Biomimetic Crystallization of Calcium Carbonate in the Presence of Water-Soluble Zwitterionic Block Copolymer

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Crystallization of calcium carbonate (CC) in aqueous solutions by gas-liquid diffusion procedure was investigated systematically in the presence of poly(4-sulfonic acid diphenylamine)-block-poly(ethylene glycol) (PSDA-b-PEG), wherein the PSDA block is a polymeric zwitterion. PSDA-b-PEG was synthesized with the reaction of tosylated PEG and amine-functionalized PSDA and was characterized by nuclear magnetic resonance. The parameters such as, block copolymer concentration, crystallization time and initial pH were considered as indicators of block copolymer's capability in controlling the morphology of CC particles. The particles were characterized by Fourier transform infrared, scanning electron microscopy, and X-ray diffraction. The results suggest that PSDA-b-PEG is a suitable template to control the growth mechanism of CC to produce meso-sized particles with different morphologies. POLYM. ENG. SCI., 59:96–102, 2019. © 2018 Society of Plastics Engineers

INTRODUCTION

Biomineralization is the formation of minerals such as calcium carbonate (CC), hydroxyapatite, silicate, and iron oxide by living organisms at the ambient temperature and pressure. In order to control and direct the crystallization during biomineralization, the living organisms use organic molecules which provide nucleation sites and orient the ions of the minerals to locate at suitable places to form some special crystal morphology. The organization style of the mineral with organic substance contributes to their unique mechanical properties. The biominerals produced by living organisms are not as brittle as the corresponding inorganic counterparts and have outstanding mechanical strength. To reveal the design strategies of these biominerals, a variety of solid inorganic materials are mineralized under the influence of organic molecules produced by the living organisms such as mollusca, birds, fishes, and mammalians [1, 2].

In the classical crystallization, atoms, ions, or molecules form limited number and shaped crystals due to the inherent crystal anisotropy. Yet, new synthetic approaches using organic templates have attracted considerable interest in a wide variety of hybrid particles to be used in modern material science [3, 4]. Biomimetic has a very high potential for the creation of new advanced hybrid materials and film with interesting features. Mimicking of natural nanocomposite materials is an early stage but there are evidences to design the creation of useful synthetic nanoscale hybrid materials and there is a need to synthesize new copolymers which can control the crystallization to produce well defined particles with unique structures from nanometer to micrometer scale [5]. It was reported that the 2D-crystallization of poly (lactic acid) can be easily succeeded by biomimetic approach [6].

A number of studies have been conducted to explore the influence of organic compounds on nucleation, growth, and morphology of inorganic materials. In order to control the nucleation and growth of the crystallization by mimicking biomineralization, numerous researchers used organic templates and additives such as bio- [7, 8] or synthetic- [9, 10] macromolecules, double hydrophilic block copolymers [9, 11, 12], Langmuir monolayers [13], low-molecular weight compounds [14], and polyelectrolytes [15–18].

CC is one of the most abundant biomineral in nature and has extensive industrial applications. It is used as processing aid, rheology and mechanical strength modifier [19, 20] and fire retardant [21]. It can be used in the surface graft copolymerization to toughen the surface of traditional polymers [22]. CC particles can be used also as a nucleating agent to adjust the size and amount of crystalline regions of traditional polymers [23, 24]. The importance of the cavities of hybrid CC particles to modify the mechanical properties has been shown [25].

Three crystalline polymorph of anhydrous CC are well-known: calcite, aragonite and vaterite. Among them, calcite is thermodynamically the most stable and vaterite is the least stable form. Vaterite can transform to calcite and aragonite in aqueous solution. The morphologies of the polymorphs: either cube- or plate-like particles for calcite, hexagonal or spherical polycrystalline particles for vaterite and needle-like particles for aragonite in aqueous solutions [26].

Cölfen and coworkers [15] used poly(sodium-4-styrenesulfonate) (PSS) as a polyelectrolyte template for the crystallization of CC. They obtained some mesocrystals with porous scaffolds composed of well-separated, but almost perfectly three-dimensionally aligned calcite nanocrystals by addition of PSS although they obtained perfect rhomboheral particles without PSS. They concluded PSS strongly binds free calcium ions and leads the mechanism from ionic growth to mesoscale assembly, and acts as a nucleation agent. It also binds selectively to the nonexposed (001) calcite face, resulting in mesostructures composed of truncated triangular units instead of the typical rhombohedra.

It was proposed that the double hydrophilic block copolymers are more successful to control the crystallization of inorganic particles in aqueous solutions compared with polyelectrolytes [9, 11, 12]. They have two blocks of which one has strong binding interaction with inorganic surfaces and the other maintains the solubility of macromolecules with no affinity to the ionic species. Cölfen and Qi [27] have shown experimentally

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Contract grant sponsor: The Scientific and Technological Research Council of Turkey (TUBITAK); contract grant number: 107T697; contract grant sponsor: TUBITAK Directorate of Science Fellowships and Grant Programmes (BIDEB)-2211; contract grant sponsor: Scientific Research Projects Coordination Center, Yildiz Technical University; contract grant number: 29-01-02-DOP03.
DOI 10.1002/pen.24871
Published online in Wiley Online Library (wileyonlinelibrary.com).
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that the presence of pure poly(ethylene glycol) (PEG) has no effect on the crystal morphology of CC whereas presence of poly (methyl acrylate) (PMA) causes large ill-defined irregular-shaped aggregates consisting of rounded particles typical for the strong interaction between the carboxylic acid groups of PMA and the crystallizing CC. Therefore, their block copolymers, PEG-b-PMA suppressed effectively crystal morphology. Effects of type, molecular weight and concentration of organic templates as well as influence of initial pH and temperature on morphologies of CC crystals were also investigated [9, 28].

On the other hand, it was shown that the type, concentration and the conformation of the amino acids and peptides strongly affect the morphology and polymorph of the precipitated CC particles [29, 30]. Especially the acidic amino acid plays an important role in the control of the polymorphs of CC since they are entrapped onto the surface of matrices. Calcite surfaces are stabilized by the binding of molecules such as peptides and proteins in order to lowers their surface energies. CC crystals allow enantioselective binding, for instance the selective binding of different amino acids onto CC crystal surfaces has been reported by Orme et al. [31]. It was revealed that that the shape of CC crystals can be effectively modified by means of chiral molecules. Very recently, Jiang et al. [32] published an elegant paper in which chiral, hierarchical vaterite toroidal suprastructures of vaterite particles were synthesized in the presence acidic D-and L-enantiomers of acidic amino acids at low supersaturation level of calcium and carbonate ions in aqueous solutions. They show also that such chiral, toroidal vaterite suprastructures cannot be synthesized using basic, neutral and achiral amino acids at the same conditions.

Similar to the proteins produced by living organisms to make biomineral, a polyswitterion carries both positive and negative charges depending on the solution pH. Thus, a polyzwitterion can be a good candidate to control the crystallization reactions of the inorganic substances. Kanapathipillai et al. [33] studied a zwitterionic pentablock copolymer as a template for calcium phosphate synthesis and obtained a mixture of amorphous and crystalline phosphates in which the crystalline component contains several inequivalent ions. They proposed this unusual phosphate phase has been nucleated by the zwitterionic polymer. Recently, Xu et al. [34] used poly(2-methacryloyl oxyethyl phosphoryl choline) zwitterionic polymer to control the crystallization of CC and barium carbonate via gas-liquid diffusion method and they obtained spherical CC particles with six flat faces distributed symmetrically on the surface and dumbbell-shaped particles with six sides.

Based on such findings and as a contribution to the existing studies, the present study research focused on a water-soluble block copolymer, namely, poly 4-sulfonic acid diphenylamine)-block-poly(ethylene glycol) (PSDA-b-PEG) to control the CC crystallization by variation of copolymer concentration, crystallization time and initial pH of the solution via gas-liquid diffusion procedure. Although it is well known that anionic groups have a specific affinity to the cations of inorganic components, the role of a polymer's cationic group in biomineralization is not adequately established. PSDA-b-PEG is not only a double hydrophilic block copolymer having both interacting and non-interacting blocks with inorganic surfaces but also it has a polyzwitterionic block similar to proteins. Therefore, this choice could be a reasonable to see the effect of the sign of template's charge on the morphology of CC since PEG block ensures the solubility of the template during the interaction of polyzwitterion with inorganic surfaces.

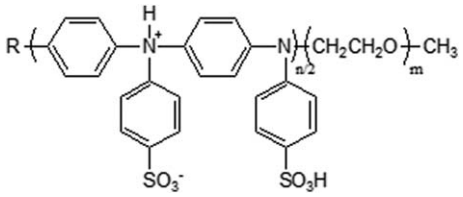

FIG. 1. Chemical structure of the PSDA-b-PEG.

EXPERIMENTAL

Synthesis of the PSDA-b-PEG

Sodium diphenylamino-4-sulfonate (SDAS) (Sigma-Aldrich, 99%), hydrochloric acid (HCl) (Merck, 37%), ammonium persulfate (Sigma-Aldrich, 98%), hydrazine monohydrate (Fluka, 98%), p-toluenesulfonyl chloride (Sigma-Aldrich, 99%), poly (ethylene glycol) ($M_n = 750$ g/mol Alfa Chemicals), sodium hydroxide (NaOH) (Fluka), HCl (Merck, 37%) ammonium hydroxide (NH_4OH) (Sigma-Aldrich) were used without further purification.

Zwitterionic block copolymer, PSDA-b-PEG (Fig. 1) was synthesized via the reaction of amine-functionalized PSDA with tosylated PEG as described in our previous study [35] and Hua and Ruckheistein's research [36]. Initially, HCl-doped PSDA was obtained by polymerization of the monomer SDAS in HCl solution and next it was neutralized with NH_4OH solution. Subsequently, the neutralized PSDA was reduced to secondary amine-functionalized end-group form by hydrazine under nitrogen atmosphere. The PEG monomethyl ether was tosylated with tosylol chloride. The PSDA-b-PEG was obtained by reacting PEG-Tos and amine-functionalized PSDA.

Crystallization of CC

All glassware was cleaned and sonicated with ethanol for 5 min, rinsed with deionized water, soaked with a H_2O:HNO_3 (65%): H_2O_2 (1:1:1, v/v/v) solution, rinsed with distilled water and dried with acetone. The crystallization of CC was carried out in glass bottles by gas–liquid diffusion reaction, as described by Addadi and coworkers [37]. Stock aqueous solution of $CaCl_2$ (1.25 mM) was freshly prepared and bubbled with argon for 1 h before use. Various amounts of polymer (5–30 mg) were added quickly into 10 mL $CaCl_2$ solutions under mild stirring. Few pieces of small coverslips were put on the bottom of the bottles for collecting the CC particles. Subsequently, the bottles were covered with punched parafilm and placed in a desiccator. Three small glass bottles of crushed ammonium carbonate were covered with punched parafilms and placed at the bottom of the desiccator. The initial pH was adjusted using dilute HCl or NaOH solutions. Next, the coverslips were taken at different times, rinsed with distilled water and ethanol, and were allowed to dry at room temperature.

Instrumentation

The synthesized block copolymer was characterized by Nuclear Magnetic Resonance (NMR) (Varian UNITY INOVA 500 MHz) spectrometer.

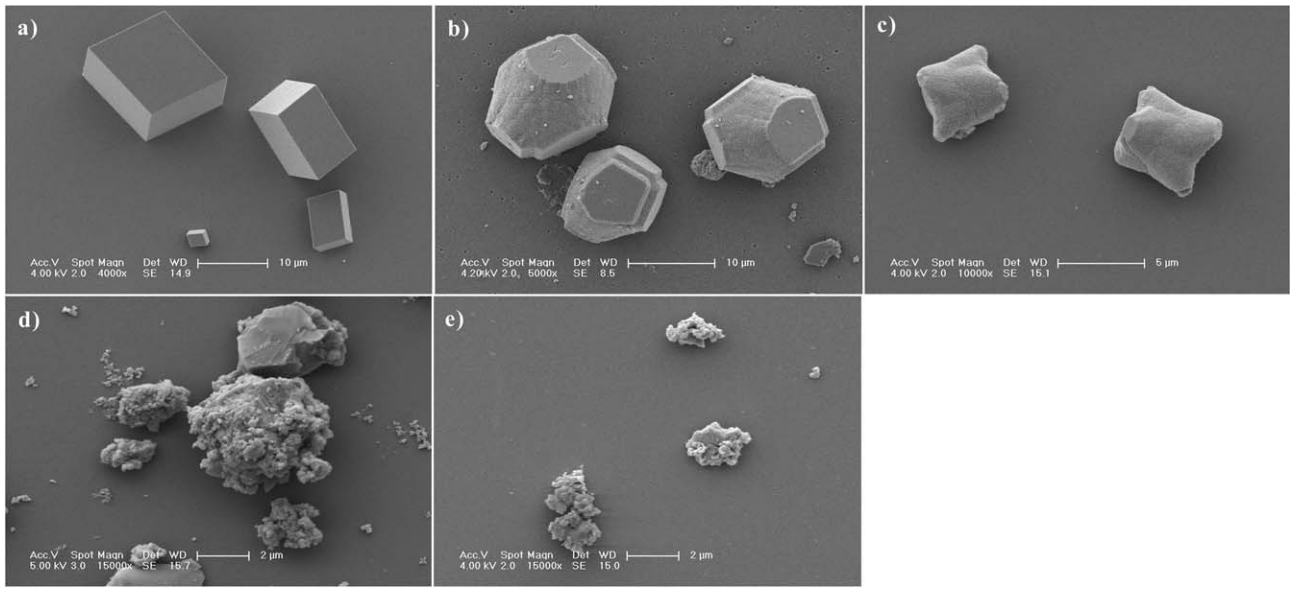

FIG. 2. Scanning electron microscopy (SEM) images of CC crystals at pH 7 after 3 h without the PSDA-b-PEG (a) and with the PSDA-b-PEG in the following concentrations (g/L): 0.5 (b), 1.0 (c), 2.0 (d), and 3.0 (e) [$CaCl_2$] = 1.25 mM.

The potentiometric titration measurements were carried out using a pH meter (Thermo Scientific, ORION 5-Star) at room temperature to determine the isoelectric point (IEP) of PSDA-b-PEG. A PSDA-b-PEG solution at a concentration of 1 g/L in a given volume was prepared and the pH value was adjusted to 1.5 by the addition of aqueous normalized HCl solution. The solution was allowed to stand overnight and then titrated with the 0.1 M standardized NaOH. Using the titration curve, the IEP of the block copolymer was determined as 6.6 by taking the average of the values of pK_{a1} and pK_{a2} [38].

The morphology of CC particles on the gold plated coverslips was examined by scanning electron microscopy (Philips XL30 ESEM-FEG/EDAX System). CC crystals were characterized by X-ray diffraction (XRD) pattern recorded on a (Rigaku D/MAX-Ultima+/PC) X-ray diffractometer and Fourier Transform Infrared (FTIR) Spectrometer. The spectra of the samples were measured using Perkin Elmer Spectrum One FT/IR spectrometer equipped with attenuated total reflectance (ATR). Spectral data were collected by contacting the fine ground powder of the samples with the diamond of the ATR cell. All spectra were obtained at 2 cm^{-1} resolution after being scanned 60 times.

RESULTS AND DISCUSSION

Characterization of the Synthesized PSDA-b-PEG

IEP where the concentrations of negative and positive charges are equal was determined as pH 6.6 by titration with NaOH solution. Lowe et al. [39] synthesized and studied solution properties of a series of zwitterionic block copolymer namely, some poly(2-[dimethylamino]ethyl methacrylate-block-2-tetrahydropyranyl methacrylate) with different copolymer compositions of which the IEPs were determined between 5.62 and 8.56 by titration. Kanapathipillai et al. [33] studied a zwitterionic pentablock copolymer containing polysulfobetaine side chains, of which the IEP value was determined around 6.3 by titration. Our result is in agreement with these IEP values in the literature.

In the ^{1}H-NMR spectrum of the block copolymer in deuterated water, the peaks of PSDA block were observed at δ 7.29-7.63 ppm (aromatic protons) and the peaks of PEG were detected at δ 3.63 ppm (OCH_2, 4H), 3.42 ppm (OCH_3, 3H), and 3.3 ppm (NCH_2, 2H), respectively. The molecular weight of PSDA block was estimated to be 5,100 g/mol by taking into account the integral ratio of aromatic protons of PSDA block to methylene protons of PEG block with a molecular weight of 750 g/mol.

CC Crystallization

The crystallization was performed via gas diffusion procedure which is a dynamic process. The concentrations of copolymer and calcium ions change continuously in the course of crystallization reaction. pH of the solution rises within an induction period of about 4 h as a result of dissolution of ammonia that is formed during the decomposition of $(NH_4)_2CO_3$ [30]. The better solubility of ammonia relative to that of CO_2 leads to the observed pH increase. It was observed also in this study that the pH of the reaction solution raised compared with initial pH values. In addition, it is also important to note that the rate of classical CC crystallization reaction considerably increase with pH of the solution.

At first, a systematic work was performed by changing the concentration of PSDA-b-PEG in a $CaCl_2$ solution at a concentration of 1.25 mM at pH7. Typical calcite rhombohedra are formed if CC is crystallized without additives via the performed gas-diffusion technique (Fig. 2a). However, the shape of calcite rhombohedra have deformed as the block copolymer concentration increases in the reaction medium from 0.5 to 3.0 g/L (Fig. 2b–e). Calcite single crystals with pseudo-dodecahedral shapes was produced via crystallization of CC at lower block copolymer

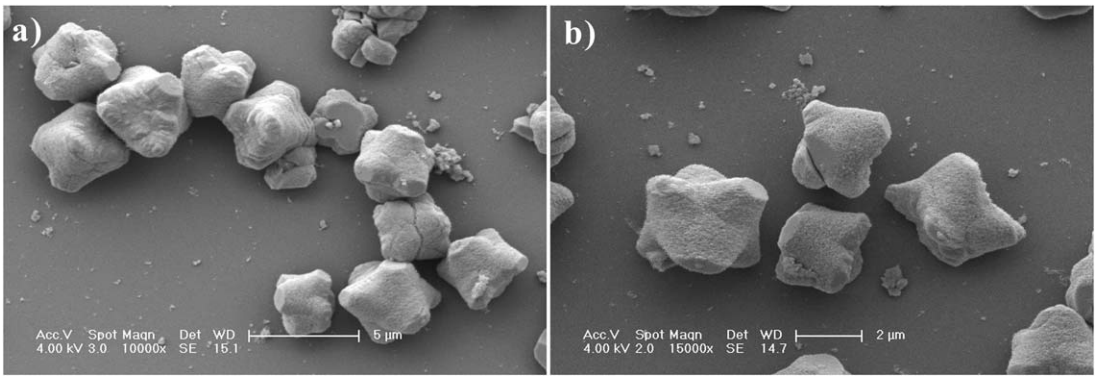

FIG. 3. SEM images of CC crystals obtained from the samples in the Fig. 2d and e after retaining them for 5 more days. The PSDA-b-PEG concentrations in g/L: 2.0 (a) and 3.0 (b) [$CaCl_2$] = 1.25 mM.

concentration (0.5 g/L) was produced after 3 h as shown in Fig. 2b. The shapes of these 10- to 15-μm sized particles are very similar to the CC particles obtained from the calcium chloride solutions including poly(4-styrene sulfonic acid-co-maleic acid) in a concentration of 0.1 g/L at ambient conditions by gas diffusion procedure [18]. The concentration of negatively sized sulfonate groups is relatively higher than that of positively signed quaternary amine groups on the PSDA block at pH 7 since its IEP is 6.6. Consequently, sulfonate groups can be tied to the calcium ions in the solution or in the calcite rhombohedra crystals formed earlier in the solution at lower copolymer concentration, that is, 0.5 g/L. It seems that the sulfonate groups of the copolymer adhere on the corners and edges rather than on the flat faces of the rhombohedra since vertices and edges of the calcite crystals disappeared however smoothness of the facets were somewhat preserved. This indicates also that the classical ionic crystallization reaction continues on the six smooth faces simultaneously with non-classical crystallization occurring on edges and corners and forming coarsened faces with curvature.

Some smaller (i.e., 5–7 μm) typical particles with six truncated conical arms are formed when the concentration of block copolymer was increased (Fig. 2c). It seems that the six truncated conical arms are formed through progressive decreasing of six smooth facets' surface areas because of decreasing classical ionic crystallization but increasing non-classical crystallization. It can be stated that, the rate of non-classical crystallization increases because of increasing sulfonate group concentration as the copolymer concentration increases. Therefore, the particles in the Fig. 2b and2c suggest that the sulfonate groups of PSDA blocks are attached to the edges and vertices (not on the smooth faces) of the rhombohedral crystals formed earlier and then the non-interacting PEG block sterically hinders the introduction of the inorganic ions into the crystal lattice on the immediate vicinity of attachment region and also acts as stabilizing moiety [9, 27].

The formation of spherical particles with six smooth facets symmetrically distributed on the surface obtained by Xu et al. [34]. This supports that a polyzwitterion can attach on the vertices and edges but does not attach to the smooth surfaces of a calcite rhombohedra at pH 7. As PSDA-b-PEG concentration increased, the size of particles decreased and their shape became ill-defined irregular (Fig. 2d and e) suggesting that PSDA-b-PEG can totally inhibit the growth of CC rhombohedral crystals at high concentrations. These results indicate that the morphology of CC particles can be adjusted with the concentration of PSDA-b-PEG.

Figure 3a and b were obtained from the samples in the Fig. 2d and e after they were retained in the reaction medium for 5 additional days. When held for longer, particles with six truncated cone-shaped arms reappeared alongside the ill-defined irregularly shaped particles. This can be attributed to the decrease in the block copolymer concentration over time since the block copolymer is trapped in the previously formed ill-defined irregular particles.

Subsequently, a set of CC crystallization experiments was conducted by altering the initial pH from 4–8 at a constant PSDA-b-PEG concentration (1.0 g/L) to reveal the influence of the initial pH on the crystal morphology. The results are depicted in the Fig. 4.

It should be noted that the induction time of CC precipitation increases significantly, thus the polymer can control the crystallization more efficiently by decreasing pH. The nucleation rate is also lower at lower pH. The lower the nucleation rate, the fewer and the bigger crystals are. At lower pHs than IEP, the zwitterionic group of the block copolymer should be charged considerably positively in acidic medium due to the formation of -(R_3N^+H)- (where R indicates phenylene groups), on the main chain by protonation and simultaneous neutralization of the pendant ionic groups as -SO_3H. Therefore, the concentration of positive charges of the block copolymer, -(R_3NH^+)- is higher than that of negatively charged sulfonate groups at lower pH. It gives chirality to the block copolymer because of the formation of the asymmetric nitrogen atom. Thus, the formation of bigger (20–30 μm) toroidal particles can be attributed to the chirality of the block copolymer at pH 4 (Fig. 4a). It can be seen that the hierarchically organized, toroid-shaped chiral superstructures with the spirally oriented morphology of assembled mineral platelets in the Fig. 4a. The shape of the particle can be comparable to the chiral toroidal vaterite particles obtained in the presence of D-enantiomer of the aspartic acid [32]. It can be stated that at pH 4, the positive charge of the PSDA block adheres to the carbonate groups on the smooth faces of the crystal lattice, and the PEG block sterically hinders the classical crystallization of the ionic species, thus resulting in a loose superstructures (Fig. 4b).

At pH 5, since the concentration of the positive charges of the block copolymer decreased, so that the concentration of

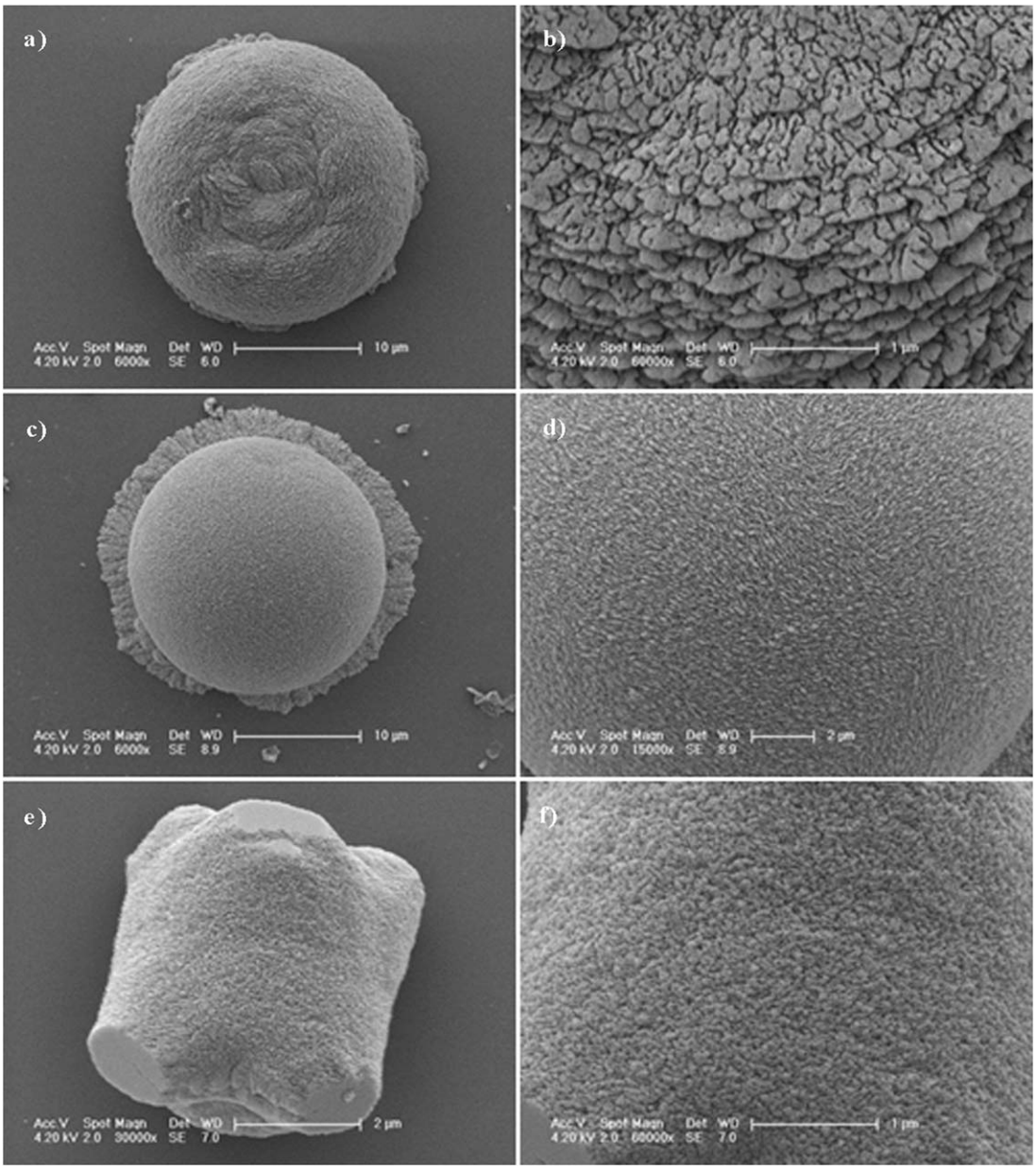

FIG. 4. SEM images of CC particles obtained from by the samples after retained for 5 more days, with their magnified views from their right sides, at different pHs: (a,b) pH 4; (c,d) pH 5, (e,f) pH 8, [PSDA-b-PEG] = 1.0 g/L, [$CaCl_2$] = 1.25 mM.

chiral groups of the polymer decreased and at the same time, the crystal growth rate increased in the case of pH 4, tighter hemispherical superstructures formed (Fig. 4c and d). A local orientation of the nanoparticles on the surface of the semispherical particle can be seen in the Fig. 4d.

The smaller (5–6 μm) particles with six truncated conical arms formed again at pH 8. In the basic medium, formation of nucleation sites and growth rate should be higher whereby the higher amount but small sized particles are formed. The block copolymer should be negatively charged because of deprotonation of aromatic amine groups in the main chain and simultaneously ionization of sulfonic acid groups. It appears that negatively charged block of the copolymer binds only to the edges and vertices of the rhombohedral calcite crystal and other water soluble block sterically inhibits the introduction of the ions into the vertices and edges of the crystal structure at higher pHs.

In order to reveal the polymorph of grown CC crystals obtained in the presence of 1.0 g/L of PSDA-b-PEG solution in the crystallization reaction, XRD and FTIR-ATR were used. The XRD pattern in the Fig. 5 suggests that the predominant polymorph in the particles is calcite.

FTIR-ATR spectra shown in the Fig. 6 were obtained from the samples obtained at different initial pH values. The non-splitting absorption bands at 709.49 and 870.64 cm^{-1} correspond to out of plane bending and in plane bending modes of the carbonate groups of the calcite, respectively. This result suggests that the composition of the sample grown at pH 8 is calcite. However, although the predominant polymorph is calcite, it

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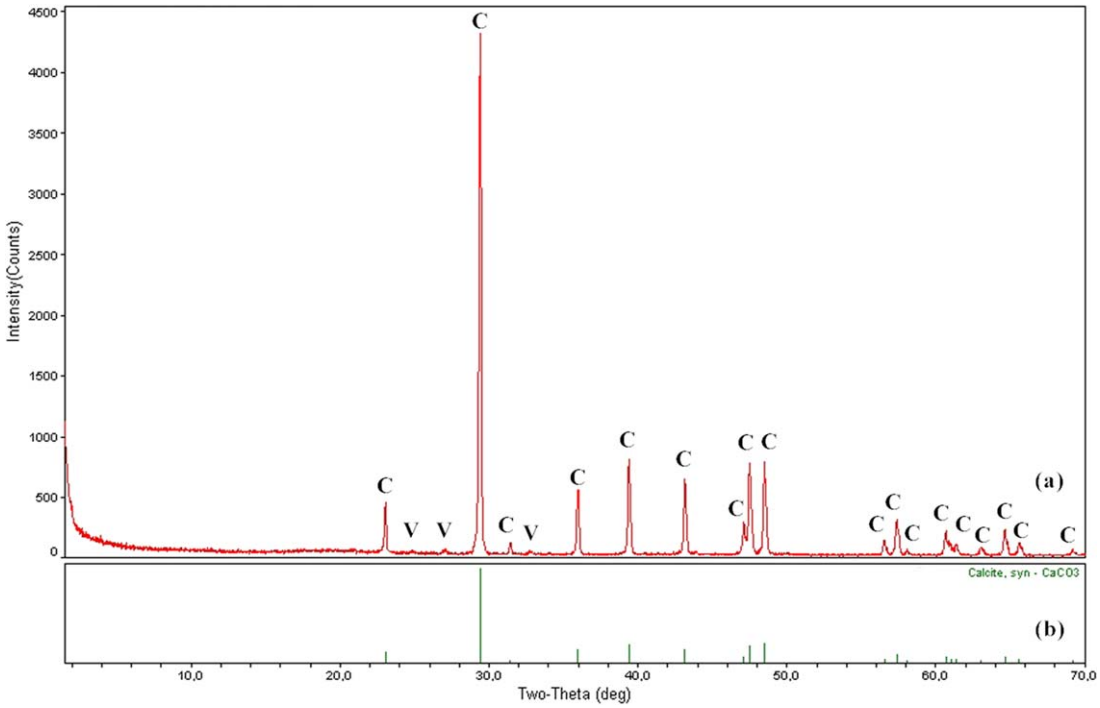

FIG. 5. XRD patterns of CC crystals grown in the presence of PSDA-b-PEG at pH 7 [PSDA-b-PEG] = 1.0 g/L (a) and pure calcite crystals as a reference (b) (V, vaterite; C, Calcite). [Color figure can be viewed at wileyonlinelibrary.com]

seems that the sample grown at pH 4 contains some vaterite polymorph since the small peaks located at 745.72 cm^{-1} can be attributed to the out of plane bending vibrations of the vaterite polymorph [18, 40, 41].

CONCLUSIONS

This is the first study in the literature which used a double hydrophilic block copolymer with a polyzwitterionic block, that is, PSDA-b-PEG to control the CC crystallization.

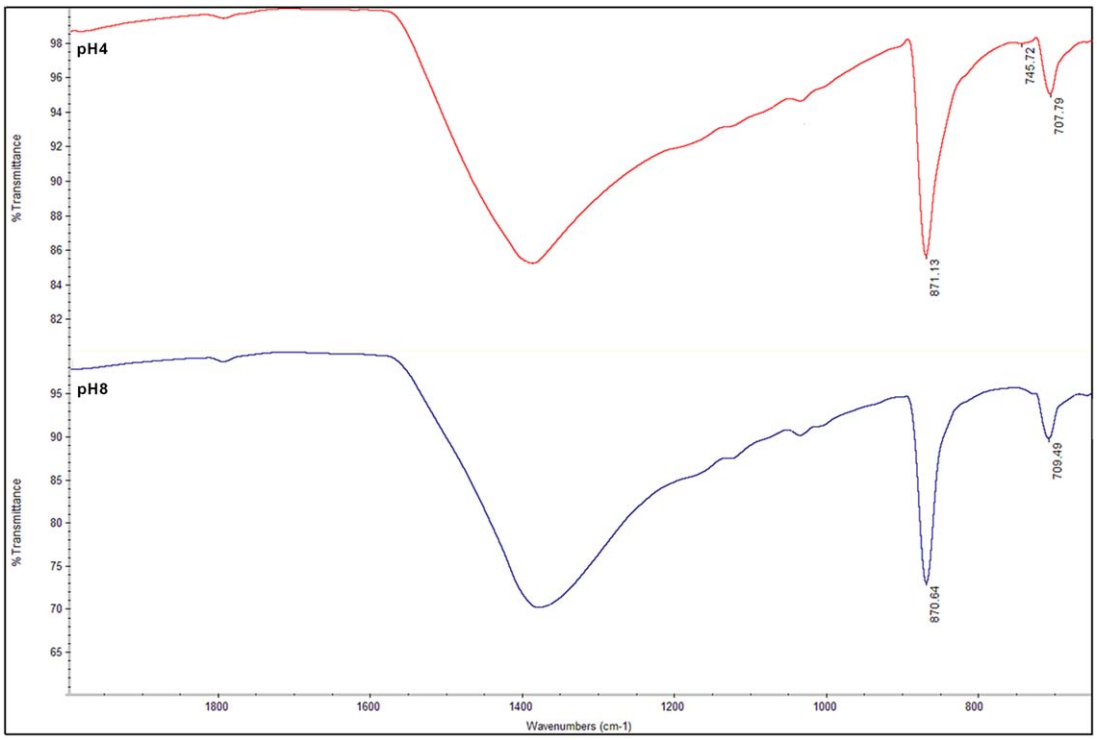

FIG. 6. FTIR-ATR spectra of CC crystals grown in the presence of PSDA-b-PEG at gas-liquid diffusion reaction at pH 4 and pH 8 [PSDA-b-PEG] = 1.0 g/L. [Color figure can be viewed at wileyonlinelibrary.com]

The findings suggest that PSDA-b-PEG can effectively control the morphology of calcite particles by variation of copolymer concentration, initial pH, and reaction time.

At higher pH than IEP, ill-defined irregular particles are formed at higher amount of PSDA-b-PEG since the polymer considerably inhibits the formation of rhombohedral calcites. The rhombohedral crystals turned into the particles with six truncated conical arms at lower concentrations. It can be stated that six truncated conical arms are formed by attachment of the PSDA block to the edges and vertices of the rhombohedra and steric hindrance of PEG block.

Somewhat chiral, toroidal particles in 15-μm size were obtained when initial pH 4 since the PSDA-b-PEG gains chirality because of formation of asymmetric nitrogen atom in acidic medium.

Semispherical particles in 15-μm size were obtained at pH 5, which do not resemble an apparent chirality.

These observations reveal that PSDA-b-PEG has considerable capacity to control the growth mechanism of CC crystallization and consequently the size and shape of the particles.

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