Dispersion Copolymerization of Acrylamide with Acrylic Acid in an Aqueous Solution of Ammonium Sulfate: Synthesis and Characterization

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ABSTRACT: Dispersion copolymerization of acrylamide with acrylic acid in an aqueous solution of ammonium sulfate using poly(2-acrylamido-2-methylpropanesulfonic acid sodium) as the stabilizer and ammonium persulfate (APS) as the initiator was investigated. The influence of initiator concentration, stabilizer concentration, ammonium sulfate concentration, chain-transfer agent concentration, and polymerization temperature on the copolymerization was discussed. The results showed that varying the ammonium sulfate concentration could affect the particle size and the intrinsic viscosity of the copolymer significantly. With increasing the stabilizer concentration, the particle size of the copolymer decreased first, and then increased, meanwhile the intrinsic viscosity of the copolymer decreased. The increase of initiator concentration, chain-transfer agent concentration, and polymerization temperature resulted in the increase in the particle size. Polydisperse spherical particles were formed in the system, and the kinetics for the dispersion copolymerization were discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3685–3690, 2006

Key words: water-soluble polymers; copolymerization; dispersions; particle size distribution

INTRODUCTION

Anionically charged water-soluble polymers are of high interest for a multitude of industrial applications[1]; the important applications include flocculation agents, oil recovery, thickening agents, drainage, and retention aids in the manufacture of paper.[2,3] In these applications, the high-molecular-weight polymers that rapidly dissolve could be desired. Early water-soluble polymers were produced by solution polymerization. To obtain high-molecular-weight polymers, it is necessary to increase monomer concentration to more than 10 wt %; the produce is a hydrated gel and cannot be easily dissolved. Therefore, it is required either to dilute produce to lower concentration or to dry it to a powder product. The shipment of a low-concentration produce increases the transport cost, whereas the heat energy required for drying to a powder is more. Additionally, three-dimensional crosslinking is brought about by heating and an undesirable water-insoluble part is produced. Using the inverse emulsion polymerization technology, high-molecular-weight polymers that rapidly dissolve can be produced. However, a disadvantage of inverse emulsion polymerization is that the emulsions contain substantial quantities of hydrocarbon liquid. The introduction of hydrocarbon liquids into the system where these water-soluble polymers are used is not always beneficial.

Dispersion polymerization is an attractive method for producing micron-size monodisperse polymer particles in a single batch process. The method may be defined as a type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a suitable polymeric stabilizer soluble in the reaction medium. The solvent selected as the reaction medium is a good solvent for both the monomer and the steric stabilizer polymer, but a nonsolvent for the formed polymer.[4] Dispersion polymerization in organic hydrocarbon media was first invented by Osmond and coworkers at ICI in the late 1960s. All of the early work was confined to polymerization in aliphatic hydrocarbon fluids as has been perfectly reviewed by Barett.[5] During the past 20 years, there has been a considerable interest in generalizing these results to more polar solvents as the continuous phase,[6–10] by which the range of mono-

mers that can be polymerized using this method was greatly widened. Up to now, styrene[7–13] and methyl methacrylate[14,15] were the most studied monomer systems. However, studies on dispersion polymerization of water-soluble monomers yielding water soluble polymers are scarce. As for as our information goes, there exist only a few published works on dispersion polymerization of acrylamide (AM)[16–21] or copolymerization of AM and hydrophilic cationic monomers[22,23] yielding water-soluble polymers in aqueous media, and the dispersion polymerization of water-soluble anionic monomers in an aqueous salt solution has been reported in some patents,[24–26] but there are no articles discussing on the polymerization characterization.

Aqueous solution of ammonium sulfate has a number of practical advantages as a dispersion medium. Its use involves low fire-risk and is free of odor and toxic effects. In addition, it is also cheap to use and the manufacturing and application equipment in which dispersions are used can readily be cleaned. At the same time, the dispersion can be directly applied as flocculants and especially as retention and drainage aids in the manufacture of paper.

In this work, we have studied the dispersion copolymerization of AM and acrylic acid (AA) in aqueous ammonium sulfate media by using ammonium persulfate (APS) as the initiator and Poly(2-acrylamido-2-methylpropanesulfonic acid sodium) (PAMPSNa) as the polymeric stabilizer. Anionic water-soluble copolymer dispersion with high solid, low viscosity, and without organic solvents was obtained using dispersion polymerization method. In the present system, the stabilizer and monomers are soluble in aqueous ammonium sulfate media, but the resulting copolymer is not. A high concentration of ammonium sulfate was used to induce the phase-out of the produced polymer by the salting-out effect.[27] The influence of initiator concentration, stabilizer concentration, salt concentration, chain-transfer agent concentration, and polymerization temperature on the polymerization characteristics are discussed.

EXPERIMENTAL

Materials

AA (A.R. grade; Beijing Yili Fine Chemicals, Beijing, China) was distilled under reduced pressure before use. AM (A.R. grade; Beijing Yili Fine Chemicals), ammonium sulfate (A.R. grade; Beijing Beihua Fine Chemicals, Beijing, China), 2-acrylamido-2-methyl-propanesulfonic acid (Shandong Souguang Chemicals, Shandong, China), APS (A.R. grade; Beijing Beihua Fine Chemicals), 2,2′-azobis(2-methylpropion-conidine)dihydrochloride (V-50, Aldrich Chemical Company), isopropanol (chain-transfer agent, A.R.

grade; Beijing Beihua Fine Chemicals), and sodium hydroxide (A.R. grade; Beijing Beihua Fine Chemicals) were used as received. Commercial distilled water was used throughout this work.

Stabilizer preparation and characterization

PAMPSNa was prepared by solution polymerization. The PAMPSNa of neutralization ratio 85% was polymerized in water at 50°C under a nitrogen atmosphere for 16 h using 0.128 wt % V-50 as initiator. After 16 h, the reaction mixture was heated to a temperature of 75°C and maintained at that temperature for 3 h. The intrinsic viscosity ([η]) of the PAMPSNa was determined in a 1 mol/L NaCl aqueous solution with an Ubbelohde capillary viscometer at 25°C. As a stabilizer, the intrinsic viscosity of PAMPSNa was 2.49 dL/g.

Dispersion copolymerization

Dispersion copolymerization was carried out in a 500-mL four-necked separable flask equipped with mechanical stirrer, a reflux condenser, and a nitrogen inlet under nitrogen. The AM and AA molar feed ratio in the monomer mixture was fixed at 70:30, and the neutralization ratio of AA by sodium hydroxide was 16%. The total monomer concentration was 15 wt %, and was kept constant in all experiments. The amount of each ingredient was kept constant in all experiments, except as indicated. Under these experimental conditions, the solution before polymerization was completely clear. After purging with nitrogen for half an hour, the polymerization was initiated by injecting the water-soluble initiator into the system at the appropriate temperature. Polymerization was allowed to proceed for 22 h until the monomer was consumed.

Copolymer characterization

The copolymer particles were photographed by an optical microscopy. Particle size and size distribution were measured with a laser particle size analyzer (LST-POPIII, OMEC Instruments Co.). The bulk viscosity of the copolymer dispersion was determined with an NDJ-4 rotation viscometer at 25°C. The polymerization conversion was determined from residual monomer of copolymer by bromating method. Copolymer was separated by dialysis using porous cellulose acetate membrane with the cutoff molecular weight of 8000 g/mol and then was oven dried exhaustively under vacuum at 40°C for 48 h. The intrinsic viscosity of the copolymer was determined in a 1 mol/L NaCl aqueous solution with an Ubbelohde capillary viscometer at 30°C.
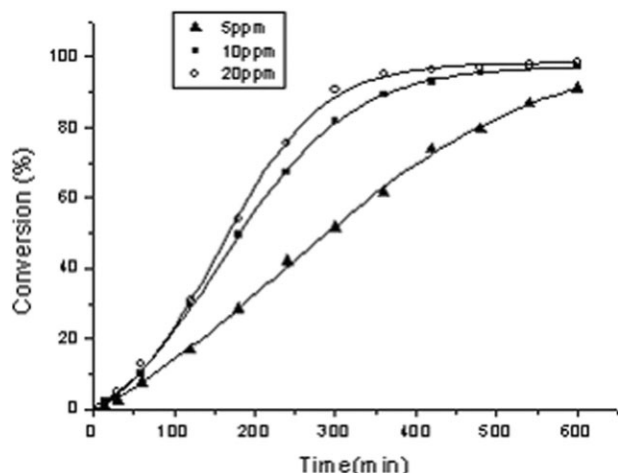
Figure 1 Conversion versus time curve for dispersion copolymerization of AM and AA with different initiator concentrations. Conditions: initiator, 5.00×10^{-4} wt %, 1.00×10^{-3} wt %, 2.00×10^{-3} wt % of total, respectively; AM/AA (70:30), 15 wt % of total; $(NH_4)_2SO_4$, 17.2 wt % of total; stabilizer, 8 wt % based on monomer; chain-transfer agent concentration, 0.13 wt % of total; reaction temp., 30°C; time, 22 h.

RESULTS AND DISCUSSION

Effect of the initiator concentration

The dependence of the conversion on the reaction time at different initiator concentrations is shown in Figure 1. The overall polymerization rate increased with an increase of the initiator concentration. The results conformed to the general polymerization kinetics. As the initiator concentration increased, the rate of free radical formation became greater. The higher rate of free radical initiation led to faster monomer consumption. The polymerization rate tended to be accelerated in the early stage of the reaction, followed by a shape change. The final conversions in all the experiments exceeded 90%.

Table I shows the effects of initiator concentration on polymerization. At lower initiator concentration, residual monomer of the copolymer dispersion was high and the dispersion was unstable because of the coalescence of particles. The polymerization conversion and the particle size increased with an increase of initiator concentration; this was in agreement with the earlier works.[7,8,12] A higher initiator concentration would lead to a greater rate of generation of unstable oligoradicals or dead polymer molecules. These generated primary particles were not stabilized enough by the stabilizer, leading to a greater rate of coagulation and resulting in larger size particles. The intrinsic viscosity of the copolymer decreased with increasing initiator concentration. This was consistent with the anticipation that high initial rate of free radical formation at high initiator concentrations led to a high de-

gree of termination, and hence the lower average molecular weight. However, when the initiator concentration was above 1.00×10^{-3} wt %, the intrinsic viscosity of the copolymer increased. Too much high initiator concentration increased the polymer ratio and the concentration of propagation chains; the system viscosity increased quickly because a lot of oligomeric radicals and dead polymer could not phase-out in a short time. There was some coagulum to be found in the system. It was the coagulum that made some of the radicals be embedded, leading to longer radical life and higher molecular weight at high initiator concentrations. Meanwhile, some of the resulting copolymer maybe slightly crosslinked intermolecules under such a high initiator concentration, which would also contribute to the intrinsic viscosity of the copolymer.

Effect of ammonium sulfate concentration

Dispersion copolymerization of AM with AA was carried out with varying ammonium sulfate concentration from 16.2 to 19.2 wt %, while the monomer, stabilizer, initiator concentration, and the chain-transfer agent concentration were fixed at 15, 8, 0.0005, and 0.13 wt %, respectively. Figure 2 shows micrograph of the particles dispersed in the original medium. It was seen that different size spherical particles were formed. The ammonium sulfate concentration had a large effect on the particle size and the intrinsic viscosity of the copolymer, as shown in Table II; the particle size decreased first, and then increased with increasing the ammonium sulfate concentration. This was in contrast with the result for the dispersion polymerization of AM in aqueous solution of ammonium sulfate,[21,22] where the particle size was nearly independent of the salt concentration or decreased with increasing ammonium sulfate concentration. Varying the ammonium sulfate concentration affected the solvency of the medium for the resulted polymer. When the salt concentration was below 16.7 wt %,

TABLE I
Effect of the Initiator Concentration on Dispersion Copolymerization of AM/AA

Initiator conc. (10^{-4} wt %)	Conversion (%)	Particle size D (μm)	$[\eta]$ (dL/g)	Size distribution (μm)
1.25	90.6		Curd	
2.50	95.6		Curd	
3.75	98.0	4.30	5.95	1.6–10.0
5.00	98.9	4.97	5.22	1.8–11.0
10.00	99.3	5.99	4.36	2.5–12.0
15.00	99.4	6.46	7.14	2.5–13.5
20.00	99.6	6.83	7.78	3.0–18.9

Conditions: 15 wt % AM/AA (70:30); $(NH_4)_2SO_4$, 17.2 wt %; stabilizer, 8 wt %; chain-transfer agent concentration, 0.13 wt %; reaction temp., 30°C; time, 22 h.
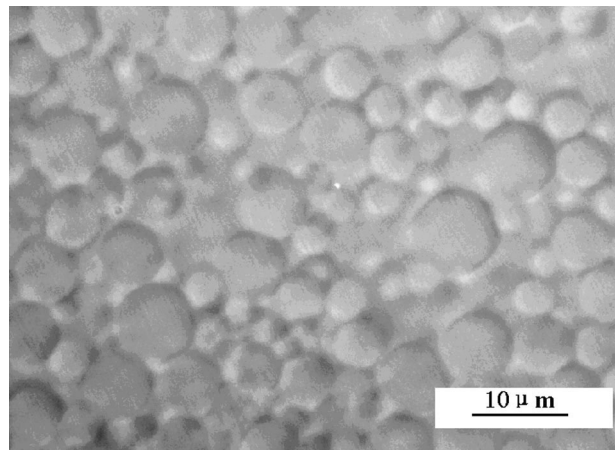
Figure 2 Photograph of copolymer particles from an optical microscopy: 15 wt % AM/AA (70:30); $(NH_4)_2SO_4$, 16.7 wt %, stabilizer, 8 wt %; initiator $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %; chain-transfer agent, 0.13 wt %; reaction temp., 30°C; time, 22 h.

dispersion copolymerization could not be successfully carried out.

The precipitating oligomer chains were directly related to their critical chains length, which depended on the solubility of the oligomer chains in the continuous phase, and was dominated by the salt concentration, monomer concentration, and temperature. At low salt concentration, the solubility of the oligomer chains became higher and the number of oligomer chains could not quickly phase-out because of poor salting-out effect, increasing the viscosity of system quickly, yielding a large lump.

As the ammonium sulfate concentration increased, the particles swollen by water became small as a result of strong electrostatic interactions. Meanwhile, increasing the ammonium sulfate concentration could also accelerate the phase-out process of the resulted polymer, but it might not increase the stabilizer adsorption rate. The stabilizer adsorption rate failed to

TABLE II
Effect of the Salt Concentration on Dispersion Copolymerization of AM/AA

Salt conc. (wt %)	Conversion (%)	Particle size D (μm)	$[\eta]$ (dL/g)	Product visc. (mPa s)
16.2		Aggregated		
16.7	97.6	6.34	5.33	275
17.2	98.9	4.97	5.22	265
17.7	98.5	4.38	5.06	175
18.2	95.8	9.61	4.33	165
19.2	98.6	13.54	3.93	205

Conditions: 15 wt % AM/AA (70:30); stabilizer, 8 wt %; initiator $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %; chain-transfer agent, 0.13 wt %; reaction temp., 30°C, time, 22 h.

TABLE III
Effect of Stabilizer Concentration on Dispersion Copolymerization of AM/AA

Stabilizer conc. (wt %)	Conversion (%)	Particle size D (μm)	$[\eta]$ (dL/g)	Product visc (mPa s)
6		Aggregated		
7	98.1	5.55	6.38	180
8	98.9	4.97	5.22	265
10	99.1	8.86	3.94	560
12	99.2	10.59	3.29	890

Conditions: 15 wt % AM/AA (70:30); initiator, $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %, $(NH_4)_2SO_4$, 17.2 wt %; chain-transfer agent, 0.13 wt %; reaction temp., 30°C; time, 22 h.

cope with the rate of new surface generation by the precipitating oligomeric radicals or the dead polymer molecules terminated in the solution phase. Hence, the coagulation rate of the unstable particles would be increased leading to bigger particles. Here, we imagined that oligoradicals or the dead polymer that deposited on the surface of growing particles had difficulty diffusing into the interior of the particles because of the internal high viscosity of the particles. So, interface coarse large particles were obtained at a high ammonium sulfate concentration.

The molecular weight decreased with an increase of ammonium sulfate concentration. It might be noted that the copolymer particles underwent significant swelling by water in the present case and the monomer should find relatively easy entry into the swollen copolymer particles through the solvent channels.[16,17] A change of ammonium sulfate concentration could lead to shift location of the polymerization.[9,28] As the ammonium sulfate concentration increased, the swelling extent of particles decreased, and the access of oligomeric radicals and monomer into the growing polymer particles was cumbered; hence, the contribution of particle phase polymerization would decrease analogously. The polymerization proceeded mainly in the solution phase, meanwhile the particles could capture dead polymer from the solution. This effect would result in a decrease of molecular weight with an increase of the ammonium sulfate concentration. Additionally, the chain transfer to the ammonium sulfate would also reduce the molecular weight of the copolymer. So the molecular weight decreased with the increasing ammonium sulfate concentration.

Effect of stabilizer concentration

As shown in Table III, the bulk viscosity of the copolymer dispersion increased with an increase of the stabilizer concentration, and the polymerization conversion slightly increased with increasing the stabilizer concentration. When the stabilizer concentration

TABLE IV
Effect of Chain-Transfer Agent Concentration on Dispersion Copolymerization of AM/AA

Chain-transfer conc. (wt %)	Conversion (%)	Particle size D (μm)	$[\eta]$ (dL/g)
0.10	99.1	4.09	7.06
0.13	98.9	4.97	5.22
0.17	98.4	6.66	4.64
0.20	98.0	8.92	4.17
0.27	97.6	10.75	3.94

Conditions: 15 wt % AM/AA (70:30); stabilizer, 8 wt %; initiator $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %, $(NH_4)_2SO_4$, 17.2 wt %; reaction temp., 30°C; time, 22 h.

was less than 7 wt %, the stabilizer was not enough to stabilize all the polymer particles precipitated from the continuous phase, and an agglomerate system was achieved. It was observed that increasing the stabilizer concentration provided more stable dispersion. A high stabilizer concentration caused faster stabilizer adsorption, and hence, for a given rate of nucleation, a greater number of particles of smaller size would be stabilized during the primary stabilization process.[12,13] When the stabilizer concentration reached 10 wt %, the particle size increased. The reason may be that PAMPSNa used as the stabilizer was a polyelectrolyte, which could enhance the stabilization of the lattice particles by the steric stabilization and the electrostatic effect,[29,30] while it could also lead to coagulation by "bridge" effect.[31] In our system, the extra stabilizer molecules may make links between particles, leading to large particles.

From the results in Table III, it was observed that the intrinsic viscosity of the copolymer decreased with an increase of stabilizer concentration. This result was in conformity with dispersion polymerization of AM in aqueous solution of ammonium sulfate[21] but was different from the results by Ray and Mandal.[16,17] The reasons for the decrease of intrinsic viscosity of the copolymer with the increase of stabilizer concentration may be (1) the stabilizer might act as a chain transfer agent, leading to lower molecular weight with an increase of stabilizer concentration and (2) since the stabilizer used in this work was a strong polyelectrolyte containing sulfonic group, the copolymer particles would be negatively charged. In our system, APS was used as the initiator. We proposed that the polymer radicals with negatively charged sulfate head groups[32] might bring out a decrease in the entry rate of oligomeric radicals into the copolymer particles because of repulsive interaction.[16,17] As the stabilizer concentration increased, the repulsive force would become stronger and the entry rate would become slower. The probability that the copolymer would be terminated in the solution phase would increase. The

particles would capture dead polymer from the solution, which would lead to lower molecular weight.

Effect of chain transfer agent concentration

Table IV shows that the polymerization conversion slightly decreased with increase of the chain-transfer agent in the feed, and the particle size increased and the intrinsic viscosity of the copolymer decreased with an increase of the chain-transfer agent concentration. The molecular weight of copolymer can be modified by the addition of a chain-transfer agent, which competes with monomer in the propagation reaction and forms a new free radical for initiation.[33] With the chain-transfer agent concentration increased, the kinetic chain length reduced and the molecular weight of the copolymer decreased. Because of the chain transfer reaction, the lowest molecular weight copolymer might have been formed at the beginning of the reaction. They remained dissolved in the solution phase rather than precipitating to form primary particles. As the result of the lower number of primary particles being initially nucleated,[34] the final particle size would be larger. Figure 3 shows the effects of the different chain-transfer agent concentrations on the particle size distribution. The particle size was relatively broad.

Effect of temperature

The effect of different temperatures on the dispersion copolymer of AM and AA, as shown in Table V, indicated that too low or too high temperature could not obtain stable dispersion. The particle sizes increased with increasing temperature, while the copolymer molecular weight decreased. The same trend was also reported for other dispersion polymerizations.[35–37] An increase in temperature caused an increase in the solubility of the oligomer chains, the rate
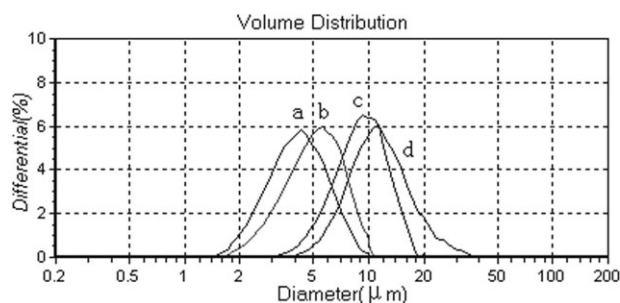

Figure 3 Distribution of particle size with different concentrations of chain-transfer agent. Conditions: 15 wt % AM/AA (70:30); stabilizer, 8 wt %; initiator $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %, $(NH_4)_2SO_4$, 17.2 wt %; reaction temp., 30°C; time, 22 h; chain-transfer agent concentration (a) 0.10 wt %, (b) 0.13 wt %, (c) 0.20 wt %, and (d) 0.27 wt %.

TABLE V
Effect of Temperature on Dispersion
Copolymerization of AM/AA

Reaction temp (°C)	Conversion (%)	Particle size D (μm)	$[\eta]$ (dL/g)	Size distribution (μm)
25		Curd		
30	98.9	4.97	5.22	1.8–11.0
35	98.6	6.36	4.15	1.8–15.0
40	99.1	8.01	3.12	3.0–18.0
45		Aggregated		

Conditions: 15 wt % AM/AA (70:30); stabilizer, 8 wt %; initiator $(NH_4)_2S_2O_8$, 5.00×10^{-4} wt %, $(NH_4)_2SO_4$, 17.2 wt %; chain-transfer agent, 0.13 wt %; time, 22 h.

constant for APS decomposition, and the rate constant for propagation; these in turn resulted in the increase in critical chain length, the concentration of precipitated chains, and the rate of growth of the particles, while the adsorption of stabilizer and the viscosity of the continuous phase were reduced. All of these could contribute to an increase in particle size. Table V also shows that the size distribution and conversion were not greatly affected by temperature.

CONCLUSIONS

In this work, the features of the dispersion copolymerization of AM with AA in an aqueous solution of ammonium sulfate using PAMPSNa as the stabilizer and APS as the initiator were investigated. High-solids, low-viscosity anionic water-soluble copolymer lattices were prepared. It was found that varying the ammonium sulfate concentration could affect the particle size and the intrinsic viscosity of the copolymer significantly. With increasing the stabilizer concentration, the particle size of the copolymer decreased first, and then increased, while the intrinsic viscosity of the copolymer decreased. The bulk viscosity of the copolymer dispersion increased with an increase of the stabilizer concentration. The increase of initiator concentration, chain-transfer agent concentration, and polymerization temperature resulted in increase in the particle size. The polymerization conversion increased with an increase in the initiator concentration and the stabilizer concentration and decreased with an increase in the chain-transfer concentration. The copolymer dispersion was stable during long storage. These results indicated that the dispersion polymerization of

AM with AA is a method for synthesis of anionic water-soluble polymers without organic solvent.

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