



Swelling/deswelling behavior of zwitterionic nanocomposite gels consisting of sulfobetaine polymer–clay networks

Kazutoshi Haraguchi^{b,*}, Jinyan Ning^a, Guang Li^a

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

^b Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Narashino, Chiba 275-8575, Japan

ARTICLE INFO

Article history:

Received 28 September 2014

Received in revised form 27 February 2015

Accepted 24 March 2015

Available online 2 April 2015

Keywords:

Nanocomposite gel

Zwitterionic polymer

Polysulfobetaine

Swelling

Thermosensitivity

Polymer–clay network

ABSTRACT

The swelling and thermosensitive behaviors of zwitterionic nanocomposite gels (Zw-NC gels) consisting of sulfobetaine polymer–exfoliated clay networks were investigated in water and aqueous NaCl solutions and compared with those of physically and chemically crosslinked zwitterionic gels and non-zwitterionic NC gels. Zw-NC gels showed different swelling behavior that was strongly dependent on the salt concentration (C_{NaCl}), clay concentration (C_{clay}), and temperature. In water, characteristic swelling-to-deswelling behavior and an abnormal increase in the degree of swelling (DS) with increasing C_{clay} (\propto crosslink density) were observed. These behaviors were in stark contrast to those obtained with other types of zwitterionic gels. In NaCl solutions, spontaneous deswelling disappeared within small C_{NaCl} , and above the critical point (0.01 M), the DS increased with C_{NaCl} via an anti-polyelectrolyte effect of the zwitterions and decreased with increasing C_{clay} . The transparency also changed depending on the C_{NaCl} , C_{clay} , swelling time, and thermosensitivity of the sulfobetaine polymer. These swelling behaviors and transparency changes of Zw-NC gels were explained by the combined effects of the zwitterionic polymers (anti-polyelectrolyte), ionic clay (polyelectrolyte), and clay as a crosslinker.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

One of the most important and essential properties of polymer hydrogels is the absorption of (i.e., swelling in) water and aqueous solutions containing various solutes. Hydrogels with a high and/or controlled absorption capability of water and solution are strongly desired and represent an area of ongoing scientific and industrial interest [1,2]. This is because it is a key component in a wide range of applications in biomedicine (e.g., wound dressing [3,4], drug delivery system [5,6], contact lens [7], injectable gel [8,9], cell culture substrate [10–12]), analytical chemistry (sensor, actuator) [13–15], cosmetic gels [16],

commodities (e.g., diaper, hygienic products) [17], industry (e.g., removal of pollutants, coatings) [18–20], and agricultural and civil engineering [18,21]. To date, extensive studies have been performed on the swelling behavior of polymer hydrogels consisting of different kinds of polymers, such as nonionic [22,23], ionic [24,25] and zwitterionic polymers [26–29], and different types of networks such as chemically crosslinked, and physically crosslinked, and specifically designed networks [30–34].

In general, the swelling capability of polymer hydrogels is determined by the osmotic pressure, which consists of mixing, elastic, and ionic terms, as expressed by Flory–Rehner theory [35]. In order to achieve a large absorption capability, it is desirable to have hydrogels composed of a highly hydrophilic polymer, with a low crosslink density in the network, and a high concentration

* Corresponding author. Tel.: +81 47 474 2567; fax: +81 47 474 2579.
E-mail address: haraguchi.kazutoshi@nihon-u.ac.jp (K. Haraguchi).

of ionic groups in the polymer chains. Lightly chemically crosslinked ionic polymers (e.g., sodium polyacrylate) are typical examples of superabsorbent polymer (SAP) gels [2,18]. However, the degree of swelling ($DS = (\text{weight of absorbed solvent})/(\text{weight of dried gel})$) of SAP gels decreases steeply when the swelling solvent is changed from water ($DS = \sim 700$) to saline ($DS = 41$), sea water ($DS = 28$), or 1 M NaCl solution ($DS = 21$) because of the disappearance of the ionic term contribution in the presence of salt (polyelectrolyte effect). Another important requirement for advanced gel materials is that they possess good mechanical properties that can withstand high levels of stress and strain under various types of deformations such as pressure, stretching, bending, and twisting [36]. In this regard, SAP gels are very weak and brittle and even become fluid when exposed to an excess amount of water.

Zwitterionic polymers, which bear both cationic and anionic groups in the same monomeric unit, have received increasing attention because of the characteristics derived from zwitterions, such as bioadhesive, antifouling and antithrombogenic properties, and mineralization scaffolds resulting from stoichiometrically balanced ampholytic structures [37–39]. Basic swelling properties of zwitterionic polymer hydrogels (Zw-gels) have been studied in water and aqueous salt solutions [26–29]. Zw-gels generally showed quite low water absorption (i.e., low DS in water, ca. 2–5) because of the hydrophobic nature of polymer chains in water, where zwitterions form inner salt structures via ion pairing [26–29,40]. In aqueous salt solutions, Zw-gels showed a higher DS than in water due to anti-polyelectrolyte effects, where the ion pairs of zwitterions formed in water dissociated in the presence of salt ions. To improve the absorption capability in water, copolymer hydrogels consisting of zwitterionic and non-zwitterionic (e.g., ionic or nonionic) units have been used [40–44]. However, the DS in water and aqueous salt solutions is still limited to fairly low values even for such zwitterionic copolymer hydrogels [28,40–44]. In addition, the zwitterionic (co)polymer hydrogels reported so far were all chemically crosslinked and thus, mechanically very weak. In fact, there have been no reports on the tensile mechanical properties of such zwitterionic (co)polymer hydrogels. Thus, the synthesis of a polymer hydrogel that can exhibit a high DS in both water and aqueous salt

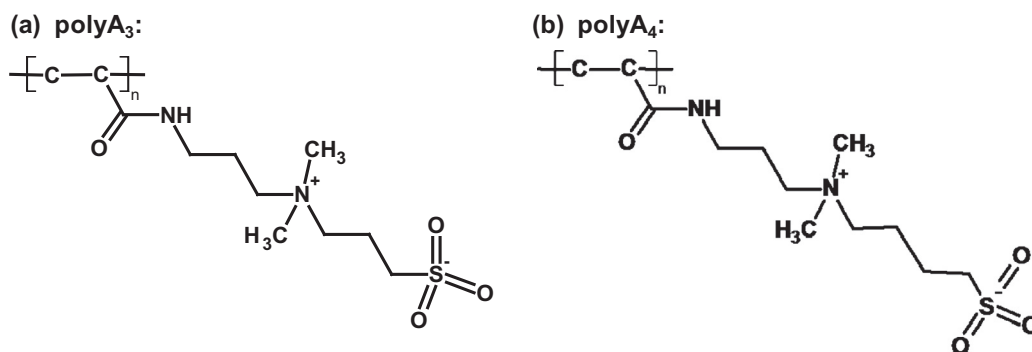
solution and simultaneously possess good mechanical properties is an important scientific and industrial target.

In a previous paper [45], we successfully prepared a new type of zwitterionic polymer hydrogel, zwitterionic nanocomposite gels (Zw-NC gels), consisting of a zwitterionic sulfobetaine polymer–clay network, that exhibited good mechanical properties. The Zw-NC gels were synthesized *in situ* by the free radical polymerization of sulfobetaine monomers in the presence of exfoliated inorganic clay platelets uniformly dispersed in aqueous media. Among several kinds of zwitterionic polymers, such as carboxybetaine, sulfobetaine, and phosphobetaine polymers, sulfobetaine polymers with a cationic quaternary ammonium group and anionic sulfonate group in the side chain, and in particular, polymers with the structure shown in Scheme 1, were selected owing to their facile synthesis, well-defined thermosensitive transition at the upper critical solution temperature (UCST), and adequately mild interaction with inorganic clay platelets. In the present study, we report the characteristic swelling behaviors of Zw-NC gels, including unique swelling-to-deswelling behavior in water, abnormal effect of crosslinker (clay) concentration on the DS, large DS in water and aqueous NaCl solutions, distinct transparency changes during swelling, and their temperature dependences related to the thermosensitive transition as compared to other (chemically and physically crosslinked) types of zwitterionic polymer hydrogels and non-zwitterionic NC gels.

2. Experimental

2.1. Materials

N-[3-(dimethylamino)propyl]acrylamide (DMAPAA), 1,3-Propanesultone (PS), and 1,4-Butanesultone (BS) were purchased from the Tokyo Chemical Industry Co., Japan. *N,N*-dimethylacrylamide (DMAA) was provided by Sigma–Aldrich Co. and Kohjin Co., Japan. DMAA was used after purification by filtration through sea sand and activated alumina. Other reagents, i.e., *N,N'*-methylenebis(acrylamide) (BIS), potassium peroxydisulfate (KPS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), and NaCl, were purchased from Wako Pure Chemical Industries, Ltd., Japan. These reagents were used without further



Scheme 1. Chemical structures of zwitterionic sulfobetaine polymers: (a) A₃ polymer, (b) A₄ polymer.

Download English Version:

<https://daneshyari.com/en/article/1395111>

Download Persian Version:

<https://daneshyari.com/article/1395111>

[Daneshyari.com](https://daneshyari.com)