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Langmuir–Blodgett films composed of amphiphilic double-decker shaped polyhedral oligomeric silsesquioxanes

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ABSTRACT

New amphiphilic polyhedral oligomeric silsesquioxanes (POSSs) were synthesized, and their monolayer behavior on a water surface and Langmuir–Blodgett (LB) film formation were studied. Two kinds of amphiphilic POSS molecules, which have two or four di(ethylene glycol) units (2OH-DDSQ and 4OH-DDSQ, respectively), were synthesized by direct hydrosilylation of di(ethylene glycol) vinyl ether with double-decker shaped polyhedral oligomeric silsesquioxanes (DDSQs). Surface pressure (π)–area (A) isotherms and Brewster angle microscope (BAM) measurements indicated that both amphiphilic DDSQs form a stable monolayer at the air–water interface. In addition, 4OH-DDSQ can be deposited on a solid substrate by the LB technique. Atomic force microscope (AFM) images of a one-layer 4OH-DDSQ film showed a homogenous uniform surface on a hydrophilic silicon substrate, whereas nanometer scale dots were formed on a hydrophobic silicon substrate. Multilayer deposition on a hydrophobic substrate resulted in an increase of dot size with increasing deposition number of layers. Moreover, homogenous multilayer films with a few voids were obtained on a hydrophilic substrate. The results indicate that 4OH-DDSQ is a good candidate for preparing hybrid nanoassemblies.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSSs) have attracted much interest because of their unique chemical structures and well-defined geometric shapes. POSSs consist of a rigid inorganic SiO core with organic coronae. The SiO core provides good thermal [1] and mechanical properties [2] as well as high optical transparency [3], which are important for applications in optics [4], catalysis [5] and electronics [6]. Organic coronae provide processability and compatibility with polymer materials, which are important for nanofillers [7,8]. The well-defined organic–inorganic architecture is suitable for creating hybrid nanostructure blocks. Controlling a structure in nanometer scale provides the highest homogeneity besides the highest reproducibility and predictability, and gives the best opportunity to tailor the properties of the materials [9]. In several reports, "bottom up" approach has already been applied to organization of POSSs at the nanometer scale [9–12]. For example, Cassagneau and Caruso [11] and Wu and Su [12] used a layer-by-layer assembly technique to prepare POSS nanocomposite thin films. Mehl and Saez [13] and Zhu and co-workers [14] attached liquid crystal mesogens to POSS and studied the self-assembled structure of the mesogen-substituted POSSs. Deng et al. used a trisilanol-POSS, a partial cage structure, to prepare a uniform Langmuir monolayer at the air–water interface. They carried out intensive study on the surface morphology and viscoelastic properties at the air–water interface of the trisilanol-POSS [15–19]. As far as we know, the trisilanol-POSS is the only monodisperse POSS material that can form a stable monolayer at the air–water interface. Unfortunately, transfer of a trisilanol-POSS monolayer onto a solid substrate to produce Langmuir–Blodgett (LB) film has not been achieved.

We have previously constructed polymer hybrid nano-sheets (LB film) containing POSS as a comonomer of an amphiphilic polymer [20]. Esker and co-workers [21] also reported polymer LB film using a telechelic polymer whose endgroups were POSS. Tsukruk and co-workers [22] prepared LB film of organic-functionalized core–shell silsesquioxane. Because these reported studies used POSS copolymers or mixed silsesquioxane as a core, they show molecular weight distribution. The main objective of the present study was to prepare LB film of POSS with a well-defined molecular structure that does not show molecular weight distribution. LB films enable molecular ordering in one, two and three dimensions, which are important for better understanding and design of POSSs as nanobuilding blocks [23].

In the present study, we prepared LB film based on monodisperse double-decker shaped polyhedral oligomeric silsesquioxanes (DDSQs) molecules. DDSQs are new members of the POSS family that can be used to prepare organic–inorganic hybrid materials

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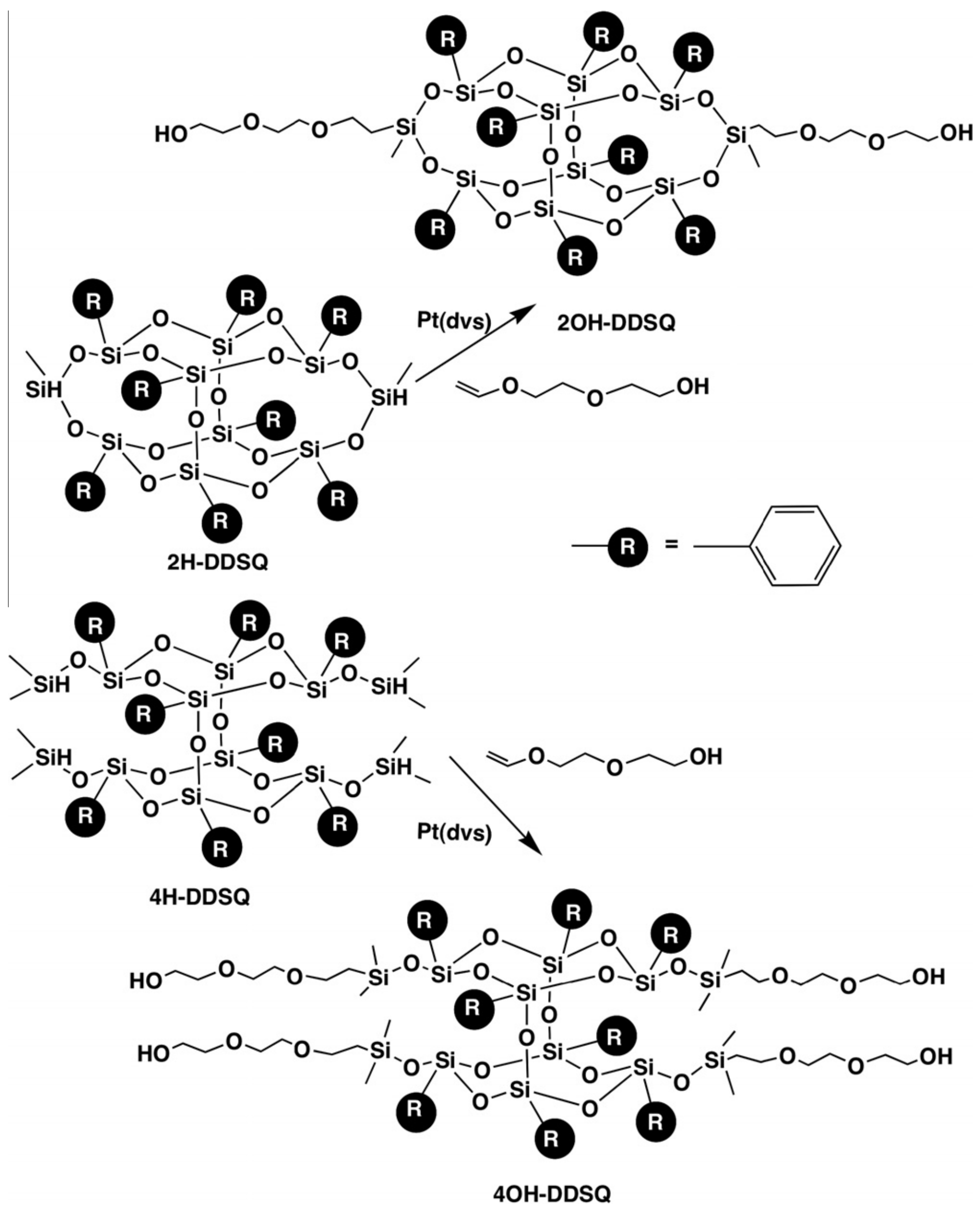
with several functions [24–27]. We synthesized amphiphilic DDSQs consisting of a DDSQ hydrophobic core and di(ethylene glycol) units as hydrophilic coronae. The DDSQs used in this study possessed precisely two or four reactive hydrosilane (SiH) groups. We attached hydrophilic di(ethylene glycol) units to the hydrosilane groups using a hydrosilylation reaction, to prepare amphiphilic DDSQs (Scheme 1). Because of the smaller number of reactive groups in DDSQs compared to the often-used octamer POSS $(RSiO_{1.5})_8$, which has eight reactive SiH groups, synthesis and purification of the amphiphilic DDSQ is simple. Moreover, the synthesized DDSQs are unique amphiphilic molecules in structure. Conventional amphiphiles take a "head-to-tail" structure, where polar hydrophilic group is a head and long hydrocarbon chain is a tail. On the other hand, the amphiphilic DDSQs take "core-coronae" structure, where DDSQ core is the hydrophobic and di(ethylene glycol) units is the hydrophilic part. Therefore, the present study proposes a new approach to form LB film using the core-coronae structure. The synthesized amphiphilic DDSQs were characterized by ^{1}H, ^{13}C and ^{29}Si NMR, FT-IR and MALDI-TOF mass spectrometry. Monolayer properties of amphiphilic DDSQs at the air–water interface were characterized by surface pressure (π)–area (A) isotherms and Brewster angle microscopy (BAM). The monolayer was transferred onto a solid substrate using a vertical dipping method. The surface morphology of the transferred film was characterized by AFM and UV–vis spectrophotometry.

2. Experimental section

2.1. Materials

Double-decker shaped oligomeric silsesquioxanes containing two SiH groups (2H-DDSQ) and four SiH groups (4H-DDSQ) were kindly donated by Chisso Corp. Anhydrous tetrahydrofuran (THF) and toluene were purchased from Aldrich and Nacalai Tesque, Inc., respectively, and were used without further purification. Platinum divinyltetramethyldisiloxane (Pt(dvs), 3 wt.% in xylene solution) was obtained from Umicore. Dichloromethane,



Scheme 1. Synthesis of amphiphilic DDSQs through direct hydrosilylation with di(ethylene glycol) vinyl ether.