Aqueous Dispersion Polymerization of Amphoteric Polyacrylamide

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ABSTRACT: The terpolymer of acrylamide (AM), dimethylaminoethyl methacrylate methyl chloride (DMC), and acrylic acid (AA) was synthesized with their molar ratio of 70 : 15 : 15 through dispersion polymerization in aqueous solution of ammonium sulfate (AS), using poly(dimethylaminoethyl methacrylate methyl chloride) (PDMC) as stabilizer and 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) as initiator. The particle size of the terpolymer ranged from 5 to 8 μm and the intrinsic viscosity was from 5.5 to 11.6 dL g^{-1}. The terpolymer had anti-polyelectrolyte effect under low AS concentration, but polyelectrolyte effect with the concentration beyond 10%. Polymerization dispersion with low apparent viscosity, uniform particles, good stability, and high molecular weight terpolymer was obtained in single stage. The effects of varying concentrations of salt, stabilizer, and monomers on particle morphology and intrinsic viscosity were investigated. With increasing concentration of AS and PDMC, the intrinsic viscosity of terpolymer increased, then decreased afterward. However, it increased gradually with increase in monomer concentration. The particle size was enlarged with increasing of AS and monomer concentration and decreasing of PDMC concentration. The optimum condition was the concentrations of salt, stabilizer, and monomers 28%, 3.0%, and 8% to 15%, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1131–1137, 2010

Key words: polyelectrolytes; dispersions; water-soluble polymers; viscosity

INTRODUCTION

Amphoteric polyacrylamide (AmPAM) carries anionic and cationic charge groups on the polymer backbone which can adsorb organic and inorganic suspension substances, respectively, to promote its flocculation properties. As compared with cationic polyacrylamide (CPAM) and anionic polyacrylamide (APAM), AmPAM has the advantages of, besides them, the anti-polyelectrolyte effect and a wide application range of pH value. So, it has attracted considerable interests around the globe.[1–3] Until now, AmPAM has been prepared by four polymerization methods below: solution polymerization,[4–6] microemulsion polymerization, inverse microemulsion polymerization,[7] and dispersion polymerization.[8]

Dispersion polymerization is a unique method due to its inherent simplicity of the single-step process in which particles ranged from 0.1 to 15 μm were formed.[9–12] Before polymerization, monomer, stabilizer, initiator, salt, and solvent formed an originally homogeneous reaction mixture. Then, the initiator decomposed and the free radicals reacted with monomer to form oligomer radicals. At a critical chain length, the oligomer precipitated and adsorbed the stabilizer to form stable particle nuclei. Once particles were formed, they absorbed monomers from the continuous phase and polymerization mainly occurred on the surface of particles.[11] Reaction media was a key factor. Appropriate solvent was insoluble for the formed polymer particles but soluble for the stabilizer and monomers. CPAM and APAM have been prepared by dispersion polymerization with organic solvents or inorganic salt solution as the reaction media.[10,13] Dispersion polymerization in aqueous salts solution has become more interesting, recently, because no organic solvents were used. Although there are many articles about CPAM or APAM, little research has been reported on the dispersion polymerization of AmPAM in aqueous medium without any organic solvents.

In this work, we developed a method for preparing AmPAM dispersion in water media. The amphoteric dispersion terpolymer of acrylamide (AM), dimethylaminoethyl methacrylate methyl chloride (DMC), and acrylic acid (AA) was synthesized in aqueous AS media by using 2,2′-azobis-(2-amidinopropane) dihydrochloride (V-50) as initiator and poly (dimethylaminoethyl methacrylate methyl chloride)

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(PDMC) as steric stabilizer. In addition to the steric stabilization, the positive charged end groups in the polymer chains of PDMC were anticipated to enhance the stabilization of the lattices by electrostatic repulsion. The effects of the concentrations of salt, stabilizer, and monomers on the dispersion polymerization were investigated. The solution properties of the terpolymer dispersion were discussed earlier.

EXPERIMENTAL

Materials

Acrylamide (AM, 99%, Dia-Nitrix. Co., Tokyo, Japan) and dimethylaminoethyl methacrylate methyl chloride (DMC, 76%, Befar Group, Binzhou, China) were both industrial grade, used without further purification. Acrylic acid (AA, Tianjin Damao Chemical Reagent Factory, Tianjin, China), ammonium sulfate (AS, Sinopharm Chemical Reagent Co., Shanghai, China), sodium hydroxide (Tianjin Bodi Chemical Co., Tianjin, China), and 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50, Wako Pure Chemical Industries, Osaka, Japan) were of analytical grade, used as received. PDMC was prepared from DMC in an aqueous solution using V-50 as initiator at 60°C. The relative molecular weight of PDMC was in the range of 1.33×10^6 to 2.90×10^6 with the following equation according to the calculation method of the Ref. 14. Deionized water, which was prepared by us, was used throughout this work.

$$[\eta] = 5.98 \times 10^{-5} \times M_w^{0.72}$$

Preparation of polymer dispersion

A given amount of monomers, AS, PDMC, and deionized water were added to a 500 mL glass reactor fitted with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube. After purging with nitrogen and controlling temperature at 60°C by means of an external heating jacket, 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 60°C for 8 h. The mixture was then allowed to cool at room temperature to yield a fine, white dispersion.

Polymer characterization

AmPAM dispersion was precipitated many times by alcohol solution (1 : 1) and acetone to purify the sample. The intrinsic viscosity [η] of the terpolymer was determined in 1*M* NaCl aqueous solution with an Ubbelohde capillary viscometer at 30°C. The total monomer conversion could be obtained by determining the residual contents of AM, AA, and DMC with bromating method,[11] where the residual monomers were presumed to be DMC. The particle size and distribution were determined by a LS230 Sizer (Beckman Coulter, CA). The samples were usually dispersed by the ultrasonic agitation before measurements. The salt water in which AS concentration was equal to that of the original dispersion was used as circulating water. This ensured that an extended electrical double layer cannot be changed artificially. The morphologies of the particles in AmPAM dispersion were obtained with optical microscope and transmission electron microscope (JEM-1200EX/S, JEOL, Tokyo Japan). The ^{1}H-NMR spectrum of DMC/AM/AA terpolymer was obtained in D_2O with a Bruker (500 MHz 1H) NMR spectrometer (Bruker Corporation, Bremen, Germany). The apparent viscosity of AmPAM solution was measured by Brookfield DV-II +Viscometer (Brookfield Engineering Laboratories, MA) at 25°C with the spindle 61.

RESULTS AND DISCUSSION

Solution properties of AmPAM

AmPAM has a prominent feature of anti-polyelectrolyte effect. Solution viscosity of polyelectrolyte, such as, CPAM or APAM, decreased with increasing of inorganic salt. As for AmPAM, it would increase on the contrary. Solution properties of AmPAM were investigated under the condition: AmPAM concentration 0.75%; molar ratio of AM : DMC : AA 70 : 15 : 15; rotor speed 1 rpm, with the results shown in Figure 1. It was indicated that AmPAM performed anti-polyelectrolyte effect only in a narrow concentration range. But with AS concentration beyond 10%, it performed polyelectrolyte effect.

Obviously, the whole system viscosity variation accompanied by rising AS concentration could be divided into three stages (see Fig. 1). In the first stage, called as "stage of anti-polyelectrolyte effect," the apparent viscosity of AmPAM solution increased rapidly with increasing of AS concentration. The AmPAM molecules in solution were promoted to stretch by a small amount of AS. Originally, the groups with positive or negative charge attracted oppositely-charged groups by electrostatic force without any small molecules. But, AS molecules can screen the electrostatic force between groups with opposite charge, then AmPAM molecules stretched largely, which caused the apparent viscosity of AmPAM solution to increase. The second stage was called as "the stable stage," AS concentration 3–10%, in which the apparent viscosity of the dispersion was nearly constant. Under this

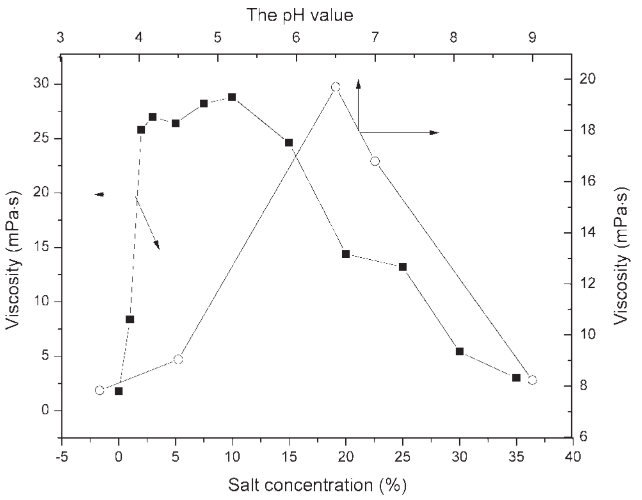

Figure 1 Solution properties of AmPAM.

condition, most of AmPAM molecules stretched to the largest extend. With the increase of AS concentration, the morphology of AmPAM molecules would not change much. So, the viscosity of AmPAM solution kept constant. The third was the stage of "the salting-out effect." When the AS concentration was beyond 10%, AmPAM was likely to be a polyelectrolyte. Excessive AS caused AmPAM molecules to coil together, similar to CPAM and APAM.[10,11] Under this condition, dispersion polymerization of AM, DMC, and AA could be carried out in aqueous AS solution.

The AmPAM solution properties were studied with various pH values when the AS concentration and polymer concentration was kept constant as 25% and 0.5%, respectively. The highest pH value was selected as 9.0 because more NaOH was needed to raise it in 20% AS solution. The rotor speed was set as 1 rpm. The data was shown in Figure 1. It was found that the solution would become low viscosity with pH value below 6.5, and turbidity below 4.5, but was colorless and transparent with pH value beyond 4.5. Because the carboxylate group was weak, low pH atmosphere was adverse to dissociation. Na^+ and NH_4^+ tend to exist as ions. So, the bond of the carboxylate group was unstable. However, the carboxylate group could bond more stably to H^+ or the quaternary group. In addition, the intertwinement, especially between the different molecules, made the bond of the carboxylate group and the quaternary group more stable. Therefore, the solution viscosity decreased with reducing pH value. Furthermore, the polymer became insoluble when the pH value was lower than 4.5. With the pH value beyond 6.5, more carboxylate group dissociated. The net charges in the molecules became less, which caused them less stretched. Then, the viscosity decreased.

^{1}H-NMR characterization

Figure 2 represents ^{1}H-NMR spectra of the AmPAM, which was purified from polymer dispersion. The

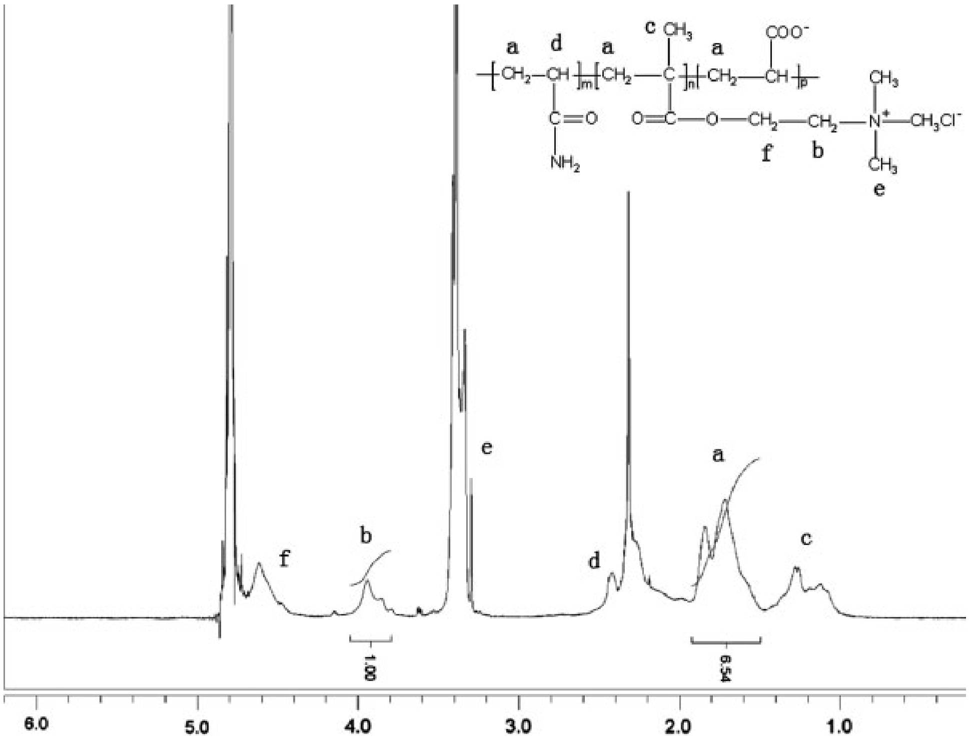

Figure 2 ^{1}H-NMR spectra of AmPAM.

TABLE I
Effect of as Concentration on Dispersion Polymerization of DMC/AM/AA

AS/wt %	η/dL g^{-1}	D_{mean}/μm	Characteristics
26	6.3	5.6 (0.9–10.1)	Milky white and high viscosity
28	7.6	6.1 (1.2–8.3)	Milky white, good fluidity, and stability
30	6.0	6.7 (1.3–8.7)	Milky white, good fluidity, and stability
32	5.5	8.3 (1.5–11.6)	Milky white and general fluidity

Synthesis conditions: Total monomer 10%; PDMC 3.0%; V-50 1.2×10^{-4}g g(monomers)$^{-1}$; M_w of PDMC 1.33×10^6.

monomers ratio of the sample (AM : DMC : AA) was 70 : 15 : 15. Each proton is readily distinguished from the resonance peaks of the terpolymer resulted from the dispersion polymerization. According to the integral area of the resonance peaks of a and b proton (CH_2 of monomers and $-CH_2-N-$ of DMC, respectively), the approximate composition of the copolymer could be calculated. The molar ratio of (AM+AA) to DMC in the copolymer is about 83/15, which is near to the ratio in the feed, 85/15. It was indicated that the conversion rate of AM was a little lower than that of DMC and AA. As mentioned earlier, with increasing of AS concentration, apparent viscosity of AmPAM solution increased gradually. It was called "anti-polyelectrolyte effect," which would not occur if only one monomer, AA or DMC, polymerized with AM. So, Figures 1 and 2 indicate that all of three monomers had participated in polymerization.

Effect of salt concentration

The polymerization experiments were carried out with varying AS concentration from 26 to 32%, whereas the concentrations of monomers, stabilizer and initiator as well as the molar ratio of AM : AA : DMC were kept constant at 10%, 3.0%, 1.2×10^{-4}g g(monomers)$^{-1}$, and 70 : 15 : 15, respectively. The effects of AS concentration on intrinsic viscosity and particle size of terpolymer dispersion were studied. The result was shown in the Table I and Figure 3. Table I indicated that the particle size increased with increasing AS concentration from 26 to 32%. However, the intrinsic viscosity of the polymer dispersion increased at first and then decreased with AS.

This result was contrasted with the result for the aqueous dispersion polymerization of CPAM, where the particle size decreased with increasing salt concentration.[13] At a relatively low concentration, AS can promote the solubility of AmPAM, but AmPAM can also be precipitated at high AS concentration. The reason may be concerned with the charge on the oligomer and the particles. In the dispersion polymerization of CPAM, both the oligomer radicals and particles had positive charges. On the contrary, as for AmPAM polymerization, the oligomer radicals had less charge than CPAM, but the particles had positive charges because of the stabilizer adsorbed on them. So, the electrostatic repulsive interaction between the oligomer radicals and the particles of CPAM polymerization was weaker than AmPAM.

The salt concentration had two effects on the dispersion polymerization. On one hand, the salting-out effect can promote the copolymer to precipitate from the reaction media. On the other hand, AS can retard the stretch of the stabilizer molecules. Under this condition, the stabilization of PDMC was weakened. Salting-out effect decreased with the decrease of the concentration, whereas the critical molecular chain length of oligomer and nucleation period increased, so the disperse particles were formed. At the same time, PDMC can stretch enough and have stronger stabilization in this case, which reduce the probability of primary particles congregation. So, the final particle size decreased. At a higher AS concentration, critical molecular chain length decreased and more primary particles were formed because the

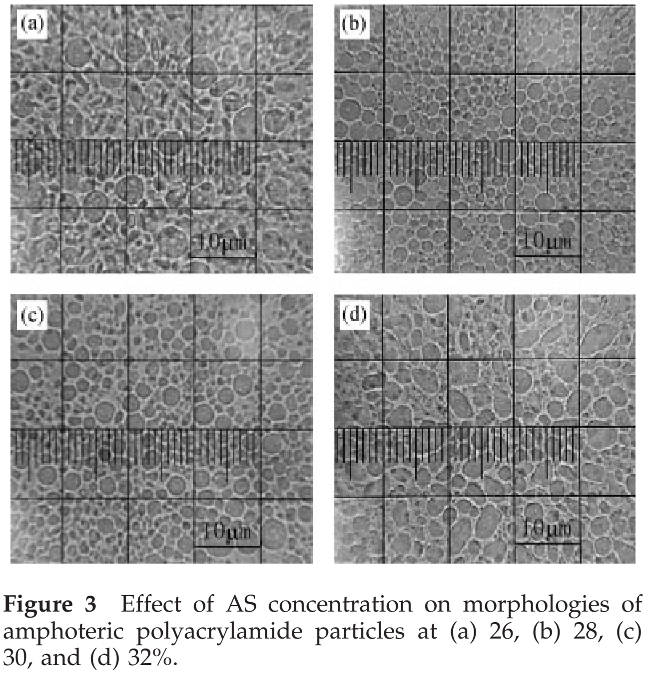

Figure 3 Effect of AS concentration on morphologies of amphoteric polyacrylamide particles at (a) 26, (b) 28, (c) 30, and (d) 32%.

TABLE II
Effect of Stabilizer Concentration on Dispersion Polymerization of DMC/AM/AA

PDMC/%	η/dL g^{-1}	D_{mean}/μm	Characteristics
1.0	3.3	7. 46 (2.2–11.4)	Grayish white, high viscosity, much adhered to the flask
2.0	7.0	6.15 (1.3–10.2)	Milky white, good fluidity, and stability
3.0	11.7	4.93 (1.0–9.4)	Milky white, good fluidity, and stability
4.0	8.1	4.16 (0.9–8.5)	Milky white, general fluidity
4.5	5.3	3.76 (0.8–8.1)	White, thicker, agglomerated after 10 days

Synthesis conditions: Total monomer 10%; AS 28%; V-50 1.2×10^{-4}g g(monomers)$^{-1}$; M_w of PDMC 2.41×10^6.

salting-out effect became stronger, which promoted the forming of smaller particles. However, the molecule of the stabilizer shrunk to a larger level. So, the stabilization of PDMC decreased and more primary particles congregated together. With excessive AS concentration, larger particles were formed because too many particles congregated. Furthermore, the particles formed were nonuniform and not smooth. In a more serious case, stable dispersion cannot be formed, but the block of the terpolymer formed. With suitable AS concentration, both salting-out effect and the stabilization of PDMC were at a good level so that uniform and smooth particles were formed. These trends were also indicated in Figure 3.

It was indicated that AS concentration had a certain effect on the intrinsic viscosity of the terpolymer. It was different from the CPAM copolymerization,[9] in which the effect of salt concentration did not seem to be strong on intrinsic viscosity. The charge of the oligomer radicals and particles played an important role. The particles had the positive charge in both case. However, oligomer radicals had less charge in AmPAM polymerization, and they had positive charge in CPAM polymerization. The particle adsorption of the oligomer radicals was affected to a certain extent, which was closely related to the intrinsic viscosity. Additionally, high concentration of AS caused the particles more compressed with high salt-out effect. Firstly, it had stronger gel-effect which causes the intrinsic viscosity high. Secondly, monomers and radicals penetrated the compressed particles with more difficulty, which caused a decrease in the monomers concentration of particles and more monomers polymerized in the continuous phase, as a result of which the intrinsic viscosity decreased. With afore mentioned effects, there was a peak of intrinsic viscosity of AmPAM at 28% with increasing of AS concentration.

Effect of PDMC concentration

The polymerization experiments were carried out with PDMC concentration from 1.0 to 4.5%, whereas the monomer, the molar ratio of AM : AA : DMC, salt, and initiator concentration were kept constant at 10%, 70 : 15 : 15, 28%, and 1.2×10^{-4}g g(monomers)$^{-1}$, respectively. The intrinsic viscosity of terpolymer was affected strongly by PDMC concentration. In dispersion polymerization, PDMC, used as stabilizer, had two kinds of roles: stabilization and salting-out effect as an organic quaternary ammonium salt. When the concentration of PDMC was low, the stabilization played a major role, which promoted particles' formation and did not congregate together. So, with the increase of PDMC concentration, the particle size decreased because of the increasing stabilization, and more monomers polymerized in the polymer phase to synthesize polymer of high molecular weight for the higher adsorption of the particles. When the concentration of PDMC was >3%, the salting-out effect of PDMC exceeded the stabilization which resulted in the molecular weight of terpolymer to decrease based on the discussion mentioned earlier.

It was also indicated in Table II that the stable dispersion could not be obtained with too low or high concentration of PDMC, which was similar to the general dispersion polymerization.[11,13,15] At low PDMC concentration, the stabilizer was not enough to stabilize the particles, which caused them to congregate together. Similarly, at too high PDMC concentration, some of them were not adsorbed on the particles. The excessive PDMC acted as flocculants, which could cause the dispersant unstable likewise. Thus, the optimum concentration of PDMC was 2.0–4.0%.

Figure 4 showed the TEM photographs of AmPAM particles in dispersion, which indicated that the morphology of particles was not clear and congregation occurred at PDMC concentration 2.0%. When PDMC concentration increased to 3.0%, the particles became uniform and clear. PDMC played a role mostly in nuclear forming and growing stage. The increase of PDMC concentration made the particle uniform and the dispersion stable.

Effect of monomer concentrations

Experiments were carried out to investigate the effect of monomer concentrations on the dispersion

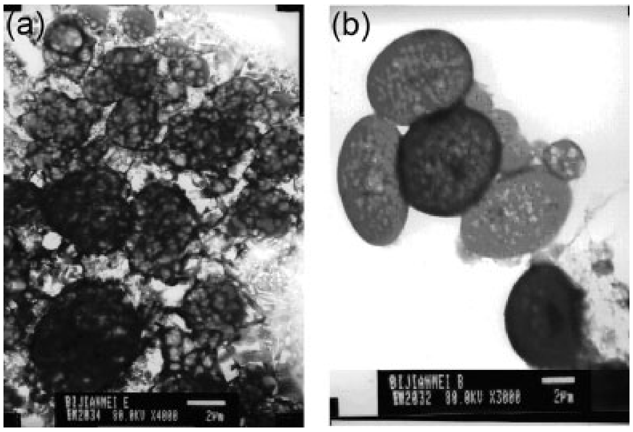

Figure 4 Effect of stabilizer concentration on morphology of amphoteric polyacrylamide particles (a) 2.0% and (b) 3.0%.

polymerization, whereas PDMC concentration, the molar ratio of AM : AA : DMC, salt, and initiator concentration were kept constant at 3.0%, 70 : 15 : 15, 28%, and 1.2 × 10^{-4}g g(monomers)$^{-1}$, respectively. The data of Table III, which were obtained from these experiments, indicated the trend of intrinsic viscosity and particle size with variety of monomer concentration. It was consistent with the trend reported in the literature.[9] It was found that polymer dispersion had a very high apparent viscosity at high monomer concentration, and a white gel would form with transparent salt solution exuded after some days.

With high monomer concentration, the contact probability between the radicals and the monomers increased. It would help to yield polymer of high molecular weight. Congregation of primary particles caused final particle size to rise. AmPAM dispersion cannot be obtained at the concentration of monomer beyond 15%. The particle stability was the key in the dispersion. There may be three reasons for this phenomenon. First, when the monomer concentration was high, the radicals had more opportunities to react with monomer and the rate of polymerization and deposition of oligomer increased. Under such condition, primary particles needed to adsorb stabilizers faster to achieve stability. If the monomer concentration was too high, these primary particles would congregate together before enough stabilizers were adsorbed. Some gel would be yielded, even the reaction system form a block with high viscosity. Second, solubility of PDMC increased with increasing monomer concentration, which caused the amount of PDMC adsorbed on particles to decrease, and changed the state of adsorption.[17,18] The stability of particles was reduced accordingly, and caused some gel formed. The dispersion became unstable finally. Third, the increase of monomer concentration changed the polarity of the reaction media. At the early stage, swelling extent of particle by the continuous phase increased, which caused the particle volume larger. In this case, the odds of contact and congregation increased. In addition, large particles needed more PDMC to reach stabilization, or congregation would occur. Based on the above analysis and the experiments data, the optimum monomer concentration was 8–15%.

TABLE III
Effect of Monomer Concentration on Dispersion Polymerization of DMC/AM/AA

Monomer/wt %	η/dL g^{-1}	D_{mean}/μm
8	9.4	4.6 (0.7–8.8)
10	11.6	5.2 (1.9–6.5)
15	14.8	6.7 (1.3–9.7)
18	Congregated	–

Synthesis conditions: PDMC 3.0%; total monomer 10%; AS 28%; V-50 1.2 × 10^{-4}g g(monomers)$^{-1}$; M_w of PDMC 2.15 × 10^6.

CONCLUSIONS

AmPAM was synthesized by dispersion polymerization in aqueous AS solution under suitable salt, stabilizer, and monomer concentrations. AmPAM performed a polyelectrolyte effect at high AS concentration, and the dispersion polymerization of AmPAM was similar to that of CPAM or APAM. The results indicated that the optimum conditions obtained the stable AmPAM dispersion was as follows: AS concentration 28%, PDMC concentration 3.0%, and monomers concentration 8–15%, respectively. The effect of AS concentration on intrinsic viscosity of polymer was different with polymerization of CPAM because of the charge of oligomer, radicals, and polymer molecule. The particle size increased with increasing of AS concentration because the stabilization of PDMC was weakened to make the particle congregate. With increasing PDMC concentration, the intrinsic viscosity of polymer increased firstly and then decreased, and the particle size gradually decreased, under the combined effect of stabilization and salting-out effect as an organic quaternary ammonium salt. Polymer of high molecular weight would be yielded with high monomer concentration, and the particle size increased because of the congregation. AmPAM obtained by dispersion polymerization performed anti-polyelectrolyte effect at low AS concentration. But, the apparent viscosity of AmPAM solution decreased when the AS concentration increased to 10% or more, which performed the polyelectrolyte effect.

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