144.8, 146.1, 149.0, 174.3.  $\delta_F$  (282.2 MHz, CDCl<sub>3</sub>): -147.5 to -140.9 (br, *meta*-F and *ortho*-F).  $T_g$ : 178 °C. TGA in N<sub>2</sub>: 25-395 °C, 2% mass loss; 395-550 °C, 46% mass loss. A film was cast of this polymer by drop deposition from a CH<sub>2</sub>Cl<sub>2</sub> solution onto a glass microscope slide followed by drying under ambient conditions for analysis by contact angle.  $\theta_{\text{water}} = 50 \pm 1^\circ$ .

**General procedure for the synthesis of poly(2), 5:** A 10mL Schlenk flask fitted with a stir bar and covered with a rubber septum was charged with **2**, DDMAT, AIBN and 2-butanone as the solvent. After five freeze–pump–thaw cycles, the flask was backfilled with N<sub>2</sub>, sealed and placed into a 68 °C oil bath to allow for polymerization. During polymerization, small aliquots (0.1 mL) of polymerization solution were withdrawn with syringe and were analyzed by <sup>1</sup>H NMR spectroscopy for the determination of monomer conversions based on the remaining vinylic proton resonances of **2** at 5.45, 5.77, and 6.39 ppm compared with methylene protons (-OCH<sub>2</sub>-) at 3.95-4.30 ppm. Finally, the flask was immersed in liquid N<sub>2</sub> to quench the polymerization. The polymer mixture was further diluted with addition of acetone and then precipitated three times into a large amount of diethyl ether. The product was collected and dried *in vacuo* at room temperature to afford **5** as yellowish solids.  $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ : 3000-2880, 1686, 1492, 1461, 1426, 1385, 1365, 1327, 1310, 1288, 1224, 1146, 1098, 1076, 1023, 956, 879, 738, 653, 566.  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, 7.27 ppm): 0.81 (br, -CH<sub>3</sub> of RAFT agent), 1.18 (br, alkyl protons of RAFT agent), 1.41-2.80 (br, protons of polymer backbone, >NCH<sub>2</sub>CH<sub>2</sub>C(=O) and >CH<sub>2</sub>C(=O)), 3.23 (br, -SCH<sub>2</sub>- of RAFT agent), 3.35-3.82 (br, -OCH<sub>2</sub>CH<sub>2</sub>N< and -CH<sub>2</sub>CH<sub>2</sub>N<). 4.17 (br, -OCH<sub>2</sub>-).  $\delta_C$  (75 MHz, CDCl<sub>3</sub>, 77.2 ppm): 18.2, 29.3, 30.7, 31.9, 36.9-39.5, 42.6, 48.5, 73.6, 113.9, 135.7, 139.0, 139.8, 142.2-149.1, 175.4.  $\delta_F$  (282.2 MHz, CDCl<sub>3</sub>, ppm): -157.8 (br, 2F, *meta*-F), -146.0 to -142.5 (m, 2F, *ortho*-F).

**Synthesis of 5a:** **5a** was prepared from the mixture of **2** (3.500 g, 11.54 mmol), DDMAT (52.5 mg, 0.144 mmol), AIBN (2.3 mg, 1.4×10<sup>-2</sup> mmol) and 1.80 mL of 2-butanone as the co-solvent. During the polymerization, the conversions of **2** were measured to be 29, 48, 60, 72 and 88% at 3, 5, 7, 9, and 14 h, respectively. The polymerization was quenched after 14 h and the isolated of **5a** was 2.89 g (92 % based on the 88% conversion of **2**).  $M_n^{\text{NMR}} = 21700 \text{ g mol}^{-1}$ ,  $M_n^{\text{GPC}} (\text{DMF}) = 54100 \text{ g mol}^{-1}$ , PDI = 1.09.  $T_g$ : 49 °C. TGA in N<sub>2</sub>: 25-320 °C, 4% mass loss; 320-445 °C, 44% mass loss; 445-550 °C, 5% mass loss. A film was cast of this polymer by drop deposition from a CH<sub>2</sub>Cl<sub>2</sub> solution onto a glass

microscope slide followed by drying under ambient conditions for analysis by contact angle.  $\theta_{\text{water}} = 42 \pm 3^\circ$ .

**Synthesis of 5b:** **5b** was prepared from the mixture of **2** (3.066 g, 10.12 mmol), DDMAT (72.8 mg, 0.200 mmol), AIBN (2.1 mg,  $1.3 \times 10^{-2}$  mmol) and 2-butanone (3.1 mL) as the solvent. During the polymerization, the conversions of **2** were measured to be 52 and 88% at 6 h and 11 h, respectively. The polymerization was quenched after 11 h and the isolated of **5b** was 1.88 g (65 % based on the 88% conversion of **2**).  $M_n^{\text{NMR}} = 13700 \text{ g mol}^{-1}$ ,  $M_n^{\text{GPC}} (\text{DMF}) = 42400 \text{ g mol}^{-1}$ , PDI = 1.06.  $T_g$ : 45 °C. TGA in  $\text{N}_2$ : 25-330 °C, 4% mass loss; 330-450 °C, 46% mass loss; 450-550 °C, 5% mass loss. A film was cast of this polymer by drop deposition from a  $\text{CH}_2\text{Cl}_2$  solution onto a glass microscope slide followed by drying under ambient conditions for analysis by contact angle.  $\theta_{\text{water}} = 44 \pm 2^\circ$ .

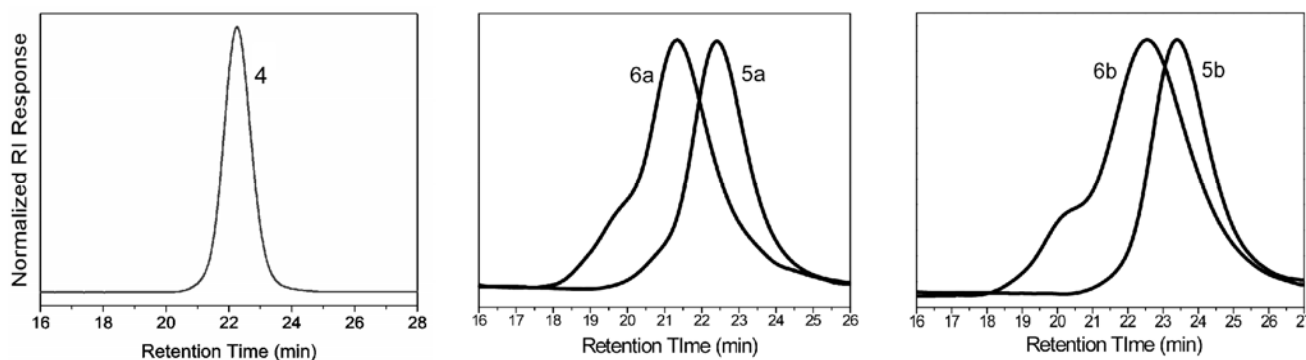
**General procedure for the synthesis of poly(2)-*b*-poly(3), 6:** A 10 mL-Schlenk flask fitted with a stir bar and covered with a rubber septum was charged with **5** as the macroCTAs, **3**, AIBN and 2-butanone as the solvent. After five freeze–pump–thaw cycles, the flask was backfilled with  $\text{N}_2$ , sealed and placed into an oil bath at 68 °C to allow for polymerization. Finally, the polymerizations were quenched and the conversions of **3** were measured by  $^1\text{H}$  NMR spectroscopy, based on the remaining vinylic proton resonances of **3** at 5.62, 6.03, and 6.62 ppm compared with methylene protons ( $-\text{OCH}_2-$ ) at 3.90-4.35 ppm. The reaction was allowed to cool to room temperature, and then opening of the flask to air. The polymer solution was precipitated three times into a large amount of hexane and the products were collected and dried *in vacuo* to yield **6** as pale yellow solids.  $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ : 3082-2880, 1686, 1654, 1648, 1492, 1460, 1426, 1384, 1364, 1328, 1310, 1288, 1222, 1145, 1117, 1098, 1077, 958, 926, 878, 769, 740, 650, 567.  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ , 7.27 ppm): 0.84 (br,  $-\text{CH}_3$  of RAFT agent), 1.22-2.83 (br, alkyl protons of RAFT agent, protons of the diblock copolymer backbones,  $>\text{NCH}_2\text{CH}_2\text{C}(=\text{O})$  and  $>\text{CH}_2\text{C}(=\text{O})$  of the repeating units of **2**, and  $-\text{OCH}_2\text{CH}_2-$  of the repeating units of **3**), 3.43-3.73 (br,  $-\text{OCH}_2\text{CH}_2\text{N}<$  and  $-\text{CH}_2\text{CH}_2\text{N}<$  of the repeating units of **2**), 3.97-4.32 (br,  $-\text{OCH}_2-$  of the repeating units of both **2** and **3**), 5.11 (m,  $-\text{CH}=\text{CH}_2$  of the repeating units of **3**), 5.83 (br, -



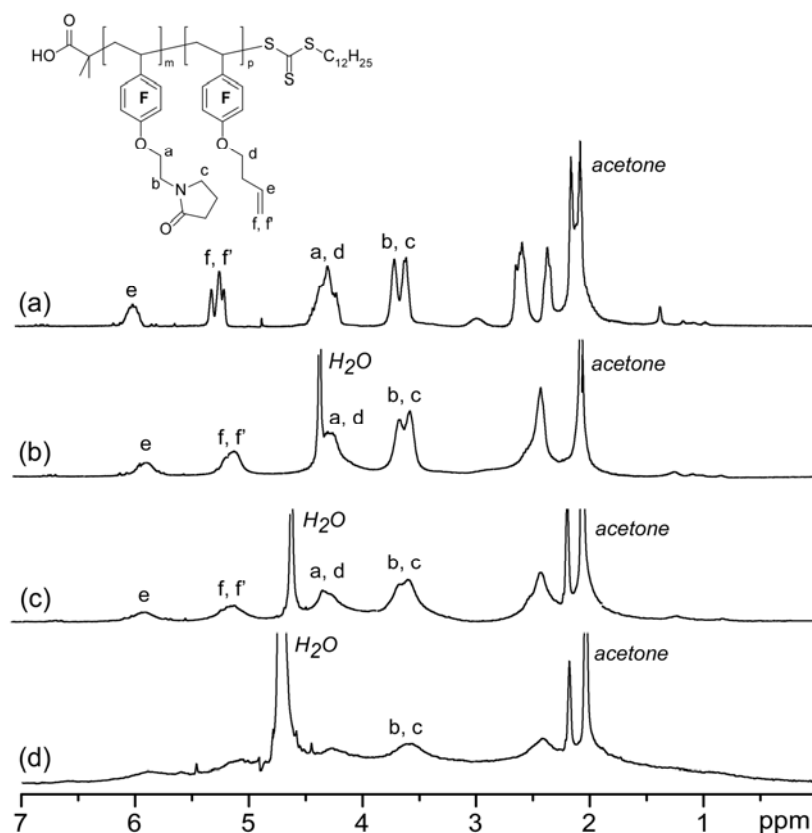
$\text{CH}=\text{CH}_2$  of the repeating units of **3**).  $\delta_C$  (75 MHz,  $\text{CDCl}_3$ , 77.2 ppm): 18.5, 31.0, 33.1, 34.3, 36.9-39.2, 42.9, 48.8, 73.8, 74.4, 113.9, 117.6, 133.6, 136.1, 139.3, 142.5, 143.2, 146.7, 175.6.  $\delta_F$  (282.2 MHz,  $\text{CDCl}_3$ , ppm): -157.7 (br, 2F, *meta*-F), -146.7 to -142.2 (m, 2F, *ortho*-F).

**Synthesis of 6a:** **6a** was prepared from the mixture of **5a** as the macroCTA ( $301 \text{ mg}$ ,  $1.39 \times 10^{-2} \text{ mmol}$ ), **3** ( $521 \text{ mg}$ ,  $1.90 \text{ mmol}$ ), AIBN ( $0.22 \text{ mg}$ ,  $1.3 \times 10^{-3} \text{ mmol}$ ) and 2-butanone ( $1.20 \text{ mL}$ ) as the solvent at  $68 \text{ }^\circ\text{C}$ . After 5 h, the conversion of **3** was measured to be 36 % by  $^1\text{H}$  NMR spectroscopy. The polymerization was then quenched and the isolated of **6a** was  $326 \text{ mg}$  (67 % based on the 88% conversion of **2**).  $M_n^{\text{NMR}} = 34000 \text{ g mol}^{-1}$ ,  $M_n^{\text{GPC}} (\text{DMF}) = 72800 \text{ g mol}^{-1}$ , PDI = 1.22.  $T_g$ :  $52 \text{ }^\circ\text{C}$ . TGA in  $\text{N}_2$ :  $25\text{-}335 \text{ }^\circ\text{C}$ , 3% mass loss;  $335\text{-}445 \text{ }^\circ\text{C}$ , 38% mass loss;  $445\text{-}550 \text{ }^\circ\text{C}$ , 11% mass loss. A film was cast of this polymer by drop deposition from a  $\text{CH}_2\text{Cl}_2$  solution onto a glass microscope slide followed by drying under ambient conditions for analysis by contact angle.  $\theta_{\text{water}} = 60 \pm 4^\circ$ .

**Synthesis of 6b:** **6b** was prepared from the mixture of **5b** as the macroCTA ( $400 \text{ mg}$ ,  $2.92 \times 10^{-2} \text{ mmol}$ ), **3** ( $768 \text{ mg}$ ,  $2.80 \text{ mmol}$ ), AIBN ( $0.75 \text{ mg}$ ,  $4.6 \times 10^{-3} \text{ mmol}$ ) and 2-butanone ( $2.0 \text{ mL}$ ) as the solvent at  $68 \text{ }^\circ\text{C}$ . After 6 h, the conversion of **3** was measured to be 48 % by  $^1\text{H}$  NMR spectroscopy. The polymerization was then quenched and the isolated of **6b** was  $560 \text{ mg}$  (73 % based on the 48% conversion of **3**).  $M_n^{\text{NMR}} = 25100 \text{ g mol}^{-1}$ ,  $M_n^{\text{GPC}} (\text{DMF}) = 56200 \text{ g mol}^{-1}$ , PDI = 1.30.  $T_g$ :  $42 \text{ }^\circ\text{C}$ . TGA in  $\text{N}_2$ :  $25\text{-}340 \text{ }^\circ\text{C}$ , 3% mass loss;  $340\text{-}450 \text{ }^\circ\text{C}$ , 40% mass loss;  $450\text{-}550 \text{ }^\circ\text{C}$ , 8% mass loss. A film was cast of this polymer by drop deposition from a  $\text{CH}_2\text{Cl}_2$  solution onto a glass microscope slide followed by drying under ambient conditions for analysis by contact angle.  $\theta_{\text{water}} = 64 \pm 2^\circ$ .

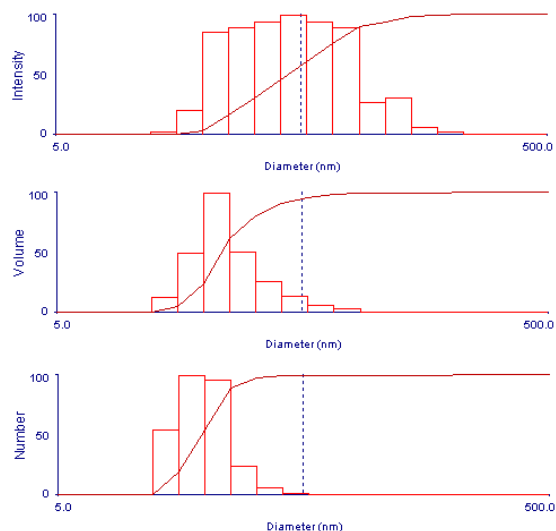


**Figure S1.** GPC traces of polymers **4-6**.



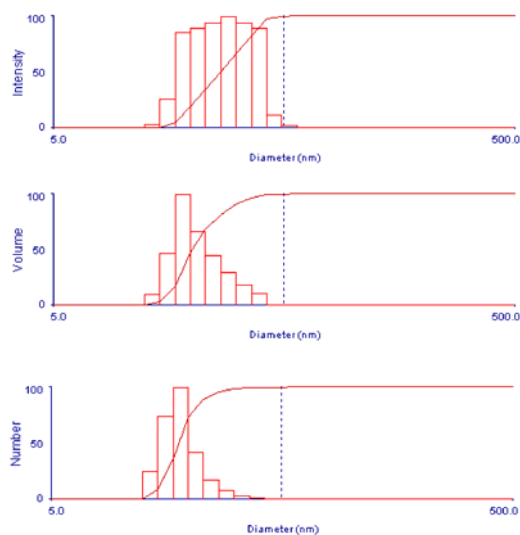
**Figure S2.**  $^1\text{H}$  NMR spectra (300 MHz) of diblock copolymer **6b** in acetone and acetone- $d_6$ /D $_2$ O mixed solvents. (a) Acetone- $d_6$ ; (b) Acetone- $d_6$ /D $_2$ O = 1/1 (v/v); (c) Acetone- $d_6$ /D $_2$ O = 1/2 (v/v); (d) Acetone- $d_6$ /D $_2$ O = 1/4 (v/v).

**Preparation of micelle solution from copolymer 6a (0.45 mg/mL).** To a solution of diblock copolymer **6a** (10 mg) in THF (8.0 mL), an equal volume of DI H $_2$ O was added dropwisely over 30 min. The reaction mixture was further stirred for 12 h at room temperature before being transferred to a pre-soaked dialysis tubing (MWCO = 6.0-8.0 kDa), and dialyzed against DI H $_2$ O for 5 days, to afford a micelle solution of **6a**, with the final polymer concentration of 0.45 mg/mL.  $D_{\text{h, int}}$  (DLS) =  $69 \pm 11$  nm,  $D_{\text{h, vol}}$  (DLS) =  $31 \pm 5$  nm,  $D_{\text{h, num}}$  (DLS) =  $24 \pm 4$  nm.  $D_{\text{av}}$  (TEM) =  $27 \pm 4$  nm.  $H_{\text{av}}$  (AFM) =  $1.5 \pm 0.4$  nm,  $D_{\text{av}}$  (AFM) =  $50 \pm 10$  nm.



**Figure S3.** DLS histogram of micelle solution from polymer **6a** (0.45 mg/mL).

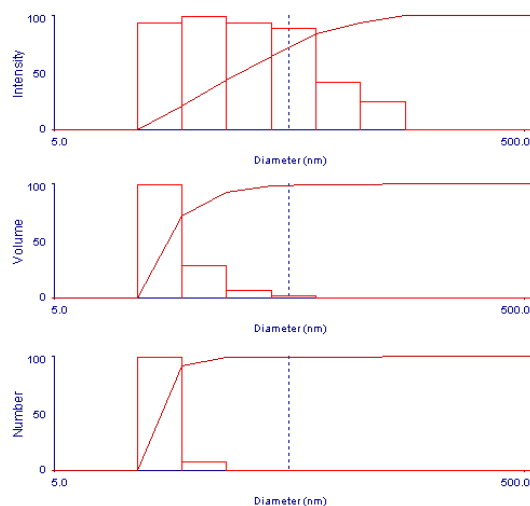
**Preparation of micelle from 6a (1.5 mg/mL).** A solution of diblock copolymer **6a** (10 mg) in THF (3.5 mL) was transferred to a pre-soaked dialysis tubing (MWCO = 6.0-8.0 kDa), and directly dialyzed against DI H<sub>2</sub>O for 5 days, to afford a micelle solution of **6a**, with the final polymer concentration of 1.5 mg/mL.  $D_{h, \text{int}}$  (DLS) =  $54 \pm 8$  nm,  $D_{h, \text{vol}}$  (DLS) =  $24 \pm 5$  nm,  $D_{h, \text{num}}$  (DLS) =  $19 \pm 3$  nm.



**Figure S4.** DLS histogram of micelle solution from polymer **6a** (1.5 mg/mL).

**Preparation of micelle from 6a (5.0 mg/mL).** A solution of diblock copolymer **6a** (20 mg) in THF (2.5 mL) was transferred to a pre-soaked dialysis tubing (MWCO = 6.0-8.0 kDa), and directly dialyzed

against DI H<sub>2</sub>O for 5 days, to afford a micelle solution of **6a** with the final polymer concentration of 5.0 mg/mL.  $D_{h, \text{int}}$  (DLS) =  $42 \pm 5$  nm,  $D_{h, \text{vol}}$  (DLS) =  $19 \pm 3$  nm,  $D_{h, \text{num}}$  (DLS) =  $15 \pm 2$  nm.

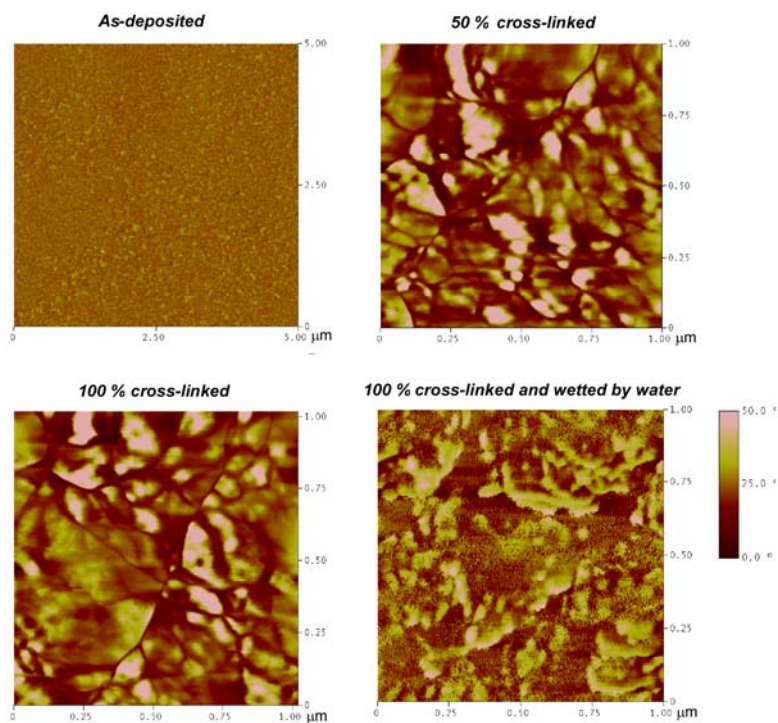


**Figure S5.** DLS histogram of micelle solution from polymer **6a** (5.0 mg/mL).

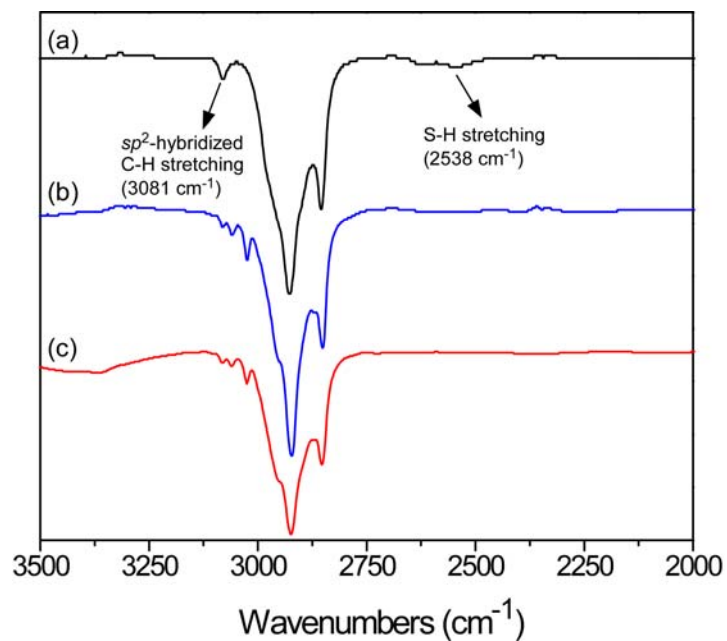
### Preparation of films from polymer **6b**

To a 3-mL vial was loaded with polymer **6b** (60 mg, 0.0024 mmol, 0.11 mmol vinyl groups), HSC<sub>10</sub>H<sub>20</sub>SH (11.4 mg, 0.055 mmol), 2,2'-dimethoxy-2-phenylacetophenone (DMPA, 1.5 mg, 0.0055 mmol) and 1,4-dioxane (1.5 mL). The solution was stirred for 30 min at room temperature and then carefully drop-deposited onto three glass microscope slides in equal amounts, followed by drying under ambient conditions in the dark for 6 h. One of the films was used as a control slide without irradiation, and the other two slides were used for the preparation of 100% cross-linked films. Another solution containing polymer **6b** (20 mg, 0.00080 mmol, 0.037 mmol vinyl groups), HSC<sub>10</sub>H<sub>20</sub>SH (1.9 mg, 0.0090 mmol), DMPA (0.5 mg, 0.002 mmol) and 1,4-dioxane (0.50 mL) was carefully drop-deposited onto a glass slide followed by drying for the preparation of the 50% cross-linked film. These films were then irradiated for 10 minutes under the F300S UV lamp to allow for “thiol-ene” cross-linking. The resulting film surfaces were analyzed with tapping mode atomic force microscopy in order to ascertain topography and roughness. One of the two 100% cross-linked slides was immersed in a chamber with artificial sea water for 18 h, followed by removal of excess water by wicking with a Kimwipe to result

in a water-wetted cross-linked film, and AFM analysis was immediately performed thereafter on the surface.



**Figure S6.** AFM phase images (2D) of the amphiphilic surface films prepared from polymer **6b**.



**Figure S7.** IR spectra of the as-prepared film of polymer **6b** with HS(CH<sub>2</sub>)<sub>10</sub>SH before cross-linking (a); 50% cross-linked film (b); and 100% cross-linked film (c).

1. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
2. J. Ma, C. Cheng, G. Sun and K. L. Wooley, *Macromolecules*, 2008, **41**, 9080-9089.
3. J. Ma, C. Cheng and K. L. Wooley, *Macromolecules*, 2009, **42**, 1565-1573.
4. A. W. Neumann and R. J. Good, *J. Surf. Colloid. Sci.*, 1979, **11**, 31-91.