Polymer 53 (2012) 3849–3860

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Film-forming amphiphilic silsesquioxane hybrids prepared by hydrolytic co-condensation of hydroxyl-functionalized and fluorinated triethoxysilanes

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ARTICLE INFO

Article history:
Received 29 March 2012
Received in revised form
15 June 2012
Accepted 24 June 2012
Available online 2 July 2012

Keywords:
Silsesquioxane
Amphiphilite
Self-standing film

ABSTRACT

Amphiphilic silsesquioxanes-based hybrids were synthesized by hydrolytic co-condensation of a hydroxyl-functionalized triethoxysilane precursor derived from 2-hydroxyethyl acrylate (HEA) and fluorinated triethoxysilane precursors derived from 1*H*,1*H*,5*H*-octafluoropentyl acrylate (OFPA) and 2,2,2-trifluoroethyl acrylate (TFEA). Hydrolytic co-condensations of two functionalized triethoxysilane precursors proceeded as homogeneous systems in *N*,*N*-dimethylformamide (DMF) to afford amphiphilic silsesquioxanes hybrids, which were soluble in a variety of solvents, depending on the composition. The structure of the constitutional unit of the hybrids was confirmed by the results of NMR and FT-IR measurements. Scanning force microscope (SFM) measurements indicated the formation of spherical hybrids having relatively narrow size distributions (average particle diameter < 3.0 nm) without aggregation. The sizes of the hybrids were also confirmed by X-ray diffraction (XRD). Flexible semi-transparent films were obtained from the amphiphilic silsesquioxane hybrids prepared by hydrolytic co-condensations at suitable feed ratios. The organic-inorganic amphiphilites exhibited a high density of chemically bonded peripheral fluoroalkyl and hydroxyalkyl groups, in which various characteristic properties involving amphiphilicity, film-forming property, refractive index, responsive surface, nanometer size, and narrow size distribution can be manipulated by varying the composition in the feed.

1. Introduction

Fluorinated silsesquioxanes comprised of a silicon-oxygen core framework and fluoroalkyl shell have attracted significant research interest, because of their wide range of applications, such as superoleophobic surfaces [1–3], low dielectric nanocomposites [4], modifiers for surface dewettability [5–8], low-refractive-index materials [9], and lithography applications [10,11]. Silsesquioxane is a family of compounds characterized by a ratio of 1.5 between the silicon and oxygen atoms, and structures can be expressed in general formula: $(R{-}SiO_{1.5})_n$ (R = substituent group and n = even number) [12–19]. In particular, much interest has been paid to cubic T_8 silsesquioxane $(RSiO_{1.5})_8$, so-called polyhedral oligomeric silsesquioxanes consisting of a rigid, crystalline silica-like core that is perfectly defined spatially (0.5–0.7 nm) and that can be linked covalently to eight R groups. A variety of fluorinated silsesquioxanes having various fluoroalkyl groups, different numbers of fluorinated substituent groups, and cage structures has been developed.

Recently, silsesquioxanes having two or more different organic groups immobilized to an inorganic core have attracted considerable attention, because of their intriguing phase behavior and enormous potential as a building block for various advanced materials [16]. For example, Tsukruk et al. reported bulk and surface assembly of amphiphilic silsesquioxane compounds with various hydrophilic and hydrophobic terminal group compositions [20]. For the synthesis of silsesquioxanes having different substituent groups, several methods have been employed, which involve co-hydrolysis/co-condensation of chlorosilanes and alkoxysilanes, corner-capping method, and synthetic modification of a pre-existing silsesquioxane compound [16]. During recent years, there has been increasing attention paid to silsesquioxanes having fluoroalkyl chain as a hydrophobic component and another organic group. The synthesis of heteroleptic silsesquioxane consisting of perfluoro, isooctyl, and amino (or alkoxy) groups was conducted by basic hydrolysis of corresponding trialkoxysilane precursors [21,22]. A number of fluorinated polyhedral oligomeric silsesquioxanes structures possessing a high degree of hydrophobicity have been prepared via a facile corner-capping methodology with various fluoroalkyl

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0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.06.044

trichlorosilanes [23]. The corner-capping methodology using incompletely condensed silsesquioxane with fluoroalkyl groups was used for the synthesis of a fluorinated polyhedral oligomeric silsesquioxane with an initiating group for atom transfer radical polymerization [24]. Fluorinated polyhedral oligomeric silsesquioxanes possessing one reactive functional group prepared by the corner-capping method were employed for preparation of various fluorinated silsesquioxanes/polymer hybrids [25–27].

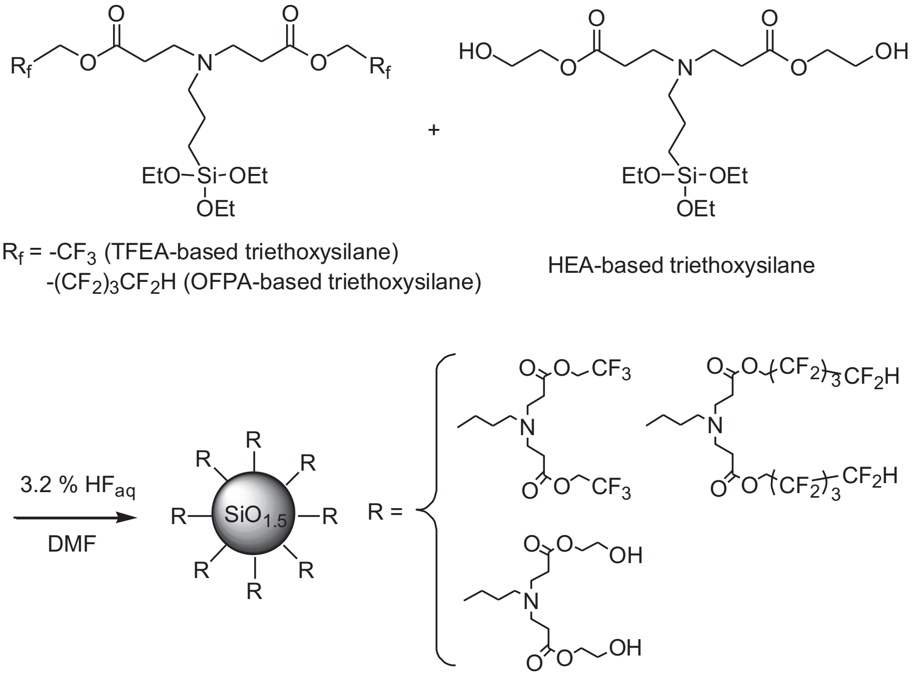
Because the synthesis of T_8 silsesquioxane requires complicated and time-consuming procedures, we are interested to develop facile synthetic methods for silsesquioxane-based nano-objects having uniform size and characteristic properties. In previous studies, a water-soluble silsesquioxane-based nanoparticle (diameter $\approx$ 3.0 nm) was synthesized by hydrolytic condensation of a functionalized precursor, *N*,*N*-di(2,3-dihydroxypropy)aminopropyltriethoxysilane, which was prepared by addition reaction of (aminopropyl)triethoxysilane and glycidol [28,29]. This facile synthetic method with short synthetic steps with high yield endowed the nanoparticles with characteristic properties such as high functionalities, good solubility in aqueous media, nanometer size, narrow size distribution, and the ability to form complexes with a weak anionic polyelectrolyte, depending on changes in the pH [29,30]. The product can be regarded as a mixture of silsesquioxanes, which are composed of various species having 12–18 Si atoms with different numbers of intramolecular cyclizations, and comprised mainly of complete and incomplete cage-like structures. The development of an easily accessible mixture of silsesquioxanes is one option for their exploitation in practical applications. A bulky functionalized triethoxysilane precursor prepared by addition reaction of (aminopropyl)triethoxysilane and 2-hydroxyethyl acrylate could be also employed for the preparation of water-soluble nanoparticles [31]. We also found that the co-condensation of the hydroxyl-functionalized triethoxysilane precursor with tetraethoxysilane [31] and titanium alkoxide [32] provided water-soluble hybrids. A similar procedure was also employed to synthesize fluorinated silsesquioxane-based hybrids having uniform size distribution, good solubility, and low-refractive-index [9]. An attractive feature of this system is that it makes it feasible to create a variety of hybrid materials having different functional organic components through the design of appropriate triethoxysilane precursors, because various vinyl monomers can be employed as starting materials.

Here, we demonstrate the synthesis of novel amphiphilic silsesquioxane hybrids having controlled number of hydrophilic and hydrophobic groups by hydrolytic co-condensations of the hydroxyl-functionalized triethoxysilane precursor derived from 2-hydroxyethyl acrylate (HEA) and fluorinated triethoxysilane precursors as shown in Scheme 1. In this study, two acrylates having different fluoroalkyl chains, 1*H*,1*H*,5*H*-octafluoropentyl acrylate (OFPA) and 2,2,2-trifluoroethyl acrylate (TFEA), were employed for the preparation of the fluorinated triethoxysilane precursors. Co-condensation of the hydroxyl-functionalized precursor (HEA-based triethoxysilane) and fluorinated precursors (OFPA-based and TFEA-based triethoxysilane) provides amphiphilic hybrid materials, in which solubility, amphiphilicity, refractive index, film-forming and various properties can be manipulated by the composition in the feed. The resulting amphiphilic silsesquioxane hybrids should have fluoroalkyl groups and hydroxyalkyl groups on the outermost surface, in addition to the tertiary amino groups and ester groups, which lead to various characteristic properties. The presence of intermolecular interactions between these functional groups of the hybrids may contribute to achieving good film-forming property, in which physically cross-linked polymer-like materials can be easily fabricated into the self-standing hybrid films.

2. Experimental section

2.1. Materials

2,2,2-Trifluoroethyl acrylate (TFEA, Tokyo Kasei Kogyo, >98%), 1*H*,1*H*,5*H*-octafluoropentyl acrylate (OFPA, Daikin Chemical, >95%), and (3-aminopropyl)triethoxysilane (Kanto Chemical, 99%) were



Scheme 1. Synthetic route for the amphiphilic silsesquioxane-based hybrids based on hydrolytic co-condensation of the hydroxyl-functionalized triethoxysilane precursor and fluorinated triethoxysilane precursors.