Supplementary Information

Construction of Supramolecular Hydrogels Using Imidazolidinyl Urea as Hydrogen Bonding Reinforced Factor

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Experimental section

Materials

Poly(ethylene glycol) (PEG, M_n = 6000) was purchased from Aladdin and dried under vacuum at 120℃ for 2 h before use. 4,4'-Dicyclohexylmethane diisocyanate (HMDI), isophorone diisocyanate (IPDI) and diphenylmethane diisocyanate (MDI) were obtained from Wanhua Chemical Group Co., Ltd. without further purification. N,N-Dimethylformamide (DMF) was dried using solvent drying system before use. The other chemical reagents were purchased from Aladdin without further purification.

Characterizations

The FTIR spectra were recorded on a Perkin Elmer 100 serial FTIR spectrophotometer equipped with universal attenuated total reflectance (ATR) in the range of 400-4000 cm^{-1}. The ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using d_6-DMSO as solvent. GPC experiments in DMF were performed on a system equipped with an isocratic pump (waters 2414), a DAWN HELEOS 18-angle laser light scattering detector (also known as multi-angle laser light scattering (MALLS) detector (Wyatt Technology, Santa Barbara, CA) and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA).

Synthesis of the copolymers

The linear multi-block copolymers were synthesized according to the procedure described in Scheme 1. A typical synthetic procedure of PHI-3 copolymers is as follows.

Poly(ethylene glycol) (3 g, 0.5 mmol) was first dried under vacuum at 120 ^oC for 2 h.

Then it was dissolved in 10 g dry DMF, followed by the addition of the mixture of 4,4'-dicyclohexylmethane diisocyanate (0.5 g, 2 mmol) and dibutyltin dilaurate (DBTDL) (20 μL) in 6 g DMF. The pre-polymerization was conducted at 85°C for 1 h. Imidazolidinyl urea (0.6 g, 1.5 mmol) dissolved in 20 g dry (DMF) was then added, and the reaction was stirred at 85°C for another 4 h. The polymer was purified by precipitation in diethyl ether. The other polymers were prepared with the same procedure.

Hydrogel preparation

The aqueous solutions of the polymers with different concentrations were obtained by dissolving certain amounts of copolymers in deionized water at 60 ^{o}C. The solutions were cooled at ambient temperature for the hydrogel formation. In order to obtain the PMI hydrogel film, the polymer was dissolved in DMF or methanol with a certain concentration, and then the solution was poured into a culture dish, followed by slow evaporation of the solvent at 60°C. The dried PMI film was immersed in water at ambient temperature until swelling equilibrium to obtain the hydrogel film.

Swelling ratio

The dried PMI film was weighed (W_0), and incubated with 10 mL water at room temperature for different times. At predetermined time intervals, the film was removed from the solution, excess water removed using filter paper, and weighed (W_t). The swelling ratio was calculated by using the formula $(W_t\text{-}W_0)/W_0$.

Rheology testing

The rheological measurements of the hydrogels were performed by employing a TA

rheometer (DHR-2). To investigate the thermoresponsive behavior of the prepared hydrogel, temperature sweep experiments were conducted within the range of 0-60℃ (γ = 0.1%, ω = 10 rad/s). The strain amplitude sweep test (γ = 0.01%-2000%) with a constant frequency of 10 rad/s at 20 ^{o}C was performed. The frequency-dependent oscillatory shear rheology (γ = 0.1%) was also measured from 0.1 to 500 rad/s. For the characterization of self-healing properties, the aqueous solution of polymer was dropped between 20 mm parallel plates with a gap of 1000 μm. After the hydrogel formation, the alternate step strain sweep test was performed at a fixed angular frequency (ω = 10 rad/s) at 20 ^{o}C. Amplitude oscillatory strains were switched from small strain (γ = 0.1%) to subsequent large strain (γ = 1000%) with 100 s for every strain interval.

Macroscopic self-healing experiment

To evaluate the self-healing ability of the prepared hydrogel, two semi-disk shaped hydrogel samples were prepared (one was stained with rhodamine B). The two fragments of hydrogels in different colors were allowed to contact immediately and heal at room temperature for 1 min. A stainless steel tweezer was used to pick up the healed hydrogel to examine the healing capability.

Measurement of mechanical properties

The mechanical properties of hydrogels were tested on a WDW-05 electromechanical tester (Time Group Inc., China) with a 50 N load cell at room temperature in air environment. Three specimens were tested. For the uniaxial tensile test, all samples were cut into dumbbell-shaped films with a dimension of 16 mm×4 mm×0.8 mm and

the extension rate was set at 50 mm min^{-1}. For cyclic tensile tests, the hydrogel specimen was stretched to a pre-set maximum strain and then returned to the initial length. For the recovery test, the sample was relaxed for different times after the first cycle, and the cyclic testing was conducted again. The dissipated energy was calculated by the area under the loading-unloading curves.

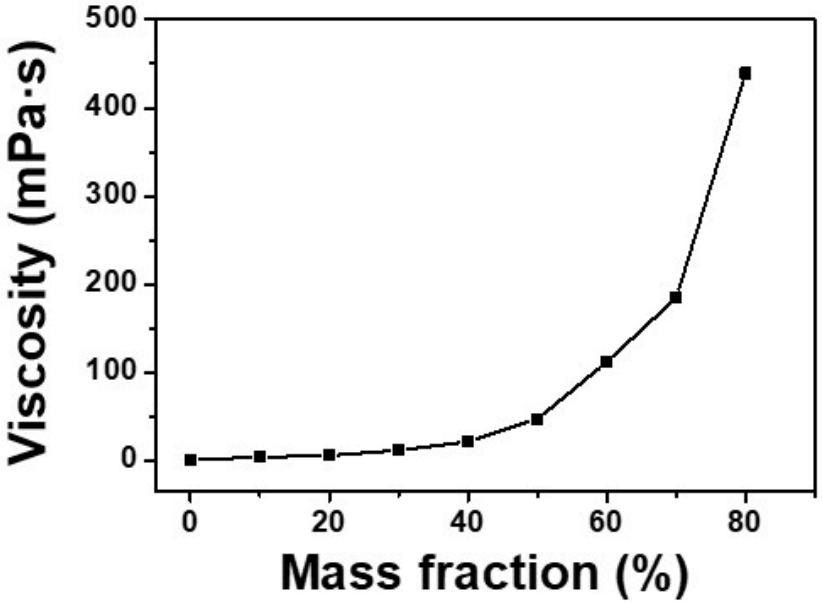

Fig. S1. The relationship between the mass concentration and viscosity of the IU aqueous solution.

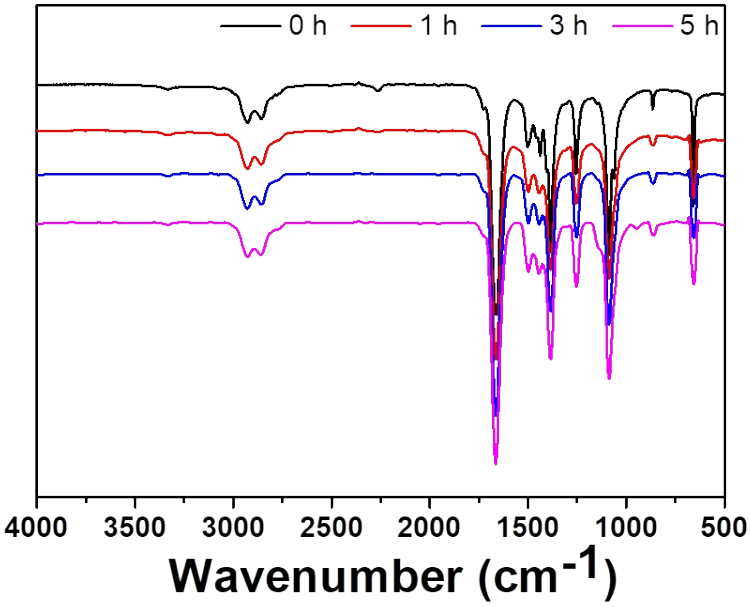

Fig. S2. FT-IR of PHI-1 solution at different times.

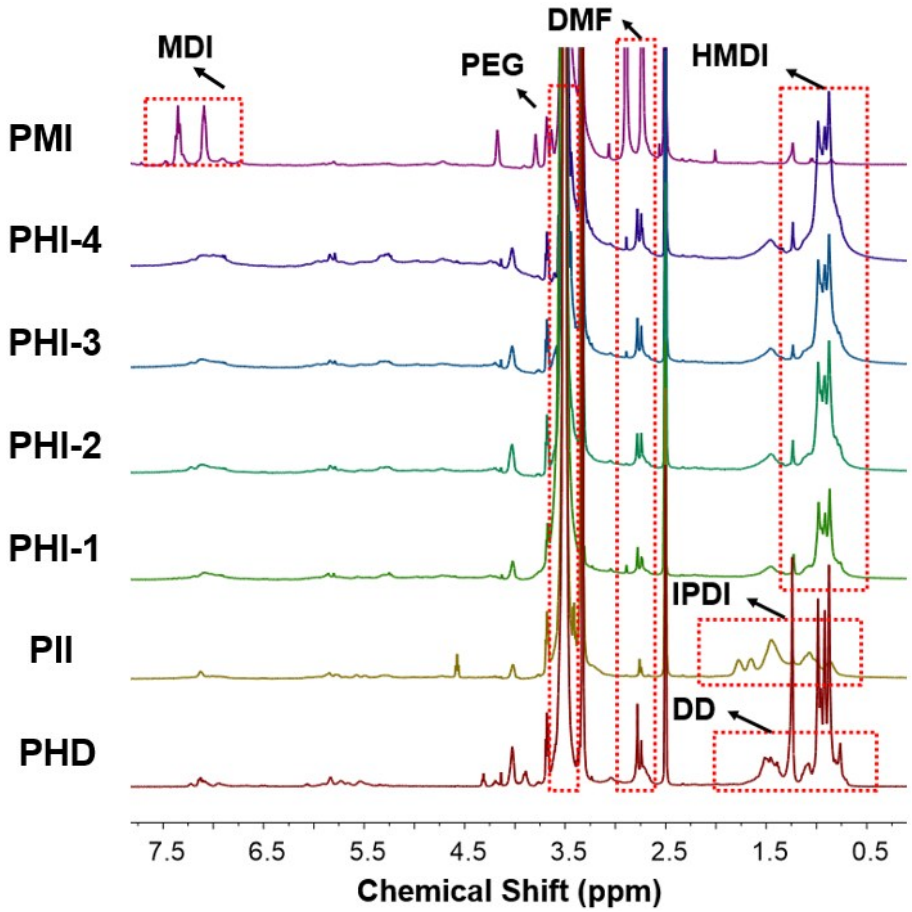

Fig. S3. ^{1}H NMR spectra of the polymers.

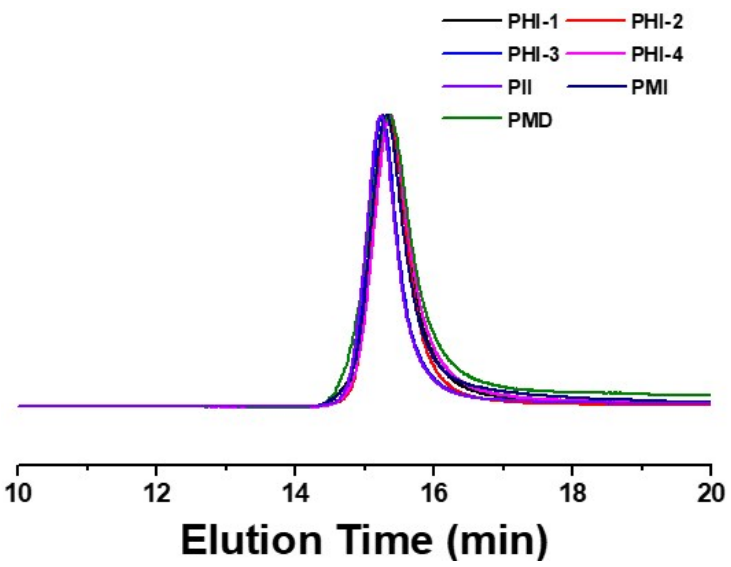

Fig. S4. GPC traces of the polymers.

Table S1. GPC analysis of the polymers.

Code	Composition	M_w (g/mol)	PDI
PII	PEG/IPDI/IU	530,000	2.5
PHI-1	PEG/HMDI/IU	560,000	1.7
PHI-2		480,000	1.9
PHI-3		460,000	2.2
PHI-4		470,000	2.9
PMI	PEG/MDI/IU	410,000	2.1
PHD	PEG/HMDI/DG	520,000	2.4

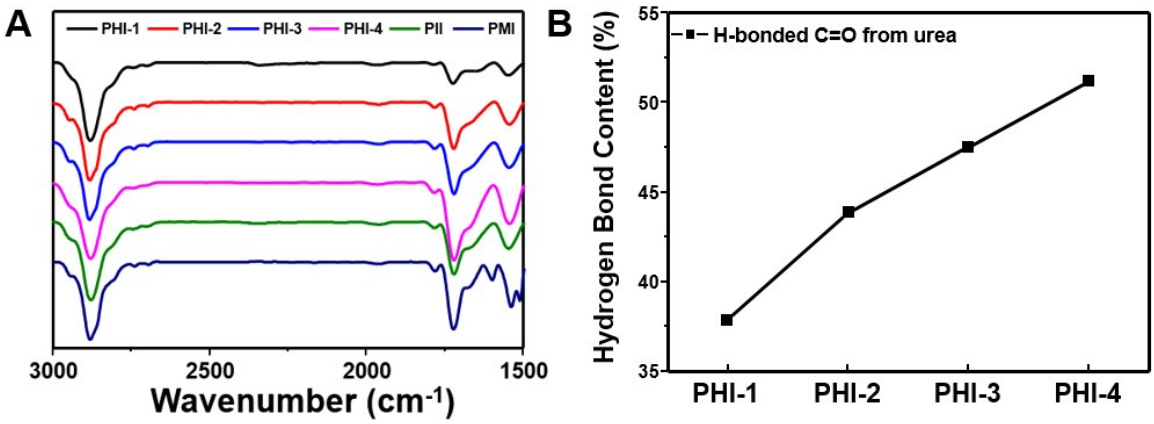

Fig. S5. A) FT-IR of the polymers. B) The content of the hydrogen bonds from urea in the PHI polymers.

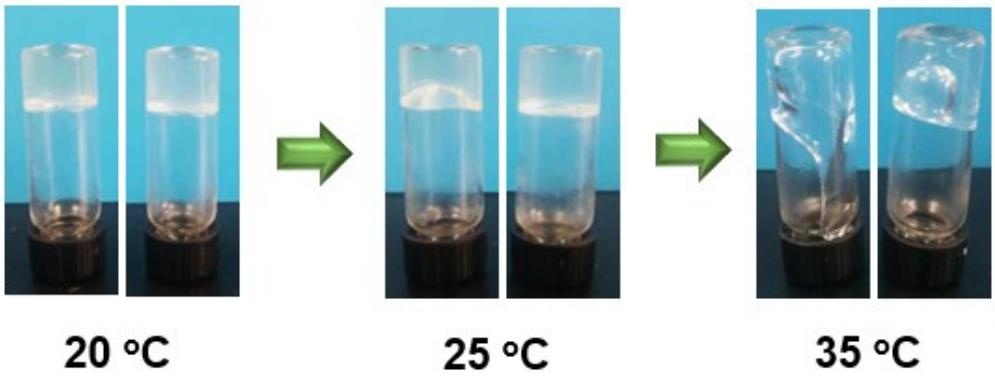

Fig. S6. Gelation test of supramolecular hydrogels with different concentrations of PHI-3 (left 25% (m/v); right 35% (m/v)) via tube inverting method at different temperatures.

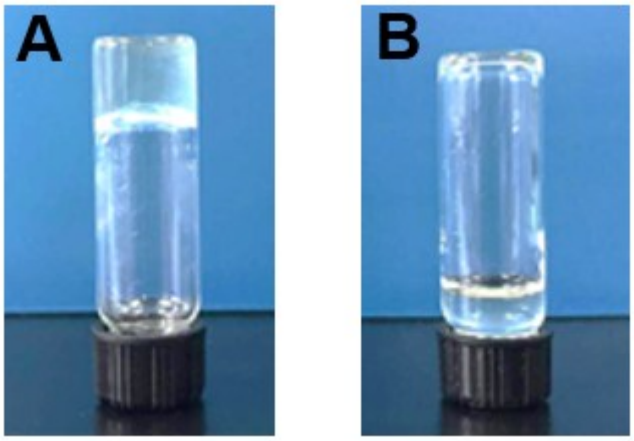

Fig. S7. Examination of the hydrogel formation in different mediums at 20 ^{o}C. The polymer concentration was 35% (m/v). A. in water; B: in 2M urea.

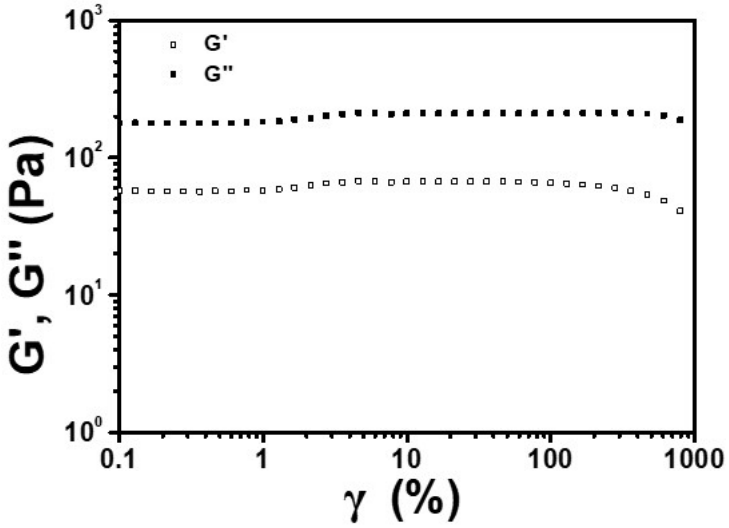

Fig. S8. Strain dependent rheology measurements of the PHD solution at 20 ℃.

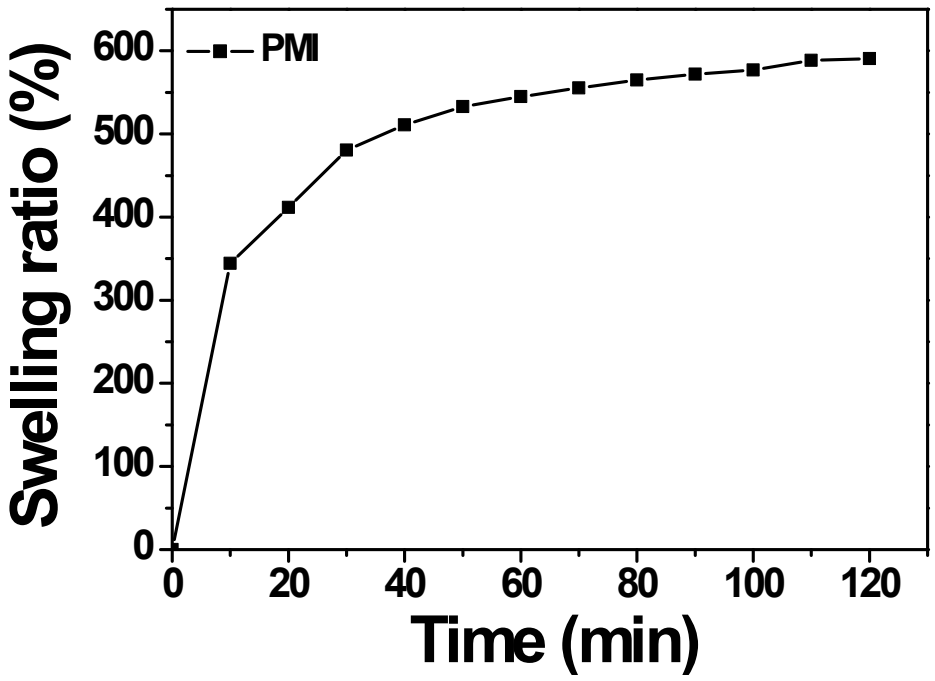

Fig. S9. Swelling ratios of PMI dried film in water.