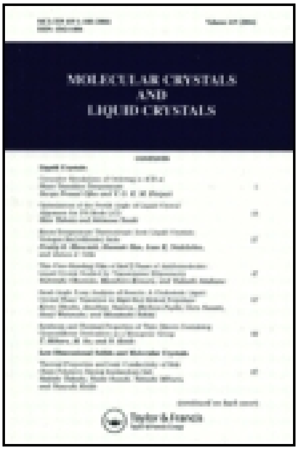

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Jung-Hyu Kim, Suck-Hyun Lee & Jae-Ho Kim (1998): Structure of Langmuir-Blodgett Films of Nitrophenyl-Prolinol Polymer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 185-188

To link to this article: http://dx.doi.org/10.1080/10587259808044487

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 185–188
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Structure of Langmuir-Blodgett Films of Nitrophenyl-Prolinol Polymer

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Abstract A fully aromatic polyester (poly-p-phenyleneterephthalates) containing N-(4-nitrophenyl)-(L)-prolinol (Poly6-NPP) as a nonlinear optical (NLO) chromophore was synthesized and characterized in the monolayer domain. Surface pressure-area ($\Pi — A$) isotherms and Brewster angle microscopy (BAM) indicated that pure Poly6-NPP formed a stable Langmuir film at the air-water interface. Although homogeneity and structural regularity of Langmuir films of Poly6-NPP were considerably improved by addition of PMMA, atomic force micrographs indicated that in the mixed Langmuir-Blodgett (LB) films segregated small islands were appeared with size of a few hundred nanometer. During the electrical poling process, surface-enhanced Raman scattering (SERS) spectra of the polymer LB films were simultaneously recorded to monitor conformational changes of NPP in the polymer matrix. SERS spectra indicated that NPP in the polymer structure underwent conformational changes from a disorganized random structure to an organized tilted orientation respect to Ag surface. This was consistent with the observation on the intensity variation of the second harmonic generation as well as on topographical images obtained by atomic force microscopy (AFM).

Keywords: nonlinear optical polymer, LB film, AFM, Brewster angle microscopy, surface-enhanced Raman scattering

INTRODUCTION

Organic polymeric NLO materials have generated great interests both in the area of fundamental research and of electroptical technology due to their large susceptibility, ease of processability and fast response time. Various methodologies in tailoring NLO chromophore (NLO-phore) and their incorporation to the polymer matrix such as LB monolayer technique, host-guest system, and covalent attachment of NLO-phore to the polymer backbone have been studied to maximize nonlinear optical efficiency as well as to minimize the relaxation of oriented chromophore. In this study, a flexible N-(4-Nitrophenyl)-L-prolinol (NPP), as the pendant NLO-phore was covalently attached to a wholly aromatic polyester (poly-p-phenylenetelephthalates) as a rigid backbone and monitored its conformational changes during the electrical poling and spontaneous relaxation process by SERS spectroscopy.

EXPERIMENTALS

The details of synthesis and purification of poly6-NPP was followed by published procedures[1]. A circular Teflon Langmuir trough (Mayer Feintechnik, Germany) was used to measure $\Pi - A$ isotherms and to prepare LB films on the solid substrates. AFM results were obtained by normal contact-mode SPM-LS (PSI, CA. USA). BAM images were acquired by using MiniBAM (Nanofilm Tech. Germany). SERS spectra were collected using a triple monochromator coupled with CCD array detector (Spex Industries, NJ, USA) and 514.5 nm of Ar^+ laser (Coherent Co. CA., USA) as an excitation source. Thermally evaporated thin Ag films on mica were used for SERS substrate.

RESULTS AND DISCUSSION

Structure of poly6-NPP is depicted in the inset of Figure 1. As shown in the structure, the NPP group is attached to the rigid polymer backbone via aliphatic flexible chain. This structure will effectively retard relaxation to a random disordered state of the aligned chromophores as suggested in the previous report[2].

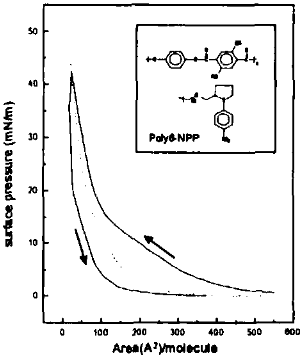

FIGURE 1. $\Pi - A$ isotherm of pure poly6-NPP on water subphase. Solid and dotted lines are the 1st and 2nd compression respectively.

It was possible to obtain reproducible $\Pi—A$ isotherms and BAM images of pure poly6-NPP at the air-water interface. As shown in Figure 1, the $\Pi—A$ isotherms the Langmuir film of the polymer is quasi-elastic and does not indicate any noticeable phase transition or collapsing point. BAM images indicated that re-expanded polymer film at the interface was gradually expanded to the initial uncompressed state. Homogeneity and structural regularity of Langmuir films of Poly6-NPP were considerably improved by addition of PMMA. However, AFM micrographs indicated that PMMA and Poly6-NPP in the mixed LB films were segregated into small islands with size of a few hundred nanometer, which is indicative of formation of disorganized multilayer structure. Before the film was poled by an electrical field, the average thickness of the film was estimated ca. 30 Å by AFM. AFM studies showed that formation of "cone-like" structure by electrical poling with a diameter ca. 60 nm as shown in Figure 2 (b). This structural feature seems to closely related to extremely high value of SHG efficiency. *In situ* SERS investigation indicated that NPP groups in the LB films were initially contacted with the substrate via NO_2 group with a tilted orientation. When an electrical field was applied, NPP aligned parallel to the electrical field and the electrical repulsive force between the substrate and NO_2 groups induced conformational change of NO_2 groups to move away to the opposite of the substrate as evidenced in Figure 3 and 4.

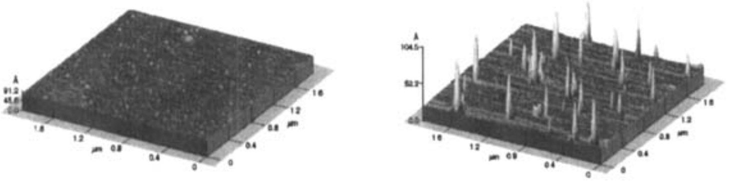

FIGURE 2. AFM images of ploy6-NPP LB films; (a) unpoled, (b) poled with 3.5 kV at 70 ℃ (transfer pressure: 20 mN/m).

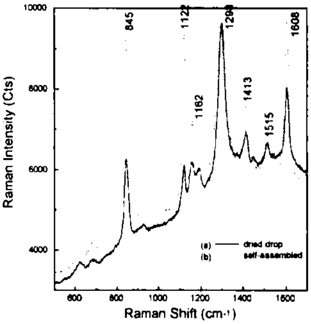

FIGURE 3. SERS spectra of poly6-NPP; (a) dried drop, (b) self-assembled film. Dried drop sample was prepared by allowing to dry a few drops of solution of the polymer on the solid substrate, whereas, for SA film the substrate was exposed to the sample for

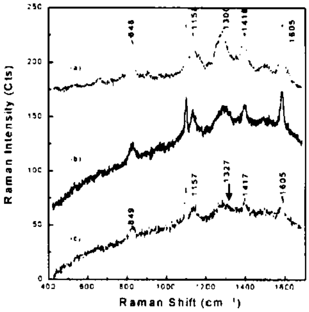

FIGURE 4. SERS spectra of poly6-NPP LB films; (a) unpoled, (b) poled with 3.5 kV at 70 ℃ for 10 min, (c) 0 kV, 25 ℃ (transfer pressure: 20

In conclusions, $\Pi - A$ isotherms and BAM reveal that pure Poly6-NPP forms a homogeneous, elastic film at the air-water interface. Prior to the electrical poling, the orientation of NPP in a dried films was flat to the substrate which was similar with that in a spin coated film, whereas both in the LB films and self-assembled films NPP showed a tilted orientation to the surface. During the electrical poling, NPP aligned parallel to the electrical field with NO_2 group toward to the opposite side of the substrate.

Acknowledgment The present study was supported by the Basic Science Research Institute Program, Ministry of Education, Korea.

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