A Convenient One-Step Preparation of Chitosan-Poly(sodium acrylate-*co*-acrylamide) Hydrogel Hybrids with Super-Swelling Properties

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ABSTRACT: Hydrogel hybrids were conveniently prepared from alkaline hydrolysis of chitosan–poly(acrylonitrile) mixture under highly practical conditions. The reaction of chitosan alkoxide anions with nitrile groups of poly(acrylonitrile) (PAN) forms crosslinking points and results in a three-dimensional network with superswelling ability in aqueous media. The hydrogel hybrid was identified using FTIR spectroscopy. The PAN content of the hydrolyzing feed affects proportionally the swelling capacity of the hydrogel hybrid. The swelling properties (capacity and rate) of the ampholytic hydrogel were investigated preliminarily. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1615–1619, 2006

Key words: chitosan; polyacrylate; hydrogel; superabsorbent; swelling

INTRODUCTION

There has been considerable interest in recent years in the development of materials with the capacity for absorbing massive amounts of water. These materials are defined as superabsorbent hydrogels. Hydrogels are crosslinked hydrophilic polymer networks, which can absorb and retain aqueous fluids within their structure without dissolution.[1–2]

Recently, much attention has been paid to chitosan as a potential polysaccharide resource. Chitosan is a biodegradable copolymer composed of D-glucosamine and *N*-acetyl-D-glucosamine.[3] Because of their excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for controlled drug delivery.[4] In recent decades, considerable interest has been focused on modification by grafting synthetic polymers onto the most abundant naturally occurring polysaccharides such as cellulose, starch, alginate, carrageenane, chitosan, and etc. Many works have been reported on the preparation of chitosan hydrogels via grafting of various hydrophilic monomers. Graft polymerization of hydrophilic monomers onto chitosan enhances hydrophilicity and water uptake capacity of the backbone.

Acrylonitrile (AN), a hydrophobic monomer, comprises nitrile group (—CN) on its structure. Graft co-polymerization of AN onto polysaccharides, such as starch[5] and chitosan,[6] have been reported. When nitrile groups are hydrolyzed, they converted to amide ($CONH_2$) and carboxyl (COOH) groups. Anionic hydrogels can be obtained by saponification of poly(acrylonitrile) (PAN)-grafted starch[7] and chitosan.[8,9] Chitosan, a basic polysaccharide, comprises amine (NH_2) groups on its backbone. Recently, an ampholytic hydrogel has been prepared through alkaline hydrolysis of chitosan-*g*-PAN copolymer.[8]

The hydrogel formation was based on early reports of Fanta et al.[10,11] published in 1982, demonstrated that PAN can simultaneously and be saponified crosslinked in aqueous alkali in the presence of starch to produce gel. In fact, crosslinks could be formed between the alkoxide ions of starch and the nitrile groups of PAN. In this work, we attempted to extend the idea in the case of a basic biopolymer. Thus, we saponifed the chitosan–PAN mixture by an aqueous alkali to yield superabsorbing hydrogel hybrids. The swelling behavior of resulted hydrogels was preliminarily investigated.

EXPERIMENTAL

Materials

Chitosan sample (DD 0.76) was prepared from chitin (extracted from shrimp shell) in our laboratory.[6] Poly-acrylonitrile (PAN) was synthesized through a method mentioned in the literature.[12] All other materials were used as received.

Synthesis of hydrogel

The temperature of hydrolysis, time of hydrolysis, and NaOH concentration can affect the saponification of the mixture of chitosan–PAN. These parameters were chosen according to previous works.[8,9] In general, chitosan (0.50 g) was dissolved in 2 wt % acetic acid (50 mL), and the solution was stirred for 20 min to complete dissolving. The chitosan solution was precipitated using NaOH (1N) solution. The precipitated chitosan was dispersed in a loosely stoppered 100-mL flask containing 40 mL aqueous sodium hydroxide (NaOH, 1N). This mixture was allowed to stir for 1 h. After 1 h, various amount of PAN (20, 40, 60, and 80 wt %) was dispersed in the chitosan mixture. Then, the dispersed mixture of chitosan and PAN was heated at 90°C, with magnetic stirring to saponify. The saponification was continued until the color of the mixture changed from deep orange-red to light yellow. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solutions. Methanol (200 mL) was added to the gelled product while stirring. After few minutes, the hyrogel light yellow precipitate was filtered, washed with fresh methanol (2 × 50 mL), and dried at 50°C for 10 h.

Sol content determination

The weighted crude product particles were dispersed in distilled water to swell completely. The gel was filtered, dewatered in excess methanol for 48 h, and dried (50°C, 3 h). The sol (soluble) content was calculated as the weight loss of the initial crude product.

Absorbency measurement

Ultimate absorbency (equilibrium swelling) of the sol-free samples was determined after using the tea bag method described elsewhere.[8] Therefore, the equilibrium swelling values were reported as the weight of fluid absorbed at equilibrium per 1 g of dried sample (g/g).

Characterization

Samples (as KBr thin disks) were characterized by FTIR on an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and characterization

The hydrogel hybrids were prepared using alkali hydrolysis of chitosan–PAN mixtures. Different hydrogels with different PAN percentages were synthesized by varying the amount of PAN. The chitosan–PAN
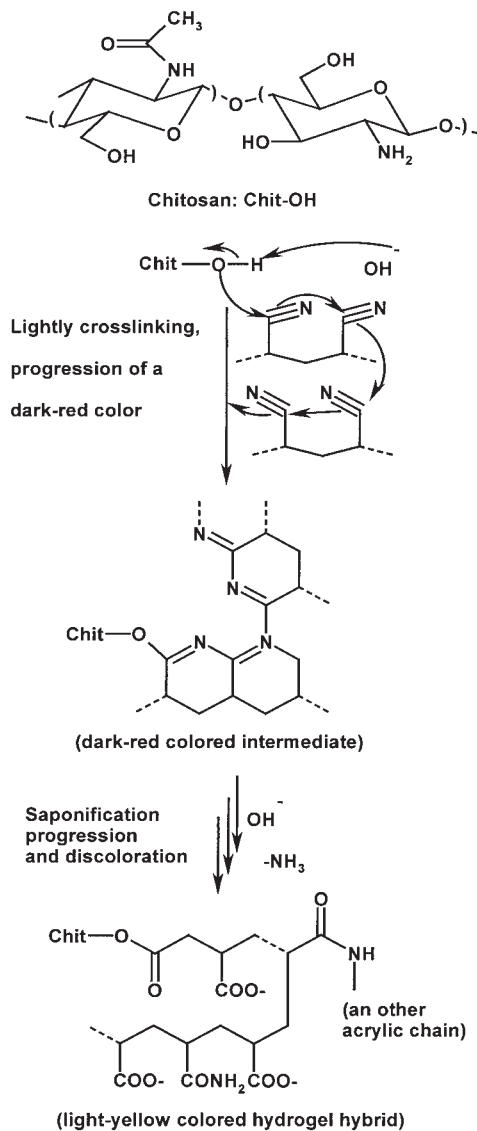
Scheme 1 Mechanism of crosslinking during saponifying nitrile groups of chitosan-PAN mixture to produce *H*-chito-PAN hydrogels.

mixtures were hydrolyzed with NaOH solution to produce superabsorbent hydrogels. During saponification, ammonia evolves and a deep red color develops due to intermediate formation of naphthyridine cyclic structures (including imine, —C≡N—, conjugated bonds) from adjacent nitrile groups. Some crosslinked domains may form if the mentioned reaction occurs between adjacent PAN pendant chains.[13,14] Also, crosslinks could be formed between the alkoxide ions of chitosan and the nitrile groups of PAN (Scheme 1).[10,11] Majority of the intermediate heterocycles are subsequently hydrolyzed with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment.

FTIR spectroscopy was used for identification of the produced hydrogels. The spectra of the initial materi-
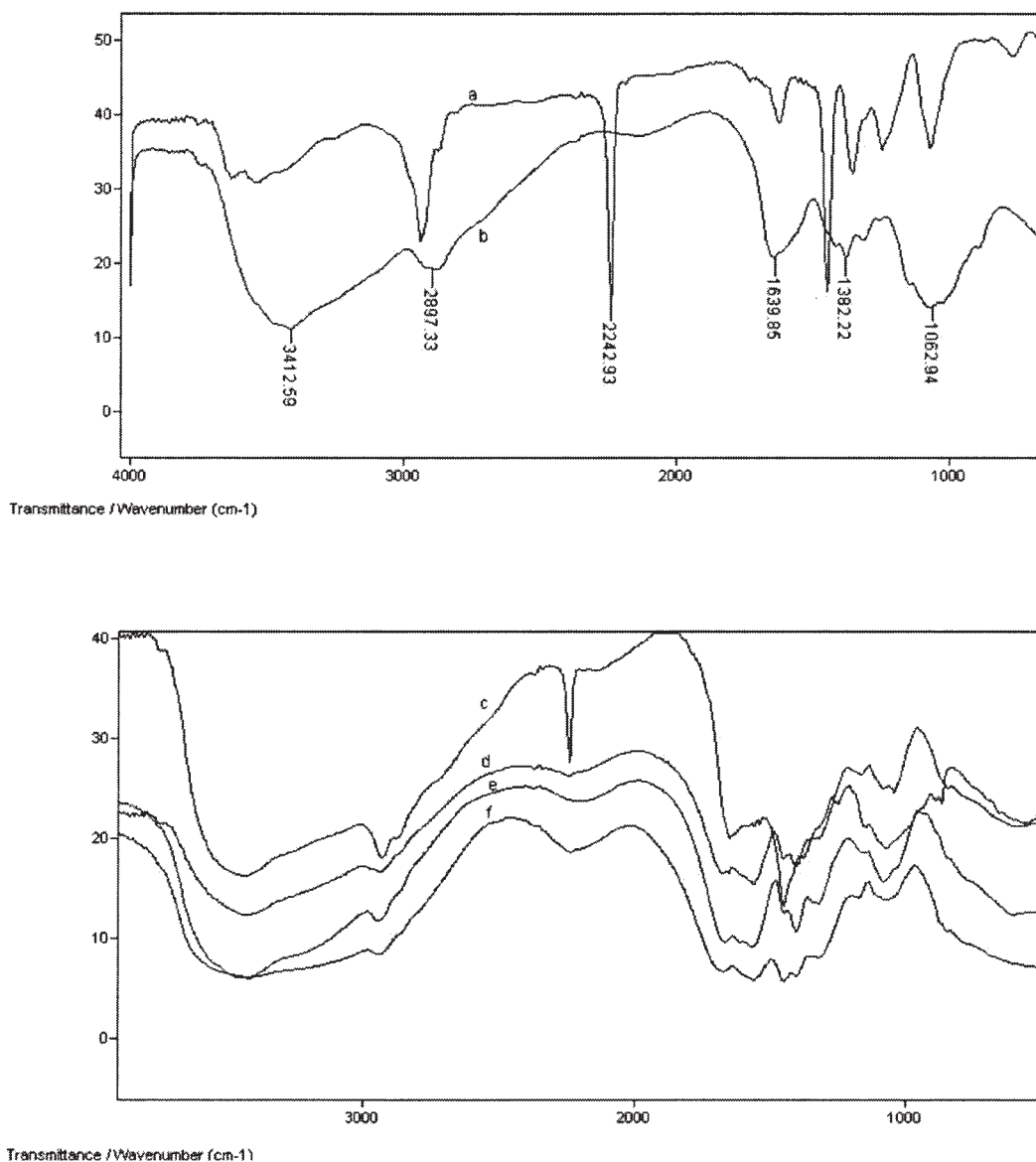
Figure 1 FTIR spectra of (a) PAN, (b) chitosan, (c) mixture of chitosan and PAN, (d) superabsorbent hydrogel from hydrolysis of chitosan–PAN mixture with 60 wt % PAN, (e) partially hydrolyzed chitosan-*g*-PAAm, and (f) hydrolyzed chitosan-*g*-PAN.

als and hydrogel are shown in Figure 1. Figure 1(a)–1(c) shows the spectra of PAN, chitosan, and chitosan–PAN mixture, respectively. Nitrile groups of PAN and chitosan–PAN mixture give an absorption band at 2242 cm^{-1}. With hydrolyzing of the nitrile groups, they convert to carboxylate and rarely carboxamide groups. Figure 1(d) shows the FTIR spectrum of the hydrogel hybrid. The very intense characteristic band at 1569 cm^{-1} is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1407 cm^{-1}, which is related to the symmetric stretching mode of the carboxylate anion.[15] The absorption band at ~1676 cm^{-1} is attributed to amide group. The FTIR spectrum of the hydrogel hybrid was also compared with the spectra of the partially hydro-lyzed chitosan-*g*-poly(acrylamide) (PAAm) and hydrolyzed chitosan-*g*-PAN. The similarity of the hydrogel hybrid with these two spectra reconfirmed the hydrogel structure as proposed in Scheme 1.

Swelling studies

Figure 2 shows the changes of swelling of hydrogels with the varying of the PAN quantity over the range of 20–80 wt % in the mixture. It is observed that by increasing the amount of PAN in the mixture, swelling of the saponified hydrogel of chitosan–PAN mixture is gradually increased. It is attributed to more population of CN groups converting to more hydrophilic groups, i.e., —COO$^-$ and —CONH$_2$. Saponified PAN
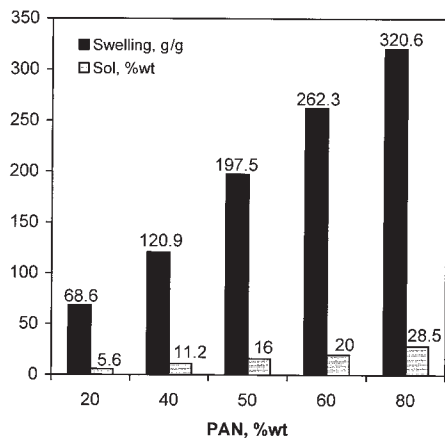
Figure 2 Water absorbency and sol content of hydrogel hybrids with different initial PAN percent made by hydrolysis of chitosan–PAN mixture.

Figure 3 Swelling dependency of superabsorbent hydrogel hybrid on pH.

in the absence of chitosan was found to be soluble in water. In fact, crosslinking takes place between chitosan alkoxide ions and nitrile groups as the initiation reaction of nitrile polymerization at the early stage of saponification (Scheme 1). However, during saponification, some of the PAN chains do not participate in reaction with alkoxide of chitosan chains, and so, they are just hydrolyzed without incorporating in the hydrogel network. As a result, these soluble poly(sodium acrylate-*co*-acrylamide) chains form the majority of the sol fraction of the final product. Therefore, as shown in Figure 2, with increase in the PAN content in the saponification feed, the sol content is increased.

Table I demonstrates the swelling capacity of the hydrogel hybrid in distilled water and salt solutions (0.15M) when PAN content of the initial reaction feed is 60 wt %. As expected, higher ionic strength (cation charge) results in lower swelling capacity.

One of the features of ionic hydrogels is their pH sensitivity. Our preliminary testing showed that the swelling-pH relationship of the chitosan-based hydrogel hybrids was very similar to what we reported most recently in the case of chitosan-*g*-poly(sodium acrylate-*co*-acrylamide) copolymer.[16] This likeness reconfirms the general chemical structure, given in Scheme 1, for the hydrogel hybrid. Since it comprises both

TABLE I
Swelling Variation of a Hydrogel Hybrid (from the Initial Reaction Feed with 60 wt % of PAN) in 0.15M of Various Salt Solutions

Swelling media	Swelling (g/g)
H_2O	262
NaCl	45
$CaCl_2$	10.5
$AlCl_3$	6.5

acidic (—COOH) and basic (—NH$_2$) groups, it is a polyampholitic gel that responds to their basic or acidic environments. To investigate the sensitivity of the hydrogel to pH, the equilibrium swelling (ultimate absorbency) of the hydrogel was studied at various pHs ranged from 1.0 to 12.0 (Fig. 3). No additional ions (through buffer solution) were added to medium for setting pH, because absorbency of a superabsorbent is strongly affected by ionic strength.[17] Therefore, stock NaOH (pH 12.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. According to Figure 3, the two sharp swelling capacity changes can be attributed to high repulsion of —NH$_3^+$ groups in acidic media (pH 3.0) and —COO$^-$ groups in basic media (pH 7.0). Chitosan is a weak base with an intrinsic pK_a of 6.5. PAA contains carboxylic groups that become ionized at pH values above its pK_a of 4.7. However, at very acidic conditions (pH < 3), a screening effect of the counter ions, i.e., Cl−, shields the charge of the ammonium cations and prevents an efficient repulsion.[17] As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). Around pH 5, the carboxylic acid component comes into action as well. Since the pK_a of the weak polyacid is about 4.6, its ionization occurring above this value may favor enhancing absorbency. At a certain pH range 4–6, the majority of the base and acid groups are as nonionized forms, and so, hydrogen bonding between amine and carboxylic acid (and probable carboxamide groups) and electrostatic attraction between ammonium and carboxylate groups may lead to a kind of crosslinking followed by a decreased swelling. At higher pHs, the carboxylic acid groups become ionized, and the electrostatic repulsive force between the charged sites (COO$^-$) causes increasing
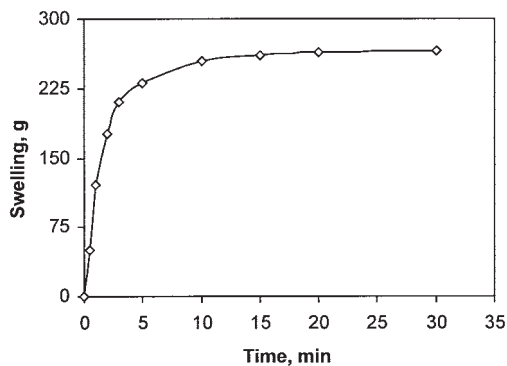
Figure 4 Representative swelling kinetics of a superabsorbent hydrogel (mesh 40–60) prepared from hydrolysis of PAN–chitosan mixture with a weight ratio of 0.6.

in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pH 8–12.

Swelling kinetics

The swelling kinetics of the hydrogel hybrid in water at 25°C is shown in Figure 4. The equilibrium-swelling ratio of the hydrogel (with 60 wt % of PAN) is 262 g/g. Initially; the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 30 min. Hydrophilic groups such as sodium acrylate and amido groups absorb the penetrating water through the formation of hydrogen bonds. The swelling is driven by repulsion of ionic and hydrophilic groups inside the network and osmotic pressure difference between the gels and the external solution. The swelling increase is fast and almost linear during the first 3 min. At this point, the swelling is ~180 g/g. Therefore, the hydrogel absorbs water with a rate of about 1 g/g s.

CONCLUSIONS

Novel hydrogel hybrids were synthesized through saponification of chitosan–PAN mixtures. Swelling capacity of the resulted hydrogel is proportionally changed with the PAN content in the initial reaction feed. On the other hand, higher content results in higher sol fraction in the hydrogel.

Our convenient preparative process comprises the following advantages: it is not involved a polymerization reaction, and so, there is no need to monomer,

crosslinker, and initiator. Consequently, problems such as polymerization control, conversion loss, and residual monomer are eliminated. Our method is a simple alkaline hydrolysis conducted under normal atmospheric conditions in a relatively short period of time. The dark red-yellow color change provides a visual practical indication for recognizing the reaction completion. The only by-product of the reaction as ammonia gas that is removed from the mixture and it can easily be absorbed by acidic solution. Meanwhile, water is the only solvent used for the reaction, and methanol is the nonsolvent to work-up the product and remove the excess alkaline. Overall, in this communication, we report a facial one-step preparative method to yield an ampholytic hydrogel hybrid with superswelling and pH-responsiveness properties. Indeed, since no toxics material is used for the synthesis, this practical approach may be preferred to as a relatively "green process." The smart ampholytic hydrogel hybrids have potential applications in controlled delivery of bioactive agents.

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