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Bio-Based Healable Non-Isocyanate Polyurethanes Driven by the Cooperation of Disulfide and Hydrogen Bonds

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Cross-linking Molecular Simulation

The Crosslink script in Materials Studio 4.2 (BIOVIA™, Dassult Systemes) software package was used for molecular modeling of the cross-linked polymer networks with the polymer consistent force field (COMPASS II). Molecular simulations were carried out with the Forcite module, using a time step of 1 fs, the Nosé–Hoover thermostat with a Q ratio of 0.01, and the Andersen barostat with a time constant of 1 ps. Amorphous cells composed of 30 molecules of CSBO that correspond to 120 cyclic carbonate functionality and equivalent amine compounds with a low density of 0.5 g cm^{-3} were constructed at room temperature and under periodic boundary conditions. The script attempts to form crosslinks between the reactive atoms, labeled as R1 (cyclic carbonate) and R2 (amine). The amorphous cells were subjected to canonical ensemble (NVT) dynamics to obtain a reasonable velocity distribution followed by 2 ns of isothermal-isobaric (NPT) dynamics with a time step of 1 fs at 298 K and 1 atm. Once the amorphous cells are equilibrated, the system searches for all close contacts between R1 and R2 within the threshold (here, <3.5 Å), and covalent bonds were created between appropriate atoms within the crosslinking cut-off distance. In this procedure, generated water molecules are removed from the cells to adjust the chemistry. After the system was subjected to NPT-based annealing, it again searches for all close contacts between R1 and R2 with a cyclic combination of bonding-minimization-dynamics until the conversion of R1 reaches the prescribed values.

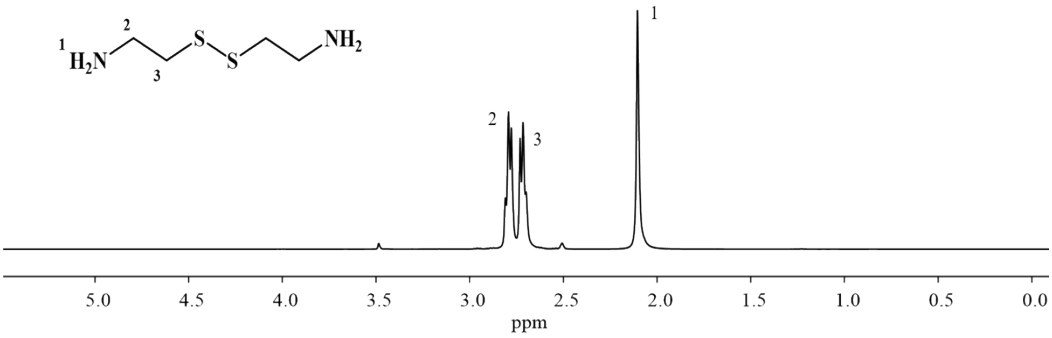

Fig. S1. ^{1}H-NMR spectra in DMSO-d_6 for CA.

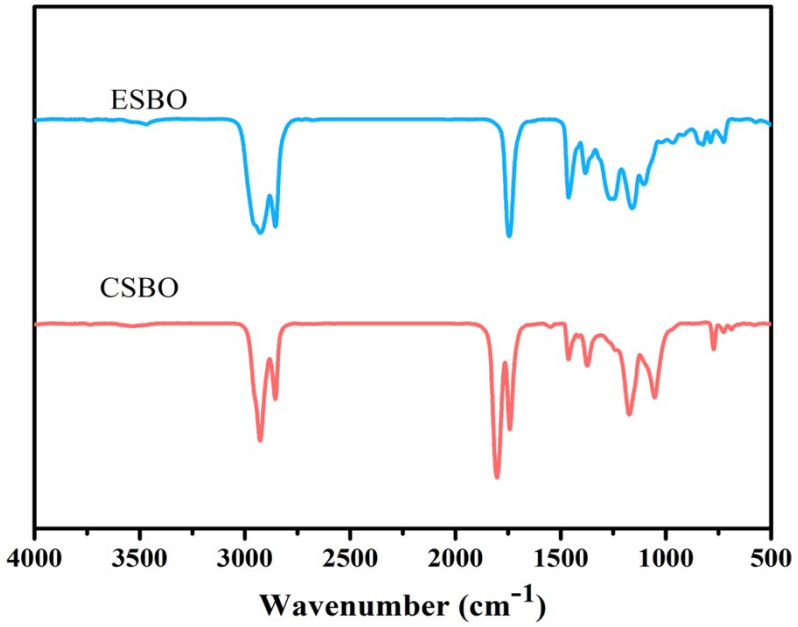

Fig. S2. FTIR spectra of ESBO and CSBO.

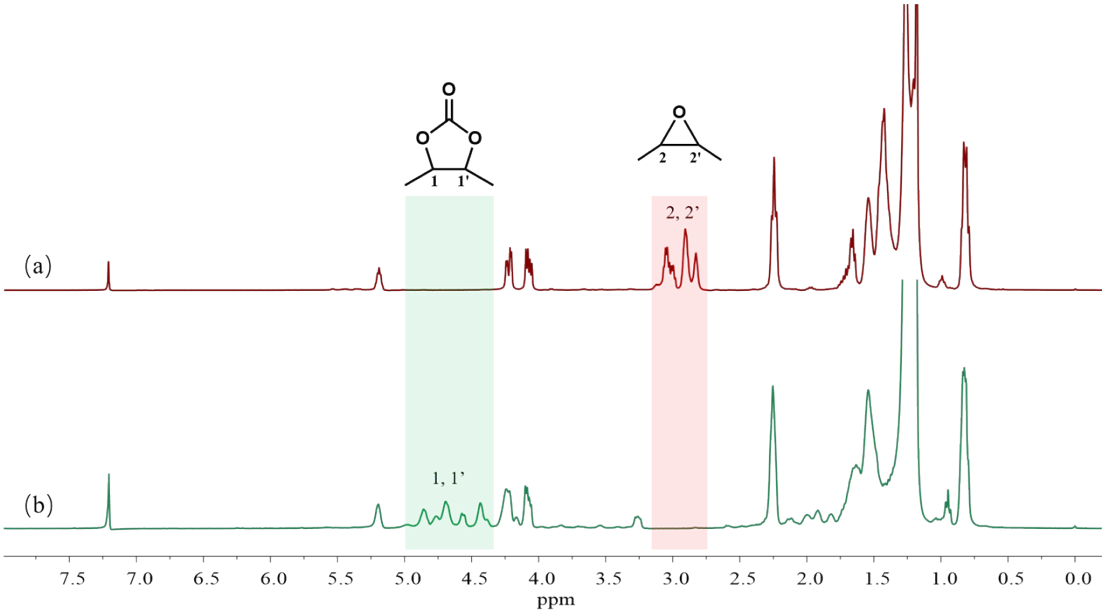

Fig. S3. ^{1}H-NMR spectra in $CHCl_3$ for (a) ESBO and (b) CSBO.

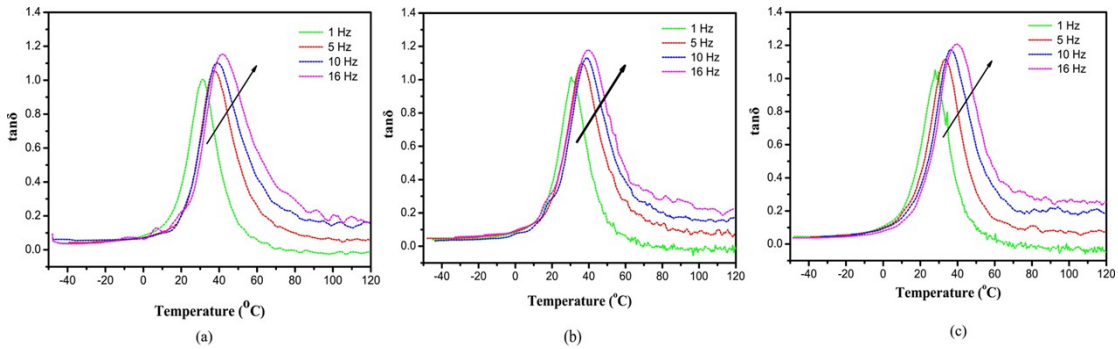

Fig. S4. Tan δ curves of (a) NIPU-6, (b) NIPU-7 and (c) NIPU-8 at different frequencies.

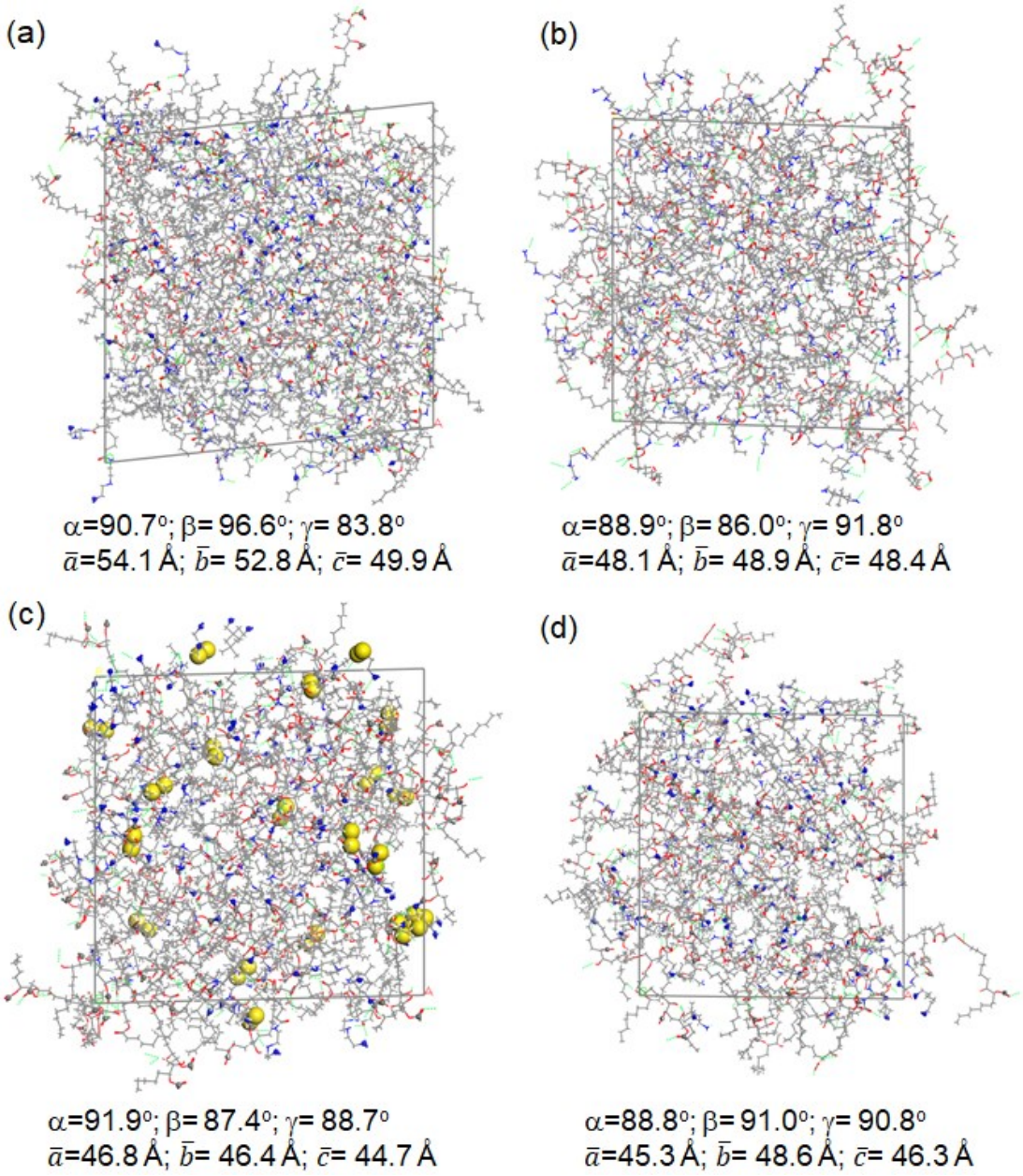

Fig. S5. Cross-linking simulations of NIPUs. Snapshots of the molecular simulation boxes of cross-linked polymers at their final stages: (a) NIPU-1, (b) NIPU-3, (c) NIPU-7, and (d) NIPU-9. Sulfur atoms in (c) present as a yellow CPK model for clarity and hydrogen bonds in all NIPUs are shown in green dotted lines.

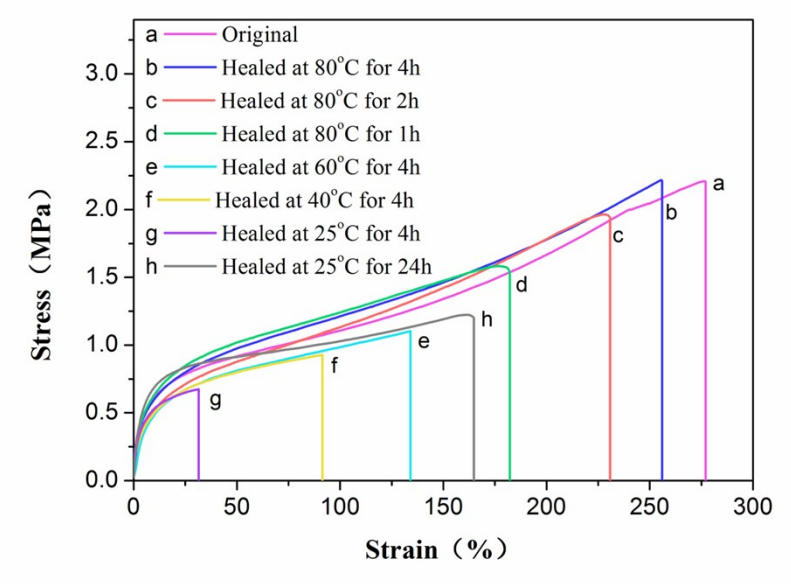

Fig. S6. Typical stress-strain curves of the original and healed specimens of NIPU-7 at different healing conditions.

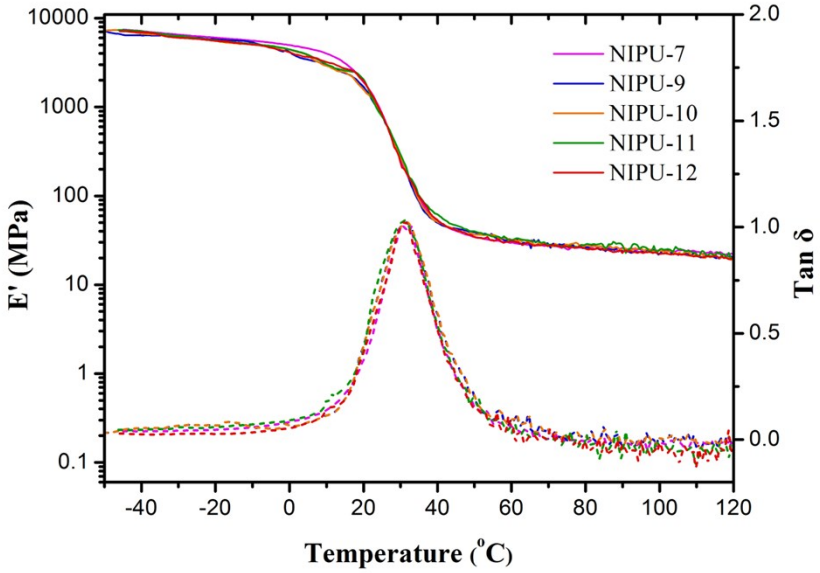

Fig. S7. DMA curves of NIPU-7 and NIPU-9 to NIPU-12.

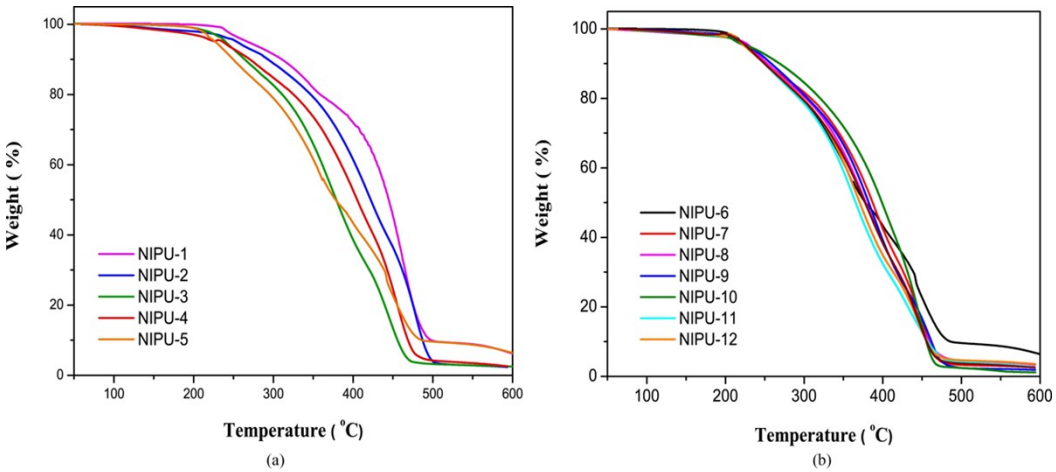

Fig. S8. TGA curves of (a) NIPU-1 to NIPU-5 and (b) NIPU-6 to NIPU-12.