

Highly Efficient Flocculant Synthesized through the Dispersion Copolymerization of Water-Soluble Monomers Induced by γ -Ray Irradiation: Synthesis and Polymerization Kinetics

Qiang Ye, Zhicheng Zhang, Xuewu Ge

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

Received 6 May 2002; accepted 12 November 2002

ABSTRACT: A water-soluble cationic copolymer dispersion was prepared by the polymerization of the cationic monomer (2-methacryloyloxyethyl)trimethyl ammonium chloride and acrylamide initiated with ^{60}Co γ -rays. The polymerization was carried out in a salt solution that did not dissolve the resulting copolymer and in the presence of a polymeric dispersant that was soluble in the salt solution. The polymerization conversion was studied gravimetrically. The bulk viscosity of the copolymer dispersion was determined with a rotation viscometer. The intrinsic viscosity of the copolymer was measured viscometrically, and the particle size was determined with an optical microscope. The

influence of some conditions on the copolymerization was studied, including the irradiation dose, dose rate, concentrations and compositions of the monomers, dispersant content, and types and contents of the inorganic salts. The flocculating characteristics of a synthetic cationic copolymer dispersion were also briefly investigated. The optimal conditions for polymerization were summarized, and some aspects of the polymerization mechanisms were examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2108–2115, 2003

Key words: dispersions; copolymerization; water-soluble polymers

INTRODUCTION

Raw water, which comes from rivers or lakes or underground, usually contains suspended matter. The suspended matter must be removed by clarification so that the water can be used in domestic and industrial applications. Flocculation is a method of dewatering suspended solids by agglomerating the solids, which materially improves the dewatering rate of many types of suspended solids, including those used in mining, papermaking, wastewater treatment, and oil-field applications. Since the early 1950s, synthetic polymer flocculants have been used in industry. Polymeric flocculating agents, which may be anionic, nonionic, cationic,^{1–3} or amphoteric,^{4,5} react with fine particles or colloids and bridge them into insoluble precipitates or flocs.

Various types of processes have been used for the preparation of polymeric flocculants, particularly water-soluble polymers. Solution polymerization is a

well-known process.^{6–8} Many patented processes use emulsion and microemulsion polymerization processes.^{9–12} However, there are a number of disadvantages associated with these. For polymers to be obtained with high molecular weights and good water solubility properties, it is necessary to retard or reduce crosslinking reactions during polymerization as much as possible. In solution polymerization, it is required that a monomer concentration of more than 10 wt % be employed to obtain a polymer with a suitably high molecular weight. The polymerization in such a high monomer concentration gives a gelatinous, hydrated polymer, which is difficult to dissolve. Therefore, it is necessary to ship the polymer product in a fluid form after further dilution or in a powdered form after drying. The shipment of the polymer in a diluted solution increases the costs of transportation, whereas shipment in a powdered form increases the cost of fuel for drying. Furthermore, when the polymer is heated in the drying process, three-dimensional crosslinking of the polymer may occur, yielding a partially water-insoluble polymer. One way of obtaining higher molecular weight polymers in a liquid form is to package the polymer in a water-in-oil emulsion^{13,14} or microemulsion.^{15,16} However, problems arise concerning smell and safety in the working environment because of a mineral oil being used as the dispersion medium. In addition, this type of polymer typically requires

Correspondence to: Q. Ye (yeqiang@ustc.edu.cn).

Contract grant sponsor: Anhui Provincial Natural Science Foundation of China; contract grant number: 01044804.

Contract grant sponsor: Research Fund for the Ministry of Science and Technology of China; contract grant number: KH1201.

more elaborate feeding equipment than that required for the solution polymers, and this has caused a great reluctance among papermakers against using this type of polymer. The inflammability of the product, as well as the wasteful use of expensive organic solvents, is the drawback of the water-in-oil emulsion polymerization process.

The goal of this study was to develop delivery systems, in liquid forms, with high active contents that did not contain hydrocarbon oil or volatile organic components and that performed comparably to analogous emulsion and powder polymer products. In 1995, Nalco Chemical Co. first introduced a line of flocculants produced by the dispersion polymerization of water-soluble cationic monomers in an aqueous salt solution as a reaction medium instead of oils and surfactants.¹⁷ This solution can dissolve the used monomers but does not dissolve the resulting polymer or copolymer, and so it gives a copolymer dispersion without gel. In wastewater treatment, the dispersion may be diluted as an aqueous solution and may be added to wastewater. This method can overcome the shortcomings of the two aforementioned types of polymerization processes and offers efficient flocculating agents. In recent years, some patents^{18–22} have also reported this unique polymerization method. However, there are no articles openly discussing the polymerization characteristics and nucleation mechanisms.

It is well known that polymers of dimethylamino-methacrylate methyl chloride quaternary (DMC) and its copolymer with acrylamide (AM) are used as effective cationic flocculants for the treatment of wastewater containing organic suspensions.^{6,23,24} Although water-soluble cationic copolymers have been recognized as being very useful in terms of technological applications and scientific investigations, until now, very few studies have been reported on the use of polymeric dispersions.²⁵ Generally, radiation polymerization is one of the most convenient methods because of its non-temperature-dependent initiation and extremely large G values (radiation chemistry yields). The radiation process can easily lead to a higher molecular weight copolymer than traditional chemical methods induced with radical initiators.^{14,26} In this study, a copolymer dispersion of a cationic monomer and AM was synthesized with ⁶⁰Co γ -rays. The influences of various polymerization parameters on the conversion percentage, the bulk viscosity of the dispersion system, the intrinsic viscosity ($[\eta]$), and the particle size were studied.

EXPERIMENTAL

Materials

AM from Hubei Daxue Chemicals, Inc. (Hubei, China), was recrystallized from acetone. Technical-grade DMC (71.2% aqueous solution) and a copolymer of dimethyl diallyl ammonium chloride and AM

TABLE I
Recipes and Synthesis Parameters for the Dispersion Polymerization Induced with γ -Ray Irradiation (T298 K)

	Standard recipe	Experimental variation	Preferred scope
Initial monomer concentration (wt%)	15.0	10.0–20.0	12.5–17.5
Monomer composition (AM/DMC w/w)	0.5	0.4–0.8	0.4–0.6
(NH ₄) ₂ SO ₄ (wt%)	15.0	5.0–25.0	12.0–20.0
Dispersant content (wt%)	2.0	0.1–3.0	1.0–2.0
Absorbed dose (kGy)	1.5	0–2.5	1.0–2.0
Dose rate (Gy/min)	30.3	18.3–85.0	18.3–50.9

(PDMA; $[\eta] = 7.8$ dL/g; cationic degree = 40%; 10% aqueous solution) were given by Xing Yu Chemicals Co., Ltd. (Wuxi, China). Ammonium sulfate (AS) and polyacrylamide [PAM; weight-average molecular weight (M_w) = 3.0×10^6] were purchased from Shanghai Chemical Reagents Co. (China). Deionized water was used throughout this work. Other reagents were AR-grade and were used as received.

Preparation and polymerization of the dispersion system

The standard recipes and synthesis parameters used in this study are given in Table I. The amount of each ingredient was kept constant in all experiments, except as indicated.

The monomer solution was prepared by the addition of monomers into an aqueous salt/polymeric dispersant (PDMA) solution. Purified nitrogen was bubbled through the aqueous solution at room temperature for about 15 min for oxygen removal. After that, the solution was directly fed into a sealed glass ampule. The ampule was then subjected to γ -ray irradiation with a ⁶⁰Co source at room temperature. The dose rate was controlled by changes in the distance between the ampule and the ⁶⁰Co source and was determined with a Fricke dosimeter. After irradiation, the polymerization product was removed from the glass ampule.

Characterization of the copolymer dispersion

The bulk viscosity of the copolymer dispersion was determined with an NDJ-1 rotation viscometer. The copolymer dispersions were observed, and their particle sizes were estimated with a Leica Galen-III biological microscope.

Copolymer characterization

The polymerized dispersion was precipitated in a large quantity of ethanol and washed with acetone.

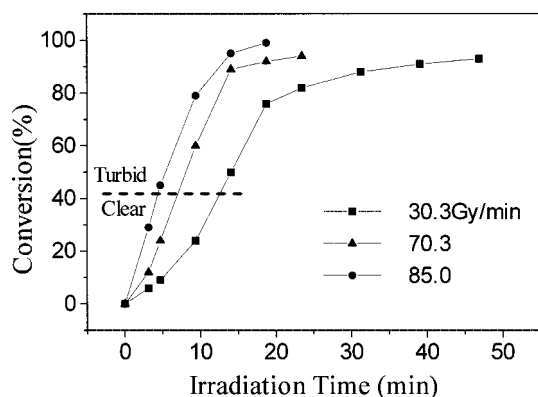


Figure 1 Conversion versus the irradiation time at three different dose rates [15 wt % monomer; 1:2 AM/DMC (w/w); 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 68 wt % H_2O ; 298 K].

The insoluble polymer was washed with a large quantity of ethanol for the removal of the inorganic salt and homopolymer of PAM, and then it was centrifuged at 4000 rpm. This operation was repeated several times. The polymer was dried to a constant weight at room temperature under vacuum. The $[\eta]$ value of the polymer was determined in a 1N NaNO_3 aqueous solution with an Ubbelohde capillary viscometer at 30°C. The IR spectra of the copolymer were recorded with a Bruker Vector-22 grating IR spectrophotometer. The samples were pulverized with potassium bromide and converted into pellets for these measurements.

RESULTS AND DISCUSSIONS

Effect of the radiation absorbed dose

Figure 1 shows the polymer conversion as a function of the irradiation time at three different dose rates. After a certain irradiation time, the turbidity of the reaction mixtures started to increase. The overall polymerization rate increased with an increase in the irradiation dose rate and with an increase in the irradiation time. The particle diameter of the polymer latex at a 93% conversion was estimated to be around $3.4 \mu\text{m}$, showing a somewhat broad size distribution (Fig. 2).

The average volume per particle increased linearly with the particle conversion only after the conversion was beyond 30% (Fig. 3). These data indicate that the number of the particles was not constant at the early stage of the polymerization, and the nucleation period was quite long. Therefore, it was followed by growth of the nuclei with the formation of new particles, resulting in a broad size distribution. The particle size and volume increased rapidly in the early stages because of the greater ability of the small particles to adsorb the polymer and because many small particles collided and formed larger particles. The viscosity increased at first as some polymer was formed and

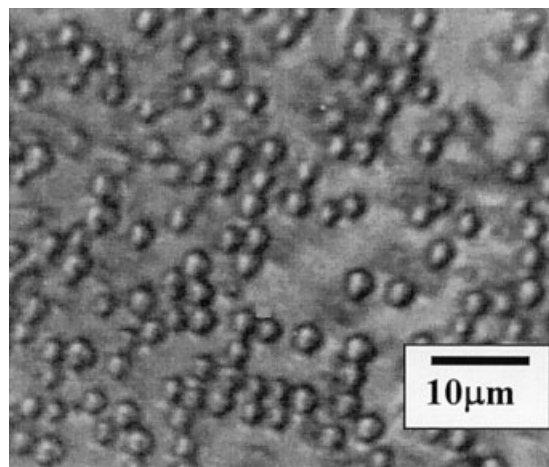


Figure 2 Photograph of polymer microspheres from a biological microscope [2-kGy irradiation dose; 30.3 Gy/min dose rate; 15 wt % monomer; 1:2 AM/DMC (w/w); 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 68 wt % H_2O ; 298 K].

then decreased as the number density of the particles in the system was reduced by these collisions.

Effect of the dose rate at a fixed radiation absorbed dose

Table II shows the effects of the dose rate on the bulk viscosity of the dispersion system and on the particle size, polymerization conversion, and polymer $[\eta]$ value at a constant radiation absorbed dose. The polymer conversion and bulk viscosity decreased as the dose rate increased.

The $[\eta]$ value of the copolymer decreased with the increase in the dose rate, whereas the particle size increased (see Table II). This was an expected behavior previously discussed in the literature.²⁷ It is thought that the dose rate affected the number of nuclei, the growth of particles, and the yield. According to the

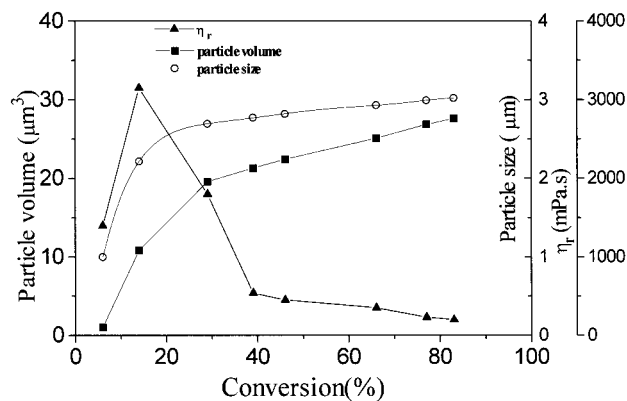


Figure 3 Relationship between the conversion and the average volume per particle, particle size, and bulk viscosity of the copolymer dispersion [30.3 Gy/min dose rate; 15 wt % monomer; 1:2 AM/DMC (w/w); 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 68 wt % H_2O ; 298 K].

TABLE II
Effect of Irradiation Dose Rate on
Dispersion Copolymerization

Dose rate (Gy/min)	Conversion (%)	Bulk viscosity (mPa.s)	d_p (μm)	Polymer [η] (dL/g)
85.0	72.3	150	4.2	3.8
70.3	75.3	160	4.0	4.0
50.9	78.9	180	3.9	4.4
30.3	83.2	200	3.0	5.1
18.3	93.3	230	2.3	6.2

Conditions: 15 wt %; monomer 1:2 AM:DMC by (w/w); 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 68 wt % H_2O ; 1.5 KGy dose; 298 K.

basic law of radical reactions, the concentration of radical reactive centers increased with the dose rate, so the average critical molecular weight of the polymer formed in the medium was reduced by termination or chain-transfer reactions. This subsequently reduced the number of chains that either aggregated or grew long enough to form nuclei. As a result, the number of particles was reduced, and the polymer particle size increased with the dose rate.

Effect of the comonomer composition and copolymer characterization

The effect of the initial monomer composition on the polymerization was studied (Table III). When the ratio of AM/DMC was reduced to 0.3, the dispersion polymerization did not occur. Instead, a translucent and viscous polymer solution formed. The reason may be that when the initial DMC content was large, the addition of a cationic monomer to a cationic end group of the growing polymer radicals was strongly influenced by electrostatic interactions. The kinetic chain length of poly(dimethylaminomethacrylate methyl chloride quaternary) was so short that the oligomer would not precipitate from the medium. When the AM/DMC ratio was about 0.4, the polymer dispersion had a low bulk viscosity. With the ratio above 0.6, the bulk viscosity of the copolymer dispersion increased quickly, as shown in Table III. This could be attributed to PAM having a much longer critical oligomeric chain length. Therefore, the viscosity of the continuous phase increased.

The polymerization conversion decreased with the increasing weight composition of AM/DMC in the feed (Table III), likely because there was a big difference between the reactivity ratios of DMC and AM ($r_1 = 1.75$ and $r_2 = 0.20$) in the solution polymerization.²⁸

The decrease in the [η] value of the copolymer with increasing DMC contents in the initial comonomer was due to the decrease in the molecular weight and the increase in the intermolecular interactions, which constricted the polymer coils.

When copolymers of DMC and AM were synthesized by variations in the feed ratios of AM to DMC, the sizes of the two characteristic peaks in the IR spectrum of the copolymer were related to its composition (Fig. 4). The peak at 1729 cm^{-1} was due to the ester group of the DMC unit, whereas the peak at 1668 cm^{-1} was due to the carbonyl group of the AM unit. The carbonyl adsorption band gradually increased with an increase in the AM/DMC ratio, whereas the ester adsorption band became weaker.

Effect of the monomer concentration

The initial monomer concentration was important because the particle number was determined by the monomer concentration very early in the reaction.²⁹ When the monomer concentration was greater than 20 wt %, the dispersion was so unstable that coagulation occurred. The effect of the monomer content on the polymerization kinetics is shown in Table IV. The bulk viscosity of the dispersion system, the particle size, the polymerization conversion, and the polymer [η] value all increased with the increase in the monomer content. The results conformed to general polymerization kinetics.

Effects of the types and concentrations of inorganic salts

In this dispersion polymerization, the viscosity was kept low for easy handling. Mixing was conducted easily, and a uniform, low-viscosity aqueous dispersion of the water-soluble cationic polymer was obtained even at a high concentration.

An inorganic salt could also be present in the aqueous medium. Many inorganic salts, such as sodium chloride, magnesium chloride, ammonium chloride, sodium sulfate, potassium sulfate, AS, sodium hydrogen sulfate, sodium carbonate, sodium hydrogen carbonate, ammonium hydrogen carbonate, and potassium hydrogen phosphate, could be used. As shown in Figure 5, the copolymer dispersions prepared in sulfate solutions had better fluidity than those of dis-

TABLE III
Effect of Comonomer Composition on
Dispersion Copolymerization

AM/DMC (w/w)	Conversion (%)	Bulk viscosity (mPa.s)	d_p (μm)	Polymer [η] (dL/g)
0.4	92.3	180	2.7	5.1
0.5	85.6	200	3.0	5.6
0.6	78.7	350	3.5	6.8
0.7	73.3	1700	6.0	7.3
0.8	63.9	3300	9.5	—

Conditions: 30.3 Gy/min dose rate; 15 wt % monomer; 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 68 wt % H_2O ; 298 K.

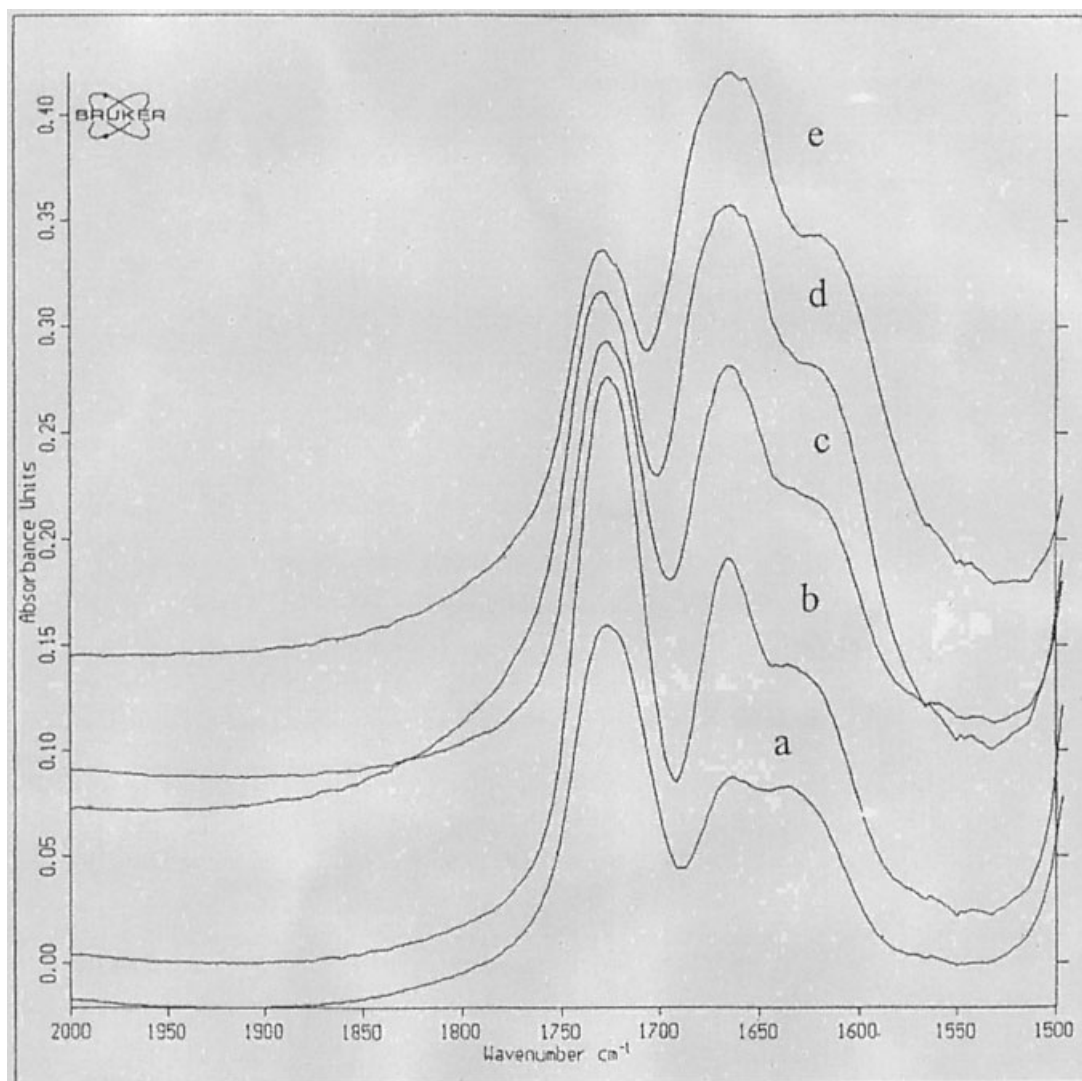


Figure 4 IR spectra of copolymers synthesized with various feed ratios of AM to DMC: (a) 0.4, (b) 0.5, (c) 0.6, (d) 0.7, and (e) 0.8.

persions prepared in carbonate or phosphate solutions. AS gave the lowest bulk viscosity in this system.

Figure 6 shows the effects of the contents of inorganic salts on dispersion copolymerization. The decrease in the $[\eta]$ value of the copolymer with in-

TABLE IV
Effect of Monomer Content on Dispersion Copolymerization

Monomer content (wt %)	Conversion (%)	Bulk viscosity (mPa s)	d_p (μm)	Polymer $[\eta]$ (dL/g)
10.0	42.3	100	1.2	7.3
12.5	65.3	160	2.0	8.9
15.0	85.6	200	3.0	11.2
17.5	89.2	1200	3.8	12.3
20.0	93.3	3300	5.3	12.8

Conditions: 30.3 Gy/min dose rate; 1:2 AM:DMC (w/w); 2 wt % dispersant; 15 wt % $(\text{NH}_4)_2\text{SO}_4$; 298 K.

creasing salt contents was due to the chain-transfer reaction to the salt. This was verified experimentally over a broad range of salt contents. The bulk viscosity of the dispersion decreased with an increase in the salt content. Because the solubility of the copolymer was reduced at higher inorganic salt contents, the critical oligomer chains were shorter. As a result, the viscosity of the continuous phase decreased.

Effect of the dispersant content on the dispersion polymerization

A water-soluble polymer (PDMA), added to the aqueous medium as a dispersant, increased the stability and fluidity of the dispersion (Table V). When the concentration of the dispersant was less than 0.1 wt %, it had little effect.

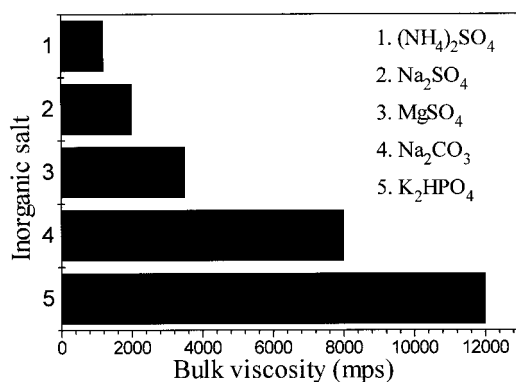


Figure 5 Effect of five types of inorganic salts on the bulk viscosity of the dispersion [30.3 Gy/min dose rate; 15 wt % monomer; 1:2 AM/DMC (w/w); 2 wt % dispersant; 12 wt % inorganic salt; 71 wt % H₂O; 298 K].

As shown in Table V, the particle size decreased as the dispersant content increased. This result may be explained by faster stabilizer adsorption at a higher dispersant content. Therefore, for a given duration, a greater number of smaller particles were stabilized during the primary stabilization process. As a result, the total interfacial area was larger, the capture ability of the primary radicals rose, and the reaction rate increased. The increase of the molecular weight with the stabilizer concentration suggests that the polymerization took place considerably inside the particle phase through the capture of oligomeric radicals from the continuous phase. These radicals subsequently underwent solid-phase polymerization and grew to higher molecular weights because of the gel effect.²⁹

Particle formation mechanism

On the basis of the aforementioned data, the following polymerization mechanism can be proposed. The system is homogeneous before the polymerization. First,

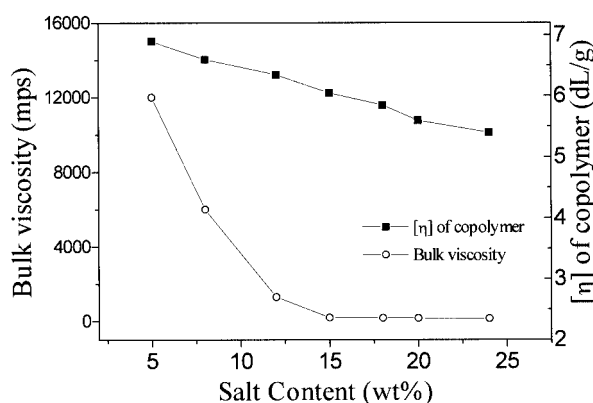


Figure 6 Effect of the content of (NH₄)₂SO₄ on the bulk viscosity of the dispersion and [η] of the copolymer Dose rate [30.3 Gy/min dose rate; 15 wt % monomer; 1:2 AM/DMC (w/w); 2 wt % dispersant; 68 wt % H₂O; 298 K].

the radiolysis of water generates e_{aq}^- , OH, and H with $G(e_{aq}^- + OH + H) = 0.6 \mu\text{mol/J}$ in pure water,³⁰ which react very rapidly with the monomer. As soon as the polymerization starts, free radicals grow in the continuous phase by the addition of monomer units until they reach their critical chain length, at which point they precipitate to form nuclei, by either a self-mechanism or an aggregation mechanism. These nuclei are unstable and quickly aggregate with one another, becoming stable (mature) particles. The mature particles capture the oligoradicals and nuclei generated in the continuous phase and, therefore, reduce the rate of particle formation. As long as enough mature particles are formed, the particle formation stage is complete. In this work, the nucleation period was quite long (the conversion was up to 30%) because of the reasonable water solubility of the polymer in the dispersion medium. The existing particles grew with the adsorption of the monomer and oligoradicals and the direct capture of unstable nuclei. At the end of the polymerization, nuclei formation stopped because of the exhaustion of either the monomer or the radicals; only mature particles were finally observed. It should be emphasized that after the particle formation stage, the number of mature particles did not change, whereas their size changed by both the polymerization inside the particles and the aggregation of small nuclei and oligoradicals from the continuous phase.

Preferred polymerization conditions

The optimal conditions for the polymerization are summarized in Table I. On the basis of the experimental data, the preferred conditions for the polymerization were as follows: radiation absorbed dose = 1000–2000 Gy, dose rate = 18.3–50.9 Gy/min, monomer content = 12.5–17.5 wt %, monomer composition (AM/DMC) = 0.4–0.6, salt content = 12.0–20.0 wt %, and dispersant content = 1.0–2.0 wt %.

TABLE V
Effect of Dispersant Content on Dispersion Copolymerization

Dispersant content (wt %)	Conversion (%)	Bulk viscosity (mPas)	d_p (μm)	Polymer [η] (dL/g)
0	54.2	3600	5.2	—
0.1	62.1	2800	4.8	—
0.3	82.1	600	4.2	5.1
1.0	84.3	260	3.6	5.4
2.0	85.6	200	3.0	5.6
3.0	88.3	160	2.7	5.7

Conditions: 30.3 Gy/min dose rate; 15 wt % monomer; 1:2 AM:DMC (w/w); 15 wt % (NH₄)₂SO₄; 68 wt % H₂O; 298 K.

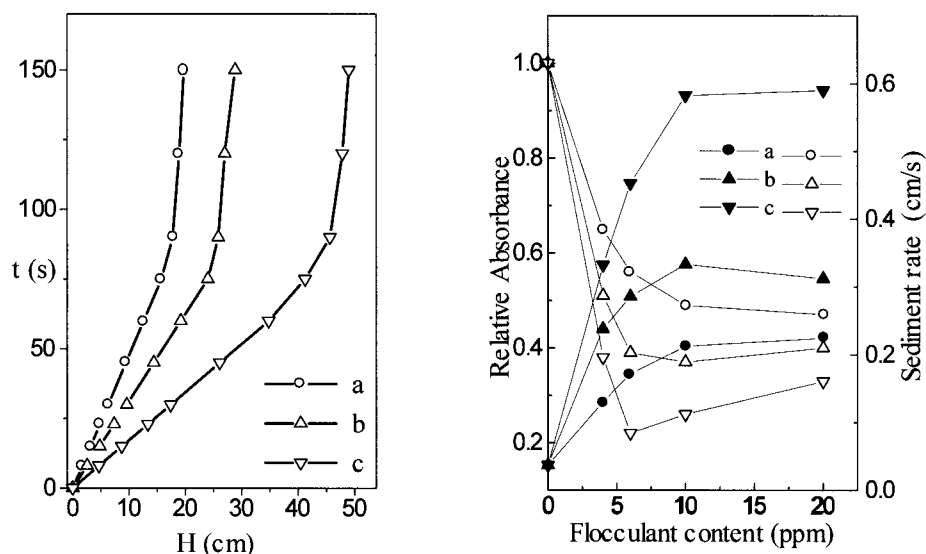


Figure 7 Flocculating characteristics of synthetic CPAM and PAM (4 wt % Kaolin; 10 ppm polymer flocculant; 100-mL sediment tube): (a) PAM ($M_w = 3.0 \times 10^6$), (b) CPAM-1 ($[\eta] = 5.84$; AM/DMC in the initial monomer composition = 0.6), and (c) CPAM-2 ($[\eta] = 5.90$; AM/DMC in the initial monomer composition = 0.4).

Studies of the flocculating characteristics of the synthetic copolymer dispersion

When the water-soluble cationic polymer dispersion prepared in this work was diluted 10 times or more, preferably around a 100 times, the polymer dispersed in the aqueous medium easily dissolved to give a uniform aqueous solution without gelation. Then, the solution could be added to wastewater, sludge, or raw materials for manufacturing papers.

The flocculating characteristics of two synthetic cationic copolymers [cationic polyacrylamide (CPAM)] were studied (see Fig. 7) with the method of Lummus.³¹ The experimental results with kaolin suspensions showed that the polymer dispersions performed well as flocculants. The sedimentation rate was about 0.4 cm/s. The relative absorbance decreased with an increase in the amount of the flocculant, but it changed little when the concentration was greater than 10 ppm. The results also show that the flocculating ability of these polymers increased with an increase in the ionic strength and molecular weight in general. It was found that CPAM had better flocculatability than PAM. This suggests that the cationic group introduced onto the polymer chain made the polymer absorb onto the kaolin particles more effectively. Therefore, the flocculatability was improved.

CONCLUSIONS

In this work, the specific features of the dispersion copolymerization of DMC and AM induced with γ -rays in a salt aqueous solution were studied. In general, the copolymer particle diameters were around 2–8 μm , and the size distribution was broad

because of the longer nucleation stage. It was discovered that the polymerization conversion increased with an increase in the dose, monomer concentration, and AM/DMC ratio. The bulk viscosity of the copolymer dispersion was enhanced with an increase in the AM/DMC ratio and the absorbed radiation dose if the polymer conversion was lower than 20%, and it was reduced with the salt content, dispersant content, and absorbed dose after 20% polymer conversion. The $[\eta]$ value of the copolymer increased with an increase in the monomer concentration and dispersant content and a decrease in the salt content, dose rate, and DMC content in the comonomer. In general, the size of the resulting copolymer particles increased with increases in the absorbed dose, dose rate, monomer concentration, and AM/DMC ratio in the comonomer and with decreasing dispersant content. The optimal conditions for the dispersion copolymerization were summarized. The copolymer dispersion worked well as a flocculant. The viscosity of the aqueous dispersion remained low, and this allowed easy handling.

References

- Kokufuta, E.; Takahashi, K. *Macromolecules* 1986, 19, 351.
- Truis, S. P.; Nicole, C.; Janice, L. B.; Patricia, D. *J Appl Polym Sci* 1994, 52, 1317.
- Ge, X. W.; Ye, Q.; Xu, X. L.; Zhang, Z. C. *Polymer* 1998, 39, 1917.
- Ge, X. W.; Sheng, M. Y.; Ye, Q.; Xu, X. L.; Zhang, Z. C. *Polym J* 1999, 31, 1243.
- Brian, A. *Prog Polym Sci* 1995, 20, 1014.
- Mabire, F.; Audebert, R.; Quivoron, C. *Polymer* 1984, 25, 1317.
- Nagai, K.; Ohishi, Y.; Inaba, H.; Kudo, S. *J Polym Sci Polym Chem Ed* 1985, 23, 1221.
- Nagai, K.; Ohishi, Y. *J Polym Sci Part A: Polym Chem* 1987, 25, 1.
- Cabestany, J.; Trouve, C.; Depernet, D. U.S. Pat. 4,396,752 (1983).

10. Cadel, J. S.; Larson, E. H. Eur. Pat. 0,176,757 (1985).
11. Davies, W. B.; Healy, J. E. U.S. Pat. 5,869,542 (1999).
12. Coville, M. W.; Dai, Q. U.S. Pat. 5,891,254 (1999).
13. Ge, X. W.; Ye, Q.; Xu, X. L.; Zhang, Z. C.; Chu, G. S. *J Appl Polym Sci* 1998, 67, 1005.
14. Ye, Q.; Ge, X. W.; Xu, X. L.; Zhang, Z. C. *J Radiat Res Radiat Process* 1998, 16, 94.
15. Ha, R. H.; Hou, S. J.; Wang, D. S.; Sun, X. M. *Acta Polym Sinica* 1995, 6, 745.
16. Huang, S. Y.; Leone-Bay, A.; Schmitt, J. M.; Waterman, P. S. U.S. Pat. 5,863,982 (1999).
17. Pearson, J. E. U.S. Pat. 5,466,338 (1995).
18. Takeda, H. U.S. Pat. 5,587,415 (1996).
19. Connors, E. J. U.S. Pat. 5,614,102 (1997).
20. Connors, E. J.; Cotter, M. L.; Chen, F. U.S. Pat. 5,696,194 (1997).
21. Wong, S. J. B. Eur. Pat. 0,821,099A1 (1998).
22. Larson, E. H.; Shultes, B.; Chiang, W. G. Eur. Pat. 0,371,822A1 (1997).
23. Mabire, F.; Audebert, R.; Quivoron, C. *J Colloid Int Sci* 1984, 97, 120.
24. Pelton, R. H.; Allen, L. H. *Colloid Polym Sci* 1983, 261, 485.
25. Zimmermann, A.; Jaeger, W.; Reichert, K. H. *Polym News* 1997, 22, 390.
26. Ge, X. W.; Ye, Q.; Xu, X. L.; Zhang, Z. C.; Sun, Q. *Radiat Phys Chem* 1997, 50, 253.
27. Ober, C. K.; Hair, M. L. *J Polym Sci Part A: Polym Chem* 1987, 25, 1395.
28. Tanaka, H. *J Polym Sci Part A: Polym Chem* 1986, 24, 29.
29. Paine, A. J. *Macromolecules* 1990, 23, 3109.
30. Buxton, G. V. In *Radiation Chemistry: Principles and Applications*; Farhataziz, R. M. A.; Rodgers, M. A. J., Eds.; VCH: New York, 1987.
31. Lummus, J. L. U.S. Pat. 3,558,545 (1971).