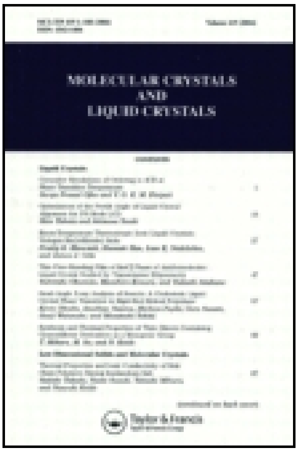

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FABRICATION OF AN ULTRATHIN FILM OF A CONJUGATED POLYMER AND AN NLO DYE

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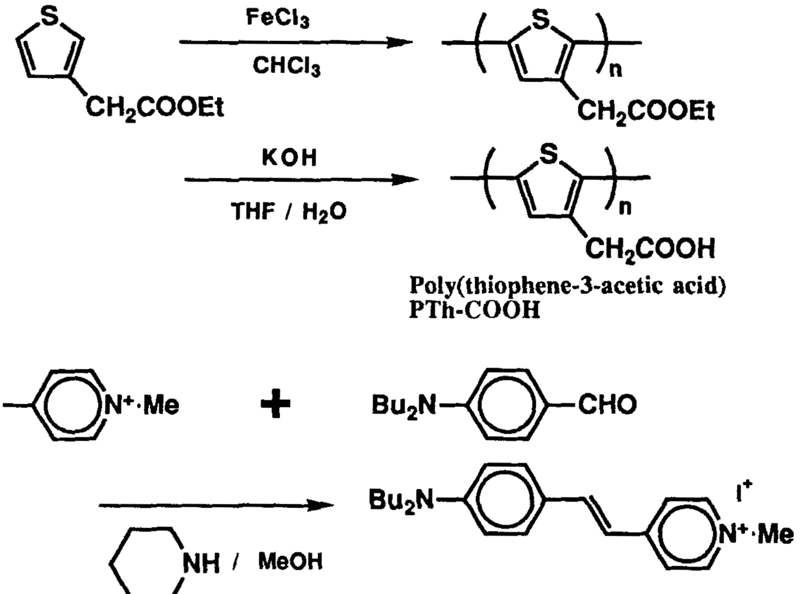
Abstract An ultrathin film of poly(thiophene-3-acetic acid) was fabricated on a glass substrate by chemical adsorption. On the film, an NLO dye was deposited. Anisotropy of UV-VIS absorption and SHG showed that the obtained film was highly oriented.

INTRODUCTION

Ultra-thin films, such as monolayer, show unique properties differently from bulk materials. Especially, ultra-thin films of conjugated polymers are expected to indicate enhanced and/or new nonlinear optical (NLO) properties due to the confinement of excited species in low dimensional structures.[1] There are many studies on Langmuir-Blodgett (LB) Films and molecular beam epitaxy (MBE) deposition for fabrication of thin films. However, the materials for these methods are limited because they have to have thermal resistance for sublimation in high vacuum or long alkyl chain for self-assembly on the surface between water and air. Furthermore, these methods require long time and expensive instruments. Recently, T.J. Marks and coworkers reported self-assemble monolayers of NLO active chromophore.[2] This method affords highly oriented structure of the chromophore. However, it still requires many step of chemical reactions and long time.

Surface-modified substrates adsorb organic molecules from its solutions by interactions such as electrostatic one. There are many combinations of surface-modifications and substances for the adsorption. Thickness of the film are varied by the concentration of the solution and density of the surface-modifying group on the surface. Self-assembly of adsorbed organic molecules on the surface may produce molecularly ordered ultra-thin films. Compared to LB film and MBE deposition methods, the deposition by the chemical adsorption is very simple and can be applied for a wide variety of materials.

Poly(thiophene-3-acetic acid) (PTh-COOH) having carboxylic acid groups as side chain is soluble in polar organic solvents such as N,N'-dimethylformamide. Rubner reported LB film of this polymer salt with a long alkyl amine.[3] However, the long alkyl chains in the polymer main chain disturbed the interaction between layers. This polymer can be adsorbed on the modified glass surface with base such as an amino group. Further, another polymer or dye with an amino group can be deposited on the polymer layer. In this study, we tried to fabricate of alternative monolayers of the polymer and stylbazolium dye (1) and characterized molecular orientation by the second harmonic generation measurement.



dye (1)

Scheme I

EXPERIMENTAL

Materials

All solvents (Aldrich HPLC grade) and chemicals were used as received. Poly(thiophene-3-acetic acid) was synthesized by the literature method. Poly(ethyl thiophene-3-acetate) was prepared by chemical oxidation of ethyl thiophene-3-acetate. Molecular weight ($\overline{M_w}$) of the poly(ethyl thiophene-3-acetate) was determined to be 1500 by GPC (elute: $CHCl_3$, polystylene standard). The polymer was hydrolyzed to be poly(thiophene-3-acetic acid). Stylbazolium dye was prepared by coupling 1,4-dimethylpyridinium iodide with p-N,N-dibutylaminobenzaldehyde (Scheme I).[4]

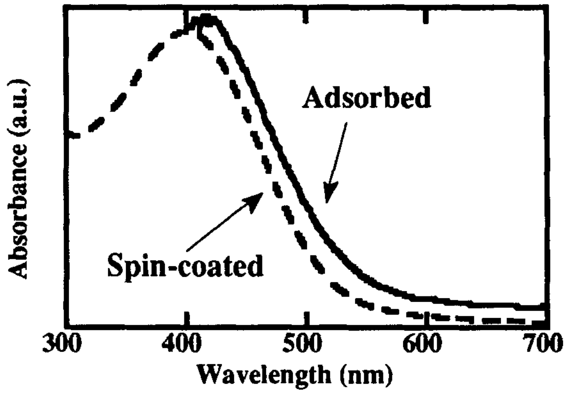


Figure 1. UV-VIS absorption spectra of the spin-coated and the adsorbed films.

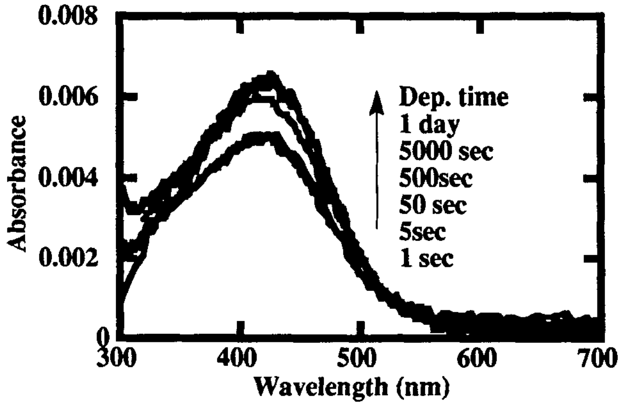


Figure 2. UV-VIS absorption spectra of the polymer film for various deposition times.

Substrate

A slide glass was heated in conc. sulfuric acid at 100 °C and washed with water. To remove residual water on the surface, the substrate was boiled in acetone and dried under vacuum at 100 °C for 1 day. Toluene saturated with water was used for surface modification. The washed slide glass was dipped into the solution (1 v/v%) of 1,1,1-triethoxypropyl-3-amine and stirred for 2 h at rt. The substrate was washed with toluene, chloroform, methanol, and water. Sequentially, it was dried under vacuum at 100 °C overnight.

Deposition of materials

Deposition of the polymer was carried out by dipping the surface modified substrate into to polymer solution (5 mg of the polymer in 1 L of dimethylformamide). After removing residual solution on the substrate by nitrogen stream, the film was dried under vacuum. Deposition of the dye was carried out by the same procedure from dye solution (5 mg of the dye in 1 L of MeOH).

UV-VIS absorption spectrum was recorded by Shimadzu UV-3100 spectrophotometer.

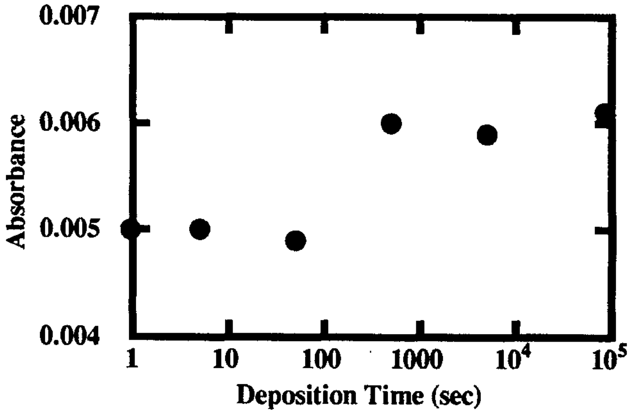
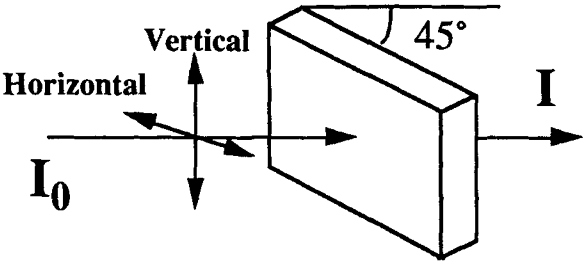


Figure 3. The absorbance of the polymer film at 420 nm as a function of deposition time.

RESULTS AND DISCUSSION

Figure 1 shows the UV-VIS absorption spectra of spin-coated and adsorbed film. Both spectra have a peak around 400 nm due to π-π^* transition in the polymer main chain. The absorption peak of the adsorbed film is red-shited compared to that of the spin-coated film. Usually, the polymer have a random coil structure in the sulution and the polymer maintains the structure in the spin-coated film. On the other hand, the conjugated polymer main-chain is expanded by the ionic interaction between the amino on the glass surface and the carboxylic group. Figure 2 shows UV-VIS absorption spectra of the polymer film for various deposition time. The growth of the polymer film is observed as increasing absorbance around 420 nm. Figure 3 shows the absorbance of the polymer films at 420 nm. The growth of the film was saturated between 50 and 500 sec. This result suggests that the polymer molecules are adsorbed on the amino groups and the grouth of the film is stopped when free amino groups are exhausted.

To characterize anisotropy of the polymer film, UV-VIS absorption spectra of the film were measured with the incident angle of 45 °(Scheme II). As shown in Figure 4, there is no difference between the two spectra. The molecules adsorbed on the surface are not aligned perpendicularly to the surface.



Scheme II

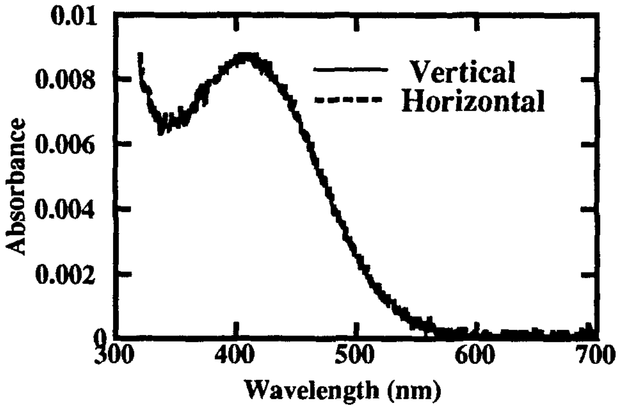


Figure 4. Anisotropy of UV-VIS absorption spectra of the film (deposition time: 5000).

On the polymer film (deposition time: 5000 sec), we tried to deposit a dye layer. Figure 5 shows the change of absorption of the polymer film. A new peak at 464 nm due to the dye absorption appeared at the deposition time of 50 sec and grows as deposition time increases. When chloroform was used as a solvent, we did not observe the absorption change and did not obtain bilayer film. For the dye adsorption, it is necessary that the ion pair of the dye molecule dissociates in the protonic solvent. These results imply that the carboxylic acid group of the polymer adsorbs the dye ions in its methanol solution and that the dye may be attached with pyridinium ion group, not with dibutylamino group.

To check the orientation of the dye molecules in the layer, the UV-VIS absorption was measured with an incident angle of 45 ° (Figure 6). Large dichromism was observed. The absorption in the spectrum for the horizontal polarized light is lager than that for vertical one. This dichromism proposes that the alignment of the dye molecules is perpendicular to the surface.[5]

Week background of second harmonic generation was observed in the pure polymer film. Figure 7 shows second harmonic generation of the polymer-dye film (deposition time of dye: 1 day). Compared to the signal from the polymer film, relatively strong signal was observed. This also proved that molecular alignment of the dye molecules. The detail analysis of the NLO property is in progress.

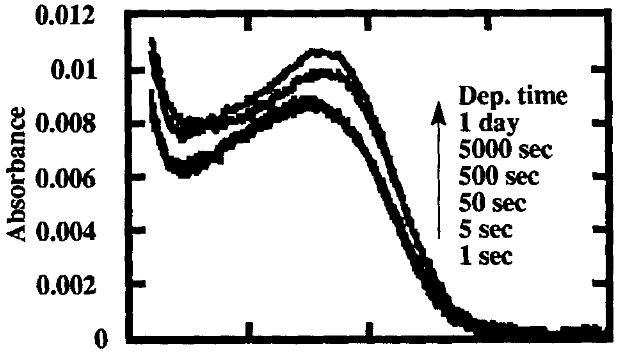


Figure 5. UV-VIS absorption spectra of the dye-polymer films for various deposition time.

CONCLUSION

The ultra-thin film of the conjugated polymer was fabricated on the aminopropylsilated glass surface by chemical adsorption method. The saturation in the growth of the film was obseved because the adsorption of the polymer occured only at the amino groups. The ionic dye can be adsorbed on the surface of the polymer film. The dye alignment of the dye molucules was estimated by the SHG measurement.

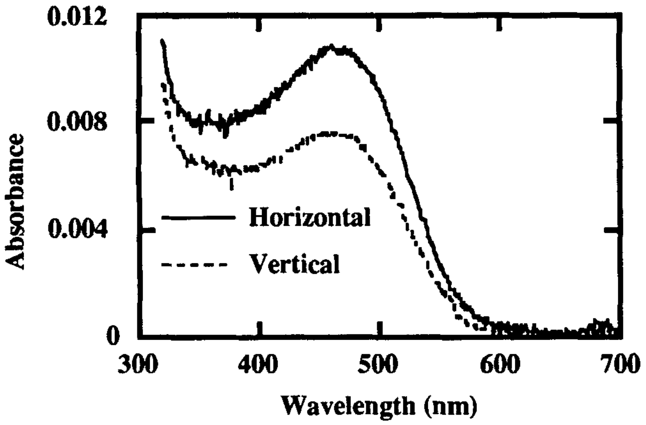


Figure 6. Anisotropy of the UV-VIS absorption in the dye-polymer film (dep. time: 5000 sec)

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