

Novel, rosin-based, hydrophobically modified cationic polyacrylamide for kaolin suspension flocculation

Haibo Zhang,^{1,2} Jianxin Jiang,² Shibin Shang ,¹ Zhanqian Song,¹ Jie Song³

¹Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Key Laboratory of Biomass Energy and Material, National Engineering Laboratory for Biomass Chemical Utilization, Key Laboratory on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, People's Republic of China

²College of Materials Science and Technology, Beijing Forestry University, Engineering Research Center of Forestry Biomass Material and Bioenergy, Ministry of Education, Beijing 100083, People's Republic of China

³Department of Chemistry and Biochemistry, University of Michigan-Flint, Flint Michigan 48502, United States

Correspondence to: S. Shang (E-mail: shangsb@hotmail.com)

ABSTRACT: A novel, hydrophobically modified cationic polyacrylamide (HMPAM) was synthesized via the copolymerization of acrylamide, diallyl dimethyl ammonium chloride (DMAAC), and diallylmethyl dehydroabiatic acid propyl ester ammonium bromide. Optimum conditions for preparing HMPAM were such that the amount of initiator was 0.075 wt % of the total monomer mass, the monomer concentration was 20 wt %, and the amount of DMAAC was 18 mol % of the total monomer molar mass. HMPAM was characterized with an UV-visible spectrometer, ¹H-NMR, Ubbelohde viscometer, rotational viscometer, and rotational rheometer. HMPAM solutions exhibited strong hydrophobic associations, and the critical association concentration of the HMPAM aqueous solution was about 0.7 wt %; the HMPAM solutions also showed salt thickening and shear resistance. The surface morphologies of the freeze-dried HMPAM samples (1 wt %) were also observed via scanning electron microscopy. Compared with unmodified cationic polyacrylamide, Synthesis of HMPAM-0.5 exhibited a stronger flocculation capacity, and the optimal transmittance of the supernatants was above 95%. HMPAM-0.5 showed significant flocculation performances for 3–4 and 3–5 wt % kaolin suspensions at 40 and 50 mg/L, respectively. Moreover, the flocculation performance was enhanced with the addition of NaCl and CaCl₂. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, *135*, 46637.

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INTRODUCTION

With industrial and economic developments, water pollution has become an important factor threatening human survival. One serious problem in wastewater treatment is the purification of high-solid-content wastewater; it is caused by soil erosion, agriculture, mining, papermaking, and industrial activities.^{1–3} To solve this issue, many technologies have been developed, including coagulation, precipitation, flocculation, membrane filtration, and adsorption.^{4,5} In particular, flocculation is regarded as one of the most common and important purification techniques used in wastewater treatment because of its low cost and high efficiency.^{6,7}

The most critical issue of flocculation is the choice of a suitable flocculant for promoting the agglomeration of suspended particles in larger flocs for separation from wastewater.^{6,8} The flocculants used

in wastewater treatment are mainly inorganic coagulants, such as poly(aluminum chloride) and ferric chloride.^{9,10} However, it has been shown that there are numerous disadvantages to using inorganic coagulants in wastewater treatment. Inorganic coagulants are sensitive to pH, and a large amount is needed for high efficiency in the flocculation process.¹¹ Moreover, using inorganic coagulants produces large volumes of metal hydroxide sludge and increases metal ions (Al³⁺) in water, which may lead to Alzheimer's disease.^{12,13}

To reduce the use of inorganic flocculants, polymers have been used as flocculants to enhance flocculation performance. In general, polymeric flocculants are water-soluble polymers, such as poly(acrylic acid), cationic polyacrylamide (CPAM), and anionic polyacrylamide.¹⁴ CPAM is a polymer used extensively as a flocculant because of its high efficiency, even when used in small

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quantities, and it can be prepared with different molecular weights, positive charge densities, and structures. The flocculation mechanism with CPAM as a flocculant can be explained with a bridging mechanism, a charge-neutralization mechanism, and a patching mechanism; of these, the charge-neutralization mechanism plays the most important role.^{15,16} CPAM with a high positive charge density is adsorbed on the surface of kaolin particles via charge neutralization, and this results in a decrease in the electrostatic repulsion between kaolin particles; this results in the formation of larger flocs. Therefore, CPAM exhibits a high flocculation efficiency.

Hydrophobically modified cationic polyacrylamide (HMPAM), in which a small amount of hydrophobic monomers (<2 mol %) is copolymerized in the polyacrylamide backbone, can improve the rheological properties of its aqueous solution.¹⁷ At high concentrations, hydrophobic groups form intermolecular interactions in aqueous solution via the hydrophobic associations of hydrophobic groups, and these produce a transient network to provide a viscosity-building capacity.^{18,19} In the flocculation process, a strong hydrophobic association formed between the flocs via HMPAM intermolecular interactions, charge neutralization, and bridging absorption to improve the flocculation performance.^{20–22}

Rosin (90% rosin acids and 10% neutral compounds) is an abundantly renewable resource extracted from various species of pine, and rosin is produced at more than 1 million tons per year.^{23,24} Rosin acids with hydrophenanthrene structures provide cycloaliphatic and aromatic structures, which give rosin and its derivatives excellent hydrophobicity.^{23–25} In general, rosin-based derivatives, such as epoxy resin, cured oil-based resin, and polyamide, are advantageous for improving the glass-transition temperature and mechanical properties of polymers.^{25,26} However, rosin-based derivatives used in water-soluble CPAM to improve their flocculation properties have rarely been reported. If rosin structures, which have renowned hydrophobicity, are incorporated into the CPAM molecular chain, strong hydrophobic associations can form between the polymer molecules. HMPAM on the surface of the flocs can form larger flocs via hydrophobic associations, and thus, the flocculation efficiency of the polymer can be improved.

In this study, we prepared HMPAM flocculant via the free-radical copolymerization of acrylamide (AM), diallyl dimethyl ammonium chloride (DMDAAC), and diallylmethyl dehydroabiatic propyl ester ammonium bromide (DMDHAE). The effects of the initiator dosage, monomer molar ratios, and monomer concentrations on the intrinsic viscosity were investigated. The rheological properties of HMPAM were evaluated with a rotational viscometer and rotational rheometer. The HMPAM solutions exhibited shear resistance, salt thickening, and hydrophobic associations when the concentration of HMPAM was greater than that of the critical association concentration (CAC). In the flocculation processes, the effects of the flocculant dosage, pH, salt concentration, and initial concentration of kaolin suspension on the flocculation performance were investigated. HMPAM exhibited a more effective flocculation performance than CPAM for various concentrations of kaolin suspensions, and flocculation performance was enhanced in the salt solutions. The flocculation

mechanism was analyzed simply. HMPAM had strong hydrophobic associations because of the incorporated rosin structure; this improved the salt resistance, viscosity, and shear resistance of HMPAM. HMPAM showed great potential for application in thickeners, rheology modifiers, and water-based coatings.

EXPERIMENTAL

Materials

Dehydroabiatic acid (~90 wt %) was purchased from Wuzhou Chemical Co. (Wuzhou, China). Oxalyl chloride (98 wt %), 3-bromopropan-1-ol (97 wt %), methyldiallylamine (98 wt %), and AM (99 wt %) were purchased from Energy Chemical Co., Ltd. (Shanghai, China). DMDAAC solution (60 wt % aqueous solution), triethylamine (99 wt %), and 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50; 97 wt %) were produced by Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium chloride (NaCl; 99.9 wt %), calcium chloride (CaCl₂; 99 wt %), and kaolin were sourced from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the reagents were used without any further purification.

Synthesis of DMDHAE

See the Supporting Information. Synthesis procedures for DMDHAE, ¹H-NMR, ¹³C-NMR, and MS are described in the Supporting Information.

Synthesis of HMPAM

Certain masses of AM, DMDAAC, and DMDHAE were dissolved in deionized water under an inert nitrogen atmosphere, and then, copolymerization was initiated with V-50 at 50 °C for 10 h. After the reaction, the copolymers were soaked in EtOH for 24 h to remove the unreacted monomer. Finally, the copolymers were dried *in vacuo* at 60 °C for 24 h. HMPAM-*x* denotes the hydrophobically modified cationic polyacrylamides, where *x* is the molar ratio of DMDHAE.

Measurements of the Intrinsic Viscosity

HMPAM was dissolved in an aqueous NaCl solution with a concentration of 1 mol/L, and the intrinsic viscosities of the polymers were measured with an Ubbelohde viscometer at 30 ± 0.1 °C.

Measurements of the Apparent Viscosity and Rheological Properties

The apparent viscosities of the copolymers were measured with a rotational viscometer (NDJ-5S, China) at 25 °C at a shear rate of 6 s⁻¹. The rheological properties of the copolymers were measured at 25 °C with a rotational rheometer (Haake Mars II, Germany) with a measured geometry (radius = 20 mm and gap = 0.10 mm). Shear property measurements were performed with shear rates ranging from 2 to 800 s⁻¹. For dynamic viscoelastic measurements, a constant strain of 1% was applied to conduct a dynamic frequency sweep within the linear region of the solution over an angular frequency range of 0.01 to 10 Hz. The storage modulus (*G'*) and loss modulus (*G''*) were recorded as functions of the frequency to obtain the dynamic mechanical spectra.

Characterization

The ultraviolet–visible (UV–vis) spectra of the DMDHAE and copolymers (at a concentration of 0.5 wt % and with deionized

water as the solvent) were measured with a UV2450 UV–vis spectrometer (Shimadzu, Japan). The surface morphology was observed with a 3400NI scanning electron microscope (Hitachi, Japan). The NMR spectrum of HMPAM was recorded with a 300 MHz spectrometer (Bruker Co., Germany) at room temperature with deuterioxide.

Flocculation Evaluation

Flocculation tests were carried out according to a method reported in the literature.²⁶ Samples (0.1 g) were dissolved in deionized water (100 mL), and the solution was then diluted to different concentrations for the tests. The kaolin suspension (3 wt %) was stirred for 15 min at 500 rpm with a magnetic stirrer. In the flocculation process, the flocculants (10 mL) and kaolin suspension (90 mL) were added in a mixing cylinder, which was stoppered. The mixture solution was shaken up and down 10 times. The supernatant (30 mL), which was below the water surface, was then collected after free settling for 30 min. The transmittance of the supernatant was measured with a UV–vis spectrophotometer at 600 nm. The time (t) of the kaolin suspension settling at a height of 40 mL was recorded. Therefore, the settlement rate was defined as $40/t$ (mL/s).

Toxicity Test

The HeLa cells were cultured in high-glucose Dulbecco's modified Eagle's medium (10% fetal bovine serum, 100 U/mL penicillin, and 100 μ g/mL streptomycin) at 37 °C in a humidified, 5% CO₂ incubator. HeLa cells were seed in a T-75 cell culture flask at a density of 1×10^5 cell/mL. After 24 h, the cell culture medium was replaced with fresh medium either without or with HMPAM. The cells were then further cultured for 72 h. The optical densities of the sample (OD_s) and the control sample (OD_c) were measured with a microplate reader at 570 nm. The cell survival rate was defined as follows:

$$\text{Cell survival rate} = \frac{\text{OD}_s}{\text{OD}_c} \times 100\%$$

RESULTS AND DISCUSSION

Synthesis of HMPAM and Measurements of the Solution Properties

HMPAM Preparation. HMPAM was prepared via the copolymerization of AM, DMAAC, and DMDHAE in deionized water via free-radical polymerization, and the synthesis route of

HMPAM is described in Figure 1. Because of the low hydrophobic content, UV spectroscopy, which has a higher sensitivity, was suitable for determining the composition of HMPAM. The UV–vis spectra for HMPAM and DMDHAE are shown in Figure 2(A). The absorption peaks at 267 and 275 nm in the spectrum for DMDHAE were attributed to the aromatic ring structure of DMDHAE. Compared with the spectrum for CPAM, the characteristic peaks for the aromatic ring (at 267 and 275 nm) appeared in the spectrum for HMPAM [Figure 2(B)]. Moreover, the intensity of the absorption peak increased with increasing amount of DMDHAE. The chemical shift at 1.3–1.8 ppm in the ¹H-NMR spectrum of HMPAM [Figure 2(B)] was assigned to the protons of –CH₂ in the polymer chain. The peaks at 1.9–2.5 ppm were attributed to the protons of –CH. The protons of N⁺–CH₃ and N⁺–CH₂ in DMAAC and DMDHAE appeared at 3.3–3.7 ppm. The proton signals of the aromatic ring were observed at 6.8–7.9 ppm. These results clearly suggest that DMDHAE was successfully copolymerized in the HMPAM copolymer structure.

Optimization of the Synthesis Conditions. The molecular weight of polyacrylamide is commonly determined via the intrinsic viscosity method. At extremely low concentration, there were no interactions between the polyacrylamide molecules, and hence, the intrinsic viscosity of the solution represents the molecular weight of polyacrylamide.

The effects of the monomer concentrations on the intrinsic viscosity are described in Figure 3(A). At first, the intrinsic viscosity increased and then decreased with increasing monomer concentration. The collision frequency of the monomer molecules was low, and this resulted in a low molecular weight of the polymers. At a high monomer concentration, the polymerization was fast and released a lot of heat; this led to a decrease in the degree of polymerization. When the monomer concentration was 20 wt %, a maximum value of the intrinsic viscosity was obtained. The effects of the initiator on the intrinsic viscosity are shown in Figure 3(B). The effects of the initiator on the intrinsic viscosity showed a similar trend as that on the effects of the monomer concentration on the intrinsic viscosity. This phenomenon occurred because the efficiency of the initiator was low because of the cage effect at relatively low concentrations, and this resulted in a low intrinsic viscosity of HMPAM; with increasing concentration of the initiator, the termination and chain-transfer rate increased, and

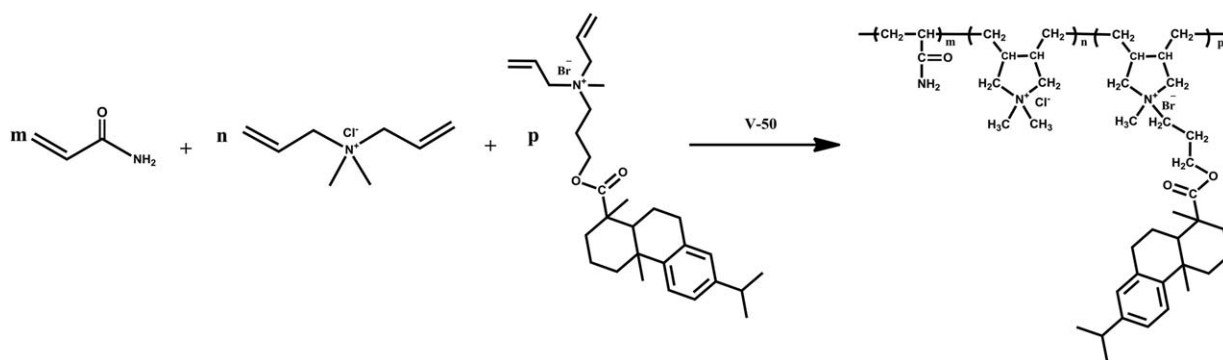


Figure 1. Synthesis route of HMPAM.

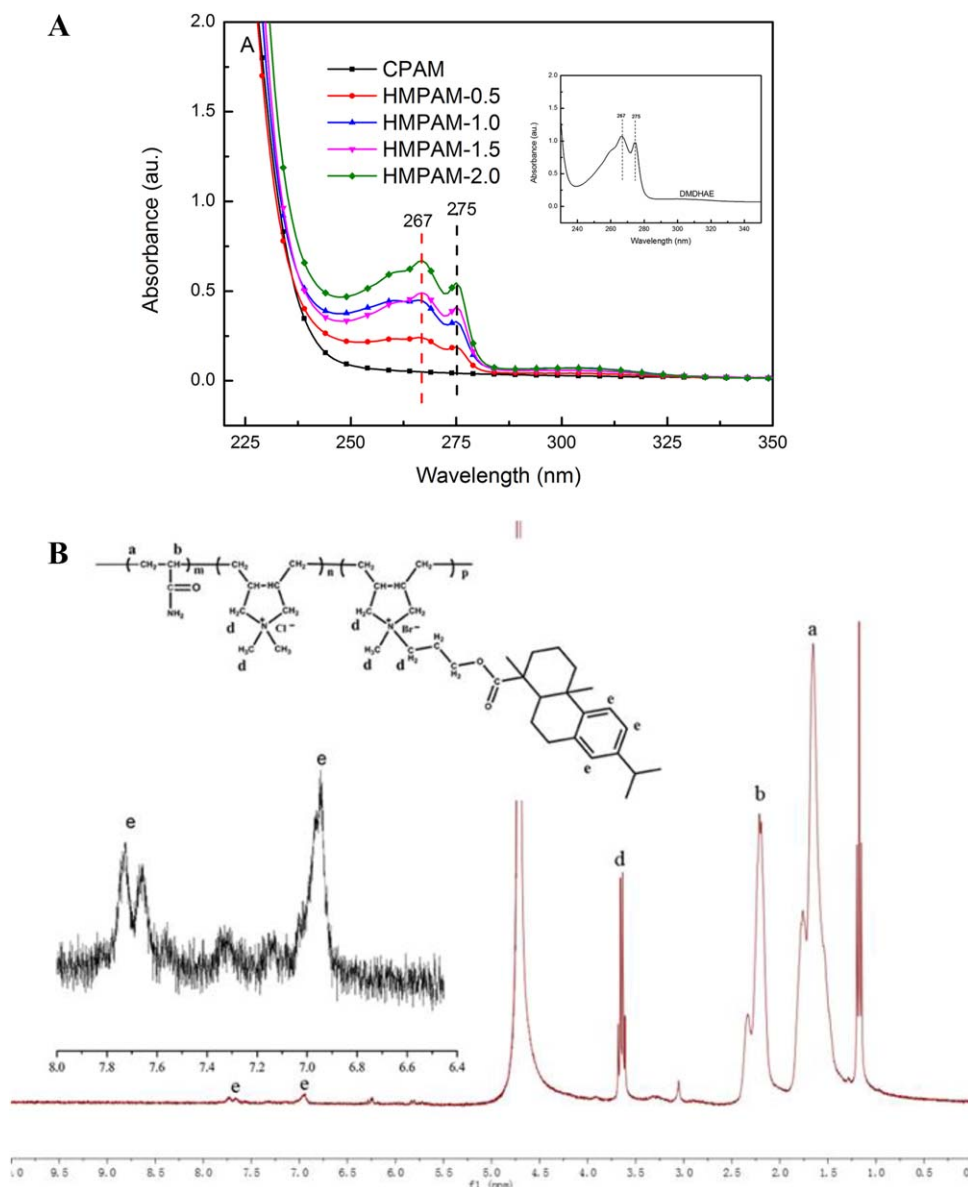


Figure 2. (A) UV-vis spectra and (B) $^1\text{H-NMR}$ spectrum of HMPAM. [Color figure can be viewed at wileyonlinelibrary.com]

this resulted in a low intrinsic viscosity.²⁷ The optimum amount of initiator was 0.075 wt % of the total monomer mass.

As shown in Figure 3(C), the intrinsic viscosity reached a maximum value when the amount of DMDAAC was 18 mol % of the total monomer molar mass. The effects of DMDHAE on the intrinsic viscosity are described in Figure 3(D). The intrinsic viscosity of HMPAM decreased with increasing molar ratio of DMDHAE. This phenomenon could be explained as follows: on the one hand, the induction period and time needed to reach the maximum temperature increased with increasing DMDHAE content, and this led to an increase in the chain-transfer rate of AM; on the other hand, DMDHAE, which had a characteristic hydrophenanthrene structure, had a large steric hindrance, and this hampered the polymerization of active centers and monomers.^{28,29}

Hydrophobic Association Properties of HMPAM. Figure 4 shows the relationships between the apparent viscosity and the concentration of polymers. The apparent viscosity increased with increasing copolymer concentration, but the apparent viscosities of HMPAM were much greater than those of CPAM at high concentrations of polymer. It was clear that the apparent viscosities of HMPAM increased sharply when the concentration of HMPAM exceeded about 0.7 wt %. This indicated that 0.7 wt % (or ~ 0.7 wt %) was the CAC for HMPAM solutions, at which point dominant associations began to change from intramolecular associations to intermolecular associations.³⁰ Transient networks were formed via hydrophobic intermolecular associations; this resulted in a high solution viscosity.³¹ Below 0.7 wt %, the apparent viscosity of CPAM was the highest; for HMPAM, the apparent viscosities decreased with increasing DMDHAE dosage. This indicated that the molecular weight at low concentrations

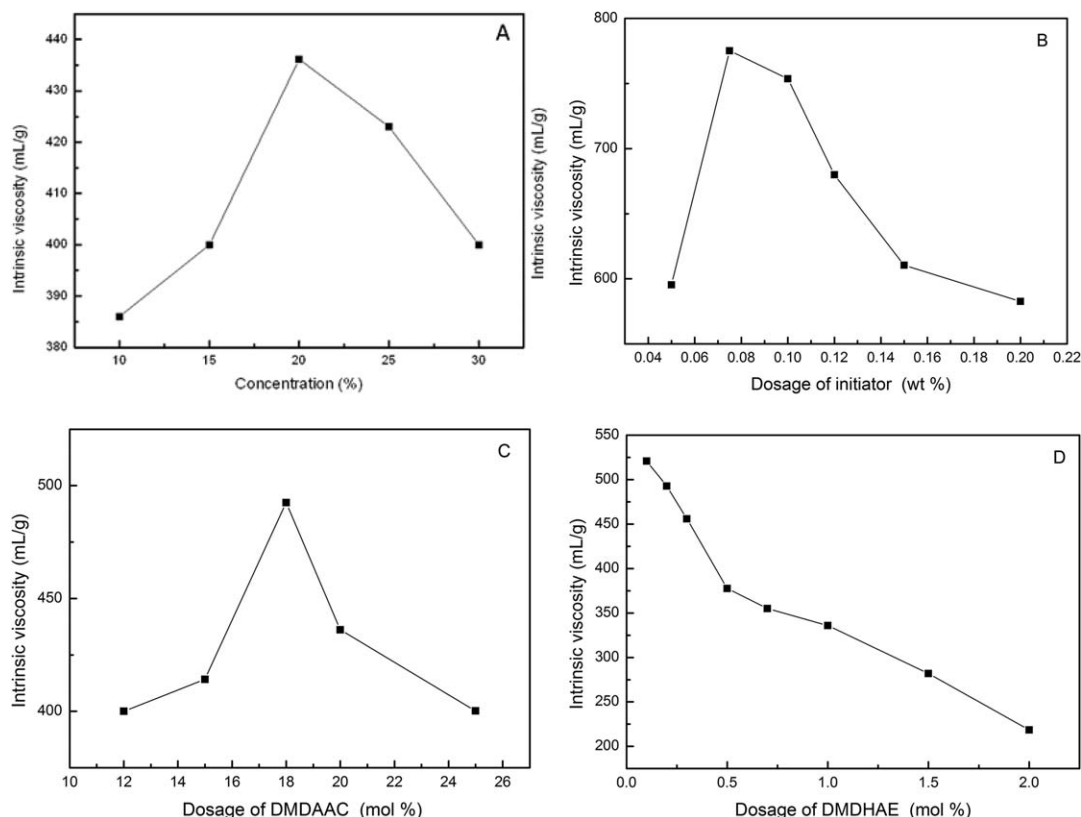


Figure 3. Effects of the synthetic factors on the intrinsic viscosity: (A) monomer concentration [$n(\text{DMDAAC})/n(\text{AM}) = 20:80$ and 0.5 wt % initiator], (B) initiator [$n(\text{AM})/n(\text{DMDAAC}) = 85:15$], (C) DMDAAC, and (D) DMDHAE [$n(\text{AM})/[n(\text{DMDAAC}) + n(\text{DMDHAE})] = 82:18$].

determined the apparent viscosities; for HMPAM, because of intramolecular associations, the HMPAM molecules, which had a small hydrodynamic volume, decreased the apparent viscosities of the solutions. Above 0.7 wt %, the apparent viscosities increased with increasing hydrophobic monomer dosage, and this was because of the increase in the degree of hydrophobic associations with increasing hydrophobic monomer content. Moreover,

HMPAM exhibited stronger hydrophobic association properties than the HMPAM modified with other hydrophobic side chains (e.g., fatty alcohol, phenyl, dialkyl, or stearic acid groups)^{17,28,32–34}, and this proved that the hydrophenanthrene structure of DMDAAC made HMPAM more hydrophobic.

The scanning electron microscopy images of CPAM and HMPAM are shown in Figure 5. The copolymers (1 wt % concentration) were dissolved in water (above CAC), and then, the samples were obtained via freezing and drying. As shown in Figure 5, the micropores of CPAM were irregular and appeared to be smooth, but HMPAM appeared to be more regular, and some of the filaments were like spider silk stuck to the micropores. This phenomenon indicated that aggregates of the HMPAM macromolecule formed via hydrophobic association with evaporated water, and this led to the formation of a network structure in the micropores.

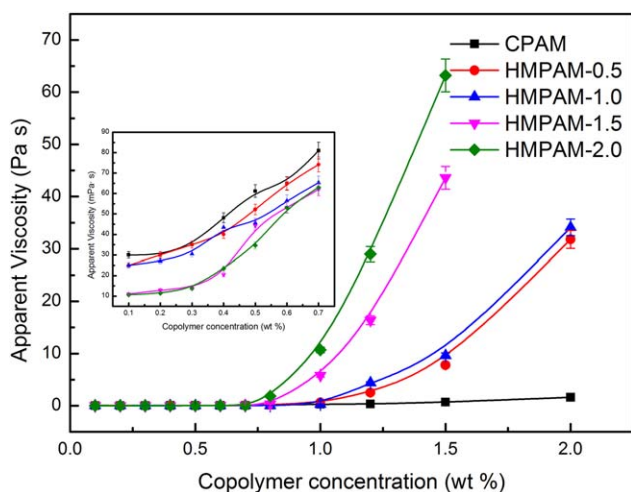


Figure 4. Apparent viscosities of aqueous solutions as a function of the copolymer concentration. [Color figure can be viewed at wileyonlinelibrary.com]

Effects of Salt on the Apparent Viscosity of HMPAM. The apparent viscosities of HMPAM exhibited remarkable salt-thickening properties, as shown in Figure 6. The apparent viscosities of CPAM sharply decreased in the salt solution, and this was because the CPAM macromolecular chains expand in the brine solution; this led to lower hydrodynamic volumes and apparent viscosities.^{32,34} However, the apparent viscosities of HMPAM dramatically increased with increasing concentration of NaCl or CaCl₂. There were two reasons for this phenomenon: (1) the polarity of the solution increased in the salt solution, and this reinforced intermolecular hydrophobic associations,

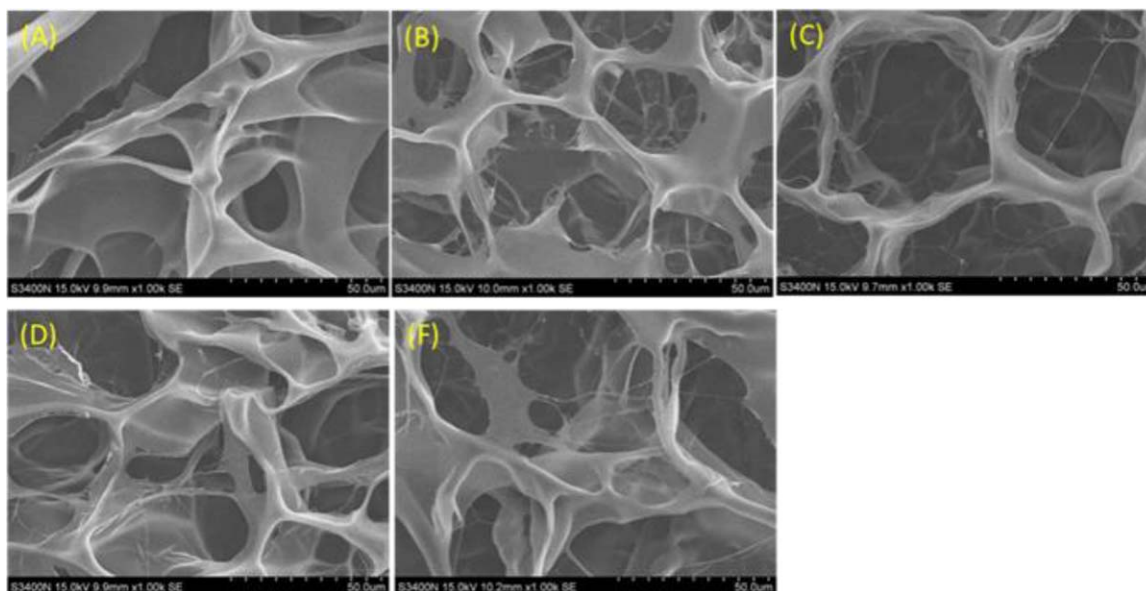


Figure 5. Scanning electron microscopy images of CPAM and HMPAM (1 wt %): (A) CPAM, (B) HMPAM-0.5, (C) HMPAM-1.0, (D) HMPAM-1.5, and (E) HMPAM-2.0. [Color figure can be viewed at wileyonlinelibrary.com]

and (2) the hydrophobic moieties of HMPAM had a low solubility in salt solution, and this resulted in an increase in the degree of hydrophobic associations.^{35,36} Because the polarity of the CaCl_2 solution was stronger than that of NaCl solution, the apparent viscosities of HMPAM in the CaCl_2 solutions were higher than those in the NaCl solutions.

Effects of the Temperature on the Apparent Viscosity of the HMPAM Solution. The effects of the temperature on the apparent viscosity of the HMPAM solution are shown in Figure 7. With increasing temperature, the apparent viscosity of HMPAM decreased dramatically, and the lower reduced rates increased with increasing DMDHAE content. These results were attributed to the destruction of intermolecular hydrophobic associations, and this reduced the degree of the physically crosslinked

network with increasing temperature and resulted in low apparent viscosities.

Shear Resistance of the HMPAM Solutions. The effects of the HMPAM solution concentrations on the shear properties of HMPAM-2.0 are shown in Figure 8(A). For the 0.8, 1.0, 1.2, and 1.5 wt % HMPAM solutions (above CAC), the apparent viscosity increased with increasing shear rate at low shear rates. However, a sharp decrease in the apparent viscosity accompanied an increase in the shear rate, and the HMPAM solutions exhibited a significant pseudo-plasticity. The phenomena could be explained as follows: at low shear rates, the intramolecular associations were destroyed, and the HMPAM molecules expanded. This enhanced the intermolecular associations; then, with increasing shear rates, the network that was formed via

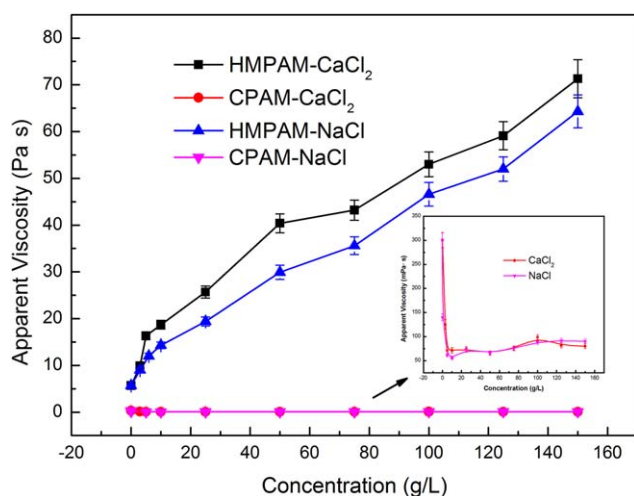


Figure 6. Apparent viscosities of the HMPAM solutions with different NaCl or CaCl_2 concentrations (1 wt % HMPAM-1.5 aqueous solution). [Color figure can be viewed at wileyonlinelibrary.com]

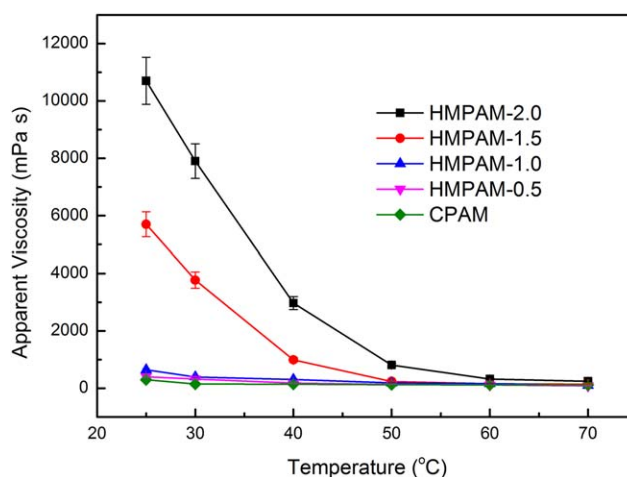


Figure 7. Effects of the temperature on the apparent viscosities of the HMPAM solutions (1 wt %). [Color figure can be viewed at wileyonlinelibrary.com]

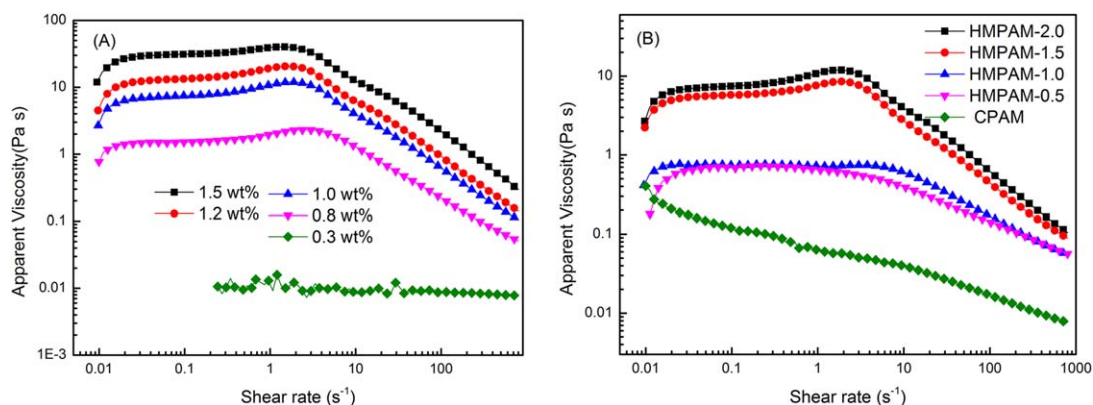


Figure 8. (A) Effects of the shear rate on the apparent viscosities of the HMPAM-2.0 solutions at different concentrations. (B) Effects of the shear rate on the apparent viscosities of HMPAM containing different amounts of DMDHAE (1.2 wt %). [Color figure can be viewed at wileyonlinelibrary.com]

intermolecular associations was broken. This resulted in a decrease in the apparent viscosity. For the 0.3 wt % HMPAM solution, the HMPAM molecules mainly formed intramolecular associations in aqueous solution, and this caused the apparent viscosity to remain almost constant with increasing shear rates. Also, the apparent viscosity increased with increasing concentration of the HMPAM solutions.

The effects of the DMDHAE dosage on the shear properties are shown in Figure 8(B). The HMPAM solutions had a higher apparent viscosity with increasing DMDHAE content of HMPAM. With increasing shear rate, the trends in the apparent viscosity of the HMPAM solutions were same as that shown in Figure 8(A). However, the apparent viscosity of the CPAM solution showed shear thinning with increasing shear rate. This showed that when the DMDHAE content was higher, the physical network in the HMPAM solution was stronger, and this led to an increase in the shear resistance of the HMPAM solutions.

Viscoelastic Properties. The viscoelastic properties of the HMPAM solutions were investigated with oscillatory-shear (frequency sweep) measurements, and the results are shown in Figure 9. At low frequency, G' was higher than G'' , and hence, the solutions exhibited viscous behavior; the elastic behavior was dominant when the value of G' was greater than the value of G'' with increasing frequency. The effects of the concentration on the viscoelasticity are shown in Figure

9(A). With increasing HMPAM solution concentration, the values of G' and G'' increased, and the crossing point (G'/G'') moved to the left. As shown in Figure 9(B), the effects of the DMDHAE content on G'/G'' and the values of G' and G'' were the same as indicated in the trends for the effects of the HMPAM solution concentration on G'/G'' and the values of G' and G'' . This indicated that the hydrophobic associations were improved with increasing concentration of the solutions and increasing content of hydrophobic monomers. When the hydrophobic associations in the HMPAM solutions were stronger, the frequency at which the solutions changed from viscous behavior to elastic behavior was lower.

Flocculation Performance

Effects of the Monomer Molar Ratio on Flocculation. As illustrated in Figure 10(A), the transmittance of the supernatant initially increased and then decreased with increasing DMDAAC content, and the value of transmittance reached a maximum when the DMDAAC content was 18 mol %. This phenomenon occurred because of the following reasons. At low dosages, low densities of positive charges were insufficient for neutralizing the negative charges of kaolin particles.¹ With excess flocculant, the surfaces of the kaolin particles interacted with the positive charges of the flocculants, and this resulted in electrostatic repulsion between the kaolin particles; thus, the transmittance of the supernatant decreased.³⁷ The values of maximum transmittance were 89.5, 83.9, 85.3, 93.77, and 91.4%, when the

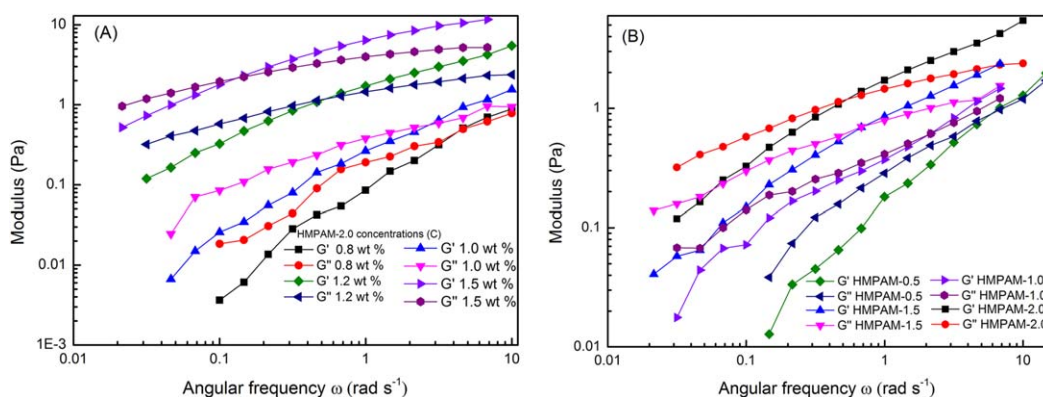


Figure 9. (A) Effects of the HMPAM-2.0 concentrations on the viscoelasticity. (B) Effects of the DMDHAE contents on the viscoelasticity (1.2 wt %). [Color figure can be viewed at wileyonlinelibrary.com]

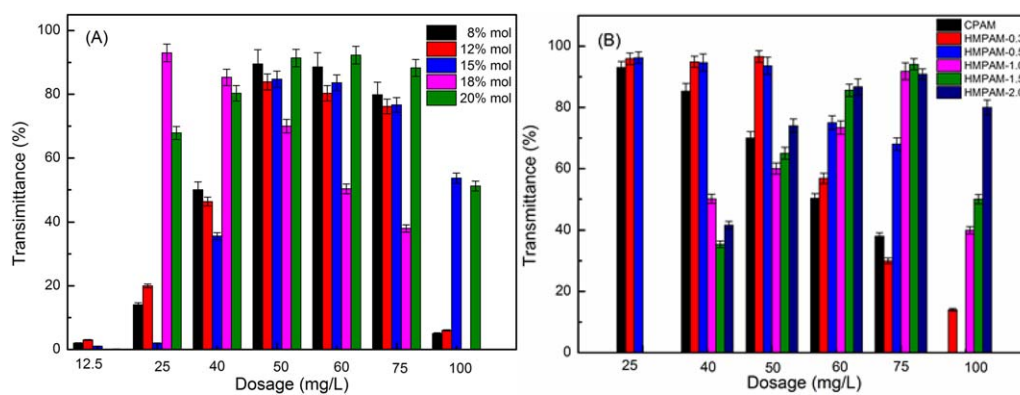


Figure 10. Effects of the (A) DMDAAC and (B) DMDHAE contents on the flocculation. [Color figure can be viewed at wileyonlinelibrary.com]

DMDAAC contents in CPAM were 8, 12, 15, 18, and 20 mol %, respectively.

The effects of the hydrophobic monomer contents on flocculation are shown in Figure 10(B). With increasing HMPAM dosage, the transmittance of the supernatant showed a similar trend with increasing CPAM dosage. Compared with CPAM, HMPAM-0.3 and HMPAM-0.5 exhibited effective flocculation properties over a wide concentration range from 25 to 50 mg/L. The optimal dosages of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 increased because of the lower intrinsic viscosities of HMPAM with high hydrophobic monomer contents. The optimal dosages of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 were each 75 mg/L.

Effects of the Initial Concentration of the Kaolin Suspension on Flocculation. The effects of the initial concentration of the kaolin suspension (1–5 wt %) on flocculation are illustrated in Figure 11. Compared with the flocculation properties of CPAM, HMPAM-0.5 had a higher flocculation capacity. The optimal dosage of CPAM was only effective for a specific concentration of kaolin suspension. The optimal dosages of CPAM were 25, 25, 25, 40, and 50 mg/L for 1, 2, 3, 4, and 5 wt % concentrations of kaolin suspension, respectively. A wide concentration range of HMPAM-0.5 was sufficient for a 3–5 wt % kaolin suspension, and the optimal transmittances of the supernatants were above 95%. The optimal HMPAM concentration ranges for 3, 4, and 5 wt % kaolin suspensions were 25–50, 40–50, and 50–75 mg/L, respectively. The transmittance of the supernatants reached 99% when the initial concentration of kaolin suspension was 5 wt %. Moreover, it was clear that 40 and 50 mg/L HMPAM-0.5 showed significant flocculation for 3–4 and 3–5 wt % kaolin suspensions, respectively. The possible reason for this may have been the formation and destruction of the hydrophobic associations between HMPAM molecules in the kaolin suspensions with various concentrations.

Effects of the pH on the Flocculation and Settlement Rates. The effects of the pH on the flocculation and settlement rates were investigated, and the results are shown in Figure 12. As shown in Figure 12(A), the transmittance of the supernatant initially increased and then decreased with increasing pH; this was because the positive charges of the flocculants were neutralized by OH^- under alkaline conditions.³⁸ The optimal pH values were 4–6 for CPAM, HMPAM-0.3, and HMPAM-0.5 and 5–

6 for HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0. As shown in Figure 12(B), the settlement rates initially decreased and then increased with increasing pH; they reached a minimum value at a pH of 6. With increasing DMDHAE contents, the settlement rates of the flocculants also decreased, and this was because a copolymer with a high intrinsic viscosity tends to form larger flocs that settle.³⁷

Effects of Salts on the Flocculation and Settlement Rates. The effects of NaCl on the flocculation and settlement rates are shown in Figure 13. As illustrated in Figure 13(A), the transmittance of the supernatant sharply decreased with increasing concentration of NaCl solution when CPAM was used as the flocculant, and this was due to the electrostatic repulsion increasing in the NaCl solution, which led to a low flocculation. When the DMDHAE content was above 0.5 mol %, HMPAM exhibited excellent flocculation in the NaCl solution, and the transmittance of the supernatants was higher than 95%. The polarity of the kaolin suspension increased with increasing concentration of NaCl solution, and this enhanced the hydrophobic associations of the HMPAM molecules, which formed larger

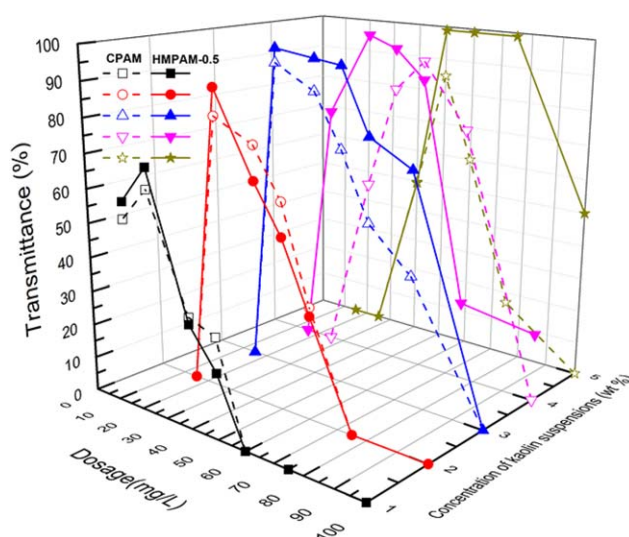


Figure 11. Effects of the initial concentration of the kaolin suspension (1–5 wt %) on flocculation. [Color figure can be viewed at wileyonlinelibrary.com]

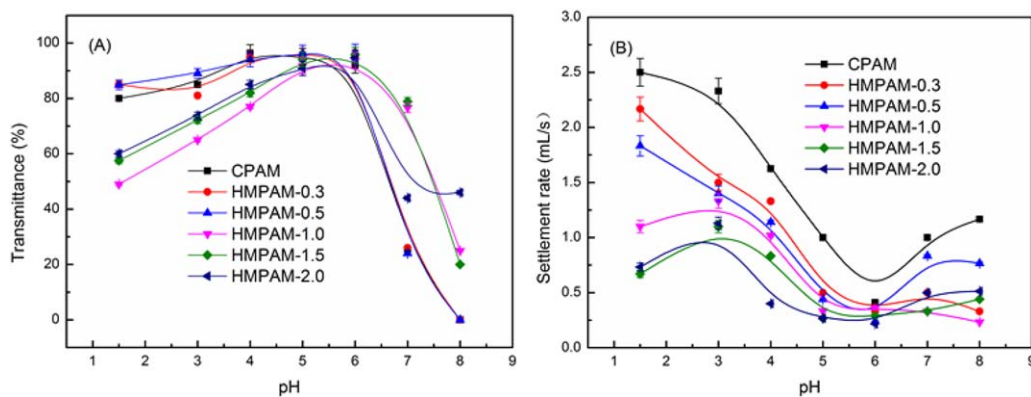


Figure 12. Effects of the pH on the (A) flocculation and (B) settlement rate. The concentrations of CPAM, HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L, and the concentrations of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 were each 75 mg/L. [Color figure can be viewed at wileyonlinelibrary.com]

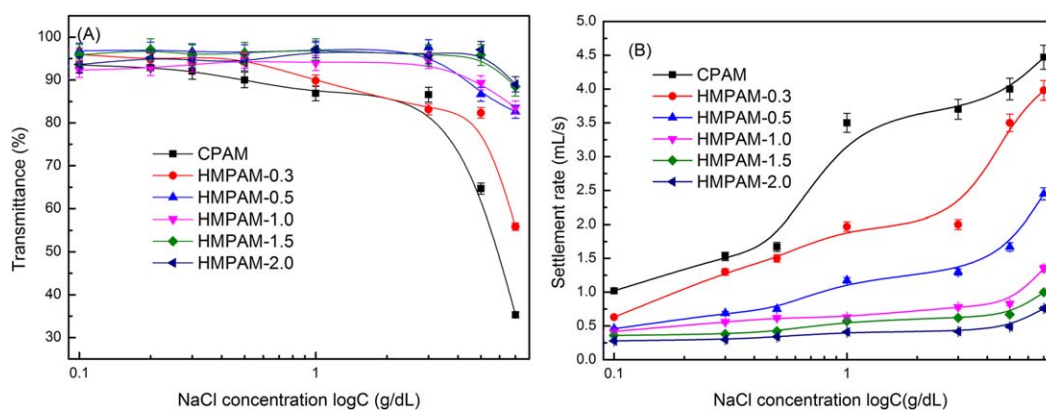


Figure 13. Effects of NaCl concentrations on the (A) flocculation and (B) settlement rate. The concentrations of CPAM, HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L; the concentrations of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 were each 75 mg/L. [Color figure can be viewed at wileyonlinelibrary.com]

flocs.²¹ Thereby, the flocculation efficiency was improved. When the concentration of NaCl was too high, the electrostatic repulsion increased, and this resulted in decreased flocculation. As shown in Figure 13(B), the settlement rates of all of the copolymers increased with the addition of NaCl. The combination of kaolin particles and HMPAM molecules was promoted to form larger flocs because of an increase in the charge density. The effects of CaCl_2 (< 1 wt %) on the flocculation and settlement

rates are shown in Figure 14. Because of the higher polarity, the flocculation of CPAM sharply decreased, and HMPAM showed better flocculation. These results indicate that HMPAM was suitable for flocculation in salt solutions.

Toxicity Tests. The results of the toxicity tests were obtained, as shown in Table I and Figure S5 (see the Supporting Information). The cells incubated with HMPAM retained the same

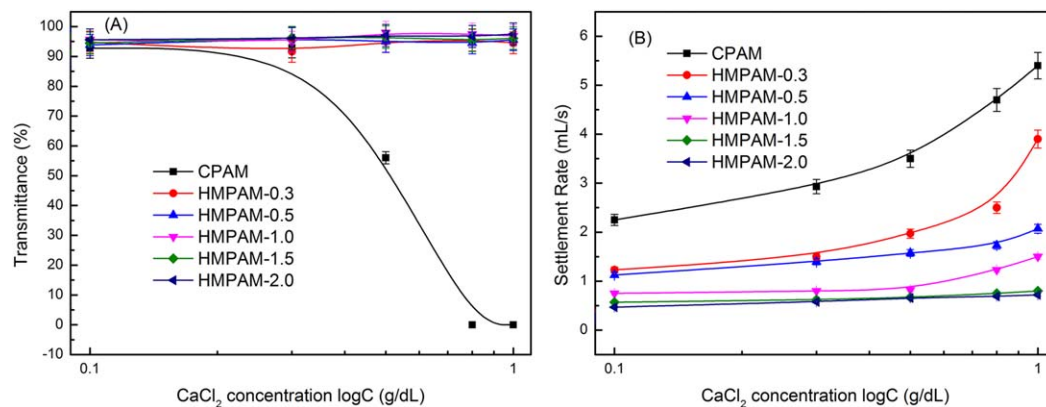
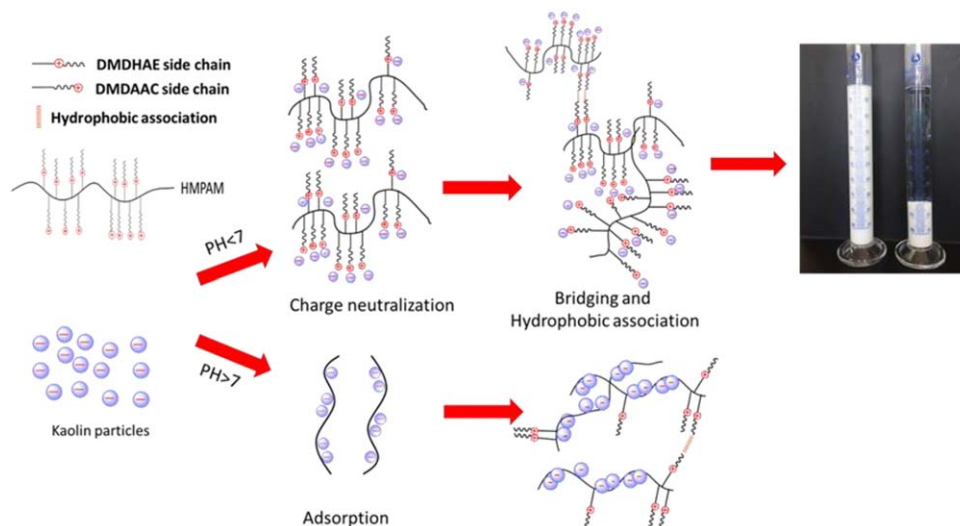


Figure 14. Effects of CaCl_2 concentrations on the (A) flocculation and (B) settlement rate. The concentrations of CPAM, HMPAM-0.3, and HMPAM-0.5 were each 25 mg/L; the concentrations of HMPAM-1.0, HMPAM-1.5, and HMPAM-2.0 were each 75 mg/L. [Color figure can be viewed at wileyonlinelibrary.com]

Table I. Cell Survival Rate of HMPM

	Cell survival rate (%)		
	500 mg/L	50 mg/L	5 mg/L
CPAM	100.4	99.85	100.3
HMPAM-0.5	101.25	100.8	101.9
HMPAM-1.0	99.8	102.45	100
HMPAM-1.5	99.1	102.2	100.8
HMPAM-2.0	96.05	100.1	102.2
Control test	99.45	99.8	102.8

**Figure 15.** Possible flocculation mechanism of a kaolin suspension with HMPAM. [Color figure can be viewed at wileyonlinelibrary.com]

phenotypical morphology as the control cells. Moreover, the cells cultured with HMPAM reached concentrations as high as 500 mg/L in 48 h, and the cell survival rate was about 100%. This demonstrated that the toxicity of HMPAM was negligible.

Flocculation Mechanism. A possible flocculation mechanism of the kaolin suspension with HMPAM is described in Figure 15. In acidic solution, HMPAM, which had positive charges, reduced the surface charges of kaolin particles through charge neutralization and the generation of numerous microflocs in water. Furthermore, these particles aggregated via regional static electricity and formed long molecular chains of HMPAM via bridging effects and hydrophobic associations to form larger flocs.³⁹ However, in an alkaline environment, OH⁻ neutralized the positive charges of flocculants, and charge neutralization exhibited an auxiliary role. Kaolin particles were mainly adsorbed on the surfaces of flocculants via van der Waals forces; this resulted in looser and lighter flocs that formed via bridging effects and hydrophobic associations during the agglomeration period.

CONCLUSIONS

In this study, we evaluated a novel rosin-based HMPAM and compared it with CPAM. HMPAM had strong hydrophobic associations because of the rosin structure introduced in HMPAM, and the CAC was about 0.7 wt %. HMPAM exhibited

excellent properties in terms of positive salinity thickening, shear resistance, and thickening. In the flocculation progress, HMPAM exhibited a flocculation capacity that was superior to that of CPAM and had a wider concentration range of flocculant than that of CPAM. HMPAM showed excellent flocculation performance in salt solution; HMPAM-0.5 also showed a significant flocculation performance for 3–5 wt % concentrations of kaolin suspensions.

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