Biomimetic Fabrication of Vaterite Film from Amorphous Calcium Carbonate on Polymer Melt: Effect of Polymer Chain Mobility and Functionality

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We demonstrate that amorphous calcium carbonate (ACC) thin film crystallization on poly(ϵ-caprolactone) (PCL), poly(bisphenol A carbonate) (PC), poly(*tert*-butyl acrylate) (PtBA), and poly(methyl methacrylate) (PMMA) substrates is affected by the chain mobility and functionality of the polymers above and below their melting and glass transition temperatures. ACC films are transformed into metastable (004) vaterite films on PCL and PMMA melts and are transformed into thermodynamically stable calcite (110) films on PC and PtBA substrates at 100 °C. On the basis of our results, we suggest that, in the melt phase, polymer chains containing ester groups trigger the formation of oriented vaterite films through interactions between the ester functionalities and ionic species present in ACC. In contrast, less reactive ester groups in polymer substrates, as well as esters in the solid phase, were found not to affect the kinetic growth of $CaCO_3$ crystals in ACC in air. A comparison of the ACC film crystallization processes on PCL and PC established a dependency on the chain mobility of the polymers, and on PtBA and PMMA, it was confirmed that the ester group reactivity also affects the crystallization of ACC films.

Introduction

Inspired by the biomineralization process observed in seashell nacre, the biomimetic mineralization of calcium carbonate has received much attention in recent times. This, combined with a broader understanding of how organic molecules in biological systems affect the nucleation and growth of biominerals, has led to the design of new hybrid materials.[1] Calcium carbonate is an attractive model mineral because its various crystal forms are easily recognizable, and its morphology has been the subject of control in biomineralization processes. Many studies have demonstrated that the macromolecules and organic molecules control the nucleation, structure, morphology, crystal orientation, and spatial confinement of the inorganic phase in solution or air conditions.[2]

Calcium carbonate has three anhydrous crystalline polymorphs with varying thermodynamic stabilities, ranging from the most stable calcite, to aragonite, through to the least stable vaterite form. Additionally there exist three metastable forms: amorphous $CaCO_3$ (ACC) and monohydrate and hexahydrate $CaCO_3$. ACC has been found to widely exist in biological organisms, is used as temporary storage deposits, and transforms with time into a crystalline form. For example biogenic single crystals of calcium carbonate are often produced by the conversion of ACC.[3] Some of them are stable and are utilized as mechanical stiffener. The in vitro formation of ACC as transient precursor phase in highly supersaturated solution has been known for a long time. ACC is readily stabilized by the macromolecules incorporated within the mineral phase and can be artificially stabilized by elimination of the remaining water in ACC after deposition from highly supersaturated solution.[4] This stabilized ACC offers an opportunity to gain a better understanding of the calcium carbonate crystallization process.[5]

Various synthetic complexes including macromolecules such as poly(acrylate), poly(Glu) or poly(Asp), stearic aicd monolayer, glycoproteins, and mercaptophenol-protected gold colloids have been investigated as potential biomineralization models in aqueous solutions.[6] Aizenberg et al.[7] previously suggested that the ACC film crystallization process occurs not by solid-state transformation but rather by mass transport between the amorphous and crystalline

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phases, in which water molecules play the role of mass transport media. Moreover, both thermodynamically stable calcite and mixtures of calcite and the less stable vaterite are formed within in vitro systems during the ACC crystallization process. The question of what might happen if ACC film crystallization is performed on polymer melts having nonionic functional groups (under low humidity conditions in air) raises some interesting issues. In principle, inorganic nuclei can be formed on organic surfaces simply by lowering the activation energy of nucleation ($\Delta G^{\ddagger}$) through interfacial recognition.[8] Different interactions between organic surfaces and inorganic ions may then create an ensemble of nucleation profiles of $\Delta G^{\ddagger}$, which theoretically could be used to kinetically control crystal polymorph formation. In view of this, we conjectured that certain polymer chain functional groups (such as esters) in the melt phase could play an important role in the nucleation of ACC films, as well as helping to stabilize the resultant film. Moreover, we speculated that at temperatures above the polymer's melting (T_m) or glass transition (T_g) temperatures, the chain mobility and chemical structure of the polymer may affect the reactivity of its functional groups, triggering the different crystal formations in ACC films.

In this study, we demonstrate how the chain mobility and functionality of selected polymer substrates, at high temperatures and at temperatures above and below their respective T_m and T_g values affect the crystallization of ACC films in air. For this purpose, ACC thin films have been deposited on selected polymer substrates that have ester groups in either their backbone or side chains.

Experimental Section

Materials. Poly(ϵ-caprolactone) (PCL) (M_n = 890 kg/mol), poly(bisphenol A carbonate) (PC) (melt index = 7.0 g/(10 min)), poly(methyl methacrylate) (PMMA; medium molecular weight), and poly(acrylic acid) (PAA; M_w = 2000 g/mol) were obtained from Aldrich and used as received. Poly(*tert*-butyl acrylate) (PtBA) was synthesized by atom transfer radical polymerization (M_n = 49 kg/mol, M_w/M_n = 1.17).

Sample Preparation. Thin, spin-coated polymer films were used as model polymer templates in this study. PCL, PC, PtBA, and, PMMA were dissolved in chloroform (50 mg/mL) and spin-coated onto cleaned silicon wafers at 2500 rpm. To improve the film adhesion properties, polymer films were annealed for 4 h under vacuum (4×10^{-5} Torr) at a temperature above their T_g (50 °C for PCL, 170 °C for PC, 70 °C for PtBA, and 120 °C for PMMA).

ACC film preparation was performed according to the reported method.[5a] A 20 mM $CaCl_2$ solution containing 20 μg/mL PAA was prepared using Milli-Q deionized water. The prepared solution was placed in a vial and polymer films were then supported (face down) over the vial. The whole system was subsequently placed in a desiccator over solid ammonium carbonate, which was then sealed and then left to form ACC films at room temperature for 1.5 h. After ACC film formation, the substrate was rinsed with water to remove any weakly bound $CaCO_3$ and then blown dry with N_2. These ACC films were crystallized at room temperature (RT) and at temperatures above and below the melting and glass transition temperatures of the polymer substrates.

Film Characterization. $CaCO_3$ thin films formed on polymer templates were observed in the reflective mode using an optical microscope (Zeiss) equipped with a cross-polarizer. High-resolution images of the deposited films (Pt-coated prior to examination) were obtained using a field emission scanning electron microscope (FE-SEM, Hitachi S-4200), at an operating voltage of 8 kV. Infrared spectroscopic analysis of $CaCO_3$ films on polymer-coated silicon wafers was performed in transmission mode (FT-IR, BIO-RAD FTS375C) and scanned from 4000 to 400 cm^{-1}. The growth of $CaCO_3$ crystals on polymer substrate was identified by X-ray diffraction, performing $\theta/2\theta$ scans in reflection mode at the 8C1 beam line at the Pohang Accelerator Laboratory (PAL), Korea.

Results and Discussion

Formation of Amorphous Calcium Carbonate Films on Polymer Substrate. PCL, PC, PtBA, and PMMA have been selected as suitable polymer substrates for the fabrication of ACC films, due to the presence of ester groups in either the polymer backbone or side chains and to their wide-ranging melting and glass transition temperatures [T_g(PCL) = −72 °C, T_m(PCL) = 60 °C, T_g(PC) = 140 °C, T_g(PtBA) = 50 °C, T_g(PMMA) = 110 °C]. Previous studies[6] have shown that the addition of soluble ionic macromolecules to the solution enables the controlled crystallization of $CaCO_3$ in aqueous solution. However, to date there have been no reports concerning the crystallization of ACC on nonionic macromolecules in air. In the work described here, the chain mobility and reactivity of the ester groups of the selected polymers are considered at temperatures higher than either their T_m or T_g. Moreover, PCL and PC have quite similar chemical structures, yet at 100 °C, the chain mobility of PCL (T_m = 60 °C) is greater than that of PC (T_g = 140 °C), providing a suitable means with which to investigate the chain mobility effect on the crystallization of ACC films. PtBA and PMMA on the other hand, have been employed to demonstrate the functionality effect on the crystallization of ACC films. Here, the bulky *tert*-butyl substituents in PtBA are known to reduce the reactivity of the ester functionality, making them less active than the ester groups in PMMA.

ACC films were fabricated on these polymer films spin-coated on Si wafers via the slow diffusion of carbon dioxide vapor, from decomposing ammonium carbonate, into the $CaCl_2$ solution at RT (1.5 h). As reported in our previous study,[5a] macroscopic and continuous ACC films with film thickness of approximately 400 nm are formed on flat substrates. Here, there were no $CaCO_3$ crystals immediately apparent on the film surface after it was taken out from solution and dried in a stream of N_2. Transmission IR analysis of the resulting ACC film revealed the presence of a carbonate out-of-plane bending adsorption at 866 cm^{-1} (ν_2), a symmetric stretch in noncentrosymmetric structures at 1070 cm^{-1} (ν_1), and a split peak at 1472 and 1384 cm^{-1} (ν_3), all peaks attributable to ACC.[4c,5a,7]

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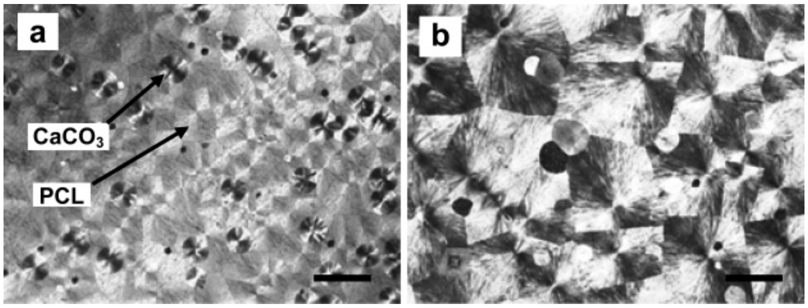

Figure 1. Polarized optical microscope images of $CaCO_3$ films deposited on poly(ϵ-caprolactone) film after removal from solution and storage in air for (a) 4 and (b) 24 h. Scale bars indicate 100 μm.

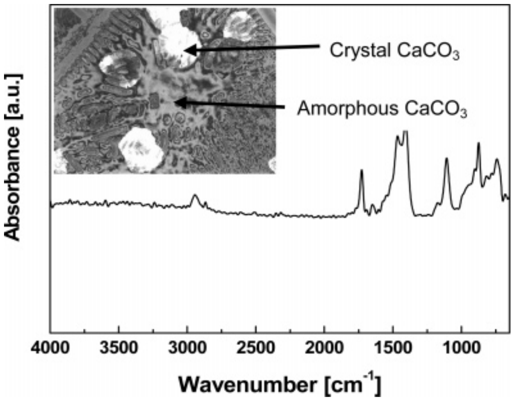

Figure 2. IR spectrum of a partially crystallized $CaCO_3$ film on poly(ϵ-caprolactone) film at 100 °C. A polarized optical microscope image is pictured in the inset.

Crystallization of ACC Films. ACC films were found to be transformed into the polycrystalline spherulitic $CaCO_3$ films on PCL film after 16 h at RT (Figure 1b). Figure 1a shows the early stage of the crystallization of ACC film on PCL film, in which $CaCO_3$ spherulite growth is clearly evident. X-ray diffraction (XRD) data of the same $CaCO_3$ film crystallized at RT indicate that spherulitic $CaCO_3$ films crystallized on all polymer templates used in this study (Figure 1b) were composed of calcite and vaterite (data not shown).[5a]

The crystallization of ACC films at RT typically occurs with the concomitant release of water and impurities.[7] However, during crystallization of ACC film at 100 °C, there is no water absorption band from partially crystallized $CaCO_3$ film in IR spectra (Figure 2). The present results indicate that the water expulsion happens so quickly at high temperature and low humidity, which means the dehydration rate is faster than the crystallization rate. This implies that the crystallization of ACC films at 100 °C is induced by thermal energy, rather than as a result of water release. This is consistent with the initial mass loss observed during the thermal dehydration of the ACC film, which is subsequently followed by crystallization to form calcite.[9]

The biomineralization process typically involves heterogeneous nucleation, relying on the strong interaction at the interface between the substrate and mineral crystal, enabling the formation of dense ceramic films on substrates having high ionic charge or polarity,[10] which interaction gives a strong effect on kinetic selection of nucleating $CaCO_3$. Kato and co-workers[11] reported that polymer film containing ionic species and ionic polymeric additives are able to trigger the controlled nucleation of $CaCO_3$ film in solution. At RT, however, the polymer substrate used in this study does not control the nucleation and growth of ACC films in air, since the polymer chains contain ester groups rather than an active ionic functional group such as carboxyl or hydroxyl functionalities. From the XRD results, it is evident that ACC films deposited on the selected polymer substrates have been transformed into uncontrolled $CaCO_3$ films composed of both calcite and vaterite at RT, due to the inability of ester groups to interact strongly with ionic species (e.g., Ca^{2+}) in the ACC film (data not shown). Consequently, it is possible to speculate that when ACC film crystallization proceeds on the selected polymer substrates at high temperature, the activated ester groups in polymer chain by thermal energy interact with the ACC films, resulting in the controlled nucleation and growth of the film. As mentioned in the Introduction, various interactions between organic surfaces and inorganic ions result in the creation of an ensemble of nucleation profiles of $\Delta G^{\ddagger}$, making it possible to kinetically control the crystal polymorph formed.

Polarized optical micrographs of crystalline $CaCO_3$ films, transformed from ACC films on selected polymer substrates at 100 °C, are shown in Figure 3. From the optical photographs of $CaCO_3$ crystal films on PCL, PC, and PtBA, it is difficult to distinguish between the crystal structure of calcite and vaterite, due to the similarity of the mosaic crystalline film. However, the appearance of microcracks in $CaCO_3$ films formed on PCL and PtBA at 100 °C is believed to be the result of polymer, and subsequently ACC film, shrinkage due to their low T_m (60 °C) and T_g (50 °C), respectively. ACC films formed on solid PC at 100 °C, on the other hand, did not shrink due to the higher T_g (140 °C). This result implies that ACC films formed on polymer melts have the capacity to move with greater ease than ACC films formed on solid substrates. The appearance of wrinkles is also apparent in the crystalline $CaCO_3$ film formed on PCL and PtBA following ACC film shrinkage at 100 °C, as confirmed in the high-magnification SEM images (Figure 4c,d). Moreover, SEM images also confirmed that the $CaCO_3$

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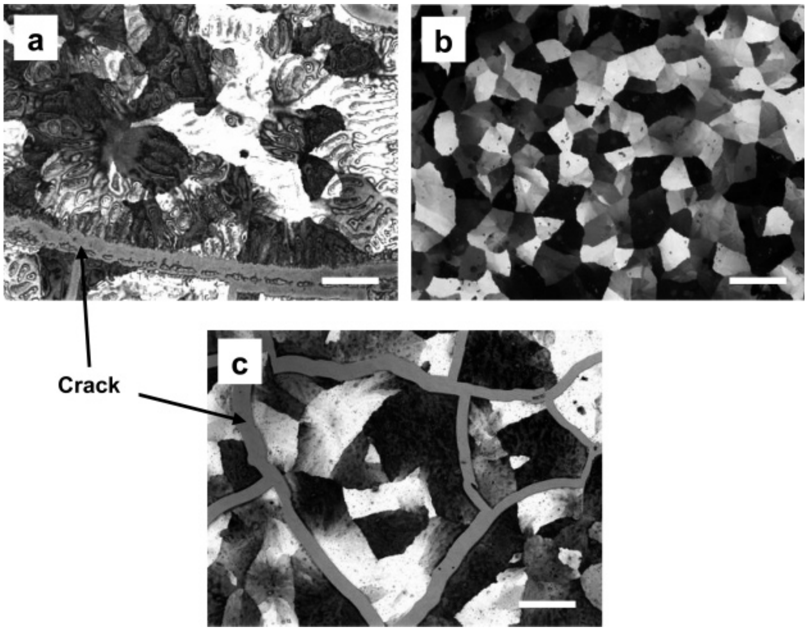

Figure 3. Optical microscopy images of $CaCO_3$ films deposited on (a) poly(ϵ-caprolactone), (b) poly(bisphenol A carbonate), and (c) poly(*tert*-butyl acrylate) crystallized at 100 °C for 40 h. Scale bars indicate 100 μm.

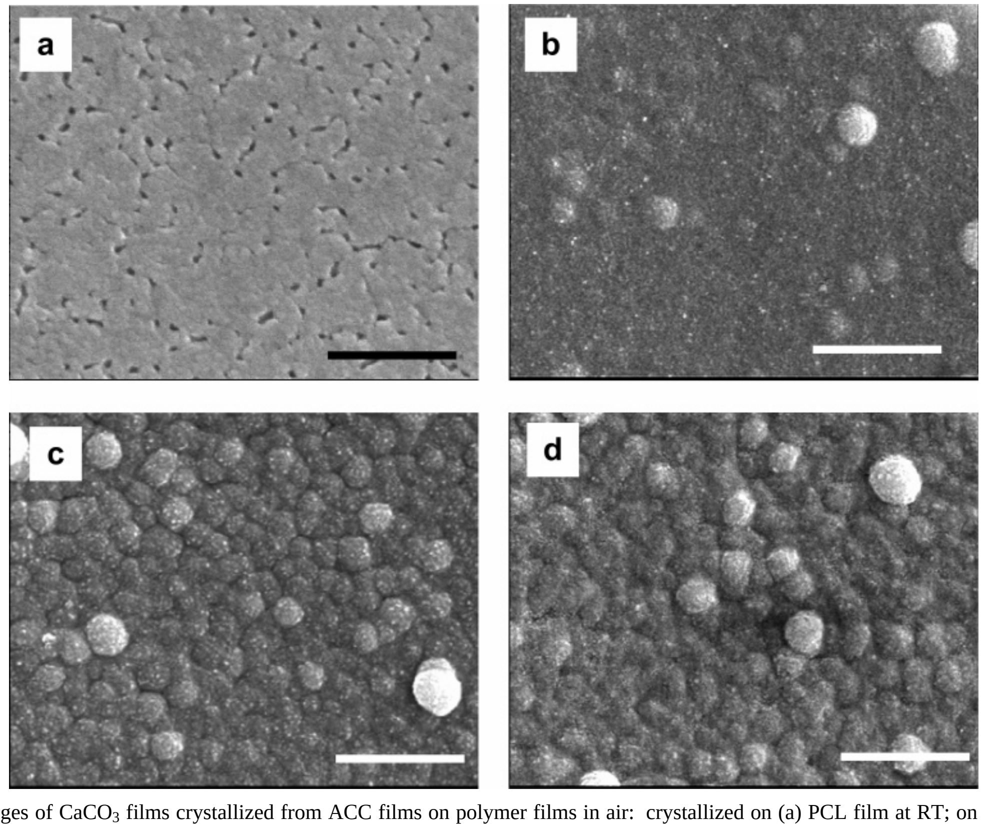

Figure 4. SEM images of $CaCO_3$ films crystallized from ACC films on polymer films in air: crystallized on (a) PCL film at RT; on (b) PC, (c) PCL, and (d) PtBA films at 100 °C. Scale bars indicate 1 μm.

film is composed of particles several tens of nanometers in size (Figure 4c,d). The appearance of several nanopores in the $CaCO_3$ film in Figure 4a is believed to be due to the release of water and impurities during crystallization of the ACC film at RT. At RT and high humidity, particles within the ACC film undergo a dissolution−recrystallization process, resulting in the formation of a flat $CaCO_3$ film consisting of nanopores.

Usually, the formation of crystalline inorganic materials is performed at very high temperatures (above 300 °C) under hydrothermal conditions. In our system, however, ACC film transformation occurs via a solid−solid phase transformation at 100 °C, rather than by mass transformation, as confirmed by the lack of water in the partially crystallized $CaCO_3$ films (Figure 2). Recent thermophysical investigations have been reported in which the crystallization of ACC occurs by thermal activation near $T = 276 \pm 10$ °C, where $\Delta H = -15.0 \pm 3$ kJ/mol was determined by differential scanning calorimetry (DSC).[12] However, these experiments were performed under nonisothermal conditions, unlike the iso-

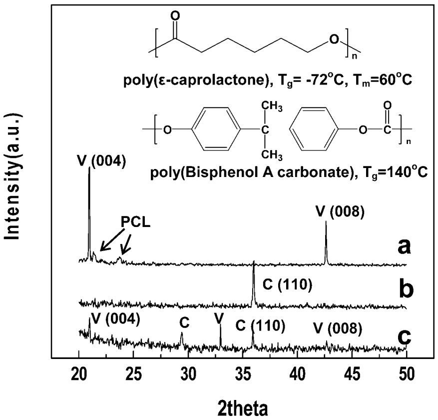

Figure 5. X-ray diffraction patterns of $CaCO_3$ films crystallized from ACC films on (a) PCL and (b) PC at 100 °C: on (c) PC at 180 °C. V and C indicate the vaterite and calcite crystals of $CaCO_3$, respectively.

thermal experiments described in the present work. Therefore, at temperatures (100 °C in the present work) lower than the reported transition temperature of 276 °C, the crystallization of ACC films is expected to occur over long periods of time (ca. 2 days).

Effect of Chain Mobility of Polymer Substrate. Crystal structures of the transformed $CaCO_3$ films were determined by means of XRD measurements with a synchrotron X-ray source, performing $\theta/2\theta$ scans, in which peaks in scattering angle represent the surface normal. Parts a and b of Figure 5 show the XRD patterns for $CaCO_3$ films crystallized on PCL and PC at 100 °C, respectively. It is evident that the XRD peaks in Figure 5a are exclusively due to the vaterite (004) plane, while the peaks in Figure 5b are due to the calcite (110) plane. The XRD data indicate that, at 100 °C, the active ester groups in the PCL melt have a sufficiently high mobility to promote stabilization of the metastable vaterite film. This was further corroborated by the XRD results obtained for the transformed $CaCO_3$ films on PC, in which the solid polyester failed to stabilize the metastable vaterite, but instead induced the formation of the stable calcite film (Figure 5b). This result is presumably due to the crystallization temperature being lower than the PC glass transition temperature T_g (140 °C), resulting in weak interactions with the ACC film.

To ascertain the chain mobility effect of ACC film formation on PC, the crystallization temperature was raised to 180 °C, 40 °C above the T_g of PC. In contrast to the formation of calcite at 100 °C, here the resulting PC melt induced the crystallization of vaterite, as confirmed by the appearance of the (004) peak in the XRD diffraction pattern (Figure 5c). This experimental result clearly suggests that polymer chain mobility exerts a large influence on the crystallization of ACC films. It is also interesting to note that the crystallized $CaCO_3$ film on PC contains calcite crystals (Figure 5c) unlike the PCL melt, in which only vaterite crystals are formed. This result may be due to the lower chain flexibility of the PC aromatic backbone in the melt, compared to the less rigid aliphatic polymers such as PCL and poly(ethylene adipate). Moreover, it is remarkable that there is a specific crystallographic orientation in which the vaterite (004) and calcite (110) planes appear parallel to the substrate (Figure 5)

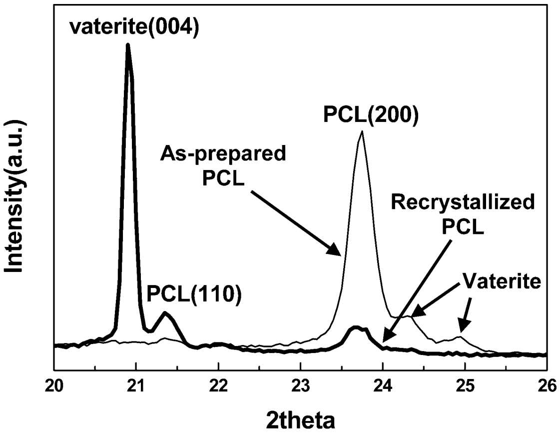

Figure 6. Out-of-plane X-ray diffraction patterns for an as-prepared (light line), and recrystallized (heavy line) poly(ϵ-caprolactone) layer between the vaterite film and a bare Si wafer.

It is also worth considering whether the reaction between the PCL chains and the overlying $CaCO_3$ film has any influence on the recrystallization of the PCL film between the bare silicon wafer and the crystalline $CaCO_3$ film. In response to this, the XRD diffraction patterns for (i) as-prepared PCL film on the bare silicon wafer and (ii) PCL layers, recrystallized at 50 °C for 2 h, sandwiched between a silicon wafer and a vaterite film crystallized at 100 °C, were compared (Figure 6). The XRD diffraction pattern for i reveals the presence of a strong (100) reflection set, but a somewhat weaker (110) set, providing confirmation that the fold planes of the crystals on PCL are parallel to the bare silicon surface. The XRD diffraction patterns for ii, on the other hand, reveal that the crystals on PCL exhibit little or no orientation when in contact with the $CaCO_3$ film. Moreover, the crystallinity of the PCL film (ii) was found to decrease due to the active interaction between the PCL chain ester groups and the ionic species within the $CaCO_3$ film.

Effect of Chain Functionality of Polymer Substrate. From the above results, we have demonstrated that the chain mobility of certain polymers is a predominant factor in the transformation of ACC films on polymer substrates. Furthermore, the reactivity of polymer chain functional groups with high chain mobility toward $CaCO_3$ films has been shown to affect the crystallization of ACC films. With regard to the effect of polymer chain functionality on the crystallization of ACC films on polymer substrate at high temperature, controlled experiments performed on PtBA and PMMA above their respective T_g reveal markedly different effects on the crystallization behavior of ACC films. The corresponding XRD patterns show that ACC films are transformed into oriented calcite (110) and vaterite (004) films on PtBA and PMMA, respectively (Figure 7). On the basis of these results, it was demonstrated that thermodynamically stable calcite films are formed on PtBA substrates, in which the ester side chain groups are protected by the bulky *tert*-butyl substituents, reducing their reactivity. The relatively active PMMA ester groups, on the other hand, trigger the formation of the thermodynamically less stable

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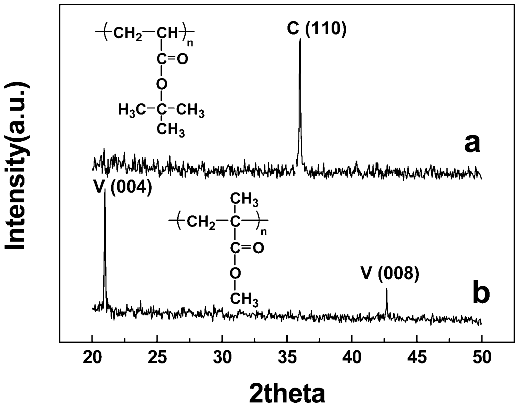

Figure 7. X-ray diffraction patterns for the $CaCO_3$ film crystallized on (a) PtBA at 100 °C and on (b) PMMA at 170 °C. Vaterite and calcite $CaCO_3$ crystals are represented by V and C, respectively.

vaterite form due to the ease with which the PMMA ester groups interact with the ionic species present within ACC films.

It can be concluded, therefore, that ACC films are transformed into oriented metastable vaterite films with the same oriented crystal (004) plane on both PCL (Figure 5a) and PMMA melts (Figure 7b), while the less reactive polymer substrates, such as PC (Figure 5b) and PtBA (Figure 7a), induce the transformation of ACC films into thermodynamically stable calcite films with the same oriented (110) crystal plane at 100 °C, despite these polymers having altogether different chemical structures. It is not clear what causes the formation of the [001] orientation in $CaCO_3$ films on certain polymer substrates at high temperature. One possible explanation may be conjectured by the occurrence of a thermally activated solid−solid phase transformation process such as a pseudo-martensitic transformation, in which the atoms move only short distances in order to join the new phase.[13,14] Recently, Addadi et al.[15] reported that some ACC films contain regions of short-range order, which sometimes resemble the crystalline form into which they are going to transform. The authors conceived that a solid−solid phase arrangement is involved in the short-range order of these ACC films, which allows them to align and coalesce.

According to Addadi et al.,[16] unlike the calcite morph, the vaterite crystalline form is rarely found in either biological or nonbiological systems. Vaterite can only be fabricated in the presence of specific additives in a controlled environment. For instance, anionic dendrimers have been shown to induce the formation of spherical vaterite particles,[17] and double hydrophilic block copolymers[18] have been shown to lead to the precipitation of spherical or hollow shell vaterite particles in solution. Recently, Park et al.[19] reported that two metastable calcium carbonate polymorphs and a hemispherical vaterite morph are formed selectively at the air/water interface by the mediation of poly(ethyleneimine) (molecular weights of ca. 25 000) dissolved in supersaturated calcium bicarbonate solution. This particular metastable vaterite is prepared by kinetically controlled crystallization through the interaction between the ionic polymer and Ca^{2+} or CO_3^{2-} ions in solution. Hosoda et al.[11] have also shown that vaterite thin films can be formed on crystalline poly(vinyl alcohol) matrixes simply by adding poly(glutamic acid) in solution.

In stark contrast to previous work, our study reveals that, under conditions of very low humidity (in air), ACC films on both PCL and PMMA melts can be transformed kinetically into metastable vaterite films through interactions between the polymer chain ester groups and certain ionic species within the ACC film. The mechanism of how polymer melts affect the transformation of ACC films into metastable $CaCO_3$ crystals is a matter for conjecture. However, from our results we speculate that calcium ions within the ACC films interact with the ester groups in the polymer melt during the initial stages of ACC film crystallization. Additionally, nucleation of the vaterite films may be induced by the selected polymer substrates (heterogeneous nucleation) through the same interactions, while calcite films may be generated by homogeneous nucleation at 100 °C.

Conclusion

We have demonstrated how the chain mobility and functionality of selected polymer substrates with ester groups in either the backbone or side chains affect the crystallization of amorphous calcium carbonate (ACC) films fabricated through biomimetic methods. While the controlled crystallization of ACC films failed to occur at room temperature on polymer substrates used in this study, the reaction between polymer chains and ACC films at high temperature resulted in the formation of metastable vaterite film, induced by the chain mobility of ester groups in the PCL and PC backbone. Moreover, the effects of polymer functionality were elucidated through controlled experiments using PtBA and PMMA, in which the more reactive PMMA polymer chains induced the formation of vaterite films above the polymer's glass transition temperature (T_g). In conclusion, we have shown that the predominant effects of polymer melt on the crystallization of ACC films are clearly dependent on the chain mobility and functionality of the polymer chains.

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