# Multi-Responsive and Tough Hydrogels Based on Triblock Copolymer Micelles as Multi-functional Macro-crosslinkers

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## Materials

Aacrylamide (AAm) and potassium peroxydisulfate (KPS) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. AAm was purified by twice recrystallization from acetone and dried under vacuum at 30 °C for 24 h before use. Pluronic F127 (PEO<sub>99</sub>-PPO<sub>65</sub>-PEO<sub>99</sub>) was provided by Sigma-Aldrich. Pluronic F127 was used as received without further processing. Dichloromethane, diethyl ether, triethylamine, and acryloyl chloride were all purchased from Aladdin Reagent Co., Ltd., China. Methyl chloride quarternized *N*,*N*-dimethylamino ethylacrylate (DMAEA-Q, 80 wt.% in aqueous solution) was purchased from Wanduo Fu Co., Ltd., China.

#### Characterization

The acrylation degree of F127DA was determined by <sup>1</sup>H NMR on a Bruker Advance III spectrometer (more than 90%) using deuterated chloroform as the solvent and calculated by the ratio of acryl protons of F127DA (dCH<sub>2</sub>,  $\delta$ = 5.8-6.4) to methyl protons in poly(propylene oxide) groups (-CH<sub>3</sub>,  $\delta$ = 1.1). The F127DA/KBr platelets were scanned by using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, America) in the range of 400-4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> by an average of 32 scans.

## **Swelling experiments**

The swelling experiments were performed by immersing the hydrogels in a large excess of water at 30 °C to reach swelling equilibrium. The equilibrium swelling ratio (ESR) was calculated by the following equation,  $\text{ESR} = (W_s - W_p)/W_p$ , where  $W_s$  and  $W_p$  are the weights of the swollen hydrogel and the as-prepared hydrogel, respectively.

## **Mechanical properties tests**

The mechanical properties of the hydrogels were measured with an Instron 5567 (Instron Inc, MA) instrument in compression mode. Five specimens were tests for each hydrogel. Each specimen was coated with a thin layer of silicon oil to prevent water evaporation.

For the compression tests were conducted at a crosshead speed of 0.13% strain per second. The stress and strain between 0.1 and 0.3 were used to calculate the initial elastic modulus (*E*). The toughness was calculated by the area under stress-stain curves. The dissipated energy was defined as the area of one cyclic curve. Cyclic compressive loading-unloading tests were performed immediately after the first loading-unloading cycle on fresh samples, the tests were conducted at a crosshead speed of 0.13% strain per second for four times.

For uniaxial tensile tests, cylindical hydrogel bars were tested at a crosshead speed of 13.6% strain per second. Cyclic tensile tests loading-unloading tests were performed immediately after the first loading-unloading cycle on fresh samples at a crosshead speed of 13.6% strain per second for four times.

**Table S1.** The average diameters of F127 and F127DA micelles were measured at 20 °C to 50 °C by dynamic light scattering. The concentration of F127DA was  $6 \times 10^{-3}$  mol/L.

Size (nm) T (°C)	F127	F127DA
20	325.6(±2.6)	326.6(±1.3)
25	349.4(±5.8)	353.5(±7.9)
30	303.6(±4.9)	299.3(±5.1)
35	285.1(±3.2)	282.3(±5.2)
40	240.8(±1.7)	239.2(±2.4)
45	247.6(±0.6)	247.6(±0.3)
50	195.2(±2.0)	194.3(±1.2)



Figure S1. <sup>1</sup>H NMR of F127DA.



Figure S2. FT-IR spectra of the synthesized M-NM and Q1M8-NM hydrogels.



**Figure S3.** (a) The dependence of compressive toughness on the DMAEA-Q content. (b) The cyclic compressive stress–time curves of Q1M8 at 90% strain. (c) The cyclic tensile stress–time curves of Q1M8 at 1000% strain.



Figure S4. The swelling behavior of QxMy gels with different formulations.