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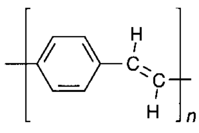
Poly(*p*-phenylenephosphaalkene): A π-Conjugated Macromolecule Containing P=C Bonds in the Main Chain[**]

Vincent A. Wright and Derek P. Gates[*]

Approximately twenty years ago, several examples of stable neutral compounds possessing acyclic (p–p) π bonds involving the heavier p-block elements were prepared.[1] Subsequently, the synthesis, structures, and reactivity of numerous low-coordinate molecules has received extensive study and continues to attract considerable attention.[2] Despite current interest in the preparation of organic macromolecules possessing π-conjugated backbones,[3] to our knowledge, the incorporation of heavy-element multiple bonds into a π-conjugated polymer is unprecedented.[4, 5] Furthermore, the incorporation of inorganic elements into the polymer backbone is synthetically challenging and often results in materials with unique properties.[6] Therefore, the development of methods to prepare π-conjugated polymers containing heavier main-group (p–p) π bonds is of fundamental interest, and may ultimately lead to materials with novel properties.[7] The poly(*p*-phenylenevinylene)s (PPVs) are an exciting class of luminescent organic macromolecules containing C=C bonds which pose many synthetic challenges.[3a,c, 8] However, the possible incorporation of other stable multiple bonds, such as the well-established P=C moiety,[9] into the PPV structure has not been explored.[10] Herein, we report the synthesis and characterization of a poly(*p*-phenylenephosphaalkene), a π-conjugated macromolecule containing phosphorus(III)–carbon double bonds in the polymer backbone.



PPV

An elegant and general route to phosphorus(III)–carbon double bonds involves the rapid and thermodynamically favorable [1,3]-silatropic rearrangement of an acylphosphane to a phosphaalkene (Scheme 1).[1a] From a preparative standpoint, this method is probably the most convenient and versatile route to phosphaalkenes with minimal steric protection.[11] We initiated our investigations by preparing model compounds **1** and **2** for the polymer **3**, under conditions chosen to mimic a typical condensation polymerization. Therefore, phosphaalkene **1** was prepared in the absence of solvent by stirring mesitylene-2-carboxylic acid chloride and PhP(SiMe$_3$)$_2$ at 50 °C for several days. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed only two signals

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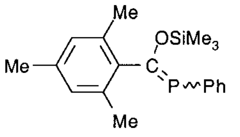

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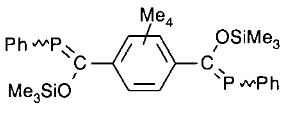

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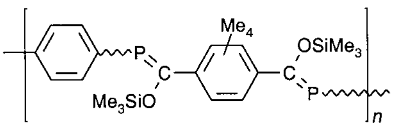

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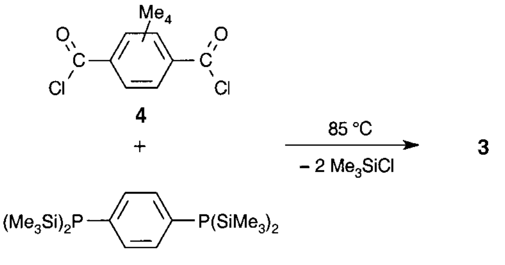

Scheme 1. The [1,3]-silatropic rearrangement of an acylphosphane to a phosphaalkene.

($\delta = 149.2$, 54 % and 134.0, 46 %), assigned to the *E* and *Z* isomers of **1**, respectively. After distillation (110 °C; 0.1 mmHg), analytically pure **1** was isolated as a pale yellow liquid (yield, 75 %).

Examples of molecules possessing two or more phosphaalkene moieties bridged by arylene spacers are uncommon;[12] furthermore, there are only two previous reports of bis(phosphaalkene)s prepared through [1,3]-silatropic rearrangement.[11b, 12b] Thus, we set out to prepare **2** from a concentrated solution of $PhP(SiMe_3)_2$ (2 equiv) and **4** in THF and hexanes. After several days of heating and monitoring by ^{31}P NMR spectroscopy, the $PhP(SiMe_3)_2$ was completely consumed, and pure **2** (yield, 42 %) was isolated as a colorless powder from a concentrated hexanes solution (−35 °C). Unexpectedly, the ^{31}P NMR spectrum of **2** in $CDCl_3$ shows eight resonances distributed over the regions expected for *E*- (44 %) and *Z*-phosphaalkene (56 %) isomers. In addition, there were six resolved signals for $OSiMe_3$ groups in the ^1H NMR spectrum. Four signals are expected for the three possible isomers (*E*,*E*; *E*,*Z*; *Z*,*Z*), thus, we postulate that the additional NMR signals arise from restricted rotation of the P = C groups about the central aryl plane in **2**.

In order to prepare the target poly(*p*-phenylenephosphaalkene), two bifunctional starting reagents (**4** and **5**) were required. The silylated phosphane **5** was prepared by treating 1,4-diphosphanobenzene[13] with MeLi (4 equiv) in diethyl ether followed by addition of Me_3SiCl (4 equiv).[14] Analytically pure **5** was obtained as a colorless solid after vacuum sublimation at 100 °C. The thermolysis of **4** and **5** was conducted just above their melting temperature (85 °C) in a vacuum-sealed Pyrex tube. In a typical experiment, after about 24 h the initially colorless, free-flowing liquid was highly viscous and yellow.[15] Poly(*p*-phenylenephosphaalkene) (**3**) was purified by precipitation of the polymer from a concentrated THF solution with cold hexanes (ca. −30 °C) and subsequent drying in vacuo. The brittle yellow solid (yield, 35 %) was dissolved in C_6D_6 and analyzed by ^{31}P NMR spectroscopy, which showed broad overlapping signals for the *E* and *Z* isomers in **3** and for the polymer end groups (see Figure 1).[16] The ^{29}Si NMR (DEPT) spectrum exhibited three signals ($\delta = 21$ and 18, **3** ($OSiMe_3$); 1.4 ppm (d), **3** $P(SiMe_3)_2$ end groups) with the signals arising from $OSiMe_3$ groups in **3** showing similar chemical shifts to those in **1** ($\delta = 21.3$, 18.2 ppm).

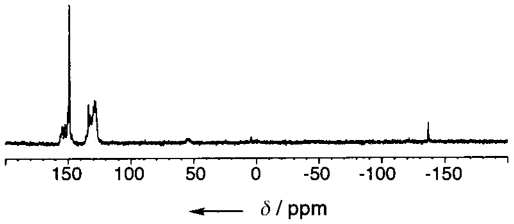

Figure 1. ^{31}P NMR spectrum (C_6D_6) of **3** (trial 2) after precipitation with hexanes.

An estimate of the molecular weight (M_n) of several samples was obtained from relative integration of the ^{31}P NMR signals for $P(SiMe_3)_2$ end groups and P=C units.[17] The results are shown in Table 1; samples of **3** had moderate degrees of polymerization ($\bar{X}_n$, *n* in **3**) between 5 and 21, not unusual for a step-growth reaction. Moreover, the elemental analyses, including chlorine analysis for two samples, were consistent with the molecular weights estimated from end-group analysis. The ^{13}C NMR spectrum exhibited resonances consistent with the assigned structure and, importantly, broad signals for the C=P moiety were detected at $\delta = 212$ and 198 ppm. The infrared spectra of films of **3** were remarkably similar to those for **1**, **2**, and other analogous phosphaalkenes.[11a] The thermal stability of **3** was assessed by thermogravimetric analysis (TGA) under dry helium. The polymer **3** was stable to weight loss up to 190 °C, whereupon approximately 40 % was lost, followed by an additional 20 % at 400 °C. After heating to 800 °C, 40 % of the mass remained as a black solid.

Table 1. Selected characterization data for **1**, **2**, and **3**.

Compound	t_{polym} [h]	$\bar{X}_n^*$	M_n^* [g mol^{-1}]	UV/Vis λ_{max} [nm]	*Z*/*E*
1			328	310	0.85
2			550	314	1.27
3 (trial 1)	21	5	2900	328	1.12
3 (trial 2)	27	21	10500	338	1.14
3 (trial 3)	28	12	6300	334	1.06
3 (trial 4)	34	12	6300	334	1.05

* M_n and $\bar{X}_n$ were estimated using end-group analysis (see ref. [17]).

The electronic structure of the new phosphaalkenes prepared was probed in THF solution (ca. 10^{-5} M) by using UV/Vis spectroscopy. Few detailed UV/Vis studies have been conducted on phosphaalkenes,[12e, 18] although there are two possible chromophores; (n – π*) and (π – π*). Typical spectra for the polymer (**3**) and model compounds (**1** and **2**) are shown in Figure 2. Broad absorbances were observed for **1** (λ_{max} = 310 nm) and **2** (λ_{max} = 314 nm). Analysis of poly(*p*-phenylenephosphaalkene) (**3**) revealed a broad absorbance (λ_{max} = 328 – 338 nm) and a tail stretching into the visible region. We speculate that the bathochromic shift observed for poly(*p*-phenylenephosphaalkene) compared with **1** and **2** suggests some degree of π-conjugation through the phenylene and P=C units. However, the red shift for **3** is less than that for *trans*-PPV compared with *trans*-stilbene (ca. 426 nm vs. 294/307 nm), which we attribute to conformational nonplanarity in the main chain, caused by the bulky C_6Me_4 groups in **3**.[19, 20] In addition, the breadth of the absorbance for **3** may be caused, in part, by the mixture of isomers present ($Z/E \approx 1.1$; compare *cis*-stilbene (276 nm) and *trans*-stilbene (294/307 nm)),[20] and/or the polydispersity of the material. Further studies are necessary to confirm the extent of π-conjugation in **3**.

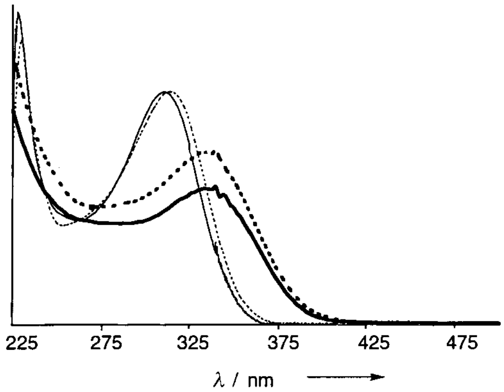

Figure 2. UV/Vis spectra of: **1** ——; **2** - - - -; **3** (trial 3) ——; **3** (trial 4) – – –.

In summary, we have prepared and characterized the first π-conjugated polymer containing P=C bonds in the main chain. Future studies will explore the scope of this synthetic methodology and attempt to develop routes to air- and moisture-stable poly(*p*-phenylenephosphaalkene)s.

Experimental Section

All manipulations were performed under a nitrogen atmosphere in a glove box or using standard Schlenk techniques. Assignment of NMR spectra were made with the aid of COSY, APT, HMQC, and HMBC experiments. The *E* and *Z* isomers of **1**, **2**, and **3** were assigned by comparison with analogous systems; the signals arising from the *E* isomer are observed downfield from those of the *Z* isomer in the ^{31}P NMR spectrum.[11, 21]

1: Bis(trimethylsilyl)phenylphosphane (5.6 g, 22.0 mmol) and mesitylene-2-carboxylic acid chloride (4.0 g, 21.9 mmol) were stirred at 50 °C, and over several days quantitative conversion to **1** was observed by ^{31}P NMR spectroscopy. Pure **1** (5.4 g, 75 %) was isolated as a pale yellow liquid after vacuum distillation (b.p. 110° C, 0.1 mmHg). **1**: ^{31}P NMR (121.5 MHz, C_6D_6): δ = 149.2 (s, 54 %, ***E*-1**), 134.0 ppm (s, 46 %, **Z-1**); ^1H NMR (400.1 MHz, $CDCl_3$): ***E*-1**: δ = 7.13 – 7.01 (m, 5 H; *o, m, p*-Ph), 6.73 (s, 2 H; *m*-Mes), 2.20 (s, 9 H; *o, p*-CH_3), 0.42 ppm (s, 9 H; $OSi(CH_3)_3$), **Z-1**: δ = 7.79 (m, 2 H; *o*-Ph), 7.35 (m, 3 H; *m, p*-Ph), 6.91 (s, 2 H; *m*-Mes), 2.48 (s, 6 H; *o*-CH_3), 2.32 (s, 3 H; *p*-CH_3), – 0.05 ppm (s, 9 H; $OSi(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): ***E*-1**: δ = 197.3 (d, ^1J (C,P) = 49 Hz; C=P), 138.5 (d, ^1J (C,P) = 39 Hz; *i*-Ph), 138.0 (d, ^2J (C,P) = 9 Hz; *i*-Mes), 137.4 (s; *p*-Mes), 134.2 (d, ^3J (C,P) = 5 Hz; *o*-Mes), 133.0 (d, ^2J (C,P) = 13 Hz; *o*-Ph), 128.0 (s; *m*-Mes), 127.7 (d, ^3J (C,P) = 6 Hz; *m*-Ph), 127.5 (s; *p*-Ph), 21.0 (s; *p*-CH_3), 19.9 (s; *o*-CH_3), 0.3 – 0.1 ppm (m; $OSi(CH_3)_3$), **Z-1**: δ = 210.2 (d, ^1J (C,P) = 41 Hz; C=P), 139.5 (d, ^1J (C,P) = 44 Hz; *i*-Ph), 138.1 (s; *p*-Mes), 136.8 (d, ^2J (C,P) = 28 Hz; *i*-Mes), 136.5 (d, ^3J (C,P) = 8 Hz; *o*-Mes), 133.3 (d, ^2J (C,P) = 13 Hz; *o*-Ph), 128.4 (s; *m*-Mes), 128.1 (s; *m*-Ph), 127.5 (s; *p*-Ph), 21.1 (s; *p*-CH_3), 20.7 (s; *o*-CH_3), 0.3 – 0.1 ppm (m; $OSi(CH_3)_3$); ^{29}Si NMR (C_6D_6, 79.5 MHz): δ = 21.3 (s), 18.2 ppm (s); UV/Vis (THF): λ_{max} (ε) = 310 nm (6000); IR (neat): $\tilde{\nu}$ = 2921 (m), 2853 (m), 1601 (w), 1456 (s), 1377 (m), 1252 (vs), 1187 (vs), 847 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 330 (3), 329 (10), 328 (44) [M^+], 253 (1), 252 (4), 251 (23) [$M^+ - C_6H_5$], 148 (9), 147 (100) [$C_{10}H_{11}O$], 74 (5), 73 (72) [C_3H_9Si]; elemental analysis: $C_{19}H_{25}OPSi$: calcd C 69.48, H 7.67, found C 69.54, H 7.60.

2: To a mixture of bis(trimethylsilyl)phenylphosphane (0.93 g, 3.7 mmol) and **4** (0.47 g, 1.8 mmol) was added hexanes:tetrahydrofuran (5 mL:2 mL) until dissolved. The solution was stirred at 85 °C in a closed vessel for a several days and ^{31}P NMR spectroscopy showed quantitative formation of **2**. The solvent was removed in vacuo giving a pale yellow oil, from which **2** was isolated (0.42 g, 42 %) as a colorless powder from hexanes at – 35 °C. **2**: ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 155.2 (s, 20 %), 154.9 (s, 4 %), 150.7 (s, 2 %), 149.5 (s, 18 %), 134.0 (s, 23 %), 131.8 (s, 4 %), 129.9 (s, 12 %), 129.6 ppm (s, 17 %); ^1H NMR ($CDCl_3$, 300.1 MHz): δ = 7.8 – 6.9 (m, 10 H; Ph-*H*), 2.39, 2.38, 2.23, 2.19, 2.11, 2.05, 2.02 (s, 12 H; Ar-C*H*$_3$), 0.38, 0.31, 0.30 (s; $OSi(CH_3)_3$, *E* isomers (44 %)), – 0.09, – 0.10, – 0.15 ppm (s; $OSi(CH_3)_3$, *Z* isomers (56 %)); ^{13}C NMR ($CDCl_3$, 75.5 MHz,): δ = 211.8 (d, ^1J (C,P) = 44 Hz; C = P, **Z-2**), 198.6 (d, ^1J (C,P) = 49 Hz; C=P, ***E*-2**), 140 – 137 (m; *i*-Ph and *i*-Ar), 134 – 132 (m; *o*-Ph), 131 – 130 (m; *o*-Ar), 128 – 127 (m; *m*-Ph and *p*-Ph), 19 – 17 (m; Ar-CH_3), 0.8 – 0.1 ppm (m; $OSi(CH_3)_3$); UV/Vis (THF): λ_{max} (ε) = 314 nm (28000); IR (neat): $\tilde{\nu}$ = 3052 (s), 2956 (vs), 2922 (sh), 1451 (sh), 1432 (s), 1251 (vs), 1192 (vs), 981 (s), 900 (sh), 854 cm^{-1} (vs); MS (EI, 70 eV): *m*/*z* (%): 553 (3), 552 (12), 551 (35), 550 (82) [M^+], 475 (4), 474 (6), 473 (26) [$M^+ -$ Ph], 443 (2), 442 (3), 441 (7) [$M^+ -$ PHPh], 371 (4), 370 (12), 369 (51) [$M^+ - P(Ph)SiMe_3$], 74 (9), 73 (100) [$SiMe_3$]; elemental analysis: calcd C 65.42, H 7.32, found C 65.32, H 7.47.

3: The same procedure was followed for each trial (1 – 4). All glassware was rinsed with Me_3SiCl and flame dried prior to use. Compounds **4** (0.601 g, 2.32 mmol) and **5** (1.00 g, 2.32 mmol) were mixed as finely ground powders, and flame sealed in vacuo in a thick-walled Pyrex tube. The sample was placed in a preheated (85 °C) oven, whereupon the solids melted forming a colorless, free-flowing liquid. After 6 – 8 h, the mixture showed an increase in viscosity and was yellow. The reaction was monitored until the liquid was almost immobile (ca. 24 h), and the yellow/orange material was removed from the oven. The tube was broken, Me_3SiCl was removed in vacuo, and the residue dissolved in a minimum amount of THF (ca. 3 mL). The viscous solution was evenly distributed over the walls of the flask, and cold hexanes (ca. – 30° C) were added rapidly to precipitate the polymer as a yellow solid. The hexanes-soluble fraction was removed and the polymer **3** remained (0.384 g, 35 %) as a bright yellow glassy solid after drying in vacuo. **3**: ^{31}P NMR ($CDCl_3$; 121.5 MHz): δ = 157 – 149 (br m; *E*-**3**), 138 – 124 (br m; *Z*-**3**), – 137 ppm (br; $P(SiMe_3)_2$ end groups; see Table 1 for *Z*/*E* ratio, and degree of polymerization for each trial). All integrations for end-group analyses are reported with a relaxation delay of 2.0 s; however, spectra were obtained by using 20 s and 30 s delays, and integrals were identical. ^{29}Si NMR ($CDCl_3$, 79.5 MHz): δ = 21.7 – 20.5 (br m), 18.4 – 17.0 (br m), 1.4 ppm (d; ^1J(Si, P) = 26 Hz, end groups); ^1H NMR ($CDCl_3$, 400.1 MHz): δ = 7.8 – 6.6 (br m; C_6H_4), 2.5 – 2.1 (br m; $C_6(CH_3)_4$), 0.5 – – 0.5 ppm (br m; $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 211.9 (br; *Z*-C=P), 197.9 (br; *E*-C=P), 142.0 (br; *i*-C_6Me_4), 139.1 (br; *i*-C_6H_4), 132.4, 130.2 (br; *o*-C_6H_4, *o*-C_6Me_4), 18.6, 17.5 (br s; $C_6(CH_3)_4$), 0.7, 0.2 ppm (br s; $OSi(CH_3)_3$); UV/Vis (see Table 1); IR (film): $\tilde{\nu}$ = 2955 (m), 2921 (m), 2849 (m), 1252 (vs), 1187 (s), 846 cm^{-1} (vs); elemental analysis: $[C_{24}H_{34}O_2P_2Si_2]_n + [C_{26}H_{43}O_2P_2Si_3Cl]$: trial 1 calcd ($n = 5$) C 59.80, H 7.32, found C 59.89, H 7.26, trial 3 calcd ($n = 12$) C 60.43, H 7.28, Cl 0.57, found C 60.27, H 7.39, Cl 0.62, trial 4 calcd ($n = 12$) C 60.43, H 7.28, Cl 0.57, found C 59.64, H 7.39, Cl 1.10.

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[16] Samples of **3** exhibit no change in their NMR spectra after several months of storage in THF solution under an inert atmosphere. Upon exposure to moisture, solutions of **3** rapidly undergo partial hydrolysis, and signals arising from -PH_2 and -$PHSiMe_3$ end groups were observed by using ^{31}P NMR spectroscopy. Excess water results in partial hydrolysis of the O-$SiMe_3$ side groups giving an enol, which tautomerizes to acylphosphane ($\delta = -16$ ppm; $^1J_{PH} = 232$ Hz).

[17] The molecular weights of **3** were estimated by integration of the $P(SiMe_3)_2$ and P=C signals in the ^{31}P NMR spectrum (relaxation delays of between 2 and 30 s resulted in identical ratios). A statistical (50:50) mixture of C(O)Cl and $P(SiMe_3)_2$ end groups was assumed; consistent with elemental analysis and the trace of C(O)Cl ($\delta =$ 170 ppm) detected in the baseline of the ^{13}C NMR spectrum. We speculate that the small resonance at 50 ppm in the ^{31}P NMR spectrum of **3** is caused by minor cross-linking of the polymer chains. To date, the sensitivity of **3** towards oxygen and moisture has precluded GPC analysis. Thus far, MALDI-TOF MS has not been successful, perhaps because of the reactivity of **3** with hydroxy-containing matrices.

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