Dyes and Pigments 82 (2009) 47–52

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The nonlinear optical properties and photoinduced anisotropy of a novel stilbene-containing fluorinated polyimide

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ARTICLE INFO

Article history:
Received 2 July 2008
Received in revised form
30 October 2008
Accepted 31 October 2008
Available online 6 December 2008

PACS:
42.65.An
42.65.Ky
78.20.Fm

Keywords:
Stilbene-containing fluorinated polyimide
Second-order optical nonlinearity
Third-order optical nonlinearity
Photoinduced anisotropy

ABSTRACT

The nonlinear optical properties and photoinduced anisotropy of a novel stilbene-containing fluorinated polyimide were investigated. Large macroscopic second-order optical nonlinearity ($d_{33} = 35.4$ pm/V) was obtained in a poled thin film using the Maker fringe method. A nonlinear absorption coefficient (β) of 0.65×10^{-5} cm/W and third-order nonlinear refractive index (n_2) of -1.13×10^{-10} cm^2/W were determined by *Z*-scan measurements. Photoinduced birefringence (Δn) of 1.02×10^{-2} was observed using a continuous Nd:YAG laser at 532 nm as pump light and a continuous diode laser at 650 nm as probe light.

1. Introduction

Recent studies have shown that organic materials exhibit promising features for optical devices. However, most of the reports focus on only one nonlinear optical property of organic materials. When an optical material is synthesized, it is expected to be fully utilized in a variety of optical devices. From the viewpoint of practical applications, stilbene-containing π-conjugated compounds are anticipated to satisfy this demand. They represent one particularly promising class of organic nonlinear materials. Various research groups have showed that this kind of organic material exhibited many applications in nonlinear optics [1], electro-optic (EO) modulators [2] and optical storage [3]. On one hand, stilbene-containing π-conjugated compounds own large second-order optical nonlinearity when their thin films are corona-poled in the air by an applied electric voltage, which makes it possible for them to be used in EO modulators. On the other hand, among many nonlinear optical materials, stilbene-containing π-conjugated compounds with extended electron delocalization seem to be promising candidates for future practical application in all optical switching devices because of their large third-order optical nonlinearity and ultra-fast response time. Furthermore, just like the azobenzene molecules, stilbene molecules have two isomeric forms: *trans*-stilbene and *cis*-stilbene [4]. Both of them can undergo *trans–cis–trans* isomerization under the irradiation of light with an appropriate wavelength and be reoriented by a linearly polarized light. This process is called photoinduced molecular reorientation of stilbene molecules, and it generates photoinduced anisotropy. Due to this special property, stilbene-containing π-conjugated compounds can be used as one kind of the most efficient optical storage and polarization holographic recording materials.

In this paper, with the purpose of obtaining an effective optical material which can be fully used in a variety of optical devices, we have synthesized a novel stilbene-containing fluorinated polyimide. In order to evaluate its suitability for the applications in nonlinear optical devices and polarization grating devices, we have studied the second-order and third-order optical nonlinearities, and the photoinduced birefringence of this polymer. Large macroscopic second-order optical nonlinearity in a poled polymer thin film was observed by using Maker fringe method [5]. By carrying out traditional *Z*-scan measurement [6], large third-order nonlinear refractive index was obtained in a polymer thin film, which was

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doi:10.1016/j.dyepig.2008.10.022

spin-coated onto a transparent optical glass substrate. Stable photoinduced molecular reorientation was observed and photoinduced birefringence with the value in order of 10^{-2} was obtained.

2. Experimental

2.1. Synthesis of the stilbene-containing fluorinated polyimide

Fig. 1 shows the synthetic routine of this novel stilbene-containing fluorinated polyimide. In this polymer molecule, a stilbene nonlinear chromophore is attached as side-chain to the fluorinated polyimide skeleton.

The synthesis of this stilbene-containing fluorinated polyimide was achieved through Mitsunobu reaction with preimidized hydrooxy-containing polyimide **1** and the chromophore **2** (Fig. 1). The polyimide **1** and chromophore **2** were prepared according to the methods reported in literatures [7,8], respectively. The hydrooxy-containing polyimide **1** (106 mg, 0.13 mmol), chromophore **2** (134 mg, 0.39 mmol) and triphenylphosphine (204 mg, 1.0 mmol) were dissolved in anhydrous THF (30 mL) successively. Diethyl azodicarboxylate (DEAD) (136 mg, 1.0 mmol) in 5 mL THF was added dropwise into solution under nitrogen at about 5 °C. The reaction mixture was stirred for 30 min, and this was followed for 3 days at room temperature. And then the mixture was poured to methanol (50 mL). The yellow solid was collected by filtration and washed with methanol (50 mL), dried under vacuum to give the stilbene-containing fluorinated polyimide. Yield: 102 mg (55.7%). ^{1}H NMR (acetone-d_6) δ: 1.07 (s, 12H, –CH_3), 2.89 (s, 4H, –CH_2–), 4.34 (s, 4H, –CH_2–), 4.53 (s, 8H, –CH_2–), 6.85–6.90 (m, 6H, ArH), 7.20–7.37 (m, 8H, ArH and CH═CH–), 7.53–7.69 (m, 8H, ArH), 7.94–8.00 (m, 4H, ArH). IR (KBr) ν: 3437 (br, –OH), 2222 (–CN).

Thermal properties of the stilbene-containing fluorinated polyimide were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperature T_g and decomposition temperature T_d of this polymer are 254 °C and about 287 °C, respectively, which indicates that it has high thermal stability. The molecular weight of this polymer was estimated by Gel Permeation Chromatography (GPC). The stilbene-containing fluorinated polyimide has a weight-average molecular weight $\overline{M}_w$ of 8.38×10^4 g/mol as well as a number-average molecular weight $\overline{M}_n$ of 3.90×10^4 g/mol based on polystyrene standard. Because they have lower average molecular weight and the flexible CF_3 groups are incorporated in the polyimide, this polymer is soluble in organic solvents such as THF, DMF, DMSO and acetone. Therefore, its polymer films can be easily prepared for measurement of macroscopic nonlinear optical coefficient and photoinduced birefringence.

Fig. 2 shows the UV–vis spectrum of polymer thin film, which was obtained using a Perkin–Elmer lamda 20 UV–vis spectrophotometer. The absorption of the polymer is negligible at 1064 nm, which indicates that it has nice optical transparence at the work wavelength of 1064 nm in the succeeding measurement of second harmonic generation (SHG). Moreover, 532 nm lies in the tail of absorption band, so the thermal effect can be neglected in the measurement of third-order nonlinear refraction at the work wavelength of 532 nm.

2.2. Measurement of the second-order optical nonlinearity

As well known, the second-order nonlinear optical interactions can occur only in noncentrosymmetric media. In order to obtain the noncentrosymmetric structure of polymer, the film was corona-poled in the air by an applied electric voltage of 4.3 kV at 160 °C for 25 min with interelectrode distance being 2 cm, and cooled down to room temperature with the field still applied.

Second harmonic generation (SHG) is known to be a fast and quantitative technique for probing materials with polar structures. In a typical SHG measurement, a sample is illuminated with a high peak-power laser beam and the generated SHG signal carrying the information of second-order nonlinear optical properties is detected. In the experiment, the second-order nonlinear coefficient d_{33} of poled polymer thin film was measured by using Maker fringe method [5]. This method was used to change the angle between the incident laser beam and the normal plane of samples by the rotation of sample so as to gain space cycle distribution of second-order harmonic signal. The second-order nonlinear optical coefficient of sample could be obtained by comparing second-order harmonic power of sample with that of the standard sample quartz. In this experiment, double optical path system with d_{33} of x-cut quartz as reference was used. A p-polarized Q-switched Nd:YAG laser with 16 ns pulse width and 50 Hz repetition frequency was used as laser source. The wavelength of fundamental light was 1064 nm and the maximum output energy was 300 mJ. The film was laid at 45° to the incident beam. The SHG signal was recorded with the help of a photomultiplier tube.

2.3. Measurement of the third-order optical nonlinearities

The nonlinear refractive index n_2 and nonlinear absorption coefficient β of the polymer thin film were evaluated by the *Z*-scan measurements [6]. If there is nonlinear absorption existing in the thin film, the closed transmittance is affected by both the nonlinear refraction and nonlinear absorption. As a result, the determination of n_2 is less straightforward from the closed aperture *Z*-scan

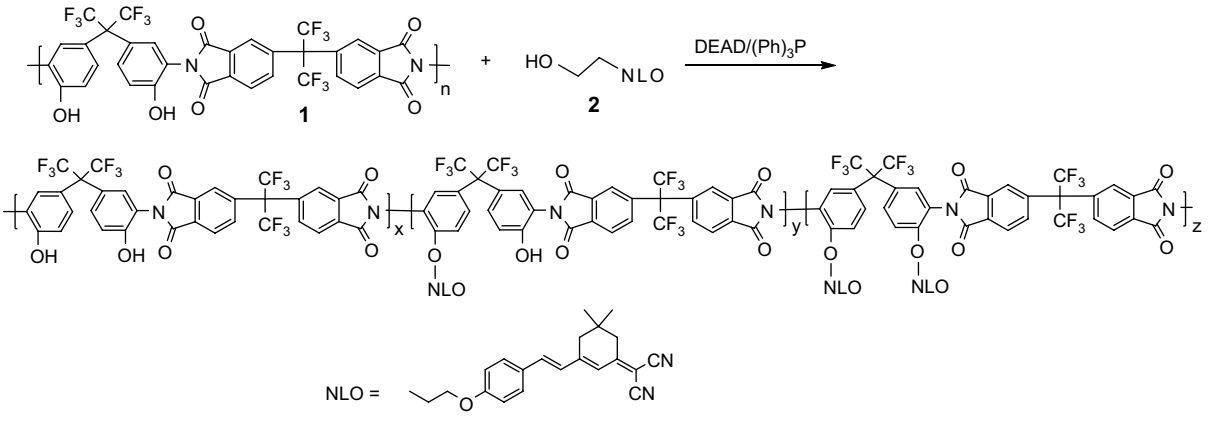

Fig. 1. Synthetic routine of the stilbene-containing fluorinated polyimide.

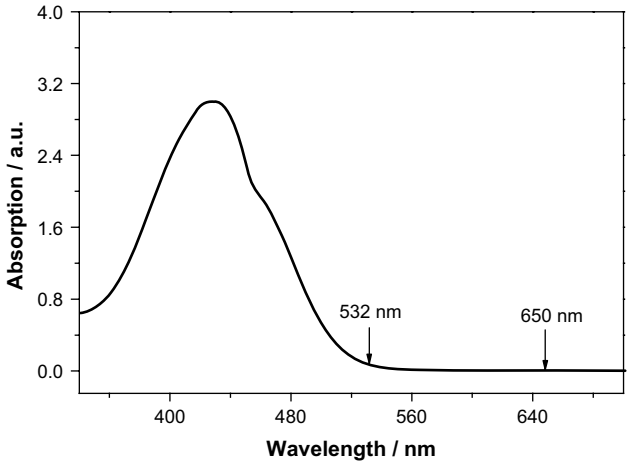

Fig. 2. The UV–vis absorption spectrum of polymer thin film.

measurement. It is necessary to separate the effect of nonlinear absorption by performing open aperture *Z*-scan experiment. In the experiment, a mode-locked Nd:YAG laser with a frequency doubled at 532 nm was used as the light source. The repetition frequency was 10 Hz and pulse duration was 38 ps, respectively. The laser beam was focused on the sample by a lens with 30 cm focal length, leading to a measured beam waist of 34.94 μm.

2.4. Measurement of the photoinduced birefringence

The optical birefringence was induced in the samples by using a continuous Nd:YAG laser at 532 nm (writing beam) with a polarization angle of 45° with respect to the polarization orientation of the probe beam (reading beam). A low-power continuous diode laser light at 650 nm passing through two crossed polarizers was used as the reading beam to measure the induced birefringence in the sample.

3. Results and discussion

3.1. Second-order nonlinear coefficient

Fig. 3 shows the second-order harmonic signal from a poled polymer thin film. The curve represented the background signal without sample before time t_1, and it represented the second-order harmonic signal of x-cut quartz between time t_1 and t_2. Between time t_2 and t_3, the curve represented second-order harmonic signal from this poled polymer thin film. After time t_3, the curve was background signal without sample.

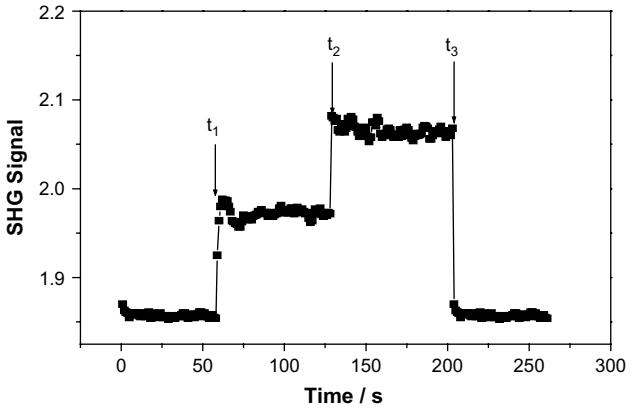

Fig. 3. The second-order harmonic signal from a poled polymer thin film.

The NLO coefficient d_{33} could be deduced by the following equation:

$$d_{33} = d^{(2)}_{zzz(\text{quartz})}[R]^{1/2}\frac{l_c^{\text{quartz}}}{l}F, \tag{1}$$

where R is the relative intensity of SHG, l_c^{quartz} is the relative length of quartz, l is the thickness of the thin film. The F of thin film can be obtained from the following equation:

$$F^2 \approx \left(0.28\frac{l_c^2}{l^2}\right)\left[1-\cos\frac{\pi l}{l_c}\right], \tag{2}$$

where l_c is the coherent length of polymer thin film. When $l < l_c$, function F is approximately a constant ($F = 1.2$). Then the second-order nonlinear refractive index d_{33} can be evaluated utilizing Eqs. (1) and (2). The thickness of the poled polymer thin film was 2.3 μm and the second-order nonlinear refractive index d_{33} was calculated to be 35.4 pm/V. The value of the second-order nonlinear refractive index is 2 times larger than those of the polymers reported in Ref. [9] and can satisfy the criteria for the practical applications.

3.2. Third-order nonlinear optical properties

Fig. 4(a–c) shows *Z*-scan experimental data for closed aperture (CA) curve, open aperture (OA) curve and closed aperture curve divided by open aperture (CA/OA) curve of the polyimide thin film. The nonsymmetrical closed aperture *Z*-scan curve in Fig. 4(a) indicated that the nonlinear absorption existed, so the nonlinear refractive index under 532 nm excitation, with division of corresponding open aperture *Z*-scan curve as shown in Fig. 4(b), could be obtained as shown in Fig. 4(c). The peak to valley configuration of curve in Fig. 4(c) suggests that the sign of nonlinear refractive index is negative, indicating a self-defocusing effect. Because the nonlinear refraction of glass substrate can be neglected, the high nonlinear optical property results from the polymer film.

The data were analyzed with the procedures described in Ref. [6]. The open aperture *Z*-scan curve displayed in Fig. 4(b) is symmetric with respect to the focus ($z = 0$), where it has a minimum transmission. The polymer thin film exhibited a reverse saturation absorption effect. The normalized transmittance for open aperture *Z*-scan experiment is given by

$$T(z, s = 1) = \sum[-q_0(z,0)]^m/(m+1)^{3/2} \quad (q_0(0) < 1), \tag{3}$$

where $q_0(z,0) = \beta I_0 L_{\text{eff}}/(1+z^2/z_0^2)$, β is the nonlinear absorption coefficient, I_0 is the intensity of the laser beam at focus $z = 0$, $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, ω_0 is the beam waist radius at the focus point and $k = 2\pi/\lambda$ is wave vector, $L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient and L is the thickness of the sample. In the experiment, $I_0 = 3.16\times10^9$ W/cm^2, $L = 0.7$ μm, $\alpha = 0.233$ μm^{-1} and $L_{\text{eff}} = 0.65$ μm. From the theoretical fit result, the nonlinear absorption coefficient was obtained to be 0.65×10^{-5} cm/W.

The nonlinear refractive index n_2 of the polymer thin film is given by

$$n_2 = \frac{\Delta T_{p-v}\lambda}{0.406(1-s)^{0.25}\cdot 2\pi\cdot L_{\text{eff}} I_0}, \tag{4}$$

where ΔT_{p-v} is the difference between normalized peak and valley transmittance, s is the aperture linear transmittance. In the

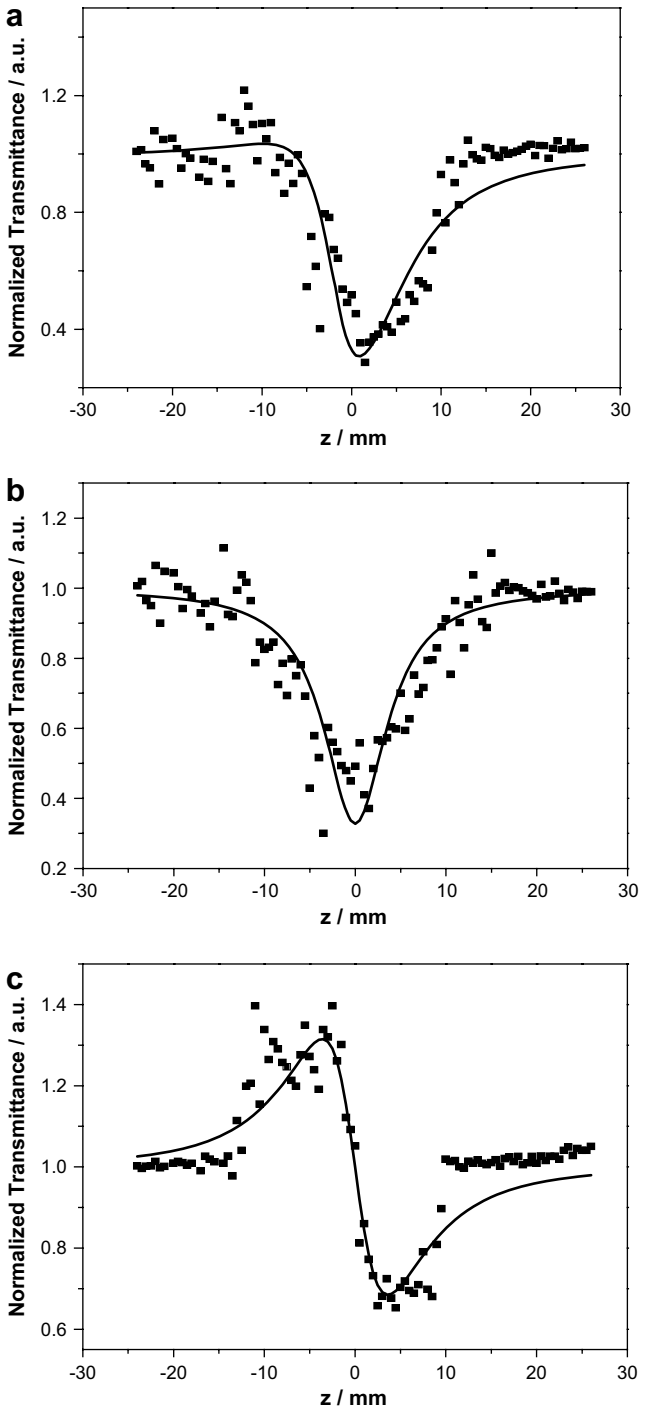

Fig. 4. *Z*-scan experimental data for the polymer thin film: (a) CA curve; (b) OA curve; (c) CA/OA curve.

experiment, the value of ΔT_{p-v} can be obtained to be 0.98 through the best theoretical fit from the results of the *Z*-scan curve as shown in Fig. 4(c), and $s = 0.40$. The third-order nonlinear index is calculated to be -1.13×10^{-10} cm^2/W. This value is much larger than those of conjugated molecules in Ref. [10].

On the basis of Schweig's nonlinear optical theory [11], the large optical nonlinearities of π-conjugated fluorinated polyimide with a stilbene nonlinear chromophore unit may be attributed to the dual contribution of the large optical nonlinearity of stilbene and the large third-order susceptibility of the configuration of the conjugative polyimide main chain, as well as the enhanced conjugation effect between stilbene pendant and conjugated backbone of polyimide. Stilbene is a well-known π-conjugated chromophore, and the attachment of stilbene pendant onto the polyimide main chain further enhances the nonlinear optical susceptibility of the polyimide [11,12].

3.3. Photoinduced anisotropy

There are few papers reporting the photoinduced anisotropy of stilbene-containing compounds except Ref. [3]. In this paper, the photoinduced anisotropy of stilbene-containing fluorinated polyimide was demonstrated by investigating the dichroism and photoinduced birefringence of the polymer thin film.

A polarized continuous argon laser beam at 488 nm was used to write on a 0.1 μm thin film of the polymer. The thin film was exposed long enough to guarantee that the molecular reorientation caused by the writing beam had reached saturation. The absorbance of the thin film was then measured for light polarized parallel and perpendicular to the polarization direction of the writing beam. The results presented in Fig. 5 show that the dichroism has been optically induced by the writing beam. The absorbance in the direction parallel to the pump polarization was obviously smaller than that in the direction perpendicular to the pump polarization. This indicates that a significant number of polymer molecules have been aligned in this direction by the writing beam. This result indicates that the polymer is an ideal polarization-sensitive material.

Fig. 6 shows temporal behavior of the signal of photoinduced birefringence under the action of pump light. The moments of turning on and off writing light are marked with arrows. Before being irradiated, the sample was an amorphous film and the polymer molecules were randomly oriented. The probe beam of 650 nm did not undergo any polarization modification when crossing the sample and no signal of photoinduced birefringence was observed. When the linear polarization 532 nm beam was turned on, the polymer molecules began to rotate by multiple *trans–cis–trans* photoinduced isomerization and *cis–trans* back thermal relaxation until the polymer molecules were aligned perpendicularly to the polarization direction of pump light. Since the dielectric constant of polymer molecules was different whether they were along the polarization direction or in the perpendicular plane, the sample exhibited anisotropy when the polymer

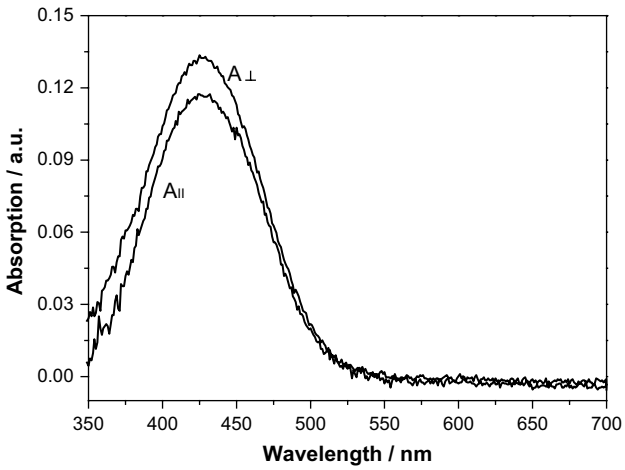

Fig. 5. Absorption spectra of the polymer thin film. The upper curve is the absorbance for light polarized parallel to the molecular orientation, while the lower curve is for light polarized perpendicular to the molecular orientation.

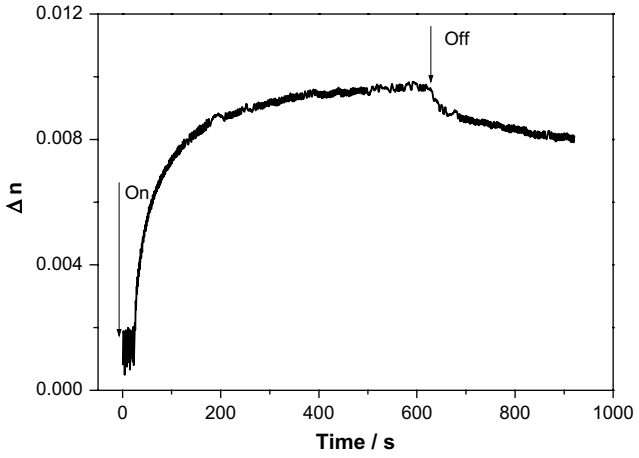

Fig. 6. Temporal behavior of the signal of photoinduced birefringence.

molecules were aligned. The polarization status of 650 nm laser was modified due to the optical anisotropy induced in the sample and the signal of photoinduced birefringence appeared. As shown in Fig. 6, the signal of photoinduced birefringence reached 50% saturation in about 45 s and 90% in about 320 s in the writing process for the light intensity of 382 mW/cm^2. When the writing beam was switched off, the signal decreased to about 80% of the saturation value. It indicated that the induced optical anisotropy was not completely preserved after the writing with linear polarized light, but a significant reorientation effect was retained.

The signal intensity can be expressed by $I_\perp = I_0 \sin^2(\pi d\Delta n/\lambda)$, where $I_\perp$ is the intensity of the transmitted light through the crossed polarizers, I_0 is the intensity of the light passing through the pair of parallel polarizers before irradiation of pump light, d is the thickness of thin film [13]. The value of the photoinduced birefringence in the polymer thin film was calculated to be 1.02×10^{-2}. Though the frequency of pump light lies in the tail of absorption band, the photoinduced birefringence of polymer thin film is very large, which indicates that the polymer film possesses good photosensitivity. The stable molecular reorientation and large photoinduced birefringence indicated that this material would be an ideal polarization-sensitive material for polarization holographic recording.

The photoinduced birefringence in the polymer thin film below or close to the glass transition temperature can be split into two modes: the initial fast one and the second slow response mode. The time dependence of the birefringence in the writing process can be fitted by the following biexponential equation [14]

$$\Delta n = A[1 - \exp(-x/t_a)] + B[1 - \exp(-x/t_b)], \quad (5)$$

where Δn represents the birefringence achieved at time t, t_a and t_b are the time constants for birefringence growth. If t_a is less than t_b, they can be regarded as the time constants for fast and slow growth rates, respectively, with fast rate coefficient A and slow rate coefficient B. Actually, the value of t_a depends on the quantum yield of the isomerization reaction, the isomerization rate and the local mobility of the stilbene nonlinear optical chromophore, which are affected by the free volume around it, the size of the stilbene moiety, and the strength of the coupling interactions between stilbene moiety and the polymer backbone. The magnitude of t_b depends mainly on the polymer mobility. Fitting the time dependence of photoinduced birefringence by the biexponential Eq. (5), the fast and slow rate constants in the writing process have been determined, respectively. Fig. 7(a) shows the optically induced birefringence curve (points) in the writing process and the solid line is a fit to a biexponential function (Eq. (5)). The fitting parameters for birefringence growth are listed in Table 1.

The relaxation of the photoinduced birefringence on removal of the writing light can also be split into an initial fast decay and a slow decay. The time dependence of the birefringence in the relaxation process can be fitted by the following equation [14]

$$\Delta n_r = C \exp(-x/t_c) + D \exp(-x/t_d) + E \quad (6)$$

where Δn_r is the relaxed birefringence after turning off the writing laser, t_c and t_d represent the time constants of the birefringence relaxation for the two kinds of motion: the fast one and the slow one. C and D are the constants related to the contribution of the two motions to the birefringence relaxation and E is the final birefringence independent of time. The fast decay would be due to the fast component of the thermal *cis–trans* isomerization and dipole reorientation, whereas the slow decay would be associated with the mobility and relaxation of the polymer backbone.

Fitting the time dependence of relaxed birefringence by the biexponential equation (Eq. (6)), the fast and slow rate constants were also obtained in the relaxation process. Fig. 7(b) shows the optically induced birefringence curve (points) in the relaxation process and the solid line is a fit to a biexponential function (Eq. (6)). The birefringence relaxation curve fitting results are listed in Table 1.

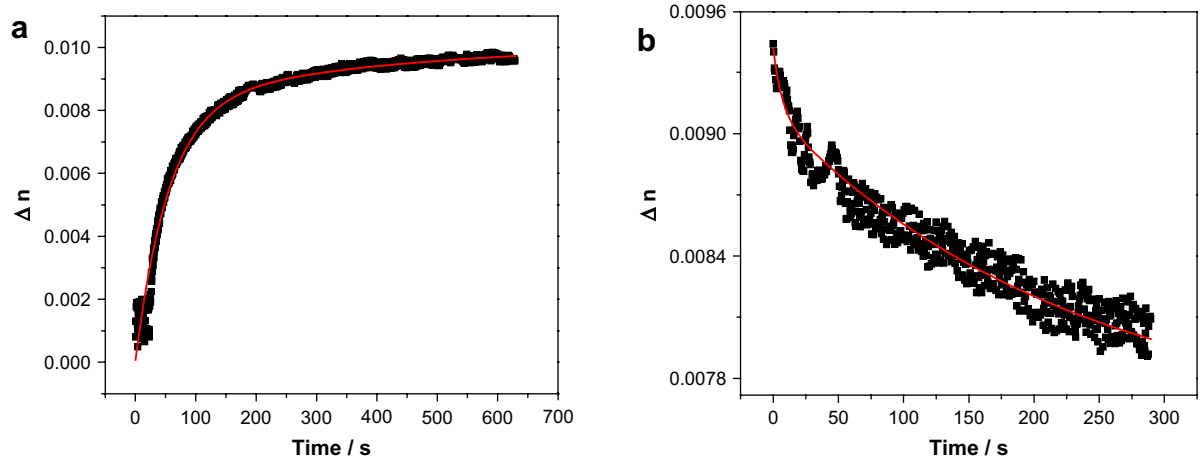

Fig. 7. (a) Optically induced birefringence curve (points) in the writing process and the solid line is a fit to a biexponential function (Eq. (5)); (b) decay of birefringence after the writing light is turned off (points) and the solid line is a fit to a biexponential function (Eq. (6)).

Table 1
The fitting parameters for the writing process and relaxation process.

Fitting parameters	Writing process	Fitting parameters	Relaxation process
A	0.00823	C	0.00031
B	0.00197	D	0.00155
A_n	0.81	E	0.00755
B_n	0.19	C_n	0.03
t_a	54.86138 s	D_n	0.16
t_b	439.30968 s	E_n	0.81
		t_c	7.14229 s
		t_d	230.2407 s

Note: $A_n = A/(A+B)$; $B_n = B/(A+B)$; $C_n = C/(C+D+E)$; $D_n = D/(C+D+E)$; $E_n = E/(C+D+E)$.

4. Conclusion

A novel fluorinated polyimide with a stilbene nonlinear chromophore unit as side-chain has been synthesized. The second-order and third-order nonlinear optical properties of this polymer have been studied by carrying out second harmonic generation (SHG) measurement and *Z*-scan measurements, respectively. The intensity of the second harmonic signal in a corona-poled polymer film has been measured. Large third-order optical nonlinearity was observed in a polymer thin film, which demonstrated strong self-defocusing refractive effect. Photoinduced optical anisotropy has been studied in a polymer thin film. Illumination with linearly polarized 532 nm light gave rise to high and stable value of birefringence in this polymer thin film. The experimental results indicate that this polymer will have potential applications in electro-optic modulators, all optical switching modulators and optical storage.

Acknowledgements

This work was supported by the National Science Foundation of China under Grant Nos. 10675083 and 20774039, the fund of the State Key Laboratory on Fiber Optic Local Area Communication Networks and Advanced Optical Communication Systems, and the National Basic Research Program of China under Grant No. 2007 CB925103.

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