Supporting Information

Regulation of Swelling Behaviour While Preserving Bulk Modulus in Hydrogels via Surface Grafting

Taihei Nishimoto, Aya M. Akimoto,* Takafumi Enomoto,
Chia-Hsuan Lin, Shyh-Chyang Luo, and Ryo Yoshida*

1. Experimental

1.1 Materials

N,N-dimethylacrylamide (DMAAm) and 1*H*,1*H*,5*H*-octafluoropentylacrylate (OFPA) were purchased from Fujifilm Wako Pure Chemical Industries (Osaka, Japan) and Tokyo Chemical Industries (Tokyo, Japan), respectively. The monomers were purified by passing them through an alumina column. *N*-(3-aminopropyl)methacrylate hydrochloride (NAPMAm) was purchased from Polyscience (Warrington, PA, USA) and used as received. The ATRP initiator, 2-bromoisobutyrate *N*-hydroxysuccinimide ester (BiB-NHS), was synthesized according to a previous paper [S1]. Trichloro(octadecyl)silane was purchased from Sigma-Aldrich (St. Louis, MO) and used as received. PFQNM-LC-A-CAL tips were purchased from Bruker (Billerica, MA, USA). All other reagents were purchased from Fujifilm Wako Pure Chemical Industries and used as received.

1.2 Preparation of base gels

DMAAm, NAPMAm, *N,N'*-methylenebis(acrylamide) (MBAAm), and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were dissolved in water. The solution was cooled in an ice bath and degassed by Ar. Subsequently, a solution of ammonium persulfate (APS) in water was added to the degassed solution, and the mixture was placed into the iced glass molds. The final feeding concentrations of $[DMAAm]_0$, $[TEMED]_0$, and $[APS]_0$ were 1.88 M, 20 mM, and 20 mM, respectively, and the fed molar ratio of $[DMAAm]_0/[NAPMAm]_0/[MBAAm]_0$ was 94/5/1. After gelation at 4 °C overnight, the prepared gels were dialyzed in water for over 3 d. Gels were formed using 40-μL glass capillaries (φ = 1.02 mm) for observation of the swelling behaviour and glass molds of 65 mm × 45 mm × 2 mm were used for the other experiments.

1.3 Preparation of IG gels

The base gels were immersed in a mixture of water and pyridine. Subsequently, ATRP initiator (BiB-NHS) and initiator-like structural compound (*N*-succinimidyl acetate) dissolved in dimethyl sulfoxide (DMSO) were added, and the mixture was stirred for 5 min. The gels were purified by dialysis in water for more than 3 d. The final volume ratio of water/pyridine/DMSO was 9/0.5/0.5, and the total fed concentration of the ATRP initiator and initiator-like structural compound was 2.25 mM. Hereafter, the obtained gels are referred to as IGχ, where χ denotes the feed molar ratio (mol%) of the ATRP initiator.

1.4 Preparation of FG gels

IG gels were immersed in a solution of OFPA, $CuBr_2$, tris[2-(dimethylamino) ethyl] amine (Me_6TREN), ascorbic acid, and

dimethylformamide. The mixture was stirred for 17 h at 40 °C. The fed concentration of $[OFPA]_0$ was 1.25 M, and the fed molar ratio of $[OFPA]_0/[CuBr_2]_0/[Me_6TREN]_0/[\text{ascorbic acid}]_0$ was 500/1/6/6. Subsequently, the gels were purified by dialysis in water for more than 3 d.

1.5 Measurement of the Total Amount of Bromine Introduced onto IG Gels

The total number of Br atoms derived from the ATRP initiator that chemically bonded to the surface area of the IG gels was measured by elemental analysis. IG gels were analyzed by ion chromatography (ICS-1600, Thermo Fisher Dionex, Thermo Fisher Scientific K.K., Waltham, MA).

1.6 Attenuated Total Reflectance (ATR)/Fourier Transform Infrared (FTIR) Measurement

The ATR-IR spectra of water and FG gels were recorded by IRSprit (Shimadzu, Co., Japan) with a diamond ATR accessory (GladiATRTM, PIKE technologies, Inc., Fitchburg, WI). SG gel samples were prepared in swollen states and scanned against an air background at wavenumbers of 4000–800 cm^{-1} with a resolution of 4.0 cm^{-1}.

1.7 Measurements of Bulk Young's Moduli of FG Gels

The stress (σ) and strain (ε) of FG0, FG25, FG50, and FG100 were obtained by pulling at a tensile speed of 5 mm/min until breakage and measuring the displacement in terms of load and distance between grade lines using a tensile test machine AGS-X (Shimadzu, Kyoto, Japan). The Young's modulus (E) was calculated from the stress–strain curve.

1.8 Observation of Swelling Behaviour of FG Gels.

Cylindrical FG0, FG25, FG50, and FG100 were first dried in air at 25 °C for 1 d and then immersed in water and kept at 21 °C. The time evolution of the size was observed by optical microscopy (VHX-900, Keyence, Osaka, Japan). The diameters of these gels were measured using ImageJ software (National Institutes of Health, Bethesda, MD).

1.9 Observation of Surface Young's Moduli of FG Gels

FG0, FG25, FG50, and FG100 immobilized on glass slides were prepared for atomic force microscopy (AFM) measurements to prevent undesired movement of the sample during the measurement. The glass slide was treated with a UV-O_3 cleaner (UV253H, Filgen, Inc., Japan) for 15 min (28 mW/cm^2) and then a solution of 3-methacryloxypropyltrimethoxysilane (MPTMS, 1 v/v%) in toluene for 18 h. The gels were fabricated on the MPTMS-modified glass slides according to the aforementioned method. The Young's moduli of the gels were determined by AFM measurements (Bioscope Resolve system, Bruker, USA). The PeakForce QNM mode in the fluid was chosen for the experiment operations with precalibrated PFQNM-LC-A-CAL tips (spring constant: 0.075–0.092 N/m, frequency: 45 kHz). A 1 μm × 1 μm image was usually obtained at a scan rate of 0.5 Hz under arbitrary operating conditions. The force volume mode was used to collect 16 force–distance curves (4 × 4 lines under 1 μm × 1 μm scan size) of each specimen under various preparation conditions. The histograms of the Young's Moduli were formed from 65,536 (256 × 256) points in a scan size of 1 μm × 1 μm using AFM NanoScope Analysis software v1.8.

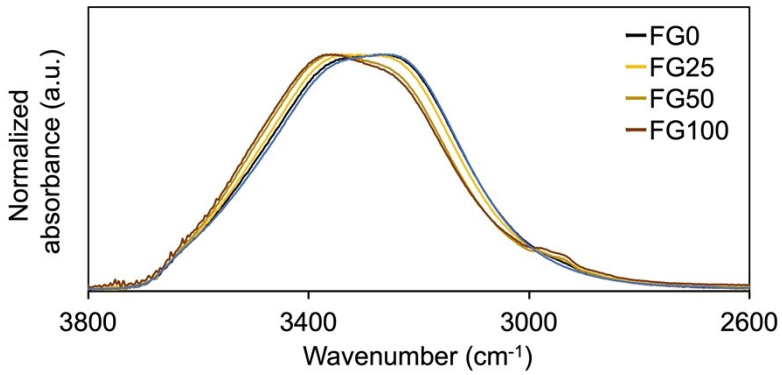

Fig. S1 Normalized ATR/FTIR spectra of the surface-grafted gels. Normalization of the spectra was performed within the range of 2600–3800 cm^{-1}.

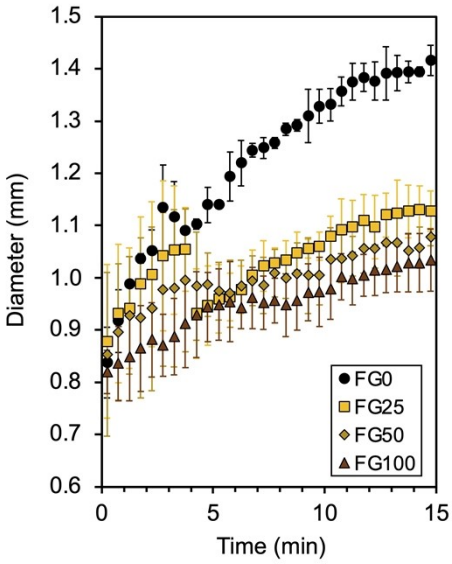

Fig. S2 Swelling behaviour of dried FG0, FG25, FG50, and FG100 upon immersion in water for 15 min. Data were obtained from three separate experiments. This graph shows Fig. 4 (a) in the manuscript with error bars.

Reference

[S1] Conradi, M.; Junkers, T. Fast and Efficient [2 + 2] UV Cycloaddition for Polymer Modification via Flow Synthesis. *Macromolecules* **2014**, *47*, 5578−5585.