

## Mixed Self-Assembled Layers of Phosphonic Acids.

Prado, M. C<sup>1,\*</sup>; Neves, B. R. A<sup>2</sup>.

<sup>1</sup> Department of Physics – Federal University of Minas Gerais, Brasil [\\_mariana@fisica.ufmg.br](mailto:_mariana@fisica.ufmg.br)

<sup>2</sup> Department of Physics – Federal University of Minas Gerais, Brasil [\\_bernardo@fisica.ufmg.br](mailto:_bernardo@fisica.ufmg.br)

Self-assembled monolayers (SAMs) of organic amphiphilic molecules on solid surfaces [1] have been extensively studied because of their technological (adhesion promoters, lubricants, nanolithography resists, surface functionalization methods) and biological applications (biomaterials, biosensors, molecular electronics). Furthermore, self-assembled bilayers (SABs) have been investigated as a model for biological membranes. SAMs and SABs of mixed molecules with different tail groups, chain length or lateral chain have an important role due to their enhanced control on surface properties. Most studied systems in this area are thiols on gold [1-2], and silanes [4] on mica and silicon. It has been shown that mixed monolayers of molecules with different chain lengths have a tendency to exhibit phase separation when the difference in the number of carbons in the chain is 4 or more [5-6] and no special care is taken prior to the deposition of the SAM [2]. This may be an advantage or a problem, so, it is necessary to study and control carefully the SAMs characteristics.

While SAMs and SABs of phosphonic acids [7-8] have been widely investigated, to the best of our knowledge, mixed self-assembled structures of these molecules have not been reported. We address here the mixed self-assembled structures formed by different mixtures of octadecylphosphonic acid (OPA, 18 carbons in the alkyl chain) and octylphosphonic acid (OcPA, 8 carbons in the alkyl chain). It has been established that an OPA SAM can be deposited on mica by immersion, spread coating and spin coating methods [8]. On the other hand, OcPA forms only SABs and multilayer aggregates [7], regardless the deposition method and substrate.

Sample characterization was performed using atomic force microscopy (AFM). Phase contrast images were useful to obtain information on layer polarity. Contact mode images of topography and friction were used to investigate possible phase separation and perform resistance tests.

Interesting features were found for samples from different OPA:OcPA ratios 2,4mM solutions on tetrahydrofuran (THF). The two most striking ones were: 1) the formation of a SAM with no detectable phase separation for up to 5:10 (OPA:OcPA) ratio, even though the molecules differ by 10 carbons in the alkyl chain length and; 2) the time evolution of both samples and solutions of higher OcPA ratios. It was found that solutions prepared with new OcPA powders, inside a glovebox with positive pressure N<sub>2</sub> atmosphere and 0% relative humidity produce mixed samples without phase separation. Without this precaution, 5:10 solutions produced samples with multilayer aggregates, most similar to those produced by pure OcPA solutions, only with more layers. Those samples, if kept on lab atmosphere, exhibited formation of rod-like structures and long branches of layers, all oriented in angles of 60° (or 120°), suggesting commensurability with the mica surface (see fig 1). It was verified that the behavior of the pure-OcPA samples was very similar to that observed on the mixture.

In order to further clarify the time evolution process, samples of pure OcPA and 5:10 mixture were prepared and kept on a desiccator. It was found that these samples do not exhibit modifications (or only very slight ones) for the three-week period they were followed, while control samples stored on normal atmosphere formed rod-like and branch structures. Finally, water was added to a new solution of 5:10 mixture prepared inside a glovebox. It was seen that this procedure produced the same kind of samples obtained using solutions prepared in normal atmosphere with old OcPA powder. Thus, it seems very clear that water molecules are responsible for the time evolution of samples and solutions (see fig 2).

Additionally, thermal and mechanical resistance tests were performed on mixed and pure OPA SAMs, revealing distinct behaviors that further support the finding of mixed homogeneous SAMs. Mixed 10:7 SAMs were permanently deformed when imaged with contact mode AFM using high cantilever deflection, while pure OPA SAMs recover the original height after the load is removed. In situ annealing studies showed that 10:10 mixed samples behave similarly to OPA SAMs. They are stable up to 80°C, but the mixed layer seems to lose material, with the formation of very small holes within the SAM. 5:10 mixed samples, when annealed, present modifications on layer stacking.

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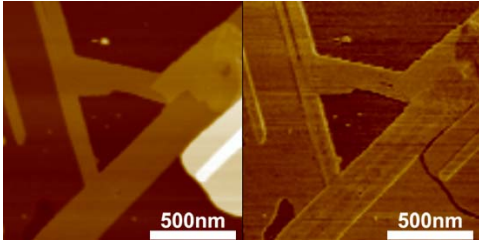


Figure 1 – AFM topography and phase contrast images of 5:10 OPA:OcPA mixture, showing branches and multilayers.

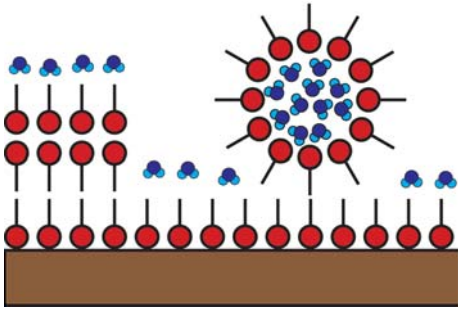


Figure 2 – Schematic illustration of the formation of rod-like structures promoted by water.