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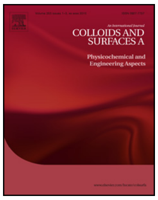

The effect of a novel polyolefine based amphiphilic copolymer on the mineralization of calcium carbonate

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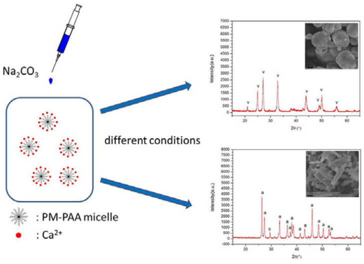
HIGHLIGHTS

- Pure spherical vaterite and rod-like aragonite can be easily obtained in the presence of PM-b-PAA.
- The mineralization temperature has the most direct influence on $CaCO_3$ mineralization.
- The increase of PM-b-PAA concentration can cause the product aggregate.
- The role of PM-b-PAA is more evident when the ratio of hydrophilic chain segment (PAA block) is larger.
- Higher pH can make the role of PM-b-PAA weaker and contribute to the formation of aragonite.

GRAPHICAL ABSTRACT



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ABSTRACT

The mineralization of calcium carbonate ($CaCO_3$) in the solution of amphiphilic block copolymers (ABCPs), polymethylene-b-poly(acrylic acid) (PM-b-PAA), is studied. Uniform vaterite and aragonite were obtained under certain conditions in the presence of PM-b-PAA. The influence of some important variables relating the mineralization including pH, the ABCPs concentration, the ratio of hydrophilic to hydrophobic chain segment of the ABCPs as well as the temperature on the crystal type and morphology of the resultant $CaCO_3$ particles has been investigated in detail. Dynamic light scattering (DLS), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermo gravimetric analyzer (TGA) were utilized to get more direct insights to the micellization behavior of PM-b-PAA and the mineralization of calcium carbonate. As all mineral proteins are generally amphiphilic, this study can enlarge our understanding of the biomineralization process and help to prepare functional materials for various applications.

1. Introduction

Biomineralization is a process by which living organisms produce inorganic minerals to meet their own needs in the form of skeletons, shells, teeth etc [1]. It is usually controlled by organic matrices consisting of water-soluble organic molecules and a water-insoluble biopolymer that regulate the crystal nucleation, morphology and crystal structure of the mineral [2–4]. $CaCO_3$ is one of the most abundant inorganic minerals in nature and has been found lots of important applications in industry, such as paints, papermaking, plastics, rubbers, and so on [5–7]. $CaCO_3$ has three anhydrous crystalline polymorphs: calcite, aragonite and vaterite. Among these three polymorphs, calcite is thermodynamically the most stable form while vaterite is the least stable [8,9]. The three polymorphs can exhibit different physicochemical properties because of their specific crystal structures [8],

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and hence it is significant to control the polymorph of $CaCO_3$ in biomineralization.

In recent years, biomimetic synthesis of $CaCO_3$ crystals in the presence of organic templates and/or additives, such as Langmuir monolayers [10–12], self-assembled monolayers [12,13], metal ions [2,14,15], biomacromolecules [16,17] and polymers [18–24], has been wildly investigated. Recent studies have shown that crystals are formed through a process of mesoscopic transformation including self-assembly or transformation of metastable or amorphous precursor particles, which is called non-classical crystallization by researchers [9,25]. These mesoscale processes are highly sensitive to a polymer additive in a variety of ways [25]. The role of additives, which modify crystal growth, is generally restricted in such a view: they can either bind ions or interact with the crystal, but it is still hard to attributed [26]. Among these researches about additives controlling mineralization, the research of using amphiphilic block copolymers (ABCPs) to regulate $CaCO_3$ mineralization is relatively less [27]. Amphiphilic block copolymers contain both hydrophilic and hydrophobic polymer chains. When dissolved in water, which is good solvent for one block and poor for another, the hydrophobic segments tend to segregate into a compact core to minimize the system energy and make the copolymer self-assemble into a variety of nano-sized, three-dimensional arrays (micelle) depending on the conditions [7,28], and this scenario can provide a suitable environment for the controlled nanoscale synthesis of biominerals [27]. As far as we know, all mineral proteins are generally amphiphilic [27]. The use of amphiphilic polymers as templates or additives to control the nucleation, growth, and alignment of inorganic particles is thus demonstrated to be a promising strategy [9]. Cölfen et al. [9] obtained triangle single crystalline calcite consisting of a large number of elongated calcite particles with well-defined faces and edges and the (001) faces of calcite were exposed in the presence of amphiphilic poly(styrene-alt-maleic acid) (PS-MA). Yue et al. [7] prepared porous calcium carbonate spheres with calcite structure using the amphiphilic PS–PAA. Yu and Cölfen et. al [29] developed a novel strategy to direct solution growth of hollow superstructures of $CaCO_3$ on the basis of controlled self-assembly and polymer concentration gradients using a double-hydrophilic block copolymer with a hydrophobic modification as a directing agent. Collectively, researches about mineralization using amphiphilic polymers as a mediator can not only enrich the understanding of the biomineralization process but also help to prepare functional materials for various applications.

To the best of authors' knowledge, the synthesis of polyolefin-b-PAA diblock copolymers is rarely reported [30] and its application to the area of mineralization has not been reported yet. In this study, we choose a kind of water soluble amphiphilic block copolymers (ABCPs), polymethylene-b-poly(acrylic acid) (PM-b-PAA), as a template to mediate the mineralization of $CaCO_3$. To our delight, pure spherical vaterite can be easily obtained in the presence of this copolymer (PM-b-PAA) while pure rod-like aragonite can also be prepared by changing the mineralization conditions. Obtaining both pure vaterite and aragonite using one same ABCP is rarely reported, although there are lots of reports about obtaining solely aragonite [31–34]/vaterite [24,35,36] or mixture of the two [27,31] in the presence of some additives. Meanwhile, the effects of pH, the ratio of hydrophilic to hydrophobic chain segment of the ABCPs, the concentration of ABCPs and temperature on the mineralization process are systematic investigated.

2. Experimental

2.1. Materials

Amphiphilic block copolymers (ABCPs), polymethylene-b-poly(acrylic acid) (PM_{214}-b-PAA_{81}, PDI: 1.09, marked ABCP A; PM_{93}-b-PAA_{94}, PDI: 1.10, marked ABCP B), were kindly supplied from Prof. Zhi Ma, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The detail about its synthesis could be found elsewhere [30]. Anhydrous calcium chloride ($CaCl_2$), anhydrous sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing and used as received.

2.2. Mineralization

The mineralization of $CaCO_3$ was carried out in glass jars with volume 50 mL. Firstly, a predetermined amount of ABCPs were dissolved in 15 mL of deionized water to prepare ABCPs homogeneous solution. Secondly, 0.12 g anhydrous $CaCl_2$ was added into the ABCPs solution and fully dissolved by ultrasonic processing and stirring. Then the solution was adjusted to a desired pH with small amount of HCl (2.5 mol/L and 0.1 mol/L) and NaOH solution (2.5 mol/L and 0.1 mol/L). The pH-adjusted solution was then kept under static conditions for 24 h at a certain temperature (25 °C, 50 °C and 80 °C) to make it stable and the interaction between Ca^{2+} and ABCPs more sufficiently. Subsequently, 1 mL Na_2CO_3 solution (the mole amount of Na_2CO_3 is the same as $CaCl_2$ previous used) was add into the polymer solution dropwise slowly under vigorous stirring and then kept the stirring 10 min. After that we kept the solution at a certain temperature (the same as the previous temperature) for 24 h to make the product further aged. Finally, the products were washed and separated by centrifugation (800 rpm) for several times. The obtained $CaCO_3$ precipitates were dried in vacuum at room temperature. In the experiments, the starting pH value was adjusted to 6, 9 and 11 on pH meter (PB-10, Sartorius). The concentration of ABCPs was prepared at 0.5 mg/mL, 1 mg/mL, 2 mg/mL and 3 mg/mL. As control experiments, the solution without ABCPs and the solution without being pH adjusted were also used in the experiments, with all the other conditions being kept the same.

2.3. Characterization

X-ray powder diffraction (XRD) data were collected on MSAL-XD2 with Cu Kα radiation ($\lambda = 0.1542$ nm) at 36 kV and 20 mA. Scanning electron microscopy (SEM) testing was carried on a field emission SEM (Hitachi S-4800) at an accelerating voltage of 10 kV. Thermo gravimetric analyzer (TGA) curves were determined by SDT-Q600 analyzer (TA Corp. US) at a heating rate of 10 °C/min in N_2 atmosphere. FTIR spectra were recorded on PerkinElmer 2000 FTIR spectrometer in transmission mode by using KBr pellets. Transmission electron microscope (TEM) analysis was performed on a HITACHI H-7650 electron microscope operated at 80 kV, the samples were transferred to copper grids with carbon film and dried in air followed by being dyed with 2% phosphotungstic acid before observation. Dynamic light scattering (DLS) results were obtained from Delsa^{TM}Nano Submicron Particle Size and Zeta Potential Analyzer (Beckman Coulter, US) with the average value of three times.

3. Results and discussion

3.1. Micellization behavior of PM-b-PAA in different concentrations

Initially the micellization behavior of the two copolymers (ABCP A and ABCP B) was investigated using TEM and DLS. Fig. 1 displays the TEM images of micelles formed by the ABCP A and ABCP B in different concentrations at pH 9. We can see that the morphology of ABCP A micelles is rod while the ABCP B micelles are spherical, the different morphology of the two ABCPs may be attributed to the different ratio of hydrophilic chain. In the ABCP A solution, the hydrophilic chain is so short that it is difficult to form spherical