

## Modification of $\beta$ -Cyclodextrin for Rapidly Decolorizing the Dye-Containing Wastewaters by Flocculation

Xiuzhi Tian, Jing Zhang, Xue Jiang

School of Textiles and Clothing, Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, Wuxi 214122, People's Republic of China

Correspondence to: X. Jiang (E-mail: jiangx@jiangnan.edu.cn)

**ABSTRACT:** To strengthen the role of polymer bridging during the flocculation process and thus raise the speed of decolorizing the dye-containing wastewaters,  $\beta$ -cyclodextrin–acrylamide–[2-(Acryloyloxy)ethyl] trimethyl ammonium chloride copolymer (poly[AM( $\beta$ -CD)-AETAC]) with relatively high intrinsic viscosity ( $84.3 \text{ mL g}^{-1}$ ) and cationicity (24.5%) was prepared by solution polymerization. The successful preparation of copolymer was demonstrated by FT-IR and  $^1\text{H-NMR}$  characterizations. Its excellent decolorization performances as a new flocculant were evaluated with the C.I. reactive orange 5 (RO 5) and C.I. reactive blue 19 (RB 19) solutions using a jar test method. Both the nature of anionic dyes and the pH of dye solutions influence the decolorization effectiveness. For both the RB 19 and RO 5 solutions ( $0.10 \text{ g L}^{-1}$ ), it can be rapidly decolorized in a wide range of pH (2–7) and flocculant concentration ( $0.12\text{--}0.26 \text{ g L}^{-1}$ ). For the given dye/flocculant solution system, both charge neutralization and polymer bridging contribute to the decolorization mechanism. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39940.

**KEYWORDS:** separation techniques; properties and characterization; polyelectrolytes

Received 17 May 2013; accepted 7 September 2013

DOI: 10.1002/app.39940

### INTRODUCTION

Treatments of the dye-containing wastewaters are challenging tasks for environmental protection.<sup>1</sup> Varied methods are always combined to accomplish the optimal purification effects.<sup>2,3</sup> Flocculation is often applied as a pre-treatment before other treatment like biological degradation or membrane filtration.<sup>4–8</sup> Because it does not destroy the dyes, which produce some even more potentially harmful and toxic by-products such as aromatic amine, but only transfer them from liquid to solid. In addition, it can also effectively remove both the suspending particles and other anionic substances in the wastewaters when polycations are used as flocculants.<sup>9</sup> That is, the turbidity as well as the color of wastewater can be largely reduced, improving the biodegradability of wastewater and simultaneously bringing on less burden of the subsequent biological treatment of wastewater. However, few of this kind of flocculants are available, e.g., inorganic aluminum salts, synthetic polyvinylpyrrolidones, polyethylenimine, reaction products of polyacrylonitrile with dicyandiamide, polyamine, and cationic polyacrylamide.<sup>10</sup>

In recent years, derivatives of natural polysaccharides consisting of cellulose, starch, and lignin, etc. have been increasingly explored for color removal based on their biodegradable, renewable, and eco-friendly aspects.<sup>11–18</sup> Beta-cyclodextrin ( $\beta$ -CD), a product from enzymatic degradation of starch and its related

compounds, has similarity to other polysaccharides. But its unique structure, relatively higher water solubility and containing 21 hydroxyl groups make it more easily be modified by chemical reactions in homogenous medium. In our previous study, amphoteric and cationic polyelectrolytes were prepared from the modification of  $\beta$ -CD and applied for color removal.<sup>19–22</sup> They were highly branched because more than one hydroxyl group of  $\beta$ -CD were substituted. Although high percentages of color removal were ultimately achieved, the speed of decolorizing the dye-containing wastewater was slow. This might be related to the weak role of polymer bridging during the flocculation process due to the relatively low molecular mass as well as the branched structure of this kind of flocculant. Accordingly, a cationic polyelectrolyte with linear backbone but side groups of  $\beta$ -CD has the potential to rapidly decolorize the dye-containing wastewaters if both its molecular mass and charge density are relatively high.

In this study, in order to reduce the second pollution from the synthesis process, solution polymerization instead of inverse emulsion polymerization was chosen to prepare the aimed flocculant. Concretely, a polymerizable  $\beta$ -CD derivative carrying monovinyl group—mono-6-(acrylamide)- $\beta$ -CD (mono-6-AM- $\beta$ -CD) was synthesized. Then, mono-6-AM- $\beta$ -CD was copolymerized with the cationic monomer [2-(acryloyloxy)ethyl] trimethyl

ammonium chloride (AETAC) in de-ionized water under nitrogen flow, using the redox initiator of ammonium persulfate (APS) and sodium bisulfite (SBS). Effects of the mole proportion of comonomers, the initiator concentration and the temperature on the copolymers' cationicities ( $\alpha$ ) and intrinsic viscosities ( $[\eta]$ ) were evaluated. The corresponding condition to prepare the copolymer with relatively high  $[\eta]$  and  $\alpha$  was determined. The copolymer synthesized under this condition was characterized by FT-IR and  $^1\text{H-NMR}$  spectra. Furthermore, its performances of color removal were studied.

## EXPERIMENTAL

### Chemicals

*p*-Toluenesulfonyl chloride (*p*-TsCl) from Tokyo Chemical Industry Co. and [2-(Acryloyloxy)ethyl] trimethyl ammonium chloride (AETAC, 80 wt % solution in water) from Sigma-Aldrich were used without any purification.  $\beta$ -CD from Wako Pure Chemical Co. was purified by re-crystallization from water twice prior to use. All other reagents of analytic grade were purchased from Sinopharm Chemical Reagent Co. (China), consisting of ammonium persulfate (APS), sodium bisulfite (SBS), acrylamide (AM),

sodium hydroxide (NaOH), sodium chloride (NaCl), acetone, and *N,N*-dimethylformamide (DMF).

Two reactive dyestuffs, C.I. reactive orange 5 (RO 5) and C.I. reactive blue 19 (RB 19) were purchased from Clariant Chemicals (China), whose structures and properties were described elsewhere.<sup>13</sup>

### Synthesis of Copolymer

The route to synthesize the copolymer was schemed in Figure 1.

First, mono-6-deoxy-6-*p*-(tolylsulfonyl)- $\beta$ -CD (mono-6-OTs- $\beta$ -CD) was synthesized according to the method reported in the literature.<sup>14</sup> Second, both mono-6-OTs- $\beta$ -CD and AM were dissolved in DMF. The mixed solution was kept at 75°C and continuously stirred for 5 h. After being cooled to room temperature, the mixture was poured into large amount of acetone. A white precipitate was collected by vacuum filtration. The crude product was dissolved in de-ionized water, precipitated by large amount of acetone, vacuum-filtrated for three times. Finally, the purified product, mono-6-AM- $\beta$ -CD, was dried in vacuum oven at 50°C for 24 h.

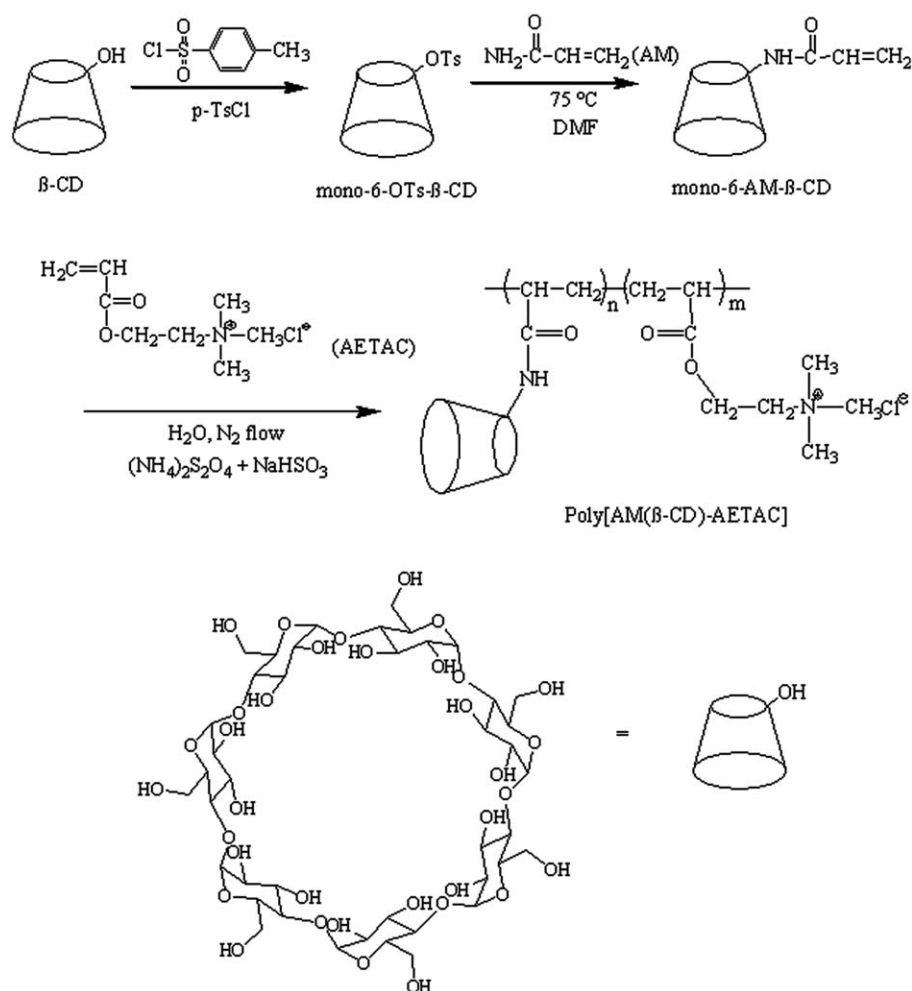


Figure 1. The schematic route to synthesize the copolymer of poly[AM( $\beta$ -CD)-AETAC].

Cationic polyelectrolytes with linear backbone but side groups of  $\beta$ -CD-poly[AM( $\beta$ -CD)-AETAC] were synthesized via AETAC and mono-6-AM- $\beta$ -CD in aqueous solution. Specifically, both AETAC and mono-6-AM- $\beta$ -CD were dissolved in de-ionized water. The monomer concentration was maintained at 20 wt %. Then, a predetermined amount of APS was added. After bubbling with N<sub>2</sub> for 15 min to remove oxygen, SBS (the same mole as APS) dissolved in de-ionized water was injected into the reaction system. The copolymerization was conducted at a constant temperature for 5 h. The mixture was poured into large amount of acetone, filtrated and vacuum-dried at 50°C for 24 h.

The crude product was dissolved in de-ionized water, purified using a dialysis bag (cut-off 8000), precipitated by large amount of acetone, filtrated and dried in vacuum oven at 50°C for 24 h.

#### Instrument Analyses

FT-IR spectra were recorded on a Nicolet is10 spectrometer in the optical range of 400–4000 cm<sup>-1</sup> by averaging 32 scans at a resolution of 4 cm<sup>-1</sup>. Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR) was obtained on a Bruker AVANCE 300 NMR spectrometer using D<sub>2</sub>O as solvent at room temperature. Viscosity measurements were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm) at 30°C in sodium chloride solution (2 mol L<sup>-1</sup>). A digital display conductivity gauge (DDS-IIA, Shanghai Tianda Instrument Co.) was used to monitor the conductivity of polymer solution during the titration by silver nitrate (0.01 mol L<sup>-1</sup>). The copolymer's cationicity ( $\alpha$ ) could be calculated according to the following equation.

$$\alpha = \frac{MV}{10^5 m} \times 100\% \quad (1)$$

where  $M$  was the relative molecular mass of AETAC (g mol<sup>-1</sup>),  $m$  was the copolymer's weight (g) and  $V$  was the volume of silver nitrate, which was consumed to attain the lowest conductivity of the copolymer solution (mL).

#### Flocculation Experiments

Flocculation experiments were referred to our previous study.<sup>13</sup> The decolorization rate (DR) was calculated by eq. (2).

$$\text{DR} (\%) = \left(1 - \frac{CV}{C_0 V_0}\right) \times 100 \quad (2)$$

where  $C_0$  and  $C$  denoted the dye concentration in the solution before and after flocculation,  $V_0$  and  $V$  were the volume of dye solution before and after flocculation, respectively.

## RESULTS AND DISCUSSION

### Determination of Copolymerization Condition

**The Mole Proportion of Co-Monomers.** The copolymer's composition depends on the feeding proportion of co-monomers and the relative monomer reactivity.<sup>23</sup> That is, a variation in the feeding composition of co-monomers who having different reactivity ratios ( $r$ ) results in a variation in the copolymer's composition and simultaneously in the copolymer's molecular mass.

In this study, a series of copolymers, poly[AM( $\beta$ -CD)-AETAC], having different values of  $\alpha$  and  $[\eta]$  were synthesized by adjusting the mole proportion of mono-6-AM- $\beta$ -CD to AETAC (1/2, 1/3, 1/4, 1/5, 1/6, and 1/10), keeping other polymerization variants constant (temperature: 70°C; time: 5 h; monomer concentration: 20 wt %; initiator dosage: 0.6 wt %, relative to co-monomers). The measured values of  $\alpha$  and  $[\eta]$  were summarized in Table I.

It could be seen that an increase in the feed composition of AETAC monomer was helpful for increasing the co-polymeric composition of AETAC moieties, but the actual composition of AETAC moieties in the copolymer increased much slower than that of AETAC monomer in the feed. Besides, the copolymer's  $[\eta]$  increased first and then decreased with increasing the feed composition of AETAC monomer. The highest value of  $[\eta]$  reached when the mole proportion of mono-6-AM- $\beta$ -CD to AETAC in the feed was 1/3. The reasons could be explained well based on the different reactivity ratios of co-monomers mono-6-AM- $\beta$ -CD ( $r_1$ ) and AETAC ( $r_2$ ).

The reactivity ratios of co-monomers mono-6-AM- $\beta$ -CD ( $r_1$ ) and AETAC ( $r_2$ ) could be defined by the equation of copolymerization.<sup>24</sup>

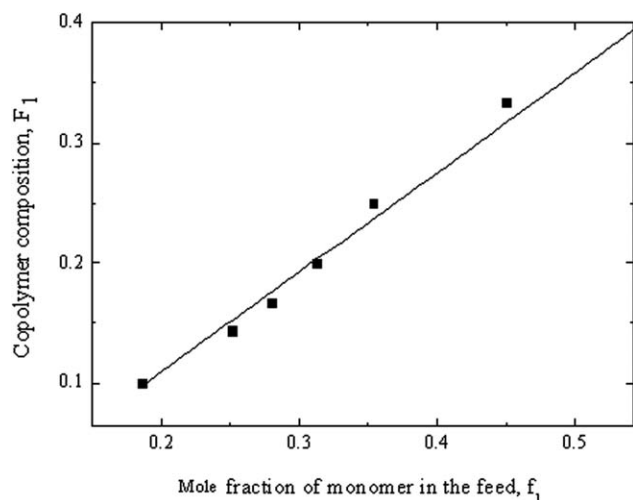
$$F_1 = \frac{f_1(1+[r_1-1]f_1)}{(r_1+r_2-2)f_1^2+2(1-r_2)f_1+r_2} \quad (3)$$

where  $f_1$ ,  $f_2$  were the mole fractions of mono-6-AM- $\beta$ -CD and AETAC in the feed, respectively.  $F_1$  was the mole fraction of AM( $\beta$ -CD) moieties in the copolymer.

The measured mole fraction of AM( $\beta$ -CD) moieties in the copolymer ( $F_1$ ) and the known mole fraction of mono-6-AM- $\beta$ -CD monomer in the feed ( $f_1$ ) were plotted in Figure 2.

**Table I.** Variation of the Copolymer's  $\alpha$  and  $[\eta]$  with the Mole Proportion of Mono-6-AM- $\beta$ -CD to AETAC

Copolymer	Mole proportion of co-monomers mono-6-AM- $\beta$ -CD/AETAC	Intrinsic viscosity ( $[\eta]$ , mL g <sup>-1</sup> )	Cationicity ( $\alpha$ , %)
1	1/1	25.9	6.3
2	1/2	32.2	15.0
3	1/3	42.5	20.8
4	1/4	40.8	24.0
5	1/5	32.1	27.0
6	1/6	28.9	30.0
7	1/10	16.8	38.7



**Figure 2.** Dependence of copolymer composition on composition of reactant mixtures for poly[AM( $\beta$ -CD)-AETAC].

The reactivity ratios of co-monomers ( $r_1$  and  $r_2$ ) could be determined using various statistical treatments of the monomer's feeding proportion and copolymer's composition.<sup>25</sup> Based on the criterion for the non-linear least-squares method of analysis as described in eq. (4).

$$\Delta = \sum_{i=1}^7 \left( \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} - F_1 \right)^2 \quad (4)$$

Selected values of  $r_1$  and  $r_2$  were substituted into eq. (4) till the sum of the squares of the differences between the observed and the computed compositions of copolymer was minimized. Accordingly, the reactivity ratios of mono-6-AM- $\beta$ -CD ( $r_1$ ) and AETAC ( $r_2$ ) were determined as 2.00 and 0.56, respectively.

Obviously, the reactivity ratio of AETAC ( $r_2 = 0.56$ ) was smaller than that of mono-6-AM- $\beta$ -CD ( $r_1 = 2.00$ ). Therefore, increasing the feed composition of AETAC monomer undoubtedly resulted in an increase of AETAC moieties in the copolymer. But for the copolymer's  $[\eta]$ , it only increased within a limited increase of AETAC monomer in the feed. When the feeding composition of AETAC monomer increased to some extent, the relative concentration of mono-6-AM- $\beta$ -CD in the feed fell largely, which would influence its participation in copolymerization regardless of its native stronger activity. Therefore, the moieties of AM( $\beta$ -CD) in the copolymer was depressed, illuminating a decrease in the copolymer's  $[\eta]$ .

**The Initiator Dosage.** Initiator is pivotal to the production of active center for free radical polymerization. Varied dosages of initiator make for different molecular masses of polymers.<sup>26</sup> In order to investigate the effect of initiator dosage on copolymerization, in this study, a series of copolymers were synthesized by adjusting the initiator dosage (0.2–1.0 wt %, relative to co-monomers), keeping other variables constant (mole proportion of mono-6-AM- $\beta$ -CD to AETAC: 1/3; temperature: 70°C;

**Table II.** Variation of the Copolymer's  $\alpha$  and  $[\eta]$  with the Dosage of Initiator

Copolymer	Dosage of initiator (relative to co-monomers, wt %)	Intrinsic viscosity ( $[\eta]$ , mL g <sup>-1</sup> )	Cationicity ( $\alpha$ , %)
8	0.2	9.8	16.1
9	0.4	22.5	23.1
10	0.6	20.7	19.6
11	0.8	19.8	15.7
12	1.0	18.4	11.8

time: 5 h; monomer concentration: 20 wt %). The measured values of  $[\eta]$  and  $\alpha$  were illustrated in Table II.

It could be seen that both the copolymers'  $[\eta]$  and  $\alpha$  increased first and then decreased with increasing the dosage of initiator. According to the theory of classic polymerization, the expedited velocity of polymerization and higher conversion of monomers were doubtlessly induced by increasing the dosage of initiator. But when an excess initiator was used (>0.4 wt %, relative to co-monomers), over-acute polymerization did lead to more chain transfers, and thus reduced the copolymer's  $[\eta]$  and  $\alpha$ .

**The Copolymerization Temperature.** Temperature is another key factor to copolymerization. In order to investigate the effect of temperature on copolymerization, in this study, a series of copolymers were synthesized at different temperature (20–70°C), keeping other variables constant (mole proportion of mono-6-AM- $\beta$ -CD to AETAC: 1/3; time: 5 h; monomer concentration: 20 wt %; initiator dosage: 0.4 wt %, relative to co-monomers). The measured values of  $[\eta]$  and  $\alpha$  were exhibited in Table III.

It could be seen that an obvious improvement of  $[\eta]$  was resulted from an increase of copolymerization temperature from 25 to 40°C. Because raising the copolymerization temperature would accelerate the formation of free radicals and diffusion of monomers. But when the copolymerization temperature was further increased over 40°C, the copolymer's  $[\eta]$  and  $\alpha$  began to decrease, which was mainly due to the poor copolymerization selectivity and accelerated chain transfer reactions.<sup>27,28</sup>

As discussed above, when the copolymer was prepared under the condition as 1/3 of the mole proportion of mono-6-AM- $\beta$ -CD to

**Table III.** Variation of the Copolymer's  $\alpha$  and  $[\eta]$  with the Copolymerization Temperature

Copolymer	Copolymerization temperature (°C)	Intrinsic viscosity ( $[\eta]$ , mL g <sup>-1</sup> )	Cationicity ( $\alpha$ , %)
13	25	74.6	21.7
14	40	84.3	24.5
15	55	66.6	22.5
16	70	42.5	20.8

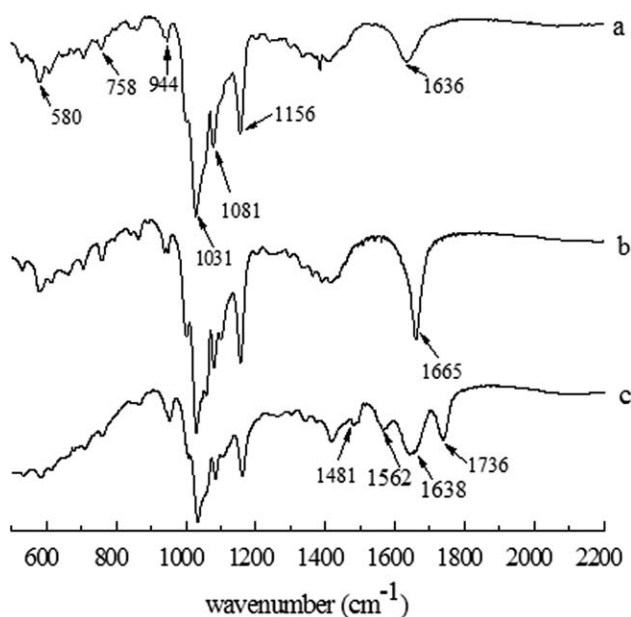
AETAC, 0.4 wt % of initiator (relative to the co-monomers), 40°C and 5 h, it had relatively high values of  $[\eta]$  (84.3 mL g<sup>-1</sup>) and  $\alpha$  (24.5%). Accordingly, poly[AM( $\beta$ -CD)-AETAC] prepared under this condition was used for the following characterizations of FT-IR and <sup>1</sup>H-NMR spectra and decolorization performances.

### Characterization of Copolymer

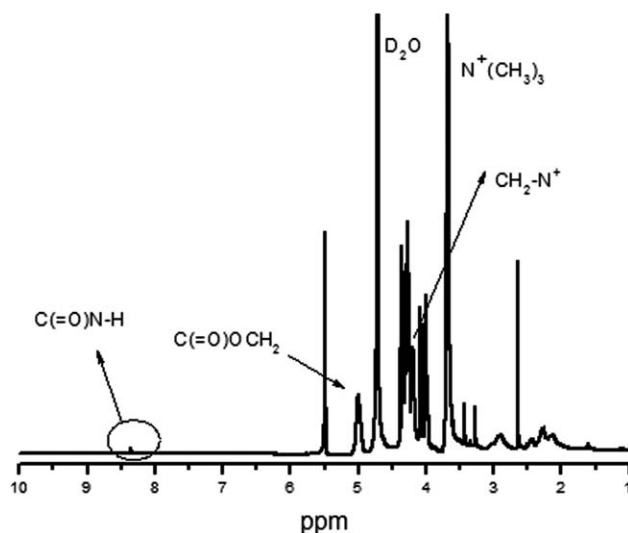
**FT-IR Spectra.** FT-IR spectra of  $\beta$ -CD, mono-6-AM- $\beta$ -CD and poly[AM( $\beta$ -CD)-AETAC] were recorded in Figure 3.

It could be seen that the characteristic peaks of  $\beta$ -CD, including 1156, 1081, 1031, 944, 758, and 580 cm<sup>-1</sup> appeared in both curves a and b.<sup>23</sup> In addition, compared with the peak at 1636 cm<sup>-1</sup> in curve a, an evidently stronger peak was found at 1665 cm<sup>-1</sup>, which could be assigned to the C(=O)NH and C=C groups in mono-6-AM- $\beta$ -CD. Accordingly, successful synthesis of mono-6-AM- $\beta$ -CD was confirmed.

On the other hand, in the wave-number range from 1640 to 1680 cm<sup>-1</sup>, only one intensive absorption peak appeared at 1665 cm<sup>-1</sup> in curve b. But two relatively weaker absorption peaks appeared in curve c, which were at 1562 cm<sup>-1</sup> and 1638 cm<sup>-1</sup>, respectively. The former was referred to the C–N stretching from amide II.<sup>13</sup> The latter was an overlapped peak corresponded to the C=O stretching from amide I and the first overtone of OH bending.<sup>13,19</sup> Besides, new peaks corresponded to the AETAC moieties appeared in curve c, which were at 1481 cm<sup>-1</sup> (bending vibration of methyl groups of ammonium), 948 cm<sup>-1</sup> (stretching vibration of quaternary ammonium), and 1736 cm<sup>-1</sup> (stretching vibration of saturated ester linkage, CH<sub>2</sub>–CH–C(=O)–O). All these meant disappearance of C=C groups in the copolymer and successful polymerization of comonomers.



**Figure 3.** FT-IR spectra of (a)  $\beta$ -CD, (b) mono-6-AM- $\beta$ -CD, and (c) poly[AM( $\beta$ -CD)-AETAC].



**Figure 4.** <sup>1</sup>H-NMR spectrum of poly[AM( $\beta$ -CD)-AETAC] in D<sub>2</sub>O.

**<sup>1</sup>H-NMR Spectrum.** <sup>1</sup>H-NMR spectrum of poly[AM( $\beta$ -CD)-AETAC] was exhibited in Figure 4.

The characteristic peaks related to the AM( $\beta$ -CD) moieties in the copolymer could be observed at 3.8–4.6 ppm and 5.55 ppm (protons in  $\beta$ -CD), 8–9 ppm [C(=O)NH], but that to vinyl group (CH<sub>2</sub>=CH) were absent at 6–7.5 ppm. Aside, the characteristic peaks attributed to the AETAC moieties in the copolymer could also clearly observed at 2.0–3.3 ppm (CH<sub>2</sub>–CH), 3.8 ppm [N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>], 4.3 ppm (CH<sub>2</sub>–N<sup>+</sup>), and 5.1 ppm [C(=O)O–CH<sub>2</sub>].

Both FT-IR and <sup>1</sup>H-NMR characterizations confirmed the successful copolymerization between mono-6-AM- $\beta$ -CD and AETAC.

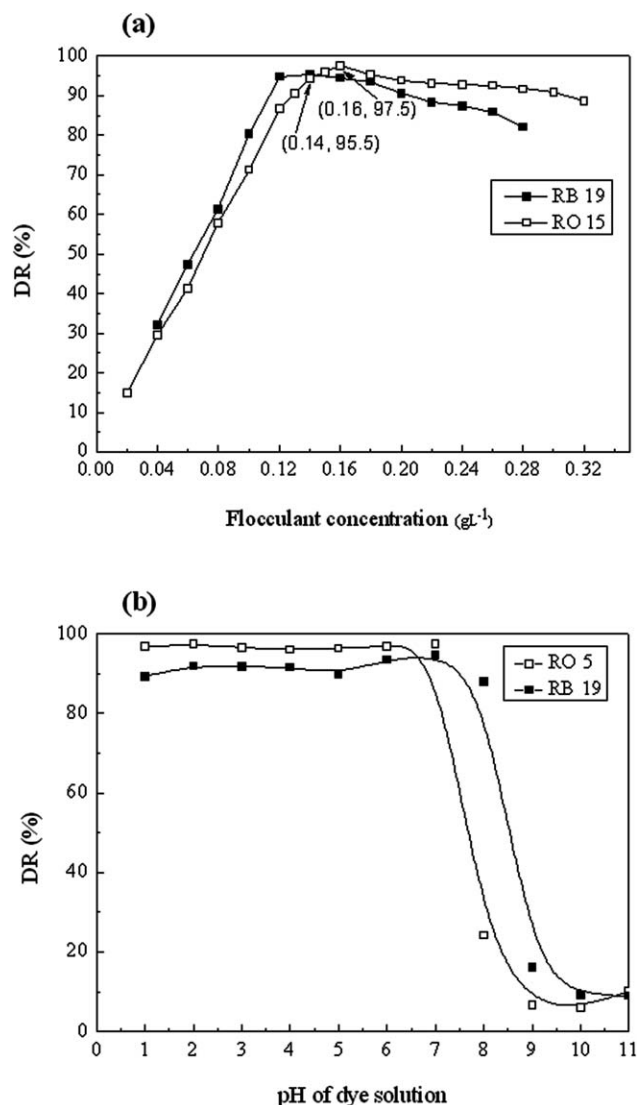
### Decolorization Performances

RB 19 and RO 5 were chosen as representatives of anionic dyes. Performances of color removal using poly[AM( $\beta$ -CD)-AETAC] as a new flocculant were investigated.

Variation of DR with different flocculant concentrations at 30°C and pH 7 was illustrated in Figure 5(a).

In Figure 5(a), DR increased first and then decreased with an increasing concentration of the given flocculant. There was an optimal flocculant concentration for the given dye/flocculant solution system. The maximum DR of RO 5 solution (97.5%), RB 19 solution (95.5%) were obtained at 0.16 and 0.14 g L<sup>-1</sup> of poly[AM( $\beta$ -CD)-AETAC], respectively. This implied that charge neutralization was one factor determining the decolorization mechanism for the given dye/flocculant solution system. It could also be seen in Figure 5(a) that relatively high DRs (>80%) were obtained in a wide range of flocculant concentration (0.12–0.26 g L<sup>-1</sup>) for both dyes solutions.

Variation of DR with different pH of dye solution at 30°C using the optimum concentration of poly[AM( $\beta$ -CD)-AETAC], e.g., 0.16 g L<sup>-1</sup> for the RO 5 solution and 0.14 g L<sup>-1</sup> for the RB 19 solution was exhibited in Figure 5(b).



**Figure 5.** Effect of (a) the flocculant concentration and (b) the pH of dye solution on the decolorization rate.

As seen in Figure 5(b) that for both dye/flocculant solution systems, high DRs ( $\geq 90\%$ ) were acquired in acidic or neutral medium. In alkaline medium, DRs decreased gradually with an increase of pH.<sup>29</sup> This further implied that charge neutralization was one factor determining the decolorization mechanism for the given dye/flocculant solution system.

On the other hand, when the pH of RB 19 solution was over 8.5, the corresponding DR was largely reduced. Comparatively, an obvious reduction of DR appeared when the pH of RO 5 solution was above 7. This indicated that for the given flocculant, the dye's nature had an important role for color removal.

It was known that the vinyl sulfone dye of RB 19 had stronger reactivity than the monochlorotriazinyl dye of RO 5. At 30°C and in alkaline medium, part of RB 19 molecules were possibly bonded with the OH groups in poly[AM( $\beta$ -CD)-AETAC].<sup>30</sup> Nevertheless, this role was simultaneously competed with the hydrolyzation of RB 19. When the pH of RB 19 solution was

increased to some extent (above 8.5), the hydrolyzation of RB 19 was instead dominant over the covalent bond of RB 19 with the given flocculant. Moreover, the hydrolyzed dyes had more negative charges than the un-hydrolyzed ones. And increasing OH<sup>-</sup> would screen more cationic charges in poly[AM( $\beta$ -CD)-AETAC]. As a result, completed charge neutralization between the given dye and flocculant was impossible and thus induced an abrupt reduction of DR at pH 8.5.

For the RO 5/flocculant solution system, the covalent bond of RO 5 with poly[AM( $\beta$ -CD)-AETAC] was impossible. Clearly, in alkaline medium, higher pH was not in favor of color removal due to the weakened electrostatic interaction between the anionic dye and cationic flocculant. Namely, the DR declined sharply when the pH of RO 5 solution was over 7.

At pH 7, 30°C and a given concentration of dye solution (0.10 g L<sup>-1</sup>), using the optimum concentration of poly[AM( $\beta$ -CD)-AETAC], e.g., 0.16 g L<sup>-1</sup> for the RO 5 solution and 0.14 g L<sup>-1</sup> for the RB 19 solution, images of the flocculation systems were recorded with a digital camera, as shown in Figure 6.

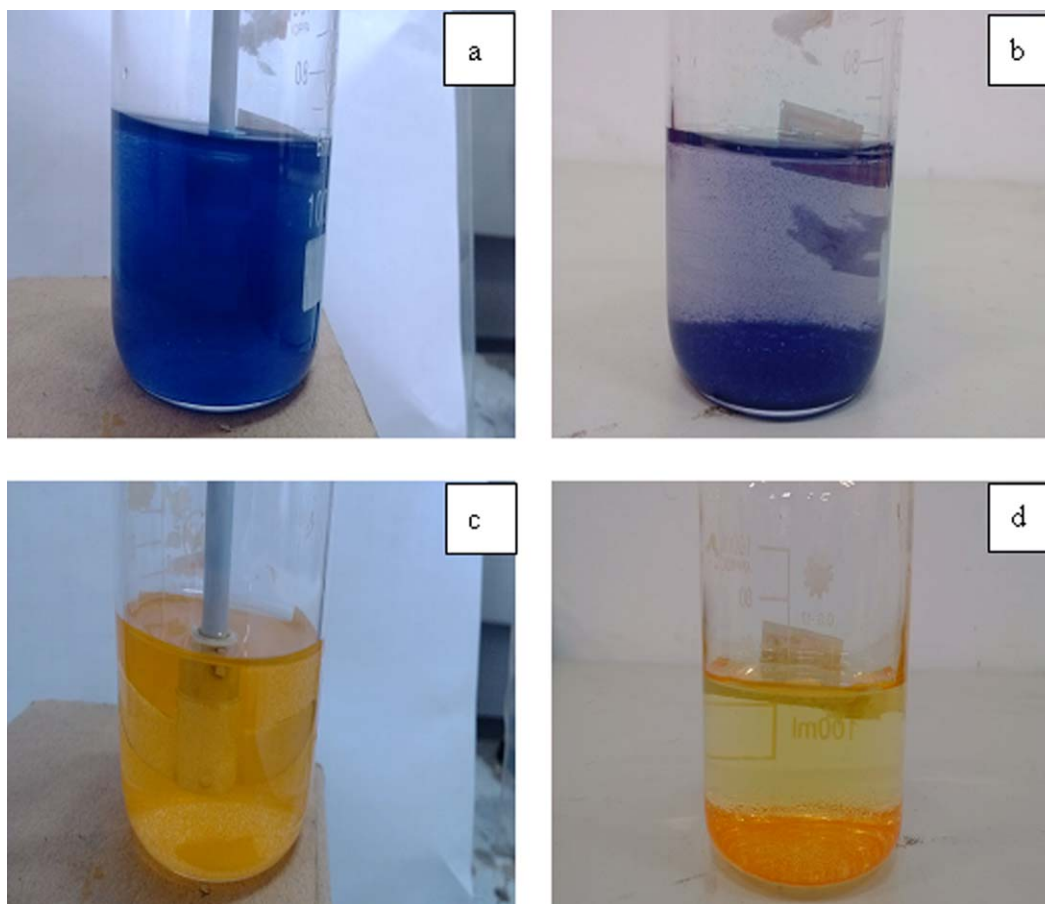
It could be seen that visible flocs were found in both flocculation systems at the end of stirring. Then after the flocculation system was placed for about 30 min, the majority of flocs were settled and high percentages of color removal came true. This explained that the goal of this study to improve the decolorization speed was achieved using this linear cationic polyelectrolyte, poly[AM( $\beta$ -CD)-AETAC], which had relatively high  $[\eta]$  (84.3 mL g<sup>-1</sup>) and  $\alpha$  (24.5%). From another point of view, this implied that polymer bridging was another factor determining the decolorization mechanism for the given dye/flocculant solution system.

## CONCLUSIONS

To prepare cationic polyelectrolytes with linear backbone and side groups of  $\beta$ -CD, a polymerizable  $\beta$ -CD derivative carrying mono-vinyl group (mono-6-AM- $\beta$ -CD) was synthesized to copolymerize with the cationic monomer of AETAC by solution polymerization using the redox initiator of APS and SBS under N<sub>2</sub> flow. FT-IR and <sup>1</sup>H-NMR spectra demonstrated the successful polymerization of co-monomers.

Variation of the copolymers' cationicities and intrinsic viscosities with the feeding composition of co-monomers, the initiator dosage and the copolymerization temperature was explained according to the calculated reactivity ratios of mono-6-AM- $\beta$ -CD ( $r_1 = 2.00$ ) and AETAC ( $r_2 = 0.56$ ). The copolymer of poly[AM( $\beta$ -CD)-AETAC] with relatively high intrinsic viscosity (84.3 mL g<sup>-1</sup>) and cationicity (24.5%) was synthesized under the condition as 1/3 of the mole proportion of mono-6-AM- $\beta$ -CD to AETAC, 0.4 wt % of initiator (relative to co-monomers), 40°C and 5 h.

As a new flocculant, poly[AM( $\beta$ -CD)-AETAC] could rapidly decolorize both the RO 5 and RB 19 solutions in a wide range of pH (2–7) and flocculant concentration (0.12–0.26 g L<sup>-1</sup>) at 30°C and 0.10 g L<sup>-1</sup> of dye solution. For the given dye/flocculant solution system, both charge neutralization and polymer bridging contributed to the decolorization mechanism.



**Figure 6.** Images of the flocculation system. (a) and (c) were recorded at the end of stirring; (b) and (d) were recorded after the flocculation systems were placed for 30 min, respectively. (At pH 7, 30°C and 0.10 g L<sup>-1</sup> of dye solution, using the optimum concentration of poly[AM( $\beta$ -CD)-AETAC], e.g., 0.16 g L<sup>-1</sup> for the RO 5 solution and 0.14 g L<sup>-1</sup> for the RB 19 solution). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## ACKNOWLEDGMENTS

Support from the National Natural Science Fund of China (Grant No. 31270632).

## REFERENCES

- Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. *Biore-source Technol.* **2001**, *77*, 247.
- Latif, A.; Noor, S.; Sharif, Q. M.; Najeebullah, M. *J. Chem. Soc. Pakistan* **2010**, *32*, 115.
- Mu, Y.; Rabaey, K.; Rozendal, R. A.; Yuan, Z.; Keller, J. *Environ. Sci. Technol.* **2009**, *43*, 5137.
- Verma, S.; Prasad, B.; Mishra, I. M. *J. Hazard. Mater.* **2010**, *178*, 1055.
- Zahrim, A. Y.; Tizaoui, C.; Hilal, N. *Desalination* **2011**, *266*, 1.
- Rodrigues, C. S. D.; Maderira, L. M.; Boaventura, R. A. R. *Environ. Technol.* **2013**, *34*, 719.
- Wang, Y.; Zhang, F.; Chu, Y. B. *Water Sci. Technol.* **2013**, *67*, 2202.
- Junior, C.; Moreira, O.; Barros, S. D.; Angelica, M.; Curveco, N. *ACTA Sci. Technol.* **2013**, *35*, 83.
- Golob, V.; Vinder, A.; Simoncic, M. *Dyes Pigments* **2005**, *67*, 93.
- Bolto, B.; Gregory, J. *Water Res.* **2007**, *41*, 2301.
- Beltran-Heredia, J.; Sanchez-Martin, J.; Delgado-Regalado, A.; Jurado-Bustos, C. *J. Hazard. Mater.* **2009**, *170*, 43.
- Fang, R.; Cheng, X.; Xu, X. *Bioresource Technol.* **2010**, *101*, 7323.
- Jiang, X.; Cai, K.; Zhang, J.; Shen, Y.; Wang, S.; Tian, X. *J. Hazard. Mater.* **2011**, *185*, 1482.
- Petter, R. C.; Salek, J. S.; Sikorski, C. T.; Kumaravel, G.; Lin, F. T. *J. Am. Chem. Soc.* **1990**, *112*, 3860.
- Sanghi, R.; Bhattacharya, B.; Dixit, A.; Singh, V. *J. Environ. Manage.* **2006**, *81*, 36.
- Song, H.; Wu, D.; Zhang, R.-Q.; Qiao, L.-Y.; Zhang, S.-H.; Lin, S.; Ye, J. *Carbohydr. Polym.* **2009**, *78*, 253.
- Song, Y.; Zhang, J.; Gan, W.; Zhou, J.; Zhang, L. *Ind. Eng. Chem. Res.* **2010**, *49*, 1242.

18. Tian, D.; Wu, X.; Liu, C.; Xie, H.-Q. *J. Appl. Polym. Sci.* **2010**, *115*, 2368.
19. Jiang, X.; Qi, Y.; Wang, S.; Tian, X. *J. Hazard. Mater.* **2010**, *173*(1-3), 298.
20. Tian, X.; Wu, D.; Zhang, J.; Wang, S.; Jiang, X. *J. Appl. Polym. Sci.* **2010**, *118*, 480.
21. Tian, X.; Ren, E.; Wang, J.; Zou, J.; Tao, Y.; Wang, S.; Jiang, X. *Carbohydr. Polym.* **2012**, *87*, 1956.
22. Xiao, H. N.; Cezar, N. *J. Colloid Interface Sci.* **2005**, *283*, 406.
23. Soykan, C.; Delibas, A.; Coskun, R. *React. Funct. Polym.* **2008**, *68*, 114.
24. O'Leary, K.; Paul, D. R. *Polymer* **2004**, *45*, 6575.
25. Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.
26. Orakdogen, N.; Okay, O. *J. Appl. Polym. Sci.* **2007**, *103*, 3228.
27. Favier, A.; Charreyre, M. T. *Macromol. Rapid Commun.* **2006**, *27*, 653.
28. Roos, S. G.; Muller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 864.
29. Joo, D. J.; Shin, W. S.; Choi, J.-H.; Choi, S. J.; Kim M.-C.; Han, M. H.; Ha, T. W.; Kim, Y.-H. *Dyes Pigments* **2007**, *73*, 59.
30. Kurbus, T.; Le Marechal, A. M.; Voncina, D. B. *Dyes Pigments* **2003**, *58*, 245.