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"Reservoir" and "barrier" effects of ABC block copolymer micelle in hydroxyapatite mineralization control

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ABSTRACT

An amphiphilic triblock poly (ethylene glycol)–block-poly (acrylate acid)–block-poly (ϵ-caprolactone) (PEG–PAA–PCL) copolymer was synthesized by sequential anionic polymerization. By comparing with diblock copolymer poly (acrylic acid)–block-poly (ϵ-caprolactone) (PAA–PCL), the triblock copolymer (PEG–PAA–PCL) micelle has core–shell–corona structure, which possesses better dispersion, could be a good candidate as structure template for the controlled mineralization of hydroxyapatite (HA). The interactions between inorganic ions and polymers were studied by using Ca^{2+} ion selective electrode and zeta potential, which indicated the "reservoir" effect of micelles and the "barrier" effect of PEG segments during mineralization process. Ca^{2+} ions can penetrate through the corona and interact with PAA segments. When PO_4^{3-} ions were added, Ca^{2+} ions diffuse out, and react with PO_4^{3-} ions to form the new apatite layer. Thus the supersaturation could be well tuned by the triblock copolymer micelles, and the nucleation and crystal growth in nano scale could be controlled by appropriate usage of this template system.

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1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (denoted as HA), a form of bioceramic material [1], is present in bone, teeth, and tendons to give these organs stability, hardness, and function [2]. Owing to its bioactive property, HA is widely used in medicine and dentistry as a material for metallic implant coatings, or for bone cavity fillings [3–5]. Controlled mineralization of HA is a hot topic in chemistry, materials, biology and nanotechnology [6–12].

HA hollow nanostructures are considered to be advantageous because of their large specific surface area and high capacity for loading drug, protein or DNA molecules. Several methods have been developed to prepare HA hollow nanostructures, for example, polyelectrolyte-mediated mineralization [13,14], ultrasonic-assisted route [15], etc. Bio-inorganic microcapsules from templating protein [16] and porous nanocomposites of PEG–PLA/calcium phosphate were reported for medicinal application [17].

In recent years, the strategy of using organic templates to control the nucleation, growth, and alignment of inorganic particles has been extensively applied to the biomimetic morphogenesis of inorganic materials with complex forms [18–25]. In the recent work, surfactants [26] and block copolymers [27–29] were used as templates to tune the morphology of HA materials, including hollow spherical morphology. In this way, the template plays an important role in the nucleation and growth of HA crystals and determines their size, morphology, and orientation in the composite material.

With the development of synthesis techniques, many functional block copolymers were designed for different applications [30–33]. However, when AB-type or ABA-type block copolymers perform as templates, their micelles will adsorb inorganic materials, then the shells become unstable, always resulting in secondary or higher-level aggregates [34], which lead to limited control in mineralization. Fortunately, the ordered self-assemblies, formed by ABC-type triblock copolymers, have more independent parameters on their phase behavior [35,36], and can be promising soft templates for regulating nano-sized inorganic materials [37]. Thus, in the present paper, an amphiphilic triblock copolymer poly (ethylene glycol)–block-poly (acrylate acid)–block-poly (ϵ-caprolactone) (PEG–PAA–PCL) was designed to act as a template to control HA mineralization. The core–shell–corona (c–s–c) structure of its aggregate [38], which is formed by the hydrophobic PCL segments (core), PAA segments with functional groups (shell) and the water-soluble PEG segments (corona), respectively, facilitates good micelle dispersion, and is hoped to perform good control on HA nano spheres mineralization.

Usually, mineralization control relies on thermodynamic or kinetic mechanisms, and in most cases, the nucleation is the key step in building up a complex structure [39]. The supersaturation is a major driving force for nucleation in solutions, thus the nucleation and growth kinetics could be tuned by adjusting solution supersaturation [40,41]. However, due to the lack of enough

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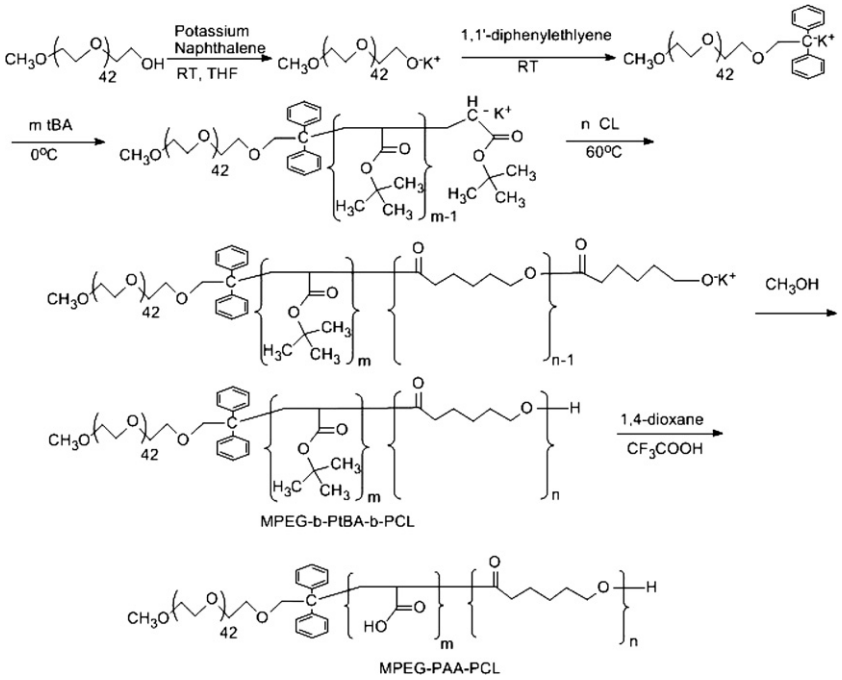

Scheme 1. Synthesis of PEG–PAA–PCL.

information such as ion distribution in the nucleation process, the mechanism of the morphology control is still not very clear from the viewpoint of supersaturation. Recently, the stable prenucleation calcium carbonate clusters were studied by measuring free Ca^{2+} concentration [42], which provided important information to mineralization control.

As an extension for the study on synthesis of hollow spherical HA [28], we present a detailed investigation on the templating effect of PEG–PAA–PCL for controlled mineralization of HA. The free Ca^{2+} concentration, zeta potential and pH value were pursued and the solution supersaturation was monitored to analyze the effect of polymer on HA formation, and we found the amphiphilic triblock copolymer PEG–PAA–PCL with a c–s–c micelle structure played a role differing from the diblock copolymer PAA–PCL. "Reservoir" and "barrier" effects of this ABC block copolymer micelle in mineralization control were proposed. We hope this study will not only provide a new understanding of the mineralization mechanism of HA, but also a way for the development of biocompatible materials by utilizing novel designed polymers. Such HA nano spheres are interesting and might be useful as novel drug delivery carriers, ceramics precursors, reinforcing fillers, or biomedical implants.

2. Experimental section

2.1. Materials

The monohydroxy capped poly (ethylene oxide) (MePEG-OH, Mn = 1900) was obtained from Aldrich Chemicals. Trace amounts of water were removed from MePEG-OH by vacuum applied to the molten polymer at 55 °C for 1 h.

Tert-butyl acrylate (tBA) obtained from Aldrich Chemicals was passed through a column of activated alumina to remove the stabilizing agents, dried over calcium hydride for 48 h at room temperature, then vacuum distilled and stored under a nitrogen atmosphere at −20 °C. The required amount of the distilled tBA was taken into a flask to which was added drop by drop 25 %wt $AlEt_3$ solution in hexane until a persistent yellow green color was observed. tBA was redistilled under reduced pressure, just prior to polymerization experiment [43].

ϵ-Caprolactone (ϵ-CL, from Aldrich Chemicals, 99%) obtained from Aldrich Chemicals was dried over calcium hydride for 48 h at room temperature, and distilled under reduced pressure just before use.

Potassium di (trimethylsilicon) amide ($[(CH_3)_3Si]_2N^-K^+$) in toluene (0.5 M) was purchased from AlfaAesar.

Tetrahydrofuran (THF) purchased from Sinopharm Chemical Reagent Co., Ltd was dried by refluxing over potassium, and distilled just before use.

Potassium naphthalene (0.5 M) was prepared by our lab: dissolving naphthalene in THF and refluxing this solution over potassium until the compound becomes dark blue, the ratio of potassium and naphthalene is 1:1.

$CaCl_2$, K_3PO_4, CF_3COOH, 1,1′-diphenylethylene, 1,4-dioxane, and petroleum ether (bp. 60–90 °C) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. All solvents were of analytical grade and were used as received, unless stated specially.

Table 1
Basic parameters of the precursor (PEG–PtBA–PCL) of the two triblock copolymers and the precursor (PtBA–PCL) of the diblock copolymers with different block lengths.

Polymer	Monomer (mmol)			Percentage of hydrolysis	Mn			PDI (GPC)
	PEG	tBA	CL		Theory	NMR	GPC	
PEG_{43}–$PtBA_{21}$–PCL_{35}	1	31.25	45.25	90	9744	8578	9234	1.37
PEG_{43}–$PtBA_{40}$–PCL_{47}	1	60.50	60.55	91	16,420	12,378	12,745	1.31
$PtBA_{32}$–PCL_{47}	0	60.50	60.55	88	14,692	9626	10,592	1.33

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