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Transition metal mediated routes to poly(arylphosphine)s: investigation of novel phosphorus containing conjugated polymers

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Abstract

Poly(aryl-*P*-alkylphosphine)s were prepared via palladium and nickel mediated coupling and the spectral and electrochemical properties of the polymers were investigated. Palladium catalyzed carbon–phosphorus bond formation was used for the preparation of poly(*p*-phenylene-*P*-alkylphoshpine)s (**1a**–**b**) via two routes. Low molecular weight polymers (1000–3000) were obtained by the condensation polymerization of 1,4-diiodobenzene with primary alkylphosphines. Higher molecular weight polymers (1000–14 000) were obtained via polymerization of *p*-bromophenylalkylphosphines (**2a**–**b**). Poly(4,4′-diphenyl-*P*-2,4,4-trimethylpentylphosphine (TMPPH$_2$)) (**4b**) was also prepared via two routes, the palladium catalyzed cross-coupling of 4,4′-diiodobiphenyl with primary alkylphosphines and the nickel mediated homo-coupling of bis-*p*-bromophenylalkylphosphines. The molecular weight of **4b** was low (1000–3000) via both routes due to poor solubility. The electronic properties of polymers **1a**–**b** were investigated with UV–vis–NIR spectroscopy and cyclic voltammetry and suggest a degree of electronic delocalization along the polymer backbone through phosphorus. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Conjugated polymers; Polymerization; Polyphosphines; Organophosphine; UV-spectrum; Electrochemistry

1. Introduction

The synthesis and physical properties of conjugated polymers have received substantial recent attention. This is due, in part, to the many interesting and useful properties of conjugated polymers. Conjugated polymers have a wide variety of optoelectric applications including sensors, light emitting diodes (LEDs) and nonlinear optical materials [1]. Synthetic polymer chemistry has provided various routes for the preparation of conjugated polymers such as poly(*p*-phenylene), poly(*p*-phenylene vinylene), and polyacetylene (Chart 1) [2]. While underivatized conjugated polymers are typically insoluble, incorporation of flexible side chains greatly enhances solubility. Upon solubilization, conjugated polymers have a unique combination of narrow band gaps, rigid-rod character, processability, and charge-transport capability, which makes them interesting and useful materials. One of the most frequently utilized methods for the preparation of soluble conjugated polymers is metal catalyzed coupling. In particular, palladium and nickel mediated coupling has been utilized for the preparation of π-conjugated polymers [3].

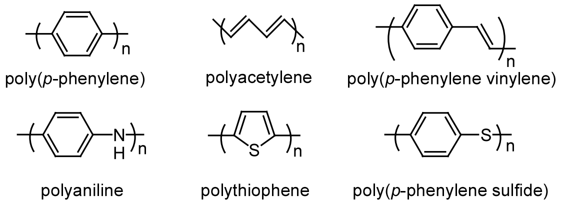

Chart 1.

While many of the important conjugated polymers have backbones constructed entirely of carbon, the incorporation of metals or heteroatoms into the path of conjugation has a profound impact on the properties of the polymer. The most important heteroatoms containing conjugated polymers include polythiophene, poly(*p*-phenylene sulfide) and polyaniline (Chart 1) [1]. The influence of the heteroatom is typically the result of the incorporation of a lone pair of electrons in the electronic delocalized system. Several other heteroatoms have been incorporated into conjugated polymers in-

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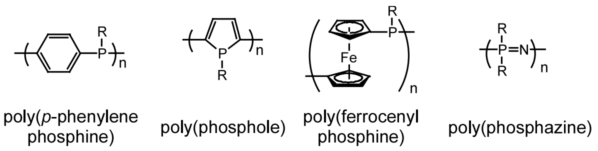
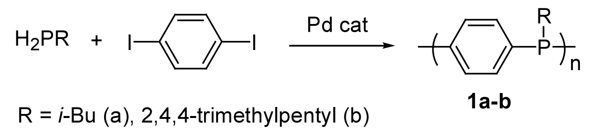


Chart 2.



Scheme 1.

cluding boron [4], poly(*p*-phenylene borane)s, and selenium [5], poly(*p*-phenylene selenide)s and poly(selenophene)s. Substantial evidence supports electronic involvement of the heteroatom in these conjugated polymers. The placement of heteroatoms directly into the path of conjugation allows fine-tuning of the electronic properties of the polymer depending upon the electronic nature of the heteroatom.

Polyaniline was one of the first π-conjugated polymers to be easily doped to afford an electronically conductive state reversibly [6]. Since this discovery polyaniline has been one of the most thoroughly investigated conjugated polymers, which has resulted in the discovery of many interesting properties including hole-transport layers for LED's and electrodes for rechargeable batteries [7]. The combination of electronic properties, ease of oxidative synthesis from aniline, and low cost make polyaniline an especially interesting material. While the oxidative polymerization of aniline predominantly yields *p*-polyaniline, some defects occur during the polymerization [8]. In order to circumvent these defects and expand the properties of polyaniline via the incorporation of substituents along the polymer chain, new methods for preparing polyanilines have been developed. Recent investigations by Buchwald [9] and Hartwig [10] have expanded the utility of palladium mediated cross coupling reactions to include carbon–nitrogen bond formation. This method couples arylhalides or -triflates with amines and has generated considerable interest for the preparation of *N*-substituted polyanilines [11], oligoanilines [12], and arylamine dendrimers [13].

While there has been considerable research on the development and investigation of palladium catalyzed carbon–nitrogen and carbon–oxygen bond formation [9,10,14], the related carbon–phosphorus and carbon–sulfur bond forming reactions have received significantly less attention [15]. The first examples of palladium catalyzed C–P bond formation included palladium catalyzed C–P(V) coupling of aryl halides with phosphonates [16] and phosphonites [17], but C–P(III) coupling was limited to silyl derivatives of primary phosphines [18]. Recent reports include efficient palladium-catalyzed coupling of aryl halides or triflates with P–H bonds of primary and secondary phosphines [19]. While many of the mechanistic details of this reaction are currently under investigation [20], it has been suggested that the mechanism is related to the proposed mechanism for palladium-catalyzed arylation of amines [21]. The mechanism involves oxidative addition of an ArX bond, base-assisted replacement of a halide by a phosphido ligand, and reductive elimination of the arylphosphine. The efficiency of palladium catalyzed C–P bond formation for condensation polymerization was first established via the preparation of easily separable supports for metal catalysts [22].

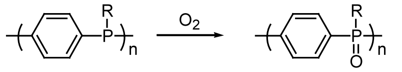
Incorporation of phosphorus into the backbone of π-conjugated polymers has been quite limited (Chart 2). Several attempts to incorporate phospholes have met with limited success; however, the oligomers are reported to have interesting optoelectric properties [23]. Phosphorus has been incorporated into poly(ferrocenylphosphine)s via ring opening polymerization of strained phosphorus bridged [1]-ferrocenophanes [24]. These polymers have been used for polymeric supports for transition metal catalysts, doped semi-conductive materials, and precursors for organometallic microstructures. Phosphorus(V) polyphosphazenes have a degree of electronic delocalization and have been commonly investigated as ionic conducting materials [25]. Phosphorus has also been incorporated into conjugated polymers inadvertently via decomposition of phosphine ligands during Suzuki or Stille coupling [26]. Nonetheless, few spectroscopic and electrochemical investigations have concentrated on the electronic effects of phosphorus incorporation into the conjugation path of conjugated polymers.

In this article we will describe several routes for the synthesis of poly(*p*-phenylene-*P*-alkylphosphine)s and related phosphine containing conjugated polymers (Chart 2). Our investigation of the spectroelectric properties of these novel polymers suggests a degree of electronic delocalization through phosphorus along the backbone of the polymer. Preliminary results of this investigation were reported in a recent communication [27].

2. Results and discussion

2.1. Polymerizations of 1,4-diiodobenzene with alkylphosphines

Initial attempts at the preparation of soluble poly(*p*-phenylene phosphine)s employed the coupling of alkyl or arylphosphines with 1,4-diiodobenzenes (Scheme 1) [27]. Polycondensations of a 1:1 mixture of diiodobenzene with primary phosphines (i-BuPH_2, 2,4,4-trimethylpentylphosphine (TMPPH_2)) were conducted with $Pd(PPh_3)_4$ in 1:1 toluene:THF with 1.1 equivalents of Et_3N. The reactions were carried out at 80 °C for 4 days and were accompanied by the appearance of a white precipitate resulting from the formation of the HI salt of Et_3N. Polymers **1a**–**b** were isolated via precipitation in nitrogen purged methanol followed by collection via filtration. The structures of **1a**–**b** are supported by ^{1}H-, ^{31}P-, and ^{13}C-NMR spectroscopy. Broad ^{1}H-, ^{31}P-, and ^{13}C-NMR resonances are observed, with integrations, chemical shifts, and scalar couplings, including ^{13}C–^{31}P scalar coupling, consistent with the anticipated polymer structures (Scheme 1). Diastereotopic ^{1}H-NMR resonances are observed for the α- and γ-protons of the 2,4,4-trimethylpentyl substituent in **1b**. Investigation of **1a**–**b** by gel permeation chromatography (GPC, THF vs. polystyrene standards) suggests that the polymer molecular weights are low ($M_n = 1000$–4000, PDI = 1.3–1.5, Table 1) which corresponds to 5–10 repeat units. Low molecular weight polymers **1a**–**b** have good solubility in THF, $CHCl_3$, and toluene but are mildly sensitive to air oxidation. Polymers **1a**–**b** are gradually converted to poly(p-phenylene-P-alkylphosphine oxide)s upon exposure to air over several days in solution and several months in the solid state (Eq. (1)) [27]. While related investigations of the palladium catalyzed synthesis of poly(N-arylaniline)s uncovered substantial quantities of cyclic oligomers [11], no evidence for cyclic phenylphosphines was uncovered.



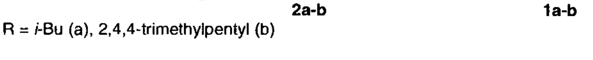
(1)

Attempts at optimization of polymerization conditions included variation of solvent, base, catalyst, and reaction time. Polymerizations were attempted in toluene, THF, DMF and dimethylacetamide. Bases investigated include DABCO, K_2CO_3, LiHMDS, and KOt-Bu. Many of the most commonly utilized palladium catalysts were investigated including dichloro-1,1′-bis(diphenylphosphino) ferrocenepalladium (Pd(DPPF)Cl_2), and palladium acetate ($Pd(OAc)_2$). The variation of polymerization conditions resulted in minor changes in the molecular weight of polymers **1a**–**b**. Longer reaction times and higher temperatures did not increase the molecular weight of polymers **1a**–**b**. We suspect that the low molecular weights of **1a**–**b** may be partially due to difficulty in obtaining an ideal 1:1 stoichiometry of the two starting materials. This could be explained by difficulties with the purification and volatility of the liquid primary alkylphosphines. Condensation polymerizations only result in the formation of high molecular weight polymers when an ideal 1:1 stoichiometry of the two difunctional monomers is used.

Table 1
Molecular weight data for polymers **1a**–**b** and **4b**

Polymer	M_n	PDI
1a [a]	1700	1.3
1b [a]	3100	1.5
1a [b]	1100	1.2
1b [b]	14 400	2.1
4b [c]	1100	1.1
4b [d]	3100	1.6

[a] Polymers prepared via Scheme 1.
[b] Polymers prepared via Scheme 2.
[c] Polymers prepared via Scheme 3.
[d] Polymers prepared via Scheme 4.

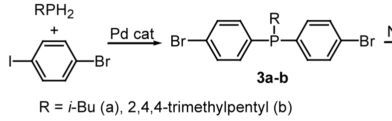


Scheme 2.

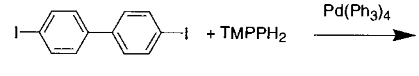
2.2. Polymerizations of 4-bromophenyl-alkylphosphines

In order to obtain higher molecular weight polymers an alternative route for the preparation of soluble poly(p-phenylene-P-alkylphosphine)s involving the cross-condensation of 4-bromophenylalkylphosphines was developed. Previous reports suggest that the first arylation of an alkyl phosphine is faster than the second, which allows the preparation of arylalkylphosphines [19b]. Addition of one equivalent of alkyl phosphines to one equivalent of 1-bromo-4-iodobenzene, one equivalent of DABCO, and 0.05 equivalent of $Pd(OAc_2)$ in toluene followed by heating at 75 °C for 4 h results in a slight darkening of the solution along with the formation of a white precipitate. After removal of the toluene by vacuum, the residue is extracted with three portions of ether. Removal of the ether by vacuum followed by distillation of the crude product affords p-bromophenylalkylphosphines (**2a**–**b**) as colorless oils in 59–68% yields (Scheme 2). While $Pd(PPh_3)_4$ was efficient for the cross coupling of 1-bromo-4-iodobenzene with alkyl phosphines, the separation of products **2a**–**b** from PPh_3 proved difficult.

Preliminary investigations using similar polymerization conditions to those described above for the condensation polymerization of dihaloaromatics with primary phosphines resulted in polymers with low molecular weight ($M_n = 1000$–3000). However, when reactions were attempted neat, polymers **1a**–**b** were prepared with significantly higher molecular weights (GPC, $M_n = 1000$–$14\,000$. PDI = 1.8–2.1, Table 1). Polymerizations were conducted in a small Teflon capped vial charged with **2a** or **b**, DABCO, and $Pd(PPh_3)_4$. The vials were heated to 130 °C allowing the reaction mixture to become a uniform viscous solu-



Scheme 3.



Scheme 4.

tion followed by gel formation after an hour. Heating of the reaction mixture was continued for variable times resulting in the formation of higher molecular weight polymers. While **1b** maintained good solubility in THF, $CHCl_3$, toluene, and NMP in all cases, when reaction times exceeded 4 days reaction mixtures of **1a** were insoluble. We suggest that this is due to the difference in solubilization of alkyl sidechain. The smaller isobutyl sidechain results in the poor solubility of **1a** while the longer 2,4,4-trimethylpentyl sidechain provides good solubility for **1b**. Polymerizations of **2a**–**b** conducted with $Pd(OAc)_2$ without solvent resulted in the formation of lower molecular weight polymers ($M_n = 1000–4000$). Attempts to conduct condensation polymerizations of 1,4-diiodobenzene with alkylphosphines (Scheme 1) without solvent proved unsuccessful due to the inhomogeneity of the reaction mixtures at high temperatures.

2.3. Polymerization of bis-p-bromophenylalkylphosphines

To further confirm the preparation of poly(*p*-phenylene-*P*-alkylphosphine)s we developed an alternative route for the preparation of related poly(arylphosphine)s utilizing traditional carbon–carbon bond forming technology. A recent report of the preparation of poly(4,4′-diphenyl-*P*-phenylphosphine oxide) ($M_n = 9000–15\,000$) by nickel-catalyzed polymerization of bis(4-chlorophenyl)phenyl phosphine oxide included an attempted preparation of poly(4,4′-diphenyl-*P*-phenylphosphine) [28]. However, the quantitative reduction of poly(4,4′-diphenyl-*P*-phenylphosphine oxide) to poly(4,4′-diphenyl-*P*-phenylphosphine) was precluded by the insolubility of the reduced polymer. Estimates from ^{31}P-NMR spectroscopy indicate that only about 35% of the polymer was reduced. The reduction of the polymer coincided with a color change from white to brownish red along with a slight red shift of the optical absorption suggesting either a decrease in the band gap resulting in extensive electron delocalization or the formation of intra-molecular donor–acceptor complexes between the phosphines and the phosphine oxides. We have investigated the direct preparation of poly(4,4′-diphenyl-*P*-alkylphosphine)s.

The synthesis of poly(4,4′-diphenyl-*P*-alkylphosphine)s was afforded via nickel catalyzed homo-coupling of bis(4-bromophenyl)-*P*-alkylphosphines (**3a**–**b**, Scheme 3) [28,29]. Bis(4-bromophenyl)-*P*-alkylphosphines (**3a**–**b**) were prepared via palladium catalyzed cross coupling of alkylphosphines with two equivalents of 1-bromo-4-iodobenzene. The structures of **3a**–**b** are supported by ^{1}H-, ^{31}P-, and ^{13}C-NMR spectroscopy. Sharp ^{1}H-, ^{31}P-, and ^{13}C-NMR resonances are observed, with integrations, chemical shifts, and scalar couplings, including ^{13}C–^{31}P scalar coupling, consistent with the anticipated structures (Scheme 3). Diastereotopic ^{1}H- and ^{13}C-NMR resonances are observed for the α- and γ-protons of the 2,4,4-trimethylpentyl substituent and the aromatic carbons in **3b**, respectively. The polycondensations of **3a**–**b** were carried out with 1.02 equivalents of $Ni(COD)_2$, 1.02 equivalents of bipyridine, in 1:1 DMF–toluene. Reaction mixtures were protected from light and heated to 60 °C for 2 h. While reaction mixtures containing **3a** formed an insoluble red solid believed to be **4a**, polymerizations of **3b** provided soluble polymer **4b** as a light yellow solid. The structure of **4b** is supported by ^{1}H-, ^{31}P-, and ^{13}C-NMR and IR spectroscopy and the molecular weight was determined by GPC ($M_n = 1100$, PDI = 1.2, Table 1). Attempts to obtain higher molecular weight polymer **4b** via nickel mediated homo-coupling of **3b** and extended reaction times resulted in insoluble polymeric materials. Polymer **4b** is oxidized slowly by atmospheric oxygen forming poly(4,4′-diphenyl-*P*-2,4,4-TMPPH oxide). While we were unable to obtain high molecular weight polymer **4b**, **3b** may be a useful material for the preparation of a variety of other phosphine containing materials.

Polymer **4b** was also prepared by the palladium catalyzed cross coupling of 4,4′-diiodobiphenyl with 2,4,4-TMPPH (Scheme 4). Reaction conditions were similar to those described above for the coupling of 1,4-diiodobenzene with alkylphosphines (Scheme 1). The spectral characterization of polymer **4b** prepared via Pd catalyzed cross-coupling was identical to polymer prepared via nickel mediated homo-coupling. The preparation of the identical polymer via two different routes provides strong additional support for the synthesis of poly(*p*-phenylene-*P*-alkylphosphine)s (**1a**–**b**). The molecular weight of **4b** prepared via palladium catalyzed cross coupling determined by GPC ($M_n = 3100$, PDI = 1.6, Table 1). The low molecular weight of **4b** prepared via two different routes suggests that the 2,4,4-trimethylpentyl substituent may be insufficient for solubilization of high molecular weight polymer.

2.4. Optical properties

While poly(p-phenylene phosphine)s are related to polyaniline, moving from the second row to the third will result in many changes in the properties of the polymers. In order to gain a better insight into the potential electronic delocalization of polymers **1a**–**b**, we prepared the corresponding alkyldiphenylphosphines and investigated the optical absorption properties of polymers **1a**–**b** and polymer model compounds isobutyldiphenylphosphine (**5a**) and 2,4,4-trimethyldiphenylpentylphosphine (**5b**) by UV–vis–NIR spectroscopy. The syntheses of **5a**–**b** were analogous to **3a**–**b**. We observe a red shift of the optical absorption upon comparing model compounds to the corresponding polymers as evidenced by the shift of the absorbance maxima for the π–π* transition for the diphenylisobutylphosphine ($\lambda_{max} = 252$ nm), when compared with polymer **1a** ($\lambda_{max} = 274$ nm) (Fig. 1). A similar trend was observed for the phenyl substituted phosphines, triphenylphosphine ($\lambda_{max} = 263$ nm), 1,4-bis(diphenylphosphino)benzene ($\lambda_{max} = 275$ nm), and poly(p-phenylene-P-phenylphosphine) ($\lambda_{max} = 291$ nm) [27]. In addition, samples of polymer **1a** precipitated in the presence of atmospheric oxygen, have additional absorption shoulders at 370 and 434 nm [27]. However, attempts to oxidize polymer **1a**, prepared and purified under nitrogen and lacking the low energy absorption shoulders, with atmospheric oxygen or [bis(trifluoroacetoxy)iodo] benzene do not result in the formation of the lower energy absorption shoulders. The low energy absorption shoulders are only present in the polymeric materials. UV–vis spectra of the polymer model compounds **5a**–**b** and 1,4-bis(diphenylphosphino)benzene do not contain these absorptions. NMR and IR spectra of polymers **1a**–**b** that contain the low energy absorption shoulders are indistinguishable from polymers that lack the absorptions. There is no evidence for the formation of phosphine oxides in samples with and without the additional absorptions. We suspect that the lower energy absorptions results from trace catalyst residues or polymer oxidation, which results in a slight unintentional doping of polymer **1a** [30]. Similar optical properties are observed for the 2,4,4-trimethylpentyl substituted model compound (**5b**) and polymer (**1b**) with absorption maxima at 252 and 273 nm, respectively. The slight red shift of the π–π* transition along with the appearance of low energy absorption bands support electronic communication via extended conjugation between phosphorus atoms along the polymer chain through the aromatic linkers. The shift in optical absorptions is similar to that observed for triphenylamine ($\lambda_{max} = 299$ nm) versus poly(N-aryl-p-phenyleneamine) ($\lambda_{max} = 333$ nm)[11] and unlike the similarity of optical absorption spectra when comparing diphenylmethane to its higher homologs [31].

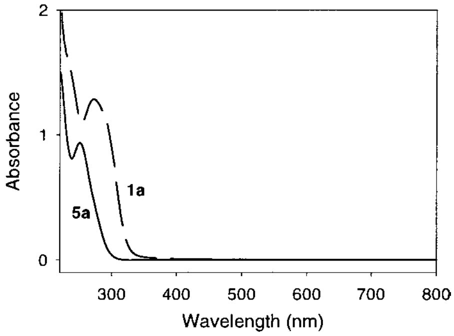


Fig. 1. UV–vis spectra for polymer **1a** and model compound **5a**.

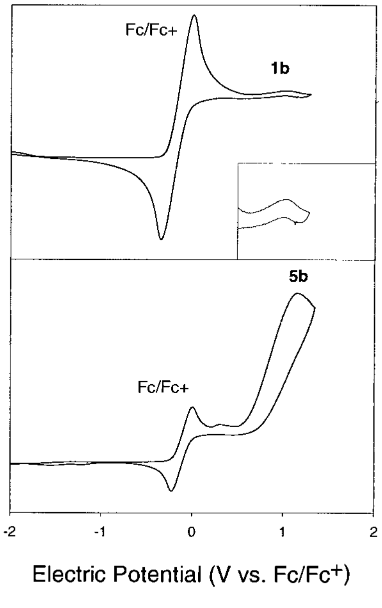


Fig. 2. Cyclic voltammograms for polymer **1b** and model compound **5b**.

2.5. Electrochemistry

Additional understanding of the electronic properties of polymers **1a**–**b** was obtained from an electrochemical investigation. Cyclic voltammetry of **1a**–**b** and **5a**–**b** was conducted in CH_2Cl_2 solution. Distinct irreversible oxidation peaks were observed for **5b** at 1.20 V versus Fc–Fc^+ while oxidation waves for **1b** were observed at 1.05 V versus Fc–Fc^+ (Fig. 2). Thus **1b** is oxidized at a 150 mV lower potential than **5b**. We observe similar behavior for the isobutyl substituted materials **5a** and **1a**. The lower oxidation potentials of polymers **1a**–**b** versus model compounds **5a**–**b** are consistent with increased electronic delocalization along the polymer chain. The shift in redox behavior between the model compounds and the polymers is consistent in both direction and magnitude with the observed shift of the optical absorption spectra providing additional support for extended conjugation in polymers **1a**–**b**.

3. Conclusions

We have described routes for the preparation of poly(arylphosphine)s via palladium catalyzed carbon–phosphorus bond formation and nickel mediated carbon–carbon bond formation. Earlier investigations that focused on the coupling of diiodobenzene with alkyl or arylphosphines resulted in the preparation of polymers **1a**–**b** with low molecular weights (1000–3000). The molecular weights of the polymers were increased (1000–14 000) via palladium-catalyzed cross coupling of difunctional monomers **2a**–**b**. The electronic properties of the materials were investigated via a combination of UV–vis–NIR spectroscopy and cyclic voltammetry. Polymers **1a**–**b** were found to have red shifted optical absorptions compared with the polymer model compounds **5a**–**b** suggesting electronic delocalization along the polymer chain through phosphorus. Cyclic voltammetry provides additional support for the electronic delocalization in polymers **1a**–**b**. While the degree and type of overlap between the lone pair on phosphorus and the adjacent aromatic groups might be questioned, our investigation provides support for electronic delocalization via an extension of conjugation through phosphorus.

With a basic understanding of the synthesis and spectroscopic properties of poly(*p*-phenylphosphine)s, we will expand our investigation via the incorporation of metals into polymers **1a**–**b**. The polymeric phosphine ligand-metal complexes may provide many interesting electronic properties. We will also conduct a detailed investigation of the source of the low energy absorption shoulders observed in samples of polymers **1a**–**b**.

4. Experimental

4.1. General comments

Organometallic reagents were stored and handled under nitrogen atmosphere in a glovebox or using Schlenk techniques. Dry, oxygen free solvents were employed throughout. Solvents were purchased from Aldrich Chemical Co. anhydrous, stored under nitrogen. All NMR spectra were acquired using a JEOL GSX 400 MHz spectrometer. Infrared spectra were recorded on a Perkin–Elmer Paragon 500 FTIR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. Molecular weights of the polymers were determined by GPC (GPC; Agilent Technology series 1100 HPLC; Detector: Differential Refractometer G1362A; Pump: Isocratic 1310A; Software: Chemstation; Column: Plgel 10^3 A) with THF as eluting solvent and polystyrene standards. Electrochemical measurements were carried out on an EG&G instruments 263A potentiostat–galvanostat using a standard cell consisting of a solid Pt working electrode and Ag/AgCl reference electrode Ag wire counter electrode. The supporting electrolyte was Bu_4NPF_6 in dry degassed methylene chloride. Ferrocene was used as an internal standard. All measurements were carried out under nitrogen. UV–vis–NIR spectra were recorded on a PE Lambda 900 UV–vis–NIR spectrometer.

4.2. Poly(p-phenylene-P-isobutylphosphine) (**1a**, Scheme 1)

A 100 ml Schlenk tube was charged with $Pd(Ph_3)_4$ (0.310 g, 0.27 mmol) and 1,4-diiodobenzene (1.77 g, 5.37 mmol) and 10 ml of 1:1 THF–toluene. To this solution was added *i*-butylphosphine (0.63 ml, 5.4 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 methanol–aqueous ammonia (500 ml) to precipitate the polymer, which was collected by filtration. The polymer was redissolved in THF, reprecipitated in methanol, filtered, washed with methanol, and dried under high vacuum for 8 h to yield polymer **1a** as a light pink solid (0.73 g, 83% yield): GPC (THF, polystyrene) $M_n = 1700$, PDI = 1.3; ^{1}H-NMR δ_H(400 MHz, $CDCl_3$) 1.01 (d, *J* 6.2, 6 H, CH_3), 1.63 (non, *J* 6.6, 1 H, CH), 1.94 (d, *J* 7.0, 2 H, CH_2), 7.33 (s, 4 H, C_6H_4); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.27 (d, J_{C-P} 9.0, CH_3), 26.22 (d, J_{C-P} -14.5, CH_2), 38.43 (d, J_{C-P} 13.3, CH); 132.66 (dd, J^2_{C-P} 19.1, J^3_{C-P} 6.1, C_6H_4); 139.53 (d, J_{C-P} -17.2, C_6H_4); ^{31}P-NMR (162 MHz, $CDCl_3$): δ -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.

4.3. Poly(p-phenylene-P-2,4,4-trimethylpentylphosphine) (**1b**, Scheme 1)

This compound was prepared via an identical procedure to that for **1a**, using 2,4,4-trimethylpentyl phosphine (0.97 ml, 5.4 mmol) instead of isobutylphosphine. This yields polymer **2a** as a light pink solid (0.98 g, 4.7 mmol, 87%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.76 (s, 9H, $(C(CH_3)_3)$, 1.00 (br, 3H, CH_3), 1.12 (mult, 1H, CH_2), 1.46 (mult, 1H, CH_2), 1.51 (br, 1H, CH), 1.88 (br, 1H, PCH_2), 2.02 (mult, 1H, PCH_2), 7.35 (br, 4H, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.32 (br, CH_3) 27.25 (br, PCH_2), 30.19 (s, $C(CH_3)_3$), 31.23 (s, $C(CH_3)_3$), 39.55 (br, CH_2), 52.77 (br, CH), 132.80 (br, C_6H_4), 139.61 (br, C_6H_4). ^{31}P-NMR (162 MHz, $CDCl_3$): δ -19.7; IR (neat, KBr, cm^{-1}) 3056, 2953, 2865, 1914, 1578, 1467, 1376, 1359, 1198, 1110, 1070, 1004, 910, 801.

4.4. *p-Bromophenylisobutylphosphine (**2a**)*

A 100 ml Schlenk tube was charged with 1-bromo-4-iodobenzene (5.00 g, 17.7 mmol), $(PPh_3)_4Pd$ (1.02 g, 0.88 mmol) and 25 ml of anhydrous toluene under nitrogen. To this solution was added isobutylphosphine (2.07 ml, 17 mmol) and triethylamine (2.47 ml, 17.7 mmol) via syringe. The reaction mixture was stirred under N_2 for 4 h at 75 °C and a substantial amount of white precipitate was observed indicating the formation of the HI salt of Et_3N. The solvent was then removed from the reaction mixture via vacuum followed by extraction of the product from the salt with three 20 ml portions of ether. Removal of solvent by vacuum followed by distillation yielded **2a** (59%, 2.47 g, 10 mmol) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.99 (d, $J = 6.6$, 6H, CH_3), 1.72 (mult, 1 H, CH), 1.85 (br, 2 H, CH_2), 4.16 (br d, $J_{PH} = 149$, 1H, PH), 7.35 (mult, 2 H, C_6H_4), 7.43 (mult, 2H, C_6H_4); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 23.76 (d, $J_{C-P} = 7.6$, CH_3), 27.32 (d, $J_{C-P} = 9.1$, CH_2), 33.18 (d, $J_{C-P} = 11.5$, CH), 122.58 (C_6H_4), 131.55 (d, J_{C-P} 6.1, C_6H_4), 134.26 (d, J_{C-P} 21, C_6H_4), 135.20 (d, J_{C-P} 7.7, C_6H_4); δ. ^{31}P-NMR (162 MHz, $CDCl_3$): δ −60.5 (d, $J_{PH} = 194$); IR (neat, KBr, cm^{-1}) 3065, 3020, 2953, 2924, 2867, 2288 (PH), 1898, 1577, 1475, 1382, 1193, 1166, 1106, 1067, 1009, 956, 936, 910, 808, 721. Anal. Calc. for $C_{10}H_{14}PBr$: C, 49.00; H, 5.76. Found: C, 49.32; H, 5.86%.

4.5. *p-Bromophenyl-2,4,4-trimethylpentylphosphine (**2b**)*

This compound was prepared via an identical procedure to that for **2a**, using 2,4,4-TMPPH (2.80 ml 15.4 mmol) instead of isobutylphosphine. This yields **2b** (68%, 3.12 g, 10.4 mmol) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.85 (s, 9H, $(C(CH_3)_3)$, 1.00 (d, $J = 6.2$, 3H, CH_3), 1.12 (mult, 1H, CH_2), 1.32 (mult, 1H, CH_2), 1.65 (mult, 1H, CH), 1.71 (mult, 1H, PCH_2), 1.82 (mult, 1H, PCH_2), 4.24 (br, 1H, PH), 7.33 (mult, 2H, C_6H_4), 7.39 (mult, 2H, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 23.75 (d, $J_{P-C} = 7.7$, CH_3) 28.61 (d, $J_{P-C} = 9.2$, PCH_2), 30.31 (s, $C(\mathbf{C}H_3)_3$), 31.24 (s, $\mathbf{C}(CH_3)_3$), 34.06 (d, $J_{P-C} = 11.5$, CH_2), 52.26 (d, $J_{P-C} = 6.9$, CH), 122.56 (s), 131.51 (d, $J_{P-C} = 5.4$, C_6H_4), 132.28 (d, $J_{P-C} = 12.2$, C_6H_4), 135.23 (d, $J_{P-C} = 16.1$, C_6H_4). ^{31}P-NMR (162 MHz, $CDCl_3$) δ −61.1 (d, $J_{P-H} = 161$); IR (neat, KBr, cm^{-1}) 3042, 3007, 2955, 2901, 2866, 2288 (PH), 1898, 1577, 1475, 1382, 1363, 1199, 1067, 1010, 809, 722. Anal. Calc. for $C_{14}H_{22}PBr$: C, 55.83; H, 7.36. Found: C, 55.51: H, 7.36%.

4.6. *Poly(p-phenylene-P-isobutylphosphine) (**1a**, Scheme 2)*

A small vial was charged with **2a** (0.20 ml, 1.0 mmol), DABCO (0.11 g, 1.0 mmol), and $Pd(PPh_3)_4$ (0.057g, 0.05 mmol) in a nitrogen filled glovebox. The vial was removed from the glove box and the reaction mixture was heated to 130 °C for 2 days. The reaction mixture melted into a viscous oil after being heated for 1 h and formed a gel after 3 h. The vial was allowed to cool followed by addition of 3 ml THF to dissolve the product. While much of the material dissolved, a mixture of crystalline white solid and amorphous red solid was not dissolved. The white crystalline solid is characteristic of the HBr salt of DABCO and we suggest that the red amorphous solid is insoluble high molecular weight polymer. The solution was added to rapidly stirring methanol (50 ml) resulting in the formation of a yellow precipitate. The precipitate was collected by filtration and dried under reduced pressure to yield **2a** (46 mg, 27%). The low yield of 2a is consistent with the poor extraction of insoluble higher molecular weight polymer. $M_n = 1100$, PDI = 1.2.

4.7. *Poly(p-phenylene-P-2,4,4-trimethylpentylphosphine) (**1b**, Scheme 2)*

A small vial was charged with **2b** (0.26 ml, 1.0 mmol), DABCO (0.11g, 1.0 mmol), and $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) in a nitrogen filled glovebox. The vial was removed from the glovebox and the reaction mixture was heated to 130 °C for 6 days. The reaction mixture melted into a viscous oil after being heated for 1 h and formed a gel after 5 h. The vial was allowed to cool followed by addition of 3 ml of THF and sonication to dissolve the product. The resulting solution was precipitated in 100 ml of rapidly stirring methanol. The tan colored solid was isolated via filtration, washed with methanol, and dried under vacuum to provide **1b** (0.205 g, 93%) $M_n = 14\,400$, PDI = 2.1.

4.8. *Bis-p-bromophenylisobutylphosphine (**3a**)*

A 100 ml Schlenk tube charged with 4-bromoiodobenzene (6.00 g, 21.2 mmol), $Pd(OAc)_2$ (0.002 g, 0.01 mmol), DABCO (2.3 g, 20 mmol), and toluene (60 ml) under nitrogen. To the reaction mixture was added isobutylphosphine (1.17 ml, 10 mmol). The reaction mixture was heated to 75 °C and allowed to stir for 90 h. The solvent was removed under reduced pressure followed by extraction with hexane (3 × 20 ml). The extracts were transferred to another Schlenk tube and the solvent was removed via vacuum. The crude product was recrystallized from hexane to yield **3a** (2.8 g, 7.0 mmol, 70%) as a white crystalline solid: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (d, $J = 6.6$, 6H, CH_3), 1.61 (non, $J = 6.4$, 1 H, CH), 1.93 (d $J = 7.0$, 2 H, CH_2), 7.25 (d $J = 7.7$, 4 H, C_6H_4), 7.44 (d $J = 7.7$, 4 H, C_6H_4); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.25 (d, $J_{C-P} = 9.2$, CH_3), 26.14 (d, $J_{C-P} = 13$, CH_2), 38.41 (d, $J_{C-P} = 13$, CH), 123.30 (s, C_6H_4), 131.71 (d, J_{C-P} 6.1, C_6H_4), 134.31 (d, $J_{\mathrm{C-P}} = 19$, C_6H_4), 138.10 (d, $J_{\mathrm{C-P}}$ 15, C_6H_4); ^{31}P-NMR(162 MHz, $CDCl_3$) δ −20.8; IR (neat, KBr, cm^{-1}) 3068, 3031, 2950, 2864, 1898, 1635, 1570, 1476, 1380, 1316, 1091, 1067, 1008, 803, 722.

*4.9. Bis-p-bromophenyl-2,4,4-trimethylpentylphosphine (**3b**)*

This compound was prepared via an identical procedure to that for **3a**, using 2,4,4-TMPPH (1.8 ml, 10 mmol) instead of isobutylphosphine to yield **3b** (3.3 g, 7.2 mmol, 72%) as a white crystalline solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.87 (s, 9H, ($C(CH_3)_3$), 1.07 (d, $J = 6.6$, 3H, CH_3), 1.18 (dd, $J = 6.4$, 14.1, 1H, CH_2), 1.52 (dd, $J = 3.5$, 13.6, 1H, CH_2), 1.57 (mult, 1H, CH), 1.89 (dd, $J = 7.6$, 13.7, 1H, PCH_2), 2.04 (dd, $J = 7.3$, 13.5, 1H, PCH_2), 7.26 (mult, 2H, C_6H_4) 7.48 (mult, 2H, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.24 (d, $J_{\mathrm{P-C}} = 9.9$, CH_3), 27.28 (d, $J_{\mathrm{P-C}} = 13.0$, PCH_2), 30.12 (s, $C(CH_3)_3$), 31.27 (s, $C(\mathbf{C}H_3)_3$), 39.52 (d, $J_{\mathrm{P-C}} = 12.2$, CH_2), 52.66 (d, $J_{\mathrm{P-C}} = 8.4$, CH), 123.23 (s, C_6H_4), 123.33 (s, C_6H_4), 131.66 (d, $J_{\mathrm{P-C}} = 6.9$, C_6H_4), 131.68 (d, $J_{\mathrm{P-C}} = 7.0$, C_6H_4), 134.28 (d, $J_{\mathrm{P-C}} = 18.4$, C_6H_4), 134.46 (d, $J_{\mathrm{P-C}} = 19.1$, C_6H_4), 138.01 (d, $J_{\mathrm{P-C}} = 13.0$, C_6H_4), 138.15 (d, $J = 14.5$, C_6H_4). ^{31}P-NMR(162 MHz, $CDCl_3$): δ −20.85; IR (neat, KBr, cm^{-1}) 3070, 3022, 2952, 2864, 1901, 1787, 1569, 1475, 1380, 1247, 1066, 1008, 802, 722. Anal. Calc. for $C_{20}H_{25}PBr_2$: C, 52.66; H, 5.52. Found: C, 52.38: H, 5.72%.

*4.10. Poly(4′,4″-diphenyl-P-2,4,4-trimethylpentylphosphine) (**4b**, Scheme 3)*

A 250 ml Schlenk tube charged with $Ni(COD)_2$ (0.14 g, 0.51 mmol) and bipyridine(0.08 g, 0.51 mmol), DMF (10 ml), and toluene (5 ml) under N_2. The mixture turns deep blue and is heated in the absence of light at 60 °C for 30 min. To the reaction mixture was added **5** (0.228 g, 0.50 mmol) dissolved in 10 ml toluene. The reaction mixture was stirred under nitrogen at 60 °C for 4 h. During this time the reaction mixture changed from blue to orange. Wet THF (20 ml) was added to stop the reaction, followed by precipitation in methanol (100 ml). Polymer **4a** was redissolved in 1:1 THF–$CHCl_3$, the solution was filtered to remove any insoluble material and the solvent was removed under reduced pressure to yield **4a** as a light yellow wax (0.09 g, 32 mmol, 63%): GPC (THF vs. polystyrene) $M_n = 1100$, PDI = 1.2; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.81 (s, 9H, ($C(CH_3)_3$), 1.09 (br, 3H, CH_3), 1.21 (br, 1H, CH_2), 1.53 (br, 1H, CH_2), 1.61 (br, 1H, CH), 1.01 (br, 1H, PCH_2), 2.11 (mult, 1H, PCH_2), 7.50 (br, 4H, C_6H_4) 7.54 (Br, 4H, C_6H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.39 (d, $J_{\mathrm{P-C}} = 10.0$, CH_3), 27.41 (d, $J_{\mathrm{P-C}} = 13.0$, PCH_2), 30.15 (s, $C(CH_3)_3$), 31.30 (s, $C(CH_3)_3$), 39.70 (d, $J_{\mathrm{P-C}} = 12.2$, CH_2), 52.80 (d, $J_{\mathrm{P-C}} = 7.6$, CH), 127.00 (d, $J_{\mathrm{P-C}} = 6.1$, C_6H_4), 127.16 (br, C_6H_4), 133.28 (d, $J_{\mathrm{P-C}} = 20$, C_6H_4), 133.48 (d, $J_{\mathrm{P-C}} = 21.4$, C_6H_4), 138.40 (br, C_6H_4), 140.59 (s, C_6H_4), 140.75 (s, C_6H_5). ^{31}P-NMR (162 MHz, $CDCl_3$): δ −20.62; IR (film, KBr, cm^{-1}) 3061, 3009, 2947, 2895, 2864, 1596, 1477, 1363, 1192, 1114, 1000, 907, 803, 730.

*4.11. Poly(4′,4″-diphenyl-P-2,4,4-trimethylpentylphosphine) (**4b**, Scheme 4)*

A 25 ml Schlenk tube charged with 4,4′-diiodobiphenyl (1.02 g, 2.5 mmol), DABCO (0.56 g, 2.5 mmol), $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol), and a stirbar in a nitrogen fillled drybox. To this reaction mixture was added 1:1 toluene:THF (15 ml). After dissolution 2,4,4-TMPPH (0.46 ml, 2.5 mmol) was added via syringe followed by heating the reaction vessel to 70 °C for 5 days. White precipitate formed during this time indicating the formation of the HI salt of DABCO. The reaction mixture was poured into rapidly stirring methanol (100 ml) to precipitate the polymer. The precipitate was collected via filtration and washed with methanol (3 × 25 ml) to yield **4a** as a light yellow solid (0.45 g, 1.5 mmol, 61%): GPC (THF vs. polystyrene) $M_n = 3100$, PDI = 1.6.

*4.12. Isobutyldiphenylphosphine (**5a**)*

In a drybox a 100 ml Schlenk tube was charged with iodobenzene (4.10 g, 20 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol), DABCO (2.25 g, 20 mmol), and a stirbar. The Schlenk tube was removed from the drybox and the reagents were dissolved in 50 ml of dry degassed toluene. To this solution was added isobutyl phosphine (1.1 ml, 10 mmol) via syringe under nitrogen. The reaction mixture was heated to 75 °C and allowed to stir for 24 h. During this time a substantial amount of white precipitate formed. The solution was transferred into a new Schlenk tube via filter cannula. The residual precipitate was extracted with hexane (3 × 15 ml) and the solvent was removed under reduced pressure to afford a light yellow oil. Hexane (20 ml) was added to precipitate any remaining catalyst. The solution was transferred to a new Schlenk tube via filter cannula. After removal of solvent via reduced pressure the crude product was distilled twice under vacuum to yield **5a** (1.8 g, 8.3 mmol, 83%) as colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.15 (d, $J = 6.6$, 6H, CH_3), 1.78 (non, $J = 6.9$, 1 H, CH), 2.10 (d $J = 7.3$, 2 H, CH_2), 7.38 (mult, 6H C_6H_5), 7.53 (mult, 4H, C_6H_4); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.43 (d, $J_{\mathrm{C-P}} = 9.8$, CH_3), 26.33 (d, $J_{\mathrm{C-P}} = 14.5$, CH_2), 38.66 (d, $J_{\mathrm{C-P}} = 13.0$, CH), 128.52 (d, $J_{\mathrm{C-P}}$ 6.1, C_6H_4), 128.55 (s, C_6H_5), 132.92 (d, $J_{\mathrm{C-P}} = 19.2$, C_6H_5), 139.59 (d, $J_{\mathrm{C-P}}$ 13.8, C_6H_5); ^{31}P-NMR(162 MHz, $CDCl_3$) δ −19.4; IR (neat, KBr, cm^{-1}) 3068, 3053, 2952, 2922, 2866, 1950, 1883, 1809, 1585, 1400, 1432, 1381, 1364, 1166, 1097, 1026, 738, 696. Anal. Calc. for $C_{16}H_{19}P$: C, 79.31; H, 7.90. Found: C, 79.15: H, 8.12%.

*4.13. 2,4,4-Trimethylpentyldiphenylphosphine (**5b**)*

This compound was prepared via an identical procedure to that for **5a**, using 2,4,4-trimethylpentyl phosphine (1.8 ml, 10 mmol) instead of isobutylphosphine. This yields **5b** (2.1 g, 7.6 mmol, 76%) as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.91 (s, 9H, $(C(CH_3)_3)$, 1.17 (d, $J = 6.6$, 3H, CH_3), 1.28 (dd, $J = 6.5$, 13.6, 1H, CH_2), 1.62 (dd, $J = 3.2$, 13.6, 1H, CH_2), 1.68 (mult, 1H, CH), 2.04 (dd, $J = 7.7$, 13.6, 1H, PCH_2), 2.18 (dd, $J = 7.1$, 13.4, 1H, PCH_2), 7.37 (mult, 3H, C_6H_5) 7.51 (mult, 2H, C_6H_5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 24.50 (d, $J_{P\text{–}C} = 9.9$, CH_3) 27.44 (d, $J_{P\text{–}C} = 13$, PCH_2), 30.26 (s, $C(CH_3)_3$), 31.37 (s, $C(CH_3)_3$), 39.78 (d, $J_{P\text{–}C} = 12$, CH_2), 52.92 (d, $J_{P\text{–}C} = 7.7$, CH), 128.45 (s, C_6H_5) 128.48 (d, $J_{P\text{–}C} = 7.1$, C_6H_5), 128.56 (d, $J_{P\text{–}C} = 7.5$, C_6H_5), 132.88 (d, $J_{P\text{–}C} = 18$, C_6H_5), 133.14 (d, $J_{P\text{–}C} = 18$, C_6H_5), 139.52 (d, $J_{P\text{–}C} = 14$, C_6H_5), 139.66 (d, $J = 14$, C_6H_5). ^{31}P-NMR (162 MHz, $CDCl_3$): δ −19.3 (s). IR (neat, KBr, cm^{-1}) 3070, 3053, 2951, 2865, 1949, 1882, 1808, 1585, 1478, 1432, 1363, 1247, 1198, 1095, 1026, 999, 738, 696, 507. Anal. Calc. for $C_{20}H_{27}P$: C, 80.50; H, 9.12. Found: C, 79.91: H, 9.35%.

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