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Enhancing Network and Collaboration
Developing Research and Education in Physics and Nuclear Energy

PROCEEDING

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Foreword

On behalf of the organizer of the 2nd Jogja International Physics Conference, I would like to give our sincere gratitude to all the participant of the conference. I would like to give our deepest appreciation and gratitude to all of keynote speakers of this conference, namely Ir. Sukarman Aminjoyo, APU (BAPETEN), Dr. Baek Jong-Bok (Korea Hidro and Nuclear Power Co. Ltd.), Prof. Ren-Tai Chiang (Univ. Of Florida and GE Energy USA), Prof. Dr. Muhammad Mat Salleh (Univ. Kebangsaan Malaysia), Prof. Yoshitsugo Tomokiyo (Kyushu Univ. Japan), Dr. Harini Sosiati (Kyushu Univ. Japan), Dr. Yoshiki Hidaka (Kyushu Univ. Japan), Dr. Yusril Yusuf (Gadjah Mada Univ.).

The second Jogja International Physics Conference is the second conference organized by the Physics Department Gadjah Mada University continuing, previously was called, the 1st Jogja Regional Physics Conference 2004. This conference is aimed for promoting, developing, and disseminating interdisciplinary research from many different fields of physics, for the betterment of human lives. The conference was intended as a forum for the physicist from different branches of physics, and different countries, especially from the Asian and surrounding region, to meet and discuss, developing research and collaboration. It is also intended as a forum for dissemination of the latest research results from many different fields of physics. As Indonesia is currently planning developing its first power plant nuclear reactor, we also hope to enhance understanding of the current result in the nuclear reactor theory and technology. The theme of the conference is *Enhancing Network and Collaboration – Developing Research and Education in Physics and Nuclear Energy*. The topics covered in this conference are from very broad spectrum of Physics, such as Nuclear Energy, Atomic Physics, Theoretical and Mathematical Physics, Computational Physics, Nanotechnology, Material Science, Geophysics, Electronics Instrumentation, Bio and Medical Physics, and Educational Physics.

In this conference there are 8 papers in the panel session, presented by eighth invited speaker in two days. For the parallel session there are 63 papers to be presented in the conference. The presented papers consist of Nuclear Energy and Atomic Physics 8 papers, Theoretical and Mathematical Physics 8 papers Computational Physics 9 papers, Nanotechnology 5 papers, Material Science 6 papers, Geophysics 10 papers, Electronics and Instrumentation 17 papers.

The committees have worked in arranging the program for the benefit of the participants. The committee hopes that this conference could enrich, enhance the physics knowlegde, and served as a forum for individuals to meet and discuss the physics current issues. We sincerely appreciate the support and encouragement from Physics Department of Gadjah Mada University, BAPETEN, Atomic and Nuclear laboratory, Electronics Instrumentations Laboratory, Geophysics laboratory, Solid state laboratory, Basics Physics Laboratory, Graduate School (Pascasarjana) in University of Gadjah Mada, and D3 Study Program. Last but not least I would also give my thanks to the student volunteers in Physics Departement.

With sincere gratitude

Chairman of the 2nd JIPC 2007

Dr. Sismanto

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Langmuir-Blodgett-Kuhn Multilayer Films of Azobenzene Containing Polyamic Acid for Liquid Crystal Optical Switching

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Abstract

Langmuir-Blodgett-Kuhn (LBK) multilayers of azobenzene polymeric containing polyamic acid were fabricated onto fused silica substrates and gold-coated optical glass slides were fabricated. UV-Vis spectroscopy was employed to investigate the optical response of multilayers films. The thickness of mono- and multilayers were measured by use of SPR spectroscopy. UV-Vis and SPR spectroscopy results show that the thickness of PAA6B monolayer is 2.5 nm. Photoisomerization studies showed the excellent reversibility of the *trans*-*cis* and *cis*-*trans* isomerization reactions of the azobenzene sidegroups within the multilayer structures. Further, these films were found to be suitable for all-optical switching devices based on liquid crystal material.

Keywords: Polyamic acid, Langmuir-Blodgett-Kuhn multilayer films, Photoisomerization, Liquid crystal optical switching

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I. Introduction

Azobenzene-containing thin polymer layers have been extensively investigated for liquid crystal (LC) alignment switching due to its importance in the LC display technology [1]. Films with highly ordered chromophores, e.g., by azobenzene moieties covalently bound to a polymer backbone are of special interest, because they provide a uniform environment for the interaction with low molecular-weight guest LCs. Amphiphilic azobenzene derivatized polymers are good candidates for such purpose, as they can be assembled into highly ordered thin layers via the Langmuir-Blodgett-Kuhn (LBK) technique [2]. It is well known that polyimide derivatives are thermally very stable and possess excellent mechanical properties [3]. By substituting long-alkyl amines, the asymmetric polyamic acid becomes amphiphilic and shows good solubility in common organic solvents such as chloroform. These properties make it easy for multilayer film formation by using Langmuir-Blodgett-Kuhn technique.

In this paper, the LBK film of polyamic acid PAA6B that was studied in term of its optical response and its application for liquid crystal optical switching will be presented.

II. Materials And Experimental Methods

II.1 Materials

The chemical structures of PAA6B displayed in Figure 1. It was synthesized through the condensation of the azobenzene-functionalized dianhydrides and commercially available diamines [4].

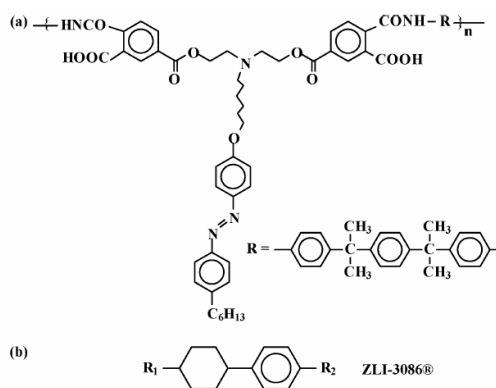


Figure 1. Chemical structure of (a). PAA6B and (b) low molecular weight nonpolar liquid crystal ZLI 3086

The introduction of the alkyl spacer between the azobenzene pendant and the polymer backbone and the alkyl tail attached to the other end of the azobenzene moiety, the polymers are sufficiently hydrophobic so that no salt-formation process by reacting PAA6B with long chain alkylamines is necessary for stabilizing the molecules at the air-water interface. The ease of

solvent evaporation in this case allows for a sufficient relaxation of the polyamic acid at the water/air interface such that abundant carboxylic and amide groups along the polymer backbone are released to the surface of the polymer coils and directed to the water subphase, while the hydrophobic tails stretch to the air. This, on one hand, stabilized the monolayer at water subphase in the Langmuir trough and, on the other hand, offers the possibility of building very stable LBK-multilayer assemblies through hydrogen bond formation by abundant carboxylic and amide groups between adjacent layers with head-to-head contact and through hydrophobic interaction by the alkyl-containing azobenzene side chains for tail-to-tail transfer.

II.2 Langmuir-Blodgett-Kuhn (LBK) Film Formation

The LBK film preparation of PAA6B was carried out on a trough film balance (FW2 Lauda) with a Milli-Q water ($R = 18.2 \text{ M}\Omega$) subphase. PAA6B was dissolved in chloroform (Aldrich, spectroscopic grade). The solution ($100 \sim 120 \mu\text{L}$, concentration $c_0 = 1.063 \text{ mg/mL}$) was then spread onto the subphase. After evaporation of the solvent (ca. 15 min), the surface area was gradually reduced with a computer controlled compression barrier, and the surface pressure was recorded. The molecular area was calculated with respect to the molecular mass of the monomeric repeat unit. The floating monolayer was compressed by moving a single barrier at a speed of 5 cm/min to surface pressure of 14 mN/m. The pressure value of 14 mN/m was chosen in order to obtain solid phase (see curve of isotherm as depicted in Figure 2). It can be calculated from this Figure that the area of PAA6B is $0.2 \text{ nm}^2/\text{molecule}$. Monolayers were transferred onto fused silica substrates or gold coated glass slides by vertical dipping with a dipping speed of 5 or 10 mm/min, respectively.

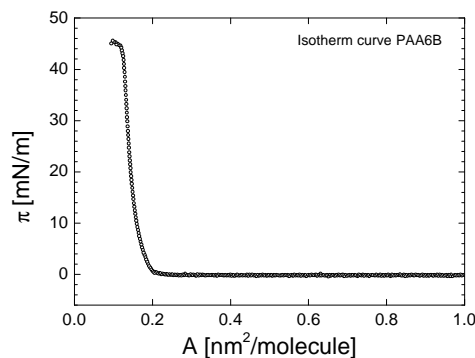


Figure 2. π -A isotherm curve of PAA6B

II.3 UV-Vis Spectroscopy

The optical density of mono- and multilayers of PAA6B were measured by using the UV-Vis-NIR spectrophotometer (Perkin Elmer model Lambda 900). The light was s-polarized which means that the electrical field vector was parallel to the film plane. The PAA6B layers were deposited onto fused silica substrate.

II.4 Surface Plasmon Resonance (SPR) Spectroscopy

The SPR studies were performed in the Kretschmann Configuration [5]. The PAA6B Langmuir layers were transferred onto Ag- and then SiO_x-coated BK7 glass slides in order to prepare LBK films of 2, 4, 6, and 8 layers, respectively. These samples were characterized by SPR spectroscopy. A 20-layer film prepared in the same way was used for the photo-isomerization study. SPR angular scans were taken with the chromophores in the as-prepared trans state and the cis state induced by UV irradiation ($\lambda = 355 \text{ nm}$).

II.5 Optical Switching Characterization

Asymmetric sandwich cells were built in the following way: four layers of PAA6B on a Ag/SiO_x-coated LaSFN9 slide and a blank quartz slide served as the two windows of a sandwich cell. Standard Polyethylene Terephthalate (PET) thin films with thickness in the micrometer range were used as spacers that controlled the distance between the two slides. The cell assembly was fixed by rapidly solidifying glue on four corners, and filled by capillary action with low molecular

weight liquid crystal ZLI-3086 (Merck). The alignment switching of the LCs upon the reversible photoisomerisation of the azobenzene-containing PAAs LBK films was studied by SPR. SPR angular scans were taken with the chromophores in both, the as-prepared trans- state and the cis state induced by UV irradiation ($\lambda=355$ nm).

III. Results And Discussions

The introduction of sterically demanding groups which reduced the $\pi-\pi^*$ complex formation, the solubility of the polyamic acids PAA6B in organic solvents, e.g., chloroform, was largely improved. This allows for an easy Langmuir-Blodgett-Kuhn (LBK) film formation from their chloroform solution on a water subphase. Figure 3 shows the changes of surface area of PAA6B in chloroform solution at surface pressure 14 mN/m as a function of time. It is clear that the polymer was stable at least after 1 hour compression, therefore, the mono- and multilayers of PAA6B is ready to be transferred into the solid substrate.

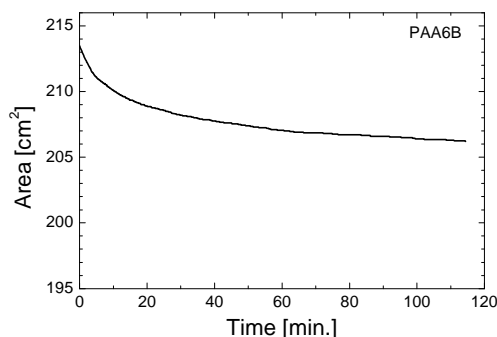


Figure 3. Stability of the PAA6B at surface pressure 14 mN/m at solid phase for 2 hours

With a dipping speed of 2 mm/min for fused silica substrates and 5 mm/min for metal-coated glass slides at a surface pressure of 14 mN/m, very regular film transfer was observed. This allows for a smooth buildup of 6 layers (Figure 4). The monotonic loss of the film on the subphase indicates a homogeneous transfer of the film onto substrate. This allowed even for the preparation of multilayers with a thickness of more than half a micron if needed, for instance, for

optical waveguide spectroscopy studies on metal-coated glass slides in which the geometrical thickness and the refractive index of the film could be determined separately [4].

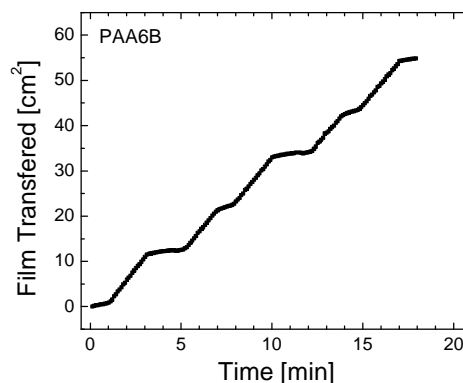


Figure 4. Deposition trace of the final 10 deposition cycles for the buildup of 6-layers on fused silica substrate. The monotonic loss of the film on the subphase indicates a homogeneous transfer of the film onto substrate.

LBK films were prepared on hydrophilic fused silica substrates at a surface pressure of $\pi = 12$ mN/m with Z-type deposition for UV-vis absorption spectroscopy measurements. The UV-vis spectra of the PAA6B films with an increasing number of layers are shown in Figure 5 (a). Furthermore, a close examination of the absorption spectra of the LBK PAA6B films in Figure 5a reveals that each spectrum exhibits a flat and nonzero absorbance in the range of $\lambda > 500$ nm, which most probably is due to reflection losses at the interfaces. The spectra consist of three peaks, i.e. at < 200 nm, 240 nm and 355 nm. The peak at $\lambda_{\text{max}} = 355$ nm is caused by an electronic transition between a molecular orbital delocalized along the polymer backbone (p- p* transition). The strong UV peak at $\lambda < 200$ nm is to transitions between localized and delocalized (s - p* transition), which are originating from the phenyl ring. The origin of the shoulder at 240 nm might be caused by charge conjugation symmetry (CCS) breaking due to the asymmetry side chain substitution (amphiphilic) [6]. Figure 5b shows the OD (ΔOD) at λ_{max} of the LBK PAA6B films plotted as a function of the number of layers deposited. It is obvious that ΔOD increases almost

linearly with the number of layers deposited. A slight deviation was found for the first layer that is probably due to the reflection losses that are more pronounced for the thinner layers and the deviation at 30 layers are caused by inhomogeneous film. By applying a linear fit, the slope of the graph leads to an approximate value of OD per layer of $(4.8 \pm 0.1) \times 10^{-3}$.

SPR measurements were performed on LBK films prepared on hydrophilic Ag/ SiO_x-coated BK7 glass substrates at a surface pressure of 14 mN/m. The numbers of layers are 2, 4, 6 and 8 layers, respectively. The experimental data are displayed in Figure 6 (a) together with the Fresnel calculation (solid lines) by assuming a refractive index of $n = 1.5$. By plotting the thickness of the films against the respective number of the transferred layers, a linear relation is found (Figure. 6b). It shows that the thickness of PAA6B monolayer is around 2.5 nm.

The photoisomerization reaction of azobenzene moieties in the PAA6B LBK films are found to be reversible and can be well controlled, as indicated by the study with SPR spectroscopy. In order to investigate the changes of PAA6B into the cis- and trans- states, the SPR spectra of a 20-layer PAA6B sample on Au-coated BK7 glass were taken with the chromophores in the film being both, in the as-prepared trans state and after UV irradiated to the cis state (Figure 7). A minor but clear shift of the resonance angle to the low incident angle was observed, therefore, it is clear that by irradiating with UV light, the trans- state of PAA6B as prepared will be aligned to the cis-state. The resonance curves are used to measure the switching behaviour of PAA6B multilayers by measuring the reflectivity at fixed angle using SPR.

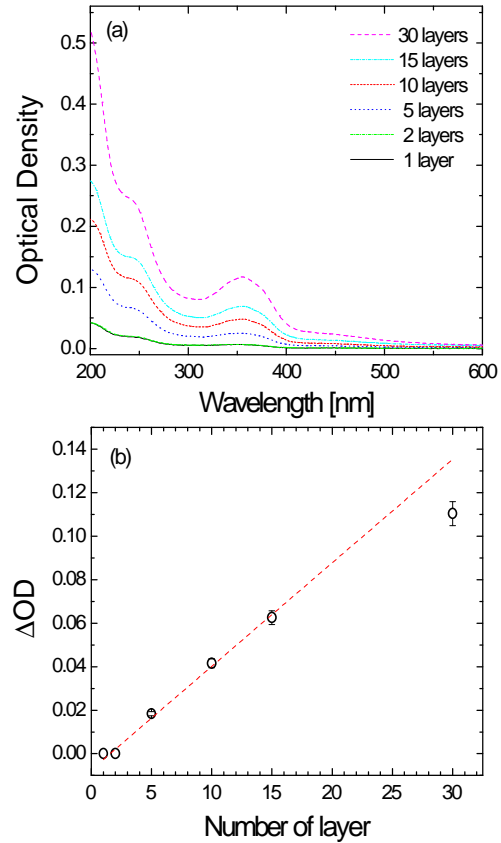


Figure 5. (a) UV-visible spectra of LBK PAA6B films transferred at a target pressure of 14 mN/m onto a hydrophilic fused silica substrate. The absorption maximum λ_{\max} of the LB film is 355 nm, (b) Plot of the change of optical density of the PAA6B film on hydrophilic fused silica against the number of layers..

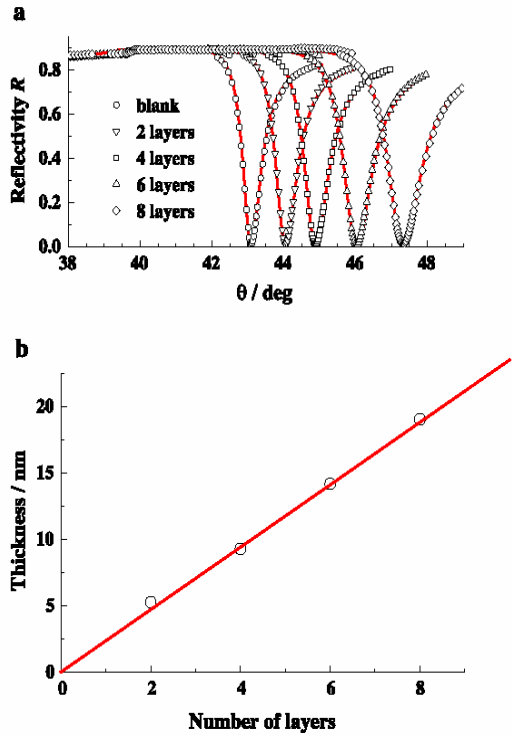


Figure 6 (a) SPR angular scans of PAA6B LBK films with different numbers of layers on Ag/SiOx-coated BK7 slides. The solid lines are curves according to Fresnel calculations. (b) The overall thickness of PAA6B LBK-films (at $n=1.5$) as a function of the number of layers deposited shows a linear dependence.

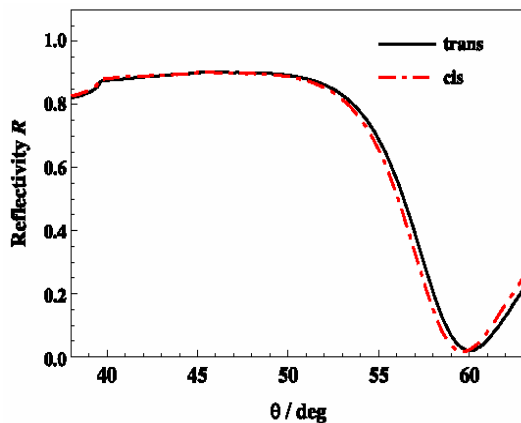


Figure 7. SPR angular scans for a 20-layer PAA6B film with the chromophores in the as-

prepared trans state (solid line) and after UV irradiation (cis state, dash-dotted line).

A hybrid Liquid Crystal cell is filled by a typical nonpolar liquid crystal, ZLI-3086 with a thickness of 20 μm . It shows under a conoscope that the PAA6B LBK layers with the azobenzene moieties in the film being in the as-prepared trans state. The LC cell is then filled with PAA6B film onto Ag/SiOx and blank quartz substrates serve as sandwich windows. This configuration was used to measure the reflectivity at fixed angle while irradiating alternately with UV light (350 nm) and visible light (> 400 nm). Figure 8 show the reflectivity changes at the angle 60° as function of time. It is clear that the PAA6B multilayer changes its configuration from trans state to cis state in 10 – 20 seconds.

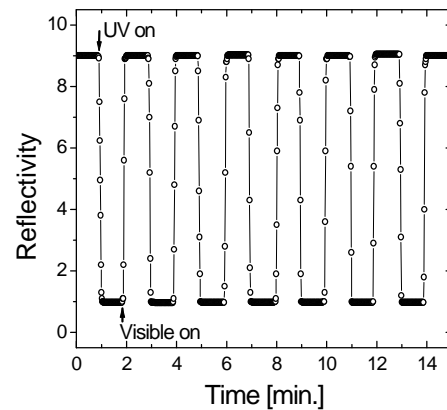


Figure 8. LC alignment switching measured with an asymmetric sandwich LC cell by using PAA6B as the photoregulation layers. UV (350 nm) and visible light (400 nm) were applied alternatively as irradiation sources.

IV. Conclusions

The asymmetric azobenzene containing polyamic acids shows good solubility in water-immiscible solvent prepared from condensation polymerization. It is also easily to be form as regular Langmuir-Blodgett-Kuhn film with well-defined internal structures. Photoisomerization of the azobenzene chromophores in the film was successfully used for the optical switching.

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