



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 24 Sep 2006

To cite this article: Hoon-Kyu Shin, Hyen-Wook Kang, Takahito Inoue, Hiroshi Yokoyama & Young-Soo Kwon (2000): Electrical Features of Surface Structure in Polymer Monolayers by Smm, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 159-162

To link to this article: <http://dx.doi.org/10.1080/10587250008024889>

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Electrical Features of Surface Structure in Polymer Monolayers by Smm

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Recent development in scanning probe microscope techniques has made it possible to investigate, not only microscopic surface topography, but also physical and chemical properties on the nanometer-scale. We observed the surface potential distribution and molecular ordering in monolayers. The SMM surface potential image clearly shows the existence of micron-sized domains in the polymer monolayers with a good correspondence to the topographical features. This is a first step towards understanding electrical phenomena in organic and inorganic materials with SMM.

Keywords: surface potential; scanning Maxwell-stress microscopy

INTRODUCTION

The horizon of organic thin film research has recently been drastically expanded toward the atomic and molecular level owing to the development and sophistication of a variety of scanning probe microscopes (SPMs)^[1]. The scanning Maxwell-stress microscope (SMM) is a variant of the AFM operated in the noncontact mode and can image the distribution of surface charge and potential over ultra-thin films with a nanometer scale resolution. In previous reports^[2,3], we

showed that the surface potential is extremely sensitive to the local arrangement of molecules in a film, drawing a few examples from phase-separated and collapsed monolayers.

In this paper, we report on a two-dimensionally crosslinked monolayer film of a phenol-formaldehyde resin. Although the thermosetting resins have been employed for various plastic applications, the LB film fabrication of commercially important resins has not been reported as yet. We also investigated the application of the SMM to structural-functional study of LB films of crosslinked polymer as well as to the formation of network monolayer in phenolic polymer films.

EXPERIMENTAL

Amphiphilic phenol, *o*-hexadecoxyphenol (*o*-HP), was synthesized by a substitution reaction of catechol, resorcinol, and hydroquinone with 1-iodohexadecane. The chemical structure was confirmed by FTIR, ¹H-NMR, and elemental analysis^[4]. Monolayers were spread on pure water or weight % aqueous formaldehyde subphase at 20 ± 1 °C. The actual SMM system consists of a commercial AFM(Nanoscope III, DI)^[2,3]. The lateral resolution was 10 nm with a potential 1 mV of sensitivity.

RESULTS AND DISCUSSION

The most stable monolayer was found on the formaldehyde subphase, and the collapse pressure showed over 15 mN/m. Phase changes of the monolayers were observed by Brewster angle microscopy (BAM) and the monolayer structures were determined by FT-IR spectroscopy^[4].

Figure 1(a) shows a $5 \times 5 \mu\text{m}^2$ SMM topographic and surface potential image (a ω -component map) recorded on the same surface. SMM images of the *o*-HP LB films on a Si wafer substrate were taken as an indirect evaluation of the film stability and domains or two-dimensional structure. When the monolayer of *o*-HP was deposited on the Si wafer substrate from a pure water subphase, the large domains were seen as bright spots in the SMM images even in the multilayers. However, a good deposit of network film was found in the monolayer films and was transferred from the acidic (pH=3.5) aqueous formaldehyde subphase.

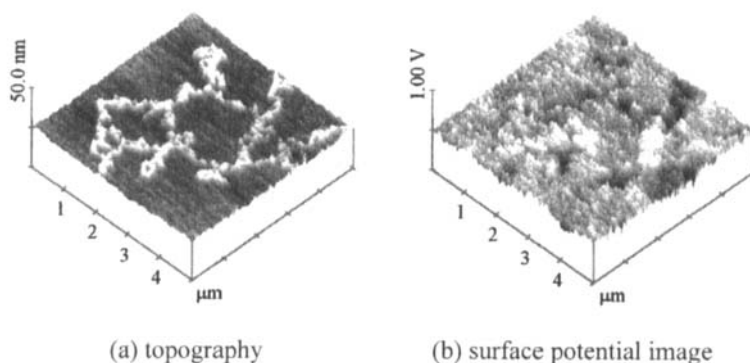


FIGURE 1. Topography (a) and surface potential (b) of phenolic polymer film on aq. 1% formaldehyde by SMM.

The substrate was a Si wafer substrate and thus the substrate potential distribution was homogeneous over the film before the LB film transfer. The spatial distribution of the surface potential was, however, created after formation on the Si wafer surface with the crosslinked network monolayer because the surface potential would be

different between the network film and the substrate. The surface potential between these two parts was attributed to the difference in the surface dipole moments due to the terminal CH_2 - and CH_3 - groups of the C-H, C-O and C=C chains, respectively^[4].

However, from a comparison between the π -A isotherms of the two-dimensional network, i.e. crosslinked phenolic polymer and formaldehyde, the chain structure is more likely. This contradiction implies the possibility of the network structure formation during the monolayer deposition and thus a further investigation with regard to the squeeze out mechanism is now in progress.

CONCLUSION

We demonstrated a molecularly-thin network film of a phenol=formaldehyde resin which is a well-known thermosetting resin. From the measured values of the surface potential with the SMM surface potentials image and those of the thickness with the SMM topographic image, the dielectric constant of the network monolayer can be obtained by the use of calculation on the assumption of the modeling. Applications of the composite network structure film toward selective permeation are expected.

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