

Photoinduced Birefringence Properties of Poly-Schiff Bases Containing Triphenylamine

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ABSTRACT: Anisotropy was induced in poly-Schiff bases containing triphenylamine with linearly polarized light at 488 nm. Both writing and relaxation processes were described with a biexponential function. The alignment process involved two response modes: a fast response mode and a slow one. The fast response mode was associated with angular-dependent trans–cis photoisomerization, whereas the slow one was attributed to the position adjustment of the rigid main chains used to obtain well-aligned monodomains. The writing rate increased with an increase in the

light intensity at a low intensity of the irradiation light. Structural factors such as main-chain rigidity seemed to play important roles in the remaining stored information. The two polymers had large photoinduced birefringence values (0.01 and 0.0015, respectively). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2274–2279, 2004

Key words: conjugated polymers; nonlinear polymers; optics

INTRODUCTION

In recent years, nonlinear optical effects in organic materials have become more interesting because of their useful applications in integrated optics, such as optical modulation, all-optical switching and optical information processing, and optical memory.^{1–4}

Polymers that incorporate both photoconductive and electrooptic functionalities can be regarded as suitable materials for a wide range of optical and electrooptic applications.^{4,5} If the electrooptic chromophores are based on an azobenzene structure, these groups can be preferentially oriented with a polarized laser for reversible optical storage and for the inscription of channel waveguides. Poled photorefractive polymers have now begun to perform competitively with traditional inorganic crystals, and they possess some advantages, such as lower cost, greater versatility, and relative ease of preparation and processing.

Photoinduced birefringence is a result of reversible trans–cis photoisomerization with respect of the N=N double bond of the azobenzene group, which

induces an angular redistribution in the orientation of the photochromic entities. Because of the selectivity of excitation, the chromophores tend toward the polarization of the acting light. After the laser pump is turned off, the stability and magnitude of the photoinduced birefringence and surface gratings are strongly associated with polymer properties, such as the concentration in the sample, glass-transition temperature, molecular weight, polarity, position of the azo group, chromophore structure, polymer main-chain rigidity, and interaction between the chromophore and the main chain. Azo dyes either dispersed or grafted into polymer matrices or into organic–inorganic composite materials have been widely researched.^{4–13}

On the other hand, it is well known that triphenylamine is a photoconductor that can be used in electrooptic cells. To the best of our knowledge, no one has researched the birefringence of poly-Schiff bases containing triphenylamine. There is a C=N double bond in the backbone of the Schiff base, different from N=N and C=C double bonds. The properties of poly-Schiff bases may be different from those of polyaniline and poly(phenylethylene).

Triphenylamine replacing an aliphatic amine should also improve the thermal and orientational stability of functional groups, such as an azo moiety, as demonstrated for all-aromatic amines, which are part of azo groups on the side chains of polymers. Another potential benefit of having a triphenylamine moiety in the backbone is the possibility of building

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variable spacers between the main chains, which would allow increasing degrees of order as the main chains become more and more decoupled from the interaction motion.

In this article, the optical storage processes of two poly-Schiff bases of the biamine triphenylamine are described. The photoinduced birefringence is examined with C=N as a function of their structure.

EXPERIMENTAL

The synthesis and characterization of the polymers have been described in detail elsewhere.¹⁴

Thin films were obtained through the dissolution of the polymer in CHCl₃, which was followed by the spin casting of the solution onto a clean glass substrate for photoinduced birefringence experiments. The solvent was allowed to evaporate for 5 h at room temperature and was subsequently heated at 60°C. Relatively homogeneous thin films 1.2 or 3.4 μm thick were obtained with this procedure, as determined by polarization microscopy.

The optically induced anisotropy was measured via the placement of a sample between two crossed linear polarizers. A low-power He-Ne laser at 632.8 nm was used as a light probe to measure the power transmitted through this optical setup. Optical anisotropy was induced in the polymer film with a polarized argon beam at 488 nm with an irradiance of 100 mW/cm² to write on the sample at a polarization angle of 45° with respect to the probe beam polarization (i.e., polarizer orientation). The sample was placed between the two crossed polarizers. The pump beam size on the sample was measured to be about 0.2 cm². The transmittance was detected with a silicon photodiode connected through a lock-in amplifier to a digital oscilloscope photomultiplier and a computer-controlled ADC (Analog Digital Converter) card and was recorded for further analysis. The probe light was modulated at about 400 Hz by a mechanical chopper. All measure-

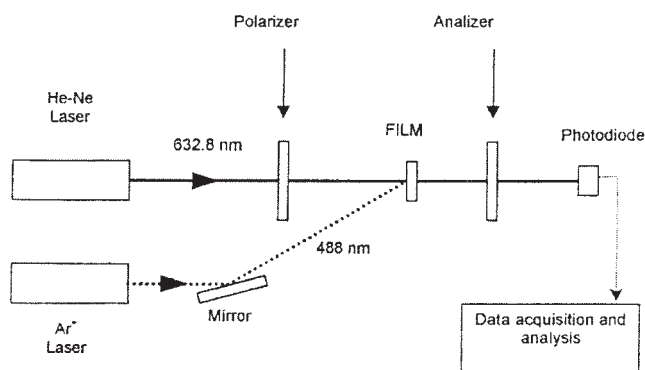


Figure 1 Experimental setup used to investigate the photoinduced alignment: polarizer and analyzer (two crossed polarizers).

ments were performed at room temperature. A typical writing unit is shown in Figure 1.^{7,8}

The structures and UV-vis spectra of poly-Schiff base 1 (PSB1) and poly-Schiff base 2 (PSB2) in CHCl₃ are shown in Figures 2 and 3. Moreover, the material should not absorb at the wavelength of the reading light.

The thermal properties of the polymers were analyzed by differential scanning calorimetry in N₂. The glass-transition temperature were 340 and 301°C, respectively.

RESULTS AND DISCUSSION

In anisotropic materials, the plane wave transmitting with different velocities and directions can show the birefringence. The value of the birefringence can be determined from changes in the polarization state of the probe laser beam, that is, the switching from linearly polarized states to circularly polarized states. Once the linearly polarized pump beam is irradiated, birefringence is induced in polymer films. The induced birefringence is characterized by the phase retardation [$\delta = (2\pi d\delta_n)/\lambda$, where d is the thickness, λ is the wavelength, and δ_n is the induced birefringence], and the corresponding Jones matrix is⁷

$$\mathbf{W} = \begin{bmatrix} \cos(\delta/2) - i \sin(\delta/2)\cos(2\alpha) & -i \sin(\delta/2)\sin(2\alpha) \\ -i \sin(\delta/2)\sin(2\alpha) & \cos(\delta/2) - i \sin(\delta/2)\cos(2\alpha) \end{bmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \quad (1)$$

where α is the angle between the optical-axis-induced birefringence and the polarization direction of the probe beam. Because the input and output polarizers are crossed, the transmitted matrix (\mathbf{T}) can be obtained as follows:

$$\mathbf{T} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & B \\ 0 & 0 \end{pmatrix} \quad (2)$$

On the action of the pump [wavelength of the pump light pump = 488 nm] laser beam, the intensity of the

He-Ne laser beam transmitted through the crossed polarizers (I) is given by

$$I = I_0 \sin^2(\pi\delta_n d/\lambda_{\text{probe}})\sin^2(2\alpha) \quad (3)$$

Solving for δ_n , when α is 45°, we obtain

$$\delta_n = \frac{\lambda_{\text{probe}}}{d\pi} \sin^{-1} \sqrt{I/I_0} \quad (4)$$

where I_0 is the probe intensity of the He-Ne laser beam transmitted when the polarization of P parallels

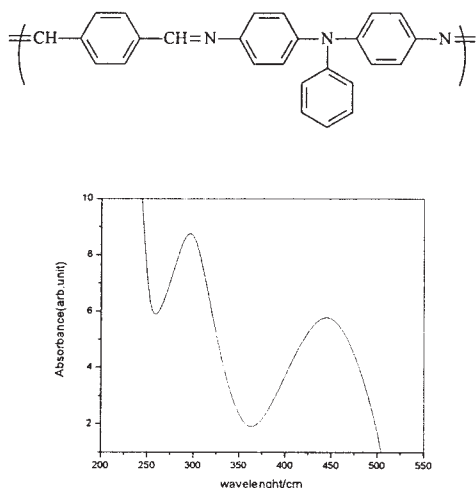


Figure 2 Structure and UV-vis absorption spectrum of PSB1.

A before the irradiation pumping light. The transmitted light intensity depends on α , and it is expected to show its maximum value when α is 45° . In our experiment, the transmitted light intensity reached the maximum value when the angle between the polarization direction on the pump beam and that of the probe beam was set to be 45° .

The value of δ_n depends on the intensity of the writing pumping light, the dye concentration, and the performance of the investigated material. From the results shown later in Figures 5 and 6, we calculated the values of δ_n to be about 0.01 and 0.0015. These large values make us think that this sort of polymer would be an ideal polarization-sensitive material for polarization holographic recording.

Photoinduced birefringence process

A typical writing sequence is presented in Figure 4. The sample was initially homogeneous and optically

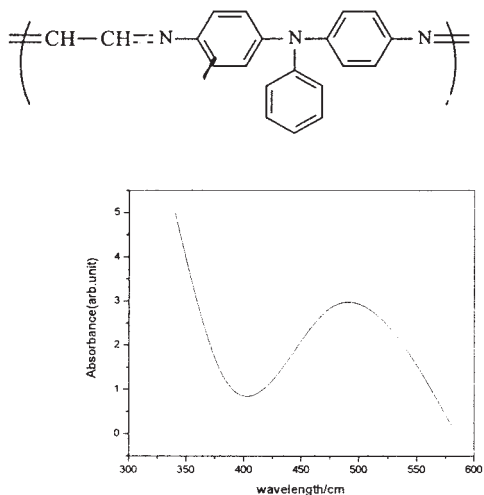


Figure 3 Structure and UV-vis absorption spectrum of PSB2.

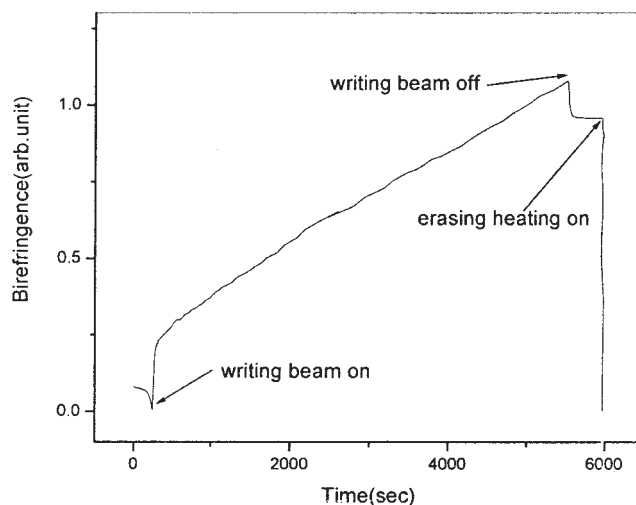


Figure 4 Write-erase profile for optically induced and erased birefringence of PSB2 with a laser beam at 632.8 nm.

isotropic, and no transmission of the probe beam through the crossed polarizers was observed. As optical anisotropy was induced by the linearly polarized argon beam being switched on in the polymer film, the probe was partially transmitted through the optical setup, and the birefringence was induced in the polymer film. As shown in Figure 5, the transmission reached 60% saturation in about 50 s and 90% in about 170 s. In PSB1, the saturation corresponded to a transmission of 0.4% of the input. This corresponded to an induced birefringence of about 0.01. Similarly, in PSB2, the saturation corresponded to a transmission of 0.073% of the input. The transmission reached 60% saturation in about 95 s and 90% in about 335 s. From this, we can conclude that PSB1 had higher birefringence than PSB2, and it could reach saturation more quickly than PSB2. This may be due to the somewhat crosslinked structure of PSB2 and the steric hindrance effect of the phenyl in PSB2, in fact, PSB1 was more inclined to orientation alignment.

During the second stage, as shown in Figure 6, the writing beam was switched off, and the transmitted signal of PSB1 decreased to about 90% of the saturation value in about 10 s. This showed that the induced optical anisotropy was not completely preserved after the writing with linear polarized light, but a significant long-term effect was nevertheless seen. When the writing beam was turned off, the birefringence values of PSB1 and PSB2 decreased to 0.0095 and 0.00096, respectively, and were 88 and 74% of the saturation values of birefringence when the writing beam was on. The induced anisotropies were stable for several months, from the time of the first test to the time at which this article was written.

During the third stage in the writing sequence, the optically induced anisotropy was erased via heating at

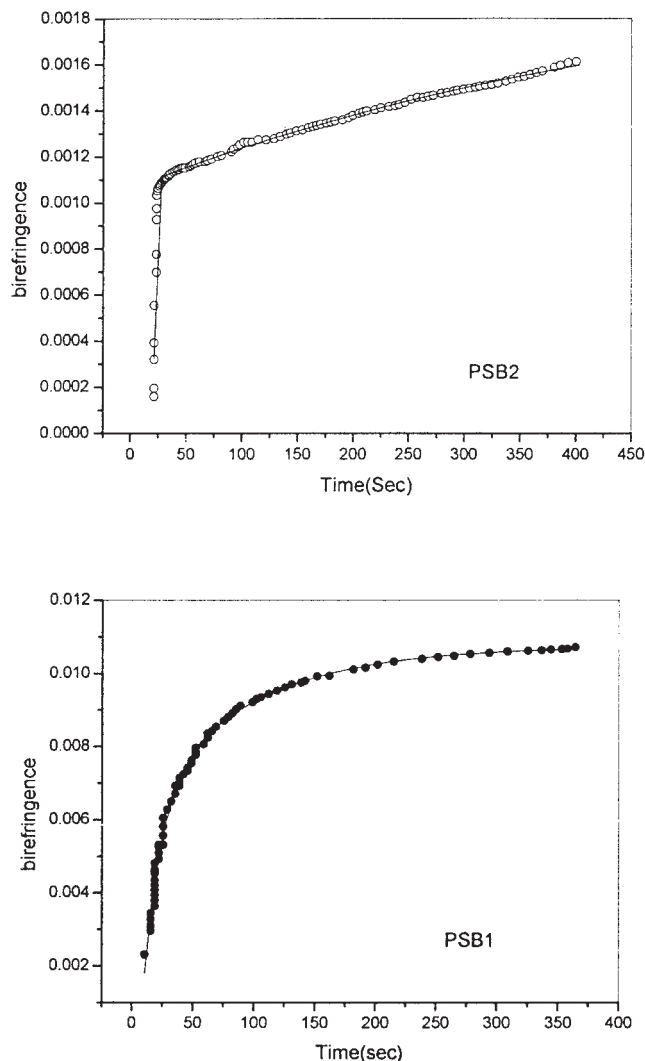


Figure 5 Photoinduced birefringence curves for PSB1 and PSB2. The solid lines are fits to biexponential functions [eq. (1) for PSB1 and eq. (2) for PSB2].

80°C. This mode of writing effectively returned the film to an optically isotropic state, thereby erasing the previously encoded information. As shown in Figure 6, the erasing time for PSB2 was about 10 s.

As indicated in the introduction, the optical anisotropy was induced birefringence in the polymer film resulting from a reorientation of the azomethine moieties. Linearly polarized light was used to cause trans-cis isomerization followed by molecular reorientation and cis-trans isomerization. The absorption and reorientation sequence was repeated until the molecule's dipole moment was lying in a direction perpendicular to the polarization direction of the writing beam. In this way, net macroscopic optical anisotropy could be induced in the film. The writing times were thus controlled by the photon flux, the trans-cis isomerization rate, and the degree of molecular reorientation attainable in a given sequence. The erasing procedure with

heating on was interpreted in a similar fashion, except that in this case thermopower was absorbed for any molecular orientation and no particular reorientation was favored; the result was a removal of the optical anisotropy of the film.

Dynamic study of photoinduced birefringence

The intensity of the transmitted reading beam increased sharply and reached saturation when the writing beam was on. The reading beam intensity decreased when the writing beam was turned off because of the relaxation of the polyazomethine conformation. The relaxation curve leveled off at a constant level, leading to a plateau. When the erasing by heating was turned on, the intensity of the transmitted beam decreased to almost zero. It was possible to repeat the cycles many times. The *in situ* birefringence curves of azomethine PSB1 and PSB2 during the writing process are shown in Figures 5 and 6.

From previous studies of photoinduced birefringence in similar azobenzene polymers, it has been

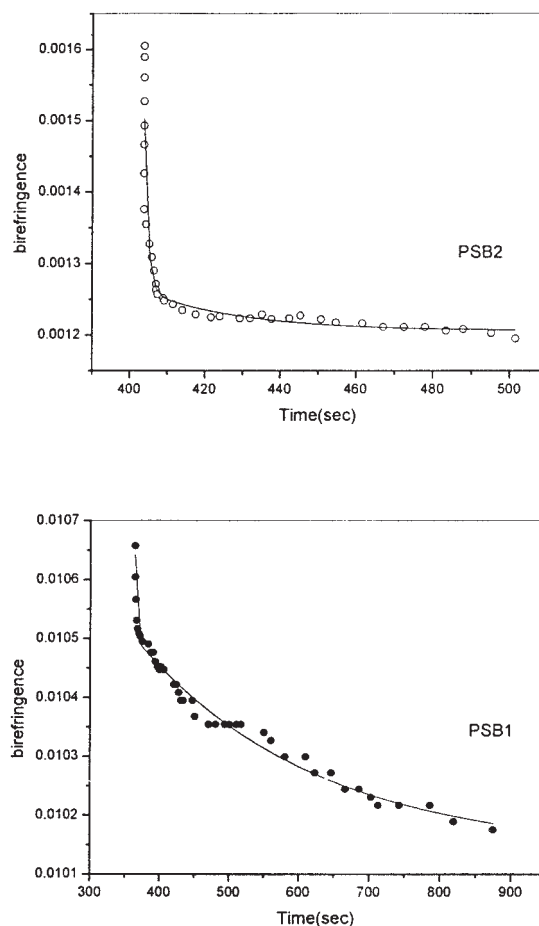


Figure 6 Decay of birefringence after the writing laser was turned for PSB1 and PSB2. The solid lines are fits to biexponential functions [eq. (1) for PSB1 and eq. (2) for PSB2].

TABLE I
Normalized Parameters Obtained from the Fitting of the Birefringence Growth Curves in Figure 5 to Eq. (1)

	PSB2	PSB1
C	-2.59064	-0.374
A	0.487	0.939
t_1	490.190	14.258
B	2.59064×10^6	0.434
t_2	1.373	87.996

shown that the growth section of the curve depicted in Figure 5 can be modeled effectively with a biexponential equation:^{4,5,7,8,13}

$$y = A[1 - \exp(-x/t_1)] + B[1 - \exp(-x/t_2)] + C \quad (5)$$

where A and B are normalized constants ($A + B + C = 1$) describing the relative contributions of two exponential growth functions described by characteristic time constants t_1 and t_2 . If t_1 is less than t_2 , then these can be regarded as the time constants for fast and slow growth rates, respectively, with fast rate coefficient A and slow rate coefficient B . C is only constant used to fit the equation (5), and x is time variate.

As shown in the previous figures, the experimental birefringence values and calculated curves matched very well. The fitting parameters are shown in Table I. The writing process consisted of two components: an initial fast mode and a slow mode. Parameters A and B in Table I represent the weighted contribution of t_1 and the slow growth component with t_2 , respectively. The magnitude of t_1 was governed by the quantum yield, the trans-cis-trans isomerization rate, and the local mobility of the azomethine groups. The magnitude of t_2 depended on the coupling interaction between the azomethine and the polymer segments and the mobility of the polymer segments. The values of t_1 and t_2 of PSB1 were different than those of PSB2. This may be due to the big differences in the steric hindrance of the phenyl in the backbone.

Dark relaxation curves of birefringence of PSB1 and PSB2 are shown in Figure 6. The solid lines are fits to the following biexponential function:

$$y = E \exp[-(x - x_0)/t_1] + F \exp[-(x - x_0)/t_2] + G \quad (6)$$

where t_1 is characteristic time constant standing for the fast exponential relaxation and t_2 is describing the slow one when t_1 is less than t_2 . G represents the fraction of the induced birefringence that is stable over time, being independent of time, and E , F are normalized coefficients standing for the contributions of the

TABLE II
Normalized Parameters Obtained from the Fitting of the Birefringence Decay Curves in Figure 6 to Eq. (2)

	PSB2	PSB1
G	4.885	6.41931×10^{-12}
x_0	333.044	318.284
E	1	1
t_1	1.058	1.542
F	3.39188×10^{-29}	2.78825×10^{-13}
t_2	25.930	260.170

two exponential relaxation functions described by t_1 , t_2 . x_0 is the only parameter used to fit equation (6). The fitting parameters are summarized in Table II. The data, similar to the growth curves, show two modes for the relaxation process. Cis-trans isomerization of the azomethine groups contributed to the initial fast decay modes, whereas interactions between the side chains and polymer backbones and the alignment of the main chain affected the slow process. There was the same significant difference between the birefringence relaxation rates of PSB1 and PSB2 as the growth behaviors.

The fitted biexponential curves lay within the experimental noise recorded by the probe beam detection equipment, and error estimates for the fits of the data to eqs. (1) and (2) were observed to be similar to those presented in previous curve-fitting publications.

The influence of the power of the writing laser on the induced birefringence was also studied, as shown in Figure 7. For the PSB2 film, the induced birefringence increased with the laser power up to about 450 mW/cm², after which it tended to saturate. This higher writing beam saturation power could be attributed to polymer rigidity. The time to achieve 50% of the maximum birefringence decreased drastically with increasing writing beam power.

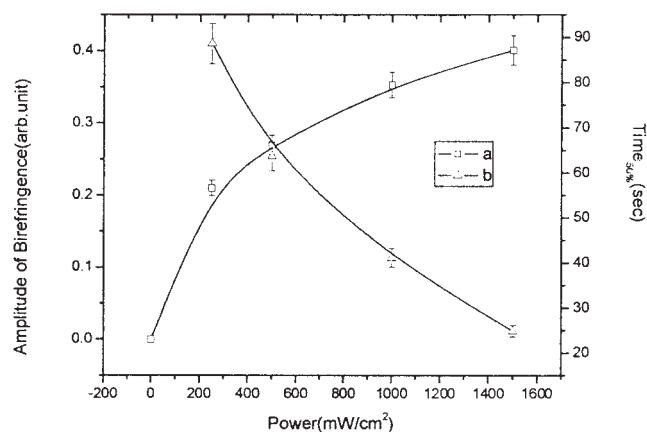


Figure 7 Dependence on the laser power (a) for the amplitude of the induced birefringence and (b) for the time to achieve 50% of the maximum birefringence in PSB2 films. The lines have been drawn as guides.

For the PSB2 film, the amplitude of the induced birefringence obtained with a pump beam power of 100 mW/cm² was 0.0015. The remaining birefringence (Fig. 6) in the film was 75% of the maximum birefringence value, being independent of the pump laser power.

CONCLUSIONS

The photoinduced birefringence was measured with a pump probe scheme in PSB1 and PSB2 films. The values of the birefringence were 0.01 and 0.0015, respectively. We described the photoinduced birefringence properties of two polymers, and we found that the writing and relaxation processes could be described by an initial fast response mode and a slow response mode. The biexponential functions yielded good fits to the writing and relaxation curves. These polymers could potentially be used in optical storage media.

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