Self-assembly of organic-inorganic hybrid nanolayers: effect of endgroup polarity on nanostructures

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1 Introduction

Molecular self-assembly (MSA) offers a convenient way to elaborate highly ordered and lightweight nanostructures with molecular-level control of material structure, composition, and dimensions. This sub-branch of supramolecular chemistry which focuses on the spontaneous and reversible construction of ordered aggregates through weak intermolecular interactions represents a facile route to produce organic-inorganic hybrid nanolayers with long-range ordering.

Over the past twenty years, many efforts have been devoted to the construction and structural optimization of well-ordered organic-inorganic nanolayers from monofunctional organosilane surfactants [1-3]. The organization process of such building blocks has been extensively investigated and is known to be governed mainly by the hydrophobic effect arising from a competition of attractive and repulsive interactions between inorganic polar heads, organic nonpolar tails, solvent and water molecules [4, 5]. Such interactions guide the nonpolar chains to aggregate and polar heads to maximize their exposure to the surrounding aqueous medium thus forming structures such as bilayers [6], micelles [7], or vesicles [8]. Finally, van der Waals forces appear between alkyl chains whereas hydrogen bonds and then stronger covalent bonds are formed between inorganic heads thus conferring thermal and mechanical stability to films [9, 10].

This study aims to investigate the effect on nanolayer structures of a second polar group located at the chain termination of alkylsilane building blocks. As intermolecular interactions which direct the assembly process are strongly dependent on the chemical composition of precursors, it is expected that the presence of a second polar endgroup will significantly affect these weak interactions thus leading to an alternative structure of nanolayers. Monofunctional hexadecyltrimethoxysilane (HDTMS) and bifunctional 11-bromoundecyltrimethoxysilane (BUDTMS) were used independently as building blocks to produce organic-inorganic nanolayers. Structures of these solid thin films were then sequentially characterized and compared after solution assembly and deposition on silicon substrates.

2 Experimental

2.1 Materials

Hexadecyltrimethoxysilane (technical, ≥ 85%) was purchased from Fluka. 11-bromoundecyltrimethoxysilane (≥ 95%) was purchased from Gelest. Hydrogen peroxide, 85%) was owned by the authors, published by EDP Sciences, 2013

http://dx.doi.org/10.1051/matecconf/20130301016

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2.3 Structural Characterization

X-ray scattering patterns were obtained either on a Bruker-AXS D8 Discover diffractometer or a Rigaku D/Max-B Geigerflex diffractometer. Both diffractometers use a Cu Ka (1.544 Å) radiation. Digital data were recorded from 2θ = 1°–16° at an angular resolution of 0.02° and angular velocity of 0.4° min⁻¹. Thin films were analyzed directly on their silicon substrates. A Dimension 3100 SPM atomic force microscope was used at room temperature to obtain topographic images of thin films. Images were recorded at a maximum resolution of 512 lines under a tapping mode. Molecular dynamics (MD) simulations were performed assuming a constant-pressure and constant-temperature (NPT) ensemble. The temperature is controlled at 300 K, and the external pressure is set at 1 atm. The consistent valence force field (CVFF) is selected to describe interactions among molecules.

3 Results

In our experimental protocol, molar ratios among components, solvent type, and precursor natures were chosen to form multilayer films with a lamellar structure where each lamella (referred to as nanolayers thereafter) is composed of tightly packed molecules oriented along the substrate normal [1, 9].

A d-spacing of 1.7 nm being very close to the length of a BUDTMS molecule, the peak at 2θ = 5.9° may correspond to a monolayer-on-monolayer packing where molecules are stacked on top of each other and oriented in the same direction. An interdigitated organization of molecules also fits a d-spacing value of 1.7 nm. In this lamellar packing mode, alkyl chains of adjacent molecules are alternately pointing up and down [3,9]. Finally, this high intensity peak may also originate from BUDTMS bilayers in which bromine atoms strongly diffract X-rays.

Molecular dynamic (MD) simulations were then conducted to determine which molecular packing is the most thermodynamically stable. As depicted in Table 1, examination of these molecular organizations reveals that the bilayered packing mode exhibits the lowest binding energy value suggesting this configuration as the most energetically favorable.
Table 1. Calculated average binding energies and layer thicknesses of BUDTMS packing modes examined by MD simulations.

<table>
<thead>
<tr>
<th>Packing Mode</th>
<th>Binding energy (kcal/mol)</th>
<th>Layer thickness (nm)</th>
</tr>
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<tbody>
<tr>
<td>Monolayer-on-monolayer</td>
<td>-31.8</td>
<td>1.63</td>
</tr>
<tr>
<td>Interdigitated Layer</td>
<td>-28.2</td>
<td>2.03</td>
</tr>
<tr>
<td>Bilayer</td>
<td>-34.9</td>
<td>3.22</td>
</tr>
</tbody>
</table>

The bilayered conformation of BUDTMS molecules in self-assembled films was further confirmed by analyzing the film topography by atomic force microscopy (AFM). As shown in Figure 3, self-assembled BUDTMS films are composed of a stacking of nanolayers (top image). Examining the height profile of these layers (bottom profile) confirm that the height of each nanolayer is ~ 3.7 nm which is in good agreement with XRD and MD simulation results that suggest a bilayered structure of layers.

4 Discussion

Experimental and simulation results suggest that our experimental protocol leads both HDTMS and BUDTMS molecules to self-assemble into a bilayered conformation even though their XRD patterns differ. Likely, this dissimilarity is due to the chemical composition of building block endgroups. Indeed, the limited number of electrons in the methyl termination of HDTMS may prevent endgroups to diffract X-rays making them invisible to XRD. In contrast, within a BUDTMS bilayer, bromine atoms form a high electron density plane in the middle of each nanolayer. The elevated number of electrons within the plane makes it visible to XRD by diffracting X-rays. As a result, BUDTMS bilayers contain two diffraction planes (i.e. the inorganic siloxane network and the plane constituted by the bromine terminations of building blocks) whereas HDTMS bilayers contain only one diffraction plane (i.e. the inorganic siloxane network). Therefore, BUDTMS bilayers are characterized by two set of diffraction peaks (d-spacing = 3.4 and 1.7 nm), while HDTMS bilayers are characterized by a unique set of diffraction peaks (d-spacing = 4.2 nm).

5 Conclusion

The effect of endgroup polarity on the nanolayer structure of self-assembled alkylsilane thin films was investigated by experimental and simulation techniques. results indicate that the weak dipole moment induced by the bromine atom at the endgroup of budtms has no remarkable effect on the self-assembly process and final nanostructure of films. indeed, both methyl-terminated hdtms and bromine-terminated budtms were found to form a lamellar structure where each lamella is composed of molecules arranged in a bilayered conformation.

Although the formation of bilayered nanolayers from monofunctional alkylsilane molecules has been extensively studied already, the ability to form such structures from bifunctional precursors is much less known. therefore, it is expected that this finding could open up a new range of potential applications of alkylsilane nanolayers by enlarging the number of precursor candidates to more complex bifunctional molecules.

References