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Preparation and applications of a variety of fluoroalkyl end-capped oligomer/hydroxyapatite composites

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Abstract

A variety of fluoroalkyl end-capped oligomers were applied to the preparation of fluorinated oligomer/hydroxyapatite (HAp) composites (particle size: 38–356 nm), which exhibit a good dispersibility in water and traditional organic solvents. These fluoroalkyl end-capped oligomer/HAp composites were easily prepared by the reactions of disodium hydrogen phosphate and calcium chloride in the presence of self-assembled molecular aggregates formed by fluoroalkyl end-capped oligomers in aqueous solutions. In these fluorinated HAp composites thus obtained, fluoroalkyl end-capped acrylic acid oligomers and 2-methacryloyloxyethanesulfonic acid oligomer/HAp nanocomposites afforded transparent colorless solutions toward water; however, fluoroalkyl end-capped *N*,*N*-dimethylacrylamide oligomer and acryloylmorpholine oligomer were found to afford transparent colorless solutions with trace amounts of white-colored HAp precipitants under similar conditions. HAp could be encapsulated more effectively into fluorinated 2-methacryloyloxyethanesulfonic acid oligomeric aggregate cores to afford colloidal stable fluorinated oligomer/HAp composites, compared to that of fluorinated acrylic acid oligomers. These fluorinated oligomer/HAp composites were applied to the surface modification of glass and PVA to exhibit a good oleophobicity imparted by fluorine. HAp formation was newly observed on the modified polyethylene terephthalate film surface treated with fluorinated 2-methacryloyloxyethanesulfonic acid oligomers and acrylic acid oligomer/HAp composites by soaking these films into the simulated body fluid.
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1. Introduction

Hydroxyapatite [HAp: $Ca_{10}(PO_4)_6(OH)_2$] has been hitherto widely studied as one of the most important biocermics for medical and dental applications such as dental implants and drug delivery systems due to its biocompatibility and chemical and biological affinity with bone tissue [1]. Well-dispersed HAp particles could increase the contact area between the polymer matrix and the inorganic reinforcing phase for interfacial bond development. However, there have been some difficulties in the development of nanophase HAp-based materials for bone replacement and tissue engineering applications, owing to the colloidal poor stability of HAp particles related to the tendency for agglomeration. Therefore, the development of such biomaterials in biomimetic and biologically inspired approaches should be focused on the preparation of nanocrystallites of inorganic biological compounds such as HAp dispersed into polymer matrices [2–4]. In fact, there have been a variety of reports on the preparation of the colloidal stable HAp–organic polymer composites [5]. For example, HAp–poly(vinyl alcohol) nanocomposites and HAp–collagen nanocomposites have been obtained by the use of in situ preparative methods with calcium ions, respectively [6].

Hitherto, we found that amphiphilic fluoroalkyl end-capped oligomers are attractive materials, because they exhibit various unique properties such as high solubility, surface-active properties, biological activities, and nanometer-size-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding nonfluorinated and randomly fluoroalkylated ones [7]. For example, self-assembled fluorinated molecular aggregates formed by fluoroalkyl end-capped acryloyl-

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morpholine oligomers could interact with fullerene and carbon nanotubes as guest molecules in aqueous media to afford a good solubility of fullerene and carbon nanotubes in water [8]. This suggests that these fluorinated molecular aggregates could provide nanometer-size-controlled suitable host moieties to interact with inorganic biological compounds such as HAp as a guest molecule in aqueous and organic media. Thus, it is strongly expected that these fluorinated oligomeric aggregates could interact with HAp to afford the corresponding fluorinated oligomer/HAp composites possessing a good dispersibility and stability in a variety of solvents. However, studies on the preparation and applications of these fluorinated polymers/HAp composites have been hitherto very limited, although such studies have been the subject of considerable research of a fundamental and an applied nature. In our continuing effort to develop colloidal stable fluorinated oligomer/inorganic biological compound composites, we have found that fluoroalkyl end-capped acrylic acid oligomers can afford corresponding fluorinated oligomer/HAp composites possessing a good dispersibility in aqueous and traditional organic media [9]. We now give a full account of the preparation and properties of a variety of fluoroalkyl end-capped oligomer/HAp composites, with particular emphasis on the formation of biologically active HAp on the polyethylene terephthalate film surface treated with these fluorinated HAp composites after exposure to simulated body fluid.

2. Experimental

2.1. Measurements

Molecular weights were measured using Shodex DS-4 (pomp) and Shodex RI-71 (detector) gel-permeation chromatography (GPC) calibrated with polystyrene standard using tetrahydrofuran (THF) as the eluent. NMR spectra and Fourier-transform infrared (FTIR) spectra were measured using the JEOL JNM-400 (400 MHz) FT NMR system (Tokyo, Japan) and a Shimadzu FTIR-8400 FTIR spectrophotometer (Kyoto, Japan), respectively. Dynamic light-scattering (DLS) measurements were measured using an Otsuka Electronics DLS-7000 HL (Tokyo, Japan), and the particle size of the composites (the mean values of four times) was determined in aqueous solutions. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1210 electron microscope (Tokyo, Japan). Scanning electron microscopy (SEM) images were measured by using JEOL JSM-5300 (Tokyo, Japan) and Hitachi S-3000H (Tokyo, Japan). Energy dispersion X-ray fluorescence spectrometry (EDX) was measured using a HORIBA EMAX-5770W (Kyoto, Japan). XRD measurements were performed by the use of a Rigaku MultiFlex (Tokyo, Japan). The contact angles were measured by the use of the Kyowa Interface Science Drop Master 300 (Saitama, Japan).

2.2. Materials

Calcium chloride and disodium hydrogen phosphate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), respectively. A variety of fluoroalkyl end-capped oligomers were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported methods [10].

2.3. Preparation of fluoroalkyl end-capped oligomer/HAp composites

A typical procedure for the preparation of fluoroalkyl end-capped oligomer/hydroxyapatite composites is as follows: To 50 mmol/dm^3 Na_2HPO_4 aqueous solution (20 ml) containing fluoroalkyl end-capped acrylic acid (ACA) oligomer [24 g/dm^3; R_F–$(CH_2CHCOOH)_n$–R_F, R_F–$(ACA)_n$–R_F; R_F = $CF(CF_3)OC_3F_7$; Mn = 2100] was added an aqueous solution (20 ml) of 84 mmol/dm^3 $CaCl_2$. The mixture was stirred with a magnetic stirring bar at room temperature for 4 h to afford the transparent colorless solution. After the solvent was evaporated by the addition of methanol under reduced pressure, the crude product obtained was dialyzed to give the white powdery product (0.33 g). The purified product thus obtained was found to exhibit a good redispersibility in water.

Other fluoroalkyl end-capped oligomer/HAp composites were also prepared under similar conditions.

2.4. Surface modification of glass and poly(vinyl alcohol) with fluorinated oligomer/HAp composites

The glass plates (10×10 mm^2 pieces) were dipped into the 4% (m/m) aqueous solutions of fluoroalkyl end-capped acrylic acid oligomer/HAp composites at room temperature and left for 5 min. They were lifted from the solution at a constant rate of 0.5 mm/min, rinsed with water, and subjected to heat treatment for 1 h at 50 °C *in vacuo*. After the heat treatment, the contact angles of water and dodecane for these glass plates were measured.

The modified poly(vinyl alcohol) (PVA) film was prepared by casting the mixtures of aqueous solutions (10 ml) of PVA (0.99 g) and the transparent colorless solutions (3 ml) containing fluoroalkyl end-capped 2-methacryloyloxyethanesulfonic acid (MES) oligomer/HAp composites (10 mg) on glass plates. The solvent was evaporated at room temperature, and the film formed was peeled off and dried at 50 °C for 72 h under vacuum to afford the modified PVA film (film thickness: 115 μm). The contact angles for dodecane of both the surface and the reverse sides of this film were measured at room temperature by the use of the contact angle measurements.

2.5. Preparation of a simulated body fluid (SBF, the Kokubo solution)

SBF (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mol/dm^3: the Kokubo solution), which has inorganic ion concentrations nearly equal to those of human blood plasma, was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 in water and buffering at pH 7.40 with tris(hydroxymethyl)aminomethane and an

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