Aqueous Dispersion Polymerization of Acrylamide with Quaternary Ammonium Cationic Comonomer

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ABSTRACT: Using aqueous solution of ammonium sulfate as medium, acrylamide (AM) and dimethylaminoethyl methacrylate methyl chloride (DMC) as main raw materials, poly(dimethylaminoethyl methacrylate methyl chloride) (PDMC) as stabilizer and 2,2′-azobis (2-amidinopropane) dihydrochloride (V-50) as initiator, the cationic polyelectrolyte of P(DMC-AM) was synthesized by aqueous dispersion polymerization. The effects of the major reaction variables on synthesis conditions, product characteristics (particle size and molecular weight), and polymerization rate were investigated. The polymerization was retarded by the presence of the ammonium sulfate. The optimum reaction conditions for obtaining a stable aqueous dispersion were concentrations of 1.8×10^{-4}–7.0×10^{-4} mol L^{-1} for V-50, 1.5–3.5% for stabilizer, and 23.2–30.0% for salt. The molecular weight of PDMC formed was 1.5×10^{5} to 7.0×10^{5}. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 134–139, 2008

Key words: aqueous dispersion polymerization; acrylamide; stabilizer; retardation

INTRODUCTION

Cationic polyacrylamides with high molecular weight and variable charge density are extensively used as flocculants for liquid/solid separation, retention and drainage aids in paper manufacture, flotation aids and demulsifiers for oil/water clarification, as soil improvers and drainage aids etc.[1–4] Various types of methods for producing the polymers have been developed, such as the polymerization of the monomers in solution or in suspension. Because of the high solution viscosity of aqueous solutions, cationic polyacrylamides have generally been handled as either dry powders (typically from about 85 wt % to about 95 wt %) or water-in-oil emulsions instead of water solutions. However, these polymers in dry-form not only require the consumption of energy in drying at elevated temperature but also subject to degradation through shear or three-dimensional polymer crosslinking. Furthermore, the crosslinking leads to the formation of water-insoluble portions resulting in incomplete dissolution of the polymers and the formation of swollen translucent particles, so called "fish-eye" particles. The disadvantage of the water-in-oil emulsion polymerization technology is that the surfactants and organic solvents which formed the continuous phase could be seen as undesirable impurities for many uses, this raises environmental concerns with respect to the use of these materials.

Dispersion polymerization in water or in an organic medium has proven to be a very useful tool in producing polymer particles of 1–20 μm.[5–8] However, while a great deal of the interest has been focused on dispersion polymerization both in nonpolar and polar media, little research had been reported on the dispersion polymerization of acrylamide (AM) in aqueous medium in the absence of organic solvents.[9–11] Dispersions produced in water might be more suitable for many applications. For example, the dispersion products having no organic solvents could be directly applied as prepared without separation and drying of solid polymers. The dispersion polymerization of AM in water/*tert*-butyl alcohol medium using poly(vinyl methyl ether) as the polymeric stabilizer has been reported.[5,6,12]

In a typical dispersion polymerization, the monomer and the initiator are both soluble in the medium, but the medium is a poor solvent for the resulting polymer. Accordingly, the reaction mixture is homogeneous at the onset and polymerization is initiated in a homogeneous solution. Depending on the solubility of the resulting oligomers in the medium, phase separation occurs at an early stage leading to nucleation and the formation of primary particles. The particles are stabilized by adsorption of a sufficient amount of stabilizers (some of the polymers also got grafted to the stabilizers[13–16]) on the

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surface to decrease the surface free energy. This has been referred to as steric stabilization. Also, the electrostatic stabilization plays a role.[17] The particles are swollen by the polymerization medium such that monomer may enter into the particles through the solvent channels. Polymerization mainly occurs in the particles until monomer is consumed.

The concentrations of the stabilizer, the salt, and the initiator play key roles in dispersion polymerization. It has been found that these variables have significant effects on the particle size, the molecular weight of the polymer, and the kinetics of polymerization process. In this case, the cationic polyelectrolyte of AM with dimethylaminoethyl methacrylate methyl chloride (DMC) was synthesized by dispersion copolymerization. The different impact of these variables on suitable synthesis conditions, product characteristics, and polymerization rate were assessed. Because of the presence of the ammonium sulfate, the polymerization rate was retarded. These phenomena have not been previously observed.

EXPERIMENTAL

Material

Acrylamide (AM) and dimethylaminoethyl methacrylate methyl chloride (DMC) were all chemical agents, used without further purification. Ammonium sulfate (AS) and 2,2'-azobis (2-amidinopropane) dihydrochloride (V-50) were of analytical grade and used as received. Poly(dimethylaminoethyl methacrylate methy chloride) (PDMC) was prepared from DMC in an aqueous solution using V-50 as initiator at 60°C. The molecular weight of PDMC was in the range of 1.0×10^5–7.0×10^5. Deionized water was routinely used.

Polymerization procedure

The polymerization procedure may be described as follows: the varying quantities of the monomers, ammonium sulfate, PDMC, and deionized water were added to a 250-mL glass reactor equipped with a stirrer, reflux condenser, thermometer, and nitrogen-inlet tube. After 30 min of stirring at room temperature under nitrogen purge, the temperature was controlled to 50°C. The polymerization was initiated by injecting the V-50 initiator into the system. Under a nitrogen atmosphere, the polymerization was allowed to proceed at a constant temperature of 50°C for 6 h. The mixture was then allowed to cool to room temperature to yield a fine, white dispersion. The agitation speed was fixed at 200 rpm throughout the experiment.

Polymer characterization

The overall monomer conversion could be calculated from a determination of the residual monomer (AM and the cationic comonomer) content using a bromating method, which was described as follows: Excess $KBrO_3$-KBr was added into the sample solution, in the presence of acid; $KBrO_3$ reacts with KBr to produce Br_2 which adds to residual monomer. Excess KI was used to reduce the residual Br_2. The amount of I_2 formed was determined by titration with $Na_2S_2O_3$ solution. A knowledge of $Na_2S_2O_3$ consumption permits the determination of the overall monomer conversion.

The intrinsic viscosity of the copolymer was determined in $1M$ aqueous NaCl solution with an Ubbelhode capillary viscometer at 30°C. The average molecular weight was calculated using the Mark-Houwink relationship[18]: $M_w = (10,000 \times [\eta]/3.73)^{1/0.66}$.

The particle size and the size distribution were measured using a laser particle size analyzer (LS230; Coulter, US) and by transmission electron microscopy (JEM-1200EX; JEOL, Japan). According to the default of the LS230 laser particle size analyzer, the D (4,3) represented D_{mean}. SD was the variance of the D (4,3). The Coefficient variation (CV) was calculated with the following relationship: CV = SD/$D_{mean} \times 100\%$, which showed the particle size distribution. The D_{mean} of the volume average particle size was taken as the average particle size. The sample was diluted to the same concentration as the original dispersion of ammonium sulfate solution.

RESULTS AND DISCUSSION

Particle size and size distribution

The plots in Figure 1 show that the particle size ranged from 0.2 to 3.8 μm with two different particle size distributions. As illustrated in Table I, the CV value in the cubing statistics was smaller than that in numerary statistics.

Effect of DMC/AM molar ratio

The data in Table II show that both the molecular weight of the polymer and the final overall conversion decreased with increasing DMC/AM molar ratio. It has been suggested that earlier termination may be induced by higher concentration of the cationic comonomer.[19] When the DMC/AM molar ratio was increased above 25/75, a stable dispersion could not be obtained. In dispersion polymerization, the entry rate of cationic comonomer into the growing particles might be retarded due to the positive charges of the particles even though a small fraction is ionized. For the polymerization of the PAM, ionization would cause the particles to undergo
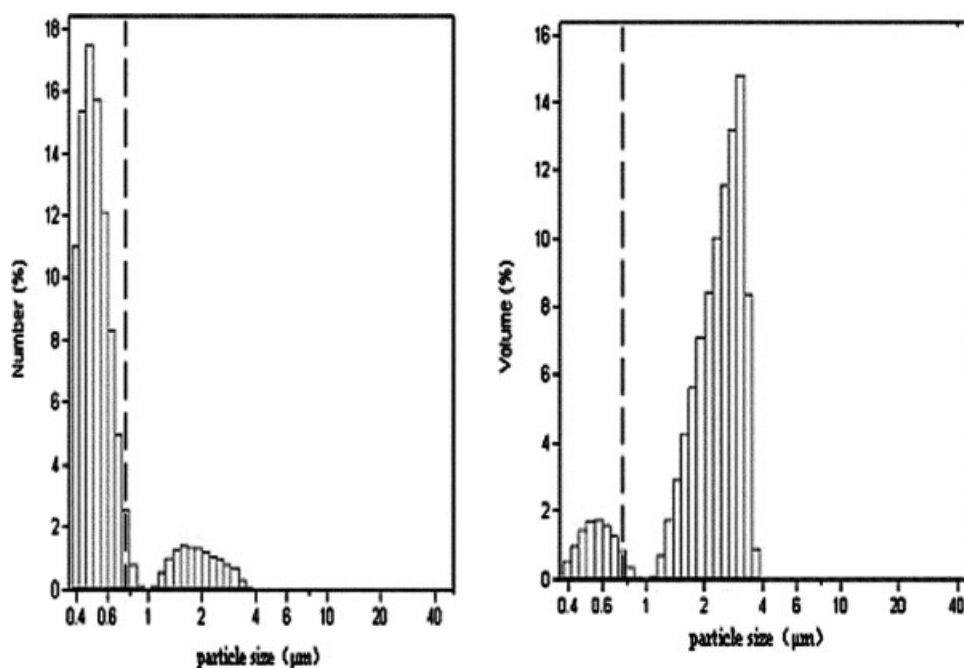
Figure 1 Particle size distribution of the dispersion copolymer.

significant swelling by water. Consequently the monomer should find relatively easy entry into the swollen particles through the solvent channels.[3]

An intriguing observation was that the particle size increased with an increase in the DMC/AM molar ratio. Because of the presence of quaternary ammonium groups in DMC and the stabilizer, it might be expected that the dispersed particles in the aqueous medium should be charged and that the particle size would become smaller with increasing content of DMC owing to electrostatic repulsion. However, as demonstrated by the data presented in Table II and Figure 2, this was not the case. In fact, the opposite occurred. The average particle size increased from 2.9 μm, 5.7 μm to 6.1 μm as the DMC/AM molar ratio was changed from 5/95, 15/85 to 25/75. As it has been suggested obviously the cationic comonomer, oligomers, stabilizer, and even the precipitated oligomers could be ionized to a considerable extent in the presence of abundant water surrounding them. The positively charged oligomers would be stabilized by electrostatic repulsion and would grow by adsorption of the monomers. Furthermore, at higher DMC/AM molar ratio, a large

number of smaller particles might be formed during the early stages of polymerization because of the presence of more ionic moieties. The absorption of stabilizer on the oligomers would be hindered by increased electrostatic repulsion. Hence, coalescence might occur more rapidly and result in the eventual formation of larger particles.

Effect of initiator concentration

The impact of the variation of initiator concentration from 1.8×10^{-4} mol L^{-1} to 7.0×10^{-4} mol L^{-1} on the molecular weight of the polymer is displayed in Figure 3. The decrease of polymer molecular weight with increasing initiator concentration is as ex-
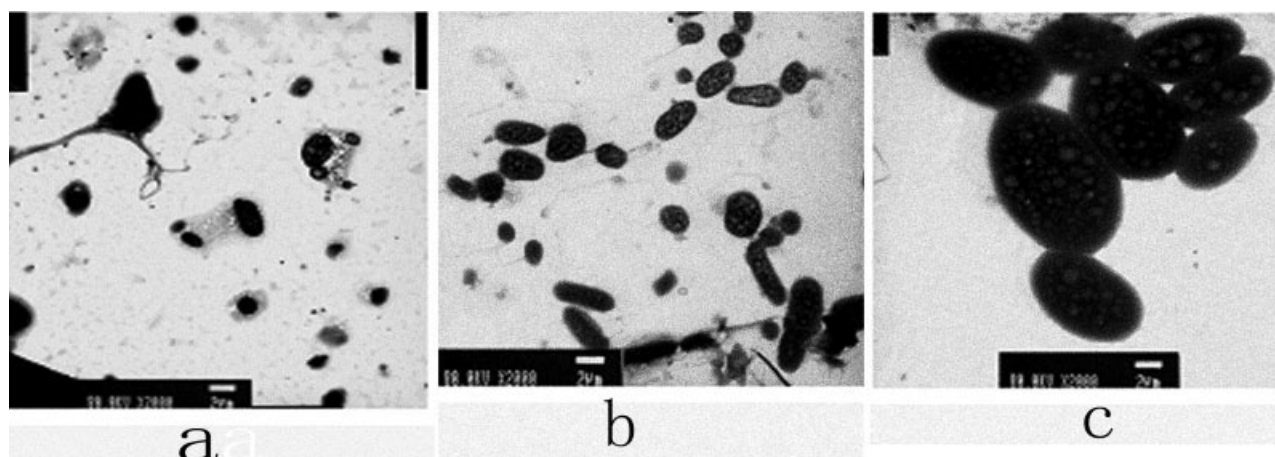
TABLE I
Particle Size and Size Distribution of the Dispersion Polymer

Statistics	D_{mean} (μm)	SD (μm)	CV (%)
Numerary statistics	0.689	0.521	75.6
Cubing statistics	2.273	0.801	35.2

TABLE II
Effect of the DMC/AM Ratio on Molecular Weight and Particle Size

DMC : AM (mol-ratio)	M_w ($\times 10^4$)	Overall conversion (%)	D_{mean} (μm)
5 : 95	689.5	94	2.9 (0.9–4.8)
7 : 93	578.8	93	3.4 (1.2–5.7)
10 : 90	564.7	90	3.9 (1.2–6.0)
12 : 88	521.6	87	4.8 (1.8–7.6)
15 : 85	434.6	85	5.7 (1.0–7.4)
20 : 80	356.4	82	6.1 (1.4–8.3)
25 : 75	Aggregated	–	–
30 : 70	Aggregated	–	–

Initiator, 2.25×10^{-4} mol L^{-1}; total monomer, 14%; PDMC, 2.3%; ammonium sulfate, 27%; temperature, 50°C; D_{mean} (μm), average of particle diameter (range of particle diameter).

Figure 2 TEM photographs of CPAM particles prepared with different levels of cationic degree (CD): (a) 5%, (b) 15%, (c) 25%.

pected.[13,14,20–22] The rate of the polymerization was proportional to the square root of the rate of initiation. An increase in the initiator concentration had a dramatic accelerating effect on the polymerization rate. On the other hand, the average chain length was lowered by an increase in the rate of initiation.[24]

As is generally observed, the particle size increased with an increase in initiator concentration. The higher initiator concentration leads to the generation of oligomers at a rate greater than that for adsorption of the stabilizers. Thus, the dispersed particles were not well stabilized and tended to coalescence rapidly and produce larger particles.[21,23,24] Moreover, the proper initiator concentration was dependent upon the temperature, the monomer concentration, and the particular polymer to be produced.

Effect of salt concentration

The salt was important in that the polymer produced in the aqueous medium would be rendered insoluble on formation and form particles of water-soluble polymers. The selection of the particular salt to be utilized was dependent upon the particular polymer to be produced, the stabilizer to be employed, and the other reaction conditions to which the dispersion was subjected. For the DMC/AM dispersion polymerization, ammonium sulfate was used as the water-soluble salt. The effects of the salt concentration on the molecular weight and particle size were studied. In particular, the effects of the salt concentration on the polymerization rate and precipitation rate were examined.

Polymerization was carried out with varying salt concentration from 18.3 to 34.2%, Monomer and stabilizer concentrations were kept constant at 14 and 2.4%, respectively. With an increase in salt concen-

tration, an increase in the molecular weight of the product was observed. The molecular weight of which oligomers precipitated varied slightly. Moreover, the period of the polymerization before the mixture became turbid was prolonged much. Data are presented in Table III. This indicates that a major portion of the polymerization occurred in the particle phase as a result of the gel effect, which became more prominent at higher salt concentration. The dispersion polymerization displayed autoacceleration in both the solution phase and the particle phase.
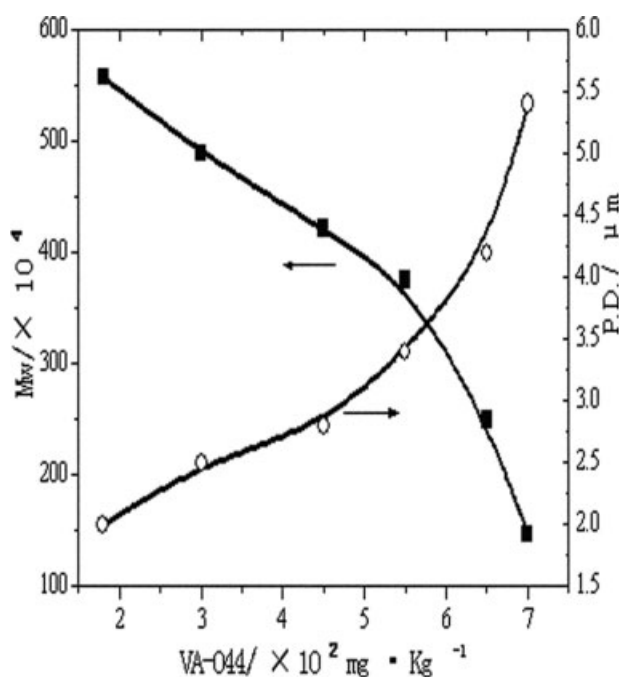
Figure 3 Effect of initiator concentration on the molecular weight of the dispersion copolymer: PDMC 2.1%; Monomer 12%; CD 10%; Temperature 50°C.

TABLE III
Effect of Salt Concentration on Polymerization Rate and Molecular Weight

V-50 ($\times 10^{-4}$ mol L^{-1})	AS (% w/v)	Precipitation[a] (min)	M_{w1} ($\times 10^4$)	M_{w2} ($\times 10^4$)	D_{mean} (μm)
2.5	23.2	90	166.3	384.0	4.3 (0.9–7.8)
2.5	26.0	120	158.5	405.3	3.4 (0.8–6.0)
2.5	28.0	150	152.7	422.6	3.1 (1.1–6.4)
2.5	30.0	210	148.4	485.9	2.9 (0.4–5.1)
2.5	32.0	Uninitiated	–		–
6.25	23.2	95	164.6	321.7	4.1 (1.3–7.6)
6.25	26.0	125	161.2	377.9	3.9 (1.5–6.7)
6.25	28.0	160	154.5	458.7	2.8 (0.5–5.4)
6.25	30.0	200	152.6	481.5	2.4 (0.6–4.4)
6.25	32.0	Uninitiated		–	–

M_{w1}, the molecular weight of the oligomers when the mixture became turbid; M_{w2}, the molecular weight of the final product; D_{mean} (μm), average of particle diameter (range of particle diameter).

[a] The period of the polymerization before the mixture became turbid.

At the same time polymerization was retarded by the presence of ammonium sulfate, independent of initiator concentration. The higher the salt concentration is the lower is the rate of precipitation or the formation of stable nucleis. The reason for the retardation is not well understood at the moment since the system is reasonably complex. Some factors that might impact the process are the initiator decomposition rate, the presence of positive charge on the comonomer, the stabilizer, and the particles. The salt might induce suppression of swelling of the oligomers and thus the extent of swelling of the particles would be reduced, leading to a lower entry rate of monomers into the particles through the solvent channels which would lead to a retardation of polymerization.

The size of the polymer particles decreased with an increase in salt concentration. It has been suggested[19,25] that the salting-out effect would be reinforced and the stabilizing action of the cationic stabilizer would also be enhanced by high ammonium sulfate concentration. Therefore, precipitation or the formation of stable nuclei would be hastened. With an increase in the salt concentration, the precipitation of shorter copolymer chains would occur and smaller particles would be obtained. The observed effect of salt concentration on particle size is consistent with this view.

It has been demonstrated that high salt concentration (above 30%) may induce excessive salting-out. This results in a high yield of the coagulum in the form of agglomerated lumps.

Effects of the concentration and the molecular weight of stabilizer

PDMC, which possesses active α–hydrogen atoms as possible chain transfer sites, was used as the stabi-

lizer to prevent agglomeration of the precipitated polymer particles during polymerization. Both the particle size and the molecular weight decreased when the stabilizer concentration was increased (see date in Table IV). This is in agreement with the results previously reported.[22,26–30] The presence of excess stabilizer might act as the chain transfer agent and lend to lower polymer molecular weight.

Particle stabilization in dispersion polymerization is usually referred to "steric stabilization" reflecting adsorption of stabilizer at the particle surface. Additionally, the charged quaternary ammonium end groups in the polymer chains of PDMC were anticipated to enhance the stabilization of the lattices by electrostatic infraction. The coexistence of the adsorption-stabilization mechanism with a graft-stabilization mechanism has often been demonstrated. As the stabilizer concentration is increased, the faster stabilizer adsorption occurs, hence, a greater number of particles with smaller size are formed during the primary stabilization process. However, when the stabilizer concentration is above 3.5% the stability of the dispersion becomes very

TABLE IV
Effects of PDMC Concentration and its Molecular Weight on Dispersion Copolymer

M_w of PDMC ($\times 10^4$)	PDMC (% w/v)	M_w ($\times 10^4$)	D_{mean} (μm)
48.6	0.8	Aggregated	–
48.6	1.5	548.7	4.3 (0.8–6.7)
48.6	2.4	462.6	3.7 (0.4–6.4)
11.5	2.4	Gellike polymer	–
70.6	2.4	Curdled	–
48.6	3.5	388.9	2.6 (0.9–5.6)
48.6	4.0	Aggregated	–

CD, 10%; total monomer, 14%; PDMC, 48.6 $\times$ 10^4; temperature, 50°C.

poor. This induces the formation of aggregated lumps separating from the medium. Moreover, the use of a stabilizer of appropriate molecular weight is necessary. A stabilizer with molecular weight less than 1.5×10^5 would results agglomeration after the particles have formed. However, when the molecular weight of the PDMC is too higher (7.0×10^5 and above), the system becomes quite viscous and the stabilizer molecules make links between particles, leading to larger particles and ultimate flocculation.

Suitable synthesis conditions

For obtaining a stable aqueous dispersion of copolymer, the variables were controlled as follows: the DMC/AM molar ratio ranged from 5/95 to 25/75, the concentrations of ammonium sulfate, the initiator and the stabilizer were in the ranges of 23.2–30.0%, 1.8×10^{-4}–7.0×10^{-4} mol L^{-1} and 1.5–3.5%, respectively, the suitable molecular weight of PDMC was from 1.5×10^5 to 7.0×10^5.

CONCLUSIONS

The cationic polyelectrolyte of DMC-AM copolymer was synthesized by dispersion polymerization, using the azo compound V-50 as initiator, PDMC as stabilizer, and an aqueous solution of ammonium sulfate as the medium.

The effects of varying the concentrations of the stabilizer, the initiator and the comonomer on the molecular weight, and the particle size were in conformity with those previously reported. A decrease in V-50 concentration and DMC/AM molar ratio resulted in a decrease of particle size and a increase in polymer molecular weight, while a decrease in stabilizer concentration induced a decrease in both particle size and polymer molecular weight. For this dispersion polymerization, the salt concentration not only affected the molecular weight and the particle size, but also retarded the polymerization rate. It is suggested that swelling of the oligomers was suppressed owing to the presence of the ammonium sulfate. As a result, the entry rate of the monomers into the particles through the solvent channels was lowered and the polymerization was retarded.

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