

## Influence of matrix polymer molecular weight on photo-induced transmission of azobenzene derivative doped in a polymer

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In order to investigate dynamic process in photo-isomerizable azo molecules, light transmission of strong excitation beam was monitored in DR1 doped PMMA thin films. The results showed quick decrease of absorbance due to photo-isomerization process which reached to a stationary state in one minute. Due to the dependence on molecular weight of the host polymer and excitation intensity, initial rising process was found to be governed by photo-isomerization rate of the guest, and magnitude of the change attained in photo-stationary state was found to be influenced strongly by host molecular weight.

Key words: azobenzene, DR1, photoisomerization, thin film.

### 1. INTRODUCTION

Extensive studies have been made for photo-induced isomerization and following dynamic processes in azobenzene derivatives, since these phenomena were very important for optical data/image processing based on induced optical constant modulation and also for microfabrication using molecular motion [1,2]. Azobenzene derivatives with push-pull type substituents as Disperse Red 1 (DR1) are in the ground *trans* state in equilibrium and are easily isomerized into *cis* state upon photon absorption, then return from the *cis* form to initial *trans* state with direction randomization. It is widely believed that these sequential processes were so quick that most molecules were in *trans* form aligned preferentially perpendicular to the actinic light field.

In order to investigate the photo-dynamic processes of azo dyes, many studies have been made in these several decades for many types of systems, of which configurations are guest-host polymer, covalently bonded azo polymer, liquid crystalline phase, sol-gel derived silica polymers and so on [3-6]. But experimental methods have not been in wide variety, but most techniques could be classified into photo-induced birefringence and diffraction observed in four wave mixing or two wave coupling geometries. Because of high sensitivity and good time resolution, undoubtedly these methods were very useful, but some inherent drawbacks make other complimentary methods important. In these techniques, it was difficult to distinguish the effects from the dye and those from matrix since both components might contribute to birefringence or change of refractive index. Additionally, in diffraction based methods, the effects from real and imaginary parts of optical constants or refractive and absorptive effects are not separable.

In this study, we employed a simple technique where intensity of transmitted excitation beam was monitored by a photodetector. With this method, it is possible to estimate the change of absorbance which is determined only by dye population and orientation distribution. We prepared thin films of DR1 doped poly-methylmethacrylate (PMMA) as a typical system to observe a temporal evolution of absorption coefficient or extinction coefficient under the irradiation of a single laser beam. Dependences on PMMA molecular weight and excitation intensity were studied to get insight into the mechanism of dye dynamics.

### 2. EXPERIMENTAL

For the fabrication of DR1 doped PMMA films, we used the dye and polymer provided by Sigma-Aldrich as purchased. Three types of PMMA with different molecular weights, namely 15,000, 120,000, and 996,000 were used. PMMA films incorporating 2wt% DR1 were fabricated from chloroform solutions with spin coating method. Absorption spectra measured with UV-1800 (Shimadzu) for these samples are shown in Fig. 1, indicating that spectral shape does not depend on the host molecular weight except for the slight blue shift observed for the sample with the highest molecular weight. Sample thickness and optical density at 532nm are summarized in Table I. The thickness was

evaluated with a surface profiler DEKTAK-6M. Because of the small values of absorbance, excitation beam intensity was almost uniform along the depth direction.

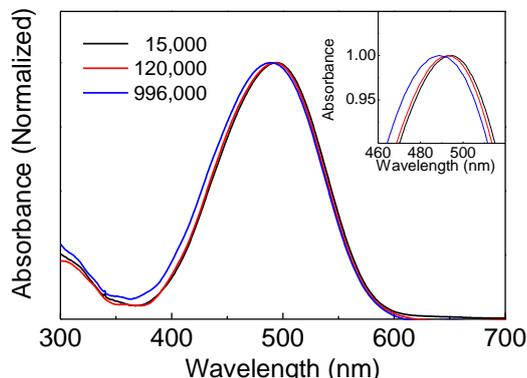


Fig. 1 Normalized absorption spectra of DR1 doped PMMA films made with three polymers of different molecular weight values. Numbers in legend indicate the molecular weight of PMMA. Inset is to show peak wavelengths clearly.

Table I. Thickness and optical density for three films of DR1 doped PMMA with different Mw values.

PMMA Molecular Weight	thickness ( $\mu\text{m}$ )	OD at 532nm
15,000	1.0	0.1690
120,000	1.2	0.1844
996,000	1.7	0.2395

Experimental setup is very simple as depicted in Fig. 2. Linearly polarized excitation beam was generated by a cw frequency-doubled YAG laser (Coherent) giving semi-Gaussian shaped beam with half-intensity diameter of 0.47mm. The peak intensity  $I$   $\text{mW}/\text{mm}^2$  can be obtained by formula  $I = P/0.963$  where  $P$  indicates the laser power given by the unit of mW. Irradiation state was switched by a mechanical shutter which repeated on and off every minute. Beam intensity was adjusted by neutral density filters. Time resolution was limited to be 0.5ms by the shutter speed.

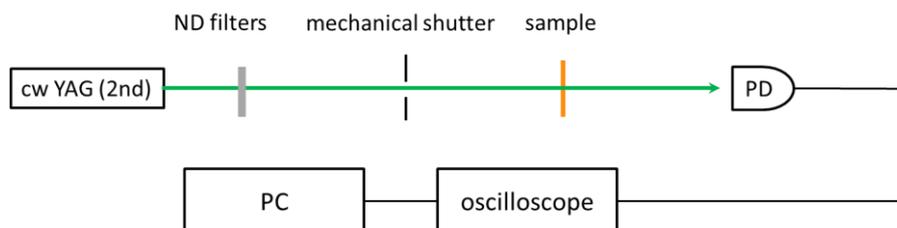


Fig.2 Schematic diagram of experimental setup.

The transmitted light intensity at time  $t$  can be converted to the change of the extinction coefficient of the sample with the following expression.

$$\Delta\kappa(t) = -\frac{\lambda}{4\pi d} \ln \left[ \frac{V(t)}{V(0)} \right] \quad (1)$$

where  $V(t)$  is output voltage of the photodetector,  $\lambda$  is the wavelength and  $d$  indicates film thickness. Since the change of the value was always negative,  $-\Delta\kappa$  values were used for  $\Delta\kappa$  in all figures and the description following.

### 3. RESULTS AND DISCUSSION

Experiments were done with three magnitudes of excitation intensities, namely 40, 80, and 160mW/cm<sup>2</sup> for all the three samples. Fig.3 shows evolutions of  $\Delta\kappa$  (a-c) in full time range of the measurements and (d-f) for the first one second. All runs showed the quick decrement (in figures, seen as increment) of absorption followed by gradual reduction approaching to photo-stationary states during the first one minute irradiation. In the repeated shining procedures, similar changes were observed with slight difference due to slower or semi-persistent components.

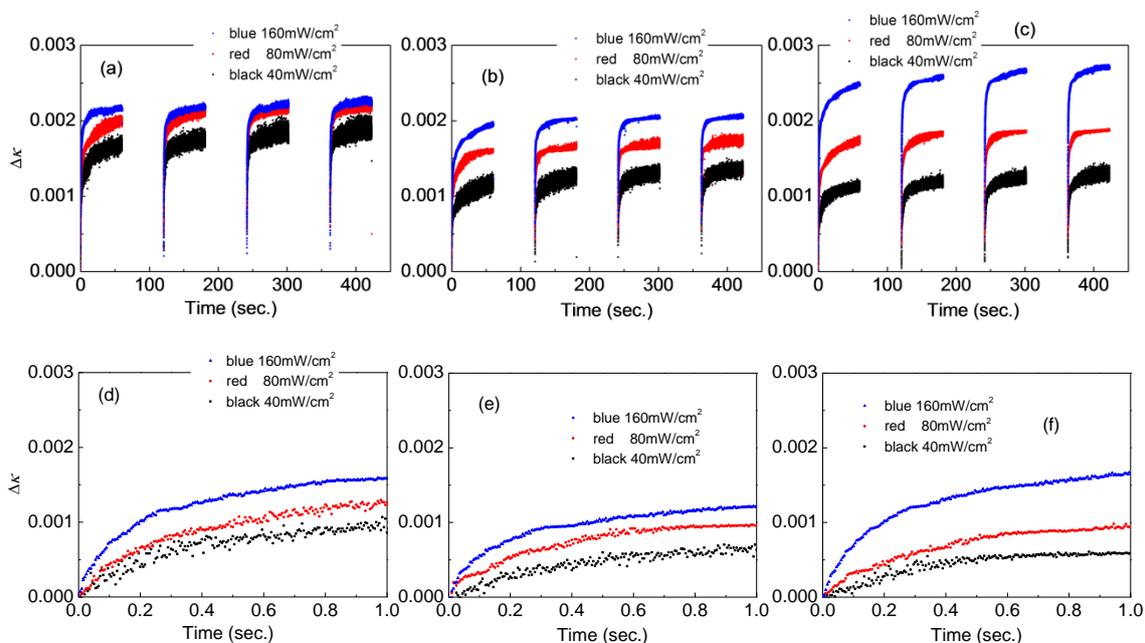


Fig. 3 Change of extinction coefficient under laser irradiation of three different intensities for three DR1/PMMA samples. Upper panels give results in full measurement time range and the lower ones give enlarged view for initial behaviors. Mw of matrix was (a)(d) 15,000, (b)(e) 120,000, and (c)(f) 996,000.

These behaviors depended on excitation intensity and also strongly on molecular weight of the host polymer. Magnitude of the change was larger when excitation intensity was stronger as expected but it was far from linear relationship, especially for the films composed of low molecular weight matrices. On the other hand, less significant difference were found in the starting behaviors as shown in Fig. 3(d-e), meaning that the rising up process was dominantly governed by incident light intensity.

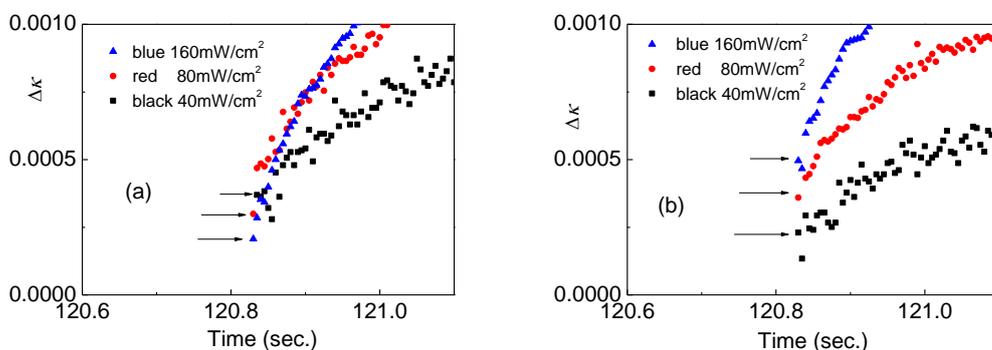


Fig. 4 Enlarged views of the data for Fig. 3 at the beginning of the second irradiation term. Arrows indicate the first data point just after shutter opening. Host Mw is (a) 15,000, and (b) 120,000.

The absorbance almost recovered during the first break period since  $\Delta\kappa$  values at the beginning of the second irradiation term were almost zero as shown in Fig. 3(a-c). However, there was an abrupt jump at the instance of shutter opening as found in Fig.4. These survived non-zero signals correlated to the magnitude attained just before the last shutter closure, since the initial values were roughly proportional to the excitation intensities. And these magnitudes gradually increased along with accumulation of total irradiation energy as known from Fig.3(a-c), indicating the growth of semi-persistent change.

Let us consider the results from three viewpoints as 1) initial build-up, 2) approach to photo-stationary state in a minute, and 3) persistent change observed at the beginning of each irradiation period.

Initial build-up gradients were roughly proportional to the excitation power. And in all three samples, shapes of build-up curves were qualitatively the same, indicating that the rate was governed by photo-isomerization of DR1 molecule. The roughly estimated response time 1sec. was consistent to the values obtained in several former studies [3,4].

The second process was dependent on the host molecular weight. When the molecular weight was small, photo-induced change saturated with weak pump power. On the other hand, final reaching points strongly depended on power for high Mw host. Since the magnitude was determined by the rate balance between photo-isomerization and relaxation, this fact indicated that relaxation was more significant for low Mw host. That might be reasonable because high molecular weight polymer would have high Tg and strongly hamper molecular motion.

The third process also might reflect the relaxation. Indeed, more prominent persistent change had been observed when covalently attached DR1 polymers were used in former studies [4]. This result indicated that high molecular weight would be somewhat effective to enhance persistency even in guest-host systems. Whether the process was determined by depopulation of *trans* state or by reorientation of *trans* molecules was not clarified in this study. In order to investigate the details of dynamic process in each time range, additional experiments and analysis are in progress.

#### 4. CONCLUSION

Temporal behaviors of DR1 doped PMMA under and after optical excitation were studied by monitoring transmission power with various intensities of excitation. Absorbance showed relative fast reduction in one second and reached to a stationary state in one minute. When molecular weight of the host was small, power dependence was less significant, indicating that relaxation force was weak in that case. Long lived components existed in all cases, although their magnitudes were smaller than the cases for covalently bonded azo polymers.

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