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# Intrinsic viscosity, surface activity, and flocculation of cationic polyacrylamide modified with fluorinated acrylate

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**Abstract** A novel cationic polyacrylamide modified with fluorinated acrylate had been synthesized of acrylamide (AM), methacryloxyethyl trimethylammonium chloride (DMC), and 2-(perfluorooctyl)ethyl acrylate (FEA) by free radical micellar copolymerization in aqueous solution utilizing cetyl trimethylammonium bromide (CTAB) as the surfactant and potassium persulfate (KPS)/sodium bisulfite (SBS) as the redox initiator. Some factors affecting synthesis, such as the amount of FEA, CTAB, and KPS, were described. Surface activity and flocculation of the polymer were studied. The results showed that with the incorporation of FEA, the intrinsic viscosity decreased until the modified polymer was not able to dissolve in water; and with the increase of CTAB and KPS, the intrinsic viscosity decreased firstly then increased slowly. The polymer exhibited good surface activity in both water and salt solution. Its flocculation properties were evaluated with kaolin suspensions using a standard jar test. The results demonstrated the superiority of the copolymer over the no-modified cationic polyacrylamide as a flocculant.

**Keywords** Cationic polyacrylamide · Fluorinated acrylate · Intrinsic viscosity · Surface activity · Flocculation

## Introduction

Flocculation is an efficient and cost-effective method for water and wastewater treatment. Flocculants are classified into two categories, inorganic and organic ones. Among the organic polymer flocculants, cationic ones present better flocculation

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ability, as they can work efficiently through both bridging and charge neutralization [1–4].

Now, acrylamide-based polymers are widely used as flocculants, rheology control agents, and additives [5–7]. Paper manufacturing, mining, and water treatment processes are among the many fields that benefit from the use of acrylamide-based polymers. Hydrophobically modified polyacrylamides (HMPAM) have been of both scientific and industrial interest in recent years. With hydrophobic association behavior, hydrophobically modified polymer has strong bridging ability, which is useful in the flocculation process. There are kinds of hydrophobically modified polymer derivations that have been used in the treatment of different kinds of wastewater [8–10].

Hydrophobically modified polyacrylamides are commonly prepared by free radical micellar copolymerization, in which the solubilization of the hydrophobic monomer within the surfactant micelles and the copolymerization occurring in the water continuous medium can be ensured. The most used hydrophobic monomers are long alkyl hydrocarbons,such as N-alkylacrylamide, n-alkyl (meth)acrylate, vinyl alkylate, styrene, and its ramification, which have been attached to an ionic or nonionic hydrophilic backbone [11–14].

Other methods are to introduce hydrophobic fluorinated groups to the polymer. Because of the low cohesive energy density and surface energy, the hydrophobic associations occurring between fluorocarbon groups are stronger than those of the corresponding hydrocarbon comonomers with the same carbon chain length. However, up to now, the studies on the fluorinated HAPAM are seldom, and moreover, they mostly focus on the non-ionic fluorinated HAPAM [15, 16]. As yet, reports about fluorinated ionic HAPAM prepared by free radical micellar copolymerization were scarcely seen.

In the present study, a novel water-soluble cationic fluorinated flocculant (FCPAM) was synthesized from acrylamide (AM), methacryloxyethyl trimethylammonium chloride (DMC), and 2-(perfluorooctyl) ethyl acrylate (FEA) by free radical micellar copolymerization in aqueous solution utilizing cetyl trimethylammonium bromide (CTAB) as the surfactant and potassium persulfate (KPS)/sodium bisulfite (SBS) as the redox initiator. Choosing 2-(perfluorooctyl) ethyl acrylate as the hydrophobic group is due to the fact that the perfluorocarbon $C_8F_{17}$ group has higher hydrophobicity compared with hydrocarbons. The effects of the content of FEA, CTAB, and KPS in the processing of synthesis on the intrinsic viscosity ($[\eta]$) of FCPAM were studied separately. Then the surface activity of AFPAM solution was also explored. And the flocculation of FCPAM were discussed in details.

## Experimental

### Materials

The structure of 2-(perfluorooctyl) ethyl acrylate (FEA) is shown in Fig. 1. Acylamide (AM) was recrystallized twice from chloroform. Potassium persulfate (KPS) and sodium bisulfite (SBS) were recrystallized from deionized water,

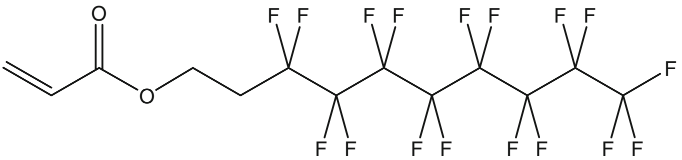
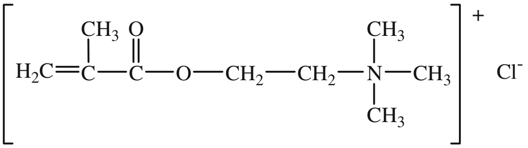


**Fig. 1** Structural formula of FEA

**Fig. 2** Structural formula of DMC



$$\left[ H_2C{=}\underset{}{\overset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{N}}}-CH_3 \right]^+ Cl^-$$

respectively. Methacryloxyethyl trimethylammonium chloride (DMC, Fig. 2), FEA, cetyl trimethylammonium bromide (CTAB), acetone, ethanol, sodium hydroxide, hydrochloric acid, and sodium chloride were obtained from commercial sources and used as received. The water was distilled and deionized.

## Preparation of FPAM

The fluorinated polymers (abbreviation as FPAM) of AM, FEA, and DMC were prepared using CTAB as the surfactant and KPS/SBS as the redox free radical initiator.

A 250-ml three-necked flask equipped with a thermometer, a mechanical stirrer, nitrogen inlet, and outlet was charged with AM, CTAB (variable), DMC (concentration was 50 mol% relative to AM), FEA (variable), and water, and then the mixture was stirred under $N_2$ until a homogeneous phase appeared in the solution. The total monomer concentration in water was constant at 10 wt% (w/w). After adding KPS (variable)/SBS (the molar ratio of KPS:SBS is 2) as initiator, the polymerization was carried out at 40 °C for 12 h.

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 to remove all traces of water, surfactant, and residual monomer before it was dried in a vacuum oven at 60 °C until a constant weight was obtained.

The cationic polymer of AM and DMC was prepared under identical experimental conditions without the addition of FEA.

## Preparation of suspension

The kaolin suspension was prepared by mixing 10 g kaolin in 5 L water, which was stirred at 500 rpm for 24 h, and then was diluted 20 times with water. The characteristics of the suspension are as followed: turbidity = 128 NTU, pH 7.5.

## Measurements

The stock polymer solutions were prepared by dissolution of an appropriate amount of polymer in deionized water or aqueous salt solution and stirred for at least 3 days.

### *Intrinsic viscosity*

Intrinsic viscosities [$\eta$] were measured by a 0.6-mm Ubbelohde capillary viscometer at 25.0 ± 0.1 °C. The kinetic energy and shear rate were found to be negligible. The density of solution was thought to be approximately the same as that of pure water. And the optimal polymer formulation was determined based on the minimum Intrinsic viscosity. All the subsequent experiments were conducted at the optimal polymer formulation.

### *Surface tension*

The surface tensions of polymer solutions were measured by a surface tensiometer (Chengde jinjian tensiometer JYW-200A) at 25.0 °C.

### *Characterization of the FCPAM*

Infrared spectra of FCPAM was recorded with a Fourier transform infrared (FTIR) spectrometer (Magna-IR 750, Nicolet Instrument Co., USA) using a potassium bromide disc technique. The study of the composition of the FCPAM was performed using X-ray photoelectron spectroscopy (XPS). The XPS was obtained by Axis Ultra, Kratos (UK) using monochromatic Al $K_\alpha$ radiation (150 W, 15 kV, 1486.6 eV). The vacuum in the spectrometer was $10^{-9}$ Torr. Binding energies were calibrated relative to the C1s peak (284.4 eV) from hydrocarbons adsorbed on the surface of the samples.

### *Flocculation tests*

The flocculation test was carried out using a standard jar apparatus (Hubei Meiyu Instrument Co., Ltd., China). The suspension was put into six 1 L beakers and the flocculants were added in as 1 g/L aqueous solution. Immediately after the polymer was added, the suspension was stirred at a high speed of 250 rpm for 2 min, followed by 100 rpm for 20 min. After the floc was settled down for 1 h, the turbidity of the supernatant liquid was measured with Digital Turbidity Meter ZD-1 (Tianjin Analytical Instrument Company, China).

# **Results and discussion**

## Synthesis studies

The hydrodynamic volume occupied by a given polymer mass is the intrinsic viscosity [$\eta$], which is a parameter that can be determined by dilute solution viscosity measurements. Intrinsic viscosity is independent of concentration (c) by virtue of extrapolation of reduced viscosity to c=o. The intrinsic viscosity of polymer is related to its relative molecular weight and its existing form of molecular chain, which is proportional to hydrodynamic volume of macromolecule coils in solution, and can reflect the convergence and crimp degree of macromolecule coils. It is an important characteristic parameter of water-soluble polymer.

## Effects of FEA amount

Figure 3 shows the effects of FEA content on the [$\eta$] of FCPAM (the mole percentage is relative to AM). Learning from the data, we know that the [$\eta$] decreases with the increasing of FEA content, and later the decrease amplitude is becoming smaller. The fluorinated monomer FEA has multiple –$CF_3$ groups, which exhibit the excellent hydrophobic performance. Therefore, the hydrophobic effect of FEA is largely stronger than methacrylic acid fluorine straight chain esters and methacrylic acid alkyl chain esters with the same fluorine atomicity.

In the dilute solution, macromolecule is isolated with each other, so there is only intramolecular interaction. In the aqueous solution, the molecular chain of PAM forms the annular or helical structure, and the chain of polymer extends; but the association of hydrophobic-associated polymer molecular dominated by intramolecular association, and increases with increment of hydrophobic groups in polymer molecular chain, which can make the shrinkage and crimp of the molecular chain, and decrease of the hydrodynamic volume. Then, the [$\eta$] reduces in macroscopic view. The incorporation of hydrophobic monomer FEA to water-soluble polymers will change the solubility of polymers. Less content of FEA cannot result to effective intermolecular association, but excessive incorporation will decrease the solubility of polymers in water. As seen in Fig. 3, when the mole content of FEA

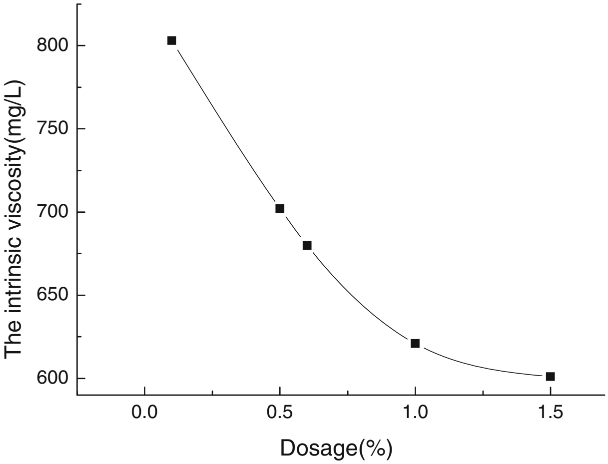


**Fig. 3** Effect of FEA content on intrinsic viscosity of FCPAM flocculant

reaches to 1.5%, the copolymer cannot be completely dissolved in water after 5 days stirring. By comprehensive consideration, the content of 1.5 mol% for FEA is suitable to the following experiments.

## Effects of CTAB amount

As FEA is insoluble in water, in the process of synthesis, a surfactant is used to solubilize FEA. After the radical free polymerization, the surfactant would be extracted out. Cationic surfactant CTAB dissolves in water and forms micellar, which can solubilize hydrophobic monomer. The number of micelle in solution will affect the hydrophobe number per micelle, control the block length and distribution of the hydrophobic groups in the macromolecules backbone, and consequently influence the viscosification effect [17, 18].

Therefore, the contents of CTAB mainly affect the distribution of hydrophobic segment on the molecular chain of FCPAM flocculant, and then affect the [$\eta$] of the FCPAM flocculant. Effects of CTAB content on the [$\eta$] of the FCPAM flocculant are shown in Fig. 4 (the mole percentage is relative to AM). It shows that the [$\eta$] decreases first and later increases with the increase of the content of CTAB. With the increasing of the content of CTAB, distribution of the hydrophobic groups in the macromolecules backbone is more evenly distributed, which leads the hydrophobic-associated interaction in the macromolecular chain strengthened, and [$\eta$] decreased. When the addition of CTAB is higher than 1.0%, there is much more micelles to be formed, so the length of hydrophobic segment in the molecular chain of FCPAM shortens, and the hydrophobic-associated interaction between hydrophobic segments in molecular chain reduces, which can make the molecular chain expand and [$\eta$] increase.

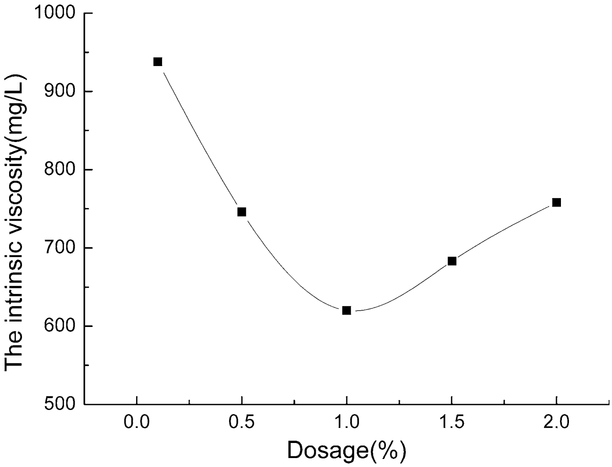


**Fig. 4** Effect of CTAB content on intrinsic viscosity of FCPAM flocculant

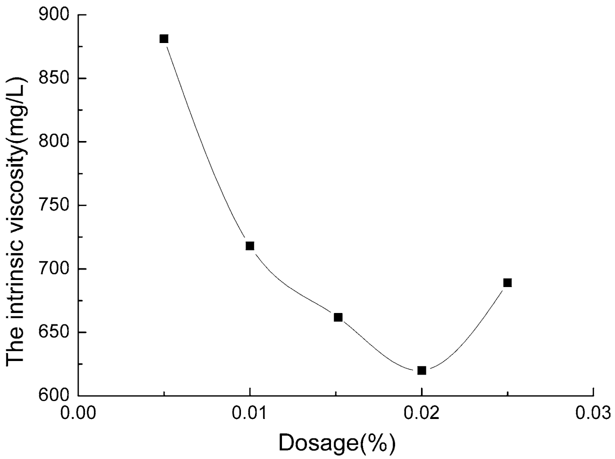


**Fig. 5** Effect of KPS content on intrinsic viscosity of FCPAM flocculant

## Effects of initiator amount

The effects of oxidant KPS content on the [$\eta$] of FCPAM are shown in Fig. 5 (the KPS concentration is relative to AM, and the molar ratio of KPS to SBS is 2). Figure 5 shows that the [$\eta$] decreases first and later increases with the increasing of the content of KPS. When the content of initiator is in a lower range, with the addition of KPS, polymerization conversion improves gradually, which lead to the increasing of the [$\eta$]. However, when the mole concentration of the KPS is higher than 0.02%, increasing the KPS content can lead the more and more smaller relative molecule mass of polymer, and lead the increasing of hydrodynamic volume; as well, the hydrophobic segment of the molecular chain reduces, so the hydrophobic-associated interaction decreases, and the [$\eta$] increases. Under the function of the two aspects, the [$\eta$] increases sharply.

## Surface activity of FCPAM

FCPAM was dissolved in water and salt solution, respectively, and the relationship between the surface tension and the FPCAM concentration is shown in Fig. 6. The results show that the change tendency of surface tension curves both in water and salt solution are similar. The surface tension drops drastically from about 68 to 51 mN/m (in water) and 63 to 40 mN/m (in salt solution) when the concentration of FCPAM increases from 0.02 to 0.1 g/L, and then the surface tension is invariable with more addition of FCPAM. It is noticeable that the surface tension in salt solution is lower than that in water all along.

The fluorinated groups in the water-soluble macromolecular make it have high surface activity in solution. The surface tension decreases quickly because of the orderly distribution of fluorinated groups on the air/water interface. At the same time, with the screening effect by counterion and the increase of polarity of the

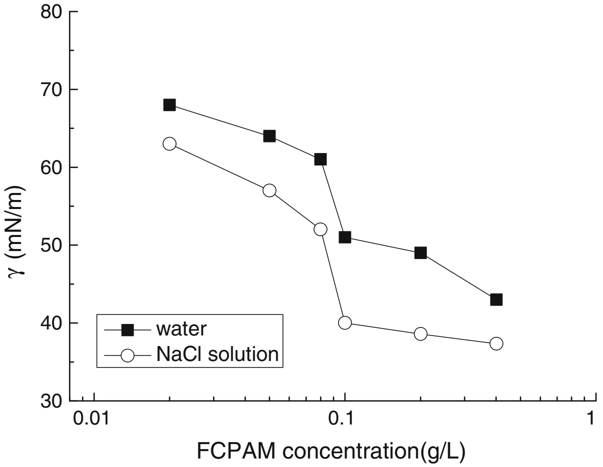


**Fig. 6** Surface tension of FCPAM in water and 0.2 mol/L salt solution as the function of polymer concentration

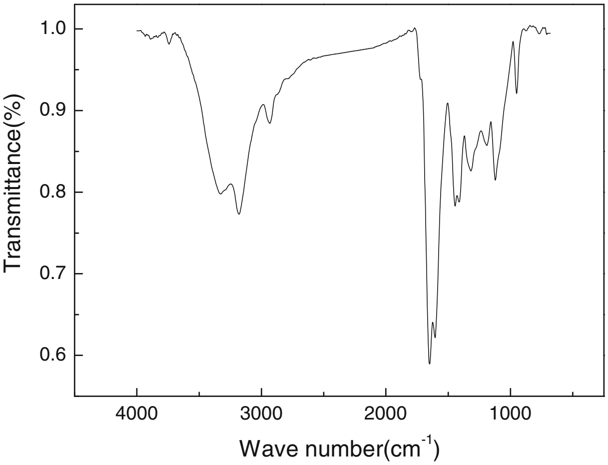


**Fig. 7** FTIR spectrum of FCPAM

medium in salt solution, the order of fluorinated groups become more tight, and thus the surface tension in salt solution is lower than that in water.

## Characterization of the FCPAM

### *FTIR spectrum*

The infrared spectrum of the FCPAM under the optimum conditions is illustrated in Fig. 7. The peaks at wavenumbers of 3326, 3179 and 1606 $cm^{-1}$ come from the

N–H groups, the one at 1,650 $cm^{-1}$ is associated with the vibrating absorption of carbonyl groups and the one at 1,412 $cm^{-1}$ is associated with the C–N groups in AM monomer. The peaks at wavenumbers of 1,445 and 951 $cm^{-1}$ are assigned to the methyl groups of quaternary ammonium in the cationic monomer. The peaks at wavenumbers of 1,318 and 1,190 $cm^{-1}$ are associated with the C–F groups in fluorinated monomer. The peaks at wavenumbers of 2932, 1412, and 770 $cm^{-1}$ come from the C–H and the one at 1,122 $cm^{-1}$ is associated with the C–O–C groups in the backbone of the copolymer. The appearance of all these peaks demonstrates that FCPAM has been successfully copolymerized with AM, DMC, and FEA.

### *XPS analysis*

XPS analysis of the composition of the FCPAM under the optimum conditions is shown in Table 1 (in wt%). From the XPS analysis, we can clearly see that the fluorinated groups are successfully introduced into the CPAM.

### *Flocculation experiment*

A comparison of turbidity removal of kaolin suspension as a function of the concentration of FCPAM at different pH values is shown in Fig. 8. With the

**Table 1** Results of X-ray photoelectron spectroscopy (XPS) analysis

| Element | F | C | N | O | Cl |
|---|---|---|---|---|---|
| Theoretical content (%) | 2.89 | 50.84 | 12.48 | 19.28 | 10.51 |
| Measurement content (%) | 2.75 | 55.57 | 11.98 | 19.35 | 10.35 |

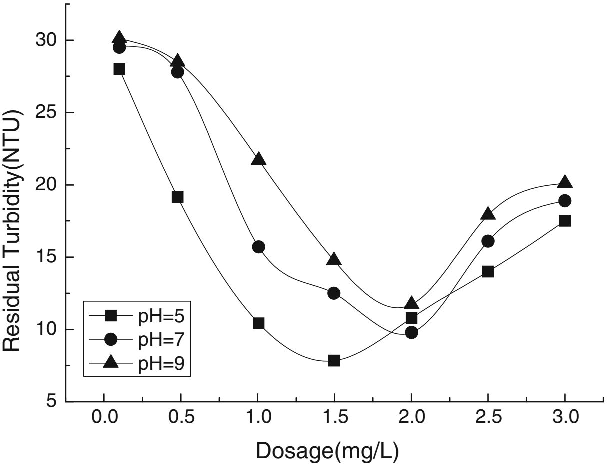


**Fig. 8** Turbidity removal of kaolin suspension as a function of the concentration of FCPAM at different pH 5, pH 7 and pH 9

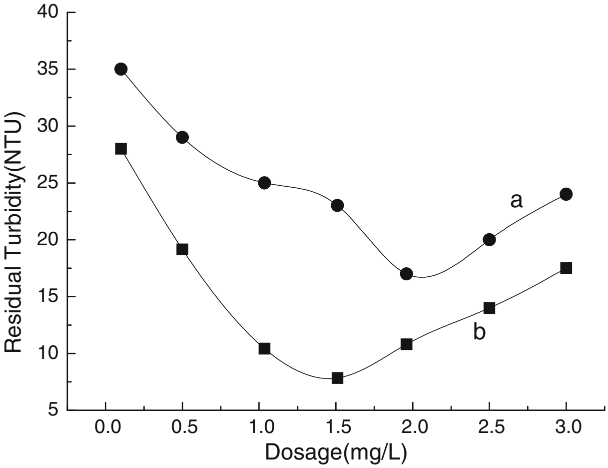


**Fig. 9** Turbidity removal of kaolin suspension as a function of the concentration of modified CPAM and no-modified CPAM at pH 5 (**a** CPAM, **b** FCPAM)

increase of the dosage, these are three similar trends on the kaolin suspension turbidity removal. The residual turbidity decreases first, and then increases. At pH 5, there was a less dosage than the other two samples when the best turbidity removal was reached, and it was the most effective pH value in turbidity removal in the flocculation.

The flocculation efficiencies of fluorinated acrylate-modified CPAM and no-modified CPAM of the kaolin suspension as a function of flocculant dosage at pH 5 are presented in Fig. 9.

As mentioned in previous articles [19], flocculation can be realized through several mechanisms. To the cationic polymers, the polymers can flocculate particles mainly through bridging and charge neutralization flocculation mechanisms. Due to the same cationic charge density, the contribution of charge neutralization is similar, but bridging function is different. Compared with CPAM, the hydrophobically modified FCPAM has stronger adsorption to kaolin particles, which is enhanced by the affinity of the hydrophobic chains to the hydrophobic kaolin particle surface. This is attributed to the strong hydrophobic association structure, which enhances the molecular anchor to the particle surface and promotes the association among polymer molecules and kaolin particles. This behavior enhances the anchor of polymer chains onto kaolin particles, and promotes the interaction between particles. As a result, the flocculation performance is enhanced.

Through the flocculation experiment, the mechanism of flocculation is proposed as follows. As FCPAM was used as a flocculant, both bridging and charging neutrality played important roles. The charge neutralization of the cationic group certainly plays a vital role, while the flocculation ability of the hydrophobically modified PAM is also realized through strong bridging mechanism. The hydrophobic chains in the macromolecule play an important role in the flocculation process. As there are strong associations between hydrophobic units, FCPAM shows self-forming behavior. With the intra- and inter-molecular associations and the affinity onto the kaolin particles, FCPAM can form a network around kaolin particles. At an appropriate concentration, flocculation happens.

## Conclusions

The water-soluble cationic fluorinated flocculant (FCPAM) was synthesized from AM, DMC, and FEA by free radical micellar copolymerization in aqueous solution utilizing CTAB as the surfactant and KPS/SBS as the redox initiator. With the incorporation of FEA, the intrinsic viscosity decreased until FEA is 1.5 mol% (concentration was relative to AM), the modified polymer was not able to dissolve in water; and with the increase of CTAB and KPS, the intrinsic viscosity decreased first then increased gradually. When the addition of CTAB and KPS was, respectively, 1.0 and 0.02 mol% (concentration was relative to AM), the intrinsic viscosity was minimum, and the hydrophobic association was strongest. Moreover, the polymer exhibited good surface activity in both water and salt solution. And the standard jar test of kaolin suspensions showed that its best flocculation properties were exhibited at pH 5. Comparison with the no-modified cationic polyacrylamide, the results demonstrated the superiority of the FCPAM as a flocculant.

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