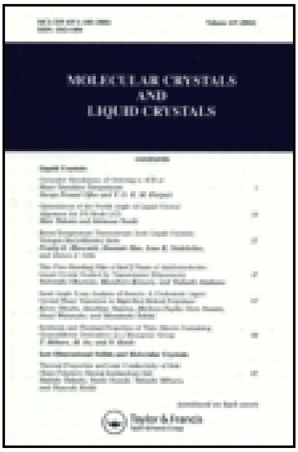

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PHOTO-MEMORY SYSTEM BASED ON THE PHOTO-ISOMERIZATION BEHAVIOR OF THE AZOBENZENE UNIT IN THE MAIN CHAIN OF POLYIMIDE LB FILMS

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Abstract Polyamic acid derivatives containing photosensitive azobenzene units in their main chain have been synthesized. Y type polyamic acid LB films were fabricated which were then converted into the polyimide LB films by chemical imidization accompanied by the elimination of long alkyl amines. The orientation of the polymer chains to the dipping direction was observed by the orientation of the chromophore in the plane direction, which depends strongly on the structure of the diamines. Aromatic diamines lead to a preferential orientation parallel to the dipping direction, while aliphatic diamines did not result in a preferential orientation. The reversible photo-isomerization was caused by both the polyamic acid and polyimide LB films. The rigid aromatic polyimides showed less reactivity compared with the more flexible aliphatic polyimides.

INTRODUCTION

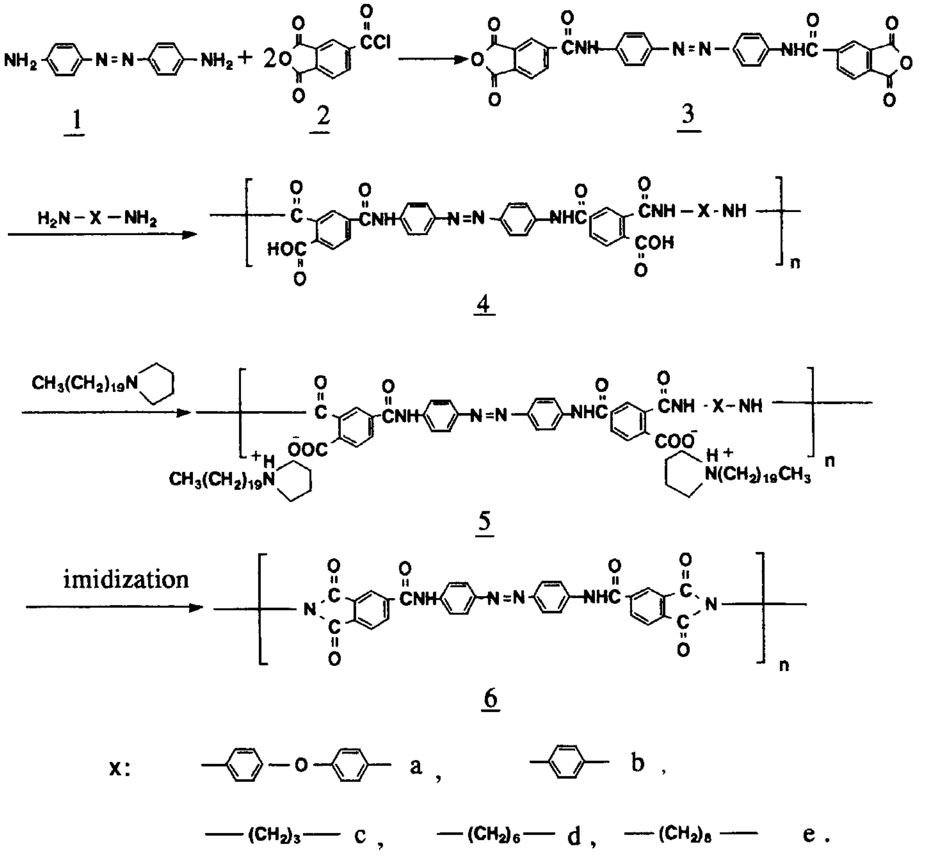
The Langmuir-Blodgett (LB) technique has recently been accepted as a method available for preparation of highly ordered and oriented polymeric multilayer films[1,2]. We have reported that polyimide LB films without alkyl spacer chains could be prepared via precursor polyamic acid long alkyl amine salt LB films[3-5]. This "precursor method" has been widely applied to preparation of non-amphiphilic polymeric LB films, such as poly(arylenevinylene)[6] and poly(thienylenevinylene)[7] LB films.

Polymeric LB films possessing functional groups have been widely investigated and are expected to be used in the fabrication of molecular devices, since they exhibit excellent thermal and mechanical stability compared with the LB films made of low molecular weight materials[1,2]. Azo dyes, causing trans-cis reversible photo-isomerization, have attracted much attentions as photosensitive molecules. Although polyimide LB films possessing azobenzene unit in the wholly aromatic system have been applied to fabricate photo-memory devices, the results were not satisfactory because the LB films were too rigid to show the photo-isomerization effect[8]. Recently, we reported a new photo-memory system of polyimide LB films having azobenzene unit as a pendant group[9]. In-plane anisotropic photo-isomerization and photo-fading behaviors were observed in these systems.

In the current work, we synthesized novel polyamic acids containing azobenzene unit in the main chain of the polymer and fabricated a new photo-memory system utilizing the LB technique.

EXPERIMENTS

Polyimide LB films presented in this study were prepared according to the procedure as shown in Scheme 1.



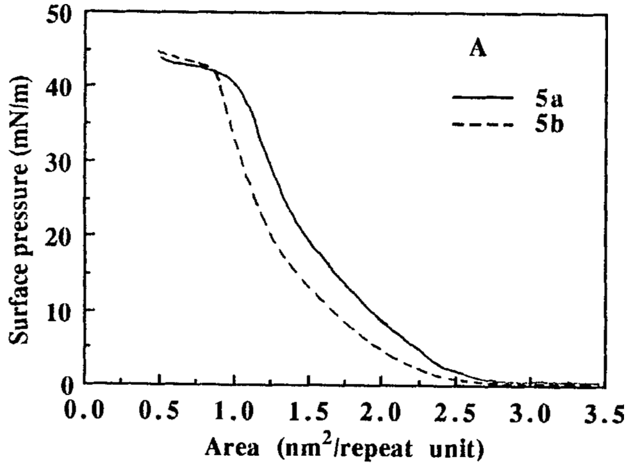
SCHEME 1

Tetracarboxylic dianhydride 3 containing azobenzene unit was synthesized by the reaction of 4,4'-diaminoazobenzene 1 and 4-chloroformylphthalic anhydride 2. The polymerization of 3 with aromatic and aliphatic diamines resulted in polyamic acids 4, which were then mixed with N-icosylpyrrolidine to form polyamic acid alkyl amine salts 5, which included aromatic 5a, 5b and aliphatic 5c, 5d, 5e, respectively. The LB films of 5 prepared by the usual LB technique were treated with a mixed solution of 10 ml of benzene, 1 ml of acetic anhydride and a few drops of pyridine for 30 minutes to form the LB films of polyimide 6.

The measurement of the surface pressure area isotherms (π-A curves) and deposition of 5 were carried out using a San-Esu FSD-20 apparatus. The transfer of the monolayer of 5 onto various substrates was achieved under an equilibrium surface pressure of 20 mN/m. Transmission FTIR spectra were measured by a JEOL JIR-MACRO 6000 FTIR spectrometer equipped with a MCT detector with a resolution of 4 cm^{-1}, where the LB films were fabricated on a CaF_2 substrate. Polarized UV-visible absorption spectra were measured using an Otsuka MCPD-1000 spectrometer. Combination of a Xenon lamp (Ushio UI-501C, 500W) and appropriate filters (λ=380 nm and λ= 500 nm) were used for photo-irradiation. The spectra changes due to the photo-isomerization were recorded by a Hitachi U-4300 spectrometer.

RESULTS AND DISCUSSION

The monolayer properties of polyamic acids were examined by their π-A isotherms in Figure 1. By mixing the polyamic acids with a long alkyl amine at the ratio of 1:2, both aromatic and aliphatic polyamic acids could form a close-packed monolayer at the relatively high surface pressures. The low compressibility in the steeply raising slope represents a solid-like arrangement of the two-dimensional array of the molecules. This suggests that the monolayer of polyamic acid is formed at the air-water interface.



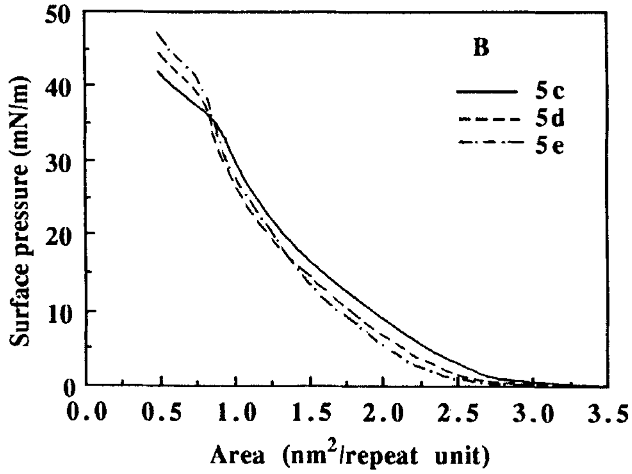


Fig. 1 π-A isotherms of 5a and 5b (A); 5c,5d and 5e (B).
Spreading solution: 0.33 mmol/l in DMAc/benzene=1/1, 20°C.

The imidization of the polyamic acid LB films was carried out by the chemical method. The chemical structure of the LB films was determined by transmission FTIR.

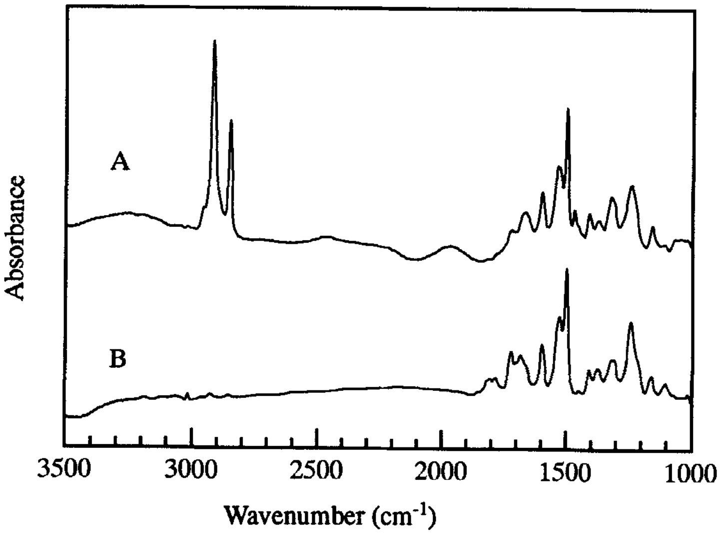


Fig. 2 FTIR transmission spectra of 5a and 6a.
Deposited 9 layers on a CaF_2 substrate.

Figure 2 shows typical FTIR transmission spectra of the LB films, where A and B represent LB films of 5a deposited 9 layers on a CaF_2 plate before and after imidization, respectively. In the spectrum of A, two intense bands at 2930 and 2860 cm^{-1} corresponding to symmetric and asymmetric methylene vibrations, $v_s(CH_2)$ and $v_a(CH_2)$, parallel to the layer plane were observed. The amide carbonyl bands at 1660 and 1480 cm^{-1} were also found in spectrum A, which disappeared in spectrum B. The latter was accompanied by the appearance of imide carbonyl bands at 1790 and 1690 cm^{-1}. These spectrum changes indicate that the polyamic acid long alkyl amine salt 5a was converted into the polyimide 6a with removal of the long alkyl amine by the chemical treatment.

Typical UV-visible absorption spectra of the LB films deposited 9 layers on the quartz plates are shown in Figure 3, where the solid line and dotted line represent polyamic acid 5b and polyimide 6b, respectively. Both the polyamic acid and polyimide have λ_{max} at around 380 nm, which is assigned to the π-π^* transition moment of the trans azobenzene group. No remarkable change of the absorption property was observed during the imidization.

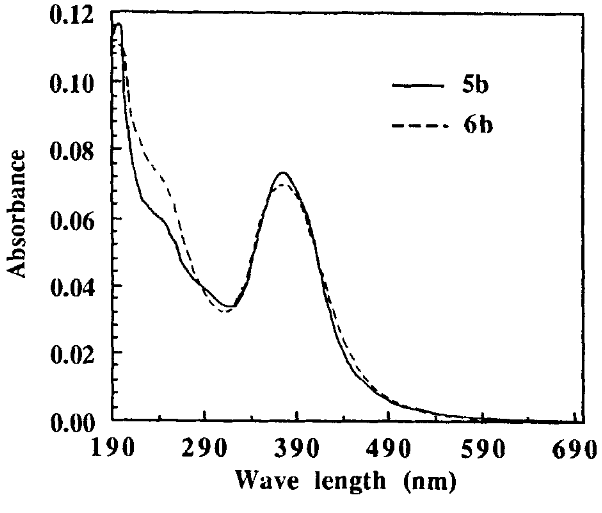


Fig. 3 Change of UV-visible absorption spectra of the LB films before (5b) and after (6b) imidization. Deposited 9 layers on a quartz substrate.

The orientation of the transition moments of the azobenzene unit (polymer backbone) were investigated by polarized UV spectroscopy. Figure 4 shows the polarized absorption spectra of 5c deposited 9 layers on the quartz plate measured with

0° and 45° incidence angles of the light with respect to the normal of the plate. The strongest absorption at 45° s-polarization indicated that the orientation of the polymer main chain was in the layer plane.

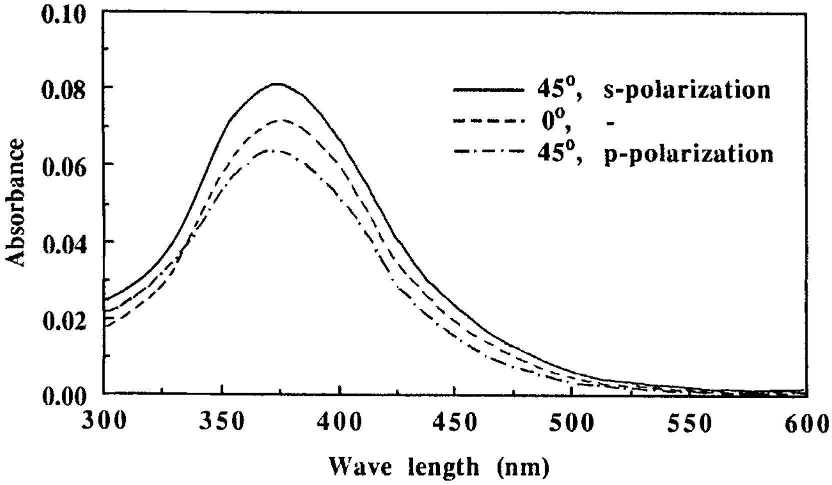
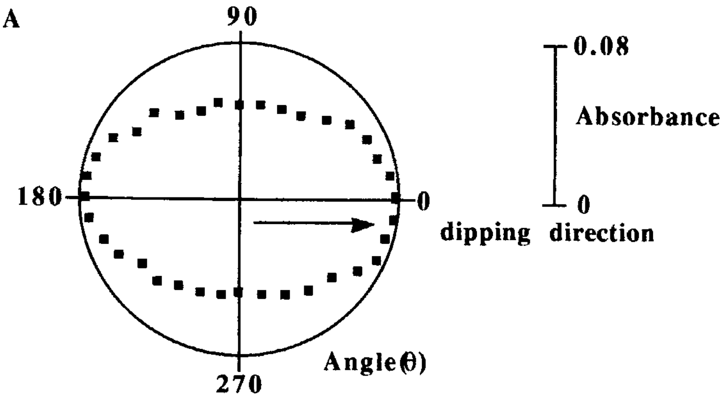


Fig. 4 Polarized UV-visible absorption spectra of 5c.
Deposited 9 layers on the quartz substrate.

Figure 5 shows the variation of absorption in the case of 5a and 5c at 380nm, where the sample was irradiated by polarized light beam normal to the plate changing the polarization angles with respect to the dipping direction. The aromatic polymer 5a in



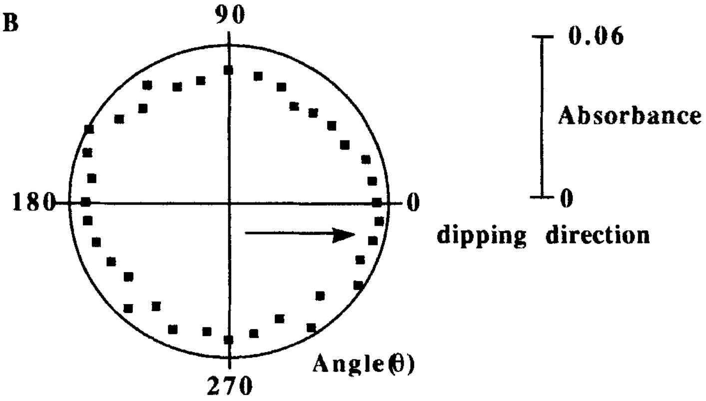


Fig. 5 Orientation of the polymer chain with respect to the dipping direction. A: 5a, B: 5c.

Fig. 5(A) exhibits a preferential orientation parallel to the dipping direction, whereas the aliphatic polymer 5c in Fig. 5(B) does not exhibit the particular orientation. Here, the absorption of the polarization direction parallel and perpendicular to the dipping direction was recorded as $A_{||}$ and $A_{\perp}$, respectively. Comparing the dichroic ratio ($D=A_{||}/A_{\perp}$) listed in Table 1, the orientation of the transition moments of the azobenzene unit was strongly dependent on the structure of the diamines (aromatic or aliphatic). In the case of the aromatic polymers, the polymer backbone was oriented preferentially parallel to the dipping direction since the dichroic ratios was greater than 1[8]. On the contrary, the dichroic ratio of the aliphatic polymers were almost 1, which indicated that the aliphatic polymer backbone oriented randomly to the dipping direction. The flexibility of the aliphatic chain in the polymer backbone restricted the formation of the highly oriented monolayer at the dipping stage.

Table 1 Orientation of the polymer backbone in polyamic acid and polyimide LB films.

LB film	Dichroism*	
	polyamic acid	Polyimide
a	1.47	1.51
b	1.24	1.21
c	0.97	1.05
d	1.09	1.13
e	1.06	1.01

* Absorbance ratio of $A_{||}$ / $A_{\perp}$ at 380 nm

The reversible photo-isomerization properties of the polymeric LB films were determined by the UV spectroscopy. the conformational change from trans to cis isomers was caused by irradiation of the light at 380 nm, whereas the reverse change from cis to trans isomers was achieved by irradiation of the light at 500 nm or thermal treatment. As shown in Figure 6, the trans to cis isomerization and its recovery were observed as decrease and increase of the absorption at 380 nm, respectively.

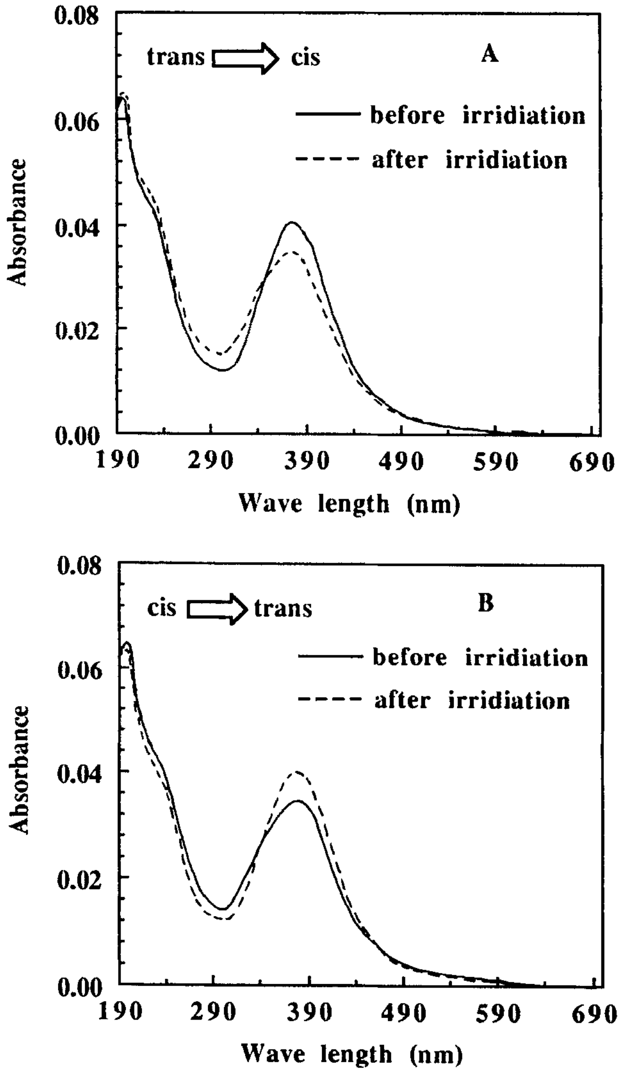


Fig. 6 Changes of UV-visible absorption spectra of 6c.
A: before and after irradiation with the light at 380 nm for 30 min.
B: before and after irradiation with the light at 500 nm for 5 min.

The photo-induced trans to cis isomerization property was compared by the decrease of the absorption after irradiation with the light at 380 nm for 30 minutes. As listed in Table 2, both the polyamic acid and polyimide LB films caused photo-isomerization to a relatively large degree. This made it possible to fabricate the photo-memory systems, where the light at 380 nm could be used for the photo-writing and that at 500 nm could be used for photo-erasing, respectively. It was noteworthy that the polyamic acid LB films had almost the same efficiency in the isomerization, which indicated that the structure of the diamines did not have any influence in the conformational change of the azobenzene unit. On the other hand, the efficiency of the isomerization of the polyimide LB films were sensitive to the structure of the polymer main chain. The conformational change in the aromatic polyimides was more difficult compared with the case of the aliphatic polyimides, because the former possessed the higher rigid chemical structure and the higher steric hindrance during the isomerization.

Table 2 Photo-isomerization efficiency of polyamic acid (5) and polyimide (6) LB films.

LB films	Isomerization (%) *	
	Polyamic acid	Polyimide
a	24.6	8.01
b	20.2	8.23
c	22.6	12.3
d	25.8	15.4
e	24.3	14.1

* Decrease in the absorbance at 380nm after irridiation with the light at 380nm for 30 min.

CONCLUSION

In conclusion, two series of polyamic acid derivatives containing the photo-sensitive azobenzene unit in the backbone were synthesized and fabricated into the polyimide LB films. The orientation of the transition moments of the azobenzene unit (polymer backbone) was anisotropic and isotropic in the layer plane with respect to the dipping direction, depending strongly on the structure of the diamines. A preferential orientation parallel to the dipping direction was obtained when the polymers contain the aromatic diamines. On the contrary, when the aliphatic diamines were incorporated into the polyimides, a random orientation was observed. The reversible photo-isomerization property of the azobenzene unit was also controlled by the structure of diamines. The conformational change was more difficult in the case that aromatic polyimides were used instead of aliphatic polyimides.

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