Experimental Research on the Respondent Behavior of a New Intelligent Hydrogel Prepared by MLTP-Initiated Polymerization

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In order to overcome the shortcomings of unitary hydrogels, a new type of binary intelligent hydrogen [P(AMPS/NIPA)], which has the characters of both PAMPS and PNIPA, was synthesized from AMPS and NIPA by Microwave Low Temperature Plasma (MLTP)-initiated polymerization. The characteristics of the binary hydrogel were studied in detail. Firstly, the effects of MLTP treatment power and time on swelling ratio were discussed, the composition and the three dimensional crosslinked network of the hydrogel were studied by means of infrared spectra and polarizing optic microscope photos. Secondly, temperature-sensitivity, swelling/deswelling kinetics and pH-sensitivity of the hydrogel were investigated, respectively. The results showed that the P(AMPS/NIPA) hydrogel prepared by MLTP-initiated polymerization had a large swelling ratio, rapid respondent speed, good temperature-sensitivity and pH-sensitivity and it was a better intelligent hydrogel with high performance.

Keywords: MLTP-initiated polymerization; P(AMPS/NIPA); intelligent hydrogel; network; temperature-sensitivity; pH-sensitivity

1 Introduction

In recent years, much attention has been paid to the investigation and application of environmental respondent, multivariate hydrogels (1−10). For the purpose of getting some special intelligent characteristics, multivariate hydrogels, which can overcome defects in the properties of unitary hydrogels, are designed and prepared with special monomers (11−16). In theory, the P(AMPS/NIPA) binary hydrogel, which is synthesized by 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and N-isopropylacrylamide (NIPA), has the properties of both PAMPS and PNIPA and shows favorable intelligent characters such as high swelling ratio, good temperature-sensitivity and pH-sensitivity, etc. Therefore, as a new type of environmental sensitivity intelligent material, it is very important to study the P(AMPS/NIPA) binary hydrogel.

Microwave low temperature plasma (MLTP), which is generated by electrical discharge at microwave-frequency (2.45 GHz), is a specially ionized gas composed of many kinds of active species, for instance, electrons, ions, radicals and photons with a wide range of energy. Compared with ordinary RF plasma generated by electrical discharge at

radio-frequency (13.56 MHz), MLTP has higher electronic density and stronger energy, which tends to engender or induce correlative physical and chemical reaction more easily. As a new polymerizing method, MLTP-initiated polymerization breaks the mode of traditional chemical-initiated method and has more peculiarities such as no initiator, speeding, simple processing and protecting environment, moreover, the products have higher purity and more degree of polymerization (17−22).

At present, the studies on P(AMPS/NIPA) binary hydrogel synthesized by MLTP-initiated polymerization have not been reported, nor have the correlative literature. In our recent work, P(AMPS/NIPA) binary hydrogel is prepared by MLTP-initiation and the influencing factors on polymerization are studied. Subsequently, we have investigated the temperature-sensitivity, pH-sensitivity and swelling/deswelling kinetics of the hydrogel and characterized the inner configuration of the hydrogel. In this article, we report the results of these investigations together with a detailed analysis and discussion about the hydrogel.

2 Experimental

2.1 Reagents and Materials

The chemical agents included sodium hydroxide(NaOH), hydrochloric acid(HCl), N,N′-methylene double acrylamide (Bis, as crosslinking agent) (all supplied by Tianjin Chemical

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Reagent Manufactory, China), 2-acrylamide-2-methylpropanesulfonic acid (AMPS) (provided by Samwing International Ltd., Switzerland), N-isopropyl acrylamide (NIPA) (provided by J&K ACROS, Belgium), nitrogen (99.99%) (provided by Tianjin Boke Gas Ltd., China). Deionized water was used to make up the solution and immerse the hydrogel.

2.2 Initiation

AMPS and NIPA monomers were mixed with a certain proportion and then placed in the airtight chamber of YZ-1 Microwave Low Temperature Plasma Processor (made by GouWei Hi-tech Ltd., China), shut down the air intake on the processor. After the system was degassed to 3Pa, the air outtake was closed. Under the vacuum condition, the monomers were vaporized till the gas pressure in the system rose spontaneously to 30 Pa. Subsequently, the MLTP of the mixed gases was generated at a power of $80 \sim 250$ W, and the mixed monomers were exposed to the plasma for $60 \sim 360$ sec. The discharge frequency was 2.45 GHz,

2.3 Polymerization

A certain quantity of crosslinking agent (Bis) and deionized water was poured into a test tube (diameter was 20 millimeter). After nitrogen bubbled in the test tube for 20 min, the monomers exposed by MLTP were simultaneously placed in, and the polymerization took place with the nitrogen condition continue. When the viscosity of the organic reactant increased, the test tube was sealed to insulate air and put into a water bath at $30°C$ to carry out the polymerization for 10 h. When the polymerization was complete, the test tube was broken carefully, the hydrogel was removed and cut into pieces 5 mm in height. In order to remove the unreacted monomers and other impurities, the samples were immersed in deionized water, renewed every day for one week and then the pure swollen hydrogels were obtained. Lastly, the swollen hydrogels were put into the DZG-40B vacuum oven (made by TianYu Experimental Instrument Ltd., China) and dried at $50°C$ to a constant weight to obtain the dry hydrogels.

2.4 Concentration

Two types of concentrations, mass fraction and mole fraction, which were denoted by W_i and X_i (i = Total monomers, Bis or AMPS, respectively), were used in the experiment.

2.5 Infrared Spectra

The dry hydrogel was powdered, mixed with KBr, and pressed to measure the infrared spectra by TENSOR37 IR spectrometer (made by the Bruker Company, Germany).

2.6 Polarizing Optics Photograph

The dry hydrogel was immersed in enough deionized water for 48 h in order to reach the swelling equilibrium completely, and then placed in a FLEXI-DRY freeze-dryer (made in Germany) and freeze-dried at $-79°C$ to a constant weight. After being freeze-dried, the sample was quickly frozen by liquid nitrogen and cut to get a transverse section. The transverse section of the treated sample was analyzed on a BA2000 polarizing optic microscope (made by Chongqing Optic Instrument Manufactory, China), the microscopic photo was taken concurrently to investigate the three-dimension crosslinked network of the P(AMPS/NIPA) hydrogel.

2.7 Temperature-Sensitivity

The temperature-sensitivity of the hydrogel was explained by means of the variation of swelling ratio at the different temperatures. After being immersed in deionized water at room temperature for 48 h to reach the swelling equilibrium, the hydrogel was put into a deionized water bath with varying temperatures from $20°C$ to $85°C$ for an hour and then the swelling ratio was measured. The swelling ratio (SR) at each determinate temperature was calculated as follows:

$$SR = (m_1 - m_0)/m_0$$

where m_0 was the weight of dry hydrogel, m_1 was the weight of the swollen hydrogel at each determinate temperature.

2.8 Swelling/Deswelling Kinetics

The swelling/deswelling kinetics of the hydrogel was investigated according to the changes in swelling ratio at regular intervals of immersion times under a constant temperature. After swelling equilibrium in the water bath of $25°C$, the hydrogel was quickly transferred into the water bath of $50°C$ and the swelling ratios were measured at predetermined time intervals for deswelling kinetics. On the contrary, the hydrogel which reached swelling equilibrium in the water bath of $50°C$ was quickly transferred into the water bath of $25°C$, and the swelling ratios were similarly measured at predetermined time intervals for swelling kinetics.

2.9 pH-Sensitivity

The pH-sensitivity of the hydrogel was illustrated by the variation of swelling ratio under the different pH values.

After being dipped in deionized water for 48 h at room temperature to reach the swelling equilibrium, the hydrogel was transferred into the solution with varying pH values from 1 to 12.4 and immersed at $25°C$ for an hour. The swelling ratios at each determinate pH value were calculated. A pH buffer solution was prepared as follows:

HCl-KCl was used for pH = $1 \sim 1.8$ and NaOH-H_3PO_4-NaH_2PO_4-Na_2HPO_4 was used for pH = $3.7 \sim 12.4$, the ionic intension adjusted with NaCl was 0.2.

3   Results and Discussion
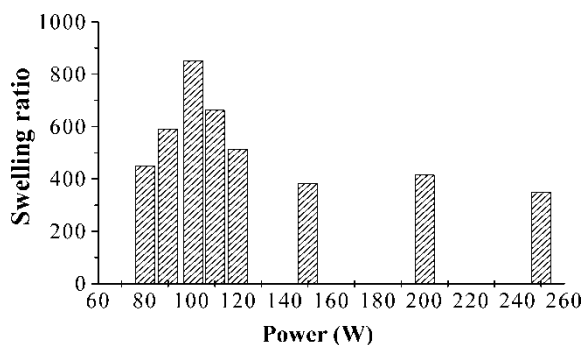
3.1   MLTP Initiation

MLTP treatment power and time are two key factors for the polymerization of AMPS and NIPA. Treatment power determines the energy and the intensity of an active species in a plasma atmosphere. Generally, the energy gained by an active species enhances with the increase of power, an appropriate exposing power is in favor of producing free radicals, accelerating chain propagation and forming a long-chain structure, as a result, a perfect network in hydrogel can be obtained and the swelling capability of the hydrogel will be improved. However, when the treatment power is excessive, oxidation and degradation of monomers will take place and branching reaction will be induced. This may result in more defects in the network and makes the polymerizing products more complicated.

In addition, the MLTP-initiating process has been directly related to the treatment time. Ensuring an appropriate exposure time may offer a sufficient reaction duration, which is beneficial to the initiation of free radicals and the chain propagation, a better effect on the swelling capacity can be expected. However, extreme exposure time will result in excess actions of active particles, which may produce more crosslinking points and make the swelling ratio decrease due to the excessive crosslinking.
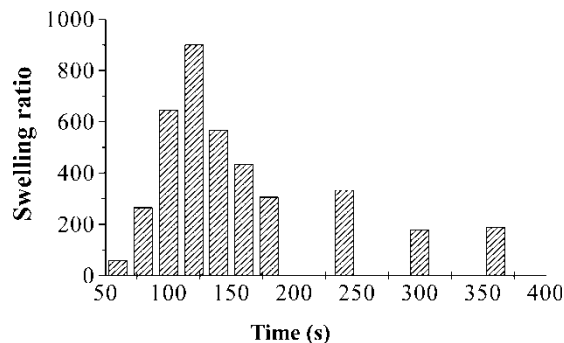
Figure 1 illustrated the swelling ratio which changed with treatment power. With the power increasing, the swelling ratio of P(AMPS/NIPA) hydrogel increased rapidly. But, after the power was beyond 100 W, the swelling ratio decreased. The relation between swelling ratio and treatment time is presented in Figure 2. It can be observed that with the increase of treatment time, the swelling ratio increased first and then decreased after the time was beyond 120 sec.

3.2   Infrared Analysis

The infrared spectra of P(AMPS/NIPA) hydrogel is shown in Figure 3. The characteristic peaks of $-SO_2-OH$ derived from
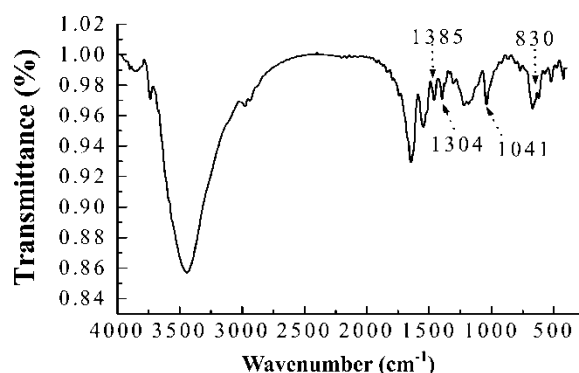

Fig. 2.   Effect of plasma treatment time on the swelling ratio. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{Bis} = 0.010$, $X_{AMPS} = 0.50$; Plasma treatment power 100 W, polymerizing temperature 30°C, polymerizing time 10 h.

AMPS, which were stretching vibration absorption of SO_2 at 1304 cm^{-1}, stretching vibration absorption of S=O at 1041 cm^{-1} and symmetrical stretching vibration absorption of S-O-C at 830 cm^{-1}, were observed clearly. As the characteristic peak of $[-CH(CH_3)_2]$ derived from NIPA, the symmetrical bending vibration absorption of isopropyl $[-CH(CH_3)_2]$ at 1385 cm^{-1} was also found.

The infrared analysis indicated that the correlative characteristic groups of both AMPS and NIPA existed in the macromolecule structure of the hydrogel, which demonstrated that copolymerization between AMPS and NIPA took place.

3.3   Three-Dimension Crosslinked Network

Polarizing optic microscope photos of a three-dimension crosslinked network of P(AMPS/NIPA) hydrogel is given in Figure 4. It shows that the copolymerization initiated by MLTP took place and the crosslinked binary hydrogel was formed. The three-dimension crosslinked network could provide many channels and spaces to pass and hold water. The size of the three-dimension crosslinked grid in the network had a direct relationship with the swelling ratio of P(AMPS/NIPA) hydrogel. In Figure 4, it can obviously be

Fig. 1.   Effect of plasma treatment power on the swelling ratio. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{Bis} = 0.010$, $X_{AMPS} = 0.50$; Plasma treatment time 120 sec, polymerizing temperature, 30°C, polymerizing time, 10 h.


Fig. 3.   Infrared spectra.

(a) $X_{Bis} = 0.010$

(b) $X_{Bis} = 0.040$

Fig. 4. Polarizing optics photos.

observed that the grid size of the network, whose X_{Bis} was 0.010, was larger than that of the network, whose X_{Bis} was 0.040. This suggests that the concentration of the rosslinking agent determined the density of crosslink, size of the three-dimension crosslinked grid and the swelling ratio of the P(AMPS/NIPA) hydrogel.

3.4 Temperature-Sensitivity

3.4.1 Effect of Total Monomers Concentration on Temperature-Sensitivity

The relation between the temperature-sensitivity of P(AMPS/NIPA) hydrogel and the total monomers concentration is given in Figure 5. It could be seen that as the total monomers concentration increased, the swelling ratios obviously declined, so did the swelling ratios at a low critical solution temperature (LCST). A possible explanation of this behavior may be associated with the 'quasi crosslinking' (23). When

(a)

(b)
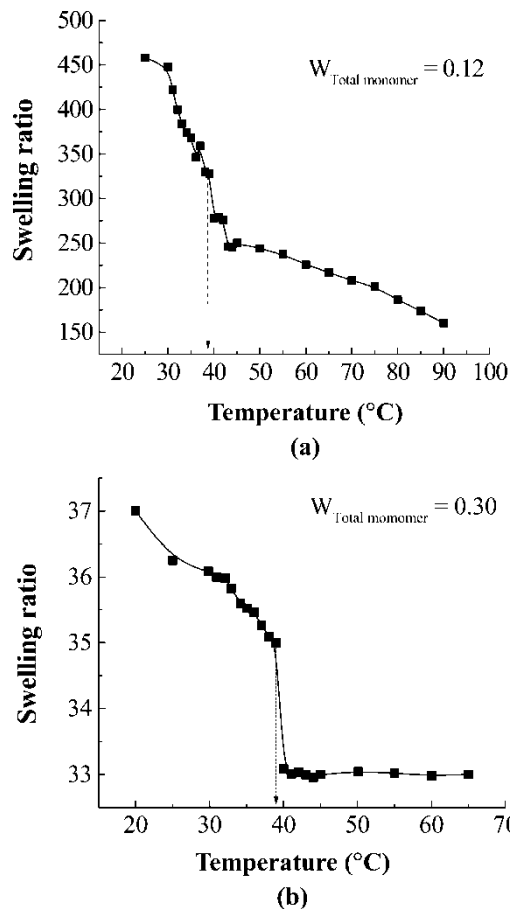
Fig. 5. Effect of total monomers concentration on temperature-sensitivity. Treatment conditions: $X_{Bis} = 0.010$, $X_{AMPS} = 0.50$; Plasma treatment time 120 sec, plasma treatment power 100 W; Polymerizing temperature 30°C, polymerizing time 10 h.

the total monomers concentration is at a high level, the physical tangle-actions among macromolecular chains may improve, which can produce many physical crosslink-nodes. The physical crosslink-nodes have the same effect as the chemical crosslink-nodes, that is, tying and bonding the network, which makes the swelling ratio decline. Therefore, increasing the total monomers concentration is disadvantageous to the swelling of hydrogel and leads to the decline of swelling ratio.

In addition, the swelling ratios of the hydrogels prepared by different total monomers concentrations decreased with the water bath temperature increasing, which showed the typical temperature-sensitivity. But, the LCST did not change, both about 38−39°C. As is known, the LCST of hydrogel is determined by the mutual effect between hydrophobic groups, the coaction between macromolecular chains and bonded water, which means that LCST has no relation with the crosslinked state (such as the grid size of network and the density of crosslink, etc.). Accordingly, the changes of total monomers concentration don't affect the LCST of P(AMPS/NIPA) hydrogel.

3.4.2 Effect of Crosslinking Agent Concentration on Temperature-Sensitivity

Figure 6 shows the temperature-sensitivity of P(AMPS/NIPA) hydrogel varied with the crosslinking agent concentration. As shown here, all hydrogels synthesized with different crosslinking agent concentrations presented the temperature-sensitivity. Nevertheless, because of the elasticity limits and the bondages in network, an increment of crosslinking agent concentration would cause an apparent decline in swelling ratio, which could weaken the temperature-sensitivity of the hydrogel. Besides, the crosslinking agent concentration didn't affect the LCST of the hydrogel, it still remained at $38-39°C$. As mentioned above, LCST had no relation with the crosslinked state, so it didn't change when the crosslinking agent concentration increased.

3.4.3 Effect of the AMPS Content on Temperature-Sensitivity

It is well known that more hydrophilic groups ($-SO_3H$) exist in the hydrogel synthesized with a higher AMPS content in mixed monomers, therefore, more hydrogen bonds will be formed in the swelling process. Contrarily,

while the deswelling process of the hydrogel takes place, more energy must be provided to break down the strong hydrogen bonds, consequently, the LCST increases. Figure 7 illustrates the temperature-sensitivity of the P(AMPS/NIPA) hydrogel correlated with the AMPS content in mixed monomers. It indicated that the swelling ratios of the hydrogels prepared by different AMPS contents decreased with the temperature increasing and had a quick decline at a determinate temperature (LCST), which showed the prominent temperature-sensitivity of the hydrogels. But, the AMPS content had a great impact on LCST, the LCST rose from $34°C$ to $65°C$, while X_{AMPS} changed from 0.10 to 0.70. This result had a special significance to the application of P(AMPS/NIPA) hydrogel, which meant that LCST could be adjusted by changing the AMPS content in mixed monomers.

In addition, the absorption capacity of P(AMPS/NIPA) hydrogel was intensively affected by the AMPS content.
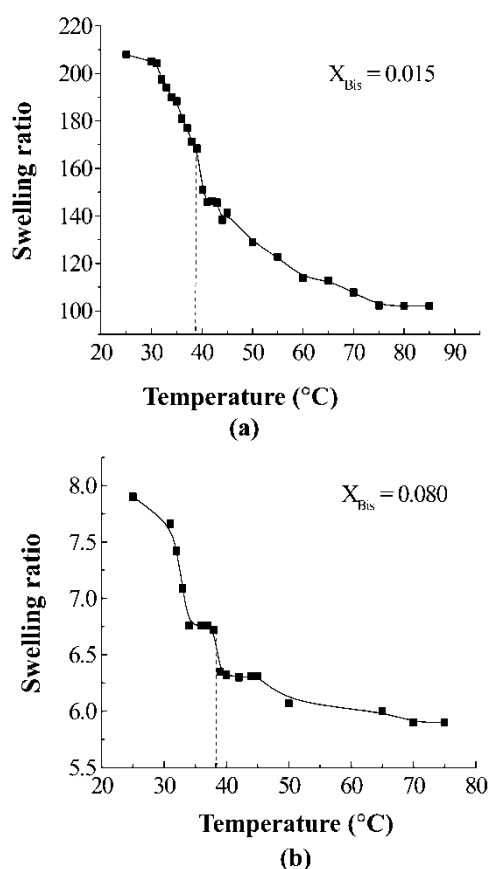
Fig. 6. Effect of crosslinking agent concentration on temperature-sensitivity. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{AMPS} = 0.50$; Plasma treatment time 120 sec, plasma treatment power 100 W; Polymerizing temperature $30°C$, polymerizing time 10 h.
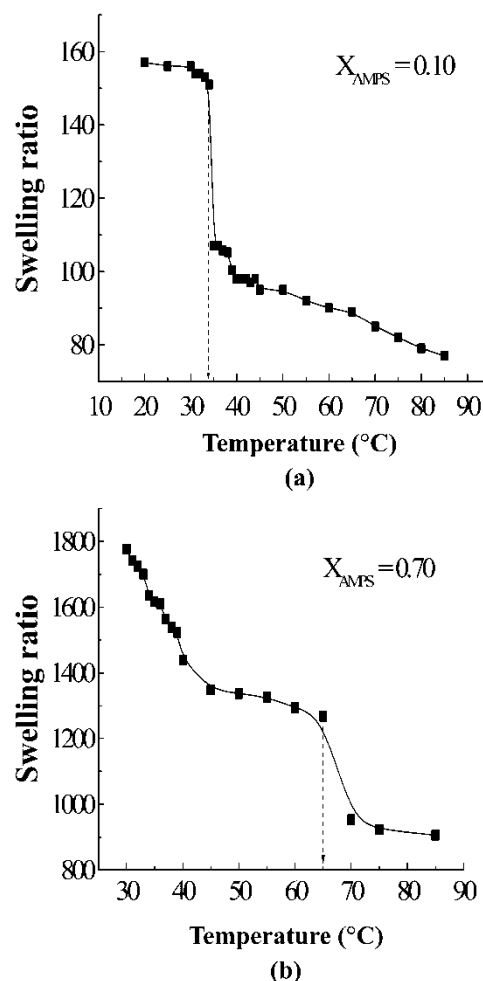
Fig. 7. Effect of AMPS content in mixed monomers on temperature-sensitivity. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{Bis} = 0.010$; Plasma treatment time 120 sec, plasma treatment power 100 W; Polymerizing temperature $30°C$, polymerizing time 10 h.

The swelling ratio increased drastically, while X_{AMPS} went up from 0.10 to 0.70. It might be due to the fact that the mutual repulsion between the strong hydrophilic groups (-SO$_3$H) on the branch chains of macromolecules was strengthened, which enlarged the hold-water space and made the hydrogel absorb more water.
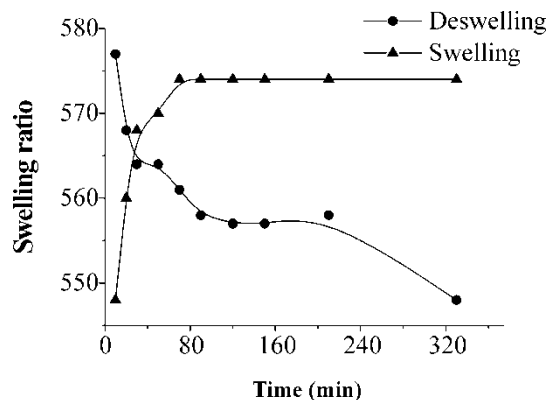
3.5 Swelling/Deswelling Kinetics

The swelling-deswelling kinetic curves of P(AMPS/NIPA) hydrogel were shown in Figure 8. It could be observed that the respondent velocities in both swelling and deswelling process were rapid, especially since the swelling velocity was apparently higher at the same time. In the swelling process, the hydrogel reached swelling equilibrium and returned to the primary state in 75 min. Furthermore, 80% of the total absorbed water was dehydrated within 2 h in the deswelling process. This result indicated good volume reversibility of the P(AMPS/NIPA) hydrogel in swelling-deswelling circulation.
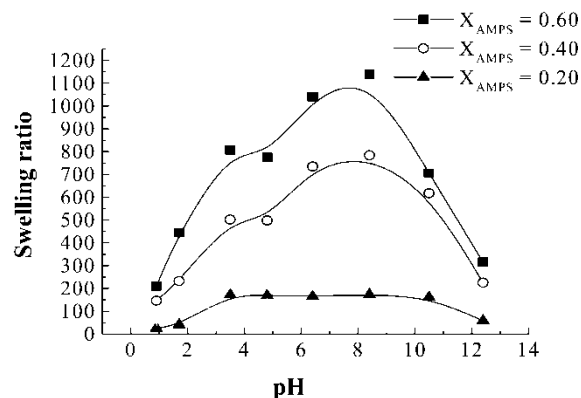
3.6 pH-Sensitivity

There are two types of groups, alkaline -NH-R group and acidic -SO$_3$H group, in the structure of P(AMPS/NIPA) hydrogel. The pH-sensitivity is possibly caused by the ionization of the two groups on the macromolecular network, that is, the ionization of alkaline -NH-R group in acidic medium of low pH value and the ionization of the acidic-SO$_3$H group in an alkaline medium of high pH value. Although many factors, such as electrostatic action between the ions on the macromolecular chains, dissociation equilibrium in network, and Donnan equilibrium inside and outside the hydrogel, can induce the pH-sensitivity, the electrostatic repulsion or attraction between ions may be the key factor.

Under acidic conditions, there are sulfonic groups (R-SO$_3$H) and amine salt ($-^+$NH$_2$RCl$^-$) rooted in the combination of

Figure. 8. Kinetic curves of swelling-deswelling. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{Bis} = 0.010$, $X_{AMPS} = 0.50$; Plasma treatment time 120 sec, plasma treatment power 100 W; Polymerizing temperature 30°C, polymerizing time 10 h.

Fig. 9. PH-sensitivity. Treatment conditions: $W_{Total\ monomers} = 0.12$, $X_{Bis} = 0.010$; Plasma treatment time 120 s, plasma treatment power 100 W; Polymerizing temperature 30°C, polymerizing time 10 h.

the secondary amide (-NH-R) and H$^+$ ion, and they can form the interaction of -RH$_2$N$^+\sim{}^-$SO$_3$-R in the entire network. The mutual attraction which resulted from the Coulomb force makes the macromolecular chain and network structure shrink, which causes the hydrogel to lose water and deswell. Particularly, under the strong acidic condition, the shrinkage was apparently reinforced.

Under alkaline conditions, the P(AMPS/NIPA) hydrogel also shrinks, which is different from the pH-sensitive of poly (acrylic acid) hydrogel (24). The deswelling phenomenon of the P(AMPS/NIPA) hydrogel in alkaline solution is probably caused by what is called 'salt effect'. With the rise of the pH value, the amount of Na$^+$ ions increases greatly. Na$^+$ ion serves as the barrier shield to sulfonic anions (SO$_3^-$) and weakens the original static repulsion between sulfonic anions, which reduced hold-water space. As a result, the hydrogel deswells or shrinks dramatically in the strong alkaline solution.

Figure 9 denoted the pH-sensitivity of P(AMPS/NIPA) hydrogel. As shown in Figure 9, the swelling ratios of the hydrogels prepared with different AMPS contents varied with pH value, they especially dropped sharply in strong acidic or alkaline solutions.

4 Conclusions

The P(AMPS/NIPA) hydrogel could be prepared by MLTP-initiated polymerization. It was proved by infrared spectrum that AMPS and NIPA were copolymerized. MLTP treatment power and time were two key factors to the polymerization. The hydrogel had a large swelling ratio, good temperature-sensitivity. Its LCST had much to do with the AMPS content in mixed monomers and could be adjusted by changing the AMPS content. The crosslinking agent concentration, as well as the total monomers concentration, determined the crosslinking density and the size of the three-dimension grid, which influenced the swelling ratio directly and had no effect on LCST. The prominent pH-sensitivity and the volume

reversibility in swelling-deswelling circulation were presented. The swelling ratio declined under both acidic and alkaline conditions, especially, an obvious shrinking which happened in a strong acidic or alkaline solution.

5 References

1. Champ, S., Xue, W. and Huglin, M.B. (2000) *Macromolecular Chemistry and Physics*, **201(17)**, 2505−2509.

2. Zhai, M.L., Chen, Y.F., Yi, M. and Ha, H.F. (2004) *Polymer International*, **53(1)**, 33−36.

3. Kim, S.J., Lee, K.J., Kim, I.Y. and Kim, S.I. (2003) *J. Macromol. Sci., Pure & Appl. Chem.*, **A40(5)**, 501−510.

4. Nonaka, T., Watanabe, T., Kawabata, T. and Kurihara, S. (2001) *J. Appl. Polym. Sci.*, **79(1)**, 115−124.

5. Pourjavadi, A., Sadeghi, M. and Hosseinzadeh, H. (2004) *Polymers for Advanced Technologies*, **15(11)**, 645−653.

6. Caykara, T. and Dogmus, M. (2005) *J. Macromol. Sci., Pure & Appl. Chem.*, **A42(1)**, 105−111.

7. Rueda, J.C., Komber, H., Cedrón, J.C., Voit, B. and Shevtsova, G. (2003) *Macromolecular Chemistry and Physics*, **204(7)**, 947−953.

8. Bryant, S.J., Davis, K.A., Luo, N., Shoemaker, R.K. and Arthur, J.A. (2004) *Macromolecules*, **37(18)**, 6726−6733.

9. Kuckling, D., Richter, A. and Arndt, K.F. (2003) *Macromolecular Materials and Engineering.*, **288(2)**, 144−151.

10. Kayaman, A.N. and Akdemir, Z.S. (2005) *Polymers for Advanced Technologies*, **16(11−12)**, 807−812.

11. Kong, H.J., Smith, M.K. and Mooney, D.J. (2003) *Biomaterials*, **24(22)**, 4023−4029.

12. Kanekiyo, Y., Sano, M., Lguchi, R. and Shinkai, S. (2000) *J. Polym. Sci. Polym. Chem.*, **38(8)**, 1302−1310.

13. Lutz, P.J. (2001) *Macromolecular Symposia*, **164(1)**, 277−292.

14. Mehrdad, M. and Doostie, L. (2005) *Drug Delivery*, **12(6)**, 343−347.

15. Sahli, N., Belbachir, M. and Lutz, P.J. (2005) *Macromolecular Chemistry and Physics.*, **206(13)**, 1257−1270.

16. Zhang, X.Z., Wu, D.Q., Sun, G.M. and Chu, C.C. (2003) *Macromolecular Bioscience*, **3(2)**, 87−91.

17. Tskhakaya, D. and Kuhn, S. (2000) Contributions to *Plasma Physics*, **40(3−4)**, 484−490.

18. Yasuda Hirotsugu, K. (2005) *Plasma Processes and Polymers*, **2(4)**, 293−304.

19. Yasuda, H. and Matsuzawa, Y. (2005) *Plasma Processes and Polymers*, **2(6)**, 507−512.

20. Abidi, N. and Hequet, E. (2004) *J. Appl. Polym. Sci.*, **93(1)**, 145−154.

21. Tae, C., Suk, C.C., Christine, T., Albrecht, L., Kaufmann, R., Rehwinkel, C. and Rossbach, V. (2000) *J. Appl. Polym. Sci.*, **76(8)**, 1207−1216.

22. Walkiewicz, P.A., Cotrino, J. and González, E.A.R. (2005) *Chemical Vapor Deposition*, **11(6−7)**, 317−323.

23. Chen, X.P., Zhu, G.Y. and Huang, Z.M. (2003) *Plastics Industry* (in Chinese) **31(4)**, 32−34.

24. Elliott, J.E., Macdonald, M., Nie, J. and Bowman, C.N. (2004) *Polymer*, **45(5)**, 1503−1510.