

Preparation of Vaterite Calcium Carbonate in the Form of Spherical Nano-size Particles with the Aid of Polycarboxylate Superplasticizer as a Capping Agent

Mohamed El-Shahate Ismaiel Saraya^{1,*}, Hanaa Hassan Abdel Latif Rokbaa²

¹Department of Chemistry, Faculty of Science, Al-Azhar University, Nasser City, P.O. 11884, Cairo, Egypt

²Department of Chemistry, Faculty of Science, Halwan University, Halwan, Cairo, Egypt

*Corresponding author: mohamedsaraya37@gmail.com

Abstract Vaterite is an important biomedical material due to its properties such as high specific surface area, high solubility, high dispersion, and small specific gravity. In this study, spherical vaterite composed of nanoparticles are synthesized by precipitation route assisted by Polycarboxylate superplasticizer (PSS). The calcium carbonate was prepared by reacting a mixed solution of Na_2CO_3 with a CaCl_2 solution at an ambient temperature, 25 °C, in the presence of polycarboxylate superplasticizer as a stabilizer. The effects of PSS on the morphology and polymorph of precipitated CaCO_3 are investigated with the help of Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and X-ray diffraction (XRD) and Transmission electron microscopy (TEM). It is supposed that the core-shell structured microspheres with the nanoparticles are attributed to the adsorption of PSS on the faces of calcium carbonate crystals. The results revealed that polycarboxylate superplasticizer can use in preparation of vaterite calcium carbonate from aqueous solutions. The prepared vaterite calcium carbonate has nanoparticles with the average particle size ranging from 15 to 26 nm as estimated using TEM.

Keywords: calcium carbonate, polycarboxylate, vaterite, Nanoparticles, SEM, TEM

Cite This Article: Mohamed El-Shahate Ismaiel Saraya, and Hanaa Hassan Abdel Latif Rokbaa, "Preparation of Vaterite Calcium Carbonate in the Form of Spherical Nano-size Particles with the Aid of Polycarboxylate Superplasticizer as a Capping Agent." *American Journal of Nanomaterials*, vol. 4, no. 2 (2016): 44-51. doi: 10.12691/ajn-4-2-3.

1. Introduction

Calcium carbonate (CaCO_3) is one of the world's most abundant materials. It has several different crystalline forms calcite, aragonite and vaterite are anhydrous crystalline polymorphs; hexahydrate and monohydrate are hydrates form. In addition, an amorphous hydrated calcium carbonate [1]. Practical, applications of the PCC are determined by its properties such as specific surface area, pore sizes, particle size distribution, polymorphic phase, purity. Calcite has crystallographic rhombohedra structure and is the most thermodynamically stable polymorph in ambient conditions. Aragonite (orthorhombic structure) forms at high temperatures, while vaterite (hexagonal structure) is the most unstable polymorph and can accompany calcite if the precipitation occurs at low temperature. The control of the precipitation process, aiming to obtain a specific morphology of the PCC is extensively studied. The operating conditions such as temperature, pH and supersaturating degree can favor the nucleation and growth of a given polymorph [2].

Calcium carbonate has great interest due to its wide industrial applications, including paper, paints, inks, plastics, adhesives, rubbers, pharmaceuticals, dental care products, cleaning agents, food stuff [3,4].

In relation to the preparation of nanoparticles, the most important aspect is the control of the polymorphism, particle size and morphology of the material. Nanoparticles with new properties such as mechanical, optical, biochemical, and catalytic have attracted many of research interest in the past years. This is mainly due to the strong functional dependence of its properties on the shapes of materials [5]. Calcium carbonate nanoparticles have numerous applications as biomaterials with different morphological structures. It is used in medicine, pharmaceutical industries, and drug delivery systems [6].

Many of works have studied the effect of organic and inorganic compounds on process of crystallization and modification of CaCO_3 such as, surfactant [7], glycine [8], polyols(ethylene glycol, glycerol, and erythritol) [9], cationic biosurfactants [10], cetyltrimethylammonium bromide (CTAB) [11], polyacrylic acids [12,13], Polyacrylamide [14], fatty acids and its salts [15,16,17], methyl methacrylate [18], polyethylene oxide [19,20], polymaleic acid [21,22], poly (styrene sulfonic acid) sodium salt [23], heavy alkylbenzene sulfonate [24], Polypeptide and polyaspartic acid [25], alginate hydrogels [26,27,28], Cellulose derivatives [29], inorganic additives [30], polysilicic acid [31] have been used. Also, Calcium carbonate was used for preparation of nanocomposites [32].

There are different techniques used for the preparation of calcium carbonate nanoparticles such as the precipitation of homogeneous solutions [33], water in- oil-in-water emulsions [34], mechanochemical and sonochemical syntheses [35,36], continuous gas-liquid membrane [37], double injection [38], precipitation [39].

Polycarboxylate water-reducer is known as polycarboxylate superplasticizer. It is a kind of copolymer which molecular structures graft carboxylic acid. Its branched structure is considered as "comb" or "graft" which is formed by polyethylene oxide, and contained other functional groups as carboxylic and sulfonic groups [40]. In the present paper, we are aimed at synthesis spherical vaterite, Where Polycarboxylate-type superplasticizer was used as stabilizer and capping agent.

2. Experimental

2.1. Materials

All chemicals are commercially available and analytical grade used without further purification. The raw materials used for synthesis were 95% CaCl_2 and 99% Na_2CO_3 , were obtained from Al-Nasser Company for Chemicals Co. (Egypt) and polycarboxylate-type superplasticizer was obtained from the Egyptian British company for special chemicals, 6th October City, Egypt. Appearance, Light brown viscous liquid; Density, $1.18 \pm 0.02 \text{ g/cm}^3$; pH =6~8; Solid content, 40 ± 1.5 . Double distilled water was

used in all experiments. The Figure 1 is shown the chemical structure of polycarboxylate-type superplasticizer.

Infrared spectra of polycarboxylate are depicted in Figure 2. The analysis result of spectra is as follows: an O-H of alcohol stretching, vibration bond at $3700\text{--}3300 \text{ cm}^{-1}$; The signals at 2960 cm^{-1} are attributed to $-\text{CH}_3-$ and $-\text{CH}_2-$ [41], peak of 1640 cm^{-1} prove the existence of ester bond; The peaks at around 1460 cm^{-1} stands for $-\text{CH}_2-$ [41], the signal at 1100 cm^{-1} [42], which proves that it contained the side chain of polyethylene glycol methyl ether in the molecular structure. Also, the signals at 1460 and 1354 cm^{-1} are the characteristic absorptions of PEO group [43], The peak at 946 cm^{-1} could respectively be assigned to the this configuration and the trans-configuration of $\text{RCH}=\text{CHR}'$ group [44], the bond 620 cm^{-1} is C-S stretching vibration [45].

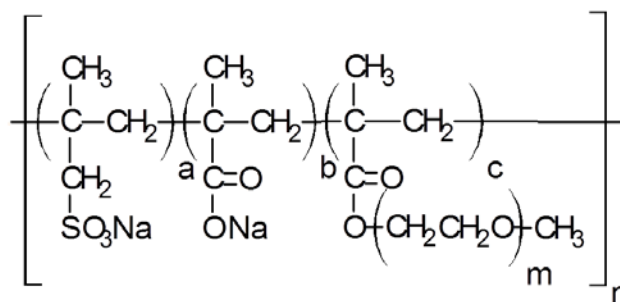


Figure 1. Chemical structure of Polycarboxylate-type superplasticizer

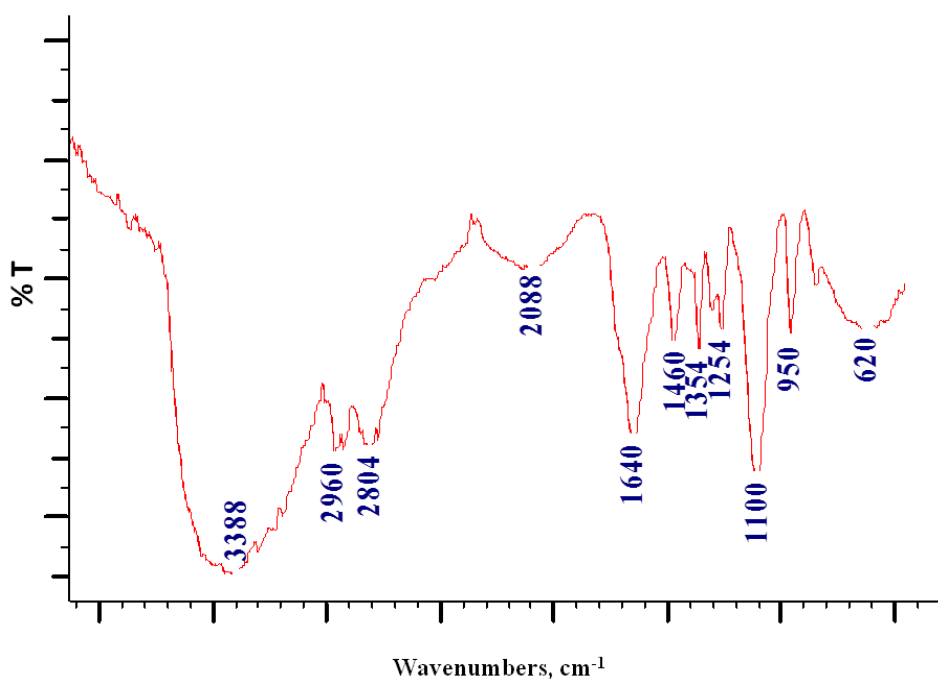


Figure 2. FT-IR spectrum of Polycarboxylate-type superplasticizer

2.2. Preparation of the Samples

Calcium carbonate precipitation experiments were carried out at 25°C , rapidly mixing, under constant and vigorous stirring (3000 RPM), equal volumes of $1.0 \text{ M Na}_2\text{CO}_3$ (pH =11.2) reacts with 0.5 M CaCl_2 (pH = 6.7) solutions in the presence of 2% polycarboxylate-type superplasticizer. The precipitated colloidal phase was filtered immediately and washed with acetone. Then the

solid was dispersed in deionized water and filtered, this process repeated three times in order to rinse the particles. After the last time particles were dried in the microwave oven. The products were slightly ground for analysis [46].

2.3. Characterization techniques used

The phases of calcium carbonate products were analyzed from the Fourier Transform Infrared (FT-IR) spectroscopy. Fourier transform Infrared (FT-IR) spectra

were measured using a Perkin Elmer 880 FT IR spectrometer with the KBr pellet method. The sample was good ground and thoroughly mixed to homogenize them. The homogenized sample was mixed with dry KBr in 1:100 mass ratios and pellet were pressed at 5 Tons. The spectra of the sample pellets were recorded by using pure KBr pellet as the blank. The X-ray diffraction (XRD) studies were performed to study the crystalline phases of synthesized calcium carbonate products. The XRD spectra were recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered Cu K α as a radiation source at 2θ scan speed of 4° min^{-1} , $k = 0.1540562 \text{ nm}$. The samples were carefully ground to a fine powder and thoroughly mixed to homogenize them and their powder XRD spectra were recorded. The resulted XRD patterns were analyzed using X Powder 12 software with the aid of ICDD PDF 2 database. Morphologies of the products were observed with the help of JEOL JSM 6360 DLA, Japan, Scanning Electron Microscope (SEM) and Transmission Electron Microscope ((TEM; Hitachi, H-800).

The molar content (%) of CaCO₃ polymorphs can be calculated according to the intensity of the (221) plane of aragonite, the (104) plane of calcite and the (110) plane of vaterite [47]:

For mixture composed of calcite, aragonite and vaterite:

$$X_a = \frac{3.1571I_a^{221}}{I_c^{104} + 3.1571I_a^{221} + 7.691I_v^{110}} \quad (1)$$

$$X_c = \frac{I_c^{104} \times X_a}{3.1571I_a^{221}} \quad (2)$$

$$X_v = 1.0 - X_a - X_c \quad (3)$$

Where X_A , X_V and X_C are the molar content (%) of aragonite, vaterite and calcite, respectively. I_A^{221} , I_C^{104} and I_V^{110} are the XRD intensity of the (221), (104) and (110) plane of aragonite, calcite and vaterite, respectively.

3. Results

3.1. Results of FT-IR Analysis

IR spectroscopy was convenient and useful to distinguish the different crystal phase of calcium carbonates, it was used to monitor effect of polycarboxylate - type superplasticizer on the crystallization of calcium carbonate. The molecular structure of calcium carbonates, containing two ions of calcium and carbonate, were simple and the vibration of carbonate ion in different calcium carbonate structures could be discriminated by IR spectra. The absorption bands of carbonate are divided into four areas: ν_1 (symmetric stretching) at 1080 cm^{-1} ; ν_2 at (out of- plane bending) 870 cm^{-1} ; at ν_3 (doubly degenerates planar asymmetric stretching) 1400 cm^{-1} and ν_4 (doubly degenerate planar bending) at 700 cm^{-1} [30,39]. The FTIR spectra of PCC products in the absence (a) and in the presence (b) of polycarboxylate are illustrated in Figure 3. For the sample without polycarboxylate (a) has bands centered at 712 , 873 and 2522 cm^{-1} reveal the presence of calcite. While in the present of polycarboxylate (b) appears new bands centered at 1085 cm^{-1} , 878 cm^{-1} , and 745 cm^{-1} and a split peak at 1440 and 1490 cm^{-1} in vaterite [48]. Also, IR spectrum of sample (b) showed strong peaks at 3396 , 2956 and 2916 cm^{-1} corresponding to OH, C-H and C-C vibrations respectively as indicated the presence of organic material [17]. These values compare with published IR data, produced by FT-IR of KBr pellets of 1420 cm^{-1} (ν_3), 876 cm^{-1} (ν_2), and 714 cm^{-1} (ν_4) for calcite and 1090 cm^{-1} (ν_1), $878/850 \text{ cm}^{-1}$ (ν_2), and $747/741 \text{ cm}^{-1}$ (ν_4) for vaterite [49]. Diagnostic peaks were therefore 712 cm^{-1} for calcite, and 747 and 1085 cm^{-1} for vaterite. Therefore, according to these results, it can be concluded that the dominant phase of all the PCC products in the presence of polycarboxylate superplasticizer is vaterite.

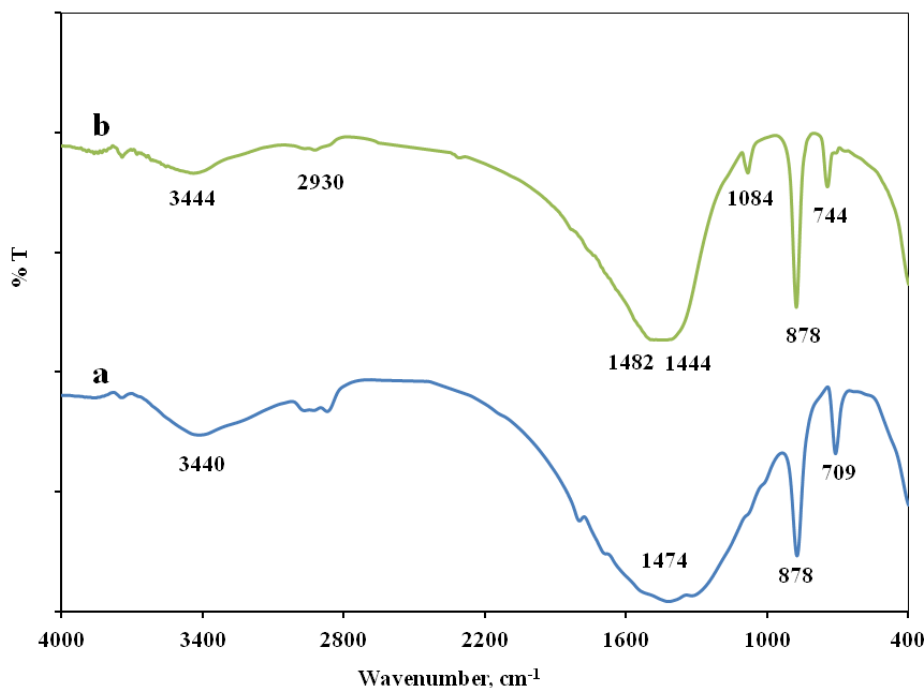


Figure 3. FTIR spectrum of CaCO₃ in absence of polycarboxylate (a) and in presence of polycarboxylate(b)

3.2. Results of XRD Analysis

X-ray diffraction was used to identify the crystalline phase of the prepared samples and the results are presented in Figure 4. XRD spectra of all samples of crystals obtained in the absence and presence of polycarboxylate-type superplasticizer are shown. Peaks characteristic of CaCO_3 are shown. The XRD peaks located at 2θ values of 29.4, 36.0, 39.4, 43.1, 47.4 and 48.5, which can be assigned to be due to those of calcite, were obtained in the absence of polycarboxylate-type superplasticizer (JCPDS 01-072-1937). In the presence of polycarboxylate-type superplasticizer the existence of calcite and vaterite (JCPDS 01-072-1937 and 00-033-0268) was demonstrated by XRD (Figure 4). The main characteristic peaks of vaterite at 2θ of 24.92°, 26.99° and 32.78° correspond to the (110), (112) and (114) crystallographic planes,

respectively [50], with no aragonite is detected. The relative contents of a different crystalline form in calcium carbonate were measured by XRD, were 91.9% calcite and 8.04% vaterite for sample prepared without PSS, while for sample prepared with PSS 10, 6% calcite and 89.4% vaterite. It can be seen that, in the presence of polycarboxylate-type superplasticizer, vaterite and calcite polymorphs occur, while in the absence of polycarboxylate-type superplasticizer, calcite is almost the only crystal form. This is mainly due to the polymer implying the inhibition of crystallization and a reduction of crystallinity. Thus, PSS in the concentration up to 2% in this system leads to the vaterite structure which remains stable for prolonged time [51]. The above results indicate that PSS favors the formation of vaterite, which agrees with the results obtained in the fast-reaction crystallization experiment carried out at ambient temperature [52,53].

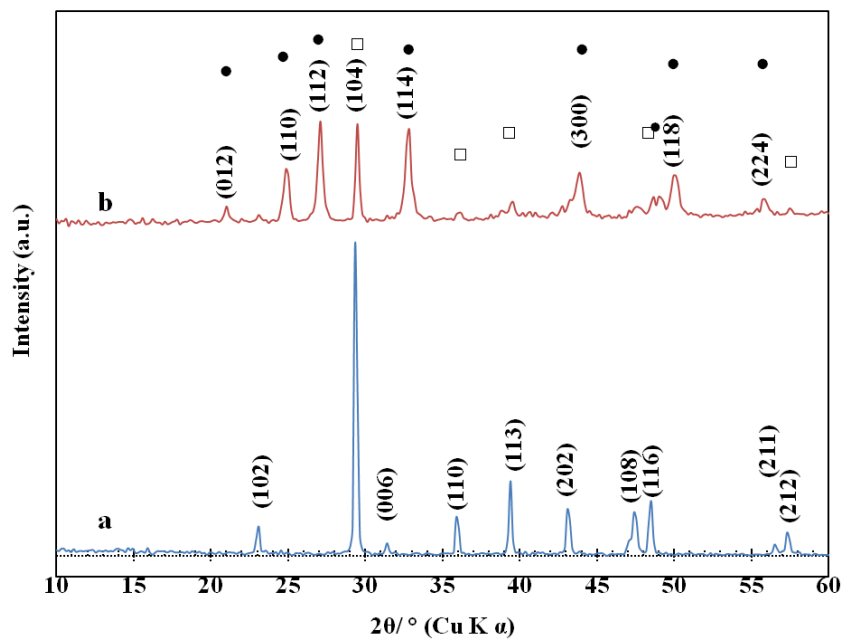


Figure 4. XRD patterns of calcium carbonate samples prepared without (a) and with (b) PSS, □ calcite, ● vaterite

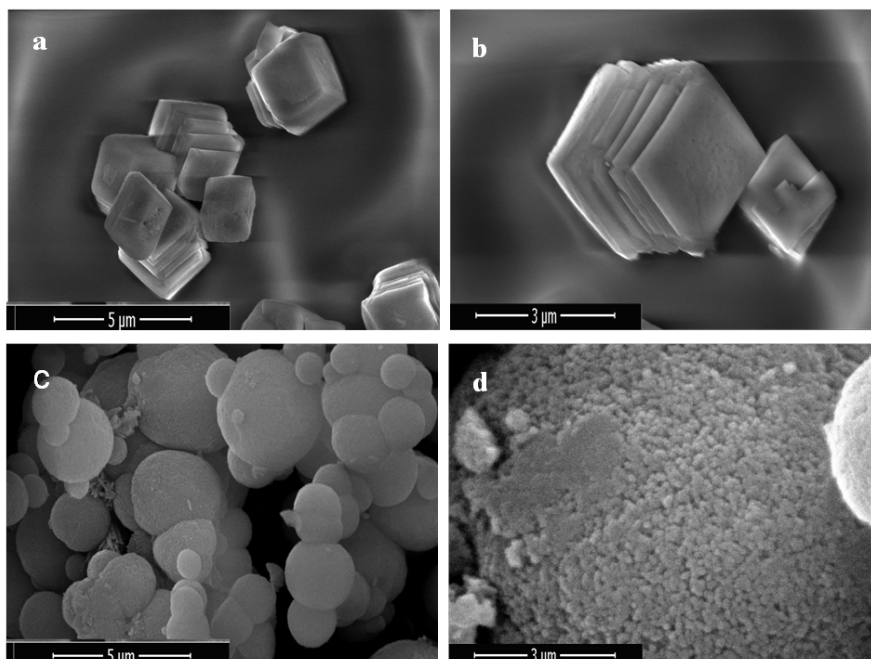


Figure 5. SEM images of CaCO_3 samples (a, b) calcite particles prepared without PSS and (c, d) vaterite particles prepared with PSS

3.3. Results of SEM and TEM analysis

Figure 5 shows that CaCO_3 were synthesized in the presence and absence of PSS. Figure 5 (a, b) indicates the morphology of CaCO_3 crystal prepared by adding PSS. The results exhibit that in the absence of the PSS system, CaCO_3 only formed common very crystalline, cubic crystal calcite crystal structure. On the other hand The PSS as modifier has an effect on crystal growth as shown in Figure 5 (c, d), the spherical morphology of final vaterite calcium carbonate are formed. These particles are in nanoscale with the average particle size ranging from

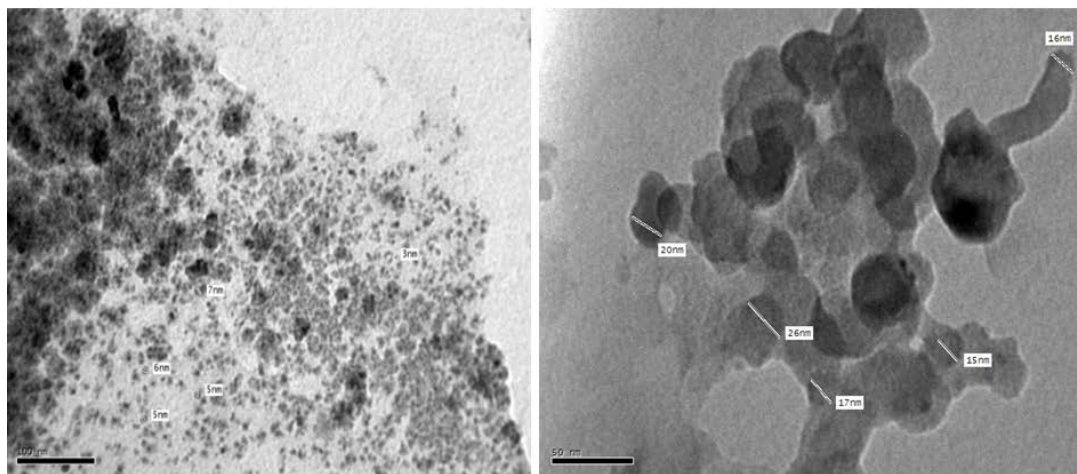


Figure 6. TEM Micrographs of CaCO_3 formed in the presence of PSS

4. Discussion

The calcite, vaterite, and aragonite are different in their crystallographic characteristics. But they composed of calcium ions and carbonate ions. Their difference lies in the ions location in the crystals, which is formed during the crystallization. In a normal condition three phases to form, three types of crystals grow simultaneously. The component of products is determined by their activity. With change of external condition, the balance of competition would change, resulting in an increase of one phase and a decrease of another phase. The growth of calcite is largely dependent on the strength of a solution, while it has less dependence on the solution velocity and ionic strength [54]. The vaterite grows as aggregated particles of small vaterite particles. The aggregation is mainly dependent on the density of vaterite nuclei, which is determined by the supersaturation as well as the transformation of vaterite to calcite and aragonite. The aragonite grows through an oriented attachment of small aragonite particles [55]. Vaterite has a different crystalline shape such as hexagonal and mono-crystalline plates, although it is rarely obtained in solution. Also, Vaterite can precipitate from solution as spherical particles spontaneously. However the mechanism of spherical particle growth is not fully recognized and is even quite often returned to be the result of nano-aggregation of precursor crystals.

Since vaterite is lowest dense phase and its nucleation rate is faster than that of calcite. But the vaterite nuclei are not thermodynamically stable that dissolving in the solution to precipitate as calcite. However, at high

15 to 26 nm as estimated using TEM. The vaterite particles have been aggregated during preparation.

TEM was also used to study the calcium carbonate crystal particles. Figure 6 (a) and Figure 6 (b) shows the TEM image of prepared calcium carbonate in the presence of PSS that reveal a spherical shape of calcium carbonate vaterite polymorphs. The nano crystal particles synthesized in the presence of PSS with individual particles measuring 15–26 nm, in addition, the shape of the particles is clear, and the difference in the particle size. PSS has been reported to strongly effect on the size and morphology of calcium carbonate nanoparticles during synthesis.

supersaturation, the dissolution of vaterite decreases and leads to the formation of metastable spherical particles of aggregates vaterite [56]. So, the direct mixing experiment with high supersaturation leads to massive formation of spherical vaterite. The massive formation of vaterite is also related to the short time of reaction because aging helps the transformation of vaterite to calcite.

Based on the Ostwald's phase rule, the least stable ACC is nucleated first and then it transforms to the most stable calcite through intermediate vaterite during the synthesis of PCC [2]. The transformation of ACC to vaterite takes place by rapid dehydration of ACC to reorganize the poorly ordered structure of ACC [57]. Kinetic studies of PCC formation given in the literature reveal that the transformation of vaterite to calcite occurs through dissolution of vaterite followed by recrystallization to achieve calcite structure [57,58,59]. The dissolution of vaterite is mainly controlled by the diffusion rate of Ca^{2+} and CO_3^{2-} ions in the solution [58]. The formation of calcite from vaterite is favored by slow diffusion rates and low concentrations of Ca^{2+} and CO_3^{2-} ions [58]. Also, the reaction temperature affects the formation of vaterite. The best temperature to stabilize vaterite is 40 °C and the amount of vaterite has been decreased with increasing temperature. This may be due to the increase of dissolution of vaterite with the increasing temperature.

The polycarboxylate - type superplasticizer is an amphiphilic copolymer that can form micelles in aqueous solution, this micelle is dynamically stable in aqueous solution. The micelles concentrate with PSS hydrophobic cores and hydrophilic side chain shells in solutions. It is speculated that block copolymer based micelles work as

“pseudonuclei” for the formation of calcium carbonate nano-crystals nuclei.

The influence of organic additives on the nucleation and crystal growth rates and its polymorphic forms, morphology, and particle size was thought to be caused by a decrease in the Ca^{2+} ion concentrations because of their reaction with carboxyl containing groups. Also, to be the adsorption of polymer on the different faces of CaCO_3 crystals, and the differences in the strength of this adsorption because of the composition of polymers i.e. The number and nature of functional groups, including polar ones, and the molecular weight, determine the final polymorphic form of the calcium carbonate precipitate [60,61].

In general, there are existing a thermodynamic/kinetic balance between calcite and metastable vaterite that can be controlled by organic additives. It is well known that metastable vaterite could transform readily and irreversibly into stable calcite form through a solvent-mediated process [62]. The stable vaterite particles can be produced in the presence of $-\text{COO}-$ functionalized which can stabilize the vaterite surfaces. The surface density of $-\text{COO}-$ functional group of the organic additive is important to control CaCO_3 morphologies and polymorphs. The formation of vaterite crystal becomes favorable to increase the density of $-\text{COO}-$ groups, due to increasing the electrostatic interaction between the carboxylic group and the Ca^{2+} . Also, the position of the carboxylate group in the polymers plays an important role in their ability to bind CaCO_3 clusters. The parallel-

oriented carboxylate groups are important for the binding to CaCO_3 clusters [63,64].

According to Colfen's results [65], the side chains of polymer are not expected to exhibit any affinity for CaCO_3 and have the potential to control the degree of surface activity. The side chains may disperse and stabilize the inorganic particles. The carboxylate groups of PSS polymer can be expected to interact with crystallized CaCO_3 through electrostatic interaction. The (0 0 1), (1 0 1), and (1 1 0) planes of vaterite are positively charged and contain exposed Ca^{2+} ; thus, the carboxylate groups of PSS polymer can adsorb on these planes [66]. The vaterite surface can be stabilized by the carboxylate groups of polymers that block the transformation of vaterite to calcite that might account for the kinetic promotion of the metastable polymorph owing to the interaction between Ca^{2+} and the carboxylate groups.

There are many studies have shown that the effect of organic additive on the stabilization of the vaterite polymorph. Jada et al. have suggested that the amount of each crystalline species, vaterite or calcite, is a function of the concentration and molecular weight of polyacrylate when CaCO_3 precipitation occurs [67]. Ouhenia et al., also reported that the crystallization of vaterite is favored in the presence of polyacrylic acid up to 50°C [68]. Song has been shown that, the CaCO_3 films obtained on the surface of chitosan films, mainly consisted of vaterite, in the presence of high concentration of polyacrylic acid, which suggests the presence of PAA plays an overwhelming part in stabilizing the vaterite [69].

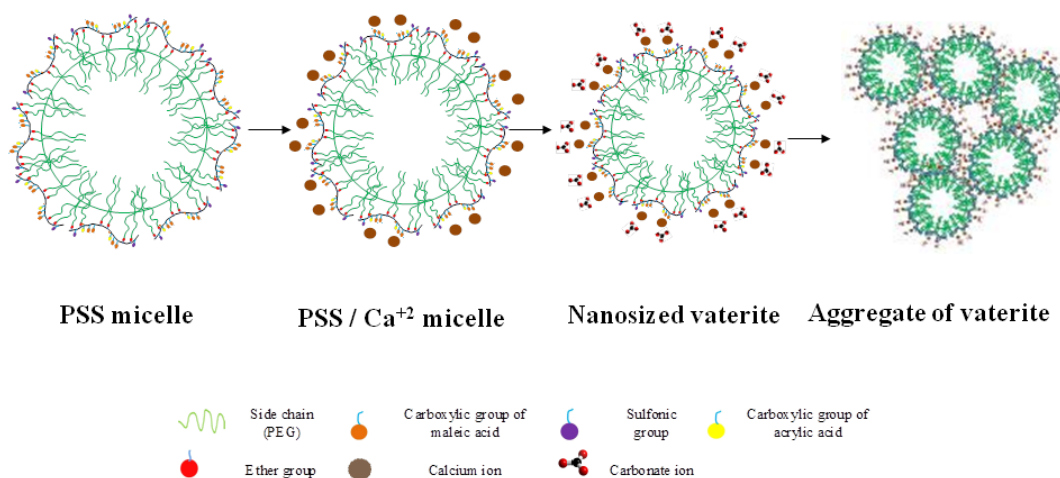


Figure 7. Shown the Schematic illustration of phase transformation process of the vaterite nanoparticles with PSS

The $-\text{COO}-$ functionalized additive in our case PSS was effectively adsorbed on the surface of the vaterite particles, which causes the stabilization of vaterite and the crystalline dissolution and recrystallization could have been inhibited with PSS segment. The carbonyl groups could interact with Ca^{2+} ions through coordination effect and form $\text{pss}/\text{Ca}^{2+}$ chelate. While the CO_3^{2-} ions encounter with the $\text{PSS}/\text{Ca}^{2+}$ chelate, the Ca^{2+} ions, on the one hand, act as the nucleating sites, on the other hand, take part in the nucleation of ACC. In the presence of pss the Ca^{2+} ions is chelated by PSS and form the $\text{PSS}/\text{Ca}^{2+}$ chelate. The CO_3^{2-} ions capture the Ca^{2+} ions and induce the formation of ACC particles, as soon as they meet with the $\text{PSS}/\text{Ca}^{2+}$ chelate. The ACC particles transform into metastable vaterite instantly, which is negatively charged on (001) planes. With the aging time prolongs, the PSS

molecules rearrange on the surfaces of vaterite particles and modulate the formation of lenticular aggregates through hydrogen bonding effect, as shown in Figure 7.

5. Conclusion

Vaterite microspheres are synthesized by a precipitation route assisted by PSS. The vaterite crystal phase of calcium carbonate is stabilized by PSS. The crystal growth process of vaterite microspheres is supposed that the nanoparticles formed and aggregated to microsphere assisted by PSS. As a result of adsorption of PSS on the surface of the vaterite particles, which causes the stabilization of vaterite and the crystalline dissolution and recrystallization could have been inhibited with PSS segment.

References

- [1] J.H. Bang, Y.N. Jang, K.S. Song, C.W. Jeon, W. Kim, M.G. Lee, S.J. Park, Effects of sodium lauryl sulfate on crystal structure of calcite formed from mixed solutions, *Journal of Colloid Interface Science* 356 (2011) 311.
- [2] I. Udrea, C. Capat, E.A. Olaru, R. Isopescu, M. Mihai, C.D. Mateescu, C. Bradu, Vaterite synthesis via gas-liquid route under controlled pH, conditions, *Industrial and Engineering Chemistry Research* 51 (2012) 8185-8193.
- [3] S. Yamanaka, N. Ito, K. Akiyama, A. Shimosaka, Y. Shirakawa, J. Hidaka, Heterogeneous nucleation and growth mechanism on hydrophilic and hydrophobic surface, *Advanced Powder Technology* 23 (2012) 268-272.
- [4] G.J. Price, M.F. Mahon, J. Shannon, C. Cooper, Composition of calcium carbonate polymorphs precipitated using ultrasound, *Crystal Growth and Design* 11 (2011) 39-44.
- [5] H. Wang, W. Huang, Y. Han, Diffusion-reaction compromises the polymorphs of precipitated calcium carbonate, *Particuology* 11 (2013) 301-308.
- [6] Y. Fukui, K. Fujimoto, Bio-inspired nanoreactor based on miniemulsion system to create organic-inorganic hybrid nanoparticle and nanofilm, *Journal of Material Chemistry* 22(2012) 3493-3499.
- [7] Y. Zhao, W. Du, L. Sun, L. Yu, J. Jiao, R. Wang, Facile synthesis of calcium carbonate with an absolutely pure crystal form using 1-butyl-3-methylimidazolium dodecyl sulfate as the modifier, *Colloid and Polymer Science* 291(2013) 2191-2202.
- [8] Y. Lai, L. Chen, W. Bao, Y. Ren., Y. Gao., Y. Yin., Y. Zhao, Glycine-Mediated, Selective Preparation of Monodisperse Spherical Vaterite Calcium Carbonate in Various Reaction Systems, *Crystal Growth & Design*, 15(3)(2015) 1194-1200.
- [9] D. B. Trushina, T. V. Bukreeva, M. N. Antipina, Size-Controlled Synthesis of Vaterite Calcium Carbonate by the Mixing Method: Aiming for Nanosized Particles, *Crystal Growth & Design*, 16(3) (2016) 1311-1319.
- [10] A. Islam, S. H. Teo, M. A. Rahman, Y. H. Taufiq-Yap, Seeded Growth Route to Noble Calcium Carbonate Nanocrystal, *PLoS one*, 10(12)(2015)0144805.
- [11] R. Na, H. B. Atchudan, I. W. Cheong, J. Joo, Facile Synthesis of Monodispersed Cubic and Spherical Calcite Nanoparticles in the Presence of Cetyltrimethylammonium Bromide, *Journal of nanoscience and nanotechnology*, 15(4)(2015) 2702-2714.
- [12] K., Hiyama, T., Nagai, A., K. Yamashita, Controlled calcite nucleation on polarized calcite single crystal substrates in the presence of polyacrylic acid, *Journal of Crystal Growth*, 415(2015).7-14.
- [13] B.P. Bastakoti, S. Guragain, Y. Yokoyama, S. I. Yusa, K. Nakashima, Synthesis of hollow CaCO₃ nanospheres templated by micelles of poly(styrene-*b*-acrylic acid-*b*-ethylene glycol) in aqueous solutions, *Langmuir* 27 (2011) 379-384.
- [14] T. J. Lee, S. J. Hong., J. Y. Park., H. J. Kim, Effects of Anionic Polyacrylamide on Carbonation for the Crystallization of Precipitated Calcium Carbonate, *Crystal Growth & Design*, 15(4), (2015).1652-1657.
- [15] S. El-Sherbiny, S. M. El-Sheikh, A. Barhoum, Preparation and modification of nano calcium carbonate filler from waste marble dust and commercial limestone for papermaking wet end application, *Powder Technology*, 279 (2015) 290-300.
- [16] J. Jiang, D. Xu, Y. Zhang, S. Zhu, X. Gan, J. Liu, From nano-cubic particle to micro-spindle aggregation: The control of long chain fatty acid on the morphology of calcium carbonate, *Powder Technology*, 270 (2015). 387-392.
- [17] H.V. Tran, L.D. Tran, H.D. Vu, H. Thai, Facile surface modification of nanoprecipitated calcium carbonate by adsorption of sodium stearate in aqueous solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 366 (2010) 95-103.
- [18] K. Fuchigami, Y. Taguchi, M. Tanaka, Synthesis of calcium carbonate vaterite crystals and their effect on stabilization of suspension polymerization of MMA, *Advanced Powder Technology* 20(2009) 74-79.
- [19] E. Y. Zeynep, D. Antoine, C. Brice, B. Frank, J. Christine, Double hydrophilic polyphosphoester containing copolymers as efficient templating agents for calcium carbonate microparticles, *Journal of Materials Chemistry B*, 3(36)(2015) 7227-7236.
- [20] X.D. Yang, G.Y. Xu, Y.J. Chen, F. Wang, H.Z. Mao, W.P. Sui, Y. Bai, H.J. Gong, CaCO₃ crystallization control by poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer and O-(hydroxy isopropyl) chitosan, *Journal of Crystal Growth* 311 (2009) 4558-4569.
- [21] M. Euvrard, A. Martinod, A. Neville, Effects of carboxylic polyelectrolytes on the growth of calcium carbonate, *Journal of Crystal Growth* 317 (2011) 70-78.
- [22] R.A., Akbour, K. Jradi, A. Jada, Crystalline Structure, Shape and Size Modifications of CaCO₃ Particles by Polyelectrolytes, *Journal of Colloid Science and Biotechnology*, 3(1) (2014) 38-45.
- [23] M. Yang, X. Jin, Q. Huang, Facile synthesis of vaterite core-shell microspheres, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 374 (2011) 102-107.
- [24] Z. Chen, S. Xiao, F. Chen, D. Chen, J. Fang, M. Zhao, Calcium carbonate phase transformations during the carbonation reaction of calcium heavy alkylbenzene sulfonate over based nano detergents preparation, *Journal of colloid and interface science* 359 (2011). 56-67.
- [25] J. Ihli, Y.Y. Kim, E.H. Noel, F.C. Meldrum, The effect of additives on amorphous calcium carbonate (acc): janus behavior in solution and the solid state, *Advanced Functional Materials*, 23(2013) 1575-1585.
- [26] T. Wang, B.X. Leng, R.C. Che, Z.Z. Shao, Biomimetic synthesis of multilayered aragonite aggregates using alginate as crystal growth modifier, *Langmuir* 26(2010) 13385-13392.
- [27] A. Rao, P. Vásquez-Quitral, M. S. Fernández, J. K. Berg, M. Sánchez, M. Drechsler, H. Cölfen, pH-dependent schemes of calcium carbonate formation in the presence of alginates, *Crystal Growth & Design*, 16(3)(2016). 1349-1359.
- [28] M.Ø. Olderøy, M. Xie, B. L. Strand, K. I. Draget, P. Sikorski, J. P. Andreassen, Polymorph switching in the calcium carbonate system by well-defined alginate oligomers, *Crystal Growth and Design* 11(2011) 520-529.
- [29] S. Kirboga, M. Öner, Application of experimental design for the precipitation of calcium carbonate in the presence of biopolymer, *Powder Technology*, 249 (2013) 95-104.
- [30] Z. Zhang, Y. Xie, X. Xu, H. Pan, R. Tang, Transformation of amorphous calcium carbonate into aragonite, *Journal of Crystal Growth* 343(2012) 62-67.
- [31] S. Bai, G. Naren, M. Nakano, Y. Okaue, T. Yokoyama, Effect of polysilicic acid on the precipitation of calcium carbonate, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 445 (2014)54-58.
- [32] W. Ye, L. Zhang, G. Feng, J. Ye, C. Li, Preparation of Calcium Carbonate and Methyl Methacrylate Nanoparticles by Seeded-Dispersion Polymerization for High Performance Polyvinyl Chloride Nanocomposites, *Industrial & Engineering Chemistry Research*, 54(30) (2015) 7459-7464.
- [33] G. X.Wu, J. Ding, J.M. Xue, Synthesis of calcium carbonate capsules in water-in-oil-in-water double emulsions, *Journal of Materials Research*, 23(2008)140-149.
- [34] A. Georgieva, B. Georgieva, Z. Bogdanov, and D. K. Stefanov, Microemulsion water-in-oil (W/O)—microreactor for synthesis of ultrafine carbonate nanostructures, *University of Ruse Union of Scientists-Ruse* 50 (2011)34-38.
- [35] Y. Kojima, K. Yamaguchi, N. Nishimiya, Effect of amplitude and frequency of ultrasonic irradiation on morphological characteristics control of calcium carbonate, *Ultrasonics sonochemistry* 17(2010) 617-620.
- [36] Y. Kojima, M. Kanai, N. Nishimiya, Synthesis of novel amorphous calcium carbonate by sono atomization for reactive mixing, *Ultrasonics sonochemistry* 19 (2012) 325-329.
- [37] Z. Jia, Q. Chang, J. Qin, A. Mamat, Preparation of Calcium Carbonate Nanoparticles with a Continuous Gas-liquid Membrane Contactor: Particles Morphology and Membrane Fouling, *Chinese Journal of Chemical Engineering* 21(2013) 121-126.
- [38] J. Chen, L. Xiang, Controllable synthesis of calcium carbonate polymorphs at different temperatures, *Powder Technology* 189 (2009) 64-69.
- [39] Y. Wang, Y.X. Moo, C. Chen, P. Gunawan, R. Xu, Fast precipitation of uniform CaCO₃ nanospheres and their transformation to hollow hydroxyapatite nanospheres, *Journal of Colloid and Interface Science* 352 (2010) 393-400.
- [40] X.L. Chen, Y.H. Fang, Z.D. Lan, Z.J. Jiang, Y. Ke, M. Q. Guan, Synthesis and Performance Research of Ester Polycarboxylate Superplasticizer, *Applied Mechanics and Materials* 204 (2012) 4147-4150.
- [41] Y.H. Fang, Z.J. Jiang, Y.L. Ke, X.L. Chen, F.L. Zheng, Z.D. Lan, M.M. Gui, Synthesis and Characterization of Comb-Like

- Polycarboxylate Superplasticizer, *Applied Mechanics and Materials* 204 (2012) 3881-3885.
- [42] S. H. Zou, W. B. Duan, X. Wang, Z. L. Gao, B. Liu, Synthesis and Effect of Polycarboxylate Superplasticizer with Two Different Molecular Polyethers as Side Chain, *Applied Mechanics and Materials*, 217 (2012) 578-581.
- [43] K. Zhou, J. Liu, Z. Li, Synthesis of A Novel Polycarboxylate Superplasticizer with High Performance, *Asian Journal of Chemistry* 23(2011) 2276-2280.
- [44] J. Zhu, G. Zhang, Z. Miao, T. Shang, Synthesis and performance of a comblike amphoteric polycarboxylate dispersant for coal-water slurry, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 412 (2012)101-107.
- [45] Z. Shen, J. Li, K. Xu, L. Ding, H. Ren, The effect of synthesized hydrolyzed polymaleic anhydride (HPMA) on the crystal of calcium carbonate, *Desalination* 284 (2012) 238-244.
- [46] H. Bala, W. Fu, Y. Guo, J. Zhao, Y. Jiang, X. Ding, Z. Wang, In situ preparation and surface modification of barium sulfate nanoparticles, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 274 (2006) 71-76.
- [47] C.G. Kontoyannis, N. V. Vagenas, Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy, *Analyst* 125 (2000) 251-255.
- [48] A. Sarkar, S. Mahapatra, Synthesis of all crystalline phases of anhydrous calcium carbonate, *Crystal Growth Design* 10 (2010) 2129-2135.
- [49] M.M.M.G.P.G. Mantilakaa, b, R.M.G. Rajapaksea, D.G.G.P. Karunaratnec, H.M.T.G.A. Pitawala, Preparation of amorphous calcium carbonate nanoparticles from impure dolomitic marble with the aid of poly (acrylic acid) as a stabilizer, *Advanced Powder Technology* 25(2014), 591-598.
- [50] C.Y. Tai, C. Chen, Particle morphology, habit, and size control of using reverse microemulsion technique, *Chemical Engineering Science* 63 (2008) 3632-3642.
- [51] E. Loste, R.M.Wilson, R. Seshadri, F.C. Meldrum, The role of magnesium in stabilising amorphous calcium carbonate and controlling calcite morphologies, *Journal of Crystal Growth* 254 (2003) 206-218.
- [52] Y. Shen, A. Xie, Z. Chen, W. Xu, H. Yao, S. Li, L. Huang, Z. Wu, X. Kong, Controlled synthesis of calcium carbonate nanocrystals with multi-morphologies in different bicontinuous microemulsions, *Materials Science and Engineering A* 443 (2007) 95-100.
- [53] D.L. Tran, V.H. Tran, T.Q. Duong, J.S. Kim, Effect of nanosized and surface-modified precipitated calcium carbonate on properties of CaCO₃/polypropylene nanocomposites, *Materials Science and Engineering A* 501 (2009) 87-93.
- [54] C.Y. Tai, W.C. Chien, C.Y. Chen, Crystal growth kinetics of calcite in a dense fluidized-bed crystallizer, *AIChE Journal* 45 (1999) 1605-1614.
- [55] G.T. Zhou, Q.Z. Yao, J. Ni, G. Jin, Formation of aragonite mesocrystals and implication for biomineralization, *American Mineralogist* 94 (2009) 293-302.
- [56] Y.S. Han, G. Hadiko, M. Fuji, M. Takahashi, Factors affecting the phase and morphology of CaCO₃ prepared by a bubbling method, *Journal of the European Ceramic Society* 26 (2006) 843-847.
- [57] J.D. Rodriguez-Blanco, S. Shaw, L.G. Benning, The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite, *Nanoscale* 3 (2011) 265-271.
- [58] Y.S. Han, G. Hadiko, M. Fuji, M. Takahashi, Effect of flow rate and CO₂ content on the phase and morphology of CaCO₃ prepared by bubbling method, *Journal of Crystal Growth* 276 (2005) 541-548.
- [59] S. Huang, K. Naka, Y. Chujo, A carbonate controlled-addition method for amorphous calcium carbonate spheres stabilized by poly(acrylic acids), *Langmuir* 23 (2007) 12086-12095.
- [60] I. Polowczyk, A. Bastrzyk, T. Kozlecki, Z. Sadowski, Calcium carbonate mineralization. Part 1: the effect of poly (ethylene glycol) concentration on the formation of precipitate, *Physicochemical Problems of Mineral Processing* 49 (2013) 631-639.
- [61] W. Li, L. Liu, W. Chen, L. Yu, W. Li, H. Yu, Calcium carbonate precipitation and crystal morphology induced by microbial carbonic anhydrase and other biological factors, *Process Biochemistry* 45(010)1017-1021.
- [62] H. ei, Q. Shen, Y. Zhao, D.J. Wang, D.F. Xu, Influence of polyvinylpyrrolidone on the precipitation of calcium carbonate and on the transformation of vaterite to calcite, *Journal Crystal Growth* 250 (2003) 516-524.
- [63] Q. Shen, Y.K. Chen, H. Wei, Y. Zhao, D.J. Wang, D.F. Xu, Suspension effect of poly(styrene-ran-methacrylic acid) latex particles on crystal growth of calcium carbonate, *Crystal Growth Design* 5 (2005) 1387-1391.
- [64] H. Wei, Q. Shen, H.H. Wang, Y.Y. Gao, Y. Zhao, D.F. Xu, D.J. Wang, Influence of segmented copolymers on the crystallization and aggregation of calcium carbonate, *Journal Crystal Growth* 303 (2007) 537-545.
- [65] H. Colfen, Double-hydrophilic block copolymers: synthesis and application as novel surfactants and crystal growth modifiers, *Macromolecular Rapid Communications* 22 (2001) 219-252.
- [66] S.H. Yu, H. Colfen, J. Hartmann, M. Antonietti, Biomimetic crystallization of calcium carbonate spherules with controlled surface structures and sizes by double-hydrophilic block copolymers, *Advanced Functional Material* 12 (2002) 541-545.
- [67] A. Jada, R. Ait Akbour, C. Jacquement, J.M. Suau, O. Guerret, Effect of sodium polyacrylate molecular weight on the crystallogensis of calcium carbonate, *Journal Crystal Growth* 306 (2007) 373-382.
- [68] S. Ouhenia, D. Chateigner, M.A. Belkhir, E. Guilmeau, C. Krauss, Synthesis of calcium carbonate polymorphs in the presence of polyacrylic acid, *Journal of Crystal Growth* 310 (2008) 2832-2841.
- [69] L.H. He, R. Xue, R. Song, Formation of calcium carbonate films on chitosan substrates in the presence of polyacrylic acid, *Journal of Solid State Chemistry* 182 (2009)1082-1087.