

# Swelling Characterizations of Chitosan and Polyacrylonitrile Semi-Interpenetrating Polymer Network Hydrogels

Seon Jeong Kim,<sup>1</sup> Su Ryon Shin,<sup>1</sup> Young Moo Lee,<sup>2</sup> Sun I. Kim<sup>1</sup>

<sup>1</sup>Department of Biomedical Engineering, Hanyang University, Seoul, Korea

<sup>2</sup>School of Chemical Engineering, Hanyang University, Seoul, Korea

Received 15 May 2002; accepted 13 June 2002

**Abstract:** Temperature- and pH-responsive semi-interpenetrating polymer network (semi-IPN) hydrogels constructed with chitosan and polyacrylonitrile (PAN) were studied. The characterizations of semi-IPN hydrogels were investigated using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). IPN hydrogels exhibited a relatively high swelling ratio, 23.31%–145.20% at room temperature. The swelling ratio of hydrogels depends

on pH and temperature. DSC was used to determine the amount of free water in IPN hydrogels. The amount of free water increased with increasing chitosan content in the semi-IPN hydrogels. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2011–2015, 2003

**Key words:** semi-IPN; hydrogel; chitosan; polyacrylonitrile; swelling behavior

## INTRODUCTION

Hydrogels are crosslinked, three-dimensional hydrophilic polymer networks, which swell but do not dissolve when brought into contact with water. In the swollen state they are soft and rubbery, resembling a living tissue; some of them also possess excellent biocompatibility.<sup>1,2</sup> The water uptake of these hydrogels may be sensitive to temperature and pH, to the ionic strength of the swelling solution, or even to the presence of a magnetic field or ultraviolet light.<sup>3</sup> They are mainly used in the fields of medicine, pharmacy, biotechnology, and agriculture. In recent years hydrogels, because of their versatile application in biomedicine and biotechnology, have been used for the immobilization of enzymes, proteins, antibodies, and antigens.<sup>4</sup>

Semi-IPNs are defined as a composition in which one or more polymers are crosslinked, linear, or branched.<sup>4,5</sup> Many hydrogels generally are formed from water-soluble polymers by crosslinking them either using radiation or chemicals or by polymerizing hydrophilic monomers in the presence of a crosslinker. Crosslinked polymers appear to be one of the candidates for improving wet strength. Semi-IPN hydrogels have been studied with a particular empha-

sis on their reversible volume changes in response to external stimuli, such as pH, solvent composition, temperature, ionic concentration, and electric field.<sup>6</sup>

Chitosan is the most facile chemical alteration and gives a useful derivative, obtained from deacetylation of chitin. Chitosan appears to be more useful than chitin for biomedical applications and dehydration of aqueous solutions because it has both hydroxyl and amino groups that can be modified easily.<sup>7,8</sup> For these uses, chitosan's key properties are biocompatibility, nonantigenicity, nontoxicity (its degradation products are known natural metabolites), the ability to improve wound healing and/or clot blood, the ability to absorb liquids and to form protective films and coatings, and the ability to selectively bind liquids, thereby lowering serum cholesterol levels.<sup>9</sup>

Crosslinked chitosan is produced via Schiff's base reaction of amino groups in chitosan and aldehyde groups in glutaraldehyde. The reaction of glutaraldehyde with primary amine groups to produce covalent glutaraldehyde crosslinking has been studied in many circumstances in order to detect the presence of free amine organic functions in simple or complex inorganic and organic compounds. Generally, three distinct structures have been suggested, and three propositions have been considered to explain this behavior: (1) there is formation of only one Schiff base, with one aldehyde group of the glutaraldehyde, the other aldehyde group remaining free and commonly used for a subsequent reaction; (2) crosslinking is formed with only one glutaraldehyde molecule and two chitosan unities, resulting in formation of two Schiff bases involving both aldehyde groups of the glutaraldehyde

Correspondence to: S. I. Kim, Sungdong, P.O. Box 55, Seoul 133-605, Korea (sunkim@hanyang.ac.kr).

Contract grant sponsor: Advanced Biometric Research Center (ABRC), supported by Korea Science and Engineering Foundation (KOSEF).

molecule; and (3) crosslinking is formed with not only with a glutaraldehyde molecule, but with the polymerization of glutaraldehyde, which forms a greater crosslinking chain as a consequence.<sup>10</sup>

PAN is a semicrystalline vinylic homopolymer with the repeating unit  $-(CH_2-CHCN)-$ , usually in atactic form.<sup>11</sup> PAN is mainly used in soft cloth furnishings, but it is also an important carbon fiber precursor. Many studies have been made of the cyclization of the side groups in the polymeric chain, most of which are concerned with heat-induced cyclization, while only a few consider PAN degradation induced by ionizing radiation.<sup>12-14</sup> PAN is one of the versatile polymers that are widely used for making membranes and offers good resistance to a wide range of solvents.<sup>15</sup> PAN shows good mechanical strength as film and is more thermally stable than poly(ethylene oxide).<sup>16</sup>

Chitosan is a hydrophilic material and is likely to impart hydrophilicity to a hydrogel prepared by formation of its composite with another mechanically stronger and hydrophobic material such as PAN. Therefore, it would be interesting to investigate the formation of composite semi-IPN hydrogel utilizing the unique properties of chitosan and PAN.

In this study we prepared semi-IPN hydrogels composed of chitosan and PAN. In this article we describe the characterization of the pH/temperature dependence of swelling behavior that results from the amino groups in chitosan. In addition, DSC studies were performed to understand the state of the swollen semi-IPN hydrogels.

## EXPERIMENTAL

### Materials

Chitosan with an average molecular weight of  $2.0 \times 10^5$  and a degree of deacetylation of 76 % was submitted from Jakwang Co., Korea. PAN with an average molecular weight of  $8.6 \times 10^3$  was purchased from Aldrich Chem. Co. Glutaraldehyde (GA), a 25 wt % solution in water, was purchased from Yakuri Chem. Co., Japan. Acetic acid and dimethyl sulfoxide were supplied by Duksan Pure Chemical Co., Ltd. (Japan).

### Preparation of semi-IPN hydrogels

Chitosan was dissolved completely in 50 wt % acetic acid. PAN was dissolved in dimethyl sulfoxide. Quantities of the chitosan/PAN mixed solution were obtained by mechanical stirring for 12 h. They then were poured into Petri dishes and dried in an oven at 60°C for 48 h. Various semi-IPN hydrogels were prepared from different compositions of chitosan/PAN. The designation of the chitosan/PAN semi-IPN hydrogels

**TABLE I**  
Water States of Chitosan/PAN Semi-IPN Hydrogels  
Estimated by DSC Analysis

Sample	Weight ratio (chitosan/PAN)	EWC (%)	Free Water (%)	Bound Water (%)
PAN		16.54	3.35	13.19
CSPA-1	1:3	20.73	3.36	17.37
CSPA-2	1:1	24.61	3.45	21.16
CSPA-3	3:1	60.03	3.68	56.35

the details of their composition are listed in Table I. The blend films were removed from the Petri dishes and washed with deionized water. The crosslinking of a sample was carried out by immersing the film in glutaraldehyde solution at room temperature. To removed the nonreactive agent, the film was dipped into deionized water for 48 h and dried in a 40°C vacuum oven for 1 week.

### Characterization

Fourier transform infrared (FTIR) spectroscopy (Nicolet Model Magna IR 550) was used to confirm the chemical structure of the semi-IPN hydrogels composed of chitosan and PAN.

The dried gels were immersed in 50 mL of deionized water at 20°C. The swelling ratio was obtained by weighing the initial and swollen samples at various time intervals. To measure the swelling ratio, pre-weighed dry samples were immersed in deionized water. After excessive surface water was removed with filter paper, the weight of swollen samples was measured at various pH, temperature, and time intervals. The swelling ratio was determined according to the following equation:

$$\text{Swelling ratio (\%)} = ((W_s - W_d)/W_d) \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  represent the weight of the swollen and dry state samples, respectively.

The equilibrium water content (EWC) was calculated from following equation:

$$\text{EWC (\%)} = ((W_e - W_d)/W_e) \times 100 \quad (2)$$

where  $W_e$  represents the weight of the swollen state at equilibrium.

The state of water in the hydrogels was investigated by differential scanning calorimetry (Du Pont Instruments DSC910) in the temperature range from  $-20^\circ\text{C}$  to  $20^\circ\text{C}$  with a heating rate of  $5^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  flow. To investigate the melting endothermic of semi-IPNs, the amounts of free water and bound water were calculated from the melting enthalpies. The following equation assumes that the heat of fusion of free

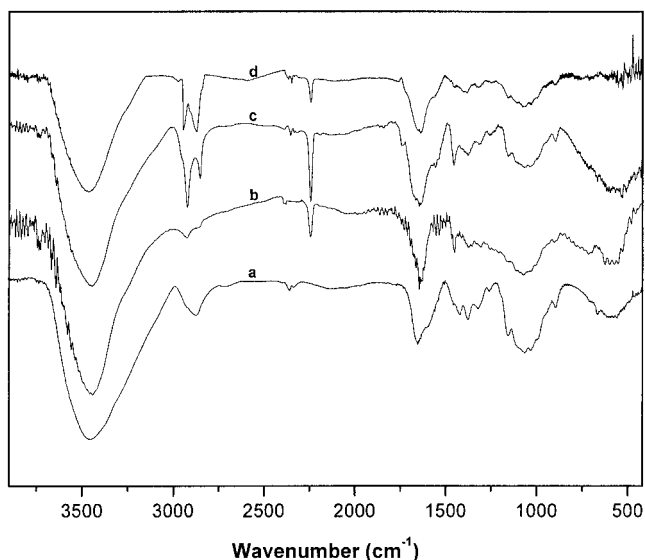
water in the hydrogel ( $Q_{\text{endo}}$ ) was the same as that in ice ( $Q_f$ ; 79.7 cal/g):

$$W_b(\%) = W_t - (W_f + W_{fb}) \\ = W_t - (Q_{\text{endo}}/Q_f) \times 100 \quad (3)$$

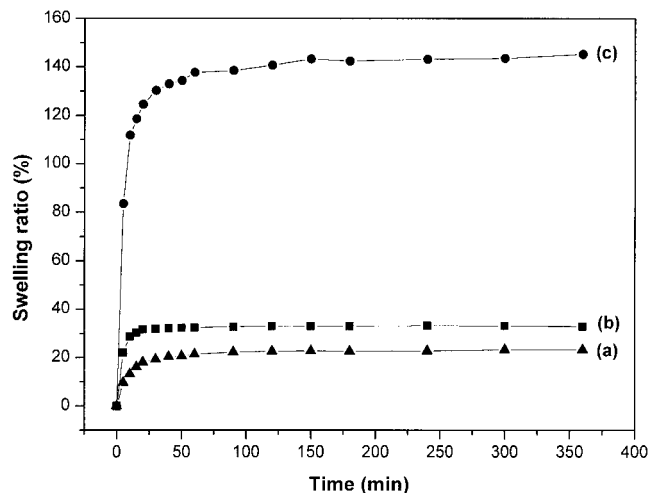
where  $W_b$  is the amount of bound water (%);  $W_f$  and  $W_{fb}$  are the amounts of free water and freezing bound water, respectively; and  $W_t$  is the equilibrium water content [EWC (%)].

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of the chitosan and chitosan/PAN semi-IPNs. Characteristic peaks of chitosan are at 3500–3450  $\text{cm}^{-1}$  of the stretching peaks of the  $\text{—NH}_2$  and hydroxyl groups, 1637  $\text{cm}^{-1}$  and 1313  $\text{cm}^{-1}$  for amide I and amide III, respectively. A peak at 1637  $\text{cm}^{-1}$  can be attributed to the amide I band caused by the remaining acetamide group in chitosan. In PAN's peaks at 2240  $\text{cm}^{-1}$ , a sharp band characterizing  $\text{C}\equiv\text{N}$  groups and 1070  $\text{cm}^{-1}$  characteristic  $\text{C—N}$  stretching vibration can be seen. For semi-IPN, a new peak appears at 1563  $\text{cm}^{-1}$  because of the imine bonds ( $\text{C=N}$ ), formed by a crosslinking reaction between amino groups in chitosan and aldehyde groups in glutaraldehyde. This may be because of the overlapping of a peak corresponding to  $\text{—NH}$  stretching in the  $\text{—NHCOCH}_3$  of the original chitosan with that of  $\text{—C=N}$  stretching of the newly formed Schiff's base between the  $\text{—NH}_2$  group of the chitosan and the  $>\text{CHO}$  group of the glutaraldehyde. The formation of Schiff's base between chitosan and glutaraldehyde has also been suggested by Uragami et al.<sup>5,7,8,17,18</sup>



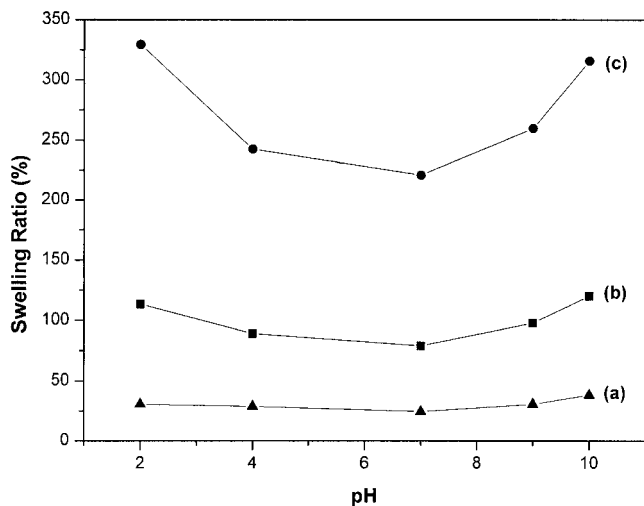
**Figure 1** FTIR spectra of chitosan and chitosan/PAN semi-IPNs: (a) chitosan, (b) CSPA-1, (c) CSPA-2, and (d) CSPA-3.



**Figure 2** Swelling kinetics of chitosan/PAN semi-IPNs at 20°C: (a) CSPA-1, (b) CSPA-2, and (c) CSPA-3.

Figure 2 shows the water-swelling ratio of semi-IPN hydrogels measured at various time intervals. These samples reveal a rapid increase in water content and reach an equilibrium within 40 min. Semi-IPN hydrogels from the combination of hydrophilic chitosan and hydrophobic PAN yield a swelling ratio. The swelling ratio of semi-IPNs varies from 23.31% to 145.23% and changes with the content of the chitosan network. In all cases the swelling ratio of the CSPA-3 semi-IPN was higher than that of the CSPA-1 and CSPA-2 semi-IPNs. It was observed that an increase in the chitosan fraction in semi-IPNs led to an increase in the equilibrium swelling ratio because chitosan has a hydrophilic content. Accordingly, CSPA-3 retained the largest amount of water among the samples studied, and no large differences could be seen between CSPA-1 and CSPA-2. This behavior may be a result not only of the degree of crosslinking of the chitosan network but also chitosan having a content that includes a large number of water-binding sites.<sup>3</sup>

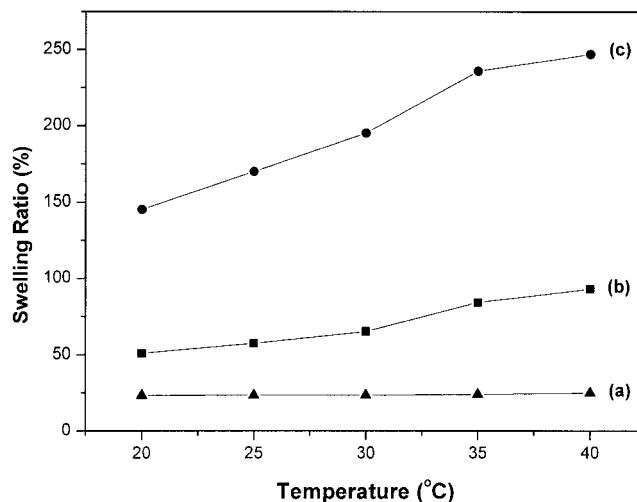
For characterization of the response of semi-IPNs to the change in the external pH condition, semi-IPNs samples were allowed to swell to equilibrium in an aqueous swelling medium of pH 2, 4, 7, 9, and 10 at 20°C. The effects of the external pH on the swelling behavior of semi-IPNs are summarized in Figure 3. The semi-IPNs swelled at pH 2 and shrunk at pH 7. At pH 2 CSPA-3, the sample that contained the greatest amount of chitosan, showed the highest swelling ratio value. Positively charged chitosan at a low pH showed a high swelling ratio because the repulsive force between the same positive charges of molecules caused the long intermolecular distances and a greater hydrophilic state.<sup>19</sup> It is known that a high concentration of a charged ionic group in gel increases swelling because of osmosis and charge repulsion.<sup>20</sup> On the other hand, in an alkaline hydrogen bonds tend to associate



**Figure 3** pH-dependent swelling behaviors of chitosan/PAN semi-IPNs at 20°C: (a) CSPA-1, (b) CSPA-2, and (c) CSPA-3.

because  $-\text{NH}_3^+$  groups can be changed into  $-\text{NH}_2$  as a result of a low concentration of  $\text{H}^+$ . In an acid solution the protonation of amino groups ( $-\text{NH}_2$ ) in chitosan gel and the dissociation of the hydrogen bonding, which induces gel swelling, develop an internal ion osmotic pressure.<sup>9</sup> It was considered that high pH sensitivity was induced mainly by chitosan, which is a weak base with an intrinsic pKa of about 6.5: that is, the semi-IPN hydrogels swelled at a low pH because of the ionic repulsion of the protonated amine groups in chitosan and collapsed at a high pH because of the influence of unprotonated amine groups.<sup>21</sup> However, Figure 3 shows the highest swelling ratio value in the swelling medium of pH 10. A higher swelling at pH 2 may be a result of the protonation of  $-\text{NH}_2$  groups, whereas at pH 10 it may be due to  $-\text{NH}^-$  group formation from the residual  $-\text{NH}_2$  groups of chitosan or slight hydrolysis of PAN and, hence, more water absorption in both cases.<sup>15</sup>

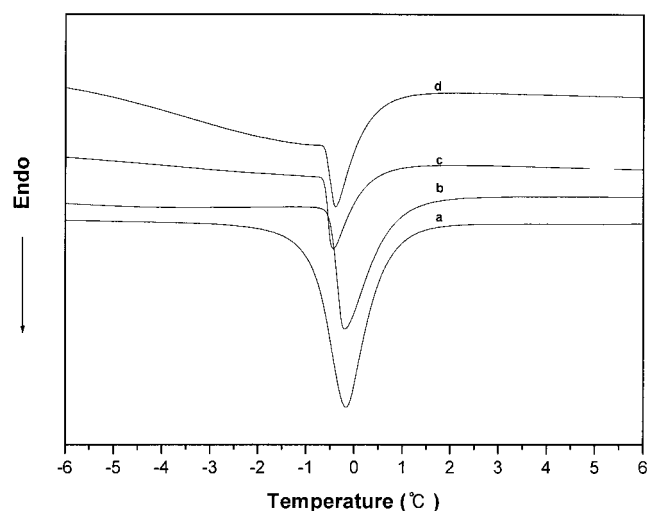
The swelling behavior of semi-IPN hydrogels was investigated as a function of temperature. As shown in Figure 4, all hydrogels had significant changes in swelling ratios over the temperature range between 20°C and 40°C. When the amounts of chitosan in the hydrogels were increased, the swelling ratios increased. The swelling ratio increased with incremental increases of temperature, and the CSPA-3 sample appeared to have the highest swelling ratio in temperature-dependent swelling behavior. The swelling ratio of the CSPA-1 and CSPA-2 sample was the lowest. A water molecule will gain an enthalpy during an increase in temperature, and the hydrophilic group in the chitosan will be turned into an intramolecular hydrogen bond in this condition.<sup>9</sup> That is, we can expect that CSPA-1 has a more compact complex structure than other samples. As temperature of the



**Figure 4** Swelling ratios as a function of temperature for chitosan/PAN semi-IPNs as a function of temperature in water: (a) CSPA-1, (b) CSPA-2, and (c) CSPA-3.

gel in swelling state increases, the swelling ratio grows. All chitosan/PAN networks exhibit a temperature-responsive swelling behavior because of the association/dissociation of the hydrogen bonding by the amine group in the chitosan.<sup>22</sup>

To further elucidate the swelling behavior of chitosan/PAN semi-IPNs, the free-water and bound-water contents were measured from DSC melting thermograms of the swollen hydrogel and calculated according to eq. (3). Figure 5 shows the DSC melting thermograms of PAN and semi-IPN hydrogels in the wet state. As a rule, DSC is used to determine the amount of free water not bound by hydrogen bonding. The fraction of free water in semi-IPN hydrogel is approximately calculated as the ratio of the endothermic peak area for a water-swollen hydrogel to melting



**Figure 5** DSC thermograms of swollen PAN and chitosan/PAN semi-IPNs: (a) CSPA-3, (b) CSPA-2, (c) CSPA-1, and (d) PAN.

endothermic heat of fusion (79.9 cal/g) for pure water, as listed in Table I. Bound water is expressed as the difference between total water and free water. The free water had no interaction with polymer chains, whereas the bound water was involved in the hydrogen bonding with polymer. The endothermic peak appeared between  $-20^{\circ}\text{C}$  and  $10^{\circ}\text{C}$ , attributed to the presence of free water in semi-IPN hydrogels. The bound water content of the chitosan/PAN semi-IPNs samples ranged between being 13.19% and 56.35% of total water. Table I shows the lowest swelling ratio and free water content for CSPA-1. Because semi-IPNs have the structure of a polyelectrolyte complex composed of chitosan, the degree of complexation should have an influence on the swelling ratio of IPNs. The polyelectrolyte complex was considered to have captured the hydrophilic group and produced the tight and ionic bonded structure. Therefore, the low swelling ratio and free water of CSPA-1 should be attributed to the compact complex structure of chitosan.<sup>23</sup>

### CONCLUSIONS

In this study we prepared semi-IPN hydrogels composed of chitosan and PAN whose various compositions resulted from crosslinking with glutaraldehyde. The swelling behaviors in the various buffer solutions were investigated. The semi-IPN hydrogels exhibited a relatively high swelling ratio as chitosan content increased. The CSPA-3 sample containing the highest chitosan content among the samples showed the highest swelling ratio of pH- and temperature-dependent swelling behaviors. The chitosan/PAN semi-IPN hydrogel exhibited a swelling change in response to external stimuli such as pH and temperature. DSC was used for the quantitative determination of the amounts of freezing and nonfreezing water. The free

water content in the semi-IPN hydrogels increased with their increasing chitosan content.

### References

1. Ju, H. K.; Kim, S. Y.; Kim, S. J.; Lee, Y. M. *J Appl Polym Sci* 2002, 83, 1128.
2. Qu, X.; Wirsén, A.; Albertsson, A. C. *Polymer* 2000, 41, 4589.
3. Lee, S. J.; Kim, S. S.; Lee, Y. M. *Carbohydr Polym* 2000, 41, 197.
4. Shin, M. S.; Kim, S. I.; Kim, I. Y.; Kim, N. G.; Song, C. G.; Kim, S. J. *J Appl Polym Sci* 2002, 84, 2591.
5. Sahiner, N.; Pekel, N.; Güven, O. *React & Funct Polym* 1999, 39, 139.
6. Kim, S. J.; Park, S. J.; Shin, M. S.; Kim, S. I. *J Appl Polym Sci* 2002, 86, 2290.
7. Kang, D. W.; Choi, H. R.; Kweon, D. K. *J Appl Polym Sci* 1999, 73, 469.
8. Peniche, C.; Waldo, A. M.; Davidenko, N.; Sastre, R.; Gallardo, A.; Roman J. S. *Biomaterials* 1999, 20, 1869.
9. Lee, W. F.; Chen, Y. J. *J Appl Polym Sci* 2001, 82, 2487.
10. Oyrton, A. C.; Monteiro, J. R.; Claudio, A. *Int J Biol Macromol* 1999, 26, 119.
11. Ulrich, H. *Introduction to Industrial Polymer*; Carl Hanser: Munchen, 1982.
12. Goodhew, P. J.; Clarke, A. J.; Bailey, J. E. *Mater Sci Eng* 1975, 17, 3.
13. Clark, A. J.; Bayley, J. E. *Nature* 1973, 243, 146.
14. Aggour, Y. A.; Aziz, M. S. *Polym Test* 2000, 19, 261.
15. Deepak, A. M.; Ashwani, K. *J Appl Polym Sci* 2000, 77, 1782.
16. Wen, T. C.; Kuo, H. H.; Gopalan, A. *Solid State Ionics* 2002, 82, 14.
17. Deepak, A. M.; Ashwani, K. *Sep Purif Technol* 2000, 21, 27.
18. Musale, D. A.; Kumar, A.; Pleizier, G. J. *J Membrane Sci* 1999, 154, 163.
19. Park S. B.; You, J. O.; Park, H. Y.; Haam, S. J.; Kim, W. S. *Biomaterials* 2001, 22, 323.
20. Shin, M. S.; Kim, S. I.; Kim, I. Y.; Kim, N. G.; Song, C. G.; Kim, S. J. *J Appl Polym Sci* 2002, 85, 957.
21. Kim, S. Y.; Cho, S. M.; Lee, Y. M.; Kim, S. J. *J Appl Polym Sci* 2000, 78, 1381.
22. Kim, S. J.; Park, S. J.; Kim, I. Y.; Shin, M. S.; Kim, S. I. *J Appl Polym Sci* 2002, 86, 2285.
23. Lee, J. W.; Kim, S. Y.; Kim, S. S.; Lee, Y. M.; Lee, K. H. *J Appl Polym Sci* 1999, 73, 113.