

Nanostructured films of novel azocompounds

Y. A. Valdez-Hernández*, E. Rivera**, M. P. Carreón-Castro*

* Instituto de Ciencias Nucleares, UNAM, México, yvaldez@nucleares.unam.mx

**Instituto de Investigaciones en Materiales, UNAM, México, riverage@iim.unam.mx

*Instituto de Ciencias Nucleares, UNAM, México, pilar@nucleares.unam.mx

ABSTRACT

The formation of Langmuir and Langmuir-Blodgett films from azocompounds like the azopolymers used in this work, that have different length of chains of ethylene glycol shows that these azocompounds are suitable to form thin films by the Langmuir-Blodgett technique, their spectroscopic and morphologic characterization confirm that the monolayer formation is stable and homogeneous in the interface air/water according to the images obtained by Brewster's angle microscopy (BAM) and their transference onto solid substrates shows a linear increase multilayer according to the UV-Visible spectra, that indicates homogeneity.

Keywords: Langmuir films, Langmuir-Blodgett films, azocompounds, azopolymers, Brewster microscopy.

1. INTRODUCTION

Actually many applications have been developed for azobenzenes exploring their important properties of photoisomerization and photonic, now their incorporation in polymers to form azopolymers is also very interesting, according to increase the potential optoelectronic and photonic applications [1, 2, 3, 4]. For study the applications the azopolymers are used in the solid state usually forming thin films built by casting or spin-coating methods. Techniques that allow control at the molecular level, such as the Langmuir-Blodgett (LB) and the Layer by Layer (LbL) methods, may lead to obtain nanostructured films with controllable thickness and architecture [5]. In the LB method, an insoluble layer of the material of interest is spread on an aqueous subphase and is compressed by constant speed, after the solid order (2-D) is obtained the layer is transferred onto a solid substrate by dipping, this substrate across the film with a constant speed. Repeated dipping on the same substrate leads to fabricate multilayers [6].

The study of the monolayer in the interface air/water is interesting too, and let us monitor the formation of the monolayer with a Brewster's Angle Microscope (BAM) that shows the behavior of the layer and all the phase transitions during the compression are observed.

2. EXPERIMENTAL

The synthesis and characterization of series *pnPEGMAN* ($n= 2, 3, 4,$ and 6) were described in reference [6]. The general structure is shown in Fig. 1

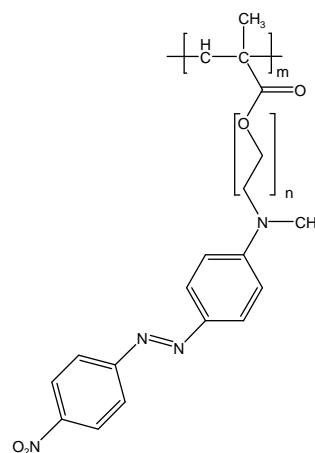


Figure 1: General structure of the azopolymers

Monolayer experiments and LB deposition were carried out at a subphase temperature of 22°C with KSV-5000 system 3 by Ltd Instruments. Ultra pure water supplied by a Milli-D coupled to a Milli-Q 185 purification system was used to prepare subphase.

Monolayers were obtained by spreading a solution of the azopolymer with a standard concentration of $1\text{mg}\cdot\text{mL}^{-1}$ in chloroform (spectra grade, Aldrich) on a ultra pure water surface. During the isotherm experiments, monolayers were compressed at a barrier speed of $10\text{mm}\cdot\text{min}^{-1}$. For the deposition onto substrates glass slides (Corning) were used pre-cleaned using sulfochromic mixture. The LB films were Z type in all cases.

UV-Visible measurements of LB films were obtained with a Varian CaryWin 100 spectrophotometer.

BAM images were obtained during compression monolayer in NIMA 622D2 through coupled to a miniBAM plus of Nanofilm Technology GmbH.

3. RESULTS

3.1 Langmuir monolayers formation and characterization

The surface pressure-area (Π -A) isotherms of the azocompounds are shown in Fig. 2.

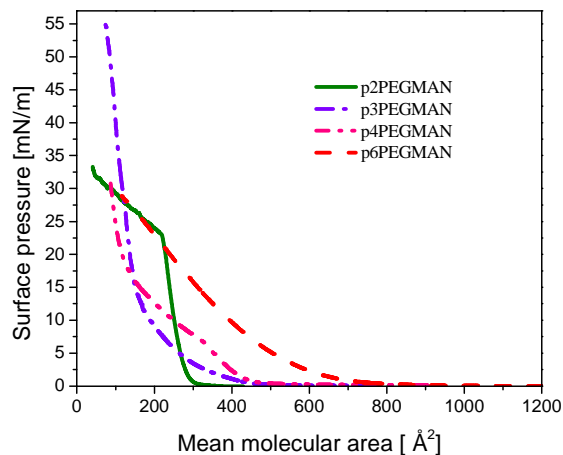


Figure 2: Surface pressure-mean molecular area isotherms of pn PEGMAN.

All the surface pressure-area isotherms are characterized by an initial long plateau region with a slow rise in different mean molecular areas, according to the size of the azopolymer, we observe a major area for azopolymer with ethylene glycol chain of 6, and the minor area is for the azopolymer with the ethylene glycol chain of 2.

For p6PEGMAN the slow rise begins at a mean molecular area about 680 \AA^2 followed by a step rise in surface pressure with a limiting mean molecular area of about 520 \AA^2 . The extrapolation through the x axis of the portion of the curves corresponding at the solid state, around $15 \text{ mN}\cdot\text{m}^{-1}$ yields an average surface area per molecule of 520 \AA^2 for p6PEGMAN 380 \AA^2 for p4PEGMAN, 180 \AA^2 for p3PEGMAN and 340 \AA^2 for p2PEGMAN. The low value for p3PEGMAN may be attributed to the formation of aggregate for the asymmetric length of the chain of ethylene glycol. The Langmuir films exhibited an excellent stability during the compression, we prove the reversibility of the monolayers under compression and decompression until surface pressure $15 \text{ mN}\cdot\text{m}^{-1}$ and all the Langmuir films are stable and reversible.

The topography of the Langmuir films were obtained by BAM imaging at different surface pressures, where the film topography during the compression of a pn PEGMAN show a stable monolayer in all the cases.

The p2PEGMAN monolayer is illustrated in Fig. 3; We can see a high order of pre-compression in the film according to the figure 3-a where the surface pressure is $0.2 \text{ mN}\cdot\text{m}^{-1}$ the domains in Fig. 3-b were observed at $4 \text{ mN}\cdot\text{m}^{-1}$ and 290 \AA^2 when the compression has been started, with compression the domains were integrated to the film forming a stable and homogeneous monolayer until surface pressure at $33 \text{ mN}\cdot\text{m}^{-1}$; after the mechanical collapse we observe fractures in the monolayer in the Fig. 3-f and the domains start again.

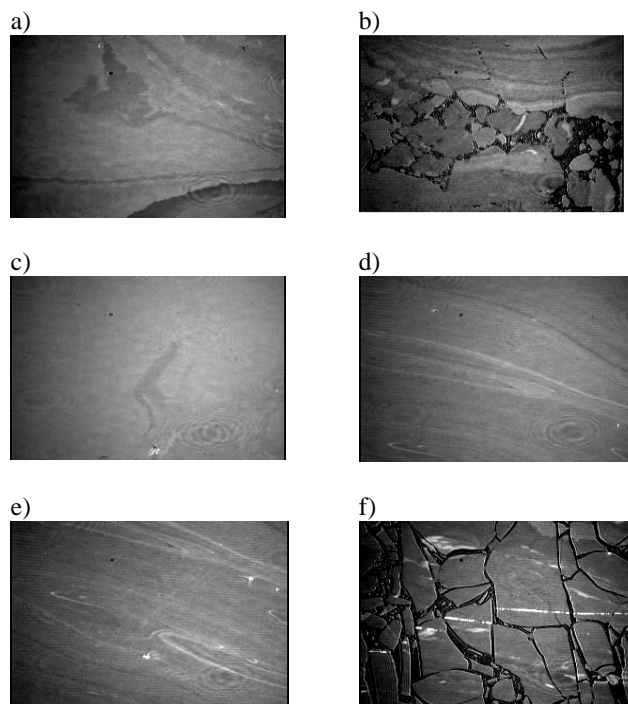


Figure 3: BAM images for p2PEGMAN at a) 0 mN/m , b) 4 mN/m , c) 22 mN/m , d) 28 mN/m , f) during decompression, collapse induced.

3.2 Langmuir-Blodgett films fabrication and characterization.

Langmuir films were transferred by using LB technique onto glass slides in all the cases; the transfer ratio is 1 ± 0.1 .

The LB films were examined by the UV-Visible spectroscopy; absorption spectra of p6PEGMAN from one to 20 layers are shown in Fig. 4, and the maximum absorption wavelength (λ) is 487 nm . Apparently no J-aggregation is present.

The absorbance at 479 nm was plotted against number of transferred layers and the relationship between absorbance and layer number was found to be linear with a linear correlation at 0.999 .

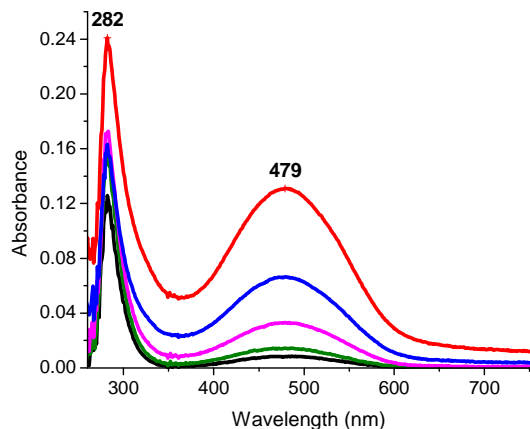


Figure 4: UV-Visible spectra of the LB Films of **p6PEGMAN** (from bottom to top: 1, 2, 5, 10 and 20 layers)

In the table 1 a resume of the maximums of absorption in UV-Visible are reported for all the azocompounds; and we can observe that the **p4PEGMAN** shows a red-shifted compared with the others azopolymers.

Azopolymer	Absorption LB films (nm)
p2PEGMAN	468
P3PEGMAN	469
P4PEGMAN	423
P6PEGMAN	479

Table 1: Resume of the maximums absorption of 20 layers from LB films and solution in chloroform

4. CONCLUSIONS

We have demonstrate that **pnPEGMAN** series forms molecular nanostructures with highly ordered and stability in monolayers; and the stability and homogeneity when are deposited onto solid substrates with the LB technique are excellent. We can conclude that the chain of ethylene glycol determine the mean molecular area and the area was decreased when the chain decreased too.

REFERENCES

[1]. Rau H. In: Rabek JK, editor. Photochemistry and photophysics, col. 2. Boca Raton, FL: CRC Press; 119, 1990.
 [2]. Natansohn A, Rochon P. Chem Rev; 102:4139-4175, 2002.
 [3]. Rivera E, Carreón-Castro M. P, Buendía I, Cedillo G, Dyes and Pigments; 68:217-226, 2006.

[4]. Rivera E, Carreón-Castro M. P, Rodríguez L, Cedillo G, Fomine S, Morales-Saavedra O, Dyes and Pigments; 74:396-406, 2007.
 [5]. Oliveira Jr ON, He J-A, Zucolotto V, Balasubramanian S, Li L, H.S.N., et al. IN: Kumar J, Nalwa HS, editors. Handbook of polyelectrolytes and their applications. Los Angeles: American Scientific publishers; 1-37, 2002.
 [6]. Oliveira Jr ON, Dos Santos Jr DS, Balogh DT, Zucolotto V, Mendoça CR, Adv Colloid Interface Sci, 116:179-192, 2005.
 [7]. García-Tenorio T, Rivera E, Carreón-Castro MP, Morales-Saavedra O, Polymer 2008, submitted.

Acknowledgements:

The authors are grateful to DGAPA-UNAM (PAPIIT 118808 and 112203). They are pleased to acknowledge Fis. Luis Flores (FC-UNAM) and Martín Cruz (ICN-UNAM) for technical assistance.