Poly(*N*-isopropylacrylamide-*co*-sodium acrylate) Hydrogels: Interactions with Surfactants

Y. M. Mohan, D. K. Joseph, K. E. Geckeler

Laboratory of Applied Macromolecular Chemistry, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, South Korea

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ABSTRACT: Poly(*N*-isopropylacrylamide-*co*-sodium acrylate) [poly(NIPAM-*co*-SA)] hydrogels were modified with three different kind of surfactants (cationic, anionic, and nonionic) to study the effect on the swelling properties. The structural variation of the surfactant-modified hydrogels was investigated in detail. The interaction between the surfactants and the hydrogel varies and strictly depends on the surfactant type. The variation in thermal stability of the modified surfactant hydrogels was investigated and compared with unmodified hydrogel. Further, the hydrogel swelling/diffusion kinetic parameters were investigated and diffusion of water into hydrogel was found to be of the non-Fickian transport mechanism. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3423–3430, 2007

Key words: *N*-isopropylacrylamide; hydrogel; swelling behavior; surfactant; networks

INTRODUCTION

A number of formulations consisting of both polymers and surfactants are found together in numerous fields, including food, surface coating, pharmaceutical, and cosmetics; therefore, it has been renowned as an important area of research from the theoretical and industrial point of view. In fact, the interaction of surfactants with water-soluble polymers was investigated extensively.[1] During the last decade, a great attention has been paid towards studies of interactions between hydrogels and surfactants.[2–5] In general, hydrogels are three-dimensional polymer networks that are capable to swell and retain water within their network structure.[6,7] Further, these hydrogel functional groups are capable to undergo quite large and abrupt physical or chemical changes in response to small external changes in the environmental conditions such as temperature, pH, ionic strength, electric and magnetic field, pressure, light intensity, solvent composition, etc.[8–11] Because of their exceptional properties such as softness, elasticity, capacity to store a massive amount of fluids within the networks, and biocompatibility, these polymeric gels have attracted great attention for their potential applications in chemical engineering, medicine, pharmaceutical, and environmental fields.[9–13] Under the intelligent hydrogels category, poly(*N*-isopropylacrylamide) (PNIPAM) was widely studied because of its phase transition temperature around 33°C, suggesting its better applicability in biomedical applications as well as a model for theoretical examination of phase transitions in the gels.[14]

The literature provides many studies for the interaction of anionic, cationic, or nonionic surfactants with PNIPAM-based gels.[15–19] Anionic surfactants have influenced to a greater extent the PNIPAM microgel properties than cationic surfactants.[13,15] It was noticed that in the presence of sodium dodecyl sulfate (SDS), the PNIPAM microgel size increased because of the aggregation of the SDS molecules within the gel networks. A pronounced increase in adsorption of SDS takes place only when most of the adsorbed PNIPAM has been depleted from the surface to form polymer–surfactant aggregates in the bulk. A few investigations committed to study the influence of surfactants on the phase transition of PNIPAM gels and the effect of surfactants on thermally collapsed PNIPAM.[20,21] The conformation transition temperature of the gels towards higher temperatures by the SDS interaction might be due to the electrostatic repulsion (expansion) of the gel networks. In contrast, cationic surfactants such as the dodecylpyridine bromide (DPB) and dodecyltrimethylammonium bromide (DTAB) were not effective to raise the conformation transition temperature of PNIPAM gels.[15,16] Further, there was not much change in the transition temperature range or swelling extent of PNIPAM gels in the case of the

Correspondence to: K. E. Geckeler (keg@gist.ac.kr).
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nonionic surfactant Triton X-100;[15] however, the addition of Triton X-100 was found to decrease the size of poly(acrylic acid) (PAAc) microgel particles.

As per our knowledge, there are very few studies done on the influence of surfactants on swelling properties of the hydrogels.[22–24] Therefore, in our present investigation we focused on the evaluation of the association of different kind of interactions of surfactants with the PNIPAM-*co*-SA hydrogel. The interaction of the surfactants with the hydrogel was demonstrated in terms of changes in the swelling capacity of gel as a function of surfactant concentration and temperature. This study also reveals how the hydrogel morphology, thermal stability, and swelling/diffusion kinetic parameter varies with different surfactants.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM), sodium acrylate (SA), *N*,*N*-methylenebisacrylamide (MBA), ammonium persulfate (APS), and *N*,*N*,N^1,N^1-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Co. The surfactants, e.g., SDS (5 m*M* in water), dodecylpyridinium chloride (DPC) (5 m*M* in water), and Tween 80 (1.5 wt % in water) were prepared by purchasing SDS, DPC, and Tween 80 from Aldrich Chemical Co. NIPAM was purified by recrystallization from a toluene–hexane (1:3) mixture. Distilled water was used for preparing all the solutions, hydrogel preparations, and for the swelling experiments.

Preparation of poly(*N*-isopropylacrylamide-*co*-sodium acrylate) hydrogels

Hydrogels composed of NIPAM and SA units were prepared by following simultaneous free-radical crosslinking polymerization using APS/*N*,*N*,N^1,N^1-tetramethylethylenediamine redox-initiator in presence of *N*,N^1-methyleneacrylamide (crosslinker).[25] The defined amounts of monomer, crosslinker, and APS were added sequentially to 10 mL of distilled water in a test tube, and the resultant solution was degassed with nitrogen gas to expel the air. Finally, the activator TMEDA was added to the polymerization mixture. The polymerization started immediately and resulted in the appearance of a strong gel within 3 min. However, we continued the polymerization reactions for a day at 25°C to get a perfect network formation with out any discontinuation to the hydrogels. After completion of the reaction period, the obtained hydrogels were completely immersed in distilled water for 3 days (refreshing the water every 5 h) at room temperature to leach out unthreaded water-soluble networks as well as unreacted materials entrapped in the hydrogel networks. Finally, the hydrogels were cut into discs and dried at 70°C *in vacuo* to a constant weight. Yields of hydrogels were found to be > 98% in all the cases. The complete reaction conditions of the hydrogel preparation and the hydrogel codes used are presented in Table I.

TABLE I
Preparation Condition and Swelling Properties of NIPAM-SA Hydrogels[a]

Hydrogel code	NIPAM (mol)	SA (mol)	MBA (mol)	S_{eq} (g/g)	EWC (%)
NISA 1	0.0077	0.0021	6.486×10^{-5}	244.74	99.82
NISA 2	0.0077	0.0021	9.729×10^{-5}	167.26	99.40
NISA 3	0.0077	0.0021	1.297×10^{-4}	120.98	99.17
NISA 4	0.0077	0.0021	1.621×10^{-4}	92.32	98.91
NISA 5	0.0077	0.0021	1.945×10^{-4}	68.25	98.53

[a] Reaction condition: [APS] = 2.19×10^{-4}; [TMEDA] = 0.86×10^{-4}; temperature = 25°C; distilled water = 10 mL.

Instrumental analysis

The completely dried surfactant-modified hydrogels (grounded powder) were used to analyze the chemical changes in the hydrogels using a Perkin–Elmer FT-IR spectrometer spectrum 2000 model in the region of 4000–400 cm^{-1}. The surface morphology of the modified hydrogels was observed with a Hitachi S-4700 (Japan) scanning electron microscope. For this analysis, specimens of the hydrogels swollen in different surfactants were lyophilized for 48 h and coated with platinum before the SEM examination. The thermal history of the modified hydrogels was investigated using TA-2050 thermal analyzer from 25°C to 700°C at 10°C/min heating rate, under nitrogen flow (40 mL/min). AFM images of the hydrogels were obtained in the tapping mode on a Dimension™ 3100 Atomic Force Microscope (Digital Instruments, Veeco Metrology).

Swelling studies

The conventional gravimetric method was employed to study the hydrogel swelling behavior. The hydrogel samples were dried in a vacuum oven at 100°C before the swelling studies. The dry hydrogel discs (~ 50 mg) were immersed in 20 mL swelling media (water or surfactant solution) and allowed to swell for 24 h to attain equilibrium swelling at 25°C. The equilibrium swelling ratio (S_{eq}) and equilibrium water content (EWC%) were calculated using eqs. (1) and (2), respectively:[26–30]

$$S_{eq} = M_e/M_d \quad (1)$$

$$\text{EWC\%} = [(M_e/M_d)/M_e] \times 100 \quad (2)$$

where M_e and M_d are the weights of water present in the swollen hydrogel at equilibrium and weight of dry hydrogel, respectively.

Swelling/diffusion kinetics evaluation

To estimate the absorption kinetic for hydrogels, the initial swelling measurements up to 60% was fitted into the exponential heuristic equation:[31]

$$F = M_t/M_\infty = kt^n \quad (3)$$

where F is the fractional uptake of water, M_t is the amount of absorbed water at time t, M_∞ is the maximum amount of water absorbed, k is the characteristic constant of the gel, and n is a characteristic exponent (diffusion constant) of the transport mode of the penetrate. This characteristic exponent can be estimated from the slope of the plot drawn for ln F versus ln t.

According to the Fick's law, a relationship for the mass transfer flux and a mutual diffusion coefficient D for a plane sheet of a hydrogel can be written as:

$$M_t/M_\infty = 1^\infty_{n=0} - \{\Sigma[8/(2n+1)^2\pi^2]x\exp[-(2n+1)^2\pi^2(Dt/L^2)]\} \quad (4)$$

where t and L denote time and the thickness of the dry hydrogel. This equation can be simplified for short time expression as:[32]

$$M_t/M_\infty = (4/\pi^{0.5})(Dt/L^2)^{0.5} \quad (5)$$

The diffusion coefficient (D) of hydrogel can be calculated from the slope of the straight-line plot M_t/M_∞ versus $t^{1/2}$.

The penetration velocity (v) or swelling rate for hydrogels was evaluated by employing Peppas and Franson method.[31] The penetration velocity was calculated from the slope of the initial portion of the penetrant uptake curve using the following equation:

$$v = [(dM_t/dt)(1/\rho)(1/2A)] \quad (6)$$

where v is the penetration velocity, dM_t/dt is the slope of the weight gain versus time curve, ρ is the density of water, A is the area of one face of the disc, and the factor 2 accounts for the fact that penetration takes place through both the faces.

RESULTS AND DISCUSSION

We chose the NISA responsive hydrogel for our investigation because the PNIPAM hydrogel is an excellent thermosensitive and biocompatible material that exhibits a sudden change in solvent-swollen weight in response to a small change in external stimuli such as pH, temperature, ionic strength, light sensitivity, and electric fields. However, at the same time it is dropping its applicability because of a fixed phase transition temperature and lower swelling capacity.[9–11] On the other hand, the swelling capacity of NIPAM hydrogels could be improved by making copolymers with SA.[33–35]

Most of the MBA-crosslinked PNIPAM hydrogels showed a swelling capacity not greater than 30 g/g. The swelling behavior of NISA hydrogels prepared with different amounts of MBA crosslinker is shown in Table I. The equilibrium swelling ratio (S_{eq}) values of these hydrogels in deionized water decrease in the order: NISA 1 > NISA 2 > NISA 3 > NISA 4 > NISA 5. It is strictly demonstrated that the equilibrium swelling capacity of the hydrogel decreased enormously with an increase in the crosslinker concentration. In fact, it is evident that a higher crosslinker content makes the gel network denser, which restricts the penetration of the water molecules into the hydrogel networks and therefore lowers their swelling capacity. Further, poly(sodium acrylate) chains in the NISA hydrogels (244–68 g/g) strongly absorbed more water, when compared with the NIPAM hydrogel (< 30 g/g). The present hydrogels with high equilibrium water content (98.53–99.82%) are suggested for being used as novel biomaterials in biotechnology.

Although these ionic hydrogels are utilized in many fields, there is very little attention focused on the interaction of surfactants with the PNIPAM gel swelling behavior.[21,22] This prompted us to study their association with surfactants in detail. Figure 1 illustrates the presence of different surfactant molecules in modified hydrogels in aqueous surfactant solutions. We suspect that this is only due to the physical absorption of surfactant molecules throughout the hydrogel networks. A clear variation can be seen in their N—H/O—H and C—H stretching peaks at 3250–3250 cm^{-1} and 3150–2850 cm^{-1} and N—H/O—H hydrogen bonding, from IR spectra of corresponding surfactant-modified hydrogels (Fig. 1). Further, the modified hydrogels showed new peaks at 1250 and 1220 cm^{-1} [NISA-SDS, Fig. 1(A)]; 777 and 685 cm^{-1} [NISA-DPC, Fig. 1(B)]; and 1736, 1112, 949, 883, and 832 cm^{-1} [NISA-Tween 80, Fig. 1(C)].

According to previous reports, the nonionic PNIPAM gels behave like ionic hydrogels through hydrophobic interactions of the ionic surfactant molecules in an adhesion process.[22–25] In this section, we report the hydrophilically modified PNIPAM hydrogel interactions with anionic, cationic, and nonionic surfactants such as the SDS, DPC, and Tween 80, respectively. From Figure 2, it is confirmed that the equilibrium swelling ratio of NISA hydrogels depended on

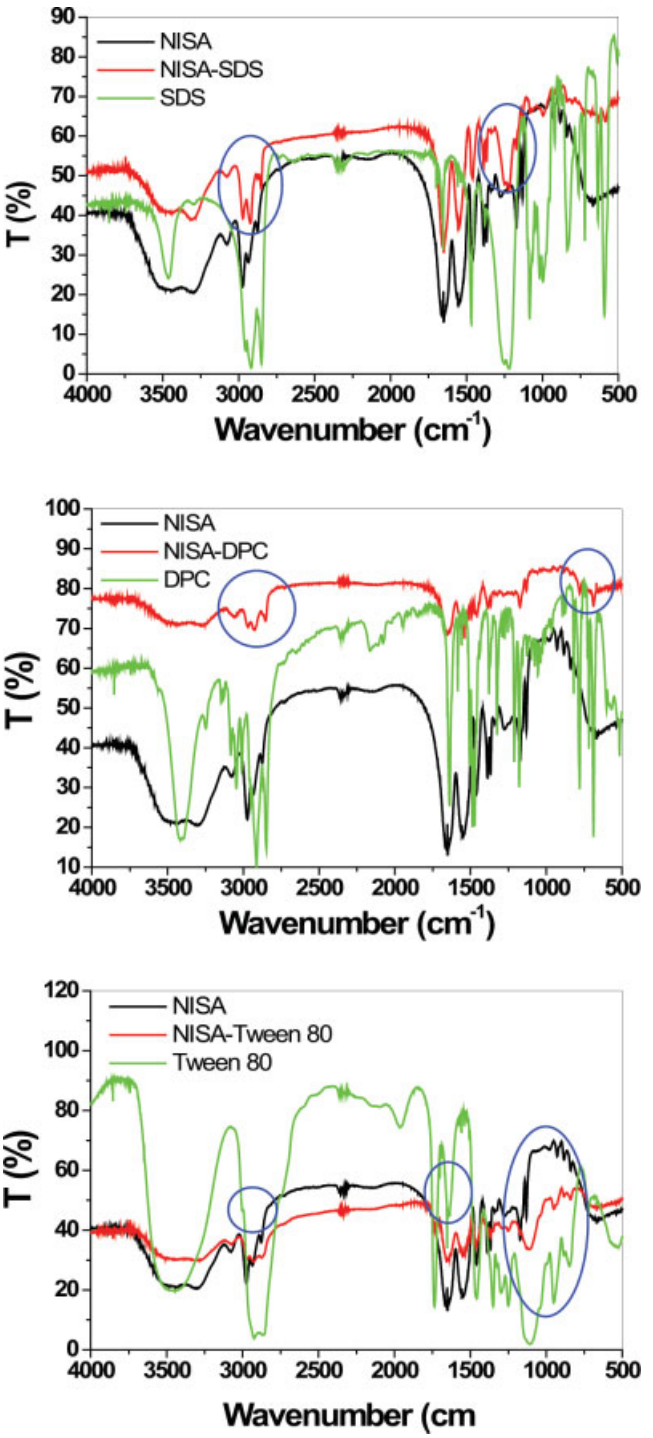

Figure 1 IR spectra of NISA hydrogel 1 and surfactant-modified NISA 1 hydrogels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the type of surfactant. A stronger swelling response was observed in the nonionic surfactant solution (1.5 wt % Tween 80) and the S_{eq} values of these hydrogels were even higher than those observed in distilled water for the NISA 4 and NISA 5 hydrogels. This might be due to the entanglement of polyethylene glycol (Tween 80) chains within the networks of the hydrogels and thus a higher hydrophilicity of the networks is attained, which ultimately promoted the water absorption capacity. In contrast, the equilibrium swelling capacity of the hydrogels in 5 m*M* cationic surfactant solution (DPC) was determined to be very low. The strong association, binding, or interaction of the cationic surfactant molecules with the counter ions or ionizable groups of hydrogels as well as the aggregation of the surfactant molecules within or over the networks of the hydrogels may be responsible for the lower swelling capacity. At the same time, the equilibrium swelling capacity of these hydrogels in an anionic surfactant solution (SDS, 5 m*M*) showed a comparatively higher swelling capacity than that of the cationic surfactant solution. This behavior is attributed to the repulsion of the counter ions of the polymeric chains with the surfactant molecules.

Figure 3 clearly demonstrates the influence of various concentrations of surfactant solutions on the equilibrium swelling ratio of NISA hydrogels. The hydrogels showed similar swelling profiles at different concentrations. Overall, the swelling capacity of the hydrogels was decreased with an increase in the concentration of the surfactant. In contrast, the NISA 1 hydrogel in Tween 80 showed an improved swelling capacity with an increase in the concentration of the swelling medium. This is reasonable because when the gels were swollen in Tween 80, the NISA 1 hydrogel was a somehow less-crosslinked hydrogel compared with the NISA 3 and NISA 5 hydrogels. Therefore, there is a higher probability for the penetration of Tween 80 molecules into the NISA 1 hydrogel net-

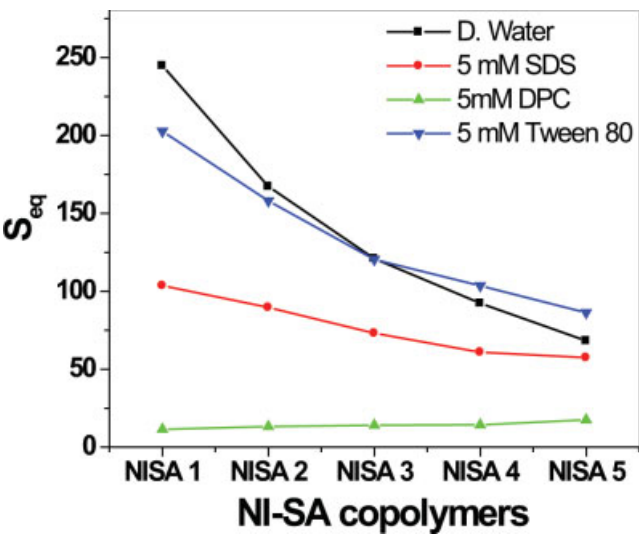

Figure 2 Hydrogels swelling behavior in different aqueous surfactant solutions (25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

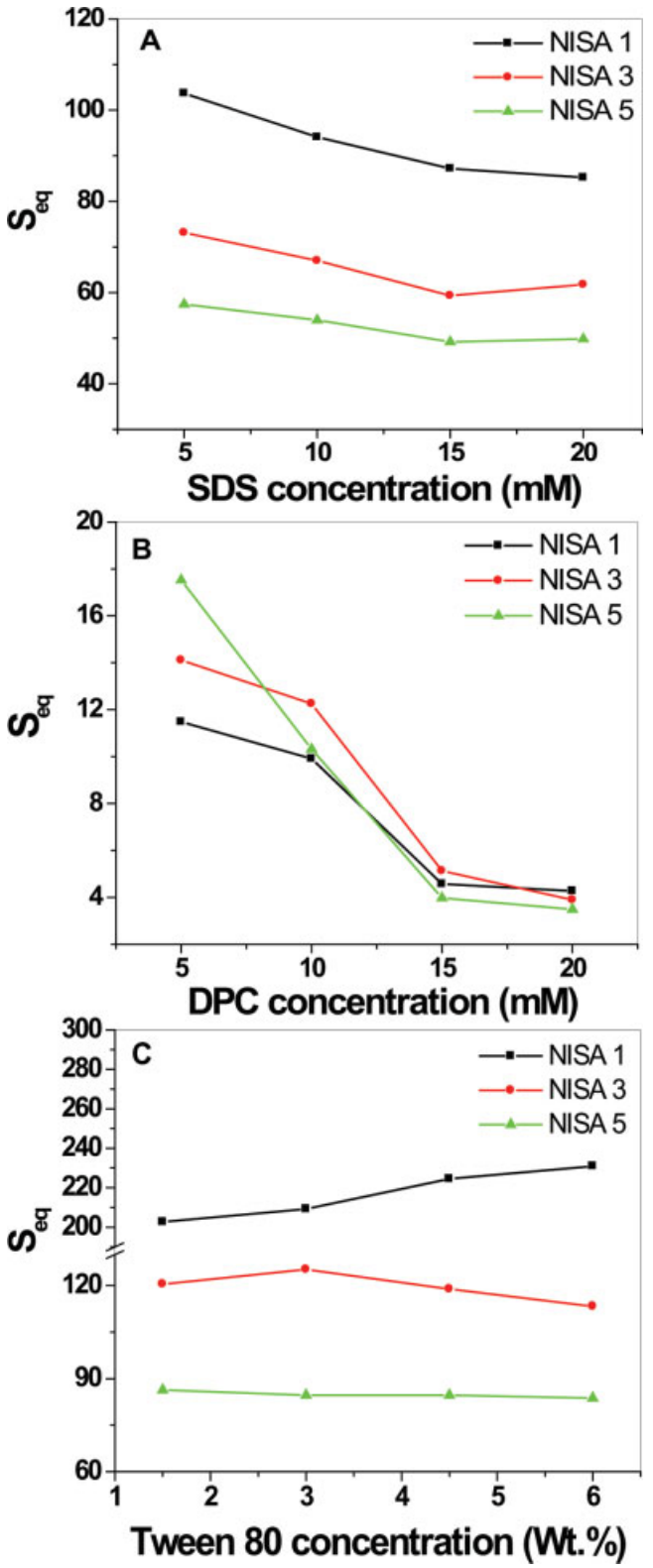

Figure 3 Hydrogel swelling pattern in (A) SDS, (B) DPC, and (C) Tween 80 (25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

works, and therefore, a higher hydrophilicity is attained, i.e., a higher water loading capacity. It was notified that the swelling behavior of the nonionic PNIPAM hydrogel in ionic surfactants was affected enormously; the LCST and volume jump during the transition increased with an increasing SDS or DTAB concentration.[22] Caykara and Birlik[23] revealed the surfactant interactions with the PNIPAM hydrogel and its hydrophobically modified hydrogel and provided possible reasons.

From these results, we can expect that the swelling behavior is dependent on the physicochemical properties of the hydrogels as well as the interactions with the surfactant molecules. The swelling capacity is dependent on the nature or type of water binding moieties such as $—O—SO_3^-$, $—N^+C_5H_5$ of the surfactant molecules. The highly repulsive site of the surfactant molecules like the $—O—SO_3^-$ towards COO^- groups of the hydrogel induce many layers within the networks of the hydrogels, which causes to develop the physical network over the hydrogel structure and therefore having the option to accommodate a massive number of water molecules within its hydrogel networks. The same pattern was well established from the SEM micrograph of NISA 2 swollen in an SDS solution [Fig. 4(A)]. In the case of DPC ($—N^+C_5H_5$), strong attractive forces engaged between the COO^- groups of NISA 2 and the positive sites of the surfactant, and these interactions lead to reducing the mesh size and thus ultimately depress the water diffusion into the hydrogel. In general, the complexation of anionic chains of hydrogel with cationic surfactant molecules forms very close and denser networks within a short span of time. Moreover, the aggregation of surfactant molecules onto the networks results in a planar view along with aggregated surfactant molecules in various parts of the hydrogel network structure as shown in Figure 4(B). As for the hydrogel swollen in the aqueous solution of the Tween 80 surfactant, the polyethylene glycol chains covered onto the networks as well as the hydrophilic chains imbedded into/onto the networks and formed a uniformly aggregated structure as shown in Figure 4(C).

The AFM images (shown in Fig. 5) furnish the information on the dry hydrogel structure after swelling in different surfactants from the atomic level with the accurate three-dimensional information. The modified NISA 1 hydrogel with different surfactants were investigated by AFM (contact mode). The morphology in the AFM images like well-defined networks, uneven physical crosslinking, and plain structure formations were observed for SDS, DPC, and the Tween 80-modified NISA 1 hydrogel. The TGA results of the hydrogel and modified hydrogels with surfactants are depicted in Figure 6. According to the TGA results, the NISA gel swollen in the DPC surfactant solution showed a higher thermal stability compared with the other modified or pristine hydrogels. It could be due to the higher physical crosslinking within the networks. The order of stability was found to be:

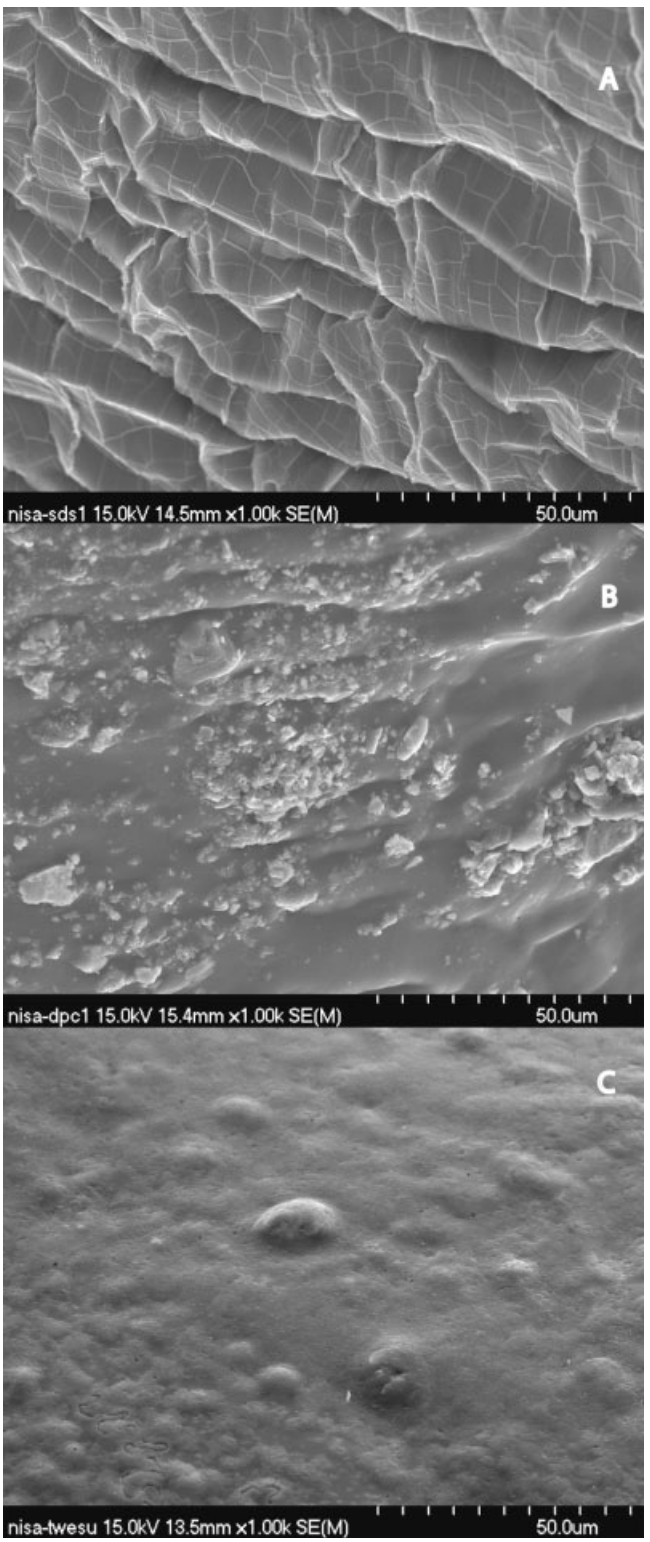

Figure 4 SEM images of modified NISA 2 hydrogel with (A) 5 m*M* SDS, (B) 5 m*M* DPC, and (C) 1.5 wt % Tween 80 aqueous solutions.

DPC-modified > unmodified gel > SDS-modified > Tween-modified gel. The DPC-modified showed a higher stability than the hydrogels modified with the surfactants SDS and Tween 80. This suggests a highly crosslinked nature, which eventually possesses a very poor swelling capacity. This could be also seen from their swelling behavior.

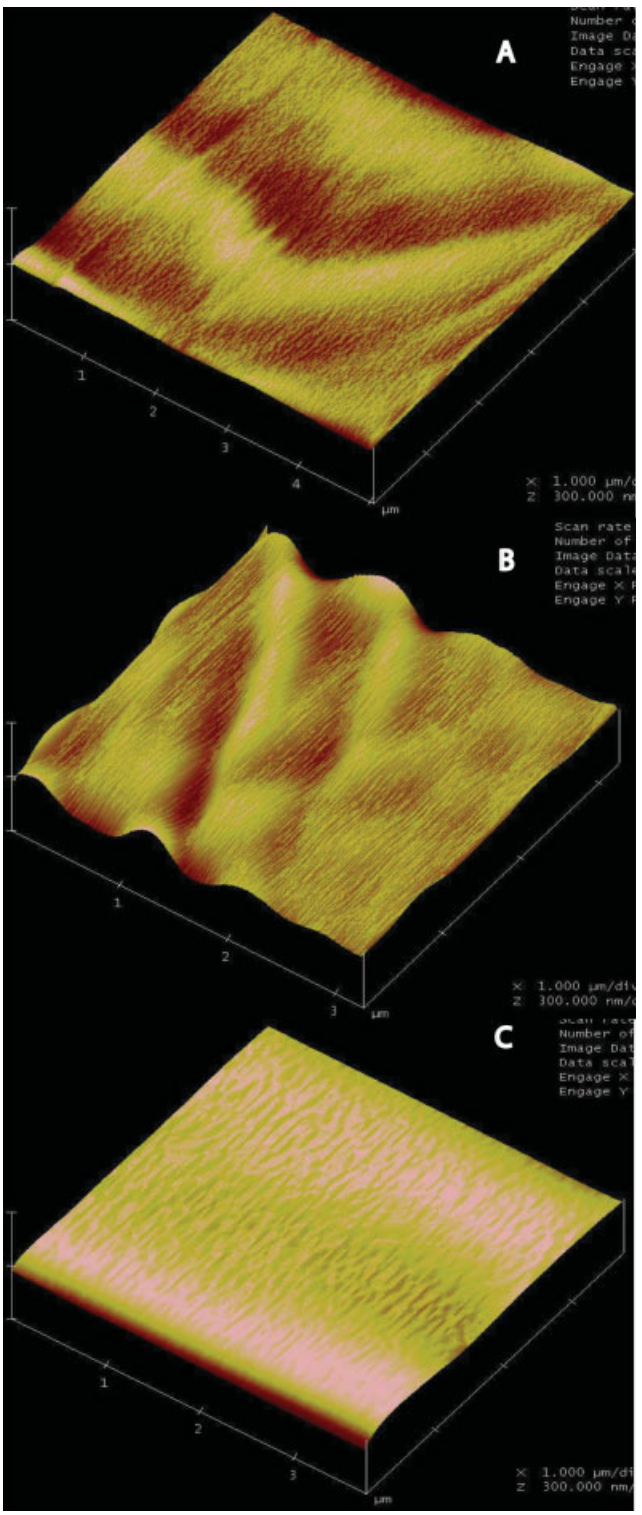

Figure 5 AFM surface images of modified hydrogel with (A) 5 m*M* SDS; (B) 5 m*M* DPC; and (C) 1.5 wt % Tween 80 aqueous surfactant solutions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Analysis of swelling and diffusion kinetic parameters[6,7,24–30]

To assess the influence of the surfactant–hydrogel interactions on the swelling/diffusion characteristics, we utilized NISA 1 hydrogel swelling data in different ionic (5 m*M*) and nonionic (1.5 wt %) surfactant solutions. Figure 7 clearly presents the pattern of various swelling/diffusion kinetic parameters such as diffusion constant (n), diffusion coefficient (D), and penetration velocity (v) of NISA 1 in various swelling media, which were calculated according to eqs. (3), (5), and (6), respectively.

The diffusion exponent or diffusion constant (n) of hydrogel can be evaluated by utilizing the swelling data of hydrogel. The value of n in eq. (3) provides an indication of the mode of transport mechanism. This value can be obtained from the slope of the plot drawn between ln F versus ln t. NISA in different surfactant solutions and distilled water showed n values between 0.62 and 0.84. That means, the water penetration into the gel is by the non-Fickian diffusion transport mechanism in distilled water or surfactant media.[6,7] The second swelling parameter, namely the diffusion coefficient (D), also varies from 0.199 to 0.249. The water penetration velocity (v) (or swelling constant, k) (g gel/g water min^{-1}) is a direct measurement for the swelling rate of the hydrogel. The swelling rate constant (k) of the hydrogel in different swelling media was calculated from the slope of the weight gain versus time. Low k values were observed for NISA 1 in SDS and DPC surfactant solutions, whereas in distilled water and Tween 80 surfactant solutions these values were found to be >1. This absolutely supports the higher swelling capacity of the gels in distilled water and Tween 80 solutions as well. From this data we conclude that the swelling/diffusion kinetic parameter of NISA hydrogel depends on the type of interactions present between the gel and swelling media (surfactant solutions).

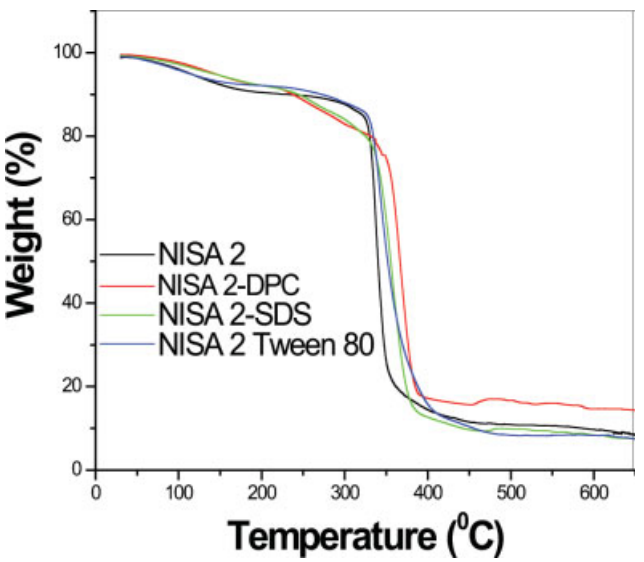

Figure 6 Thermograms of pure and modified hydrogels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

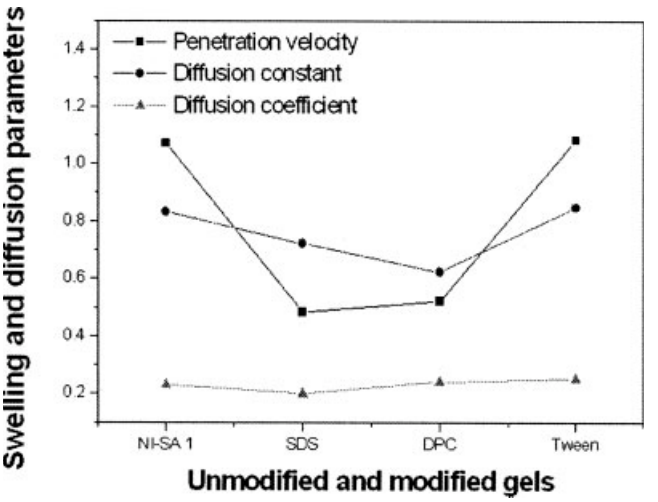

Figure 7 Swelling/diffusion kinetic parameters of modified and unmodified hydrogels.

CONCLUSIONS

Poly(*N*-isopropylacrylamide-*co*-sodium acrylate) hydrogels with different network content were prepared by free-radical polymerization, employing different amounts of MBA. A detailed swelling behavior study of these hydrogels was performed in distilled water and surfactant solutions. The swelling/diffusion kinetic parameters suggest that the interaction between the surfactant and gels varies with a change of the surfactant. The morphological changes in the hydrogel networks were analyzed by SEM and AFM. Thermal studies also suggest that there is a greater degree of interaction between the DPC-gel, since opposite charges lead to physical crosslinking.

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