Determinations of Optical Field Induced Nonlinearities in Azo Dye Doped Polymer Film

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1. Introduction

Saturable dye doped polymer films have been widely used for optical data storage (Pham et al., 1997), nonlinear optical wave mixing processes (Sharma et al., 1994) such as degenerate and non-degenerate multiwave mixing (Fragnito et al., 1987), optical phase conjugation (Fujiiwara et al., 1985), two beam coupling and polarization holograms (Huang et al., 1993). The optical field induced (photo-structural) changes of azo dye molecules embedded in polymer matrix lead to remarkable changes of nonlinear optical properties, including scalar effects like nonlinear refractive index and nonlinear absorption, and vector effects like photoinduced birefringence (PIB) and photoinduced dichroism (PID). Nonlinear optical materials exhibiting PIB and PID, such as azo dye doped polymers, amorphous chalcogenide semiconductor films and others have been intensively investigated due to their potential applications in many fields, particularly for polarization (or vector) holograms (Kwak et al., 1988 & Nikolova et al., 1988), nonlinear optical image processing (Kwak et al., 1989), and multispot arrays generation for digital optical computing systems (Kwak et al., 1992). It has been now widely accepted that the physical origin of the PIB and PID in azo dye doped polymer is attributed to the trans-cis photoisomerization of azo molecules via photoinduced molecular reorientation (Nikolova et al., 1988 & Sekkat et al., 1995 & Egami et al., 1997 & Yaroshchuk et al., 2003).

In this Chapter, we report on the determinations of the optical nonlinearities of azo dye doped polymer film by means of the holographic gratings as a scalar effect and the photoinduced birefringence as a vector effect, and present on the transient behaviors of the diffraction efficiency and the PIB, revealing the stretched exponential responses, which cannot be explained by the conventional photo-process model (Nikolova et al., 1988). A stretched exponential time response, which is also known as Kohlrausch-Williams-Watts (KWW) response, is frequently observed in amorphous polymers, glasses and other disordered materials. Although several authors have proposed some of the empirical models to explain the stretched exponential relaxation phenomena in amorphous materials (Johanson et al., 2007 & Benatar et al., 1993 & Dureiko et al., 1998 & Palmer et al., 1984), those models cannot be directly applied to the diffraction efficiency and the PIB kinetics observed in azo dye doped polymer.
The purpose of this work is to propose a novel approach to explain the transient behaviors of the diffraction efficiency and the photoinduced birefringence and to compare with the experimental data. A three state model for photoisomerization is presented to analyze the stretched exponential kinetic behaviors by employing an empirical stretched exponential time response in the trans-cis photoisomerization of azo molecules. Finally, we have conducted the Z-scan experiments to determine the sign of the optical non-linearities.

2. Theory

2.1 Three state model for photoisomerization with stretched exponential kinetics

In this section, we will present a three state model for photoisomerization, describing the transient behaviors of both the diffraction efficiency of the holographic gratings and the photoinduced birefringence. We consider a three state system consisting of trans, trans* and cis states, which is illuminated by a linearly (say, x-) polarized single pump beam for PIB, or coherent two pump beams for holographic gratings, as shown in Fig. 1. It is assumed that under the influence of the amorphous natures of azo dyes in polymeric environment, the dye molecules embedded in a polymer matrix exhibit the stretched exponential time response below the glass transition temperature (Huang et al., 1993). We empirically introduce a relaxation time dispersion function or stretched exponential time (KWW) response function, 

\[ g(t) = \beta (t / \tau)^{\beta - 1}, \]

where \( \tau \) is a characteristic time of azo molecules with polymer matrix and the parameter \( \beta (0 \leq \beta \leq 1) \) is a stretched exponent that quantifies the extent of the deviation from pure exponentiality (i.e., \( \beta = 1 \)), or equivalently, the degree of the relaxation time dispersion. The stretched exponential kinetics of glasses or amorphous materials has been related to the high degree of disorder, which leads to the existence of a large number of metastable states (Palmer et al., 1984).

![Fig. 1. (a) Three state model for trans-cis photoisomerizations, (b) geometry for describing the interactions of the trans molecules with the polarized optical beam intensity \( I(r) \).](www.intechopen.com)

The optical transition rate from trans to trans* state and thermal relaxation rate from cis to trans states are assumed to have a form of the stretched exponential time response and can be written as 

\[ W_{\text{trans-cis}} = q \sigma, I g(t) = q \sigma, I \beta (t / \tau)^{\beta - 1} \]

and 

\[ A_{\text{cis-trans}} = g(t) / \tau = \beta t^{\beta - 1}/\tau^\beta, \]

respectively. Here, \( q = \Phi / \hbar \omega \) is a constant depending on the molecular surroundings, where \( \Phi \) is the quantum yield for trans to cis state and \( \hbar \omega \) is the photon energy, so the dimension of \( q \) is the inverse of energy (i.e., \( J^{-1} \)). The anisotropic molecular absorption cross section is
the interactions of the cis state, which is illuminated by a linearly (say, x-) polarized single pump beam for PIB, or to photoinduced birefringence. We consider a three state system consisting of transient behaviors of both the diffraction efficiency of the holographic gratings and the photoinduced birefringence and to compare with the experimental data. A three state model for photoisomerization is presented to analyze these behaviors by employing an empirical stretched exponential time response function, below the glass transition temperature (Huang et al., 1993). We empirically introduce a coherent two pump beams for holographic gratings, as shown in Fig. 1. It is assumed that the optical transition rate from trans-cis transition, the trans* state becomes a quasi-steady state, so the three state system reduces to the two state system by eliminating the number density of the trans* state. Taking into account of the relaxation time dispersion of each isomer states, we readily have the rate equations for trans and cis states as;

\[ \frac{dN_{\text{trans}}}{dt} = -W_{\text{trans-cis}} N_{\text{trans}} + A_{\text{cis}} N_{\text{cis}} \]  
\[ \frac{dN_{\text{cis}}}{dt} = W_{\text{trans-cis}} N_{\text{trans}} - A_{\text{cis}} N_{\text{cis}} \]

where \( N_{\text{trans}} \) and \( N_{\text{cis}} \) are the number densities of trans and cis states. For PIB, caused by a linearly polarized single beam, the optical transition rate \( W_{\text{trans-cis}} \) has a strongly angular dependency, whereas for the case of the diffraction gratings, the angular dependence of the optical transition rate \( W_{\text{trans-cis}} \) is negligible and should be ensemble averaged for all \( \theta \) (0 ≤ \( \theta \) ≤ 2π), because the grating spacing of about a few \( \mu \text{m} \) is very much larger than the trans or cis molecular sizes. With this in mind, the optical transition rates are given by \( W_{\text{trans-cis}} = \beta(t/\tau)^{p-1} q q_1 I \cos^2 \theta \) for PIB, and \( W_{\text{trans-cis}} = \beta(t/\tau)^{p-1} q q_1 I/2 \) for intensity gratings.

2.2 Diffraction efficiencies of holographic gratings

We present the transient diffraction efficiency of holographic gratings, which is constructed by a spatially modulated intensity grating, \( I(x) \). The solutions of Eqs. (1) are given by

\[ N_{\text{trans}}(t) = N_0 \frac{1}{1 + S(x)} \left[ 1 + S(x) \exp \left\{ -\left(1 + S(x)\left(\frac{t}{\tau}\right)\right)^{\theta} \right\} \right] \]  
\[ N_{\text{cis}}(t) = N_0 \frac{S(x)}{1 + S(x)} \left[ 1 - \exp \left\{ -\left(1 + S(x)\left(\frac{t}{\tau}\right)\right)^{\theta} \right\} \right] \]

which has been made use of the initial conditions of \( N_{\text{trans}}(0) = N_0 \), \( N_{\text{cis}}(0) = 0 \) and \( N_s = N_{\text{trans}}(t) + N_{\text{cis}}(t) \) is the total number density of isomers. Here, \( S(x) = I(x)/I_s \) is the saturation parameter, and \( I_s = 2/\tau q q_1 = 2\omega \mu /\Phi q_1 \) is the saturation intensity for the holographic grating, \( I(x) \) is the intensity grating. The saturation parameter \( S(x) \) represents the spatially modulated intensity distribution of two writing beams, and is expressed as (Fragnito et al., 1987; Kwak et al., 1988)

\[ S(x) = S_s + S_1 \cos Kx \]
where $S_0 = (I_a + I_s)/I_s$, $S_1 = 2\sqrt{I_a I_s}/I_s$ with the two writing beam intensities $I_a$ and $I_s$, $K = 2\pi/\Lambda$ is the magnitude of the grating wave vector and $\Lambda$ is the grating period. The refractive index change is assumed to be proportional to the changes of population density of Eqs.(2) and then is given by

$$n(x,t) = n_o + \Delta n(x,t) = n_o + \Delta n \frac{S(x)}{1 + S(x)} \left( 1 - \exp \left[ -\left( 1 + S(x) \left( \frac{L}{\tau} \right)^\beta \right) \right] \right),$$

(4)

where $n_o$ is the linear refractive index, $\Delta n$ is the nonlinear refractive index, and $\Delta n$ is the maximum nonlinear refractive index change. Following the same procedures of the literatures (Fragnito et al., 1987; Kwak et al., 1988) and using the residue calculus in the complex plane, we have the nonsinusoidal phase gratings of the form:

$$\Delta n(x,t) = \sum_{h=-\infty}^{\infty} \Delta n_h(t) \exp[ihKx],$$

(5a)

where $\Delta n_h(t)$ is the $h$th diffraction amplitudes of the phase gratings and are given by

$$\Delta n_h(t) = \delta n \left[ 1 - C_h + \exp \left[ -\left( 1 + S_h \left( \frac{t}{\tau} \right)^\beta \right) \right] - D_h(t) + \sum_{n=-\infty}^{\infty} C_n D_{-n}(t) \right],$$

(5b)

$$\Delta n_h(t) = \delta n \left[ - C_h + \exp \left[ -\left( 1 + S_h \left( \frac{t}{\tau} \right)^\beta \right) \right] - D_h(t) + \sum_{n=-\infty}^{\infty} C_n D_{-n}(t) \right], \quad (h \neq 0),$$

(5c)

Here, the Fourier coefficients, $C_h$ and $D_h$ are given by

$$C_h = \left( \frac{S(1 + S_0) - S_0^2 - 1 - S_0}{S^4(1 + S_0)^2 - S_0^2} \right)^{1/2},$$

(6a)

$$D_h(t) = I_h \left[ S \left( \frac{t}{\tau} \right)^\beta \right], \quad D_h(t) = 2(-1)^h I_h \left[ S \left( \frac{t}{\tau} \right)^\beta \right], \quad (h \neq 0),$$

(6b)

where $I_h(\bullet)$ denotes $h$th-order modified Bessel function of the first kind. The Fourier coefficients have the properties of $C_h = C_{-h}$, $D_h = D_{-h}$ for $I_h(\bullet) = I_{-h}(\bullet)$. These high-order Fourier coefficients result from the nonsinusoidal spatial modulation of the population grating due to the saturation effect. A precise knowledge of the amplitudes of the gratings, particularly for the first-order diffraction, is of fundamental significance for understanding the physical mechanism of the grating formations in saturable absorber. Henceforth we only consider the time evolution of the first-order spatial harmonic grating. Furthermore, we have numerically confirmed that the contribution of the high-order coefficients greater than 2 (i.e., $C_{\pm2}$ and $D_{\pm2}(t)$) to the resultant grating amplitude can be negligibly small for all
time regime, within less than 10%. The diffraction efficiency of the first-order harmonic grating for Bragg condition is then approximately given by (Kogelnik et al., 1969)

\[
\eta \approx \sin^2\left(-\frac{\pi \delta n L}{\lambda' \cos \theta}\right) C_i + \exp\left[-\left(1 + S_0\right)\left(\frac{t}{\tau}\right)^\beta\right] \left(D_i(t) - C_iD_i(t) - C_iD_0(t)\right)
\]

where \( L \) is the thickness of the sample, \( \lambda' \) is the wavelength of read-out beam, \( \theta \) is the incident half-angle between the two writing beams, \( \tau \) is the characteristic lifetime of the material in grating formation, and \( \beta \) is the stretched exponent.

Fig. 2. Theoretical predictions of (a) first-order time dependent diffraction efficiency for several saturation parameters with \( \beta = 0.35 \), \( \tau = 35\text{sec} \) and \( \delta n = 5 \times 10^{-4} \), and (b) steady-state value of diffraction efficiency against saturation parameter, which is independent of the stretched exponent.

Fig. 2(a) represents the theoretical predictions of time-dependent diffraction efficiency for several saturation parameters \( S_0 \). It is shown that as increasing the saturation parameters the transient peaks of the diffraction efficiency reveal much higher than the steady state values. Figure 2(b) depicts the steady-state values of diffraction efficiency as a function of the saturation parameter \( S_0 \). As increasing the saturation parameter, the diffraction efficiency rapidly increases to a maximum value and then gradually decreases and eventually fades away.

2.3 Photoinduced birefringence

We will develop a theory describing the transient behaviors of the photoinduced birefringence (PIB) observed in azo dye doped polymer film by adopting a stretched exponential response, which cannot be explained by the conventional photo-process (Nikolova et al., 1988). For a linearly polarized (say, x-polarized) beam, we have the number densities of the states from the rate equation of Eqs.(1):
\[ N_r(\theta,t) = \frac{N_0}{2\pi} \frac{1}{1 + S \cos^2 \theta} \left[ 1 + S \cos^2 \theta \exp \left( -\left(1 + S \cos^2 \theta \left( \frac{t}{\tau} \right)^\theta \right) \right) \right], \]  
(8a)

\[ N_c(\theta,t) = \frac{N_0}{2\pi} \frac{S \cos^2 \theta}{1 + S \cos^2 \theta} \left[ 1 - \exp \left( -\left(1 + S \cos^2 \theta \left( \frac{t}{\tau} \right)^\theta \right) \right) \right]. \]  
(8b)

It is noted that the saturation parameter, \( S = 1/I_s \) for PIB is a spatially uniform, and the total number density at polar angle \( \theta \), \( N_r(\theta,t) + N_c(\theta,t) = N_0/2\pi \) is strongly angular dependent and the saturation intensity, \( I_s = 1/\tau \sigma \sigma_i = \hbar \omega/\Phi \sigma_i \) is different from that of the holographic gratings. For an axially symmetric configuration about the polarization axis as in Fig. 1(b), the populations of \( \text{trans} \) and \( \text{cis} \) molecules are strongly anisotropic in space and only a function of the polar angle \( \theta \). In the laboratory frame, the macroscopic susceptibility of oriented molecules is given by

\[ \chi_y(t) = \chi_{\text{polym}} + \int d\Omega_{\mu\nu} \cos \mu \cos \nu \chi_i(t) \chi_c(t), \quad (i,j = x,y) \]  
(9)

where \( \cos \mu \) and \( \cos \nu \) are direction cosines of the electric dipole moment vector \( \bar{\mu} \) relative to the \( i, j = (x,y) \) axes of the laboratory frame as in Fig. 1(b), and \( d\Omega_{\mu\nu}(\theta,t) = [\alpha_r N_r(\theta,t) + \alpha_c N_c(\theta,t)] d\theta \) is the total susceptibility of the group of molecules oriented in an angle \( d\theta \). Since the host polymer is optically isotropic, the linear susceptibility for the polymer \( \chi_{\text{polym}} \) is included. Here, the macroscopic (isotropic) linear susceptibility is \( \chi_L = \chi_y(0) \delta_y = \chi_{\text{polym}} + \alpha_r N_0 \) with the isotropic condition of \( \chi_{\text{ss}}(0) = \chi_{\text{yy}}(0) \) due to amorphous nature of the sample, where \( \alpha_r (X = T,C) \) is the complex linear polarizability of the \( \text{trans} \) or \( \text{cis} \) isomers, and \( \delta_y \) is the Kronecker delta function. The photoinduced nonlinear susceptibility \( \delta \chi_y(t) \) is given by

\[ \delta \chi_y(t) = \frac{\delta \chi_c}{N_0} \int_0^\infty N_c(\theta,t) \cos \mu \cos \nu \ d\theta, \]  
(10)

where \( \delta \chi_c = (\alpha_c - \alpha_r) N_0 \), \( \cos \mu_x = \cos \theta \) and \( \cos \mu_y = \sin \theta \). Substituting Eq. (8b) into Eq. (10) and using the residue calculus of the complex plane, after some calculations, we have the photoinduced nonlinear susceptibilities for directions parallel and perpendicular to the direction of linearly polarized pump beam as

\[ \delta \chi_y(t) = \delta \chi_o \left[ A_{\theta,\alpha} \left( 1 - \exp \left[ -\left(1 + \frac{S}{2} \right) \left( \frac{t}{\tau} \right)^\theta \right] \right) \right], \]  
(11a)

\[ + 2 \exp \left[ -\left(1 + \frac{S}{2} \right) \left( \frac{t}{\tau} \right)^\theta \right] \sum_{m=1}^\infty A_{\theta,\alpha} \left[ \frac{S}{2} \left( \frac{t}{\tau} \right)^\theta \right] \]
where \( I_n \) \((m = 1, 2, 3, \ldots)\) is the modified Bessel function of the \( m \)th order of first kind. Here, we present some of coefficients \( A_{w,i} \) \((m = 0, 1, 2, 3, \ldots\) and \( i = x, y \)) as follows:

\[
A_{w,x} = \frac{(8 + 8S^2)\sqrt{1 + S} - 4(2 + S)}{8S^2\sqrt{1 + S}}, \quad A_{w,y} = \frac{(8 + 8S^2)\sqrt{1 + S} - 4(2 + 3S + S^2)}{8S^2\sqrt{1 + S}}
\]

\[
A_{w,i} = \frac{4(2 + S)\sqrt{1 + S} - (8 + 8S^2)}{2S^2\sqrt{1 + S}}, \quad A_{w,y} = \sqrt{1 + S} \frac{4(2 + S)\sqrt{1 + S} - (8 + 8S^2)}{2S^3},
\]

\[
A_{w,i} = \sqrt{1 + S} \frac{4(2 + 3S + S^2)\sqrt{1 + S} - (32 + 48S + 18S^2 + S^4)}{2S^4}, \quad \ldots
\]

The complex refractive index changes can be written as \( \tilde{n}(\omega') = \tilde{n}_0(\omega') + \delta \tilde{n}(\omega') \), where \( \tilde{n}_0(\omega') = \sqrt{1 + \chi_{\text{polymer}} + \alpha_i N_0} \) is the complex linear refractive index including the background refractive index of the polymer matrix and \( \delta \tilde{n}(\omega') = \delta \chi_n / 2\tilde{n}_0(\omega') \) is the complex nonlinear refractive index changes. The complex refractive indices are also written as \( \tilde{n} = n_i - i\kappa_i \), in which \( n = \text{Re}[\tilde{n}] \) represents the anisotropic refractive index change, and \( \kappa_i = \text{Im}[\tilde{n}] = \lambda' \alpha_i / 4\pi \) depicts the anisotropic absorption index change, where \( \alpha_i = 4\pi\kappa_i / \lambda' \) is the anisotropic absorption coefficient and \( \lambda' \) is the wavelength of the probe beam. The photoinduced birefringence (PIB) is given by \( \Delta n(t) = \text{Re}[\delta \chi_{\text{ss}} - \delta \chi_{\text{ss}}]/2n_0(\lambda') = \delta n_i(t) - \delta n_y(t) \) and the photoinduced dichroism (PID) is expressed as \( \Delta \kappa(t) = \text{Im}[\delta \chi_{\text{ss}} - \delta \chi_{\text{ss}}]/2n_0(\lambda') = \delta \kappa_i(t) - \delta \kappa_y(t) \).

Using Eqs. (11) and (12) the PIB kinetics can be approximately written as

\[
\Delta n(t) = \delta n \left\{ B_0 \left[ 1 - J_0(\bullet) \exp \left\{ - \left(1 + \frac{S}{2} \right) \left( \frac{t}{\tau} \right)^\theta \right\} \right] \\
+ B_1 I_1(\bullet) + B_2 I_2(\bullet) + B_3 I_3(\bullet) \exp \left\{ - \left(1 + \frac{S}{2} \right) \left( \frac{t}{\tau} \right)^\theta \right\} \right\}
\]

(13)

where \( \delta n = \text{Re}[\delta \chi_n]/2n_0 \) is the maximum PIB change and the coefficients \( B_m \) are given by

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$$B_o = \frac{2 + S - 2\sqrt{1 + S}}{2S\sqrt{1 + S}}, \quad B_i = \frac{\sqrt{1 + S}(16 + 8S + 2S^2) - 4(4 + 4S + S^2)}{4S^2\sqrt{1 + S}},$$
$$B_2 = \frac{(2 + S)(4\sqrt{1 + S}(2 + S) - (8 + 8S + S^2))}{S^4\sqrt{1 + S}},$$
$$B_3 = \frac{(2 + S)(2\sqrt{1 + S}(16 + 16S + 3S^2) - (32 + 48S + 18S^2 + S^3))}{S^4\sqrt{1 + S}},$$

(14)

Since the contribution of high-order coefficients larger than \(m=3\) to the PIB kinetics can be negligibly small, in what follows, we will use the approximated analytic formula, Eq. (13) with Eq. (14). Figure 3(a) represents the theoretical kinetics of normalized PIB divided by the maximum PIB change \(\tilde{\Delta}_n\) and compares the PIB kinetics of stretched exponent \((\beta = 0.35)\) with the pure exponentiality \((\beta = 1)\) for several saturation parameters, which reveals quite distinct transient behaviors at early time. It follows that as time goes to infinity the steady state value of PIB comes together with that of the pure exponentiality whatever one may take the stretched exponents. Figure 3(b) depicts the normalized steady state value of PIB divided by \(\tilde{\Delta}_n\) as a function of the saturation parameter. Using Eq. (13) with Eq. (14) the steady state value of PIB is uniquely determined by \(\Delta_{n_s} = B_o\Delta_n = \Delta_n\left(2 + S - 2\sqrt{1 + S}\right)/(2S\sqrt{1 + S})\). As increasing the saturation parameter, the PIB rapidly increases to a maximum value and then gradually decreases.

Fig. 3. (a) Comparisons of normalized PIB kinetics with a stretched exponent (solid lines: \(\beta = 0.35\)) and the pure exponentiality (dotted lines: \(\beta = 1\)) for several saturation parameters \(S\), and (b) normalized steady state PIB divided by the maximum PIB change against saturation parameter. Steady state values of PIB is independent of the stretched exponent.

3. Experimental Results and Discussions

3.1 Sample preparation of azo dye doped polymer films

Methylorange doped PVA (MO/PVA) films are fabricated and are used as nonlinear media for investigating the transient behaviors of the holographic gratings and the photoinduced birefringence. PVA of 6wt% was melted by distilled water by means of double boiler processing. Small amount of azo dye was doped into PVA solution and is thoroughly mixed by agitator for about 24 hours. The MO/PVA mixture was coated on glass substrates by gravity deposition technique and baked at 50°C for about 1 hour in a heating oven. We
fabricated several MO/PVA films for various MO concentrations of 0.01wt%, 0.02wt%, 0.05wt%, 0.08wt%, 0.12wt% and 0.14wt%.

![Absorbance of MO/PVA films against wavelength for various MO concentrations.](image)

The thickness of the film was approximately 20μm. The absorption spectra of MO/PVA films for various MO concentrations are measured by using a spectrophotometer and are shown in Fig. 4. The linear absorbance has the maximum values for the wavelength region of blue-green light, while for the red wavelength region it shows nearly transparent, irrespective of MO concentrations. The pure PVA film without azo dye reveals no absorption for visible lights.

### 3.2 Determinations of optical nonlinearity by holographic gratings

![Experimental setup for recording holographic gratings and for measuring the diffraction efficiencies.](image)

Figure 5 shows the experimental setup measuring the real-time diffraction efficiency of the holographic gratings. Two coherent Ar-ion laser beams with the same linear polarization and the wavelength of 488 nm were used to construct the holographic gratings, and a He-Ne
laser beam of 633nm wavelength was used for measuring the diffracted efficiencies. The incident half-angle between the two writing beams was approximately $\theta = 12^\circ$ and the beam intensity ratio of the two writing beams was kept to be unity. The read-out beam was incident by Bragg angle and the real-time first-order diffraction efficiencies were measured for various writing beam intensities and MO concentrations. The intensity of read-out beam was very small compared to the writing beam intensity, not to affect the grating formations.

Figure 6 represents the real-time first-order diffraction efficiencies of holographic gratings for the concentration of 0.05wt% MO/PVA film with the theoretical predications according to Eq. (7). As clearly seen Fig. 6, theoretical curves are in good agreements with the experimental data. It is also found that as increasing the writing beam intensity the transient peak of the diffraction efficiency at early time, which is higher than the steady-state value, was observed, as theoretically predicted. Figure 7(a) represents the steady state diffraction efficiency as a function of total writing beam intensity at several MO concentrations with the theoretical predictions of Eq. (7), whose steady-state value is determined by $\eta \approx (C_1 \pi \delta n L/\lambda \cos \theta)^2$. It is also clear that the maximum nonlinear refractive index change $\delta n$ is linearly proportional to the MO concentration, as shown in Fig. 7(b).

From the best curve fitting to the data, we estimated the following physical parameters as: $\delta n = -(4.8 \pm 0.5) \times 10^{-4}$ of the maximum nonlinear refractive index change, $I_s = 500 \pm 20 \text{mW/cm}^2$ of the saturation intensity, $\tau = 31.5 \pm 1.5 \text{sec}$ of the characteristic lifetime and $\beta = 0.3 \pm 0.02$ of the stretched exponent in holographic gratings. It should be emphasized that the nonlinear refractive index change has the negative sign, which is experimentally confirmed by the Z-scan experiment.
confirmed by the Z-scan experiment. That the nonlinear refractive index change has the negative sign, which is experimentally and was very small compared to the writing beam intensity, not to affect the grating formations.

For various writing beam intensities and MO concentrations. The intensity of read-out beam incident by Bragg angle and the real-time first-order diffraction efficiencies were measured. The intensity ratio of the two writing beams was kept to be unity. The read-out beam was incident half-angle between the two writing beams was approximately.

A laser beam of 633nm wavelength was used for measuring the diffracted efficiencies. The theoretical predictions of Eq. (7), whose steady-state value is determined by.

Efficiency as a function of total writing beam intensity at several MO concentrations with the peak of the diffraction efficiency at early time, which is higher than the steady-state value,

As clearly seen Fig. 6, theoretical curves are in good agreements with the experimental data. It is also found that as increasing the writing beam intensity the transient.

Figure 7(a) represents the steady state diffraction onation of 0.05wt% MO/PVA film with the theoretical predications according for the concentration of 0.05wt% MO/PVA film. From the best curve fitting to the data, we estimated the following physical parameters as:

\[ I \equiv I_0 \pm \frac{\beta \cdot \cos \theta}{n \delta \lambda} \]

\[ \delta n \equiv \frac{\beta \cdot \cos \theta}{n \delta \lambda} \]

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Fig. 7. (a) Steady-state diffraction efficiency against writing beam intensity for various MO concentrations and (b) maximum nonlinear refractive index change versus MO concentration. The solid lines are theoretical curves.

3.3 Determinations of nonlinear characteristics by photoinduced anisotropy

In order to measure the photoinduced birefringence kinetics of MO/PVA film we performed the pump-probe experiment. Figure 8 shows the experimental geometry for pump-probe technique to measure the PIB kinetics. We used a linearly polarized Ar-ion laser beam of 488nm wavelength as a pump beam and a linearly polarized He-Ne laser beam of 633nm wavelength as a probe beam. The wavelength of the probe beam is far away from strong absorption region as shown in Fig. 4 and that the probe beam intensity is taken to be so weak (about 5 mW/cm²) that it cannot influence the optical properties of the sample.

Fig. 8. Experimental setup for pump probe technique to measure PIB kinetics (M: mirror, P1, P2: polarizers, A: analyzer, S: shutter).

The polarization direction of the pump beam is controlled by a quarter wave plate and a polarizer. The intensity of the probe beam transmitted through the analyzer is adjusted to be zero (i.e., to be crossed) without the sample. The film is then placed between the crossed polarizer and analyzer in the path of the probe beam. When the polarizer and analyzer are crossed, the transmittance of the probe beam intensity is given by (Kwak et al., 1992; Yang et al., 2009)

\[ T = \sin^2 \left( \frac{\beta \cdot \cos \theta}{n \delta \lambda} \right) \]

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\[ T = \sin^2 \left( \frac{\beta \cdot \cos \theta}{n \delta \lambda} \right) \]
\[ T = \exp\left(-\alpha L\right) \sin^2 2\phi \left[ \cosh\left(\frac{\Delta \alpha L}{2}\right) - \cos\left(\frac{2\pi \Delta n L}{\lambda'}\right) \right] \]  

(15)

where \( \alpha = (\alpha_+ + \alpha_-)/2 \) is the average absorption coefficient, measured with an unpolarized probe light. \( \Delta \alpha = \alpha_+ - \alpha_- \) represents the photoinduced dichroism (PID), \( \Delta n = n_+ - n_- \) is the photoinduced birefringence (PIB), \( \phi \) is the relative polarization angle between the linearly polarized probe beam and pump beam, \( L \) is the sample thickness and \( \lambda' \) is the wavelength of the probe beam. If one neglects PID of the sample (i.e., \( \Delta \alpha = 0 \)), Eq. (15) provides the PIB transmittance readout by a linearly polarized probe beam:

\[ T = \exp\left(-\alpha L\right) \sin^2 2\phi \sin^2 \left(\frac{\pi \Delta n L}{\lambda'}\right) \]  

(16)

For maximal readout the PIB the relative polarization angle between the linearly polarized probe and pump beams is chosen as \( \phi = \pi/4 \). Furthermore, if one may neglect the average absorption coefficient at the wavelength of the probe beam, the PIB kinetics can readily be described by the simple formula of \( \Delta n(t) = (\lambda'/\pi L) \sin^{-1} \sqrt{T} \) with the theoretical one, \( \Delta n(t) = \text{Re} \left[ \delta n_{ss} - \delta n_{ss} \right] / (2n_0(c')) \). Actually, it has experimentally shown that the PID signal was seldom or never detected at 633nm wavelength of the probe beam.

![Figure 9](image_url)

(a) Experiments  
(b) Theory

Fig. 9. (a) Experimental data for PIB kinetics against time for various pump beam intensities at MO concentration of 0.08wt% and (b) the corresponding theoretical curves fitted by using Eq. (16) with \( \beta = 0.34 \pm 0.04 \).

Figure 9 represents the time-dependent PIB data obtained at 0.08wt% MO/PVA film for various pump beam intensities with theoretical predictions of Eq. (16), showing excellent agreements with the experiments. As clearly seen in Fig. 9(a), the PIB kinetics cannot be described by a single exponential kinetics. The stretched exponential PIB kinetics seems to be quite good predictions for the entire time range, indicating the amorphous nature of MO/PVA. From the best curve fitting to the data, we estimated the following physical parameters as: for 0.08wt% of MO concentration, the maximum PIB change,
\[ \delta n = -(7.4 \pm 0.6) \times 10^{-2}, \] the saturation intensity, \( I_s = 31 \pm 2 \text{mW/cm}^2, \) the characteristic lifetime, \( \tau = 75 \pm 5 \text{sec} \) and the stretched exponent, \( \beta = 0.34 \pm 0.04. \]

Figure 10. Variations of steady state of PIB against pump beam intensity for various MO concentrations. Solid lines are the theoretical curves.

Figure 10(a) represents the steady state values of PIB as a function of pump beam intensities for various concentrations of azo dye (MO). As increasing the pump beam intensity the steady state values of PIB for a MO concentration rapidly increase to its maximum value and then gradually decrease. The steady-state value of PIB is uniquely determined by \( \Delta n_u = B_s \delta n = \delta n \left( 2 + S - 2\sqrt{1 + S} \right) / \left( 2S\sqrt{1 + S} \right) \) as theoretically predicted. The solid lines are the theoretical predictions. Figure 10(b) shows that the maximum PIB change, \( \delta n \) against the concentration of MO. As described above, \( \delta n \propto (\alpha_c - \alpha_r)N_o \), is linearly proportional to the total number density of azo dye \( N_o \).

### 3.4 On the sign of the optical nonlinearities in azo dye doped polymer

In the previous sections, we have measured only the magnitudes of the optical nonlinearities by means of the holographic gratings (i.e., scalar effects) and the photoinduced birefringence (i.e., vectorial effects) in azo dye doped polymers. One of the simplest ways to determine the sign of the optical nonlinearities is the Z-scan method (Sheik-Bahae et al., 1990). The Z-scan technique is a simple, highly sensitive single beam method that uses the principle of spatial beam distortion to measure both the sign and the magnitude of the optical nonlinearities of materials. The optical material is scanned along the z-axis in the back focal region of an external lens and measures the far-field on-axis (i.e., closed aperture) transmittance and the whole (i.e., open aperture) transmittance as a function of the scan distance \( z \). We have performed the Z-scan experiment by using a He-Ne laser beam, whose photon energy corresponds to the transparent region, as shown in Fig. 4. Figure 11 represent the typical experimental data for Z-scan in azo dye doped polymer films. It is obvious from Fig. 11 that the peak followed by a valley transmittance obtained from the closed aperture Z-scan data indicates the sign of the nonlinear refractivity is negative (i.e., self-defocusing), and that the sign of the nonlinear absorption coefficient is also negative from the open aperture Z-scan (i.e., photobleaching). It is also noted that the closed aperture Z-scan data shows severe asymetric behaviors, revealing the large nonlinear
phase shifts (Kwak et al., 1999). Asymmetric behaviors of closed aperture Z-scan data cannot be described by the conventional Z scan theory (Sheik-Bahae et al., 1990).

By employing the complex beam parameter formulation, we have the large phase shift closed aperture Z-scan transmittance, including both of the effects of nonlinear absorption and nonlinear refraction as follows (Kwak et al., 1999):

\[
T_{\text{close}}(z) = \frac{1}{1 - \frac{4(x - \eta)}{(1 + x^2)(1 + q_o)} \Delta \Phi_o + \frac{4(1 + \eta^2)}{(1 + x^2)(1 + q_o)^3} \Delta \Phi_o^2} \tag{17}
\]

where \(x = z / z_o\) is the dimensionless distance from a focus of an external lens, \(z_o\) is the Rayleigh diffraction length, \(\Delta \Phi_o = k \Delta n_o L_{\text{eff}}\) is the on-axis nonlinear phase shift at focus, \(k\) is the wave number, \(\Delta n_o = \gamma I_o\) is the nonlinear refractive index change, \(\gamma\) is the nonlinear refraction coefficient, \(I_o\) is the on-axis intensity at focus, \(L\) is the sample thickness, \(L_{\text{eff}} = [1 - \exp(-\alpha_o L)] / \alpha_o\) is the effective length of the sample, \(\alpha_o\) is the linear absorption coefficient. Here, the coupling factor, \(\eta = \beta / 2k\gamma\) is the ratio of the imaginary part to the real part of the complex nonlinearity, which is inversely proportional to the figure of merit (FOM), defined as FOM = \(\gamma / \beta\) (Lenz et al., 2000), where \(\beta\) is the nonlinear absorption coefficient. The nonlinear absorptive and refractive contributions to the closed aperture Z-scan transmittance are coupled in terms of \(\eta\) or FOM. For a CW laser beam, the open aperture Z-scan transmittance is given by (Kwak et al., 1999):

\[
T_{\text{open}}(z) = \frac{\ln(1 + q_o)}{q_o} \tag{18}
\]

where \(q_o = \beta L_{\text{eff}} / (1 + x^2)\). Once the nonlinear absorption coefficient \(\beta\) is unambiguously extracted from an open aperture Z-scan, one can use the closed aperture Z-scan transmittance to determine the remaining unknown coefficient \(\gamma\) or \(\Delta \Phi_o\) from Eq. (17).
The solid lines in Fig. 11 depict the theoretical curves, showing excellent agreements with experimental data. We have obtained the nonlinear coefficients for several azo dye concentrations:

\[ \gamma(0.05\text{wt\%}) = -2 \times 10^{-5} \text{cm}^2/W, \quad \beta(0.05\text{wt\%}) = -2.75 \text{cm}/W \quad \text{and} \quad \Delta \Phi_o(0.05\text{wt\%}) = -1.99, \]
\[ \gamma(0.08\text{wt\%}) = -4.8 \times 10^{-5} \text{cm}^2/W, \quad \beta(0.08\text{wt\%}) = -4.02 \text{cm}/W \quad \text{and} \quad \Delta \Phi_o(0.08\text{wt\%}) = -4.78. \]

4. Conclusion

We have presented on the determinations of the optical nonlinearities of azo dye doped polymer film by means of the holographic gratings as a scalar effect and the photoinduced birefringence as a vector effect. We have measured the diffraction efficiency of the holographic gratings and the photoinduced birefringence caused by a linear polarized pump beam as a function of time for various laser beam intensities and azo dye concentrations. It is found that the real time behaviors of both of the diffraction efficiencies and the photoinduced birefringence reveal the stretched exponential kinetics. A three state model for photoisomerization is proposed to analyse the stretched exponential kinetic behaviors. Theoretical predictions are in good agreements with the experimental data.

To determine the sign of the optical nonlinearities we have conducted the Z-scan experiments and found that the sign of the nonlinear refractivity of azo dye doped polymer (MO/PVA) film is negative (i.e., self-defocusing) from the closed aperture Z-scan, and that the sign of the nonlinear absorption coefficient is also negative (i.e., photobleaching) from the open aperture Z-scan.

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