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Electronic Supplementary Information

Catalyst-Free Dynamic Exchange of Aromatic Schiff Base Bonds and Its Application to Self-Healing and Remolding of Crosslinked Polymer

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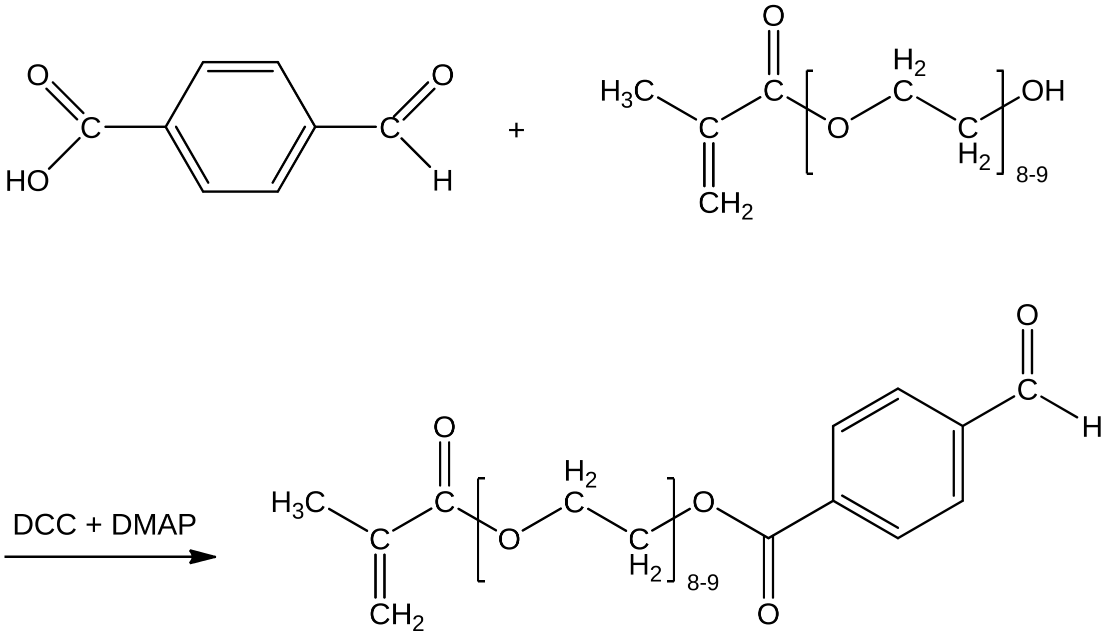


Fig. S1. Synthesis of polyethylene glycol methacrylate ester benzaldehyde (PEGMA-BZ).

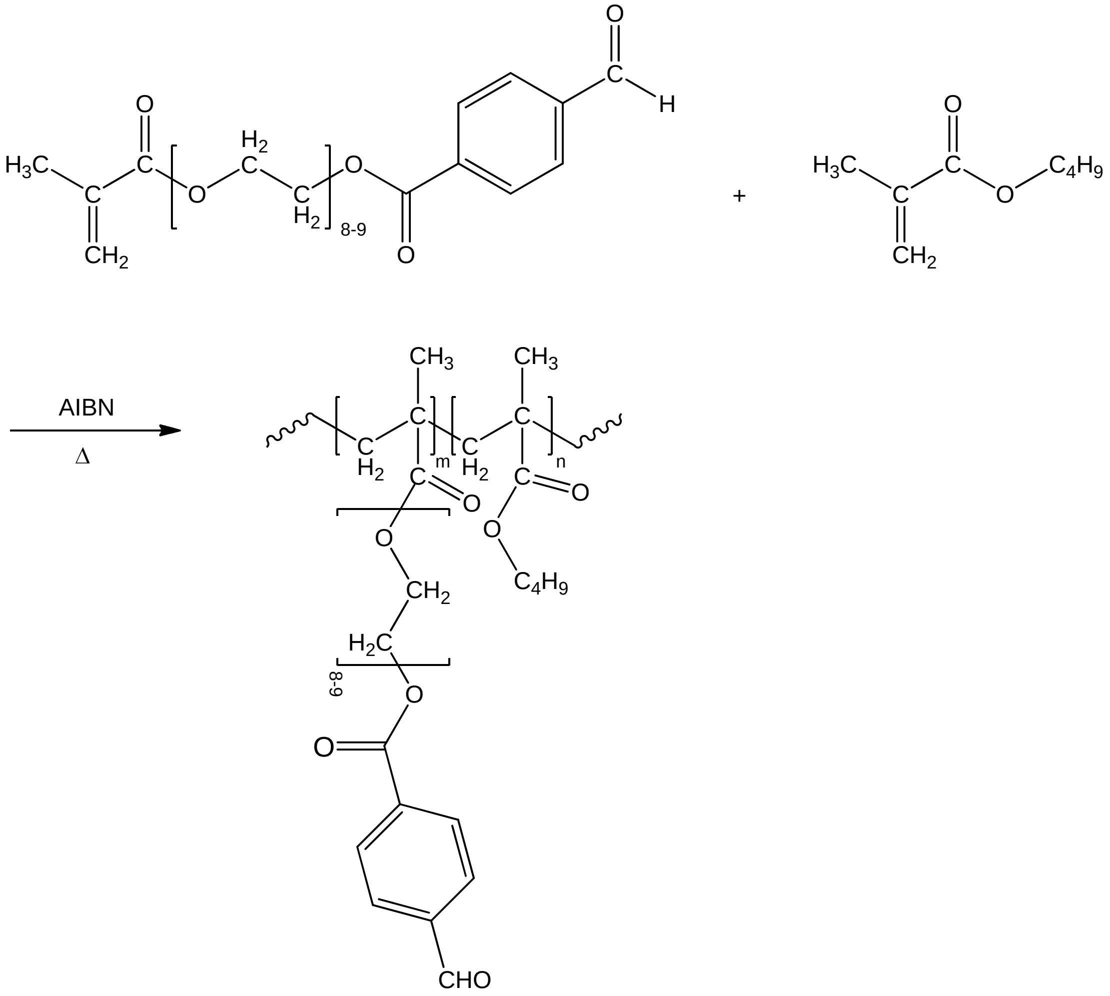


Fig. S2. Synthesis of aldehyde-functionalized polyacrylate.

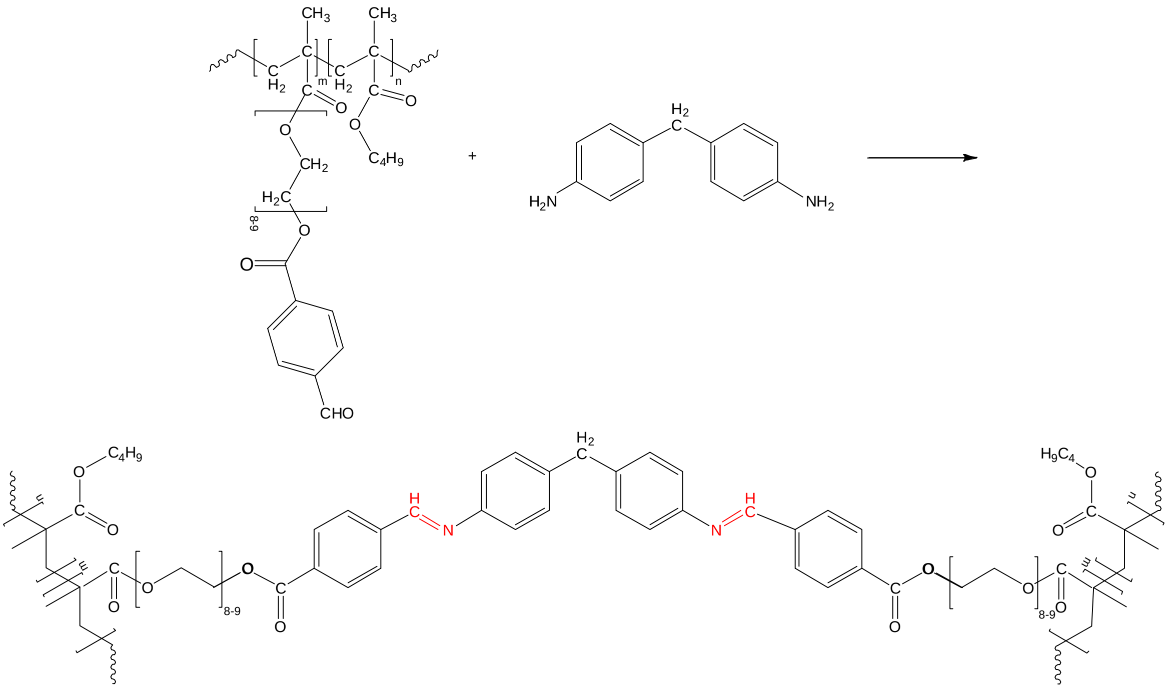


Fig. S3. Synthesis of Schiff base bonds crosslinked aldehyde-functionalized polyacrylate (PA-SH).

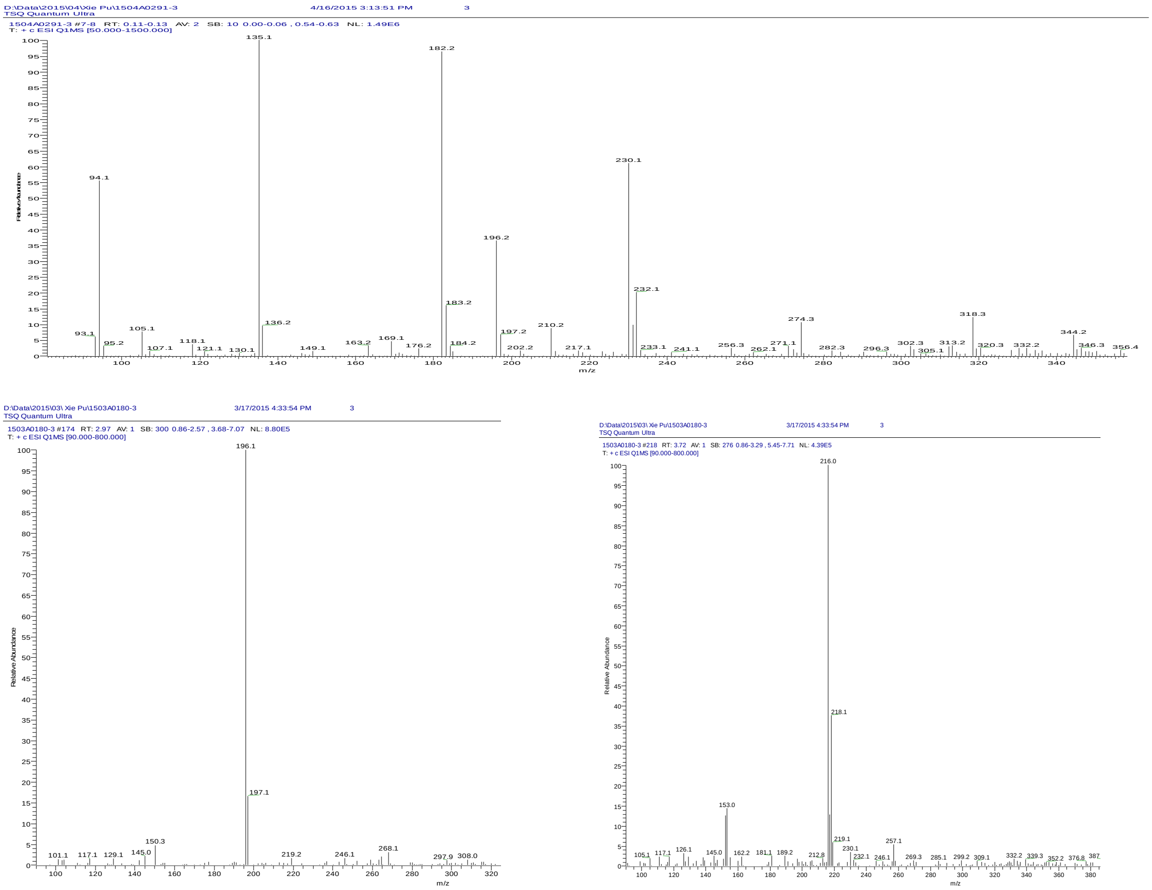
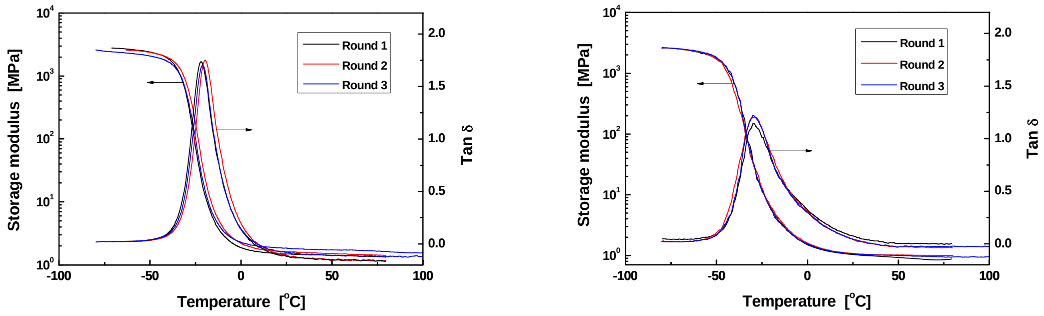


Fig. S4. Mass spectra showing appearance of the exchange products (N-(4-methylbenzylidene)aniline (m/z = 195) and N-benzylidene-3-chloroaniline (m/z = 215.5)) between equimolar benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline in methanol (0.005 mol/L) at room temperature for 12 h.



(a) (b)

Fig. S5. Temperature dependences of storage modulus and tan *δ* of (a) PA-SH and (b) PA-ref measured by repeated DMA scans.

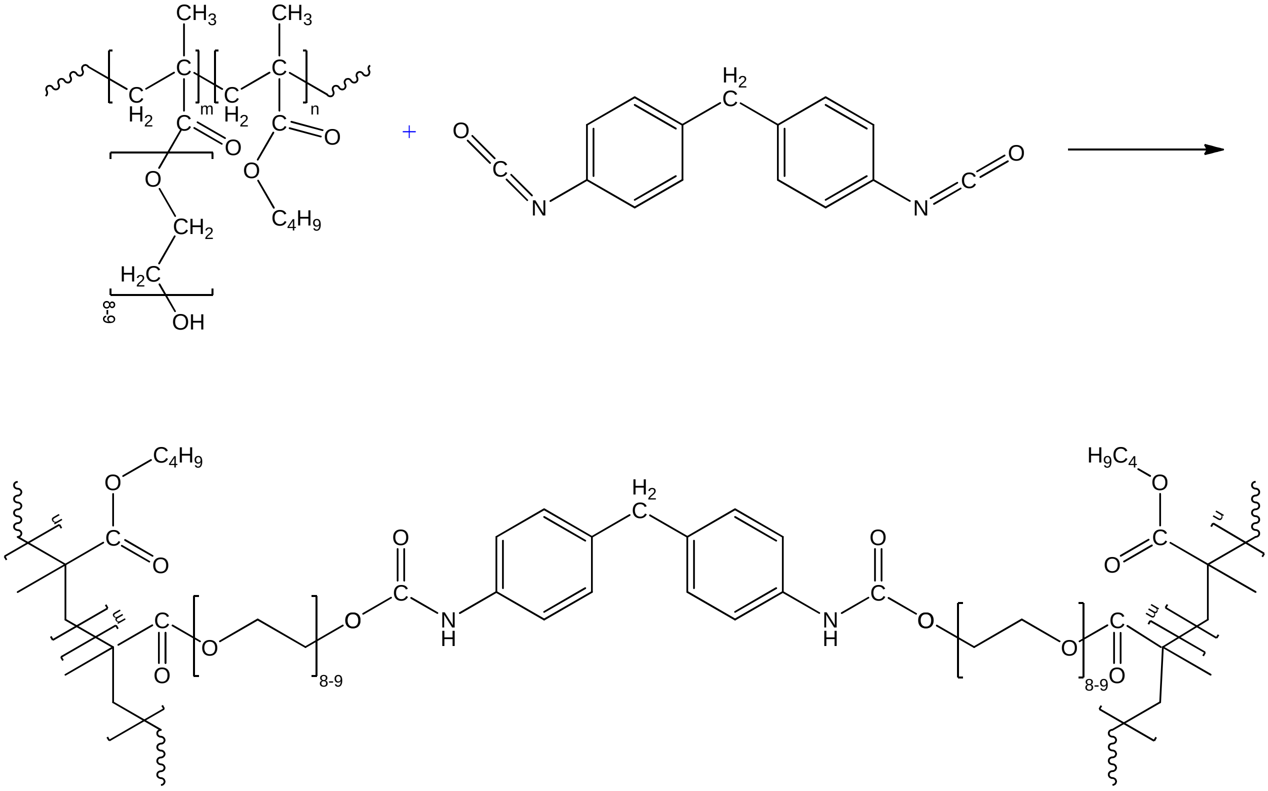
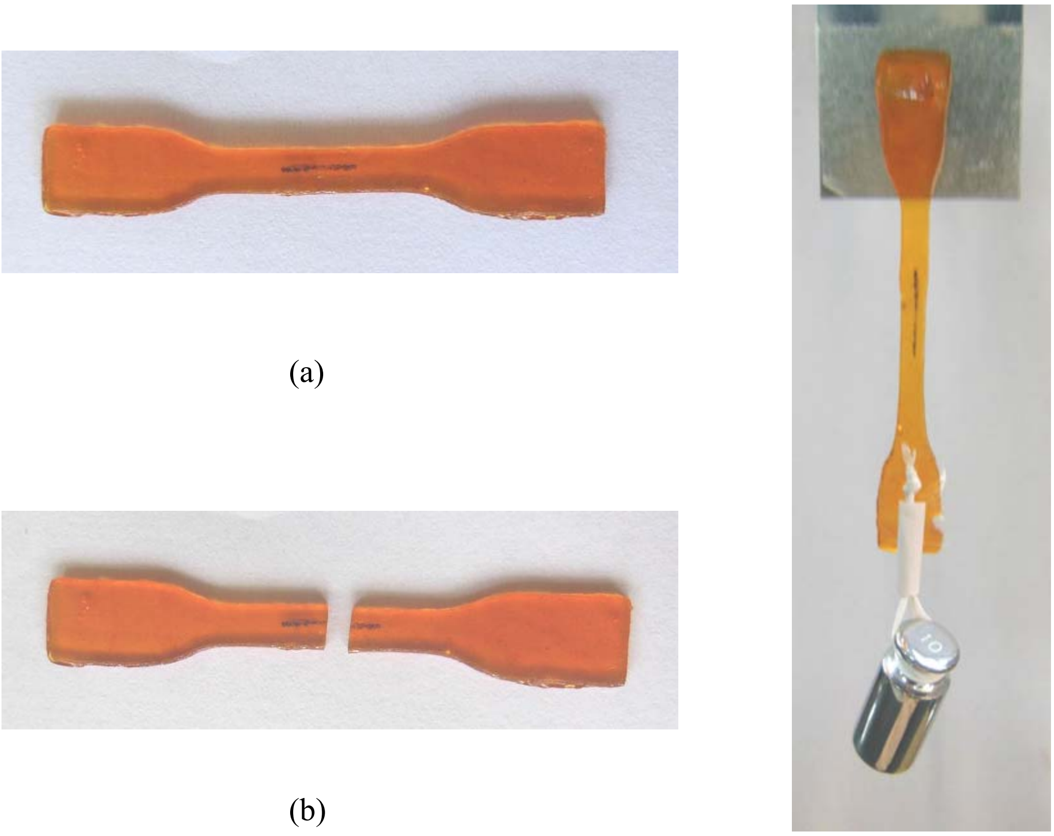


Fig. S6. Synthesis of control polymer PA-ref.



(a)

(b)

(c)

Fig. S7. Macro-repairing of a PA-SH specimen at 25 °C in air. The virgin specimen (a) was firstly cut (b), and then the broken halves were recombined for healing. After 24 h, the specimen looks like the original one without any shape change, and can bear a weight (c).

Experimental details

Materials: Poly(ethylene glycol) methacrylate (PEGMA, M_n = 500), 4-carboxybenzaldehyde, benzylideneaniline, N-(4-methylbenzy-lidene)-3-chloroaniline and methylene diphenyl diisocyanate (MDI) were supplied by Sigma-Aldrich. Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 2,2-azobisisobutyronitrile (AIBN), and 4,4'-diaminodiphenyl methane (DDM) were provided by Aladdin Chemical. Butyl acrylate was purchased from Tianjin Fuchen Reagent Factory, China. Tetrahydrofuran (THF), diethyl ether, dioxane, n-hexane, and chloroform were supplied by Guangzhou Reagent Chemical Factory, China.

Preparation of polyethylene glycol methacrylate ester benzaldehyde (PEGMA-BZ, Fig. S1): Poly(ethylene glycol) methacrylate (10 g) and 4-carboxybenzaldehyde (4.2 g) were dissolved in anhydrous THF (120 ml).

Afterwards, nitrogen was introduced for 10 min, and the THF solution (30 ml) of DCC (10.3 g) and DMAP (0.82 g) was added dropwise at -20 °C. Then, the system was heated to 30 °C allowing for reaction of 24 h. When the solid deposit was filtered off and most of THF was removed by a rotary evaporator (about 10 ml remained), diethyl ether (100 ml) was incorporated. Again, the precipitate was filtered off and the solvents were evaporated. The resultant canary yellow liquid product with yield of ~70% was vacuum dried for 24 h. The product of PEGMA-BZ was characterized by infrared and nuclear magnetic resonance (^{1}H NMR) spectroscopy to confirm its molecular structure (**Fig. S8** and **S9a**).

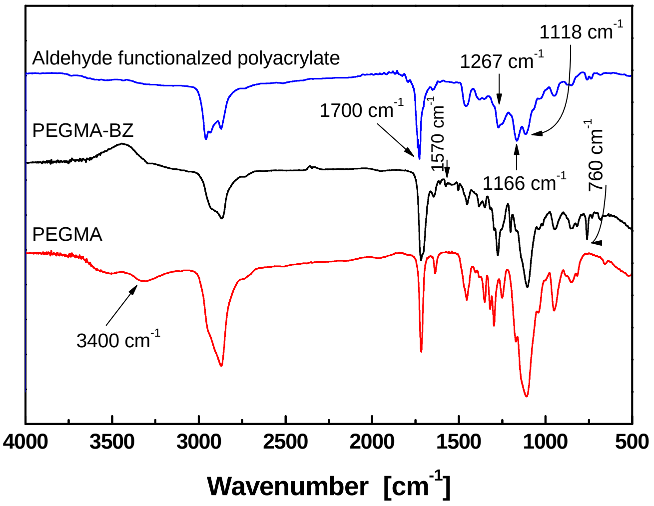
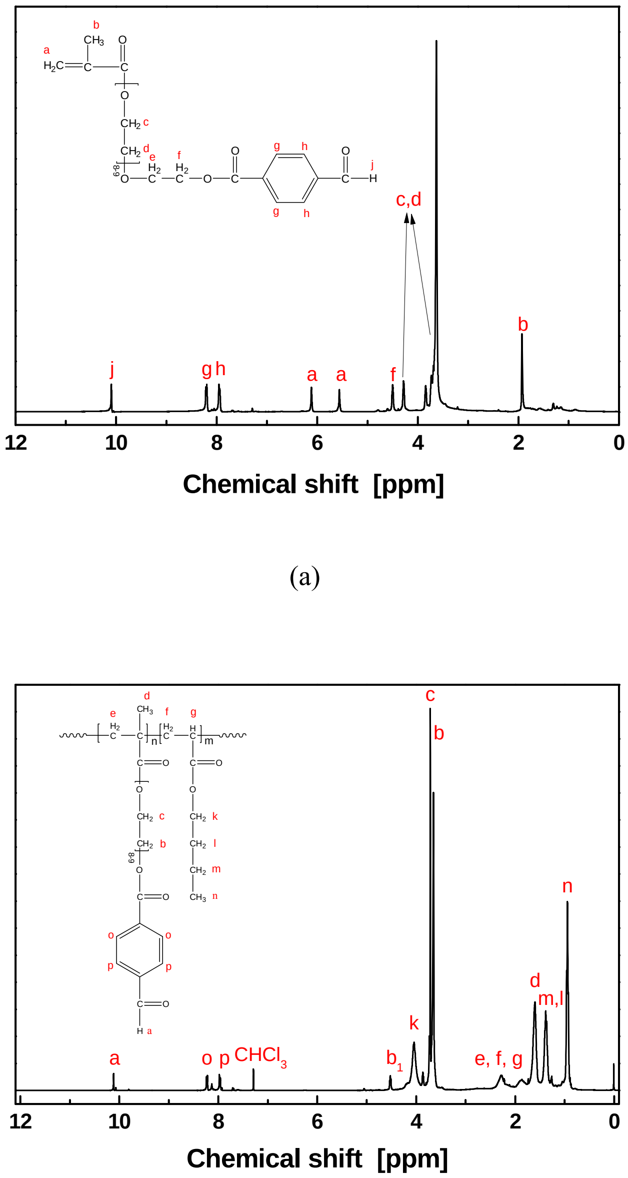


Fig. S8. FTIR spectra of PEGMA-BZ and aldehyde-functionalized polyacrylate with that of PEGMA as reference. Compared to PEGMA, the strong adsorption at 3400 cm^{-1} is no longer observed on the spectrum of PEGMA-BZ. Instead, the adsorptions of phenyl ring appear at 1570 and 760 cm^{-1} on the spectrum of PEGMA-BZ. The results evidence the generation of PEGMA-BZ. On the other hand, there are three peaks at 1267, 1166 and 1118 cm^{-1} on the spectrum of aldehyde-functionalized polyacrylate assigning to C-O-C bonds in addition to the carboxyl peak at 1700 cm^{-1}.



(a)

(b)

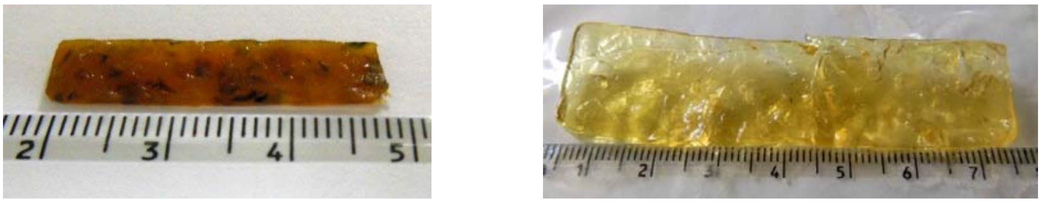
Fig. S9. ^{1}H NMR spectra of (a) PEGMA-BZ and (b) aldehyde-functionalized polyacrylate in $CDCl_3$.

Preparation of aldehyde-functionalized polyacrylate (Fig. S2): PEGMA-BZ (5 g) and butyl acrylate (10 g) were dissolved in dioxane (100 ml), and then argon was introduced for 10 min. When the system was heated to 60 °C, AIBN (0.4 g) was added and the reaction proceeded at 65 °C for 24 h. Afterwards, the system was cooled down to room temperature and the solvent was evaporated. The produced sticky fluid was washed by cold n-hexane for several times and vacuum dried at room temperature for 24 h. Fourier transform infrared (FTIR) and ^{1}H NMR spectroscopy were also used to identify the product (**Fig. S8** and **S9b**). Number average molecular weight and polydispersity index of the polymer, determined by gel permeation chromatography (GPC), are 3.0×10^4 and 1.9, respectively.

Preparation of Schiff base bonds crosslinked aldehyde-functionalized polyacrylate (PA-SH, Fig. S3): Aldehyde-functionalized polyacrylate (7 g) was dissolved in chloroform (5 ml), which was then mixed with chloroform solution (5 ml) of DDM (0.28 g). The mixture was poured into the mold for curing at room temperature. After 4 h, the crosslinked polymer was cut into pieces and vacuum dried at 40 °C for 10 h. Finally, the dried fragments were put into the mold again and compressed at 60 °C for 1-2 h under a pressure of 4.5 MPa for further characterization.

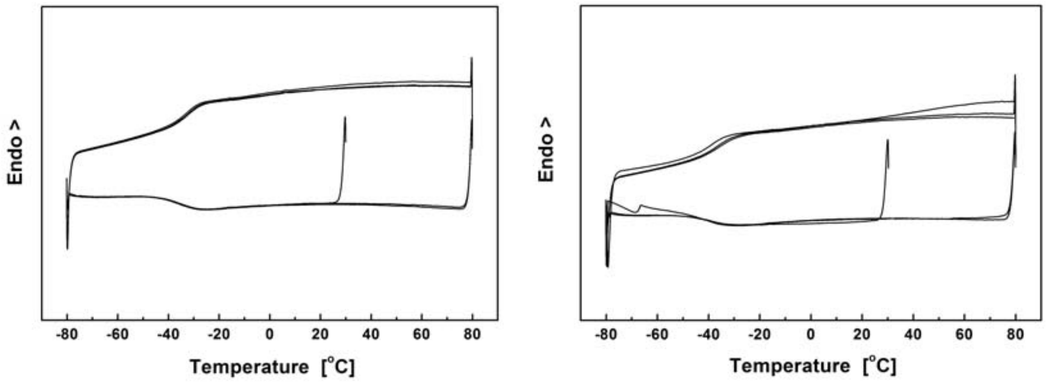
To verify whether the polymer is crosslinked, PA-SH was immersed in the good solvent THF for 24 h at room temperature. The material was not dissolved but still maintained its structural integrity, exhibiting only volume expansion (**Fig. S10**). In addition, cyclic differential scanning calorimetry (DSC) measurement of the specimen (**Fig. S11a**) indicates that the curves overlap with each other without additional exotherm. Glass transition temperature, T_g, of -33 °C does not change with the repeated scan. These suggest that the polymer has been fully cured, and the yield of imine bonds is almost 100 %.

For the convenience of discussion, PEGMA was copolymerized with butyl acrylate at molar ratio of $n_{(PEGMA)}/n_{(BA)} = 1/9$, and then the copolymer was crosslinked by MDI to yield the control (named as PA-ref, **Fig. S6**). Finally, PA-ref was also molded following the procedures described above. Multiple DSC scans manifest that the crosslinked structure of PA-ref with T_g of -40 °C has been fixed under the given conditions (**Fig. S11b**).



(a) (b)

Fig. S10. (a) PA-SH before swelling, and (b) PA-SH after swelling in THF for 24 h at room temperature.



(a) (b)

Fig. S11. Repeated DSC heating-cooling scans of (a) PA-SH and (b) PA-ref.

Model exchange experiments: Equimolar solutions of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline in methanol (0.005 mol/L) were mixed under stirring at 25 °C in air. Samples were extracted by syringe after different times to estimate the time dependence of the exchange reaction with high-performance liquid chromatography (HPLC).

Characterization: HPLC analyses were carried out at 25 °C on an Agilent 1100 using acetonitrile as eluent at a flow rate of 1 ml/min with UV detection at 280 nm.

Electron spin resonance (ESR) spectra were obtained from a Bruker A300-10-12 spectrometer in N_2 at 25 °C with 1,1’-diphenyl-2-picrylhydrazyl (DPPH) as the reference. The filed modulation amplitude was changed from 0.2 to 1 G, depending on the linewidth and the signal strength.

GPC measurements were performed on a Waters 1515 instrument using polystyrene as the calibration standard and THF as the eluent at a flow rate of 1 mL/min. The samples were dissolved in THF (6 mg/mL) in advance, and both the sample solutions and the THF mobile phase were filtered through 0.1 μm polytetrafluoroethylene filters. FTIR spectra were collected by a Bruker EQUINOX 55 spectrophotometer. ^{1}H NMR spectra were recorded by a Bruker Avance III (400 MHz) with $CDCl_3$ as solvent.

DSC tests were conducted on a PerkinElmer DSC 8500 to determine glass transition temperatures, T_g, and to monitor the completeness of the curing reaction of the crosslinked polymer. The samples were repeatedly scanned from -80 to 80 °C at identical heating and cooling rates of 10 °C/min.

Dynamic mechanical analysis (DMA) was performed using a Mettler Toledo Instruments DMA SDTA861 in the tensile mode under 1 Hz applying a heating ramp of 3 °C/min in nitrogen. The molecular weight between cross-links in the cured materials, M_c, was calculated from:

$M_c = 3(1 - 2/\Phi)\rho RT/E'$

where E' is the storage modulus at the rubbery plateau zone as measured by DMA at $T = T_g + 30$ °C, ρ is the density, R is the gas constant, T is the absolute temperature, and Φ is the functionality of the crosslinked polymer.

Rheological data were obtained from ARES-RFS rheometer (TA Instruments) with 25 mm parallel-plate geometry (disk-shaped specimens: 10 mm in diameter and 2 mm in thickness). Strain sweep experiments were performed at a frequency of 1 rad/s to determine the region of linear response. Frequency sweeps from 0.01 to 300 Hz at 0.2% strain were conducted at different temperatures.

Stress relaxation and creep behavior were measured at 25 °C according to ASTM D638-98 with 01dB-MetraviB DMA-25N. For stress relaxation, tensile mode was applied at a constant strain of 8 % of failure strain of the specimen. Creep data were collected under a constant compression of 1.5 N.

Self-healing capability was characterized by tensile tests, which were performed in air at 25 °C on dumbbell-shaped specimens according to ISO527-2 and using a SANS CMT 6000 universal tester at a cross-head speed of 50 mm/min. The specimen was firstly cut into half and then manually recombined. After rehabilitation at 25 °C for a preset period of time, the healed specimen was subjected to tension again. Healing efficiency was calculated from the ratio of tensile strength of healed specimens to that of virgin specimens.