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Carbohydrate Polymers 73 (2008) 315–321

Carbohydrate Polymers

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# A multifunctional hydrogel with high conductivity, pH-responsive, thermo-responsive and release properties from polyacrylate/polyaniline hybrid

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Received 2 November 2007; received in revised form 24 November 2007; accepted 26 November 2007
Available online 5 December 2007

## Abstract

Polyacrylate/polyaniline (PAC/PANI) hybrid was synthesized by a two-step aqueous polymerization method, which aniline monomer was absorbed in the network of polyacrylate and followed by a polymerization reaction between aniline monomers. The PAC/PANI hydrogel possessed a conductivity of 2.33 mS cm$^{-1}$. A conduction mechanism with charge carriers (protons) hopping along the polyaniline chain was suggested. The PAC/PANI hydrogel had predominant pH- and thermo-sensitive properties. The hydrogel showed two sharp water adsorbed peaks at pH 4–6 and pH $> 12$. The swelling sensitive temperature of PAC/PANI hydrogel was about 30 °C. PAC/PANI hydrogel possessed loading and releasing properties. The release obeyed an anomalous mechanism.

*Keywords:* Polyacrylate/polyaniline; Conducting hydrogel; pH-responsive swelling; Thermo-responsive swelling; Release property

## 1. Introduction

Superabsorbent polymers have stronger hydrophilic groups and lightly crosslinked network structure (Wu et al., 2006). Not only it is able to absorb a large amount of water to form a stable hydrogel, but also the absorbed water is hardly removed under some pressure. About three decades ago (Omidian, Rocca, & Park, 2005), superabsorbent polymers were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where an excellent water holding property was prime importance. Recently, many researches focus on the superabsorbent polymer for developing new applications, such as, conducting materials, sensors and release materials, biomaterials, wave-absorbing materials (Abd El-Rehim, 2005; Dispenza, Presti, Belfiore, Spadaro, & Piazza, 2006; Ito et al., 2003; Lee & Chen, 2005; Li, Guo, Wei, MacDiarmid, & Lelkes, 2006; Richter, Howitz, Kuckling, & Arndt, 2004; Siddhantaa & Gangopadhyay, 2005; Wada, Nohara, & Iwakura, 2004; Wu, Lin, & Zhou, 2000; Wu, Wei, Lin, & Lin, 2003; Wu et al., 2006), it is expected to prepare a multifunctional superabsorbent material to meet applications requirement by modifying, grafting, copolymering and other methods.

Here, polyaniline is integrated with polyacrylate to form polyacrylate/polyaniline (PAC/PANI) hybrid and hydrogel. Polyaniline is a typical conducting polymer. Polyacrylate is a superabsorbent polymer, its swelling behavior is sensitive to the pH value and temperature, thus the resulted polyacrylate/polyaniline hydrogel possess conductivity, pH- and thermo-sensitivity. Furthermore, the hydrogel have porous structure and hydrophilic groups, which endows the hydrogel with a controlled release property. In this way, a multifunctional hydrogel can be obtained, the multifunctional hydrogel is likely to be used as conducting materials, sensors, release materials and biomaterials (Abd El-Rehim, 2005; Li et al., 2006; Richter et al., 2004; Siddhantaa & Gangopadhyay, 2005; Wada et al.,

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doi:10.1016/j.carbpol.2007.11.036

2004). In this paper, polyacrylate/polyaniline hybrid was synthesized by two-step aqueous polymerization. Meanwhile, the pH-responsive swelling, temperature-responsive swelling and release property for PAC/PANI hydrogel was investigated.

## 2. Experiment

### 2.1. Materials

Acrylic acid monomer (AA) and aniline monomer (ANI) was reduced distilled prior to use, respectively. Potassium hydroxide was used to neutralize acrylic acid monomer and produce potassium acrylate (AC). Potassium persulfate (KPS) was purified by recrystallization from 66 wt% ethanol/water solution before being used, which was used as a radical initiator for the polymerization reaction of polyacrylate (PAC) and polyaniline (PANI). *N*,*N*′-methylene bisacrylamide was used as a crosslinker for preparation of PAC.

### 2.2. Preparation of polyacrylate superabsorbent polymer

Polyacrylate superabsorbent polymer was prepared by modifying the procedure from reference (Lin, Wu, Yang, & Pu, 2001; Tang, Lin, & Wu, 2007; Wu, Lin, Li, & Wei, 2001). A mixed solution of AA monomer, potassium acrylate, crosslinker was made by agitating AA monomer (15 g), crosslinker (*N*,*N*′-methylene bisacrylamide, 0.006 g), potassium hydroxide (7 g, to partially neutralize acrylic acid) in distilled water (15 ml) at ambient temperature. Under a nitrogen atmosphere, the mixture solution was stirred and heated to 80 °C in a water bath for 15 min, and then the initiator potassium persulfate (0.15 g) was added, the reaction system was stirred for a few minutes until the polymerization reaction completed. A jell-like intermediate product was filtered through Whatman filter paper No. 54 and then immersed in excess distilled water to remove any impurities. After vacuum drying at 80 °C for more than 3 h to constant weight, milled and sifted using a 40-mesh screen, a powdered PAC superabsorbent polymer thus was obtained.

### 2.3. Preparation of PAC/PANI

Using the PAC superabsorbent polymer, a polyacrylate/polyaniline (PAC/PANI) was prepared according to following procedure. Under vigorous agitating, 5 g of PAC superabsorbent polymer powdered was immersed in a predetermined amount ANI aqueous solution at ambient temperature for 30 min, which resulted in the absorption of ANI monomer inside of the PAC network and the formation of a swollen sample. The swollen sample was dispersed in a solution of 100 ml containing a suitable amount of initiator potassium persulfate, which caused an in situ polymerization between ANI monomers and formed PANI inside the network of PAC. The polymerization reaction took place at room temperature. After that, similar to the preparation of PAC superabsorbent polymer, the intermediate product was filtrated, washed, dried, milled and sifted, finally a PAC/PANI hybrid powder thus was obtained.

### 2.4. The measurement of swelling property of PAC/PANI

The swelling ratio is the criterion of describing water absorption capacity. The measurement of the swelling ratio of PAC/PANI was conducted by a tea-bag method, and using distilled water as liquids to be absorbed. The tea bags used in the method was made of 40 meshes nylon net. The weight of the wet nylon net was measured and marked as $W_n$. The weight of dry PAC/PANI was marked as $W_d$. After weighing, the test sample was placed into the tea-bag, then the tea-bag with sample inside was suspended and fully immersed into distilled water 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 swollen sample was measured and marked as $W_t$. The swelling ratio of PAC/PANI was calculated according to the follow equation:

$$\text{Swelling ratio(SR)(g/g)} = \frac{(W_t - W_d - W_n)}{W_d} \quad (1)$$

### 2.5. The measurement of conductivity of PAC/PANI hydrogel

The dry powdered PAC/PANI hybrid of 3 g was immersed in excessive distilled water at room temperature for at least 3 h to reach swelling equilibrium, which resulted in the absorption of water inside of the network of the PAC/PANI hybrid and the formation of a semitransparent PAC/PANI hydrogel. The unabsorbed water was removed by filtrating over a 40-mesh nylon net and hanging up for 25 min. The electrical conductivity of the PAC/PANI hydrogel was measured by inserting a Pocket Conductivity Meter (HANNA8733) in a cylinder containing the PAC/PANI hydrogel of 30 g.

### 2.6. The measurement of pH-sensitive properties of PAC/PANI hydrogels

Buffer solutions with pH 1–14 were used to study the pH-sensitivity swelling of PAC/PANI hydrogel. The desired basic and acidic pHs were adjusted by NaOH and HCl solutions, respectively. The pH values were precisely checked by a pH-meter (Leici/E-201-C, accuracy ± 0.01). Then, 0.50 g of dried sample was used for the swelling measurements in buffers according to the above method described in Section 2.4.

### 2.7. The measurement of temperature-sensitive properties of PAC/PANI hydrogel

The thermo-sensitive swelling of the PAC/PANI hydrogels under different temperatures was studied in distilled water in term of swelling ratio as a function of temperature. The swelling ratio of PAC/PANI hydrogel was measured after reaching a measuring temperature for 30 min. About 0.50 g of dried sample was used for measuring the swelling ratio of sample according to the above method described in Section 2.4.

### 2.8. Drug loading and release

The drug loaded and released property was evaluated by using methylrosaniline chloride as drug target. PAC/PANI dried samples were immersed in the drug target aqueous solution with different concentrations (0.03, 0.06 and 0.10 mg/ml) for 12 h at room temperature. The loaded and released amount were determined spectrophotometrically ($\lambda = 270 \pm 1$ nm) with a UV-3100 UV–vis–IR spectrophotometer (Shimadzu Corporation, Japan). The regression equation of methylrosaniline chloride solution working curve was $A = 45.45\ c = .022$, $r = .9994$.

### 2.9. FTIR spectra

The sample was identified by IR spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets.

## 3. Results and discussion

### 3.1. FTIR spectrum of PAC/PANI hybrid

The PAC/PANI hybrid was characterized by FTIR spectrum. In Fig. 1, the absorption peak at 3331 $\text{cm}^{-1}$ belongs to a N—H bending, 2946 $\text{cm}^{-1}$ ascribes to a —$CH_2$— stretching, 1710 $\text{cm}^{-1}$ attributes to a C=O bending and 1123 $\text{cm}^{-1}$ belongs to a C—H bending of polyacrylate, respectively. The absorption peak at 1565 $\text{cm}^{-1}$ is due to a quinoid ring stretching, 1491 $\text{cm}^{-1}$ attributes to benzene ring stretching, 1298 $\text{cm}^{-1}$ and 1235 $\text{cm}^{-1}$ are stretching vibrations for N—H connecting between benzene ring and quinoid ring and between benzene ring and benzene ring of polyaniline, respectively. The results indicate the formation of PAC/PANI hybrid.

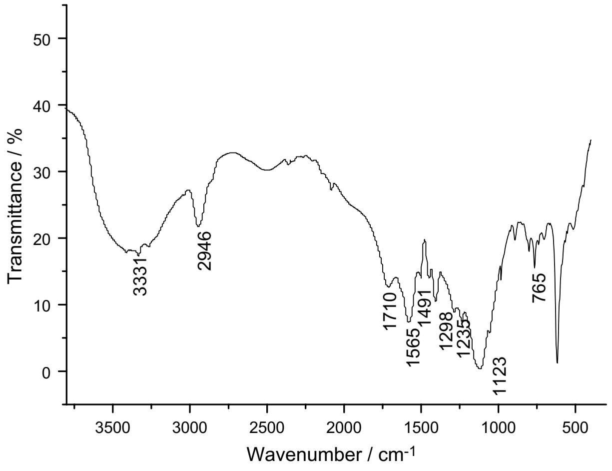

Fig. 1. FTIR spectrum of polyacrylate/polyaniline hybrid.

### 3.2. Influence of preparation conditions on the conductivity of hydrogel

A suitable mass ratio of AC to ANI is crucial for the conductivity of PAC/PANI hydrogel. As is shown in Fig. 2a, with the increase of mass ratio of acrylic acid monomer to aniline monomer, the conductivity of the hydrogel increases gradually, and then decreases after reaching a highest conductivity of 2.33 mS $\text{cm}^{-1}$ with the mass ratio of acrylic acid to aniline of 12. Obviously, a higher mass ratio of acrylic acid to aniline means lower concentration of aniline, which causes a polyaniline chain weakening. A lower mass ratio of acrylic acid to aniline also cannot absorb enough aniline monomer inside of polyacrylate network to construct a suited polyaniline chain, due to the osmosis character of aniline monomer and polyacrylate network. Above two cases cannot form an interpenetrating network to conduct electrons and bring to the decrease of conductivity of the hydrogel.

The polyaniline chain is formed inside of the polyacrylate network in aqueous solution system based on the polymerization reaction (reactions I and II). The concentration of aniline affects the reaction (II) and the conductivity of hydrogel. From Fig. 2b, it can be seen that the concentration of aniline an increase from 0.63 wt% to 1.0 wt% causes the conductivity to increase, beyond the concentration of 1.0 wt%, the conductivity decrease.

$$N(\text{acrylate}) \xrightarrow[\text{first polymerization}]{\text{crosslinker+initiator}} \text{polyacrylate} \tag{I}$$

$$N(\text{aniline}) + \text{polyacrylate} \xrightarrow[\text{second polymerization}]{\text{initiator}} \text{polyacrylate/polyaniline} \tag{II}$$

According to the mass law, a lower aniline concentration causes a slower velocity for the second polymerization reaction between aniline monomers, a lower polyaniline yield, and a lower conductivity. On the other hand, due to the osmosis character of aniline monomer and polyacrylate network, only part aniline monomers penetrate into polyacrylate network and polymerize to form polyaniline chain. Under a higher aniline concentration, mostly aniline monomers and oligomer exist outside of polyacrylate network, and are washed out in the preparation process. Consequently, higher aniline concentrations do not produce a higher polyaniline chain density in the network of polyacrylate and a higher conductivity. In our experiment conditions with the aniline monomer concentration of 1.0 wt%, the hydrogel possesses a highest conductivity.

### 3.3. Conductivity mechanism of the hydrogel

Compared the conductivities of the hydorgels and in their corresponding filtrate liquids in Fig. 2. Obviously,

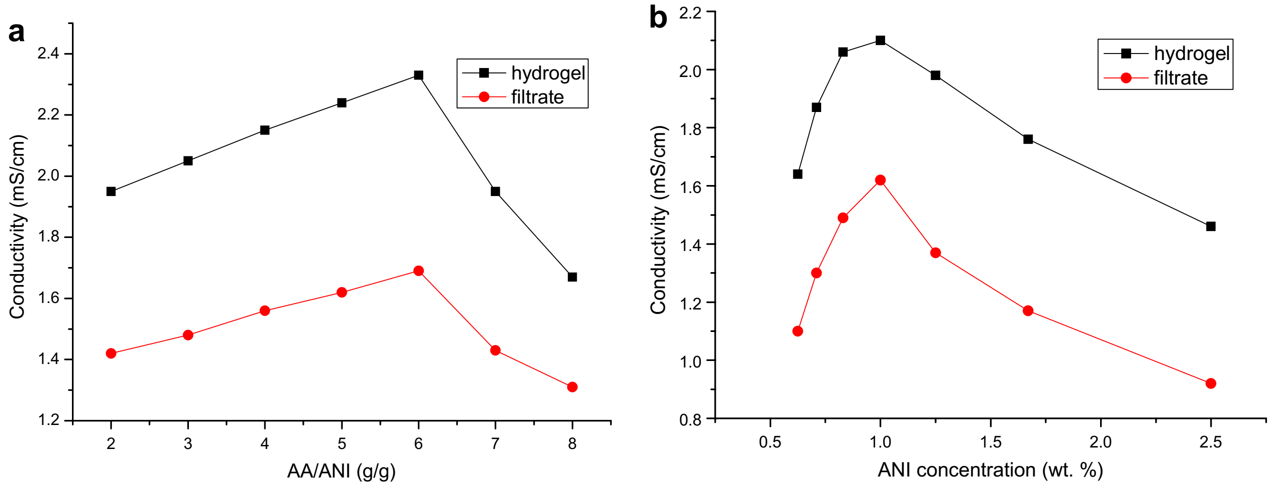

Fig. 2. Influence of preparation conditions on the conductivity of the hydrogel: (a) The ratio of AA to ANI at ANI concentration = 1.0 wt%; (b) ANI concentration at ratio of AA to ANI = 8 (Preparation conditions: Mass ratio of KPS to ANI 1.0, react at 20 °C for 6 h).

the conductivity of the PAC/PANI hydrogels are higher than that of their corresponding filtrate, which suggests that the conductivities of hydrogels mainly come from the polyaniline china (by protons hoping) in the interpenetrating networks structure of PAC/PANI, instead of the liquid in hydrogel (by ions hoping) in our conditions.

On the other hand, from Fig. 2, the conductivity of the hydrogel evidently depends on the ratio of aniline monomer and the concentration of aniline monomer, which implies that aniline chain play an important rule in the conductivity of the hydrogel, in other words, the aniline chain in the interpenetrating networks structure of PAC/PANI govern the conductivity of the hydrogel.

The dependence of temperature on the conductivity of the hydrogel shows that the conductivity rises with the increase of temperature (Fig. 3). The conductivity-temperature behavior of the PAC/PANI hydrogel can be described by Arrhenius equation.

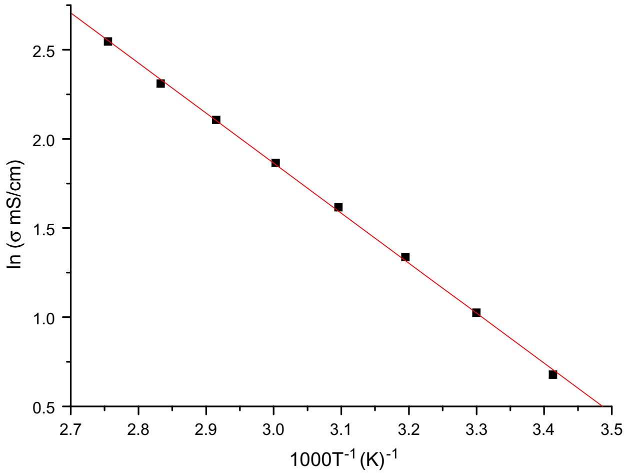

Fig. 3. The conductivity–temperature relationship of hydrogel (preparation conditions: Mass ratio of AA to ANI 12, mass ratio of KPS to ANI 1.0, ANI concentration 1.0 wt%, react at 20 °C for 6 h).

$$\sigma(\mathrm{T}) = A\exp\left[\frac{-E_{\mathrm{a}}}{R}T\right] \tag{2}$$

where $E_a$ is the activation energy, $R$ is the molar gas constant, $A$ is a constant, and $T$ is absolute temperature. According to the experimental data, the $E_a$ is calculated as 0.225 eV and the $A$ is 14.88. The Arrhenius behavior of conductivity, with an activation energy value of 0.225 eV suggests that conduction is due to charge carriers (protons) (Konsta, Daoukaki, Pissis, & Vartzeli, 1999) hopping along the polyaniline chain rather than to cooperative motions of polymer chains.

### 3.4. Swelling behaviors responding to pH and temperature

The swelling of PAC/PANI hydrogel was investigated at different pHs ranged from 1.0 to 14.0. The result is shown in Fig. 4a. From Fig. 4a, PAC/PANI do not possess the maximum of swelling ratio at pH 7, which is different from the cross-linked polyacrylate that is researched most universally. This is due to that PAC/PANI is consisted of polyacrylate and polyaniline, and polyaniline shows an ampholyte and alkalescence. The two sharp water absorbent peaks can be ascribed to high repulsion of $=\mathrm{NH}^{+}-$ group on the polyaniline chine in acidic media and $-\mathrm{COO}^{-}$ group on the polyacrylate networks in basic media. The repulsion action between these groups promote the swelling of hydrogel and cause a higher swelling ratio. Moreover, due to stronger repulsion force between $-\mathrm{COO}^{-}$ groups than between $=\mathrm{NH}^{+}-$ groups, higher swelling ratio is shown in basic media than in acidic media.

At very acidic condition ($\mathrm{pH} < 3$), a screening effect of the counter ions, i.e. $\mathrm{Cl}^{-}$, shields the charge of the cations ($-\mathrm{NH}^{+}-$) and prevents an efficient repulsion (Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004). Therefore, an obviously reduced final absorbency appears. Under this acidic condition, anionic carboxylate groups are protonated, so the polymeric network collapsed. At

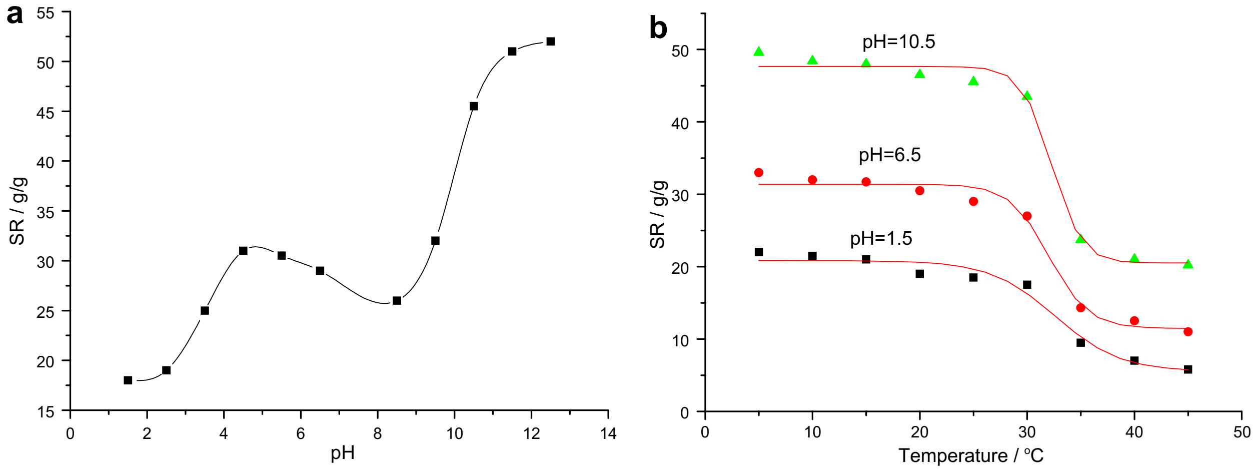

Fig. 4. Dependence of swelling ratio (SR) of the hydrogel on (a) pH at 25 °C and (b) temperature (Samples prepared conditions was the same as Fig. 3).

about pH 4.5, the carboxylic acid component comes into action as well. Since the p$K_a$ of the aniline monomer is about 5.3, its ionization occurs above this value. That may enhance absorbency. However, in pH range 6–8 closed with neutrality, most base and acid groups are non-ionization, so H-bonding between amine and carboxylic acid or carboxamide groups may result in a kind of cross-linking followed by a decreased swelling. With farther increase of pH, ionization of carboxylic acid groups happens, and the electrostatic repulsive force between the —COOK groups leads to high swelling. Analogous viewpoints were reported in the poly(aspartic acid) (Zhao, Su, Fang, & Tan, 2005) and chitosan-*g*-poly (AA-co-AAm) systems (Konsta et al., 1999).

### 3.5. Swelling behaviors responding to temperature

It is well known that the hydrogels with suitable hydrophilic–hydrophobic balance may exhibit thermosensitivity, i.e. sharp decrease in volume in aqueous environment with high temperature. Fig. 4b shows the temperature-dependant swelling of PAC/PANI hydrogels when media temperature increases from 5 to 45 °C. It can be seen that the swelling ratio decreases with the increase of temperature in the region of 30–45 °C. Swelling behavior of the hydrogel depended on temperature is ascribed to the intramolecular hydrophobic interaction, the H-bonding with water (Dergunov, Nam, Doldina, & Nurkeeva, 2004), and the porosity (Mahdavinia et al., 2004) of the hydrogel.

From the thermodynamics aspects, the $\Delta H$ that water molecules enter the networks of polymer and cause a hydrogel swelling is negative due to the formation of hydrogen bond, and $\Delta S$ for the hydrogel swelling is also negative for the formation of cage structures and enhancement of the ordered degree of water molecules. According to $\Delta G = \Delta H - T\Delta S$, increasing temperature is disadvantageous for the swelling of hydrogel. If $T = T_C$, $\Delta G = 0$; $T > T_C$, $\Delta G > 0$, which results in a deswelling and a decrease of the hydrogel volume.

Swelling temperature-sensitive property is studied on the hydrogel swelling kinetics. Fig. 5 represents the dynamic swelling behavior of a PAC/PANI hydrogel in water. It can be found that water uptake depended linearly on $t^{1/2}$ ($r^2 > .99$) for all the hydrogels studied, i.e. Fickian behavior is maintained in spite of the swelling of the polymer network. The slope for PAC/PANI hydrogels at 5, 25 and 37 °C is 1.37, 1.23 and 0.46, respectively. Nevertheless, the high values in three cases shows that water molecules easily penetrate the free pore volume. Similar phenomena also were reported in polyquaternium-4 (PQ-4) and polyquaternium-10 (PQ-10) systems (Rodriguez, Alvarez-Lorenzo, & Concheiro, 2003). The faster swelling velocity constant for the PAC/PANI hydrogel from the slope at lower temperature than that at higher temperature suggests that the swelling depends on the diffusion of water molecules, and the interaction between the water molecules and PAC/PANI matrix.

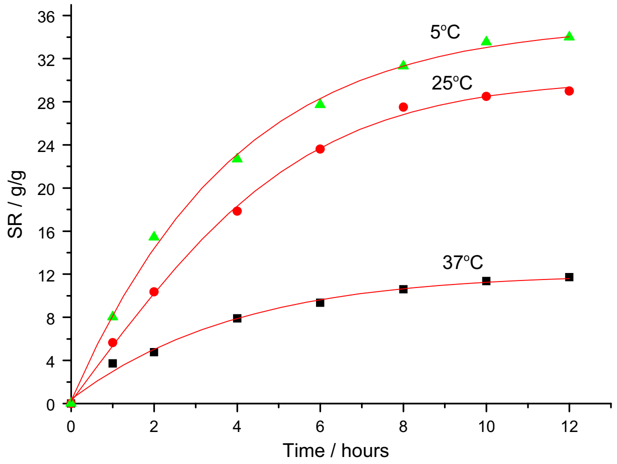

Fig. 5. Dependence of SR on time at pH of 6.5 (Samples prepared was the same as Fig. 3).

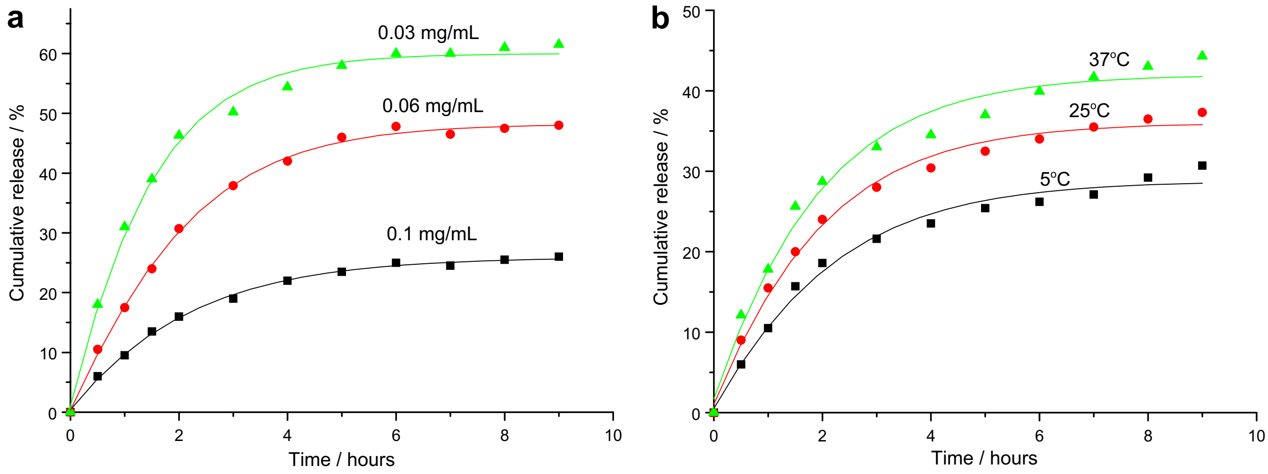

Fig. 6. Methylrosaniline chloride release (a) under different loaded amount and at 25 °C (b) under different temperature at loaded 0.06 mg/ml (pH at 6.5, samples prepared was the same as Fig. 3).

### 3.6. Methylrosaniline chloride loading and releasing

The PAC/PANI possesses porous structure and the property of semipermeable film (Tang et al., 2007; Wu et al., 2001), which is possible to be used in drug load and release. Using methylrosaniline chloride with different concentrations as targets, the cumulative release of methylrosaniline chloride at different loading amount were measured and shown in Fig. 6a.

The influence of temperature on drug release is shown in Fig. 6b, it can be seen that with the increase of temperature, the cumulative release amount and release velocity increase. This is due to that a higher temperature makes a higher kinetic energy of methylrosaniline chloride molecule and weakens the interaction between matrix and methylrosaniline chloride molecules.

Modeling of the controlled release from polymeric devices has been the subject of considerable research over the past 25 years (Stephens, Li, Robinsona, Chen, & Chang, 2000). Higuchi derived a simple relationship that described drug release from a matrix as a function of time Eq. (3) (Higuchi, 1963).

$$\frac{M_t}{M} = kt^{1/2} \tag{3}$$

where $M_t$ and $M_\infty$ are the masses of drug released when the time equals $t$ and $\infty$, respectively. It can be considered that the release of the drug is linear with the square roots of time.

Peppas extended the Higuchi model to a more generalized form:

$$\frac{M_t}{M} = kt^n \tag{4}$$

where $n$ is the diffusional exponent. Information about the release mechanism can be gained by fitting the release data (for the first 60% dissolved) and comparing the values of $n$ to the semi-empirical values for various geometries reported by Peppas (Peppas & Ritger, 1987). For a cylindrical geometry, value of $n$ of .45 (or less) is corresponding to a pure Fickian diffusion mechanism. Value of $n$ greater than .89 indicates a relaxation controlled-release mechanism, and $n$ value between .45 and .89 indicates an anomalous release mechanism. Despite the approximations, it is found that these relationships could be applied to release data, indicating that the diffusion-based models of Higuchi and Peppas describe drug release from a polymeric system quite well.

According to Eq. (4) and Fig. 6a, the relationship between $\ln M_t$ on $\ln t$ was made and the result is shown in Fig. 7. The diffusional exponent $n$ values for .10, .06 and .03 mg/mL are .62, .58 and .46, respectively. Diffusional exponent $n$ values for PAC/PANI hydrogel with different loading amount between .45 and .89 indicate an anomalous release mechanism, which may be the result of cooperate effect, including the methylrosaniline chloride concentration difference between the exterior and the interior of PAC/PANI hydrogel, and the interaction between methylrosaniline chloride and PAC/PANI matrix. The higher

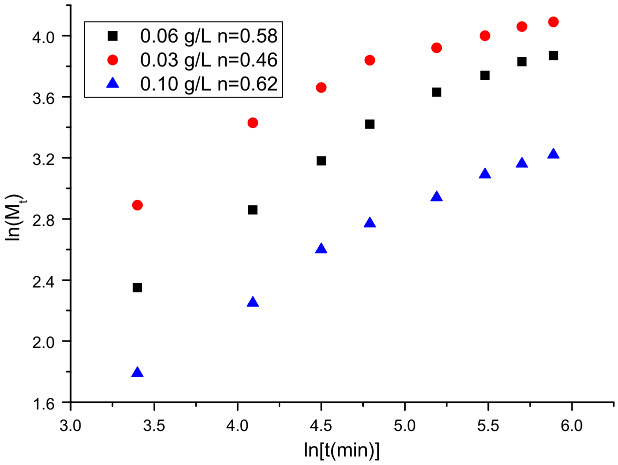

Fig. 7. The relation of $\ln M_t$–$\ln t$ for polyacrylate/polyaniline hydrogel with different loading amount.

*n* value for higher methylrosaniline chloride concentration indicates that the interaction is enhanced further.

## 4. Conclusions

Polyacrylate/polyaniline (PAC/PANI) polymer was prepared by a two-steps aqueous polymerization. Firstly, the polyacrylate superabsorbent polymer was synthesized by a routine aqueous polymerization. Secondly, aniline monomer was absorbed inside of polyacrylate network, then, PAC/PANI hybrid was prepared by a polymerization reaction. When immersed the PAC/PANI hybrid in distilled water, a hydrogel with a conductivity of $2.33\ \mathrm{mS\ cm^{-1}}$ was obtained. The researches on the conductivity of filtrate liquid and the Arrhenius behavior of conductivity of the hydrogel suggest that the conduction is due to charge carriers (protons) hopping along polyaniline chain. Due to the bifunctional groups —NH— and —COOH in PAC/PANI, the PAC/PANI hydrogel has predominant pH- and thermo-sensitive swelling properties. The hydrogel shows two sharp water absorbent peaks at pH 4–6 and $\mathrm{pH} > 12$. The sensitive temperature of PAC/PANI hydrogel to swelling is about 30 °C. Based on the porous structure, the PAC/PANI hydrogel possesses loading and releasing property. Diffusional exponent *n* values for PAC/PANI hydrogels between .45 and .89 indicates an anomalous release mechanism, which may be due to the concentration difference between the exterior and the interior of PAC/PANI hydrogel, and the interaction between methylrosaniline chloride and PAC/PANI matrix.

## Acknowledgements

The authors thank for jointly support by the National Natural Science Foundation of China (No. 50572030 and No. 50372022), the Key Scientific Technology Program of Fujian, China (No. 2005HZ01-4 and No. 2007HZ0001-3), the Key Project of Chinese Ministry of Education (No. 206074) and Specialized Research Fund for the Doctoral Program of Higher Education (No. 20060385001).

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