

# Synthesis and Flocculation Properties of Poly(diallyldimethyl ammonium chloride–vinyl trimethoxysilane) and Poly(diallyldimethyl ammonium chloride–acrylamide–vinyl trimethoxysilane)

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**ABSTRACT:** Poly(diallyldimethyl ammonium chloride–vinyl trimethoxysilane) [P(DADMAC–VTMS)] and poly(diallyldimethyl ammonium chloride–acrylamide–vinyl trimethoxysilane) [P(DADMAC–AM–VTMS)], the latter a new cationically charged and hydrophobically modified flocculant, were obtained by radical polymerization initiated by potassium persulfate. The effects of the vinyl trimethoxysilane (VTMS) feed ratio on the intrinsic viscosity and solubility of the polymers were examined. The effects of the flocculants on turbidity removal, decolorization, and oil removal in water treatment were also studied. The introduction of VTMS increased the intrinsic viscosities of P(DADMAC–VTMS) and P(DADMAC–AM–VTMS) in comparison with the viscosities of poly(diallyldimethyl ammonium chloride) and poly(diallyldimethyl ammonium chloride–acrylamide), respectively, but reduced their solubilities. The introduction of VTMS also enhanced the flocculation properties of P(DADMAC–VTMS) and P(DADMAC–AM–VTMS), including turbidity removal, decolorization, and oil removal. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 335–342, 2002; DOI 10.1002/app.10339

**Key words:** water-soluble polymers; radical polymerization; modification; copolymerization; polyamides

## INTRODUCTION

Flocculation is one of the most important decontamination processes in drinking or wastewater treatment. The flocculant is undoubtedly the most important factor in this process, and effective and multifunctional flocculants are constantly being sought. Cationic, quaternary ammo-

nium polyelectrolytes have been the subject of increased research efforts in recent years because of their diverse commercial applications. Among the most prominent water-soluble and cationic ammonium polymers are the homopolymers and copolymers of diallyldimethyl ammonium chloride (DADMAC).<sup>1</sup> Many studies have been reported on the uses of the homopolymers or copolymers of DADMAC as primary flocculants or flocculant aids in the destabilization of colloidal suspensions, the clarification of industrial wastewater, the separation of solid–liquid systems, the treatment of sewage, and so forth.<sup>2–8</sup>

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**Table I** Copolymerization of DADMAC with VTMS

Sample	DADMAC Feed Ratio (mol %)	VTMS Feed Ratio (mol %)	Initial DADMAC Concentration (wt %)	Yield (%)	$[\eta]$ (dL/g)	Cationicity (mol %)
1	100	0	65	96	1.96	100
2	99.5	0.5	65	92	2.01	99.5
3	99	1	65	95	1.97	99
4	97	3	65	91	2.19	97
5	95	5	65	89	2.14	95
6	93	7	65	92	2.17	93
7	90	10	65	94	2.19	90

The copolymerization of DADMAC with other monomers can improve the properties and broaden the utility of the polymers. Acrylamide (AM) is often employed as a comonomer because of its reasonable cost, the ease of its polymerization, and the high quality of the products.<sup>9</sup> However, with industrial development, various types of wastewater are released. In this situation, it is impossible for a flocculant to achieve all effects. Fortunately, modification, grafting, and other means can improve the properties of polymers for various industrial purposes.<sup>2,10–14</sup> Hydrophobically functionalized water-soluble polymers have shown excellent flocculation properties in the treatment of wastewater containing oil droplets or other hydrophobic substances.<sup>15,16</sup> As a hydrophobic monomer, vinyl trimethoxysilane (VTMS) can be polymerized with DADMAC.<sup>17–19</sup> The cationically charged, hydrophobically modified polymer poly(diallyldimethyl ammonium chloride–vinyl trimethoxysilane) [P(DADMAC–VTMS)] exhibits improved performance and activity in water treatment (e.g., the breaking of reverse emulsions and the removal of emulsified or dispersed oil from wastewater).<sup>17</sup> However, like poly(diallyldimethyl ammonium chloride) (PDADMAC), P(DADMAC–VTMS) does not have a high intrinsic viscosity ( $[\eta]$ ) or molecular weight because of the low activity of the DADMAC monomer. This must lead to deficient adsorption bridging when P(DADMAC–VTMS) is used as a flocculant in water treatment. For this reason, poly(diallyldimethyl ammonium chloride–acrylamide–vinyl trimethoxysilane) [P(DADMAC–AM–VTMS)], which has not been reported previously, with its cationic groups, hydrophobic groups, and high values of  $[\eta]$ , is expected to have excellent flocculation properties.

This work was undertaken in the course of developing cationic and hydrophobic polyelectro-

lytes that could be used as effective flocculants. For this purpose, the copolymerization of DADMAC with VTMS and the tripolymerization of DADMAC, AM, and VTMS were investigated, and the effects of the VTMS feed ratio on the  $[\eta]$  values and solubility of the polymers are discussed. The flocculation properties of the synthesized polymers, such as the effects on turbidity removal, decolorization, and oil removal, are also studied in this article.

## EXPERIMENTAL

### Materials

DADMAC was prepared and purified in the laboratory as a 70% aqueous solution.<sup>20,21</sup> AM, commercially available, was recrystallized from acetone. VTMS, as a 98% solution obtained from the Haerbin Chemical Graduate School (Haerbin, Heilongjiang Province, China), was used without further purification. Potassium persulfate (KPS) and ethylenediamine tetraacetic acid tetrasodium salt ( $\text{Na}_4\text{EDTA}$ ) were analytical-reagent-grade. Potassium poly(vinyl sulfate) (PVSK) and toluidine blue were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Absolute alcohol, acetone, and NaCl were chemical-purity-grade. Kaolinite and activated red (K-2BP) were industrial products.

### Synthesis of P(DADMAC–VTMS) and P(DADMAC–AM–VTMS)

P(DADMAC–VTMS) and P(DADMAC–AM–VTMS) were polymerized under the conditions shown in Tables I and II, respectively. To a three-necked, round-bottom flask (250 mL) equipped with a me-

**Table II** Tripolymerization of DADMAC, AM, and VTMS

Sample	DADMAC Feed Ratio (mol %)	AM Feed Ratio (mol %)	VTMS Feed Ratio (mol %)	Initial DADMAC Concentration (wt %)	Yield (%)	[ $\eta$ ] (dL/g)	Cationicity (mol %)
1	70	30	0	50	95	3.97	52.3
2	69.65	29.85	0.5	50	92	4.18	50.5
3	69.3	29.7	1.0	50	89	4.45	51.7
4	50	50	0	40	96	5.08	37.7
5	49.75	49.75	0.5	40	90	5.25	36.9
6	49.5	49.5	1.0	40	93	5.51	36.4
7	30	70	0	20	95	6.50	22.8
8	29.85	69.65	0.5	20	91	6.76	23.0
9	29.7	69.3	1.0	20	94	7.09	21.9
10	20	80	0	15	93	8.00	16.2

chanical stirrer, a nitrogen inlet, and a nitrogen outlet were added the desired quantities of DADMAC and VTMS or DADMAC, AM, and VTMS. Na<sub>4</sub>EDTA (0.02% based on the total weight of the reactants) was added. The concentration of DADMAC was then adjusted to a desired value by the addition of deionized water. The solution was purged with nitrogen at room temperature for 1 h. Solid KPS (1% based on the total weight of the reactants) was added, and the mixture was purged continuously for 10 min. The mechanical stirrer was then started, and the flask was sealed with a blanket of nitrogen gas and placed in a bath maintained at 35 (20 h), 60 (3 h), and 80°C (2 h) to complete the polymerization. During the process, some deoxygenated, deionized water was added as needed to control the bulk viscosity and maintain mixing.

The resulting polymer was precipitated by the addition of the dilute mixture dropwise to a large amount of acetone and rapid stirring. The polymer was washed several times with small amounts of absolute alcohol and vacuum-dried to a constant weight at 50°C. The polymer yield ( $W$ ) was calculated with the following equation:

$$W = \frac{(\text{g of polymer recovered}) \times 100}{\text{g of total monomers added}}$$

#### [ $\eta$ ]

The viscosities of the product polymers in 1M aqueous NaCl solutions were measured with an Ubbelohde viscometer (4 mL, 0.6 mm) at 30  $\pm$  0.1°C. [ $\eta$ ] was obtained by extrapolation of both

reduced viscosities ( $\eta_{sp}/c$ ) and inherent viscosities ( $\ln \eta_r/c$ ) to infinite dilution.

#### Cationicity

The molar fractions of VTMS in P(DADMAC–VTMS) and P(DADMAC–AM–VTMS) were not more than 10 and 1%, respectively, so the cationicity of P(DADMAC–VTMS) could be assumed to be the DADMAC feed ratio in the copolymerization, and the cationicity of P(DADMAC–AM–VTMS) could be determined by the colloid titration method suitable for determining the cationicity of poly(diallyldimethyl ammonium chloride–acrylamide) [P(DADMAC–AM)].<sup>9</sup> For the titration of cationic polymers, 1/400N PVSK was used as the titrant, and toluidine blue was used as an indicator.

The quantity of VTMS introduced into P(DADMAC–VTMS) or P(DADMAC–AM–VTMS) was below the detection limit of IR, NMR, or <sup>13</sup>C-NMR.

#### Coagulation Method

The flocculation properties of the polymers were evaluated by jar tests with kaolinite suspensions, dye liquor, and oily wastewater. The kaolinite suspensions were prepared by the addition of kaolinite (15.625 g) to distilled water (50 L). Na<sub>2</sub>CO<sub>3</sub> (1.6 g) was added to make the alkalinity 0.8–1.0 mequiv/L.<sup>22</sup> The dye liquor was prepared by the addition of activated red (5 g) to tap water (50 L) and mixing to homogeneity. The oily wastewater was taken from the oil separator of the Jinan Refinery Plant and had a pH of 7.6 and a chemical oxygen demand of 234.0 mg/L.

The jar tests were run on a PB-700 jar tester (Phipps & Bird Co., Richmond, VA). To 500 mL of the test sample, a known quantity of polymer was added. The test water was then rapidly stirred at 120 rpm for 2 min, slowly stirred at 60 rpm for 7 min, and then allowed to settle for 10 min. Supernatant samples were then withdrawn from a position about 2 cm below the water surface for the following measurements.

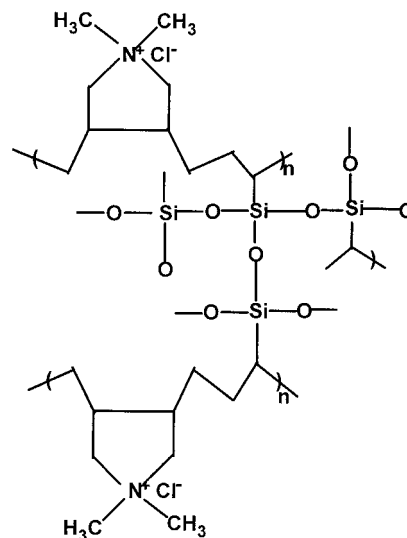
The turbidity was measured on a 2100N IS turbidimeter (Hach Co., Loveland, CO). In this project, the effect of the flocculants on decolorization was expressed as the absorbance reduction of the dye liquor. The absorbance was measured on a DR/4000 spectrophotometer (Hach) at 550 nm, the wavelength of the maximum absorbance of the activated red solution. The oil content was determined by the ether extraction of the oil from the wastewater and the subsequent measurement of its ultraviolet absorbance at 225 nm relative to a standard. Measured by the aforementioned methods, the turbidity of the original kaolinite suspensions, the absorbance of the original dye liquor, and the oil content of the original oily wastewater were 202 NTU, 1.866, and 93.57 mg/L, respectively.

## RESULTS AND DISCUSSION

### Effects of the VTMS Feed Ratio on the Copolymerization of DADMAC with VTMS

By changing the VTMS feed ratio from 0 to 10%, fixing the initial concentration of DADMAC at 65%, and keeping other reaction conditions constant as described earlier, we investigated the effects of the VTMS feed ratio on the copolymerization, and the results are listed in Table I.

The VTMS feed ratio had no effect on the polymer yield, but with increasing VTMS feed ratio,  $[\eta]$  for P(DADMAC-VTMS) tended to increase slightly. From tests on the solubility behavior, it was also found that the greater the VTMS feed ratio was, the worse the solubility of the vacuum-dried P(DADMAC-VTMS) was. When the VTMS feed ratio reached 10%, it became very difficult to dissolve the polymer in water. With a VTMS feed ratio greater than 10%, the polymer only swelled in water and could not untangle and move away from the solid polymer mass. This behavior can be explained as follows: after copolymerizing with DADMAC in an aqueous solution, VTMS crosslinked P(DADMAC-VTMS) by hydrolysis



**Figure 1** Crosslinked structure of hydrolyzed P(DADMAC-VTMS).

and polycondensation.<sup>17</sup> The crosslinked structure of P(DADMAC-VTMS) is shown in Figure 1.

### Effects of the VTMS Feed Ratio on the Tripolymerization of DADMAC with AM and VTMS

In the tripolymerization of DADMAC, AM, and VTMS, the VTMS feed ratio was changed from 0 to 1.0%. Because AM is highly reactive, this led to a high polymerization rate that made the reaction system difficult to control. Therefore, according to the AM feed ratio, the initial concentration of DADMAC was adjusted to a suitable value, and other reaction conditions were kept constant. The results of tripolymerization are listed in Table II. With a decreasing DADMAC feed ratio and an increasing AM feed ratio, the cationicities of the tripolymer decreased and  $[\eta]$  increased as expected.<sup>23</sup> As with P(DADMAC-VTMS),  $[\eta]$  for P(DADMAC-AM-VTMS) increased with the VTMS feed ratio. It was found from the solubility tests that when either the AM feed ratio was increased or the VTMS feed ratio was changed from 0.5 to 1.0%, the solubility decreased. The tripolymer with a VTMS feed ratio of more than 1.0% only swelled in water. Normally, DADMAC monomers polymerize by incorporating both allyl bonds within the same molecule to form a linear polymer chain. A small proportion of DADMAC monomer, however, can polymerize via the incorporation of only one of its allyl bonds, thereby leaving

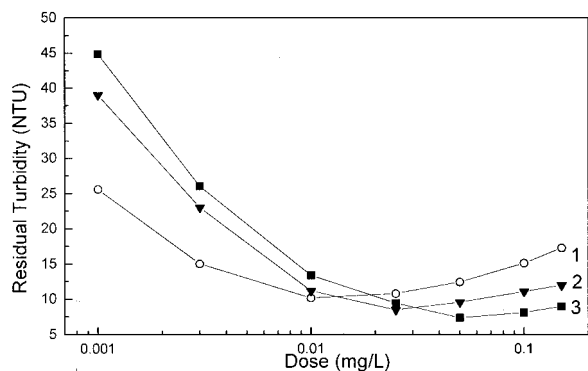


a pendent double bond in the molecule. These pendent double bonds can subsequently initiate branching to produce crosslinked polymers that have a reduced solubility in water.<sup>24</sup> It is possible that the tendency of DADMAC to polymerize via branching or crosslinking, in combination with the greater reactivity of AM, can result in the formation of nonlinear polymers. In addition, the hydrolysis of VTMS makes the polymers further crosslinked. Therefore, the upper limit of the VTMS feed ratio (1.0%) in the tripolymerization is much lower than that in the copolymerization (10%). Whether the flocculant can be used conveniently depends on the solubility of the polymer. In addition, the solubility of the polymer has an effect on the flocculation performance. Therefore, the VTMS feed ratio in the aforementioned polymerization reaction must be strictly controlled.

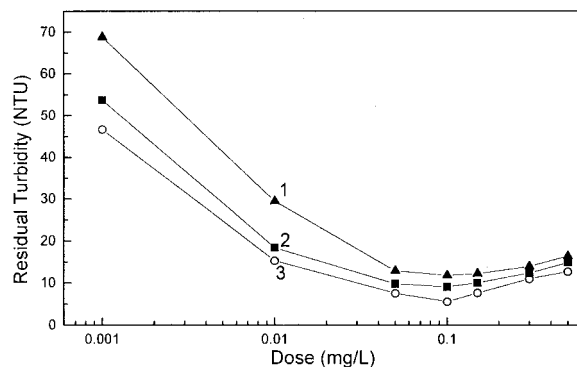
## Flocculation Evaluation

### Effect on Turbidity Removal

The properties of P(DADMAC-VTMS) synthesized under the same reaction conditions except for the VTMS feed ratio (0, 5, and 10%), were investigated, and the results are shown in Figure 2. P(DADMAC-VTMS) had a similar effect on turbidity removal as PDADMAC. With the PDADMAC or P(DADMAC-VTMS) dose increasing, the residual turbidities of the kaolinite suspensions decreased first and then increased. The doses of flocculants had optimum ranges, resulting from overdosed flocculants with positive charges, which neutralized the kaolinite particles



**Figure 2** Turbidity removal by PDADMAC and P(DADMAC-VTMS): (1) PDADMAC,  $[\eta] = 1.96$  dL/g; (2) P(DADMAC-VTMS),  $[\eta] = 2.14$  dL/g, VTMS feed ratio = 5%; and (3) P(DADMAC-VTMS),  $[\eta] = 2.19$  dL/g, VTMS feed ratio = 10%.



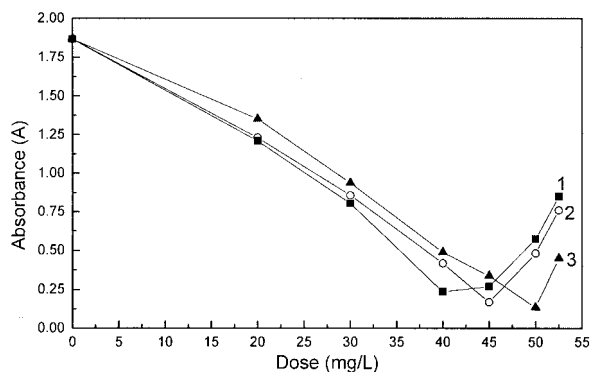
**Figure 3** Turbidity removal by P(DADMAC-AM) and P(DADMAC-AM-VTMS): (1) P(DADMAC-AM),  $[\eta] = 5.08$  dL/g, cationicity = 37.7%; (2) P(DADMAC-AM-VTMS),  $[\eta] = 5.01$  dL/g, cationicity = 35.6%, VTMS feed ratio = 0.5%; and (3) P(DADMAC-AM-VTMS),  $[\eta] = 5.12$  dL/g, cationicity = 36.2%, VTMS feed ratio = 1%.

by changing the electric charges on the surfaces from negative to positive. The optimum dose of P(DADMAC-VTMS) was greater than that of PDADMAC because of its lower cationicity. However, it was more effective in removing turbidity. The differences can be attributed to the incorporation of VTMS, which made P(DADMAC-VTMS) bulky and fluffy, improved its hydrophobicity, and, therefore, enhanced the interaction between P(DADMAC-VTMS) and the hydrophobic kaolinite particles.

The effects of P(DADMAC-AM-VTMS) with similar values of  $[\eta]$  and cationicity but different VTMS feed ratios of 0, 0.5, and 1.0% were investigated, and the results are shown in Figure 3. P(DADMAC-AM-VTMS) and P(DADMAC-AM) also had optimum doses like P(DADMAC-VTMS) and PDADMAC. Compared with P(DADMAC-AM), P(DADMAC-AM-VTMS) had a narrower optimum dose range but showed a better effect on turbidity removal, especially with a higher VTMS content. The introduction of VTMS obviously optimized the structure of P(DADMAC-AM-VTMS), which contributed to a better coagulation performance. From these results, we can conclude that, although cationicity and  $[\eta]$  generally were the key factors in influencing the coagulation performance, in this case the structure of the flocculant had the more important effect on the coagulation performance.

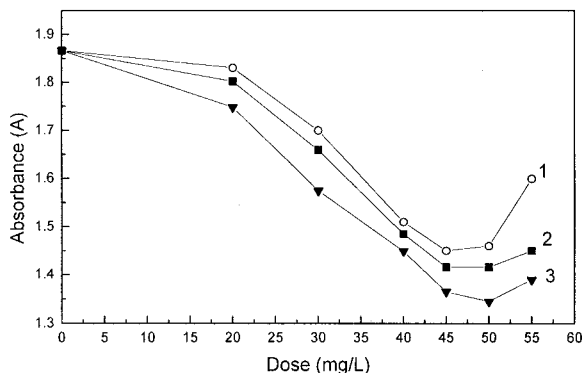
### Effect on Decolorization

Decolorization by the polymers is shown in Figures 4 and 5. PDADMAC and P(DADMAC-

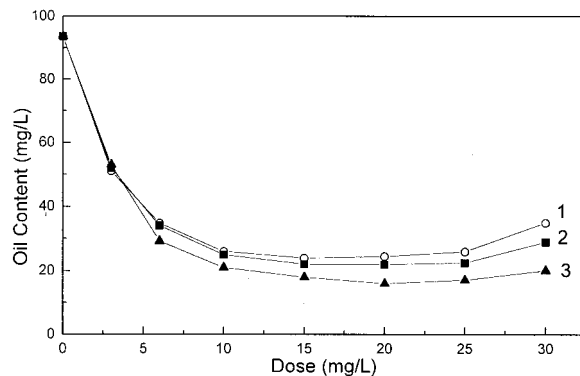


**Figure 4** Decolorization by PDADMAC and P(DADMAC-VTMS): (1) PDADMAC,  $[\eta] = 1.96$  dL/g; (2) P(DADMAC-VTMS),  $[\eta] = 2.14$  dL/g, VTMS feed ratio = 5%; and (3) P(DADMAC-VTMS),  $[\eta] = 2.19$  dL/g, VTMS feed ratio = 10%.

VTMS) were more effective at decolorization than P(DADMAC-AM) and P(DADMAC-AM-VTMS). For a soluble dye such as activated red, the mechanism of the decolorization of the flocculants is probably as follows. The cationic flocculants make the dye molecules separate from the water as neutral species by neutralizing their negative charges, then aggregating them by adsorption-bridge formation, and finally precipitating and removing them from the water. Therefore, the greater the flocculant cationicity is, the better the decolorization efficiency is. Moreover, P(DADMAC-VTMS) was better than PDADMAC, and P(DADMAC-AM-VTMS) was better than P(DADMAC-



**Figure 5** Decolorization by P(DADMAC-AM) and P(DADMAC-AM-VTMS): (1) P(DADMAC-AM),  $[\eta] = 5.08$  dL/g, cationicity = 37.7%; (2) P(DADMAC-AM-VTMS),  $[\eta] = 5.01$  dL/g, cationicity = 35.6%, VTMS feed ratio = 0.5%; and (3) P(DADMAC-AM-VTMS),  $[\eta] = 5.12$  dL/g, cationicity = 36.2%, VTMS feed ratio = 1%.

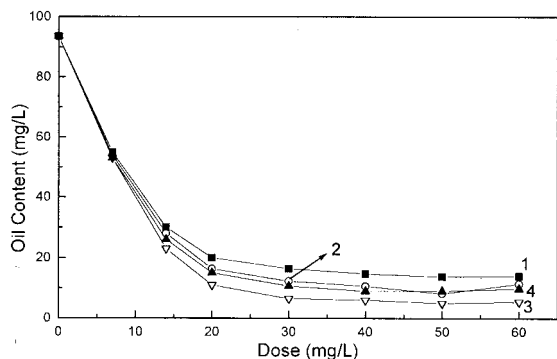


**Figure 6** Oil removal by PDADMAC and P(DADMAC-VTMS): (1) PDADMAC,  $[\eta] = 1.96$  dL/g; (2) P(DADMAC-VTMS),  $[\eta] = 2.14$  dL/g, VTMS feed ratio = 5%; and (3) P(DADMAC-VTMS),  $[\eta] = 2.19$  dL/g, VTMS feed ratio = 10%.

AM); that is, the effects on decolorization by the flocculants increased with their VTMS feed ratio. This effect could be attributed to VTMS, which made P(DADMAC-VTMS) and P(DADMAC-AM-VTMS) bulky and fluffy, improving their hydrophobicity. At the same time, the hydrolysis of VTMS in an aqueous solution could result in P(DADMAC-VTMS) and P(DADMAC-AM-VTMS) having relatively low contents of hydroxyl groups. The hydrophobic and hydroxyl groups enhanced interactions, such as coulombic attraction, hydrogen bonding, and hydrophobic association, between P(DADMAC-VTMS) or P(DADMAC-AM-VTMS) and the dye molecules.

#### Effect on Oil Removal

Oil removal by the selected polymers is shown in Figures 6 and 7. With increasing flocculant doses, the oil content curves decline sharply, reach a plateau, and rise slightly. This can be explained by the following mechanism.<sup>15,16</sup> The oil droplets emulsified in water generally carry a negative surface charge that helps to stabilize the emulsion and keep the droplets dispersed. The cationic polymers can neutralize the negative surface charge. Once the charge is neutralized, the droplets may begin to approach each other and agglomerate or coalesce because the electrostatic repulsion responsible for a significant portion of the emulsion's stability has been eliminated. However, using too much cationic polymer would result in oil droplets that are again charge-stabilized, but this time with a cationic charge instead of an anionic charge. Because PDADMAC and



**Figure 7** Oil removal by P(DADMAC-AM) and P(DADMAC-AM-VTMS): (1) P(DADMAC-AM),  $[\eta] = 5.08$  dL/g, cationicity = 37.7%; (2) P(DADMAC-AM-VTMS),  $[\eta] = 5.01$  dL/g, cationicity = 35.6%, VTMS feed ratio = 0.5%; (3) P(DADMAC-AM-VTMS),  $[\eta] = 5.12$  dL/g, cationicity = 36.2%, VTMS feed ratio = 1%; and (4) P(DADMAC-AM),  $[\eta] = 8.00$  dL/g, cationicity = 16.2%.

P(DADMAC-VTMS) had higher cationicities, they took on the obvious characteristic of restabilizing the oil droplets, as shown in Figure 6. This was not evident for P(DADMAC-AM) and P(DADMAC-AM-VTMS) because of their lower cationicities (Fig. 7). At the same time, the optimum dose for PDADMAC or P(DADMAC-VTMS) was smaller than that for P(DADMAC-AM) or P(DADMAC-AM-VTMS), as evidenced by a comparison of Figures 6 and 7.

It is clear that in their optimum dose ranges P(DADMAC-AM) and P(DADMAC-AM-VTMS) can result in a much lower oil content than PDADMAC or P(DADMAC-VTMS), which shows that  $[\eta]$  or the molecular weight of the flocculants also has an important effect on oil removal, just as the cationicity in decolorization. When P(DADMAC-AM) or P(DADMAC-AM-VTMS) as a cationic polymer with high molecular weight was used for charge neutralization, it accelerated the oil separation because the polymer was attracted to the oil droplet by coulombic attraction, hydrogen bonding, and other intermolecular forces.

From Figures 6 and 7, it can be seen that P(DADMAC-VTMS) had a better effect on oil removal than PDADMAC and P(DADMAC-AM-VTMS) had a better effect than P(DADMAC-AM), even if they had relatively lower  $[\eta]$  values sometimes. This can be explained by their structure. The incorporation of VTMS gave polymers with a small content of hydrophobic groups, which aggregated or associated in a manner similar to a surfactant in an aqueous solvent. Al-

though conventional polymers can only attach themselves to oil droplets by coulombic attraction, hydrogen bonding, and other mechanisms, the hydrophobic groups of P(DADMAC-VTMS) and P(DADMAC-AM-VTMS) could also be attached by hydrophobic-group/hydrophobic-oil-droplet association. Although coulombic attraction still appeared to be the strongest type of attraction, the hydrophobic association or hydrophobic effect appeared to add a significant strengthening to this attraction, as evidenced by improved emulsion breaking and oil removal in Figures 6 and 7.

In addition, the cationic groups of P(DADMAC-VTMS) and P(DADMAC-AM-VTMS) caused an expansion of the polymer in solution, an improvement in polymer solubility, and an enhancement of the attractive interaction between the polymer chains and the oil droplets that normally had negative surface charges. The synergism between the cationic groups and the hydrophobic groups gave P(DADMAC-VTMS) and especially P(DADMAC-AM-VTMS) excellent performance in oil removal and set these flocculants apart from conventional cationic flocculants.

## CONCLUSIONS

P(DADMAC-VTMS) and P(DADMAC-AM-VTMS), the latter a new cationically charged and hydrophobically modified flocculant, were prepared. The introduction of VTMS made  $[\eta]$  for P(DADMAC-VTMS) higher than  $[\eta]$  for PDADMAC and  $[\eta]$  for P(DADMAC-AM-VTMS) higher than  $[\eta]$  for P(DADMAC-AM). However, their solubilities decreased mainly because of the hydrolysis of VTMS, which crosslinked the polymers. The upper limits of the VTMS feed ratio in the copolymerization of DADMAC and VTMS and in the tripolymerization of DADMAC, AM, and VTMS were 10 and 1%, respectively.

This introduction of hydrophobic groups to P(DADMAC-VTMS) and P(DADMAC-AM-VTMS) enhanced their flocculation performance in turbidity removal, decolorization, and oil removal. Because of the synergism between the introduced hydrophobic groups and the intrinsic cationic groups, P(DADMAC-VTMS) had much better flocculation properties than PDADMAC, and P(DADMAC-AM-VTMS) had much better flocculation properties than P(DADMAC-AM). Of the studied flocculants, P(DADMAC-AM-VTMS) gave the best performance in oil removal.

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