

Thermal stability of self-assembled surfaces and micropatterns made of ladder polysilsesquioxanes



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ABSTRACT

Self-assembled films made of ladder [2-(carboxymethylthio)ethyl]-polysilsesquioxanes adsorbed on mica are stable within a wide temperature range (293–373 K). A thermally induced transformation, resulting in a significant decrease of free surface energy but not in a collapse of macromolecules in the adsorbed film was observed only at 393 K. The unique behaviour has been ascribed to a specific rearrangement of hydrogen bonds between COOH groups. It is irreversible under ambient conditions, but the structural features and properties of the self-assembled film can be reverted to the primary state if the sample is kept in humid atmosphere (steam). Wetting angle measurements as well as microscopic (AFM) and spectroscopic (ATR FTIR, ARXPS) studies were carried out to evaluate changes in the surface morphology and its physiochemical properties. The studied [2-(carboxymethylthio)ethyl]-polysilsesquioxanes were also used as a printing ink on native mica. The micropatterns exhibited all the characteristic properties of the self-assembled films, which can be exploited for the formation of precisely localized surface textures of specific chemical composition and specific free surface energy.

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1. Introduction

Polymer brushes chemically tethered to solid supports provide a highly interesting alternative to self-assembled monolayers of small molecules (SAMs) due to the intrinsically large size of the building blocks and entropic contribution to the film morphology. Covering planar substrates with stimuli-responsive polymers is an attractive route for the preparation of “smart” surfaces with controlled wettability that can be used as chemical and optical sensors, nanoactuators and biomaterials [1–10]. Responsive properties of smart surfaces can be controlled by phase transition mechanisms induced reversibly by external stimuli including e.g. light irradiation, electrical potential, temperature, pH or interactions with selected liquids and solids [1,11–15] or their combinations [12,16–18]. Most of these changes are entropy-driven but enthalpy-controlled switchable bio-surfaces have been prepared as well [19].

The change of properties in stimuli-responsive surface-grafted polymers (especially those temperature, pH or solvent induced) almost always involves chain shape transformation from “brush-

like” to collapsed coil (“mushroom”) structure [2,20–22]. The effect depends on molecular weight of polymer chains and their grafting density [23] as well as the type of bonding with the support (covalent grafting vs physiochemical interactions). Covalent bonds anchor macromolecules and prevent their diffusion on the surface. For example, well defined and stable polymer brushes can be prepared on activated mica substrate by direct grafting of poly(-sodium acrylate) [24] and poly(*tert*-butyl acrylate) [25]. On the other hand deposition of poly(isoprene-*b*-ethylene oxide) on freshly cleaved mica by physical adsorption resulted in ultraflat nanoislands of well-defined monomolecular thickness that evolved rapidly into surface micelles [26]. A similar micellar structure was reported for pH responsive poly[2-(dimethylamino)ethyl methacrylate]-*b*-poly[2-(diethylamino)ethyl methacrylate] adsorbed on mica [27].

We have recently reported formation of superhydrophilic and reactive surfaces by adsorption and self-assembly of linear polysilsesquioxanes functionalized with side 2-(carboxymethylthio) ethyl groups (LPSQ-COOH) on native mica [28]. The specific structure of LPSQ-COOH (rigid double-chain backbone surrounded by reactive carboxylic groups) makes the polymer suitable for planar adsorption on reactive surfaces and determines the arrangement of layered assemblies. Flexibility of the double-strand siloxane backbone in LPSQ is smaller than that of their linear single-chain

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analogues. Devitrification of LPSQ-COOH and its precursor LPSQ-Vi occurs, respectively at 234 K and 230 K [28,29]. It suggests that both polymers have almost the same degree of rotational freedom. It facilitates self-assembling and adjustment of the adsorbed species for the formation of well-organized nanolayers of LPSQ-COOH at the solid/liquid interface. The multipoint substrate-adsorbate and adsorbate–adsorbate interactions are based on the formation of surface salts between COOH groups and K^+ ions that belong to the mica substrate [28]. Potassium ions bind electrostatically the alternating aluminosilicate sheets in mica, which can be exfoliated along the plane located in the K^+ layer. The oligomers of LPSQ-COOH are immobilized unilaterally, with their siloxane backbone parallel to the surface. The specific arrangement of poly(silsesquioxane) chains results in exceptionally high free surface energy of the adsorbed film.

Such hydrophilic surfaces and interfaces attract growing attention due to their specific surface energy and antifouling properties [30,31]. It was of interest to study their stability and sensitivity to external stimuli. In this paper we present a detailed analysis on thermal stability of the structure and properties of LPSQ-COOH adsorbed and self-assembled on mica support. Wetting angle measurements, Atomic Force Microscopy (AFM), Attenuated Total Reflectance Fourier-Transform Infra-Red Spectroscopy (ATR FTIR) and Angle-resolved X-ray Photoelectron Spectroscopy (ARXPS) were applied for the studies. It was found that the structure of the adsorbed film of LPSQ-COOH and its characteristic high surface energy (γ_s) endure for a long time and within a wide temperature range (293–373 K). However, a drastic decrease of wettability was observed at $T = 393$ K due to a very specific thermal rearrangement of hydrogen bonds between COOH groups (Scheme 1). The rearrangement is durable at ambient conditions, but can be reversed by exposing the sample to gas phase boiling water (steam), which led to restoration of the original structure of LPSQ-COOH coating and its hydrophilicity. Quite uniquely, thickness of the adsorbed coating did not change throughout all the temperature cycle. The observed increase of surface energy does not involve collapse of macromolecules typically observed for thermoresponsive polymers. Such behaviour is quite unique and was not observed for polysilsesquioxane hybrids with thermosensitive side groups (derivatives of N-isopropylacrylamide and N,N-dimethylacrylamide) [32–39].

LPSQ-COOH can be also used for printing well-defined micropatterns on mica. The produced designs show all the characteristic properties of the adsorbed LPSQ-COOH films, including the thermally induced surface energy change. Such a precise surface

patterning with smart hydrophilic/hydrophobic materials can be applied in microfluidics, biotechnology and for the preparation of water-harvesting, non-biofouling coatings or photonic structures.

2. Experimental

2.1. Materials

Ladder [2-(carboxymethylthio)ethyl]polysilsesquioxanes (LPSQ-COOH) terminated with trimethylsilyl groups were obtained as previously described [28]. Solvents [tetrahydrofuran (THF) (Chempur, analytical grade) and methanol (Chempur, analytical grade)] were purified according to the literature procedures [40]. Rectangular tiles of muscovite mica (V-1 grade, SPI Supplies/Structure Probe, Inc.) were freshly cleaved before use by removing the top layer with an adhesive tape. Microcapillaries with $1 \mu\text{m} \pm 10\%$ tip were made of borosilicate glass tubes (O.D.: 1.0 mm, I.D. 0.50 mm, 10 cm length; Intracel, UK) using a P-97 Flaming/Brown Micropipette Puller (Sutter Instruments).

2.2. Experimental procedures

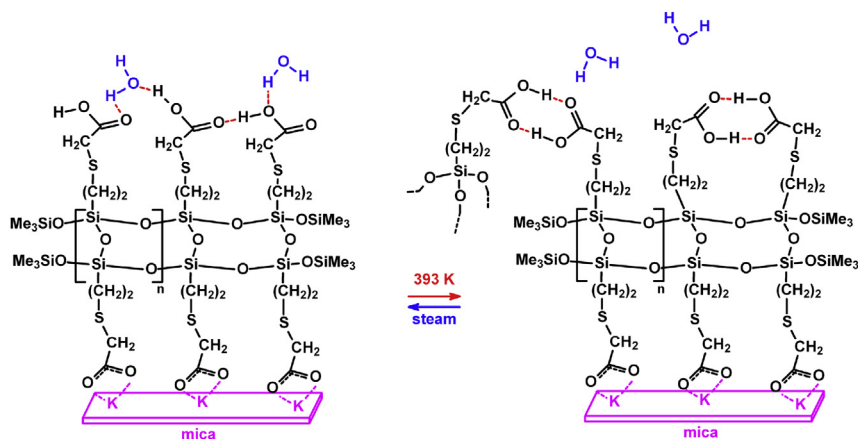
2.2.1. Preparation of thin films of polymeric linear silsesquioxanes on mica

LPSQ-COOH were dissolved in pure THF at 0.05%wt concentration. The solutions were filtered through a $0.2 \mu\text{m}$ PTFE filter. Dip coating was carried out at room temperature by immersion of a freshly cleaved muscovite mica support in the polymer solution for 15 min. Supports were moved vertically (immersion/extraction rate: 4 mm/s) with a motorized linear slide (Zaber Technologies Inc.), then placed in a closed container and left for drying at room temperature for one day.

Samples used for thermal ageing studies were placed on a heating plate under a glass cover and heated in air at selected temperatures (311 K, 333 K, 373 K, 393 K) for a given time (Fig. 1). In order to recover the original hydrophilicity after the thermal treatment, the samples heated at 393 K were placed in a closed chamber containing a cup with boiling water. They were kept in the chamber for 7 h (near 100% relative humidity, boiling water was left to cool down slowly to room temperature, samples were shielded against incidental direct contact with condensed H_2O) then the samples were left to dry at room temperature for 4 days.

2.2.2. Surface micropatterning

Patterned samples were prepared using a micropipette filled



Scheme 1. Thermally induced structural rearrangement in LPSQ-COOH adsorbed on mica.

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