

Synthesis and Characterization of Self-oscillating P(AA-co-AM)/PEG Semi-IPN Hydrogels Based on a pH Oscillator in Closed System^{*}

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Abstract Various semi-interpenetrating polymer network (semi-IPN) hydrogels composed of pore-forming agent polyethylene glycol (PEG), acrylic acid (AA) and acrylamide (AM) were prepared by using free radical polymerization with a two-step method. The chemical structures of the synthesized hydrogels were characterized by FTIR spectroscopy and the morphologies were studied by scanning electron microscopy (SEM) method. The swelling properties, such as the pH-responsive behavior, salt sensitivity, oscillatory swelling/de-swelling behaviors in different solutions with various pH values and self-oscillating behaviors in bath pH oscillator were investigated in detail. The results revealed that the prepared hydrogels exhibited high pH sensitivity and excellent salt sensitivity when the pH values of the medium changes from 3.0 and 7.0 and well reversible properties by undergoing a number of swelling/de-swelling cycles. In particular, the hydrogels exhibited self-oscillation behavior in a closed system containing BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H^+ . This study may create a new possibility as biomaterial for new self-walking actuators and other devices.

Keywords: P(AA-co-AM)/PEG semi-IPN hydrogel; Self-oscillating; pH-responsive.

INTRODUCTION

The stimuli-responsive hydrogels are soft and smart materials, which could undergo significant changes of volume or shape in response to a variety of environmental stimuli, such as temperature, pH, electrical fields, *etc*^[1–6]. In the past few years, considerable researches have focused on responsive hydrogels due to their various applications in artificial organ^[7], enzyme^[8, 9], tissue engineering^[10], controlled drug release^[11–13], biosensor^[14], on-off switches^[15] and so on^[16, 17]. However, these smart hydrogels exhibit only one behavior: either swelling or de-swelling in response to environment stimulus. Recently, another type of hydrogels which exhibit swelling/de-swelling recycle in the automatic and periodic chemical oscillating systems, so they are called as self-oscillating hydrogels^[18]. Self-oscillating hydrogel systems could be designed as following^[19–22]: combined responsive hydrogels with chemical oscillating reaction, such as Belousov-Zhabotinsky (BZ) reaction. The BZ reaction is a well known oscillation system^[23, 24] which involves the oxidation of malonic acid by bromate ions in acidic medium with metal catalyst like $\text{Ru}(\text{bpy})_3^{2+}$. Yoshida and his coworkers^[25–27] bonded covalently $\text{Ru}(\text{bpy})_3^{2+}$ to polymer chains to prepare the self-oscillating hydrogels. The periodic change of Ru between its oxidation and reduction states in BZ reaction led to the hydrophilicity/hydrophobicity alter dynamically and thereby exhibited rhythmic swelling/deswelling behavior. Crook *et al.*^[28] synthesized poly(methacrylic acid) gels which oscillate in a Landolt pH-oscillator based on BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H_2SO_4 pH oscillator. However, the applications of this

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kind of self-oscillating hydrogels reported are limited due to the low sensitivity and response rate.

The purpose of this study is to prepare a new kind of self-oscillating and transfer the chemical energy of chemical oscillating reactions to the mechanical energy of hydrogel automatic responses. A series of P(AA-co-AM)/PEG semi-IPN hydrogels were prepared using the familiar two-step method for it is easy to operate and has high yield. The prepared hydrogels have excellent swelling/de-swelling behavior, salt sensitivity and good pH reversibility. The BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H_2SO_4 pH oscillator in closed system was chosen to investigate the self-oscillating behavior of the hydrogels and the results indicated obvious oscillating in volume. This self-oscillating P(AA-co-AM)/PEG hydrogels might create new applications of hydrogels as materials for new self walking actuators and other devices. Moreover, due to the biocompatibility of PAA and PEG would lead to more applications in biomaterial fields.

EXPERIMENTAL

Materials

Acrylamide (AM, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), polyethylene glycol (PEG2000, Shanghai Zhongqin Chemical Reagent Co., Ltd., Shanghai, China), *N,N'*-methylenebisacrylamide (MBA, Shanghai Zhongqin Chemical Reagent Co., Ltd., Shanghai, China), ammonium persulfate (APS, Yantai Shuangshuang Chemical Co., Ltd., Shandong, China), $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, KBrO_3 , Na_2SO_3 , H_2SO_4 were of analytical grade and used as received. Acrylic acid (AA, Tianjin Kaixin Chemical Industry Co., Ltd., Beijing, China) was distilled under reduced pressure before use. Deionized water was used through all the experiments.

Preparation of the PEG/PAA Semi-IPN Gel

The semi-IPN hydrogels of P(AA-co-AM)/PEG were prepared through free radical polymerization with a two-step method. The synthetic route is shown in Fig. 1. Typically, 10.0 g of AA was diluted with distilled water (10 mL) and neutralized with sodium hydroxide solution. Then a certain quality of AM was added and mixed sufficiently at room temperature. After deoxygenating by bubbling with nitrogen for 30 min during stirring, the mixed solution was heated to 65 °C and lasted for 5 min. Then, 0.005 g of MBA and 0.045 g of APS were added and the mixture was stirred at 65 °C for 30 min. The solution of PEG and another 0.005 g of MBA and 0.045 g of APS were introduced into the reactor quickly. At the same time, the reactor was cooled to avoid implosion for some time and then heated under 65 °C for 4 h and the hydrogels was obtained. To remove the residual monomer and cross-linking agent, the dried semi-IPN hydrogels were cut into pieces and put into deionized water for a month and the water refreshed several times. The composition and designation of P(AA-co-AM)/PEG semi-IPNs were listed in Table 1.

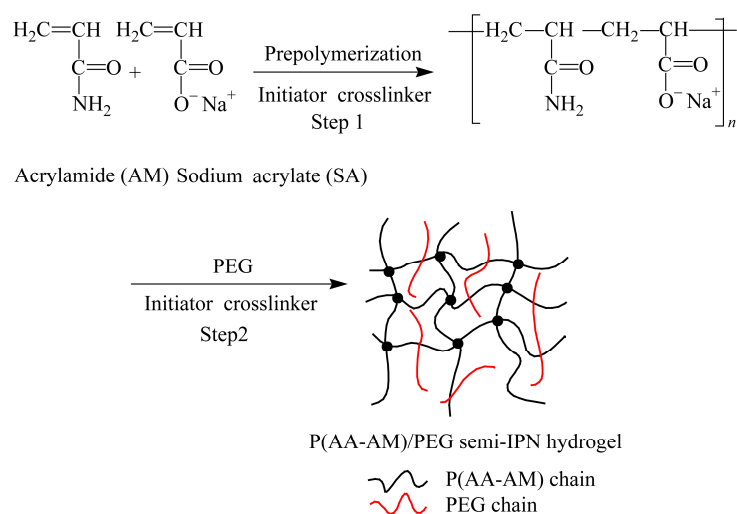


Fig. 1 Preparation of poly(AA-co-AM)/semi-IPN hydrogel

Table 1. Composition and designation of P(AA-co-AM)/PEG semi-IPN hydrogels

Samples	AA (g)	AM (g)	PEG (g)	APS (g)	MBA (g)
semi-IPN1	10.0	2.0	0.3	0.1	0.01
semi-IPN2	10.0	2.0	0.5	0.1	0.01
semi-IPN3	10.0	2.0	0.7	0.1	0.01
semi-IPN4	10.0	2.0	0.9	0.1	0.01
semi-IPN5	10.0	2.0	1.1	0.1	0.01
semi-IPN6	10.0	1.5	0.3	0.1	0.01
semi-IPN7	10.0	2.0	0.3	0.1	0.01
semi-IPN8	10.0	2.5	0.3	0.1	0.01
semi-IPN9	10.0	3.0	0.3	0.1	0.01
semi-IPN10	10.0	3.5	0.3	0.1	0.01

Characterization

FTIR spectroscopy

The chemical structure of the obtained hydrogels was investigated by using FTIR spectroscopy, which were recorded over the range of 400–4000 cm^{-1} by KBr pellet method. The samples were dried at 60 °C under vacuum for FTIR measurements. The FTIR spectroscopy was obtained on an FTS3000 spectrometer (DIGILABGON, USA).

Scanning electron microscopy (SEM)

To identify the morphological differences of the semi-IPN hydrogels, the swollen hydrogel samples were frozen-dried for three days to remove water completely, sputter-coated and imaged by using a JSM-5600LV scanning electron microscope (JSM-5600LV, Japan).

Swelling Properties of the Hydrogels

Measurement of swelling ratio

The totally dried hydrogels was weighed and immersed into excess of swelling medium. At various time intervals, the samples were removed from the solution, wiped with wet filter paper, weighed and replaced into the same solution again. The mass measurement was performed until equilibrium swelling was attained. The swelling ratio (SR) was calculated according to the following equation:

$$\text{SR} = (M_s - M_d)/M_d \quad (1)$$

where M_s and M_d are the masses of the equilibrium swollen hydrogels sample in solution and completely dried state, respectively.

pH sensitivity of the hydrogels

The hydrogels in swollen state were cut into regular cylinders (ϕ 10 mm $\times$ 10 mm) and immersed into absolute alcohol to obtain networks and followed by drying at 40 °C under vacuum condition. Then cylindrical particles with diameter and highness of 1.2 mm were received. In the pH sensitivity experiment, the dried samples were immersed into excess of swelling buffer solutions with various pH values and constant ionic strength 0.1 mol/L. At various time intervals, the samples were removed from the solution, wiped with filter paper and measured the diameters using a digital vernier caliper then replaced back into the same solution. The diameter measurements were continued until the constant date was attained for each sample. To achieve good measuring results, ternate parallel samples were carried out. The swelling measurements in different pH value solutions were measured on the basis of the relative volume swelling ratio Q , which was calculated according to the following equation:

$$Q = (D_s/D_d)^3 \quad (2)$$

where D_s is the diameter of the equilibrium swollen gel sample in solution and D_d is the diameter in dried state.

Salt sensitivity of the hydrogels

In order to evaluate the effect of salt on the swelling of the resulting materials, the swollen samples in deionized

water were weighted and then immersed in NaCl aqueous solutions of various concentrations. The weight of de-swelling sample was measured at different intervals until the weight did not change. The equilibrium lose water content (LWC) of the hydrogels was calculated according to the following equation:

$$\text{LWC}(\%) = [(W_s - W_d)/W_s] \times 100 \quad (3)$$

where W_s is the mass of the swollen sample in water and W_d is mass of the equilibrium de-swollen sample in NaCl aqueous solution.

Oscillatory swelling/de-swelling behavior of the hydrogels

The swollen samples in water were first placed in pH = 3.0 buffer solution and allowed to swell to equilibrium state, and then transferred into pH = 7.0 buffer solution for 2 h. This cycle was repeated several times and the diameters of samples were measured before each immersion. The relative volume swelling ratio Q of cycle-swollen samples were calculated according to the Eq. (2).

Self-oscillatory of the hydrogels in batch pH oscillator

The swollen samples were fixed by one end and suspended in a pH oscillator containing H_2SO_4 (0.03 mol/L), KBrO_3 (0.195 mol/L), Na_2SO_3 (0.225 mol/L) and $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (0.06 mol/L) in batch reactor (volume = 50 mL). At the same time, the pH value change of the system was monitored continuously with a pH meter (PHSJ-4F) connected with computer. The dimensional changes of the hydrogels were measured with a digital vernier caliper at various time intervals.

RESULTS AND DISCUSSION

FTIR Spectra of Hydrogels

The FTIR spectra of the AM, PEG, PAA, P(AA-co-AM)/PEG are presented in Fig. 2. In spectrum a (Fig. 2a), the absorption peaks at 3353 cm^{-1} , 1673 cm^{-1} , 1564 cm^{-1} and 1349 cm^{-1} are attributed to the N—H stretching vibration, the C=O stretching vibration, the N—H bending vibration and the C—N stretching vibration in AM respectively. In spectrum b (Fig. 2b), the peak at 3425 cm^{-1} is the O—H stretching vibration absorption peak and the strong peak around 1111 cm^{-1} corresponds to the C—O—C stretching vibration of PEG. The strong peaks in spectrum c (Fig. 2c) at 1712 cm^{-1} and 1411 cm^{-1} are attributed to the asymmetric stretching vibration and symmetric stretching vibration of C=O in carboxylate, respectively. The peak at 3425 cm^{-1} is attributed to the O—H stretching of AA. For the spectrum d (Fig. 2d) of P(AA-co-AM)/PEG semi-IPN hydrogels, the absorption peaks at 3426 cm^{-1} and 1110 cm^{-1} are due to the O—H stretching vibration absorption and the C—O—C stretching vibration of PEG, which indicates that PEG molecular chains have been introduced into the hydrogels.

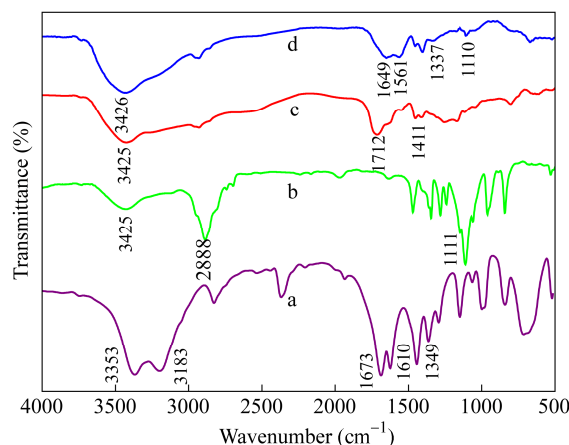


Fig. 2 The FTIR spectra of (a) AM, (b) PEG, (c) PAA and (d) P(AA-co-AM)/PEG

The characteristic absorption peaks around 1673 cm^{-1} , 1564 cm^{-1} and 1349 cm^{-1} attributed to the $\text{C}=\text{O}$ stretching vibration, the $\text{N}-\text{H}$ bending vibration and the $\text{C}-\text{N}$ stretching vibration shift to 1649 cm^{-1} , 1561 cm^{-1} and 1337 cm^{-1} , respectively due to the chemical environment differences. These observations clearly indicate that the semi-IPN hydrogels of $\text{P}(\text{AA-co-AM})/\text{PEG}$ were prepared successfully.

Morphology Analysis of Hydrogels

It is important to study the morphology because the swelling behaviors of the $\text{P}(\text{AA-co-AM})/\text{PEG}$ semi-IPN hydrogels are relevant to it. The morphologies of the semi-IPNs are shown in Fig. 3. It was found that different PEGs induced different hydrogel morphologies and the $\text{P}(\text{AA-co-AM})/\text{PEG}$ semi-IPN2 hydrogels exhibit a highly porous and loose structure with uneven distribution and irregular pores. The larger specific surface area and pores are beneficial for water molecules diffusion into the hydrogels. However, the morphology of semi-IPN5 is different from that of semi-IPN2 as shown in Fig. 3(c). The structure is closer and the pores are smaller than those in semi-IPN2.

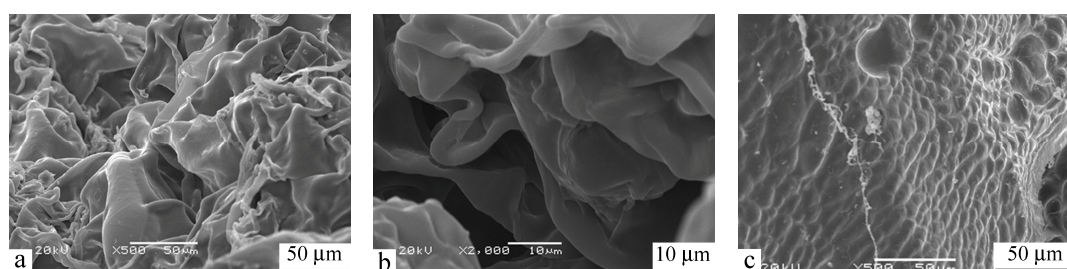


Fig. 3 SEM images of $\text{P}(\text{AA-co-AM})/\text{PEG}$ semi-IPN hydrogels: (a), (b) semi-IPN2 and (c) semi-IPN5

Effect of PEG Content on Swelling Property

In order to evaluate the effect of the composition on the swelling properties of the hydrogels, 10 kinds of hydrogels with different compositions were synthesized as shown in Table 1.

Just as we all know, PEG is used as pore forming agent in hydrogels' synthesis process. The effect of PEG content on the swelling behaviors in deionized water is presented in Fig. 4. It can be seen from Fig. 4, the swelling ratio increases with the increasing of PEG in the range of 0.3–0.5 g and reaches maximum value when the amount of PEG is 0.5 g. Then the swelling ratio decreases with the increasing of PEG content. This phenomenon may be attributed to the PEG influencing the crosslink density^[29] and the hydrophilic/hydrophobic balance of $\text{P}(\text{AA-co-AM})/\text{PEG}$ hydrogels. Due to the numerous proper pores in the network, water molecules can diffuse easily. However, the density and strength of the hydrogels increase and the interior diameter decreases with more PEG addition, the diffusion of water molecules into the hydrogels becomes more and more difficult.

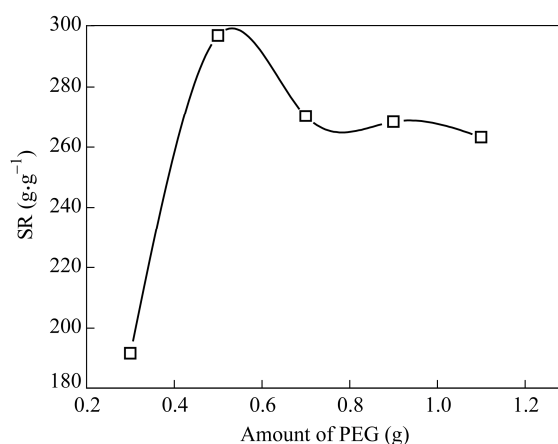


Fig. 4 The effect PEG on the swelling ratio of $\text{P}(\text{AA-co-AM})/\text{PEG}$ hydrogels

Effect of AM Content on Swelling Property

There existed a minimum of SR dependent on the content of AM as shown in Fig. 5. The SR decreased when the amount of AM increased from 1.5 g to 2.5 g. However, the further increasing of AM led to the SR increasing accordingly. It may be because the hydrophilic ability of COO^- is better than that of $-\text{CONH}_2$, so SR would decrease with the increase of AM. On the other hand, AM is a nonionic monomer, it almost does not ionize in solution^[30]. When the appropriate amount AM added in AA, the perfect network of hydrogels formed, which may benefit water entering inside of hydrogels. Therefore, as AM increased, SR would increase. But when the amount of AM exceeded 0.5 g, the SR of semi-IPN hydrogels decreased with the increasing the AM. It may be the result of the effective cross-link densities of the hydrogels increased with increasing the monomer concentration. The probability of cyclization and multiple cross-linking reactions increased as the initial monomer concentration increased^[31].

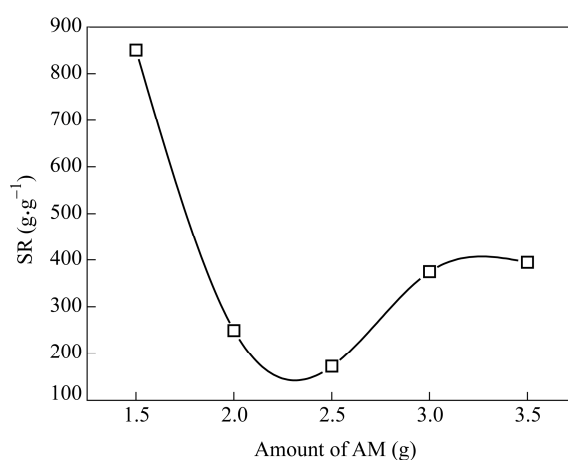


Fig. 5 The swelling ratio of P(AA-AM)/PEG semi-IPN2 hydrogel versus the amount of AM

Salt Sensitivity of the Semi-IPN Hydrogel

Considering the important effect of salt on water absorbency capacity of the hydrogels, the equilibrium dehydration behaviors of the prepared hydrogels in NaCl aqueous solutions were investigated. Figure 6 shows the LWC of the semi-IPN hydrogels in NaCl aqueous solutions of various concentrations. It indicates the LWC of the semi-IPN hydrogels increases with increasing of the NaCl concentrations. According to the Donnan osmotic pressure equilibrium^[32, 33], the osmotic pressure within the hydrogels decreases with the increasing of freely moving counter ions in solution and the network structure of the hydrogels shrinks. As demonstrated by Fig. 7, due to the non-ionic property of AM and the hydrophobicity of $-\text{CONH}_2$ groups, the tolerance to salt of the prepared hydrogels increases with the increasing content of the AM.

pH Sensitivity of the Hydrogels

Figure 8 shows the effect of pH values on the volume swelling ratio of the semi-IPN2 in the range of pH value from 2.0 to 9.0 at room temperature. It can be seen that the swelling ratio of the hydrogels increases quickly with the increasing of pH value in the range of 2.0–9.0. However, only a small change in pH value when it is around 4.0, may produce a large change in the swelling ratio. Thus, increasing the pH values from 3.0 to 5.0, the swelling ratio greatly enhanced from 2.5 to 20.0. The main reason may be due to the dissociation constant (pK_a) being 4.25. When pH value is lower than 4, the ionization degree of AA is low and AA in the hydrogels exists as $-\text{COOH}$ groups. So the electrostatic repulsion of the negatively charged carboxylate groups attached to the polymer chains is so weak that the pores inside the hydrogels are not expanded effectively and plenty water molecules can't spread into the hydrogels. With the pH increasing in the range of 3.0 to 5.0, the $-\text{COOH}$ groups on polymer chains are ionized into $-\text{COO}^-$ and the electrostatic repulsion between $-\text{COO}^-$ increases distinctly and tends to expand the network of hydrogels, so it begins to swell, which makes water enter inside of hydrogels

easily and the swelling ratio increases abruptly. Further increasing of pH from 6.0 to 9.0, the ionization rate of AA in the polymer chain becomes slower and slower, the swelling ratio change is also similar to that.

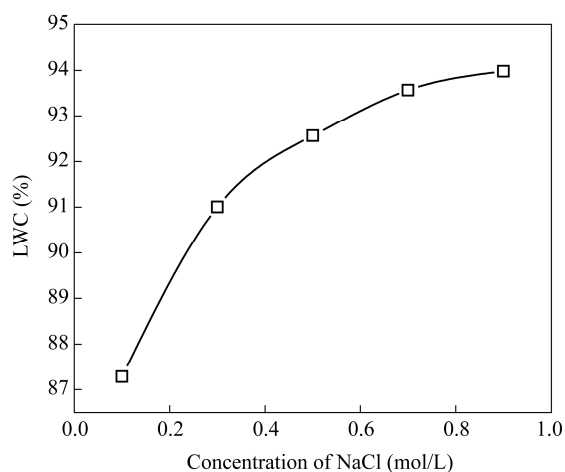


Fig. 6 The lose water content of P(AA-co-AM)/PEG semi-IPN2 hydrogel versus the concentration of NaCl in solution

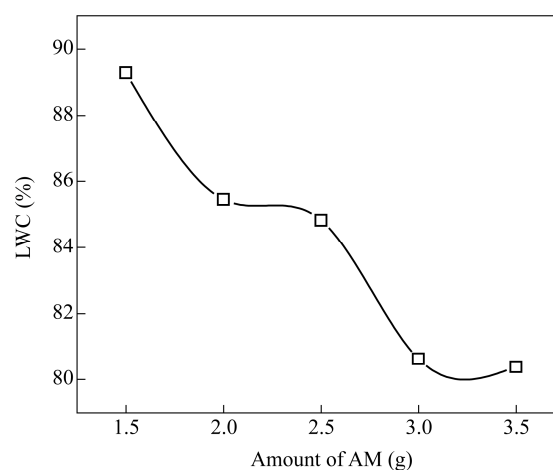


Fig. 7 The lose water content of P(AA-co-AM)/PEG hydrogel containing different contents of AM in 0.1 mol/L NaCl solution

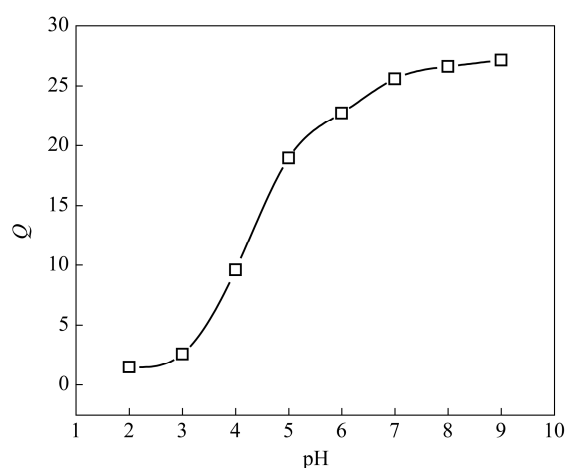


Fig. 8 The relative volume swelling ratio of P(AA-AM)/PEG semi-IPN2 hydrogel versus the pH value

Oscillatory Swelling/De-swelling Behavior

The oscillatory swelling/de-swelling experiments were also performed to investigate the reversible swelling behavior and the response rate of the prepared hydrogels to the pH of the external environment. Figure 9 illustrates the oscillatory swelling/de-swelling of the prepared hydrogels between buffer solutions of pH being 3.0 and 7.0 with ionic strength constant (0.1 mol/L). The sample was immersed into the buffer solution with pH = 3.0 to swelling equilibrium and then transferred into the buffer solution with pH = 7.0, it began to swell quickly. When it returned back to the solution with pH = 3.0, the sample shrunk and the volume swelling ratio was about 12. Then the sample was transferred into the solution with pH = 7.0 again, it swelled fast. It can be seen from Fig. 8 that semi-IPN hydrogels present favorable reversibility with quick swelling, shrinking and re-swelling even after several recyclings. In addition, we also found that the hydrogels was not broken and the shape kept very well after several recyclings, which indicated the hydrogels with good flexibility and toughness. It would be a desirable characteristic for a pH-sensitive control-release system and the hydrogels could be expected to be applied as a pH-responsive material in many biological fields.

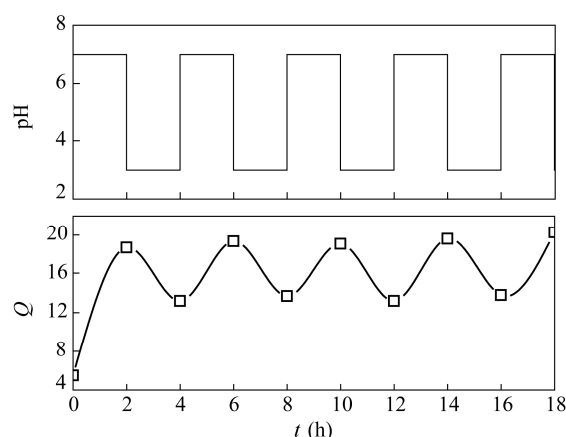


Fig. 9 Relative volume swelling ratio oscillation behavior of P(AA-co-AM)/PEG semi-IPN2 hydrogel in the solutions of pH = 3.0 and pH = 7.0

Self-oscillatory in Closed pH Oscillator

The BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H^+ system in acidic media is known to exhibit oscillating behavior in which the pH changes periodically between 2.5 and 7.0^[34, 35], so it was chosen to evaluate the self-oscillating behaviors of the resulting hydrogels. Figure 10 shows the volume swelling ratio changes of P(AA-co-AM)/PEG hydrogel (lower) with pH (upper) in the pH oscillator in batch system at 37 °C. The sample swelled in response to the increasing of pH until pH = 7.0 by addition of SO_3^{2-} in the pH oscillator. The total swelling ratio is about 2 times of that at pH = 2.5. Following a slow decrease of pH of the oscillator, the hydrogels reversed to shrink to the original size. The shrinking speed was slower than the swelling rate, and it took almost 45 min for it to restore to its original size. This slower shrinking speed may be attributed to the dense polymer network and the strong hydrogen bonding interaction between the carboxylic groups of hydrogels, which slow down the diffusion of water inside the hydrogels. In addition, the swelling ratio in the pH oscillator is smaller in contrast to which in buffer solutions of pH being 3.0 and 7.0 with ionic strength constant (0.1 mol/L). These results are reasonable due to the ionic strength. The ionic strength of the pH oscillator is several times more than that in the above described buffer solutions of pH = 3.0 and 7.0. The increasing of the ionic strength significantly decreases the swelling ratio, and it can also be seen from Fig. 6.

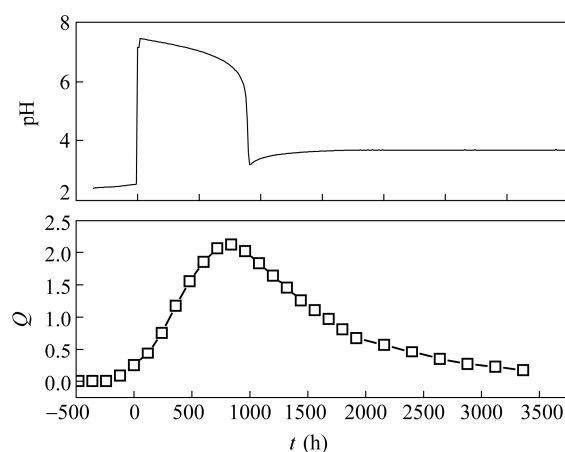


Fig. 10 Relative volume swelling ratio changes of P(AA-co-AM)/PEG semi-IPN2 hydrogel (lower) and pH in a closed pH oscillator at 37 °C

CONCLUSIONS

P(AA-co-AM)/PEG semi-IPN hydrogels were synthesized using two-step free radical polymerization in the present work. PEG is used as pore forming agent in hydrogels' synthesis process, the PEG content in the hydrogels affects the pore's diameter and water molecule diffusion. The prepared hydrogels are sensitive to pH value and salt in external environment and have excellent reversibility of pH-response. Also the response of the present hydrogels in the BrO_3^- - SO_3^{2-} - $\text{Fe}(\text{CN})_6^{4-}$ - H^+ oscillating system indicates good swelling/de-swelling self-oscillating behavior coupled with pH oscillator. As a result, the prepared hydrogels with pH-dependent and self-oscillating characteristics may be expected to use in bioengineering and biotechnology.

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