

## SUPPORTING INFORMATION FOR

### Synthesis, Self-assembly and Self-healing Properties of Organic-inorganic ABA Triblock Copolymers with Poly(POSS acrylate) Endblocks

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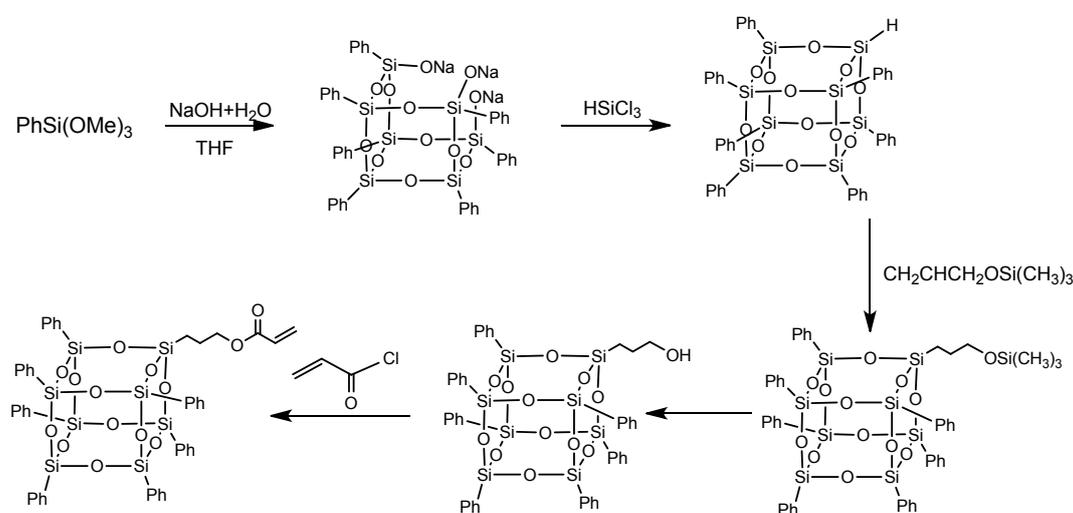
## 1. Materials and Synthesis

### 1.1 Materials

Phenyltrimethoxysilane [ $\text{PhSi}(\text{OMe})_3$ ] was supplied by Zhejiang Chemical Technology Co. Ltd., China; it was purified with distillation under reduced pressure. Trichlorosilane, allyloxytrimethylsilane, acryloyl chloride and triethylamine were purchased from TCI Co., Shanghai, China and used as received. The organic solvents such as tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), methanol, toluene, diethyl ether and dichloromethane were of chemically pure grade, obtained from commercial sources. Before use, THF and toluene were dried with distillation over metal sodium and stored in the presence of 4Å molecular sieves.

### 1.2 Synthesis of 3-Acryloxypropylheptaphenyl POSS (POSS-Acrylate)

The route of synthesis for 3-acryloxypropylheptaphenyl POSS (POSS-Acrylate) is depicted in Scheme S1.



**Scheme S1** Synthesis of 3-acryloxypropylheptaphenyl POSS

#### 1.2.1 Synthesis of Heptaphenylhydro POSS (POSS-H)

First, heptaphenyltricycloheptasiloxane trisodium silanolate [ $\text{Na}_3\text{O}_{12}\text{Si}_7(\text{C}_6\text{H}_5)_7$ ] was synthesized by following the method of literature [1]. Phenyltrimethoxysilane [ $\text{C}_6\text{H}_5\text{Si}(\text{OMe})_3$ ] (74.250 g, 0.375 mol), sodiumhydroxide

(6.525 g, 0.15 mol), deionized water (8.500 g, 0.48 mol) and THF (350 mL) were added to a flask equipped with a condenser and a magnetic stirrer, After refluxing at 75 °C for 5 h, the reaction was performed on room temperature for additional 15 h. All the solvents and other volatile components were removed *via* rotary evaporation. After drying *in vacuo* at 40 °C for 4 h, the product [*i.e.*, Na<sub>3</sub>O<sub>12</sub>Si<sub>7</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>7</sub>] (52.200 g) was obtained with the yield of 98%.

Second, hydroheptaphenyl POSS (denoted POSS-H) was synthesized *via* the silylation reaction of Na<sub>3</sub>O<sub>12</sub>Si<sub>7</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>7</sub> with trichlorosilane. Typically, Na<sub>3</sub>O<sub>12</sub>Si<sub>7</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>7</sub> (34.800 g, 34.9 mmol) and THF (250 mL) were added to a flask and then the flask was immersed into an ice-water bath for 1.5 h. Thereafter, trichlorosilane (7.89g, 52.35 mmol) was added quickly. The reaction was performed at 0 °C for 1 h and at room temperature for 12 h. After filtering out the insoluble component (*i.e.*, sodium chloride), the solvent together with other volatile compounds was removed *via* rotary evaporation. The solids were washed with 200 mL of methanol three times and dried *in vacuo* at 30 °C for 4 h. The product (19.700 g) was obtained with the yield of 59.6%. <sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>): 7.30–7.55, 7.70–7.87 (35H, C<sub>6</sub>H<sub>5</sub>-), and 4.50 (s, Si-H) (See Figure S1).

### 1.2.2 Synthesis of 3-Hydroxypropylheptaphenyl POSS (POSS-OH)

First, 3-trimethylsilylheptaphenyl POSS was synthesized *via* the hydrosilylation reaction of POSS-H with allyloxytrimethylsilane. POSS-H (10.000 g, 10.45 mmol), allyloxytrimethylsilane (6.750 g, 51.93 mmol), and anhydrous toluene (80 mL) were added to a flask containing a magnetic stirrer. The flask was purged with highly pure nitrogen for 30 min, and then Karstedt catalyst (0.03ml) was added with vigorous stirring. The reaction was performed at 95 °C for 36 h to attain a complete reaction. The toluene and excess allyloxytrimethylsilane were removed *via* rotary evaporation and the product (10.250 g) was obtained with the yield of 90%.

Second, 3-hydroxypropylheptaphenyl POSS was prepared *via* the deprotection reaction of 3-trimethylsilylpropylheptaphenyl POSS. The above 3-trimethylsilylpropyl heptaphenyl POSS (10.000 g, 9.2 mmol) was dissolved in 200 mL of dichloromethane and then 200 mL of methanol was added with vigorous stirring. The reaction was performed at room temperature for 6 h. Thereafter,

methyltrichlorosilane (2.300 g, 20.87 mmol) was added. The solvent and excess methyltrichlorosilane were removed *via* rotary evaporation. The resulting product (1.800 g) was obtained *via* washing with methanol for three times.  $^1\text{H}$  NMR (ppm,  $\text{CDCl}_3$ ): 7.30–7.55, 7.70–7.87 (*m*, 35H,  $\text{C}_6\text{H}_5$ -), 3.61 (*t*, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 1.78 (*m*, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ), 0.90 (*t*, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) (See Figure S1).

### 1.2.3 Synthesis of 3-Acryloxypropylheptaphenyl POSS (POSS-Acrylate)

3-Hydroxypropylheptaphenyl POSS (5.070 g, 5 mmol), triethylamine (1.012 g, 10 mmol) and dichloromethane (50 mL) were added to a flask and then acryloyl chloride (0.905 g, 10 mmol) was dropwise added. With vigorous stirring, the reaction was carried out at room temperature for 24 hours and then the reacted mixture was washed with deionized water three times and the organic layer was collected and concentrated *via* rotary evaporation. The concentrated mixture was dropwise added to 200 mL of methanol to afford the precipitates. After dried *in vacuo* at 40 °C for 2 hours, the product (*i.e.*, 3-acryloxypropylheptaphenyl POSS (POSS-acrylate) (4.500 g) was obtained with the yield of 84%.  $^1\text{H}$  NMR (ppm,  $\text{CDCl}_3$ ):  $^1\text{H}$  NMR (ppm,  $\text{CDCl}_3$ ): 7.30 ~ 7.55, 7.70 ~ 7.87 (*m*, 35H,  $\text{C}_6\text{H}_5$ ), 6.38, 5.79 (*t*, 2H,  $-\text{CH}_2\text{CHCOO}$ ), 6.10 (*t*, 1H,  $-\text{CH}_2\text{CHCOO}$ ), 4.15 (*t*, 2H,  $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OOC}$ ), 1.92 (*m*,  $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OOC}$ ) and 0.93 (*t*, 2H,  $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OOC}$ ) (See Figure S1).

### 1.3 Synthesis of 5-Acetamidopentylacrylate (AA)

First, ethyl acetate (500 mL) and 5-amino-1-pentanol (25.000 g, 242.5 mmol) were charged to a flask with vigorous stirring. Thereafter, acetic anhydride (28.034 g, 274.6 mmol) was added dropwise and the reaction was carried out for 2 hours. Methanol (75 mL) and  $\text{K}_2\text{CO}_3$  (27.6 g, 20.0 mmol) were added with vigorous stirring for 5 min, the insoluble component was filtrated out and the filtrate was subjected to rotary evaporation to afford 5-acetamido-1-pentanol (33.5 g) with the yield of 95 %.

Second, to a flask, 5-acetamido-1-pentanol (25.000 g, 172.0 mmol), trimethylamine (26.107 g, 258.0 mmol) and dichloromethane (300 mL) were charged with vigorous stirring; after that, acryloyl chloride (23.349 g, 258.0 mmol) was dropwise added within 30 min. The reaction was performed at room temperature for

24 hours. Thereafter, the reacted mixture was washed with the aqueous solutions of NaOH (1.0 M, 200 mL) and HCl (1.0 M, 200 mL) and the saturated solutions of NaCl (250 mL), respectively. The organic layer was dried with anhydrous MgSO<sub>4</sub>. After rotary evaporation, the product (32.210 g) was obtained with the yield of 93 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 6.32 (*t*, 1H, CH<sub>2</sub>=CH-), 6.17 (*t*, 1H, CH<sub>2</sub>=CH), 5.93 (*t*, 1H, CH<sub>2</sub>=CH-), 4.14 (*t*, 2H, CH<sub>2</sub>=CHCOOCH<sub>2</sub>), 3.01 (*t*, 2H, CH<sub>2</sub>=CH-COO-(CH<sub>2</sub>)<sub>4</sub>-CH<sub>2</sub>-), 1.77 (*s*, 3H, CH<sub>3</sub>-C=O), 1.57 ~ 1.63 (*m*, 2H, CH<sub>2</sub>=CH-COO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.37-1.41 (*m*, 2H, CH<sub>2</sub>=CHCOO(CH<sub>2</sub>)<sub>3</sub>-CH<sub>2</sub>-), 1.28 ~ 1.33 (*m*, 2H, CH<sub>2</sub>=CH-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-) (See Figure S2).

## 2. Measurements and Techniques

### 2.1 Nuclear Magnetic Resonance (<sup>1</sup>H NMR) Spectroscopy

The <sup>1</sup>H NMR spectroscopy was carried out on a Varian Mercury Plus 500 MHz NMR spectrometer at 25 °C. Deuterium chloroform (CDCl<sub>3</sub>) or/and deuterium dimethyl sulfoxide (DMSO-d<sub>6</sub>) was used to dissolve the samples.

### 2.1 Gel Permeation Chromatography (GPC)

The GPC measurements were conducted on a Waters 1515 system equipped with three Waters RH columns (*i.e.*, RH1, RH3 and RH4) and a water 2414 refractive index detector; N,N'-dimethylformamide (DMF) containing 0.01 M LiBr was used as the eluent at the flow rate of 1 mL × min<sup>-1</sup>; the molecular weights were expressed with polystyrene standards.

### 2.3 Dynamic Light Scattering (DLS)

The DLS measurements were performed on a Malvern Nano ZS90 analyzer with a He-Ne laser; the wavelength was λ = 633 nm and the scattering angle was 90°. The block copolymers (10 mg) were dissolved in 0.5 mL of THF and the solution was dropwise added 50 mL of ultra-pure water with vigorous stirring; the THF in the suspensions was removed *via* rotary evaporation.

### 2.4 Transmission Electron Microscopy (TEM)

The TEM measurements were performed on a JEOL JEM-2010 high-resolution transmission electron microscope. To investigate the self-assembly morphology of the triblock copolymers in aqueous solutions, the specimens were prepared by dropping the above aqueous suspensions at the concentration of  $0.2 \text{ g} \times \text{L}^{-1}$  onto copper grids and the water was removed *via* a freeze-drying approach. To observe the morphologies of the samples in bulks, the ultrathin sections were cut from the samples in bulks with a diamond knife under a cryo condition with liquid nitrogen and the specimens were subjected to the morphological observation without a staining step.

### *2.5 Small Angle X-ray Scattering (SAXS)*

The SAXS measurements were performed on a small angle X-ray scattering station (BL16B1) of Shanghai Synchrotron Radiation Facility (SSRF), China. The measurements were carried out at room temperature; two-dimensional diffraction patterns were recorded using a CCD detector. The intensity profiles were output as the plot of scattering intensity ( $I$ ) *versus* scattering vector ( $q$ ),  $q = (4\pi/\lambda) \sin(\theta/2)$  and  $\theta$  is the scattering angle.

### *2.6 Differential Scanning Calorimetry (DSC)*

The DSC measurements were conducted on a TA Instruments Q2000 differential scanning calorimeter in a dry nitrogen atmosphere. The samples (5 ~ 10 mg) were first heated up to 120 °C and held at this temperature for 3 min and then quenched to -80 °C to erase the thermal history. Thereafter, the samples were reheated from -80 to 120 °C at the heating rate of  $20 \text{ }^\circ\text{C} \times \text{min}^{-1}$  to record the thermograms. Glass transition temperature ( $T_g$ ) was taken as the midpoint of the heat capacity change.

### *2.7 Thermal Gravimetric Analysis (TGA)*

The TGA measurements were conducted on a TA Instruments Q5000 thermal gravimetric analyzer from 50 °C to 800 °C at the heating rate of  $20 \text{ }^\circ\text{C} \times \text{min}^{-1}$  in air

atmosphere.

### 2.8 Rheological Analysis

The rheological measurements were also carried out on a TA Q-800 DMTA apparatus in a dynamic shearing mode at 25 °C. The rectangular specimens with the dimension of  $10 \times 10 \times 2 \text{ mm}^3$  were measured in a sandwich configuration in the range of frequency from  $10^{-1}$  to  $10^2$  Hz; the amplitude of shear with 10 mm was used.

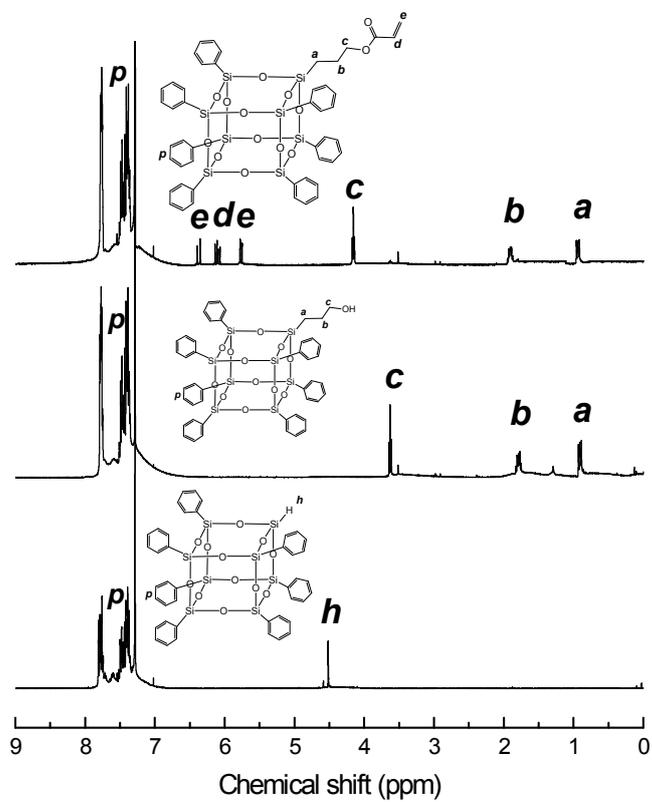
### 2.9 Self-healing Properties and Tensile Tests

The tensile tests were performed with a WDW-2 universal electron testing machine (Songdun Instruments Co. Ltd., Shanghai, China). Dogbone-shaped specimens were prepared *via* casting the concentrated solutions of the triblock copolymers into Teflon molds at 60 °C. The majority of solvent was evaporated at 60 °C for 12 hours and the residual solvent was removed *in vacuo* at 60 °C for two weeks. The specimens had the dimension of  $25 \times 4.75 \times 0.6 \text{ mm}^3$  in the central section. Before the measurements the specimens were annealed at 60 °C for 12 hours. At room temperature, the tensile tests were carried out with strain rate of  $100 \text{ mm} \times \text{min}^{-1}$ . For each sample, five successful tests were conducted to report the parameters of tensile mechanical properties.

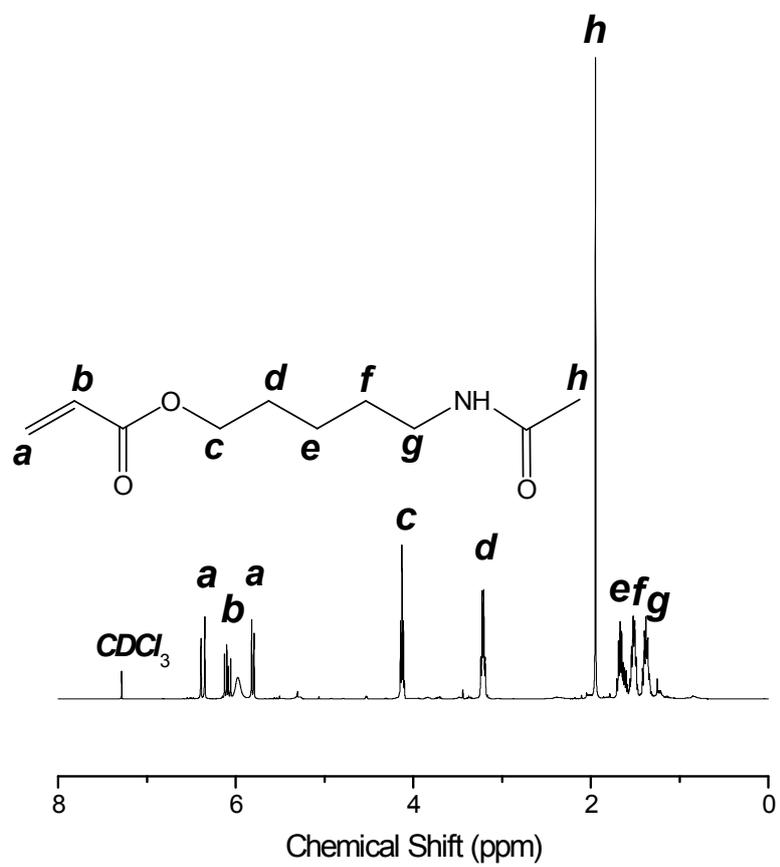
## 3. REFERENCES

1. K. Ohno, S. Sugiyama, K. Koh, Living radical polymerization by polyhedral oligomeric silsesquioxane-holding initiators: precision synthesis of tadpole-shaped organic/inorganic hybrid polymers. *Macromolecules* **2004**, *37*, 8517-8522.

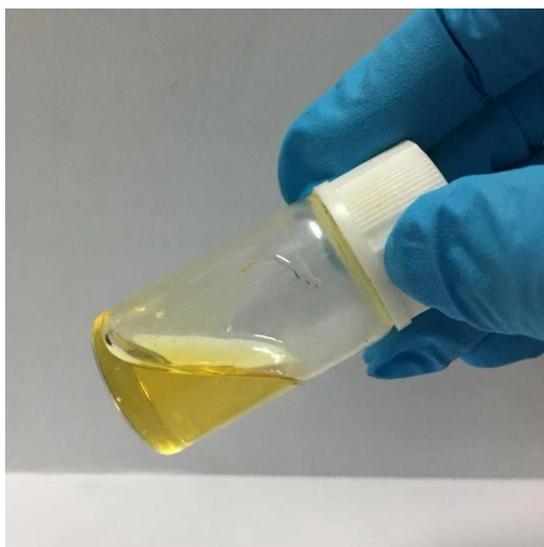
## 4. FIGURES



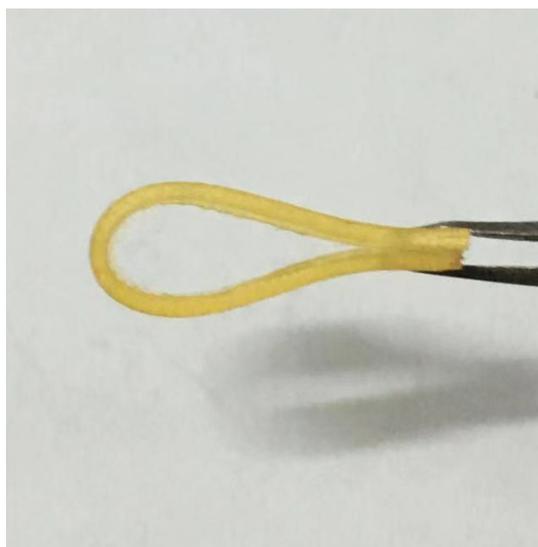
**Figure S1**  $^1\text{H}$  NMR spectra of POSS-acrylate, POSS-OH and POSS-H



**Figure S2** <sup>1</sup>H NMR spectrum of 5-acetamidopentyl acrylate

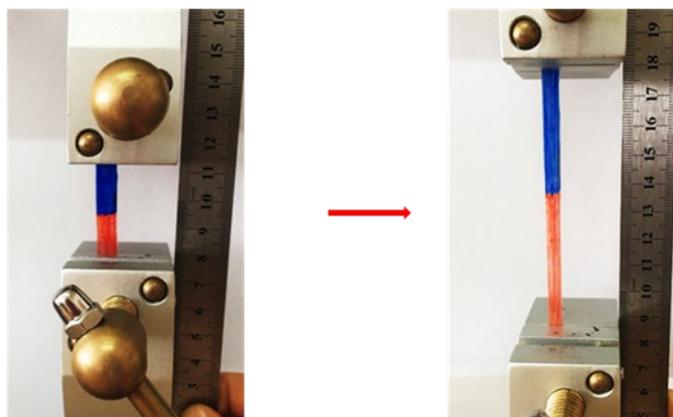
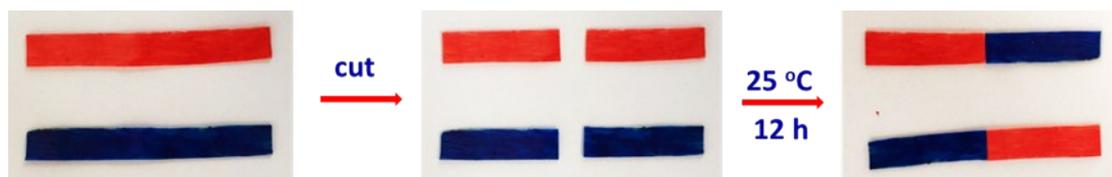


PAA ( $M_n=32,000$  with  $M_w/M_n=1.09$ )



PAA-P(POSS)11

**Figure S3** Photographs of PAA-CTA and PAA-P(POSS)11



**Figure S4** Photographs of PAA-P(POSS)18 for the self-healing measurements;