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Preparation and property of soluble azobenzene-containing substituted poly(1-alkyne)s optical limiting materials

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Abstract

Two novel poly(1-alkyne)s containing azobenzene nonlinear optical chromophoric group, poly(4-(4-[4-(*n*-dodecyloxy)phenylazophenyl]carbonyl)oxy-1-butyne) (P**1**) and poly(11-(4-[4-(*n*-dodecyloxy)phenylazophenyl]carbonyl)oxy-1-undecyne) (P**2**), were synthesized by $[Rh(nbd)Cl]_2$–Et_3N catalysts and characterized by FTIR, ^1H NMR, GPC and UV–vis techniques. Their optical limiting and nonlinear optical properties were investigated using 8 ns pulse at 532 nm. The results show that these soluble functional poly(1-alkyne)s possess good optical limiting properties and large nonlinear optical properties.

Keywords: Polyacetylene; Optical limiting; Nonlinear optics; Azo dyes; Chromophore

1. Introduction

The optical materials in recent years have received a significant attention owing to the growing needs for protection of optically sensitive devices and human eyes from laser damage in both civilian and military applications due to the fast development of modern laser technology [1,2]. Conjugated polymer optical limiting materials are considered to be promising materials, mainly because they offer many advantages such as large third-order nonlinearities, fast response times, high damage thresholds, ease of processing, structural modification, and their applicability over a wide range of wavelengths [3–9].

Polyacetylene, the structurally simplest conjugated polymer with alternating single and double bonds, is endowed with large third-order nonlinear susceptibility and good conductivity [12]. However, its insolubility and instability, as well as its improcessability, limit its practical applications as a functional material. Attachments of suitable substituents to the polyacetylene backbone will not only improve its solubility and stability but also endow polyacetylene with novel properties such as liquid crystallinity, photo- and electroluminescence, optical activity (chirality), photoconductivity and gas permeability [10–16].

Recently, we have successfully synthesized a series of functional polyacetylenes containing azobenzene [8,9]. These polyacetylenes have not only the large third-order nonlinear susceptibility, but are also endowed with novel optical limit properties. In this paper, we adopt a flexible alkyl chain as spacer to incorporate the rigid nonlinear optical chromophore group into polyacetylene and a long alkyloxyl chain as a substituent of chromophoric pendant to improve the solubility of functional polyacetylene to prepare two novel soluble functional poly(1-alkyne)s and investigated their optical limiting and nonlinear optical properties (Scheme 1).

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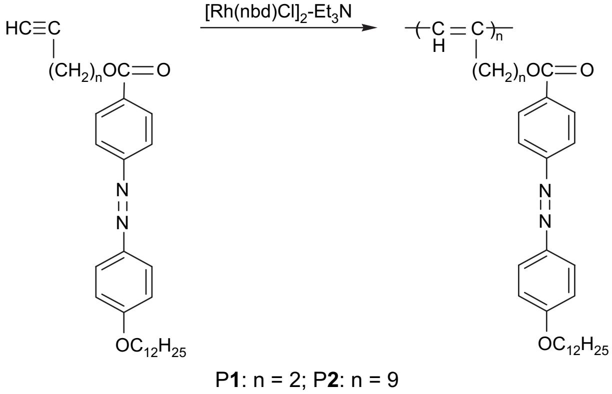

Scheme 1. Synthetic route for **P1** and **P2**.

2. Experimental

2.1. Materials and measurements

Norbornadienerhodium(I) chloride dimer [$[Rh(nbd)Cl]_2$] was purchased from Aldrich and kept in inert-atmosphere glovebox, used as received without further purification. The synthesis of the monomers was performed according to Ref. [17]. Dioxane, toluene and THF were distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine was distilled from potassium hydroxide immediately prior to use. Methanol was used to precipitate the polymer products.

The FTIR spectra were recorded as KBr pellets on a Nicolet 170SX spectrometer. The ^{1}H NMR spectra were collected on an AVANCE/DMX-300 MHz Bruker NMR spectrometer using chloroform-*d* as solvent. Tetramethylsilane (TMS) or chloroform-*d* was used as internal reference for the NMR analysis. The UV–vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm square quartz cell. Molecular weights of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) using 12 monodisperse polystyrenes (molecular weight range 10^2–10^7) as calibration standards.

The optical limiting properties were carried out with a Q-switched ns/ps Nd:YAG laser system continuum with pulse width of 8 ns at 1 Hz repetition rate and 532 nm wavelength. The experimental arrangement is similar to that in the literature [8,9]. The transverse mode of the laser pulses is nearly Gaussian. The input laser pulses were splitted into two beams by an attenuator (Newport). One was employed as reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens with 30 cm focal length. The sample was positioned at the focus and housed in quartz cells with a thickness of 5 mm. 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 were performed by *Z*-scan technique using the same laser system as in the optical limiting experiment. The experiment was set up as in Refs. [8,9]. The solution sample was contained in a 2 mm quartz cell and moved along the axis of the incident beam (*z* direction). The input energy was 100 μJ.

2.2. Polymerization

Into a baked 20-mL Schlenk tube with a side arm was added 1 mmol of the monomer. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Three milliliters of dioxane was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 4.6 mg (0.01 mmol) $[Rh(nbd)Cl]_2$ and 2.02 mg (0.02 mmol) Et_3N in 2 mL of dioxane, which was transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C under nitrogen for 6 h. The mixture was then diluted with 5 mL of dioxane and added dropwise to 200 mL of methanol under stirring. The precipitate was centrifuged and redissolved in THF. Then the THF solution was readded dropwise into 200 mL of methanol to precipitate the polymer. The dissolution–precipitation process was repeated three times, and finally isolated precipitant was dried under vacuum at 40 °C.

P1: yellow-brown powder; yield: 71.7%; $M_w = 13{,}900$, M_w/M_n: 2.1 (GPC, polystyrene calibration; Table 1, no. 5). FTIR (KBr), ν (cm^{-1}): 3067 (=C–H), 1718 (C=O), 1609, 1498, 1463 (–Ar), 1265, 1139 (C–O–C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.88 (br, 3H, CH_3), 1.28 (br, 18H, $O(CH_2)_2(CH_2)_9CH_3$), 1.82 (br, 2H, $OCH_2CH_2C_{10}H_{21}$), 2.70 (br, 2H, $=CCH_2(CH_2)_8$), 4.05 (br, 2H, $OCH_2C_{11}H_{23}$), 4.75 (br, 2H, $=CCH_2CH_2(CH_2)_7$), 6.19 (br, *cis* = C–*H*), 6.72, 7.92, 8.20 (br, Ar–*H* and *trans* = C–*H*).

P2: yellow-brown powder; yield: 69.9%; $M_w = 15{,}700$, M_w/M_n: 2.4 (GPC, polystyrene calibration; Table 1, no. 10). FTIR (KBr), ν (cm^{-1}): 3063 (=C–H), 1718 (C=O), 1601, 1497, 1463 (–Ar), 1247, 1147 (C–O–C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 0.88 (br, 3H, CH_3), 1.28 (br, 30H, $O(CH_2)_2(CH_2)_9CH_3$ and $=C(CH_2)_6(CH_2)_3$), 2.01 (br, 6H, $OCH_2CH_2C_{10}H_{21}$ and $=C(CH_2)_6(CH_2)_2CH_2$), 4.04 (br, 2H, $OCH_2C_{11}H_{23}$), 4.37 (br, 2H, $=C(CH_2)_8CH_2$), 6.99, 7.87, 8.15 (br, Ar–*H* and *trans* = C–*H*).

Table 1
Polymerization of the monomer **1** and **2**[a]

No.	Solvent	Time (h)	Temp (°C)	Yield (%)	M_w[b]	M_w/M_n[b]
Monomer **1**						
1	THF	3	30	42.7	6700	1.7
2	Toluene	3	30	48.9	9800	1.5
3	Dioxane	3	30	55.6	9400	1.5
4	Dioxane	3	60	64.4	10,200	1.9
5	Dioxane	6	60	77.7	13,900	2.1
6	Dioxane	12	60	64.5	14,500	2.5
7	Dioxane	6	90	69.7	9600	2.8
Monomer **2**						
8	Dioxane	3	30	24.37	800	1.8
9	Dioxane	3	60	53.2	15,300	2.2
10	Dioxane	6	60	69.9	1500	2.4
11	Dioxane	12	60	69.5	11,300	2.7
12	Dioxane	6	90	57.7	7700	1.5

[a] Carried out using $[Rh(nbd)Cl]_2$–Et_3N as catalyst under nitrogen, $[M] = 0.2$ mol/L, [cat.] = 2 mmol/L, [cocat.] = 4 mmol/L.

[b] Determined by GPC in THF based on polystyrene standards.

3. Results and discussion

3.1. Polymerization

The polyacetylene directly linked by azobenzene is insoluble in almost all organic solvents [18] while P**1** and P**2** are completely soluble in common organic solvents, such as $HCCl_3$, THF and dioxane. P**1** prepared in 1,4-dioxane instead of THF or toluene as the solvent at 30 °C shows higher yield and higher molecular weight (Table 1, nos. 1, 2 and 3). Suitable elevating temperatures and delaying times can increase the yield and molecular weight. The highest yield and the highest molecular weight for both P**1** and P**2** happened at 60 °C for 6 h although that for P**2** at 30 °C only possesses a low yield (Table 1, no. 8).

3.2. Polymer structure

Fig. 1 shows the FTIR spectra of the monomer **2** and its polymer P**2**. As shown in Fig. 1, monomer **2** exhibits the characteristic $\equiv C{-}H$ and $C{\equiv}C$ stretching vibrations at 3277 and 2127 cm^{-1}, respectively, which completely disappear in the spectrum of its polymer P**2**, suggesting that the triple bond of monomer **2** has converted to double bond of polyacetylene (P**2**) backbone.

Fig. 2 shows the ^1H NMR spectra of the monomer **1** and its polymer P**1** in chloroform-*d*. In the ^1H NMR spectra of P**1** the characteristic acetylenic moiety resonance absorption peak at 2.03 ppm disappears and the absorption of the propargyl carbon at δ 2.40 ppm is obviously widened owing to its transformation to the allylic structure via the polymerization of acetylene and a new broad peak appears in the olefin absorption region (δ 6.03–6.42 ppm) corresponding to the *cis* olefin absorption of P**1**, further confirming that $C{\equiv}C$ has changed into $C{=}C$ group.

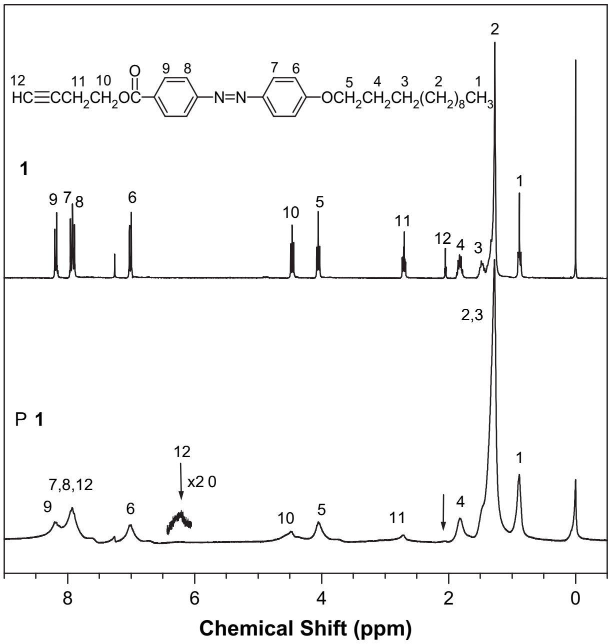

Fig. 2. ^1H NMR spectra of P**1** (sample from Table 1, no. 5) and its monomer **1** (in chloroform-*d*).

The electronic absorption spectra of these polymers in the $HCCl_3$ solutions are displayed in Fig. 3. P**1** and P**2** exhibit a strong absorption peak at ~360 nm corresponding to the $\pi{-}\pi^*$ electronic transitions of the azobenzene chromophores and the backbone absorption is found at wavelengths longer than 400 nm and well extends to 600 nm with low intensities. P**1** and P**2** only display weak ground state electron absorption at 532 nm wavelength, hinting that P**1** and P**2** may possess small ground state absorption cross-section for the laser with 532 nm wavelength.

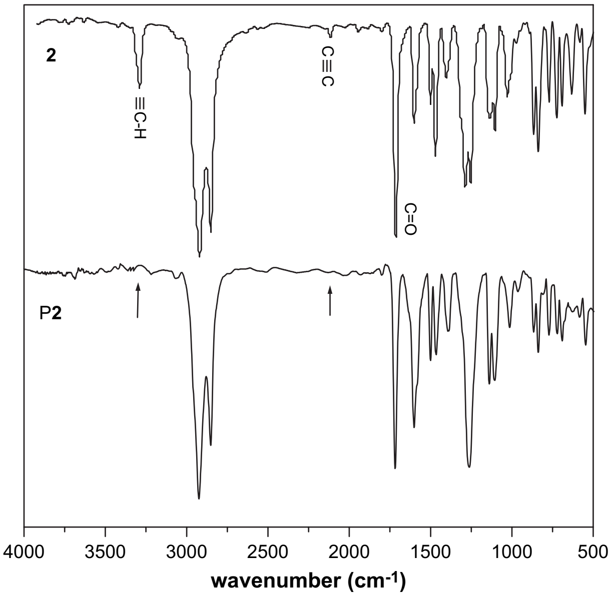

Fig. 1. FTIR spectra of P**2** (sample from Table 1, no. 10) and its monomer **2**.

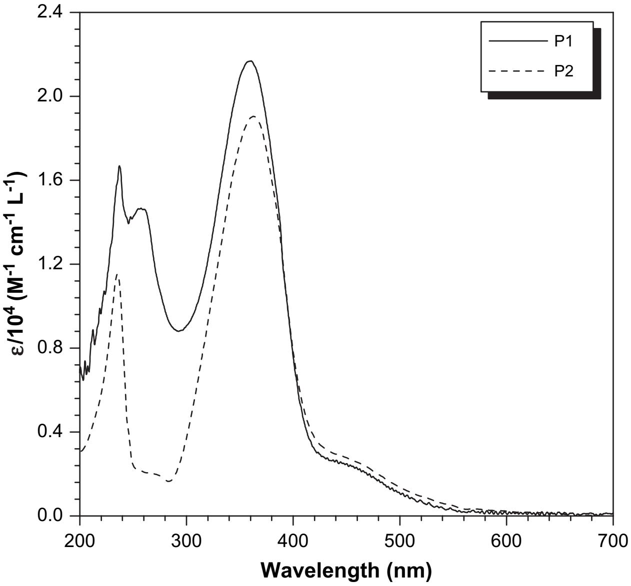

Fig. 3. UV–vis spectra of P**1** and P**2** in $CHCl_3$.

3.3. Nonlinear optical property

The nonlinear coefficients of the polymers are measured by *Z*-scan technique. The *Z*-scan experimental results of P**1** and P**2** are shown in Figs. 4 and 5, respectively. The results of *Z*-scan with and without an aperture show that all the polymers have both nonlinear absorption and nonlinear refraction. Thus, the third-order nonlinear susceptibility ($\chi^{(3)}$) of the polymers results from dual attributed to nonlinear absorption (α_2) of and nonlinear refraction (n_2) of the molecules. The $\chi^{(3)}$ of P**1** and P**2** were calculated to be 1.26×10^{-10} and 0.99×10^{-10} esu according to our experimental data and the calculation method reported in Refs. [8,9,19], which is almost three orders of magnitude larger than those of poly(phenylacetylene) [20,21], larger than that of *ortho*-substituted poly(phenylacetylene) [22,23] and carbazyl or anthryl substituted polyacetylene [24]. Thus, the incorporation of azobenzene into polyacetylene effectively enhances the third-order susceptibility of polyacetylene.

Based on the Schuling's nonlinear optical theory of the relationship between molecular structure and optical property, that is, the third-order nonlinear optical susceptibility (γ) depends on γ_e^0, a term related to the movement of electron, and β, the second-order nonlinear optical susceptibility [25], the large optical nonlinearities of these polymers may be attributed to the electronic interaction of the large second-order nonlinear optical chromophore (azobenzene) and the third-order conjugative polyacetylene main chain. Simultaneously, it is also seen that the third-order nonlinear susceptibility of P**1** is larger than that of P**2**, which may result from the decrease of the electronic interactions of azobenzene with polyacetylene main chain with the increase of the spacer.

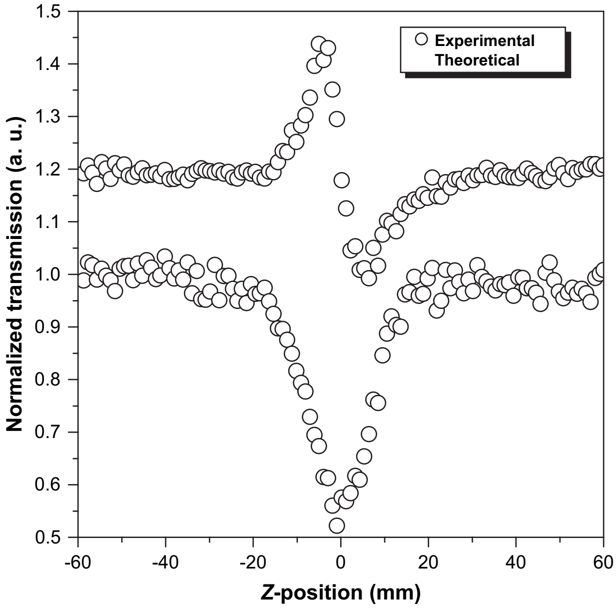

Fig. 5. *Z*-scan data of P**2** (sample from Table 1, no. 10).

3.4. Optical limiting property

Fig. 6 shows the optical limiting (OL) behaviors of P**2** at the different concentrations. As shown in Fig. 6, the transmitted fluence of the polymer solution ($c = 0.38$ mg/mL, $T = 55\%$) increases linearly with the incident fluence at very low incident fluence but starts to deviate at a high incident fluence. With a further increment of the incident fluence, the transmitted fluence reaches a plateau and is saturated at 0.252 J/cm^2 (defined as limiting amplitude; that is, the maximum output intensity), showing obvious optical limiting

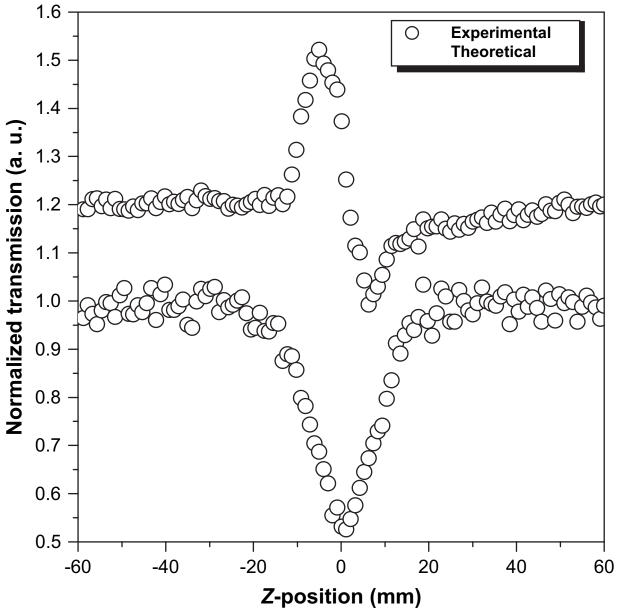

Fig. 4. *Z*-scan data of P**1** (sample from Table 1, no. 5).

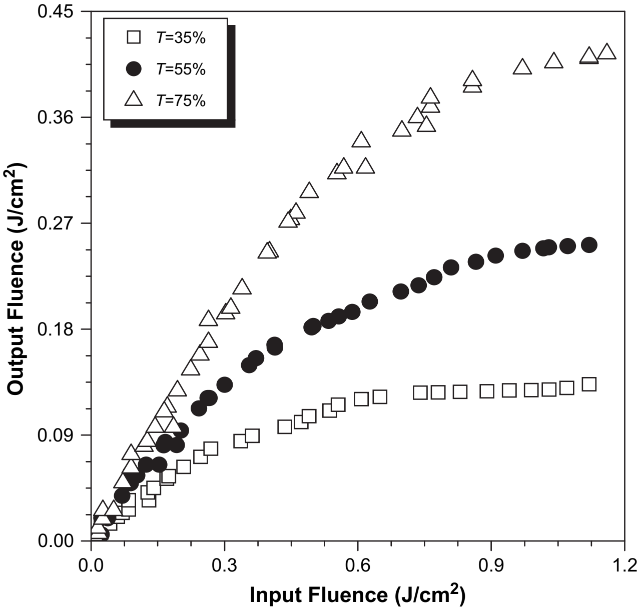

Fig. 6. Optical limiting properties of P**2** (sample from Table 1, no. 10) solution with different linear transmittance.

property. Simultaneously, we also measured the UV–vis absorption spectrum of the **P2** solution before and after the laser irradiation and found that the pattern and its intensity of UV–vis absorption spectrum have almost no change, hinting that the **P2** possesses good photostability. In contrast, the transmittance of the poly(PA) solution continually increases instead of decreasing due to the laser-induced photolysis of the polyacetylene chains [4], indicating that polyacetylene is endowed with a novel optical property–optical limiting property by the incorporation of azobenzene and good photostability. Simultaneously, we also found that the limiting effect is affected by concentration and increases with concentration. For example, the limiting amplitude of the sample varies from 0.252 to 0.131 J/cm^2 when the solution concentration increases from 0.38 mg/mL ($T = 55\%$) to 0.72 mg/mL ($T = 35\%$). Similar results were also found by Kojima and our previous publications [4,8,9,26], which may be due to more molecules per unit volume.

Fig. 7 shows the optical limiting performance of **P1** and **P2** at the same linear transmittance ($T = 55\%$). As shown in Fig. 7, **P1** and **P2** both show the obvious optical limiting property. Their optical limiting amplitudes are 0.223 and 0.252 J/cm^2 for **P1** and **P2**, respectively. **P1** exhibits the better optical property than **P2**, which is consistent with the result of the nonlinear optical property.

The optical limiting mechanisms of organic compounds are often based on two-photon absorption (TPA) or reverse saturable 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, rather than a picosecond time scale, owing to the different excited-state lifetimes involved in a multilevel energy process [27]. In this work, the polymers are excited by the laser with 8 ns pulse width at 532 nm wavelength. Therefore, we consider that the optical limiting properties of **P1** and **P2** may originate from RSA.

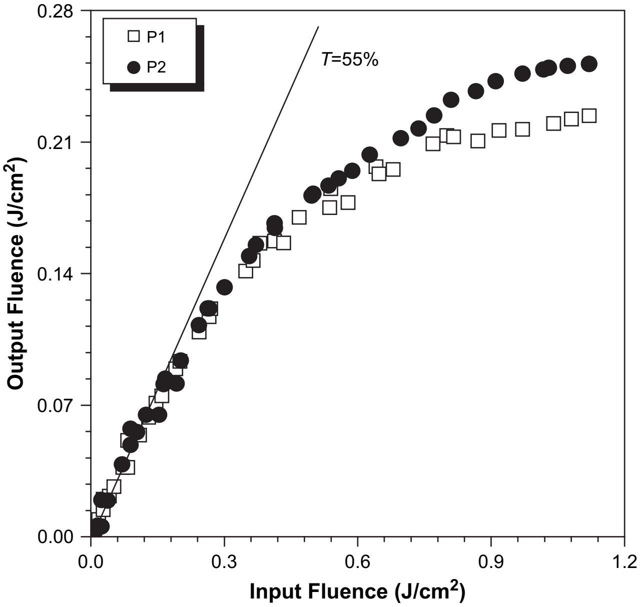

Fig. 7. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light, of chloroform solution of **P1** (sample from Table 1, no. 5) and **P2** (sample from Table 1, no. 10) with a linear transmission of 55%.

The optical limiting property for RSA mechanism mainly depends on the ratio of the excited state absorption cross-section (σ_{ex}) to the ground state absorption cross-section (σ_0) of molecules, which was defined as $\sigma_{ex}/\sigma_0 = \ln T_{sat}/\ln T_0$. T_{sat} is a saturated transmittance for high degrees of excitation [28]. In our experimental setup, we can use the transmittance at 1.1 J/cm^2 to calculate the lowest bound for σ_{ex}/σ_0 although we are unable to reach the saturable transmittance for these compounds. As shown in Fig. 7, the corresponding value of σ_{ex}/σ_0 for **P1** is calculated to be 5.62, while σ_{ex}/σ_0 for **P2** is 5.20, further conforming that **P1** shows better optical limiting property than **P2**.

4. Conclusions

Two new soluble azobenzene-containing poly(1-alkyne)s are synthesized by $[Rh(nbd)Cl]_2$–Et_3N as catalyst and characterized. The incorporation of azobenzene chromophoric pendant effectively enhances the nonlinear optical properties of polyacetylene and endows polyacetylene with novel optical limiting properties. Polymer having shorter spacer lengths shows better performances and larger third-order nonlinear optical susceptibility.

Acknowledgements

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