

Electronic Supplementary Information

Improved Mechanical Properties of Polyacrylamide Hydrogels Created in the Presence of Low-Molecular-Weight Hydrogelator

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Materials and Methods

The compounds 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HEPP) and sodium dodecyl sulfate (SDS) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used without further purification. All solvents were purchased from Wako Pure Chemical Industries, Ltd. (WAKO) and used without further purification. Acrylamide (AAM, 98%, TCI) and methylene bisacrylamide (BIS, 95%, WAKO) were purified via re-crystallisation from methanol. The compound C8NG (white crystals) was synthesised following literature procedures.¹⁻³ Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K.).

Photoinduced radical polymerization was performed using a HLR100T-2 UV curing unit (equipped with a high-pressure mercury lamp, MIZUKA PLANNING Co., Ltd.) as the light source and a UVA 365 UV light metre (UVA radiometer, LUTRON ELECTRONIC ENTERPRISE CO., LTD.) as an illuminometer with optical filters {neutral density filter: ND20, ultraviolet optical filter (HOYA

Bandpass Filter): U-360, which passes around 360 nm light, HOYA CANDEO OPTRONICS CORPORATION).

Degree of swelling (q) of the hydrogel was estimated by use of the following equation,

$$q = (W_s - W_d) / W_d$$

where W_s is the weight of the swollen state of hydrogel after washing and W_d is the weight of the dried state of hydrogel obtained after removing of water by vacuum evaporation until a constant weight is obtained.

Solid-state ^{13}C CP/MAS NMR spectra were obtained using an AVANCEIII500 (125 MHz, Bruker BioSpin K. K.) spectrometer with a 4 mm CP/MAS probe and adamantane as the standard. Elemental analyses were performed using a JM10 elemental analyser (J-SCIENCE LAB CO., Ltd.). Infrared spectroscopy was performed on a Nicolet iS5 FT-IR (THERMO FISHER SCIENTIFIC K.K.) using the ATR method (ZnSe prism).

Compression tests were performed using an AGS-5KNG universal tester (SHIMADZU CORPORATION) at 5 mm/min. The measurement temperature and relative humidity were set at 25 °C and 60 RH, respectively.

SEM images were recorded with an SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel of hydrogel) was freeze-dried and placed on a conductive tape on the SEM sample stage. Pt, as a conductive material, was used as a coating on the sample (Pt coating is 10-nm thick).

Synthesis of polymer hydrogels from molecular hydrogels (Fig. S1)

Polymer hydrogels, or BIS cross-linked PAAm, were prepared using C8NG/SDS molecular hydrogels as a template via photoinduced radical polymerisation. First, a mixture (10 ml) composed of 2.00 M AAm (as a monomer), an aqueous solution containing crystalline C8NG at x wt% ($x = 0, 3, 5$ or 10), 0.5 wt% SDS, 0.02M BIS (as the cross-linker) and 2mM HEPP (as a water-soluble photoinduced radical initiator) in a 20 mL vial was heated in the dark at 100 °C for 30 min in a dry bath to dissolve the C8NG. The dissolved mixture was then allowed to stand at room temperature until the translucent C8NG/SDS molecular hydrogel was formed. The formation of the molecular hydrogel was confirmed using the vial inversion method. The mixture was allowed to stand for 1 h at room temperature and gelation was visually evaluated by inverting the vial. If the mixture did not drop after vial inversion, the mixture was considered to form a gel. Next, the photoinitiated radical polymerization of AAm and BIS with the transparent molecular hydrogel was performed by irradiating the mixture with 10 mW/cm² ultraviolet light for 5 min at 25 °C. After irradiation, the mixture of polymer and molecular hydrogels was immersed and washed in 70 °C water for 48 h to dissolve the C8NG (up to 3.0–10.0 wt%), SDS components of the molecular gel and any unreacted AAm, BIS and HEPP. The removal of the initiator, monomers, C8NG and SDS was confirmed by elemental analysis of the vacuum-dried hydrogels after washing, as described above.

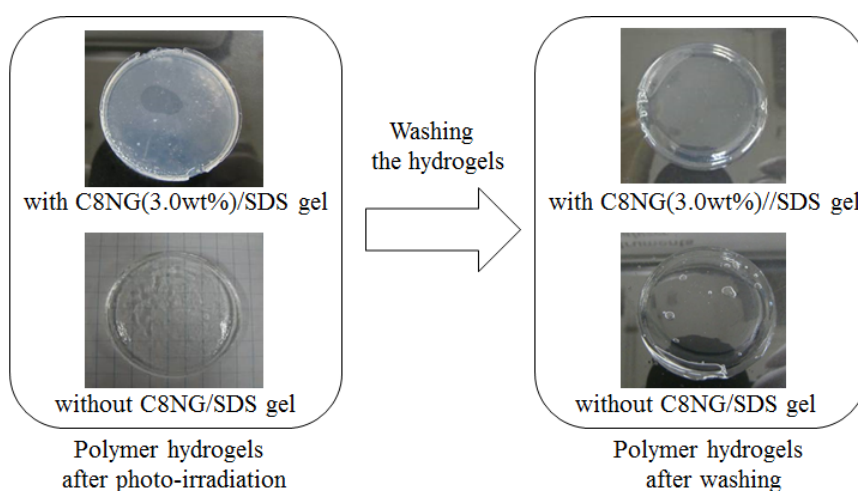


Fig. S1 Images of the polymer hydrogels (PAAm gel) before and after washing.

Estimation of the number of water molecules in the hydrogels (Tables S1 and S2)

Elemental analysis of the washed and vacuum-dried hydrogels was performed (Table S1). The number of water molecules present in the washed and dried hydrogels was then estimated on the basis of the elemental analysis results for each sample (Table S2). The data in Table S2 indicates that all of the unreacted monomers and molecular hydrogel components were removed from the polymer hydrogels through the washing process.

Table S1 Elemental analysis results for the washed and dried hydrogels

Conc. of C8NG	0.0 wt%	3.0 wt%	5.0 wt%	10.0 wt%
C/%	47.42	47.86	47.96	48.03
H/%	7.32	7.34	7.31	7.32
N/%	18.37	18.41	18.51	18.53

Table S2 Calculated values considering the presence of water in the washed and dried hydrogels

Conc. of C8NG	0.0 wt%	3.0 wt%	5.0 wt%	10.0 wt%
Estimated H ₂ O ^a				
/number of water molecules	30	26	25	24
C/% (estimated) ^b	47.39 (0.03) ^c	47.82 (0.04)	47.93 (0.03)	48.04 (0.01) ^d
H/% (estimated) ^b	7.36 (0.03)	7.33 (0.01)	7.32 (0.01)	7.31 (0.01)
N/% (estimated) ^b	18.31 (0.06)	18.48 (0.07)	18.52 (0.01)	18.56 (0.03)

a: Estimated data for the elemental analysis considering the presence of H₂O molecules provided above the line.

b: Estimated number of H₂O molecules in 100 AAm monomers with 1 BIS crosslinker.

c: Blue values: negative deviation from the EA in Table S1.

d: Red values: positive deviation from the EA in Table S1.

Fig. S2

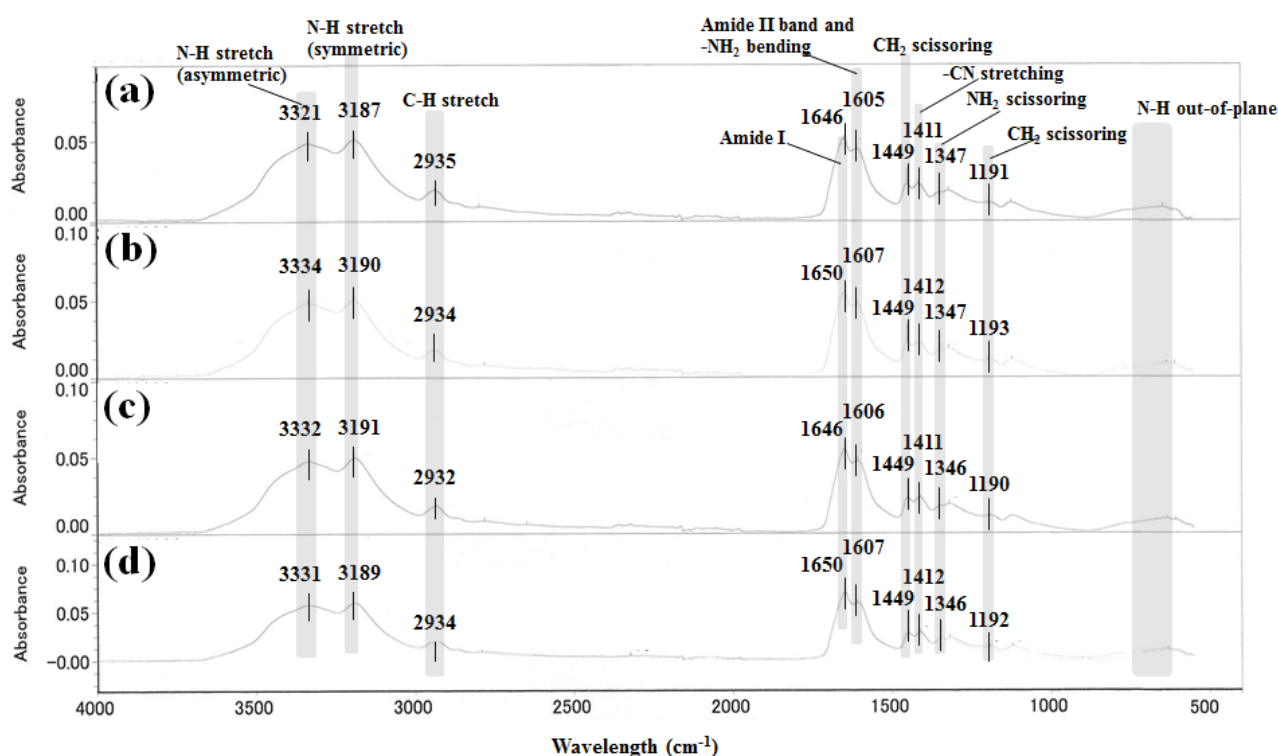


Fig. S2 FT-IR spectra of xerogels of the PAAM polymer hydrogels prepared using the molecular gel templates: (a) C8NG 0.0 wt%/SDS 0.5 wt%, (b) C8NG 3.0 wt%/SDS 0.5 wt%, (c) C8NG 5.0 wt%/SDS 0.5 wt% and (d) C8NG 10.0 wt%/SDS 0.5 wt%.

The peaks of FT-IR spectra are attributed as described in Fig. S2. These results correspond well with the results of PAAM in the literature.^{4,5} In addition, there no peak attributable to the stretching of the sulfur-oxygen single bond (1060 cm^{-1}) in SDS.⁶ From these results, it is thought that the removal of SDS was successfully performed and no significant chemical change in the molecular structure of PAAM gel thorough washing process was observed in the Ft-IR spectra. In addition, no chemical change in the molecular structure of PAAM both with and without templating was also observed in the FT-IR spectra.

Fig. S3

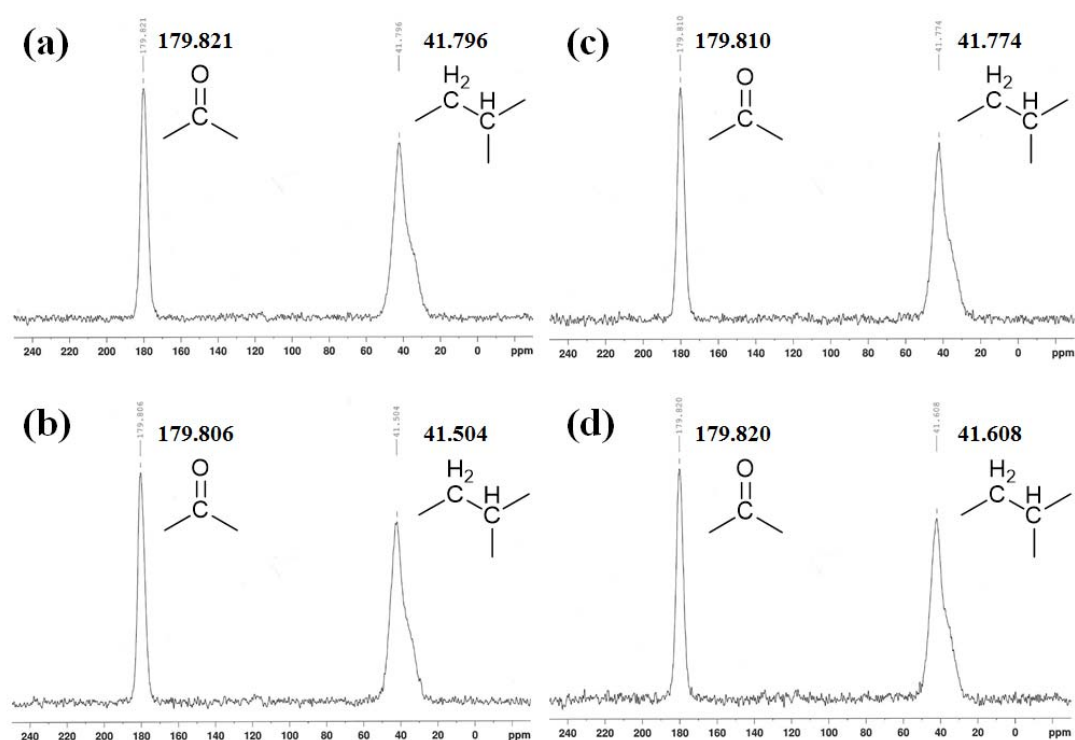


Fig. S3 Solid-state ^{13}C CP/MAS NMR spectra of xerogels of the PAAm polymer hydrogels prepared using the molecular gel templates: (a) C8NG 0.0 wt%/SDS 0.5 wt%, (b) C8NG 3.0 wt%/SDS 0.5 wt%, (c) C8NG 5.0 wt%/SDS 0.5 wt% and (d) C8NG 10.0 wt%/SDS 0.5 wt%.

In the spectra, the peak at ca. 180 ppm is attributed to the carbonyl carbon in the amide moiety and the peak at ca. 42 ppm is attributed to the CH_2 and CH in the main chain of PAAm. These results correspond well with the results of PAAm (M_w 5,000,000) in the literature obtained by ^{13}C CP/MAS measurement.⁷

Fig. S4

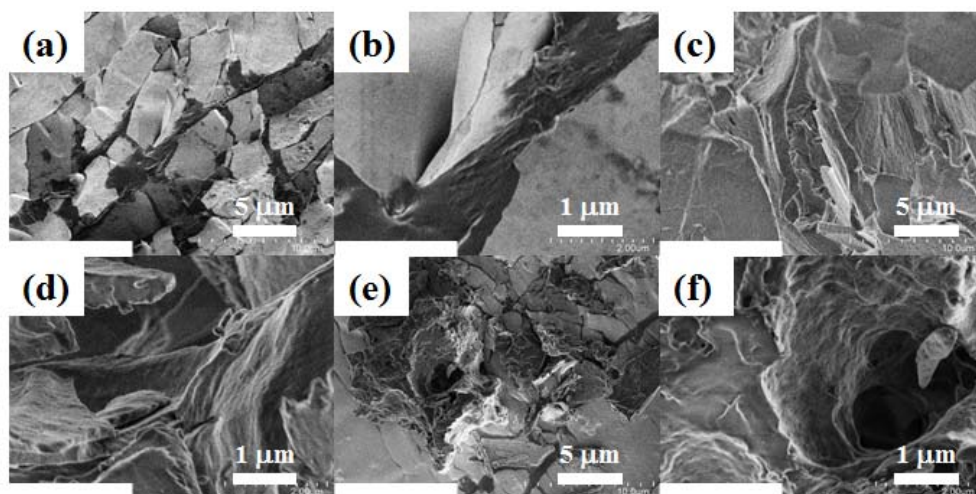


Fig. S4 SEM images of xerogels prepared from the corresponding C8NG/SDS molecular hydrogels: (a and b) C8NG 3.0 wt%/SDS 0.5 wt%, (c and d) C8NG 5.0 wt%/SDS 0.5 wt% and (e and f) C8NG 10.0 wt%/SDS 0.5 wt%.

Acknowledgments

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