

# Synthesis of a New Intelligent Hydrogel Initiated by Microwave Low Temperature Plasma

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Received 15 April 2006; accepted 30 March 2007

DOI 10.1002/app.26777

Published online 12 July 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new kind of dualistic intelligent hydrogel [P(AMPS/NIPA)], which has the characters of both PAMPS and PNIPA, was introduced. For the purpose of synthesizing the P(AMPS/NIPA) hydrogel, the polymerization between 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and *N*-isopropylacrylamide (NIPA), which was initiated by the microwave low temperature plasma, was investigated. The influencing factors such as plasma-treating time and power, concentration of monomers and crosslinking agent, mole fraction of AMPS in mixed monomers, and temperature of polymerization were

analyzed and discussed in detail. The optimal synthesizing condition of P(AMPS/NIPA) was determined according to the variety in the swelling ratio of the hydrogel. IR spectra and microscopic photos were made to characterize the functional groups and the three-dimension crosslinked network of the dualistic intelligent hydrogel. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1368–1374, 2007

**Key words:** synthesis; intelligent; hydrogels; plasma polymerization; swelling; crosslinking

## INTRODUCTION

A polymer hydrogel, which consists of a three-dimension crosslinked network, can intelligently modulate the swelling ratio (SR) in accordance with the environmental stimulation such as pH value, temperature, free ion, etc. At present, many multivariate hydrogels, which can overcome the defects in the properties of unitary hydrogels, had been designed and prepared with special monomers.<sup>1–14</sup> As we know, PNIPA hydrogel belongs to nonionic hydrogel and is a typical temperature-sensitivity hydrogel. Because there is no hydrophilic group in the structure, the SR of PNIPA hydrogel is very low, which limits the application of PNIPA hydrogel in many fields. On the contrary, PAMPS hydrogel, as a typical bibulous hydrogel, has many strong hydrophilic groups ( $-\text{SO}_3\text{H}$ ) in the structure, and so it can exhibit a prominent drinking capacity and has a high SR, which can reach more than 1000-fold. In addition, because of the actions of the sulfonic groups and the amide groups in the macromolecular chain, PAMPS hydrogel may have a good pH-sensitivity, but its temperature-sensitivity is very poor. In theory, the P(AMPS/NIPA) dualistic hydrogel should have the properties of both PAMPS and PNIPA, and shows favorable intelligent characters

(such as high SR, good temperature-sensitivity, pH-sensitivity, etc.), which makes the P(AMPS/NIPA) hydrogel become a new environmental-respondent, intelligent material. Therefore, it is a significant work to synthesize and study the P(AMPS/NIPA) dualistic 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. Consequently, better effects can be expected when MLTP-initiated polymerization takes place.<sup>15–19</sup>

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, simplifying process, and protecting environment, besides, the products have higher purity and more degree of polymerization.<sup>20–25</sup>

In our recent work, the P(AMPS/NIPA) hydrogel is prepared, and its intelligent characters are investigated. The main purpose of this work is to synthesize the P(AMPS/NIPA) hydrogel with 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and

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*N*-isopropylacrylamide (NIPA) by means of MLTP-initiated polymerization. Since the polymerization is directly affected by many factors, we focus on the study of the key parameters such as MLTP treatment power and time, concentration of monomers and crosslinking agent, mole fraction of AMPS in mixed monomers and polymerizing temperature. The results of these investigations together with a detailed analysis and discussion are very significant to working out the optimum synthesizing condition.

## EXPERIMENTAL

### Reagents and materials

The chemical agents included sodium hydroxide (NaOH), hydrochloric acid (HCl), *N,N'*-methylenebisacrylamid (Bis, as crosslinking agent) (all supplied by Tianjin Chemical Reagent Manufactory, China), AMPS (provided by Samwing International, Switzerland), *N*-isopropyl acrylamide (NIPA; provided by J&K ACROS, Belgium), nitrogen (99.99%; provided by Tianjin Boke gas, China). Deionized water was used to make up the solution and immerse the hydrogel.

### Methods

#### Initiation

AMPS and NIPA monomers were mixed with a certain proportion ( $X_{AMPS} = 0.1\text{--}0.9$ ) and then placed in the airtight chamber of YZ-1 Microwave Low Temperature Plasma Processor (made by GouWei Hi-Tech, China), shut down the air intake on the processor. After the system was degassed to 3 Pa, the air outtake was closed. Under the circumstance of vacuum, 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 power of 80–250 W, and the mixed monomers were exposed to the plasma for 60–360 s. The discharge frequency was 2.45 GHz.

#### Polymerization

A certain quantity of crosslinking agent (Bis) ( $X_{Bis} = 0.005\text{--}0.08$ ) and deionized water was poured into a test tube whose diameter was 20 mm. After nitrogen-bubbled in the test tube for 20 min, the monomers exposed by MLTP were simultaneously placed in, and then the polymerization took place together with the continuation of the nitrogen condition. When the viscosity of the organic reactant increased, the test tube was sealed to insulate air and put into the water bath of 30°C to carry out the polymerization for 10 h. When the polymerization was completed, the test tube was broken carefully, and the

hydrogel was fetched out and cut to pieces of 5-mm height. To remove the unreacted monomers and other impurities, the samples were immersed in deionized water renewed everyday for 1 week, and then the pure swollen hydrogels were obtained. Last, the swollen hydrogels were put into the DZG-40B vacuum oven (made by TianYu experimental instrument, China) and dried at 50°C to a constant weight to get the dry hydrogels.

#### Swelling ratio

The dry hydrogel was immersed in deionized water for 48 h to swell fully, and then taken out. After the excess water on the sample surface was wiped off with filter paper, the weight of the swollen hydrogel was measured. The swelling ratio (SR) of the hydrogel was calculated as follows:

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

where  $m_0$  is the weight of dry hydrogel and  $m_1$  is the weight of swollen hydrogel.

#### Concentration

To be convenient for the experiment, mass fraction and mole fraction, which were denoted by  $W_i$  and  $X_i$  ( $i = \text{Monomers, Bis, or AMPS}$ ), were used as two types of concentrations and calculated as follows.

$$W_{\text{Monomers}} = [(Q_{NIPA} + Q_{AMPS})/Q_{NIPA} + Q_{AMPS} + Q_{Bis} + Q_{\text{water}}] \quad (1)$$

$$X_{Bis} = [M_{Bis}/(M_{AMPS} + M_{NIPA} + M_{Bis})] \quad (2)$$

$$X_{AMPS} = [M_{AMPS}/(M_{AMPS} + M_{NIPA})] \quad (3)$$

where  $Q_{NIPA}$ ,  $Q_{AMPS}$ ,  $Q_{Bis}$ , and  $Q_{\text{water}}$  indicate the weight of NIPA, AMPS, Bis, and water, respectively, and  $M_{NIPA}$ ,  $M_{AMPS}$ , and  $M_{Bis}$  indicate the mole number of NIPA, AMPS, and Bis, respectively.

#### Infrared spectrum

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

#### Microscopic photograph

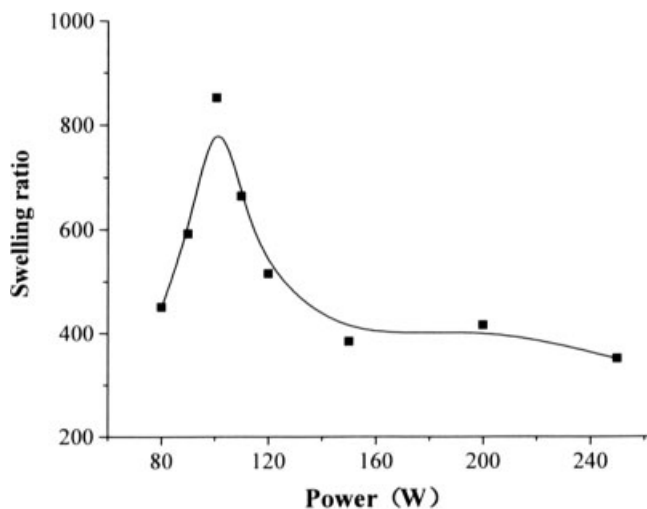
The dry hydrogel was immersed in enough deionized water for 48 h in order to reach the swelling equilibrium entirely, placed in a FLEXI-DRY freeze-dryer (made in Germany), and then freeze-dried at

$-79^{\circ}\text{C}$  to a constant weight. After freeze-dried, the sample was quickly frozen by liquid nitrogen and cut to get transverse section. The transverse section of the treated sample was analyzed on a BA2000 polarizing optic microscope (made by Chongqing Optic Instrument Manufactory, China) and on a Stereoptic microscope XTS30 (made by Beijing TEK Optic Instrument, China), respectively. The microscopic photos were synchronously taken to investigate the three-dimension crosslinked network of P(AMPS/NIPA) hydrogel.

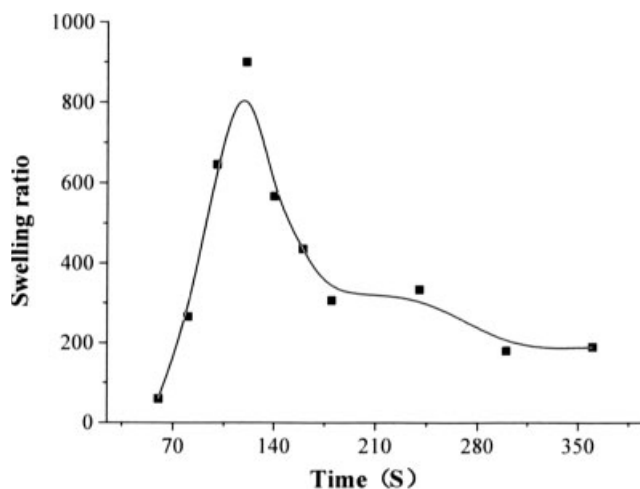
## RESULTS AND DISCUSSION

### Effect of plasma treatment on the swelling ratio

MLTP treatment power and time are the two key factors to the MLTP-initiated polymerization. Generally, the treatment power determines the energy and intensity of active particles in plasma atmosphere, and the energy gained by active particles increases with the increase in the treatment power. An appropriate exposing power is in favor of producing free radicals, accelerating chain propagation, and forming long-chain structure. It is certain that under the condition of an optimized exposing power, a good network structure will be formed and the swelling capability of hydrogel will be improved. However, when the treatment power is over high, oxidation and degradation of the monomers will take place and branching reaction will be induced, which may result in more defects in the network and make the polymerizing products more complicated. As a result, the SR decreases. Figure 1 illustrates that the SR changed with the treatment power. With the



**Figure 1** Effect of plasma-treatment power on the swelling ratio. Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.50$ ; plasma-treating time 120 s; plasma-treating power 80–250 W; polymerizing temperature  $30^{\circ}\text{C}$ ; polymerizing time 10 h.



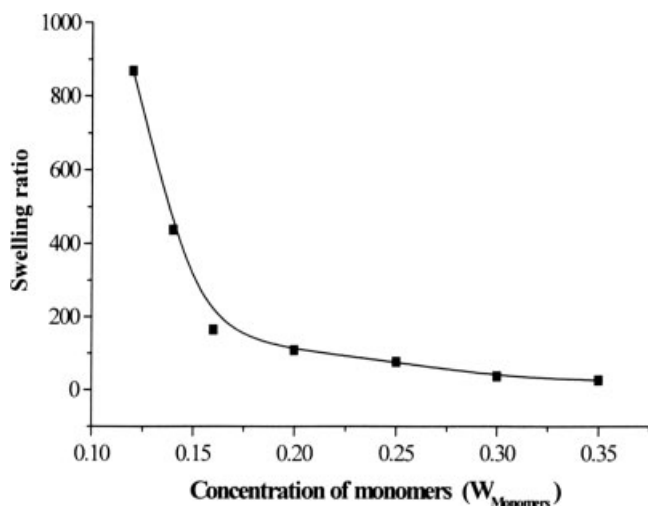
**Figure 2** Effect of plasma-treatment time on the swelling ratio. Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.50$ ; plasma-treating time 60–360 s; plasma-treating power 100 W; polymerizing temperature  $30^{\circ}\text{C}$ ; polymerizing time 10 h.

increase in power, the SR of P(AMPS/NIPA) hydrogel increased rapidly. But, after the power was beyond 100 W, the SR decreased.

Furthermore, MLTP-initiating process is correlated with the treatment time. When the treatment time is too short, the actions of active particles cannot take effect and the free radicals cannot be induced. Ensuring that an appropriate exposing time may offer a sufficient reacting 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, an overlong exposing time will bring on excess actions of active particles, which may produce more crosslinking points and make the SR decrease due to the excessive crosslinking. Figure 2 presents the relation between SR and treatment time. It could be observed that with the increase in treatment time, the SR increased first and then decreased after the time was beyond 120 s.

### Effect of concentration of monomers on the swelling ratio

The relation between the SR of P(AMPS/NIPA) hydrogel and the concentration of monomers was given in Figure 3. Generally, with the concentration of monomers ( $W_{\text{monomers}}$ ) increasing, the absolute amount of the chemical crosslinking points cannot be increased, but the physical tangly actions between macromolecular chains, which is called “quasi-crosslinking,” increase greatly. The “quasi-crosslinking” has the same effects as the chemical crosslinking, which makes the bondage action of the hydrogel network enhance and results in the decrease of SR. It was observed from Figure 3 that with the

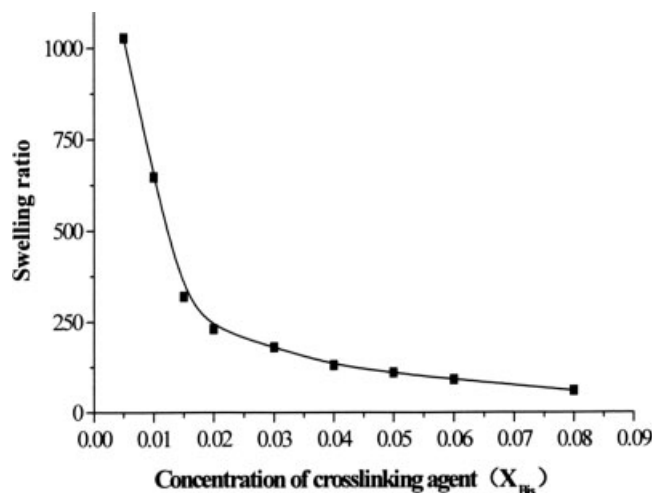


**Figure 3** Effect of concentration of monomers on the swelling ratio. Treating condition:  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.50$ ,  $W_{\text{Monomers}} = 0.12\text{--}0.35$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h.

concentration of monomers increasing, the SR declined. Especially, it should be mentioned here that when the concentration of monomers is too low, the strength and the keeping-shape ability of the hydrogel will get worse, which makes the hydrogel lose the applying value.

#### Effect of concentration of crosslinking agent on the swelling ratio

Figure 4 shows the SR of P(AMPS/NIPA) hydrogel variation with the concentration of crosslinking agent. As shown here, with the increase in the con-

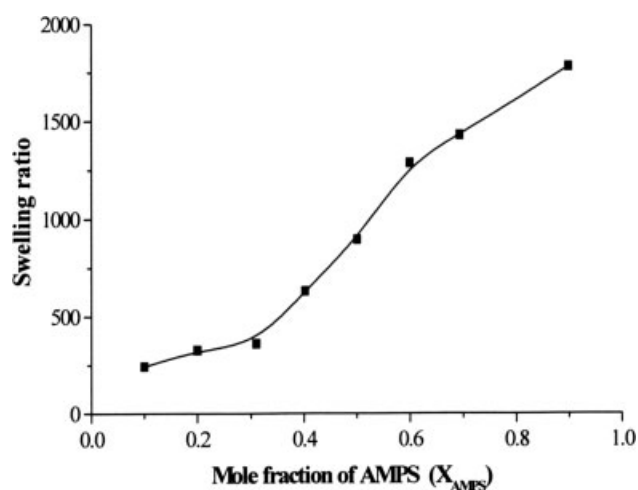


**Figure 4** Effect of concentration of crosslinking agent on the swelling ratio. Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{AMPS}} = 0.50$ ,  $X_{\text{Bis}} = 0.005\text{--}0.08$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h.

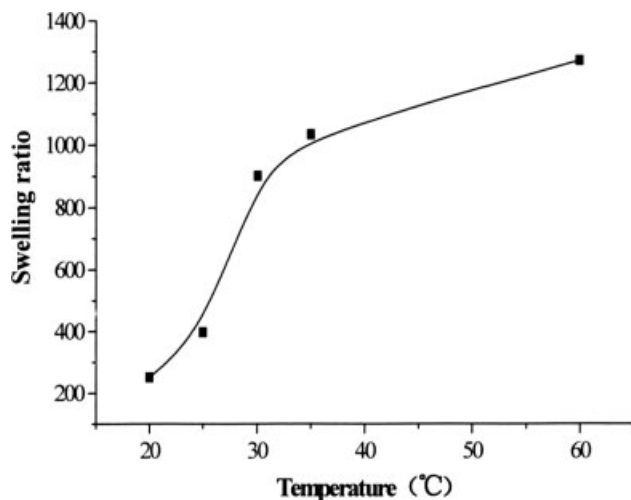
centration of crosslinking agent ( $X_{\text{Bis}}$ ), the crosslinking density in the hydrogel network increased, and the drinking channels of the network were lessened and shortened due to so many crosslinking points. As a result, the bondage action of the network increased, which is disadvantageous to absorbing water, therefore, the drinking capability and the SR of the hydrogel decreased greatly. Usually, the SR can be enhanced by means of reducing the crosslinking agent concentration. But, an overflow crosslinking agent concentration will lead to a poor strength and a bad keeping-shape ability of the hydrogel, even shapelessness.

#### Effect of mole fraction of AMPS on the swelling ratio

Figure 5 indicates the relation between SR of P(AMPS/NIPA) hydrogel and mole fraction of AMPS in mixed monomers. It could be observed that with the mole fraction of AMPS ( $X_{\text{AMPS}}$ ) increasing, the SR rose apparently. Generally, water in swollen hydrogel has three kinds of forms. The first sort of water, which is called "free water," is contained by crosslinked network and its properties are the same as those of ordinary water. The second sort of water, which is called "bond water," is combined with hydrophilic groups by means of hydrogen bond.  $-\text{SO}_3\text{H}$  in AMPS is a strong hydrophilic group and prone to forming strong hydrogen bond with water, which may enhance the drinking and swelling capacity of the hydrogel. The last sort of water, whose properties are between the two sorts of water mentioned earlier, is called "tie water," which has a weak reciprocity with hydrogel. When there



**Figure 5** Effect of mole fraction of AMPS on the swelling ratio. Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.1\text{--}0.9$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h.



**Figure 6** Effect of polymerizing temperature on the swelling ratio. Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.50$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing time 10 h; polymerizing temperature 20–60°C.

are no ionic hydrophilic groups in the hydrogel, little or no “tie water” exists. After the anion monomer (AMPS) is introduced, the amount of anion in the hydrogel network increases, that is, more hydrophilic groups ( $-\text{SO}_3\text{H}$ ) will exist in the P(AMPS/NIPA) hydrogel as the increase of AMPS mole fraction will engender a great quantity of bond water and make the SR raise. In addition, because the anions, as electriferous groups, arrange regularly and repulse each other, the crosslinked network is enlarged and can hold more free water, which also makes the SR increase. As shown in Figure 5, with the increase in  $X_{\text{AMPS}}$ , the SR of the hydrogel increased apparently.

#### Effect of polymerizing temperature on the swelling ratio

Figure 6 demonstrates the dependence of the SR to polymerizing temperature. It could be observed that with the increase of the polymerizing temperature, the SR increased. Usually, it is considered that a high temperature in polymerizing process is advantageous to raising reactive speed and shortening reactive time. But a higher reactive speed will result in the “burst-polymerization,”<sup>26</sup> which can increase the defects in the network and decrease the swelling capacity. Moreover, because of the strong energy and the high density of MLTP active particles, an overhigh polymerizing temperature will increase reactive point, broaden distribution of polymer molecular weight, and weaken crosslinking integrality, which make the drinking capability of the hydrogel decline. Therefore, an appropriate polymerizing

temperature is beneficial to forming a perfect drinking structure for P(AMPS/NIPA) hydrogel.

#### Contrast with chemical-initiated polymerization

The striking contrast of the SRs between MLTP-initiated and chemical-initiated polymerization with different mole fraction of AMPS was given in Figure 7.

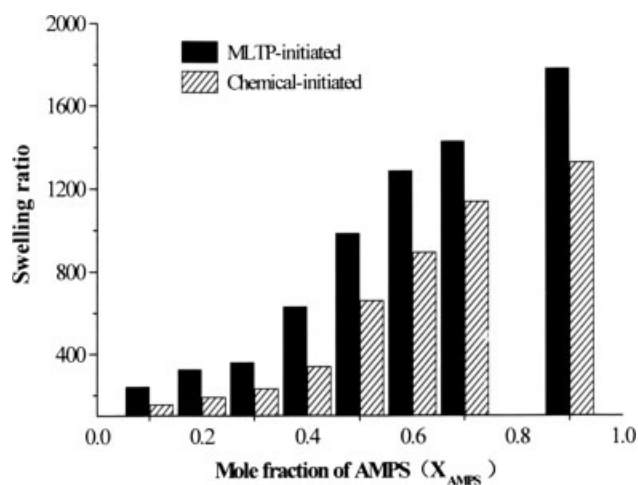
Generally, MLTP is easy to induce physical and chemical reaction due to its high electronic density and strong energy. After the mixed monomers are exposed by MLTP at an appropriate exposing power and time, more free radicals are produced, which is in favor of advancing radical reaction, accelerating chain propagation, and improving degree of polymerization. As a result, a long-chain structure and a perfect network can be obtained and the swelling capability of the hydrogel will be improved greatly.

It is shown in Figure 7 that compared with the chemical-initiated method, MLTP-initiated polymerization brought on a better-drinking capability, and higher SRs of P(AMPS/NIPA) hydrogels prepared with different mix ratios could be obtained.

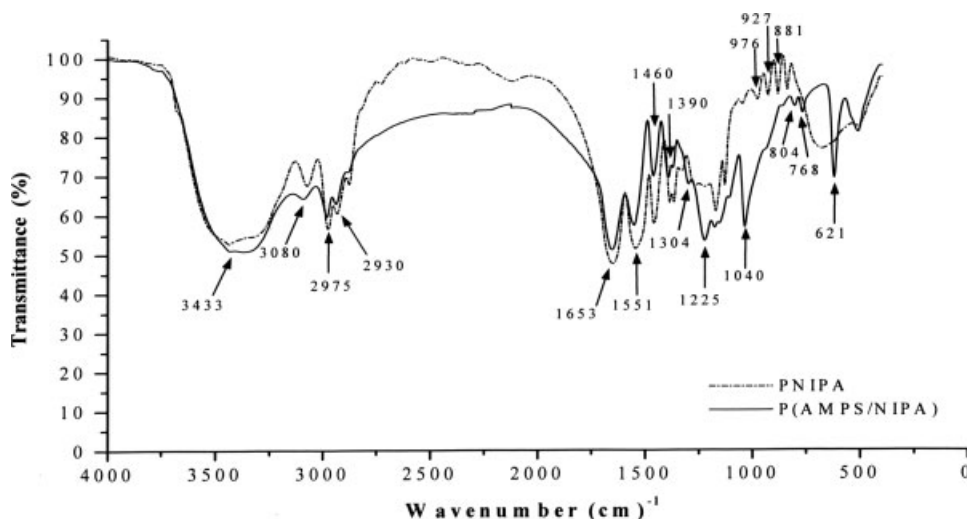
#### Infrared spectrum

To testify that the copolymerization between AMPS and NIPA took place, infrared spectra of PNIPA and P(AMPS/NIPA) hydrogels were measured respectively and the results were shown in Figure 8.

Both AMPS and NIPA are secondary amide compounds and have the character of secondary amide.



**Figure 7** Contrast between MLTP and chemical-initiated polymerization. MLTP-initiated:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.1-0.9$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h; chemical-initiated:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.1-0.9$ ,  $C_{\text{AIBN}} = 0.01$  (AIBN: azodiisobutyronitrile, as initiator); polymerizing temperature 20°C; polymerizing time 5 h.



**Figure 8** Infrared spectra of PNIPA and P(AMPS/NIPA). Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.010$ ,  $X_{\text{AMPS}} = 0.50$  [For P(NIPA):  $X_{\text{AMPS}} = 0$ ] plasma-treating time 120 s, plasma-treating power 100 W polymerizing temperature 30°C, polymerizing time 10 h.

The main difference in their molecular structures is that the sulfo group characteristic exists in AMPS.

In the infrared spectrum of P(AMPS/NIPA), there were characteristic peaks of PNIPA, such as stretching vibration absorptions of N—H of secondary amide at 3433 and 1460  $\text{cm}^{-1}$ , stretching vibration absorption of secondary amide at 3080  $\text{cm}^{-1}$ , stretching vibration absorptions of C—H of methyl and methylene at 2975 and 2930  $\text{cm}^{-1}$ , stretching vibration absorption of C=O of secondary amide at 1653  $\text{cm}^{-1}$ , bending vibration absorption of N—H of secondary amide at 1551  $\text{cm}^{-1}$ , symmetrical bending vibration twin-absorption of isopropyl at 1390  $\text{cm}^{-1}$ , etc.

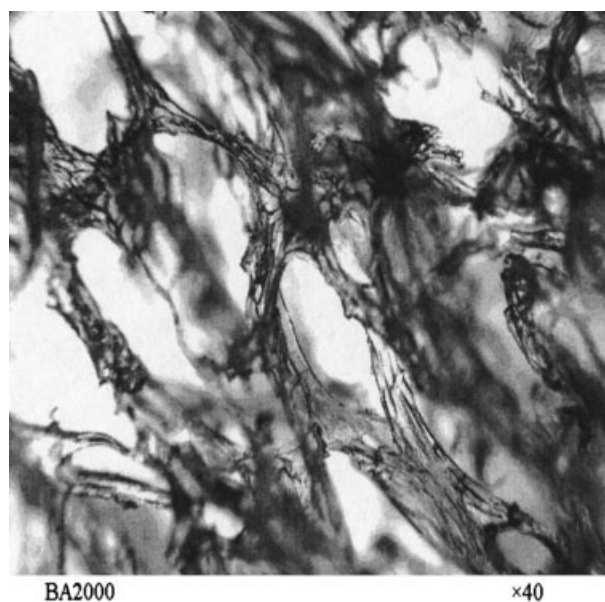
Especially, in the infrared spectrum of P(AMPS/NIPA), the stretching vibration absorption of  $\text{SO}_2$  at 1304  $\text{cm}^{-1}$ , the symmetrical stretching vibration absorption of S=O at 1225  $\text{cm}^{-1}$ , the stretching vibration absorptions of S—O—C at 804 and 768  $\text{cm}^{-1}$ , and the stretching vibration absorption of S—O at 621  $\text{cm}^{-1}$ , which derived from  $-\text{SO}_3\text{H}$  in AMPS, were shown obviously. Therefore, it could be judged that the copolymerization between AMPS and NIPA took place.

Moreover, some nonplanar rocking vibration absorptions of C=C at 976, 927, and 881  $\text{cm}^{-1}$  could be found in the infrared spectrum of PNIPA, which meant that the PNIPA sample for IR spectrum contained some double-bond compounds. The reason for this might be that under the experimental condition mentioned in Figure 8, the addition polymerization of NIPA, which was initiated by MLTP, could not be completed perfectly. More unreacted NIPA monomer, which contains "C=C" configuration, existed in PNIPA and could not be removed entirely by means of ordinary water-immersion method. On the contrary, because of the perfect addition polymerization

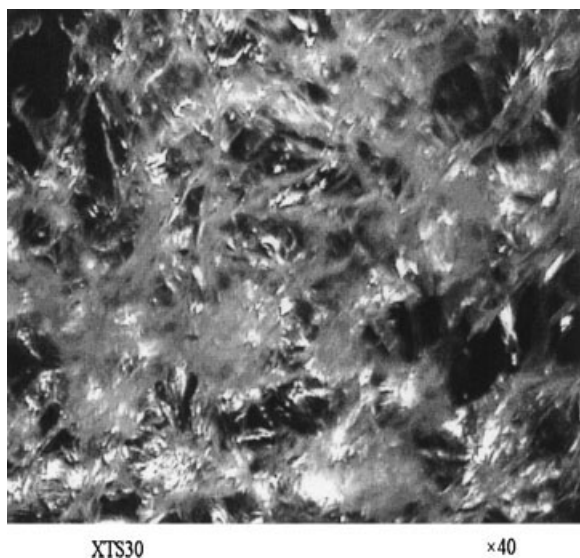
between AMPS and NIPA under the experimental condition, which was the optimum synthesizing technique for P(AMPS/NIPA), the similar nonplanar rocking vibration absorptions of C=C did not appear in the infrared spectrum of P(AMPS/NIPA).

#### Microscopic analysis of three-dimension crosslinked network structure

Polarizing and Stereoscopic microscope photos of the transverse sections of the freeze-dried P(AMPS/NIPA) hydrogel are shown in Figures 9 and 10.



**Figure 9** Polarizing optic microscope of P(AMPS/NIPA). Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.02$ ,  $X_{\text{AMPS}} = 0.50$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h.



**Figure 10** Stereoptical microscope of P(AMPS/NIPA). Treating condition:  $W_{\text{Monomers}} = 0.12$ ,  $X_{\text{Bis}} = 0.02$ ,  $X_{\text{AMPS}} = 0.50$ ; plasma-treating time 120 s; plasma-treating power 100 W; polymerizing temperature 30°C; polymerizing time 10 h.

The three-dimension crosslinked network structure, which provided enough channels to pass water and enough spaces to hold water, was observed clearly from the photos. The size of three-dimension crosslinked grid in the network had direct relationship with the SR of P(AMPS/NIPA) hydrogel. It was also proved that the copolymerization between AMPS and NIPA, which was initiated by MLTP, took place and the crosslinked dualistic hydrogel was formed.

### CONCLUSION

During the polymerization between AMPS and NIPA, which was initiated by MLTP, plasma-treatment power and time, concentration of monomers and crosslinking agent, mole fraction of AMPS in two monomers, and polymerizing temperature had direct influence on the SR of the hydrogel. The synthesizing technics of the P(AMPS/NIPA) dualistic hydrogel could be optimized.

The chemical configuration and the functional groups of P(AMPS/NIPA) hydrogel were analyzed

by infrared spectra, which indicated that copolymerization between AMPS and NIPA took place.

Polarizing and Stereoptical microscope photos proved the formation of the three-dimension cross-linked network, which made the P(AMPS/NIPA) hydrogel absorb water and swell greatly.

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