

## Supporting Information for:

### Crystallization driving thermoresponsive transition of a liquid crystalline polymer

Yuewen Yu,<sup>a</sup> Guangran Shao<sup>a</sup> and Wangqing Zhang<sup>\*,a,b</sup>

<sup>a</sup> Key Laboratory of Functional Polymer Materials of the Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

E-mail: [wqzhang@nankai.edu.cn](mailto:wqzhang@nankai.edu.cn).

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.

#### 1. Synthesis and characterization of the MAS monomer

The MAS monomer was synthesized with the method discussed previously,<sup>S1</sup> and its <sup>1</sup>H NMR spectra is shown in Figure S1.

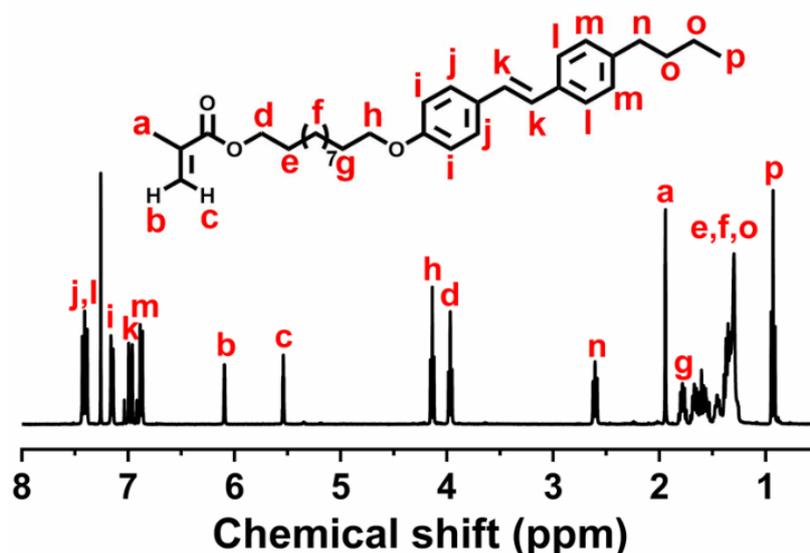


Figure S1. <sup>1</sup>H NMR spectra of MAS monomer

#### 2. Synthesis and characterization of PMAS

PMAS with different degree of polymerization (DP) was synthesized by solution RAFT polymerization of MAS in THF at 70 °C using CDTPA as CTA and AIBN as

initiator as shown in Scheme S1. Taking PMAS<sub>73</sub> as a typical example, the synthetic procedure of PMAS<sub>73</sub> is described. In a 10 mL Schlenk flask with a magnetic bar, MAS (1.104 g, 2.25 mmol), CDTPA (0.010 g, 0.025 mmol), AIBN (1.368 mg, 0.0083 mmol) dissolved in THF (6.30 g) were added. The flask was immersed in ice water and the flask content was degassed by three freeze-pump-thaw cycles to remove oxygen. Then the flask was placed in an oil bath at 70 °C. After polymerization for 10 h with 80.7% monomer conversion, which is determined by <sup>1</sup>H NMR using 1,3,5-trioxane as an internal standard, polymerization was quenched by rapid cooling upon immersion of the flask into iced water. To collect PMAS<sub>73</sub>, the polymer was precipitated in the THF/n-butanol mixture (2/1 by volume), and the precipitate was washed twice with the THF/n-butanol mixture, and finally dried at room temperature under vacuum overnight.

The theoretical molecular weight of PMAS was calculated by Eq S1 listed below.

$$M_{n,th} = [\text{monomer}]_0 \times M_{\text{monomer}} / [\text{RAFT}]_0 \times \text{Conversion} + M_{n, \text{RAFT}} \quad (\text{S1})$$

**Scheme S1.** The synthesis of the PMAS by RAFT polymerization.

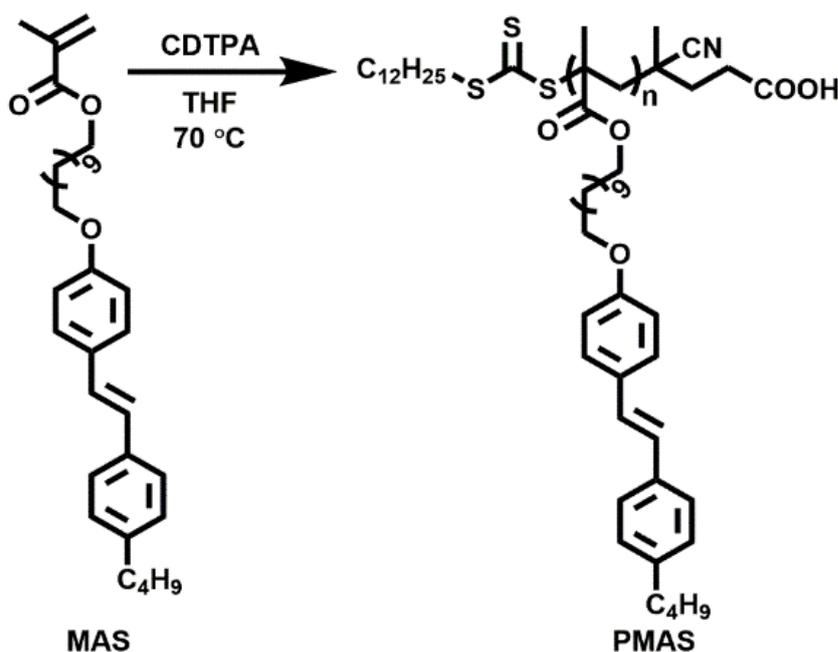
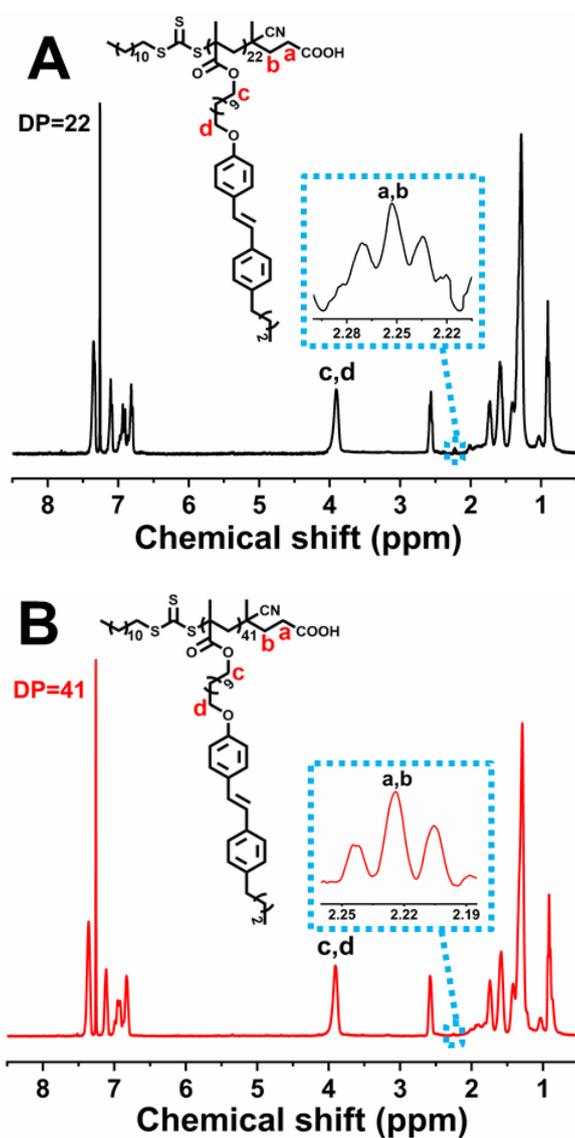
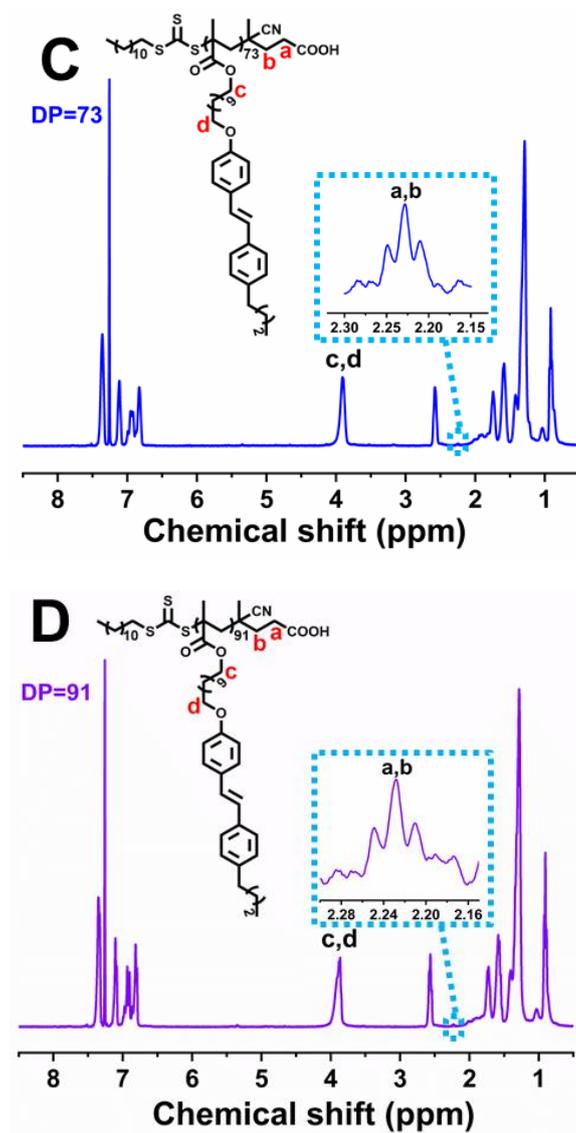


Figure S2 shows the  $^1\text{H}$  NMR of the synthesized PMAS with different DPs. By comparing the chemical shifts at  $\delta \approx 2.23$  ppm corresponding to the RAFT moieties and  $\delta = 3.88$  ppm assigned to the PMAS backbone, the molecular weight  $M_{n,\text{NMR}}$  of PMAS is obtained.





**Figure S2.**  $^1\text{H}$  NMR spectra of PMAS with different DPs: (A) PMAS<sub>22</sub>, (B) PMAS<sub>41</sub>, (C) PMAS<sub>73</sub>, (D) PMAS<sub>91</sub>.

Figure S3 shows the TGA or DTG of the synthesized PMAS<sub>73</sub>. At temperature below 300 °C, traced or almost no weight loss is detected. The weight loss occurs at temperature from 300 to 490 °C and reaches to 94% at 490 °C, caused by the cleavage of covalent bonds of polymer.

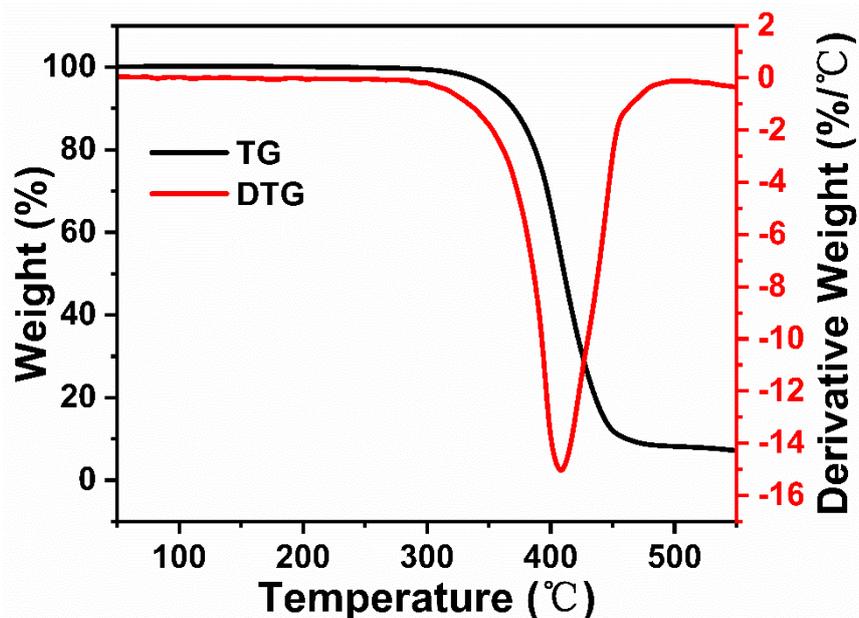
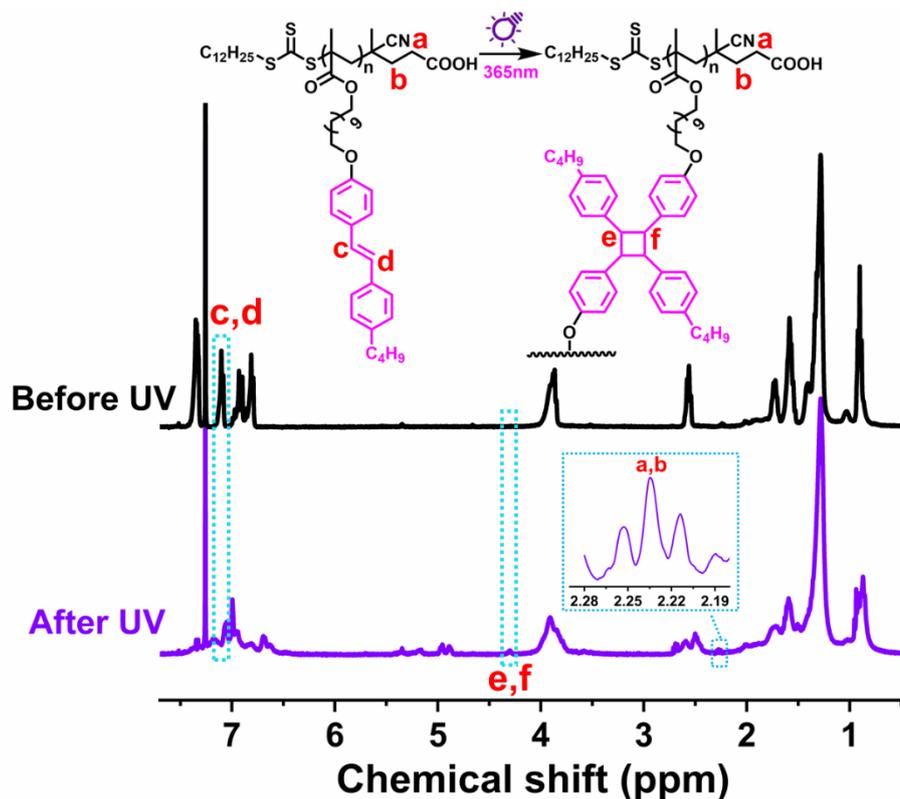


Figure S3. TGA and DTG curves of PMAS<sub>73</sub>.

### 3. Photodimerization of PMAS

PMAS was dissolved in 1,4-dioxane at 65°C to make 20 wt% solution. The PMAS solution was exposed to 365 nm ultraviolet light (UV light, intensity  $\approx 15 \text{ mW/cm}^2$ ) for different time under vigorous stirring. Figure S3 shows the  $^1\text{H}$  NMR spectra of PMAS<sub>73</sub> before and after 365 nm UV light irradiation for 3 h. After UV light irradiation, a new absorption at  $\delta = 4.31 \text{ ppm}$  appears, indicating the photodimerization. By comparing the chemical shifts at  $\delta = 2.23 \text{ ppm}$  corresponding to the RAFT moieties and  $\delta = 4.31 \text{ ppm}$  assigned to the four-membered rings, the dimerization degree (DD) of PMAS, 92%, can be approximately obtained. It is found that DD by  $^1\text{H}$  NMR is higher than those calculated by UV-vis analysis as discussed subsequently.



**Figure S4.**  $^1\text{H}$  NMR spectra of PMAS<sub>73</sub> before and after 365 nm UV light irradiation for 3 h, recorded in  $\text{CDCl}_3$ .

The UV-vis spectra of PMAS<sub>73</sub> in 1,4-dioxane under 365 nm UV light irradiation (15 mW/cm<sup>2</sup>) for different time are shown in Figure 5B. From the absorbance at 307 nm of the stilbene group before ( $A_0$ ) and after UV light irradiation ( $A_t$ ) for certain time, the dimerization degree (DD) of PMAS can be approximately obtained following Eq S2 listed below, and the results are summarized in Figure 5C.

$$\text{DD} = 1 - A_t/A_0 \quad (\text{S2})$$

#### 4. Solubility and thermoresponse of PMAS

The solubility of 1.0 wt% PMAS in various solvents at three temperatures, 5 °C, 25 °C and the temperature close to the boiling point of the solvent, was judged by the transparency of the solution with naked eyes. Through this, the suitable solvent was

chosen. The UCST of the PMAS thermoresponsive polymer was determined by turbidity analysis at 500 nm on a Varian 100 UV-vis spectrophotometer equipped with a thermo-regulator ( $\pm 0.1$  °C) with the heating/cooling rate at  $1.0$  °C  $\text{min}^{-1}$ , in which UCST was determined at 50% change of the transmittance. In order to obtain a well-dispersed polymer solution, ultrasonic dispersion and refrigeration were sometimes necessary.

## **5. Formation of PMAS particles**

The PMAS particles were prepared by dissolving the polymer in a given solvent at temperature above UCST to make 0.20 wt% solution. Then, temperature decreased below UCST and turbid dispersion was observed. The turbid dispersion was deposited on a piece of copper grid (for TEM observation) or silicon wafer (for SEM observation), and solvent was removed by evaporated at room temperature, and then PMAS particles formed on the copper grid or silicon wafer were checked.

## **References**

- (S1) Asaoka, S.; Uekusa, T.; Tokimori, H.; Komura, M.; Iyoda, T.; Yamada, T.; Yoshida, H. *Macromolecules* **2011**, *44*, 7645-7658.