Effect of Polyethylene Glycol on Phase and Morphology of Calcium Carbonate

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ABSTRACT: Calcium carbonate ($CaCO_3$) with different phases and morphologies were prepared and characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. The effect of polyethylene glycol (PEG) with different molecular weight and concentrations on the phase and morphology of $CaCO_3$ was studied. The results showed that aragonite was the only phase in the solution without PEG, while calcite phase could be obtained by the use of PEG as the additive. The possible crystallization mechanism for the formation of $CaCO_3$ polymorphs in the presence of different PEG was also discussed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 319–324, 2011

Key words: crystallization; templates; growth

INTRODUCTION

$CaCO_3$ is widely used in various fields as additives to plastics, medical supply, papers, paints, the adhesives, and the rubbers. Besides, it involved in many industrial processes as pigment, brightener filler, adsorbent, etc.[1–3] There are three polymorphs for $CaCO_3$ crystals: calcite, aragonite, and vaterite. They have the crystal system of rhombohedral, orthorhombic, and hexagonal, respectively. At standard atmospheric pressure and room temperature, calcite is the thermodynamic stable phase, aragonite is a metastable phase and vaterite is an unstable phase.[4–8]

The control of crystal polymorphs is of fundamental importance because the morphology and physicochemical properties depend on each polymorphous crystal. Recently, the nucleation and crystal growth of $CaCO_3$ have been extensively investigated. Different polymorphs of $CaCO_3$ have been synthesized in the presence of different templating agents, such as metal ions,[9–12] polyacrylamide,[13–15] cetyltrimethyl ammonium bromide,[14] amino acid,[16] polypropylene acid,[17] sodium dodecyl benzene sulfonate,[18] polyvinyl alcohol,[19] proteins,[20] cellulose,[21] and polyethylene glycol (PEG),[22–24] to effectively control the crystal growth of $CaCO_3$. Among various templates, PEG is of particular interest due to the following reasons. First, PEG is an inexpensive, innocuous, nonvolatile nonionic surfactant and it has excellent water-solubility, lubricating property, and high stability at room temperature. Second, PEG has a wide molecular weight distribution and different chain length. The different polymer chain with diverse framework could provide a new kind of organization to metal atoms along the polymer backbone, which could afford different assemblage ways for the final products. Furthermore, PEG is a polymer containing hydrophilic groups (i.e., ─OH and ─O─). It can act as a donor to metal ions to form metal complexes with diverse conformations, which makes it possible to control the morphology of the crystals.[25]

Although PEG is an attractive polymer, the influence of PEG on phase and morphology of $CaCO_3$ crystal has not been widely studied. Wang et al. studied the influence of PEG on $CaCO_3$ crystal, however, they only prepared aragonite whiskers by using PEG 20,000 with a sort of concentration.[26] Compared with their work, both calcite and aragonite of $CaCO_3$ were synthesized in this article by using PEG with different molecular weight and concentrations. The effect of molecular weight and concentration of PEG on phase and morphology of $CaCO_3$ was investigated. Furthermore, the possible crystallization mechanism for the formation of different $CaCO_3$ polymorphs was proposed.

EXPERIMENTAL

Preparation

$CaCl_2$, Na_2CO_3, PEG400, and PEG4000 were purchased from Kelong Reagents Company of Chengdu, PEG10000 were purchased from Shanghai Reagents Company. All of the reagents were of analytical

grade and were used without further purification. Deionized water was used throughout.

In a typical synthetic procedure 80 mL of $CaCl_2$ and PEG mixed aqueous solution was put into a 250-mL flask, thereinto, the concentration of $CaCl_2$ is 0.05 mol L^{-1}, PEG is 0.002, 0.005, and 0.01 mol L^{-1}, respectively. Then the mixed solution was heated from 25 to 80 °C and then 80 mL of Na_2CO_3 (0.05 mol L^{-1}) solution was dropped into the mixed solution with the rate of about 1 mL min^{-1}. The resulting mixture was stirred for about 3 h with a paddle-type impeller at a constant rate of 300 rpm. After cooling to room temperature, the obtained precipitate was filtered off, washed with deionized water and dried in infrared drying oven.

Characterization

Powder XRD data were collected on a Rigaku D/MAX-rA Diffractometer with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 100 mA. The grain morphologies and particle sizes of samples were examined on a Philips Inspect F scanning electron microscope at an accelerating voltage of 10 kV or Hitachi S-450 scanning electron microscope at an accelerating voltage of 20 kV. All the surfaces of the samples were dried and sputter coated with gold prior to examination. The FTIR spectra (KBr pellets) were recorded by a Nicolet 170SX spectrometer.

RESULTS AND DISCUSSION

Influence of different molecular weight of PEG

Figure 1 shows the XRD patterns of different $CaCO_3$ crystals obtained in the presence of different PEG. All the diffraction peaks in Figure 1(a, c) are in accordance with the standard JCPDS file (aragonite, 05-0453) and JCPDS file (calcite, 83-0578), respectively, indicating that the two samples in Figure 1(a, c) are pure aragonite and calcite phase, respectively. However, the samples in Figure 1(b,d) are the mixture of aragonite and calcite phase.

To further confirm the phases of as-prepared $CaCO_3$ crystals, SEM was carried out to examine their morphologies(Fig. 2). It is well known that needle-like $CaCO_3$ is the typical morphology of aragonite and rhombohedral $CaCO_3$ is the typical morphology of calcite. As expected, the SEM micrographs of the obtained $CaCO_3$ crystals contains needle-like crystals in Figure 2(a), rhombohedral shape crystals in Figure 2(c), and both kinds of crystals in Figure 2(b) and Figure 2(d). These results are in well accordance with those of XRD.

Figure 3 shows FTIR spectra of the obtained products. The vibration bands in the range of 1628–1644 cm^{-1} and 1419–1498 cm^{-1} can be assigned to the
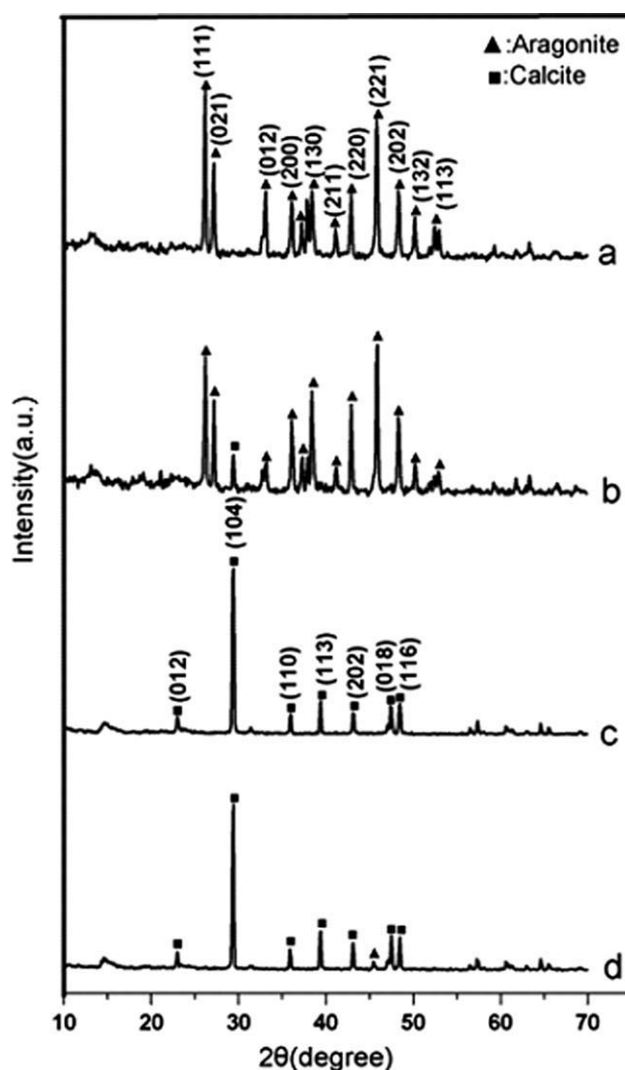
Figure 1 XRD images of CaCO3 crystals obtained in solutions with different molecular weight of PEG (a) without PEG; (b) with 0.01 mol L^{-1} PEG400; (c) with 0.01 mol L^{-1} PEG4000; (d) with 0.01 mol L^{-1} PEG10000.

stretching vibration of carbonyl group and carbonate group, respectively. Vibration bands at 1079 and 854 cm^{-1} can be assigned to the characteristic symmetric carbonate stretching (v_1 mode) and a carbonate out-of-plane bending (v_2 mode) vibrations of aragonite, respectively. At the same time, vibration band at 875 cm^{-1} can be assigned to the v_2 mode of calcite, while vibration bands at 710 and 711 cm^{-1} can be assigned to the v_4 modes of calcite.[18] It should be noted here that the absorption peaks of calcite can not be observed clearly in Figure 3(b), which can be explained by the fact that calcite is a minor phase in the product, as shown in Figure 2(b).

Influence of the concentrations of PEG

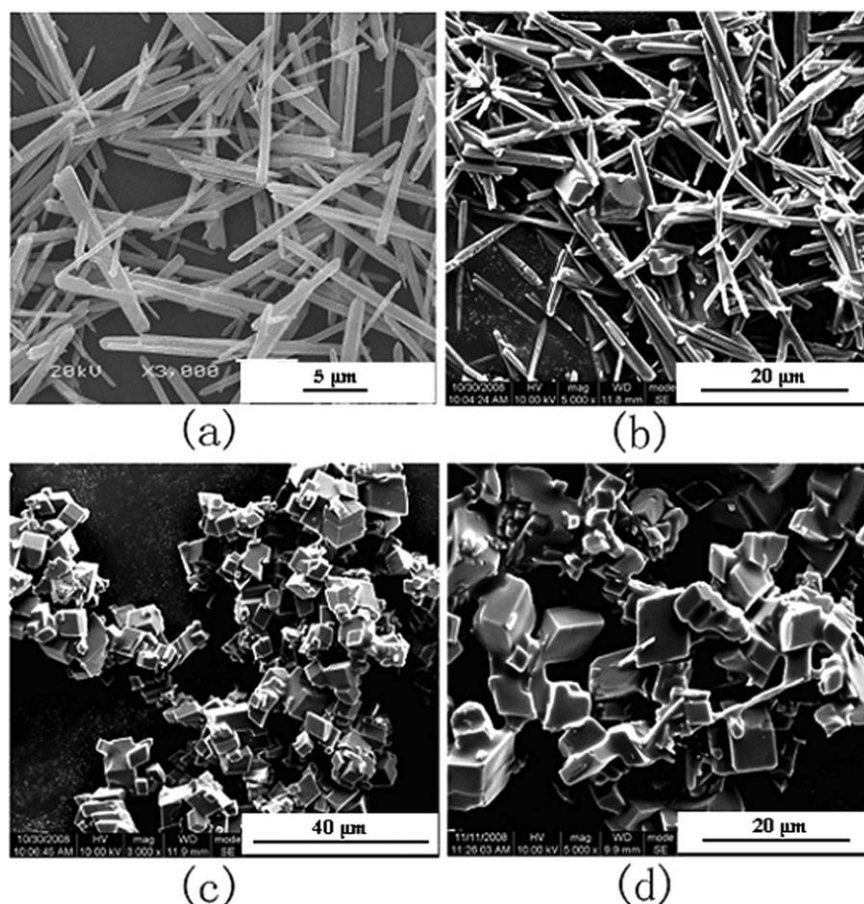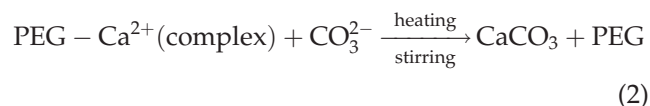Figure 4 shows the XRD patterns of the obtained $CaCO_3$ samples prepared by the use of PEG400,

Figure 2 SEM images of CaCO3 crystals obtained in solutions with different molecular weight of PEG (a) without PEG; (b) with 0.01 mol L^{-1} PEG400; (c) with 0.01 mol L^{-1} PEG4000; (d) with 0.01 mol L^{-1} PEG10000.

PEG4000, and PEG10000, respectively. As can be seen, only aragonite appears in 0.002 and 0.005 mol L^{-1} PEG400 solutions and only calcite appears in PEG4000 solution. Both aragonite and calcite appear in PEG10000 and 0.01 mol L^{-1} PEG400 solutions. Furthermore, calcite somewhat increases with the increase of PEG400 and PEG10000 concentration. The influence of PEG4000 concentration on the formation of CaCO$_3$ crystal is unobvious under the experimental conditions. The influence of PEG molecular weight and concentration on phase of CaCO$_3$ crystal is summarized in Table. I.

Figure 5 shows the corresponding SEM micrographs of the CaCO$_3$ crystals. It is shown that only calcite appears in PEG4000 solution, both calcite and aragonite can be obtained in PEG400 and PEG10000 solutions and calcite increases a bit with the increase of PEG400 and PEG10000 concentration. The results are consistent with those of XRD analyses. In addition, the average length of the needle-like crystal obtained in 0.002 mol L^{-1} PEG10000 solution is about 28 μm, which is longer than that of about 21 μm obtained in 0.002 mol L^{-1} PEG400 solution.

Proposed formation mechanism

From the aforementioned experiments, it is clear that PEG plays a crucial role in the formation of CaCO$_3$ crystals. Because of the lone pair electrons on the oxygen atoms of PEG, there is strong electrostatic interaction between PEG and Ca^{2+} ions. PEG can combine with Ca^{2+} ions and easily adsorb on the surfaces of CaCO$_3$ crystals. The formation of CaCO$_3$ is based on the reactions as follows:

$$PEG + Ca^{2+} \longrightarrow PEG - Ca^{2+}(complex) \qquad (1)$$

$$PEG - Ca^{2+}(complex) + CO_3^{2-} \xrightarrow[\text{stirring}]{\text{heating}} CaCO_3 + PEG$$

$$(2)$$

When the surface of the CaCO$_3$ crystal adsorbs PEG, the activities of the crystal are greatly suppressed.[27] From the viewpoint of kinetics of crystal growth, when the crystal adsorbs PEG on some surface, the crystal growth rate in some certain direction will be slowed down, which would lead to anisotropic growth of the crystals. As a result, calcite appears in solutions with PEG while only aragonite appears in the solution without PEG.
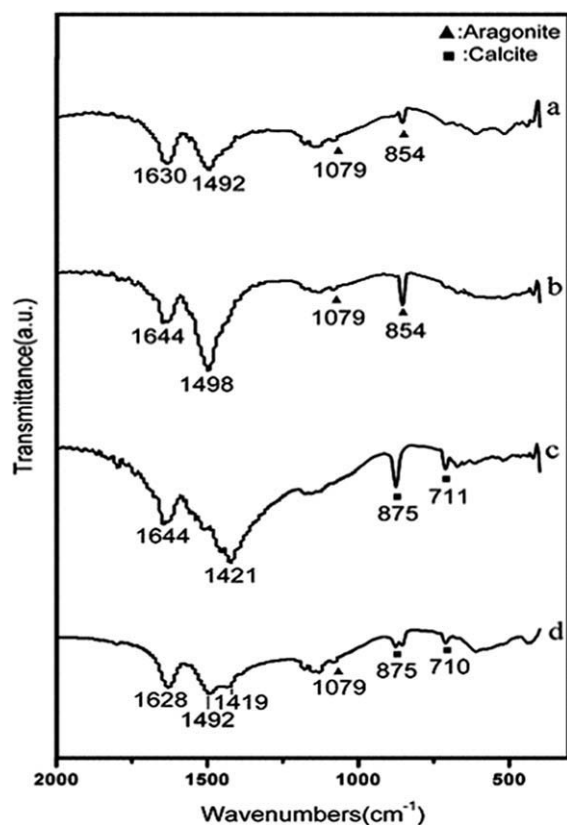
Figure 3 FTIR images of CaCO3 crystals obtained in solutions with different molecular weight of PEG (a) without PEG; (b) with 0.01 mol L^{-1} PEG400; (c) with 0.01 mol L^{-1} PEG4000; (d) with 0.01 mol L^{-1} PEG10000.

TABLE I
The Influence of PEG Molecular Weight and Concentration on Phase of CaCO$_3$ Crystal

PEG molecular weight	Concentration (mol L^{-1})	Phase
400	0.002	Aragonite
	0.005	Aragonite
	0.010	Aragonite + Calcite
4000	0.002	Calcite
	0.005	
	0.010	
10000	0.002	Aragonite + Calcite
	0.005	Aragonite + Calcite
	0.010	Aragonite + Calcite

In addition, the length of PEG molecular chain, viscosity of the solution, and the shape of PEG adsorption layer are all important factors for the formation of different morphologies of CaCO$_3$. The possible formation process of CaCO$_3$ crystal in the presence of PEG is shown in Figure 6. It is clear that the two different ways could lead to the formation of aragonite or calcite under the experimental conditions.

From the fact that calcite and aragonite can be obtained in PEG400 and PEG10000 solutions while only calcite is obtained in PEG4000 solutions, we can speculate that PEG4000 can confine the growth of CaCO$_3$ crystal in multidirection and it is especially effective for the formation of calcite under the experimental conditions. The possible reason is that long-chain polymers are easily intertwisted together,[27] which
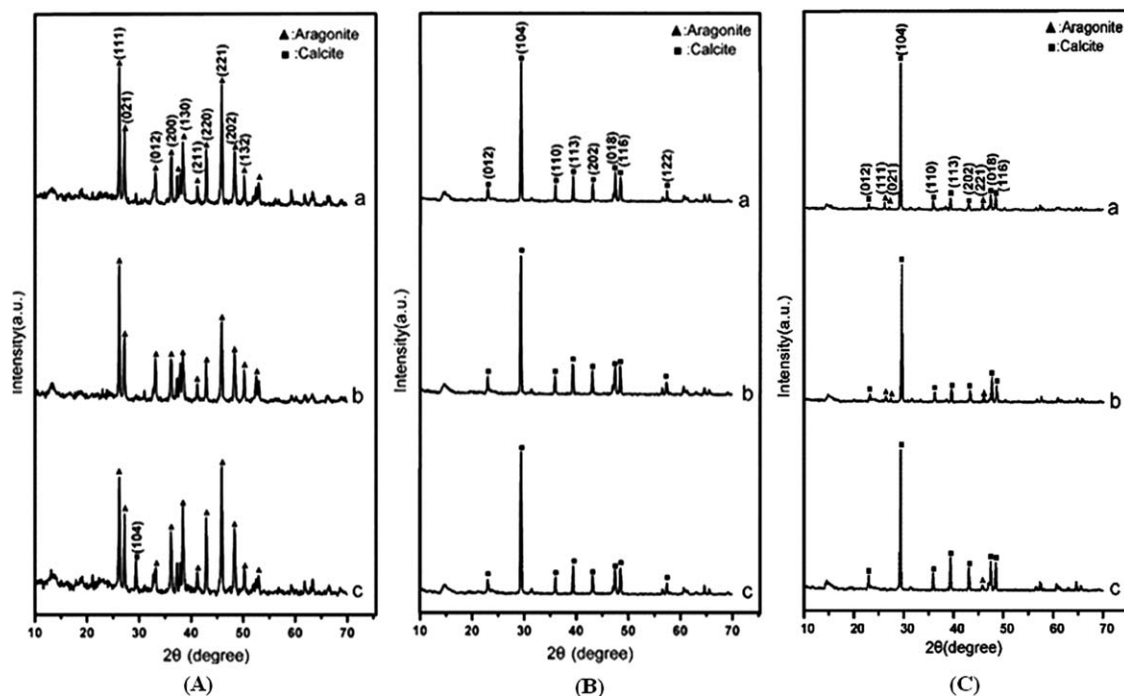

Figure 4 XRD images of CaCO3 crystals obtained in PEG solutions with different concentrations (A) PEG400; (B) PEG4000; (C) PEG10000; (a) 0.002 mol L^{-1}; (b) 0.005 mol L^{-1}; (c) 0.01 mol L^{-1}.
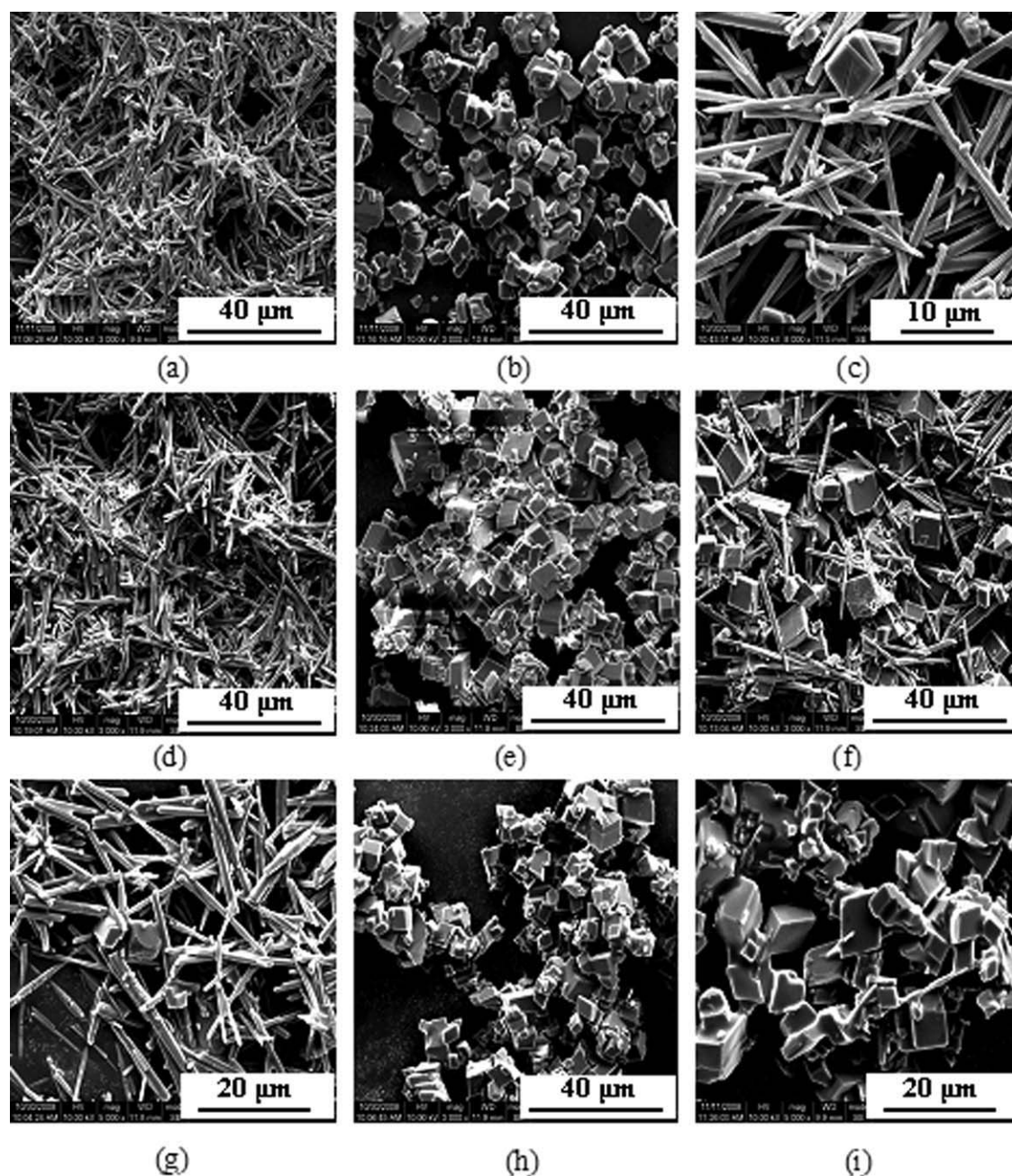
Figure 5 SEM micrographs of CaCO3 crystals obtained in PEG solutions with different concentrations (a, d, g) with 0.002, 0.005, and 0.01 mol L^{-1} PEG400, respectively (b, e, h) with 0.002, 0.005, and 0.01 mol L^{-1} PEG4000, respectively (c, f, i) with 0.002, 0.005, and 0.01 mol L^{-1} PEG10000, respectively.

has a disadvantage for the formation of 1D aragonite, while short-chain polymers greatly decrease the intertwisting possibilities, hence only rhombohedral $CaCO_3$ particles are formed in PEG4000 solutions and the main phase obtained in PEG400 solutions is aragonite. This is similar to the previous research done by Li et al.[28]

However, as the PEG10000 molecular chain is longer than PEG4000, there is strong steric hindrance to enwind $CaCO_3$, at the same time, according to the previous reports,[23,29] with the increase of molecular weight, the viscosity of solution increases and the influence on the $CaCO_3$ crystal growth decreases, thus

aragonite crystals are formed in PEG10000 solution besides calcite. Furthermore, the cavity formed by PEG10000 adsorption layer is larger, the needle-like crystal obtained in 0.002 mol L^{-1} PEG10000 solution is longer than that obtained in 0.002 mol L^{-1} PEG400 solution. The similar phenomenon is also found in the formation of ZnO with different length of PEG.[27]

From the above discussion, it can be seen that the amount of calcite crystals somewhat increases with the concentration of PEG400 and PEG10000 increases. The possible reason is that with the increase of PEG concentration, solution viscosity and the adsorption
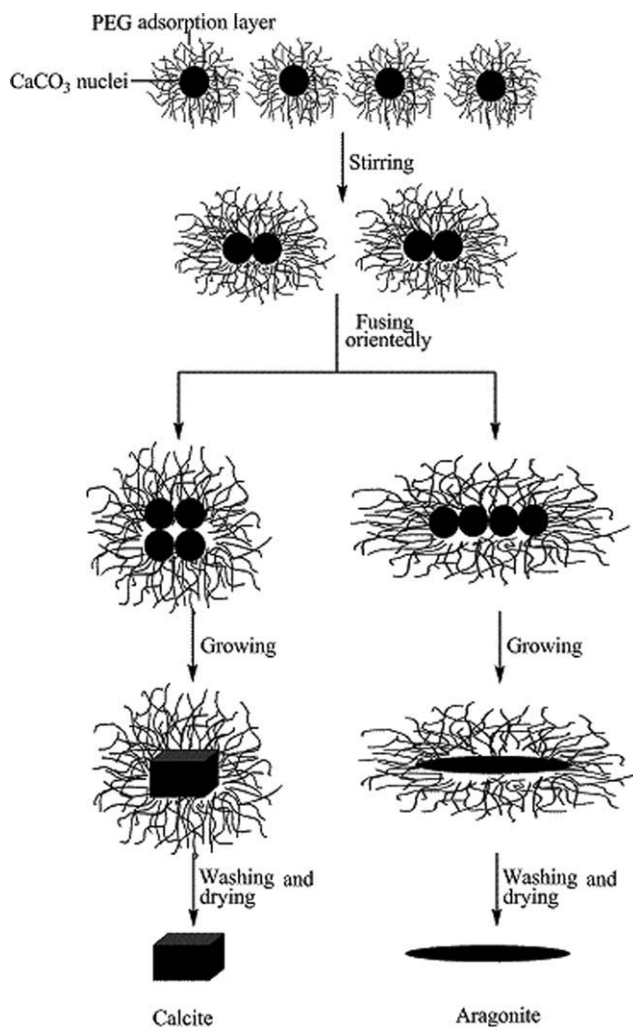
Figure 6 The possible formation process of CaCO3 crystal in the presence of PEG.

layer thickness increase simultaneously,[30,31] the electrostatic attraction between PEG and CaCO₃ crystal is enhanced and not only comes from the single direction. Thus a low concentration of PEG cannot confine several areas of the crystal, while a relatively high concentration of PEG confines more than one aspects of the crystal, which leads to the formation of calcite.

Thereby, it is clear that PEG plays an important role in determining both phase and morphology of CaCO₃. Further work is in progress to investigate the detailed mechanism.

CONCLUSION

PEG templates have been used to tune the growth of CaCO₃ crystals. Both aragonite and calcite phases were obtained in the presence of PEG400 and PEG10000 and only calcite appeared in PEG4000 solution. In contrast, only aragonite appeared in the solution without PEG. Furthermore, the needle-like CaCO₃ crystal obtained in 0.002 mol L^{-1} PEG10000

solution is longer than that obtained in 0.002 mol L^{-1} PEG400 solution. At the same time, calcite somewhat increases with the increase of PEG400 and PEG10000 concentration, while the influence of PEG4000 concentration on CaCO₃ crystal is unobvious. The results show that both molecular weight and concentration of PEG are important factors in affecting the phase and morphology of CaCO₃.

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