State of Water in the pH-Sensitive Chitosan–Polyether Semi-IPN Hydrogel

INTRODUCTION

Hydrogels are highly swollen, hydrophilic polymer networks that can absorb large amounts of water and drastically increase in volume. It is well-known that the physicochemical properties of the hydrogel depend not only on the molecular structure, the gel structure, and the degree of crosslinking but also on the content and state of water in the hydrogel. Since the inclusion of water significantly affects the performance of hydrogels, a study on the physical state of water in the hydrogels is of great importance because it might offer useful suggestions on their microstructure and the understanding of the nature of interactions between absorbed water and polymers.

The structure of water in hydrogels and of water adsorbed to polymers has been investigated by numerous workers.[1-18] According to their results, the water in hydrogels can be generally classified into three species: nonfreezing bound, freezing intermediate, and freezing free water. Different techniques such as dilatometry,[1-3] specific conductivity,[1,3] infrared spectroscopy,[4-6] FT Raman spectroscopy,[7] NMR spectroscopy,[8-10] and differential scanning calorimetry (DSC)[1,8,10-18] were employed to study the extent of bound water and the existence of structured water in the gels in order to understand the properties of water and its interactions with the polymers.

The bulk of investigations on the state and role of water in synthetic polymers has been focused on poly(vinyl alcohol) (PVA),[15] poly(2-hydroxyethyl methacrylate) (PHEMA),[8-10] poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone) (polyMMA-co-VP)[10,17,18] interests, which is due to their biological compatibility and use in medical applications. In our previous studies, we have prepared a semi-IPN hydrogel based on crosslinked chitosan with glutaraldehyde interpenetrating polyether polymer network (semi-IPN) and discussed its pH-sensitivity, swelling and release kinetics, and structural changes of the gel in different pH solutions.[19-21] A study on the state of water and its interaction with the polymer network in the chitosan–polyether semi-IPN hydrogel is necessary because of prominent applications of this hydrogel in biomedical area. In this paper, we employ the widely used DSC method to probe the distribution of different types of water in swollen hydrogels with different water content in distilled water or in buffer solution at a specified pH, and the technique of infrared spectroscopy is used to get information on molecular interactions, especially those involving water molecules.

EXPERIMENTAL

Materials

Chitosan was kindly provided by the Department of Materials Science and Engineering, Tianjin University. Be-
fore use, it was purified through the method of dissolving in acetic acid and separating with alkali. The viscosity-average molecular weight of the chitosan purified was 9.0×10^5, calculated by the Mark-Houwink Equation:[22] $[\eta] = K_m M^\alpha$, where $K_m = 1.81 \times 10^{-3}$, $\alpha = 0.93$, and the N-deacelylation degree was 60%. Poly(oxypropylene glycol), polyether N330, was obtained from Tianjin No. 3 Petroleum Chemical Engineering Factory. The average molecular weight was 3000 ± 100. Polyether N330 has three functional hydroxyl groups. Glutaraldehyde, acetic acid, and other reagents were chemical grade.

Synthesis of Chitosan–Polyether Semi-IPN

The semi-IPN was prepared according to the method described previously.[19-21] 1.5 g chitosan was dissolved in 48.0 g 0.25N acetic acid and mixed with 1.4 g polyether N330. Then, 0.8 g 0.5% glutaraldehyde solution was poured into a frame mold and maintained at 45°C for film formation. The semi-IPNs obtained were swollen in pH = 7.0 buffer solution at 37°C for 4 h to reach equilibrium and then dried completely at 70°C.

Swelling Measurements

Swelling samples were cut into disks and were swollen in distilled water or buffer solutions with an ionic strength of $0.1M/L$ in various pH at 25°C. The degree of swelling, W, is expressed as the percentage of water in hydrogel during a definite time interval

$$W = \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of hydrogel}} \times 100 \quad (1)$$

In the case of equilibrium swelling, W becomes the familiar equilibrium water content (EWC).

IR Spectroscopy

Semi-IPN films casted of approximately 6 μm in thickness were swollen in pH = 7.0 or 1.25 buffer solutions for 1 h. Some of the films were dried completely in vacuum at 70°C for several days to get dry films, and others were dried partially with water content of about 30–40% to get wet films. Chitosan and polyether N330 were also dried completely. All the infrared spectra were obtained with a Nicolet 5DX FTIR spectrometer.
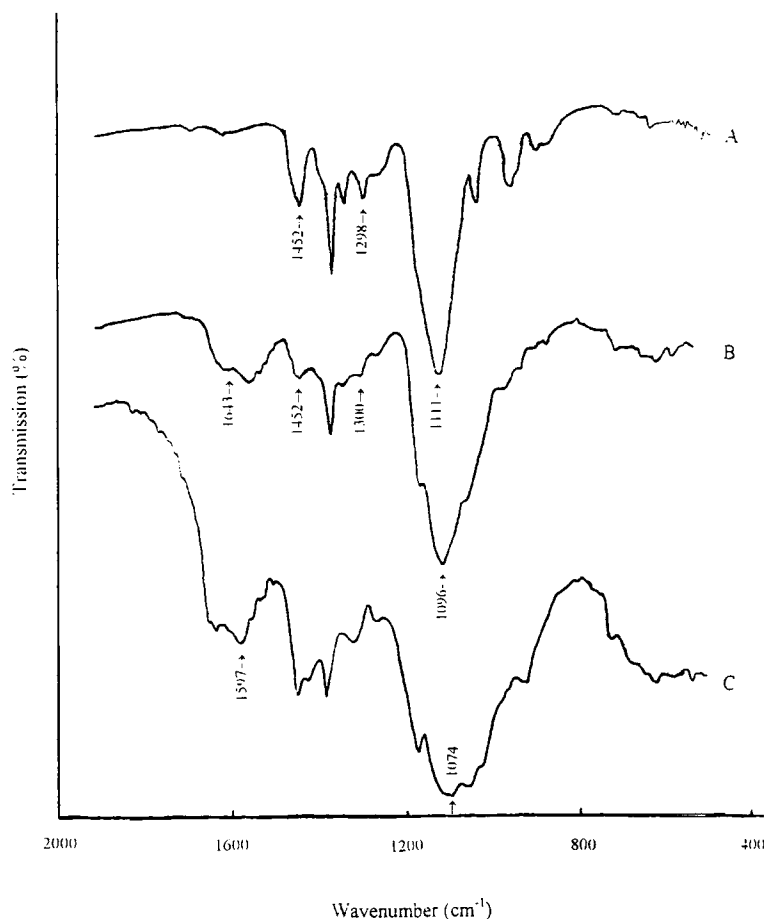
Figure 1   IR spectra of (A) polyether, (B) semi-IPN dry gel, and (C) chitosan.

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-2C was used to measure the phase transition of water sorbed by the hydrogels. The xerogels of known dry weight were swollen in distilled water or pH = 1.25 buffer solution at 25°C, and the hydrogels with different swelling degree were surface-dried with a filter paper and transferred to aluminum pans; the excess water was allowed to evaporate on the micro-balance to the desired water content before the pans were sealed. The weights of hydrogel samples were ca 4 mg. Samples were cooled from room temperature down to 210 K and then heated to 300 K at a heating rate of 5 K/min. The heat of fusion was calculated from the thermogram area using pure water as a standard; therefore, the weight of freezing water in the hydrogel can be calculated. The percentage of nonfreezing water (W_{nf}) was calculated by subtracting the total percentage of freezing water (W_{tf}) from the water content, W, in the hydrogel. As indicated in eq. (1), W is calculated on the basis of the total mass of hydrogel; the same applies to W_{nf} and W_{tf}.

RESULTS AND DISCUSSION

IR Spectra Analysis

Figure 1 shows the IR spectra of polyether (A), semi-IPN dry gel (B), and chitosan (C). The peak at 1597 cm^{-1} in IR spectrum of chitosan [Fig. 1(C)] can be assigned to the amino absorption peak.[20] In contrast with spectra (A) and (C), it was noticed that in the spectrum of the semi-IPN (B), the peak for the amino in chitosan, became weaker; and there was a new peak at 1643 cm^{-1}, which can be attributed to the formation of C $=$ N due to imine reaction between amino groups from chitosan and aldehyde groups in glutaraldehyde.[20,21] The peaks at 1452 and 1300 cm^{-1} are characteristic peaks from polyether within the gel. The peaks at 1111, 1096, and 1074 cm^{-1} in spectra [Fig. 1(A–C)] are due to C $-$ O stretching vibration in polyether, chitosan/polyether gel, and chitosan, respectively.[20] The type of hydrogen bounding within the semi-IPN may be complicated because there are several groups that can form hydrogen bonds in chitosan.[23] Furthermore, polyether may form a new type of hydrogen bonding with these groups

Figure 2   IR spectra of dry gels: (A) chitosan–polyether semi-IPN and (B) IPN swollen in pH = 1.25 medium.

competitively. It has been reported previously that within the semi-IPN, there is a new type of hydrogen bonding between amino hydrogen and polyether oxygen.[19] Therefore, as the amino groups in the network are protonized in acidic medium, the hydrogen bonding dissociates, and the gel is obviously swollen. In Figure 2, by contrast with the spectrum in Figure 2(A), there are two new bands at 1624 and 1518 cm^{-1} assigned to NH_3^+ absorption peaks[20] in the spectrum in Figure 2(B)], which can confirm the —NH_3^+ formation when the gels were swollen in pH = 1.25. Meanwhile, in comparison to Figure 2(A), the wave number of C—O stretching in Figure 2(B) shifts to 4
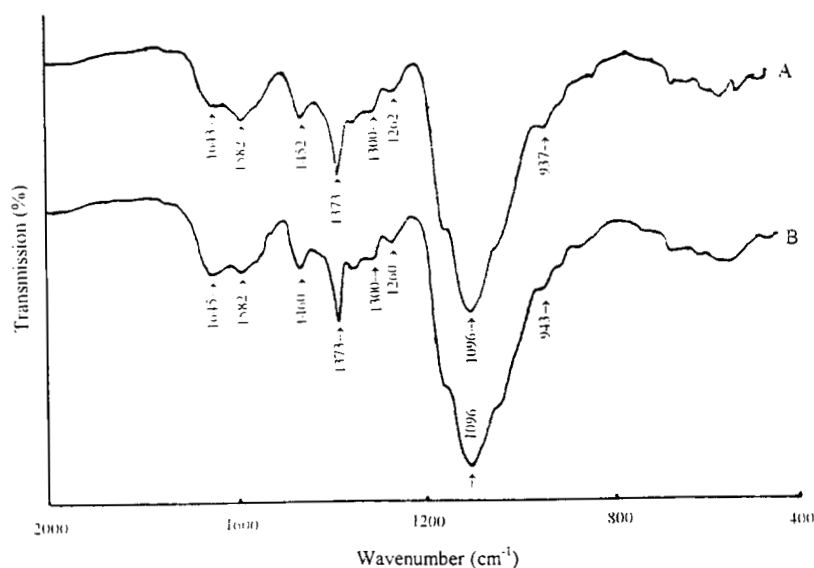

Figure 3   IR spectra of the (A) dry and (B) wet semi-IPN gel swollen in pH = 7.0 buffer solution.
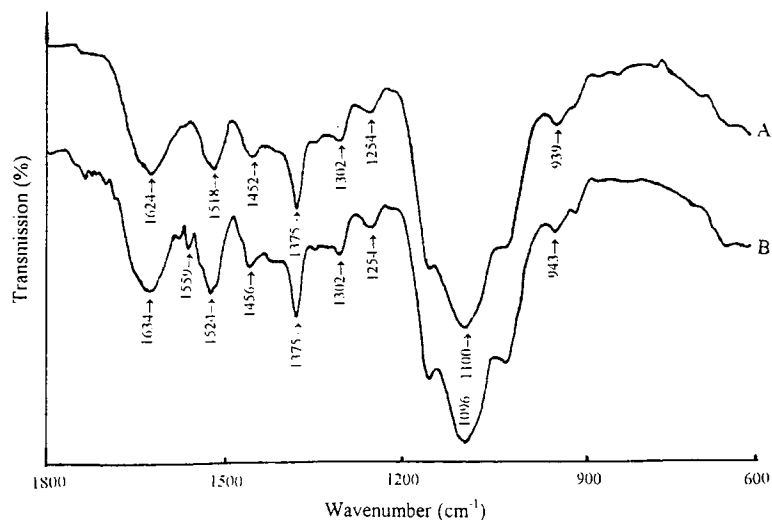
Figure 4 IR spectra of the (A) dry and (B) wet semi-IPN gels swollen in pH = 1.25 buffer solution.

Table I Main Bands in Infrared Spectra of Dry and Wet Semi-IPN Film

| Swollen Medium | Band Position (cm^{-1}) | | Assignment |
	Dry Film	Wet Film	
pH = 7.0	1643	1645[a]	C=N stretching and HOH bend
	1582	1582	C—N absorption or NH deformation
	1452	1460	—CH$_2$—O symmetric deformation of —CH$_2$ from polyether[b]
	1373	1373	CH$_3$ symmetric deformation
	1300	1300	Probable OH deformation from polyether
	1262	1260	OH deformation from chitosan
	1096	1096	The sum of C—O stretching in the ether bond of polyether and —OH in chitosan
	937	943	Assignment uncertain
pH = 1.25	1624	1634	NH$_3^+$ deformation
		1559	Assignment uncertain
	1518	1524	NH$_3^+$ deformation
	1452	1456	—CH$_2$—O symmetric deformation of —CH$_2$ from polyether[b]
	1375	1375	CH$_3$ symmetric deformation
	1302	1302	Probable OH deformation from polyether
	1254	1254	OH deformation from chitosan
	1100	1096	The sum of C—O stretching in the ether bond of polyether and —OH in chitosan
	939	943	Assignment uncertain

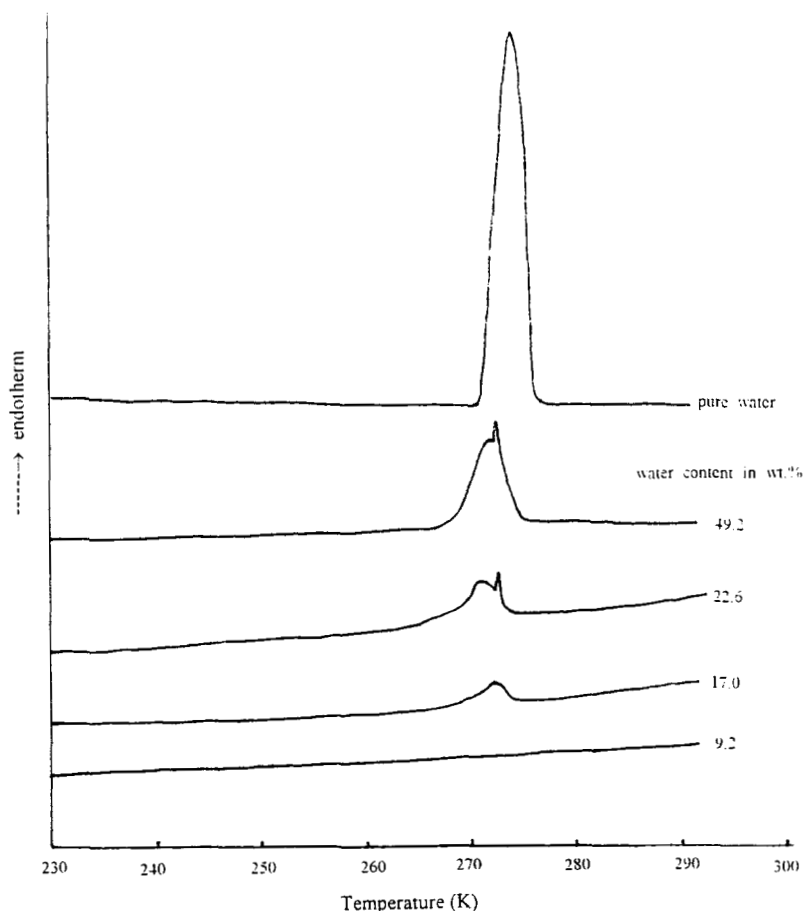[a] Overlapped by H$_2$O absorption.
[b] See Yao et al.[19]

Figure 5 DSC melting thermograms of frozen waters in the chitosan–polyether semi-IPN hydrogels with different water contents swollen in distilled water.

cm^{-1} higher frequency after the sample was swollen in pH = 1.25 to form NH$_3^+$, which may lead to the disassociation of the hydrogen bonding between amino and oxygen in polyether and an increase of the frequency of C — O stretching.[19]

Figures 3 and 4 demonstrate the IR spectra of the dry and wet gel swollen in pH = 7.0 and pH = 1.25, respectively. Table I lists the main absorption bands in the spectra of dry and wet semi-IPN gels. From Figure 3 and Table I, we have found that the absorption band around 1643 cm^{-1} became broader and stronger because of being overlapped by the absorption of H$_2$O assigned to HOH bend vibration. Being affected by water, the absorption due to CH$_2$ — O symmetric deformation of methylene groups from polyether shifts from 1452 to 1460 cm^{-1}. It suggested that the interfacial water may be associated with hydro-

Table II   The Concentration of Three Kinds of Water in the Semi-IPN Hydrogel Swollen in Distilled Water

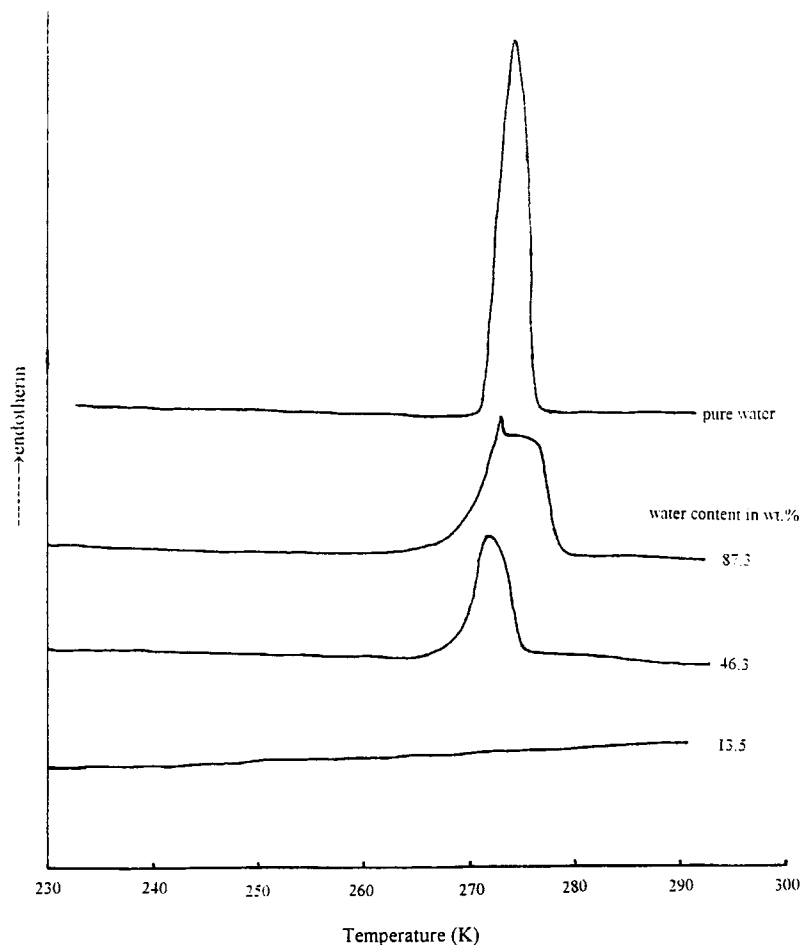| Total Water Content W (wt %)	Total Freezing Water Content W_{tf} (wt %)				Nonfreezing Bound Water W_{nf} (wt %)
	W_{tf} (wt %)	T_1 (K)	W_{fb} (wt %)	T_2 (K)	
9.2	0	—	0	—	9.2
17.0	0	—	1.7	272	15.3
22.6	0.9	273	3.0	271	18.7
49.2	a	a	a	a	19.2

[a] Difficult to be well-resolved.

Figure 6 DSC melting thermograms of frozen waters in the chitosan–polyether semi-IPN hydrogels with different water contents swollen in pH = 1.25 buffer solution.

phobic interactions. The frequencies of amino band and C — O stretching band alter slightly in the presence of water, which indicated that there is strong intermolecular hydrogen-bonding between amino groups and polyether oxygen in the original semi-IPN hydrogel, when the gel swells in pH = 7.0 buffer solution. This is the reason of the low swelling degree for the hydrogel in pH 7.0. However, water may bind to hydroxyl and amide groups in the chitosan-polyether semi-IPN hydrogel.

In contrast to the hydrogel swollen in pH = 7.0 buffer solution, the spectrum of the hydrogel swollen in pH = 1.25 buffer solution is largely affected by water. When the semi-IPN swelled in pH = 1.25 buffer solution, the amino groups in the network protonized, leading to the dissociation of the hydrogen-bonding between amino group and polyether oxygen and swelling. From Figure 4 and Table I, one see that the 1624 and 1518 cm^{-1} bands of the dry gel due to NH deformation shifts toward higher frequencies of 1634

Table III   The Concentration of Different Types of Water in the Semi-IPN Hydrogel Swollen in pH = 1.25 Buffer Solution

Total Water Content W (wt %)	Total Freezing Water Content W_{tf} (wt %)	Nonfreezing Bound Water W_{nf} (wt %)
13.46	0	13.46
46.30	40.58	5.72
87.31	78.26	9.05

and 1524 cm^{-1}, respectively, when the gel contains water, which is probably because of hydrate–ion interaction. A decrease of the frequency of C — O stretching from 1100 cm^{-1} to 1096 cm^{-1} may be caused by the formation of strong hydrogen bonds between the O — H hydrogen of water and oxygen in polyether.[7]

DSC Analysis

In DSC measurements, generally, freezing free water is defined as the unbound water in the polymer, having transition temperature, enthalpy, and shape of the DSC curves similar to those of pure water.[13] Freezing bound water is the intermediate water having a phase transition temperature lower than 273 K. Nonfreezing bound water is one that has no detectable phase transition over the temperature range usually associated with the water freezing–melting transition from 200 to 273 K.[24]

The DSC curves obtained for the semi-IPN hydrogel with different water content swollen in distilled water are shown in Figure 5, together with that of pure water. It is seen that no thermal transition is observed for a hydrogel sample with 9 wt % water content; the hydrogel with low water content of 17 wt % shows a single broad endothermic peak at a temperature little lower than 273 K, while the hydrogel with 23 wt % of water exhibits two endothermic peaks, suggesting the existence of two states of freezing water in the hydrogel. The sharp peak for freezing free water has a transition temperature close to the freezing point (273 K) of pure water. The freezing bound water is distinguished by the low onset temperature of the melting endotherm graph and its broad temperature range, which suggests that the freezing bound water exists in a range of environments.[14] The hydrogel with an equilibrated water content of 49 wt % shows two sharper and broader endothermic peaks, but these two peaks are difficult to be well resolved, probably because the heating rate was high.[17] Table II gives the contents of the three different kinds of water in the semi-IPN hydrogels swollen in distilled water. From the DSC results, it has been suggested that only nonfreezing water exists in the polymer network up to a certain percentage of water content before freezing water can be detected.[1,8,10,18] Furthermore, it implied that the uptake of water into a polymeric network was to be in the following order: nonfreezing, freezing bound, and freezing free water;[8,18] i.e., the freezing free water is the last type emerging after the nonfreezing and freezing bound types have reached their maximum contents.

Figure 6 shows the DSC curves obtained for the semi-IPN hydrogels with different water contents swollen in pH = 1.25 buffer solution for different time intervals, and Table 3 indicates the content of different types of water in the semi-IPN hydrogel swollen at the pH = 1.25 buffer solution. The result is similar with that of Figure 5. The results range from none to one peak to two endothermic ones in the DSC curves as the total water content increases, but the shape of peaks are different from those in Figure 5, which is perhaps because of the presence of

salts. It is surprising that the nonfreezing bound water contents in the hydrogels are not high. As the hydrogen bonding between amino groups and polyether oxygen disrupt in the acidic medium, the polymer network relaxes and absorbs large amount of water. Perhaps there are interactions among water molecules and ion clusters, polyether oxygen sites, and other polar groups in the polymer, which can be seen from IR spectra analysis. The water includes bound and intermediate types. Others are bulk-like water clustered in the micropores inside the relaxed semi-IPN networks.

CONCLUSION

Three types of water could exist in the pH-sensitive chitosan-polyether semi-IPN hydrogels swollen in distilled water or pH = 1.25 buffer solution as follows: nonfreezing bound water molecules that were strongly bound to specific sites, such as polyether oxygen, hydroxyl, amide groups, or ion clusters within the polymer network, and which exhibited no phase transition over the range of 210–300 K; freezing intermediate water, which corresponded to the broad component of the melting endotherm and was loosely bound to the hydrophilic sites in the polymer network and/or to the nonfreezing species; and the sharp component (hump) of the peak, representing freezing free water.

REFERENCES

1. H. B. Lee, M. S. John, and J. D. Andrade, *J. Colloid Interface Sci.,* **51,** 255 (1975).
2. M. Aizawa and S. Suzuki, *Bull. Chem. Soc. Jpn.,* **44,** 2967 (1971).
3. S. Choi and M. S. John, *J. Colloid Interface Sci.,* **61,** 1 (1977).
4. C. Toprak, J. N. Agar, and M. Falk, *Trans. Faraday Soc.* **I.** 803 (1979).
5. E. G. Chatzi, H. Ishida, and J. L. Koenig, *Appl. Spectrosc.,* **40,** 847 (1986).
6. H. Kusanagi and S. Yukawa, *Polymer,* **35,** 637 (1994).
7. B. H. Stuart, *Polym. Bull.,* **33,** 681 (1994).
8. Y. K. Sung, D. E. Gregonis, M. S. John, and J. D. Andrade, *J. Appl. Polym. Sci.,* **26,** 3719 (1981).
9. A. Y. Nosaka, K. Ishikinayama, M. Todoki, and H. Tanzana, *J. Appl. Polym. Sci.,* **39,** 2443 (1990).
10. F. X. Quinn, E. Kampff, G. Smyth, and V. J. McBrierty, *Macromolecules,* **21,** 3191–3198 (1988).
11. E. Ahad, *J. Appl. Polym. Sci.,* **22,** 1665 (1978).
12. S. P. Rowland, Ed., *Water in Polymers,* ACS Symposium Series 127, American Chemical Society, Washington, D.C., 1980. p. 273.
13. K. Nakamura, T. Hatakeyama, and H. Hatakeyama, *Polymer,* **24,** 871 (1983).

14. N. S. Schneider, J. L. Illinger, and F. E. Karasz, *J. Appl. Polym. Sci.,* **47,** 1419 (1993).

15. W. I. Cha, S. H. Hyon, and Y. Ikada, *Makromol. Chem.,* **194,** 2433 (1993).

16. D. S. G. Hu and M. T. S. Lin, *Polymer,* **35,** 4416 (1994).

17. M. B. Ahmad and M. B. Huglin, *Polym. Int.,* **33,** 273 (1994).

18. M. B. Ahmad and M. B. Huglin, *Polymer,* **35,** 1997 (1994).

19. K. D. Yao, T. Peng, M. F. A. Goosen, J. M. Min, and Y. Y. He, *J. Appl. Polym. Sci.,* **48,** 343 (1993).

20. T. Peng, K. D. Yao, C. Yuan, and M. F. A. Goosen, *J. Polym. Sci., Part A: Polym. Chem.,* **32,** 591 (1994).

21. K. D. Yao, T. Peng, M. X. Xu, and C. Yuan, *Polym. Int.,* **34,** 213 (1994).

22. G. A. F. Robert and I. G. Domszy, *Int. J. Biol. Macromol.,* **4,** 373 (1982).

23. F. G. Pearson, R. H. Marchessanlt, and C. Y. Liang, *J. Polym. Sci.,* **43,** 101 (1960).

24. A. Higuchi, J. Komiyama, and T. Lijima, *Polym. Bull.,* **11,** 203 (1984).

Yun Lin Guan[1,*]
Lei Shao[1]
Kang De Yao[2]

[1]Department of Applied Chemistry
Tianjin University
Tianjin 300072
China
[2]Department of Materials Science and Engineering
Tianjin University
Tianjin 300072
China

* To whom correspondence should be addressed.