CALCIUM CARBONATE AND POLY(2-ACRYLAMIDO-2-METHYLPROPANESULFONIC ACID-CO-ACRYLIC ACID)

Marcela MIHAI* and Bogdan C. SIMIONESCU

“Petru Poni” Institute of Macromolecular Chemistry of Roumanian Academy,
41 A Grigore Ghica Vodă Alley, 700487 Iași, Roumania

Received May 29, 2018

Calcium carbonate minerals are the most abundant biogenic minerals, both in terms of the amounts produced and their widespread distribution. Adapting the design concepts from nature is a promising pathway to develop advanced materials. The organisms' main strategy to control mineralization is by using organic molecules as insoluble organic matrices, able to generate the proper environment for crystallization and to influence the nucleation processes, or soluble organic additives, which can influence crystals texture and morphology. There is a

significant interest in using soluble additives, which vary from small molecules to large polymers, to control crystallization and generate crystals with complex morphologies. In this context, the aims of the review was to investigate the morphogenesis of calcium carbonate tuned by a strong/weak anionic copolymer, poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) (PAMPSAA), and different parameters – polymer presence and concentration, inorganic compound concentration, pH, and polyelectrolytes complexes.

INTRODUCTION

Nature produces a variety of self-organized and hierarchical microscopic skeletal structures from inorganic and organic components. Such complex, three-dimensional structures, if fabricated synthetically, could have numerous important applications. As an example, porous inorganic microspheres with controlled meso- and macro-porosity might find uses in catalysis, separation technology, and biomedical engineering.¹⁻⁵ Calcium-based minerals represent more than 50% of the 60 different known biominerals. Calcium carbonate is a common mineral that exists as three different anhydrous polymorphs, *i.e.* calcite, aragonite and vaterite, all

of which occur in calcified tissues, and two metastable precursor phases during the initial stages of crystal formation, the monohydrate (monohydrocalcite) and hexahydrate (ikaite) forms of CaCO_3 . Calcium carbonate crystals exhibit different types of morphologies: synthetic calcites normally crystallize out as rhombohedra, aragonites form clustered closely-packed needle-like structures and vaterites invariably exhibit floret-like morphology.

Since the morphology and physicochemical properties, such as solubility and density, depend on each polymorphous crystal, the polymorphic control of the crystals is very important in industrial processes. Most research in calcium

* Corresponding author: marcelas@icmpp.ro

carbonate microparticles synthesis has been done using the mixing of solutions containing calcium and carbonate ions.³⁻⁵ During the fast-reactive crystallization processes, the calcium ions and carbonate groups combine into the amorphous CaCO_3 , the most instable solid-state phase.⁶ Then, the initially formed CaCO_3 is transformed within a few minutes to a mixture of several crystalline CaCO_3 . The transformed carbonates are vaterite and calcite at low temperatures (14-30 °C) and aragonite and calcite at high temperatures (60–80 °C).⁷ The stability of these CaCO_3 crystalline polymorphs decreases in the following order: calcite > aragonite > vaterite.⁸ Actually, the stability and lifetime of these polymorphic species mainly depend on their own solubility in aqueous solution. The spontaneous precipitation of calcium carbonate from aqueous supersaturated solutions depends mainly on supersaturation and the presence of additives, which may act as a nucleation initiation point.

The application of CaCO_3 particles is determined by a number of strictly defined parameters such as morphology, structure, size, specific surface area, chemical purity, and so on.⁹⁻¹¹ Among these factors, particle morphology is the most important one. As a consequence, controllable synthesis of calcium carbonate crystals with uniform size and morphology has been attracting considerable attention due to their fascinating mechanical and optical properties. A promising approach was proved to consist in the use of organic additives and/or templates to control the nucleation, growth, and alignment of inorganic materials. Such an exploration of bioinspired morphosynthesis strategies using self-assembled organic superstructures, organic additives, and/or templates with complex functionalization patterns to template inorganic materials with controlled morphologies and textures has received much attention.^{3-5,12-15} pH-sensitive polymers, which are polyelectrolytes that bear in their structure weak acidic or basic groups that either accept or release protons in response to changes in environmental pH, can be incorporated into inorganic/organic hybrid materials that show both the advantages of inorganic materials (high mechanical stability) and conventional weak polyelectrolyte based materials (the controlled release/uptake properties of the composite microparticles resulting from changes in, among others, pH values and ionic strength).^{5,12,16,17} Besides the common applications of polyelectrolytes in controlled release, the inorganic/organic materials can be also applied as mechanically stable microreactors for

enzymatic reactions and synthesis employing gas phase reagents acting as hollow catalytic microcontainers. The inorganic part can also find medical applications that, together with encapsulated drug material, can provide synergistic curing effects, i.e. the application of hydroxyapatite-containing capsules in bone repair.

In this context, the aim of the review was to investigate the morphogenesis of calcium carbonate in the presence of a macromolecular compounds, namely the strong/weak anionic copolymer which contains 55 mol.-% 2-acrylamido-2-methylpropanesulfonic acid and 45 mol.-% acrylic acid (PAMPSAA), as a function of different parameters – polymer presence, polymer concentration, inorganic compound concentration, pH, and polyelectrolyte complexes.

CALCIUM CARBONATE POLYMORPHS

Amorphous calcium carbonate is considered a precursor in spontaneous precipitation at high supersaturation, being an unstable solid phase that rapidly transforms into a more stable anhydrous state.¹⁸ Amorphous calcium carbonate has a spherical shape of diameter less than 1 μm and turns into a few minutes in vaterite and calcite at 14-30 °C and in aragonite and calcite at 60-80 °C.¹⁹ Calcium carbonate hexahydrate, which crystallizes as well-defined rhombohedral crystals with 10-40 μm in diameter, is a form more stable as compared to amorphous calcium carbonate, keeping it in shape for several days at temperatures below 0 °C, then converting to calcite.²⁰ The monohydrate consists of aggregate platelets in the form of particles of 2-4 μm .²¹ Vaterite is the least stable anhydrous form under normal conditions and exists as polycrystalline spherical particles that can be easily transformed into one of the more stable forms (aragonite, calcite) in contact with water. Due to this instability, vaterite is less present in nature, although it has been identified in sediments, metamorphic rocks or shells.²² More often, vaterite is found together with aragonite and calcite, therefore its investigation is quite difficult.²³ Aragonite is a polymorph of calcium carbonate found in nature in the nacre structure, at about 95%.²⁴ Aragonite is considered the most stable polymorph at high pressures, its shape being that of orthorhombic rods.²⁵ Calcite is the most thermodynamically stable form of calcium carbonate at normal temperature and pressure. Therefore, most of the applications of calcium carbonate are in fact those of calcite or combinations

of calcite and vaterite. Calcite has a rhombohedral shape with well-defined facets.

CALCIUM CARBONATE CRYSTALLIZATION MECHANISMS

Crystallization of calcium carbonate takes place in nature through inorganic precipitation, its organization being influenced by the biological environment.²⁶ Calcium carbonate can also be produced in the laboratory, in or without the presence of the biological environment, the latter being a biomimetic crystallization. The kinetic control of the crystallization process is based on the modification of nucleation activation barriers, the growth and phase transformation.² Thus, crystallization is a sequential process involving structural and compositional modifications of amorphous precursors and crystalline intermediates, and not a single-step process.²⁷ These phase transformations take place along a series of increasingly stable intermediates and depend on the activation free energies of their interconversions, being strongly influenced by the additives.²⁸ The appropriate structural changes occur by dissolution and re-nucleation processes on the surface and / or inside of the preformed particles. Crystallization kinetics can be controlled by modifying interactions between nucleation centres and soluble molecules.²⁹ This can influence the structure of the nuclei, the particle size, the texture and the stability of the intermediate phases.

Jongen *et al.*³⁰ have proposed an aggregated mediated crystallization mechanism, where the aggregation of the crystalline preformed blocks represent a mesoscale assembly process leading to the monocrystals with iso-oriented mosaic textures. The process takes place by fusing the primary nanoparticles into colloidal aggregates, followed by their internal restructuring to produce a crystallographically continuous particle. Alternatively, the nanoparticles can align to produce oriented nanocrystals.³¹ These aggregation-mediated crystallization mechanisms are characteristic of metallic oxides,³² but have also been encountered with calcium carbonate³³ in the presence of some block-copolymer macromolecules.³⁴ Li *et al.*³⁵ have proposed a CaCO_3 crystallization mechanism based on strong interactions between organic molecules and inorganic nuclei that allow the formation of colloidal aggregates containing primary hybrid particles with metastable amorphous centres. In time, amorphous nanoparticles crystallize, the process being coupled with mesophase

transitions involving adsorption of polymers or surfactants on the surface. By modifying the molar ratio of anions to cations, the binding interactions between organic molecules and the inorganic surface can be modified, leading to the formation of particles with different morphologies.

Mihai *et al.*³⁶ proposed a pathway for the formation of CaCO_3 capsules in the presence of pectins and nonstoichiometric polyelectrolyte complexes. The process involves the following steps: (1) interaction of calcium ions with ionic or ionizable groups along the polymer chain or on uncomplexed nanoparticle fragments with gel-forming microparticles and crystallization of calcium carbonate in calcium rich areas; (2) growth of calcium carbonate crystals with microparticle formation (in the first minute of crystallization); (3) dissolution of the less stable (amorphous and vaterite) CaCO_3 fractions mainly by dissolving the core of the microparticles; (4) secondary nucleation of the calcite crystalline polymorph on the external surface; (5) progressive increase of the thickness of the crystalline wall as the core is emptied, yielding hollow microspheres.

In the case of biomineralization, organic molecules are used as precipitation initiators or as selective inhibitors.³⁷ The precipitate forms on the surface of the insoluble organic matrix, which has a structural role and contains nucleation points. Biological precipitation of CaCO_3 occurs through two general mechanisms,³⁸ namely microbial / biologically induced precipitation or biologically-influenced precipitation. Biologically induced precipitation is the direct result of microbial activity that generates the biochemical conditions necessary to facilitate precipitation, while biologically-influenced precipitation is a passive indirect process resulting from interaction between extracellular biopolymers and geochemical environments.³⁹ Braissant *et al.* states that the precipitation of calcium carbonate depends on the alkalinity of the carbonate and the availability of free calcium ions.⁴⁰ The concentration of these two components must be higher than saturation, and, in the absence of organic molecules and under relatively low supersaturation conditions, the formation of calcium carbonate follows a homogeneous classical crystallisation pattern. In this case, the partial CO_2 pressure plays a major role in determining the balance of ionic charges. Calcite surface is negatively charged in CO_2 -free water and becomes more positively charged with increasing CO_2 concentration. Thus, a continuous dissolution and re-precipitation of the ions takes place on calcite surface.⁴¹

Under high supersaturation conditions, crystallization/precipitation of calcium carbonate takes place in a very short time interval, in several stages.⁴² Initially, in a monophasic homogeneous system, the dissolved monomer units (cations or anions) can associate forming chained or compact structures. After reaching a critical level of supersaturation, a phase separation occurs with the formation of dense liquid droplets, bi-continuous liquid structures or solid nuclei with amorphous or crystalline structures. Over time, liquid precursors and / or solid nuclei convert into nanoparticles, which may be stable, can grow into larger amorphous or crystalline particles, possibly with amorphous transformations in crystalline, or can aggregate randomly or in an ordered manner. The final products obtained by maturing can be colloidal nanoparticle suspensions, amorphous microparticles or crystals of different aspects, depending on the reaction conditions and the presence of the additives.

The use of non-biological macromolecules in the crystallization medium may result in crystals having special morphologies. Gower *et al.*⁴³ used poly(aspartic acid) to obtain helix crystals on their surface. Falini *et al.*⁴⁴ used poly(aspartic) and poly(glutamic) acids to obtain calcite, aragonite and vaterite crystals, depending on the ratio of the polymers. Guillemet *et al.*⁴⁵ used a poly(ethylene oxide) and polyacrylic-based composites to stabilize spherical amorphous calcium carbonate particles. Previous studies showed that protein macromolecules, as soluble or insoluble matrix, affect the crystallization of CaCO_3 .⁴⁶ Various self-assemblies of organic compounds, especially the acidic macromolecules, are shown to be responsible for nucleation and / or stabilization of the particular CaCO_3 polymorphs.^{2-5,47-49} The functional groups (especially the carboxylic ones) on the gel-like structures influence the formation of crystals due to electrostatic forces, spatial location, match of crystal lattices, stereochemistry.⁵⁰⁻⁵³ Several studies dealt with the *in-vitro* effects of various additives (surfactants, polymers and block copolymers, proteins) on the morphology and size of CaCO_3 particles.⁵⁴⁻⁵⁷

Co-precipitation with different excipients such as divalent cations, organic solvents and macromolecules (natural or synthetic) showed a strong effect on the morphology of the formed CaCO_3 materials.^{3-5,14,16,58-61} Difficulties in understanding their roles arise from the complexity of the investigation of such mechanisms in the solid-liquid system and the large ability of CO_3^{2-} anions

to form different supramolecular structures. Thus, is still far away from fully understanding the formation of CaCO_3 composites with various shapes, polymorphs, composition, and stability, etc. in either natural or mimic systems, especially those mediated by biomacromolecules or synthetic polymers.

A wide range of copolymers, typically comprising a nonionic block and an ionic block bearing side groups such as carboxylates, sulfonates, and phosphates,⁶²⁻⁶⁶ have been shown to mediate the formation of calcite particles with morphologies including hollow spheres, spherules, and dumbbells. The purpose for tuning the copolymer structure is huge since, for example, subtle changes in the relative block lengths can lead to significant changes in particle morphology.⁶³ Furthermore, variation of the composition and pH of the crystallizing solution can change the mode of interaction between the developing particles and the copolymer chains, resulting in large morphological effects.

CALCIUM CARBONATE POLYMORPHS STABILITY

Changing the thermodynamic parameters of the system can lead to the instability of different polymorphs and implicitly to their evolution towards other more stable structures. The polymorphs modification and the transition to other phases is based on the modification of mineral structure as a result of the tendency to reach the thermodynamic equilibrium state. The mechanisms of the changes can be understood by following their structural aspects, *i.e.* structural phase transformations.

The trend of the evolution of phase transformations in natural systems is described by Ostwald's law:⁶⁷ when a compound with several possible polymorphic changes crystallizes, the first formed is that which is thermodynamically unstable under the given conditions, and then it gradually turns into more stable phases. This trend is governed by the crystal nucleation energy that depends on their surface energy (nucleation energy decreases with surface energy), and thus by the ability of crystals to adsorb outer particles. Thus, the presence of foreign particles of the chemical composition of the polymorphic phase may inhibit stable phase nucleation. Consequently, the existence of metastable phases in natural rocks is not unusual. All endogenous rocks formed at pressures and / or high temperatures are metastable systems and evolve

slowly to stable phases under normal pressure and temperature conditions. Reconstructive transformations imply a major reorganization of the crystalline structure by breaking the interatomic bonds and rebuilding new connections, requiring high activation energies for switching from one level of free energy to another. Since high temperature intervals are required to reorganize the structure, these transformations are irreversible. Kinetically, these transformations are very slow, so that the stability of the evolutionary phases of the structure depends very much on the evolution of pressure and temperature parameters. If the change is slow, the structure can adapt and the system goes through successive steady states; if the change is rapid, undefined metastable phases remain in the system indefinitely. The structural changes in reconstructive transformations are reflected by the values of some characteristic parameters of the structure: symmetry, interatomic distances, binding angles, atom coordinates in the elemental cell, atom coordination, density. In the case of CaCO_3 , it was considered that, during the first crystallization stage, unstable amorphous phase formation takes place, which subsequently transforms into a metastable phase of vaterite or aragonite and then is further transformed into a calcite stable phase. The precipitation of polymorphs depends on different factors such as temperature, environmental pH, concentration of individual components, oversaturation, ionic strength or impurities.

The pH of the initial reaction mixture influences the CaCO_3 binding strength which is responsible for the formation of different polymorphs.⁶⁸⁻⁷⁰ It was shown that starting from a mixture of CaCl_2 and NaHCO_3 solutions in which the $\text{Ca}^{2+} / \text{CO}_3^{2-}$ concentration ratio was of 1: 1 and 10: 1 at a temperature close to 0 °C and a pH of 13.4 only ikaite was formed. At the same temperature, but at pH = 9.0, the precipitation yielded to vaterite and only a very small percentage of ikaite. These polymorphs were obtained irrespective of the concentration ratio of Ca^{2+} and CO_3^{2-} , this demonstrating that the selection of polymorphs was influenced by solution pH. The influence of pH on polymorphs can be attributed to the concentration of HCO_3^- and CO_3^{2-} ionic species.

Weiss *et al.*⁶⁸ studied the influence of temperature on calcite, aragonite and vaterite polymorphs production starting from ammonium carbonate and calcium acetate. The authors synthesized CaCO_3 at different temperatures between 25–80 °C and noticed that at temperatures in the 25–30 °C range the formation of vaterite was

favoured. With increasing the temperature, an increase in the dimensions of the vaterite crystals was observed, and at temperatures above 50 °C mainly calcite was obtained. The aragonite polymorph was formed above 70 °C. Chen *et al.*⁷¹ studied the effect of temperature on polymorphs precipitation in the 30–80 °C temperature range, using 1:1 $\text{CaCl}_2 / \text{NH}_4\text{HCO}_3$ ratio. The results showed the formation of vaterite particles of lamellar structure at 30–40 °C, of a mixture of calcite, aragonite and vaterite polymorphs at 50–70 °C and of aragonite at 80 °C. These results were explained by thermodynamic calculations confirming that the value of the $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$ ratio decreases with increasing temperature, thus favoring the formation of vaterite at low temperature and of aragonite at high temperatures.

Pai *et al.*⁷² and Yan *et al.*⁷³ have studied the influence of the rate of stirring of the reaction mixture on the formation of polymorphs. Thus, calcium carbonate microparticles were obtained by the addition of NaHCO_3 to an aqueous solution of CaCl_2 and polyelectrolytes. Particles morphology and type of polymorphs were adjusted by varying the mixing rate. It has been noticed that at higher stirring rates nanocrystalline spherical particles are formed and at low stirring nanostructured calcite particles of rhombohedral morphology are formed.

COMPOSITES BASED ON PAMPSAA

The crystallization of CaCO_3 from aqueous solutions tuned by PAMPSAA has been followed by colloidal crystallization from inorganic supersaturated solution.¹² The process was initiated by rapid mixing of equal volumes of CaCl_2 and Na_2CO_3 solutions, in the presence of PAMPSAA.

As shown in SEM images in Figure 1b, spherical particles, of about 8–10 μm in diameter were obtained, smoother and bigger comparative with CaCO_3 microparticles prepared in the same supersaturation conditions (Figure 1a). The CaCO_3 microspheres revealed a bimodal particle size distribution (span = 1.4), the median diameter, $d(0.5)$, being $7.4 \pm 0.24 \mu\text{m}$. As shown in Figure 1b, the presence of PAMPSAA during composite microparticle formation determines an increase in particle size ($d(0.5) = 11.2 \pm 1.31 \mu\text{m}$) and mean volume weighted ($[D4,3] = 12.1$), and a decrease in specific surface area ($\text{SSA} = 1.1$). At the same time, a bimodal distribution was observed for composite $\text{CaCO}_3/\text{PAMPSAA}$ microspheres (span = 1.8).

Fig. 1 – SEM micrograph for (a) CaCO_3 and (b) $\text{CaCO}_3/\text{PAMPSAA}$ microparticles (scale bar 10 μm) and some particle size distribution statistics (mass median diameter, volume weighted mean diameter, the width of the particles size distribution and the specific surface area); (c) circularity vs particle size obtained by FPIA measurements; (d) FTIR spectrum of $\text{CaCO}_3/\text{PAMPSAA}$ particles.

The representation of circularity vs particle size of the $\text{CaCO}_3/\text{PAMPSAA}$ particles obtained by Flow Particle Image Analysis (FPIA) measurements are included in Figure 1c. The zones marked with red squares represent: I – fine fraction, II – needle-like fraction, III – coarse grain fraction, IV – smaller size and lower circularity indicating crushing, V – larger size and lower circularity indicating agglomeration, VI – larger size with no reduction in circularity indicating chemical size enlargement, VII – spherical particles. Circularity analysis shows an average value of 0.908 ± 0.084 , with $\sim 90\%$ of particles under 10 μm , for CaCO_3 and 0.941 ± 0.153 , with $\sim 94\%$ of particles under 20 μm , for $\text{CaCO}_3/\text{PAMPSAA}$. For both samples the circularity distributions showed a relatively broad polydispersity. Moreover, the representation of circularity vs particle size shows similar polydispersities for both investigated samples, with larger and more circular particles obtained for $\text{CaCO}_3/\text{PAMPSAA}$ sample.

The chemical composition of the CaCO_3 and carbonate/PAMPSAA microparticles was evaluated by infrared spectroscopy. FTIR spectra of both

CaCO_3 and $\text{CaCO}_3/\text{PAMPSAA}$ particles (Figure 1d) show the fundamental bands of vaterite⁷⁴: 1089 cm^{-1} - the symmetric stretch (ν_1), 878 cm^{-1} - the carbonate out-of-plane bending absorption (ν_2), a split peak at 1413 and 1490 cm^{-1} (ν_3 - asymmetric stretch) and at 745 cm^{-1} - the carbonate in-plane bending absorption (ν_4). The small bands at 850 (ν_2) and 713 (ν_4) cm^{-1} are characteristic for calcite. The increase of calcite characteristic bands in $\text{CaCO}_3/\text{PAMPSAA}$ particles suggested that the polyanion favors the formation of this most stable polymorph. Besides the differences in bands intensity, due to different ratio between vaterite/calcite phases, some other absorption bands, located at 1403 and 1799 cm^{-1} , are detected in the spectrum of $\text{CaCO}_3/\text{PAMPSAA}$, these being ascribed to the copolymer adsorbed on the surface or trapped into the as-prepared particles.

XRD diffractogram (Figure 2) show peaks at $2\theta = 24.89^\circ, 27.06^\circ, 32.78^\circ, 43.84^\circ, 49.09^\circ, 50.08^\circ$ and 55.81° corresponding to the (110), (112), (114), (300), (304), (118) and (224) planes of vaterite, as well as peaks at $2\theta = 29.45^\circ, 35.97^\circ, 39.43^\circ$ and 47.15° assigned to (104), (110), (113)

and (024) planes of calcite. The XRD patterns demonstrate that the composite particles are composed mainly of vaterite (hexagonal structure)

and calcite (rhombo-H-axes structure), these results being in agreement with FTIR observations (Figure 1d).

Fig. 2 – XRD patterns of $\text{CaCO}_3/\text{PAMPSAA}$ microparticles; blue and green marks represent the calcite and vaterite polymorph, respectively.

Fig. 3 – (a) SEM images of $\text{CaCO}_3/\text{polyanion}$ particles prepared with constant inorganic concentration (0.2 M) and different initial concentrations of polymers; scale bar – 10 μm ; (b) mean particles size (closed symbols) and circularity (open symbols); (c) particles charge density, CD (closed symbols) and apparent zeta-potential values, ζ_{app} , (open symbols).

The CaCO_3 and $\text{CaCO}_3/\text{PAMPSAA}$ microspheres were characterized by XPS and the relative atomic concentrations of C, O, Ca, S and N on particles surface were determined. The C/Ca ratio of CaCO_3 microparticles is relatively low (~ 0.83) compared to the theoretical ratio (1.0), whereas the O/Ca ratio is higher (3.5) than the theoretical one (3.0). Similar results were reported in the literature⁷⁵ and were ascribed to vaterite crystallization form. For the $\text{CaCO}_3/\text{PAMPSAA}$ sample the C content is 5.74 %, lower than that of CaCO_3 ; the differences consists from adventitious carbon and PAMPSAA contribution. The C/Ca ratio is very close to the theoretical ratio in carbonate (0.988%), whereas the O/Ca ratio is much higher (5.48 %) due to copolymer contribution. The atomic concentration of nitrogen (0.91%) and atomic ratio $\text{N/Ca} = 0.16$, suggest that the copolymer content in hybrid particles is 6.25 times lower than the inorganic part, very close to the ratio used in the preparation of hybrid particles ($\text{CaCO}_3/\text{polymer} = 6.6$).

INFLUENCE OF PAMPSAA CONCENTRATION

The influence of PAMPSAA concentration on $\text{CaCO}_3/\text{polymer}$ composite microparticles formation has been followed by varying polymer concentration (0.1–0.5 wt.%) and keeping constant the inorganic concentration (0.2 M).⁷⁶

As expected, polymer concentration has an important role in particles surface morphology (Figure 3a) and mean size (Figure 3b). Thus, the size of PAMPSAA based particles decrease with increasing polymer concentration on the investigated concentration range (0.1 – 0.5 wt.%). Moreover, as compared to the typical cauliflower shape of bare CaCO_3 particles prepared with the same initial inorganic concentration,⁷⁷ low amounts of PAMPSAA (0.1 and 0.2 wt%) induced the formation of smoother particles, with very small grain size. A further increase of initial polymer concentration up to 0.5 wt.% determines the appearance of some agglomerated features evident on the particles surface, with the simultaneous decrease of composite particles size, as also observed by FPIA (Figure 3b). The features on the surface are probably given by the formation of denser cross-linked networks with increasing the calcium content into the composite particles. Similar curves shapes were obtained for the electrokinetic properties, such as charge density and apparent zeta-potential values, which were

determined as depending on the initial concentration of PAMPSAA (Figure 3c). Polymer presence increased the negative values of charge density and of the apparent zeta-potential, as compared to bare CaCO_3 particles.

To evidence the presence of the polymers on the surface of the composite materials, XPS spectra were recorded. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley.⁷⁸ The high-resolution spectra were deconvoluted by means of a computer routine (Kratos Analytical, Manchester, U.K.). The maximum information depth of the XPS method is about 8 nm for the C 1s region.⁷⁹ Calcium can be considered as label for the inorganic phase, and therefore, changes in the relative content of Ca 2p can be explained by the distribution of the organic phase in the inorganic phase. The use of PAMPSAA to control the crystallization process influences the $[\text{Ca}]:[\text{O}]_{\text{spec}}$ ratios. Even if the majority of oxygen is part of the inorganic phase, the polymers also contribute to total oxygen content of the sample. Therefore, the decrease of the $[\text{Ca}]:[\text{O}]_{\text{spec}}$ ratios for PAMPSAA-based samples suggests an increase of oxygen content, and sustain polymer presence in the composite microparticle. The increase of the initial amount of PAMPSAA during the crystallization process lowered the $[\text{Ca}]:[\text{O}]_{\text{spec}}$ ratio. These findings are in good agreement with the results from SEM images for the sample with 0.4 wt % PAMPSAA (Figure 3a), which show some irregularities on particles surface. Furthermore, electrokinetic measurements verified a stronger negative character of the surfaces of these composite particles (Figure 3c).

As mentioned above, calcium can be considered as a label element for the inorganic phase, while the majority of nitrogen is introduced by the PAMPSAA polymer. Hence, the increase of the relative amount of nitrogen ($[\text{N}]:[\text{C}]_{\text{spec}}$) is an evidence for the presence of the polymer on composite particle surfaces. The sulphonate groups of the PAMPSAA polymer should also introduce sulphur in composite particle surface. According to the stoichiometry of the polymer chain, the $[\text{N}]:[\text{S}]$ ratio should be $[\text{N}]:[\text{S}] = 1$. However, for all composite particle surfaces lower amounts of sulphur were observed. It is assumed that as first step of crystal formation, when calcium ions were added to polymer solution, the high affinity of polymer sulphonate groups to calcium ions fixes

these ions irreversibly in their immediate environment. The further growth of CaCO_3 crystals takes place around these nucleation centres. Thus, the sulphonate groups appear shielded by calcium, while the amide groups are just surrounded by the calcium carbonate crystals. Moreover, polymer chain flexibility can further influence their arrangements into the composites and on their surface. The chain structure of PAMPSAA was 3D optimized (using ACD/Lab 6.0 software) and its interaction with Ca^{2+} ions is schematically represented in Figure 4.

As shown in Figure 4, intra- and inter-chains ionic crosslinks in $\text{CaCO}_3/\text{PAMPSAA}$ composites can occur: inter-chains, between the $-\text{SO}_3^-$ groups of different PAMPSAA molecules, and intra-chain, between $-\text{SO}_3^-$ and $-\text{COO}^-$ or two $-\text{COO}^-$ groups on the same polymeric chain. Thus, the $\text{CaCO}_3/\text{PAMPSAA}$ composite particles may have on the surface some free $-\text{SO}_3^-$ groups, which can be detected by XPS. To identify the polymer and evaluate its contributions to the C 1s and N 1s peaks, high-resolution element spectra were recorded (Figure 5).

Fig. 4 – Schematic representation of the chain structure of PAMPSAA 3D optimized (using ACD/Lab 6.0 software) and its interaction with Ca^{2+} ions.

Fig. 5 – High-resolution C1s and N1s element spectra of $\text{C}_{0.2}\text{PAMPSAA}_{0.4}$ composite particles.

The shape of the C 1s spectrum is characterized by carbon atoms constituents of the carbonate group and carbon atoms showing the presence of surface contaminants. The carbonate groups (CO_3^{2-}) of the inorganic CaCO_3 phase were clearly identified as component peaks CO_3 (the binding energies for these component peaks were not different from the binding energy determined for the CO_3 component peak of the bare CaCO_3 sample. Component peaks *A* at 285.00 eV arose from photoelectrons escaped from saturated hydrocarbons (C_xH_y). The C 1s spectrum of the CaCO_3 /PAMPSAA composite sample (Figure 5) shows two component peaks, *D* and *F*, which were assigned to the carbonyl carbon atoms of the polymer amide groups ($\text{O}=\text{C}-\text{NH}-\text{C}$) and the carbonyl carbon atoms of the carbonic acid groups ($\text{O}=\text{C}-\text{OH}$) and their corresponding carboxylates ($\text{O}=\text{C}-\text{O}^- \leftrightarrow {}^-\text{O}-\text{C}=\text{O}$). Beside the carbon atoms in α -position to the strongly electronegative carbonyl carbon atoms amine-sided $\text{C}-\text{N}$ bonds of the amide groups and $\text{C}-\text{S}$ bonds also contributed to component peak *B*. The N 1s spectrum of PAMPSAA-based composite sample showed with component peak *K* (at 399.77 eV) nitrogen atoms of the polymer's amide groups ($\text{O}=\text{C}-\text{NH}-\text{C}$).

INFLUENCE OF INORGANIC CONCENTRATION

Composite microparticles were also prepared by using 0.2 wt.% PAMPSAA and different calcium and carbonate concentration in the starting solution (0.05–0.3 M).⁷⁶ The morphology of particles was evidenced by SEM (Figure 6a), the particles mean size and circularity by FPIA (Figure 6b) and the electrokinetic values were investigated with the PCD Particle Charge Detector and Zetanosizer (Figure 6c).

As shown in Figure 6, the inorganic content has an important role on particle size and morphology. Thus, at very low inorganic content (0.05 and 0.1 M) the formation of a mixture of particles with irregular shapes and a large size distribution is observed. The further increase of calcium and carbonate concentration in the initial solutions leads to the formation of bigger and more spherical shaped particles for both polymer-based composites. Taking into account the microparticles shape as observed in the images included in Figure 6 one can assume that PAMPSAA favours the formation of vaterite polymorph at inorganic concentrations higher than 0.1 M. The particles

size significantly increases with increasing inorganic concentration from 0.05 M to 0.3 M, irrespective of polyanion structure. However, as shown in Figure 6b (closed symbols), polymer presence leads to the formation of slightly smaller particles as compared to bare CaCO_3 particles prepared with the same inorganic concentration. At the same time, the particles circularity (empty symbols in Figure 6b) increases with inorganic concentration up to 0.15 M and remains almost constant at higher concentrations, irrespective of polymer presence. The presence of polymers during particle preparation increases particle charge density, CD (closed symbols in Figure 6c), irrespective of inorganic ions concentration. This behavior is an evidence of the presence of polymer in composite particles. Less negative CD values were obtained with increasing inorganic concentration due to the decrease of polymer content into the composites, irrespective of the used polymer. The presence of PAMPSAA in CaCO_3 microparticles has been also confirmed by the zeta-potential values (Figure 6c, open symbols). The negative zeta-potential values determined for the differently prepared samples followed the same trend as CD and can be explained considering that the macromolecules have been intertwined in the carbonate particles.

INFLUENCE OF INITIAL pH

The formation of hollow shells of calcium carbonate has been also followed by the principle of controlled nucleation and growth, using the same polyanion substrate, PAMPSAA, changing the calcium and carbonate ions content in the starting solutions, when the pH of the mixture was 11 (as compared to pH = 9 in a previous study).⁷⁰ Previous studies show that above pH = 10, carbonate ions become the dominant species in the reaction mixture.^{4,80} Therefore, the formation mechanisms of empty particles is expected to take place in two steps: (1) interaction of acidic groups along the polymeric chain with carbonate ions forming gel microparticles, thus providing the template upon which crystallization can occur; (2) calcium carbonate crystallization promoted by the calcium rich sites at template surface. The tendency of the system to crystallize on gel particle surface led to the formation of a shell of calcium carbonate. Figure 7 shows the comparative SEM micrographs of calcium carbonate crystals formed with and without added strong/weak anionic copolymer PAMPSAA.

Fig. 6 – (a) SEM images of CaCO_3 /polyanion particles prepared with 0.2 wt.% PAMPS concentration and different concentrations of calcium and carbonate ions; scale bar – 10 μm ; (b) mean particles size (closed symbols) and circularity (open symbols); (c) particles charge density, CD (closed symbols) and apparent zeta-potential values, ζ_{app} , (open symbols).

Fig. 7 – (a) SEM images of CaCO_3 particles formed at pH = 11, for different PAMPSAA contents; (b) particle size distribution vs particle diameter; (c) XRD patterns of particles.

Fig. 8 – Wide-scan XPS survey spectra of CaCO_3 /PAMPSAA particles prepared at pH = 11 and high-resolution XPS scans of N1s and S 2s.

As can be seen in Figure 7a, without a polymeric template a mixture of spherical and cubic particles has been obtained, whereas in the presence of the PAMPSAA copolymer (Figure 7b) hollow-structured spherical particles were formed. Increasing polymer concentration from 0.02 to 0.04 wt%, a slight increase of particles size was observed, probably due to the formation of larger gel particles in the initial step of hollow-structured particles preparation. As Figure 7b shows, a clear bimodal distribution in particle size was observed for the CaCO_3 microparticles. The diameter corresponding to the first maximum in volume percent (D_m), located at $\sim 6.9 \mu\text{m}$, is close to the sizes observed in the micrograph shown in Figure 7a, whereas the second D_m , located at $\sim 41.7 \mu\text{m}$, can be ascribed to the agglomerated structures. The presence of PAMPSAA during the composite hollow particle formation causes a decrease in particle size up to $\sim 6.5 \mu\text{m}$, the polymer content of 0.04 wt.% leading to the formation of well-structured hollow shells. Also, a bimodal distribution was observed for composite microspheres, but with a lower particle agglomeration tendency, the second maximum of particles size being much lower, irrespective of polymer concentration.

The XRD patterns of carbonate particles obtained in absence or presence of PAMPSAA aqueous solutions (Figure 7c) demonstrate that CaCO_3 samples contain two polymorph fractions, vaterite (hexagonal) and calcite (rhombohedral). The lattice constants for each polymorph detected in CaCO_3 sample were similar to those determined in our previous study ($a = b = 4.988 \text{ \AA}$ and $c = 17.061 \text{ \AA}$ for calcite and $a = b = 7.147 \text{ \AA}$ and $c = 16.917 \text{ \AA}$ for vaterite).⁷⁷ In the PAMPSAA containing samples only calcite polymorph was detected, in agreement with the results reported in other studies,^{4,52} where it was observed that

calcium carbonate crystallization on gel particle surface takes place mainly in the form of calcite.

The CaCO_3 /PAMPSAA hollow microspheres, prepared at pH = 11, were characterized by XPS and the relative atomic concentrations of C, O, Ca, S and N on particles surface were determined. Figure 8 shows the XPS wide-scan spectra of the microspheres, as well as the high-resolution scans of N1s and S 2s for both samples.

The presence of PAMPSAA on the surface of composite particles is clearly evidenced in the XPS wide scan spectra by the appearance of the N 1s, S 2s, and S 2p peaks (Figure 8). The atomic concentration of N and S in each sample, determined by XPS, and the corresponding atomic ratio Ca/N and Ca/S, are very close to the ratio used during the preparation of the particles and shows that almost all copolymer was trapped into the particles.

Particles charge density, CD, slowly increased when the polymer has been involved in particles preparation: from -10.61 meq/g for CaCO_3 particles up to -15.22 meq/g for sample with 0.02 wt.%, and -17.7 meq/g for sample with 0.04 wt.% PAMPSAA. This behaviour is an evidence of polymer presence in the composite particles. However, the small increase of particles CD can be ascribed to their formation mechanism, where the polymer is located mainly inside the particles, and the calcite on the surface. The presence of PAMPSAA in CaCO_3 microparticles has been also confirmed by the zeta-potential values. The zeta-potential of a colloidal particle is mainly determined by its surface charge. Negative zeta-potential average values of -21.5 , -30.3 and -37.1 mV were measured for the particles without or with 0.02 and 0.04 wt.% PAMPSAA, respectively. This increase of negative zeta-potential of the surface followed the same trend as CD and can be explained

by the fact that PAMPSAA macromolecules have been intertwined in the carbonate particles.

CaCO₃/NPEC COMPOSITES

Even if there are numerous studies on polyanions control of CaCO₃ growth, the use of non-stoichiometric polyelectrolyte complexes (NPEC) as templates for controlling CaCO₃ crystals growth has been reported up to now only by our group.^{36,76,81} Polyelectrolyte complexes (PECs) are obtained by mixing aqueous solutions of oppositely charged polymers.⁸² PECs are of interest due to their facile preparation and responsiveness to environmental stimuli. Moreover, using water as a solvent, PECs are attractive for biomedical applications. At relatively low concentrations and when one of the components is taken in excess, PEC formation can lead to stable colloidal dispersions.⁸³⁻⁸⁵ The characteristics of the polyelectrolyte components (molecular weight, nature of ionic groups, charge density, and architecture) and the solvent (ionic strength, pH) determine the internal structure of the particles.

In this context, the formation of CaCO₃/polymer composite microparticles was followed using NPEC with negative charges in excess.⁷⁶ To prepare the NPEC, chitosan (CS) was used as polycation and PAMPSAA as polyanion. Dispersions of NPEC were prepared at room temperature, by mixing the solutions of oppositely charged polyelectrolytes in appropriate proportions. Thus, the NPEC dispersions used in this study differs by the ratios between the negative and positive charges (n^+/n^-) – 0.2 and 0.4. Therefore, different charge densities (CD), zeta-potential values (ZP),

particle sizes (D_h) and size distributions (PI) are obtained (Table 1).

The difference in particles size and surface charge (CD and ZP) with the variation of the ratio between charges (n^+/n^-) can be ascribed to polymer presence in the composite microparticles.

The CaCO₃/NPEC composite samples were coded C_xN_y, where x is the molar concentration of Na₂CO₃ and CaCl₂ aqueous solutions (0.2 M), and y is the molar ratio of NPEC dispersion. Table 2 shows the electrokinetic results (CD and ZP) and FPIA mean diameter and circularity for as prepared composites.

Compared with the starting NPEC dispersions, the charge densities of the particles and their ZP values sharply decrease following composite formation (Table 2) up to close to bare CaCO₃ particles values.^{77,86} This can be considered as a hint of the good NPEC embedment into the composites. However, compared to the particles prepared with the same polyanion and the same CaCO₃ content (Figure 3), higher particles sizes were obtained when NPECs were used (Table 2). One can assume that the use of complex nanoparticles as template may restrict CaCO₃ growth, even if the polyanion in excess can act as a ligand for NPEC and CaCO₃ nanocrystals.

As shown in Figure 9, particles surface morphologies are very similar, irrespective of NPEC molar ratio, and differ from those of the particles prepared with the polyanion as a template (Figure 3). These observations are in agreement with the values of the parameters listed in Table 2, when almost the same values were obtained for the investigated parameters for all NPEC tested as a template in CaCO₃ composite preparation.

Table 1

Some characteristics of NPEC dispersions as a function of the positive and negative charges ratio (n^+/n^-): charge density (CD), zeta-potential (ζ_{app}), hydrodynamic diameter (D_h) and size distributions (PI)

NPEC	n^+/n^-	CD*, meq/g	ζ_{app} *, mV	D_h , nm	PI
PAMPSAA/CS	0.2	-74.9 ± 0.9	-26.1 ± 0.5	172.1 ± 2.5	0.066 ± 0.004
	0.4	-49.3 ± 0.6	-21.5 ± 0.4	184.8 ± 3.6	0.079 ± 0.011

* determined at pH = 8

Table 2

Electrokinetic results (charge density - CD and zeta-potential - ζ_{app}) and FPIA mean diameter (D_m) and circularity (C) for NPEC based composites, with initial inorganic concentration of 0.2 M

Sample	n^+/n^-	CD, meq/g	ζ_{app} , mV	D_m , nm	C
C _{0.2} NPEC _{0.2}	0.2	-12.2 ± 0.8	-11.6 ± 0.5	10.75 ± 1.51	0.983 ± 0.011
C _{0.2} NPEC _{0.4}	0.4	-11.7 ± 0.5	-11.4 ± 0.8	10.85 ± 1.28	0.987 ± 0.009

Fig. 9 – SEM images of CaCO_3 /NPEC particles prepared with constant inorganic concentration (0.2 M) and different NPEC molar ratios between charges; scale bar – 10 μm .

Table 3

XPS determined atomic composition of samples with NPEC dispersions with $n^-/n^+ = 0.4$

	$\text{C}_{0.2}\text{N-PAMPSAA}_{0.4}$
$[\text{N}]:[\text{C}]_{\text{spec}}$	0.025
$[\text{O}]:[\text{C}]_{\text{spec}}$	0.519
$[\text{S}]:[\text{C}]_{\text{spec}}$	0.009
$[\text{Ca}]:[\text{C}]_{\text{spec}}$	0.124

To determine the polymorph content on the CaCO_3 particles obtained in the presence of NPECs aqueous dispersions and compare it with the results on the composites prepared in the presence of polyanions, the X-ray diffractograms were registered. XRD semi-quantitative analysis results were obtained with an EVA soft from DiffracPlus package and an ICDD-PDF2 database, based on the patterns' relative heights. The polymorph ratio in the investigated composite particles is slightly influenced by the ratio between organic and inorganic part and the use of NPECs with polyanion excess. Thus, when the synthetic PAMPSAA polyanion was used the calcite polymorph growth was almost inhibited (just 6.5 - 7.5 % calcite in PAMPSAA -based samples), irrespective of polymer content into the composites. Using NPECs based on PAMPSAA, a slight increase of calcite polymorph was noticed (up to ~12%), irrespective of their molar ratios between charges. The calcite crystallite size increases significantly when PAMPSAA based NPECs are used, the highest value of about 77 nm being obtained when the molar ratio between charges was lower ($\text{C}_{0.2}\text{N-PEC}_{0.2}$).

The atomic compositions of samples prepared with NPEC dispersions with $n^-/n^+ = 0.4$, determined by XPS, are summarized in Table 3.

The relative Ca 2p atomic concentration values are lower than those obtained for the samples prepared with PAMPSAA alone. Obviously, the polymer content on the surface of the particles is increased. On the other hand, the low values of

charge densities and zeta-potential values demonstrate that sample surfaces can be considered as largely electrically neutralized. The addition of chitosan as polycation did not significantly affect the shapes of the C 1s and N 1s spectra, the high-resolution C 1s and N 1s element spectra being very similar to the spectra shown in Figure 5. Compared to the unmodified CaCO_3 sample, the C 1s spectra of composite samples clearly show that the intensities of the component peaks CO_3 are clearly decreased. From these findings it can be concluded that the surfaces of the inorganic phase also contain polymeric material. Chitosan, which was used as polycation to form polyelectrolyte complexes, carries primary amino groups. Component peaks *L* on N 1s element spectra show that these amino groups are partly protonated. Nitrogen atoms of non-protonated amino and amide groups contributed to component peaks *K*.

The use of NPEC as templates in composite formation strongly decreases the particles charge densities and their zeta-potential values, comparative with starting NPECs dispersions, suggesting their uniform embedment into the composites. The NPEC initial dispersion characteristics such as molar ratio, particles size and charge density slightly affect the CaCO_3 /NPEC composite particles surface morphology and electrokinetic parameters, almost the same values being obtained for the investigated parameters for all NPECs tested as template in CaCO_3 composite preparation.

CONCLUSION

Given the present state of knowledge, the prospects for finding simple, tough explanations for different effects of biomineralization mechanisms still represent challenges for further investigations. Moreover, bioinspired mineralization can transfer biomineralization principles to the synthesis of organic-inorganic materials, offering a large playground to develop future materials. Understanding the biological concepts, mechanisms, functions and design features and applying them to the development of new synthetic advanced materials and devices represent a very attractive subject for modern studies. This paper is intended to be a short review on some insight on composite materials, mainly in respect to calcium carbonate and poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) (PAMPSAA), tuning the materials properties by different parameters: polymer presence and concentration, inorganic concentration, pH, and polyelectrolyte complexes.

Acknowledgement. This work was supported by a grant of Roumanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project nr. 26PCCDI/2018, Integrated and sustainable processes for environmental clean-up, wastewater reuse and waste valorisation (SUSTENVPRO), within PNCDI III.

REFERENCES

1. R. J. Park and F. C. Meldrum, *Adv. Mater.*, **2002**, *14*, 1167-1169.
2. H. Cölfen and S. Mann, *Angew. Chem. Int. Ed.*, **2003**, *42*, 2350-2365.
3. S. Ouhenia, D. Chateigner, M.A. Belkhiria, E. Guilmeaub and C. Krauss, *J. Cryst. Growth*, **2008**, *310*, 2832-2841.
4. M. F. Butler, W. J. Frith, C. Rawlins, A. C. Weaver and M. Heppenstall-Butler, *Cryst. Growth Des.*, **2009**, *9*, 534-545.
5. J. Wang, J.-S. Chen, J.-Y. Zong, D. Zhao, F. Li, R.-X. Zhuo and S.-X. Cheng, *J. Phys. Chem. C*, **2010**, *114*, 18940-18945.
6. M. G. Lioliou, C. A. Paraskeva, P. G. Koutsoukos and A. C. Payatakes, *J. Colloid Interf. Sci.*, **2007**, *308*, 421-428.
7. F. Lippmann, "Sedimentary Carbonate Minerals", Springer, Berlin, 1973.
8. J.-P. Andreassen, *J. Crystal Growth*, **2005**, *274*, 256-264.
9. C.X. Zhang, J.L. Zhang, X.Y. Feng, W. Li, Y.J. Zhao and B.X. Han, *Colloids Surf. A*, **2008**, *324*, 167-170.
10. A.W. Xu, M. Antonietti, H. Cölfen, Y.P. Fang, *Adv. Funct. Mater.*, **2006**, *16*, 903-908.
11. Q. Zhang, L. Ren, Y. Sheng, Y. Ji and J. Fu, *Mat. Chem. Phys.*, **2010**, *122*, 156-163.
12. M. Mihai, F. Bucătaru, M. Aflori and S. Schwarz, *J. Cryst. Growth*, **2012**, *351*, 23-31.
13. C. Wang, H. Liu, Q. Gao, X. Liu and Z. Tong, *Carbohydr. Polym.*, **2008**, *71*, 476-480.
14. H. Wakayama, S. R. Hall and S. Mann, *J. Mat. Chem.*, **2005**, *15*, 1134-1136.
15. J. Yu, J. C. Yu, L. Zhang, X. Wang and L. Wu, *Chem. Commun.*, **2004**, *21*, 2414-2415.
16. F. Jiang, Y. Yang, L. Huang, X. Chen and Z. Shao, *J. Appl. Polym. Sci.*, **2009**, *114*, 3686-3692.
17. M. Mihai and E. S. Dragan, *J. Mat. Sci.*, **2011**, *46*, 5723-5731.
18. D. C. Bassett, B. Marelli, S. N. Nazhat and J. E. Barralet, *Adv. Funct. Mater.*, **2012**, *22*, 3460-3469.
19. H. Elfil and H. Roques, *Desalination*, **2001**, *137*, 177-186.
20. L. Brecevic and D. Kralj, *Croat. Chem. Acta*, **2007**, *80*, 467-484.
21. F. Krauss and W. Schriver, *Z. Anorg. Allgem. Chem.*, **1930**, *188*, 259-273.
22. D. L. G. Rowlands and R. K. Webster, *Nature Phys. Sci.*, **1971**, *229*, 158.
23. O. Söhnel and J. W. Mullin, *J. Cryst. Growth*, **1982**, *60*, 239-250.
24. X. Li, W.-C. Chang, Y. J. Chao, R. Wang and M. Chang, *Nano Let.*, **2004**, *4*, 613-617.
25. G.-T. Zhou, J. C. Yu, X.-C. Wang, L.-Z. Zhang, *New. J. Chem.*, **2004**, *28*, 1027-1031.
26. S. Mann, *Angew. Chem.*, **2000**, *112*, 3532-3548.
27. J. Rieger, E. H. Mdicke, I. U. Rau and D. Boeckh, *Tenside Surf. Deterg.*, **1997**, *34*, 430-435.
28. D. Gebauer, H. Cölfen, A. Verch and M. Antonietti, *Adv. Mater.*, **2009**, *21*, 435-439.
29. N. A. J. M. Sommerdijk and G. de With, *Chem. Rev.*, **2008**, *108*, 4499-4550.
30. N. Jongen, P. Bowen, J. Lemaitre, J. C. Valmalette and H. Hofmann, *J. Colloid Interf. Sci.*, **2000**, *226*, 189-198.
31. R. L. Penn and J. F. Banfield, *Geochim. Cosmochim. Acta*, **1999**, *63*, 1549-1557.
32. S. H. Lee, Y. S. Her, E. Matijevic, *J. Colloid Interface Sci.*, **1997**, *186*, 193-202.
33. S. H. Yu, H. Cölfen, J. Hartmann and M. Antonietti, *Adv. Funct. Mater.*, **2002**, *12*, 541-545.
34. H. Cölfen, *Macromol. Rapid Commun.*, **2001**, *22*, 219-252.
35. M. Li and S. Mann, *Adv. Functional Mater.*, **2002**, *12*, 773-779.
36. M. Mihai, S. Racovita, A.-L. Vasiliu, F. Doroftei, C. Barbu-Mic, S. Schwarz, C. Steinbach and F. Simon, *ACS Appl. Mater. Interf.*, **2017**, *9*, 37264-37278.
37. K. Mann, F. Siedler, L. Treccani, F. Heinemann and M. Fritz, *Biophys. J.*, **2007**, *93*, 1246-1254.
38. J. Trichet and C. Defarge, *Bull. Inst. Oceanogr. Monaco*, **1995**, *14*, 203-236.
39. A. W. Decho, *Ecological Eng.*, **2010**, *36*, 137-144.
40. O. Braissant, A. W. Decho, C. Dupraz, C. Glunk, K. M. Przekop and P. T. Visscher, *Geobiology*, **2007**, *5*, 401-411.
41. R. Eriksson, J. Merta and J. B. Rosenholm, *J. Colloid Interf. Sci.*, **2008**, *326*, 396-402.
42. J. Rieger, M. Kellermeier and L. Nicoleau, *Angew. Chem. Int. Ed.*, **2014**, *53*, 12380-12396.
43. L. A. Gower and D. A. Tirrell, *J. Cryst. Growth*, **1998**, *191*, 153-160.
44. G. Falini, S. Fermani, M. Gazzano and A. Ripamonti, *J. Chem. Soc. Dalton*, **2000**, *21*, 3983-3987.
45. B. Guillemet, M. Faatz, F. Grohn, G. Wegner and Y. Gnanou, *Langmuir*, **2006**, *22*, 1875-1879.
46. X. Q. Li, Z. Feng, Y. Xia and H. C. Zeng, *Chem. Eur. J.*, **2012**, *18*, 1945-1952.

47. G. Falini, S. Albeck, S. Weiner, L. Addadi, *Science*, **1996**, 271, 67–69.
48. K. Sawada, *Pure Appl. Chem.* **1997**, 69, 921–928.
49. J. D. Rodriguez-Blanco, P. Bots, N. J. Terrill, S. Shaw and L. G. Benning, *Geochim. Cosmochim. Acta*, **2010**, 74, A876–A889.
50. O. Grassmann, G. Muller and P. Lobmann, *Chem. Mater.* **2002**, 14, 4530–4535.
51. T. Kato, T. Suzuki, T. Amaniya, T. Irie, M. Komiyama and H. Yui, *Supramol. Sci.*, **1998**, 5, 411–415.
52. M. F. Butler, N. Glaser, A. C. Weaver, M. Kirkland and M. Heppenstall-Butler, *Cryst. Growth Des.*, **2006**, 6, 781–794.
53. O. Grassmann and P. Lobmann, *Biomaterials*, **2004**, 25, 277–282.
54. A. Barhoum, H. Rahier, R. E. Abou-Zaied, M. Rehan, T. Dufour, G. Hill and A. Dufresne, *ACS Appl. Mater. Interf.*, **2014**, 6, 2734–2744.
55. Y. Zhao, W. Du, L. Sun, L. Yu, J. Jiao and R. Wang, *Colloid. Polym. Sci.*, **2013**, 291, 2191–2202.
56. Y. V. Nelyubina and K. A. Lyssenko, *Chem. Eur. J.*, **2012**, 18, 12633–12636.
57. M. Fujiwara, K. Shiokawa, M. Araki, N. Ashitaka, K. Morigaki, T. Kubota and Y. Nakahara, *Cryst. Growth Des.*, **2010**, 10, 4030–4037.
58. H. Matahwa, V. Ramiah and R.D. Sanderson, *J. Cryst. Growth*, **2008**, 310, 4561–4569.
59. Y. Yao, W. Dong, S. Zhu, X. Yu and D. Yan, *Langmuir*, **2009**, 25, 13238–13243.
60. Y. Wang, Y.X. Moo, C. Chen, P. Gunawan and R. Xu, *J. Coll. Interf. Sci.*, **2010**, 352, 393–400.
61. Q. Zhang, L. Ren, Y. Sheng, Y. Ji and J. Fu, *Mat. Chem. Phys.*, **2010**, 122, 156–163.
62. L. Qi, J. Li and J. Ma, *Adv. Mater.*, **2002**, 14, 300–303.
63. A.N. Kulak, P. Iddon, Y. Li, S.P. Armes, H. Colfen, O. Paris, R.M. Wilson and F.C. Meldrum, *J. Am. Chem. Soc.*, **2007**, 129, 3729–3736.
64. H. Wei, Q. Shen, H. Wang, Y. Gao, Y. Zhao, D. Xu and D. Wang, *J. Cryst. Growth*, **2007**, 303, 537–545.
65. J. Yu, M. Lei, B. Cheng and X. Zhao, *J. Cryst. Growth*, **2004**, 261, 566–570.
66. H. Colfen, L. Qi, *Chem. Eur. J.*, **2001**, 7, 106–116.
67. H. Ahari, A. Lough, S. Petrov, G.A. Ozin and R. L. Bedard, *J. Mater. Chem.*, **1999**, 9, 1263–1274.
68. C. A. Weiss, K. T. Cancel, R. Moser, P. G. M. Allison, C. Malone, *J. Nanotech. Smart Mater.* **2014**, 1, 105, 1–6.
69. M. Mihai, G. Mountrichas, S. Pispas, I. Stoica, M. Aflori, M. Auf der Landwehr, I. Neda and S. Schwarz, *J. Appl. Cryst.*, **2013**, 46, 1455–1466.
70. M. Mihai, F. Bucătariu and F. Doroftei, *Rev. Chim.*, **2013**, 64, 338–342.
71. J. Chen and L. Xiang, *Powder Technology*, **2009**, 189, 64–69.
72. R. K. Pai, K. Jansson and N. Hedin, *Cryst. Growth Des.*, **2009**, 9, 4581–4583.
73. F. Yan, S. Zhang, C. Guo, X. Zhang, G. Chen, F. Yan and G. Yuan, *Cryst. Res. Technol.*, **2009**, 44, 725–728.
74. M. Sato and S. Matsuda, *Zeitsch. Kristall.*, **1969**, 129, 405–410.
75. M. Ni and B. D. Ratner, *Surf. Interface Anal.*, **2008**, 40, 1356–1361.
76. M. Mihai, S. Schwarz and F. Simon, *Cryst. Growth Des.*, **2013**, 13, 3144–3153.
77. M. Mihai, M.-D. Damaceanu, M. Aflori and S. Schwarz, *Cryst. Growth Des.*, **2012**, 12, 4479–4486.
78. D.A. Shirley, *Phys. Rev. B*, **1972**, 5, 4709–4714.
79. M.P. Seah and W.A. Dench, *Surf. Interf. Anal.*, **1979**, 1, 2–11.
80. J. Yu, H. Guo, S. A. Davis and S. Mann, *Adv. Funct. Mater.*, **2006**, 16, 2035–2041.
81. M. Mihai, S. Schwarz, F. Doroftei and B. C. Simionescu, *Cryst. Growth Des.*, **2014**, 14, 6073–6083.
82. S. Dragan and M. Cristea, in “Recent Research Developments in Polymer Science”, Pandarai S. G. (Ed.), Transworld Research Network, Trivandrum, Kerala, 2003, Vol 7, p. 149–181.
83. H.-M. Buchhammer, M. Mende, M. Oelmann, *Progr. Colloid Polym. Sci.*, **2003**, 124, 98–102.
84. S. M. Hartig, G. Carlesso, J. M. Davidson, A. Prokop, *Biomacromolecules*, **2007**, 8, 265–272.
85. M. Mihai, C.A. Ghiorghiță, I. Stoica, L. Niță, I. Popescu and G. Fundueanu, *Express Polym. Lett.*, **2011**, 5, 506–515.
86. M.-D. Dămăceanu, M. Mihai, I. Popescu, M. Brumă and S. Schwarz, *React. Funct. Polym.*, **2012**, 72, 635–641.