Synthesis and Characteristics of an Amphoteric Semi-IPN Hydrogel Composed of Acrylic Acid and Poly(diallydimethylammonium chloride)

Jia Wei, Shimei Xu, Ronglan Wu, Jide Wang, Yi Gao

College of Chemistry and Chemistry Engineering, Xinjiang University, Urumqi, Xinjiang, 830046, China

ABSTRACT: Semi-interpenetrating polymer network (IPN) hydrogels, with acrylic acid (AA) and poly(diallydimethyl-ammonium chloride) (PDMDAAC), were constructed by a sequential IPN method. The characterizations of the IPN hydrogels were investigated by FTIR, DTA, and swelling tests under various conditions. The prepared semi-IPN hydrogels exhibited relatively high swelling capacity, in the range of 477–630 g/g at 25°C. The results show that the swelling capacity of AA/PDMDAAC semi-IPN hydrogels was pH and temperature dependent. Swelling behaviors were also studied in the different salt solutions. Swelling kinetic parameters are given. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 345–350, 2007

Key words: hydrogels; interpenetrating networks (IPN); swelling; kinetics

INTRODUCTION

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymer networks synthesized in juxtaposition.[1] The presence of entangled crosslinks increases the miscibility of the polymers compared with that of usual blends and leads to a material with good dimensional stability. The semi-IPNs differ from IPNs in that they are composed of a noncrosslinked polymer entrapped into another polymer network.[2] IPNs now have gained more and more applications in industry and other fields, with IPNs showing the possibility for an even wider range of applications.[3] Studies of hydrogels are paid much attention, not only from a chemical perspective, but also for their uses in chemical engineering, pharmaceuticals, food processing, biochemistry, biology, and medicine.

At present, most of researches about IPN hydrogels concern the intelligent hydrogel that can reversibly change their volume and shape in response to external stimuli, such as changes in pH and electric field.[4–7] In terms of the superabsorbent hydrogel, however, much interest has been focused on copolymeric or grafting copolymeric anionic hydrogels.[1,8,9] The poor resistance to salt solution has limited the application. Few researches show that the amphoteric hydrogels present special characteristics. Tamagawa et al. have discussed the reversible hardness variance of amphoteric hydrogel produced by acrylamide and acrylic acid (AA).[10] It was reported that in certain conditions, amphoteric hydrogel shows so-called antielectrolyte property, e.g., with increase of salt concentration in the solution, the swelling capacity increases.[11–14] Gazizov et al.[15] have studied the behavior of amphoteric hydrogels based on vinyl 2-aminoethyl ether and sodium acrylate under the influence of pH, ionic and solvent composition, temperature, and electric field. This would be applied in agriculture, especially in some farmland with salina.

Based on the work described earlier, we tried to synthesis a new amphoteric IPN hydrogel and studied its swelling behaviors. AA was chosen as the base material in this study because of its high water affinity and commercial availability. Diallydimethyl-ammonium chloride (DMDAAC) was chosen as the cationic monomer with extraordinary hydrophilicity. However, poly(AA-*co*-DMDAAC) itself did not have enough mechanical strength in the swollen state; so the IPN structure was considered.

In this study, AA/PDMDAAC semi-IPN hydrogel was prepared, and the effect of time, temperature, pH, and concentration of various salt solutions on the swelling capacity were investigated.

EXPERIMENTAL

Materials

AA was purchased from Tianda Chemical Co. (Tianjin, China); *N,N*-methylenebisacrylamide (MBAAm) was purchased from Shanghai Chemical Co. (Shanghai, China) DMDAAC (60 wt % aqueous solution) was purchased from Shandong Luyue Chemical Co.

Correspondence to: J. Wang (awangjd@xju.edu.cn).

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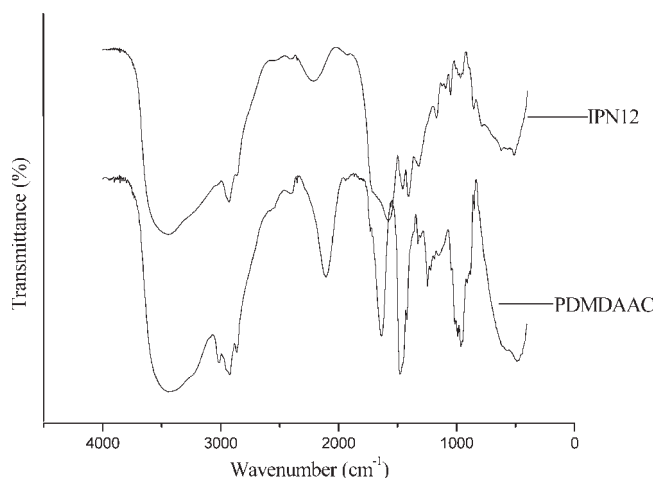DISCOVER SOMETHING GREAT

Figure 1 FTIR spectra of the PDMDAAC and the hydrogel IPN12.

(Shandong, China); ammonium persulfate (APS) was purchased from Xi'an Chemical Co. (Xi'an, China); sodium chloride, calcium chloride, and ferric chloride were purchased from Tianjin Baishi Chemical Co. (TianJin, China). All the chemicals were of reagent grade and used without further purification.

Synthesis of PDMDAAC

Monomer initiator (APS; 1 wt %) was added into the 60% DMDAAC aqueous solution. Nitrogen was bubbled through the monomer solvent mixture in three-necked flask to remove oxygen dissolved in the reaction mixture. The mixture was stirred for 2 h at 60°C. The product was poured into acetone and absolute alcohol, respectively, to wash away the reactants and to form precipitation. The precipitation was dried for 24 h in air.

Preparation of semi-IPN hydrogels

The semi-IPN hydrogels were prepared using the sequential IPN method. The mass ratio of AA and PDMDAAC are 1 : 2, 1 : 1, and 2 : 1 (with ratio of anionic to cationic groups 1.12 : 1, 2.24 : 1, and 4.48 : 1), and the semi-IPN hydrogels were named IPN12, IPN11, and IPN21, respectively. The AA was neutralized by the 40% NaOH solution, with the dropper in ice water, till the neutralization degree of AA is 75% (n/n). Then the AA was polymerized in the presence of PDMDAAC aqueous solution, using APS and MBAAm as the initiator and crosslinking agent, respectively. The initiator content was 1 wt % of monomer, and that of the crosslinking agent was 0.02 wt % of monomer. The mixture was stirred for 2 h at 50°C in three-necked flask, and nitrogen was bubbled all the time. The product was washed by distilled water three times, infused in 60% alcohol solution for 24 h, and dried for 12 h. The product was then smashed into granules with 0.55 mm aver-

age diameter. The PAA hydrogel was synthesized in the same way with the absence of PDMDAAC.

Sorption experiment of semi-IPN hydrogels

The hydrogels were immersed in distilled water or salt solutions for 3 h. The swelling capacities Q (g/g) of the IPN hydrogels were calculated with the following equation.

$$Q = (M - M_0)/M_0$$

where M (g) is the weight of the swollen hydrogel at a given time and M_0 (g) is the weight of the dry hydrogel.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectroscopy (Bruker Eqinox55) was used to confirm the structure of the AA/PDMDAAC semi-IPN hydrogels. Figure 1 shows the FTIR spectra of PDMDAAC and the IPN12 hydrogel. In the FTIR spectrum of PDMDAAC, $-CH_3$ stretching was confirmed at 1419 cm^{-1}, 2865 cm^{-1} attributed to $-CH_2$ groups, and C$-$N stretching at 1246 cm^{-1}. In the FTIR spectrum of the IPN12, the absorption peaks belonging to the two components were confirmed: the peak at 1409 cm^{-1}, attributed to $-C=O$ stretching of the AA; 1468 and 2922 cm^{-1} attributed to $-C-H_3$ stretching of PDMDAAC, 1050 cm^{-1} attributed to $-C-O$ stretching, 2928 cm^{-1} attributed to $-CH_2$ stretching, and 1169 cm^{-1} attributed to C$-$N stretching.

Differential thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) curves for thermal degradation of the semi-
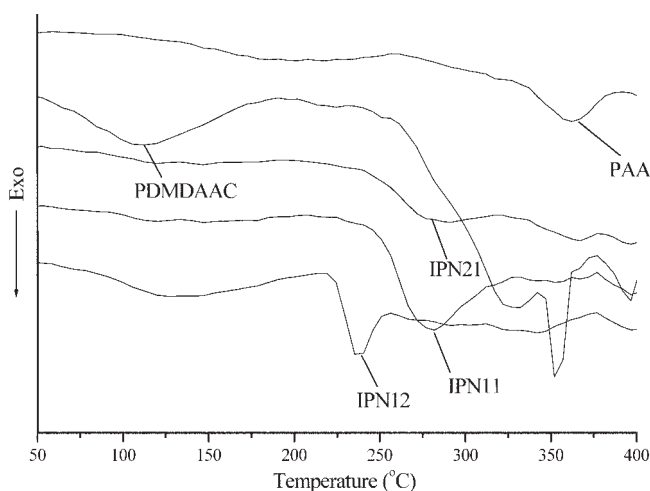

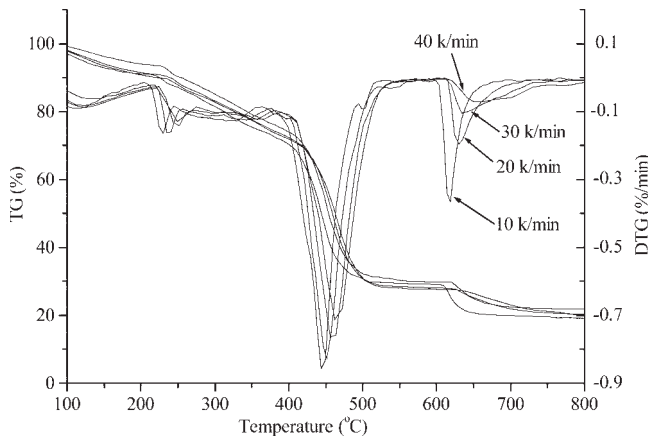**Figure 2** DTA thermograms of the semi-IPN hydrogels, PAA, and PDMDAAC.

Figure 3 TG and DTG of the IPN21.

IPN hydrogels, PAA, and PDMDAAC are shown in Figure 2, using a heating rate of 20 K/min in an air atmosphere. It can be seen that the thermal degradation of the PDMDAAC, IPN12, IPN11, IPN21, and PAA occurs in different stages.

It is known that DTA measurement gives some useful results for the structural information of semi-IPN hydrogels. The DTA curves of PDMDAAC, IPN12, IPN11, IPN21, and PAA show maximum peaks at 110, 238, 280, 290, and 360°C, respectively. The DTA peaks for semi-IPN lie between those of the two native compounds. The rise in temperature could be due to a net increase of the PAA. As the content of the PAA increases, the temperature of semi-IPN hydrogels thermal degradation is rising. It can be confirmed that the hydrogels were of semi-IPN structure.

To further obtain the active energy of the degradation of the IPN, its TG curve is recorded at different heating rates of 10, 20, 30, and 40 K/min under an air atmosphere. Figure 3 shows the TG and DTG of the IPN21. The active energy of decomposition (E; J/mol) is obtained from the following equation:[16]

$$E = -R/0.4567[d \log \beta/d(1/T)]$$

where β is the heating rate (K/min), R is the gas constant (8.314 J/mol K), and T is the absolute temperature. The E value is calculated as 26.64, 118.06, and 140.36 kJ/mol. At the first stage with 20.69% weight loss, it is due to the decomposition of ammonium group in the polymer bone. The polymer side chain is found to break when the temperature is higher than 400°C with a 51.97% weight loss, followed by a total collapse of a polymer bone.

Dynamics of semi-IPN21

Figure 4 shows sorption kinetics and time-dependent sorption behavior of semi-IPN hydrogels IPN21. The hydrogels swelled so rapidly and reached equilibrium within about 2 h. The sample IPN21 appeared to have the highest equilibrium water capacity at 45°C, while it had the lowest at 25°C. Since the carboxyl group is hydrophilic, IPN21 hydrogel shows highest water uptake with more hydrophilic groups within its structure, resulting in the highest Q in all sorption experiments. The sorption data were analyzed using the following equation:

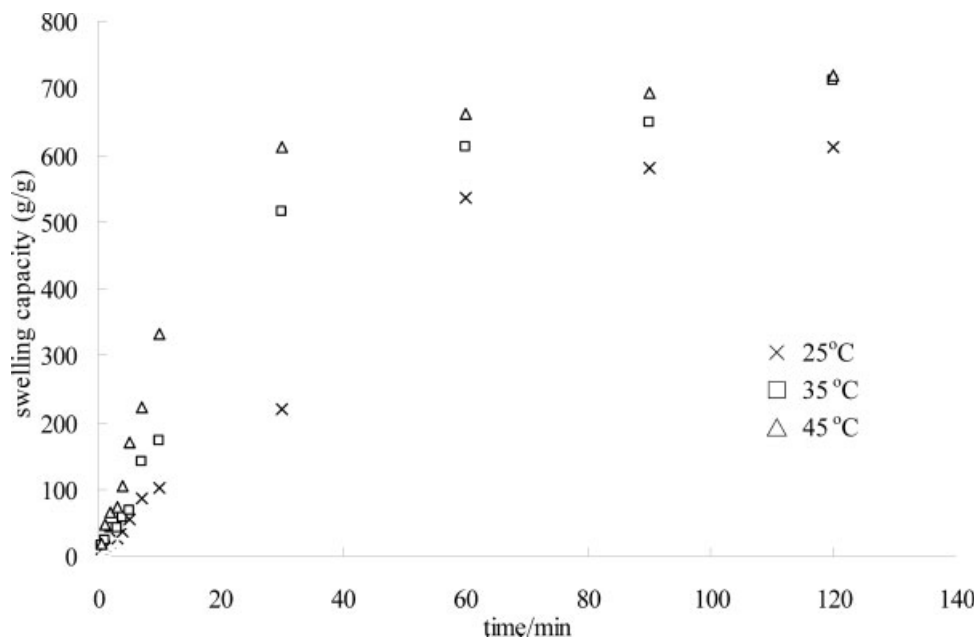$$\frac{M_1}{M_\infty} = Kt^n \quad (M_t/M_\infty < 0.6)$$

Figure 4 Dynamics sorption behavior of semi-IPN hydrogels IPN21.

TABLE I
Characteristic Constant (*K*), Kinetic Exponent (*n*),
Correlation Coefficient (*R*), and Initial Diffusion
Coefficient (*D*) for Semi-IPN21

Temperature (°C)	K	n	R	D ($\times 10^{-10}$cm^2/s)
25	0.0273	0.7662	0.9700	9.438
35	0.0357	0.7852	0.9680	17.51
45	0.0542	0.9080	0.9821	52.65

where M_t and M_∞ represent the amount of weight of the swollen hydrogel at times t and equilibrium time, respectively, k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrating molecule. When $n < 0.5$, the diffusion belongs to Fickian type; $0.5 < n < 1$ indicates non-Fickian or anomalous transport, while $n = 1$ implies case-II or relaxation-controlled transport.[17] It is indicted in Table I, that at different temperature, the diffusion mechanism is inclined to non-Fickian type.

Diffusion coefficients of IPN21 at 25, 35, and 45°C were calculated by utilizing diffusion equations first developed by Crank and Park.[18] For a single step in controlled humidity, the diameter of the IPN granule, L, the initial kinetics of sorption into the bulk may be described by the following equation:

$$\frac{M_1}{M_\infty} = \left(\frac{4}{L}\sqrt{\frac{D}{\pi}}\right)\sqrt{t} \quad (M_t/M_\infty < 0.6)$$

where M_t is the amount adsorbed at time t, M_∞ is the amount adsorbed at thermodynamic equilibrium, t is the equilibrium time, and D is the diffusion coefficient. It is found that the speed of diffusion increases obvi-
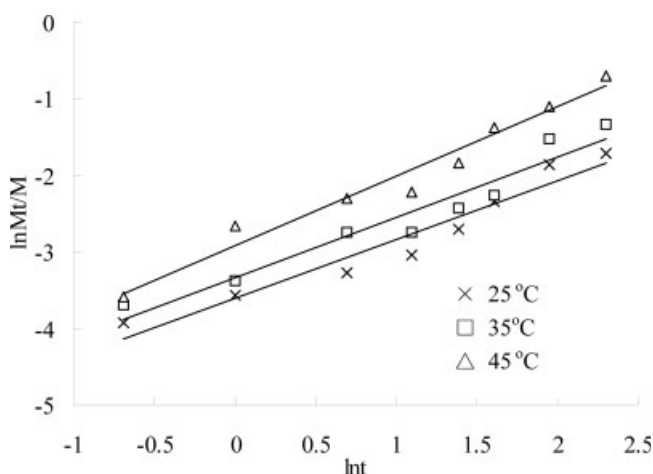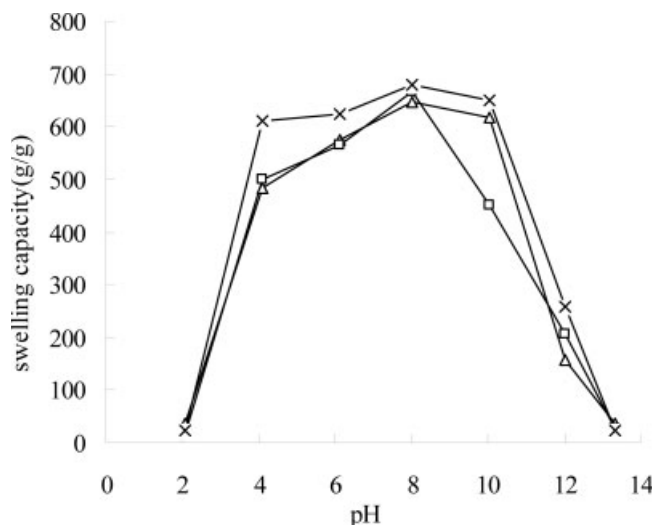
Figure 6 Swelling behavior as a function of pH △ IPN12; □ IPN11; × IPN 21.

ously as the temperature rises. The hydrogel reaches equilibrium water uptake within 90 min even at different temperatures (Fig. 5).

pH

The pH-sensitive characteristics of IPN hydrogels were studied using swelling tests, in the pH range from 2 to 14 at room temperature. As shown in Figure 6, the swelling ratios of the semi-IPN hydrogels increased with increasing pH values, while these values decreased at pH range from 10 to 14. In the acid medium (pH < 4), COO$^-$ groups lie in COOH form; therefore, the hydrogen bonds are easily formed, so the net-
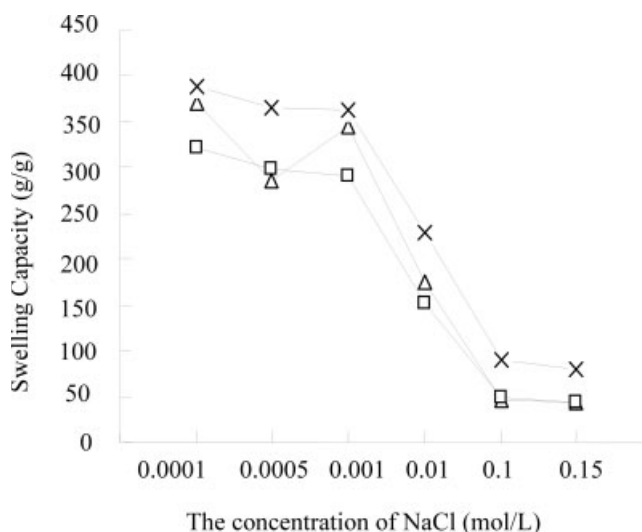
Figure 5 Plots of logarithms of Mt/M versus plots of logarithms of time.

Figure 7 Swelling behavior as a function of the concentration of NaCl △ IPN12; □ IPN11; × IPN 21.

work becomes compact. While in the strong alkaline medium, the COOH groups are ionized to COO^- forms that cause the increase of ionic concentration and the decrease of osmotic pressure. Electrostatic attraction between COO^- and quaternary ammonium in PDMDAAC also causes the shrink of the network. All these lead to the decrease of the swelling ratio of IPN hydrogel.

Different salt solutions

The effect of the salt concentration in aqueous solution on the equilibrium swelling was studied for the semi-IPN hydrogels. Figures 7–9 show the equilibrium swelling ratios of the IPN hydrogels in various aqueous NaCl, $CaCl_2$, and $FeCl_3$ solutions at room temperature.

From Figures 7–9, it can be seen that the swelling ratios decreased with increasing salt solution concentration. The NaCl swelling ratio of IPN12, IPN11, and IPN21 is 371, 322, and 388 g/g at 10^{-4} mol/L, respectively, while as the concentration increases to 0.1 mol/L, the swelling ratio falls to 42, 44, and 79 g/g, respectively. The Donnan osmotic pressure equilibrium shows that an increase in the movable counter-ions of a solution leads to a decrease in the osmotic pressure within the gel, which causes the gel to shrink. For $CaCl_2$ solution, the value is from 325, 362, and 440 g/g to 21, 11, and 16 g/g at corresponding concentration, respectively. The hydrophilic groups within the polymer chelate with Ca^{2+} ion, producing excessive crosslinking spot. So hydrogels show a reduced swelling ratio.

But for $FeCl_3$ solution, the property of antielectrolyte was shown. When the concentration is 5 $\times$ 10^{-4} mol/L, the swelling capacity of IPN12,
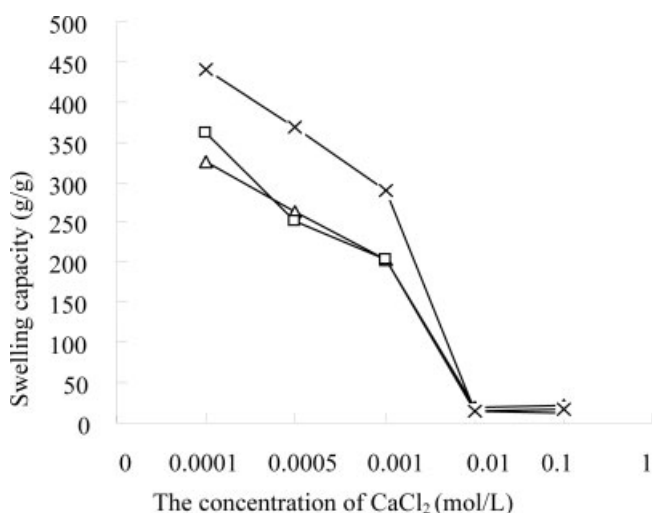
Figure 8 Swelling behavior as a function of the concentration of $CaCl_2$ △ IPN12; □ IPN11; × IPN 21.
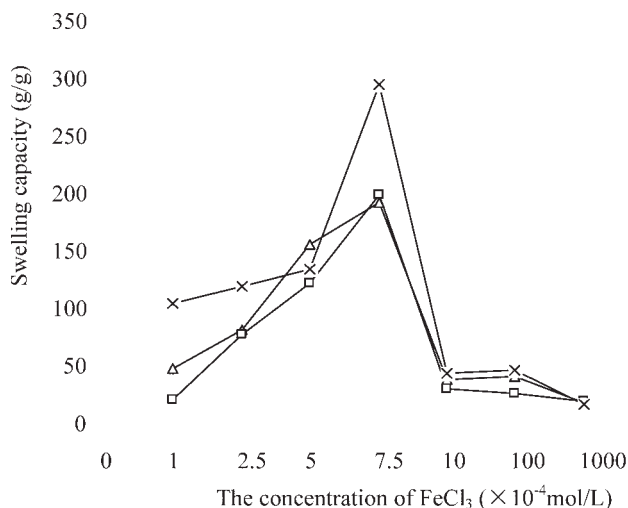
Figure 9 Swelling behavior as a function of the concentration of $FeCl_3$ △ IPN12; □ IPN11; × IPN 21.

IPN11, and IPN21 reaches to the highest value, about 172, 183, and 278 g/g, respectively, instead of a decrease. The inter-reactions of cationic and anionic groups are shielded by the ionization groups in the electrolyte solution. This leads to the decreased crosslinking made by inter-reaction between cationic and anionic groups. As a result, the networks of semi-IPN hydrogels are given further expanding space and the swelling ratio increases correspondingly.

CONCLUSIONS

Semi-IPN hydrogels were prepared from AA and PDMDAAC by the sequential IPN method. The semi-IPN hydrogels exhibited relatively high swelling ratios as the AA content was increased. The IPN21 sample, containing the highest amount of AA, showed the highest swelling ratio in the pH- and temperature-dependent swelling behavior studies. The dynamic diffusion coefficients of IPN21 at 25, 35, and 45°C were calculated, and the system exhibited non-Fickian diffusion mechanism. Semi-IPN hydrogels show a high swelling ratio in a wide range of pH (4–10), which makes them an extensive application. The high swelling ratio in the salt solution indicates that semi-IPN hydrogels have excellent salt resistance. Besides, hydrogel shows antielectrolyte property in $FeCl_3$ solution.

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