

Synthesis in Inverse Emulsion and Decolorization Properties of Hydrophobically Modified Cationic Polyelectrolyte

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ABSTRACT: Poly(acrylamide-diallyldimethyl ammonium chloride-vinyl trimethoxy silane) [P (AM-DAD-MAC-VTMS)] was prepared by inverse free-radical emulsion polymerization technique. VTMS segment was hydrolyzed and condensed to form three dimensional networks. The effects of different factors, such as hydrophobic monomer feed ratio, cationic monomer feed ratio, pH value, and NaCl concentration, on decolorization efficiency were studied. Moreover, the decolorization mechanism was also explained by analyzing FTIR spectra and

UV-vis spectra. The introduction of VTMS on flocculant enhanced removal efficiency of dye molecules. With the increasing VTMS, adsorption and net roofing-sweeping action of hydrophobically modified cationic polyacrylamide played the dominant role in the decoloring process of anion dye. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1602–1609, 2011

Key words: copolymerization; cross-linking; inverse emulsion polyacrylamide; water-soluble polymers

INTRODUCTION

In the past decade, great interests had been taken in treatment of waste-waters from paper-making, printing and dyeing, cosmetics and textile industries. The effluents from such industries contain considerable original dyes or their hydrolysates. Good water-solubility of dyes made it difficult to remove color. Moreover, the presence of slight dyes in aqueous liquor also could produce an obvious colorization¹ and reduce light penetration, which significantly effects photosynthetic activity in aquatic life.² Almost all synthetic dyes can cause physical and chemical reaction of recycle water and worsen the environment, which would threaten human health. For these reasons, many treatment methods have been used to treat dye waste-waters, especially reactive dyes. Most of strategies, such as adsorption,^{3,4} electrochemical treatment,^{5–7} oxidation,^{8,9} and biological degradation,^{10,11} although effective, are expensive or can cause secondary pollution.

Physical or chemical flocculation process has been widely used in treatment of dye waste-water. Although inorganic flocculants may be a choice for pretreatments

to remove suspended particles and coloring materials before biological treatment, strongly pH dependent and high residual ions of Fe²⁺, Fe³⁺, or Al³⁺ limit its full scope application. Fe²⁺ and Fe³⁺ can form new colors to dye waste-water, and Al³⁺ has been regarded as potential danger for human being. Polymeric flocculants are becoming popular in dye waste-water treatment, because of their natural inertness to pH changes, low dosage, and easy handling.^{12–15} Cationic polyacrylamides have been recognized as effective at decolorization, but their effectiveness mainly depend on high cationicity. At low cationicity, cationic polyacrylamides were scarcely applied in decolorization because of poor decolorization efficiency.¹⁶

Flocculants modified with organosilicons have been studied to improve flocculating properties at decolorization, turbidity removal, dewatering, etc.^{17–21} Vinyl trimethoxy silane (VTMS) was commonly used as cross-linking agent because of hydrolysis and condensation reaction of methoxyl group. Kerr and Ramesh²⁰ and Zhao et al.²¹ studied copolymerization of VTMS and Diallyldimethylammonium chloride (DADMAC) or terpolymerization of VTMS, acrylamide (AM), and DADMAC in water solution, but a distinguished drawback was that VTMS hydrolyzed before copolymerization, and was unfavorable for further copolymerization with another comonomers, which would effect the characteristic of final product. Moreover, there were

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disadvantages of low solid content and hard after-treatment by solution polymerization. To avoid these drawbacks, the article adopted the inverse emulsion polymerization technique, which was commonly used to prepare polyelectrolyte.^{22–24} In the system, VTMS was dissolved in oil phase (kerosen) to avoid hydrolysis before copolymerization. VTMS could copolymeriz with AM and DADMAC in aqueous phase by diffusion. High temperature in later period of reaction makes methoxy group of VTMS segment hydrolyze and condense, and then building three dimensional networks. In this article, the synthetic polymer was tested for simulative dye waste-water by jar tests. The purpose of this study is to apply inverse emulsion polymerization to synthesize hydrophobically modified polyelectrolyte, and discuss the applicability of the polymer at low cationicity as decolorization agent for the removal of reactive brilliant red and decolorization mechanism between hydrophobically cationic polyacrylamide and anionic dye.

EXPERIMENTAL

Chemicals

The AM purchased from Damao (Tianjin, China) was used without further purification. DADMAC, as a 65% aqueous solution, was obtained from Luyue Chemical (Shandong, China). VTMS, CP grade, came from Qufu Chengguang Chemical (Shandong, China). The compound 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044) was kindly provided by Guangchuangjing import and export corporation (Shanghai, China), was used as an initiator. Span80 and Tween80 were used as mixed surfactants. Kerosene was directly used as disperse phase without purification. Reactive brilliant red X-3B, industrial grade, was used to prepared dye solution as stimulant waste-water. Other reagents were analytical grade, purchased from Liaodong chemical reagent (Dalian, China), which were used as received. The structures of these comonomers and reactive brilliant red X-3B and AM were illustrated in Figure 1.

Synthesis of P (AM-DADMAC-VTMS)

Inverse emulsion polymerization technique was used to synthesize a hydrophobically cationic flocculant in a 250 mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a nitrogen outlet, and a condenser. Aqueous phase (45 wt %) was prepared by adding the water-soluble monomers of AM and DADMAC to deionized water, and then mixed 4 wt % surfactants, disperse medium [wt(Oil) : wt(H₂O) = 0.8:2] and hydrophobic monomer were added into reactor one after another. The reactor

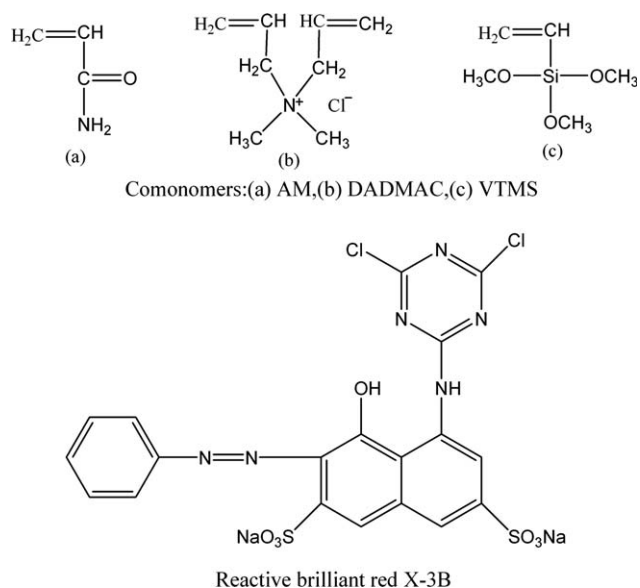


Figure 1 Structures of comonomers and reactive brilliant red X-3B.

was stirred at a speed of 800 rpm and continuously sparged with nitrogen to remove any residual oxygen at room temperature for 30 min. Adding water-soluble initiator (0.1 wt % of total weight of comonomers), the reactor was run into warm-up oil bath maintained at 40°C for 2 h, 60°C for 1 h, and 80°C for 1 h to complete the polymerization. The reaction of cross-linking and hydrolysis of Si—OCH₃ was easy to be carried out at higher reacting temperature (80°C) when the system was near to 7. The resulting emulsion was precipitated by the dropwise addition of excess amount of mixed solvents of acetone and ethanol (50 : 50 wt %), and by stirring rapidly. The solid powders were washed several times with acetone and then dried in vacuum oven at 75°C.

Some main FTIR (KBr, cm⁻¹) peaks as follows: 3414, 3186 (—NH₂), 2926 (N⁺—CH₃), 2856 (—CH₂), 1668 (—C=O); 1455, 1418(—CH₂ and —CH of hexa—heterocycle); 1098 (Si—O—Si), 965 (Si—OH).

Characterizations of terpolymers

The copolymer yield was calculated by the ratio of weight of recovered copolymer to weight of total monomers.

The intrinsic viscosity of copolymers in 0.01 mol L⁻¹ NaCl solution was measured with an Ubbelohde viscometer at 30 ± 1°C. Cationicity (*I*) was measured by the method of AgNO₃ titration. The mass percent of cationic group was calculated with the equation as follows:

$$I = \frac{207.7C(V - V_0)}{1000m} \times 100\%$$

where *C* is the concentration of AgNO₃ solution and *m* is the weight of sample. *V* and *V*₀ were AgNO₃

TABLE I
Characterization of Copolymers

Sample	AM feed ratio (mol %)	DADMAC feed ratio (mol %)	VTMS feed ratio (mol %)	Yield (%)	$[\eta]$ in 0.01N NaCl (dl/g)	Cationicity (wt %)
1#	80	20	0	83.25	9.45	27.17 (36.23)
2#	79.84	19.96	0.2	80.63	9.59	26.18 (36.10)
3#	79.68	19.92	0.4	73.97	10.07	26.02 (35.95)
4#	79.52	19.88	0.6	81.62	10.86	26.73 (35.85)
5#	79.36	19.84	0.8	89.77	11.06	26.48 (35.71)
6#	79.20	19.80	1.0	85.15	11.94	26.40 (35.57)
7#	59.52	39.68	0.8	67.73	8.70	33.59 (59.52)
8#	69.44	29.76	0.8	88.70	10.02	30.49 (48.68)
9#	89.28	9.92	0.8	94.61	12.35	18.32 (19.81)

The numbers in parentheses represent theoretical values of cationicity.

solution volume demanded for blank and samples, respectively.

The contents of silicon in terpolymers were measured on Optima 2000 DV inductively coupled plasma emission spectrometer.

Flocculation procedure

The flocculation properties of the copolymers were carried out by jar tests. About 1 g/L dye solution was prepared by adding 0.1 g dye to 100 mL deionized water. The jar tests were run by adding a known quantity of flocculants to 1 L the test sample. The test waste-waters were rapidly stirred at 250 rpm for 7 min, slowly stirred at 60 rpm for the next 8 min, and then settled for 30 min. Most of flocs settled on bottom of the beaker within 30min. However, smaller flocs suspended in liquid need more time to settle. Therefore, an equivalent method, flocculant-treated dye solutions being filtrated, was adopted to save time, and then the filtrates were collected to measure residual dye concentration. The decolorization efficiency was expressed as removal ratio (R) and the equation was described as follows:

$$R = \frac{C_0 - C}{C_0} \times 100\%$$

where C_0 is the initial concentration of dye solution and C is residual dye concentration after being decolorized.

Residual dye concentration was determined from absorbance of clear solution by using a HP8453 UV-vis spectrophotometer. In pH influence experiments, the pH of dye solution was adjusted to different values with 0.1 mol L⁻¹ hydrochloric acid and 0.1 mol L⁻¹ sodium hydroxide solution before flocculants addition and stirring. Concentration-absorbance standard curve was established in the following Section.

Concentration-absorbance standard curve

The standard equation of relationship between concentration (C) and absorbance (A) of dye solution was established according to Lambert's law and Beer's Law as follows:

$$C = 99.904A - 0.8453 (R^2 = 1)$$

RESULTS AND DISCUSSION

Effects of comonomers feed ratio on terpolymer characterizations

A significant effort was made in this study to synthesize a series of hydrophobically cationic polyacrylamides in inverse emulsion. Keeping constant of aqueous concentration (45 wt %), weight ratio of aqueous and oil phases (2 : 0.8) and initiator concentration, some effects of VTMS and cationic monomer feed ratio on intrinsic viscosity, cationicity, and yield of copolymers were investigated, and the results were shown in Table I.

VTMS feed ratio had no obvious effect on terpolymers yield. However, with the increase of DADMAC, terpolymers yields and intrinsic viscosity decreased. Intrinsic viscosity of terpolymers increased slightly with the addition of VTMS feed ratio. Actual values of cationicity were less than theoretical values, because of lower reactivity of DADMAC comparison with that of AM. The dissolvability of copolymers decreased with increasing VTMS feed ratio. Although cationic monomer of DADMAC was low activity, cross-linking of unreacted double bonds hardly was the key factor of insolubility, because of good heat-conductivity in inverse emulsion polymerization. Hydrolysis and condensation of Si-OCH₃ at higher reaction temperature caused the decrease of terpolymer solubility (Fig. 2).

Characterization

In the FTIR spectrum of sample 6# (Fig. 3), the broad peaks at 3414 and 3186 cm⁻¹ were assigned to the

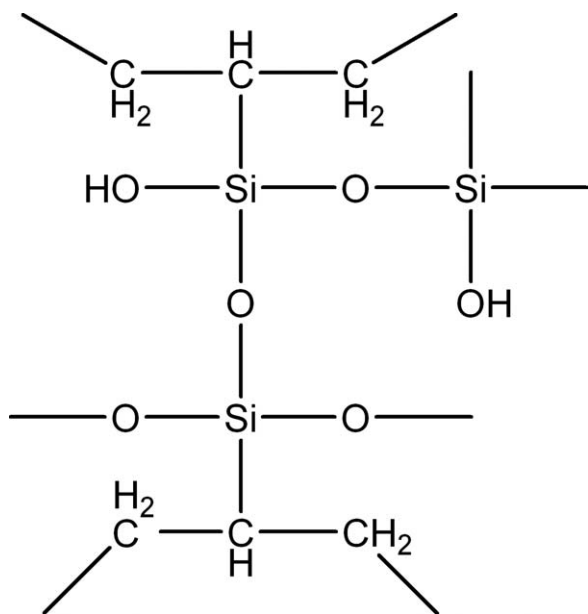


Figure 2 Cross-linking structure of copolymer.

amino stretch of amide and the strong and sharp peak at 1668 cm^{-1} was assigned to the carbonyl stretch of amide. In addition, the peak at 2926 cm^{-1} was assigned to methyl group connected to quaternary ammonium, and the absorption peaks at 1455 and 1418 cm^{-1} were ascribed to $-\text{CH}$ and $-\text{CH}_2$ of hexa-heterocycle. The weak peaks at 1098 and 950 cm^{-1} were ascribed to antisymmetric stretching vibration of $\text{Si}-\text{O}-\text{Si}$ and stretching vibration of $\text{Si}-\text{OH}$, respectively. These peaks indicated the introduction of VTMS into the terpolymer.

Because of VTMS chain segment $<1.0\text{ mol } \%$ in copolymer, it was hard to estimate silicon content from FTIR spectrum and elemental analysis. Therefore, micro silicons in terpolymers were measured by using inductively coupled plasma emission spectrometer

TABLE II
The Content of Silicon in Copolymers

Samples	Actual value (wt %)	Theoretical value (wt %)
2#	0.0331	0.0624
3#	0.0923	0.1282
4#	0.1411	0.1831
5#	0.1974	0.2466
6#	0.2680	0.3100

(Table II). Low activity of VTMS decreased the actual values of silicon content than theoretical values.

Decolorization efficiency and its influencing factors

Effects of VTMS feed ratio on decolorization

Flocculants with different content of hydrophobic group were used to test decolorization efficiency (Fig. 4). With increasing VTMS feed ratio, decolorization efficiency of P (AM-DADMAL-VTMS) was increased. Removal ratio increased initially and then decreased with increasing dose of each flocculant. There was an optimal dose existed for each flocculant. The maximum removal ratio of copolymers, only, is 65.0% when the molar ratio of VTMS is 0.4% , but then it is 94.2% when the molar ratio of VTMS is 1.0% .

The reason of flocculating efficiency increase with the increase of VTMS feed ratio is because of the hydrolysis and cross-linking of VTMS segment built three dimensional networks. Dye molecules entered the meshes and adhered to flocculant molecules. The meshes were stuff full by dye molecules step by step, and flocs became close-grained. At the same time, flocs sizes increased by adsorption and net roofing-sweeping action of flocculant molecules. With the increase of flocs size, flocs separated from water.

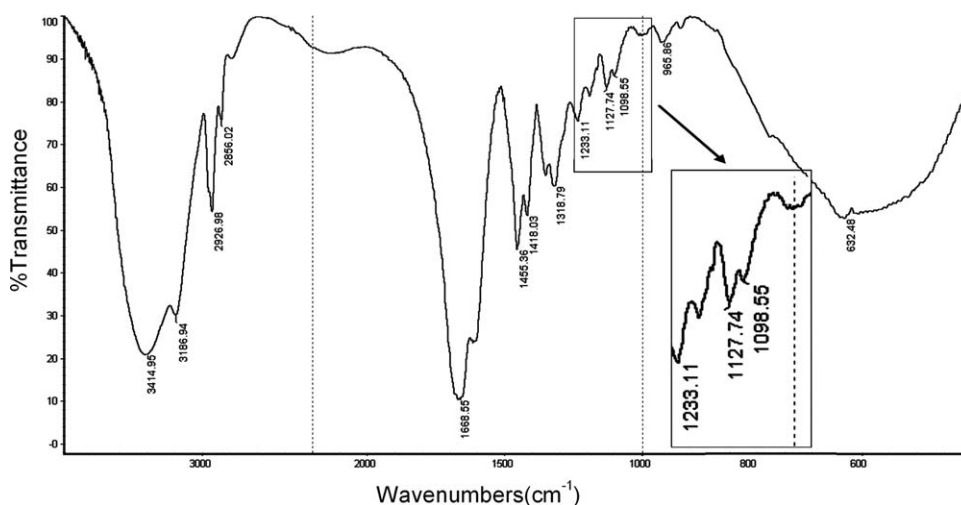


Figure 3 FTIR spectrum of copolymer.

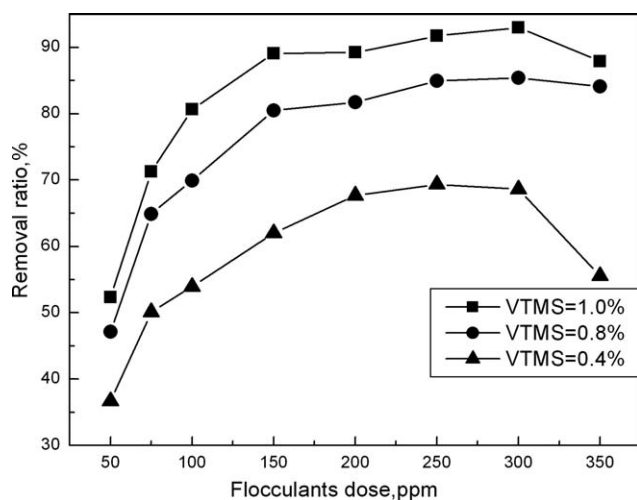


Figure 4 Effect of VTMS feed ratio on decolorization.

In addition, Si—OH of terpolymers might react with OH group of reactive brilliant red, which strengthened interaction between dye molecules and flocculants. However, this needs to be proved furtherly.

Effects of cationic monomer feed ratio on decolorization

Charge-neutralization for cationic polyacrylamide also plays an important role during decolorization process. Decolorization efficiency of P (AM-DADMAC-VTMS) with various cationicity was investigated (Fig. 5). Three flocculants had similar tendency on decolorization, but removal ratio decreased with the increase of cationic monomer feed ratio. DADMAC had lower reactivity than AM, so molecular weight of copolymers reduced with increasing cationic monomer feed ratio. Low molecular weight

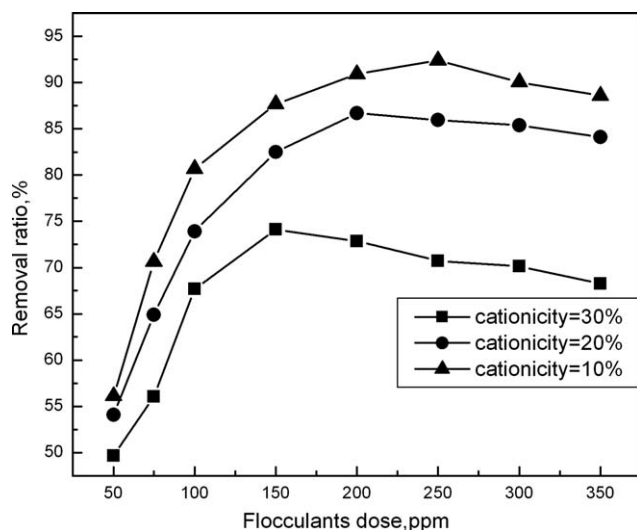


Figure 5 Effect of cationic monomer feed ratio on decolorization.

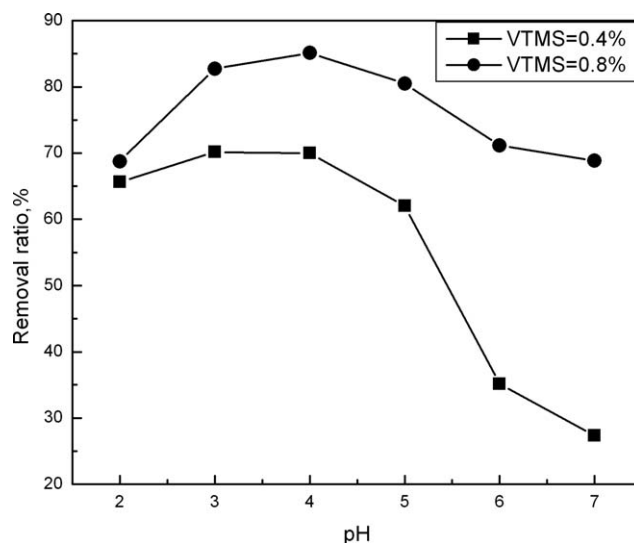


Figure 6 Effect of pH on decolorization.

copolymers have poor bridging function and does not cause flocs to precipitate. Removal ratio increased first and then decreased with increasing dose of P (AM-DADMAC-VTMS). Overdose of flocculant changed the electric charges on the surfaces from negative to positive, which decreased the electrostatic attraction between dye molecules and flocculants.

Effects of pH on decolorization

In flocculation processes using polymer flocculant, pH plays an important role in determining efficiency. Previous studies have reported that color removal was highly dependent on the pH.²⁵⁻²⁷ The effect of pH on the reactive dye removal showed that reactive dye had better removal ratio between pH = 2 and 5 for the flocculants with similar cationicity and various VTMS content (Fig. 6). This was the reason that Na⁺ prevented the electro-ionization of SO₃⁻Na from dye molecules and improved the hydrophobicity of dye molecules. Moreover, there was maximum intermolecular adsorption, between VTMS groups and dye molecules of flocculants, because of the association behavior of hydrophobic groups of flocculants under the pH range. However, too much H⁺ reduced hydrogen bonds between dye molecules and flocculants. Therefore, multifunctions mentioned above lead to the presence of optimal applied-range of pH.

Effects of NaCl on decolorization

Some previous studies^{12,13} reported that, the presence of inorganic electrolytes screens the charged groups of cationic polymers and anionic dyes, and weakens the function of charge-neutralization

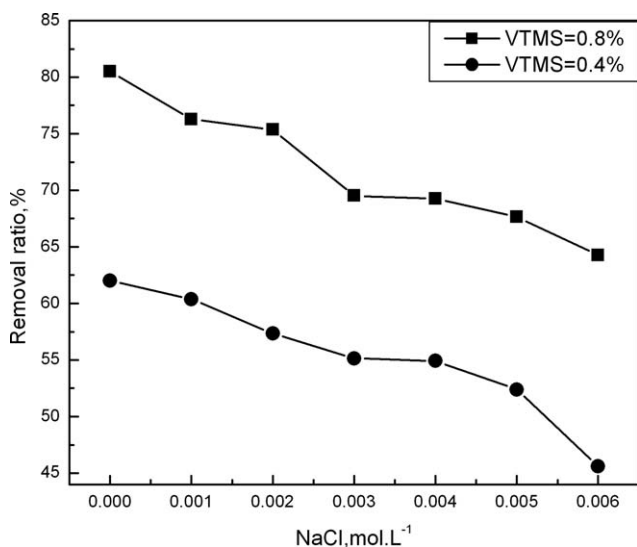


Figure 7 Effect of NaCl on decolorization.

between cationic group of polycations and anionic group of dyes. To investigate further, the contribution of the electrostatic force between P (AM-DADMAC-VTMS) and reactive brilliant red X-3B, NaCl was added to anionic dye solution before adding the flocculants and stirring. With increasing NaCl concentration, removal ratio decreased, and the flocculant with 0.8% VTMS group had better decolorization efficiency than that with 0.4% (Fig. 7). The data indicated that the introduction of VTMS enhanced

the interaction between dye molecules and flocculants and improved decolorization efficiency.

Decolorization mechanism of hydrophobically cationic polyacrylamide

FTIR spectra analysis

To investigate the chemical interaction between P (AM-DADMAC-VTMS) and anionic dye molecules, the FTIR spectra of P (AM-DADMAC-VTMS), reactive brilliant red X-3B and complex of dye-flocculant were compared with each other (Fig. 8). The adsorption peak of quaternary ammonium of P (AM-DADMAC-VTMS) at 2926 cm^{-1} became weak in intensity. The band of sulfonic group at 1053 cm^{-1} in spectrum of dye shifted to 1042 cm^{-1} in floc. The peak of Si—O—Si shifted from 1098 cm^{-1} in P (AM-DADMAC-VTMS) spectrum to 1109 cm^{-1} in floc. Band of Si—OH at 965 cm^{-1} disappeared in floc, but two new peaks appeared at 1538 and 1492 cm^{-1} , assigned to phenyl group. These changes indicated sulfonic groups in dye molecules reacted with quaternary ammonium and produced new ion bond like $\text{N}^+(\text{CH}_2)_2\text{SO}_3^-$. Si—OH of P (AM-DADMAC-VTMS) might reacted with OH of dye molecules.

Uv-vis spectra analysis

UV-vis spectra of residual dye solution flocculated by P (AM-DADMAC-VTMS) were displayed

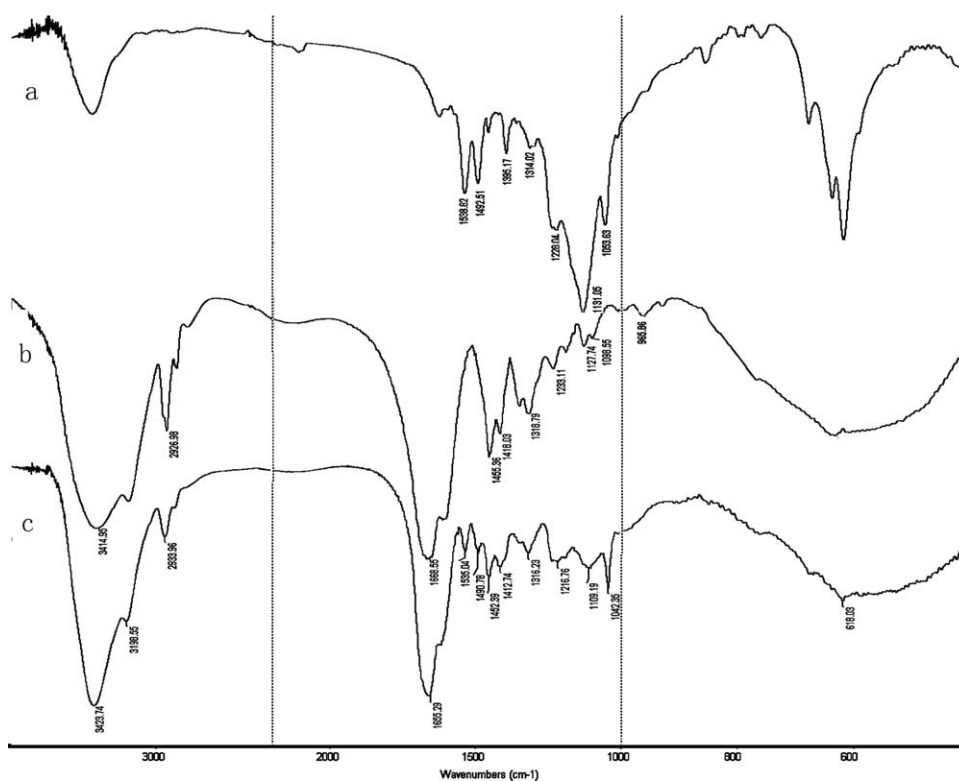


Figure 8 FTIR spectra of (a) X-3B, (b) Copolymer, and (c) complex of dye-flocculant.

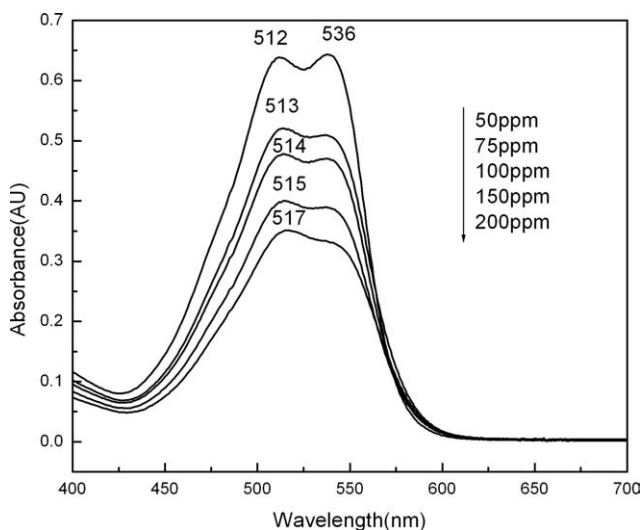


Figure 9 UV-vis spectra of residual dye solution (VTMS = 0.4%).

(Figs. 9, 10). With the addition of dose, removal ratio increased. The Figure 9 was UV-vis spectra of residual dye solution treated by the flocculant with 0.4 mol% VTMS feed ratio. The two characteristic peaks of residual dye solution made red shifts from 512 and 536 nm to 517 and 537 nm with the addition of dose of flocculant, and the absorption peak at 517 nm had higher intensity than that at 537 nm. The spectral changes (Fig. 9) reflect electrostatic interaction plays the determining role at lower VTMS feed ratio. P (AM-DADMAC-VTMS) with lower VTMS chain segments had similar decolorization mechanism to cationic polyacrylamide, such as P (AM-DMC).¹²

Spectral changes of residual dye solution treated by the flocculant with higher VTMS feed ratio were shown in Figure 10. With increasing the dose of flocculant,

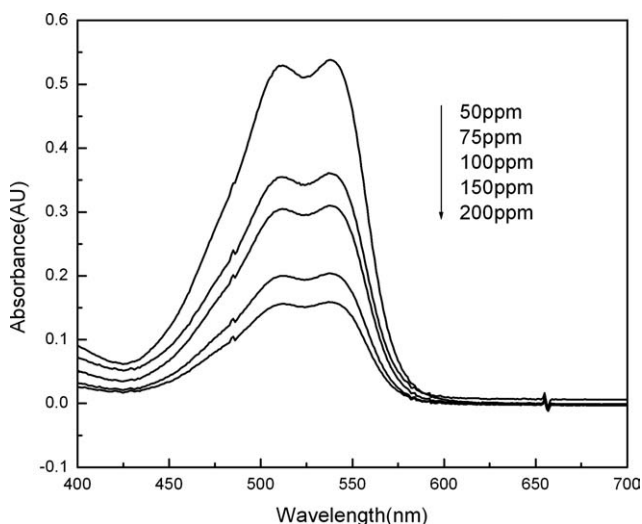


Figure 10 UV-vis spectra of residual dye solution (VTMS = 0.8%).

culant, peaks intensities decreased, but the shifts of characteristic peaks did not change. Moreover, the absorption intensities of characteristic peaks (Fig. 10) were lower than that (Fig. 9) at the same dose. These disclosed that three dimensional network structures were beneficial to molecular adsorption and net roofing-sweeping action, and with the increasing VTMS feed ratio, molecular adsorption and net roofing-sweeping action displaced charge-neutralization step and step and became the key factor of decolorization. These were in agreement with the effect of VTMS feed ratio on decolorization and FTIR spectra analysis.

CONCLUSIONS

Inverse emulsion polymerization technique was used to synthesis P (AM-DADMAC-VTMS) by free-radical copolymerization of two water-soluble monomers, AM and DADMAC, with a hydrophobic comonomer, VTMS. VTMS segment hydrolyzed and condensed to form three dimensional networks. The introduction of VTMS to P (AM-DADMAC-VTMS) enhanced its discoloring ability. The higher the content of VTMS was, the greater discoloring performance, but the worse copolymer solubility was. The introduction of VTMS segments enhanced the interaction between flocculant molecules and organic dye molecules, which speeded up the flocs to separate from the water.

With the increasing VTMS feed ratio, three dimensional networks increased and molecular adsorption and net roofing-sweeping action improved. As a result, adsorption and net roofing-sweeping action of hydrophobically modified cationic polyacrylamide substituted for charge-neutralization little by little and played the dominant role in the process of anion dye.

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