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Oppositely Charged Polyelectrolytes form Tough, Self-healing and Rebuildable Hydrogels

Feng Luo[1], Tao Lin Sun[1], Tasuku Nakajima[1], Takayuki Kurokawa[1], Yu Zhao[2], Koshiro Sato[2], Abu Bin Ihsan[1], Xu Feng Li[2], Hong Lei Guo[2] and Jian Ping Gong[1]*

[1]Faculty of Advanced Life Science, Hokkaido University, Sapporo 060-0810, Japan
[2]Graduate School of Life Science, Hokkaido University, Sapporo 060-0810, Japan
*Corresponding author: gong@mail.sci.hokudai.ac.jp

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Recent progresses in developing tough hydrogels promise the great potential of this class of soft and wet materials as biomaterials, soft robotics, smart actuators and sensors.[1-10] Any practical application of these hydrogels as smart materials, however, requires a combination of mechanical properties including stiffness, strength, toughness, and self-healing. For instance, along with the high strength and toughness, a cartilage substitute material requires a high stiffness to bear the load, while a blood vessel substitute material requires flexibility. Self-healing not only merits the long term durability of the load-bearing materials, but also gives possibility to reconstruct the material with desired shape from its microgels. While many hydrogels possess some of these requirements, it is a challenge to develop hydrogels satisfying all of these criteria.[2, 11-13] In this work, we report a new class of physical hydrogels that possess these multiple functions. These hydrogels are obtained from concentrated solution of oppositely charged polyelectrolytes. After dialysis of their small counter ions, the oppositely charged polyelectrolytes form polyion complexes of a wide strength distribution, which give dynamic crosslinking of an extremely wide life time scale. The strong, long life time bonds serve as permanent cross-linking, imparting elasticity, whereas the weak, short life

time bonds function as reversible crosslinking that break and reform at deformation to dissipate energy. By this mechanism, the weak bonds serve as reversible sacrificial bonds, and give the hydrogels high toughness and self-healing properties.[12, 14] The polyion complex (PIC) gels from various combinations of polyelectrolytes contain *c.a.* 50 wt% water, and exhibit fracture strength as high as several MPa, tearing fracture energy up to 10,000 J/m^2 at maximum. The cut pieces of the gels can heal together in ambient condition with the aid of saline solution. Based on this fact, one can build a tough bulk hydrogel with tailor-made shape and/or designed spatial distribution from its microgels as building blocks. It is also confirmed that the PIC hydrogels are nontoxic to human cell. This polyion complex approach is general and easily applicable to various biopolymers and/or synthetic polyelectrolytes. These gels might open new avenue of tough hydrogels for load-bearing biomaterials, such as articular cartilage and sports guard materials.

The difficulty in developing polyion complex (PIC) hydrogels is the fast complexation reaction. Mixing of bulk solutions of polyanion and polycation usually leads to inhomogeneous precipitation, where strong polyion complexes are formed at the interface of the two solutions, which quenches the further reaction.[15-17] Because of this, materials based on polyion complexes are usually limited to thin films formed by layer-by-layer reaction.[18-23] To overcome this difficulty, we polymerized one of the polyelectrolyte from its monomers solution in the presence of another oppositely charged polymer at 1:1 charge ratio (**Figure 1**). The latter is either synthesized from its monomers in advance or a pre-existing polymer. The as-polymerized samples form soft and stretchable hydrogels when the overall concentration of the two components is well above the entanglement concentration.

First, we show a typical example of the PIC hydrogels synthesized from two oppositely charged monomers by two-step polymerization. The first monomer is 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC) and the second monomer

is sodium *p*-styrenesulfonate (NaSS) (**Figure 1**). The PIC hydrogels such prepared are referred to as PMPTC/PNaSS (See Experimental section).

Figure 2a shows the tensile stress-strain curves of PMPTC/PNaSS sample, in the as-prepared state and after the dialysis. The as-prepared sample is soft and highly stretchable, while after dialysis in water it shows the tensile fracture stress of 3.7 MPa, modulus of 5.4 MPa and work of extension (=the area under the stress-strain curve) of 14.8 MJ/m^3. These mechanical properties are at least two orders of magnitude larger than that of the as-prepared hydrogels and are comparable to that of rubber. For uniaxial compression, the PIC hydrogel can stand a stress of 17.5 MPa with a strain of 95% and never broken. The gel is so tough that it has a high resistance against the defect, as seen by the suture test (**Figure 2b and Movie S1**). The huge change in mechanical performance from as-prepared to equilibrium PIC hydrogels indicates that abundant of inter-chain complexes are formed during dialysis in water. This can also be confirmed by the 50 vol% shrinkage of the hydrogel after equilibrium in water (inset picture of **Figure 2a**).

Distinct yielding and large hysteresis are observed for the first loading-unloading cycle (**Figure 2c**). The sample shows notable residual strain right after the unloading, indicating the plastic deformation. It is surprising to find that the residual strain decreases with increasing waiting time and disappares after certain waiting time (~ 120 min), which means the plastic deformation completely disappear. The second loading-unloading curve gradually recovers back to the first loading-unloading curve with the increase of the waiting time and completely overlaps to the first one when the residual strain disappears. This indicates that the polyion complex could reversibly break and reform. The full recovery also indicates that only the reversible ion complexes are broken during deformation, and no breaking of primary chains occurs. The hysteresis area enclosing by the first loading-unloading cycle is up to 85% of the overall area below the loading curve (work of extension). This indicates that 85% of the energy used for deformation of the sample is dissipated by the breaking of the relatively weak

ion complexes of the gel. The waiting time dependence of the residual strain and the hysteresis ratio estimated from the hysteresis area change (**Figure 2d**) indicate that the recovery involves both a quick process and a slow process, similar to that of polyampholyte gels and ionomers. [12, 24] This two-stage recovery process is related to the competition between the elasticity of primary chain and the strength of temporarily reformed bonds during the unloading process. The complete self-recovery, which almost overlaps to its original stress-strain curve, is observed up to a loading strain of 700% (**Figure. S1**), which is close to the fracture strain of 750–800%. These results suggest that there is no flow of the polymer chains until fracture, and the strong, long life time ion complexes serve as permanent crosslinking in the observation time scale. This structural character has a similar function as double network system.[25] That is, the strong bonds serve as permanent crosslinkers in the observation time, imparting elasticity, whereas the weak bonds serve as reversible crosslinkers that break and re-form by deformation to dissipate energy, as reversible sacrificial bonds.

The PIC physical hydrogels show excellent volume and mechanical stability in saline solution even up to the ionic strength of the physiological condition (0.154 M NaCl) (**Figure 3**). Addition of more salts (C_{NaCl}: 0.3-2.5 M) leads to decreasing of Young's modulus and fracture stress, while the breaking strain increases dramatically. These results indicate that some ionic bonds of PIC hydrogels are destroyed in the concentrated NaCl solution.[26-27] It is interesting to observe that the change in the volume ratio Q_v ($=V_{salt}/V_{water}$) is as small as 110% in 1.0 M NaCl concentration although the modulus is decreased by a factor more than 10. This excellent size stability is also observed in wide temperature range from 0 to 90 °C and pH range of 0-14 (**Figure S2**).

Based on the reversible ionic bonds and saline softening effect, the cut surfaces of the gel can be healed with the aid of saline solution. As shown in **Figure 4a**, the gel was cut into two pieces and the cut surfaces were dipped in 3 M NaCl for 2 min, and then were brought

together to form a contact. The sample after 12 hrs healing time exhibits 66% cure in terms of the work of extension (**Figure 4b**). Although the healed sample is weaker than the virgin sample, its strength is still very high (Modulus: 4.5 MPa; Strength: 2.2 MPa; Strain: 630%). We also find that when two pieces of gels are put together without cuts, they can also self-adhesive to each other with the aid of saline solution. In distinct contrast, the sample shows almost no self-healing or self-adhesive at room temperature without dipping in concentrated salt before contact. This result gives a new approach for effective self-healing of stiff and tough hydrogels consisting of ionic bonds at ambient temperature. The image of the self-healed sample during tensile test is presented in **Movie S2**.

As the PIC hydrogel is self-healable in room temperature with the aid of saline solution, we can build a tough self-glued bulk hydrogel from its microgels as building blocks. To do this, the bulk gel is dried and then grinded into small particles of tens of μm (**Figure 4c-I**). The powders are filled into a mold of heart shape and then are added with several drops of 3 M NaCl solution to make the powders glue together. After dialysis in pure water, we obtain a bulk gel with the heart shape (**Figure 4c-II**). The self-glued hydrogels, also containing about 55 wt% water, have high strength (fracture stress 1.5 MPa) and stiffness (modulus ~ 4 MPa), as demonstrated in **Figure 4c-III**. The self-glued bulk sample also sustains strain as large as ~ 400% (**Figure 4b**) and shows completely recovered after deformation.

The PIC hydrogels also have excellent biocompatibility as confirmed by the cytotoxicity test (**Figure S3**). This result endows the potential of such hydrogels as structural biomaterials. The biocompatibility is presumably due to the effect in similar to the zwitter-ion polymers.

This polyion complex approach is general, permitting us to obtain very tough PIC hydrogels from a wide variety of polyelectrolyte combinations. Some examples using different ionic monomer combinations (**Figure 1**) are summarized in **Table 1**. The mechanical properties of these hydrogels strongly depend on the chemical structure. For example, the combination of acryloyloxethyltrimethylammonium chloride (DMAEA-Q) and NaSS form very tough PIC

hydrogels, the Young's modulus (E), fracture stress (σ_b), work of extension (W_b) and tearing fracture energy (T) of PDMAEA-Q/PNaSS is up to 7.9 MPa, 5.1 MPa, 18.8 MJ/m^3 and 11,800 J/m^2, respectively. On the other hand, the PIC hydrogels from the combination of anionic sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and cationic MPTC are very soft and stretchable. The PNaAMPS/PMPTC hydrogel has a modulus of 0.03 MPa, a fracture stress of 0.02 MPa and a breaking strain of 3500%. The gel is very tough and blunting occurs in tearing test, indicating a high resistance against crack propagation. Moreover, it should be noticed that the toughness of the PIC hydrogels is independent of the polymerization sequence, the samples either polymerized first from cationic monomer or anionic monomer give the similar properties, as shown in **Table 1**. By virtue of this method, biopolymer-based hydrogels can also be prepared. For example, CS/PDMAEA-Q gel with excellent toughness was prepared from biopolymer chondroitin sulfate (CS) and DMAEA-Q.[28] With appropriate chemical structures and optimal formulation, the PIC hydrogels are strong and tough, reaching the high modulus of rubbers (tens of MPa) while maintaining the toughness (fracture energy) in the order of 10 kJ/m^2, comparable with rubbers [29], soft tissues [30], tough DN hydrogels [31].

Previously, we have developed tough and self-healing physical hydrogels from linear polyampholytes (PA) that are synthesized from random copolymerization of oppositely charged monomers.[12, 32] The randomly dispersed opposite charges along the polymer chains form ionic bonds of a wide strength distribution through inter-chain and intra-chain complexation. As a result, the PA gels have a wide hierarchical time scale of crosslinking dynamics. By the similar mechanism to PIC hydrogels, these PA gels are also viscoelastic, tough, and self-healing. [12] The polyampholyte approach, however, has several drawbacks. 1) The charge sequence is random and not controllable, and it depends on the reactivity ratio of the oppositely charged monomers which varies with monomer combination; 2) The polyelectrolyte chains are in globule conformation due to intra-chain ion bonds. Because of

this, the inter-chain ion bonds that contribute to the elasticity of the gels only form at extremely high concentration. By using oppositely charged homo-polymers, one has three advantages over the polyampholytes. 1) A well-defined primary structure of the polymer chains; 2) There is no intra-chain ion complexation, and the polymers are in the extended coil conformation. The latter greatly favours the chain entanglement and inter-chain complexation even at relatively low polymer concentration. For example, the critical concentration to form homogeneous polyion complex hydrogel PMPTC/PNaSS is 0.2 M while polyampholyte P(MPTC-co-NaSS) could not form hydrogels when the concentration is below 1.3 M; [12] 3) The ion complexes are more stable, and the mechanical properties are much higher than that of polyampholyte (PA) hydrogels with the same combination. For example, P(DMAEA-Q-co-NaSS) hydrogel synthesized at the optimized condition showed E, σ_b, W_b of ~ 0.07 MPa, ~ 0.2 MPa, ~ 1.6 MJ/m^3, respectively.[33] These values are lower than those of the PDMAEA-Q/PNaSS hydrogel shown in **Table 1**. The PIC gels also have a much better stability than the PA gels in saline solution, which is important for biological application.

We can also rebuild tough bulk hydrogels from self-healing hydrogels of different chemical structrues. For example, **Figure 4d-I** shows a "W" shape gel rebuilt from two kinds of microgels, the left half of "W" is from the PIC microgels, PMPTC/PNaSS (white) and the right half is from polyampholyte (PA) microgels, P(DMAEA-Q-co-NaSS) (pink). The latter has a very high self-healing ability.[12] As the PIC hydrogel is much stiffer than the PA hydrogel, by stretching, the right half of the "W" deforms more (**Figure 4d-II**). Based on this result, hydrogels with designed spatial distribution of chemical and mechanical properties might be obtained, which is promising for the 3D/4D printing and additive manufacturing of hydrogels.[34-36]

Above all, we report a new class of physical hydrogels which consist of oppositely charged polyelectrolytes. This structure, having a double-network feature, renders the high strength and toughness of the materials. Owing to the reversible, inter-polymer bonding, the materials are self-healable and rebuildable at ambient condition with the aid of saline solution which is promising for the 3D/4D printing and additive manufacturing of hydrogels. Since these properties are generic for polyion complexes, hydrogels from various combinations of biopolymer and/or synthetic polyelectrolytes could be developed. Therefore, these gels might open new avenue of tough hydrogels.

Experimental

Typical PIC hydrogel was synthesized by sequential homo-polymerization of cationic and anionic monomers. The sample is referred as PM_1/PM_2 (C_m-f-x_1-x_2), where P is abbreviation of poly-, and M_i, (i = 1,2) are the abbreviated monomer name in the ith step polymerization. C_m is the overall molar concentration at the second component polymerization, f is the molar fraction of anionic monomer, and x_1 and x_2 are initiator concentration of the first and second polymerization (mol%) in relative to the corresponding monomers. For example, to synthesize (PMPTC/PNaSS) hydrogel, PMPTC was first synthesized from an aqueous solution of 1 M MPTC containing x_1=0.05 mol-% initiator, 2-oxoglutaric acid by UV light irradiation (light intensity ~ 4 mW/cm^2) for 8h. The achieved PMPTC was dried and made into powder. And then, the powder was mixed with NaSS monomer with the charge fraction of the second monomer NaSS, f =[NaSS]/([MPTC]+ [NaSS])=0.5. After well dispersion in aid of 0.5 M NaCl to form a mixture solution of C_m=[MPTC]+[NaSS]=1.5 M at 60 °C, the mixture containing x_2=0.1 mol-% initiator in relative to the second monomer was polymerized by UV light for 8 h in a reaction cell consisting of a pair of glass plates with 1.5 mm spacing. In sequent, the as-prepared hydrogel was 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

(*d*) shrank from 1.5 mm to *c.a.* 0.8 mm. The sample thus prepared is referred as PMPTC/PNaSS (1.5-0.5-0.05-0.1).

The tensile test was carried out on a commercial tensile tester (Tensilon RTC-1150A, Orientec Co.) at a stretch velocity 100 mm/min, using gels cut into the dumbbell-shape with the size of length 35 mm (*L*), gauge length 12 mm (L_0), and width 2 mm (*w*). The compressive measurement was performed using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.) at a strain rate of 10% / min. using gels cut into disc shape with diameter 15 mm. In both measurements, the sample thickness was 0.8 mm (*d*). All of mechanical tests were performed at room temperature in air. For the cyclic tensile test, both loading and unloading were performed at constant velocity of 100 mm/min and carried out in a water bath to prevent water evaporating from the samples.

For self-healing test, the dumbbell-shape gel was cut into two equal pieces by a sharp blade and then the two cut surfaces was dipped in 3 M NaCl for 2 min. In sequent, the two cut surfaces were contacted together in air for 12 hours sealed by plastic wrap, and finally dialyzed in large amount of water (water was changed every day for at least 5 days).

To build bulk gel from its microgels, the hydrogel was dried at 100°C for 12 h and then grinded into powders with tens of μm. The powders were filled in free-shape plastic mould and several drops of 3 M NaCl solution were added to glue microgel powders. After holding for one hour for self-adhesion, the sample was dialysis in water to form bulk gel. Water was changed every day for at least 5 days. At last, size of glued bulk gel shrinkage was less than 5%.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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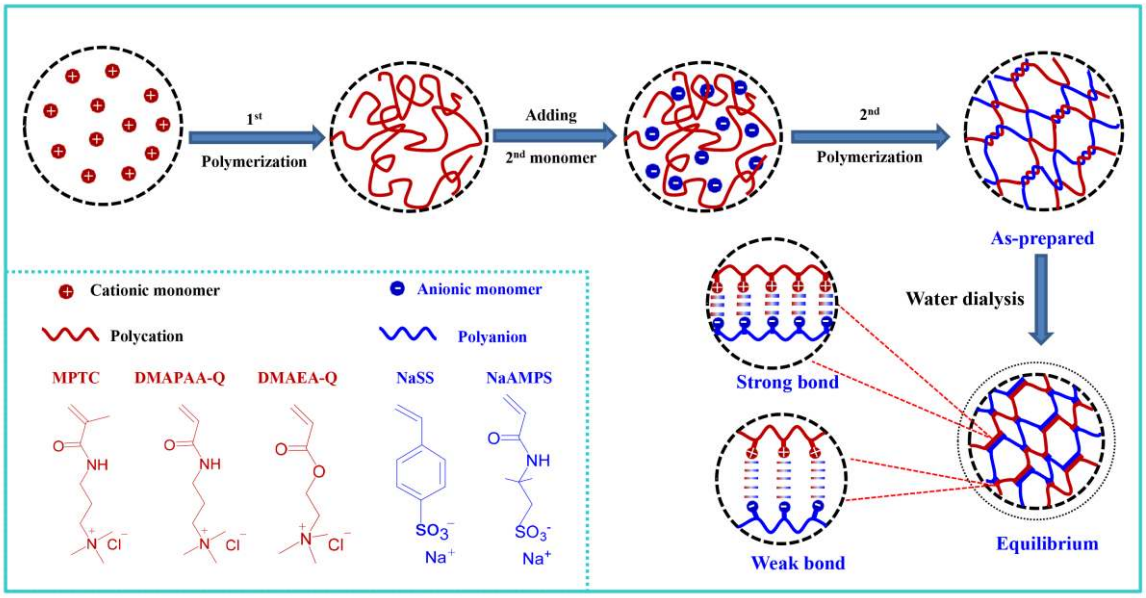

Figure 1. Schematics of preparation of polyion-complex (PIC) hydrogels and the chemical structures of monomers used in this work.

Cationic monomer was homopolymerized in the first step and then is mixed with the anionic monomer. After well dispersion, the anionic monomer is polymerized in the second step to form soft PIC hydrogel (as-prepared). By immersing the sample in water, small counter ions and co-ions of the polymer are removed from the sample (dialysis). As a result, high density of weak ionic bonds and strong ionic bonds are formed to give tough PIC hydrogel (equilibrium).

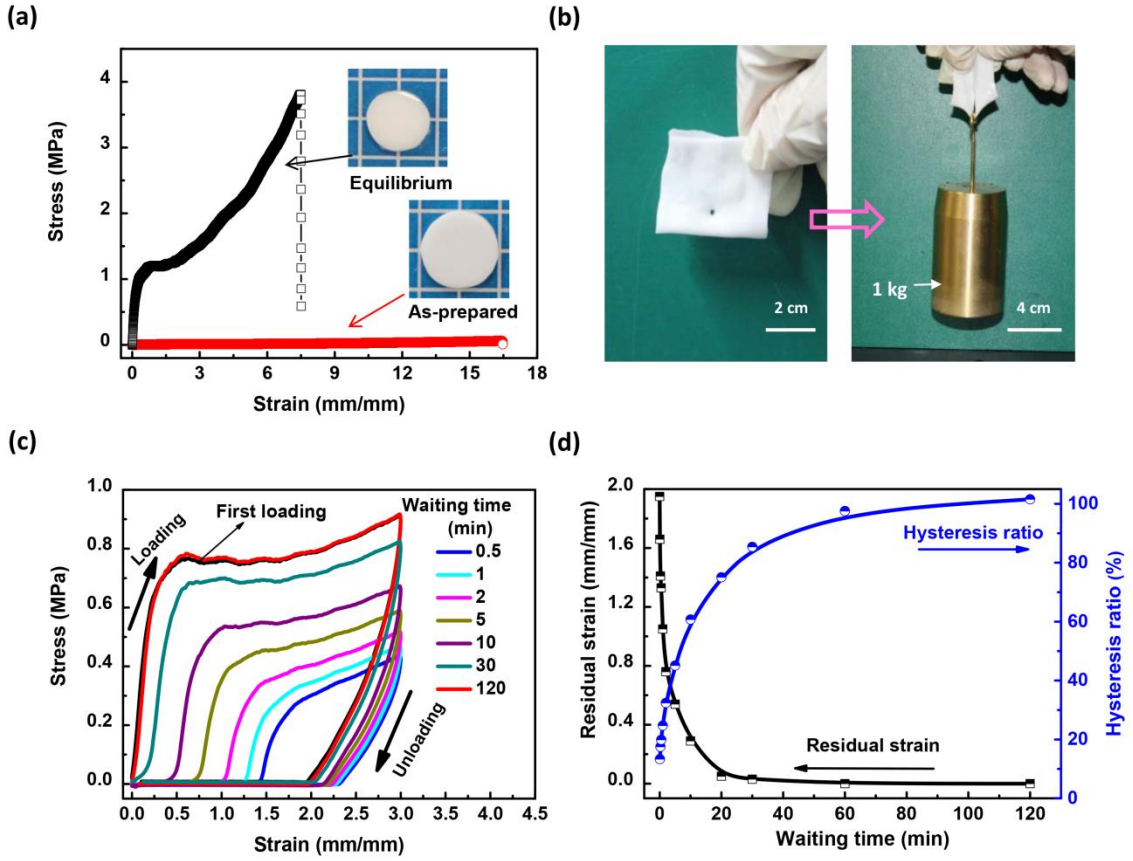

Figure 2. Mechanical behaviors of a typical polyion complex (PIC) hydrogel, PMPTC/PNaSS. a) Tensile stress-strain curves for a PIC hydrogel in as-prepared state (circles) and in water equilibrium state (squares). Inset images show the equilibrium and as-prepared PIC hydrogels. Compared with as-prepared one, the equilibrium one shrinks about 50 vol%. After equilibrium in water, the counter ions of the polyelectrolytes are dialyzed from the gel and inter-chain polyion complexation are formed. The scale of a white grid in background is 5mm×5mm. b) The sample shows notch-insensitivity as demonstrated by the suture test. A hole is made in the hydrogel, using a sharp awl and a 1 kg weight is hung to the gel via the hole. c) Recovery of the stress-strain curve for different waiting time performed by cyclic tensile test. d) Waiting time dependence of the residual strain and hysteresis ratio (area ratio of the second hysteresis loop to the first). Sample code: PMPTC/PNaSS (1.5-0.5-0.05-0.1).

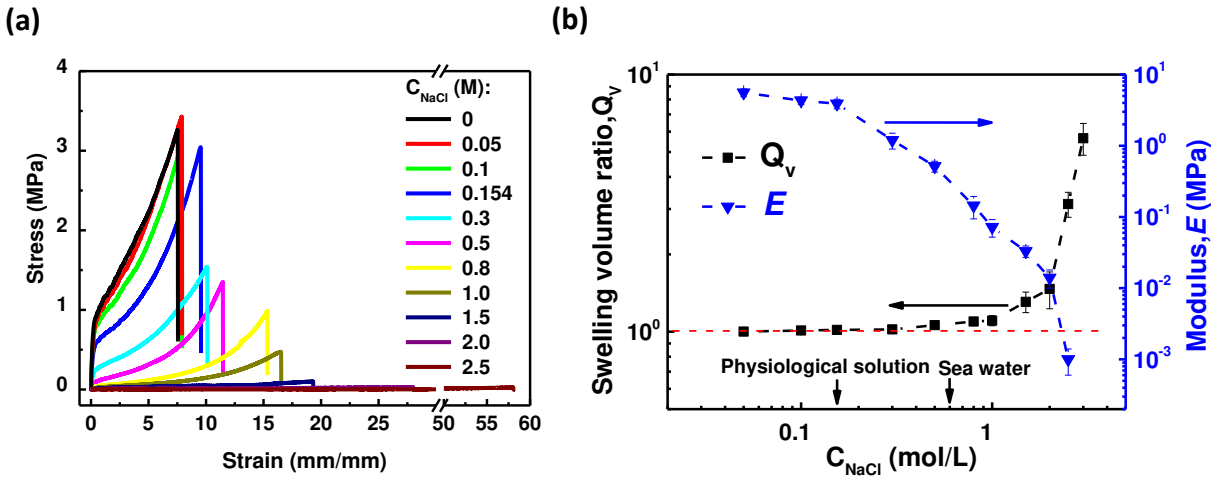

Figure 3. a) Tensile behaviors of the PMPTC/PNaSS hydrogels after immersing in saline solutions of different concentration C_{NaCl} and b) the volume ratio $Q_v(=V_{salt}/V_{water})$ and Young's modulus *E* on the concentrations of saline solution C_{NaCl}. Sample code: PMPTC/PNaSS (1.5-0.5-0.05-0.1).

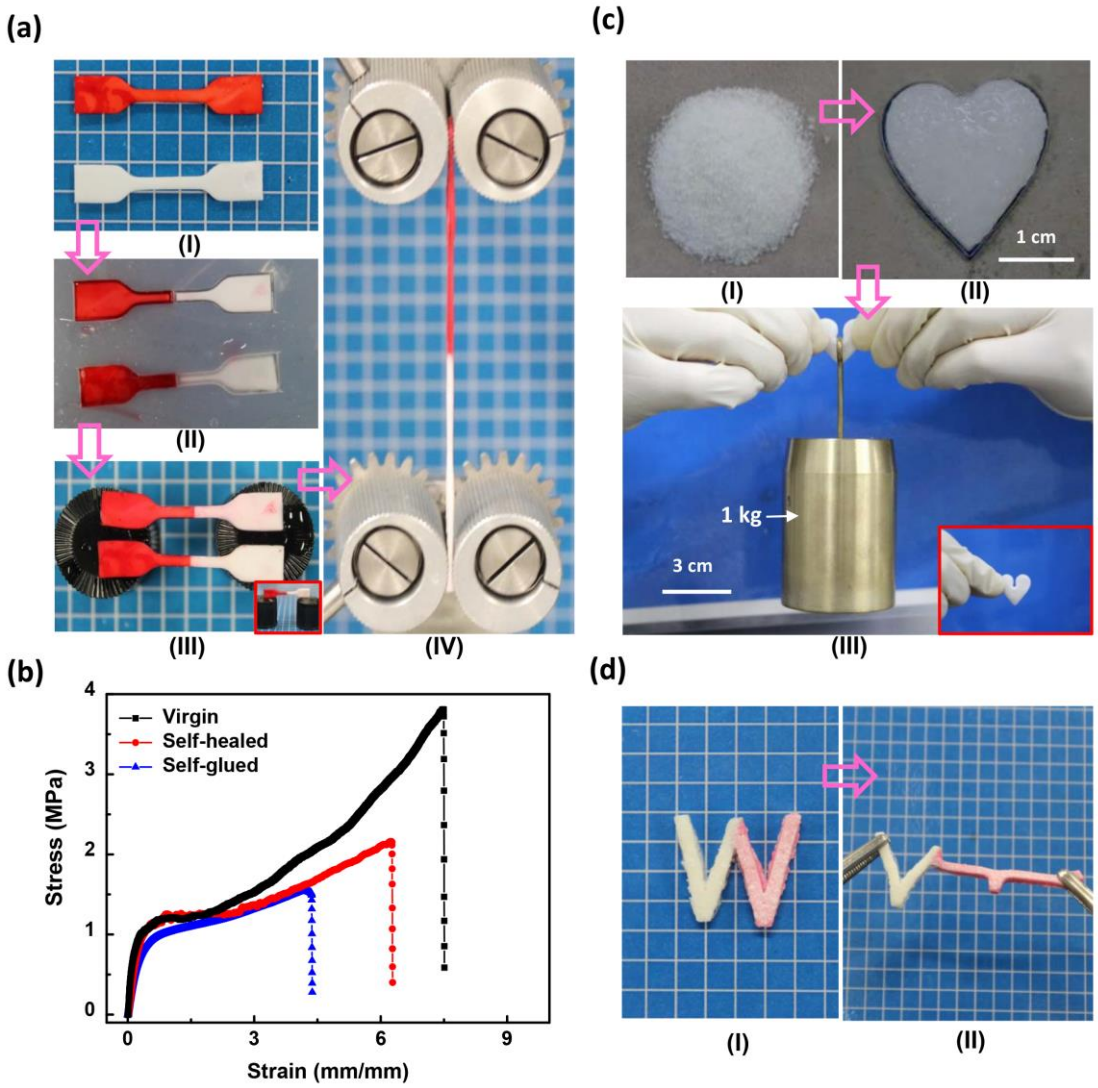

Figure 4. a) Self-healing behavior of the PMPTC/PNaSS hydrogels assisted by 3M NaCl solution. (I) Two pieces of virgin PIC hydrogels, one of them is dyed by congo red; (II) The cut samples were reattached by embedding the two cut pieces in a silicone rubber mold with the same size of the sample. Before reattaching, the cutting surfaces of the samples were dipping in 3M NaCl solution for 2 min; (III) the self-healed samples after 12 hrs healing time; (IV) photograph demonstrating the large deformation of self-healed samples. b) Stress-strain curves of the virgin, self-healed and self-glued bulk samples. c) Shelf-gluing behavior of PIC microgels. PMPTC/PNaSS microgel powders can self-glued to form desired-shape and show high mechanical performances. (I) Dry hydrogel powders; (II) heart shape hydrogel from

hydrogel powders; (III) a weight of 1kg was hung to the “heart” shape bulk hydrogel with thickness of 3 mm (diameter of hook is 2 mm) and inset picture shows the virgin shape of sample. d) Self-glued bulk hydrogel with spatial distribution of chemical and mechanical properties. (I) a “W” shape sample constructed from microgels of stiff polyion complex (PIC) (left half, white, PMPTC/PNaSS) and soft polyampholyte (PA) (right half, pink, P(NaSS-co-DMAEA-Q)); (II) The microgels of two different modulus are glued together so strongly that they do not break by stretching. Sample code: PIC hydrogel PMPTC/PNaSS(1.5-0.5-0.05-0.1). The scale of each white grid in background (a, d) is 5×5mm.

Table 1. Physical properties of various PIC hydrogels.

Sample code (C_m-f-x_1-x_2) [1]	E (MPa) [2]	ε_b	σ_b (MPa)	W_b (MJ/m^3)	T (kJ/m^2)	c_w, (%)
PMPTC/PNaSS (1.5-0.5-0.05-0.1)	5.4±0.6	7.5±0.9	3.7±0.4	14.8±1.1	8.6±0.8	51.3±2.5
PNaSS/PMPTC (1.5-0.52-0.05-0.1)	4.4±0.7	8.3±0.8	3.3±0.3	13.4±0.9	7.7±0.5	57.8±3.9
PDMAEA-Q/PNaSS (1.5-0.52-0.05-0.1)	7.9±0.6	7.5±0.8	5.1±0.6	18.8±1.9	11.8±1.2	42.5±4.2
PNaSS/PDMAPAA-Q (1.5-0.53-0.05-0.1)	0.28±0.07	11.8±1.2	0.8±0.1	3.2±0.5	Blunting [4]	47.6±4.1
PNaAMPS/PDMAEA-Q (1.5-0.53-0.05-0.1)	0.09±0.01	24.4±2.6	0.2±0.03	2.1±0.4	Blunting	50.3±5.4
PNaAMPS/PMPTC (1.5-0.52-0.05-0.1)	0.03±0.01	34.7±4.6	0.02±0.005	0.6±0.07	Blunting	64.5±5.9
CS/PDMAEA-Q [3]	0.16±0.05	8.2±1.1	0.4±0.07	1.8±0.4	Blunting	59.6±5.2

1) C_m is the overall monomer concentration (M) during the polymerization of the second polyelectrolyte in the presence of the first polyelectrolyte. f is the molar fraction of the anionic monomer, x_1 and x_2 are the initiator concentrations (mol%) in respective to its monomer of the first and 2nd polymerization, respectively.

2) The parameters E, ε_b, σ_b, W_b, T and c_w are Young's modulus, fracture strain, fracture stress, work of extension at fracture, tearing fracture energy and the water content, respectively. Tearing fracture energy was tested by trouser tear test as our previous report (Reference 12).

3) PDMAEA-Q was polymerized at 0.54 M with 0.1 mol% initiator, in the presence of 150g/L chondroitin sulfate (CS). The molecule weight of CS unit is 458.14 g/mol. The DMAEA-Q monomer unit is 1.65 times of CS unit.

4) 'Blunting' means the crack of sample does not propagate in trouser tear test.

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Oppositely Charged Polyelectrolytes form Tough, Self-healing and Rebuildable Hydrogels

Feng Luo[1], Tao Lin Sun[1], Tasuku Nakajima[1], Takayuki Kurokawa[1], Yu Zhao[2], Koshiro Sato[2], Abu Bin Ihsan[1], Xu Feng Li[2], Hong Lei Guo[2] and Jian Ping Gong[1]*

Key words: Polyion-complex, hydrogel, tough, self-healing, rebuildability

A series of strong and tough polyion complex (PIC) hydrogels have been synthesized by sequential homo-polymerization of cationic and anionic monomer. Owing to the reversible, inter-polymer ionic bonding, the materials are self-healable at ambient condition with the aid of saline solution. Furthermore, self-glued bulk hydrogels of various shapes can be built from their microgels, which is promising for the 3D/4D printing and additive manufacturing of hydrogels.