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咔唑-苯并噻唑类衍生物薄膜的线性及非线性光学性质

宋秋艳[1],陈根祥[2],赵明根[3],李桐[1]

(1 北京交通大学 光波技术研究所,全光网络与现代通信网教育部重点实验室,北京 100044)

(2 中央民族大学 理学院,北京 100081)

(3 忻州师范学院化学系,山西 忻州 034000)

摘 要:以咔唑为电子供体,苯并噻唑为电子受体,合成了两种新型咔唑-苯并噻唑衍生物 3-(2-苯并噻唑-2-基乙烯基)-N-乙基咔唑和 3,6-二(2-苯并噻唑-2-基乙烯基)-N-乙基咔唑,通过核磁共振和分光光度计对其结构进行表征.利用刮刀法制备质量分数为 4%的衍生物/聚酰亚胺的复合薄膜.采用透射光谱法和单光束 *Z*-扫描技术分别测试了衍生物的线性和三阶非线性光学特性. *Z* 扫描实验结果表明 3-(2-苯并噻唑-2-基乙烯基)-N-乙基咔唑薄膜的非线性吸收系数和非线性折射系数分别为 $\beta_1=-2.118\ 9\times10^{-10}$ cm/W、$r_1=2.285\ 2\times10^{-14}$ cm^2/W,具有反饱和吸收特性和自聚焦效应;同时 3,6-二(2-苯并噻唑-2-基乙烯基)-N-乙基咔唑薄膜的非线性吸收系数与非线性折射系数分别为 $\beta_2=-1.275\ 6\times10^{-9}$ cm/W、$r_2=-7.039\ 9\times10^{-14}$ cm^2/W,具有反饱和吸收特性和自散焦效应.

关键词:电子供体-受体;咔唑;苯并噻唑;有机薄膜;透射光谱法;*Z* 扫描技术;三阶非线性光学特性

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Linear and Nonlinear Optical Properties of Carbazole-Benzothiazole Derivatives Doped Polyimide Films

SONG Qiu-yan[1], CHEN Gen-xiang[2], ZHAO Ming-gen[3], LI Tong[1]

(1 *Key Lab of All Optical Network and Advanced Telecommunication Network of Ministry of Education, Institute of Lightwave Technology, Beijing Jiaotong University, Beijing* 100044, *China*)

(2 *College of Science, Minzu University of China, Beijing* 100081, *China*)

(3 *Department of Chemistry, Xinzhou Teachers University, Xinzhou, Shanxi* 034000, *China*)

Abstract: Two novel carbazole-benzothiazole derivatives 3-((2-benzothiazole-2-yl) ethenyl)-N-ethyl-carbazole and 3, 6-bis ((2-benzothiazole-2-yl) ethenyl)-N-ethyl-carbazole containing carbazole as a donor and benzothiazole as an acceptor were synthesized and characterized by 1H-NMR spectra and UV-Visible spectrophotometer. The compound-doped polyimide thin film with mass fraction 4% were prepared by doctor blading on the glass substrate. The linear and nonlinear optical properties of the thin film were studied using the transmission spectrum method and *Z*-scan technique with 30 ps pulses at 1 064 nm, respectively. The values of the nonlinear absorption coefficient and nonlinear refractive index of the two thin films were $\beta_1=-2.118\ 9\times10^{-10}$ cm/W, $r_1=2.285\ 2\times10^{-14}$ cm^2/W, $\beta_2=-1.275\ 6\times10^{-9}$ cm/W, $r_2=-7.039\ 9\times10^{-14}$ cm^2/W, respectively. The *Z*-scan results revealed that the first compound-doped polyimide thin film exhibited reverse saturable absorption and self-focusing effect while the second

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First author(Corresponding author): SONG Qiu-yan (1986—), female, Ph. D student, mainly focuses on nonlinear optics. Email:10111004@bjtu.edu.cn

Responsible author: CHEN Gen-xiang (1965—), male, professor, Ph. D degree, mainly focuses on photoelectronic device. Email:gxchen_bjtu@163.com

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compound-doped polyimide thin film exhibited reverse saturable absorption and self-defocusing effect.

Key words: Electron donor-acceptor; Carbazole; Benzothiazole; Organic thin film; Transmission spectrum method; *Z*-scan technique; Third-order nonlinear optical property

OCIS Codes: 190.4400; 190.4710; 310.3840; 310.6860

0 Introduction

With the rapid development of nonlinear optics, nonlinear optical materials are spewing out including organic materials, inorganic materials, semiconductors and organometallics. Particularly, owing to the large and ultrafast nonlinear optical response, organic materials have attracted more attentions of worldwide scientists[1-3].

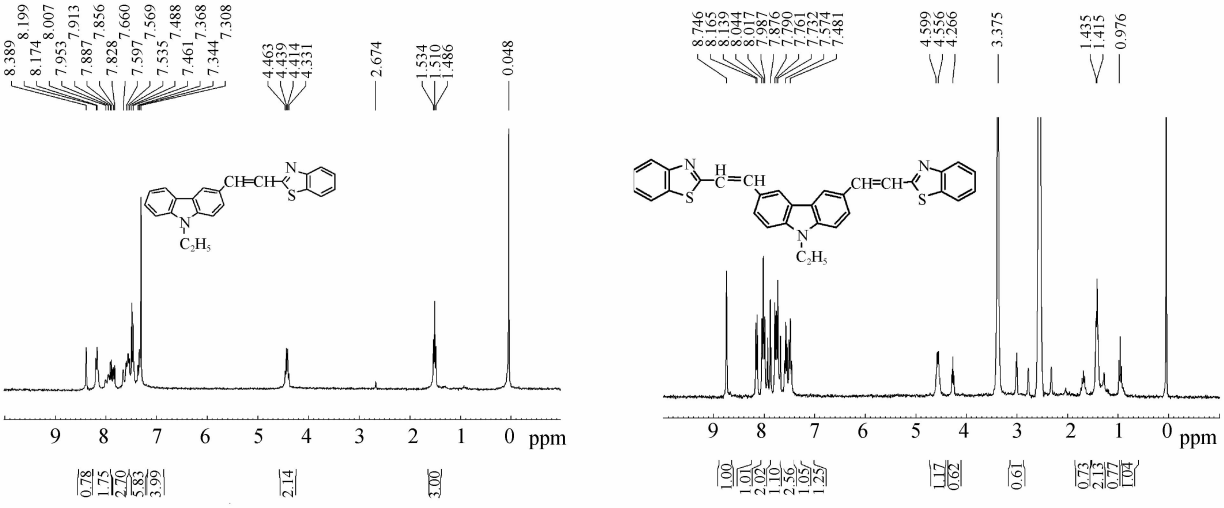
In order to gain novel organic materials with superior properties, it need to investigate the relationship between the molecular structures with the nonlinear optical efficiency[4]. Currently, the π-conjugated organic materials have emerged as a promising class of third-order Nonlinear Optical (NLO) materials. Their nonlinear optical properties are mainly concerned with electron donor, electron acceptor and π-conjugated bridge[5-8]. Heterocyclic groups have excellent ability of push or pull electronic, which contain with nitrogen, sulfur, or oxygen atom. Such as, carbazole is an electron-donor and benzothiazole is an electron-acceptor. Meanwhile, introducing heterocyclic into nonlinear optical system can improve the thermal stability of the organic molecular system[9-15].

In this paper, two carbazole-benzothiazole derivatives 3-((2-benzothiazole-2-yl) ethenyl)-N-ethyl-carbazole(compound 1) and 3,6-bis((2-benzothiazole-2-yl) ethenyl)-N-ethyl-carbazole (compound 2) were designed and synthesized. They are D-π-A type and A-π-D-π-A type, respectively. They all use carbazole as donor and benzothiazole as acceptor. Two such compounds were synthesized and characterized by NMR and UV-Visible. The third-order nonlinear optical properties were studied using *Z*-scan method.

1 Experiments

1.1 Compound molecular structures characterization

The two novel carbazole-benzothiazole derivatives compound 1 and compound 2 were synthesized. Their molecular structures were characterized by 1H-NMR spectra and illustrated in Fig. 1.



(a) 1H-NMR spectra of compound 1 (b) 1H-NMR spectra of compound 2

Fig. 1 Molecular structures and 1H-NMR spectral of two compound 1 and 2

1.2 Preparation films

In order to study the linear and nonlinear optical properties of the two organic compounds, Polyimide (PI) was chosen as the matrix because it was a transparent polymer in the optical communication wavelength. And its glass transition temperature was greater than 200℃. In addition, polyimide had excellent electrical, thermal and mechanical properties[16].

The compound 1/compound 2-doped PI thin films were fabricated as follows. First, the quartz glass substrates (20 × 20 × 1.1 mm^3) were washed with distilled water, acetone, ethanol and distilled water in turn, and dried them in oven at 100℃ for 30 min. They would be used later on. Second, 5mg of compound 1 was dissolved in a quantity of N, N-dimethylformamide (DMF) via ultrasonication for 1 h. Subsequently, 1.2g of PI/DMF solution with mass fraction 10% was mixed with the above compound 1/DMF solutions via ultrasonication for 3 h. The same method applied to the

compound 2.

Then, the prepared solutions were coated by doctor blading on the glass substrate. After 10 hours' standing at room temperature, cured films were gained. These films were then respectively dried at 60℃, 80℃ for 1 hour, and every 10℃ dried 10minutes at 90℃ to 200℃. Finally, then remove the thin films from the substrate using boiling method around 90℃. The compound 1/PI thin films and the compound 2/PI thin films with mass fraction 4% were using the following relation:

$$M(\mathrm{wt}\%)=(m_0/m_o+0.1\cdot m_p)\cdot 100 \quad (1)$$

where, m_o and m_p are the weight of organic molecule and polymer, respectively.

2 Results and discussion

2.1 UV-Visible spectra

Absorption spectra of the thin films were measured by Lambda 950 UV/VIS Spectrophotometer of PerkinElmer. The UV-Visible spectra of the compound 1/PI thin film, compound 2/PI thin film and PI thin film were shown in Fig. 2. The typical characteristic absorption behavior of the compound 1 and compound 2 were observed in the spectra. The absorbance of the compound 1/PI thin film and compound 2/PI thin film around 430 nm wavelength is biggest and up to 2.3. This result suggests that the chromophores were affected by the different acceptors, donors and conjugation lengths. Compared with compound 1/PI thin films, the UV-Visible spectrum of compound 2/PI thin films moved to longer wavelength. In other words, the increase in the degree of π delocalization results in a red shift of the absorption peak wavelength.

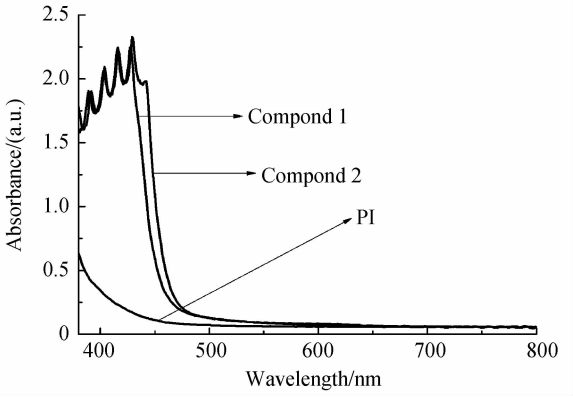


Fig. 2 UV-Vis absorption spectra of compound 1/PI compound 2/PI and PI

2.2 Linear optical properties

2.2.1 *The linear absorption*

According to the Bouguer - Lambert - Beer law, the light incident intensity will change with the change of the propagation distance and satisfy the following Eq. 2

$$I(x)=I_0\exp(-\alpha_0 CL) \quad (2)$$

And, the light transmittance is the ratio of transmission intensity to incident intensity. So

$$\alpha_0=-\ln T/CL \quad (3)$$

where, α_0 is the linear absorption coefficient, L is the thickness of the thin film, C is solution concentration and when the sample is thin film, C is equal to 1.

So, in this paper Eq. 3 is simplified into Eq. 4

$$\alpha_0=-\ln T/L \quad (4)$$

2.2.2 *The linear refractive index and thickness*

In order to determine the linear refractive index and thickness of thin films, there adopted the transmission spectrum method for. The method system was surrounded by air with refractive index $n_0=1$[17-18].

For single layer medium thin film, the relevant parameters were shown in Fig. 3. We mainly discussed

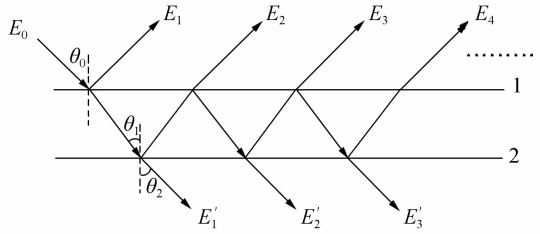


Fig. 3 System of multiple beam interference of thin film

the incident waves were vertical incidence to the thin film samples in this paper. So, $\theta_0=0$, $\cos\theta_0=\cos\theta_1=\cos\theta_2=1$.

Using Fresnel formula, we obtained Eq. 5 and Eq. 6 as follows

$$n=\{[1+(1-T_{\min})^{1/2}]/[1-(1-T_{\min})^{1/2}]\}^{1/2} \quad (5)$$

$$L'=\lambda_1\lambda_2/2(n_1\lambda_2-n_2\lambda_1) \quad (6)$$

where, $T_{\min}$ is the transmission minimum, n is the linear refractive index, n_1 and n_2 are the refractive indices at two adjacent extremes of the same type at λ_1 and λ_2, the thickness of the thin film L, is estimated as the average value of L'.

We get the transmission (T) of compound 1-doped PI thin film and compound 2-doped PI thin film using Lambda 950 UV-Vis Spectrophotometer. Finally, all the results are shown in Table 1.

Table 1 Linear optical parameters of PI, compound 1/PI and compound 2/PI by the transmission spectrum method

	Compound 1/PI	Compound 2/PI	PI
$\alpha_0/(\times 10^3\ \mathrm{m}^{-1})$	7.871 4	9.19	7.952
n_0	1.433 1	1.441 3	1.425 3
L/μm	15.7	13.7	15.2

2.3 Third-order nonlinear optical properties

Compared with the previous measurements, the z-scan technique has the advantages of high sensitivity and simple experiment device in the study of nonlinear optics. So, third-order nonlinear optical properties of

the sample thin films were measured by the Z-scan technique. Z-scan is a single beam technique for measuring both the nonlinear refractive index and the nonlinear absorption coefficient. The measurements were performed using EKSPLA PL2143B, a mode-locked Nd∶YAG laser with pulse widths of 30 ps and were carried out at 1064nm laser beam, which was focused by 15 cm focal length lens, as depicted in Fig. 4. The laser beam passed splitting mirror and was split into two beams. They were detected by energy probe and laser energy meter of Israel Ophir. We adopted single pulse mode in order in order to avoid accumulated thermal effect[19-24].

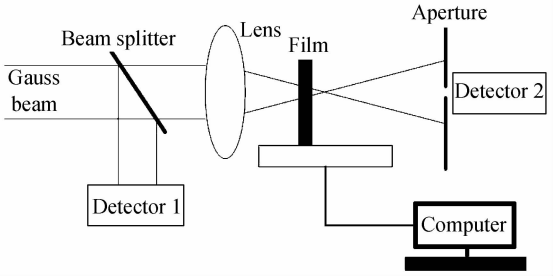


Fig. 4 Schematic experimental setup of Z-scan method

When the intensity of the incident laser beam is sufficient to induce nonlinearity in the thin film, the thin film will either converges or diverge the beam and its absorption coefficient will depend light intensity. So, we measured the transmittance of the thin film through a finite aperture as the thin film is moved along the propagation path of a focused laser beam. Removing the aperture, the totally transmitted light is collected and detected by the energy probe for each position of the sample. In this case, the Z-scan is referred to as 'Open Aperture' (OA) Z-scan. The OA Z-scan recordings can show a minimal transmittance or a maximal transmittance, corresponding to reverse saturable absorption or saturable absorption, respectively. And the magnitude and sign of the nonlinear absorption coefficient of the thin films are easily deduced from the above mentioned OA Z-scan. Placing the aperture, a small part of the laser beam is collected after passing the aperture. The magnitude and sign of the nonlinear refractive index of the thin films were obtained by dividing the CA data by the corresponding OA data. The curve obtained after this division is referred to as 'divided' Z-scan. The 'divided' Z-scan can show a 'peak-valley' form or a 'valley-peak' form, corresponding to self-defocusing or self-focusing effect.

The normalized transmittance as a function of film position for OA Z-scan case and 'divided' Z-scan case were respectively given by[25-27]

$$T(z,s=1)=1-\frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}(1+x^2)} \tag{7}$$

$$T(z,\Delta\Phi_0)=1+\frac{4\Delta\Phi_0 x}{(x^2+1)(x^2+9)} \tag{8}$$

where T is the normalized transmittance, β is the third-order nonlinear absorption coefficient, $x=z/z_0$, z_0 is the Rayleigh range, $I_0=E_0/\pi\omega_0{}^2\tau$ is the peak on-axis irradiance, E_0 is the energy on the focus, τ is the pulse width, ω_0 is the waist radius, $L_{\text{eff}}=[1-\exp(\alpha_0 L)]/\alpha_0$ is the effective length, L is the thickness of the thin film, α_0 is the linear absorption coefficient at the laser excitation wavelength, $\Delta\Phi_0$ is the on-axis nonlinear phase shift at the focus and it is related with the nonlinear refraction parameter through the equation $\Delta\Phi_0=2\pi\gamma I_0 L_{\text{eff}}/\lambda$, γ is the third-order nonlinear refractive index and s is the linear transmittance of the aperture.

Accordingly, the imaginary part and the real part of third order nonlinear optical susceptibility are related to the nonlinear absorption coefficient and the nonlinear refraction coefficient, respectively, and can be calculated by the following equations[27-28]

$$\chi_R^3=2n_0^2\cdot\varepsilon_0\cdot c\cdot\gamma \tag{9}$$

$$\chi_I^3=\frac{\varepsilon_0\cdot c^2\cdot n_0^2}{\omega}\cdot\beta \tag{10}$$

$$\chi^3=\chi_R^3+\mathrm{i}\chi_I^3 \tag{11}$$

where n_0 is the linear refractive index, ε_0 is the permittivity of free space, and c is velocity of light in vacuum, ω is the incident frequency.

In order to confirm that the measured nonlinear optical phenomena originate from compound, the z-scan curve of the PI film was measured under the same measuring condition as shown in Fig. 5 and Fig. 6. From Fig. 5 and Fig. 6, it obtained that the PI showed better saturable absorption and weak self-focusing effect.

The OA Z-scan data and 'divided' Z-scan data of compound 1/PI and compound 2/PI were shown in Fig. 5 and Fig. 6. It was obvious that the compound 1/PI films exhibited a transmittance minimum around the focal point corresponding to reverse saturable

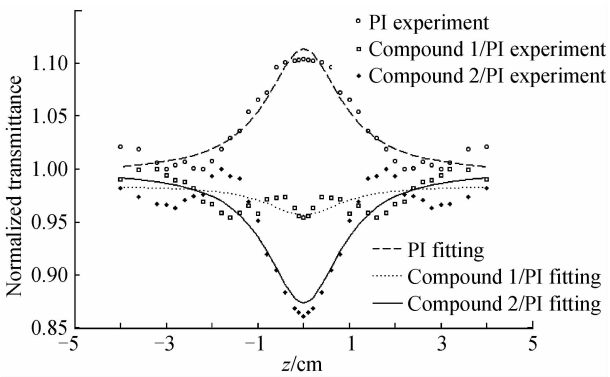


Fig. 5 Open-aperture curve of PI, compound 1/PI and compound 2/PI

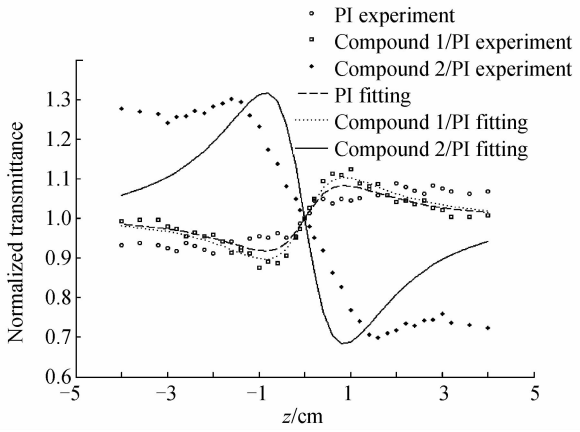


Fig. 6 Divided Z-scanning curve of PI, compound 1/PI and compound 2/PI

absorption and a valley-peak form corresponding to self-focusing effect. For the compound 1, the nonlinear absorption coefficient was bigger and the nonlinear refractive index was smaller than the compound 1/PI because the PI showed better saturable absorption and weak self-focusing effect. And the compound 2/PI films exhibited a transmittance minimum around the focal point corresponding to reverse saturable absorption and a peak-valley form corresponding to self-defocusing effect. For the compound 2, the nonlinear absorption coefficient and the nonlinear refractive index were bigger than the compound 2/PI because the PI showed better saturable absorption and weak self-focusing effect.

For obtaining the nonlinear absorption coefficient of PI, compound 1/PI and compound 2/PI, Eq. (7) had been employed to fit the OA Z-scan data and is given in Fig. 5, respectively. For obtaining the nonlinear refractive index of PI, compound 1/PI and compound 2/PI, Eq. (8) had been employed to fit the OA Z-scan data and is given in Fig. 6, respectively.

The nonlinear absorption coefficient and the nonlinear refractive index of PI, compound 1/PI and compound 1/PI were shown in Table 2.

Table 2 Nonlinear optical parameters of PI, compound 1/PI and compound 2/PI by the Z-scan method

	PI	Compound 1/PI	Compound 2/PI
$\beta/(\times10^{-10}\ \mathrm{cm}\cdot\mathrm{W}^{-1})$	9.128 0	−2.099 4	−10.837
$\gamma/(\times10^{-14}\ \mathrm{cm}^2\cdot\mathrm{W}^{-1})$	1.893 5	2.284 7	−7.039 9

The above results suggested that 1) The absorbance of the compound 1-doped PI thin film and compound 2-doped PI thin film around 430nm wavelength was biggest and up to 2.3. Compared with compound 1-doped PI thin film, the UV-Vis spectrum of compound 2-doped PI thin film moved to longer wavelength. 2) The linear refractive index of compound 2/PI was bigger than compound 1/PI. 3) Compound 1/PI exhibited reverse saturable absorption and self-focusing effect while compound 2/PI exhibited reverse saturable absorption and self-defocusing effect. The nonlinear absorption coefficient and the nonlinear refractive index of compound 2/PI was bigger than compound 1/PI. This finding was in good agreement with results previously reported.

3 Conclusions

Due to the requirements of the organic third-order NLO materials, carbazole-benzothiazole derivatives compound 1 and compound 2 were synthesized and doped with PI in this paper. The compound 1-doped PI film and the compound 2-doped PI film with mass fraction 4% were prepared by doctor blading on the glass substrate. Their structures were confirmed by 1H-NMR. The UV - Vis spectrum revealed its transmittance nature in the ultraviolet-visible region. Their linear properties were investigated by the transmission spectrum method. The third-order nonlinear optical parameters were obtained from the OA Z-scan and 'divided' Z-scan employing a 30ps Nd: YAG laser at 1064 nm.[29] The values of the nonlinear absorption coefficient and nonlinear refractive index of the two thin films were $\beta_1=-2.118\ 9\times10^{-10}$ cm/W, $\gamma_1=2.285\ 2\times10^{-14}$ cm^2/W, $\beta_2=-1.275\ 6\times10^{-9}$ cm/W, $\gamma_2=-7.039\ 9\times10^{-14}$ cm^2/W, respectively. The results suggested that the larger nonlinearity could be obtained in carbazole-benzothiazole systems by increasing the molecular conjugation length. And carbazole-benzothiazole derivatives will be intensively used in the optoelectronic devices, such as optical limiters, all-optical switches and all optical wavelength convertor etc.

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