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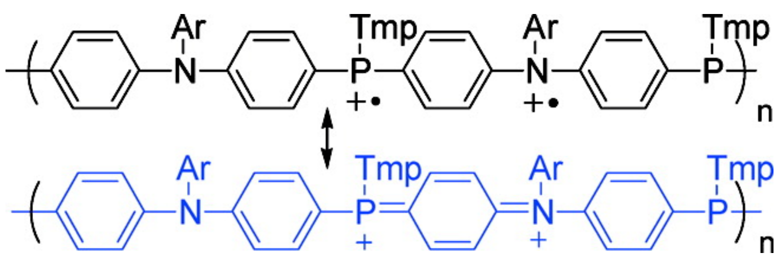

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Poly-*p*-phenylene Phosphine/Polyaniline Alternating Copolymers: Electronic Delocalization through Phosphorus

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Abstract: Phosphorus-containing poly(*N*-arylaniline)s and related polymer model compounds have been prepared. The spectroscopic and electronic properties of the materials were investigated via UV−vis−NIR spectroscopy and cyclic voltammetry. PPPP−PANI copolymers containing *p*-phenylene diamine units in the polymer backbone have electronic and spectroscopic properties characteristic of aromatic substituted *p*-phenylene diamines. Copolymers containing $-(-C_6H_4-P-C_6H_4-P-C_6H_4-)-$ linkages between nitrogen centers show evidence for weak electronic delocalization along the polymer chain. The electrochemical and spectroscopic properties support strong electronic delocalization in copolymers containing $-(-P-C_6H_4-N-C_6H_4-)-$ repeat units. The presence of a single diphenylphosphine bridge between nitrogen centers provides an efficient mode of electronic delocalization between nitrogen centers. PPPP oxide−PANI copolymers and related polymer model compounds were also prepared and investigated. The resemblance of PPPP oxide−PANI copolymers to isolated *p*-phenylene diamines or triarylamines suggests electronic isolation of the amine fragments in the polymer. The conversion of phosphorus(III) phosphines to phosphorus(V) phosphine oxides inhibits electronic delocalization through phosphorus, further supporting delocalization of the lone pair of electrons on phosphorus in PPPP−PANI copolymers. PPPP−PANI copolymers are a new type of π-conjugated polymer with low oxidation potentials and electronic delocalization through phosphorus along the polymer chain.

Introduction

The preparation of conjugated polymers containing metals or other modifiable atoms in the conjugation path has been of great interest.[1] Conjugated polymers have delocalized electrons along the polymer backbone that result in useful electronic properties including conductivity and electroluminescence.[2−4] The presence of metals or heteroatoms allows a site for chemical or electrochemical modification of the electronically active polymer. The modifications allow tuning of the electronic properties of the polymer. This tunability has been used for sensor, switching, magnetic, and other applications.[1,5,6] While several metals and heteroatoms, sulfur and nitrogen, in particular, have been incorporated into conjugated polymers,[1b,d] incorporation of phosphorus has only recently been investigated.[7−13]

Incorporation of phosphorus into the backbone of π-conjugated materials has been accomplished in a number of ways (Chart 1), but evidence for delocalization of the lone pair on phosphorus is limited. Reports on the preparation and investigation of phosphole-containing conjugated oligomers[8] and polymers support the presence of extended π-delocalization.[9] However, involvement of the lone pair on phosphorus in the extended π-delocalization is limited.[10] Phosphorus(III)−carbon double bonds and phosphorus(III)−phosphorus(III) double bonds have been incorporated into conjugated materials in the form of "phospha"-PPVs[11] and "diphospha"-PPVs.[12] Related diphosphine-containing materials have interesting electronic properties, suggesting possible use as a molecular switch.[13] While the phosphorus analogues of PPV have interesting electronic and spectroscopic properties, they have limited interactions of the lone pair on phosphorus with the π-delocalized system. Poly(*p*-phenylene phosphine)s are the only ex-

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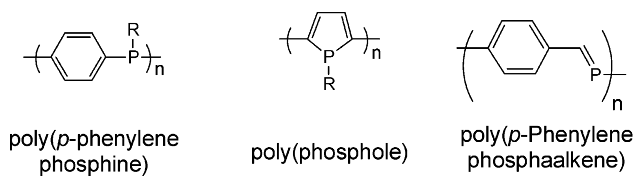
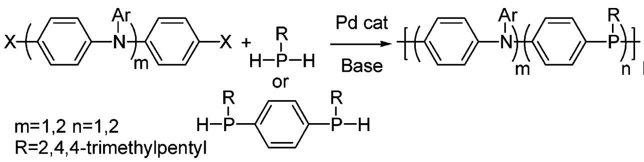
Chart 1



Scheme 1



amples where the lone pair on phosphorus is involved in extended delocalization.[14] Other examples supporting overlap of the lone pair on phosphorus with p orbitals on carbon include phosphanylcarbenes reported by Bertrand and co-workers.[15] The X-ray structure of a phospanyl(mesityl)carbene contains a phosphorus atom in a planar environment consistent with electronic donation of the lone pair into the vacant orbital of the carbene. These results suggest that the lone pair on phosphorus has good overlap with the electron-deficient p orbital on carbon. However, further investigation is required to determine the extent of delocalization of the lone pair of electrons on phosphines and related phosphorus(III) species.

The preparation and investigation of oligo(*N*-phenylaniline),[16,17] poly(*N*-arylaniline)s,[18] and poly(phenylenesulfide)−polyaniline alternating copolymers[19−21] have been reported. In most cases the electronic and spectroscopic properties are similar to polyaniline. However, the substituted polymers have good solubility in organic solvents, providing superior processability. Incorporation of poly(phenylenesulfidephenyleneamine) as a hole transport layer in trilayer light-emitting diodes has been shown to promote hole injection from ITO into the emissive layer.[22] In this article we describe the synthesis of poly(*p*-phenylene phosphine)−polyaniline alternating copolymers (PPPP−PANI, Scheme 1). PPPP−PANI copolymers are prepared via palladium-catalyzed C−P or C−N bond-forming reactions. Depending on the structure of the comonomers used for polymerization, PPPP−PANI copolymers have been prepared with main-chain alternating units comprised of $-(-N-C_6H_4-P-C_6H_4-)-$, $-(-N-C_6H_4-N-C_6H_4-P-C_6H_4-)-$, or $-(-N-C_6H_4-P-C_6H_4-P-C_6H_4-)-$. Investigation of the spectroscopic and electrochemical properties of these novel polymers supports electronic delocalization through phosphorus along the backbone of the polymer upon chemical or electrochemical oxidation.

Results

Synthesis of Monomers for Polymerization. The preparation of PPPP−PANI copolymers can be conducted by either N−C or P−C bond-forming reactions. Efficient palladium-catalyzed C−N bond-forming reactions have recently been developed by Hartwig[23] and Buchwald,[24] while the related palladium-catalyzed P−C bond-forming reactions have also been reported.[25] We attempted to prepare PPPP−PANI copolymers via both N−C and P−C bond-forming reactions and discovered that condensation polymerization via P−C bond formation is more effective for polymerization reactions. While palladium-catalyzed C−N bond-forming reactions have been used to generate poly(*N*-arylamine)s,[18] the polymerization procedures typically utilize hindered phosphine ligands, which allow the generation of reactive Pd(0) monophosphine complexes.[26] Attempts to prepare PPPP−PANI copolymers using similar conditions were ineffective. The problems encountered during attempts to prepare PPPP−PANI copolymers via C−N bond-forming reactions are likely due to the presence of high concentrations of unhindered phosphine comonomers. Alternative attempts to conduct C−N bond-forming polymerizations with PdBINAP or PdDPPF generated only low molecular weight oligomers. Therefore, palladium-catalyzed C−N and C−P bond-forming reactions were used to prepare the appropriate monomers for polymerization, and P−C bond-forming reactions were used for polymerization reactions.

The preparation of 1,4-bis(*N*-4′-iodophenyl,-*N*-4′′-*n*-butylphenylamino)benzene (**2**) followed a two-step procedure. First, reaction of 1,4-dibromobenzene with excess (5 equiv) 4-butylaniline catalyzed by Pd(DPPF)Cl_2 (2.5 mol %) in toluene with 2.2 equiv of NaO*t*-Bu was conducted for 2 days at 100 °C. Purification via column chromatography yields light yellow crystals of 1,4-bis(*N*-4′-*n*-butylphenylamino)benzene (**1**, 65% yield). Conversion of diamine **1** to **2** is achieved by reaction of **1** with excess 1,4-diiodobenzene catalyzed by Pd(DPPF)Cl_2 (5 mol %) in toluene with 2.2 equiv of NaO*t*-Bu for 7 days at 100 °C. This provides **2** as a yellow solid (20% yield).

Following related procedures *N*,*N*-bis-*p*-bromophenyl-*p*-anisidine (**3**) was prepared via the palladium-catalyzed cross coupling of *p*-anisidine with dibromobenzene. Compound **3** was isolated as a white crystalline material in 61% yield. Attempts to prepare *N*,*N*-bis-*p*-bromophenyl-*p*-*n*-butylaniline via palladium-catalyzed cross coupling of dibromobenzene with *n*-butylaniline provided only low yields of the monosubstituted product. While **3** is a good starting material for the preparation

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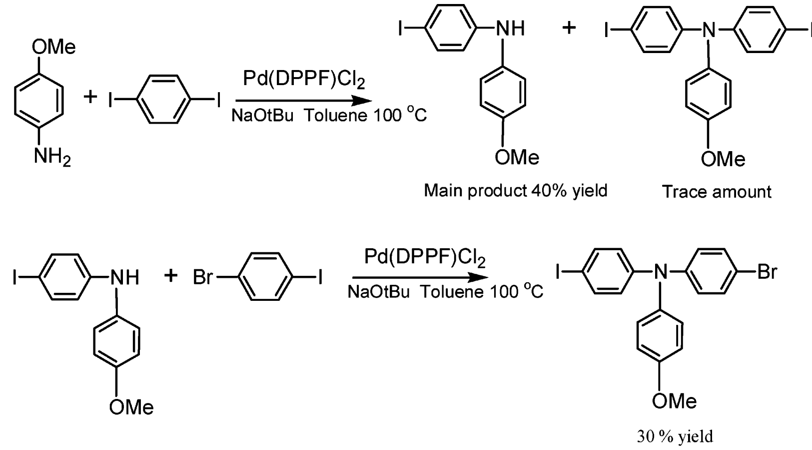
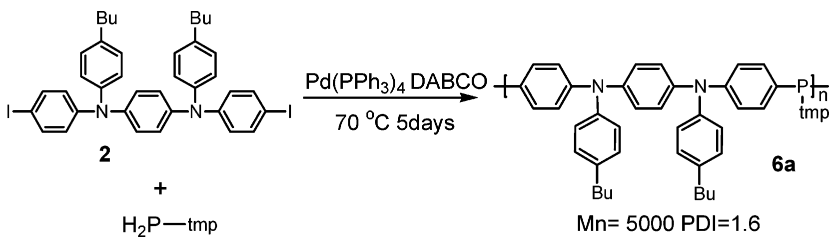
Scheme 2



4

Scheme 3



2

6a

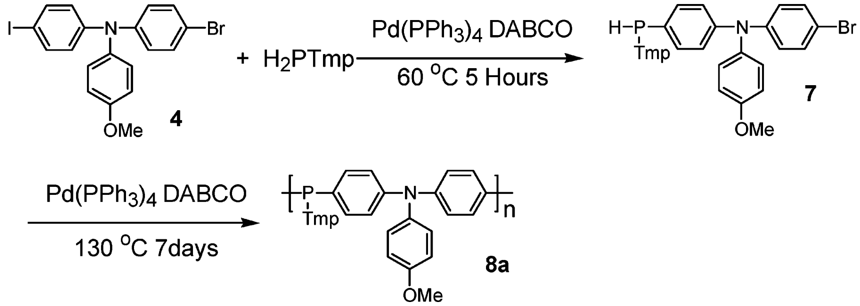
of PPPP−PANI copolymers with a backbone consisting of $-(-N-C_6H_4-P-C_6H_4-P-C_6H_4-)-$, as described below, attempts to utilize **3** for the preparation of PPPP−PANI copolymers with a $-(-N-C_6H_4-P-C_6H_4-)-$ backbone proved difficult due to the high reaction temperatures (∼130 °C) required to prepare high-molecular weight polymers and the low boiling point of the comonomer 2,4,4-trimethylpentylphosphine (78 °C). Therefore, we attempted to prepare the more reactive *N*,*N*-bis-*p*-iodophenyl-*p*-anisidine. Surprisingly, the Pd(DPPF)-Cl_2-catalyzed coupling of *p*-anisidine with 1,4-diiodobenzene provided a moderate yield of *N*-*p*-iodophenyl-*p*-anisidine (40%) but only a trace amount of the desired *N*,*N*-bis-*p*-iodophenyl-*p*-anisidine (Scheme 2). Several attempts were conducted using either Pd(DPPF)Cl_2 or Pd$(OAc)_2$/BINAP as the catalyst, but significant quantities of *N*,*N*-bis-*p*-iodophenyl-*p*-anisidine were not observed under any reaction conditions. Alternatively, isolation and purification of *N*-*p*-iodophenyl-*p*-anisidine did allow the preparation of *N*-*p*-bromophenyl-*N*-*p*-iodophenyl-*p*-anisidine (**4**). Palladium-catalyzed coupling of *N*-*p*-iodophenyl-*p*-anisidine with 1-bromo-4-iodobenzene produced **4** as a light yellow low melting solid in 21% isolated yield (Scheme 2). Oddly, attempts to prepare **4** from *N*-*p*-iodophenyl-*p*-anisidine and 1,4-dibromobenzene were unsuccessful.

The synthesis of PPPP−PANI with a $-(-N-C_6H_4-P-C_6H_4-P-C_6H_4-)-$ backbone is most easily achieved via preparation of a diphosphine monomer. Reaction of 2,4,4-trimethylpentylphosphine with 1,4-diiodobenzene was catalyzed by Pd$(OAc)_2$ (0.5 mol %) in the presence of 2.2 equiv of DABCO. The reaction mixture was heated for 24 h at 70 °C to yield 1,4-bis(*P*-2′,4′,4′-trimethylpentylphosphino)benzene (**5**) as a colorless oil in 48% yield after purification. All purification procedures including extractions and solvent removal were conducted under an inert atmosphere to prevent conversion of the secondary phosphines to phosphine oxides.

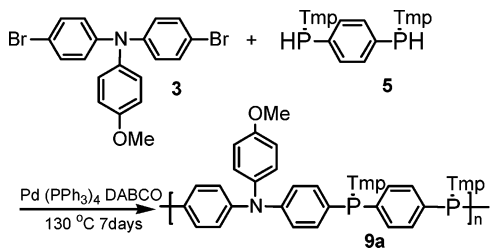
Synthesis of PPPP−PANI Copolymers. PPPP−PANI copolymers were afforded via palladium-catalyzed P−C bond formation. The appropriate primary phosphine or secondary diphosphine was coupled to dihaloaromatic amines or dihaloaromatic diamines. In all cases the polymerizations were conducted with a 1:1 stoichiometry of phosphine and dihaloaromatic amine or diamine with 2 mol % Pd$(PPh_3)_4$ as the catalyst and 2.2 equiv of DABCO as a base without added solvent. Attempts to prepare PPPP−PANI copolymers via reactions in organic solvents (THF or toluene) resulted in low molecular weight materials due to poor solubility of the polymers. PPPP−PANI copolymers are sensitive to oxidation, forming phosphine oxides in solution exposed to air over several days. In the solid state air oxidation is much slower. While most of the polymers have good solubility in THF, $CHCl_3$, and NMP, some of the isolated material is not soluble in organic solvents (THF, NMP, $CHCl_3$, etc.). IR spectra of the insoluble fractions are identical to those of the soluble PPPP−PANI copolymers. The similarity of the IR spectra is consistent with identical polymer structure but higher molecular weight for the insoluble material.

Polymer **6a** contains a $-(-N-C_6H_4-N-C_6H_4-P-C_6H_4-)-$ backbone and is prepared by the palladium-catalyzed coupling of **2** with 2,4,4-trimethylpentylphosphine (H_2PTMP) (Scheme 3). The polymerization reaction is conducted at 70 °C for 5 days. During this time the reaction mixture went from a light yellow viscous liquid to a dark gel. Isolation of **6a** is afforded via suspension in THF with sonication followed by precipitation in N_2-purged MeOH. One-half of the precipitated polymer does not redissolve in THF after precipitation. The soluble fraction has broad ^1H and ^{31}P resonances with integrations, chemical shifts, and scalar couplings consistent with the anticipated polymer structures. IR spectra of the insoluble fraction are similar to IR spectra of the soluble polymer,

Scheme 4



Scheme 5

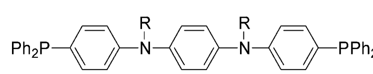


suggesting that the insoluble material is a higher MW fraction of the polymer. Investigation of the soluble fraction by gel permeation chromatography (SEC, THF vs polystyrene standards) suggests that the molecular weight of **6** is low (M_n = 5000, PDI = 1.6), corresponding to an average of nine repeat units. While shorter reaction times result in lower quantities of insoluble polymer, the soluble fraction has a similar molecular weight, consistent with precipitation of higher molecular weight **6a**.

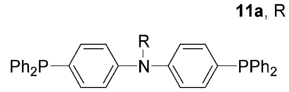
The preparation of a PPPP−PANI copolymer containing a $-(-N-C_6H_4-P-C_6H_4-)-$ backbone structure (**8a**) was conducted with palladium-catalyzed cross-coupling of a 1:1 mixture of **4** and H_2PTMP (Scheme 4). The polycondensations involve a two-step procedure. First, the reaction mixture was heated to 60 °C for 5 h, allowing the aryl iodide to couple with the primary phosphine, generating a difunctional intermediate in situ (**7**, Scheme 4). Upon formation of **7** the reaction temperature was increased to 130 °C for 7 days. The initial phase of the reaction consumes all of the volatile H_2PTmp, allowing higher reaction temperatures during polymerization. The reaction mixture was a light yellow viscous liquid before heating, which was converted to a gel after the first 4 h of heating and then formed a hard black solid. Resulting polymer **8a** was suspended in THF over 5 h via sonication followed by precipitation in nitrogen-purged methanol and collection via filtration. Only about one-third of the collected solid dissolved in THF or NMP; the remaining material was insoluble in organic solvents. ^{1}H and ^{31}P NMR spectra of the soluble fraction of **8a** support the expected structure. Investigation of the soluble fraction of **8a** by gel permeation chromatography (SEC, THF vs polystyrene standards) suggests that the molecular weight is low (M_n = 3000, PDI = 1.5), corresponding to seven repeat units. Shorter reaction times resulted in smaller quantities of insoluble polymer, but the molecular weight of the soluble fraction was largely unchanged.

Synthesis of PPPP−PANI copolymer containing a $-(-N-C_6H_4-P-C_6H_4-P-C_6H_4-)-$ backbone (**9a**, Scheme 5) was achieved via palladium-catalyzed cross coupling of **3** with **5**. The polymerization was conducted at 130 °C for 7 days, resulting in formation of a hard black solid **9a**. The black solid was suspended in THF with sonication over 5 h, precipitated in nitrogen-purged methanol, and collected via filtration. All of the precipitate can be redissolved in THF. The structure of **9a** is supported by ^{1}H and ^{31}P NMR spectroscopy. Size-exclusion chromatography of **9a** (SEC, THF vs polystyrene standards) suggests that the polymer molecular weight is moderate (M_n = 11 K, PDI = 1.9), corresponding to 16 repeat units. The higher molecular weight of **9a** vs **6a** and **8a** is likely due to the greater proportion of solubilizing 2,4,4-trimethylpentyl substituents providing enhanced solubility of the higher molecular weight fraction. In addition, PPPP−PANI copolymer **9a** contains a single dominant signal observed by ^{31}P NMR spectroscopy (>95%), suggesting higher molecular weight polymer by end-group analysis. Related low estimates of the molecular weight of phosphine-containing polymers have been reported.[27]

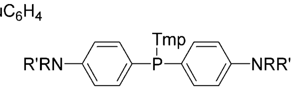
Synthesis of Polymer Model Compounds. The synthesis of polymer model compound **10a** was conducted via the palladium-catalyzed cross coupling of 2.0 equiv of diphenylphosphine with 1.0 equiv of *N*,*N*-bis-*p*-bromophenyl-*p*-anisidine (**3**). The neat reaction mixture was heated for 2 weeks at 130 °C followed by extraction with hot hexane to provide crude **10a**. Recrystallization in hexanes yields light yellow crystals (**10a**, 45% yield). Polymer model compound **11a** was prepared and purified using similar conditions to those for **10a** except 2 equiv of diphenylphosphine and 1 equiv of 1,4-bis(*N*-4′-iodophenyl,-*N*-4″-*n*-butylphenylamino)benzene (**2**) were used as staring materials. Alternatively, polymer model compound **12a** was prepared by reacting H_2PTmp with an excess amount of **3**.



11a, R = *n*-BuC_6H_4



10a, R = *p*-MeOC_6H_4



12a, R = C_6H_4-*p*-OCH_3, R′ = C_6H_4-*p*-Br

Synthesis of PPPP Oxide−PANI Copolymers and Model Compounds. Poly(*p*-phenylene phosphine oxide)−PANI copolymers (**6b**, **8b**, and **9b**) are formed by reaction with hydrogen peroxide (Scheme 6).[28] Modified copolymers (**6b**, **8b**, and **9b**) were purified by precipitation into hexane and characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies and size-exclusion chromatography (SEC). The quantitative nature of the trans-

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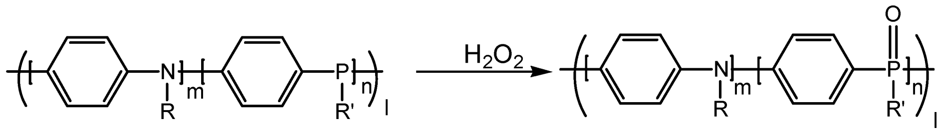
Scheme 6



6a, 8a, 9a, and **13a** → **6b, 8b, 9b,** and **13b**

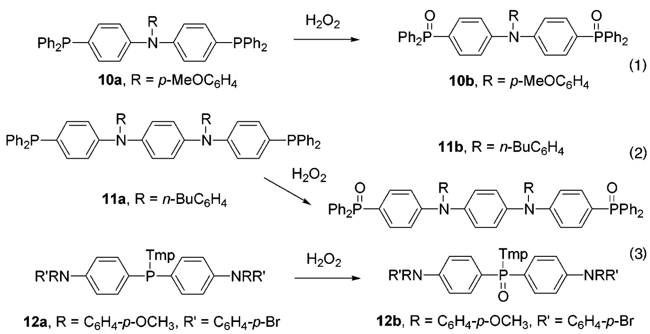
6: R = *p*-*n*-Bu-C_6H_4-;
R' = 2,4,4-trimethylpentyl;
m = 2; n = 1

8: R = *p*-$CH_3OC_6H_4$-;
R' = 2,4,4-trimethylpentyl;
m = 1; n = 1

9: R = *p*-$CH_3OC_6H_4$-;
R' = 2,4,4-trimethylpentyl;
m = 1; n = 2

13: R' = 2,4,4-trimethylpentyl
m = 0, n = 1

formations is easily monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR resonances for poly(*p*-phenylene phosphine oxide)−PANI copolymers are between 30 and 32 ppm. The molecular weight of PPPP oxide−PANI copolymers as estimated by SEC is about one-half of that observed for the PPPP−PANI copolymers (M_n = 2200, **6b**; 1500, **8b**; 5000, **9b**). The change in M_n suggests a significant alteration in the conformation of the copolymers upon conversion of the phosphines to phosphine oxides. Polymer model compounds **10a, 11a,** and **12a** were modified and characterized via related methods to the PPPP−PANI copolymers (eqs 1−3).



Cyclic Voltammetry of PPPP−PANI Copolymers and Model Compounds. The structural similarity of PPPP−PANI copolymers **6a**, **8a**, and **9a** with polyaniline and poly(*p*-phenylene phosphine)s suggests a potential for similar electrochemical properties. Previous investigations of poly(*p*-phenylene-*P*-2,4,4-trimethylpentylphosphine) (**13a**) support electronic delocalization through phosphorus along the polymer backbone.[14] Poly-[18] and oligo(*N*-arylaniline)s[17] have similar electrochemical properties to polyaniline, consistent with the formation of delocalized radical cations along the polymer chain. To understand the electrochemical properties of **6a**, **8a**, and **9a**, we conducted cyclic voltammetry of the polymers and polymer model compounds **10a, 11a**, and **12a** in CH_2Cl_2 solution. The cyclic voltammetry data is summarized in Table 1. Cyclic voltammetry of **6a** reveals three irreversible oxidations at 0.15, 0.45, and 0.83 V vs Fc/Fc$^+$. The first two oxidations occur at similar oxidation potentials to those reported for *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine (0.13 and 0.65 V vs Fc/Fc$^+$)[17] and polymer model compound **11a** (0.21 and 0.52 V vs Fc/Fc$^+$, Table 1). The stepwise oxidation of aryl-substituted *p*-phenylene diamines to form $-(-NC_6H_4N-)-^+$ and $-(-NC_6H_4N-)-^{+2}$ fragments has been thoroughly investigated.[29] Therefore, the first two oxidation peaks are assigned to loss of electrons from the *p*-phenylene diamine fragment of **6a**. The third peak at 0.83 V is at a similar potential to that reported for **13a** and is likely to result from removal of an electron from an orbital located primarily on phosphorus.[14b]

Table 1. Cyclic Voltammetry Data for PPPP−PANI Copolymers and Model Compounds

compound	E_{1ox} [a]	E_{2ox} [b]	E_{3ox} [c]
6a	0.15	0.45	0.83
6b	0.36	0.73	
8a	0.09	0.83	
8b	0.67		
9a	0.50	0.79	
9b	0.63		
10a	0.60	0.82	
10b	0.67		
11a	0.21	0.52	0.75
11b	0.29	0.66	
12a	0.33	0.74	
12b	0.62		
13a	0.89		

[a] Standard cell consisting of a Pt working electrode, Ag/AgCl reference electrode, and Pt wire counter electrode. Scan rate is 50mV/s. [b] Polymer solution (1.0 mM) in 0.1 M Bu_4NBF_4 supporting electrolyte was in dry degassed methylene chloride. Ferrocene (1.0 mM) was used as an external standard. [c] The electrical potential of Fc/Fc$^+$ was set to 0.00 V.

Cyclic voltammetry of **9a** provides quite different results. Two oxidation peaks are observed at 0.50 and 0.79 V vs Fc/Fc$^+$. The first peak occurs at a lower potential than tri-*p*-anisylamine (0.68 V vs Fc/Fc$^+$)[30] but higher than the first oxidation peak of *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine. The oxidation potentials of **9a** are similar to polymer model compound **10a** (0.60 and 0.82 V vs Fc/Fc$^+$). **10a** contains a single triarylamine center substituted by two triarylphosphines. For both **9a** and **10a** the first oxidation is assigned to loss of an electron from a nitrogen-centered orbital, while the second oxidation occurs from a phosphorus-centered orbital.

Intermediate results to those obtained for **6a** and **9a** are observed for **8a**. Cyclic voltammetry of **8a** reveals two distinct oxidation peaks at 0.09 and 0.83 V vs Fc/Fc$^+$. The first oxidation peak occurs at a 0.41 V lower potential than **9a** but has a similar potential to the first oxidation peak of **6a** and **11a**. Since **8a** does not contain $-(-NC_6H_4N-)-$ units, a stepwise oxidation

(29) (a) Bailey, S. E.; Zinc, J. I.; Nelsen, S. F. *J. Am. Chem. Soc.* **2003**, *125*, 5939−5947. (b) Lambert, C.; Noll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434.
(30) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498−3503.

to generate $-(-NC_6H_4N-)-^{+}$ and $-(-NC_6H_4N-)-^{+2}$ is not possible. There is only one oxidation peak below 0.75 V, suggesting a single oxidation from a nitrogen-centered orbital. The oxidation peak at 0.83 V is assigned to loss of an electron from a phosphorus-based orbital. Presumably, the low oxidation potential observed for the first oxidation peak of **8a** results from electronic communication between two adjacent triphenylamine units through the connecting phosphorus. This interpretation is supported by investigation of model compound **12a**. The first oxidation potential of **12a** (0.33 V) is between that of **8a** and **11a** as one might expect for a single polymer repeat unit. Both **8a** and **12a** contain two nitrogens connected by a $-(-C_6H_4-P-C_6H_4-)-$ linkage. If the linkage between triphenylamine fragments contains a bisphosphine linkage $-(-C_6H_6-P-C_6H_4-P-C_6H_4-)-$ (**9a**) or the triphenylamine units are not connected as in **10a**, the first oxidation peak is observed at a significantly higher potential (0.50 and 0.60 V vs Fc/Fc$^+$, respectively). The electrochemical properties of **8a** and **12a** are unique and observed only when there is a single $-(-C_6H_4-P-C_6H_4-)-$ linkage between nitrogen centers. Related unique properties are observed for UV−vis−NIR spectra of **8a** as discussed below.

Cyclic Voltammetry of PPPP Oxide−PANI Copolymers and Model Compounds. The electrochemical properties of PPPP oxide−PANI copolymers were investigated with cyclic voltammetry (CV). Oxidation potentials of PPPP oxide−PANI copolymers and model compounds are summarized in Table 1.

Cyclic voltammetry of **6b** reveals two reversible oxidations at 0.36 and 0.73 V vs Fc/Fc$^+$. The first two oxidations for **6b** occur at slightly higher oxidation potentials than **6a** and are similar to polymer model compound **11b** (0.29 and 0.66 V vs Fc/Fc$^+$). The electrochemical oxidations of **6b** are assigned to the loss of electrons from the *p*-phenylene diamine fragments.

The electrochemical properties of **8b** and **9b** differ from those of **6b** and are consistent with the absence of *p*-phenylene diamine units. Quasi-reversible oxidations are observed for **8b** and **9b** at 0.67 and 0.63 V vs Fc/Fc$^+$, respectively. Polymer model compound **10b** is structurally related to polymers **8b** and **9b** containing a triarylamine substituted by two *p*-phenyl phosphine oxides. Alternatively, polymer model compound **12b** contains a phosphine oxide substituted by two arylamines. The reversible oxidations of **10b** (0.67 V vs Fc/Fc$^+$) and **12b** (0.62 V vs Fc/Fc$^+$) are analogous to **8b** and **9b**. The equivalence of the oxidation potentials for **8b**, **9b**, **10b**, and **12b** and similarity to related substituted triarylamines supports oxidation of electronically isolated triarylamine fragments in polymers **8b** and **9b**. The loss of the difference in oxidation potentials between **8a** and **9a** upon conversion to the phosphine oxides **8b** and **9b** is consistent with a loss of electronic delocalization in **8a** upon conversion to **8b**.

UV−Vis−NIR Spectroscopy of PPPP−PANI Copolymers. UV−vis absorption spectra of neutral polymers **6a**, **8a**, and **9a** are similar, containing absorption maxima at 319, 335, and 338 nm, respectively. The absorptions are assigned to $\pi-\pi^*$ transitions characteristic of aromatic compounds. Upon chemical oxidation of polymers **6a**, **8a**, and **9a** with $NOBF_4$ the spectral properties retain many similarities. The UV−vis−NIR absorptions are summarized in Table 2. The chemical oxidations require an excess amount of oxidant to remove sequential electrons from the polymer chain. The oxidation potential of

Table 2. UV−Vis−NIR Data for the Chemical Oxidation of PPPP−PANI Copolymers and Polymer Model Compounds

	neutral[a]		first oxidation[b]		second oxidation[c]	
6a	319	30	275	12	419	14
			417	16	669	7.7
			929	14		
8a	335	19	295	12	275	13
			356	20	353	13
			833	1.0	670	2.0
					725	2.0
9a	302	30	287	20	277	22
	338	32	357	29	355	22
			836	2.0	654	3.0
					727	3.0
10a	336	33	353	25		
			798	10		
11a	324	41	372	13	422	13
			419	20	663	23
			954	18	810	8.0
12a	314	34	336	29	358	24
			809	2.0	668	5.0
					751	10
13a	277	28	285	20		
			350	5.0		
			670	1.0		
			739	1.0		

[a] The wavelength maximum and apparent extinction coefficient per unit of polymer ($\epsilon_{max} \times 10^{-3}$) are provided for each major absorption. [b] The spectral characteristic of the first new species generated upon stepwise chemical oxidation. [c] The spectral characteristic of the second new species generated upon stepwise chemical oxidation.

NO has been reported to be between 1.05[31] and 1.20[32] V vs Fc/Fc$^+$, suggesting that $NOBF_4$ is a strong enough oxidant to fully oxidize **6a**, **8a**, and **9a**. While we do not have a full understanding of the requirement for excess oxidant, the oxidations are reproducible; similar results were observed using different oxidants and correlate well with the cyclic voltammetry data.

Stepwise titration of **6a** with the one-electron oxidant $NOBF_4$ in CH_2Cl_2 results in the appearance of a narrow band at 417 nm and a very broad absorption in the NIR centered at approximately 929 nm (Figure 1). The NIR absorption is typically attributed to intramolecular charge transfer in *p*-phenylenediamines.[29] Continued addition of $NOBF_4$ results in a gradual transition to new absorptions at 419 and 669 nm (Figure 1). Similar results are obtained for the chemical oxidation of the polymer model compound **11a**. Addition of $NOBF_4$ provides a new broad absorption centered at 954 nm, while further addition of oxidant shifts the absorption to shorter wavelength ($\lambda_{max} = 868$ nm). Continued addition of $NOBF_4$ results in a further shift of the absorptions to 663 nm. The absorptions are consistent with stepwise oxidation of the 1,4-phenylene diamine fragment to form $-(-NC_6H_4N-)-^{+}$ and $-(-NC_6H_4N-)-^{+2}$. Similar absorptions have been reported for the radical cation and dication of TPD[33] and *N*,*N*,*N*,*N*-tetra-*p*-methoxyphenyl-1,4-phenylenediamine.[29b]

Chemical oxidation of **8a** provides related spectral changes to those observed for **6a**. Stepwise titration of CH_2Cl_2 solutions

(31) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. VII, p 325.
(32) Castellano, C. E.; Calandra, A. J.; Arvia, A. J. *Electrochim. Acta* **1974**, *19*, 701−712.
(33) (a) Cornil, J.; Gruhn, N. E.; dos Santos, D. A.; Malagoli, M.; Lee, P. A.; Barlow, S.; Thayumanavan, S.; Marder, S. R.; Armstrong, N. R.; Bredas, J. L. *J. Phys. Chem. A* **2001**, *105*, 5206−5211. (b) Low, P. J.; Paterson, M. A. J.; Puschmann, H.; Goeta, A. E.; Howard, J. A. K.; Lambert, C.; Cherryman, J. C.; Tackley, D. R.; Leeming, S.; Brown, B. *Chem. Eur. J.* **2004**, *10*, 83−91.

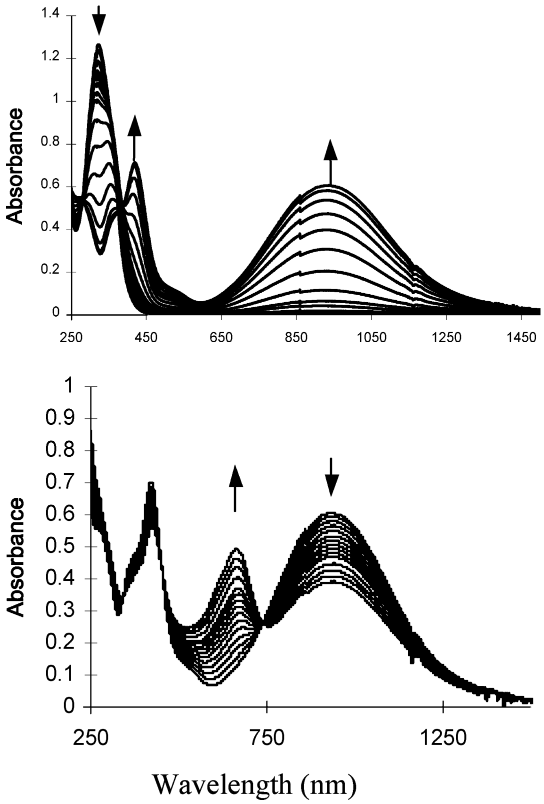


Figure 1. UV−vis spectra of the chemical oxidation of polymer **6a** (3.5×10^{-5} M) with $NOBF_4$ (0.6 equiv per aliquot). (Top) Addition of 0.0−9.6 equiv of $NOBF_4$. (Bottom) Addition of 9.6−19.2 equiv of $NOBF_4$.

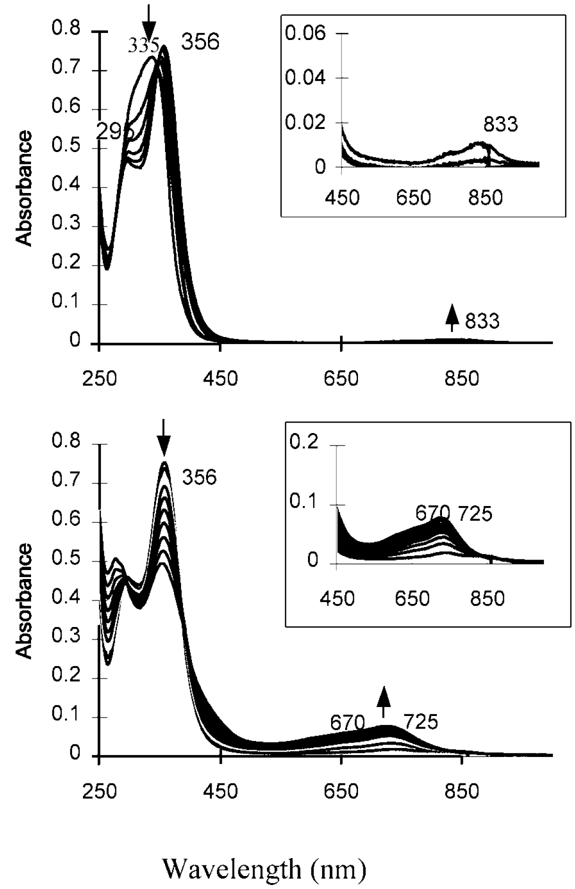


Figure 2. UV−vis spectra of the chemical oxidation of polymer **8a** (2.3×10^{-5} M) with $NOBF_4$ (0.75 equiv per aliquot). (Top) Addition of 0.0−6.0 equiv of $NOBF_4$. (Bottom) Addition of 6.0−13.5 equiv of $NOBF_4$.

of **8a** with $NOBF_4$ is consistent with the appearance of two species (Figure 2). The addition of low concentrations of $NOBF_4$ results in the appearance of a sharp band at 353 nm and a broad band centered at 833 nm (Figure 2). The change in absorption spectra upon oxidation is accompanied by isosbestic points at 250 and 360 nm, consistent with the presence of two species. Continued addition of $NOBF_4$ causes the disappearance of the absorption at 833 nm and appearance of new absorptions at 356, 670, and 725 nm (Figure 2). While the chemical oxidation of polymer **8a** is similar to model compound **12a**, it is quite different than the chemical oxidation of model compound **10a**. Stepwise oxidation of **12a** results in the appearance of a sharp absorption at 336 nm and broad absorption at 809 nm. Further addition of oxidant results in disappearance of the bands at 336 and 809 nm along with appearance of new bands at 358, 668, and 751 nm. Isosbestic points were observed, supporting the presence of two different species. The stepwise oxidation of **10a** results in the appearance of two absorptions at 353 and 798 nm. The oxidation product of **10a** has similar spectral characteristics to the second oxidation state of **8a** and **12a**. Broad absorptions above 800 nm are only observed in **8a** and **12a** but not **10a**. The lack of the low-energy absorption at low concentrations of oxidant for **10a** suggests that the presence of two nitrogen centers connected by a $-(-C_6H_4-P-C_6H_4-)-$ linkage is a requirement for observation of this species. While aromatic−NO^+ complexes have been characterized, the presence of the absorption band at 833 nm at low concentrations of oxidant for **8a** and **12a** and absence of a similar band for **10a** are inconsistent with an aromatic or phosphine NO^+ complex.[34]

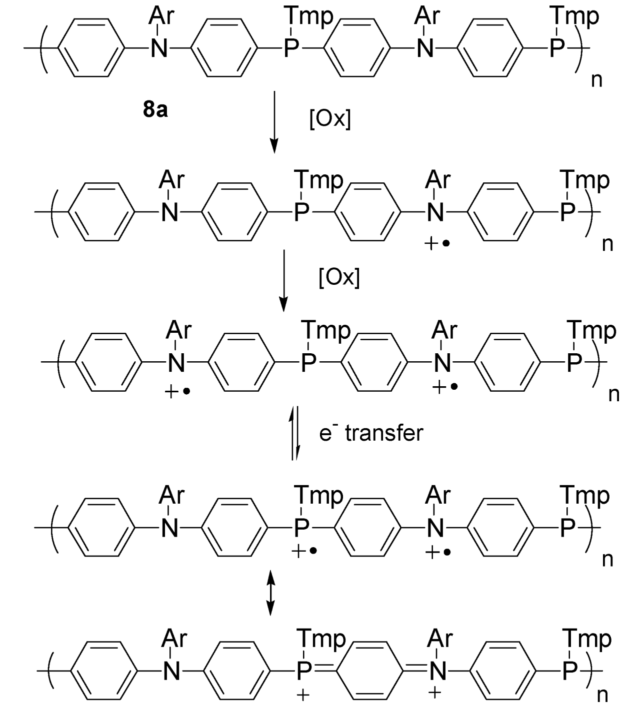
(34) Kim, E.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962−4974.

The results strongly support electronic communication between the two nitrogen centers through a phosphine center in **8a** and **12a**. The proposed structure of the different oxidation states of **8a** is depicted in Scheme 7. An explanation for these observations is provided below.

The spectral properties of **9a** are similar to those reported for **8a**. Sequential chemical oxidation of **9a** results in the formation of two new species. The first species contains absorption maxima at 357 and 836 nm, while the second species possesses absorption maxima at 355, 654, and 727 nm. Conversion to each new oxidation species is accompanied by isosbestic points, supporting the presence of two different oxidation states of **9a**.

Reinvestigation of the stepwise chemical oxidation of PPPP homopolymer **13a** was also conducted.[14] Stepwise addition of $NOBF_4$ to CH_2Cl_2 solutions of **13a** resulted in the appearance of new absorption bands at 350, 670, and 739 nm. The two new absorption bands at 670 and 739 nm upon oxidation of **13a** occur at similar wavelengths to those observed for **10a** and the second oxidation state of **8a**, **9a**, and **12a**. The similarity of these absorption bands suggests that chemical oxidation of phosphine and amine centers in PPPP−PANI copolymers and model compounds cannot be distinguished by UV−vis−NIR spectroscopy. Therefore, observation of absorption bands between 650 and 800 nm in **8a** and **9a** can be attributed to concurrent amine and phosphine oxidations. Related chemical oxidations of triphenylphosphine provided a new absorption at 336 but no absorption above 400 nm. The different spectroscopic

Scheme 7



properties of **13a** and triphenylphosphine provides additional support for electronic delocalization of poly(*p*-phenylene phosphine)s. Addition of a large excess amount of oxidant to **8a**, **9a**, **10a**, **12a**, or **13a** or storage of the oxidized species for over 1 h results in decomposition of the oxidized species, as evidenced by the appearance of new absorptions between 300 and 650 nm. While the new species appear to be stable, we have been unable to isolate or characterize the decomposition products.

UV−Vis−NIR Spectroscopy of PPPP Oxide−PANI Copolymers and Model Compounds. The spectroscopic properties of PPPP oxide−PANI copolymers **6b**, **8b**, and **9b** and the polymer model compounds **10b**, **11b**, and **12b** were investigated by UV−vis−NIR spectroscopy. The UV−vis−NIR spectral data is summarized in Table 3.

UV−vis absorption spectra of polymer **6b** and model compound **11b** are nearly identical with strong absorptions in the ultraviolet region (λ_{max} = 315 and 316 nm, respectively). Stepwise chemical oxidation of **6b** via addition of $NOBF_4$ results in the appearance of new absorption bands centered at 415 and 935 nm (Figure 3). The broad band at 935 nm is similar to absorptions observed for other phenylene diamines upon removal of a single electron, generating a radical cation.[30] The presence of an isosbestic point at 370 nm supports the presence of two distinct species. Further addition of $NOBF_4$ alters the spectral properties of **6b**. The absorptions at 415 and 935 nm decrease, while absorptions at 426 and 652 nm increase (Figure 3). The new absorptions are similar to those reported for dicationic *p*-phenylene diamines.[29] Polymer model compound **11b** has comparable spectral properties upon oxidation, generating spectral properties consistent with radical cations (λ_{max} = 416 and 898 nm) at low concentrations of $NOBF_4$ and a dication at high concentrations of oxidant (λ_{max} = 436 and 668 nm). The UV−vis−NIR spectra of **6b** and **11b** are dominated by the *p*-phenylene diamine fragments and show little evidence of electronic delocalization along the polymer chain in **6b**.

Table 3. UV−Vis−NIR Absorption Data for **6b** and **8**−**13b**

	neutral[a]		first oxidation[b]		second oxidation[c]	
8b	339	19	295	11		
			348	15		
			724	1.0		
6b	316	30	415	17		
			935	14	652	24
9b	342	32	278	21		
			340	23		
			721	1.0		
10b	339	33	354	24		
			714	12		
11b	315	41	416	24	668	49
			898	19		
12b	326	36	364	23		
			669	8.0		
			751	14		
13b	243	31				

[a] The wavelength maximum and extinction coefficient ($\epsilon_{max} \times 10^{-3}$) are provided for each major absorption. [b] The spectral characteristic of the first new species generated upon stepwise chemical oxidation. [c] The spectral characteristic of the second new species generated upon stepwise chemical oxidation.

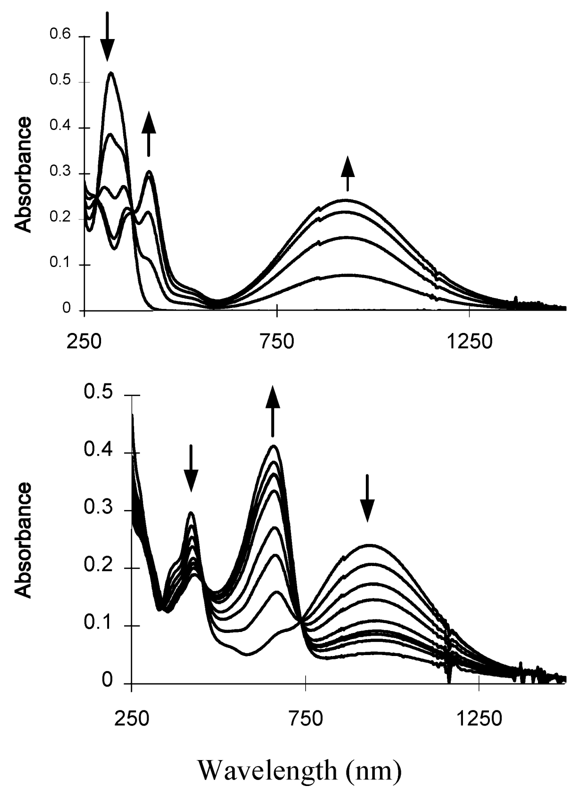


Figure 3. Chemical oxidation of polymer **6b** (1.8×10^{-5} M) with $NOBF_4$ (1.25 equiv per aliquot). (Top) Addition of 0.0−6.25 equiv of $NOBF_4$. (Bottom) Addition of 6.25−16.25 equiv of $NOBF_4$.

The absorption spectra of polymers **8b** and **9b** and model compounds **10b** and **12b** are also similar (λ_{max} = 339, 342, 339, and 324 nm, respectively). Upon stepwise chemical oxidation of **8b** with $NOBF_4$ new absorptions centered at 348 and 724 nm appear, consistent with the formation of arylamine radical cations (Figure 4).[29] Similar absorptions are observed for **8b** (λ_{max} = 340 and 721 nm), **9b** (λ_{max} = 354 and 714 nm), and **12b** (λ_{max} = 374 and 751 nm) upon chemical oxidation. Interestingly, the broad absorptions observed for **8a** (λ_{max} = 833 nm), **9a** (λ_{max} = 836 nm), and **12a** (λ_{max} = 809 nm) at low concentrations of oxidant are not observed for **8b**, **9b**, and **12b**. The lack of low-energy absorptions at low concentrations of

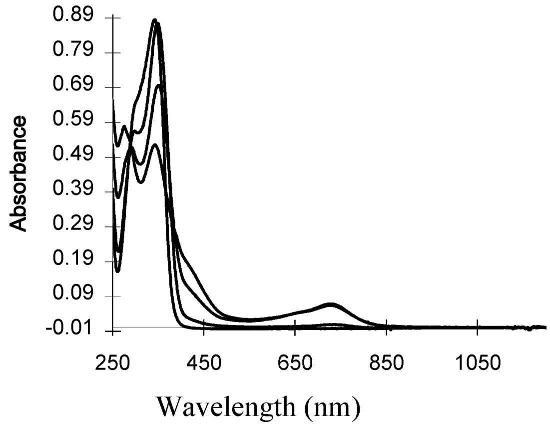


Figure 4. Chemical oxidation of polymer **8b** (4.6×10^{-5} M) with $NOBF_4$ (0.5 equiv per aliquot). Addition of 0.0−1.5 equiv of $NOBF_4$.

oxidant for **8b** and **9b** provides additional support for electronic delocalization through phosphorus in polymers **8a** and **9a**. Finally, reinvestigation of the chemical oxidation of **13b** via stepwise addition of $NOBF_4$ resulted in no observed spectral changes, as expected due to a lack of nonbonding electrons on phosphorus in **13b**.

Discussion

The synthetic, spectroscopic, and electrochemical investigation of PPPP−PANI copolymers and related model compounds provides strong evidence for involvement of the lone pair of electrons on phosphorus in extended electronic delocalization.

Cyclic voltammetry of PPPP−PANI copolymers (**6a**, **8a**, and **9a**) and model compounds (**10a**, **11a**, and **12a**) provides evidence for multiple oxidations. In all cases the first oxidation is consistent with removal of an electron for an aromatic amine. The first oxidation potentials have the following order **10a** > **9a** > **12a** > **11a** > **6a** > **8a**. There are several interesting aspects of the ordering of the oxidation potentials. Model compound **10a** has the highest oxidation potential. This is not surprising since **10a** is an aromatic amine with two *p*-diphenylphosphine substituents. While there is potential for delocalization of the nitrogen-based radical cation onto the *p*-diphenylphosphines, the high oxidation potential, comparable to tri-*p*-anisylamine (0.67 V vs Fc/Fc^+), suggests insignificant electronic delocalization. Since **10a** and **9a** are both anisidines containing $-(-P-C_6H_4-N-C_6H_4-P-)-$ linkages, one would anticipate that in the absence of electronic delocalization the oxidation potentials would be very similar. The oxidation potential of polymer **9a** is 100 mV lower than that of **10a**. While the difference in oxidation potentials could be attributed to the different substituents on phosphorus, we suggest that it is the result of weak electronic delocalization between adjacent nitrogen centers via the $-(-C_6H_4-P-C_6H_4-P-C_6H_4-)-$ linkage. Further support for this assignment is discussed below.

Polymer **6a** and model compound **11a** have low first oxidation potentials (0.15 and 0.21 V vs Fc/Fc^+, respectively) and a low second oxidation potential, as expected for *p*-phenylene diamines. However, the first oxidation potential for **6a** is 60 mV lower than that of **11a**. While this difference is small, it is consistent with weak electronic delocalization between *p*-phenylene diamine units via a $-(-C_6H_4-P-C_6H_4-)-$ linkage. However, the strongest evidence for electronic delocalization of the lone pair on phosphorus is found in the oxidation potentials of **8a** and **12a**. Surprisingly, polymer **8a** has the lowest first oxidation potential of all PPPP−PANI copolymers (0.09 V). The first oxidation potential of **8a** is 60 mV lower than that of **6a**. While this can be partially explained by different substituents on nitrogen, *p*-*n*-butylphenyl vs *p*-methoxyphenyl, electronic donation of the *p*-methoxyphenyl substituent cannot fully explain the extremely low oxidation potential of **8a.** A correspondingly low oxidation potential is observed for model compound **12a** (0.33 V). The oxidation potential of **12a** is 270 mV lower than that of **10a** and 240 mV higher than that of **8a**. Assuming that electronic delocalization is negligible in **10a**, one could assume that **12a** has about one-half of the delocalization of **6a**. This is fully consistent with strong electronic delocalization between adjacent nitrogen centers through a $-(-C_6H_4-P-C_6H_4-)-$ linkage. **12a** contains a single $-(-N-C_6H_4-P-C_6H_4-N-)-$ unit, while **8a** has a $-(-N-C_6H_4-P-C_6H_4-)_n-$ repeat unit in the polymer backbone. Related changes in the the oxidation potentials of oligo- and poly-*N*-arylanilines have been reported in support of electronic delocalization.[17,18] Further support of electronic delocalization through phosphorus is provided upon conversion of PPPP−PANI copolymers to PPPP oxide−PANI copolymers.

Comparison of the oxidation potentials of PPPP−PANI copolymers **6a, 8a,** and **9a** with PPPP oxide−PANI copolymers **6b**, **8b**, and **9b** suggests changes in the electronic structure upon modification (Table 1). The first oxidation peak shifts to a higher electrochemical potential for all PPPP oxide−PANI copolymers (**6b**, **8b**, and **9b**), as expected for more electron-deficient compounds. In addition, one less oxidation is observed for all PPPP oxide−PANI copolymers. This oxidation is primarily assigned to removal of an electron from a phosphorus-centered orbital. The absence of this oxidation wave is consistent with conversion of nonbonded electrons to a bonding pair. The shift of the first oxidation potential upon conversion of the phosphines to phosphine oxides is relatively small for model compounds **10a** (70 mV) and **11a** (80 mV). Slightly larger shifts are observed for PPPP−PANI copolymers **6a** (210 mV) and **9a** (120 mV). While the small shifts in oxidation potentials for **10a** and **11a** are consistent with a change in electron density from electron-donating phosphines to electron-withdrawing phosphine oxides, the larger shifts for **6a** and **9a** suggest a loss of the weak electronic delocalization through the $-(-C_6H_4-P-C_6H_4-)-$ or $-(-C_6H_4-P-C_6H_4-P-C_6H_4-)-$ linkages as described above

The large shift in oxidation potentials of **8a** and **12a** upon conversion to **8b** and **12b** cannot be explained by a change in the electron density of the phosphorus center. The first oxidation potentials of **8a** and **12a** are shifted by 580 and 290 mV, respectively, upon conversion to **8b** and **12b**. The large difference in the first oxidation potential of **8a** relative to **8b** is consistent with a significant change in electronic delocalization. The dramatically lower oxidation potential of **8a** (0.09 V) compared to **10a** (0.60 V) is attributed to electronic delocalization between two adjacent nitrogen centers through the connecting phenyl phosphine linkage. However, upon conversion of phosphines to phosphine oxides the oxidation potential of **8b** is identical to that of **10b** (0.67 V), which is consistent with a loss of delocalization. Conversion of the phosphorus(III) centers in **8a** to phosphorus(V) centers in **8b** results in elimination of unshared electrons on phosphorus and coincides with a dramatic increase in oxidation potential. This strongly suggests that the lone pair of electrons on phosphorus in **8a** is delocalized in an extended π-conjugated system along the polymer backbone. Related differences in the electronic structure of **8a** and **12a** are observed by UV−vis−NIR spectroscopy as described below.

UV−vis−NIR spectra of the chemical oxidation of PPPP−PANI copolymers and model compounds fall into three categories. In the first category the UV−vis−NIR spectra of polymer **6a** and model compound **11a** are dominated by the *p*-phenylene diamine fragments.[29] The second category contains model compound **10a**, which has spectra consistent with oxidation of an isolated aromatic amine.[29] The third category contains polymers **8a** and **9a** and model compound **12a**. These compounds' spectra contain additional features not observed in isolated aromatic amines. At low concentrations of oxidant a new species is observed, which contains a broad absorption with a maximum between 809 and 836 nm. We assign this feature to a charge-transfer band associated with charge transfer between two adjacent nitrogen centers through *p*-phenylene phosphine linkages. The presence of this new band correlates with changes in the oxidation potentials of **8a**, **9a**, and **12a** as discussed above. While one might anticipate that a similar band would be observed for **6a**, the absorption occurs at a similar wavelength to the absorption associated with the charge-transfer band of the *p*-phenylenediamine radical cation. The extinction coefficient of **6a** (12 000) is much larger than that of **8a**, **9a**, and **12a** (1000−2000). Therefore, it is unlikely that one would be able to observe the N−P−N charge-transfer band in **6b**.

The UV−vis−NIR spectral properties of PPPP oxide−PANI copolymers are consistent with a loss of electronic delocalization through phosphorus upon conversion of the phosphine to phosphine oxide. There are only two types of PPPP oxide−PANI copolymers or model compounds. While **6b** and **11b** have spectra characteristic of *p*-phenylene diamines, **8b**, **9b**, **10a**, and **12a** have spectra characteristic of isolated aromatic amines. The unique spectral properties assigned to charge transfer between two adjacent nitrogen centers through *p*-phenylene phosphine linkages in **8a**, **9a**, and **12a** are lost upon conversion of the phosphorus(III) phosphines to phosphorus(V) phosphine oxides.

A proposed mechanism for the oxidation of **8a** is depicted in Scheme 7. The first oxidation removes an electron from every other nitrogen. The broad absorption at 833 nm is characteristic of an intramolecular charge-transfer band from an electron-rich nitrogen to a nitrogen-based radical cation. The second oxidation provides radical cations at either amines or phosphines adjacent to the initial site of oxidation. While one might anticipate that phosphine oxidations would occur at higher potential than amine oxidations, the anaerobic oxidation potentials for triphenylamine[30] and triphenylphosphine[35] in acetonitrile (+0.98 vs SCE and +0.830 vs Ag/0.1 M $AgNO_3$, respectively) are similar. The quinoidal resonance form of **8a**$^{2+}$ (Scheme 7) is a likely source of the unique spectroscopic and electrochemical properties of **8a** and **12a**. While there is limited experimental evidence for species containing $[R_2P{=}CR_2]^+$ fragments,[36] as depicted in Scheme 7, there is substantial computational support for π conjugation.[37]

Conclusions

We have shown that phosphorus-containing poly(*n*-arylaniline) (PPPP−PANI) can be prepared via palladium-catalyzed carbon−phosphorus bond formation. Spectroscopic and electrochemical investigations of PPPP−PANI copolymers strongly support electronic delocalization through P(III) centers along the polymer backbone. Conversion of phosphorus(III) phosphines to phosphorus(V) phosphine oxides inhibits electronic delocalization through phosphorus, further supporting delocalization of the lone pair of electrons on phosphorus. PPPP−PANI copolymers are a new type of π-conjugated polymer with low oxidation potentials and electronic delocalization through phosphorus along the polymer chain.

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Supporting Information Available: Experimental procedures for the preparation of PPPP−PANI copolymers and polymer model compounds, UV−vis spectra of the chemical oxidation of **9a**, **9b**, **10a**, **10b**, **11a**, **11b**, **12a**, **12b**, **13a**, and **13b**, and cyclic voltammographs of **6a**, **6b**, **8a**, **8b**, **9a**, **9b**, **10a**, **10b**, **11a**, **11b**, **12a**, and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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