

Studies of Precipitated Polymerization of Acrylamide with Quaternary Ammonium Cationic Comonomer in Potassium Citrate Solution

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ABSTRACT: Copolymer particles consisting of acrylamide (AM) and cationic comonomer 2-methyl acryloyloxyethyl trimethyl ammonium chloride (DMC) were prepared by precipitation polymerization in an solution of potassium citrate using ammonium persulfate ((NH₄)₂S₂O₈) and sodium sulfite (Na₂SO₃) as an initiator. The product poly(acrylamide-2-methyl acryloyloxyethyl trimethyl ammonium chloride) [Poly(DMC-AM)] is a water-soluble cationic polyelectrolyte. The solubility of DMC, AM and Poly(DMC-AM) in potassium citrate solution were measured, combined with the theory of solubility parameter, and the experiment results indicate that the solubility of DMC and AM is much higher than that of Poly(DMC-AM), and also the mechanism of copolymer precipitated in salt solution was discussed. The factors influencing the conversion of comonomers were exam-

ined, such as salt mass fraction, polymerization temperature, monomers mass fraction, initiator mass fraction, and so on. The results of experiments indicate that the best conditions are salt mass fraction = 57%, monomers mass fraction = 3%, $m(\text{DMC}) : m(\text{AM}) = 3 : 1$, initiator mass fraction = 0.08%, polymerization temperature = 50°C, reaction time = 2 h, and the conversion is 86.4%. And the qualitative analysis experimental method for copolymer by infrared absorption spectrum show that [Poly(DMC-AM)] was successfully synthesized by precipitation polymerization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2479–2484, 2007

Key words: potassium citrate solution; precipitation polymerization; acrylamide; 2-methyl acryloyloxyethyl trimethyl ammonium chloride; initiator

INTRODUCTION

In the past several years, the production of poly(acrylamide-2-methyl acryloyloxyethyl trimethyl ammonium chloride) [Poly(DMC-AM)] has grown rapidly for their various commercial applications. This cationic water-soluble copolymer is used for retention aids in papermaking, as flocculent and disinfectant in the sewage treatment, and as stabilizers for emulsion polymerization in cosmetics, and so on.^{1,2} Now, its preparation method most used are the homogeneous aqueous solution polymerization, the dispersed polymerization (emulsion polymerization and aerosol polymerization), and the precipitation polymerization,^{3,4} but they are still deficiently suited in preparing the high electric-charge density cationic polyelectrolyte. In the precipitation polymerization, people mostly use the organic solvent or the component solvent to take the response medium in the reacting system, and also use precipitating agent

joined in the reacting system to achieve the effect of precipitation polymerization. For example, Song and Cho⁵ put acrylamide and acryloyloxyethyl dimethylbenzyl ammonium chloride in an aqueous solution of ammonium sulfate, and successfully prepared cationic polyelectrolyte by dispersion polymerization. But Song's preparation way also has the insufficiency; for instance, copolymer particle size is too small, the product separation needs the seepage membrane, and the operation is complicated.

In this kind of precipitation polymerization, instead of using an organic solvent, the aqueous medium is used, which usually contains a high concentration of a water-soluble salt to induce the phase-out of the resulting polymer by the salting-out effect. We use potassium citrate solution, which is friendly to the environment as reaction medium. The copolymer of AM and DMC are prepared by precipitation polymerization in the solution of potassium citrate and in the presence of ammonium persulfate and sodium sulfite as an initiator. Also, the factors influencing the conversion of monomers were examined. By this way, copolymer particle size is moderate, and filtering copolymer from the reacting system can use the reduced pressure distillation, simplified the separation flow.

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EXPERIMENTAL

Materials

The AM monomer was purchased from Fushun Longfeng Chemical Co. and was used either as received or after recrystallization from methanol. DMC was obtained from SNF Chemicals in France as an aqueous solution (80%). Potassium citrate as the salt, ammonium persulfate and sodium sulfite as initiator were used as received without further purification.

Procedure

Appropriate amounts of AM, DMC, potassium citrate, and distilled water were taken in a 250-mL three-necked separable flask equipped with a stirrer and a nitrogen inlet tube. After monomers and salt were dissolved in the distilled water, the reaction mixture was purged with a gentle stream of nitrogen for 30 min. As the temperature control started, the copolymerization was initiated by injecting the water-soluble initiator into the system. Maintaining of the temperature was continued for 2–6 h. Responded intermixture liquid after filters by reduced pressure distillation obtains the granulated primary product. After the primary product was washed three times by ethyl alcohol, dried it at 60°C, the white powdery solid was the product.

Determination and attribute

Infrared absorption spectrum of copolymer was measured by Vector-22 infrared spectrograph from German Bruker Instrument Co. Dried copolymer was redissolved in water. According to GB12005.3-89 "Determination for residual acrylamide of polyacrylamide-Bromating method" we measured residual monomer of product. Potassium ion concentration of product was measured using PXS-215 Ionic activity apparatus with PK-1 cationic selective electrodes, then accounted rudimental potassium citrate concentration of product.

The expressions of total monomer conversion X :

$$X = \frac{m_1 - m_2 - m_3}{m} \times 100\%$$

m_1 is the quality of dried copolymer, m_2 is the quality of residual monomer of product, m_3 is the quality of rudimental potassium citrate of product, and m is the quality of total monomer.

RESULTS AND DISCUSSIONS

Precipitation polymerization in the potassium citrate solution

Expression of the solvent characteristic was used by the solubility parameter. The component solvent is

prepared by two mutually soluble solvents according to the certain proportion; its solubility parameter can be approximately expressed:⁶

$$\delta_m = \varphi_1 \delta_1 + \varphi_2 \delta_2$$

δ_m is the solubility of solute in component solvent; δ_1 is the solubility of solute in the first solvent; δ_2 is the solubility of solute in the second solvent; φ_1 is the percentage of the first solvent in component solvent; φ_2 is the percentage of the second solvent in component solvent.

When φ_1 and φ_2 reach the certain value, the component solvent regarding the monomer was still a good solvent, but regarding the copolymer was a poor solvent. Therefore, the proportion of potassium citrate and water has decided the monomer and copolymer solubility in potassium citrate solution. And the premise of copolymer prepared by precipitation polymerization in the salt solution is: (1) DMC and AM could be dissolved in potassium citrate solution; (2) copolymer of DMC and AM could be prepared by free radical polymerization in the presence of initiator; (3) copolymer could not be dissolved in potassium citrate solution and phase separation happened.

To be advantageous for comparing solubility of monomer with copolymer in the potassium citrate solution, the weight of DMC, AM, and potassium citrate solution was regulated to 100 g. Figure 1 is the maximum soluble amount of DMC, AM, P(DMC-AM) dissolved in different concentration of potassium citrate solution. As shown in Figure 1, the monomer and also the copolymer solubility became lower with increasing salt concentration, but the solubility of monomer were always much more than that of copolymer. When salt concentration is 50%

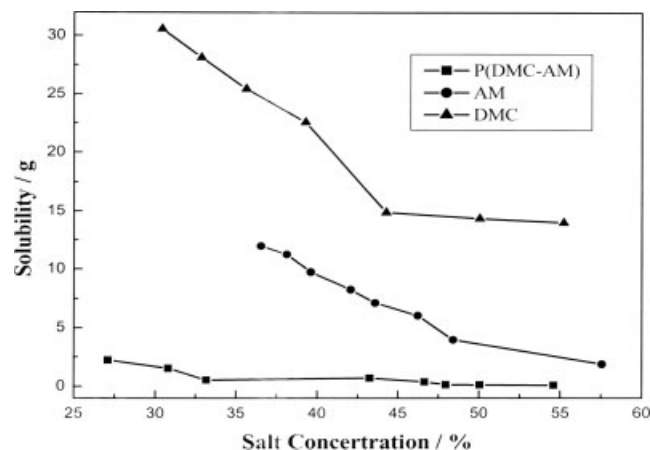


Figure 1 Soluble amount of 2-methyl acryloyloxyethyl trimethyl ammonium chloride (DMC), acrylamide (AM), and poly(DMC-AM) [Poly(DMC-AM)] in potassium citrate solution.

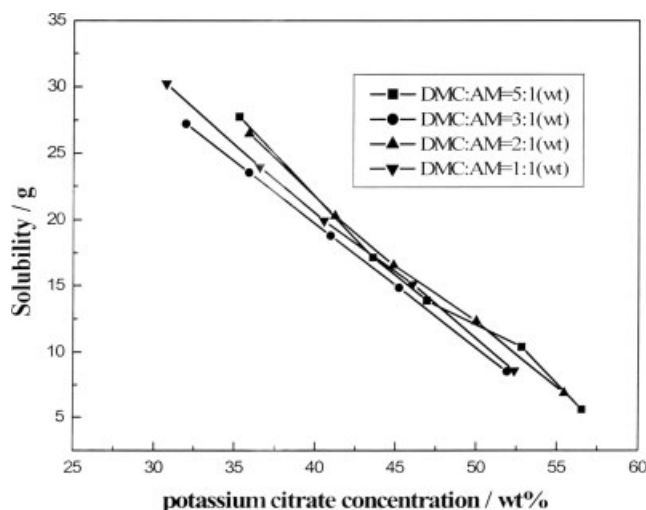


Figure 2 Solubility of mixture with different $m(\text{DMC})$ and $m(\text{AM})$ ratio in potassium citrate solution.

(weight/weight), DMC soluble amount compared to P(DMC-AM) more than 14 g, AM soluble amount compared to P(DMC-AM) more than 5 g. Therefore, the reacting system conforms to the premise (1) and (3) in the precipitation polymerization.

Figure 2 is the maximum soluble amount of different proportion of DMC and AM dissolved in different concentration of potassium citrate solution under room temperature. As shown in Figure 2, when salt concentration was above 50%, the mixed monomer soluble amount was still more than 6 g. Two kinds of monomers in this reacting system could be mixed and dissolved well, and DMC and AM could have the copolymerization after the initiation. As a result, after DMC and AM was dissolved in salt solution, the solubility of monomers could satisfy the request of precipitation polymerization.

In Figure 2, when salt concentration was 50% and $m(\text{DMC}) : m(\text{AM})$ (weight of AM) = 3 : 1, the mixed monomer soluble amount was 10.2 g, and DMC solubility was 7.5 g. And in Figure 1, DMC solubility was 14.5 g when salt concentration was 50%. Therefore, the solubility of DMC in Figure 2 decreased more than that in Figure 1, and DMC and AM solubility influenced each other in the salt solution. Although decreasing solubility of mixed monomer was still much higher than copolymer, this reacting system could satisfy the request of precipitation polymerization.

Effect of potassium citrate concentration on total monomer conversion

In this reacting system, the salt concentration is extremely important because of the salting-out effect. The experiment indicated that Poly(DMC-AM) could not precipitate from salt solution if salt concentration

was below 45%. Therefore, the critical salt concentration of precipitation polymerization was 45%, and the potassium citrate concentration in saturated salt solution was 61%.

As shown in Figure 3, the total monomer conversion increased with increasing salt concentration. The solubility of DMC and AM decreased with increasing salt concentration, at the same time, the solubility of Poly(DMC-AM) also decreased. In Figure 1, the solubility of Poly(DMC-AM) was 0.6 g when salt concentration was 45%, and the solubility of Poly(DMC-AM) was only 0.1 g when salt concentration was 48%. So with the increasing salt concentration, more copolymer precipitated, more monomer copolymerized, and conversion increased.

We discovered in the experiment the maximum concentration of potassium citrate, which can achieve in this system is 57% as monomer total mass fraction was 4% and initiator total mass fraction was 0.08%. And the total monomer conversion was 84.2% when salt concentration was 57%. So, we choose 57% to be the best concentration of potassium citrate in this reacting system.

Effect of initiator concentration on total monomer conversion

As shown in Figure 4, with increasing the initiator concentration, the conversion increased during the early stage, but decreased at the later stage. Because of the increasing of primary radical $\text{S}_2\text{O}_8^{2-}$ and SO_3^- concentration, initiation rate increased and copolymerization rate increased. Increasing of initiator concentration brought on increasing of active site concentration, so conversion increased. When initiator concentration

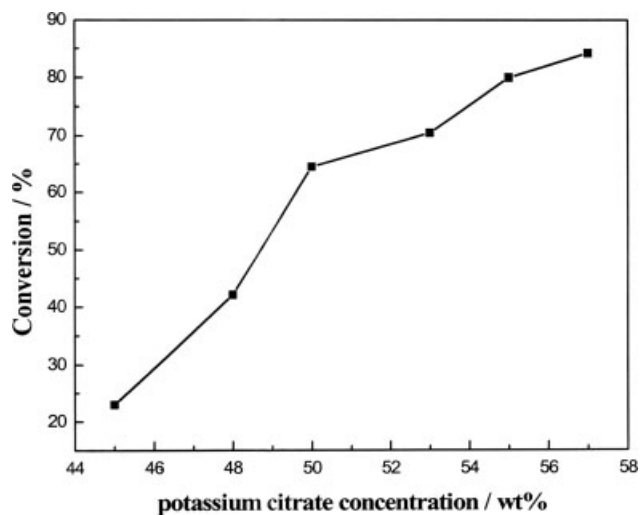


Figure 3 Effect of potassium citrate concentration on conversion. Monomer total mass fraction 4%; $m(\text{DMC})/m(\text{AM})$ was 3; initiator total mass fraction 0.08%; 2 h.

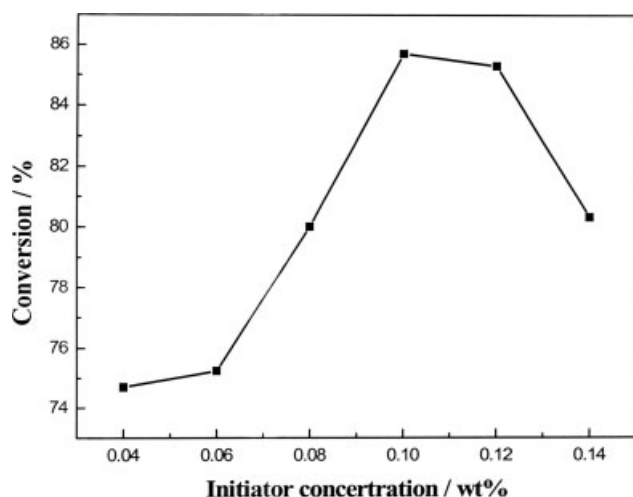


Figure 4 Effect of initiator concentration on conversion. Monomers total mass fraction 4%; $m(\text{DMC})/m(\text{AM})$ was 3; potassium citrate mass fraction 55%; 2 h.

was above 0.12%, there were too many radicals in the solution and the termination reaction between radicals increased, so that conversion decreased. Figure 4 show maximum total monomer conversion was 85%, as the initiator concentration was 0.10%. Therefore, 0.10% was the best initiator concentration in this system.

Effect of monomer ratio and monomer concentration on conversion

As measured by infrared spectrograph, we did not find DMC characteristic peak of IR in product if $m(\text{DMC}) : m(\text{AM})$ was below 1. Flocculation polymer was found in the reacting system and the separation was difficult if $m(\text{DMC}) : m(\text{AM})$ was above 6. So, for two kinds of monomer ratio, it ranged from 1 to 6. When salt concentration was 55%, the maximum concentration of total monomer was 6%, and monomer concentration ranged from 1 to 6%. Figure 5 was the experimental result.

As shown in Figure 5, conversion increased with increasing the DMC concentration, and the maximum conversion was 80% when $m(\text{DMC}):m(\text{AM})$ was 3. Along with DMC concentration continuously increased, conversion decreased. The reason was DMC activeness was much lower than AM,^{7,8} DMC could not carry on the full copolymerization with AM, and the product included massive residual DMC monomer, so conversion decreased. Figure 5 also shows conversion decreased with increasing the total monomer concentration. Conversion was 85.4% as monomer concentration was 1%, and 84.3% as monomer concentration was 3%. Considered the output of the product, the total monomer concentration chosen was 3% and $m(\text{DMC}) : m(\text{AM})$ was 3 to be the best copolymerization condition.

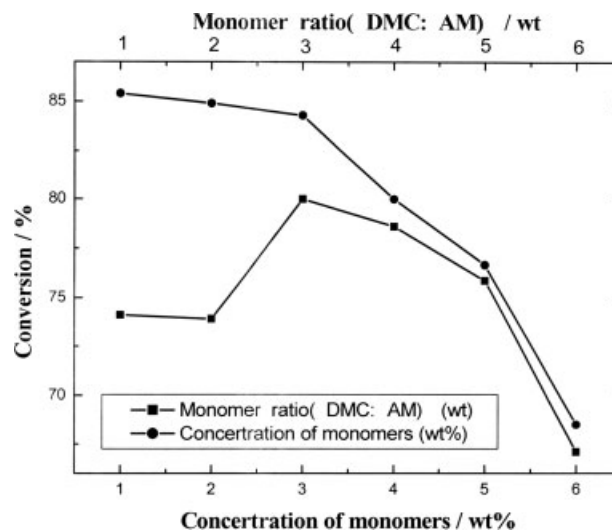


Figure 5 Effect of monomer ratio and monomer concentration on conversion. Initiator total mass fraction 0.08%; potassium citrate mass fraction 55%; 2 h.

Effect of reaction temperature on conversion

As shown in Figure 6, with increasing the reaction temperature, the conversion increased during the early stage, and decreased at the later stage. The maximum conversion was 86% when reaction temperature was 50°C. The polymerization rate constant K and the temperature T relations follow the Arrhenius equation:⁹ $K = Ae^{-E/RT}$. Increasing the reaction temperature, polymerization rate constant K increased, the time required to achieve the high conversion rate reduced. Meanwhile, along with temperature continuously increased, the active chain termination probability increased. So, the best reaction temperature was 50°C.

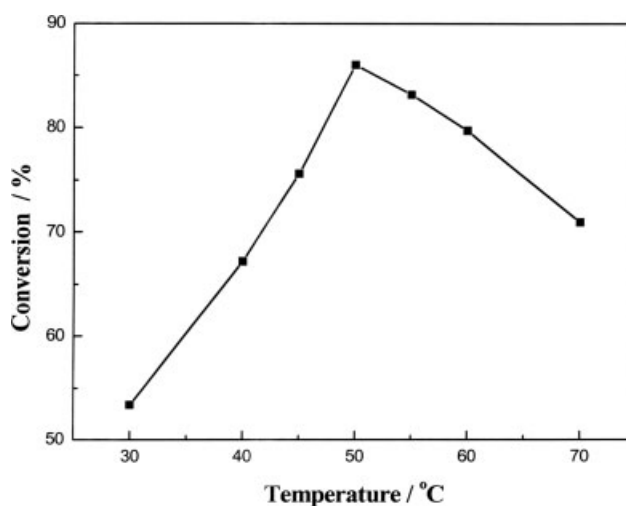


Figure 6 Effect of reaction temperature on conversion. Monomer total mass fraction 4%; $m(\text{DMC})/m(\text{AM})$ was 3; initiator total mass fraction 0.08%; potassium citrate mass fraction 55%; 2 h.

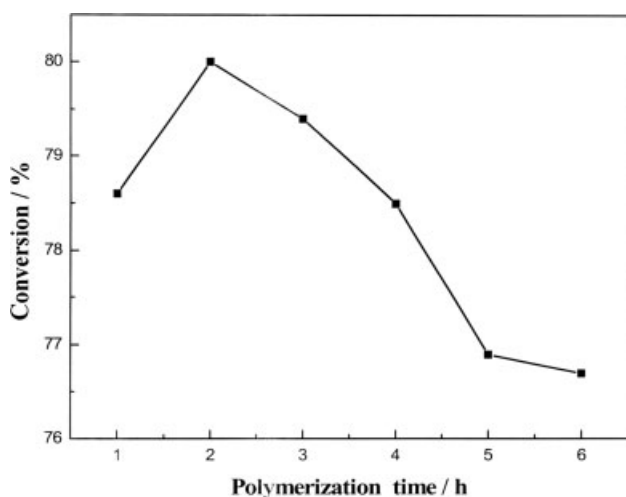


Figure 7 Effect of reaction time on conversion monomers total mass fraction 4%; $m(\text{DMC})/m(\text{AM})$ was 3; initiator total mass fraction 0.08%; potassium citrate mass fraction 55%.

Effect of reaction time on conversion

Figure 7 was the effect of reaction time on conversion, with increasing reaction time, radical increased, the polymerization rate and copolymer chain increased, conversion increased. The total monomer conversion was 80% when reaction time was 2 h. Conversion decreased if reaction time was above 2 h. The explanation of this reason was that some of polymer could be dissolved in a long time rapid stirring. Therefore, with the increasing stir time, the monomer conversion decreased apparently, as a result, the best reaction time 2 h was obtained.

Condition test

According to the result, the best conditions were potassium citrate concentration 57%, total monomer concentration 3%, $m(\text{DMC}) : m(\text{AM}) = 3$, $m((\text{NH}_4)_2\text{S}_2\text{O}_8) : m(\text{Na}_2\text{SO}_3) = 1$, initiator concentration 0.10%, reac-

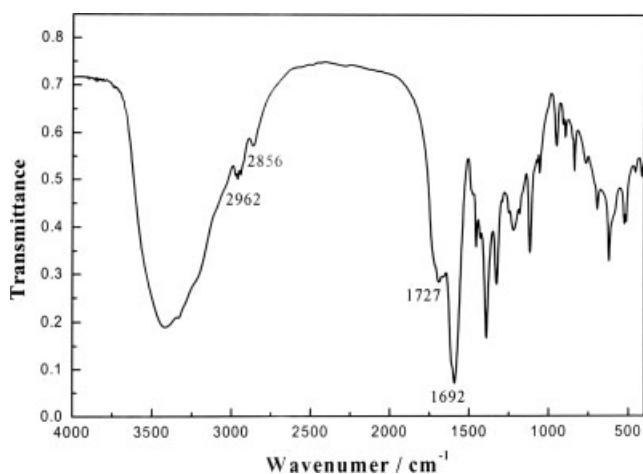


Figure 8 IR spectrum of copolymer.



Figure 9 The system after copolymerization.

tion temperature 50°C, reaction time 2 h. Under these conditions, we carried on the duplicated confirmation experiment, and the total monomer conversion was 86.4%.

Infrared absorption spectrum of copolymer

Figure 8 was infrared absorption spectrum of product with washed by ethyl alcohol. Comparing with characteristic absorption peak of organic functional group, characteristic absorption peak in 1727 cm^{-1} was "C—O—C=O," 1692 cm^{-1} was "NH₂—C=O," 2856 cm^{-1} was "CH₂—CH₂," 2962 cm^{-1} was "C—H," and there were not characteristic absorption peak "C=C" near 3020 cm^{-1} . Therefore, the IR data indicated that the product included AM and DMC organic functional group, and the product was Poly(DMC-AM).

Figure 9 was the copolymerization system which obtained after a rapid stirring (100 rpm/min). It was found from Figure 9 that milky precipitation was obtained without the formation of any coagulum, and this phenomenon indicated that precipitation particles could be easily dispersed in salt solution.



Figure 10 The delaminating of product after resting 20 min.

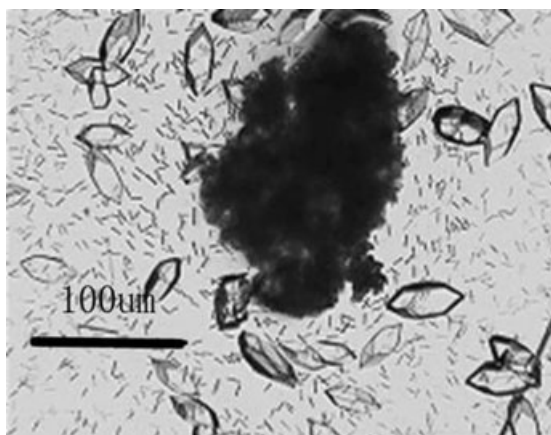


Figure 11 Micrograph (highly contrasted) of copolymer particles of Poly(DMC-AM).

Figure 10 was the copolymerization system which obtained after resting 20 min. It was found from Figure 10 that the system of Figure 9 delaminated with a precipitation particles layer on the top and a salt solution layer below. It can be interpreted the results of experiments as follows: the density of precipitation particles is lower than that of salt solution, as a result, the polymerization system delaminated after resting 20 min.

Figure 11 were the micrograph of copolymer particles. It can be seen from Figure 11 that particles form of polymer and diamond form of potassium citrate crystals appeared in our polymerization system, and the average particles diameter was 120 μm . The experimental results reveal special examples that there was a salt separating out phenomenon in our polymerization procedure. The explanation of this result is as follows: the polymer particles were porous and some water was absorbed by this porous structure, as a result the salt solution achieved a super saturation situation leading to the salt separating out phenomenon under high salt mass fraction solution.

CONCLUSIONS

Copolymer particles consisting of acrylamide (AM) and cationic monomer 2-methyl acryloyloxyethyl trimethyl ammonium chloride (DMC) were prepared by precipitation polymerization in an aqueous solution of potassium citrate using ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and sodium sulfite (Na_2SO_3) as an initiator. Under the best conditions: potassium citrate concentration 57%, total monomer concentration 3%, $m(\text{DMC}) : m(\text{AM}) = 3$, $m((\text{NH}_4)_2\text{S}_2\text{O}_8) : m(\text{Na}_2\text{SO}_3) = 1$, initiator concentration 0.10%, reaction temperature 50°C , reaction time 2 h, the total monomer conversion was 86.4%.

As shown in the figure, when potassium citrate concentration increased from 45 to 50%, the solubility of DMC, AM, Poly(DMC-AM) all decreased, but the decreasing scope of Poly(DMC-AM) solubility was far more than that of DMC and AM. Therefore, after free radical polymerization of DMC and AM in the salt solution, copolymer could be precipitated and phase separation was appeared.

As shown in the infrared absorption spectrum of copolymer, the carbonyl groups of DMC and the amino groups of AM were found in the polymer, and there were not characteristic absorption peak "C=C." These indicated that copolymer was Poly(DMC-AM).

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