

POLY(MALEIC ANHYDRIDE-*CO*-ACRYLIC ACID)/POLY(ETHYLENE GLYCOL) HYDROGELS WITH pH- AND IONIC-STRENGTH-RESPONSES

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Abstract Poly(maleic anhydride-*co*-acrylic acid), P(MA-AA), was synthesized by the free-radical copolymerization of maleic anhydride with acrylic acid, and fast responsive pH-sensitive poly(maleic anhydride-*co*-acrylic acid)/polyethylene glycol, P(MA-AA)/PEG, hydrogels were prepared using PEG as macromolecular cross-linking agent. FT-IR and ¹H-NMR spectrometry were applied to characterize the structure of P(MA-AA). The influences of pH and ionic strength on the swelling behavior of P(MA-AA)/PEG hydrogels and the swelling-deswelling changes along with the repeated changes between acid and alkali conditions were studied. The results showed that there was a hundredfold difference in the swelling ratios between the conditions of acid and alkali, and the swelling capability could not be weakened after multiple swelling-deswelling cycles. The results of swelling kinetics demonstrated that the response rate of P(MA-AA)/PEG hydrogels was very fast, because the swelling transition points always occurred at 10 min. The pH-responsive hydrogels reported here might be a smart material for potentially applications in many areas, including biosensors, drug-delivery devices and tissue engineering.

Keywords: pH-response; P(MA-AA); Macromolecular cross-linking agent; External cross-linking.

INTRODUCTION

Hydrogels, especially intelligent hydrogels, have attracted a great deal of researchers' attention due to their intriguing properties and potential applications^[1–4]. One of the most notable properties of the intelligent hydrogels is that they could undergo substantial and abrupt volume change in response to the external stimulus, such as pH, temperature, ionic strength, electric field, *etc*^[5–9]. The volume transitions of hydrogels have prompted researchers to investigate the application of the smart materials in sensors, actuators, artificial muscles, drug-delivery systems, tissue engineering, *etc*^[2, 10–12].

pH-responsive hydrogels are the most extensively investigated intelligent hydrogels. They are capable of changing their shape and volume with a slight variation of external pH, so they have been widely used in medicine such as drug-delivery^[10–13]. The pH-responsive behavior of hydrogels is caused by the presence of ionizable groups in the polymeric chains. It has been known that a hydrogel bearing weakly acidic pending groups exhibits pH-responsive due to the alternant changes of COOH/COO[−] on pH. Because of the electrostatic repulsion among COO[−], the pH-responsive hydrogel expands smoothly with pH increasing. A lot of pH-responsive hydrogels like acrylic copolymer hydrogels and poly(acrylic acid) derivative hydrogels have been synthesized and their swelling behaviors have been extensively studied^[11, 13–18], but hydrogels with large responsibility, fast response rate and excellent reversible changes with changing environmental stimuli at the same time are rarely found. In order to improve the pH-responsibility and response rate of the hydrogels, maleic anhydride was introduced into poly(acrylic acid) chains to increase the amount of COOH groups.

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The preparation technology is the prerequisite to devise new polymer hydrogels and obtain a wide range of applications. Up to now, a number of studies in preparing hydrogels have focused on copolymerization of water-soluble monoene/diene or polyene (cross-linker) monomers^[3–5, 12, 18, 19]. However, hydrogels can also be prepared by external cross-linking of macromolecular chains. Compared with chain addition polymerization, the main advantage of this method is that the initial macromolecular chains could be prepared in a variety of ways. Therefore, there are more choices for monomers and synthesis technologies and there is more room for the design and regulation of chemical structure. The variety of existing water-soluble polymers is limited, and many researchers are studying the non-environment sensitive PVA/dialdehyde cross-linking system^[20–22]. Liu has prepared pH-responsive hydrogel nanofibers by external cross-linking^[23, 24], which implies the applicative value of external cross-linking hydrogels in a certain extent.

In the last several decades, PEG has been widely used in biomedical applications because of its extreme hydrophilicity, biocompatibility and low toxicity^[11, 12, 25, 26]. In this paper, long-chain PEG4000 was used as macromolecular cross-linking agent to increase chain length between crosslinking points, and to enhance the response rate and the swelling ratio of the hydrogel. In order to examine the effects of maleic anhydride and macromolecular cross-linking agent, the influences of pH and ionic strength on swelling ratio of P(MA-AA)/PEG hydrogels, and the swelling-deswelling changes along with the repeated changes between acid and alkali conditions were mainly studied.

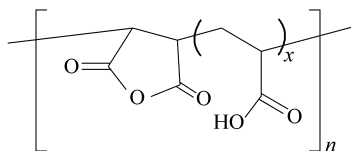
EXPERIMENTAL

Materials

Acrylic acid (AA) (AR, Tianjin Guangfu Fine Chemical Research Institute) was distilled under reduced pressure before use. Maleic anhydride (MA) (AR, Tianjin Fuchen Chemical Reagent Factory) was recrystallized in chloroform before use. Benzoyl peroxide (BPO) (AR, Shenyang Xinxu Reagent Factory) was recrystallized twice from chloroform-methanol (1:1) mixture and dried under vacuum before use. 1,4-Dioxane (AR) and tetrahydrofuran (THF) (AR) (Tianjin Tiantai Fine Chemical Co., Ltd.) were purified by refluxing with metallic sodium followed by distillation. Benzene (AR), *n*-hexane (AR), diethyl ether absolute (AR) and polyethylene glycol 4000 (PEG) (LR) (Tianjin Tiantai Fine Chemical Co., Ltd.) were used without further purification.

Preparation of P(MA-AA)

P(MA-AA) was prepared by the free-radical copolymerization of MA with AA in 1,4-dioxane based on Guner's methods^[27, 28]. 230 mL of 1,4-dioxane, 64.8 g of AA and 88.2 g of MA were added into a 500 mL three-necked flask ordinarily. Nitrogen was bubbled through the mixture to remove oxygen for 10 min, and then 0.2183 g of BPO was added as an initiator. The reaction was carried out with stirring for 10 h at 70°C under a nitrogen atmosphere. The P(MA-AA) was isolated from the reaction mixture by precipitation with *n*-hexane. Then the obtained copolymers were purified by precipitating twice from 1,4-dioxane solution with *n*-hexane and were washed three times with a mixed solvent of *n*-hexane, benzene and diethyl ether (1:1:1, *V/V/V*). At last the product was dried in vacuum at 50°C to a constant weight with a yield of 75%. The structure of P(MA-AA) is represented schematically as follows:



Preparation of P(MA-AA)/PEG Hydrogels

A certain amount of PEG-4000 was added to a test tube, in which 0.8500 g of P(MA-AA) was dissolved in 10 mL of purified THF. Then H₂SO₄ (0.5 mL) and THF (3 mL) were added to the above mixture. After mixing uniformly, nitrogen was bubbled through the reaction mixture to remove oxygen for 10 min, followed by sealing the test tube and reacting at 68°C. 2 mL of THF was injected into the test tube after hydrogel formed to prevent the evaporation of THF (the recipe is given in Table 1). The obtained hydrogels were immersed in distilled

water at room temperature for a week after finishing the reaction, and the distilled water was refreshed at set time intervals to remove THF, unreacted chemicals and sols.

Characterization

The FT-IR spectra of the copolymer and hydrogels were recorded using a VECTOR22 spectrometer (Bruker, Germany). P(MA-AA) was dissolved in THF and was cast as a thin film on a KBr pellet. The dried P(MA-AA)/PEG hydrogels mixed with KBr powder were compressed into a pellet for the test. The spectra were recorded in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} .

^1H -NMR spectrum of the hydrolyzed P(MA-AA) was recorded with a Varian 300 spectrometer in deuterated dimethylsulfoxide (DMSO-d_6).

Measurement of Swelling Ratio

The aqueous solutions with different pH were prepared by adding HCl or ammonia in distilled water. The pH dependence of equilibrium swelling ratio of P(MA-AA)/PEG hydrogels was studied within the range of pH = 2 to pH = 11. First, each hydrogel sample was immersed in the solution of pH = 2 for swelling equilibration, and the solution was refreshed twice in order to keep the pH unchanged during the process of equilibration. The hydrogel was repeatedly weighted and reimmersed in the solution until the hydrogel weight reached a constant value. This weight was the equilibrium swollen weight (W_s) of the hydrogel at this pH. After equilibration at pH = 2, the hydrogel sample was then transferred into the solutions of pH = 3, and got W_s by the same way. Values of W_s at pH = 4 to 11 were obtained in turn. At last, the sample was dried in vacuum at 35°C until the weight was constant, which was called the dry weight (W_d) of the hydrogel. The equilibrium swelling ratio (SR) was calculated as follows:

$$\text{SR} = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

Measurement of Response Rate

For sample C has the best swelling capability, it was taken as an example to study the response rate of P(MA-AA)/PEG hydrogels when pH value changed. The hydrogel sample was immersed in a certain pH value solution, and the solution was replaced twice to keep the pH unchanged. The hydrogel was filtered and weighed until the weight was constant. Then, the hydrogel was transferred into another pH solution, and the sample was filtered and weighed at a set time intervals until the weight was constant. The solution was refreshed after each weighting.

The Swelling-Deswelling Repeatability

Sample C was taken as an example to study the repeatability of swelling-deswelling with altering changes between acid and alkali solutions. The sample was immersed in the solution of pH = 2 for 10 min and weighed, and then the sample was transferred into the solution of pH = 10 and weighed after it was immersed for 20 min. After that, the sample was transferred into the solution of pH = 2 again. The above cycle was repeated 20 times, and the solution was replaced twice to keep the pH unchanged during each process of swelling or deswelling.

Effect of Ionic Strength

The effect of ionic strength on swelling ratio of P(MA-AA)/PEG hydrogels was conducted by immersing the sample in NaCl solution with different ionic strength. The solution was replaced twice to keep the ionic strength unchanged. The equilibrium swollen weight of the hydrogel was measured. Sample C was also taken as the example.

RESULTS AND DISCUSSION

FT-IR Analysis

The FT-IR spectra of P(MA-AA) and P(MA-AA)/PEG hydrogels are shown in Fig. 1. It is obvious that the characteristic signals of C=O of a five-membered ring of anhydride are observed at 1845 cm^{-1} (asymmetric)

and 1778 cm^{-1} (symmetric) in the P(MA-AA) spectrum. The peaks at 3060 cm^{-1} and 1720 cm^{-1} correspond to O—H and C=O stretching vibration in carboxyl groups. The results demonstrate that P(MA-AA) was successfully synthesized.

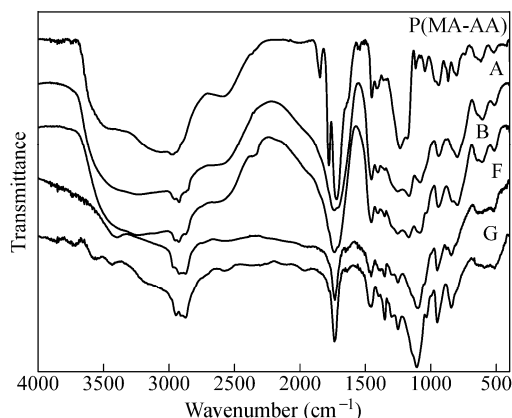


Fig. 1 FT-IR spectra of P(MA-AA) and P(MA-AA)/PEG hydrogels

In spectra of P(MA-AA)/PEG hydrogels, the characteristic bands of 1845 cm^{-1} and 1778 cm^{-1} for anhydride units in the copolymer P(MA-AA) disappear, which means that anhydride units have been fully esterified or hydrolyzed. From sample A to G, the amount of PEG linked to P(MA-AA)/PEG hydrogels increases with the increase of PEG used according to the comparison between bands of C=O (1735 cm^{-1}) in carboxyl and C—O—C (1100 cm^{-1}) in ether.

¹H-NMR Analysis

The ¹H-NMR spectrum of the hydrolyzed copolymer is shown in Fig. 2. The spectrum displays characteristic peaks at $\delta = 1.23\text{--}1.94$ (peak c, CH groups), $\delta = 2.00\text{--}2.40$ (peak b, CH₂ groups), $\delta = 12.02\text{--}12.92$ (peak d, COOH groups) which are related to AA units, and $\delta = 2.54\text{--}2.96$ (peak a, CH groups), $\delta = 12.02\text{--}12.92$ (peak d, COOH groups) which are related to hydrolyzed MA units. The integration of ¹H-NMR spectrum indicate that the molar ratio of MA:AA in the P(MA-AA) is 1.04:2.

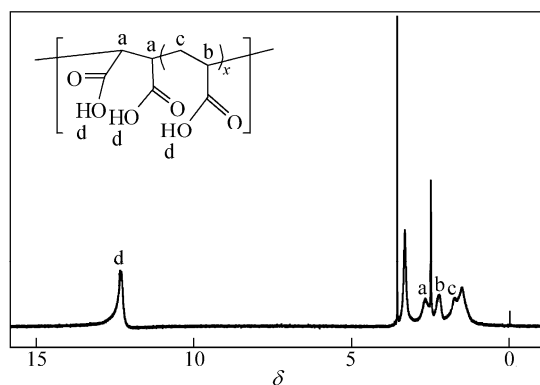


Fig. 2 ¹H-NMR spectrum of hydrolyzed P(MA-AA)

Gel Yield and Gel Fraction

Gel yield is the mass of hydrogel after it was dried in vacuum at 35°C , and gel fraction is the ratio of gel yield to total mass of the raw materials (Table 1). The gel yield increases with the increase of PEG content, which is the result of increasing reaction probabilities between anhydride and hydroxyl groups.

Table 1. Detail experiment information and results

Sample ID	P(MA-AA) (g)	PEG (g)	PEG ^a (mol%)	THF (mL)	<i>M</i> ^b (h)	<i>N</i> ^c (h)	<i>T</i> (°C)	Yield (g)	<i>F</i> _{gel} ^d (%)
A	0.8509	0.2002	1.4	10	60	80	68	0.6589	62.68
B	0.8515	0.6002	4.2	10	48	78	68	0.8204	56.51
C	0.8500	1.0000	7.0	10	44	76	68	0.5382	29.09
D	0.8500	1.6002	11.2	10	34	76	68	1.0075	41.12
E	0.8502	2.0003	14.0	10	28	72	68	1.1549	40.51
F	0.8505	3.0010	21.0	10	25	72	68	1.8951	49.20
G	0.8502	4.0001	28.0	10	22	72	68	1.9270	39.72

^a The molar percentage of PEG relative to the incorporated MA unit; ^b Reaction time before the gelatin forms;

^c Reaction time after the gelatin forms; ^d Gel fraction

Table 1 shows that gel fraction declines with the increase of PEG. As PEG-4000 is a long-chain molecule with only two reactive groups (hydroxyl) in the molecular chain, the reaction probability with P(MA-AA) is low. Some hydroxyl groups at the ends of PEG may be embedded in molecular coils so that they have few opportunities to react with anhydride in P(MA-AA). Although the PEG may react to the hydrogels and the cross-linking density increases with the increase of PEG used, the increased mass of PEG reacted to the hydrogel is much less than the PEG used, so the gel fraction is in a declining tendency.

It is noticeable that the sample C in Table 1 is not consistent with the rule of gel yield and gel fraction with the sample composition. We think this may be due to the microgels in the hydrogel system. During the process of preparing hydrogel, the system is composed of macrogels and microgels, and the microgels will be filtered together with the sols from the system in the process of sample purification, then the macrogels is obtained as gel sample. In the preparation of P(MA-AA)/PEG hydrogels, the content of the formed microgels will increase greatly with PEG increase when the content of the cross-linking agent PEG is quite few, while as the PEG content increases to a certain value, the macrogels and microgels will be connected and form a large gelation network. We guess that the sample C is at the critical state, and there are a large number of microgels in the hydrogel system. So the value of gel yield and gel fraction is quite small.

pH-response of P(MA-AA)/PEG Hydrogels

The swelling ratio at different pH is adopted to evaluate the pH-response of P(MA-AA)/PEG hydrogels. In this experiment, the swelling ratios at a series of pH (from pH = 2 to pH = 11) were measured, and the results are shown in Figs. 3 and 4.

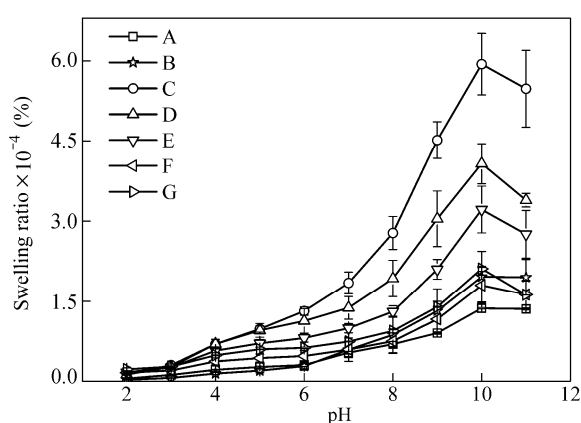


Fig. 3 Swelling ratio of P(MA-AA)/PEG hydrogels at different pH

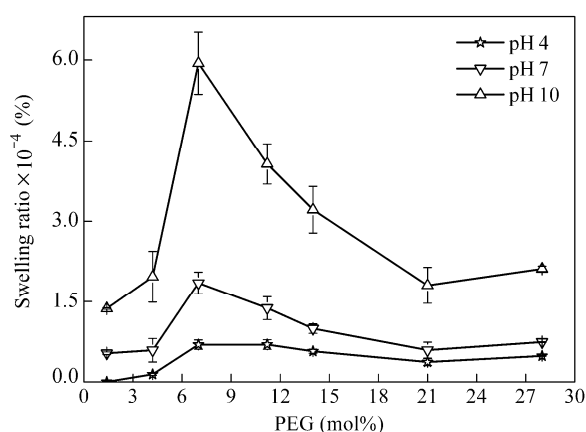


Fig. 4 Effect of PEG content on swelling ratio

As shown in Figs. 3 and 4, the swelling ratio of P(MA-AA)/PEG hydrogels increases obviously with the increase of pH, especially when pH > 7, which can be attributed to the fact that the anhydride units are fully

hydrolyzed into carboxyls for the hydrogels immersed in water. With the increase of pH, the force of hydrogen bonds among the COOH groups in the backbone disappears and the COOH groups are ionized into COO⁻ forms. Electrostatic repulsion among COO⁻ groups makes the backbones of P(MA-AA) extended, so the average pore size in P(MA-AA)/PEG hydrogels increases, and the swelling ratio increases as well.

In Fig. 3, it is found that the swelling ratio of the hydrogels decreases suddenly from pH = 10 to pH = 11, which is the result of salt effect. There are lots of NH₄⁺ in the solution at higher pH, which shield COO⁻. So, the electrostatic repulsion disappears, and then the backbones of copolymer contract to irregular coils which causes the average pore size in P(MA-AA)/PEG hydrogel reduced, and the swelling ratio decreases.

From Fig. 4, we notice that the swelling ratio of P(MA-AA)/PEG hydrogels increases when PEG increases from 1.4 mol% to 7.0 mol% (from sample A to sample C), which may be the result of that cross-linking agent in sample A and B is too little to cross-link completely and the cross-linking density is relatively small. There are lots of pendant P(MA-AA) chains extend in water, but they couldn't save water after filtration. The swelling ratio decreases with increasing PEG from 7.0 mol% to 21.0 mol% and 28.0 mol% (from sample C to F, G), which should be attributed to the high reticulation densities. The chain length between two cross-linking points is shorter and pore size in hydrogels is smaller when the cross-linking agent increases.

The swelling ratio of hydrogels in alkali is almost a hundred times larger than that in acid condition. It is because that COOH density is high on backbone and long chain molecules used as cross-linking agent. In order to make the hydrogels more sensitive to pH, maleic anhydride has been introduced into poly(acrylic acid) chains. Electrostatic repulsion between two COO⁻ groups makes the molecule chain more extended after the COOH groups are ionized to COO⁻ in alkali condition. Long-chain PEG was adopted as cross-linking agent to prepare hydrogels, so the average pore size in the P(MA-AA)/PEG hydrogels was relatively big. Therefore, the swelling ratio of the prepared hydrogels changed remarkably with changing pH.

Swelling Kinetics

Time-dependent swelling of P(MA-AA)/PEG hydrogels with different pH are provided in Fig. 5. The picture of the hydrogels (sample C) at pH = 10 and pictures of the hydrogels at different times after addition of pH = 2 solution are shown in Fig. 6. It is obvious that the swelling transition points are almost in the same position at 10 min. It demonstrates that the response rate of P(MA-AA)/PEG hydrogels is very fast. The hydrogels could completely swell within 20 min from pH = 2 to pH = 10, while they also could contract completely within 10 min from pH = 10 to pH = 2, which is due to the high density of COOH on backbone in hydrogels and long chain molecules used as cross-linking agent. The COOH groups are quickly ionized to COO⁻ when the hydrogels are immersed in alkali solution. The molecular chains extend rapidly, which is caused by the disappearance of hydrogen-bonding forces and appearance of electrostatic repulsion among COO⁻ groups, so the hydrogels swell quickly. COO⁻ and H⁺ are combined into COOH rapidly when the hydrogels are immersed

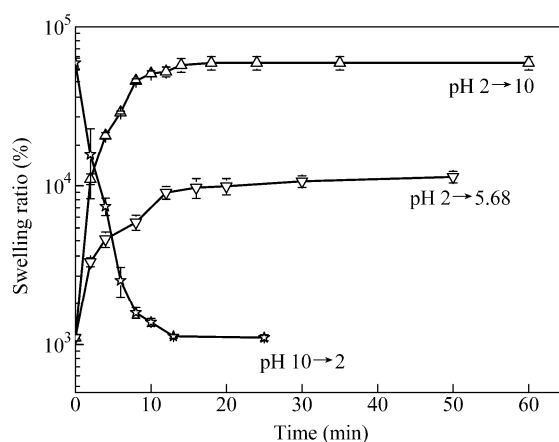


Fig. 5 Effect of pH on swelling kinetics

in acid solution. The hydrogels deswell rapidly because of the disappearance of electrostatic repulsion among anions and the appearance of hydrogen bonds. Compared with small molecular cross-linking agent, the average pore size is larger in hydrogels when macromolecule is adopted as cross-linking agent, so it is easier for water molecules to diffuse through the hydrogels.

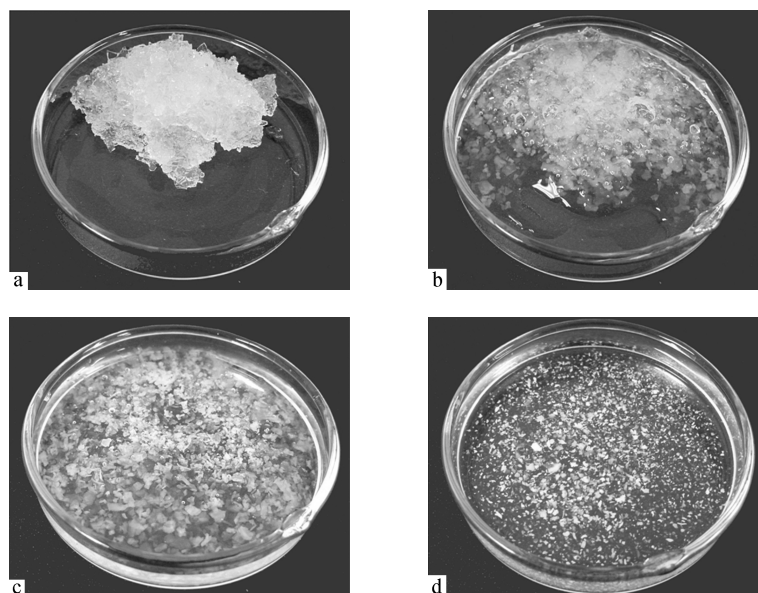


Fig. 6 Pictures of hydrogels taken under different conditions

a) pH = 10; b) 10 s after the pH = 2 solution was added; c) 1 min after the pH = 2 solution was added; d) 10 min after the pH = 2 solution was added.

In addition, it takes less time to reach the equilibrium for P(MA-AA)/PEG hydrogels in alkali condition than in neutral condition. The hydrogels can reach the equilibrium state within 20 min from pH = 2 to pH = 10, while they are still swelling slowly till 50 min from pH = 2 to pH = 5.68. The reason is that the hydrogen bonds break rapidly and then the COOH groups are ionized to COO⁻ in alkali condition, but the COOH groups can't be ionized completely in neutral condition. In alkali condition hydrogen bonds do not work any more and strong electrostatic repulsion exist among COO⁻ groups, but there are only parts of hydrogen bonds that don't work in neutral condition.

Effect of Swelling-Deswelling Recurrent Times on Swelling Ratio

It is important to achieve reversible swelling-deswelling of the hydrogels for their practical applications. The effect of swelling-deswelling recurrent times of P(MA-AA)/PEG hydrogels in acid-alkali solution on swelling ratio is shown in Fig. 7. From Fig. 7, it can be seen that the hydrogels have excellent swelling-deswelling repeatability. The swelling capability and the response rate are not weakened after 20 cycle times. It indicates that the inherent structures haven't been broken during swelling-deswelling cycles. The prepared P(MA-AA)/PEG hydrogels can be used as pH-sensitive materials due to their favorable repeatability and great transformation in swelling ratio (nearly 100 times).

Effect of Ionic Strength on Swelling Ratio

The effect of different ionic strengths on swelling ratio of P(MA-AA)/PEG hydrogels is shown in Fig. 8. The swelling ratio of the P(MA-AA)/PEG hydrogels decreases dramatically as the ionic strength increases from 0.0001 mol·L⁻¹ to 0.1 mol·L⁻¹, and then it maintains constant with further increasing ionic strength to 1.0 mol·L⁻¹, which indicates that P(MA-AA)/PEG hydrogel is quite sensitive to ions. The reduction of the swelling ratio with ionic strength is very common for carboxyl-containing hydrogels. On one hand, the chemical

potential is higher in hydrogel than in ionic solution, and osmotic pressure is the drive force for water exuding from hydrogel. On the other hand, negative electrostatic repulsion is depressed by the shielding of Na^+ counter ions. Electrostatic repulsion disappears and it causes the chains to shrink. Therefore, P(MA-AA)/PEG hydrogels also can be used in ions detecting and absorbing in solution.

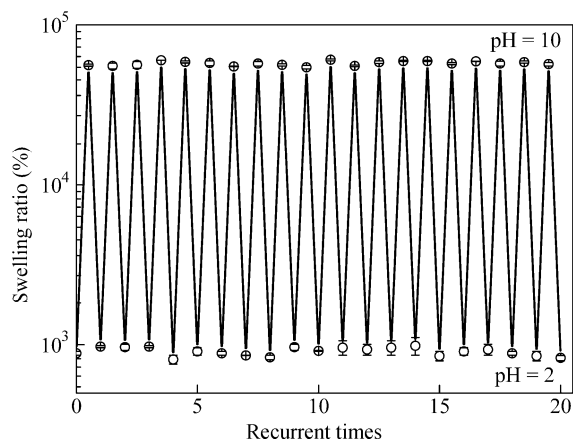


Fig. 7 Effect of swelling-deswelling recurrent times on swelling ratio

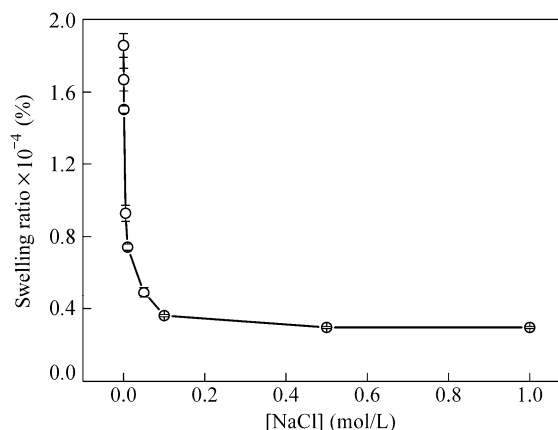


Fig. 8 Effect of ionic strength on swelling ratio

CONCLUSIONS

In this paper, fast responsive pH-sensitive P(MA-AA)/PEG hydrogels were obtained by using PEG as a macromolecular cross-linking agent. The hydrogels have excellent swelling-deswelling repeatability when the conditions of acid and alkali were repeatedly changed, and there is a hundredfold difference among swelling ratios. In addition, the swelling capability could not be weakened by multiple swelling-deswelling cycles.

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