NIR driven fast macro-damage repair and shear-free reprocessing of thermoset elastomers via dynamic covalent urea bonds

*Zhanhua Wang,[1] Maoyu Yang,[1] Xiaorong Wang[2], Guoxia Fei,[1] Zhuo Zheng,[1] Hesheng Xia[1,]**

[1]State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, P. R. China. E-mail: xiahs@scu.edu.cn

[2]School of Petrochemical Engineering, Liaoning Shihua University, Fushun, Liaoning 113001, China

Experimental section

Materials: Amine-terminated polysiloxane (DMS-A12: M_n = 900-1000 g/mol) were purchased from Gelest, Inc. Isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), 4,4′-methylenebis-(cyclohexyl isocyanate), 4,4′-diphenylmethane diisocyanate, and HDI trimer were obtained from best-reagent companies. All of the other regents were used as received.

Preparation of polydopamine nanoparticles (PDAs): For a typical synthesis of PDAs with an average size of 340 nm, the aqueous ammonia solution (NH_4OH, 5 mL, 28–30%) was mixed with ethanol (80 mL) and deionized water (180 mL) under stirring at 30 °C for 30 min. Dopamine hydrochloride (1 g) was dissolved in deionized water (20 mL) and then added into the above mixture. The color of this solution immediately turned pale brown and gradually changed to dark brown. The reaction was allowed to proceed for 24 h. The PDAs were obtained by freeze drying after centrifugation and washed with water three times.

Preparation of PUA-PDMS/PDAs composites: 25 mg polydopamine nanoparticles was dispersed in 20 mL anhydrous tetrahydrofuran at room temperature and ultrasonicated for 20 min. 4 g DMS-A12 and 0.76 g IPDI were added to the solution and stirred for 1 h, then 0.2 g tri-HDI was added into the solution, the mixture was stirred at room temperature for 20 min, and then poured into a PTFE mold. The THF was evaporated at room temperature for 5 days. The PUA-PDMS composite elastomers with graphene or nanotube as fillers were prepared by using the same procedure just by replacing polydopamine nanoparticles with graphene or nanotube. The same procedure was also used for preparing the PUA-PDMS elastomer without PDAs fillers.

Self-healing experiments: The damage sample was exposed to an 808 nm near-infrared (NIR) light with diverse irradiation intensities and times (for scratches: 2 W/cm^2, 5 min; for hole repair: 3 W/cm^2, 10 min). The distance between the sample and the light was 2 cm.

Reprocessing experiments: The samples were first cut into small pieces and then put into a mold which was then irradiated by NIR light with an intensity of 150 W/cm^2. The distance between the mold and the light was 8 cm.

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. PUA-PDMS/PDAs composites were characterized by IR spectroscopy on a Fourier transform infrared spectrometer (FTIR; Nicolet 560) in the frequency range of 400–4000 cm^{-1}. NMR experiments were conducted by 1H NMR (Bruker ARX-400 at 400 MHz) with DMSO-d^6 as solvent. The morphology of polydopamine particles was observed on an FEI-inspect SEM with an acceleration voltage of 15 kV. Stress-relaxation analysis experiments were performed in tensile geometry on a DMA Q800 apparatus (TA Instrument), and rectangular samples were utilized (ca. 0.5 mm (T) × 3 mm (W) × 20 mm (L) and a gauge length of ~8 mm). For the stress-relaxation analysis, the built-in stress relaxation mode was used. Samples were equilibrated at a set temperature for 5 min, and then subjected to a constant strain of 10%. The stress decay over time was monitored. 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. Dynamic rheological measurements were carried out in a dynamic rheometer (Bohlin Gemini 2000, Malvern, British) in constant-strain mode by controlling the strain at 1%. The diameter of the plate was 25 mm, and the gap was about 1 mm. All of the samples were tested from 60 to 180 °C at a heating rate of 3 °C/min in the frequency of 1 Hz. The temperature variation under NIR light irradiation was recorded by a Testo 875i Infrared Thermal Imager.

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 (M062X method was also adopted, and the results were consistent). 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.

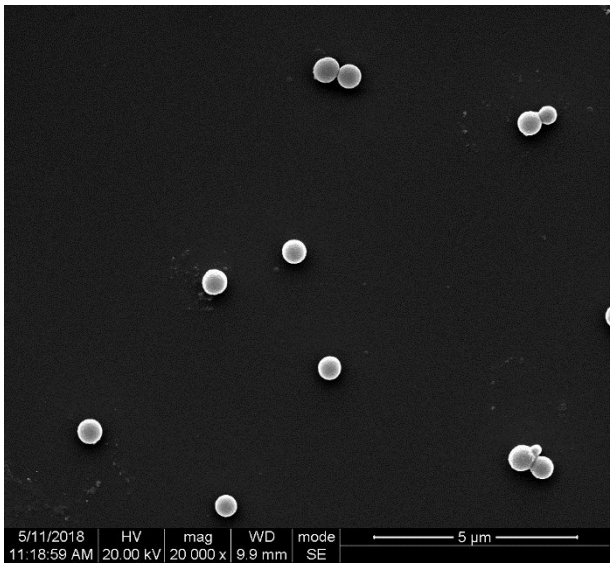

Figure S1. SEM image of the polydopamine nanoparticles.

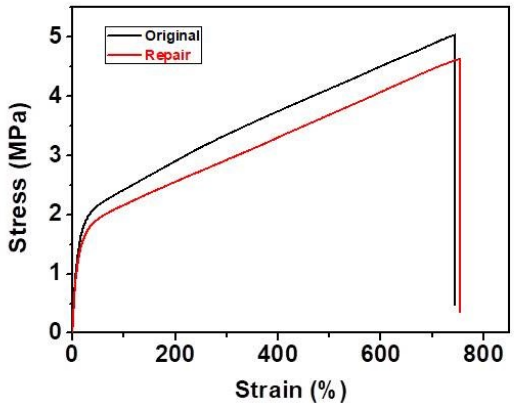

Figure S2. Strain-stress curves of the original and repaired PUA-PDMS/PDAs composites.

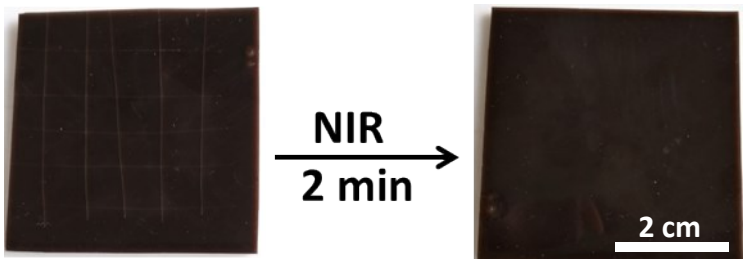

Figure S3. Optical images of a PUA-PDMS/PDAs composite damaged by blade with many scratches, and after NIR exposure for 2 min.

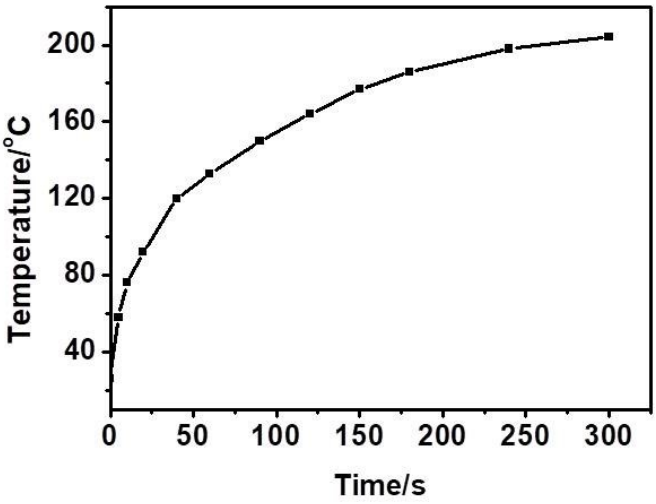

Figure S4. Temperature variation of the PUA-PDMS/PDAs composites as a function of NIR exposure time.

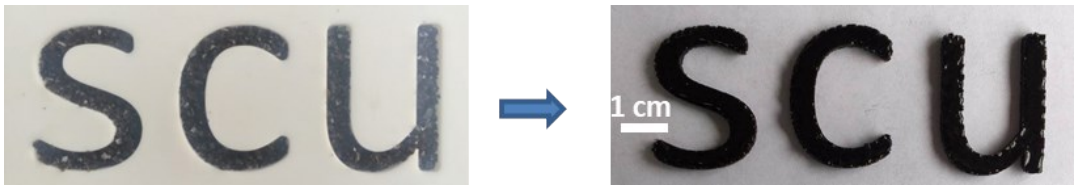

Figure S5. Optical images showing the reprocessing in a "SCU" shape mold.

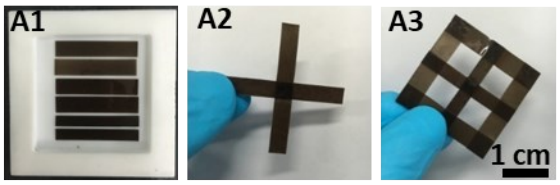

Figure S6. Optical images showing the fabrication process of a "田" shape product by NIR exposure. All of the overlapped areas are irradiated by NIR, which causes strong adhesion between each other due to the reversible urea bonds.

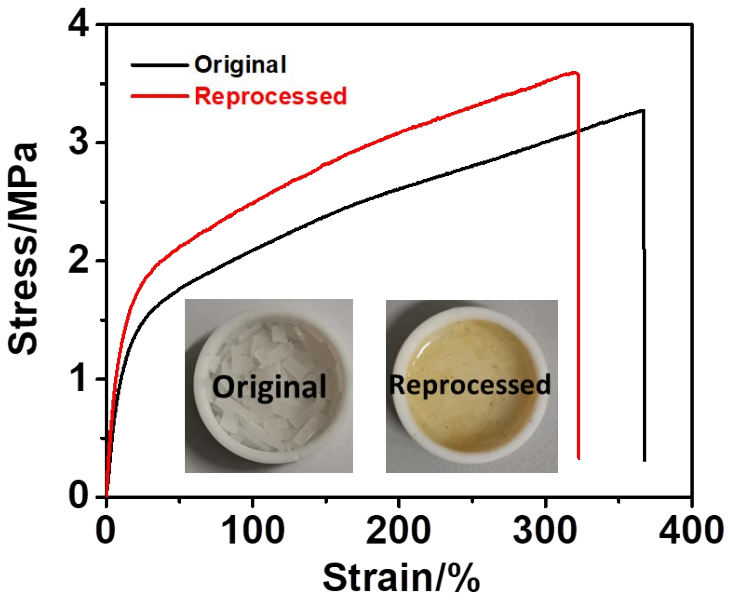

Figure S7. Stress-strain curve of the original and reprocessed PUA-PDMS elastomer without PDAs. Inset are the optical pictures of PUA-PDMS elastomer pieces (left) after being heated at 200 °C for 5 min (right).

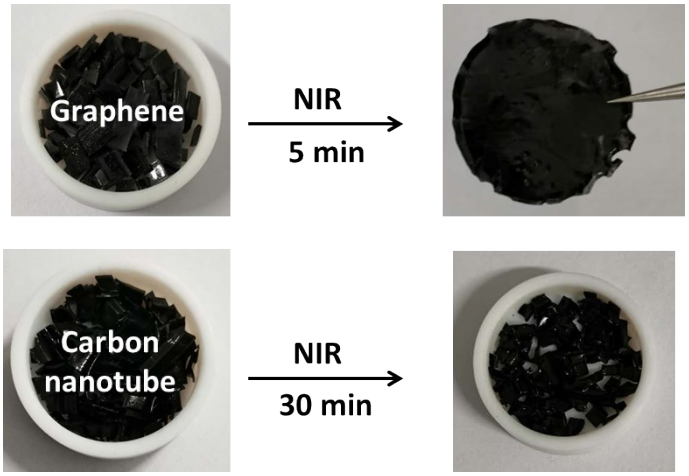

Figure S8. Optical pictures of small pieces of PUA-PDMS elastomers with graphene or carbon nanotube as fillers (left) after being irradiated by NIR light (right).

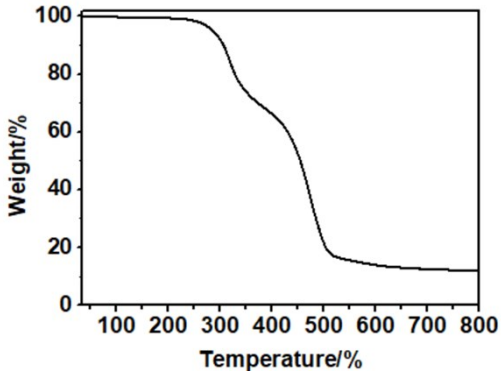

Figure S9. TGA curve of PUA-PDMS/PDA composites.

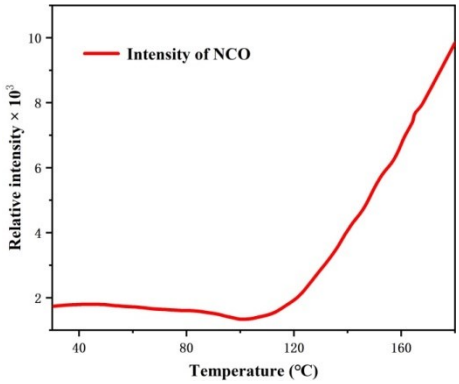

Figure S10. Relative FTIR peak intensity curves of the isocyanate group from a linear PUA-PDMS at about 2260 cm^{-1} which was normalized by C-H (3000-2800 cm^{-1}) recorded as a function of temperature.

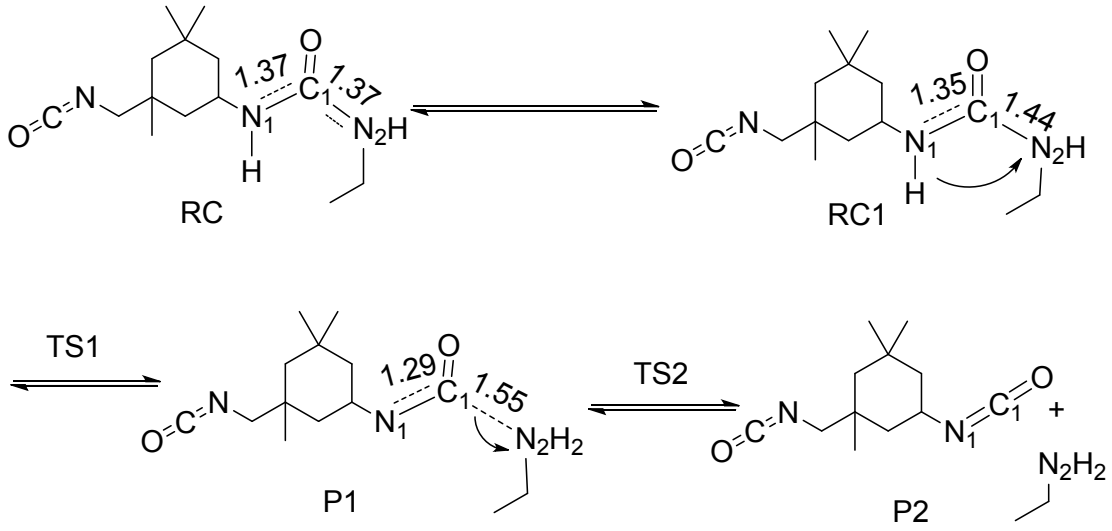

Figure S11. Schematic illustration of the mechanism of the reversible dissociation and re-formation of a urea compound formed by IPDI and ethyl amine.

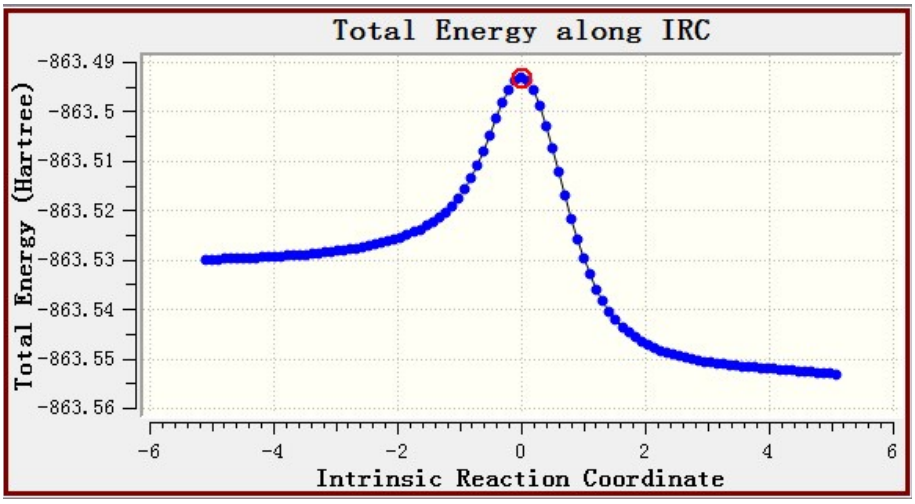

Figure S12. Intrinsic reaction coordinate of TS1.

Figure S13. Optical images of the PUA-PDMS/PDAs composite pieces made from hexamethylene diisocyanate (A) and 4,4′-methylenebis-(cyclohexyl isocyanate) (B) before and after NIR exposure.

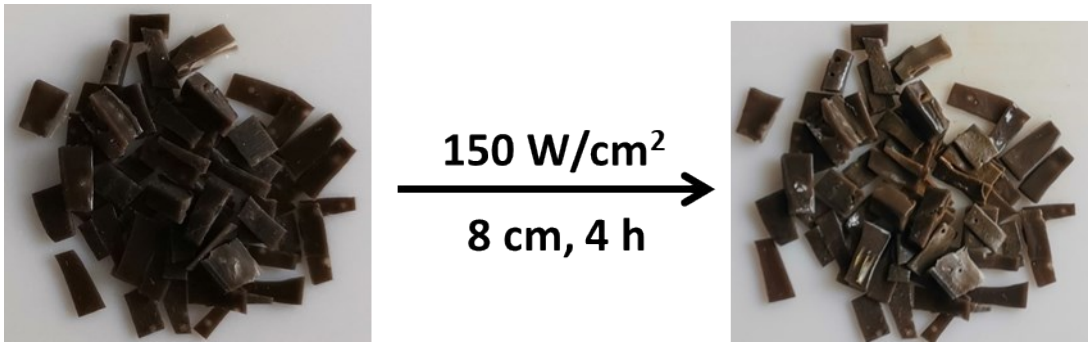

Figure S14. Optical images of the PUA-PDMS/PDAs composite pieces made from 4,4′-diphenylmethane diisocyanate before and after NIR exposure.

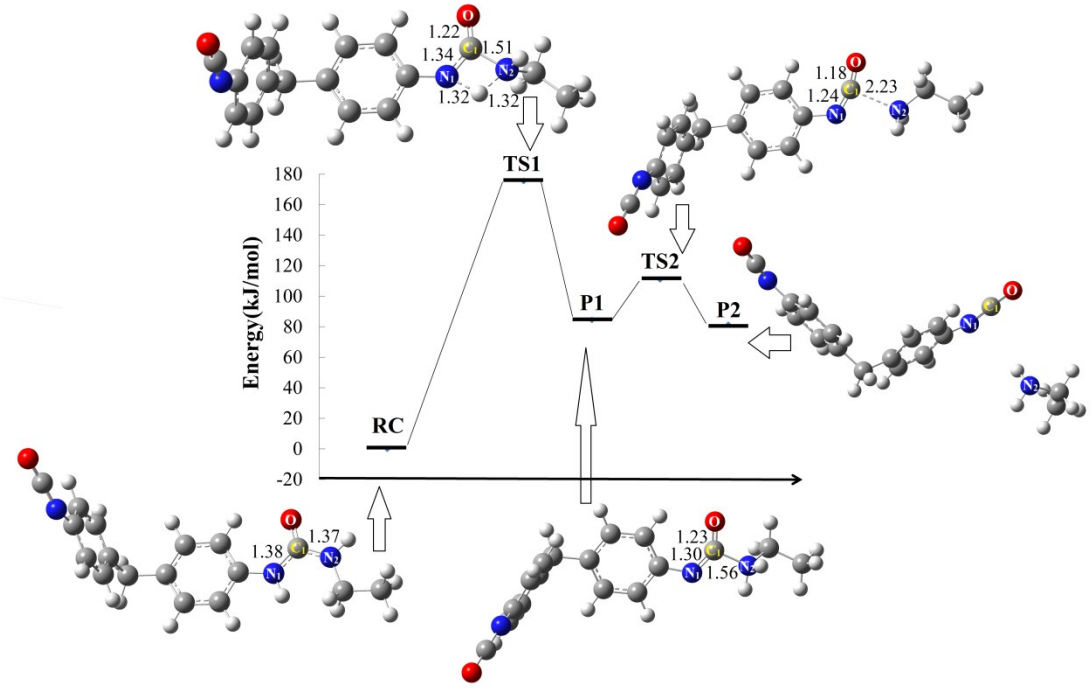

Figure S15. Energy profile of the decomposition reaction of the model urea compound formed by 4,4′-diphenylmethane diisocyanate and ethyl amine.

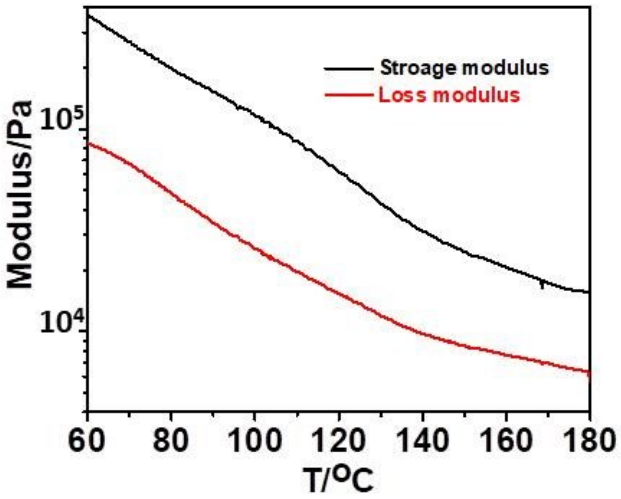

Figure S16. Storage modulus (G′) and loss modulus (G″) of the PUA-PDMS/PDAs composites made from an aromatic isocyanate (4,4′-diphenylmethane diisocyanate) as a function of temperature.

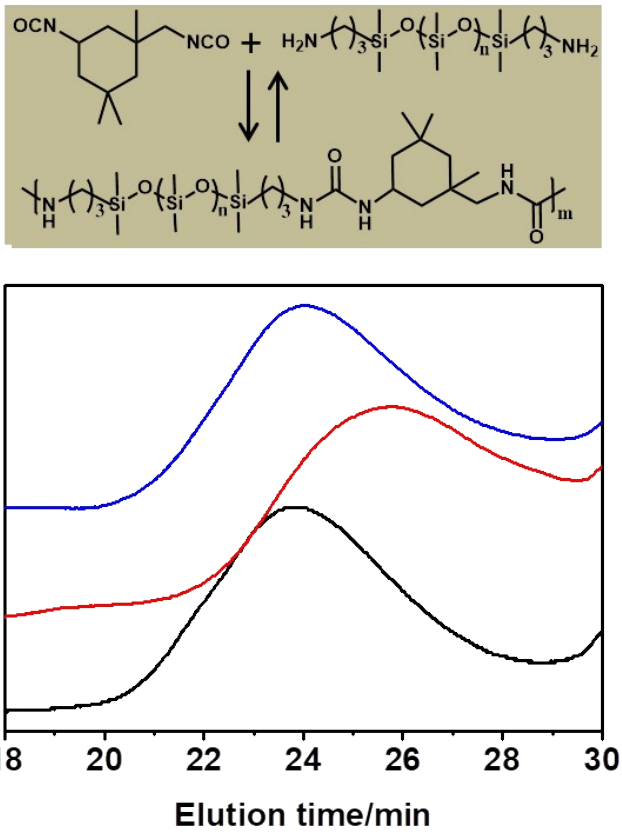

Figure S17. GPC curves of a linear PUA-PDMS. Black curve: a linear PUA-PDMS formed by IPDI and DMS-A12 with a 1:1 ratio; red curve: the linear PUA-PDMS was dissolved in toluene and then 1 equivalent DMS-A12 was added into the solution and incubated at 120 °C for 12 h; blue curve: another equivalent IPDI was added into the solution and stirred for 20 min, and then evaporate the toluene room temperature for 12 h and then 80 ^{o}C for another 12 h.

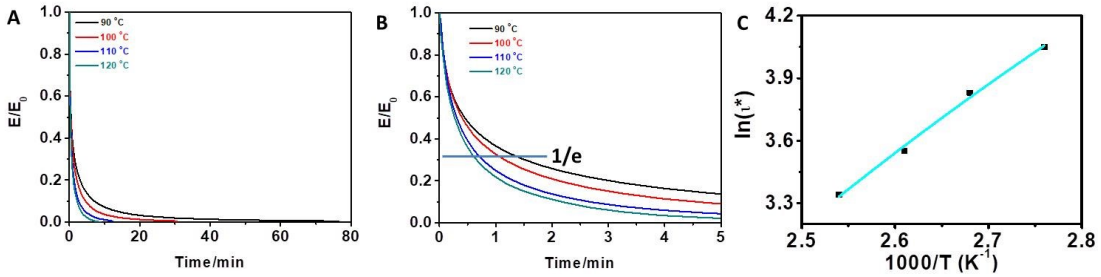

Figure S18. Normalized stress–relaxation curves of PUA-PDMS/PDAs composite at various temperatures (Black: 90 °C, red: 100 °C, blue: 110 °C, dark cyan: 120 °C) as a function of time (A: 0-80 min; B: 0-5 min). C: Fitting line of the relaxation times according to the Arrhenius equation, and the relaxation activation energy obtained from the slope.

The stress-relaxation properties of dynamic cross-linked elastomers conform to the Maxwell model, and the relaxation modulus can be described by the follow equation：

$$E = E_0 e^{(-t/\tau)}$$

where E is the tensile stress relaxation modulus, τ is the relaxation time. The relaxation time τ could be determined as the time when E/E_0 = 1/e. Compared to traditional thermoset elastomers, the stress/modulus of dynamic-covalent cross-linked elastomers will relax to zero much faster. The relaxation times are controlled by the associative exchange reactions, and the temperature dependence of the relaxation time can be described by the following Arrhenius equation[54]:

$$\tau(\mathrm{T}) = \tau_0 e^{(Ea,r/RT)}$$

where τ(T) is the relaxation time at the temperature T, τ_0 is a constant, $E_{a,r}$ is the relaxation activation energy and R is the gas constant.

Table S1. The relative energy and Boltzmann distribution of the first 100 conformations with lower energy for chair/boat conformation

chair conformation			boat conformation		
RC label	rel. E (kJ/mol)	Boltzmann Dist	**RC** label	rel. E (kJ/mol)	Boltzmann Dist
M0001	**0**	**0.179**	**M0001**	**0**	**0.232**
M0002	1.31	0.105	M0002	0.95	0.158
M0003	1.78	0.087	M0003	1.73	0.115
M0004	2.23	0.073	M0004	2.15	0.097
M0005	2.58	0.063	M0005	2.97	0.07
M0006	2.66	0.061	M0006	3.29	0.061
M0007	2.76	0.059	M0007	3.56	0.055
M0008	3.07	0.052	M0008	3.94	0.047
M0009	3.9	0.037	M0009	4.42	0.039
M0010	3.99	0.036	M0010	4.85	0.033
M0011	4.31	0.031	M0011	4.87	0.033
M0012	4.78	0.026	M0012	6.11	0.02
M0013	4.81	0.026	M0013	7.85	0.01
M0014	5.37	0.02	M0014	10.34	0.004
M0015	5.43	0.02	M0015	11.14	0.003
M0016	5.88	0.017	M0016	11.25	0.002
M0017	6.34	0.014	M0017	11.32	0.002
M0018	6.4	0.014	M0018	11.55	0.002
M0019	6.61	0.012	M0019	12.06	0.002
M0020	7.64	0.008	M0020	12.23	0.002
M0021	8.09	0.007	M0021	12.4	0.002
M0022	8.09	0.007	M0022	12.71	0.001
M0023	8.24	0.006	M0023	13.18	0.001
M0024	8.31	0.006	M0024	13.37	0.001
M0025	8.59	0.006	M0025	13.44	0.001
M0026	8.95	0.005	M0026	13.5	0.001
M0027	9.29	0.004	M0027	13.91	0.001
M0028	10.18	0.003	M0028	14.1	0.001
M0029	10.48	0.003	M0029	14.52	0.001
M0030	10.56	0.003	M0030	15.33	0
M0031	12.59	0.001	M0031	15.55	0
M0032	12.7	0.001	M0032	15.55	0
M0033	12.78	0.001	M0033	15.95	0
M0034	12.95	0.001	M0034	16.58	0
M0035	13.95	0.001	M0035	16.91	0
M0036	14	0.001	M0036	16.95	0
M0037	14.27	0.001	M0037	17.07	0
M0038	14.55	0.001	M0038	17.54	0
M0039	15.13	0	M0039	17.82	0

M0040	15.16	0	M0040	18.03	0
M0041	15.18	0	M0041	18.08	0
M0042	15.37	0	M0042	18.11	0
M0043	15.55	0	M0043	18.22	0
M0044	15.67	0	M0044	18.36	0
M0045	15.67	0	M0045	18.37	0
M0046	15.77	0	M0046	19.3	0
M0047	16.14	0	M0047	19.35	0
M0048	16.17	0	M0048	19.44	0
M0049	16.18	0	M0049	19.46	0
M0050	16.5	0	M0050	19.66	0
M0051	16.58	0	M0051	19.96	0
M0052	17.03	0	M0052	20.54	0
M0053	17.2	0	M0053	20.74	0
M0054	17.44	0	M0054	21.01	0
M0055	18.02	0	M0055	22.54	0
M0056	18.03	0	M0056	22.93	0
M0057	18.5	0	M0057	23.01	0
M0058	18.52	0	M0058	23.13	0
M0059	18.58	0	M0059	23.43	0
M0060	18.65	0	M0060	23.74	0
M0061	19	0	M0061	24.29	0
M0062	21.3	0	M0062	24.42	0
M0063	21.43	0	M0063	26.01	0
M0064	21.51	0	M0064	26.79	0
M0065	21.67	0	M0065	26.87	0
M0066	21.84	0	M0066	27.14	0
M0067	21.91	0	M0067	27.84	0
M0068	22.33	0	M0068	28.32	0
M0069	24.18	0	M0069	28.66	0
M0070	24.31	0	M0070	29.14	0
M0071	24.79	0	M0071	29.55	0
M0072	25.2	0	M0072	29.64	0
M0073	25.38	0	M0073	29.74	0
M0074	26.13	0	M0074	29.75	0
M0075	26.36	0	M0075	29.82	0
M0076	27.15	0	M0076	30.03	0
M0077	27.3	0	M0077	30.38	0
M0078	27.61	0	M0078	30.43	0
M0079	28.03	0	M0079	30.78	0
M0080	28.17	0	M0080	31.03	0
M0081	28.29	0	M0081	31.13	0
M0082	28.4	0	M0082	31.28	0

M0083	28.46	0	M0083	31.48	0
M0084	28.52	0	M0084	31.76	0
M0085	29.32	0	M0085	31.84	0
M0086	29.88	0	M0086	32.05	0
M0087	30.01	0	M0087	32.08	0
M0088	31.19	0	M0088	32.35	0
M0089	31.82	0	M0089	32.55	0
M0090	31.87	0	M0090	32.98	0
M0091	33.84	0	M0091	33.94	0
M0092	34.24	0	M0092	34.45	0
M0093	35.92	0	M0093	34.63	0
M0094	37.49	0	M0094	37.47	0
M0095	37.88	0	M0095	37.78	0
M0096	38.44	0	M0096	37.99	0
M0097	39.89	0	M0097	38.88	0
M0098	40.51	0	M0098	39.82	0
M0099	40.63	0	M0099	40.28	0
M0100	41.64	0	M0100	41.33	0