Dispersion Polymerization of Acrylamide with Quaternary Ammonium Cationic Comonomer in Aqueous Solution

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ABSTRACT: Copolymer particles consisting of acrylamide (AM) and acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) were prepared by dispersion polymerization in an aqueous solution of ammonium sulfate and in the presence of poly(acryloyloxyethyl trimethyl ammonium chloride) (PAOTAC) as the stabilizer. The average particle size ranged from 4 to 7 μm, and M_w and M_n were 2–6 $\times 10^6$ g/mol and 1–3 $\times 10^6$ g/mol, respectively. The effects of the AM/AODBAC ratio, monomer, initiator, salt, and stabilizer concentration on the particle size and molecular weight were studied. Increase of the AODBAC/AM ratio resulted in a decrease in the molecular weight and an increase in particle size. With the increase of the AODABA/AM ratio, the dispersion became less stable during long storage. Due to the presence of the salt, ionization of the quaternary ammonium groups in the dispersed particles is considered significantly suppressed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1101–1108, 2003

Key words: dispersion polymerization; acrylamide; acryloyloxyethyl dimethylbenzyl ammonium chloride; poly(acryloyloxyethyl trimethyl ammonium chloride); aqueous solution

INTRODUCTION

In the past several years the production of cationic water-soluble homopolymers and copolymers with acrylamide has grown rapidly for their various commercial applications. These polymers are used for retention aids in papermaking, as flocculent and biocides in wastewater treatment, and as stabilizers for emulsion polymerization in cosmetics.[1–4] For the same applications, high molecular weight polyacrylamide (PAM) has been widely used because of effectiveness and low price, but it is nonionic. If a polymer has charged groups on its chain, it will be more effective as a flocculent and as a retention aid in papermaking. Hence, many cationic polymers are prepared by copolymerizing acrylamide (AM) with monomers having cationic charge groups,[5–9] and this led to the development of water-soluble cationic polyelectrolytes having marked utility in many applications.[10–15]

For the preparation of cationic polyelectrolytes, acrylamide has been frequently copolymerized with diallydimethyl ammonium chloride (DADMAC),[16–24] but solution polymerization and inverse emulsion polymerization were almost exclusively employed. On the other hand, very few reports in the literature deal with dispersion copolymerization of AM with cationic monomers. Recent advances for the dispersion copolymerization in aqueous media are generally regarded as proprietary information by industrial laboratories, and technical information is not readily disseminated except through the patent literatures.[25–27]

Dispersion polymerization is an attractive alternative to other polymerization methods for the preparation of dispersed polymer particles of micron size in a single step.[28–40] Dispersion polymerization of hydrophobic polymers in organic media has been studied by many researchers. However, there exist only a few works on dispersion polymerization of water-soluble polymers in aqueous media. Ray and Mandal[39,40] carried out the dispersion polymerization of acrylamide, but they used water/*tert*-butyl alcohol media. The dispersion polymerization of acrylamide in aqueous media without an organic solvent has appeared only in a few numbers of patents.[25,41] In this kind of dispersion polymerization, instead of using an organic solvent, the aqueous medium usually contains a high concentration of a water-soluble salt in order to induce the phase-out of the resulting polymer by the salting-out effect. Although the aqueous medium contains a high concentration of the salt, it does not cause any problem in practical applications because the amount of the dispersion employed is very small (on the order of 0.1 wt % or less) compared with the amount of the particles suspended in liquids. If a polymer can be finely dispersed by dispersion polymerization in an aqueous medium having no organic solvent, it can be directly applied as prepared, especially to flocculation and papermaking. Compared with precipitation and solution polymerization, it may not need separation and drying of solid products and redissolution of the products for applications.

DADMAC seems to be the most frequently used cationic comonomer. Other comonomers that have appeared in academic articles are amide-type monomers such as quaternized dimethylaminoethyl acrylamide,[7] methacrylamidopropyltrimethyl ammonium chloride,

TABLE I
Effect of the Composition of AM and AODBAC on the Charge Density and Particle Size

AODBAC : AM (mol-ratio)	Charge density of AODBAC measured/theor. (μ eq/g)[b]	Mw ($\times10^6$)	Mn ($\times10^6$)	Conversion of AODBAC (%)	Overall conversion of monomer (%)	AODBAC composition in copolymer (%)	P.D. (μm)
0 :100[a]	—	2.495	1.021	—	90	—	2.7 (2.2–4.5)
05 : 95	328/561	3.832	1.755	58.46	90	3.25	3.9 (1.9–6.7)
10 : 90	768/999	3.667	2.029	76.88	92	8.36	4.3 (2.4–7.1)
15 : 85	1123/1351	3.289	2.436	83.12	85	14.7	5.8 (2.4–8.0)
20 : 80	1414/1640	2.721	2.100	86.22	80	21.6	6.7 (3.5–8.5)

The monomer, salt, stabilizer, and initiator concentrations were kept constant at 5.5%, 25%, 0.5%, and 1.84×10^{-4} mol/L, respectively.

[a] 5% AM, 30% AS, 0.6% PAOTAC, 1.84×10^{-4} mol/L AIBA (without AODBAC).

[b] Total charge density—charge density of the stabilizer.

P.D.: average particle size (range of particle diameter).

etc., and ester-type monomers such as acryloyloxyethyltrimethyl ammonium chloride (AOTAC), etc.[9] In a previous work, we successfully carried out dispersion polymerization of acrylamide in aqueous media without an organic solvent and found the stable conditions for the dispersion polymerization.[42] In this work we synthesized cationic polyelectrolytes by dispersion copolymerization of acrylamide with acryloyloxyethyl dimethylbenzyl ammonium sulfate chloride (AODBAC) in aqueous media without using an organic solvent. As the water-soluble salt, ammonium sulfate was used. The cationic comonomer, AODBAC, was chosen because it can be easily synthesized and has not appeared in academic research. As the stabilizer, poly(acryloloxy ethyltrimethylammonium chloride) (PAOTAC), the same one in the previous work, was used. As the synthesis variables, concentrations of the monomers, salt, stabilizer, and initiator as well as the composition of monomers were varied. The copolymers were characterized with respect to the molecular weights, particle size, size distribution, and copolymer composition. Discussion was made for the effects of cationic comonomer on the stable synthesis conditions, product characteristics, and polymerization reaction rate. In addition, a simple experiment was made to test the flocculation ability of the copolymer.

EXPERIMENTAL

Materials

The AM monomer was purchased from Duksan Chemical Co., and was used either as received or after recrystallization from methanol. Ammonium sulfate (AS; Samchun Chem., EP) as the salt and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA; Aldrich Chem.) as the initiator were used as received without further purification. AOTAC was obtained from CPS Chemicals (West Memphis, AR) as an aqueous solution (80%) inhibited approximately 600 ppm of hydroquinone monomethylether and was purified by repeated extraction and crystallization from acetone. PAOTAC was prepared from AOTAC in an

aqueous solution using AIBA as the initiator at 45°C.[43,44] PAOTAC had a Brookfield viscosity of 121,600 cps. This corresponds to the molecular weight of ca. 200,000 if it is assumed that the behavior of PAOTAC is similar to that of PAM. AODBAC was synthesized from 2-(dimethylamino) ethyl acrylate (DMAEA) and benzyl chloride according to the procedure in the literature.[45] The concentration of AODBAC was determined by titration of chloride with silver nitrate using sodium chromate as a visual indicator.[46] The water used was triple distilled from NANO pure UV of Barnstead, USA.

Procedure

Varying quantities of the ingredients (Tables I and II) were added to a 250-mL three-necked separable flask equipped with a stirrer, a reflux condenser, and a nitrogen inlet tube. After purging with N$_2$ and starting the temperature control, the polymerization was initiated by injecting the water-soluble initiator into the system. The temperature was maintained at 45 ± 1°C. Polymerization was allowed to continue for 20 h until the monomer was consumed. Solid products could be obtained by freeze-drying from water after dialysis to remove the reaction medium. The charge density of copolymers was measured by a particle charge detector, PCD 02 of MÜTEK in order to determine the copolymer composition. The instrument serves to detect the point of neutral charge—i.e., the isoelectric point, by polyelectrolyte titration, which is a charge-compensating method using polyions of opposite charge. Sodium polyethensulphonate (Pes-Na) of MÜTEK was used as the reference substance for determining the exact concentration of AODBAC in the copolymer.[47] The consumption of a defined titer indicates the original surface charge density, in μeq/g, of macromolecules and particles. Molecular weights were calculated using a VISCOTEK GPC with TOSOH G6000 columns in acetic acid and sodium acetate as solvent. Both the UV and refractive index detectors were employed, and the calculation of molecular

TABLE II
Results of Copolymerization of Acrylamide and AODBAC in Ammonium Sulfate Solution Using AIBA as the Initiator in the Presence of PAOTAC as the Stabilizer at 45°C

Expt. no.	AODBAC/AM (% w/v)	AS (% w/v)	PAOTAC (% w/v)	AIBA ($\times 10^{-4}$ mol/L)	Mw ($\times 10^6$)	Mn ($\times 10^6$)	M.W.D.	Conversion (%)	P.D. (μm)
1	6	25	0.5	1.84	5.059	2.473	2.046	83	3.6 (2.3–4.5)
2	6	25	0.5	2.76	4.652	2.332	1.995	85	3.7 (1.8–4.8)
3	6	25	0.5	3.68	4.538	2.257	2.037	84	4.4 (2.7–5.6)
4-1	6	25	0.5	4.6	4.037	2.155	1.873	86	4.6 (2.5–6.1)
4-2	6	25	0.5	4.6	3.655	1.244	2.938	88	4.9 (3.1–6.8)
2	6	25	0.5	2.76	4.652	2.332	1.995	85	3.7 (1.8–4.8)
6	8	25	0.5	2.76	5.282	1.529	3.455	86	5.8 (2.4–7.1)
7-1	10	25	0.5	2.76	aggregated				
7-2	10	25	0.5	2.76	5.581	2.635	2.22	92	6.4 (2.3–7.4)
8	8	21	0.5	1.84	5.107	2.358	2.166	89	6.3 (3.1–7.6)
9	8	23	0.5	1.84	6.088	2.066	2.947	85	5.9 (2.8–6.9)
10	8	25	0.5	1.84	6.743	3.126	2.157	87	5.2 (2.5–7.2)
11-1	8	27	0.5	1.84	aggregated				
11-2	8	27	0.5	1.84	6.184	2.473	2.501	91	4.3 (2.1–6.8)
12-1	5.5	25	0.2	1.84	aggregated				
12-2	5.5	25	0.2	1.84	3.76	1.644	2.26	82	6.7 (2.9–8.2)
13	5.5	25	0.5	1.84	3.667	2.029	1.807	86	5.9 (2.6–7.8)
14-1	5.5	25	1.0	1.84	3.096	1.428	2.168	89	3.8 (2.4–7.1)
14-2	5.5	25	1.0	1.84	aggregated				

Molar ratio of AODBAC/AM = 1 : 9.
AM: acrylamide, AS: ammonium sulfate, PAOTAC: poly(acryloylxyethyl trimethylammonium chloride).
AIBA: 2,2'-azobis(2-methyl propionamidine) dihydrochloride, P.D.: average particle size (range of particle diameter).

weights was carried out by using a standard curve based on the polyacrylamide standards. Particle size was measured with image-analyzer (Bum Mi Universe Co.) and polarizing microscope (OLYMPUS BH-2). The image analysis procedure consists of a calibration sequence for size and contrast to ensure high reproducibility, a neighborhood contrast threshold algorithm, a particle selection criterion, and finally particle measurement. Using a reference slide and a contrast level predetermined by a software program for detecting the local contrast sets the microscope illumination.[42]

Conversion-time data were obtained by using a dilatometer. The aqueous solution of acrylamide was charged in a stirred bulb, and the height of liquid in the attached capillary was measured with time. From the decrease of the volume of the system, the conversion with time was calculated by assuming that the conversion is proportional to the volume decrease. The final conversion of copolymer-acrylamide and AODBAC was determined from the weight of the polymers obtained by precipitation in isopropyl alcohol.

A simple experiment was made to test the flocculation performance of the copolymer. Prior to this experiment, the dispersion of the copolymer or the PAM sample was dialyzed as follows: the dispersion was diluted with water, and then the polymer was separated by dialysis using a porous cellulose acetate membrane with the cutoff molecular weight of 3500 and then dried by lyophilization. The dried copolymer was redissolved in water. A solution of AODBAC-AM copolymer (see Figure 1) was added to a CaCO₃ suspension in water and the turbidity was measured with

time. The CaCO₃ particles had the average particle size of about 4 μm. For comparison, the same experiment was made with a solution of PAM prepared in the previous work.[42] To the CaCO₃ suspension of 100 g with the solid content of 10 wt %, 0.05 g of each polymer was added. The turbidity was measured by a Hach DR 2010 portable turbidimeter.

RESULTS AND DISCUSSION

Particle size and distribution

Figures 2 and 3 show some representative micrographs of the particles dispersed in the original medium. It was seen that spherical as well as oval or nonspherical particles were formed, and large particles were mostly nonspherical. The formation of non-
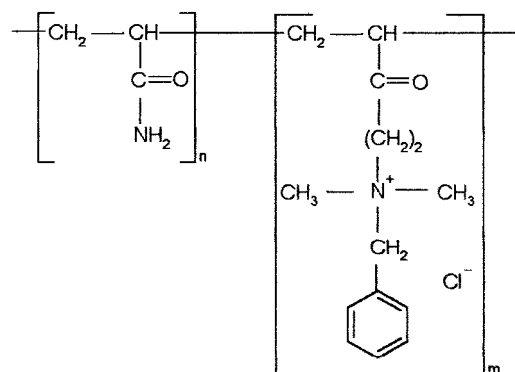

Figure 1 Chemical structure of copolymer of AM and AODBAC.

spherical particles suggests that coalescence of small particles has taken place during the course of polymerization. From the pictures, the particle size distributions were determined, as shown in Figure 4. The average particle diameters and the range of the particle size are given in Tables I and II. The average particle size ranged from 4 to 7 μm, and this is contrasted with that of PAM particles prepared by the same dispersion polymerization in the previous work where the average size of the PAM particles was 2-4 μm, about half of the above.[42] The particle size distribution was observed to skew to larger size particles in most cases and to be relatively broad. This result is somewhat different from that for the PAM particles in the previous work, which were more symmetric and narrower.

A drop of the aqueous dispersion was redispersed in acetone, and the particle size and distribution was measured. As shown in Figures 5 and 6, the particle size distributions were nearly the same between the dispersion in the aqueous medium and that in acetone. This suggests that the number of effective positive charges in the particles dispersed in the aqueous medium is considerably small; otherwise the particles dispersed in acetone would have come out to be significantly smaller.

Due to the presence of quaternary ammonium groups in AODBAC and the stabilizer, one would have expected that the dispersed particles in the aqueous media be charged and thus expanded owing to electrostatic repulsion between polymer chains. However, comparison of the size of particles dispersed in acetone with that in the aqueous media suggests that the quaternary ammonium groups may not be fully ionized. One reason for this is considered due to the presence of the salt (ammonium sulfate) in relatively high concentration. The salt would induce the salting-out effect as well as suppression of ionization of the quaternary ammonium salt. Another is the concentrated state of the particle phase that was formed by
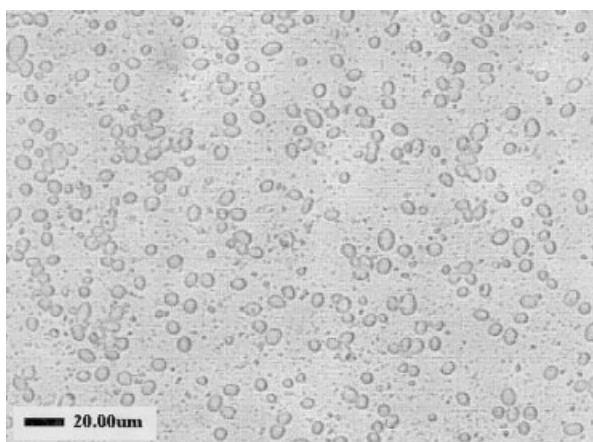

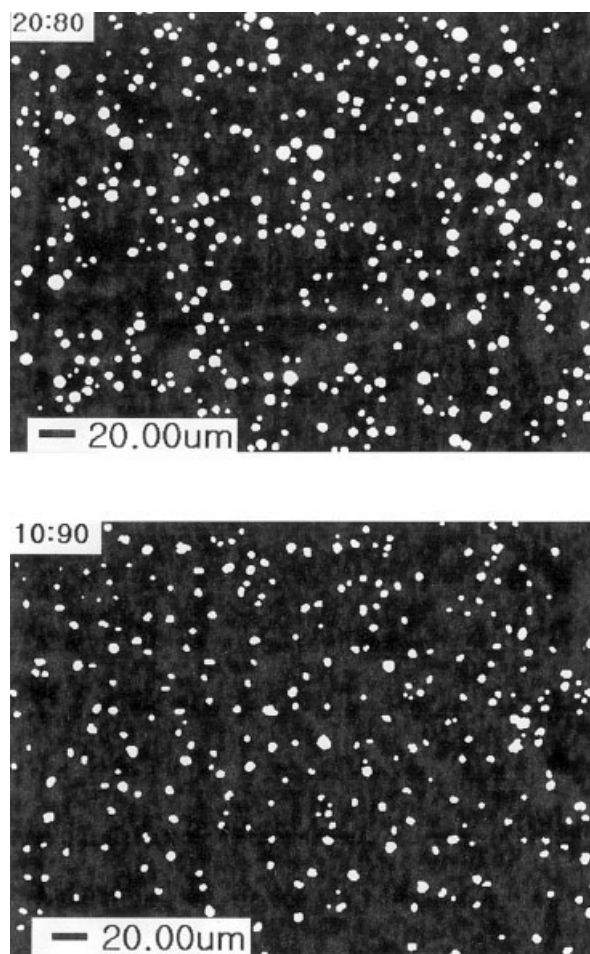**Figure 3** Micrographs (highly contrasted) of copolymer particles of AODBAC and AM with different compositions: 25% AS, 0.5% PAOTAC, 1.84×10^{-4} mol/L AIBA.(a) 5.5% AODBAC/AM (20:80); (b) 5.5%AODBAC/AM (10:90).

precipitation from the solution phase. The quaternary ammonium groups may be ionized to a greater extent in the homogeneous solution phase, but in the particle phase the concentration of the quaternary ammonium groups will be denser and thus the fraction of ionized groups will become much smaller. In addition, contrary to the expectation, stabilization of the particles owing to the electrostatic repulsion would not satisfactorily be accomplished. The larger particle size and skewed, broader distribution in this work than in the PAM case indicate that coalescence of the particles have taken place to a greater extent.

Effect of AODBAC/AM ratio

The particle size increased with increasing content of AODBAC. If the particles of cationic copolymer are charged, one may anticipate that the particle size will become smaller with increasing content of AODBAC due to electrostatic repulsion. However, the result was opposite to this. In dispersion polymerization, the following process is usually suggested to occur for particle formation and growth[33]: (1) At the start of the
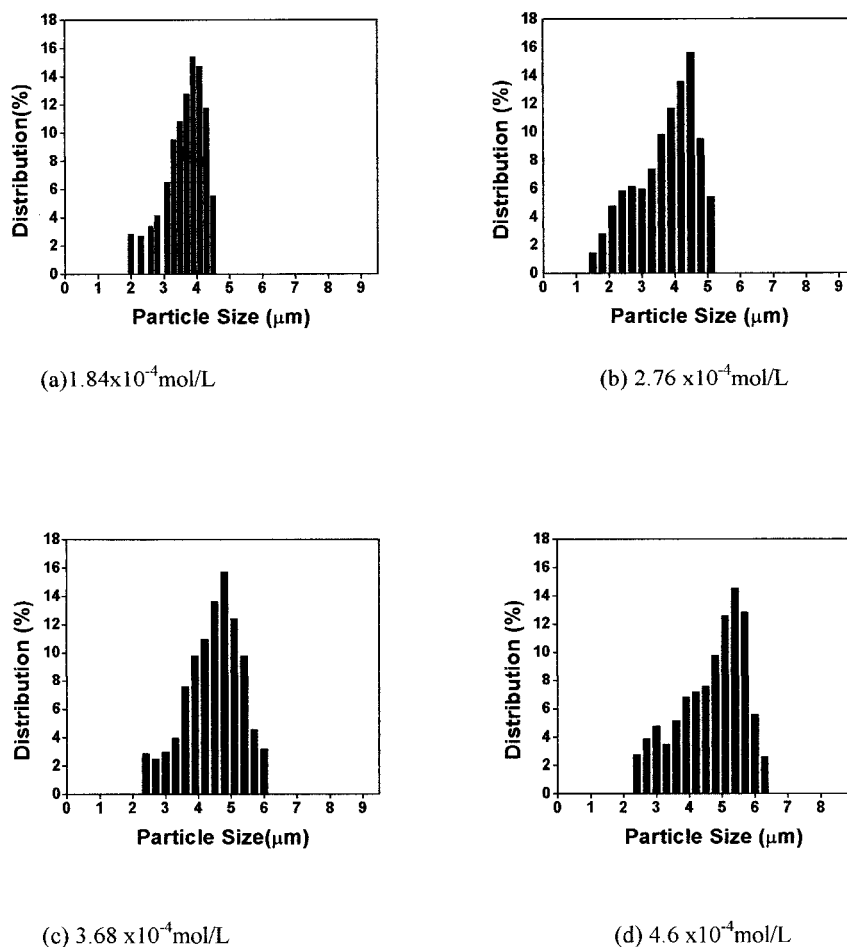

Figure 2 Micrographs (original) of copolymer particles of AODBAC and AM with different compositions: 25% AS, 0.5% PAOTAC, 1.84×10^{-4} mol/L AIBA. (a) 5.5% AODBAC/AM (20:80); (b) 5.5%AODBAC/AM (10:90).

(a)1.84x10^{-4}mol/L

(b) 2.76 x10^{-4}mol/L

(c) 3.68 x10^{-4}mol/L

(d) 4.6 x10^{-4}mol/L

Figure 4 Distribution of particle size with different amounts of initiator: 6% AODBAC-AM, 25% AS, 0.5% PAOTAC; (a) 1.84 × 10^{-4} mol/L (b) 2.76 × 10^{-4} mol/L (c) 3.68 × 10^{-4} mol/L (d) 4.6 × 10^{-4} mol/L.

process, monomer, stabilizer, and initiator are present in a homogeneous solution of continuous phase. (2) The initiator decomposes and the free radicals react with monomer to form oligomeric radicals. (3) At a critical chain length, the oligomers precipitate and adsorb stabilizer to form stable particle nuclei. (4)
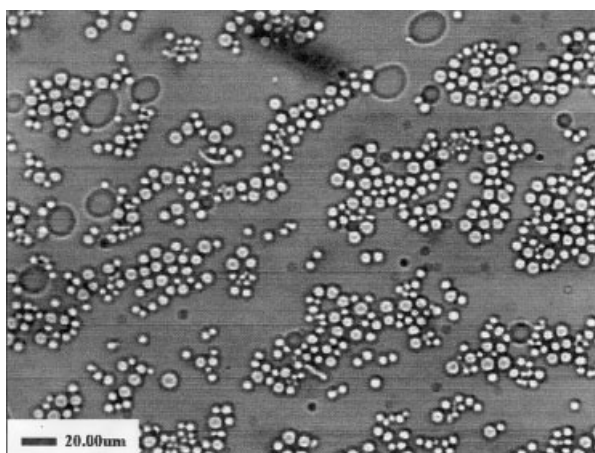
Once particles have been formed, they absorb monomer from the continuous phase and the polymerization mainly takes place within the particle. However,
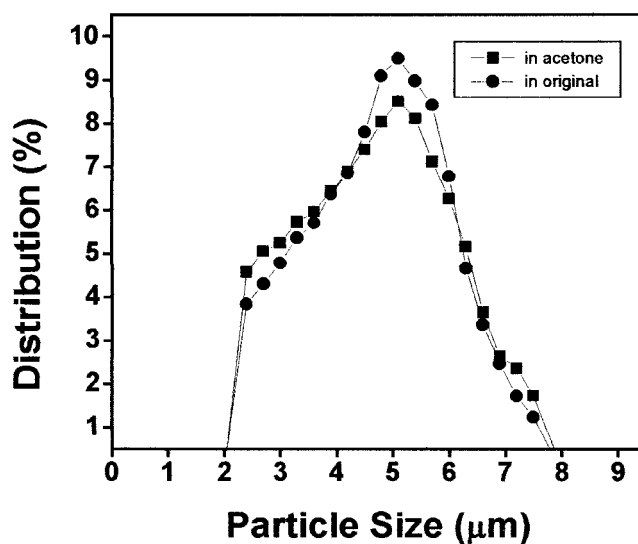

Figure 5 Micrographs of copolymer particles of AODBAC and AM redispersed in acetone: 8% AODBAC/AM (10:90), 25% AS, 0.5% PAOTAC, 1.84 × 10^{-4} mol/L AIBA (Expt. No. 10).

Figure 6 Size distribution of the particles in the original medium and redispersed in acetone: 8% AODBAC/AM (10:90), 25% AS, 0.5% PAOTAC, 1.84 × 10^{-4} mol/L AIBA (Expt. No. 10).
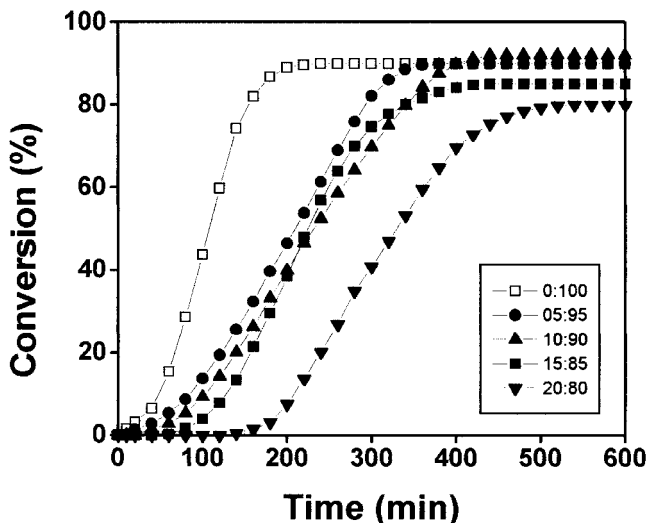
Figure 7 Conversion vs time curve for dispersion polymerization of AODBAC and AM with different molar ratios of AODBAC/AM: 20:80, 15:85, 10:90, 05:95, 0:100, respectively.

there may be some differences for this system. As discussed above, the cationic comonomer, oligomers, and stabilizer in the solution phase can be ionized more due to abundant water surrounding them and even the precipitated oligomers can still be ionized to a considerable extent due to the short chain length. Due to the positive charges, adsorption of the stabilizer on the oligomers will be hindered, but the charged oligomers will be stabilized by them owing to the electrostatic repulsion and will grow by absorption of the monomers. As the particle size becomes larger, the fraction of ionized groups will become smaller, and beyond a certain point coalescence of the particles will become significant. As the AODBAC/AM ratio increases, a larger number of smaller particles might be present during the early stage due to more ionized groups, but at a later stage the coalescence may occur more rapidly, resulting in larger particles eventually. One additional factor that can be considered is that the adsorption rate of the stabilizer may be slower on larger particles, resulting in less effective stabilization.

In addition, it was observed that the dispersed state of AODBAC-AM copolymer was less stable than that of PAM during long storage. For the latter the dispersed state sustained stable for longer than 6 months, while for the former sedimentation occurred within a few months and it occurred faster with a higher AODBAC/AM ratio. This is probably due to the larger particle size compared with the PAM particles. When the AODBAC/AM ratio was above 20/80, the polymerization system became half-muddy and stable dispersion could not be obtained.

Figure 7 shows the polymerization rate (R_p) with varying the comonomer/monomer feed ratio. By the presence of the comonomer, the polymerization rate appeared to be retarded. As the ratio increased, retardation of the polymerization became more pro-

nounced. However, once the polymerization started regularly, the polymerization went on with about the same rate regardless of the comonomer content, although it was quite slower compared with the case without the comonomer. In an earlier work on copolymerization of AM with AOTAC by employing solution polymerization in which $K_2S_2O_8$ was used as the initiator,[9] retardation of polymerization did not seem to occur. The reason for the retardation in this work is not well understood at the moment since the system is different and more complex. Several factors may be considered such as efficiency of the initiator radicals for combination with each monomer, the positive charges of the comonomer, oligomers, stabilizer and particles containing the stabilizer and copolymer, and the effect of salt. At least, it may be suggested that the entry rate of the cationic comonomer into the growing particles may be retarded due to the positive charges of the particle even though a small fraction was ionized. Another factor may be that the AODBAC molecule is bulkier than AM, which will have a slower diffusion rate especially in the particle.

As shown in Table I, the final overall conversion became lower with increasing AODBAC/AM ratio and the molecular weight also became lower. It is also considered due to the retarding effect of the comonomer, inducing earlier termination with higher concentration of AODBAC.

For use as cationic flocculants, charge density in the polymer is very important because it is closely related to properties of the polymer.[10,12] The total charge density of the copolymers was measured, and after subtracting the charge density of the stabilizer the conversion of AODBAC was determined as shown in Table I. At low AODBAC/AM ratio, the conversion of AODBAC was quite lower compared with the overall conversion. This means that the AODBAC composition in the copolymer is lower than the feed composition. As the AODBAC/AM feed ratio increased, the conversion of AODBAC increased and at the ratio of 20/80 it became greater than the overall conversion.

Effect of initiator (AIBA) concentration

The set of Experiments 1 through 4-2 in Table II shows the effects of the variation of initiator concentration from 1.84 to 4.6×10^{-4} mol/L while the monomer and stabilizer concentrations were fixed at 6 and 0.5%. As is generally observed, the molecular weight of the polymers decreased with the increase of initiator concentration.[27,30–32,52] While the rate of polymerization increases with increase of the initiator concentration, the average numbers of monomer molecules consume per each radical will be smaller, resulting in lower molecular weight.[51] The particle size increased with increase of the initiator concentration. This is commonly observed in dispersion polymerization. The most commonly offered explanation is that a greater

initiator concentration generates more oligomers and the dispersed particles are not stabilized enough by the stabilizer, leading to a greater rate of coalescence and resulting in larger particles.[27,30,31]

Effect of monomer concentration

Experiments 2, 6, 7-1, and 7-2 in Table II indicated that the molecular weight and the particle size increased with increasing monomer concentration. This is the usual trend reported in the literature.[28,31,32,43,44] The increase of the monomer concentration increases the solubility of the polymer formed in the medium and thus increases the critical length for the precipitation of the oligomers. Also, the solvency for the stabilizer increases and consequently adsorption on the formed copolymer was reduced. These two effects may account for the increase of the particle size. As the monomer concentration was increased above 10%, stable dispersion could not be obtained when 0.5% PAOTAC and 2.76×10^{-4} mol/L AIBA were used.

Effect of salt concentration

The polymerization experiments were carried out with varying salt concentration from 21 to 27%, while the monomer, stabilizer, and initiator concentrations were kept constant at 8, 0.5, and 1.84×10^{-4} mol/L, respectively. The effect of salt concentration did not seem to be strong on the molecular weight of polymers. A similar trend was also observed for the dispersion polymerization of PAM.[42] The particle size decreased with increasing salt concentration. This is contrasted with the result for the dispersion polymerization of PAM, where the particle size was nearly independent of the salt concentration.[42] A similar discussion as mentioned above may be applicable. When the salt concentration is low, the salting-out effect will be reduced and the extent of ionization will be high. In addition, the stabilizing action of the cationic stabilizer will also be diminished. The precipitation or the formation of stable nuclei will be deterred to a certain stage where the copolymer chains are sufficiently long, but after that the formed particles may coalescence rather in a rapid rate. When the ammonium sulfate concentration was below 21%, it was difficult to get a stable dispersion and usually a single body of homogeneous gel was obtained. As the salt concentration increases, the precipitation of the copolymer with shorter chains will occur and the stabilizer will become more effective, resulting in smaller particles. However, when the salt concentration is too high, the salting-out effect becomes too excessive and it will be difficult to get stable dispersion. When the salt concentration was above 27%, it was difficult to get a homogeneous solution of the monomers due to limited solubility and high yield of the coagulum was obtained in the form of agglomerated lumps separated from the medium.

Effect of stabilizer concentration

The PAOTAC concentration was varied between 0.2 and 1.0 wt %. Table II showed that the particle size decreased when the stabilizer concentration increased. This is on the expected line and is in agreement with the results reported in the literature.[28,31,32,43–45] With increasing amount of the stabilizer, a greater number of particles of smaller size will be stabilized owing to a larger surface area for stabilization. However, when the stabilizer concentration was too high (1.5% and above), the dispersion became very unstable, giving agglomerated lumps separated from the medium. When the amount of the stabilizer is too excessive, it seems to promote the agglomeration. This is probably due to that the extra stabilizer molecules do not participate in stabilization but rather they may make links between the particles, inducing agglomeration. The molecular weight of the copolymers does not seem to depend strongly on the stabilizer concentration.

Stable synthesis conditions

The concentration ranges for obtaining stable aqueous dispersion of the AODBAC-AM copolymer were as follows: For the total monomer concentration, it ranged from 5 to 10%. This is similar to the PAM case.[42] For the ammonium sulfate concentration, it was from 21 to 27%. This is somewhat lower compared with the PAM case, in which it was from 24 to 30%. This is probably due to the ionic character of the comonomer. For the concentration of the stabilizer, PAOTAC, it was from 0.2 to 1.0%. This is also lower that for the PAM case, which was from 0.6 to 1.8%. This is also considered due to the ionic character of the comonomer, and the copolymerized oligomers may serve as a stabilizer to a certain extent. The optimum concentrations for the total monomer, salt and stabilizer were 5.5–8, 25, and 0.5%, respectively. The optimum AODBAC/AM mole ratio may be 10/90.

Flocculation test

A simple test was made to compare the flocculation ability of a dispersion product of the AODBAC-AM copolymer prepared in this work and that of PAM in the previous work.[42] The dispersions were added to a CaCO$_3$ suspension sample and the turbidity change was measured with time. As is shown in Figure 8, the copolymer showed far superior performance to the PAM. This is certainly due to the cationic groups that enhance the flocculation. Work is in progress in our laboratory to investigate the flocculation performance in more details.

CONCLUSIONS

Dispersed particles of copolymer of AODBAC-AM were prepared by dispersion polymerization in aque-
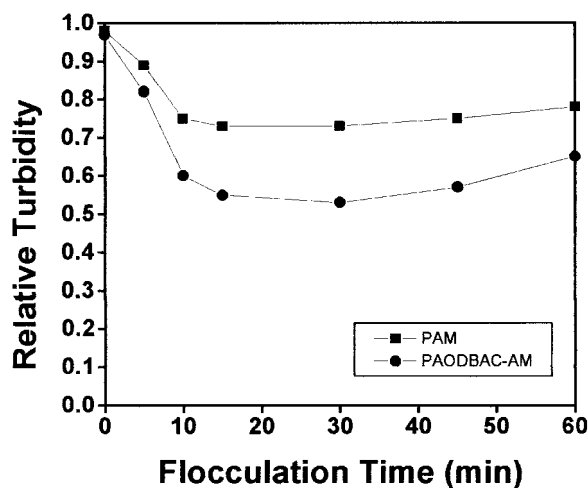
Figure 8 Change of turbidity of CaCO₃ suspension after addition of PAM and PAODBAC-AM dispersions; solid content of CaCO₃ suspension = 10 wt %, polymer dose = 5 mg/g CaCO₃, polymer content of PAM dispersion = 8 wt %, polymer content of PAODBAC-AM (10:90) dispersion = 8 wt %.

ous salt solution of ammonium sulfate by using PAO-TAC as the stabilizer. The stable conditions for the dispersion copolymerization were investigated, and it was found that the stable ranges for the salt and stabilizer concentration were somewhat lower than those of for the preparation of PAM dispersion. This is probably due to the ionization of the cationic comonomer. The effects of concentrations of the initiator, monomers, and stabilizer on the molecular weight and particle size were in conformity with those usually reported in other works. With increase of the AOD-BAC/AM ratio, the rate of polymerization became more retarded and the molecular weight decreased, but the particle size increased. The concentration of the salt did not appear to affect the molecular weight strongly, but the particle size decreased with increase of the salt concentration until it was not too high. It was suggested that the extent of ionization of the quaternary ammonium groups in the comonomer and the stabilizer, under the influence of the salt present, might be related to the particle size. During the early stage the extent of ionization may be high, but at a later stage where the particle precipitates and grows to above a certain size, the extent of ionization will be greatly reduced, leading to coalescence of particles. The average particle size was 4–7 μm. This was larger than that of PAM particles prepared by the same method, and the copolymer dispersion was less stable during long storage. However, the copolymer dispersion was more effective for flocculation than the PAM dispersion.

References

1. Pabon, M.; Selb, J.; Candau, F. Polymer, 1999, 40, 3101–3106.
2. Laird, D. A. Soil Sci 1977, 162, 826.
3. Otsubo, Y. Hetero Chem Rev 1996, 3, 347.
4. Fan, A.; Turro, N. J.; Somasundaran, P. Colloids and Surface A: Physicochemical Eng. Asp, 2000, 162, 141.
5. McCormick, C. L.; Blackmon, L. P. Polymer 1986, 27, 1971.
6. Rojas, O. J.; Claesson, P. M.; Muller, D.; Neuman, R. D. J Colloid Interface Sci 1998, 205, 77.
7. Ni, H.; Hunkeler, D. Polymer 1997, 38, 667.
8. Mikaelkjellin, U. R.; Claesson, P. M.; Audebert, R. J. Colloid Interface Sci 1997, 190, 476.
9. Tanaka, H. J Polym Sci Polym Chem Ed 1986, 24, 29.
10. Dautzenberg, H.; Jaeger, W. Polyelectrylytes; Hanser Publishers: Munich, Germany, 1994.
11. Thomas, W. M.; Wang, D. W. Encycl Polym Sci Eng 1988, 1, 169.
12. Butler, G. B. Polymeric Amines and Ammonium Salts; Pergamon: New York, 1980.
13. Hoover, M. F. J Macromol Sci, Chem 1970, A4, 1327.
14. Destais, N.; Ades, D.; Sauvet, G. Polym Bull 2000, 44, 401.
15. Petzhold, L. C.; Stefens, J.; Monteavaro, L. L.; Stadler, R. Polym Bull 2000, 44, 477.
16. Butler, G. B.; Bunch, R. L. J Am Chem Soc 1949, 71, 3120.
17. Pledger, H., Jr.; Young, T. S.; Butler, G. B.; Hogen-Esh, T. E. J Makromol Sci, Chem 1985, A22, 415.
18. Lin, Y. Q.; Pledger, H., Jr.; Butler, G. B. J Macromol Sci, Chem 1998, A 25, 999.
19. Lin, Y. Q.; Butler, G. B. J Macromol Sci, Chem 1989, A 26, 681.
20. Subramanian, R.; Zhu, S.; Pelton, R. H. Colloid Polym Sci 1999, 277, 939.
21. Brand, F.; Dautzenberg, H.; Jaeger, W.; Hahn, M. Angew Makromol Chem 1997, 41, 248.
22. Matsumoto A.; Wakabayashi, S.; Oiwa, M.; Butler, G. B. J Makromol Sci, Chem 1989, A26, 1475.
23. Boothe, J. E.; Flock, H.G.; Hoover, M. F. J Macromol Sci, Chem 1970, A4(6), 1419.
24. Butler, G. B. Acc Chem Res 1982, 15, 370.
25. Hymo Corp. Jpn Pat 11335505, 1999.
26. W. R. Grace & Co.—Conn., US Pat 5 529 699, 1995.
27. Nalco Chemical Company, US Pat 6 025 426, 2000.
28. Barrett, K. E. J., Ed. Dispersion Polymerizaton in Organic Media; Wiley: New York, 1975.
29. Almog, Y.; Reich, S.; Levy, N. Br Polym J 1982, 14, 131.
30. Lok, K. P. ; Ober, C. K. Can J Chem 1985, 63, 209.
31. Ober, C. L.; Lok, K. P.; Hair, M. L. J Polym Sci Polym Lett Ed 1985, 23, 103.
32. Ober, C. K.; Lok, K. P. Macromolecules 1987, 20, 268.
33. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Polym Chem Ed 1986, 24, 2995.
34. Paine, A. J.; McNulty, J. J Polym Sci Part A: Polym Chem 1990, 28, 2569.
35. Saenz, J. M; Asua, J. M. J Polym Sci Part A: Polym Chem 1996, 34, 1977.
36. Corner, T. Colloids and Surfaces 1981, 3, 119.
37. Lacroix-Desmazes, P.; Guyot, A. Macromolecules 1982, 29, 4508.
38. Kawaguchi, S.; Winnik, M. A.; Ito, K., Macromolecules, 1996, 29, 4465.
39. Ray, B.; Mandal, B. M. Langmuir 1997, 13, 2191.
40. Ray, B.; Mandal, B. M. J Polym Sci: Part A, 1999, 37, 493.
41. Kyoritsu Yuki Co. Ltd. Eur Pat 0 183 466, 1985.
42. Cho, M. S.; Yoon, K. J.; Song, B. K. J Appl Polym Sci 2002, 83, 1397.
43. Hildebrandt, V.; Reichert, K. H. Angew Makromol Chem 1997, 245, 165.
44. Reichert, K. H. Eur Polym J 1984, 20, 505.
45. Lacroix, C.; Hess, R. Eur Pat 0329512, 1989.
46. ASTM Standards D4458–85, 1987.
47. Bley, L. Paper Technol 1992, 4. 33.
48. Takeda, H.; Kawano, M. Eur Pat 0183466, 1985.
49. Odian, G. Principles of Polymerization; John Wiley & Sons: New York, 1970.
50. Kobayashi, S.; Uyama H.; Yamamoto, I.; Matsumoto, Y. Polym J 1990, 22, 759.
51. Tuncel, A.; Kahraman, R.; Piskin, E. J Appl Polym Sci 1994, 51, 1485.
52. Shen, S. E.; Sudol, D.; El-Aasser, M. S. J Polym Sci Part A: Polym Chem 1994, 32, 1087.