Synthesis of Microporous pH-sensitive Polyacrylic Acid/Poly (ethylene glycol) Hydrogels Initiated by Potassium Diperiodatocuprate (III)

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A B S T R A C T

A copolymer hydrogel of polyacrylic acid poly(ethylene glycol) was prepared by potassium diperiodatocuprate (III). In this work we considered many reaction conditions which can affect the conversion and hydrogel efficiency, such as reaction time, concentration of initiator, reactants and cross-linking agent. In the optimal conditions, temperature was 35ºC, concentration of potassium diperiodatocuprate (III) was 1.76×10^{-3} mol/L, the weight ratio of polyacrylic acid-poly(ethylene glycol) was 5:1 with reaction time of 80 min, cross-linker was 0.1 mg/mL, hydrogel efficiency (HE) could reach 0.90 and total conversion was 0.98. At the same time the effects of pH, pore-forming agent of the hydrogel and cross-linker on swelling ratio were also investigated. The maximum swelling ratio of the hydrogel was obtained at pH 7 while the pore-forming agent was 0.08 mg/mL, the weight ratio of polyacrylic acid-poly(ethylene glycol) was 25:1, and the cross-linker was 0.05 mg/mL. The hydrogel was synthesized successfully as confirmed by infrared spectroscopy, and the experimental result indicated that potassium diperiodatocuprate (III)/poly(ethylene glycol) redox system was an efficient initiator for this reaction. Meanwhile, we also used scanning electron microscope (SEM) to study the structure of the hydrogel. SEM showed that there are many micropores formed in the microporous hydrogel compared to the traditional hydrogel, which obviously improved the swelling capacity.

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INTRODUCTION

Hydrogels are formed by physically or chemically cross-linked three-dimensional polymer network capable of holding a large amount of water while at the same time maintaining their shape [1]. Since 1970s, many research works on hydrogels have been focused on the properties and related environmental sensitivity issues towards higher efficiency of synthetic methods [2-9]. Much of the research has shown that, the synthetic methods could be generalized as ionic polymerization, free radical polymerization, and freezable cross-linking polymerization, and in this respect the hydrophilic properties of some

hydrogels may change abruptly even if the polymerization conditions (such as temperature, pH, solvent, ion concentration, etc) change slightly. In the above three methods, the free radical polymerization has been most widely used, because it can initiate polymerization in mild conditions. A system initiated by potassium persulphate (KPS) is the most popular approach to synthesize hydrogels. Although KPS is a convenient and low-cost initiator, it initiates cross-linking polymerization at high temperature and requires N,N,N',N'-tetramethylethylenediamine (TEMED) as an accelerator which has limited attraction in industry [10]. Therefore, finding a new initiator to initiate the free radical polymerization is of outmost importance.

The supernormal valence transition-metals such as Ce(IV), Mn(III) as oxidants and polymer as reductant for a redox system which initiates the radical grafting or block copolymerization is a convenient, low-cost, and high efficient system [11-18]. These supernormal valence transition-metals, however, must be implemented in the acidic medium. In recent years, we have made some achievements on polymerization initiated by supernormal valence transition-metals, such as diperiodatocuprate (III) (DPC) [19-21], diperiodatoargentate (III) [22-23] and diperiodatonickelate (IV) [24-25]. It has been demonstrated that they are not only an efficient initator but also can initiate polymerization in alkaline solution supplied by Ce(IV), Mn(III). This work has been an attempt to study a copolymer hydrogel of polyacrylic acid (PAAc)-poly(ethylene glycol) (PEG) synthesized by potassium diperiodatocuprate in an alkaline solution. The results indicate that DPC/PEG redox system is an efficient initiator for the reaction under study and the swelling ratio of the hydrogel change abruptly in pH 7 when the concentration of the pore-forming is 0.15mg/mL and the cross-linker is 0.05mg/mL.

EXPERIMENTAL

Materials and Equipment
The solution of DPC was prepared according to reference [20]. The concentration of DPC was measured by its absorption at λ=414 nm using a Shimadzu UV-265 spectrophotometer (Japan). AAc of analytical

reagent grade, was purchased from Huadong reagent factory (Tianjin), which was counteracted by sodium hydroxide before use. PEG (Senchang reagent factory, MW=2000, Tianjin) was used as received. N,N'-Methylenebisacrylamide as a cross-linker and calcium carbonate as a pore-forming agent were used as received (Senchang reagent factory). Other reagents were all analytical reagents and used as received.

Experimental Procedure
The required amounts of PEG solution, sodium acrylate (AS), cross-linking agent, pore-forming agent and water were introduced into a glass tube, flushed with pure nitrogen and then the reaction system was maintained at 35±0.1ºC in a thermostatic reservoir. An appropriate amount of DPC was then added under nitrogen, held at 35±0.1°C for a period of time, then stopped by addition of hydrochloric acid. The copolymer and hydrogel were precipitated in methanol, filtered through a weighed sintered glass crucible, and then the hydrogel was left in hydrochloric acid (1 mol/L) for 24 h to extract the entire pore-forming agent. At the end the hydrogel was dried under vacuum to constant weight, and the weight of PEG was subtracted from the constant weight till the weight of PAAc was obtained. The homopolymer of PAAc and uncross-linked copolymer PAAc-PEG were removed from the hydrogel by exhaustive 48 h Soxhlet extraction with water. The final hydrogel was then dried to a constant weight.

The total conversion (TC) and hydrogel efficiency (HE) were defined and calculated as follows:

TC = weight of PAAc / weight of AAc charged

HE = weight of hydrogel/weight of PEG+PAAc

The swelling capacity was determined as follows:

$$S(g/g)=(m_2-m_1)/ m_1$$

where m_2 is the weight (g) of swollen hydrogel and m_1 is the weight (g) of dried hydrogel, respectively.

Measurements
The FTIR spectrum of hydrogel was recorded on an FTS-40 spectrometer (Bruker IFS-25.US) using potassium bromide pellets technique. An AMKAY-1000B Scanning electron microscope was used to observe the morphologies of PAAc-PEG hydrogel and the microporous PAAc-PEG hydrogel.

Table 1. Effect of weight ratio of AAc/PEG on total conversion and hydrogel efficiency.

AAc(g)/PEG(g)	5	10	15	20	25	30
Total conversion	0.98	0.97	0.95	0.92	0.84	0.77
Hydrogel efficiency	0.90	0.90	0.82	0.74	0.64	0.50

[DPC] = 1.76×10^{-3} mol/L, Time = 80 min, T = 35ºC, cross-linker = 0.1 mg/mL.

Table 2. Effect of DPC concentration on total conversion and hydrogel efficiency.

[Cu(III)$\times 10^3$ mol/L]	0.72	1.05	1.41	1.76	2.11	2.48
Total conversion	0.63	0.75	0.82	0.90	0.85	0.71
Hydrogel efficiency	0.51	0.58	0.70	0.74	0.70	0.62

W(AAc)/W(PEG) = 20, Time = 80 min, T = 35ºC, cross-linker = 0.1 mg/mL.

RESULTS AND DISCUSSION

Effect of Weight Ratio of AAc/PEG on Total Conversion and Hydrogel Efficiency

Keeping all the other variables unchanged, the effects of weight ratio of AAc/PEG on total conversion and hydrogel efficiency have been investigated, and the results are shown in Table 1. It can be observed that both these properties have shown reductions as the weight ratio of AAc/PEG has been increased all along in the studied range. The declined trend of the above properties may be explained as follows: AAc is poly-merized with PEG and it is cross-linked mostly when the monomer concentration is low, so the total conver-sion and hydrogel efficiency are initially high. However, with increasing monomer concentration, at the final stage the initiator and cross-linker are almost exhausted, and induce the homopolymer of PAAc and uncross-linked PAAc-PEG copolymer to increase, i.e. leading to decreased total conversion and hydrogel efficiency.

Effect of DPC Concentration on Total Conversion and Hydrogel Efficiency

Table 2 shows the effect of initiator concentration on total conversion and hydrogel efficiency. It can be seen that both increased significantly first, reached a maximum and then decreased. The initial increasing trend may be attributed to the initiator being used up mostly in polymerization and cross-linking reaction in low DPC concentration. When the DPC concentration is very high, abundance of primary radical not only initiates the polymerization but accelerates the termi-nation rate by coupling and oxidation. Thus the total conversion and hydrogel efficiency are all increased.

Effect of Reaction Time on Total Conversion and Hydrogel Efficiency

The effect of reaction time on total conversion and hydrogel efficiency was investigated while the other reaction conditions being maintained unchanged. The results are shown in Table 3. The initial increase in total conversion and hydrogel efficiency has clearly

Table 3. Effect of reaction time on total conversion and hydrogel efficiency.

Reaction time (min)	20	30	40	50	60	80	120
Total conversion	0.42	0.60	0.73	0.81	0.89	0.92	0.95
Hydrogel efficiency	0.33	0.48	0.59	0.70	0.72	0.72	0.74

[DPC] = 1.76×10^{-3} mol/L, W(AAc)/W(PEG) = 20, T = 35ºC, cross-linker = 0.1 mg/mL.

Table 4. Effect of the cross-linker on total conversion and hydrogel efficiency.

Cross-linking agent (mg/mL)	20	30	40	50	60
Total conversion	0.91	0.91	0.91	0.90	0.92
Hydrogel efficiency	0.46	0.66	0.74	0.80	0.82

[DPC] = 1.76×10^{-3} mol/L, W(AAc)/W(PEG) = 20, Time = 60 min, T=35ºC.

indicated that both DPC and macroradicals could keep its activity for a period of time. The following trend of leveling off can be attributed to the decrease in monomer concentration and initiator concentration.

Effect of the Cross-linker on Total Conversion and Hydrogel Efficiency

Table 4 shows the cross-linker influence on total conversion and hydrogel efficiency. It is observed from the table, that the total conversion has changed a slightly, however, and the hydrogel efficiency has increased along with the increasing concentration of the cross-linker. This phenomenon may be attributed to the increasing amount of cross-linker, which has only accelerated the cross-link reactions to produce more hydrogel and therefore the hydrogel efficiency has increased.

Effect of Weight Ratio of AAc/PEG and pH on the Swelling Ratio

The effects of weight ratio of AAc/PEG and pH on the swelling ratio were investigated and are shown in Figure 1. It has been shown that for a given pH, the swelling ratio (S) increases steadily with the increasing weight ratio of AAc/PEG. The increase tendency of the S could be explained as follows: because of the good water-solubility of PAA, the increasing amount of AA could make the molecular chain becoming longer and form much bigger cross-link network which would improve the swelling ratio. In addition, in every increase in AAc/PEG weight ratio, a decreased initial rate of swelling ratio is observed as pH increases. It is well known that water is a kind of good solvent for PEG and PAA because of the hydrogen bonding between the polymers and water, and thus the PEG and PAA would be in a stretched state.
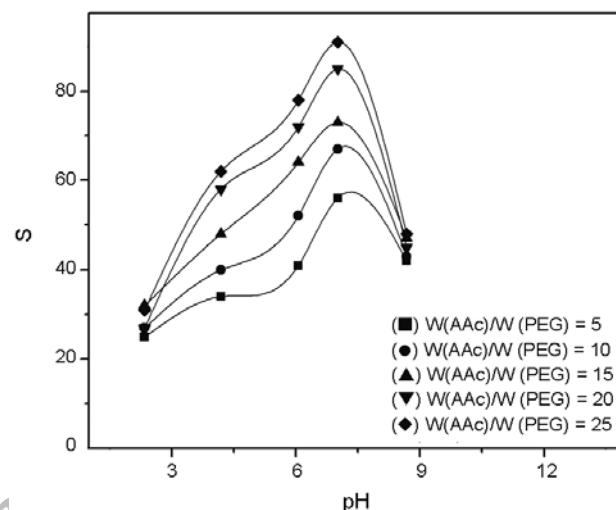

Figure 1. Effect of weight ratio of AAc/PEG and pH on swelling ratio $[CaCO_3]$ = 0.08 g/mL, cross-linker = 0.05 mg/mL.

If by adding some ionic solvent into the system that would destroy the hydrogen bonding between the bases and water molecules, the molecular chain would curl into a quasi-spherical configuration. Therefore in acidic condition the hydrogel cross-link network is shrinked and with increasing pH the interaction of oxygen atom and carboxyl with hydrogen ion become weak, and the cross-link network is dilated. At pH 7, the cross-link network is at its maximum.

Effect of the Pore-forming Agent on Swelling ratio [26]

When the other reaction conditions were invariable, the effect of pore-forming agent on swelling ratio was investigated and it is shown in Figure 2. Along with the increasing of pore-forming agent, the swelling ratio increased steadily to a certain value, then it naturally declined. As we know, the pore-forming agent (calcium carbonate) could not dissolve in alkaline water reaction system, when the number of the undissolved pore-forming agent is small; the pore-forming agent is enchased in the hydrogels, which destroys the compact structure of the hydrogels and decreases the cross-linking density after the pore-forming agent dissolves in the hydrochloric acid forming micropores. So the swelling ratio improves with the increasing of pore forming agent concentration. However, when the number of undissolved
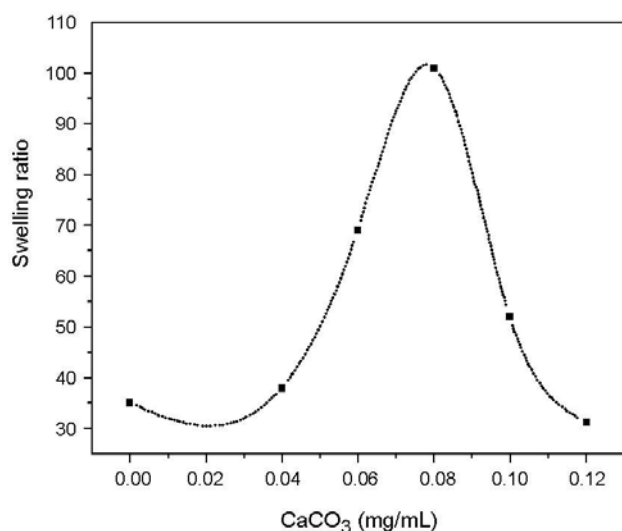
Figure 2. Effect of the pore-forming agent on swelling ratio W(AAc)/W(PEG)= 25, pH=7.01, cross-linker = 0.05 mg/mL.

Figure 3. Effect of the cross-linker on swelling ratio W(AAc)/W(PEG) = 25, pH = 7.01, $[CaCO_3]$= 0.08g/mL.

pore-forming agent is abundant, the pore-forming agent could form little conglomeration and it is filled with the whole hydrogels. The compact structure of the network is then destroyed entirely when the pore-forming agent dissolves in hydrochloric acid and forms plenty of holes. So the swelling ratio is decreased.

Effect of the Cross-linker on Swelling Ratio
Figure 3 shows the effect of cross-linker on the swelling ratio. From the curve we have found that the swelling ratio is decreased with increasing concentra-
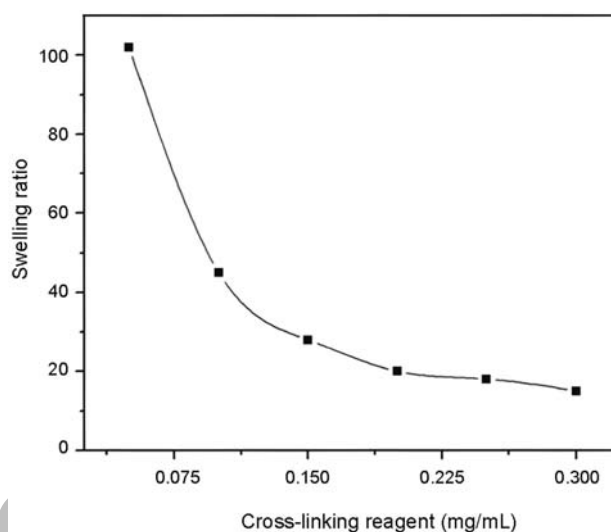
tion of cross-linker. The increase in cross-linker concentration has resulted in cross-link density and therefore the cross-link network area is reduced, followed by decrease in the swelling ratio.

Blocking Formation
The IR spectra of PAAc-PEG hydrogel is shown in Figure 4. The absorption band at 3398 cm^{-1} can be assigned to –OH of the PEG segment. The band at 2943 is due to C–H_{atr} and C–H_{def} of –CH_2–. Absorptions at 1578 and 1410 cm^{-1} are due to the

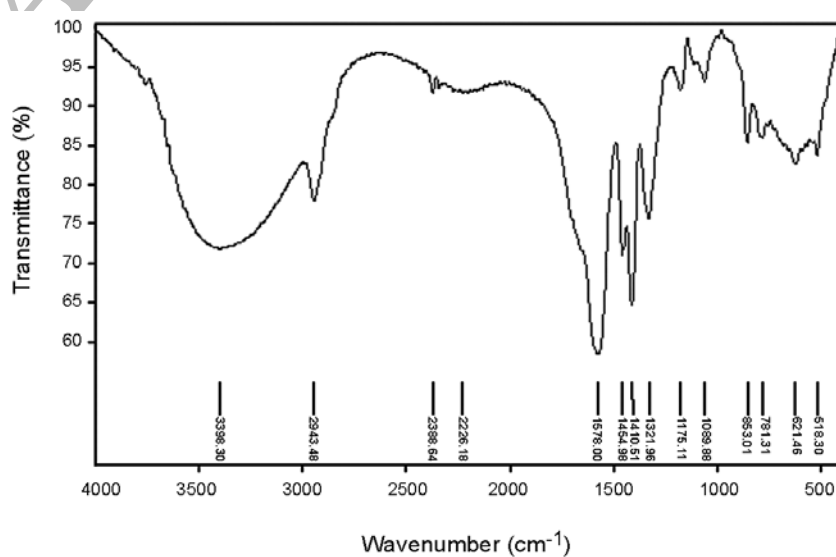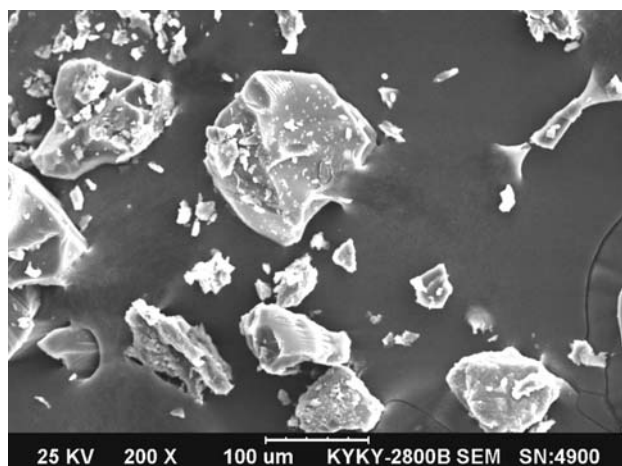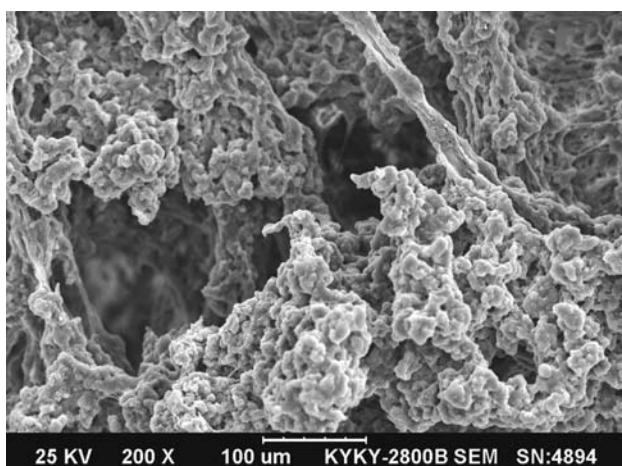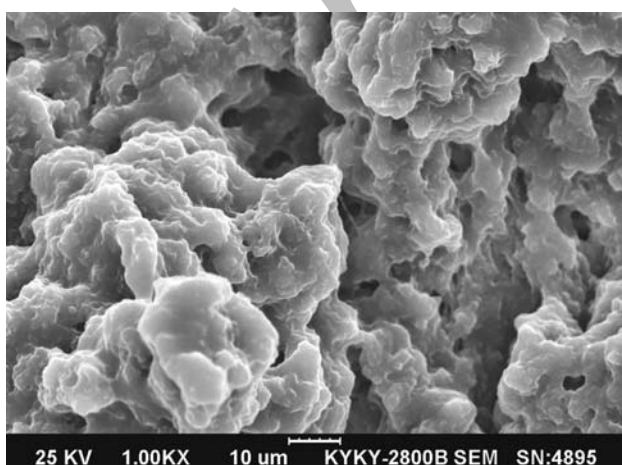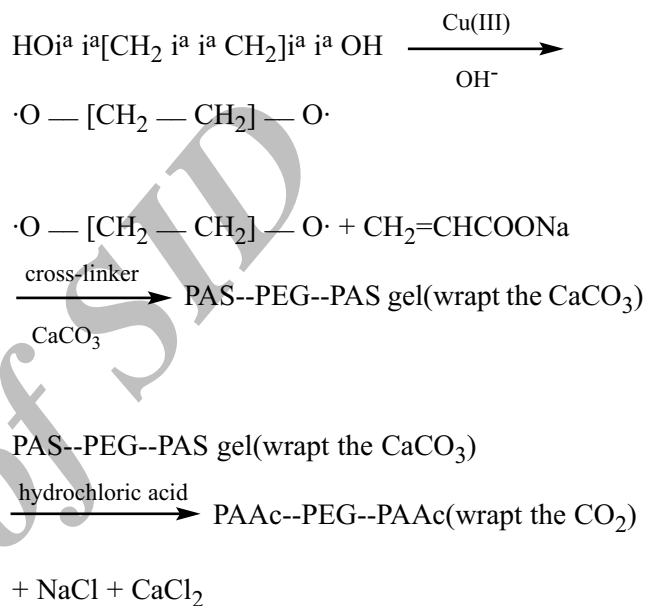**Figure 4.** IR spectra of PAAc-PEG hydrogel.

(a)

(b)

(c)

Figure 5. SEM of PAAc-PEG-PAAc hydrogel and PAAc-PEG-PAAc microporous hydrogel, (a) PAAc-PEG-PAAc hydrogel; 200×; (b) PAAc-PEG-PAAc microporous hydrogel, 200× (c) PAAc-PEG-PAAc microporous hydrogel, 1.00 K×.

carboxyl of PAAc. This is a clear indication of the presence of PAAc segment in the hydrogel.

A plausible initiation mechanism [27-28] may be proposed as follows:

$$HOiªiª[CH_2 iª iª CH_2]iª iª OH \xrightarrow[OH^-]{Cu(III)}$$

$$\cdot O — [CH_2 — CH_2] — O\cdot$$

$$\cdot O — [CH_2 — CH_2] — O\cdot + CH_2=CHCOONa$$

$$\xrightarrow[CaCO_3]{cross-linker} PAS\text{--}PEG\text{--}PAS \text{ gel(wrapt the } CaCO_3)$$

$$PAS\text{--}PEG\text{--}PAS \text{ gel(wrapt the } CaCO_3)$$

$$\xrightarrow{hydrochloric\ acid} PAAc\text{--}PEG\text{--}PAAc(\text{wrapt the } CO_2)$$

$$+ NaCl + CaCl_2$$

Morphological Studies (SEM)

The morphological characteristics of PAAc-PEG and microporous PAAc-PEG hydrogels have been studied by SEM. As shown in Figure 5, it can be observed that the surface of the PAAc-PEG hydrogel (a) is smooth and there are more holes in the microporous PAAc-PEG hydrogel (b), (c). This may be attributed to the pore-forming agent dissolved in hydrochloric acid and being left as microporous, which shortened the water pervasion time in the hydrogel, increased the cross-link network area and improved the swelling capacity of the hydrogel.

CONCLUSION

In this work, the microporous hydrogel has been obtained with satisfactory results by using DPC in an aqueous alkaline medium. In the optimal conditions: temperature (35ºC), concentration of [DPC] (1.76×10^{-3} mol/L), weight ratio of AAc/PEG (5:1), reaction time (80 min), cross-linker (0.1mg/mL)], hydrogel efficiency could reach 0.90 and total conversion was 0.98. The swelling ratio of the hydrogel reached maximum at pH 7 when the weight ratio of AAc/PEG was 25:1, the pore-forming was 0.08 mg/mL, and the

cross-linker was 0.05 mg/mL. The proof of hydrogel was obtained from IR analysis. Based on the SEM result, it was found that the microporous hydrogel could improve the swelling capacity.

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