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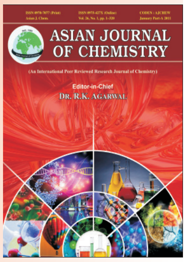

REVIEW

Synthesis and Application of Hydrophobically Associating Cationic Polyacrylamide

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The progress using micellar polymerization to synthesize an effective hydrophobically associating cationic polyacrylamide for treatement of wastewater was reviewed. Special emphasis was put on its preparation condition and reaction mechanism, as well as the applicability of dealing with some typical polluted water from paper making industry and oil contamination. Based on discussions above, future research perspectives on its synthesis and application were proposed.

Keywords: Hydrophobic association, Polyacrylamide, Micellar polymerization, Wastewater treatment.

INTRODUCTION

Polyacrylamide is a class of water-soluble polymers with unique features which is widely used in oil exploitation, chemical industry, water treatment and other fields[1-5]. Because of poor resistance to temperature, salt and shear, the application of the ordinary polyacrylamide has been greatly restricted[6]. In the mid-1980s, Evani and Rose[7] put forward the concept of hydrophobically associating polymers for the first time, which refers to a polymer formed by introducing a small amount of hydrophobic groups on the macromolecular chains. Despite small amount of hydrophobic group, hydrophobically associating cationic polyacrylamide (HACPAM) is still water-insoluble when introduced into the cationic polyacrylamide hydrophilic macromolecular chains. The hydrophobic group that bridges between organic matter and HACPAM molecule in water solution may form a tiny hydrophobic region promoting particle aggregation. This effect is referred to as hydrophobic association[8].

The hydrophobic association, effectively strengthening the absorption and aggregation of flocculants and organic matter, contributes to removing organic compounds from wastewater[9-10]. Molecular chain on the HACPAM with cationic group and hydrophobic groups could cause charge neutralization and hydrophobically association with the organic pollutants in the wastewater[11], and thus will have a good application prospect in the field of wastewater treatment, such as paper making industries wastewater, petrochemical wastewater, printing and dyeing wastewater, leather wastewater, *etc*[12]. Hydrophobic monomers could be solubilized better in the micelle by micellar copolymerization method and the mixing between the hydrophobic and hydrophilic monomers could be easily achieved[13], because of the high efficiency of the micellar copolymerization and the easy controlling of the length of structure of hydrophobic block in the chain of the resulting polymer, as well as convenient operation. So micellar polymerization is the most common method of synthesis of hydrophobically associating cationic polyacrylamide[14].

This review examines preparation condition and reaction mechanism as well as its application in the treatment of some typical polluted water, including paper making wastewater and water from oil contamination. Finally, the main conclusions and future perspectives are presented.

Micellar polymerization of hydrophobically associating cationic polyacrylamide

Monomer: Acrylamide (AM) was the main monomer used in the hydrolysis or polymerization process while other some specific hydrophilic monomers added containing ammonium group or sulfonate functional group[15], could improve intrinsic viscosity and water solubility of polymerization product. In addition to those monomers above, neutral or amphoteric single body as the comonomers viable for the polymization process are also adopted, such as dimethyl diallyl ammonium chloride (DMDAAC), methacryloxypropyltrimethoxy silane (MAPMS) methacryloyloxy ethyl trimethyl ammonium chloride (DMC) and acrylic acid (AA)[15-19]. The frequently-used hydrophobic monomers for polymization reaction were styrene and its derivatives or acrylate [*i.e.* butyl acrylate (BA), octadecyl acrylate (OA)][20]. The hydrophobic interaction of the hydrocarbon chain-containing polymers was weaker than that of the fluorocarbon chain-containing polymers[21]. Therefore, the hydrophobically associating ability of the polymer that used fluorocarbon chain-containing polymers as hydrophobic monomers would be significantly improved resulting in a stronger adsorption-bridging ability, salt tolerance and temperature resistance.

N-Substituted acrylamide for excellent polymerizability with N-substituted acrylamide was extensively applied to the industrial production. When the hydrophobic monomer was N-mono-substituted acrylamides, the polymer composition of the product changed significantly with each monomer conversion rate. Thus, its flocculation performance changed. Ren *et al.*[22] studied the flocculation performance and sludge dewatering ability of cationic polyacrylamide containing three different alkyl groups (ethyl, butyl, octyl), respectively, revealing that the cationic polyacrylamide containing octyl group had better flocculation and dewatering efficiency. Dragan *et al.*[23] studied the effect of the length of the hydrophobic chain on turbidity removal efficiency. Cationic polyacrylamide with longer hydrophobic chain had better turbidity removal performance and temperature resistance. Ghimicia *et al.*[24] carried out the study of hydrophobically modified cationic polyacrylamide on turbidity removal performance and the same conclusion was also drawn.

Candau *et al.*[14,25] indicated that during the micellar polymerization, using N,N-disubstituted acrylamide as the hydrophobic monomer, the polymer composition of the product mainly kept identical with initial monomer ratio. In the initial stage of polymerization, due to the high conversion rate of hydrophobic monomers, the polymerization activity of the acrylamide and the hydrophobic monomers depended on the polarity of the solvent. This was the result of different N-H bond in the role of polar and non-polar solvent and the N-H bond having the different degrees of reaction in the polar and non-polar solvent. The polymerization activity of the N-substituted acrylamide would be increased in the non-polar solvent, so the polarity of the solvent had no effect on its polymerization activity. N-H group of N, N-disubstituted acrylamide did not possess the N-H bond and its polymerization activity was independent of the polarity of the solvent. Thus, the composition ratio of N, N-disubstituted acrylamide as hydrophobic monomers kept constant with the initial monomer ratio[26]. Hence, the acrylamide initial concentration was in the range of 1 to 50 % while the hydrophobic monomer molar concentration 0.5 -2 % (relative to the water-soluble monomer)

Surfactant: Micellar polymerization was often added surfactant to solubilize the hydrophobic monomer, while the amount of surfactant significantly affected the solubility and the intrinsic viscosity of the polymerization product. Recent studies showed that the concentration of the surfactant referred to distributed manner of the hydrophobic monomer on the polymer molecule chain. The surfactants were divided into: cationic, such as cetyltrimethyl ammonium bromide (CTAB), anionic, such as sodium dodecyl sulfonate (SDS); non-ionic, such as dodecyl alcohol polyoxyethyleneether (C12E15), polyethylene glycol octylphenyl ether (Triton X-100)[27]. The cationic and non-ionic surface active agent were always used to synthesize cationic polyacrylamide. Candau *et al.*[14] indicated that the typical surfactant concentration was 1 to 3 %. In the earlier studies, the concentration of the surfactant was only adjusted to improve the efficiency of the solubility of the hydrophobic monomers. Later research found that the surfactant not only affecting the efficiency of the solubility of the polymerization product and reaction rate, but also affecting the microscopic structure of the polymerization product as an important factor. The characteristics of common surfactants were listed in the Table-1[28].

The addition of surfactant during the polymerization increased the complexity of purification. However, it was the simplest and most commonly used method of synthesis of HACPAM. In order to simplify the subsequent operations, surface active monomer was synthesized to be used as a hydrophobic monomer and such monomers themselves had both a hydrophilic group and a hydrophobic group. Because of their surface activity, they could be dissolved in the reaction medium in micellar form without adding surfactant. These kinds of monomers were referred to as a surface-active monomer (surfomers).

Initiator and initiation temperature: Initiator system and initiator dosage selected by micellar polymerization were similar to other ways of polymerization of acrylamide and potassium persulfate (KSP)[20,29] was the most commonly used water-soluble initiator and the initiator dosage was generally the mass ratio of 0.1 to 1 %. Other water-soluble initiators: redox initiators such as ammonium persulfate-sodium bisulfite[21,30-32]; water-soluble azo initiator such as azobisisobutylamidine hydrochloride; redox composite initiator such as potassium persulfate-sodium thiosulfate-azobis isobutyryl cyanide[33]. But few studies were carried out by the separate use of an oil-soluble initiator such as azobisisobutyronitrile initiator. At

TABLE-1
CHARACTERISTICS OF SURFACTANT

Surfactant	m.f.	m.w. (g/moL)	Ionic type	Critical micelle concentration (mM)	HLB	Aggregation no.
Cetyltrimethyl Ammonium Bromide (CTAB)	$C_{16}H_{33}N(CH3)_3^+Br^-$	364.4	cationic	0.9	/	91
Sodium Dodecyl Sulfonate (SDS)	$n\text{-}C_{12}H_{25}SO_4^-Na^+$	288.3	anionic	8.2	17.2	62
Polyethylene glycol octylphenyl ether (Triton X-100)	$p\text{-}t\text{-}C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$	628	Non-ionic	0.28	13.5	135

present the influences of the solubility of initiator on the structure and the flocculation performance of the polymerization product had never been reported. However, some mechanism studies found that even using the oil-soluble initiator, the polymerization reaction was also carried out in the water phase[34]. The polymerization temperature of micellar polymerization was usually 50 °C by thermostatic water bath. But using a redox initiator, the polymerization could be carried out at a relatively low temperature (25-30 °C)[14,27,35].

Mechanism of polymerization: The method of micellar polymerization was first proposed by Evani and Rose[7] and even now their original experimental steps were still widely used. As research continued, Biggs *et al.*[36,37] put forward the most likely polymerization mechanism:

(1) With the decomposition of the initiator in the aqueous phase, a water-soluble free-radical was generated and polymerization reaction of water-soluble monomer occurred in the aqueous phase.

(2) When the head of the chain growth macroradicals collided with the micelles solubilizing hydrophobic monomer, it would make a number of hydrophobic monomer molecules enter into micelles and then got the introduction of a short hydrophobic chains and the formation of the micro-area of the hydrophobic block structure.

(3) And then the head of radicals left micelles, the reaction of the water-soluble monomer in the aqueous phase had been carried out, until a collision with another micelles again, introducing a short hydrophobic chain, forming micro-area of a hydrophobic block structure.

(4) Due to the higher activity of macroradicals, chain growth rate constant was greater than the rate constant of the chain termination. These steps were repeated several times until the macromolecular radical termination.

(5) Owing to the polymerization reaction in the aqueous phase and micelles were carried out respectively, the hydrophobic chains formed by the hydrophobic monomer in the polymerization product was based on the random distribution block form[38,39]. Schematic representation of the micellar copolymerization mechanism could be seen in the Fig. 1.

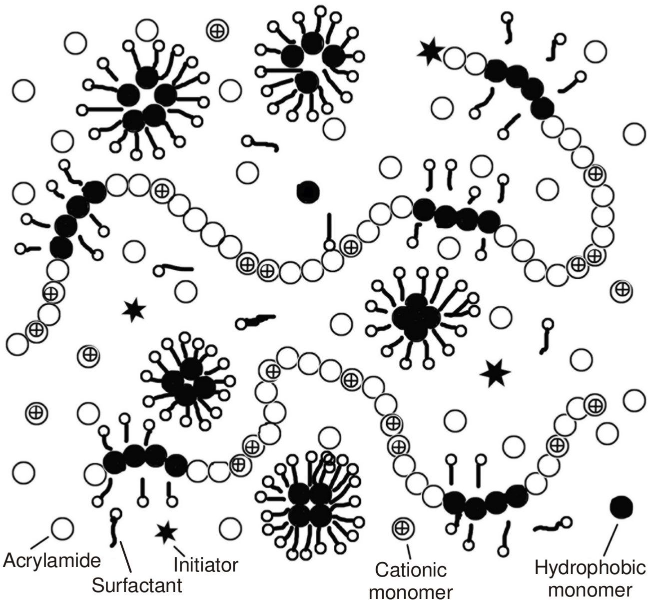

Fig. 1. Schematic representation of the micellar copolymerization mechanism

Application of hydrophobically associating cationic polyacrylamide in wastewater treatment

Treatment of simulating wastewater: Owing to the single component of simulating wastewater and its convenience for investigating flocculation-coagulation effect of flocculant under laboratory conditions, it was widely adopted by most researchers. Chen *et al.*[40] using butyl acrylate (BA) as hydrophobic monomer, synthesized hydrophobically associating cationic polyacrylamide P(AM-DMDAAC-BA) by micellar polymerization method processing to treat diatomite wastewater and when dosage was 25 mg/L, butyl acrylate 3 %, better turbidity removal was achieved. Lee *et al.*[30,31] synthesized some cationic hydrophobic monomers containing different hydrophobic groups and it revealed that polyacrylamide containing hexyl group had the highest molecular weight when the turbidity removal rate of kaolin wastewater was 99 %. Ren *et al.*[41] synthesized hydrophobically modified polyacrylamide with N,N-substituting acrylamide and when it was used to process kaolin wastewater, turbidity removal performance was superior to unmodified polyacrylamide. Shang *et al.*[42] also synthesized hydrophobically modified cationic flocculant P(AM-DMC-MAPMS) to treat kaolin wastewater and reactive brilliant red X-3B wastewater, better turbidity removal and decoloration effect were both achieved and the more MAPMS content, the better the flocculation effect was made. Dragan *et al.*[23] synthesized a series of cationic polyacrylamide containing hydrophobic chains of different lengths and investigated the treatment effect of montmorillonite wastewater, finding that the best turbidity removal was obtained at 25 °C and the longer the hydrophobic chain, the better effects of temperature resistance, salt tolerance and turbidity removal can be obtained.

Treatment of papermaking wastewater: The characteristics of the wastewater produced by the paper industry were the complexity of wastewater quality, high quantity of wastewater effluent and high CODcr. It was one of the most difficult to dispose in industry and it was usually treated by biochemical processing[43]. But recently attention was paid to treating paper making wastewater by flocculation-coagulation process. Ariffin *et al.*[44] treated pulp and papermaking wastewater by using the polydimethyl diallyl ammonium chloride (PDMDAAC) and polyacrylamide as flocculants and good coordination flocculation effect was achieved and better performance of turbidity removal, CODcr removal and TSS removal were made. Wang *et al.*[45] conducted the treatment of papermaking wastewater by using starch modified cationic polyacrylamide, with the maximum removal rate of turbidity and lignin 98.7 % and 82.5 %, respectively.

However, there were a lot of researches about applications of HACPAM as flocculant for treatment of papermaking wastewater as well and their flocculation performance was better than traditional cationic polyacrylamide. Li *et al.*[33] had synthesized P(AM-DMDAAC-OA) by using octadecyl acrylate (OA) as hydrophobic monomer and researched flocculation effect of the paper mill wastewater by adding P(AM-DMDAAC-OA). Due to the strong hydrophobic interaction of P(AM- DMDAAC-OA), its flocculation performance was better than that of polymeric ferric sulfate and polyacrylamide. Yang[46] had made a study of treatment of papermaking wastewater with synthetic hydrophobic polyacrylamide by using methacryloyloxy ethyl Dimethyloctyl bromide (ADMOAB) as hydrophobic monomer and the CODcr removal rate for optimal conditions was 74.1 %, sludge filter cake moisture content by dehydration treatment after flocculation dropped to 67.7 %.

Treatment of oily wastewater: Main chains of hydrophobically associating cationic polyacrylamide were connected with some hydrophobic groups. In the aqueous phase, hydrodynamic volume of HACPAM decreased due to the hydrophobic interaction and at the same time oily wastewater having a higher content of hydrophobic organic compounds could be formed micelles with a hydrophobic group in the flocculant. Due to cationic groups on the flocculant could better charge neutralization with the negative surface charge of the oil droplets. Therefore hydrophobically associating cationic polyacrylamides were widely used in the treatment of wastewater containing oil. Li *et al.*[47] had synthesized hydrophobically associating cationic polyacrylamide P (AM-DMDAAC-BA) by using butyl acrylate as hydrophobic monomer to process sewage from the Shengli Oilfield lump Union Station,the effect of which showing that the maximum oil removal rate was up to 93 % under optimal conditions and comparing with other flocculants, the introduction of hydrophobic groups was more conducive for oil removal. Zhao *et al.*[48] had used vinyl trimethoxysilane(VTMS) as hydrophobic monomer to synthesize P(DMDAAC-AM-VTMS), and it had better oil removal performance than PDADMAC. Yang *et al.*[49] also synthesized P(AM-DMDAAC-BA) and investigated its oil removal performance, the result of which displaying that the largest oil removal rate was 93.4 % at the dosage of 50 mg/L, synergy with $Al_2(SO_4)_3$ for oil removal and better than other conventional commercially available polyacrylamide flocculant.

Conclusion

This paper reviewed the major advances achieved in the field of hydrophobically associating cationic polyacrylamide prepared by micellar polymerization. A characteristic feature of this technique was the production of copolymers with a multiblock. Synthesis of hydrophobically associating cationic polyacrylamide was similar to polyacrylamide synthesis. However, micellar polymerization was generally required to incorporate both hydrophilic and hydrophobic monomers into the polymer.

Hydrophobically associating cationic polyacrylamide had better water treatment performance and the widely extensive application could be predicted in the near future. Although great progress had been made in the synthesis and application of hydrophobic associating cationic polyacrylamide, further and extensive research about the microstructure of block structure and more effective ways of controlling block distribution were expected. A further study conducting to improve intrinsic viscosity and charge density of the polymerization product should be highly concerned. Hydrophobically associating cationic polyacrylamide had many unique properties. Some latest developments reported in the current researches dealing with a better understanding of synthesis of HACPAM were addressed, thus pinning hope on the design of HACPAM has a higher instinct viscosity and better flocculation-coagulation performance.

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