

SUPPORTING INFORMATION FOR

Shape Memory and Self-healing Properties of Poly(acrylate amide) Elastomers Reinforced with Polyhedral Oligomeric Silsesquioxanes

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EXPERIMENTAL

Materials

5-Acetylaminopentyl acrylate (AA) was prepared by following the method of literature with slight modification [1] (See Supporting Information, SI). 3-Methacryloxypropylheptaphenyl polyhedral oligomeric silsesquioxane (MAPOSS) was synthesized with a corner-capping reaction of heptaphenyltricycloheptasiloxane trisodium silanolate with 3-methacryloxypropyltrichlorosilane as detailed elsewhere [2]. 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid was synthesized by following the method reported by McCormick *et al* [3]. 2,2-Azobisisobutylnitrile (AIBN) was purchased from Shanghai Reagent Co., China; it was purified with recrystallization from ethanol. The organic solvents such as toluene, tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were obtained from commercial sources.

Synthesis of 3-Methacryloxypropylheptaphenyl POSS (MAPOSS)

First, heptaphenyltricycloheptasiloxanetrisodiumsilanolate[Na₃O₁₂Si₇ (C₅H₆)₇] was synthesized with the method described by Fukuda *et al* [4]. Typically, phenyltrimethoxysilane (45.540 g, 0.23 mol), THF (250 ml), distilled water (5.250 g, 0.29 mol) and NaOH (3.950 g, 0.1 mol) were charged into a flask equipped with a reflux condenser and a magnetic stirrer. The mixture was refluxed in an oil bath at 70 °C for 5 hours with vigorous stirring and then cooled to room temperature. With continuous stirring for additional 15 hours at room temperature, all the volatile components were removed *via* rotary evaporation to obtain the white solids. The white solids were then dried *in vacuo* at 60 °C for 24 h to get the products (32.000 g) with the yield of 98.9%.

Second, 3-methacryloxypropylheptaphenyl POSS (MAPOSS) was synthesized *via* the corner capping reaction of Na₃O₁₂Si₇(C₅H₆)₇ with 3-methacryloxypropyl trichlorosilane (See Scheme S1). Typically, Na₃O₁₂Si₇ (C₅H₆)₇ (10.022 g, 8.8 mmol) was charged to a flask equipped with a magnetic stirrer, 200 ml of anhydrous THF was added with vigorous stirring. The flask was immersed into an ice-water bath and purged with highly pure nitrogen for 1 hour. After that, 3-methacryloxypropyl trichlorosilane (2.981 g, 11.5 mmol) was quickly added to the flask. With vigorous stirring, the corner capping reaction was carried out at 0°C for 3 hours and at room temperature for 24 hours. The insoluble solids (*i.e.*, sodium chloride) were filtered out and then the solvent together with other volatile compounds was removed *via* rotary evaporation to afford the white solids. The crude product was washed with 100 ml of methanol three times until the methanol layer was clear. The white solids were collected by filtration and dried *in vacuo* at 40 °C for

24hours. The product (6.120 g) was obtained with the yield of 58.0%. ^1H NMR (CDCl_3 , ppm): 7.35-7.53, 7.73-7.81 [*m*, 5H, protons of aromatic ring]; 6.09, 5.53 [*s*, 2H, $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CO}$]; 4.14 [*t*, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si}$]; 1.93 [*m*, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}$ and (*s*, 3H, $\text{CH}_2\text{C}(\text{CH}_3)\text{CO}$); 0.93 (*t*, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}$). ^{29}Si NMR (CDCl_3 , ppm): -64.61, -77.70, -78.03.

Synthesis of 5-Acetamidopentylacrylate (AA)

First, to a flask, ethyl acetate (500 mL) and 5-amino-1-pentanol (50.010 g, 485.4 mmol) were charged and then acetic anhydride (56.130 g, 549.1 mmol) was added dropwise with vigorous stirring and the reaction was carried out for 2 hours. Thereafter, methanol (150 mL) and K_2CO_3 (55.050 g, 39.8 mmol) were added with vigorous stirring for 5 min followed by filtration of solids and the filtrate was subjected to rotary evaporation to afford 5-acetamido-1-pentanol (89.6 g) with the yield of 92.5%.

Second, to a flask, 5-acetamido-1-pentanol (25.110 g, 173.2 mmol), EDC (60.040 g, 312.9 mmol), DMAP (40.310 g, 330.4 mmol) and dichloromethane (500 mL) were charged with vigorous stirring; the reaction was performed at room temperature for 24 hours. Thereafter, the reacted mixture was diluted by adding dichloromethane (500 mL) and the 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 NaHCO_3 (250 mL) and NaCl (250 mL), respectively. The organic layer was dried with anhydrous MgSO_4 for 12 hours. With rotary evaporation, the crude product was then obtained and purified by passing silica column. The product (32.510 g) was obtained with the yield of 90 %. ^1H NMR ($\text{DMSO-}d_6$, ppm): 7.79 (*s*, 1H, $-\text{CH}_2\text{CH}_2\text{NHC=O}$), 6.32 (*t*, 1H, $\text{CH}_2=\text{CH-}$), 6.17 (*t*, 1H, $\text{CH}_2=\text{CH}$), 5.93 (*t*, 1H, $\text{CH}_2=\text{CH-}$), 4.09 (*t*, 2H, $\text{CH}_2=\text{CHCOOCH}_2$), 3.01 (*t*, 2H, $\text{CH}_2=\text{CH-COO-(CH}_2)_4\text{-CH}_2$ -), 1.77 (*s*, 3H, $\text{CH}_3\text{-C=O}$), 1.57 ~ 1.63 (*m*, 2H, $\text{CH}_2=\text{CH-COO-CH}_2\text{-CH}_2$ -), 1.37-1.41 (*m*, 2H, $\text{CH}_2=\text{CHCOO(CH}_2)_3\text{-CH}_2$ -), 1.28 ~ 1.33 (*m*, 2H, $\text{CH}_2=\text{CH-COOCH}_2\text{CH}_2\text{CH}_2$).

Measurement and Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^1H NMR spectroscopy was carried out on a Varian Mercury Plus 400 nuclear magnetic resonance spectrometer. The polymer was dissolved in deuterium dimethylsulfone ($\text{DMSO-}d_6$) and the solution was measured with tetramethylsilane (TMS) as the external reference.

Dynamic Light Scattering (DLS)

The DLS experiments were conducted on a Nano ZS90 (Malvern Instrument, Malvern, Worcestershire, UK) equipped with a He-Ne laser operating at the wavelength of $\lambda = 633$ nm. P(AA-stat-MAPOSS8.7) was dispersed in N,N-dimethylformamide (DMF) at the concentration of $0.2 \text{ g} \times \text{L}^{-1}$. The measurements were carried out at 25, 60, 90 and 140 °C, respectively. At a specific temperature, the dispersion was maintained at 30 min with vigorous stirring before the measurements were performed.

Thermal Gravimetric Analysis (TGA)

The TGA measurements were carried out on a TA Instrument Q5000 thermal gravimetric analyzer in air atmosphere from 25 to 800 °C at the heating rate of $20 \text{ }^\circ\text{C} \times \text{min}^{-1}$. The temperature of initial degradation (T_d) was taken as the onset temperature at which 5 wt % of weight loss occurred. The TGA curves of plain PAA and P(AA-*r*-MAPOSS)s are shown in Figure S4.

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. 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 θ is the scattering angle.

Transmission Electron Microscopy (TEM)

The samples were dispersed in DMF and the suspensions were dropped onto 200 mesh copper grids followed by solvent evaporation at 60 °C for 12 hours and the film specimens were used for morphological observation. The TEM measurements were carried out on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV.

Rheological Measurements

The rheological measurements at 50 °C were carried out on a TA Q-800 DMTA apparatus in dynamic shearing mode with three parallel plates with a sandwich

configuration. The parallel plates had the area of $10 \times 10 \text{ mm}^2$ and a gap of 5.58 mm. The shear rate was varied from 0.01 to 100 Hz with the amplitude of 10 μm .

Self-healing and Tensile Mechanical Tests

The tensile mechanical tests were carried out on an Instron 4465 mechanical test machine at room temperature. The dumbbell-shaped specimens which were scaled down from ASTM standard were prepared and the specimens had the central dimension of $40 \times 8 \times 2 \text{ mm}^3$. The loading rate was $100 \text{ mm} \times \text{min}^{-1}$; at least five parallel measurements were performed.

Shape Memory Measurements

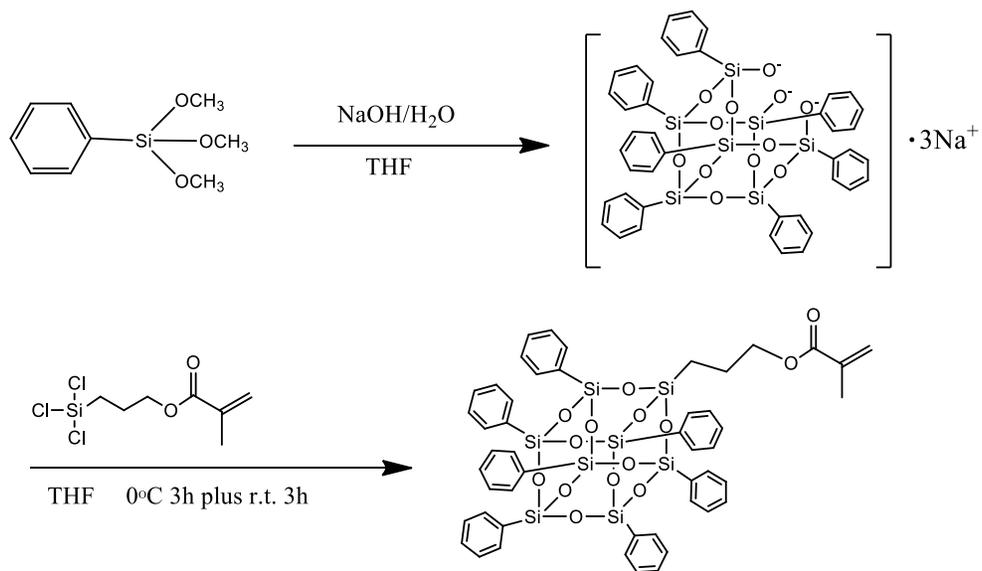
The above specimens were also used for shape memory tests. Before the measurements, all the specimens were annealed at $60 \text{ }^\circ\text{C}$ for 12 hours to remove the thermal history. The specimens were deformed into “O” shapes at room temperature and then transferred into a refrigerator at $-20 \text{ }^\circ\text{C}$ for 30 min to fix the temporary shapes. The specimens with the temporary shapes were taken out and placed on a hot stage at $30 \text{ }^\circ\text{C}$ and shape recovery of specimens was recorded with a digital video camera.

For one-way shape memory measurements, the rectangular specimens with the dimension of $20 \times 4 \times 2 \text{ mm}^3$ were prepared. The measurements were carried out on a TA Q800 dynamic mechanical thermal analyzer (DMTA). First, the specimens were heated up to $60 \text{ }^\circ\text{C}$ at which the specimen was stretched with the stress up to $\sigma = 0.1 \text{ MPa}$ at the loading rate of $0.01 \text{ MPa} \times \text{min}^{-1}$. Maintaining the stress condition, the specimens were cooled to $-20 \text{ }^\circ\text{C}$ at the rate of $3 \text{ }^\circ\text{C} \times \text{min}^{-1}$ and then the load was released. Lastly, the specimens were heated up to $60 \text{ }^\circ\text{C}$ at the rate of $3 \text{ }^\circ\text{C} \times \text{min}^{-1}$. The above steps were repeated five times and the change in strain was recorded to evaluate the fixity of temporary shape, recovery of original shape and the repeatability of shape memory.

REFERENCES

1. Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z., Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* **2012**, *4*, 467-472;
2. Wang, L.; Li, J.; Li, L.; Zheng, S., Organic-inorganic hybrid diblock copolymer composed of poly(ϵ -caprolactone) and poly(MA POSS): Synthesis and its nanocomposites with epoxy resin. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 2079-2090;
3. Wang, R.; McCormick, C. L.; Lowe, A. B., Synthesis and evaluation of new dicarboxylic acid functional trithiocarbonates: RAFT synthesis of telechelic poly(n-butyl acrylate)s. *Macromolecules* **2005**, *38*, 9518-9525;
4. Ohno, K.; Sugiyama, S.; Koh, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Oikawa, H.; Yamamoto, Y.; Ootake, N.; Watanabe, K. *Macromolecules* **2004**, *37*, 8517.

SCHEMES



Scheme S1 Synthesis of 3-methacryloxypropylheptaphenyl POSS (MAPOSS)

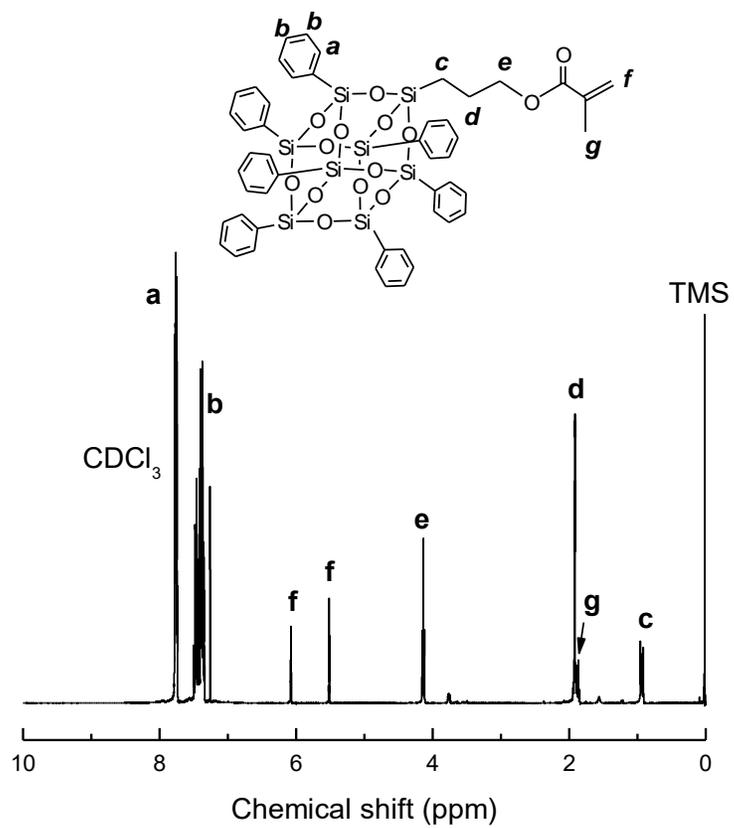


Figure S1 ¹H NMR spectrum of 3-methacryloxypropylheptaphenyl POSS (MAPOSS)

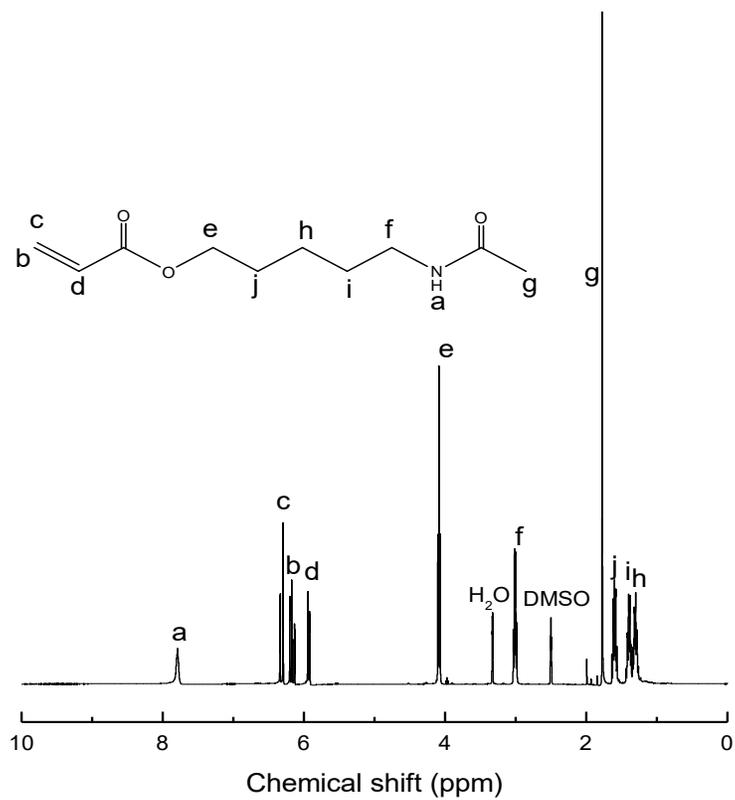


Figure S2 ¹H NMR spectrum of 5-acetamidopentyl acrylate (AA)

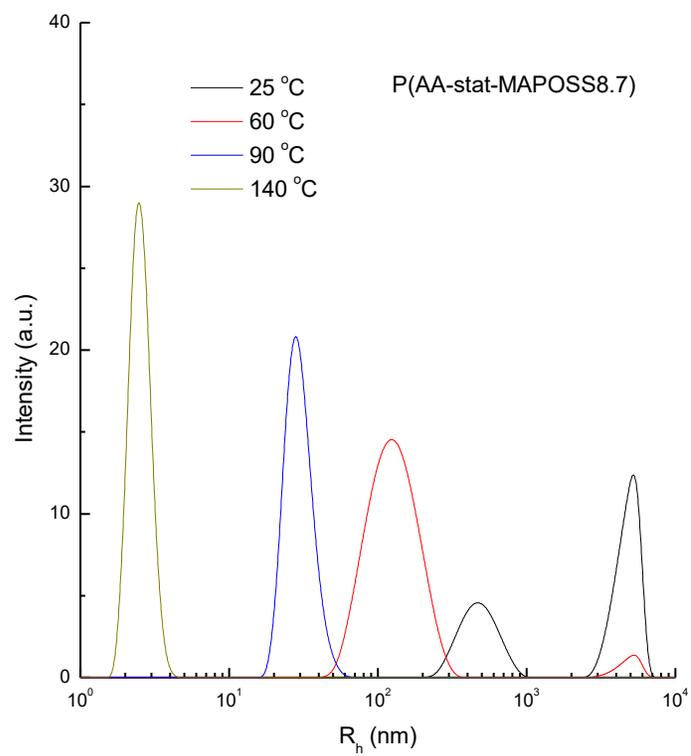


Figure S3. Hydrodynamic radius of the self-assembled nanoobjects of P(AA-*r*-MAPOSS8.7) in the solution of DMF at the concentration of 0.1 wt% at 25, 60, 90 and 140 °C.

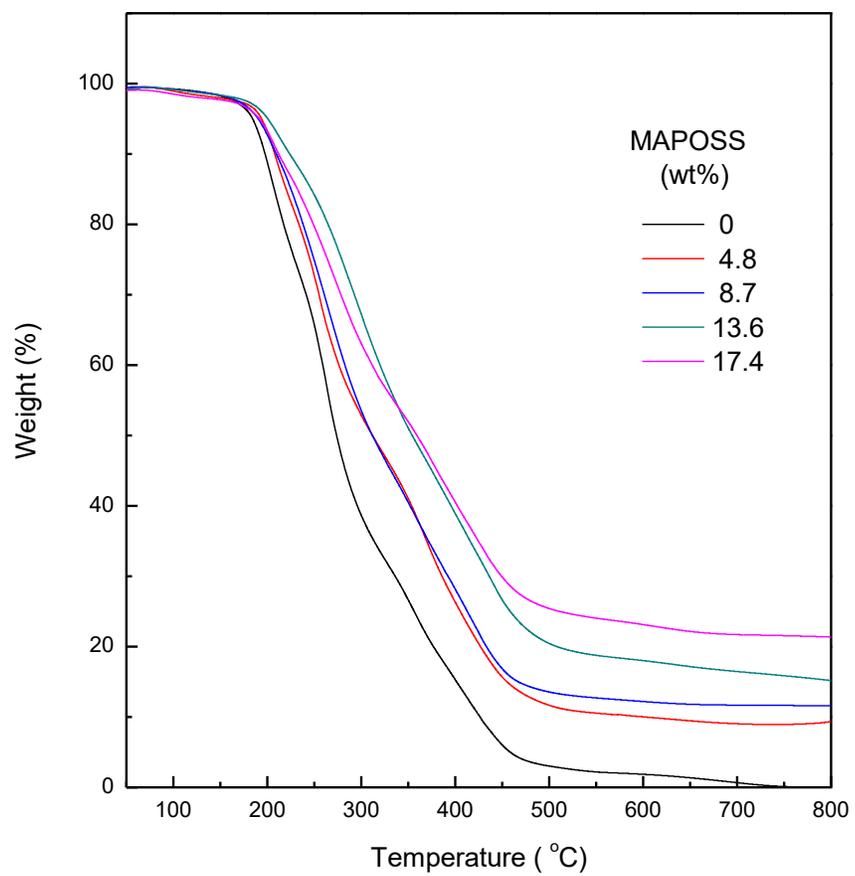


Figure S4 TGA curves of PAA and P(AA-*r*-MAPOSS)s



Figure S5 The physical gel of P(AA-*r*-MA POSS17.4) in DMF at the concentration of 15 wt% at room temperature

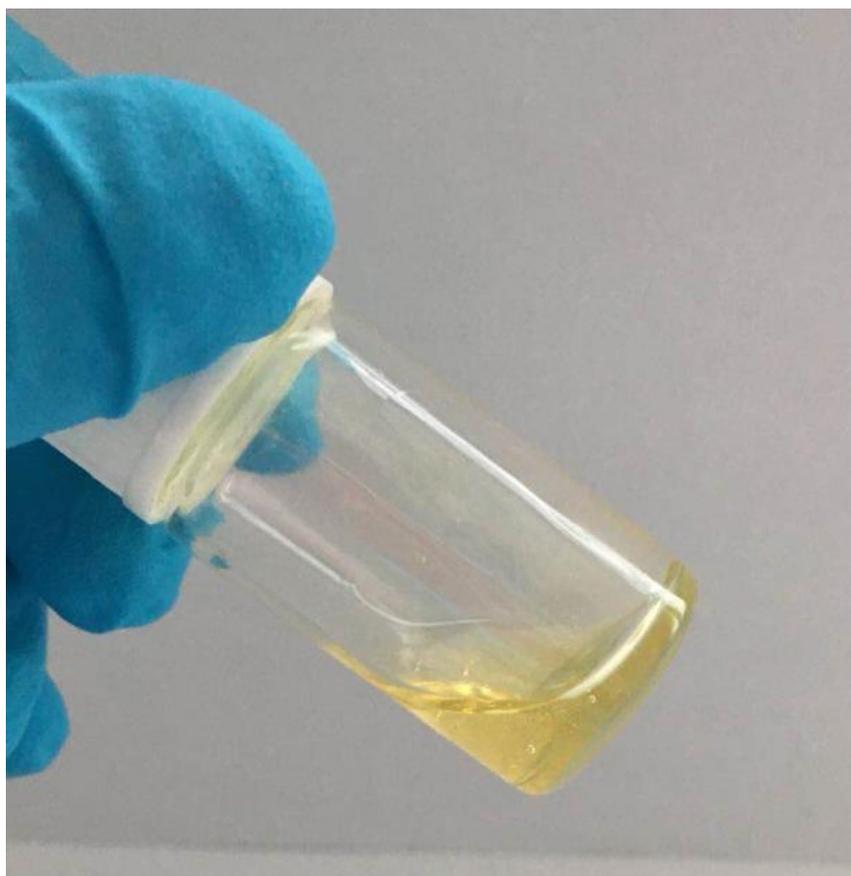


Figure S6 Photo of PAA ($M_n=20,000$ with $M_w/M_n=1.27$) at room temperature