

Synthesis, Characterization, and Flocculation Properties of Poly(acrylamide-methacryloxyethyltrimethyl Ammonium Chloride-Methacryloxypropyltrimethoxy Silane)

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ABSTRACT: A novel hydrophobically modified and cationic flocculant poly(acrylamide-methacryloxyethyltrimethyl ammonium chloride-methacryloxypropyltrimethoxy silane) (P(AM-DMC-MAPMS)) was synthesized by inverse emulsion polymerization. The molecular structure of hydrophobically cationic polyacrylamide (HCPAM) was characterized by FTIR and ¹H-NMR. The effects of DMC and MAPMS feed ratio on intrinsic viscosity and solubility were measured. The effects of hydrophobically cationic flocculants on reactive brilliant red X-3B solution and kaolin

suspension were studied. It was found that the introduction of MAPMS could increase the intrinsic viscosities of P(AM-DMC-MAPMS) and enhance the flocculation properties to anionic dye solution and kaolin suspension, but reduced their water-solubility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1594–1599, 2009

Key words: cationic polymerization; emulsion polymerization; copolymerization; water-soluble polymers; flocculation

INTRODUCTION

Cationic polyacrylamides (CPAM) have been widely used as retention aids in paper-making, as flocculants for waste-water and suspension, as surfactants for tertiary oil recovery,^{1–4} etc. In the past decade, many researchers have taken up interest in hydrophobically modified and cationic polyacrylamide.^{5–8} These hydrophobically cationic polymers exhibited excellent flocculating properties and unique rheological characteristic in aqueous solution.^{9,10} Above a certain polymer concentration, apparent viscosity has a sharp increase in aqueous solution attributing to the association of a few hydrophobic units incorporate into a hydrophilic backbone and build a transitory three-dimensional network. The preparation of hydrophobic polyelectrolyte can be carried out by chemical modification and free radical copolymerization. The former method has been applied to a precursor polymer or natural polymer,⁴ for example, cellulose. The latter method of copolymerization technique mainly applied in copolymer base of acrylamide and cationic monomers and their derivatives.^{11–13} However, one unavoidable drawback in the copolymerization comes from the insolubility of the hydrophobic monomer in water. At present, various types of processes were used to overcome this problem by carrying out the

polymerization reaction in a mixture of solvents, in which both monomers are soluble,^{14–16} or by running a micellar polymerization,^{17–19} in which the presence of surfactant enhances dissolving capacity of hydrophobic monomer in water. However, few literatures reported that the inverse emulsion polymerization was used to synthesize hydrophobically CPAM, in which the soluble monomers can dissolve in water and hydrophobic monomer can dissolve in oil, and the surfactants ensure the emulsion stability and that the hydrophobic monomer diffuse to copolymerize with water-soluble monomer. The inverse emulsion polymerization technique has the advantages of highly reactive speed ratio, high molecular weight, high solid content, and easiness in posttreatment, and so forth.^{20,21} The inverse emulsion polymerization technique was used in this article.

In this work, the synthesis, characterization, and flocculation properties of poly(acrylamide-methacryloxyethyltrimethyl ammonium chloride-methacryloxypropyltrimethoxy silane) (P(AM-DMC-MAPMS)) by inverse emulsion polymerization technique were investigated, and the effects of the introduction of MAPMS on intrinsic viscosities, solubility, and flocculating performance were discussed.

EXPERIMENTAL

Materials

Acrylamide, obtained from Damao Co. (Tianjin, China), was recrystallized from acetone. 2,2'-Azobis[2-(2-

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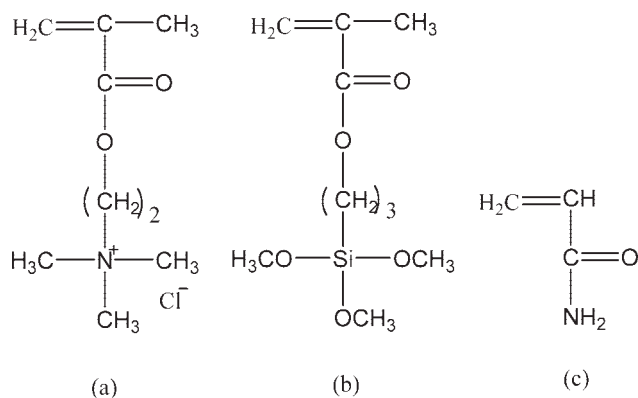


Figure 1 Structures of the comonomers: (a) DMC; (b) MAPMS; (c) AM.

imidazolin-2-yl)propane] dihydrochloride (VA-044), provided by Guangchuangjing Import and Export Corp. (Shanghai, China), was used as an initiator; methacryloxyethyltrimethyl ammonium chloride (DMC), 78 wt % aqueous solution, was purchased from Wanduofu Chemical Co. (Shandong, China); methacryloxypropyltrimethoxy silane (MAPMS), CP-grade, was obtained from Qufu Chengguang Chemical Co. (Shandong, China). Sorbitan Monooleate (Span 80) and Tween80 were used as nonionic surfactants. Reactive brilliant red X-3B and kaolin were obtained from Jinxi Xiliucheng Dyestuff Chemical Factory (Tianjin, China) and Chemical Reagent Company of China Medicines Corp. (Shanghai, China), respectively, CP-grade, flocculated. Other reagents were ACS-grade, purchased from Liaodong Chemical Reagent Co. (Dalian, China), which were used as received. The structures of these comonomers as well as AM are illustrated in Figure 1.

Synthesis of P(AM-DMC-MAPMS)

The inverse emulsion polymerizations were carried out in a 250-mL four-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a nitrogen outlet, and a condenser. The inverse emulsions were prepared by pouring the aqueous phase (AM, DMC, and H₂O) in the flask followed by the oil phase (Span80, Tween80, and kerosene). After stirring for 10 min, hydrophobic monomer was added into the inverse emulsion. The solution was continuously sparged with nitrogen to remove any residual oxygen at room temperature for 30 min. Adding initiator (VA-044), the copolymerization was processed in warm-up oil bath at 40°C for 2 h, and then at 60°C for 2 h. The resulting emulsion was cooled at room temperature and then precipitated in mixed solution of acetone and ethanol.

FTIR (cm⁻¹) absorption peaks: 3354 (—NH₂), 2972 (—CH₃), 1728 (—COO— for DMC and MAPMS), 1665 (C=O for AM), 1474, 1455 (—CH₃ and —CH₂—

deformation vibration, respectively), 1090 and 1049 (Si—O—CH₃), 954 (N⁺).

¹H-NMR (δ, ppm) peaks: 3.93 (—COOCH₂—), 3.59 (Si—OCH₃), 3.39 (Si—CH₂), 3.11–3.08 (N⁺—CH₃), 2.26 (N⁺—CH₂—), 2.10–1.94 (—CH₂—C—C=O), 1.65 (—O—CH—), 1.05 (—CH₂—), 0.74 (—CH₃).

Conversion determination

The copolymer yield was calculated according to the following equation:

$$\text{Yield (\%)} = \frac{\text{weight of recovered copolymer}}{\text{weight of total monomers}} \times 100. \quad (1)$$

Copolymer characterization

The intrinsic viscosity of copolymers were measured in 0.01N NaCl with an Ubbelohde viscometer at (30 ± 1)°C. The samples of copolymers were coagulated with mixing solvent of acetone and ethanol. The precipitated copolymer, washed with mixing solvent few times, was dissolved in deionized water and reprecipitated. The sample was then dried under vacuum 24 h at 75°C. All determinations were carried out on 0.005 g/dL. [η] was obtained by one-point method with the following equation:

$$[\eta] = \frac{1}{c} \sqrt{2(\eta_{sp} - \ln \eta_r)}, \quad (2)$$

where η_{sp} and η_r are specific viscosity and relative viscosity, respectively.

Characterization

The Fourier transform infrared (FTIR) spectrums (in KBr pellets) were measured on a Nicolet 20DXB FTIR spectrophotometer. Samples were pressed into KBr pellets. ¹H-NMR spectrum was measured on a Bruker Unity 400 NMR spectrometer at room temperature, with D₂O as solvent and tetramethylsilane (TMS) as internal reference. The transmittance and absorbance were obtained on a HP8453 ultraviolet (UV) spectrophotometer.

Flocculation procedure

The flocculation properties of the copolymers were carried out by jar tests with solution of reactive brilliant red X-3B and suspension of kaolin. The concentration of reactive brilliant red solution was 1.0 g/dL. The suspensions were prepared by the addition of 1.0 g kaolin to 1 L deionized water.

The jar tests were run by addition a known quantity of polymer to 1 L the test sample, which were

stirred at 200 rpm for 10 min and at 60–70 rpm for 5 min. Before measuring, decolorized dye solution was filtrated and kaolin suspension settled for a few minutes.

The decolorization ratio of filtrate was expressed by removal ratio (R):

$$R = \frac{C_0 - C}{C_0} \times 100\%, \quad (3)$$

where C_0 is the initial concentration of dye solution and C is the dye concentration after being decolorized.

The dye concentration was gained by the standard curve of absorbance to concentration, which was measured at 541 nm, the wavelength of the maximum absorbance of the dye solution. Supernatant samples of kaolin suspension were withdrawn to measure transmittance at 550 nm.

RESULTS AND DISCUSSION

Synthesis and characterization

A significant effort was made in this study to synthesize a series of hydrophobically cationic polyacrylamide. In the inverse emulsion polymerization, changing the MAPMS feed ratio from 0 to 1.0% and cationic monomer feed ratio from 10 to 30%, keeping aqueous phase concentration at 45% (w/w), oil phase and water phase volume ratio at 0.5, initiator concentration at 0.08% (w/w). We investigated the effects of MAPMS and cationic monomer feed ratio on the intrinsic viscosity of polymers, and the results are shown in Table I.

Feed ratio of DMC and MAPMS had no obvious effect on the terpolymer yield. In 0.01N NaCl solution, $[\eta]$ for terpolymers increase all through with increasing MAPMS and DMC feed ratio as expected. However, it is found that the greater the MAPMS feed ratio was, the worse the solubility of terpolymers was, which can be explained as follows: Si-

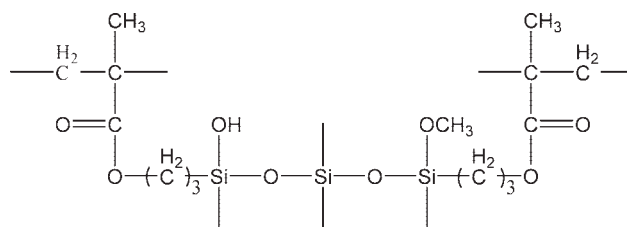


Figure 2 Crosslinked structure of hydrolyzed terpolymer.

OCH₃ from MAPMS units hydrolyzes to form Si-OH and then crosslink gently at higher reactive temperature. Gentle crosslink enhanced the length of the molecular chain, but also decreased water solubility. The crosslinked structure of P(AM-DMC-MAPMS) is shown in Figure 2.

The terpolymers were deposited in mixing solvent of acetone and ethanol, and dried in vacuum oven at 75°C. Samples were characterized by FTIR spectrum and ¹H-NMR spectrum. The FTIR spectrum (Fig. 3) of terpolymers showed strong stretching vibration peaks at 3354 and 1665 cm⁻¹ for amino group and carbonyl group of amide, respectively. The stretching vibration peaks of -CH₃ for DMC and MAPMS appeared at 2972 cm⁻¹. The peak at 1728 cm⁻¹ represented carbonyl group of ester for DMC and MAPMS. The absorption peaks between 1474 and 1455 cm⁻¹ represented deformation vibration for -CH₃ and -CH₂-, respectively. The peak at 954 cm⁻¹ indicated the presence of N⁺ group. Compared with Figure 2(a), the peaks in Figure 2(b) at 1090 and 1049 cm⁻¹ were ascribed to Si-O-C group stretching vibration, and the peak at 880 cm⁻¹ was assigned to Si-OH, which was hydrolysis product of Si-OCH₃. The peak for Si-CH₂- did not appear

TABLE I
Terpolymerization of AM, DMC, and MAPMS

Sample	AM feed ratio (mol %)	DMC feed ratio (mol %)	MAPMS feed ratio (mol %)	Yield (%)	$[\eta]$ in 0.01N NaCl (dL/g)
1	90	10	0	98.7	8.13
2	89.55	9.95	0.5	99.1	8.37
3	89.1	9.9	1.0	99.3	9.45
4	80	20	0	87.1	10.51
5	79.6	19.9	0.5	92.5	11.11
6	79.2	19.8	1.0	88.9	11.35
7	70	30	0	96.2	13.28
8	69.65	29.85	0.5	98.1	15.27
9	69.3	29.7	1.0	94.8	17.09

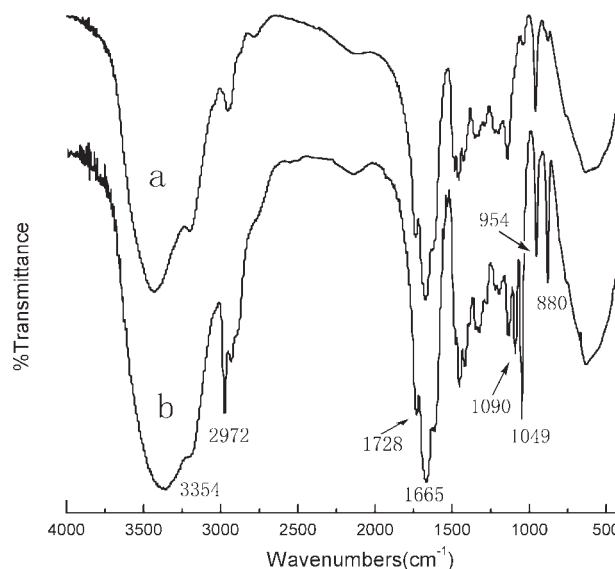


Figure 3 FTIR spectrums of copolymers: (a) P(AM-DMC); (b) P(AM-DMC-MAPMS).

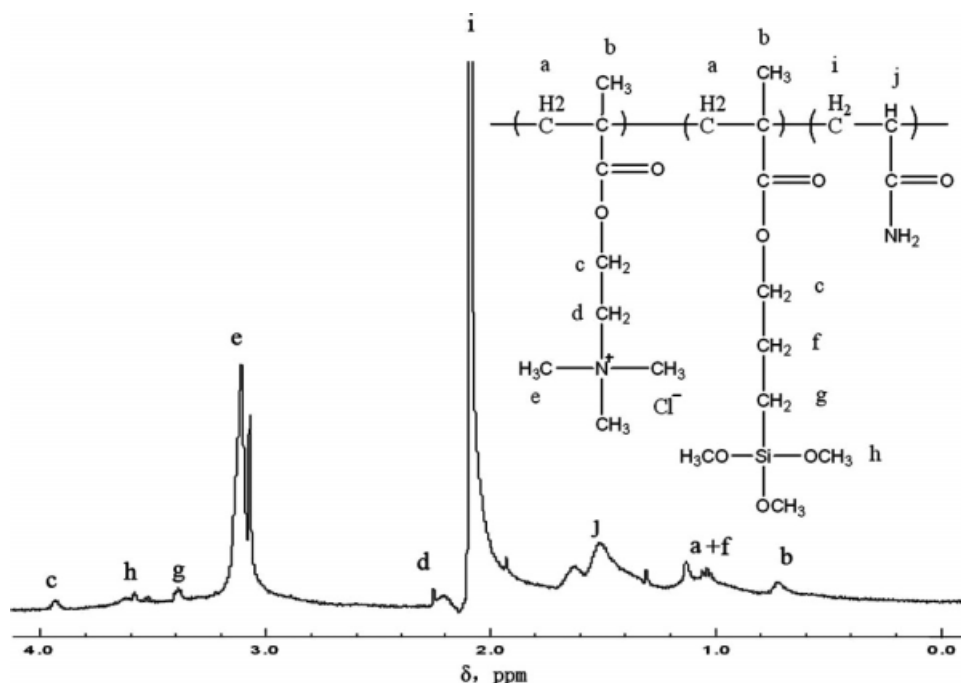


Figure 4 $^1\text{H-NMR}$ spectrum of P(AM-DMC-MAPMS).

because of the content of hydrophobic monomer less than 1% (mol).

The $^1\text{H-NMR}$ spectrum of polymer was shown in Figure 4. The signal at 3.93 ppm was originated from methylene of ester (c). The multiple signals around at 3.59–3.52 ppm were attributed to Si-O-CH_3 (h). The next multiple signals around at 3.40–3.38 ppm were regarded as the Si-CH_2- (g). The strong signals around at 3.10 ppm were ascribed to N^+-CH_3 (e). The signal at 2.26 ppm represented N^+-CH_2- (d). The sharp signal at 2.10 ppm was attributed to $-\text{CH}_2-$ (i) of acrylamide chain. The peaks around at 1.65 and 1.05 ppm were attributed to $-\text{CH}-$ and $-\text{CH}_2-$ (j, a + f), respectively. The peak at 0.75 ppm were regarded as $-\text{CH}_3$ (b) of DMC and MAPMS. Accordingly, the results confirmed the terpolymer was synthesized.

Flocculation properties

The effects of hydrophobic monomer feed ratio on decolorization ratio of reactive brilliant red X-3B

Decolorization by HCPAM is shown in Figure 5. HCPAM was more effective than P(AM-DMC) on decolorization of reactive brilliant red X-3B. The decolorized efficiency increased with hydrophobic monomer feed ratio. When the dose of HCPAM with $[\eta] = 11.35 \text{ dL/g}$ and MAPMS = 1.0% is 180–200 mg/L, the dye can be removed absolutely. The mechanism of the decolorization of P(AM-DMC-MAPMS) can be described as follows. The hydrophobically cationic flocculants not only make the anionic dye separate

from the water by charge neutralization and adsorption-bridge, but also the hydrophobic groups enhance the interaction between organic dye molecules and flocculants. Other possible reason can be explained from the molecular structures of the active brilliant red X-3B and P(AM-DMC-MAPMS): the ester interchange reaction of Si-O-CH_3 of flocculants with OH of active brilliant red may takes place in the process of flocculating, which strengthens dye to removal from the water.

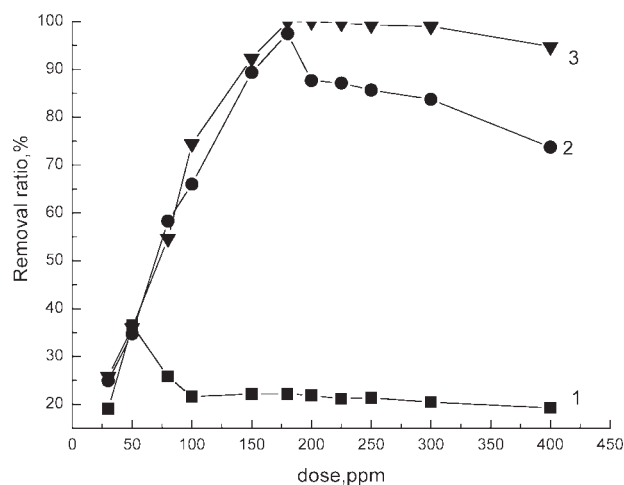


Figure 5 Decolorization by HCPAM with different cationicity: (1) $[\eta] = 9.45 \text{ dL/g}$, cationicity = 30%; (2) $[\eta] = 11.35 \text{ dL/g}$, cationicity = 20%; (3) $[\eta] = 17.09 \text{ dL/g}$, cationicity = 10%.

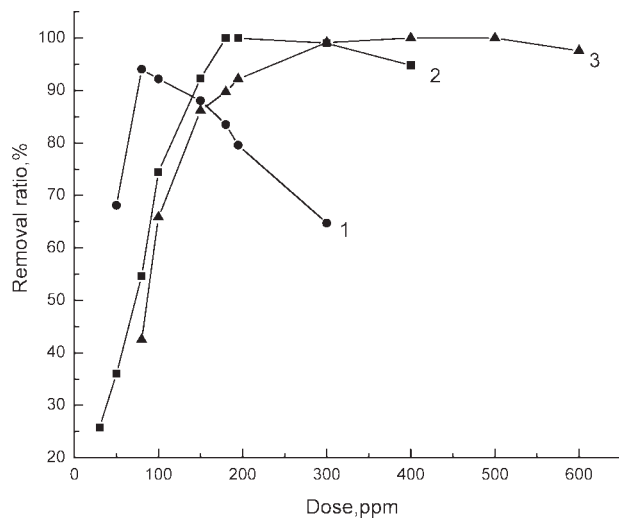


Figure 6 Decolorization by HCPAM with various MAPMS feed ratio: (1) P(AM-DMC), $[\eta] = 10.51$ dL/g; (2) HCPAM, $[\eta] = 11.11$ dL/g, MAPMS = 0.5%; (3) HCPAM, $[\eta] = 11.35$ dL/g, MAPMS = 1.0%.

The effects of cationicity on decolorization ratio of reactive brilliant red X-3B

From the curves of Figure 6, the flocculants with high cationic density, low molecular weight, and that with low cationic density, high molecular weight have both not good flocculating performance. The former could not remove dye molecules from water completely because of the weak function of adsorption-bridge, which made the granules difficult to go down. The latter did not exhibit excellent performance when the dose was less than 300 ppm, which could be explained that low charge density could not neutralize the anionic charge and adsorb the dye molecules to go down. The signal 2 of Figure 6 showed superexcellent performance, and the removal ratio of dye molecules can top to 100% when the dose less than 180 ppm. All mentioned earlier indicated that the optimal discolored performance can be met only by using the flocculants with suitable charge density and molecular weight.

The effect of flocculation time on transmittance of kaolin suspension

The Figure 7 showed the relationship of transmittance change with flocculating time. The flocculation performance increased with hydrophobic monomer. When without adding any flocculants, the transmittance of kaolin suspension only reached to 72% in 35 min. However, the addition of flocculants greatly improved the flocculation performance. Moreover, the flocculants of HCPAM had higher speed of sedimentation than that of CPAM. The reason could be attributed to the incorporation of MAPMS group, which made HCPAM bulky and fluffy, improved

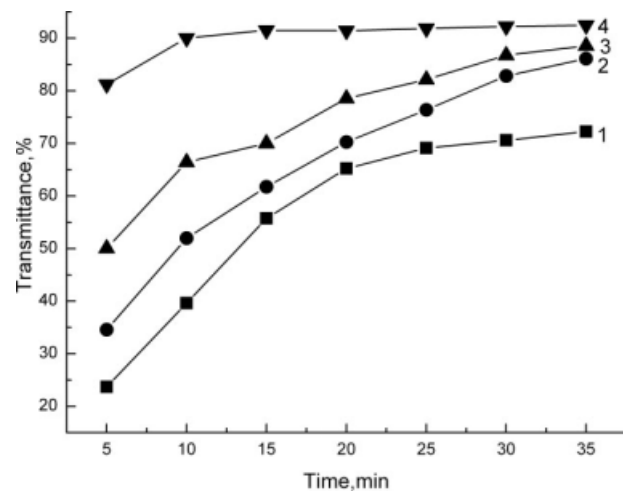


Figure 7 Transmittance change with time: (1) without flocculant; (2) P(AM-DMC); (3) P(AM-DMC-MAPMS), MAPMS = 0.5%; (4) P(AM-DMC-MAPMS), MAPMS = 1.0%.

the floccule hydrophobicity, and consequently improved the interaction between HCPAM and kaolin particles and speeded up the floccule to remove from water solution. The signal 4 showed excellent flocculation performance that the transmittance exceeded 90% when the suspensions settled for 10 min, therefore, the addition of HCPAM decreased flocculation time and increased flocculation performance comparison with that of CPAM.

The effects of flocculation dose on transmittance of kaolin suspension

The flocculation time was fixed at 15 min. The curves of the effects of flocculation dose on transmittance of kaolin suspensions were shown in Figure 8. Three flocculants had a similar effect on

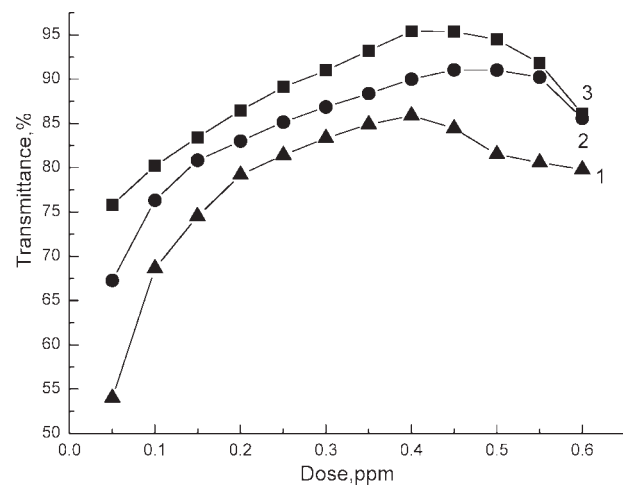


Figure 8 Transmittance change with dose : (1) P(AM-DMC); (2) P(AM-DMC-MAPMS), MAPMS = 0.5%; (3) P(AM-DMC-MAPMS), MAPMS = 1.0%.

transmittance change of kaolin suspension. With the dose increasing, the transmittance of kaolin suspensions increased first and then decreased. The different flocculants had different optimum dose ranges. Under the optimum dose, the suspension particles could not be neutralized completely. However, above the dose, the negative charges on surfaces of suspension particles were neutralized by flocculants with cationic charges, moreover, the excess dose of which made the suspensions stabilization again by changing the electric charges on the surfaces from negative to positive. At the condition of the same dose, HCPAM was a better effect on flocculation of kaolin suspensions compared with CPAM, especially with a higher MAPMS content. From these results, we could draw the conclusion that the introduction of MAPMS optimized the structure of HCPAM, which exhibited a more important influence on the flocculation of kaolin suspensions when cationicity and intrinsic viscosity, which generally were the key factors of charge neutralization and adsorption-bridge, had similar values.

CONCLUSIONS

A novel hydrophobically modified and cationic flocculant P(AM-DMC-MAPMS) was synthesized by radical copolymerization in inverse emulsion. The structure of P(AM-DMC-MAPMS) was proved by FTIR and $^1\text{H-NMR}$ spectra. The introduction of MAPMS made the intrinsic viscosity of P(AM-DMC-MAPMS) higher than that of P(AM-DMC), however, solubility decreased.

The introduction of MAPMS to P(AM-DMC-MAPMS) enhanced flocculation performance. The greater flocculation performance was, the higher

MAPMS feed ratio was. The introduction of MAPMS improved the interaction between flocculant molecules and organic dye molecules or suspended particles, speeding up the floccus to go down. All of the studied flocculants, P(AM-DMC-MAPMS) gave the best flocculation performance all through.

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