[Contribution from the Monsanto Chemical Company, Chemical Research Department, Research and Engineering Division]

Effect of Polyelectrolytes on the Precipitation of Calcium Carbonate

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The effect of polyelectrolytes on the precipitation of $CaCO_3$ has been examined. The following were observed: the time before precipitation commences is prolonged, the rate of precipitation is decreased and the quantity of $CaCO_3$ eventually precipitated is reduced. The $CaCO_3$ crystals are also distorted. An explanation involving polymer adsorption is presented to account for these observations.

Introduction

There are numerous examples in the literature[1] describing the effects of foreign substances, chiefly dyes and colloids, on the crystallization of sparingly soluble salts. These effects are predominantly concerned with alterations in crystal habit.

In this paper are described some observations on the effect of two synthetic polyelectrolytes, sodium polymethacrylate (NaPMA) and the ammonia adduct of isobutylene/maleic anhydride copolymer (IBMA), on the precipitation of calcium carbonate.

Experimental

Reagent grade calcium nitrate and sodium carbonate were used. The low molecular weight polymethacrylic acids were prepared by the mass polymerization of glacial methacrylic acid at 100° using various concentrations of benzoyl peroxide as catalyst and bromoform or bromotrichloroethane as transfer agent. The intrinsic viscosities were determined in methanol at 26°. The intrinsic viscosity–molecular weight relation is known.[2] The degree of polymerization (D.P.) of the high molecular weight polymethacrylic acid was around 6000. The isobutylene/maleic anhydride copolymer was made by treating maleic anhydride, dissolved in benzene, with a slight excess of isobutylene in the presence of 0.1% of dibenzoyl peroxide in a sealed tube at 54° for 14 hours. The isobutylene/maleic anhydride copolymer was then treated with ammonia gas until two moles of NH_3 had been absorbed per mole of copolymer unit. It is believed that this material is a half amide, half ammonium salt. The equivalent weight was taken as the sum of the molecular weights of isobutylene and the half amide, half ammonium salt of maleic anhydride.

Mixtures containing a constant amount of stock solution of Ca^{++} and various quantities of polyelectrolyte stock solution were prepared. A constant amount of $CO_3^=$ stock solution was added to each mixture. The final concentrations of Ca^{++} and $CO_3^=$ were such that in the absence of polyelectrolyte $CaCO_3$ precipitated instantly. Precipitation of polymethacrylate by Ca^{++} prohibited the use of very low concentrations of NaPMA. After addition of the $CO_3^=$, the solutions were agitated thoroughly and immediately transferred to a turbidity cell. Turbidities were measured with a light scattering photometer built in the laboratories of Cornell University and designed by Professor Debye. Measurements were made at room temperature. Specimens of the crystals were collected for microscopic examination after equilibrium was attained.

To determine the quantity of $CaCO_3$ prevented from precipitating, solutions were prepared in the fashion described above and permitted to stand for two days to attain equilibrium. The $CaCO_3$ precipitates were then filtered, dissolved in acid, reprecipitated with oxalate and the calcium oxalate determined by titration with standard permanganate.

The extent of adsorption of polyelectrolytes by $CaCO_3$ was measured by precipitating $CaCO_3$ in the presence of polyelectrolyte and analyzing the supernatant for polymer as described below.

The scheme of polymer analysis consisted of adding a definite amount of a polycation, the acetate salt of poly-β-dimethyl aminoethylmethacrylate, to the solution to be analyzed. The turbidity of the resulting suspension of the polycation–polyanion coprecipitate was measured. A working curve relating turbidity with concentration of polyanion was constructed.

Results

The general nature of the precipitation in the presence of polyelectrolyte is revealed in Fig. 1, in which data from several of the turbidity–time experiments with NaPMA are collected. Three distinct features are evident. (1) The time elapsed before $CaCO_3$ begins to precipitate increases as the polymer concentration increases. To relate this induction period with polymer concentration, the two linear portions of each curve were extrapolated to the point of intersection. This point is arbitrarily defined as the induction period. The connection between the induction period and the concentration of polymer is shown in Table I. (2) After initiation of precipitation, the rate of precipitation decreases as the polymer concentration increases. (3) The total quantity of $CaCO_3$ eventually precipitated decreases as the polymer concentration increases. The moles of $CaCO_3$ prevented from precipitating per equivalent of polyanion is defined as the sequestering constant. These data are recorded in Table II.

Table I

Effect of Polymer Concentration of the Induction Period: Concentration of Solutions 5.2 × 10^{-3} *M* Ca^{++}, 4.6 × 10^{-3} *M* Na_2CO_3

Polymer concn.	Induction period, min.
0.0128 *N* NaPMA(DP6000)	17
.1038 *N* NaPMA(DP6000)	27
.0153 *N* NaPMA(DP6000)	19
.0168 *N* NaPMA(DP6000)	44
.0179 *N* NaPMA(DP6000)	61
.0204 *N* NaPMA(DP6000)	158
.0230 *N* NaPMA(DP6000)	255
> .0250 *N* NaPMA(DP6000)	No precipitation
.0125 *N* NaPMA(DP54)	124
.0125 *N* NaPMA(DP118)	112
.0125 *N* NaPMA(DP296)	126
.0125 *N* NaPMA(DP385)	40
.0125 *N* NaPMA(DP6000)	29
.00174 *N* IBMA	10
.00204 *N* IBMA	~40
.0088 *N* IBMA	No precipitation

Photographs of crystals obtained from the experiments with NaPMA are shown in Fig. 2. As the concentration of polymer is increased the usual rhombs of calcite become more distorted. In the more concentrated polymer solutions the crystals

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[1] H. E. Buckley, "Crystal Growth," John Wiley and Sons, Inc., New York, N. Y., 1951.

[2] N. M. Wiederhorn and A. R. Brown, *J. Poly. Sci.*, **8**, 651 (1952).

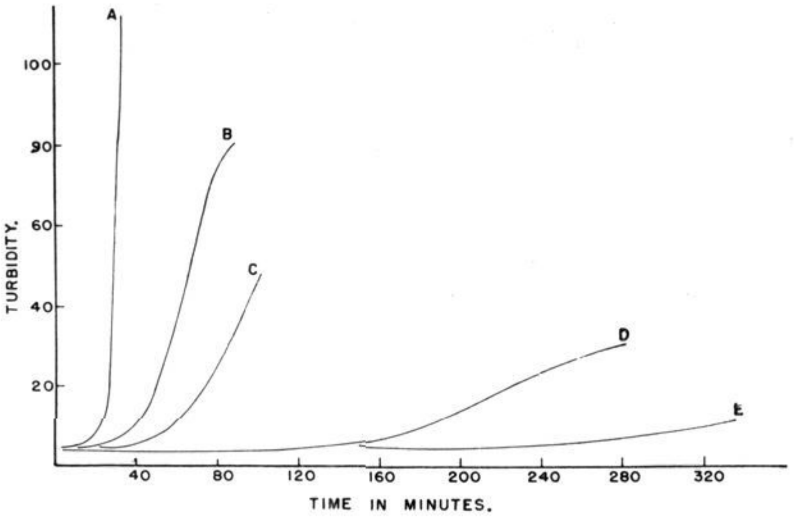

Fig. 1.—Effect of NaPMA(DP6000) concentration on the precipitation of $CaCO_3$: concentration of solutions, 0.0052 M Ca^{++}, 0.0046 M Na_2CO_3; normality of NaPMA, (A) 0.0138; (B) 0.0168; (C) 0.0179; (D) 0.0204; and (E) 0.0230.

exhibit no external signs of a definite structure. X-ray powder spectrograms of the most distorted crystals indicated that the calcite structure had been retained. It is surprising that the size of the crystals first decreases and then increases as the concentration of NaPMA is increased.

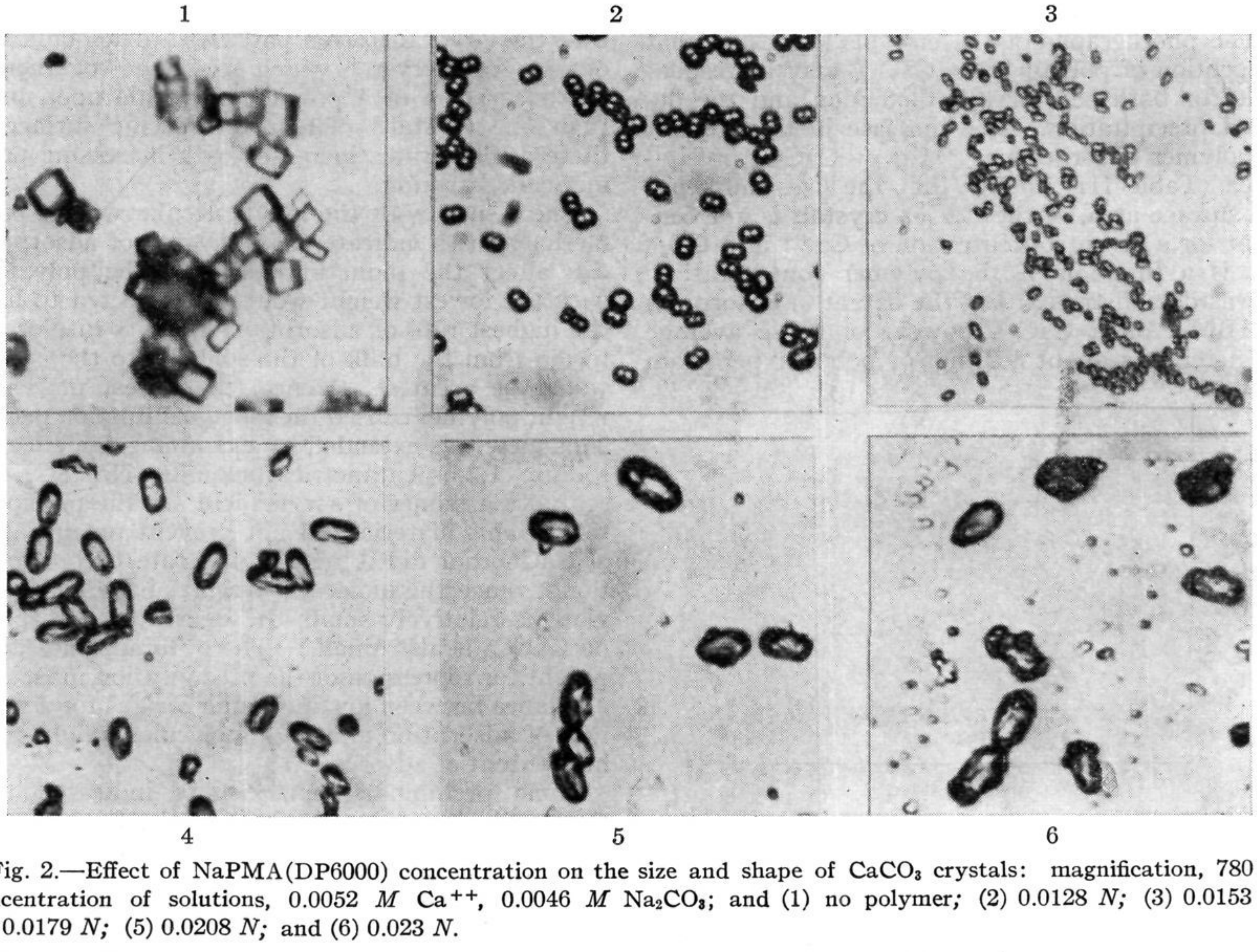

Fig. 2.—Effect of NaPMA(DP6000) concentration on the size and shape of $CaCO_3$ crystals: magnification, 780×; concentration of solutions, 0.0052 M Ca^{++}, 0.0046 M Na_2CO_3; and (1) no polymer; (2) 0.0128 N; (3) 0.0153 N; (4) 0.0179 N; (5) 0.0208 N; and (6) 0.023 N.

For NaPMA, no difference could be detected in polymer concentration in solution before and after precipitation of $CaCO_3$. The adsorption results with IBMA are given in Table III. Qualitatively, the effects of these polyelectrolytes resemble those of the condensed phosphates on the precipitation of $CaCO_3$.[3]

TABLE II

$CaCO_3$ ANALYSES ON SOLUTIONS (5.2×10^{-3} M Ca^{++}, 4.6×10^{-3} M Na_2CO_3) CONTAINING POLYELECTROLYTE

Polymer concn.	Mmoles $CaCO_3$ pptd./ 100 ml. soln. 1	2	Av.	"Sequestering constant"
0	0.430	0.430	0.430	
0.0130 N NaPMA(DP6000)	.253	.250	.252	0.138
.0182 N NaPMA(DP6000)	.188	.178	.183	.136
.0208 N NaPMA(DP6000)	.147	.165	.156	.133
.0125 N NaPMA(DP54)	.281	.287	.284	.117
.0125 N NaPMA(DP118)	.261	.260	.261	.135
.0125 N NaPMA(DP296)	.242	.266	.254	.141
.0125 N NaPMA(DP385)	.258	.246	.252	.142
.00058 N IBMA			.361	2.38
.00116 N IBMA			.331	1.71
.00174 N IBMA			.309	1.39
.00232 N IBMA			.300	1.12
.00290 N IBMA			.292	0.95
.025 N NaPTC	.391	.393	.392	.015
.0175 N NaPTC	.395		.395	.020

Discussion

One might suspect that the repression of the precipitation merely involved sequestration of the calcium ions by the polyions, presumably as gegenions or by chelation. Evidence for this view is found in the data on NaPMA (Table II). For NaPMA, the moles of $CaCO_3$ prevented from precipitating

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[3] R. F. Reitemeier and T. F. Buehrer, *J. Phys. Chem.*, **44**, 535 (1940).

TABLE III

ADSORPTION OF IBMA DURING PRECIPITATION OF $CaCO_3$

Solutions 0.005 mole Ca^{++}, 0.005 mole Na_2CO_2

Mg. IBMA/100 ml. soln. Initial	Final	Difference	$CaCO_3$ pptd. g./100 ml. soln.	Mg. IBMA adsorbed/g. $CaCO_3$ pptd.
2.408	1.932	0.476	0.0371	12.8
2.408	2.005	.403	....	..
4.816	4.144	.672	.0354	19.0
4.816	4.188	.628	.0346	18.2
9.632	7.95	1.682	.0307	54.8
9.632	7.88	1.752	.0313	55.9

per equivalent of polyanion was constant, 0.135. For IBMA, this quantity is much higher and is not constant. This suggests that the IBMA inhibited crystal growth to a considerable extent so that many non-filterable small crystals of $CaCO_3$ were not recovered. In addition, copolymers of maleic anhydride generally bind Ca^{++} to a greater extent than polymethacrylate.[4]

A sequestration mechanism alone cannot account for the distortion of the crystals and the large difference in the induction period that exists between the high and the low molecular weight polymethacrylates. Since the sequestering constant is the same for all the polymethacrylate samples, factors other than sequestration are involved.

The photographs of the crystals suggested that adsorption of polyanion on $CaCO_3$ may be responsible for both the marked distortion and the delayed precipitation. The increase in the amount of polymer adsorbed per gram of $CaCO_3$ precipitated (Table III) implies that the size, and hence the surface area, of the $CaCO_3$ crystals is not constant for a given concentration of Ca^{++} and $CO_3^{=}$ but is a function of the polymer concentration. It was demonstrated that the extent of adsorption of IBMA on a $CaCO_3$ powder of 0.2 μ average diameter was about 1.2 mg. of polymer per gram of $CaCO_3$ and that it was independent of polymer concentration.

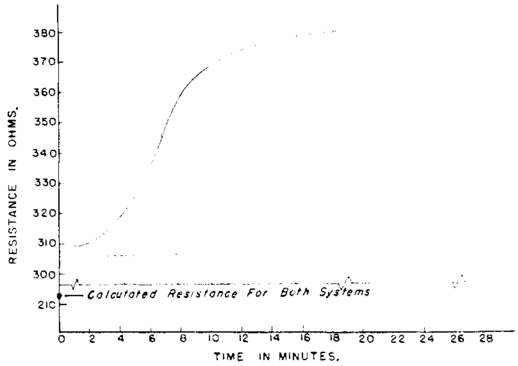

Fig. 3.—Change of resistance during precipitation of $CaCO_3$: concentration of solutions, 0.0052 M Ca^{++}, 0.0046 M Na_2CO_3; upper curve—no polymer; lower curve—0.00176 N IBMA.

It is generally agreed that the process of crystallization proceeds by two steps[5]: (1) formation of sub-microscopic nuclei or "germs" and (2) subsequent growth of the nuclei to macroscopic proportions. A few resistance measurements on the components of the Ca^{++}–$CO_3^{=}$–polyelectrolyte system provided some insight into the mechanism of the $CaCO_3$ precipitation, both in the presence and absence of polyelectrolyte. The change of resistance during precipitation is illustrated in Fig. 3. The first measurable resistance of a Ca^{++} and $CO_3^{=}$ solution is far higher than the calculated value. This indicates that the rate of formation of nuclei is very rapid. Thereafter, the measurable change of resistance is caused by the addition of ions to the nuclei to form crystals, this step being rate determining. The presence of the polyelectrolyte is manifested solely in the second stage of the precipitation process. The mechanism whereby the polyelectrolyte retards the addition of ions to the submicroscopic nuclei probably involves the adsorption of polyions on the nuclei.

The apparent increase in particle size of the $CaCO_3$ at higher polymer concentrations, as shown in the photographs, may be explained on the basis that the larger distorted particles are agglomerates of very small crystals which are bound together by the adsorption of a polymer molecule upon more than one crystal.[6] The total specific surface of these agglomerates increases with increasing polymer concentration.

The results with the low molecular weight polymethacrylates indicate that the rate of adsorption can affect the induction period. The polyanion with the lowest weight would be expected to have the highest rate of adsorption since its rate of diffusion from the bulk of the solution to the crystal would be greatest, Hence, the lowest molecular weight polymer caused the longest induction period. This view was extended by examining the effect of sodium 1,3,5-pentanetricarboxylate (NaPTC), essentially a trimer of acrylic acid, on the precipitation. This material did not prevent precipitation of $CaCO_3$ nor did it repress the rate of precipitation. Since the molecular weight of the tricarboxylate is relatively small, the degree of adsorption on $CaCO_3$ is also small.[6] The optimum molecular weight for repression of the precipitation must give a balance between low molecular weight for a rapid rate of adsorption and high molecular weight for a high extent of adsorption.

Some preliminary experiments indicated that these polyelectrolytes prevented the formation of the aragonite form of $CaCO_3$ when the precipitations were carried out at 90°.

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(4) (a) H. Morawetz, *J. Phys. Chem.* **58**, 619 (1954); (b) H. P. Gregor, *et al.*, *ibid.*, **59**, 990 (1955).

(5) H. Reiss and V. K. LaMer, *J. Chem. Phys.*, **18**, 1 (1950).

(6) R. A. Ruehrwein and D. W. Ward, *Soil Science*, **73**, 485 (1952)