Preparation of Polyacrylamide Aqueous Dispersions Using Poly(sodium acrylic acid) as Stabilizer

Xiaoguang Liu,[1,2] Qiang Chen,[1,2] Kun Xu,[1] Wende Zhang,[1] Pixin Wang[1]

[1]*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*
[2]*Graduate School, Chinese Academy of Sciences, Bejing 100049, China*

ABSTRACT: High-solids, low-viscosity, stable polyacrylamide (PAM) aqueous dispersions were prepared by dispersion polymerization of acrylamide in aqueous solution of ammonium sulfate (AS) using poly (sodium acrylic acid) (PAANa) as the stabilizer, ammonium persulfate (APS) or 2,2′-Azobis (N,N′-dimethyleneisobutyramidine) dihydrochloride (VA-044) as the initiator. The molecular weight of the formed PAM, ranged from 710, 000 g/mol to 4,330,000 g/mol, was controlled by the addition of sodium formate as a conventional chain-transfer agent. The progress of a typical AM dispersion polymerization was monitored with aqueous size exclusion chromatography. The influences of the AS concentration, the poly(sodium acrylic acid) concentration, the initiator type and concentration, the chain-transfer agent concentration and temperature on the monomer conversion, the dispersion viscosity, the PAM molecular weight and distribution, the particle size and morphology were systematically investigated. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2693–2701, 2009

Key words: water-soluble polymers; dispersions; radical polymerization; phase separation

INTRODUCTION

Polyacrylamide (PAM) and acrylamide (AM)-based (co)polymers are among the most commercially important water-soluble polymers and are the focus of extensive research in academic and industrial laboratories. PAM is used in numerous application areas, including flocculants in wastewater treatment application, drag reduction agents and drilling fluids in enhanced oil recovery, additives in papermaking, etc.[1,2]

Various types of methods for producing AM-based polymers have been developed, such as aqueous solution polymerization, inverse (micro) emulsion polymerization, inverse (micro) suspension polymerization, and precipitation polymerization.[3–12] Because of the high viscosity of aqueous solution, PAM has generally been handled as dry powders or water-in-oil emulsions. However, the drying process not only requires the consumption of energy intensive but also subject to degradation through shear. Additionally, three-dimensional crosslinking of the polymer may occur, yielding a partially water-insoluble polymer. The water-in-oil emulsions are easy to handle, however they are associated with several inherent disadvantages. For example, the hydrocarbon continuous phase and surfactant system, which play an important role in producing liquid products, are no longer helpful in the end use application of the polymers and will become pollutants to the environment.

During the 1980s, a new method of dispersion polymerization in salt aqueous media was developed.[13] This polymerization process permits the manufacture of high molecular weight water soluble polymers based on AM as water dispersions. The water dispersions have the property of going instantaneously into solution on dilution with water. This is a very desirable property for PAM because the dissolution of dry PAM powder is a slow process, and gels are often formed during dissolution, particularly when the molecular weight is in the ultrahigh range. In addition, the dispersions are manufactured in water instead of in a hydrocarbon and surfactant system. Thus, no oil or surfactants are released to the environment with the application of these polymers.

Dispersion polymerization may be defined as a type of precipitation polymerization in which the polymerization of the monomers is carried out in the presence of a suitable polymeric stabilizer soluble in a reaction medium.[14,15] Both the monomer and the stabilizer are soluble in the medium but insoluble for the formed polymer. Dispersion polymerization is a very useful method in producing

polymer particles of 0.1–20μm in a single step. General Dispersion polymerization is highly sensitive to small changes in reaction parameters, and the diameter of producing particles is strongly dependent on numerous polymerization parameters. In the last decades, there has been a considerable interest in using more polar solvents or supercritical carbon dioxide as the continuous phase to polymerize organic monomers.[16–25] However, studies on producing water-soluble polymers by dispersion polymerization are rather scarce. Ray and Mandal reported the dispersion polymerization of AM in *t*-butyl alcohol water media using poly(vinyl methyl ether) as the polymeric stabilizer and 2,2′-azobisisobutyronitrile or ammonium persulfate (APS) as the initiator.[26,27] Subsequently, some researchers have also carried out the dispersion polymerization of AM in alcohol aqueous media.[28–30] Recently, Cho et al. reported the dispersion polymerization of AM in aqueous ammonium sulfate (AS) media using poly(acryloyloxyethyltrimethyl ammonium chloride) as the stabilizer and 2,2′-azobis(2-methyl propionamidine) dihydrochloride (AIBA) as the initiator.[31] However, the AM concentration is usually lower.

In this article, we present a study of the dispersion polymerization of AM in aqueous solution of AS using poly(sodium acrylic acid) (PAANa) as the stabilizer, APS or 2, 2′-Azobis (N,N′-dimethyleneisobutyramidine) dihydrochloride (VA-044) as the initiator, and HCOONa as a chain-transfer agent. The aim of the work is to evaluate the conditions for preparing of the stable high molecular weight PAM aqueous dispersions with a high concentration of the polymer, a low concentration of the stabilizer, and a low dispersion viscosity; moreover, the preparation of aqueous dispersions also do not require organic solvents, such as alcohol. Therefore, we have determined the solubility of AM in different concentration aqueous solutions of AS, selecting the most favorable conditions for dispersion polymerization corresponding to high monomer concentration.

EXPERIMENTAL

Materials

Acrylic acid (AA, A.R. Grade, Beijing Yili Fine Chemicals) was distilled under reduced pressure before use. AM (A.R. Grade, Beijing Yili Fine Chemicals), (AS, A.R. Grade, Beijing Beihua Fine Chemicals), APS (A.R. Grade, Beijing Beihua Fine Chemicals), 2,2′-Azobis(N,N′-dimethyleneisobutyramidine)dihydrochloride (VA-044) (Wako Chemicals), sodium formate (NaOOCH, A.R. Grade, Shanghai Chemicals Reagent), and sodium hydroxide (A.R. Grade, Beijing Beihua Fine Chemicals) were used as received, respectively. Deionized water was used

throughout this work. Other reagents were A.R grade and used as received.

Stabilizer preparation and characterization

PAANa was prepared in our laboratory by free radical aqueous solution polymerization. The 16 wt % aqueous solution of sodium acrylic acid was made and polymerized at 40°C under a nitrogen atmosphere for 45 h using 0.66 wt % VA-044 as initiator. After 45 h the solution was heated to 90°C and maintained the temperature for 8 h. The molecular weight and distribution of PAANa was measured with aqueous size exclusion chromatography (SEC). As the stabilizer, the weight-average molecular weight and polydispersity index (PDI) of PAANa were 1,080,000 g/mol and 3.52, respectively.

Preparation of aqueous dispersions

Varying quantities of the ingredients containing AM, AS, stabilizer, chain-transfer agent, and deionized water were added to a 500 mL four-necked separable flask equipped with an anchor-like paddle stirrer, a reflux condenser, and a nitrogen inlet. After purging with nitrogen for half-an-hour and controlling the temperature in a water bath, the polymerization was initiated by injecting the water-soluble initiator APS or VA-044 solution into the reaction system under stirring. Polymerization was allowed to proceed for 22 h under N_2. The amount of each ingredient was kept constant in all experiments, except as indicated.

Characterization

A drop of the final polymer dispersion was placed on the clean glass microscope slide and to be photographed by an MOTIC digital optical microscopy (DMB5) to observe the shape of polymer particles.

The particle sizes were measured with a laser particle size analyzer LST-POP (III) (632.8 nm, 2 mW He–Ne Laser, OMEC Instruments). The volume-average particle size $D_{4/3}$ was regarded as the average particle diameter. $D_{4/3}$ of particles was calculated assuming spherical particle morphology. The samples were usually dispersed by the ultrasonic agitation before measurements.

The dispersion viscosity was determined with an NDJ-4 rotational viscometer at 25°C.

The monomer conversion was determined by bromometric method.[32]

Polymer was separated by dialysis using porous cellulose acetate membrane with the cutoff molecular weight of 8000 g/mol, and then precipitated by a large quantity of acetone. The samples were dried under vacuum at 40°C for 60 h. The molecular weight distribution was determined by aqueous SEC at room
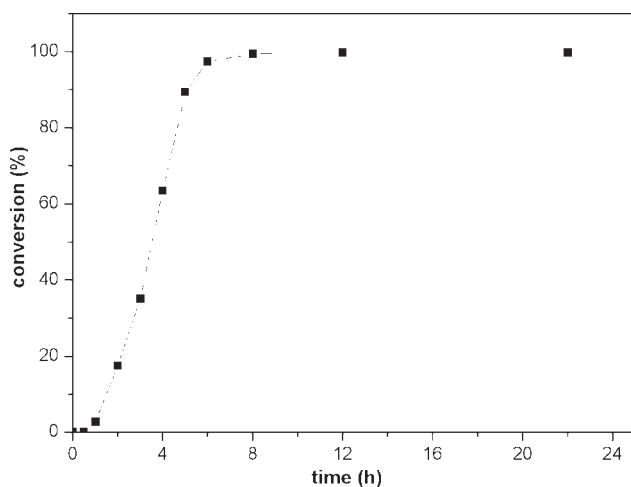
Figure 1 Conversion versus time plot for dispersion polymerization of AM conditions: 20 wt % monomer concentration (based on total); PAANa 2 wt % (based on monomer); 33.77 wt % AS aqueous solution; $(NH_4)_2S_2O_8$, 3.12×10^{-3} mol % (based on monomer); chain-transfer agent, 6×10^{-2} wt % (based on monomer); reaction temperature 30°C. stirring speed 300 rpm.

temperature (ca. 30°C) with a Waters 515 HPLC pump, two columns (a guard column and Ultrahydrogel-2000 and Ultrahydrogel-1000 column from Waters) connected in series, and a Waters 2414 refractive index detector. An aqueous solution of 0.1 mol/dm^3 $NaNO_3$ was used as a mobile phase at a flow rate of 0.5 mL/min. PAANa (M_w 1300 g/mol $\sim$ 1,360,000 g/mol) obtained from Waters was used as calibration standards. However, because the hydrodynamic volumes of the standards were not likely to be the same as those of PAM of the same molecular weights, the SEC traces were used only to calculate the PDI. The actual molecular weights of the samples were obtained by the viscometric method, for which the intrinsic viscosity ([η]) was determined in a 0.5 mol/L NaCl aqueous solution with an Ubbelhode capillary viscometer at 25.0°C. The viscosity-average molecular weight (M_v) was calculated with the following Mark–Houwink equation[33]:

$$[\eta] = 7.19 \times 10^{-5} M_v^{0.77} (\text{dl/g})$$

RESULTS AND DISCUSSION

The progress of dispersion polymerization of AM

The progress of a typical AM dispersion polymerization in the presence of NaOOCH was monitored with aqueous SEC. Aliquots taken from the polymerization at given time intervals were analyzed to determine monomer conversion as a function of time and to follow changes in M_v and PDI during the course of the reaction. In the system, the stabi-

lizer cannot be removed from the final dispersions. To decrease the effect of the stabilizer on the M_v and PDI of resultant PAM, we choose the lower stabilizer concentration to study the progress of dispersion polymerization of AM.

Figure 1 depicts the monomer conversion as a function of reaction time. The conversion versus time curve was typically S-shaped. After a brief inhibition period, the reaction conversion increases quickly to about 89% within 5 h. As the reaction progresses to higher conversion, the rate of monomer consumption continually decreases, and the reaction is near completion. The decrease in the rate of monomer consumption is readily attributed to growing PAM chains encountering lower monomer concentration at progressively higher conversion. During the monomer consumption up to 63% conversion, the M_v slightly decreases, and the PDI slightly increases (Fig. 2), that is caused by an increase in the population of lower molecular weight PAM fractions. The decrease in M_v and concurrent increase in PDI with increasing conversion are both attributed to the greater probability of chain-transfer events occurring as the monomer supply is exhausted at higher conversion (i.e. for a propagating PAM radical, transfer to NaOOCH becomes more likely than addition to AM monomer with increasing conversion).

The effects of the AS concentration

As far as our information goes, there are two kinds of ways to carry out the dispersion polymerization of AM in aqueous media, one is using polar organic/water mixed solvent, and the other is adding inorganic salt to water. In the present investigation, the high concentration aqueous solution of AS was used to induce the phase separation of the resultant PAM by the salting-out effect.[34–36]
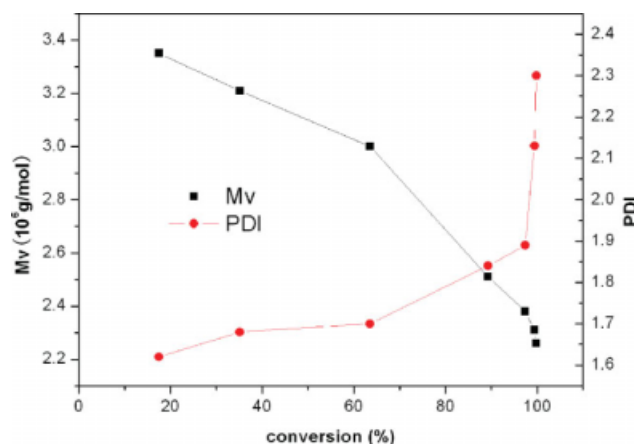

Figure 2 M_v and PDI as a function of conversion for dispersion polymerization of AM. See Figure 1 for conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
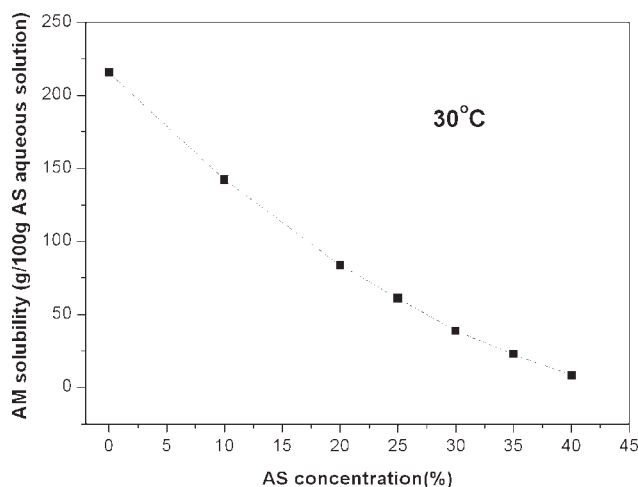
Figure 3 AM solubility in $(NH_4)_2SO_4$ solution with different concentrations at 30 °C.

Figure 3 shows the maximum soluble amount of AM dissolved in different concentration aqueous solutions of AS at 30°C. As shown in Figure 3, the solubility of AM in aqueous solution of AS becomes lower with increasing AS concentration. The solubility of monomer can satisfy the request of the dispersion polymerization of AM. In the article, the effects of AS concentration on the dispersion polymerization of AM were studied in the range of 28.0 wt %–35.0 wt %, while the monomer, the stabilizer, the initiator concentration, and the chain-transfer agent concentration were fixed at 20 wt %, 4 wt %, 3.12×10^{-3} mol %, and 6×10^{-2} wt %, respectively.

As shown in Table I, when the AS concentration is less than 28.0 wt %, the resultant polymer cannot be separated quickly because of the poor salting-out effect, and the formed higher molecular weight PAM precipitate from the medium, and then another part of lower molecular weight PAM remains soluble in the medium, resulting in a high in-process viscosity, and yielding a gel-like polymer solution.

The increase of AS concentration seems to have no strong effects on the monomer conversion, M_v and PDI. This is in conformity with the Cho et al.'s report.[31] However, the obtained particle sizes decrease first; reach a minimum at 33.77 wt % and then increase with the increasing salt concentration. This is contrasted with the result for the dispersion copolymerization of AM with quaternary ammonium cationic monomer, where the particle sizes decrease with increasing salt concentration.[37] When the monomer concentration and polymerization temperature are fixed, a decrease in the AS concentration will increase the solubility of PAM in the system, the phase separation will be postponed, and the critical phase separation concentration of PAM becomes larger, leading to quickly coalescence of the particle, yielding a larger particle. At the same time, it may be

noted that the PAM particles underwent significant swelling by water in the present case. With the decrease in the salt concentration the swelling ratio of particle will become larger. This also will result in larger particles obtained at a low salt concentration. However, at a high salt concentration, the strong salting-out effects will result in formed polymer phase separation quickly, but it may not increase the stabilizer's adsorption rate. The stabilizer's adsorption rate fails to cope with the rate of new surface generation. Here, we imagine that the formed polymer that deposit on the surface of the particle have difficulty in diffusing into the interior of the particle because of the high internal viscosity of the particles. So larger particle with interface coarse are obtained.

Figure 4 shows the micrograph of the particles dispersed in the original medium. It can be seen that AS concentration has a remarkable influence on the particle morphology, and polydisperse spherical particles are obtained in a narrow concentration range.

When the AS concentration is lower than 33.7 wt %, the shapes of the particles are irregular or ellipsoidal instead of spherical. The formation of nonspherical particles suggests that the coalescence of particles has taken place during the course of polymerization. One would have expected that coalescence should yield spherical particles because that would have led to more effective minimization of surface energy. However, the internal viscosity of the particles can be great enough to prevent easy diffusion of molecules between the coalescing particles. In addition, shearing stress during polymerization should have contributed to the formation of nonspherical particles.

The effects of the PAANa concentration

The effects of PAANa concentration on the dispersion polymerization of AM are shown in Table II. With the increase of the PAANa concentration, the dispersions viscosity quickly increases, and the

TABLE I
Effects of AS Concentration on Dispersion Polymerization of AM

Salt Conc. (wt %)	$D_{4/3}$ (μm)	Conversion (%)	M_v (10^6 g/mol)	PDI
28.0		Coagulum		
32.0	28.60	99.7	2.20	2.63
33.2	11.00	99.7	2.24	2.54
33.7	10.54	99.7	2.25	2.49
34.2	12.14	99.8	2.29	2.54
35.0	13.88	99.7	2.35	2.83

Conditions: 20 wt % monomer concentration (based on total); PAANa 4 wt % (based on monomer); $(NH_4)_2S_2O_8$, 3.12×10^{-3} mol % (based on monomer); chain-transfer agent, 6×10^{-2} wt % (based on monomer); reaction temperature 30°C; stirring speed 300 rpm; reaction time 22 h.
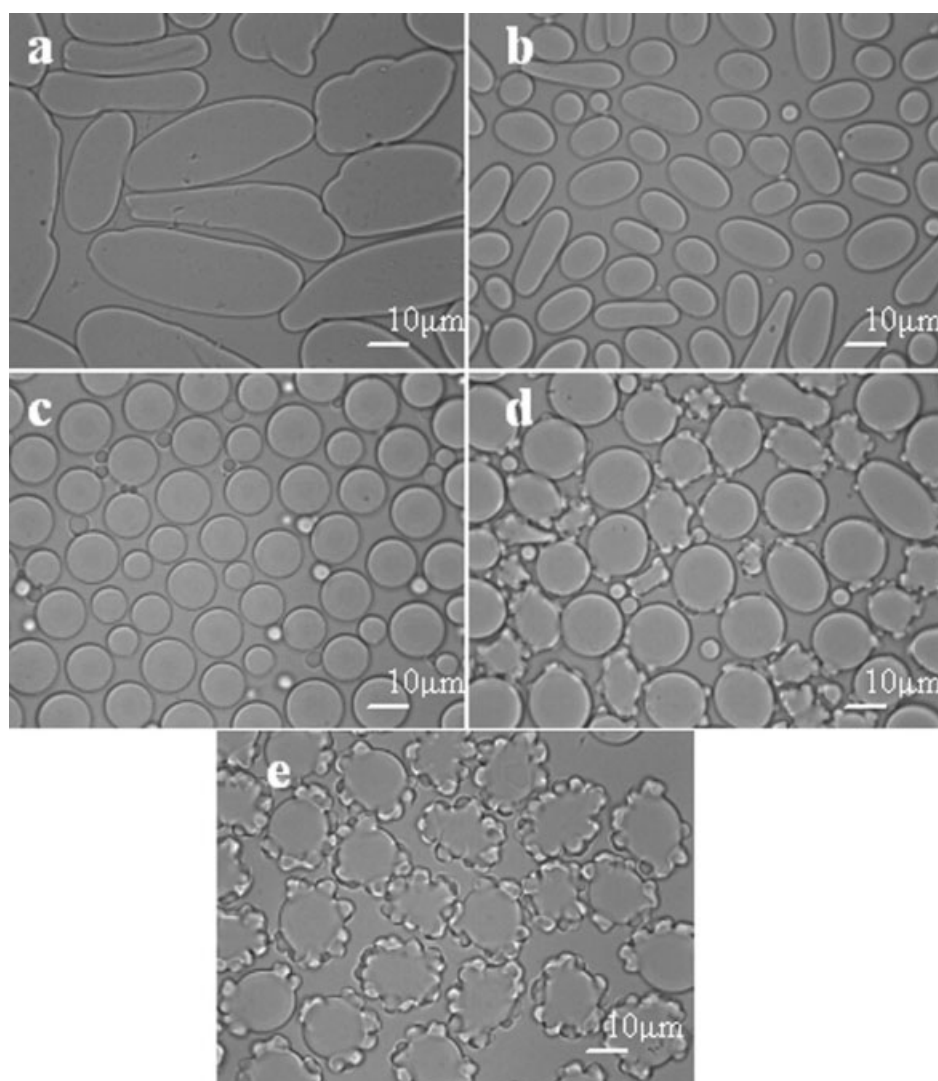
Figure 4 Photographs of PAM particles prepared with different AS concentrations: a: 32.0 wt %, b: 33.2 wt %, c: 33.7 wt %, d: 34.2 wt %, e: 35.0 wt %; see Table I for other conditions.

monomer conversion, M_v and PDI are not obviously change. A likely explanation of this result may be the presence of the PAANa in the polymerization media did not give rise to significant chain-transfer to stabilizer. The molecular weight of the polymer did not depend strongly on the stabilizer concentration as reported by Song et al.[37] The particle sizes decrease first, reach a minimum at 4 wt % and then increase with increasing PAANa concentration. The similar trend was also observed for the dispersion copolymerization of AM and AA.[32,38]

Figure 5 shows the photographs of PAM particles at different stabilizer concentrations. It can be seen that the ellipsoidal particles are formed when the PAANa concentration is 2 wt %. Increasing PAANa concentration to 8 wt %, the interface coarse particles are obtained. This result attributes to the salt effect of PAANa. The PAANa as the stabilizer is a kind of polyelectrolyte, which can protect the particles against coalescence and provide the stabilizer of the dispersions by the steric stabilization and the electrostatic effect,[39–42] while the PAANa is also a kind of

TABLE II
Effects of Stabilizer Concentration on Dispersion Polymerization of AM

Stabilizer Conc. (wt %)	$D_{4/3}$ (μm)	Conversion (%)	M_v (10^6 g/mol)	PDI	Dispersion Visc. (mPa s)
2	12.71	99.8	2.26	2.43	129
4	10.54	99.7	2.25	2.49	313
6	11.86	99.8	2.23	2.46	950
8	13.08	99.7	2.22	2.55	3248

Conditions: 20 wt % monomer concentration (based on total); 33.77 wt % AS aqueous solution; $(NH_4)_2S_2O_8$, 3.12×10^{-3} mol % (based on monomer); chain-transfer agent, 6×10^{-2} wt %; reaction temperature 30°C; stirring speed 300 rpm; reaction time 22 h.
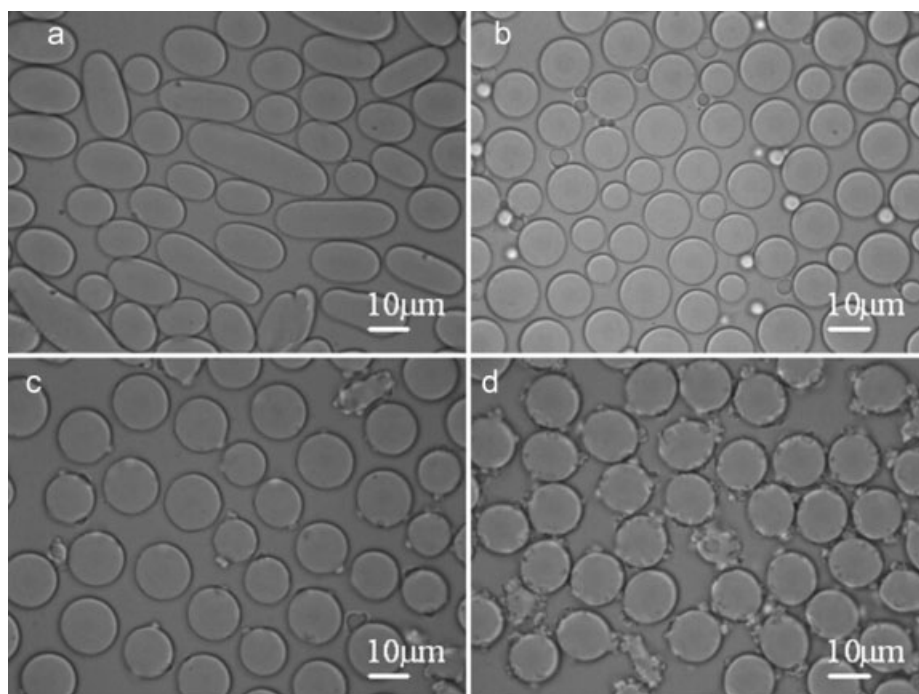
Figure 5 Photographs of PAM particles prepared with different stabilizer concentrations: a: 2 wt %. b: 4 wt %, c: 6 wt %, d: 8 wt %; see Table II for other conditions.

carboxylate sodium salt, which can also induce the phase separation of the resultant polymer.

The effects chain-transfer agent concentration

In the system, the M_v of the formed PAM was controlled by addition of sodium formate to the polymerization media as a conventional chain-transfer agent.[43,44] Figure 6 shows that monomer conversion

slightly changes with the increase of the chain-transfer agent concentration in the feed, and the molecular weight of the resultant PAM obviously decreases with increasing the chain-transfer agent concentration. This is because the chain-transfer agent competes with the monomer in the propagation reaction and forms a new free radical for initiation. The M_v for PAM synthesized in the presence NaOOCH ranged from 710, 000 to 4,330,000 g/mol, depending on the ratio of monomer to chain-transfer agent used. The SEC traces (Fig. 7) of the six PAM samples
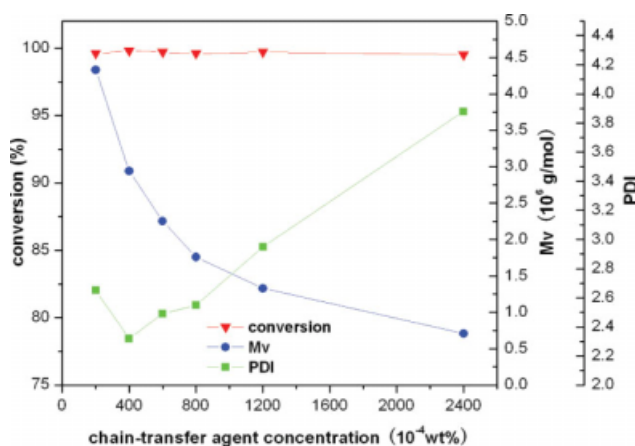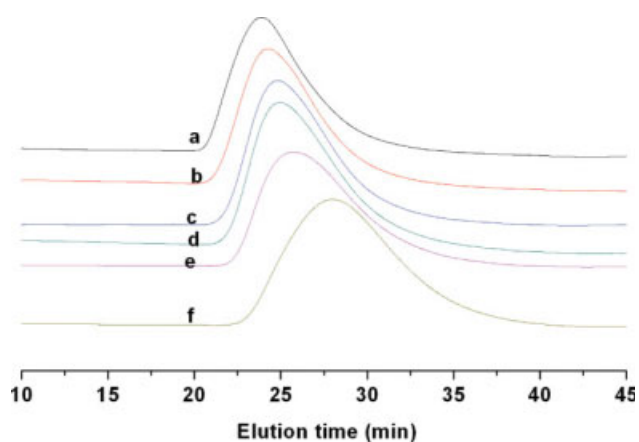

Figure 6 Effects of chain-transfer agent concentration on dispersion polymerization of AM. Conditions: 20 wt % monomer concentration; PAANa 4 wt % (based on monomer); 33.77 wt % AS aqueous solution; $(NH_4)_2S_2O_8$ 3.12 × 10^{-3} mol % (based on monomer); reaction temperature 30°C; stirring speed 300 rpm; reaction time 22 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 SEC traces of PAM obtained for different chain-transfer agent concentrations: a: 2 × 10^{-2} wt %, b: 4 × 10^{-2} wt %, c: 6 × 10^{-2} wt %, d: 8 × 10^{-2} wt %, e: 12 × 10^{-2} wt %, f: 24 × 10^{-2} wt %; see Figure 6 for other conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Effects of the Initiator Type and Concentration on Dispersion Polymerization of AM

Initiator type	Initiator Conc. (10^{-3} mol %)	Conversion (%)	M_v (10^6 g/mol)	PDI
APS	1.56	89.2	2.32	1.92
APS	2.34	94.5	2.26	2.26
APS	3.12	99.7	2.25	2.49
APS	6.24	99.8	2.12	2.52
APS	12.48	99.9	2.10	2.54
VA-044	1.17	39.9	2.79	1.70
VA-044	1.95	68.1	2.74	1.75
VA-044	2.34	89.0	2.48	1.90
VA-044	3.12	97.5	2.39	2.19
VA-044	12.48	99.7	2.35	2.57

Conditions: 20 wt % monomer concentration; PAANa 4 wt % (based on monomer); 33.77 wt % AS aqueous solution; chain-transfer agent, 6×10^{-2} wt % (based on monomer); reaction temperature 30°C; stirring speed 300 rpm; reaction time 22 h.

were unimodal, and the PDI (Fig. 6) of the PAM samples prepared with NaOOCH ranged from 2.32 to 3.88. At proper chain-transfer agent concentration the PDI is low, and too high chain-transfer agent concentration will lead to the higher PDI.

The effects of the initiator type and concentration

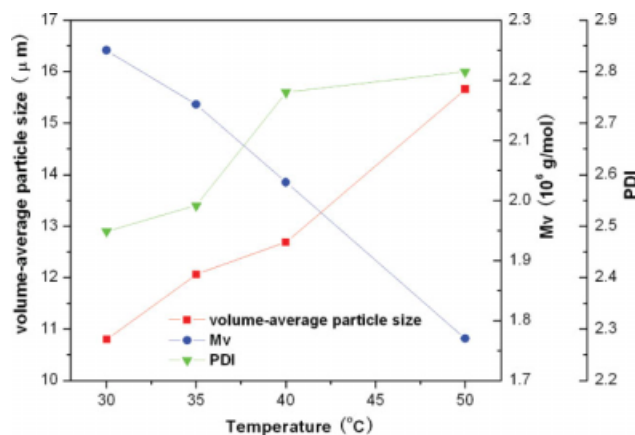Table III shows the effects of the initiator type and concentration on dispersion polymerization of AM.

Figure 8 Effects of temperature on the dispersion polymerization of AM. Conditions: 20 wt % monomer concentration; PAANa 4 wt % (based on monomer); 33.77 wt % AS aqueous solution; $(NH_4)_2S_2O_8$, 3.12×10^{-3} mol % (based on monomer); chain-transfer agent, 6×10^{-2} wt % (based on monomer); stirring speed 300 rpm; reaction time 22 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Whatever APS or VA-044 used as initiator, the monomer conversion increases with the increase of the initiator concentration. The decrease in M_v with the increase of initiator concentration is accompanied by an increase in PDI. That is caused by an increase in the population of lower molecular weight fractions. The results are in agreement
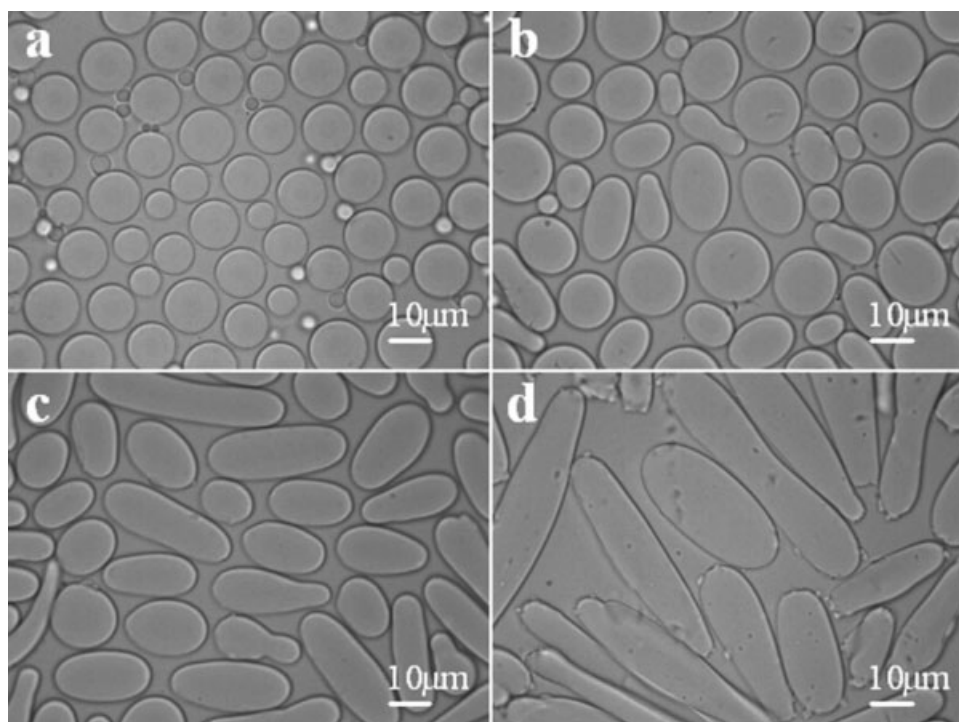

Figure 9 Photographs of PAM particles prepared with different reaction temperatures: a: 30°C, b: 35°C, c: 40°C, d: 50°C; see Figure 8 for conditions.

with the results of the progress of dispersion polymerization.

From Table III, it can be observed that the APS as initiator leads to higher monomer conversion and lower molecular weight, compared with those of the similar molar feed VA-044 as initiator. A possible reason is the different decomposition rate of initiator in salt media.

The effects of temperature

The effects of different temperature on the dispersion polymerization of AM are shown in Figure 8. The particle sizes increase with increasing the reaction temperature. The same trend is also reported for other dispersion polymerization.[21,38,45,46] An increase in temperature in this polymerization system leads to the following effects: (1) an increase in the critical phase separation concentration of the polymer due to the increase in the solvency of the continuous phase; (2) an increase in the concentration of precipitated polymer chain due to increase in the decomposition rate of the initiator and the propagation rate of oligomer radical; (3) an increase in the solubility of the stabilizer molecular in the growing particle's surface. All these effects may contribute to an increase in the particle sizes.

The decrease in M_v and concurrent increase in PDI with increasing temperature are attributed to the greater probability of chain-transfer events at higher reaction temperature.

Figure 9 shows the particle morphology at different temperatures. The particle shapes changed from spherical to ellipsoidal with increasing temperature. This may be due to the increase in the solvency of the continuous phase and the increase in the concentration of precipitated polymer chain.

CONCLUSION

A series of high-solids ($\geq$20 wt %), low-viscosity, stable PAM aqueous dispersions were prepared by the dispersion polymerization of AM in aqueous solution of AS using PAANa as the stabilizer. NaOOCH was used as a chain-transfer agent to control the PAM molecular weight. The M_v for PAM synthesized ranged from 710, 000 to 4,330,000 g/mol, depending on the amount of NaOOCH added to the polymerization medium. In the system, the monomer conversion increased with increasing the initiator concentration, and high conversion was reached (>99%). Increasing the stabilizer concentration led to higher dispersion viscosity. The particle morphology was affected significantly by the polymerization factors. Only in the proper reaction condition, polydisperse spherical particles were formed.

The PAM aqueous dispersions were stable during long storage.

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