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Two-steps synthesis of a poly(acrylate–aniline) conducting hydrogel with an interpenetrated networks structure

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Abstract

A two-steps aqueous polymerization method is used to prepare poly(acrylate–aniline) conducting hydrogel. When the preparation conditions for the second step were optimized as mass ratio of acrylic acid monomer to aniline monomer 12, mass ratio of initiator to aniline monomer 1.0, concentration of aniline 1.0 wt%, reaction at 20 °C for 6 h, the hydrogel with water absorbency of 150 times possessed a conductivity of 2.33 mS cm^{-1}. The influence of initiator, aniline monomer, acrylic acid monomer, reaction temperature and time on the conductivity of hydrogel was investigated. An interpenetrated networks structure model with a three-dimensional network of polyacrylate and a one-dimensional chain of polyaniline for poly(acrylate–aniline) conducting hydrogel was proposed.

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Keywords: Poly(acrylate–aniline); Conducting hydrogel; Two-steps aqueous polymerization; Interpenetrated network structure; Superabsorbent polymer

1. Introduction

Conducting hydrogel is a novel functional material that has been developing recently. It is possible to be used as conducting film, coating, sensor, conducting fiber, wave-absorbing material and so on (Ali, 2006; Emirkhanian et al., 2006; Li, Guo, Wei, MacDiarmid, & Lelkes, 2006). The conducting hydrogel often was prepared by copolymerizing or doing conducting materials with/to hydrophilic monomers/polymers (Aouada et al., 2006; Dispenza, Presti, Belfiore, Spadaro, & Piazza, 2006; Gyurcsányi, Rangisetty, Clifton, Pendley, & Lindner, 2004). Based on a superabsorbent polymer polyacrylate, we developed a novel method with two-steps aqueous polymerization to prepare a conducting hydrogel.

Superabsorbent polymers have a network structure with a suitable degree of crosslinking (Lee & Chen, 2005; Wu, Lin, Zhou, & Wei, 2000; Zhang, Li, & Wang, 2006). Not only is it able to absorb hundred to thousand times its own mass of water to form a stable hydrogel, but the absorbed water is also hardly removed under some pressure. On the other hand, polyaniline is a polymer with higher conductivity. Based on the conductivity of polyaniline and the colloid stability of superabsorbent polymer, a copolymer conducting hydrogel with an interpenetrated networks structure can be formed by two-steps polymerizations. In this paper, the synthesis conditions of poly(acrylate–aniline) were optimized and an interpenetrated networks structure model with a three-dimensional network of polyacrylate and a one-dimensional chain of polyaniline for poly(acrylate–aniline) conducting hydrogel is proposed. Simple preparation procedure and higher conductivity for poly(acrylate–aniline) hydrogel make it possible to be used in the fields of coatings, sensors, conducting films and wave-absorbing materials.

2. Experiment part

2.1. Materials

Acrylic acid monomer and aniline monomer were distilled under reduced pressure prior to use, respectively.

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Potassium hydroxide was used to neutralize acrylic acid monomer to produce potassium acrylate. Potassium persulfate (KPS) was a radical initiator for the synthetic reaction of polyacrylate and polyaniline. *N*,*N*′-Methylene bisacrylamide, used as a crosslinker for preparation of polyacrylate, was purified by recrystallization from 66 wt% ethanol/water solution before using.

2.2. Preparation of polyacrylate superabsorbent polymer

Polyacrylate superabsorbent polymer was prepared by modifying the procedure from reference (Lin, Wu, Yang, & Pu, 2001; Wu, Lin, Li, & Wei, 2001; Wu, Zhong, Lin, Wei, & Xie, 2006). A mixed solution of acrylic acid monomer, potassium acrylate, crosslinker was made by agitating acrylic acid monomer (15 g), crosslinker (*N*,*N*′-methylene bisacrylamide, 0.006 g), potassium hydroxide (9.33 g) 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 (0.15 g) was added, the reaction mixture 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 drying under vacuum at 80 °C for more than 3 h to constant weight and milled and sifted using a 40-mesh screen, a powdered product polyacrylate superabsorbent polymer thus was obtained.

2.3. Preparation of poly(acrylate–aniline) conducting polymer

On the basis of the polyacrylate superabsorbent polymer, a poly(acrylate–aniline) conducting polymer was prepared according to the following procedure. Under vigorous agitation, 5 g powdered polyacrylate superabsorbent polymer was immersed in a predetermined amount of aniline aqueous solution at ambient temperature for 30 min, which resulted in the absorption of aniline monomer in the polyacrylate 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 a polymerization between aniline monomers and formed polyaniline inside the network of polyacrylate. The polymerization reaction took place at room temperature. After that, similar to the preparation of polyacrylate superabsorbent polymer, the intermediate product was filtered, washed, dried milled and sifted, finally a powdered poly(acrylate–aniline) conducting polymer thus was obtained.

2.4. Measurement and characterization

The powdered conducting polymer of 3 g was immersed in distilled water of 500 ml 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 conducting polymer and the formation of a conducting hydrogel. The unadsorbed water was removed by filtering over a 40-mesh stainless steel screen and hanging up for 25 min. The electrical conductivity of the hydrogel was measured by inserting a Pocket Conductivity Meter (HANNA8733) in a cylinder containing the conducting hydrogel (water absorbency about 150 times) of 30 g.

SEM photographs of the conducting hydrogel were taken using Hitachi S-5200 scanning electron microscope. The sample was identified by IR spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets.

3. Results and discussion

3.1. IR spectrum of poly(acrylate–aniline) conducting polymer

The conducting polymer was characterized by FT-IR spectrum. In Fig. 1, the absorption peak at 3331 cm^{-1} belonged to a N–H bending, 2946 cm^{-1} ascribed to a $-CH_2$-stretching, 1710 cm^{-1} attributed to a C=O bending and 1123 cm^{-1} belonged to a C–H bending of polyacrylate, respectively. The absorption peak at 1565 cm^{-1} belonged to a quinoid ring stretching, 1491 cm^{-1} attributed to benzene ring stretching, 1298 cm^{-1} and 1235 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 polyacrylate and polyaniline in the conducting hydrogel.

3.2. Influence of the amount of initiator on the conductivity of hydrogel

The conductivity of the conducting hydrogel depends on polyaniline chain, and the formation of the polyaniline

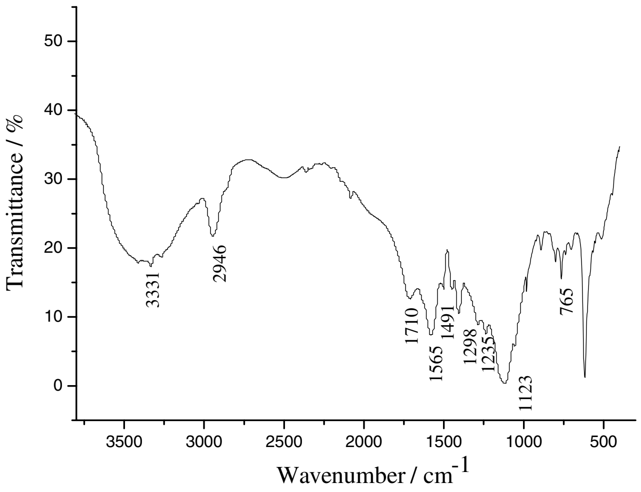

Fig. 1. FT-IR spectrum of the conducting hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 12, mass ratio of KPS to aniline 1.0, aniline concentration 1.0 wt%, reaction at 20 °C for 6 h).

chain is initiated by potassium persulfate (KPS), so the amount of initiator KPS affects the conductivity of the hydrogel. As are shown in Fig. 2, the electrical conductivity of the hydrogel increases with the increase of the mass ratio of KPS to aniline monomer in the range of 0.2–1.0, beyond a mass ratio of 1.0, the conductivity decreases. Clearly, a lower amount of KPS does not produce enough crosslink points to construct a polyaniline chain and a conducting channel, and results in the decline of the conductivity of the hydrogel. On the other hand, KPS is not only an initiator, but also an oxidizer, excessive KPS causes a side reaction for oxidizing polyaniline, which results in the devastation of the polyaniline chain to some extent, a conducting channel cannot run through the material effectively, therefore, the conductivity of the hydrogel decreases. According to Fig. 2, the mass ratio of KPS to aniline monomer 1.0 is the better.

3.3. Influence of aniline concentration on the conductivity of hydrogel

The polyaniline chain is formed inside of the polyacrylate network in aqueous solution system based on the polymerization reaction (Eqs. 1 and 2). The concentration of aniline affects the reaction (2) and the conductivity of hydrogel. From Fig. 3, it can be seen that the concentration of aniline an increase from 0.625 wt% to 1.0 wt% causes the conductivity to increase but beyond the concentration of 1.0 wt%, the conductivity decreases.

$$n(\text{acrylate}) \xrightarrow[\text{aqueous polymerization}]{\text{crosslinker+initiator}} \text{polyacrylate} \tag{1}$$

$$n(\text{aniline}) + \text{polyacrylate} \xrightarrow[\text{aqueous polymerization}]{\text{initiator}} \text{poly(acrylate–aniline)} \tag{2}$$

According to mass law, a lower aniline concentration causes a slower velocity for the polymerization reaction between aniline monomers, a lower polyaniline yield, and a lower conductivity. On the other hand, due to the osmosis character of aniline monomers 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 the highest conductivity.

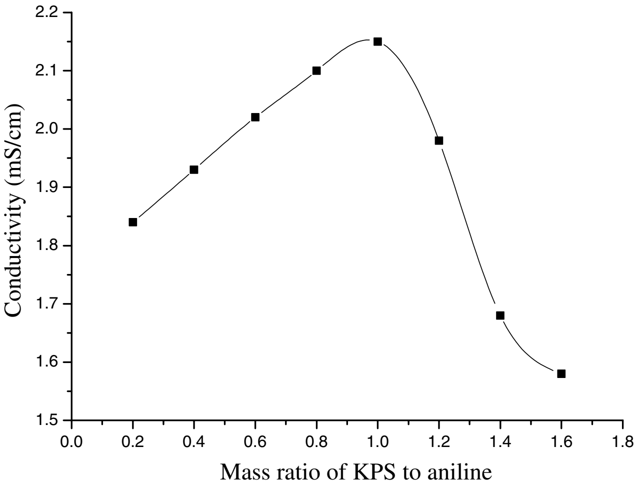

Fig. 2. The influence of KPS amount on the conductivity of hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 8, aniline concentration 1.0 wt%, reaction at 20 °C for 6 h).

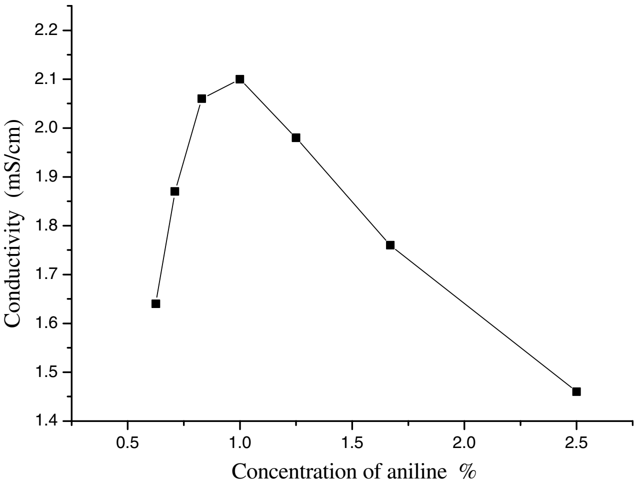

Fig. 3. Influence of aniline concentration on the conductivity of hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 8, mass ratio of KPS to aniline 1.0, reaction at 20 °C for 6 h).

3.4. Influence of the amount of acrylic acid monomer on the conductivity of hydrogel

The conductivity of hydrogel depends on the amount of polyacrylate in the copolymer. As is shown in Fig. 4, with the increase of mass ratio of acrylic acid monomer to aniline monomer, the conductivity of hydrogel increases gradually, and then decreases after reaching the highest conductivity of 2.33 mS cm^{-1} with mass ratio of acrylic acid to aniline of 12. As is known, an interpenetrated network is formed by integrating a polyaniline chain and a polyacrylate network. A suitable mass ratio of acrylic acid to aniline is significant. Obviously, a higher mass ratio of acrylic acid to aniline means lower concentration of aniline which causes the weakening for polyaniline chain. 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. The above two cases cannot form an interpenetrated network to conduct electrons and bring about a decrease of conductivity of the hydrogel.

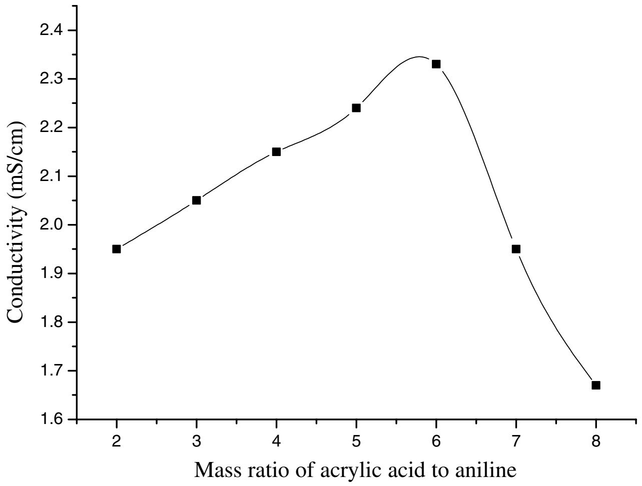

Fig. 4. Influence of aniline amount on the conductivity of hydrogel (preparation conditions: mass ratio of KPS to aniline 1.0, aniline concentration 1.0 wt%, reaction at 20 °C for 6 h).

3.5. Influence of reaction temperature and time on the conductivity of hydrogel

The reaction temperature and time also affect the structure and conductivity of polymer hydrogel. From Fig. 5, it is obvious to see that the conductivity of the hydrogel increases and then decreases with the reaction time prolonging for three temperature curve, and the higher temperature, the shorter reaction time for reaching the highest conductivity. Higher reaction temperature resulting in a shorter reaction time is accorded with the general rule of chemical reactions. But potassium persulfate is an initiator for polymerizing aniline monomer, also being a stronger oxidizer for oxidizing aniline monomer or polymer. A longer reaction time brings about a side reaction for oxidizing polyaniline, which results in the breakage of the polyaniline conducting chain to some extent and decline of the conductivity of the materials.

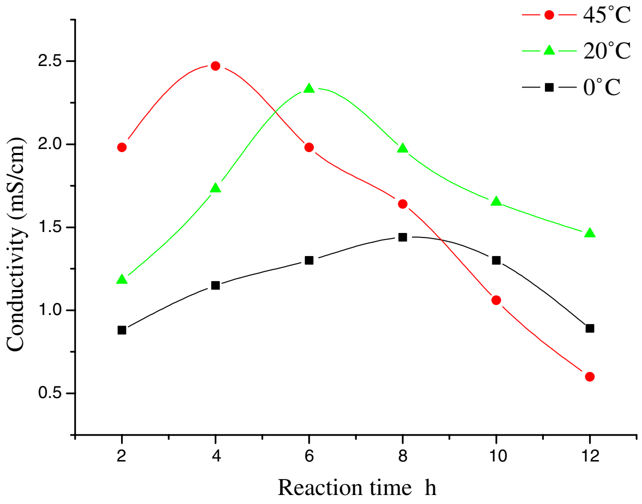

Fig. 5. Influence of reaction temperature and time on the conductivity of hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 12, mass ratio of KPS to aniline 1.0, aniline concentration 1.0 wt%).

3.6. Influence of temperature on the conductivity of hydrogel

The dependence of temperature on the conductivity of hydrogel shows that the conductivity rises with the increase of temperature (Fig. 6). Obviously, this is due to the fact that the electrons move faster under higher temperature than under lower temperature. The conductivity–temperature behavior of the conducting hydrogel can be described by the Arrhenius equation:

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

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, the E_a is calculated as 10.78 kJ mol^{-1} and the A is 0.317.

3.7. Interpenetrated networks structure model for poly(acrylate–aniline) conducting hydrogel

The microscope structure of poly(acrylate–aniline) hydrogel is shown in Fig. 7. It can be seen that an even porous network structure is formed in the hydrogel. According to above discussions, an interpenetrated network structure model for poly(acrylate–aniline) conducting hydrogel is proposed, and the sketch figure is shown in Fig. 8. As we know that a polyacrylate network is formed after the first polymerization reaction (Lin et al., 2001; Wu et al., 2001). Since aniline monomer is absorbed inside of the polyacrylate network, the polyaniline chain is formed inside of the polyacrylate network during the second polymerization process. Due to bifunctional group of aniline monomer, the polyaniline exists only in chain state configuration instead of network state configuration. Additional, the polyacrylate network and polyaniline chain may integrate by physical or chemical combination, owing to –COOH, –COO$^-$ groups on the polyacrylate network

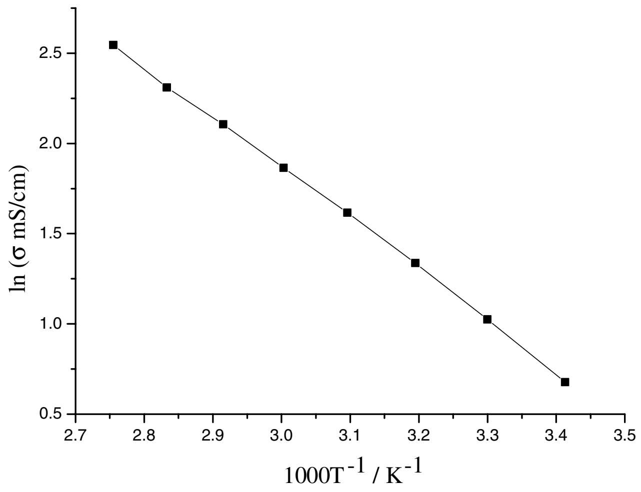

Fig. 6. The conductivity–temperature relationship of hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 12, mass ratio of KPS to aniline 1.0, aniline concentration 1.0 wt%, reaction at 20 °C for 6 h).

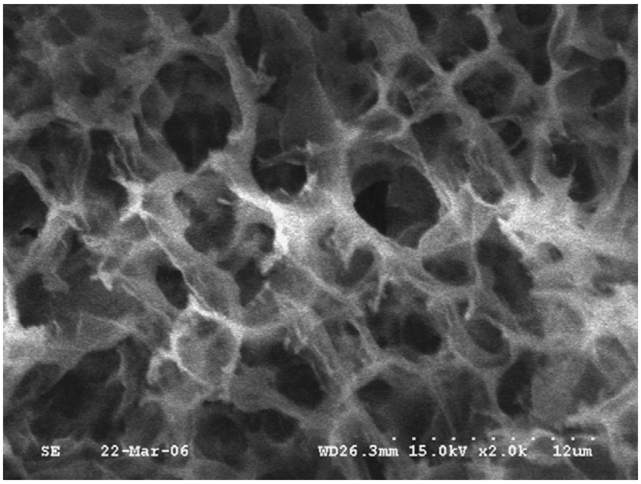

Fig. 7. SEM of the hydrogel (preparation conditions: mass ratio of acrylic acid to aniline 12, mass ratio of KPS to aniline 1.0, aniline concentration 1.0 wt%, reaction at 20 °C for 6 h).

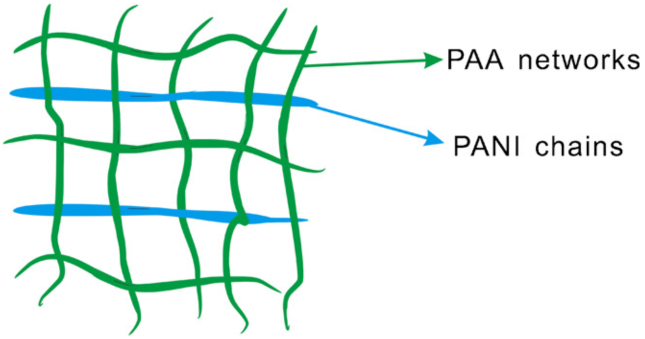

Fig. 8. Interpenetrated networks structure model.

and $-NH_2$ group on the polyaniline chain. Once the second chain of polyaniline is formed, whole system becomes an interpenetrated network structure, and an electrical conductive channel is formed with polyaniline chain. Based on the interpenetrated network structure model, the influence of initiator, acrylic acid monomer, aniline monomer, reaction time and temperature on the electrical conductivity of hydrogel can be explained, which further confirms the rationality of the structure model.

4. Conclusions

(1) Poly(acrylate–aniline) conducting copolymer is prepared by a two-steps aqueous polymerization. First, the polyacrylate superabsorbent polymer is synthesized by a routine aqueous polymerization. Second, the aniline monomers are absorbed inside of polyacrylate network and then are polymerized and formed a poly(acrylate–aniline) copolymer. When immersing the copolymer in distilled water, a conducting hydrogel is obtained.

(2) An interpenetrated networks structure model with a three-dimensional network of polyacrylate and a one-dimensional chain of polyaniline for poly(acrylate–aniline) conducting hydrogel is proposed. Based on the structure model, the influence of initiator, aniline monomer, acrylic acid monomer, reaction temperature and time on the conductivity of the hydrogel can be explained.

(3) When the preparation conditions for second step are optimized as mass ratio of acrylic acid monomer to aniline monomer 12, mass ratio of initiator to aniline monomer 1.0, concentration of aniline 1.0 wt%, reaction at 20 °C for 6 h, the hydrogel with water absorbency of 150 times possesses a conductivity 2.33 mS cm^{-1}.

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