

Synthesis and Characteristics of the Interpenetrating Polymer Network Hydrogel Composed of Chitosan and Polyallylamine

Mi-Seon Shin,¹ Seon Jeong Kim,¹ Sang Jun Park,¹ Yong Hee Lee,² Sun I. Kim¹

¹Department of Biomedical Engineering, Hanyang University, Seoul 133-791, Korea

²School of Information & Communication Engineering, Halla University, Wonju, Korea

Received 29 July 2001; accepted 14 January 2002

ABSTRACT: A temperature- and pH-dependent hydrogel was studied with interpenetrating polymer network (IPN) hydrogels constructed with water-insoluble chitosan and polyallylamine. Various IPNs were prepared from different weight ratios of chitosan–polyallylamine. Crosslinked-IPN hydrogels exhibited relatively high equilibrium water content (EWC) in the range 80–83%. The EWC of IPN hydrogels depended on pH and the amount of complex, which is the content of chitosan and polyallylamine. The differential scanning calorimeter (DSC) thermogram of fully swollen

IPN hydrogels appeared between 3 to 4 °C. The IPNs exhibited two glass-transition temperatures (T_g s), indicating the presence of phase separation in the IPNs as exhibited by dielectric analysis (DEA). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 498–503, 2002

Key words: chitosan–polyallylamine interpenetrating polymer network (IPN) hydrogels; swelling behavior; thermal properties

INTRODUCTION

Hydrogels and conducting polymers are two of the most promising types of polymers being used for new material development. Both hydrogels and conducting polymers are stimuli-responsive materials whose dynamic characteristic is reasonably well understood. Hydrogel transitions (volume changes) occur in response to changing environmental conditions, such as temperature,^{1,2} pH,³ solvent composition,⁴ and electrical stimuli.⁵ Conducting polymers also undergo chemical and physical changes in response to electrical stimuli. Ion exchange capacity,⁶ protein affinity,⁷ or enzyme bioactivity,⁸ tensile strength,⁹ conductivity,¹⁰ and optical properties.^{11–14} all change in response to the imposition of appropriate electrical potentials. Hydrogels are hydrophilic polymeric networks that may absorb water in the amount from 10% up to thousands of times their dry weight. As a water content of polymer, the chains extend and exert a resistive force because swelling places the chains into less entropically desired configurations. Polymer complexes are formed by the association of two or more complementary polymers, and may arise from electrostatic forces, hydrophobic interaction, hydrogen bonding, van der Waals forces, or combinations of these interactions.

The formation of complexes may strongly affect the polymer solubility, rheology, conductivity, and turbidity of polymer solutions. Similarly, the mechanical properties, permeability, and electrical conductivity of the polymeric systems may be greatly affected by complexation.

Membrane of ionic polymer hydrogel has been known to be bent in an electric field.

These materials have been attracting much attention in medical and mechanical engineering fields. In the application of these materials to active catheter, micromachine, and micromanipulator, quick response in bending is required to obtain high performance of those membranes. Also, hydrogels have been used in the medical device industry as contact lenses, artificial corneas, dressings and coatings for sutures, catheters, and electrode sensors.

Recently, attention has been focused on employing natural polymers, such as cellulose,¹⁵ starch,¹⁶ gelatin,^{17,18} and chitosan^{19,20} to compose hydrogels with a specific response to a biological environment. In particular, chitosan possesses excellent biocompatibility and mechanical properties and has been used as biomedical materials. In recent literature, Yao reported on the chitosan semi-interpenetrating polymer network (IPN) hydrogels crosslinked with glutaraldehyde and studied their swelling kinetics.^{21,22} Wang et al. blended chitosan and PAAc and used glutaraldehyde to crosslink chitosan.²³

Polyallylamine is one of the pH-sensitive polymers that contains ionizable groups as the cationic polyelec-

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

trolyte. Therefore, polyallylamine was used as cationic polyelectrolyte source in this work. We synthesized IPN hydrogels composed of chitosan and polyallylamine, and focused on the pH- and thermo behaviors of IPN hydrogels based on chitosan and polyallylamine.

EXPERIMENTAL

Materials

Chitosan with an average molecular weight of 2.0×10^5 and a degree of deacetylation of 76% was submitted from Jakwang Company, Korea. Polyallylamine was purchased from Sigma Aldrich, and the average molecular weight was 6.5×10^4 . 2,2-Dimethyl-2-phenylacetophenone (DMPAP) and methylenebisacrylamide (MBAAm) were purchased from Sigma Aldrich and were used for hydrogels preparation without further purification. All other chemical reagents were used extra pure grade.

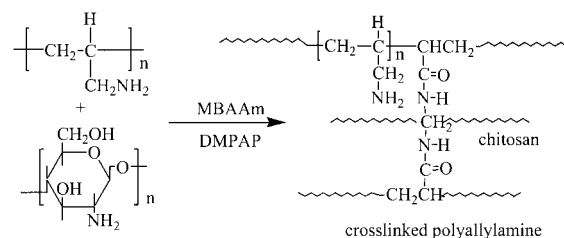
Preparation of IPN hydrogels

IPNs were prepared by nearly the same method submitted in a previous paper. Polyallylamine was mixed with 1 wt % DMPAP and 0.5 mol % MBAAm in tetrahydrofuran (THF) as initiator and crosslinker, respectively. Chitosan was dissolved in 1 wt % acetic acid aqueous solution to prepare 2 wt % chitosan solution. Later, 2 wt % chitosan solution was added the polyallylamine reaction mixture. This mixture was heated at 65 °C for 3 h, and then the polyallylamine network was formed by ultraviolet (UV) irradiation. The solutions were poured in a Petri dish, and dried at 50 °C for 12 h. After 12 h, the dry film was obtained and washed with deionized water to remove any unreacted materials that were not incorporated into the network.

Characterization

Fourier transform infrared (FT-IR) spectroscopy (Bruker Model EQUINOX 55) was used to confirm the chemical structure of IPN hydrogels. To measure the equilibrium water content (EWC), preweighed dry samples were immersed in various buffer solutions. After excessive surface water was removed with the filter paper, the weight of swollen samples was measured at various pH and time intervals. The procedure was repeated until there was no further weight increase and 5 times. Values of EWC were determined according to the following equation:

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



Scheme 1 The reaction of IPNs composed of chitosan-polyallylamine.

where W_s and W_d represent the weight of swollen and dry states samples, respectively. To investigate the melting endothermic of IPNs, the measurement of differential scanning calorimetry (DSC) was conducted by TA Instruments DSC 2010, in aluminum pans at 5 °C/min scanning rate under N_2 flow. Dielectric measurements were conducted to observe the glass transition temperature (T_g) and relaxation behaviors of samples. Measurements of dielectric constant, ϵ' , and dielectric loss factor, ϵ'' , were carried out using the dielectric analysis (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was done from -60 to 200 °C at a rate of 3 °C/min with dry nitrogen adjusted to a flow rate of 50 mL/min. Applied frequencies were 100, 500, and 1 kHz.

RESULT AND DISCUSSION

The IPNs composed of chitosan and polyallylamine were synthesized by radical polymerization using DMPAP and 0.5 mol % MBAAm as initiator and crosslinker, respectively. The reaction of IPNs based on chitosan and polyallylamine is shown in Scheme 1. In FT-IR spectra, characteristic peaks of chitosan-polyallylamine IPNs were located at 3500–3450 cm^{-1} of stretching peaks for the $-NH_2$ and hydroxyl group, 1700 cm^{-1} for carbonyl, and 1650 and 1550 cm^{-1} for amides I and II, respectively.

All swelling behavior is plotted on the average of five trials. Swelling kinetics and temperature-dependent swelling behaviors of IPN hydrogels in pH 7 buffer solution at 35 °C are plotted in Figure 1. All hydrogels swelled rapidly and reached equilibrium within 2 h. The EWC increased with increments of temperature and time. Sample CPAA51 had the highest swelling ratio of the temperature-dependent swelling behaviors, and EWC of CPAA11 had the lowest. Therefore, we can expect that CPAA11 has a more compact complex structure than other IPNs. Temperature-dependent swelling behaviors of hydrogels in pH 7 buffer solution in the temperature range 25–45 °C are plotted in Figure 2. As the temperature of the gel in the swelling state increased, the EWC grew higher. All chitosan-polyallylamine networks exhib-

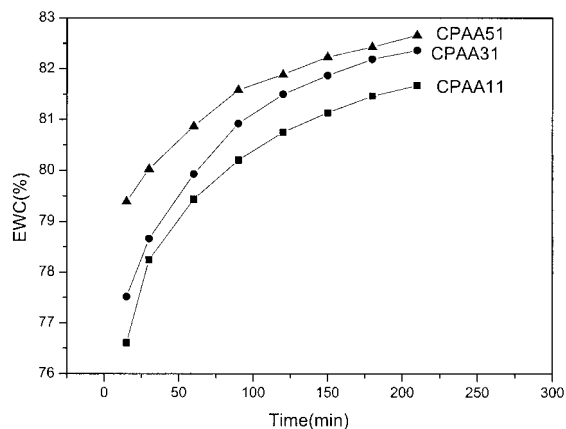


Figure 1 The time-dependent swelling behavior of IPN hydrogels at pH 7 and 35 °C (CPAA11, CPAA31, and CPAA51 have weight ratios of chitosan to polyallylamine of 1:1, 3:1, and 5:1, respectively).

ited a temperature-responsive swelling behavior due to the association/dissociation of the hydrogen bonding by the amine group in the chitosan and polyallylamine within the IPNs.

The pH-dependent swelling behavior was observed at 35 °C, with changes in pH 2–10 buffer solution, as shown in Figure 3. The hydrogels showed a lower specific solution content at basic pH as compared with acidic pH. It is well known that a high concentration of charged ionic group in the gel increases swelling due to osmosis and charge repulsion. Thus, when the degree of ionization of gel bound groups is decreased, swelling decreases. Because the swelling process of gels involves the ionization of amino groups at the acid in acidic (pH 2) buffer solution, the acid would be attached to the gels by the ionic bonds. Therefore, the weight of the gels increased in the acidic (pH 2) buffer. At high pH, because the aggregation, intermolecular interactions, and protonation of amino groups have already reached their maximum, the swellability of

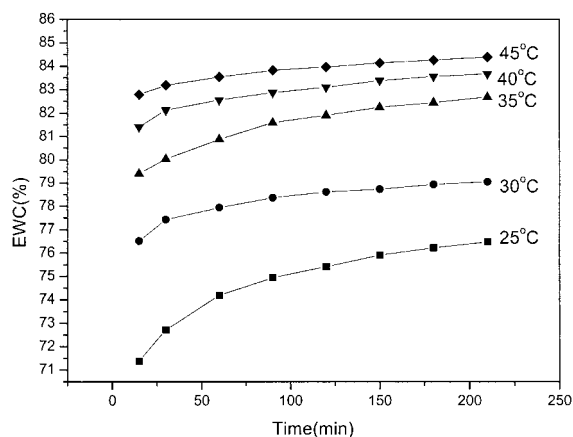


Figure 2 The temperature-dependent swelling behavior of CPAA51 in pH 7 buffer solution.

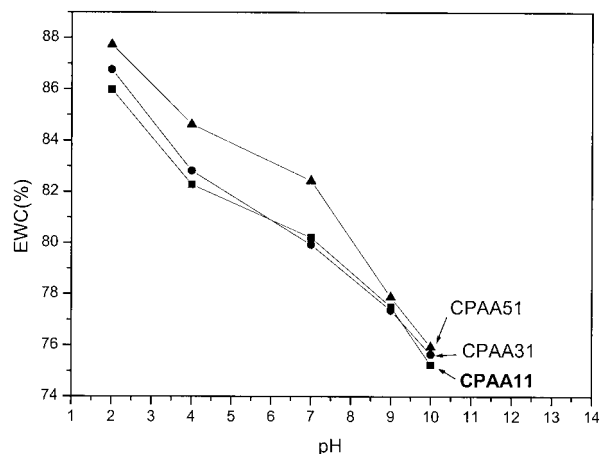


Figure 3 The pH-dependent swelling behavior of IPN hydrogels at 35 °C: CPAA11, CPAA31, and CPAA51.

the hydrogel becomes unchanged when the buffer pH is >7 . This pH-sensitive behavior is typical of ionic hydrogels.

Because the IPN hydrogel CPAA51 possesses more chitosan in its structure, the swelling degree may be the highest among the other IPNs, resulting in the highest total water content at all conditions of experiments. In addition, the sample CPAA11 that contained the lowest content of chitosan among samples showed the lowest EWC value at all pHs. In summary, the EWC of IPN hydrogels depends on pH and the amount of complex, which is the content of chitosan and polyallylamine.

The DSC melting thermograms of polyallylamine and IPN hydrogels in the dry state are shown in Figure 4. Polyallylamine reveals a sharp melting endothermic peak at 110 °C, whereas weak and broad melting endothermic peaks of polyallylamine segments in the IPNs, caused by crosslinking reaction and

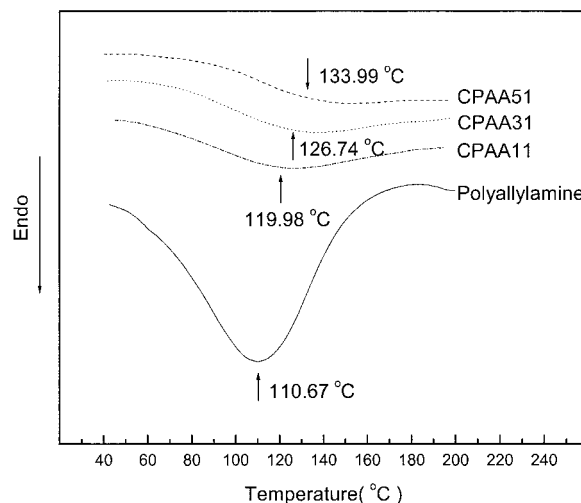


Figure 4 The DSC thermogram of IPN hydrogels: CPAA11, CPAA31, CPAA51, and polyallylamine.

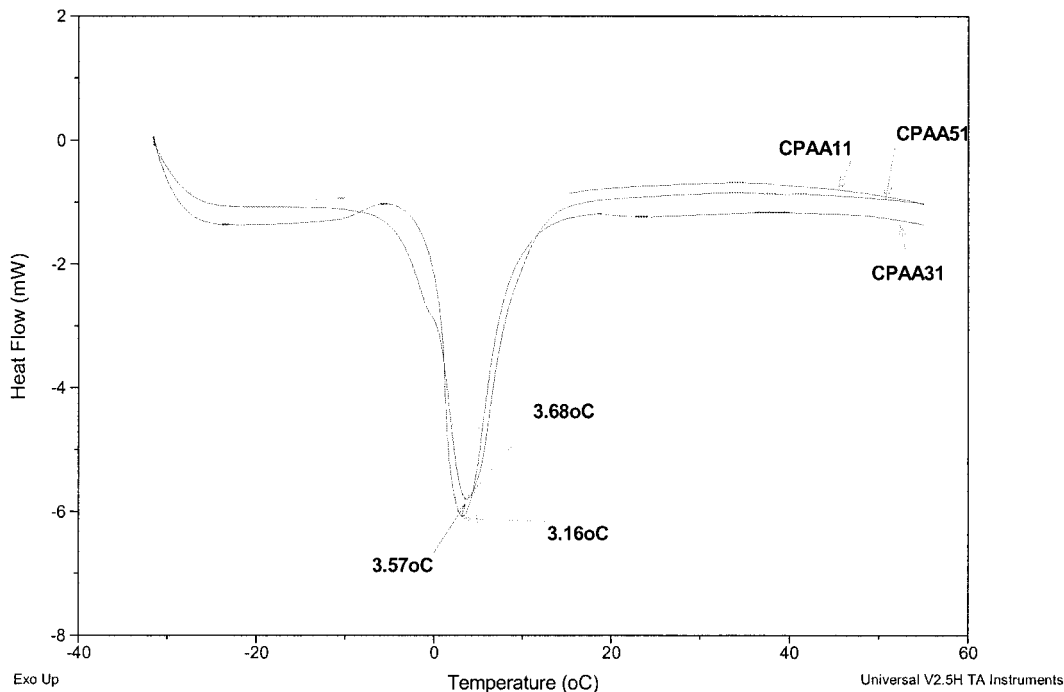


Figure 5 The DSC thermogram of hydrogels that were fully swollen at pH 7: CPAA11, CPAA31, and CPAA51.

IPNs formation, appeared between 120 and 134 °C. On the other hand, the melting temperature (T_m) of chitosan network cannot be determined from DSC analysis. Although chitosan has crystalline regions, T_m is not found because of rigid-rod polymer backbone having strong inter- and/or intramolecular hydrogen bonding.²⁴ This behavior is frequently detected in many polysaccharides, such as cellulose and chitin derivatives.²⁵ Also, DSC is used for the quantitative determination of the amounts of freezing and non-freezing water. The heat of melting of the freezing water (intermediate and free water) was determined from the area under the endothermic curve and was calibrated using pure distilled water as a standard, as described in Mansor and Malcolm's work.²⁶ The DSC thermogram of fully swollen IPN hydrogels is shown in Figure 5. The endothermic peak of swollen gel appears between 3 to 4 °C. The fraction of free water is approximately estimated by the ratio of endothermic peak, integrated between these ranges, to the melting endothermic peak of heat of fusion for pure water. Bound water is expressed as the difference between total water and free water. EWC values, free water contents, and bound water contents are calculated and listed in Table I. Free water contents in the IPN hydrogel of CPAA51, CPAA31, and CPAA11 were 67.28, 56.34, and 55.34% at pH 7, respectively. The CPAA11 shows the lowest EWC and free water content. This result confirmed that CPAA11 has a more compact structure than CPAA51 or CPAA31. The fraction of free water in total water is approximately calculated as the ratio of the endothermic peak area for water-

swollen hydrogel to melting endothermic heat of fusion (79.9 cal/g) for pure water. The following equation assumes that the heat of fusion of free water in the hydrogel was the same as that of the ice:²⁷

$$W_b(\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{\text{endo}}/Q_f) \times 100 \quad (2)$$

where W_t is the equilibrium water content (EWC, %), W_b is the amount of the bound water (%), W_f and W_{fb} are the amount of free water and the freezing bound water, respectively, and Q_{endo} and Q_f are the heat of fusion of free water in sample and that of the ice (79.9 cal/g), respectively.

Generally, the three kinds of water in hydrogels are referred to as follows:

- (1) Nonfreezing water or "bound water": this term refers to the water molecules that are bound to polymer molecules through hydrogen bounds and are immobilized. This kind of water shows

TABLE I
Water State of IPN Hydrogels Calculated by Differential Scanning Calorimetry

Sample	EWC (%)	Free water (%)	Bound water (%)
CPAA51	82.43	67.28	15.15
CPAA31	82.19	56.34	25.85
CPAA11	81.46	55.34	26.12

^aAll samples were swelled in pH 7 at 35 °C.

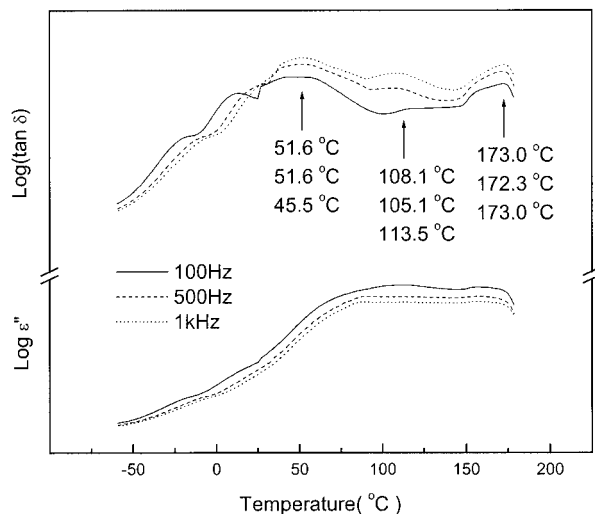


Figure 6 The dielectric analysis of CPAA51 IPN.

no endothermic peak in the temperature range -70 – 0 °C.

- (2) Intermediate water or "secondary bound water": other water molecules that interact with polymer molecules are referred to as intermediate water. This kind of freezing water has a melting point <0 °C.
- (3) Free water: water molecules that do not take part in hydrogen bonding with polymer molecules are called free water because of their greater degree of mobility in comparison with other water molecules. Free water is freezing water showing a melting point at 0 °C. It has a transition temperature, enthalpy, and DSC curves similar to those of pure water.

In the present study, the EWC in DSC test was calculated in pH 7 buffer solution at 35 °C. The free water has good mobility because it has no interaction with polymer chains. However, the bound water is involved in the hydrogen bonding with polymer.

In general, the T_g of crosslinked polymer is difficult to detect using the ordinary DSC technique. Therefore, in this study, the more sensitive dielectric analysis (DEA) was employed to determine the T_g of each component in the IPNs. The $\log(\tan \delta)$ -to-loss factor ($\log \epsilon''$) of the IPN depending on temperature at 100 Hz, 500 Hz, and 1 kHz is shown in Figure 6. Three relaxation peaks appeared at ~ 50 , 110, and 170 °C in the IPN. The T_g of chitosan appears at >150 °C.²⁸ Accordingly, the temperature of the maximum $\tan \delta$, at ~ 170 °C, is considered to be the T_g of chitosan. Another maximum $\tan \delta$ temperature at 110 °C was thought to be the T_m of polyallylamine segments in IPN, as indicated by DSC analysis. The lower maximum $\tan \delta$ temperature was taken to be the T_g of polyallylamine segments in IPN. In fact, the T_g of

polyallylamine itself was -26 °C, as indicated by DSC analysis in this work. DEA showed that the T_g in IPNs was much higher than that of polyallylamine and nearly shifted up to 50 °C. From the result of DEA, the IPNs exhibited two T_g s, indicating the presence of phase separation in the IPN.

CONCLUSIONS

We prepared IPN hydrogels based on chitosan and polyallylamine by crosslinking for the network formation. Chitosan dissolved in aqueous acetic acid solution gave a homogeneous viscous polyelectrolyte solution. By heating the solution, the reaction was initiated. All hydrogels exhibited a high EWC in the range 80 – 83% . Prepared IPNs were characterized and confirmed by FT-IR, DSC, and DEA.

The pH- and temperature-sensitive characteristics of hydrogels were studied by a swelling test under various pH conditions at 35 °C. The CPAA51 sample appeared to have the highest swelling ratio in pH- and temperature-dependent swelling behavior. CPAA11 exhibited the lowest EWC value among the three IPN hydrogels because of the low free water content and relatively high content of bound water, as evidenced by DSC analysis. This result means that CPAA11 has the most compact complex structure in comparison with CPAA51 and CPAA31. From the result of DEA, the IPNs exhibited two T_g s, indicating the presence of phase separation in the IPN. These pH-sensitive hydrogels have potential use in biomedical application, such as controlled-release systems.

We are continuing our preparation of full IPN systems. Further work, including the electrostatic interactions, is under way in our laboratory and will be reported in the near future.

This work is the result of research activities at the Advanced Biometric Research Center (ABRC), supported by Korea Science and Engineering Foundation.

References

1. Aoki, T.; Kawashima, M.; Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. *Macromolecules* 1994, 27(4), 947.
2. Sasase, H.; Aoki, T.; Katono, H.; Sanui, K.; Ogata, N. *Makromol Chem Rapid Commun* 1992, 13, 577.
3. Hu, Y.; Horie, K.; Tori, T.; Ushiki, H.; Tang, X. *J Polym* 1993, 25(2), 123.
4. Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1984, 81, 6379.
5. Tanaka, T.; Nishio, I.; Sung, S. T.; Ueno-Nishio, S. *Science* 1982, 218, 467.
6. Ge, H.; Wallace, G. G. *React Polym* 1992, 18, 133.
7. Hodgson, A. J.; Lewis, T. W.; Maxwell, K. M.; Spencer, M. J.; Wallace, G. G. *J Liq Chromatogr* 1990, 13, 3091.
8. Lu, W.; Zhou, D.; Wallace, G. G. *Anal Commun*, in press.
9. Burford, R. P.; Murray, P.; Spinks, G. M.; Wallace, G. G. *Synth Met*, in press.
10. John, R.; Wallace, G. G. *J Electroanal Chem* 1993, 354, 154.

11. Sapp, S. A.; Sotzing, G. A.; Reddinger, J. L.; Reynolds, J. R. *Adv Mater* 1996, 8, 808.
12. Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem Mater* 1996, 8, 882.
13. Hyodo K. *Electrochim Acta* 1994, 39, 265.
14. Chandrasekhar, P.; Masulautis, A. M.; Gumbs, R. W. *Synth Met* 1990, 36, 303.
15. Oliverira, W. D.; Glasser, W. G. *J Appl Polym Sci* 1996, 61, 81.
16. Pascual, B.; Castellano, I.; Vazquez, B.; Gurruchaga, M.; Goni, I. *Polymer* 1996, 37, 1005.
17. Rathna, G. V. N.; Rao, D. V. M.; Chatterji, P.R. *JMS-Pure Appl Chem A* 1996, 33, 1199.
18. Vazquez, B.; Gurruchaga, M.; Goni, I. *Polymer* 1995, 36, 2311.
19. Guan, Y. L.; Shao, L.; Liu, J.; Yao, K. D. *J Appl Polym Sci* 1996, 61, 2325.
20. Guan, Y. L.; Shao, L.; Liu, J.; Yao, K. D. *J Appl Polym Sci* 1996, 62, 1253.
21. Yao, K. D. *J Polym Sci, Part A; Polym Chem* 1994, 32, 1213.
22. Yao, K. D.; Liu, J.; Cheng, G. X.; Zhao, R. Z.; Wang, W. H.; Wei, L. *Polym Int* 1998, 45, 191.
23. Wang, H.; Li, W.; Li, Y.; Wang, Z. *J Appl Polym Sci* 1997, 65, 1445.
24. Lee, S. J.; Kim, S. S.; Lee, Y. M. *Carbohydr Polym* 2000, 41, 197.
25. Kim, S. S.; Kim, S. J.; Moon, Y. D.; Lee, Y. D. *Polymer* 1994, 35, 3212.
26. Mansor, B. A.; Malcolm, B. H. *Polym Int* 1994, 33, 273.
27. Albin, G.; Horbett, T. A.; Ranteri, B. D. *J Controlled Release* 1995, 2, 153.
28. Nam, S. Y.; Lee, Y. M. *J Membr Sci* 1997, 135, 161.