

Supplementary Information

A New Recyclable Polymer Based on Diels-Alder Crosslinking Networks Derived from Anisaldehyde

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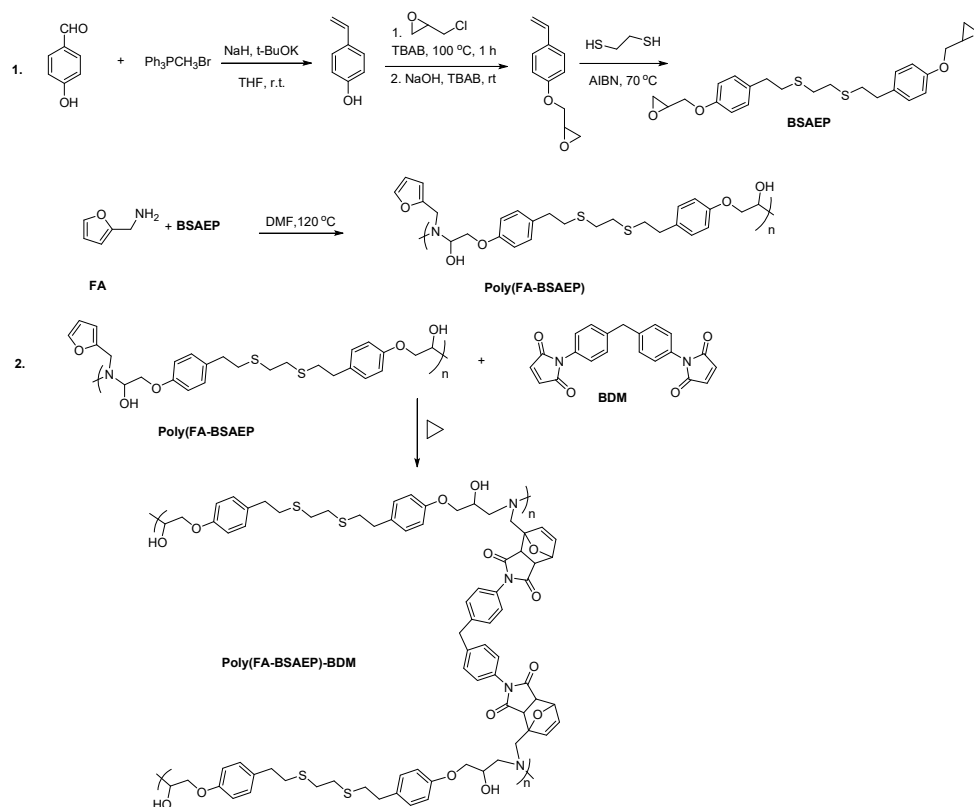
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Materials and instruments

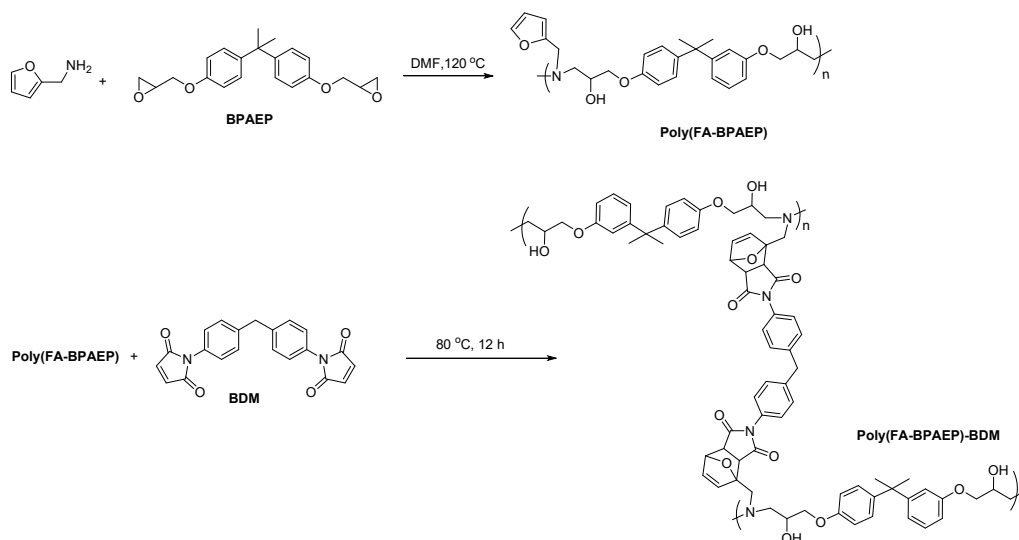
4,4'-Bismaleimidodiphenylmethane by Shanghai Meryer Chemical Technology Co. Ltd, China. 1,2-Ethanedithiol was provided by TCI Co. Epichlorohydrin, sodium hydride, azodiisobutyronitrile, tetrabutylammonium bromide and all ultra-dry solvents (including toluene, tetrahydrofuran) were provided by Beijing InnoChem Science & Technology Co., Ltd. Methyltriphenylphosphonium bromide and potassium tert-butoxide were purchased from Shanghai Haohong scientific Co., Ltd. Bisphenol A epoxy resin was bought from Bidepharm.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer (Switzerland) with CDCl_3 or $\text{DMSO-}d_6$ as the solvent. Fourier transform infrared spectra (FT-IR) were characterized on Thermo Scientific Nicolet spectrometer (USA) using a Smart Orbit Diamond, and the scanning range was from 400 to 4000 cm^{-1} . Elemental analysis tests were conducted on the VARIO EL CUBE elemental analyzer (ELEMENTAR, Germany). High-resolution mass spectra (HRMS) were characterized on a XEVO G2 TOF instrument produced in Waters company

(USA). Gel permeation chromatography (GPC) analysis was conducted on a Waters 1515 chromatography instrument (USA) with polystyrene as the standard and tetrahydrofuran as a solvent at a flow rate of 1 mL·min⁻¹. Differential scanning calorimetry analysis (DSC) were operated with a Q2000 DSC (TA, USA) at a heating rate of 10 °C min⁻¹ between 40 and 200 °C under N₂ flow with a flowing rate of 50 mL min⁻¹. Thermogravimetric analysis (TGA) was detected on Germany Mettler Toledo apparatus at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under N₂ with a flowing rate of 50 mL min⁻¹. Dynamic mechanical analysis (DMA) was recorded on a DMA 1 mechanical analyzer (Mettler Toledo, Germany) with a heating rate of 5 °C min⁻¹ in air. UV–vis–near-infrared (NIR) spectra were detected on a Varian CARY 5000 detector in the wavelength range from 300 to 2000 nm.



Scheme S1. The synthetic route of **Poly(FA-BSAEP)-BDM**



Scheme S2. The synthetic route of **Poly(FA-BPAEP)-BDM**

Synthesis of 4-vinylphenol

To a stirring solution of methyltriphenylphosphonium bromide (64.35 g, 0.18 mol) in a 500 ml three-mouth flask with THF (200 mL), then potassium tert-butoxide (36.81 g, 0.33 mol) and NaH (1.97 g, 0.08 mol) were added. After addition, the mixture was stirred for an additional 15 minutes at room temperature. Then a solution of 4-hydroxybenzaldehyde (20.00 g, 0.16 mol) in THF (50 mL) was added dropwise to the mixture. After stirred at room temperature for 3 h, the reaction system was neutralized with dilute HCl and extracted with ethyl acetate. The organic layer was collected, washed with saturated brine, dried over anhydrous Na_2SO_4 , and filtered. After removal of the solvent under reduced pressure, the obtained product was purified by column chromatography of silica gel using a mixture of petroleum ether and ethyl acetate (9:1, v/v) as the eluent to give 4-vinylphenol as a white solid in a yield of 99%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, δ): ^1H NMR 9.52 (s, 1H), 7.37 – 7.21 (m, 2H), 6.84 – 6.70 (m, 2H), 6.68 – 6.51 (m, 1H), 5.58 (dd, $J = 17.6, 1.0$ Hz, 1H), 5.04 (dd, $J = 10.9, 1.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.59 (s), 141.62 (s), 133.47 (s), 132.64 (s), 120.55 (s), 115.81 (s).

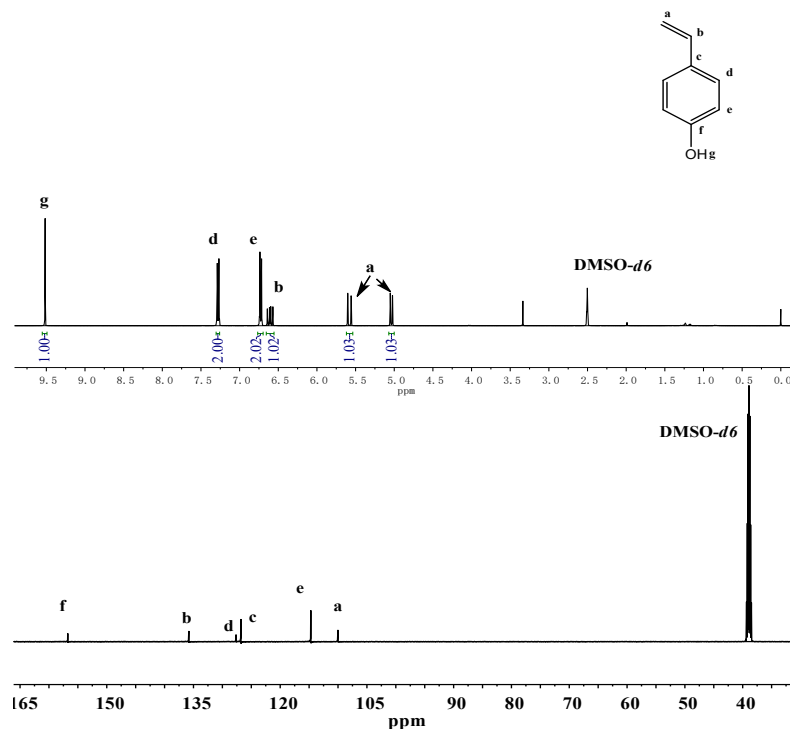


Fig.S1. ¹H NMR and ¹³C NMR spectra of 4-vinylphenol monomer (DMSO-*d*₆)

Synthesis of 2-((4-vinylphenoxy)methyl)oxirane

4-vinylphenol (14.00 g, 0.12mol) and **TBAB** (1.88 g, 0.12mol) were added to a three-mouth flask, dissolved with epichlorohydrin and reflux at 100 ° C. After 3 hours, the solution was cooled to room temperature and the aqueous solution of NaOH (20 wt %) was added. The mixture was stirred vigorously for 3 h and extracted with dichloromethane. Then, the organic layer was washed with saturated brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum. The crude 2-((4-vinylphenoxy)methyl)oxirane was purified by column chromatography on SiO₂ using a mixture of petroleum and ethyl acetate (9:1, v/v) to give pure product as a colorless liquid in a yield of 86%.

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.6 Hz, 1H), 6.87 (t, *J* = 10.0 Hz, 1H), 6.64 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.60 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.9 Hz, 1H), 4.05 (ddd, *J* = 16.8, 11.0, 4.4 Hz, 1H), 3.32 (qd, *J* = 5.8, 3.1 Hz, 1H), 2.97 – 2.65 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 158.28 (s), 136.15 (s), 130.98 (s), 127.45 (s), 114.67 (s), 111.91 (s), 68.75 (d, *J* = 11.2 Hz), 50.13 (s), 44.68 (s).

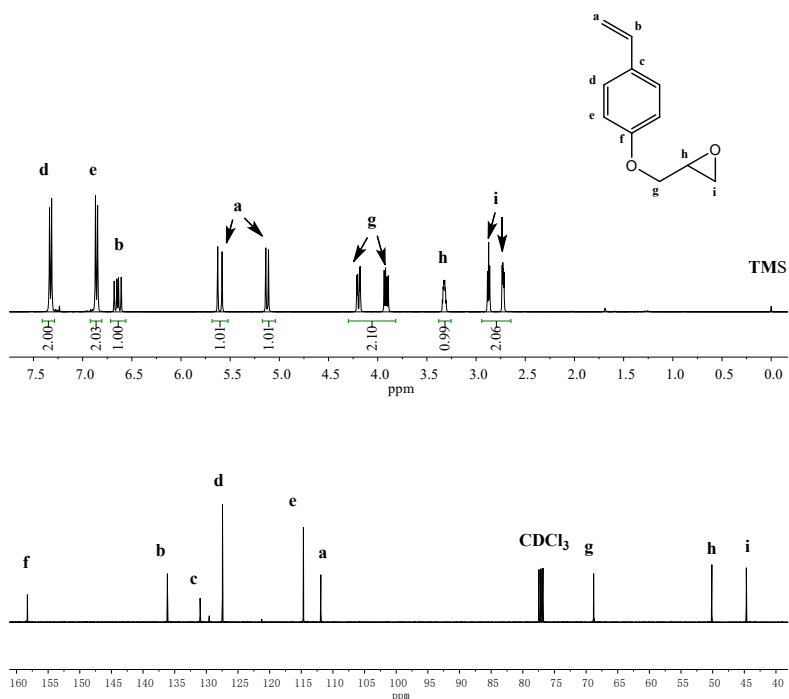


Fig. S2. ¹H NMR and ¹³C NMR spectra of BSAEP monomer (CDCl₃)

Synthesis of 1,2-bis((4-(oxiran-2-ylmethoxy)phenethyl)thio)ethane (BSAEP)

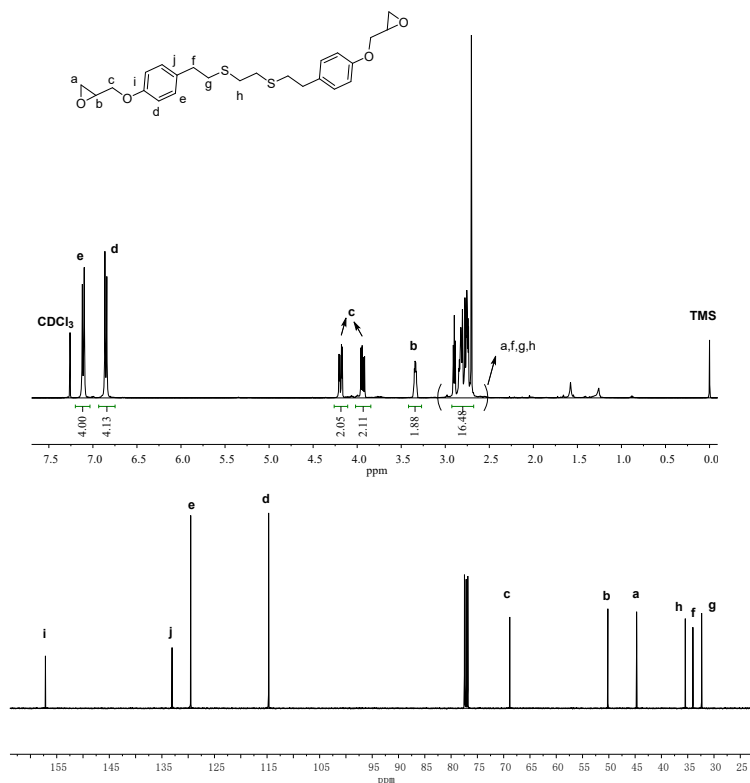


Fig. S3. ¹H NMR and ¹³C NMR spectra of 2-((4-vinylphenoxy)methyl)oxirane monomer (CDCl₃)

Preparation of linear epoxy polymer containing furan group (Poly(FA-BSAEP) and Poly(FA-BPAEP))

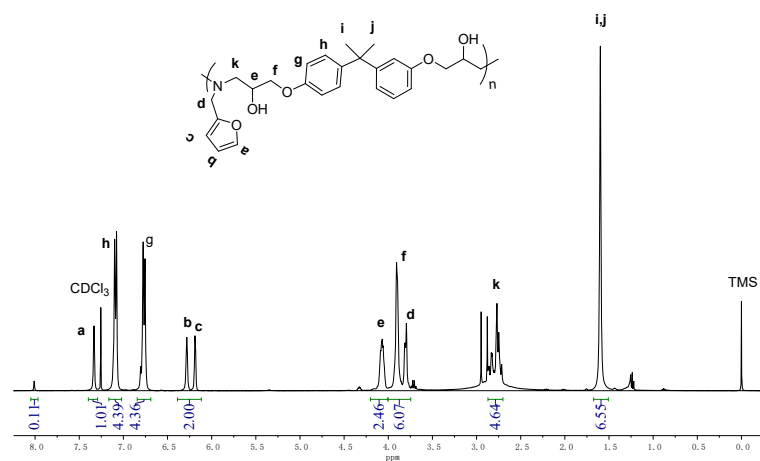


Fig. S4. ^1H NMR spectra of Poly(FA-BPAEP) monomer (CDCl_3)

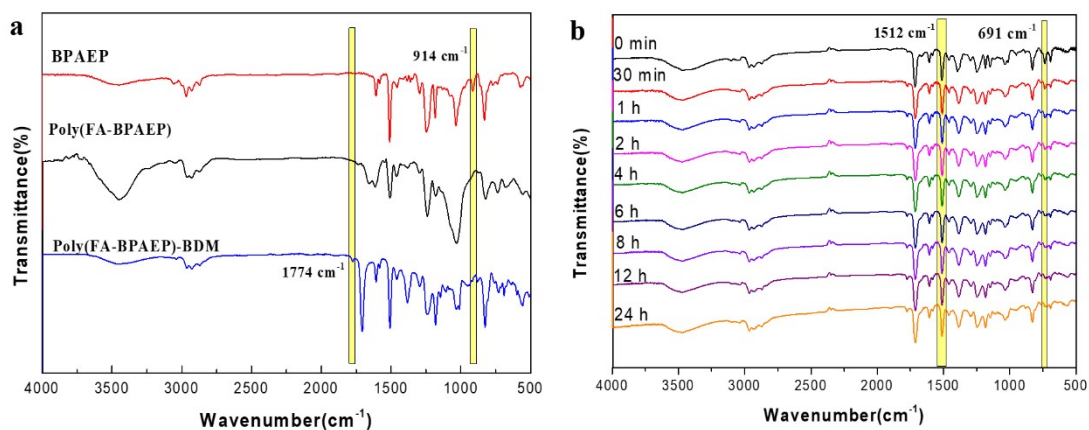


Fig.S5. FT-IR curves (a) of the BPAEP, Poly(FA-BPAEP) and Poly(FA-BPAEP)-BDM , FT-IR curves (b) of the Poly(FA-BPAEP) reacted with BDM at 80°C for different holding times.

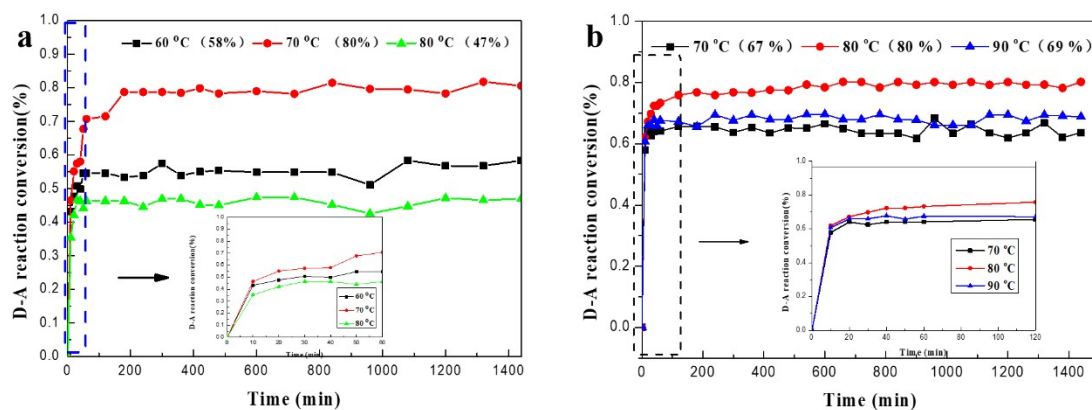


Fig. S6. Reaction degree of the Poly(FA-BSAEP) (a) or Poly(FA-BSAEP) (b) with BDM at different temperature

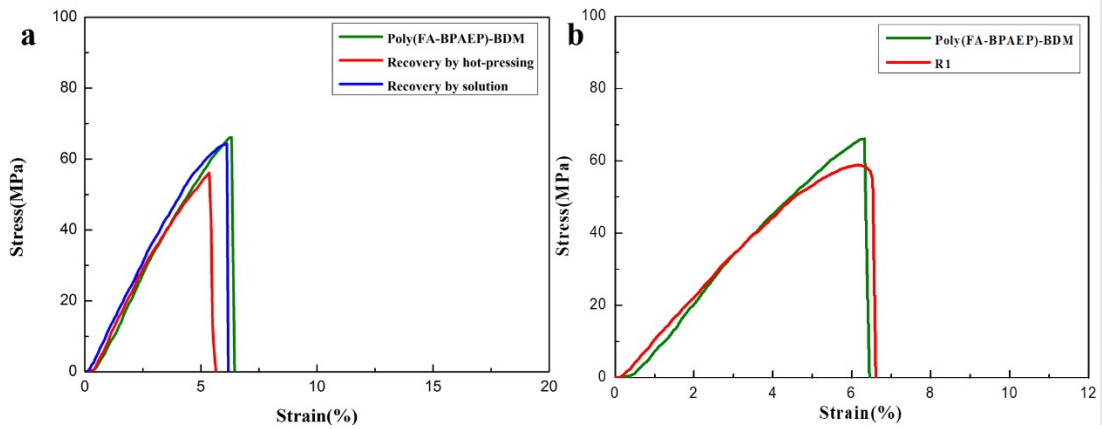


Fig. S7. The tensile tests of reprocessed Poly(FA-BPAEP)-BDM (a. processing using different methods, b. recycle by hot-pressing)

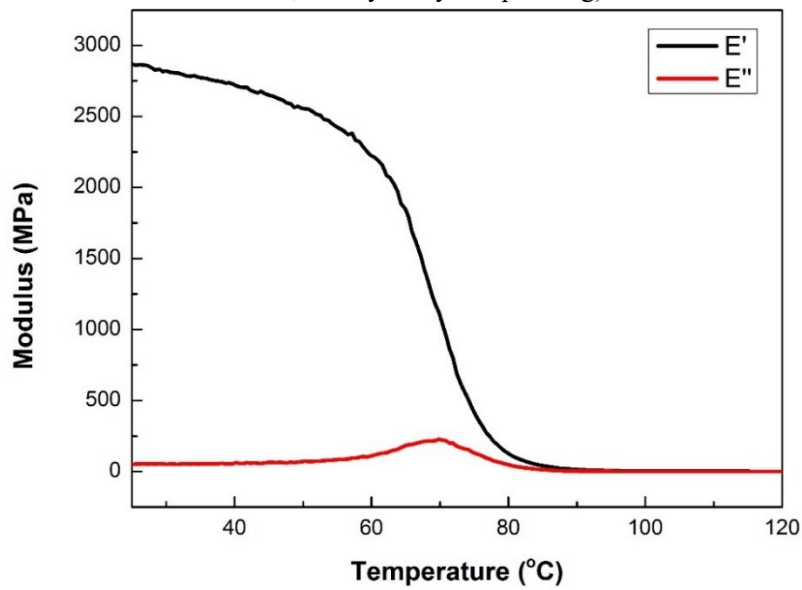


Fig.S8. DMA curves of Poly(FA-BPAEP)-BDM

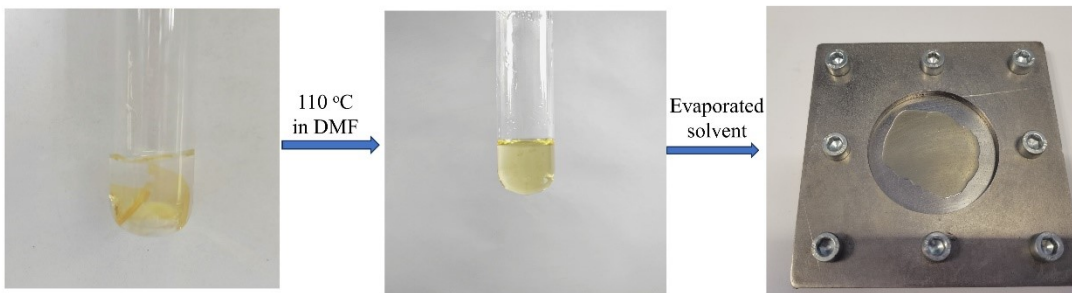


Fig.S9 Recovery of Poly(FA-BSAEP)-BDM by solution method

Table S1. The tensile properties of reprocessed **Poly(FA-BSAEP)-BDM** and **Poly(FA-BPAEP)-BDM**

Name	strength (Mpa)	Elongation (%)	Young's Modulus
Poly(FA-BSAEP)-BDM	79.7	12.2	8.6
Poly(FA-BSAEP)-BDM (R1)	80.0	11.2	8.8
Poly(FA-BSAEP)-BDM (R2)	78.2	9.7	9.2
Poly(FA-BSAEP)-BDM (R3)	77.9	9.4	10.3
Poly(FA-BPAEP)-BDM	66.1	6.3	13.8
Poly(FA-BPAEP)-BDM (R1)	56.1	5.4	13.2