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Precursor and Substituent Effects on the Alternate Adsorption of Polycation and Anionic Dyes as Studied by Second Harmonic Generation and Absorption Spectroscopies

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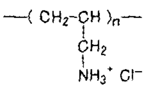
An alternately assembled polycation-anionic dye film was prepared on a precursor assembly of poly(allylamine)hydrochloride (PAH) and poly(sodium styrenesulfonate) (PSS) or of poly (diallyldimethyl)ammonium chloride (PDDA) and PSS. The (PAH/PSS) precursor assembly gave better adsorptivity to the anionic dye than the (PDDA/PSS) one. Four kinds of anionic dyes (EB-T, AR-17, AR-18, AR-27) with different numbers of sulfonate substituents were compared. The extent of dye assembling was higher for the dye with a smaller number of sufonate substituents. Second harmonic generation (SHG) was clearly observed from the films. The SHG signal and the absorption intensity correlated well up to four polycation/dye bilayers, while further assembly did not increase the SHG signal appreciably. Second order nonlinear coefficients for ten bilayer assemblies were the order of pm/V.

key words: Later-by-layer, alternative adsorption, polycation, anionic dye, second harmonic generation

INTRODUCTION

Fabrication of organic nonlinear optical (NLO) films is receiving much attention for possible applications in optoelectronic devices. Assembling of NLO chromophores in a stable noncentrosymmetric alignment is an important key to demonstrate macroscopic second-order NLO properties. Several attempts have been made to achieve noncentrosymmetric ordering, such as the Langmuir-Blodgett method [1], poling in electric fields [2], spin-coating [3], polymer-casting on water [4], and self-assembling [5-7]. Preparation of NLO films by self-assembly is relatively new. Marks et al [5] reported multilayers of NLO chromophores by sequential build-up of layers of silane coupling agent, chromophore, and capping agent, via covalent bonding. Katz et al [6] prepared a multilayer of polar chromophores via zirconium phosphonate/phosphate coordinative bonding.

Recently, a novel method for preparing a thin film by alternate electrostatic adsorption of polycation and polyanion [8,9], or polycation and low-molecular weight species [10,11], have been successful for generating NLO responses [12-18]. We previously reported SH responses from polycation-polyanion [12] and polyion-dye [13,14] films. In this study, we have investigated the effects of precursor layers as well as the number of sulfonate substituents of the dye on the degree of adsorption of the dye molecule in the polyion-dye alternate films, using the second harmonic generation (SHG) and the absorption spectroscopies.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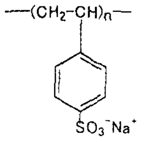
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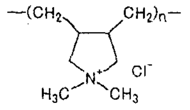
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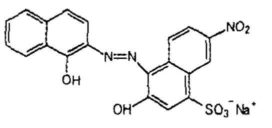
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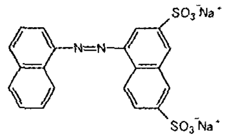
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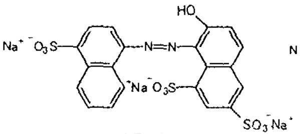
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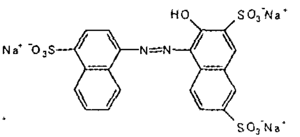
AR-27

MATERIALS AND METHODS

The experimental setup for second harmonic generation (SHG) measurements is identical to the one described previously [13]. Briefly, p-polarized fundamental light (1064 nm) from a Nd:YAG laser (~20 mJ, 7 ns, 10 Hz) irradiated the sample film and the p-polarized component of the transmitted SH light (I_{pp}) was detected. All measurements were carried out in

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air. Absorption spectra were recorded with a Shimadzu UV-2200 spectrophotometer.

Poly(allylamine)hydrochloride (PAH: Aldrich, MW 50000-70000), poly(diallyldimethylammonium chloride) (PDDA: Aldrich), poly(sodium styrenesulfonate) (PSS: Aldrich, MW 70000), Acid Red 17 (AR-17, Aldrich), Acid Red 18 (AR-18, Aldrich), Acid Red 27 (AR-27, Aldrich), and Eriochrome Black T (EB-T: Dojindo) were used as received. Polyions were dissolved in deionized water at appropriate concentrations: 1 mg/ml for PAH, 3 mg/ml for PSS, and 0.3 mg/ml for PDDA. A fused quartz glass substrate (40 × 13 × 1 mm) was washed in alkaline aqueous alcohol (1% KOH, 60% ethanol) with sonication to generate anionic charges on the surface by partial hydrolysis. Thus, the PAH or the PDDA layer could be formed on the substrate surface. The $(PAH/PSS)_n$ or the $(PDDA/PSS)_n$ (n: number of bilayers, n=1-5) precursor films were also prepared on the substrate by alternate adsorption of the polycation and PSS. The outermost layer of the precursor film was always negative. The $(PDDA/dye)_n$ (n=1-10) assembly was superimposed on the precursor film by immersing the substrate in aqueous PDDA (0.3 mg/ml) and dye (1×10^{-4} M) solutions for 20 min alternately with intermediate water washing.

RESULTS AND DISCUSSION

First, the polycation (PAH or PDDA) layer was formed on the substrate surface, and then EB-T was adsorbed on the polycation layer, giving the (polycation/EB-T) bilayer assembly. Figure 1 shows the absorption spectra of these bilayer assemblies. The absorption band around 520 nm is due to EB-T. It is clear that the adsorbed quantities of EB-T are almost identical in PAH and PDDA. As shown in Figure 2, SH responses were clearly observed from the both bilayer assemblies. The interference pattern of the SH signal due to the interference of SH waves from the both surfaces of the substrate is destructive, suggesting uniform quality of the layer structure for each assembly. According to the projection model [19], the polarized SH signal, I_{pp}, is given by

$$I_{pp} = K(1.5\tan^2\theta\sin\theta\cos\theta + \sin^3\theta)^2, \qquad (1)$$

where θ and θ show the incident angle of the laser light and the average tilt angle of molecular hyperpolarizability, respectively, and K is a proportionality constant[19]. Solid lines are the best fits Eq (1), taking θ = 40°(a) and 43°(b).

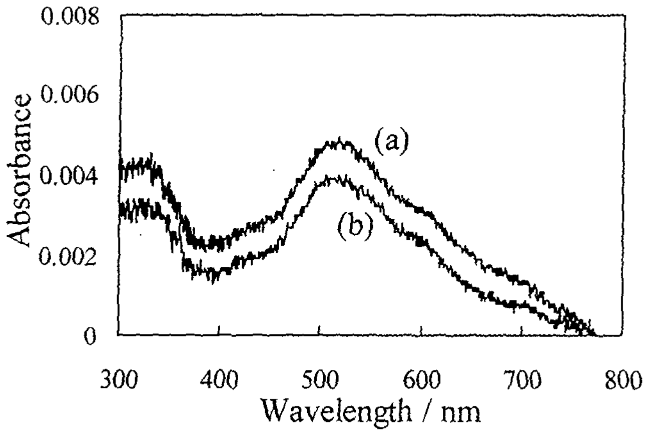

Figure 1. Absorption spectra of (PAH/EB-T) (a) and (PDDA/EB-T) (b) bilayers.

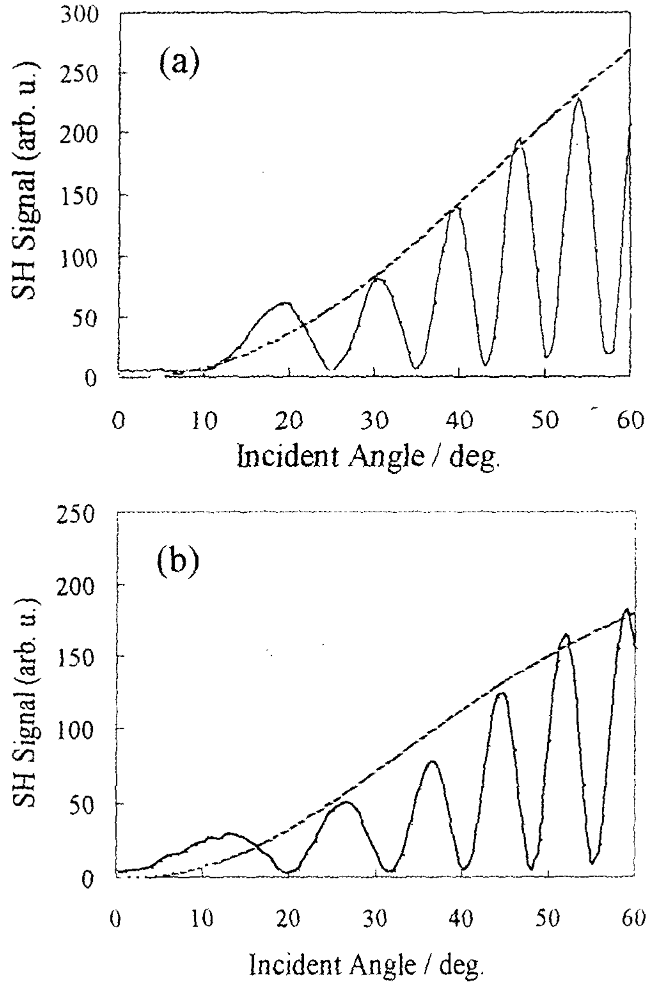

Figure 2. Angular dependencies of SH signals from (PAH/EB-T) (a) and (PDDA/EB-T) (b) bilayers. Dotted lines show the best fits to the Eq (1), where θ values are: 40° (a) and 43° (b).

Effects of the number of precursor bilayers were compared between PAH and PDDA. The $(PAH/PSS)_n$ or the $(PDDA/PSS)_n$ (n=1-5) precursor film was prepared, and then the (PDDA/EB-T) bilayer was superimposed on the precursor film. The adsorption behavior of EB-T molecules was investigated by absorption and SHG measurements. Since SHG is a two-photon process for excitation, the intensity of SH signal is proportional to the square of the concentration of SHG-active species in the film. Thus, the second harmonic field $E_{2\omega}$ (square root of I_{pp}) should reflect the concentration of noncentrosymmetrically aligned dye molecules in the

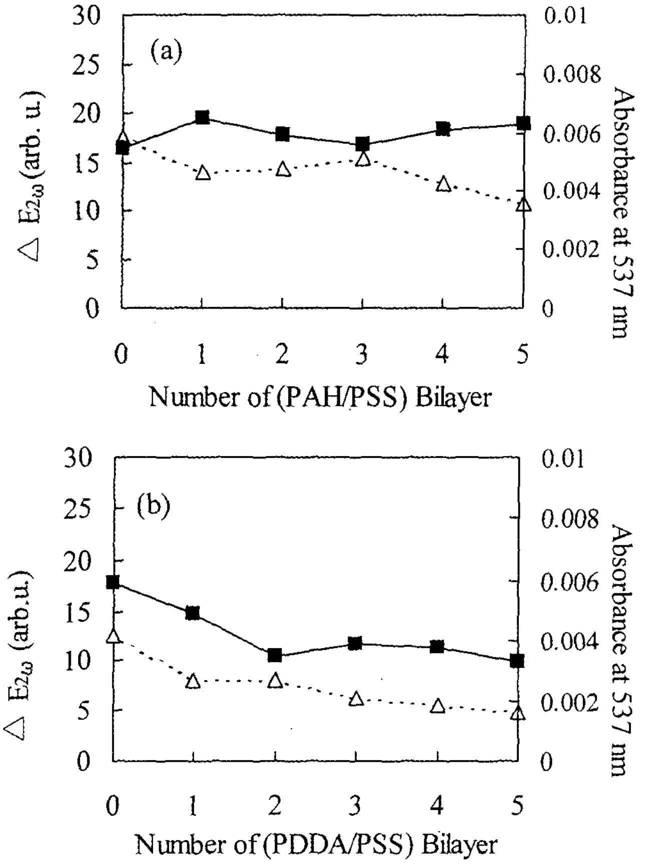

Figure 3. Effects of the number of layers on the subsequent adsorption of the (PDDA/EB-T) bilayer on the precursor films of $(PAH/PSS)_n$ (a) and $(PDDA/PSS)_n$: (b) for n=0-5: △ $E_{2\omega}$, ■ absorbance at 537 nm.

film. As shown in Fig. 3, absorbance at 537 nm are almost identical in the PAH/PSS precursor films, indicating constant quantity of adsorption. While, the $E_{2\omega}$ value at 45° incident angle tended to decrease slightly with increasing the number of (PAH/PSS) bilayer. Thus, slight disordering of molecular alignment for the thicker precursor film is suggested. In the case of the (PDDA/PSS) precursor films, both the absorbance at 537 nm and the $E_{2\omega}$ value decreased with increasing the number of bilayer, indicating the reduction of adsorption quantity in the thicker precursor film. Thus, the (PAH/PSS) precursor films gives better performance for the noncentrosymmetric adsorption of EB-T molecules.

However, most EB-T molecules were desorbed into the aqueous PAH solution from the (polycation/EB-T) bilayer, when the (polycation/EB-T) bilayer was immersed into the aqueous PAH solution to superimpose the subsequent PAH layer, probably due to the high hydrophilicity of PAH. On the other hand, no appreciable desorption of EB-T molecules was observed on immersion of the (polycation/EB-T) bilayer into the aqueous PDDA solution, probably because of lower hydrophilicity of PDDA as compared with PAH. Accordingly, the combination of the (PAH/PSS) precursor film and the (PDDA/EB-T) assembly gave the best performance for the practical fabrication of polycation-dye assemblies. For practical use, we have used the $(PAH/PSS)_2$ precursor film.

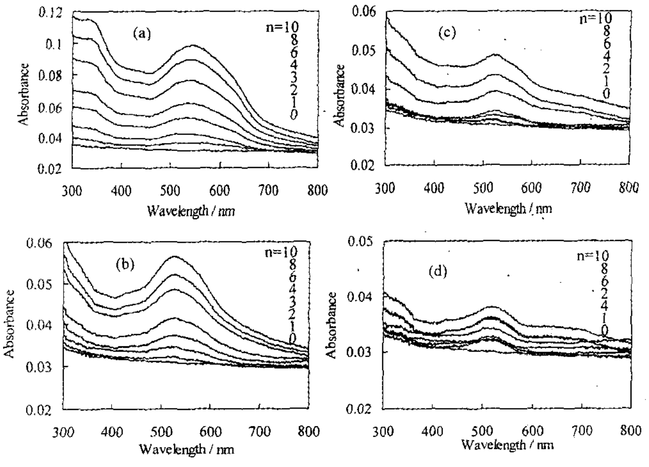

Figure 4. Absorption Spectra of $(PDDA/dye)_n$ assemblies (n = 0, 1, 2, 3, 4, 6, 8, 10) on $(PAH/PSS)_2$ precursor films: (a) EB-T, (b) AR-17, (c) AR-27, (d) AR-18.

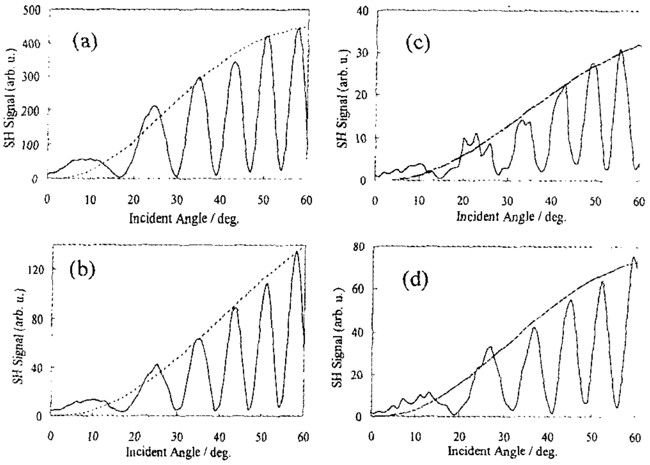

Figure 5. Angular dependencies of SH signals from $(PDDA/dye)_4$ assemblies on $(PAH/PSS)_2$ precursor films: (a) EB-T, (b) AR-17, (c) AR-27, (d) AR-18. Dotted lines show the best fits to the equation (1), where θ values are: (a) 47°, (b) 41°, (c) 43°, (d) 45°.

Absorption spectra of $(PDDA/dye)_n$ (n=0,1,2,3,4,6,8,10) assemblies deposited onto $(PAH/PSS)_2$ precursor films are shown in Figure 4. The absorption intensity satisfactorily increased with the number of dye layers, except AR-18 (d). The mean concentration of adsorbed dye at each one step was the order of EB-T (4×10^{-10} mol cm^{-2}) > AR-17 (8×10^{-11} mol cm^{-2}) > AR-27 (3×10^{-11} mol cm^{-2}) (AR-18 (2×10^{-11} mol cm^{-2}), inverse order of the number of sulfonate substituents.

All $(PDDA/dye)_n$ assemblies showed clear SH responses, as typically shown in Figure 5 for $(PDDA/dye)_4$ assemblies prepared on the $(PAH/PSS)_2$ precursor layers. Solid lines are the best fits to the equation (1), taking $\theta = 47 \pm 1°$ (a), 41 ± 1° (b), and 43 ± 1° (c), 45 ± 1° (d), respectively. If the adsorption quantity as well as the similar degree of non-

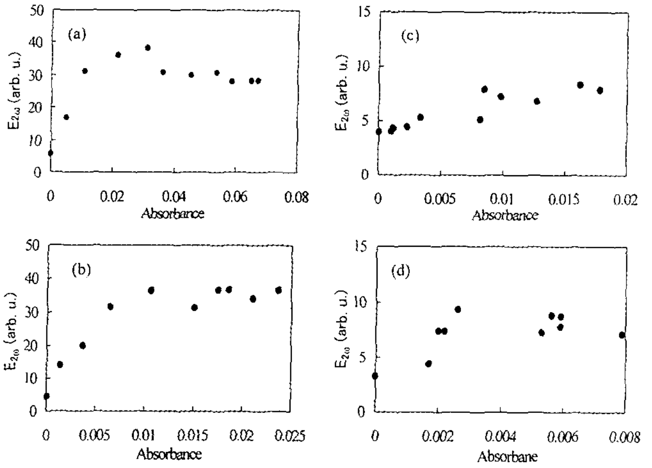

Figure 6. Relationships between $E_{2\omega}$ and absorbance for $(PDDA/dye)_n$ assemblies (n = 0-10) on $(PAH/PSS)_2$ precursor films: (a) EB-T, (b) AR-17, (c) AR-27, (d) AR-18. Absorption wavelengths: (a) 537 nm, (b)522 nm, (c)522 nm, (d) 507 nm.

centrosymmetric orientation are achieved for each assembly, the linear relationship between the $E_{2\omega}$ value and the absorbance is expected. As shown in Figure 6 (a), the $E_{2\omega}$ value of EB-T increased up to four cycles of (PDDA/EB-T) adsorption, but did not increase beyond five cycles. Thus, disordering of the EB-T molecules is occurring in upper layers. The $E_{2\omega}$ value tended to saturate rather gradually in AR-17 (Figure 6 (b)). In the case of AR-27, the SH response was certainly observed but was considerably smaller than EB-T and AR-17, mainly due to lower adsorption quantity [21]. The adsorptivity of AR-18 was very poor, and the relationship between the $E_{2\omega}$ value and the absorbance was much worse than the others. Unfortunately, we could not evaluate the direction of the dipole moment of the dye. However, the angular dependency of the SH signal (Figure 5) did not vary substantially on the number of PDDA/dye bilayers in each dye assemblies. Thus, saturation profiles of the SH signals in EB-T and AR-17 must be ascribed not to orientational change of the dye molecule but to gradual disordering of molecular alignment in upper layers.

The second order NLO coefficients of the $(PDDA/dye)_{10}$ assemblies were determined to be 1.6 (EB-T), 1.9 (AR-17), 0.46 (AR-27), and 0.40 (AR-18) pm/V, respectivey, by using a Y-cut quartz crystal as a reference NLO material (0.3pmV). The values were somewhat smaller than that obtained for the 5 bilayer films obtained from PDDA and a polyanion with an SHG-active chromophore [15]. Some factors should be taken into account to explain the difference of those NLO coeficients: concentration of adsorbed SHG-active chromophore, hyperpolarizability of SHG active chromophore, degree of noncentrosymmetric alignemt.

In conclusion, we have demonstrated here that the precursor film substantially affected the noncentrosymmetric adsorption of the anionic dye and that the number of sulfonate substituents profoundly affect the degree of adsorption and SHG response in polycation/dye alternate assemblies. Use of zwitter-ionic dyes will be fascinating to achieve more definite structures as well as to improve the SHG performance. The work is in progress along this line.

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