

Supporting Information

Post Polymerization Modification of Poly(Dihydropyrimidin-2(1H)-thione)s via the Thiourea-haloalkane Reaction to Prepare Functional Polymers

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Experimental Section

1. Materials

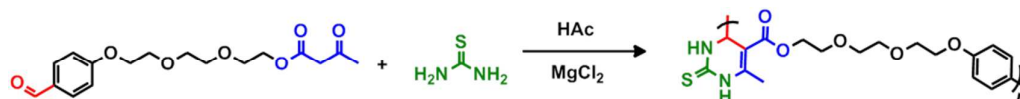
5-Bromo-1-pentene (Ouhe, 98%), 3-mercapto-1,2-propanediol (J&K, 99%), 6-chloro-1-hexyne (J&K, 99%), 3-phenylpropargyl chloride (Sigma, 97%), thiourea (Ouhe, $\geq 99.0\%$), sodium iodide (NaI, Heowns, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aladdin, 99%) and 1,1,4,7,7-pentamethyldiethylenetriamine (J&K, 98%) were used as purchased. 2-(2-(2-(4-Formylphenoxy)ethoxy)ethoxy)ethyl 3-oxobutanoate¹ and 1-azido-3-propanol² were synthesized as previous literatures. CuBr was washed by acetic acid prior to use.

2. Instrumental Analysis

Gel permeation chromatography (GPC) analyses of polymers were performed using N,N-dimethyl formamide (DMF) containing 50 mM LiBr as the eluent. The GPC system was a Shimadzu LC-20AD pump system consisting of an auto injector, a MZ-Gel SDplus 10.0 μm guard column ($50 \times 8.0 \text{ mm}$, 10^2 \AA) followed by a MZ-Gel SDplus 5.0 μm bead-size column ($50 - 10^6 \text{ \AA}$, linear) and a Shimadzu RID-10A refractive index detector and a Shimadzu SPD-10A UV detector. The system was calibrated with narrow molecular weight distribution polystyrene standards ranging from 200 to 10^6 g mol^{-1} . ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400MHz) spectrometer for all samples. UV-Visible absorption spectra were recorded on UV/Vis/NIR Perkin-Elmer lambda750 spectrometer (Waltham, MA, USA) using quartz cuvettes of 1 cm path length. The fluorescence measurements were

obtained on a Perkin-Elmer LS-55 spectrometer equipped with quartz cuvettes of 1 cm path length. Different scanning calorimetry (DSC) was performed using TA instruments Q2000 operated at a scanning rate of 10 °C/min. The thermal stability was measured with a TA-Q50 TGA under air atmosphere.

3. Biginelli polymerization



The AB monomer 2-(2-(2-(4-formylphenoxy)ethoxy)ethoxy)ethyl 3-oxobutanoate (10.1 g, 30 mmol) was dissolved with thiourea (4.56 g, 60 mmol) in acetic acid (15 mL). Then magnesium chloride (0.28 g, 3 mmol) was added to the mixture. The system was stirred at 100 °C for 9 h. Samples were taken periodically for ¹H NMR (Fig. S1) and GPC analyses for conversion and molecular weight determination, respectively. The final polymer was simply purified by precipitation in water and ultrasonic washing with water and diethyl ether followed by filtration.

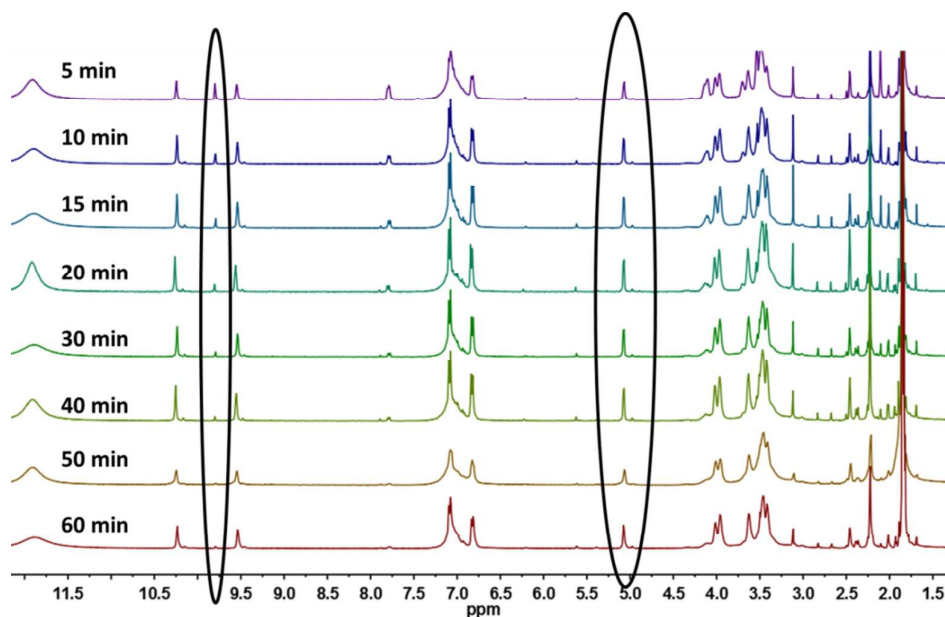
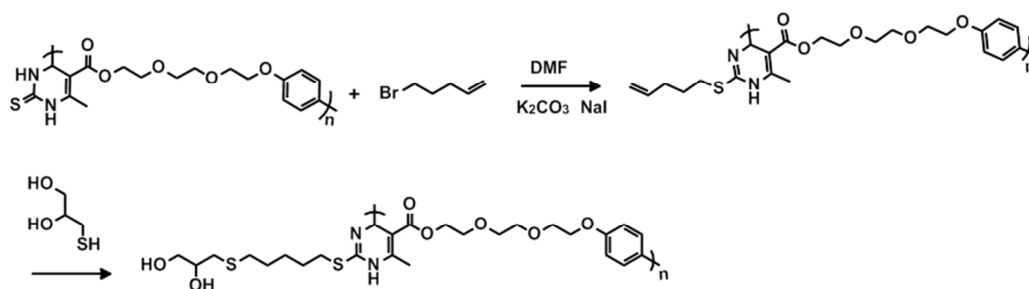


Fig. S1. ¹H NMR analysis (DMSO-d₆, 400 MHz) of the crude of the condensation

polymerization of 2-(2-(2-(4-formylphenoxy)ethoxy)ethoxy)ethyl 3-oxobutanoate and thiourea.

4. Post-polymerization modification (PPM)

4.1. PPM of P1 with 5-bromo-1-pentene and the followed thiol-ene reaction



P1 (756 mg, 2 mmol) was dissolved with 5-bromo-1-pentene (358 mg, 2.4 mmol) in 10 mL of dry DMF. Potassium carbonate (331 mg, 2.4 mmol) and sodium iodide (446 mg, 2.4 mmol) were added to the mixture. The system was stirred at 80 °C for 12 h. The final polymer (P2) was simply purified by precipitation into cold water, and then ultrasonic washing with water and diethyl ether for three times followed by filtration as a brown powder (780 mg, ~ 87.6%).

P2 (89 mg, 0.2 mmol) was dissolved with 3-mercapto-1,2-propanediol (43 mg, 0.4 mmol) in 2 mL of THF. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 16 mg, 0.06 mmol) was added to the mixture. After purging with nitrogen for 30 min, the system was stirred at 25 °C under a UV lamp (365 nm) for 12 h. The final polymer (P2') was simply purified by precipitation into diethyl ether, and then ultrasonic washing with diethyl ether for three times followed by filtration as a yellow powder (95 mg, ~ 85.6%).

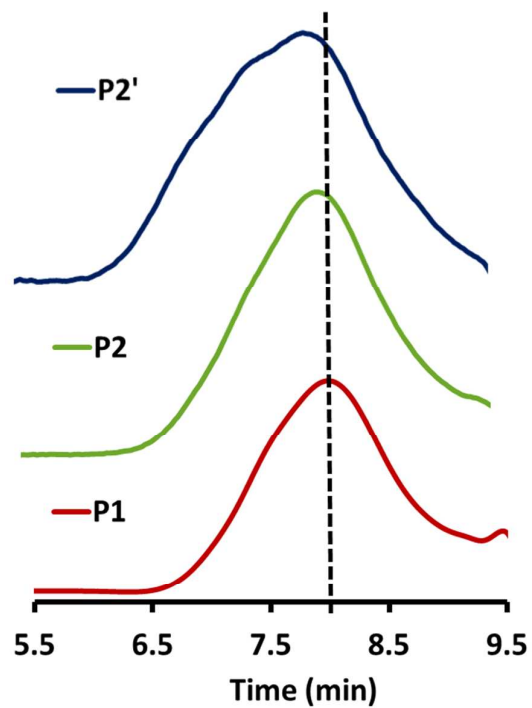


Fig. S2. GPC curves of P1 ($M_{n\text{GPC}} \sim 23100$, PDI ~ 1.45), P2 ($M_{n\text{GPC}} \sim 29000$, PDI ~ 1.44) and P2' ($M_{n\text{GPC}} \sim 33000$, PDI ~ 1.74).

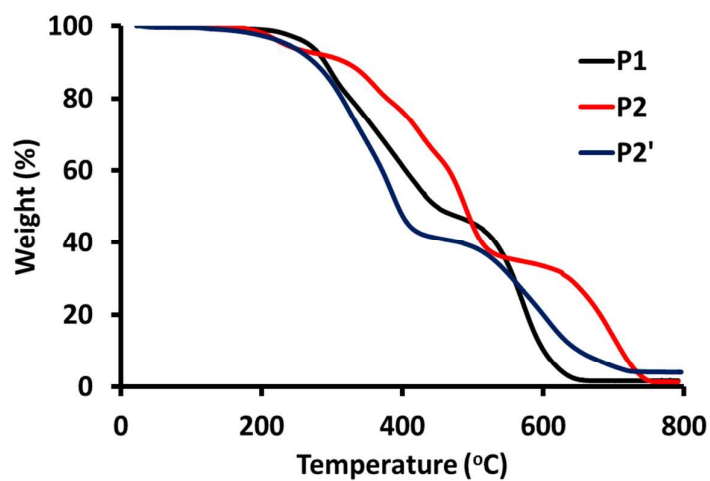
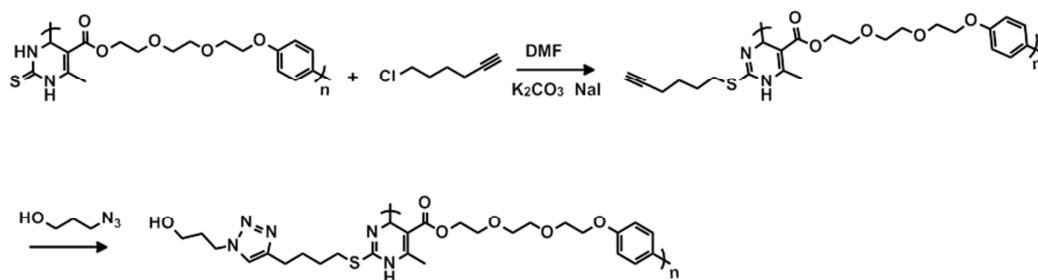


Fig. S3. TGA curves of P1, P2 and P2'.

4.2. PPM of P1 with 6-chloro-1-hexyne and the followed CuAAC click reaction



P1 (756 mg, 2 mmol) was dissolved with 6-chloro-1-hexyne (279 mg, 2.4 mmol) in 10 mL of dry DMF. Potassium carbonate (331 mg, 2.4 mmol) and sodium iodide (446 mg, 2.4 mmol) were added to the mixture. The system was stirred at 80 °C for 12 h. The final polymer (P1-alkynyl) was simply purified by precipitation into cold water, and then ultrasonic washing with water and diethyl ether for three times followed by filtration as a brown powder (854 mg, 93.2%).

P3 (92 mg, 0.2 mmol) was dissolved with 1-azido-3-propanol (30 mg, 0.3 mmol) in 2 mL of THF. CuBr (44 mg, 0.3 mmol) and 1,1,4,7,7-pentamethyldiethylenetriamine (66 μ L, 0.6 mmol) were added to the mixture. After purging with nitrogen for 30 min, the system was stirred at 25 °C for 12 h. The crude polymer was simply precipitated into water, and the collected powder was washed by water for three times to remove metal salt, and then by diethyl ether to get the final polymer (P3') as a yellow powder (101 mg, ~91.0%).

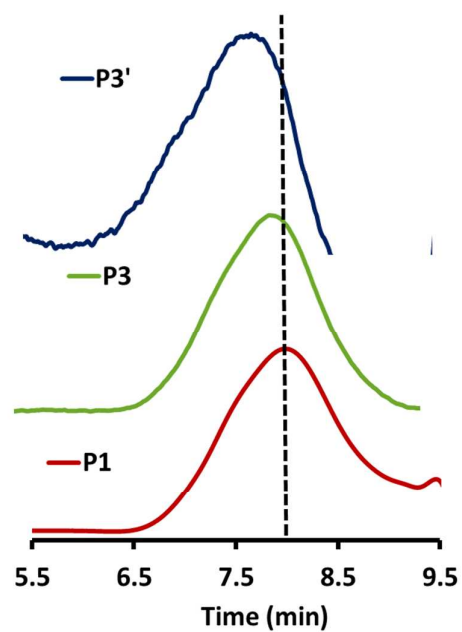


Fig. S4. GPC curves of P1, P3 ($M_{n\text{GPC}} \sim 29200$, $\text{PDI} \sim 1.45$) and P3' ($M_{n\text{GPC}} \sim 44800$, $\text{PDI} \sim 1.45$).

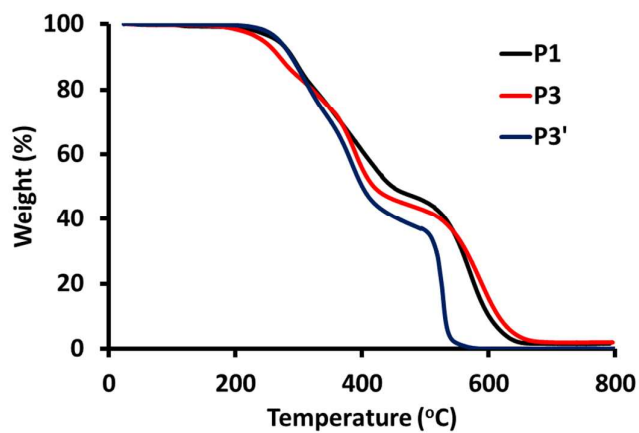
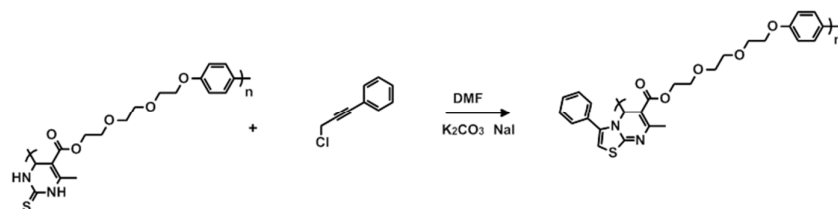


Fig. S5. TGA curves of P1, P3 and P3'.

4.3. PPM of P1 with 3-phenylpropargyl chloride



P1 (378 mg, 1 mmol) was dissolved with 3-phenylpropargyl chloride (180 mg, 1.2 mmol) in 10 mL of dry DMF. Potassium carbonate (166 mg, 1.2 mmol) and sodium iodide (223 mg, 1.2 mmol) were added to the mixture. The system was stirred at 80 °C for 12 h. The final polymer (P4) was simply purified by precipitation into cold water, and then ultrasonic washing with water and diethyl ether for three times followed by filtration as a brown powder (452 mg, 91.9%).

P4 has an absorption peak at 390 nm in the ultraviolet absorption spectrum while the maximum absorption peak of original polymer (P1) is at 310 nm (**Fig. S6**).

P4 has an excitation wavelength at 448 nm and an emission wavelength at 518 nm, while P1 has an excitation wavelength at 400 nm and an emission wavelength at 480 nm (**Fig. S7**).

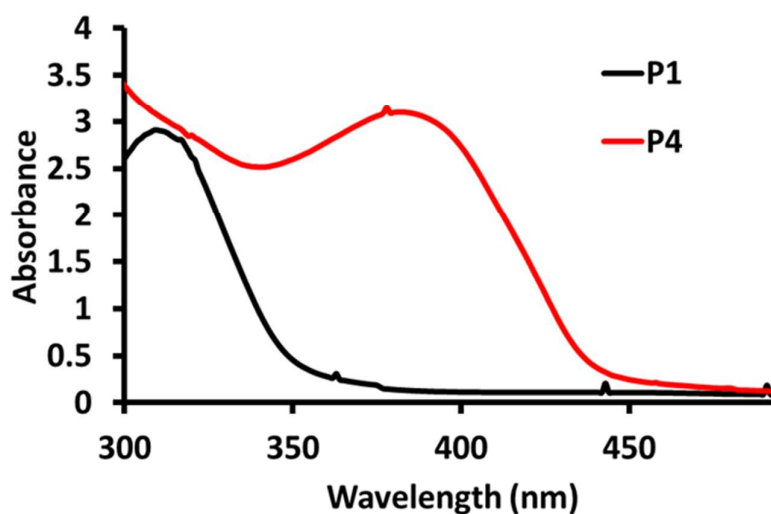


Fig. S6. Ultraviolet absorption spectra of P1 and P4.

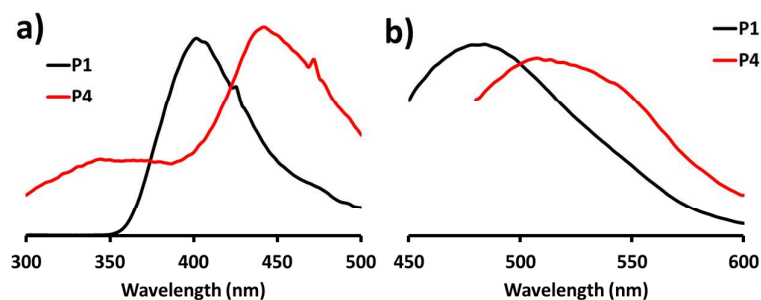


Fig. S7. a) Excitation spectra of P1 and P4. b) Emission spectra of P1 and P4.

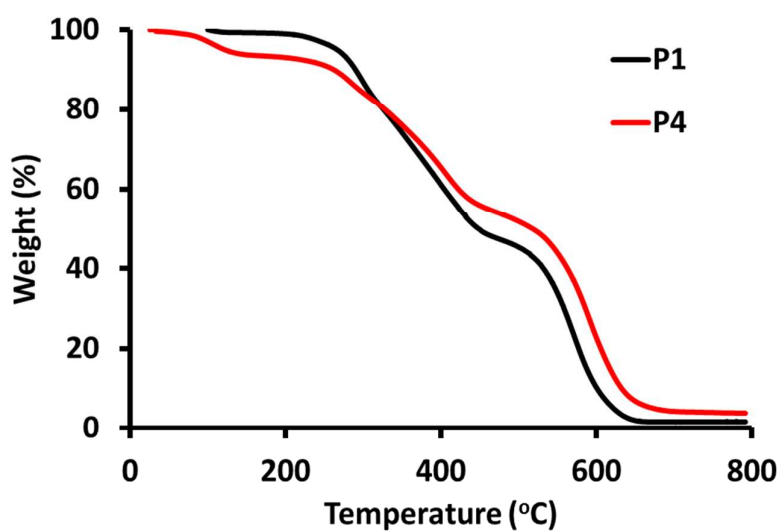


Fig. S8. TGA curves of P1 and P4.

4. Different scanning calorimetry (DSC) analyses of different polymers

DSC was performed using TA instruments Q2000 operated at a scanning rate of 10 °C/min from 0 °C to 200 °C for six polymers (P1, P2, P2', P3, P3' and P4) (**Fig. S9**).

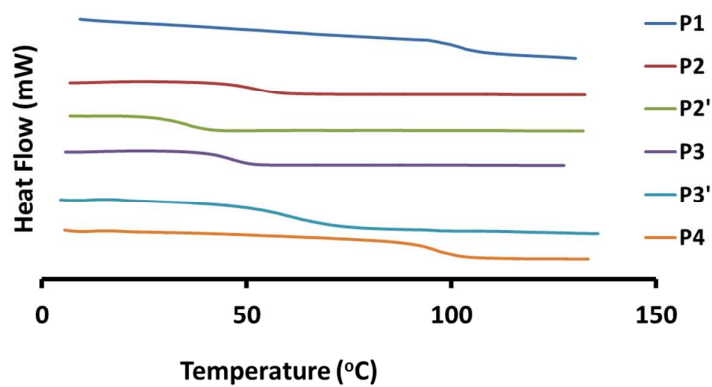


Fig. S9. DSC traces for heating (10 °C/min) of six polymers.

Reference

1. Zhao, Y.; Yu, Y.; Zhang, Y.; Yang, B.; Zhang, Q.; Wei, Y. *Polym. Chem.* **2015**, DOI: 10.1039/c5py00684h.
2. Badiang, J. G.; Aubé, J. J. *Org. Chem.* **1996**, 61, (7), 2484-2487.