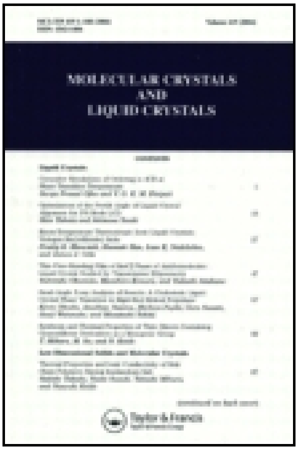

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Photoinduced Maxwell-Displacement-Current Acr-Oss Polyamic Acid and Azobenzen Langmuir-Blodgett Films

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PHOTOINDUCED MAXWELL-DISPLACEMENT-CURRENT ACR - OSS POLYAMIC ACID AND AZOBENZEN LANGMUIR-BLODGETT FILMS

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Abstract Maxwell-displacement-current (MDC) measuring technique has been applied to the investigation of polyamic acid and azobenzen Langmuir-Blodgett films by alternating photoirradiation with visible light and ultraviolet light. MDCs across multilayer films were generated alternatingly due to the cis-trans photoisomerization of AZBPAA films. It was also found that the photoexcited electron transfer also made a contribution to the generation of MDCs with ultraviolet irradiation. Finally, MDCs across AZBPAA monolayers were found to be suppressed as a result of the deposition of PAA layers onto the AZBPAA monolayers, possibly due to the inhibitation in the cis-trans photoisomerization.

1. INTRODUCTION

Recently, much attention has been paid to the Langmuir-Blodgett(LB) technique in the field of organic material electronics[1,2]. Using this technique, mono- and multilayer systems are produced for the realization of novel electronic phenomena which are available in organic material electronics. For the past few years, we have been developing a maxwell-displacement-current-measuring technique which allows molecular motions to be probed without destroying monolayer films on a water surface and as well as on solid substrate[3].

MDCs flow across multilayer films due to the orientational change in polar molecules and due to the electron transfer in the films. The motion of polar molecules and electrons in multilayer films strongly depends on the film structure and the constituent molecules. Thus the MDCs give information concerning the relationship between the structure of

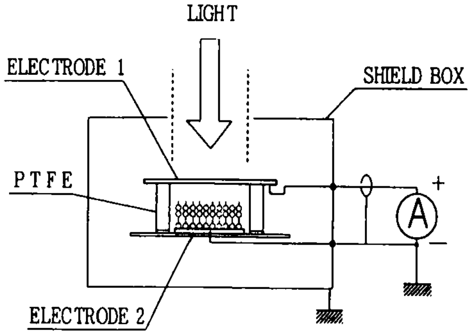

FIGURE 1
Maxwell-displacement-current-measuring system.

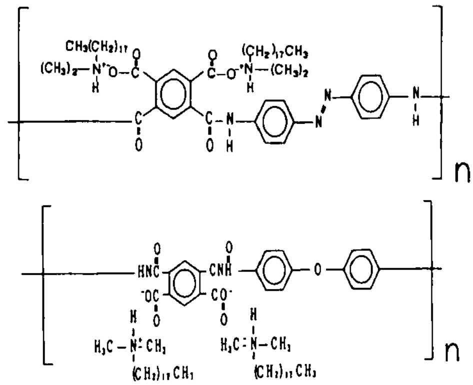

FIGURE 2
Molecules used in the present investigation. (a)AZBPAA, (b)PAA

multilayers and the electrical properties of the films.

In our pervious study[3], we examined the MDCs across single monolayers of azobenzen polyimide(AZBPAA) and polyamic acid(PAA), and clarified the dynamical motion of charged particles in the monolayers. However we are not certain of the relationship between the structure of multilayer films and the generation of MDCs.

In the present investigation, we examined the MDCs across multilayer films consisting of azobenzen and polyamic acid polyimide Langmuir-Blodgett films.

2. EXPERIMENTAL

2.1. Experimental set-up

Figure 1 shows the experimental setup used in the present investigation. It was the same as in the previous study[4]. Electrode 2 was a glass slide coated with multilayer films. Electrode 1 was an S_nO_2-coated glass slide without monolayers. Electrodes 1 and 2 were supported with a polytetrafluorethylene(PTEE) sheet in order to electrically isolate the two electrodes from each other. The two electrodes were parallel to each other at a spacing of about 100 μm. The working area of each sample was about 6.25 cm^2.

Each sample was put into an electrically shielded box, and electrodes 1 and 2 were then connected to each other through a sensitive ammeter (Keithley 617), of which the internal electrical resistance was negligibly small. Ultraviolet and visible light outputs from a 500-W xenon lamp

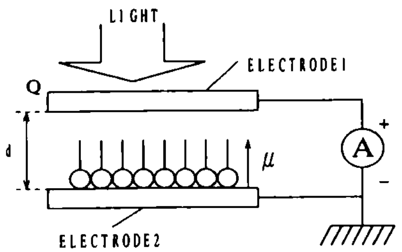

FIGURE 3
A model of displacement current generation.

(Ushio UI-501C) were separated using appropriate band-pass filters and they were then applied to the sample from the side of electrode 1 at intensities of 0.4 and 0.8 mW/cm ^{2} by the application of ultraviolet light(λ_1) with a wavelength of 380 nm and of visible light (λ_2) with a wavelength of 450 nm, respectively. The displacement current was measured in a manner similar to that in the previous papers[5,6].

2.2. Materials and Samples

LB films used here were AZBPAA and PAA, whose chemical structures are shown in Fig.2. Single monolayers of AZBPAA and PAA formed on a pure water surface were transferred onto S_nO_2-coated glass slide (25 mm x 25 mm) at a surface pressure of 30 mN/m and a temperature of 20℃ by means of the conventional LB technique.

The transfer went quit well at the deposition ratio of nearly unity. AZBPAA and PAA monolayers were deposited in a Y-type fashion. We prepared samples with the structure of ITO/AZBPAA(1,3,5)/air-gap/ITO, ITO/PAA(2)/AZBPAA(1)/air-gap/ITO, ITO/PAA(1,3,5)/air-gap/ITO and ITO/AZBPAA(1)/PAA(2)/air-gap/ITO, where the number in the parentheses represents the number of deposited layers, and ITO represents conducting electrode.

2.3. MDC-measurement

Figure 3 illustrates a model of displacement current generation. Displacement current flows through the circuit during the photoirradiation as a result of the change in the induceded charge Q_1 on electrode 1. Briefly, charge Q_1 is given by[4]

$$Q_1 = -\frac{S}{d}\sum_{i=1}^{k} n_i \mu_i \qquad (1)$$

Here $\mu_i (i = 1,2,\ldots,k)$ is the vertical component of average dipole moment of molecules in the i -th layer, S is the area of working electrode, $n_i (i = 1,2,\ldots k)$ is the density of molecules on electrode 2 of the i -th layer, k is the number of layers deposited on electrode 2, and d is the distance between electrode 1 and electrode 2. If displacement current I is generated only due to a change in the vertical component of dipole moment of the molecules, the current I is given by

$$I = -\frac{dQ_1}{dt} = \frac{S}{d}\frac{d}{dt}\sum_{i=1}^{k} n_i \mu_i \tag{2}$$

Therefore, the current flows in a direction from electrode 1 to electrode 2 (positive direction) when the Q_1 increases by photoirradiation. In contrast, the current flows in the opposite direction when the Q_1 decreases by photoirradiation.

3. RESULTS AND DISCUSSION

Figure 4 shows typical examples of displacement current of ITO/AZBPAA(5)/air-gap/ITO and ITO/PAA(2)/AZBPAA(1)/air-gap/ITO by alternating irradiation by lights λ_1 and λ_2 (repeated twice), respectively. The trace of MDCs were nearly the same between the two samples as shown in the figures (a) and (b). The MDCs were generated in a positive direction when λ_2 light was irradiated, whereas it was generated in the opposite direction when light λ_1 was applied. This result indicates that MDCs were generated due to the photoisomerization in AZBPAA layers with alternating photoirradiation of light λ_1 and λ_2.

In contrast, for ITO/PAA(1,3,5)/air-gap/ITO structures, the MDC was not

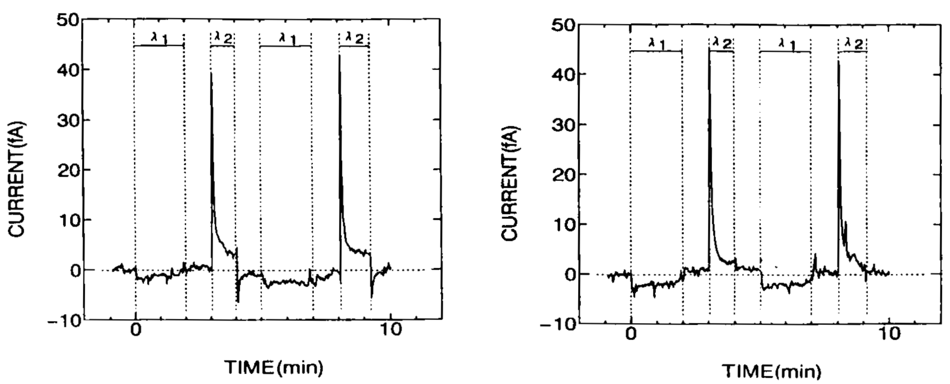

FIGURE 4
A typical example of MDC alternating irradiation with UV (λ 1, 380 nm in wavelength) and visible light(λ 2, 450 nm in wavelength).
(a)ITO/AZBPAA(5)/air-gap/ITO, (b)ITO/PAA(2)/AZBPAA(1)/air-gap/ITO

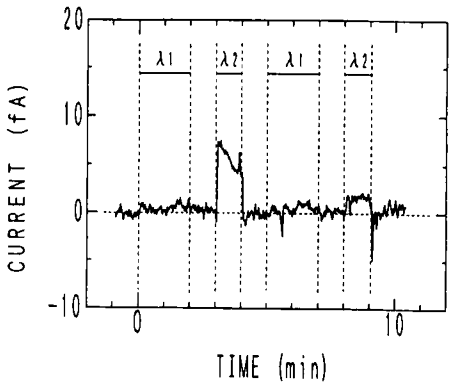

FIGURE 5
MDC across ITO/PAA(3)/air-gap/ITO structure by alternating irradiation with UV(λ 1, 380 nm in wavelength) and visible light(λ 2, 450 nm in wavelength).

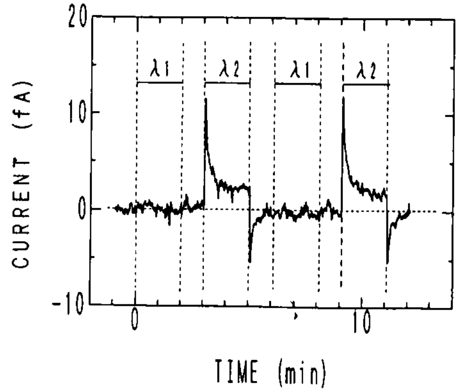

FIGURE 6
Typical of MDC by alternating irradiation with UV (λ 1, 380 nm in wavelength) and visible light(λ 2, 450nm in wavelength) of ITO/AZBPAA(1)/PAA(2)/air-gap/ITO structure.

generated by photoisomerization, whereas it was generated by photoirradiation with visible light λ_2 possibly due to the electrons which were photoexcited in PAA layers and subsequently transferred in the direction from PAA to ITO (see Fig.5)[5,6]. MDCs due to the electron transfer were also observed for ITO/AZBPAA(1,3,5)/air-gap/ITO and ITO/PAA(2)/AZBPAA(1)/air-gap/ITO structures.

Figure 5 shows a typical example of MDCs generated from ITO/AZBPAA(1)/PAA(2)/air-gap/ITO. The MDCs were very small in comparison with those seen in Fig. 4(a) and 4(b), indicating that the cis-trans photoisomerization of AZBPAA monolayers was suppressed as the result of the deposition of PAA monolayers onto AZBPAA layers.

Finally we compared the magnitude of MDCs flowing across the samples used in the present study, and summarized the results in Table 1. Table 2 shows the ratio of the intensity of absorption spectra of cis and trans form AZBPAA LB films deposited on S_nO_2-coated glass slide at a wavelength of 380 nm. The absorbances of cis and trans form films were measured after the 3-hour UV application and 5-min visible light application, respectively. It was again suggested that the cis-trans photoisomerization in AZBPAA films was suppressed as a result of the deposition of PAA LB films onto the films. Finally it should be noted that for the sample with a structure of ITO/PAA(1)/AZBPAA(2)/PAA(2)/air-gap/ITO. The absorption spectra exhibited the cis-trans photoisomerization although the MDCs were suppressed. Further experimental research is required.

TABLE 1 The magnitude of MDCs by alternating irradiation with UV (λ 1, 380 nm in wavelength) and visible light(λ 2, 450 nm in wavelength).

film / light	AZBPAA(5)	PAA(2)/ AZBPAA(1)	PAA(3)	AZBPAA(1)/ PAA(2)
λ 1	- 3 fA	- 3 fA	0 fA	0 fA
λ 2	+ 40 fA	+ 40 fA	+ 5 fA	+ 10 fA

* AZBPAA and PAA films were prepared on SnO2-coated glass slide.

TABLE 2 Ratio of the intensity of absorption spectra in cis and trans form films.

film / ratio	AZBPAA(3)	AZBPAA(5)	PAA(2)/ AZBPAA(1)	AZBPAA(1)/ PAA(2)
$\frac{Icis}{Itrans}$	0.0087	0.01	0.0075	0.0001

4. CONCLUSIONS

We investigated the photoinduced Maxwell-displacement-current generated across multilayer films consisting of polyamic acid and azobenzen polyimide Langmuir-Blodgett films by photoirradiation. MDCs were found to be generated due to the cis-trans photoisomerization by irradiation with ultraviolet and visible light. It was found that the generation of MDCs across azobenzen films was suppressed as the result of the deposition of PAA monolayers on them.

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