

Flocculation and Sedimentation of Cane Sugar Juice Particles with Cationic Homo- and Copolymers

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ABSTRACT: Rapid flocculation and sedimentation of suspended particles in primary cane sugar juice is achieved using a high molecular weight anionic polymer flocculant. This work reports on efforts to enhance the performance of an anionic flocculant by the addition of cationic polymers. Homopolymers of poly(trimethylammonium ethyl methacrylate chloride) (TMAEMAC) and cationic copolymers of poly(trimethylammonium ethyl acrylate chloride) (TMAEAC) and acrylamide were synthesized and their performance, to enhance the flocculation and sedimentation of cane sugar juice particles, was evaluated by turbidity and settling rate measurements. The charge-patch mechanism best explains the performance of the homopolymers, whereas the action of

the copolymers is attributed to the bridging mechanism. The results of this work indicate that the copolymers are more effective than the homopolymers to aid flocculation and sedimentation of the cane sugar juice particles, and that the best-performing polymers are those that act by the bridging mechanism. Addition of increased amounts of anionic flocculant did not confer an improvement, suggesting that the cationic bridging flocculant targets a different population of particles that is largely responsible for the residual turbidity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 316–325, 2003

Key words: polyelectrolytes; cane sugar juice; flocculation; colloids; water-soluble polymers

INTRODUCTION

Removal of impurities (consisting of both soluble and insoluble nonsugar compounds) from cane sugar juice by clarification is an essential part of the process of raw sugar manufacture. In the Australian cane sugar milling industry, the clarification process is best described as simple defecation. This process is based on the addition of lime as lime saccharate (i.e., lime dissolved in sugar syrup) to heated juice at about 76°C to increase the juice pH to between 7.8 and 8.0 and prevent inversion of sucrose.¹ This is followed by secondary heating of the limed juice under pressure to approximately 103°C and flashing to remove dissolved air. The deaerated juice then enters the clarifier. At this stage the juice contains insoluble calcium salts formed from the reaction between free calcium ions supplied by the lime saccharate and inorganic phosphate from the raw cane sugar juice. These precipi-

tated calcium phosphate microfloc particles act as a sweep flocculant in the clarifier, removing suspended matter from the juice and adsorbing dissolved molecules and ions. The particle size in primary juice is between 0.5 and 5 microns in diameter,¹ with a number concentration between 2.5×10^8 and 1.2×10^9 L⁻¹.² To increase the settling rate of the calcium phosphate microfloc particles and improve the efficiency of separation of the liquid–solid system, an anionic flocculant [a high molecular weight copolymer of acrylamide (AAM) and sodium acrylate] is added to the juice. The clarified juice is collected from the top of the clarifier and sent to the evaporator station for concentration.

Adsorption of an AAM–sodium acrylate copolymer to microfloc particles may proceed by any of three mechanisms³: (1) attraction of the negatively charged acrylate groups to positive charges on the surface of the microfloc particles; (2) attraction of the negatively charged acrylate groups to dipositive ionic “bridges” (e.g., Ca²⁺), which are adsorbed to negative charges on the microfloc particles; and (3) hydrogen or dipolar bonding between the AAM groups and the microfloc particles. In cane sugar juice, although binding of microflocs most likely proceeds primarily by calcium bridging of the charged acrylate group,⁴ it is still possible that the other two mechanisms may be important under some conditions. In the flocculation of colloidal silica (present in cane sugar juice),⁵ similar effective-

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ness was seen with copolymers of AAm containing either a cationic or anionic comonomer, suggesting that the uncharged polar amide groups are more important in binding to silica.⁶ Whatever the chemical basis of adsorption to particle surfaces, it is clear that the physical properties of the flocculant are responsible for the distinctive features of flocculation. Under shear, large flocs joined by dynamic polymer bridges will be stronger than the brittle flocs formed by primary coagulation, allowing aggregation in the shear-controlled (orthokinetic) domain rather than the simple-diffusion (perikinetic) domain.⁷ This in turn will lead to geometric rather than arithmetic growth, giving the distinctive rapid flocculation and macroscopic morphology of flocs generated using a polymeric flocculant.⁸

In a system as complex as unclarified cane sugar juice, it is evident that no single flocculant will give optimal removal of all suspended particles. This is because of the polydispersity and chemical heterogeneity of the suspended particles. In the treatment of coal fines and other industrial applications, the combination of a relatively low molecular weight cationic polymer and a high molecular weight anionic flocculant has been shown to impart improvements in clarification.^{9–12} The cationic polymer most likely aggregates small, highly charged particles that are not adsorbed by the anionic flocculant. The mechanism of this process is related to the density of the charges on the polymers vis-à-vis the density of charges on the particle surfaces. The three main mechanisms for the process are charge–charge annihilation, charge–patch flocculation, and cationic bridging.

A number of cationic polymers have been claimed to enhance the flocculation of cane sugar juice.^{5,13} However, the authors are aware of the inconclusive results from some Australian sugar mills that have tested cationic polymers in combination with an anionic flocculant. This study forms part of an ongoing effort to synthesize and optimize cationic polymers to enhance the clarification of cane sugar juice, where they are used in combination with a high molecular weight poly(AAm-co-sodium acrylate). In an early stage of the investigation, tests carried out on commercial cationic homopolymers of poly(trimethylammonium ethyl methacrylate chloride) (TMAEMAC) and cationic copolymers of poly(trimethylammonium ethyl acrylate chloride) (TMAEAC) and AAm were the only ones to show reasonable effectiveness in improved cane sugar juice clarification.³ As a result, a number of these polymers with varying molecular weights (estimated in terms of intrinsic viscosity, a good empirical measure of random-coil volume) were prepared and tested for their effectiveness to enhance flocculation. The cationic monomer contents of the copolymers prepared were also varied.

EXPERIMENTAL

Materials

Acrylamide monomer (AAm; Aldrich Chemical, Milwaukee, WI) was recrystallized from chloroform. The TMAEAC and TMAEMAC quaternary ammonium monomers were obtained as aqueous solutions of dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate quaternized with methyl chloride (75 wt % for TMAEMAC and 80 wt % for TMAEAC; Aldrich) inhibited with approximately 600 ppm of hydroquinone monoethylether. It has been demonstrated that these monomers can be purified by repeated extraction with acetone,¹⁴ and this was the procedure followed. Glacial acrylic acid (Sumika Co., Singapore), inhibited with 200 ppm of hydroquinone monomethylether, was degassed but not otherwise purified before polymerization. Toluene (BDH, Toronto, Canada) and hexane (certified ACS; BDH) were used without further purification.

The redox initiators sodium metabisulfite and potassium bromate (BDH) were used without further purification. The organic initiator, 2,2-azobis-isobutyronitrile (AIBN) was recrystallized from methanol and light petroleum ether. The chain-transfer agents 2-thioethanol and dodecanthiol (Aldrich) and isopropanol (BDH) were used without further purification, whereas thioglycolic acid (Aldrich) was purified by distillation.

Homopolymer synthesis

Homopolymers of the quaternary cationic monomer TMAEMAC were produced by free-radical polymerization using AIBN as initiator in three different solvents (water, methanol, and isopropanol) and three different chain-transfer agents (CTA): thioglycolic acid (TGA), thioethanol, and sodium formate.

Cationic monomer (10 g), solvent (90 mL), and CTA were combined and sparged continuously with nitrogen for 1 h to remove any residual oxygen. The initiator was then added under nitrogen as a solution in 5 mL of *N,N*-dimethylformamide (DMF). The reaction mixture was stirred at 60°C under nitrogen. Samples prepared in aqueous solution were then cooled to room temperature, diluted with Milli-Q deionized water (Millipore, Bedford, MA), and dialyzed for 4 to 5 days against deionized water using a cellulose membrane to remove the residual monomer. The polymer solutions were then freeze-dried to remove water. Polymers prepared in methanol solution were precipitated in acetone, filtered, and dried under vacuum. When isopropanol was used as the polymerization solvent, the polymer precipitated as it was generated. After filtering and drying under vacuum, the polymer was dissolved in water, dialyzed against distilled water to remove residual isopropanol, then freeze-dried.

TABLE I
¹H-NMR Spectra of Homo- and Copolymers

	Poly(TMAEMAC)	Poly(TMAEMAC-co-AAm)	Poly(TMAEAC-co-AAm)
α-CH ₃	1.07	1.1	—
Backbone-CH ₂ -(TMAEMAC/TMAEAC)	2.0	unclear	1.9
-NCH ₂ -	3.6	3.6	3.6
-OCH ₂ -	4.3	4.3	4.3
-N ⁺ -(CH ₃) ₃	3.16	3.15	3.14
Backbone-CH-(TMAEAC)	—	—	2.4
Backbone-CH ₂ -(acrylamide)	—	1.6	1.6
Backbone-CH-(acrylamide)	—	2.1	2.1

The polymers were characterized by proton nuclear magnetic resonance spectroscopy (¹H-NMR, 200 MHz Bruker apparatus; Bruker Instruments, Billerica, MA) to determine the composition, and by viscometry using an Ubbelohde viscometer (25°C, 1M NaCl), to determine the intrinsic viscosity (IV). Table I gives details of the ¹H-NMR spectra of the synthesized homopolymers and copolymers. The IV measurements were carried out by staff at Ciba Specialty Chemicals (Wyang NSW, Australia).

Table II indicates the reaction conditions used for poly(TMAEMAC) homopolymer synthesis and the IV determined for each homopolymer. The use of methanol as a solvent results in a homopolymer with the highest molecular weight, given that precipitation of the polymer will lead to a greatly reduced rate of propagation. Sodium formate and TGA in high concentration appear to be ineffective chain-transfer

agents in aqueous solution, for reasons that are as yet unclear.

Copolymer synthesis

In this work, most copolymers were synthesized by heterophase water-in-oil (inverse-emulsion) free-radical polymerization using a redox initiation system. Sample TMAEAC 2 was synthesized in aqueous solution according to the procedure of Mabire et al.¹⁵

To carry out the polymerizations, aqueous solutions of AAm and cationic monomer containing a small amount of potassium bromate were dispersed in hydrocarbon oil (LT20; Conoco, Victoria, Australia), with sorbitan monooleate as emulsifier and ethylenediaminetetraacetic acid (EDTA; Aldrich) as a chelating agent to remove the inhibitor. The aqueous phase was dispersed in the oil phase at 1000 rpm using an Ultra-

TABLE II
 Conditions for the Synthesis of Poly(TMAEMAC) Homopolymers

Sample	[AIBN] (mol L ⁻¹ × 10 ³)	Solvent	[CTA] (mol L ⁻¹ × 10 ³)	Reaction time (h)	Intrinsic viscosity (L g ⁻¹)
1	1.6	isopropanol	—	3	2.3 ± 0.2
2	0.6	water	0.7	24	2.4
3	0.6	water	sodium formate 0.95	24	1.5
4	1.2	water	TGA 0.48	24	0.5
5	1.2	isopropanol	TGA 0.48	24	0.27
6	1.2	water	1.75	24	1.8
7	1.2	methanol	sodium formate 0.48	24	2.8
8	1.2	water	TGA —	24	1.16
9	1.2	water	0.48	24	0.27
10	1.2	water	thioethanol 0.96	24	0.6
11	1.2	water/isopropanol	thioethanol —	24	0.3
12	1.8	water	—	24	2.6
13	0.6	water	—	24	0.7
14	1.8	water	9.0	24	1.26
			TGA		

TABLE III
Conditions for the Synthesis of TMAEMAC:AAM Copolymers

Sample	TMAEMAC (mol)	Acrylamide (mol)	Chain-transfer agent	Composition (mol % TMAEMAC)	Intrinsic viscosity (L g ⁻¹)
1§	0.192	1.125	2-Propanol	26	5.2
2§	0.360	2.000	None	39	10.1
3	0.360	2.000	None	42	5.9
4	0.170	2.000	None	48	7.0

Turrax, after which the system was purged with nitrogen overnight (at 25°C and at 200 rpm) to remove residual oxygen, which can inhibit the radical reactions. An initiator solution containing sodium metabisulfite was then injected in aliquots to start the polymerization and the progress of the exothermic reaction monitored. All polymerizations were isothermal at 40 ± 0.5°C and were carried out under nitrogen with equal volumes of water and oil, corresponding to 570 g of aqueous phase and 430 g of organic phase. Samples for characterization were obtained by precipitation in acetonitrile, a solvent in which the monomer is soluble and the polymer insoluble, while the immiscible oil and emulsifier form a separate liquid phase. Tables III and IV indicate the conditions used for preparation of TMAEAC/AAM and TMAEMAC/AAM copolymers and the composition and intrinsic viscosity were determined for each copolymer. Details of the ¹H-NMR spectra of the copolymers are given in Table I.

A number of polymerizations were carried out with a "burn-out" stage, which involves the addition late in the reaction of a relatively large excess of redox initiator to ensure the polymerization of any monomer remaining. This procedure leads to the presence of a population of relatively low molecular weight copolymer with a high acrylamide content, resulting from the high flux of radicals and the likely composition of the feed in the final stages of the reaction. These syntheses are marked with the symbol "§" in Tables III and IV.

Table III shows that the products formed from TMAEMAC/AAM are enriched in cationic monomer in comparison with the feed at all times. This is consistent with most literature reports of reactivity ratios for these monomers¹⁶⁻¹⁸ in which TMAEMAC- and

AAM-terminated polymer radicals have been found to react preferentially with TMAEMAC. This suggests that a synthetic protocol in which the monomers are fed in continuously under starved-feed conditions (i.e., monomer concentration near zero at all times) would be more successful in achieving a controlled copolymer composition.

Flocculation tests

Fresh primary cane sugar juice was collected from a sugar factory in the Mackay region, Australia, and used immediately to prevent juice deterioration and changes in juice properties. The zeta potential of the particles in the primary juice was between -2 and -5 mV (measured with a Brookhaven ZetaPlus instrument, Holtsville, NY). This low zeta potential suggests that the particles are easily coagulated.

The cationic polymer (to give a final concentration of 5, 10, or 40 ppm) was added at two points in the clarification process, either before or after lime saccharate addition. In the clarification experiments, the juice at 76°C was adjusted to pH 7.8 with lime saccharate and heated to boiling. At this point the cationic polymer was added for determinations carried out after liming. After boiling for 90 s the juice was poured into a vessel containing 3.0 mL of 0.1% commercial anionic flocculant solution (a copolymer of acrylamide and sodium acrylate) to give a final anionic flocculant concentration of 3 ppm. The mixture was stirred gently twice and poured into a 1-L settling tube. The tube was placed into a clarification box containing 60-W bulbs to maintain the temperature of the juice and allow the settling rate of the floc particles to be monitored visually. As the tube was placed in the box, a timer was started. The settling rate of the flocculated

TABLE IV
Conditions for the Synthesis of TMAEAC:AAM Copolymers

Sample	TMAEAC (mol)	Acrylamide (mol)	Composition (mol % TMAEAC)			Intrinsic viscosity (L g ⁻¹)
			30 min	8 h	24 h	
1	0.150	0.600	40	20	20	13.9
2	0.150	0.360	—	31	—	4.6
3	0.560	0.560	50	45	38	6.5
4	0.150	1.500	35	20	—	18.8 ^a

^a The intrinsic viscosity value for the sample obtained after 8 h of polymerization time.

TABLE V
Relative Turbidity Values of Primary Cane Sugar Juice Treated with Poly(TMAEMAC)

Sample	Intrinsic viscosity (L g ⁻¹)	Homopolymer concentration (ppm)			
		5	10	40	200
1	2.30	1.10	0.98	0.68	
2	2.40	1.01	1.23	0.99	
3	1.50	1.20	1.70	0.94	
4	0.50	1.09	1.55	1.01	
5	0.27	0.97	0.98	0.69	0.64
7	2.80	0.91	0.85	1.10	
9	0.27	1.10	1.00	0.78	0.65
11	0.30	0.87	1.02	0.79	
14	1.26	0.86	0.93	0.74	0.64

particles was determined by measuring the height of the settled precipitate at 30 s and then each minute thereafter. The initial settling rate was obtained from a graphical analysis of the data. The precipitate height at 15 min was recorded as "final mud level." Every fourth aliquot was prepared using the same procedure without the addition of the polymer, to provide a set of controls adequate for the highly variable process stream.

The screening of cationic polymers was based primarily on settling rate and turbidity measurements. Settling rate data are reported as the relative settling rate of the suspended particles to the settling rate of the controls, attributed to the high variability of primary sugar juice from the process stream. Turbidity of the clarified juice was measured as the "absorbance" at 900 nm in 1-cm glass cells against distilled water. The relative turbidity was defined as the 900-nm adsorption obtained in the presence of a cationic polymer divided by the 900-nm adsorption for the relevant control sample clarified with the anionic polymer flocculant only. This term was used in preference to absolute turbidity, again because of the high variability of the process stream.

RESULTS AND DISCUSSION

Results of synthesized homopolymers

Low molecular weight poly(TMAEMAC)s were investigated because these had been more effective than high molecular weight polymers in preliminary work carried out by the authors.³

Turbidity results

The relative turbidity results obtained using the homopolymers are summarized in Table V. The best overall performance was achieved at high concentrations of cationic polymer, with homopolymers 4 and 8 giving a significant improvement in clarity at a concentration of 40 ppm.

No strong correlation between the turbidity results and IV measurements can be seen, although the performance of the polymer is generally better at lower IV (e.g., homopolymers 4, 6, and 7).

Settling rates

A typical plot of the settling rate as a function of homopolymer concentration is shown in Figure 1. All the homopolymers showed a clear decline in settling rate with increasing concentration.

Table VI shows the slopes determined for plots of settling rate (in cm⁻¹ × final mud level in cm as a normalization factor) as a function of homopolymer concentration. The results confirm that the homopolymers have a negative impact on floc settling rates. Values of settling rate obtained for the extrapolation of these curves to zero polymer concentration were comparable to those found in the presence of the anionic flocculant alone.

As with the turbidity results, there was no clear correlation between polymer behavior and the IV results, although the homopolymer with the highest IV had the most marked effect on settling rate.

Mode of action of homopolymer

The decline in settling rate with increasing homopolymer concentration indicates that the presence of poly(TMAEMAC) must be in some way interfering with the activity of the anionic flocculant in accelerating settling. Because the charge density on the anionic flocculant is quite low and cane sugar juice has a high concentration of negatively charged species, it is unlikely that the cationic homopolymer is either binding to the flocculant or significantly reducing the size of the anionic polymer coils by screening the charge repulsion holding it in an extended conformation. The most likely explanation for the effect lies in the presence of poly(TMAEMAC) on the physical process of flocculation. One possibility is that the aggregates

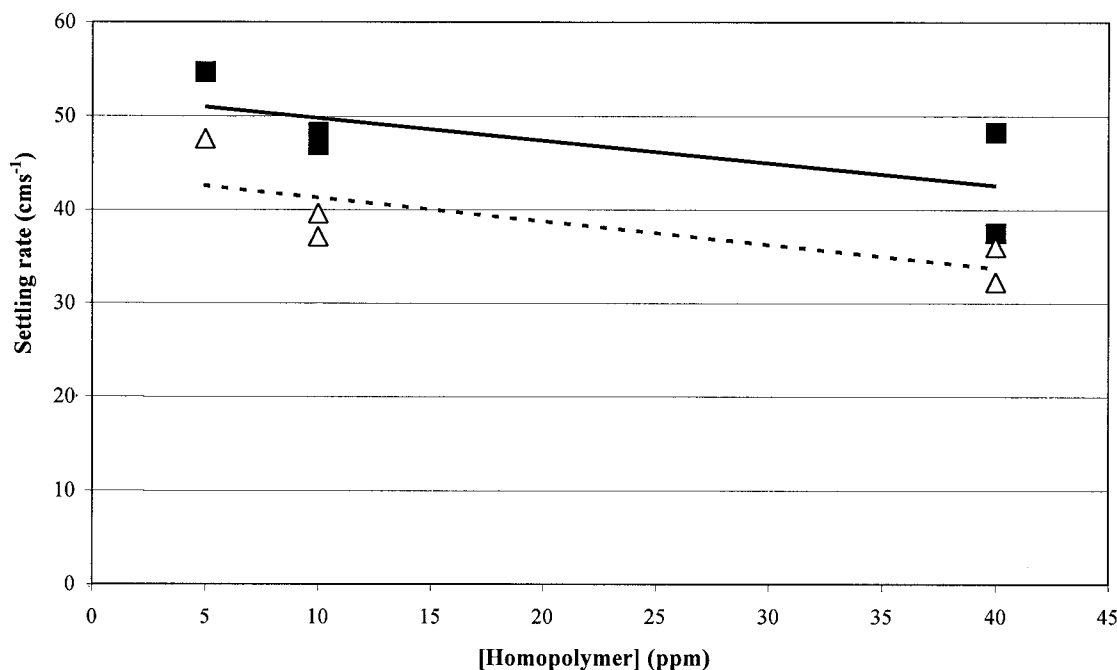


Figure 1 Settling rate over first 30 s (■) and 60 s (△) for clarifications done with homopolymer TMAEMAC 9 as a function of concentration.

formed by the action of poly(TMAEMAC) cannot readily participate in the geometric growth of the primary flocs because of their relatively high charge density and may physically prevent the bridging of the primary flocs (i.e., microflocs) by the anionic high molecular weight polymer to form fast-settling macroflocs. In coagulation of a polydisperse material, large low charge density particles such as flocs formed by very high molecular weight polymers will aggregate chiefly by a shear-dominated mechanism that is selective for coagulation of equal-sized particles. Small-size high charge density particles that are in the matrix, on the other hand, will have a much weaker selectivity for same-size aggregation attributed to elec-

trostatic repulsive forces and will grow arithmetically and independent of the primary flocs. The only role left for these aggregates is to increase turbidity.

The most probable mechanism in which the poly(TMAEMAC) aids coagulation of cane juice particles is by a charge-patch mechanism. A low degree of surface coverage provides the most rapid aggregation of particles and polymer, and at higher polymer concentrations the homopolymer would be expected to act as an electrosteric stabilizer. If simple charge-charge annihilation or bridging flocculation was responsible for coagulation, the settling rate might be expected to increase with increasing polymer concentration. Furthermore, none of the juices treated with the homopolymers showed mud levels different from that of the control, indicating that the dominant factor in mud structure remained the flocculation of the microflocs by the anionic high molecular weight polymer and strengthening the postulate that the cationic homopolymer is not binding to the anionic flocculant or significantly screening its self-repulsion.

A charge-patch mechanism is consistent with the weak dependency of turbidity on polymer concentration. It is probable that a complex function of molecular weight, concentration, and degree of hydrolysis is responsible for the observed turbidity results, and that an investigation in a system of more controlled composition than process-stream primary cane juice will be necessary to determine the contribution of each factor.

TABLE VI
Concentration Dependency of Settling Rates for Primary Cane Juice Particles Treated with Poly(TMAEMAC)

Sample	Intrinsic viscosity (L g ⁻¹)	Slope of initial settling rate versus polymer concentration (cm ² s ⁻¹ ppm ⁻¹)
1	2.40	-1.26
2	1.50	-0.53
3	0.50	-0.25
4	0.27	-0.06
5	2.80	-3.8
7	0.27	-0.24
9	0.30	-1.2
11	2.30	-0.28
14	1.26	-0.12

TABLE VII
Relative Turbidity Values in Primary Cane Sugar Juice
Treated with Poly(TMAEMAC-co-AAm) and
Poly(TMAEAC-co-AAm) Copolymers

Cationic monomer	Cationic monomer (mol %)	Copolymer concentration (ppm)	
		10	40
TMAEMAC (before liming)			
1a	26 ^a	0.87	0.74
1b	26	0.74	0.76
2a	39 ^a	0.89	0.62
2b	39	1.14	1.00
3	42	1.02	1.08
4	48	1.43	0.84
TMAEMAC (after liming)			
1a	26 ^a	0.88	0.69
1b	26	0.90	0.71
2a	39 ^a	1.03	0.77
2b	39	1.11	0.71
3	42	0.89	0.63
4	48	0.87	0.62
TMAEAC (before liming)			
—	13 ^b	0.85	0.59
1 (8 h)	20	1.06	0.67
2 (8 h)	31	0.83	0.71
3 (8 h)	45	1.00	0.61
3 (24 h)	37.5	1.00	0.61
4 (8 h)	20	0.94	0.6
TMAEAC (after liming)			
—	13 ^b	1.22	0.83
1 (8 h)	20	0.90	0.54
2 (8 h)	31	0.75	0.5
3 (8 h)	45	0.87	0.62
3 (24 h)	37.5	0.85	0.54
4 (8 h)	20	0.83	0.64

^a Polymer prepared with a "burn out" step, containing more low molecular weight acrylamide-rich copolymer.

^b Commercial polymer.

Results of synthesized copolymers

The second main class of polymers identified to give enhanced flocculation in trials with commercial polymers were high molecular weight polymers of AAm containing moderate levels of quaternary ammonium monomers such as TMAEAC or TMAEAMAC. Preliminary indications based on studies of commercial polymers suggested that high molecular weight copolymers of low to moderate cationic monomer content would be most effective as flocculants in this application.³

Turbidity results

The relative turbidities of the copolymers at concentrations of 10 and 40 ppm are given in Table VII. Three of the copolymers conferred a greater reduction in turbidity than the most effective commercial copolymer investigated. Overall, the main trend that can be observed for both TMAEAC and TMAEMAC copoly-

mers is their increasing effectiveness in reducing turbidity with increasing concentration, both before and after liming.

With regard to the point of addition of copolymer during the clarification stage, addition of the copolymer after liming was generally more effective in reducing turbidity than addition before liming. The only exceptions to this rule are the commercial sample and two of the TMAEMAC samples containing 26 and 39 mol % TMAEMAC, respectively.

A weaker than expected relation between turbidity reduction and variation in cationic monomer composition was observed. For TMAEMAC copolymers added before liming, a rise in turbidity with cationic comonomer content was seen. The other copolymers showed a weak tendency toward reduced turbidity at increasing cationic content, as illustrated in Figure 2. In absolute terms TMAEAC copolymers were normally more effective than TMAEMAC containing copolymers of equivalent IV.

To clarify the contribution of molecular size to the effectiveness of the polymers in flocculation, the relative turbidities obtained were also plotted as a function of intrinsic viscosity (Fig. 3).

Settling rates

The relative settling rates obtained in the presence of the copolymers are shown in Table VIII. Settling rates were generally higher than those of the controls, and are higher after liming than before liming, and with TMAEAC- rather than TMAEMAC-containing copolymers. The settling rate generally increased with copolymer concentration, rather than decreasing, as was observed for TMAEMAC homopolymer.

With increasing proportion of cationic comonomer in the polymer, the settling rate generally fell for TMAEAC copolymers and for TMAEMAC copolymers added before liming. However, for TMAEMAC copolymers added after liming, there was a trend to higher settling rates at higher cationic comonomer concentration.

Mode of action of copolymer

For the copolymer flocculant aids, reductions in turbidity were normally accompanied with relatively poor effectiveness in increasing the settling rate. This is the customary result in bridging flocculation, where rapid geometric growth leading to very rapid settling can generate aggregates that do not interact with small, highly charged particles and leave residual turbidity.

The increased rate of settling observed at increased concentrations of flocculant is the expected result if a bridging mechanism is applicable. When the settling rate is plotted as a function of intrinsic viscosity of the

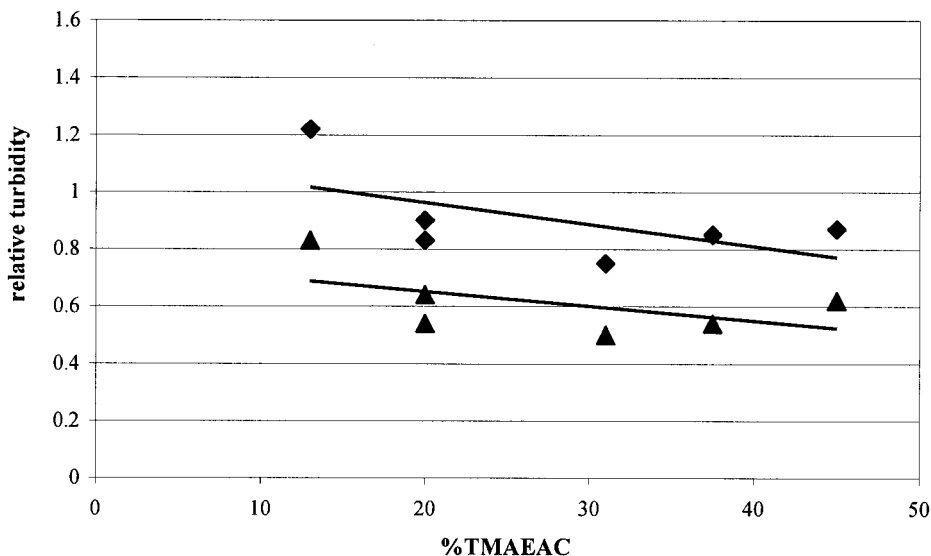


Figure 2 Dependency of relative turbidity in clarified primary sugar juice on copolymer composition, % TMAEAC in copolymer added after liming at concentrations of 10 ppm (◆) and 40 ppm (▲).

copolymer (Fig. 4), settling rates are greater at higher intrinsic viscosities (corresponding to lower cationic comonomer content), except in the case of TMAEMAC copolymers added before liming. This trend is expected for polymers acting by a bridging mechanism, in which case the settling rate is known to increase with increasing IV.⁷

After liming, a trend to greater effectiveness at lower intrinsic viscosity is seen at 40 ppm (Fig. 3), and to a lesser extent at 10 ppm. This is the expected trend if the copolymers favor a bridging mechanism with increasing IV because the larger coils will act in a similar fashion as the high molecular weight anionic

flocculant already present and tend to miss the smaller juice particles responsible for turbidity. The accelerated settling rates observed before liming are connected with the type and nature of the juice particles and the overall charge on the particles. After liming, the calcium phosphate formed during clarification carries a positive charge that partially neutralizes the negative charge of the juice particles. This allows for easier aggregation of the particles.

This trend is reversed before liming (at 40 ppm) because there is greater effectiveness of the copolymer at higher intrinsic viscosity. As the copolymers are added before liming, the surface charges of the parti-

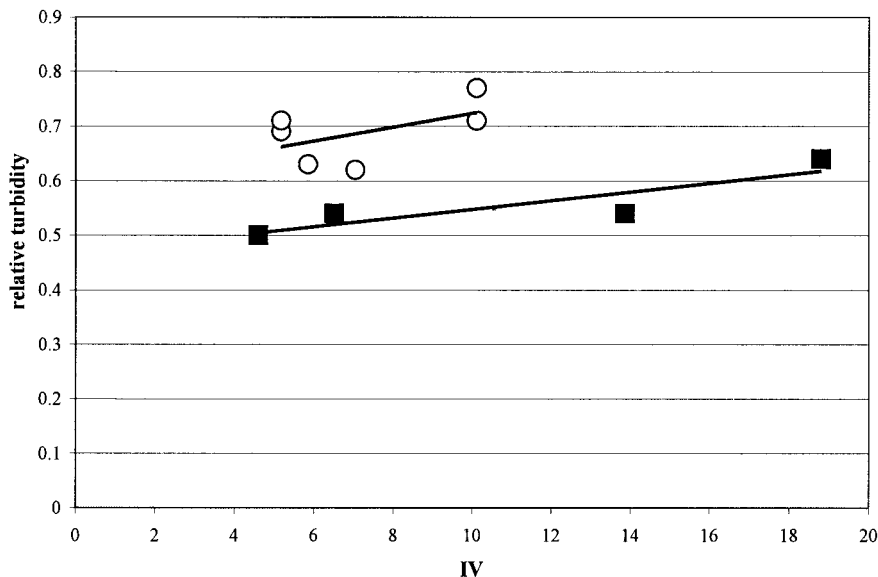


Figure 3 Dependency of relative turbidity of clarified primary cane sugar juice on intrinsic viscosity of copolymer. Results are for 40 ppm copolymer added after liming, TMAEAC (■) and TMAEMAC (○).

TABLE VIII
Relative Settling Rates in Primary Sugar Juice Treated
with Poly(TMAEMAC-*co*-AAM) and Poly(TMAEAC-
***co*-AAM) Copolymers**

Cationic monomer	Cationic monomer (%)	Relative settling rate at	
		10 ppm	40 ppm
TMAEMAC (before liming)			
1a	26 ^a	1.22	2.05
1b	26	1.37	1.22
2b	39	0.57	0.79
3	42	0.60	0.38
4	48	0.25	0.60
TMAEMAC (after liming)			
1a	26 ^a	1.15	0.57
1b	26	1.06	1.19
2b	39	2.2	0.71
4	48	1.71	4.02
TMAEAC (before liming)			
— ^b	13 ^b	0.91	0.81
1 (8 h)	20	1.17	3.05
1 (24 h)	20	1.33	2.17
2	31	0.91	1.02
3 (8 h)	45	0.38	1.26
3 (24 h)	37.5	0.67	0.95
4 (8 h)	20	0.48	1.04
TMAEAC (after liming)			
— ^b	13 ^b	0.90	1.97
1 (8 h)	20	0.71	0.83
1 (24 h)	20	0.98	2.16
2	31	1.62	1.71
3 (24 h)	37.5	1.48	1.41
4 (8 h)	20	1.70	3.05

^a Polymer prepared with a "burn out" step, containing more low molecular weight acrylamide-rich copolymer.

^b Commercial polymer.

cles will be relatively strong (no lime for neutralization) and would require larger polymer coils at high concentrations to provide more bridging sites to effect

particle binding. It is also possible that when the copolymers are added before liming the smaller molecular weight polymer fractions are more likely to act as nuclei for calcium phosphate particle formation and hence cannot act as effective coagulants.¹⁹

The reduction in turbidity observed with increasing cationic content is probably related to stronger binding between the polymer and the particles as a result of the increasing positive charge of the polymer. This would be expected to lead to denser flocs and a slower transition to geometric growth.

The typical bridging flocculant behavior is clearest for poly(TMAEMAC-*co*-AAM), which is generally less effective in improving clarified juice turbidity and more effective in increasing the settling rate. This is interpretable in terms of the effect of the α -methyl group on the backbone in retarding chain collapse, giving less dense flocs and a more rapid transition to geometric growth. The more rapid relaxation of the poly(TMAEAC-*co*-AAM) would result in somewhat denser flocs and the capture of more target particles before the transition to geometric growth.

The weak relationship between turbidity and the cationic content of the copolymer may be attributed to the variable composition within each polymer sample. The feed composition is a function of conversion, and each sample consists of a distribution of copolymer chains of different composition, ranging in extreme cases from copolymers rich in cationic comonomer formed early in the reaction to what is essentially low molecular weight poly(acrylamide) formed in the final stages of the reaction. A further source of concern is the fact that the molecular weights of the copolymers have not been kept constant in this work, so that the results reported will reflect both the changes in composition and molecular weight. Assuming that

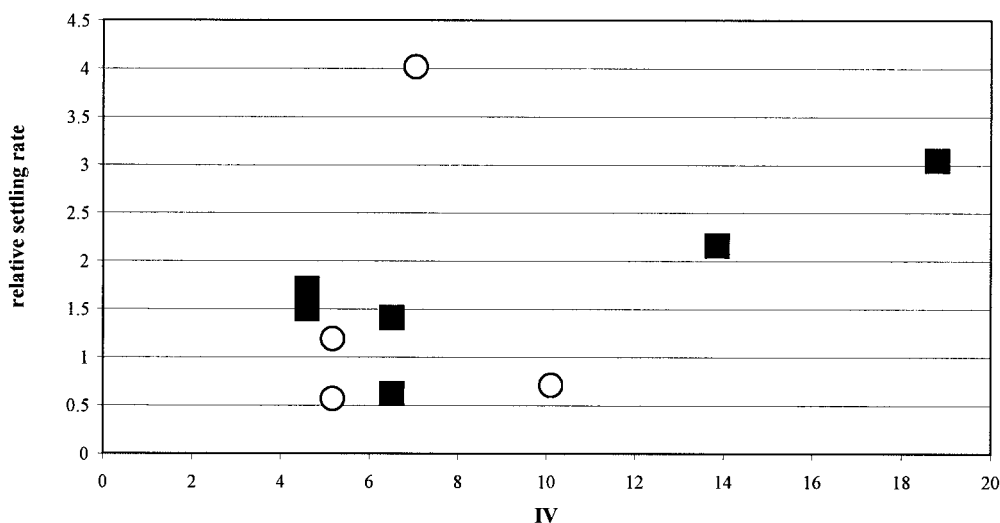


Figure 4 Dependency of settling rate of primary juice particles on intrinsic viscosity of copolymer. Results are for 40 ppm flocculant aid added after liming, TMAEAC (■) and TMAEMAC (○).

TMAEAC and TMAEMAC have a similar effect on chain expansion, the measured intrinsic viscosities should give the relative molecular weights of the copolymers.

Finally, it should be noted that simply adding increasing amounts of commercial anionic flocculant to the cane sugar juice conferred little improvement in either turbidity or settling rate, suggesting that the improvement seen is not simply a matter of the amount of bridging flocculant present, but that the cationic flocculants are targeting a different population of suspended material.

CONCLUSIONS

Measurements of turbidity and settling rate have shown that copolymers synthesized from AAm and the quaternary ammonium compounds TMAEAC/TMAEMAC are more effective than homopolymers of TMAEMAC as flocculant aids in improving the clarity of cane sugar juice. These copolymers have been found in a number of cases to be more effective than the best commercial copolymer identified for the flocculation and sedimentation of cane sugar particles. It was also found that addition of the copolymer after liming, rather than before liming, was a more effective procedure for enhancing both juice clarity and settling rate of the juice particles. The reduction of clarified juice turbidity by 50% is significant and the faster settling rate obtained may lead to arguments for reduced clarifier capacity. Also, with the reduced residence time of the clarified juice in the clarifier, sucrose inversion, degradation of reducing sugars to organic acids, and formation of color bodies will be minimized. The reduction of up to 50% in turbidity is expected to have an impact on the quality of raw sugar produced.

It is probable that the charge-patch mechanism is operative with poly(TMAEMAC), and there is no simple modification to these species that could make the homopolymer significantly more effective for turbidity removal.

The particles most likely responsible for residual turbidity in juice clarified using an anionic flocculant only are small and bear a high negative charge. It is postulated that cationic copolymers of IV high enough to act by a bridging mechanism are the most effective polymers to aid flocculation and sedimentation of cane sugar juice. It is anticipated that testing various

combinations of the prepared copolymers and anionic flocculants with different degrees of hydrolysis may provide valuable information for the synthesis of superior polymer additives. Such investigations may also lead to the identification of synergistic combinations of anionic and cationic bridging flocculants with significantly enhanced clarification performance.

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References

- Doherty, W. O. S.; Edey, L. A. *Proc Aust Soc Sugar Cane Technol* 1999, 21, 381.
- Bennett, M. C. *Int Sugar J* 1957, 59, 176.
- Fellows, C. M.; Doherty, W. O. S.; Cheung, W. H. *Zuckerindustrie* 2000, 125, 101.
- Crees, O. L.; Senogles, E.; Whayman, T. J. *Appl Polym Sci* 1991, 42, 837.
- Kampen, W. H. *Int Sugar J* 1997, 99, 1183.
- Mühle, K. In: *Coagulation and Flocculation*; Dobias, B., Ed.; Marcel Dekker: New York, 1993.
- Han, M.; Lawler, D. F. *J Am Water Works Assoc* 1992, 84, 79.
- Fellows, C. M.; Lin, Y.; Li, G.; Gorjian, S. In: *Shear-Induced Aggregation in "Bridging" Flocculation*, Proceedings of the 9th Asian Chemistry Congress, Federation of Asian Chemical Societies, Brisbane, Australia, 2001.
- Elvin, J. R. In: *Decolorization and Clarification of Sugar Solutions using Color Precipitants and Flocculants*, Proceedings of the Workshop on Separation Processes in the Sugar Industry, New Orleans, LA, 1996.
- Kitchener, J. A.; Slater, R. W. *Trans Faraday Soc* 1966, 62, 267.
- Moody, G. M. *Filtr Sep* 1995, 32, 329.
- Rose, G. R.; St. John, M. R. In: *Encyclopedia of Polymer Science and Technology*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985.
- Moodley, M. *The Application of Cationic Flocculants as Decolorising Agents in the Sugar Industry*; SMRI Technical Report, 1993, 1648.
- Hunkeler, D. J. Ph.D. Thesis, McMaster University, 1990.
- Mabire, F.; Audebert, R.; Quivoron, C. *Polymer* 1984, 25, 1317.
- Baade, W.; Hunkeler, D.; Hamielec, A. E. *J Appl Polym Sci* 1989, 38, 185.
- Ha, R.; Hou, S. *Gaofenzi Xuebao* 1993, 5, 570.
- Yang, Y.; Yu, H.; Bao, Y. *Shiyong Huagong* 1988, 17, 21.
- Gorjian, S.; Fellows, C. M.; Doherty, W. O. S.; Cheung, W. H. *Zuckerindustrie* 2001, 126, 259.