



Research papers

Impurities in pluronic triblock copolymers can induce the formation of calcite mesocrystals

Anna S. Schenk, Yi-Yeoun Kim, Alex N. Kulak, Fiona C. Meldrum*

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

ARTICLE INFO

Article history:

Received 22 June 2011

Received in revised form 6 December 2011

Accepted 8 December 2011

Available online 16 December 2011

Editor: U. Brand

Keywords:

Calcite

Mesocrystal

Calcium carbonate

Block copolymer

ABSTRACT

An interesting recent report by Zhou et al. (Chemical Geology, 2010, 279, 63–74) describes the formation of calcite mesocrystals with very well-defined, prismatic morphologies in the presence of F-68, a pluronic triblock copolymer. That this can be achieved with a polymer which is a linear, nonionic polyoxyethylene-polyoxypropylene runs counter to the current understanding that face-selective adsorption of a polymer on the precursor mineral building blocks is required for mesocrystal formation. In this paper we contrast the effect of analytical grade F-68 and the same polymer after purification by dialysis, and show that a strong morphological effect on calcite precipitation is only achieved with the analytical grade polymer. We therefore suggest that low molecular weight impurities present within analytical grade F-68 may have been responsible for the formation of CaCO_3 mesocrystals rather than the F-68 macromolecules themselves.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Non-classical crystallisation mechanisms, where crystals grow by the transformation of amorphous precursor phases (Addadi et al., 2003) or through the aggregation of precursor units (Song and Colfen, 2010; Yuwono et al., 2010), are currently receiving considerable interest. These processes operate in many systems, and in aqueous solution at least, they may ultimately prove to be the norm rather than the exception. Focussing specifically on aggregation-based crystal growth, a large number of crystals are now known to grow by this mechanism (Song and Colfen, 2010). While the earliest examples demonstrated the formation of single crystals through the oriented aggregation of precursor crystallites in the absence of additives (Penn and Banfield, 1998; Penn and Banfield, 1999), it is now recognised that soluble additives can also assist in this process and that crystallographic continuity can sometimes be achieved via mineral bridges between the separate crystallite units (Oaki et al., 2006; Song and Colfen, 2011). Where the final crystal product retains a memory of the precursor particles from which it forms, it is termed a “mesocrystal” or “mesoscopically-structured crystal” (Cölfen and Antonietti, 2008).

Calcium carbonate mesocrystals, in particular, have received considerable attention, in part due to their potential relevance to biomineralisation processes (Song et al., 2009). Indeed, a number of studies of CaCO_3 biominerals such as sponge spicules (Sethmann and

Worheide, 2008), coral (Vielzeuf et al., 2010) and sea urchin spines (Oaki and Imai, 2006) have suggested that they may comprise a nanoparticulate ultrastructure, and therefore that they may be mesocrystals. CaCO_3 mesocrystals form in the presence of organic additives which direct their growth and control their final structure. The intracrystalline macromolecules isolated from CaCO_3 biominerals are characteristically highly acidic (Gotliv et al., 2005; Evans, 2008), and the available literature demonstrates that the synthetic additives which are most effective in controlling calcium carbonate precipitation are also negatively charged (Meldrum and Colfen, 2008). This is further reflected in the fact the synthetic CaCO_3 mesocrystals have been formed in the presence of highly charged polyelectrolytes and copolymers such as poly(styrene sulphonate) (Wang et al., 2005) and styrene-*alt*-maleic acid (Xu et al., 2008). It was therefore with great interest that we noted a recent article which reported the formation of calcite mesocrystals in the presence of a pluronic triblock copolymer (Zhou et al., 2010). As a non-ionic species this polymer would not be expected to have such a significant effect on CaCO_3 precipitation (Robinson et al., 2002). In this article we further investigate this result, and suggest that the effect attributed to the pluronic triblock copolymers may actually have been due to impurities present with this commercial polymer sample.

2. Experimental methods

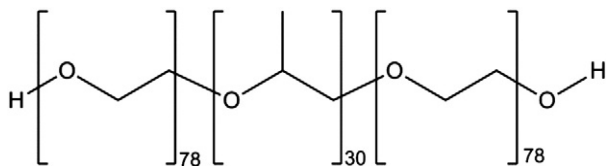
2.1. Materials

All chemicals employed were commercially available and were purchased from the specified suppliers: $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich),

* Corresponding author.

E-mail address: F.Meldrum@leeds.ac.uk (F.C. Meldrum).

Pluronic F-68 ($M_w = 8350$ g/mol; Sigma-Aldrich), $(\text{NH}_4)_2\text{CO}_3$ (Sigma-Aldrich) and H_2SO_4 (95–97%; Sigma Aldrich). The chemical structure of the polymer is shown below. All reactant solutions were prepared from deionised Millipore water.



2.2. Purification of the polymer

In order to purify the polymer additive, an aqueous solution of F-68 was dialysed against Millipore DI water (MWCO: 3500 Da). Dialysis was carried out for 4 days and the surrounding water was exchanged twice-daily. After purification, the polymer was isolated as a solid by freeze-drying.

2.3. Characterisation of the polymer

Structural information about the polymer additives before and after dialysis was obtained by infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopy. IR was carried out using a Perkin Elmer ATR-IR instrument, while proton NMR spectra were recorded of the polymer dissolved in D_2O on a Varian Inova 500 MHz instrument, at 20 °C.

2.4. Precipitation and characterisation of calcium carbonate crystals

Calcium carbonate was precipitated using the ammonium carbonate diffusion technique. Reactant solutions containing $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (10 mM) and either purified or non-purified F-68 at concentrations of 2.5 mM–5 mM were prepared by vigorous mixing, and 10 mL was then transferred to Petri dishes. Glass cover slides acting as substrates for the mineral precipitation were cleaned by immersion in Piranha solution (75 vol% H_2SO_4 and 25 vol% H_2O_2) and were placed at the base of the Petri dishes. These were subsequently covered with Parafilm (punched with 5 needle holes) before being placed in sealed desiccators along with two Petri dishes, each containing 3 g of crushed ammonium carbonate. These were also covered with Parafilm which was pierced with 5 needle holes. In keeping with the experiments performed by Zhou et al., a bottle filled with 100 mL sulphuric acid was also inserted in the desiccator to allow the partial absorption of NH_3 vapour. After a crystallisation time of 7 days, the glass slides were removed from the solution and were washed first with Millipore DI water and then ethanol. The crystals were then characterised by light microscopy and scanning electron microscopy (SEM) where samples for SEM were coated with a Pt/Pd alloy and were then examined using a Jeol Neoscope, JCM-5000. Polymorph identification was carried out by Raman Microscopy, using a Renishaw inVia Raman microscope operating with a 785 nm laser.

3. Results

In common with the observations of Zhou et al. (2010), calcium carbonate particles precipitated in the presence of 2.5 mM non-purified polymer were calcite (as confirmed using Raman microscopy) and showed significant deviation from the equilibrium rhombohedral form of pure calcite. The crystals were elongated, showed highly roughened surfaces, and were typically capped by {104} faces (Fig. 1a). Examination of the crystals using scanning electron microscopy (SEM) showed their morphologies more clearly (Fig. 1b).

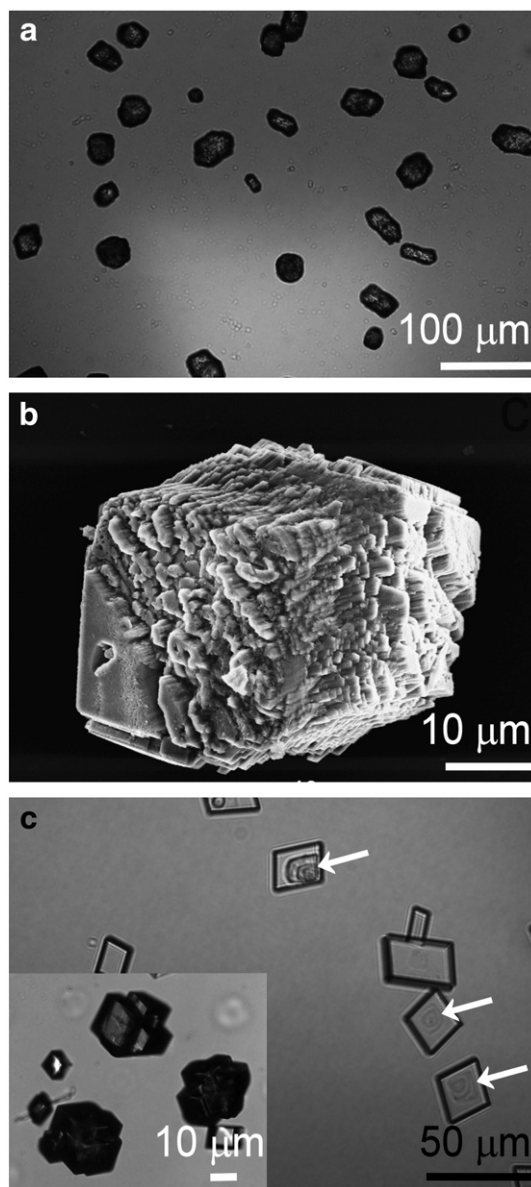


Fig. 1. (a and b) Calcite crystals precipitated in the presence of non-purified F-68 polymer at $[\text{Ca}^{2+}] = 10$ mM and $[\text{F-68}] = 2.5$ mM, where (a) shows an optical micrograph and (b) an SEM image of a typical crystal. (c) An optical micrograph of rhombohedral calcite crystals obtained from a 10 mM Ca^{2+} and 2.5 mM F-68 solution, where the polymer had been purified by dialysis prior to use. Hopper-type crystals exhibiting cavities in the centre are indicated by white arrows. The inset shows crystals precipitated under the same conditions but with an elevated concentration of the purified polymer additive of $[\text{F-68}] = 5$ mM.

Calcium carbonate was also precipitated in the presence of 2.5 mM F-68 polymer which had been prior-purified using dialysis. This was the highest polymer concentration employed by Zhou et al. in their study (Zhou et al., 2010). In this case, only rhombohedral calcite particles, defined by smooth {104}-type surfaces, were obtained (Fig. 1c). Some of the particles showed cavities in their centres (indicated by white arrows), which is characteristic of hopper crystals (Kim et al., 2009). The effect of raising the polymer concentration yet further to 5 mM was also investigated, but again no elongated crystals were obtained. As shown in the inset in Fig. 1c, only inter-grown rhombohedra were produced at these solution concentrations.

The polymer itself was also characterised before and after purification to confirm that the pluronic was retained after purification and to attempt to identify the presence of possible impurities. IR spectroscopy

Download English Version:

<https://daneshyari.com/en/article/4699517>

Download Persian Version:

<https://daneshyari.com/article/4699517>

[Daneshyari.com](https://daneshyari.com)