



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

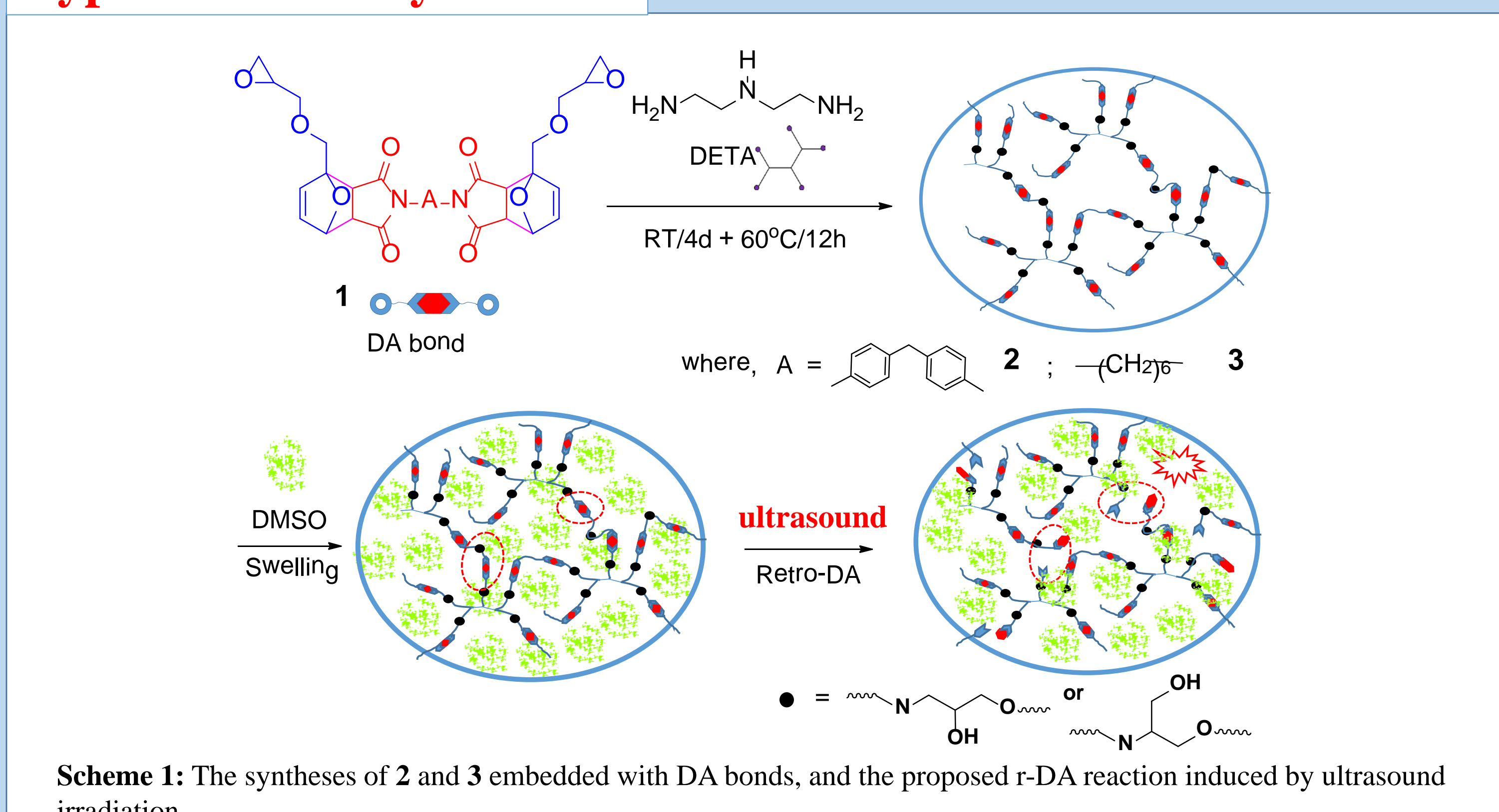
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**Introduction:** The degradation and reuse of epoxy thermosets have significant impact on the environments. We report that an epoxy-amine thermoset embedded with Diels–Alder (DA) bonds was transformed into soluble polymers via sonochemistry under mild temperature (ca. 20°C) for the first time. Sonication could effectively induce the position-oriented cleavage of DA bonds (i.e., retro-DA) of the fully swelled epoxy thermoset in dimethyl sulfoxide (DMSO), leading to the soluble polymers. Of importance, such sonochemical process could be regulated on demand via switching on-and-off of the sonication. The obtained soluble polymers could be re-cured to form epoxy-amine thermosets via DA reaction.

## Hypothesis and Synthesis



## Results

**Table 1.** Soluble epoxy polymers from sonochemical reaction of the epoxy thermosets in the selected solvents.

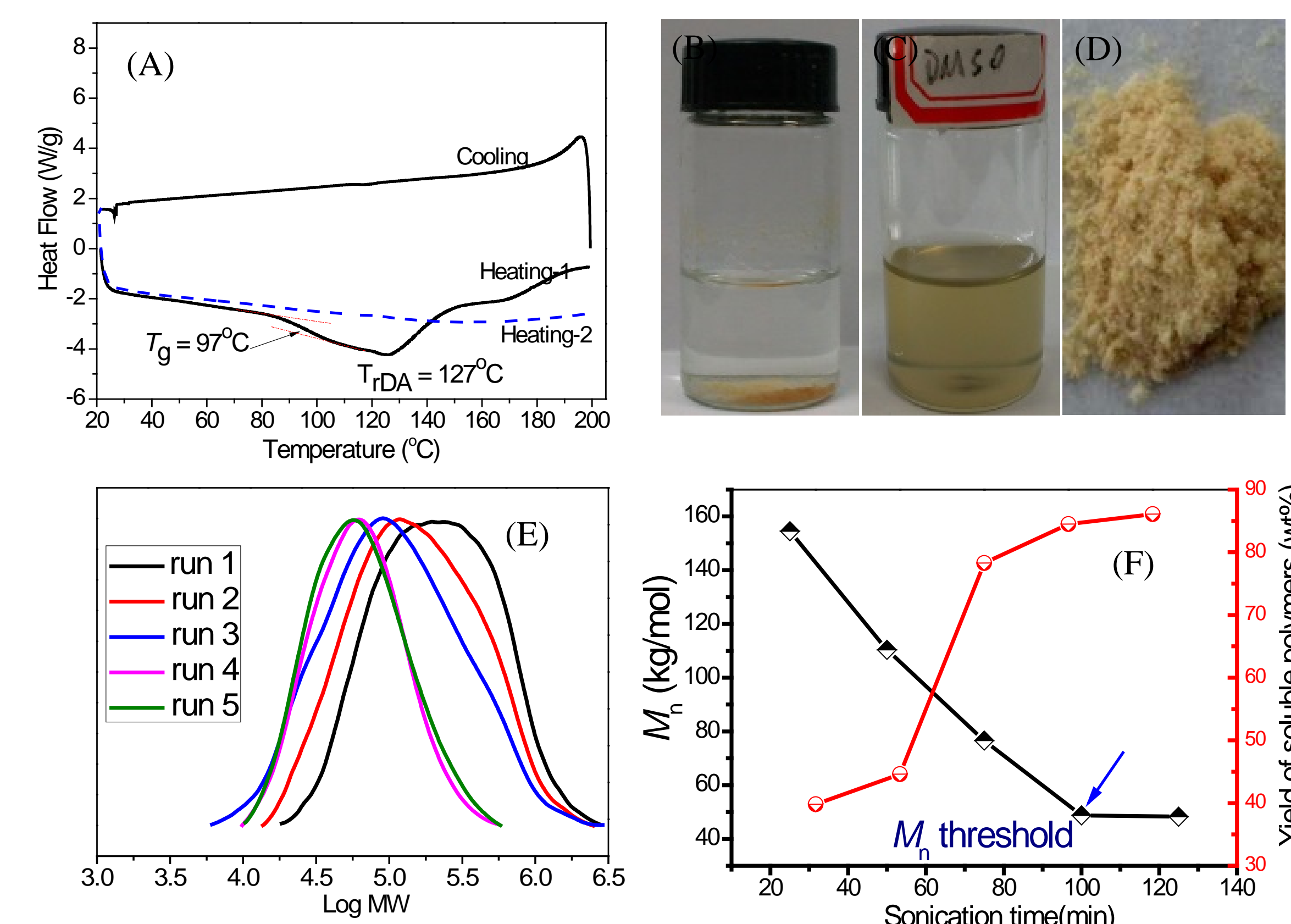
Run	Solvent	Intensity (%)	Time <sup>[a]</sup> (min)	Yield of soluble polymers (%) <sup>[b]</sup>	M <sub>n</sub> (kg/mol) / PDI <sup>[c]</sup>
1	DMSO	30	25	39.8	154.5/2.2
2	DMSO	30	50	44.6	110.4/2.3
3	DMSO	30	75	78.3	76.6/2.7
4	DMSO	30	100	83.5	48.8/1.6
5	DMSO	30	125	84.1	48.3/1.7
6	DMSO	40	50	71.1	86.8/2.5
7	DMSO	50	50	77.9	82.7/2.6
8	NMP	30	75	16.9	577.1/1.5
9	DMF	30	75	3	-/-
10 <sup>[d]</sup>	DMSO	30	125	84.5	48.6/1.6
11 <sup>[d]</sup>	NMP	30	125	46.9	106.2/2.0

**Conditions:** 100.0 mg **2** in 10.0 ml solvent; ice bath; sonication mode: 3s on and 3s off, and 10 min as one cycle (i.e.: 5 min sonication on per cycle), the next cycle was then started after a stop time of 2 min. The maximum ultrasonic power of the instrument was 650 W, an Ø6 mm amplitude transformer was immersed into the solvent in a 25 ml vial under N<sub>2</sub> atmosphere. [a] the total time of the on mode of the sonicator; [b] calculated from the residual solid after sonication, centrifugation and completely dried process; [c] determined by gel permeation chromatography in DMF, 60 °C, PMMA standard; [d] the FHM/DETA thermoset (**3**).

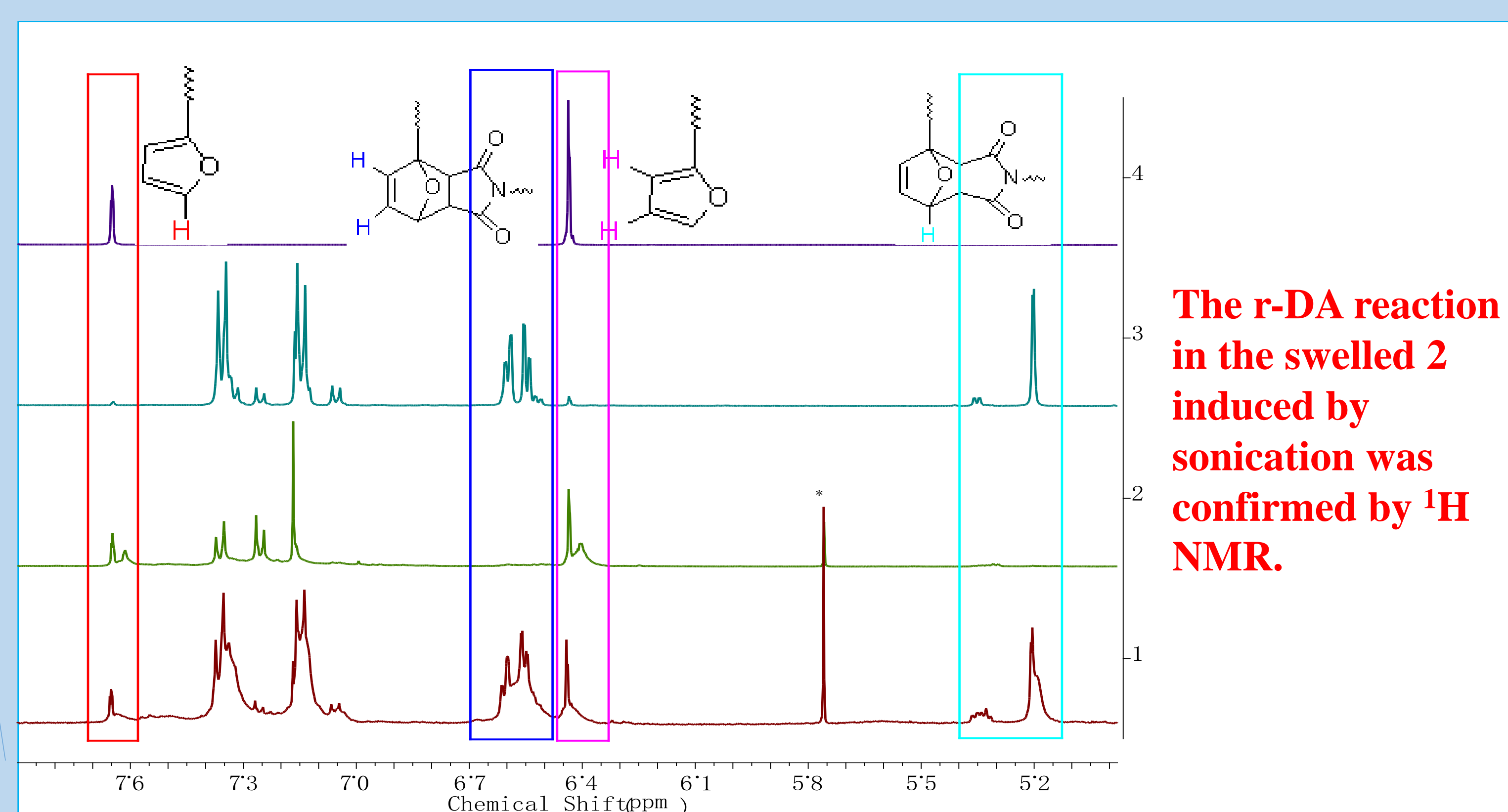
## Proposed mechanism

The partial degradation of **2** to soluble polymers is a combination of the swelling and pulling-out effect caused by ultrasound irradiation in DMSO. The effective swelling of **2** is the prerequisite for converting the cross-linked network into soluble polymers, while the strong solvent-polymer interaction could facilitate the extraction of a polymer chain from the swelled layer of the thermoset.

**Conclusions:** We reported the first example of force-induced transformation of the epoxy thermoset into a soluble and reusable polymer via partial position-oriented cleavage of DA bonds in the thermoset in DMSO. This force-induced degradation protocol provides an unprecedented, useful and efficient way to recycle the epoxy thermosets with dynamic covalent bonds like DA groups under mild conditions.

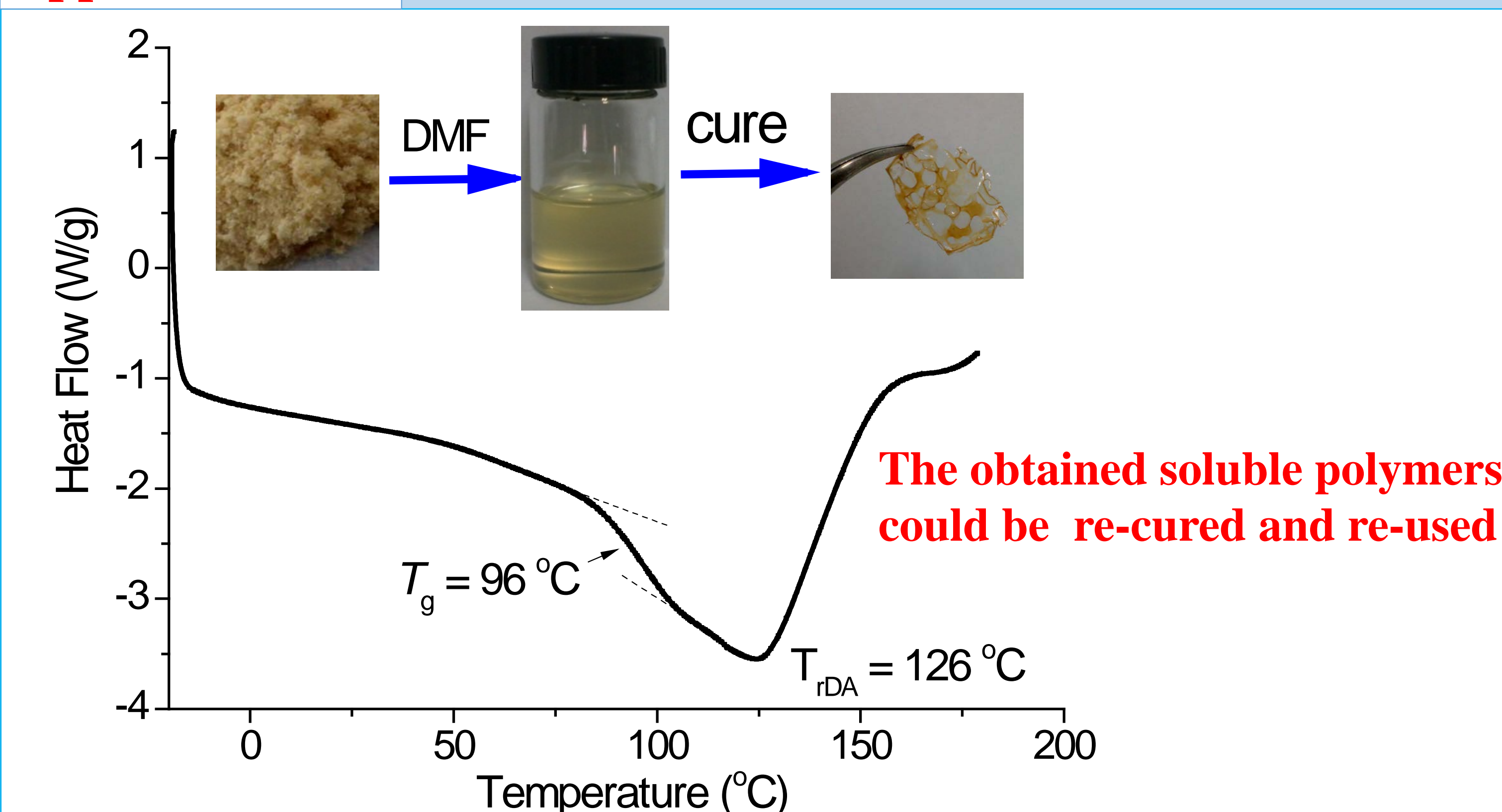


**Figure 1.** (A) DSC result of **2** (inserted image) under N<sub>2</sub> atmosphere (10 °C/min); (B) the powders of **2** swelled in DMSO for at least 4h; (C), the solution obtained from (B) via sonication in DMSO for 75 min (ice bath); (D), the solid polymers from (C); (E), GPC curves of the soluble polymers (runs 1-5 in Table 1); (F), the yield and M<sub>n</sub> of the resultant soluble polymers as a function of sonication times.



**Figure 2.** <sup>1</sup>H-NMR spectra (400 Hz, d<sub>6</sub>-DMSO): 1) the soluble polymer of run-5 in Table 1; 2), heat-degraded product of **2** at 130 °C for 30 min; 3), FDB; 4), FGE.

## Application



**Figure 3.** DSC result of the re-cured sample (inserted chart) from the recycled epoxy polymer in DMF (cure condition: 70 °C/2 d).

**References:** 1, Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F., *Science* 2002, 295 (5560), 1698-1702; 2, Wiggins, K. M.; Syrett, J. A.; Haddleton, D. M.; Bielawski, C. W., *J Am Chem Soc* 2011, 133 (18), 7180-7189.

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