

# **Supporting information**

## **For**

### **Sonochemical Transformation of Epoxy-amine Thermoset into Soluble and Reusable Polymers**

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### Experimental section for the synthesis of the FHM/DETA thermoset (3):

#### Synthesis of 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione) (HBMI)

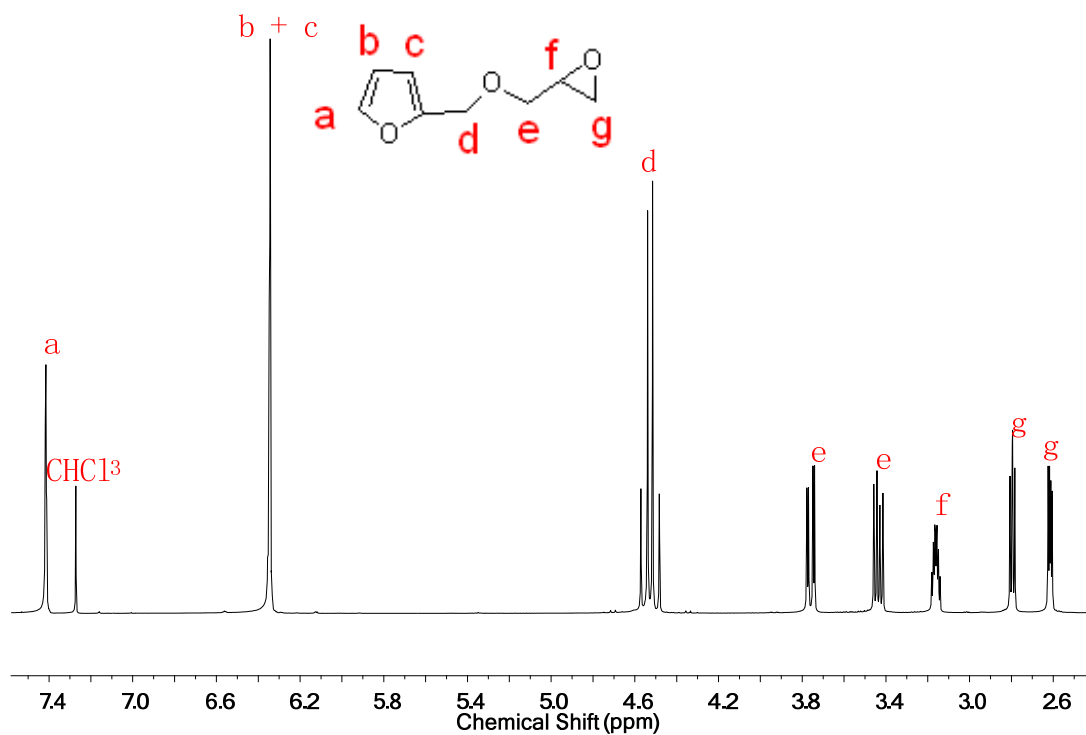
Firstly, 6.00 g (61.2 mmol) maleic anhydride was dissolved in 60 mL CH<sub>2</sub>Cl<sub>2</sub>. The solution was charged into a 250 mL three-necked round-bottom flask equipped with magnetic stirring. Then, 3.21 g (27.7 mmol) 1,6-hexamethylenediamine in 60 mL CH<sub>2</sub>Cl<sub>2</sub> was slowly dropped into the solution by a constant dropping funnel at 0 °C and stirred for an overnight at room temperature. After the reaction, CH<sub>2</sub>Cl<sub>2</sub> was evaporated and 120 mL acetone was added to dissolve the residue. 0.14 g (0.56 mmol) nickel(II) acetate and 1.60 mL (11.4 mmol) triethylamine were added to the solution under stirring. The mixture was heated at 65 °C for 2 days. The mixture was cooled to room temperature and acetone was evaporated and the residue was poured into ice water (400 mL) and stirred for 30 minutes while NaHCO<sub>3</sub> was added to neutralize the acids. The mixture was filtered and washed with water until the filtrate was colorless. Then the filter cake was dried in vacuum oven to give the compound **2** (63%) as white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.69 (s, 4H), 3.50 (t, *J* = 7.2 Hz, 4H), 1.71 – 1.44 (m, 4H), 1.30 (dd, *J* = 8.9, 5.4 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.41, 142.89, 110.30, 109.58, 70.57, 64.97, 50.68, 44.18.

#### Synthesis of 2,2'-(hexane-1,6-diyl)bis(4-((oxiran-2-ylmethoxy)methyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione) (FHM)

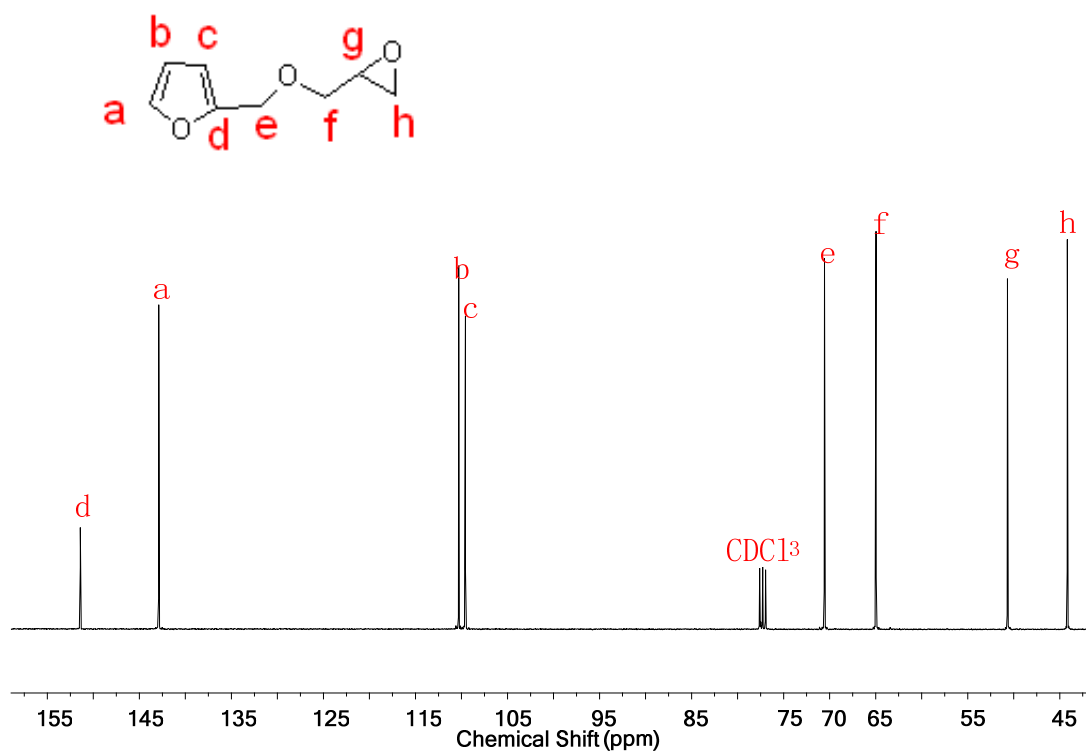
FGE (5 g, 32.5 mmol) and HBMI (4 g, 14.5 mmol) and EtOAc (60 mL) were added in a 250 mL three-necked round-bottom flask equipped with magnetic stirring and condenser and a thermometer. The solution was refluxed at about 78 °C for 24 h under N<sub>2</sub> atmosphere. Then cooled down to room temperature. Concentrated and the residue was purified by chromatography on a silica gel column with mixed solvent of CHCl<sub>3</sub>/MeOH = 100/1 (*R<sub>f</sub>* = 0.43) to obtain the aimed colorless viscous liquid. <sup>1</sup>H NMR (400 MHz, DMSO) δ 6.52 (2H), 5.15 (1H), 4.18 (1H), 3.87 – 3.61 (2H), 3.37 (1H), 3.33 – 3.23 (2H), 3.19 – 2.87 (3H), 2.75 – 2.70 (1H), 2.59 – 2.52 (1H), 1.39 (2H), 1.16 (2H). <sup>13</sup>C NMR (100 MHz, DMSO) δ 176.19, 175.18 – 174.64, 137.48, 136.52, 90.08, 80.27, 72.18 – 71.80, 68.2, 50.19, 49.45, 47.98, 43.23, 38.79, 26.73, 25.27.

The synthesis of **3** was the same with that of **2**.

## Figures and Schemes:

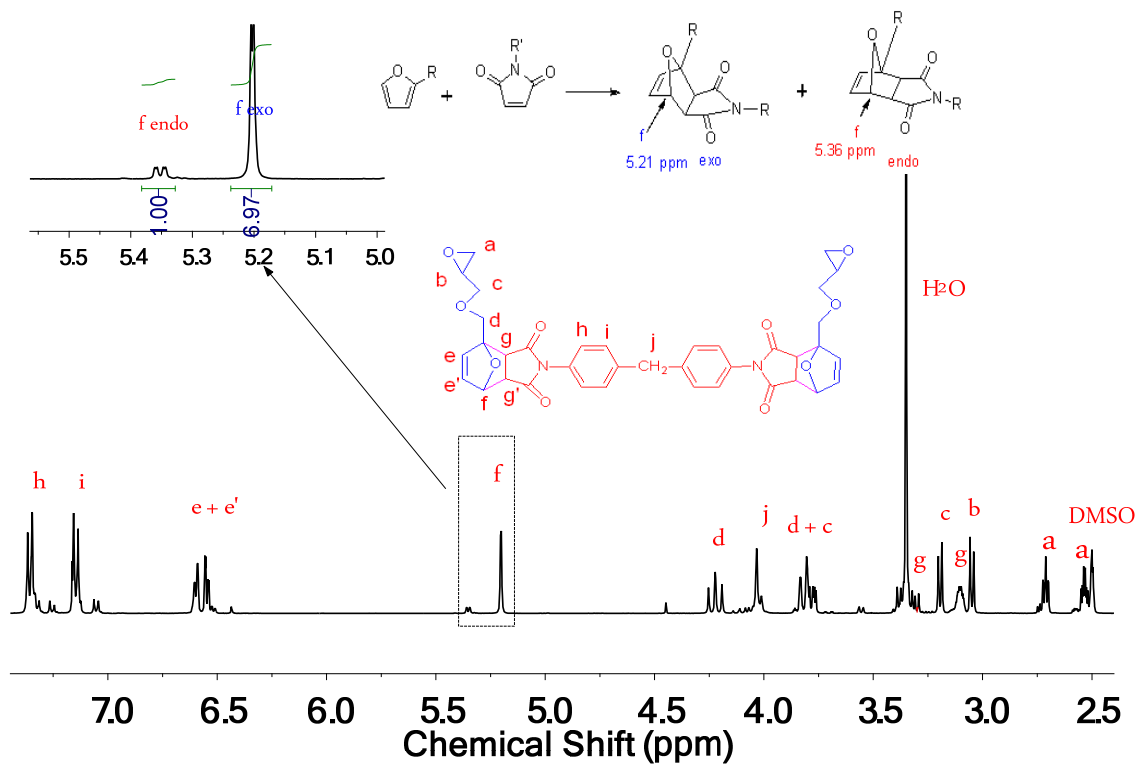


(A)

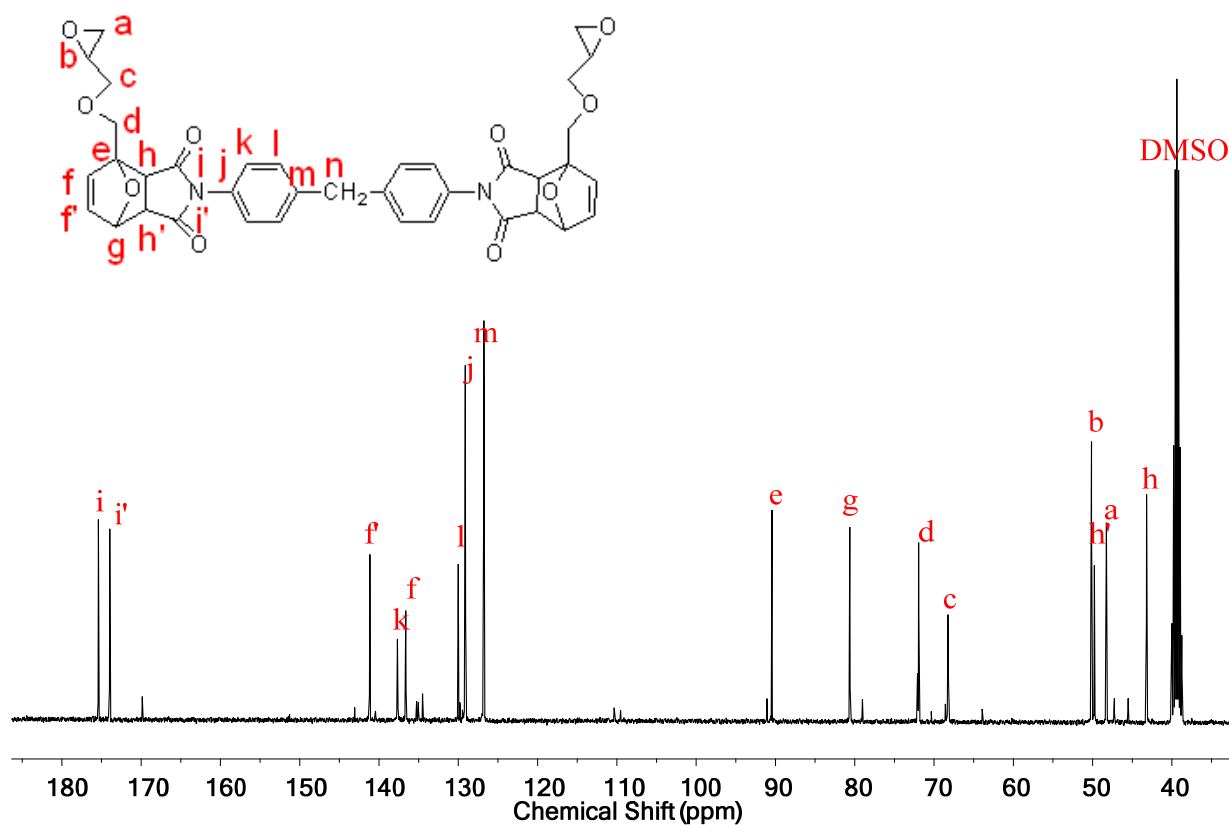


(B)

**Figure S1** (A) <sup>1</sup>H-NMR spectrum (400 MHz, CDCl<sub>3</sub>) of FGE; (B) <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of FGE.

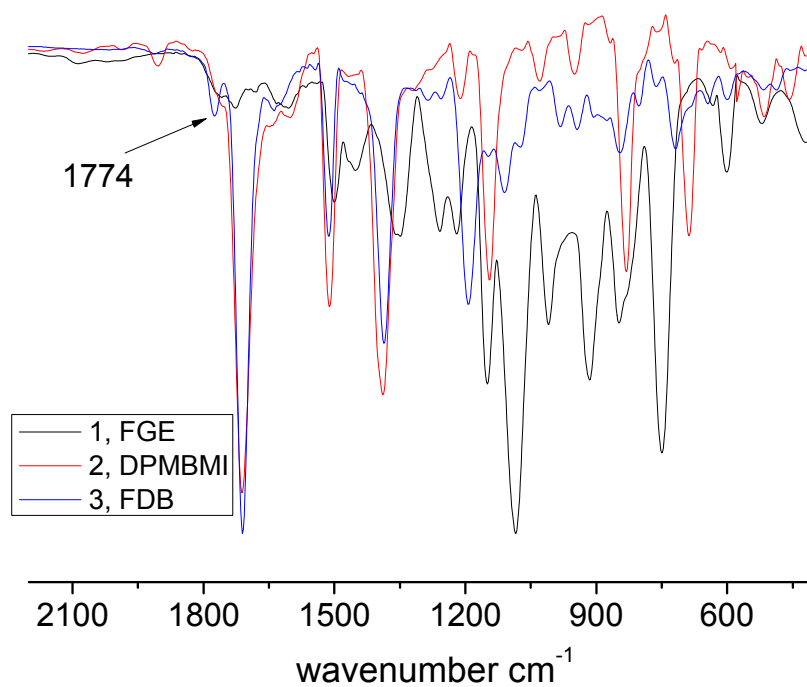


(A)

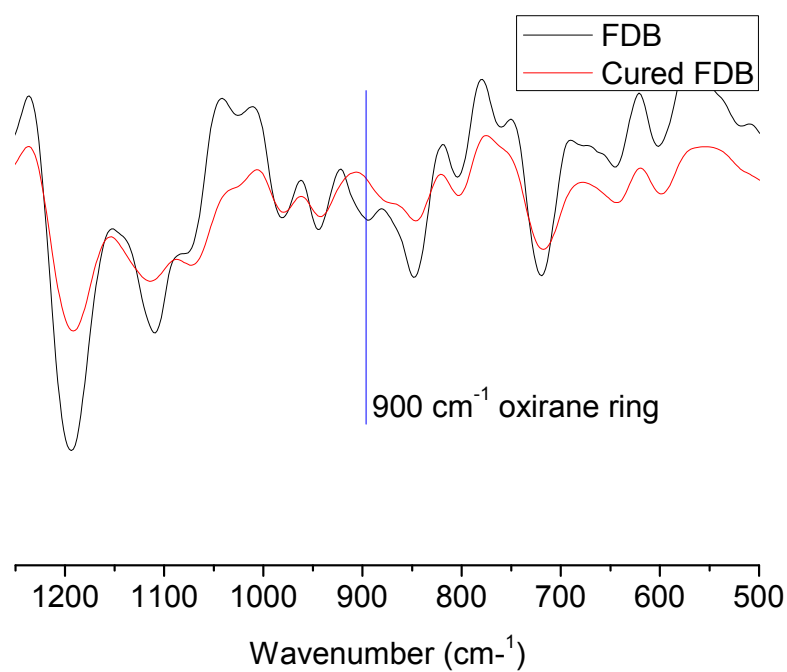


(B)

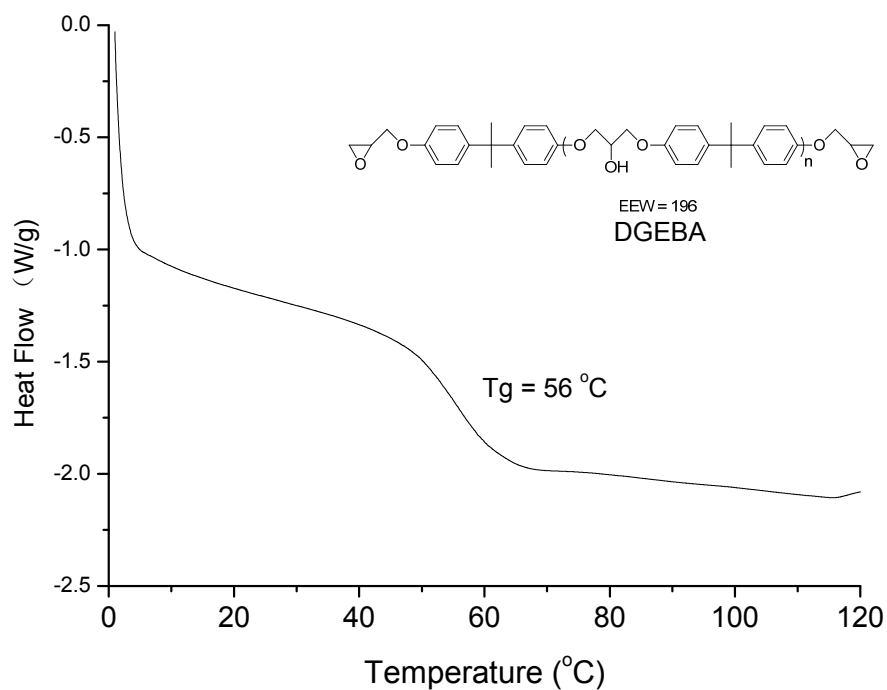
**Figure S2** (A)  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{DMSO}-d_6$ ) of FDB; (B)  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{DMSO}-d_6$ ) of FDB.



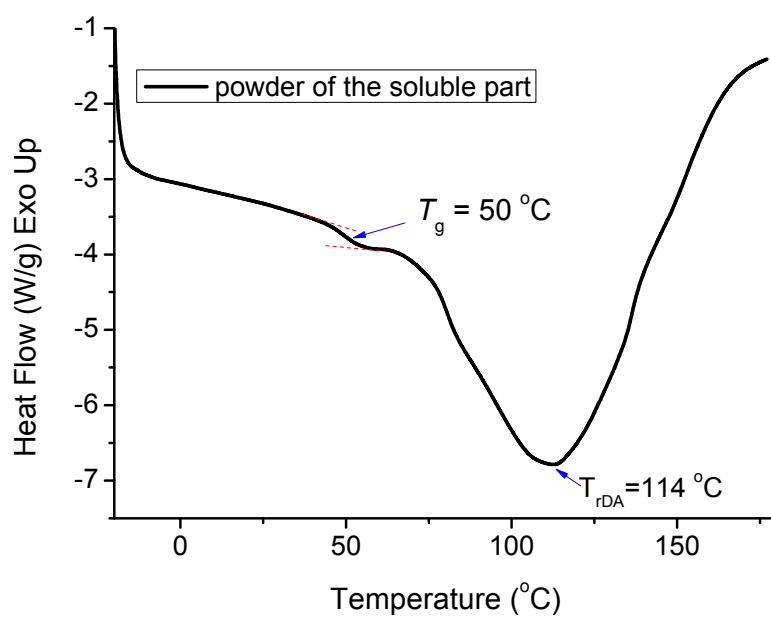
**Figure S3** FT-IR spectra of FGE, DPMBMI and FDB. The absorption peak found at  $1774\text{ cm}^{-1}$ , which is specific to DA adducts of maleimides.<sup>1</sup>



**Figure S4** FT-IR spectra of FDB and FDB/DETA thermoset.

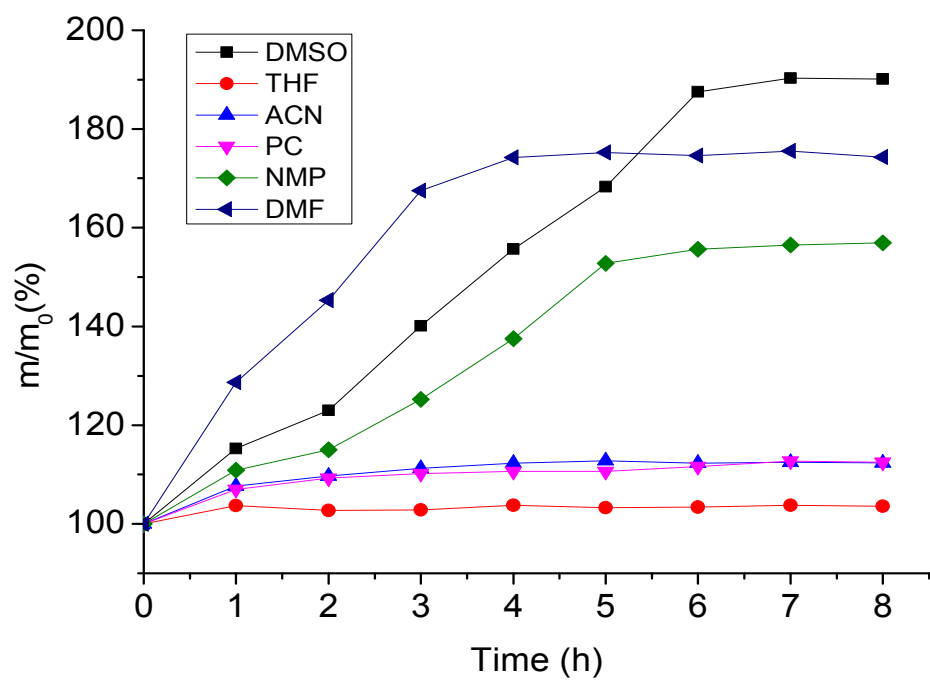


(A)

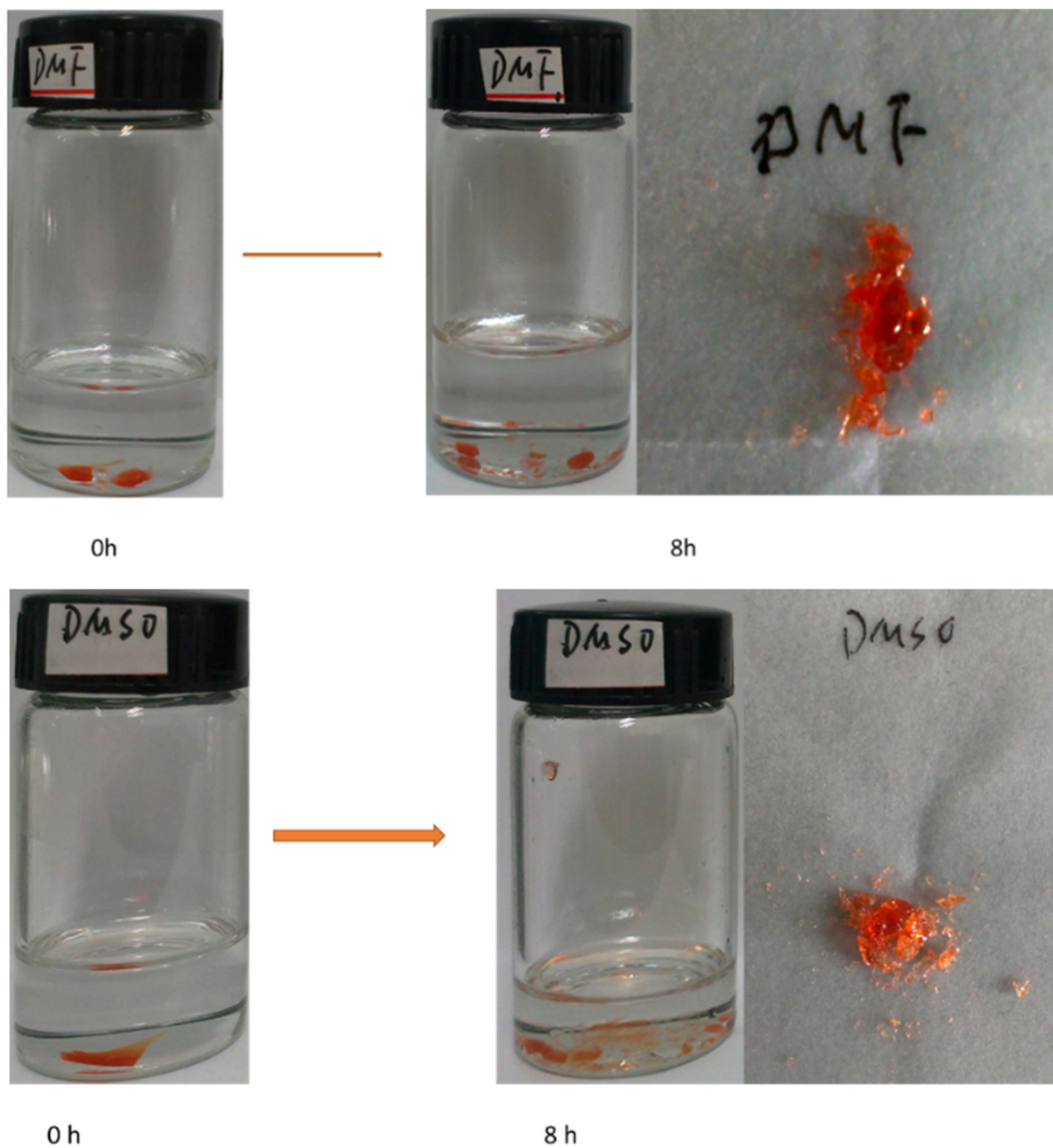


(B)

**Figure S5** DSC results of: (A) of the DGEBA/DETA thermoset. DGEBA: DETA = 1: 0.13 (weight ratio), curing procedure: RT \* 4 d + 60 °C \* 12 h; (B) the soluble part after sonication in DMSO (dried).



(A)





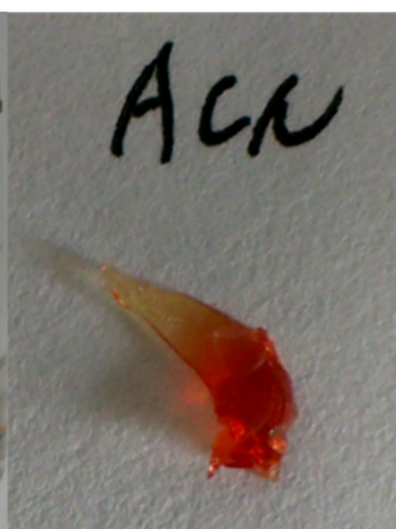
0h



8h



0h



8h

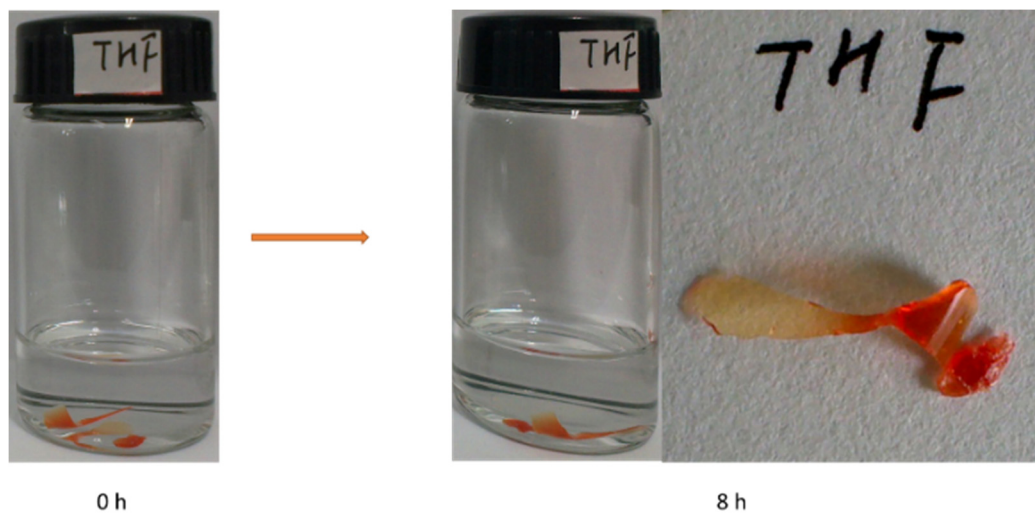


0h



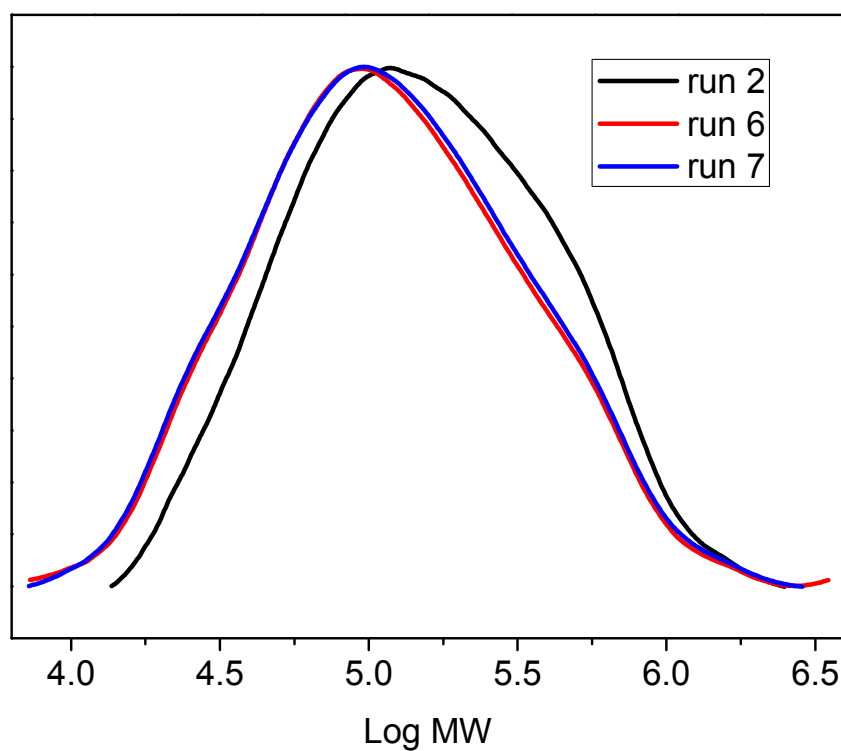
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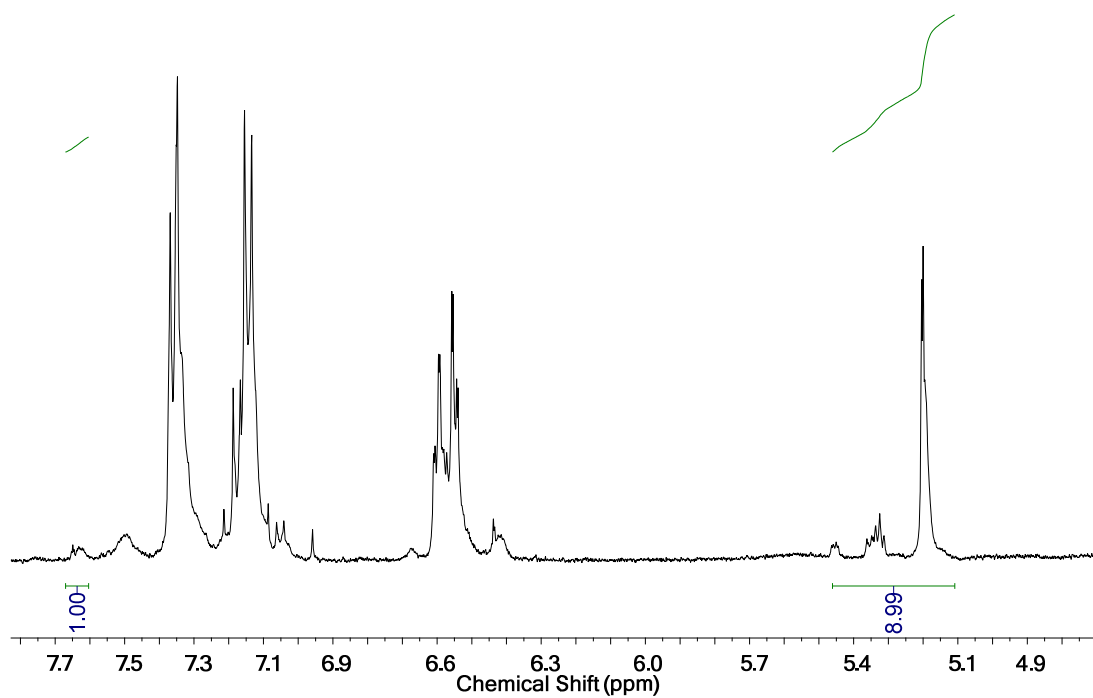


(B)

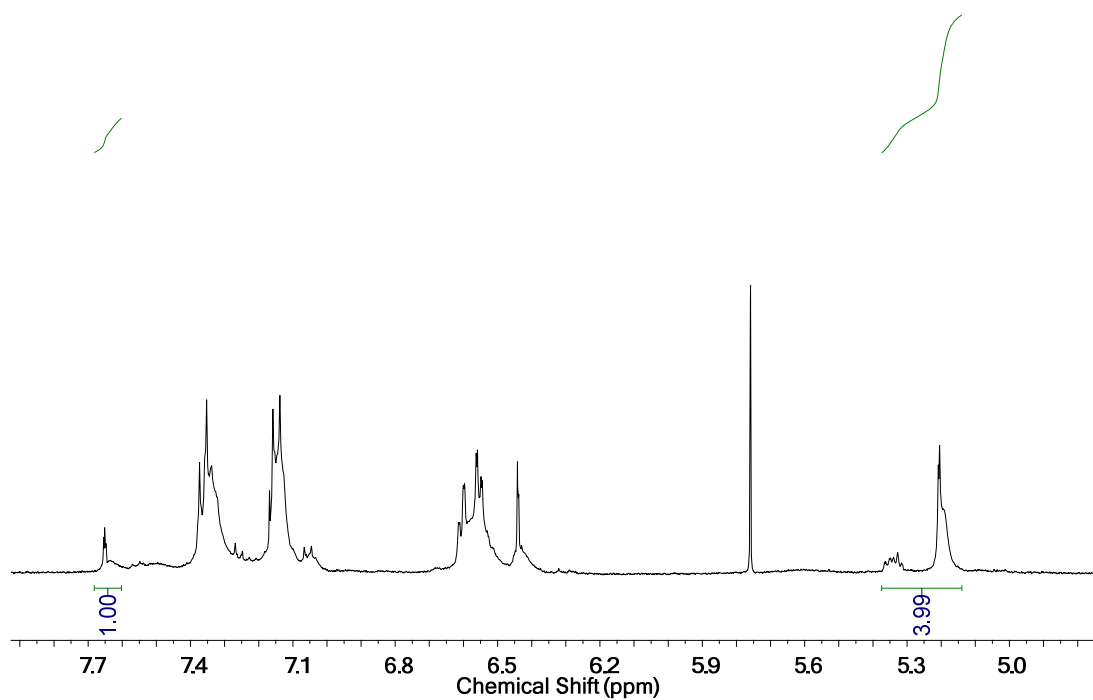
**Figure S6** Swelling degree of the FDB/DETA thermoset (**2**) in various solvents as a function of immersion time (A) and the digital photos of **2** in DMSO, THF, DMF, NMP, ACN and PC at 0 h and 8 h respectively (B). The swelling degree was defined as  $m/m_0 \times 100\%$ ,  $m_0$ : the original mass of the dried sample,  $m$ : the mass of the sample picked out at different time points, the solvent at the surface of the sample was absorbed by dried filter paper.



**Figure S7** GPC curves of the obtained soluble polymers. Curves 2, 6,7 are corresponding to the entries 2,6,7 in Table 1 in the text.

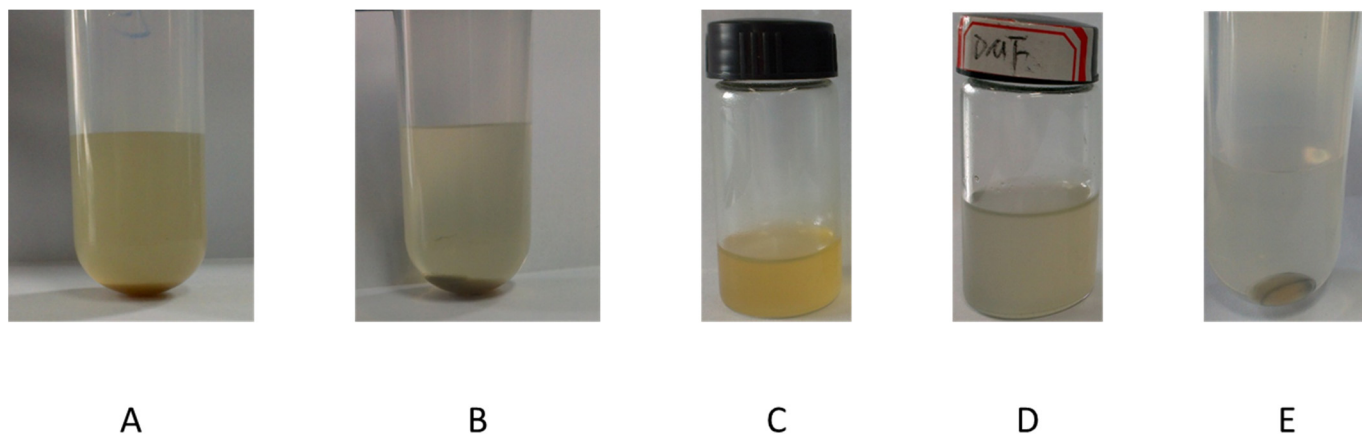


(A)

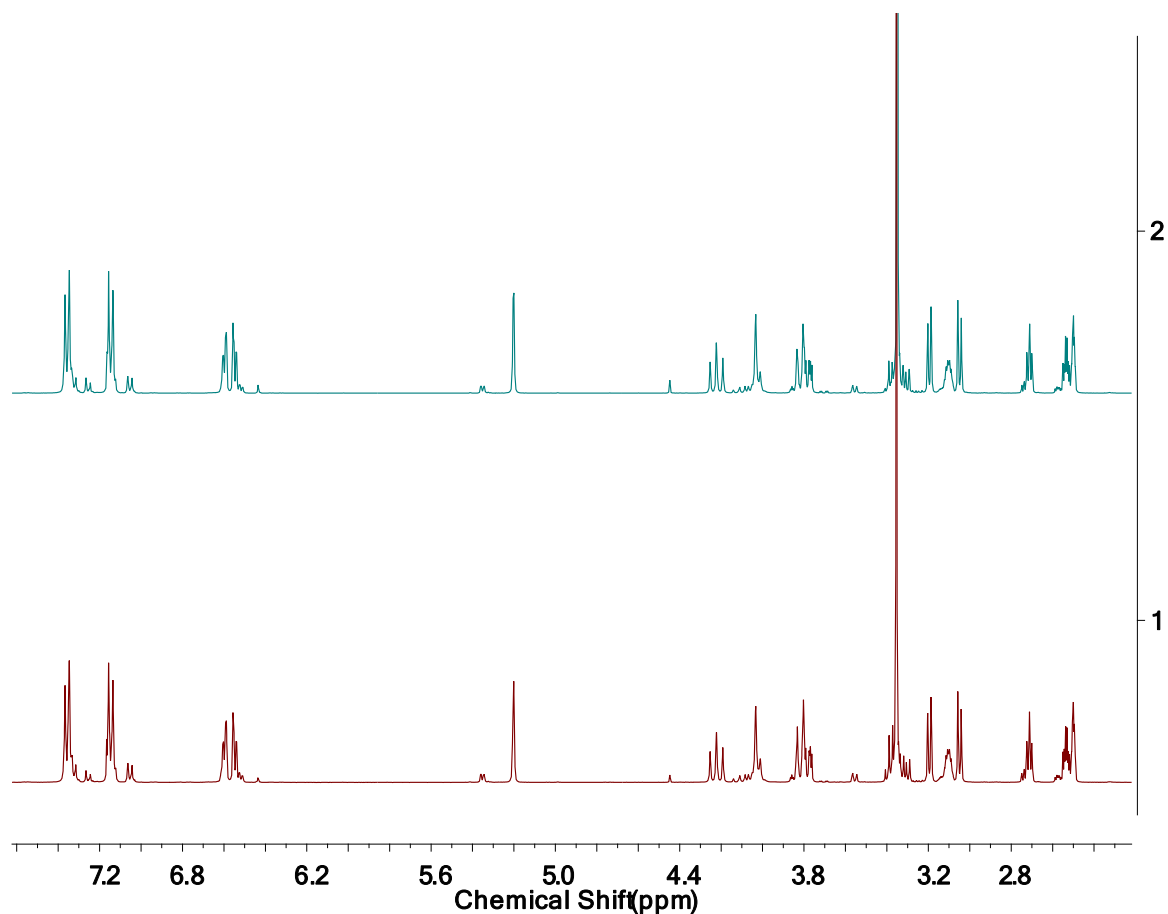


(B)

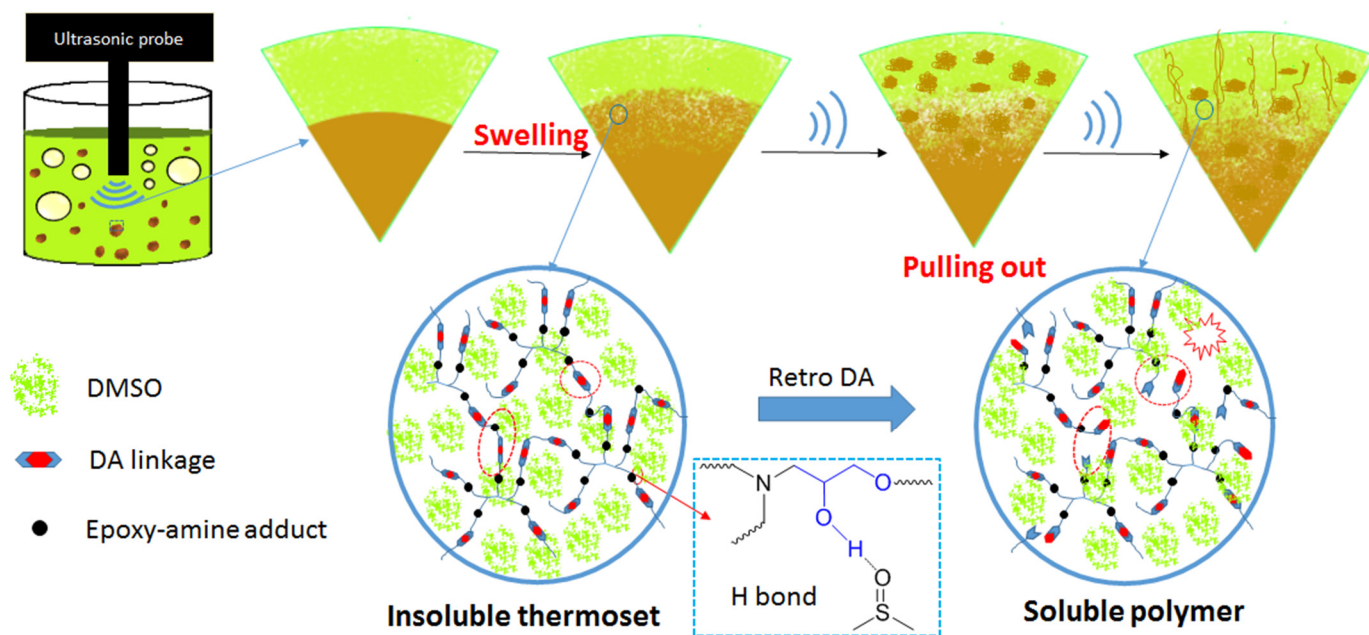
**Figure S8**  $^1\text{H}$  NMR spectra of the ultrasonic degradation product. (A): polymer from entry 3 in Table 1. The ratio of r-DA =  $1/(1+9) \times 100\% = 10\%$ ; (B): polymer from entry 5 in Table 1. The ratio of r-DA =  $1/(1+4) \times 100\% = 20\%$ .



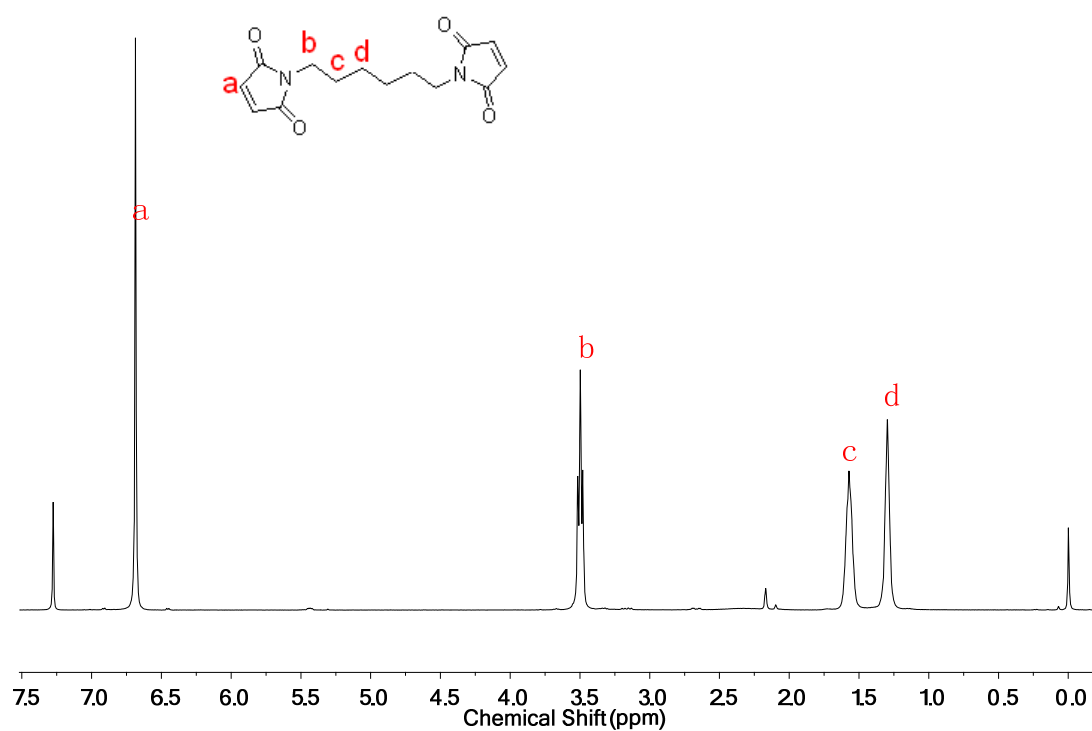
**Figure S9** Digital images: the DGEBA/DETA thermoset that was sonicated in DMSO for 125 min (**A**) and after centrifugation (**B**); **C**, the FDB/DETA thermoset was sonicated in DMSO without ice bath (ca.40 °C); **D** and **E**, the FDB/DETA thermoset was sonicated in DMF before and after centrifugation.



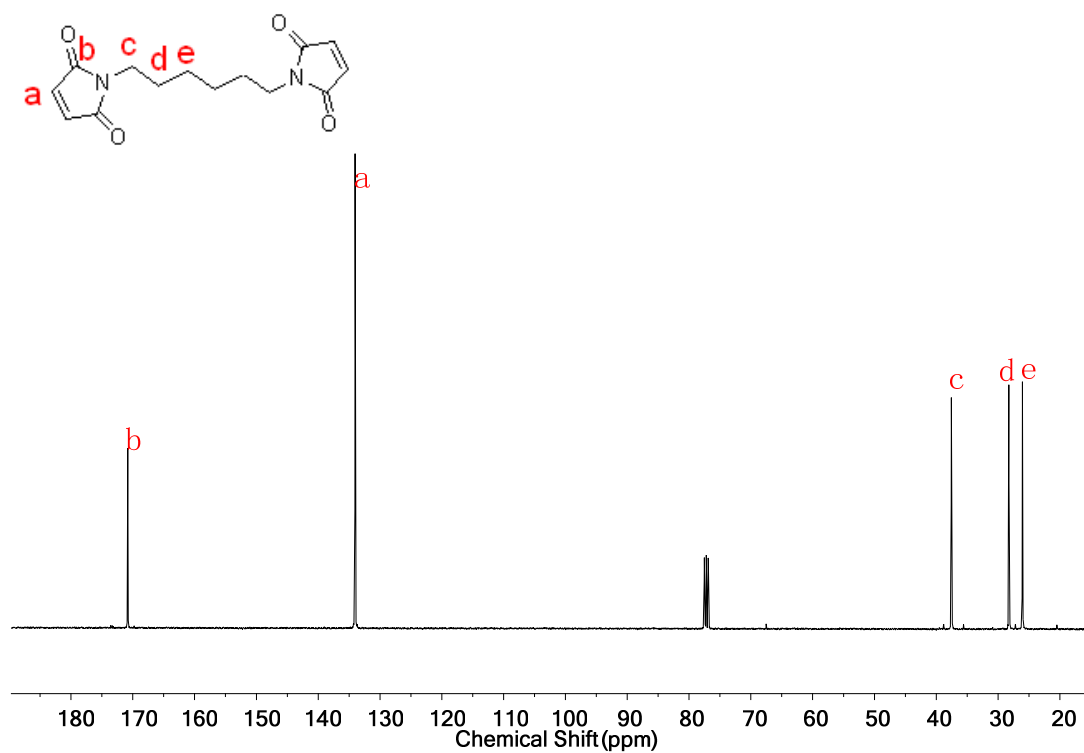
**Figure S10**  $^1\text{H}$  NMR spectra of FDB: 1, before sonication; 2, after sonication. ( $d_6$ -DMSO, 400 MHz).



**Figure S11** Cartoon schematic diagram of the “swell-pullout” mechanism for the mechanical transformation of FDB/DETA thermoset into soluble polymers in DMSO at room temperature.

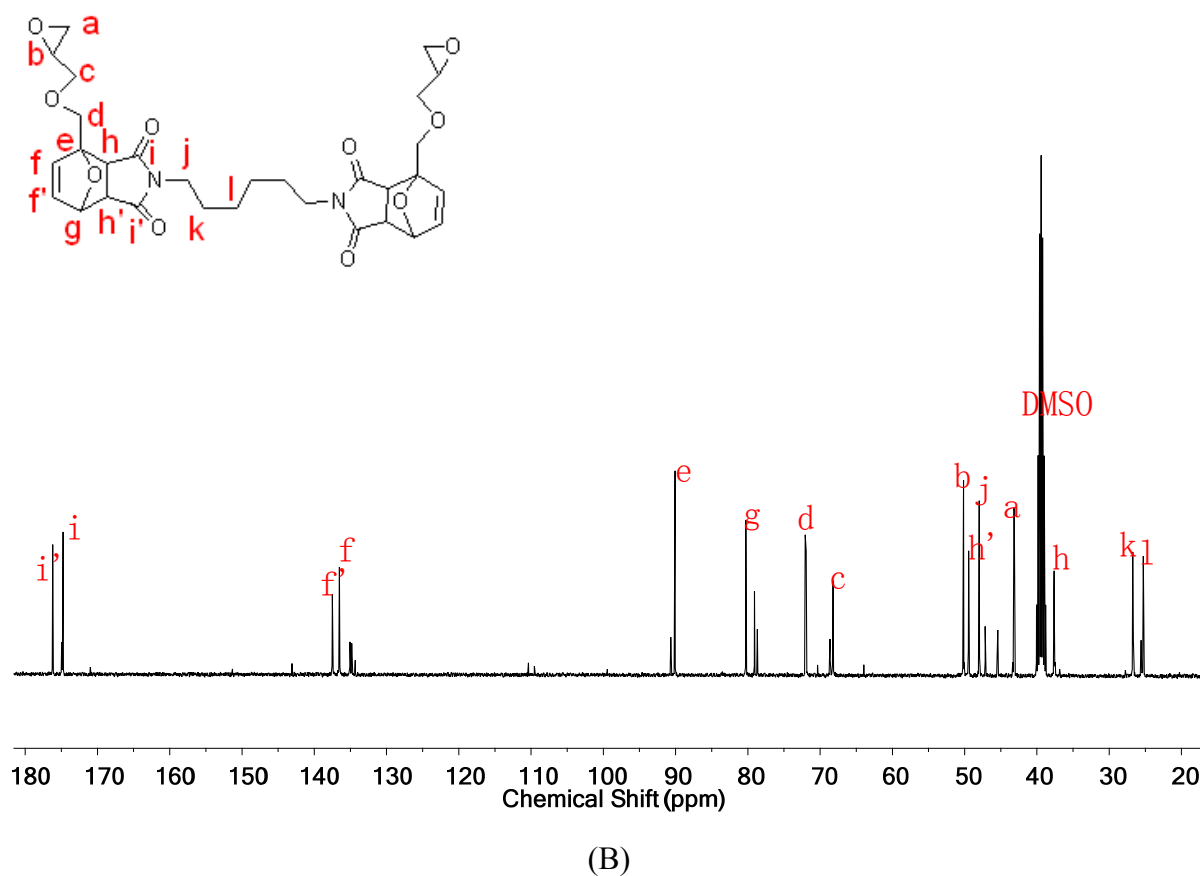
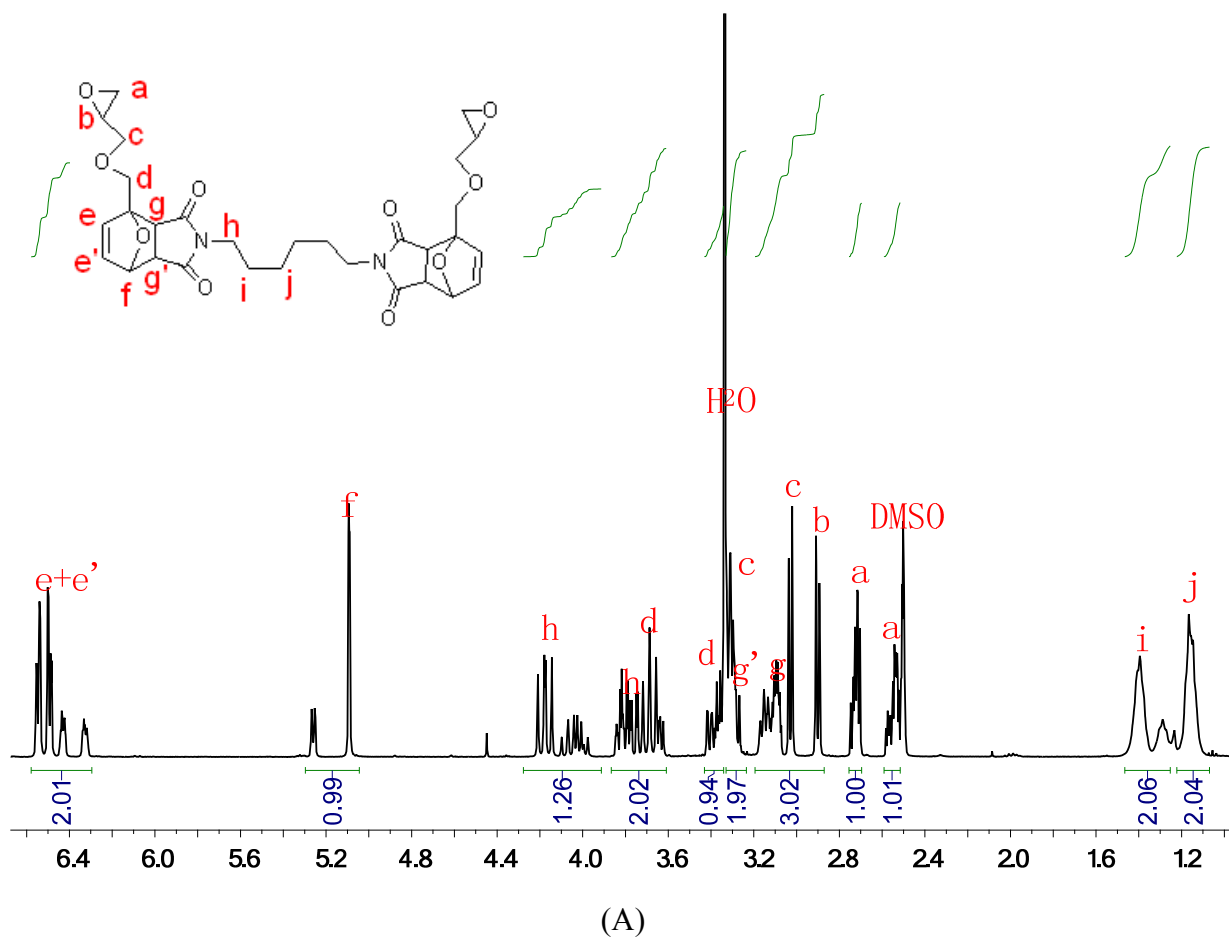


(A)

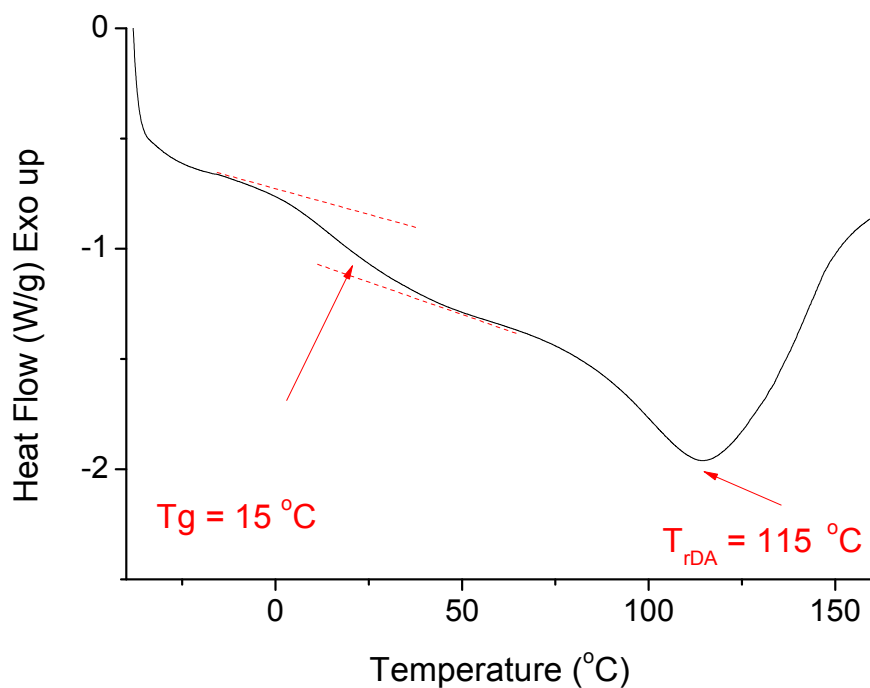


(B)

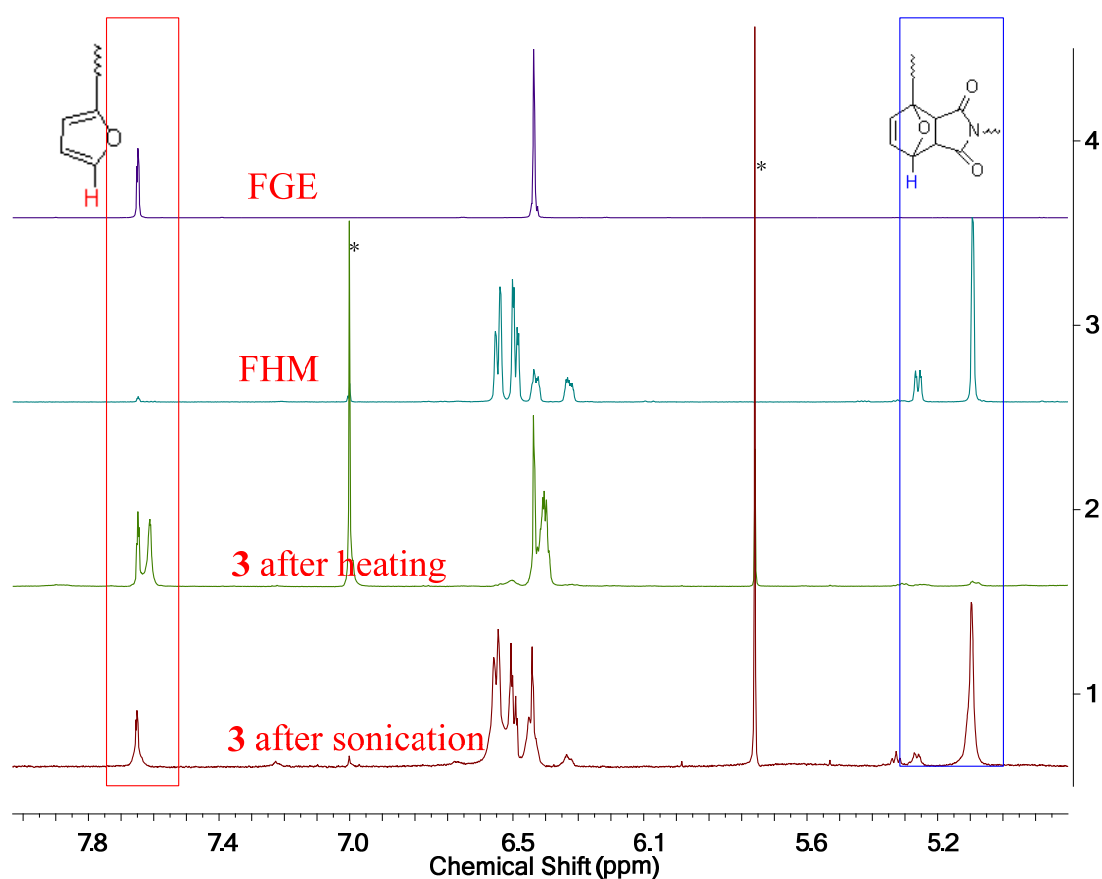
**Figure S12** <sup>1</sup>H-NMR spectrum (400 MHz, CDCl<sub>3</sub>) (A) and <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) (B) of HBMI.



**Figure S13** (A) <sup>1</sup>H-NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) and (B) <sup>13</sup>C NMR spectrum (100 MHz, DMSO-*d*<sub>6</sub>) of FHM.



**Figure S14** DSC curve of FHM/DETA. FHM: DETA = 1: 0.07(weight ratio), RT \* 4 d + 60 °C \* 12 h.



**Figure S15**  $^1\text{H}$ -NMR spectra: 1) the soluble part of entry 10 in Table 1; 2), heat-degraded product of the **3** at 130 °C for 30 min in DMSO- $d_6$ ; 3), FHM and 4), FGE(400 MHz, DMSO- $d_6$ ).

[1] a) Y. Imai, H. Itoh, K. Naka, Y. Chujo. *Macromolecules*, **2000**, 33: 4343-4346; b) Q. Tian, Y. C. Yuan, M. Z. Rong, M. Q. Zhang. *J Mater Chem*, **2009**, 19: 1289-1296.