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Articles

Synthesis and Properties of First Well-Defined Phosphole-Containing π-Conjugated Polymers

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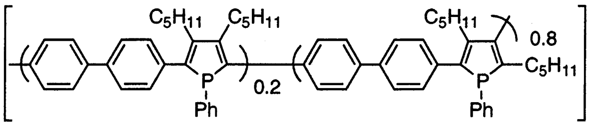
ABSTRACT: Novel π-conjugated polymers **10a**−**c** having the phosphole unit were prepared by palladium complex-catalyzed coupling of bis(*p*-bromophenyl)phosphole (**7**) with diethynylarenes **9a**−**c**. The obtained polymers **10a**−**c** were regio-regulated with the 2,5-substituted phosphole unit and characterized by ^{1}H and ^{31}P NMR. Polymers **10a**−**c** were found to be an extended π-conjugated system according to the results of the UV−vis absorption spectra. In the fluorescence emission spectra of **10**, moderate emission peaks were observed in the visible region. These polymers showed electron-donating properties in cyclic voltammometry measurements.

Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers[1] due to their intriguing properties such as electrical conductivity,[2] electroluminescence,[3] liquid crystallinity,[4] third-order nonlinear optical properties,[5] and chemical sensing.[6] Among these polymers, π-conjugated polymers bearing a heteroaromatic unit as a π-electron system, especially the heterocyclopentadienes such as thiophene, pyrrole, and silole, have been synthesized, and their conductive and photochemical behaviors have been investigated extensively.[1] On the other hand, few phosphole-containing π-conjugated polymers are known,[7] despite their numerous applications to organic and organometallic chemistry.[8] Tilley and co-workers reported the first synthesis of a phosphole-containing π-conjugated polymer (**1**) with both 2,4- and 2,5-substituted phosphole units by zirconocene coupling of dialkyne and the following reaction of zirconacyclopentadiene-containing polymer with $PhPCl_2$, which exhibited an emission peak at 470 nm in the visible bluish-green region with a large Stokes shift of 162 nm.[7a] Although oligophospholes have been synthesized and characterized in detail by Mathey et al.,[7b−d] to our knowledge, there have been no well-defined and well-characterized π-conjugated polymers having a phosphole unit in the main chain as a repeating unit.[7e] The π-conjugated polymers consisting of the regio-regulated phosphole unit would provide efficient optical and/or electronic properties. Here, we report the preparation and physical properties of novel π-conjugated polymers having a 2,5-substituted phosphole skeleton in the main chain.



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Results and Discussion

The preparation route for monomer **7** is summarized in Scheme 1. The chemoselective $PdCl_2(PPh_3)_2$/CuI-catalyzed cross-coupling[9] of 1,4-bromoiodobenzene (**2**) and 1,7-octadiyne (**3**) provided 1,8-bis(4-bromophenyl)-octa-1,7-diyne (**4**) in 58% yield. Then, the treatment of **4** with zirconocene, generated by the reaction of zirconocene dichloride with Bu^{n}Li,[10] gave the red solution of zirconacyclopentadiene (**5**), which was used in situ for the next step. After **5** was converted into **6** with 2 equiv of CuCl,[11] $PhPCl_2$ was added to give the desired monomer (**7**) having phosphole as a core in 49%

Scheme 1

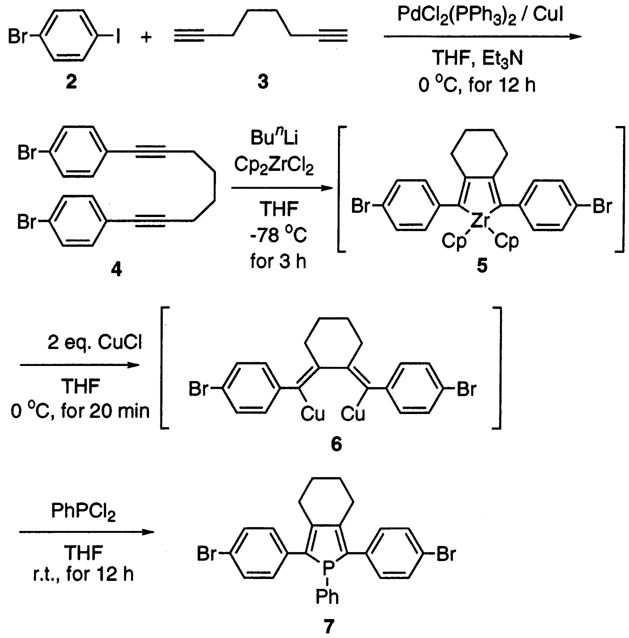

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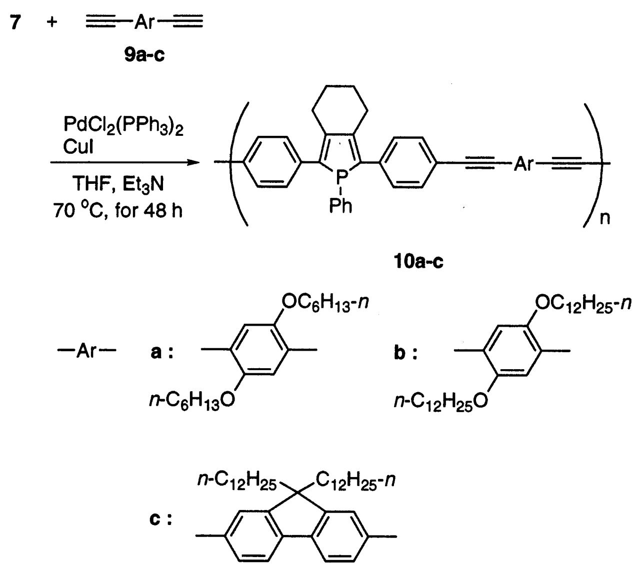
Table 1. Syntheses and Optical Properties of Polymers 10a–c[a]

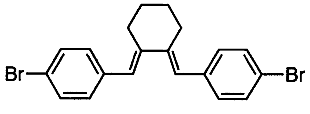
						UV λ_{max}[c]		PL λ_{max}[c,d]	
run	polymer	yield[a] (%)	M_w[b]	M_n[b]	M_w/M_n[b]	nm	log ϵ[c]	nm	Φ_F[e]
1	**10a**	46	15 400	10 200	1.5	410	4.53	490	0.09
2	**10b**	51	14 000	10 000	1.4	414	4.52	487	0.14
3	**10c**	16	9 000	6 800	1.3	382	4.80	435	0.08

[a] Isolated yields after reprecipitation into MeOH. [b] GPC ($CHCl_3$), polystyrene standards. [c] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [d] Excited at 410 nm. [e] The quantum yield (Φ_F) was calculated in $CHCl_3$ at room temperature by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard.

Scheme 2



yield on the basis of **4**. In the absence of CuCl, the reaction of **5** with $PhPCl_2$ gave the corresponding monomer (**7**) in low yield (~10%), and a large amount of hydrolyzed bis(*p*-bromophenyl)diene (**8**) was obtained as a byproduct after treatment. Comonomers **9a–c** were prepared as described in the literature.[12,13]



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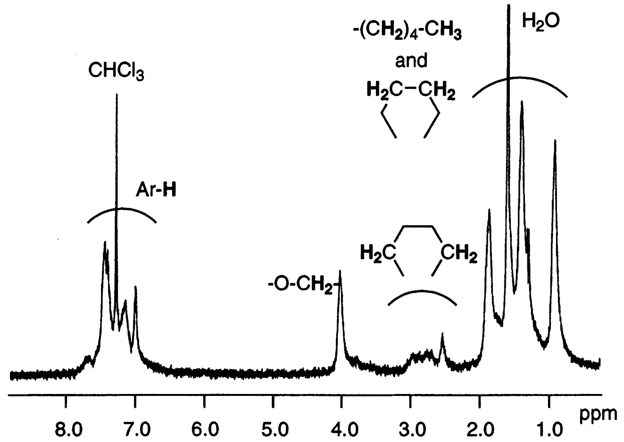


Figure 1. ^{1}H NMR spectrum of **10a** in $CDCl_3$.

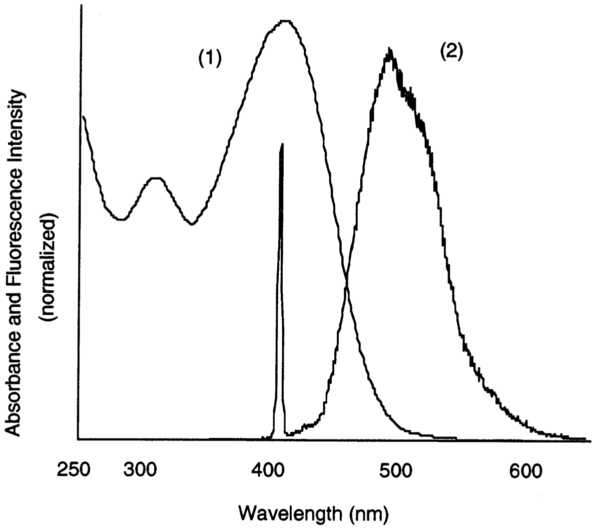
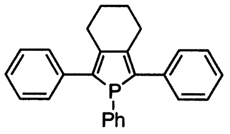


Figure 2. (1) Absorption spectrum of **10a** in $CHCl_3$ and (2) fluorescence spectrum of **10a** in 2.0×10^{-6} M $CHCl_3$ solution (excitation wavelength at 410 nm).

Polymers **10a–c** were synthesized using the Heck–Sonogashira reaction,[9] as shown in Scheme 2. The results obtained from the reaction of bis(*p*-bromophenyl)phosphole (**7**) with the comonomers **9a–c** under optimum conditions are listed in Table 1. For example, the polymerization of **7** with **9a** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$/CuI in THF–Et_3N at 70 °C for 48 h under a nitrogen atmosphere proceeded smoothly to give the corresponding polymer **10a** in 46% isolated yield as a yellow powder (Table 1, run 1). The structures of polymers **10a–c** were confirmed by ^{1}H and ^{31}P NMR spectra. The ^{1}H NMR spectrum of polymer **10a** as the representative polymer is shown in Figure 1. The peaks at 0.88, 1.2–1.8, and 4.0 ppm are the protons of the alkoxy side chain. In addition, the cyclic methylene protons in the phosphole moiety are found at around 1.8 ppm (overlapping) and at 2.5–3.0 ppm. The peaks at 7.0–7.5 ppm are assigned to the aromatic protons. The ^{31}P NMR spectrum of **10a** shows only one signal at 13.2 ppm derived from the phosphole unit. No signals of phosphorus nuclei coordinated to palladium center were observed. The molecular weight measurements were performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). Polymer **10a** had a number-average molecular weight (M_n) of 10 200, which corresponds to a degree of polymerization of 15, with M_w/M_n of 1.5. All polymers **10a–c** were soluble in common solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene. These polymers were stable in air as a solid but were gradually oxidized to phosphole oxide in a homogeneous solution.

Table 1 also summarizes some properties of polymers **10a–c** obtained above. The absorption and emission spectra of polymer **10a**, as a typical representative example, are shown in Figure 2. In a dilute chloroform solution at room temperature, **10a** exhibited a strong UV absorption maximum at about 410 nm attributed to π–π* transition, which was red-shifted from compound **11** (λ_{max} = 354 nm).[14] This result indicates the effective expansion of the π-conjugation system in the titled polymer. In the fluorescence emission spectrum of the solution of **10a** in chloroform (2.0×10^{-6} M) at room temperature on excitation at 410 nm, the emission peak of **10a** was observed at 490 nm in the visible blue to green region. The emission peak maximum was independent of the concentration of the polymer solution, and in the film state the weak peak maximum at around 490 nm was observed. The absorption and emission spectra of polymer **10a** have a Stokes shift of 80 nm, which is smaller than that observed for polymer **1** (λ_{max} = 308 nm, λ_{em} = 470 nm) reported by Tilley and co-workers.[7a] This result implies that incorporation of an ethynylene unit due to the good coplanarity of the polymer backbone and incorporation of a dialkoxy-substituted benzene ring leads to a large bathochromic shift of λ_{max} with respect to polymer **10a**. In addition, the regioregularity of polymer **10a** would result in this absorption behavior. For polymers **10a** and **10b**, the shapes and peaks of the absorption spectra were almost the same and independent of the length of the alkoxy side chain (runs 1 and 2). On the other hand, in the fluorescence emission spectrum of the solution of copolymer **10c** having an alternating fluorene unit in chloroform on excitation at 390 nm, a peak at 435 nm was observed in the visible blue region (run 3). Polyfluorene and fluorene-containing polymers have attracted more attention in recent years due to their efficient blue PL and EL properties.[15] Optical properties of these phosphole-containing polymers can be tuned by modifying the nature of the comonomer. Polymers **10a**–**c** exhibited moderate quantum efficiencies in chloroform solution (Table 1), and a typical value for these polymers is higher than 0.08 by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard.[16]



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λ_{max} = 354 nm, λ_{em} = 466 nm$^{ref. 14}$

The electrochemical behavior of polymers **10a**–**c** was also investigated by the measurement of cyclic voltammetry in 0.1 M CH_2Cl_2 solution of $Bu^n{}_4NPF_6$ at the sweep rate of 200 mV s^{-1}, in the potential range from 0 to +2.0 vs Ag/Ag$^+$. Polymer **10a** was electrochemically active and gave a single broad oxidation peak at 1.2 V irreversibly (Figure 3). Réau, Nyulászi, and co-workers reported that 2,5-diphenylphosphole (**11**) has an E_{pa} = +0.69 V in 0.2 M $Bu^n{}_4NPF_6$ in CH_2Cl_2.[14] The oxidation peak of **10a** was highly broadened and anodic shifted in comparison with that of **11**. Such a broadening and a shift of the peak have been reported for electrochemically active π-conjugated polymers.[17]

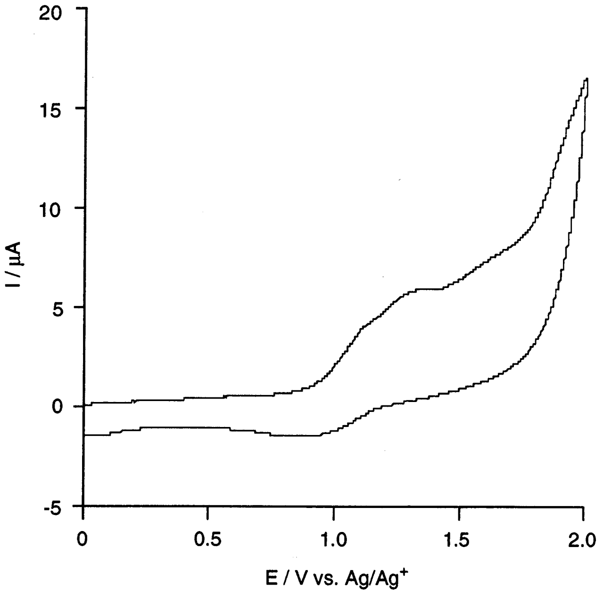

Figure 3. Cyclic voltammogram of **10a** measured in 0.1 M CH_2Cl_2 solution of Bu_4NPF_6 using Pt electrode (vs Ag/Ag$^+$) at the sweep rate of 200 mV/s.

In conclusion, we have synthesized the first well-defined and well-characterized π-conjugated polymers which have phosphole as a repeating unit in the main chain. The extension of π-conjugation via the polymer backbone was observed according to the UV–vis absorption spectra. The obtained polymers are efficient emitters of green (**10a,b**) and blue light (**10c**). Modifying the nature of the phosphorus moiety and changing the comonomer can tune optical and electrochemical properties of the polymers. In this study, we showed that 2,5-substituted phosphole units are attractive building blocks for the preparation of novel π-conjugated polymers. Further studies on the reactivities of these polymers and their applications for the soluble polymer-supported catalyst in organic chemistry are in progress.

Experimental Section

General. The NMR spectra were measured on a JEOL JNM-EX270 instrument for solutions in $CDCl_3$ with Me_4Si as an internal standard (^1H and ^{13}C) or with H_3PO_4 as an external standard (^{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. Cyclic voltammetry was carried out with a BAS CV-50W electrochemical analyzer in CH_2Cl_2 solution of 0.1 M $Bu^n{}_4NPF_6$ as a supporting electrolyte. A platinum wire auxiliary electrode and a Ag/AgCl RE-5 reference electrode were used in the CV measurement. Column chromatography was performed with Wakogel C-300 silica gel.

Materials. THF was distilled from sodium benzophenone ketyl under nitrogen. NEt_3 was distilled from KOH under nitrogen. 1-Bromo-4-iodobenzene, 1,7-octadiyne, $PdCl_2(PPh_3)_2$, CuI, CuCl, Cp_2ZrCl_2, $PhPCl_2$, and Bu^nLi (1.6 M in hexane) were obtained commercially and used without further purification. 1,8-Bis(*p*-bromophenyl)octa-1,7-diyne (**4**),[18] 2,5-dialkoxy-1,4-diethynylbenzenes (**9a** and **9b**),[12] and 9,9-didodecyl-2,7-diethynylfluorene (**9c**)[13] were prepared as described in the literature.

1-Phenyl-2,5-bis(*p*-bromophenyl)phosphole (7). A 100 mL Pyrex flask was charged with Cp_2ZrCl_2 (1.56 g, 5.3 mmol) and 30 mL of anhydrous THF under argon. This solution was cooled to −78 °C, and Bu^nLi (6.8 mL of 1.6 M hexane solution, 11 mmol) was added dropwise. The resulting solution was stirred at −78 °C for 15 min, and **4** (2.2 g, 5.3 mmol) in 20 mL of anhydrous THF was added slowly. The reaction mixture was warmed to room temperature and stirred for 3 h. The mixture was cooled to 0 °C, and then CuCl (1.1 g, 11 mmol) was added directly under a flow of argon. After stirring for 20 min, $PhPCl_2$ (1.4 g, 5.3 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 water. The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the residue was subjected to column chromatography on SiO_2 with degassed hexane/$CHCl_3$ under argon to give the product **7** (1.4 g, 2.6 mmol, 49% yield on the basis of **4**) as a yellow solid. ^1H NMR (270 MHz, $CDCl_3$): δ 1.74 (m, 4H), 2.69 (m, 2H), 2.77 (m, 2H), 7.16 (m, 2H), 7.24 (d, $J = 8.1$ Hz, 4H), 7.37 (d, $J = 8.1$ Hz, 4H), 7.42 (m, 3H). ^{13}C-$\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 22.3, 27.5, 120.5, 127.0, 128.3 (d, $J = 11.0$ Hz), 130.1, 130.7 (d, $J = 7.3$ Hz), 130.8, 132.8 (d, $J = 14.6$ Hz), 133.2 (d, $J = 15.9$ Hz), 137.5, 147.2 (d, $J = 13.4$ Hz). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +14.4 ppm. HRMS (FAB) calcd for $C_{26}H_{21}{}^{79}Br_2P$ M^+: 521.9749, found 521.9750.

Polymerization. A typical procedure is as follows. A mixture of **7** (0.34 g, 0.50 mmol), **9a** (0.22 g, 0.50 mmol), $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol), CuI (5.0 mg, 0.025 mmol), Et_3N (5.0 mL), and THF (20 mL) was placed in a 100 mL Pyrex flask under a nitrogen atmosphere. The reaction was carried out at 70 °C 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 MeOH (50 mL) to precipitate the polymer. The resulting polymer **10a** was filtered, washed with MeOH, and dried in vacuo to give 0.16 g (0.23 mmol, 46%) as a yellow powder.

10a. Yield: 46%. ^1H NMR (270 MHz, $CDCl_3$): δ 0.88 (br, 6H), 1.24−1.84 (m, 20H), 2.50−2.95 (m, 4H), 4.00 (br, 4H), 6.97−7.42 (m, 15H). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +13.2.

10b. Yield: 51%. ^1H NMR (270 MHz, $CDCl_3$): δ 0.86 (br, 6H), 1.19−2.95 (m, 48H), 3.92 (br, 4H), 6.91−7.63 (m, 15H). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +12.5.

10c. Yield: 16%. ^1H NMR (270 MHz, $CDCl_3$): δ 0.60 (br, 4H), 0.85 (br, 6H), 1.05−1.67 (m, 36H), 1.70−2.00 (m, 8H), 3.08 (br, 4H), 7.32−7.70 (m, 19H). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ +12.2.

Note Added after ASAP Posting

This article was released ASAP on 3/5/2003. A value was changed from 0.0025 to 0.025 mmol on page 4, paragraph 1, sentence 2. The correct version was posted on 3/20/2003.

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