

Synthesis, Characterization and Optical Properties of Poly(aryleneethynylene)s Containing BODIPY*

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Abstract Poly(aryleneethynylene)s containing BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) (P1) were prepared by palladium-catalyzed Sonogashira polymerization of 2,6-diiodo-functionalized BODIPY monomer (M1) with 1,4-diethynyl-2,5-didodecyl-oxybenzene monomer (M2). The structures of the monomer (M1) and copolymer (P1) were confirmed by ¹H-NMR and Fourier transform infrared (FTIR) spectroscopies; their optical properties were characterized by UV-Vis absorption, photoluminescence (PL) spectroscopy and the Z-scan technique. Both UV-Vis absorption and fluorescence emission of copolymer P1 red-shifted to longer wavelengths (λ_{abs} : from 502 nm to 542 nm; λ_{em} : from 511 nm to 631 nm) relative to those of the monomer M1 due to the π -conjugation extension of the copolymer. The third-order nonlinear optical coefficient ($\chi^{(3)}$) of copolymer P1 was 1.94×10^{-10} esu, which is almost two or three orders of magnitude greater than that of common conjugated polymers without BODIPY moiety.

Keywords: BODIPY; Conjugated polymers; Nonlinear optics; Synthesis.

INTRODUCTION

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) was discovered by Treibs and Kreuzer as early as 1968^[1], however, its potential as a highly fluorescent dye was only recognized in the mid-1990s. Over the past three decades, BODIPY has risen in popularity for its superior properties over other dyes^[2, 3] for the following reasons: (1) BODIPY is a small molecule whose strong UV-absorbance leads to relatively sharp fluorescence peaks with high quantum yields, (2) BODIPY derivatives are relatively insensitive to the polarity and pH of their environment and reasonably stable in physiological conditions and (3) the optical properties can be easily tuned by small modifications to the BODIPY core. Consequently, these physical and chemical properties have resulted in BODIPY's popularity for wide spread applications in chemical sensors^[4–7], light-harvesting systems^[8–11], fluorescent labels^[12] and photodynamic therapy^[13–15].

Recently, Li and colleagues reported the first application of BODIPY dyes in nonlinear optical (NLO) materials^[16]. They found that the BODIPY component in the π -conjugated copolymers played decisive roles in the nonlinear optical properties of the material, and the third-order nonlinear optical coefficients of the copolymers were enhanced gradually with the increased incorporation of the BODIPY component. Similarly, we investigated the effect of the position number of the BODIPY core at which it is conjugated to polyacetylene backbones on the material's nonlinear optical properties^[17]. We found that the BODIPY position at which the dye was joined with the polyacetylene backbones had a significant effect on the resulting nonlinear optical

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properties, with the position 3 variant possessing ~15 times greater third-order nonlinear optical coefficients than those with the position 8 variant.

In continuation of our interests in developing BODIPY-based NLO materials, here, we report the synthesis of a new BODIPY-based conjugated copolymer P1 by palladium-catalyzed Sonogashira coupling reaction and investigate its photophysical and nonlinear optical properties.

EXPERIMENTAL

Instruments

Fourier transform infrared (FTIR) spectra were recorded using KBr pellets on a Nicolet 5700 spectrometer. ^1H -NMR spectra were recorded at room temperature on a Bruker Avance 400. UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 750 UV-Vis spectrophotometer. Fluorescence emission spectra were measured on a HITACHI F-2700 spectrofluorometer. Fluorescence quantum yields of monomer and copolymer were measured in THF and calculated by using cresyl violet excited at 570 nm in methanol as the reference ($\Phi_f = 0.55$). Thermogravimetric analyses (TGA) of the polymers were performed under nitrogen with a PerkinElmer TGA 7 at a heating rate of 20 K/min. The molecular weights of the polymers were determined (relative to polystyrene standard) by gel permeation chromatography (GPC) with a Waters Associates liquid chromatograph equipped with a Waters 515 high-performance-liquid-chromatography pump, a Wyatt injector with a stand kit, a CBL Model 200 column heater and a Wyatt Optilab T-rEx differential refractometer. All the polymer solutions were prepared in tetrahydrofuran (THF; ~4 mg/mL) and filtered through 0.45 μm poly(tetrafluoroethylene) (PTFE) syringe-type filter before injection 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 35 $^\circ\text{C}$.

The nonlinear optical property of the copolymer was measured by Z-scan technique. The test 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 set-up used was described previously^[18,19]. Briefly, the relation between the normalized transmittance $T(z)$ and z position was obtained by moving the samples in a 2 mm quartz cell along the axis of the incident beam (z direction) with respect to the focal point. The input energy was 100 μJ . The incident and transmitted energies were detected simultaneously by an energy meter (Laser Precision Corporation Rjp-735).

Materials

Unless otherwise stated, all reagents were commercially obtained from Energy Chemical Company, and used without further purification. 1,4-Diethynyl-2,5-didodecyloxybenzene (M2)^[20] and EOE-BODIPY^[21] were prepared according to published procedures. THF and triethylamine were distilled immediately prior to use from sodium benzophenone ketyl and potassium hydroxide, respectively.

Synthesis of 4,4-Difluoro-1,3,5,7-tetramethyl-2,6-diiodo-8-(3,4-bis(ethoxycarbonyl)methoxy)phenyl)-4-bora-3a,4a-diaza-s-indacene (M1)

Iodic acid (528 mg, 3 mmol) in 5 mL of water was added dropwise to a reaction mixture of EOE-BODIPY (528 mg, 1 mmol) and iodine (762 mg, 3 mmol) in 50 mL of $\text{C}_2\text{H}_5\text{OH}$. The mixture was stirred for 3 h, and then the unreacted iodine was quenched with sodium thiosulphate. The resulting solution was concentrated under reduced pressure, dissolved in CH_2Cl_2 , and washed twice with water. The organic layer was collected, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/EtOAc = 3:1, V/V) as eluent to give brown powder (740 mg, 94% yield). FTIR (KBr), ν (cm^{-1}): 2956, 2927, 2856 (CH_3); 1720 ($\text{C}=\text{O}$); 1545, 1510, 841 (Ar); 1105 ($\text{C}-\text{O}-\text{C}$). ^1H -NMR (500 MHz, CDCl_3 , δ): 6.98 (d, 1H, $J = 8.2$ Hz), 6.81 (d, 1H, $J = 8.2$ Hz), 6.71 (s, 1H), 4.78 (s, 2H), 4.70 (s, 2H), 4.27 (q, 2H, $J = 7.2$ Hz), 4.20 (q, 2H, $J = 7.2$ Hz), 2.62 (s, 6H, CH_3 ortho to N), 1.44 (s, 6H), 1.29 (t, 3H, $J = 7.2$ Hz), 1.24 (t, 3H, $J = 7.2$ Hz).

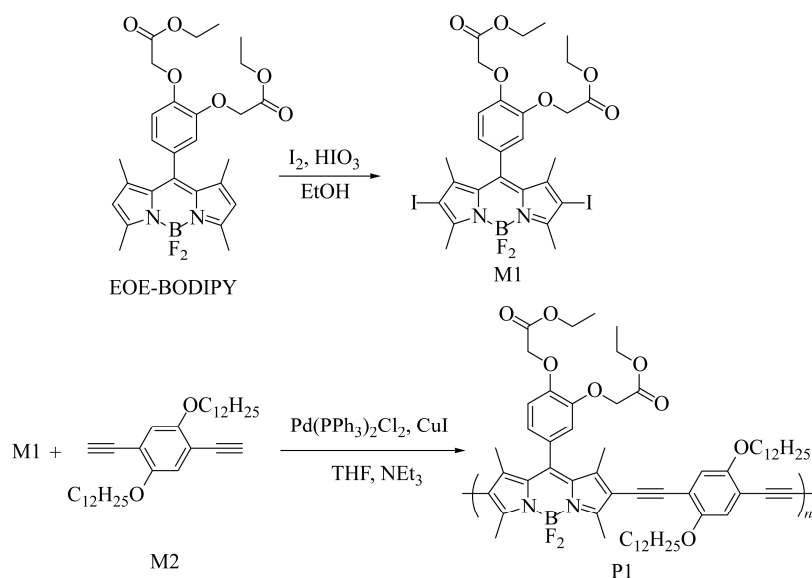
Synthesis of Copolymer (P1)

M1 (234 mg, 0.3 mmol), M2 (148 mg, 0.3 mmol), CuI (3 mg, 0.015 mmol), and Pd(PPh₃)₂Cl₂ (10 mg, 0.005 mmol) were added to a degassed mixture of solvents containing anhydrous THF (10 mL) and anhydrous NEt₃ (1 mL) in 25 mL flask under a nitrogen atmosphere. The mixture was refluxed for 48 h. After removal of the solvent, the residue was dissolved in THF (4 mL), and added to 100 mL of methanol to precipitate the polymer. The precipitate was centrifuged and redissolved in THF (4 mL). The THF solution was again added dropwise to 100 mL of methanol to precipitate the polymer. This dissolution-precipitation process was repeated three times, and the obtained polymer was dried in a vacuum oven at 45 °C for 24 h to a constant weight (177 mg). The result product was dark-brown powder; yield 58%. $M_w = 8.9 \times 10^3$; $M_w/M_n = 1.7$ (GPC, polystyrene calibration). FTIR (KBr), ν (cm⁻¹): 2927, 2860 (CH₃); 1716 (C=O); 1545, 1510, 841 (Ar); 1105 (C—O—C). ¹H-NMR (500 MHz, CDCl₃, δ): 6.95–6.68 (br, Ar—H), 4.72–4.64 (br, Ar—OCH₂ linked at BODIPY), 4.23–4.11 (br, —OCH₂), 3.90 (br, Ar—OCH₂), 2.65 (br, CH₃ linked at 3,5 position of BODIPY), 1.74–1.72 (br, Ar—OCH₂CH₂), 3.90 (br, CH₃ linked at 1,7 position of BODIPY), 1.34–1.15 (br, —OCH₂CH₂(CH₂)₇), 0.79 (br, CH₃).

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The synthetic route for the BODIPY monomer M1 and its copolymer P1 is outlined in Scheme 1. Diiodination of EOE-BODIPY resulted in monomer M1, which was further reacted with 1,4-diethynyl-2,5-didodecyloxybenzene under Sonogashira conditions to afford the copolymer P1. The resulting copolymer P1 was soluble in common organic solvents including THF, toluene, CHCl₃ and CH₂Cl₂. Gel permeation chromatography (GPC) in THF relative to polystyrene standards revealed the number-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of 8900 and 1.7, respectively. The chemical structures of the monomers and copolymer were characterized by spectroscopic techniques, including FTIR and ¹H-NMR spectroscopies, giving satisfactory spectral data corresponding to their expected molecular structures.



Scheme 1 The synthetic route of copolymer P1

The FTIR spectrum of copolymer P1 is shown in Fig. 1; for comparison, the spectra of the two monomers, M1 and M2, are also given. As depicted in Fig. 1, M2 had the characteristic stretching vibrations of $\equiv\text{C—H}$ and $\text{C}\equiv\text{C}$ bonds of monosubstituted acetylene group at 3290 and 2105 cm⁻¹, respectively. However, these two

characteristic stretching vibrations completely disappeared in the spectrum of copolymer P1, while a new peak at 2185 cm^{-1} appeared. These spectral changes indicate that the triple bond of monosubstituted acetylene is completely consumed during the polymerization and converted to $\text{C}\equiv\text{C}$ bonds of disubstituted acetylene along the main chain in the polymer.

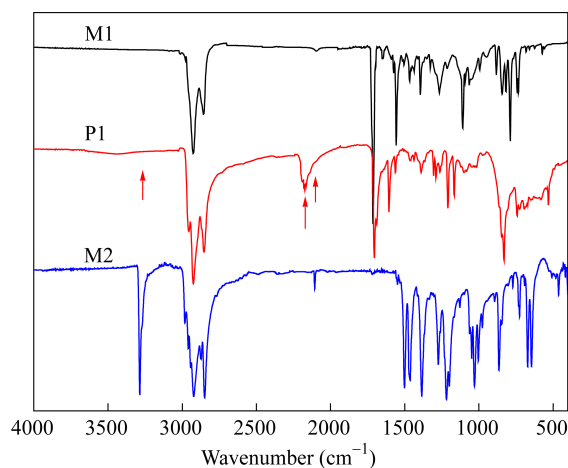


Fig. 1 FTIR spectra of the two monomers and copolymer P1

NMR spectroscopy further confirms that the two monomers have been successfully polymerized. Figure 2 shows ^1H -NMR spectra of the monomers and copolymer in CDCl_3 . As shown in Fig. 2, the resonance peaks in ^1H -NMR spectrum of copolymer P1 were a little broader than its two monomers. As expected, all peaks attributable to the two monomers appeared in the ^1H -NMR spectrum of their copolymer P1 with the exception of the singlet proton at $\delta = 3.25$, corresponding to the ethynyl protons in M2, indicating that M1 underwent efficient Sonogashira reaction with M2^[22, 23].

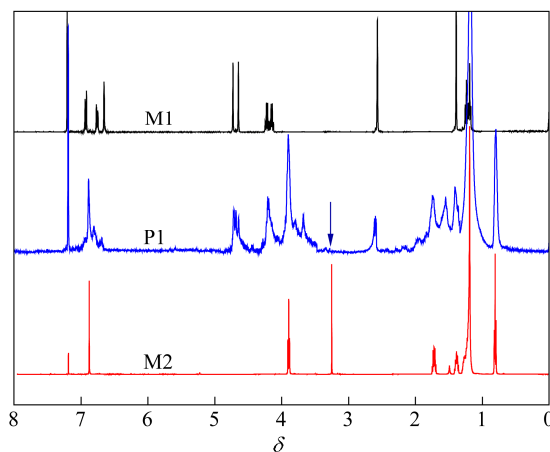


Fig. 2 ^1H -NMR spectra of the two monomers and copolymer P1

Thermal Properties

The thermal stability of copolymer P1 was evaluated by thermogravimetric analysis (TGA) at a heating rate of 20 K/min under a nitrogen atmosphere. EOE-BODIPY was also measured under the same conditions. From Fig. 3, it is evident that EOE-BODIPY and copolymer P1 lost 5% of their weight at $236\text{ }^\circ\text{C}$ and $307\text{ }^\circ\text{C}$, respectively, indicating that copolymer P1 is more thermally stable than its monomer.

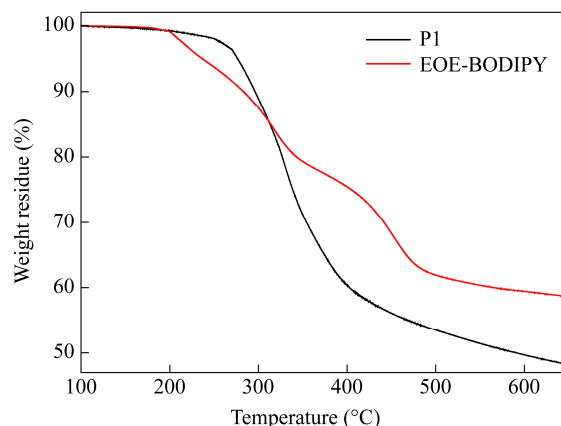


Fig. 3 TGA thermograms of EOE-BODIPY and copolymer P1 measured under nitrogen at a heating rate of 20 K/min

Optical Properties

The optical properties of copolymer P1 were characterized using UV-Vis absorption and PL measurements together with EOE-BODIPY for comparison (Fig. 4). EOE-BODIPY showed the typical absorption and emission spectra of the BODIPY chromophore, that is, the strong $S_0 \rightarrow S_1$ ($\pi-\pi^*$) transition at 502 nm, the weak $S_0 \rightarrow S_2$ ($\pi-\pi^*$) transition at 350 nm, and bright ($\Phi_f \sim 1.0$) and sharp emission at 511 nm. Following the Sonogashira reaction of polymerization, both the absorption and emission peaks of copolymer P1 exhibited a broadening of the peaks and significant red-shifts to 542 nm (absorption) and 631 nm (emission) relative to EOE-BODIPY, which is a consequence of the π -conjugated system being extended^[17, 20]. However, the absolute quantum yield (Φ_f) of the copolymer was a small fraction of the EOE-BODIPY quantum yield (decrease from ~ 1.0 to 0.04). The decreased quantum yield is possibly due to self-absorption stemming from the overlap of P1 emission spectrum with its absorption spectrum^[24, 25].

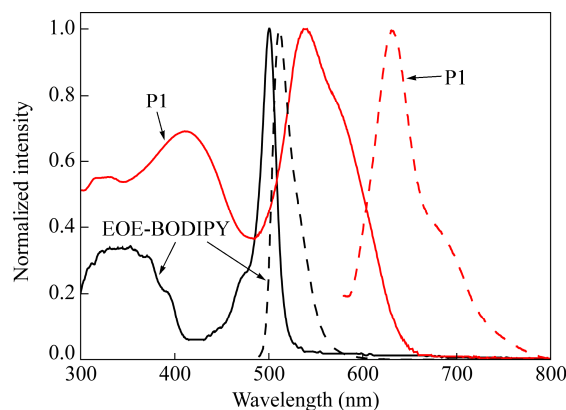


Fig. 4 Normalized absorption (solid line) and emission (dash line) spectra of EOE-BODIPY and copolymer P1 in THF

Nonlinear Optical Properties

The nonlinear optical properties of copolymer P1 were investigated, and its nonlinear optical coefficients were measured using Z-scan technique. As shown in Fig. 5, copolymer P1 displayed reverse saturable absorption and nonlinear refraction. The third-order nonlinear optical coefficient ($\chi^{(3)}$) of copolymer P1 is calculated to be 1.94×10^{-10} esu, according to previous reports^[26], which is almost two or three orders of magnitude greater than that of common conjugated polymers, such as poly(phenylene ethynylene) and poly(phenylacetylene)^[27, 28]. Thus, the incorporation of the BODIPY moiety into poly(phenylene ethynylene) effectively improves its third-

order susceptibility. This work paves the way for designing new soluble functional conjugated polymers with improved nonlinear optical properties.

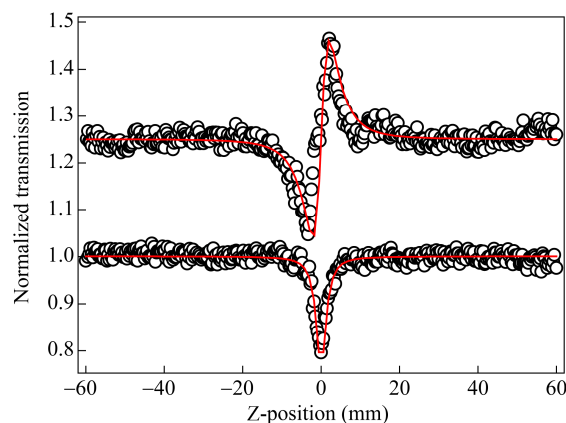


Fig. 5 Normalized transmission curves of Z-scan data with (upper curve) and without (lower curve) an aperture (linear transmission of $s = 0.1$) of copolymer P1 in THF measured using 8 ns pulses at 532 nm (The solid lines indicate the theoretical fitting curves.)

CONCLUSIONS

We have successfully synthesized a novel poly(aryleneethynylene)s containing BODIPY by palladium-catalyzed Sonogashira polymerization. The UV-Vis absorption and PL spectra of the copolymer red-shifted to longer wavelengths (λ_{abs} : from 502 nm to 542 nm; λ_{em} : from 511 nm to 631 nm) relative to those of the BODIPY monomer due to extended π -conjugation in the copolymer. The third-order nonlinear optical coefficient ($\chi^{(3)}$) of the BODIPY conjugated copolymer is found to be greater than that of previously reported NLO polymer materials that do not incorporate BODIPY. This work provides new information regarding the design of conjugated NLO polymer materials having improved third-order nonlinear optical coefficients.

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