Supplementary Information

A surface-grafted hydrogel demonstrating thermoresponsive adhesive strength change

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EXPERIMENTAL

Materials.

N,*N*-dimethylacrylamide (DMAAm) was purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan) and purified by passing it through an alumina column. *N*-(3-aminopropyl)methacrylate hydrochloride (NAPMAm) was purchased from Polyscience (Warrington, PA, USA) and used as received. *N*-isopropylacrylamide (NIPAAm) was kindly provided by KJ Chemicals (Tokyo, Japan) and recrystallized in toluene/hexane before use. The initiator of atom transfer radical polymerization (ATRP), 2-bromoisobutyrate *N*-hydroxysuccinimide ester (BiB-NHS), was synthesized based on the method published in a previous paper.[S1] All other reagents were purchased from FUJIFILM Wako Pure Chemical Co. and used as received.

Preparation of NG (non-grafted) gels

DMAAm (2.788 mL), NAPMAm hydrochloride (268.0 mg), *N*,*N*-methylenebis(acrylamide) (MBAAm) (231.3 mg), and *N*,*N*,*N'*,*N'*-tetramethylethylene (TEMED) (45.0 μL) were dissolved in pure water (19 mL). The solution was placed in an ice bath and bubbled for 30 min to replace oxygen in the solution with argon. Next, holes of dimensions of approximately 4 cm × 6 cm were cut using a cutter into 2 mm- thick silicone sheets, and the sheets were placed between glass slides that had been irradiated with UV/ozone for 10 min on both sides and fixed with vinyl tape. Ammonium peroxodisulfate (APS) (68.5 mg) dissolved in 1 mL of pure water was added to the prepared solution containing monomers, mixed, and rapidly poured into the holes of the silicone sheet (2 mm thick). After carefully removing the glass slide to expose the gel, a cylindrical mould (7 mm in diameter) was used to cut a disc of the gel, which was dialyzed in pure water for 2 d.

Preparation of the ATRP initiator-grafted gel

The NG gel was immersed in a mixture of pure water (28 mL), BiB-NHS (79.2 mg), and pyridine (1 mL) for 5 min at 25 °C. The unreacted ATRP initiator was removed via dialysis against water for two days.

Preparation of the surface-grafted (SG) gel

The ATRP initiator-grafted gel was immersed in 20 mL of an aqueous solution containing NIPAAm (181.1 mg), $CuBr_2$ (28.9 mg), tris[2-(dimethylamino)ethyl]mine (Me_6TREN) (107 μL),

and L-ascorbic acid (35.3 mg), and activators regenerated by electron transfer for ATRP (ARGET ATRP) reaction for 3 h at 25 °C. The unreacted reagents were removed via dialysis against water for five days.

Confocal laser microscopy with the Nile Red

The SG gel was immersed in an aqueous solution containing Nile Red (2 μM) for 1 week. Thereafter, the SG gel was cut at the cross section with a scalpel and placed on a stage heater controlled at 25 or 40 °C in water. After 30 min of incubation, the gel was observed using a confocal laser microscope (λ_{ex} = 488 nm, λ_{em} = 588-678 nm)) (FV3000, Olympus, Co., Tokyo, Japan).

Movie S1

The movie (165x speed) showing the SG gel at 25 °C being placed on a stage heater set at 40 °C for 30 min.

Contact angle measurements

The static contact angle was measured using a DMs-401 automatic contact angle meter and FAMAS analysis software (Kyowa Interfaces Science, Co., Ltd., Japan) by dropping a drop of water on the NG and SG gel surfaces on a heater controlled at 25 or 50 °C in air. The contact angles were recorded immediately after a drop of water (2 μL) was gently dropped onto the samples.

Evaluation of adhesive strength

The adhesion strength between the gel and Bakelite plate was measured using the apparatus developed in this study. Immediately before to performing the adhesion measurement, the weight of the gel sample (w) was measured on a precision balance and the water content of the gel sample was calculated by using the weight of the gel after drying (w_{dry}) and calculating as following equation 1.

$$Water\ content\ (\%) = \frac{(w - w_{dry})}{w} \times 100 \quad (1)$$

A disc gel piece was fixed to the parallel-plate spring of the device at the time of measurement. The size of the gel surface fixed to the parallel-plate spring was measured using calipers to define the adhesive area. A Bakelite plate to be adhered was placed on a stage with a motor, and the position of the motor was adjusted to adhere to the hydrogel piece fixed to the parallel plate spring. Subsequently, measurements were performed at an ascent/descent speed of 2.0 mm/s. The conditions were fixed at an ascent distance of 1.5 mm and a descent distance of 6.0 mm. Holding time for adhesion was 10 seconds. During the measurements, a Bakelite plate was placed on top of a plate heater, and the temperature was regulated.

Reference

S1) K. Matsukawa, T. Masuda, A. M. Akimoto and R. Yoshida, *Chem. Commun*., 2016, **52**, 11064.