Inhibition of Calcium Oxalate Monohydrate by Poly(acrylic acid)s with Different End Groups

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ABSTRACT: Water-soluble low molecular weight polymers are known to affect the crystal habit of scale-forming minerals and their rates of deposition. Poly(acrylic acid) (PAA) and poly(maleic acid) are commonly used to control scale formation in sugar mill evaporators. Calcium oxalate (both mono- and dihydrate) forms the bulk of the hard intractable scale found in Australian sugar mills, causing efficiency losses of significant economic importance. In this work, the formation of calcium oxalate monohydrate in a synthetic juice solution was investigated in the presence of PAAs of varying molecular weights and end-group functionality and a strong dependency on both of these factors was observed. Terminal functionality was controlled using three chain-transfer agents (CTA): thioethanol, thioglycolic acid, and dodecanthiol. Effectiveness of inhibition varied with CTA in the order thioethanol ~ thioglycolic acid > dodecanthiol for all molecular weights. This suggests that polymer end groups play a role in scale inhibition. The polymers that were prepared with dodecanthiol accelerated rather than inhibited calcium oxalate formation, implying a different mode of action on calcium oxalate crystallization. Consistent with previous reports for other scales, the calcium oxalate inhibition tests show optimum effectiveness for PAAs of molecular weight 2000–4000. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2035–2041, 2004

Key words: acrylic acid; precipitation polymerization; scale inhibitors; molecular weight determination; chain

INTRODUCTION

Formation of scale on equipment surfaces is a problem in many areas such as industrial water systems, secondary oil recovery using water-flooding techniques, desalination, and sugar mill evaporators. In the sugar milling industry, the deposition on evaporator units of mineral salts such as calcium oxalate (monohydrate and dihydrate), calcium magnesium aconitate, amorphous silica, calcium sulfate dihydrate, calcium carbonate, and calcium phosphate is of major economic importance.[1,2] Water-soluble low molecular weight polymers are often used as scale inhibitors in such systems. The effect of these species on the crystal habit of scale-forming minerals and on their rates of precipitation has been the subject of numerous investigations.[3] Senogles and Doherty[1] investigated the use of low molecular weight polymeric additives such as poly(acrylic acid) (PAA) and poly(maleic acid) to control scale formation in Australian sugar mills. They demonstrated changes in calcium oxalate nucleation and crystal growth processes and, attributed the changes to the adsorption of polymers on the surfaces of calcium oxalate crystallites.

In this work the formation of calcium oxalate in a synthetic sugar juice solution was investigated in the presence of PAA species of varying molecular weights while the same temperature, solution pH, and polymer concentration were maintained. Another variable that may determine the effectiveness of an inhibitor is the identity of the terminal functional group of the PAA chain. Three chain-transfer agents (CTAs) were therefore selected to control both molecular weight and end-group functionality of PAA: (1) thioethanol, which introduces an –OH group on the chain terminus; (2) thioglycolic acid, which introduces a –COOH group; and (3) dodecanthiol, which introduces a $-C_{12}H_{25}$ group. The CTAs were selected for their effect on the ability of PAA to bind to calcium oxalate crystallites, on the basis of their relative affinity for ionic substrates. It was anticipated that the –COOH-terminated polymers would be most successful in binding to forming calcium oxalate surfaces, whereas the –OH-terminated polymers would be somewhat less effective and the $-C_{12}H_{25}$-terminated polymers least effective.

EXPERIMENTAL

Acrylic acid can be polymerized in bulk[5] or in aqueous or organic media by methods such as inverse-suspension[6,7] or inverse-emulsion[8] polymerization. The rate of polymerization is dependent on the nature of the polar solvent, the ionic strength, and the pH (for re-

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TABLE I
Poly(acrylic acids) Prepared with Different Chain-Transfer Agents (CTA)

Type of CTA	CTA concentration (mol L^{-1})	AIBN concentration (mol L^{-1})	Reaction time (h)	Molecular weight (M_n)
None	0.00	0.024	24	12,800
Thioglycolic acid	0.01	0.012	24	9300
	0.02	0.018	24	5900
	0.025	0.024	2	5900
	0.05	0.024	24	4200
	0.10	0.024	24	3300
	0.18	0.024	2	3100
	0.40	0.024	24	1600
	1.0	0.024	2	1300
Thioethanol	0.018	0.018	3	4500
	0.018	0.018	6	3900
	0.018	0.018	16	4000
	0.025	0.024	2	5600
	0.064	0.024	2	3500
	0.120	0.024	2	3000
Dodecanthiol	0.025	0.024	2	14,500
	0.025	0.024	18	7800
	0.050	0.024	2	15,900
	0.050	0.024	24	11,800
	0.10	0.024	24	5600
	0.10	0.024	2	5700
	1.0	0.024	24	2900
	1.0	0.024	2	2800

actions carried out in aqueous solution).[9] The maximum rate of polymerization occurs near the pK_a of acrylic acid, suggesting that the cross-propagation reaction between the acid and salt forms of acrylic acid may be favored. The use of a precipitation polymerization method has been reported to overcome the strong solvent dependency of the polymerization rates and eliminate contamination of polymer by emulsifying agents.[10] The method uses an aromatic hydrocarbon such as toluene, which is a solvent for the monomer and a nonsolvent for the polymer. Because the purity of the polymer will influence scale inhibition tests, precipitation polymerization was used in this study.

Synthesis

Glacial acrylic acid (Sumika Co., Singapore) was supplied inhibited with 200 ppm of hydroquinone monomethylether and was degassed, but not otherwise purified, before polymerization. Toluene (BDH, Toronto, Canada) and hexane (Certified ACS, BDH) were used without further purification. Azobisisobutyronitrile (AIBN; Aldrich Chemical, Milwaukee, WI) initiator was recrystallized from methanol and light petroleum ether. The chain-transfer agents 2-thioethanol and dodecanthiol (Aldrich) were used without further purification and thioglycolic acid (Aldrich) was purified by distillation.

Acrylic acid (10 g, 0.14 mol), toluene (90 mL), and a known amount of CTA were added to a three-neck flask. A number of different CTAs at various concentrations were used to give a range of molecular weights and end-group functionalities (Table I). The reaction mixture was sparged continuously with nitrogen for 1 to 2 h at room temperature to remove any residual oxygen, and a known amount of AIBN was added under nitrogen as a solution in 5 mL *N*,*N*-dimethylformamide. The reaction mixture was stirred at 50°C for 2 to 24 h under nitrogen. The precipitated polymers were filtered off, washed with *n*-hexane, and dried to constant weight under air at 60°C for about 12 h.

Polymer characterization

Gel permeation chromatography

The synthesized PAAs were characterized by aqueous-phase gel permeation chromatography (GPC) to estimate the number-average molecular weight M_n. GPC analysis was carried out using a Waters gel permeation chromatograph (Model 441; Waters Chromatography Division/Millipore, Milford, MA) with an Erma dRI Model ERC 750 detector. M_n was determined using (a) 0.5*M* $LiNO_3$ and (b) 0.5*M* NaCl buffered to pH 9 as eluent. For method (a), M_n was estimated using poly(ethylene oxide) (PEO) standards (four standards covering the molecular weight range

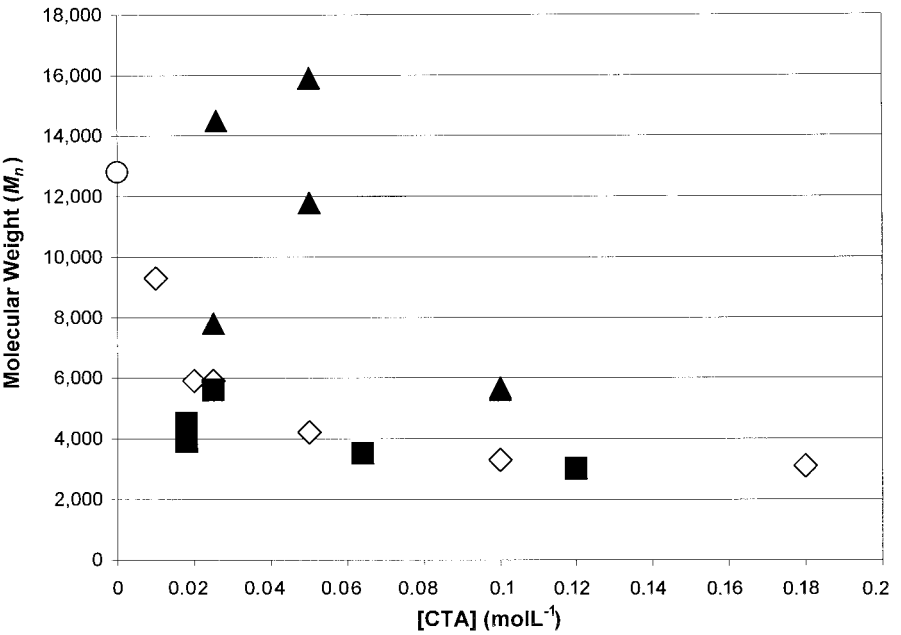

Figure 1 Dependency of molecular weight on the concentration of chain-transfer agents. No CTA, ○; thioglycolic acid, □; thioethanol, ■; dodecanthiol, ▲.

from 29,600 to 761,300, Mark–Houwink parameters $K = 3.47 \times 10^{-4}$, $a = 0.700$[11]). For method (b), these same PEO standards were used and a calibration was done using Mark–Houwink parameters for poly(sodium acrylate) under the given conditions $K = 2.44 \times 10^{-5}$, $a = 0.887$.[12] Because there were differences in the M_n values determined by the two approaches, the M_n values given in Table I were scaled from values obtained in separate runs with $LiNO_3$ to agree with the results for two samples that gave similar results with NaCl.

Figure 1 illustrates the dependency of M_n on the concentration and type of CTA for concentrations up to 0.02 mol L^{-1}. As expected, lower molecular weight polymers are obtained at higher concentrations of CTA. However, a marked difference is seen between the effectiveness of the different chain-transfer agents, as shown in Figure 1. At similar CTA concentrations, both thioethanol and TGA gave comparable M_n values, whereas dodecanthiol gave higher values. Literature values of chain-transfer coefficients for CTAs for thioethanol and alkyl thiols are very similar for acrylate and methacrylate polymers,[11] making the large difference between the effectiveness of thioethanol and dodecanthiol surprising. A possible explanation for thioglycolic acid producing polymers of lower molecular weight than dodecanthiol is that as a more polar species it is preferentially concentrated near the growing polymer chains, rather than being distributed evenly throughout the toluene solution.

At low CTA concentrations, a trend to lower molecular weight at longer reaction times can be seen. This is to be expected, given the normal termination mechanisms in a system such as the one employed where the initiator concentration remains relatively constant (the half-life for AIBN at 50°C in toluene is about 90 h[11]), whereas the monomer concentration is declining. At higher concentrations of CTA, this effect is masked by chain transfer to the thiol.

NMR spectroscopy

The synthesized PAAs were examined by ^{1}H-NMR to locate groups associated with the CTAs. Typical NMR spectra for PAA prepared with each of the CTA are presented in Figure 2. The broad signal at about 4.4 ppm is assigned to protons on the thioether methylenes attached to no other functional group; that is, PAA—CH_2SCH_2 – for thioethanol and dodecanthiol and PAA—CH_2S– for thioglycolic acid–terminated PAAs. The broadness of the signal is indicative of a covalent bond between CTA and the polymer chain and not attributed to unreacted CTA. The M_n value was then estimated from the ratio of end groups to the signals from the backbone methine and methylene resonances, assuming an incorporation of one CTA molecule per polymer molecule. In general, the NMR method for M_n determination gave results similar to those obtained in Table I (±20%).

Calcium oxalate monohydrate inhibition test

Calcium oxalate inhibition was tested using a solution with sucrose and organic and inorganic ion concen-

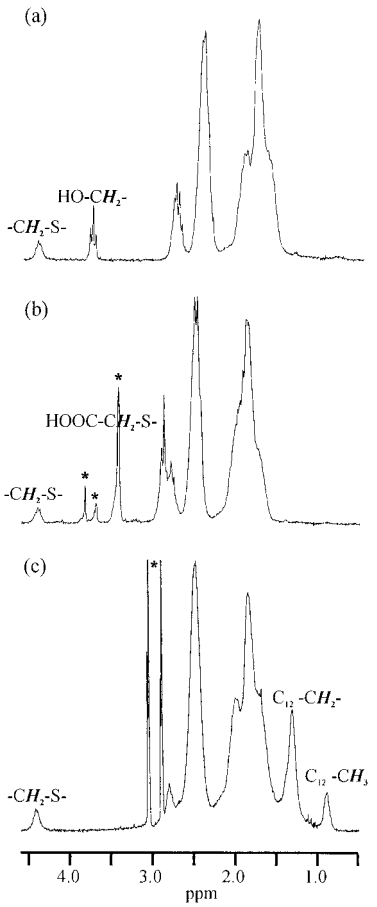

Figure 2 ^{1}H-NMR spectra of poly(acrylic acid) with (a) thioethanol end groups, (b) thioglycolic acid end groups, and (c) dodecanthiol end groups. Signals wholly or partly derived from low molecular weight impurities are marked with an asterisk.

trations equivalent to those found in cane sugar juice. Table II shows the composition of the synthetic juice used in this study. The juice was adjusted to pH 7.0 with sodium hydroxide, filtered through a 0.45-μm membrane, and used within 24 h of preparation.

The evaluation of polymers for calcium oxalate monohydrate inhibition involved adding 200 mL of synthetic juice to an ultraclean 250-mL beaker with no cracks or surface imperfections. Exactly 40 ppm of oxalic acid was added to the juice followed by 3 ppm polymer. The mixture was boiled, with stirring, at atmospheric pressure until visible turbidity indicated calcium oxalate monohydrate precipitation. The beaker was then removed from heat, covered, and cooled to room temperature, upon which sucrose concentration was determined by measurement of the refractive index of the solution. The effectiveness of the polymer for the desired application is best determined by the extent to which it retards the onset of turbidity in comparison to a solution to which no polymer was added. This is expressed in terms of percentage inhibition (I), defined as

$$I = \frac{S\% - 17\%}{46\%} \quad (1)$$

where S% is the percentage of sucrose in the final turbid solution and 17% is the percentage of sucrose in juice concentrated without the use of a scale inhibitor. The term 46% is the difference between S% and 63%, the target concentration of sucrose in the product emerging from the final evaporator stage in the factory.

Scanning electron microscopy

The crystal sizes and shapes of calcium oxalate formed in the presence and absence of polymers were examined in a JEOL 5410LV scanning electron microscope (JEOL, Peabody, MA) operating at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Calcium oxalate monohydrate inhibition

The I values obtained for the PAAs are given in Table III, together with figures for the commercial PAA scale inhibitors Antiprex A and Evaptreet XY. Selected values are displayed graphically in Figure 3, showing I as a function of M_n for each series of PAAs investigated. Each data point is an average of a number of experiments with an error of $\pm$2%.

The effectiveness of the polymers in preventing calcium oxalate formation improves at lower PAA molecular weight. For PAAs prepared with thioethanol and thioglycolic acid, optimal scale inhibition occurs at M_n between 2000 and 4000. Dodecanthiol-terminated PAAs, however, give relatively poor scale inhibition whatever their molecular weight.

Crystal morphologies of calcium oxalate monohydrate

Scanning electron microscopy (SEM) was carried out on the calcium oxalate monohydrate samples obtained from the inhibition tests. A number of representative SEM images are shown Figures 4, 5, and 6. Figure 4 is

TABLE II
Synthetic Juice Formulation

Compound	Juice (mol L^{-1})
Sucrose	0.3768
Calcium chloride dihydrate	0.0061
Magnesium sulfate heptahydrate	0.0037
Potassium chloride	0.0210
Sodium gluconate	0.0018
Citric acid	0.0005
Aconitic acid	0.0110

TABLE III
Effect of Poly(acrylic acid) Species on Calcium Oxalate Inhibition

Type of CTA	Molecular weight (M_n)	Percentage inhibition (I)
None	12,800	13
Thioglycolic acid	9300	−2
	5900	39
	5900	7
	4200	28
	3300	63
	3100	54
	1600	37
	1300	7
Thioethanol	4500	43
	3900	78
	4000	43
	5600	13
	3500	50
	3000	91
Dodecanthiol	14,500	−7
	7800	−4
	15,900	−7
	11,800	9
	5600	−7
	5700	2
	2900	11
	2800	15
Antiprex A		89
Evaptreet XY		91

the micrograph for calcium oxalate monohydrate prepared in the absence of polymer. The crystals are not well developed, with an irregular laminar appearance. When calcium oxalate monohydrate is prepared in the presence of PAA with –COOH end groups (i.e., with thioglycolic acid), an effective scale inhibitor, some of the crystals are cruciform, although a large majority of the crystals have poorly developed faces, approaching spherical symmetry (Fig. 5). However, when calcium oxalate monohydrate is prepared in the presence of PAA with the $-C_{12}H_{25}$ end group (i.e., with dodecanthiol), a poor scale inhibitor, uniformly produced platelike structures are formed (Fig. 6). The small crystal sizes formed suggests that "shock" crystallization has occurred.

The best PAA scale inhibitors prepared show equivalent effectiveness to commercial antiscalants (Table III). It is suggested that the PAA acts to inhibit scale formation by adsorption to the surface of growing calcium oxalate crystallites, preventing crystallite growth. The observed optimum in inhibition efficiency as a function of molecular weight (Fig. 3) may be explained with reference to two conflicting size-related trends. As PAA increases in size, its adsorption will become less reversible because of the increasing number of carboxylic acid groups per polymer that can interact with the surface. Above an optimum molecular weight, however, the polymer chain will not be able to relax completely on the crystallite surface within the time scale of interparticle interactions and monolayer growth.[1] This will reduce the proportion of acid groups able to interact directly with the crystallites, and this extended polymer may also behave as a coagulant/flocculant, aggregating and bridging crys-

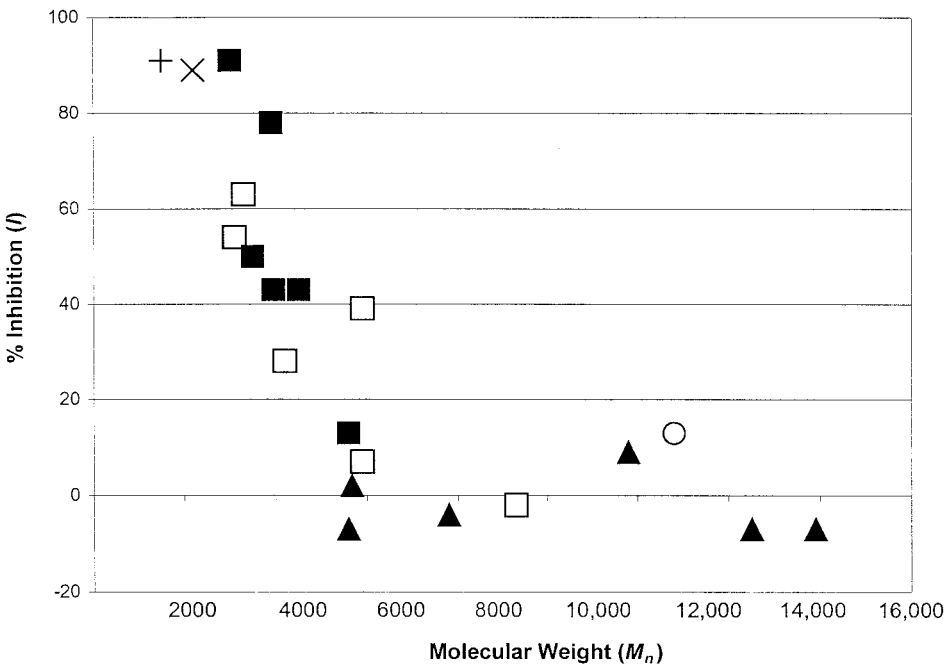

Figure 3 Relationship between molecular weight and calcium oxalate monohydrate inhibition: No CTA, ○; thioglycolic acid, □; thioethanol, ■; dodecanthiol, ▲; Antiprex A, +; and Evaptreet XY, ×.

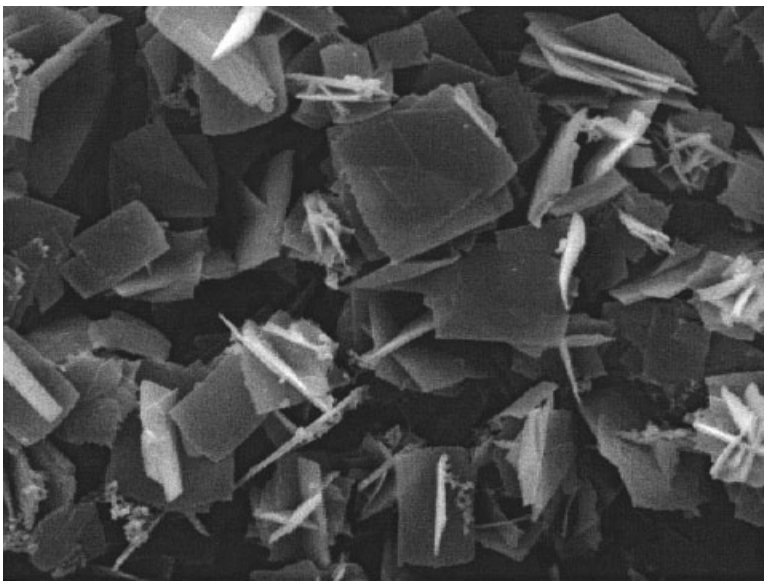

Figure 4 Calcium oxalate monohydrate (width of micrograph = 26.4 μm) in the absence of an additive.

tallites to give qualitatively less effective inhibition. This result is consistent with previous reports for a number of scales and antiscalants.[13,14] It is also probable that at an optimum molecular weight, the polymer is able to completely wrap around the crystallites and cause repulsion between them, thus enhancing inhibition.

Thioglycolic acid (i.e., –COOH) and thioethanol (–OH) derived end groups are expected to have a much higher degree of adsorption than that of dodecanthiol because they are capable of polar interactions with the crystallites, and are seen to be effective in reducing the rate of crystal growth from their effect on morphology (Fig. 5). The $C_{12}H_{25}$ end group will not adsorb to the calcium oxalate surface, and because of its size could provide a reservoir of thermal energy for desorption of the polymer from the crystallite surface. Furthermore, the hydrophobic character given to PAA by the $C_{12}H_{25}$ end group could result in the formation of an insoluble complex with calcium. The calcium–polymer complex microparticles would then act as seeds for "shock" crystallization of calcium oxalate (Fig. 6). Even at a low polymer molecular weight where the polymer backbone chain is short, the dan-

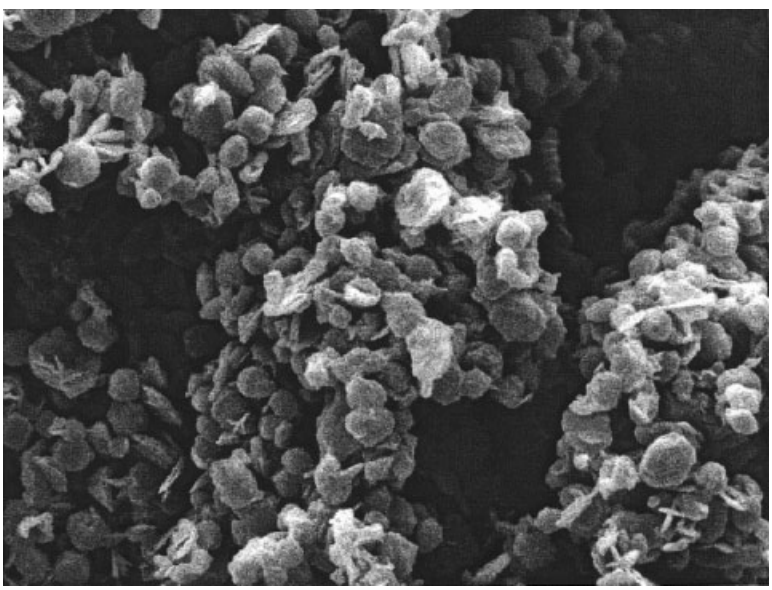

Figure 5 Calcium oxalate monohydrate prepared in the presence of PAA with thioglycolic acid (width of micrograph = 26.4 μm).

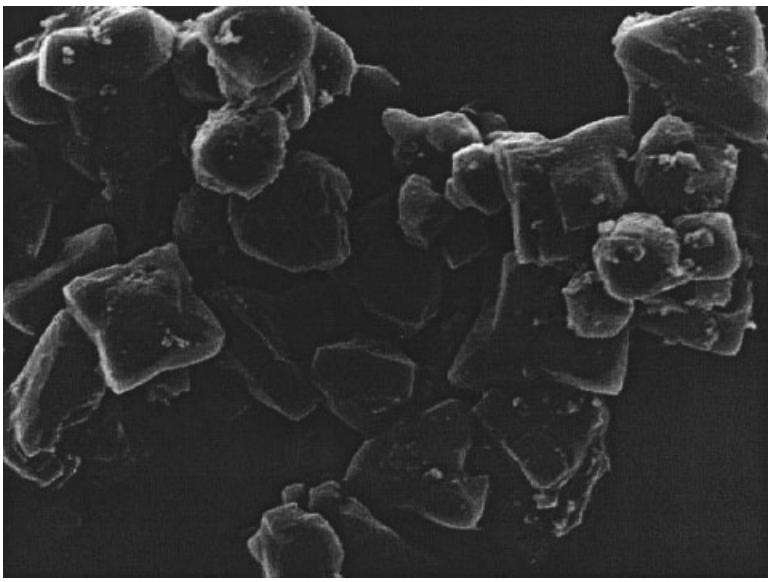

Figure 6 Calcium oxalate monohydrate prepared in the presence of PAA with dodecanthiol (width of micrograph = 26.4 μm).

gling hydrophobic chain ends of $-C_{12}H_{25}$ may foster aggregation of the calcium oxalate crystallites and therefore cause rapid calcium oxalate precipitation.

The enhanced growth of calcium oxalate observed under some conditions in this work when $C_{12}H_{25}$-terminated polymers were used suggests that the use of such an additive in a sugar factory would result in the formation of calcium oxalate at an earlier stage in the multistage juice evaporation process. Calcium phosphate, the major component of scale in the earlier evaporator units, is regarded as "soft scale" because it is readily removed by acid, and earlier formation of calcium oxalate scale will give a composition of mixed calcium phosphate and calcium oxalate in the early effects. Once the calcium phosphate is dissolved the calcium oxalate component of the scale will be easily dislodged and removed.

CONCLUSIONS

Inhibition tests of calcium oxalate monohydrate formation using PAAs of varying molecular weights gave marked differences in inhibition behavior observed for different chain-transfer agents independent of the molecular weight determined, with effectiveness declining with end-group type in the order thioethanol $\sim$ thioglycolic acid $>$ dodecanthiol. This suggests that polymer end groups play a role in the adsorption of polyacrylic acid to the growing calcium oxalate crystallite surface. The PAAs with end groups that are capable of adsorption onto the crystallite surface were significantly more effective than those with end groups less likely to adhere to the crystallite surface.

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