Supporting Information

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm) was kindly provided by KJ Chemicals (Tokyo, Japan) and purified by recrystallization in toluene/hexane. *N*-(3-Aminopropyl)methacrylamide (NAPMAm) was purchased from Polyscience (Warrington, PA) and used as received. *N*,*N*′-methylenebisacrylamide (MBAAm) was purchased from Acros Organics (Geel, Belgium) and used as received. Ammonium persulfate (APS) was purchased from Kanto Chemical (Tokyo, Japan). 8-Anilino-1-naphthalenesulfonic acid (ANS) and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) were purchased from Tokyo Chemical Industry (Tokyo, Japan). *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), ethyl 2-bromoisobutyrate (EBiB), copper(II) bromide ($CuBr_2$), dehydrated dimethyl sulfoxide (DMSO), and dehydrated *N*,*N*-dimethylformamide (DMF) were purchase from Wako Pure Chemical Industries (Osaka, Japan). Water used in this study was purified by a water purifier (WA200, Yamato Scientific, Tokyo, Japan). 2-Bromoisobutanoic acid *N*-hydroxysuccinimide ester (abbreviated as NHS-initiator) and 5-acryloylfluorescein (abbreviated as FLAAm) were synthesized as reported.[S1,S2] 0.2 M Phosphate buffer (pH 7.5) was prepared by mixing disodium hydrogenphosphate and sodium dihydrogenphosphate (purchased from Wako Pure Chemical Industries) in aqueous solution. 40-μL glass capillaries (inner diameter = 1.02 mm) were purchased from Hirschmann Laborgeräte (Eberstadt, Germany).

Synthesis of the cylindrical poly(NIPAAm-*r*-NAPMAm) gel

NIPAAm (0.806 g), NAPMAm (0.0268 g), MBAAm (0.0347 g), and TEMED (11.2 μL) were dissolved in water (4.5 mL), and the solution was degassed by Ar bubbling and cooled to 0 °C. Then a solution of APS (0.0171 g) in water (500 μL) was added, and the pre-gel solution was placed into 40-μL glass capillaries (ϕ = 1.02 mm). The loaded capillaries were maintained at 4 °C for 8 h. After this time, the cylindrical poly(NIPAAm-*r*-NAPMAm) gels (length = 20–30 mm) were obtained. The gels were purified by dialysis in water for one week.

Immobilization of the ATRP initiator on the surface of the poly(NIPAAm-*r*-NAPMAm) gel

Poly(NIPAAm-*r*-NAPMAm) gels were immersed in 0.2 M phosphate buffer (pH 7.5, 27 mL) and heated to 60 °C, causing gel shrinkage. NHS-initiator (0.790 g) dissolved in dimethylsulfoxide (3 mL) was then added, and the mixture was stirred for 5 min. Then, the gels were purified by dialysis in water for one week.

Grafting of PNIPAAm to the surface of the poly(NIPAAm-*r*-NAPMAm) gel

Initiator-immobilized poly(NIPAAm-*r*-NAPMAm) gels were immersed in a solution of NIPAAm (0.679 g), Me_6TREN (160 μL), $CuBr_2$ (13.4 mg), ascorbic acid (52.9 mg), and H_2O (30 mL), and the mixture was stirred for 3 h at 25 °C. Then, the gels were purified by dialysis in water for one week. Unmodified poly(NIPAAm-*r*-NAPMAm) gels and PNIPAAm surface-grafted poly(NIPAAm-*r*-NAPMAm) gels are abbreviated as NG gel and SG gel, respectively.

Differential scanning calorimetry of the surface-grafted gel

To measure the lower critical solution temperature (LCST) of the grafted polymer and the volume phase transition temperature (VPTT) of the polymer network, differential scanning calorimetry (DSC) was performed for both SG and NG gels under an N_2 gas atmosphere (using a DSC1, Mettler-Toledo, Tokyo, Japan). The temperature was raised from 10 to 60 °C at a heating rate of 10 °C/min. The samples were prepared by cutting the cylindrical gels into fragments, each weighing several milligrams. The LCST and VPTT were defined by the peak tops of endothermic peaks.

Cross-sectional observation of the surface-grafted gel

To evaluate the spatial distribution of the surface-grafted polymer on the gel, FLAAm was copolymerized with NIPAAm by ARGET ATRP to graft a fluorescent polymer to the SG gel. Initiator-immobilized poly(NIPAAm-*co*-NAPMAm) gels were immersed in the mixture of NIPAAm (0.678 g), FLAAm (2.40 mg), Me_6TREN (160 μL), $CuBr_2$ (13.4 mg), ascorbic acid (52.9 mg), *N*,*N*-dimethylformamide (15 mL), and water (15 mL), and the mixture was stirred for 3 h at 0 °C. Then the gels were purified by dialysis in DMF for 3 days, followed by dialysis in water for 4 days. This gel is abbreviated as FSG gel. The cylindrical FSG gel was sliced into a disk shape (thickness < 1 mm) and placed on a glass plate with the flat area face-up. Then the gel was observed by fluorescence microscopy (λ_{ex} = 494 nm, λ_{em} = 521 nm) (DFC 360FX, Leica, Mannheim, Germany).

Measurement of the swelling ratio of the gels

NG and SG gels were immersed in water and maintained for 1 h at each temperature, ranging from 25 to 50 °C in 1 °C steps. Then the gels were observed by optical microscopy (VHX-900, Keyence, Osaka, Japan). The diameters of the gels were measured using Image J. Swelling ratios were calculated by dividing the diameter of the swollen gel by the inner diameter of the mold glass capillary. To visualize the hydration and dehydration of the polymer network, NG and SG gels were immersed in aqueous solutions containing ANS (10 mg/L) overnight, and the gels were subsequently observed by fluorescence microscopy at 25 °C (below volume phase transition temperature (VPTT)) and 40 °C (above VPTT) in the ANS solution (λ_{ex} = 388 nm, λ_{em} = 470 nm). Images were recorded after the gels were maintained for 10 min at each temperature.

Kinetic analysis of shrinking and swelling of the gels

For shrinkage analysis, NG and SG gels were immersed in water and kept at 25 °C overnight. Then, the gels were placed in hot water (40 °C), and volume changes were observed using an optical microscope. The diameters of these gels were measured using Image J. Swelling analysis was done in the same way, but reversing the temperature and drying the gels before immersing them in water at 40 °C.

References

S1 M. Conradi and T. Junker, *Macromolecules*, 2009, **42**, 6348.

S2 M. J. Serpe, C. D. Jones and L. A. Lyon, *Langmuir*, 2003, **19**, 8759.

SUPPORTING FIGURES

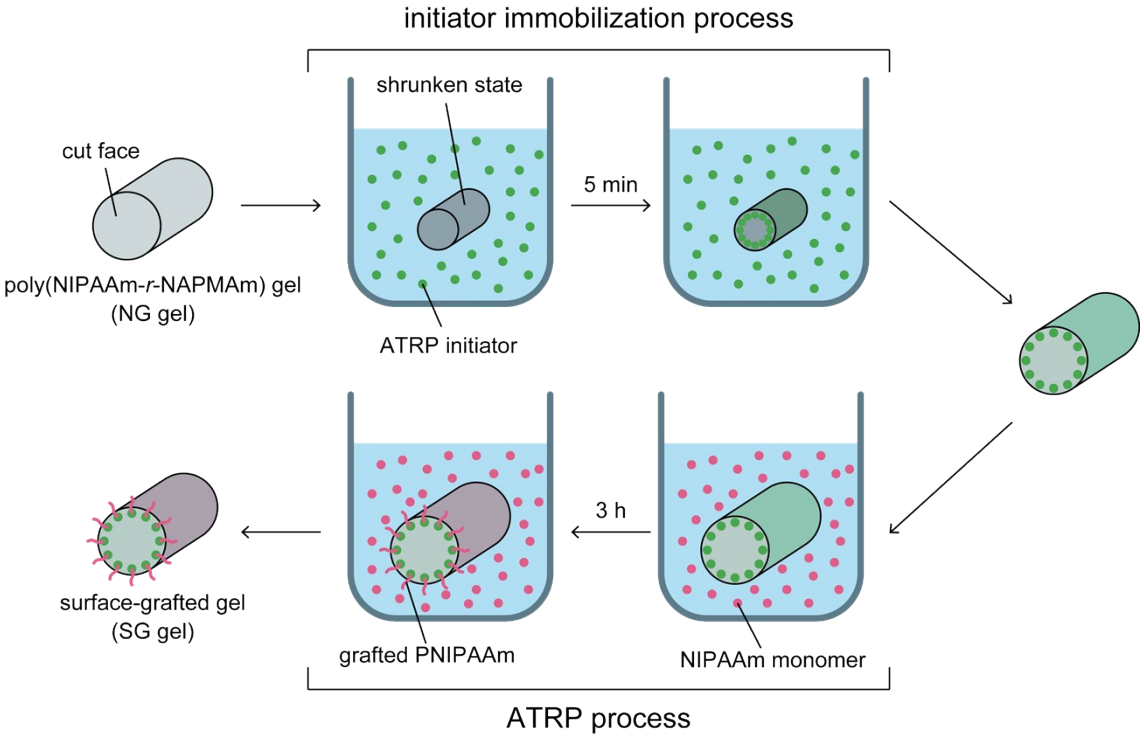

Fig. S1 Schematic image of synthetic process of surface-grafted gels (SG gel). First poly(NIPAAm-r-NAPMAm) cylindrical hydrogels were synthesized (upper left). Then ATRP initiators were immobilized only to the surface of the gels by reacting at higher temperature than VPTT (upper middle two). Finally, PNIPAAm was grafted from the initiators by ARGET ATRP (lower middle two), and the surface-grafted hydrogels were obtained (lower left).

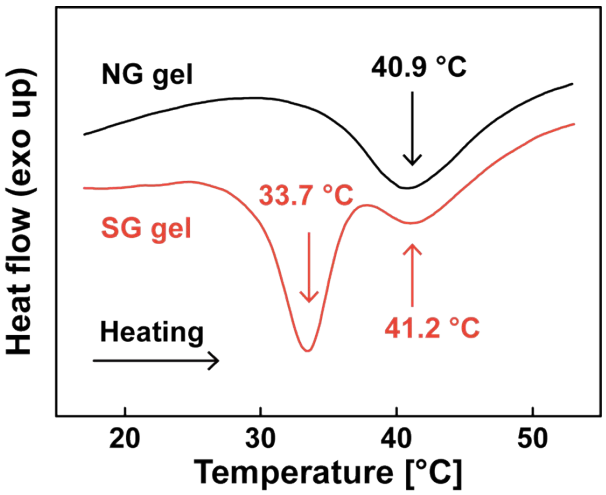

Fig. S2 DSC thermograms of the SG gel (red line) and NG gel (black line).

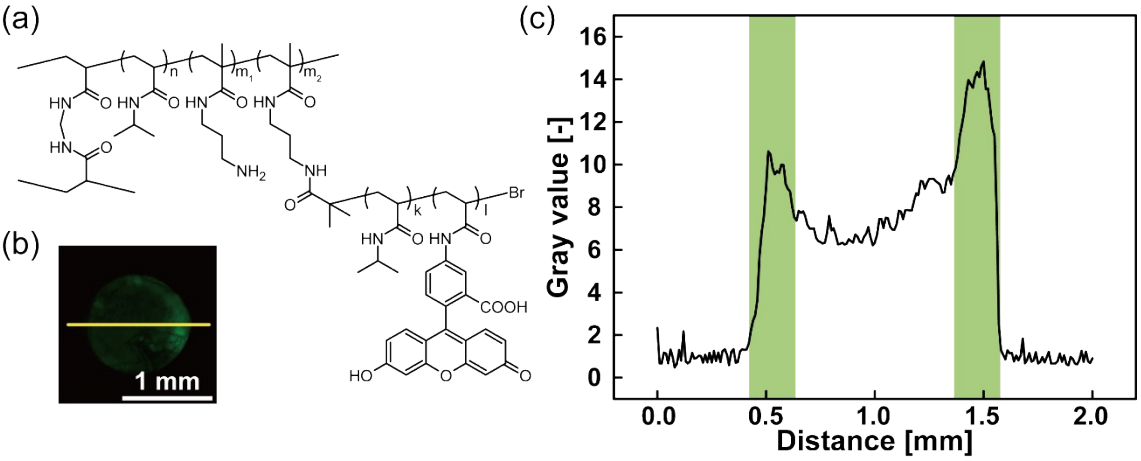

Fig. S3 (a) Chemical structure and (b) fluorescence image of the FSG gel. (c) The distribution of fluorescence intensity across the diameter of the gel disk (shown by the yellow line in (b)).

SUPPORTING MOVIE

Shrinking behavior of NG gel (left) and SG gel (right) induced by temperature increase (25→40°C) (played at 150x speed). At approximately 3 s, one crack started to appear lengthways and one breadthways at around 1/4th distance from the bottom.