

POLYELECTROLYTE NANORING STRUCTURES: CRITICAL PARAMETERS GOVERNING FORMATION AND STRUCTURAL ANALYSIS.

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Abstract- Recently we have presented new polyelectrolyte nanoring structures formed by self-assembly of poly(ethylenimine) and poly(sodium 4-styrenesulfonate) during sequential adsorption observed by AFM microscope in liquid cell technique¹. In this work, filter pore size and carbonate ion concentration are identified as critical parameters for their formation. We show how these two parameters modulate the nanorings formation as a consequence of the hydrophobic polyelectrolyte domains formed into the polyelectrolyte solutions and the screening effect produced by the divalent carbonate ions present also in solutions. Also, we propose a simple model for nanoring formation; this simple model explains some uncompleted and overlapped nano-rings.

Introduction

Self-assembled polyelectrolyte films on surfaces have attracted much attention during the last decade for their potential in technological and biological applications.² Their buildup is based on first principles: dissociation of polyelectrolytes in aqueous solution releases counterions leaving ionized groups along the polymer chain.³ These polyelectrolytes are then adsorbed onto a charged surface producing a charge inversion on the surface that promotes the adsorption of a second charged polyelectrolyte of opposite electrical charge.⁴ Alternating adsorption of anionic and cationic polyelectrolytes produces multilayer films having a fine control on the film architecture and thickness.⁵ Surface structure of the polyelectrolyte film is an important property for any application and evidently depends on factors as the polyelectrolyte hydrophobic nature, substrate charge density, pH and ionic strength, etc. In the past, Scanning Electron Microscopy (SEM)⁶ and Atomic Force Microscopy (AFM)⁷ have been used to observe film surface structure. However, pre-treatment of samples prior observation limits these techniques. Alternatively, Liquid-cell AFM was recently proposed as an *in situ* technique to monitor the surface during the self-assembly of the film to avoid preparation artifacts.⁸ This technique has revealed the presence of nanoring like structures in the surface after successive adsorption of poly(ethylenimine) and poly(sodium 4-styrenesulfonate) polyelectrolytes.¹ At present, many questions are open in the understanding of the nanoring structure observed by liquid cell AFM. This work is addressed to investigate the effect of filter pore size and carbonate ions concentration on the nanoring structure.

Experimental section:

Polyelectrolytes and Buffer Solution Preparation: Polyelectrolyte solutions are prepared using Poly(ethylenimine) (PEI) ($M_w \approx 7 \times 10^4$ Da) and poly(sodium 4-styrenesulfonate) (PSS) ($M_w \approx 7 \times 10^4$ Da both from Sigma, France) at 1 mg/ml in concentration. Tris(hydroxymethyl) aminomethane (TRIS) 25mM, 2-(N-morpholino)ethanesulfonic (MES) 25mM and NaCl 100 mM, (all from Sigma), were used to prepare the buffer solution. All solutions were prepared with degassing ultrapure water (Mill Q-Plus system, Millipore) with resistivity of 18.2 MΩcm. Polyelectrolyte solutions were filtered with 0.10, 0.22 or 0.45 pore size filters (Millex PVDF, Millipore, USA) prior to injection to liquid cell AFM.

Nanoring formation: A liquid cell is used to obtain *in situ* contact mode images AFM (Nanoscope IIIa Digital Instruments Santa Barbara, CA, USA). Cantilevers with a spring constant of 0.03 N/m (MLCT-AUHW, Park Scientific, USA) were used, following tips silanization with octadecyltrichlorosilane (OTS, 95%, Aldrich, USA) in order to turn them hydrophobic tips. The glass slides are mounted on AFM piezoelectric, following the cell is closed with a silicone o-ring (Digital Instruments, CA, USA). Nanorings are prepared and imaged as follow: buffer is injected into the AFM liquid-cell and an image of the glass

surface is taken as reference. PEI solution is injected and let in contact with the substrate for 15 min, rinsed with 5 ml of buffer and the PEI film surface is finally imaged. PSS deposition and imaging follow a similar procedure that of for PEI. Polyelectrolyte solutions were filtered with 0.10, 0.22 and 0.45 μm filter pore size and exposure times to air were of 3, 12 and 24 hours. Height and friction images are captured simultaneously, only the height images are reported. Images are taken at 1 Hz scan rate with a resolution of 512 x 512 pixels. At 5 and 10 μm^2 scanning were taken.

Results and Discussion

In Figure 1, we observe different nanoring sizes depending on the exposure time to air with a fixed filter pore size of 0.22 μm , while in Figure 2 nanoring sizes is depending of filter pore size with a fix exposure time to air of 3 h. this is directly related to the carbonate ions concentration. From these images, we can observe that the nanoring distribution is homogenous on the surface and the nanoring size is nearly constant in each case.

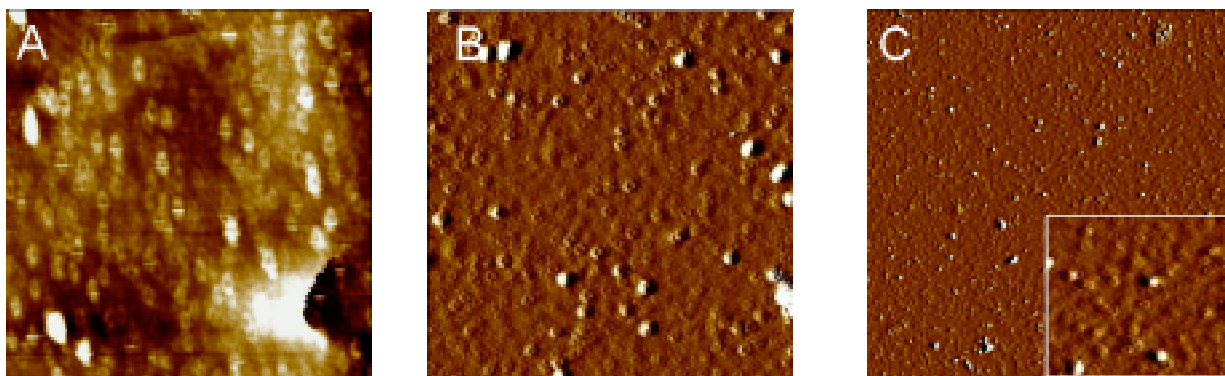


Figure 1. Nanoring obtained with polyelectrolyte solutions filtered with a 0.22 μm filter and different exposure times to air. A) nanorings obtained after 24 h with an external diameter (D) of 420 ± 22 nm. B) after 12 h; $D = 309 \pm 27$ nm. C) after 3 h; $D = 187 \pm 8$ nm. Scan size for all images is 10×10 μm , a zoom of 5×5 μm is also shown in Fig. 1C.

Using filter pore size of 0.22 μm , after 24, 12 and 3 hours we obtain nanorings of 420 ± 22 nm, 309 ± 27 nm and 187 ± 8 nm in external diameter. Equivalently, large pore filters of 0.45 μm produce nanorings with an average diameter of 731 ± 50 nm, nanorings are bigger than those formed with filter of 0.2 μm giving 413 ± 27 nm and 0.1 μm giving 213 ± 32 nm. In all the experiments the nanoring external diameter dispersion is less than 18% indicating a relative narrow nanoring distribution.

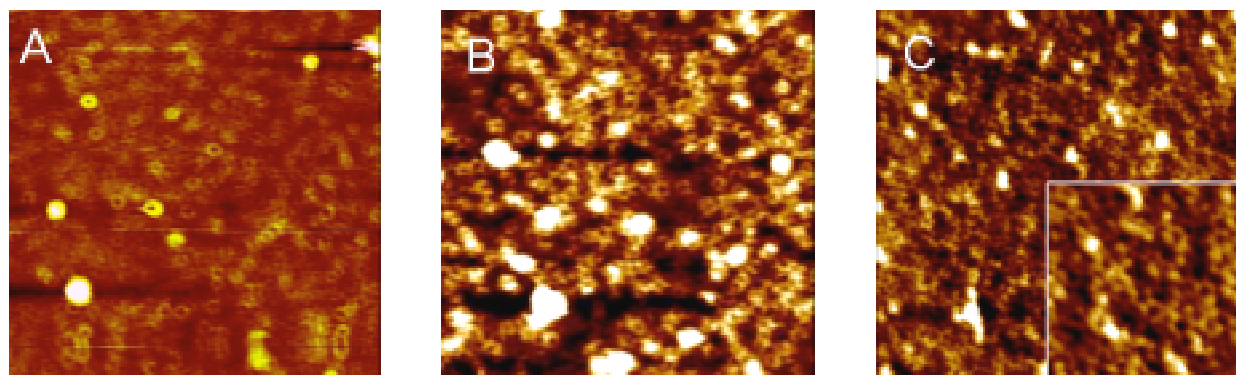


Figure 2. Nanoring obtained with filtered polyelectrolyte solutions at an exposure time of 3 hours: A) filter of 0.45 μm in pore size gives nanorings of 731 ± 50 nm in external diameter, B) filter of 0.22 μm gives $D = 413 \pm 27$ nm and C) filter of 0.10 μm gives $D = 213 \pm 32$ nm. Scan size for all images is 10×10 μm , a zoom of 5×5 μm is also shown in Fig. 2C.

When the images were analyzed by number of nanorings per surface we also find that the number of nanorings per surface unit is strongly dependent on size. While the external diameter of the rings increases, the nanorings number per surface decreases. Additionally, the mean surface coverage is approximately to $18 \pm 11 \%$ for all the nanorings reported here. In spite of this broad distribution, the surface coverage is far away of the maximum surface coverage obtained for a random sequential adsorption (RSA) process that gives a value equal to 54.7% .⁹ This indicates again the important role of electrostatic interactions in the processes of nanorings formation.

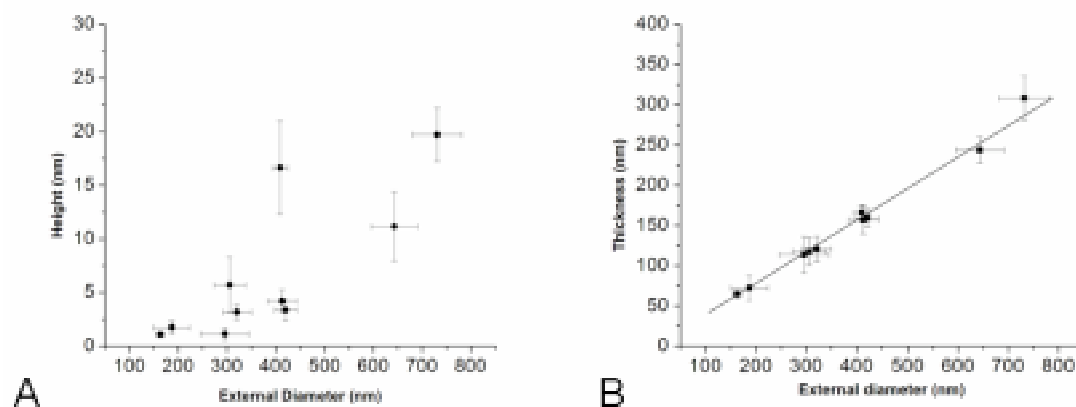


Figure 3 A) Screening effect is correlated between height and nanoring external diameter B) Linear behavior between thickness and external diameter for the nanorings. This indicates uniform nanoring growth that justifies a constant value for the ratio between external and internal nanoring diameter of $23 \pm 5 \%$.

An analysis of nanorings dimensions gives us additional information. The height and thickness, defined as $\frac{1}{2}(D-d)$, of the nanorings with the external diameter are shown in Figure 3A and 3B, respectively, where the external diameter of nanorings is ranging from 180 to 730 nm and height is always of few nanometers (2 to 20 nm). It is very remarkable the linear dependence between the thickness and the external diameter indicates a uniform nanoring growth. Statistical analysis of these results shows that the ratio between external and internal nanoring diameter, for all experiments is roughly constant. Internal diameter represents $23 \pm 5 \%$ of the external diameter in all the cases. This confirms that the structures are growing in a homogenous way and this behavior is independent of the external conditions during nanoring formation.

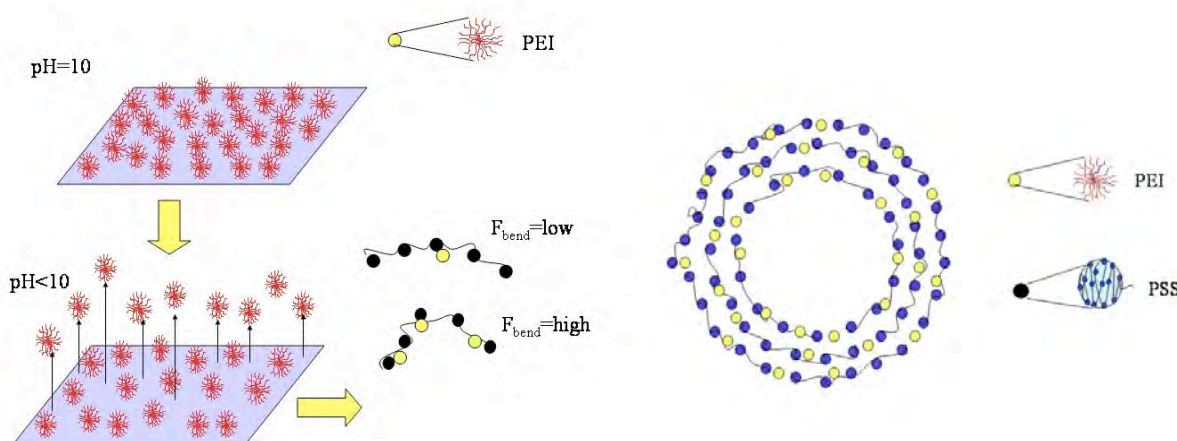


Figure 4 The simple mechanism of nanoring formation is showed; the PEI conformation is highly branched in this case red balls represent the PEI molecules. The PSS conformation is a pearl necklace and in this case the blue balls represent a pearl formed by several monomers of PSS. The final conformation of two polyelectrolytes is like a ring.

A simple model of nano-ring formation is proposed here. It is based on pH change during the adsorption sequence of PEI and PSS. In solution PEI and PSS have a pH 10 and 6 respectively, this indicate that PEI is weak (only the primary groups are charged) and PSS is strong charged. Therefore when we deposited the PEI on the surface, the PEI chains are weakly attached to the surface because the interaction among molecules is weak. When PSS is injected there is a pH change in solution, this pH change produces that some PEI chains are released to the bulk because the volume interaction among PEI molecules is stronger. Therefore PEI-PSS complex are formed. These PEI molecules modify the original PSS curvature. A varieties of curvatures are formed in the PEI-PSS complex, These curvatures depend on the number of PEI molecules. The PEI-PSS complexes produce different curvatures which are reflected in the nano-rings thickness. Therefore, Nano-ring formation involves two effects: the bending by PEI molecules and the semicircular conformation of PSS. A schematic representation of this model is show in figure 4. These bending may be the origin of the nano-ring formation.

Under this model the carbonate ions decreases the pH of the solutions, so at high carbonate ions concentration a low pH is found and then they produce large nano-rings.

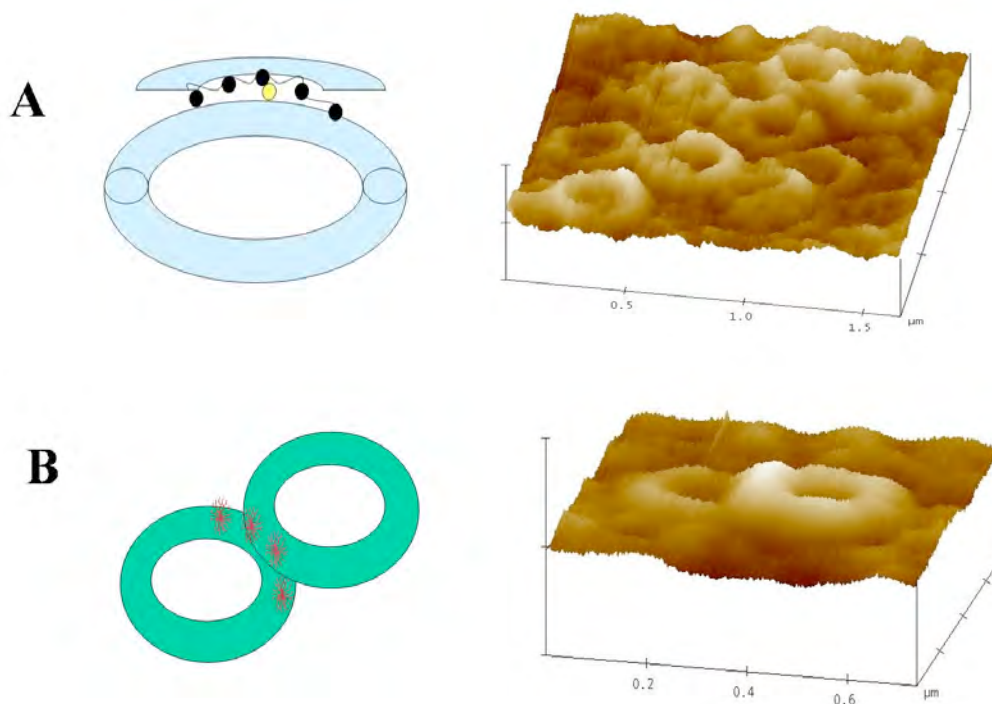


Figure 5 In some cases we observed uncompleted (A) and overlapped (B) structures, this is due to the role of PEI of glue between these structures, this experimental observation are in agreement with the model proposed here.

The images showed in the figure 5 can be explained by this simple model, in this figure we observe some uncompleted and overlapped nanorings. These structures are formed for several PSS chains and these chains are put together by PEI molecules. This is possible because the branched PEI molecules are playing the role of glue between structures.

Conclusions:

We show that the formations of nanoring structures are governed by two critical parameters: filter pore size and carbonate ions concentration in the polyelectrolyte solutions. The filtering of PSS forms a homogenous size of polyelectrolyte domains in solution and they are also present in the structure of the

nanorings. Also we propose simple model for the nano-ring formation, this model is based on the pH change in the solution when PSS polyelectrolyte is injected after the adsorption of PEI molecules and on the conformational changes of the PSS chain produced during the adsorption processes. Additional experimental and theoretical work is necessary to prove nanorings formation and to be better the model. Applications as protein immobilization or nanopatterning can be also envisaged for this novel structure. The experimental results presented in this work can be useful for these purposes.

Acknowledgements. This work was partially supported Mexico-France Program: SEP-CONACYT-ANUIES-ECOS France (M01-S01) and “Inmovilización de proteínas sobre superficies biocompatibles” PROMEP/103.5/04/2278, J.L.M. and F.T. thank Conacyt.

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