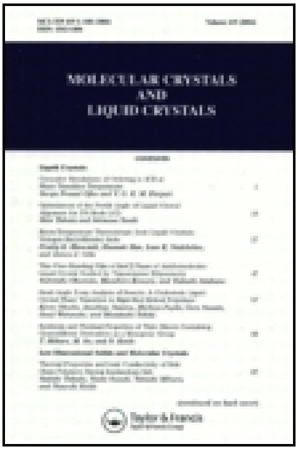

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Reversible Photochromic Behaviors of Fatty Acids with Azobenzene Chromophore in Thin Film Assemblies

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The mechanism of reversible photoinduced anisotropy of an azobenzene derivative was investigated by measuring optical retardation and UV/Vis dichroism. During the relaxation period, the cis-trans thermal back relaxation and orientational relaxation of azobenzene groups occur. It is believed that the orientational relaxation of trans and cis azobenzene groups to relieve the strains is a more dominant contribution to the decrease of the optical anisotropy in the film.

Keywords: azobenzene; optical anisotropy; phoisomerization

INTRODUCTION

The photochemical isomerization of azobenzene has been a subject of much investigation due to its potential use in optical devices. Azobenzene derivatives are particularly attractive materials and have been widely investigated for a long time due to their reversible trans-cis photoisomerization. Furthermore, an induction of optical anisotropy in azobenzene films by the use of linearly polarized light provides a new approach to alignment of liquid crystal molecules and an optical storage medium.[1,2] In the present study, reversible photoinduced anisotropy of an azobenzene derivative 4-octyl-4'-(5-carboxy-pentamethyleneoxy)-

azobenzene (ABD) was investigated as a potential application for the optical storage medium. The macroscopic alignment of the molecules induced by polarized light was detected by measuring the UV/Vis dichroism and optical retardation of the sample.

EXPERIMENTAL

The azobenzene containing fatty acid used in this study was ABD of Dojindo Laboratories. Guest-host type samples were prepared by dissolving ABD in cyclohexanone solutions of polymethylmethacrylate (ABD:PMMA 10:90). Solutions were filtered and deposited by spin coating onto a quartz plate. Films were then heated for one hour at 60 °C to remove any remaining solvent. The optical anisotropy in the films was induced by using an Altech 500 W high pressure mercury lamp with a Glan-Taylor polarizer. A thick glass plate was used to remove UV light with shorter wavelength (< 330 nm) and band pass filters (365 nm and 436 nm) were employed to produce monochromatic light. UV/Vis spectra of the films were obtained using a Hitachi U-2000 double beam spectrometer. In-situ monitoring of photoinduced anisotropy of the films was carried out by measuring the transmitted intensity of a prove beam (He-Ne laser) while the films were exposed to the mercury lamp with a power of 50 mW/cm^2.

RESULTS AND DISCUSSION

A typical sequence of inducing and erasing optical anisotropy in the ABD/PMMA (10:90) film with polarized light (>330 nm) is shown in Fig. 1. An initially isotropic film was placed between crossed polarizers and no transmission of the probe beam was observed. After the film was exposed to the linearly polarized light, the transmission increased to approach a saturated level. Only azobenzene groups parallel to the polarization direction of irradiated beam are selectively activated for photoisomerization and inducing both trans-cis and cis-trans isomerization

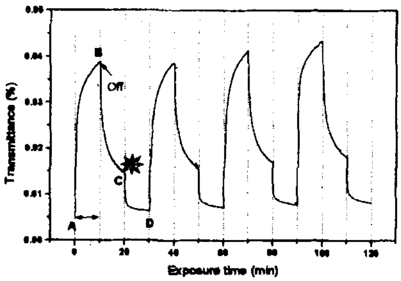

FIGURE 1. Inducing and erasing optical anisotropy on ABD film

processes. This leads to redistribution of azobenzene groups in the film and resulting that initially homogeneous distribution of the azobenzene groups becomes perpendicularly aligned to the polarization direction of the light. At a second stage (position B), the polarized beam was turned off and the transmitted light signal was seen to decrease. At a third stage (position C) in the sequence in Fig. 1, the induced anisotropy disappeared by irradiating the film with unpolarized light. This unpolarized beam randomizes the azo molecules and thus removes optical anisotropy in the film.

Figure 2 shows the UV/Vis spectral responses of ABD in PMMA matrix after the film was irradiated with 365 nm UV light. The absorption peak at 352 nm is due to π - π^* transition of the trans azobenzene chromophore with the transition moment parallel to its long axis.[3] The 352 nm band gradually decreases its intensity with irradiation time and a new band at 440 nm corresponding to the cis isomer is observed. The conversion of the cis isomer to the trans isomer was also observed for the film with irradiation of 436 nm light.

At each stages of one sequence in Fig. 1 (positions A, B, C, and D), UV/Vis spectra of the ABD film were obtained to understand the molecular mechanism of inducing and erasing the optical anisotropy. Although the anisotropy induction mechanisms during irradiation are well understood as explained in the previous paragraph, detailed relaxation mechanisms after light is off are not clearly known. It is believed that there are at least two separate relaxation processes including well-known cis-trans thermal back relaxation. In Fig. 3 (B and C), the trans azobenzene band of 352 nm increases its intensity slightly indicating the return to photochemical equilibrium from the photostationary state. However, the change in the intensity of 352 nm band is too small to ascribe the change observed in optical anisotropy only to the thermal back relaxation. During irradiation, angular redistribution of azobenzene groups through photoisomerization may impose significant strains on polymer chains and azobenzene groups. It is thus believed that an orientational relaxation of trans and cis azobenzene groups to relieve the strains may be a more dominant contribution to the decrease of the optical anisotropy in the film during the relaxation process.

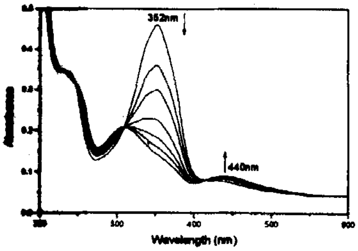

FIGURE 2. The changes of UV/Vis spectra of ABD film with irradiation of 365 nm light.

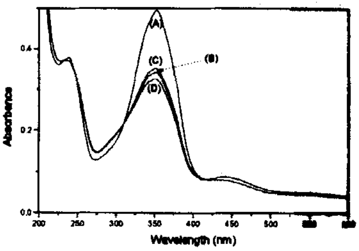

FIGURE 3. UV/Vis spectra of ABD film obtained at each positions marked in Fig. 1.

Acknowledgments

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