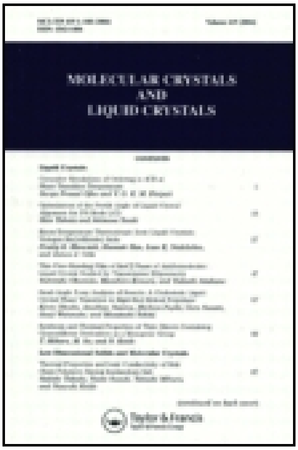

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New Memory Systems Constructed with Polyimide LB Films Having Azobenzene Pendant Groups: Behavior of In-Plane Anisotropic Photoisomerization, Photoinduced Optical Anisotropy, and Anisotropic Photofading

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NEW MEMORY SYSTEMS CONSTRUCTED WITH POLYIMIDE LB FILMS HAVING AZOBENZENE PENDANT GROUPS: BEHAVIOR OF IN-PLANE ANISOTROPIC PHOTOISOMERIZATION, PHOTOINDUCED OPTICAL ANISOTROPY, AND ANISOTROPIC PHOTOFADING

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Abstract Polyamic acids functionalized by azobenzene units possessing p-methoxy (3a) and p-nitro (3b) subtituents as pendant groups were newly synthesized for photomemory materials. Langmuir-Blogdett (LB) films of polyimides 5a and 5b were prepared by "Precursor Method" via LB films of polyamic acid long alkyl amine salts 4a and 4b. FTIR transmission and RA spectroscopy revealed conformational change of the pendant azobenzene groups between polyamic acid and polyimide LB films. Three kinds of new photomemory systems were fabricated using the polyimide LB films. In the beginning, the polyimide LB film of 5a performed in-plane anisotropic trans-cis photoisomerization on irradiation of the linearly polarized light at 400 nm. The reversible change (erase) was achieved by irradiation at 500 nm. Second, reversible photoinduced optical anisotropic property was observed in this LB film of 5a, which was caused by the alternative polarized light at 400 nm and nonpolarized light at 500 nm. The anisotropic property was erased by irradiation of the nonpolarized light at 400 nm. The third example was in-plane anisotropic photofading in the LB film of 5b. After irradiation of the polarized argon ion laser to the LB film, decrease in absorption due to photobleaching of chromophore was observed selectively in the parallel plane to the incident polarization.

INTRODUCTION

The Langmuir-Blodgett (LB) technique is one of the excellent technologies to manipulate the materials at the molecular level. Recently, many kinds of LB films have been investigated and applied to molecular devices, where polymeric LB films possessing functional groups have been expected as promising those candidates because they exhibit excellent thermal and mechanical stability compared with those of low molecular weight materials.[1,2] We have been developed unique polymeric LB films possessing no long alkyl chain by means of "Precursor Method".[3-5] The basic concept of this method was that nonamphiphilic and insoluble polymeric LB films were prepared via amphiphilic and soluble polymeric precursor LB films. For instance, the LB films of thermally and mechanically stable polyimides were prepared via the LB films of amphiphilic polyamic acid long alkyl amine salts. It has been also demonstrated that some functional groups can be incorporated into polyimide LB films.[6-8]

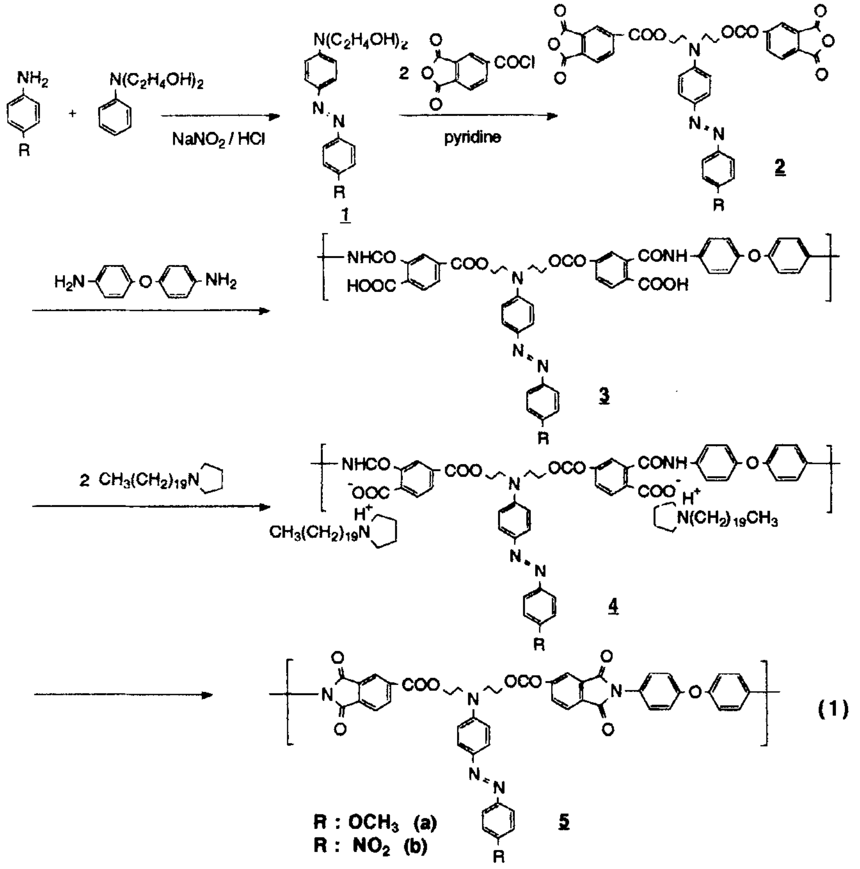
The photochromic behavior is the photoinduced reversible isomerization of a specific organic molecule between two isomers having different colors. Azobenzenes are typical photochromic molecules, which generally have strong anisotropy of absorptions between parallel and perpendicular directions along the molecular axis. They are also known as photochromic molecules based on trans-cis reversible isomerization. The isomerization from trans to cis form is carried out by irradiation of the light around at 400 nm corresponding to π–π^* transition moment, while the cis form can be reversed to the trans form by either irradiation of visible light or thermal treatment. LB films possessing azobenzene groups have been prepared to fabricate the photomemory devices.[2] Some attempts were disappointed, because the LB films were too rigid to show the photochromic behavior of azobenzene groups. We also synthesized polyamic acids having azobenzene units in their backbone. Polyimide LB films were also prepared from the polyamic acids to examine the molecular orientation of Langmuir (L) and LB films. However, photoisomerization of azobenzene unit was not observed in LB films of polyimides.[9]

In this study, we prepared the novel polyamic acid and polyimide LB films possessing azobenzenes as pendant groups. Conformational investigation of the LB films was also determined by infrared transmission and reflection-absorption (RA) spectroscopy.[10-12] After these investigations, we discussed about new kinds of memory systems in the polyimide LB films using the linearly polarized photoirradiation, which consisted of the in-plane anisotropic photoisomerization and the photoinduced optical anisotropic property[14-16] of methoxy substituted azobenzene pendant group, and in-plane anisotropic photofading in the LB film possessing nitro substituted azobenzene group.

EXPERIMENTS

Eq. (1) shows a synthetic rout of pendant type polyamic acids for LB films presented in this study. 4-Methoxy and 4-nitro 4'-[bis(2-hydroxyethyl)amino]azobenzenes 1 was synthesized by the reaction of the corresponding aniline derivatives and bis(hydroxyethyl)aniline in the presence of sodium nitrite and hydrochrolic acid.[17] Esterification of 1 with 4-chloroformylphthalic anhydride lead to the azo dye monomer tetracarboxylic dianhydride 2, which afforded polyamic acid 3 by the reaction with 4,4'-diaminodiphenyl ether.

Spreading solution of polyamic acid long alkyl amine salt 4 were prepared by mixing the solution of polyamic acid 3 at a concentration of 1.0 mmol/l in a mixture of



(1)

N,N-dimethylacetamide (DMAc) and benzene (1:1 by volume) with the solution of N-icosylpyrrolidine in the same solvent system in the ratio of 1:2 by volume.[3] The measurement of surface pressure-area (π-A) isotherms and the deposition of the monolayer films were carried out by the commercial Langmuir trough (San Esu Seiki) using a Wilhelmy's plate. The compression speed of a moving barrier was kept constant at 20 mm/min and the dipping speed of substrates was 8 mm/min for both down and upward strokes. After deposition of the monolayer films onto substrates, imidization was carried out by heating at 120°C for 30 min in vacuo. Infrared spectra were measured by a JEOL JIR-MACRO 6000 FTIR spectrometer equipped with a MCT (mercury cadmium telluride) detector with a resolution of 4 cm^{-1}. A reflection attachment (IR-RSC150) was used for RA spectroscopy. The p-polarized infrared beam by a polarizer (IR-OPT02) was incident on the sample plane at 80° from the surface normal. Two thousands scans were accumulated to obtain a spectrum possessing acceptable signal/noise ratio. Xenon lamp (USHIO UI-501C) of 500 W and appropriate interface filters (MELLES GRIOT) and argon ion laser (Spectra-Physics, Model 164) operated at 458 nm with the intensity of 33 mW/cm^2 were used for photoirradiation. The spectrum change and the polarized absorption spectra were followed by a Hitachi U-3400 spectrometer and a Otuka MCPD-1000 multichannel spectrophotometer with a polarizer.

RESULTS AND DISCUSSION

Preparation and Characterization of LB Films

Polyamic acids, 3a and 3b, synthesized for the present study had azobenzene groups substituted by methoxy and nitro functional groups, which were electron donating and withdrawing groups, respectively. Figure 1 shows the π-A curves of polyamic acid alkyl amine salts 4a and 4b. The surface pressure started to increase at relatively large area and then raised steeply up to 40 mN/m where condensed monolayers were formed. Both L films of 4a and 4b possessing the different substituents should have a similar conformation on the water surface because these two monolayers traced the similar curves each other. Monolayers on the water surface could be transferred onto various solid substrates by means of the vertical dipping method (LB method) with the Y-type deposition starting a transfer to the hydrophilic surface in the first up mode.

Figure 2 represents FTIR transmission spectra of the LB films of 4b and 5b deposited 7 layers on both sides of CaF_2 plates. The latter LB film was obtained by heating the LB film of 4b at 120°C for 30 min in vacuo. In the spectrum of the precursor LB film of 4b (Figure 2a), two intense bands at 2922 and 2853 cm^{-1} corresponding to

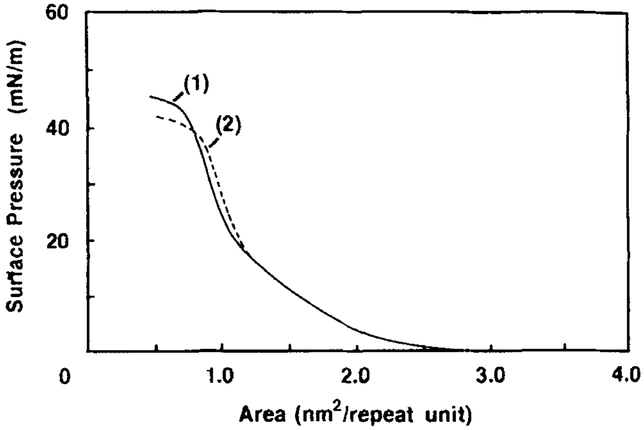


FIGURE 1 π-A curves of monolayers of 4a (1) and 4b (2), spreading from 0.33 mmol/l in DMAc/benzene =1/1 at 20°C.

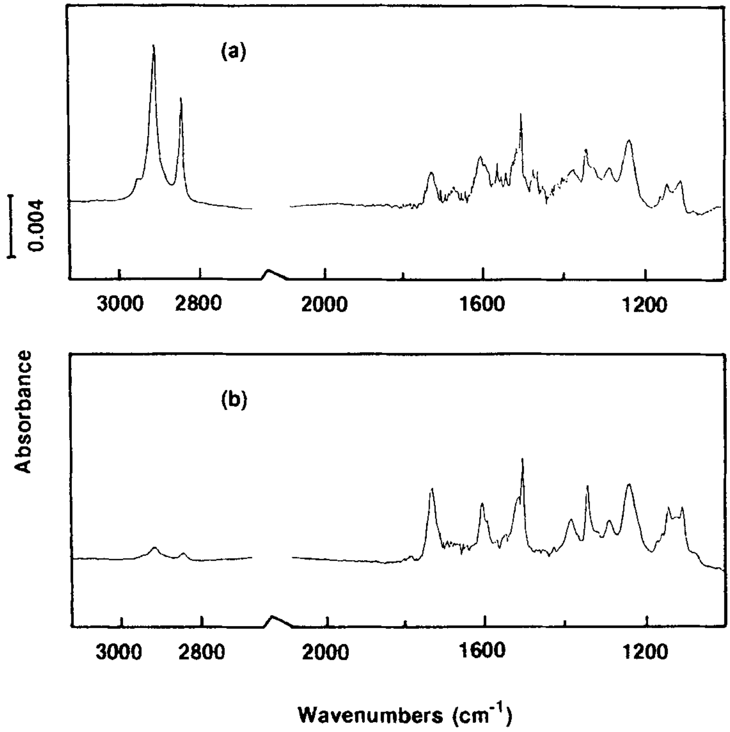


FIGURE 2 FTIR transmission spectra of the LB films of 4b (a) and 5b (b). Seven layers LB films were deposited on both sides of CaF_2 plates.

CH_2 antisymmetric and symmetric stretching modes of hydrocarbon chain and a weak band of CH_3 asymmetric stretching at 1960cm^{-1} were observed. These absorptions and amide carbonyl absorptions at 1674 and 1559 cm^{-1} disappeared in the IR spectrum of the polyimide LB film of 5b (Figure 2b), where characteristic absorptions of imide carbonyl at 1780 and 1727 cm^{-1} coinciding with the ester carbonyl band were newly observed. These spectrum changes indicated that the chemical structure of the polyamic acid long alkyl amine salt 4b was converted into the polyimide 5b with removal of the long alkyl chains by heat treatment.

The conformation of the polyamic acid LB film in addition to the characterization of the pendant groups were determined by means of FTIR transmission and RA spectroscopies. Since the electric field vector of IR beam is perpendicular to the surface plane in RA measurements, the relative intensity of the bands with the transition moment perpendicular to the surface should be enhanced in RA spectra. And the

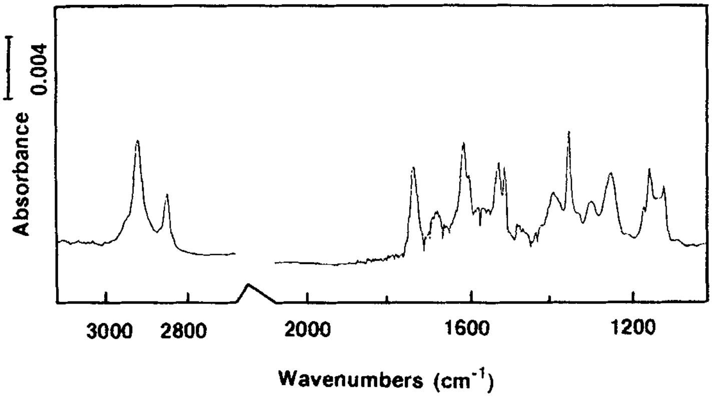


FIGURE 3 FTIR RA spectrum of the LB film of 4b. Seven layers LB film was deposited on Ag evaporated glass.

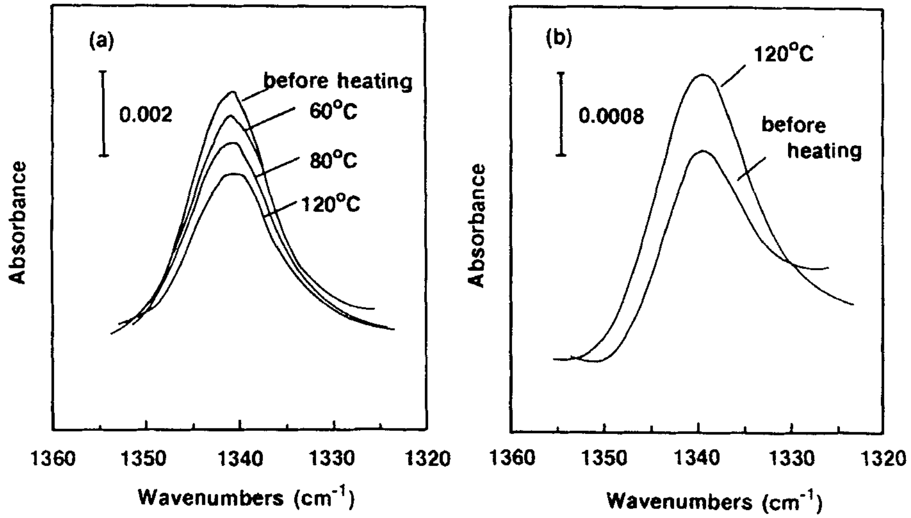


FIGURE 4 FTIR RA (a) and transmission (b) spectra of the symmetric NO_2 stretching mode of 4b at elevated temperature.

orientation of the particular groups can be evaluated by comparing the relative intensity of the absorption in RA spectra with these in transmission spectra, where the electric field vector of the IR beam is parallel to the surface of the LB films.[10-12] As shown in Figure 3, a weak band at 2871 cm^{-1} due to symmetric CH_3 stretching was observed in the FTIR RA spectrum of 7 layers LB film of 4b deposited on a silver evaporated glass. Comparing with transmission spectrum in Figure 2a, the relative intensity of symmetric and antisymmetric CH_2 bands were observed with weaker intensity in the RA spectrum. Since it has been known that vibrational planes of symmetric and antisymmetric CH_2 stretching are perpendicular to the axis of alkyl chain, these spectra indicated that alkyl chains tended to orient perpendicular to the film surface. However, the tilting angle of the alkyl chains was not so large compared with that in fatty acid LB films showing larger difference in the intensities between two spectra.[6-8] On the other hand, the relative intensity at 1338 cm^{-1} corresponding to symmetric NO_2 stretching was also observed in RA spectrum. The transition moment of symmetric NO_2 stretching should be almost parallel to the molecular axis of azobenzene group. Figure 4 shows the change of symmetric NO_2 band at 1338 cm^{-1} measured by FTIR RA and transmission spectra with heating at elevated temperature. Upon heating the LB film of 4b, the intensity in RA spectra (Figure 4a) decreased, while that in transmission spectra (Figure 4b) increased. These observation indicated that the azobenzene group, which had been oriented perpendicular to the film surface in the precursor LB film of polyamic acid long alkyl amine salt, lay on the surface in the polyimide LB film. Azobenzene group possessing methoxy substituent in the LB films of 4a and 5a should play the same conformational behavior of those of 4b and 5b, because π-A curves of 4a and 4b were almost identical as shown in Figure 2.

The conformational change of pendant groups between the precursor and polyimide LB films was also examined by UV spectra. Figure 5 shows pairs of absorption spectra of 9 layers LB films of 4a and 5a, and 4b and 5b deposited on quartz plates. The respective absorption bands centered at 405 nm and 475 nm in the LB films of 4a and

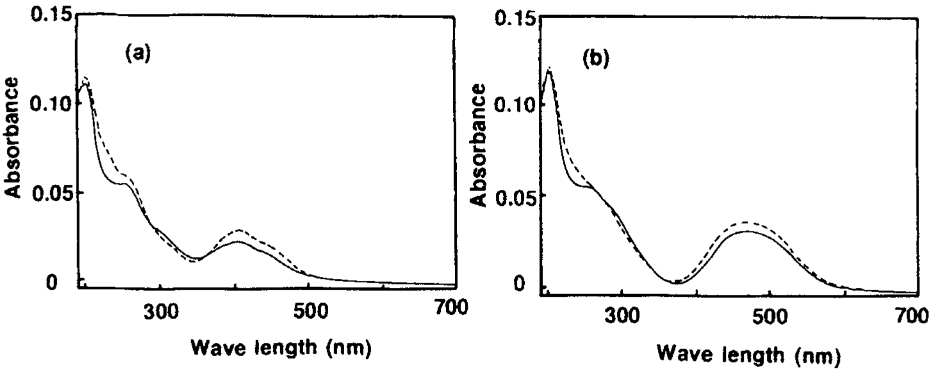


FIGURE 5 Change of UV spectra of the LB films before and after heat treatment of 4a (a) and 4b (b): 4a and 4b are solid lines, and 5a and 5b are dotted lines.

4b were assigned as π–π* transition moment of the trans azobenzene groups. In the spectrum of the LB film of 4b, λ_{max} sifted to longer wave length because of the strong electron withdrawing property of the nitro group. After imidization, the LB films of 5a and 5b did not show any shift in λ_{max}, while the intensity of absorption increased in both cases. Since the electric field vector of UV light was parallel to the film surface, the spectrum change between the precursor and polyimide LB films suggested the conformational change of azobenzene pendant groups during heating. In the precursor LB films of 4a and 4b, pendant groups were assumed to align to the perpendicular direction of the surface, while they lay on the surface after heat treatment. Consequently, the absorption of azobenzene groups in the polyimide LB films of 5a and 5b, in which π–π* transition moment was parallel to the electric field of UV light, was larger than that in the LB films of 4a and 4b. This assumption of conformational change was consistent with the results in the FTIR measurements discussed above.

In-Plane Anisotropic Photoisomerization of LB Film of Polyimide 5a

The spectrum change due to trans-cis photoisomerization was observed in the LB film of the precursor 4a upon irradiation of the light at 400 nm and the spectrum recovery was achieved by irradiation at 500 nm. The slower thermal recovery was also observed in dark for more than 30 min at room temperature. The LB film of polyimide 5a also afforded the same but smaller spectrum change. The smaller spectrum change should be caused by the close-packed multilayer structure of the polyimide LB film accompanied by elimination of the long alkyl chains during imidization. In our previous work, it was reported that any spectrum change was not observed in the polyimide LB films because of the rigid structure of polyimide, where the azobenzene group was incorporated in the polymer backbone.[9] However, it is interesting that the reversible photoisomerization was observed in the LB film of polyimide 5a having azobenzene unit as the pendant group, which was allowed a structural change.

Photoisomerization experiments described above were done using the nonpolarized isotropic irradiation of UV light. Next, we examined the in-plane anisotropic photoisomerization behavior of the LB films 4a and 5a. Figure 6a shows representative spectrum change of the LB film of 4a with irradiation of the linearly polarized light at 400 nm for 10 min, where the polarized plane was parallel to the dipping direction. The large spectrum change caused by the trans to cis photoisomerization was observed in both parallel and perpendicular planes to the polarization of the irradiated light. This spectrum change was reversible to the initial state rapidly with irradiation of light at 500 nm for 1 min. Thus, any anisotropic response against the irradiation of the polarized light was not observed in this spectrum. When the polarized light in the same wave length was irradiated to the LB film of 5a, the spectrum change was larger in the parallel plane to the light polarization than that in the perpendicular plane as shown in Figure 6b. Such difference in photoresponse of the LB films of 4a and 5a against the polarized light should be attributed to the specific conformation of azobenzene group in the polyimide LB films, in which they lay flat on the surface to the random direction. Because the electric field vector of the polarized light was parallel to the surface, the sensitivity of the anisotropic photoresponse against the light was rather small in the polyamic acid LB film, where the π–π* transition moment should align to the perpendicular direction of the surface. On the other hand, the anisotropic photoresponse increased in the polyimide LB film, whose π–π* moment of azobenzene group was parallel to the electric field vector of the incident light. The anisotropic trans-cis photoisomerization of azobenzene units in LB films has not been reported so far, and should be useful to fabricate a memory device. However, it is difficult to retain the optical anisotropic state for a long period because of the thermal relaxation to the initial conformation.

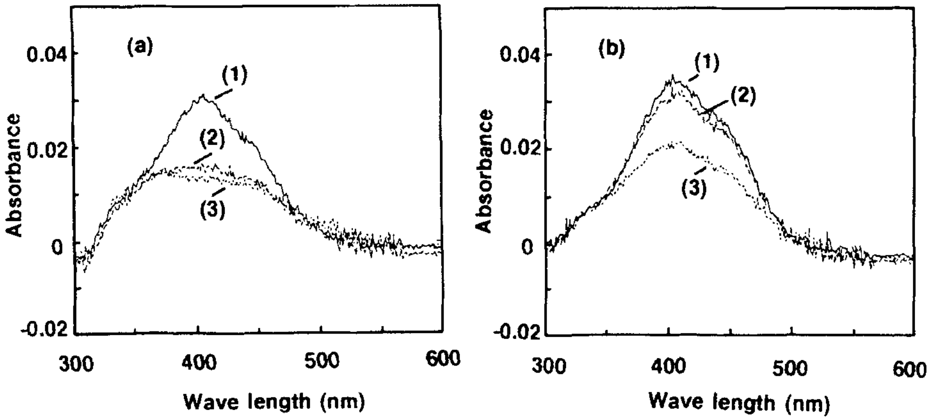


FIGURE 6 Polarized absorption spectra of the LB films of 4a (a) and 5a (b): before irradiation (1) ; after irradiation, observed parallel (2) and perpendicular (3) to polarization of the irradiated light.

Photoinduced Optical Anisotropy in LB Film of Polyimide 5a

After the LB film of 5a was irradiated by the polarized light at 400 nm (Figure 6b), the conformational change from cis to trans was caused by irradiation of nonpolarized light at 500 nm. Spectrum recovery of Figure 6b after irradiation at 500 nm is shown in Figure 7a. It was noteworthy that increase of the absorption in the perpendicular plane against the polarization of the irradiation light was observed, on the other hand, that in the parallel plane decreased comparing with the initial spectrum. The result obtained here suggested that the reorientation of azobenzene pendant group was occurred during trans-cis photoisomerization and cis-trans recovery. This phenomenon is known as a photoinduced optical anisotropy.[15,16] Azobenzene trans-cis and cis-trans transition follows a fundamental role in the longitudinal molecular axis rotation, leading to a change in the dye molecule orientation.

Photoinduced optical anisotropy is considered to be a new kind of aim of in-plane optical recording as follows. In the beginning, the LB film of 5a had no in-plane anisotropic character. The stage shown in Figure 7a, obtained after irradiation of the polarized light at 400 nm and subsequent irradiation of visible light at 500 nm, is a written state. This thermally stable state could be erase by the irradiation of the nonpolarized light at 400 nm and subsequent irradiation of visible light as shown in Figure 7b, where dichromism was disappeared and the two absorption bands in perpendicular and parallel plane were equal each other. This reversible photoinduced optical anisotropy could be repeated many times by irradiation of alternative polarized and nonpolarized light. Thus, the polyimide LB film of 5a demonstrated new in-plane optical anisotropy after one cycle of trans-cis photoisomerization induced by the linearly polarized light and successive cis-trans recovery using the visible light. Furthermore, we could successfully fabricated reversible ON/OFF optical anisotropic device, because the written information could be erased by irradiation of the nonpolarized light.

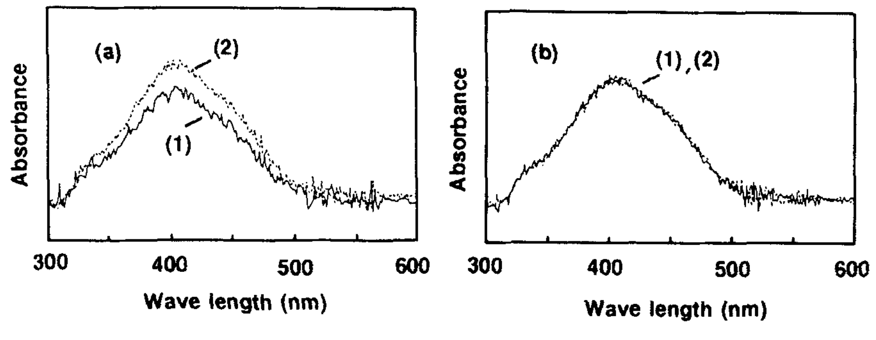


FIGURE 7 Polarized absorption spectra of the polyimide LB film of 5a: (a) the LB film of 5a was irradiated by the polarized light at 400 nm, and successively, the conformational change from cis to trans was caused by irradiation of nonpolarized light at 500 nm. (b) the LB film of 5a at stage of (a) was irradiated by the nonpolarized light at 400 nm, and successively, irradiated by nonpolarized light at 500 nm. Spectra (1) and (2) were measured with polarization parallel and perpendicular to the irradiated polarization, respectively.

Laser Induced Optical Anisotropy in LB Film of 5b

Although photofading phenomenon, which is usually attended irreversible spectrum change, is observed in dye chemistry, potential applications of photobleaching to photodevices have not been reported so far. If in-plane selective photobleaching, whose optical axis is parallel to the incident polarization, can be achieved by the linearly polarized irradiation, it is possible to fabricate a new type of photon mode memory system written by the polarized beam.

When argon ion laser light at 458 nm was irradiated to the polyimide LB film of 5b having p-nitroazobenzene group, the decrease in absorption at 480 nm was observed. This spectrum change should be due to the photofading caused by the photobleaching process, because the spectrum did not recover by irradiation of the visible light. On the other hand, any spectrum change in UV region (200-300 nm) of polyimide backbone

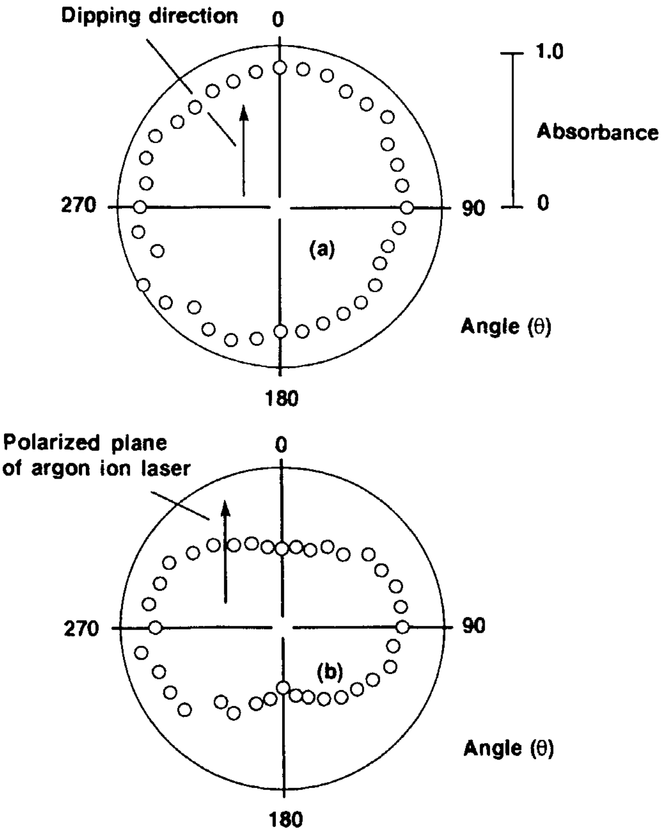


FIGURE 8 Polarized absorption diagrams of the LB film of 5b at 480 nm as a function of the angle between the plane of dipping and polarized direction before (a) and after (b) irradiation of argon ion laser.

was not observed even after irradiation of the laser beam, that indicated the photobleaching was achieved only in the azobenzene unit. Figure 8a and 8b show the polarized absorption diagrams rotating the LB films of 5b by 10° at 480 nm before and after irradiation of the linearly polarized argon ion laser, respectively. The absorption is displayed as a function of the angle between the film dipping direction (0° and 180° planes) and the polarized plane of absorption spectra. The distance between the center of the diagram and the white circles is absorbance. Argon ion laser was irradiated from the normal direction to the LB film, whose polarized direction was parallel to the film dipping direction. In the diagram of Figure 8a, any anisotropy of absorption was not observed in the film surface, thus the orientational distribution was concluded to be quite isotropic before the laser irradiation. On the other hand, the polarized diagram in Figure 8b was obtained after irradiation of the linearly polarized argon ion laser. The decrease in the absorption was maximized in the region centered at the laser polarization. While, the azobenzene groups, in the region of the angle 30-40° toward the perpendicular axis, was not affected by the incident beam. It is interesting that we could not observe any recovery of the decrease in the absorption intensity. Thermal recovery of the optical anisotropy like Figure 6b is a serious problem for the fabrication of the photon mode memory system. The optical anisotropy shown in Figure 8b demonstrated the thermal stability for more than 20 h at 100°C. The dichroic ratio calculated from the respective intensity of the absorptions in the parallel and perpendicular planes was more than 2. The time dependence of photobleaching ratio, calculated from the equation of $(A^0-A^t)/A^0$ (A is absorbance in the parallel plane), reached about 0.5 (equilibrium) after 40 min of irradiation. While, the maximum dichroic ratio was about 2.3, which tended to decrease with longer irradiation.

CONCLUSION

In conclusion, three types of optical memory systems in the polyimide LB films were fabricated. The first was the in-plane anisotropic photoisomerization of the LB films of 5a caused by irradiation of the polarized light. The second was the photoinduced optical anisotropy observed in the LB film of 5a, which was applied to the erasable optical memory. These properties were based on the azobenzene trans-cis photoisomerization. The third was the photon mode recording system written by the laser photobleaching of the chromophore in the LB film of 5b. The resulting LB film had a large dichromism and performed a good thermal stability.

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