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Preparation and optical properties of poly(4-ethynyl-4′-[*N*,*N*-diethylamino]azobenzene-*co*-phenylacetylene)

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Abstract

A novel soluble functional polyacetylene copolymer (poly(EAAB-*co*-PA)) of 4-ethynyl-4′-[*N*,*N*-diethylamino]azobenzene (EAAB) and phenylacetylene (PA) was synthesized. The structures and properties of the polymers were characterized and evaluated by FTIR, UV–vis, ^{1}H NMR, GPC, optical limiting, and nonlinear optical analyses. The results show that poly(EAAB-*co*-PA) has the large third-order nonlinear susceptibility, which are two orders of magnitude larger than those of poly(PA) and novel optical limiting property.

Keywords: Nonlinear optics; Optical limiting; Substituted polyacetylene; Azo dyes; Z-scan; Chromophore

1. Introduction

Organic π-conjugate polymers as the third-order nonlinear optics (NLO) materials have been widely investigated in the last few years [1,2]. Polyacetylene, a prototypical conjugated polymer shows the large third-order electric susceptibility $\chi^{(3)}$ and fast response time [3]. However, its insolubility, instability and improcessability limit its practical applications as a functional material. Attachment of functional substitutents to the polyacetylene backbone, however, not only has helped to solve the problems but also endows the resultant polymers with novel properties. A few substituted polyacetylene having nonlinear optical property were synthesized, which are soluble in common organic solvents and stable in air even at elevated temperature. For instance, the third-order nonlinear optical coefficients of poly(phenylacetylene) film and its solution were determined by using third harmonic generation (THG) technique and Z-scan technique, respectively, to be about 10^{-13} esu [4]. Sone et al. investigated the NLO properties of *cis*-rich (Rh-produced) and *trans*-rich (Mo produced) poly(*o*-trifluoromethyl(phenylacetylene)) films and found that the third-order nonlinear optical coefficient of *trans*-polyacetylene is two orders larger than that of *cis*-polyacetylene [5]. Masuda synthesized carbazoly or anthryl substituted polyacetylene and the polyacetylene copolymer of 1-naphthylacetylene and 9-anthrylacetylene [6,7]. These substituted polyacetylenes have the large third-order nonlinear optical coefficient, ranging form 10^{-12} to 10^{-10} esu.

In this paper, we report the preparation of a novel soluble functional polyacetylene copolymer of acetylene bearing substituted azobenzene chromophore and phenylacetylene (Scheme 1). The substituted azobenzene moiety was bonded to the polymer main chain to endow polyacetylene novel optical property.

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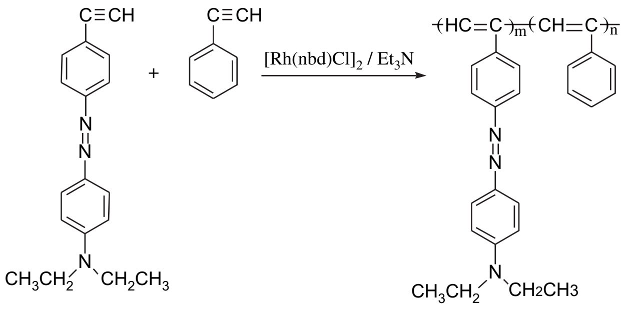

Scheme 1. The synthetic route of poly(EAAB-*co*-PA).

2. Experimental

2.1. Materials

Norbornadienerhodium(I) chloride dimer ([Rh(nbd)Cl]$_2$), tungsten(VI) chloride (WCl$_6$), molybdenum(V) chloride (MoCl$_5$) and tetraphenyltin (Ph$_4$Sn) were all purchased from Aldrich and kept in inert-atmosphere glovebox, used as received without further purification. Phenylacetylene (PA) was purchased from Fluka, distilled from calcium hydride under reduced pressure before use. The synthesis and characterization of the (4-ethynyl-4′-[*N*,*N*-diethylamino]azobenzene) (EAAB) monomer are described elsewhere.

2.2. Instruments

The FTIR spectra were recorded as KBr pellets on a Nicolet 170sx spectrometer. The ^{1}H NMR spectra were colleted on an AVANCE/DMX-500 MHz Bruker. 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 nonlinear optical property of the sample measured by *Z*-scan technique was performed with a Q-swithed ns/ps Nd:YAG laser system continuum with pulse width of 8 ns at 1 Hz repetition rate and 532 nm wavelength. The experiment was set-up as in Ref. [8]. The solution sample was contained in a 2-mm quartz cell. The relation between the normalized transmittance $T(z)$ and z position was obtained by moving the samples along the axis of the incident beam (z direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by an energy meter (Laser Precision Corporation Rjp-735). The input energy was 180 μJ.

The investigation of the OL properties of the samples was carried out by using the same laser system as in the Z-Scan experiment. The experimental arrangement is similar to that reported in the literature [9].

2.3. Polymerization

EAAB (277 mg, 1 mmol) was added into a baked 20-mL Schlenk tube equipped with a side arm. The tube was evacuated under vacuum and then flushed three times with dry nitrogen through the side arm. Phenylacetylene (204 mg, 2 mmol) in THF (5 mL) was injected into the tube. The catalyst solution was prepared in another tube by dissolving 13.2 mg (0.03 mmol) [Rh(nbd)Cl]$_2$ and 6.06 mg (0.06 mmol) Et$_3$N in THF (3 mL). This solution was transferred to the EAAB solution through a hypodermic syringe. The reaction mixture was stirred at room temperature under nitrogen for 3 h and then the reaction was quenched with 5 mL of THF containing a small amount of methanol. After the diluted reaction mixture was filtered, the soluble filtrate was added dropwise into 300 mL of methanol under stirring to precipitate the polymer product. Then the product was redissolved in THF, and added dropwise through a cotton filter into methanol (300 mL). The dissolution/precipitation process was repeated three times, and the final isolated precipitate was dried to a constant weight under vacuum at 40 °C. A red-brown powder was obtained (58%). M_w: 76 100, M_w/M_n: 7.05 (GPC, polystyrene calibration). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 1.23 (br., 3H, NCH$_2$C*H*$_3$), 3.37 (br., 2H, NC*H*$_2$CH$_3$), 5.83 (br., *cis* olefin proton), 6.47–7.88 (br., aromatic protons and *trans* olefin proton). IR (KBr), ν (cm^{-1}): 3046 (=C–H), 2967 (–CH$_3$), 2920 (–CH$_2$), 1600, 1508, 821, 738, 692 (–Ar).

3. Results and discussion

3.1. Polymerization

Table 1 lists the results of the polymerization. From Table 1, we observe that the [Rh(nbd)Cl]$_2$–Et$_3$N catalyst exhibited high activity in the polymerization of EAAB, while classical metathesis catalysts, such as WCl$_6$/Ph$_4$Sn and MoCl$_5$/*n*-Bu$_4$Sn show no activity, which is attributed to catalyst deactivation by the azo group. However, the resulting poly(EAAB) was insoluble in almost all solvents, possibly because the rigid planar *p*-azobenzene groups adopt stacked structures. A similar result was reported by Terguchi and Masuda [10]. To solve the solubility, we selected phenylacetylene, whose homopolymer possesses good solubility and film-forming ability to copolymerize with EAAB. When EAAB was polymerized with phenylacetylene at a molar ratio of 1:1 (Table 1, No. 6), the

Table 1
The results of polymerization

No.	EAAB:PA (molar feed ratio)	Catalyst	Time (h)	Yield (%)	$\overline{M}_w$ ($\times10^3$)[a]	$\overline{M}_w/\overline{M}_n$
1	1:0	WCl$_6$	24	0		
2	1:0	WCl$_6$–Ph$_4$Sn	24	0		
3	1:0	MoCl$_5$	24	0		
4	1:0	MoCl$_5$–Ph$_4$Sn	24	0		
5	1:0	[Rh(nbd)Cl]$_2$–Et$_3$N	3	53[b]		
6	1:1	[Rh(nbd)Cl]$_2$–Et$_3$N	3	28	7.73	3.2
7	1:2	[Rh(nbd)Cl]$_2$–Et$_3$N	3	58	76.1	7.1

[a] Determined by GPC in THF.
[b] Not dissolved in THF.

resulting copolymer was partially soluble in THF and $CHCl_3$. When the molar feed ratio of EAAB and phenylacetylene was further increased to 1:2 (Table 1, No. 7), however, the resultant copolymer was completely soluble in THF and $CHCl_3$, indicating that the solubility of functional polyacetylene can effectively be adjusted by a copolymerization method.

3.2. Structure characterization

Fig. 1 displays the FTIR spectra of EAAB, poly(PA) and poly(EAAB-*co*-PA) (Table 1, No. 7). The spectrum of poly(EAAB-*co*-PA) is similar to that of the EAAB monomer, with the exceptions that the characteristic $\nu_s(\equiv C-H)$ and $\nu_s(C\equiv C)$ absorption bands disappear at 3275 and 2100 cm^{-1}, which proves that C≡C of EAAB was transferred into C═C band. The $\delta_s(C-H)$ vibration band of monosubstituted aromatic rings at 738 and 692 cm^{-1} from the poly(PA) segment clearly appears in the poly(EAAB-*co*-PA) copolymer, further confirming that phenylacetylene copolymerized with the EAAB monomer.

Fig. 2 displays ^1H NMR spectra of EAAB, poly(PA), and poly(EAAB-*co*-PA) (Table 1, No. 7) in *d*-chloroform. From Fig. 2, it can be seen that the characteristic single peak for the resonance of the proton of the ethynyl group in EAAB is located at 3.17 ppm. This peak disappears, however, after copolymerization with phenylacetylene, and a new broad peak appears in the olefin absorption region (δ 5.8–6.0) in the ^1H NMR spectra of the poly(EAAB-*co*-PA) copolymer. This peak corresponds to that of the *cis* olefin proton of poly(EAAB-*co*-PA), which proves that the transformation of C≡C bonds to C═C units has occurred. The aromatic proton peaks of EAAB are obviously widened and shifted to higher field after the copolymerization with phenylacetylene and the characteristic resonance of the poly(PA) aryl protons at 6.93 ppm also clearly appear in the spectrum of poly(EAAB-*co*-PA), further supporting the conclusion that phenylacetylene indeed copolymerized with EAAB.

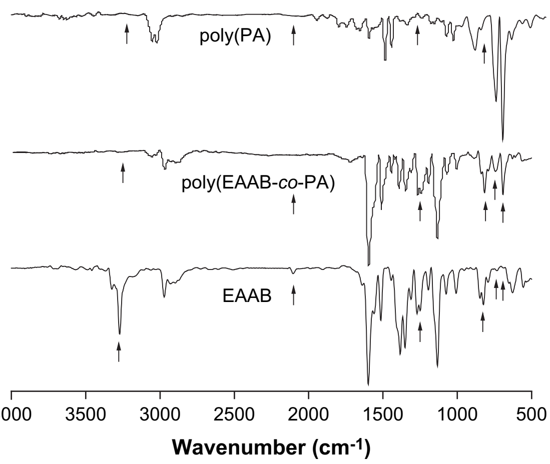

Fig. 1. IR spectra of poly(PA), EAAB and poly(EAAB-*co*-PA) (KBr, sample from Table 1, No. 7).

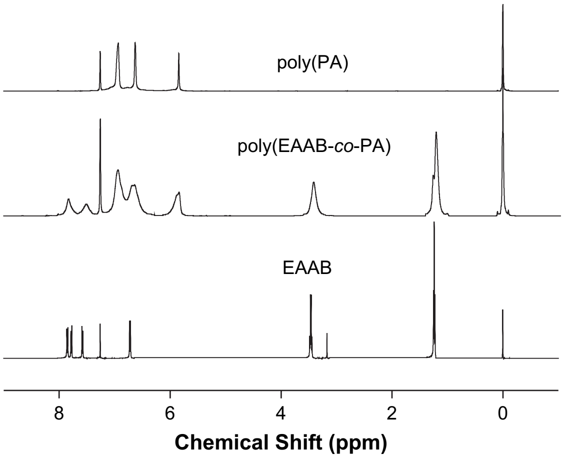

Fig. 2. ^1H NMR spectra of poly(PA), EEAAB and poly(EAAB-*co*-PA) (sample from Table 1, No. 7).

The ^1H NMR spectrum was also used to determine the segment content of the copolymer. The content of poly(EAAB) may be estimated by directly comparing the peak area associated with the methylene protons in the poly(EAAB) segment (δ 3.47 ppm) and the peak area corresponding to aryl and olefin protons in the poly(EAAB-*co*-PA) copolymer based on the following.

$$\text{Poly(EAAB) content (mol\%)} = \frac{\frac{1}{4}\times A_{3.47}}{\frac{1}{4}\times A_{3.47}+\frac{1}{6}\times\left(A-9\times\frac{1}{4}\times A_{3.47}\right)}\times 100\%$$

where $A = A_{5.84} + A_{6.63} + A_{6.94} + A_{7.49} + A_{7.82}$, corresponds to the absorption peak area of aryl protons and olefin proton (*trans* and *cis* olefin) of the poly(EAAB-*co*-PA) copolymer, $(1/4)A_{3.47}$ is associated with the peak areas of one methylene proton of the poly(EAAB) segment and $9(1/4)A_{3.47}$ corresponds to the peak areas of eight aryl protons and one olefin proton (*trans* and *cis* olefin) of the poly(EAAB) segment. So, nominator is associated with the peak area of one proton of the poly(EAAB) segment and denominator is associated with the peak area of one proton of the poly(EAAB-*co*-PA) copolymer. Thus, the poly(EAAB) segment content in the poly(EAAB-*co*-PA) copolymer was calculated to be 42.8%.

Fig. 3 displays the electronic absorption spectra of poly(EAAB-*co*-PA), recorded at 20 °C using a Shimadzu UV-265 spectrometer. Poly(EAAB-*co*-PA) exhibits two strong absorption peaks at 245 and 435 nm, which correspond to the absorption bands of the phenyl groups mainly from the poly(PA) segment and the $\pi-\pi^*$ transition of the azobenzene chromophore from the poly(EAAB) segment, respectively, providing a further confirmation that EAAB and phenylacetylene have copolymerized.

3.3. Nonlinear optical property of the copolymer

The nonlinear absorption coefficient of poly(EAAB-*co*-PA) was measured by using Z-scan technique. In our experiment,

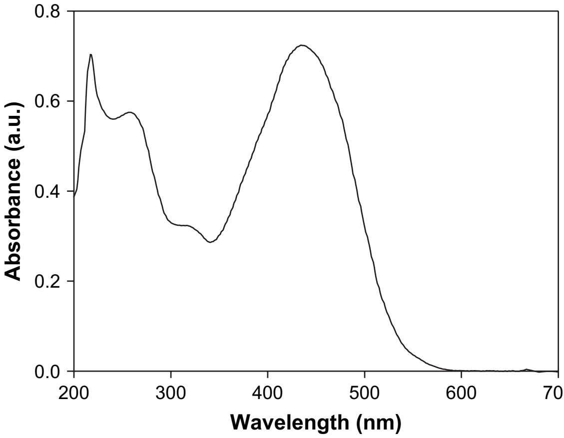

Fig. 3. UV–vis spectrum of poly(EAAB-*co*-PA) (sample from Table 1, No. 7).

the samples were moved along the direction of laser beam around the focus ($z = 0$) forward or backward. The transmittance was simultaneously recorded by a power meter with and without an aperture in the far field of lens as the function of sample position. The results of Z-scan with and without an aperture showed that poly(EAAB-*co*-PA) has both nonlinear absorption (Fig. 4a) and nonlinear refractive coefficients (Fig. 4b). Thus, the $\chi^{(3)}$ measured in this experiment was attributed to nonlinear absorption of molecules (α_2) and nonlinear refractive index of molecules (n_2).

In theory, the normalized transmittance for the open aperture can be written as [8,11]

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

where $q_0(z) = \alpha_2 I_0(t) L_{\mathrm{eff}} / \left(1 + z^2/z_0^2\right)$, α_2 is the nonlinear absorption coefficient, $I_0(t)$ the intensity of laser beam at focus ($z = 0$), $L_{\mathrm{eff}} = \left[1 - \exp(-\alpha_0 L)\right]/\alpha_0$ 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 poly(EAAB) is determined to be 4.87×10^{-10} m/W by fitting the experimental data using Eq. (1).

The normalized transmission for the closed aperture Z-scan is given by [8,11]

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

where $x = z/z_0$ and $\Delta\phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\phi = 2\pi I_0(1 - \mathrm{e}^{-\alpha_0 L}) n_2/\lambda\alpha_0$. Thus, the nonlinear refractive coefficient of poly(EAAB) is determined to be 1.24×10^{-17} m^2/W by fitting the experimental data using Eq. (2).

The $\chi^{(3)}$ can be calculated by the following equation [8,11]

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

where ε_0 is the permittivity of vacuum, c the speed of light, n_0 the refractive index of the medium and $\omega = 2\pi c/\lambda$. Thus, the nonlinear susceptibility of poly(EAAB-*co*-PA) is determined to be 4.62×10^{-11} esu. The third-order susceptibility of poly(EAAB-*co*-PA) is almost two orders of magnitude larger than that of poly(phenylacetylene) [4,12–14]. Thus, the introduction of the poly(EAAB) segment effectively increases the third-order nonlinear optical property of poly(PA).

3.4. Optical property of the copolymer

Fig. 5 shows the optical responses of poly(EAAB-*co*-PA) solutions ($T = 77\%$) and the solution of poly(PA) ($T = 75\%$) [15]. From Fig. 5, it can be seen that at very low laser fluence, the transmitted fluence of the poly(EAAB-*co*-PA) solution ($T = 77\%$, $c = 0.11$ mg/mL) linearly increases with the incident fluence obeying the Beer–Lambert law.

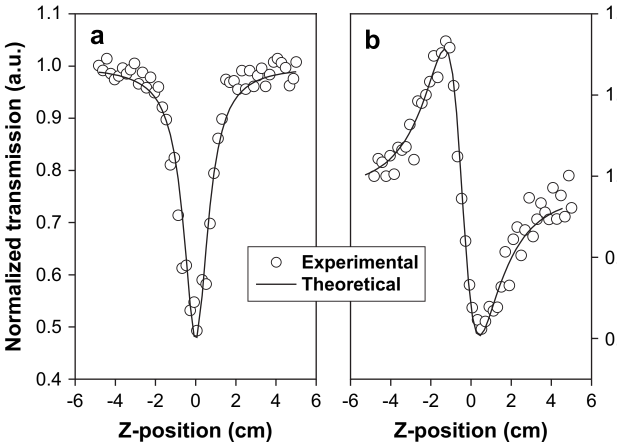

Fig. 4. (a) Z-scan data of open aperture: (dot line) experimental data; (solid line) theoretical curve. The theoretical curve is fitted by using Eq. (1) with the nonlinear absorption coefficient α_2. (b) Z-scan data of close aperture: (dot line) experimental data; (solid line) theoretical curve. The theoretical curve is fitted by using Eq. (2) with the nonlinear refractive coefficient n_2.

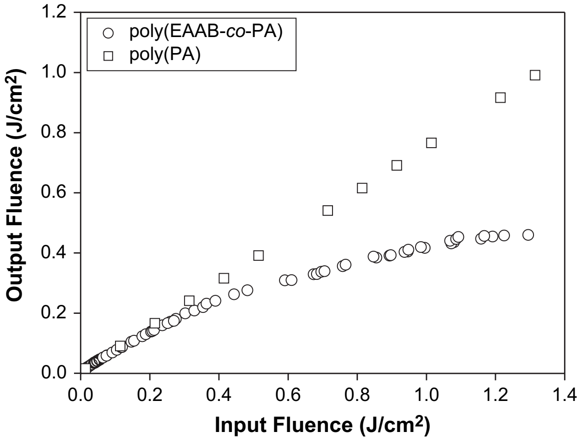

Fig. 5. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light, of the poly(EAAB-*co*-PA) solution with a linear transmission of 77%. The open circles correspond to experimental results of poly(EAAB-*co*-PA). Data for poly(PA) (open square) with a linear transmission of 75% is shown for comparison.

However, when the incident fluence reaches 0.215 J/cm^2, the transmitted fluence of the poly(EAAB-*co*-PA) solution starts to deviate from linearity (defined as limiting threshold, that is, the incident fluence at which the output fluence starts to deviate from linearity). With further increase in the incident fluence, the transmitted fluence reaches a plateau and is saturated at 0.442 J/cm^2 (defined as the limiting amplitude, that is, the maximum output intensity), showing the optical limiting property. In contrast, the transmitted fluence of the poly(PA) solution ($T = 75\%$, $c = 4.0$ mg/mL) successively linearly increases with an increase in the incident influence, that is, poly(PA) hasn't the optical limiting property even if the concentration of the poly(PA) solution is 36 times more than that of the poly(EAAB-*co*-PA). Thus, the incorporation of the conjugated chromophores into polyacetylene endows polyacetylene a novel optical limiting property.

4. Conclusion

A novel functional polyacetylene copolymer bearing an azobenzene nonlinear optical chromophore was synthesized using $[Rh(nbd)Cl]_2$–Et_3N as catalyst and characterized by FITR, ^{1}H NMR, UV–vis and GPC. The nonlinear optical and optical limiting properties of this functional polyacetylene copolymer were investigated using 8 ns Nd:YAG laser system at 532 nm. The results show that the incorporation of nonlinear optical chromophore into polyacetylene effectively enhances the third-order nonlinear susceptibility of poly(phenylacetylene) and endows poly(phenylacetylene) a new good optical limiting property. This work paves the way for new nonlinear optical and optical limiting materials.

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