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Tuning of morphology and polymorphs of carbonate/polymer hybrids using photoreactive polymer templates

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We here report the use of photolithographic polymer thin films as matrices for the formation of inorganic/organic polymer thin-film hybrids and the tuning of their structures. Poly(vinyl alcohol) derivatives bearing photoreactive styrylpyridinium moieties (PVA-SbQs) are used as matrices for the crystallization of $CaCO_3$ and $SrCO_3$. Thin-film hybrids are formed on the matrices in the presence of poly(acrylic acid). The polymorphs and morphologies of the $CaCO_3$ nanocrystals assemblies are tuned by the photoreaction and the polymer structures of the matrices. Hybrid $CaCO_3$ films exhibiting complex shapes and different surface structures are formed on the photoimaged PVA-SbQ matrix. Crystallization of $SrCO_3$ on the photoimaged matrix leads to selective formation of film hybrids on the UV-irradiated areas. These approaches may have great potential in controlling the complex structures of inorganic/polymer composite materials.

Introduction

Biominerals are inorganic/organic composites formed by living organisms.[1-3] They have hierarchically ordered structures and show high optical, mechanical, and biological functionalities and unique properties that cannot be achieved by a simple combination of their organic and inorganic constituents. The formation processes of biominerals have provided attractive models for the development of hybrid materials because self-organized elaborate structures were obtained under mild conditions with biomacromolecule templates.[3-8] Inspired by biomineralization, control of the crystallization of $CaCO_3$ using synthetic templates has been studied for the last two decades.[7-15] Soluble polyelectrolytes,[16–19] solid templates,[20–26] and combinations of these materials[27–35] have been used for controlling the crystallization of $CaCO_3$ to develop novel hybrid materials.

It is known that crystal morphologies can be tuned by specific interactions between crystalline planes and the functional groups of the additives[3,20,21,29] and/or diffusion-limited crystal growth processes.[30–33,36-40] The formation of periodic relief structures consisting of $CaCO_3$ and related minerals has been achieved using gels as template for crystallization.[32,33] Amorphous calcium carbonate (ACC)[41–47] stabilized through interaction with micro-structured templates has been used to prepare complex structures.[20–26] The ACC molded in the solid templates is then transformed into crystalline material. Positional control of $CaCO_3$ crystal growth has been achieved using functionalized solid substrates with microstructures such as self-assembled monolayers (SAMs)[20] and photolithographed polymer matrices.[23,33] The interactions between the functional groups and ions induce a high local concentration of ions, resulting in hetero-nucleation on the substrates.[20,21] Highly ordered alignments of the functional groups of SAMs are also useful for polymorph and orientation control of the obtained $CaCO_3$ crystals. Matching between the lattice of the inorganic crystal and the substrate is important for the selection of polymorph and crystallographic orientation.

We have developed $CaCO_3$/polymer hybrid films showing ordered morphologies and crystallographic orientations by exploiting cooperative effects between soluble acidic polymers and polymer matrices.[7,11,12,27–35] These ordered $CaCO_3$/polymer hybrids show functionality as diffraction gratings[30] and substrates for cellular engineering.[31,48] In our previous studies,[33] we obtained $CaCO_3$ films comprising nanocrystal assemblies with complex morphologies on a matrix of poly(vinyl alcohol) bearing styrylpyridinium moieties (PVA-SbQ). Photoimages written in the matrices were transferred to the $CaCO_3$ crystals by self-organization of the regular surface-relief structures in the nonirradiated areas of the matrices. However, in this case, only vaterite $CaCO_3$ crystals were formed in the photoimaged structures.[33] If this photoimaging crystallization approach could be applied to the formation of other polymorphs[8] of $CaCO_3$ and a wider variety of inorganic crystals,[21,31,49,50] a new synthetic methodology for hybrid materials could be achieved.

In the present study, we examined the effects of the structures of the photoreactive polymer templates and the period of UV irradiation on the crystallization of $CaCO_3$ and $SrCO_3$. Photoreactive PVA-SbQs with lower degrees of hydrolysis than that of the polymer used in the previous study were synthesized from PVA as polymers for the matrices used to control crystal growth.[33] These less-hydrolyzed PVA matrices form hydrogels in aqueous solution and their properties, which are modified by the crosslinking reaction, and considerably affect the crystal growth of $CaCO_3$.[32]

Experimental Section

Materials

Poly(vinyl alcohol) (PVA: M_w = 1.24 × 10^5–1.86 × 10^5, 88% hydrolyzed) and poly(acrylic acid) (PAA: M_w = 1.8 × 10^3) were purchased from Sigma-Aldrich Japan. Terephthalaldehyde, 4-picoline, 1,3-propanediol, and iodomethane were obtained from Tokyo Chemical Industry (Japan). Calcium chloride and ammonium carbonate were purchased from Wako (Japan). All reagents were used without further purification. Silica gel column chromatography was carried out with silica gel 60 (spherical, 40–50 µm) from Kanto Chemical (Japan).

Characterization

Polarizing optical microscopy images were taken with an Olympus BX51 polarizing optical microscope. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4700 field-emission SEM and a Keyence VE-9800 SEM operated at 5 kV. Samples were coated with platinum using a Hitachi E-1030 ion sputter coater. Laser Raman spectra were recorded using a JASCO NR-1800. ^{1}H (400 MHz) NMR spectra were obtained on a JEOL LAMDA 400 spectrometer. UV-visible (UV-Vis) absorption spectra were recorded with a JASCO V-670 spectrophotometer and an Agilent 8453 spectrophotometer.

Preparation of the polymer matrices for the crystallization

The photoreactive PVA-SbQs (PVA-SbQ**1, 2**) were synthesized according to the procedures reported in previous papers, and were characterized using UV-Vis absorption spectra and NMR measurements.[33,51,52] The polymer matrices were prepared by spin-coating of a 4 wt% solution of the PVA-SbQ in dimethylsulfoxide on glass substrates.[33] UV irradiation of the dried polymer matrices was performed with a high-pressure mercury lamp (USHIO, 365 nm, 15 mW cm^{-2}). An annealed PVA-SbQ matrix was prepared by thermal procedures[32,54,55] of the dried matrix before the UV-irradiation.

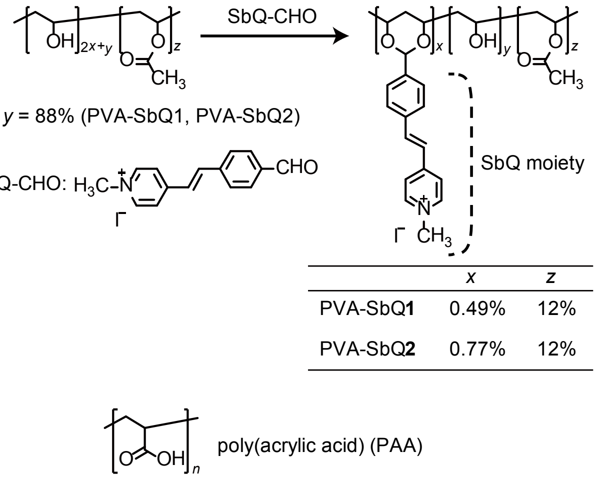
Crystallization of $CaCO_3$ and $SrCO_3$

Purified water obtained from an Auto pure WT100 purification system (Yamato, Tokyo, Japan) was employed in the crystallization of $CaCO_3$. First, PAA was added to an aqueous solution of calcium chloride ($[Ca^{2+}]$ = 10 mM, [PAA] = 2.5 × 10^{-3} wt%).[33] The solution was then transferred to a vessel containing the polymer matrix and the vessel was placed in a closed desiccator at 30 °C with a vial of ammonium carbonate. $SrCO_3$ was crystallized in the same manner using strontium chloride solution ($[Sr^{2+}]$ = 10 mM, [PAA] = 1.0 × 10^{-2} wt%) instead of the calcium chloride solution.

Results and Discussion

Crystallization of $CaCO_3$ on photoreactive polymer matrices

PVA-SbQs with different degrees of substitution of photoreactive SbQ moieties (PVA-SbQ**1, 2**) were synthesized according to previous reports (**Scheme 1**, Supplementary Information, **Fig. S1**).[33,51,52] The amount of photoreactive SbQ moiety substituted into PVA-SbQ**1** (0.49 mol%) is similar to that of the PVA-SbQ used in the previous study (0.44 mol%), while PVA-SbQ**2** contained a higher concentration of SbQ moiety (0.77 mol%).



	x	z
PVA-SbQ**1**	0.49%	12%
PVA-SbQ**2**	0.77%	12%

Scheme 1 Structures of photoreactive polymers (PVA-SbQ**1, 2**) and PAA used for the crystal growth.

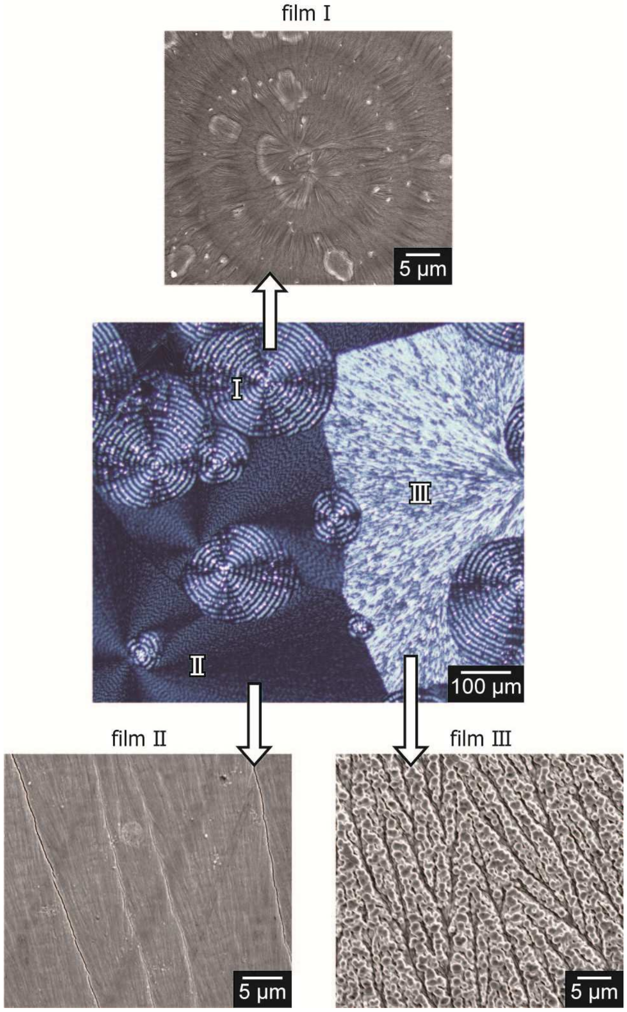


Fig. 1 Polarizing optical microscopy (POM) image of $CaCO_3$ films formed on PVA-SbQ**1** matrix UV irradiated for 10 min, and scanning electron microscopy (SEM) images of the $CaCO_3$ films **I**, **II**, and **III** shown in the POM image

The matrices for the crystal growth were prepared by spin-coating of these polymers onto glass substrates and subsequent UV irradiation. The matrices were then immersed into aqueous solution of calcium chloride (10 mM) containing poly(acrylic acid) (PAA). $CaCO_3$ was crystallized on the matrix by slowly diffusing ammonium carbonate vapor into the calcium chloride solution at 30 °C for 16 h.

$CaCO_3$/polymer films exhibiting different morphologies and polymorphs were formed on polymer matrices and the structures of the hybrid films were dependent on the photoreaction of the matrices. **Figure 1** shows polarizing optical microscopy (POM) and scanning electron microscopy (SEM) images of the $CaCO_3$ crystals grown on the PVA-SbQ**1** matrix with UV irradiation for 10 min. Three types of $CaCO_3$ nanocrystals assemblies are formed on the matrix. The Raman spectra[53] of these films suggest that their polymorphs were different (Supplementary Information, **Fig. S2**). Film **I** displayed concentric ring patterns in its POM and SEM images (Fig. 1, top). The concentric birefringence pattern of film **I** indicates that the *c* axes of the nanocrystals in the disklike $CaCO_3$ film were alternately aligned perpendicularly (dark ring areas) and parallel (bright ring areas) to the radial direction of the disk.[31] The periodic patterning of crystallographic orientations induce the formation of three-dimensional ordered structures[31] and such ordered structures have been reported to be useful as substrates for cultivation of pre-osteoblast cells.[48] The polymorph of film **I** was calcite and its thickness was about 0.4 μm (Supplementary Information, **Fig. S3**). Film **II** showed darker mosaic textures under crossed polarizers and its surface morphology was flat (Fig. 1, bottom left). The *c* axes in the darker areas of the mosaic texture were also perpendicularly oriented. Film **III** displayed a dendritic surface morphology (Fig. 1, bottom right) and brighter birefringence than the vaterite film **II**. Films **II** and **III** consisted of vaterite. Cross-sectional observation revealed that film **III** (thickness: 0.7–0.8 μm) was thicker than film **II** (thickness: 0.3 μm) (Supplementary Information, Fig. S3). The thickness and the parallel *c* axis orientation were the reasons for the brighter birefringence of film **III**.

UV irradiation for longer periods increased the fraction of concentric calcite film **I** and decreased that of dendritic vaterite film **III** (**Fig. 2a**). Further UV irradiation more than 120 min resulted in the dominant formation of calcite film **I** on the PVA-SbQ**1** matrix. For PVA-SbQ**2**, which has a higher substitution of SbQ (PVA-SbQ**1**: 0.49 mol%, PVA-SbQ**2**: 0.77 mol%), calcite film **I** and flat vaterite film **II** were formed, but dendritic film **III** is not obtained (Fig. 2b). In addition, for the PVA-SbQ**2** matrix UV irradiation for only 20 min was enough to cause dominant formation of calcite film **I**.

The obtained $CaCO_3$ crystals exhibited different structures. This observation suggests that the degree of crosslinking in the PVA-SbQ**1** and **2** matrices affected the morphologies and polymorphs of the formed $CaCO_3$ films. The increased degree of crosslinking in the matrix may have exerted effects on crystallization conditions such as the diffusion rate and concentrations of ions in the polymer matrix. It has been reported that diffusion-controlled crystal growth leads to the formation of various types of patterned crystals.[49–53] We assume that the morphologies of the $CaCO_3$ crystals obtained in the present study were generated through competition between the consumption and diffusion of the ions in the gel matrices. Increases in the amount of SbQ moieties in the polymer matrices and the UV-irradiation period both increased the amount of photocrosslinking, and thus caused similar effects on the formation of the three types of $CaCO_3$.

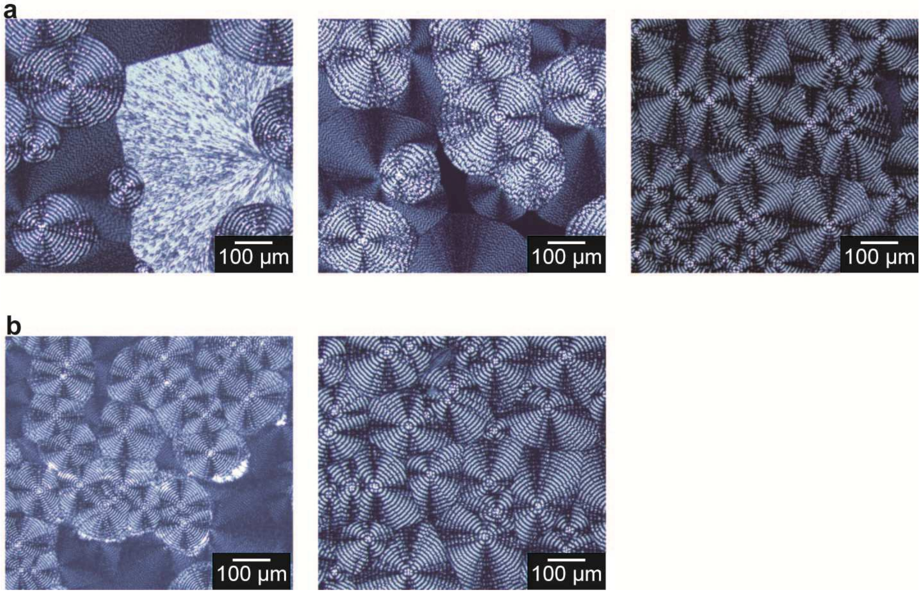


Fig. 2 (a) POM images of $CaCO_3$ crystals formed on PVA-SbQ**1** matrices with UV irradiation for 10 min (left), 20 min (center), and 120 min (right). (b) POM images for $CaCO_3$ crystals formed on PVA-SbQ**2** matrices UV-irradiated for 10 min (left) and 20 min (right).

We previously reported that the polymorphs of $CaCO_3$ films formed on the PVA matrices are tuned by the thermal conditions used to prepare the matrices.[32,54,55] Highly crosslinked PVA hydrogel matrices prepared by annealing for a longer period induce the nucleation of calcite on the surface of the matrix,[31,32] while a slightly crosslinked PVA hydrogel matrix induces the formation of aragonite crystals inside the matrix.[32] PVA-SbQ matrices highly crosslinked through longer photoirradiation also induced the formation of calcite in the present study. We assume that the diffusion of ions and/or ACC into the highly crosslinked matrix was inefficient and that the PAA in the solution affected nucleation on the surface of the matrix, resulting in the formation of calcite.

Effects of SbQ groups in the polymer matrices on the $CaCO_3$ crystallization were studied by crystallization using PVA-SbQs matrices prepared through thermal procedures without UV-iiradiation. Vaterite films showing regular-surface relief structures were mainly formed onto the annealed[32,54,55] PVA-SbQ**1** and **2** matrices (**Fig. 3**, Supplementary Information, **Fig. S4**). Smaller disklike films were composed of calcite. These films displayed crossed extinction patterns under crossed polarizers. While it is reported that aragonite $CaCO_3$ are selectively formed on annealed PVA matrices,[29,32,54,55] the photo-crosslinked nor the annealed PVA-SbQ matrices did not induce the nucleation of aragonite. Selective formation of aragonite on the PVA matrix may have occurred because of the lattice matching between aragonite $CaCO_3$ and crystalline PVA.[29,55] It is assumed that crystalline domains were not formed in the PVA-SbQ matrices because of bulky SbQ groups, and that aragonite was not formed without the presence of crystalline domains of PVA. Since the similar crystal films were obtained onto the annealed PVA-SbQ**1** and **2** matrices, it is suggested that the SbQ moieties did not significantly affect the crystallization of $CaCO_3$.

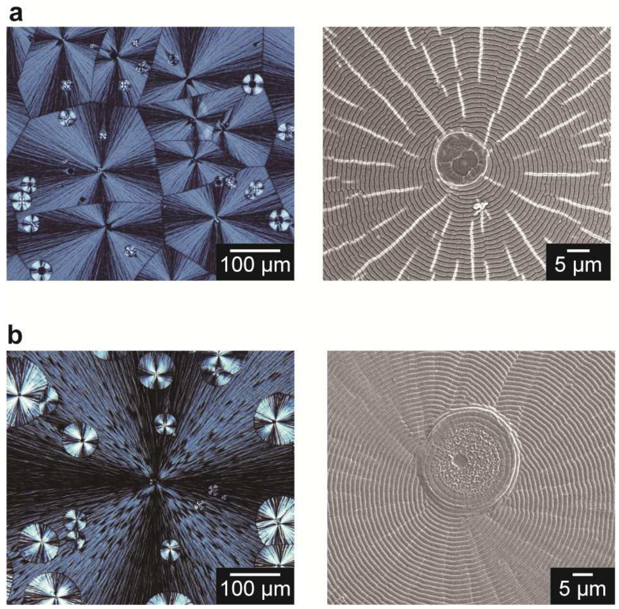


Fig. 3 $CaCO_3$ crystals grown on (**a**) PVA-SbQ**1** and (**b**) PVA-SbQ**2** matrices prepared through thermal procedures (annealed at 180 °C for 10 min): left: POM images; right: SEM images.

Photoimaging and tuning of $CaCO_3$/polymer hybrids with various structures

We prepared various $CaCO_3$/organic films with imaged and hierarchically ordered by using the photoimaged polymer matrices of PVA-SbQ**1** and **2** (**Fig. 4**). Photoimaging of PVA-SbQ**1** resulted in the formation of vaterite films with the imaged shape and a small amount of calcite film **I** (Fig. 4a). The vaterite films consisted of the flat film **II** on the UV-irradiated areas and film **IV**, which exhibits self-organized regular surface-relief structures on the nonirradiated areas. The periodicity of the regularly aligned grooves on the surface of film **IV** is about 1–2 µm. Thickness of the film **IV** was about 800 nm (Fig. S3). The structures of vaterite film **II** and **IV** are the same as those of vaterite films formed on the highly hydrolyzed PVA-SbQ matrices used in the previous study,[33] although concentric calcite films **I** formed on the highly hydrolyzed matrix.

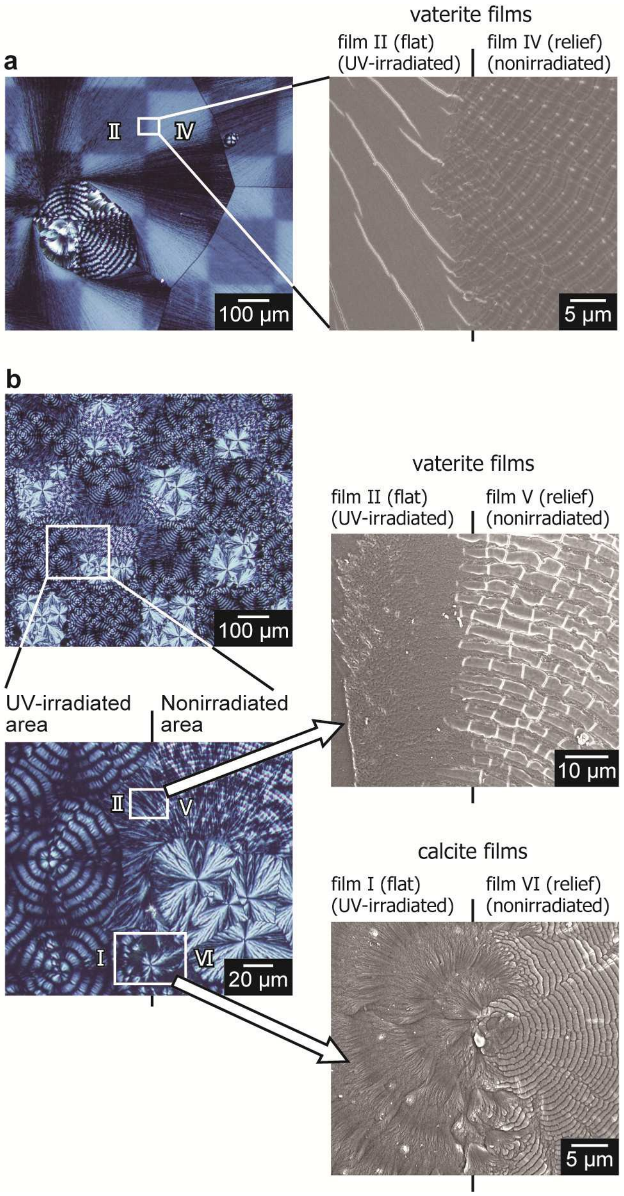


Fig. 4 $CaCO_3$ films formed on photoimaged (**a**) PVA-SbQ**1** and (**b**) PVA-SbQ**2** matrices (irradiated period: 10 min): left: POM images; right: SEM images.

Crystallization on photoimaged PVA-SbQ**2** matrix (Fig. 4b) resulted in the formation of calcite films and vaterite films with photoimaged structures. Two types of $CaCO_3$ films showing brighter birefringence, vaterite film **V** and calcite film **VI** were formed on the nonirradiated areas, while concentric calcite film **I** and flat vaterite film **II** were grown on the UV-irradiated areas (Fig. 3b). Thicknesses of film **V** and **VI** are about 800 nm (Fig. S3). Vaterite film **V** exhibited concentric regular surface-relief structures and the distances between the grooves were 5–7 µm.

The calcite film **VI** also displayed regular surface-relief structures, the periodicity of which was about 1 µm. On the boundary areas, the morphologies of the $CaCO_3$ films were changed but the polymorphs were not changed. The degree of crosslinking in the hydrogel matrices affected both the self-organized structures and the polymorphs of the crystals,[32] and their morphologies were even more highly dependent on the degree of crosslinking.

Table 1 $CaCO_3$ films formed on the PVA-SbQ matrices.

$CaCO_3$ films	Morphology	Crystallographic orientation	Polymorphs	Matrix polymer	UV irradiation period
film **I**	smooth surface-relief	periodical	calcite	PVA-SbQ**1, 2**	≥ 60 min (PVA-SbQ**1**), ≥ 20 min (PVA-SbQ**2**)
film **II**	flat	periodical	vaterite	PVA-SbQ**1, 2**	10–60 min (PVA-SbQ**1**) ≤ 10 min (PVA-SbQ**2**)
film **III**	dendritic	dendritic	vaterite	PVA-SbQ**1**	≤ 10 min (PVA-SbQ**1**)
film **IV**	regular surface-relief	radial	vaterite	PVA-SbQ**1**	no
film **V**	regular surface-relief	radial	vaterite	PVA-SbQ**2**	no
film **VI**	regular surface-relief	radial	calcite	PVA-SbQ**2**	no

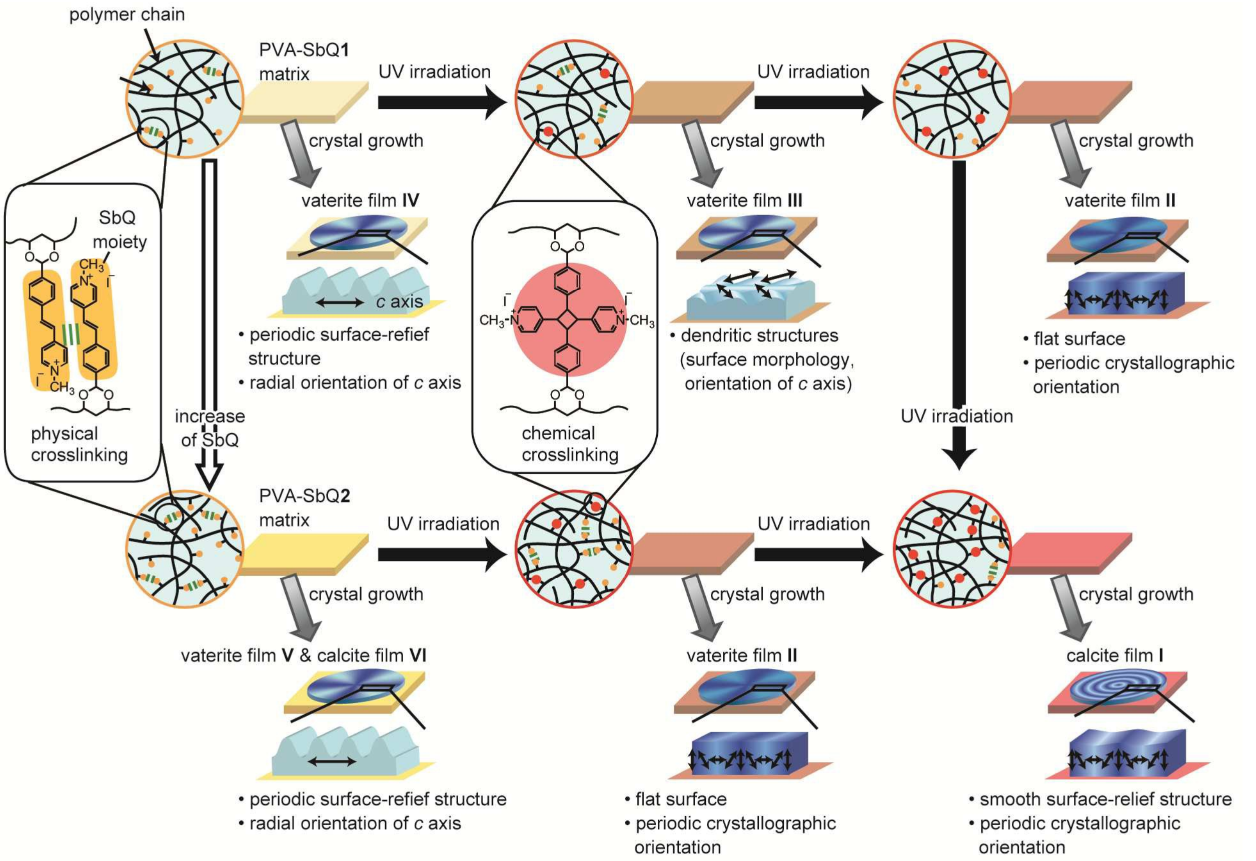


Fig. 5 Schematic of the tuning of $CaCO_3$ crystals formed on the PVA-SbQ matrices

The results of $CaCO_3$ crystallization on the PVA-SbQ matrices are summarized in **Fig. 5** and **Table 1**. The vaterite film **IV,** and vaterite film **V** and calcite film **VI** were formed on the nonirradiated areas of the PVA-SbQ**1** and **2** matrices, respectively. These $CaCO_3$ films displayed periodic surface relief structures. The polymer matrices may have formed swollen hydrogels in the aqueous solution because aggregated non-reacted SbQ groups may function as physical crosslinking points.[30,32,33] The thicker crystal film **V** and **VI** with regular surface-relief structures were formed onto the well-swollen hydrogel matrices. UV irradiation caused the formation of covalent crosslinking points and the polymer matrices became less swellable (Supplementary Information, **Fig. S5**), resulting in the formation of denser polymer networks. Dense polymer networks physically suppress ion diffusion and permeation, which is a key factor in the self-organization of patterned crystals and their morphological changes.[30-33,39-43] Indeed, the increase in the amount of crosslinking points in the PVA-SbQ**1** and **2** matrices led to the formation of dendritic vaterite film **III** and flat vaterite film **II**. In addition, we previously reported that increase of crosslinking points in the PVA gel matrix induced the morphological change of aragonite $CaCO_3$ films from concentric surface-relief structures into dendritic structures.[32] It has been known that dendritic assemblies of nanocrystals are obtained under lower degree of supersaturation than that for the formation of the circular supherulites.[37] We assume that the lower supersaturation degree and limited diffusion of the ions caused by the denser polymer networks induced the morphological changing of the vaterite films. For the highly crosslinked PVA-SbQ matrices, the concentric calcite film **I** was selectively formed because of the nucleation on the surface of the polymer matrices.[31,32]

Formation of $SrCO_3$/polymer hybrid films with photoimaged structures

It is of interest to examine the effects of photoreactive polymer matrices on the crystallization of other carbonate crystals such as $SrCO_3$. $SrCO_3$ crystallization using photoimaged PVA-SbQ matrices led to the formation of $SrCO_3$ films with the photoimaged structures (**Fig. 6**, Supplementary Information, **Fig. S6**). The $SrCO_3$ films formed on the nonirradiated areas of the PVA-SbQ**1** matrix showed brighter birefringence and periodic surface-relief structures with higher regularity than those of the crystal film on the UV-irradiated areas. In contrast, the use of PVA-SbQ**2** matrices with photoimaged matrices resulted in selective formation of $SrCO_3$ on the photoirradiated areas of the matrices (Fig. 6b).

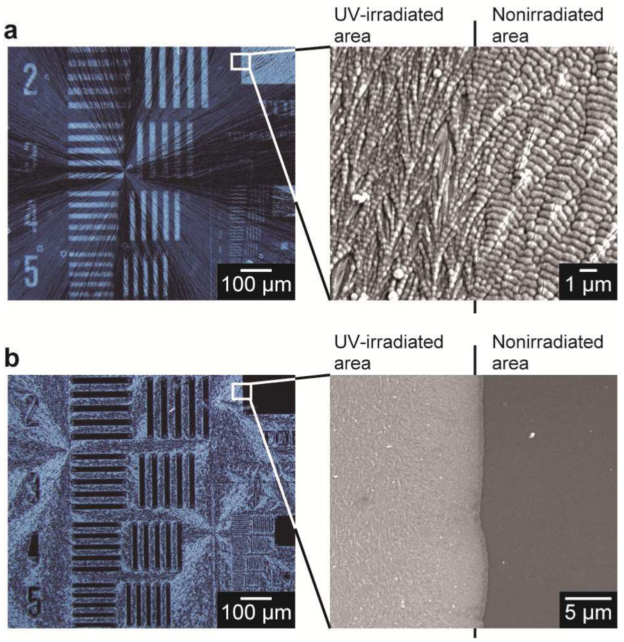


Fig. 6 $SrCO_3$ films formed on photoimaged (a) PVA-SbQ**1** and (b) PVA-SbQ**2** matrices (irradiation period: 20 min); left: POM images; right: SEM images.

The effects of the degree of crosslinking of the PVA-SbQ were studied by using of the PVA-SbQ**1** and **2** matrices crosslinked through a thermal process (Supplementary Information, **Fig. S7**). $SrCO_3$ films were obtained in the presence of PAA for PVA-SbQ**1** matrices annealed at 160 °C and 175 °C (10 min). The PVA-SbQ**2** matrix annealed at 175 °C also induces the formation of $SrCO_3$ films in the presence of PAA. However, the PVA-SbQ**2** matrix annealed at 160 °C did not show any function as a matrix for the crystallization of $SrCO_3$.

These results indicate that the SbQ moieties of the polymer matrices inhibit the crystallization of $SrCO_3$ on the matrix and that this inhibition becomes less effective when the polymer chains are highly crosslinked. The selective crystallization of $SrCO_3$ on the photoimaged PVA-SbQ**2** matrix was caused by such interaction between the SbQ moieties. In contrast, the PVA-SbQ**1** matrix, which had a lower concentration of SbQ moiety, did not show such inhibition effects even though the polymer chains were less crosslinked. The morphological changes of the $SrCO_3$ films on the photoimaged PVA-SbQ**1** matrices may have been caused by the different swelling behaviors of the matrices.[33,49]

Conclusion

We have developed inorganic/polymer composites with photoimaged structures on photoreactive polymer matrices. The polymorphs of the $CaCO_3$ crystals formed on the polymer matrices were tuned by the UV irradiation period and the structure of the photoreactive polymer. Differences in the degree of crosslinking in the polymer matrices affected the formation of the calcite and vaterite structures of $CaCO_3$. For $SrCO_3$, photoimaging of PVA-SbQ led to the on-off switching of the crystallization as well as morphological tuning of the crystals. The approach reported here may have great potential for the development of complex and hierarchical structures from nanocrystalline materials under mild conditions.

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Notes and references

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A table of contents entry

Tuning of morphology and polymorphs of carbonate/polymer hybrids using photoreactive polymer templates

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Crystallization of inorganic carbonate on photolithographic polymer matrices led to development of inorganic/organic hybrid materials with photo-controlled and self-organized structures.