

# Synthesis and Characterization of Novel Twin-Tailed Hydrophobically Associated Copolymers and Their Applications to Cr(III) Removal from Aqueous Solutions

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**ABSTRACT:** Water pollution is one of the most serious environmental problems facing society. The objective of this study was to provide an efficient and inexpensive way of removing Cr(III) from polluted water. Novel twin-tailed hydrophobically associating copolymers (PAAD) were prepared by micellar copolymerization of acrylamide (AM) and sodium 2-acrylamido-2-methylpropane sulfonate with *N,N*-dibutylmethacrylamide in an aqueous solution. The PAAD series, comprising copolymers of different molecular weights (ranged from 1.42 to  $1.78 \times 10^6$  g/mol) and compositions was characterized by gel permeation chromatography–multiangle laser light scattering,  $^1\text{H}$  NMR and FTIR spectroscopy, and elemental analysis. The surface activity, morphology, and aggregation properties of PAAD samples were measured by surface tension and dynamic light scattering. A schematic representation of the formation of  $\text{Cr}(\text{OH})_3$  and its precipitation using PAAD samples as coagulant aid is discussed in the article. In addition, the  $\text{Cr}(\text{OH})_3$ –copolymer interaction, as investigated by precipitation experiments, demonstrated that these copolymers have good  $\text{Cr}(\text{OH})_3$  binding capacity and potential as coagulant aid for the removal of Cr(III) from polluted water. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41028.

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## INTRODUCTION

Many water-soluble, hydrophobically modified polyacrylamides have attracted increasing attention because of their good performance and fundamental importance in several industries.<sup>1,2</sup> These polyacrylamides exhibit unique molecular self-assembly behavior and solution properties and are involved in a multitude of important biological functions and industrial applications.<sup>3–6</sup> In particular, hydrophobically modified polyacrylamides containing twin-tailed units, which offer excellent viscosity-building capacity, form a transient network structure by intermolecular hydrophobic association and have applications in water treatment, oil recovery, and pharmacy.<sup>7–9</sup> It is well known that the incorporation of a small amount of hydrophobic units (<5 mol %) into the hydrophilic backbone of polyacrylamide results in systems with unique rheological properties due to hydrophobic interactions.<sup>10</sup>

Water pollution is one of the most serious environmental problems that society faces. The use of Cr-based chemicals in industrial processes such as leather tanning, mining of chrome ores, textile industry, metal cleaning, plating, and electroplating leads to the contamination of natural waters, mainly because of improper disposal methods.<sup>11</sup>

Cr is a heavy metal that is especially toxic to humans and aquatic life.<sup>12</sup> The discharge of effluents containing Cr(III) into groundwater caused livestock death and pollution of soil and water.<sup>13</sup> Accumulation of Cr(III) ions can inhibit various enzyme systems of living organisms and also affect the ecology of the environment when it is present in large amounts. Long-term exposure to trivalent chromium is known to cause allergic skin reactions and cancer.<sup>14</sup> Hence, the removal of Cr(III) is of great importance.

Cr(III) cannot be destroyed chemically, nevertheless, many different technologies such as chemical precipitation, ion exchange, and biological operations are available for the removal of Cr(III) from wastewater. The conventional method for Cr(III) removal is the precipitation of  $\text{Cr}(\text{OH})_3$  by increasing the pH to 9–10 using lime.<sup>15–18</sup> However, because  $\text{Cr}(\text{OH})_3$  is amphoteric, the precipitation of Cr(III) from suspensions under neutral to alkaline conditions is generally difficult. Thus, the objective of this study is to provide an efficient and inexpensive way of removing Cr(III) from suspensions of  $\text{Cr}(\text{OH})_3$ .

Little work has been reported on the application of metal salts of hydrophobically associating copolymers for Cr(III) removal.

**Table I.** Composition of PAAD Samples

Sample	Feed molar ratio of AM/AMPS-Na/DBMAAM	Elemental analysis				Actual Molar Ratio of AM/AMPS-Na/DBMAAM <sup>a</sup>
		C (wt %)	H (wt %)	N (wt %)	S (wt %)	
PAAD-1	94.5 : 5 : 0.5	50.078	7.019	18.95	0.716	94.41 : 5.12 : 0.47
PAAD-2	94 : 5 : 1	50.180	7.041	18.89	0.720	93.90 : 5.15 : 0.95
PAAD-3	93.5 : 5 : 1.5	50.284	7.062	18.84	0.713	93.52 : 5.10 : 1.38
PAAD-4	93 : 5 : 2	50.393	7.085	18.77	0.720	92.95 : 5.15 : 1.90

<sup>a</sup>Determined by elemental analysis.

Herein, the micellar copolymerization of hydrophobically associating polyacrylamides containing twin-tailed units is explored. A detailed characterization of the copolymers via <sup>1</sup>H NMR and FTIR spectroscopy and elemental analysis (EA) is presented. To provide detailed information about the performance of PAAD (see below for its chemical composition) in Cr(III) removal, precipitation measurements were used to investigate the effect of the addition of PAAD in various concentrations to suspensions of Cr(OH)<sub>3</sub>.

## EXPERIMENTAL

### Materials

Acrylamide (AM, Tianjin Chemical Reagent Co.) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS, Shanghai Chemical Reagent Co.) were thrice recrystallized and dried at room temperature. Sodium 2-acrylamido-2-methylpropane sulfonate (AMPS-Na) stock solution was prepared by adding 10 mL of 30% NaOH solution to 20 g AMPS dissolved in about 40 mL of distilled water under cooling. After adjusting the pH to 7 with 1M NaOH, distilled water was added to make up the volume to 100 mL. 2,2'-Azobis (2-methylpropionamide) dihydrochloride (AIBA, Qingdao Run Xing Photoelectric Materials Co.) and sodium dodecyl sulfate (SDS, Shanghai Chemical Reagent Co.) were used as received. The twin-tailed hydrophobic monomer *N,N*-dibutylmethacrylamide (DBMAAM, 90%) was prepared according to the literature<sup>19</sup>; <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O): δ 0.95–0.98 (6H, t, —N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> CH<sub>3</sub>)<sub>2</sub>), 1.30 (4H, m, —N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> CH<sub>3</sub>)<sub>2</sub>), 1.55 (4H, m, —N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> CH<sub>3</sub>)<sub>2</sub>), 3.30–3.38 (4H, t, —N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> CH<sub>3</sub>)<sub>2</sub>), 1.95 (3H, s, CH<sub>3</sub>—C=), 4.95, 5.12 (2H, d, d, CH<sub>2</sub>=). Analytical reagents were used as received (Kermel).

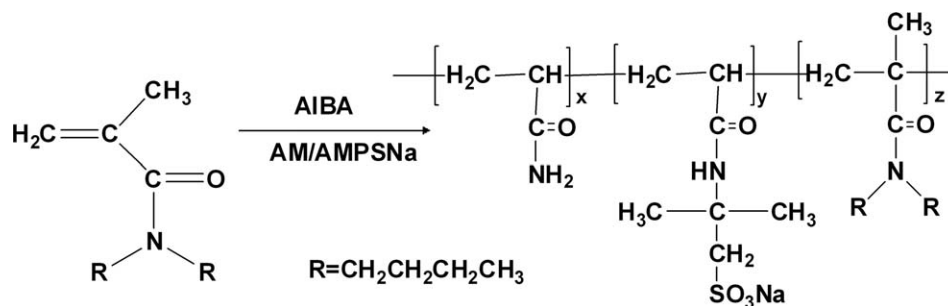
### Polymerization of PAAD

All samples were prepared using micellar copolymerization.<sup>20,21</sup> PAAD-*n* (*n* = 1–4) was synthesized with different ratios of AM/AMPS-Na/DBMAAM, shown in Table I, under otherwise identical conditions.

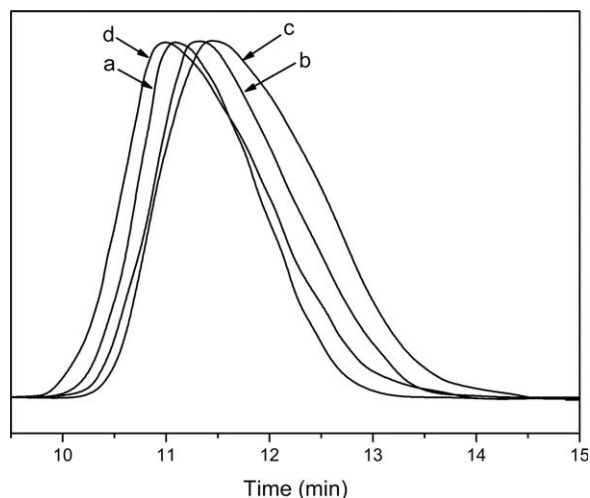
Each reaction was conducted in a 250 mL, three-necked, round-bottomed flask equipped with a condenser, magnetic stirrer, and nitrogen inlet/outlet. Because of the viscosity of the reaction mixture, especially during the latter stages of polymerization, the total monomer concentration was kept below 3 wt %. The synthesis was carried out with a range of DBMAAM concentrations (0.5–2.0 mol %) and 5 mol % AMPS-Na, as indicated in Table I, which summarizes the details of the copolymers synthesized herein.

The reactor was purged with nitrogen for 30 min to remove trapped air before being loaded with the desired mixture of sodium dodecyl sulfate (SDS), AM, AMPS-Na, DBMAAM, and deionized water. When the mixture was homogeneous, an aqueous AIBA solution was added to the reactor. The reaction was carried out at 56°C for 10 h under nitrogen flow and vigorous stirring. After cooling the final reaction mixture, the aqueous polymer solutions were precipitated using ethanol, and the precipitate was washed with ethanol five times to remove emulsifiers and residual monomers, dried under vacuum at 50°C for 4 days, and stored in a desiccator. The detailed synthesis of PAAD is shown in Scheme 1.

The weight-average molecular weights (*M<sub>n</sub>*) of the synthesized copolymers determined by gel permeation chromatography–multiangle laser light scattering (GPC-MALLS) are also shown in Table I.



**Scheme 1.** Synthesis of PAM/AMPS-Na/DBMAAM (PAAD).



**Figure 1.** MALLS-GPC traces of PAAD-1(a), PAAD-2(b), PAAD-3 (c), PAAD-4 (d).

### Characterization

Elemental analyses were performed on a Vario E1 III analyzer (Elementar, Hanau, Germany).

All  $^1\text{H-NMR}$  experiments were performed on an AVANCE400 NMR spectrometer (Bruker, Switzerland).  $\text{D}_2\text{O}$  and TMS were used for field-frequency locking and as internal standard, respectively.

FTIR spectra were recorded on a Tensor 27 spectrometer (Bruker, Switzerland) in the frequency range  $4000\text{--}400\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$  over 16 scans using KBr pellets as matrix for the samples.

GPC-MALLS measurements used an aqueous gel permeation chromatograph coupled to a Wyatt Technology DAWN HELEOS 18 angle (from  $15^\circ$  to  $165^\circ$ ) light scattering detector with a Ga-As laser (658 nm, 40 mW). The mobile phase contained 0.1M aqueous NaCl filtered through Millipore  $0.2\text{ }\mu\text{m}$  hydrophilic membranes. PAAD was dissolved in 0.1M aqueous NaCl solution and filtered (pore size:  $0.8\text{ }\mu\text{m}$ ). The resulting 0.1 mg/mL PAAD solution was injected at a flow rate of 1.0 mL/min. A differential refractive index detector (Optilab-REX) was used to measure the differential refractive indices ( $dn/dc$ ) of different copolymer solutions at 658 nm and  $25^\circ\text{C}$ .

DLS experiments were performed on DAWN HELEOS, Wyatt QELS, and Optilab DSP instruments after filtering all samples through Millipore  $0.45\text{ }\mu\text{m}$  hydrophilic membranes.

Surface tension measurements were performed at  $25^\circ\text{C}$  on a Kruss K12 Processor Tensiometer equipped with a Wilhelmy plate.

### Precipitation Experiments for Cr(III)

Dissolution of a weighed quantity of  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  in distilled water yielded a solution of 1.0 g/L Cr(III).  $\text{Cr}(\text{OH})_3$  suspensions were adjusted to pH 10 by adding  $\text{Ca}(\text{OH})_2$ . All precipitations were performed at  $25^\circ\text{C}$  and with different concentrations of PAAD to select the optimal PAAD dose as coagulant aid. The Cr(III) ion concentration in the supernatant was determined by

atomic absorption spectrophotometry (Varian Spectra HP 3510).

For the above measurements, all PAAD sample solutions were gently stirred until all bubbles disappeared and kept for several days. The polymer stock solutions were diluted with water to the desired concentration and stored overnight for equilibration prior to measurements. Every solution stood unstirred for at least 24 h before each experiment to allow for the relaxation of any structure formed during stirring.

## RESULTS AND DISCUSSION

### Evaluation of PAAD

PAAD, containing different quantities of monomers, was characterized by EA, as shown in Table I. The actual mole ratio of AM/AMPS-Na/DBMAAM was calculated via the weight percentages of carbon, hydrogen, nitrogen, and sulfur, as listed in Table I. As evident from Table I, the mole percent of hydrophobe incorporated in PAAD was always found to be less than the mole percent in the feed.

Figure 1 depicts the GPC curves of PAAD, the weight-average molecular weights, and polydispersity indexes (PDIs) of PAAD, as determined by gel permeation chromatography–multi-angle light scattering (GPC-MALLS). These results are also listed in Table II. All PAAD samples exhibited low polydispersity between 1.35 and 1.48, whereas the molecular weights of DDSFAM were ascertained to be in the range  $(1.42\text{--}1.78) \times 10^6\text{ g/mol}$  by GPC-MALLS.

It is known that the incorporation of hydrophobic units into the hydrophilic backbone of polyacrylamide results in PAAD with unique hydrophobically associated properties due to hydrophobic interactions. Candau and his coworkers<sup>22,23</sup> reported that the high concentration of hydrophobic monomers in micelles favored their incorporation as blocks in the backbone of hydrophobically modified polyacrylamide. Hence, in our work, the sequence distribution of the hydrophobic monomers DBMAAM in PAAD was controlled by varying the number of hydrophobes per micelle,  $N_H$ , which was calculated using the following equation:

$$N_H = ([\text{DBMAAM}] \times \text{Nagg}) / ([\text{SDS}] - \text{cmc}) \quad (1)$$

where  $[\text{DBMAAM}]$  is the initial molar concentration of the hydrophobic twin-tailed monomer,  $[\text{SDS}]$  is the molar surfactant concentration, cmc is its critical micellar concentration and Nagg is its aggregation number. For our system, the Nagg of

**Table II.** Values of  $N_H$  and GPC-MALLS Results of PAAD

Sample	$N_H^a$	$M_n\text{ (g mol}^{-1}\text{)}^b$	$(M_w/M_n)^b$
PAAD-1	1.53	$1.63 \times 10^6$	1.35
PAAD-2	3.09	$1.52 \times 10^6$	1.40
PAAD-3	4.49	$1.42 \times 10^6$	1.48
PAAD-4	6.18	$1.78 \times 10^6$	1.42

<sup>a</sup>The number of hydrophobic monomers per micelle,  $N_H$ , calculated according to equation (1) based on the DBMAAM content determined by EA.

<sup>b</sup> $M_n$  and polydispersity measured by GPC-MALLS.

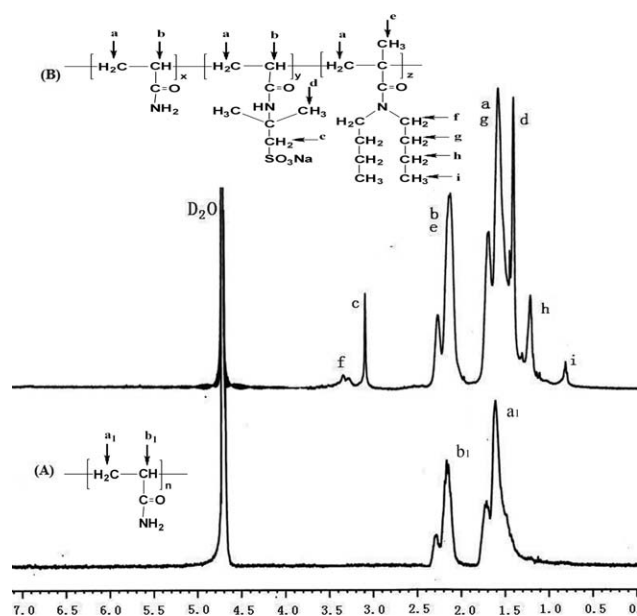


Figure 2.  $^1\text{H}$  NMR spectra of PAM (a) and PAAD-3 (b).

SDS was  $\sim 62$  and the cmc of SDS was  $9.3 \times 10^{-3}$  M. The  $N_H$  of the samples was calculated according to equation (1) based on the DBMAAM content determined by EA. The value of  $N_H$ , which determines the distribution of DBMAAM blocks in PAAD, indicates the hydrophobicity of PAAD in water. The results are shown in Table II.

### $^1\text{H}$ NMR Spectra

Figure 2 displays the  $^1\text{H}$  NMR spectra of PAAD-3 and PAM as typical cases. Compared with the unmodified polyacrylamide (PAM), the formation of PAAD (i.e., PAAD-3) reveals new broad signals at 3.13 ppm (peak c) and 1.30–1.35 ppm (peak d), which correspond to the protons of  $-\text{CH}_2-\text{SO}_3\text{Na}$  and methyl groups ( $-\text{CH}_3$ ) of AMPS-Na. The twin-tailed chain of the hydrophobic group of the copolymer is evidenced by peaks at 3.25–3.40 (f), 1.45 (g), 1.10–1.25 (h), and 0.75–0.85 ppm (i). Because peak e could be masked by peak b of the copolymers, direct proof of the

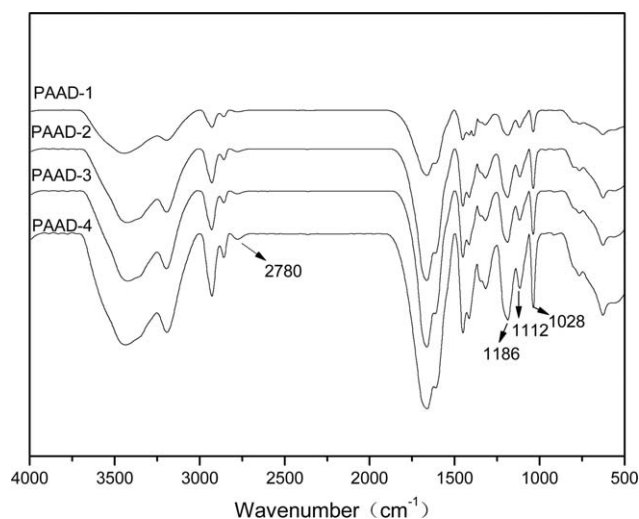


Figure 3. FT-IR spectra of PAAD- $n$  ( $n = 1-4$ ).

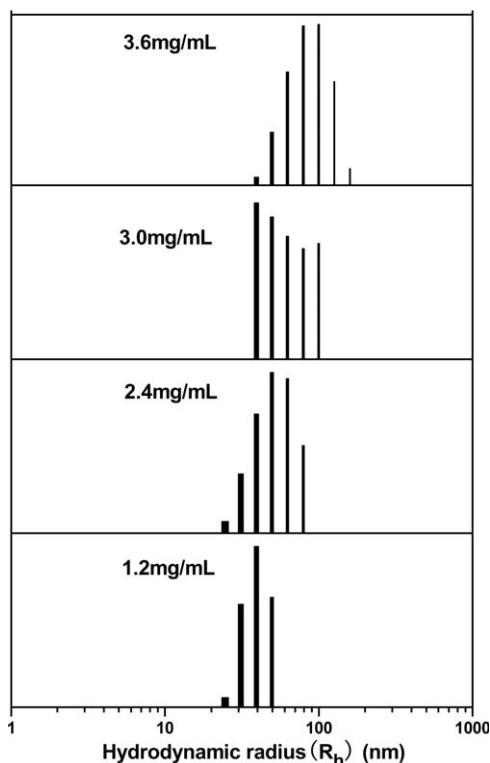


Figure 4. Distribution of the hydrodynamic radius of PAAD-1 in solution at pH 10 and different copolymer concentrations.

linkage of the methyl group ( $-\text{CH}_3$ ) to the copolymer backbone is extremely difficult by  $^1\text{H}$  NMR spectroscopy.

### FTIR Spectra

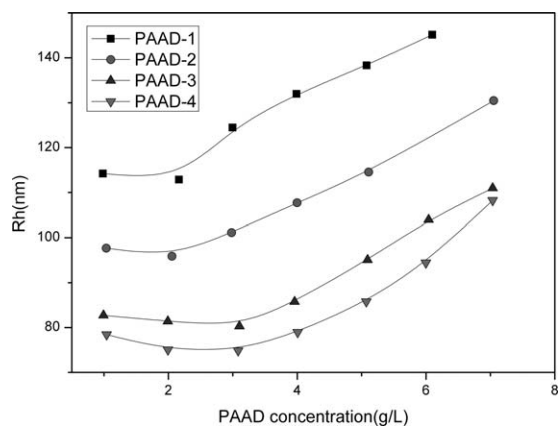
Figure 3 shows the FTIR spectra of PAAD- $n$  ( $n = 1-4$ ). The characteristic absorption peaks of sulfonic acid groups in copolymers at 1186, 1112, and  $1028\text{ cm}^{-1}$  indirectly confirm the existence of AMPS-Na in PAAD. Moreover, a comparison of the absorption intensity of peaks ( $2780\text{ cm}^{-1}$ ) arising from protons of the methylene bridges connected to the acrylamido group ( $-\text{CON}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$ ) of DBMAAM in PAAD revealed that the intensity of the band increased gradually with DBMAAM content from PAAD-1 to PAAD-4.

### DLS Measurements

The behavior of polymer solutions is determined by the competition between intramolecular and intermolecular interactions, which control the size of aggregates in solution. The size of the aggregates was determined by DLS measurements.<sup>24,25</sup> Figure 4 shows the distribution of the hydrodynamic radius ( $R_h$ ) in solutions of pH 10 at different concentrations of PAAD-1. The distribution of  $R_h$  broadens and the mean hydrodynamic radius increases with concentration of PAAD-1 from 1.2 to 3.6 mg/mL, indicating the dependence of the aggregate size on the molecular association of twin-tailed hydrophobic groups.

The distribution of the hydrodynamic radius and the average hydrodynamic radius of PAAD, obtained from DLS experiments, at different concentrations and pH 10 is shown in Figure 5. The average hydrodynamic radius first decreases and then increases rapidly with increasing concentration of PAAD. This





**Figure 5.** Variations in the hydrodynamic radius of PAAD in solution at pH 10.

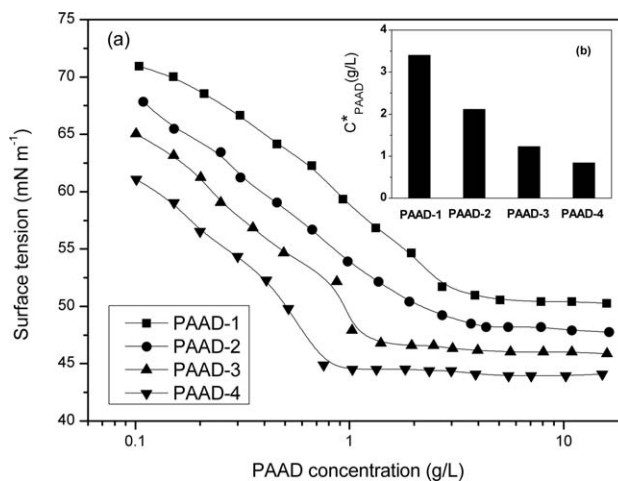
behavior can be explained by the intramolecular hydrophobic association of PAAD moieties at low concentrations, which lead to coil contraction and a decrease in Rh, and intermolecular hydrophobic association at higher concentrations, which lead to an increase in Rh.

#### Surface Tension Measurements

Figure 6(a) displays the relationship between surface tension and PAAD concentration at 25°C. The critical association concentrations of PAAD ( $C^*_{PAAD}$ ) in aqueous solution are shown in Figure 6(b). Figure 6 illustrates that the surface tension of PAAD decreases significantly with increasing copolymer concentration below  $C^*_{PAAD}$ , whereas solutions with copolymer concentrations above  $C^*_{PAAD}$  exhibit surface activity. Moreover,  $C^*_{PAAD}$  decreases rapidly with increasing hydrophobic content in PAAD, indicating that the hydrophobic twin-tailed groups in copolymers could effectively promote the surface activity of PAAD in aqueous solution. A decrease in  $C^*_{PAAD}$  could be attributed to an increased aggregation of PAAD molecules at the air–solution interface at high PAAD concentrations.

#### Precipitation of Cr(III)

We have also investigated the effect of PAAD concentration on the precipitation of  $Cr(OH)_3$  suspensions under alkaline conditions. Figure 6 shows the images of the sedimentation of



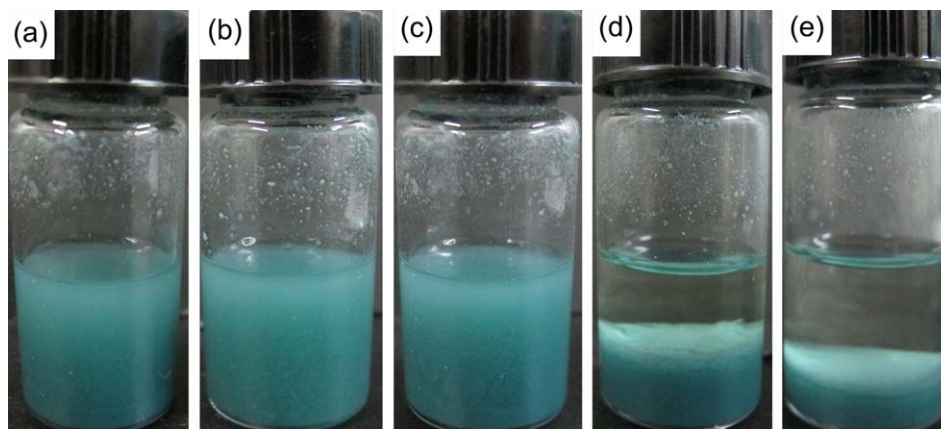
**Figure 6.** Variation in surface tension with PAAD concentration at 25°C.

$Cr(OH)_3$  at pH 10 obtained in the absence [Figure 7(a)] and presence of PAAD-4 at different concentrations. At PAAD-4 concentrations of 0.1 and 0.5 g/L, shown in Figures 7(b) and 7(c), the morphology was similar to that obtained in the absence of PAAD-4, and no precipitation of  $Cr(OH)_3$  was observed. However, at higher PAAD-4 concentrations (1.0 and 2.0 g/L),  $Cr(OH)_3$  precipitated from the suspension, as shown in Figures 7(d) and 7(e), forming a relatively dense layer. In particular, the precipitation of  $Cr(OH)_3$  obtained at 2.0 g/L was thinner and firmer than that at 1.0 g/L.

The improvements and removal rates in the precipitation of  $Cr(OH)_3$  obtained using PAAD samples as a coagulant aid with varying polymer dose are shown in Table III. The optimal PAAD doses for the removal of Cr(III) through precipitation of  $Cr(OH)_3$  were larger than the  $C^*_{PAAD}$  values obtained from surface tension measurements. Hence, the above results unveil the dependence of  $Cr(OH)_3$  precipitation on the molecular association of the hydrophobic groups of PAAD in solution.

#### Schematic Representation of the Precipitation of $Cr(OH)_3$ Using PAAD Samples as Coagulant Aid

Based on the results discussed above, we propose a schematic representation of the formation of  $Cr(OH)_3$  and its



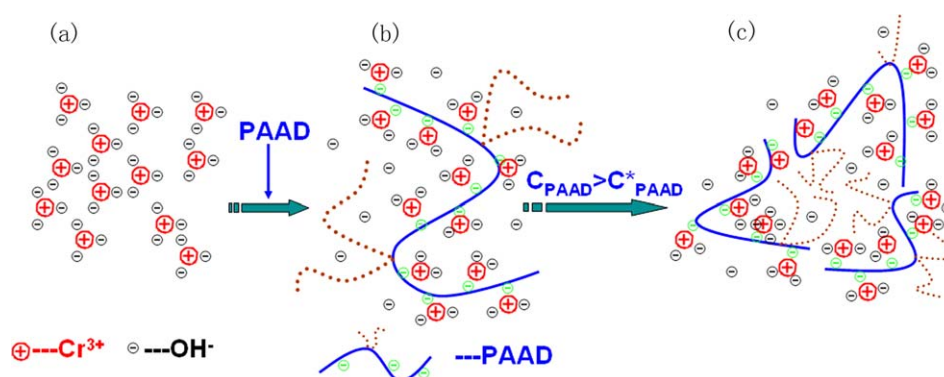
**Figure 7.** Images of  $Cr(OH)_3$  deposited in the absence (a) and presence of PAAD-4 at different concentrations: (b) 0.1 g/L, (c) 0.5 g/L, (d) 1.0 g/L, and (e) 2.0 g/L, wherein pH=10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Effect of Polymer Dose on the Precipitation of Cr(OH)<sub>3</sub> Using PAAD Samples as a Coagulant Aid at pH 10

Samples	PAAD-1				PAAD-2			
	1	2	3	4	0.5	1	2	3
Cr(III) concentration of supernatant fluid (mg/L)	908.17	890.74	828.68	0.42	978.14	815.28	796.52	0.39
Removal rates of Cr (III) (%)	81.837	82.185	83.426	99.992	80.437	83.694	84.070	99.992

Samples	PAAD-3				PAAD-4			
	0.5	1	2	3	0.1	0.5	1	2
Cr(III) concentration of supernatant fluid (mg/L)	960.78	780.22	0.42	0.21	950.03	720.15	0.35	0.03
Removal rates of Cr (III) (%)	80.784	84.396	99.992	99.996	80.999	85.597	99.993	99.999

**Figure 8.** Schematic representation of the formation of Cr(OH)<sub>3</sub> and its precipitation using PAAD samples as coagulant aid in solution at pH 10. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

precipitation using PAAD samples as coagulant aid, shown in Figure 8. As discussed previously,<sup>26,27</sup> Cr(III) can exist in solutions of pH 10 as Cr(OH)<sub>3</sub>; the optimal condition and a model for the precipitation of Cr(OH)<sub>3</sub> from suspension is shown in Figure 8(a). In general, the negative charge (–SO<sub>3</sub><sup>–</sup>) on PAAD will be attracted by the positively charged Cr(III), primarily coordinated by hydroxide and water, as proposed in Figure 8(b). Meanwhile, it is more likely that the amines on PAAD are complexed to solid Cr(OH)<sub>3</sub> at surface sites, causing the particles to aggregate with the polymer. As shown in Figure 7 above, the precipitation of Cr(OH)<sub>3</sub> increased with increasing PAAD concentration in solution, which can be explained by the hydrophobic association of PAAD copolymers for PAAD concentrations above the C\*<sub>PAAD</sub> values, thereby forming a hydrophobic core in water, schematically shown in Figure 8(c), and acting as nucleus for Cr(OH)<sub>3</sub> binding to PAAD.

## CONCLUSIONS

Novel twin-tailed hydrophobically associating copolymers (PAAD) were prepared using micellar radical polymerization, and their potential as coagulant aid for the precipitation of Cr(OH)<sub>3</sub> suspensions under alkaline conditions was investigated. The chemical structure of PAAD was determined by

elemental analysis, <sup>1</sup>H NMR and FTIR spectroscopy, and the molecular weights of the copolymers obtained from GPC-MALLS ranged from 1.42 to 1.78 × 10<sup>6</sup> g/mol. The aggregation properties of PAAD samples were studied by DLS. The critical association concentrations of the copolymers, measured by surface tension, decreased with an increase in the DBMAAM content in the copolymers. The precipitation experiments of Cr(III) indicated its high potential for practical application as a coagulant aid.

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