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Free reprocessability of tough and self-healing hydrogels based on polyion complex

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Supporting information

Experimental section

Materials

Commercially available anionic monomer, sodium *p*-styrenesulfonate (NaSS); cationic monomer, 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC); UV initiator, α-ketoglutaric acid; and NaCl were all purchased from Wako Pure Chemical Industries, Ltd. Iron oxide powder (Fe_3O_4) was purchased from Kanto Chemical Co., Inc. All materials were used as received. Millipore de-ionized water was used in all of the experiments.

Measurements

Tensile test. The tensile tests were carried out on a commercial tensile tester (Tensilon RTC-1310A, Orientec Co.) at a stretch velocity 100 mm/min. The samples (sheets and films) were cut into dumbbell-shape with initial gauge length 12 mm (L_0). The nominal stress, σ, was estimated from the load divided by the cross-sectional area of the undeformed sample. The strain, ε, was estimated from the clamp displacement divided by L_0. The Young's modulus, E, was estimated as the slope of the stress-strain curve within a strain range of ε=0.03-0.1. The work of extension was estimated by the area under the stress-strain curve. The values of all the mechanical properties were calculated as averages for at least three specimens. All of the measurements were performed in air at a room temperature of about 25 °C.

GPC Analysis. Molecular weights (M_w) of PNaSS and PMPTC were determined by GPC measurement using a HITACHI L-7110 pump and a HITACHI 7490 RI detector, using a method the same as in a previous study[1] with a slight modification: a buffer solution of

0.1M Na_2SO_4 was used as an eluent at 40 °C, and flow rate was 0.4 mL/min.

Synthesis of polyion-complex (PIC) hydrogel

The PIC hydrogel PMPTC/PNaSS was synthesized by sequential homo-polymerization of cationic and anionic monomers, according to our previous report.[2] PMPTC was first synthesized from an aqueous solution of 1 M MPTC containing 0.05 mol% initiator, 2-oxoglutaric acid by UV light irradiation (light intensity ~ 4 mW/cm^2) for 8 h. The achieved PMPTC was dried and made into powder. Next the powder was mixed with NaSS monomer with the charge fraction of the second monomer NaSS, f =[NaSS]/([MPTC]+ [NaSS])=0.5. After well dispersed with the addition of 0.5 M NaCl to form a solution of [MPTC]+[NaSS]=1.5 M at 60 °C, 0.1 mol% initiator is added relative to the second monomer and the solution was polymerized by UV light for 8 h in a reaction cell consisting of a pair of glass plates with 1.5 mm spacing. The as-prepared hydrogel was then dialyzed in large amount of water to remove their mobile counter ions and co-ions from the polymers. After dialysis, the thickness of the sample shrank and the equilibrium hydrogel was obtained.

Dissolving the PIC hydrogel into solution: The PIC hydrogel of PMPTC/PNaSS was cut into small pieces and then completely disassociated into 4M NaCl to produce a uniform solution at 60°C. PIC solutions with different polymer concentrations from 20 to 80 g/L were prepared.

Reforming thin film by curtain coating: A small amount of PIC solution with 50 g/L polymer concentration was dropped on a glass sheet, and immediately the glass sheet was tilted slightly to form uniform coating layer on the glass surface (see Fig. 2a-I). Then, the

coated glass was put into a large amount of water for dialysis. After changing water every day for at least 3 days, a tough PIC thin film was obtained.

Reforming sheet by mold-dialysis: The PIC solution of 80 g/L polymer concentration was poured into a mold consisting of a pair of multi-hole plastic sheets (d: 1.0 mm) with 3 mm spacer and two selectively permeable membranes (see Fig. 2a-II)). Then, the mold was immersed into water and dialyzed by a large amount of water to remove their mobile counter ions and produce the sheet (changing water every day for at least 5 days).

Reforming fiber by injecting spinning: The PIC solution of 50 g/L polymer concentration was injected by a syringe with a pipe diameter of 0.9 mm into water that was quickly flowing by a magnetic stirrer at 500 rpm (see Fig. 2a-III and Move 1). The viscous PIC solution injected was drawn by the force of rotating water and was crosslinked by dialysis to form hydrogel fiber. Then, the fiber was further dialyzed by a large amount of water to get a tough fiber (changing water every day for at least 3 times).

Reforming capsule by dropping-dialysis: The PIC solution of 20 g/L polymer concentration was slowly dropped by a syringe with a pipe diameter of 0.9 mm into water that was under stirring by a magnetic stirring at 100 rpm (see Fig. 2a-IV and Move 2). The droplet formed capsule by dialysis. Then, the capsule was further dialyzed in a large amount of water to get the stable hollow capsule (changing water every day for at least 3 times). The thickness of capsule wall can be tuned by polymer concentration.

Reforming polyampholyte (PA) hydrogel sheet

The polyampholyte hydrogel P(MPTC-co-NaSS),consisting of [MPTC]+[NaSS]=2.0 M, [NaSS]/([MPTC]+ [NaSS])=0.52 and 0.05 mol% initiator α-ketoglutaric acid, obtained according to our previous report was cut into small pieces and then completely disassociated in 4M NaCl to produce a uniform solution at 60°C.[3] PA solution of 80 g/L polymer concentrations was prepared. Then the PA solution was reformed by the same method as that of PIC hydrogel sheet by mold-dialysis method described above.

Building PIC hydrogel by direct blending oppositely charged polymers

Positively charged PMPTC and negatively charged PNaSS were separately polymerized from their aqueous solutions of 1 M monomer containing 0.05 mol% 2-oxoglutaric acid UV initiator. The polymerizations were performed at UV light intensity of ~ 4 mW/cm^2 for 8h. The achieved PMPTC and PNaSS was dried and made into powder. Then, the PMPTC and PNaSS powder were mixed and disassociated in 4M NaCl aqueous solution at 60°C to get a solution of 150 g/L total polymer concentration. Finally, the mixture was formed into a sheet by the same method as that of the PIC sheet by mold-dialysis. It should be noted that the mixture with polymer concentration 80 g/L (the same as the concentration of PIC solution from two-step sequential polymerization) could not form a uniform sheet. The samples thus obtained are denoted as PMPTC/PNaSS-b.

Supplementary Movie S1

A movie showing preparation of the PIC fiber.

Supplementary Movie S2

A movie showing preparation of the PIC capsules.

Supplementary Movie S3

A movie shows the movement of magnetic PIC/Fe_3O_4 capsules under a magnetic field. The oval magnetic PIC/Fe_3O_4 capsules dance in the rotating magnetic field.

References

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