

PREPARATION AND RETENTION PERFORMANCE OF CROSS-LINKED AND HYDROPHOBICALLY ASSOCIATING CATIONIC POLYACRYLAMIDE

Wei-Bing Wu,^{a,b,*} Jun Gu,^a Yi Jing,^a Xiao-Fan Zhou,^a and Hong-Qi Dai^a

“Water-in-water” emulsions of cross-linked and hydrophobically associating cationic polyacrylamide (CHCPAM) with cationic groups (methacryloethyl trimethyl ammonium chloride, DMC), hydrophobic groups (octadecyl methacrylate, OA), and cross-linked groups (N, N'-methylene bisacrylamide, MBA) were prepared by dispersion polymerization. The structure of the copolymer was confirmed by FTIR and ¹HNMR analyses. The prepared “water-in-water” emulsions possessed high solids content, low viscosity, good stability, and water solubility. Optical microscope images showed that the diameters of most emulsion particles were several microns. Appropriate concentrations of OA and MBA for a stable dispersion system were in the range of 0 to 0.1 wt% and 0 to 50 ppm. “Water-in-water” emulsions of CHCPAM can be directly used as a retention aid without further processing. They have a comparative retention rate, better anti-shearing ability, and better salt resistance, compared to commercial CPAM. The cross-linked structure of CHCPAM contributed to the anti-shearing ability. Intermolecular and intramolecular hydrophobic association of CHCPAM was the most important factor in improving resistance to salt.

Keywords: Hydrophobic association; Cross linking; Polyacrylamide; Dispersion polymerization; “Water-in-water”

Contact information: a: Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing, 210037, China; b: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510641, China * Corresponding author: wbwu@yahoo.cn

INTRODUCTION

As a kind of water-soluble polymer with the function of charge interaction, cationic polyacrylamide (CPAM) is widely used as a multi-functional additive in the papermaking industry (Wen *et al.* 2008). Most CPAM products, both in China and worldwide, are of linear structure, which usually creates problems associated with reconfiguration and diffusion when such products are used as retention and drainage aids (Liu *et al.* 2006). Due to their electrically charged nature and linear structure, their application is limited in the case of modern paper machines having closed white water systems as well as high shear force (Hulkko and Deng 1999; Shi *et al.* 1997; Yuan *et al.* 2011). Recently, highly branched polyelectrolytes have been developed that have much higher flocculation efficiency than linear CPAM (Peng and Zhao 2007; Shi *et al.* 1997). Similar to a highly branched polymer, a cross-linked cationic polyacrylamide (CCPAM) can keep its 3D conformation after it is adsorbed to a solid surface due to its compact

structure (Valette *et al.* 2002). The resulting molecular shape gives better performance for dissolved and colloidal substance (DCS) fixation to the fibers due to the extension of the polymer outside the electrostatic double layer of the surface (Ondaral *et al.* 2008). In addition, CCPAM polymers can maintain the linkage between fibers even under high shear force because of the cross-linked structure (Neff and Ryles 1994). Additionally, hydrophobically associating cationic polyacrylamide (HACPAM) is another kind of water-soluble polymer with hydrophobic groups in the main chain (Chen *et al.* 2012; Feng *et al.* 2005). In the polymer solution, an intermolecular and intramolecular hydrophobically associating interaction can form reversible and “physical” reticulation (Yang *et al.* 2010; Li *et al.* 2011), which is similar to the cross-linked CPAM. Even more important is that the charge of the medium when HACPAM is used as retention aid will have little interference on the flocculation effect from hydrophobic interaction and physical reticulation.

Conventional CPAMs are solutions, powders, or water-in-oil emulsions. All of them have disadvantages in synthesis or use (Feng *et al.* 2009), such as low solids content, difficulty in controlling the molecular weight, and high transport cost. The procedure of producing and dissolving CPAM powder is very complex and expensive; it requires special smashing, drying, mixing, and heating equipment. “Water-in-oil” emulsions require additional phase inversion reagents, and high amounts of hydrocarbon compounds enter the water system of papermaking complexes. Waste and pollution cannot be avoided in the production process. The disadvantages of these three types of CPAM limit their application in the papermaking industry. Thus, looking for less expensive and more environmentally friendly ways to synthesize CPAM has become the focus for current research.

Dispersion polymerization is a useful method for preparing micron-size mono-dispersed polymer particles in a single batch process. The method may be defined as a type of precipitation polymerization in which the polymerization of the monomers is carried out in the presence of a suitable polymeric stabilizer, soluble in a reaction medium. Both the monomers and the stabilizer have to be soluble in the medium, but the formed polymer must be insoluble (Kawaguchi and Ito 2005). During the past 20 years, there has been considerable interest in using more polar solvents as the continuous phase, an approach by which more monomers can be polymerized. Until now, styrene (Paine *et al.* 1990; Lee *et al.* 2006) and methyl methacrylate (Kim *et al.* 2006) have been the most studied monomer systems. Utilizing dispersion polymerization in an aqueous solution is an attractive way to produce water-soluble PAM. However, related studies are rather scarce. Some researchers have carried out dispersion polymerization of acrylamide (Ray and Mandal 1997; Wu *et al.* 2010) in aqueous alcohol media or hydrophilic cationic monomers (Chen *et al.* 2006) in aqueous salt media. Recently, “water-in-water” dispersion polymerization of acrylic acid in an aqueous solution of ammonium sulfate was reported (Liu *et al.* 2007; Wang *et al.* 2009). In this paper, cross-linked and hydrophobically associating cationic polyacrylamide (CHCPAM) “water-in-water” emulsions were synthesized by dispersion polymerization and their retention performance was studied.

EXPERIMENTAL

Materials

Acrylamide (AM) methacrylateethyl trimethyl ammonium chloride (DMC, 78%) was of chemical grade; bleached broad-leaved pulp (44 °SR) and ground calcium carbonate (GCC) were supplied by Gold East Paper Co. Ltd. The $(\text{NH}_4)_2\text{SO}_4$, NaCl, N, N'-methylene bisacrylamide (MBA), octadecyl methacrylate (OA), ammonium persulfate (APS), NaHSO_3 , and ethanol were all analytical grade.

Preparation of CHCPAM “Water-in-Water” Emulsions

Synthesis of CHCPAM by dispersion polymerization in aqueous phase typically proceeds as follows: In a four-neck flask equipped with thermometer and mixer, stabilizer PVP K30 (1.5 g), $(\text{NH}_4)_2\text{SO}_4$ (10.0 g), AM (10.0 g), DMC (1.0 g), and a specified amount of OA (listed in Table 1) were dissolved in distilled water (60 g). After a homogeneous solution formed in the flask, the solution was diluted to 88 g with distilled water and deoxygenated by bubbling nitrogen gas for 30 min at room temperature. Then the flask was placed in a 45 °C water bath. The APS (0.2 g) and NaHSO_3 (0.2 g) dissolved in distilled water (8 g) were added continuously, and the addition was completed within 1 h under nitrogen protection at a stirring rate of 200 rpm. Thirty minutes later, continuous addition of a specified amount of MBA (listed in Table 1) in ethanol (2 g) was completed within 1 h. The mixture was then heated to 60 °C and reacted for 24 h. After cooling to room temperature, milky white emulsions were obtained and kept in a cool, dark place.

Detection and Characterization

The prepared emulsion was dialyzed in distilled water, precipitated in ethanol, and dissolved in distilled water again. The above process was repeated three times to obtain pure CHCPAM. The resulting solid was dried in a vacuum at 40 °C for 24 h. The apparent viscosity (η) was measured with a NDJ-79 viscosimeter at 30 °C. The morphology of the CHCPAM emulsion was observed with an Olympus CX21 digital optical microscope. The particle size was estimated using an image analysis system (Image-pro Express 4.0, Media Cybernetics Inc.) and ^1H NMR spectroscopy was obtained in D_2O from a Bruker DRX (500 MHz, relative to TMS). The molecular weight (M) was measured using method GB 12005.10-92.

Retention Experiment

Pulp (2 g, oven dried) in 800 mL water was disintegrated at 3000 rpm in a fluffer, then 10 wt% GCC (relative to oven dry pulp) was added under stirring. Afterwards, the mixture was diluted to 1000 mL. The first pass retention rate (FPR) and first pass retention rate of fines (FPR_f) were detected according to the standard procedure from DDJ-DFR05 dynamic drainage jar. The filtrate was divided into two parts, and their concentrations were measured. Then, they were filtered and dried at 105 °C for 4 h. The ash content was calculated after calcination in a muffle furnace at 800 °C for 3 h.

RESULTS AND DISCUSSION

Physical and Chemical Character of CHCPAM

The prepared CHCPAM had the appearance of a milky white “water-in-water” emulsion, where no traditional “oil” phase exists, but a small amount of dispersant is used to stabilize the system. Figure 1 shows the optical images of such a “water-in-water” emulsion. Most of particles were spherical, but oval and nonspherical particles were also observed. The formation of large particles and nonspherical particles indicates that the coalescence of small particles had taken place during the polymerization process. The particle size of the “water-in-water” emulsions was estimated to be in the range of several hundred nanometers and several micrometers with a comparatively broad size distribution.

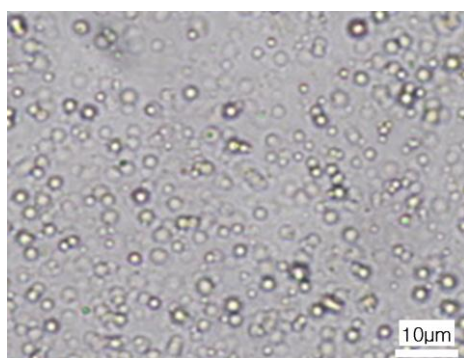


Fig. 1. Optical images of typical CHCPAM emulsion

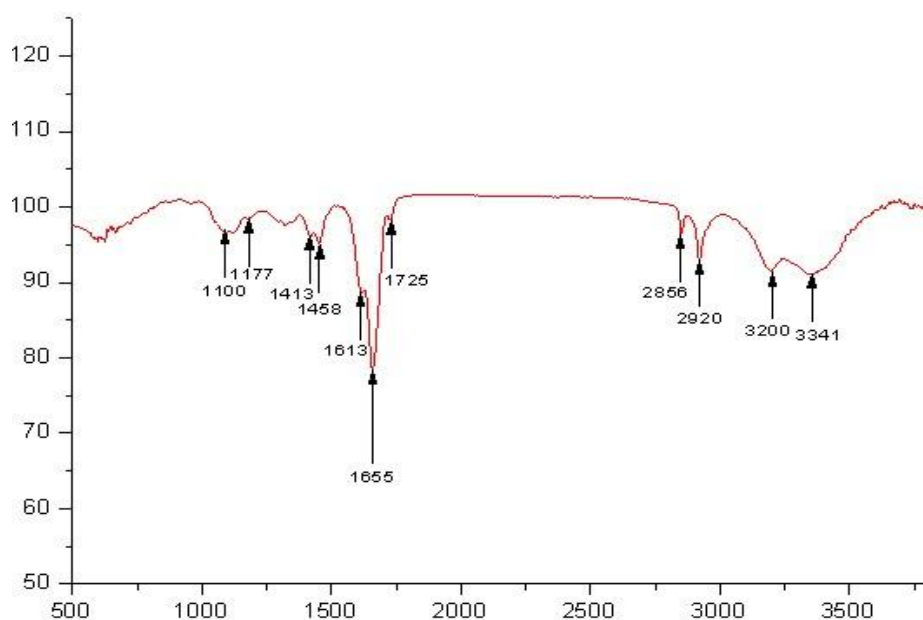


Fig. 2. FTIR spectrum of typical CHCPAM copolymer

The solids contents of the prepared CHCPAM emulsions were around 10 wt%, which is much higher than commercial CPAM solution. The viscosity (η) of the “water-in-water” emulsion was found to be much lower than that of polymer solution at the same concentration. The solubility of CHCPAM emulsion in water was also investigated. The “water-in-water” emulsions could be diluted to any concentration, requiring no dissolving time, while the preparation of 1 wt% CPAM solution from purified CPAM powder requires 1 h in order to become fully dissolved under stirring. The emulsions also have good stability, since they can be stored for several months without precipitation.

Figure 2 illustrates the FTIR spectrum of representative CHCPAM. The peaks at wave numbers 3341 and 3200 cm^{-1} are assigned to the amido function. The peak at 2920 cm^{-1} is associated with the C-H stretching vibration of the backbone of the CHCPAM. The peak at 1725 cm^{-1} is assigned to the carbonyl groups of ester in DMC and OA. The intense peak at 1655 cm^{-1} comes from the vibrating absorption of carbonyl groups in AM. The peaks at 1458, 1413, and 1177 cm^{-1} are attributed to methyl groups of ammonium and quaternary ammonium in DMC moiety (Wang *et al.* 2006). The appearance of these adsorption peaks proves the successful copolymerization of main monomers.

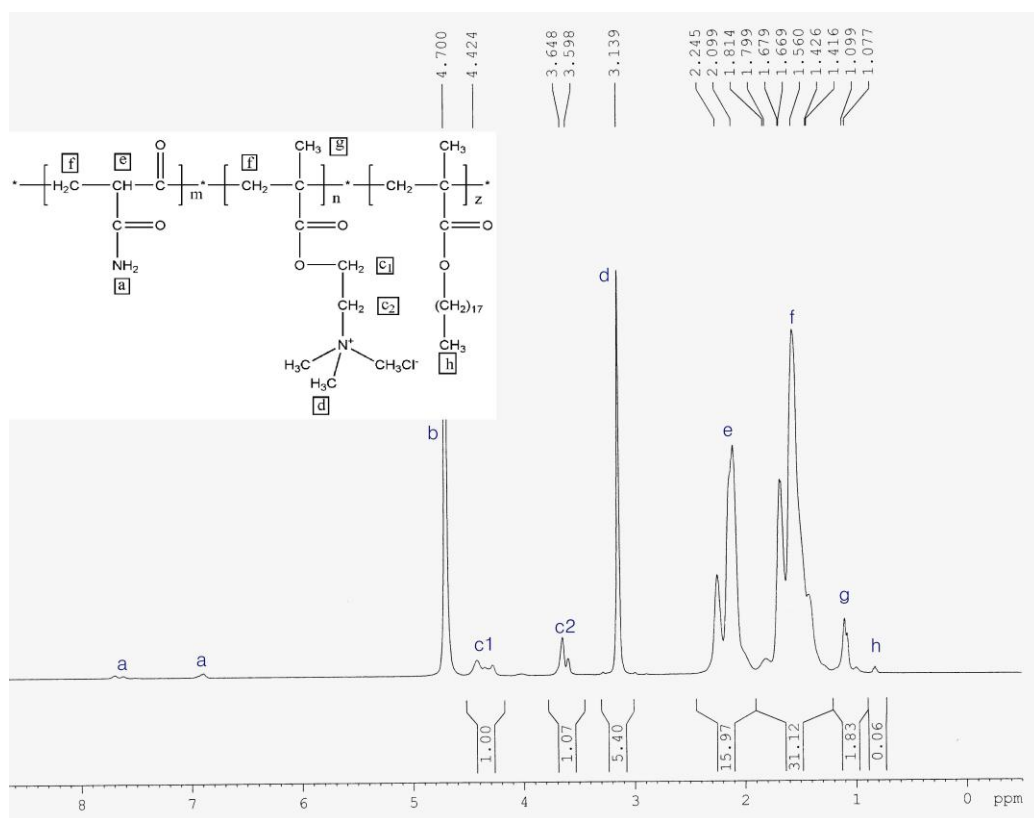


Fig. 3. ^1H NMR spectrum of typical CHCPAM copolymer

Figure 3 shows the ^1H NMR spectrum of CHCPAM in D_2O . The approximate composition of the copolymer is analyzed from the spectrum. All the ^1H signals of different groups are marked with letters to correspond with the molecular structure, except for the signals of D_2O at 4.7 ppm (b). ^1H signals from the backbone methine and

methylene protons appear in the range of 1.07 to 2.25 ppm (e, f, g). The $-NH-$ and $-NH_2-$ groups usually give rise to weak signals at 6.91 and 7.77 ppm (a) in D_2O . A sharp singlet at 3.14 ppm (d) is assigned to the three equivalent methyl groups of ammonium. 1H signals from the methyl group of OA moiety appear at 0.85 ppm (h). The analytical results of the 1H NMR spectrum provide further support for the formation of copolymerization of AM, OA, and DMC. Since the added amount of MBA is extremely low, the characteristic peaks are not observed in the spectrum.

Effects of MBA and OA on the Polymerization System

There are many factors that influence the synthesis of CHCPAM “water-in-water” emulsions by dispersion polymerization. In these experiments, stable “water-in-water” emulsions were formed when C_{AM} was lower than 15 wt%, while gel was obtained at high C_{AM} (>20 wt%). Therefore C_{AM} in the subsequent experiments was fixed at 10 wt%. This paper mainly focused on the effect of the concentrations of cross-linked reagent (C_{MBA}) and hydrophobic monomer (C_{OA}) on the dispersion polymerization.

A cross-linked reagent has important effects on the properties of CHCPAM “water-in-water” emulsion. MBA is an effective cross-linked reagent with two active double bonds, which can change a linear chain into a netlike structure (Lee *et al.* 2006). Table 1 presents η and M values of CHCPAM with different dosages of MBA. With an increase in the dosage of MBA, both η and M first increased and then decreased. In these experiments, the inflection point appeared at the 5 ppm dosage. When the dosage of MBA is lower than the value of the inflection point, polymer chains are inclined to form branched structures rather than netlike structures, since a small quantity of cross-linked reagent cannot result in enough joints between polymer chains. In this range, branched polymers have long polymer chains and a stretching structure. The increase in M was observed before the inflection point. This may be explained by the fact that the extent of branching of the polymer rises when more MBA is added. However, when the dosage of MBA exceeds the inflection point, the increasing joints between polymer chains tend to result in netlike structures rather than branched structures. Since polymer could become locally densified with excessive cross-linking, M was calculated based on the viscosity method and was found to decrease after the inflection point. The effect of the MBA dosage on η was the same as that on M . An inflection point at 5 ppm also was apparent, as shown in Table 1. For “water-in-water” dispersion polymerization, there are some free polymers dissolved in the disperse phase besides those embedded in the emulsion particles. At a relatively low dosage of MBA before the inflection point, the increase in η can be attributed to the increase in the M of free dissolved branched CHCPAM, which will cause the enhanced interaction between polymer chains in the disperse phase. At a relatively high dosage of MBA after the inflection point, netlike CHCPAMs tend to be formed. They are more easily captured by emulsion particles since they are less soluble. Therefore, fewer free polymers are dissolved in the disperse phase, and η is reduced. The number of emulsion particles is another reason for the change of η . It is known that η is also related to the interaction between emulsion particles. More particles lead to stronger interaction between polymer chains and a larger η . The number of emulsion particles is inversely proportional to their average diameter (D_{av}) at the same C_{AM} . The change in D_{av} shown in Table 1 indicates that the number of emulsion particles first increased and then

decreased with an increase in the dosage of MBA. The trend is in accordance with that of η . A possible reason for the reduction of D_{av} before the inflection point is that emulsion particles are more stable when branched CHCPAM macromolecules are absorbed on them. The increase in D_{av} after the inflection point may be attributed to the formation of netlike CHCPAM with compacted structure, which causes the coagulation of small particles.

Hydrophobic monomers have the function of forming netlike structures in a manner similar to cross-linked monomers. The difference is that the netlike structure is not covalently linked; instead it is hydrophobically associated. Table 1 lists the η and M with different dosages of OA. The corresponding η of emulsion shows a descending trend when the dosage of OA is increased. On the contrary, the M of CHCPAM shows an ascending trend. The increase in M can be attributed to the hydrophobic associations between polymer chains, which cause larger measured values of M_w . It is believed that intermolecular hydrophobic associations can, to some extent, form “branched” polymers like cross-linked reagents, which further cause an increase in the measured value of M . However, the above relationship between the dosage of OA and M does not exist throughout the range of experimentation. In these experiments, there was a sharp decline in M when the dosage of OA was more than 0.2%. Intermolecular and intramolecular hydrophobic associations that are too intense will result in the shrinkage of polymer and a reduction in the measured value of M . In most situations, an inverse correlation between D_{av} and M has been noted for dispersion polymerization (Cho *et al.* 2002). The result was different in these experiments possibly due to the cross-linking effect and hydrophobic association.

Table 1. Details of CHCPAM Emulsions under Different Polymerization Conditions

Sample	P-0	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10	P-11
$C_{AM}(\%)$ *	10	10	10	10	10	10	10	10	10	10	10	10
$C_{DMC}(\%)$ *	1	1	1	1	1	1	1	1	1	1	1	1
$C_{OA}(\%)$ *	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0	0.025	0.050	0.075
$C_{MBA}(\text{ppm})$ *	0	0	2	5	10	15	25	50	10	10	10	10
$D_{av}(\mu\text{m})$	2.3	2.7	2.3	1.5	1.8	1.9	2.5	2.7	2.6	2.4	2.2	2.0
$\eta(\text{mPa}\cdot\text{s})$	620	240	600	2130	2000	1850	380	200	3650	2950	2800	2600
$M(\times 10^4 \text{ g/mol})$	26.3	19.8	31.5	81.9	61.5	51.6	26.0	22.6	32.6	40.6	42.5	48.4

* relative to the mass of reaction mixture; C_{DMC} : The concentration of DMC; P-C: Commercial CPAM ($M \approx 2,700,000 \text{ g/mol}$)

Retention Performance of CHCPAM

Effect of the dosage of CHCPAM

The dosage of CHCPAM is a very important factor that not only relates to the retention performance, but is also regarded as the main reference index of economic evaluation. Figure 4 presents FPR and FPR_f of several types of CPAM with different dosages of CHCPAM. At the same dosage, P-4 had a comparative retention rate to P-C

and a better retention rate than P-0, P-1, and P-8. P-1 and P-8 showed better retention performance compared to P-0. This means that both the cross-linking effect and hydrophobic association can enhance the flocculation ability. With an increase in the CHCPAM dosage, both FPR and FPR_f first increased and then dropped appreciably. The change in FPR_f is more notable. The reason for the decrease in the retention rate at large dosages may be that excessive CPAM causes too much cationic local charge and plays the role of dispersant. In addition, excessive CPAM could result in large flocs and affect paper formation. The optimal dosage was about 600 ppm, based on the mass of oven-dry pulp.

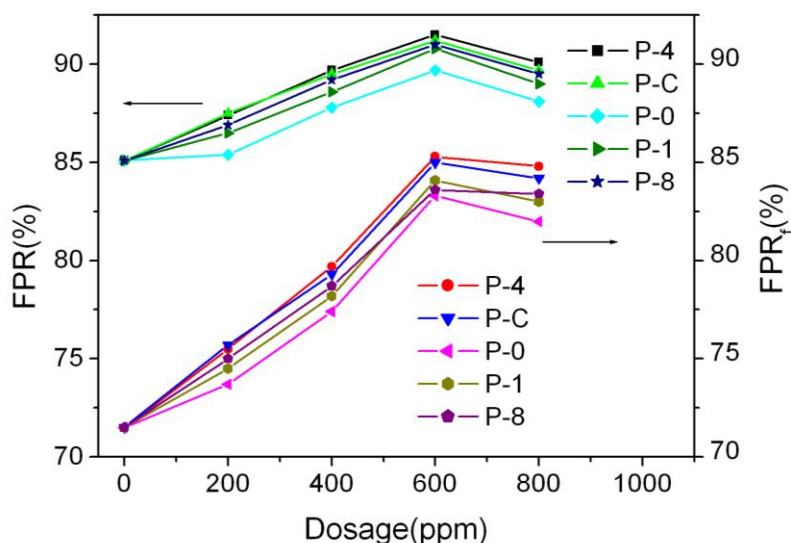


Fig. 4. Retention rate of several selected CHCPAM at different dosages (relative to the oven-dry pulp). Contacting time: 90 s; Stirring rate of shearing: 650 r/min; Stirring rate of drainage: 300 r/min

Effect of shear force

Shear stress is an important factor affecting retention aid performance. Besides the enhancement of the contact and interaction of fibers, fine fibers, and fillers, shear stress can limit the production of large flocs and improve paper formation. However, high shear stress will destroy the formed flocculation and further reduce the retention efficiency (Shin *et al.* 1997). The strong shear stress in the wet end of modern paper machine requires a new type of retention aid. CHCPAM is specially designed for high shear stress conditions.

Figure 5 shows the relationship between the retention performance and stirring rate. As the stirring rate was increased, FPR and FPR_f of P-4, P-1, and P-8 dropped appreciably, while those of P-0 and P-C decreased markedly. This means that both the hydrophobic association and cross-linked structure existing in CHCPAM improved the anti-shearing ability. This ability was further enhanced when the two functions appeared simultaneously, since P-4 showed better retention performance than P-1 and P-8. The main reason is that the hydrophobic association and cross-linking effect can increase the number of junctures among molecular chains. Flocculation bridged by CHCPAM is prone to be preserved under high shear force.

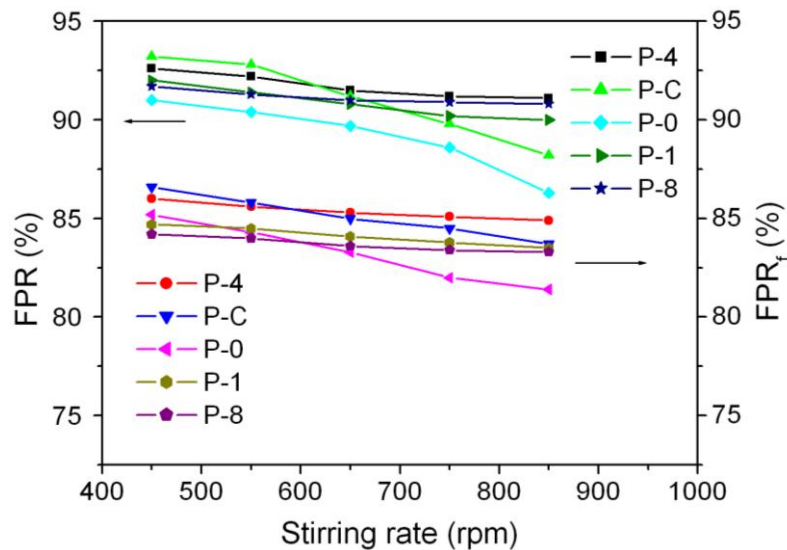


Fig. 5. Retention rates of several selected CHCPAM at a different stirring rate of shearing. The dosage of CHCPAM: 600 ppm; Contacting time: 90 s; Stirring rate of drainage: 300 r/min.

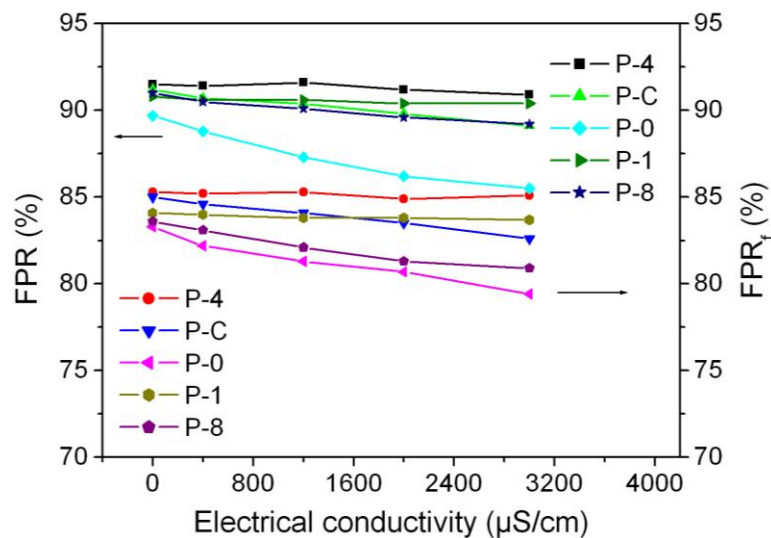


Fig. 6. Retention rates of several selected samples at different electrical conductivity. The dosage of CHCPAM: 400 ppm, Contacting time: 90 s, Stirring rate of contacting: 650 r/min; Stirring rate of drainage: 300 r/min

Effect of electrical conductivity

Closed white water systems typically have much more DCS than open systems due to the use of little fresh water. In the complete closure of white water circuit, the electrical conductivity can be considerably high because of the continuously accumulated inorganic salts. This can lead to the loss of paper quality (Hulkko and Deng 1999). When added to the slurry, common CPAM intensely adsorbed to the fiber surface and formed flocculation by the charge patch or bridging function. However, high electrical conduc-

tivity will weaken the efficiency of ionic additives due to charge shielding. To conquer this defect, hydrophobic groups were copolymerized into the polyacrylamide chains.

Figure 6 illustrates the retention performance under differing electrical conductivity. When the electrical conductivity increased, the retention rates of P-4 and P-1 with hydrophobic groups remained almost constant, while those of P-C, P-0, and P-8 without hydrophobic groups showed an obvious decrease. The difference in the salt resistance is mainly attributed to the hydrophobic association function, which is not influenced by the charge shielding. In addition, the intermolecular and intramolecular hydrophobic associations can form physical and reversible “networks” with good extensibility and trapping ability (Li *et al.* 2011), which can improve the performance of flocculation based on the charge function. Because P-4 shows the best retention performance over the entire range of electrical conductivity, the described effect can be proven.

CONCLUSIONS

CHCPAM with cationic, cross-linked, and hydrophobic moiety in the polymer chain was prepared by “water-in-water” dispersion polymerization. The CHCPAM emulsions are of relatively high solids content, low apparent viscosity, and good solubility. As a retention aid, CHCPAM possess better anti-shearing ability and salt resistance than a commercial CPAM.

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REFERENCES CITED

- Chen, D. N., Liu, X. G., Yue, Y. M., Zhang, W. D., and Wang, P. X. (2006). “Dispersion copolymerization of acrylamide with quaternary ammonium cationic monomer in aqueous salts solution,” *Eur. Polym. J.* 42, 1284-1297.
- Chen, H., Ye, Z., Han, L., and Luo, P. (2012). “Studies on the self-assembly behavior of the hydrophobically associating polyacrylamide,” *J. Appl. Polym. Sci.* 123, 2397-2405.
- Feng, Y. J., Billon, L., and Grassl, B. (2005). “Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification. II. Properties of non-hydrolyzed polymers in pure water and brine,” *Polymer* 46, 9283-9285.

- Feng, Y. J., Lv, Y. L., and Li, X. J. (2009). "Polyacrylamide based "water-in-water" emulsion: A novel environmental-friendly polymeric material," *Appl. Tech.* 17, 11-15.
- Hulkko, V. M., and Deng Y. (1999). "Effects of water-soluble inorganic salts and organic materials on the performance of different polymer retention aids," *J. Pulp Pap. Sci.* 25, 378-383.
- Kawaguchi, S., and Ito, K. (2005). "Dispersion polymerization," *Adv. Polym. Sci.* 175, 299-328.
- Kim, O. H., Lee, K., Kim, K., Lee, B. H., and Choe, S. (2006). "Effect of PVA in dispersion polymerization of MMA," *Polymer* 47, 1953-1959.
- Lee, K., Jung, H., Kim, S. Y., Lee, B. H., and Choe, S. (2006). "Synthesis and characterization of cross-type vinylurethane macromonomer (C-VUM) and their application in the dispersion polymerization of styrene," *Polymer* 47, 1830-1836.
- Li, P., Shen, Y., and Yang, X. (2011). "Solution properties and flocculation of hydrophobically associating cationic fluorinated polyacrylamide," *Polym. Bull.* 67, 961-973.
- Liu, W. X., and Qiu, H. Y. (2006). *Wet End Chemistry*, Chemical Industry Press, Beijing.
- Liu, X., Xiang, S., Yue, Y., Su, X., Zhang, W., Song, C., and Wang, P. (2007). "Preparation of poly(acrylamide-co-acrylic acid) aqueous latex dispersions using anionic polyelectrolyte as stabilizer," *Colloid Surf. A-Physicochem. Eng. Asp.* 311, 131-139.
- Neff, R. E., and Ryles, R. G. (1994). "Cross-linked cationic polymeric microparticles," US Patent, US 5340865.
- Ondaral, S., Usta, M., Gumusderelioglu, M., Wagberg, L., and Ondaral, M. (2008). "Fixation of dissolved and colloidal substances on fibers and silicon oxides surfaces using water soluble cross-linked cationic polymers," *Cell. Chem. Tech.* 42, 61-69.
- Paine, A. J., Luymes, W., and McNulty, J. (1990). "Dispersion polymerization of styrene in polar solvents: Influence of reaction parameters on particle size and molecular weight in poly(N-vinylpyrrolidone)-stabilized reactions," *Macromolecules* 23, 3104-3109.
- Peng, X., and Zhao, J. (2007). "Synthesis and application of polyoxyethylene-grafted cationic polyamidoamine dendrimers as retention aids," *J. Appl. Polym. Sci.* 106, 3468-3473.
- Ray, B., and Mandal, B. M. (1997). "Dispersion polymerization of acrylamide," *Langmuir* 13, 2191-2196.
- Shin, J.-H., Han, S. H., Sohn, C., Ow, S. K., and Mah, S. (1997). "Highly branched cationic polyelectrolytes: Filler flocculation," *Tappi J.* 80(11), 179-185.
- Valette, L., Pascault, J.-P., and Magny, B. (2002). "Methacrylic cross-linked polymer microparticles: Synthesis by dispersion polymerization and particle characterization," *Macromol. Mater. Eng.* 287, 31-40.
- Wang, J. P., Chen, Y. Z., Ge, X. W., and Yu, H. Q. (2006). "Gamma radiation- induced grafting of a cationic monomer onto chitosan as a flocculant," *Chemosphere* 66, 1752-1757.

- Wang, L.-J., Wang, J.-P., Zhang, S.-J., Chen, Y.-Z., Yuan, S.-J., Sheng, G.-P., and Yu H.-Q. (2009). "A water-soluble cationic flocculant synthesized by dispersion polymerization in aqueous salts solution," *Sep. Purif. Tech.* 67, 331-335
- Wen, Z. Q., Zhong, H., Fu, J. G., and Zhang, W. X. (2008). "Research survey on cationic polyacrylamide flocculant," *Mater. Res. Appl.* 2(2), 98-102.
- Wu, Y., Wang, C., and Xu, J. (2010). "Aqueous dispersion polymerization of amphoteric polyacrylamide," *J. Appl. Polym. Sci.* 115, 1131-1137.
- Yang, Z. L., Gao, B. Y., Li, C. X., Yue, Q. Y., and Liu, B. (2010). "Synthesis and characterization of hydrophobically associating cationic polyacrylamide," *Chem. Eng. J.* 161, 27-33.
- Yuan, G., Dai, H., Ye, C., Zhang, Y., and Wang, Z. (2011). "Adsorption of Ca(II) from aqueous solution onto cellulose fiber and its impact on the papermaking process," *BioResources* 6(3), 2790-2804.

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