

## Supporting Information for

### **Synthesis and Phase Behavior of a New 2-Vinylbiphenyl-Based Mesogen-Jacketed Liquid Crystalline Polymer with High Glass Transition Temperature and Low Threshold Molecular Weight**

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## Experimental Section

**Synthesis of the Initiator 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine.** The initiator, 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine, was prepared as described in the literature.<sup>1</sup> The <sup>1</sup>H NMR spectrum is shown in Figure S1.

<sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 0.66 (s, 3H, -CH<sub>3</sub>), 1.03 (s, 3H, -CH<sub>3</sub>), 1.16 (s, 3H, -CH<sub>3</sub>), 1.29 (s, 3H, -CH<sub>3</sub>), 1.37–1.59 (m, 9H, -CH<sub>2</sub>-; -CH<sub>3</sub>), 4.75–4.80 (q, 1H, -CH-), 7.20–7.24 (m, 1H, Ar-H), 7.28–7.33 (m, 4H, Ar-H). <sup>13</sup>C NMR (100 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 17.24, 20.35, 23.55, 34.14, 34.47, 40.39, 59.67, 83.11, 126.60, 126.75, 127.98, 145.85. MS (HR-ESI): found (M + H)<sup>+</sup>/<sub>z</sub>, 262.21636; calcd. (M + H)<sup>+</sup>/<sub>z</sub>, 262.21709.

**Synthesis of 4,4'-Bis(methoxy)biphenyl-2-carbaldehyde (MBP).** In this step, a typical Suzuki cross-coupling reaction was used to synthesize the target compound. A mixture of 2-bromo-5-methoxybenzaldehyde (4.04 g, 19.0 mmol), 4-(methoxy)phenylboronic acid (3.92 g, 26.0 mmol), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 5.26 g, 38.0 mmol), and the catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> (1.13 g, 0.980 mmol) in a 250 mL three-necked round-bottomed flask were purged with argon for 30 min to exclude oxygen. Then 100 mL of acetonitrile/water (3/1, v/v) mixture was added, followed by refluxing at 90 °C for 35 h. The mixture was cooled to ambient temperature. After evaporation of acetonitrile under reduced pressure, the residue was extracted with ethyl acetate five times. The organic phase was dried with anhydrous magnesium sulfate and concentrated by rotary evaporator. Subsequently, the crude product was obtained by silica gel column chromatography with dichloromethane/petroleum ether (1/1, v/v) as the eluent. The product was obtained as a pale yellow powder. Yield: 91%. The <sup>1</sup>H NMR spectrum is shown in Figure S2.

<sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 3.86–3.89 (d, 6H, -OCH<sub>3</sub>), 6.97–7.00 (m, 2H, Ar-H), 7.17–7.20 (dd, 1H, Ar-H), 7.26–7.28 (m, 2H, Ar-H), 7.34–7.36 (d, 1H, Ar-H), 7.49 (d, 1H, Ar-H), 9.95 (s, 1H, -CHO). MS (ESI): found (M + H)<sup>+</sup>/<sub>z</sub>, 243.09; calcd. (M + H)<sup>+</sup>/<sub>z</sub>, 243.10.

**Synthesis of the Monomer 4'-(Methoxy)-2-vinylbiphenyl-4-methyl Ether (MVBPE).** In

this step, a typical Wittig reaction was used to obtain the monomer. A solid of methyltriphenylphosphonium bromide (5.37 g, 15.0 mmol) in a 250 mL round-bottomed flask was purged with argon for 30 min and cooled to 0 °C. Then 50 mL of distilled tetrahydrofuran (THF) was added as solvent and stirred for a while. Afterwards, 2.4 M n-BuLi in hexanes (6.00 mL, 15.0 mmol) was added slowly under argon protection. The solution was stirred for 1 h. A mixture of 4,4'-bis(methoxy)biphenyl-2-carbaldehyde (2.69 g, 11.0 mmol) in 40 mL of distilled THF was slowly added over 30 min under argon protection. The reaction mixture was then stirred for another 1 h. The solution was partially concentrated by rotary evaporator, and petroleum ether (500 mL) was added. The suspension was filtered through a silica gel pad. The residue was washed with petroleum ether three times. The organic phase was concentrated and purified by silica gel column chromatography with petroleum ether/dichloromethane (3/1, v/v) as the eluent to obtain the monomer as a white solid. Yield: 87%.

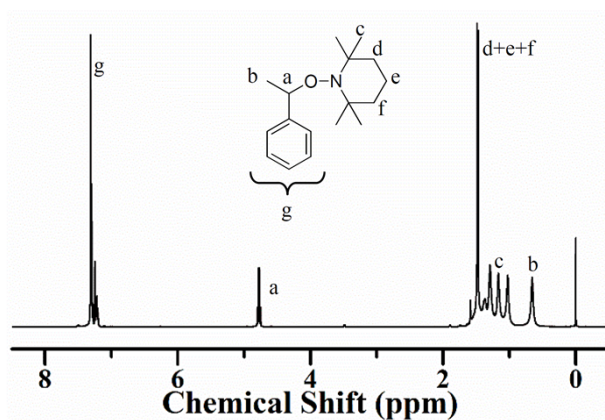
$^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm,  $\text{CDCl}_3$ ): 3.83–3.85 (d, 6H,  $-\text{OCH}_3$ ), 5.17–5.20 (dd, 1H,  $=\text{CH}_2$ ), 5.65–5.70 (dd, 1H,  $=\text{CH}_2$ ), 6.67–6.74 (dd, 1H,  $-\text{CH}=\text{}$ ), 6.86–6.89 (dd, 1H, Ar–H), 6.91–6.94 (m, 2H, Ar–H), 7.14–7.15 (d, 1H, Ar–H), 7.18–7.25 (m, 3H, Ar–H).  $^{13}\text{C}$  NMR (100 MHz,  $\delta$ , ppm,  $\text{CDCl}_3$ ): 55.31, 55.38, 110.64, 113.47, 113.64, 114.62, 130.99, 131.23, 132.98, 133.50, 136.19, 136.90, 158.58, 158.80. MS (HR-ESI): found  $(\text{M} + \text{H})^+/\text{z}$ , 241.12203; calcd.  $(\text{M} + \text{H})^+/\text{z}$ , 241.12285. EA: found C, 79.96; H, 6.72. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_2$ : C, 79.97; H, 6.71.

**Polymerization.** All the polymers were obtained via nitroxide-mediated living radical polymerization (NMP) in anisole. In a typical polymerization procedure, which resulted in PMVBP-1, the monomer MVBP (0.81 g, 3.37 mmol), the initiator 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (36.4 mg, 0.140 mmol), and anisole (0.808 mL) were placed in a polymerization tube with a magnetic stir bar. After stirring and degassing by three freeze-pump-thaw cycles, the tube was sealed under vacuum and subsequently transferred into an oil bath at 130 °C for 48 h. Then it was quenched in liquid nitrogen and broken. The product was diluted with THF and finally precipitated into a large volume of methanol to obtain a white product. To

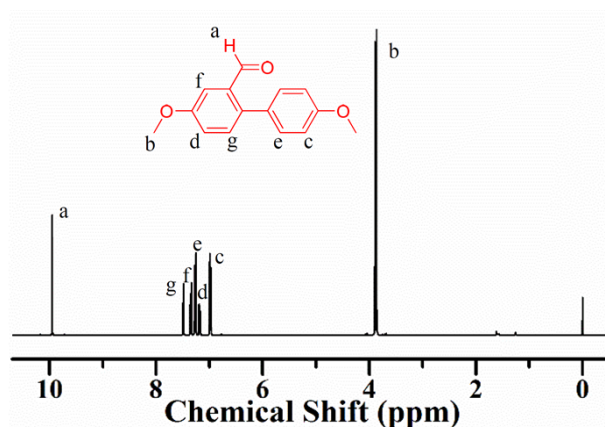
remove the unreacted monomer, the product was redissolved in THF and reprecipitated into methanol until the disappearance of the monomer peak in the GPC curve. After purification, the polymer was dried under vacuum for 24 h. Yield: 50%. Then, by changing the composition of reactants while maintaining the same polymerization time of 48 h, other samples were obtained.

$^1\text{H}$  NMR of PMVBP-4 (400 MHz,  $\delta$ , ppm,  $\text{CDCl}_3$ ): 0.18–1.72 ( $-\text{CH}_2-$ ), 3.18–4.12 ( $-\text{OCH}_3$ ), 5.40–7.20 (Ar-H).

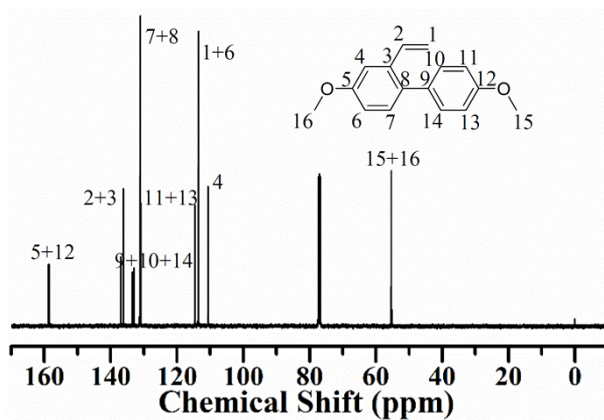
## Results and Discussion



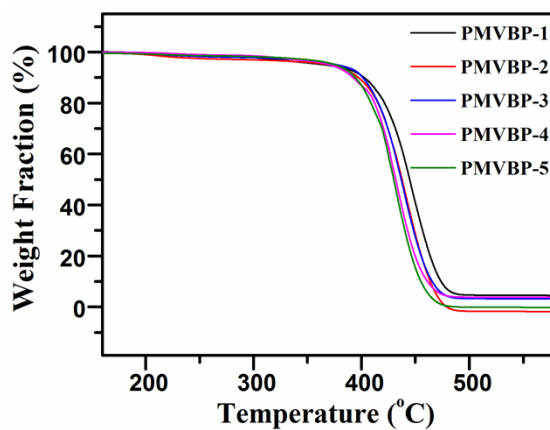
**Figure S1.**  $^1\text{H}$  NMR spectrum of the initiator.



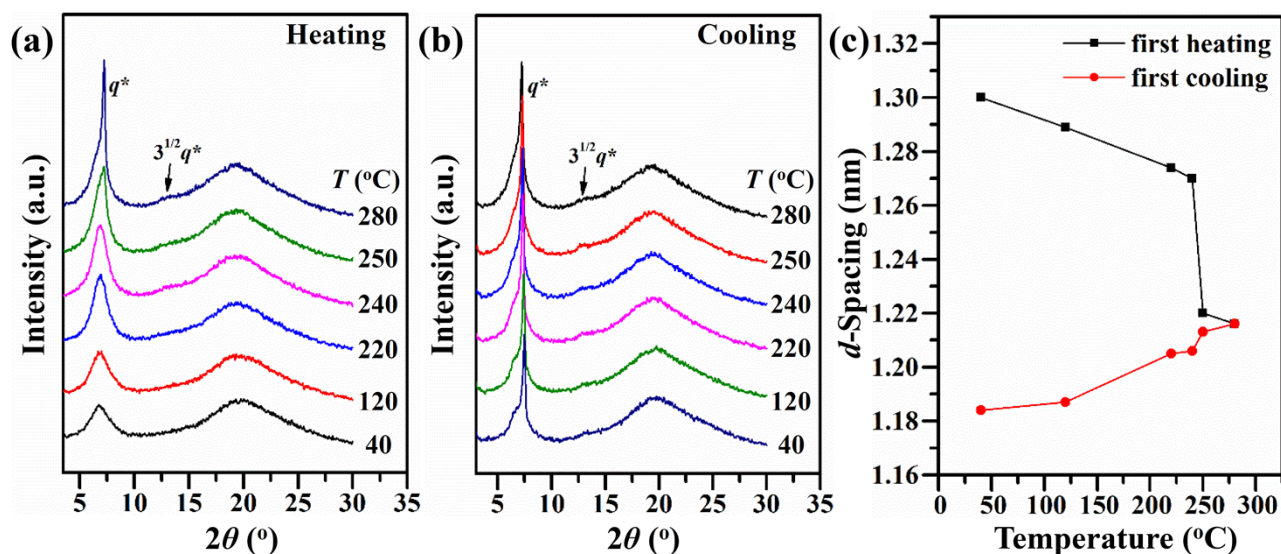
**Figure S2.**  $^1\text{H}$  NMR spectrum of MBP.



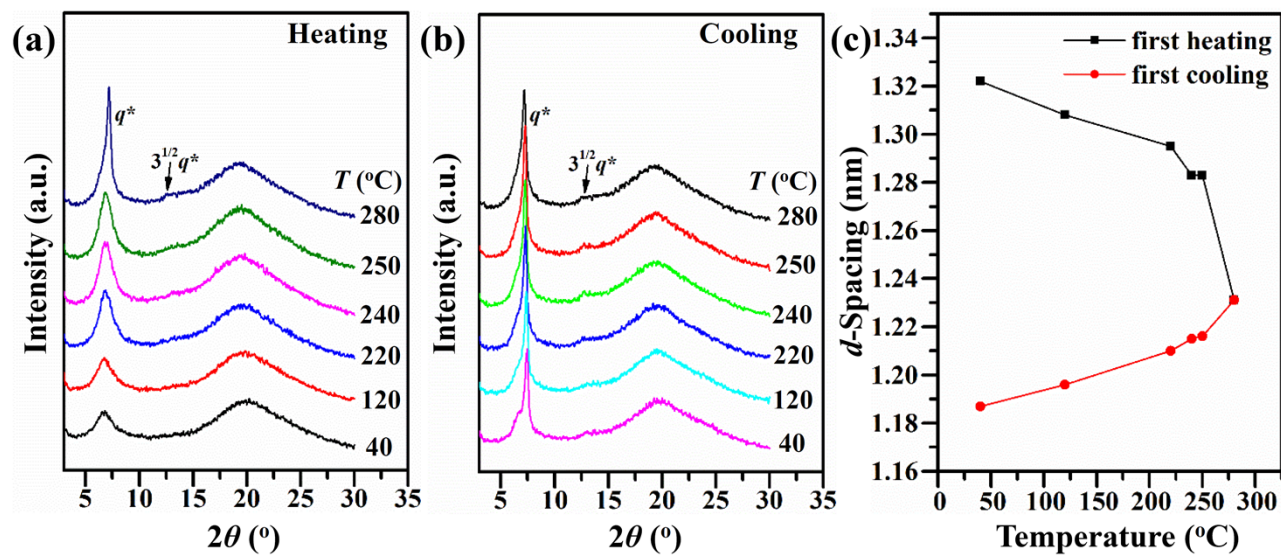
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of MVBP.



**Figure S4.** TGA curves of PMVBPs at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under the nitrogen atmosphere.



**Figure S5.** 1D WAXD patterns of PMVBP-3 during the first heating (a) and the subsequent cooling (b) processes under a nitrogen atmosphere and the  $d$ -spacing of the low-angle halo/peak as a function of temperature (c) during the first heating and the subsequent cooling processes as shown in (a) and (b).



**Figure S6.** 1D WAXD patterns of PMVBP-5 during the first heating (a) and the subsequent cooling (b) processes under a nitrogen atmosphere and the  $d$ -spacing of the low-angle halo/peak

as a function of temperature (c) during the first heating and the subsequent cooling processes as shown in (a) and (b).

### References

- (1) Ghani, M. A. A.; Abdallah, D.; Kazmaier, P. M.; Keoshkerian, B.; Buncel, E. *Can. J. Chem.* **2004**, *82*, 1403-1412.