Colloid Polym Sci (2005) 284: 175–182
DOI 10.1007/s00396-005-1355-9

ORIGINAL CONTRIBUTION

Jin Zhao
Yanjun Li
Qinglin Kuang
Guoxiang Cheng

Effects of Hydroxypropylmethylcellulose macromolecules used as organic template on the crystallization of $CaCO_3$

Received: 28 December 2004
Accepted: 3 May 2005
Published online: 5 July 2005

J. Zhao · Y. Li · Q. Kuang · G. Cheng (✉)
School of Materials Science
and Engineering, Tianjin University,
Tianjin 300072, China
E-mail: gxcheng@tju.edu.cn
Tel.: +86-22-87894012

Abstract Hydroxypropylmethylcellulose (HPMC) was used as an organic template to synthesize calcium carbonate. Crystals were synthesized in HPMC solution and HPMC hydrogel, respectively. For the mineralization system of HPMC solution, the effects of adding HPMC and rotating the reaction system on the crystal polymorph and morphology of $CaCO_3$ were investigated by X-ray diffractometer (XRD) and scanning electron microscope (SEM). The results showed that the presence of HPMC induced the formation of aragonite. And its content became higher when the concentration of solution increased or when rotating the system with the presence of HPMC. Moreover, it can be seen from SEM that bundle-like $CaCO_3$ appeared and became more with the increase of concentration. The structure and shape of the crystal had close relationship with the condition of mineralization. On the other hand, for the first time, $CaCO_3$ was synthesized in HPMC gel, SEM results indicated that a special structure, a long bar with some slight slots at intervals on the surface, of the crystals which may be caused by the network structure of the gel was found. Thermogravimetry (TG) results showed that $CaCO_3$ crystal products contained some HPMC. Further research on how the gel network modulates the growth of crystals is left to be done in the future.

Keywords HPMC · Calcium carbonate · Organic template · Mineralization · Hydrogel

Introduction

In nature, biological minerals associate with organic macromolecules containing certain kinds of functional groups which can mediate the crystallization behaviors of the minerals [1, 2]. The process of synthesis of these inorganic substances is called biomineralization [3]. The study on biomineralization has shown that the organic polymers play important roles in the whole process by acting as templates that serve as a pattern for the production of a second structure [4]. However, the templating mechanisms are poorly understood.

Calcium carbonate ($CaCO_3$) is an abundant component in fish otoliths, human brain stones, gallstones, and, notably, in the nacreous layer of mollusc shells [5] and exhibits polymorphic variation. Calcite is the most stable form of $CaCO_3$, while aragonite that is more unstable than calcite is its polymorph. Therefore, to investigate the influence of organic template on the selectivity of polymorph is of great interest in biomineralization research. Many researches have been focused on the effect of templating species on polymorph type and morphology of $CaCO_3$ crystal. In these studies, organic template used were in the form of solid matrices [6, 7], or in state of hydrogel [8, 9] or solution [10–12]. It was found that acidic functional groups, such as carboxylic acid group, along the macromolecular chains influenced the nucleation and crystal growth of $CaCO_3$

[13, 14]. Moreover, the physical network structure of the hydrogel and the secondary structure of the macromolecules like the conformation also affected the formation of the crystal [9, 13].

In this study, hydroxypropylmethylcellulose (HPMC) that has polyhydroxy groups on the molecular chains was used as the organic template to investigate the effect of polymers possessing weak polarity groups on the control of the crystallization of $CaCO_3$, on which only few efforts were made [15, 16]. Hydroxypropylmethylcellulose was in the state of solution and hydrogel, respectively. The structure of calcium carbonate obtained was studied by a X-ray diffractometer (XRD). Scanning electron microscope (SEM) was employed to investigate morphologic features of the crystals of calcium carbonate.

Experimental methods

Materials

Hydroxypropylmethylcellulose was purchased from Shandong Heda Co. (Shandong, China). The viscosity of 2 wt% solution is about 17,000 mPa·s at 20 °C. Na_2CO_3 and $CaCl_2$ were all of analytical reagent grade. Deionized water was from Nankai University (Tianjin, China) and was used throughout the experiment.

Mineralization studies in HPMC solution [17]

A certain amount of Na_2CO_3 powder was evenly placed at the bottom of a 250-ml beaker, while a certain amount of $CaCl_2$ powder at the bottom of a 100-ml one. Then the 100-ml beaker was put into the 250-ml beaker. After that, HPMC solution with different concentration (0.2 wt%, 0.5 wt%) was slowly added into both of the beakers along their walls until the final surface of the solution reached about 5 mm above the edge of the 100-ml beaker. A control experiment using deionized water instead of HPMC solution was also carried out. All the sample systems were left tranquilly at room temperature for about 12 days. Then the $CaCO_3$ crystals that were leached out through a vacuum pump were rinsed with deionized water, dried for 48 h in a vacuum oven and sealed in a desiccator before being analyzed.

By using the method described above, sample systems with different concentration (0.2 wt%, 0.5 wt%) of HPMC and control system without the presence of HPMC were made. Then all of them were suspended from a rotation equipment with a rotating speed of 20 r/min. After 12 days of rotating, 2 h for each day, the systems were treated as above before being analyzed.

Mineralization studies in HPMC gel

Certain amount of $CaCl_2$ powder was put into 0.5 wt% HPMC solution under constant stirring to form a final solution of which the concentration of $CaCl_2$ was 3 wt%. Ten milliliter of the solution was added into a test tube placed in a 65 °C water bath to gel. About 10 ml 3 wt% of Na_2CO_3 solution was poured on the gel that was formed. After 3 days of mineralization, the gel containing $CaCO_3$ crystal was allowed to be cooled to reverse back into solution. Rest of the experiment was conducted as above before being analyzed.

Characterization of the crystals

The morphology of the product was viewed through SEM (Philips XL30, Philips, Netherlands). The crystals were also investigated by XRD (D/MAX-2500, Rigaku, Japan). The work condition of XRD was CuK_α radiation, the λ of which was 1.54056Å via a rotating anode at 40 kV and 50 mA. The scanning range of scattering angles (2θ) was from 3 ° to 80 °. The data were collected in step of 0.02 °.

Thermogravimetry (TG) assay

Crystals obtained were analyzed by using a ZRY-2P integrated thermal analysis apparatus (Shanghai Zufa Co., China). The assay was carried out in the temperature range of 21–600 °C and at a rate of 15 °C/min.

Results and discussion

Synthesis of $CaCO_3$ crystal in deionized water without HPMC

$CaCO_3$ crystals which were synthesized in deionized water without HPMC existing was characterized by XRD and SEM. Calcite was formed by contrasting with the standard pattern card of $CaCO_3$. The characteristic diffraction peak of calcite located in $2\theta = 23.022$, 29.450, 35.965, 39.401, 47.489 and 48.512, which was shown in Fig. 1. The morphology of the $CaCO_3$ exhibited spherical structure and layered, rhombohedral structure (Fig. 2a, b).

Synthesis of $CaCO_3$ crystals in HPMC solutions

$CaCO_3$ crystals were synthesized in 2 wt% HPMC solution and 5 wt% HPMC solution. X-ray diffractometer results indicated that besides the calcite, aragonite of which the characteristic diffraction peak

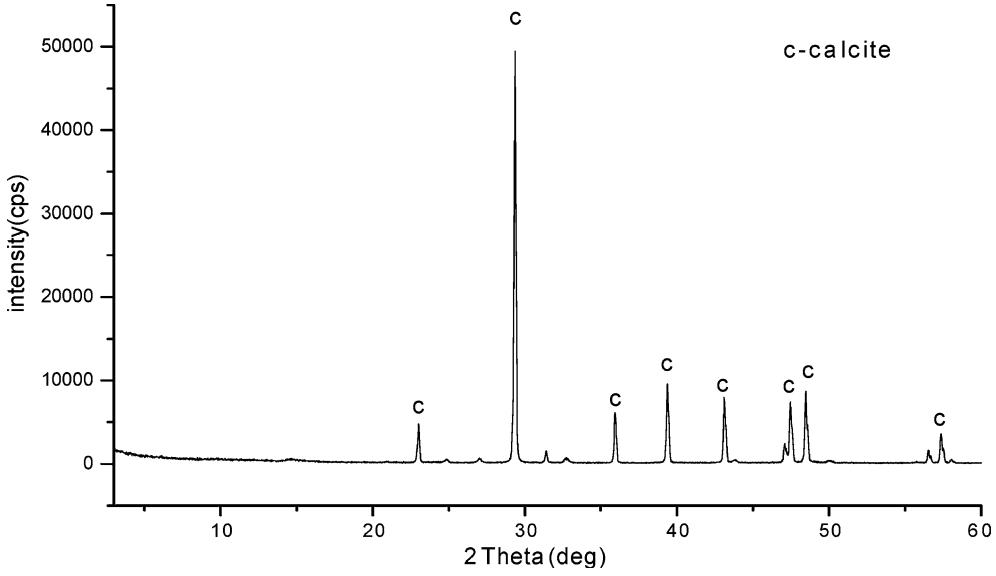

Fig. 1 X-ray diffractometer (XRD) spectrum of $CaCO_3$ crystals obtained in the control system

located in $2\theta = 26.212$, 27.215, 32.741, 37.883 and 45.852 appeared in both of the reaction system (Fig. 3). Therefore it was obvious that a small quantity of HPMC can induce the formation of aragonite which is one of the unstable $CaCO_3$ crystalline forms in nature. This result is similar with some of the other researches [15, 16]. In those reports, PVA, which possesses polyhydroxy functional groups, enhanced the selectivity of the aragonite formation. Based on the definition that the content of aragonite can be calculated as the ratio of the strongest peak of aragonite to the strongest peak of calcite [14], the effect of HPMC solution with different concentration on crystallization of calcium carbonate were summarized in Table 1. The content of aragonite had a tendency to increase as the concentration of HPMC solution increased. It is well known that the critical nucleation free energy of aragonite (ΔG^*) is larger than that of calcite. In terms of nucleation, Gibbs free energy formula [17],

$$\Delta G = B\sigma^3 V^2/(kT\ln S)^2 \quad (1)$$

where B, σ, V, k, T and S are constant, interface energy, molecular volume, Boltzmann constant, absolute temperature, and supersaturation, respectively.

It can be concluded that the existence of HPMC molecules may increase the ionic supersaturation (S) and form a scale of local supersaturation microenvironment. As this happened, the addition of HPMC caused a reduction of the nucleation free energy (ΔG) of calcium carbonate to a value below the ΔG^* of aragonite. Thus aragonite was formed. Moreover, ΔG continued to decrease as more HPMC was added into the system. Hence it was more likely to form aragonite and the content of aragonite was higher in 5 wt% HPMC solution than in 2 wt% solution.

Morphologies of calcium carbonate crystals obtained from HPMC solution were different from those precipitated from deionized water (Fig. 2c, d). The crystals formed in 2 wt% and 5 wt% HPMC solution was composed of spherical $CaCO_3$, layered, rhombohedral $CaCO_3$ and a small amount of bundle-like $CaCO_3$ which was made up of dozens of crystal whiskers. As these bundle-like crystals were not found in the control system, they were probably composed of aragonite. It can also be seen that the ratio of length to radius of the whiskers in 2 wt% solution were lower than those in 5 wt% solution and the content of these bundle-like structures became higher along with the increase of the concentration of the solution (Table 1). The spherical $CaCO_3$ had some evident porous defect and was in inferior shape compared with those prepared in the control system. All these phenomena seemed due to the reaction between the HPMC and Ca^{2+} through the polyhydroxy groups on the macromolecule of HPMC. This reaction may cause steric obstacle for small crystallite fusing with each other to reduce surface energy to form $CaCO_3$ spheres. Thus porous defect and inferior shape developed. On the other hand, when this reaction occurred, the growth of the crystal was prone to orient alongside certain direction, while showed slow growth rate on the surface perpendicular to this certain direction because of the great steric obstacle caused by the HPMC macromolecules. Then the whiskers bonded with each other and formed bundle-like structures. The more the HPMC was added, the greater the obstacle encountered by the crystal transverse growth. That is to say, the ratio of length to radius of the whisker became higher when concentration of HPMC solution increased.

As for the circumstance of rotating the reaction system, calcite precipitated from the reaction system at a

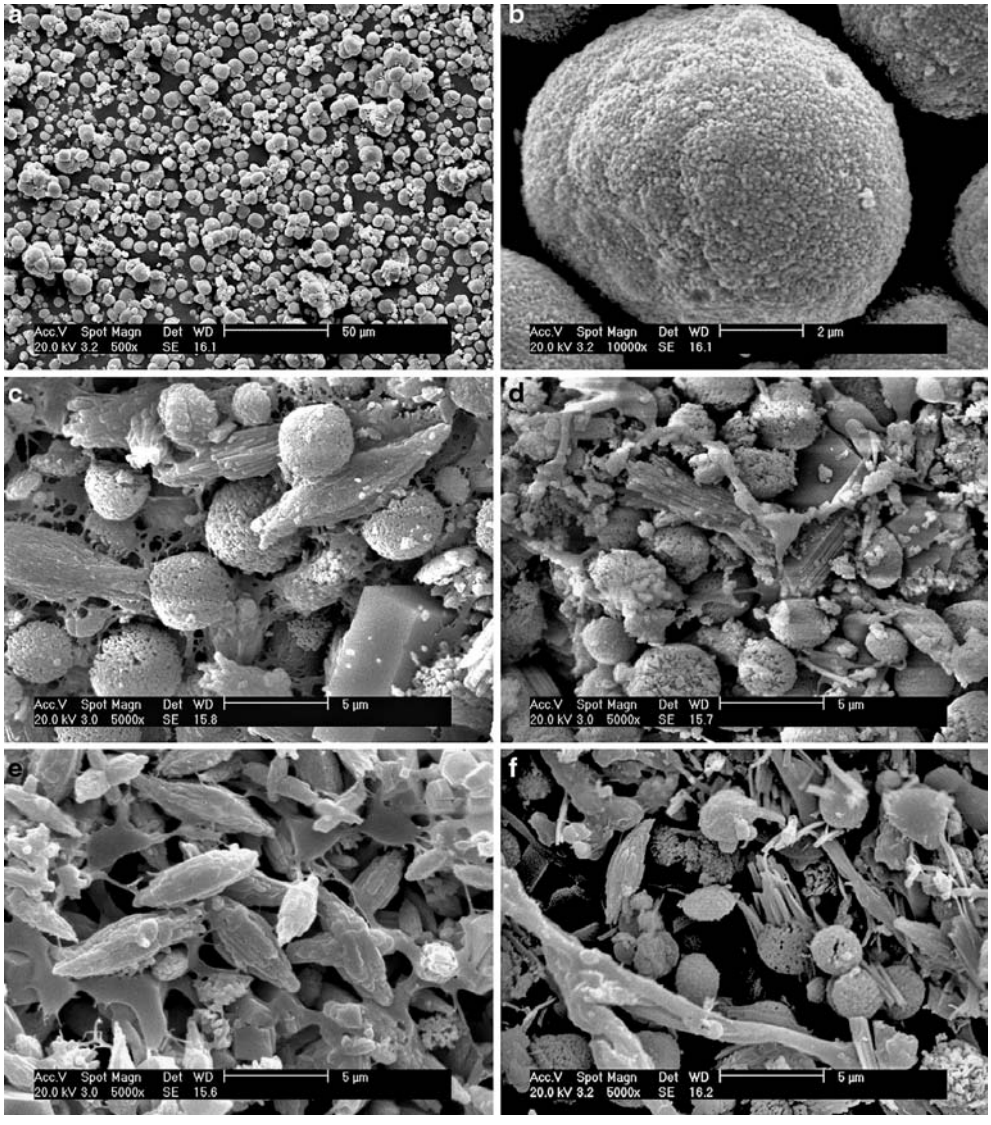

Fig. 2 The SEM micrograph of $CaCO_3$ crystals crystals obtained in HPMC solutions after incubation at room temperature for 12 days: **a, b** control system, **c** 0.2 wt% still system, **d** 0.5 wt% still system, **e** 0.2 wt% rotation system, **f** 0.5 wt% rotation system

rotating speed of 20 r/min without HPMC, while calcite and aragonite were all found when HPMC was added (Fig. 4). That is to say, the condition that rotated the system alone cannot arouse the formation of aragonite. The vital factor lied on the influence of HPMC on the whole process. However, the relative diffraction peak strength of aragonite exhibited obvious increase compared with the peak strength of the still system, namely the content of aragonite became higher (Table 1). To meet the lowest energy principle, unstable polymorph of $CaCO_3$, aragonite, will transform to the most stable form of $CaCO_3$, calcite, with time extending. It is often found that less stable forms are stabilized kinetically [13]. In this regard, to rotate the system conduced to stabilize aragonite. It means the chance for aragonite to transform to calcite is declined. Thus the content of aragonite increased. On the other hand, even though rotation may stabilize less stable form, it was impossible to form aragonite in the system without HPMC, because it was short of the supersaturation microenvironment.

The morphologies of the crystals formed under the rotation condition were shown in Fig. 2e, f. Spindly bundle-like structure became more and shape of $CaCO_3$ spheres became even more inferior. It seemed that shear stress caused by rotation destroyed the integrity of the crystal spheres and also conduced to form crystal whiskers. Detail of the mechanism was on investigation.

Synthesis of $CaCO_3$ crystals in HPMC gel

It is well known that HPMC can form thermoreversible hydrogel caused by thermally induced hydrophobic interaction [18]. Therefore, 0.5 wt% HPMC solution

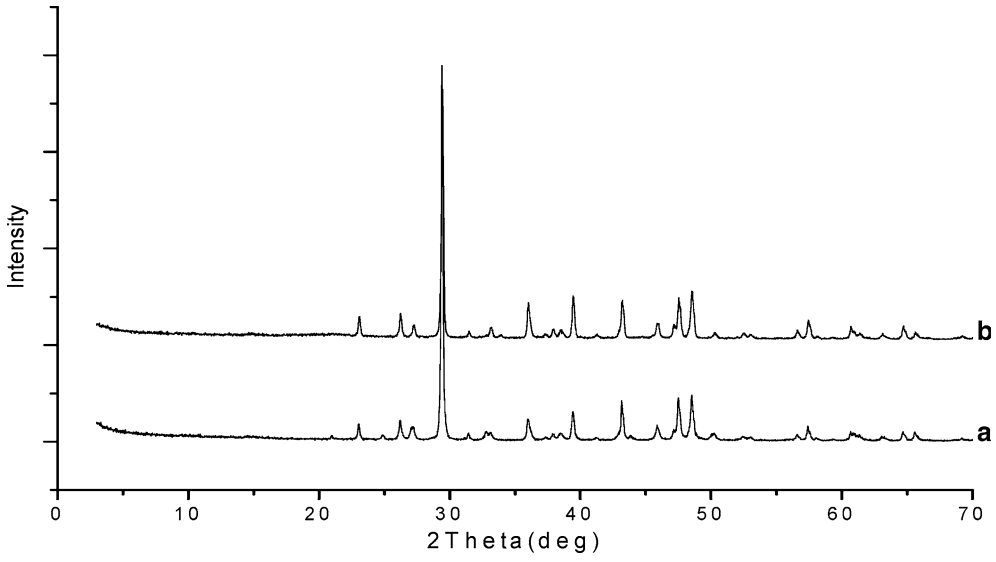

Fig. 3 The XRD spectrum of $CaCO_3$ obtained in the presence of HPMC with different concentration (still reaction system):

Table 1 The obtained crystals of $CaCO_3$ in the absence and presence of HPMC (taken and calculated from the results of XRD)

Reaction system	Concentration of HPMC solution (wt%)	Crystal type	Strongest characteristic peak intensity(cps)	Content
Still	0	Calcite	2,740	1
	0.20	Calcite	34,646	0.94
		Aragonite	2,007	0.06
	0.50	Calcite	24,277	0.90
		Aragonite	2,515	0.10
Rotation	0	Calcite		1
	0.20	Calcite	30,307	0.85
		Aragonite	3,811	0.15
	0.50	Calcite	12,790	0.79
		Aragonite	2,643	0.21

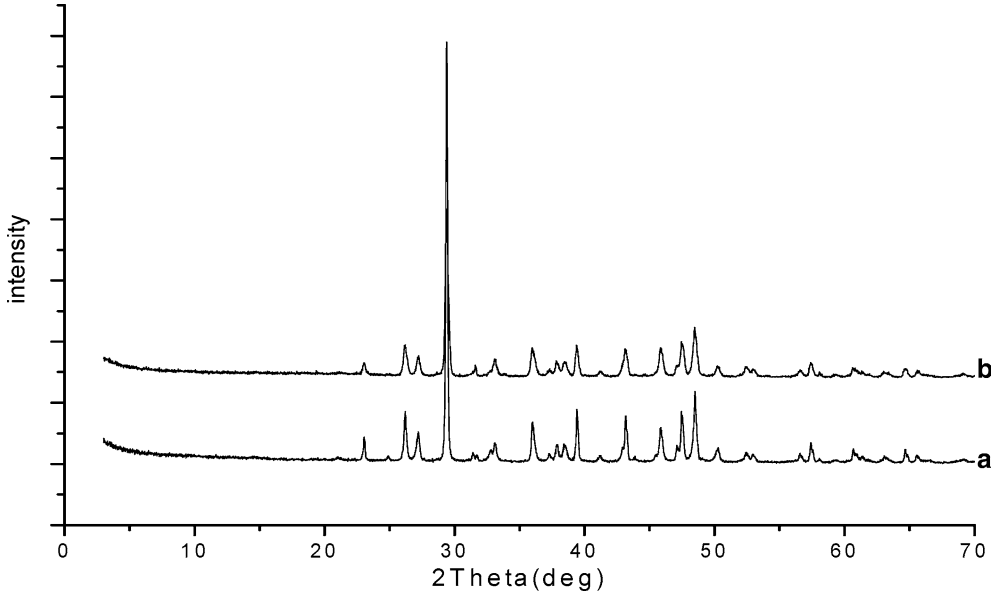

Fig. 4 The XRD spectrum of $CaCO_3$ crystals obtained in the presence of HPMC with different concentration (rotation reaction system): **a** 0.2 wt%, **b** 0.5 wt%

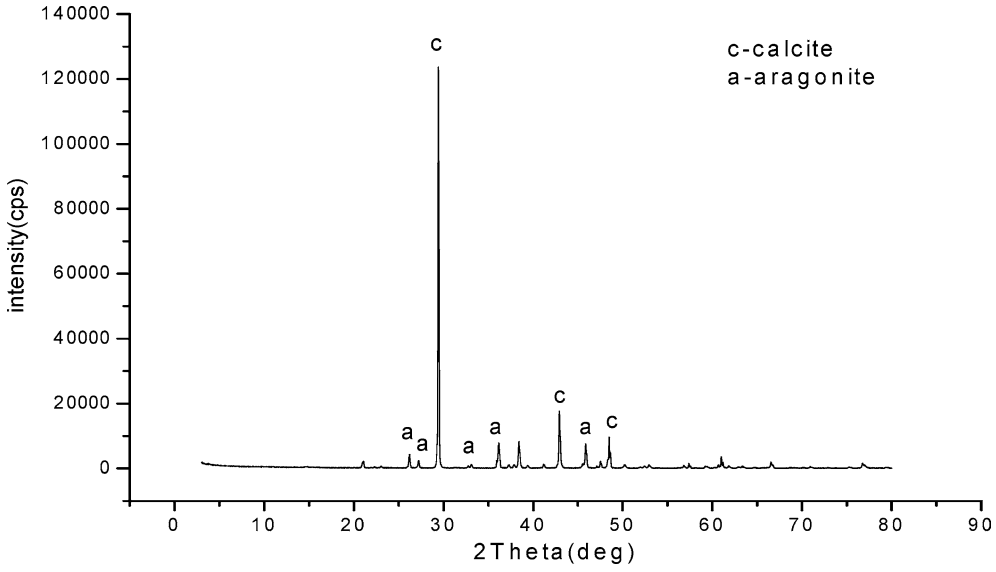

Fig. 5 The XRD spectrum of $CaCO_3$ crystals obtained in 0.5 wt% HPMC gel after incubation at 65 °C for 3 days

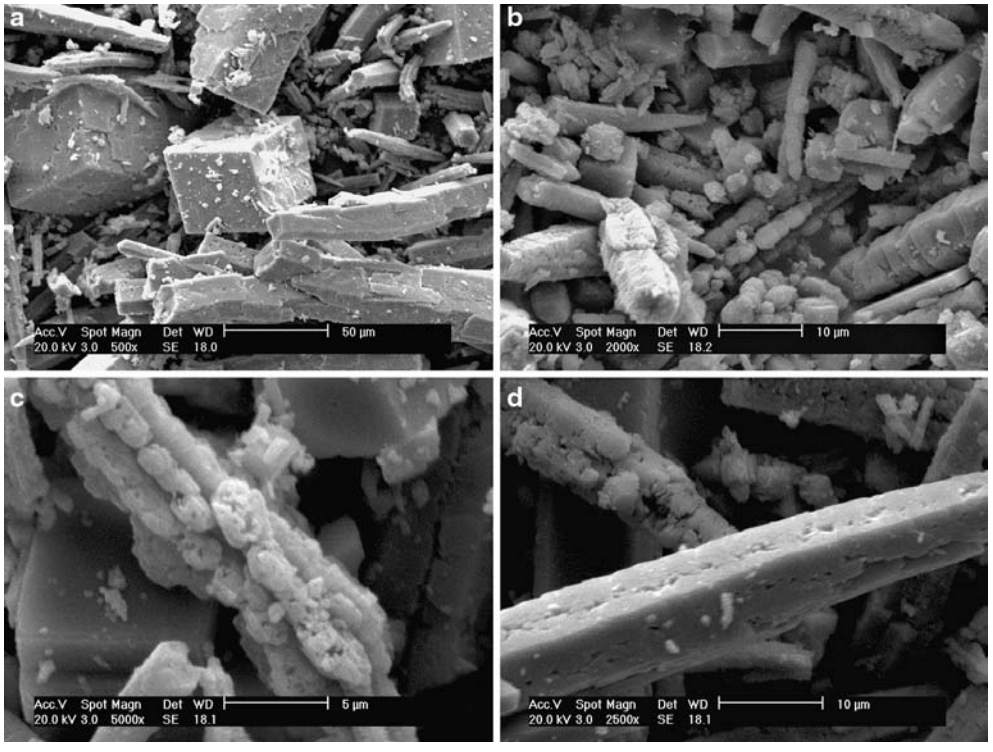

Fig. 6 The SEM micrograph of $CaCO_3$ crystals obtained in 0.5 wt% HPMC gel after incubation at 65 °C for 3 days

was heated to gel. The XRD spectrum of $CaCO_3$ formed in gel was shown in Fig. 5. Characteristic diffraction peaks of calcite and aragonite were detected. The content of aragonite was 4%. Scanning electron microscope showed that most of the crystals were in the shape of long bars. Rod-like aragonites were also obtained in agarose gels [19]. Yet crystals formed in HPMC gel exhibited a more interesting morphology. Some of these long bars formed through small short bars arranging in a specific order (Fig. 6), while some of them existed with many slight slots at intervals along their rough surface. On the one hand, the influence of polyhydroxy groups on water structure and hydration/dehydration steps could be responsible for the kinetics of crystallization processes [11]. On the other hand, the growth of the crystal was also regulated and restricted by the

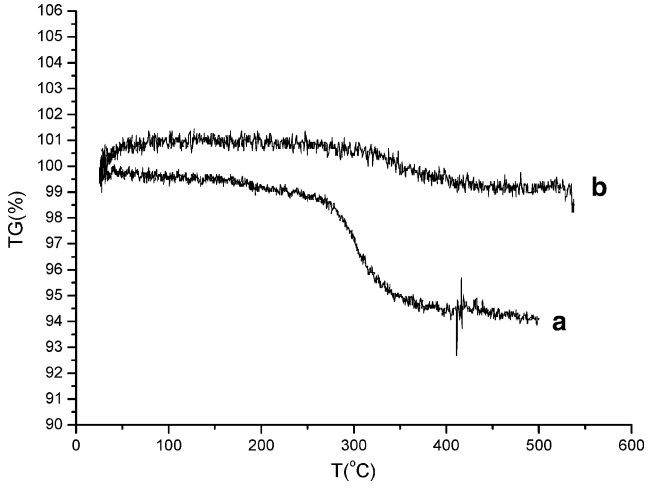

Fig. 7 The TG curves: **a** crystal products obtained from 0.2 wt% HPMC solution, **b** crystal products obtained from 0.5 wt% HPMC gel

three-dimension network structure of HPMC gel. As this special crystal morphology was not reported to the best of our knowledge, further investigation will be given later.

TG assays

The crystal obtained from the reaction system was analyzed via TG assays. Take samples precipitated from 0.2 wt% HPMC solution and samples formed from 0.5 wt% HPMC hydrogel, for example, it can be seen from the thermogravimetry curves (Fig. 7) that there was weight loss around 300 °C and 380 °C respectively, caused by the decomposition of HPMC which may be contained in the $CaCO_3$ crystal products. Weight loss ratio was 3.9 and 1.4%, respectively. It showed that the content of HPMC contained in the crystals powder was 3.9 and 1.4%, respectively. This result further indicated that there was some interaction between the template macromolecules and $CaCO_3$ crystals regardless of the systems of HPMC solution or HPMC gel.

Conclusions

$CaCO_3$ crystals were synthesized both in HPMC solution and in HPMC thermal reversible gel. With regard to the former, the presence of HPMC resulted in the formation of thermodynamically unstable aragonite besides the stable calcite. X-ray diffractometer indicated that the content of aragonite became higher when the concentration of HPMC solution increased. The crystals were composed of spherical $CaCO_3$, layered, rhombohedral $CaCO_3$ and bundle-like $CaCO_3$ which did not exist with the absence of HPMC. The shape of $CaCO_3$ spheres were inferior and the content of those bundle-like $CaCO_3$ increased with the increase of the concentration. To rotate the reaction system aroused the increase in the content of aragonite. The shear stress seemed to benefit the formation of crystal whiskers while destroying the integrity of the crystal spheres.

With regard to the crystals formed in HPMC gel, aragonite was also obtained. The morphology of the crystals was quite extraordinary. They were long bars with slight slots at intervals on the surface. Some of them were made up of little short bars. This may have some relation with the influence of polyhydroxy groups on the hydration/dehydration steps and the network structure of HPMC gel.

And also TG assay indicated that there was a little HPMC contained in $CaCO_3$ crystal products.

Acknowledgements The authors would like to thank the National Natural Science Foundation of China (No. 50373032), the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, P.R.C.(2002-123) and the Key Research Project of Ministry of Education, P.R.C. (No.02041) for supporting this research work.

References

1. Kato T, Suzuki T, Amaniya T, Irie T, Komiyama M (1998) Effects of macromolecules on the crystallization of $CaCO_3$ the formation of organic/inorganic composites. Supramol Sci 5:411–415
2. Arias JL, Ferna'ndez MS (2003) Biomimetic processes through the study of mineralized shells. Mater Characterization. 50:189– 195
3. Endo H, Schwahn D, Cölfen H (2004) An analysis of calcium carbonate/polymer hybrid crystals applying contrast variation SANS. Physica B 3:200–202
4. Chan CS, Stasio GD, Welch SA et al (2004) Microbial polysaccharides template assembly of nanocrystal fibers. Science 303: 1656–1658
5. Litvin AL, Valiyaveettil S, Kaplan DL, Mann S (1991) Template-directed synthesis of aragonite under supramolecular hydrogen-bonded Langmuir monolayers. Adv Mater 9(2):124–127
6. Sukun Z, Gonsalves KE (1995) Synthesis of calcium carbonate-chitosan composites via biomimetic processing. J Appl Polym Sci 56(6):687–695
7. Fendler JH, Meldrum FC (1997) The colloid chemical approach to nanostructured materials. Adv Mater 7(7):607–632

8. Grassmann O, Obmann PL (2004) Biomimetic nucleation and growth of $CaCO_3$ in hydrogels incorporating carboxylate groups. Biomaterials 25:277–282
9. Grassmann O, Obmann PL (2003) Morphogenetic control of calcite crystal growth in sulfonic acid based hydrogels. Chem Eur J 9(6):1310–1316
10. Estroff LA, Hamilton AD (2001) At the interface of organic and inorganic chemistry: bioinspired synthesis of composite materials. Chem Mater 13(10):3227–3235
11. Naka K, Chujo Y (2001) Control of crystal nucleation and growth of calcium carbonate by synthetic substrates. Chem Mater 13(10):3245–3259
12. Marentette JM, Norwig J, Stockelmann E, Meyer WH, Wegner G (1997) Crystallization of CaC03 in the presence of PEO-block-PMAA copolymers. Adv Mater 9(8):647–651
13. Naka K, Chujo Y (2003) Effect of anionic dendrimers on the crystallization of calcium carbonate in aqueous solution. C R Chim 6:1193–1200
14. Tong H, Ma W, Wang L, Wan P, Hu J, Cao L (2004) Control over the crystal phase, shape, size and aggregation of calcium carbonate via a l-aspartic acid inducing process. Biomaterials 25:3923–3929
15. Didymus JM, Oliver P, Mann S, DeVries AL, Hauschka PV, Westbroek P (1993) Biomimetic approaches to crystal engineering: influence of low molecular weight and macromolecular organic additives on the morphology of calcium carbonate. J Chem Soc Faraday Trans 89:2891–2900
16. Lakshminarayanan R, Valiyaveettil S, Loy GL (2003) Selective Nucleation of calcium carbonate polymorphs: role of surface functionalization and poly(vinyl alcohol) additive. Cryst Growth Des 3(6):953–958
17. Guo Y, Zhang X, Jiang K, Zhou J, Hu Z, Yang X, Yang L (2001) Biomimetic synthesis of calcium carbonate with the existence of the polymer matrices. Acta Chim Sin 59(5):755–762
18. Sarkar N, Walker LC (1995) Hydration-dehydration properties of methylcellulose and hydroxypropylmethylcellulose. Carbohydr Polym 27:177–185
19. Yang D, Qi L, Ma J (2003) Well-defined star-shaped calcite crystals formed in agarose gels. Chem Commun 10:1180–1181