β-Cyclodextrin Modified Cationic Acrylamide Polymers for Flocculating Waste Drilling Fluids

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ABSTRACT: In this article, the P(AM/A-β-CD/DMDAAC) is used as flocculant. The synthesis and characterization of the cationic poly-acrylamide flocculant modified by β-cyclodextrin have been studied in the early article. This article stresses its excellent flocculated performance and mechanism. In the flocculated process, the bridging flocculation played a dominant role. Through the flocculation experiments, it can be seen that the flocculating rate of the P(AM/A-β-CD/DMDAAC) on four solutions can go up to 93.4%, 89.7%, 85.1%, and 96.7%, respectively. As can be seen from experiment data, the flocculated property of P(AM/A-β-CD/DMDAAC) is superior to polyacrylamide and poly (dimethyl diallyl ammonium chloride). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40197.

INTRODUCTION

Aggregation processes play a critical role in many industrial and environmental strategies. A better understanding and control of particle aggregation can serve a wide range of traditional industries such as wastewater treatment.[1] Flocculation is widely used in many wastewater systems for which the removal of suspended matter is an important waste stream cleanup stage. All types of industrial wastewater treatment is a few application areas of flocculation. In recent years, the organic polymer flocculants are being paid more attention because of its good properties, such as less doses, wider range of pH, better performances on salt resistance, and so on. As a typical flocculant, polyacrylamide and its derivatives are widely used to turn off colloidal stability and thus initiate flocculation. And the cationic polyacrylamide flocculants are extensively applicated in the process of wastewater treatment because the suspended colloidal particles in the sewage are negatively charged. During cationic polyacrylamide-induced flocculation, polymer adsorption onto colloid surfaces is vital.[2] On the basis of the polymer adsorption theory under equilibrium conditions, many flocculation mechanisms have been proposed, such as bridging, patching, and charge neutralization mechanisms.[3] For cationic polyacrylamide of high molecular weight, the increased ionic strength can reduce the slectrical double-layer thickness of a particle and thus can enable two particles to approach one another more closely, which decreases the bridging distance. Therefore, the polymer must span in order to induce flocculation.[4] Dimethyl diallylammonium chloride is an important cationic monomer due to its properties of higher charge density and water soluble. Because of cationic modified polyacrylamide flocculants with low relative molecular mass, not conducive to flocculate with pollutants exposure and settlement, preparation with macromolecular side base of acrylamide polymer is particularly important. In the study of the host compounds, whose structures have been confirmed cyclodextrin (CD) with a large proportion, and its inclusion effect for surfactant has been proved to be relatively stable.[5,6]

The focus of this article is to illustrate the flocculent property of a cationic polyacrylamide flocculant modified by β-cyclodextrin and to compare the flocculent property of the polymer with polyacrylamide and poly(dimethyl diallyl ammonium chloride), respectively.

EXPERIMENTAL

Materials and Synthesis of P(AM/A-β-CD/DMDAAC)

The materials and synthesis of P(AM/A-β-CD/DMDAAC) were given by an early article.[5] In addition, the synthetic process of P(AM/A-β-CD/DMDAAC) was shown in Figure 1.
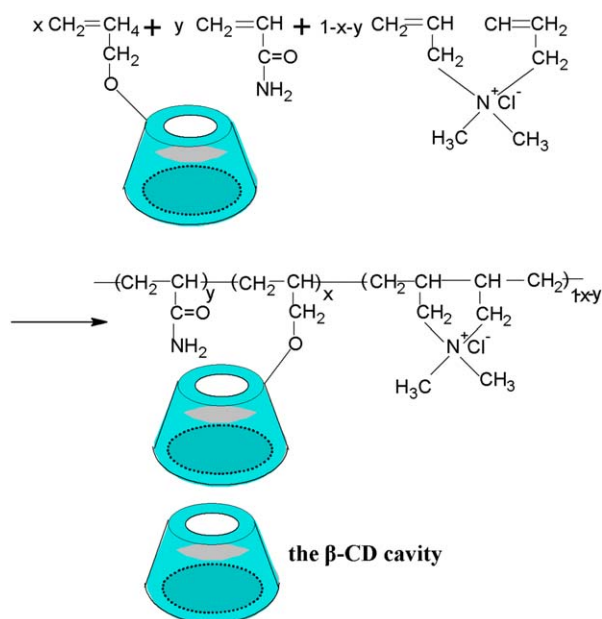
CHARACTERIZATION

Infrared Spectroscopy

The IR spectra of P(AM/A-β-CD/DMDAAC) was recorded by a Nicolet Nexus 470 spectrometer (on KBr tablets). The infrared spectra was obtained in the range of 4500–500 cm^{-1}.[5,6]

Scanning Electron Microscope

The surface morphologies of P (AM/A-β-CD/DMDAAC) was scanned by the scanning electron microscope (SEM;PHLIPS-XL30, Holland).[5,6]

Figure 1. The synthetic process of P (AM/A-β-CD/DMDAAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flocculation Experiments

To compare the flocculated effect of the polymer with PAM and PDMDAAC, the flocculation experiments of kaolin, surfactant, oily wastewater, and waste drilling fluids were carried out. Kaolin and sodium dodecyl sulfonate were purchased from the Kelong Chemical Reagent Factory (Chengdu, China).[7] The oil-field wastewater was obtained from Liaohe oil field, which was used in the flocculation experiments. In addition, the waste drilling fluids was provided by Southwest Petroleum University (Chengdu, China).The kaolin and the surfactant solutions were prepared with kaolin and sodium dodecyl sulfonate at a concentration of 2000 mg/L, respectively. The aqueous solutions of P (AM), P (DMDAAC) and P(AM/A-β-CD/DMDAAC) were respectively prepared with deionized water. Specifically, the simulation solutions of 100 mL were transferred into the measuring cylinder with a plug and then the flocculants were added. The mixtures in the measuring cylinder were inverted 10 times repeatedly. Thereafter, the solutions were allowed to be settled for 50 min.After settling, samples were collected at the top of the settling measuring cylinder (top 30 mm of water surface) using a pipette and analyzed by UV spectrophotometer to measure the light transmittance at wavelength of 670 nm.[8,9]

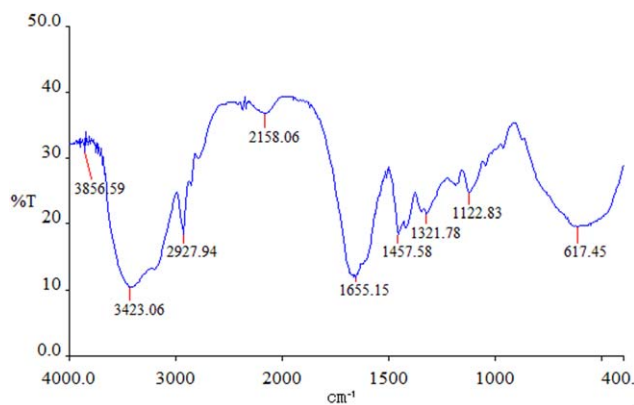The Flocculating rate was calculated by eq. (1):

$$\text{Flocculating rate } (\%) = (T_0 - T)/T_0 \times 100 \qquad (1)$$

where T_0 and T were the light transmittance of the solutions before and after flocculation, respectively.[10–12]

RESULTS AND DISCUSSION

FTIR Spectra

The FTIR spectra of P (AM/A-β-CD/DMDAAC) was illustrated in the previous study.[5] And the FTIR spectra of P (AM/A-β-CD/DMDAAC) was listed in Figure 2.
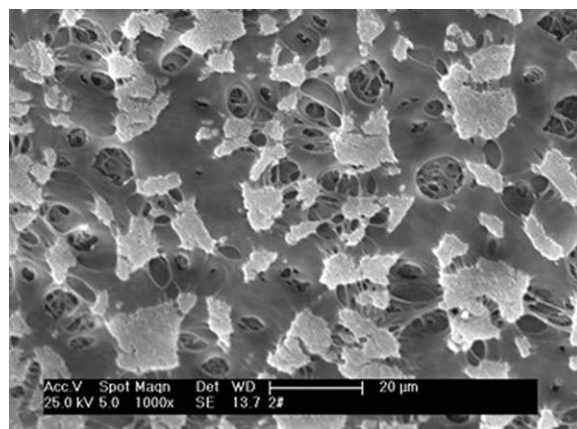

Figure 2. The FTIR spectra of P (AM/A-β-CD/DMDAAC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

From Figure 2, the stretching vibration peaks of N—H and C=O bond in the amide groups(-CONH$_2$) appeared at 3450 cm^{-1} and 1655 cm^{-1}, respectively. The peaks at 930 cm^{-1} and 575 cm^{-1} corresponded to the skeleton vibrations of allyl-β-cyclodextrin. Both of them proved that the cationic acrylamide polymer contained the structures of AM and A-β-CD. Furthermore, the stretching vibration peak of C—H bond of methyl and methylene in DMDAAC appeared at 2927 cm^{-1}, and the bending vibration absorption peak of double methyl bonded with N$^+$ presented at 1457 cm^{-1}. The peaks at 1321 cm^{-1} and 966 cm^{-1} were respectively assigned to the symmetric bending vibration peak of methyl and the stretching vibration absorption peak of quaternary ammonium (–(CH2)N(CH3)2Cl). Above all, a conclusion could be reached that cationic acrylamide polymer contained the structures of AM, A-β-CD and DMDAAC.

Surface Morphologies

Similarly, the surface morphologies of P (AM/A-β-CD/DMDAAC) can also be seen from the early article.[5] The scanning electron microscopy image of P(AM/A-β-CD/DMDAAC) indicated that the cationic polymer was typical gel-network structure (seen in Figure 3[5,6]). This was because that several -OH groups of β-CD had been replaced by allyl groups, and then polymerization of allyl-β-CD with AM and DMDAAC happened,which led to the formation of supramolecularchain aggregates. In addition, the

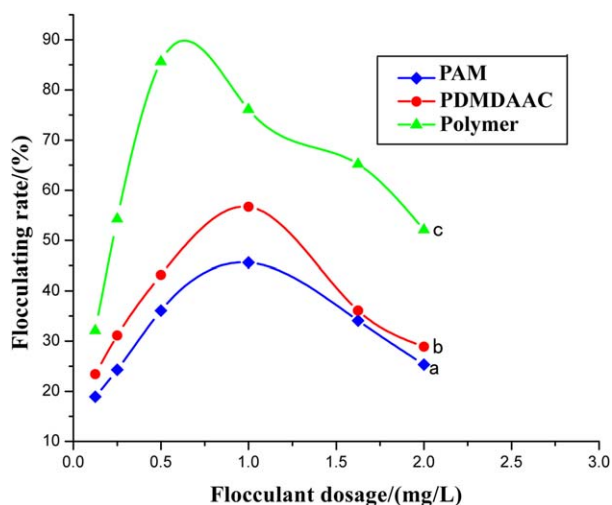**Figure 3.** The SEM image of P (AM/A-β-CD/DMDAAC).
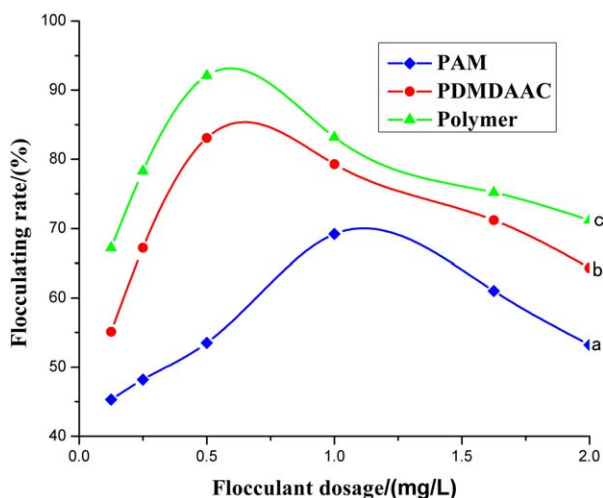
Figure 4. The comparison of flocculation property of kaolin among polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. The comparison of flocculation property of oilfield wastewater among polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intermolecular or intramolecular association and cross-linking reaction between gels brought about the formation of three-dimensional network structure, which contained a lot of cavities.
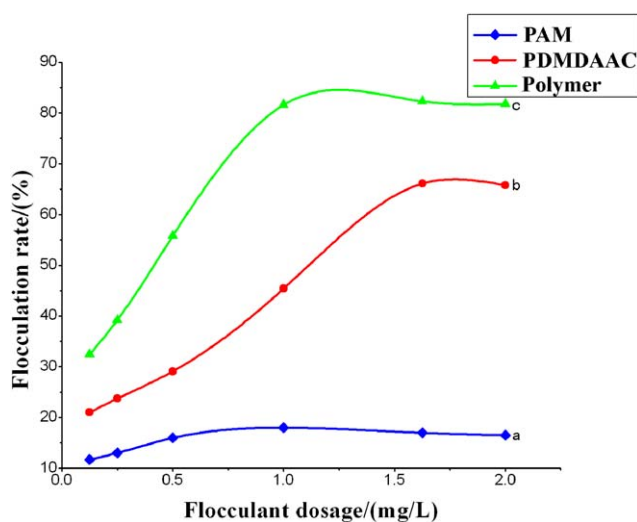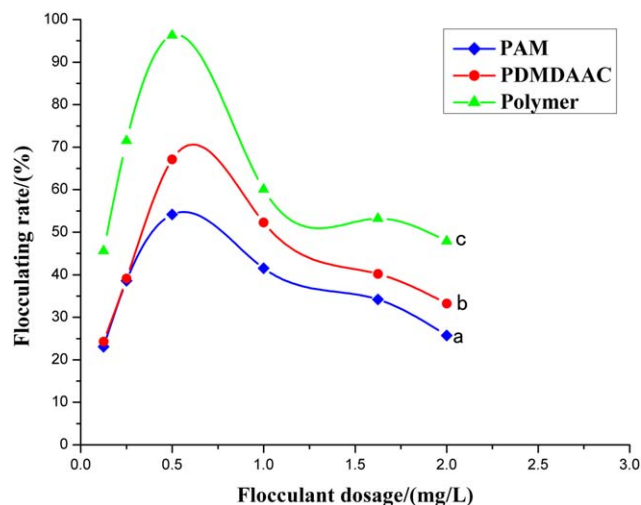
Flocculation Experiments

In the flocculation experiments the flocculating rates were measured as a function of flocculant dosage.[13,14] And the results were shown in Figures 4–7.

As can be seen from Figure 4, there were no marked difference of the flocculation trends of three types of flocculant on kaolin. Namely with the increase of flocculant dosages, the flocculating rates firstly increased sharply and then reached the maximum, then went down slowly and finally tended to be stable. However, the flocculation effect of the polymer was superior to the other two under the same conditions. This difference occurred because the positively charged DMDAAC well maintained in side chain of AM/A-β-CD/DMDAAC can flocculate the nega-

tively charged kaolin through electrical neutralization.[15] Moreover, the high molecular polymer with β-CD can extend the chain through intermolecular and intramolecular hydrogen bonds and is more conducive to the settling of flocs.[16–18]

Figure 5 shows that the flocculation trends of surfactant were also similar, and the flocculation property of the polymer was the best.

As the flocculant dosages were too low, the flocculation capability of the polymer was much better than PAM and PDMDAAC. When the flocculant dosages rose to an excess, the flocculating rate of the polymer reached the maximum. This occurs due to the inclusion function of cyclodextrin and electric neutralization of DMDAAC. The primary hydroxyl groups and the secondary hydroxyl groups in β-CD form a complex network of intramolecular hydrogen bonds to give a polar hydrophilic outer shell

Figure 5. The comparison of flocculation property of surfactant among polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. The comparison of flocculation property of waste drilling fluids among polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and a relatively hydrophobic cavity, thus β-CD can generate host/guest inclusion complexes by inclusion with suitable hydrophobic molecules. Because of the special β-CD cavity structure, the polymer host has good weak inclusion relations with surfactant to form the host/guest systems.[19,20] Moreover, the negative charges on the surface of particles are balanced by positively charged DMDAAC.

In addition, the flocculation rates of olifield wastewater were shown in Figure 6.

It was clear from Figure 6 that the flocculation rates of P (DMDAAC) and P (AM/A-β-CD/DMDAAC) were larger than that of PAM at the same condition.

When the flocculant dosages were over 20 mg/kg, the flocculation rates increased significantly. The reasons were as follows. There were lots of groups containing charges in the polymer macromolecule chain, and the intramolecular repulsion as well as the hydration of polar groups kept macromolecule main chain in loose stretching.[21] When the concentration reached to a certain degree, the space network structures formed in the polymer. Then the hydrodynamic volume rose, and flocculation property increased.

Finally, Figure 7 revealed the polymer has excellent flocculation effect on waste drilling fluids.

Because of the special β-CD cavity, the polymer can identify guest molecules and form the stable host/guest systems. Furthermore, the waste drilling fluids contain various particles, such as suspended particles, surfactants, organic matter, and so on. As mentioned above, the polymer contained β-CD can effectively flocculate the kaolin, the sodium dodecyl sulfonate and the olifield wastewater compared with PAM and PDMDAAC, respectively. Thus it is obvious that the flocculation property of the cationic polymer on waste drilling fluids is prior to PAM and PDMDAAC.[22,23]

In addition, the four figures also showed the comparison of the same flocculant polymer on flocculating different solutions. From the Figures 4(a), 5(a), 6(a), and 7(a). It can be seen that the flocculation trends of PAM were no marked difference on kaolin, surfactant, and waste drilling fluids, and the flocculation effect on kaolin was far better than on the surfacant and waste drilling fluids. Furthermore, the flocculation effect of PAM on the oilfield wastewater was not very satisfactory, it might be because the main oil containing wastewater was mostly negative. As can be seen from the Figures 4(b), 5(b), 6(b), and 7(b), PDMDAAC could much better flocculate the kaolin and the oilfield wastewater. This reasons might be because through the electricity neutralization, the positively charged PDMDAAC could adsorb the negatively charged particles. Thus the flocculation happened.

Similarly it was clearly observed from Figures 4(c), 5(c), 6(c), and 7(c) that compared with the other simulated water samples on the same condition, the flocculating performance of cationic acrylamide polymer on waste drilling fluids was best. It was due to the following reasons. On the one hand, the waste drilling fluids contained suspended particles negatively chared, oil content, surfacant, and so on. On the other hand, with AM, A-β-
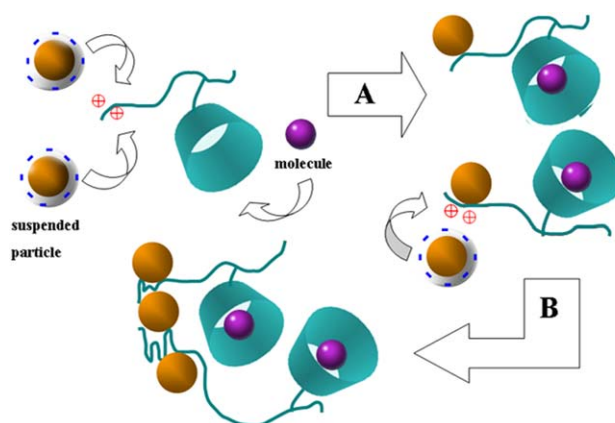
Figure 8. The flocculation mechanism of the cationic polyacrylamide flocculant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CD, and DMDAAC structures, the polymer not only could adsorb negatively charged particles, but also envelope surfactants and other components by cyclodextrin cavity.

Flocculation Mechanism

The flocculation mechanism of the cationic polyacrylamide flocculant prepared by redox free-radical copolymerization is known as Bridging Flocculation.[24–26] This occurs by the interaction of only a few segments of the polymer chain with the surface of a particle, with the remainder of the polymer extending into the solution phase.[27,28] As other particles approach the polymer, they also interact with the polymer, and thus a bridge is formed between particles. This is shown schematically in Figure 8.

In the Step A, the polymer adsorbs to a particle through the inclusion effect of the β-CD cavity or the electrical neutralization. During the entire process, it is quite possible that the polymer molecules undergo conformational changes to adjust to the interaction with the particle, although this depends somewhat on the type of dispersion and the polymer concentration.[29–31] In the Step B, the other segment of the particle attaches to another polymer chain to form a bridge.[32,33] Generally, several polymer chains will form bridges between adjacent particles, and more than one particle will be attached in the resultant floc. The polymers may also undergo vast conformational changes after adsorption, which can assist in bringing the particles closer together to cause agglomeration.[34–36]

Flocculation Kinetics

The approach in describing the flocculation kinetics of the polymer is by measuring the rate of floc growth.[37,38] It separated the total number of particles into N_1 particles and N_2 polymer.[39,40] The adsorption rate of polymer is given by the disappearance rate of the N_2 term as follows:

$$-dN_2/dt = k_A N_1 N_2 \qquad (2)$$

where k_A is the collision rate constant.[41–43] Integration of eq. (2) yields

$$-\ln(N_{2,0}/N_2) = k_A N_{1,0} t \qquad (3)$$

where the subscript 0 refers to the initial particle and polymer numbers.

From eq. (3), the time of adsorption t_A for a fraction x of polymer is

$$t_A = [\ln(1-x)]/k_A N_{1,0} \qquad (4)$$

Similarly, the flocculation time t_f (with a rate constant of k_f) is

$$t_f = 1/k_f N_{1,0} \qquad (5)$$

The ratio t_A/t_f is indicative of the kinetics of flocculation. The article assumed that the particle and polymer molecules were spherical with radii a_1 and a_2, respectively. The ratio becomes

$$t_A/t_f = -4[\ln(1-x)]a_1 a_2/(a_1+a_2)^2 \qquad (6)$$

As can be seen from the flocuulation experiments, the experiment result was consident with the above theoretical equations.

CONCLUSIONS

In the article, to introduce the inclusion function of β-cyclodextrin into acrylamide polymers, the novel cationic polymer was synthesized by aqueous free-radical copolymerization. Furthermore, FIIR and SEM characterizations confirmed the synthetic product contained the structures of AM, A-β-CD, and DMDAAC. Through the flocculation experiments, it was found that the introduction of β-cyclodextrin moieties could effectively compensate the weakness of PAM and PDMDAAC to improve the performance.

ACKNOWLEDGMENTS

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