Supporting Materials

Solving the harshly recyclable issues of conventional thermosetting polyurea elastomers based on commercial raw materials in a facile way

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Characterization:

The differential scanning calorimetry (DSC) curve was measured via 204 instrument (NETZSCH, Germany) from -70 to 150 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT-Q600 thermal analyzer from 25 to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Soxhlet extraction experiment was performed by using the conventional Soxhlet extraction apparatus consisting of a condenser, a Soxhlet chamber, and an extraction flask. About 1 g HTPU-x sample and massive solvent of THF were packed in filter paper and placed in Soxhlet chamber. Samples were extracted under continuous reflux in THF at 90 °C for 24 h. After cooling to room temperature, the residual samples were washed by using new THF after three times. After that, the residual samples were dried under vacuum at 80 °C for 12 h. The gel contents were calculated using equation (1):

$$\text{Gel content} = (m_{\text{residual mass}}/m_{\text{total mass}})*100\% \quad (1)$$

Where $m_{\text{residual mass}}$ and $m_{\text{total mass}}$ are the sample mass before and after extracting.

The experiment of the small molecular model was conducted as follows: Firstly, the different intermediates, containing the different isocyanate monomers of HDI, IPDI and HMDI, were synthesized via dropping the solution of isopropylamine into the different isocyanate monomers in a molar ratio of 1:2 in ice bath. And then the mixture of the reacted products was purified through repeated washing by water. Secondly, the purified intermediate was mixed with excessive benzyl

isocyanate in Dimethyl Sulphoxide (DMSO-D6) reagent at 120 °C for 12 h for sufficiently dynamic exchange reaction. Finally, the dynamic exchange reaction between classic urea bond, which simultaneously contains the different isocyanate monomers of HDI, IPDI or HMDI and the sterically hindered isopropylamine similar to poly (propylene oxide) diamine, and benzyl isocyanate can be observed from the ^{1}H NMR spectra of the mixed products. Comparison of the ^{1}H NMR spectra between the intermediate before dynamic exchange reaction and the mixed products after dynamic exchange reaction.

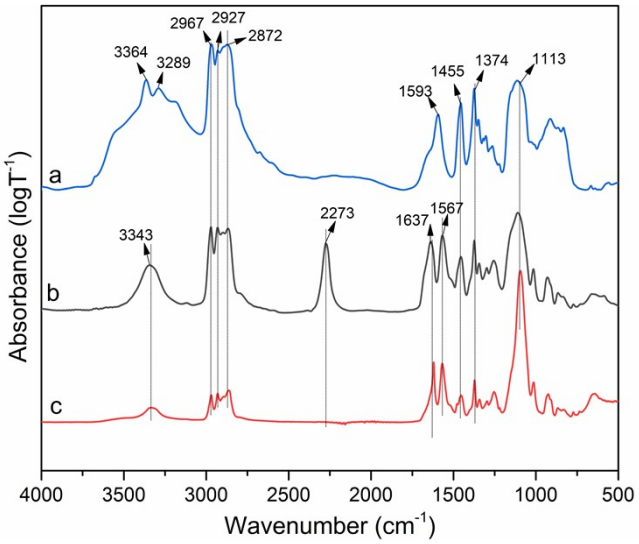

Fig. S1 (1) FTIR spectra of raw materials, prepolymer and TPUEs during the synthetic process: (a) Poly (propylene oxide) diamine D2000 by using infrared spectrophotometer, (b) the prepolymer terminated by isocyanate monomer of IPDI by using infrared spectrophotometer, (c) PUA-IPDI by using infrared spectrophotometer the model of attenuated total reflection (ATR).

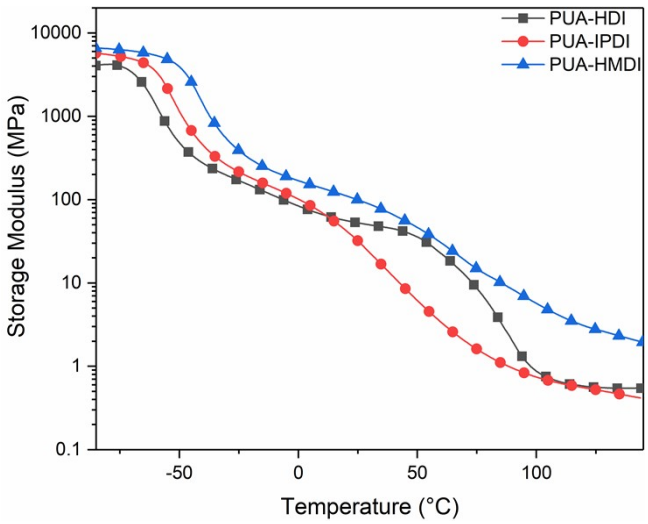

Fig. S2 Storage modulus of TPUEs *vs.* temperature curves measured by DMA.

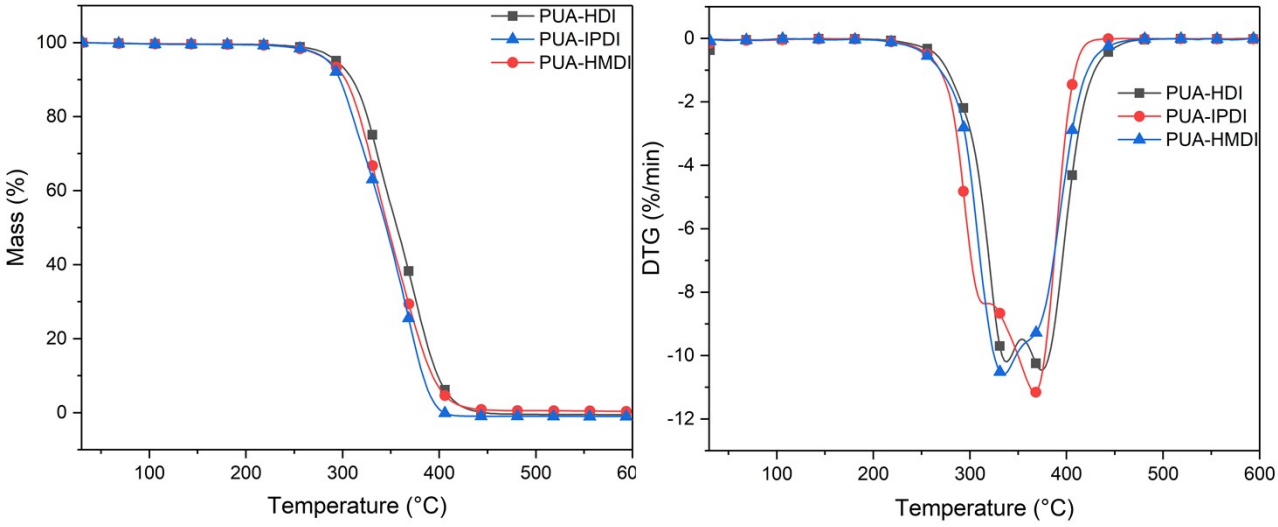

Fig. S3 TG curve of TPUEs at 10 °C min^{-1} under N_2 condition measured by thermal analyzer.

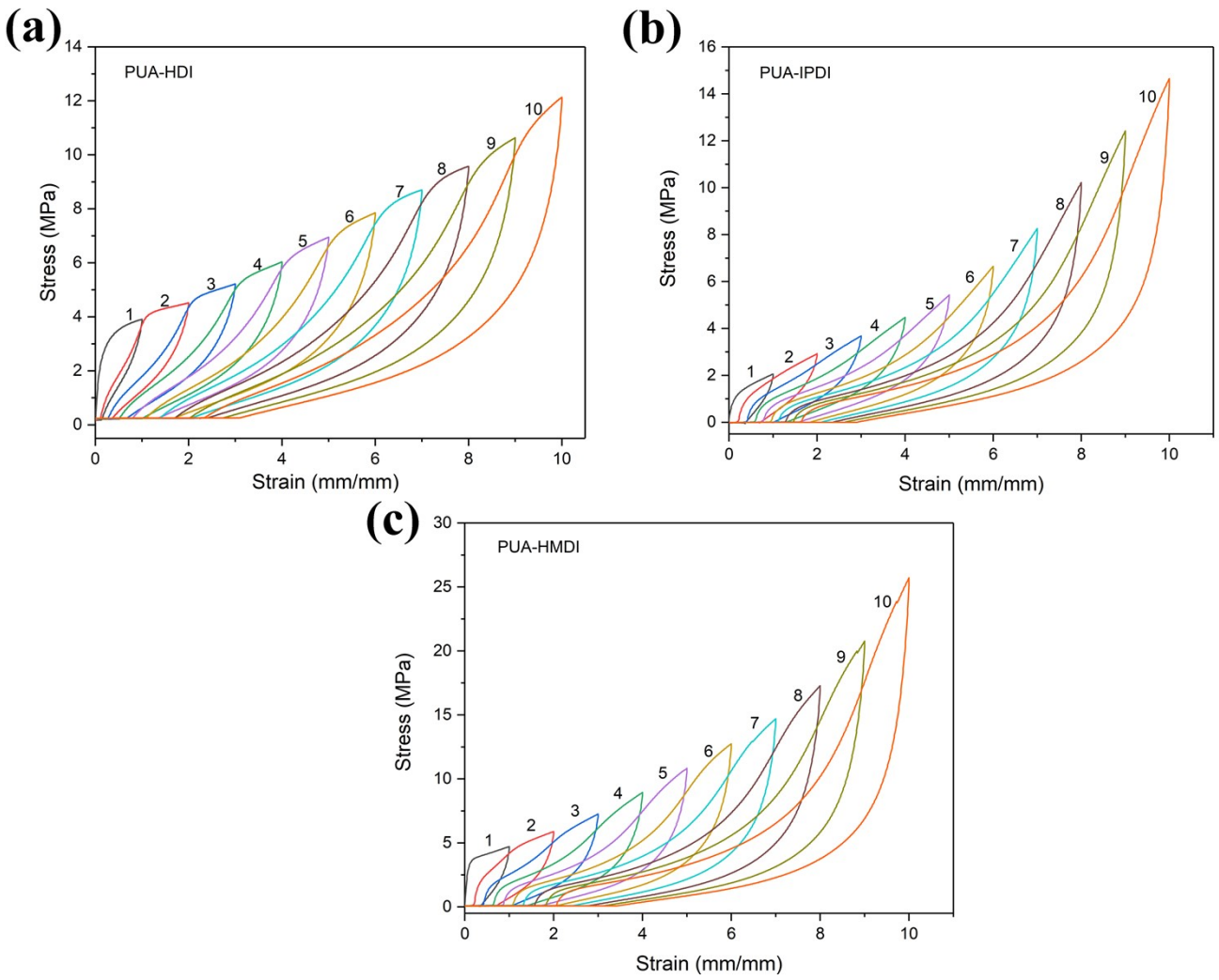

Fig. S4 Successive loading-unloading curves with increasing strains from 100% to 1000% of TPUEs for ten cycles tested by universal testing machine: (a) PUA-HDI, (b) PUA-IPDI, (c) PUA-HMDI.

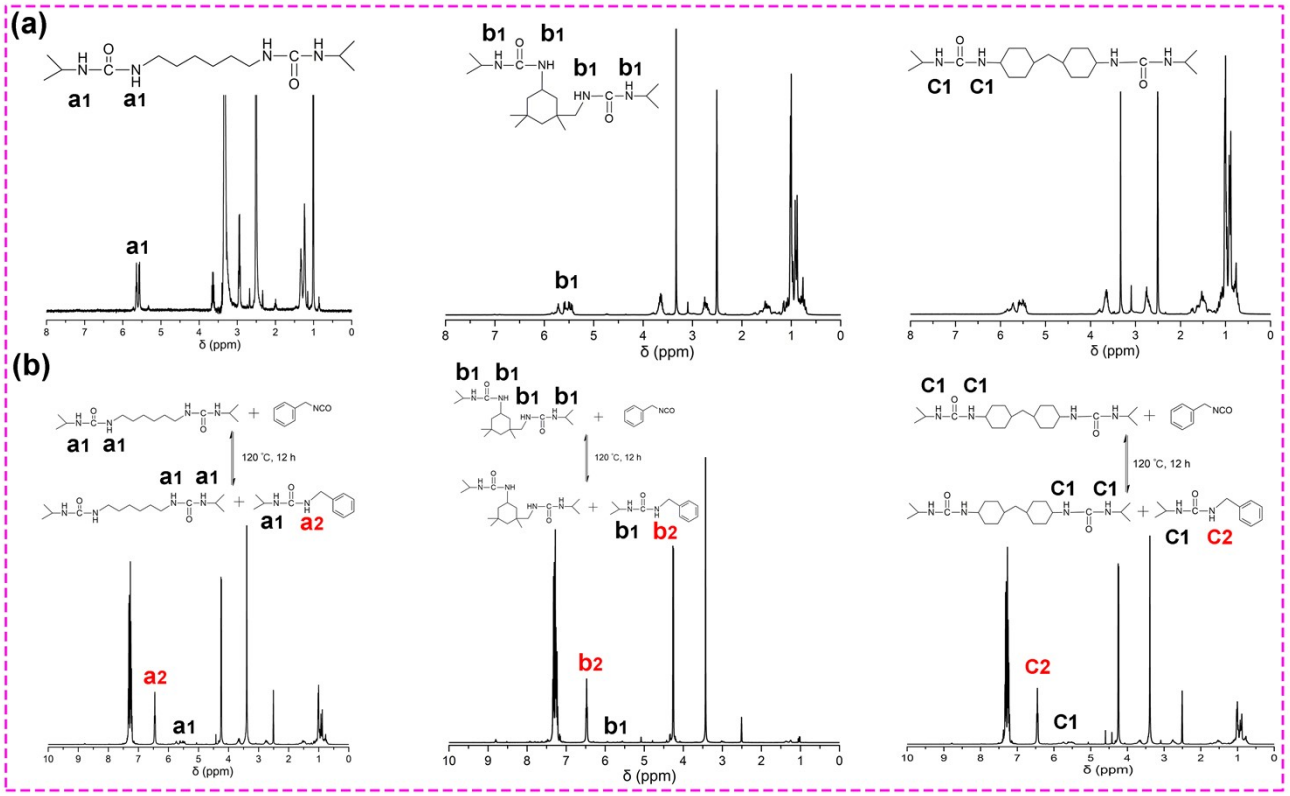

Fig. S5 (a) The chemical structure and the ^{1}H NMR spectra of the various intermediates containing the different isocyanate monomers of HDI, IPDI or HMDI with the sterically hindered isopropylamine. (b) Chemical structures and ^{1}HNMR spectra of the small model compounds of dynamic exchange reaction between the various intermediates and benzyl isocyanate mixtures reacted in DMSO-D6 at 120 ℃ for 12 h.

As shown in Fig. S5, the results of ^{1}H NMR spectra showed that the reduction of the **a1, b1 and c1** belong to the various intermediates containing the different isocyanate monomers of HDI, IPDI or HMDI before the dynamic exchange reaction. Obviously, the growth of the **a2, b2 and c2** peak belong to the new product of 1-benzyl-3-isopropylurea, confirming the dynamic nature of the devised classic urea bonds based on the various isocyanate monomers.

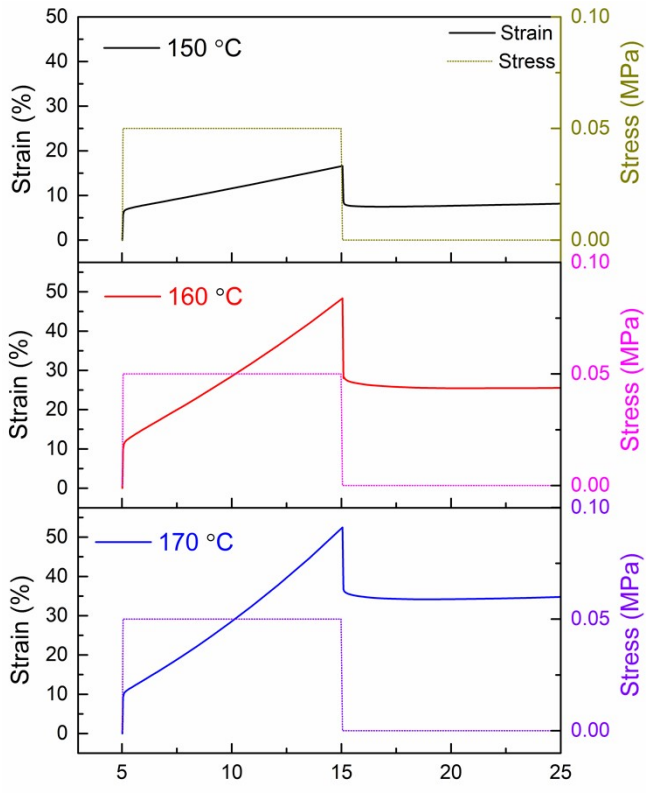

Fig. S6 Creep and recovery curves of PUA-HMDI at different temperature measured by DMA in a creep mode.

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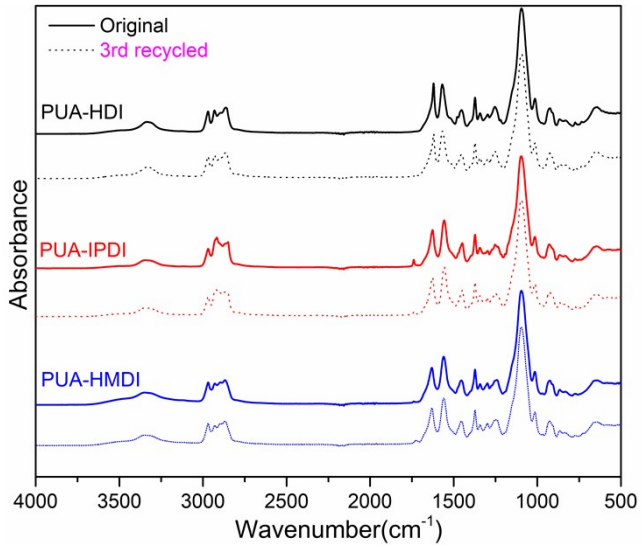


Fig. S7 FTIR spectra of TPUEs before (solid line) and after (dot line) three times reprocessing by using infrared spectrophotometer.

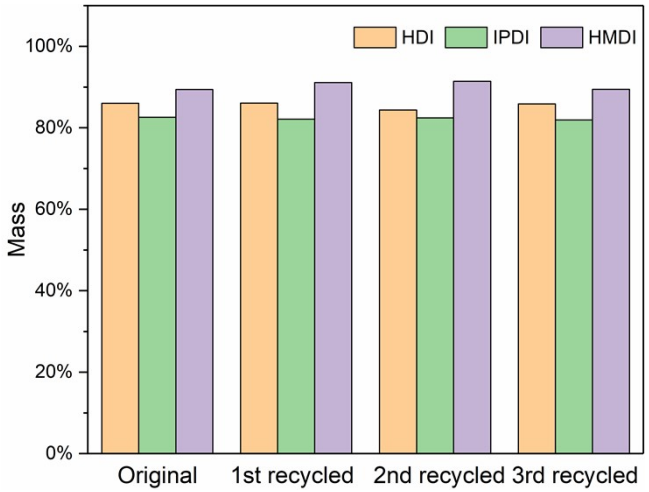
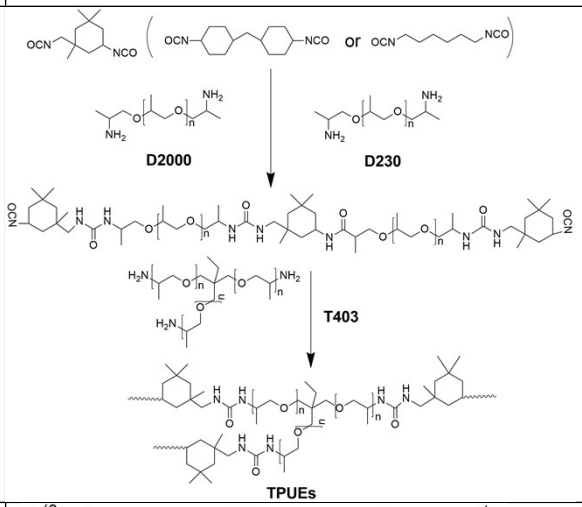
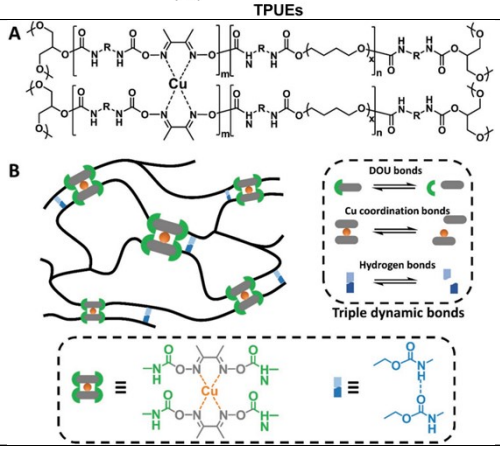
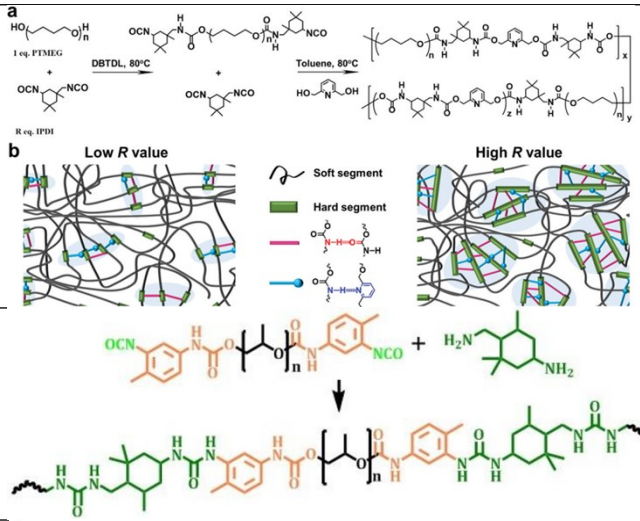
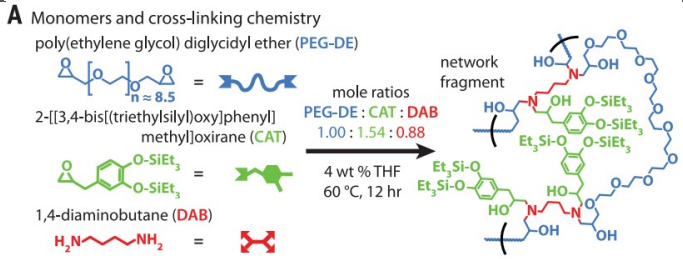
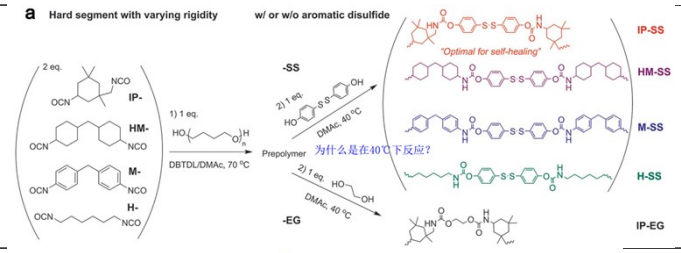
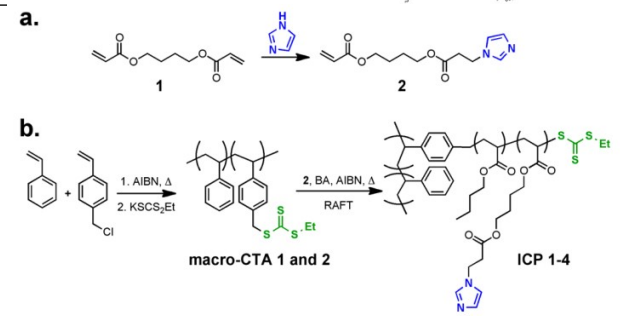
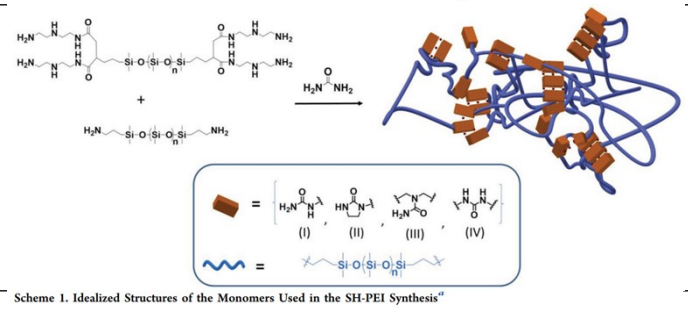
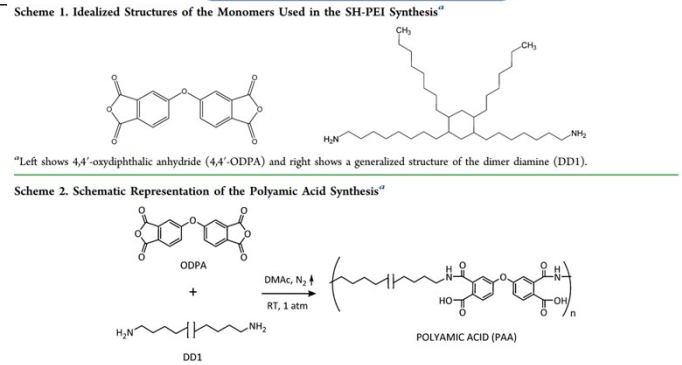
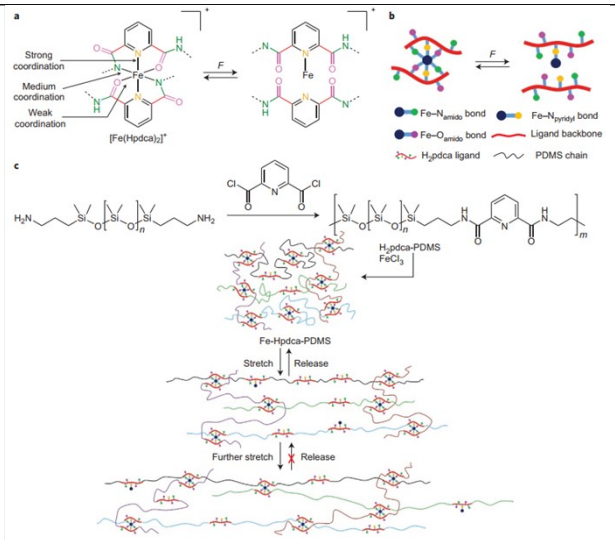
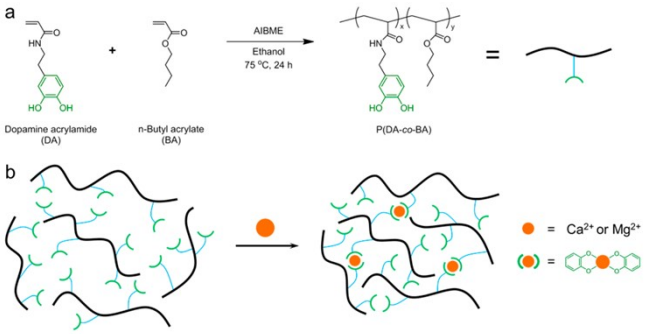
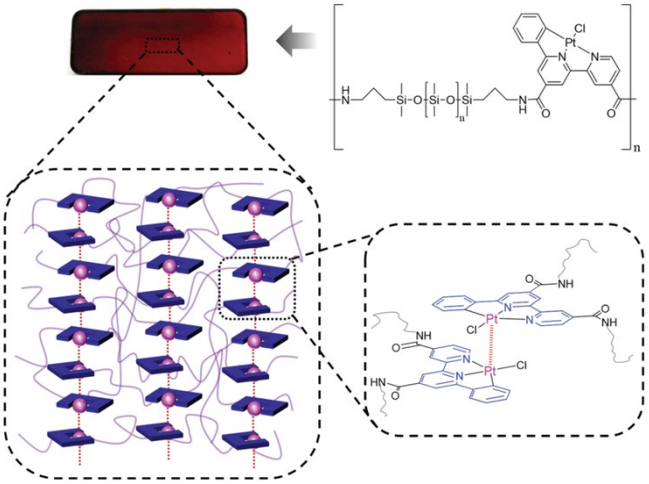
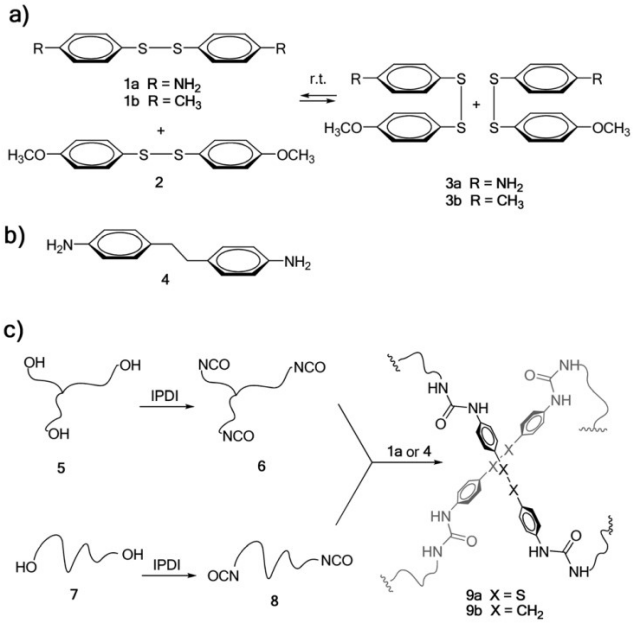


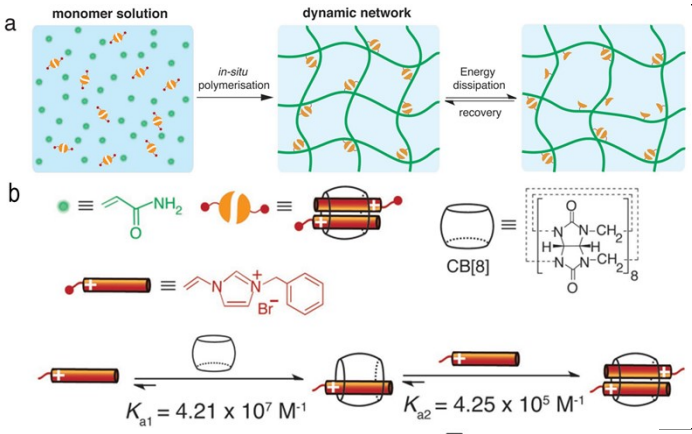
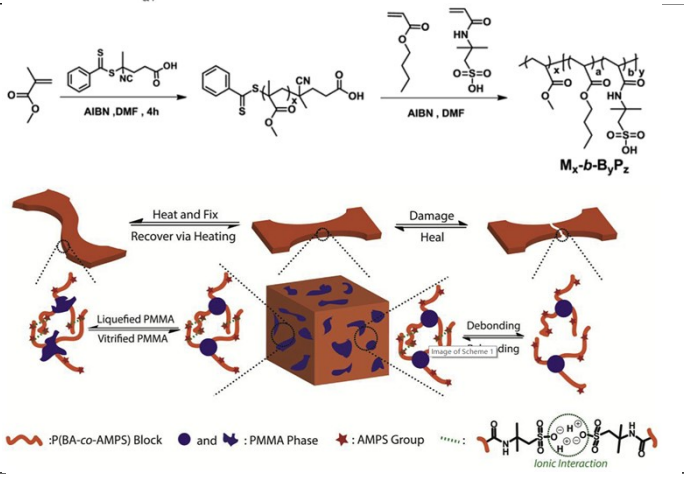
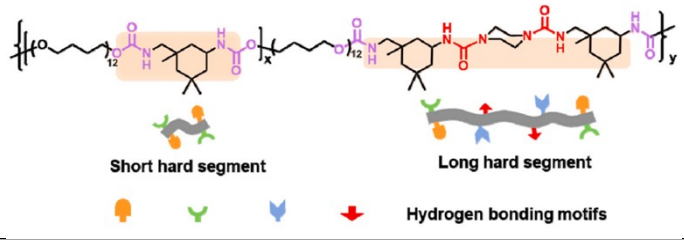
Fig. S8 Gel contents of original and reprocessed TPUEs via the swelling experiment.

Table S1 Comparison of mechanical properties of these TPUEs with the dynamic materials and commercial elastomers in the previous literatures.

Ref.	Respective chemical structural information	Breaking strengths (MPa)	Elongations at break (%)	Toughness (MJ m^{-3})
This work		16	1654	130.1
		28.8	1752	339.2
		31.4	1421	276.6
22		14.8	1182	87

41		29	1710	121.8
40		4.83	2010	65.49
27		21.9	170	22
36		6.76	923	26.9
42		1.25	470	9.8
43	 Scheme 1. Idealized Structures of the Monomers Used in the SH-PEI Synthesis[a]	1.11	984	7.14
44	 [a]Left shows 4,4′-oxydiphthalic anhydride (4,4′-ODPA) and right shows a generalized structure of the dimer diamine (DD1). Scheme 2. Schematic Representation of the Polyamic Acid Synthesis[a] [a]DD1 structure is shown in a simplified way where the brackets refer to the branched section, which can be positioned at different places along the main C18 chain.	4.4	560	12

45		0.23	1850	3.8
46		3.5	310	6.8
47		0.3	1400	3.4
48		0.81	3100	13

49		0.5	4500	11
50		11.6	366	29
51		38.5	1416	134.6