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Preparation and Optical Limiting Properties of Polyurethane Containing Long Conjugated Chromophores

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Two functional polyurethanes (**P1** and **P2**) bearing a large π electron conjugated chromophoric pendant were synthesized and characterized by FT-IR, ^{1}H-NMR and UV-Vis absorption spectra. Their optical limiting properties were evaluated. The results show that **P1** and **P2** show novel optical limiting properties, which are assigned to a long π electron conjugated chromophoric pendant. It was found that their optical limiting properties were affected simultaneously by solution concentration and **P2** displays a better optical limiting property than **P1** at the same solution transmittance, although that **P1** has larger $\chi^{(3)}$ (4.28×10^{-11} esu) than **P2** (0.87×10^{-11} esu), and their optical limiting mechanism is investigated.

Keywords: optical limiting; polyurethanes; synthesis; NLO

1 Introduction

With the development of laser equipment and technology, the research on materials and devices for protection of optically sensitive devices and human eyes from laser damage has drawn much interest in recent years (1). Among the organic materials, some NLO polymers are considered to be promising materials, mainly because they offer many advantages such as good optical limiting properties, a high optical damage threshold, fast time response, and good processability to form optical devices (2–6).

To enhance the application viability of the polymer materials in optical limiter, it is necessary to improve their optical limiting properties, as well as thermal stability. Polyurethanes exhibiting excellent mechanical and thermal properties have drawn both scientific and industrial attention. Many polyurethanes containing different chromophore groups were synthesized and their nonlinear optical properties were investigated (7–15). However, little attention has been devoted to optical limiting properties (16). In previous work (17), we investigated the influence of different electron conjugation bridge structures of the polyurethanes on their optical properties. In this work, to further understand the relationship between structure and optical properties of polyurethanes, we synthesized two substituted polyurethanes. They contain the same electron conjugation bridge structures, but a different acceptor in long conjugated NLO-chromophores (Scheme 1) and the effect of molecular structures with different donor/acceptor groups on the optical limiting properties is investigated.

2 Experimental

2.1 Chemicals

4-Methylpyridine and methyl iodide were purchased from Aldrich Chemical Company. 4-Aminobenzadehyde, *N,N*-dihydroxyethylaniline, dibutyltin dilaurate and 1,4-butanediol were purchased from Shanghai Chemical Reagent Company. Dibutyltin dilaurate and 1,4-butanediol were distilled before use. 4,4′-Methylenebis(phenyl isocyanate) (MDI) was purchased from Bayer and purified by distillation under reduced pressure before use. *N,N*-Dimethylformamide (DMF) was purified by distillation over CaH_2 prior to utilization. Triethylamine was distilled from potassium hydroxide prior to use.

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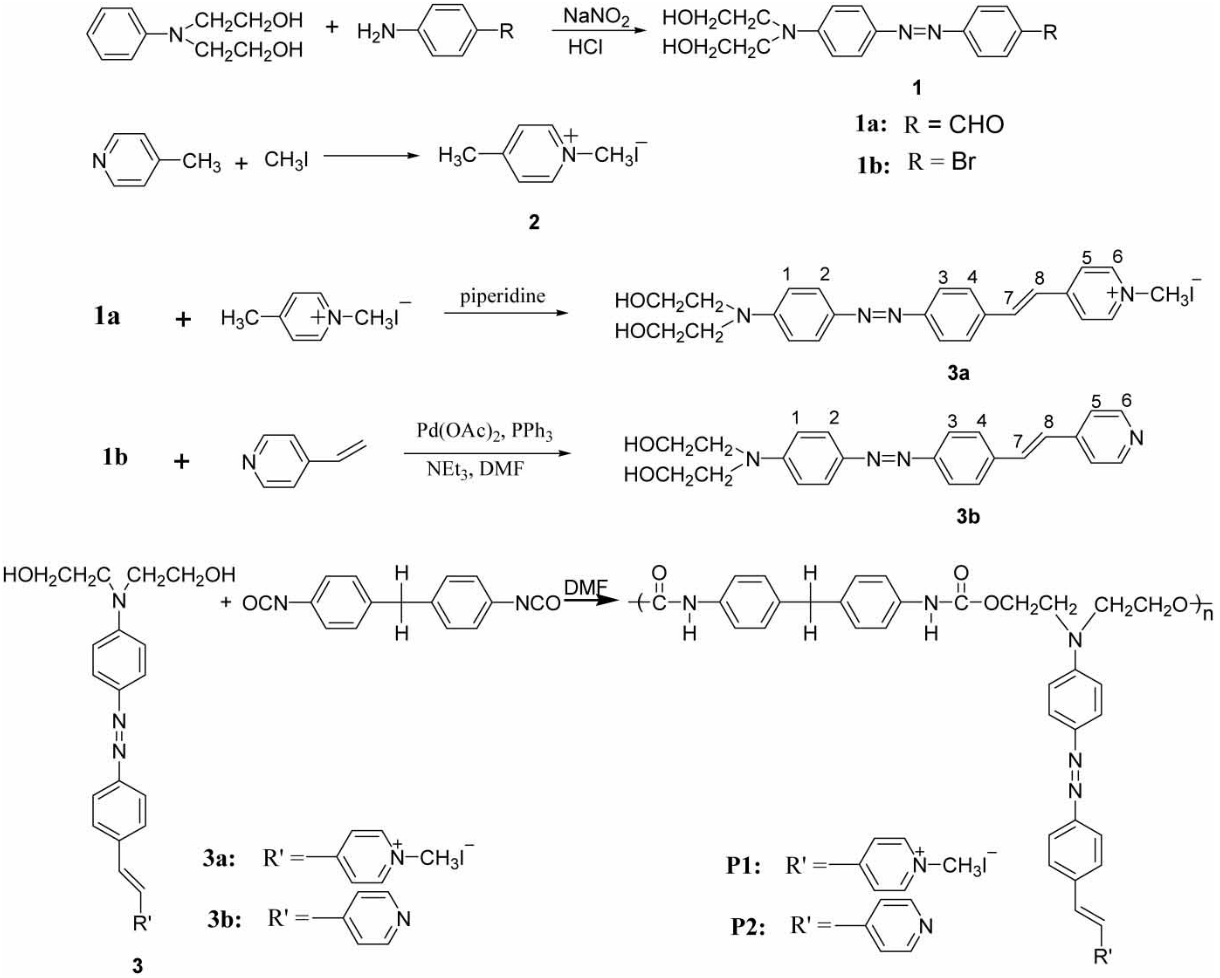

Sch. 1. Synthetic scheme of the functional polyurethanes.

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2.2 Testing

The FT-IR spectra were recorded as KBr pellets on a Nicolet 170sx spectrometer. ^{1}H-NMR spectra were collected on an AVANCE/DMX-300 MHz Bruker NMR spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1 cm^2 quartz cell. Molecular weights of the polymers were estimated on a KNAVER Vapor Pressure Osmometer. Thermal analyses of the polymer were performed on a Perkin-Elmer TGA (Thermogravimetric analysis) and a Perkin-Elmer DSC (differential scanning calorimeter) under nitrogen at a heating rate of 20°C/min and 10°C/min, respectively.

The investigation of the optical limiting properties of the samples was carried out by using a frequency doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser, which provides linearly polarized 8 ns optical pulses at 532 nm wavelength with a repetition of 1 Hz. The experimental arrangement is similar with that in the literature (18). The samples were housed in quartz cells with a path of 5 mm. The input laser pulses adjusted by an attenuator (Newport) were split into two beams. One was employed as a reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens with a 300 mm focal length. The samples were positioned at the focus. The incident and transmitted laser pulses were monitored by two energy detectors, D_1 and D_2 (Rjp-735 energy probes, Laser Precision).

The nonlinear optical properties of the samples were performed by a *Z*-scan technique with the same laser system as in the optical limiting experiment with a pulse width of 8 ns at 1 Hz repetition rate and 532 nm wavelength. The experiment was set up as in the literature (19). The solution sample was contained in a 2 mm quartz cell. The input energy was 100 μJ. The radius ω at beam waist was 50 μm. The samples were moved along the axis of the incident beam (*z* direction). The experimental data were collected utilizing a single shot at a rate of 1 pulse/min to avoid the influence of thermal effect.

2.3 Synthesis

2.3.1 Synthesis of 4-{p-[(N,N-dihydroxyethyl) amino]phenylazo}benzaldehyde (1a)

4-Aminobenzaldehyde (2.46 g, 20 mmol) was dissolved in 8 mL conc. hydrochloric acid. After cooling to 0°C, an ice-

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water solution of sodium nitrite (1.36 g, 20 mmol) was added to the above solution and stirred for 30 min. Then, the mixture was added dropwise to a 400 mL aqueous buffer solution of acetic acid-sodium acetate (pH $\approx$ 6) containing 3.81 g (21 mmol) *N,N*-dihydroxyethylaniline and stirred for 1 h at 0~5°C. The resulting precipitate was filtered and rinsed with water twice. The crude product was recrystallized from ethanol twice to give orange crystals in 85% yield. FTIR (KBr): 3408 (OH), 2956, 2882 (CH_2), 2754 (CHO), 1670 (C=O), 1598, 1515 (Ar); ^{1}H-NMR (300 MHz, DMSO-d_6), $\delta = 3.57$ (4H, d, CH_2CH_2OH), 3.61 (4H, d, CH_2CH_2OH), 4.86 (2H, s, O*H*), 6.88 (2H, d, H^1), 7.81 (2H, d, $J = 8.4$ Hz, H^2), 7.92 (2H, d, H^3), 8.04 (2H, d, $J = 9.2$ Hz, H^4), 10.06 (1H, s, C*H*O) (see Scheme 1).

2.3.2 Synthesis of 4-bromo-4′-(N,N-di-2-hydroxyethyl) azobenzene (1b)

This was prepared as above from 4-bromoaniline. The crude product was recrystallized from ethanol twice to give yellow crystals in 83% yield. FTIR (KBr): 3280 (OH), 2945, 2882 (CH_2), 1597 (Ar); ^{1}H-NMR (300 MHz, DMSO-d_6), $\delta = 3.55$ (4H, t, J = 5.5 Hz, CH_2CH_2OH), 3.60 (4H, t, CH_2CH_2OH), 4.84 (2H, s, *OH*), 6.86 (2H, d, J = 9.1 Hz, H^1), 7.70 (2H, d, J = 8.9 Hz, H^4), 7.76 (2H, d, H^3), 7.85 (2H, d, H^2).

2.3.3 Synthesis of 4-methyl-N-methylpyridinium iodide (2)

Following Reference (20), compound 2 was obtained as white solid, yield 92%. ^{1}H-NMR (DMSO-d_6): $\delta = 2.56$ (3H, s, CH_3), 4.20 (3H, s, CH_3I), 7.0 (2H, d, H^5), 8.90 (2H, d, H^6).

2.3.4 Synthesis of trans-4-[4-{p-[(N,N-dihydroxyethyl)amino]phenylazo}styryl]-N-methylpyridinium iodide (3a)

9.9 g (0.03 mol) **1** and 7.9 g (0.03 mol) **2** were dissolved in 90 mL absolute ethanol. Five drops of piperidine were added into the solution. This solution was then heated to reflux overnight. After cooling, the solution was filtered, and the solid was recrystallized from ethanol twice to give a deep red solid in 65% yield. FTIR (KBr): 3381 (O-H), 2931 (CH_3, CH_2), 1618, 1593, 1512 (Ar); ^{1}H-NMR (DMSO-d_6): $\delta = 3.57$ (4H, d, CH_2CH_2OH), 3.59 (4H, d, CH_2CH_2OH), 4.25 (3H, s, CH_3), 4.86 (2H, s, O*H*), 6.88 (2H, d, $J = 9.2$ Hz, H^1), 7.60 (1H, d, H^7), 7.79 (2H, d, H^3), 7.86 (2H, d, H^2), 7.88 (2H, d, $J = 8.4$ Hz, H^4), 8.07 (1H, d, $J = 16.3$ Hz, H^8), 8.24 (2H, d, H^5), 8.87 (2H, d, $J = 8.7$ Hz, H^6).

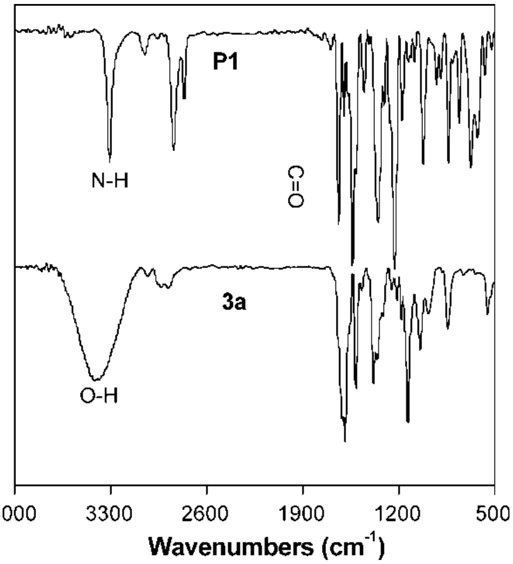

Fig. 1. IR spectra (KBr) of compound **3a** and **P1**.

2.3.5 Synthesis of 4-(N,N-dihydroxyethylamino)-4′-(pyridine-4-vinyl)-azobenzene (3b)

This was prepared from 4-bromo-4′-(*N,N*-dihydroxyethyl-amino)azobenzene and vinylpyridine. The process was described in detail elsewhere (16). The precipitation was recrystallized from ethanol three times to give a red-brown powder in 80% yield. FTIR (KBr): 3483 (OH), 2943(CH_2), 1598, 1512, 823 (Ar); ^{1}H-NMR (DMSO-d_6): $\delta = 3.56$ (4H, t, J = 6.0 Hz, CH_2CH_2OH), 3.60 (4H, t, CH_2CH_2OH), 4.88 (2H, s, OH), 6.86 (2H, d, J = 8.9 Hz,H^1), 7.37 (1H, d, J = 16.3 Hz, H^7), 7.64 (2H, d, J = 7.7 Hz, H^4), 7.72 (1H, d, H^8), 7.77 (2H, d, H^3), 7.80 (2H, s, H^2), 7.82 (2H, d, J = 8.1 Hz, H^5), 8.58 (2H, d, H^6).

2.3.6 Synthesis of the Polyurethanes

All the polymerization reactions and manipulations were performed under nitrogen, except for the purification of the polymers, which was conducted in open atmosphere. A typical procedure is given below: In a 100 mL four-neck cylindrical vessel, equipped with a mechanical stirrer, 2.62 g (10 mmol) of MDI was added slowly to a solution of 5.30 g (10 mmol) **3a** and 0.1 mL of dibutyltinlaurate in 50 mL of anhydrous *N,N*-dimethylformamide. The resulting solution was reacted at 80°C for 8 h. After cooling to room temperature, the reaction solution was poured dropwise into 250 mL of methanol. The resulting polyurethane was collected by filtration and redissolved in DMF and precipitated into methanol for purification. The dissolution-precipitation process was repeated three times, and the final isolated precipitant was dried under vacuum at 50°C.

P1 Deep red solid; yield: 91.5%; $M_n = 8\,800$ (VPO); FTIR (KBr, ν (cm^{-1})): 3311 (N-H), 1645 (C = O), 1618, 1593, 1512 (Ar), 1230 (C-O-C); ^{1}H-NMR (DMSO-d_6): $\delta = 3.05 \sim 4.41$ (br, CH_3, $N(CH_2CH_2O)_2$, $N(CH_2CH_2O)_2$ and -ArCH_2Ar-), 6.87 ~ 8.93~ (br, Ar-*H* and -*CH*=*CH*-), 9.60 (s, 2H, *NH*CO).

P2 was prepared as above from **3b**. Deep red solid; yield: 92.7%; M_n 11 700 (VPO); FTIR (KBr, ν (cm^{-1})): 3303 (N-H), 1648 (C=O), 1615, 1596, 1512 (Ar); ^{1}H NMR (DMSO-d_6): $\delta = 3.05 \sim 4.35$ ($N(CH_2CH_2O)_2$, $N(CH_2CH_2O)_2$, -$CH_2C_2H_4CH_2$- and -ArCH_2Ar-), 6.75 ~ 8.63 (Ar-*H* and -*CH*=*CH*-), 9.60 (*NH*CO-).

Table 1. Polymerization results and characterization data

Sample	Yield (%)	M_n	T_g ($°C$)	T_d ($°C$)	α_2 (m^2/W)	n_2 (m^2/W)	$\chi^{(3)}$ (esu)
P1	91.5	8800	213	294	4.00×10^{-11}	3.29×10^{-17}	4.28×10^{-11}
P2	92.7	11700	224	302	8.75×10^{-12}	6.25×10^{-18}	0.87×10^{-11}

3 Results and Discussion

3.1 Structure Characterization of the Polyurethanes

Both polymers were well characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained (see Experimental section for details). Figure 1 shows the FTIR spectra of **3a** and **P1**. The characteristic O-H stretching vibration of compound **3a** is located at $3381 cm^{-1}$, which disappears and the characteristic stretching vibrations ν_s (N-H) and ν_s (C═O) at 3311 and $1645\ cm^{-1}$ are found in the spectrum of its polymer. The similar results were also found in the IR spectra of compound **3b** and **P2**, displaying the formation of the urethane group (17).

The excellent solubility of both polymers enables characterization of their molecular structure by a solution spectroscopic method in common solvents. Figure 2 shows the ^{1}H-NMR spectra of compound **3a** and **P1** in DMSO-d_6. As seen in Figure 2, the hydroxyl proton of compound **3a** absorbs at $\delta = 4.86$ ppm, which disappears in the spectrum of its polymer. A new broad resonance peak assigned to the amine proton absorption at δ 9.61 ppm appears upon the spectrum of **P1**, further displaying the formation of urethane linkage and is consistent with result of FTIR spectra. All the other resonance peaks of the segment of **3a** and 4,4′-methylenebis(phenyl isocyanate) appear in the spectrum of **P1**. Similar phenomena are also found in the NMR spectra of compound **3b** and **P2**. The relative ratio of integration of these protons are also consistent with the proposed structures, as shown in Scheme 1, confirming that functional polyurethane polymers are yielded.

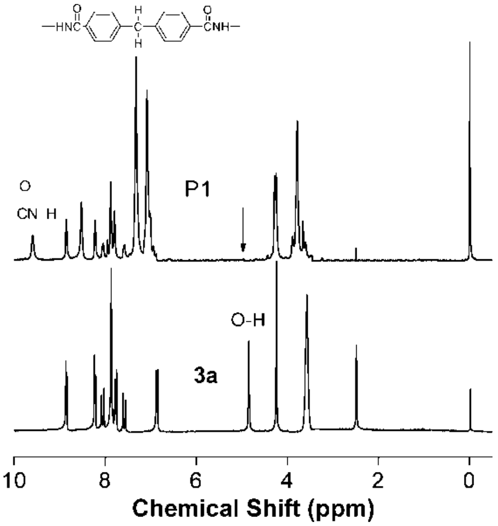

Fig. 2. ^{1}H-NMR spectra of compound **3a** and P1 in DMSO-d_6.

3.2 Thermal Properties of the Polyurethanes

The thermal behavior of two polymers were investigated by TGA and DSC. All the results are summarized in Table 1. The polymers are thermally stable. Their TGA thermograms are shown in Figure 3. The decomposition temperature (T_d), defined as the temperature of 5% wt loss of P1 is 294°C and T_d of **P2** is up to 302°C, and the glass transition temperature (T_g) of P1 and **P2** are 213°C and 224°C, respectively. The result indicates that both polymers exhibit good thermal stability and high glass transition temperature (9, 10), which may results from a protective 'jacket' formed via the strong electronic interaction among the polarized azobenzene group in the side chain, shielding the polyurethane backbone from thermal attack. The similar phenomena were found in Masuda (21) and our previous work (5, 6).

3.3 Optical Properties of the Polyurethanes

Figure 4 shows the UV-Vis spectra of compound **3a**, **3b**, along with **P1** and **P2** in DMF. It can be seen in Figure 4 that compound **3a** and **3b**, exhibit strong absorption peak at 502 and 465 nm, respectively, which are associated with the π-π^* transition of the extended π electron conjugated NLO

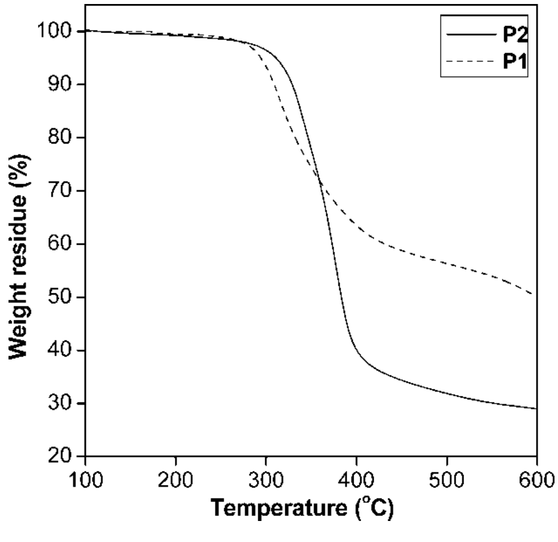

Fig. 3. TGA thermograms of **P1** and **P2** measured under nitrogen at a heating rate of 20°C/min. Data of **P1** (dash line) and **P2** (solid line) are shown for comparison.

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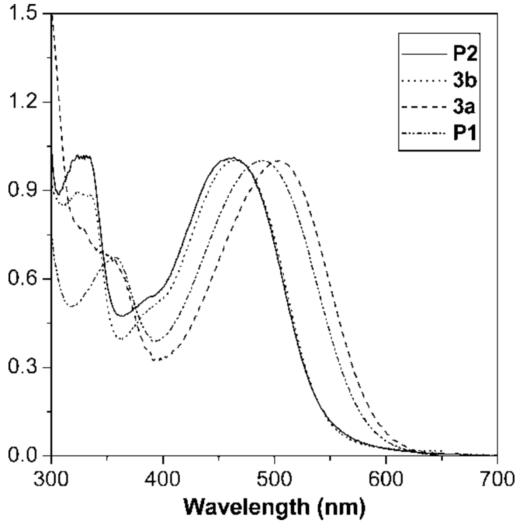

Fig. 4. UV-Vis spectra of compound **3a** (dash line), **3b** (dot line), **P1** (dash dot line)and **P2** (solid line) in DMF solution.

chromophores. Compared with that of compound **3b**, the absorption peak of compound **3a** significantly shows red-shift, which may result from a larger dipole effect of strong electron accepted group *N*-methypyridinium iodide in compound **3a**. However, after being incorporated into the polymer chain, their polymers display the different degree blue-shift and the maximum absorption wavelength at 488 nm for **P1** and 459 nm for **P2**, indicating the presence of the electronic interaction between the chromophore moieties and the polymer chain (9, 10, 22).

The nonlinear coefficients of polymers were measured by using a *Z*-scan technique. The concentrations of **P1** and **P2** solutions used were 0.060 and 0.063 mg/mL, respectively. The results of *Z*-scan with and without an aperture showed that **P1** and **P2** have both nonlinear absorption and nonlinear refractive (Figures 5 and 6). Thus, the $\chi^{(3)}$ measured in this experiment was attributed to dual contributions of nonlinear absorption coefficient of molecules (α_2) and nonlinear refractive index of molecules (n_2).

In theory, the normalized transmittance for the open aperture configuration can be written as (19) (Equation (1)):

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, for|q_0| < 1 \qquad (1)$$

where $q_0\ (z) = \alpha_2\ I_0\ (t)L_{eff}\ /(1+z^2\ /z_0^2)$, α_2 is the nonlinear absorption coefficient, I_0(t) the intensity of laser beam at focus ($z = 0$), $L_{eff} = [1\ -\ \exp\ (-\alpha_0 L)]/\alpha_0$ is the effective thickness with α_0 the linear absorption coefficient and L the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. Thus, the nonlinear absorption coefficient of **P1** and **P2** are determined to be 4.00×10^{-11} and 8.75×10^{-12} m/W respectively by fitting the experimental data using Equation (1).

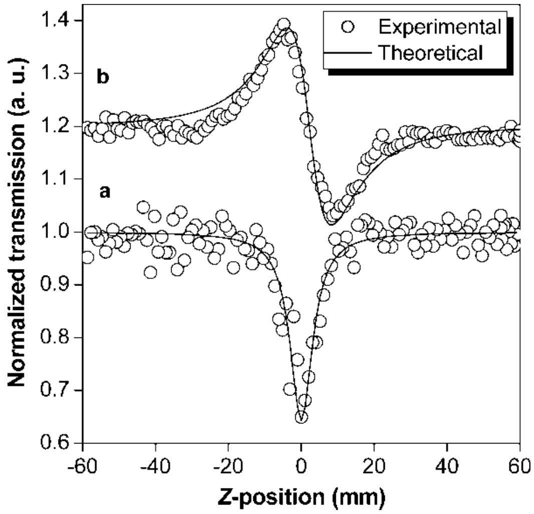

Fig. 5. *Z*-scan data of **P1**. (a) *Z*-scan data of open aperture. (open circles) experimental data; (solid line) theoretical curve; (b) *Z*-scan data of close aperture. (open circles) experimental data; (solid line) theoretical curve.

The normalized transmission for the closed aperture *Z*-scan is given by (19) (Equation (2)):

$$T(z, \Delta\phi) = 1 + \frac{4\Delta\phi x}{(x^2+9)(x^2+1)} \qquad (2)$$

where x $= z/z_0$ and $\Delta\phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\phi = 2\pi I_0(1 - e^{-\alpha_0 L})n_2/\lambda\alpha_0$. Thus, the nonlinear refractive coefficient of **P1** and **P2** are determined to be 3.29×10^{-17} and 6.25×10^{-18} $\mathrm{m^2/W}$ by fitting the experimental data using Equation (2). The sign of n_2 is determined to be negative, hinting the optical nonlinear refraction is a

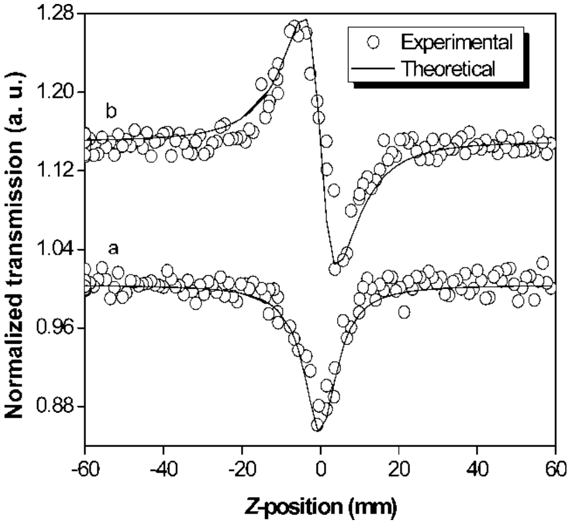

Fig. 6. *Z*-scan data of **P2**. (a) *Z*-scan data of open aperture (open circles) experimental data; (solid line) theoretical curve; (b) *Z*-scan data of close aperture. (open circles) experimental data; (solid line) theoretical curve.

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self-defocusing process. The $\chi^{(3)}$ can be calculated by the following Equation (3) (19):

$$|\chi^{(3)}| = \sqrt{\left|\frac{cn_0^2}{80\pi}\cdot n_2\right|^2 + \left|\frac{9\times 10^8 \varepsilon_0 n_0^2 c^2}{4\pi\omega}\cdot \alpha_2\right|^2} \qquad (3)$$

where ε_0 is the permittivity of vacuum, c the speed of light, n_0 the refractive index of the medium and $\omega = 2\pi c/\lambda$. The calculation results of the nonlinear susceptibility of **P1** and **P2** are 4.28×10^{-11} and 0.87×10^{-11} esu, respectively. Evidently, the nonlinear susceptibility increases with the acceptor strength.

3.4 Optical Limiting Properties of the Polyurethanes

Figure 7 shows the optical limiting behaviors of **P1** with concentration of 0.060 mg/mL and **P2** with concentration of 0.063 mg/mL at the same linear transmittance ($T = 60\%$) in DMF. As shown in Figure 7, at very low incident fluence, the output fluence of **P1**, **P2** solutions with 60% transmittance linearly increases with the incident fluence obeying the Beer–Lambert law. However, at high incident fluence (limiting threshold, defined as the incident fluence at which transmittance start to deviate from linearity), the transmittance of the solution decreases and a nonlinear relationship is observed between the output and input fluence. With a further increase in the incident fluence, the transmitted fluence reaches a plateau, showing the good optical limiting property. From Figure 7, we can see that **P1** shows the limiting threshold at 0.17 J/cm^2 while **P2** is at 0.15 J/cm^2. Thus, different from their nonlinear optical properties, **P2** exhibits better optical limiting properties than **P1** at the same transmittance although that **P1** has larger $\chi^{(3)}$ than **P2**, which may be originated from the stronger ground electronic absorption of **P1** than that of **P2** at 532 nm wavelength. Similar phenomenon was found in our previous work (17). Simultaneously, we measured the UV-Vis absorption spectrum of the **P1** and **P2** solution before and after the laser irradiation and found that the pattern and intensity of UV-Vis absorption spectrum have almost no change, hinting that both polymers possess good photostability.

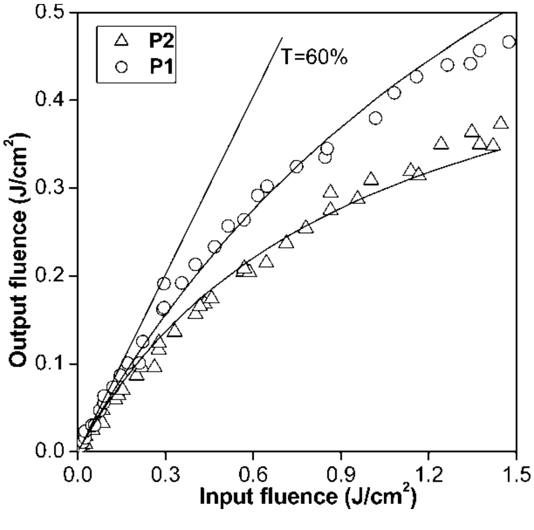

Fig. 7. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light, of DMF solution of **P1** (c = 0.060 mg/mL) and **P2** (c = 0.063 mg/mL) with a linear transmission of 60%. The open circles and open triangles correspond to experimental results of **P1** and **P2**, respectively.

3.5 Optical Limiting Mechanism of the Polyurethanes

The optical limiting mechanisms of organic compounds are often based on two-photon absorption (TPA) or reverse saturated absorption (RSA). Generally, TPA-based optical limiting effect can be yielded in principle under the laser irradiation of picosecond or shorter pulses. RSA is achieved on a nanosecond or longer time scale, owing to the different excited-state lifetimes involved in a multilevel energy process (23). In this work, the polymers are excited by the laser with 8 ns pulse width at 532 nm wavelength and the transmittance of all these polymers solutions decreases with the increase of the incident fluence. Therefore, we consider that the optical limiting properties of **P1** and **P2** may mainly arise from RSA.

Based on Golovlev's phenomenological model (24), the experimental data can be fitted perfectly using Equation (4):

$$\Phi_{out} = \frac{T_0\Phi_{in}}{1+(1-T_0)\Phi_{in}/\Phi_{n\mathrm{ln}}} \qquad (4)$$

where T_0 is the linear transmittance of the sample, Φ_{out} is output fluence, Φ_{in} is input fluence, $\Phi_{n\mathrm{ln}}$ is the parameter characterizing of the nonlinear absorption of the material and a small magnitude of $\Phi_{n\mathrm{ln}}$ will ensure better optical limiting performance of the sample. Thus, $\Phi_{n\mathrm{ln}}$ of **P1** and **P2** are determined to be 0.68 J/cm^2 and 0.38 J/cm^2 by fitting the experimental data using Equation (4) and **P2** has larger $\Phi_{n\mathrm{ln}}$ than **P1**, which is consistent with their optical limiting properties. The fitting result indicated that the RSA process is the most likely mechanism for the optical limiting behavior of **P1** and **P2**.

Figure 8 shows the optical limiting behaviors of **P1** with different concentration. It can be found that the limiting effect was affected by concentration, with higher concentration solutions exhibiting better performances. For example, the limiting threshold of **P1** solution decreases from 0.17 to 0.15 mJ/cm^2 when linear transmittance decreases from 60% (c = 0.060 mg/mL) to 40% (c = 0.156 mg/mL). On the contrary, the threshold increased from 0.17 to 0.29 mJ/cm^2 when linear transmittance was increased to 75% (c = 0.036 mg/mL). Similar results were also found by Kojima Y and our previous publications (5, 25). It is the reason that the solution with a higher concentration has more molecules per unit volume, which should absorb the energy of the harsh laser more efficiently.

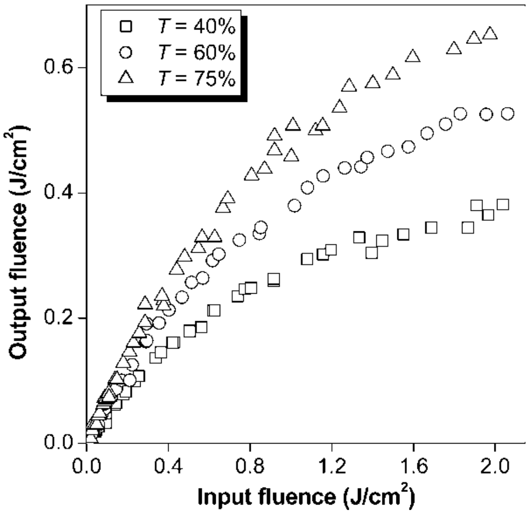

Fig. 8. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light, of DMF solution of **P1** with different linear transmissions 40% (open squares), 60% (open circles), 75% (open triangles).

4 Conclusions

We have successfully synthesized two novel functional polyurethanes bearing long D-π-A conjugated chromophores in high yield. The both polymers show novel optical limiting properties. Their optical limiting properties are mainly originated from reverse saturated absorption (RSA). Different from their third order nonlinear optical properties, **P2** with weak acceptor group displays better optical limiting property than **P1** with stronger acceptor group at the same transmittance. Simultaneously, it is found that both polymers exhibit good thermal stability, which may result from a protective 'jacket' formed via the strong electronic interaction among the polarized azobenzene group in the side chain, shielding the polyurethane backbone from thermal attack.

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