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[17] Crystal data for **1**: crystal dimensions 0.15 × 0.30 × 0.60 mm, monoclinic, space group $P2_1/c$, $a = 21.14(1)$, $b = 27.16(1)$, $c = 19.274(9)$ Å, $\beta = 104.99(1)^\circ$, $V = 10689(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.321$ g cm^{-3}, $2\theta_{max} = 43.8^\circ$, Mo$_{K\alpha}$ ($\lambda = 0.710730$ Å), θ-2θ scan, $T = 298$ K, 13445 measured reflections, 12909 independent reflections ($R_{int} = 0.0268$), 12391 reflections included in the refinement. Lorentz, polarization corrections were applied, $\mu = 0.867$ mm^{-1}, $(\Delta/\sigma) = 0.095$, 1262 parameters refined, $R1 = 0.0624$ (for 8482 reflections with $I > 2\sigma(I)$), $wR2 = 0.1453$ (on F^2). Max./min. residual peaks in the final difference map 0.619/−0.414 e Å^{-3}. A crystal of **1** was mounted in a glass capillary with drops of mother liquor because of its sensitivity to air exposure. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 using SHELXL-93. All non-hydrogen atoms were refined anisotropically, except for the solvent molecules, which were refined isotropically. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. CCDC-180394 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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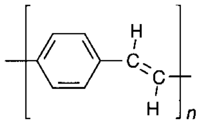
Poly(*p*-phenylenephosphaalkene): A π-Conjugated Macromolecule Containing P=C Bonds in the Main Chain[**]

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).[11a] 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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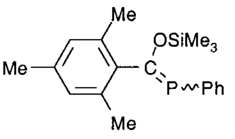

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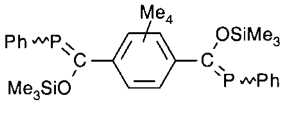

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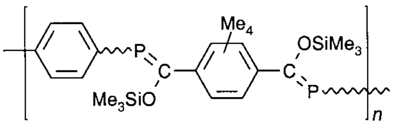

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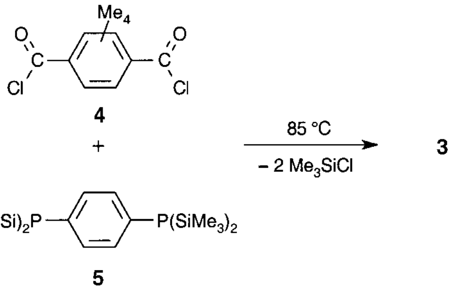

Scheme 1. The [1,3]-silatropic rearrangement of an acylphosphane to a phosphaalkene.

($\delta = 149.2$, 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 ^{1}H 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$_3$SiCl (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$_6$D$_6$ 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).

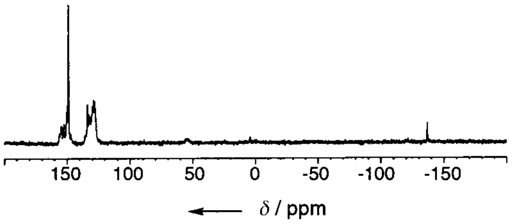

Figure 1. ^{31}P NMR spectrum (C$_6$D$_6$) of **3** (trial 2) after precipitation with hexanes.

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 $\lambda_{\max}$ [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** ($\lambda_{max} = 310$ nm) and **2** ($\lambda_{max} = 314$ nm). Analysis of poly(*p*-phenylenephosphaalkene) (**3**) revealed a broad absorbance ($\lambda_{max} = 328–338$ 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**.

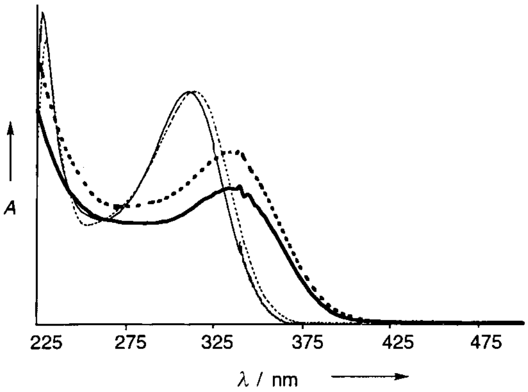

Figure 2. UV/Vis spectra of: **1** ——; **2** - - - -; **3** (trial 3) ——; **3** (trial 4) – – –.

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): $\delta = 149.2$ (s, 54 %, ***E*-1**), 134.0 ppm (s, 46 %, ***Z*-1**); ^{1}H NMR (400.1 MHz, $CDCl_3$): ***E*-1**: $\delta = 7.13–7.01$ (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**: $\delta = 7.79$ (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**: $\delta = 197.3$ (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**: $\delta = 210.2$ (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): $\delta = 21.3$ (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): $\delta = 155.2$ (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 %); ^{1}H NMR ($CDCl_3$, 300.1 MHz): $\delta = 7.8–6.9$ (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,): $\delta = 211.8$ (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): $\delta = 157–149$ (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): $\delta = 21.7–20.5$ (br m), 18.4–17.0 (br m), 1.4 ppm (d; ^1J(Si, P) = 26 Hz, end groups); ^{1}H NMR ($CDCl_3$, 400.1 MHz): $\delta = 7.8–6.6$ (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): $\delta = 211.9$ (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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