

Synthesis of amphiphilic triblock copolymers and application for morphology control of calcium carbonate crystals

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Abstract

A series of amphiphilic triblock copolymers poly(ethylene glycol)-*block*-poly(acrylic acid)-*block*-poly(*n*-butyl acrylate) (PEG-*b*-PAA-*b*-PnBA) differing only in the relative block lengths were synthesized by the acid-catalyzed elimination of the *tert*-butyl groups from poly(ethylene glycol)-*block*-poly(*tert*-butyl acrylate)-*block*-poly(*n*-butyl acrylate) (PEG-*b*-PtBA-*b*-PnBA), which was synthesized by atom-transfer radical polymerization (ATRP). The degree of polymerization, molecular weight and percentage of hydrolysis of the product PEG-*b*-PAA-*b*-PnBA were studied by gel permeation chromatography (GPC), NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS). Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to study the aggregation states of copolymers in water solution. The radii of the copolymer micelles shrink as Ca^{2+} is introduced into the solutions. The crystallization behaviors of calcium carbonate controlled by copolymer **1** (PEG₁₁₂-*b*-PAA₈₆-*b*-PnBA₆₀) and copolymer **2** (PEG₁₁₂-*b*-PAA₄₀-*b*-PnBA₇₂) differing mainly in the length of PAA block were systematically studied. It was found that the crystallization products are composed of calcite and vaterite, and the ratio of vaterite to calcite increases with increasing the concentration of copolymer **1**. For copolymer **2**, however, only calcite is obtained at all the concentration range investigated in this work.

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1. Introduction

From a number of carbonate minerals, CaCO_3 is by far the most important in nature and abundant in geological scales and in biominerals – mainly as exoskeleton in shells or cell walls or as mechanical support in spicules and spines. Calcium carbonate has three anhydrous crystalline polymorphs which have typical morphologies: vaterite (polycrystalline sphere), aragonite (needle), and calcite (rhomboheda) in the order of decreasing solubility and increasing stability [1]. The three

polymorphs have markedly different physicochemical characteristics, and it is often found that less stable forms are stabilized kinetically.

Biomimetic synthesis of CaCO_3 crystals in the presence of organic templates and/or additives has been intensively studied in recent years. The mineralization of CaCO_3 induced by double-hydrophilic polymers [2–5] like PEG-*b*-PAA has been extensively investigated. Cölfen and Qi [6] reported that the precipitate of CaCO_3 in the presence of pure PEG, which mainly promotes solubilization in water as the block of PEG-*b*-PAA copolymer, is just the same as that in the absence of additives, and the crystals are all calcite. However, the crystal shape changes greatly when pure PAA is added. The functional parts are the carboxyl groups of the PAA block,

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and the crystals grow along a certain direction as a result of the interaction of carboxyl groups with Ca^{2+} [7]. When these two different polymers are combined together, i.e., by using a block copolymer of PEG-*b*-PAA as a modifier, the morphology of the CaCO_3 crystals is greatly changed.

The design of a block which strongly interacts with calcium ions implies hydrophilicity, so that no superstructure formation in the sense of micellization can be expected when dissolving double-hydrophilic block copolymers in water. The amphiphilic character of a block copolymer can lead to self-assembly behavior similar to that of low molecular weight ionic surfactants, and this opens numerous avenues for the generation of new properties and uses. Among the family of amphiphilic block copolymers, poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) gains much attention, as it self-associates in aqueous solution to form micelles with PS block as core and PAA block as corona [8]. In reference solutions of the amphiphilic diblock copolymer PnBA-*b*-PAA is soluble in water and forms globular micelles with a hydrophobic core and a tethered corona forms the polyelectrolyte block [9]. In comparison with other systems, this system has the advantage that the core of the micelles is in the liquid state and not in the glassy state at room temperature (T_g was measured in the bulk by DSC for the PnBA block: $T_g = -55^\circ\text{C}$).

Since amphiphilic diblock copolymers can simultaneously form self-assembled nanostructures, including rod, wire, lamella, sphere, vesicle, and LCM (large compound micelle), they are potentially useful as soft templates for regulating nanometer-sized inorganic materials. In comparison with diblock copolymers, linear ABC triblock copolymers have more independent parameters on their phase behavior, thus displaying a variety of different morphologies [10]. As far as we know, there is no example of using ABC type amphiphilic triblock copolymers as templates to control the crystallization of calcium carbonate. Therefore, in the present paper we synthesized a new class of amphiphilic triblock copolymers, which tend to form a globular micelles in water solution. In the formed micelles, the single hydrophobic block forms the core and two flanking hydrophilic blocks form the corona. The self-assembled micelle morphology of the amphiphilic triblock copolymer could be extraordinarily effective for controlling the crystallization behavior of calcium carbonate.

2. Experimental

2.1. Materials

Monomethyl ether poly(ethylene glycol) (PEG_{112} , $M_n = 5000 \text{ g mol}^{-1}$) was obtained from Alfa and CuBr was prepared according to the literature [11]. Toluene, ether, tetrahydrofuran (THF), dichloromethane and magnesium sulfate were purchased from Beijing Corporation of Chemical Reagent and used as received. Triethylamine (TEA) was purchased from Tianjin Damao Corporation of Chemical Reagent and dried over KOH. 2-Bromoisobutyl bromide (BrBBR, 98%), ethyl 2-bromoisobutyrate (98%) and trifluoroacetic acid (TFA, 98%) were purchased from Alfa and used as received.

tert-Butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) were purchased from Alfa (98%) and Tianjin Corporation of Chemical Reagent, respectively, both of which were treated with CaH_2 and purified by distillation to remove inhibitor before use. N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA, 99%) was obtained from Aldrich and used after distillation. Alkaline alumina (200–300 mesh, 70%) was obtained from Shanghai Wusi Corporation of Chemical Reagent and used as received. Calcium chloride dihydrate (Sigma–Aldrich, 99+%) and sodium carbonate anhydrous (Acros, 99.5%) were used as received.

2.2. Characterization

GPC was performed on a Waters 515 HPLC pump equipped with a Waters 2414 differential refractometer. Three Waters Styragel columns (HT2, HT3, and HT4) were used. THF was used as eluent at a flow rate of 1 mL/min at 35°C . Polystyrene standards were used for calibrations. ^1H NMR spectra of the precursor and the final products were recorded at room temperature with a Bruker AV-400 NMR spectrometer in CDCl_3 (d_1) and DMSO (d_6), respectively, with tetramethylsilane (TMS) as internal standard. The MALDI experiments were performed with a Bruker reflectron TOF mass spectrometer equipped with a nitrogen laser emitting at 337 nm (Biflex III, Bruker Daltonics Co.). Solutions of the samples (1 g/L) were prepared in 1% trifluoroacetic acid of acetonitrile/water mixed solvents and 4-hydroxyl- α -cyano cinnamic acid (CCA), which was used as the matrix, was also dissolved in the solvents. Matrix and polymer solutions (both in the same solvent) were mixed in a 1:1 ratio, and ca. 0.5 μL of the final mixture was applied to the MALDI sample target.

The dynamic light scattering was performed on ALV/DLS-5022F equipped with a 22 mW UNIPHASE He–Ne laser source ($\lambda_0 = 632 \text{ nm}$). The measurements were carried out at 90° scattering angle at 25°C . The stock solutions were filtered through filters of 0.45 μm pore size into the scattering cells with diameter of 10 mm. The obtained results were processed by ALV software. TEM was performed on a Hitachi-800 microscope operating at an accelerating voltage of 100 kV. For the observations of the size and distribution of the copolymer aggregates, samples were deposited from aqueous solutions (about 1 g/L) onto copper grids, which had been precoated with a thin film of Formvar. Water was allowed to evaporate from the grids at atmospheric pressure and room temperature.

The X-ray diffraction (XRD) patterns of the CaCO_3 crystals were recorded on a Rigaku D/max 2400 X-ray powder diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation (40 kV, 120 mA). Powder samples were mounted on a sample holder and scanned at a scanning speed $2^\circ/\text{min}$ between $2\theta = 20^\circ$ and 60° . FT-IR spectra were recorded on a Bruker EQUINOX55 using KBr pellets. Each sample was recorded with 32 scans at a spectral resolution of 4 cm^{-1} . All samples were Pt-coated before they were examined by a JEOL-JSM-6700F Field Emission Scanning Emission Microscope (FE-SEM), fitted with a field emission source, and operated at an accelerating voltage of 5 kV. Thermogravimetric analyses (TGA) were

made with a Perkin–Elmer TGA-7m. Samples were heated at 20 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere.

2.3. Polymer synthesis

2.3.1. Synthesis of PEG₁₁₂-Br macroinitiator

The preparation of PEG₁₁₂-Br macroinitiator was carried out by a reaction between PEG and BrBBR according to the literature [12].

2.3.2. Synthesis of PEG₁₁₂-b-PtBA-Br

In Schlenk flask, PEG₁₁₂-Br (5 g, 0.001 mol) and CuBr (0.144 g, 0.001 mol) were degassed by vacuum-nitrogen for three times to remove the oxygen. The deoxygenated acetone (5 mL), *t*BA (14 mL, 0.1 mol) and PMDETA (0.209 mL, 0.001 mol) were added into the flask, which was then placed in an oil bath at 60 °C and stirred for different reaction times to control the different lengths of PAA block. Ether was added dropwise to deposit the reaction mixture, which was then dissolved by THF. After removal of the copper catalyst by filtration through an activated (alkali) alumina column, the unreacted monomer *t*BA was removed by precipitation in ether twice and the isolated diblock copolymer was concentrated with rotary evaporation and then dried under vacuum for 24 h to obtain a canary spumescence solid.

2.3.3. Synthesis of PEG₁₁₂-b-PtBA-b-PnBA

In Schlenk flask, PEG₁₁₂-b-PtBA-Br (5 g, 0.5 mmol) and CuBr (0.072 g, 0.6 mmol) were added and the flask was cycled between vacuum and nitrogen three times to remove the oxygen. The deoxygenated acetone (3 mL), *n*BA (7.1 mL, 0.05 mol) and PMDETA (0.0865 mL, 0.5 mmol) were added into the flask and stirred for several minutes, which was then placed in an oil bath at 60 °C and stirred for 12 h. Hexane was added dropwise to deposit the reaction mixture, which

was then diluted by THF. After removal of the copper catalyst by passing the solution through an activated alumina column, the unreacted monomer *n*BA was removed by precipitation in hexane twice and the separated triblock copolymer was concentrated with rotary evaporation and then dried under vacuum for 24 h to obtain a canary sticky solid.

2.3.4. Preparation of PEG₁₁₂-b-PAA-b-PnBA

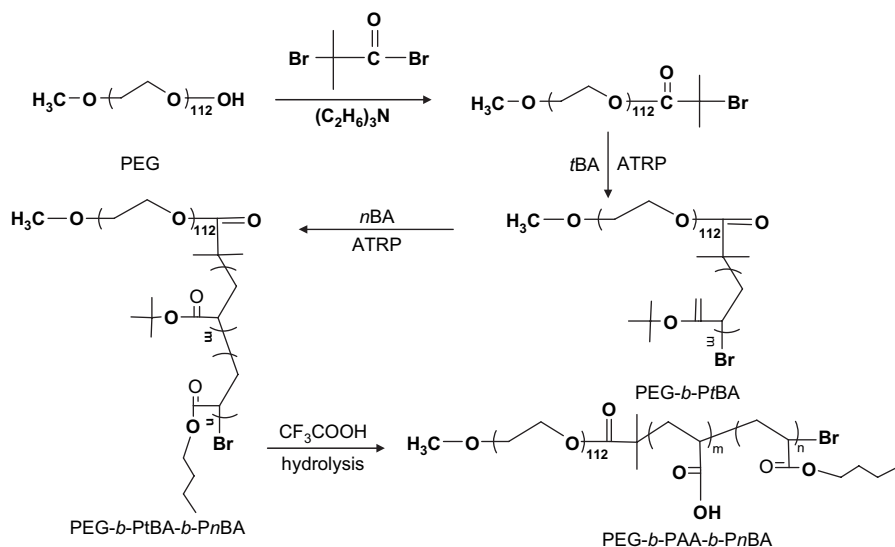
The block copolymer PEG-*b*-PtBA-*b*-PnBA was dissolved in dichloromethane and a fivefold molar excess TFA (with respect to the *tert*-butyl group) was added. This mixture solution was then stirred at room temperature for 24 h. The resulting PEG-*b*-PAA-*b*-PnBA started to precipitate out from the reaction mixture by hexane twice. They were filtered, washed with dichloromethane, and dried under vacuum to constant weight.

2.4. Preparation of pure polymer solution

Triblock polymer PEG-*b*-PAA-*b*-PnBA (0.2 g) was dissolved in 20 mL deionized water and adjusted to pH ca. 7–8 by using 1 mol/L NaOH or HCl aqueous solution. The solution was transferred to a dialysis bag (MEMBRA-CEL MD44-14, molecular weight cut-off = 14 000) and dialyzed against distilled water for 7 days by changing water one time a day in order to eliminate trifluoroacetic acid remained in the product. The dialyzed solution was fixed to 100 mL as 2000 ppm stock solution.

2.5. CaCO₃ crystallization with dynamic stirring method

The precipitation of CaCO₃ was carried out in a glass vessel at a constant temperature of 25 °C. The stock polymer solution was diluted to different concentrations and CaCl₂ was added into 10 mL polymer solution to maintain the concentration of CaCl₂ at 0.2 mol/L. Aqueous solution of Na₂CO₃



Scheme 1. Schematic illustration for the synthesis of the amphiphilic triblock copolymer PEG-*b*-PAA-*b*-PnBA using ATRP method.

Table 1

Basic parameters of the precursor (PEG-*b*-PtBA-*b*-PnBA) of the three triblock copolymers with different block lengths

Samples	Monomer conversion (%)	DP	Percentage of hydrolysis	M_n			PDI (GPC)
				Theor	^1H NMR	MALDI-TOF-MS	
1	82	PEG ₁₁₂ - <i>b</i> -PtBA ₈₆ -PnBA ₆₀	89	26 100	23 600	25 600	1.07
2	80	PEG ₁₁₂ - <i>b</i> -PtBA ₄₀ -PnBA ₇₂	92	23 000	19 300	19 900	1.12
3	87	PEG ₁₁₂ - <i>b</i> -PtBA ₁₈ -PnBA ₇₈	91	18 000	17 300	18 300	1.07

(10 mL, 0.2 mol/L) was mixed with the above solution under vigorous shaking using a magnetic stirrer. The concentrations of the polymer in the final mixture solutions were as follows: 50, 100, 500, and 1000 ppm. The resultant mixture was incubated for 10 h to induce the formation of white precipitates. After decantation, the formed crystals of CaCO₃ were washed with distilled water and ethanol three times, dried at 40 °C overnight, and then submitted for SEM, FT-IR, XRD, and TGA characterization.

3. Results and discussion

3.1. Synthesis of triblock copolymer

The synthetic route for an amphiphilic triblock copolymer is outlined in Scheme 1. The ATRP of PtBA using PEG₁₁₂-Br macroinitiator gave the diblock copolymer PEG-*b*-PtBA, which subsequently transformed to the triblock copolymer PEG-*b*-PtBA-*b*-PnBA. The final amphiphilic copolymer PEG-*b*-PAA-*b*-PnBA was obtained by hydrolysis of PtBA into PAA using trifluoroacetic acid in dichloromethane. The percentages of hydrolysis of the three triblock copolymers are all more than the recognized complete hydrolysis value (85%), which could be thought that the hydrolysis of PtBA into PAA is 100%. The molecular weight of the precursor (PEG-*b*-PtBA-*b*-PnBA) of the three triblock copolymers differing only in the relative block lengths, determined by ^1H NMR and MALDI-TOF-MS methods, are summarized in Table 1. The PAA block length in the three triblock copolymers changes from 86 (copolymer 1) to 40 (copolymer 2), and finally to 18 (copolymer 3), i.e., the main difference among the three copolymers is the content of PAA block, which follows the order of $1 > 2 > 3$.

Because the GPC and NMR results of three copolymers are similar, only one kind of copolymer was chosen as the model. Fig. 1 shows the GPC traces of the precursors PEG-Br, PEG-*b*-PtBA and PEG-*b*-PtBA-*b*-PnBA of copolymer 2. These polymers were characterized by GPC with linear polystyrene standards in THF. Even though the M_n obtained by this method is questionable, it is worthy to determine the polydispersity index (PDI). It revealed that the polymer precursors have low PDI (PDI < 1.5, which is the theoretical value for the controlled/‘living’ free radical polymerization), and with every subsequent reaction the entire distribution curves moved smoothly toward higher molecular weight and the polydispersities remained low with the increasing monomer conversion. The symmetric peak without a shoulder in the high-molecular-weight region indicates no detectable coupling

termination, and the PDI of the copolymer as low as 1.07 demonstrates that the copolymers have uniform molecular weight.

Fig. 2 shows the ^1H NMR spectra of polymers PEG-Br, PEG-*b*-PtBA, PEG-*b*-PtBA-*b*-PnBA, and PEG-*b*-PAA-*b*-PnBA of copolymer 3. In Fig. 2a, peak *a* is assigned to the methylene group of PEG, and peaks *b* and *c* to the methyl protons of *t*BA and the methine group of PtBA, and peaks *c* and *d* to the methine group and the methyl group of PnBA, respectively. Peaks *b* and *d* attributed to PtBA and PnBA, respectively, appear with every subsequent reaction demonstrating the successful copolymerization. After hydrolysis of the PtBA, the sharp peak *b* disappears (Fig. 2b), which indicates the removal of *tert*-butyl groups and the formation of an amphiphilic block polymer as expected. The percentages of hydrolysis of the copolymers were determined by calculating the ratio of the integrated peak areas of the unhydrolyzed part to the original part of *tert*-butyl group ($\delta = 1\text{--}2$ ppm).

3.2. Self-association of triblock copolymers in water

As the PAA block length is very short such as copolymer 3 (PEG₁₁₂-*b*-PAA₁₈-*b*-PnBA₇₈), its aqueous solution becomes turbid. The subsequent study of TEM, DLS and effect on the crystallization of CaCO₃ were not performed on copolymer 3 because of its insolubility in water. The characteristics of the triblock copolymer aggregates 1 and 2 in an aqueous phase were investigated by DLS and TEM. The typical TEM micrographs are presented in Fig. 3 for copolymers 1 (PEG₁₁₂-*b*-PAA₈₆-*b*-PnBA₆₀) and 2 (PEG₁₁₂-*b*-PAA₄₀-*b*-PnBA₇₂). The

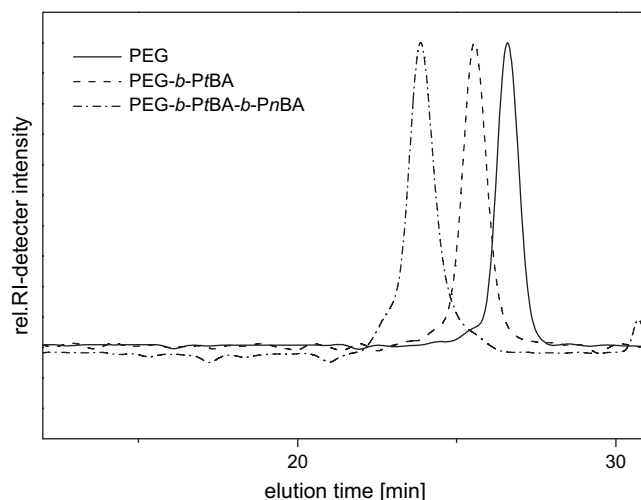


Fig. 1. GPC traces of precursors of copolymer 2.

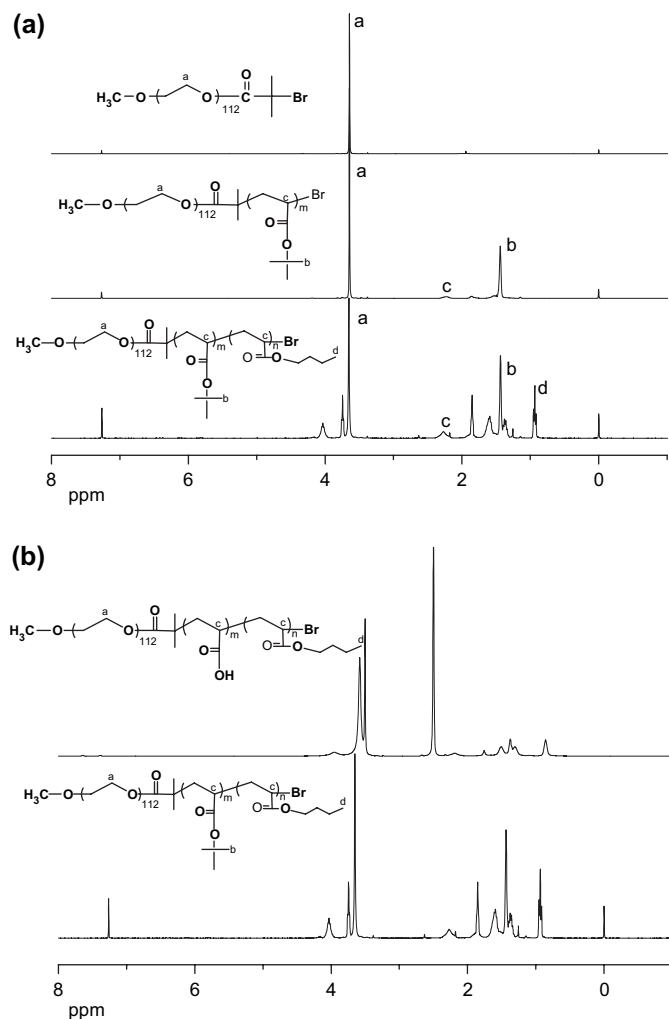


Fig. 2. ^1H NMR spectra of: (a) PEG-Br, PEG-*b*-PtBA, and PEG-*b*-PnBA in CDCl_3 ; (b) PEG-*b*-PtBA-*b*-PnBA before and after hydrolysis in CDCl_3 and DMSO , respectively.

two aggregates are both close to spherical particles with an average diameter between 80 and 120 nm, characteristic of the “dried” micelle. It is generally recognized that amphiphilic block copolymer molecules tend to self-associate and form micelle-like aggregates of spherical geometry because of the

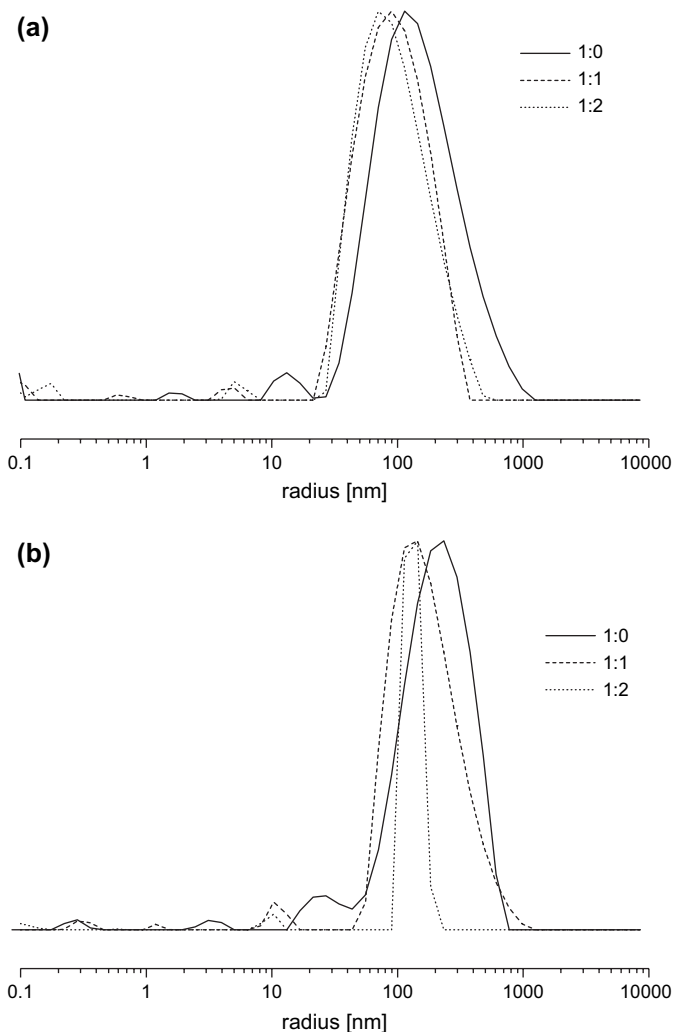


Fig. 4. DLS measurement of: (a) copolymer 1 in water at 90° (1:0, 1000 ppm polymer, $R_h = 106.04$ nm; PDI = 0.377; 1:1, 1000 ppm polymer/ Ca^{2+} , $R_h = 74.70$ nm; PDI = 0.292; 1:2, 1000 ppm polymer/ Ca^{2+} , $R_h = 74.82$ nm; PDI = 0.295); (b) copolymer 2 in water at 90° (1:0, 1000 ppm polymer, $R_h = 148.80$ nm; PDI = 0.378; 1:1, 1000 ppm polymer/ Ca^{2+} , $R_h = 131.47$ nm; PDI = 0.335; 1:2, 1000 ppm polymer/ Ca^{2+} , $R_h = 137.94$ nm; PDI = 0.36).

large repulsive segmental interactions and solubility differences between blocks. The structure of a spherical micelle consists of a core formed by the aggregated insoluble blocks

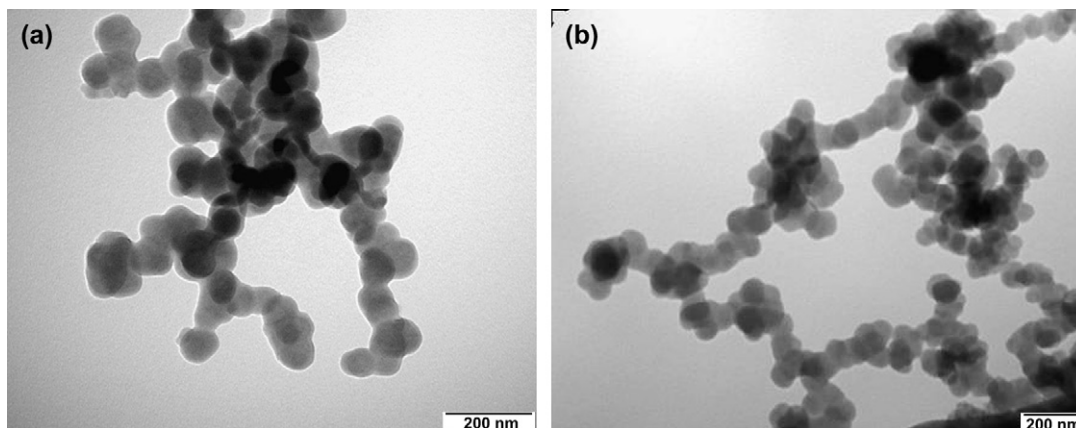


Fig. 3. TEM images of copolymers: (a) 1 and (b) 2 in aqueous solutions.

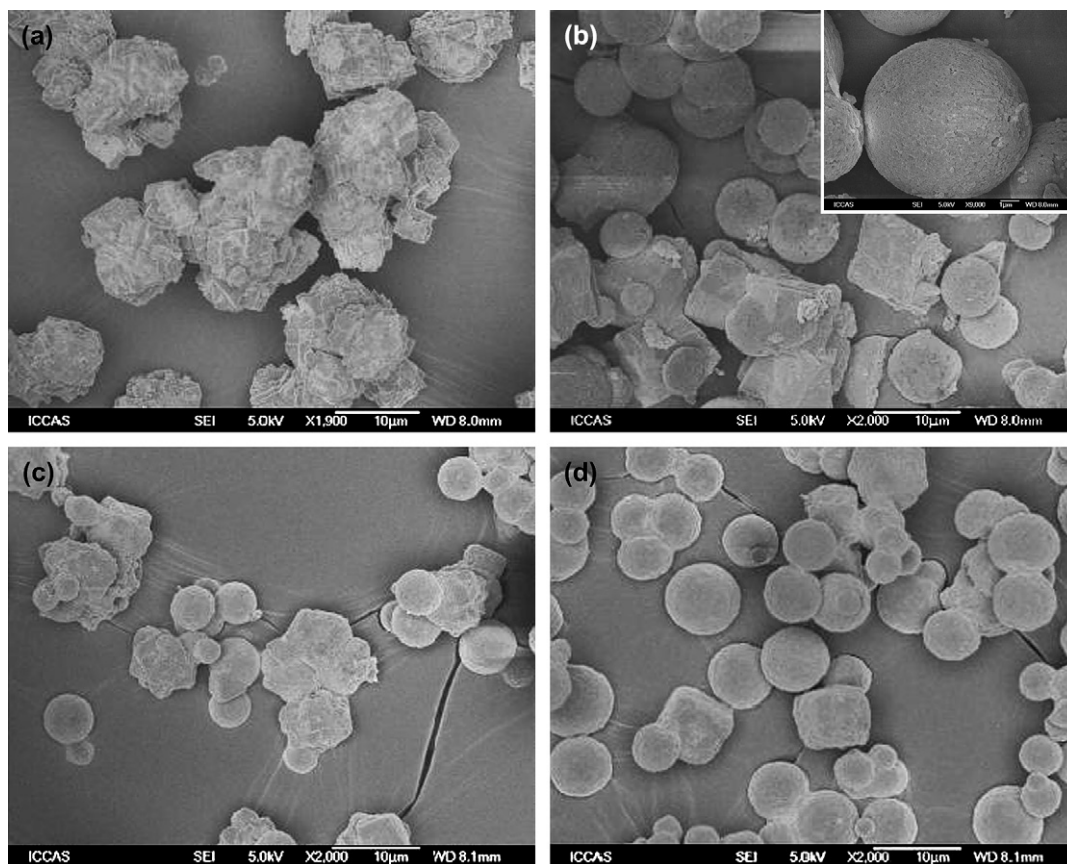


Fig. 5. SEM images of CaCO_3 prepared using dynamic method in the presence of triblock copolymer **1**: (a) 50, (b) 100, (c) 500, and (d) 1000 ppm.

of the copolymers, surrounded by a spherical corona shell formed by the soluble blocks. Eisenberg and Zhang [13] reported that the aggregates having a core which is much smaller than the corona are referred to as star micelles. Micelles of another kind, namely crew-cut micelles, are characterized by a bulky core and a relatively short corona. The block copolymer in our case spontaneously forms star micelles consisting of a collapsed PnBA core and a stretched PAA and a PEG corona in water. The hydrogen bonding between the carboxylic acid groups of PAA and the oxygen atoms of PEG may exist in the corona of the micelle [14].

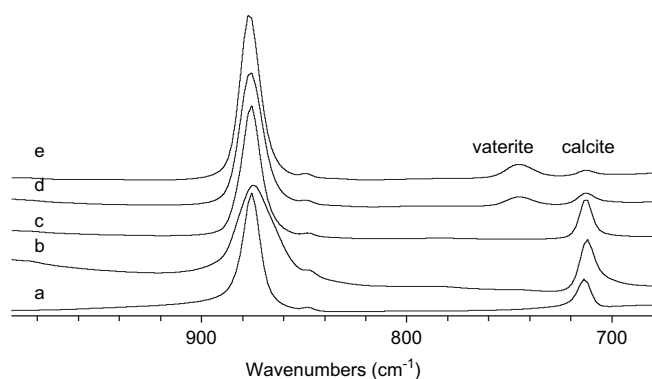


Fig. 6. FT-IR spectra of CaCO_3 crystallized from the solution of triblock copolymer **1**: (a) 0, (b) 50, (c) 100, (d) 500, and (e) 1000 ppm.

DLS shown in Fig. 4 was used to measure the mean hydrodynamic radius (R_h) of the micelles. After adding Ca^{2+} , the R_h decreased from 106 to 74 nm for copolymer **1** and from 148 to 131 nm for copolymer **2**. The shrinkage effect of Ca^{2+} on the copolymer **1** with longer PAA block is greater than copolymer **2** with shorter PAA block. The change of micellar scales in solution by adding Ca^{2+} maybe as a result of the shrinkage

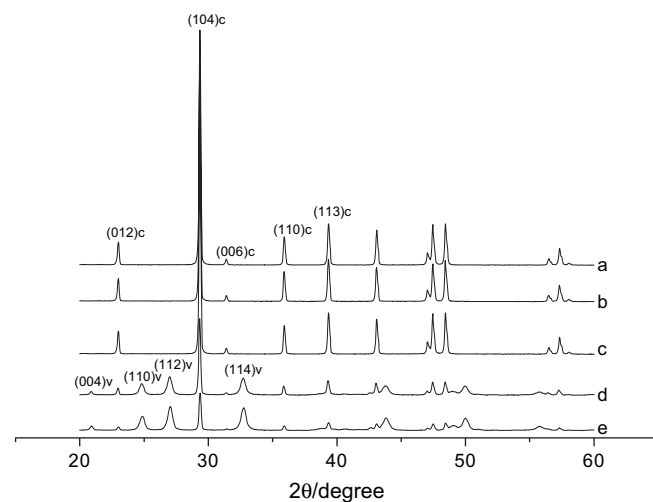


Fig. 7. XRD spectra of CaCO_3 crystallized from the solution of triblock copolymer **1**: (a) 0, (b) 50, (c) 100, (d) 500, and (e) 1000 ppm.

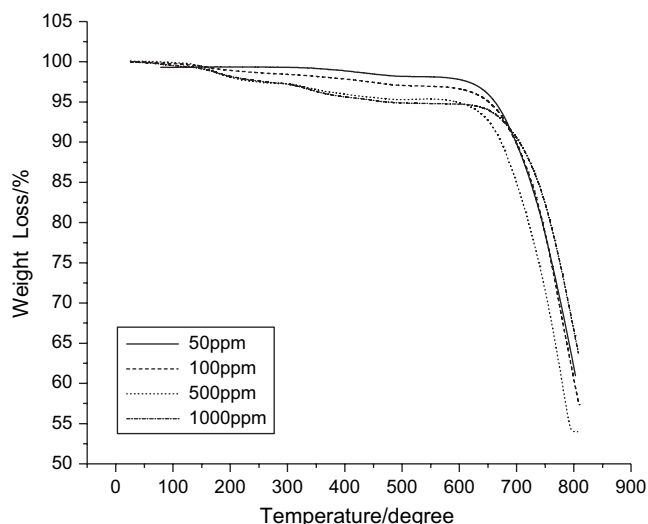


Fig. 8. TGA thermograms of CaCO_3 crystallized from the solutions of triblock copolymer 1.

of the corona because of binding of the Ca^{2+} ions to the carboxylate anions, which were present in the solution as a result of the slight dissociation of the poly(acrylic acid) blocks [15]. The introduction of Ca^{2+} increases the counterion concentration outside of the corona, thus lowering the thickness of the diffuse double layer. Part of Ca^{2+} goes into the bulk phase

and binds with carboxylate anions, which shields the effective charge. The strong anion repulsion among the hydrophilic blocks therefore weakens and the blocks are more curled, resulting in the decrease of the micellar size.

3.3. Influence of the triblock copolymers on the crystallization of CaCO_3

In a blank experimental condition (without any additive), CaCO_3 crystallization only resulted in the clearly defined rhombohedral crystals characteristic of calcite. The two triblock copolymers (copolymers 1 and 2) were used as additives and showed different effects on the polymorph and morphology of CaCO_3 . Under the control of copolymer 1, the concentration has an apparent effect on the polymorph of CaCO_3 (Fig. 5). At low concentration (50, 100 ppm), rhombohedral calcite was obtained similar to pure water system. With increasing polymer concentration, the amount of spherical vaterite increases, whose surface is smooth as shown in the inset in Fig. 5b. FT-IR and XRD results under stirring conditions and in the presence of the polymer are summarized in Figs. 6 and 7, respectively. The peaks at 712 and 745 cm^{-1} correspond to characteristic carbonate infrared vibration for calcite and vaterite, respectively. Peaks at $2\theta = 24.88^\circ$, 27.04° and 32.77° are assigned to (110), (112) and (114) planes of the diffraction of vaterite, and $2\theta = 29.39^\circ$ to (104) plane of the diffraction of

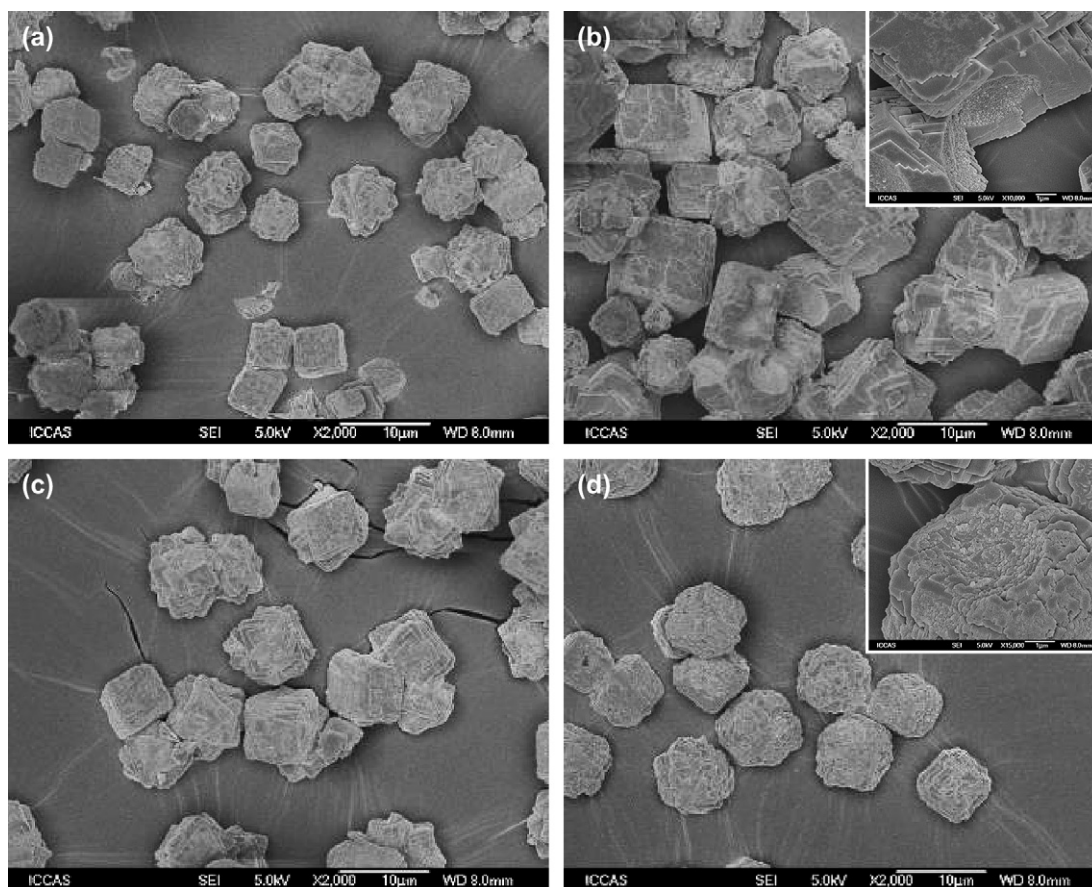


Fig. 9. SEM images of CaCO_3 prepared using the dynamic method in the presence of triblock copolymer 2: (a) 50, (b) 100, (c) 500, and (d) 1000 ppm.

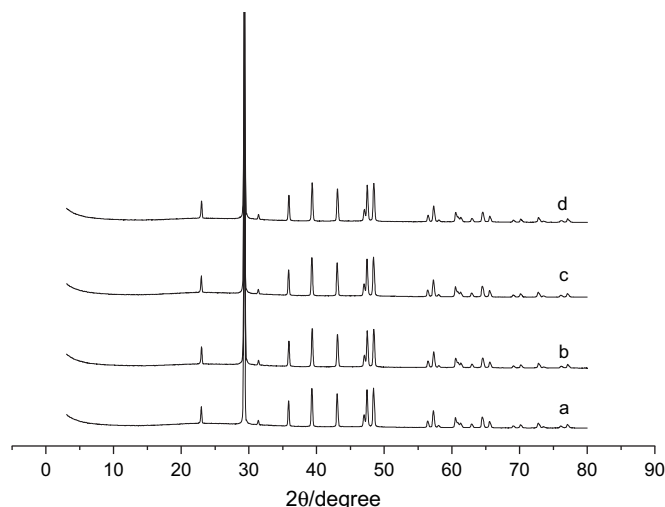


Fig. 10. XRD spectra of CaCO_3 crystallized from the solution of triblock copolymer **2**: (a) 50, (b) 100, (c) 500, and (d) 1000 ppm.

calcite. Therefore, the CaCO_3 particles are a mixture of calcite and vaterite. The organic additives absorbed on crystal surfaces and/or embedded in CaCO_3 particles can be detected by TGA analyses (Fig. 8). All the TGA measurements showed two decomposing processes. The first decomposing onset at ca. 220 °C corresponds to the carbonization of copolymer molecules, and the second one at ca. 620 °C corresponds to the decomposition of CaCO_3 crystals. The weight loss during the first decomposition course is ca. 2.0 or 5.0% in the presence of 100 or 1000 ppm of copolymer **1**, respectively, while the residual mass (i.e., only the CaCO_3 crystals) is determined to have a weight loss of ca. 30%. Therefore, Fig. 8 further proved that copolymer molecules are chemically interacted and/or absorbed on the surfaces of the precipitated CaCO_3 crystals. According to Ref. [6], the PEG corona would not play the role of template for the CaCO_3 crystallization, whereas the PAA corona would act as templates for the CaCO_3 crystallization. The preferential nucleation of vaterite in the dynamic crystallization experiments implies that the interaction between Ca^{2+} and the carboxyl groups of the PAA block might account for the kinetic promotion of the metastable polymorph of vaterite.

Under the control of copolymer **2**, only calcite was obtained at all the four concentrations (50, 100, 500, 1000 ppm) (Fig. 9). The surface of calcite is not typical rhombohedral with some defects (the inset in Fig. 9b and d). The corresponding XRD pattern (Fig. 10) showed only sharp calcite reflections, indicating that the phase structure consists of well-crystallized calcite crystals. These results indicate that copolymer **2** has a weak influence on the morphology and phase structure, which can be ascribed to the fact that the amount of carboxylic acid groups of copolymer **2** is too short to bind enough calcium ions.

4. Conclusions

A series of amphiphilic triblock copolymers, $\text{PEG}_{112}\text{-}b\text{-PAA-}b\text{-PnBA}$, which contain one hydrophobic segment of a PnBA block and two hydrophilic segments of PAA and PEG blocks, differing in the length of PAA blocks were synthesized by ATRP method. Due to the amphiphilic characteristic and unique structure of single molecule on the nanometer scale, the polymers were used to modify the crystal growth of CaCO_3 . In the presence of copolymer **1** with longer PAA block, CaCO_3 crystals are composed of calcite and vaterite, and the vaterite content increases with increasing the polymer concentration. For copolymer **2**, however, only calcite can be obtained at all the concentration range investigated in this work.

Based on the experimental results, it is proposed that the synthesized ABC triblock copolymers construct a shell structure on CaCO_3 crystals with the end block of PnBA forming an inert shell and the outmost block of PAA rendering the crystal polymorph. The current investigations have demonstrated that by precisely designing composition of block copolymers with various functional blocks, ABC type copolymers may play a role as ideal templates for regulating inorganic materials to form multifarious morphologies.

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