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# Synthesis and optical properties of azobenzene-containing poly(1-alkyne)s with different spacer lengths and ring substituents

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## Abstract

Poly(1-alkyne)s containing azobenzene pendants with different spacer lengths and ring substitutents –{HC=C[(CH$_2$)$_m$COO–C$_6$H$_4$–N=N–C$_6$H$_4$–NO$_2$]}$_n$– P**1**($m$) $m=3$, 8 and –{HC=C[(CH$_2$)$_m$COO–C$_6$H$_3$-*o*-Br–N=N–C$_6$H$_4$–NO$_2$]}$_n$– P**2**($m$) $m=3$, 8} are designed and synthesized. The polymers are prepared in satisfactory yields with high molecular weights ($M_w$ up to $3.3\times10^4$ Da) by [Rh(nbd)Cl]$_2$–Et$_3$N in THF or dioxane. Their structures and properties are characterized and evaluated by IR, UV, NMR, TGA, nonlinear optical and optical limiting analyses. All the polymers are completely soluble in common organic solvents and lose 5% of their weights at temperatures of ~270 °C. The spacer length and the pendant substitutent affect the nonlinear optical and optical limiting properties of the polymers, with **1**(3) showing superior properties than its counterparts **1**(8) and **2**(3) with long methylene spacers and bromide substitutents on the azobenzene pendants, respectively.

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

## 1. Introduction

Conjugated organic materials exhibiting strong nonlinear optical properties and fast response time have attracted considerable interest in recent years because of their usages in a variety of optical devices. In particular, their applicability for optical limiters has received significant attention owing to the growing needs for protection of human eyes and optical sensors from intense laser beams [1–5]. Polyacetylene, a prototypical conjugated polymer, shows large third-order electric susceptibilities $\chi^{(3)}$ and fast response time [6]. However, its intractability and instability have significantly limited its practical applications as a specialty material. Incorporation of functional pendants into the polyacetylene structure has dramatically improved its solubility and stability and has generated substituted polyacetylenes with enhanced optical properties. Sone found that the third-order nonlinear optical coefficient of *trans*-poly[*o*-trifluoromethyl(phenylacetylene)] film prepared by Mo catalyst is about two times larger than its *cis*-counterpart synthesized by Rh catalyst [7]. Masuda found that substituents on the *ortho*-positions of the phenyl rings of poly(phenylacetylene)s [7–9] and incorporation of bulky and planar aromatic rings such as carbazole, naphthalene, or anthracene into the polyacetylene main chains [10–12] can effectively improve the third-order nonlinear optical susceptibilities of the resulting polymers. Schuling once found that the third-order nonlinear optical susceptibility ($\gamma$) depends on $\gamma_e^0$, a term related to the movement of electron, and $\beta$, the second-order nonlinear optical susceptibility [13].

Azobenzene is a well-known second-order nonlinear optical active chromophore. Polyacetylenes containing such chromophore are expected to show novel optical properties.

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Thus, in this paper, we report our recent work on the attachment of azobenzene as pendants into the poly(1-alkyne) structures and present how the structural variation affects their nonlinear optical and optical limiting properties.

## 2. Experimental section

### 2.1. Materials

2,5-Norborndienerhodium(I) chloride dimer [Rh(nbd)Cl]$_2$ was purchased from Aldrich, kept under an inert-atmosphere in a glove box, and used as received without further purification. 5-Hexynoic acid and 10-undecynoic acid were purchased from Tokyo Kasei (TCI). 4-Nitroaniline, phenol, 2-bromophenol, 1,3-dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) were purchased from Shanghai Chemical Reagent Company. Dioxane, THF, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Triethylamine was distilled from potassium hydroxide prior to use. Methanol was used to precipitate the resulting polymer products.

### 2.2. Instruments

The IR spectra were recorded as KBr pellets on a Nicolet 170s× spectrometer. The $^1$H NMR spectra were recorded on an AVANCE/DMX-300 MHz Bruker NMR spectrometer using chloroform-*d* or DMSO-*d* as the solvent. Tetramethylsilane (TMS) or chloroform-*d* or DMSO-*d* was used as the internal reference for the NMR analyses. Elemental analyses were conducted using an Elemental Vario EL-III apparatus. Melting points (mp) were measured on a Yanaco micro melting point apparatus. UV spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm-square quartz cell; the molar absorptivities ($\varepsilon$) 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. The 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 polymer solutions were prepared in THF (ca. 2 mg/mL) and filtered through 0.45-μm PTFE syringe-type filters before 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 detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) was used for calibration purposes.

The optical limiting properties 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 experimental arrangement is similar to that in the literature [14]. 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 utilizing two energy detectors, $D_1$ and $D_2$ (Rjp-735 energy probes, Laser Precision).

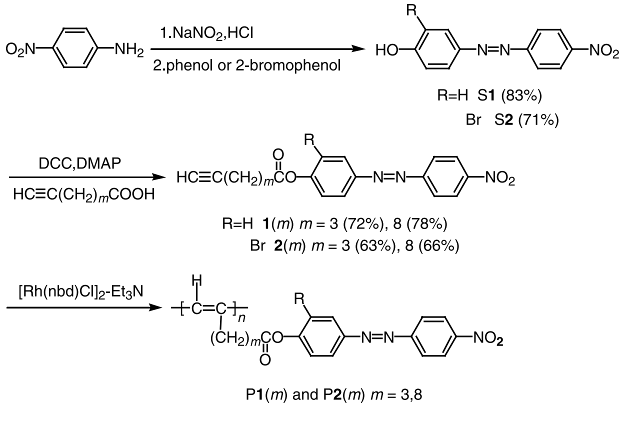
The nonlinear optical properties of the polymers were evaluated by a Z scan technique using the same laser system as in the optical limiting experiment. The experimental set-up can be found in the literature [15]. The input energy was 100 μJ. The sample solution was placed in a 2 mm quartz cell and moved along the axis of the incident beam (*z*-direction).

### 2.3. Synthesis of the monomers

The monomers were prepared according to the reactions shown in Scheme 1.The detailed experimental procedures are given below.

#### 2.3.1. 4′-Nitro-4-hydroxylazobenzene (S1)

2.76 g (20 mmol) 4-nitroaniline was dissolved in 8 mL concn. hydrochloric acid. After cooling to 0 °C, an ice-water solution of sodium nitrite (1.38 g, 20 mmol) was added dropwise to the resulting solution and stirred for 30 min. 1.97 g (21 mmol) phenol was dissolved in 15 mL aqueous NaOH (0.84 g, 21 mmol) solution. Then this solution was



Scheme 1.

added to 400 mL an aqueous buffer solution of $1\mathrm{NH_4Cl}$–$\mathrm{NH_3{\cdot}H_2O}$ (pH∼9). The so-formed diazonium chloride solution was added to the buffer solution and stirred for 2 h at 0∼5 °C. The mixture was adjusted to pH∼6 using aqueous HCl solution and the resulting precipitate was filtered, rinsed with water twice. The crude product was recrystallized from ethanol twice to give a red powder in 83% yield (4.03 g). IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3416 (OH), 1593 (Ar), 1508, 1335, 855 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, DMSO-$d_6$), $\delta$ (ppm): 8.37 (2H, d, H$^9$), 7.99 (2H, d, $J=8.7$ Hz, H$^8$), 7.94 (2H, d, H$^6$), 6.98 (2H, d, $J=8.5$ Hz, H$^5$), 5.34 (1H, s, OH) (for the numbering of the phenyl protons, Fig. 2).

### 2.3.2. 4′-Nitro-3-bromo-4-hydroxylazobenzene (S2)

This compound was prepared by coupling reaction of 4-nitroaniline with 2-bromophenol, using procedures as described above. Red power; yield 71%. IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3439 (OH), 1592 (Ar), 1520, 1343, 857 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, DMSO-$d_6$), $\delta$ (ppm): 8.37 (2H, d, H$^9$), 8.18 (1H, s, H$^7$), 7.99 (2H, d, $J=8.8$ Hz, H$^8$), 7.94 (1H, d, H$^6$), 7.17 (1H, d, $J=8.6$ Hz, H$^5$), 6.47 (1H, s, OH).

### 2.3.3. 5-{[(4′-Nitro-4-azobenzene)oxy]carbonyl}-1-pentyne *1*(3)

5-Hexynoic acid (1.23 g, 11 mmol), 4′-nitro-4-hydroxylazobenzene (2.43 g, 10 mmol), and DMAP (12 mg, 0.1 mmol) were dissolved in dry THF (200 mL) in a 500 mL flask under nitrogen. The solution was cooled to 0 °C with an ice-water bath, to which 2.2 g DCC (11 mmol) in 50 mL THF was added with stirring via a dropping funnel with a pressure-equalization arm. The reaction mixture was stirred at room temperature for 72 h. After filtering out the crystalline urea by-product, the solution was concentrated by a rotary evaporator. The crude product was purified by column chromatography ($\mathrm{Al_2O_3}$, ethyl acetate: Petroleum ether = 1:3 as eluent) and finally recrystallized from acetone–ethanol to yield 2.42 g (72%) of red crystals. IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3273 (≡C–H), 2933, 2848 ($\mathrm{CH_2}$), 2113 (C≡C), 1746 (C=O), 1595 (Ar), 1519, 1349, 860 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$), $\delta$ (ppm): 8.39 (2H, d, H$^9$), 8.02 (2H, d, $J=8.9$ Hz, H$^6$), 8.01 (2H, d, H$^8$), 7.30 (2H, d, $J=8.2$ Hz, H$^5$), 2.78 (2H, t, $J=7.3$ Hz, $\equiv\mathrm{CCH_2CH_2C}H_2$), 2.39 (2H, t, $\equiv\mathrm{CC}H_2\mathrm{CH_2}$), 2.01 (2H, td, $J=7.1$ Hz, $\equiv\mathrm{CCH_2C}H_2$), 1.96 (1H, s, HC≡). $T_\mathrm{m}=100$–101 °C. Elem. Anal. Calcd for $\mathrm{C_{18}H_{15}N_3O_4}$: C 64.09; H 4.45; N 12.46. Found: C 64.15; H 4.48; N 12.38.

### 2.3.4. 10-{[(4′-Nitro-4-azobenzene)oxy]carbonyl}-1-decyne *1*(8)

Monomer **1**(8) was prepared in a similar fashion. Yellow solid; yield 78%. IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3276 (≡C–H), 2930, 2856 ($\mathrm{CH_2}$), 2115 (C≡C), 1760 (C=O), 1585 (Ar), 1522, 1352, 858 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$), $\delta$ (ppm): 8.39 (2H, d, H$^9$), 8.03 (2H, d, H$^6$), 8.01 (2H, d, $J=8.9$ Hz, H$^8$), 7.29 (2H, d, $J=8.3$ Hz, H$^5$), 2.61 [2H, t, $J=7.4$ Hz, $\equiv\mathrm{CCH_2CH_2(CH_2)_4CH_2C}H_2$], 2.20 (2H, td, $\equiv\mathrm{CC}H_2\mathrm{CH_2}$), 1.95 (1H, s, HC≡), 1.78 [2H, tt, $\equiv\mathrm{CCH_2CH_2(CH_2)_4C}H_2$], 1.54 (2H, tt, $J=7.5$ Hz, $\equiv\mathrm{CCH_2C}H_2$), 1.38 [8H, tt, $\equiv\mathrm{CCH_2CH_2(C}H_2)_4$]. $T_\mathrm{m}=94$–95 °C. Elem. Anal. Calcd for $\mathrm{C_{23}H_{25}N_3O_4}$: C 67.81; H 6.14; N 10.32. Found: C 67.75; H 6.11; N 10.36.

### 2.3.5. 5-{[(4′-Nitro-3-bromo-4-azobenzene)oxy]carbonyl}-1-pentyne *2*(3)

It was prepared by reaction of 4′-nitro-3-bromo-4-hydroxylazobenzene with 5-hexynoic acid, using the procedures for the synthesis of **1**(3). Red crystals; yield 63%. IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3300 (≡C–H), 2933, 2857 ($\mathrm{CH_2}$), 2120 (C≡C), 1756 (C=O), 1586 (Ar), 1518, 1350, 858 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$), $\delta$ (ppm): 8.38 (2H, d, H$^9$), 8.22 (1H, s, H$^7$), 8.02 (2H, d, $J=8.9$ Hz, H$^8$), 7.99 (1H, d, H$^6$), 7.34 (2H, d, $J=8.6$ Hz, H$^5$), 2.84 (2H, t, $J=7.4$ Hz, $\equiv\mathrm{CCH_2CH_2C}H_2$), 2.41 (2H, td, $\equiv\mathrm{CC}H_2\mathrm{CH_2}$), 2.05 (1H, s, HC≡), 2.04 (2H, t, $J=7.1$ Hz, $\equiv\mathrm{CCH_2C}H_2$). $T_\mathrm{m}=104$–105 °C. Elem. Anal. Calcd for $\mathrm{C_{18}H_{14}BrN_3O_4}$: C 51.92; H 3.37; N 10.10. Found: C 51.91; H 3.32; N 10.23.

### 2.3.6. 10-{[(4′-Nitro-3-bromo-4-azobenzene)oxy]carbonyl}-1-decyne *2*(8)

It was prepared by esterification of 4′-nitro-3-bromo-4-hydroxylazobenzene with 10-undecynoic acid, again using DCC as dehydrating agent. Yellow solid; yield 66%. IR (KBr), $\nu$ ($\mathrm{cm^{-1}}$): 3303 (≡C–H), 2931, 2853 ($\mathrm{CH_2}$), 2116 (C≡C), 1757 (C=O), 1596 (Ar), 1530, 1346, 859 ($\mathrm{NO_2}$). $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$), $\delta$ (ppm): 8.39 (2H, d, H$^9$), 8.24 (1H, d, H$^7$), 8.04 (2H, d, $J=8.8$ Hz, H$^8$), 7.99 (1H, d, H$^6$), 7.34 (1H, d, $J=8.5$ Hz, H$^5$), 2.67 [2H, t, $J=7.5$ Hz, $\equiv\mathrm{CCH_2CH_2(CH_2)_4CH_2C}H_2$], 2.20 (2H, td, $\equiv\mathrm{CC}H_2\mathrm{CH_2}$), 1.95 (1H, s, HC≡), 1.82 [2H, tt, $\equiv\mathrm{CCH_2CH_2(CH_2)_4C}H_2$], 1.53 (2H, tt, $J=7.5$ Hz, $\equiv\mathrm{CCH_2C}H_2$), 1.34 [8H, tt, $\equiv\mathrm{CCH_2CH_2(C}H_2)_4$]. $T_\mathrm{m}=98$–99 °C. Elem. Anal. Calcd for $\mathrm{C_{23}H_{24}BrN_3O_4}$: C 56.79; H 4.94; N 8.64. Found: C 56.84; H 4.98; N 8.59.

### 2.4. Polymerization

All the polymerization reactions and manipulations were performed under pre-purified nitrogen using Schlenk techniques either in vacuum-line system or in an inert-atmosphere glove box, except for the purification of the polymers, which were done in open air. Typical procedures for the polymerization are given below: 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-milliliter 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) $\mathrm{[Rh(nbd)Cl]_2}$ and 2.02 mg (0.02 mmol) $\mathrm{Et_3N}$ in 2 mL 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 dioxane and added dropwise to 200 mL methanol under stirring. The precipitate was centrifuged and redissolved in THF. The THF solution was added dropwise into 200 mL methanol to precipitate the polymer. The dissolution–precipitation process was repeated three times, and the final precipitate was dried under vacuum at 40 °C to a constant weight.

### *2.4.1. Poly(5-{[(4′-nitro-4-azobenzene)oxy]carbonyl}-1-pentyne) P**1**(3)*

Red–brown powder; yield 68.9%. $M_w$ 31,200; $M_w/M_n$: 2.5 (GPC, polystyrene calibration; Table 1, No. 3). IR (KBr), $\nu$ (cm$^{-1}$): 3102 (=C–H), 2930 ($CH_2$), 1761 (C=O), 1600 (Ar), 1522, 1348, 863 ($NO_2$). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.35, 7.96, 7.30 (br., Ar–H and *trans* =C–H), 2.74 (2H, br., $=CCH_2CH_2CH_2$), 2.39 (2H, br., $=CCH_2CH_2$), 2.01 (2H, br., $=CCH_2CH_2$).

### *2.4.2. Poly(10-{[(4′-nitro-4-azobenzene)oxy]carbonyl}-1-decyne) P**1**(8)*

Red–brown powder; yield 63.5%. $M_w$ 16,900; $M_w/M_n$: 2.4 (GPC, polystyrene calibration; Table 1, No. 6). IR (KBr), $\nu$ (cm$^{-1}$): 2930, 2856 ($CH_2$), 1760 (C=O), 1585 (Ar), 1520, 1344, 852 ($NO_2$). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.39, 8.01, 7.29 (br., Ar–H and *trans* =C–H), 2.60 [2H, br., $=CCH_2CH_2(CH_2)_4CH_2CH_2$], 2.27 (2H, br., $=CCH_2CH_2$), 1.76 [2H, br., $=CCH_2CH_2(CH_2)_4CH_2$], 1.58 (2H, br., $=CCH_2CH_2$), 1.38 [8H, br., $=CCH_2CH_2(CH_2)_4$].

### *2.4.3. Poly(5-{[(4′-nitro-3-bromo-4-azobenzene)oxy]carbonyl}-1-pentyne) P**2**(3)*

Red–brown powder; yield 59.7%. $M_w$ 26,200; $M_w/M_n$: 2.1 (GPC, polystyrene calibration; Table 1, No. 9). IR (KBr), $\nu$ (cm$^{-1}$): 3102 (=C–H), 2930 ($CH_2$), 1761 (C=O), 1600 (Ar), 1523, 1345, 852 ($NO_2$). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.34, 8.17, 7.96, 7.64, 7.30 (br., Ar–H and *trans* =C–H), 6.11 (br. *cis* =C–H), 2.75 (2H, br., $=CCH_2CH_2CH_2$), 2.50 (2H, br., $=CCH_2CH_2$), 2.04 (2H, br., $=CCH_2CH_2$).

### *2.4.4. Poly(10-{[(4′-nitro-3-bromo-4-azobenzene)oxy]carbonyl}-1-decyne) P**2**(8)*

Red–brown powder; yield 55.4%. $M_w$ 18,700; $M_w/M_n$: 2.6 (GPC, polystyrene calibration; Table 1, No. 12). IR (KBr), $\nu$ (cm$^{-1}$): 2931, 2853 ($CH_2$), 1757 (C=O), 1596 (Ar), 1528, 1345, 863 ($NO_2$). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (ppm): 8.37, 8.22, 7.91, 7.29 (br., Ar–H and *trans* =C–H), 2.66 [2H, br., $=CCH_2CH_2(CH_2)_4CH_2CH_2$], 2.21 (2H, br., $=CCH_2CH_2$), 1.88 [2H, br., $=CCH_2CH_2(CH_2)_4CH_2$], 1.55 (2H, br., $=CCH_2CH_2$), 1.38 [8H, br., $=CCH_2CH_2(CH_2)_4$].

## 3. Results and discussion

### *3.1. Monomer synthesis*

We designed the molecular structures of four 1-alkyne derivatives containing azobenzene pendants and elaborated a two-step reaction route for their synthesis (Scheme 1). Diazotization of 4-nitroaniline with phenol or 2-bromophenol gives azobenzene derivatives S**1** or S**2**. Respective esterification of S**1** and S**2** with alkynoic acids in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) produces the pure monomers in 63–78% yields after purification by column and recrystallization. We characterized all the intermediates and monomers by standard spectroscopic methods and obtained satisfactory analysis data corresponding to their molecular structures.

### *3.2. Polymerization reactions*

We first attempted to polymerize **1**(*m*) and **2**(*m*) by classic metathesis catalysts of $WCl_6$ and $MoCl_5$ but no polymeric products are obtained. The catalysts may be toxic by the polar azo groups in the monomers, leading to failure in the polymerization. Since organorhodium complexes are found to be tolerant of polar functional groups in the

Table 1
Polymerization of **1**(*m*) and **2**(*m*)

| No. | Monomer | Temp. (°C) | Yield (%) | $M_w$[a] | $M_w/M_w$[a] |
|---|---|---|---|---|---|
| 1 | **1**(3) | 30 | 48.7 | 18,100 | 2.5 |
| 2 | **1**(3) | 30 | 56.4 | 24,600 | 2.3 |
| 3 | **1**(3) | 60 | 68.9 | 31,200 | 2.5 |
| 4 | **1**(3) | 90 | 64.5 | 27,800 | 2.6 |
| 5 | **1**(8) | 30 | 7.8 | 8600 | 1.3 |
| 6 | **1**(8) | 60 | 63.5 | 16,900 | 2.4 |
| 7 | **1**(8) | 90 | 61.2 | 15,800 | 2.5 |
| 8 | **2**(3) | 30 | 50.4 | 33,100 | 2.8 |
| 9 | **2**(3) | 60 | 59.7 | 26,200 | 2.1 |
| 10 | **2**(3) | 90 | 54.9 | 27,400 | 2.6 |
| 11 | **2**(8) | 30 | 5.7 | 7200 | 1.3 |
| 12 | **2**(8) | 60 | 55.4 | 18,700 | 2.6 |
| 13 | **2**(8) | 90 | 47.8 | 15,900 | 2.3 |

Polymerization catalyzed by $[Rh(nbd)Cl]_2$–$Et_3N$ in THF (No. 1) or dioxane (No. 2–13) for 24 h.

[a] Estimated by GPC on the basis of a polystyrene calibration.

acetylenes, we thus tried to polymerize the monomers using $[Rh(nbd)Cl]_2$–$Et_3N$ as catalyst [16]. Polymerization of **1**(3) in THF at 30 °C gives a polymer with an $M_w$ of $1.8\times10^4$ Da in a moderate yield (Table 1, No. 1). Changing the solvent to dioxane increases the yield and molecular weight, which become even higher when the polymerization is conducted at elevated temperatures. Unlike **1**(3), the reaction of **1**(8) at 30 °C only produces a trace amount of polymeric product. Increasing the polymerization temperature, however, has dramatically activated the catalyst and completely soluble polymers are obtained in over 60% yield.

The polymerization behaviors of **2**(3) are similar to those of **1**(3) and the reaction conducted in dioxane gives high molecular weight polymers in satisfactory yields, irrespective of the polymerization temperature. Similar to **1**(8), the polymerization of **2**(8) carried out at 30 °C produces only a polymer in a low yield. The yield and molecular weight, however, are boosted more than 7- and 2-folds, respectively, when the polymerization is performed at high temperatures.

### *3.3. Structural characterization*

All the purified polymers give satisfactory spectroscopic data corresponding to their expected molecular structures (Section 2 for details). An example of the IR spectra of monomer **1**(3) and its polymer P**1**(3) are given in Fig. 1. Monomer **1**(3) exhibits characteristic ≡C–H and C≡C stretching vibrations at 3277 and 2127 $cm^{-1}$, respectively, which completely disappear in the spectrum of its polymer P**1**(3), suggesting that the triple bond of the **1**(3) has been converted to double bond polyacetylene backbone of P**1**(3).

The $^1H$ NMR spectra of P**1**($m$) and P**2**($m$) are shown in Fig. 2. The spectrum of P**2**(3) shows no acetylene proton of **2**(3) at $\delta$ 2.05 ppm. On the other hand, a new broad resonance peak corresponding to the *cis*-olefin proton absorption is observed at $\delta$ 6.11 ppm. The absorption of the propargyl proton at $\delta$ 2.41 ppm also becomes broadened upon polymerization owing to its transformation to the allylic structure by the acetylene polymerization [17]. The *cis*-content of P**2**(3) is calculated to be 14.8% based on the method reported by Simionescu and Tang [18,19], Other polymers also give satisfactory analysis data corresponding to their molecular structures. No absorptions are found in the olefin absorption region of $\delta$ 5.8–6.0 ppm, suggesting that these polymers possess predominantly *trans*-configurations.

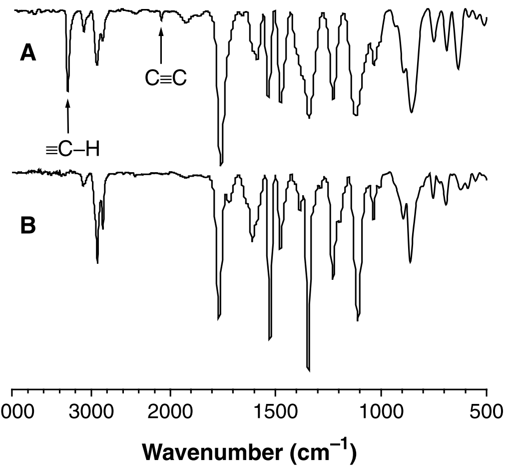


Fig. 1. IR spectra of (A) **1**(3) and (B) its polymer P**1**(3).

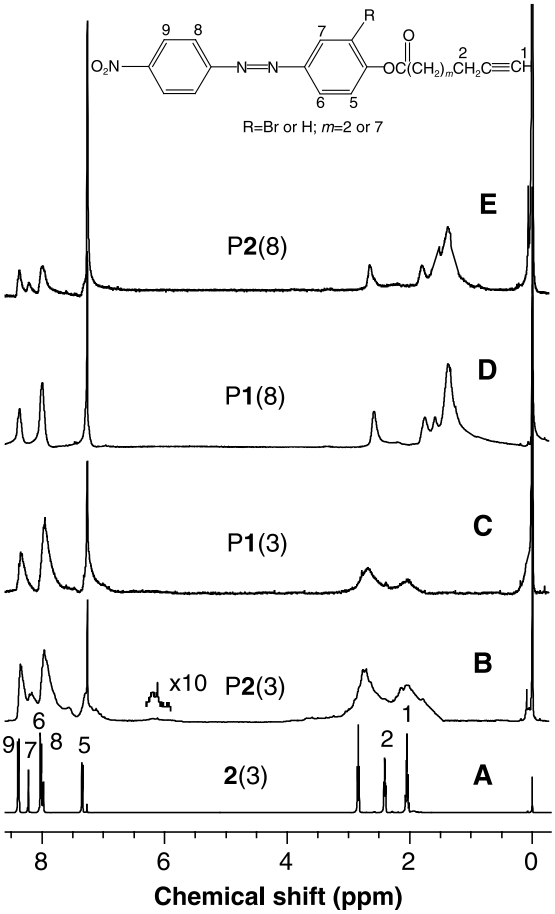


Fig. 2. $^1H$ NMR spectra of (A) monomer **2**(3) and polymers (B) P**2**(3), (C) P**1**(3), (D) P**1**(8), and (E) P**2**(8) in chloroform-$d$ (samples taken from Table 1, No. 3, 6, 9, and 12).

The UV spectra of the polymers in chloroform are shown in Fig. 3. P**1**(3) exhibits two absorption peaks at 240 and 340 nm associated with corresponding the π–π* transitions of the phenyl and azobenzene chromophores, respectively. The backbone absorption is found at wavelengths longer than 400 nm and well extends to 600 nm with low intensities. The steric effect of the bulky azobenzene pendants may force the double bonds of the polyacetylene main chains out of planarity, leading to low absorptivity. The ground state electronic transitions of the polymers are not affected by the spacer length and the substitutent on the azobenzene ring: The UV profiles of P**1**(8), P**2**(3), and P**2**(8) are practically the same to that of P**1**(3).

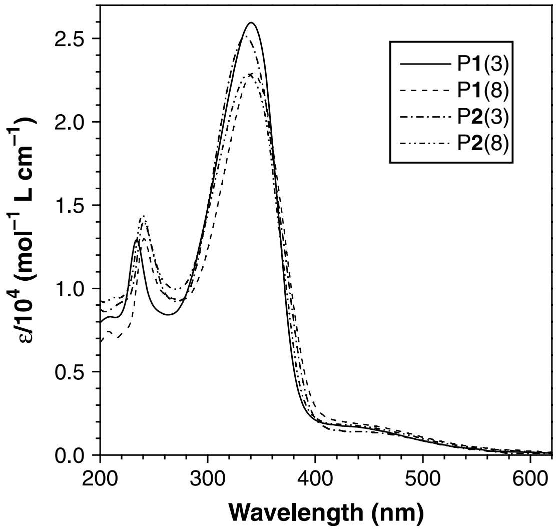


Fig. 3. UV spectra of chloroform solutions of **P1**(3), **P1**(8), **P2**(3), and **P2**(8) (samples taken from Table 1, No. 3, 6, 9, and 12).

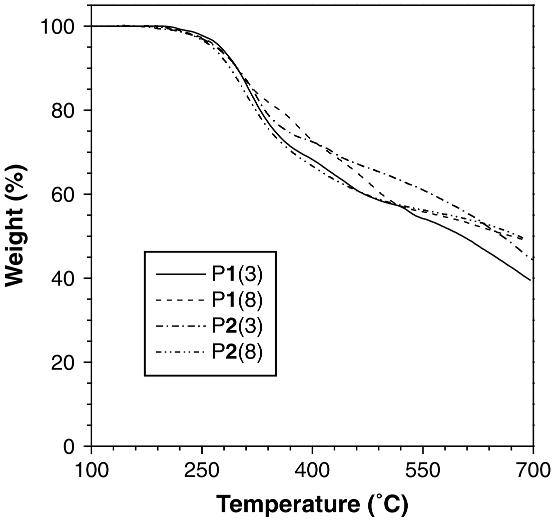


Fig. 4. TGA thermograms of **P1**(3), **P1**(8), **P2**(3), and **P2**(8) (samples taken from Table 1, No. 3, 6, 9, and 12) recorded under nitrogen at a heating rate of 20 °C/min.

### 3.4. Thermal properties

The poly(1-alkynes) such as poly(1-butyne) and poly(1-hexyne), which may be regarded as the parent forms of **P1**(*m*) and **P2**(*m*), are so unstable that even the isolation process of the polymer products from the polymerization reactions leads to degradation [20,21]. Thus, the initially precipitated poly(1-alkyne) products in methanol are white and fibrous; they change to yellow powders after drying under vacuum. Poly(1-hexyne) starts to lose its weight at 150 °C, and heating for a few minutes at the temperature easily changes the yellow powder to a brown gummy fluid [21]. On the other hand, except for the polymerization reactions, which were carried out under an atmosphere of dry nitrogen, all the handlings, including the isolation, purification, and storage of **P1**(*m*) and **P2**(*m*), were done in an open atmosphere, during which no any changes in the color and form of the polymer products were observed. As shown in Fig. 4, all the polymers decompose at a temperature as high as 270 °C, irrespective of the spacer length and substitutent on the azobenzene ring. Thus, the incorporation of the rigid azobenzene group into poly(1-alkynes) had endowed the polymers with high thermal stability. The thermal stability enhancement of **P1**(*m*) and **P2**(*m*) may be due to the 'jacket effect' of the aromatic azobenzene pendants. That is, the alternating-double-bond backbone of the polymers is surrounded by a rigid 'jacket' formed through the strong intra- and interchain molecular electronic interaction of the polarized aromatic azobenzene groups, shielding the polymer main chains from the thermal attack. Similar results are also found by Masuda, Tang and our previous work [16,17,22–25], respectively.

### 3.5. Optical limiting property

Fig. 5 shows the optical limiting performances of **P1**(8) in THF with different concentrations. The transmitted fluence of all the solutions increases linearly with the incident fluence at low fluence region but starts to depart and reaches a plateau at high incident fluence. In our optical limiting experiment, we investigated the photostability of **P1**(8) by three repeated experiments, finding that the optical limiting properties of **P1**(8) are rather stability. Simultaneously, we also checked the FT-IR and UV–vis spectrum of **P1**(8) before and after the laser irradiation in our optical limiting experiment and found that the FT-IR and UV–vis absorption spectra of FTIR and UV–vis absorption spectra did not change, hinting that the **P1**(8) possesses good photostability. In contrast, the transmittance of the poly(PA) solution continually increase instead of decrease due to the laser-induced photolysis of the polyacetylene chains [26],

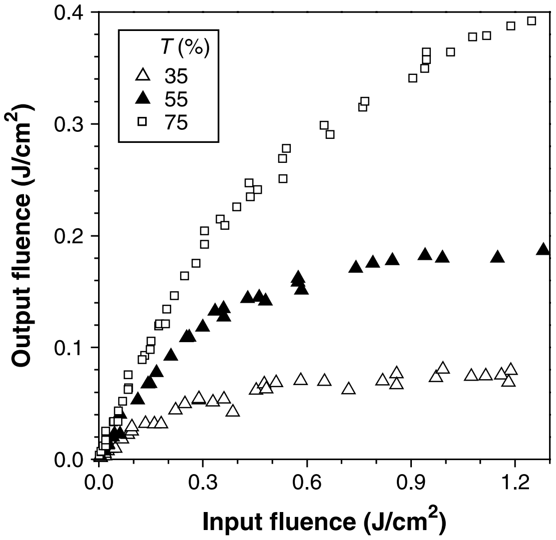


Fig. 5. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light of THF solutions of **P2**(3) (sample taken from Table 1, No. 6) with different linear transmittances.

indicating that the incorporation of azobenzene makes polyacetylene to be endowed with a new optical property—optical limiting property and good photostability. Furthermore, the light limitation is affected by the concentration and becomes better in solutions with high concentrations. For example, the limiting threshold (incident fluence at which the output fluence starts to deviate from linearity) and limiting amplitude (the maximum output intensity) of the sample vary from 0.166 to 0.095 and 0.180–0.070 J/cm$^2$, respectively, when the solution concentration increases from 0.46 ($T=55\%$) to 0.83 mg/mL ($T=35\%$). Similar results are also found by Kojima and our previous publications [26–31]. Solutions with higher concentrations have more molecules per unit volume, which should be able to absorb the energy of harsh laser light more efficiently. On the contrary, the optical limiting performances of the polymers become poorer when the solution is diluted. For example, the limiting threshold of the sample changes from 0.166 to 0.245 J/cm$^2$ when the solution concentration decreases from 0.46 ($T=55\%$) to 0.21 mg/mL ($T=75\%$).

Fig. 6 shows the optical limiting properties of the polymers at the same linear transmittance ($T=75\%$) and the results are summarized in Table 2. All the polymers are good optical limiters, especially for those with short spacer lengths. For example, the limiting threshold and limiting amplitude of P**1**(3) are 0.245 and 0.349 J/cm$^2$, respectively, which are 1.3 and 1.2 times lower than those of P**1**(8). The optical limiting properties are also influenced by the ring substitutent and become poorer in polymers with bromine functionalities on the azobenzene pendants, as suggested by the higher limiting threshold (0.295 J/cm$^2$) and limiting amplitude (0.393 J/cm$^2$) of P**2**(3) than P**1**(3).

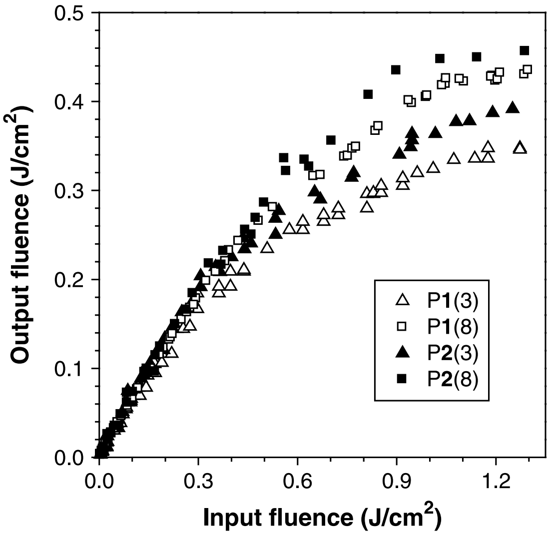


Fig. 6. Optical responses to 8 ns, 1 Hz pulses of 532 nm laser light of THF solutions of P**1**(3), P**1**(8), P**2**(3), and P**2**(8) (samples taken from Table 1, No. 3, 6, 9, and 12) with a linear transmission of 75%.

### 3.6. Nonlinear optical property

The nonlinear absorption coefficients of the polymers are measured by Z scan technique. The results of Z scan with and without an aperture show that all the polymers have both nonlinear absorption and refraction. Thus, the $\chi^{(3)}$ of the polymers should be dual attributed to nonlinear absorption ($\alpha_2$) of and refractive ($n_2$) of the molecules. The Z scan results of P**2**(3) are shown exemplarily in Fig. 7.

In theory, the normalized transmittance for the open aperture can be written as [15,32]

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

where $q_0(z) = \alpha_2 I_0(t) L_{\text{eff}}/(1+z^2/z_0^2)$ with $\alpha_2$, nonlinear absorption coefficient; $I_0(t)$, intensity of laser beam at focus ($z=0$); $L_{\text{eff}} = [1-\exp(-\alpha_0 L)]/\alpha_0 =$ effective thickness with $\alpha_0$, linear absorption coefficient; $L$, sample thickness; $z_0$, diffraction length of the beam, and $z$, sample position. Thus, the nonlinear absorption coefficients of the polymers can be determined by fitting the experimental data using Eq. (1).

The nonlinear refractive index $n_2$ is given by [15,32]

$$n_2 = \frac{\lambda \alpha_0}{2\pi I_0 \left(1-\mathrm{e}^{-\alpha_0 L}\right)} \frac{\Delta T_{\text{p-v}}}{0.416(1-S)^{0.25}} \qquad (2)$$

where $\Delta T_{\text{p-v}}$ is the difference between the normalized transmittance values at the valley and peak portions and $S$ is the aperture size ($S=0.12$). Thus, the nonlinear refractive coefficients of the polymers can be determined by using Eq. (2).

The $\chi^{(3)}$ can be calculated by the following equation [15, 30]

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

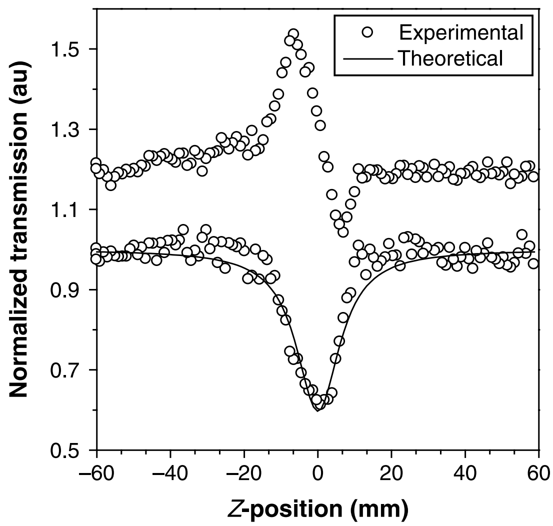


Fig. 7. Z scan data of P**2**(3) (sample taken from Table 1, No. 6) in THF.

Table 2
Properties of the polymers

| Polymer | Thermal stability[a] $T_d$ (°C) | Limiting threshold[b] (J/cm$^2$) | Limiting amplitude[c] (J/cm$^2$) | Nonlinear optical values[d] $\alpha_2$ (m/W) | $n_2$ (m$^2$/W) | $\chi^{(3)}$ (esu) |
|---|---|---|---|---|---|---|
| **P1**(3) | 275 | 0.245 | 0.349 | $5.36\times10^{-10}$ | $5.68\times10^{-17}$ | $1.43\times10^{-10}$ |
| **P1**(8) | 263 | 0.322 | 0.429 | $4.70\times10^{-10}$ | $4.54\times10^{-17}$ | $1.15\times10^{-10}$ |
| **P2**(3) | 268 | 0.295 | 0.393 | $4.69\times10^{-10}$ | $5.09\times10^{-17}$ | $1.22\times10^{-10}$ |
| **P2**(8) | 271 | 0.344 | 0.450 | $4.12\times10^{-10}$ | $3.07\times10^{-17}$ | $7.78\times10^{-11}$ |

[a] Temperature for 5% weight loss.
[b] Incident fluence at which the output fluence starts to deviate from linearity.
[c] Maximum output intensity.
[d] Measured by Z scan technique with an 8 ns Nd:YAG laser system at 1 Hz repetition rate and 532 nm wavelength.

where $\varepsilon_0$, permittivity of vacuum; $c$, speed of light; $n_0$, refractive index of the medium, and $\omega=2\pi c/\lambda$. The calculation results of the nonlinear optical coefficients of the four polymers are shown in Table 2. From Table 2, we can see that the nonlinear susceptibilities of all the polymers are as high as $\sim10^{-10}$ esu, which are almost three orders of magnitude larger than those of poly(phenylacetylene) [8,9,33,34], and larger than poly(*N*-carbazolyacetylene) [10], poly(1-naphtylacetylene) [11], and the copolymer of 1-naphthylacetylene and 9-anthrylacetylene [11], respectively. Thus, the attachment of azobenzene moieties into the polyacetylene main chain has enhanced the nonlinear optical properties of polyacetylenes significantly. Simultaneously, we also found from Table 2 that the nonlinear susceptibility of polymers are lower with increasing spacer lengths or bromine substitutent on the azobenzene rings. This result is similar to the results obtained from optical limiting analysis.

## 4. Conclusions

Functional polyacetylenes containing azobenzene pendants are synthesized in satisfactory yields by [Rh(nbd)Cl]–Et$_3$N catalyst. All the polymers are soluble in common organic solvents such as CHCl$_3$ and THF and possess high thermal stability. Their optical limiting and nonlinear optical properties are investigated by an 8 ns Nd:YAG laser system at 532 nm wavelength. Results show that the optical limiting and nonlinear optical performances are affected by the spacer length and ring substitutent, with polymers having longer spacer lengths and bromine functionality on the azobenzene ring show inferior properties.

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