Measurement of Electro-optic Response of Self-Assembled Monolayer by Attenuated Total Reflection

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Abstract A monolayer film consisting of a layer-pair of cationic polymers with nonlinear optical active rod-like pendent group and anionic molecules were fabricated on a thin film using electrostatic self assembly technique. The surface plasmon resonance spectroscopy enabled the determination of the anisotropic dielectric constants and the thickness of each organic layer. A linear change in the modulation of the reflection curve upon application of a modulating electric field was observed, which is from the electro-optic response of polar-ordered hemicyanine pendent group.

1. Introduction

Some organic films possessing high second-order optical nonlinearities show potential for utilization in nonlinear optical devices. In order to obtain the second-order nonlinear optical (NLO) properties, the organic films must be non-centrosymmetric. Usually, an electrical poling field has been applied to the organic and/or polymeric films to achieve the non- centrosymmetry. Besides of the poling method, several novel methods to create the non-centrosymmetric structures incorporating organic NLO molecules have been developed during the past decade. These include Langmuir-Blodgett (LB) films, covalent self-assembled monolayer structures (CSA), and materials formed by electrostatic self-assembly (ESA). These techniques have been extensively developed to obtain a ultra-thin film with non-centrosymmetry. However, LB film and CSA film have several limitations for a further progress toward NLO applications, such as thermal and temporal unstability. As an alternative approach, the fabrication of layer-pairs by consecutive adsorption of polyanions and polycations, i.e., the ESA method, has been introduced, which goes through the fabrication process of the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion at room temperature. [DHS1992] [D1997] Monolayer and multilayer formations of ESA has highly stability-some reports were demonstrated its thermal and long term stability, even over 1 year.[HFMLC1999] In particular, the assembly of non-centrosymmetric multilayers through ESA is a promising technique for preparing second-order NLO films because their non-centrosymmetric structure permits a stabilized dipole orientation of the NLO chromorphores without the need of a high electric field poling. Recently, it has been shown that the second harmonic generation (SHG) was observed in the ESA films. [HFMLC1999]

In this paper, we report the electro-optic effect in the ESA monolayer film with substantial second-order NLO susceptibility, in the attenuated total reflection (ATR) geometry, which is known as a sensitive optical probe for the ultra thin film.[CGPC1987] From ATR measurements, we determined the anisotropic dielectric constants and the thickness of each organic layer and observed the E-O effects from the modulated reflectance.

2. Experimental

For sample, one of the new amphiphilic rod like polymers with pendent hemicyanine group, $POST_4$-amide, (2, 5 - [(E) – *N* – methyl – 4 - [2 - [4 - [(L) - prolinoxylphenyl] ethenyl] –pyridinium *p*-toluensulfonate]]), was used. (**Figure1**) The UV-VIS absorption spectra of the polymeric dye $POST_4$-amide show the absorption peak at 478 nm and transparent over 600 nm as shown in Ref [IKKL2000].

A glass, coated with a silver (Ag) layer (50nm) by vacuum evaporation (10^{-6} Torr) was used as a substrate for fabrication of ESA film. After washing and drying the silver coated substrate, the adsorption of a negatively charged acid, MPA (mercaptopropionic acid) was carried out in 5mM aqueous solution at room temperature during 90min onto the silver-coated substrate. Next, the $POST_4$-amide was subsequently adsorbed onto the MPA/Ag coated substrate during 30min at room temperature.

For the EO measurement, we made EO cell by attaching another transparent electrode (ITO, indium thin oxide) to the POST4-amide coated MPA/Ag substrate with 8μm air gap. The Prism/Ag/MPA/$POST_4$-amide/Air/ITO EO cell was put in optical contact through an index matching oil with the base of a right angle prism (BK7, n=1.51508).

The prism EO cell was mounted on a goniometer and the reflected light (633nm, p-pol.) on the monolayer through the prism was recorded directly as a function of incident angle θ. For the electric field modulation, external electric field was applied to the Ag and the ITO electrodes and the modulation of reflectivity was detected through a lock-in amplifier.

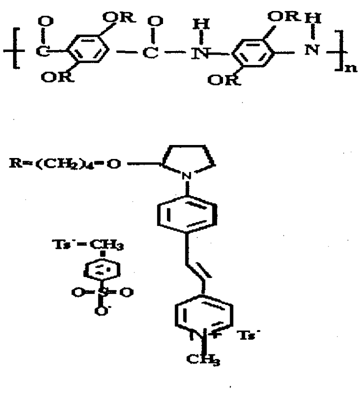


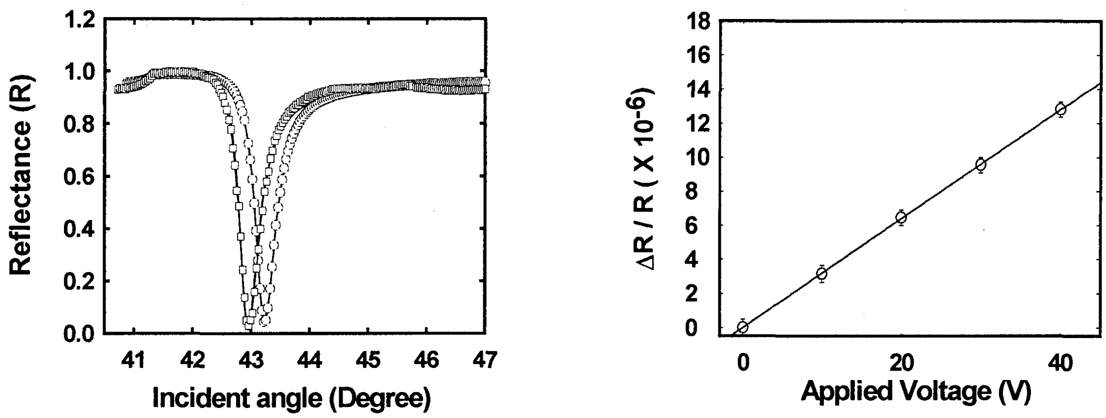
Figure 1. POST4-amide chemical structure

3. Results and Discussions

At first, we observed and analyzed ATR curves from the Prism/Ag/MPA/$POST_4$-amide/air. The observed ATR data points and fitted curves of Prism/Ag/air(square), Prism/Ag/MPA/POST4-amide/air(circle) system are shown in **Figure 2(a)**. From the theoretical analysis, the dielectric constant and thickness, d, of Ag layer were ε=-17.34+i0.66 and d=45.62nm. We also obtained the in plane and normal components of dielectric constant for the monolayer system using by 5-layer model [Y1998]. $POST_4$-amide, ε_{33}=2.93+i0.38 and ε_{11}=2.31 +i0.66 with the thickness of 1.9nm. 33 and 11 stand for the surface normal and the in-plane parallel directions, respectively.

In this ATR configuration, the modulation of the refractive index of the ESA monolayer by through the EO response results in the modulations in the peak position and width of plasmon resonance curve, which can be monitored through the reflectivity modulation at a fixed incidence angle. As shown in **Figure 2(b)**, the observed ΔR/R is linearly proportional to the applied voltage, indicating linear E-O effect.

In order to verify that the E-O modulation signal is due to the nonlinearity of $POST_4$-amide monolayer, we measured ΔR/R from a MPA monolayer on Ag and $POST_4$-amide on Ag under the same strength of applied electric field. The resulting ΔR/R from both MPA/Ag and $POST_4$-amide/Ag were comparable to the noise level, one order of magnitude smaller than that from $POST_4$-amide/MPA/Ag monolayer. It means that ΔR/R does not come from the Ag film, MPA or disordered $POST_4$-amide on Ag. From these, it is clear that the ordered $POST_4$-amide monolayer is responsible for the modulation of reflectance (ΔR/R)



(a) (b)

Figure 2. **(a)** Reflectivity R as a function of the incident angle in prism/Ag/air system (square) and prism/Ag/MPA/$POST_4$-amide/air system (circle). Solid curves are the least –squared fits. **(b)** The dependence of modulated reflectivity on the applied voltage of $POST_4$-amide monolayer in ATR geometry.

4. Conclusion

In summary, a simple ATR technique was employed to measure the electro-optic effect in ESA ultra thin monolayer film. From the plasmon resonance curves, the anisotropic dielectric constants and thicknesses of each layer were determined through the electromagnetic wave boundary condition analysis. A linear change in the modulation of the reflection curve upon application of a modulating electric field was observed, which is from the electro-optic response of polar-ordered hemicyanine pendent group.

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