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SUPPORTING INFORMATION

Crosslinking of Linear Poly(*n*-butyl acrylate)-POSS Copolymers *via* Dynamic Urea Exchange Enables Self-healing, Reprocessing and Shape Recovery

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1. Materials

Phenyltrimethoxysilane [$PhSi(OMe)_3$] was purchased from Zhejiang Chemical Technology Co. Ltd., China. Before use, it was purified by distillation under reduced pressure. Sodium hydroxide (NaOH) was supplied by Admas Reagent Co., China. The organic solvents such as tetrahydrofuran (THF), 1,4-dioxane and methanol were of chemically pure grade, obtained from commercial sources. Prior to use, THF was distilled over metal sodium and then stored in the presence of 4Å molecular sieves.

2. Synthesis of Heptaphenyl POSS Acrylate

First, heptaphenyltricycloheptasiloxane trisodium silanolate [$Na_3O_{12}Si_7(C_6H_5)_7$] was synthesized by following the method of literature by Seino *et al* [1]. To a flask equipped with a condenser and a magnetic stirrer, THF (350 mL), deionized water (7.450 g, 0.41 mol) and sodium hydroxide (5.540 g, 0.14 mol) were charged and then phenyltrimethoxysilane (63.760 g, 0.32 mol) was dropwise added. The mixture was refluxed for 5 hours and at room temperature for additional 19 hours. After reaction, the solvent was removed *via* rotary evaporation. After drying *in vacuo* at 40 °C for 6 hours, the product (44.800 g) was obtained with the yield of 98%.

Second, the corner-capping reaction of $Na_3O_{12}Si_7(C_6H_5)_7$ with 3-(trichlorosilyl)propyl acrylate was carried out. To a flask, heptaphenyltricycloheptasiloxane trisodium silanolate [$Na_3O_{12}Si_7(C_6H_5)_7$] (34.860 g, 35.0 mmol) and anhydrous tetrahydrofuran (300 mL) were charged with vigorous stirring and then 3-(trichlorosilyl)propyl acrylate (17.332 g, 70.00 mmol) was quickly added. The reaction was performed at 0 °C for 1 hour and then at room temperature for 18 hours. The insoluble solids were filtered out and the remaining solvent was removed *via* rotary evaporation. The raw product was washed with methanol for three times (100 mL × 3) and dried *in vacuo* at 40 °C for 6 hours. The product (*i.e.,* POSS acrylate) was obtained with a yield of 45%. ^{1}H NMR (ppm, $CDCl_3$): 7.30 ~ 7.55, 7.70 ~ 7.87 (*m,* 35H, $C_6\boldsymbol{H}_5$-), 6.39 (*dq,* 1H, -OCOCH=C$\boldsymbol{H}_2$), 6.11 (*t*, 1H, -OCOC$\boldsymbol{H}$=CH_2), 5.78 (*dq*, 1H, -OCOCH=C$\boldsymbol{H}_2$), 4.21 (*m,* 2H, -$CH_2CH_2C\boldsymbol{H}_2$OCO-), 1.95 (*m,* 2H, -$CH_2C\boldsymbol{H}_2CH_2$OCO-) and 0.98 (*m*, 2H, -C$\boldsymbol{H}_2CH_2CH_2$OCO-).

REFERENCE

Reference 1. M. Seino, T. Hayakawa, Y. Ishida, M.-a. Kakimoto, K. Watanabe, H. Oikawa, *Macromolecules,* **2006,** *39,* 3473-3475**.**

Measurement and Techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^{1}H NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The P(BA-*stat*-POSS-*stat*-HUB) copolymers were dissolved with deuterated chloroform ($CDCl_3$) and the solutions were measured with deuterated chloroform ($CDCl_3$) as an internal reference.

Gel Permeation Chromatography (GPC)

The GPC was conducted using a Waters 1515 HPLC system equipped with three Waters RH columns (RH1, 3, 4) and a RI detector. The GPC was used N, N-dimethylformamide (DMF) containing 0.01 M lithium as the eluent. The values of molecular weights were calculated relative to polystyrene standards.

Thermogravimetric Analysis (TGA)

The TGA measurements were carried on TA Q5000 thermogravimetric analyzer. In air atmosphere, the samples (about 5.0 mg) were heated from room temperature to 800 °C at the heating rate of 20 °C × min^{-1}.

Transmission Electron Microscopy (TEM)

The TEM measurements were performed on a JEOL JEM-2010 high resolution transmission electron microscope at an acceleration voltage of 120 kV. For the specimens of networks, the samples were sliced by using an ultrathinmicrotome machine and the sections with the thickness of 70 ~ 100 nm; the sustained sections were placed in 200 mesh copper grids for observations.

Stress Relaxation Measurements

The stress relaxation curves were performed on a TA Q-800 apparatus in a stress relaxation mode with an iso-strain value set at 5%. The temperatures varying from 100 to 140 ºC.

Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA measurements were performed on a TA Q-800 apparatus. The rectangular specimens with the dimensions of 15 (length) × 4.5 (width) × 1 mm (thickness) were equilibrated to -80 °C for 5min and then ramped to 150 °C at a rate of 3 °C/min and frequency of 1 Hz.

Rheological Measurements

The rheological measurements were performed on a DHR-2 stress-controlled rheometer (TA, USA). First, the linear viscoelastic (LVE) regime of each circular specimen with the diameter of 20 mm was determined by applying strain sweeps. The strain amplitude sweeps were performed at 35 ºC with the strain range from 0.01 to 100 % a constant angular frequency of 1.0 rad × s^{-1}.

Tensile Mechanical Tests

The tensile tests were performed with a WDW-2 electron universal testing machine (Songdun Instruments Co. Ltd., Shanghai, China). The experiments were carried out with an elongation rate of 100 mm × min^{-1} at room temperature. For each sample, three specimens with the dimension of 20 × 4.75 × 0.75 mm^3 were tested and then averaged results were reported.

Surface Contact Angle Analysis

The surface contact angle tests were carried out on the DSA30 contact angle analyzer (Krüss GmbH, Germany). By using ultrapure water and ethylene glycol as the probe liquids respectively, the static contact angles were measured.

TABLES

Table S1 Mechanical properties of P(BA-POSS-HUB) networks

Samples*	σ_b (MPa)[a]	E (MPa)[b]	ε_b (%)[c]
P(BA_{75}-$POSS_{15}$-HUB_{10})	0.15 ± 0.02	0.43 ± 0.02	44.75 ± 0.4
P(BA_{65}-$POSS_{15}$-HUB_{20})	1.46 ± 0.08	2.47 ± 0.05	62.00 ± 2.4
P(BA_{55}-$POSS_{15}$-HUB_{30})	7.77 ± 0.3	58.84 ± 0.3	45.92 ± 1.8
P(BA_{45}-$POSS_{15}$-HUB_{40})	11.06 ± 0.5	730.55 ± 4.0	3.14 ± 0.04

*: the digits after the names of comonomers stand for the mass percentage of monomer; *a*: tensile strength; *b*: Young's modulus; *c*: elongation at break

Table S2 Mechanical properties of P(BA- POSS-HUB) networks

Samples*	σ_b (MPa)[a]	E (MPa)[b]	ε_b (%)[c]
P(BA_{75}-$POSS_{5}$-HUB_{20})	0.24 ± 0.02	1.64 ± 0.03	16.91 ± 0.1
P(BA_{70}-$POSS_{10}$-HUB_{20})	0.55 ± 0.05	1.92 ± 0.03	35.01 ± 1.5
P(BA_{65}-$POSS_{15}$-HUB_{20})	1.46 ± 0.08	2.47 ± 0.05	62.00 ± 2.4
P(BA_{60}-$POSS_{20}$-HUB_{20})	2.03 ± 0.12	3.00 ± 0.08	73.60 ± 3.6

*: the digits after the names of comonomers stand for the mass percentage of monomer; *a*: tensile strength; *b*: Young's modulus; *c*: elongation at break

Table S3 Static contact angles and surface free energy of P(BA-POSS-HUB) networks

Sample	Static contact angle (degree)		Surface free energy (mN ×m^{-1})		
	θ_{H2O} (deg)	$\theta_{ethylene\ glycol}$ (deg)	γ_s^d	γ_s^L	γ_s
P(BA_{75}-$POSS_5$-HUB_{20})	75.2±0.1	48.4±0.2	24.65	9.95	33.59
P(BA_{70}-$POSS_{10}$-HUB_{20})	86.2±0.3	63.4±0.2	19.73	6.54	26.14
P(BA_{65}-$POSS_{15}$-HUB_{20})	90.9±0.2	72.4±0.3	13.52	6.83	20.34
P(BA_{60}-$POSS_{20}$-HUB_{20})	97.1±0.4	79.8±0.2	12.21	4.76	16.97

Water: γ_L = 72.8mN/m, γ_L^d = 21.8 mN/m, γ_L^p = 51.0 mN/m; ethylene glycol: γ_L = 48.3 mN/m, γ_L^d = 29.3 mN/m, γ_L^p = 19.0 mN/m [2].

REFERENCE

Reference 2. A. Adamson, *Physical Chemistry of Surfaces,* fifth ed., Wiley-Interscience: New York, **1990**.

Table S4 Shape recovery and fixity of P(BA-POSS- HUB) networks

Samples*	Shape Recovery (%)	Shape fixity (%)
P(BA_{75}-$POSS_{15}$-HUB_{10})	93.1± 0.2	82.6 ± 0.3
P(BA_{65}-$POSS_{15}$-HUB_{20})	96.5± 0.1	85.5± 0.5
P(BA_{55}-$POSS_{15}$-HUB_{30})	96.2± 0.3	87.2 ± 0.1
P(BA_{70}-$POSS_{10}$-HUB_{20})	97.1± 0.1	75.1± 0.3
P(BA_{60}-$POSS_{20}$-HUB_{20})	96.5± 0.2	88.2± 0.3

*: the digits after the names of comonomers stand for the mass percentage of monomer

FIGURES

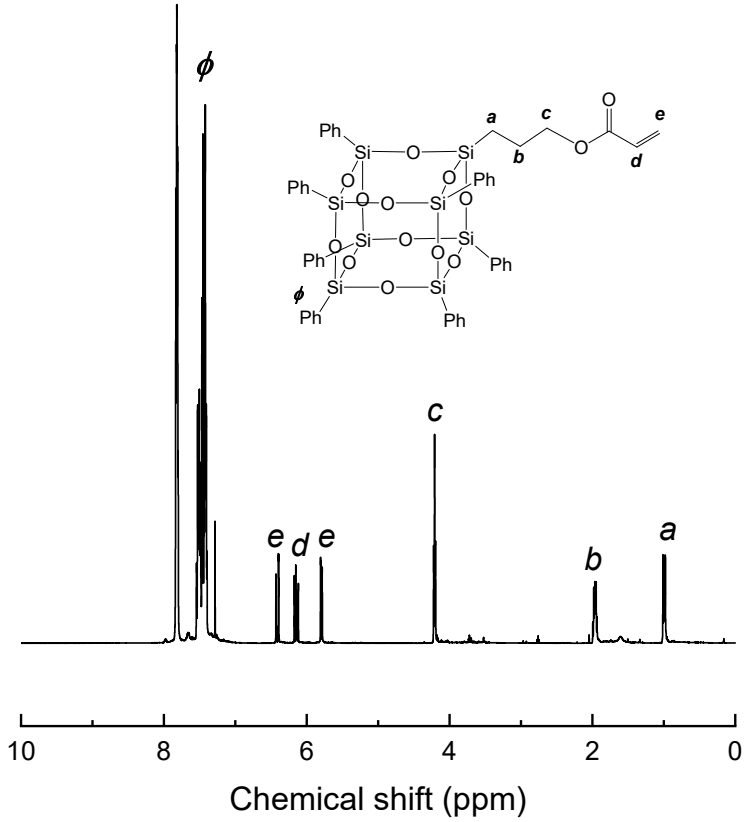

Figure S1 ^{1}H NMR spectrum of heptaphenyl POSS acrylate (denoted POSS acrylate)

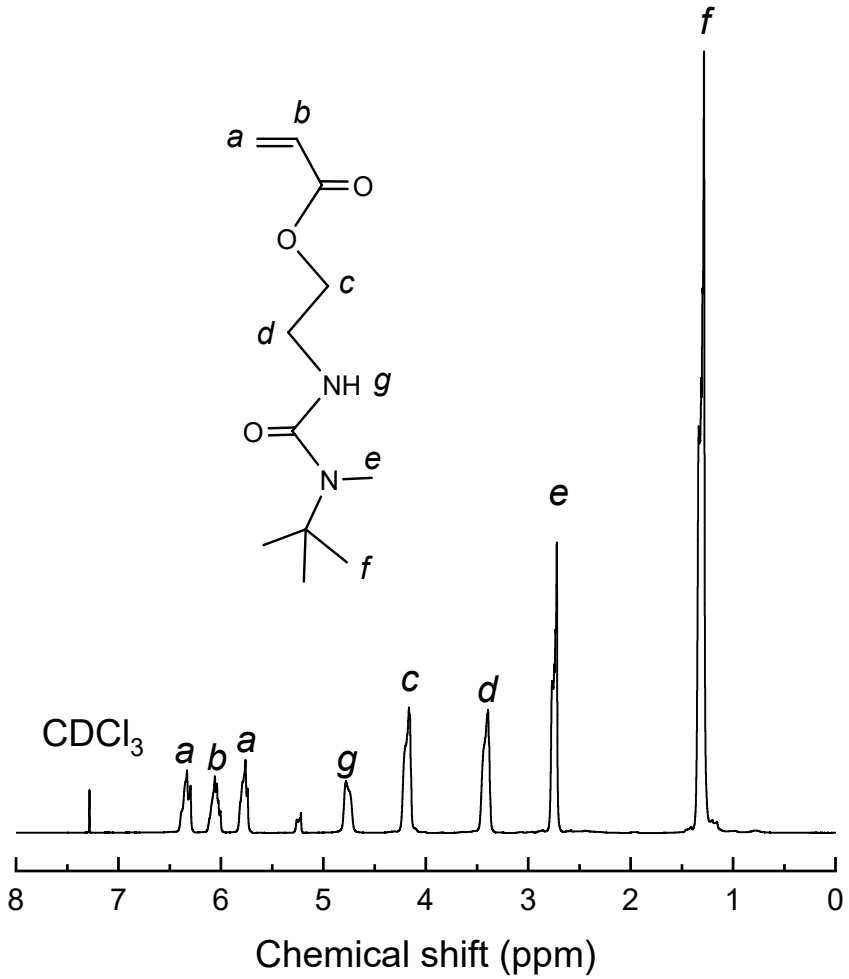

Figure S2 ^{1}H NMR spectrum of 2-(3-(*tert*-Butyl)-3-methylureido)ethylacrylate

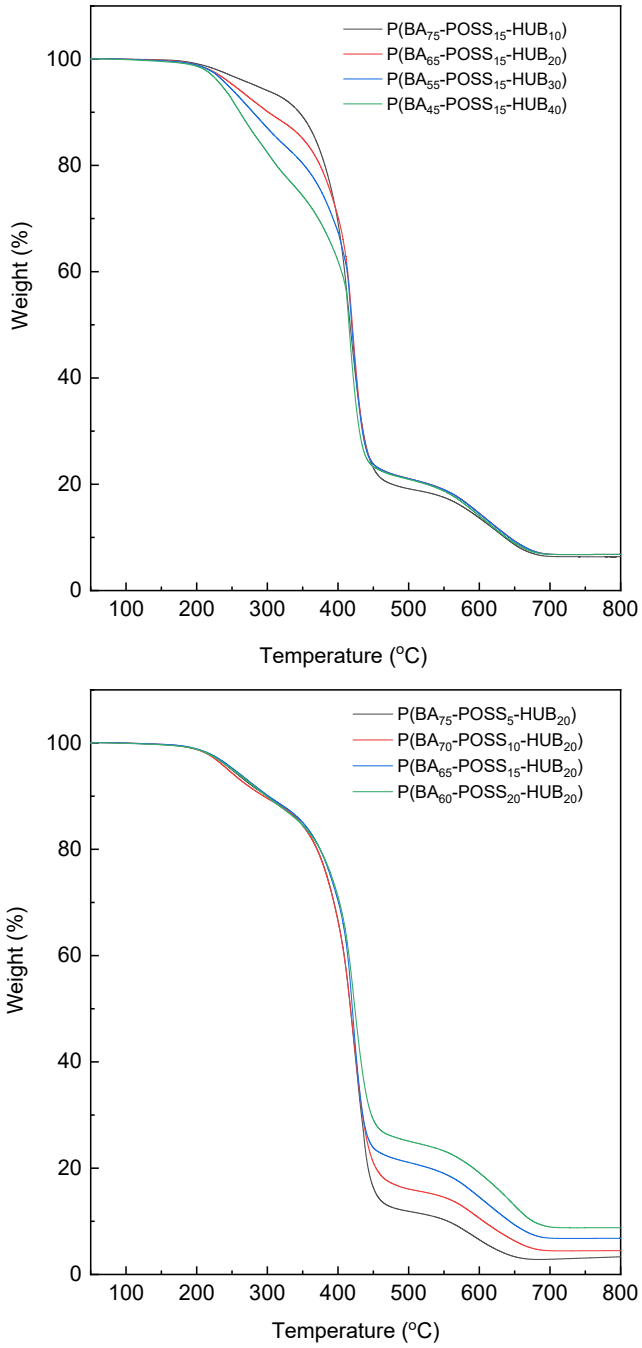

Figure S3 TGA curves of P(BA-POSS-BMEA) copolymers in an air atmosphere and at the heating rate of 20 °C× min^{-1}

Figure S4 Photographs for P(BA_{65}-$POSS_{15}$-$BMEA_{20}$) copolymer: A) the solution of 1,4-dioxane at the concentration of 1 g × mL^{-1}; B) the mixture after 1,2-bis(tert-butyl)ethylenediamine (50 mol% with respective of the quantity of BMEA) was added and reacted at 80 °C

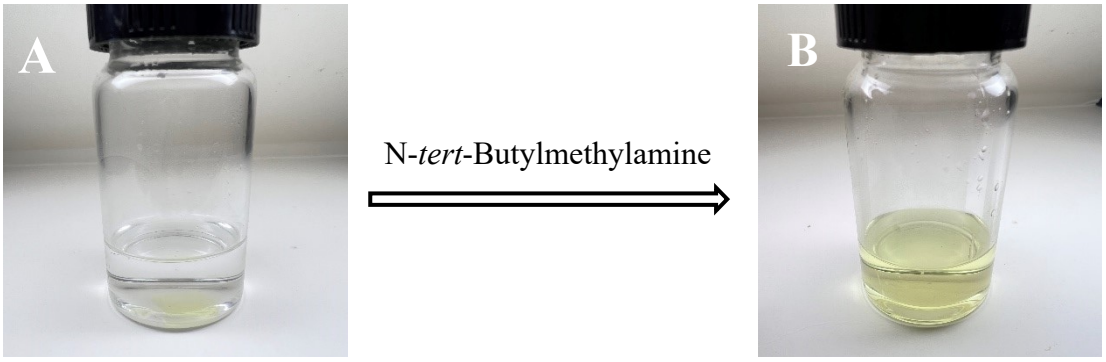

Figure S5 Photographs of solubility tests for P(BA_{75}-$POSS_{15}$-HUB_{10}) network: A) swollen with 1,4-dioxane for 12 hours; B) held at room temperature for 12 hours after *N-tert*-butylmethylamine was added

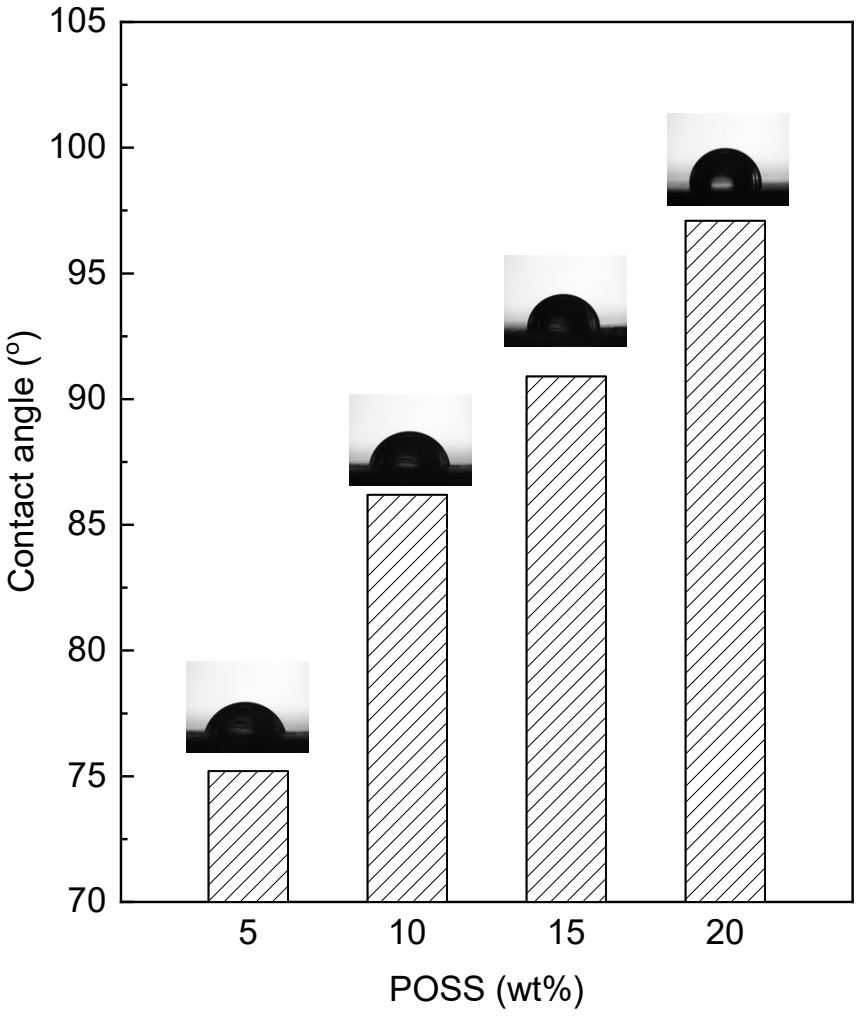

Figure S6 Plot of water contact angles of P(BA-POSS-HUB) networks as a function of POSS contents

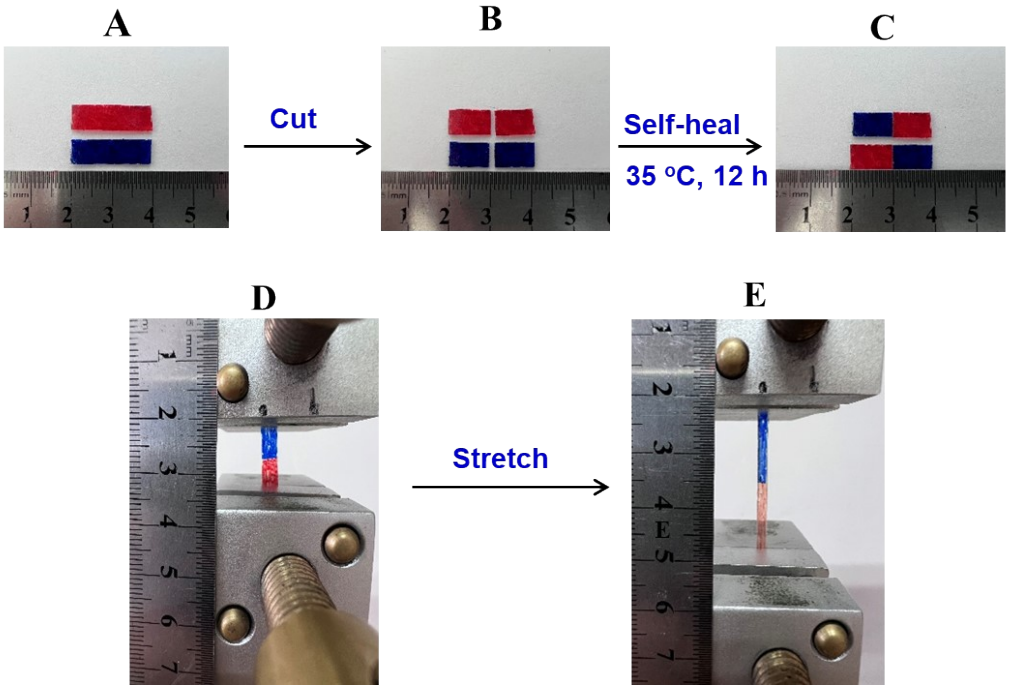

Figure S7 Photographs of P(BA_{75}-$POSS_{15}$-HUB_{10}) for self-healing test: A) Two original specimens were colored in red and blue; B) they were cut into four halves; C) two halves with different colors were exchanged and put in contact for self-healing at 35 °C for 12 h; D) the healed specimen was used for stretching; E) the healed specimen can be uniaxially stretched at the elongation of ε = 135 % without break

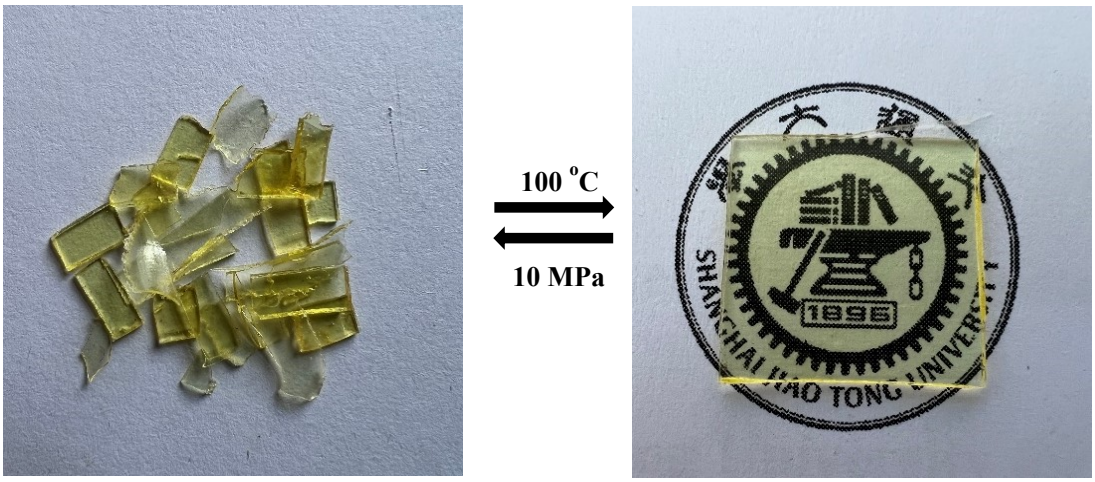

Figure S8 Photographs of P(BA_{55}-$POSS_{15}$-HUB_{30}) for the reprocessing test

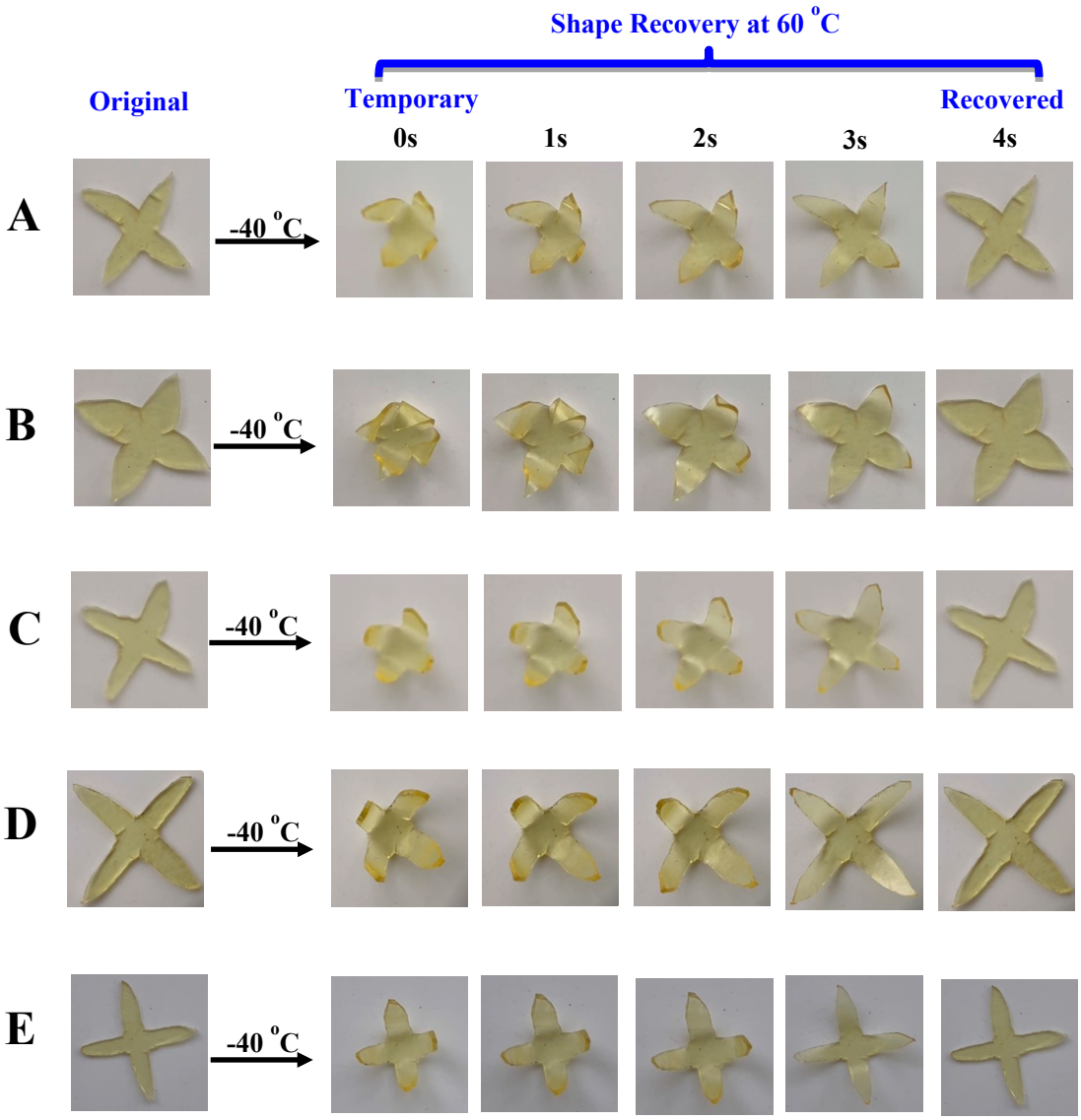

Figure S9 Shape recovery processes of A: P(BA_{75}-$POSS_{15}$-HUB_{10}), B: P(BA_{65}-$POSS_{15}$-HUB_{20}), C: P(BA_{55}-$POSS_{15}$-HUB_{30}), D: P(BA_{70}-$POSS_{10}$-HUB_{20}) and E: P(BA_{60}-$POSS_{20}$-HUB_{20}) for the their temporary shapes at 60 °C

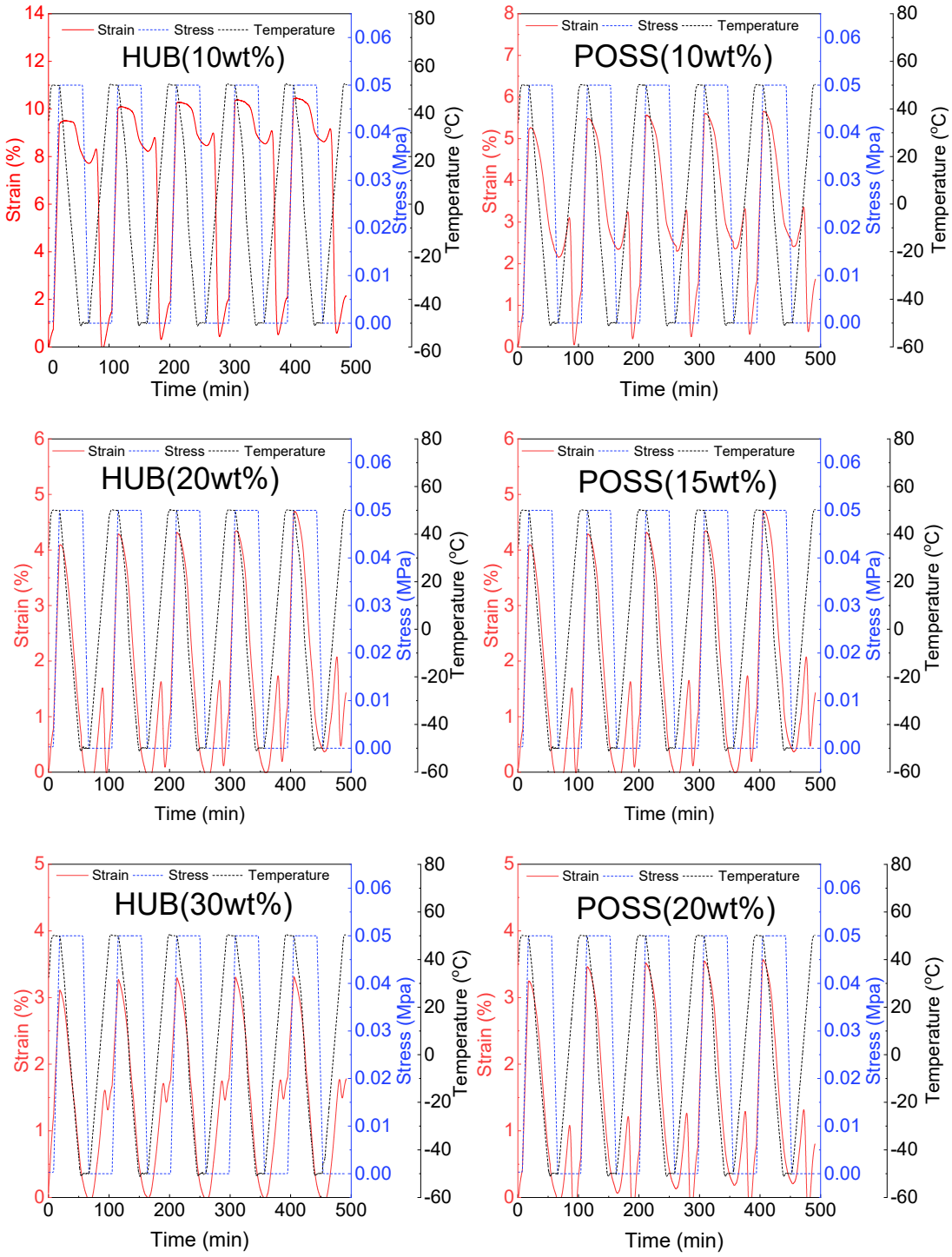

Figure S10 One-way shape memory cycles curves of P(BA-POSS-HUB) networks: Left) 15 wt% of POSS; right) 20 wt% of HUBs