

Supporting Information for

Synthesis and Properties of a Coil-*g*-Rod Polymer Brush by Combination of ATRP and Alternating Copolymerization

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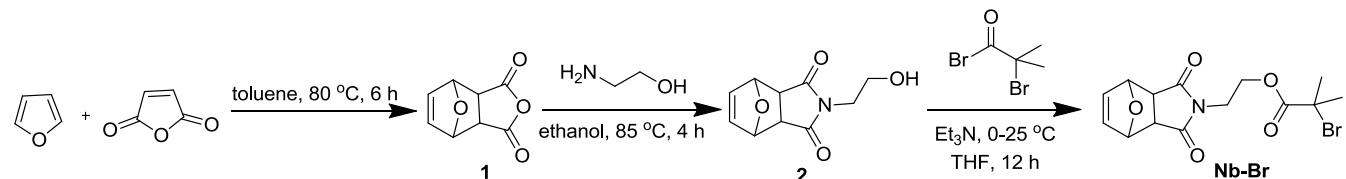
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Synthetic Procedures

1.1. Synthesis of Nb-Br

Nb-Br was synthesized according to the literature, and the detailed route is shown in Scheme S1.^{1,2}

Scheme S1. Synthesis of initiator



1.1.1. Synthesis of 4,10-dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1). Maleic anhydride (10.0 g, 102 mmol) and 50 mL of toluene were charged into a 100 mL three-necked flask with a magnetic stir bar, and the flask was put into an oil bath at 80 °C for a while. Furan (11.0 mL, 153 mmol) was added into the flask, and the mixture was heated for 6 h and then cooled to ambient temperature. After one hour, a white solid was precipitated out. It was filtered and washed with 3×30 mL of petroleum ether. The chemical structure of the product (1) was confirmed by ¹H NMR (Figure S1). ¹H NMR (400 MHz, DMSO-*d*₆, δ , ppm): 3.31 (s, 2H, CH), 5.35 (s, 2H, CHO), 6.58 (s, 2H, CH_{vinyl}).

1.1.2. Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2). The above product 1 (5.00 g, 30.0 mmol) was dissolved in 15 mL of ethanol, and then a solution of ethanolamine (1.90 mL, 31.5 mmol) in 10 mL of ethanol was added dropwise. The mixture was refluxed for 4 h and then cooled to ambient temperature. After 12 h, the resulting white crystal was filtered and washed with 3×30 mL of petroleum ether. The chemical structure of the product (2) obtained was also verified by ¹H NMR (Figure S2). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 2.90 (s, 2H, CH), 3.70 (t, 2H, NCH₂), 3.77 (t, 2H, OCH₂), 5.28 (s, 2H, CHO), 6.53 (s, 2H, CH_{vinyl}).

1.1.3. Synthesis of Nb-Br. The alcohol 2 (3.14 g, 15.0 mmol) and 3.14 mL of Et₃N were dissolved in 100 mL of THF, and the mixture was cooled to 0 °C. After a solution of 2-bromo

isobutyryl bromide (1.40 mL, 11.1 mmol) in 50 mL of THF was added dropwise, the mixture was stirred at 0 °C for 3 h and then at ambient temperature overnight. The resulting solids were filtered out, and the solution was concentrated by a rotary evaporator to give a raw product which was purified by silica gel column (100% dichloromethane). Yield: 82%. ¹H NMR (Figure S3) (400 MHz, CDCl₃, δ , ppm): 1.90 (s, 6H, CH₃), 2.88 (s, 2H, CH), 3.82 (t, 2H, NCH₂), 4.34 (t, 2H, OCH₂), 5.27 (s, 2H, CHO), 6.52 (s, 2H, CH_{vinyl}). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 30.59 (1C, CH₂), 37.44 (1C, NCH₂), 47.43 (2C, CH), 55.50 (1C, C(CH₃)₂Br), 62.03 (1C, OCH₂), 80.72 (2C, CHO), 136.33 (2C, CH_{vinyl}), 171.66 (1C, CO_{ester}), 175.87 (2C, CO_{imide}). Anal. Calcd. for C₁₄H₁₆NO₅: C, 46.95; H, 4.50; N, 3.91. Found C, 47.00; H, 4.60; N, 3.91. HRMS (ESI): calcd. (M + Na)^{+/z}, 382.01; (M + K)^{+/z}, 397.98; found (M + Na)^{+/z}, 382.0; (M + K)^{+/z}, 398.0.

1.2. Synthesis of MPCS

As a regularly used monomer in our group, MPCS was synthesized according to our previous report,³ and its purity was confirmed by ¹H NMR (Figure S4).

1.3. Synthesis of Nb-PMPCS

All Nb-PMPCS samples were polymerized in a similar way. In a typical experiment, MPCS (2.02 g, 5.00 mmol), Nb-Br (0.0900 g, 0.250 mmol), CuBr (0.0360 g, 0.250 mmol), PMDETA (0.0430 g, 0.250 mmol), and chlorobenzene (8.08 g) were charged into a glass tube with a magnetic stir bar. The glass tube was degassed by three freeze-thaw cycles and sealed under vacuum. After polymerization at 85 °C for 1 h, the tube was dipped into liquid nitrogen. Then the solution was diluted with 20 mL of dichloromethane, passed through a neutral alumina column to remove the Cu(I) catalyst, and precipitated in 400 mL of methanol. After filtration and being dried in vacuum at ambient temperature for 24 h, Nb-PMPCS was obtained as a white powder.

Results

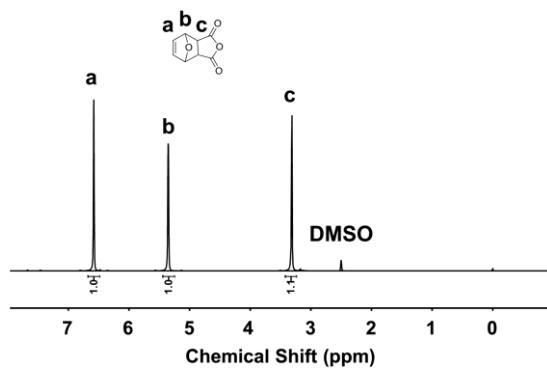


Figure S1. ^1H NMR spectrum of **1** in $\text{DMSO}-d_6$.

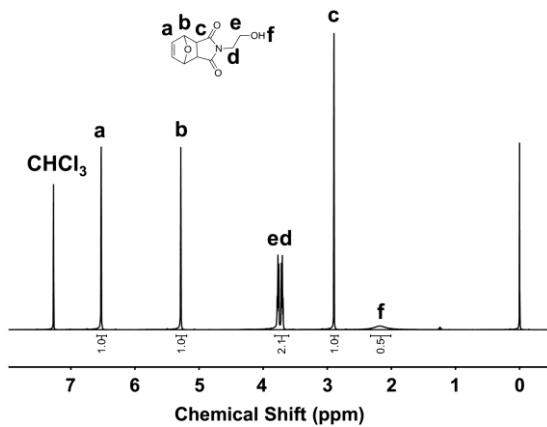


Figure S2. ^1H NMR spectrum of **2** in CDCl_3 .

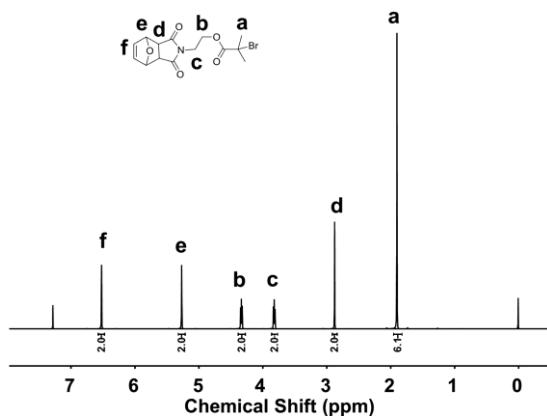


Figure S3. ^1H NMR spectrum of Nb-Br in CDCl_3 .

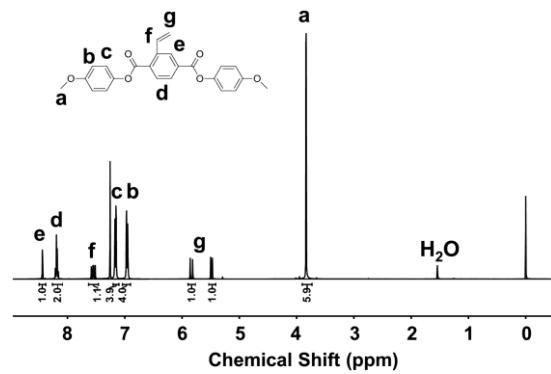


Figure S4. ^1H NMR spectrum of MPPCS in CDCl_3 .

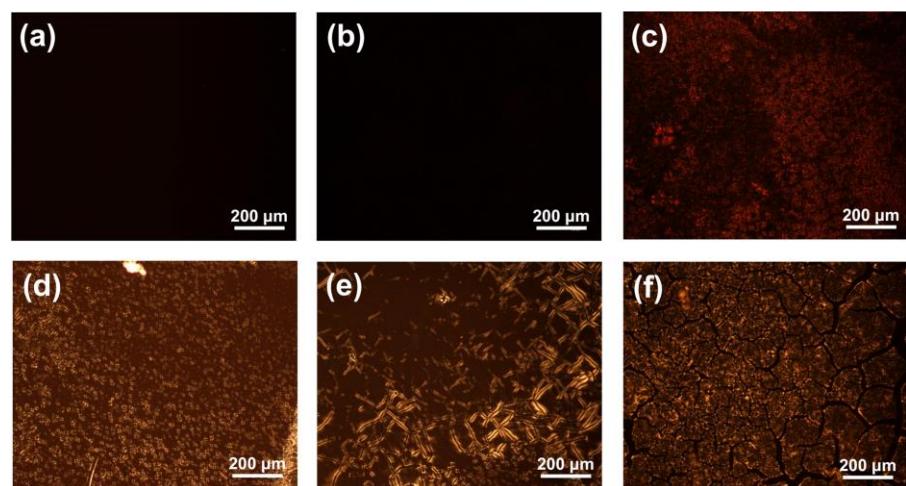


Figure S5. PLM micrographs of MI-PMPPCS 1 (a), Brush 1 (b), MI-PMPPCS 3 (c), Brush 3 (d), MI-PMPPCS 4 (e), and Brush 4 (f) at 240 $^{\circ}\text{C}$.

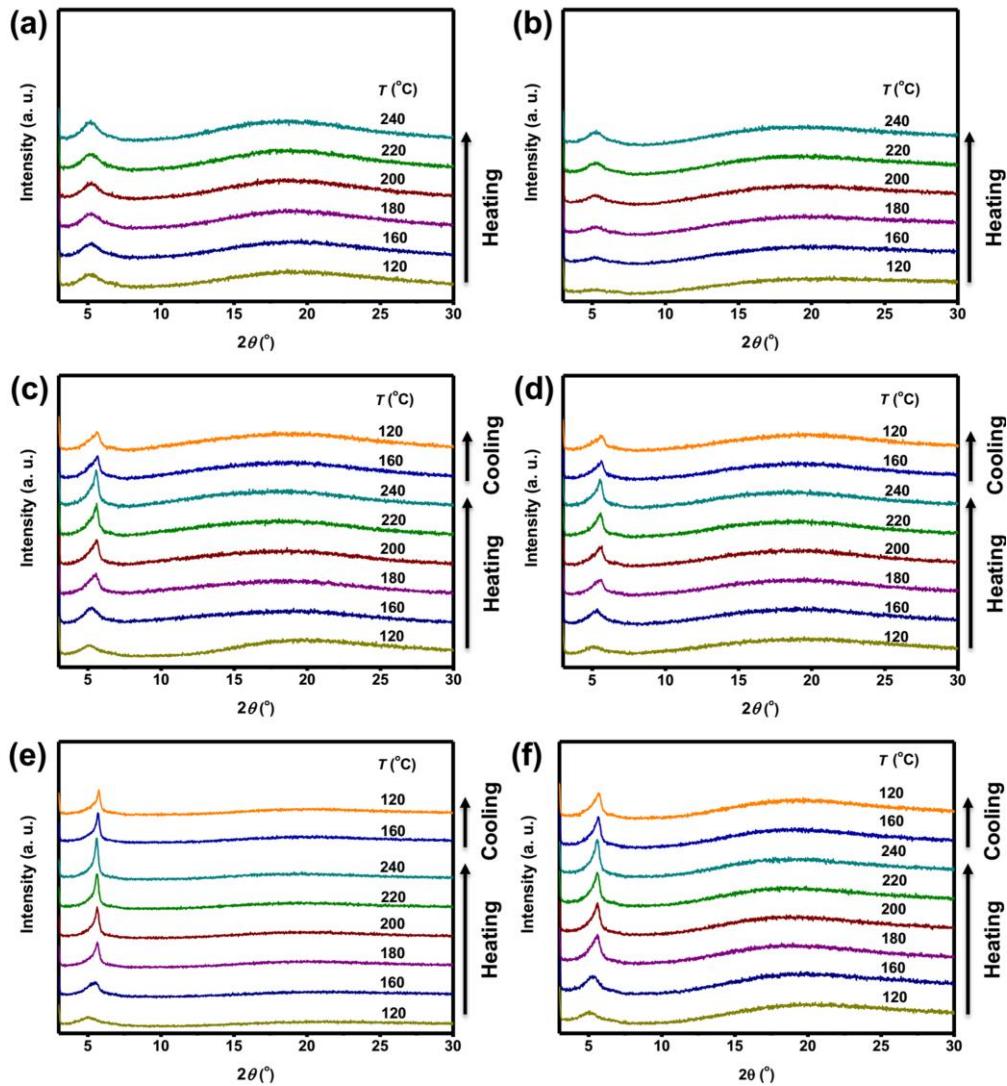


Figure S6. 1D WAXD profiles of MI-PMPCS 1 (a), Brush 1 (b), Brush 2-2 (c), Brush 2-3 (d), MI-PMPCS 4 (e), and Brush 4 (f).

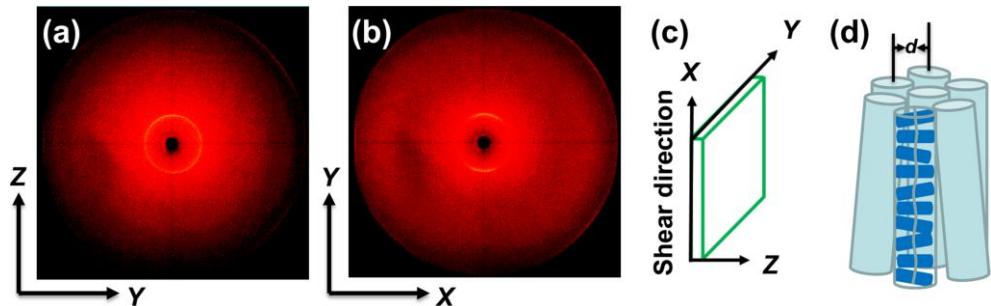


Figure S7. 2D WAXD patterns of a sheared film sample of MI-PMPCS 3 with the X-ray beam along X (a) and Z (b) directions, the shearing geometry (c), and the schematic drawing of the Φ_N phase formed by MI-PMPCS 3 (d).

References:

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