Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

From Plastic to Elastomers: Introducing Reversible Copper-Thioether Coordination in CO_2-based Polycarbonate

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1. General Information

1.1 Materials

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. Chemicals were obtained from Energy Chemical and used as received without further purification unless otherwise stated. Solvent and epoxides were purified by distillation from calcium hydride and stored under Argon atmosphere prior to use. The carbon dioxide gas (99.999%) was purchased from Changchun Juyang Co. Ltd. and used as received.

1.2 Characterization

^{1}H NMR. Solution ^{1}H NMR spectra were collected at ambient temperatures using Bruker ARX-300 and ARX-400 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference. Solvent proton shifts (ppm): $CDCl_3$, 7.26 (s) .

Gel permeation chromatography (GPC). The molecular weight and molecular weight distribution of the polycarbonates were determined by gel permeation chromatography (GPC) at 35 °C in polystyrene standard on Waters e2695 GPC instrument with dichloromethane as the eluent, where the flow rate was set at 1.0 mL min^{-1}.

Infrared spectroscopy. The infrared spectroscopy test was conducted on the Bruker Fourier Transform Infrared Spectroscopy INVENIO R IFS 66 V/S with a diamond as the reflecting crystal.

Differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-7 instrument under N_2 atmosphere. The sample was first heated from −50 °C to 150 °C at 10 °C min^{-1} and then rapidly quenched to −50 °C, followed by a second heating process to obtain the glass transition temperature (T_g).

Thermogravimetric analyses (TGA). Thermogravimetric analyses (TGA) were measured on a Perkin-Elmer DSC-7 instrument under N_2 atmosphere with a heating rate of 10 °C min^{-1} from 25 °C temperature to 450 °C.

Elemental Analysis. The elemental analysis was conducted on elementar vario EL cube using pre-dried sample.

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Configured samples were tested on ICP-OES ICAP 6300.

Uniaxial tensile testing. Uniaxial tensile testing was evaluated in a screw-driven universal testing machine (Z010, Zwick Co., Germany) equipped with a 10 KN electronic load cell and mechanical grips. The sample was shaped into a dumbbell-shaped specimen (thickness:1.01mm; length: 49mm; width: 4.1mm) and was conducted at 25 °C using a cross-head rate of 5 mm min^{-1} according to the ASTM standard.

Hardness Tests (Shore A). The hardness of the material was measured using a shore A durometer (model LX-A-Y from RS PRO, Corby, UK). The sample was shaped into a rectangular specimen with 7.1 mm thickness.

Dynamic mechanical analysis (DMA). Dynamic mechanical analysis (DMA) were performed on TA Q850 in a single cantilever mode. The sample was shaped into a rectangular specimen (thickness:1.50 mm; length: 35 mm; width: 13.6 mm) under the 5.0 um amplitude and 1 Hz frequency with the ramp rate at 3.0 °C min^{-1}

2. Synthetic procedures

2.1 Preparation of the DMC catalyst (Zn-Co-DMC).

20 ml of $K_3[Co(CN)_6]$ solution (0.2 M) was added dropwise in 45 min into a $ZnCl_2$ solution (11.42 g of $ZnCl_2$ in a mixture solution of 60 ml deionized water and 30 ml tert-butanol) under vigorous stirring at 50 °C, and the white suspension was centrifuged at 5000 rpm after 60 min. The isolated slurry was resuspended with vigorous stirring in a solution of tert-butanol and deionized water (1 : 1, v/v) for 30 min. This process was repeated several times, with a gradually increasing proportion of tert-butanol against water. Finally, the solid was re-suspended in neat tert-butanol and stirred for 30 min, centrifuged and dried under vacuum at 50 °C until a constant weight was reached. The obtained product was denoted as Zn-Co-DMC.

2.2 General terpolymerization procedure

In a glove box, 6 mg DMC, 20 ml CH_2Cl_2, corresponding ratio CHO and VCHO were added into a pre-dried 75 mL autoclave equipped with a magnetic stir. The autoclave was assembled and immersed in an oil bath whose temperature was 75 °C. The 3 MPa CO_2 was pressurized, and the mixture system was stirred for 5 min to reach the bath temperature. The polymerization was terminated after 12h by cooling the autoclave to room temperature. After releasing CO_2, a small aliquot of the copolymerization mixture was taken out for ^1H NMR spectroscopy and the remained crude mixture was dissolved in CH_2Cl_2, then precipitated in methanol to remove byproducts and excess reactant. This process was repeated three times to yield a purified product. The product was dried under a vacuum at 65 °C for 12 h. The yield product was labeled as P (X%), which X% respected the content of VCHC linkage in the polymer.

2.3 General thiol-ene click reaction

A 250 mL flask was charged with polycarbonate (3 g) and AIBN at [AIBN]: [alkene]=0.33:1. The mixture was degassed for 10 min then refilled with argon. Hexanethiol/dodecylthiol (20-fold of alkene) and anhydrous THF were injected into the flask followed by heating at 60 °C for 24 h. The solution was precipitated from THF into methanol to remove byproducts and excess reactants. This process was repeated three times to yield a purified product. The product was dried under a vacuum at 60 °C for 12 h. The yield product was labeled. For example, P (50%-6) respected that the polymer, with 50% content of VCHC linkage, was clicked with hexanethiol.

2.4 General Cu-S coordination reaction

A 250 mL flask was charged with grafted polycarbonate and CH_2Cl_2. The mixture was degassed for 10 min and then refilled with argon. Certain ratio (according to the molar amount of S) of CuI was dissolved in CH_3CN and then was injected into the flask slowly. The mixture was stirred with a magnetic stir for 3 h, and then was heated at 60 °C to reflux for 1 h. The solvent was removed by volatilization. To purify the polymers, the product was washed with acetonitrile and then was dried under a vacuum at 30 °C for 24 h. The yield product was labeled as P(100%-12-X%), which X% represented the molar ratio of CuI to S in the polymer. The addition of CuI according to the molar of CuI = X%*(the molar of S in the polymer) =X%*(the weight of polymer/ the relative molecular mass of the repeating unit). In this system, the relative molecular mass of the repeating unit is 370.

2.5 ICP-AES analysis

The polymer (0.95mol) was calcined at 600 °C in muffle for 1.5 h. The resulting residue was dissolved with nitric acid and was transferred into a 100 mL volumetric flask. Then the solution was diluted with water to volume. Transfer 5.0 mL of this solution for ICP-AES Analysis.

2.6 Cyclic tensile testing

Under room temperature, the dumbbell-shaped specimen was loaded on a universal testing machine and was stretched to 300% strain at 25 °C using a cross-head rate of 5 mm min^{-1} according to the ASTM standard. After that, the stress was slowly relieved to zero and the dumbbell-shaped specimen was removed from the machine and relaxed for another 2 minutes in a 75 °C oven for recovery. Then, the specimen was cold to room temperature before another test. The process was repeated five times.

2.7 Thermal reprocessing testing

The tensile testing was conducted with the pressed spline. After stretching, the spline was cut into pieces and repressed under the same process condition. The obtained splines were subjected to another stretching experiment.

2.8 Self-healing testing.

Dumbbell-shaped specimens were cut into two pieces in the middle, and the two parts were placed in contact with each other. Press the two parts for minutes and transfer the specimens into ovens with configured temperatures for different times. The incision was observed with naked eyes and a optical microscope. The quantitative repair effect can be determined by the strength and elongation at break of the tensile test at 25 °C using a cross-head rate of 5 mm min^{-1} according to the ASTM standard.

3. Supplemental figures and tables.

Table S1. Influence of the reaction conditions on the copolymerization of CHO/CO_2.

Entry[a]	T (°C)	P (MPa)	Conv. (%)[b]	CU (%)[c]
1[d]	80	3	82	94
2	80	3	>99	96
3	80	2	93	88
4	80	4	>99	96
5	60	3	56	95
6	100	3	>99	97

[a] The polymerization reactions were carried out under for 12 h in a 75 mL autoclave with 196.8 mmol CHO, 6 mg DMC and 20 ml CH_2Cl_2 unless otherwise noted. [b] The conversion of epoxy monomers, determined by ^1H NMR spectroscopy. [c] The molar ratio of carbonate unit content in polymer, according to CU (%) = (mole number of carbonate linkage) / (total mole number of carbonate and ether linkage). [d] No CH_2Cl_2 was added in this polymerization.

From crude product:

Conv. (%) = 1 - $A_{3.1\text{-}3.2} / (A_{4.5\text{-}5.2} - 2A_{5.6\text{-}5.9} + A_{3.3\text{-}3.7} + A_{3.1\text{-}3.2})$

From purified product

CU (%) =1 – $A_{3.3\text{-}3.7} / (A_{4.5\text{-}5.2} - 2A_{5.6\text{-}5.9} + A_{3.3\text{-}3.7})$

CHC linkage (%) = 1- $A_{5.6\text{-}5.9} / (A_{4.5\text{-}5.2} - 2A_{5.6\text{-}5.9} + A_{3.3\text{-}3.7})$

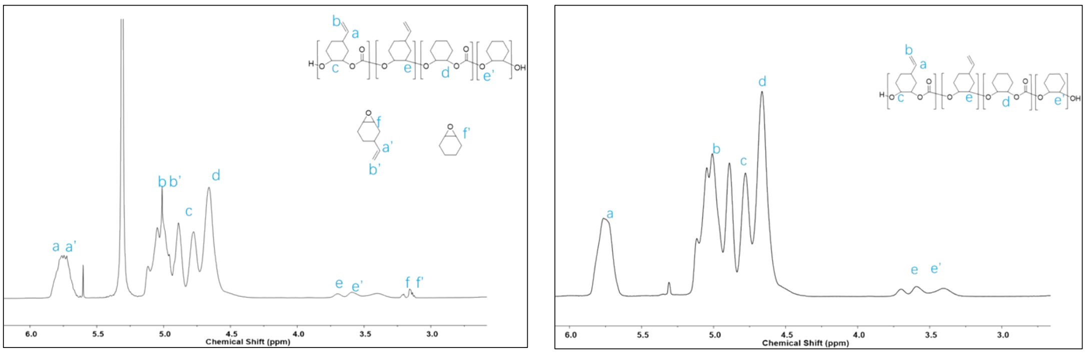

Fig. S1 The calculation method for definitions through the ^1H NMR of crude product and purified product.

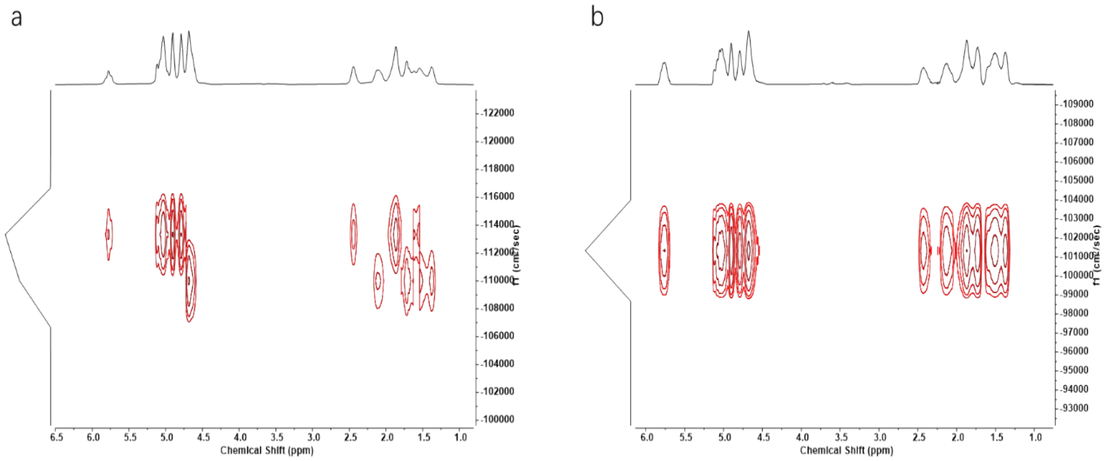

Fig. S2 The 2D DOSY of (a) the mixture of PCHC/PVCHC; (b) the terpolymer from VCHO/CHO/CO_2.

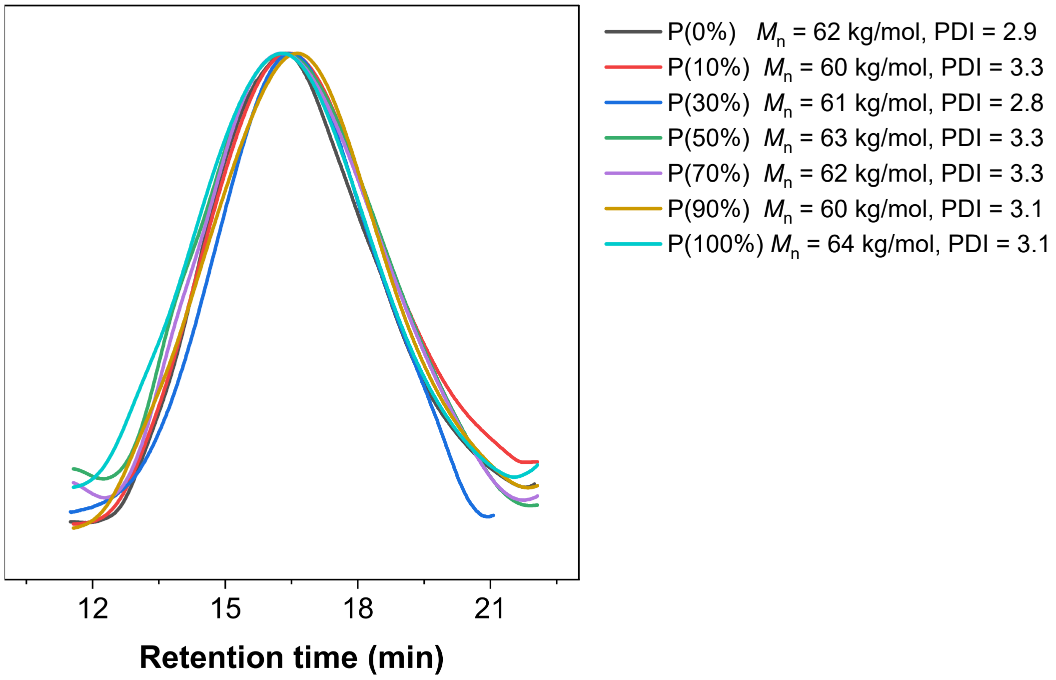

Fig. S3 GPC trace of CHO/VCHO/CO_2 polymers with different content of vinyl groups (entries 1-7, Table 1).

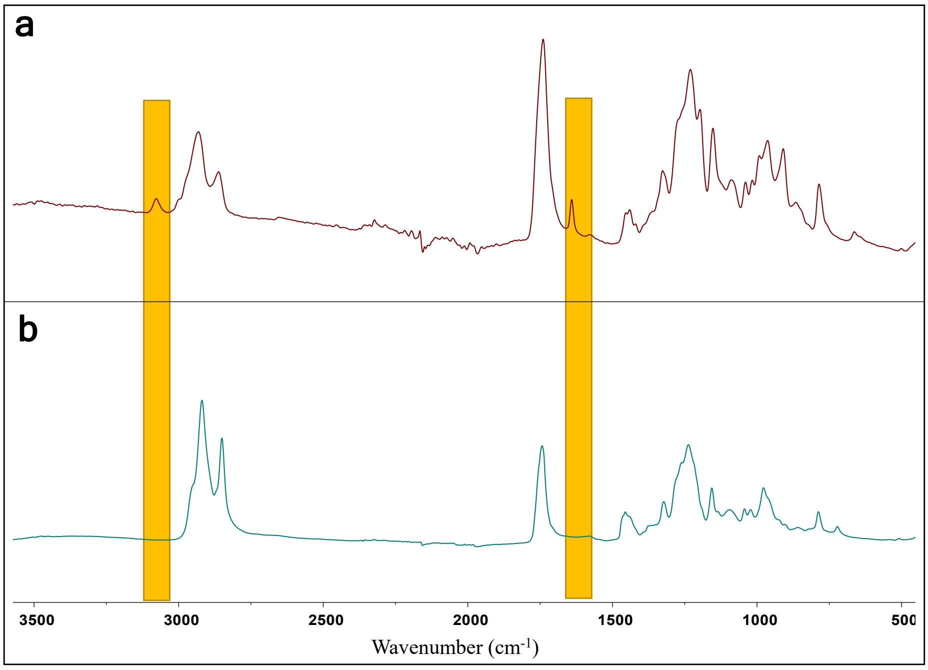

Fig. S4 The respective spectrum of FT-IR. (a) The sample P(100%); (b) The sample P(100%-12).

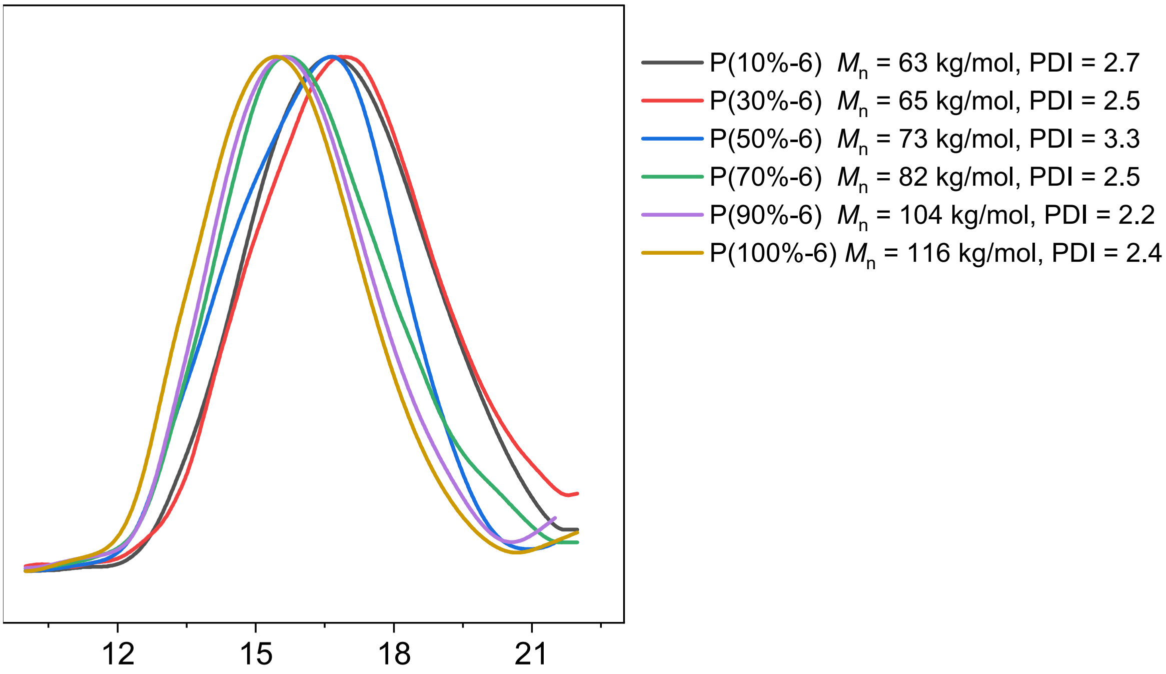

Fig. S5 GPC trace of polymers clicked with hexanethiol (entries 2-7, Table 2).

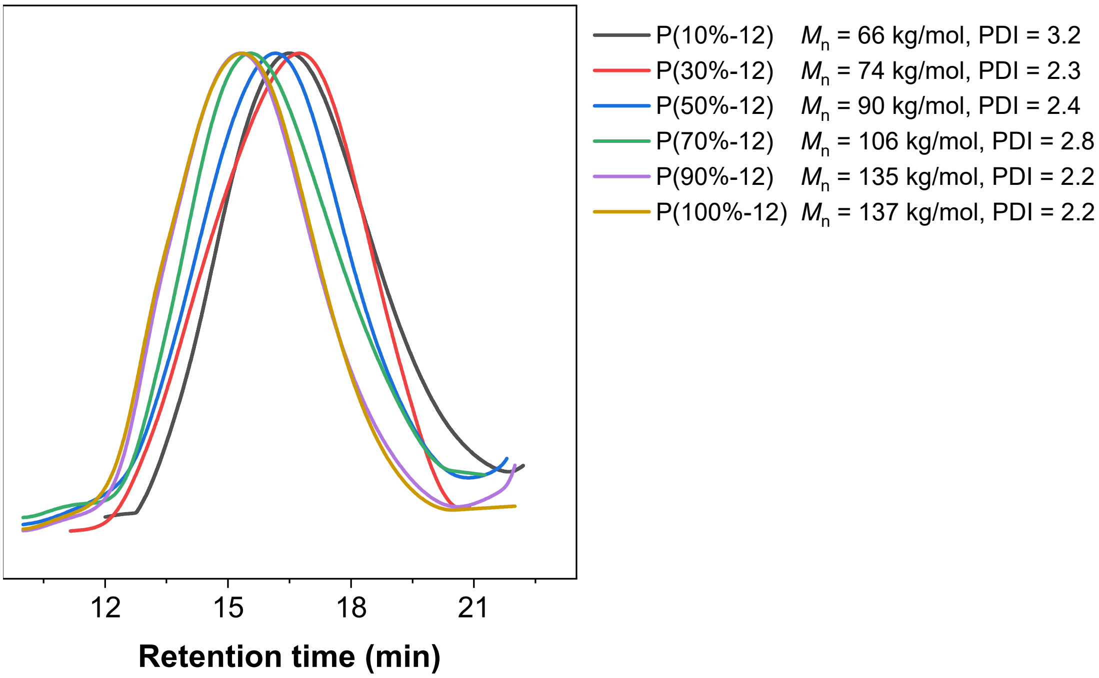

Fig. S6 GPC trace of polymers clicked with dodecylthiol (entries 9-13, Table 2).

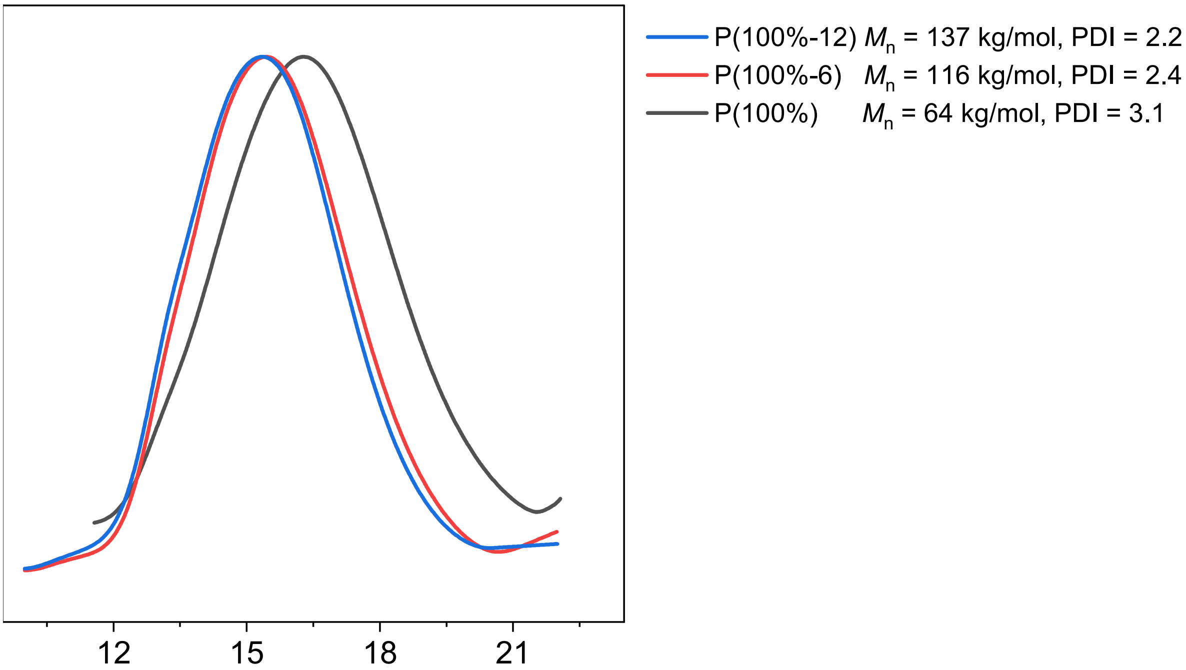

Fig. S7 The shift of GPC trace of polymers when clicked with hexanethiol or dodecylthiol.

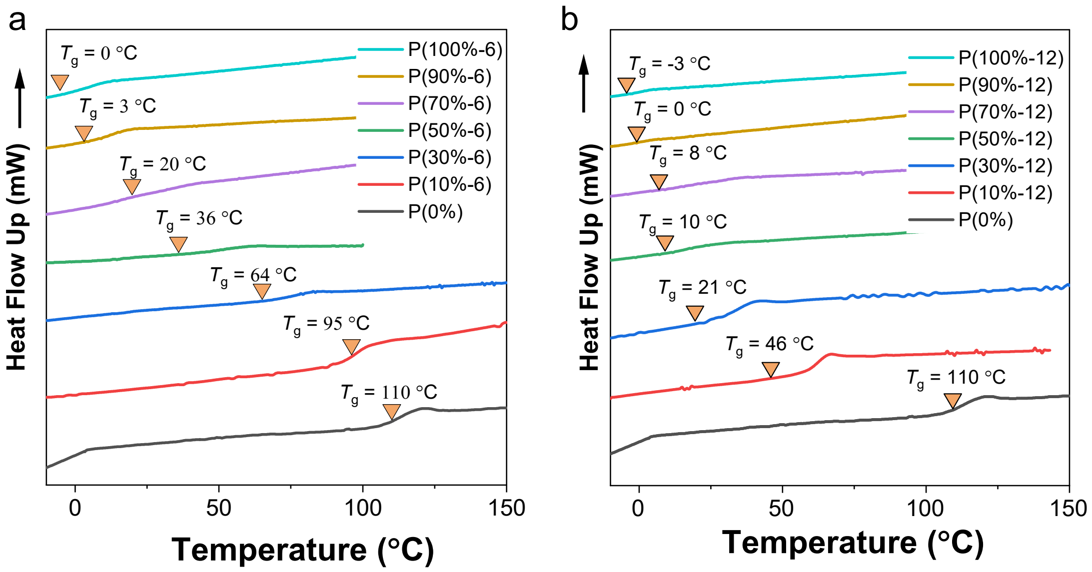

Fig. S8 DSC traces of polymer with different content of grafted groups via click reaction with (a) hexanethiol; (b) dodecylthiol.

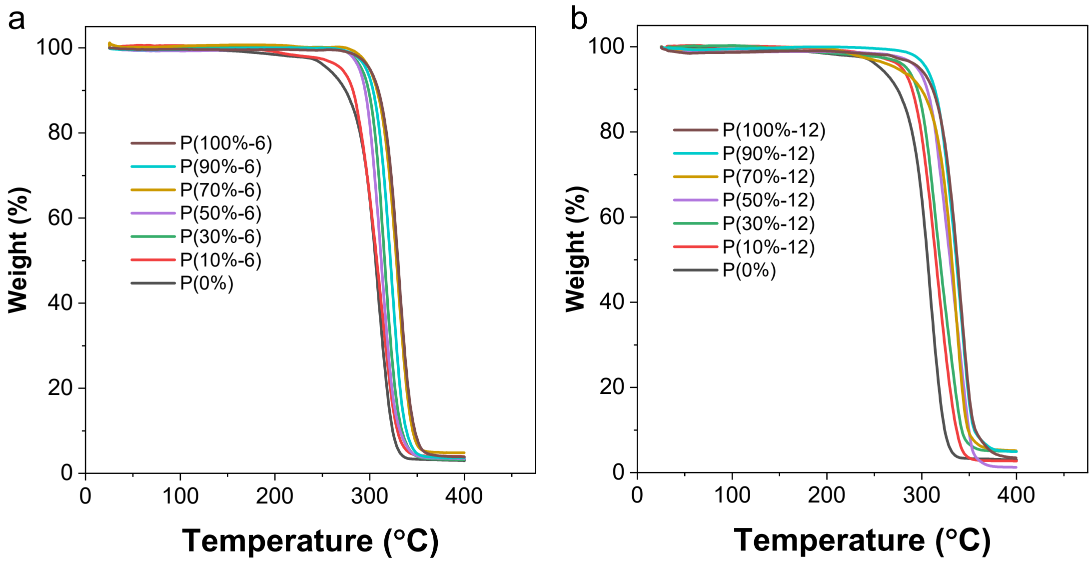

Fig. S9 TGA traces of polymer with different content of grafted groups via click reaction with (a) hexanethiol; (b) dodecylthiol.

Table S2. Mechanical properties of the terpolymers.

Sample	Tensile strength (MPa)[a]	Tensile modulus (MPa)[a]	Elongation at break (%)[a]
P(0%)	38	1800	3
P(100%)	43	2200	4

[a] The tensile test was conducted at 25 °C using a cross-head rate of 5 mm min^{-1} according to the ASTM standard.

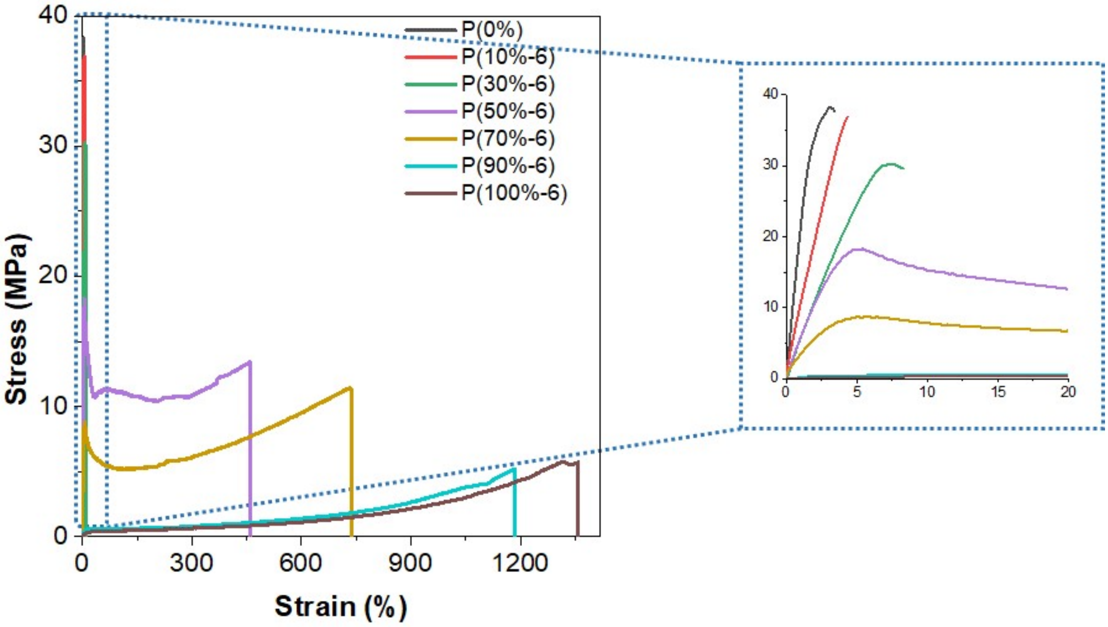

Fig. S10 Representative engineering stress versus strain curves for polymers with different content of grafted groups via click reaction with hexanethiol (entries 1-7, Table 2).

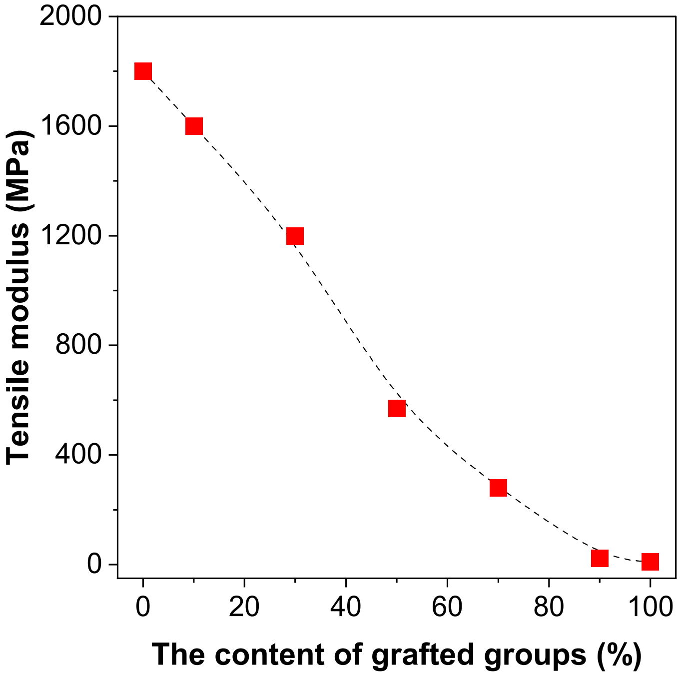

Fig. S11 The variation of tensile modulus of polymers with different content of grafted groups via click reaction with hexanethiol (entries 1-7, Table 2).

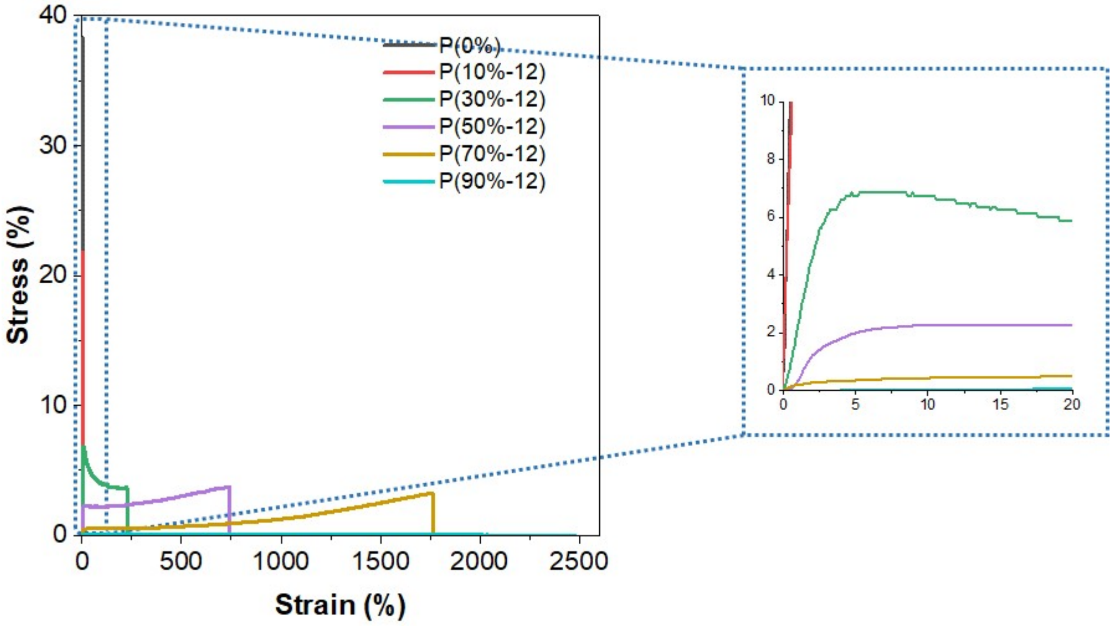

Fig. S12 Representative engineering stress versus strain curves for polymers with different content of grafted groups via click reaction with dodecylthiol (entries 8-13, Table 2).

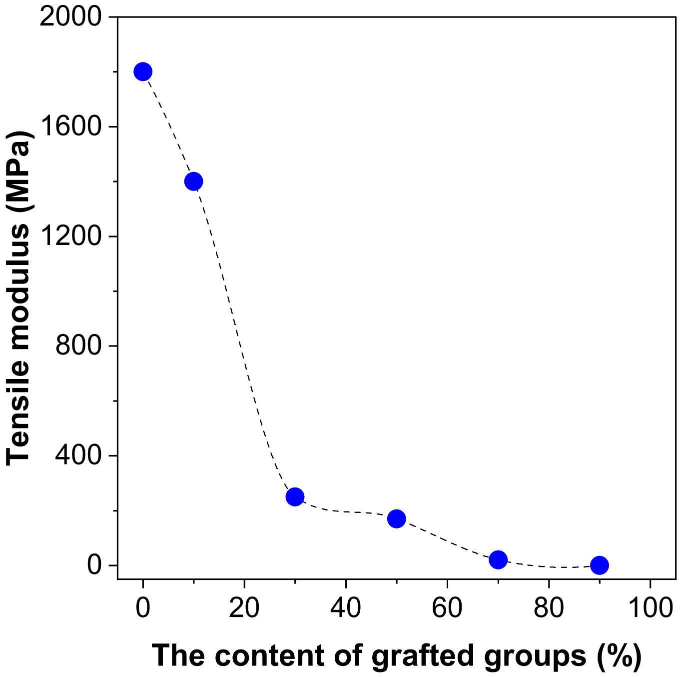

Fig. S13 The variation of tensile modulus of polymers with different content of grafted groups via click reaction with dodecylthiol (entries 8-13, Table 2).

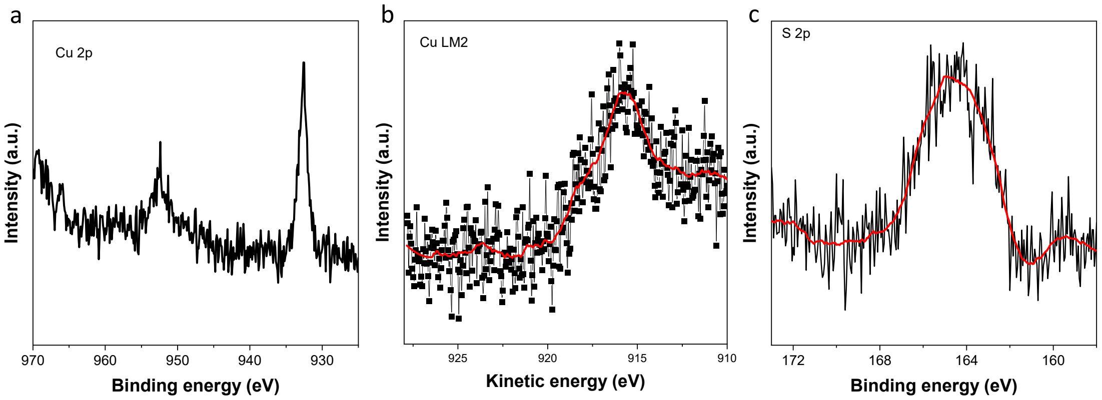

Fig. S14 XPS of polymer coordinated with CuI after heated.

Table S3. Elemental Analysis of polymer coordinated with CuI.

Sample[a]	$C_{measured}$ (%)[b]	$H_{measured}$ (%)[b]	$C_{expected}$ (%)[c]	$H_{expected}$ (%)[c]
P (100%-12-10%)	63.9	9.4	64.8	9.8
P (100%-12-20%)	60.6	9.1	61.8	9.3
P (100%-12-30%)	57.8	8.7	59.0	8.9
P (100%-12-40%)	55.3	8.2	56.5	8.5

P (100%-12-50%)	53.8	7.9	54.2	8.2

[a] The sample was dried before the test.

[b] The data was measured by elementar.

[c] The expected data was calculated according to C(%) = (the weight of C)/(the total weight of the polymer) = (the number of C in the polymer* the relative atomic mass of C)/ (370 + the ratio of Cu/S*191). The H (%) was calculated in the similar way.

Table S4. ICP-AES Analysis of polymer coordinated with CuI.

Sample[a]	Measured (ppm)[b]	Expected (ppm)[c]
P (100%-12-10%)	58	60
P (100%-12-20%)	114	121
P (100%-12-30%)	155	181
P (100%-12-40%)	240	240
P (100%-12-50%)	308	302

[a] The sample (0.95 mmol) was calcined at 600 °C for 1.5 h. The resulting residue was dissolved with nitric acid and was transfer into a 100 mL volumetric flask. Then, the solution was diluted with water to volume. Transfer 5.0 mL of this solution for ICP-AES analysis.

[b] The results were detected by ICP-AES.

[c] The expected content of Cu was calculated according to Cu (ppm) = the relative atomic mass of Cu * the ratio of Cu/S* the molar of the polymer/ 100ml*1000.

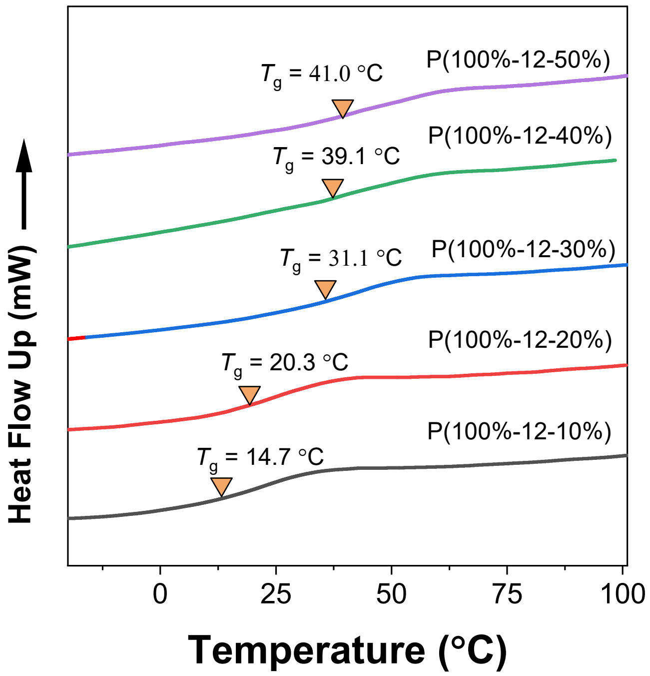

Fig. S15 Related DSC traces of the polymers when coordinated with different content of CuI.

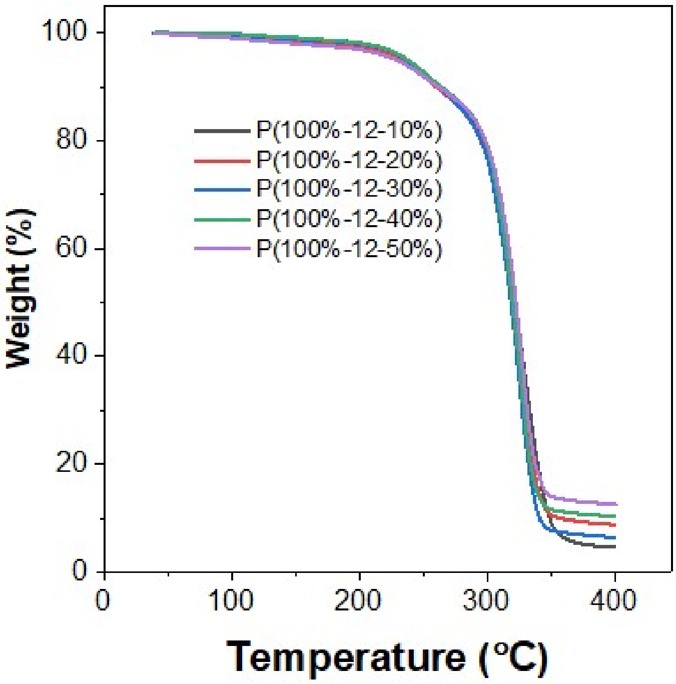

Fig. S16 Related TGA traces of the polymers when coordinated with different content of CuI.

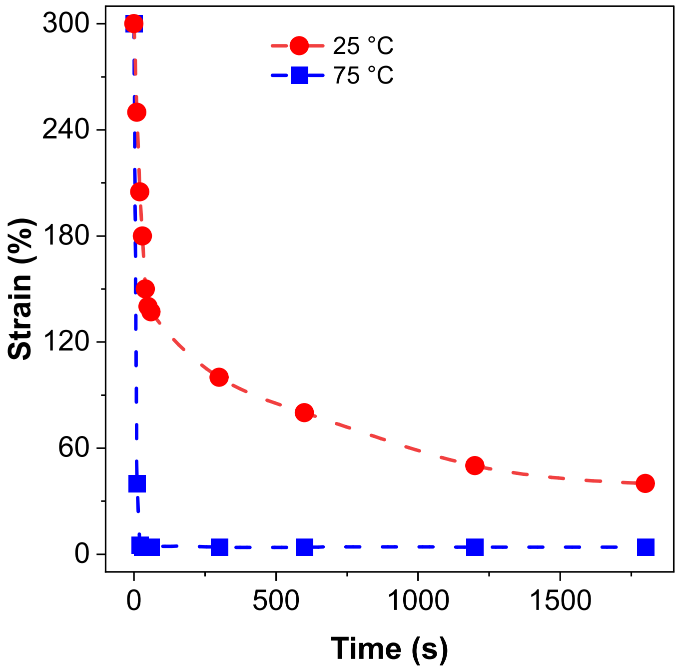

Fig. S17 The recovery testing of residual strain versus time under 25 °C and 75 °C respectively.

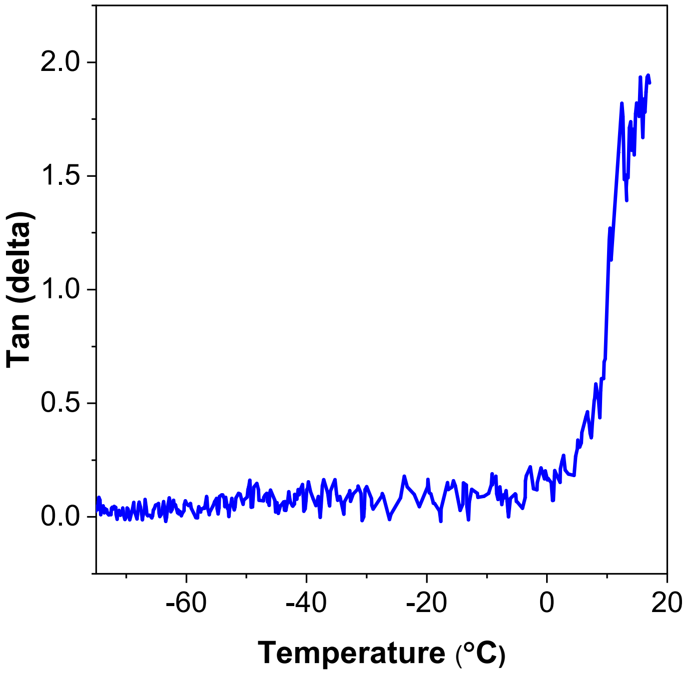

Fig. S18 Temperature Dependence of Tan (delta) from DMTA using P(100%-12) as sample.

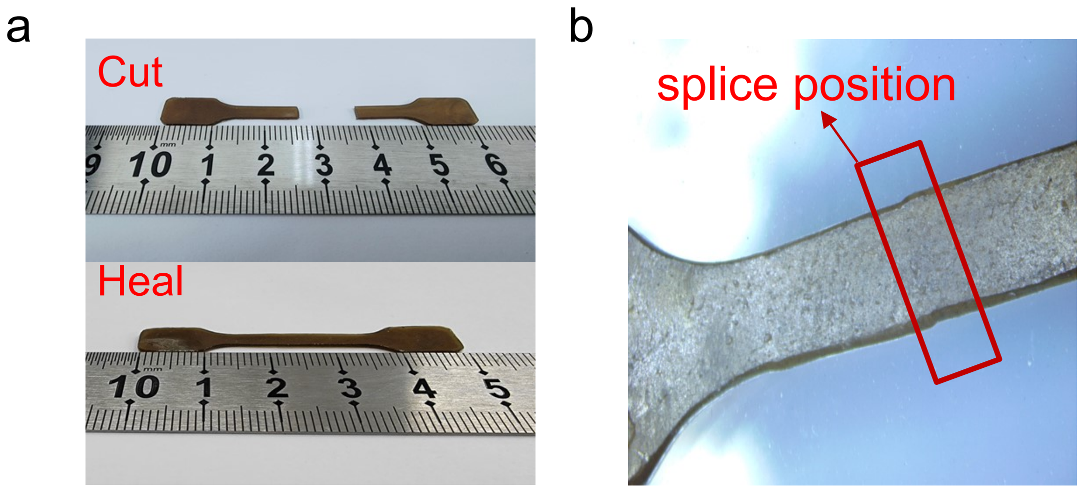

Fig. S19 The self-healing test and DMTA test of P(100%-12-20%). a) The photo showed the process of cutting and healing; b) The photo of the fracture via optical microscope after healing at 75 °C for 24 h.

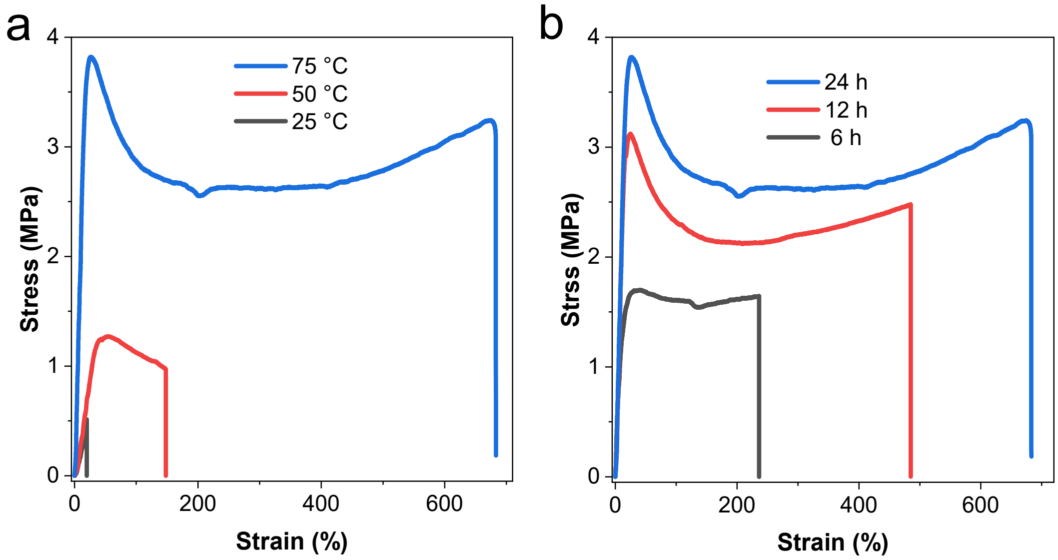

Fig. S20 Representative engineering stress versus strain curves for polymers spline exposed to a)different temperatures for 24 h; b) different time at 75 °C.

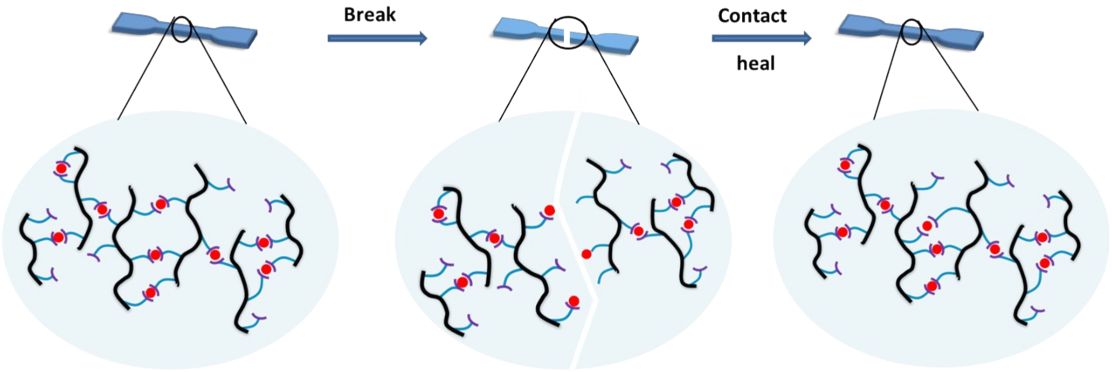

Fig. S21 The possible change in the microstructure of polymers for the phenomenon of self-healing process.