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Synthesis and optical properties of polyacetylenes containing nonlinear optical chromophores

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Abstract

High molecular weight polyacetylenes bearing nonlinear chromophoric pendants poly[4-ethynyl-4′-(*N*,*N*-diethylamino)azobenzene-*co*-phenylacetylene]s [poly(EAAB-*co*-PA)s] were synthesized in moderate yields by $[Rh(nbd)Cl]_2$–Et_3N. The azo unit in the copolymers can be effectively controlled by the monomer feed ratio. Whereas the homopolymer of EAAB possessed low solubility, all the copolymers, however, dissolved readily in common organic solvents when the poly(EAAB) molar content was less than 41.7%. The structures and properties of the polymers were characterized and evaluated by UV, NMR, optical limiting, and nonlinear optical analyses. All the copolymers possessed high stereoregularity and thermal stability (≥ 300 °C). They can attenuate intense laser pulses, with solutions of high concentrations showing better performances. The third-order nonlinear susceptibility of the copolymers was as high as 4.62×10^{-11} esu, which are two orders of magnitude larger than those of poly(PA), and larger than that of poly(*N*-carbazoylacetylene), and poly(1-naphthylacetylene).

Keywords: Functional polyacetylene; Optical limiting; The third-order nonlinear optics

1. Introduction

With the fast development of modern laser technology, there is a growing need in nonlinear optical materials for passive-mode optical limiting applications to protect optically sensitive devices and human eyes from laser damage in both civilian and military applications [1,2]. An ideal optical limiter exhibits linear transmittance at low laser incident fluence, but becomes opaque at high laser incident fluences. The widely investigated optical limiters are organic dyes such as porphyrins, metallophthalocyanines, and fullerenes and nanoscale materials including suspended carbon black and carbon nanotubes [3–12].

Recently, conjugated polymers have also attracted great interest as optical limiting materials due to their large third-order nonlinearity, fast nonlinear response time, high damage threshold, ease of processing, versatile structural modification, and their applicability over a wide wavelength range [13–24]. Polyacetylene is the simplest conjugated polymer with alternating double bonds and has been found to exhibit good third-order nonlinear optical properties [25]. Unfortunately, its insolubility, instability and improcessability have limited its practical applications. Attachment of functional substituents to the polyacetylene backbone, however, not only has helped to solve the problems but also endows the resultant polymers with novel properties. While some works on the synthesis of polyacetylenes with nonlinear optical (NLO) properties have been reported [26–32], a few papers, however, present the use of substituted polyacetylenes as optical limiting (OL) materials [16,17].

Thus, in order to enrich the research field of OL polyacetylenes, in this paper, we synthesized a group of

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soluble functional polyacetylenes containing NLO chromophores (Scheme 1). The copolymers exhibit novel NLO and OL properties originated from their unique molecular structures.

2. Experimental section

2.1. Materials

Bis(triphenylphosphine)palladium(II) chloride [$Pd(PPh_3)_2Cl_2$] and norbornadienerhodium(I) chloride dimer $[Rh(nbd)Cl]_2$ were purchased from Aldrich, kept under an inert-atmosphere in a glove box, and used as received without further purification. Phenylacetylene (PA) was purchased from Fluka, distilled from calcium hydride under reduced pressure, and stored in sealed ampoules in a dark, cool place before use. 2-Methyl-3-butyn-2-ol and 4-bromoaniline were purchased from Aldrich. *N*,*N*-Diethylaniline was purchased from Shanghai Chemical Reagent Company and distilled before use. Dioxane, THF, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine was distilled from potassium hydroxide prior to use. Technical grade methanol was used to precipitate the polymers.

2.2. Instruments

The FT-IR spectra were recorded on a Nicolet 170s× spectrometer. The ^1H and ^{13}C NMR spectra were recorded on an AVANCE/DMX-500 MHz Bruker NMR spectrometer using chloroform-*d* as the solvent. Tetramethylsilane (TMS) or chloroform-*d* was used as the internal reference for the NMR analyses. Elementary analyses were conducted using an Elementar Vario EL-III apparatus. Melting points (mp) were measured on a Yanaco micro melting point apparatus. UV–vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm-square quartz cell. The molar absorptivities (ε) of the polymers were calculated on the basis of their repeat units. Thermogravimetric analyses (TGA) of the polymers were performed on a Perkin–Elmer TGA 7 under nitrogen at a heating rate of 20 °C/min. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of Styragel columns (HT3, HT4, and HT6; molecular weight range: 10^2–10^7), a column temperature controller, a Waters 486 wavelength-tunable UV–vis detector, a Waters 410 differential refractometer, and a system DMM/scanner possessing an 8-channel scanner option. All the polymer solutions were prepared in THF (ca. 2 mg/mL) and filtered through 0.45-μm PTFE syringe-type filters before being injected into the GPC system. THF was used as the eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 30 °C and the working wavelength of the UV–vis detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) was used for calibration purposes.

The optical limiting properties of poly(EAAB-*co*-PA) were measured in THF solutions. Testing was performed 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 transverse mode of the laser pulses is nearly Gaussian. The input laser pulses were split 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 housed in quartz cells with a thickness of 5 mm. The incident and transmitted laser pulses were monitored by utilizing two energy detectors, D_1 and D_2 (Rjp-735 energy probes, Laser Precision) [33].

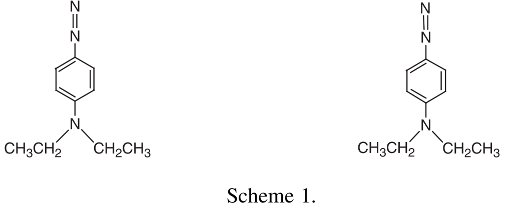
The nonlinear optical properties of the samples were carried out using the same laser system above at the input energy 180 μJ. The experimental set up was similar to that given in the literature [34]. The concentration of poly-(EAAB-*co*-PA) used was 0.35 mg/mL.

2.3. Synthesis of the functional monomer

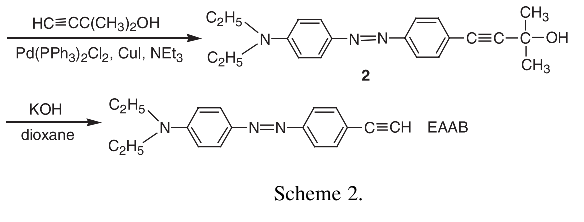
The monomer 4-ethynyl-4′-(*N*,*N*-diethylamino)azobenzene (EAAB) was prepared according to Scheme 2. The detailed experimental procedures are given below.

2.3.1. 4-Bromo-4′-[(N,N-diethyl)amino]azobenzene (*1*)

4-Bromoaniline (3.44 g, 20 mmol) was dissolved in an ice-water solution containing sodium nitrite (1.36 g, 20 mmol). After cooling to 0 °C, the solution was added to conc. hydrochloric acid (8 mL) and stirred for 30 min.



Scheme 1.



Scheme 2.

The mixture was then added dropwise to an buffered aqueous solution (acetic acid/sodium acetate, pH ∼ 6) containing 3.13 g *N*,*N*-diethylaniline (21 mmol) and stirred for 2 h at 0–5 °C. The resulting precipitate was filtered and rinsed twice with water. The crude product was recrystallized twice from ethanol/petroleum ether (4:1 vol. ratio) to provide yellow crystal powder (5.64 g, 85%). IR (KBr), ν (cm^{-1}): 2945, 2882, 1595. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.24 [t, $J=7.1$ Hz, 6H, $N(CH_2CH_3)_2$], 3.46 [q, 4H, $N(CH_2CH_3)_2$], 6.73 [d, $J=7.7$ Hz, 2H, Ar–H *ortho* to $N(CH_2CH_3)_2$], 7.58 (d, $J=8.5$ Hz, 2H, Ar–H *ortho* to Br), 7.71 (d, 2H, Ar–H *meta* to Br), 7.85 [d, 2H, Ar–H *meta* to $N(CH_2CH_3)_2$].

2.3.2. 2-Methyl-4-[p-(N,N-diethylamino)azobenzene]-3-butyn-2-ol (2)

2-Methyl-3-butyn-2-ol (0.86 mL, 8.4 mmol) was added to a solution of $PdCl_2(PPh_3)_2$ (49 mg, 0.07 mmol), CuI (7 mg, 0.036 mmol), and 4-bromo-4′-[*N*,*N*-diethylamino] azobenzene (2.32 g, 7 mmol) in triethylamine (10 mL) and THF (65 mL) under a nitrogen atmosphere. The mixture was heated under reflux for 4 h. After cooling to room temperature, the precipitate was filtered and the filtrate was concentrated. The crude product was purified by aluminium oxide column using ethyl acetate/petroleum ether mixture (1:4 v/v) as eluent. Recrystallization from ethanol gave a yellow powder in 85% yield (1.95 g). IR (KBr), ν (cm^{-1}): 3413 (OH), 2975, 2920, 2121 (C≡C), 1598. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.24 [t, $J=7.1$ Hz, 6H, $N(CH_2CH_3)_2$], 1.64 [s, 6H, $C(CH_3)_2$], 2.03 (s, 1H, OH), 3.46 [q, 4H, $N(CH_2CH_3)_2$], 6.72 [d, $J=9.1$ Hz, 2H, Ar–H *ortho* to $N(CH_2CH_3)_2$], 7.50 (d, $J=8.4$ Hz, 2H, Ar–H *ortho* to C≡C), 7.76 (d, 2H, Ar–H *meta* to C≡C), 7.87 [d, 2H, Ar–H *meta* to $N(CH_2CH_3)_2$]. ^{13}C NMR (125 Mz, $CDCl_3$), δ (ppm): 12.9 (NCH_2CH_3), 31.7 (CH_3), 44.9 (NCH_2), 65.9 [$OC(CH_3)_2$], 82.5 (Ar–C≡), 95.4 [$\equiv CC(CH_2)_3$], 111.2 [aromatic carbons *ortho* to $N(CH_2CH_3)_2$], 122.3 (aromatic carbons *meta* to C≡C), 123.5 (aromatic carbon attached to C≡C), 125.7 [aromatic carbons *meta* to $N(CH_2CH_3)_2$], 132.6 (aromatic carbons *ortho* to C≡C), 143.4 [aromatic carbon *para* to $N(CH_2CH_3)_2$], 150.6 [aromatic carbon attached to $N(CH_2CH_3)_2$], 152.9 (aromatic carbon *para* to C≡C).

2.3.3. 4-Ethynyl-4′-[N,N-diethylamino]azobenzene (EAAB)

Potassium hydroxide (672 mg, 12 mmol) was added with stirring to a solution of **2** (5.03 g, 15 mmol) in dry dioxane (150 mL) under nitrogen. The reaction mixture was then heated under reflux for 3 h. After cooling to room temperature, the precipitate was filtered and the filtrate was concentrated. The crude product was purified by aluminium oxide column chromatography using ethyl acetate/petroleum ether mixture (1:4 v/v) as eluent. Recrystallization from ethanol/petroleum ether gave a deep-red powder (2.71 g, 65%). IR (KBr), ν (cm^{-1}): 3275 (≡C–H), 2974, 2929, 2100 (C≡C), 1600, 1508, 821. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.24 [t, $J=7.1$ Hz, 6H, $N(CH_2CH_3)_2$], 3.17 (s, 1H, ≡CH), 3.47 (q, 4H, NCH_2), 6.72 [d, $J=9.2$ Hz, 2H, Ar–H *ortho* to $N(CH_2CH_3)_2$], 7.58 (d, $J=8.5$ Hz, 2H, Ar–H *ortho* to C≡CH), 7.78 (d, 2H, Ar–H *meta* to C≡CH), 7.86 [d, 2H, Ar–H *meta* to $N(CH_2CH_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 12.8 (NCH_2CH_3), 44.8 (NCH_2), 78.7 (HC≡C), 83.9 (HC≡C), 111.1 [aromatic carbons *ortho* to $N(CH_2CH_3)_2$], 122.2 (aromatic carbons *meta* to C≡CH), 122.6 (aromatic carbon attached to C≡CH), 125.7 [aromatic carbons *meta* to $N(CH_2CH_3)_2$], 133.0 (aromatic carbons *ortho* to C≡CH), 143.3 [aromatic carbon *para* to $N(CH_2CH_3)_2$], 150.5 [aromatic carbon attached to $N(CH_2CH_3)_2$], 153.2 (aromatic carbon *para* to C≡C). Elem. Anal. Calcd for $C_{18}H_{19}N_3$: C 77.98; H 6.86; N 15.16. Found: C 77.68; H 6.80; N 15.06.

2.4. Polymerization

All the polymerization reactions and manipulations were performed under pre-purified nitrogen using Schlenk techniques either in vacuum-line systems or in an inert-atmosphere glove box, except for the purification of the polymers, which was conducted in open atmosphere. A typical procedure for the copolymerization of EAAB and PA is given below: monomer 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 (408 mg, 4 mmol) in toluene (5 mL) was injected into the tube. The catalyst solution was prepared in another tube by dissolving 22 mg (0.05 mmol) $[Rh(nbd)Cl]_2$ and 10.1 mg (0.1 mmol) Et_3N in toluene (3 mL). This solution was transferred to the EAAB solution through a hypodermic syringe. After stirring at room temperature under nitrogen for 3 h, the reaction was quenched with 5 mL of toluene containing a small amount of methanol, and 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 finally isolated precipitant was dried under vacuum at 40 °C to a constant weight. A deep-brown powder was obtained (77%). M_w 211, 100; M_w/M_n 2.8 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3041, 2970, 2924, 1598, 1506, 821, 738, 692. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 1.22 [br, $N(CH_2CH_3)_2$], 3.38 (br, NCH_2), 5.85 (br, *cis* olefin proton), 6.47–7.88 (br, aromatic protons and *trans* olefin proton). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 12.7 (NCH_2CH_3), 44.7 (NCH_2), 111.0 [aromatic carbons *ortho* to $N(CH_2CH_3)_2$], 121.9 (aromatic carbons *meta* and attached to C≡C), 125.2 [aromatic carbons *meta* to $N(CH_2CH_3)_2$], 126.8, 127.9 [aromatic carbons of the poly(PA) segment], 132.0 (aromatic carbons *ortho* to C≡C and HC=), 139.5, 143.0 (=C–Ar), 143.5 [aromatic carbon *para* to $N(CH_2CH_3)_2$], 149.8 [aromatic carbon attached to $N(CH_2CH_3)_2$], 152.1 (aromatic carbon *para* to C=C).

2.5. Determination of component contents

We used IR spectroscopy to estimate the content of poly(EAAB) in the copolymers [17,35,36]. To establish a calibration curve, we prepared poly(PA)/poly(EAAB) mixtures with known quantities and ground them thoroughly with KBr in agate mortars to ensure intimate mixing. The out-of-plane bending δ_s (C–H) of monosubstituted aromatic rings in poly(PA) occurred at 692 cm^{-1}, while poly(EAAB) do not show any absorption in this wavelength. On the contrary, poly(EAAB) exhibited a ν_s (C_R–N) stretching at 1266 cm^{-1} owing to its aromatic tertiary amine functionality. No such band, however, was found in poly(PA). Thus, we can use the phenyl absorption at 692 cm^{-1} as internal standard and build a calibration curve by plotting the intensity ratios of the absorption bands at 1266 and 692 cm^{-1} (I_{1266}/I_{692}) against the poly(EAAB) content (cf. Fig. 2). The amount of azo unit in the copolymers can then be established by the following linear relationship:

$$\text{Poly(EAAB) content (mol\%)} = 33.9\frac{I_{1266}}{I_{692}} - 1.0 \qquad (1)$$

3. Results and discussion

3.1. Monomer synthesis

To prepare polyacetylenes with novel optical properties, we synthesized a phenylacetylene monomer containing an azobenzene pendant and established a multi-step reaction route for its synthesis (Scheme 2). We first coupled 4-bromoaniline with *N*,*N*-diethylaniline in the presence of $NaNO_2$ and HCl. The resultant product was then reacted with 2-methyl-3-butyn-2-ol using $Pd(PPh_3)_2Cl_2$ as catalyst. The 2-propyl-2-ol group in **2** was cleaved in dioxane KOH solution, giving the desirable monomer EAAB in a high yield.

3.2. Polymerization reactions

We first tried to polymerize EAAB by $[Rh(nbd)Cl]_2$, a well-known catalyst for the polymerizations of phenylacetylenes (PAs), with a small amount of Et_3N. Reaction conducted in THF, however, yielded a polymer that could hardly dissolve in any common organic solvents (Table 1, no. 1). Similar result was also found by Masuda [37], probably due to the stacking of the planar *p*-azobenzene groups. To improve the solubility of resultant polymers, we copolymerized EAAB with different amounts of PA in THF. As shown in Table 1, when the molar ratio of EAAB to PA was 1:1, the resultant copolymer was only partially soluble in THF and $CHCl_3$. Completely soluble polymers were, however, obtained when we increased the amount of PA by one fold. The reaction also worked well in other solvents, with reactions performed in toluene producing polymers with high molecular weights in high yields. Further increment of the concentration of PA lead to much better results: the highest yield and molecular weight could reach 85% and 210×10^3 Da, respectively.

3.3. Structural characterization

All the copolymers were well characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained (Section 2 for details). Fig. 1 shows the FTIR spectra of EAAB, poly(EAAB), poly(PA), and poly(EAAB-*co*-PA) (Table 1, no. 8). The monomer EAAB showed characteristic ≡C–H and C≡C stretching vibrations at 3275 and 2100 cm^{-1}, respectively, which disappeared in the spectrum of its copolymer. The characteristic out-of-plane bending vibrations δ_s (C–H) of ploy(PA) at 738 and 692 cm^{-1} were also found in poly(EAAB-*co*-PA), suggesting that PA is successfully incorporated into the copolymer. The intensity of the absorption band at 692 cm^{-1} became stronger in copolymers with high PA fraction, enabling us to manipulate their molecular structures by varying the monomer feed ratio. To confirm whether the resultant polymer is copolymer or mixtures of poly(EAAB) and poly(PA), we added the reaction solution dropwise into methanol through a filter during precipitation to remove the insoluble polymer (poly(EAAB)). Then redissolved the obtained precipitation in THF, a good solvent for poly(PA) but nonsolvent for poly(EAAB), and readded dropwise the solution into methanol to purify the resulting polymer through a filter. The redissolution/reprecipitation procedure

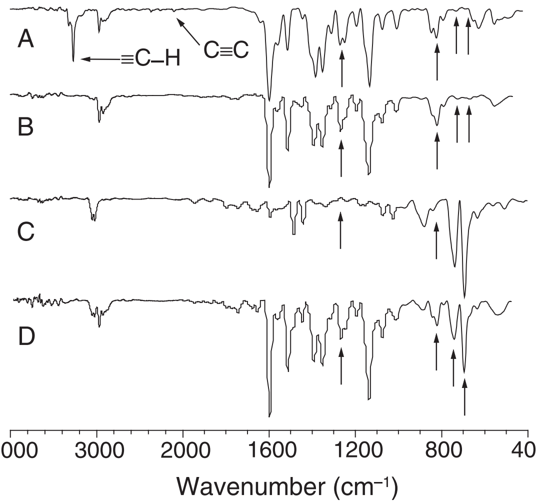


Fig. 1. IR spectra of (A) EAAB, (B) poly(EAAB), (C) poly(PA), and (D) poly(EAAB-*co*-PA) (sample from Table 1, no. 8).

Table 1
Copolymerization of EAAB with phenylacetylene (PA)

No.	[EAAB]:[PA]	Solvent	Yield (%)	M_w[a]	M_w/M_n[a]
1	1:0	THF	53[b]		
2	1:1	THF	28	7730	3.2
3	1:2	THF	58	76,100	7.1
4	1:2	Dioxane	61	92,500	3.0
5	1:2	Toluene	74	141,800	2.3
6	1:4	THF	61	63,300	6.8
7	1:4	Dioxane	64	89,600	3.0
8	1:4	Toluene	77	211,100	2.8
9	1:6	Toluene	80	118,800	2.7
10	1:8	Toluene	85	116,200	2.7
11	0:1	Toluene	90	118,200	1.4

Carried out under nitrogen for 3 h using $[Rh(nbd)Cl]_2$–Et_3N as catalyst; [EAAB] = 0.125 M, [Rh] = 3.75 mM, $[Et_3N]$ = 7.5 mM.

[a] Determined by GPC in THF on the basis of a polystyrene calibration.

[b] Not dissolved in THF.

of the above-purified polymer was repeated more than three times again and the obtained polymers displayed almost the same IR spectra as before. We also performed a same experiment on a mixture of poly(EAAB) and poly(PA). The similar dissolution–precipitation process of mixture of poly(EAAB) and poly(PA) was repeated three times and the obtained polymers displayed almost the same IR spectra as that of poly(PA), and no characteristic absorption band of aromatic tertiary amine functionality of poly(EAAB) at 1266 cm^{-1} in the spectrum of the obtained polymer because poly(EAAB) was insoluble during the dissolution-precipitation process. By these two comparative experiments, it can be concluded that poly(EAAB) and poly(PA) are joined together by covalent bond, not mixture.

Since poly(EAAB) and poly(PA) exhibited their characteristic absorption bands at 1266 and 692 cm^{-1}, respectively, we can thus determine the content of poly(EAAB) in the copolymers, using the absorption at 692 cm^{-1} as an internal reference. A calibration curve of I_{1266}/I_{692} ratio against the poly(EAAB) content was constructed (Fig. 2), utilizing data from the IR spectra of poly(PA)/poly(EAAB) mixtures of known quantities. The component content in the copolymers was determined and the results are shown in Table 2. It is noteworthy that when the molar feed ratio of EAAB to PA was 1:2, the nonlinear optical content in the resultant polymer was 41.7%, which is higher than the theoretical value of 33.3%. Other copolymers prepared by different monomer feed ratios also showed higher azo contents than the calculated values, possibly due to the higher reactivity of EAAB than PA.

Because the copolymers are soluble, we can characterize their structures by 'wet' spectroscopic methods. Fig. 3 shows the ^{1}H NMR spectra of EAAB, poly(PA), and poly(EAAB-*co*-PA)s in chloroform-*d*. The acetylene proton of EAAB absorbed at δ 3.17 ppm, which disappeared in the spectra of its copolymers. A new broad resonance peak corresponding to the *cis* olefin proton absorption at δ 5.8–6.0 ppm was emerged upon polymerization [38], suggesting that the acetylene triple bond of EAAB has been transformed to the olefin backbone carbons of poly(EAAB-*co*-PA)s. The *cis* content of the copolymers can

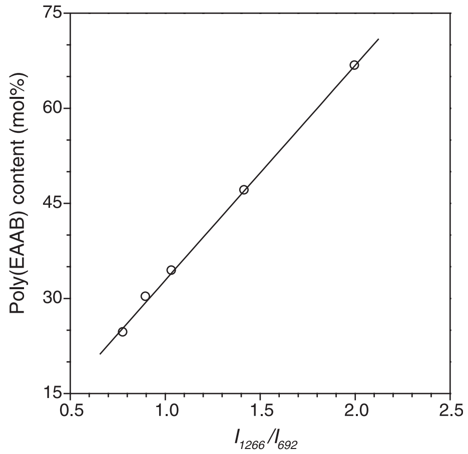


Fig. 2. Calibration curve for the determination of poly(EAAB) content in poly(EAAB-*co*-PA) using the intensity ratios of the absorption bands of poly(PA) at 692 cm^{-1} and poly(EAAB) at 1266 cm^{-1}.

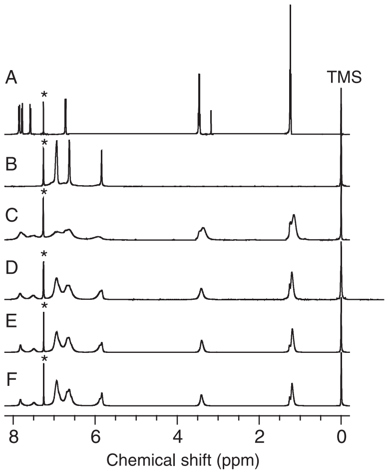


Fig. 3. ^{1}H NMR spectra of (A) EAAB, (B) poly(PA), and (C)–(F) poly(EAAB-*co*-PA)s of different compositions [samples from Table 1, nos. 3 (C), 8 (D), 9 (E), and 10 (F)].

Table 2
Poly(EAAB) and *cis* contents of the copolymers

No.	[EAAB]:[PA]	Solvent	Poly(EAAB) content (mol%)[a]	*cis* content (%)[b]	Solubility[c]
1	1:0	THF	100		×
2	1:1	THF	56.4		Δ
3	1:2	THF	41.7	90.1	○
4	1:2	Dioxane	40.1		○
5	1:2	Toluene	37.0		○
6	1:4	THF	22.7		○
7	1:4	Dioxane	22.2		○
8	1:4	Toluene	21.3	91.7	○
9	1:6	Toluene	16.7	93.1	○
10	1:8	Toluene	15.9	95.3	○
11	0:1	Toluene	0	98.7	○

[a] Estimated from IR spectra.
[b] Calculated from ^{1}H NMR spectra using Eq. (1).
[c] Tested in THF; ×, insoluble; Δ, partially soluble; ○, soluble.

be determined by the following equation [38]:

cis content (%)

$$= \frac{A_{5.84}}{A - \left(8\frac{1}{4}A_{3.14} + 5\frac{1-m}{m}\frac{1}{4}A_{3.14}\right)} \times 100\% \qquad (2)$$

where m is the poly(EAAB) segment content (mol%), $A = A_{5.84} + A_{6.63} + A_{6.94} + A_{7.49} + A_{7.82}$, $8(1/4)A_{3.47}$ corresponds to the eight azobenzene protons of the poly(EAAB) segment, and $5((1-m)/m)(1/4)A_{3.47}$ represents the five phenyl protons of the poly(PA) segment. Thus, the nominator corresponds to the peak area of one *cis* olefin proton and the denominator is associated with the peak area of one olefin proton (both *cis* and *trans* forms). As shown in Table 2, all the copolymers possessed high *cis* content or stereoregularity and increased with an increase in poly(PA) unit. No unexpected signals were observed and all the characteristic aromatic resonance peaks of EAAB and poly(PA) were also found in the spectra of the copolymers, further substantiating their structures, as shown in Scheme 1.

We also analyzed their structures by ^{13}C NMR spectroscopy. The spectrum of the copolymer displayed no carbon peaks of the ethynyl group of EAAB at δ 78.7 and 83.9 ppm, owing to their transformation to the olefin backbone carbons by the polymerization. The phenyl absorptions of poly(PA) at δ 126.9, 127.7, and 127.9 ppm were also found, suggesting that PA is successfully incorporated into the copolymer [39]. Two new peaks appear at δ 132.0 and 143.0 ppm, unambiguously due to the carbon resonances of the double bond polyacetylene main chain (Fig. 4).

The UV spectra of EAAB, poly(EAAB-*co*-PA), and poly(PA) are shown in Fig. 5. Poly(EAAB-*co*-PA) exhibited two strong absorption peaks at 245 and 435 nm. Compared the spectrum with those of EAAB and poly(PA), it became clear that the peaks at 245 and 435 nm are originated from the phenyl absorptions of the poly(PA) segment and the π–π^* transitions of the azobenzene chromophores of the poly(EAAB) segment, respectively. The backbone absorptions were found at wavelengths longer than 300 nm but were overwhelmed by the transitions of the azobenzene pendants.

3.4. Thermal properties

We examined the thermal stabilities of poly(PA) and poly(EAAB-*co*-PA)s by TGA analysis. As shown in Fig. 6, the decomposition temperature, defined as the temperature of 5% weight loss, of poly(PA) was ca. 293 °C while that of the copolymers (Table 1, no. 5 and nos. 8–10) was ≥300 °C. Thus, the copolymers exhibit much better thermal stability than poly(PA), which may results from a protective

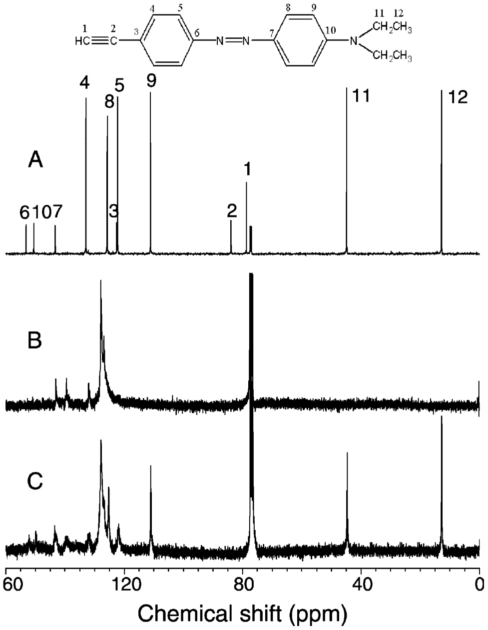


Fig. 4. ^{13}C NMR spectra of (A) EAAB, (B) poly(PA), and (C) poly(EAAB-*co*-PA) (sample from Table 1, no. 8) in chloroform-*d*.

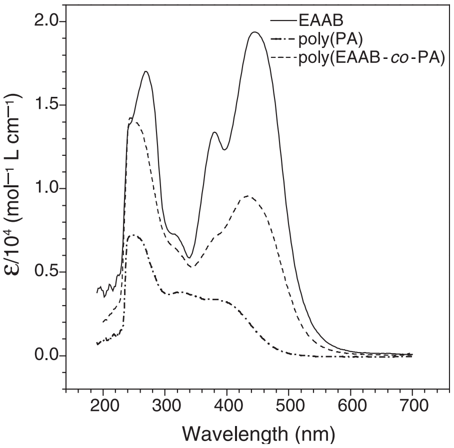


Fig. 5. UV spectra of THF solutions of EAAB, poly(PA), and poly(EAAB-*co*-PA) (sample from Table 1, no. 8).

'jacket' formed via the strong electronic interaction among the polarized azobenzene group, shielding the polyacetylene backbone from thermal attack [37,40].

3.5. Optical limiting property

Fig. 7 shows the optical limiting (OL) behaviors of poly(EAAB-*co*-PA). The transmitted fluence of the polymer solution with a concentration of 0.18 mg/mL increased linearly with the incident fluence but started to deviate at a value of 0.177 J/cm^2 (defined as limiting threshold; that is, the incident fluence at which the output fluence starts to deviate from linearity). With a further increment of the incident fluence, the transmitted fluence reached a plateau and was saturated at 0.299 J/cm^2 (defined as limiting amplitude; that is, the maximum output intensity). It is well known that the transmitted fluence of poly(PA) successively linearly increases with the incident influence and does not limit harsh laser pulses [16]. Thus, the incorporation of conjugated azobenzene pendants into the polyacetylene backbone has endowed the resultant polymer with novel OL properties. The limiting effect was affected by concentration, with solutions of high concentration exhibiting better performances. For example, the limiting threshold of the sample decreased from 0.177 to 0.123 J/cm^2, while the limiting amplitude changed from 0.299 to 0.148 J/cm^2 when the solution concentration was increased from 0.18 to 0.35 mg/mL. Similar results were also found by Kojima and our previous publications [16,17,41]. The solution with a high concentration has more molecules per unit volume, which should absorb the energy of the harsh laser more efficiently. That is why the threshold increased from 0.177 to 0.215 mJ/cm^2 when the solution concentration was lowered to 0.11 mg/mL.

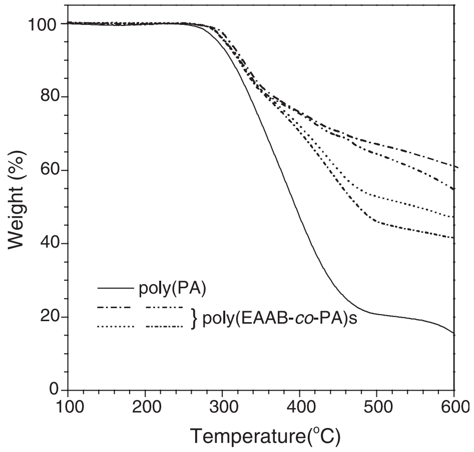


Fig. 6. TGA thermograms of poly(PA), and poly(EAAB-*co*-PA)s of different compositions [samples from Table 1, nos. 5 (dash dot), 8 (dash dot dot), 9 (short dash), and 10 (short dash dot)] measured under nitrogen at a heating rate of 20 °C/min.

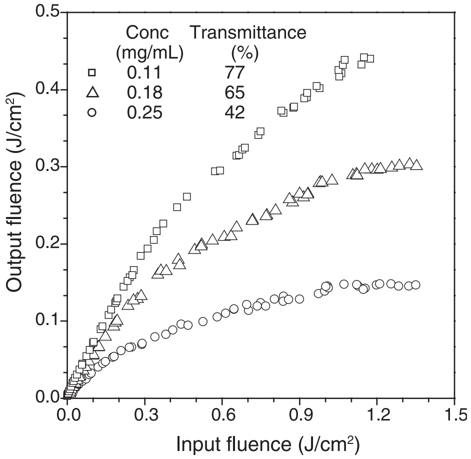


Fig. 7. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light of poly(EAAB-*co*-PA) (sample from Table 1, no. 3) solution with different concentrations.

3.6. Nonlinear optical property

The nonlinear optical property of poly(EAAB-*co*-PA) was measured using *Z*-scan technique. The *Z*-scan experimental results of poly(EAAB-*co*-PA) are shown in Fig. 8.

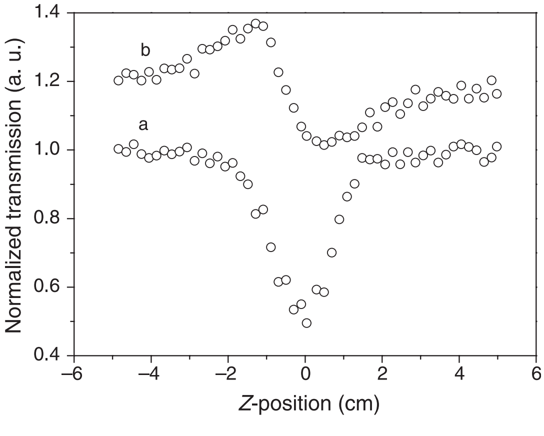


Fig. 8. (a) *Z*-scan data of open aperture. (b) *Z*-scan data of close aperture.

The results of *Z*-scan with and without an aperture indicated that poly(EAAB-*co*-PA) exhibited both nonlinear absorption and nonlinear refractive behavior. Thus, the $\chi^{(3)}$ of poly(EAAB-*co*-PA) was attributed to the nonlinear absorption and nonlinear refraction of molecules. The third-order nonlinear susceptibility of poly(EAAB-*co*-PA) was calculated to be 4.62×10^{-11} esu according to our experimental data and the calculation method of the third-order nonlinear susceptibility reported in references [34,42,43], which is almost two orders of magnitude larger than those of poly(phenylacetylene) [24–26], larger than that of poly(*N*-carbazolyacetylene) [29], poly(1-naphtylacetylene) [30], and the copolymer of 1-naphthylacetylene and 9-anthrylacetylene [30], respectively.

4. Conclusions

We have successfully synthesized a group of functional polyacetylene copolymers bearing azobenzene pendant groups using $[Rh(nbd)Cl]_2$–Et_3N as catalyst. The solubility and the amount of nonlinear optical unit in the resultant copolymers can be effectively controlled by varying the monomer feed ratio. The copolymers exhibited higher thermal stability than poly(PA), novel optical limiting and large third-order nonlinear susceptibility. Thus, this method provides a new strategy for the preparation of soluble polyacetylenes with novel optical limiting and nonlinear optical properties.

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