

## Supporting Information

# Tunable interfacial adhesion based on orthogonal supramolecular forces

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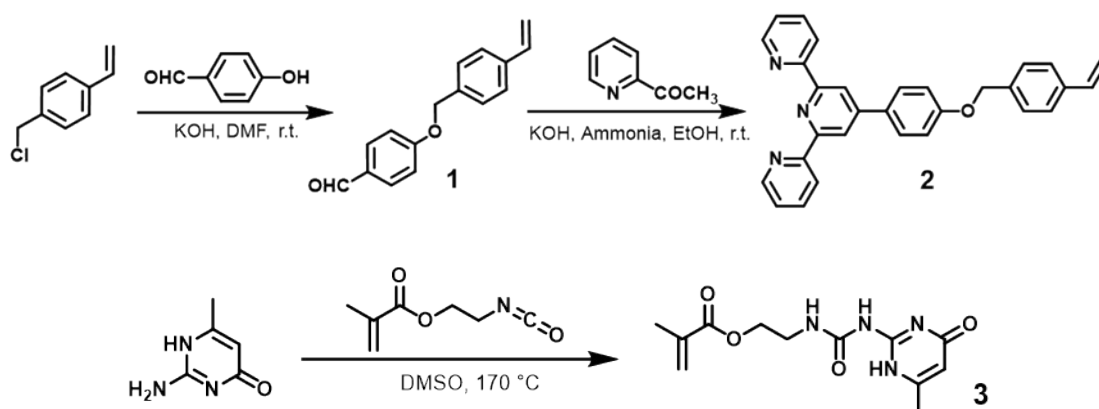
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## 1. Materials and instruments

All these materials were of analytical grade and were used without further purification. Compounds **1** and **2** were both synthesized according to literature procedures.<sup>1,2</sup> For analysis of chemical structures, <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded through a Bruker Advance 400 MHz spectrometer. High-resolution electrospray ionization mass spectra (ESI-MS) was performed via using a Bruker microOTOF II. The molecular masses of polymers were recorded by using gel permeation chromatography (GPC) measurements which were conducted in tetrahydrofuran (THF) on an Elite P230pII HPLC system. Fourier transform infrared (FT-IR) spectra were collected by using an FT interferometer (Equinox 55, Bruker, Germany). The thermal properties of the polymer were examined through applying a thermogravimetric analyzer (TGA, 4000 PerkinElmer) under N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup> ranging from 0 to 600 °C. Differential scanning calorimetry (DSC, Q2000, TA) was manipulated at a rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. Scanning electron microscopic (SEM) images of freeze-dried gels were obtained using a Hitachi SU8010 instrument. The rheological properties of the gels were measured via using a rheometer MCR 302 (Anton Paar, Austria), with a 25 mm diameter parallel plate attached to a transducer. The frequency sweep was performed over the frequency range of  $\omega = 0.1 - 100 \text{ rad s}^{-1}$  at a fixed strain of 1% at 25 °C. The tensile tests of the gels were investigated using an electronic universal testing machine (CMT4104, Shenzhen Sans Testing Machine Co.) with a tensile rate of 6 mm min<sup>-1</sup>. The gels **G1-G5** were prepared by immersing the **P1**, **P3**, **P4** and **P5** in Zn<sup>2+</sup> solutions (MeCN/CHCl<sub>3</sub>: 1/10, vol/vol), while **P2** was dissolved in pure CHCl<sub>3</sub> solutions at room temperature. For these studies gels were all 20 mm long, 5 mm wide, and 1 mm in thick. As for adhesive gels (**AG1-AG7**), the detailed preparation steps were shown in below. Therein, the preparation steps of adhesive gels **AG1**, **AG3**, **AG4** and **AG5** were similar, thus, take **AG1** as an example here. Firstly, adhesive gel **AG1** was fabricated by contacting gel **G1** together when Zn<sup>2+</sup> solutions (MeCN/CHCl<sub>3</sub>: 1/10) was added onto the interface. Apart from this, adhesive gel **AG2** was produced via mutual adhesion of gel **G2**. With regard to adhesive gels **AG6** as well as **AG7**, they were generated through adding distinct types of competitive molecules. Cyclen solutions (1.74×10<sup>-4</sup> mol/L, dissolved in CHCl<sub>3</sub>) was injected into adhesive gel **AG3** by using needles, adhesive gel **AG6** was thus produced. Besides, adhesive gel

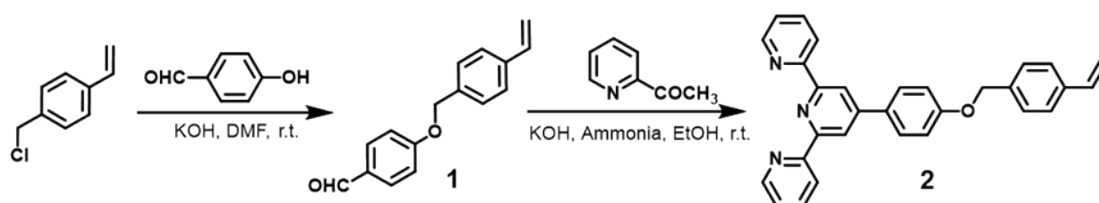
AG7 was generated upon the addition of UPy monomer solutions ( $2.50 \times 10^{-4}$  mol/L, dissolved in  $\text{CHCl}_3$ ), likewise, the solutions was injected into adhesive gel AG3.

## 2. Synthesis and characterization of compounds 2 and 3



**Scheme S1** Synthetic routes of compounds **1** and **2**.

### 2.1 Synthesis and characterization of compound 2



First, 4-hydroxybenzaldehyde (2.45 g, 20.0 mmol) and 4-vinylbenzyl chloride (3.58 g, 20.0 mmol) were dissolved in DMF (50.0 mL), then the solid KOH (1.12 g, 20.0 mmol) was added into the solution. At room temperature, the mixture was stirred for 12 h. To precipitate the product, the water (600 mL) was added, also used to wash the product. Next, the product was dried by the vacuum at 60 °C. While the redundant 4-vinylbenzyl chloride was eliminated via triturating the product in hexane (50.0 mL). The final product was washed with additional hexane, dried by positive air flow to give compound **2**.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 – 8.61 (m, 6H), 7.87 (t,  $J = 6.9$  Hz, 4H), 7.48 – 7.40 (m, 4H), 7.37 – 7.32 (m, 2H), 7.10 (d,  $J = 8.6$  Hz, 2H), 6.74 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.78 (d,  $J = 17.6$  Hz, 1H), 5.27 (d,  $J = 10.9$  Hz, 1H), 5.13 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,

CDCl<sub>3</sub>) δ 172.85, 167.33, 156.75, 154.48, 148.32, 136.11, 125.83, 106.69, 63.07, 38.76, 18.95, 18.29. HRMS (ESI<sup>+</sup>) Calcd for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 442.1910, found: 464.1716.

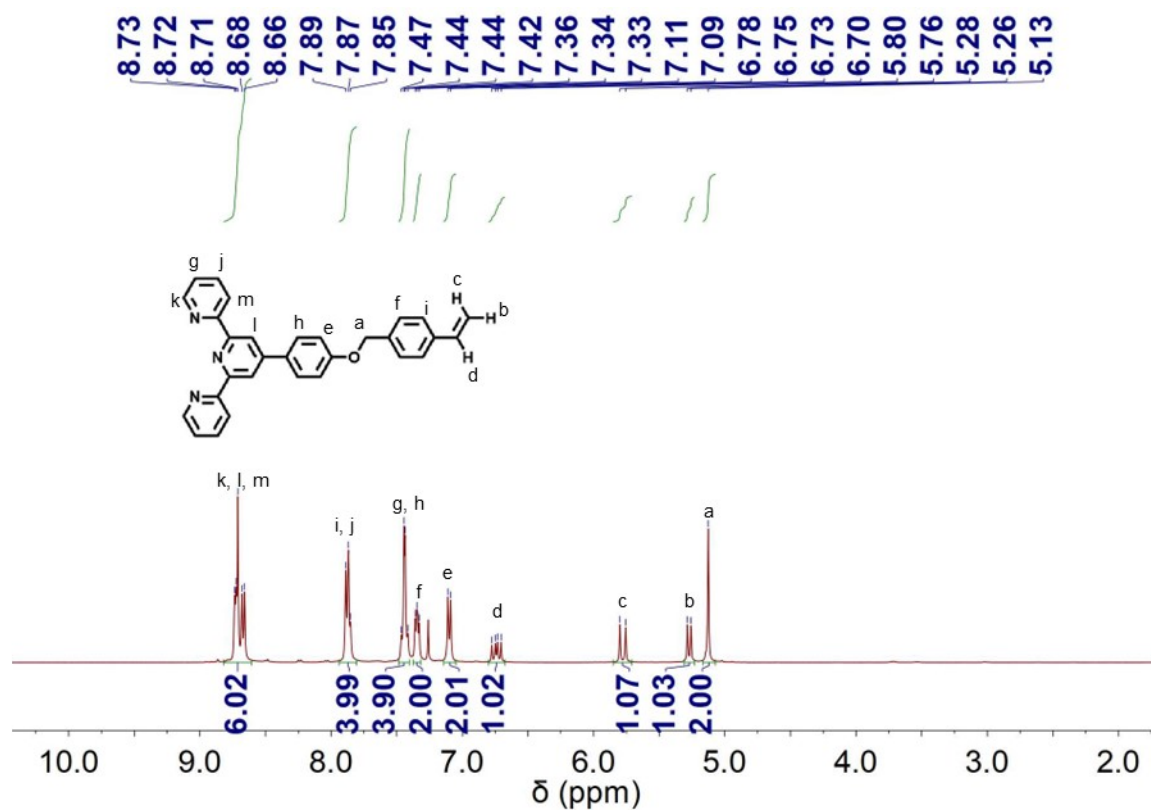


Figure S1  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 298 K) of 2.

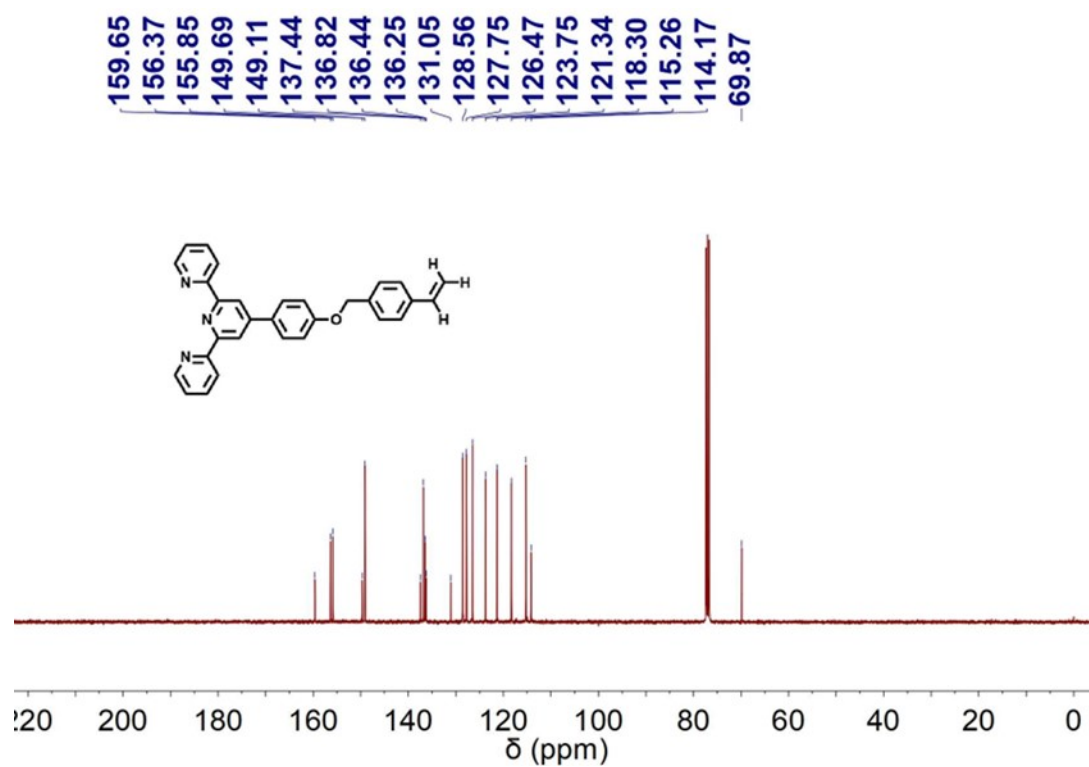
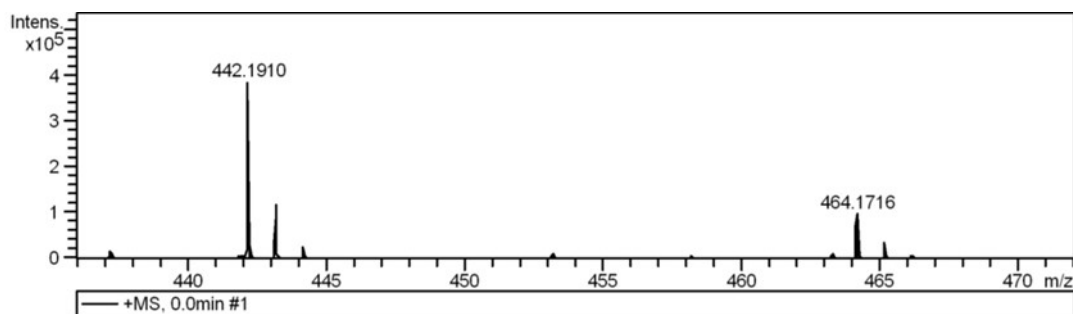
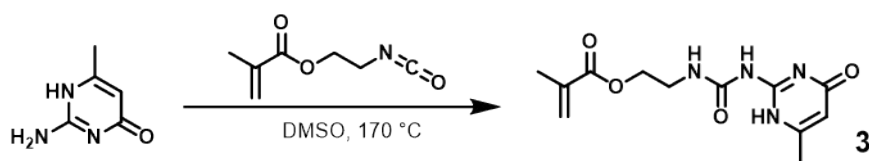


Figure S2  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 298 K) of 2.



**Figure S3** HR-ESI+-MS spectrum of **2**.

## 2.2 Synthesis and characterization of compound **3**



First, with heating to 170 °C, 6-methylisocytosine (2.94 g, 23.5 mmol) was dissolved in DMSO. Then the flask containing solution was taken out. Upon the addition of 2-isocyanatoethyl methacrylate (ICEMA) (4.00 g, 21.8 mmol) into flask, the reaction became violently, then the water was used to quench it which inhibited the polymerization. The precipitated white solid was washed with cyclohexane. Finally, cyclohexane was employed to washed the product, then the compound **3** was dried under reduced pressure.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.96 (s, 1H), 11.95 (s, 1H), 10.50 (s, 1H), 6.17 (s, 1H), 5.78 (s, 1H), 5.54 (s, 1H), 4.26 (t,  $J = 5.7$  Hz, 2H), 3.57 (q,  $J = 5.7$  Hz, 2H), 2.23 (s, 3H), 1.93 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.85, 167.33, 156.75, 154.48, 148.32, 136.11, 125.83, 106.69, 63.07, 38.76, 18.95, 18.29. HRMS (ESI $^+$ ) Calcd for  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_4$   $[\text{M}+\text{Na}]^+$ : 303.1069, found: 303.1123.

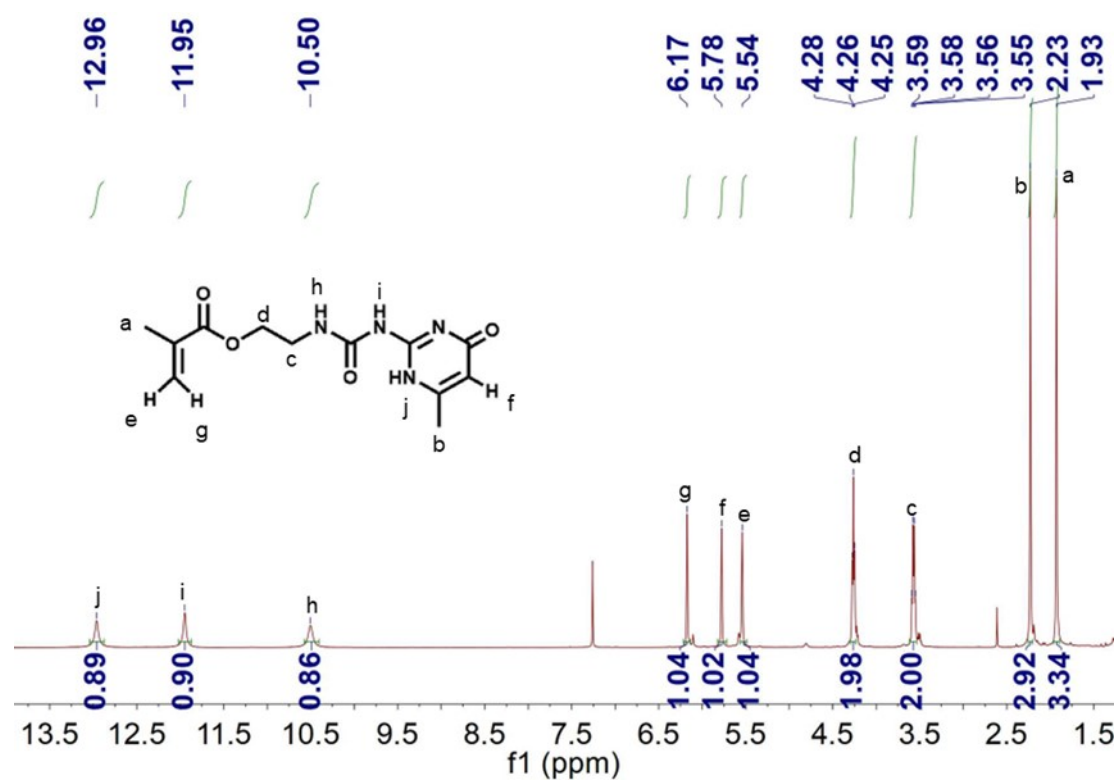


Figure S4 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of 3.

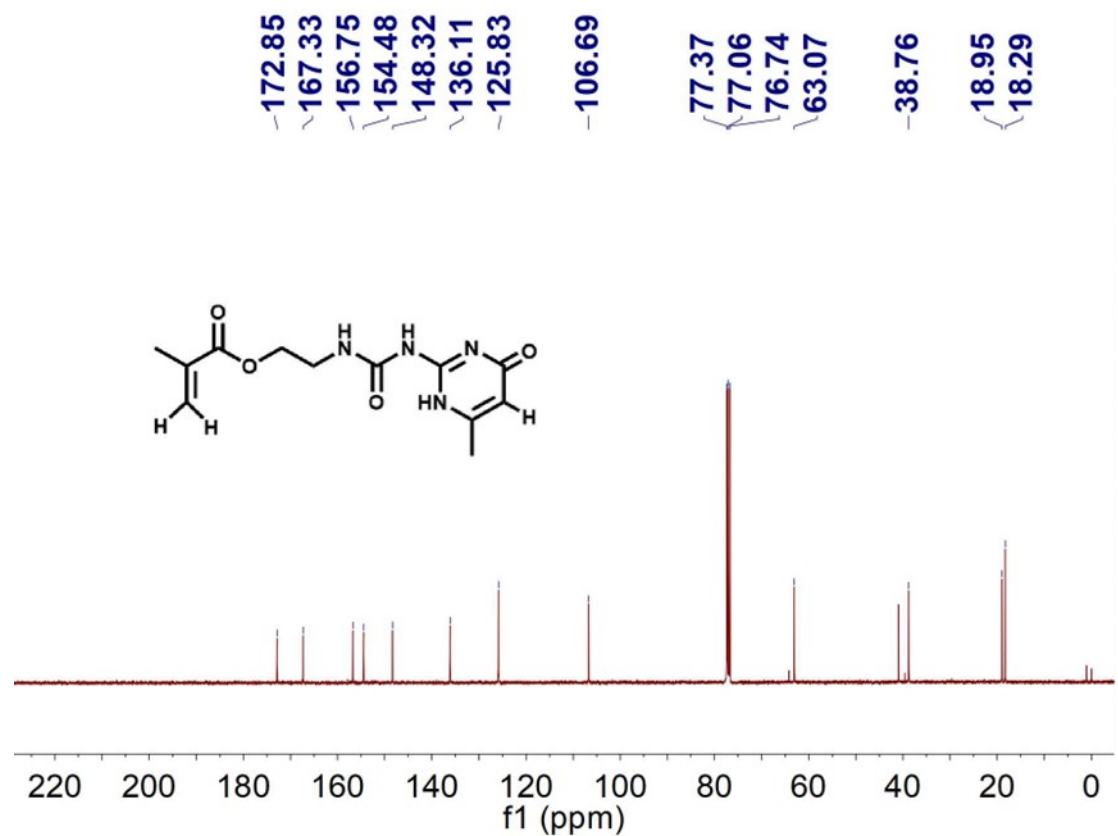
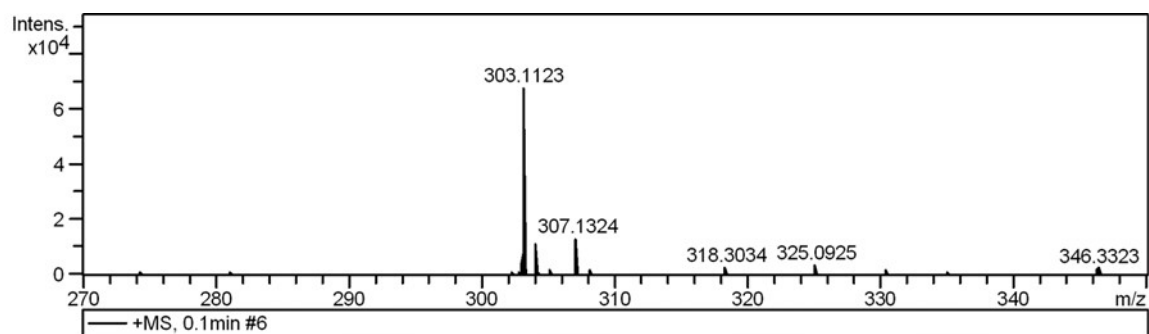
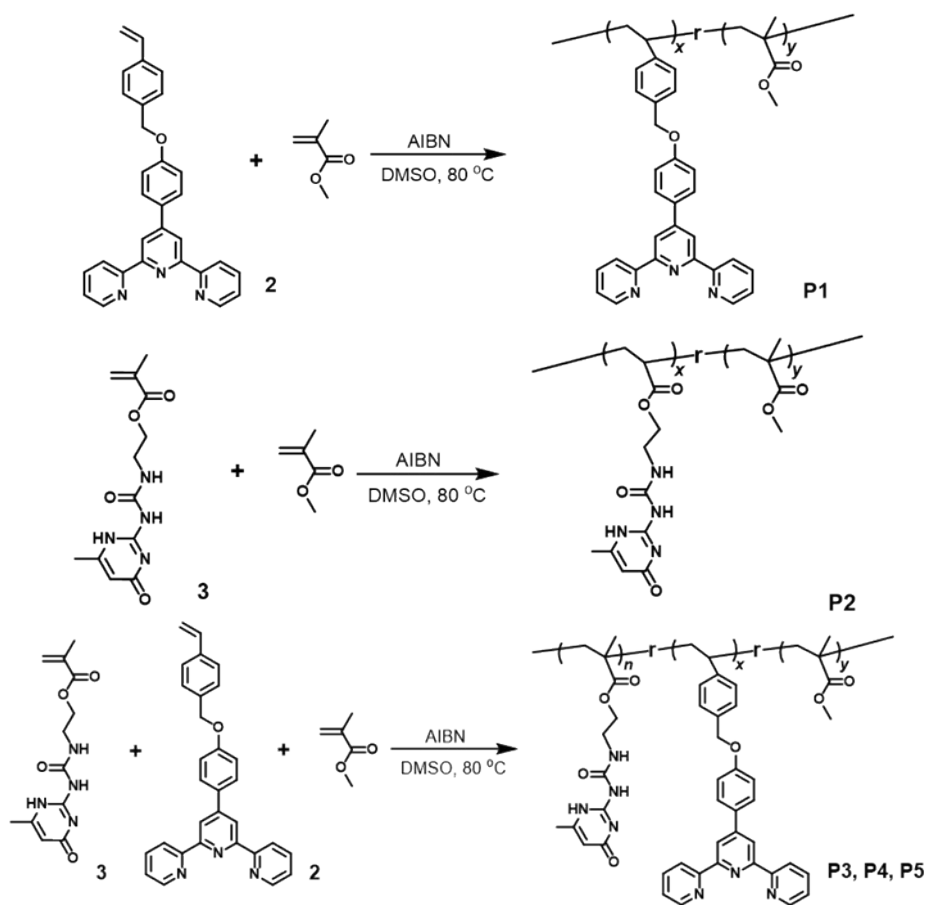


Figure S5 <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of 3.



**Figure S6** HR-ESI<sup>+</sup>-MS spectrum of **3**.

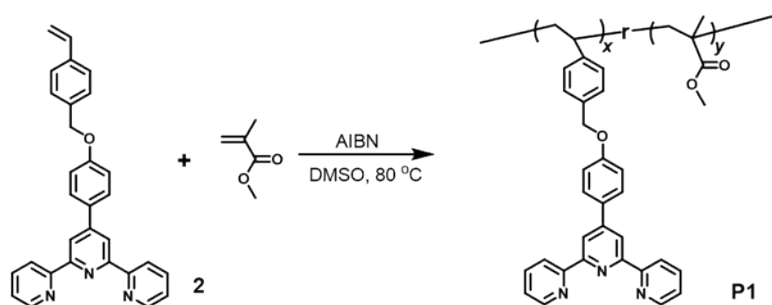
### 3. Synthesis and characterization of polymers **P1**, **P2**, **P3**, **P4** and **P5**



**Scheme S2** Synthetic routes of polymers **P1**, **P2**, **P3**, **P4** and **P5**



### 3.1 Synthesis and characterization of polymer **P1**



Polymer **P1** was prepared from compound **2** and methyl methacrylate by free radical polymerization. The molar ratio of compound **2** to methyl methacrylate was controlled at 1:100. DMSO as solvent, then compound **2** (397 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 900 mmol) was added. Meanwhile, azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen ( $N_2$ ) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. Next, the resulting solution was added into methanol (500 mL), then the precipitated yellow solid was obtained through vacuum filtration. These two steps were repeated for three times, finally, polymer **P1** was produced after being dried with vacuum.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.70 (d,  $J = 20.4$  Hz, 1H), 7.89 (s, 3H), 7.06 (s, 2H), 5.06 (s, 2H), 3.59 (s, 59H), 2.61 (s, 62H), 2.07 – 1.50 (m, 49H), 1.42 (s, 6H), 1.20 (s, 4H), 1.05 – 0.45 (m, 58H).

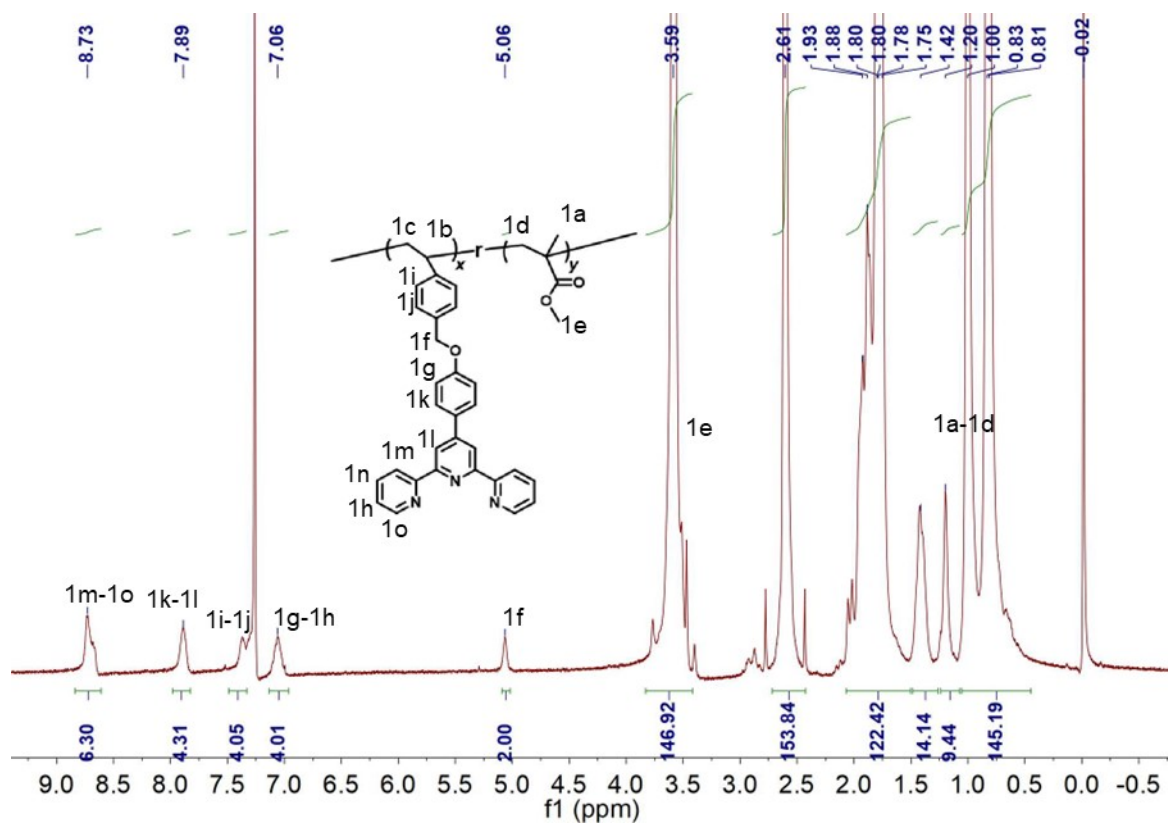


Figure S7  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 298 K) of P1.

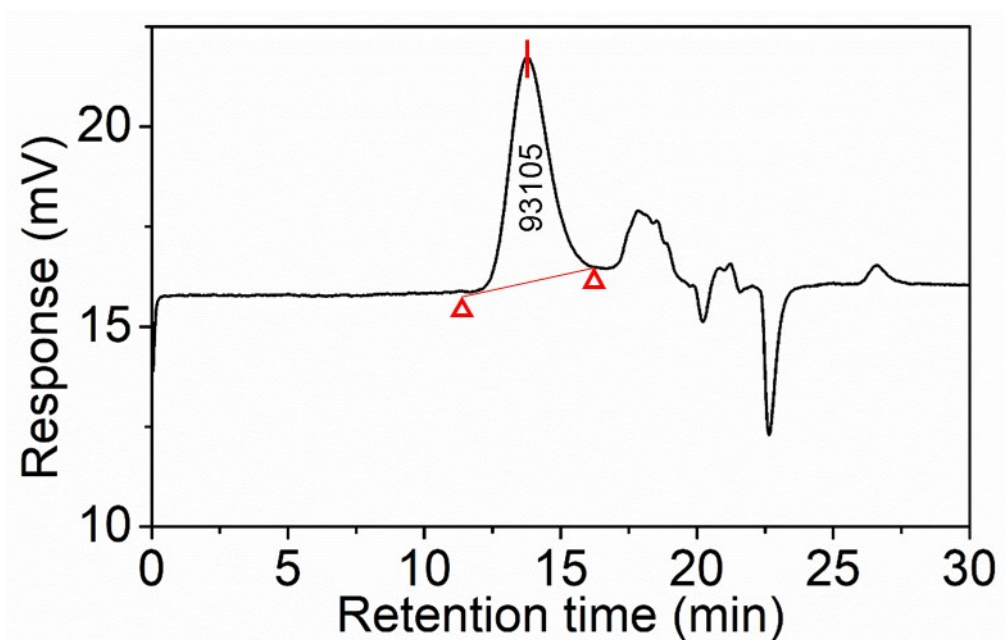


Figure S8 GPC trace of P1.

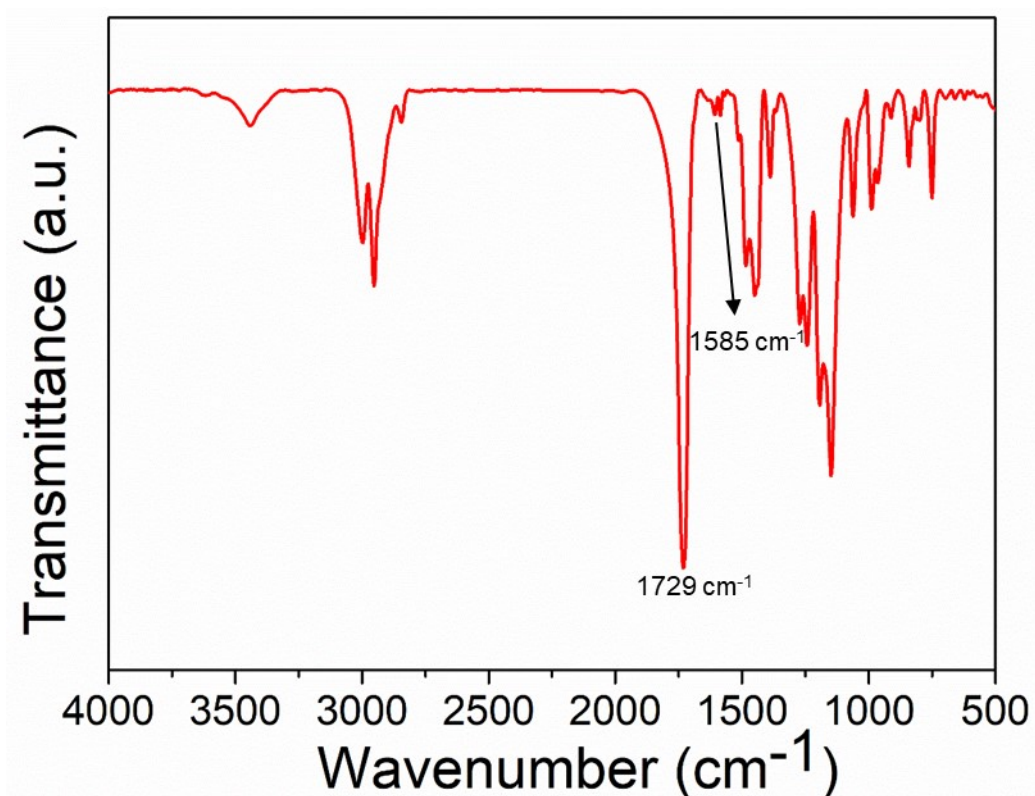
$M_n$	$M_w$	$M_p$	$M_z$	$\bar{D}$
$5.51 \times 10^4$	$1.02 \times 10^5$	$9.31 \times 10^4$	$1.61 \times 10^5$	1.85

**Table S1** GPC analysis of **P1**.

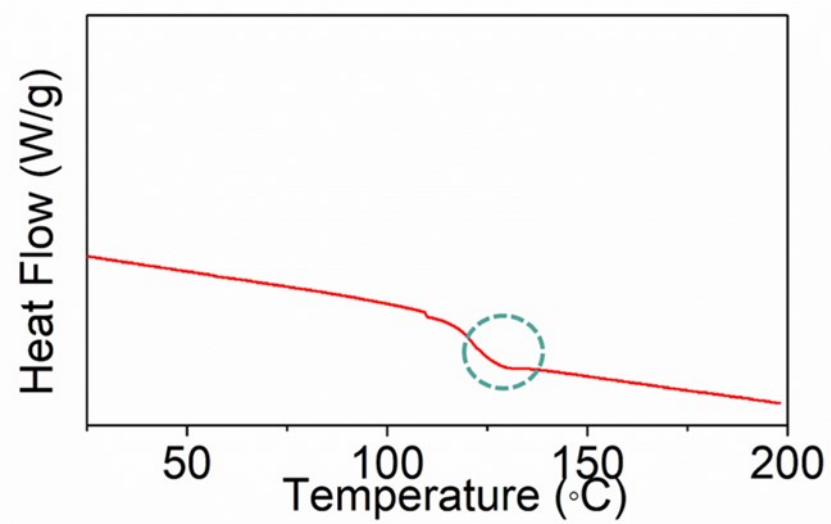
The ratio of x/y was (2)/(146.92/3), namely 2/48.97, for polymer **P1**, as calculated based on the integrations of the peaks corresponding to protons H<sup>1f</sup>, H<sup>1e</sup>. According to  $M_n$  and the ratio of x/y, the values of x and y were calculated to be 19.06 and 466.9.

Values	x	y
<b>P1</b>	19.06	466.9

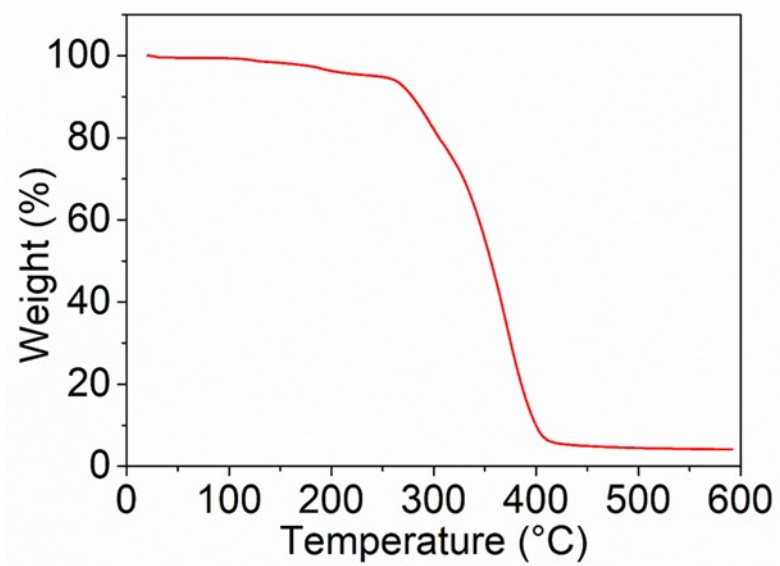
**Table S2.** The calculated values of x and y for **P1**.



**Figure S9** FT-IR spectrum of **P1**.

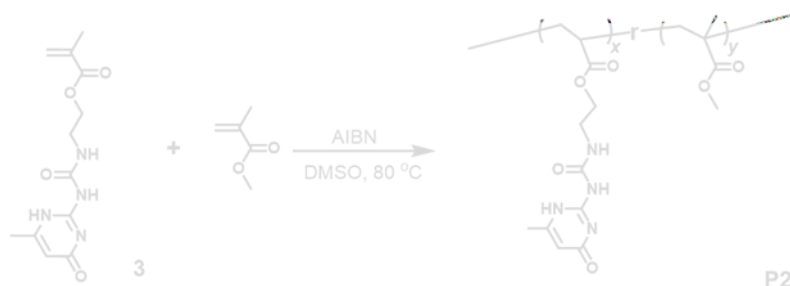


**Figure S10** DSC spectrum of **P1**.



**Figure S11** TGA trace of **P1**.

### 3.2 Synthesis and characterization of polymer **P2**



Polymer **P2** was prepared from compound **3** and methyl methacrylate by free radical polymerization. The molar ratio of compound **3** to methyl methacrylate was also controlled at 1:100. DMSO as solvent, then compound **3** (252 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 90.0 mmol) was simultaneously added. And azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen (N<sub>2</sub>) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. The resulting solution was added into methanol (500 mL), then the precipitated white solid was obtained by using vacuum filtration. These two steps were again repeated for three times, then polymer **P2** was produced after being dried with vacuum.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.95 (s, 1H), 11.95 (s, 1H), 10.46 (s, 1H), 5.82 (s, 1H), 4.07 (s, 1H), 3.58 (s, 400H), 2.73 – 0.50 (m, 848H).

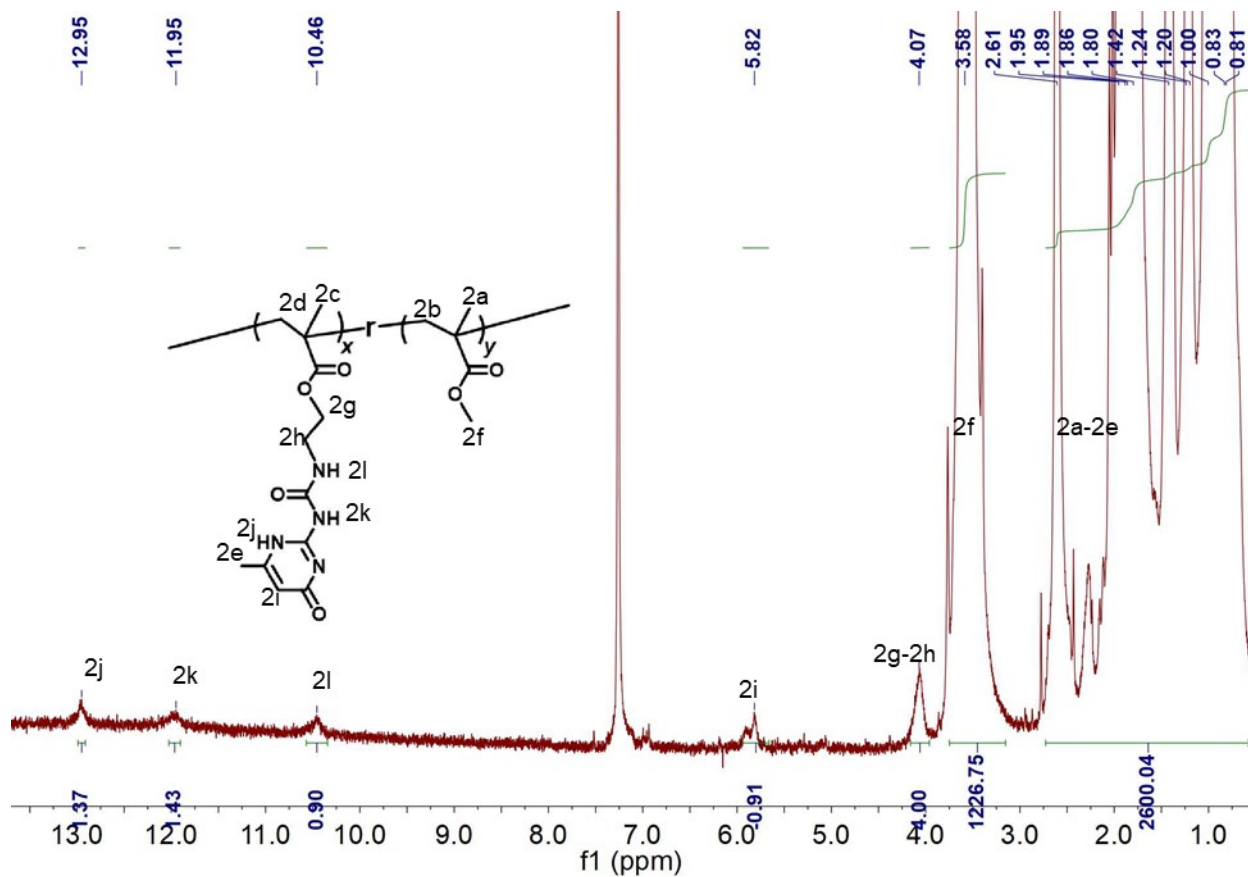
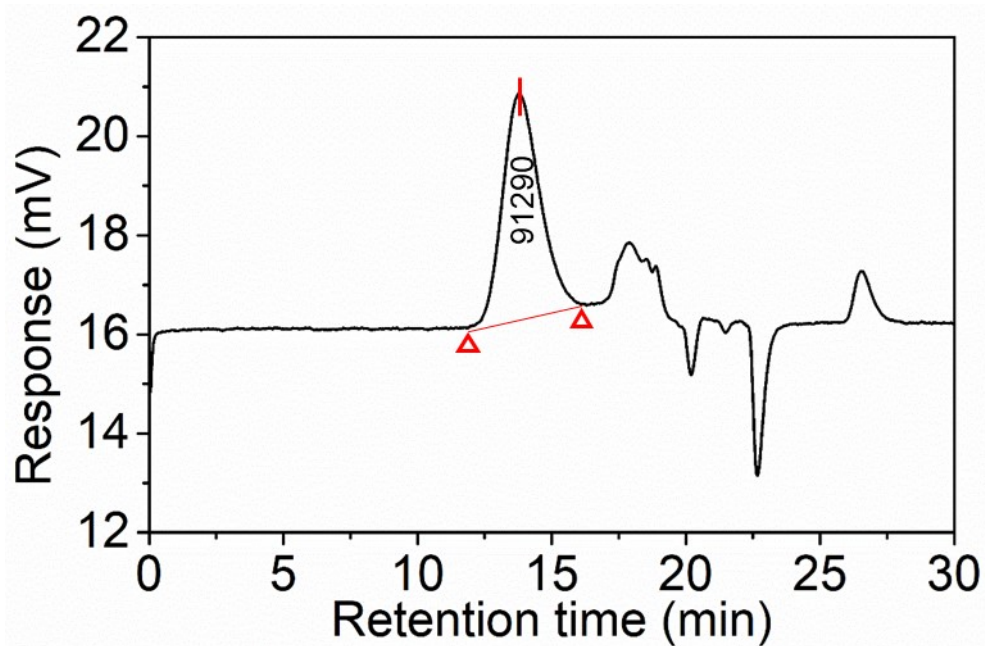


Figure S12 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of P2.



**Figure S13** GPC trace of **P2**.

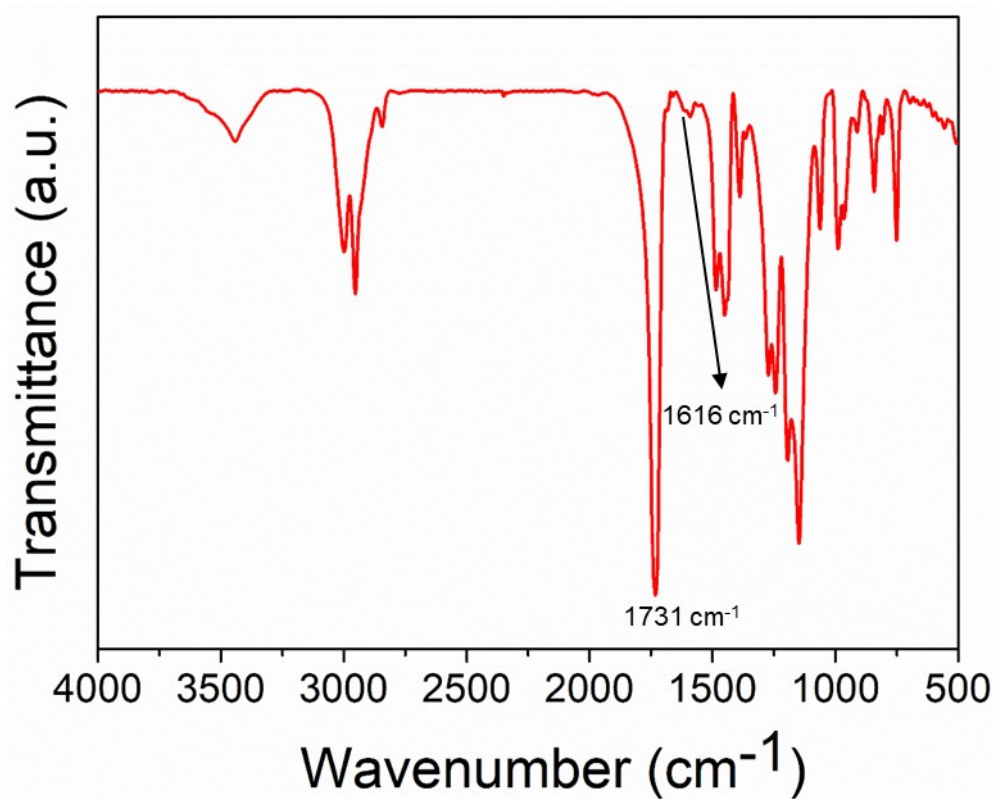
$M_n$	$M_w$	$M_p$	$M_z$	$\bar{D}$
$5.77 \times 10^4$	$1.00 \times 10^5$	$9.13 \times 10^4$	$1.54 \times 10^5$	1.73

**Table S3** GPC analysis of **P2**.

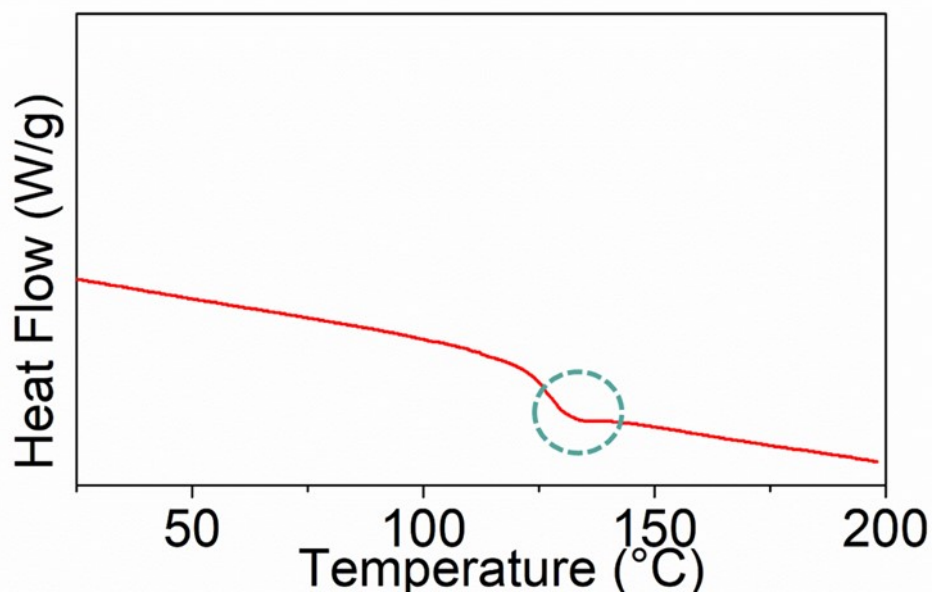
The ratio of x/y was (0.9)/(1226.75/3), namely 2/408.92, for polymer **P2**, as calculated based on the integrations of the peaks corresponding to protons H<sup>2i</sup>, H<sup>2f</sup>. According to  $M_n$  and the ratio of x/y, the values of x and y were calculated to be 2.78 and 569.2.

Values	x	y
<b>P2</b>	2.78	569.2

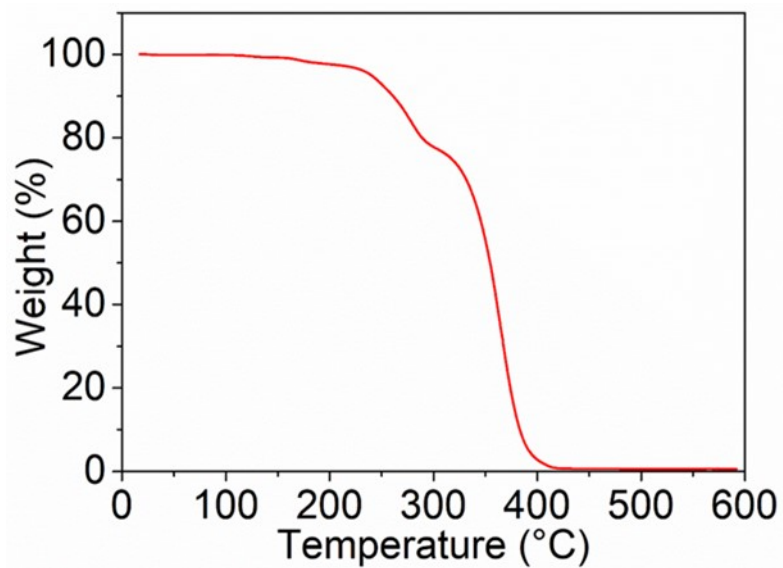
**Table S4.** The calculated values of x and y for **P2**.



**Figure S14** FT-IR spectrum of **P2**.



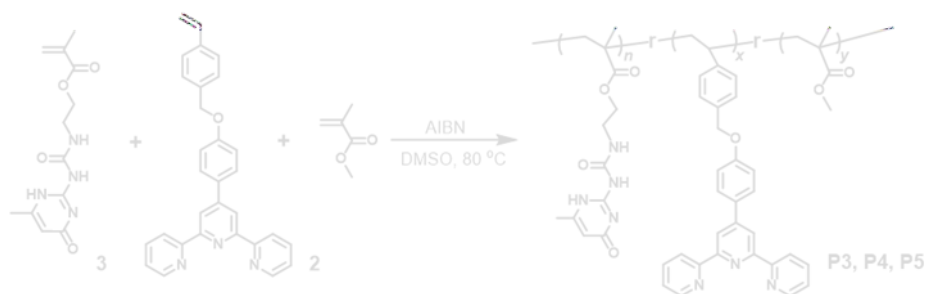
**Figure S15** DSC spectrum of **P2**.



**Figure S16** TGA trace of **P2**.



### 3.3 Synthesis and characterization of polymer **P3**, **P4** and **P5**



Polymer **P3**, **P4** and **P5** was prepared from compound **2**, compound **3** and methyl methacrylate by free radical polymerization. In **P3**, the molar ratio of compound **2**, compound **3** and methyl methacrylate is 1:1:100. While in **P4**, the molar ratio changed to 0.6:1:100. And in **P5**, this molar ratio transformed to 0.3:1:100. The preparation steps of the three polymers are the same, so taking **P3** as an example. DMSO as solvent, then compound **2** (397 mg, 0.800 mmol), compound **3** (252 mg, 0.800 mmol) and methyl methacrylate (9.00 g, 90.0 mmol) was simultaneously added. And azobisisobutyronitrile (AIBN) (22.0 mg, 0.130 mmol) acted as initiator was added. A stream of nitrogen ( $N_2$ ) was bubbled through the reaction mixture for 15 min. Then the mixture was heated to 80 °C, stirred for 10 h. The polymerization was quenched by freezing the reaction mixture in ice water. The resulting solution was added into methanol (500 mL), then the precipitated white solid was obtained by using vacuum filtration. These two steps were again repeated for three times, then polymer **P3** was produced after being dried with vacuum. **P4** and **P5** could be obtained in the same way.

**P3**:  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  12.92 (s, 1H), 11.88 (s, 1H), 10.42 (s, 2H), 8.67 (d,  $J = 15.0$  Hz, 66H), 7.84 (s, 44H), 7.03 (s, 35H), 5.87 – 5.71 (m, 11H), 5.03 (s, 22H), 4.66 (d,  $J = 7.6$  Hz, 26H), 4.03 (d,  $J = 7.9$  Hz, 20H), 3.56 (s, 3580H), 2.88 – 0.02 (m, 13470H).

**P4**:  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  12.92 (s, 1H), 11.93 (s, 1H), 10.41 (s, 1H), 8.66 (s, 3H), 7.85 (s, 2H), 7.03 (s, 2H), 5.79 (s, 1H), 5.05 (s, 2H), 4.04 (s, 3H), 3.56 (s, 214H), 2.92 – 0.51 (m, 591H).

**P5**:  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  12.95 (s, 1H), 11.93 (s, 1H), 10.43 (s, 1H), 8.68 (s, 2H), 7.86 (s, 1H), 7.05 (s, 1H), 5.80 (s, 1H), 5.06 (s, 1H), 4.07 (s, 2H), 3.58 (s, 133H), 2.86 – 0.24 (m, 363H).

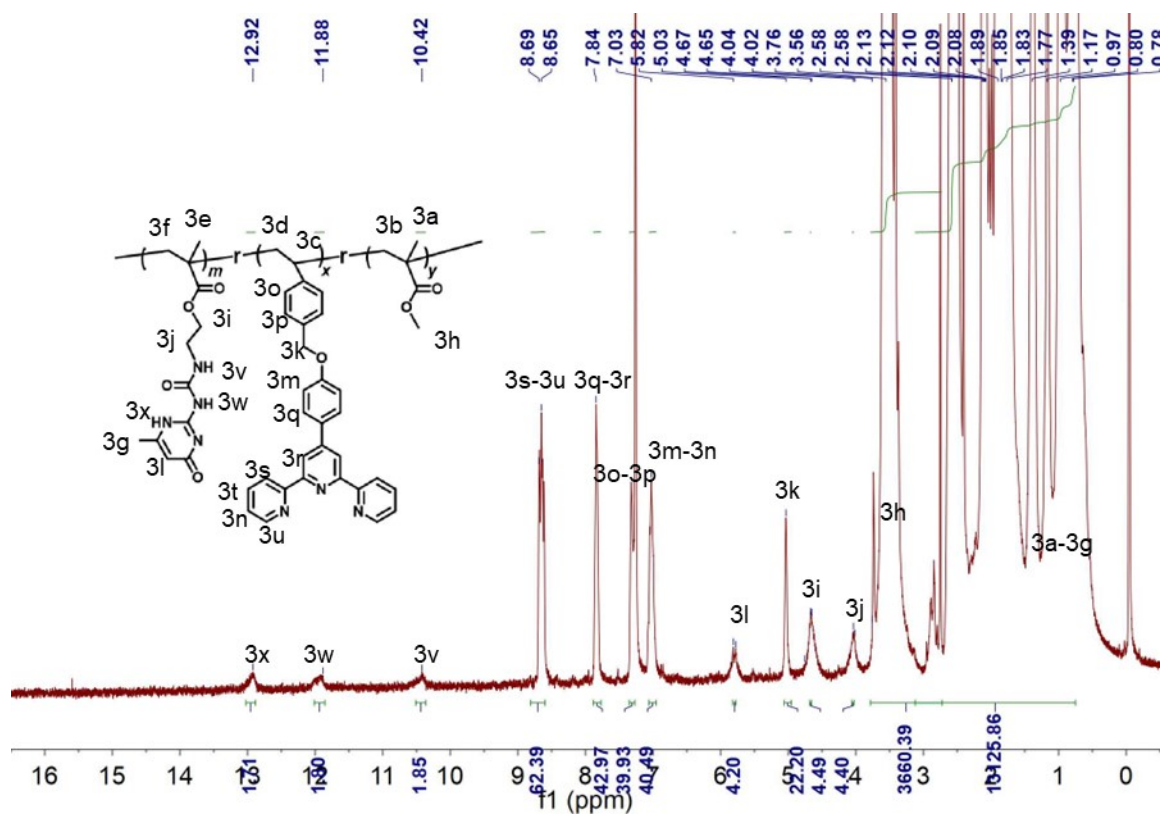


Figure S17 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of P3.

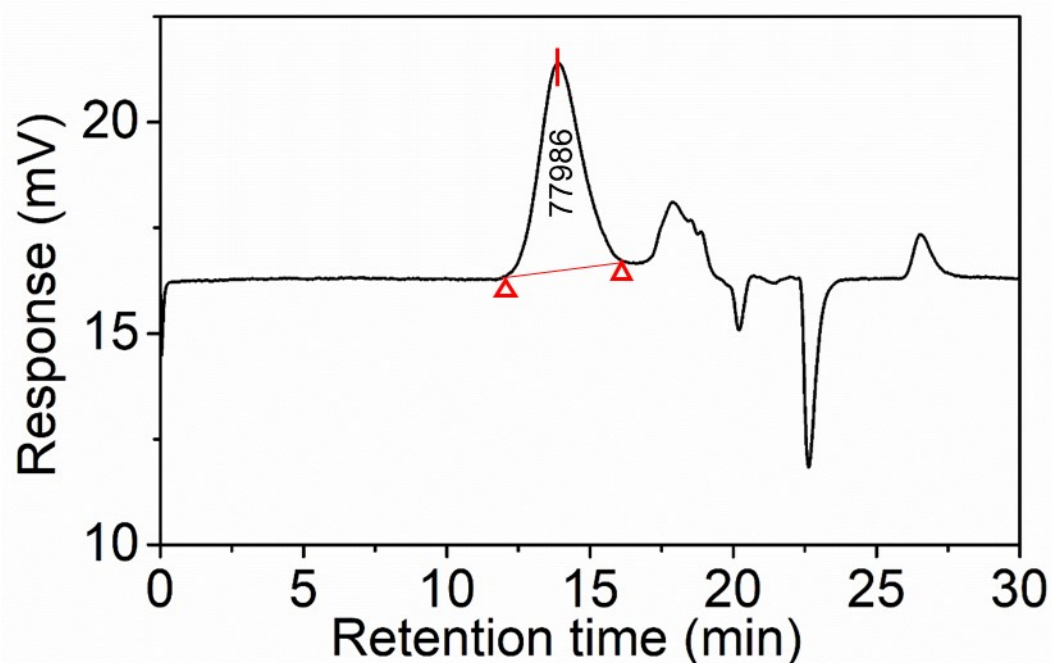


Figure S18 GPC trace of P3.

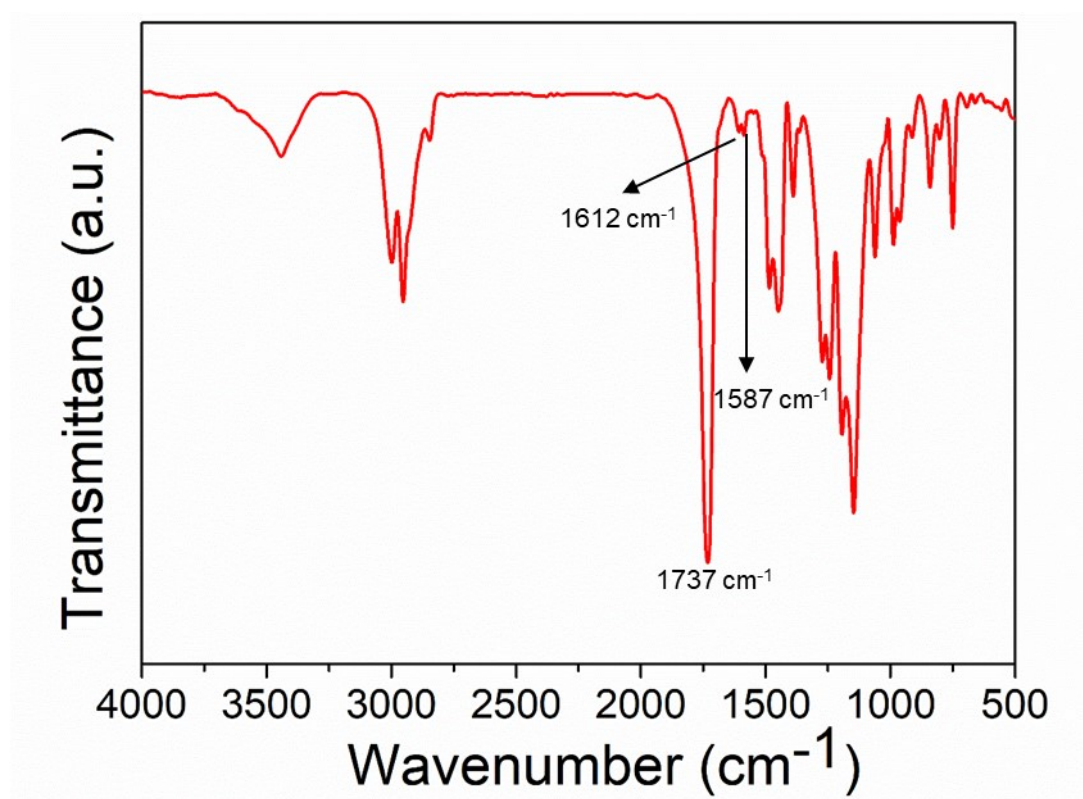
$M_n$	$M_w$	$M_p$	$M_z$	$\bar{D}$
$4.85 \times 10^4$	$9.41 \times 10^4$	$7.80 \times 10^4$	$1.63 \times 10^5$	1.94

**Table S5.** GPC analysis of **P3**.

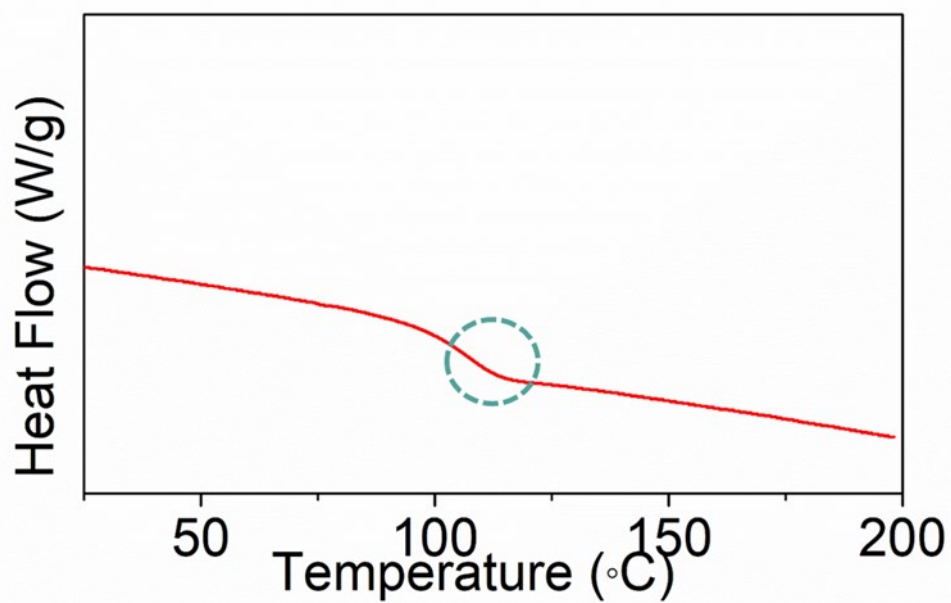
The ratio of m/x/y was (4.2)/(22.2/2)/(3660.39/3), namely 4.2/11.1/1220.13, for polymer **P3**, as calculated based on the integrations of the peaks corresponding to protons H<sup>3l</sup>, H<sup>3k</sup> and H<sup>3h</sup>. According to  $M_n$  and the ratio of m/x/y, the values of m, x and y were calculated to be 1.59, 4.2 and 462.06.

Values	x	y	z
<b>P3</b>	1.59	4.2	462.09

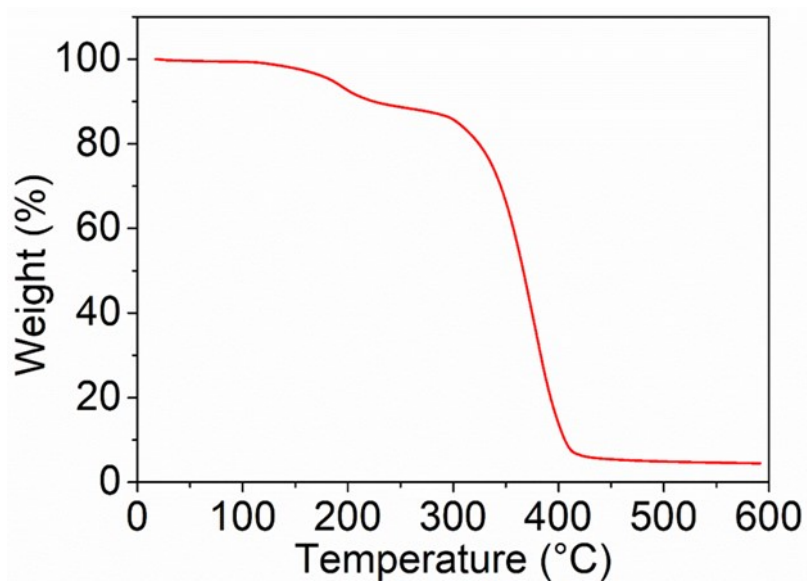
**Table S6.** The calculated values of x and y for **P3**.



**Figure S19** FT-IR spectrum of **P3**.



**Figure S20** DSC spectrum of **P3**.



**Figure S21** TGA trace of **P3**.

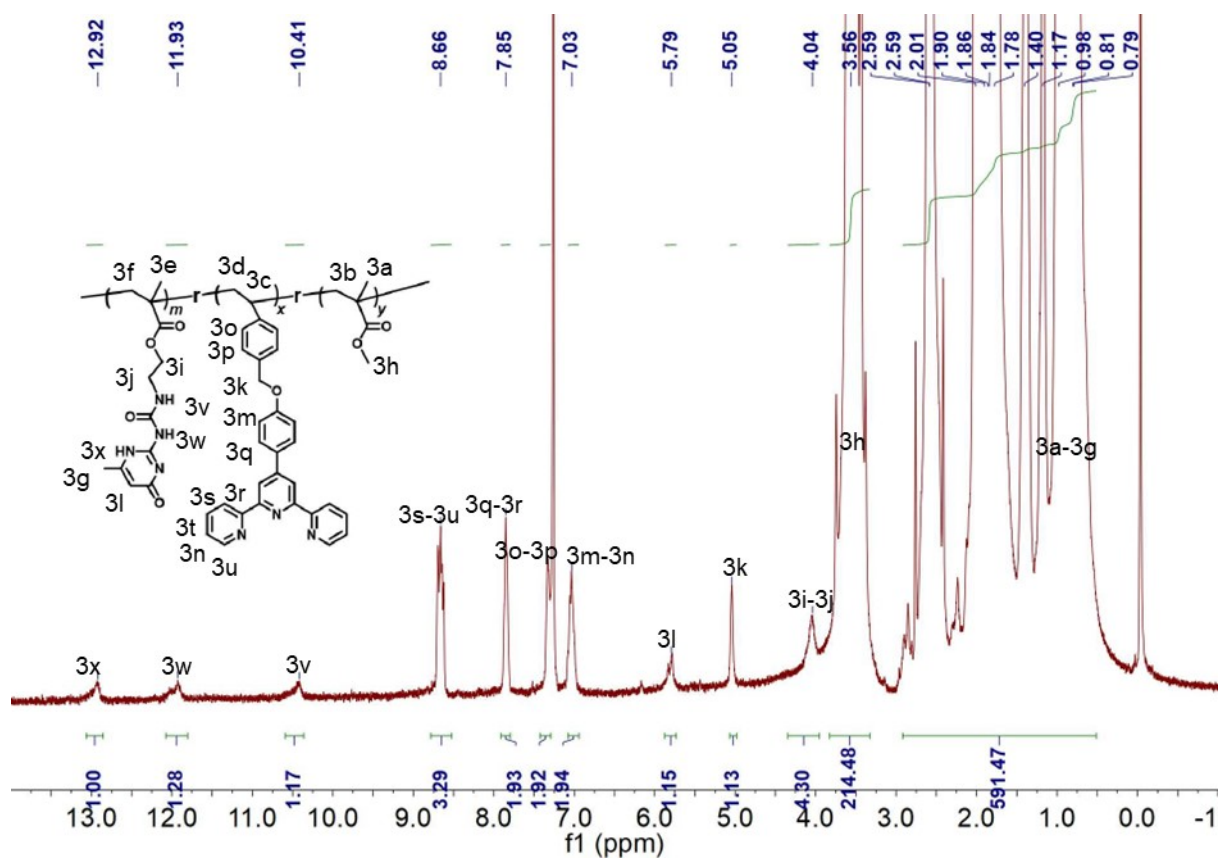


Figure S22 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of P4.

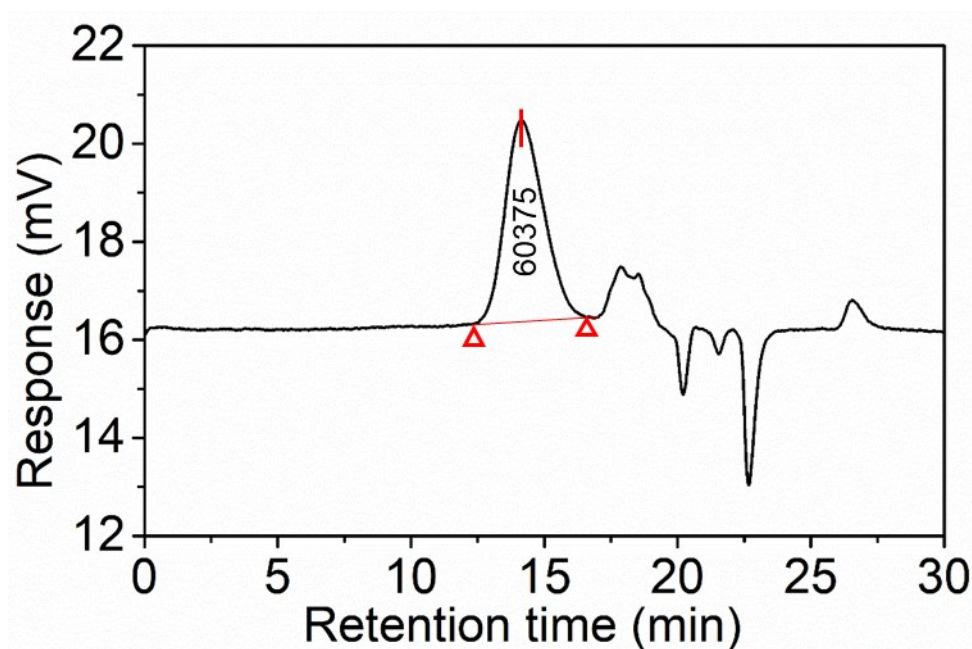


Figure S23 GPC trace of P4.

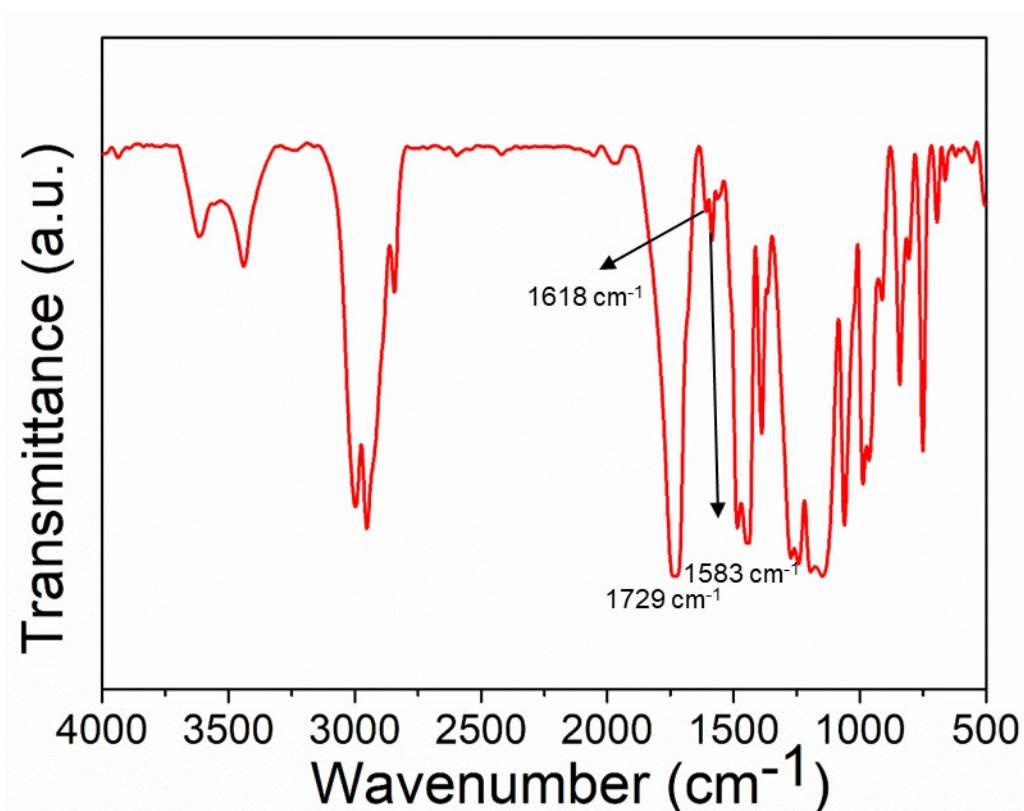
$M_n$	$M_w$	$M_p$	$M_z$	$D$
$3.73 \times 10^4$	$6.53 \times 10^4$	$6.04 \times 10^4$	$1.03 \times 10^5$	1.75

**Table S7** GPC analysis of **P4**.

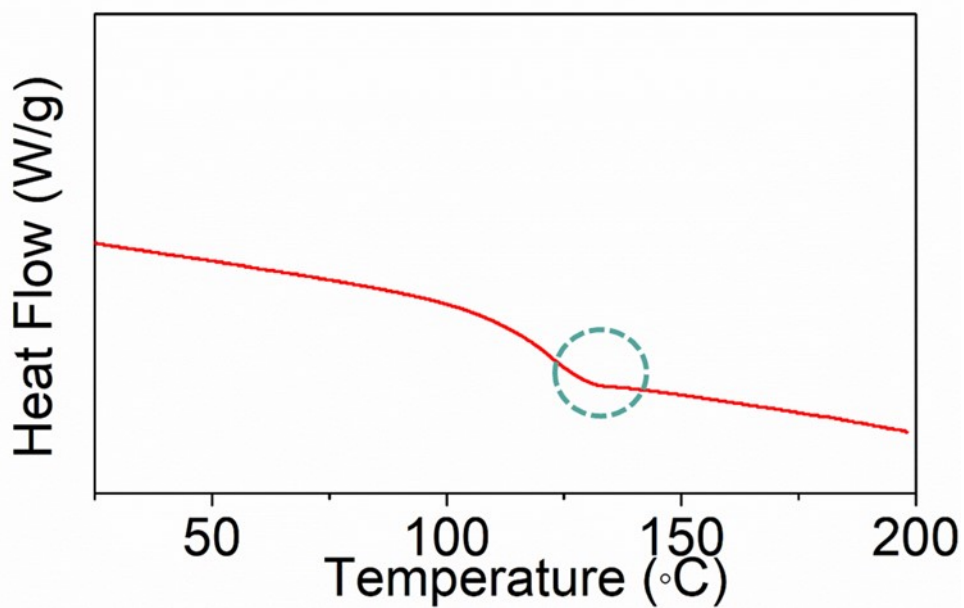
The ratio of m/x/y was (1.15)/(1.13/2)/(214.48/3), namely 1.15/0.56/71.5, for polymer **P4**, as calculated based on the integrations of the peaks corresponding to protons H<sup>4l</sup>, H<sup>4k</sup> and H<sup>4h</sup>. According to  $M_n$  and the ratio of m/x/y, the values of m, x and y were calculated to be 5.56, 2.7 and 345.3.

Values	x	y	z
<b>P4</b>	5.56	2.7	345.3

**Table S8** The calculated values of x and y for **P4**.



**Figure S24** FT-IR spectrum of **P4**.



**Figure S25** DSC spectrum of **P4**.

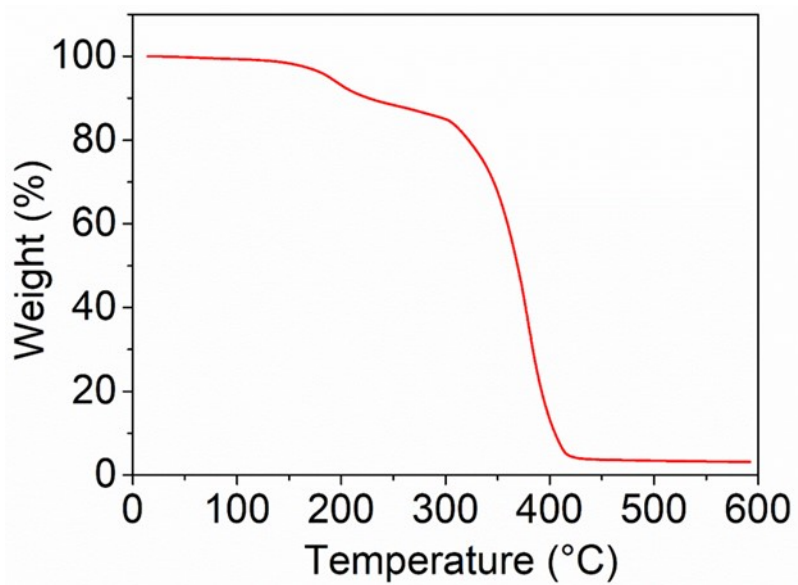


Figure S26 TGA trace of P4.

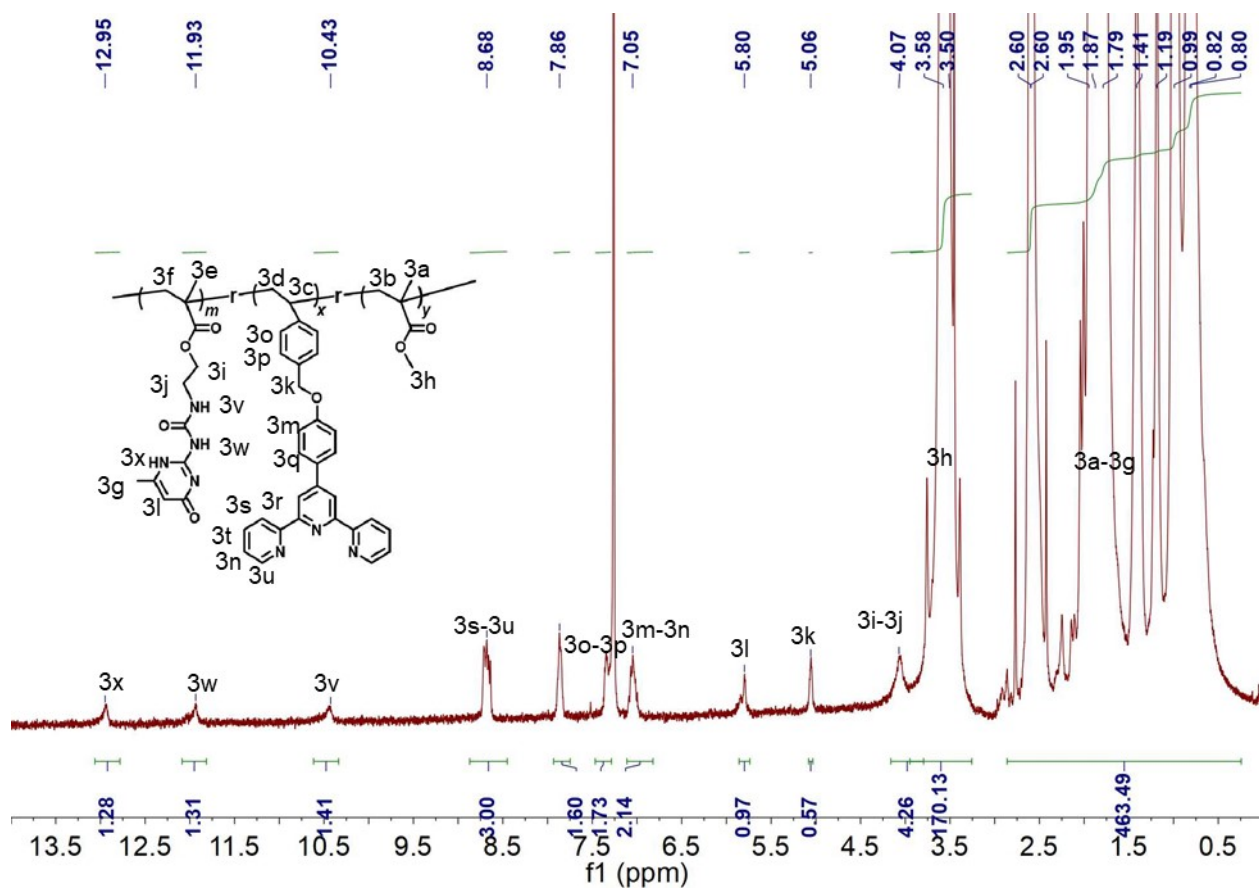
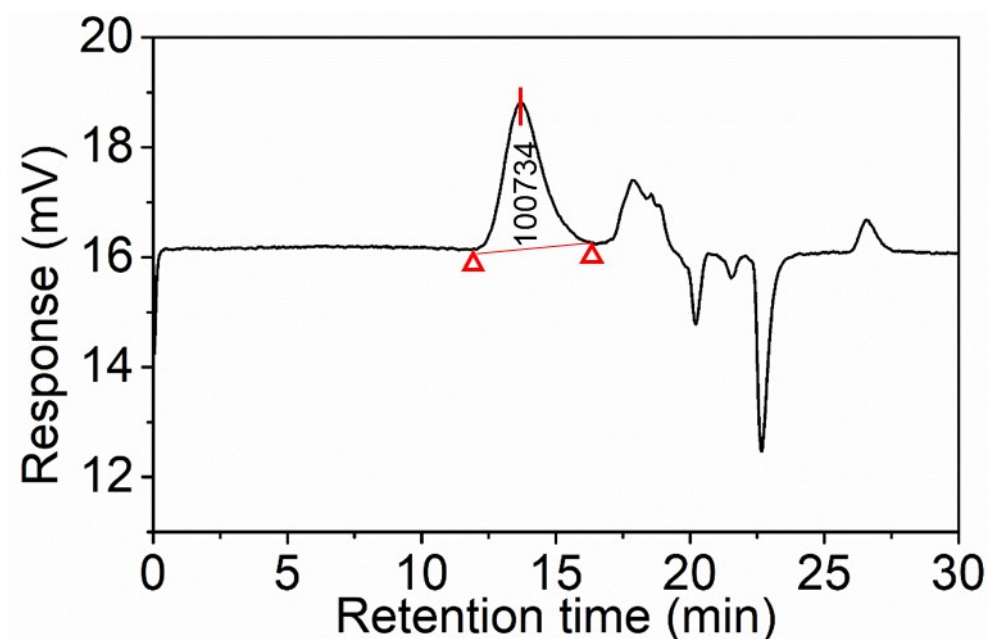


Figure S27 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of P5.





**Figure S28** GPC trace of **P5**.

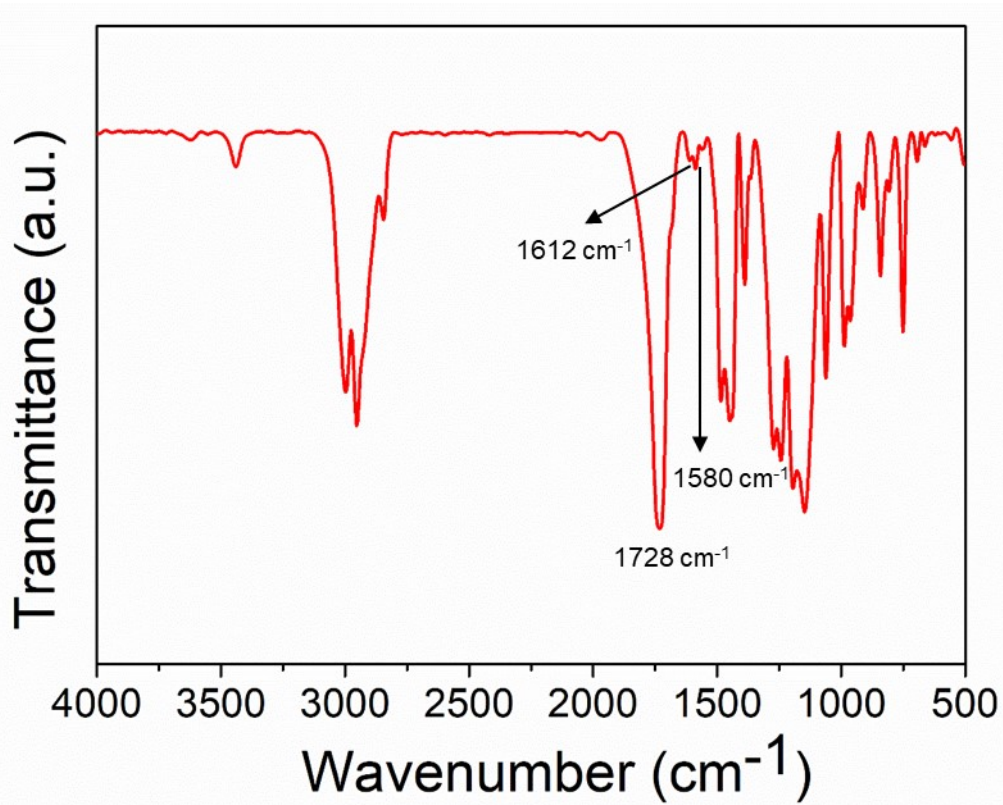
$M_n$	$M_w$	$M_p$	$M_z$	$\bar{D}$
$6.32 \times 10^4$	$1.10 \times 10^5$	$1.01 \times 10^5$	$1.69 \times 10^5$	1.75

**Table S9** GPC analysis of **P5**.

The ratio of m/x/y was (0.97)/(0.57/2)/(170.13/3), namely 0.97/0.285/56.71, for polymer **P5**, as calculated based on the integrations of the peaks corresponding to protons  $H^{5l}$ ,  $H^{5k}$  and  $H^{5h}$ . According to  $M_n$  and the ratio of m/x/y, the values of m, x and y were calculated to be 9.9, 2.9 and 578.44.

Values	x	y	z
<b>P5</b>	9.9	2.9	578.44

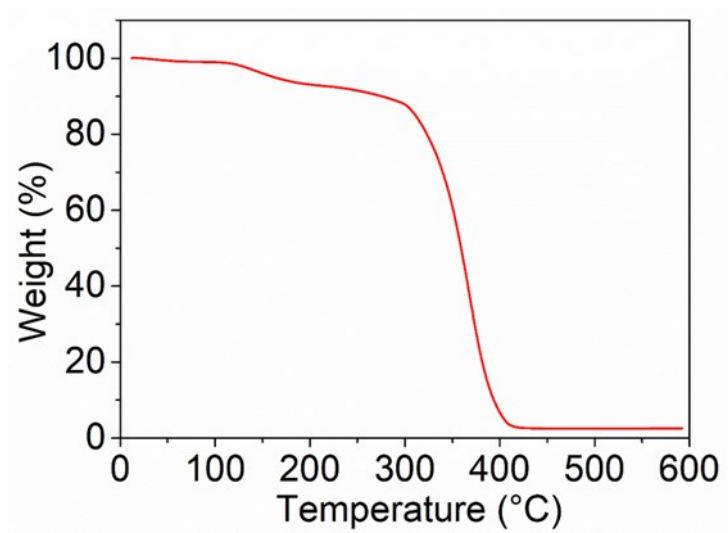
**Table S10** The calculated values of x and y for **P5**.



**Figure S29** FT-IR spectrum of **P5**.



**Figure S30** DSC spectrum of **P5**.



**Figure S31** TGA trace of **P5**.

#### 4. Rheological properties and SEM images of adhesive gels AG4 and AG5

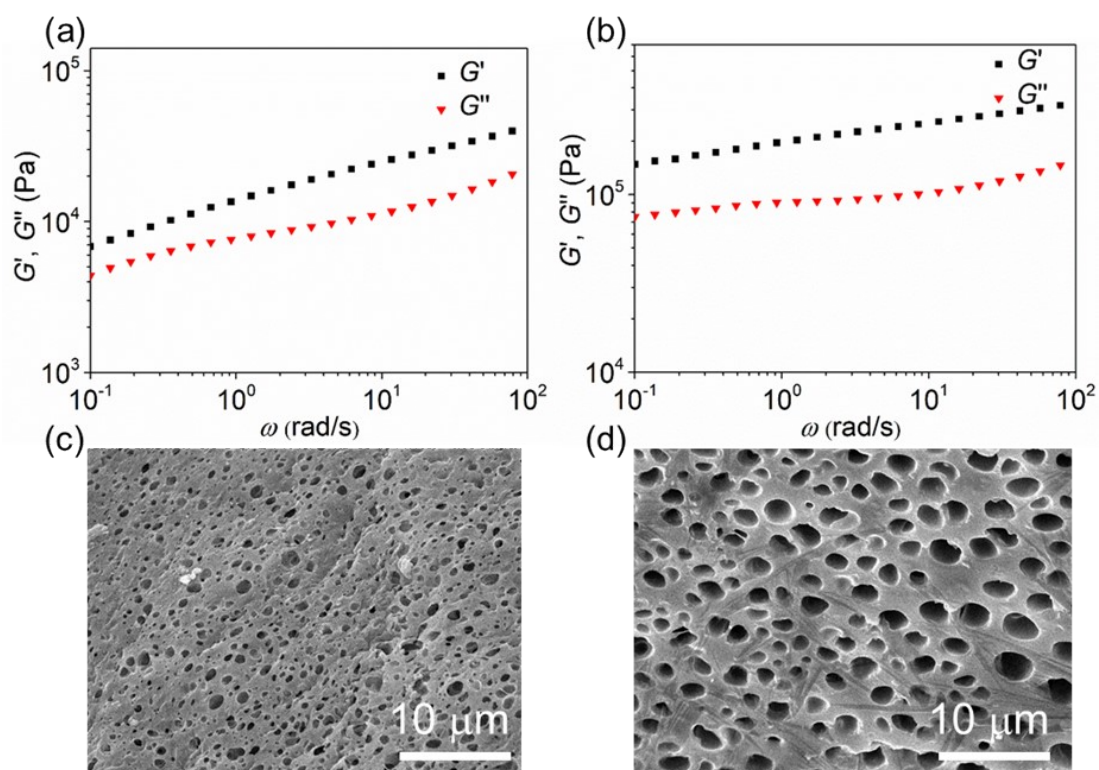


Figure S32 Rheological behaviors of (a) AG4, and (b) AG5. SEM images of (c) AG4, and (d) AG5.

#### 5. Supporting references

- 1 K. Yamauchi, J. R. Lizotte and T. E. Long, *Macromolecules*, **2003**, *36*, 1083-1088.
- 2 C. Yang, J. Xu, Y. Zhang, Y. Li, J. Zheng, L. Liang and M. Lu, *J. Mater. Chem. C*, **2013**, *1*, 4885-4901.