

Synthesis and Properties of Substituted Polyacetylenes Containing Pyrene Moieties in the Side Group

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Abstract

A novel phenylacetylene derivative containing a pyrene group was synthesized and polymerized with various Rh complex catalysts. The obtained polymers were soluble in common organic solvents such as chloroform and THF. The M_w and M_w/M_n were estimated as ca. 12000–18000 and 1.3–1.7 respectively, and the polymer yields were estimated as around 57–72%. The characteristic absorptions of $\equiv\text{C-H}$ (3200 cm^{-1}) and $\text{C}\equiv\text{C}$ (2100 cm^{-1}) stretchings seen in the monomer spectra have completely disappeared in the polymer spectra from IR spectrum. $^1\text{H NMR}$ analysis confirmed that the acetylene triple bonds transformed to polyene double bonds. These polymers were found to be thermally stable based on TGA data. The synthesized polymers exhibited blue fluorescence. The fluorescence quantum yield in solution was high at 0.37–0.41. Furthermore, the obtained polymer had a long fluorescence lifetime.

In the past few decades, conjugated polymers have been investigated intensively due to their promising electrical and optical properties, making them useful materials for electronic and photonic devices such as field-effect transistors and light emitting diodes (LEDs).^{1–3} Polyacetylene (PA), as the simplest conjugated polymer, exhibits high conductivity when doped with an appropriate dopant, such as iodine.⁴ However, the application of PA in electronic devices is not feasible due to its lack of solution processability and air stability.^{5–7} Through the introduction of various groups, such as alkyl and aryl groups, to the polymer chain, the solubility and stability of polyacetylenes (PAs) can be greatly improved.^{8,9} Among the various PAs, poly(phenylacetylene)s (PPAs) have been found to possess photoconductivity,^{10,11} third-order nonlinear optical properties, light emission,^{12–14} light emissivity,^{15,16} helical chirality,^{17,18} liquid crystallinity,^{19,20} and gas permeability.^{21,22} In general,

substituted polyacetylenes can be obtained by the polymerization of the corresponding acetylenic monomers with group 5 (Nb, Ta), 6 (Mo, W), and 9 (Rh) transition metal catalysts. Being sensitive to air and moisture, Nb, Ta, Mo, and W catalysts cannot be applied for the polymerization of substituted acetylenes bearing polar groups due to their deactivation. On the other hand, Rh catalysts display remarkable activity for the polymerization of monomers containing polar groups owing to their low oxophilicity. In addition, Rh catalysts exhibit activity even in polar and protic solvents. However, they suffer from the disadvantage of being effective only for monosubstituted acetylenes. Attracted by these properties and the corresponding potential applications, many research groups have been working on the synthesis of novel substituted PPAs. Acetylene monomers could only be polymerized by Rh-based catalysts and the obtained polymers were found to have unusually high *cis*-polyene contents (90%). Pyrene is a fluorescent substance emitting blue light, is photoconductive,²³ and has been widely studied as an organic EL material.^{24,25} However, since the solubility is a problem with pyrene alone, the introduction of substituents, such as an ethynyl group,²⁶ which has been reported to have high fluorescence characteristics, has been considered.²⁷ In this article, we describe a synthetic design different from previous reports, that is, synthesis of an acetylene monomer containing an amide bond with a pyrene group at the end. Introduction of a pyrene²³ to the side chain of acetylene extends the conjugated chain and would impart excellent heat resistance and fluorescence.²⁶ These monomers were polymerized with Rh complexes. The synthesis and characterization of these novel fluorescent substituted polyacetylenes are described herein.

Experimental

Materials. 2-Methyl-3-butyn-2-ol (Tokyo Kasei), bis-(triphenylphosphine)palladium(II) chloride (Tokyo Kasei),

copper(I) iodide, ethyl 3-iodobenzoate (Tokyo Kasei), 1-aminopyrene (Tokyo Kasei), *N,N'*-dicyclohexylcarbodiimide (DCC, Tokyo Kasei), *N*-(4-pyridyl)dimethylamine (DMAP, Wako Pure Chemical), (bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer ([Rh(nbd)Cl]₂, Aldrich), chloro(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(cod)Cl]₂, Aldrich), and 2,5-norbornadiene (Tokyo Kasei) were all purchased and used without further purification. The solvents were treated as follows: tetrahydrofuran (THF) was dried over calcium hydride, triethylamine (Et₃N) over potassium hydride, and chloroform under nitrogen. Other chemicals were obtained from Kanto Kagaku Co. and were used as received.

Monomer and Catalyst Synthesis. Synthesis of 4-Ethynylbenzoic Acid (1): The reaction procedures are similar to these reported elsewhere.²⁸ To a 200-mL three-necked flask were added methyl ethyl-4-iodobenzoate (5.0 g, 25.7 mmol), 2-methyl-3-butyn-2-ol (2.51 mL, 25.7 mmol), Ph₃P (0.075 g, 0.28 mmol), CuI (23 mg, 0.12 mmol) in 93.2 mL of dry Et₃N and 7 mL of dry pyridine. [PdCl₂(Ph₃P)₂] (326 mg, 3.8 mmol) was then added to the above mixture under nitrogen. After refluxing for 4 h at ca. 80 °C, the mixture was cooled to room temperature and filtered to remove the insoluble trimethylamine hydrobromide. The salt was washed with trimethylamine and ethyl ether until the ether washings were clear. The combined filtrates were reduced to dryness under reduced pressure, and the crude product was washed with water. The residue was dried under vacuum to yield 3.12 g of methyl 4-(3-hydroxy-3-methylbut-1-ynyl)benzoate. The above solid was dissolved in 300 mL of refluxing solution of *n*-butanol with 3.2 g of KOH. After refluxing for 10 min, the mixture was cooled in an ice bath. After filtration, the collected residue was acidified to pH 2 by HCl. The mixture was extracted with ethyl acetate. After removing the solvent, the residue was dried under vacuum to yield 2.31 g of 4-ethynylbenzoic acid **1** as a yellow solid (yield 76.2%) (Figure 1). IR (KBr): 650 (C≡CH), 1750 (C=O), 2200

(C≡C), 3200 (C≡CH), 3400 (-COOH). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 4.5 (s, C≡CH, 1H), 7.6, 8.0 (d, Ar-H, 4H), 13.1 (s, -COOH, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 82.2, 83.1, 126.8, 131.1, 132.5, 167.0.

Synthesis of 4-Ethynyl-*N*-pyrenylbenzamide (EPBA) (2). First, (0.217 g 1.0 mmol) of 4-ethynylbenzoic acid, (0.146 g, 1.0 mmol) of 1-aminopyrene, (0.040 g, 3.2 mmol) of DMAP, and (0.068 g, 0.4 mmol) of *p*-toluenesulfonic acid monohydrate were dissolved in 10 mL of dry dichloromethane. To the dichloromethane solution, 0.82 g (4 mmol) of DCC was added dropwise with stirring. The reaction mixture was stirred for 24 h at room temperature. After the solvent was removed, the crude product was washed with saturated sodium hydrogen carbonate aqueous solution, 0.1 M HCl aqueous solution, and water. The organic phase was dried over Na₂SO₄ and concentrated by rotary evaporation. The residue was purified by recrystallization from MeOH and acetone to afford solid EPBA **2** in 85% yield. The data are as follows. Yield: 85.0, brown powder (Figure 1). IR (cm⁻¹, KBr): 650 (C≡CH), 1750 (C=O), 2200 (C≡C), 3200 (C≡CH), 3300 (-NH). ¹H NMR (400 MHz, CDCl₃, ppm): δ 3.0 (s, C≡CH, 1H), 4.5 (s, -NH 1H), 7.6, 7.8 (d, Ar-H, 4H), 8.0–8.5 (m, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 51.2, 82.2, 83.1, 126.8, 125–135 (Pyrene), 139.7, 131.1, 132.5, 180.0.

Synthesis of [Rh(nbd){B(C₆H₅)₄}] Catalyst. Synthesis of this catalyst was carried out according to the method reported by Schrock et al.²⁹ RhCl₃·3H₂O (250 mg) was dissolved in water (1 mL), and Na[B(C₆H₅)₄] (1 g) in methanol (20 mL) was added. 2,5-Norbornadiene (nbd; 1 mL) was then added and the solution was allowed to stand until crystals were deposited. The yellow crystalline product was filtered and air-dried. The desired complex was obtained in a yield of ca. 68.2%.

Polymer Synthesis (3). All the polymerizations were carried out in a glass tube equipped with a three way stopcock under nitrogen. The polymerization conditions were as follows:

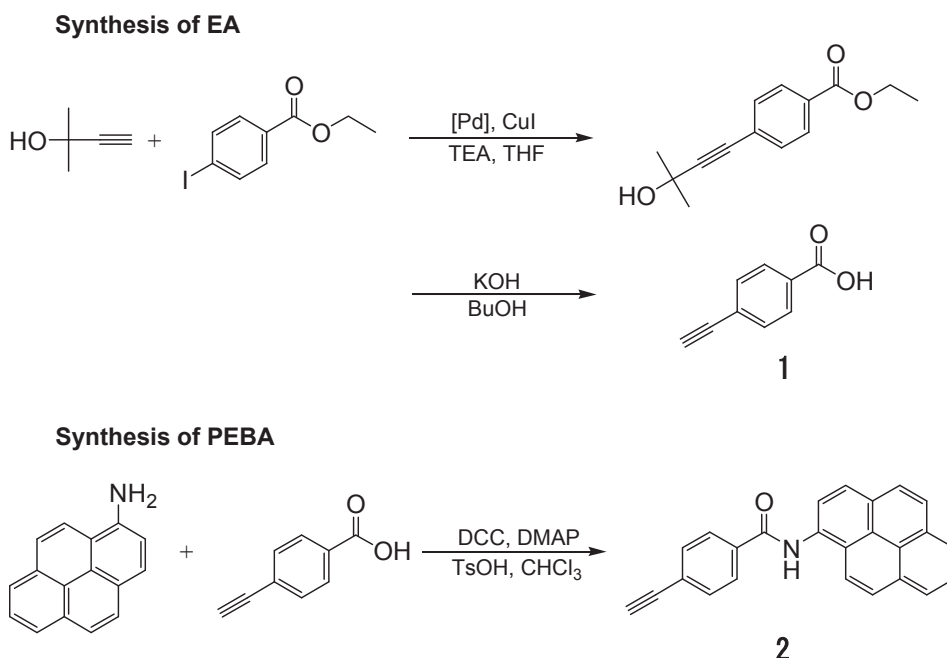


Figure 1. The synthetic route of 4-ethynylbenzoic acid (**1**) and 4-ethynyl-*N*-pyrenylbenzamide (EPBA) (**2**).

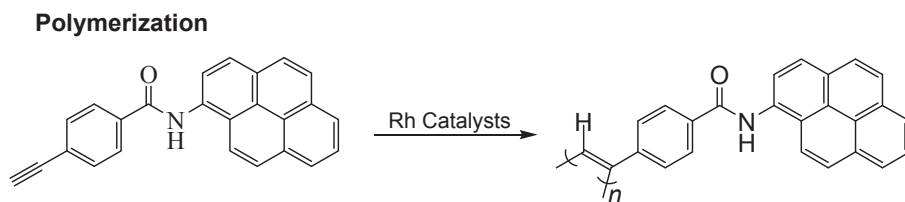


Figure 2. Synthesis of poly(EPBA) (**3**).

Table 1. Synthesis of polymers

Cat.	Monomer		Yield ^{b)}		$M_n^c)$	$M_w^c)$	$M_w/M_n^c)$	State
	/g	/mmol	/g	/%				
nbd ^{d)}	0.1	0.29	0.065	65	1.5×10^4	2.4×10^4	1.6	Orange powder
cod ^{d)}	0.1	0.29	0.057	57	1.2×10^4	1.6×10^3	1.3	Orange powder
B ^{d)}	0.1	0.29	0.072	72	1.8×10^4	3.0×10^4	1.7	Orange powder

a) $[M] = 0.29 \text{ mmol L}^{-1}$, $[Rh] = 2.9 \times 10^{-3} \text{ mmol L}^{-1}$, $[TEA] = 0.5 \text{ mmol L}^{-1}$, solvent THF. b) Acetone-insoluble part. c) Determined from GPC calibrated by polystyrene standard. d) nbd: $[Rh(\text{norbornadiene})\text{Cl}_2]$, cod: $[Rh(\text{cyclooctadiene})\text{Cl}_2]$, B: $[Rh(\text{nbd})\{\text{B}(\text{C}_6\text{H}_5)_4\}]$.

A solution of EPBA (0.1 g, 0.29 mmol), $[Rh(\text{nbd})\text{Cl}_2]$ (1.3 mg, $2.9 \times 10^{-3} \text{ mmol}$) and trimethylamine (0.045 ml, 0.5 mmol) in distilled dry tetrahydrofuran (2.0 ml) was kept at room temperature for 24 h in a glass tube under nitrogen. The polymers were isolated by precipitation in a large amount of methanol with stirring. The precipitate was collected by filtration and dried under vacuum to give poly(EPBA) **3** (Figure 2). IR (cm^{-1} , KBr): 650 ($\text{C}\equiv\text{CH}$), 1750 ($\text{C}=\text{O}$), 2200 ($\text{C}\equiv\text{C}$), 3200 ($\text{C}\equiv\text{CH}$), 3300 ($-\text{NH}$). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 3.0 (s, $\text{C}\equiv\text{CH}$, 1H), 4.5 (s, $-\text{NH}$ 1H), 7.6, 7.8 (d, Ar-H, 4H), 8.0–8.5 (m, 9H).

Results and Discussion

Measurement. Infrared absorption spectra (FT-IR) measurements were carried out using a JASCO FT-IR-615 spectrometer. Raman measurements were carried out using a JASCO NRS-3000 Laser Raman Spectrophotometer. Thermogravimetric analysis (TGA) was performed with a Rigaku Thermoplus instrument at a heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen or air atmosphere. Gel permeation chromatography (GPC) was carried out on a TOSOH HLC-8220 instrument using THF as an eluent at 25°C . The GPC calibration curve was obtained with linear polystyrene standards. UV–vis absorption measurements were performed with a V-670 UV–vis spectrometer. The dry THF solvent was used as the reference. Fluorescence spectrum measurements were carried out using a JASCO FP-6500. The dry THF solvent was used as the reference. Fluorescence lifetime measurements were carried out using a HORIBA modular fluorescence spectrophotometer Fluorolog-3. $^1\text{H NMR}$ (400 MHz) and $^{13}\text{C NMR}$ (100 MHz) spectra were recorded on a Varian Mercury plus spectrometer (Varian Technologies Co., Ltd., Japan) at room temperature using deuterated chloroform (CDCl_3) or dimethyl sulfoxide ($\text{DMSO}-d_6$) as the solvent and tetramethylsilane (TMS) as the internal standard.

Synthesis and Characterization. The starting acetylene compounds based on 2-methyl-3-butyn-2-ol were obtained according to Figure 1 using a Sonogashira cross-coupling reaction. The cross coupling of ethyl-4-iodobenzoate with excess 2-methyl-3-butyn-2-ol afforded 4-ethynylbenzoic acid in 76.2%

yield. 4-Ethynyl-*N*-pyrenylbenzamide (EPBA) was condensed using DCC with 1-aminopyrene and 4-ethynylbenzoic acid to give the product **2** in 85.0% yield. The synthetic procedures have not yet been optimized. Figure 2 shows the results of the polymer synthesis. All polymers were obtained in yields of around 57–72% as orange powders using various Rh catalysts (Table 1). The molecular weights were measured by GPC (using the polystyrene standard). All the polymers possessed moderate molecular weights ($M_w = 12000\text{--}18000$), and their polydispersities (M_w/M_n) were in the range of ca. 1.3–1.7. Thus, it is concluded that these monomers gave polymers having relatively high molecular weights in good yields. At the optimal ratio between initiator and catalyst of 100:1, high monomer conversions were observed. These results are somewhat better than those of polyacetylenes by Rh catalysts.³⁰ The characteristic absorptions of $\equiv\text{C}-\text{H}$ (3200 cm^{-1}) and $\text{C}\equiv\text{C}$ (2100 cm^{-1}) stretchings seen in the monomer spectra have completely disappeared in the polymer spectra (Figure 3a). Figure 3b shows the $^1\text{H NMR}$ spectrum of poly(EPBA). In the $^1\text{H NMR}$ spectra of the polymers, the signals at around 3.1 ppm assigned to the acetylenic proton ($\equiv\text{CH}$) of the monomer were undetectable. The polymer obtained with the Rh catalyst in the present study also showed a singlet peak around 6.1 ppm, corresponding to the *cis* structure observed. The obtained polymers were soluble in organic solvents such as toluene, chloroform and THF. We used Raman technique to study the stereostructure of the polymer backbones. The Raman spectra revealed of poly(EPBA) possesses a *cis*-polyene structure (Figure 3c). The peaks at 1537, 1340, and 962 cm^{-1} can be assigned to the stretching $\text{C}=\text{C}$ band in *cis*-polyacetylene (although it is partially overlapped with that of the phenyl ring), the stretching vibration of *cis* C–C bond coupled with the single bond connecting the main chain and phenyl ring, and the C–H deformation band of the *cis* main chain, respectively.

On the other hand, the scattering peaks corresponding to the *trans* form, which appear at around 1190 cm^{-1} ,^{31,32} are very weak. Therefore, the resulting polymers are *cis*-rich polyacetylenes. This result is consistent with that usually found in the monosubstituted polyacetylenes obtained from Rh-

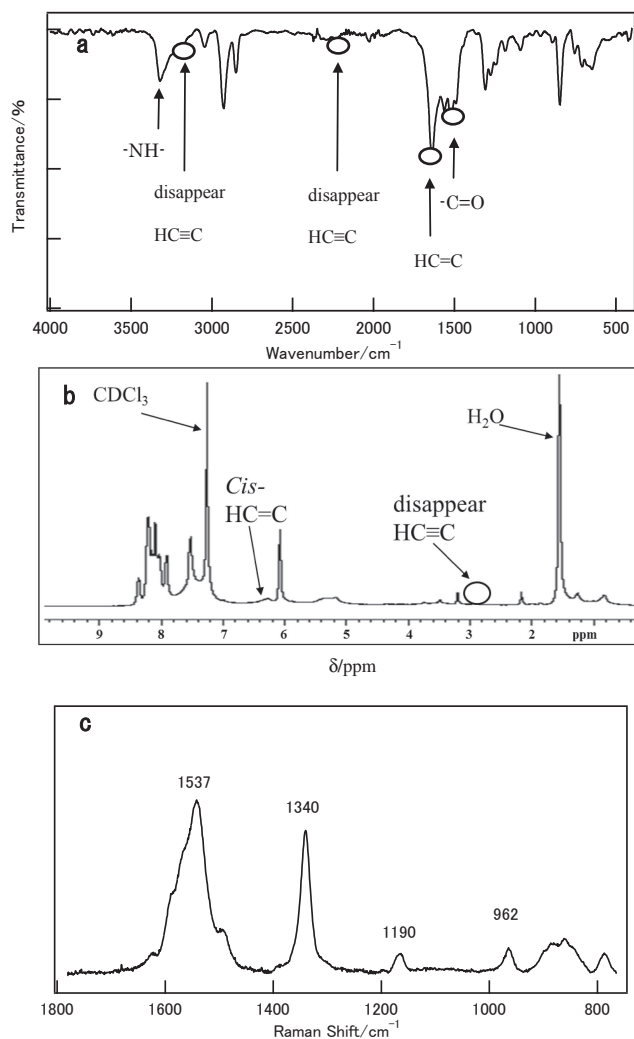


Figure 3. (a) FT-IR spectra of the corresponding poly(EPBA). (b) ^1H NMR spectrum of poly(EPBA) in CDCl_3 . (c) Raman spectra recorded from the poly(EPBA).

catalyzed polymerization, of which the main-chain is stereoregularly *cis*-transoid.

Thermal stability of the poly(EPBA) was investigated by TGA and compared with pristine PPA. The TGA curves are presented in Figure 4 and weight loss behaviors of the species are tabulated at Table 2. The TGA results show that the temperatures for 10% weight loss of the samples are 414 and 405 °C in the air and nitrogen atmosphere, respectively. The thermal stability of the polymers is considerably improved in comparison with PPA which degrades at about 290 °C.³³

On the other hand, the thermal data also reveals that the char yield of the poly(EPBA) is enhanced approximately fifteen fold compared to PPA because of the presence of more rigid and bulky pyrene group. Another noticeable feature is that the weight loss difference at 600 °C between the polymer before and after modification.

Photophysical Properties. The optical absorption and photoluminescence (PL) emission properties of poly(EPBA) in dilute solution ($1 \times 10^{-5} \text{ M}$) are shown in Figure 5. In dilute solution, poly(EPBA) has a rather broad absorption in the 320–375 nm region with an absorption maximum (λ_{max}) at 348

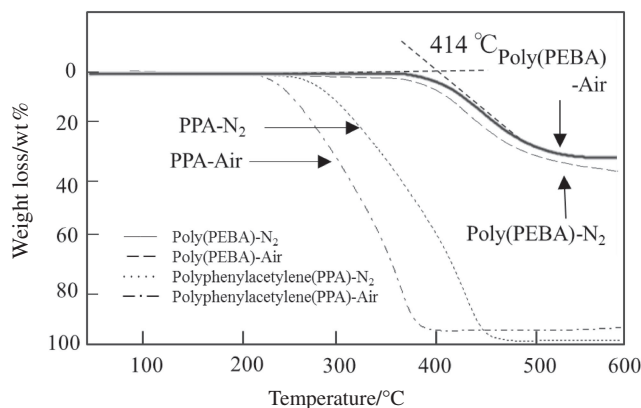


Figure 4. TGA results of poly(EPBA) and PPA measured under nitrogen atmosphere and air.

Table 2. Thermal properties of poly(EPBA)

Polymer	$T_{5\%}^{\text{a)}$ /°C	$T_{10\%}^{\text{b)}$ /°C	$Y_c^{\text{c)}$ at 600 °C/%
Poly(EPBA)- N_2	414.2	431.2	67.7
Poly(EPBA)-Air	405.0	414.5	60.5
PPA- N_2	296.3	301.4	4.1
PPA-Air	232.7	266.6	2.3

- a) $T_{5\%}$: The temperature for which the weight loss is 5%.
 b) $T_{10\%}$: The temperature for which the weight loss is 10%.
 c) Y_c : Char yields.

nm. Furthermore, absorption peaks at 243 and 273 nm, can be observed, considered to be derived from the -NH- and benzene ring absorption peaks, respectively.³⁴

Additionally, the maximum wavelength of the blue wavelength 420 nm was subjected to fluorescence spectroscopy, confirming the broad fluorescence peak. The peak of the excimer fluorescence derived from pyrene was not observed. This emission was observed as blue light by the naked eye. The fluorescence quantum yield in solution was high at 0.37–0.41.^{35,36} Additionally, the fluorescent assessment was subjected to fluorescence lifetime measurements, and two components were observed as shown in Figure 6, with fluorescence lifetime of 24 and 107 ns. In general, organic compounds have lifetime of 1 ns,³⁷ so these lifetimes are considered to be long.³⁸ This is because the preventing excimer fluorescence. Thus, the lifetime is long because there is no energy loss. From the above results, highly efficient fluorescence nature is observed, which is expected to be available to the new fluorescent materials. Figure 6. Fluorescence decay curves of poly(EPBA) in THF.

Conclusion

In summary, we designed and synthesized a novel acetylene monomer and polymer containing pyrene units and investigated the chemical and physical properties of the macromolecules. Our results can be summarized as follows:

1. The monomer was prepared by a three step reaction route. At each step, products were obtained in at least 60% yields, and their structures were confirmed by various measurements.
2. Rh catalysts initiate the polymerization of the monomers, furnishing polymers in high yields. The $[\text{Rh}(\text{nbd})\{\text{B}(\text{C}_6\text{H}_5)_4\}]$ catalyst was the most effective in our polymerization.

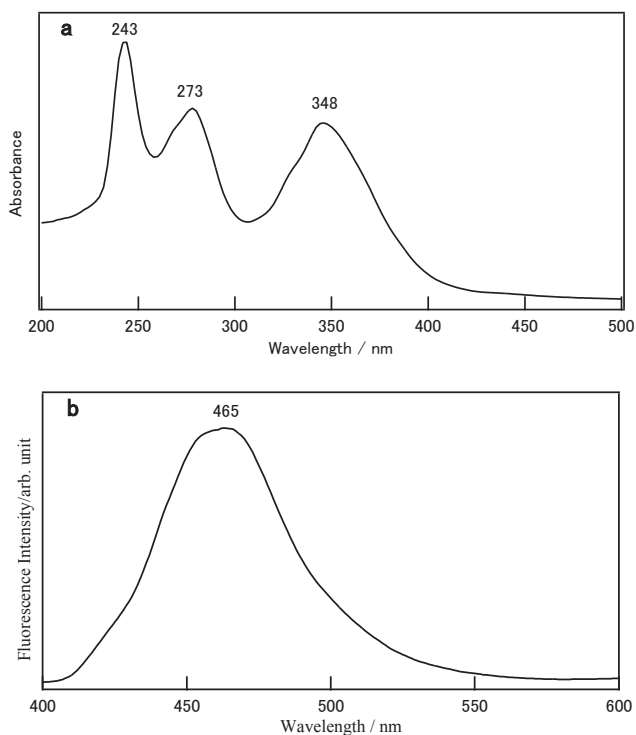


Figure 5. (a) UV-vis absorption spectrum of poly(EPBA) in THF. (b) Photoluminescence spectrum of poly(EPBA) in THF.

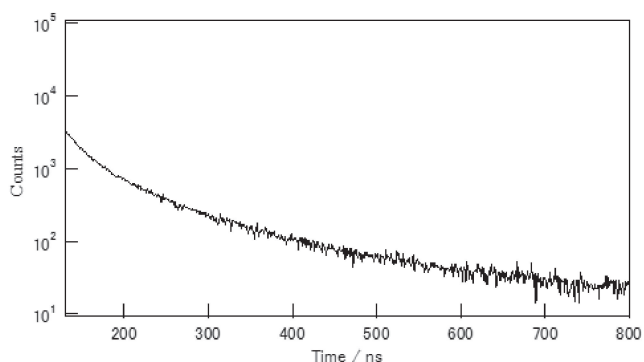


Figure 6. Fluorescence decay curves of poly(EPBA) in THF.

3. All the polymers were thermally stable, losing little of their weight when heated to 414 °C. Furthermore, they were stable in air, thus, the structure of the pyrene group affected the fluorescence lifetime. The structure–property relationship revealed in this study is expected to help guide future structural design endeavors in the development of fluorescence polyacetylenes with desirable properties.

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