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## Photoinduced Orientation of Azobenzene Chromophores in Polymer Films

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## Photoinduced Orientation of Azobenzene Chromophores in Polymer Films

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In situ dynamical studies of photoinduced orientation of the azobenzene group in polymer films were carried out using real-time visible absorption and birefringence measurements. From these studies, the mechanisms of the photoinduced birefringence generation in the polymer films can be explained based on trans-cis isomerization, thermal back relaxation, and angular relaxation of reoriented trans isomers.

**Keywords:** photoinduced; anisotropy; azobenzene; relaxation; polymer

### INTRODUCTION

It is well known that azobenzene containing polymers show various potential applications and thus have received much attention in the last few years. The main interest of these systems is their birefringent properties when they are irradiated with a linearly polarized light. This birefringence in the films originates from the reorientation of azobenzene groups through trans-cis-trans isomerization cycles, which create an excess of azobenzene groups oriented perpendicular to the irradiated polarized light direction. Such a photoinduced isomerization of azobenzene groups has been a subject of much investigation due to its potential use as an optical storage medium.<sup>1</sup> In the present study, in situ dynamical studies of photoinduced orientation of the azobenzene derivatives in the polymer

films were carried out using real-time visible absorption and birefringence measurements.

## EXPERIMENTAL

The guest-host type sample was prepared by dissolving both Disperse Red 1 (DR1) and polymethylmethacrylate (PMMA) (10/90) into cyclohexanone, and spin-coated on a quartz plate. The side-chain type polymer was DR1-attached PMMA (10/90) and prepared the same way as the guest-host type sample. The optical anisotropy in the films was induced using a linearly polarized light ( $> 330$  nm) from the Nanotech 500 W high-pressure mercury lamp with an irradiance of  $50 \text{ mW/cm}^2$ . The birefringence was measured in-situ using a He-Ne laser and Glan-Thompson polarizers. In-situ measurements of visible absorption (at 546 nm) of the films were carried out by monitoring the absorbance in the parallel and perpendicular directions with respect to the pump light polarization.

## RESULTS AND DISCUSSION

A typical sequence of writing and erasing optical anisotropy in the films with a polarized light is shown in Fig. 1. During the writing period (A $\rightarrow$ B), the polarized pump beam is turned on, activating the trans-cis-trans isomerization cycles which result in the excess orientation of the azobenzene groups perpendicular to the irradiated polarized light direction. It is clear that the level-off of birefringence was achieved, and the saturation was higher in the side-chain type polymer than in the guest-host type polymer films. This is due to the difference in mobility of azobenzene groups in the guest-host type and in the side-chain type

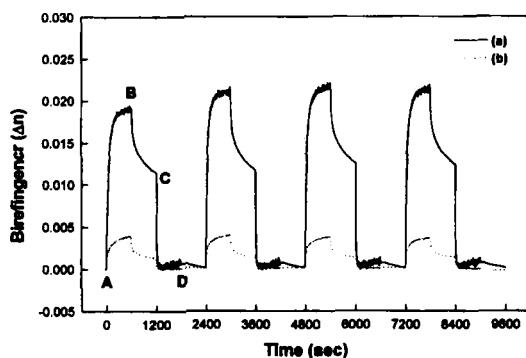


FIGURE 1. Typical writing and erasing curves for (a) the side-chain type polymer and (b) the guest-host type dye doped polymer. A→B: writing (polarized light), B→C: relaxation (pump off), C→D: erasing.

samples. During the writing period, three molecular level processes are competing one another. These are the photo-isomerization from trans (parallel to the polarization direction of the irradiated light) to cis isomers; cis to trans (both to parallel and perpendicular) thermal back relaxation; and angular relaxation of the reoriented trans (perpendicularly reoriented trans) azobenzene groups. Since one end of azobenzene is tethered to the polymer backbone in the side-chain type whereas not in the guest-host type, it is easy to understand that the difference in angular relaxation process is the main reason for the observed difference in the induced anisotropy. For the relaxation period (B→C), only thermal back relaxation and angular relaxation occur. Because of the same reason as in the writing period, the decrease of birefringence in the guest-host type sample is much larger than that in the side-chain type. Using results of in-situ measurements of visible absorption of the films, the amounts of all trans isomers in the films are expressed by the structural absorbance,  $T_0 = (2 A_{\perp} + A_{\parallel})/3 A_0$ , while the differences in the amount of trans isomers between the parallel

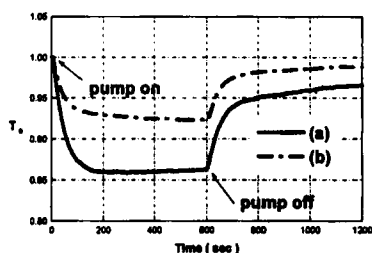


FIGURE 2. Time dependence of structural absorbance ( $T_0$ ).  
(a) side-chain, (b) guest-host.

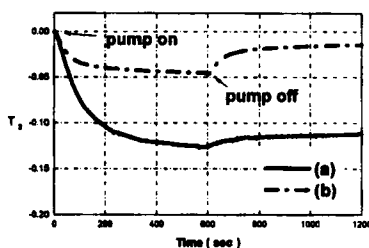


FIGURE 3. Time dependence of linear dichroism ( $T_2$ ).  
(a) side-chain, (b) guest-host

and perpendicular directions are expressed by the linear dichroism,  $T_2 = (A_{\parallel} - A_{\perp})/3A_0$ . As seen in Fig. 2 and Fig. 3,  $T_2$  continues changing at the photo-stationary state (after 200 sec) where the rate of photo-isomerization is the same as that of thermal back relaxation. This is due to the contribution of the angular relaxation which leads to the change only in  $T_2$ . At the relaxation period, the recovery of  $T_0$  is about the same for both types of samples, while the recovery of  $T_2$  is much larger for the guest-host type sample. This is because the rate of the thermal back relaxation, which is the only contribution to the change in  $T_0$ , is almost the same for both types of samples. However, since  $T_2$  is dependent on both thermal and angular relaxation processes, the recovery is faster for the guest-host type where the rate of angular relaxation process is much faster than in the side-chain type sample.

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### References

- [1] M. S. Ho, and A. Natansohn, *Macromol.*, **28**, 6124 (1995).