



Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Tough polyion-complex hydrogels from soft to stiff controlled by monomer structure

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ARTICLE INFO

Article history:

Received 8 December 2016

Received in revised form

10 February 2017

Accepted 11 February 2017

Available online xxx

Keywords:

Tough hydrogel

Polyion-complex

Monomer structure

Stiffness

Dynamic relaxation spectrum

Time-temperature superposition

Phase separation

ABSTRACT

Tough hydrogels with adjustable stiffness are expected for adapting application as various biomaterials. Oppositely charged polyelectrolytes form tough and self-healing physical polyion-complex (PIC) hydrogels via formation of inter-chain ionic bonds with a wide distribution in bond strength. The strong bonds serve as permanent crosslinking to impart elasticity and the weak bonds as reversible sacrificial bonds to dissipate energy and to self-heal. In this work, we fabricate four PIC hydrogels using four positively charged trimethyl-ammonium monomers with slightly different chemical moieties and a same negatively charged polymer. The obtained PIC hydrogels all show high toughness but large difference in stiffness, extensibility, and self-recovery kinetics. With slight difference in the monomer structure of the polycations, the modulus of the hydrogels varies over two orders in magnitude, from 0.36 to 56 MPa, and the difference in elongation at break is up to five times. The presence of acryloyl moiety and methyl moiety increase the stiffness of the hydrogels. In the temperature range studied, all the four PIC hydrogels exhibit the rheological simple behaviours, following the time-temperature superposition principle. The four samples show quite different dynamic relaxation spectra over wide frequency range, revealing large difference in the strength distribution of dynamic ionic bonds. SEM observation reveals quite different phase separation structure for the four samples, in which the polymer chain stiffness should play an important role. This understanding of structure-properties of the PIC hydrogels will merit the designing of various supramolecular tough hydrogels and therefore broaden the scope of hydrogels for the applications as biomaterials.

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1. Introduction

Hydrogels are good candidates for biomaterials. Developing robust hydrogels with excellent mechanical properties has drawn great attention in recent years, because the traditional hydrogels are soft and weak [1–8]. Any load-bearing biomaterial requires a proper stiffness in addition to high toughness. For instance, cartilage substitute materials require a relatively high stiffness to bear the load, and blood vessels substitute materials require softness

and flexibility in relative to cartilage materials.

During the past decade, great progress has been made in developing hydrogels with excellent mechanical performances [9,10]. For example, double-network hydrogels [11] and nano-composite hydrogels [12,13], are both stiff and tough, slide-ring hydrogels [14] and tetra-arm poly(ethylene glycol) hydrogels [15,16], are soft and stretchable. These achievements greatly promote the potential application of hydrogels as biomaterials. Among them, the double network (DN) strategy has been shown to be extraordinarily effective in improving the toughness of hydrogels, and the “sacrificial bond” mechanism was shown to efficiently dissipate energy during the deformation [17]. Since the rupture of covalent bonds in traditional DN gels is irreversible, DN gels exhibit permanent softening after large deformation, which might be a limitation in many practical applications. To address this problem, physically reversible bonds including hydrogen bonds [18],

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metal–ligand interactions [19], ionic bonds [20,21], Van der Waals interactions [22], π – π interactions [23], and hydrophobic interactions [24], were built in hydrogels as a reversible “sacrificial bond” to replace the irreversible covalent bonds.

In our previous work, taking advantage of the reversible ionic bonds, a novel class of tough hydrogels was developed based on the polyion-complex formation. Such hydrogels are obtained by two-step homo-polymerization of oppositely charged cationic monomer and anionic monomer at relatively high concentration [25]. The oppositely charged polyelectrolytes form polyion complexes (PIC) with a wide distribution in ionic bond strength through multiple bonds formation, which gives dynamic crosslinking with very wide distribution in lifetime. For a given observation time, if the lifetime of an ionic-bond is longer than the observation time, this bond serves as permanent crosslinking to maintain the shape of the gel (strong bond). In contrast, if the lifetime of an ionic-bond is shorter than the observation time, this bond serve as reversible sacrificial bond, breaking to dissipate energy and re-forming to impart self-healing (weak bond). Thus, PIC hydrogels show many amazing properties, such as high toughness, high stability, self-recovery, self-healing, self-glued and rebuild-ability (recyclability) [26].

To satisfy the “real world” applications, it is important to develop various types of PIC hydrogels with tunable stiffness to adapt various requirements of biomaterials. As the Young's modulus of the hydrogels are related to the crosslinking density, the strategy to obtain PIC hydrogels of varied stiffness is to tune the strength and distribution of ionic bonds. As report in physical polyampholyte hydrogels that are another tough system also based on ionic bonds [27], we found that the hydrophobic moiety of the ionic monomer has a synergistic effect in stabilizing the ionic interaction. The more hydrophobic of the monomer in the gel, the stronger the ion bond is. These results suggest that the mechanical properties of the hydrogels strongly related to the chemical structure of the ionic monomers. However, to the best of our knowledge, few systematic works have been reported on tuning the mechanical properties (i.e. stiffness, toughness) of physical hydrogels by the structure of ionic monomers.

In this work, we study the PIC hydrogels formed by ionic monomers with different chemical structures and ascertain the structure - properties relationship. Four positively charged trimethylammonium monomers with slightly different chemical structures were used to fabricate PIC hydrogels with a same negatively charged polymer. The differences in the mechanical behaviors of the four PIC hydrogels are investigated. This paper will pave the way for designing a series of tough hydrogels with required stiffness.

2. Experimental section

2.1. Materials

The schematic illustration for the PIC hydrogel and chemical structures of the ionic monomers used in this work are shown in Fig. 1. Oppositely charged polyelectrolytes form tough and self-healing physical hydrogels via formation of inter-chain ionic bonds. Sodium *p*-styrenesulfonate (NaSS) is used as the anionic monomer; methacrylateethyl trimethyl ammonium chloride (MATAC), acryloyloxethyltrimethylammonium chloride (DMAEA-Q), 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC) and 3-acrylamidopropyl trimethyl-ammonium chloride (DMAPAA-Q) are used as the four cationic monomers. The former two cationic monomers contain acryloyl moiety and the latter two contain acrylamido moiety, and one of the acryloyl moiety or acrylamido moiety contains methyl side group. Depending on the

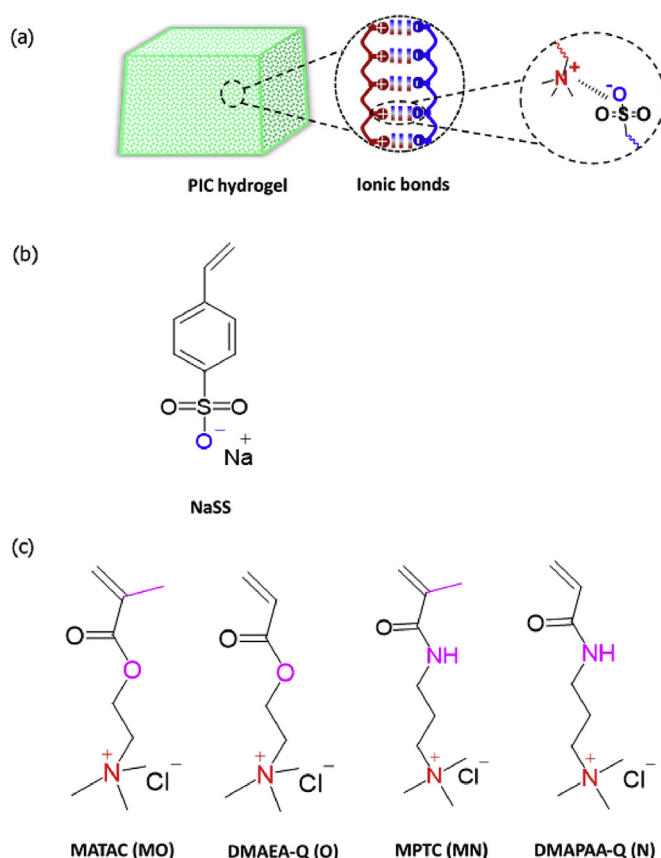


Fig. 1. Schematic illustration for the polyion complex (PIC) hydrogel and chemical structures of ionic monomers used to synthesize the PIC hydrogels in this study. (a) Illustration for the PIC hydrogel. (b) Anionic monomer: NaSS. (c) Cationic trimethylammonium monomers: MATAC (MO), DMAEA-Q (O), MPTC (MN), and DMAPAA-Q (N).

structure, the MATAC, DMAEA-Q, MPTC and DMAPAA-Q are shortly named as MO, O, MN and N, respectively, where M represents acrylate with methyl group, O represents acryloyl and N represents acrylamido. These ionic monomers, UV initiator, α -ketoglutaric acid, and NaCl are all purchased from Wako Pure Chemical Industries, Ltd. All materials are used as received. Millipore de-ionized water is used in all of the experiments.

2.2. Synthesis of polyion-complex (PIC) hydrogels

The PIC hydrogels were synthesized by sequential homo-polymerization of anionic and cationic monomers, as described in our previous report [25]. Typically, the anionic polymer, PNaSS, was first synthesized from an aqueous solution containing 103.095 g of NaSS (0.5 mol) and 0.0365 g of α -ketoglutaric acid (initiator, 0.25 mmol) in 500 ml de-ionized water by UV light irradiation (light intensity ~ 4 mW/cm²) for 8 h. The obtained PNaSS was dried and made into powders (without further purification). Then, the powders were mixed with cationic monomers at the 1:1 charge ratio. In a typical reaction procedure, 100 ml homogeneous aqueous solution containing 15.464 g of PNaSS, 15.577 g of MO (0.075 mol, taken MO as an example), 2.922 g of NaCl (0.05 mol), and 0.011 g of α -ketoglutaric acid (0.075 mmol) was prepared at 60 °C. The solution was irradiated with UV light for 8 h to carry out polymerization in a reaction cell consisting of a pair of glass plates with a 1.5 mm-thick silicone spacer. The as-prepared hydrogel was then dialyzed in a large amount of water to remove their mobile counter ions, residual chemicals, and low molecular weight polymers from

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