

Thermoreversible Hydrogels. VII. Synthesis and Swelling Behavior of Poly(*N*-isopropylacrylamide-*co*-3-methyl-1-vinylimidazolium iodide) Hydrogels

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ABSTRACT: A series of *N*-isopropylacrylamide/3-methyl-1-vinylimidazolium iodide (NIPAAm/MVI) copolymer gels were prepared from the various molar ratios of NIPAAm, cationic monomer MVI, and *N,N'*-methylene bisacrylamide (NMBA) in this study. The influence of the amount of MVI in the copolymer gels on the swelling behaviors was investigated in various aqueous saline solutions. Results showed that the swelling ratios (SRs) of copolymer gels were significantly greater than those of NIPAAm homopolymer gels, and the higher the MVI content, the higher the volume phase transition temperature. The SRs for the NIPAAm/MVI copolymer gels decreased with an increase of the salt concentration. In various saline solutions, results showed that the effect of divalent ions on the SR was greater than that of monovalent ions for these hydrogels. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3242–3253, 1999

Key words: thermoreversible hydrogel; *N*-isopropylacrylamide-*co*-3-methyl-1-vinylimidazolium iodide copolymer gel; swelling ratio

INTRODUCTION

Hydrogel is a kind of polymer that can be swollen but cannot be dissolved in water. There are some hydrogels whose SR can be modulated by environmental stimuli such as: temperature,^{1,2} pH,^{3,4} chemicals,⁵ photoirradiation,⁶ and electric field.⁷ The collapse of a gel in response to environmental changes was predicted by Dusek and Patterson⁸ and intensively investigated by Tanaka and coworkers.^{9–13} Thermosensitive hydrogel, one kind of these environmental stimuli responsive hydrogels, collapses by elevating temperature through the lower critical solution temperature (LCST). The volume change occurs within a quite narrow temperature range. An on-off switch according to the environmental temperature can change the

permeability of water through the gel. Therefore, such materials can be used in many fields such as drug delivery system,^{14,15} extraction,¹⁶ and enzyme activity control.¹⁷

N-isopropylacrylamide hydrogel demonstrates a nearly continuous volume transition and associated phase transition from a highly swollen gel network at low temperature to a collapsed phase near its critical point between approximately 31 and 35°C.¹⁸ Hirotsu¹⁹ investigated the phase behaviors of NIPAAm gel/water/alcohol system and explained their thermoshinking by the destruction of hydrogen bonds between water molecules and NH or CO of NIPAAm.

Tanaka and coworkers have previously studied NIPAAm gels containing sodium acrylate (SA) in pure water.^{12,13,20} Their results indicate that incorporation of a small amount of anionic SA into NIPAAm networks produced continuous swelling transition in macroscopic gels at critical temperature. Moreover, the volume phase transition

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temperature increased monotonically as a function of SA content. Some NIPAAm gels containing cationic comonomer have been reported by Beltran et al.^{21,22} They reported the behaviors and properties of NIPAAm gels containing cationic comonomer methacrylamidopropyl trimethylammonium chloride (MAPTAC). Their results showed that the SR of the gel in water and in salt solution at low ionic strength was highly dependent on the degree of gel ionization and the temperature range increased strongly with gel ionization. In addition, the volume change appeared to become less dramatic as the percentage of cationic monomer was increased.

A series of cationic monomers and their corresponding polymers were prepared and the properties in the aqueous salt solution were investigated in the previous reports.^{23–25} In our previous reports, a series of NIPAAm/trimethyl acrylamidopropyl ammonium iodide (TMAAI) and NIPAAm/trimethyl methacryloyloxyethyl ammonium iodide (TMMAI) copolymer gels were prepared.^{24,25} The influence of the content of TMAAI or TMMAI in the copolymer gel on the swelling behavior in aqueous salt solutions was investigated. To further investigate the influence of the structure of cationic monomer in the copolymer gel on the swelling behavior, a series of NIPAAm/3-methyl-1-vinylimidazolium iodide (NIPAAm/MVI) copolymeric gels are prepared. The influence of molar ratio of NIPAAm/MVI and the effect of various salt solutions on swelling behaviors for these copolymer gels are also investigated.

EXPERIMENTAL

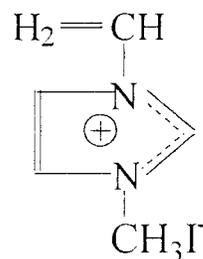
Materials

N-isopropylacrylamide (NIPAAm) (Fluka Chemical Co.) was recrystallized in *n*-hexane before use

in order to remove an inhibitor. 1-Vinylimidazole (Fluka Chemical Co., Switzerland); methyl iodide (TCI Co., Tokyo, Japan); *N,N'*-methylene bisacrylamide (NMBA) (SIGMA Chemical Co., St. Louis, MO) as a crosslinker; and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Fluka Chemical Co.) as an accelerator were used as received. Ammonium peroxydisulfate (APS; Wako Pure Chemical Co. LTD, Osaka, Japan) as an initiator was further purified by recrystallization.

Synthesis of Monomer

The monomer 3-methyl-1-vinylimidazolium iodide (MVI) was prepared according to the literature.²⁶ The structure is as follows:



Preparation of Hydrogels

Various ratios of NIPAAm, MVI, and 3 mol % NMBA based on total monomer content were dissolved in 10 mL of deionized water. To this solution, 3 wt % APS and 3 wt % TEMED as redox initiator were added, and the mixture was immediately injected into the space between two glass plates. The gel membrane thickness (2 mm) was adjusted with a silicone spacer between two glass plates. Polymerization was carried out at room temperature for 1 day. After the gelation was completed, the gel membrane was cut into disks, 10 mm in diameter, and then immersed in an

Table I Characterization of NIPAAm/MVI Copolymer Gels

Sample No.	Feed Composition (%)		Cloud Point Effect ^a	Cloud Point Temperature (°C)	Swelling Ratio (25°C) (g H ₂ O/g dry gel)
	NIPAAm	MVI			
MVI0	100	0	st	30 ~ 35	14.1
MVI1	99	1	st	35 ~ 40	30.6
MVI2	98	2	st	45 ~ 50	44.3
MVI3	97	3	vw	45 ~ 50	56.6
MVI5	95	5	vw	45 ~ 50	83.0
MVI6	94	6	vw	45 ~ 50	87.9

^a st = strong; vw = very weak.

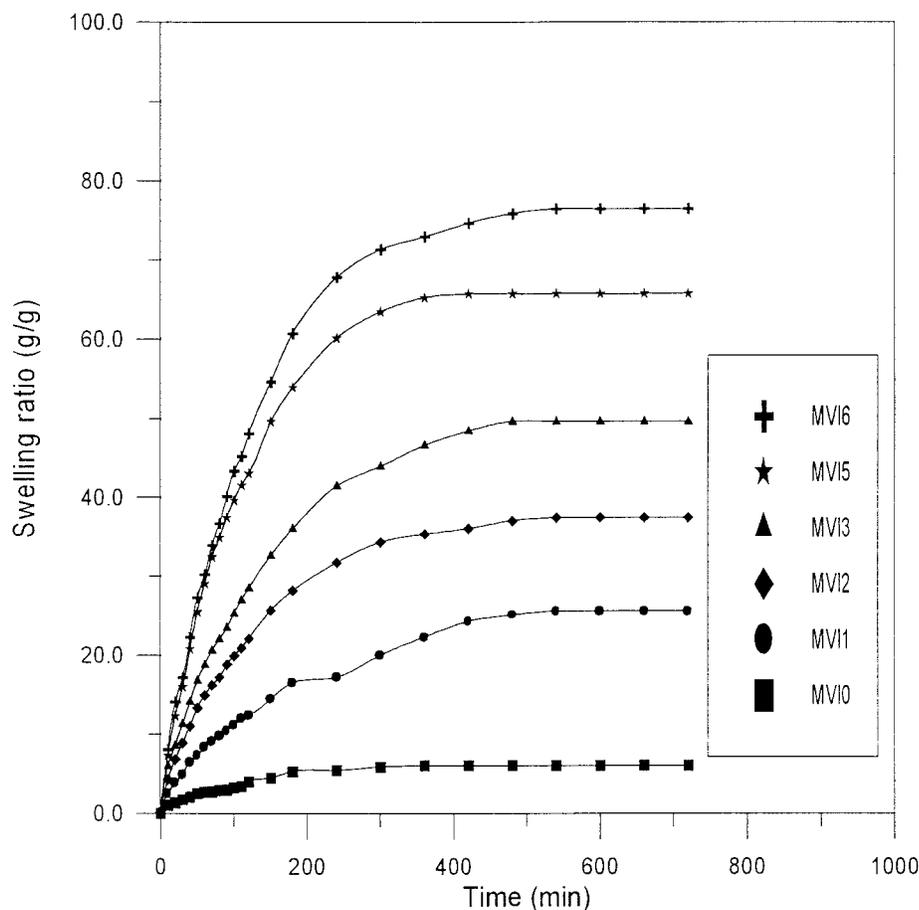


Figure 1 SR as a function of time for NIPAAm/MVI copolymer hydrogels at 30°C.

excess amount of deionized water for 7 days to remove the residual unreacted monomer. Swollen polymer gels were dried at room temperature for 1 day, and these samples were further dried in a vacuum oven for 2 days at 60°C.

Measurement of SR

The dried gels were immersed in an excess amount of deionized water or various saline solutions of different concentrations at 25°C until swelling equilibrium was attained. Each sample was then removed from the water bath and its respective vial, tapped with filter paper to remove excess surface water, and weighed as the wet weight (W_w). Dry weight (W_d) was determined after drying the gel in a vacuum oven for 2 days. SR was calculated from the following formula:

$$SR = \frac{W_w - W_d}{W_d} \quad (1)$$

Dynamic Swelling

The dried gels were immersed in an excess amount of deionized water at different temperatures. The SR was obtained by weighing the initial and swollen samples at various time intervals. The amount of water sorbed M_t was reported as a function of time, and the equilibrium sorption at infinitely long time was designated M_∞ . The following equation can be used to calculate the diffusion coefficient D for $M_t/M_\infty \leq 0.8$.²⁷

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \times \left(\frac{D_t}{L^2} \right)^{1/2} \quad (2)$$

where t is the time and L is the initial thickness of the dried gel.

RESULTS AND DISCUSSION

The swelling behavior of the hydrogels depends on the nature of the polymer and environmental

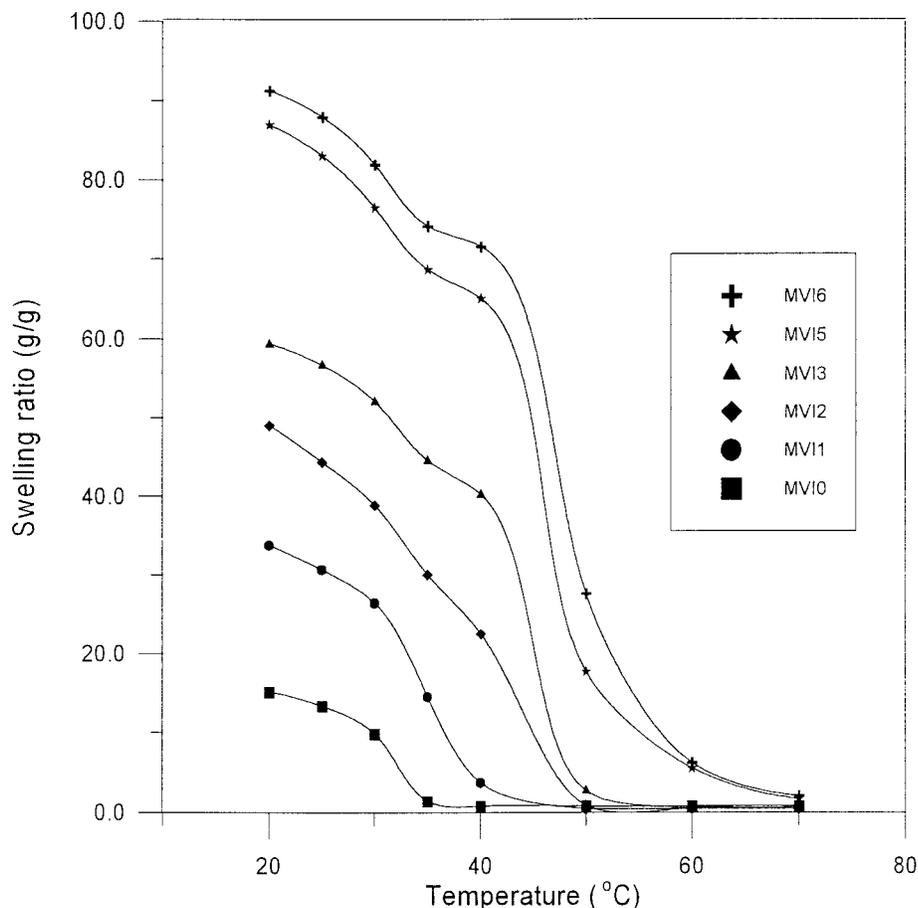


Figure 2 SR as a function of temperature for NIPAAm/MVI copolymer hydrogels.

conditions. The polymer's nature involves the nature of the charge, ion content, and crosslinking agent content.

Characterization of NIPAAm/MVI Copolymer Gels

Some characteristics of the NIPAAm/MVI copolymer gels for various feed compositions shown in Table I exhibit that the cloud point effects of the copolymer gels are weaker with an increase of the content of MVI monomer. The volume phase transition temperatures increase with an increase of the content of MVI in the copolymer composition; that is, from 30 to 50°C for MVI0–MVI6. This result is similar to the results for NIPAAm/TMAAI and NIPAAm/TMAAI copolymer gels.^{24,25} This is because addition of MVI monomer into gel composition makes the gel become more hydrophilic.

In comparison with NIPAAm/TMAAI and NIPAAm/TMAAI copolymer gels, the SRs for the gels presently under investigation are significantly greater than those for the other two series

gels, but a contrary result in cloud point effect for the present gels is observed. This could be the result of the presence of the imidazolium ring—a rigid structure and less hydrophilic group—in the copolymer gel, which occupied a larger space in the gel structure. The increase of the volume phase transition temperature was lower in the gels under study, so the hydrophilicity of the monomer MVI was lower than that of the TMAAI and TMAAI monomer.^{24,25} We also observed that the gels under investigation are more easily subject to collapse.

Effect of MVI Content on SR

As shown in Figure 1, the SRs as a function of time for NIPAAm/MVI copolymer gels at 30°C in deionized water indicate that the SRs increase with MVI content. According to Flory's swelling theory,²⁸ it is well known that the SR has a relation to ionic osmotic pressure, crosslinking density, and the affinity of the hydrogel for water.

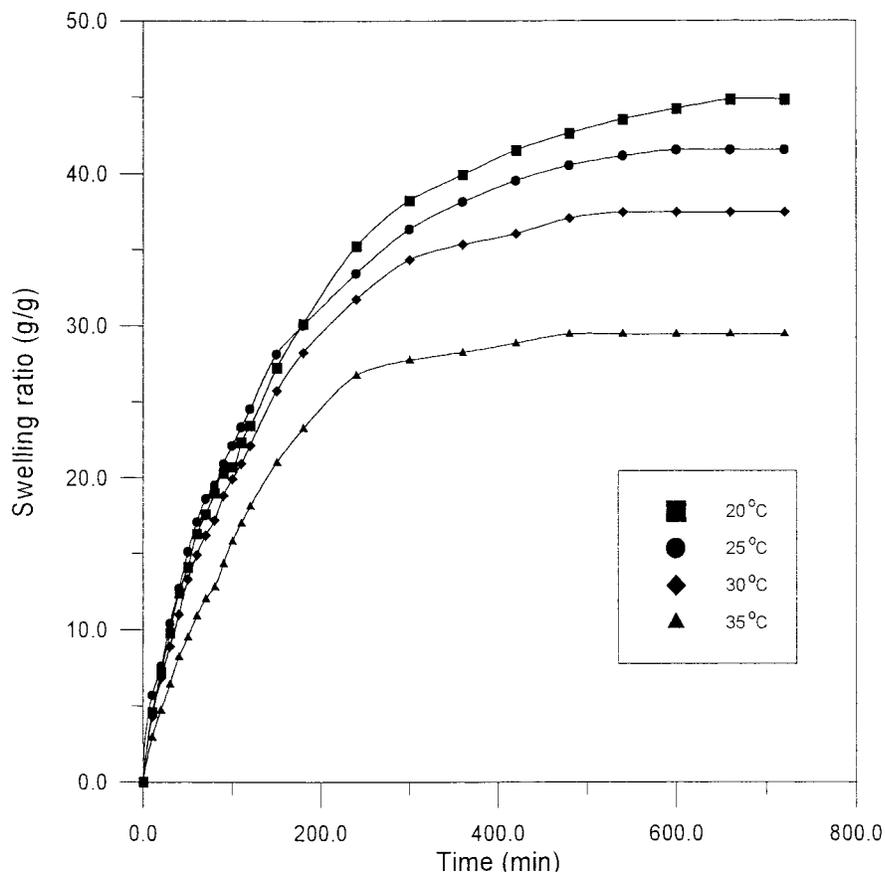


Figure 3 A typical SR as a function of time for MVI2 at different temperatures.

The crosslinking density was fixed in a series of different compositions of NIPAAm/MVI copolymer hydrogels, so the influence of the SR of the hydrogels is the affinity of hydrogel for water and total charges inside the gel. Because the MVI monomer is a hydrophilic cationic monomer, the greater the MVI content, the greater the affinity of the gel for water, and the higher the SR of the hydrogel. In other words, MVI monomer is ionized in aqueous solution; the mutual repulsion of their charges causes the expansion of the polymer chain, which leads to a higher SR of the hydrogel with a greater content of MVI. This result conforms to that reported in previous studies.^{24,25}

Effect of Temperature on SR for NIPAAm/MVI Copolymer Gels

The effect of temperature on the equilibrium-swelling ratio (SR_{eq}) for a series of NIPAAm/MVI copolymer gels shown in Figure 2 indicates that the higher the temperature, the lower the SR_{eq} ; and the greater the MVI content, the higher the

volume phase transition temperature. For NIPAAm gel, the hydrophilic group (amido, —NHCO—) in the polymer structure would transform from an intermolecular hydrogen bond with surrounding water at low temperature (below gel transition temperature) to an intramolecular hydrogen bond at higher temperature. This phenomenon makes the SR of the gel rapidly decrease at the gel transition temperature. The results also indicate that the greater the MVI content, the greater the hydrophilic ability of the gel, and the stronger the affinity of the hydrogel for water. The result is that, as the temperature increases, the gel is not as easily subject to shrinkage. These results conform to our previous studies for NEPAAm/AAm or NTHFAAm/AAm hydrogels.^{29,30}

Investigation of Water Diffusion in Xerogels

As shown in Figure 3, typical SRs as a function of time for sample MVI2 copolymer gel at various temperatures indicate that the SR decreases with in-

Table II Initial Diffusion Coefficient of Water D , Kinetic Exponent n , and Characteristic Constant K of Water Penetrating into NIPAAm/MVI Copolymer Gels at Various Temperatures

Sample No.	Temp. (°C)	n	$K \times 10^3$	$D \times 10^8$ (cm ² /sec)	SR _{eq} ^a (g/g)	T_{eq} ^a (h)	Initial Rate (g/min)
MVI0	20	0.545	4.5	6.44	14	16	0.061
	25	0.510	6.2	6.51	12	12	0.044
	30	0.507	6.6	9.21	6	6	0.029
	35	—	—	—	0.6	1	0
MVI1	20	0.523	5.50	6.22	27.7	10	0.097
	25	0.581	2.95	6.42	26.9	10	0.099
	30	0.654	1.41	6.61	25.6	9	0.092
	35	0.621	2.29	8.07	12.4	9	0.049
MVI2	20	0.595	2.82	6.58	42.1	11	0.152
	25	0.605	2.69	6.90	40.2	10	0.157
	30	0.665	1.69	9.03	37.4	9	0.154
	35	0.735	0.89	10.8	29.4	8	0.129
MVI3	20	0.577	3.31	7.57	52.7	11	0.202
	25	0.665	1.51	8.42	51.9	10	0.206
	30	0.643	1.91	8.87	49.6	8	0.200
	35	0.668	1.70	10.5	39.3	8	0.165
MVI5	20	0.709	1.15	9.29	71.8	10	0.295
	25	0.749	0.85	10.3	69.5	8	0.299
	30	0.751	0.91	12.0	65.7	7	0.293
	35	0.778	0.69	12.2	64.0	7	0.282
MVI6	20	0.713	1.02	10.1	81.5	10	0.319
	25	0.703	1.17	10.8	79.0	8	0.321
	30	0.721	1.07	12.4	76.4	7	0.309
	35	0.718	1.12	13.3	69.5	6	0.303

^a SR_{eq} = equilibrium swelling ratio, T_{eq} = equilibrium time.

creasing temperature. The equilibrium absorption time (T_{eq}) decreases with MVI content in the hydrogels, as can be observed in Table II. As more cationic groups are incorporated into the gel, the equilibrium swelling can be reached more quickly. This is related not only to the LCST but also the amount of ionic charged group in the individual gel matrix. As the charge density rises, the driving force for swelling also increases. Swelling kinetics can generally be described in two terms: the diffusion rate of solvent into the gel and the relaxation rate of the polymer network.

To obtain a more quantitative understanding of the nature of the sorption kinetic in MVI series gels, the initial swelling data were fitted to the exponential heuristic equation:^{31,32}

$$\frac{M_t}{M_\infty} = kt^n \quad (3)$$

where k is a characteristic constant of the gel and n is a characteristic exponent of the mode transport of the penetrate; n and k were calculated

from the slopes and intercepts of the plot of $\log(M_t/M_\infty)$ against $\log(t)$ at various temperatures, respectively. For Fickian kinetics in which the rate of penetrate diffusion is rate limiting, $n = 0.5$, whereas values of n between 0.5 and 1 indicate the contribution of non-Fickian processes such as polymer relaxation. The results shown in Table II indicate that the swelling exponents n for all NIPAAm/MVI copolymer gels at various temperatures are between 0.5 and 1.0. These results indicate that the swelling transport mechanism is a non-Fickian transport.

The measurement techniques of diffusion coefficient in polymers have been the subject of considerable discussion by Crank and Park.³³ The measurement technique used in this experiment is based on the initial rates of sorption.³⁴ It is possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted against the square root of time. Equation (2) was used to calculate the diffusion coefficient (D). The data shown in Table II indicate that the diffusion coefficients for various

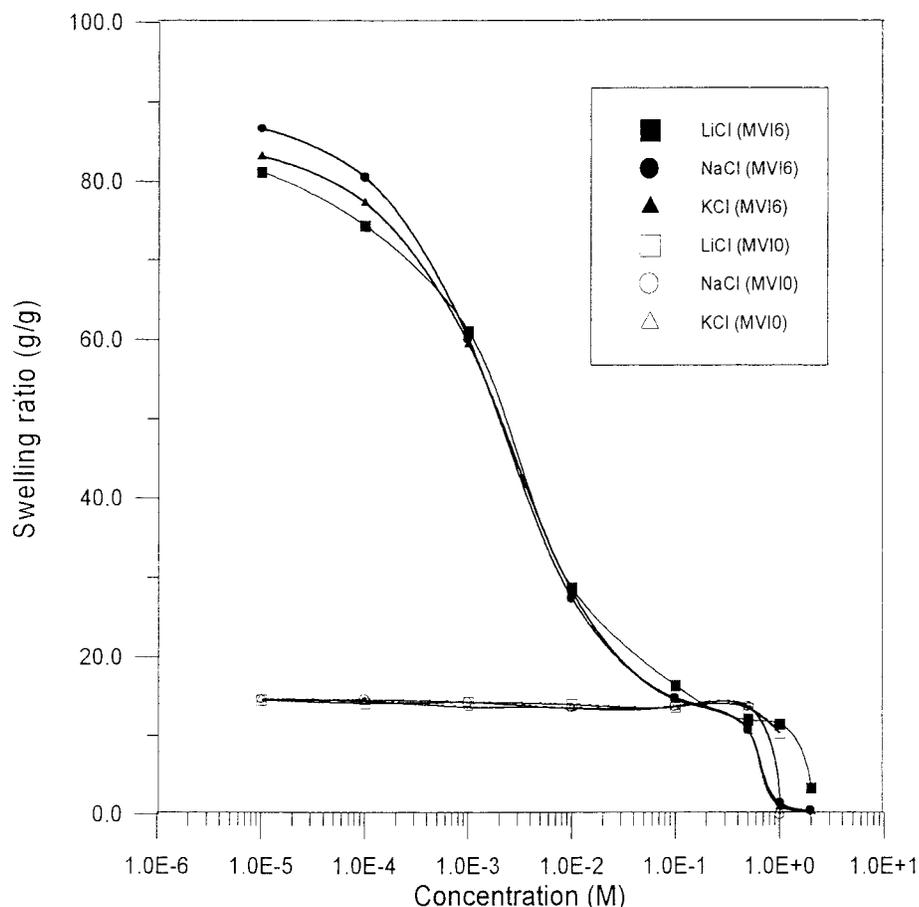


Figure 4 SR for MVI0 and MVI6 in various salt solutions with different monovalent cations at 25°C.

NIPAAm/MVI copolymer gels increased with an increase of temperature. The SR_{eq} and equilibrium time decreased with an increase of temperature. The initial absorption rates (at initial 3 h) also decreased with increasing temperature but increased with an increase of MVI content for these copolymer gel series.

Effect of Various Salt Solutions on the SR

To investigate the influence of various salt solutions on the swelling behavior of the NIPAAm/MVI copolymer gel, samples MVI6 and MVI0 were chosen to compare and discuss in subsequent sections.

The Influence of Different Monovalent Cations with a Common Anion (Cl^-) on the SR

Figure 4 shows the SR of samples MVI0 and MVI6 as a function of the salt concentration for LiCl, NaCl, and KCl solutions. The results shown in Fig-

ure 4 indicate that the SRs for MVI0 keep an approximately constant value at the range of the salt concentration from 1×10^{-5} to $0.1M$. Because the total fixed charge for pure NIPAAm gel is zero, the concentration of fixed charge referred to unswollen network is zero, according to Flory's swelling theory.²⁸ This implies that the SR of MVI0 could not be affected by the external dilute salt solution. But the SR of the NIPAAm gel rapidly decreases when the concentration of salt solutions is over $0.1M$, and shows the tendency in the order of $LiCl > NaCl = KCl$ (contract to zero SR). This evidence can be explained by the fact that the hydration force of Li^+ is greater than that of Na^+ and K^+ , so the hydrated lithium ion can easily hydrogen-bind onto the amido group of the NIPAAm gel. Hence, the SR of poly(NIPAAm) gel has a higher value in the concentrated LiCl solution. The SR of sample MVI6, however, was influenced by the affinity to water and the fixed charge of gel, because the side chain of MVI would bear a positive charge.

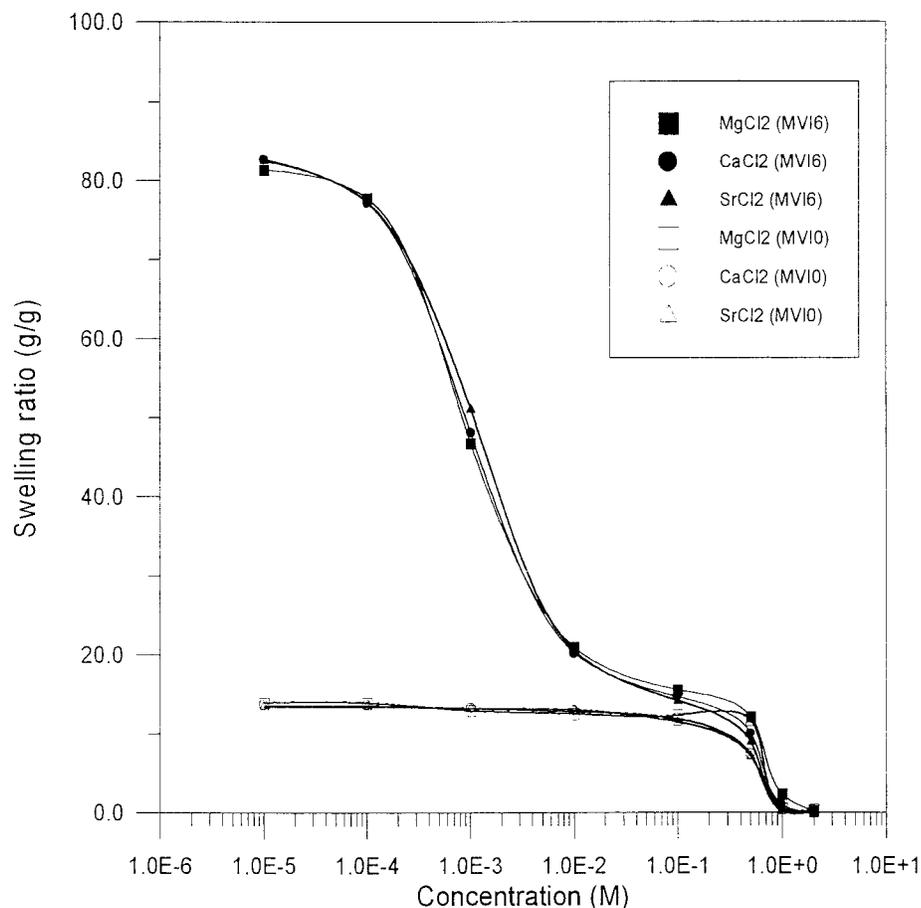


Figure 5 SR for MVI0 and MVI6 in various salt solutions with different divalent cations at 25°C.

The SRs for MVI6 gradually decrease with an increase of salt concentration. This behavior can readily be explained on the basis of a simple physical argument. At low ionic strength, the concentration of charges within the gel exceeds the concentration of salt in the external solution; a large ion-swelling pressure causes the gel to expand, thereby lowering the concentration of co-ions within the gel. As the external salt concentration rises, the difference between the internal and external ion concentration decreases and the gel deswells; the gel continues to deswell with rising external salt concentration until the mobile-ion concentrations inside and outside the gel are approximately equal. These phenomena can also be explained on the basis of repulsion between fixed charged groups on the gel. At low ionic strength, repulsion is long range and the gel expands to minimize the repulsive free energy; as ionic strength increases, repulsion is shielded and the gel deswells (shielding effect).

The Influence of Different Divalent Cations with a Common Anion (Cl^-) on the SR

Figure 5 shows the SRs for MVI0 and MVI6 xerogels in salt solutions of MgCl_2 , CaCl_2 , and SrCl_2 . The swelling behaviors for MVI0 in these salt solutions have the same tendency as those in the salt solutions of LiCl , NaCl , and KCl . However, the swelling behavior for MVI6 gradually decreases and converges to zero with an increase of the concentration of divalent salts from 10^{-5} to $2M$. On the other hand, comparing Figure 5 with Figure 4 on the salt concentration from 10^{-4} to $10^{-2} M$, the SR for MVI6 in divalent salt solution is lower than that in monovalent salt solution. This result implies that the effect of divalent ions on the SR for MVI6 is greater than that of monovalent ions.

The Influence of Different Halide Ions with a Common Cation (K^+) on the SR

The influences of different halide ions with a common cation (K^+) on the SR for MVI6 and MVI0

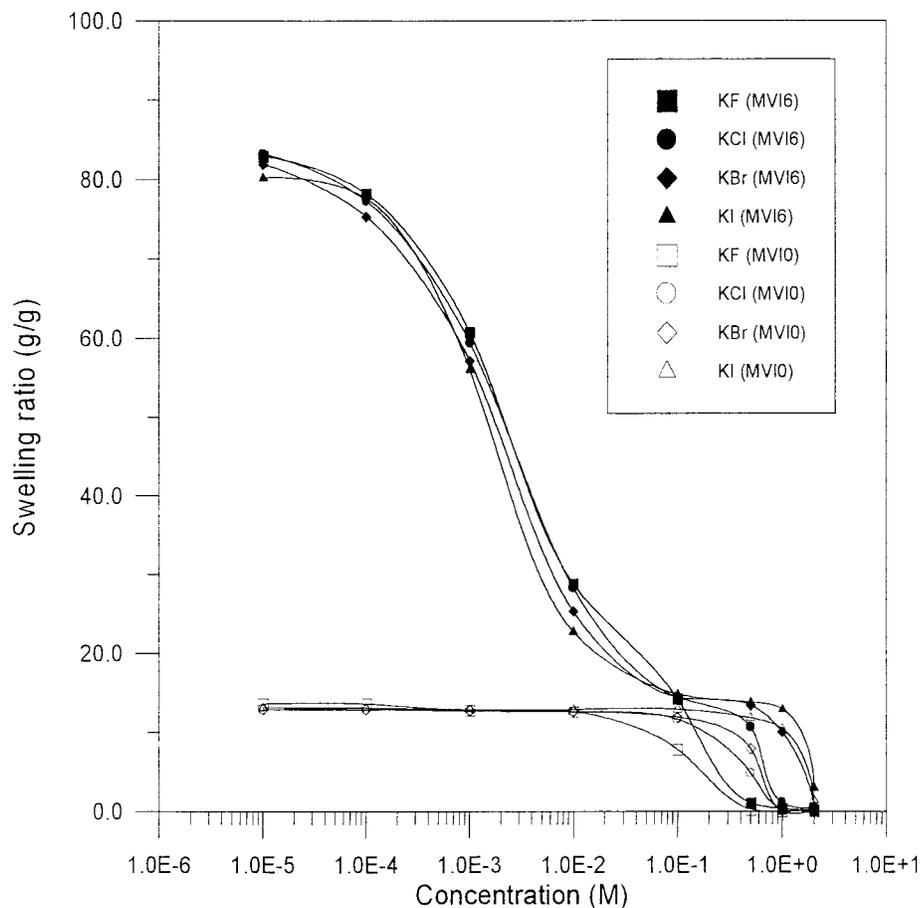


Figure 6 SR for MVI0 and MVI6 in various salt solutions with different halide ions at 25°C.

are shown in Figure 6. The results indicate that the SR for MVI6 decreases with an increase of the salt concentration from 10^{-5} to $2M$. The result also shows that the deswelling curve is divided into two parts. The SR of the gels in different salt solutions is in the order $KF > KCl > KBr > KI$ when the salt concentration is below $0.1M$. This is because the larger anion with common positive charge (charge density is smaller) is easily polarized and bound to the quaternary ammonium group (R_4N^+) on the chain. The positive charge on polymer side chain could therefore become effectively neutralized by the larger anion (I^-) and the SR decreased. When the salt concentration is greater than $0.1M$, the tendency of the SR is in the order $KF < KCl < KBr < KI$, due to the fact that the polyelectrolytic behavior of the gels was shielded by the salt effect. This deswelling behavior is similar to that of the poly(NIPAAm) gel (MVI0). The SRs for MVI0 in the KF, KCl, KBr, and KI solutions keep constant value at low con-

centration ($<0.1M$), but decreases in the order $KF < KCl < KBr < KI$. The result is the same as the behavior of sample MVI6 at high concentration ($>0.1M$).

The Influence of Different Acidic Ions with a Common Cation (Na^+) on the SR

The influence of monovalent acidic groups (ClO_4^- , NO_3^- , and CH_3COO^-) with a common cation (Na^+) on the SR for MVI0 and MVI6 copolymer gel is investigated. The results shown in Figure 7 indicate that the tendency of the SR for MVI6 gel is in the order $CH_3COO^- > NO_3^- > ClO_4^-$ as the concentration of salts is lower than $0.1M$. The reason is that the acetate ion (CH_3COO^-) is a weak acid group and easily forms an acetic acid in aqueous solution. Therefore, the ionic intensity is very small and cannot effectively neutralize the charges of the polycations. The polymer side chain is attracted by the acid ion (ClO_4^-), and this attraction causes the poly-

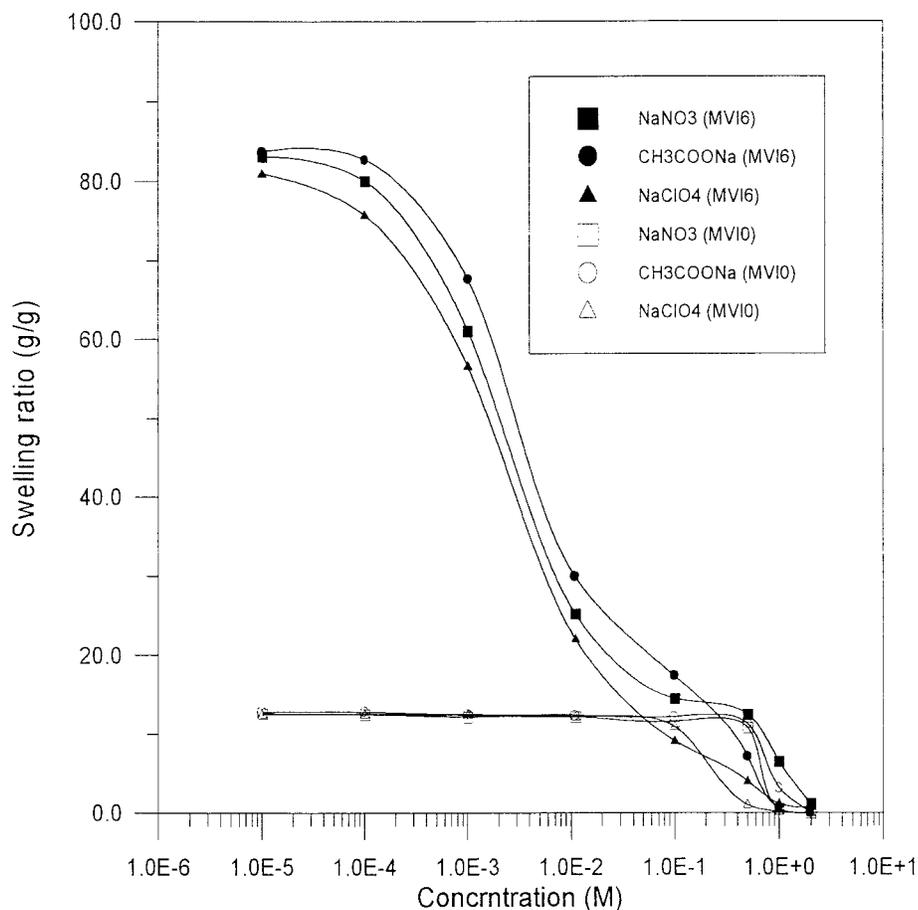


Figure 7 SR for MVI0 and MVI6 in various salt solutions with different monovalent anions at 25°C.

meric chain not to expand and agglomerate in the solution. The result shown in Figure 7 also shows that the tendency of the SR for MVI6 gel is in the order $\text{NO}_3^- > \text{CH}_3\text{COO}^- = \text{ClO}_4^-$ at high concentration ($>0.1M$) of NaNO_3 , CH_3COONa , and NaClO_4 solutions.

The SR of MVI0 keeps constant value at low concentration ($<0.01M$), but decreases rapidly at high concentration. The tendency of SR is in the order $\text{CH}_3\text{COO}^- < \text{ClO}_4^- < \text{NO}_3^-$. From the preceding result, we know that the swelling behaviors of sample MVI6 are like those of an uncharged hydrogel in high concentration of salt solutions and is similar to sample MVI0.

For the various divalent anions, the data (see Fig. 8) show that the SRs decrease with an increase of concentration of salt solution. For Figure 8, the SR for MVI0 rapidly decreases from 12 to zero at $10^{-3}M$ to $10^{-1}M$ of various salt solutions. But the SR for MVI6 shows a two-stage decrease; that is, the first stage is from 10^{-4} to $10^{-1}M$, and the

second stage is from 10^{-1} to $1M$ for various divalent anions. Comparing these two gels, it is known that the first stage deswelling behavior for MVI6 is attributed mainly to the MVI component, and their SRs show a decrease in the order $\text{CO}_3^{2-} > \text{SO}_3^{2-} > \text{S}_2\text{O}_3^{2-}$. This deswelling behavior can be explained by Pearson theory.^{23,35} The second-stage deswelling behavior for the MVI6 gel is also consistent with the deswelling behavior of MVI0. By comparing Figure 8 with Figure 7 on the salt concentration from 10^{-4} to $10^{-2}M$, we also find that the SRs for MVI6 in divalent anions are lower than those in monovalent anions.

From the preceding results, we find that the swelling behaviors for these series gels are extremely similar to those for NIPAAm/TMAAI and NIPAAm/TMAAI gels. Hence, we can conclude that the swelling behavior of cationic polyelectrolyte gel is not affected by the difference in structure of the cationic monomer incorporated into NIPAAm gel, but is readily af-

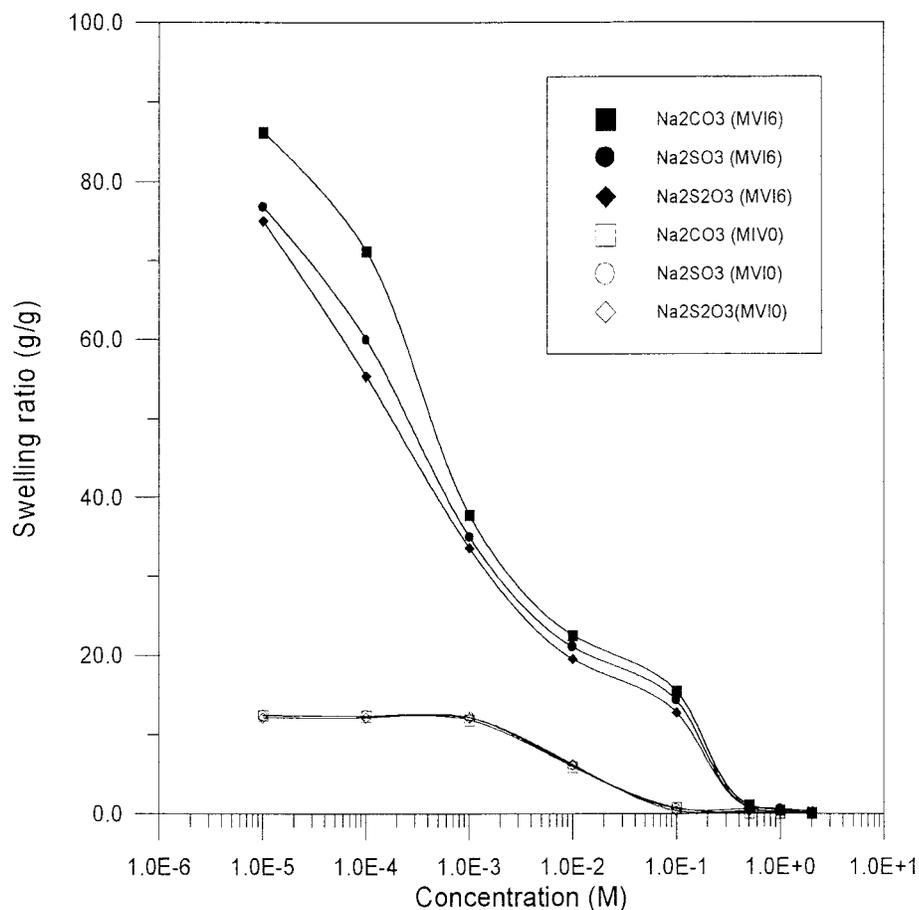


Figure 8 SR for MVI0 and MVI6 in various salt solutions with different divalent anions at 25°C.

ected by the charge density of the copolymer gel.

CONCLUSIONS

The SRs of NIPAAm/MVI copolymer gels increase with an increase of MVI content, and the equilibrium absorption time of hydrogels is shorter. In addition, the greater the MVI content, the greater the affinity of the hydrogels for water. The volume phase transition temperature increases as the MVI content increases.

In diffusion transport mechanism, the results indicate that the swelling exponents n for all NIPAAm/MVI copolymer gels at various temperatures are at values between 0.5 and 1.0. This implies that the swelling transport mechanism belongs to a non-Fickian transport. The diffusion coefficients (D) for various copolymer gels increase with an increase of temperature.

The effect of salt solution on the SR for this series of gels shows a polyelectrolytic behavior. The SRs of various copolymer gels decrease with an increase of salt concentration. When the salt concentration is between 0.1 and 2M, various copolymeric gels exhibit uncharged swelling behavior. In other words, the swelling behavior may be changed at higher concentration. Finally, the effect of divalent ions on the SR is greater than that of monovalent ions for the hydrogels.

REFERENCES

1. Bae, Y. H.; Okano, T.; Kim, S. W. *J Polym Sci B Polym Phys* 1990, 28, 923.
2. Ricka, J.; Tanaka, T. *Macromolecules* 1984, 17, 2916.
3. Hirokawa, E.; Tanaka, T. *J Chem Phys* 1984, 81, 6379.
4. Hoffman, A. S. *J Controlled Release* 1987, 6, 297.

5. Ishihara, K.; Muramoto, N.; Shinohara, I. *J Appl Polym Sci* 1984, 29, 211.
6. Kungwachakun, D.; Irie, M. *Makromol Chem Rapid Commun* 1988, 9, 243.
7. Eisenberg, S. R.; Grodzinski, A. J. *J Membr Sci* 1984, 19, 173.
8. Dusek, K.; Patterson, D. *J Polym Sci A Polym Chem* 1968, 6, 1209.
9. Tanaka, T. *Phys Rev Lett* 1978, 40, 820.
10. Tanaka, T.; Nishio, T.; Sun, S.; Nishio, S. *U. Sci-ence* 1982, 218, 467.
11. Tanaka, T.; Fillmore, D.; Sun, S.; Nishio, I.; Swislow, G.; Shah, A. *Phys Rev Lett* 1980, 45, 1637.
12. Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1987, 87, 1392.
13. Matsuo, E. S.; Tanaka, T. *J Chem Phys* 1988, 89, 1696.
14. Hoffman, A. S.; Afrassabi, A.; Dong, L. C. *J Controlled Release* 1986, 4, 213.
15. Bea, Y. H.; Okano, T.; Kim, S. W. *Makromol Chem Rapid Commun* 1987, 8, 481.
16. Freltas, R. F. S.; Cussler, E. L. *Sep Sci Technol* 1987, 22, 911.
17. Dong, L. C.; Hoffman, A. S. *J Controlled Release* 1986, 4, 223.
18. Heskins, M.; Guillet, J. E. *J Macromol Sci Chem* 1968, A2, 1441.
19. Hirotsu, S. *J Phys Soc Jpn* 1987, 56, 233.
20. Hirose, Y.; Amiya, T.; Hirokawa, Y.; Tanaka, T. *Macromolecules* 1987, 20, 1342.
21. Beltran, S.; Baker, J. P.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* 1991, 24, 549.
22. Beltran, S.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. *J Chem Phys* 1990, 92, 2061.
23. Lee, W. F.; Tsai, C. C. *J Appl Polym Sci* 1994, 52, 1447.
24. Lee, W. F.; Hsu, C. H. *Polymer* 1998, 39, 5393.
25. Lee, W. F.; Hsu, C. H. *J Appl Polym Sci* 1998, 69, 1793.
26. Salamone, J. C.; Snider, B.; Israel, S. C.; Taylor, P.; Raia, D. C. *Polym Prepr* 1972, 13(1), 271, 1973, 14(2), 778.
27. Kabra, B. G.; Gehrke, S. H.; Hwang, S. T. *J Appl Polym Sci* 1991, 42, 2409.
28. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1953; Chapter XIII.
29. Hung, G. C. M.S. Thesis, Tatung Institute of Technology, Taipei, Taiwan, 1995.
30. Lee, W. F.; Hung, G. C. *J Appl Polym Sci* 1997, 64, 1477.
31. Franson, N. M.; Peppas, N. A. *J Appl Polym Sci* 1983, 28, 1299.
32. Kormsmeier, R. W.; Merrwall, E. W.; Peppas, N. A. *J Polym Sci Polym Phys Ed* 1986, 24, 409.
33. Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: London, 1968; Chapter 1.
34. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Caledon Press: Oxford, 1975; Chapter 10.
35. Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1984; p 218.