Effect of the Anionic-Group/Cationic-Group Ratio on the Swelling Behavior and Controlled Release of Agrochemicals of the Amphoteric, Superabsorbent Polymer Poly(acrylic acid-*co*-diallyldimethylammonium chloride)

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ABSTRACT: A series of amphoteric, superabsorbent polymers [poly(acrylic acid-*co*-diallyldimethylammonium chloride)] with different molar ratios of anionic groups to cationic groups were prepared by solution polymerization to investigate their swelling behaviors and the controlled release of agrochemicals. Various factors, including the solution pH, the concentrations of different salt solutions, and the temperature, were studied. The dynamic parameters of hydrogels at different temperatures suggested that diffusion was Fickian at lower temperatures, whereas non-Fickian diffusion prevailed at higher temperatures. A copolymer hydrogel with a low anionic-group/cationic-group ratio showed a higher swelling capacity in water and higher salt tolerance. Also, the anionic-group/cationic-group ratio was not the dominant factor in determining the water retention. A poly(acrylic acid-*co*-diallyldimethylammonium chloride) hydrogel could control the release of agrochemicals effectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 986–991, 2006

Key words: hydrogels; hydrophilic polymers; kinetics (polym.); swelling

INTRODUCTION

Superabsorbent polymers have received much more attention in recent years because of their wide applications in many fields, such as disposable diapers, soil-improvement agents, drug delivery systems, and absorbent pads.[1–6] Usually, anionic monomers, especially acrylic acid (AA) and its derivates, are the main monomers for synthetic absorbent polymers,[7–10] which have great absorption capacity but weak salt tolerance. To improve the swelling ability in salt solutions, more interest has been focused on introducing a nonionic monomer into the poly(acrylic acid) chain,[11–13] but this leads to a reduction of the absorption capacity in water. Besides, some crosslinkers with certain molecular masses and polar groups are used to improve swelling in salt solutions.[14] In comparison, amphoteric, absorbent polymers have been reported that, under some certain conditions, show potential salt tolerance.[15–18] Cai and Gupta[19] found antipolyelectrolyte swelling behavior in divalent salt solutions for the *N*-isopropylacrylamide/[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide hydrogel. Lu et al.[20] prepared an absorbent dimethylaminoethyl methacrylate/AA copolymer initiated by microwaves, and the amphoteric hydrogel had better salt tolerance. Kudaibergenov et al.[21] studied the behavior of amphoteric hydrogels based on vinyl 2-aminoethyl ether and sodium acrylate under the influence of the pH, ionic and solvent compositions, temperature, and electric field. With good biocompatibility and peculiar characteristic, amphoteric, absorbent polymers are applied to the therapy of cardiovascular diseases,[22] intelligent materials,[23] and the controlled release of drugs.[24]

However, more attention in the literature has been paid to the investigation of optimal synthetic conditions. No previous attempt has appeared to further study the effect of the anionic-group/cationic-group ratio (A/C ratio) in amphoteric polymers on the swelling ability. In this study, we prepared a series of diallyldimethylammonium chloride (DMDAAC)/AA amphoteric copolymer hydrogels by aqueous polymerization. Relations between the A/C ratio and swelling behav-

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iors of these copolymers were studied. Also, the controlled release of agrochemicals was investigated.

EXPERIMENTAL

Materials

AA (Tianda Chemical Co., Tianjin, China), DMDAAC (60 wt % aqueous solution; Shandong Luyue Chemical Co., Shandong, China), *N,N'*-methylenebisacrylamide (NMBA; Shanghai Chemical Co.), ammonium persulfate (APS; Xi'an Chemical Co., Xian, China), sodium hydroxide, hydrochloric acid, sodium chloride, calcium chloride, and ferric chloride (Tianjin Bashi Chemical Co., Tianjin, China) were all analytical-grade and were used as received without further purification.

Preparation of the amphoteric copolymer poly(acrylic acid-*co*-diallyldimethylammonium chloride) [poly(AA-*co*-DMDAAC)]

A sodium acrylate solution with a neutralization degree of 75% was first prepared by the slow dropping of a 40% NaOH solution into a flask containing AA with strong stirring at 0°C (cooled in an ice bath). Then, the aforementioned AA monomer solution, a DMDAAC monomer solution, and the crosslinker NMBA (0.1 wt % of the weight of the monomer) were added to a 250-mL, four-necked flask, which was equipped with a mechanical stirrer and a reflux condenser and purged with nitrogen. After 30 min, an APS solution (2.5 wt % of the weight of the monomer) was added to the reaction system. The reaction was carried out at 60°C for 3 h. The resulting product was washed several times with a 70% methanol solution and then dried to a constant weight. The product was smashed, and then the size of its particles was measure with scanning electron microscopy (1430VP, Leo, Germany). The nitrogen content was measured with the Kjeldahl method; the concentration of carboxyl groups was measured according to Mattisson and Legendre's work.[25]

Swelling measurements

The dry hydrogel (0.1 g) was dispersed in 200 mL of distilled water (or various salt solutions). After a certain time, the swelling sample was filtered through a 100-mesh nylon bag. The water sticking to the bag surface was removed and then weighed. The swelling ratio [Q (g/g)] was calculated as follows:

$$Q = \frac{W_t - W_0}{W_0} \quad (1)$$

where W_t (g) is the weight of the swollen hydrogel at a given time and W_0 is the weight in the dry state.

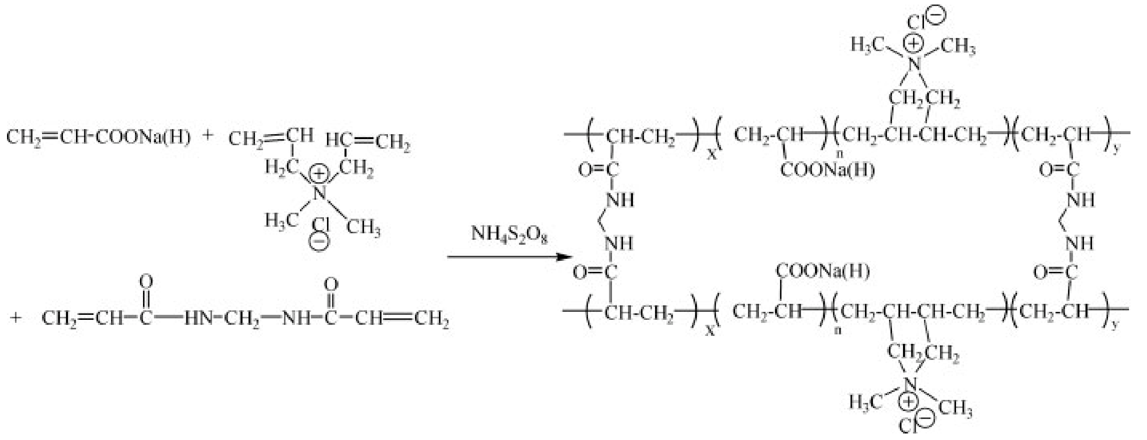
Measure of the water-retention capacity

A weighed dry hydrogel was placed in a 50-mL beaker with 50 mL of distilled water to reach the swelling equilibrium, and the total weight (M_0) was recorded. It was then weighed at different time intervals (M_t), with 50 mL of distilled water free of the sample used as a reference. The water-reduced ratio [s (%)] was calculated according to the following equation:

$$s(\%) = \frac{M_0 - M_t}{50} \times 100 \quad (2)$$

Release of ammonium nitrate

Hydrogels with different A/C ratios and a loading of 50 mg of NH_4NO_3 were transferred into 50 mL of distilled water and were allowed to release NH_4NO_3 at 25°C. The conductivity of the solutions was measured at certain time intervals with a conductivity meter (DDS-310, Shanghai Kangyi Instrument Co., Shanghai, China). The released NH_4NO_3 concentration was calculated by reference to a standard curve.



Scheme 1 Preparation process for the poly(AA-*co*-DMDAAC) hydrogel.

TABLE I
Nitrogen and Carboxyl Contents of Poly(AA-*co*-DMDAAC)

	No. 1	No. 2	No. 3
Nitrogen (wt %)	1.77	0.98	0.49
Carboxyl group (wt %)	45	44	40
A/C ratio (mol/mol)	8	14	25

RESULTS AND DISCUSSION

The preparation process of the poly(AA-*co*-DMDAAC) hydrogel can be proposed as shown in Scheme 1. The swelling behavior of the absorbent polymer depends on the composition of the polymer and the characteristic of the external solution. In the experiment, a series of amphoteric, absorbent poly(AA-*co*-DMDAAC) polymers with different A/C ratios (see Table I) were synthesized to investigate the effects of the composition and external solution on the swelling behaviors.

Effect of the solution pH

Although the amphoteric copolymers were synthesized with different A/C ratios, they showed almost the same trend for the swelling change with the various pH values of the solutions. Figure 1 indicates that the swelling ratios of three kinds of copolymers showed a sharp increase when the pH increased from 2 to 4 and then remained almost constant until pH 11. With a further pH increase to 14, the swelling ratios decreased remarkably. The amphoteric hydrogel did not show a maximum swelling ratio at pH 7, although the swelling ratio was strongly influenced by the ionic strength. Similar results have been reported for poly(aspartic acid),[26] which is a polyampholyte and is partially acidic. The obvious changes were due to the presence of different interacting species in the swelling medium depending on the pH. Like the —NH_2 group, which accepts protons, becoming —NH_3^+ under an acidic condition, the ammonium group keeps an unchangeable form in a wide range of pHs; therefore, the aforementioned changes are attributed to the change in the form of the carboxyl groups as well as the interaction between the ammonium and carboxyl groups. Therefore, at pH < 4, —COOH groups become the dominant involved species, and they reduce the charge density on the polymer chains, thus causing the network to shrink. In addition, the hydrogen bond is inclined to form under an acidic condition, so the network becomes compact. At pH $>$ 11, the COO^- groups are involved, and excessive Na^+ reduces the osmotic pressure inside the polymer gel, leading to decreased swelling. In a pH range of 4–11, there are two contrary factors in the polymer solution: COO^-–COO^- and ammonium–ammonium repulsion tends to lead to a higher swelling capacity. Meanwhile, the static attraction between ammonium and carboxyl groups, as well as the buffer system composed of COO^- and COOH, will restrict the swelling to some degree. As a result, the swelling ratio remains almost constant.

Effect of the kind and concentration of the salt solution

Ammonium groups have been reported to be salt-tolerant in the case of poly(ethylene oxide ethylene imine) hydrogels,[27] so it is thought that a lower A/C ratio can lead to a higher swelling ratio in a salt solution. Figures 2–4 support that conclusion. However, no obvious antielectrolyte swelling behaviors

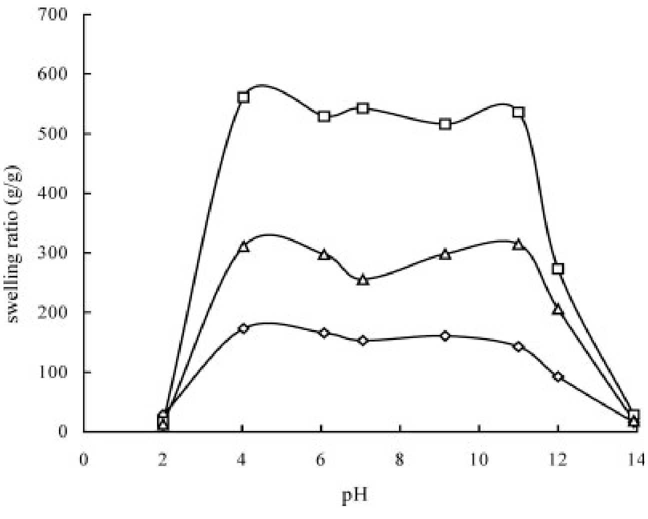


Figure 1 Effect of the solution pH on the swelling ratio: (□) no. 1, (△) no. 2, and (◇) no. 3.

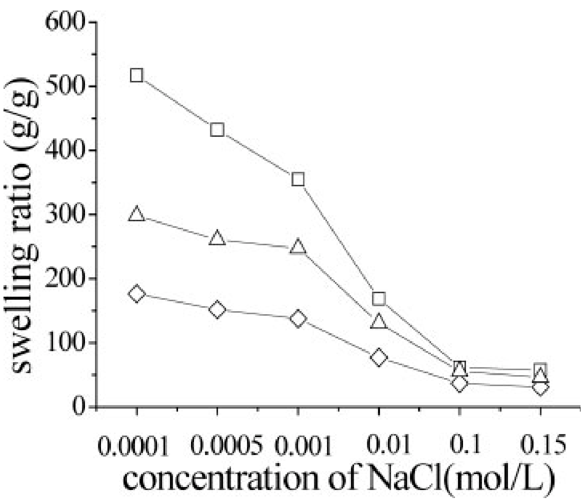


Figure 2 Effect of the NaCl concentration on the swelling ratio: (□) no. 1, (△) no. 2, and (◇) no. 3.

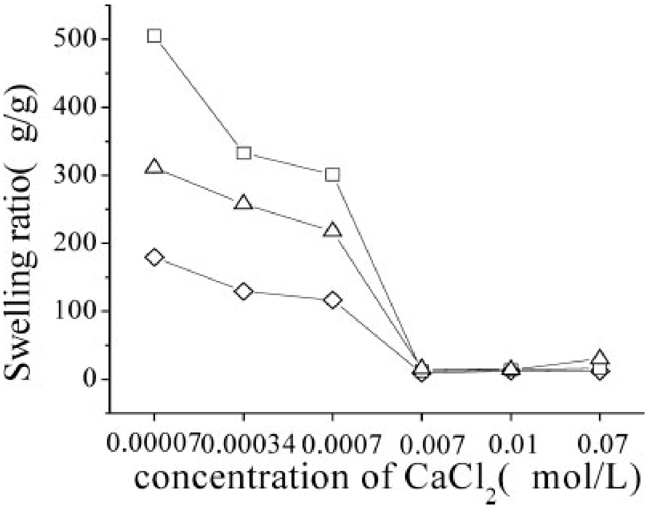


Figure 3 Effect of the $CaCl_2$ concentration on the swelling ratio: (□) no. 1, (△) no. 2, and (◇) no. 3.

for the three polymer hydrogels were observed. This can be explained as follows: the addition of salt may not break the interchain association, or the polymer gels mainly show anionic properties because all A/C ratios are above 1.

The figures further show that the swelling ratios in NaCl solutions are higher than those in $CaCl_2$ and $FeCl_3$ solutions. It can be explained that multivalent salt ions (Ca^{2+} or Fe^{3+}) reduce the network space as a kind of crosslinker. However, the swelling ratios for different A/C ratio samples do not show obvious differences at a high concentration. It can probably be explained that excessive salts shield the repulsion between hydrophilic groups and greatly reduce the osmotic pressure, thus eliminating the swelling gap caused by different amounts of groups.

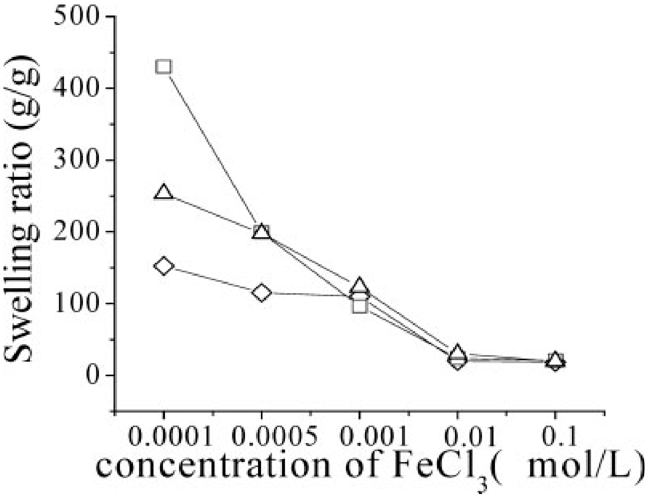


Figure 4 Effect of the $FeCl_3$ concentration on the swelling ratio: (□) no. 1, (△) no. 2, and (◇) no. 3.

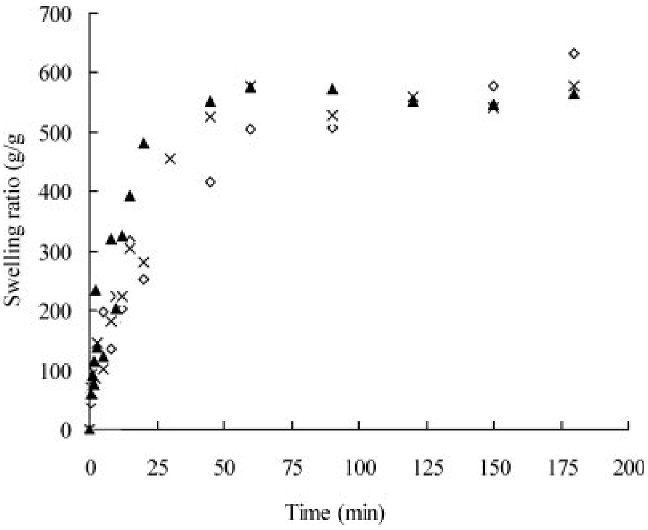


Figure 5 Effect of the temperature on the swelling ratio: (◇) 30, (×) 40, and (▲) 50°C.

Swelling kinetics

Sample 1 (particle diameter = 64 μm) is used to investigate the swelling kinetics. The swelling ratios at different temperature from 30 to 50°C and for various times from 0 to 180 min are shown in Figure 5. Initially, the rate of water absorption sharply increases, and then it levels off. The swelling equilibrium is achieved after 1 h. According to the following equation[28], the corresponding dynamic parameters have been calculated (they are listed in Table II):

$$\frac{M_t}{M_e} = Kt^n \quad (M_t/M_e < 0.6) \tag{3}$$

where K is a characteristic constant of the hydrogel and n is a kinetic exponent of the mode of solute transport. M_t/M_e is the swelling ratio at time t and equilibrium. When $n < 0.5$, the diffusion is Fickian; $0.5 < n < 1$ indicates non-Fickian or anomalous transport, whereas $n = 1$ implies case II or relaxation-controlled transport.[29] It is indicated in Table II that the swelling exponent is less than 0.5, suggesting the Fickian diffusion mechanism at 30°C, 40°C, whereas n is 0.5895, implying non-Fickian diffusion at 50°C. At $0 < M_t/M_e < 0.6$, the curve can be

TABLE II
Dynamic Parameters of Copolymer 1 at 30–50°C

Temperature (°C)	K	n	R_1	$D \times 10^9$ (cm^2/s)	R_2
30	0.0975	0.4317	0.9940	1.06	0.9924
40	0.1089	0.4572	0.9770	1.68	0.9774
50	0.1434	0.5895	0.9863	3.24	0.9719

R_1 is the correlation coefficient for k and n, and R_2 is the correlation coefficient for D.

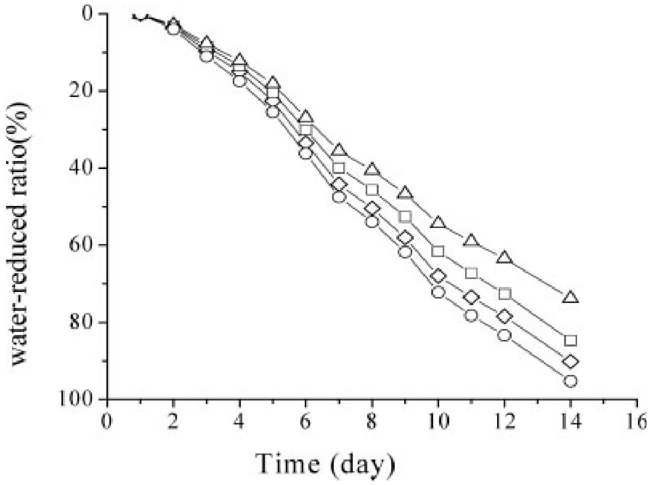


Figure 6 Water-retention capacity of the amphoteric copolymers: (□) no. 1, (△) no. 2, (◇) no. 3, and (○) blank.

thought to be a linear plot of M_t/M_e against $t^{1/2}$. The initial swelling parameters have been determined with the following equation:[28]

$$\frac{M_t}{M_e} = \left(\frac{4}{L}\sqrt{\frac{D}{\pi}}\right)\sqrt{t} \tag{4}$$

where L (cm) is the diameter of the dry sample and D ($\times$ 10^{-9} cm^2/s) is the diffusion coefficient. D is 1.06×10^{-9}, 1.68×10^{-9}, and 3.24×10^{-9} when the temperature varies from 30 to 50°C, respectively. This can be attributed to the fact that with the temperature increasing, D increases, thus tending to favor anomalous or relaxation-controlled transport. The value of n indicates the non-Fickian type. It can be explained that the relaxation caused by electrostatic repulsion between COO— groups or ammonium groups is comparable to the osmotic pressure caused by a concentration gap inside and outside a hydrogel at higher temperatures. This result is different from our previous work[30] for a zwitterionic *N*-carboxymethyl-*N,N*-dimethyl-*N*-allylammonium/AA hydrogel, for which no obvious gap has been found in D as the temperature increases; this is probably because network shrinkage, tending to lower D, is comparable to thermal activation, which increases D. In this case, it is suggested that thermal activation governs the dependence of D on the temperature.[31]

Water-retention capacity

As previously discussed, an amphoteric hydrogel with a lower A/C ratio exhibits higher swelling in a salt solution because of the potential salt tolerance of cationic ammonium groups. However, this conclusion fails to account for water-retention behaviors.

As shown in Figure 6, a hydrogel with a lower A/C ratio does not exhibit better water-retention capacity. This could be caused by other factors besides the A/C ratio. Water involved in the hydrogel network can be classified as free, freezing bound, and nonfreezing bound.[32] Free water is similar to pure water, which is not involved in the formation of H bonding with polymer molecules. Freezing bound water, or intermediate water, interacts weakly with polymer molecules. Nonfreezing water, also known as bound water, is water with its molecules bound to the polymer molecules via hydrogen bonds. Therefore, it is difficult to lose bound water. Different from —NH_2 groups, ammonium groups in an amphoteric hydrogel cannot take part in the formation of hydrogen bonding. Therefore, a good water-retention property in a hydrogel with more ammonium groups is not found. Although COOH groups tend to form hydrogen bonding with H_2O, an increase in the number of COOH groups is not followed by an improvement in the water-retention capacity. This may partly be attributed to the steric structure that hinders the formation of hydrogen bonding to some degree.

Release of the agrochemical ammonium nitrate

Figure 7 shows the release behaviors of amphoteric copolymers loading ammonium nitrate. The loaded hydrogel can control the release of ammonium nitrate effectively. The mechanism of controlled release is that different salt concentrations outside and inside the hydrogel create high osmotic pressure. Water is inclined to diffuse from the surrounding solution to the hydrogel, thus coming out of ammonium nitrate. However, the amount of controlled released is not proportional to the swelling ratio.

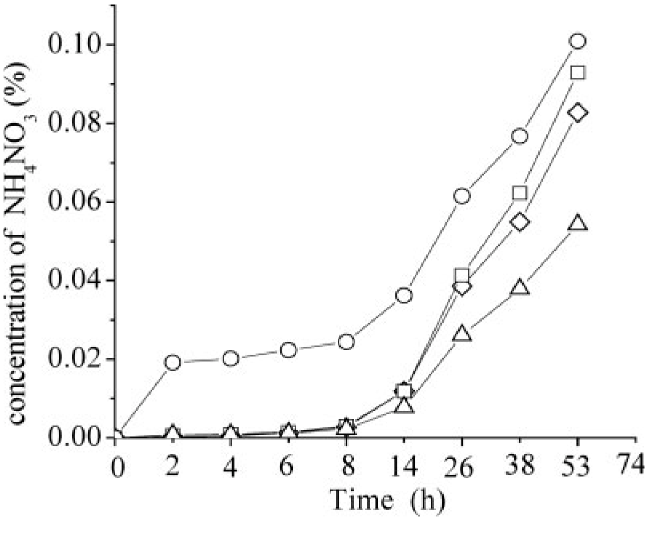


Figure 7 Effect of the amphoteric copolymers on the released concentration of NH_4NO_3: (□) no. 1, (△) no. 2, (◇) no. 3, and (○) blank.

The absorbency of water makes a transition of the polymer matrix from the glassy state to the rubbery state, creating a gel layer as a barrier opposing water and ammonium nitrate transport. The different swelling-controlled mechanisms for hydrogels with different A/C ratios, as well as mechanistic aspects, control the mechanism of controlled release of ammonium nitrate.

CONCLUSIONS

This investigation has revealed that the swelling ratio of amphoteric copolymer poly(AA-*co*-DMDAAC) is heavily dependent on the A/C ratio. A hydrogel with a low A/C ratio shows a higher swelling ratio and better salt tolerance. The amphoteric hydrogels maintain a high swelling ratio over a wide range of pHs. The water-absorbing processes shift from the Fickian type to the non-Fickian type when the temperature increases from 30 to 50°C with an increase in D. The water-retention capacity is not proportional to the number of COOH groups in the amphoteric hydrogels, even though the formation of hydrogen bonding contributes to the water-retention capacity. The amphoteric hydrogels can control the release of the agrochemical ammonium nitrate remarkably, and this makes them good candidates for potential soil-improvement agents.

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