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A Fluorescent (*E*)-Poly(*p*-phenylenephosphaalkene) Prepared by a Phospha-Wittig Reaction

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A soluble (*E*)-poly(*p*-phenylenephosphaalkene) having sterically encumbering ligands has been prepared by a phospha-Wittig reaction. This material exhibits a bathochromic shift with respect to *E*-PPV and with respect to representative model oligomers. We also report the first fluorescence study of a poly(*p*-phenylenephosphaalkene) and find that this material exhibits fluorescence, though with modest intensity relative to similarly sized carbon-based analogues.

Polymers featuring π-conjugation along the main chain are currently of great interest and importance.[1] Many such materials have been synthesized that incorporate heteroatoms in their backbones, notably poly(thiophene) and poly(aniline). Interaction of accessible lone pairs of electrons on these elements allows potential participation in π conjugation (n−pπ interactions) and leads to interesting and unique properties versus all-carbon analogues. Several recent investigations have focused on the incorporation of other elements, notably phosphorus, into oligomers[2] and polymers[3] featuring possible π conjugation (Chart 1).[4] Possibly the most familiar synthetic polymers incorporating phosphorus are the polyphosphazenes and related systems that have been the subject of a large body of work.[5] Such polymers clearly display valuable properties but do not display the type of extended π conjugation that is sought in the current study.

Phosphorus has become an attractive candidate for replacement of carbon in pπ−pπ conjugated materials due to its similar electronegativity; indeed, phosphorus has often been referred to as a "carbon copy",[6] and calculations predict similar conjugative abilities for phosphorus and carbon in olefinic type bonds.[7] Very recently, poly(*p*-phenylenephosphaalkene)s (**B**) have been prepared and shown to exhibit properties expected for conjugation.[3b] We have been working to prepare building blocks for integrating P═C units within a stable extended framework. Recently, we described tetraarylbenzenes and their use for preparing diphosphaalkenes.[8] The diphosphaalkenes were quickly prepared in good yields via a transient di-"phospha-Wittig"[9] reagent (Scheme 1). This type of phospha-Wittig reaction[10] generally proceeds in quantitative yield by NMR spectroscopic analysis and often gives >90% isolated yield, making this synthetic methodology amenable to the strict requirements of a successful step polymerization.[11] The preliminary study reported herein represents the first application of a phospha-Wittig reaction,

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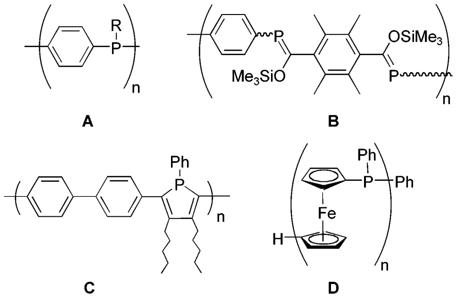
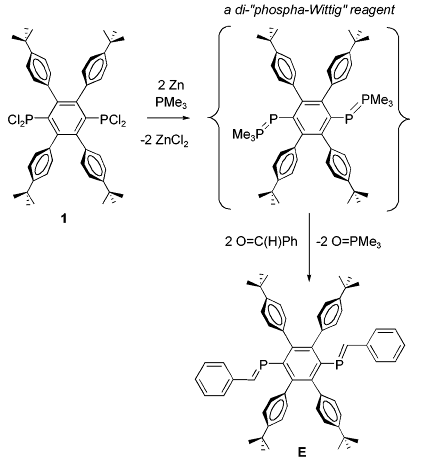
10.1021/ic0345471 CCC: $25.00

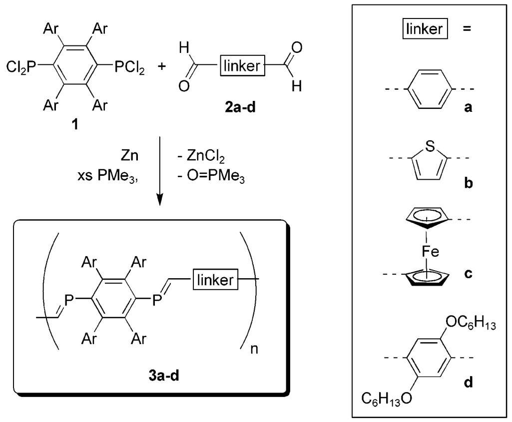
Chart 1. Some Polymers with Possible π Conjugation Involving Phosphorus



Scheme 1



Scheme 2



a novel analogue of the classic organic reaction, to polymer synthesis.

In order to extend the phospha-Wittig methodology in Scheme 1 for polymer synthesis, conjugated dialdehydes were used in place of benzaldehyde (Scheme 2). Mixtures of **1**, dialdehydes **2a**−**c**, zinc dust, and PMe_3 were allowed to stir in THF overnight. In each case, highly colored materials were obtained; however, full characterization of these polymers (**3a**−**c**) was thwarted by their very limited solubility in organic solvents, a difficulty also observed for unsubstituted PPV.[1a] Analysis of the soluble fractions of the reaction mixtures showed the presence of $O{=}PMe_3$ as the only phosphorus containing species, indicating the intended coupling most likely occurred. To overcome this obstacle, dialdehyde **2d**[12] was chosen for reaction with **1**, as its hexyloxy side chains should engender solubility as they often do for PPVs. This approach indeed leads to the successful synthesis of a hexanes-soluble poly(*p*-phenylenephosphaalkene) **3d** as an orange powder after stirring the reactants for 8 h at room temperature.[13] Spectroscopic analysis (^{31}P NMR) confirms the complete consumption of **1**, and after removal of volatiles in vacuo, only peaks assignable to **3d** and to trimethylphosphine oxide are present (Figure 1). The two broad ^{31}P NMR resonances for **3d** represent internal and end group P═C units, and the integrations of these signals parallel the ^{1}H NMR spectral results. An additional significant aspect of this phospha-Wittig reaction is that only *E*-phosphaalkenes are produced, making this method ideal for the preparation of π conjugated materials.

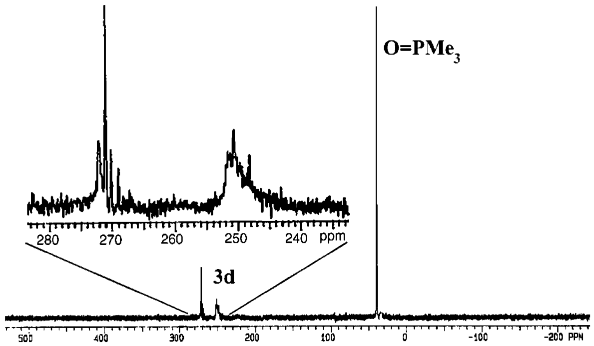
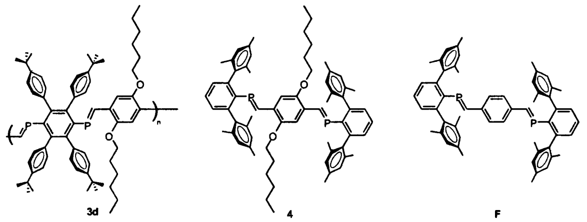


Figure 1. ^{31}P NMR spectrum for crude reaction mixture of **3d** after removal of volatiles.

Chart 2



End group analysis (^{1}H NMR integrations of phosphaalkene versus aldehydic protons) indicates that the average degree of polymerization is 6, corresponding to a material with an average of 12 (P═C) units per chain with a modest M_n estimated at 6500 g mol^{-1}. Bis-phosphaalkene **4** (Chart 2) was also prepared as an oligomeric model for **3d**, and absorption and fluorescence spectra (Figure 1) were collected for the two materials. The absorption maximum of 445 nm for **3d** represents a substantial red shift as compared to the only other known poly(*p*-phenylenephosphaalkene)[3b] (**B**, λ_{max} = 338 nm, *Z*/*E* = 1.14) and even a 19 nm red shift versus *E*-PPV (λ_{max} = 426 nm),[14] despite the modest conjugation length in **3d**. The absorption maximum for polymer **3d** is identical to that for model compound **4**; thus, the increased color of the former material arises from the broader absorp-

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(13) **3d** (24.8%): ^{1}H NMR ($CDCl_3$) δ 0.89−1.31 (br, 58H), 3.40−3.90 (br, 4H), 6.50−7.20 (br, 18H), 8.40−8.80 (br, 2H), 10.32 (br, 0.17H per repeat unit); ${}^{31}P\{{}^1H\}$ NMR($CDCl_3$) δ 250.5 (br, internal P═C), 270.6 (s, end group P═C).

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tion that extends further into the visible region compared to the latter. These data can also be compared to absorption data for two other structurally related diphosphaalkenes **E** and **F** (Chart 2 and Scheme 1) that display $\lambda_{\max}$ values of 349 and 411 nm, respectively. The lower energy transition (presumably $\pi-\pi^*$) for **F** may be ascribed in part to the fact that better conjugation of the two P═C units occurs across the less hindered phenylene linker. The significant bathochromic shift (34 nm) in the $\pi-\pi^*$ transition of **4** compared to that of **F** is largely attributable to the electronic effects due to substitution of the central ring in **4** with strongly electron-donating alkoxy groups. Similar effects are well established in PPV systems,[15] as demonstrated by the progressively lower energy $\pi-\pi^*$ transition upon comparing unsubstituted PPV (426 nm), poly(phenylenevinylene-*alt*-2,5-di-*n*-alkoxyphenylenevinylene)s (~459 nm),[16] and poly-(2,5-dimethoxyphenylenevinylene)s (~474 nm).[17]

Both **3d** and **4** showed fluorescence (Figure 2), with the fluorescence intensity per P═C unit in the polymer observed to be a factor of 3.3 greater than that of **4** and approximately 8% that of *E*-stilbene. The weaker fluorescence intensity in **3d** versus its all-carbon analogues may be due to quenching by the phosphorus lone pair, or simply a heavy atom effect.[18] The steric bulk employed in our choice of linker also endows **3d** with a good degree of air stability, with no change being observed by ^{31}P NMR after the solid was allowed to stand open to air for one week. The steric factors in **3d** thus aid thermal stability compared to **B**, although the stabilization is not complete, as solutions of this material still undergo reaction with air and moisture.

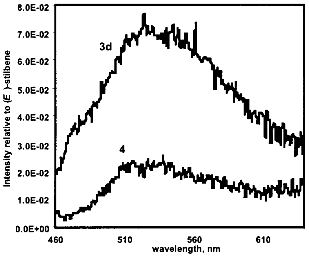

Figure 2. Fluorescence spectra of **3d** and **4** ($CHCl_3$) relative to (*E*)-stilbene.

In summary, a soluble (*E*)-poly(*p*-phenylenephosphaalkene) with modest air stability imparted by sterically encumbering ligands has been prepared by a phospha-Wittig reaction. This material exhibits a bathochromic shift with respect to unsubstituted *E*-PPV. We also report the first fluorescence study of a poly(*p*-phenylenephosphaalkene) and find that this material does exhibit fluorescence, though with modest intensity relative to carbon-based analogues. Current efforts are underway to access soluble analogues of **3a**−**c**, as well as to optimize experimental conditions for maximum degree of polymerization of the resultant polymers.

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Supporting Information Available: Full experimental details for synthesis and characterization of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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