Dynamic covalent urea bonds
and their potential for self-healing polymer materials

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Materials

Amine-terminated polysiloxane (DMS-A12: M_n = 900-1000 g/mol, DMS-A15: M_n = 3000 g/mol; DMS-A21: M_n = 5000 g/mol) and (20-25% aminopropylmethylsiloxane) -dimethylsiloxane copolymer (AMS-1203: M_n = 25000 g/mol) were purchased from Gelest, Inc. Hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), HDI trimer, zinc acetate, magnetism acetate, zinc trifluoromethanesulfonate, and anhydrous tetrahydrofuran were obtained from best-reagent companies. All of the other regents were used as received.

Polymer preparation

Preparation of PDMS-$Zn(OA_C)_2$ materials.

P1: 25 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature; 1.95 g DMS-A21 and 0.05 g AMS-1203 were added to the solution and stirred for 1 min, then 0.045 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P2: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature; 1.96 g DMS-A21 and 0.04 g AMS-1203 were added to the solution and stirred for 1 min, then 0.076 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P3: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran; 1.93 g DMS-A21 and 0.07 g AMS-1203 were added into the solution and stirred for 1 min, and then 0.082 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P4: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature; 1.90 g DMS-A21 and 0.1 g AMS-1203 were added into the solution and stirred for 1 min, and then 0.089 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P5: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran; 1.76 g DMS-A15 and 0.06 g AMS-1203 was added to the solution and stirred for 1 min, and then 0.114 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P6: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature; 1.57 g DMS-A12 and 0.16g AMS-1203 were added into the solution and stirred for 1 min, and then 0.304 g HDI was added, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h at 40 °C in vacuum for 24 h.

P7: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature; 2.00 g DMS-A12 and 0.32 g IPDI were added into the solution and stirred for 20 min. Next, 0.20 g tri-HDI was added to the above solution, the mixture was stirred at room temperature for 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h and the sample was subsequently dried at 40 °C in vacuum for 24 h.

P8: 50 mg $Zn(OA_C)_2$ was dissolved in 8 mL anhydrous tetrahydrofuran at room temperature, and 2 g DMS-A21 and 0.080 g IPDI were added into the solution and stirred for 20 min. Next, 0.013 g tri-HDI was added to the above solution, the mixture was stirred at room temperature for another 5 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 16 h and the sample was subsequently dried at 40 °C in vacuum for 24 h.

GC-MS

15.7 mg $Zn(OA_C)_2$ was dissolved in 2 mL DMSO-D6, 10 mg 1,3-diethylurea and 92.4 mg benzylamine were added into the solution and stirred at 80 °C for 72 h under the continuous flow of argon gas. The 5 μL of the reaction mixture was collected from the reaction vial, which was subsequently added to 0.5 mL of 1,2-dichloroethane and 0.5 mL of water. The ether layer was separated from the water layer, and 2 μL of extracted ether layer was injected into the GC-MS.

Characterization

The weight-average molecular weight of the synthesized PU-PDMS was determined by gel permeation chromatography (GPC; HLC-8320) with THF as an eluent phase and PMMA as a standard sample. PDMS-PUR-$Zn(OAc)_2$ was characterized by IR spectroscopy on a Fourier transform infrared spectrometer (FTIR; Nicolet 560) in the frequency range of 400–4000 cm^{-1}, and further analyzed by ^1H NMR (Bruker ARX-400 at 400 MHz). Thin slices of the PDMS-$Zn(OAc)_2$-II (P7) were cut with a diamond knife at -140 °C (below the glass-transition temperature of PDMS). These specimens were then placed on a copper grid with an eyelash tool and examined through a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI). Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument at a linear heating rate of 10 °C/ min from 30 to 800 °C under a nitrogen atmosphere. Dynamic Mechanical Thermal Analysis (DMTA) experiments were performed using a TA Instrument Q800 machine in the dual cantilever mode. The test temperatures ranged from -30 to 150 °C and the heating rate was 3 °C/min. The strain amplitude used was 50 μm, and the stretching frequency was 1 Hz. Mechanical tensile-stress experiments were conducted on an Instron 5567 machine (USA) at room temperature with a strain rate of 50 mm/min. The dimension of specimens was 35 × 8 × 0.7 mm^3. At least four samples of each loading fraction were tested. GC and GC-MS analyses were performed by taking 50 μL aliquots of the reaction studied in DMSO-d_6 and inject these in a vial filled with 500 μL water and

500 μL 1,2-dichloroethane. The sample was gently mixed by shaking, and injections on the GC and GC-MS were from the 1,2-dichloroethane layer.

Computational Methods

The geometries of all the reactants, products and transition states (TS) were optimized at the B3LYP/6-311+G(d,p) level of theory. Frequency analysis was carried out on all stationary points to confirm their nature (minimum, TS) on the potential energy surface. The universal solvation model SMD was used to mimic the solvent dimethyl sulfoxide (DMSO) for the calculation of the free energy of solvation. All calculations were carried out with the Gaussian16 software package, and Gaussview 6.0 was used as visualization software.

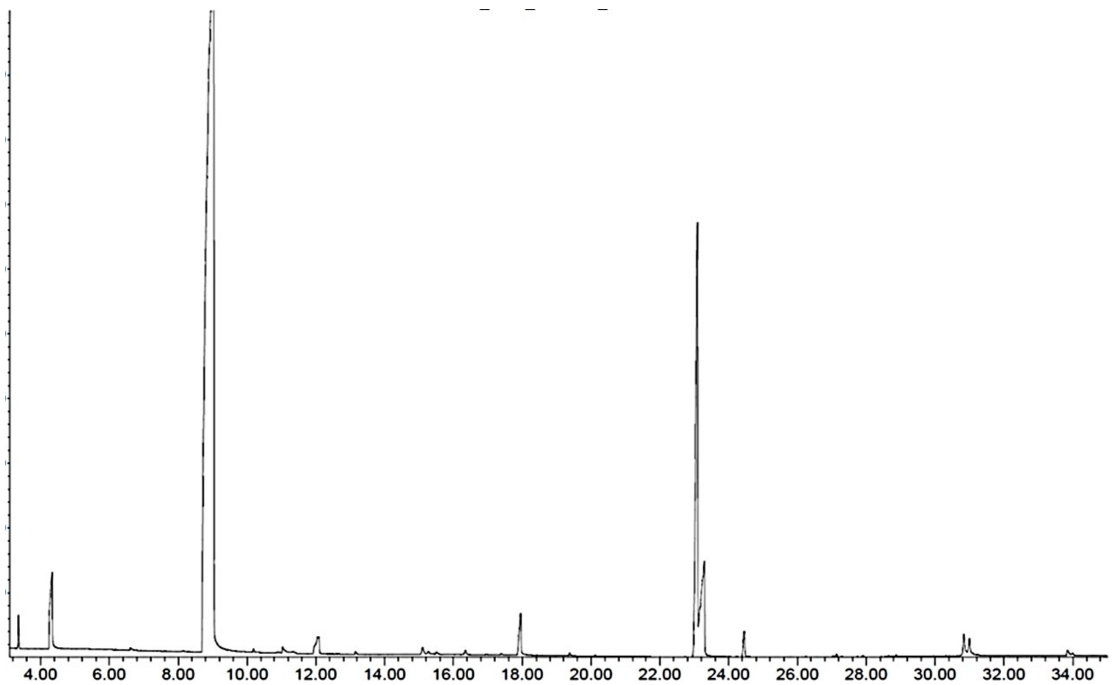

Figure S1. GC-MS spectra of 10:1:1 ratio of Benzylamine, 1,3-diethylurea and $Zn(OAc)_2$ in DMSO heated at 80 ^{o}C for 72 h. 5 µl of reaction mixture was added to 0.5 ml of 1,2-dichloroethane and 0.5 ml of water and 2 µl of extracted ether layer was injected into GC-MS. The transamination products along with starting materials were observed at the retention times of 1,3-diethylurea, benzyl amine, 1-benzyl-3-ethylurea, 1,3-dibenzylurea of 12 min, 9 min, 23 min, and 31 min, respectively.

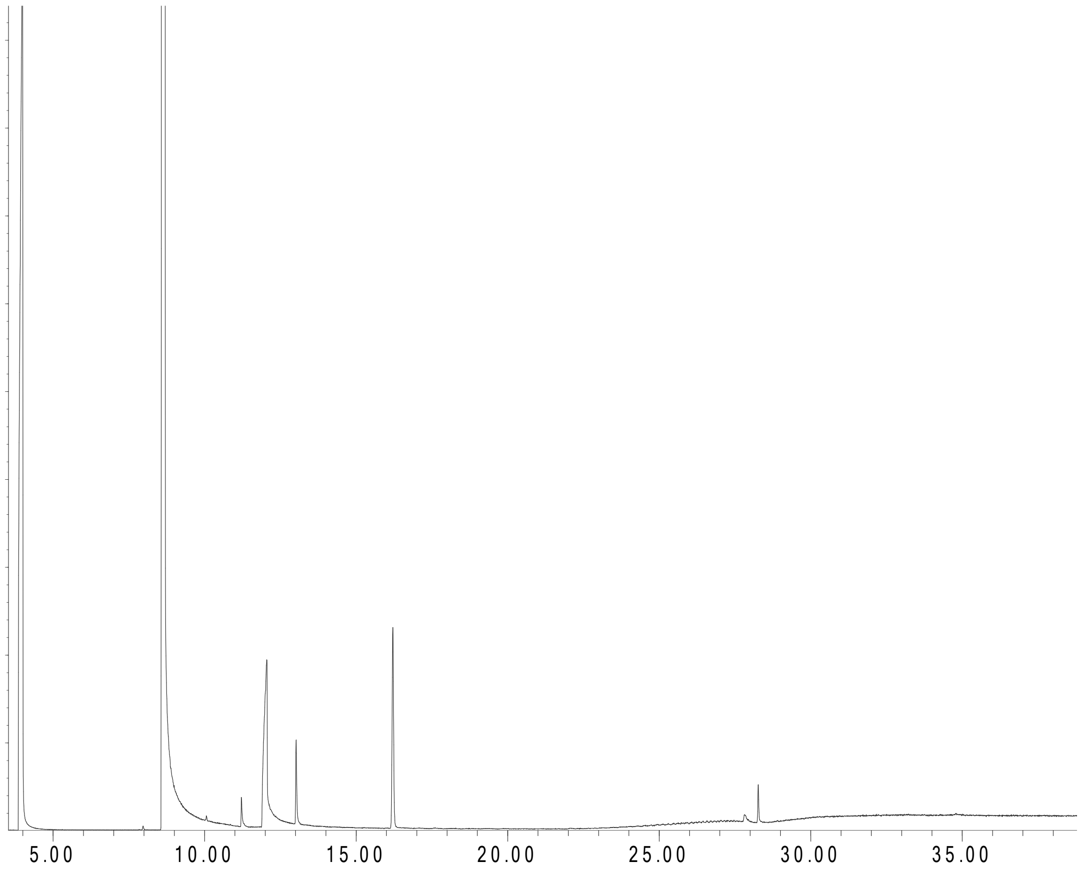

Figure S2. GC-MS spectra of 10:1 ratio of benzylamine, 1,3-diethylurea in DMSO heated at 80 ^{o}C for 72 h. The transamination products were **NOT** observed at expected retention times of 23 and 31 min, and shows that Zn(OAC)2 plays a vital role in the dynamic urea bond formation.

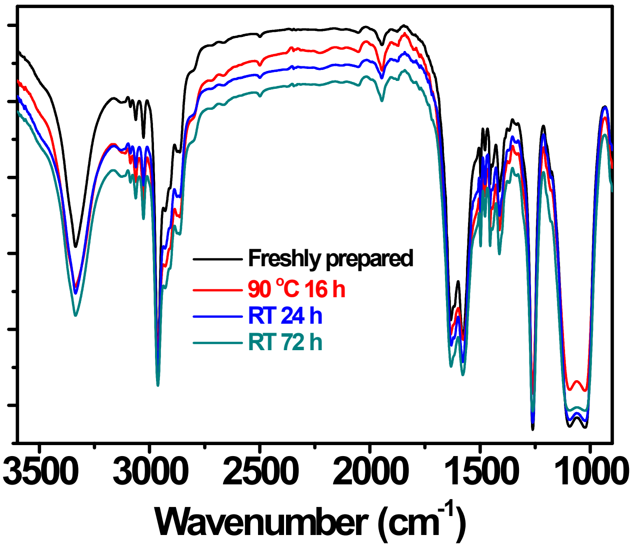

Figure S3. FTIR spectra of a linear PDMS-Zn$(OAc)_2$. Freshly prepared sample (black curve, top); the fresh sample was heated at 90 °C for 16 h (red curve), and then cooled down to room temperature for 24 h (blue curve), and finally kept at room temperature for 72 h (dark cyan curve, bottom).

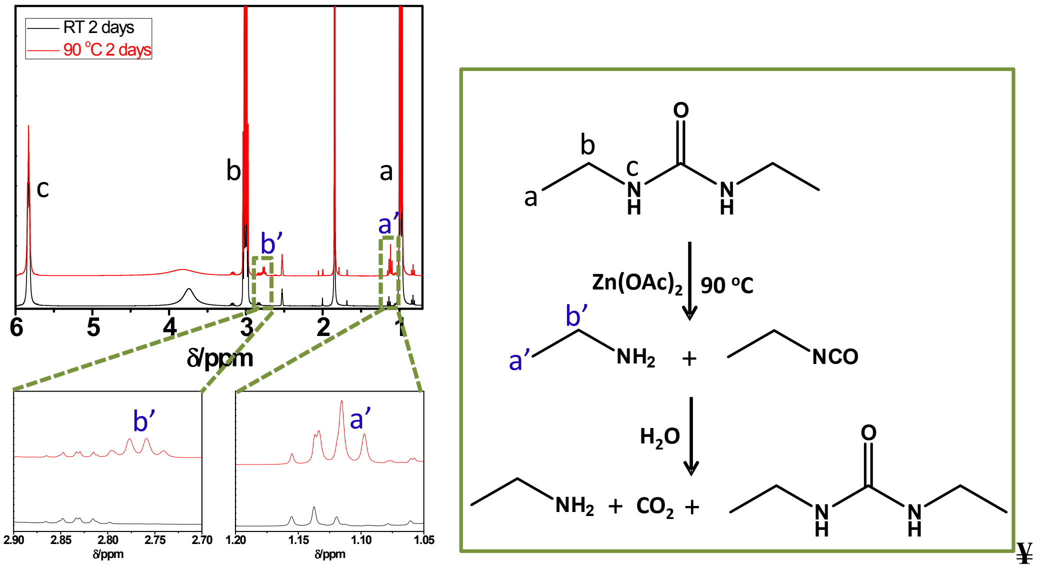

Figure S4. Left: NIR spectra of 1,3-diethylurea and $Zn(OAc)_2$ mixture in DMSO at room temperature and 90 °C for 48 h. Right: Schematic illustration of the reaction of 1,3-diethylurea and $Zn(OAc)_2$ mixture in DMSO at 90 °C.

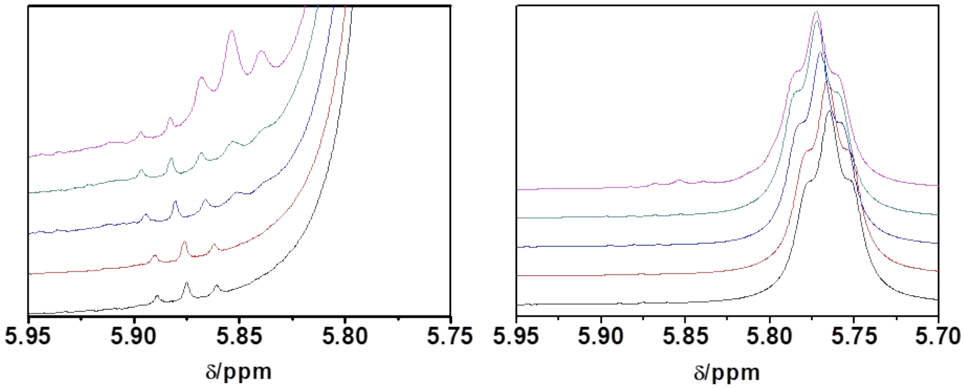

Figure S5. NMR spectra of a mixture of 1,3-diethylurea, 2-(p-toly)ethylamine and Zn(OAc)2 in DMSO at different temperatures. Black curve: room temperature; red curve: 60 °C, blue curve: 70 °C; cyan curve: 80 °C; pink curve: 90 °C.

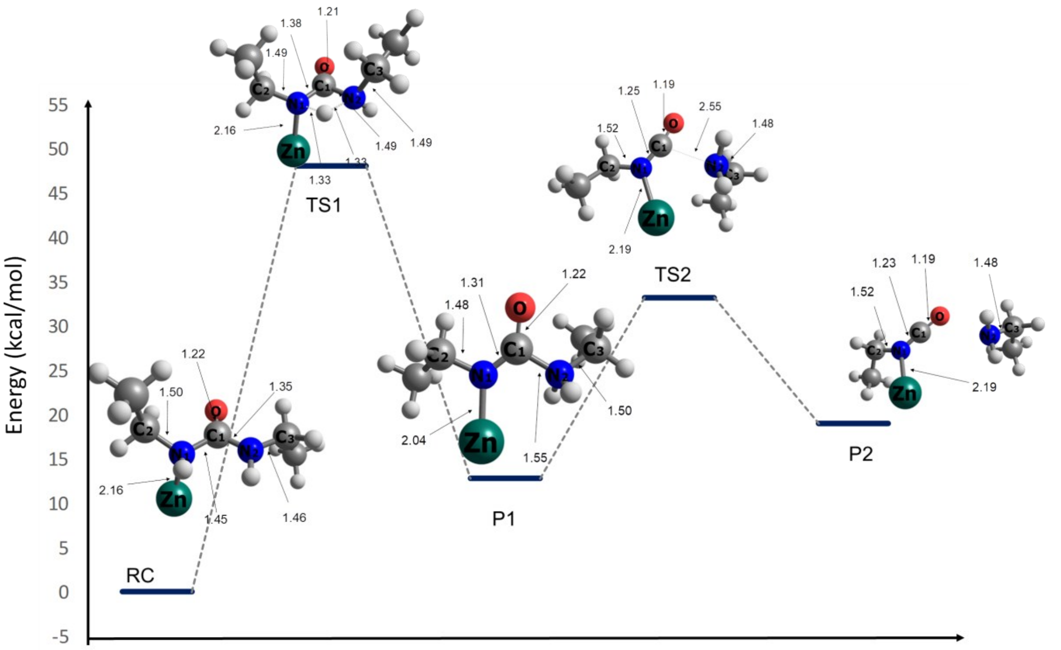

Figure S6. Energy profile of the Zn (II) catalyzed-decomposition reaction of diethylurea into ethyl isocyanate and ethyl amine. Zn atom is coordinated to the N atom from which the initial proton is transferred (N^1).

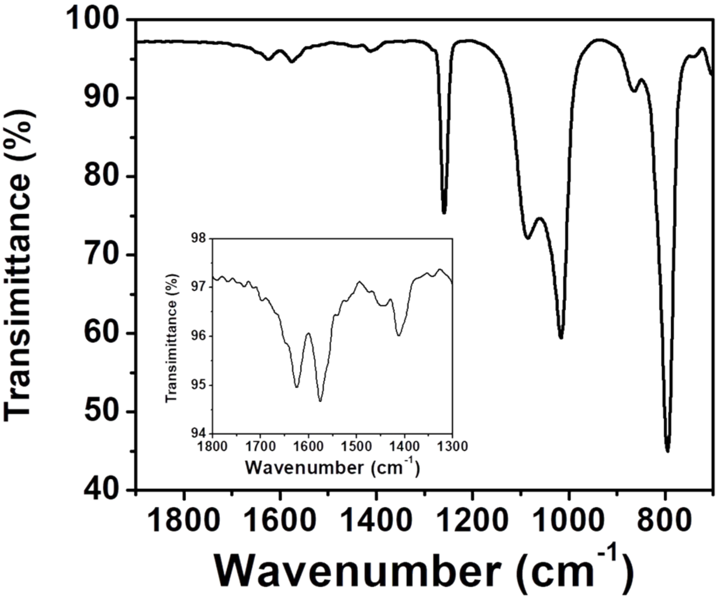

Figure S7. ATR-IR spectra of the PDMS-Zn(OAc)$_2$-I (P4) networks.

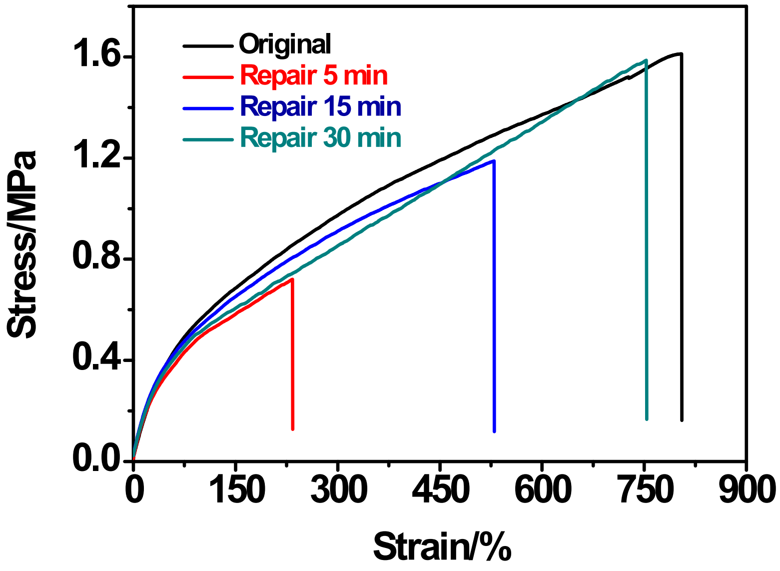

Figure S8. Stress-strain curves of the original PDMS-Zn(OAc)$_2$–II (P8) films and the self-healing films after thermal treatment at 70 °C for different repair times.

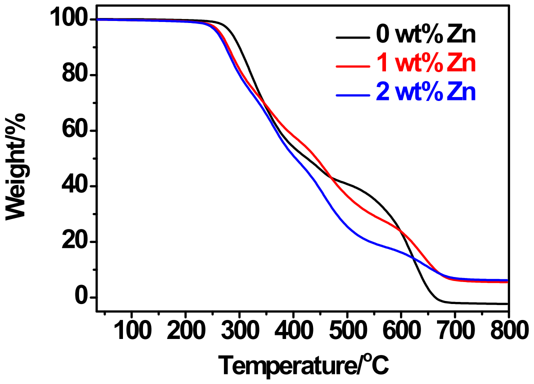

Figure S9. TGA curves of PDMS-Zn(OAc)$_2$-II with different concentration of Zn(OAc)$_2$

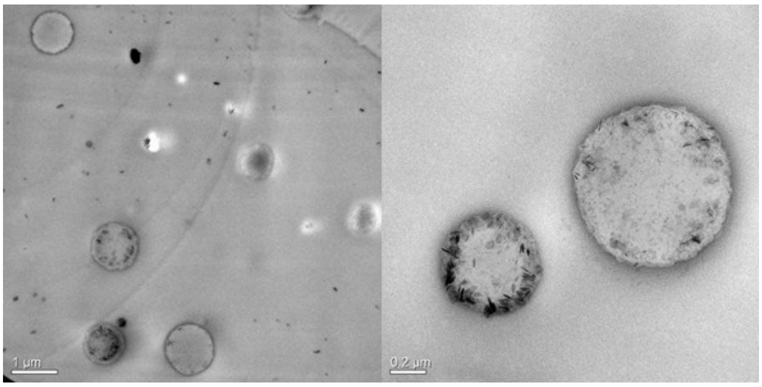

Figure S10. TEM images of T PDMS-Zn(OAc)$_2$-II (P7).

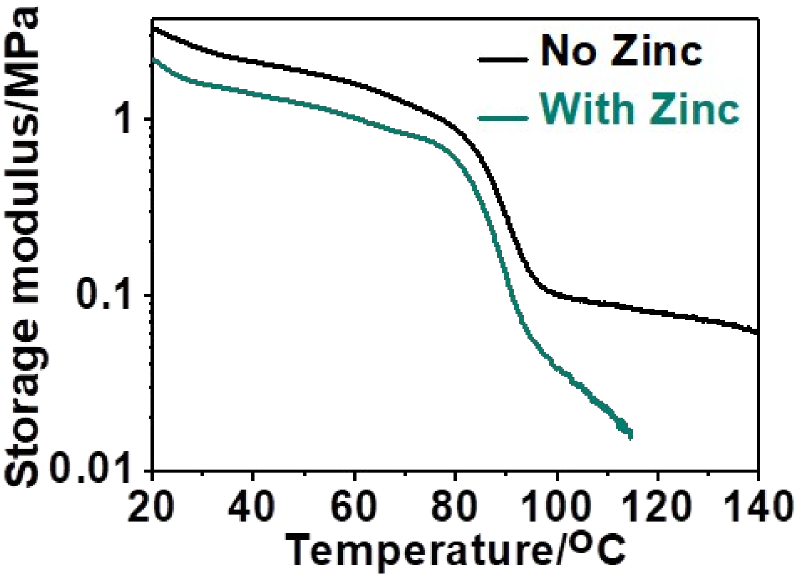

Figure S11. DMA curve of the PDMS network without zinc salts (black curve) and PDMS-Zn(OAc)2-I (P4) networks (dark cyan curve).

Table S1. Tensile strength, elongation at break and healing efficiency of PDMS-$\mathrm{Zn(OAc)_2}$-I networks with different ratio and compositions.

Sample No.	Pristine sample		Healed sample		Healing efficiency/%	
	Tensile strength/MPa	Strain at break/%	Tensile strength/MPa	Strain at break/%	Tensile strength	Strain at break
P2	1. 0 ± 0.05	970 ± 17	0.94 ± 0.02	950 ± 10	94	98
P3	0.63 ± 0.04	547 ± 47	0.62 ± 0.02	512 ± 39	98	94
P4	0.97 ± 0.16	229 ± 34	0.97 ± 0.03	218 ± 21	100	95
P5	0.81 ± 0.09	349 ± 3	0.75 ± 0.12	326 ± 12	93	93
P6	3.31 ± 0.37	135 ± 24	▯	▯	▯	▯

$\mathrm{Zn(OAC)_2}$: 2.5 wt%

P2: DMS-A21 : AMS-1203 : HDI = 191 : 1 : 226

P3: DMS-A21 : AMS-1203 : HDI = 110 : 1 : 139

P4: DMS-A21 : AMS-1203 : HDI = 76: 1 : 106

P5: DMS-A15 : AMS-1203 : HDI = 191 : 1 : 226

P6: DMS-A12 : AMS-1203 : HDI = 191 : 1 : 226