Electronic Supplementary Material (ESI) for Polymer Chemistry

Self-Healable and Recyclable Triple-Shape PPDO-PTMEG Co-network Constructed through Thermoreversible Diels-Alder Reaction

Jingjing Zhang, Ying Niu, Caili Huang, Zhongtao Chen, chao Chen[a], Keke Yang* and Yuzhong Wang*

Materials

Furfuryl alcohol (Aladdin), 1,1,1,3,3,3-Hexafluoroisopropanol (Aladdin), tris(2-aminoethyl)amine (Alfa Aesar), exo-3,6-epoxy-1,2,3,6-tetrahydroxyphthalic anhydride1 (Alfa Aesar), 6-hexamethylene diisocyanate (HDI, Sigma-Aldrich) were used without further purification. Dihydroxyl terminated poly(tetramethylene oxide) glycol (PTMEG-diol) (M_n = 2900 g/mol, Reagent grade) was purchased from Aldrich Co., and *p*-dioxanone (PDO) was provided by the pilot plant of the center for degradable and flame-retardant polymeric materials (Chengdu, China), and dried over C_aH_2 for 48 h, then diatilled under a reduced pressure of 70 Pa just before used. N,N-dimethylformamide (DMF) was used was dried over 4 A molecular sieve for 72 h, distilled under reduced pressure of 70 Pa just before use. $CHCl_3$ was washed three times by distilled water,dried by refluxing over P_2O_5 and distilled just before use. 1, 1, 1, 3, 3, 3-Hexafluoroisopropanol, pentane and methanol were used without further purification. Tris(2-maleimide ethyl)amine were synthesized as previously reported.

Analytical Methods

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Fourier transform infrared spectrometer in a range of wave numbers from 4000 to 700cm^{-1}. The resolution and scanning time were 4 cm^{-1} and 32 times, respectively. The samples were milled into powders and then mixed and laminated with KBr.

The chemical structures and number-average number (M_n) of the obtained samples were characterized at 400 MHz using Bruker AV400 spectrometer in $CDCl_3$, with tetramethylsilane as the internal standard.

The molecular weights were obtained at 35 ℃ by gel permeation chromatography (GPC), using a Waters GPC device equipped with a 1515 pump, a Waters model 717 autosampler, and a 2414 refractive index detector. Chloroform was employed as the eluent at a flow rate of 1.0 mL min^{-1}, and a sample concentration of 2.5 mg mL^{-1} was used.

The UV-vis spectra were measured by a VARIAN CARY-50 spectrophotometer. The films were prepared by casting the PPDO-PTMEG solution onto quartz substrates.

Swelling and gel content were measured by immersing the samples in chloroform at room temperature, and then dried them in vacuum until constant weight. The percentages were obtained by the following equations:

$$\text{Swell\%} = \frac{(W_1 - W_0)}{W_0} \times 100 \qquad (1)$$

where W_0 is weight of dried film and W_1 is weight after chloroform absorption.

$$\text{Gel\%} = \frac{W_2}{W_0} \times 100 \tag{2}$$

where W_0 is the weight of initial dried film and W_2 is the weight of dried film after immersing in chloroform.

DSC measurement was performed with TA Q200 DSC (USA) in aluminum pan under nitrogen atmosphere. The samples were cooled to -50 ℃ then heated to 180 ℃ at 10 ℃ min^{-1} and kept for 5 min to remove thermal history, then were cooled to -50 ℃ at a rate of 10 ℃ min^{-1}, and finally were reheated to 180 ℃at the same rate.

The shape memory effect (SME) was conducted on a bending test.

An optical microscope (Nikon ECLIPSE LV100POL, Japan) equipped with a temperature controller (Instec HSC621V, USA) was used to probe the self-healing of PPDO-PTMEG co-network. The sample was heated to 65 ℃ and kept for 5 min, heated to 110 ℃ and kept for 5 min, then heated to 125 ℃ and kept this temperature until the fracture matched, lastly, Cooled to 75 ℃ for 15 h. The process was monitored by taking photomicrographs, using computer with a CCD camera.

The samples of gauge-centered edge-cracks and undamaged with an average thickness of 0.73mm and a width of 4.23 mm were tested by Instron Universal Testing Machine (Model 4302, Instron Engineering Corporation, Canton,MA) under a 200 N load cell and uniaxially stretched to a displacement at 5mm min^{-1}. After that, the sample was heated to 150℃ leading to full re-D-A reaction, and then loaded in a convection oven for 15h at 75℃. This loading-recovery process was repeated. The self-heal efficiency was defined as:

$$\eta\% = \frac{P_{\text{healed}}^{\text{max}}}{P_{\text{virgin}}^{\text{max}}} \times 100 \tag{3}$$

Synthesis of macromonomers, bisfuranic terminated poly (tetramethylene oxide) (PTMEG-BF)

Under N_2 atmosphere, firstly, poly (tetramethylene oxide) glycol was terminated by 6-hexamethylene diisocyanate (PTMEG-NCO), the NCO-terminated of PTMEG-diol was prepared in bulk. PTMEG was placed in a two-necked flask, which was dried under vacuum at 100 ℃ for 2 h and purged with nitrogen three times. After melting in the oil bath (T = 150 ℃), predetermined amount of HDI was injected under N_2 and stirred vigorously. 1.5 h later, quenched with ice water. Crude product was purified by dissolving in $CHCl_3$ and then precipitating in excessive pentane. Then PTMEG-NCO was dissolved in DMF and heated to 75 ℃, under exclusion of water, furfuryl alcohol (n (PTMEG-NCO): n (Furfuryl alcohol) = 2 : 3) was added. After 48 h, the crude product was precipitated in water.

The FTIR spectra of PTMEG, PTMEG-NCO and PTMEG-BF were illustrated in Fig. S2. It can be seen clearly that the characteristic absorptions at 2950 cm^{-1} and 1120 cm^{-1}, which belonged to C—H absorption of CH_2 groups and the bond vibration of ether, were found among them. A broad peak corresponding to O—H stretching vibration of the terminal —OH appeared at about 3482 cm^{-1} assigning to PTMEG. However, the intensity of —OH stretching vibration sharply decreased in PTMEG-NCO, the intensive absorption peak at 2273 cm^{-1}, combining with new peaks at 3350 cm^{-1} and 1586 cm^{-1}, which were corresponding to the N—H and C—N stretching of the urethane groups, indicating free isocyanate groups in the chain termini of PTMEG-NCO. As to PTMEG-BF, the absorption peak at about 2273 cm^{-1} assigning to PTMEG-NCO disappeared, which demonstrated that the free isocyanate groups of PTMEG-NCO were consumed completely.

The chemical structure and number-average molecular weights of PTMEG-BF were characterized by ^1H NMR spectra (shown in Fig. S1). We can see that resonances located at 3.41 ppm (δH^g) and 1.62 ppm (δH^h) were attributed to the two methylene of PTMEG, respectively. The signals occurring at 3.16 ppm (δH^d), 1.62 ppm (δH^e) and 1.33 ppm (δH^f) were assigned to the methylene protons of HDI. Furthermore, the signals of 7.41 ppm (δH^a), 6.39 ppm (δH^b), 6.36 ppm ($\delta H^{b'}$) and 5.04 ppm (δH^c) were assigned to furfuryl. The number-average molecular weight (M_n) of PTMEG-BF could be determined according to the following equations:

$$D_p = \frac{I_g}{I_c} \qquad (3)$$

$$M_n = D_p \times 72 + 266.3 \times 2 + 18 \qquad (4)$$

Where D_p was the polymerization degree of PTMEG-BF, I_g and I_c were the intensity of methylene groups that closed to the ether linkage of PTMEG and furan, respectively. The value 72 represented the molecular weight of the repeating units of PTMEG, and 266.3×2 was the terminal HDI and furfuryl alcohol, 18 was the terminal H and —OH of PTMEG. M_n=3968 g/mol.

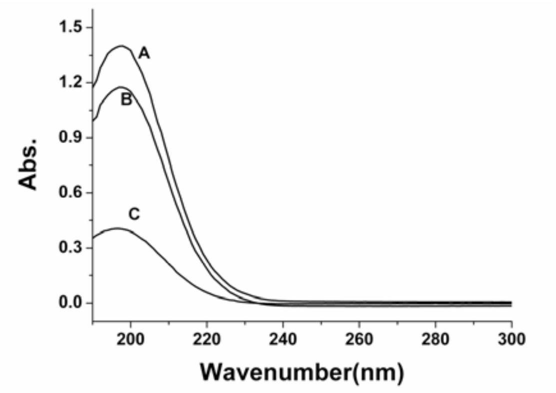

Fig. S1 **UV** absorption spectra of furfuryl alcohol obtained at each reaction time. A: 0 h B: 15 h C: 48 h

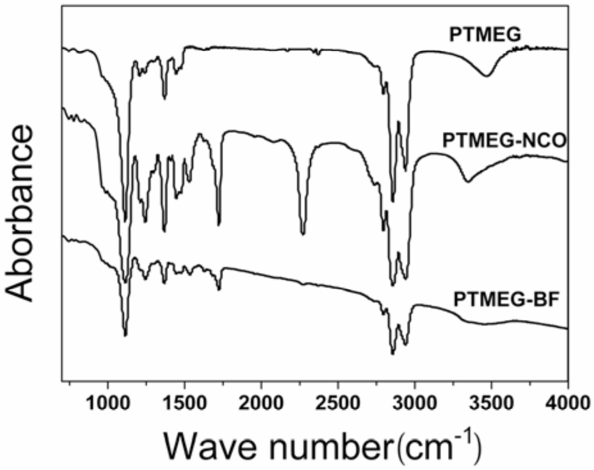

Fig. S2 FTIR spectra of PTMEG, PTMEG-NCO and bisfuranic terminated poly(tetramethylene oxide) (PTMEG-BF)

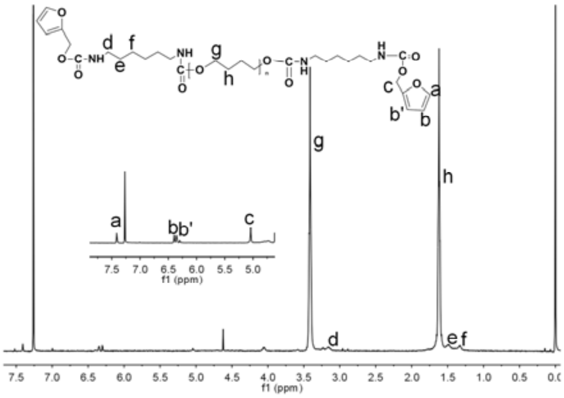

Fig. S3 ^{1}H NMR spectra of PTMEG-BF.

Synthesis of macromonomers, bisfuranic terminated poly (p-dioxanone) (PPDO-BF)

The PPDO-BF was synthesized by two steps: in the first step, the PPDO-K, which was terminated with furan in one side, another was hydroxyl, was synthesized through the ring-opening polymerization of PDO initiated by furfuryl alcohol. The experiment process was as follows: under N_2 atmosphere, anhydrous PDO (135 g / 1.32 mol) and furfuryl alcohol (1.85 g / 0.019 mol) were charged into a rigorously dried flask that immersed into a preheated oil bath (T = 80 ℃), 0.19 mL $SnOct_2$ toluene solution (0.2 mol/mL) as a catalyst was injected, then proceeding for 40 h. Crude product was purified by dissolving in $CHCl_3$ and then precipitating in excessive methanol. After dried in vacuum at 60 ℃ until constant weight. Then in the second step, PPDO-F are coupled with 6-hexamethylene diisocyanate, PPDO-BF was obtained. It was carried out in detail as follows: PPDO-K was charged and dried under vacuum at 60 ℃ for 2 h, purging three times with dry nitrogen, the reactor was immersed into a preheated oil bath (T = 142 ℃) with persistent stirring, predetermined amount of HDI was injected to actuate the coupling reaction as soon as reactants were molten completely. 1.5 h later, Crude product was purified by dissolving in $CHCl_3$ and then precipitating in excessive methanol. Then dried them in vacuum at 60 ℃ until constant weight.

The chemical structure and number-average molecular weights of PPDO-F and PPDO-BF were characterized by ^{1}H NMR spectra (shown in Fig. S4 and Fig. S5). Fig. S4 revealed that the peak of 4.36 ppm (δH^f), 4.18 ppm (δH^d) and 3.80 ppm (δH^e) were assigned to the three menthylene of PPDO, respectively, and the signals occurring at 7.43 ppm (δH^{a}), 6.43 ppm (δH^{b}), 6.37ppm ($\delta H^{b'}$) and 5.14 ppm (δH^{c}) were assigned to furfuryl. Furthermore, the signals of 3.76 ppm ($\delta H^{e'}$) and 3.70 ppm ($\delta H^{f'}$) were assigned to the terminal methylene group of PPDO. The number-average molecular weight (M_n) of PPDO-F could be determined according to the following equations:

$$D_p = \frac{I_f}{I_c} \tag{5}$$

$$M_n = D_p \times 102 + 200.10 \tag{6}$$

Where D_p was the polymerization degree of PPDO-F, I_f and I_c were the intensity of methylene groups of PPDO and furan, respectively. The values 102 represented the molecular weight of the repeating units of internal PPDO, and 200.10 was the molecular weight of terminal units of PPDO and furfuryl alcohol. M_n=4855 g/mol.

As to PPDO-BF, it was found that all the characteristic signals ascribed to both repeated segments of PPDO-F were presented. However, the signals which belonged to terminal methylene group of PPDO-F (3.76 ppm ($\delta H^{e'}$), 3.70 ppm ($\delta H^{f'}$)) disappeared respectively, indicating that all the terminal hydroxyl groups had thoroughly reacted. Furthermore, the shifts of three kinds of methylene protons of HDI are observed at 1.49 ppm (δH^{h}), 3.16 ppm (δH^{g}) and 1.33 ppm (δH^{i}), indicating that the chain extending reaction was sufficiently preceded. The number-average molecular weight (M_n) was different, it can be determined according to the following equations:

$$D_p = \frac{I_f}{I_c} \times 2 \tag{7}$$

$$M_n = D_p \times 102 + 200.10 \times 2 + 168 \tag{8}$$

Where D_p was the polymerization degree of PPDO-BF, I_f and I_c were the intensity of methylene groups of PPDO and furan, respectively. The value 102 represented the molecular weight of the repeating units of internal PPDO, and 200.10×2 was the molecular weight of terminal units of PPDO and furfuryl alcohol, and 168 was HDI. M_n=9640 g/mol.

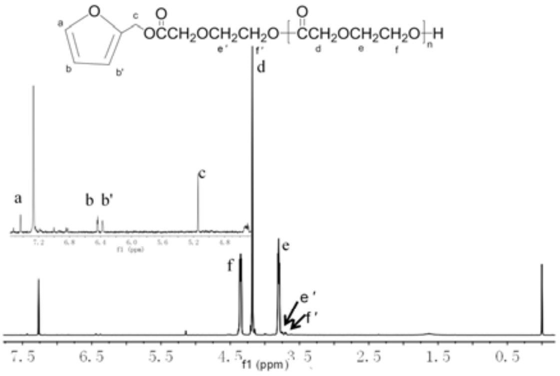

Fig. S4 ^{1}H NMR spectra of PPDO-F.

Fig. S5 ^{1}H NMR spectra of PPDO-BF.

Preparation of the PPDO-PTMEG co-network by D-A reaction

Bisfuranic terminated PTMEG-BF (0.5 g) and PPDO-BF (0.5 g) were dissolved in 3 mL 1,1,1,3,3,3-Hexafluoroisopropanol at ambient temperature, then 0.06 g tris(2-maleimide ethyl)amine was added. Then the bubbles were removed under vacuum, the residue, very viscous liquid, was poured into a glass mold at 75 ℃ for 15 h. The flat sheet is obtained at 0.5 mm in average.

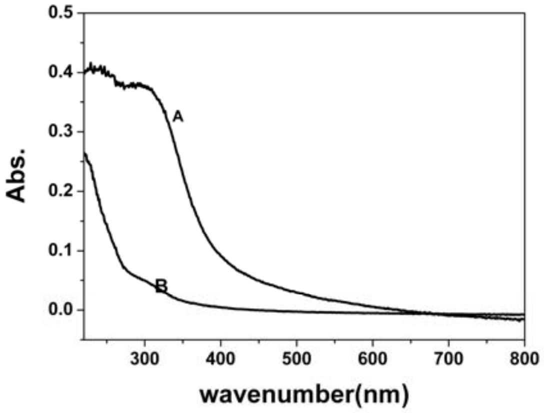

Fig. S6 UV absorption spectra obtained at each D-A reaction time. A: 0 h B: 15 h.

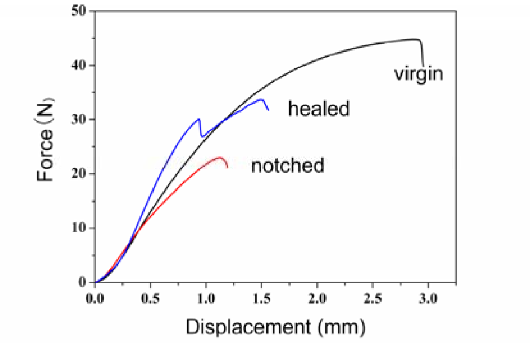

Fig. S7 Force vs displacement curves for the virgin, damaged and healed state of PPDO-PTMEG co-network.