

## Novel Clickable and Fluorescent Poly(siloxane amine)s for Reusable Adhesive and Reprocessable Elastomer

Jie Zhou,<sup>a</sup> Linlin Wang,<sup>a</sup> Lei Li<sup>\*a</sup> and Shengyu Feng<sup>\*a,b</sup>

### Experimental Section

#### Materials

1,3-Bis(3-glycidyloxypropyl)tetramethyldisiloxane, n-butylamine, 2-propynylamine, furfurylamine, ethanolamine, piperazine,  $\beta$ -mercaptoethanol, 2,2-dimethoxy-2-phenylacetophenone, chloroform-d ( $\text{CDCl}_3$ ), 4,4'-bismaleimidodiphenylmethane (BMI) and 4-aminophenyl disulfide were purchased from Sigma-Aldrich or Aladdin Co., Ltd (China). Tetrahydrofuran (THF), Chloroform, *N,N*'-dimethylformamide (DMF), dichloromethane and petroleum ether were provided by Tianjin Guangfu Fine Chemical Research Institute (China). All the reagents and solvents were used as received apart from some chemicals that were distilled prior to polymerization.

#### Characterization and measurements

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were analyzed on a Bruker AVANCE 400 MHz spectrometer at 25 °C with  $\text{CDCl}_3$  as the solvent and without tetramethylsilane (TMS) as the internal reference for chemical shifts ( $\delta$ , ppm). Fourier transform infrared spectra (FT-IR) were recorded on a Bruker TENSOR 27 infrared spectrophotometer with the KBr pellet technique from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ . Differential scanning calorimetry (DSC) was measured through SDTQ 600 of TA Instrument, and the polymers were heated from -140 °C to 200 °C at a rate of 10 °C/min under the nitrogen flow. Thermogravimetric analysis (TGA) was carried out by a TA SDTQ600 from room temperature to 700 °C at a rate of 10 °C/min under a  $\text{N}_2$  atmosphere. The fluorescence (excitation and emission) spectra of the polymers were performed on a Hitachi F-4500 fluorescence spectrophotometer using a monochromated Xe lamp as an excitation source. Gel permeation chromatography (GPC) measurements were performed with a Waters liquid chromatography equipped with a 2414 refractive index detector. The column temperature was set at 40 °C and the flow rate of THF was stable at 1.0 mL/min. The thiol-ene photoreaction was carried on using a Spectroline Model SB-100P/FA lamp (365 nm, 100 W). The UV intensity was 4500  $\mu\text{W}\cdot\text{cm}^{-2}$  fixed at a distance of 38 cm. The lap shear strength values between the cross-linked P3/BMI and the stainless steel plates were measured on a WDW-5 universal testing

machine (KeXin Testing Machine Co., Ltd). The tensile speed was set at 5 mm/min until the sample was damaged to separate at 25 °C. The adhesive area between two stainless steel plates was 25.4×12.5 mm<sup>2</sup> according to the ASTM D1002-10 standard document. Mechanical tensile tests of the elastomers were implemented by the Instron 3343 material testing system with a speed of 20 mm/min. For all the tensile tests, the samples were cut into dumbbell-shaped specimens with a size of 40×5×1 mm<sup>3</sup>.

### Synthesis of the poly(siloxane-amine)s (P1-P5)

General synthesis procedure: 1,3-bis(3-glycidyloxypropyl)tetramethyldisiloxane (5 mmol, 1.817 ml) and the amine monomers were added into a round-bottom flask with a molar ratio of 1:1, and stirred by a mechanical stirrer at 60 °C for 24 h. Subsequently, the crude mixture was precipitated in petroleum ether for three times to give corresponding poly(siloxane-amine) **P1**, **P2**, **P3** or **P4**. For the synthesis of polymer **P5**, the mixture of THF and DMF (volume ratio = 10:1) was used as the solvent because of the poor solubility of piperazine in the epoxy monomer.

### Post-modification of P2 by thiol-alkyne reaction

Polymer **P2** (0.039 mmol, 0.209 g), β-mercaptoethanol (4 equiv. per alkyne unit) and 2,2-dimethoxy-2-phenylacetophenone (2.8 wt%, 0.01 g) were dissolved in a minimum amount of THF. Then the mixture was subjected to UV irradiation for 2 h. Subsequently, the crude mixture was precipitated in petroleum ether to give post-modified polymer **P2F**.

### Thermoreversibility of P3/BMI network

To test the thermoreversibility of the cross-linked **P3/BMI** network, **P3** (0.043 mmol, 0.2 g) and **BMI** (0.156 g) were dissolved in a certain amount of DMF with equal molar ratio of functional groups. Then the mixture was heated at 60 °C for 24 h to give a gel, which turned into the liquid state after further heating at 120 °C for 5 min. The original gel restored after heating at 60 °C for 24 h.

### Adhesion Test

Adhesion properties were determined by lap shear strength test. Prior to mount the adhesives, the stainless steel plates were polished with sandpaper, washed with acetone and dried through vacuum overnight. **P3** and **BMI** were dissolved in a minimum amount of DMF with equal molar

ratio of functional groups and then evenly spread onto two stainless steel plates. The adhesive area was fixed at  $25.4 \times 12.5 \text{ mm}^2$ . The sample was clamped by two clips at ambient temperature for 12 h and then subjected to heating at  $60^\circ\text{C}$  for 24 h. The lap shear strength was measured using a mechanical testing machine at a tensile speed of 5 mm/min at room temperature. After the measurement, the separated plates were clung together, heated at  $120^\circ\text{C}$  for 5 min and subsequently at  $60^\circ\text{C}$  for 24 h. The adhesion strength was analyzed again. This process was repeated one more time. Seven parallel samples were tested and averaged results were reported with error bars showing standard deviation.

### **Preparation of the P4-disulfide elastomer**

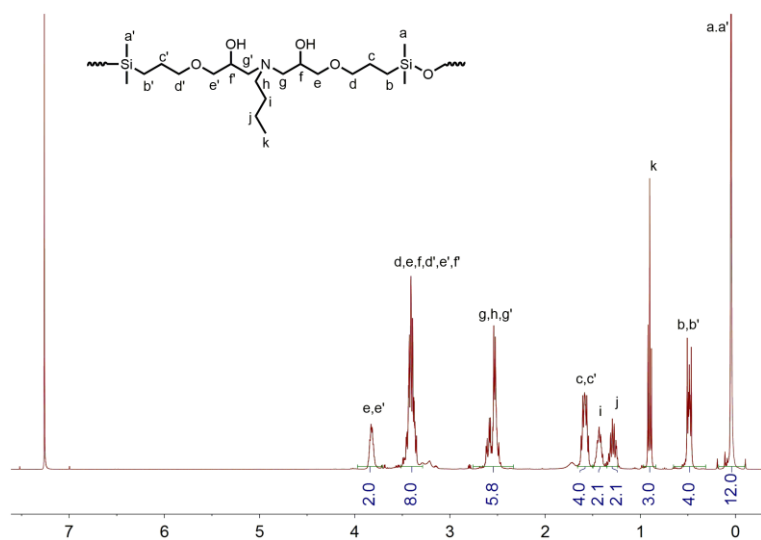
1,3-Bis(3-glycidyloxypropyl)tetramethyldisiloxane (12.6 mmol, 4.58 ml), ethanolamine (9 mmol, 0.539 ml), and 4-aminophenyl disulfide (1.8 mmol, 0.447 g) were mixed in a 1:1 molar ratio of epoxy and NH groups. The homogeneous mixture was poured into a teflon plate mold and subjected to the pre-curing process at room temperature for 12 h. Then the mold was placed into a drying oven at  $60^\circ\text{C}$  for 24 h followed by heating at  $80^\circ\text{C}$  for another 12 h. The obtained sample was peeled off from the teflon mold and cut into several dumbbell-shaped specimens with a size of  $40 \times 5 \times 1 \text{ mm}^3$  for tensile tests.

### **Solution procession of the P4-disulfide elastomer**

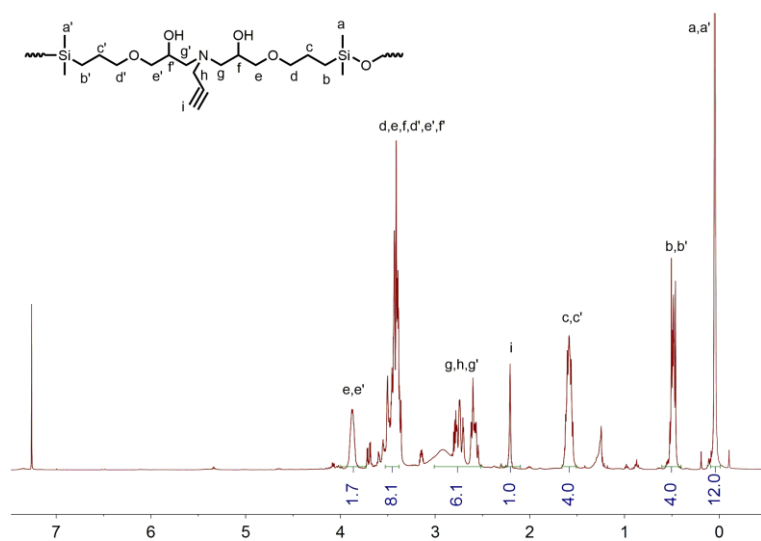
P4-disulfide elastomer were added to a vial containing DMF and 3eq. 4-aminophenyl disulfide. The solution was heated at  $130^\circ\text{C}$  for 4h to give a homogeneous solution. According to the composition of original P4-disulfide elastomer, corresponding amounts of 1,3-bis(3-glycidyloxypropyl)tetramethyldisiloxane and ethanolamine were supplemented to the above solution to reach the equal molar ratio of epoxy and amine groups. The mixture was poured into a teflon plate mold. After vacuum volatilizing at room temperature for 24 h, the mold was placed in a drying oven at  $60^\circ\text{C}$  for 24 h followed by curing at  $80^\circ\text{C}$  for another 12 h. Tensile measurement was performed to evaluate its mechanical property.

### **Hot-press of the P4-disulfide elastomer**

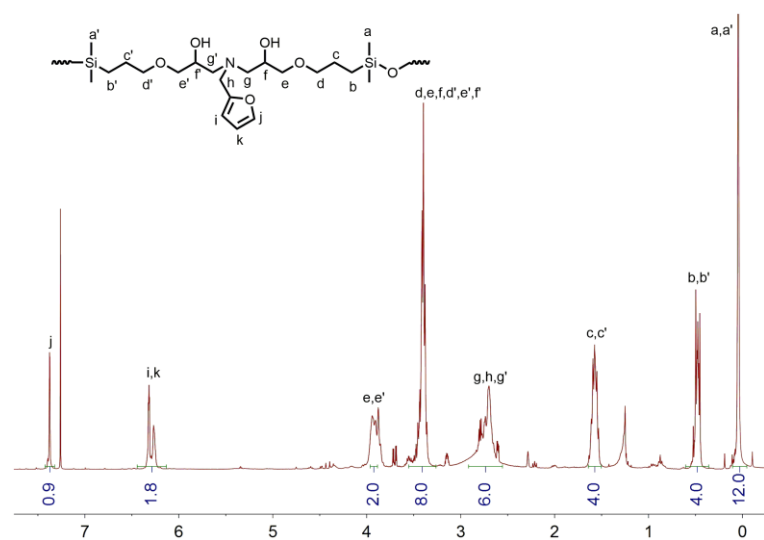
The fractured materials of P4-disulfide elastomer were collected together and introduced into a steel mold ( $150 \times 100 \times 1 \text{ mm}^3$ ), which was pressed at  $150^\circ\text{C}$  for 2 h under 1 MPa. Tensile measurement was performed to evaluate its mechanical property.



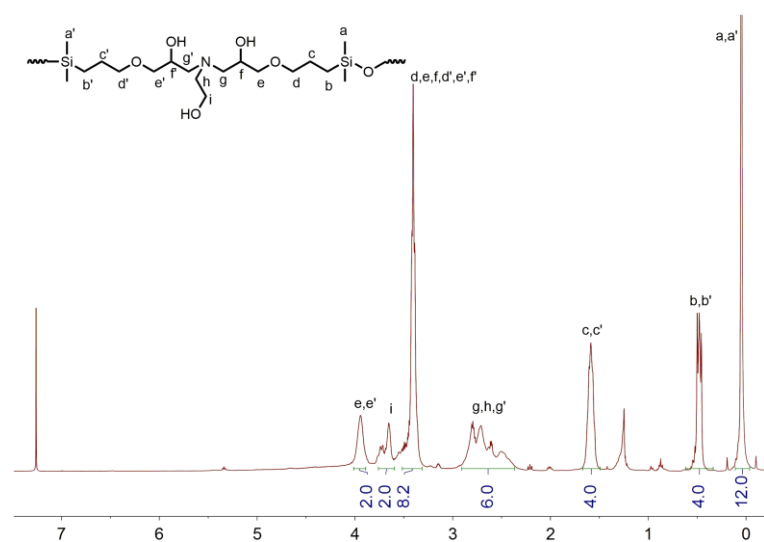
**Fig. S1**  $^1\text{H}$  NMR spectra of polymers **P1** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)



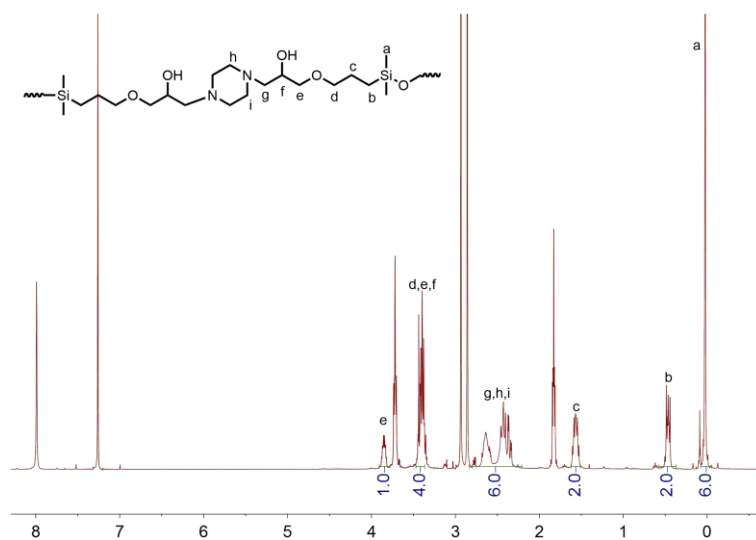
**Fig. S2**  $^1\text{H}$  NMR spectra of polymers **P2** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)



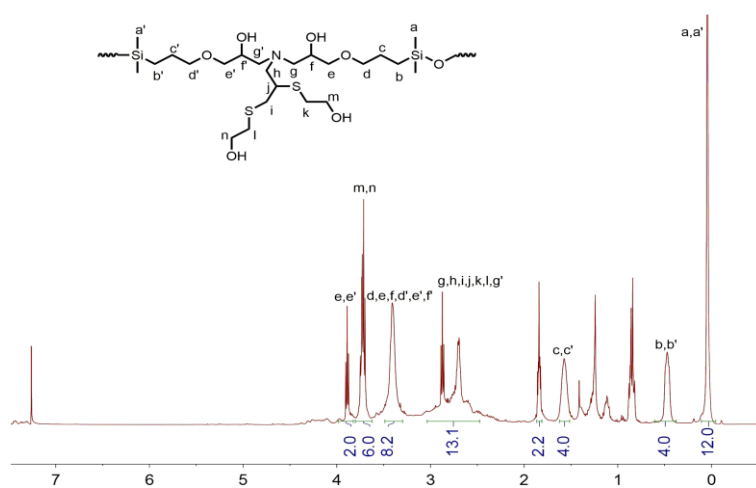
**Fig. S3**  $^1\text{H}$  NMR spectra of polymers **P3** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)



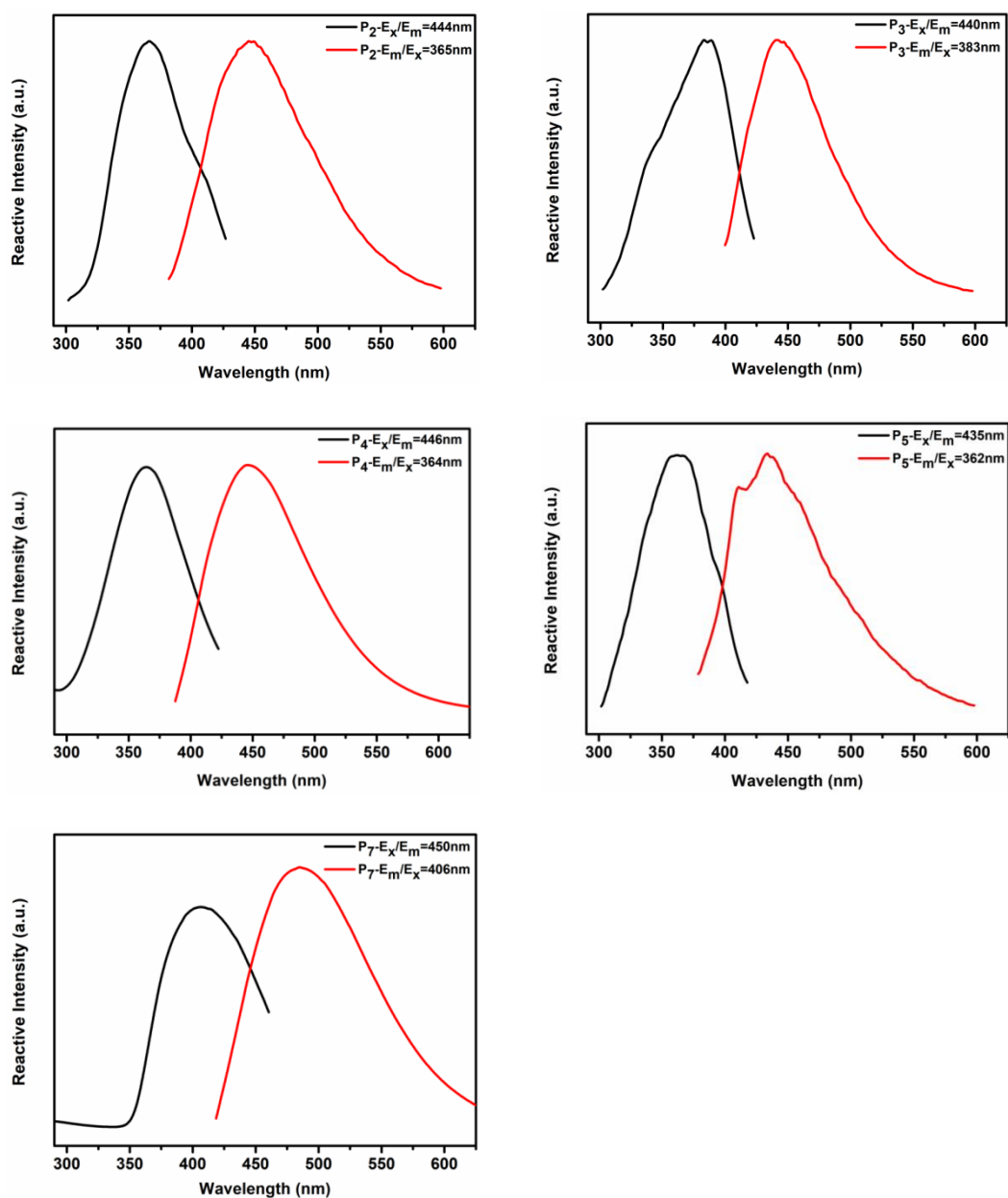
**Fig. S4**  $^1\text{H}$  NMR spectra of polymers **P4** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)



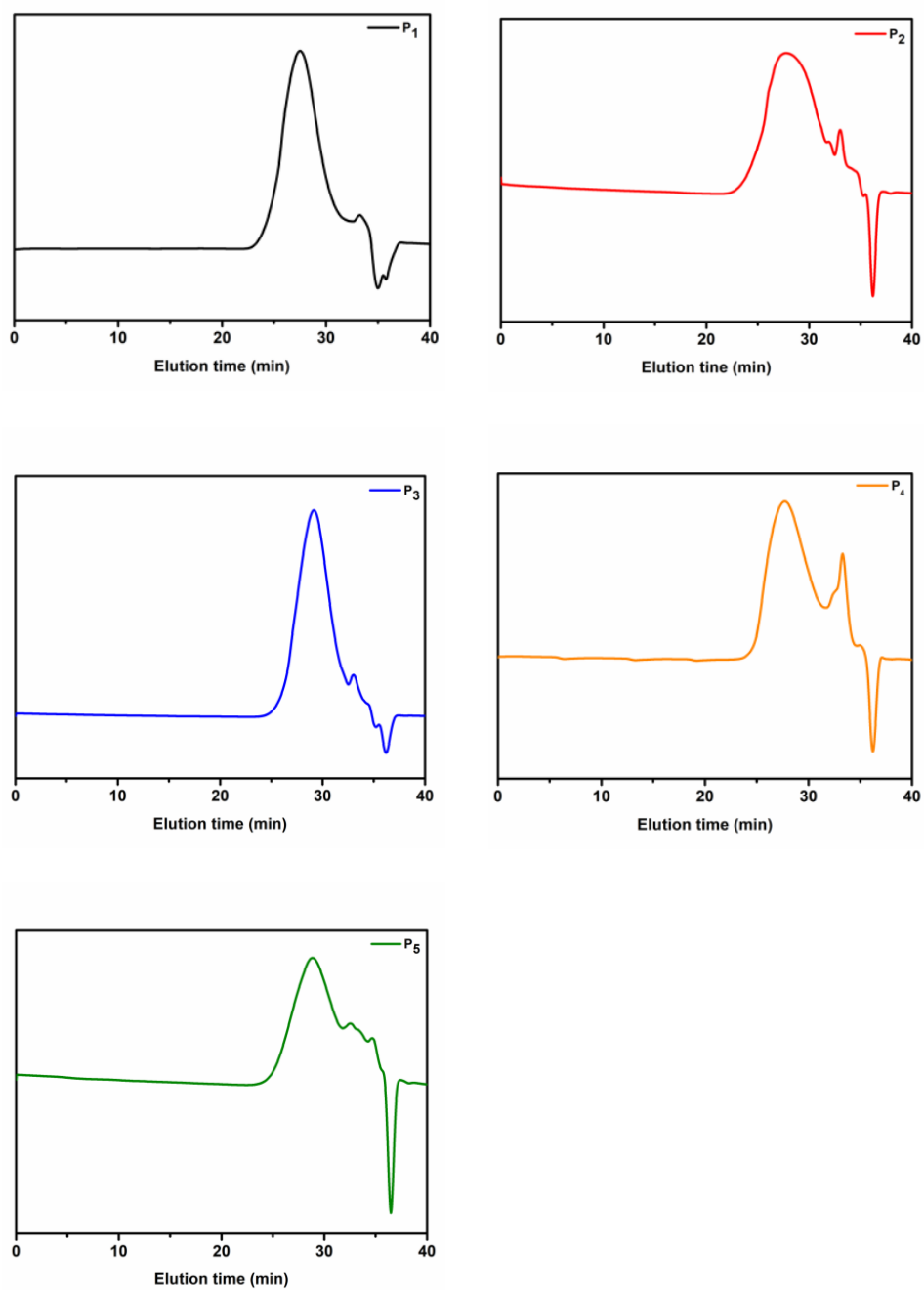
**Fig. S5**  $^1\text{H}$  NMR spectra of polymers **P5** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)



**Fig. S6**  $^1\text{H}$  NMR spectra of polymers **P2F** in  $\text{CDCl}_3$ . ( $\delta$ , ppm)

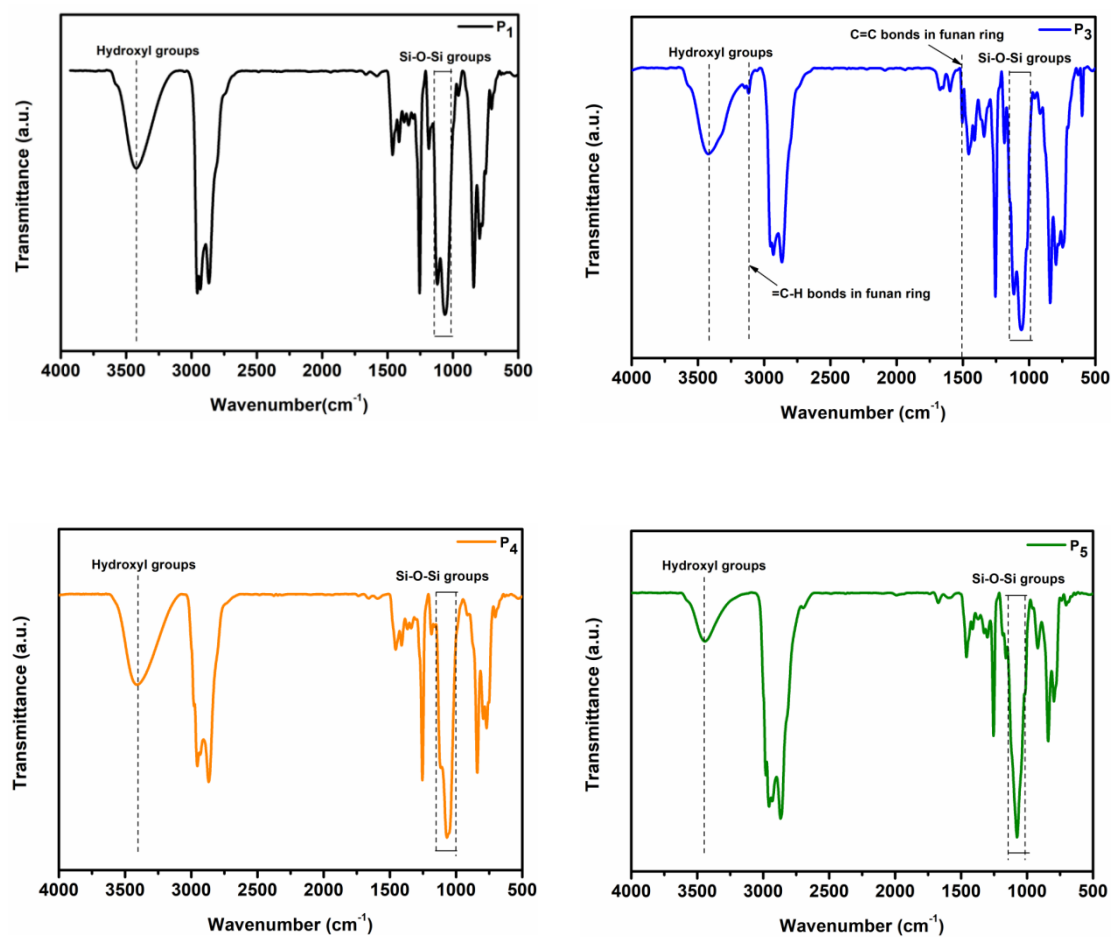


**Fig. S7** Fluorescence excitation and emission spectra of polymers **P2**, **P3**, **P4**, **P5** and **P2F** in THF solution.



**Fig. S8** GPC curves of polymers **P1**, **P2**, **P3**, **P4** and **P5**.





**Fig. S9** FT-IR spectra of polymers **P1**, **P3**, **P4** and **P5**.