Preparation of Poly(*p*-phenylene vinylene) Derivatives by a Debromination-Chain Polymerization-Debromination Sequence

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Abstract— A debromination-chain polymerization-debromination (DPD) route to poly(*p*-phenylene vinylene) (PPV) derivatives is reported. In contrast to existing chain polymerization routes for the preparation of PPV derivatives, this route takes advantage of a symmetric monomer to preclude head-to-head or tail-to-tail coupling that ultimately leads to alkyne or alkyl defects in the polymer chain. Mechanistic studies were performed and revealed that the DPD route can be carried out with the desirable intermediacy of a soluble, isolable polymer precursor. Unsubstituted PPV, poly(*p*-(2,5-dihexyloxyphenylene)vinylene) and a PPV derivative with a sterically encumbering side chain were all readily prepared by the new DPD route. 2016 Elsevier Science. All rights reserved

Keywords: conjugated polymer, polymer synthesis, PPV, chain polymerization, defects

1. Introduction

Poly(*p*-phenylene vinylene) derivatives (PPVs) are some of the most-studied organic semiconducting conjugated polymers (CPs) for optoelectronic devices,[1, 2] and are leading candidates to serve as active components in organic photovoltaics[3] and display applications.[4, 5] Unfortunately, several of the more common synthetic avenues that can be used to prepare high molecular weight PPVs, such as Gilch, Wessling and Vanderzande routes,[6-8] involve polymerization of asymmetric active monomers and thus lead to polymers with small percentages of defects in the conjugated backbone (Scheme 1A). Even a small amount of such defects can diminish or alter the optoelectronic performance of PPVs leading to irreproducible performance [9, 10] or performance deficiencies.[11-15] It is therefore worthwhile to pursue routes that produce PPV derivatives wherein the incidence of deleterious defects is reduced. In seeking a low-defect route to PPV derivatives, it was hypothesized that chain polymerization of a symmetrically-substituted monomer (Scheme 1B) would lower the possibility of

SCHEME 1 Defects derived from several common routes to PPVs (A) and proposed low-defect route (B)

defects resulting from head-to-head and tail-to-tail coupling.

Herein we describe conditions to accomplish the desired transformation shown in Scheme 1B, application of the transformation to prepare three PPV derivatives, and efforts to elucidate the possible mechanism of the polymerization. We also compare the absorption and emission spectra and electrochemical properties of polymer prepared by the new debromination-polymerization-debromination route to corresponding properties of polymers prepared by the common Gilch route.

SCHEME 2 Proposed mechanism for DPD route to PPV

2. Results and Discussion

The proposed route shown in Scheme 2B was devised to generate the symmetric, chain-polymerizable monomer (**3**). This route was particularly attractive because one can envision isolation of processable precursor polymer **4**. This route would thus maintain the attractive features that have made the other processable precursor routes (i.e., Scheme 1A) so useful. The most convenient route that was found for the generation of quinoideal **3** was debromination of the 1,4-bis(dibromomethyl)arene precursors **1** by diethylphosphite. Diethylphosphite (in the presence of a mild base) is a well-known reducing reagent and dehalogenating agent.[16-18] Its affordability also makes it a convenient reagent for scalable polymer production. We were further encouraged in pursuing this route because *electrochemical* reduction of bis(dibromomethyl)arene precursors such **1** yields PPV derivatives.[19] Initial tests were therefore

carried out to evaluate the viability of the proposed debromination–polymerization–debromination (DPD) route outlined in Scheme 2. Initial efforts employed diethylphosphite as the reducing agent and mild bases such as Hünig's base, $\text{N}(\text{C}_2\text{H}_5)_3$ (TEA) or Cs_2CO_3 . Each base worked equally well in initial trials, so TEA was selected for subsequent studies on the basis of its affordability, ease of removal following reaction, and lack of metal ions that could potentially contaminate polymer products.

Table 1 summarizes the versatility of the DPD route toward accessing parent PPV (**P1a**), a PPV derivative with electron-donating substituents (**P1b**), and a PPV derivative with a sterically encumbered *o*-aryl substituent (**P1c**). In all cases, the 1,4-bis(dibromomethyl)aryl monomer was heated for 12 h at 55 °C with 6 equiv diethylphosphite and 6 equiv base in 10:1 THF/methanol. The unsubstituted PPV (**P1a**) obtained was insufficiently soluble for NMR spectroscopic or GPC analysis. PPV derivatives **P1b** and **P1c** were more soluble and GPC analysis revealed that the new DPD route afforded PPV-type polymers with molecular weights and polydispersity indices (PDI) nearly identical to those obtained via the widely-used Gilch route at the same initial monomer concentration (Table 1).

The lower incidence of bromide-containing defects

TABLE 1 DPD polymerization results and comparison to **P1b** prepared by the Gilch route.^a

Polymer	M_n (g/mol)	M_w (g/mol)	PDI	Residual Br (%) ^b
P1b (DPD)	36,000	101,000	2.8	2.31
P1b (Gilch) ^c	34,100	102,000	3.0	7.34
P1c (DPD)	41,800	127,000	3.1	2.1

^a GPC analysis was not possible for **P1a** due to prohibitive insolubility.

^b Residual Br was determined from elemental microanalysis.

^c The precursor for the Gilch route was α,α' -dibromo-2,5-dihexyloxy-*p*-xylene.

in polymers prepared via the new route was confirmed by elemental microanalysis (for C, H, N, Br, P, O, and in the case of **P1c** iodine analysis as well). The lack of any residual P or N in the elemental microanalysis also rules out the introduction of new defects containing these elements such as ammonium or phosphonate ester units in place of bromide. Nonzero values for Br obtained for **P1b–P1c** prepared by the DPD route presumably arise when the growing PPV chains precipitate from solution above a certain molecular weight.[7] It is

important to note that there are twice as many bromo substituents per repeat unit in the precursor monomer for the DPD route compared to the precursor monomer in the Gilch route (Scheme 1A, top pathway). Nonetheless, **P1b** produced by the DPD protocol features less than one third the number of unreacted bromides compared to **P1b** produced by the Gilch route. Furthermore, mass balance analysis of **P1a–P1c** obtained via the DPD route indicate ~97.5% efficiency in Br removal before the polymer precipitates from the reaction solution, compared to 93% for the Gilch route. This contrast indicates that bromide removal by the DPD route is approximately six times as efficient at removing bromine from the polymer chain compared to Gilch conditions at the same initial monomer concentration in THF. Furthermore, ^1H and ^{13}C NMR spectroscopic analysis of **P1b** and **P1c** prepared as in Scheme 2 reveal no evidence for alkane or alkyne defects of the type shown in Scheme 1A. However, Bunz has noted that such ^{13}C NMR analysis of polymers is not a valid way to assess the presence of minor impurities.[20] A small molecule model study was thus undertaken to assess the possible presence of alkyne defects in a highly concentrated solution. Specifically, 1,2-dibromo-1,2-diphenylethane was reacted under the same conditions as were used to prepare polymers by the DPD route. As anticipated, the crude reaction product was *trans*-stilbene in 100% spectroscopic yield. The ^{13}C NMR spectrum of the crude reaction product is shown in Figure 1. It is clear from the spectrum in Figure 1 that there is no evidence for

FIGURE 1 Carbon-13 NMR spectrum for crude reaction product upon reaction of 1,2-dibromo-1,2-diphenylethane under DPD conditions and magnified region with an arrow indicating where alkyne defects would occur (inset)

TABLE 2 Electrochemical and Photophysical data for **P1b** prepared by DPD and Gilch routes.^a

	DPD	Gilch
λ_{max} (nm)	464	481
λ_{em} (nm)	548	557
Φ (%) ^b	0.18	0.18
τ (ns) ^c	0.70(5)	0.60(7)
Ionization Energy (eV)	6.27	6.01
Electron Affinity (eV) ^d	2.97	2.27
E_{opt} (eV) ^e	2.30	2.24

^a Photophysical and electrochemical data were acquired in dichloromethane.

^b Photoluminescence quantum yield.

^c Photoluminescence lifetime at room temperature.

^d Calculated from the optical bandgap and electrochemically-determined ionization energy

^e Optical bandgap.

alkyne defects, which would be expected to produce a resonance at 89.43 ppm.[21]

Photophysical and electrochemical data (Table 2) for **P1b** produced by the DPD route compare favorably with the PPV materials prepared by Horner-Wittig and Gilch routes. Cyclic voltammetry (CV) showed the oxidation onset for **P1b** prepared via the standard Gilch route occurred at only a slightly lower energy than **P1b** prepared via DPD and the bandgap potentials estimated from the red edge onset of absorption of **P1b** from the DPD and Gilch routes, respectively, were calculated to be 6.27 and 6.01 eV (Table 2).

Subsequent analysis of the Gilch route **P1b** by differential pulse voltammetry (DPV) revealed a minor peak at 1.7 V, presumably corresponding to oxidation of alkyne defects, as well as a smaller peak at 1.9 V, corresponding to oxidation of the target (entirely phenylenevinylene) backbone segment's valence band. In contrast, the DPV of DPD route **P1b** was dominated by the peak at 1.9 V, with no evidence of the peak attributable to alkyne defects.

Having demonstrated that PPV derivatives with similar properties to those prepared by the Gilch route are accessible via the DPD route, it was of interest to gather evidence for the proposed mechanism outlined in Scheme 2.

The formation of the required anion [$^-\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$][22-24] can be observed by ^{31}P NMR spectroscopy.[25] In the current case, the formation of the anion under our reaction conditions was further confirmed via deuterium exchange of DOCH_3 with diethylphosphite to form $\text{DP}(\text{O})(\text{OC}_2\text{H}_5)_2$ (^{31}P NMR:

6.21 ppm, t, $J_{D-P} = 106$ Hz). Once formed, the anion debrominates *gem*-dibromides,[22, 26] here yielding **2**. Anion **2** is not isolable, rapidly eliminating Br⁻ to yield **3**. Efforts to observe **3** by ¹H NMR spectroscopy at -80 °C in THF-*d*₈[27, 28] were inconclusive due to the very slow rate of reaction of **1** at that low temperature. It was possible, however, to isolate and characterize processable precursor polymer **4** (Elemental analysis: calc'd for C₂₀H₃₀Br₂O₂: C, 51.97; H, 6.54; Br, 34.57; Found: C, 51.42; H, 6.46; Br, 33.54) via reaction of **1** with 1 equiv diethylphosphite at room temperature (20 °C) in the presence of TEA or cesium carbonate and methanol. The bromine analysis was slightly low for isolated **4**, presumably due to a small amount of debromination to form olefinic linkages. It should also be noted that lower molecular weights and polydispersity are observed in **4** ($M_n = 10733$, $M_w = 28493$, PDI = 2.64) produced at this low temperature than are attained for **P1a** and **P1b** at the higher reaction temperatures of the DPD conditions. Because diethylphosphite is well-known to mediate debromination of vicinal dibromides to produce olefins,[18, 29, 30] it was not surprising that exposure of isolated **4** to additional diethylphosphite and base at 55 °C led to the formation of PPV derivatives just as in the one-pot reaction of **1** with excess diethylphosphite and base. This is an important control, however, to demonstrate that **4** is a viable species on the path from **1** to **P1**.

Because compound **1a** has also been shown to form PPV derivatives via electrochemically-induced polymerization,[19] it was also of interest to determine whether the electrochemical reduction of precursor polymer **4** to give **P1** could be affected in the same way. Simple cyclic voltammetric analysis of **4** under rigorously oxygen- and water-free conditions revealed no redox processes within the CH₂Cl₂ solvent window. However, holding the cell at a constant reducing potential (-1.5 V) for 2 min before acquiring a CV resulted in the appearance of multiple irreversible oxidation and reduction peaks and a gradual darkening of the solution consistent with PPV formation. Characterization of these electrochemical processes is underway and will be reported separately.

Another important consideration in these types of polymerization reactions is the relative contribution of radical versus anionic polymerization. Following standard procedures that have been developed to probe the mechanism of the other routes shown in Scheme 1A,[6, 31, 32] the current polymerization sequence was attempted in the presence of either TEMPO, which would quench active species in a

radical chain polymerization, or water, which would quench the active species in anionic chain polymerization.[33] When the one pot DPD sequence was attempted in the presence of TEMPO or open to ambient oxygen, the polymerization reaction did not take place, supporting the expected radical chain polymerization mechanism.[32] Furthermore, polymerization was not hampered by addition of 10 vol. % water to the reaction solvent, suggesting that anionic polymerization may not be a major contributor to polymerization of **3**. [6, 31, 33-35]

In the current case, polymerization was actually *faster* in the presence of water. This makes sense because phosphite-mediated dehalogenation sometimes *requires* water or an alcohol for the reaction to take place.[26, 30] In the current case, the rate enhancement is attributable to the irreversible reaction of water with BrP(O)(OEt)₂ to push equilibrium ii (Scheme 2) towards formation of **3**. This is why the optimized route utilizes as solvent a 10:1 mixture of THF and methanol (methanol will serve the same role as water in equilibrium ii). Taken together, all of the above data are consistent with the proposed mechanism and literature precedent for related debromination and chain polymerization reactions.

3. Conclusions

In conclusion, a facile new route to PPV derivatives has been developed. The new route appears to lead to fewer alkyne defects than are found in PPV derivatives produced by the Gilch route. The mechanism of this reaction takes advantage of a debromination-chain polymerization-debromination sequence and appears to proceed through an isolable polymer precursor. Additional studies are underway to optimize the route and to explore its full scope / functional group tolerance.

4. Experimental

4.1 Reagents and General Methods

Reagents were obtained from Aldrich Chemical Co., TCI America, Acros or Alfa Aesar and used without further purification. Solvents were purified by passage through alumina columns under a dry N₂ atmosphere employing an MBraun solvent purification system. Air sensitive operations were carried out in an MBraun dry box or using standard Schlenk line techniques under N₂. NMR spectra were obtained using a Bruker Avance 300 spectrometer operating at 300 MHz for protons. All spectra were collected at 25 °C and referenced to TMS or residual

solvent signals.

Gel permeation chromatography (GPC) data were collected using polystyrene as a standard (Polymer Labs Easical PS-2) using a Waters 2695 Alliance System with UV-vis detection for samples in CHCl_3 or a Waters 515 HPLC pump coupled with a Waters 2414 refractive index detector for samples in THF. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. Thermal gravimetric analysis (TGA) was performed on a TA Hi-Res TGA2950 instrument.

4.2 General Spectroscopic Methods

Photoluminescence (PL) spectra were acquired on a Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra were recorded on a Varian Cary 50 Bio absorption spectrophotometer. Samples for all absorbance and PL spectra used tetrahydrofuran (THF) as solvent in Spectrosil quartz cuvettes having a path length of 1 cm. Initial solutions for PL analysis were filtered prior to analysis. The THF solvent for all optical measurements was purified and made anhydrous/anaerobic by passage through alumina columns under a N_2 atmosphere employing an MBraun solvent purification system. Photoluminescence quantum yields were measured relative to quinine bisulfate ($\Phi = 0.564$) in 0.1 N aqueous sulfuric acid. Polymer concentrations are reported as moles of repeat unit per L.

4.3 Electrochemistry

All electrochemical experiments were performed on a CH Instruments Electrochemical Workstation 660D using an airtight 3-electrode cell under a nitrogen atmosphere. A gold working electrode and tungsten wire counter electrode were used, along with a silver wire quasi-reference electrode. Measurements were made using anhydrous CH_2Cl_2 with 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte. Ferrocene (FeCp_2) was chosen as the internal standard. All reported potentials were collected with a 100 mV s^{-1} scan rate and were referenced to SCE by shifting $[\text{FeCp}_2]^{+/0}$ to 0.46 V.

4.4 General Procedure for preparation of poly(*p*-phenylene vinylene) derivatives (**P1a-c**)

A 0.100 mmol sample of the requisite 1,4-bis(dibromomethyl)benzene derivative was mixed with 6 equiv. of diethyl phosphate and 6 equiv. of base (ethyl-diisopropylamine, cesium carbonate or triethylamine) in 5 mL of anhydrous THF with 0.5 mL of methanol. The solution was allowed to reflux

at 55 °C for 12 h. Solvent was then removed under reduced pressure. The crude polymer was then redissolved in minimal dichloromethane then added dropwise into 15 mL of methanol. Polymer solids were obtained as powders via precipitation from methanol and recursive rinsing with methanol, followed by drying in vacuo.

4.5 Preparation of **4**

A 0.500 g (0.804 mmol) sample of 1,4-bis(dibromomethyl)-2,5-bis(hexyloxy)benzene was mixed with 0.123 g (0.884 mmol) of diethylphosphite and 0.288 g (0.884 mmol) of cesium carbonate in 20 mL of anhydrous tetrahydrofuran under nitrogen. A 2.0 mL aliquot of methanol was then added via syringe. The reaction mixture was stirred at room temperature for 6 h then poured into 75 mL of dichloromethane. The combined organics were rinsed with water (2×50 mL aliquots) and the organic layer collected. Solvent was removed under reduced pressure to yield a pale yellow solid that formed as a thin film in the flask. The crude polymer was taken up in minimal dichloromethane and reprecipitated into methanol. The resultant yellow material was dried in vacuo to give the final product **4** (0.35 g, 94%). GPC: $M_n = 10733$, $M_w = 28493$, PDI = 2.64. Elemental analysis: calc'd for $\text{C}_{20}\text{H}_{30}\text{Br}_2\text{O}_2$: C, 51.97; H, 6.54; Br, 34.57; Found: C, 51.42; H, 6.46; Br, 33.54.

5. Acknowledgements

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GRAPHICAL ABSTRACT

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A debromination-chain polymerization-debromination route to poly(*p*-phenylene vinylene) (PPV) derivatives has been devised. The use of a symmetric monomer precludes head-to-head or tail-to-tail defects, producing more uniform PPV via an isolable, soluble polymer precursor.