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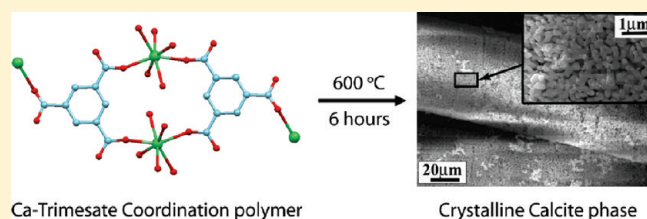
Published as part of the virtual special issue on Structural Chemistry in India: Emerging Themes

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S Supporting Information

ABSTRACT: Selective formation of different polymorphs of calcium carbonate (CaCO_3) in the solid state using aromatic organic acids as ligands for Ca^{2+} coordination has been reported. The formation of pure calcite and vaterite phase in bulk amount can be nicely captured by the choice of suitable solid state routes, employed in the preparation of precursor Ca-carboxylic acid complexes. Calcite can be solely obtained via crystallization of Ca-carboxylic acid complexes in a water–methanol binary solvent system followed by thermal agitation at 600°C for 6 h. However, vaterite has been primarily obtained under similar conditions upon heating the crystalline powders of the precursory complexes prepared by the solid state grinding technique. The results obtained suggest that solid state techniques could give an alternative and versatile tool for controlling both the structure and the polymorphism of inorganic materials. The formation of intertwined aragonite rods from using trimesic acid as an organic additive instead of ligand is also noteworthy.



1. INTRODUCTION

Biomineralization is an intricate process that relies on precise physiological control of solution and interface properties.¹ Despite much research of the process, mechanistic details of biomineralization are only beginning to be understood, and studies of additives seldom investigate a wide space of chemical conditions in mineralizing solutions.² Calcium carbonate (CaCO_3), as one of the most ubiquitous existing biominerals, has received much attention in various fields. According to thermodynamics, calcite is the most stable crystalline phase of CaCO_3 at ambient temperature and pressure (RT), although conditions can be altered such that the other polymorphs are stabilized.^{1a} Vaterite and aragonite, a metastable phase, are the main forms of CaCO_3 existing in organisms.³ However, vaterite is expected to have potential applications for different purposes because of its properties such as high specific surface area, high solubility, high dispersion, and lower density compared with the other two crystalline phases.⁴

The development of chemical routes leading to controlled and selective preparation is an important requirement in the synthesis of crystalline materials for various applications. In organisms, these crystals have a wide range of naturally occurring crystal habits and are normally found assembled into hierarchical structures that result in differences with intriguing properties.⁵ Scientists inspired by these results have attempted to fabricate CaCO_3 crystals with different morphologies and properties and have investigated the formation mechanisms outside of biological organisms by mimicking the biomineralization processes.⁶ The importance of calcium carbonates in nature has led to extensive

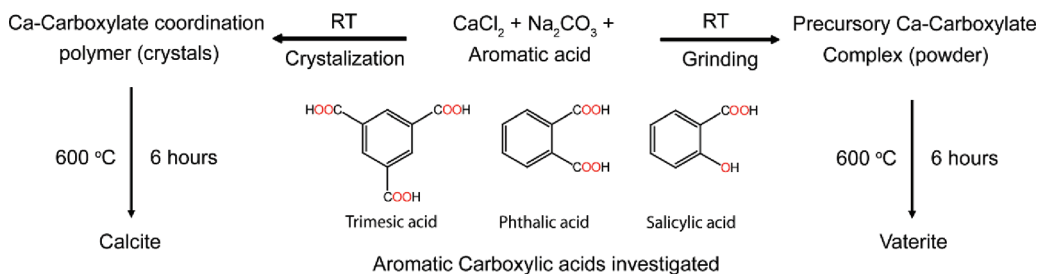
studies of CaCO_3 crystallization using two main bioinspired methods: (i) templating by structured organic surfaces,⁷ such as self-assembled monolayers (SAMs), Langmuir monolayers, bio-macromolecules, and functionalized polymers; and (ii) solution precipitation with growth modifiers,⁸ such as ions, proteins, and synthetic polymers. Although these methods independently offered a certain level of control over crystal orientation, or polymorph and morphology, fine-tuning of the polymorph selection with identical crystal morphology in the solid state is one experiment that has not been reported yet, and the crystals grown were often diverse in sizes and shapes within a single sample. There is a vast amount of previous literature describing the effect of various carboxylates as additives on the precipitation of calcium carbonate preferably because additives can dramatically affect particle shape and size and therefore can be used in a particle engineering sense. However, the controlled preparation of different polymorphs of calcium carbonate with identical morphologies within a single sample in bulk quantity has always been a challenging task.

In continuation of our study in the field of mineralization and inorganic material chemistry,⁹ we represent here an entirely different approach toward preparing specific polymorphs of CaCO_3 with novel morphologies using Ca(II) -carboxylate precursor complexes. The development of metal complexes that assemble into hierarchical supramolecular structures in the

Received: November 19, 2010

Revised: April 12, 2011

Scheme 1. Representation of the Formation of Pure Calcite and Vaterite from Ca-Carboxylic Acid Complexes Following Different Solid State Routes Followed by Thermal Decomposition along with the Molecular Structures of Aromatic Carboxylic Acids Investigated in This Work



crystal is of great interest because of their potential in designing new materials with desirable optical and magnetic properties.¹⁰ In this study, calcite has been exclusively obtained via thermal decomposition of crystals of the precursor complex, whereas vaterite has been primarily obtained under similar conditions upon heating the crystalline powders of the precursory complexes prepared by the solid state grinding technique. The role of solvents both aqueous and nonaqueous in controlling the morphology of polymorph of the calcium minerals has also been monitored and discussed. Polymorphs of calcite and vaterite crystals with uniform nucleating plane, shape, morphology, and size were synthesized for the first time, employing carboxylic acid as ligands in the preparation of precursory complexes for the synthesis of CaCO_3 minerals in the solid state. This approach provides the ability to tune the polymorph specificity, orientation, and morphology of the resulting minerals as well as bulk synthesis of pure mineral phase (Scheme 1).

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization. All reagents and solvents were obtained from commercial sources and used as received without further purification. Distilled water was used throughout the experiment. The IR spectra were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range $4000\text{--}400\text{ cm}^{-1}$. Powder X-ray diffraction data were recorded using a Seifert powder X-ray diffractometer (XRD 3003TT) with a $\text{CuK}\alpha$ source ($\lambda = 1.54\text{ \AA}$) on a glass surface of an air-dried sample. The thermal analyses of the polymorphs were performed by using an SDTA 851 e TGA thermal analyzer (Mettler Toledo) with a heating rate of $2\text{ }^\circ\text{C per min}$ in a N_2 atmosphere. Scanning electron micrograph (SEM) images were obtained by means of a LEO-1430 VP electron microscope on samples glued on an aluminum stub and gold sputtered.

2.2. Synthesis of Precursor Complexes. In our effort to obtain the single crystals of Ca-carboxylate coordination polymers in a comparatively bulk quantity, an equivalent amount of CaCl_2 and aromatic carboxylic acids (1 g each) were dissolved in 10 mL of water, and Na_2CO_3 (equivalent to the number of acid groups present in the aromatic carboxylic acids) was added at once while stirring. When the solution mixture became homogeneous, 10 mL of methanol was added and refluxed for about 4 h. The solution was then filtered into a beaker and kept for slow evaporation of solvents at RT. Crystals suitable for single crystal analysis were grown over a period of 1 week. The crystals were collected by filtration, then washed with acetone and diethyl ether, and finally dried at RT for carrying out the further experiments involving crystals of Ca-carboxylate coordination polymers.

The Ca-carboxylate precursory complexes were prepared by mixing an equivalent amount of CaCl_2 and aromatic carboxylic acids (1 g each)

in the presence of Na_2CO_3 (equivalent to the number of acid groups present in the aromatic carboxylic acids). The mixture was then thoroughly ground in a mortar over the duration of 2 h when crystalline powder of the precursor complexes was formed. The formation of the crystalline precursor complexes has been confirmed by powder X-ray diffraction (PXRD) and Fourier transform-infrared (FT-IR) patterns. The so-formed precursor complexes were used for the bulk preparation of polymorphs of CaCO_3 (Figures S13–S18, Supporting Information).

In a typical experiment involving the crystallization of CaCO_3 in the presence of 1 mol % of trimesic acid (additive) in different polar solvents, 1 mM of trimesic acid was mixed with 100 mM of CaCl_2 solution in the desired solvent ($\text{H}_2\text{O}/\text{EtOH}/\text{DMSO}$) with constant stirring at RT. Meanwhile, 100 mM Na_2CO_3 solution in Milli-Q water was added dropwise with constant stirring over a period of 12 h. The resulting mixture kept at RT with much mechanical disturbance. The crystal formation in the solution can be observed as an increase in the turbidity of the solution with time. When there was a large number of precipitate present in the reaction vessel, the crystalline products were collected through centrifugation at 10 000 rpm and washed with methanol/acetone several times to remove the organic additive and then finally with diethyl ether. The crystals were dried in air for 24 h and kept in desiccators before analysis.

2.3. X-ray Crystallography. In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, and then it was mounted on the tip of a glass fiber and cemented using epoxy resin. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $298(3)\text{ K}$, with increasing ω (width of 0.3° per frame) at a scan speed of 5 s/frame . The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP¹¹ software. Multiscan empirical absorption corrections were applied to the data using the program SADABS.¹² Structures were solved by direct methods using SHELXS-97¹³ and refined with full-matrix least-squares on F^2 using SHELXL-97.¹⁴ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon atoms were geometrically fixed and the positional and temperature factors are refined isotropically. Structural illustrations have been drawn with ORTEP-3¹⁵ for Windows. Parameters for data collection and crystallographic refinement parameters of Ca-trimesic acid precursor complex is summarized in Table 1.

3. RESULTS AND DISCUSSION

Carboxylic acid is well-known to strongly bind Ca(II) ion, and aromatic scaffolds provide rigidity to the formed complexes. For the preparation of Ca minerals in a comparatively bulk amount, we have chosen two different routes for the synthesis of CaCO_3 polymorphs. First is via a crystallization process, in which the crystals of Ca-Carboxylate coordination polymers were

prepared by slow evaporation of a 1:1 H₂O–MeOH mixture which was then recovered and subjected to heat at 600 °C for 6 h to obtain the thermodynamically most stable calcite phase of the mineral. Second is via a solid state grinding method, in which aromatic acids and CaCl₂ were thoroughly grounded in the presence of Na₂CO₃ to obtain the powders of precursor complexes. The powder of precursor complexes was then heated at 600 °C for 6 h, which yielded the least stable vaterite phase of the mineral. Interestingly, following the crystallization route, we ended up with the stable calcite phase of the mineral. But all three single crystals resulted in the formation of the calcite phase with different morphologies having similar shapes and sizes within a single sample. One explanation for the probable change in morphology is that the different hierarchical supramolecular architectures resulted because of coordination modes adopted by

the Ca(II) ions in the presence of different carboxylic acids in the solid state. On the basis of their binding modes and overall 3D structure in the solid state, different morphologies will be obtained upon thermal agitation.

3.1. Single Crystal Structural Analysis. The Ca-trimesate coordination polymer crystallizes in monoclinic space group *P*2₁/*c*. Structural investigation reveals that each Ca²⁺ ion is coordinated to seven oxygen atoms in a distorted octahedral fashion. Four water molecules (O4, O5, O6, and O7) are coordinated to Ca²⁺ ion in the equatorial plane. Each Ca²⁺ ion is further coordinated to three encircling ligand molecules via three oxygen atoms (O1, O3, and O5) of carboxylic acid occupying the axial positions. Four equatorial oxygen atoms lie exactly on the equatorial plane, and the Ca²⁺ ion is deviated at 0.377 Å from the equatorial plane (Figure 1b). The proton H4 bonded to O5 of one of the carboxylate groups forms a strong hydrogen bond O5–H5···O6 linking the trimesic acid anions in chains. All four water molecules are not only involved in the coordination of Ca but also form strong hydrogen bonds to carboxylate oxygen and to the other coordinated water molecules. Overall, it forms a polymeric layered structure, where trimesic acid unit is packed in an alternate up and down fashion. Coordination polymers of Ca²⁺ ion derived from phthalic acid and salicylic acid have similar kinds of coordination modes involving carboxylate oxygen atoms and water molecules but with different supramolecular frameworks. Although the crystal structures of coordination polymer of Ca-phthalic acid¹⁶ and Ca-salicylic acid¹⁷ are previously reported, however, we have resolved the structures as a feature of our work.

3.2. Formation of Calcite Phase from Crystals of Ca-Carboxylates Coordination Polymers. Single crystal of the Ca-trimesate complex is rectangular in shape with a dimension of 20–30 μm. Calcite formed upon heating the crystals of Ca-trimesate complex at 600 °C for 6 h in a muffle furnace have a structure that resembles sea urchin skeletal plates. Formation of calcite has also been established by PXRD analysis with a characteristic pattern at 2θ = 29 which corresponds to the [104] plane¹⁸ (Figure 2a). An FT-IR spectrum also shows characteristic stretching frequencies at 878 and 718 cm^{−1} consistent with the literature data.¹⁹ FT-IR spectrum shows that vibrational bands at about 878 and 718 cm^{−1} can be attributed to ν₂ and ν₄ modes of calcite, respectively. A higher magnification SEM image shows that the calcite aggregates are not perfectly spherical and are aggregated into a particular oval shape within the sample having a uniformity of shape and size to be an order of

Table 1. Crystallographic Refinement Parameters of Ca-TMA Precursor Complex

CCDC no.	648775
fw	320.27
empirical formula	C ₉ H ₁₂ CaO ₁₀
temp, K	273(2)
radiation	MoKα
wavelength	0.71073 Å
size, mm	0.45 × 0.36 × 0.31
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	10.202(4)
<i>b</i> , Å	16.449(7)
<i>c</i> , Å	7.476(3)
β, deg	102.316(2)
<i>V</i> , Å ³	1225.66(9)
<i>Z</i>	4
ρ _{calc} mg/m ³	1.730
μ	0.560
<i>F</i> (000)	512
GOF(<i>S</i>)	1.006
final <i>R</i> indices	<i>R</i> ₁ = 0.0731
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.2037
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0810
	<i>wR</i> ₂ = 0.2096
refinement	full-matrix least-squares on <i>F</i> ²

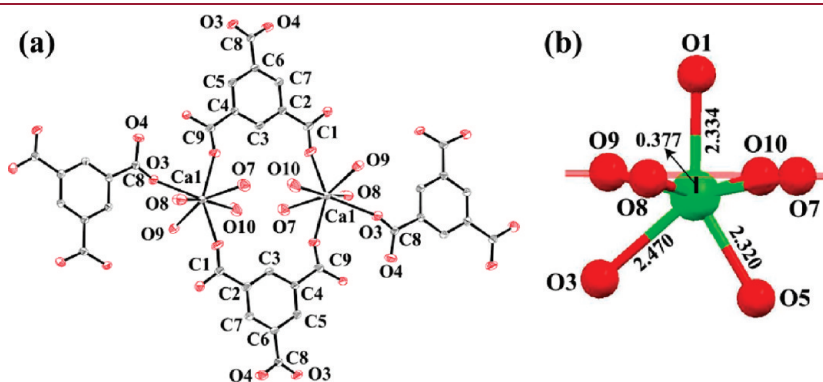


Figure 1. (a) ORTEP plot (50% probability ellipsoids) of the Ca-trimesic acid coordination polymer with the atom numbering scheme; (b) ball and stick representation of the coordination of Ca²⁺ ion depicting the deviation of the Ca²⁺ from the equatorial plane of the coordinating water molecules.

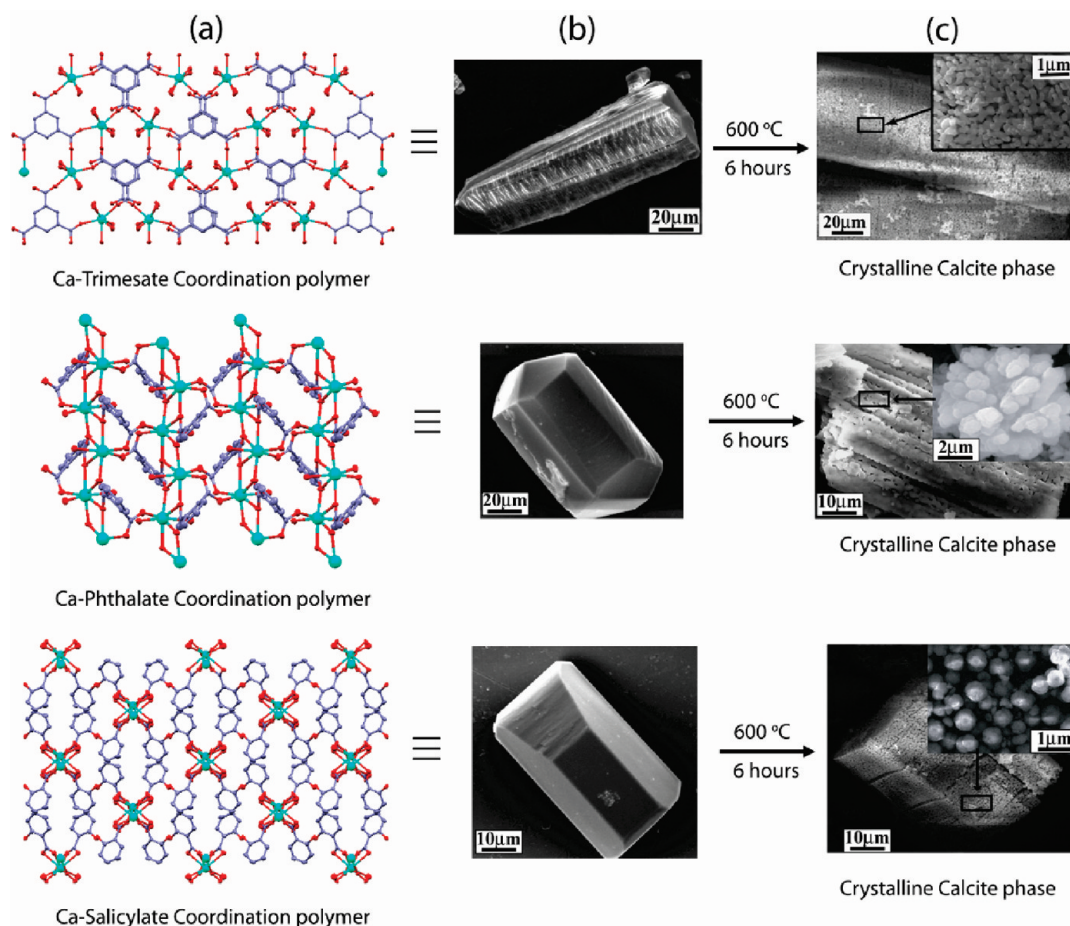


Figure 2. (a) Crystal structure representation of the supramolecular networks of three Ca-carboxylate coordination polymers; (b) SEM micrograph images of the single crystals obtained for the three Ca-carboxylate coordination polymers; (c) SEM micrograph images of the single crystals obtained after thermal agitation of the three Ca-carboxylate coordination polymers forming stable calcite phase.

0.5–1 μm consistent with ordering within the aggregate (inset, Figure 2a). Thermogravimetric analysis (TGA) shows that the crystals are stable up to 325 $^{\circ}\text{C}$ with a two-step thermal decomposition to form calcite. The mass loss at about 100 $^{\circ}\text{C}$, obtained by the TG curve, demonstrates that water gets desorbed from the surface of the crystal of Ca-trimesic acid coordination polymer fabricated in the mixed solvent of water and methanol (1:1). The weight loss in the range of 320–420 $^{\circ}\text{C}$ corresponds to the loss of four coordinating water molecules.

In order to validate whether thermal agitation of the crystals of other Ca-carboxylate complexes yields a similar calcite phase, we have subjected the crystals of phthalate¹⁶ and salicylate¹⁷ complexes to heat under similar conditions. It was found that pure calcite was obtained in both cases (Figure 2b,c). The TGA curve (Figure S7, Supporting Information) shows that the crystals of Ca-phthalic acid coordination polymers are stable up to 430 $^{\circ}\text{C}$ with a sharp single-step thermal decomposition to form calcite. The mass loss at about 160 $^{\circ}\text{C}$, obtained by the TG curve, demonstrates that water gets adsorbed or absorbed on the surfaces of the crystal of Ca-phthalic acid coordination polymer fabricated in the mixed solvent. The vaporizing temperature of water is increased because of the interaction between water and Ca^{2+} or with the coordinating acid groups in the system. A higher magnification SEM image shows that the calcite aggregates formed upon calcination of Ca-salicylic acid are aggregated into

a particular overall shape within the sample having a uniformity of shape and size to be an order of 2 μm consistent with ordering within the aggregate. TGA curve shows that the crystals of Ca-salicylic acid coordination polymers are stable up to 230 $^{\circ}\text{C}$ (Figure S9, Supporting Information) with a two-step thermal decomposition to form calcite. The weight loss in the range of 200–300 $^{\circ}\text{C}$ corresponds to the loss of four coordinating water molecules followed by gradual decomposition to form calcite.

3.3. Formation of Vaterite Phase from Powders of Ca-Carboxylates Precursor Complexes. In our effort to validate the occurrence of different polymorphs of Ca minerals, we have adopted another strategy whereby the Ca-trimesate precursor complexes were prepared by a solvent-free solid state grinding method in the presence of Na_2CO_3 (equivalent to the number of acid groups present in the aromatic acid). This solvent-free solid-state method is both operationally simple and green in nature. In a typical experiment, a 3:1 mixture of aromatic acid and CaCl_2 were thoroughly ground with a pestle in a mortar at RT in open atmosphere until the mixture turned into a melt. The melt was then washed several times with methanol to get rid of excess unreacted and surface adsorbed aromatic acid. The precursor complex thus obtained was air-dried before characterization. The powders of the precursor complex were further heated at 600 $^{\circ}\text{C}$ for 6 h in a muffle furnace to obtain primarily the vaterite phase of

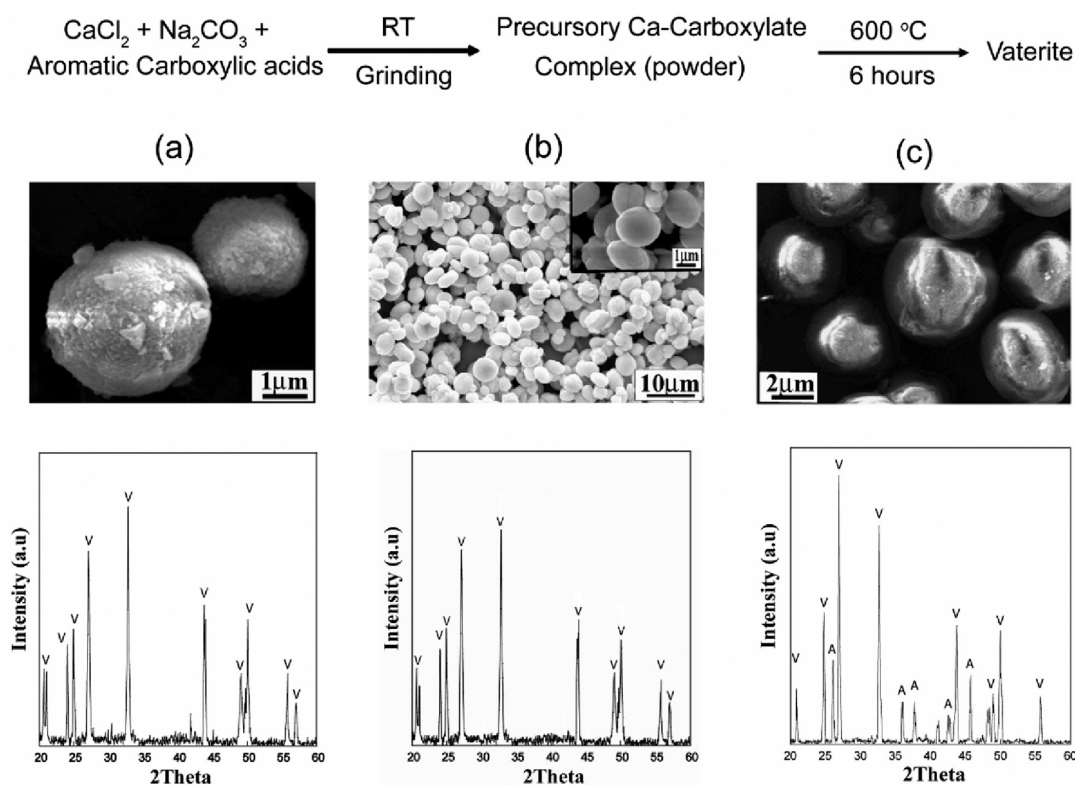


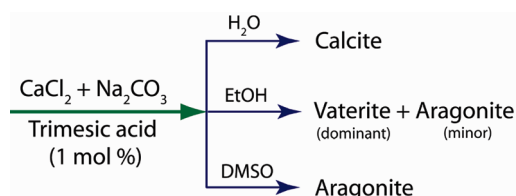
Figure 3. SEM micrograph images of the spherical vaterite formed after thermal treatment of the powders of precursory (a) Ca-trimesate complex; (b) Ca-phthalate complex; (c) Ca-salicylate complex and their corresponding powder XRD patterns.

the mineral (Figure 3a). We believe that the aromatic acid helps in the formation of the solid state self-assembled three-dimensional (3D) superstructure, which on thermolysis via a calcination–reconstruction process forms primarily the vaterite phase of the mineral.

The formation of precursory complex and exclusive occurrence of crystalline vaterite upon heating was confirmed by PXRD and FT-IR patterns. In the FT-IR spectrum, the bands at about 1080 and 745 cm^{-1} (Figure S19, Supporting Information) can be attributed to the characteristic symmetric carbonate stretching (ν_1 mode) and ν_4 mode of vaterite, respectively.²⁰ A higher magnification SEM image shows that the morphology of the as-obtained vaterite is perfectly spherical with an average diameter of $2\text{ }\mu\text{m}$ (Figure 3a). Similarly, when the powders of Ca-phthalic acid precursor complex have been subjected to calcination under similar conditions, vaterite was obtained as the exclusive phase of the mineral confirmed by PXRD with characteristic peaks²¹ at approximately 25 [110], 27 [112], and 33 [114] in 2θ and FT-IR patterns (Figure 3b). However, thermal treatment of the powders of Ca-salicylic acid precursor complex under similar conditions yielded vaterite, syn (lattice: hexagonal, SG: $P6_3/mmc$, Oxford PXRD database, (PDF No. 01-072-0506) as the major phase (76.37%) along with aragonite (23.63%) as a minor phase (SG: $Pmcn$, [111], Oxford PXRD database, PDF No. 00-005-0453). The occurrence of a mixture of crystalline vaterite and aragonite has been confirmed by PXRD and FT-IR patterns (Figure 3c).

3.4. Fabrication of CaCO_3 Polymorphs by Suitable Choice of Solvents. An in vitro study of biomineralization provides valuable information for the design of organic templates. Here we have tuned the growth of various CaCO_3 polymorphs by using

Scheme 2. Schematic Representation of the Solvent Induced Polymorphism of CaCO_3 in the Presence of 1 mol % of Trimesic Acid in Different Polar Solvents



trimesic acid as organic additive in aqueous and nonaqueous solvents viz. EtOH and DMSO. Although nonaqueous solvent is not biologically relevant, to study the mechanism of mineralization and role of various additives and solvents in this processes we have carried out these experiments in nonaqueous medium. The objective behind choosing polar nonaqueous solvents is due to their high miscibility with water and to validate the effect of protic and aprotic solvents viz. EtOH and DMSO respectively in the process of mineralization. As shown in Scheme 2, it is clear that calcite is the most stable phase in water, and nonaqueous solvents play an important role in stabilizing the metastable phases of CaCO_3 . When we carried out crystallization in ethanol, a mixture of aragonite and vaterite was formed, whereas in DMSO the formation of pure aragonite was observed. From this investigation, it is evident that both aqueous as well as nonaqueous solvents play an important role in CaCO_3 polymorphism, and by the suitable choice of solvent or solvent mixtures we can tune their polymorphism.

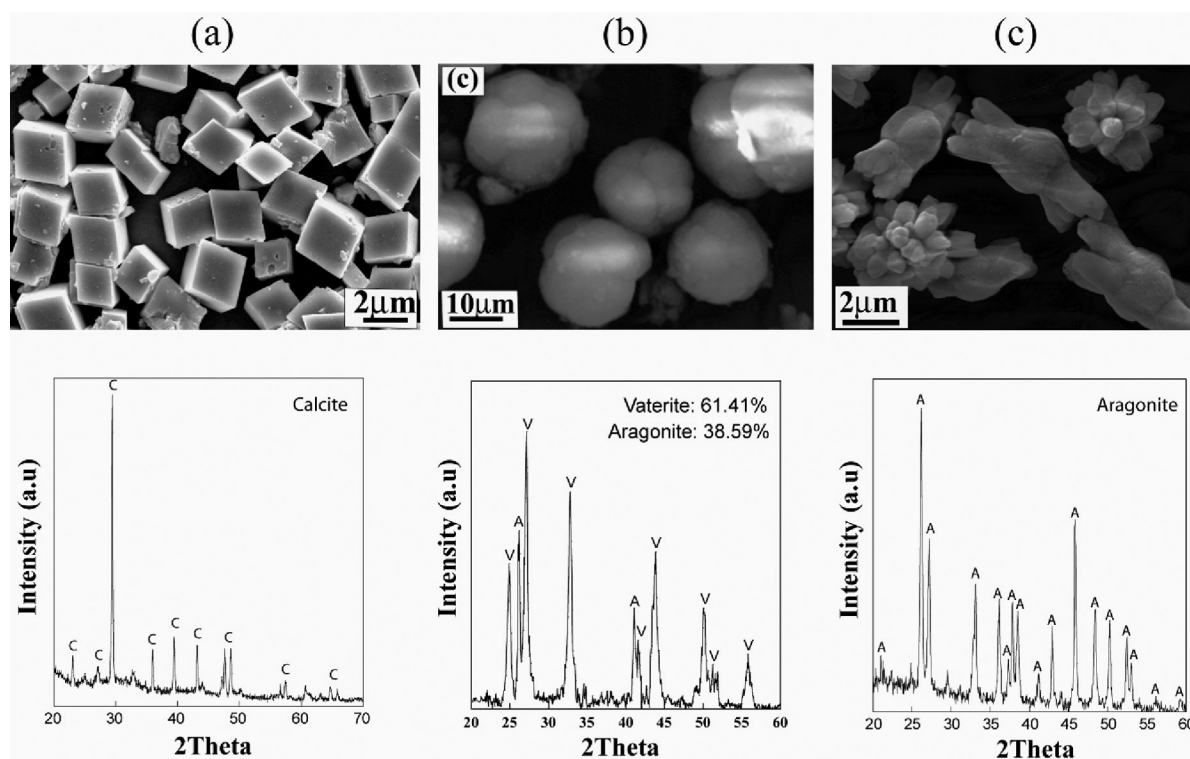


Figure 4. SEM micrograph images of the (a) rhombohedral calcite formed in water; (b) spherical vaterite formed in ethanol; (c) intertwined aragonite rods formed in DMSO employing 1 mol % of trimesic acid in the respective solvents and their corresponding powder XRD patterns.

When we carried out CaCO_3 crystallization in the presence of 1 mol % of trimesic acid in water, we ended up with a thermodynamically stable calcite polymorph at RT (characteristic PXRD pattern at $2\theta = 29$ corresponds to the $[104]$ plane). These results confirm that in water, calcite is the only and most stable polymorph at RT. The SEM images show regular rhombohedral shaped calcite as it ensues from XRPD and FT-IR diagrams (Figure 4a). However, when a similar crystallization experiment was carried out in EtOH, spherical shaped morphology of vaterite was obtained as the major phase unlike in water (Figure 4b). The sample was composed of hexagonal vaterite, syn polymorph ($P63/mmc$, Oxford PXRD database, PDF No. 01-074-1867) as the major phase (61.40%) and a substantial amount of orthorhombic aragonite ($Pmcn$, $[111]$) (38.59%) as it follows from the XRPD and FT-IR results. When DMSO was employed as the solvent in the mineralization process of CaCO_3 , pure aragonite was obtained with intertwined rod like morphology reflecting the polymorphism of CaCO_3 in a suitable choice of solvents (Figure 4c). This kind of rod-like morphology is typical of aragonite, and its occurrence is confirmed by the results obtained by XRPD with characteristic pattern at $2\theta = 26.23$ which corresponds to the $[111]$ plane²¹ (SG: $Pmcn$, Oxford PXRD database, PDF No. 00-005-0453) and FT-IR, but intertwined aragonite rods have not been reported to our knowledge. In FT-IR spectrum, the bands at about 1086, 852, and 702 cm^{-1} (Figure S22, Supporting Information) demonstrated that pure aragonite was fabricated. The bands at about 852 and 702 cm^{-1} can be attributed to out-of-plane bending vibrations (ν_2 mode) and in-plane bending modes of aragonite, respectively.²²

The energy of a crystal is made up of two components: a surface component and a bulk component.²³ The surface energies of calcite, aragonite, and vaterite were previously calculated.²⁴

In our experimental conditions with pure water as solvent, the surface energy may be significant. Calcite is the thermodynamically most stable one among CaCO_3 polymorphs. Thus, pure calcite was fabricated in water. However, aragonite or vaterite may be formed when there is a competition between the surface and bulk components to predominate in the crystallization of CaCO_3 , which may be responsible for the precipitation of a mixture of both ethanol and pure aragonite in DMSO as solvent. The stability of calcite, aragonite, and vaterite needs further investigation by measuring (or calculating) the influence of a solvent (water, ethanol, and DMSO) on those faces determining the equilibrium shape of the crystal.

4. CONCLUSION

To conclude, we found a novel route for CaCO_3 polymorphs discrimination in the solid state using aromatic carboxylic acids as coordinating ligands to form Ca-carboxylate coordination polymers. We have chosen two different routes for the synthesis of CaCO_3 polymorphs. First is via crystallization process, in which the single crystals of Ca-carboxylate coordination polymers were synthesized. The second is via solvent-free solid-state grinding method, where Ca-carboxylates precursor complexes were obtained. On thermal treatment of the crystals of Ca-carboxylate coordination polymers, the thermodynamically most stable calcite polymorph was obtained. On the other hand, from the powders of precursory Ca-carboxylate complexes primarily vaterite, the metastable phase of CaCO_3 was obtained. These results suggest that solid state techniques could give an alternative and versatile tool for controlling both the structure and the polymorphism of inorganic materials. Discrimination between the CaCO_3 polymorphs has also been achieved by the choice of

suitable solvents employing 1 mol % of trimesic acid acting as an organic template (additive). Pure calcite was fabricated with water as solvent, whereas pure aragonite was fabricated with DMSO as solvent. A mixture of vaterite and aragonite was obtained with ethanol as solvent having a greater proportion of vaterite in the sample. From this investigation, it is evident that both aqueous as well as nonaqueous solvents play an important role in CaCO_3 polymorphism, and by the suitable choice of solvent or solvent mixtures their polymorphism can be tuned.

■ ASSOCIATED CONTENT

S **Supporting Information.** Crystallographic files in CIF format and additional crystallographic data, FT-IR and PXRD spectra, and TGA-DSC plots are available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

G.D. gratefully acknowledges DST (SR/S1/IC-01/2008) and CSIR (01-2235/08/EMR-II) New Delhi, India, for the financial support, DST-FIST for single crystal X-ray diffraction facility and Central Instrument Facility at IIT Guwahati. S.K.D acknowledges IIT Guwahati, India, for a senior research fellowship.

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