A Multifunctional Hydrogel with High-Conductivity, pH-Responsive, and Release Properties from Polyacrylate/Polyptrrole

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ABSTRACT: A simple, two-step aqueous polymerization was introduced to synthesize a polyacrylate (PAC)/polypyrrole (PPy) hydrogel. The hydrogel had a semi-interpenetrating network (semi-IPN) structure with a loose, three-dimensional PAC network and a one-dimensional PPy conjugated chain. The presence of PPy led to a higher conductivity (9.1 mS/cm) for the PAC/PPy hydrogel. Because of the acrylate group on PAC and the imine group on PPy, the hydrogel showed typical pH sensitivity with two water absorption peaks at pH 4–6 and pH > 11. The loose semi-IPN structure endowed the hydrogel with good load and release functions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1376–1383, 2010

Key words: adsorption; conducting polymers; hydrogels; interpenetrating networks (IPN); polypyrroles

INTRODUCTION

Superabsorbent polymers are structurally loosely crosslinked three-dimensional (3D) network hydrophilic polymers;[1] they are able to absorb considerable amounts of liquid to form stable hydrogels and do not dissolve in the liquid. About 3 decades ago,[2] superabsorbent polymers were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where excellent water-holding properties were emphasized. Recently, many researchers have focused their attention on superabsorbent polymers for the development of new applications, such as conducting materials, biomaterials, sensors, and release materials.[3–10] They expected to prepare multifunctional soft matters from superabsorbents to meet application requirements by modification, grafting, copolymerizing, and other methods.

Conducting hydrogels are novel functional materials that were recently developed. Conducting hydrogels are often prepared by the copolymerization or doping of conducting materials with/to hydrophilic monomers/polymers.[11,12] Polypyrrole (PPy) is one of the most extensively studied conductive polymers because of its good conductivity, low cost, easy synthesis, and good environmental stability.[8,13] On the basis of the superabsorbent polymer polyacrylate (PAC) and the conducting PPy, a novel hydrogel with multifunctional properties is expected.

In this study, we introduced a one-dimensional PPy conjugated chain into a 3D PAC network to form a novel hydrogel by a two-step aqueous polymerization. We expected the obtained hydrogel to be a semi-interpenetrating network (semi-IPN). On the basis of the PPy conjugated chain, bifunctional groups of —NH— on PPy and —COOH (or —COO⁻) on PAC, and the semipermeable membrane structure of the PAC/PPy, a novel multifunctional hydrogel with high-conductivity, pH-sensitive, drug-loading, and release properties was obtained. It could be used in fuel cells, supercapacitors, dye sensitive solar cells, rechargeable lithium batteries, conducting films, coatings, sensors, conducting fibers, and so on[4,14–20] because of to its high conductivity, colloidal stability, low cost, and simple preparation.

EXPERIMENTAL

Materials

Acrylic acid (AA) and pyrrole (Py) monomers were distilled under reduced pressure before use. Potassium hydroxide (KOH) was used to neutralize the AA monomer to form acrylate (AC) monomer and

to adjust the pH values of the solution. Potassium persulfate was used as a radical initiator for the synthetic reaction of PAC, and iron chloride (FeCl$_3$) was used as an oxidant and adulterant for PPy. N,N'-Methylene bisacrylamide, used as a crosslinker for the preparation of PAC, was purified by recrystallization from a 66 wt % ethanol/water solution. Methylrosaniline chloride (MC) was used as a drug target with a solution concentration of 1 wt %. All of the materials were purchased from Shanghai Chemical Reagents Co. (Shanghai, China).

Preparation of the PAC superabsorbent polymer

The PAC superabsorbent polymer was prepared by modification of the procedure from refs. [21–23]. A mixed solution consisting of the AA and AC monomers was made by agitation of 15 g of AA in 15 mL of KOH in deionized water at ambient temperature. Under a nitrogen atmosphere, the mixture solution was stirred and heated to 80°C in a water bath for 10 min; then, the initiator (mass ratio of potassium persulfate to AA = 0.3 wt %, 0.045 g) was added, and the reaction mixture was stirred for a few minutes until polymerization reaction completed. A jell-like intermediate product was filtered and then immersed in excess deionized water to remove any impurities and chains with low molecular weights. After the product was dried *in vacuo* at 80°C for more than 3 h to a constant weight and milled with a 40-mesh screen, a powdered PAC superabsorbent polymer was obtained.

Preparation of the PAC/PPy composite

On the basis of the PAC superabsorbent polymer, a PAC/PPy with a semi-IPN structure was prepared according to following procedures. Under vigorous agitation, 5 g of powdered PAC superabsorbent polymer was immersed in a predetermined amount of Py aqueous solution at ambient temperature for 30 min, which resulted in the absorption of Py monomers inside the PAC 3D network and the formation of a swollen sample. The swollen sample was dispersed in a solution of 100 mL containing a suitable amount of the oxidant FeCl$_3$, which caused an *in situ* polymerization between the Py monomers and the formation of PPy inside the PAC 3D network. The polymerization reaction took place at room temperature. After the complete reaction, the hydrogel was filtered, rinsed, and dried; finally, a black, powdered PAC/PPy composite was obtained.

Measurement of the pH sensitivity

The swelling ratio (SR) is the criterion used to evaluate the water absorption capacity of hydrogels. The

measurement of SR of the PAC/PPy conducting hydrogel was carried out by a tea-bag method and with solutions with pH values ranging from 1.5 to 12.5 as liquids to be absorbed. The tea bag used in the method was made of 40-mesh nylon netting. The weight of the wet nylon net was measured and marked as W_n. The weight of the dry PAC/PPy composite was marked as W_d. The test sample of the PAC/PPy composite, after weighing, was placed into the tea bag, and then, the tea bag with the sample inside was suspended and fully immersed into liquids to be absorbed at 25°C. After 24 h, the tea bag was hung in the air for 15 min, and then, the weight of the tea bag, including the swollen resin was measured and marked as W_t. SR of the PAC/PPy hydrogel was calculated from eq. (1):

$$SR(g/g) = \frac{W_t - W_d - W_n}{W_d} \tag{1}$$

Measurement of the conductivity

The powdered composite (3 g) was immersed in deionized water (500 mL) at room temperature for at least 3 h until it reached swelling equilibrium, which resulted in the absorption of water inside the network of the PAC/PPy composite and the formation of a conducting hydrogel. The unadsorbed water was removed by filtration over a 40-mesh stainless steel screen and hanging up for 25 min. The hydrogel samples (pure PAC and PAC/PPy) were washed three times to remove impurities. The conductivities of these hydrogels were measured by the insertion of a Pocket Conductivity Meter (HANNA8733, Hanna Instruments, USA) in a cylinder containing a swollen hydrogel (30 g).

Measurement of the load and release

The drug load and release properties were evaluated with MC as a drug target. The PAC/PPy composite dried samples were immersed in drug target aqueous solutions with different concentrations (0.03, 0.06, and 0.10 mg/mL) for 12 h at 37°C. The loading amounts were measured with an ultraviolet -visible-infra (UV -Vis-IR) spectrophotometer (Shimadzu UV-3100, Shimadzu Corporation, Japan) at maximal absorption wave number (λ_{max}) = 270 ± 1 nm with a glass cell of 15 mm to measure the color intensity of MC. The MC loading amount (q_e; mg/g) was obtained according to eq. (2):[24,25]

$$q_e = \frac{C_0 - C_{eq}}{m} V \tag{2}$$

where C_0 is the initial concentration of the MC solution (mg/L), C_{eq} is the equilibrium concentration

(mg/L), V is the volume of the MC solution (L), and m is the mass of the dried PAC/PPy composite (g).

The PAC/PPy hydrogel loaded MC was immersed in 10 mL of deionized water (pH = 6) to measure the MC release from the hydrogel. We measured the release amount spectrophotometrically ($\lambda = 270 \pm 1$ nm) by taking the sample from the solution and returning it to each vessel periodically so that the liquid volume was kept constant. The absorption peak area (A) and the concentration (C, mg/L) of MC had good linear relationship. The regression equation was $A = 45.45\ C - 0.022$ with a correlation coefficient $r = 0.9994$.

RESULTS AND DISCUSSION

### Fourier transform infrared (FTIR) spectra of the PAC/PPy composite

The FTIR spectra[26,27] of PAC and PAC/PPy are shown in Figure 1. For the curve of PAC, the absorption peak at about 3500 cm^{-1} was attributed to the O—H stretching, the peak at about 2888 cm^{-1} was attributed to —CH$_2$— dissymmetrical stretching, the peak at about 1690 cm^{-1} was attributed to C=O stretching, the peak at about 1123 cm^{-1} was attributed to C—H bending, and the peaks at 1570 and 1407 cm^{-1} resulted from C=O bending in the carboxylic acid and carboxylate groups, respectively. The peak at about 1250 cm^{-1} corresponded to O—H distortion in the carboxylic acid group, the peak at about 1180 cm^{-1} was attributed to C—O stretching vibrations, the peak at about 1456 cm^{-1} belonged to —COO$^-$ stretching, and the peak at about 1319 cm^{-1} was attributed to C—C stretching. For the curve of PAC/PPy, the absorption peak at about 3118 cm^{-1} was attributed to O—H stretching, the absorption

peak at about 1542 cm^{-1} was attributed to C=C stretching, the peak at about 1452 cm^{-1} was attributed to C—N stretching, the peak at about 1311 cm^{-1} was attributed to C—H and N—N distortion, and the peak at about 891 cm^{-1} was attributed to C—H bending of PPy. The introduction of the absorption peaks of PPy to the PAC superabsorbent indicated the integration of PAC and PPy. PAC is a typically anionic polyelectrolyte in which a large amount of —COOH groups are ionized to —COO$^-$ groups under the neutralization of KOH, whereas PPy doped with Fe^{3+} ion is a cationic polyelectrolyte. The peak at about 1690 cm^{-1} corresponding to C=O stretching on PAC shifted to about 1716 cm^{-1}. The peaks at about 1570 and 1407 cm^{-1} were weakened. Particularly, —COO$^-$ stretching disappeared. All of these changes indicated strong interactions between —COO$^-$ on PAC and PPy doped with Fe^{3+}.
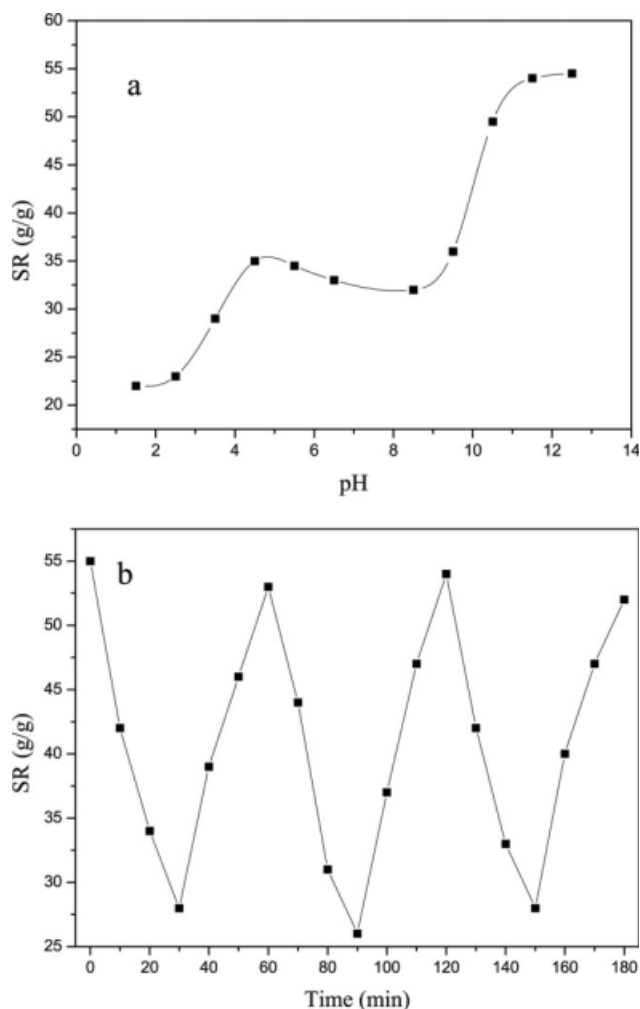
pH sensitivity of the PAC/PPy hydrogel

The swelling properties of the PAC/PPy hydrogel were investigated at pH values ranging from 1.0 to 14.0. As shown in Figure 2(a), the PAC/PPy hydrogel showed two sharp water-absorbent peaks at pH 4–6 and pH > 11. This was because the PAC/PPy hydrogel consisted of acidic PAC and slightly basic PPy. The sharp water absorption peak at pH 4–6 was ascribed to the high repulsion of the —NH$_2$$^+$— groups on the PPy in the acidic media, whereas the absorption peak at pH > 11 was ascribed to the —COO$^-$ groups on the PAC in the basic media. The electrostatic repulsions between these groups promoted the swelling of the hydrogel and caused a higher SR. The electrostatic repulsive force between the —COO$^-$ groups was higher than that between the —NH$_2$$^+$— groups, so the SR at pH > 11 was higher than that at pH 4.

Under acidic conditions (pH < 3), a screening effect of the counterions, that is, Cl$^-$, shielded the charge of the cations (—NH$_2$$^+$—) and prevented an efficient repulsion.[28] Therefore, the water absorbency of the hydrogel was smaller. Under these acidic conditions, the anionic —COO$^-$ group was protonated, so the polymeric network collapsed. With increasing pH of the solution, the concentration of the Cl$^-$ ions decreased, which resulted in a decrease in the shield effect of the Cl$^-$ ions and an increase in the repulsive effect between the —NH$_2$$^+$— groups. At around pH 4.5, the water absorbency of the hydrogel reached a higher value. However, in certain pH values, ranging from 6 to 8, close to neutrality, most base and acid groups were not ionized, so H bonding between imine and carboxylic acid may have resulted in a kind of crosslinking followed by decreased swelling. In basic conditions (pH > 7), the —COOH group gradually ionized to a —COO$^-$
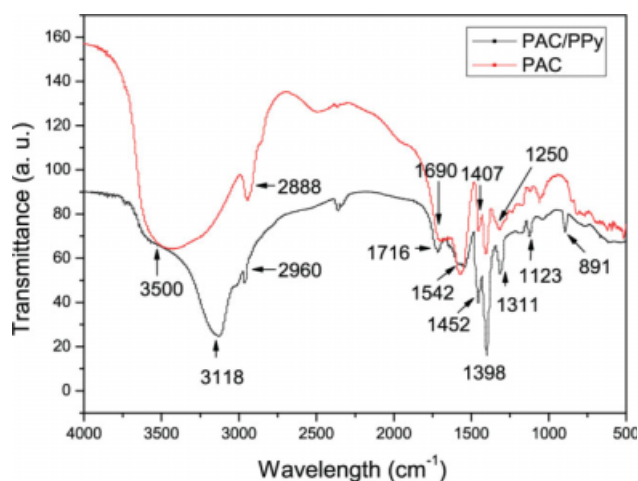
Figure 1 FTIR spectra of the PAC superabsorbent polymer and PAC/PPy composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the drive of electrostatic repulsions and osmotic pressure.

Hydrogel conductivity

The conductivity of the hydrogel depended on the preparation conditions. The influence of $FeCl_3$ dosage on the conductivity of the PAC/PPy hydrogel is shown in Figure 3(a). The conductivity of the hydrogel increased with increasing molar ratio of $FeCl_3$ to Py in the range 1.4–2.0; beyond a molar ratio of 2.0, the conductivity of the hydrogel decreased.

We believe that the conduction of the PAC/PPy hydrogel came from the PPy chain.[32] The length of the π-conjugated chain of PPy affected the conductivity of the hydrogel. In our system, $FeCl_3$ had two functions: one was as a dopant, and the other was as an oxidant. When the molar ratio of $FeCl_3$ to Py

Figure 2 (a) Dependence of the SR of hydrogel on the pH (preparation conditions: mass ratio of PAC to Py = 20, molar ratio of $FeCl_3$ to Py = 2.0, $FeCl_3$ concentration = 0.050M, and reaction at 45°C for 5 h) and (b) on–off switching behaviors as reversible swelling (pH 11.5) and deswelling (pH 1.5).

group, and the electrostatic repulsive force between the —COO⁻ groups led to high swelling. Analogous viewpoints were reported for poly(aspartic acid),[29] poly(N-isopropylacrylamide)/poly(acrylic acid),[30] and chitosan-g-poly(acrylic acid-co-acrylamide) systems.[31]
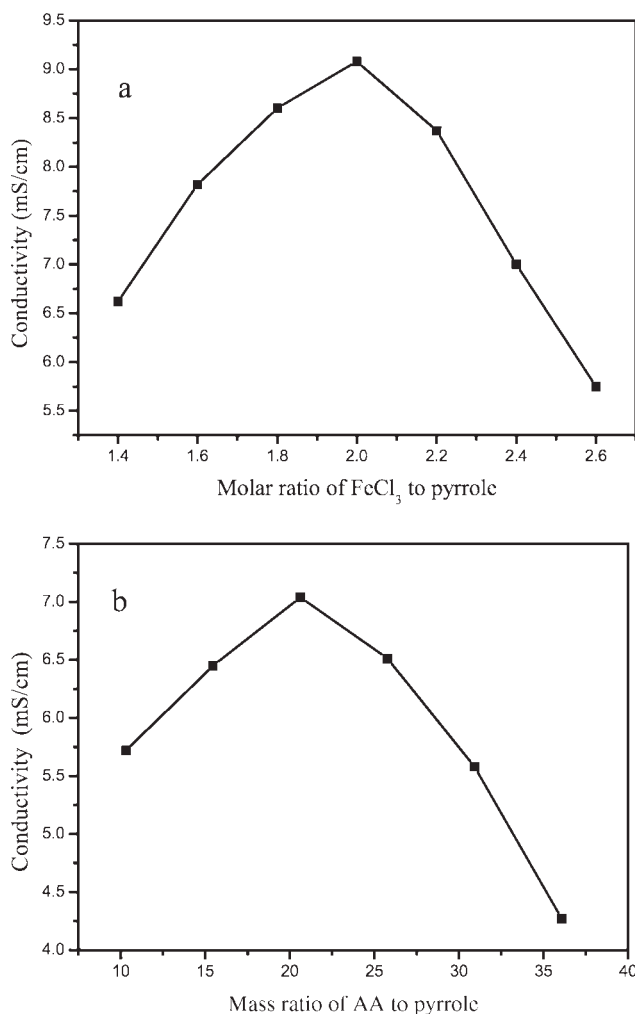
Because of the different swelling behaviors of the PAC/PPy hydrogel in acidic and alkaline solutions, we investigated the reversible swelling–deswelling behavior of the hydrogels in buffer solutions of pH 1.5 and 11.5 [Fig. 2(b)]. At pH 1.5, the hydrogels shrank rapidly because of the protonation of carboxylic acid groups and the production of hydrogen bonds, similar to the increase in the crosslinkage of hydrogels, which resulted in the diminution of network space and hydrophilic capability. The result was the diffusion of superfluous water and the shrinkage of the hydrogels. Once the hydrogel was immersed at pH 11.5, the hydrogel swelled under

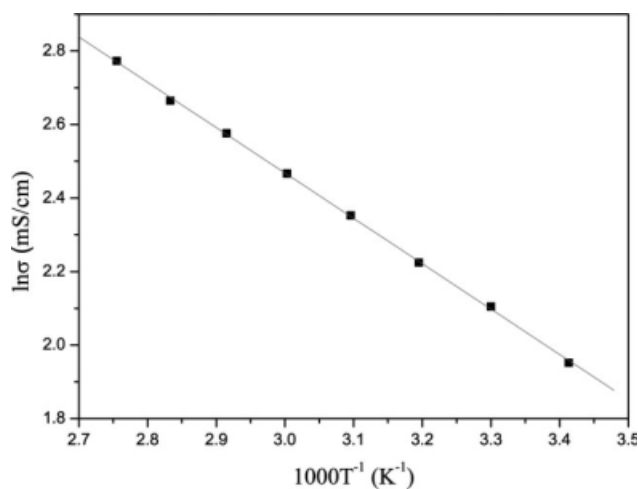**Figure 3** (a) Conductivity of the PAC/PPy hydrogel versus the molar ratio of $FeCl_3$ to Py (preparation conditions: mass ratio of PAC to Py = 25, and reaction at 45°C for 5 h) and (b) conductivity of the PAC/PPy hydrogel versus the mass ratio of PAC to Py (preparation conditions: molar ratio of $FeCl_3$ to Py = 1.4 and reaction at 45°C for 5 h).

was less than 2.0, as a p-type dopant, the $FeCl_3$ mainly played an electron-acceptor rule. Fe^{3+} accepted electrons from the π-valence band of PPy to form movable carriers in PPy, which changed the band-gap energy of π electrons in PPy, decreased the resistance of the carrier motion, and increased the conductivity of the composite with increasing Fe^{3+} dosage. On the other hand, according to the Nernst equation, as an oxidant, the oxidation potential and oxidation ability of Fe^{3+} increased with increasing $FeCl_3$ dosage. When the $FeCl_3$ dosage exceeded a molar ratio of 2.0, the higher oxidation potential of Fe^{3+} caused an overoxidation and disjunction of the PPy chains; the access of carrier motion was destroyed, and the conductivity decreased with increasing $FeCl_3$ dosage. In our conditions, the molar ratio 2.0 was better.

Figure 3(b) shows the influence of the PAC amount on the conductivity of the hydrogel. With increasing mass ratio of PAC to Py, the conductivity of the hydrogel increased gradually and then decreased after it reached the highest conductivity of 7.2 mS/cm with a mass ratio of PAC to Py of 20. It is well known that a semi-IPN structure is formed by the integration of PPy chains and PAC networks. A suitable mass ratio of PAC to Py is significant. In the case of a higher mass ratio of PAC to Py, less Py was absorbed, and the resultant PPy conducting channels could not formed. However, at a lower mass ratio of PAC to Py, a lower AC dosage could not produce an effective 3D network of PAC, and the Py monomer could not be absorbed into the network to form a PPy conducting channel effectively. In the previous two cases, a semi-IPN could not be formed to conduct electrons; this resulted in a decrease in the conductivity of the hydrogel.

Other preparation conditions, such as the mass ratio of PAC to Py, $FeCl_3$ concentration, reaction time, and reaction temperature, also affected the structure and conductivity of the PAC/PPy hydrogel. After a series of comparison experiments, the optimal reaction conditions were determined as follows: molar ratio of $FeCl_3$ to Py = 2.0, mass ratio of PAC to Py = 20, $FeCl_3$ concentration = 0.050M, reaction temperature = 45°C, and reaction time = 5 h. Under these conditions, the PAC/PPy hydrogel possessed a conductivity of 9.1 mS/cm.

The PAC/PPy hydrogels possessed both ionic and electronic conductivities; ionic conduction came from H^+ and $-COO^-$ on PAC because PAC was only a weak polyelectrolyte. The ionic conductivity of the pure swollen PAC hydrogel was measured as 2.3×10^{-4} S/cm or less, which was much lower than that for the PAC/PPy hydrogel (at least 5.5 mS/cm), as shown in Figure 3. Therefore, the conductivity of the PAC/PPy hydrogel mainly resulted from the electronic conduction by the PPy compo-

Figure 4 Conductivity of the PAC/PPy hydrogel versus the temperature (preparation conditions: molar ratio of $FeCl_3$ to Py = 2.0, mass ratio of PAC to Py = 20, concentration of $FeCl_3$ = 0.050M, and reaction at 20°C for 6 h).

nent. The result was consistent with conducting hydrogels consisting of polyaniline nanoparticles and pyrrolidone,[33] polyaniline–polyacrylamide, and polyaniline–poly(2-acrylamido-2-methyl propanesulfonic acid) semi-IPN hydrogels.[34]

Figure 4 shows the influence of the temperature on the conductivity of the PAC/PPy hydrogel. The conductivity of the hydrogel rose with increasing temperature. The conductivity–temperature behavior [$\sigma(T)$] of the conducting hydrogel could be described by the Arrhenius equation:

$$\sigma(T) = A \exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

where E_a is the activation energy, R is the molar gas constant, A is a constant, and T is the absolute temperature. According to the experimental data and eq. (3), E_a was calculated as 0.99 eV, and A was 17.12. The Arrhenius behavior of the conductivity with an activation energy value of 0.99 eV suggested that conduction was due to charge carriers hopping along the PPy conjugated chains rather than to the cooperative motions of polymer chains.[31]

Release of PPy from the PAC/PPy hydrogel

To study the stability of the hydrogel and the release of PPy from the PAC/PPy hydrogel, 5 g of the hydrogel sample was immersed in 500 mL each of acidic, neutral, and alkaline aqueous solutions with pH values of 2.5, 6.8, and 11.5, respectively. The release amount of PPy from the PAC/PPy hydrogel was measured with a Shimadzu UV-3100 UV–vis IR spectrophotometer at a λ_{max} of 450 nm for pure PPy.[35] The amount of PPy released from the
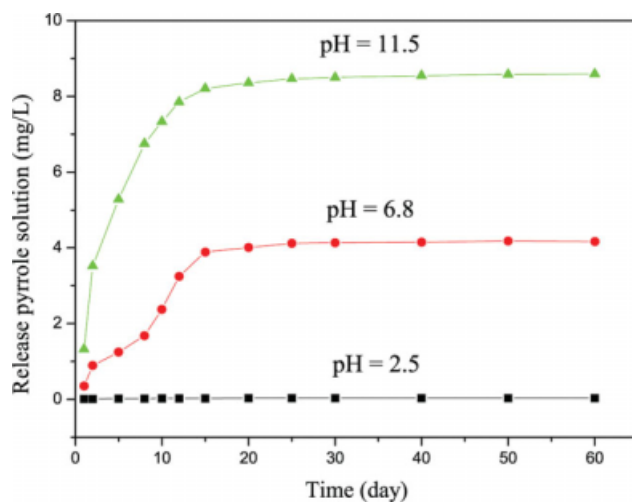
Figure 5 Py release from the PAC/PPy hydrogel in solutions with different pH's (preparation conditions: molar ratio of FeCl$_3$ to Py = 2.0, mass ratio of PAC to Py = 20, FeCl$_3$ concentration = 0.050M, and reaction at 45°C for 5 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydrogel was evaluated by the absorbency of solutions and a working curve.

The PPy release amount into surrounding solutions with various pH values was measured and is plotted in Figure 5. There was little PPy release when the PAC/PPy hydrogel was immersed in the acidic aqueous solution. In acidic conditions, such as at pH 2.5, the anionic —COO$^-$ group on PAC with a high hydrophilicity was protonated and changed into a relatively low-hydrophilic —COOH group. Furthermore, Cl$^-$ ions shielded the charge of the —NH$_2^+$— on PPy. On the basis of these reasons, the hydrogel network collapsed and shrank, as illustrated in Figure 2. On the other hand, the hydrogen bond between —COOH and —NH$_2^+$— dramatically increased; this enhanced the crosslinkage of the hydrogel to a certain extent.[36,37] The shrinkage of the hydrogel network and the hydrogen bond interaction prevented PPy from being released from the PAC/PPy hydrogel. With increasing pH to 6.8, the —COOH and —NH— groups on the PAC/PPy hydrogel were not ionized, which resulted in swelling of the hydrogel and the breakage of partial hydrogen bonds; thus, PPy was released with prolonged immersion time. With further increases in pH up to 11.5, the —COOH group ionized to a —COO$^-$ group, and —NH$_2^+$— changed to —NH—; this increased the electrostatic repulsion for —COO$^-$ groups on the PAC network. Additionally, the hydrogen bond between the two components decreased. These factors accelerated the diffusion of PPy from the expanded PAC/PPy hydrogel.

The conductivity of the hydrogel was measured to study PPy release from the PAC/PPy hydrogel.

Before measurements of conductivity, the hydrogel samples were rinsed several times with deionized water to reduce the influence of ions. The dependence of the conductivity of the hydrogel on time immersed in acidic, neutral, and alkaline solutions is shown in Figure 6. With increasing pH value for the surrounding solution, the conductivity of the PAC/PPy hydrogel decreased. This was because the PPy chains diffused out from the PAC/PPy hydrogel network, and the electronic conductivity decreased gradually, especially at pH 11.5, which was consistent with Figure 5.

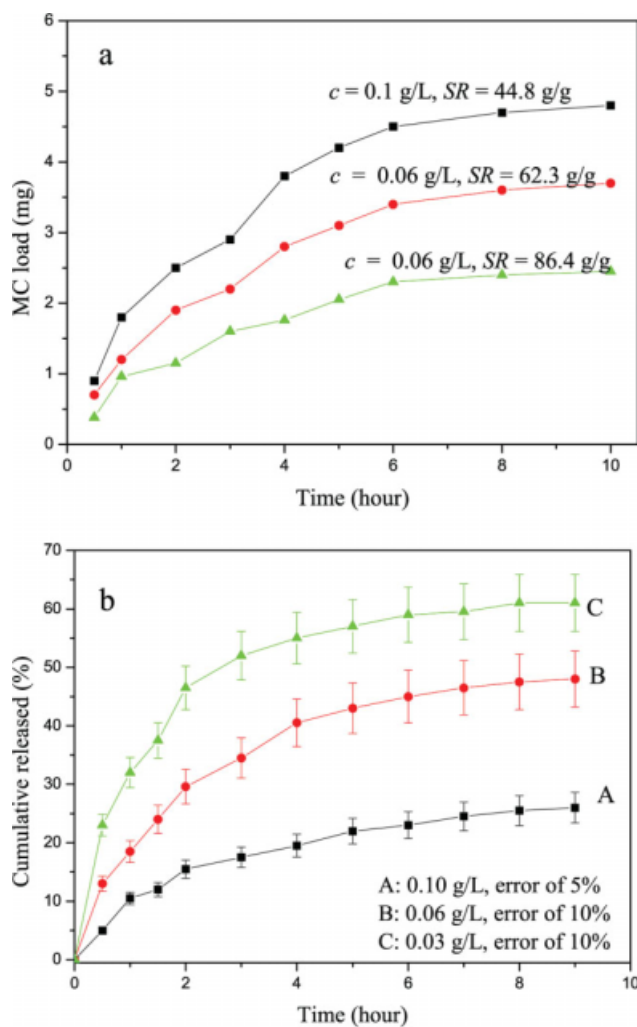## Load and release of MC from the PAC/PPy hydrogel

The PAC/PPy hydrogel possessed semipermeable membrane properties; this enables possible use in drug-release applications. With MC as targets, the load and cumulative release of MC were measured.

Figure 7(a) shows the MC load in the PAC/PPy hydrogel in different loading solutions. The MC loaded amount increased with prolonged loading time and finally reached equilibrium. For the same hydrogel and time, the MC load increased with increasing MC concentration in the solution. It is understandable that higher MC concentration led to more MC penetration into the PAC/PPy hydrogel because of the semipermeable membrane properties of the PAC/PPy hydrogel. The SRs of the hydrogels decreased with increasing MC concentration in solution, which was the result of the salt resistance of the ionic hydrogel.[38]

Figure 7(b) shows the cumulative release of MC from the PAC/PPy hydrogel. The hydrogel with the
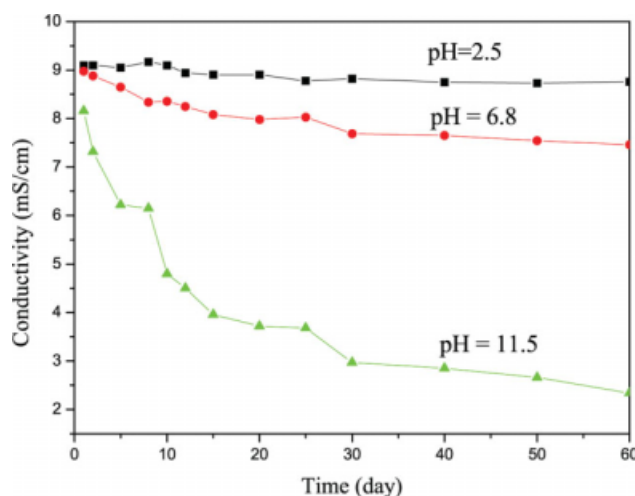
Figure 6 Conductivity of the PAC/PPy hydrogel in solutions with different pH's (preparation conditions: molar ratio of FeCl$_3$ to Py = 2.0, mass ratio of AA to Py = 20, FeCl$_3$ concentration = 0.050M, and reaction at 45°C for 5 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 MC (a) load and (b) release profiles for the PAC/PPy hydrogel in MC concentrations (c) of 0.1, 0.06, and 0.03 g/L at 37°C (preparation conditions: molar ratio of FeCl$_3$ to Py = 2.0, mass ratio of PAC to Py = 20, FeCl$_3$ concentration = 0.050M, and reaction at 45°C for 5 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

smaller MC load presented faster release than those hydrogels with larger MC loads. As shown in Figure 7(a), the smaller MC load meant a higher SR for the hydrogel, the hydrogel had a looser space, and loaded MC was easy to release from the hydrogel; this resulted in a faster release rate and a higher release percentage.

CONCLUSIONS

A PAC/PPy semi-IPN hydrogel was prepared by a two-step aqueous polymerization. First, the PAC superabsorbent polymer was synthesized by a routine aqueous polymerization. Second, the Py monomer was absorbed into the PAC network followed by *in situ* polymerization to form a PAC/PPy hydrogel. The optimal synthesis conditions were as fol-

lows: molar ratio of FeCl$_3$ to Py = 2.0, mass ratio of AA to Py = 20, FeCl$_3$ concentration = 0.050M, polymerization temperature = 45°C, and reaction time = 5 h.

Because of the bifunctional groups —NH— and —COOH on PAC/PPy, the PAC/PPy hydrogel exhibited predominantly pH-sensitive swelling. The hydrogel showed two sharp water absorption peaks at pH 4–6 and pH > 11. A typical on–off behavior was found at acidic and basic conditions with the pH sensitivity.

On the basis of the PPy conjugated chains, the PAC/PPy hydrogel possessed a conductivity of 9.1 mS/cm under the optimal conditions, and the hydrogel basically kept its conductivity in acidic and neutral media.

On the basis of the loose semipermeable membrane structure, the PAC/PPy hydrogel possessed load and release functions. The hydrogel with the smaller MC load presented a faster release than those hydrogels with larger MC loads.

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