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Gamma radiation-induced dispersion polymerization in aqueous salts solution for manufacturing a cationic flocculant

Li-Juan Wang, Jian-Ping Wang, Shi-Jie Yuan, Shu-Juan Zhang, Yong Tang, Han-Qing Yu*

Department of Chemistry, University of Science & Technology of China, Hefei 230026, China

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ABSTRACT

A water-soluble cationic flocculant, a copolymer of acrylamide (AM) and acryloylamino-2-hydroxypropyl trimethyl ammonium chloride (AMHP), was synthesized through dispersion polymerization method in aqueous ammonium sulfate ($(NH_4)_2SO_4$) solution. The polymerization was initiated by gamma-radiation using poly(2-methylacryloylxyethyl trimethyl ammonium chloride) (PDMC) as the stabilizer. The obtained copolymer was characterized by using Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), colloidal titration and optical microscopy. Its flocculation properties were evaluated with 0.25 wt% kaolin suspensions using a standard jar test. The zeta potential of supernatant at different flocculant dosage was simultaneously measured. The results demonstrate the superiority of the copolymer over the commercial polyacrylamide as a flocculant.

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1. Introduction

Flocculation is an efficient and cost-effective method for water and wastewater treatment [1–3]. Flocculants are classified into two categories, i.e., inorganic and organic ones. Inorganic flocculants are usually salts of multivalent metals like aluminium or iron. Compared with the organic flocculants, they have several disadvantages, e.g., greater dosage, larger volume of sludge and pH sensitivity [4]. On the other hand, synthetic organic polymers have some advantages, such as inertness to pH changes, formation of large cohesive flocs and versatile tailor ability [5]. Among the organic polymer flocculants, cationic ones have better flocculation ability, as they can work efficiently through both bridging and charge neutralization [6–10].

The water-soluble cationic flocculants could be prepared through solution polymerization [11–13], emulsion polymerization [14], and microemulsion polymerization [15]. However, there are some shortcomings in these processes. In order to produce high-molecular-weight polymers with the solution polymerization method, the monomer concentration has to be kept over 10 wt%. This will result in a gelatinous and crosslinking polymer, which is difficult to dissolve in water. The emulsion polymerization could cause environmental pollution problems, because this process needs a large amount of organic solvents. Similar to the emulsion polymerization, microemulsion polymerization also has problems of smelling and safety in the working environment because a mineral oil is used as the dispersion medium. In addition, the inflammability of the product and the wasteful utilization of expensive organic solvents are the drawback of the water-in-oil emulsion polymerization process.

Dispersion polymerization is an attractive alternative to produce micro-sized polymer particles in a single-step process. Dispersion polymerization of hydrophobic polymers in organic media has been extensively studied [16–18]. However, so far information on the dispersion polymerization of cationic water-soluble polymers in aqueous media is still limited [19–21].

In the present work, a novel water-soluble cationic flocculant was synthesized from acrylamide (AM) and a cationic monomer, acryloylamino-2-hydroxypropyl trimethyl ammonium chloride (AMHP), using the dispersion polymerization method in aqueous ammonium sulfate ($(NH_4)_2SO_4$) solution. Compared with other grafting approaches, gamma ray radiation is highly efficient and cost-effective. In addition, it does not cause further contamination. The formed cationic acrylamide copolymer (CPAM) was characterized using Fourier-transform infrared (FTIR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR), inherent viscosity, colloidal titration and optical microscopy. Its flocculation ability was also tested with kaolin suspensions (0.25 wt%) using the jar test method.

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* Corresponding author. Fax: +86 551 3607592.
E-mail address: hqyu@ustc.edu.cn (H.-Q. Yu).

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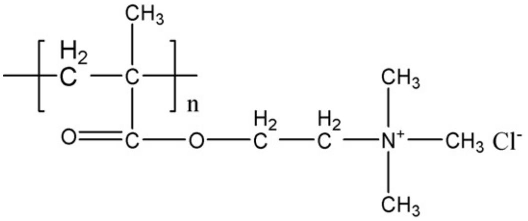

Fig. 1. Chemical structure of stabilizer PDMC.

2. Materials and methods

2.1. Materials

Epoxypropyl trimethyl ammonium chloride (ETA), AM, $(NH_4)_2SO_4$, potassium persulfate (KPS), sodium chloride (NaCl), 2-methylacryloylxyethyl trimethyl ammonium chloride (DMC), acetone, ethanol, and polyacrylamide (PAM, average molecular weight of 3.0×10^6) purchased from Shanghai Chemical Reagent Company, China, were all of analytical reagent grade and used without further purification. Potassium polyvinylsulfate (PVSK, esterification degree of 98.6%) was purchased from Wako Pure Chemical Inc. Ltd., Japan. Kaolin (6250 mesh, 2 μm) was obtained from Sanhe Kaolin Ltd., China. Doubly distilled water was used throughout the experiments except for the jar test.

2.2. Solution polymerization

The polymeric stabilizer poly(2-methylacryloylxyethyl trimethyl ammonium chloride) (PDMC) was prepared in aqueous solution using KPS (8.3×10^{-4} mol/l) as the initiator at $80 \pm 1\,^\circ C$ for 5 h. DMC concentration was kept at 1.21 mol/l throughout the experiments. Prior to polymerization, the solutions were deoxygenated through purging nitrogen for 30 min. As a stabilizer, the intrinsic viscosity of PDMC was 1.2 dl/g, which was determined in a NaCl solution of 1 mol/l with an Ubbelode capillary viscometer at $30 \pm 0.2\,^\circ C$. The chemical structure of PDMC is shown in Fig. 1.

2.3. Synthesis of the cationic monomer AMHP

AMHP was synthesized from AM and ETA in an aqueous solution. In the experiments, the molar ratio of ETA to AM was 1.0–1.6. In addition, the copolymer used in the characterization and flocculation tests was also synthesized at this ratio. All the reagents were added to a 250-ml three-necked flask equipped with a stirrer and a thermometer. The reaction was allowed to continue for 5 h at $55 \pm 1\,^\circ C$ until ETA was consumed. The reaction degree was determined by measuring the variation of the epoxy value after the reaction. Later, the solution was measured for its volume in this test. Then, it was moved into a sealed glass reagent bottle for the subsequent use.

2.4. Dispersion polymerization

The synthesis of the copolymer of AM and AMHP was performed using dispersion polymerization method in aqueous $(NH_4)_2SO_4$ solution. The monomer solution (prepared as described above, 250.0 g/l) and stabilizer (PDMC, 2.4, w/v%) were mixed and dissolved in the $(NH_4)_2SO_4$ solution (20, w/v%) in Pyrex glass vessel under stirring at ambient temperatures. Then, the solution was bubbled with nitrogen for 30 min to remove oxygen. After that, the mixed solution was irradiated in a ^{60}Co-γ-ray field at a dose rate of 15.64 Gy/min for 3 h at ambient temperatures. The reactions occurred as shown in Fig. 2.

After irradiation, the polymerization product was removed from the glass vessel and the copolymer was purified with the following procedures: the dispersion was diluted with water, and then was dialyzed using a porous cellulose acetate membrane with the cutoff molecular weight of 4200. Later, the sample solution was precipitated in acetone and was separated by filtration. The homopolymer formed in the reaction was removed through Soxhlet extraction using ethanol for 24 h. The copolymer of AM and AMHP was then dried in a vacuum oven at $60\,^\circ C$ until a constant weight was obtained.

2.5. Characterization of the copolymer CPAM

Infrared spectra of CPAM were recorded with a Fourier-transform infrared (FTIR) spectrometer (Magna-IR 750, Nicolet

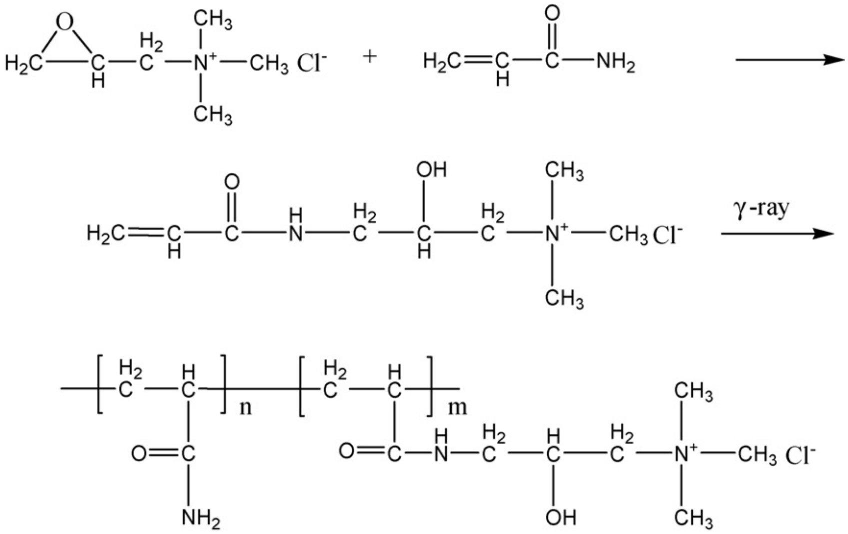

Fig. 2. Synthesis reactions of AMHP and CPAM.

Instrument Co., USA) using a potassium bromide disc technique. The nuclear magnetic resonance (NMR) spectrum of the dried copolymer sample was obtained in deuterium oxide (D_2O) with a Bruker (300 MHz ^1H) NMR spectrometer. The inherent viscosity $[\eta]$ of the copolymer was measured in a 1 mol/l NaCl aqueous solution with an Ubbelohcle capillary viscometer at $30 \pm 0.2\,^\circ C$. Its charge density was measured by colloidal titration, while the particle sizes were estimated using an image analysis system (Image-pro Express 4.0, Media Cybernetics Inc., USA) with a digital optical microscopy (BX41, OLYMPUS Co., Japan).

2.6. *Jar test*

Flocculation capacity of the copolymer CPAM and PAM was evaluated using 0.25 wt% of kaolin suspensions. The flocculants in solution form were added into each of 500-ml kaolin suspensions. The suspensions were immediately stirred at a constant speed of 200 rpm for 2 min, followed by a slow stirring at 40 rpm for 10 min. Thereafter, the suspensions were allowed to be settled for 5 min. At the end of settling, the solution transmittance was measured with a spectrophotometer (UV-9100, Ruili Co., China) at a wavelength of 630 nm. The zeta potential of the supernate was measured using the Nano Zeta Sizer (ZEN3600, Malvern, Inc., UK) at 25 °C.

3. Results and discussion

3.1. *Characterization of the cationic copolymer*

3.1.1. *FTIR spectrum*

The infrared spectrum of the copolymer is illustrated in Fig. 3. The peaks at wavenumbers of 3435, 1345 and 1115 cm^{-1} are attributed to the hydroxyl groups in AMHP. The strong peak at wavenumber of 1654 cm^{-1} is associated with the vibrating absorption of carbonyl groups in AM. The strong peak around 3400 cm^{-1} could be assigned to the extension vibration of N–H, and the band at 1597 cm^{-1} was the characteristic peak of primary amine N–H vibration. The peaks at wavenumbers of 1454 and 954 cm^{-1} are assigned to the methyl groups of ammonium and quaternary ammonium in PDMC [22], respectively. The peak at 2923 cm^{-1} comes from the C–H stretching vibration of the backbone of the copolymer. The appearance of all these peaks demonstrates that AMHP had been successfully copolymerized with AM.

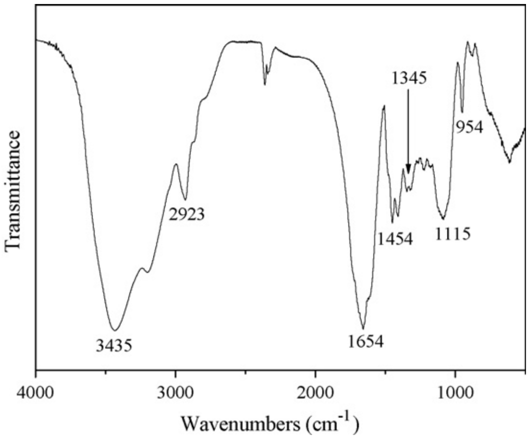

Fig. 3. FTIR spectrum of the copolymer.

3.1.2. ^1H *NMR spectrum*

The ^1H NMR spectrum of the copolymer solution in D_2O is shown in Fig. 4. The ^1H NMR spectrum shows a sharp singlet at 3.31 ppm (g), assigned to the three equivalent methyl groups of

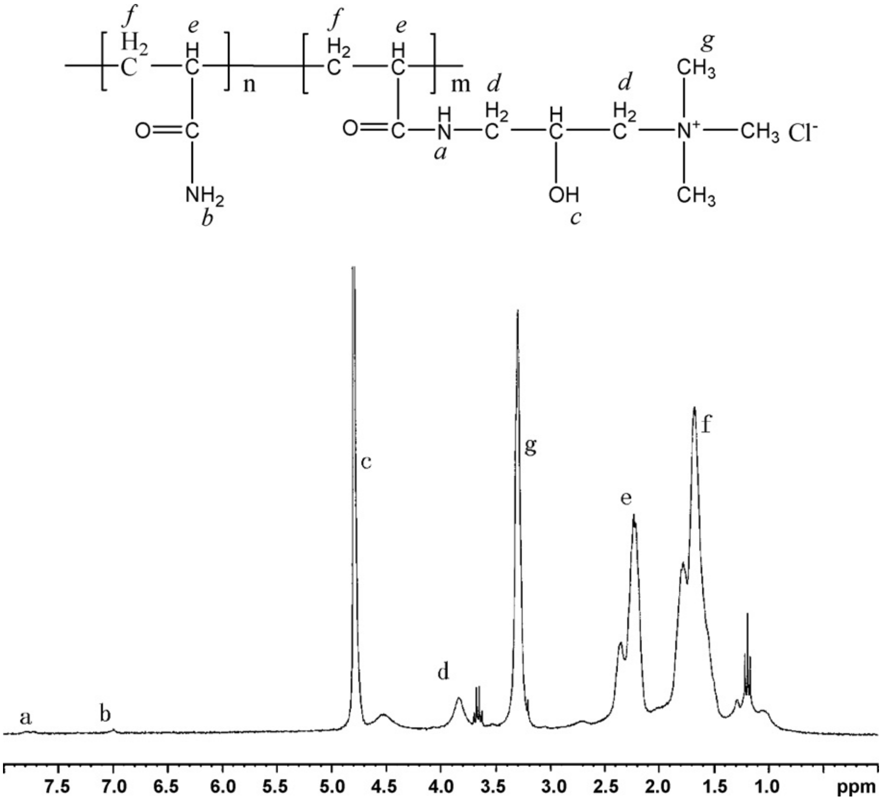

Fig. 4. ^1H NMR spectrum of the copolymer.

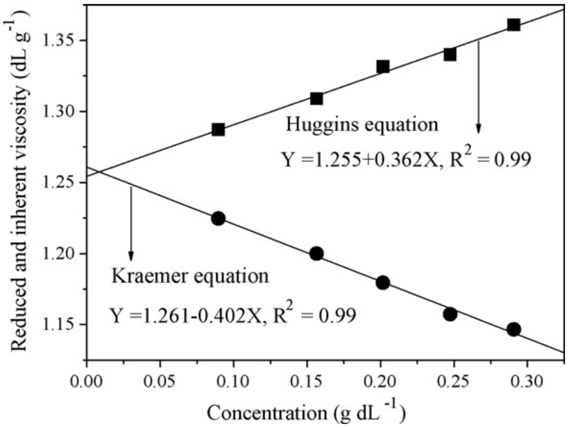

Fig. 5. Intrinsic viscosity of the copolymer calculated using the reduced viscosity and inherent viscosity equations.

ammonium. ^{1}H signals from the backbone methine and methylene protons appear in the ranges of 2.36–2.25 (e) and 1.98–1.69 ppm (f), respectively. Fig. 4 also shows that the–NH–and–NH_2 groups give rise to weak signals at 7.79 (a) and 7.00 ppm (b), respectively. The analytical results of the ^{1}H NMR spectrum provide further support for the formation of the copolymer of AM and AMHP.

3.1.3. Inherent viscosity measurement and colloidal titration

The measured inherent viscosity of the copolymer is shown in Fig. 5. With the Huggins and Kraemer equations [23], the inherent viscosity was calculated to be 1.258 dl/g, suggesting that the copolymer solution had viscous effects even at a low concentration. This suggests that the monomer AM and AMHP were successfully copolymerized. The charge density of the copolymer was 1.12 mmol/g, indicating that the mole ratio of AM to the cationic group AMHP ranged from 9.4 to 1.0 in the copolymer.

3.2. Particle size and distribution

Spherical, oval or nonspherical particles were formed in the dispersion polymerization, and most of large-sized particles were nonspherical (Fig. 6). The formation of nonspherical particles suggests that coalescence of small particles had taken place in the polymerization process. The particle diameter of the copolymer was estimated to be 2.64 ± 0.35 μm with a broad size distribution (Fig. 7).

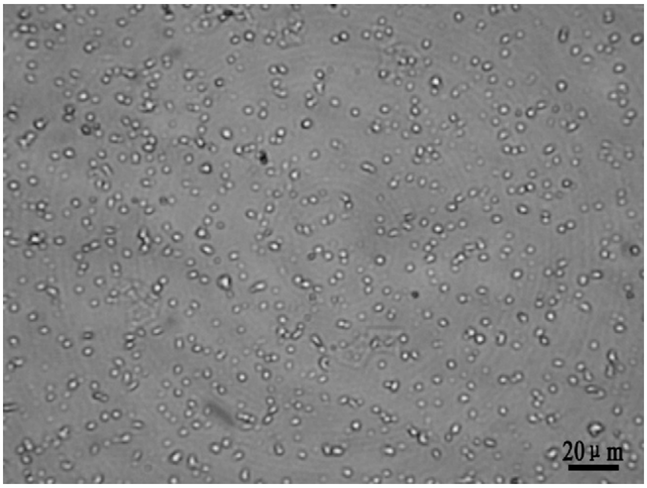

Fig. 6. Imaging of the copolymer particles.

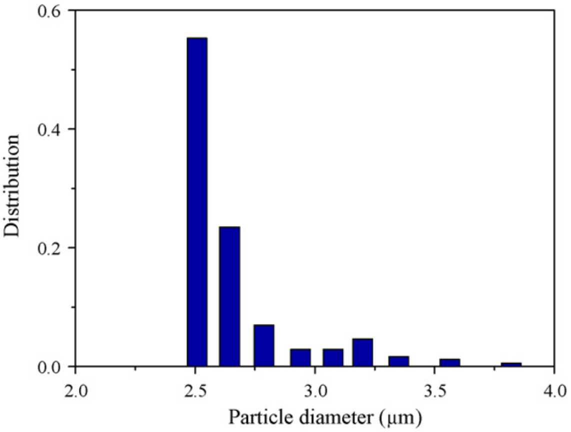

Fig. 7. Particle size distribution of the copolymer particles.

3.3. Flocculation tests

The flocculation results of the cationic copolymer and PAM at pH of 4.0, 7.0 and 10.0 are illustrated in Fig. 8(A–C). Compared with PAM, the cationic copolymer showed better flocculation ability under all conditions, especially under both neutral and alkaline conditions. At pH 4.0 (Fig. 8A), the turbidity of the kaolin suspension was 15 NTU after being flocculated by the copolymer at a dosage of 0.2 mg/l, but 30 NTU by PAM with initial turbidity of 204 NTU. Under neutral conditions (pH 7.0, Fig. 8B), at the optimal dosage of 4 mg/l, the turbidity of the kaolin suspension was 23 NTU after being flocculated by the copolymer, but 128 NTU by PAM. On the other hand, at pH 10.0 (Fig. 8C), the turbidity of the kaolin suspen-

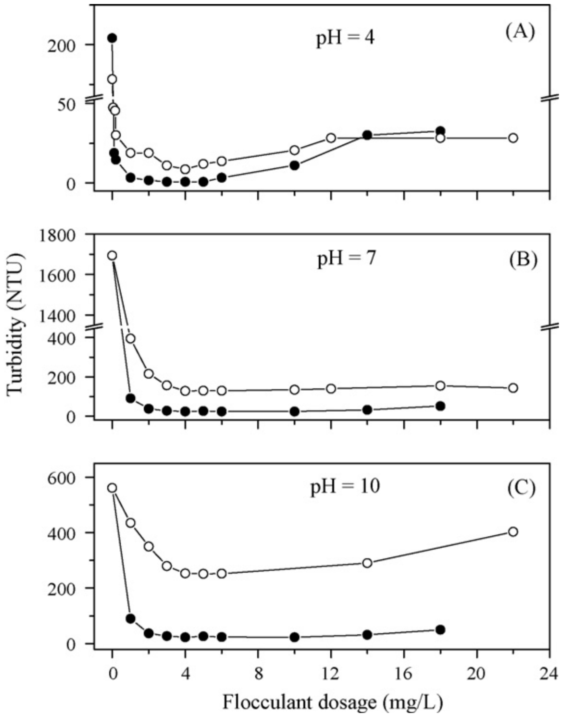

Fig. 8. Flocculation performance of PAM and the copolymer in kaolin suspension of 0.25% (w/v) at pH 4.0, 7.0 and 10.0. The solid spots are for the copolymer and the open ones for PAM.

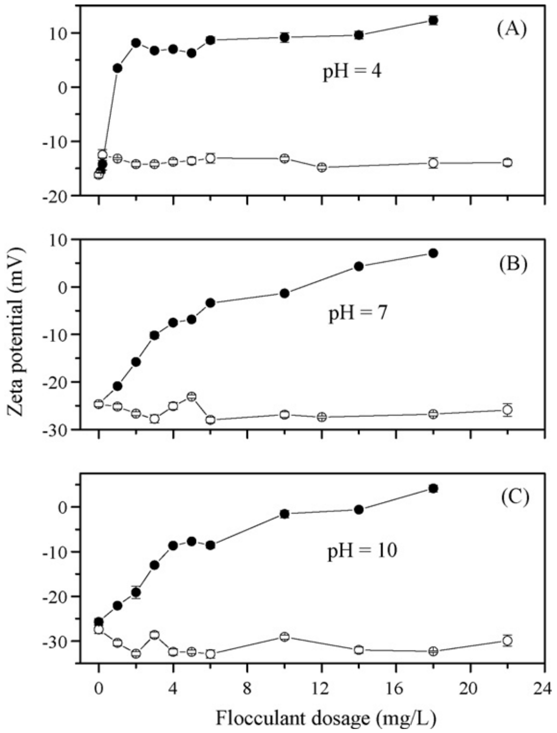

Fig. 9. Zeta potentials of the supernatant of PAM and the copolymer in kaolin suspension of 0.25% (w/v) at pH 4.0, 7.0 and 10.0. The solid spots are for the copolymer and the open ones for PAM.

sion was about 25 NTU after the flocculation with the copolymer at a dosage range of 3.0–6.0 mg/l, while PAM showed poor flocculation effect on the suspension with a turbidity of 250 NTU. In addition, the copolymer had a greater flocculation capacity than PAM under alkaline conditions. The turbidity of the kaolin suspension significantly increased with the flocculation by PAM beyond a dosage of 6 mg/l, but it was not true for the case of the copolymer. This is one of the advantages of the copolymer synthesized in this work. The flexible copolymer chain increased the flocculant flexibility, which was in favor of the binding intensity between flocculants and colloids. Therefore, the re-dispersion resulting from the competition of bridging could be avoided to some extent.

Fig. 9(A–C) shows the zeta potentials of the supernatant in the kaolin suspension flocculated with the copolymer and PAM at pH 4.0, 7.0 and 10.0. The zeta potential of the supernatant flocculated by the copolymer increased rapidly with an increase in flocculant dosage at a low level, but no significant change in zeta potential was observed for the supernatant flocculated by PAM. As CPAM was used as a flocculant, the charge neutralization of the cationic group certainly plays a vital role, while the flocculation ability of PAM was realized through bridging effect only. In addition, the zeta potential did not reach the zero even at the optimal dose of the copolymer (Fig. 9). This demonstrates that both bridging and charging neutrality played important roles in the flocculation process when the copolymer was used as flocculant.

4. Conclusions

A novel flocculant, copolymer of AMHP and AM, was obtained through dispersion polymerization. The FTIR and ^{1}H NMR spectra of the copolymer showed the existence of copolymerization between AM and AMHP. The copolymer solution had viscous effects at low concentrations, indicating that AM and AMHP were successfully copolymerized. The mole ratio of AM to the cationic group AMHP was 9.4–1 in the copolymer, and the dispersion particle size was estimated as $2.64 \pm 0.35\ \mu$m. The flocculation experimental results demonstrated the superiority of the copolymer product over PAM as a flocculant under both neutral and alkaline conditions. The zeta potential profiles of the supernatant flocculated by the copolymer indicate that both bridging and charge neutralization played important roles in the flocculation process of the copolymer.

References

[1] M.I. Aguilar, J. Saez, M. Llorens, A. Soler, J.F. Ortuno, Microscopic observation of particle reduction in slaughterhouse wastewater by coagulation–flocculation using ferric sulphate as coagulant and different coagulant aids, Water Res. 37 (2003) 2233–2241.
[2] A.L. Ahamad, S. Ismail, S. Bhatia, Optimization of coagulation–flocculation process for palm oil mill effluent using response surface methodology, Environ. Sci. Technol. 39 (2005) 2828–2834.
[3] H. Tanaka, H. Ichiura, A novel and simple method for determining the cationic demand of suspensions using chromophoric labeled cationic polymers, Colloids Surf. A 159 (1999) 103–107.
[4] S.K. Rath, R.P. Singh, Flocculation characteristics of grafted and ungrafted starch, amylose, and amylopectin, J. Appl. Polym. Sci. 66 (1997) 1721–1729.
[5] R.P. Singh, B.R. Nayak, D.R. Biswal, T. Tripathy, K. Banik, Biobased polymeric flocculants for industrial effluent treatment, Mater. Res. Innovat. 7 (2003) 331–340.
[6] B. Pushparaj, E. Pelosi, G. Torzillo, R. Materassi, Microbial biomass recovery using a synthetic cationic polymer, Bioresour. Technol. 43 (1993) 59–62.
[7] J.P. Wang, Y.Z. Chen, X.W. Ge, H.Q. Yu, Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology, Colloids Surf. A 302 (2007) 204–210.
[8] R.J. Zemaitaitiene, E. Zliobaite, R. Klimaviciute, A. Zemaitaitis, The role of anionic substances in removal of textile dyes from solutions using cationic flocculant, Colloids Surf. A 214 (2003) 37–47.
[9] L. Huang, H.N. Xiao, Y.H. Ni, Cationic-modified microporous zeolites/anionic polymer system for simultaneous removal of dissolved and colloidal substances from wastewater, Sep. Purif. Technol. 49 (2006) 264–270.
[10] V. Goloba, A. Vinderb, M. Simonic, Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents, Dyes Pigments 67 (2005) 93–97.
[11] H. Tanaka, Copolymerization of cationic monomers with acrylamide in an aqueous solution, J. Polym. Sci. Polym. Chem. 24 (1986) 29–36.
[12] T. Okada, I. Ishigaki, T. Suwa, S. Machi, Synthesis of cationic flocculant by radiation-induced copolymerization of methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate with acrylamide in aqueous solution, J. Appl. Polym. Sci. 24 (1979) 1713–1721.
[13] F. Mabire, R. Audebert, C. Quivoron, Synthesis and solution properties of water soluble copolymers based on acrylamide and quaternary ammonium acrylic comonomer, Polymer 25 (1984) 1317–1322.
[14] H. Ono, Y.L. Deng, Flocculation and retention of precipitated calcium carbonate by cationic polymeric microparticle flocculants, J. Colloid Interf. Sci. 188 (1997) 183–192.
[15] Coville, W. Michael, Dai, Qi, U.S. Pat 5,891,254 (1999).
[16] K. Nakamura, K. Fujimoto, H. Kawaguchi, Dispersion polymerization of methyl methacrylate using macro-azo-initiator, Colloids Surf. A 153 (1999) 195–201.
[17] K. Ishizu, S. Shiratori, Microsphere synthesis by dispersion copolymerizations using poly(*t*-butyl methacrylate) macromonomers in nonaqueous media, J. Colloid Interf. Sci. 236 (2001) 266–269.
[18] D.G. Yu, J.H. An, S.D. Ahn, S.R. Kang, K.S. Suh, Titanium dioxide/P(St-*co*-DVB)-MAA hybrid composite particles prepared by dispersion polymerization, Colloids Surf. A 266 (2005) 62–67.
[19] Q. Ye, Z.C. Zhang, X.W. Ge, Highly efficient flocculant synthesized through the dispersion copolymerization of water-soluble monomers induced by γ-ray irradiation: synthesis and polymerization kinetics, J. Appl. Polym. Sci. 89 (2003) 2108–2115.
[20] B.K. Song, M.S. Cho, K.J. Yoon, D.C. Lee, Dispersion polymerization of acrylamide with quaternary ammonium cationic comonomer in aqueous solution, J. Appl. Polym. Sci. 87 (2003) 1101–1108.
[21] D.N. Chen, X.G. Liu, Y.M. Yue, W.D. Zhang, P.X. Wang, Dispersion copolymerization of acrylamide with quaternary ammonium cationic monomer in aqueous salts solution, Eur. Polym. J. 42 (2006) 1284–1297.
[22] J.P. Wang, Y.Z. Chen, X.W. Ge, H.Q. Yu, Gamma radiation-induced grafting of a cationic monomer onto chitosan as a flocculant, Chemosphere 66 (2007) 1752–1757.
[23] Q. Wang, P.R. Ellis, S.B. Ross-Murphy, J.S. Grant Reid, A new polysaccharide from a traditional Nigerian plant food: Detarium senegalense Gmelin, Carbohyd. Res. 284 (1996) 229–239.