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# Determination of transition rate constants of *trans–cis* isomerization in a poly(malonic ester) containing disperse red 1

H. D. Shin, W. J. Joo, C. H. Oh, and P. S. Kim Department of Physics, Hanyang University, Seoul 133-791, Korea

Y. K. Han

Department of Chemistry, Hanyang University, Seoul 133-791, Korea

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We suggested a simple method for obtaining the quantitative transition rate constants of *trans-cis* isomerization in the pseudo-stilbene-type of azobenzene molecule. The absorbances of the solution and film of a poly(malonic ester) containing disperse red 1(PDR1) were measured with the pumping beam intensity, and analyzed by the rate equation for the fractions of *trans* and *cis* conformers. The rate constants of PDR1 solution and film were successfully determined. © 2002 American Institute of Physics. [DOI: 10.1063/1.1487825]

# I. INTRODUCTION

The polymers containing azobenzene molecules have received considerable attention because of the merits of fabrication, reversibility, high birefringence, and photochromic property for optical data storage.<sup>1-3</sup> The origin of optical data storage is founded on the photoinduced birefringence caused by the reorientation of the azobenzene molecule. The reorientation is dependent on the rigidity of matrix, spacer length, temperature, light intensity, and so forth.<sup>4,5</sup> The mechanism of the reorientation is mainly founded on the trans-cis isomerization that changes the shape of mesogens (rod-shaped trans conformer and banana-shaped cis conformer).<sup>6</sup> Recently, several experimental results that cannot be explained by the trans-cis isomerization were reported. The birefringence induced by pumping at the absorption edge of the *cis* conformer was reported,<sup>7,8</sup> and Andreienko et al. showed that the threshold pumping intensity for the Freedericksz transition decreased greatly in azobenzene polymers.9 Therefore, a detailed study of the exact process of the photoinduced birefringence is necessary. In order to determine the contribution of isomerization to the photoinduced birefringence, the transition rate constants of trans-cis isomerization should be obtained quantitatively.

There are a lot of reports to determine the parameters, such as absorbance and quantum yields from the rate equation of trans-cis isomerization. In particular, Fischer reported a method to obtain the absorbance of pure cis conformers,<sup>10</sup> and several researchers suggested methods to obtain the quantum yields.<sup>11-14</sup> However, there are several problems in the previous methods for determining the transition rate constants of trans-cis isomerization. Each parameter had to be separately measured and calculated for obtaining the transition rate constants. Moreover, the thermal isomerization was almost neglected in the case of azobenzene-type and aminoazobenzene-type molecules, because thermal cis-trans isomerization operates very slowly.10-12,14 But, in the case of the pseudo-stilbene-type molecule with relatively fast thermal  $cis \rightarrow trans$  isomerization, the thermal isomerization should be considered for determining the rate constants. Therefore, another simple method is needed for determining the quantitative rate constants of *trans-cis* isomerization in the pseudo-stilbene-type of azobenzene molecule.

In this article, we analyzed the rate equation of the *trans-cis* isomerization and suggested a simple method for determining the quantitative transition rate constants of *trans-cis* isomerization. With this method, we obtained the rate constants of *trans-cis* isomerization in a poly(malonic ester) containing disperse red 1(PDR1).

## **II. EXPERIMENT**

### A. Polymer material

The polymer used in our experiments was a poly(malonic ester) (PDR1) with two symmetrical disperse red 1 [Fig. 1(a)], which is characterized spectroscopically by the  $\pi \rightarrow \pi^*$  band of the *trans* conformer that overlaps with the weak  $n \rightarrow \pi^*$  band of the *cis* conformer around the wavelength of 500 nm [Fig. 1(b)].<sup>6</sup>

New thermotropic liquid crystalline malonic ester monomer (MDR1) was synthesized by reacting malonyl dichloride and disperse red 1 in tetrahydrofuran (THF) at 0 °C for 24 h. It was then condensed with 1,6-dibromohexane in THF in the presence of sodium hydride at 65 °C for 24 h to give a poly-(malonic ester) (PDR1) with two symmetrical disperse red 1s a photoresponsive group. The polymeric thin films were cast from the polymer solution (5 wt %) in CHCl<sub>3</sub> onto a glass plate for 30 s using a spin coater.<sup>15</sup>

# **B.** Experimental setup

We prepared an experimental setup for the real-time measurements of the absorbance in PDR1 solution and film, as shown in Fig. 2. The sample was irradiated by a pumping beam (2) from a second harmonic generated Nd:YAG laser (Coherent 532-200) with the wavelength of 532 nm. The Nd:YAG laser was a continuous wave laser, and the intensity of the pumping beam was controlled by a variable attenuator. The absorbance change was measured with a reading beam



FIG. 1. (a) Chemical structure of PDR1. (b) Absorption spectrum of PDR1.

(1) split by a beam splitter. The intensity of the reading beam (1) was attenuated by a variable attenuator as small as 10  $\mu$ W/cm<sup>2</sup>. Both pumping and reading beams were circularly polarized to prevent them from inducing any anisotropy. Since the pumping beam and reading beam were coherent, energy transfer between the two beams could occur through the formation of a grating. To avoid this coupling effect, the phase of the pumping beam was modulated at about 1 kHz by a piezoelectric transducer. The reading beam was detected by a photodiode (Hamamatsu, S1336-18BQ) interfaced with a computer, in which the data transfer rate was about 80 Hz. To determine the absorbance of the pure *cis* conformers using Fischer's method,<sup>6</sup> an argon ion laser at 514 nm was used



FIG. 2. Experimental setup for real-time measurement of the absorbance of the PDR1 polymer sample in pumping and relaxation periods (M=mirror, B.S.=beam splitter, Q.W.P.= $\lambda/4$  wave plate, V.A.=variable attenuator, and P.Z.T.=piezoelectric transducer).

as another light source. The absorbance was measured when the pumping beam was turned on (pumping period) and off (relaxation period).

### **III. THEORY**

When azobenzene molecules are irradiated by a monochromatic beam, the rate equation for the fractions of *trans* and *cis* conformers can be expressed by<sup>11</sup>

$$\frac{dC(t)}{dt} = l \times I \times T(t) - m \times I \times C(t) - n \times C(t)$$
$$= l \times I \times [1 - C(t)] - m \times I \times C(t) - n \times C(t), \qquad (1)$$

$$[T(t)=1-C(t)]$$
  
=  $l \times I - [(l+m) \times I + n] \times C(t),$  (2)

where *I* is the pumping beam intensity. C(t) and T(t) are the fractions of *cis* and *trans* conformers at time *t*, respectively. The transition rate constants correspond to the following reactions:

- $l: T+h\nu \rightarrow C$  (photoisomerization);
- $m: C+h\nu \rightarrow T$  (photoisomerization);
- $n: C \rightarrow T$  (thermal isomerization).

The first two terms on the right-hand side of Eq. (1) are related to the *trans* $\rightarrow$ *cis* and *cis* $\rightarrow$ *trans* photoisomerizations, and the third term is related to the thermal *cis* $\rightarrow$ *trans* isomerization. The transition rate constants, *l* and *m*, are dependent on the absorption coefficients, quantum yields and a function  $[(1 - e^{-D(t)})/D(t)]$ , where D(t) is the measured absorbance in pumping period or relaxation period.<sup>11</sup> Because the variation of the function is very small (less than 2%) during illumination, we can consider this function as a constant parameter. In the pumping period, the fraction of *cis* conformers is given from Eq. (2) by

$$C(t) = \frac{l \times I}{(l+m) \times I+n} \times (1 - e^{-\{(l+m) \times I+n\} \times t}).$$
(3)

As can be seen in Eq. (2), the fraction of *cis* conformers changes by a single exponentially growing function of time in the pumping period. Since the *trans* and *cis* conformers coexist in the polymer sample, and each conformer has its own absorption coefficient, the measured absorbance [D(t)]of the polymer sample is given by

$$D(t) = T(t) \times D_{trans} + C(t) \times D_{cis}$$
  
=  $D_{trans} + \frac{(D_{cis} - D_{trans}) \times l \times I}{(l+m) \times I + n}$   
 $\times (1 - e^{-\{(l+m) \times I + n\} \times t\}})$   
=  $D_{trans} - M \times (1 - e^{-k \times t}),$  (4)

where  $D_{trans}$  and  $D_{cis}$  represent the absorbances of the pure *trans* conformer and the pure *cis* conformer, respectively.  $D_{trans}$  is determined when the sample was kept in the dark for a long time, and  $D_{cis}$  can be calculated by Fischer's

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FIG. 3. Absorbances at 532 nm in the PDR1 solution with time at various pumping beam intensities: (a) in the pumping period; (b) in the relaxation period.

method with the pumping beam of high power.<sup>8</sup> For simplicity, the time constant (k) in the pumping period is defined as

$$k = (l+m) \times I + n \tag{5}$$

and the magnitude of absorbance change (M) is as

$$M \equiv D_{trans} - D(\infty) = \frac{(D_{trans} - D_{cis}) \times l \times I}{(l+m) \times I + n}.$$
 (6)

Since the  $D_{trans}$  is bigger than  $D_{cis}$  in our experimental condition, the *M* value is positive, and the measured absorbance also changes by the single exponential decaying function of time.

The magnitude of absorbance change (M) and the time constant (k) in the pumping period are dependent on the pumping beam intensity and the transition rate constants. Therefore, from analyzing the values of M and k for the various pumping beam intensities, we can determine the transition rate constants. The values of M and k can be obtained by fitting the measured curve of D(t) in the pumping period to Eq. (4).

The process to change the fractions of *trans* and *cis* conformers in relaxation periods is only the thermal isomerization. That is, the absorbance change in the relaxation period is independent of the pumping beam intensity and can be described only by the thermal rate constant *n*. Therefore, the thermal rate constant (*n*) can be obtained by fitting the measured curve of absorbance [D(t)] in the relaxation period to a single exponential growing function:

$$D(t) = D(\infty) + M \times (1 - e^{-n \times t}).$$
<sup>(7)</sup>

By again fitting the k values with the pumping beam intensity to Eq. (5), the value of l+m can be determined. Finally, with the obtained values of parameters such as  $D_{trans}$ ,  $D_{cis}$ , n and l+m, the individual values of l and m can be obtained by fitting the M values with the pumping beam intensity to Eq. (6).



FIG. 4. (a) Time constant in the pumping period and (b) magnitude of absorbance change vs pumping beam intensity in the PDR1 solution.

### **IV. RESULTS**

k

Figure 3 shows the absorbance [D(t)] for a diluted solution of PDR1 at various pumping beam intensities during pumping (a) and relaxation (b) periods. The magnitude of absorbance change *M* increased with the intensity of the pumping beam [Fig. 3(a)], and was saturated at 15 mW/cm<sup>2</sup> of the pumping beam intensity. The solid lines are the fitted curves with Eq. (4) by nonlinear least-squares fitting method. The values of *M* and *k* obtained from the fitting are shown in Fig. 4. By fitting the curve of Fig. 3(b) with Eq. (7), the value of *n* was determined to be  $0.053 \pm 0.003$  irrespective of the pumping beam intensity. The value of  $D_{trans}$  was found to be 0.288 at 532 nm.  $D_{cis}$  was calculated to be 0.173 using Fischer's method with high pumping beam intensity,<sup>5</sup> so  $D_{trans} - D_{cis}$  was 0.115.

Figure 4(a) shows the time constants (k) with the pumping beam intensity, and the value of l+m was obtained by fitting the plots of k with Eq. (5) in which the already determined value of n was included:

$$x = (l+m) \times I + 0.053. \tag{8}$$

In this case, the linear least-square fitting method was used. As a result, the value of l+m was determined to be  $0.077\pm0.003$ . Figure 4(b) shows the magnitudes of absorbance change *M* with the pumping beam intensity. The curve of Fig. 4(b) was fitted by Eq. (6) with the parameters obtained above, such as l+m, *n*, and  $D_{trans}-D_{cis}$ :

$$M = 0.115 \times \left[ \frac{l \times I}{0.077 \times I + 0.053} \right].$$
(9)

In this case, the nonlinear least-square fitting method was used. As shown in Fig. 4(b), the fitting result matched well with the experimental one. As a result, the values of *l*, *m*, and *n* were determined to be  $0.032\pm0.0001$ ,  $0.045\pm0.0001$ , and  $0.053\pm0.003$ , respectively. Therefore, the rate equation of both conformers in the PDR1 solution can be represented quantitatively as

$$\frac{dC}{dt} = 0.032 \times I \times T - 0.045 \times I \times C - 0.053 \times C.$$
(10)

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FIG. 5. Absorbances in the PDR1 film with time at various pumping beam intensities: (a) in the pumping period; (b) in the relaxation period.

The same method as in the case of the solution was used for obtaining the rate constants of the *trans-cis* isomerization with some adjustments for the case of the PDR1 film. The intensity dependence of the absorbance was similar to the case of solution (Fig. 5), but as shown in Fig. 5(a), the variation of absorbance was slower than that of the PDR1 solution. The magnitude of absorbance change was not saturated even though the pumping beam intensity was as large as 80 mW/cm<sup>2</sup>. Moreover, there might be another effect besides the thermal isomerization in the relaxation period, since the curve of D(t) in the relaxation period did not match with a single exponential growing function but with a biexponential growing function. Paik et al. reported that the anomalous fast relaxation component was caused by cis conformers trapped in a strained conformation, and a slow one was due to the thermal isomerization.<sup>16</sup> Therefore, we used a bi-exponentially growing function to obtain the time constants of the thermal isomerization.

$$D(t) = D(\infty) + M_{\text{fast}} \times [1 - \exp(-n_{\text{fast}} \cdot t)]$$
  
+  $M_{\text{slow}} \times [1 - \exp(-n_{\text{slow}} \cdot t)],$  (11)

where  $n_{\text{fast}}$  and  $n_{\text{slow}}$  are the time constants of fast and slow components of relaxation, and  $M_{\text{fast}}$  and  $M_{\text{slow}}$  are the magnitudes of fast and slow components, respectively. In order to consider both the rate constants, a thermal rate constant (n')of  $cis \rightarrow trans$  isomerization was newly defined by

$$n' = \frac{M_{\text{fast}}}{M_{\text{fast}} + M_{\text{slow}}} \times n_{\text{fast}} + \frac{M_{\text{slow}}}{M_{\text{fast}} + M_{\text{slow}}} \times n_{\text{slow}}.$$
 (12)

As the fitting result, the value of  $M_{\text{fast}}/(M_{\text{fast}}+M_{\text{slow}})$  was 0.58±0.005. The values of  $n_{\text{fast}}$  and  $n_{\text{slow}}$  were 0.333 ±0.003 and 0.033±0.002, respectively. So, the defined thermal rate constant (n') was determined by 0.21±0.004.

Figure 6 shows a similar tendency to that of the PDR1 solution in Fig. 4. The time constants (k) with the pumping beam intensity are shown in Fig. 6(a), and the plots in Fig. 6(b) are the values of M.  $D_{trans}-D_{cis}$  was determined to be



FIG. 6. (a) Time constant in the pumping period and (b) magnitude of absorbance change vs pumping beam intensity in the PDR1 film.

0.088 using the ratio between the absorbances of *trans* and *cis* conformers  $(D_{trans}/D_{cis})$  in the case of the PDR1 solution.

Finally, the rate constants of isomerization were determined by  $l = 0.0084 \pm 0.00006$ ,  $m = 0.0336 \pm 0.00006$ , and  $n' = 0.21 \pm 0.004$ . Comparing these constants with those of the PDR1 solution, the time constant (n') of the film was about four times higher than that of the solution, because the strained *cis* conformers induced the fast anomalous relaxation. Also, both *l* and *m* were smaller than those of the solution, because of very low quantum yields in the film.<sup>17</sup>

# **V. CONCLUSION**

A simple method was suggested for determining the transition rate constants of *trans-cis* isomerization quantitatively in the pseudo-stilbene-type of azobenzene molecule. The absorbances of the PDR1 solution and film were measured with the pumping beam intensity, and analyzed by the rate equation for the fractions of *trans* and *cis* conformers. As the results in the PDR1 solution, the rate constants l, m, and n were determined to be  $0.032\pm0.0001$ ,  $0.045\pm0.0001$ , and  $0.053\pm0.003$ , respectively. In the PDR1 film, the rate constants l, m, and n' were  $0.0084\pm0.00006$ ,  $0.0336\pm0.00006$ , and  $0.21\pm0.004$ , respectively.

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