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Synthesis of Conjugated Polymers Containing Phosphole with the 5-Member Fused Carbocycle

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Summary

Novel conjugated polymers **9a–c** possessing the phosphole ring with the 5-member fused carbocycle were synthesized by palladium catalyzed coupling reaction of 1-phenyl-2,5-bis(*p*-bromophenyl)phosphole **7** with diethynylarenes **8a–c**. The obtained polymers **9a–c** had the regio-regulated 2,5-substituted phosphole ring in the polymer main chain, and were characterized by ^{1}H, ^{13}C, ^{31}P NMR, and FTIR. The ^{31}P NMR spectra revealed that the extension of π-conjugation changed the phosphole ring angles. The optical properties of polymers **9a–c** were independent of the size of the fused carbocycle.

Introduction

Over the years, organic conjugated polymer bearing a five-membered heteroaromatic ring, e.g., thiophene, pyrrole, and silole, have received considerable attention for applications in electronic and optic devices such as light emitting diodes (LEDs), thin-film transistors, photovoltaic cells, and chemical sensors [1]. Each heteroaromatic moiety has a distinctive aromatic character and electron density, which reflects the nature of each heteroatom. The introduction of various types of heteroaromatic units into conjugation systems makes it possible to alter the electrical and optical properties of the target compounds at a molecular level [2]. Among the five-member heteroaromatic rings, phosphole is an interesting building block for the construction of conjugation systems due to its low aromatic character and versatile reactivity at the phosphorus center [3]. Since the appearance of the first report on phosphole in 1953 [4], phosphole chemistry has undergone gradual development [5]. In particular, Réau and co-workers have recently carried out an extensive study on phosphole-containing conjugation systems [6]. In view of the increasing importance of the conjugated systems comprising phosphole, studies on the synthesis of conjugated polymers possessing the phosphole unit in the polymer main chain is worth investigating. However, the use of phosphole as the building block for the conjugated polymers has not received considerable attention [3d,6,7]. Tilley and co-workers reported the first synthesis of phosphole-containing conjugated polymer **1** with both 2,4- and 2,5-substituted phosphole rings; the polymer was synthesized using the zirconacyclopentadiene intermediate [8] (Figure 1). Réau's group synthesized conjugated polymer **2** comprising phosphole and thiophene units by the electrolytic polymerization [6a] (Figure 1). In addition, we also synthesized conjugated polymers **3** by the Sonogashira-coupling reaction, which contained a regio-regulated phosphole ring with a six-member fused carbocycle [9].

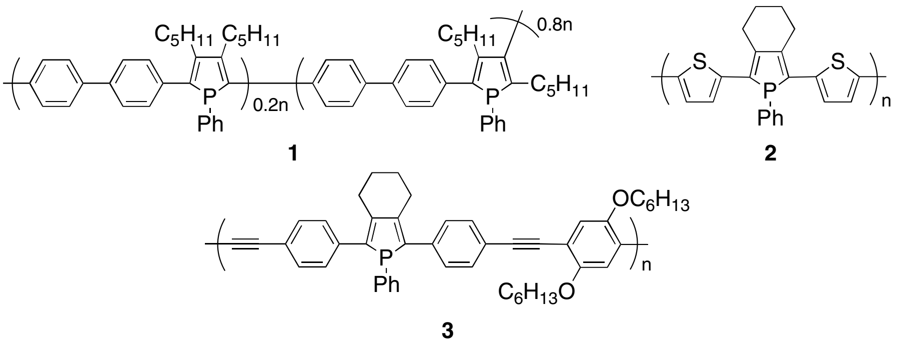


Figure 1. Phosphole-containing conjugated polymers **1** [8], **2** [6a], and **3** [9].

In this study, we synthesized 2,5-substituted phosphole monomer **7** with a five-member fused carbocycle and prepared novel conjugated polymers **9a–c** that contained this phosphole unit in the conjugated main chain. Further, the characterization and the optical properties of these polymers **9a–c** are discussed.

Experimental

General

NMR spectra were recorded on JEOL JNM-EX270 spectrometer or JEOL EX400 spectrometer. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard (for ^1H and ^{13}C) or H_3PO_4 as an external standard (for ^{31}P). UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI 8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. All experiments were performed under dry argon. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. NEt_3 was distilled from potassium hydroxide under nitrogen. 1-Bromo-4-iodobenzene, 1,6-heptadiyne, zirconocene dichloride, $PdCl_2(PPh_3)_2$, *n*-BuLi, CuCl, and $PhPCl_2$ were obtained commercially, and used without further purification. 2,5-Dihexyloxy-1,4-diethynylbenzenes **8a** and 9,9-dihexyl-2,7-diethynylfluorene **8b** were prepared as described in the literature [10,11]. 1,4-Diethynyl-tetrafluorobenzene **8c** was prepared as described in the literature with minor modification [12].

Synthesis

*1,7-Bis(4-bromophenyl)hepta-1,6-diyne **4***

A 200 mL flask was charged with 1-bromo-4-iodobenzene (14.7 g, 50 mmol), 1,7-heptadiyne (2.4 g, 25 mmol), $PdCl_2(PPh_3)_2$ (0.88 g, 1.25 mmol), CuI (0.25 g, 1.25 mmol), 100 mL of anhydrous THF, and 30 mL of dry NEt_3. The reaction was carried out at 0 °C for 12 h with stirring. The reaction mixture was filtered to eliminate ammonium salts. Solvent was evaporated and then purified by column chromatography (SiO_2, hexane). Recrystallization from methanol provided a white solid (4.5 g, 11 mmol, 45% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.89 (quin, J = 7.0 Hz, 2H), 2.57 (t, J = 7.0 Hz, 4H), 7.26 (d, J = 8.1 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.7, 27.7, 80.3, 90.3, 121.7, 122.7, 131.4, 133.0; HRMS (FAB) calcd for $C_{19}H_{14}{}^{79}Br_2$ M^+: 399.9462, found 399.9466; IR (film) 2236 cm^{-1}. Anal. Calcd for $C_{19}H_{14}Br_2$: C, 56.75; H, 3.51; Br, 39.74%. Found: C, 56.81; H, 3.44; Br, 39.71%.

*1-Phenyl-2,5-bis(4-bromophenyl)phosphole **7***

A 100 mL flask was charged with Cp_2ZrCl_2 (0.73 g, 2.5 mmol) and 20 mL anhydrous THF under argon. This solution was cooled to -78 °C and *n*-BuLi (3.2 mL of 1.6 M hexane solution, 5.0 mmol) was added dropwise. The resulting solution was stirred at -78 °C for 30 min. 1,7-Bis(4-bromophenyl)hepta-1,6-diyne **4** (1.0 g, 2.5 mmol) in 30 mL THF was added slowly. The resulting solution was warmed to room temperature and stirred for an additional 6 h. The mixture was cooled to 0 °C, and then CuCl (0.49 g, 5.0 mmol) was added directly under a flow of argon. The color of the solution changed from light red to dark green. After stirring for 30 min, $PhPCl_2$ (0.44 g, 2.5 mmol) was added slowly by a syringe. The reaction mixture was stirred overnight, and the solvent was removed under reduced pressure. The crude residue was dissolved in degassed $CHCl_3$ and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$. Solution was plugged through basic alumina column to remove zirconium species. Solvent was evaporated and the residue was subjected to column chromatography (silica gel, degassed hexane/$CHCl_3$ under argon) to give the pure product **7** (0.42 g, 0.82 mmol, 33%) as a bright yellow solid. ^1H NMR (270 MHz, $CDCl_3$): δ 2.33 (m, 1H), 2.42 (m, 1H), 2.71 (m, 2H), 2.92 (m, 2H), 7.16 (m, 2H), 7.31-7.39 (m, 11H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 29.1, 30.1, 118.5, 120.2, 128.8, 129.5, 131.6, 133.2, 134.2, 134.9, 136.6, 155.3; $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +35.6 ppm; HRMS (FAB) calcd for $C_{25}H_{19}{}^{79}Br_2P$ M^+: 507.9591, found 507.9585.

*1,4-Diethynyl-tetrafluorobenzene **8c***

A 100 mL flask was charged with 1,4-dibromotetrafluorobenzene (2.0 g, 6.5 mmol), trimethylsilylacetylene (1.9 g, 20 mmol), $PdCl_2(PPh_3)_2$ (0.46 g, 0.65 mmol), CuI (0.12 g, 0.65 mmol), NEt_3 (10 mL), and THF (35 mL). The reaction was carried out at 70 °C for 6 h with stirring. After the reaction, the mixture was filtered to eliminate ammonium salts and then treated with 0.5 M aqueous KOH solution (2.0 mL). The organic layer was concentrated, and the crude residue was dissolved in pentane, followed by washing with water. The organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was dissolved in a small amount of MeOH, and then reprecipitated from water to obtain **8c** (0.62 g, 3.1 mmol, 48%) as a white solid. Spectral data of **8c** matched the literature values [12].

Polymerization

A typical procedure is as follows [13]. A mixture of **7** (0.77 g, 1.50 mmol), **8a** (0.49 g, 1.50 mmol), $PdCl_2(PPh_3)_2$ (53 mg, 0.075 mmol), CuI (14 mg, 0.075 mmol), NEt_3 (10 mL), and THF (30 mL) was placed in a 100 mL flask under an argon atmosphere. The reaction was refluxed for 48 h with stirring. After the reaction, precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and poured into degassed MeOH (50 mL) to precipitate the polymer. All work-up procedures were carried out under an argon atmosphere. The resulting polymer **9a** was filtered, washed with MeOH, and dried in vacuo to give 0.67 g (1.00 mmol, 67%) as a dark yellow powder.

9a. Yield: 67%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (br, 6H), 1.26 (m, 8H), 1.42 (br, 4H), 1.74 (br, 4H), 2.22 (br, 2H), 2.70 (m, 4H), 3.91 (m, 4H), 6.7-7.6 (m, 15H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 25.6, 29.1, 29.2, 29.4, 31.5, 69.7, 82.3, 94.9, 112.6, 114.6, 116.8, 117.7, 121.1, 127.6, 128.1, 128.5, 131.2, 131.8, 133.7, 153.4, 157.3; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ +27.2 ppm. IR (film) 2203 cm^{-1}.

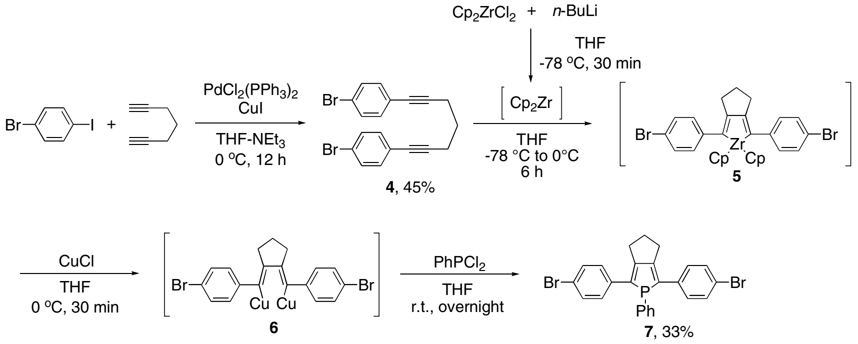
9b. Yield: 88%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.60 (br, 4H), 0.76 (br, 6H), 1.04 (br, 12H), 1.96 (br, 4H), 2.31 (br, 2H), 2.79 (m, 4H), 6.9-7.7 (m, 19H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.9, 22.6, 23.7, 29.4, 29.7, 31.5, 40.3, 55.2, 73.0, 84.6, 120.0, 120.8, 121.1, 121.8, 126.5, 128.4, 129.1, 129.9, 131.2, 131.8, 132.2, 133.4, 133.9, 151.2, 157.4; $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ +27.3 ppm. IR (film) 2203 cm^{-1}.

9c. Yield: 34%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.25 (br, 2H), 2.46 (m, 2H), 2.71 (br, 2H), 6.7-7.6 (m, 13H); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ +27.3 ppm. IR (film) 2210 cm^{-1}.

Results and Discussion

The synthetic route to prepare the phosphole monomer **7** is shown in Scheme 1. 1,7-Bis(4-bromophenyl)hepta-1,6-diyne **4** was prepared in 45% yield by the reaction of two equivalents of 1-bromo-4-iodobenzene with 1,6-heptadiyne in the catalytic system of $PdCl_2(PPh_3)_2$/CuI in THF-Et_3N at 0 °C for 12 h. Subsequently, the treatment of **4** with zirconocene, which was formed by the reaction of zirconocene dichloride with *n*-BuLi [14], yielded a red solution of zirconacyclopentadiene intermediate **5**. After this intermediate **5** was converted into **6** with two equivalents of CuCl [15], $PhPCl_2$ was added to obtain the desired monomer **7** in 33% yield. The structure of monomer **7** was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectra and HRMS. In the ^{31}P NMR spectrum, a singlet peak was observed at δ + 35.6 ppm (Figure 2). Co-monomers **8a** and **8b** were prepared as described in the literature [10,11], and co-monomer **8c** was prepared by a modified procedure [12].

Scheme 1



The procedure for polymer synthesis is outlined in Scheme 2, and the results are summarized in Table 1. The polymerization of **7** with **8a** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$/CuI in THF-Et_3N at 70 °C for 48 hours under an argon atmosphere proceeded smoothly to yield the corresponding polymer **9a** in 67% yield as a dark yellow powder (Table 1). The structures of polymers **9a–c** were also characterized by ^{1}H, ^{13}C, and ^{31}P NMR and FT-IR spectra. The ^{31}P NMR spectrum of **9a** exhibited a strong peak at δ +27.2 ppm, as shown in Figure 2. This ^{31}P signal (δ +27.2 ppm) of polymer **9a** was shifted upfield in comparison with that of monomer **7** (δ+35.6 ppm) after the formation of the conjugated polymer. Réau and co-workers reported that the size of the fused carbocycle on the phosphole ring influenced the angles around the phosphorus atom, resulting in the shift of ^{31}P signals [6b]. These findings imply that an extension of π-conjugation by polymerization modifies the phosphole ring angles. On the other hand, the change of ^{31}P chemical shifts of polymers **9a–c** was not remarkable (δ+ 27.2, δ + 27.3, and δ +27.3 ppm for **9a**, **9b**, and **9c**, respectively) regardless of the

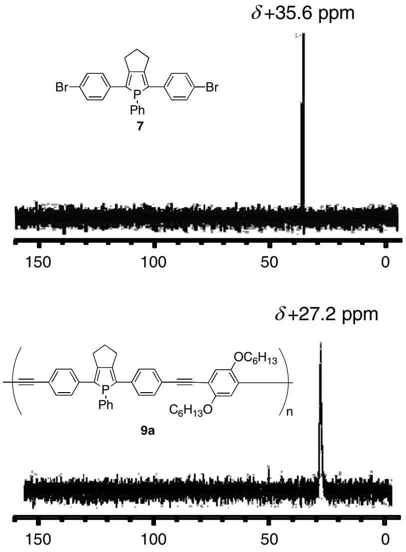
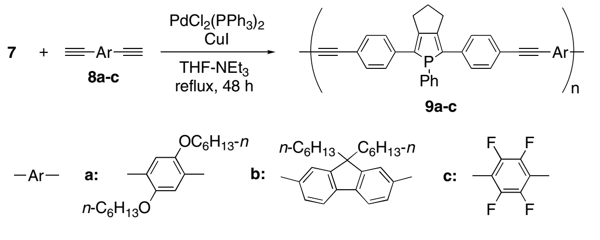


Figure 2. ^{31}P NMR spectra of monomer **7** and polymer **9a**.

Scheme 2



electronic characteristic of co-monomer units; this was because the lone pair of the phosphorus atom slightly participated in the conjugation system.

Table 1. Synthesis of Polymers **9a–c**

Polymer	Yield[a] (%)	M_w[b]	M_n[b]	M_w/M_n[b]
9a	67	5000	3500	1.41
9b	88	4700	3800	1.23
9c	34	7000	6800	1.03

[a] Isolated yield after reprecipitation. [b] GPC ($CHCl_3$), polystyrene standards.

The molecular weight measurement was performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards, and the results are listed in Table 1. Polymer **9a** had a number-average molecular weight (M_n) of 3500, which corresponded to a degree of polymerization of approximately 5. Polymers **9a** and **9b** were soluble in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene, while polymer **9c** was partly soluble in THF and $CHCl_3$. Polymers **9a–c** were relatively stable in the solid state in air; however, they were gradually oxidized in a homogeneous solution.

Table 2. Optical Properties of Polymers **9a–c**

Polymer	UV		PL	
	λ_{max}[a] (nm)	$\log\varepsilon$	λ_{max}[a,b] (nm)	Φ_F[c]
3	410	4.53	490	0.09
9a	398	4.39	466	0.39
9b	408	5.30	479	0.23
9c	395	4.00	470	0.18

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ at room temperature.
[b] Excited at the absorption maximum. [c] The quantum efficiency (Φ_F) was calculated in dilute $CHCl_3$ at room temperature by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard.

The optical properties of polymers **9a–c** were exmined, and the results are summarized in Table 2. The absorption and emission spectra of all the polymers were recorded in a dilute $CHCl_3$ solution at room temperature, and those of polymer **9a** are shown in Figure 3 as a representative example. Polymer **9a** exibited a strong UV absorption maximum (λ_{max}) at 398 nm, which could be attributed to the π–π* transition. This

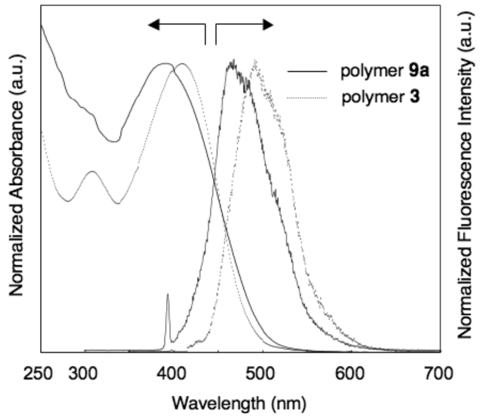


Figure 3. UV-vis absorption spectra of polymer **9a** and **3** in $CHCl_3$ (3.0×10^{-5} M), and fluorescence emission spectra of **9a** and **3** in $CHCl_3$ (2.0×10^{-6} M) at room temperature.

absorption was bathochromically shifted with respect to the absorption of monomer **7** (λ_{max} = 378 nm). Figure 3 shows the absorption and emission spectra of polymer **3**, which possesses the phosphole unit along with the six-member carbocycle, and Table 2 also shows optical data on polymer **3** [9]. As observed in Figure 3, the effect of the size of the fused carbocycle was not pronounced for the π–π^* transition of the conjugated polymer chain. The absorption maximum of polymer **9a** (λ_{max} = 398 nm) was approximately 10 nm of shorter wavelength than that of polymer **3** (λ_{max} = 410 nm), as shown in Figure 3 and Table 2. This difference is probably related to the conjugation length due to the difference in M_n (M_n is 3500 and 10200 for polymers **9a** and **3**, respectively). The general trends were similar for polymers **9b** and **9c**, which had absorption maxima at 408 and 395 nm (Table 2), respectively. The fluorescence emission spectrum of the solution of **9a** in chloroform (2.0×10^{-6} M) at room temperature upon excitation at 390 nm exhibited an emission peak at 490 nm in the visible bluish green region. The maximum emission peak of **9a** also exhibited a shorter wavelength than that of polymer **3**. Polymers **9a–c** exhibited moderate quantum efficiencies in a chloroform solution (Table 2). The efficiencies were estimated by using 9-anthracenecarboxylic acid in CH2Cl2 as a standard [16].

In conclusion, we successfully synthesized novel conjugated polymers possessing 2,5-diphenylphosphole with a 5-member fused carbocycle as a repeating unit in the main chain. It was inferred from the ^{31}P NMR measurement that the extension of π-conjugation by polymerization changed the phosphole ring angles. The optical properties of the polymers were independent of the size of the fused carbocycle. Further studies on the application of phosphole-containing conjugated polymers to optical devices and the enhancement of their device performance are currently in progress.

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16. The absorbance of each sample was below 0.05 at the excitation wavelength at 350 nm, in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{unk} = \Phi_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{D,std}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_D is the refractive index [CH_2Cl_2 ($n_D = 1.424$) and $CHCl_3$ ($n_D = 1.446$) were used]