Supporting information for

Self-Healing Elastomers Assembly Towards Three-Dimensional Shape Memory Devices

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Experimental Section

Raw materials

2-Methoxyethyl acrylate (MEA) was purchased from Alfa Aesar, and used without further purification. N,N-dimethylacrylamide (DMAA,99%, Kohjin Co., Japan) was purified by reduced pressure distillation and filtering through activated alumina. Potassium persulfate (KPS) (99.5%, Bodi Co., China) and N,N,N’,N’-tetramethyldiamine (TEMED) (99%, Sinopharm Chemical Reagent, China) were used as received without further purification. The water used in all experiments was purified by a Millipore Direct-Q purification system and bubbled with N_2 for 3h before use.

Preparation of samples

The appropriate amount of MEA and DMAA were added in ultrapure water with N_2 gas bubbling for 1 h to remove any soluble O_2. After vigorous stirring for another 15 min, the solution was cooled to 0℃ before catalyst (TEMED, 8μL) and initiator (0.01g in 0.5ml water) were added. Finally, the final mixture was transferred to a tailored glass tube and polymerized at 60℃ for 12h to obtain the desired hydrogels. The hydrogels obtained were washed thoroughly with distilled water to remove the unreacted monomer and other impurities, and the water on the surface of hydrogels was then swept by filter paper. The resulting gels were subsequently dried at room temperature for 24 h followed by drying for 24 h at 80℃ under vacuum in order to obtain the elastomer samples.

Measurements and characterizations:

FT-IR spectra were performed with a Nicolet 6700 instrument (Thermal Scientific, USA) by the KBr method in the range 500-4000 cm^{-1}. The mechanical properties of polymers were measured on an ASG-J electronic universal testing machine (Shimadzu Co., Japan) at room temperature. Clubbed samples with size of Φ3mm× 40mm (gauge length, 20 mm) were used for tensile tests with a crosshead speed of 20mm/min. Plate samples with size of 40mm×4mm×0.5mm was used for dynamic mechanical analysis with a TA Q800 Dynamic Mechanical Analysis (DMA) instrument (TA Instrument Inc.) in the shear mode. The dynamic storage and loss moduli were determined at a frequency of 10 Hz and a heating rate of 3℃/min as a function of temperature from -50℃ to 100℃. The MD copolymer elastomers were cut into completely separate pieces using a razor blade and healing experiments were performed by gently contacting the cut faces together at room temperature and healed at 90℃ for various time.

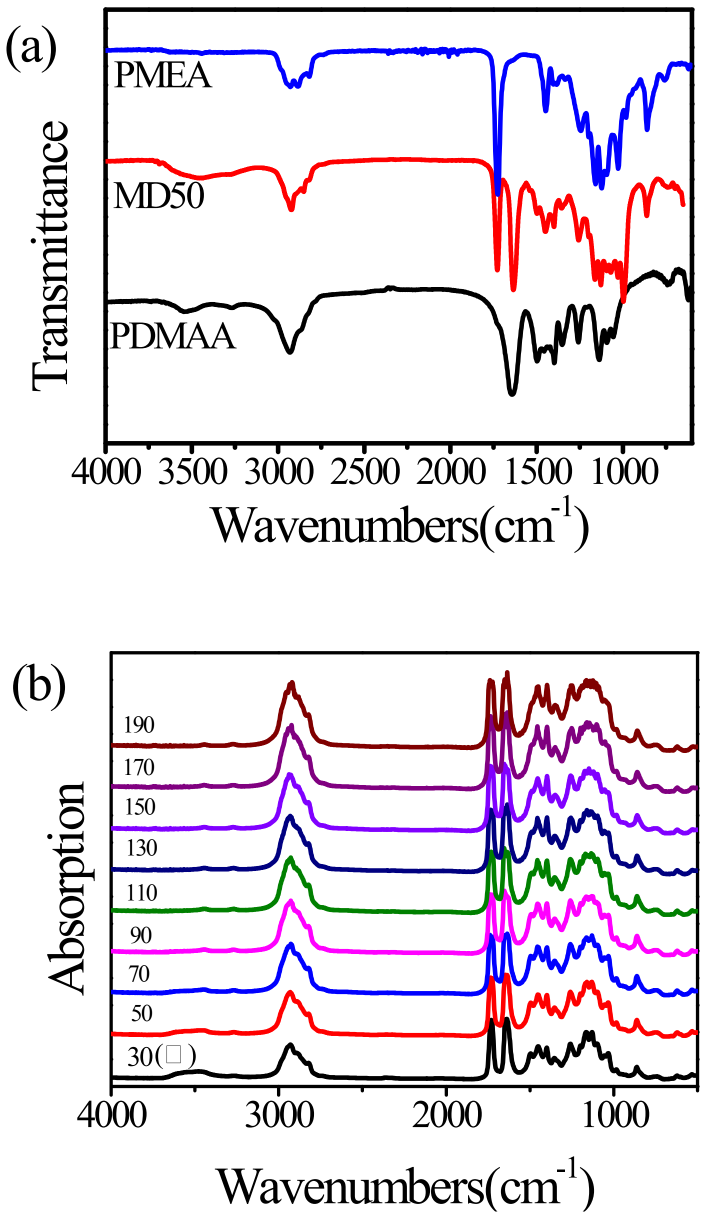

Figure S1. FT-IR spectra image of MDx copolymer and temperature-variable FT-IR spectra image of MD50 copolymer film.

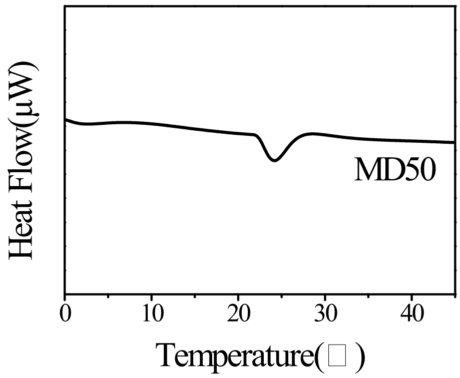

Figure S2. DSC isotherms of the self-healing MD50 copolymer elastomer.

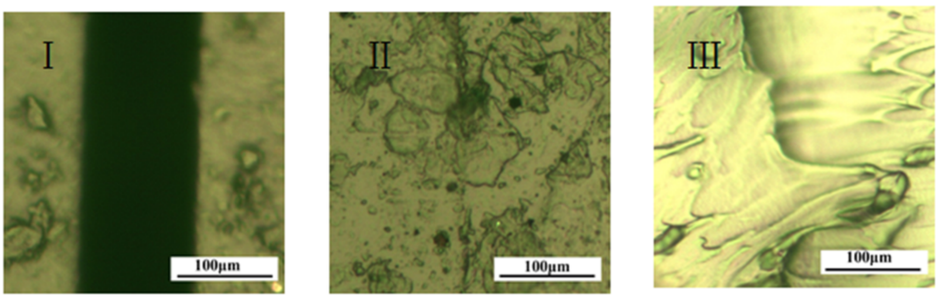

Figure S3. The representative optical microscope images for self-healing behavior: (Ⅰ) the gaps with the depth ~0.50 mm; (Ⅱ) after healed 12 h at 90℃; (Ⅲ) after stretched to about 200% strain.

To investigate the physical details of the self-healing behaviour of elastomeric materials, the healing process of MD50 sample was monitored by using optical microscope. Figure S3 presents the optical microscope images showing the evolution of the scratch on the surface of MD50 sample (the thickness of sample is ~0.65mm and the depth of scratch is ~0.50mm). As shown in Figure S2 (Ⅰ), the scratch on the surface of the sample was clearly observed with the width of ~120μm. The width of scratch decreased significantly at initial several minutes at 90℃. After healing for 12h, the optical microscope image of the sample [shown in Figure 3b (Ⅱ)] confirmed that the fracture surfaces were sufficiently healed such that the gaps were indiscernible. The resulting healed sample can be subsequently subjected to ~200% strain without failure, and the corresponding optical microscope image was shown in Figure 3b (Ⅲ).

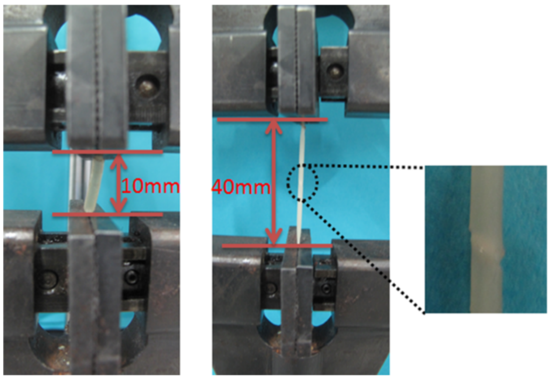

Figure S4. The cross-sectional pictures of the sample of MD50 elastomer under the tensile test.

Figure S5. The cubic device constructed using MD50 copolymer elastomer can bear load of 500g (comparable to 400 times the weight of itself) without failure.

Table S1. Summary of the mechanical and self-healing properties of MD elastomers.

Sample	Young's Modulus(Mpa)	Yield strength(Mpa)	Ultimate strain(%)	Ultimate stress(Mpa)	Recovery of strain(%)	Recovery of stress(%)	Recovery of yield strength (Mpa)
MD45	34.95±1.3	4.18±0.5	353.92±6.2	5.84±0.3	36.58±1.1	65.74±2.7	4.23±0.7
MD50	40.30±0.8	7.01±0.4	569.50±10.8	12.27±0.2	83.83±2.5	98.21±1.6	7.24±0.3
MD55	52.09±3.5	14.42±1.2	373.41±7.4	14.46±0.6	30.49±5.3	80.30±6.4	14.59±2.6