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Tropone-Containing Conjugated Polymer, Part V

Influence of Fused Benzene Ring upon Photophysical Properties

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Summary

p-Phenylenevinylene type (**P1**), *p*-phenylene type (**P2**), and *p*-phenyleneethynylene type (**P3**) conjugated polymers containing tropone in the main chain were obtained by Heck reaction, Suzuki coupling, and Sonogashira coupling, respectively. The carbonyl stretching vibration peaks in the IR spectra were always detected at the lower wavenumber region compared with that of tropone. **P1** and **P2** in chloroform had the absorption peak maximum at 515 nm and 400 nm, respectively. The fluorescence from these polymer solutions was almost quenched, in contrast to previously reported **P4** bearing benzotropone unit (λ_{em} = 566 nm). The acid-doping to **P1** did not bring about any spectral change in the UV spectra. From the powder XRD pattern, **P1** was found to have the π-stacked structure in the solid state.

Introduction

Excellent photophysical and electrochemical properties of conjugated polymers stem from the π-electron delocalization along the main chain, which enable the application for various optoelectronic materials such as light-emitting diodes, transistors, and sensors. The variation of the chemical structure connecting aromatic rings significantly affects the optical properties of conjugated polymers. For example, poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenyleneethynylene) (PPE), and poly(*p*-phenylene) (PPP) have much different absorption and emission characteristics. The fusion of the additional aromatic and aliphatic rings to the aromatic segment in the conjugated polymer can also manipulate the optical properties. Poly(isothianaphthene) [1] and poly(thienothiophene) [2], which have fused benzene and thiophene rings, respectively, are the small band gap polymers due to the contribution of the quinoid structure. The nitrogen-containing heteroaromatic rings such as oxadiazole decrease the electron injection barrier of the polymer to be applicable to the material for the electroluminescent device [3]. Furthermore, the π-stacking of conjugated polymers is very important factor to gain the desirable function, especially in the solid state, because the dramatic spectral change is often observed between in the solution and film states.

We previously reported a series of benzotropone-containing polymers to reveal their optical properties [4]. It is known that the fusion of the benzene ring to tropone leads to a less polarization of the carbonyl group and hence a loss of the 6π aromatic character [5]. Accordingly, we designed novel conjugated polymers (**P1**, **P2**, and **P3**) containing tropone *without* the fused benzene ring to compare the optical properties with those of benzotropone-containing PPV type conjugated polymer (**P4**) (Figure 1). The acid-doping experiment was also performed to control the absorption and emission properties of the polymer.

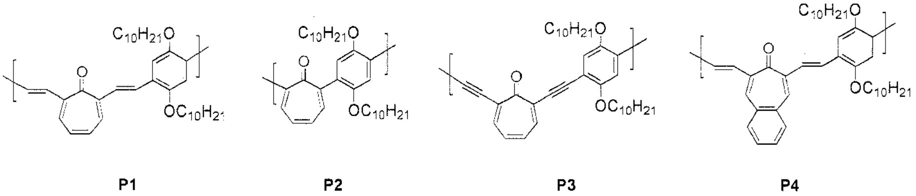

Figure 1. Chemical Structure of Tropone-Containing Polymers (**P1**, **P2**, and **P3**) and Benzotropone-Containing Polymer (**P4**).

Experimental Section

Materials and Instruments

All the reagents for the monomer synthesis were used as received. 1,4-Diethenyl-2,5-bis(decyloxy)benzene [6], [2,5-bis(decyloxy)-1,4-phenylene]diboronic acid [7], and 1,4-diethynyl-2,5-bis(decyloxy)benzene [8] were prepared according to the previous methods. All the polymerization solvents were dried by common methods and distilled under nitrogen before use. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer with tetramethylsilane (^{1}H NMR, $\delta = 0.00$) or $CDCl_3$ (^{13}C NMR, $\delta = 77.0$) as an internal reference peak. Infrared (IR) spectra were recorded on a Nicolet Impact 400D FT-IR spectrophotometer. Elemental analyses were performed with a Yanaco MT-3 CHN corder. Gel permeation chromatography (GPC) analyses were carried out on a Tosoh DP-8020 [TSK gel Multipore H_{XL}-M with tetrahydrofuran (THF) as an eluent] equipped with a refractive index detector (RI-8010) on the basis of standard polystyrene samples. Ultraviolet (UV) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2100 spectrophotometer and Jasco FP-777 spectrofluorometer, respectively, with an 1 cm quarts cell. Optical properties of thin films of the polymer were obtained by spin-coating onto a quarts glass from their toluene solutions. Thin films were dried for 6 h at room temperature in a vacuum. Cyclic voltammetries were recorded on a BAS CV-50W Electrochemical Analyzer. The polymer films casted on a Pt electrode were scanned positively and negatively in an anhydrous acetonitrile solution (0.1 M) of tetrabutylammonium perchlorate (TBAP). Powder X-ray diffraction (XRD) data were obtained with a Rigaku RINT 2500TN.

Monomer Synthesis [9]

A mixture of 1.09 g (10.3 mmol) of tropone, 8.23 g (51.5 mmol) of bromine, and 2.58 g (31.2 mmol) of sodium acetate in 54 mL of acetic acid was stirred at 80 °C for 3 h and heated to reflux for 1 h. After the reaction, the solution was cooled and acetic acid was removed under the reduced pressure. Purification by a column chromatography (SiO_2, methylene chloride : hexane = 9 : 1 as an eluting solvent) gave 2,7-dibromotropone in 0.58 g (21 %) as a pale yellow powder. ^1H NMR (200 MHz, DMSO-d_6, δ (ppm)) 8.40 (2H, dd, *J* = 6.66, 3.64 Hz), 7.13 (2H, dd, *J* = 6.65, 3.64 Hz). ^{13}C NMR (50 MHz, DMSO-d_6, δ (ppm)) 174.7, 140.9, 138.8, 133.7. IR (KBr disk, cm^{-1}) 3048.9, 2919.7, 1616.9, 1602.7, 1589.1 ($\nu_{C=O}$), 1567.8, 1481.1, 1446.4, 1348.6, 1251.6, 1199.5, 1079.9, 991.2, 958.5, 914.3, 768.5, 736.7, 669.2, 614.2, 432.0. Elemental Analysis, Calcd for $C_7H_4Br_2O$: C, 31.86 % H, 1.53 %, Found: C, 31.73 %, H, 1.55 %.

*Synthesis of a PPV type Polymer (**P1**)*

A mixture of 0.008 g (0.038 mmol) of $Pd(OAc)_2$, 0.155 g (1.89 mmol) of NaOAc, 0.100 g (0.380 mmol) of 2,7-dibromotropone, and 0.168 g (0.380 mmol) of 1,4-diethenyl-2,5-bis(decyloxy)benzene in 6 mL of 1-methyl-2-pyrrolidinone (NMP) was stirred for 1.5 h at room temperature and 4 h at 80 °C under nitrogen. The polymer was precipitated from methanol and dried *in vacuo* to obtain a violet powder (**P1**) in 0.12 g (56 %). ^1H NMR (200 MHz, $CDCl_3$, δ (ppm)) 8.13-6.72 (aromatic + vinylene protons), 4.05 (*trans* OCH_2), 3.62 (*cis* OCH_2), 1.85-1.83 (OCH_2CH_2), 1.60-1.26 (C_7H_{14}), 0.87-0.84 (CH_3). ^{13}C NMR (50 MHz,$CDCl_3$, δ (ppm)) 184.9, 179.1, 151.3, 146.5, 145.2, 140.7, 138.5, 133.3, 131.7, 130.4, 129.3, 127.6, 127.0, 126.6, 110.2, 109.5, 31.7, 29.5, 29.4, 29.2, 28.6, 26.1, 22.5, 13.9. IR (KBr disk, cm^{-1}) 2921.6, 2852.2, 2602.7, 2358.3, 2341.6, 1608.3, 1567.8 ($\nu_{C=O}$), 1494.6, 1467.6, 1421.3, 1387.4, 1330.6, 1250.9, 1203.4, 1024.0, 972.0, 747.1, 721.1.

*Synthesis of a PPP type Polymer (**P2**)*

To a stirred solution of 0.100 g (0.380 mmol) of 2,7-dibromotropone and 0.182 g (0.380 mmol) of [2,5-bis(decyloxy)-1,4-phenylene]diboronic acid in 6 mL of THF was added 0.207 g (1.50 mmol) of K_2CO_3 in 1.5 mL of H_2O and 0.043 g (0.038 mmol) of $Pd(PPh_3)_4$ under nitrogen. After refluxing for 12 h, the polymer was precipitated from methanol. After drying *in vacuo*, a yellow powder (**P2**) was obtained in 0.11 g (56 %). ^1H NMR (200 MHz, $CDCl_3$, δ (ppm)) 7.35-7.30 (aromatic protons), 6.97-6.90 (tropone protons), 3.86-3.79 (OCH_2), 1.59-1.43 (CH_2), 1.21-1.19 (C_7H_{14}), 0.91-0.83 (CH_3). ^{13}C NMR (50 MHz, $CDCl_3$, δ (ppm)) 185.6, 149.6, 148.6, 135.5, 131.7, 131.0, 125.4, 116.1, 69.5, 34.1, 31.8, 30.2, 29.6, 29.5, 29.3, 25.9, 22.6, 14.0. IR (KBr disk, cm^{-1}) 2922.3, 2850.7, 1623.8, 1591.0 ($\nu_{C=O}$), 1496.5, 1467.6, 1411.6, 1378.9, 1345.8, 1261.2, 1209.2, 1028.0, 860.6, 800.3.

*Synthesis of a PPE type polymer (**P3**)*

To stirred mixture of 0.100 g (0.380 mmol) of 2,7-dibromotropone and 0.167 g (0.380 mmol) of 1,4-diethynyl-2,5-bis(decyloxy)benzene in 14 mL of toluene and 2 mL of triethylamine was added 0.026 g (0.038 mmol) of $PdCl_2(PPh_3)_2$ and 0.007 g (0.038 mmol) of CuI under nitrogen. The polymerization was performed for 2 h at room temperature, and the polymer was precipitated from methanol. After drying *in vacuo*, a black powder (**P3**) was obtained in 0.19 g (88 %). IR (KBr disk, cm^{-1}) 2921.6 , 2850.3, 1598.7 ($\nu_{C=O}$), 1494.6, 1465.6, 1434.8, 1417.4, 1375.0, 1274.8, 1267.3, 1209.2, 1039.3, 863.6, 822.4.

Results and Discussion

Polymerization and Characterization

Monomer (2,7-dibromotropone) was synthesized by the bromination of tropone with bromine in the presence of sodium acetate in acetic acid. The structure and purity of the monomer was confirmed by the NMR, IR, and elemental analysis. Polymers (**P1**, **P2**, and **P3**) were obtained by Heck reaction, Suzuki coupling, and Sonogashira coupling, respectively. When the reaction ended, the polymers were precipitated from methanol. The polymerization of **P1** proceeded smoothly to obtain a violet powder in 56 % yield. The number-averaged molecular weight (M_n) of **P1** was estimated from the GPC analysis to be 4000, which corresponds to the repeating unit of eight. The polydispersity index (M_w/M_n) was about 1.4. The structure of **P1** was confirmed by the NMR (^{1}H and ^{13}C) and IR spectra. **P1** was predominantly consisted of the *trans*-vinylene conformation from the result of the ^{1}H NMR spectrum (Figure 2) as with **P4** that was prepared by Wittig polycondensation in our laboratory. The aromatic proton signals were divided into three portions and they were difficult to be assigned, but the total integral ratio agreed with the theoretical value. The IR spectrum of **P1** indicated that the stretching vibration of the tropone carbonyl group ($\nu_{C=O}$) was observed at 1568 cm^{-1}, which shifted to the lower wavenumber region compared with that of tropone (1638 cm^{-1}). Likewise, soluble **P2** was obtained as a yellow powder in 55 % yield (M_n = 6800, M_w/M_n = 1.3). The IR spectrum of **P2** indicated that $\nu_{C=O}$ was found at 1590 cm^{-1}. While **P1** and **P2** were soluble in common organic solvents such as chloroform, THF, and toluene, **P3** was sparingly soluble in organic solvents irrespective of the polymerization condition. Therefore the structure of **P3** was only confirmed by the IR spectrum, where $\nu_{C=O}$ was observed at 1599 cm^{-1}. Accordingly, the $\nu_{C=O}$ values were considered to be associated with the effective conjugation length of the polymer (*vide infra*).

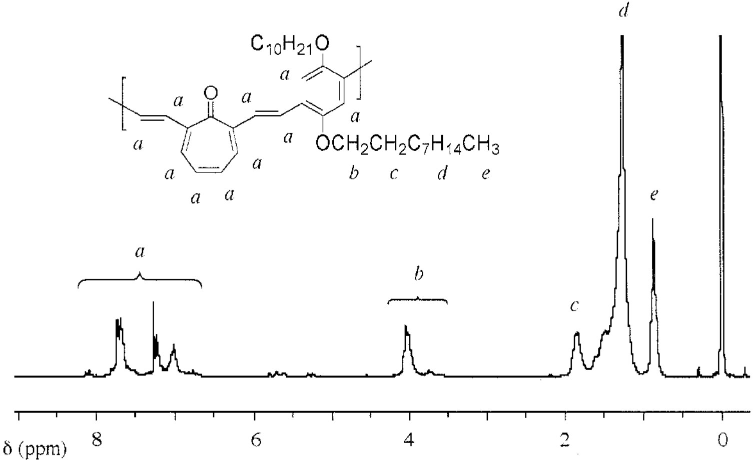

Figure 2. ^{1}H NMR Spectrum of **P1** in $CDCl_3$ (200 MHz).

Optical Properties in Solution and Solid States

The UV spectra of **P1**, **P2**, and **P4** in the chloroform solution had a maximum absorption wavelength at 515 nm, 400 nm and 434 nm, respectively, as shown in Figure 3. Although both **P1** and **P4** had a similar PPV type backbone and the content of the *trans*-vinylene conformation was almost the same (ca. 80 %), **P1** bearing tropone demonstrated a red shift of the maximum peak as much as 81 nm from that of **P4** bearing benzotropone. This result seems to be inconsistent with the optical property of the low molecular weight benzenoid compounds, where the annulation of benzene most likely extends the π-conjugation of the system to result in a red shift of the UV spectra. In the case of tropone-containing conjugated polymers, π-conjugation length might be associated with the degree of polarization of the tropone carbonyl group. The carbonyl group of **P1** polarizes better than that of **P4**, judging from the IR spectra of **P1** ($\nu_{C=O}$ = 1568 cm^{-1}) and **P4** ($\nu_{C=O}$ = 1603 cm^{-1}), which well reflects the characteristic of tropone and benzotropone [5]. It can be considered that the partially generated positive charge in **P1** moves along the polymer backbone to cancel the main chain distortion, resulting in the longer effective conjugation length. This account agrees with our previous observation that the carbonyl stretching vibration peak shifts to the lower energy region as the effective conjugation length became longer from monomer to polymer. The maximum absorption wavelength of **P2** blue shifted from that of **P1**, which originated from the steric repulsion between tropone and alkoxy-substituted benzene. The cut-off wavelengths in the UV spectra of **P1** and **P2** (**P1**: 691 nm and **P2**: 508 nm) were observed at the much longer wavelength than those of conventional PPV and PPP without the tropone segment.

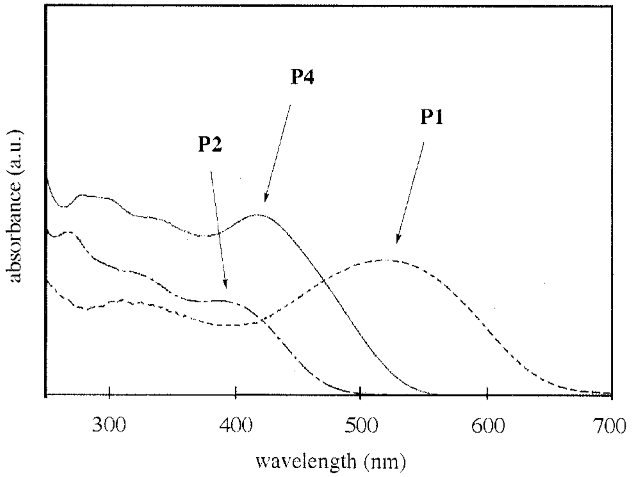

Figure 3. UV Spectra of **P1**, **P2**, and **P4** in chloroform (1.0 x 10^{-5} M).

The fluorescence spectra of **P1**, **P2**, and **P4** in the chloroform solution are shown in Figure 4. **P4** emitted an orange fluorescence at 566 nm, while the emission from **P2** was very weak and **P1** was non-emissive polymer. As described above, the carbonyl group of **P1** polarizes better than that of **P4** and hence the excitation energy of **P1** (and also **P2**) might be consumed by the motional energy of the carbonyl stretching vibration to result in the non-radiative decay.

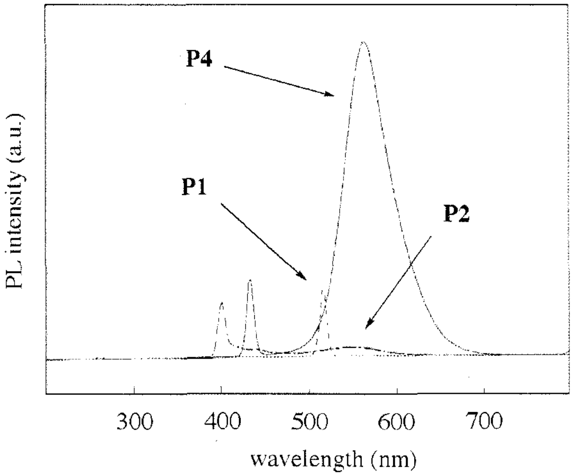

Figure 4. PL Spectra of **P1**, **P2**, and **P4** in chloroform (1.0 x 10^{-5} M).

The optical and electrochemical properties of **P1** and **P4** are summarized in Table 1. Comparing the absorption maximum peaks in the solution and solid states, **P1** showed a red shift by 12 nm and **P4** only shifted by 2 nm. From these results, it can be expected that **P1** has an aggregated structure than **P4** in the solid state. The electrochemical properties of **P1** and **P4** in the film state were investigated by using CV. Both polymers exhibited irreversible p- and n-doping processes. The electrochemical band gaps of the polymers could be calculated from the difference of onset potentials in the oxidation and reduction processes, which approximately match with the optical band gaps estimated from the absorption edge in the UV spectra of the polymer films. **P1** had a relatively narrow band gap energy.

Table 1. Optical and Electrochemical Properties of **P1** and **P4**.

Polymer	λ_{max} (nm)		Band gap (eV)	
	Solution state[a]	Film state[b]	UV[c]	CV[d]
P1	515	527	1.55	1.60
P4	434	436	1.93	2.04

[a]Measured in the chloroform solution (1.0 x 10^{-5} M). [b]Measured in the spin-coated film on the quartz grass. [c]Calculated from the absorption edge. [d]Calculated from the oxidation and reduction onset potentials.

We subsequently performed a proton-doping experiment by exposing polymer films to the vapor of trifluoroacetic acid. The absorption peak at 434 nm observed in the virgin **P4** decreased and the absorption peak at 300 nm increased, keeping an isosbestic point at 380 nm [10]. On the contrary, the UV spectral pattern of **P1** did not change at all. It is supposed that the degree of π-electron delocalization in **P4** can be altered by the proton-induced polarization of the carbonyl group, but the carbonyl group of **P1** naturally polarizes and is not influenced by the protonation.

Powder XRD Study

Figure 5 illustrates powder XRD patterns of **P1** and **P4**. **P4** showed two distinct peaks at 2θ = 4.2° and 19.7°. The d spacing values corresponding to these peaks were calculated to be 21 Å and 4.5 Å, which can be assigned to distances between polymer chains separated by the decyloxy chains and by the π-stacking interaction, respectively. While **P1** showed similar peaks at d = 21 Å and 4.0 Å, they were broader than those of **P4**. By comparing the d spacing values, **P1** is considered to have a stronger tendency to form π-π stacking structure rather than **P4**, which may be correlated with the planar polymer chain caused by the polarization of the tropone carbonyl group (*vide supra*).

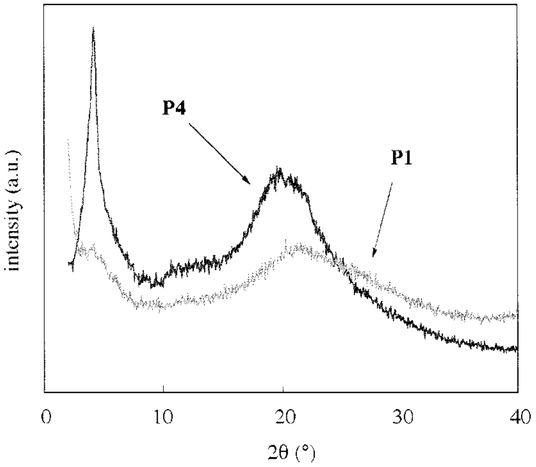

Figure 5. Powder XRD patterns of **P1** and **P4**.

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