Role of Polyelectrolytes in Crystallogenesis of Calcium Carbonate

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Summary: The effects anionic polyelectrolytes, having various molecular weights and repeating unit structures, on the crystallization of calcium carbonate in supersaturated solutions are studied. The induction times of the crystals grown in the presence of the polymers were optically evaluated; X-ray diffraction and Scanning Electronic Microscopy (SEM) analyses were performed to determine, respectively, their crystalline structures and morphologies. The polyelectrolyte is found to lengthen the induction time and to reduce the size of $CaCO_3$ nanocrystallites, to an extent depending on the interaction efficiency between the polymer anionic repeating units and the calcium ions. Further, depending on their sizes and their crystalline structures (calcite, vaterite) the nanocrystallites aggregate and yield final calcium carbonate particles having various sizes and morphologies. The data indicate that nanocrystals having vaterite structure, as determined by X-ray analysis, give spherical $CaCO_3$ final particles, while nanocrystals having calcite structure lead to either acicular or flower shapes of $CaCO_3$ final particles.

Keywords: crystallization; electron microscopy; filler; mineral; polyelectrolytes

Introduction

Calcium carbonate ($CaCO_3$) either natural or precipitated is widely used as mineral filler in the plastics industry. [1,2] This filler is added to the polymer matrix in order to improve the quality of the final product and to fulfil different requirements (enhanced mechanical properties, better stability, low raw material coasts). This mineral and others calcium-containing salts are also the major constituents of mollusc shells in which various forms and crystalline structures of $CaCO_3$ are observed. In these systems acidic proteins are located at the surfaces of polymeric tissues matrices and are responsible for both the nucleation and the growth of $CaCO_3$ crystals. [3] Such control exerted by the proteins during the biomineralization process is not clearly understood.

Several studies dealt with the effects of various additives (surfactants, polymers, proteins and block copolymer) on the morphology and size of $CaCO_3$ particles. [4–11] However, more investigations are still needed to elucidate the mechanisms by which such additives affect the $CaCO_3$ nanocrystals structures and their aggregation to yield various morphologies of $CaCO_3$ final particles. Thus, the aim of the present work is to throw light on the mechanism by which polyelectrolytes affect the crystalline structure, the size and the shape of $CaCO_3$ particles.

Experimental

The anionic polyelectrolytes used in the present work are: sodium polystyrene sulfonate, PSS, $M_w = 1.0\ 10^6$ g mol^{-1}, sodium polyacrylate, PAA, $M_w = 2.1\ 10^3$ g mol^{-1}, sodium polyvinyl sulfonate, PVSA, $M_w = 30–60\ 10^3$ g mol^{-1} and sodium poly (maleic acid-co-olefin), PMACO,

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$M_w = 12.0\ 10^3$ g mol^{-1}. All the polyelectrolytes were purchased from Aldrich and used as received without further purification. The sodium carbonate anhydrous (Na_2CO_3), and the calcium nitrate tetrahydrate Ca $(NO_3)_2$ $4H_2O$, were purchased, respectively, from Fluka Chemie AG, and from Prolabo.

Supersaturated solutions for crystal growth experiments were prepared, at ambient temperature, by addition of sodium carbonate (Na_2CO_3) to calcium nitrate (Ca $(NO_3)_2$ $4H_2O$) solutions in a water-jacketed Pyrex glass vessel of 300-ml capacity. [7] Prior the beginning of the precipitation, the polymer aqueous solution were first added to calcium nitrate solution, and the mixtures were stirred for about few minutes prior the addition of sodium carbonate solution. The final polyelectrolyte concentration varied in the range 0.9–1.42 g/l. It should be emphasized that prior the $CaCO_3$ precipitation takes place, the PSS-calcium mixtures at the equilibrium, form homogenous solutions. At the end of the precipitation, $CaCO_3$ crystals were recovered by filtration and the dried particles were gold coated in vacuum and examined by Scanning Electron Microscope (SEM).

In order to determine the kinetic of $CaCO_3$ crystal growth, the time dependence of the turbidity during the precipitation reaction of $CaCO_3$ particles were measured in the absence and the presence of various polyelectrolytes. Such measurements were made at 25 °C by using a spectrofluorimeter Shimadzu RF-5001 PC, operating at the same emission and excitation wavelength $\lambda = 500$ nm.

Results and Discussions

Modification of Induction Time by the Polyelectrolyte

The measurements of the turbidity versus time during the precipitation reaction of $CaCO_3$ particles in the absence or in the presence of various polyelectrolytes give sigmoidal curves, in all instances, and an example is shown for the precipitation of $CaCO_3$ in the presence of PSS, at polyelectrolyte concentration, $C_{PSS} = 1.42$ g/l, (Figure 1). From the intercept of the tangent at the inflection point with the time axis, the induction time, τ, i.e. the period of time preceding the crystal growth, was determined (Figure 1). In the following the sursaturation ratio, S/S_0, will be considered, where S is the actual ionic product of the solution, $S = [Ca_2^+]\ [CO_3^{2-}]$ and S_0 is the solubility product of calcium carbonate. At temperature T = 25 °C, for vaterite and calcite $CaCO_3$ polymorphs, S_0 is equal to, respectively, $1.22\ 10^{-8}$ and $3.32\ 10^{-9}$ mol^2 l^{-2}.

In the absence of any additives the measured induction time, τ_0, is 40 seconds for $CaCO_3$ calcite precipitation at T = 25 °C, and at ionic product $S = 2.016\ 10^{-6}$ mol^2 l^{-2}, ($S/S_0 = 607$).

However, at the same value of $S = 2.016\ 10^{-6}$ mol^2 l^{-2}, ($S/S_0 = 165$), and in the presence of PSS ($C_{PSS} = 1.42$ g/l), the measured induction time, $\tau = 5524$ seconds indicates retarding effect of the polymer on the precipitation of the mineral. Such retarding effect results from the complexation between the calcium ions and the negatively charged sulfonate spaced groups of PSS leading hence to reduction of the available calcium ions in the crystallization medium. In all instances, the logarithm plot of the induction time, τ, versus the

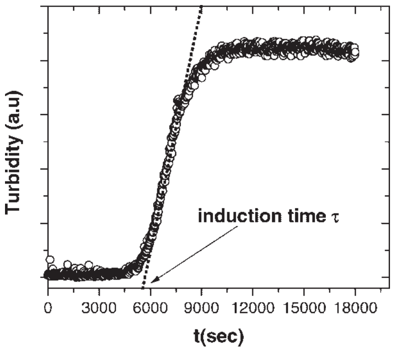

Figure 1.
Measurement of the induction time of the $CaCO_3$ particles prepared in the presence of PSS, $C_{PSS} = 1.42$ g/l, $[Ca^{2+}] = [CO_3^{2-}] = 0.00142$ M.

sursaturation ratio, S/S_0, is straight line (Figure 2) and shows, as expected, a decrease of the induction with the increase of S/S_0. The data indicate that the induction time is lengthened in the presence of the polyelectrolytes. Hence by extrapolating all the linear curves to low values of S/S_0 ratio (Figure 2), the induction time τ decreases in the order: $\tau_{PAA} > \tau_{PMACO} > \tau_{PVSA} > \tau_{PSS} > \tau_0$.

These variations of the induction time result from the complexation between the anionic polyelectrolyte groups (sulfonate, acrylate, maleic acid) and the calcium ions. Such complexation leads to the reduction of the mutual repulsion between the polyelectrolyte segments [12,13] and its efficiency decreases in the order: PAA > PMACO > PVSA > PSS.

Modification of the Crystal Size, Morphology and Structure by the Polyelectrolyte

It should be emphasized that the crystallization of $CaCO_3$ from supersaturated solution and in the absence of any additives gives birth to agglomerate of primary particles having rhombohedral morphology and size of few microns. The SEM micrograph of the $CaCO_3$ particles prepared in the presence of PSS ($C_{PSS} = 1.42$ g/l), (Figure 3) or in the presence of PVSA ($C_{PVSA} = 1.00$ g/l), (Figure 4), shows homogenous spherical $CaCO_3$ particles having mostly vaterite crystalline structures. The mean sizes of $CaCO_3$ particles obtained in the presence of PSS and PVSA are equal to, respectively, 2 and 0.7 μm. The smaller particle size obtained in the presence of PVSA as compared to PSS results from the more efficient complexation of calcium ions by the PVSA anionic groups.

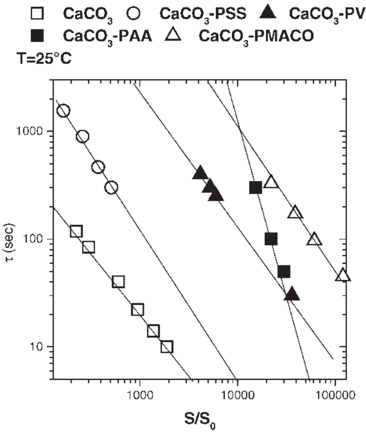

Figure 2.
Variation of the induction time τ, with the sursaturation, S/S_0.

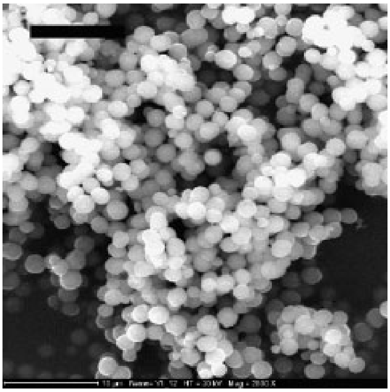

Figure 3.
SEM micrograph of $CaCO_3$ particles prepared in the presence of PSS. Scale bar = 10 microns.

The SEM micrographs (Figure 5) and (Figure 6) of the $CaCO_3$ particles prepared in the presence of PAA ($C_{PAA} = 0.14$ g/l) and PMACO ($C_{PMACO} = 0.90$ g/l) show $CaCO_3$ particles having, respectively, flowers and acicular shapes Such crystals have mostly calcite

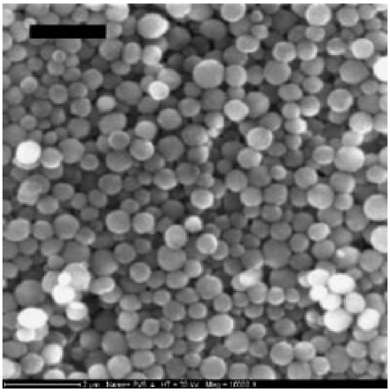

Figure 4.
SEM micrograph of $CaCO_3$ particles prepared in the presence of PVSA. Scale bar = 2 microns.

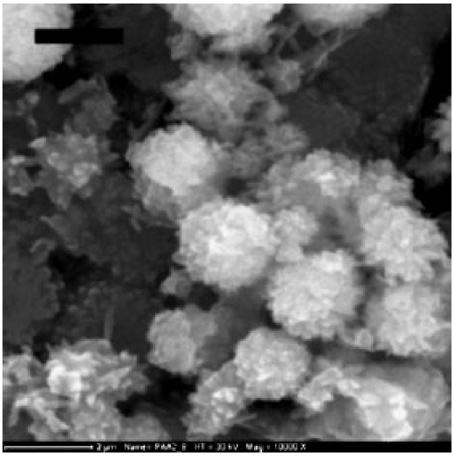

Figure 5.
SEM micrograph of $CaCO_3$ particles prepared in the presence of PAA. Scale bar = 2 microns.

structures (>90%) as determined by X-ray analysis, and the final $CaCO_3$ particle consists of aggregated rhombohedral nanocrystallites.

It should be emphasised that the $CaCO_3$ mineral exists in various polymorph phases [14] that are, in order of decreasing solubility: calcium carbonate hexahydrate, calcium carbonate monohydrate, vaterite, aragonite and calcite.

The first two polymorphs are unstable and are converted into the thermodynamically most stable calcite. [15,16] Further, the vaterite $CaCO_3$ particles can be formed without any additives. This phase is also unstable but it is first formed in the precipitation medium under spontaneous conditions and converts rapidly, in the absence of additives, into calcite. [7] However, the vaterite phase may be stabilized in the presence of additives, as shown in the present study, the PSS and PVSA polyelectrolytes stabilize the vaterite $CaCO_3$ polymorph. It should be recalled that with these two additives the interactions of calcium ions with the anionic groups of the polymers were found to be less efficient as compared to the PAA and PMACO polymers. Two main mechanisms are involved when dealing with the $CaCO_3$ crystallization in the presence of polyelectrolytes. The first one occurs at earlier precipitation stages (nucleation) and involves calcium exchange and/or calcium complexation with the anionic groups of the polyelectrolyte. The polyelectrolyte in this earlier precipitation satges lengthens the induction time and controls the unit cell structure of the nanocrystallites. The second mechanism explaining the shape and the size modifications of the final $CaCO_3$ particle involves preferential adsorption of polyelectrolyte on the nanocrystal surfaces during the growing process. The role of the polyelectrolyte in this process is to stabilize the crystal planes having high surface energies. Such crystal planes due to their large growth rates will disappear and will not be expressed in the nanocrystal equilibrium morphology, in the absence of any additives. However, they will appear in the equilibrium nanocrystal morphology, in the presence of the polyelectrolyte, owing to the surface energy reduction by the adsorbed polymer.

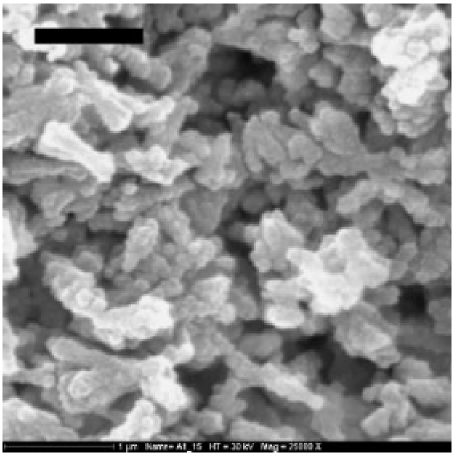

Figure 6.
SEM micrograph of $CaCO_3$ particles prepared in the presence of PMACO. Scale bar = 1 micron.

The adsorption process of polyelectrolyte on the $CaCO_3$ nanocrystal involves mainly electrostatic interaction and leads to surface charge compensation and size reduction of the crystal. The resulting nanocrystals are then less charged and aggregate in the aqueous medium to yield the final $CaCO_3$ particle. Finally, the aggregation of nanocrystals that leads to various shapes of the final $CaCO_3$ particles is function of their sizes and surface charges, which are in turn under control of the polyelectrolyte present in the crystallization medium.

Conclusion

The crystallization of calcium carbonate ($CaCO_3$) from supersaturated solutions and in the presence of various anionic polyelectrolytes was studied. The nucleation, the growth, the shape and the size of the final $CaCO_3$ particle are function of the polyelectrolyte structure used in the crystallization medium. Moreover, the crystalline structures of the $CaCO_3$ crystal, calcite, vaterite or the calcite-vaterite mixture are also dependent on the concentration and the nature of the polyelectrolyte. Such various $CaCO_3$ particle sizes, morphologies and crystalline structures are related to the efficiency of interaction that occurs between the polyelectrolyte surface groups and the calcium ions, during the nucleation and the crystal growth processes. The Final $CaCO_3$ particle results from aggregation of less surface charged nanocrystallites. The mechanisms by which the polymer affects the $CaCO_3$ morphogenesis involve ion exchange of the polyelectrolyte counterions and/or ion complexation between the macromolecule units and the crystal lattice calcium ions. In addition during the crystal growth, preferential adsorption of the polyelectrolytes takes place, which tend to reduce the crystal size.

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