Photodimerization of Anthracene Having Dendritic Substituent within the Vaterite Crystal of $CaCO_3$

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(Received June 13, 2002; CL-020500)

Crystallization of $CaCO_3$ in the presence of poly(amidoamine) (PAMAM) dendron containing an anthryl group at the focal point and carboxylate groups at the external surface resulted in the formation of spherical vaterite crystals. Furthermore, photodimerization reaction of anthracene unit proceeded within the vaterite crystals upon irradiation.

Polymer-inorganic hybrid materials have received considerable attention in the past decade.[1] However, much less is known about an organic reaction within such hybrid materials. Calcium carbonate ($CaCO_3$) is one of the most popular candidate for construction of a composite material. In particular, controlling polymorph of $CaCO_3$ has been extensively reported in the view point of analogy with biomineralization.[2–5] Naka et al. reported that crystallization of $CaCO_3$ in the presence of poly(amidoamine) (PAMAM) dendrimer containing carboxylate groups at the external surface resulted in the formation of spherical vaterite crystals.[5] Since the selectivity of polymers for certain crystal faces appears to be highly dependent on the secondary structure of the macromolecules, organic reaction within the crystal should potentially affect mineral crystal growth and morphology. Hence photoreactivity of dendrimer within the vaterite crystal is quite important. Recently, we have reported that the PAMAM dendron having an anthryl group at the focal point acted as photoresponsive dendrimer.[6] This paper describes the crystallization of $CaCO_3$ in the presence of anthracenyl dendron (**1**). Furthermore, photoreactivity of **1** within the vaterite crystal was investigated. To our knowledge, this is the first example of a photoreaction by the use of $CaCO_3$ crystals as a matrix.

The precipitation of $CaCO_3$ in the presence of the dendron **1** was carried out under the same conditions as used by Naka et al.[5] To a solution of dendron **1** (0.33 mmol) in water (130 ml, pH 8.5) were added simultaneously aqueous solutions of $CaCl_2$ (0.5 M, pH 8.5) and $(NH_4)_2CO_3$ (0.5 M, pH 10.2) at 25 °C under a nitrogen atmosphere. After gentle stirring for 4 days, the crystalline $CaCO_3$ was washed with water to remove contaminating dendrimers that were not involved in the crystals and separated by filtration. The yield of the crystalline product was 93%. The dendrimer content in the crystalline $CaCO_3$ was approximately 5 wt% determined by elemental analysis and UV-vis spectrum. These results indicate that the anionic dendrimer was bound to the crystalline $CaCO_3$.

The crystal phase of $CaCO_3$ obtained in the presence of the PAMAM dendrimer was characterized by FTIR analysis, XRD analysis, and SEM observation. The IR spectrum of the crystalline $CaCO_3$, obtained in the presence of dendron **1**, shows bands at 878 and 745 cm^{-1} indicated the formation of vaterite while bands at 874 and 712 cm^{-1} characteristic of calcite were scarcely observable as shown in Figure 1.[7] By contrast, according to IR spectroscopy, the crystal phase of $CaCO_3$ obtained in the absence of the dendrimer was calcite. Crystal phases $CaCO_3$ were further confirmed by XRD; in the presence of dendrimer, the precipitate consisted almost of vaterite (>98%) while in the absence of dendrimer, the reflections were characteristic of calcite as shown in Figure 2.

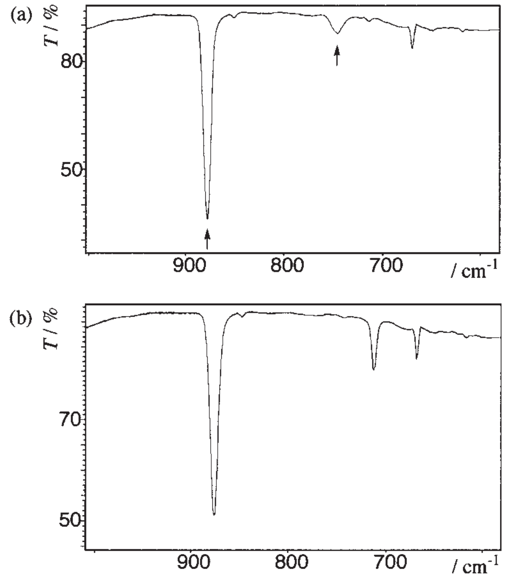


Figure 1. FTIR spectra of $CaCO_3$ grown (a) in the presence of dendron **1**, (b) in the absence of dendron **1** (the peaks corresponding to vaterite are indicated by arrows).

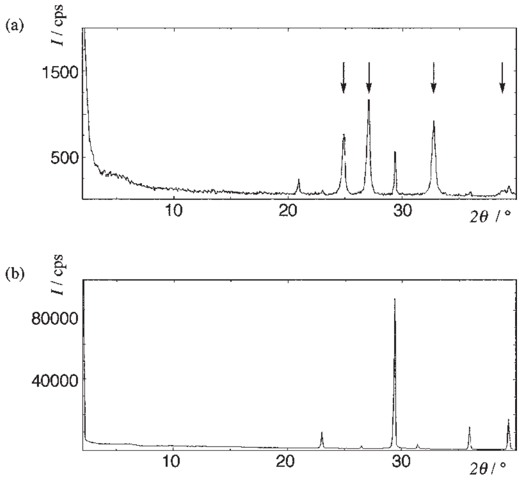
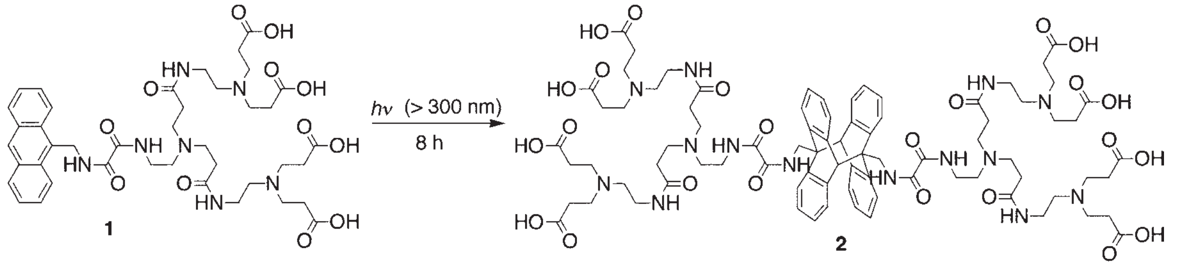


Figure 2. X-ray diffraction patterns of crystalline $CaCO_3$ grown (a) in the presence of dendron **1**, (b) in the absence of dendron **1** (the peaks corresponding to vaterite are indicated by arrows).



Scheme 1. Photodimerization of anthracene having dendritic substituent within the vaterite crystal of CaCO$_3$.

SEM observations showed that the vaterite particles were spherical (Figure 3a) with an average particle diameter of 7–8 μm. On the other hand, the calcite crystals, which were obtained in the absence of dendrimer, were rhombohedral (Figure 3c). Interestingly, the globular structure of vaterite was formed by gathering of nanocrystals of CaCO$_3$, of which size was approximately 40 nm (Figure 3b). It is well known that vaterite transforms readily and irreversibly into the thermodynamically stable calcite form via a solvent-mediated process.[8] Vaterite crystal obtained from the solution of PAMAM dendron **1** is quite stable for one month and transforms very slowly into calcite (18% per 24 h) in solution. Hence the vaterite surface is stabilized by the carboxylate-terminated dendron in aqueous solution to prevent phase transformation as mentioned by Naka et al.[5] In marked contrast with Naka's dendrimer, dendron **1** has only four carboxyl groups at the terminals. However, both of them can affect the crystallization of CaCO$_3$ to give vaterite.

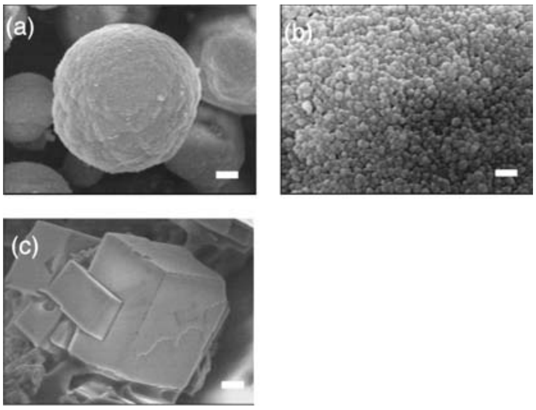


Figure 3. Scanning electron micrographs of crystalline CaCO$_3$ grown (a) in the presence of dendron **1**, scalebar = 1 μm; (b) in the presence of dendron **1**, scalebar = 0.1 μm; (c) in the absence of dendron **1**, scalebar = 1 μm.

In order to clarify the photoreactivity of the anthracene moiety within the CaCO$_3$ crystal, we examined the [4 + 4] photocycloaddition of dendron **1** incorporated into CaCO$_3$. The dendrimer-CaCO$_3$ composite material (600 mg) was placed between Pyrex plates and irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 8 h to give dendrimer **2** in 81% yield, which was confirmed by UV-vis spectrum and ^{1}H, ^{13}C NMR spectra of acidic D$_2$O solution of CaCO$_3$ containing reaction product (Scheme 1).[9] The crystal phase of CaCO$_3$ was not changed after the photodimerization of dendron **1**. Compared with photodimerization in aqueous solution (yield 100%), photoreactivity of **1** within the CaCO$_3$ was maintained despite effects of light scattering and low concentration.

The results described herein show the first example of the photoreaction within the vaterite crystal of CaCO$_3$ as a matrix. It is notable that there is no effect of anthracene unit for the selective crystallization of calcium carbonate. Further work is in progress to explore the applications and advantages of the polymer-inorganic hybrid material containing photoreactive dendrimer.

This work was partly supported by Research Foundation for the Electrotechnology of Chubu, Grant-in-Aid for COE Research (No. 10CE2003), and Priority-Area-Research (B) (No. 12129205) by the Ministry of Education, Science, Sports and Culture of Japan. We are grateful to Prof. Dr. Keiichi Satoh, Niigata University, for fruitful discussions on this topic.

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9 Selected data for dendrimer **2**: ^{1}H NMR (D$_2$O) δ 2.10–2.25 (m, 24H), 2.25–2.55 (m, 12H), 2.55–2.80 (m, 24H), 2.92–3.26 (m, 12H), 4.56 (s, 4H), 4.05 (s, 2H) 6.75–7.05 (m, 16H); ^{13}C NMR (D$_2$O) δ 33.2, 34.1, 36.7, 37.5, 42.6, 49.3, 50.3, 51.4, 124.9, 126.3, 126.8, 127.0, 128.8, 141.7, 143.3, 144.6, 160.7, 175.2, 181.1.