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Synthesis and flocculation performance of graft copolymer of *N*-vinylformamide and poly(dimethylaminoethyl methacrylate) methyl chloride macromonomer

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Abstract A comb-structured polymeric flocculant was synthesized by the aqueous copolymerization of *N*-vinylformamide (NVF) with poly(dimethylaminoethyl methacrylate) quats (methyl chloride) macromonomer. The effects of temperature and macromonomer concentration on the copolymerization kinetics were determined experimentally. The copolymerization reactivity ratio was measured to be 3.82 and 6.39 for NVF and macromonomers with 50 and 100

repeating units when copolymerized with NVF. The copolymer samples were also subjected to a flocculation performance test and were found to be more effective than linear random cationic copolymers in terms of cationic content, flocculation rate, final turbidity levels, and floc strength.

Keywords *N*-Vinylformamide · Macromonomer · Water-soluble polymers · Flocculation

Introduction

N-Vinylformamide (NVF), an isomer of acrylamide, has low toxicity and high reactivity for polymerization and modification. Poly(NVF) (PNVF) and its derivatives comprise a novel class of water-soluble polymers [1]. They have potential applications in areas such as wastewater treatment, sludge dewatering, and paper-making [2, 3].

The essential roles played by PNVF-class polymers in these applications are as flocculants. These polymers can flocculate colloidal particles from an aqueous phase, thereby either recovering valuable materials or removing unwanted solids. The two basic mechanisms used to explain the flocculation process are charge neutralization and chain bridging [4, 5]. Charge neutralization accounts for the electrostatic attraction by addition of counterions into colloids. For negatively charged waterborne colloidal particles, low-molecular-weight cationic polymers (coagulant) are often used for the purpose. The chain bridging mechanism is governed by an irreversible multipoint adsorption of polymer chains onto the surface of colloidal particles. A polymer chain

can subsequently bring particles together by attaching to different particle surfaces, making high-molecular-weight polymers, such as PNVF and polyacrylamide (PAM), most useful.

In reality, most water-soluble polymeric flocculants put both flocculation mechanisms into action. The cationic charge centers provide firm attraction to particle surfaces, while the long polymer chains extend from one particle to another. To date, most commercial polymer flocculants are linear copolymers with randomly distributed cationic charges along the polymer chain. Typical representatives are modified PAM or copolymer of acrylamide with cationic comonomers, usually polyquats, polyimines, or polyamines [6–8].

It is desirable to control the charge density distribution within the molecular structure to improve the flocculation performance of these flocculants. A proposed graft copolymer with a long nonionic polymer chain as a backbone and grafted cationic polymer side chains appears to have a better charge density distribution than traditional random linear copolymers [9, 10]. Instead of having randomly distributed cationic charges along the backbone chain, the graft copolymer has

locally concentrated cationic charge clusters to provide locally strong polymer–surface interaction. At the same time, the high-molecular-weight backbone enables multipoint adsorption onto particle surfaces and interparticle extension.

In this work, graft copolymers of NVF and poly(dimethylaminoethyl methacrylate) (PDMAEMA) quats were synthesized by free-radical copolymerization in an aqueous solution. The copolymerization kinetics and the cationic macromonomer incorporation rate were obtained. The copolymerization reactivity ratios were measured with two macromonomers having different molecular weight. The flocculation performance of the graft copolymer was assessed and compared to that of random linear copolymer counterparts.

Experimental

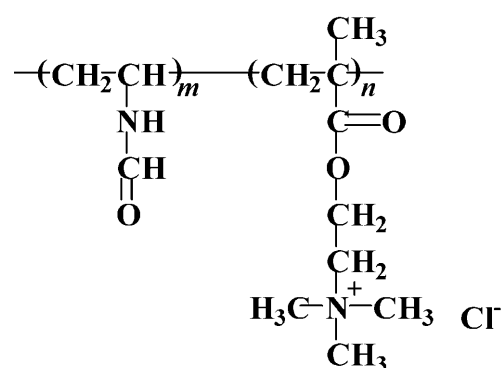
Materials

NVF monomer (Aldrich) was distilled under vacuum at 70 °C and stored at –15 °C before polymerization. Two PDMAEMA macromonomers bearing unsaturated diallyl end groups were synthesized by an anionic polymerization method [11]. The macromonomers (for graft copolymerization) were dissolved in dimethyl sulfonate and quarternized to form PDMAEMA quats by benzyl chloride (Aldrich) at room temperature for 8 h. Dimethyl sulfate was added at the end and the mixture was stirred for an additional hour to ensure complete quarternization. The quarternized macromonomer was precipitated and dried in a vacuum at room temperature. One quarternized macromonomer had a number-average molecular weight of 14,100 (equivalent to 50 repeating units) and a polydispersity index of 1.10; the other had a number-average molecular weight (100 repeating units) of 28,200 and a polydispersity index of 1.11. If only dimethyl sulfate was used to quarternize the macromonomer, the hydrolysis of the sulfate under the subsequent aqueous copolymerization conditions would result in strong acidity of the solution, which would hydrolyze NVF monomer and no polymer would be formed. Methyl iodine was also excluded as a quarternizing agent because the I[–] ion it brought into the macromonomer was an inhibitor to the following free-radical polymerization. DMAEMA methyl chloride (DMAEMA-MCQ, 70 wt% aqueous solution, Dajac Lab, Pa.) was used for the copolymerization with NVF to produce random copolymers for comparison purposes. The molecular structures of the random and graft copolymers are presented in Fig. 1. After copolymerization, the diallyl end group of the macromonomer formed a five-membered ring similar to that formed in the polymerization of diallyldimethyl ammonium chloride [12].

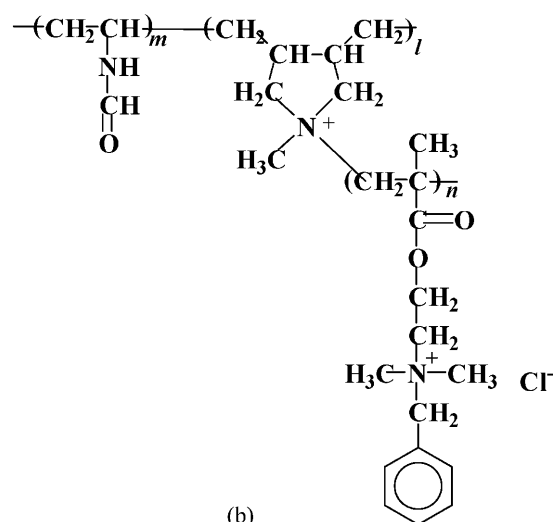
A TiO₂ aqueous suspension was used as the model system for flocculation performance evaluation. The suspension contained 45 mg TiO₂ powder (Aldrich, $\rho = 3.9$ g/ml) dispersed in 1 l deionized water with an ionic strength of 10^{–3} M NaCl. The stock suspension was stirred for 24 h to ensure complete wetting of the TiO₂ particles. Prior to the flocculation tests, an ultrasonic bath for 10 min was used to completely disperse the TiO₂ particles.

Copolymerization

The free-radical copolymerization of NVF and comonomers (PDMAEMA quat or DMAEMA-MCQ) was carried out in an aqueous solution. The initiator, 2,2'-azobis(2-methylpropanamide)



(a)



(b)

Fig. 1 Molecular structure of **a** random linear copolymer and **b** graft copolymer

dihydrochloride (AIBA) (Aldrich), was recrystallized twice before use.

A given mixture of NVF, comonomer, AIBA, and water was charged into a set of glass ampoules. After three freeze–thaw degassing cycles, the ampoules were immersed in a water bath at the polymerization temperature. The ampoules were taken out at different time intervals and the contents were quenched by freezing. The reactant mixture was dissolved in water and the polymer was precipitated in methanol. All the samples were dried under vacuum at room temperature for 48 h. The polymerization conversion, x , was calculated using

$$x = \frac{W_p}{M_0}, \quad (1)$$

where W_p is the mass of copolymer and M_0 is the total initial charge of the monomers.

Copolymer samples having different cationic content ranging from 0 to 10 mol% were synthesized for flocculation performance evaluation and reactivity ratio measurement. The cationic content in the copolymer was measured using a 200 MHz NMR spectrometer. An example NMR spectrum is given in Fig. 2. The molar percentage of NVF can be calculated from the ratio of the peak areas of NVF (M_1) and macromonomers (M_2). Equations (2) and

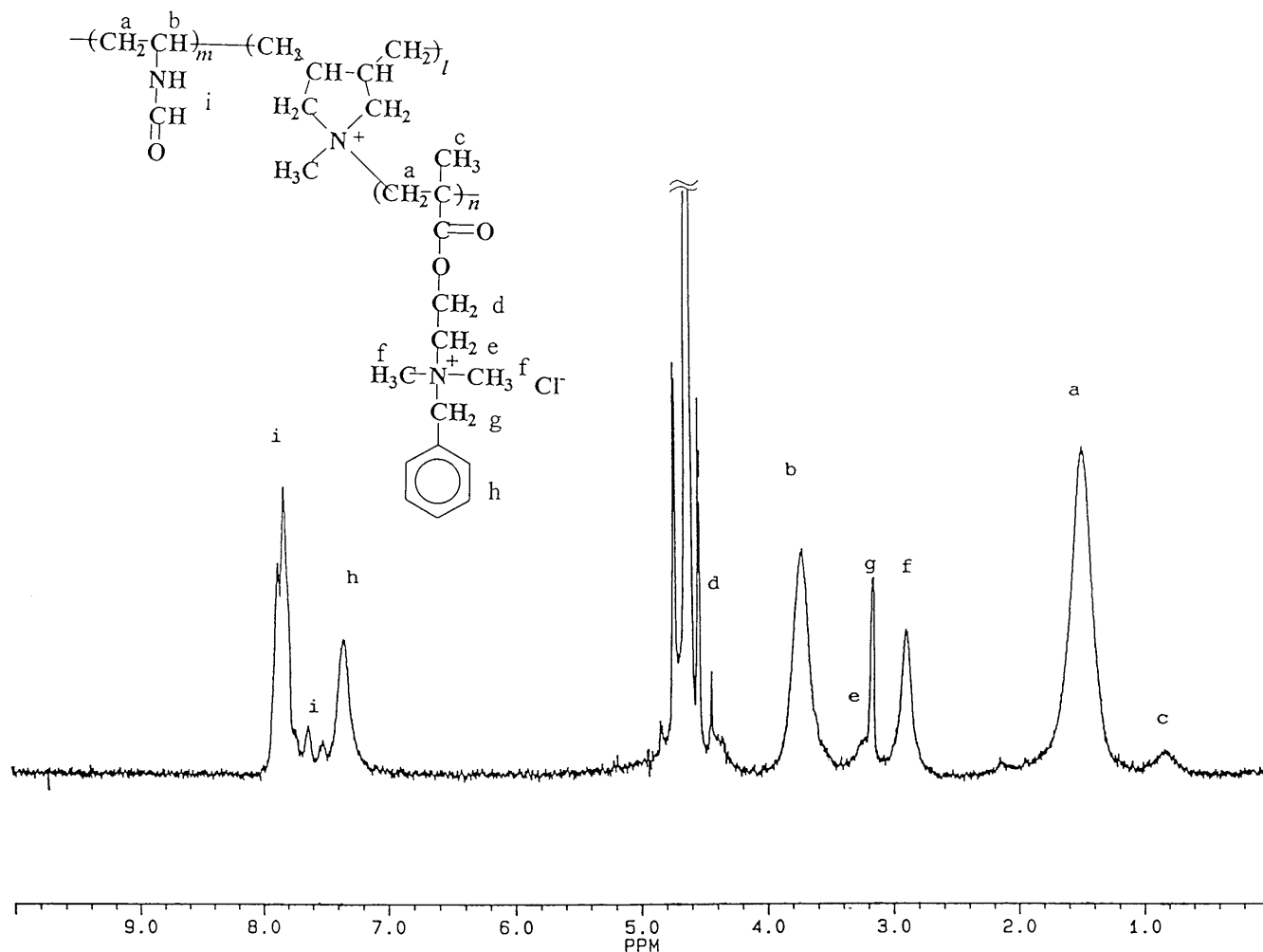


Fig. 2 ^1H NMR spectrum of *N*-vinylformamide (NVF)/poly(dimethylaminoethyl methacrylate) methyl chloride quat (PDMAEMA-MCQ) macromonomer copolymer in D_2O

(3) were used to calculate the fractional conversions of NVF and macromonomer.

$$x_1 = \frac{w_1 x}{M_{0,1}}, \quad (2)$$

$$x_2 = \frac{(1-w_1)x}{M_{0,2}}, \quad (3)$$

where x_1 and x_2 are the fractional conversions of NVF and macromonomer and $M_{0,1}$ and $M_{0,2}$ are the initial mass of NVF and macromonomer, respectively. w_1 is the weight percentage of NVF in the final copolymer which can be translated from the NVF molar percentage obtained from NMR measurements.

Intrinsic viscosity measurement

The intrinsic viscosity of the linear and graft copolymer samples was measured using a Cannon Ubbelohde (50, M545) viscometer. A 0.2 M NaNO_3 water solution was used as the solvent for all the samples. Each sample solution was subjected to 0.45- μm filtration before injection into the viscometer. The temperature of the viscosity measurement was maintained at 25 ± 0.1 $^\circ\text{C}$.

Flocculation test and turbidity measurement

The pH value of the stock suspension was adjusted to a value of 8 according to a zeta-potential (surface charge) measurement to ensure the negative surface charge of the TiO_2 particles [9]. This was done by adding a small amount of 0.01 M NaOH solution. The turbidity of the TiO_2 suspension samples with and without polymers was measured using a Hach 2100P portable turbidimeter (Hach, Loveland, Colo.).

The flocculation experiments followed the procedures of a previous report [9]. A preset amount of polymer was added to 180 ml pH-stabilized TiO_2 suspension with constant stirring. Samples were taken out at 0, 5, 10, 15, 30, 45, and 60 min into the experiment and their turbidity was measured. The relative turbidity was the ratio of the turbidity measured at a given time to the initial turbidity ($T_r = T_t/T_0$).

Results and discussion

Copolymerization

The kinetics of copolymerization of NVF with macromonomers at 50 $^\circ\text{C}$ is shown in Figs. 3 and 4. (Fig. 3: macromonomer with 50 DMAEMA units; Fig. 4:

macromonomer with 100 DMAEMA units). The total monomer concentration was 40 wt%. The initial macromonomer feed was presented as the mass percentage of macromonomer in the NVF/macromonomer mixture.

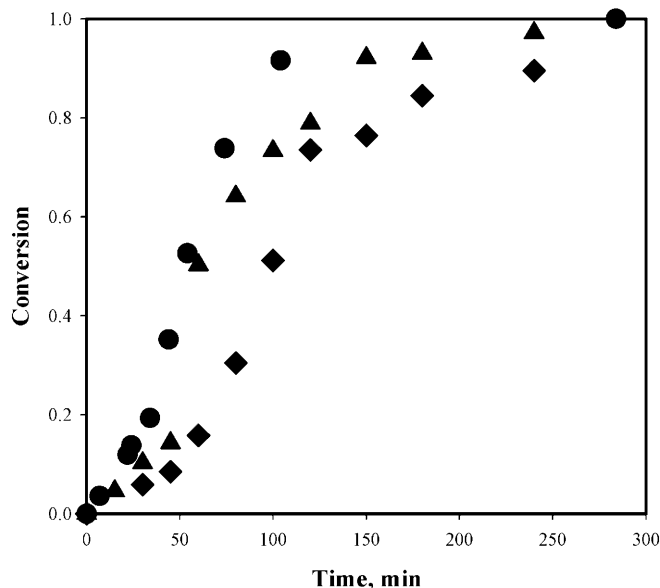


Fig. 3 Aqueous copolymerization kinetics of NVF/DMAEMA-MCQ (50 repeating units) at 50 °C, 3.0×10^{-3} mol/l 2,2'-azobis(2-methylpropionamide) dihydrochloride (AIBA), 40 wt% total monomer concentration: homopolymerization (circles); 10 wt% macromonomer (triangles); 20 wt% macromonomer (diamonds)

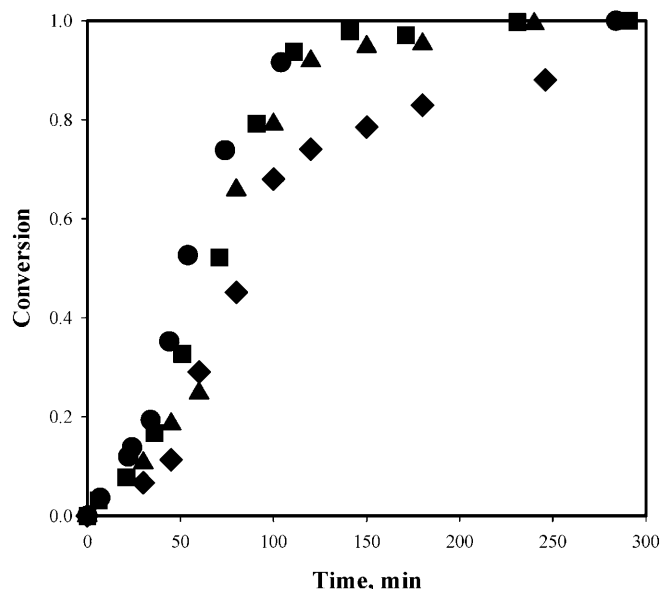


Fig. 4 Aqueous copolymerization kinetics of NVF/DMAEMA-MCQ (100 repeating units) at 50 °C, 3.0×10^{-3} mol/l AIBA, 40 wt% total monomer concentration: homopolymerization (circles); 5 wt% macromonomer (squares); 10 wt% macromonomer (triangles); 20 wt% macromonomer (diamonds)

The initiator (AIBA) concentration was 3.0×10^{-3} mol/l. Both figures show comparison with NVF homopolymerization. Increasing the macromonomer concentration in the reaction mixture reduced the polymerization rate as well as the final monomer conversion.

The effect of temperature on the copolymerization kinetics is shown in Fig. 5. The polymerization rate increased with temperature. The final conversion remained almost the same.

All the kinetics experiments clearly showed the “gel effect”. This phenomenon was also observed in NVF homopolymerization [13] and was caused by the diffusion control of the chain radical termination. Addition of macromonomers, which were essentially short-chain-length polymers, to the reaction mixture would increase the initial viscosity and create more resistance to the diffusion of polymer chain radicals. This should yield a more severe “gel effect” as is actually shown in the figure that the copolymerizations with higher macromonomer content (e.g., 20 wt% macromonomer) exhibited a higher curvature (more autoacceleration) trend at the initial stage of polymerization.

An example of the conversion of the individual comonomers as a function of the total monomer conversion is shown in Fig. 6. The initial feed of macromonomer (50 repeating units) was 20 wt% of the total monomer mass. At every stage of the copolymerization, the NVF conversion was always higher than that of the macromonomer. The NVF monomer was more active than the macromonomer during the

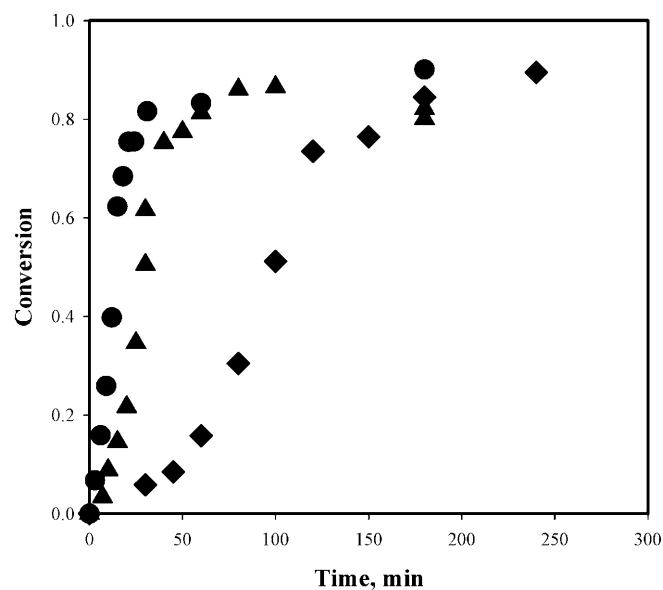


Fig. 5 Aqueous copolymerization kinetics of NVF/DMAEMA-MCQ (50 repeating units) at different temperatures, 3.0×10^{-3} mol/l AIBA, 40 wt% total monomer concentration, 20 wt% macromonomer: 70 °C (circles); 60 °C (triangles); 50 °C (diamonds)

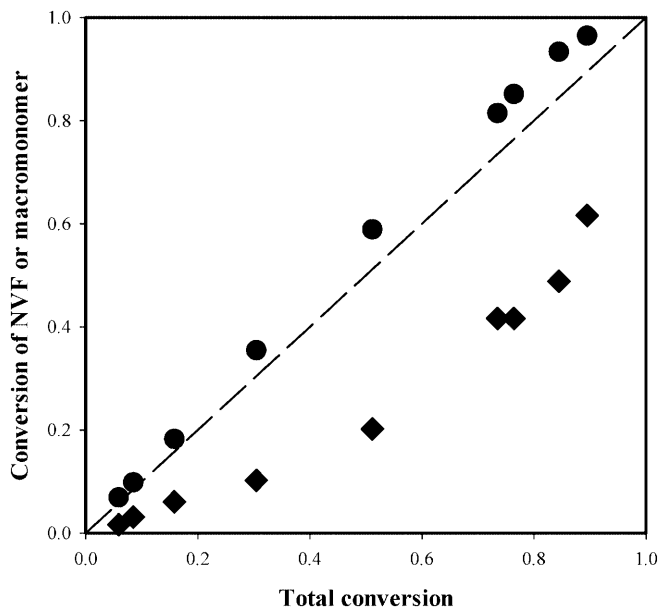


Fig. 6 Plot of fractional conversion of NVF and macromonomer (50 repeating units) against total monomer conversion in the aqueous copolymerization, 50 °C, 0.2 wt% AIBA, 40 wt% total monomer concentration, 20 wt% macromonomer: NVF (circles); macromonomer (diamonds)

copolymerization. The incorporation of the macromonomer into the copolymer remained low until the end of the copolymerization.

Reactivity ratios

The reactivity ratios are the most important parameters in describing the relative activities of a comonomer pair in polymerization. In a binary system that follows the terminal model, Eq. (4) can be used to determine the instantaneous copolymer composition,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]r_1[M_1] + [M_2]}{[M_2]r_2[M_2] + [M_1]} \quad (4)$$

The reactivity ratios r_1 and r_2 are defined as K_{p11}/K_{p12} and K_{p22}/K_{p21} , respectively. $K_{p_{ij}}$ is the propagation rate constant of monomer i onto a polymer chain radical ending with a j monomeric unit ($i, j = 1$ or 2). In the case of NVF (M_1) and PDMAEMA quats macromonomer (M_2) copolymerization, the molar concentration of M_2 is very low; thus,

$$[M_1] \gg [M_2] \quad (5)$$

and Eq. (4) can therefore be simplified to [14]

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (6)$$

Equation 6 can be integrated to yield

$$r_1 = \frac{\ln(1 - x_1)}{\ln(1 - x_2)} \quad (7)$$

Equation (7) is used to estimate r_1 for different macromonomers. It gives a ratio of the reactivity of NVF and macromonomer toward the NVF radical. Within the scope of this study, r_2 cannot be determined owing to the extremely low molar concentration of macromonomer in the experiments. Also, in an aqueous medium, once a macromonomer is added and a macromonomer radical is thus formed at the end of a growing chain, the highly concentrated charges on the pendent graft makes it almost impossible to react with another macromonomer, i.e., $K_{p22} \approx 0$; therefore r_2 is assumed to be negligible ($r_2 \approx 0$).

To estimate r_1 , a series of NVF/macromonomer copolymer samples were synthesized by free-radical polymerization with various initial monomer ratios. The initial feed ratios of the macromonomer were 10, 20, 30, 40, and 50 wt% of the total monomer mass and the total monomer concentration was 40 wt%. The initiator (AIBA) concentration was 3.0×10^{-3} mol/l. The total conversion of each copolymerization run was kept at less than 15% to avoid a possible composition drift effect. These copolymer samples were purified as described in the Experimental section and their composition was measured by H NMR spectroscopy.

The $-\ln(1 - x_1)$ versus $-\ln(1 - x_2)$ plots of the previous copolymers samples are shown in Fig. 7. The slopes of the regression line through the experimental points are equal to r_1 . For the macromonomer with 50 repeating units, r_1 was estimated to be 3.82. For macromonomer with 100 repeating units, r_1 was 6.39. This suggested a chain length effect of the macromonomer on the diallyl group activity. A macromonomer with a shorter chain length is more reactive than one with a longer chain length in copolymerization. This phenomenon was also observed in other monomer/macromonomer copolymerization studies [15, 16] that reported a reduction in K_p with increasing macromonomer molecular weight. This lower copolymerization reactivity is attributed to the lower segmental diffusion rate of a longer macromonomer chain. It is more difficult for a macromonomer with 100 repeating units to react with a PNVF radical than for a macromonomer with 50 repeating units.

Flocculation tests

Several graft copolymer samples were synthesized with different cationic contents using the two macromonomers. For reference and comparison purposes, several random linear copolymers of NVF with DMAEMA-MCQ were also prepared and tested. All these poly-

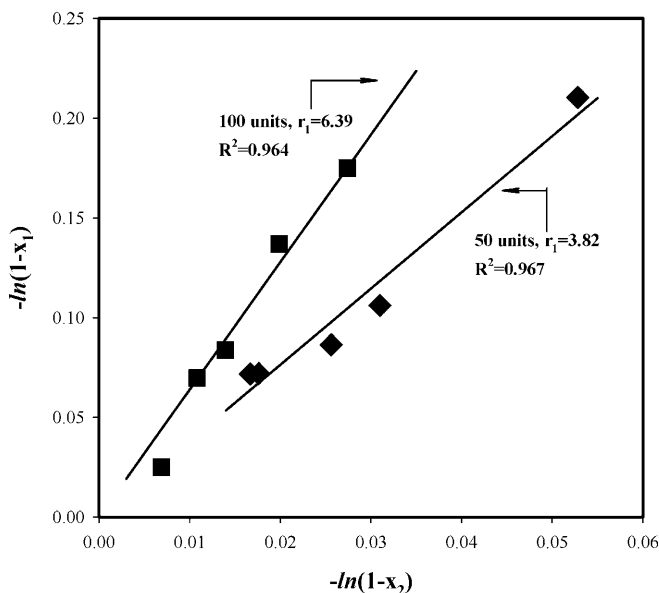


Fig. 7 Plot to determine the copolymerization reactivity ratio (r_1) of the NVF/macromonomer comonomer pair. r_1 is the slope of the fitting line. 50 repeating units (diamonds); 100 repeating units (squares)

mer samples were synthesized by aqueous free-radical polymerization with 40 wt% monomer concentration and 3.0×10^{-3} mol/l initiator (AIBA) concentration. The copolymer samples used for the flocculation tests are listed in Table 1. The molar contents of the cationic charge groups are listed as well as the total monomer conversions. The intrinsic viscosities corresponding to the samples in Table 1 are listed in Table 2. Because there is no reliable and accurate method for estimating the molecular weight of grafted cationic copolymers, only the intrinsic viscosity data are reported here as a

molecular-weight indicator when samples are compared to each other. Generally, the viscosity decreased with increasing cationic content in the copolymer. This indicated a decreasing trend in the molecular weight with increasing cationic content for both the linear and the graft copolymers.

The results of the relative turbidity (T_r) measurements are shown in Figs. 8, 9, and 10. The T_r value is plotted against the flocculation time up to 60 min. The polymer dose was 5 mg/g TiO_2 . The cationic charge levels of the seven random linear copolymer samples tested were 1.86, 2.61, 3.57, 9.33, 11.29, and 13.34 mol% (the mole percent is the number of the DMAEMA units over the total number of the monomeric units). The charge levels of the copolymer samples having the 50-unit grafts were 3.85, 4.93, 5.18, and 7.99 mol% (the mole percent is with respect to the DMAEMA monomeric unit and should not be confused with the macromonomer unit in the chain). The charge levels of the 100-unit graft copolymers were 0.68, 2.39, 3.54, 5.72, 8.81, and 9.48 mol%. A general trend of the T_r versus t curves was a dramatic reduction in the turbidity within 20 min followed by a leveling off.

It was also observed that, in some cases, the turbidity increased with time after the initial drop, but did not recover to the original turbidity level. This can be attributed to the breakup of the flocculated TiO_2 colloidal particles by the continuous stirring of the dispersion. Most random linear samples as well as the 3.85 and 4.93 mol% 50-unit graft samples showed the turbidity recovery effect. The flocs with the graft copolymers appeared to have greater strength than those formed by the linear samples. The copolymer samples with longer grafts (100 units) gave stronger flocs than the samples with shorter grafts (50 units).

Table 1 *N*-Vinylformamide (NVF) cationic copolymers used for flocculation tests. The first numbers in columns 3–5 are the mole percentage (mol%) of the cationic charge. The numbers in parentheses are the total monomer conversion (wt%)

Number	Initial macromonomer content (wt%)	Random	100-unit graft	50-unit graft
1	5	1.9 (100)	0.68 (100)	–
2	10	2.6 (100)	2.4 (99)	–
3	20	3.6 (72)	3.5 (91)	3.9 (89)
4	30	9.3 (90)	5.7 (85)	4.9 (91)
5	40	11.3 (90)	8.8 (84)	5.2 (84)
6	50	13.3 (70)	9.5 (74)	8.0 (68)

Table 2 Intrinsic viscosity of NVF cationic copolymers used for flocculation tests

Number	Initial macromonomer content (wt%)	Random	100-unit graft	50-unit graft
1	5	6.39	4.38	–
2	10	4.61	3.10	–
3	20	4.95	2.76	2.23
4	30	2.93	0.71	3.83
5	40	2.90	0.49	0.33
6	50	2.57	0.40	0.16

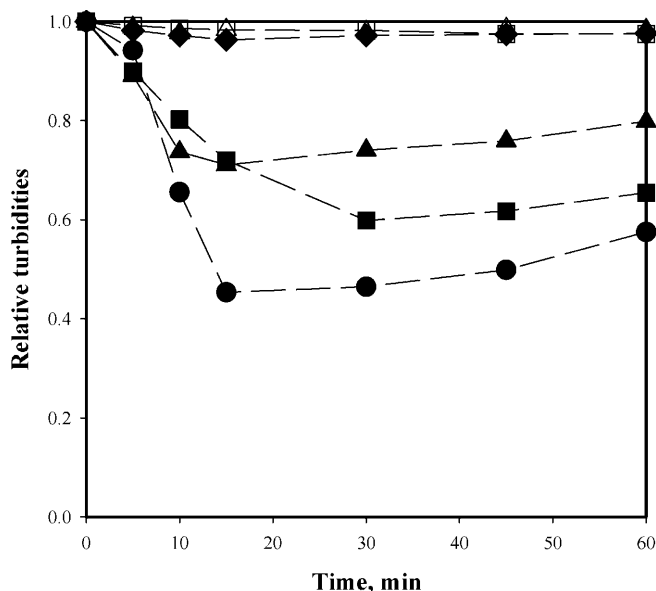


Fig. 8 Relative turbidity change in 60 min by the use of random linear copolymer samples, 5 mg copolymer/g TiO_2 dose. Cationic charge (mol%): 1.9 (open triangles); 2.6 (open squares); 3.6 (diamonds); 9.3 (filled triangles); 11.3 (filled squares); 13.3 (circles)

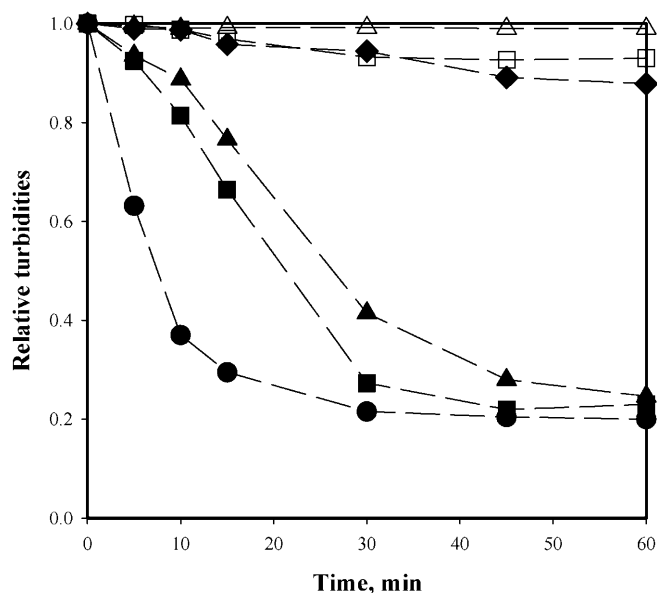


Fig. 10 Relative turbidity change in 60 min by the use of graft copolymer (100 repeating units) samples, 5 mg copolymer/g TiO_2 dose. Cationic charge (mol%): 0.68 (open triangles); 2.4 (open squares); 3.5 (diamonds); 5.7 (filled triangles); 8.8 (filled squares); 9.5 (circles)

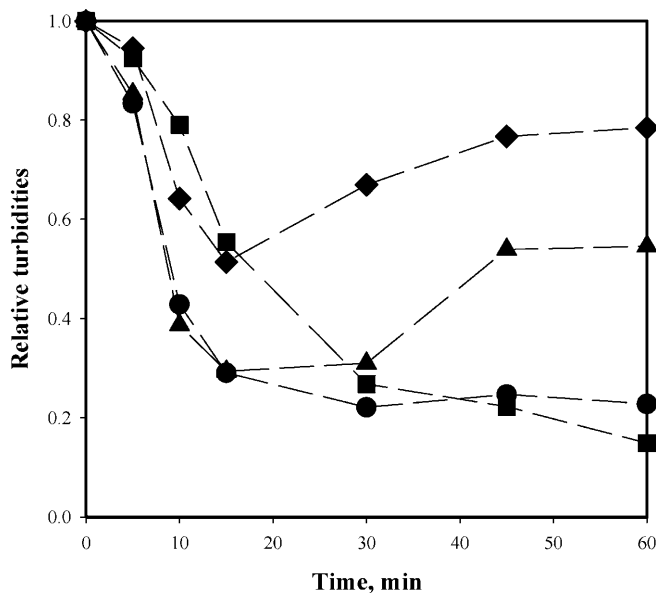


Fig. 9 Relative turbidity change in 60 min by the use of graft copolymer (50 repeating units) samples, 5 mg copolymer/g TiO_2 dose. Cationic charge (mol%): 3.9 (diamonds); 4.9 (triangles); 5.2 (squares); 8.0 (circles)

The reduction in turbidity strongly depends on the charge content level. At low cationic levels, no significant impact on the turbidity was observed for all the polymer samples. Increasing the charge content improved the flocculation and thus lowered the turbidity.

Compared to their random linear counterparts, the graft copolymers gave improved flocculation performance using samples with the same or lower molar cationic content. The comb-branched graft copolymers appear to be more effective than the random linear copolymers in flocculating the model TiO_2 suspension. For example, the best flocculation performance among the linear random samples was at a cationic content of 13.34 mol%. The sample reduced the relative turbidity to 40% in 15 min and reached a final level of about 60% of the initial turbidity. In contrast, the graft copolymer samples having as low as 6 mol% cationic content (above 5.18 mol% for the 50-unit graft, above 5.72 mol% for the 100-unit graft) achieved a lower final relative turbidity (20–30%) than that of the previously described random sample (with 13.34 mol% cationic content). The graft copolymers having the same levels of cationic charge as their linear counterparts acted faster and achieved a lower final turbidity (7.99 mol% 50-unit graft and 8.81 mol% 100-unit graft with 9.33 mol% linear copolymer).

The turbidity reduction data also show less dependence on the molecular weight than on the cationic content. For noncharged polymers, such as PAM, it is necessary to have a certain molecular weight (about 10^6) to be an effective flocculant; however, the cationic charged copolymer samples (both linear and graft) having higher cationic content usually have better turbidity reduction even with lower intrinsic viscosity, i.e., lower molecular weight. For example, the best

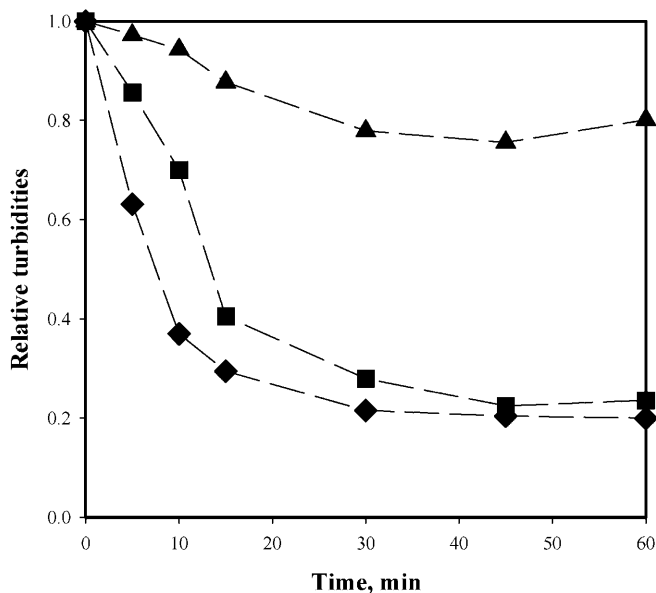


Fig. 11 Relative turbidity change in 60 min by the addition of graft copolymer (100 repeating units, 9.48 mol% cationic charge) but with different doses (mg copolymer/g TiO₂): 1 (triangles); 2 (squares); 5 (diamonds)

performance was for a 100-unit graft copolymer containing 9.5 mol% cationic content. It had the lowest intrinsic viscosity (0.4) among the grafted copolymers. For linear random copolymer samples, the sample with the best performance had the highest cationic content, 13.34 mol%, but had the lowest intrinsic viscosity, 2.57.

The flocculation performance is also a function of the polymer dose. Tests were also conducted at reduced polymer doses, 1 and 2 mg copolymer/g TiO₂. At a TiO₂ dose of 1 mg/g, none of the samples tested (random or grafted copolymers) showed significant flocculation impact on the model suspension system. At a TiO₂ dose of 2 mg/g, only the 100-unit graft copolymer with 9.48 mol% cationic content significantly reduced the turbidity. The effect of polymer dose on turbidity is shown in Fig. 11.

The reason for the flocculation performance enhancement of the graft copolymers lies in their chain structure and cationic charge distribution. For a charged polymeric flocculant to be effective, both flocculation mechanisms – chain bridging and charge neutralization – must be at work simultaneously. The comb-branched

graft copolymer provides highly concentrated cationic groups (clusters of DMAEMA quats), enabling strong adsorption with particle surfaces. The PNVF backbone free of charges brings particles together by anchoring its grafts to different particle surfaces. However, in a linear random copolymer, individual cationic charges are randomly distributed along the chain. The local cationic charge density may not be high enough to provide firm attraction at the adsorption sites. Meanwhile, charges situated on the bridging segments are simply wasted.

The observations in this work agree with a previous investigation [10] using poly(diallyldimethyl ammonium chloride) grafted onto PAM via a γ -ray irradiation method. However, the use of the monodispersed PDMAEMA quat macromonomer in preparing the NVF copolymer presented in this work ensures a comb-branched copolymer structure in the absence of gel formation. The comb-branched copolymer structure has been shown to improve flocculation performance compared to the random copolymer. Future work should be directed towards the control of backbone length, graft length, graft frequency and distribution in the polymer preparation, and the examination of their effects on the flocculation performance of the products.

Conclusion

Graft copolymers samples were synthesized by copolymerizing NVF and PDMAEMA quats (nearly monodispersed molecular weight cationic macromonomer) in an aqueous solution. The polymerization kinetics and copolymer compositions were investigated at various experimental conditions. The copolymerization reactivity ratio of the comonomer pair (NVF/macromonomer) was determined to be 3.82 and 6.39 for the two macromonomers with 50 and 100 repeating units. The flocculation performance of the graft copolymer was also tested on a TiO₂ aqueous dispersion model system. The graft copolymers were found to be more effective than their random linear counterparts. The comb-branched structure of the graft copolymer effectively combines the chain bridging and charge neutralization mechanisms – stronger attachment to the particle surfaces owing to concentrated cationic clusters on side chains and charge-free backbones bridging different particles together.

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