Microspheres of Calcium Carbonate Composite Regulated by Sodium Polyacrylates with Various Ways

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ABSTRACT: Microspheres of calcium carbonate ($CaCO_3$)/ sodium polyacrylate (PAAs)/H_2O composite were synthesized by adding PAAs to the supersaturated solution of $CaCO_3$. It was found that the sizes of microsphere were influenced by the concentration and average molecular weight (M_w) of PAAs. Particularly, the polymorph of $CaCO_3$ in the microspheres could be regulated by M_w of PAAs, that is, the formation of aragonite was induced by PAAs with lower M_w, while the amorphous calcium carbonate (ACC) was facilitated by PAAs with a higher one. Both polymorphs in produced microspheres were stable in air for longer than 3 months. In addition, it was revealed that the formation of calcite crystals was suppressed by a highly concentrated solution of PAAs. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3686–3692, 2009

Key words: mineralization; hybrid; morphology; particle; aggregation

INTRODUCTION

As an important mineral in nature, calcium carbonate has three anhydrous crystalline polymorphs: calcite, aragonite, and vaterite. There are also two well-defined hydrous crystalline polymorphs: calcium carbonate monohydrate ($CaCO_3 \cdot H_2O$) and calcium carbonate hexahydrate ($CaCO_3 \cdot 6H_2O$) as well as one amorphous form, amorphous calcium carbonate (ACC), existing in nature.[1,2] Aragonite is the thermodynamic metastable polymorph of calcium carbonate and is widely found in biological minerals, such as the shell of mollusk.[3] *In vitro*, it relatively rapidly transforms into a more stable polymorph, calcite.[4] However, due to its extraordinary high toughness arising from the absence of any easy cleavage plane, aragonite crystals have received more attention recently.[5,6] In addition, ACC, which plays an important role in life as the temporary storage of calcium salts,[7,8] could be instantly formed from the highly saturated solution of $CaCO_3$ and transformed into the crystalline polymorph rapidly in solution and humid air.[9,10] The coexistence of ACC and aragonite in nacre gives rise to the high mechanical strengthen of the mollusk shell.[11–13] Therefore, how to obtain the stable aragonite, ACC, and their composites *in vitro* is very topical in the field of biomineralization.

Many efforts have been made in recent years to control the crystallization of $CaCO_3$ and regulate its morphology by additives.[14–17] It was reported that the biological macromolecules extracted from the aragonite layer of the mollusk shell were capable of inducing the formation of aragonite spherulites *in vitro* when preadsorbed on a substrate of β-chitin/silk fibroin, but this fraction only induced the formation of needle-shaped aragonite crystals.[18,19] When thin films of aragonite were synthesized on the chitosan matrices in cooperation with Mg^{2+} and poly(aspartate) or sodium polyacrylate (PAAs),[20–22] some regular aragonite spherical particles about 200 μm were also obtained under the coeffect of soluble collagen and Mg^{2+}.[23]

It was suggested that the formation and stabilization of aragonite and ACC are dependent on the regulation from the biological macromolecules or synthesized polymers with the carboxyl groups.[24–26] Therefore, poly(acrylic acid) (PAA) and its salt have been extensively used to regulate the crystallization of $CaCO_3$.[27–30] It has been shown that ACC and vaterite particles were synthesized by PAA ($M_w = 5000$) through a carbonate controlled-addition method or by the delayed addition method.[31,32] The higher concentration of PAA in the solution was inclined to the formation of irregular particles of $CaCO_3$; the crystallization of vaterite and aragonite was favored in the presence of PAA at high

temperature.[17,33,34] Also the effects of M_w of PAAs and the ratios of $[COO^-]/Ca^{2+}$ on the crystallization and polymorph of $CaCO_3$ as well as the stability of formed $CaCO_3$ composite have been investigated in a certain extent.[35,36]

However, it is still far away to fully understand the formation processes of $CaCO_3$ composite with varied shapes, polymorph, composition, and stability, etc. in either the natural or mimic system, especially those mediated by biomacromolecules or synthetic polymers. For instance, there were few reports about the formation of regular aragonite and ACC microspheres regulated by PAAs with different molecular weights in the supersaturated solution of $CaCO_3$.[37] In this work, we selectively synthesized the aragonite and ACC microspheres composite, which could be kept in air for more than 1 month, by adding different M_w PAAs into a supersaturated solution of $CaCO_3$. Moreover, the effects of the concentration and M_w of PAAs on the size and polymorph of the microspheres were investigated in detail, and the mechanism of the formation and stabilization of the composite microspheres of aragonite and ACC is suggested.

MATERIALS AND METHODS

Materials and equipment

$CaCO_3$ powder (calcite > 99.0%), PAA ($M_w = 100$ kDa) and PAAs ($M_w = 5.1$, 8, and 15 kDa) were purchased from Sigma-Aldrich (St. Louis, MO). Aqueous solutions (5 mg/mL) of PAAs with different average molecular weight were prepared as follows: PAAs solution ($M_w = 5.1$, 8, and 15 kDa) was made by dissolving PAAs directly in MilliQ water (relative resistivity: maximum 1.8×10^7 Ω cm), but PAAs solution with $M_w = 100$ kDa was obtained by adjusting pH value of PAA aqueous solution to 6–9 with NaOH. The glass and silicon slides used as substrate for collecting samples were cleaned and sonicated in ethanol for 5–10 min, then rinsed with deionized water and soaked in a mixture of $H_2O/HNO_3(65\%)/H_2O_2$ (v/v/v = 1 : 1 : 1), further rinsed by deionized water and MilliQ water, and finally dried in air with acetone.[38,39] All the glassware in the experiment were immersed in a mixture of $H_2O/HNO_3(65\%)/H_2O_2$, rinsed with deionized water and MilliQ water, and then dried in air.

Preparation of microspheres of calcium carbonate

The supersaturated solution of $CaCO_3$ was prepared following the procedure described in literature.[29] The concentration of Ca^{2+} ions in the supersaturated solution of $CaCO_3$ was adjusted to 8 mmol/L by MilliQ water. The solutions of PAAs with different M_w were added to the supersaturated solution of $CaCO_3$. The molar ratio of carboxyl groups on PAAs chains to Ca^{2+} ions in the solution was from 0.006 to 0.264, corresponding to the concentration of PAAs in solution from 5 to 200 μg/mL. The resulting solution was transferred to the glassware and kept at 30°C in a water bath for 24 h. The samples collected on the glass and silicon slides were rinsed with deionized water and then dried in air for the characterization of scanning electron microscope (SEM) and X-ray diffraction (XRD). The samples for thermogravimetric analysis (TGA) and FTIR measurement were centrifuged, rinsed, and lyophilized.

Structure and morphology

The morphologies of the samples on the glass slides were examined by using TS 5136 SEM (Brno, Czech) at 20 kV after being sputtered with gold. The polymorph of the samples on the silicon slides was characterized by XRD and recorded on Philips X'Pert Pro diffractometer (Almelo, The Netherlands) with Cu Kα radiation ($\lambda = 1.541$ Å) at 40 kV and 40 mA. FTIR spectra of the samples were recorded in KBr disc on Nicolet (Waltham, MA) Nexus 470 FTIR spectrometer from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution. TGA analysis was performed at 10 K/min on Perkin-Elmer (Waltham, MA) Pyris 1 TGA under 40 mL/min air.

Dynamic light scattering measurement

Dynamic light scattering (DLS) measurement of the supersaturated solution of $CaCO_3$ adding 200 μg/mL PAAs of different M_w was carried out on Malvern (Worcestershire, UK) Autosize 4700 laser light scatter at 30°C.

RESULTS AND DISCUSSION

The effect of the concentration of PAAs on the formation of the microspheres of $CaCO_3$

Below 10°C, no $CaCO_3$ crystals formed in the supersaturated solution of $CaCO_3$ because of the highly concentrated CO_2 dissolved in solution, but if this supersaturated solution was incubated at 30°C for 24 h, many rhombohedral and needle-shaped crystals precipitated in the supersaturated solution.

However, when PAAs was added to the supersaturated solution, a large number of smooth microspheres were presented. These microspheres were fairly stable in solution and air for at least 3 months without any change in their morphology. With an increase in the concentration of PAAs 8 kDa, both the size and the amount of microspheres increased (Fig. 1). At the low concentration of PAAs 8 kDa (below 20 μg/mL), there were still a few of rhombohedral or irregular crystals presented in solution

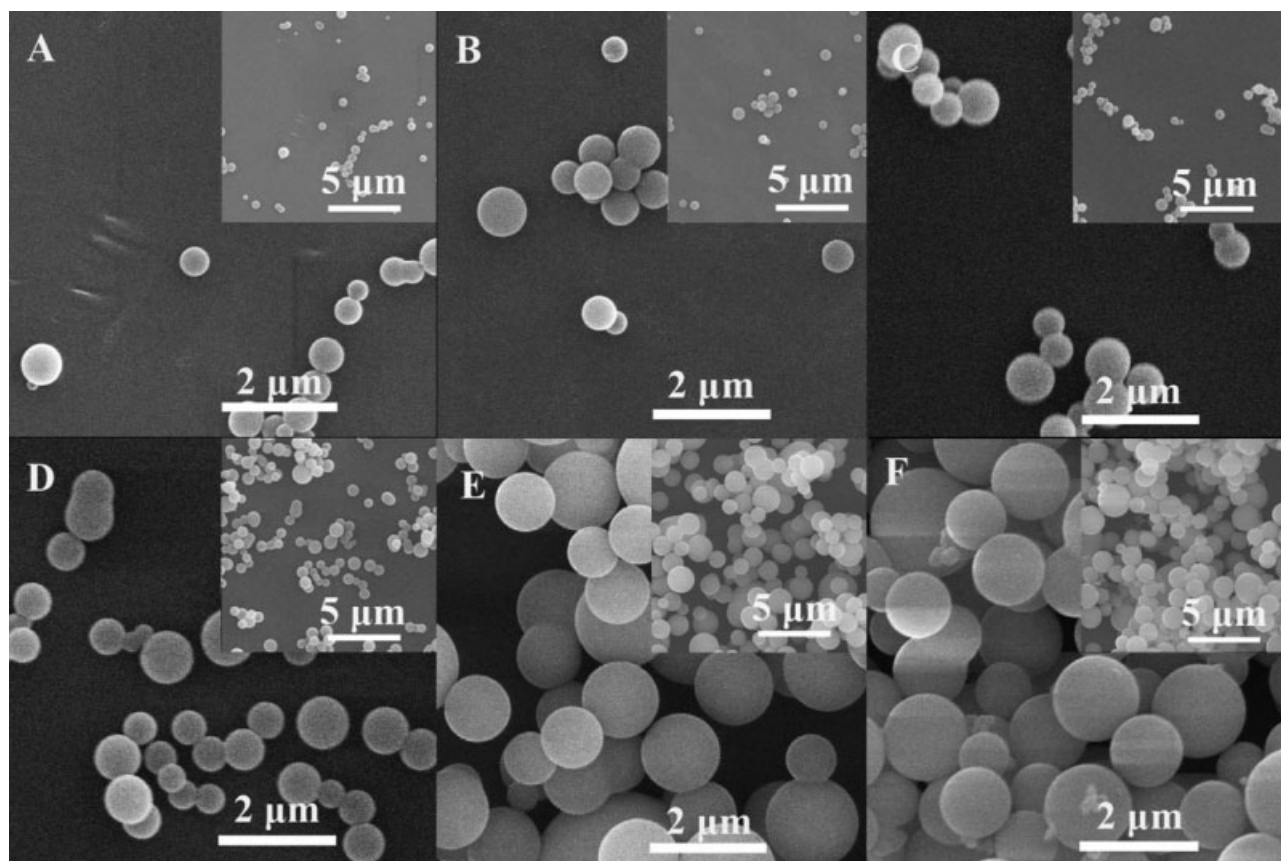**Figure 1**　Representative SEM micrographs of the microspheres formed of $CaCO_3$ with different concentrations of PAAs 8 kDa (A, 5 μg/mL; B, 10 μg/mL; C, 20 μg/mL; D, 50 μg/mL; E, 100 μg/mL; F, 200 μg/mL).

besides the microspheres. The results of the XRD pattern showed three diffraction peaks at 29.7°, 33.2°, and 48.1° (Fig. 2), which were attributed to calcite and aragonite, respectively.[20,29] This revealed that not only the microspheres of aragonite but also a tiny amount of calcite crystals had been formed. When the concentration of PAAs 8 kDa increased above 20 μg/mL, only microspheres were obtained in solution. The diffraction peak at 33.2° and 48.1° appearing in the XRD pattern indicated that the polymorph of $CaCO_3$ in the microspheres is almost all aragonite. It suggests that the aragonite microspheres can be induced by PAAs 8 kDa in the supersaturated solution of $CaCO_3$ and the size of microspheres is regulated by the concentration of PAAs 8 kDa. Moreover, the formation of calcite crystals was restrained while the concentration of PAAs 8 kDa increased.

The influence of PAAs 5.1 and 15 kDa on the crystallization of $CaCO_3$ was also investigated (Table I), and similar results were obtained as those of PAAs 8 kDa, suggesting that both the size and the polymorph of the obtained microspheres were controlled by the concentration of PAAs at a certain range of the M_w of PAAs. However, for the case of the smallest M_w PAAs in our experiment (PAAs 5.1 kDa),
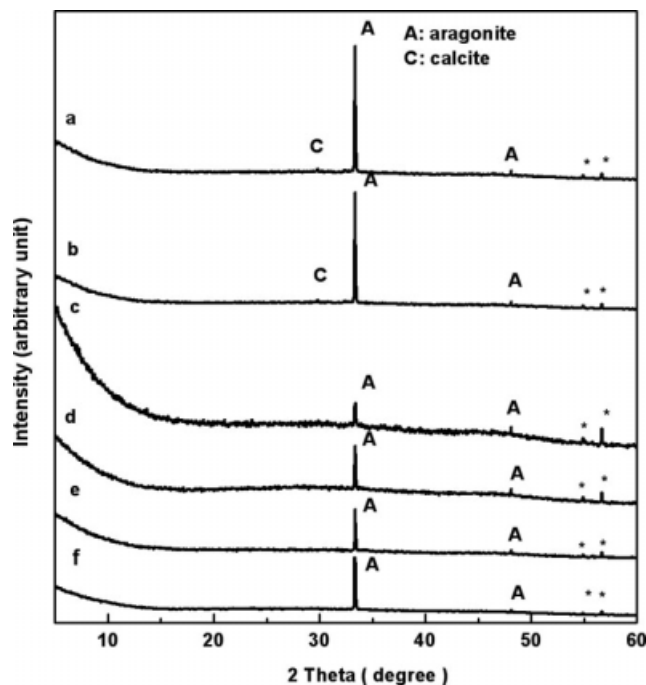

Figure 2　XRD patterns of the microspheres of $CaCO_3$ formed with different concentrations of PAAs 8 kDa (curve a: 5 μg/mL; curve b: 10 μg/mL; curve c: 20 μg/mL; curve d: 50 μg/mL; curve e: 100 μg/mL; curve f: 200 μg/mL; *: from the diffraction of sodium salts).

TABLE I
The Effect of PAAs on the Diameter and Polymorph of the Microspheres of CaCO$_3$

Conc. (µg/mL)	PAAs 5.1 kDa		PAAs 8 kDa		PAAs 15 kDa		PAAs 100 kDa	
	Diameter (µm)[a]	Polymorph	Diameter (µm)	Polymorph	Diameter (µm)	Polymorph	Diameter (µm)	Polymorph
5	0.11 ± 0.05	A/C	0.55 ± 0.08	A/C	0.51 ± 0.12	A/C+V	0.38 ± 0.11	ACC/C
10	0.27 ± 0.13	A/C	0.63 ± 0.09	A/C	0.66 ± 0.08	A/C	0.55 ± 0.07	ACC/C
20	0.29 ± 0.07	A	0.66 ± 0.12	A	0.93 ± 0.19	A	0.67 ± 0.14	ACC
50	0.41 ± 0.12	A/C[b]	0.70 ± 0.12	A	1.01 ± 0.32	A	0.77 ± 0.09	ACC
100	0.66 ± 0.15	A	1.29 ± 0.27	A	1.41 ± 0.45	A	0.83 ± 0.12	ACC
200	0.81 ± 0.11	A/C[b]	1.38 ± 0.19	A	1.79 ± 0.74	A	0.82 ± 0.13	ACC

A, aragonite; C, calcite; V, vaterite; ACC, amorphous calcium carbonate. The details may be found in Supporting Information.
[a] $N = 30$.
[b] Trace of calcite coexisted in the sample.

there were still a few of rhombohedral or irregular crystals formed even if the concentration of PAAs was reached as high as 200 µg/mL. Thus, it implies that the size and polymorph of microspheres were regulated not only by the concentration of PAAs but also by the M_w of PAAs.

The effect of M_w of PAAs on the formation of the microspheres of CaCO$_3$

To further understand the regulation of PAAs, the effects of M_w of PAAs on the size and polymorph of the microspheres of CaCO$_3$ were studied extensively. The results showed that with small M_w PAAs (PAAs 5.1, 8, and 15 kDa), the diameter of the microspheres increased obviously with increments of M_w of PAAs [Fig. 3(A–C) and Table I]. In addition, the amount of PAAs influenced the polymorph of the microspheres: when the concentration of PAAs was lower than 20 µg/mL, microspheres of aragonite and rhombohedral or irregular crystals of calcite co-formed in solution but when the concentration of PAAs exceeded 20 µg/mL, only microspheres of aragonite were obtained (Fig. 2, curves c–f, and Table I).

As for the PAAs with large M_w (i.e., PAAs 100 kDa), both the size and the morphology of microspheres of CaCO$_3$ changed significantly [Fig. 3(D) and Table I]. The diameter of microspheres was rather smaller than those of the small M_w PAAs but still increased slightly as the concentration of PAAs 100 kDa was increased. In addition, conglutination also occurred among these microspheres. According to the XRD results, the polymorph of CaCO$_3$ in these microspheres is ACC, especially when the concentration of PAAs 100 kDa was larger than 20 µg/mL (Fig. 4, curve d, and Table I). This was also confirmed by the characteristic absorption peak presented at 866 and 1414 cm^{-1} as well as the absence of one at 713 cm^{-1} in the FTIR spectra.[9,30] Moreover, our experiment also indicated that the prepared aragonite microspheres could be kept in air for more than 1 month without transforming to calcite, while ACC microspheres were stable for at least 3 months.

Investigation of the composition of the microspheres of aragonite and ACC

Based on the results above, PAAs played a crucial role in regulating the formation of the microspheres
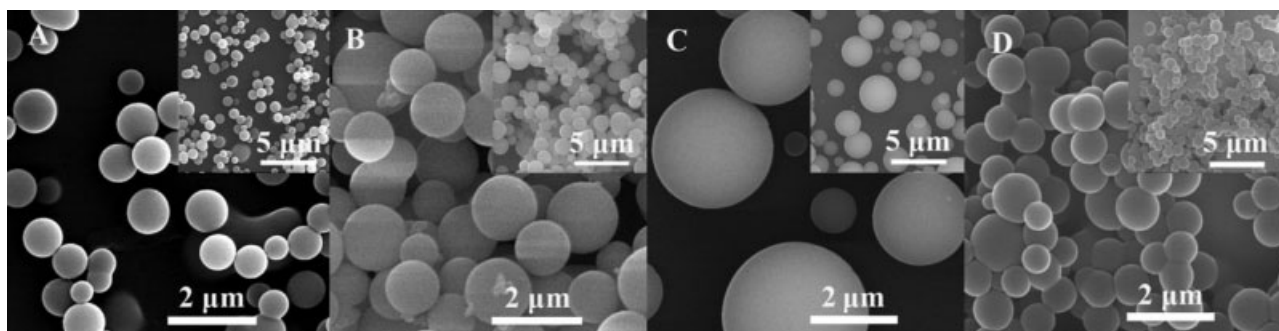

Figure 3 Representative SEM micrographs of the microspheres of CaCO$_3$ formed with 200 µg/mL PAAs (A, PAAs 5.1 kDa; B, PAAs 8 kDa; C, PAAs 15 kDa; D, PAAs 100 kDa).
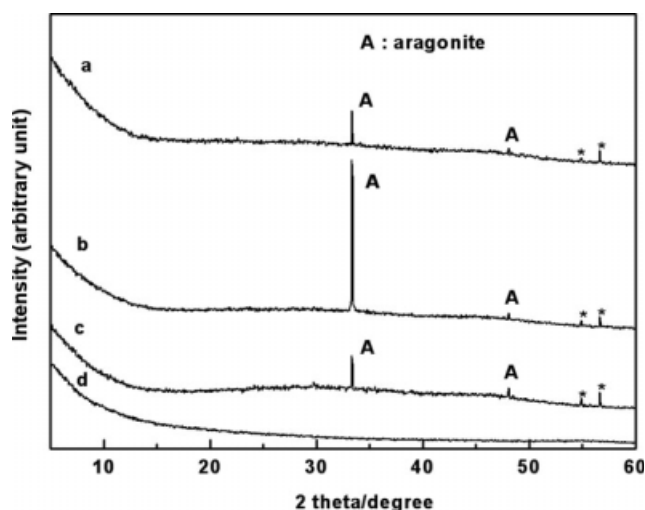
Figure 4 XRD of the microspheres of $CaCO_3$ formed with 200 µg/mL PAAs (curve a: PAAs 5.1 kDa; curve b: PAAs 8 kDa; curve c: PAAs 15 kDa; curve d: PAAs 100 kDa).

of $CaCO_3$. Therefore, to further understand the function of PAAs in the course of the crystallization of $CaCO_3$, the composition of the microspheres of aragonite and ACC were investigated first. TGA results indicated that all the curves of microspheres obtained by addition of PAAs 8, 15, and 100 kDa (the amount of microspheres prepared by PAAs 5.1 kDa was too little to be investigated by TGA) consisted of three parts (Fig. 5): the first part was the weight loss below 480°C owing to the loss of water; the second part was the weight loss in the temperature range from 480 to 630°C resulting from the decomposition of the PAAs; and the last part was the weight loss of 630–740°C arising from the decomposition of $CaCO_3$ to CaO,[32,40] suggesting that
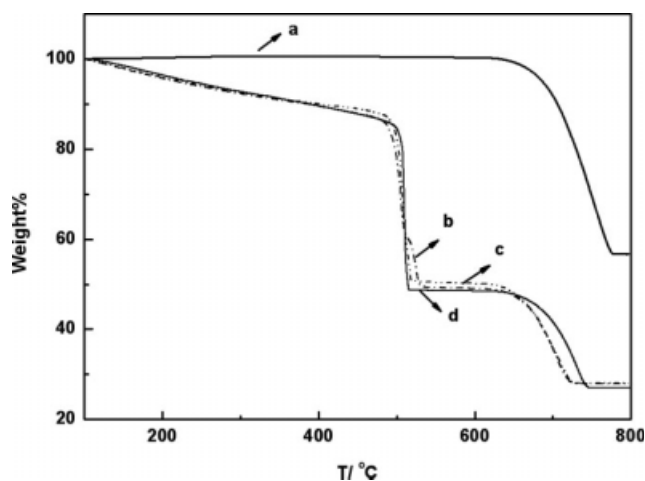
the microspheres obtained were composites composed of $CaCO_3$, H_2O, and PAAs.

The content of PAAs and $CaCO_3$ in the microspheres could be estimated by subtracting the weight loss of water from the weight loss above 630°C and the decomposition of $CaCO_3$ to CaO. Accordingly, the content of water in the composite microspheres of $CaCO_3$ obtained by 200 µg/mL PAAs 8, 15, and 100 kDa was 14.4, 12.7, and 14.6 wt %, respectively. The content of PAAs was 35.6, 37.1, and 37.4 wt %, suggesting that the contents of binding water in the composite microspheres of $CaCO_3$ (1.4–1.7 moles of H_2O for 1 mole of $CaCO_3$ due to the strong bind ability of PAAs with H_2O[41]) were higher than that of the biogenic ACC (1 mole of H_2O for 1 mole of $CaCO_3$).[42] As water molecules play an important role in the stabilization of ACC, it might be reasoned that the water content of the prepared microspheres of ACC and aragonite is important to the achieving of stability in air.

The mechanism of the formation of the microspheres of $CaCO_3$

With a view of exploring the mechanism of the formation of the microspheres in the supersaturated solution of $CaCO_3$, the growth of microspheres was tracked by DLS and XRD (Figs. 6 and 7). The DLS results indicated that upon addition of low M_w PAAs (e.g., PAAs 8 kDa), the clear solution of $CaCO_3$ turned turbid immediately, and that particles of $CaCO_3$ of about 500 nm were first formed in the solution. The diameter of these particles increased gradually and finally reached about 1500 nm 8 h later. XRD confirmed that the initial particles were ACC, and then their polymorph transformed into

Figure 5 TGA curves of the microspheres of $CaCO_3$ obtained without PAAs (curve a) and with 200 µg/mL PAAs 8 kDa (curve b), PAAs 15 kDa (curve c), and PAAs 100 kDa (curve d).
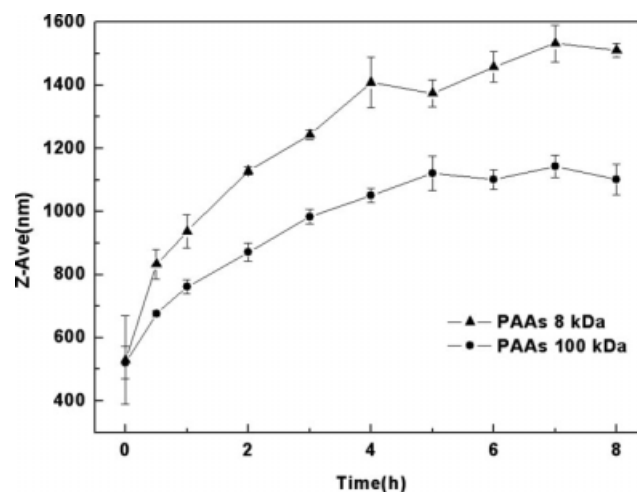

Figure 6 The change of Z-Ave of the particles formed in the supersaturated solution of calcium carbonate with 200 µg/mL PAAs 8 kDa and PAAs 100 kDa.
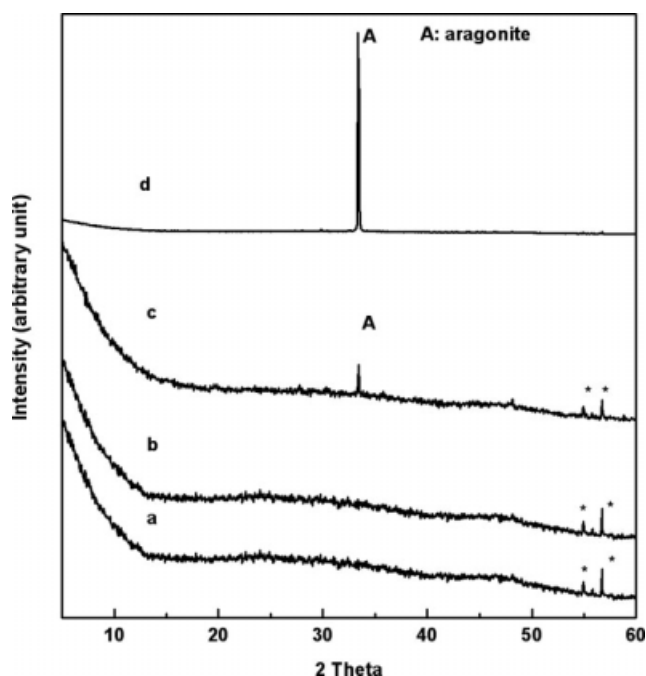
Figure 7 The change of XRD of the particles of $CaCO_3$ with 200 μg/mL PAAs 8 kDa at different times (curve a: 0 min; curve b: 5 min; curve c: 15 min; curve d: 30 min; *: from the diffraction peaks of sodium salts).

aragonite around 15 min later. In the case of higher M_w PAAs (i.e., PAAs 100 kDa), the initial ACC particles had a diameter of about 500 nm that increased to 1000 nm in 8 h. The polymorph remained amorphous.

Because of the complexation between Ca^{2+} and the carboxyl groups of PAAs, a great number of Ca^{2+} ions were bound onto the side group of PAAs, resulting in immediate formation of different kinds of complex in the solution. Therein, the interaction between PAAs 8 kDa and Ca^{2+} gave rise to the formation of the pseudobridge with Na^+ or bidentate intermediates, whereas the high M_w PAAs ($M_w \geq 30$ kDa) would result in the forming of the bidentate intermediates.[41] Therefore, with the addition of PAAs into the supersaturated solution of $CaCO_3$, due to the enrichment of Ca^{2+} in the coils of PAAs, the local supersaturated level of $CaCO_3$ increased dramatically, leading to the large formation of ACC particles. Meanwhile, the crystallization mechanism of $CaCO_3$ converted from ionic growth to mesoscale assembly of nanoparticles as the addition of PAAs in the solution.[43,44] The initial particles of $CaCO_3$ were unstable and inclined to aggregate and dehydrate to reduce its interfacial energy.[45] Upon the augmentation of the concentration of PAAs, more particles of ACC were formed instead of the formation of the calcite crystals because the latter were inhibited by the concentrated PAAs in the solution. The further aggregation of ACC particles made the

microspheres of $CaCO_3$ much larger with the increasing the concentration of PAAs in the solution.

In the supersaturated solution of $CaCO_3$ with PAAs, the crystallization of $CaCO_3$ by the mechanism of mesoscale assembly of ACC particles was under kinetic control of nucleation and growth. The crystallization began with ACC, proceeded through a series of thermodynamic metastable intermediates, such as vaterite and aragonite, and finally transformed into the stable calcite by the mechanism of dissolution–recrystallization.[44] However, the different polymorph of $CaCO_3$ can be obtained through kinetics intervention at different stages by additive during the process of ACC crystallization.[27] With the shorter molecular chains, the low M_w PAAs such as PAAs 5.1, 8, and 15 kDa can adopt the proper conformation to achieve the best matching between the carboxyl groups of PAAs and Ca^{2+} in the crystalline plane of {012} in aragonite, which makes PAAs chains bind tightly on the crystalline plane of aragonite and stabilize the formation of aragonite. On the other side, the less interaction between the low M_w PAAs and Ca^{2+} leads to the relatively weak ability of adjusting the crystallization of calcium carbonate.[41] The crystallization of ACC during the assembly of particles was not inhibited entirely and ACC transformed to aragonite, but further polymorph transformation was inhibited by PAAs chains bound on the crystalline plane of aragonite and resulted in the formation of the microspheres of aragonite. However, PAAs 100 kDa exhibited the strong binding strength on the surface of ACC particles because of its longer molecular chain. The crystallization of ACC was inhibited completely by PAAs chains through preventing the process of dissolution–recrystallization of ACC and eventually this resulted in the formation of microspheres of ACC.

CONCLUSIONS

The formation of composite microspheres of $CaCO_3$/PAAs/H_2O formed through the addition of PAAs to induce the crystallization of the supersaturated solution of $CaCO_3$ was investigated. It revealed that the size of the microspheres obtained was influenced by both molecular weight and concentration of PAAs involved, while the polymorph of $CaCO_3$ in the composite was only regulated by M_w of PAAs. The low and high M_w PAAs can induce the formation of the microspheres of aragonite and ACC, respectively. All presented aragonite and ACC microspheres were stable in air at least for 3 months. Moreover, the result suggested that the formation of calcite was inhibited to a certain extent by the concentrated PAAs in the supersaturated solution of $CaCO_3$. It may expect that such microspheres of aragonite or ACC have widely potential

applications in various fields (e.g., paper, rubber, pharmaceutical, plastics, paint industries, etc.), as the morphology, polymorph, as well as the size of CaCO$_3$ can be controlled to a certain degree.

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