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Soluble functional polyacetylenes for optical limiting: Relationship between optical limiting properties and molecular structure

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ABSTRACT

Four polyacetylenes containing chromophores with different conjugation bridge structure or terminal substituents were designed and prepared by using $[Rh(nbd)Cl]_2$ as catalysts, respectively. Their structures and properties were characterized and evaluated by IR, NMR, UV, TGA, optical limiting and nonlinear optical analyses. All the polymers show high thermal and photo stability and novel optical limiting properties. The functional polyacetylene with stilbene pendant shows better optical limiting property than that with azobenzene chromophore pendant. Their optical limiting mechanisms are mainly originated from reverse saturable absorption of molecules. Their nonlinear optical properties are significantly affected by their molecular structures and the shorter spacer group will be beneficial in increasing the electronic interaction between chromophore pendant and polyacetylene conjugation backbone to result in higher third-order optical nonlinearity.

1. Introduction

With the rapid development of new laser technology, the optical limiting materials for protection of optically sensitive devices and human eyes from laser damage in both civilian and military applications in recent years have received significant attention [1–7]. Among the materials, the π-conjugated NLO polymers are considered to be promising materials, mainly because they offer many advantages such as ultrafast time response, high damage threshold, easy molecular design, and good processability to form optical devices. Polyacetylene (PA), the structurally simplest conjugated polymer with alternating single and double bonds, exhibits good third-order electric susceptibilities ($\chi^{(3)}$) and fast response time (the order of several picoseconds) [8–10]. However, the insolubility and instability of this polymer have limited its practical applications as a functional material. Much attention has been redirected to the polyacetylene derivatives substituted by functional group. These functional group substituted polyacetylenes display liquid crystallinity [11–14], photo- and electro-luminescence [15–19], optical activity (chirality) [20,21], photoconductivity [22], gas permeability [23,24], and optical nonlinearity [25–30]. Recently, we have successfully prepared a group of functional polyacetylenes with large third-order nonlinear optical susceptibilities and novel optical limiting properties by copolymerizing phenylacetylene with 4-ethynyl-4′-(*N*,*N*-diethylamino)azobenzene [4]. However, these copolymerized phenylacetylenes possess poorer film-forming properties and limited chromophoric content. To increase chromophoric content and processability, our group has also prepared a series of azobenzene-containing functional poly(1-alkyne)s with different spacer lengths and terminal alkyloxy chains, and found that the azobenzene pendant endowed polyacetylene with novel optical limiting properties and high thermal stability. Simultaneously, flexible spacer between polyacetylene main chain and azobenzene pendant, and the terminal flexible group on azobenzene pendant still impart polyacetylene good solubility and film-forming properties [5,31–33]. To enhance the application of the π-conjugated NLO polymer materials on optical limiters, it is necessary to further understand the relationship between the optical limiting property and the molecular structures of the materials. In this paper, we designed and synthesized four soluble functional polyacetylenes containing chromophore with different conjugation bridge structure or different substituents (Chart 1), and carefully investigated the effects of molecular structures on optical limiting properties of the resultant polymers and their optical limiting mechanisms.

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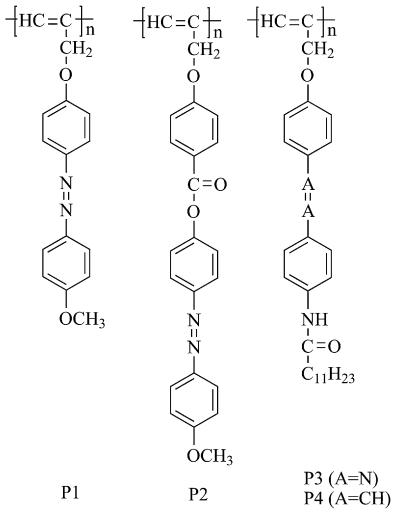

Chart 1.

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. 4-Methoxyaniline, 4-nitroaniline, 1-(bromomethyl)-4-nitrobenzene, phenol, and propargyl bromide 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. Technical grade methanol was used to precipitate the polymers.

2.2. Instruments

The FT-IR spectra were recorded as KBr pellets on a Nicolet 170sx spectrometer. ^{1}H NMR spectra were collected on an AVANCE/DMX-300 MHz Bruker NMR spectrometer. Tetramethylsilane was used as the internal reference for the NMR analyses. Elementary analyses were conducted on Vario EL-III elementary analysis apparatus. UV–vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm square quartz cell. EI-MS spectra were recorded with a Micromass GCT-MS mass spectrometer. Thermal analyses of the polymers were performed on a Perkin Elmer TGA (Thermogravimetric analysis) under nitrogen at a heating rate of 20 °C/min. 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 investigation of the optical limiting properties of the samples was carried out by using a frequency doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser, which provides linearly polarized 4 ns optical pulses at 532 nm wavelength with a repetition of 1 Hz. The experimental arrangement is similar with that in the literature [34]. The samples were housed in quartz cells with a path of 2 mm. The input laser pulses adjusted by an attenuator (Newport) were split into two beams. One was employed as a reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens with a 300 mm focal length. The samples were positioned at the focus. The incident and transmitted laser pulses were monitored by two energy detectors, D1 and D2 (Rjp-735 energy probes, Laser Precision).

The nonlinear optical properties of the samples were performed by a Z-scan technique with the same laser system as in the optical limiting experiment with a pulse width of 4 ns at 1 Hz repetition rate and 532 nm wavelengths. The experiment was set up as in the literature [35]. The solution sample was contained in a 2 mm quartz cell. The input energy was 40 μJ. The radius ω_0 at beam waist was 70 mm. The samples were moved along the axis of the incident beam (z direction). The experimental data were collected utilizing a single shot at a rate of 1 pulse/min to avoid the influence of thermal effect.

2.3. Monomer synthesis

2.3.1. Synthesis of 4-((4-methoxyphenyl)diazenyl)phenol (**1a**)

4-Methoxyaniline (9.85 g, 0.08 mol) was dissolved in 32 mL conc. hydrochloric acid. After cooling to 0 °C, an ice-water solution of 5.52 g (0.08 mol) sodium nitrite was added dropwise and stirred for 30 min. Phenol (7.88 g, 0.084 mol) was dissolved in 60 mL aqueous NaOH (3.36 g, 0.084 mol) solution. Then this solution was added to 2 L aqueous buffer solution of NH_4Cl–$NH_3\cdot H_2O$ (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 dark red piece crystals in 85% yield. FT-IR (KBr), ν (cm^{-1}): 3418 (OH), 2918, 2843 (CH_3), 1588, 1508, 1458 (CH═CH), 1238 (C–O–C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, CH_3), 5.24 (s, 1H, OH), 6.93 (d, 2H, $J = 8.8$ Hz, H^7), 6.99 (d, 2H, $J = 9.0$ Hz, H^2), 7.83 (d, 2H, $J = 8.8$ Hz, H^6), 7.87 (d, 2H, $J = 9.0$ Hz, H^3). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C 68.41, H 5.30, N 12.27. Found: C 68.37, H 5.26, N 12.34.

2.3.2. Synthesis of 4-((4-nitrophenyl)diazenyl)phenol (**1b**)

This was prepared as above from 4-nitroaniline. The crude product was recrystallized from ethanol twice to give orange crystals in 87% yield. FT-IR (KBr), ν (cm^{-1}): 3416 (OH), 1593, 1508, 1458 (Ar), 1335 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (s, 1H, OH), 6.98 (d, 2H, $J = 8.5$ Hz, H^7); 7.94 (d, 2H, $J = 8.5$ Hz, H^6), 7.83 (d, 2H, $J = 8.7$ Hz, H^3), 7.87 (d, 2H, $J = 8.7$ Hz, H^2). Anal. Calcd for $C_{12}H_9N_3O_3$: C 59.26, H 3.73, N 17.28. Found: C 59.17, H 3.70, N 17.32.

2.3.3. Synthesis of 1-(4-methoxyphenyl)-2-(4-(prop-2-ynyloxy)phenyl)diazene (**M1**)

Sodium hydroxide (0.8 g, 0.02 mol) was added to a solution of 4.56 g (0.02 mol) **1a** in 50 mL ethanol. After the reaction mixture was stirred at room temperature for 1 h, 3.57 g (0.03 mol) propargyl bromide was added dropwise to the mixture. The resulting mixture was heated under reflux overnight. Ether was added to the mixture, and the organic phase was washed with water. The organic phase was dried over $MgSO_4$. After the removal of the solvent with a rotary evaporator, the residue was recrystallized from ethanol twice to give orange piece crystals in 84% yield. FT-IR (KBr), ν (cm^{-1}): 3276 (≡C–H), 3053 (═C–H), 2912, 2840 (CH_3, CH_2), 2129 (C≡C), 1596, 1500, 1465 (CH═CH), 1251 (C–O–C), 844 (*p*-Ar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (t, 1H, $J = 2.4$ Hz, ≡CH), 3.91 (s, 3H, CH_3), 4.79 (d, 2H, $J = 2.4$ Hz, OCH_2), 7.02 (d, 2H, $J = 8.8$ Hz, H^7), 7.10 (d, 2H, $J = 8.8$ Hz, H^2), 7.90 (d, 4H, $J = 8.8$ Hz, $H^{3,6}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.2 (C^8), 158.9 (C^1), 147.2 (C^5), 146.6 (C^4), 123.9 (C^6), 114.6 (C^7), 113.7 (C^2), 76.7 (*C*≡), 75.4 (≡CH), 55.5 (OCH_2), 55.1 (OCH_3). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C 72.16, H 5.30, N 10.52. Found: C 72.13, H 5.23, N 10.57. MS (EI), m/z [M^+]: 266.1057, calcd: 266.1055.

2.3.4. Synthesis of 1-(4-nitrophenyl)-2-(4-(prop-2-ynyloxy)-phenyl)diazene (**2b**)

This was prepared as above from **1b**. The crude product was recrystallized from ethanol twice to give brown piece crystals in