

Electronic Supplementary Information for

Preparation of Superhydrophobic Films based on the Diblock Copolymer

P(TFEMA-*r*-Sty)-*b*-PCEMA

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Materials and reagents

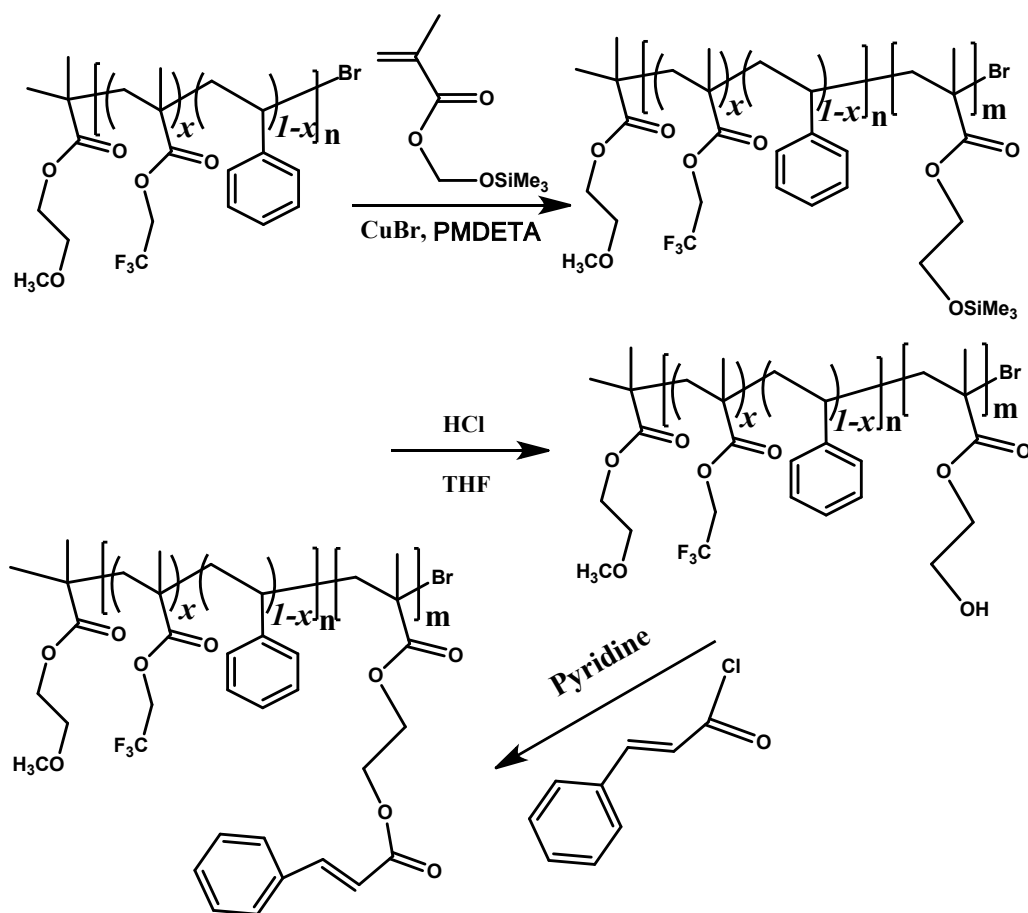
2,2,2-Trifluoroethyl methacrylate (TFEMA) was purchased from Harbin Xuefugui Chemical Co., Ltd (China), and was purified according to a previously reported procedure.¹⁻³ Styrene (Aladdin, 99%) was distilled over calcium hydride under reduced pressure prior to use. (Trimethylsilyloxy)ethyl methacrylate (HEMA-TMS) was synthesized and purified according to a previously reported procedure.⁴ Methoxyethyl 2-bromoisobutyrate (MEBrIB) was synthesized according to a previously reported procedure and its structure and purity were confirmed via ¹H NMR spectroscopy.¹⁻³ Copper(I) bromide (CuBr, Fluka, 98+%) was purified via stirring in acetic acid at 80 °C for over 8 h before it was subsequently washed with

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methanol and then dried under vacuum at room temperature. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was used as received. Cyclohexanone (Aladdin, 99%) was stirred overnight with calcium hydroxide before it was distilled under reduced pressure before use. Cinnamoyl chloride (Aldrich, 98%, predominantly *trans*) was used as received without further treatment. Pyridine (Aladdin, 99%) was of analytical grade and distilled over calcium hydride prior to use. Dichloromethane (CH₂Cl₂, Aladdin, 99%), tetrahydrofuran (THF, Aladdin, 99%), and hexane (Aladdin, 99%) were all of analytical grade and were distilled over sodium prior to use.

Preparation of the macroinitiator and the diblock copolymer

The macroinitiator and the diblock copolymer were prepared via atom transfer radical polymerization (ATRP) methods, as ATRP could be used to prepare well-defined polymers.⁵ The synthesis of the macroinitiator P(TFEMA-*r*-Sty)-Br and the corresponding polymerization kinetics have been recently reported.¹ Statistical copolymers with low polydispersity indices (M_w/M_n) were prepared using MEBriB as the initiator, and CuBr/PMDETA as the catalyst system in cyclohexanone at 85 °C. Illustrated in Scheme S1 is the synthetic route for preparing the diblock copolymer starting from the macroinitiator.



Scheme S1. Synthetic pathway followed during the preparation of poly[2,2,2-trifluoroethyl methacrylate-*r*-styrene]-*block*-poly[(2-cinnamoyloxyethyl methacrylate)] (P(TFEMA-*r*-Sty)-*b*-PCEMA) from P(TFEMA-*r*-Sty)-Br.

1. Synthesis of the macroinitiator P(TFEMA-*r*-Sty)-Br

ATRP was used to prepare P(TFEMA-*r*-Sty)-Br. The copolymerization of styrene and TFEMA was performed in a home-made dual-flask apparatus in which two 25 mL flasks were connected together via a glass pipe with a diameter of 0.8 cm and a length of 5 cm. In a typical procedure, cyclohexanone (4.03 mL), TFEMA (2.50 g, 14.9 mmol), styrene (1.56 g, 14.9 mmol), MEBriB (0.067 g, 0.3 mmol), and PMDETA (0.052 g, 0.3 mmol) were added into one of the flasks in the set, while CuBr (0.043g, 0.3 mmol) was loaded into the other flask containing a magnetic stir

bar. The liquid mixture in the first flask was bubbled with argon for half an hour before it was subjected to three freeze-pump-thaw cycles, and then transferred to the flask containing CuBr. At this point, the dual-flask set was transferred to a preheated oil-bath that was heated at a constant temperature of 85 ± 1 °C. The reaction was stopped by freezing the flask with liquid nitrogen prior to the introduction of air. Subsequently, the bluish reaction mixture was diluted with 15 mL of THF and passed through a neutral alumina column to remove any copper-ligand complexes. The filtrate was concentrated to ~5 mL via rotary evaporation before it was precipitated from 100 mL of methanol or hexane. The crude product was further purified by re-dissolution into 5 mL of THF and precipitation from 100 mL of methanol or hexane thrice before it was dried under vacuum overnight. The precipitate was centrifuged and then vacuum-dried at room temperature for 24 h to generate 3.17 g of the polymer as a white powder in an 80% yield. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 6.55-7.21 ppm (m, $-\text{C}_6\text{H}_5$), δ 2.78-4.35 ppm (m, $-\text{CH}_2\text{CF}_3$), δ 1.11–2.78 ppm (m, $-\text{CH}_2$ and $-\text{CH}=\text{}$), δ 0.25–1.11 ppm (br, $-\text{CH}_3$). According to our kinetic investigations,¹ the copolymer should possess 41 TFEMA units and 38 styrene units.

2. Synthesis of P(TFEMA-*r*-Sty)-*b*-PHEMA

Initially, the diblock copolymer P(TFEMA-*r*-Sty)-*b*-PHEMA-TMS was prepared by chain extension using P(TFEMA-*r*-Sty)-Br as a macroinitiator. The product of this reaction was then hydrolyzed by HCl to yield P(TFEMA-*r*-Sty)-*b*-PHEMA. In summary, acetonitrile (2.52 mL), HEMA-TMS (6.28 g, 30.8 mmol), and PMDETA (11.9 mg, 0.07 mmol) were added into one side of a dual-flask set, while P(TFEMA-

r-Sty)-Br (0.67 g, 0.06 mmol), CuBr (8.9 mg, 0.06 mmol) and CuBr₂ (1.39 mg, 0.006 mmol) were added to the other flask. The liquid reactants were subjected to three freeze-pump-thaw cycles before they were transferred to the flask containing the macroinitiator and CuBr. The yellow solution was stirred to dissolve the solid and then placed into an oil bath that was preheated to 70 ± 1 °C. The reaction was stopped by freezing the flask with liquid nitrogen and subsequently introducing air. The reaction mixture was then diluted with 15 mL of THF and passed through a neutral alumina column to remove the copper complex. The filtrate was diluted to ~80 mL with THF before the addition of 3 mL of water and 0.3 mL of 1 M HCl. After it was stirred for 4 h, the mixture was concentrated to ~20 mL via rotary evaporation prior to the addition of 150 mL of distilled water to precipitate the polymer. The precipitate was washed with water and hexane before it was dried under vacuum at room temperature, thus yielding 3.21 g of the product as a white fluffy solid in a 63% yield. ¹H-NMR (DMSO-*d*₆, 400 MHz): δ 6.55-7.21 (m, -C₆H₅), δ 2.78-4.35 ppm (m, -CH₂CF₃, br, -COOCH₂, br, -CCH₂OH), δ 1.11-2.78 ppm (m, -CH₂ and -CH=), δ 0.25-1.11 ppm (br, -CH₃).

3. Synthesis of P(TFEMA-*r*-Sty)-*b*-PCEMA

Cinnamation was achieved according to a method reported in the literature.⁶ In particular, 1.51 g of P(TFEMA-*r*-Sty)-*b*-PHEMA (containing 9.1 mmol of hydroxyl groups) was dissolved in 30 mL of dry pyridine. Subsequently, 3.83 g of cinnamoyl chloride (22.9 mmol, 2.5 mol equiv) was also dispersed into 30 mL of dry pyridine and added into the first pyridine solution. This mixture was stirred overnight at

room temperature. The pyridine salt that had formed was separated via centrifugation at 3000 g and the supernatant was concentrated to ~10 mL before it was precipitated from 150 mL of methanol. The precipitate was redissolved in 10 mL of THF and again precipitated from methanol. This precipitation procedure was repeated once again. The resultant product was dried at room temperature under vacuum to obtain 2.39 g of a white powder in a 79% yield. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.63 ppm (d, $=\text{CHC}_6\text{H}_5$), δ 6.55-7.21 (m, $-\text{C}_6\text{H}_5$), δ 6.45 ppm (d, $-\text{CH}=\text{CHC}_6\text{H}_5$), δ 2.78-4.35 ppm (m, $-\text{CH}_2\text{CF}_3$, br, $-\text{COOCH}_2$, br, $-\text{COOCH}_2$), δ 1.11–2.78 ppm (m, $-\text{CH}_2$ and $-\text{CH}=\text{}$), δ 0.25–1.11 ppm (br, $-\text{CH}_3$).

The disappearance of the ethylene peaks corresponding to the hydroxyl ethyl group at ~3.8 ppm and the emergence of the doublet at ~4.3 ppm corresponding to the ethylene group of CEMA suggests the complete cinnamation of PHEMA.⁷

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