

Synthesis and Swelling Behavior of Thermosensitive IPN Hydrogels Based on Sodium Acrylate and *N*-isopropyl acrylamide by a Two-Step Method

Wen-Fu Lee, Hsiang-Cheng Lu

Department of Chemical Engineering, Tatung University, Taipei, Taiwan

Correspondence to: W.-F. Lee (E-mail: wflee@ttu.edu.tw)

ABSTRACT: A series of interpenetrating polymer network (IPN) hydrogels having higher swelling ratio (SR) and thermosensitivity were synthesized from sodium acrylate (SA) and *N*-isopropyl acrylamide (NIPAAm) by a two-step method. A series of the porous poly(sodium acrylate -*co*-1-vinyl-2-pyrrolidone) [poly(SA-*co*-VP)], (SV), hydrogels were prepared from acrylic acid having 90% degree of neutralization and VP monomer in the first step. The second step is to immerse the SV dried gels into the NIPAAm solution containing initiator, accelerator, and crosslinker to absorb NIPAAm solution and then polymerized to form the poly(SA-*co*-VP)/poly(NIPAAm) IPN hydrogels (SVN). The effect of the different molar ratios of SA/VP and the content of NIPAAm on the swelling behavior and physical properties of the SVN hydrogels was investigated. Results showed that the SVN hydrogels displayed an obviously thermoreversible behavior when the temperature turns across the critical gel transition temperature (CGTT) of poly(NIPAAm) hydrogel. The pore diameter distributions inside the hydrogel also indicated that the pore sizes inside the SVN hydrogels were smaller than those inside the SV hydrogels. At the same time, the more proportion of SA was added into the hydrogel, the larger pore diameter of the SV hydrogel was formed. The results also showed that the SR decreased with an increase of the VP content in the SV hydrogel and more obviously decreased in the SVN hydrogels. The SVN networks also showed stronger shear moduli than SV hydrogels. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: superabsorbent; interpenetrating polymer network; thermosensitivity; *N*-isopropyl acrylamide; pore size distribution

Received 18 August 2009; accepted 25 April 2012; published online

DOI: 10.1002/app.37971

INTRODUCTION

Superabsorbent polymer is a crosslinked, three-dimensional polymer and it contains strong hydrophilic groups such as –OH and –COO[−] groups. Superabsorbents have superior water absorbency compared with general water-absorbing materials, in which the absorbed water was hardly removable even under high temperature and pressure. The first superabsorbent polymer was reported by the U.S. Department of Agriculture in 1961,¹ and much attention was paid to their applications. The application of superabsorbent polymers was widely used in medical materials and personal hygiene products due to their highly absorbency and holds the water.^{2,3} Some superabsorbent polymeric materials prepared with inversed suspension polymerization were reported in previous reports.^{4–12}

The volume variation of the general temperature-sensitive gels was caused by different hydrophilic and hydrophobic polymeric chains in different temperatures. It is well known that poly(NI-

PAAm) gels occurred a dramatic volume phase transition in water above or below their critical gel transition temperature (CGTT), about 32°C. That is, when a swollen poly(NIPAAm) hydrogel is immersed into water above its CGTT, deswelling immediately occurred at the gel surface. On the contrary, poly(NIPAAm) gel become hydrophilic when immersed into water below its CGTT. Because poly(NIPAAm) gel had this behavior, it was used for thermosensitive gels.¹³

Interpenetrating polymer network (IPN) is a mixture of two or more polymer networks which are at least partially interlaced on a molecular segmental scale but not covalently bonded to each other. Recently, the semi- or full IPN–poly(NIPAAm) hydrogels were used to improve mechanical properties without weakening the thermal sensitivity of the hydrogel because of their higher polymer mass per unit volume in an IPN system. Most of the reported semi- or full-IPN based on poly(NIPAAm) hydrogels have used other network components whose chemical structure is different from NIPAAm to form IPN with

© 2012 Wiley Periodicals, Inc.

Table I. The Feed Compositions, Yields, Equilibrium Swelling Ratio and Swelling Equilibrium Time of SV Hydrogels^a

Sample codes	SA (mol %)	VP (mol %)	Yield ^b (%)	Equilibrium swelling ratio (g/g)	Equilibrium time (min)
SV40	60	40	94.8	98	108
SV20	80	20	95.2	97	122
SV10	90	10	96.6	163	135
SV0	100	0	95.8	190	243

^aDEAP was 1 mol % and neutralization degree of acrylic acid is 90%, ^b $\text{Yield}_{\text{SV}} = \frac{\sum W_{\text{monomer}}}{W_{\text{Hydrogel}}}$
 W_{monomer} : Sum of the weight of SA and VP.
 W_{Hydrogel} : Weight of the SV hydrogel.

poly(NIPAAm).^{14–20} For example, a semi-IPN hydrogel based on crosslinked polyacrylamide and poly(NIPAAm) were prepared by Muniz and Geuskens to greatly increase the elastic modulus and mechanical properties of the hydrogel.^{14,15} Dhara et al.¹⁶ synthesized full gelatin/poly(NIPAAm) IPN hydrogel, and then the volume phase transition in aqueous medium was investigated to understand the role of intermolecular interactions and molecular structure. However, the thermosensitivities of these IPNs were partially weakened due to the introduction of non-thermosensitive gelatin moiety into the IPN network system. In addition, Chu et al. reported IPN-poly(NIPAAm) hydrogels from two poly(NIPAAm) networks and the IPN hydrogels greatly improved mechanical properties and also exhibited improved intelligent characteristics that depended on the composition ratio of the two network components.²¹ A high mechanical strength hydrogel from poly(acrylamide)/poly(acrylamide) with interpenetrating network structure by two-steps synthesis method was reported by Tang et al.²² A series of semi-IPN and IPN hydrogels based on chitosan or gelatin/NIPAAm were prepared and their swelling behavior, thermosensitive, and mechanical properties as well as drug release behavior were investigated in our previous studies.^{23–25}

In a previous study,²⁵ a series of superabsorbents based on sodium acrylate (SA)/1-vinyl-2-pyrrolidone (VP) containing silver nanoparticles had been reported to investigate their swelling and antibacterial properties. In this study, the main purpose is to offer the thermosensitivity to the SA/VP superabsorbent. To approach this purpose, a series of IPN hydrogels with higher swelling ratio (SR) and thermosensitivity were designed from combining SA and NIPAAm. Hence, a series of IPN hydrogels were synthesized from SA and NIPAAm by a two-step method. The effect of the different molar ratios of SA/VP and the content of poly(NIPAAm) on the swelling behavior, physical properties, and pore diameter inside the IPN hydrogels was investigated.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAAm) (Wako Pure Chemical, Tokyo, Japan) was recrystallized in *n*-hexane before use. VP was purchased from Aldrich (St. Louis, MO). Sodium hydroxide was purchased from Nihon Shiyaku Industries (Osaka, Japan). Acrylic acid (AA) was purified by vacuum distillation at 40°C/5

mm Hg (Fluka Chemical, Buchs, Switzerland). Ammonium persulfate (APS) and diethoxyacetophenone (DEAP) as initiator were purchased from Wako Pure Chemical Co. *N,N'*-methylene-bis-acrylamide (NMBA) as a crosslinker was obtained from Sigma Chemical (St. Louis, MO). Cyclohexane and methanol were of reagent analytical grade.

Preparation of SA Monomer Solution

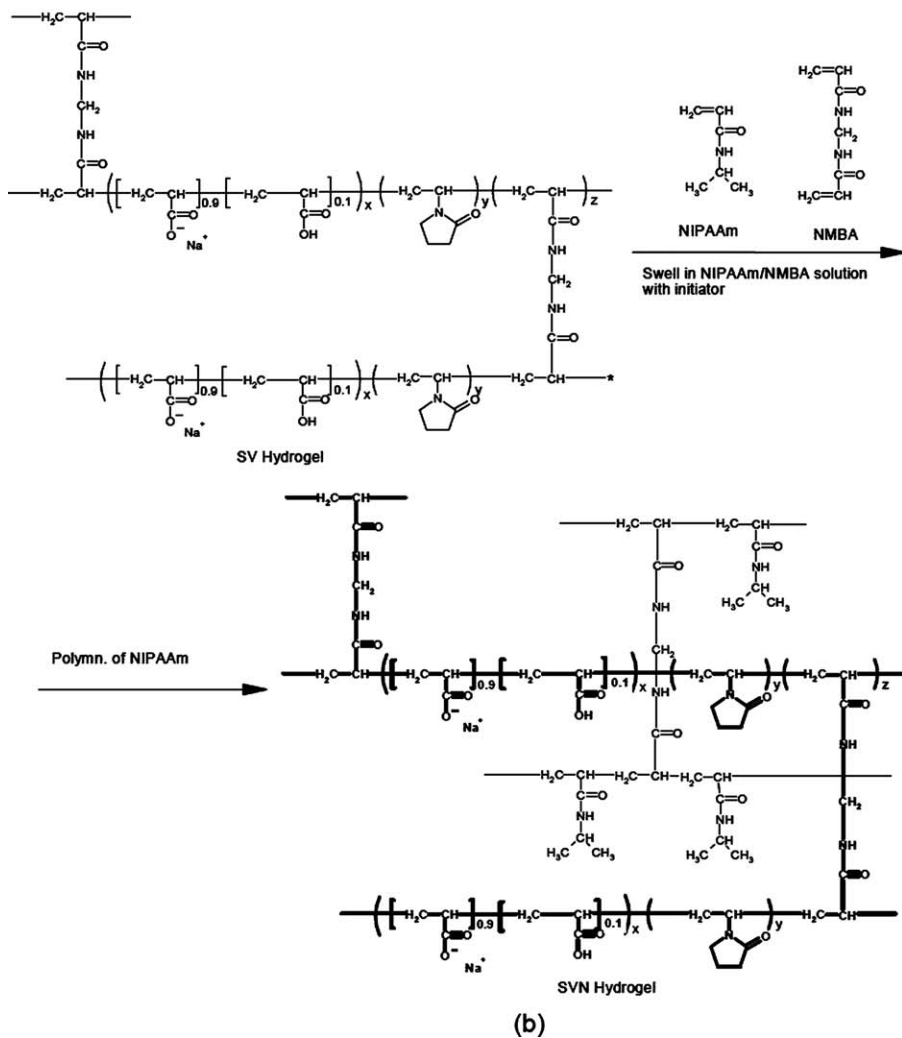
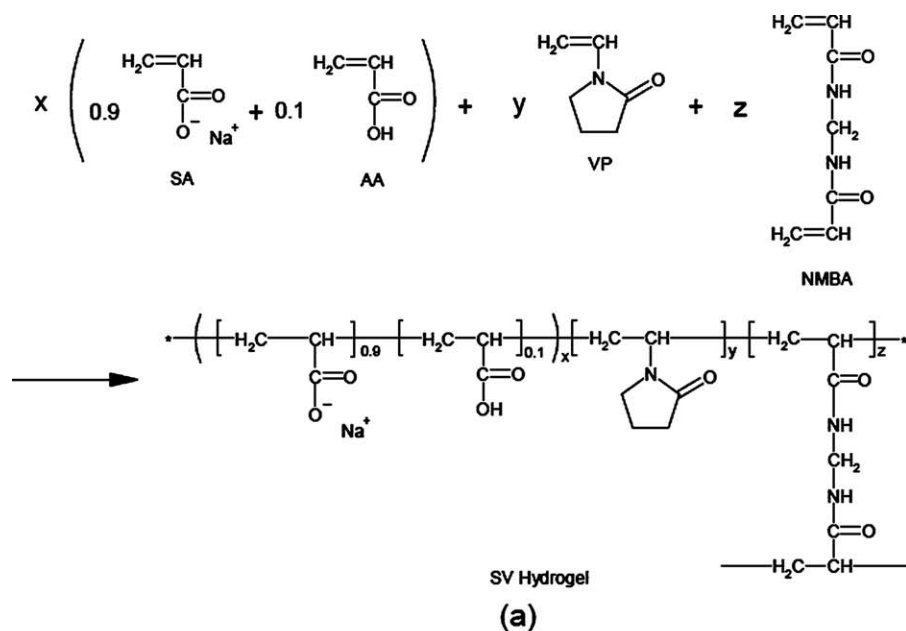
SA monomer solution was prepared from acrylic acid (AA) and sodium hydroxide, the degree of neutralization of AA was 90% as previously reported.⁴

Preparation of SV Hydrogels

SA and VP with different molar ratios were dissolved in 10 mL deionized water. To this solution, 1 mole% NMBA and 1 mole% DEAP were added and well mixed. Finally, the monomer solution was injected into the space between two glass plates, then photo-polymerized by UV lamp with full wavelength at 4°C for 20 min. After gelation was completed, the gel membrane (2-mm thickness) was cut into discs, 8-mm diameter. The gels were then immersed in an excess amount of methanol, and then washed two times by the mixture of water and methanol (1 : 9 in volume ratio). Finally, the product was frozen in –50°C and then freeze-dried for 3 days. The feed compositions and yields of SV copolymeric hydrogels are shown in Table I. The yield was about 95%. The process of polymerization reaction of the SV hydrogel is shown in Scheme 1(a).

Preparation of SVN Hydrogels

The SVN hydrogels were prepared according to the following procedure. Ten milliliters of 1M NIPAAm aqueous solution was prepared in advance, 3 mol % NMBA and 3 mol % APS based on NIPAAm were then added and well mixed. Dried SV discs were immersed into this NIPAAm aqueous solution at 25°C for 12 h to load NIPAAm solution into the SV hydrogel and the equilibrium swollen gels were obtained. Finally, the swollen gels were immersed into 6 mol % TEMED solution to perform a polymerization of NIPAAm and formed poly(NIPAAm) network interpenetrating the SV gel network. The polymerization reaction took place at 25°C for 1 day. After that, the SVN hydrogels were washed with deionized water for three times, then dried in 70°C for 3 days. The process of polymerization reaction of the SVN hydrogel is shown in Scheme 1(b). The yields of poly(NIPAAm) in SVN hydrogels shown in Table II decreases from 9.7% for SV0N hydrogel to 3.8% for SV40N hydrogel.



Scheme 1. The process of polymerization reaction of the (a) SV hydrogel and (b) SVN hydrogel.

Table II. The Yields of Poly(NIPAAm), Equilibrium Swelling Ratio, and Swelling Equilibrium Time of SVN Hydrogels

Sample codes	NIPAAm (M)	NMBA (mol %)	Yield of poly(NIPAAm) ^a (%)	Equilibrium swelling ratio (g/g)	Equilibrium time (min)
SV40N	1	3	3.8	16.1	110
SV20N			7.7	18.9	110
SV10N			8.3	24.1	134
SVON			9.7	27.6	243

$$^a\text{Yield}_{\text{poly(NIPAAm)}} = \frac{W_{\text{SVN}} - W_{\text{SV}}}{W_{\text{NIPAAm}}}$$

where W_{SVN} is the weight of SVN hydrogels, W_{SV} is the weight of the SV hydrogel, and W_{NIPAAm} is the initial weight of the 1M NIPAAm.

Measurement of the Weight Ratio of Poly(NIPAAm) in the IPN Hydrogels

The weight ratios of the SVN to SV hydrogels were calculated by eq. (1) and the weight ratios of poly(NIPAAm) in the SV hydrogels were calculated by eq. (2).

$$R = \frac{W_{\text{SVN}}}{W_{\text{SV}}} \quad (1)$$

$$R' = \frac{W_{\text{PNIPAAm}}}{W_{\text{SV}}} = \frac{W_{\text{SVN}} - W_{\text{SV}}}{W_{\text{SV}}} = R - 1 \quad (2)$$

where W_{SVN} is the weight of IPN hydrogel, W_{PNIPAAm} is the weight of the poly(NIPAAm), and W_{SV} is the weight of SV hydrogel.

Measurement of Physical Properties

The dried gels were immersed in 30 mL of deionized water at 25°C for 1 day to approach equilibrium. The diameters and thicknesses of the gels were recorded. The mechanical strengths of the hydrogels were measured by uniaxial compression experiment with universal tester (LLOYD LRX; J. J. Lloyd, Poole, UK). The shear modulus (G) was calculated by the eq. (3).^{26,27}

$$\tau = F/A = G(\lambda - \lambda^{-2}) \quad (3)$$

where τ is the compression stress, F is the compression load, A is the cross-sectional area of the swollen gels, and λ is the compression strain (L/L_0), where L is the thickness of the wet gel after compression, and L_0 is the thickness of the dried gels. At low strain, a plot of shear stress versus $-(\lambda - \lambda^{-2})$ would yield a straight line whose slope is shear modulus (G). The effective crosslinking density (ρ_x) can then be calculated from shear modulus and polymer volume fraction (v_2) as follows:^{26,27}

$$\rho_x = Gv_2^{-1/3}/(RT) \quad (4)$$

where R is the gas constant and T is the absolute temperature.

Measurement of Pore Size Distribution

The pore size inside the swollen gels at 25°C was measured using a capillary flow porometer (PMI, Ithaca, New York). The tested hydrogels were cut to fit the sample chamber. The swollen gel was placed in the sample chamber, the gel was then

sealed with o-rings between the top and bottom of the adapter plates. The test was performed by increasing the nitrogen pressure from 1 to 20 psi and measured the flow rate through the swollen gel. The flow rate, pore size diameter, bubble point pressure, and pore size distribution were measured during the test.

Measurement of Swelling Kinetics

The swelling kinetics of the hydrogels was measured at 25°C. After wiping off water on the surface with filter paper, the SR of the gel was recorded during the course of swelling at regular time intervals. The SR was calculated by eq. (5):

$$\text{SR} = \frac{W_w - W_d}{W_d} \quad (5)$$

where W_w is the weight of wet gel at different times and W_d is the weight of the dry gel.

Measurement of Deswelling Kinetics

The kinetic of deswelling behavior of the hydrogels was measured at 45°C. Before the measurement of deswelling kinetics, the hydrogels were reached swollen equilibrium in deionized water at 25°C. The weights of the hydrogels were recorded during the course of deswelling at regular time intervals after wiping off water on the surface with filter paper. The deswelling ratio (DSR) (%) is defined as follows:

$$\text{DSR}(\%) = (\text{SR}/\text{SR}_{\text{eq}}) \times 100\% \quad (6)$$

where the SR_{eq} is the SR of the gel at equilibrium.

Equilibrium SR at Different Temperatures

The equilibrium SR of the gel was measured after wiping off water on the surface with filter paper in the temperature range from 25 to 45°C. Gel samples were immersed into excess deionized water for 24 h at every temperature. The SR_{eq} at different temperatures were calculated as eq. (5).

Swelling–Deswelling Behavior of the IPN Hydrogels

Pre-weighed dried gels were immersed in deionized water at 25°C to reach equilibrium at first. The IPN hydrogels were then transferred to 45°C at each fixed time interval (2 h), then immediately transferred the IPN hydrogels to 25°C. The

Table III. The Weight Ratio of SVN/SV and NIPAAm/SVN in IPN Hydrogels

Sample code	SV40N	SV20N	SV10N	SV0N
W_{SVN}/W_{SV} (g/g)	3.62 ± 0.22	4.91 ± 0.17	5.03 ± 0.21	5.65 ± 0.22
$W_{PNIPAAm}/W_{SV}$ (g/g)	2.62 ± 0.16	3.97 ± 0.22	4.06 ± 0.23	4.69 ± 0.16
$W_{PNIPAAm}/W_{SVN}$ (%)	72.4 ± 7.2	80.8 ± 6.11	80.7 ± 6.57	83.0 ± 4.60

measurement of the SR for the hydrogels was performed by repeating above steps for 20 h.

Morphologies

Samples were equilibrated in deionized water for 1 day, and then the swollen gels were frozen-dried for 3 days. The hydrogels were immersed in liquid nitrogen and fractured. The fractured specimens were examined for morphological details by using scanning electron microscopy (SEM) (JEOLJXA 6700, Tokyo, Japan) with an acceleration voltage of 15 kV. The specimens were coated a gold metal layer to provide proper surface conduction.

RESULTS AND DISCUSSION

Preparation of SVN Hydrogels

The dried SV hydrogels were immersed into the NIPAAm solution to load the NIPAAm solution into the SV hydrogels and then polymerized. The yields of poly(NIPAAm) in SVN hydrogels were shown in Table II. The results showed that the yields of poly(NIPAAm) in the SVN hydrogels decreased with an increase of VP content in the SV hydrogels.

The effect of VP content in the SV hydrogels on the weight ratio of NIPAAm and SVN IPN hydrogels is shown in Table III. The results in Table III indicate that the weight ratios of W_{SVN}/W_{SV} and $W_{PNIPAAm}/W_{SV}$ decrease with an increase of VP content in the SV hydrogels. For example, the weight ratios of W_{SVN}/W_{SV} from 5.65 (g/g) for SV0N gel decreased to 3.62(g/g) for SV40N gel. The content of poly(NIPAAm) gel in SVN IPN gels also decreased from 83% (SV0N) to 72.4% (SV40N) when the molar ratios of SA decreased to 60% (SV40N). This is because SA contains much strong hydrophilic groups such as $-\text{COO}^-$ groups, SV0 hydrogel with higher SR can absorb more NIPAAm in solution than other SV hydrogels and has higher yield (9.7%) of poly(NIPAAm) in the SV0N IPN hydrogels. Hence, the content of poly(NIPAAm) in SVN IPN hydrogels

would be decreased with an increase of VP content in the SV hydrogels.

Physical Properties Measurement

The shear moduli and crosslinking densities of the SV and SVN hydrogels are listed in Table IV. The results showed that the crosslinking densities and gel strengths for SV hydrogels increased with increasing of the VP molar ratio in SV hydrogels. That is, the crosslinking density and gel strength increase from 0.65×10^{-5} (mol/cm³) and 4.81 kPa for SV0 hydrogel to 1.59×10^{-5} (mol/cm³) and 17.66 kPa for SV40 hydrogel. When the NIPAAm network was incorporated into the pore inside the SV hydrogels to form an SVN hydrogels, the gel strength from 6.29 kPa for SV0N increases to 26.28kPa for SV40N and gel strengths for SVN hydrogels are higher than SV hydrogels; On the other hand, the crosslinking densities from 0.39×10^{-5} (mol/cm³) for SV0N increases to 1.08×10^{-5} (mol/cm³) for SV40N, but the crosslinking densities for SVN hydrogels are lower than SV hydrogels. Compare these two series, the largest gain in “G” occurs from SV40 to SV40N (17.66–26.28 kPa) due to the largest content of VP. In addition, the gel strength of the hydrogels is mainly dependent on the polymer volume fraction or SR for high absorbent materials according to eq. (4). In this IPN system, the second poly(NIPAAm) network interpenetrating into the porous SV network can compact the hydrogel’s structure, and decrease their SRs, and strengthen the weak SV network.

Pore Diameter Distribution Inside the SV and SVN Hydrogels

The pore size distributions for the pores inside the SV and SVN hydrogels were measured with a capillary flow porometer and the results are shown in Figure 1(a–d). The pore size distributions shown in Figure 1 are ranged from 40 to 80 microns for SV40, 24 to 200 microns for SV20 (the pores over 1000 microns were distributed in the surface and edge of gel disc), 85–400 microns for SV10, respectively. The SV0 hydrogel is too weak to test in this experiment and not shown in Figure 1(d). The results indicated that the range of the pore size distribution increased as the content of SA increased. This is because SA has strong hydrophilicity and can absorb more water that caused larger pore in the gel. But when the pores inside the SV hydrogels were filled with poly(NIPAAm) gel, the pore sizes inside the gels would be decreased. The results shown in Figure 1(a–d) indicated that the pore sizes decreased with an increase of NIPAAm in SVN hydrogels. That is, the pore diameter was distributed from 5 to 15 microns for SV40N hydrogel that containing minimum SA and distributed from 7 to 200 microns for SV0N hydrogels. Comparing the pore diameters inside the SV and SVN hydrogels in Figure 1(a–d), we can find that the larger and coarser pores inside the SV hydrogels were almost completely filled and leveled up by poly(NIPAAm) moiety, this is

Table IV. Shear Moduli and Crosslinking Densities of the Present Hydrogels

Sample codes	$\rho \times 10^5$ Wet gel (mol/cm ³)	G (kPa)
SV40	1.59	17.66
SV20	1.39	12.93
SV10	0.74	5.73
SV0	0.65	4.81
SV40N	1.08	26.28
SV20N	0.66	14.50
SV10N	0.59	12.16
SV0N	0.39	6.29

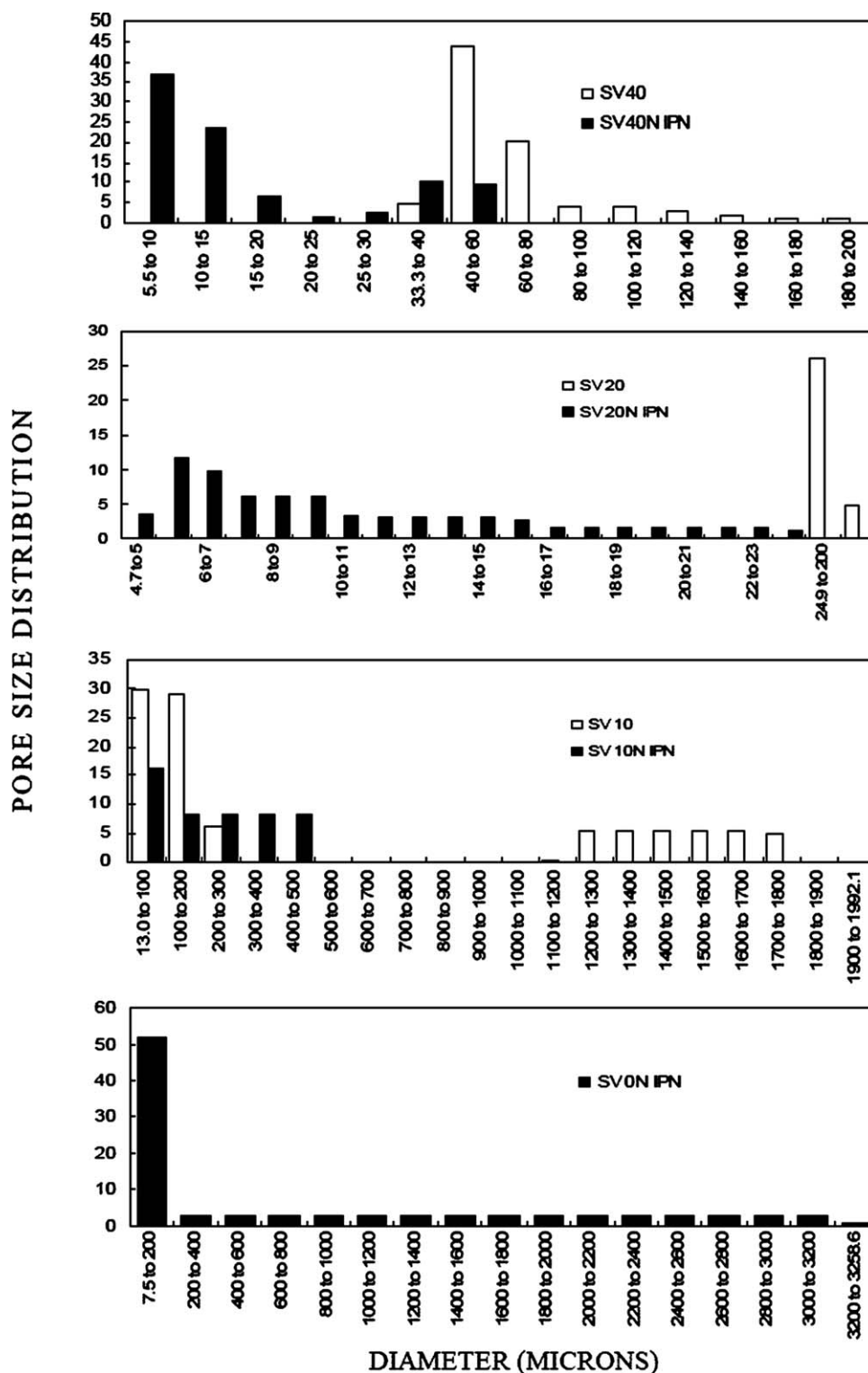


Figure 1. The pore diameter distribution for (□) SV and (■) SVN series hydrogels.

the reason why the pore diameters of SVN hydrogels were narrower and smaller than those of SV hydrogels.

Swelling Behaviors of the SV gels and the SVN Hydrogels

It is well-known that the SR or water absorbency of poly(sodium acrylate) is dependent on the ionic osmotic pressure

within the gel network due to the presence of mobile counterions (Na^+) or on the repulsion force of anionic ion fixed on the gels. The SRs as a function of time for the SV and SVN hydrogels at 25°C are shown in Figures 2 and 3, respectively. The results indicated that the SRs for the SV hydrogels decreased with an increase of VP content in the SV hydrogels.

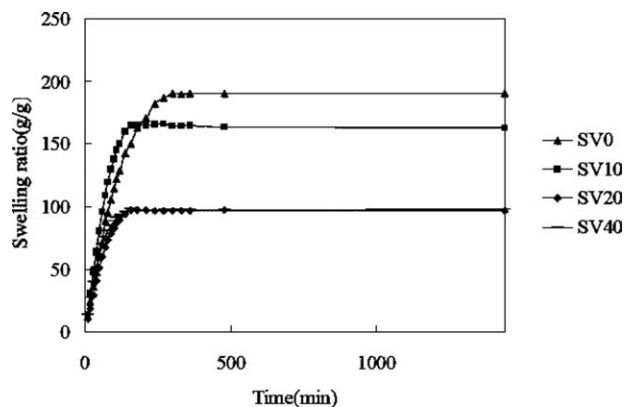


Figure 2. The SRs as a function of time for the SV hydrogels at 25°C.

The equilibrium SR decreases from 190 (g H₂O/g sample) for SV0 to 98 (g H₂O/g sample) for SV40 hydrogel (also see Table I). This is because the ionic osmotic pressure within the gel network or the repulsion force of anionic ion fixed on the gels decreased with an increase of VP content in the gels. Similarly, the results in Figure 3 also showed that the SRs also decreased with a decrease of SA content in SVN hydrogels. The equilibrium SR decreases from 27.6 (g H₂O/g sample) for SV0N to 16.1 (g H₂O/g sample) for SV40N hydrogel (also see Table II). Comparing the SV and SVN hydrogels, the SRs for SVN hydrogels are much lower than those of SV hydrogels. This is attributed to the increased matrix density or polymer mass per unit volume or the more compact structure in IPNs, which would decrease the available space for water during the swollen state.²¹ In addition, the repulsion force between the ionic charges on the SV hydrogels decreases when the SV network was filled with the poly(NIPAAm) gel. That made the water be not able to accommodate into the matrix of SVN hydrogels. But, comparing the swelling equilibrium time (shown in Tables I and II) of an SV hydrogel with the corresponding SVN hydrogel show that the swelling equilibrium times for the two series hydrogels are not significantly affected by the poly(NIPAAm) moiety.

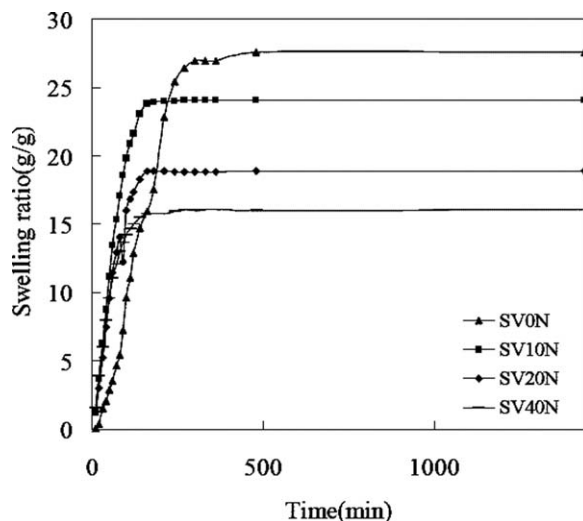


Figure 3. The SRs as a function of time for the SVN hydrogels at 25°C.

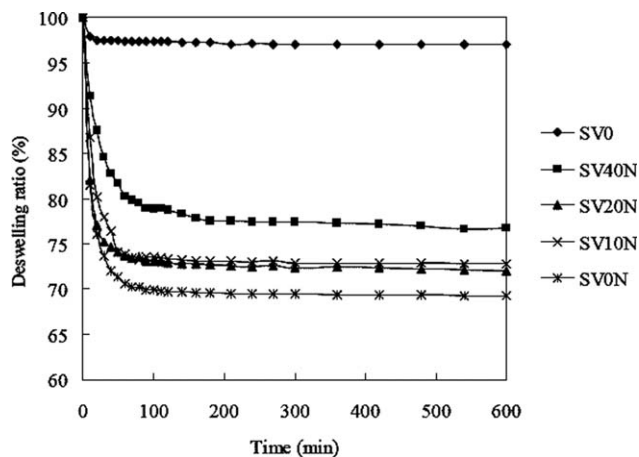


Figure 4. Deswelling profiles of SVN hydrogels at 45°C.

Deswelling Behaviors of the SVN Hydrogels

The deswelling profiles of SVN hydrogels at 45°C are shown in Figure 4. The results indicate that the SV hydrogels had no obvious shrinkage (only 3% of DSR for SV0) during deswelling process because no thermosensitive moiety, poly(NIPAAm), was imbibed into the SV hydrogels. However, the DSR of the SVN hydrogels increased from 23% (SV40N) to 31% (SV0N) as the content of poly(NIPAAm) increased from 3.8% to 9.7% in the IPN networks such as SV40N < SV20N < SV10N < SV0N and exhibited obvious thermosensitivity. The deswelling profiles also showed that the deswelling equilibrium times of the IPN gels were approached at 30–50 min for all these gels.

Effect of Temperature on Equilibrium SRs of the SVN Hydrogels

The effect of temperature on the equilibrium SRs of the SVN hydrogels at various temperatures from 25°C to 55°C is shown in Figure 5. The results show that the equilibrium SRs for other SVN hydrogels decrease as the temperature increases and have a broadening gel transition in the range of the temperature from 30 to 35°C, that is the CGTT of poly(NIPAAm) gel, except

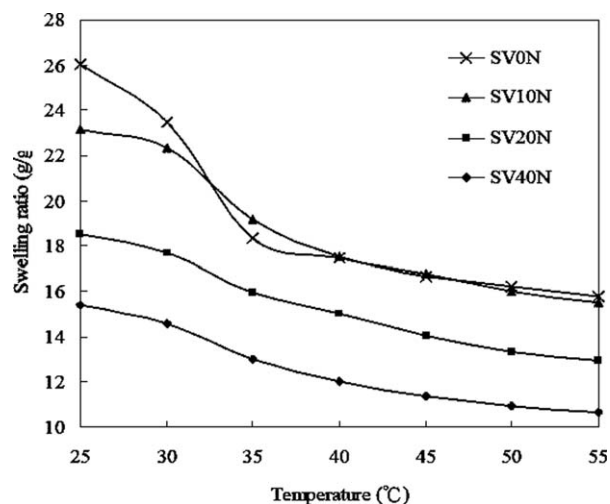


Figure 5. Equilibrium SRs of SVN hydrogels at various temperatures.

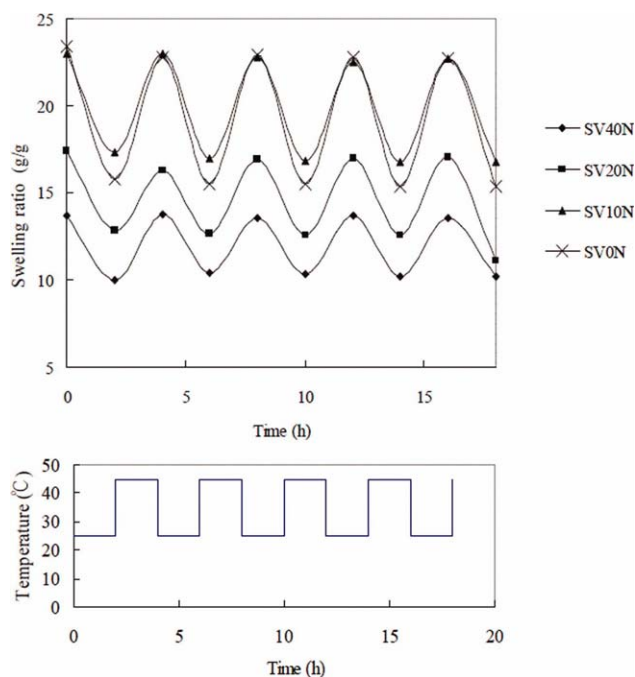


Figure 6. Swelling–deswelling behaviors of SVN hydrogels between 25°C and 45°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SV0N (with the most Poly(NIPAAm)) hydrogel exhibits a somewhat sharp transition at its CGTT. Because the addition of poly(NIPAAm) component into the SV hydrogels would endow the

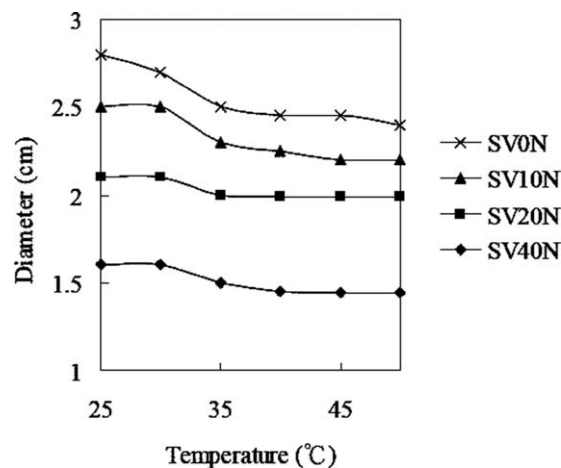


Figure 8. Effects of temperature on gel diameter of SVN hydrogels.

hydrogels with a thermosensitive behavior, the SVN hydrogels containing higher content of poly(NIPAAm) would be more obviously affected by temperature. Hence, the results in Figure 5 indicate that the SV0N gel shows the significant thermosensitivity around the CGTT.

Swelling–Deswelling Behaviors of SVN Hydrogels

The swelling–deswelling behaviors of the SVN hydrogels between 25 and 45°C were measured at fixed time interval (2 h) and shown in Figure 6. The results indicate that the SV hydrogels containing poly(NIPAAm) moiety showed significant

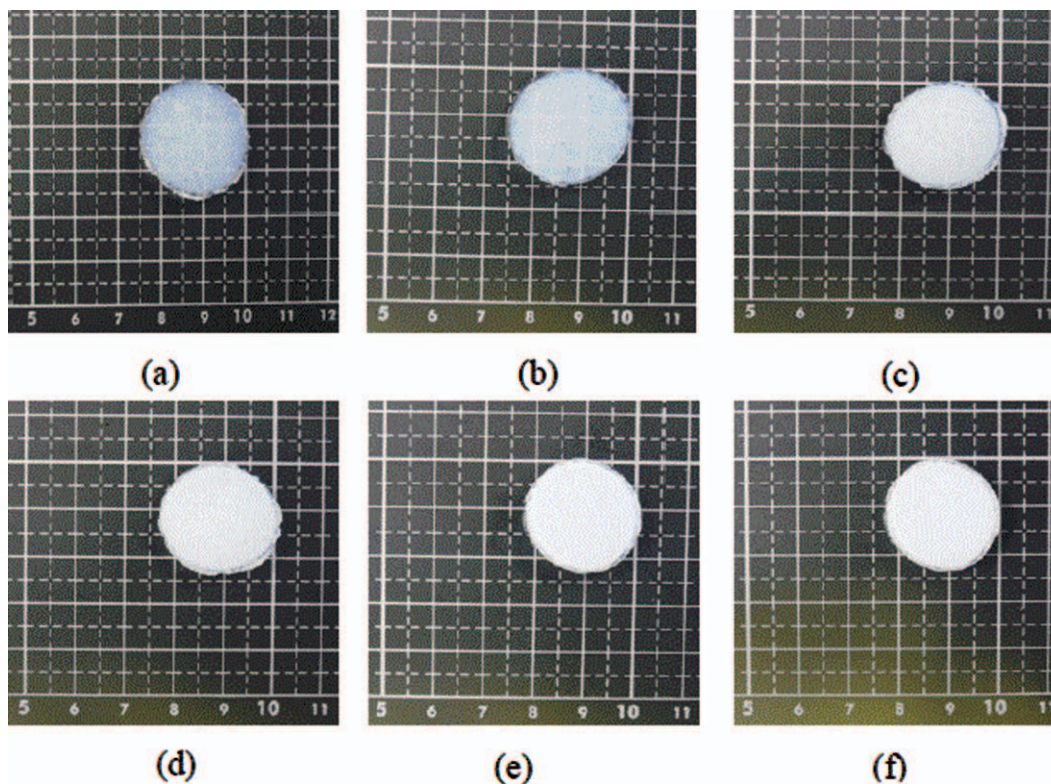


Figure 7. Effect of temperature on dimension and appearance of SV10N hydrogel at (a) 25°C, (b) 30°C, (c) 35°C, (d) 40°C, (e) 45°C, and (f) 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

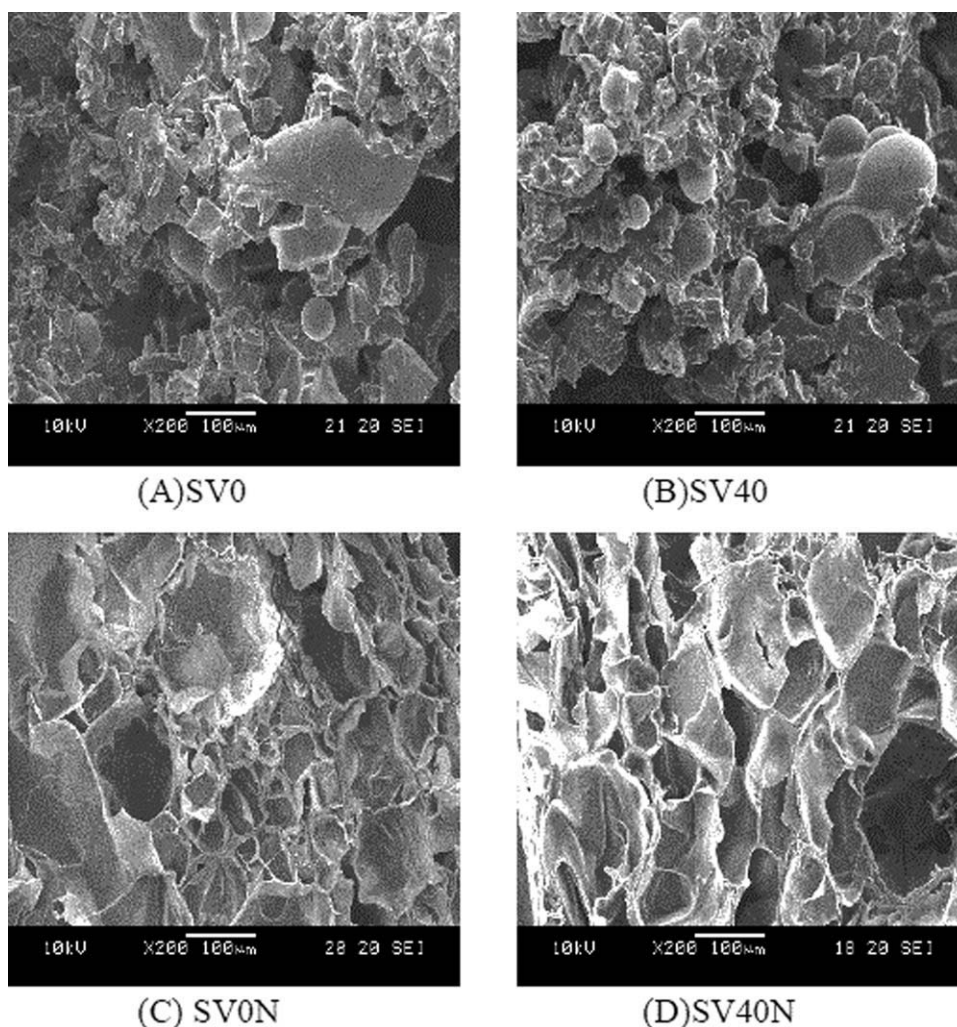


Figure 9. Representative cross-sectional morphologies observed by SEM for (a) SV0, (b) SV40, (c)SV0N, and (d) SV40N hydrogels.

thermoreversibility under swelling–deswelling process. The results also indicate that SV0N hydrogel has a maximum swelling–deswelling range of 35.6%, and SV40N hydrogel has a minimum swelling–deswelling range of 27%. This result explicitly indicated that the swelling–deswelling range was mainly affected by the content of poly (NIPAAm) in the SVN hydrogels.

Effect of Temperature on the Dimension and Appearance of SVN Hydrogels

The effect of temperature on the dimension and appearance of SVN hydrogels is typically shown in Figure 7 for SV10N hydrogel. The results in Figure 7 show that the changes of diameter and appearance of the SV10N hydrogel were observed as the water temperature was switched from 25 to 50°C. When the water temperature is higher than 32°C, the appearance of SV10N hydrogel was changed from transparent to opaque because a collapsed phase transition of the poly(NIPAAm) component was occurred under water above CGTT. The gels would be shrunk as the temperature increased; the diameters of SV10N hydrogel at various temperatures were measured and shown in Figure 8. The results in Figure 8 indicate that the transition of diameter profiles for the SVN hydrogels also

occurred at the temperature range of 30–35°C. This result conforms to the above-mentioned results for the temperature effect on equilibrium SRs of the SVN hydrogels.

Morphologies

To investigate how affect the internal structures of the SV hydrogels while NIPAAm component was incorporated into the hydrogels, the cross-sectional SEM images of swollen and freeze-dried gels were measured and shown in Figure 9 for SV and SVN hydrogels, respectively. The results shown in Figure 9(a, b) exhibit that the cross-sectional surface displays rough and uneven morphologies and more irregular pores. But, when the NIPAAm moiety was incorporated into SV hydrogels, their cross-sectional surfaces became level and showed regular macroporous morphologies in SVN hydrogels.

CONCLUSIONS

SVN hydrogels containing SV and poly(NIPAAm) two networks were successfully synthesized by a two-step method. Some conclusions can be drawn as follows. The thermosensitivity of the SV gels can be successfully endowed by immersing of NIPAAm solution into the SV hydrogels and the thermosensitivities of

the SVN hydrogels are more obvious as the content of poly(NIPAAm) moiety in the SVN hydrogels increased. The gel strength could be strengthened but the pore size and SR of the SV network were significantly decreased when the poly(NIPAAm) network was added into the SV hydrogels. The results of morphology and pore size distribution show that the rough and uneven surface and irregular pores inside SV hydrogels would be modified by imbibing poly(NIPAAm) moiety into SV hydrogels and the pore size distribution of the SVN hydrogels become narrower and smaller as the content of poly(NIPAAm) moiety increase in the SVN hydrogels.

ACKNOWLEDGMENTS

The authors thank the National Science Council of the Republic of China for financial support under grant NSC 96-2221-E-036-006.

REFERENCES

1. U. S. Department of Agriculture. *U. S. Pat.* 3,981,100 (1961).
2. Buchholz, F. L. Superabsorbent Polymers Science and Technology; Buchholz, F. L.; Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994.
3. Hogari, K. Ashya, F. Advances in Superabsorbent Polymers; American Chemical Society: Washington, DC, 1994.
4. Lee, W. F.; Huang, Y. L. *J. Appl. Polym. Sci.* **2001**, *81*, 1827.
5. Lee, W. F.; Yang, L. G. *J. Appl. Polym. Sci.* **2004**, *92*, 3422.
6. Lee, W. F.; Chen, Y. C. *J. Appl. Polym. Sci.* **2004**, *94*, 2417.
7. Lee, W. F.; Chen, Y. C. *Eur. Polym. J.* **2005**, *41*, 1605.
8. Zhang, Y.; Wang, L.; Li, X.; He, P. J. *Polym. Res.* **2011**, *18*, 157.
9. Xie, Y.; Wu, J.; Lin, J.; Wei, Y.; Zhong, J. *Polym. Polym. Compos.* **2007**, *15*, 29.
10. Liu, M.; Liang, R.; Zhan, F.; Liu, Z.; Niu, A. *Polym. Int.* **2007**, *56*, 729.
11. Bahaj, H.; Benaddi, R.; Bakass, M.; Bayane, C. *J. Appl. Polym. Sci.* **2010**, *115*, 2479.
12. Xie, J.; Li, N.; Huang, K.; Han, X. *Adv. Mater. Res.* **2011**, *239(Pt. 1)*, 851.
13. Ricka, J.; Tanaka, T. *Macromolecules* **1984**, *17*, 2916.
14. Muniz, E. C., Geuskens, G. *Macromolecules* **2001**, *34*, 4480.
15. Muniz, E. C., Geuskens, G. J. *Membr. Sci.* **2000**, *172*, 287.
16. Dhara, D., Rathna, G. V. N., Chatterji, P. R. *Langmuir* **2000**, *16*, 2424.
17. Qiu, Y., Park, K. *Adv. Drug Deliv. Rev.* **2001**, *53*, 321.
18. Ju, H. K.; Kim, S. Y.; Lee, Y. M. *Polymer* **2001**, *42*, 6851.
19. Wang, M.; Fang, Y.; Hu, D. *React. Funct. Polym.* **2001**, *48*, 215.
20. Lu, X.; Zhai, M.; Li, J.; Ha, H. *Radiat. Phys. Chem.* **2000**, *57*, 477.
21. Zhang, X. Z.; Wu, D. Q.; Chu, C. C. *Biomaterials* **2004**, *25*, 3793.
22. Tang, Q.; Wu, J.; Lin, J.; Sun, H.; Ao, H. *e-Polymers* **2008**, *21*, 1.
23. Lee, W. F.; Chen, Y. J. *J. Appl. Polym. Sci.* **2001**, *82*, 2487.
24. Lee, W. F.; Lee, S. C. *J. Appl. Polym. Sci.* **2005**, *98*, 1092.
25. Lee, W. F.; Huang, Y. C. *J. Appl. Polym. Sci.* **2007**, *106*, 1992.
26. Peppas, N. A.; Barr-Howell, B. D. Hydrogels in Medicine and Pharmacy; CRC Press: Boca Raton, 1986; Vol. 1, p 27.
27. Treloar, L. R. G. The Physics of Rubber Elasticity; Clarendon Press: Oxford, 1975.