

## Supporting Information for

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

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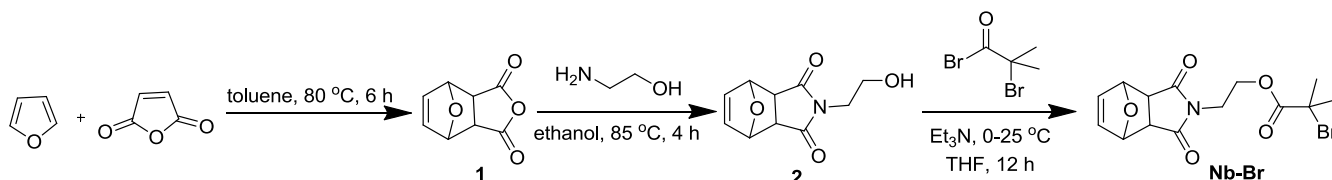
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## Synthetic Procedures

### 1.1. Synthesis of Nb-Br

Nb-Br was synthesized according to the literature, and the detailed route is shown in Scheme S1.<sup>1,2</sup>

#### 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 <sup>1</sup>H NMR (Figure S1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 3.31 (s, 2H, CH), 5.35 (s, 2H, CHO), 6.58 (s, 2H, CH<sub>vinyl</sub>).

**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 <sup>1</sup>H NMR (Figure S2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 2.90 (s, 2H, CH), 3.70 (t, 2H, NCH<sub>2</sub>), 3.77 (t, 2H, OCH<sub>2</sub>), 5.28 (s, 2H, CHO), 6.53 (s, 2H, CH<sub>vinyl</sub>).

**1.1.3. Synthesis of Nb-Br.** The alcohol **2** (3.14 g, 15.0 mmol) and 3.14 mL of Et<sub>3</sub>N 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%. <sup>1</sup>H NMR (Figure S3) (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.90 (s, 6H, CH<sub>3</sub>), 2.88 (s, 2H, CH), 3.82 (t, 2H, NCH<sub>2</sub>), 4.34 (t, 2H, OCH<sub>2</sub>), 5.27 (s, 2H, CHO), 6.52 (s, 2H, CH<sub>vinyl</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 30.59 (1C, CH<sub>2</sub>), 37.44 (1C, NCH<sub>2</sub>), 47.43 (2C, CH), 55.50 (1C, C(CH<sub>3</sub>)<sub>2</sub>Br), 62.03 (1C, OCH<sub>2</sub>), 80.72 (2C, CHO), 136.33 (2C, CH<sub>vinyl</sub>), 171.66 (1C, CO<sub>ester</sub>), 175.87 (2C, CO<sub>imide</sub>). Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>NO<sub>5</sub>: C, 46.95; H, 4.50; N, 3.91. Found C, 47.00; H, 4.60; N, 3.91. HRMS (ESI): calcd. (M + Na)<sup>+</sup>/<sub>z</sub>, 382.01; (M + K)<sup>+</sup>/<sub>z</sub>, 397.98; found (M + Na)<sup>+</sup>/<sub>z</sub>, 382.0; (M + K)<sup>+</sup>/<sub>z</sub>, 398.0.

## 1.2. Synthesis of MPCS

As a regularly used monomer in our group, MPCS was synthesized according to our previous report,<sup>3</sup> and its purity was confirmed by <sup>1</sup>H 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

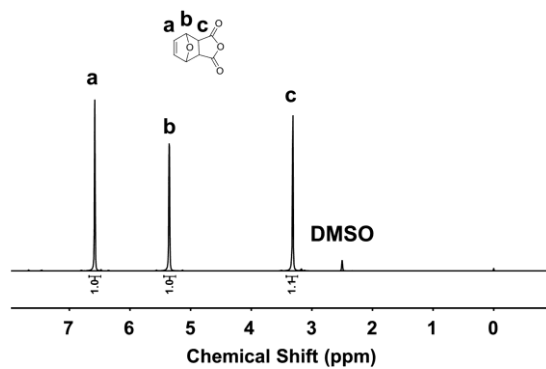


Figure S1. <sup>1</sup>H NMR spectrum of **1** in DMSO-*d*<sub>6</sub>.

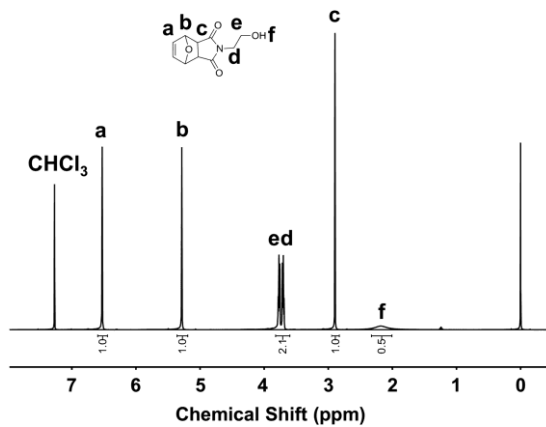


Figure S2. <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub>.

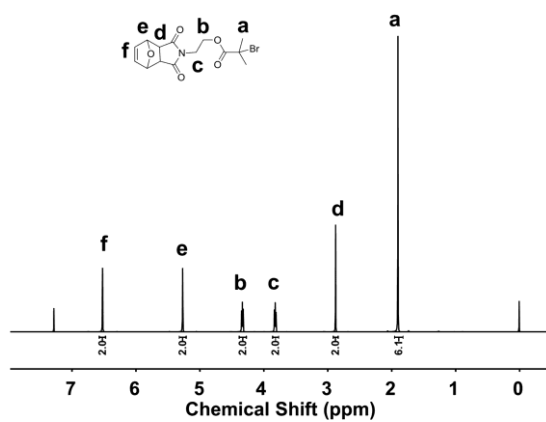


Figure S3. <sup>1</sup>H NMR spectrum of Nb-Br in CDCl<sub>3</sub>.

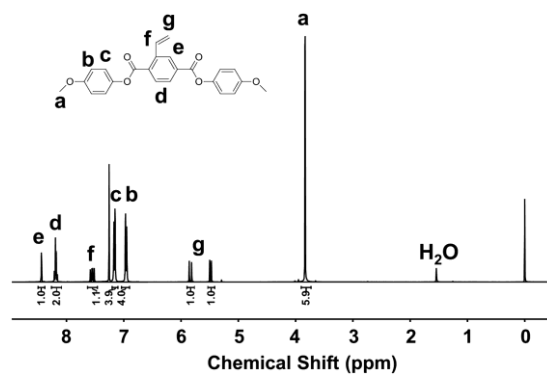


Figure S4.  $^1\text{H}$  NMR spectrum of MPCS in  $\text{CDCl}_3$ .

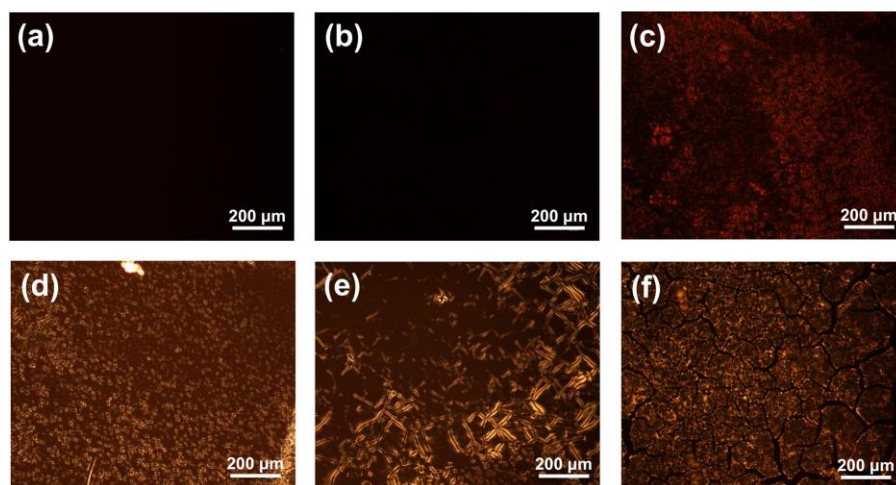


Figure S5. PLM micrographs of MI-PMPCS 1 (a), Brush 1 (b), MI-PMPCS 3 (c), Brush 3 (d), MI-PMPCS 4 (e), and Brush 4 (f) at  $240^\circ\text{C}$ .

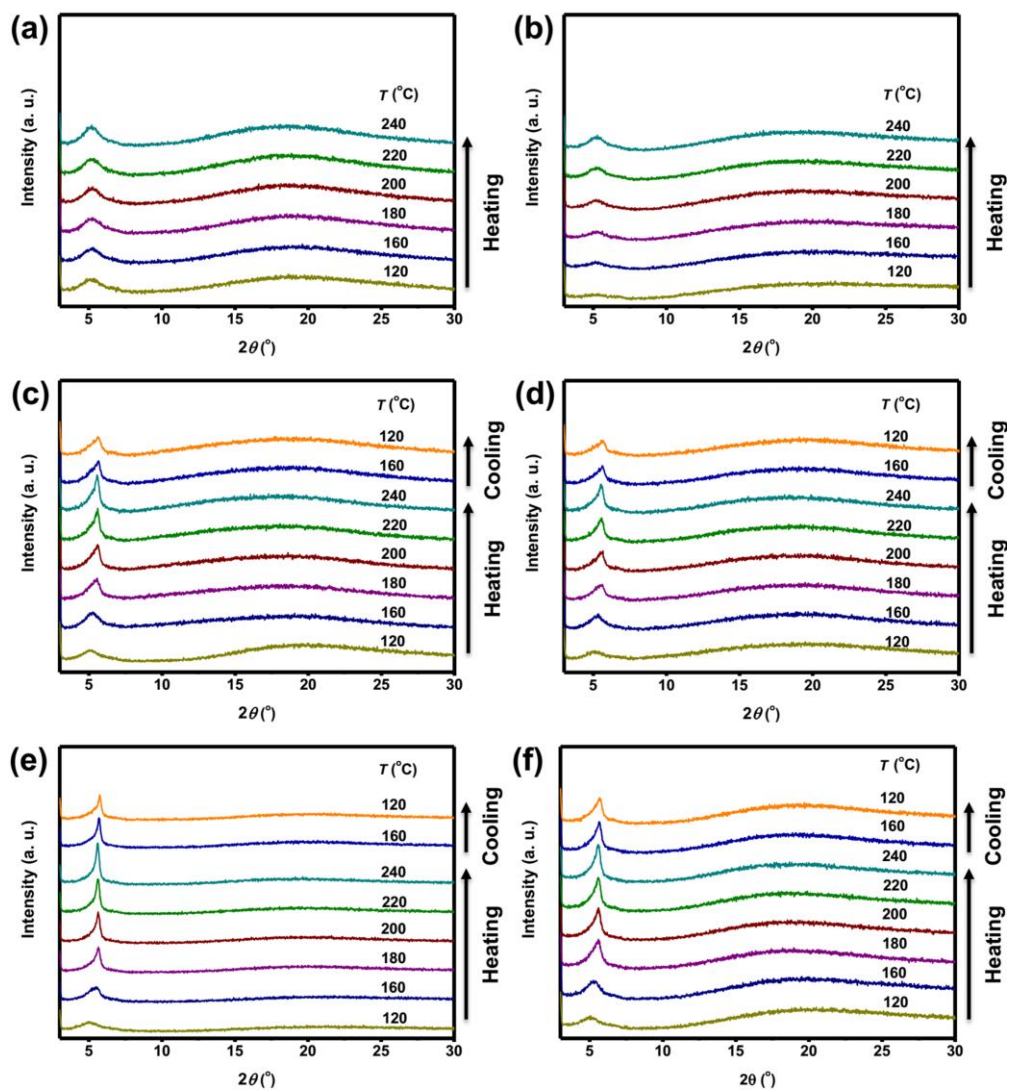


Figure S6. 1D WAXD profiles of MI-PMPCS 1 (a), Brush 1 (b), Brush 2-2 (c), Brush 2-3 (d), MI-PMPCS 4 (e), and Brush 4 (f).

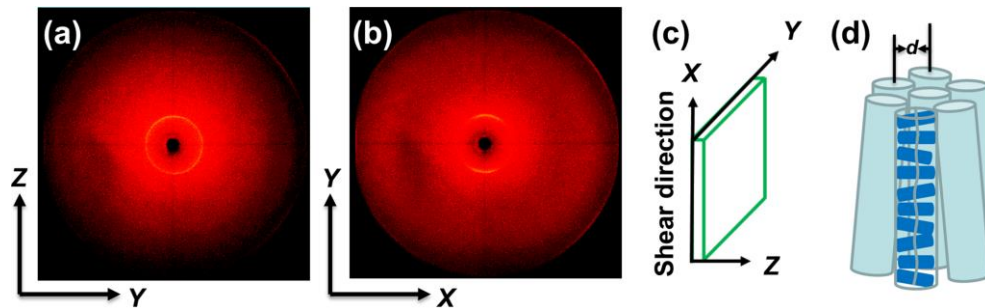


Figure S7. 2D WAXD patterns of a sheared film sample of MI-PMPCS 3 with the X-ray beam along  $X$  (a) and  $Z$  (b) directions, the shearing geometry (c), and the schematic drawing of the  $\Phi_N$  phase formed by MI-PMPCS 3 (d).

#### References:

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