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Synthesis and characterization of poly(*p*-phenylenephosphine)s

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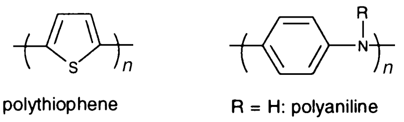
***P*-Substituted poly(*p*-phenylenephosphine)s were prepared *via* palladium catalyzed carbon–phosphorus bond formation.**

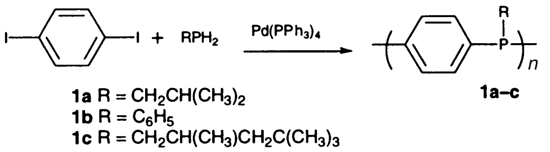
There has been substantial recent interest in the synthesis and properties of π-conjugated polymers. These polymers have found important uses for a variety of optoelectric applications such as rechargeable battery electrodes, light-emitting diodes, and chemical sensors.[1] While many conjugated polymers contain only sp and sp^2 hybridized carbon atoms along the polymer backbone, two of the most important and widely investigated conjugated polymers, polyaniline[2] and polythiophene,[3] contain heteroatoms as a vital component of the conjugation path (Scheme 1). Other interesting conjugated polymers have been prepared which contain heteroatoms in the backbone including poly(*p*-phenyleneborane)s,[4] poly(*p*-phenyleneselenide)s,[5] and poly(*p*-phenylenesulfide).[6] The presence and properties of the heteroatom have a profound impact on the optoelectronic properties of the polymer. A substantial increase in the doped conductivity is observed upon moving from poly(*p*-phenyl-eneoxide) to poly(*p*-phenylenesulfide).[6] While phosphorous containing polymers have found a variety of important uses including flame retardants, ionic conduting materials, and easily separable supports for metal catalysts,[7] the incorporation of phosphorus into the backbone of a conjugated polymer has been limited. The few cases include poly(ferrocenylphosphine),[8] oligophospholes,[9] and the trace incorporation of phosphorus into soluble poly(*p*-phenylene)s *via* catalyst ligand decomposition.[10]

Palladium catalysis has been used extensively in organic chemistry for the formation of new sp^2–sp^2 and sp^2–sp hybridized carbon–carbon bonds with high yields and is useful for the preparation of π-conjugated polymers.[11] Recent investigations by Buchwald[12] and Hartwig[13] have expanded the utility of palladium mediated cross coupling to include carbon–nitrogen bond formation. The new synthetic method couples arylhalides or aryltosylates with amines and has generated considerable interest for the preparation of arylamine containing materials such as polyanilines, oligoanilines, and arylamine dendrimers.[14] Analogous nickel[15] and palladium[16] mediated carbon–phosphorus bond forming reactions have been reported and recently utilized for the synthesis of phosphorus containing polymers.[7e] We report the synthesis and optoelectric investigation of the phosphorus analog to *N*-substituted polyanilines, *P*-substituted poly(*p*-phenylenephosphine)s, *via* palladium catalyzed carbon–carbon phosphorus bond formation.

In this paper, we describe the palladium catalyzed condensation polymerization of monoalkyl and monoaryl phosphines with 1,4-diiodobenzene (Scheme 2). A typical experiment is conducted as follows. Palladium tetrakis(triphenylphosphine) (0.310, 0.27 mmol) and diiodobenzene (1.77 g, 5.37 mmol) were dissolved in 1 : 1 dry oxygen free THF–toluene (10 ml). To this solution was added isobutylphosphine (0.63 ml, 5.37 mmol) followed by triethylamine (2.0 ml). Upon the addition of the triethylamine a white precipitate was observed indicating the formation of $Et_3N·HI$. The reaction mixture was heated at 70 °C for 72 h and turned burnt orange. The reaction mixture was poured into rapidly stirring 5 : 1 MeOH–aq. NH_3 (500 ml) to precipitate the polymer, which was collected by filtration. The polymer was redissolved in THF, reprecipitated in MeOH, filtered, washed with MeOH, and dried under high vacuum for 8 h to yield polymer **1a** as a light pink solid (0.73 g, 83% yield).



Scheme 1 Heteroatom containing conjugated polymers.



Scheme 2 Synthesis of poly(*p*-phenylenephosphine)s.

The structures of polymers **1a**–**c** are supported by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy and the molecular weights are estimated by gel permeation chromatography (Table 1).† The ^1H NMR spectra of **1a** contain four broad resonances with appropriate chemical shifts and integrated intensities. The ^{31}P NMR spectra contain a single broad resonance at −19.81 ppm suggesting that the environment is similar for most of the P nuclei. The ^{13}C NMR spectra contain five resonances each with scalar coupling to ^{31}P. The resonance at 132.66 ppm is coupled to two different ^{31}P nuclei characteristic of ^2J (^{31}P–^{13}C, 19.1 Hz) and ^3J(^{31}P–^{13}C, 6.1 Hz) as expected for the C nuclei not directly bound to P.[17] The IR spectra include absorptions characteristic of aromatic ring stretches but contain no observable P=O absorptions. Polymers **1a** and **c** are entirely soluble in THF, toluene, and $CHCl_3$ while **1b** is only partially soluble.

The UV-visible spectra of polymers **1a**–**c** in $CHCl_3$ suggest significant π-conjugation along the polymer backbone *via* the lone pair on P. A red shift of the optical absorption upon increasing the number of phenyl phosphine units is observed, as evidenced by the shift of the absorbance maximum for the π–π* transition for the following series of phosphines: triphenylphosphine (λ_{max} = 263 nm), 1,4-bis(diphenylphosphino)benzene (**2**) (λ_{max} = 275 nm), and polymer **1b** (λ_{max} = 291 nm). In addition, polymer **1b** has a second small absorption maximum at 434 nm (Fig. 1). We suspect that this lower energy absorption results from an n–π* transition. The absorption is observed due to an increase in intensity resulting from electron delocalization in the polymer.

Table 1 Optical and molecular weight data for polymers **1a**–**c**

Polymer	R	M_n[a]	n[b]	PDI	λ_{max} Abs
1a	Isobutyl	1,700	10	1.3	278, 415
1b	Phenyl	1,300	7	1.4	291, 434
1c	2,4,4-Trimethylpentyl	3,100	14	1.5	276, 422

[a] Molecular weights were determined by GPC *vs*. polystyrene standards in THF. [b] The value *n* corresponds to the average number of repeat unit in the polymer.

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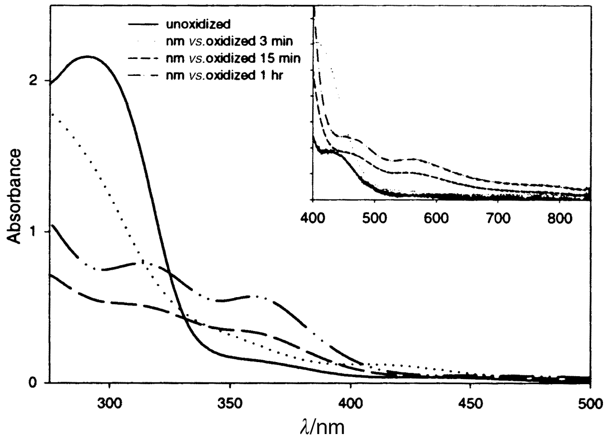

Fig. 1 UV-visible spectra of the oxidation of polymer **1b** with $FeCl_3$ in $CHCl_3$.

Chemical oxidation provides additional support for the electronic delocalization of poly(*p*-phenylenephosphine)s. Oxidation of polymer **1b** with $FeCl_3$ in the absence of O_2 and H_2O results in the formation of several new absorption bands and a shift of the band edge past 800 nm (Fig. 1). The spectral properties of these polymers are related to poly(*N*-arylaniline)s.[14*a*] The NMR spectra of polymers **1a–c** are also altered upon oxidation with $FeCl_3$. We are unable to observe ^{31}P or ^{1}H NMR spectra for oxidized polymers **1a–c**. The lack or severe broadening of NMR resonances is consistent with paramagnetism resulting from declocalized electrons along the polymer chain. The oxidized polymer is stable in solution for several hours in the absence of O_2 and H_2O. While we do not fully understand the spectroscopic properties of these polymers, the data support an extension of the conjugation path through P and electronic delocalization along the polymer chain.

Since phosphines are well known to undergo rapid oxidation to phosphine oxides, we investigated the oxidation of the polymers by hydrogen peroxide (Scheme 3). Addition of (30%) H_2O_2 to $CHCl_3$ solutions of **1b** resulted in a color change to deep red along with a dramatic change of the UV-visible spectroscopic properties, the primary absorption (291 nm) is blue shifted while the low energy band (434 nm) is red shifted to 550 nm and severely broadened. A change in the structure of the polymer is supported by NMR and IR spectroscopy. The ^{31}P NMR absorption for polymer **1b** cleanly shifts from −5.2 ppm to 28.6 ppm suggesting near quantitative conversion of **3b**.‡ IR spectra of polymer **3b** contain two strong absorptions at 1120 and 1188 cm^{-1} characteristic of phosphine oxides.[18] Polymers **1a–c** are mildly sensitive to atmospheric oxygen and are converted to **3a–c** over 4–6 days in solution ($CHCl_3$) and 4–6 months in the solid state.

We have described the synthesis and spectroscopic investigation of a series of poly(*p*-phenylenephosphine)s. Polymers **1a–c** were synthesized *via* palladium catalyzed cross coupling of diiodobenzene with primary phosphines. The investigations suggest significant electronic delocalization through P along the backbone of the polymer. We are currently further evaluating the properties of these interesting polymers and investigating additional routes to incorporate P into conjugated polymers.

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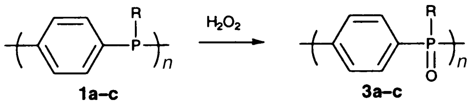

Scheme 3 Oxidation of poly(*p*-phenylenephosphine).

Notes and references

† Characterization data for polymer **1a**. δ_H(400 MHz, $CDCl_3$) 1.01 (d, *J* 6.2, 6H, CH_3), 1.63 (non, *J* 6.6, 1H, CH), 1.94 (d, *J* 7.0, 2H, CH_2), 7.33 (s, 4H, C_6H_4); δ_C(100 MHz, $CDCl_3$) 24.27 (d, J_{CP} 9.0, CH_3), 26.22 (d, J_{CP} −14.5, CH_2), 38.43 (d, J_{CP} 13.3, CH), 139.53 (d, J_{CP} −17.2, C_6H_4), 132.66 (dd, J^2_{CP} 19.1 J^3_{CP} 6.1, C_6H_4); δ_P(162. MHz, $CDCl_3$) −19.81 (s); ν(film, KBr)/cm^{-1} 2953, 2924, 2867, 2360, 1474, 1461, 1455, 1381, 1364, 1110, 1046, 1014, 1004, 814, 795, 758, 547; (Calc. for $C_{10}H_{13}P$: C, 73.13; H, 7.98. Found: C, 64.08; H, 7.20%). While the absolute values of the elemental analysis are a few percent low the calculated and found C : H ratios are 9.17 and 8.90 respectively; we suspect the difference in absolute values is the result of polymer end-groups. Assuming the polymers are quantitatively capped with *p*-iodophenyl substituents provides better correlation to experimental elemental analysis. (Calc. for $C_{106}H_{134}P_{10}I_2$; C, 64.56; H, 6.86%).

‡ The chemical shift for the ^{31}P NMR resonances of Ph_3P and $Ph_3P{=}O$ are −4.6 ppm and 29.7 ppm respectively.

1 *Conjugated Polymers: The Novel Science of Technology of Highly Conducting and Nonlinear Optically Active Materials*, ed. J. L. Bredas and R. Silbey, Kluwer Academic Publishers, Dordrecht, 1991; J. M. Tour, *Chem. Rev.*, 1996, **96**, 537; T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.

2 A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.*, 1989, **31**, 317.

3 A. O. Patil, A. J. Heeger and F. Wudl, *Chem. Rev.*, 1988, **88**, 183.

4 N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **88**, 10 776.

5 E. Tsuchida, M. Jikei, K. Miyatake, K. Yamamoto and H. Nishide, *Macromolecules*, 1993, **26**, 4732.

6 R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer and L. W. Shacklette, *Chem. Rev.*, 1982, **82**, 209.

7 (*a*) W. C. Kuryla and A. J. Papa, *Flame Retardancy of Polymeric Materials Vol. 1–5*, Marcel Dekker, New York, 1973; (*b*) H. Ghassemi and J. E. McGrath, *Polymer*, 1997, **38**, 3139; (*c*) D. B. Bergbreiter and Y. Liu, *Tetrahedron Lett.*, 1997, **38**, 7843; (*d*) H. R. Allcock, D. L. Olmeiger and J. M. O'Connor, *Macromolecules*, 1998, **31**, 753; (*e*) T. Kanbara, S. Takase, K. Izumi, S. Kagaya and K. Hasegawa, *Macromolecules*, 2000, **33**, 657.

8 T. J. Peckham, J. A. Massey, C. H. Honeyman and I. Manners, *Macromolecules*, 1999, **32**, 2830.

9 E. Deschamps, L. Ricard and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1994, **96**, 537.

10 F. E. Goodson, T. I. Walow and B. M. Novak, *Macromolecules*, 1998, **31**, 2047.

11 M. Rehahn, A.-D. Schluter, G. Wegner and W. J. Feast, *Polymer*, 1989, **30**, 1060; D. L. Trumbo and C. S. Marvel, *J. Polym. Sci. Part A: Polym. Chem.*, 1987, **25**, 839.

12 J. P. Wolfe, S. Wagaw and S. L. Buchwald, *J. Am. Chem. Soc.*, 1996, **118**, 7215; J. P. Wolfe, S. Wagaw, J.-F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805.

13 M. S. Driver and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 7217; J. F. Hartwig, *Acc. Chem. Res.*, 1998, **31**, 852.

14 (*a*) F. E. Goodson, S. I. Hauck and J. F. Hartwig, *J. Am. Chem. Soc.*, 1999, **121**, 7527; (*b*) J. Louie, J. F. Hartwig and A. J. Fry, *J. Am. Chem. Soc.*, 1997, **119**, 11 695; (*c*) R. A. Singer, J. P. Sadighi and S. L. Buchwald, *J. Am. Chem. Soc.*, 1988, **120**, 213; (*d*) J. P. Sadighi, R. A. Singer and S. L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 4960.

15 D. Cai, J. F. Payack, D. R. Bender, D. L. Huges, D. L. Hughes, T. R. Verhoeven and P. J. Reider, *J. Org. Chem.*, 1994, **59**, 1780.

16 T. Hirao, T. Masaunaga, N. Yamada, Y. Oshiro and T. Agawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 909; S. E. Tunney and J. K. Stille, *J. Org. Chem.*, 1987, **52**, 748; O. Herd, A. Hessler, M. Hingst, M. Tepper and O. Stelzer, *J. Organomet. Chem.*, 1996, **522**, 69; J. H. Hillhouse, U.S. Patent No. 5550295 (to Cytec), 1996; M. A. Zhuravel, PhD Thesis, Darmouth College, Hannover, NH, 2000.

17 F. W. Wehrli, A. P. Marchand and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd ed., John Wiley Sons, New York, 1988, Chapter 2.

18 L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, 1964, **20**, 467.