# Supporting Information

## Injectable Shear-Thinning Hydrogel with Enhanced Strength and Temperature Stability by POSS End-Group Aggregation

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### General Information

**Materials.** All chemicals except POSS were purchased from Energy and Aladdin. The reagent aminopropyllsobutyl POSS were provided by Hybrid Plastics. The dialysis tubes (MWCO 8000-14000) were purchased from YuanYe Biological Technology. All anhydrous solvents mentioned were distilled from $CaH_2$. Polyethylene glycol (PEG) was dried in vacuum oven for 4 hours before using.

**Measurements.** Gel permeation chromatography (GPC) was performed on a Waters 410 system using DMF as eluent at 50 °C and with polymethyl methacrylate (PMMA) as standard. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1011 machine operated at 100 kV. The samples were drop cast from their solution onto copper grids coated with a thin layer of carbon. Hydrodynamic diameters were measured with a Brookhaven 90Plus size analyzer. Scanning electron microscopy (SEM) was performed on a FEI XL-30 at an accelerating voltage of 10 kV, the working distance is 25 mm for the Sample P1-POSS and 26 mm for the Sample P1-Octyl. All hydrogel samples at certain concentration were dehydrated by freeze-drying and the cross-section of hydrogels were coated with a thin layer of gold before testing. The rheological properties of these hydrogels were measured by a stress-controlled rheometer (Anton Paar, MCR301) with a constant gap distance

(0.104 mm) and diameter (25 mm) of cone-plate geometry. A constant strain of 3% was applied for the frequency sweeps and frequency of 1 Hz was applied for the strain sweeps. For temperature sweeps, a 1 Hz frequency and 3% strain were used. The high strain and low strain used in the self-healing experiments were 100 % and 0.1% respectively at 1Hz frequency. All rheological tests were conducted at 20 °C unless mentioned otherwise and silicone oil was used during testing to avoid evaporation.

**Synthesis.** The amonium chloride-terminated PEG was synthesized according to literature procedures.[1,2] The P1-POSS and P1-Octyl were achieved by following process: First, the amonium chloride-terminated PEG (Mn =10000 g/mol) was washed by saturated $NaHCO_3$ solution to obtain amino-terminated PEG. Next, amino-terminated PEG (3.2 g, 0.3 mmol) was dissolved in 50ml anhydrous N,N-dimethylformamide at room temperature in a $N_2$-filled round-bottom flask. Then HDI (60 μl, 0.375 mmol) was added dropwise into the solution. The mixture was stirred for 1 h at room temperature and heated up to 60 ºC for another 2 h. After the solution cooled down to room temperature, POSS (0.131 g, 0.15 mmol) or octylamine (0.02 g, 0.15 mmol) was added to react overnight. The resulting solution was precipitated in diethyl ether, yielding white solid, which was collected and dried at 40 ºC in the vacuum oven. P2-POSS and P2-Octyl were synthesized with the above procedures under different reactant ratio. P1-POSS: $^1$H NMR (400 MHz, $CDCl_3$, T = 295 K) δ 4.22 (t, 4H, $CH_2OCO$), 3.96–3.35 (m, $OCH_2$), 3.19 (m, 8H, $CH_2N$), 2.31 (t, 4H, $CH_2CO$), 1.21−1.70 (m,14H, $CH_2CH_2N$, $CH_2CH_2CO$ and $CH_2$), 0.5−1.0 (m, $CH_2CH(CH_3)_2$). P1-Octyl: $^1$H NMR (400 MHz, $CDCl_3$, T = 295 K) δ 4.22 (t, 4H, $CH_2OCO$), 3.96–3.35 (m, $OCH_2$), 3.22 (m, 8H, $CH_2N$), 2.31 (t, 4H, $CH_2CO$), 1.21−1.70 (m, 14H, $CH_2CH_2N$, $CH_2CH_2CO$ and $CH_2$), 0.89 (t, $CH_3$).

**Hydrogel formation.** To prepare hydrogels at different concentrations, typically the copolymer was dissolved in deionized water at 70 ºC for 1 hour under constant stirring and then cooled to room temperature. Before all others characterization studies, the hydrogels were put into a refrigerator at 4 ºC overnight to ensure complete gelation.

**Hydrogel erosion.** The erosion of hydrogels was measured in regard to weight loss under aqueous environment. 100 mg of each kind of hydrogel was put into a 1.5 ml of eppendorf tube, then 1 ml PBS (pH = 7.4) was added on the top of the gels and these gels were incubated at 37 °C. The PBS was replaced with fresh one at specified time intervals (24 hours) and the weight of hydrogels remained was compared with initial weight. The weight loss of gels was calculated to quantify the erosion rate.

**In vitro cytotoxicity.** All materials were dialyzed for at least 3 days with water changed 3-4 times a day before testing. L929 fibroblast cells were purchased from Shanghai Cell Bank of the Chinese Academy of Sciences, and were maintained in Dulbecco's modified eagle medium (DMEM) contain containing 10% FBS, 100 U/ml penicillin, and 100 mg/ml streptomycin. The cells were seeded in 96-well platesat 6000 cells per well, and then incubated in a humidified atmosphere of 5% $CO_2$ at 37 °C for 24 h. Then 100μL of copolymers in DMEM in given concentrations from 0.1 to 5 mg/ml were added.After 24 h incubation, the cytotoxic activity of the copolymers was quantitatively analyzed by MTT assays.

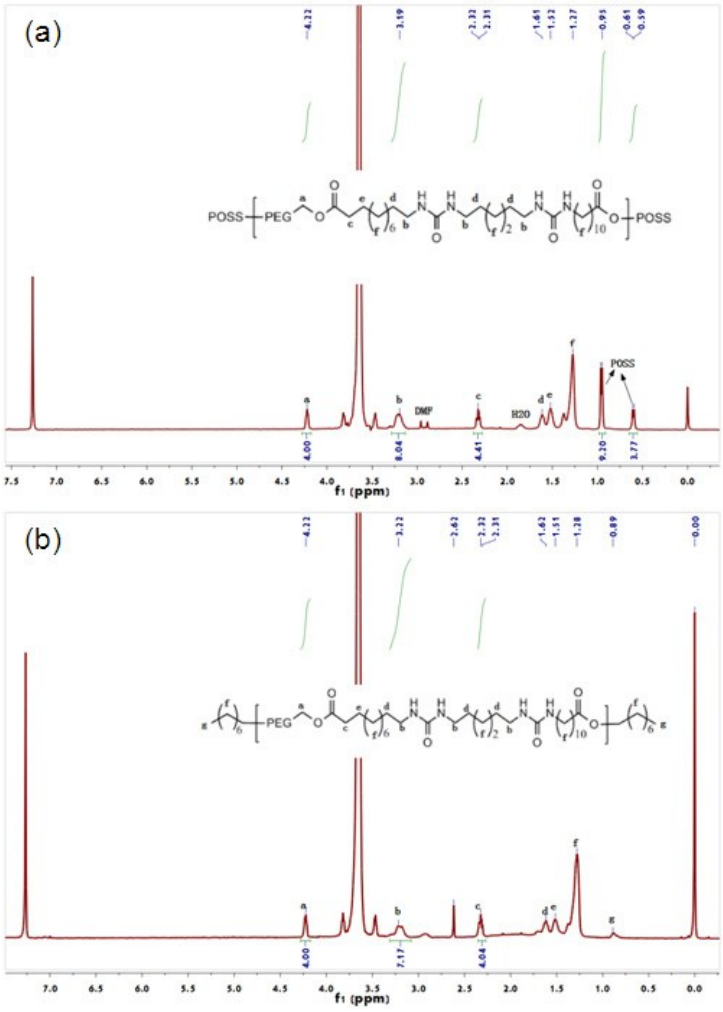


**Figure S1.** $^{1}$H NMR spectra of (a) P1-POSS and (b) P1-Octyl.

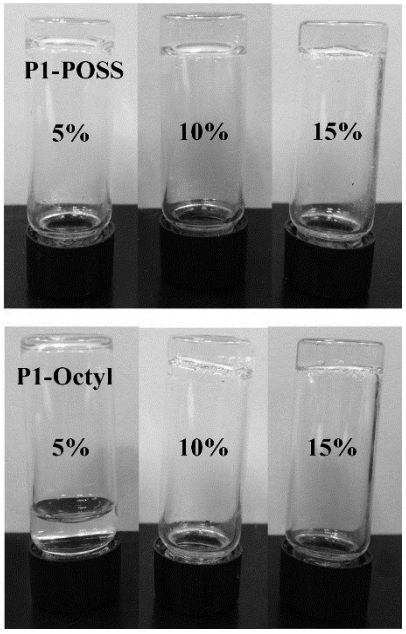


**Figure S2.** Photographs of P1-POSS and P1-Octyl hydrogels at different concentration. The P1-Octyl cannot gel at 5 wt %, while the P1-POSS forms gel at 5 wt %.

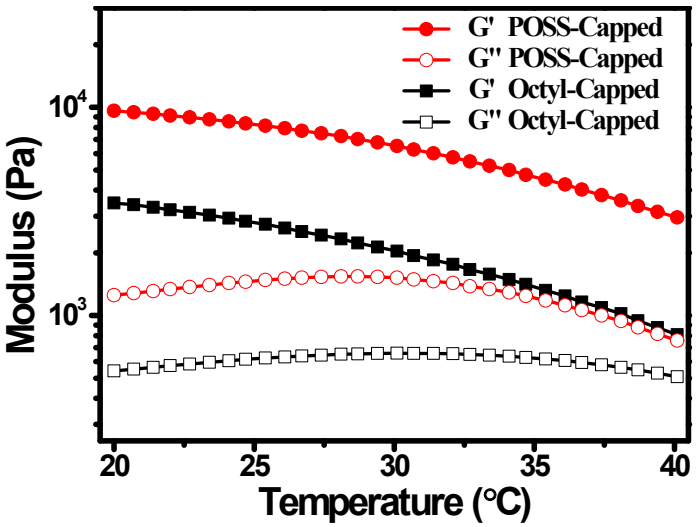


**Figure S3.** Rheological properties of P2-POSS and P2-Octyl hydrogels with temperature at 10 wt % concentration (6.28 rad/s and 3% strain).

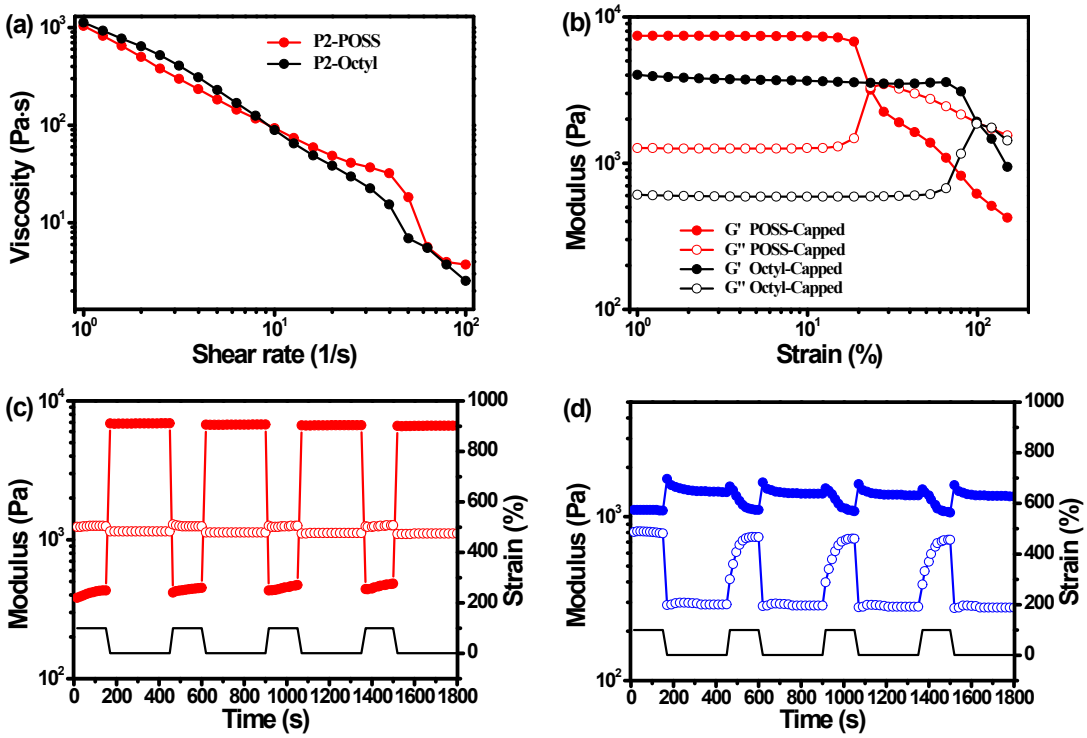


**Figure S4.** (a) Viscosity change with shear rate and (b) storage and loss modulus in strain sweeps of 10 wt % P2-POSS and P2-Octyl hydrogels. Dynamic strain tests of 10 wt % (c) P2-POSS, and (d) P2-Octyl hydrogels in four cycles (solid circle: G′, open circle: G″, line: 1%-100% strain). The measurements were all carried out at 6.28 rad/s.

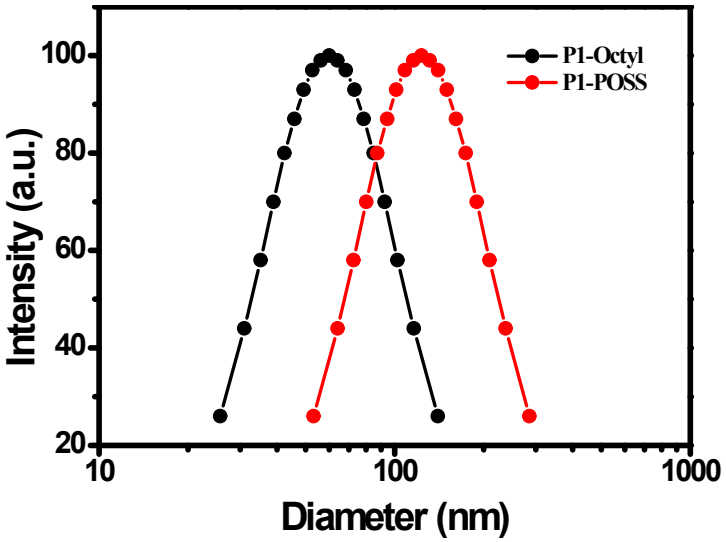


**Figure S5.** Hydrodynamic diameters of P1-POSS and P1-Octyl in 0.5 wt % solution.

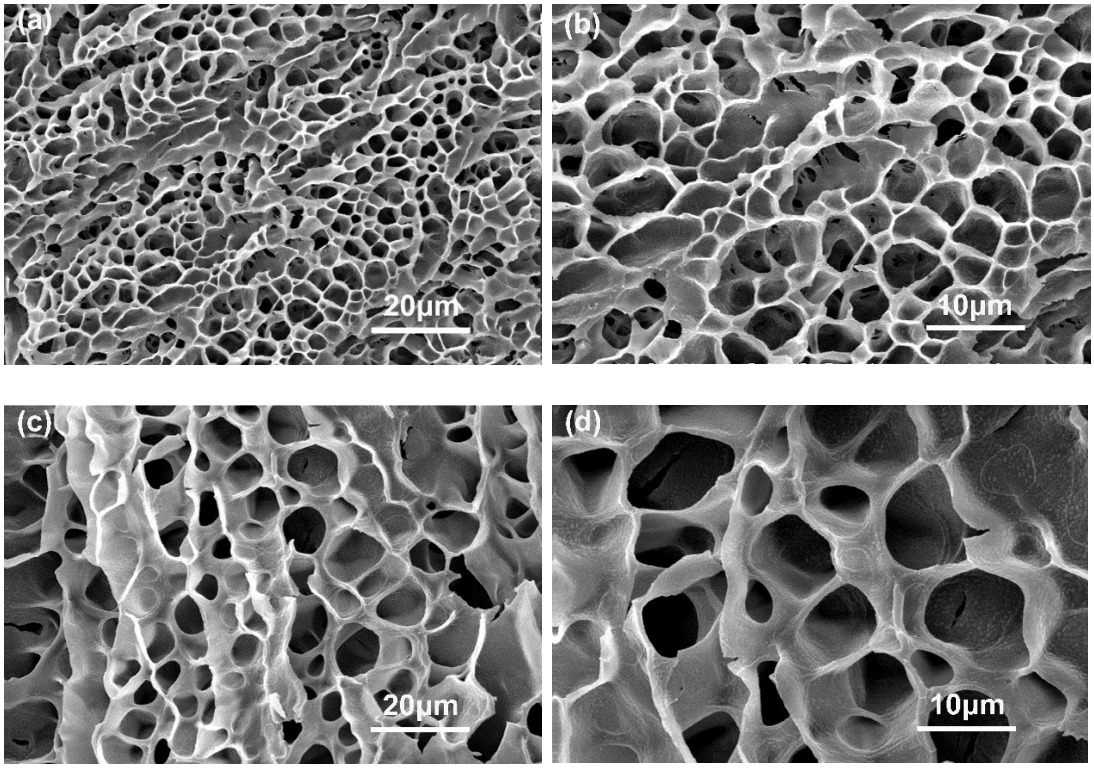


**Figure S6.** The SEM graphs of (a and b) P1-POSS and (c and d) P1-Octyl hydrogels at 15 wt %concentration.

References:

1 G. Bottari, D. A. Leigh, E. M. Pérez, *J. Am. Chem. Soc.,* 2003, **125**, 13360-13361.

2 G. M. Pawar, M. Koenigs, Z. Fahimi, M. Cox, I. K. Voets, H. M. Wyss, R. P. Sijbesma, *Biomacromolecules,* 2012, **13**, 3966-3976.