

Precipitation Polymerization of Acrylamide with Quaternary Ammonium Cationic Monomer in Potassium Carbonate Solution Initiated by Plasma

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ABSTRACT: Precipitation polymerization of 2-(methacryloyloxyethyl) trimethyl ammonium chloride (DMC)-co-acrylamide (AM) [poly(AM-DMC)] has been successfully performed in potassium carbonate (K_2CO_3)-water media by plasma initiation. K_2CO_3 solution was selected because not only the higher solubility of AM and DMC comparing with that of poly(AM-DMC), but the higher intrinsic viscosity of poly(AM-DMC) could be obtained. A set of experiments was performed using different K_2CO_3 concentration (from 50 down to 10% (w/w)),

thus the precipitation architecture was not obtained below 20% (w/w). And particles size, particles size distribution (7–120 μm), and intrinsic viscosity of poly(AM-DMC) (ranging up to 455 cm^3/g) were also summarized in this article. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4060–4067, 2007

Key words: plasma-initiated polymerization; precipitation polymerization; potassium carbonate solution; 2-(methacryloyloxyethyl) trimethyl ammonium chloride; acrylamide

INTRODUCTION

There has been a considerable interest in the homopolymerization and copolymerization of cationic vinyl monomers, because the cationic polyelectrolyte obtained has wide range of applications in water treatment, paper making, antistatic treatment of textiles, etc.¹ In these applications, polymers of very high intrinsic viscosity are desired from the point of view of effectiveness and cost. However, these polymers in dry form are difficult to dissolve. Moreover, their solutions are difficult to handle or too dilute for applications because of their giving rise to gel. Methods of overcoming these problems of solution application have been proposed. The radiation-induced copolymerization of 2-(methacryloyloxyethyl) trimethyl ammonium chloride (DMC) with acrylamide (AM) in aqueous solution has been studied² and chemical-induced aqueous solution^{3,4} and inverse microsuspension⁵ copolymerization has also been described in some literatures. The use of organic or inorganic salt solution as an attractive alternative to traditional liquid solvents for polymer synthesis is an interesting topic in both academia and industry^{6–8} because of its advantages such as inexpensive, relatively nontoxic, nonflammable, and environmentally benign. Among the different classes

of salts, we found that K_2CO_3 was an interesting one for polymerization because of the solubility of a wide range of monomers and insolubility of polymer, therefore, a majority of the work in radical polymerization in K_2CO_3 solution has focused on precipitation polymerization. In this article, we first investigated using the plasma-initiated polymerization of DMC with AM in K_2CO_3 solution to prepare pure cationic polyelectrolyte. It is found that using plasma initiation, we could easily produce a copolymer with a higher intrinsic viscosity (455 cm^3/g) compared to that of polymer prepared from traditional chemical initiator (380 cm^3/g).⁹ Furthermore, the effects of particles size, particles size distribution, and intrinsic viscosity of poly(AM-DMC) were also discussed in this article.

EXPERIMENTAL

Materials and equipments

AM (Fushun Long Feng Chemicals, 99.9%) and DMC (Xing Yu Chemicals, 80% (w/w)) were used without further purification. K_2CO_3 (AR) and ethanol (AR) were used as received. A plasma reactor chamber ($\Phi 20 \times 200$ mm) and two parallel electrodes (30×200 mm) were constructed by self-command. The Glow discharge frequency was 13.56 MHz. Vacuum meter (Model Fzh-2B) and Vacuum pump (Model K-150A) were manufactured by Bei Yi. PXS-215 ion electrodes was manufactured by Zhengzhou Technology.

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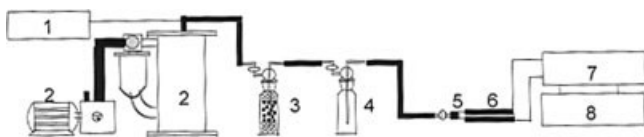


Figure 1 Schematic diagram of experimental apparatus (1) vacuumeter, (2) vacuum pump, (3) dryer, (4) bumper, (5) tubular-type reactor chamber, (6) electrode, (7) radio-power supply, and (8) matching power supply.

Synthesis of poly(AM-DMC)

Plasma-induced polymerization is a two-step procedure: (1) first, the reactant (usually monomer solution) is activated with radio-frequency inert cold plasma under vacuum to form free radicals; (2) second, the induced reactant is placed in a thermostated water bath to carry out its postpolymerization. Figure 1 showed a schematic diagram for the plasma-induced procedure.

In this article, a representative plasma initiated polymerization procedure used to synthesize a linear copolymer was as follows: to a self-command plasma reactor chamber, 3.55 g of AM (0.5 mol), 2.6 g of 80% (w/w) DMC (0.1 mol), and 117 g of 25% (w/w) K_2CO_3 solution were added in a tubular-type reactor sequentially. The mixture was stirred for 10 min until AM was dissolved completely, and then degassed the reactor three times with vacuum pump to remove oxygen (because oxygen plays an important role in radical polymerization and it would consume free radicals generated by plasma). Before plasma initiation, nitrogen was introduced for 30 min and degassed the chamber with vacuum bump to keep pressure at 133 Pa. At this time, the reaction solution was cooled to $-9^\circ C$ to restrict the solvent starting evaporating and to ensure the stability of free radicals in solution state, and plasma was then ignited at a frequency of 13.56 MHz, and discharge power was loaded directly to the reactor chamber for 60 s. After this initiating procedure, with the 133 Pa pressure and a rapid stirring (100 rpm/min), the reactor chamber was placed in a carriage, which was submerged in a thermostated water bath at $50^\circ C$ to finish its postpolymerization procedure. The precipitation particles would be appeared within 10 min, and then the solution in the reactor chamber was stirred for 5 h to complete postpolymerization, and the milky precipitation was obtained without the formation of any coagulum. The final product was filtered, washed with 95% (w/w) cold ethanol (with cooling to help precipitation) to remove any residual monomers and K_2CO_3 (K_2CO_3 can be easily dissolved in ethanol solution). At last, the product was dried under vacuum at $50^\circ C$, 0.05 MPa, and pure cationic polyelectrolyte was obtained.

IR measurement

IR spectra were run on a FIR spectrometer in 400–4000 cm^{-1} waves, KBr disc.

Intrinsic measurement

The intrinsic viscosity of the copolymer was determined in 1N NaCl aqueous solution with Ubbelode capillary viscometer at $(30 \pm 0.1)^\circ C$.

Particles size and particles size distribution measurement

After the initiating process, the reactor chamber was then placed in a water bath at $50^\circ C$, and stirred using a magnetic stirrer (100 rpm/min) for 5 h. The average particles size (\bar{D}_n) of the copolymer was measured from electron micrographs. One drop of the precipitation latex was placed on a glass board, and it was then used for drop microscopy. The diameters of the copolymer particles were measured from the electron micrographs using a lens with a scale printed on it. About 600 particles were used to calculate the \bar{D}_n using the following formula (agglomerated particles of two or more original particles were excluded from the count):

$$\bar{D}_n = \frac{\sum_{i=1}^n d_i}{n}$$

RESULTS AND DISCUSSION

In this reaction system, use of plasma as an initiated method and K_2CO_3 -water as a media gave stable precipitations, and a copolymer with a much higher intrinsic viscosity compared to that of polymer prepared from traditional chemical initiator could be easily obtained. The explanation of this result was that the free radicals generated by plasma might be because of precipitation polymerization playing a more important role in high concentration salt solution than that of generated by classical initiator. The particles polymer could be dried easily because of its small particles size and narrow particles size distribution, unlike those prepared using aqueous solution, which could be easily obtained gel and difficult to dry.² This improved performance of the method was attributable to much lower solubility of copolymer in K_2CO_3 solution than that of monomers. Using of plasma as an initiated method also had no impurity introduction. The residual monomers and K_2CO_3 could be easily dissolved in ethanol solution; as a result, the pure copolymer would be finally obtained with our expectation.

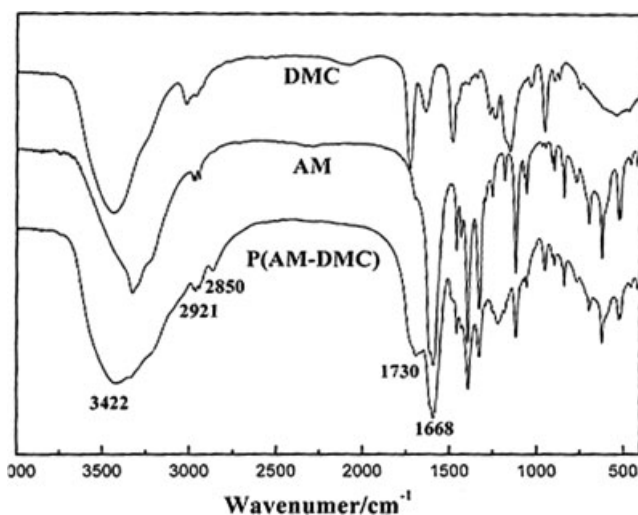


Figure 2 IR spectrum of DMC, AM, and poly(AM-DMC).

IR analysis

IR spectra of AM, DMC, and poly(AM-DMC) was in Figure 2, and IR analysis was in Table I.

The solubility of AM, DMC, and poly(AM-DMC) in different K₂CO₃ concentration and temperature

In a precipitation polymerization process, the polymerization takes place in a medium, which is a solvent for the monomer and a nonsolvent for the polymer. To overcome the aforementioned problems, a large amount of organic and inorganic salts solution were used for the production of poly(AM-DMC) utilize precipitation polymerization. Finally, K₂CO₃ was selected not only because in which solution the solubility of AM and DMC were higher than that of poly(AM-DMC) (Figs. 3–5), but also high intrinsic viscosity of copolymer could be obtained.

AM solubility

The equation of AM solubility in different K₂CO₃ concentration and different temperature was as follows:

$$S_{AM} = 48.5 + 0.0204 T^2 + 0.472T - 0.0386TC + 0.0375C^2 - 2.35C \quad R^2 = 0.9854 \quad (1)$$

TABLE I
IR Spectrum Analysis of Poly((2-methacryloyloxyethyl)thrimethyl ammonium chloride-co-acrylamide)

| Wave number (cm ⁻¹) | Explanation |
|---------------------------------|---|
| 1668 | NH ₂ -C=O characteristic ⁹ |
| 1730 | -O-C=O characteristic ⁹ |
| 3422 | C=O expansion vibration peak |
| 2921, 2850 | CH ₃ -, -CH ₂ - expansion vibration |

where T is the temperature of K₂CO₃ solution, $T \in [20,40]$, (°C); where C is the mass K₂CO₃ concentration, $C \in [20,50]$, (w/w %); where S_{AM} is AM solubility in K₂CO₃ solution, (g/100 g); where R^2 is R square.

DMC solubility

The equation of DMC solubility in different K₂CO₃ concentration and different temperature was as follows:

$$S_{DMC} = 17.2 + 0.02168 T^2 + 0.3192 T - 0.03496 TC + 0.02188 C^2 - 0.9560 C \quad R^2 = 0.9637 \quad (2)$$

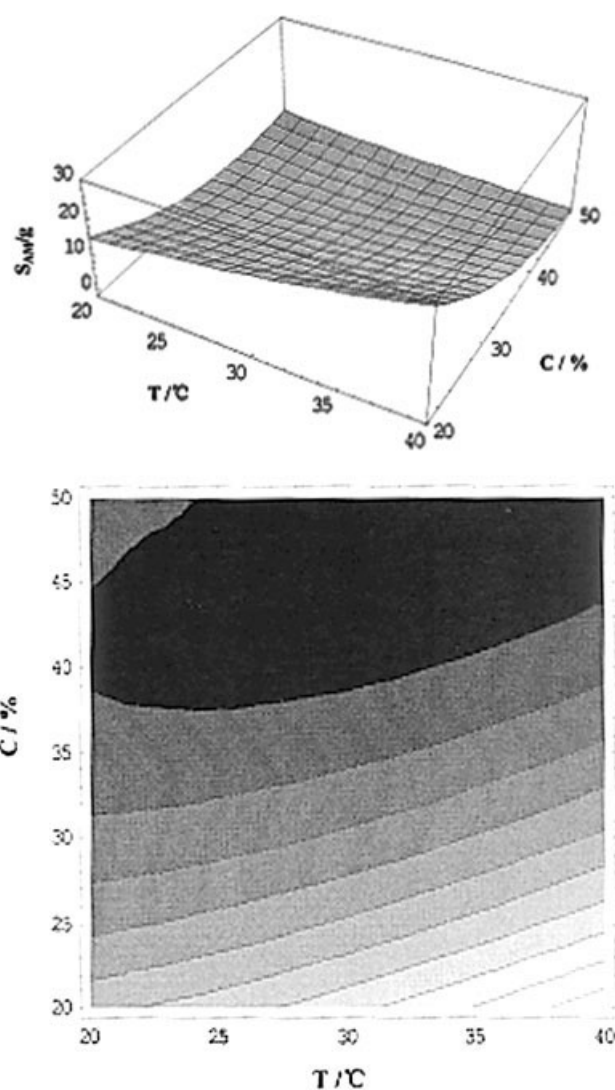


Figure 3 AM solubility in K₂CO₃ solution with different temperature and different concentration where T is the temperature of K₂CO₃ solution, $T \in [20,40]$, (°C); where C is the mass concentration of K₂CO₃ solution, $C \in [20,50]$, (w/w %); where S_{AM} is AM solubility in K₂CO₃ solution, (g/100 g).

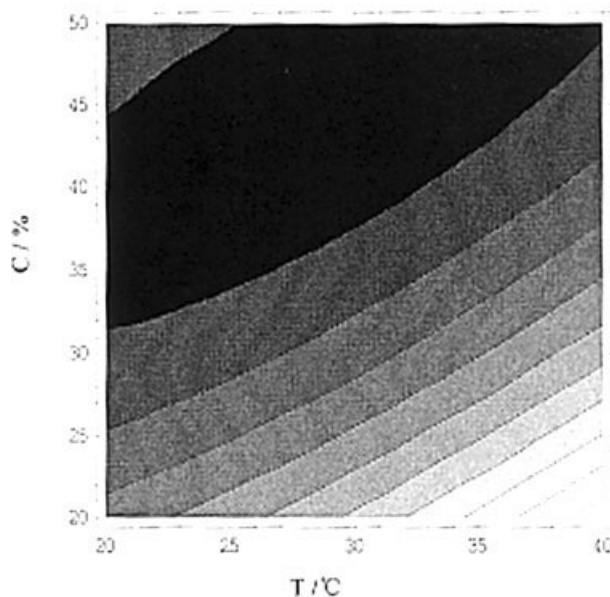
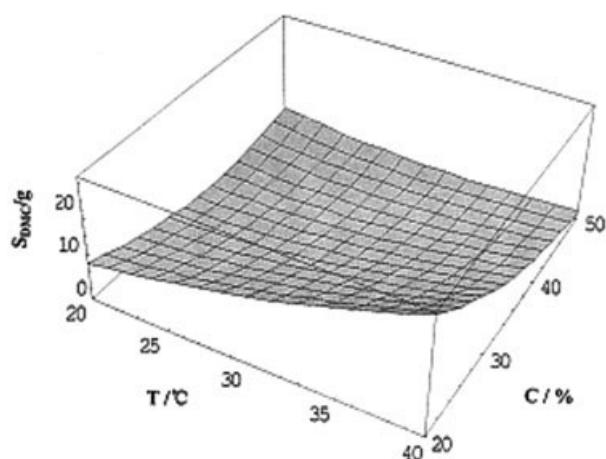


Figure 4 DMC solubility in K_2CO_3 solution with different temperature and different concentration, where T is the temperature of K_2CO_3 solution, $T \in [20,40]$, ($^{\circ}C$); where C is the mass concentration of K_2CO_3 solution, $C \in [20,50]$ (w/w %); where S_{DMC} is DMC solubility in K_2CO_3 solution, (g/100 g).

where T is the temperature of K_2CO_3 solution, $T \in [20,40]$, ($^{\circ}C$); where C is the mass of K_2CO_3 concentration, $C \in [20,50]$ w/w %; where S_{DMC} is DMC solubility in K_2CO_3 solution, (g/100 g); where R^2 is R square.

Poly(AM-DMC) solubility

The equation of poly(AM-DMC) solubility in different K_2CO_3 concentration and different temperature was as follows:

$$\begin{aligned}
 S_{poly(AM-DMC)} = & 0.3448 - 0.00000716 T^2 \\
 & + 0.002448 T - 0.00003364 TC \\
 & + 0.00001352 C^2 - 0.0013 C \\
 & R^2 = 0.9913 \quad (3)
 \end{aligned}$$

where T is the temperature of K_2CO_3 solution, $T \in [20,40]$ ($^{\circ}C$); where C is the mass of K_2CO_3 concentration, $C \in [20,50]$ (w/w %); where $S_{poly(AM-DMC)}$ is poly(AM-DMC) solubility in K_2CO_3 solution, (g/100 g); where R^2 is R square.

The nearly same slopes for Figures 3–5 suggests that the solubility of AM, DMC, and poly(AM-DMC) increase with the decreasing of K_2CO_3 concentration and increasing temperature, in addition, the solubility of AM and DMC are far more higher than that of poly(AM-DMC) in a certain K_2CO_3 concentration and a certain temperature. For example, the solubility of AM and DMC are 13.406 and 9.843 g in $30^{\circ}C$ in 25% K_2CO_3 solution (w/w), however, the solubility of poly(AM-DMC) is only 0.3625 g.

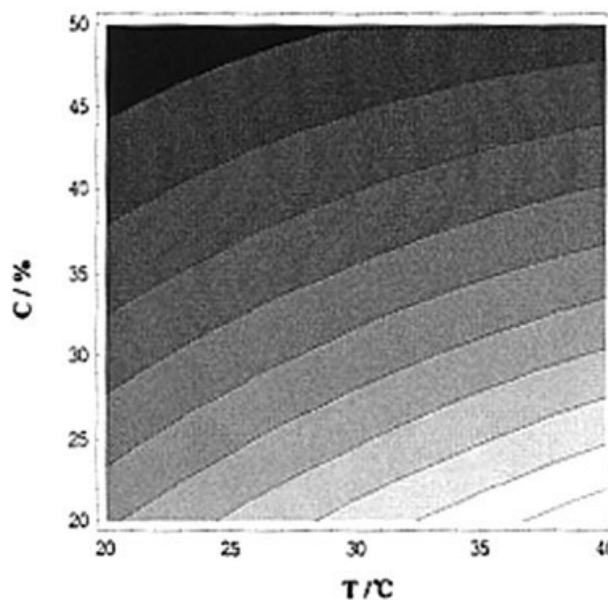
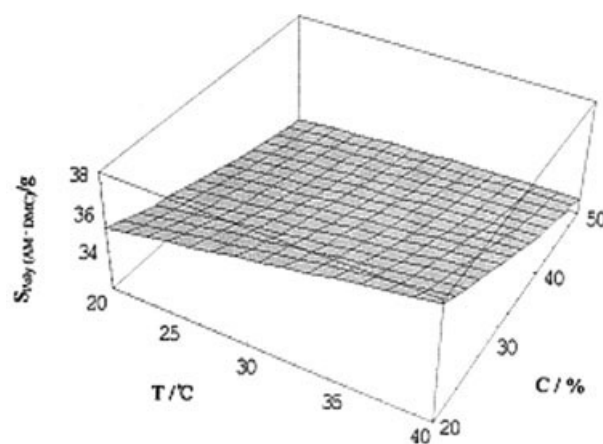


Figure 5 Poly(AM-DMC) solubility in K_2CO_3 solution with different temperature and different concentration where T is the temperature of K_2CO_3 solution, $T \in [20,40]$, ($^{\circ}C$); where C is the mass concentration of K_2CO_3 solution, $C \in [20,50]$, (w/w %); where $S_{poly(AM-DMC)}$ is poly(AM-DMC) solubility in K_2CO_3 solution, (g/100 g).

The analysis of K_2CO_3 concentration

To investigate the effect of K_2CO_3 concentration on intrinsic viscosity of the copolymer, a set of experiments were carried out by keeping fixed at 0.047 of the weight fraction of the total monomers. The tested K_2CO_3 concentration can be divided in two classes: below 20% (w/w) and between 20 and 50% (w/w). In each class, intrinsic viscosity of the copolymer was tested. A first set of experiments of poly(AM-DMC) were performed using different K_2CO_3 concentration (below 20% (w/w)), thus the precipitation architecture was not obtained. When poly(AM-DMC) was performed using K_2CO_3 concentration, which were between 20 and 50% (w/w), the precipitation architecture was obtained (below 20% (w/w) K_2CO_3 solution, poly(AM-DMC) can be easily solved; and above 50%, it is difficult for the monomer AM and DMC to solve.)

Intrinsic viscosity analysis

For some precipitation architecture, such as precipitation polymerization of poly(acrylonitrile), the reason of precipitation is that poly(acrylonitrile) cannot be dissolved in its monomer, however, the reason of this precipitation is that poly(AM-DMC) cannot be easily dissolved in the mixture, which is composed of AM, DMC, and K_2CO_3 mixed with water. Furthermore, chain transmission constant also plays an important role in precipitation architecture: the less chain transmission constant of the solution system, the higher molecular weight polymer could be obtained. With our expectation, a high intrinsic viscosity ($455 \text{ cm}^3/\text{g}$) of copolymer was obtained with our research. It can be seen from Figure 6 that the intrinsic viscosity of poly(AM-DMC) increased with the increasing of K_2CO_3 concentration in 20–25% (w/w), but beyond 25% (w/w), it decreased. The result can be explained by solubility parameter.

Solubility parameter of solution is used to express the solvent characteristic. The component solvent is prepared by two mutually soluble solvents according to the certain proportion, and its solubility parameter can be approximately expressed:¹⁰

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

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

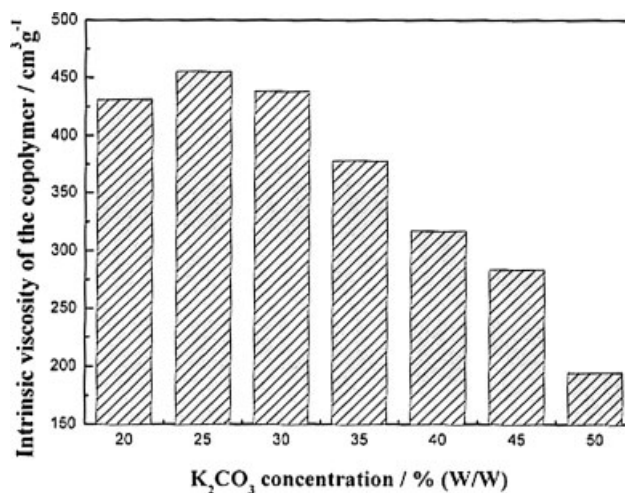


Figure 6 The effects of K_2CO_3 concentration on intrinsic viscosity of the copolymer polymerization temperature 30°C , polymerization time 24 h, discharge time 35 s, discharge power 60 W, monomer concentration 8% (w/w), AM:DMC was 5 : 1 (w/w).

copolymer was a poor solvent. Therefore, the proportion of K_2CO_3 and water has decided the monomer and copolymer solubility and the intrinsic viscosity of poly(AM-DMC) in K_2CO_3 solution.

Increasing of K_2CO_3 concentration can change solubility parameter δ_m of reaction solution, and the higher of K_2CO_3 concentration, the much of solubility parameter changed. As a result, the value between δ_m and δ_p (solubility parameter of polymer) widely changed, and the polymer cannot be easily dissolved into solution leading to salt out. Apparently, particles polymer generated in a very short time in the solution system. In this short reaction time, the chain of macromolecular radical should be short, however, the form of curliness of chain radical play an important role, and it imbed inside of the particles to prevent termination between two chains, and the chain radicals still increased inside of particles, therefore, a higher molecular weight polymer was obtained. So, we achieved a result without our expectation: with the increase of K_2CO_3 concentration (between 20 and 25% (w/w)), the intrinsic viscosity of poly(AM-DMC) increased. When the concentration of K_2CO_3 over 25% (w/w), on the contrary, with the increase of concentration of K_2CO_3 , not only the particles polymers generated in a shorter time, but the chain radicals was much shorter. The degree of chains curliness was no more in compact, and it was difficult for monomers to diffuse into particle; as a result, lower molecular weight polymer was obtained. So, we achieved a result that with the increase of concentration of K_2CO_3 (between 25 and 50% (w/w)), the intrinsic viscosity of poly(AM-DMC) decreased. The final result showed that there was a peak value of K_2CO_3 concentration (25% (w/w)), and in this peak

value, we could obtain the highest intrinsic viscosity of poly(AM-DMC).

Particles size analysis

In K_2CO_3 - H_2O medium, K_2CO_3 was contributed to separate the increasing big molecules and steady precipitation; therefore, both particles size and particles size distribution were mostly depended on the K_2CO_3 concentration. In the case of K_2CO_3 , which allows effective stabilization of poly(AM-DMC) particles, a further set of experiments was aimed to investigate the effect of the K_2CO_3 concentration on the poly(AM-DMC) particles and particles size distribution. It can be seen from Figure 7 that the average particles size did not increase with increasing K_2CO_3 concentration, but showed the maximum value at 25% (w/w) and it was also showed the same trend in Figure 6. It was because intrinsic viscosity was the intrinsic exhibition of copolymer molecular weight, and intrinsic viscosity increased with the increasing of molecular weight. However, over-long molecular chains result in curliness, and exposed active chains would be entwisted into big-gish particles before it became steady. As a result, both intrinsic viscosity and average particles size showed the maximum value at 25% (w/w) K_2CO_3 solution with $455 \text{ cm}^3/\text{g}$ and $120 \mu\text{m}$.

Particles size distribution analysis

Figure 8 was the particles size distribution analysis in 25% K_2CO_3 solution (w/w), which showed that it

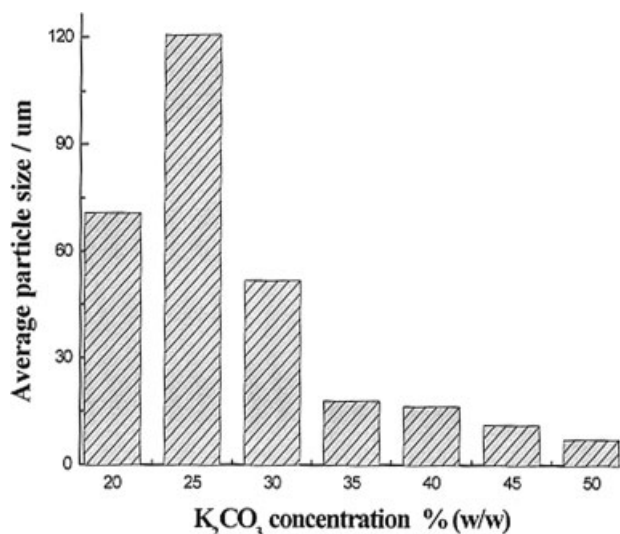


Figure 7 The effects of K_2CO_3 concentration on average particles size polymerization temperature 30°C , polymerization time 24 h, discharge time 35 s, discharge power 60 W, monomer concentration 8% (w/w), AM : DMC was 5 : 1 (w/w).

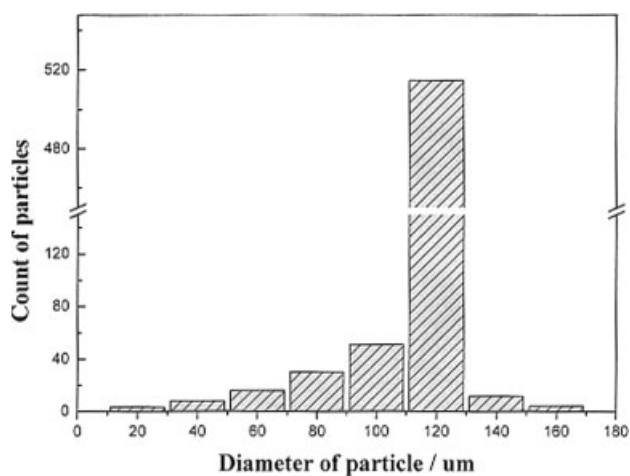


Figure 8 Particles size distribution histogram of poly(AM-DMC) produced with 25 w/w % K_2CO_3 solution. Polymerization temperature 30°C , polymerization time 24 h, discharge time 35 s, discharge power 60 W, monomer concentration 8% (w/w), and AM:DMC was 5 : 1 (w/w).

was constituted by discrete particles having a narrow scope of 20–160 μm and an average diameter of 120 μm , and also the percentage of 120 μm particles was 80.4% in amount.

Particles analysis

The particles micrographs of the samples are showed in Figure 9(a–g). With the increasing of K_2CO_3 concentration, the particles size showed the maximum value at 25%. Otherwise, salting out was a special phenomenon of precipitation polymerization in salt solution. It can be seen that the needle-shape K_2CO_3 crystalloid separated out in 40–50% (w/w) K_2CO_3 solution, and then the amount of needle K_2CO_3 crystalloid increase with the increasing of K_2CO_3 concentration.

CONCLUSIONS

Precipitation polymerization of poly(AM-DMC) has been successfully performed in potassium carbonate-water media by plasma initiation. Potassium carbonate solution is the right media, which is a solvent for AM and DMC and a nonsolvent for poly(AM-DMC), otherwise, high intrinsic viscosity of poly(AM-DMC) also received. A set of experiments were performed using different K_2CO_3 concentration (from 50 down to 10% (w/w)), thus the precipitation architecture was not obtained below 20% (w/w). When it was performed using K_2CO_3 concentrations, which were between 20 and 50% (w/w), the precipitation architecture was obtained, and particles sizes, particles size distribution (7–120 μm), and intrinsic vis-

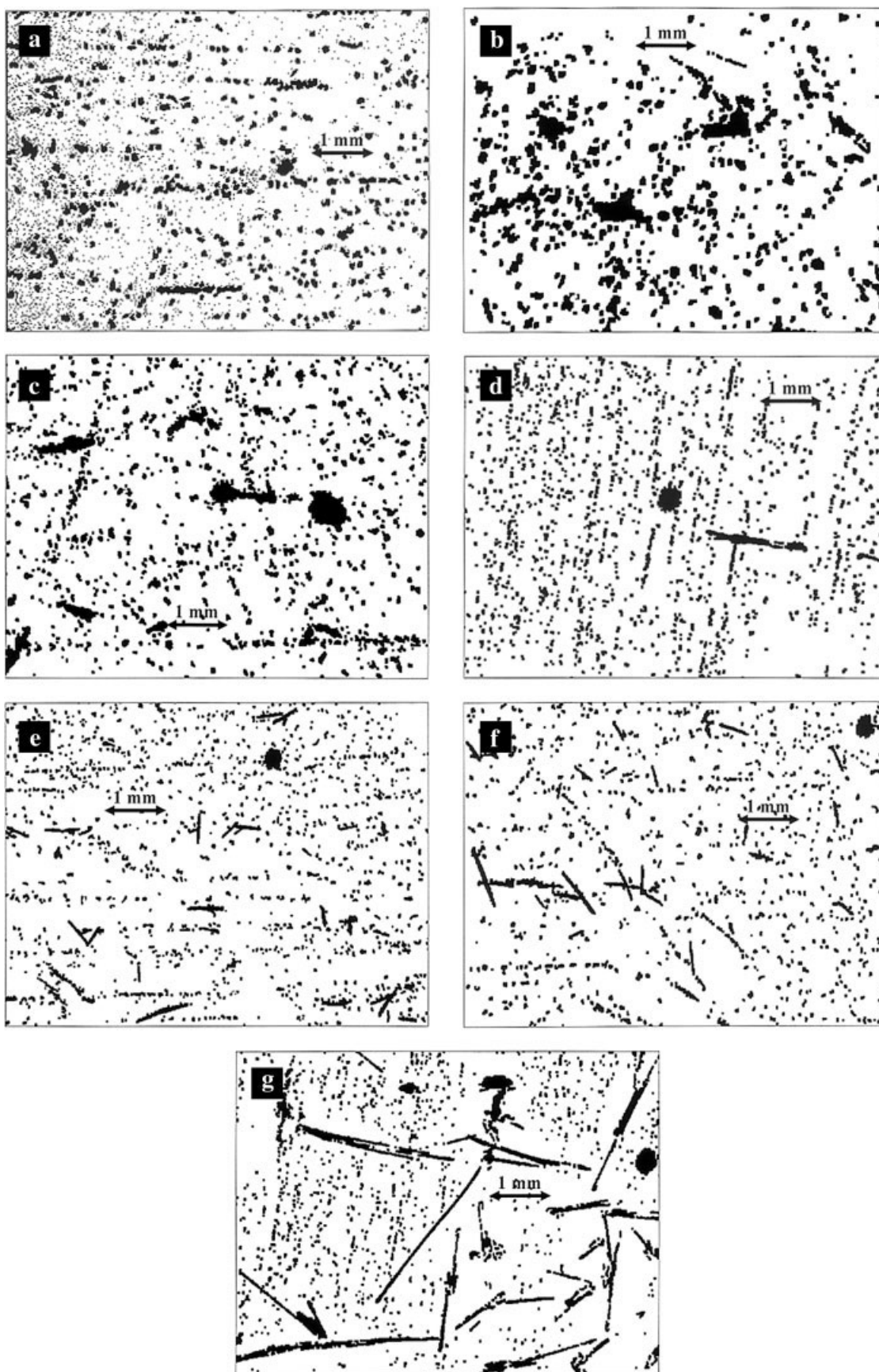


Figure 9 (a) Particles micrographs of the samples prepared in 20% (w/w) K_2CO_3 solution; (b) particles micrographs of the samples prepared in 25% (w/w) K_2CO_3 solution; (c) particles micrographs of the samples prepared in 30% (w/w) K_2CO_3 solution; (d) particles micrographs of the samples prepared in 35% (w/w) K_2CO_3 solution; (e) particles micrographs of the samples prepared in 40% (w/w) K_2CO_3 solution; (f) particles micrographs of the samples prepared in 45% (w/w) K_2CO_3 solution; (g) particles micrographs of the samples prepared in 50% (w/w) K_2CO_3 solution.

cosity of poly(AM-DMC) (ranging up to 455 cm³/g) were also summarized in this article.

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