

Super tough, ultra-stretchable, and thermo-responsive hydrogels with functionalized triblock copolymer micelles as macro-crosslinkers

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Materials

The acrylamide (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 (PEO₉₉-PPO₆₅-PEO₉₉) 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.

Experimental section

Preparation of Pluronic F127 Diacrylate (F127DA)

F127DA was synthesized according to a well established literature procedure.¹ 10g F127 and ten-fold molar excess triethylamine were dissolved in 100mL anhydrous dichloromethane under nitrogen atmosphere, then the ten-fold molar excess acryloyl chloride in a dropping funnel were introduced to the three-neck flask. The mixture was stirred at 25 °C under nitrogen for 24h, then the precipitated triethylammonium chloride was filtered away and the above filtrate was precipitated by adding into anhydrous diethyl ether. The resulting product was dried under vacuum at 30 °C for 24 h.

Synthesis of nano-micellar hydrogels and PAAm hydrogels.

NM gels were synthesized via a one-step sequential free-radical polymerization. Firstly, AAM and F127DA were mixed in water. After bubbling under a nitrogen atmosphere for at least 30 mins, 0.1 mol% of the initiator potassium persulfate (KPS) with respect to AAM were added into the mixture. Using a syringe, the solution was poured into a mold fabricated by spacing two glass plates with a 4 mm silicone rubber spacer. The mold was heated at 50 °C for 12 h in a water bath for the polymerization and gelation. The PAAm hydrogels were synthesized almost the same like NM gels, with the same concentration of AAM, initiator, and cross-linker under the same condition. The only difference is the use of N, N'-methylenebis(acrylamide) (MBAA) as cross-linker.

Characterisation

The acrylation degree of F127DA was determined by ¹H 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_2 , $\delta = 5.8-6.4$) to methyl protons in poly(propylene oxide) groups ($-CH_3$, $\delta = 1.1$).

The F127DA/KBr platelets were scanned by using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, America) in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} by an average of 32 scans.

The F127DA micelle size and its distribution were measured by dynamic light scattering (DLS) using a Zeta particle size analyzer (Nano-ZS, Malvern, England) at different temperatures.

Dynamic mechanical analysis of the hydrogels were carried out by using an Anton Paar Physica MCR301 rheometer equipped with a Peltier device for temperature control. A frequency of 1 Hz and a deformation amplitude $\gamma = 0.5\%$ were selected to ensure that the oscillatory deformation is within the linear regime. The gel samples were scanned from 25 °C to 50 °C with a heating rate of 1 °C/min.²

The swelling experiments were performed by immersing the hydrogels in a large excess of water at 25 °C to reach swelling equilibrium. The equilibrium swelling ratio (ESR) was calculated by the following equation, $ESR = (W_s - W_d)/W_d$, where W_s and W_d are the weights of the swollen hydrogel and the corresponding dried hydrogel, respectively.

The compressive and tensile measurements of the hydrogels were performed by using an Instron model 5567 testing machine (Instron Corporation, MA). The compression tests were conducted at a crosshead speed of 10% strain per min. 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-strain curves. The dissipated energy was defined as the area of one cyclic curve. Cyclic compression tests were conducted at a crosshead speed of 10% strain per min for four times. For uniaxial tensile tests, cylindrical hydrogel bars were tested at a crosshead speed of 80 $mm\ min^{-1}$. Cyclic tensile tests loading-unloading tests were performed immediately after the first loading-unloading cycle on fresh samples at a crosshead speed of 80 $mm\ min^{-1}$ for four times. The samples after cyclic tests were kept in silicone oil at different temperatures for different durations. Then cyclic tensile tests were conducted on these samples for a comparison with the previous data. The residual strain was measured by the equation, $\varepsilon = (e_t - e_0)/e_0$, where e_t is the length of hydrogels after storing t hours, and e_0 is the original length of the sample.

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

T (°C) \ Size (nm)	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)

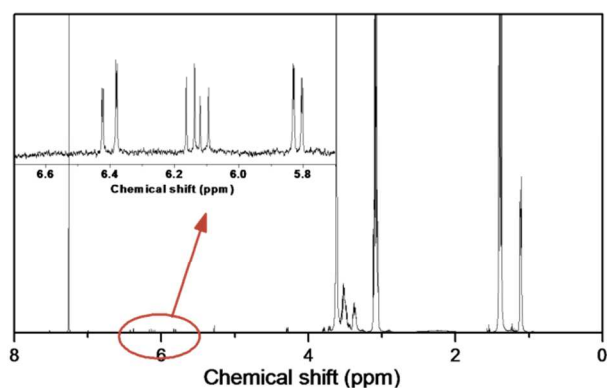


Figure S1. ^1H NMR of the synthesized F127DA.

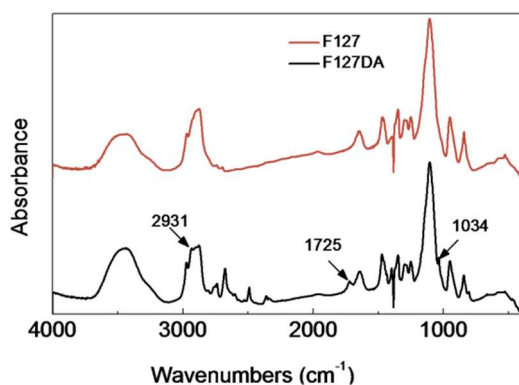


Figure S2. FTIR spectrum of the synthesized F127DA.

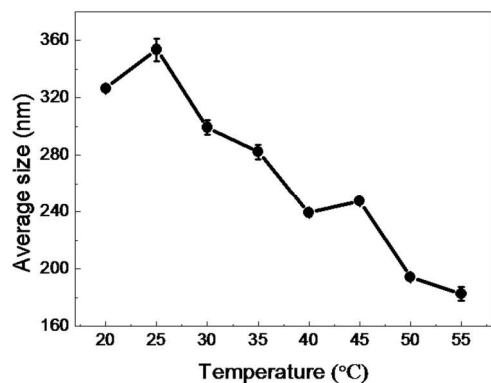


Figure S3. The average diameters of the F127DA micelles were measured at 20 °C to 55 °C by dynamic light scattering. The concentration of F127DA was 6×10^{-3} mol/L.

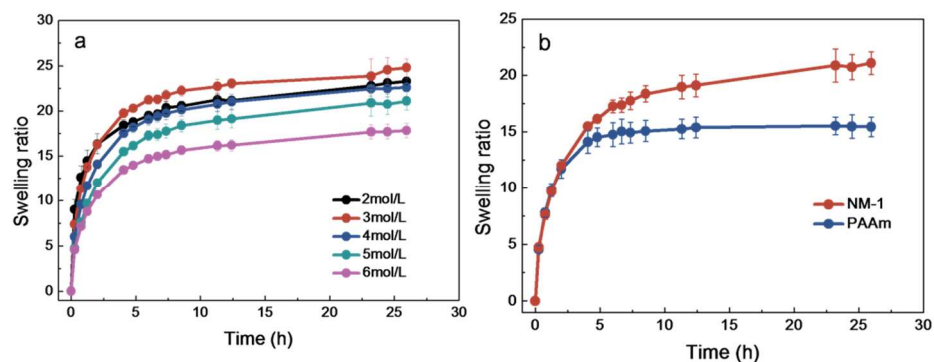


Figure S4. The swelling curves of (a) the NM gels with different C_{AAm} values and (b) PAAm gels and NM gels, the concentration of AAm were 5 mol/L, the concentration of cross-linker of both hydrogels were 6×10^{-3} mol/L, respectively.

REFERENCES

1. Lee, S.-Y.; Tae, G. *Journal of Controlled Release* 2007, 119, (3), 313-319.
2. Baskan, T.; Tuncaboylu, D. C.; Okay, O. *Polymer* 2013, 54, (12), 2979-2987.