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PHENYLATED POLY(P-PHENYLENE VINYLENES) PREPARED VIA THE CHLORINE PRECURSOR ROUTE (CPR)

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Abstract

The synthesis of several highly phenylated PPV derivatives by a chlorine precursor route (CPR) was investigated in order to understand its scope. Three 1,4-bis(chloromethyl)benzene monomers were prepared via a robust and versatile synthetic procedure involving the Diels-Alder reaction. The monomers were then polymerized to the corresponding precursor polymers with about 1.0 equivalent of potassium t-butoxide in THF. Only one monomer gave a soluble precursor polymer while the other two gave insoluble precursor polymers. The soluble precursor polymer was deposited as thin films and then converted to the corresponding PPV derivative, which showed green photoluminesence and electroluminesence.

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Introduction

The discovery of electroluminescence, (EL), in poly(phenylene vinylene), (PPV), has stimulated considerable interest in conjugated polymers for a variety of applications [1]. The two major approaches to the fabrication of conjugated polymer thin films are the precursor approach and the side chain approach [1]. The former relies on the preparation of a soluble precursor polymer which can be spin cast into thin films. These are then converted to the final conjugated polymer films through solid-state thermo- or photo-conversion. The side chain approach involves the polymerization of a monomer containing soluble substituents or side groups to afford a soluble conjugated polymer that can be cast into thin films directly without conversion. Unfortunately, the side chain approach does not work in all cases because of polymer product gellation during polymerization. The precipitation may be caused by high molecular weight, semicrystallinity and/or cross-linking of the product. As a result, the desired soluble product is obtained in very low yields (<10%). This problem can be avoided by preparing a soluble precursor polymer which can be converted to the final conjugated polymer. Three precursor routes, namely the sulfonium precursor route (SPR), the halogen precursor route (HPR), and the xanthate precursor route (XPR), have been used for the fabrication of PPV LEDs [1]. These three precursor routes are highly complementary to each other and have led to the synthesis of a wide range of PPV derivatives. Because of various synthetic difficulties, SPR approach is limited and is useful mainly for the preparation of PPV. In general, XPR is useful for the preparation of PPV and those PPV derivatives with small side groups such as methyl and methoxy groups [2]. The chlorine precursor route (CPR), one of many halogen precursor routes is useful for the preparation of PPV with relatively large side groups such as phenyl, phenoxy and hexyloxy [3].

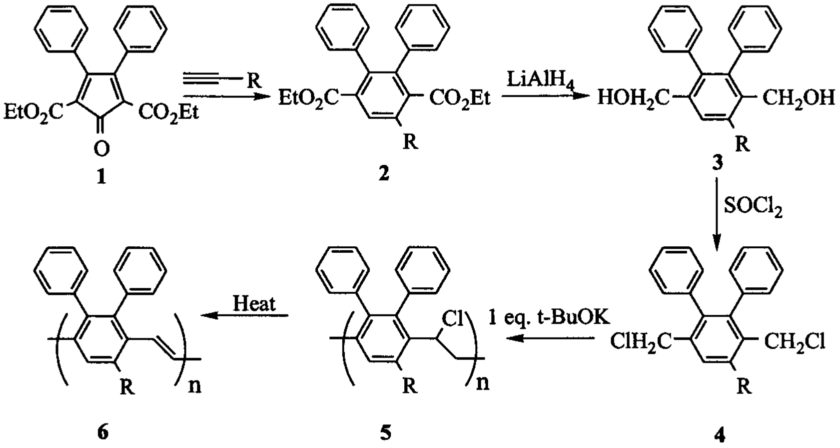
We have focused our research on the fabrication of PPV derivatives based LEDs via CPR [4-7]. We have found that CPR is a versatile, robust and simple route for the preparation of a wide range of PPV derivatives [8,9]. Here we report the synthesis of three new highly phenylated PPVs using CPR. The objective of this work is to explore the versatility and to define the scope of CPR for the preparation of PPV derivatives with phenyl substituents. In addition we hope to be able to tune the color emission of HP-PPV's by the use of bulky phenyl groups.

Results and Discussion

The three 1,4-bis(chloromethyl)benzene monomers were prepared via a robust and versatile synthetic procedure involving the Diels-Alder reaction as shown in Scheme 1. The Diels-Alder reaction of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (**1**) with the substituted acetylenes: phenylacetylene, 4-fluorophenylacetylene or 4-biphenylacetylene. gives **2a**, **2b**, or **2c**, respectively. The diesters **2a**, **2b** and **2c** are then reduced with $LiAlH_4$ in THF to give the dialcohols **3a**, **3b** and **3c**. The three 1,4-bis(chloromethyl)benzene monomers **4a**, **4b**, and **4c**, are obtained by chlorination of the three dialcohols **3a**, **3b** and **3c** with $SOCl_2$ in methylene choride.

We chose to prepare the fluorinated monomer **4b** since the strongly electronegative fluorine atom may decrease the polarizability of the π electrons on the aromatic rings thereby increasing the solubility. This has been demonstrated for fluoro-substituted poly(2,6 diphenylphenylene ether)s which showed enhanced solubility relative to the non-fluorinated polymer[10]. The monomers **4a**, **4b** and **4c** were then polymerized by treatment with about 1.1 equivalent of potassium t-butoxide (t-BuOK) in THF to give the chlorine precursor polymer **5a**, **5b** and **5c** respectively. The polymerization of **4a** and **4b** via CPR gave insoluble chlorine precursor polymers. No further characterizations were performed on these two insoluble precursor polymers. The polymerization of **4c** gave a soluble precursor polymer **5c** which was spin cast into thin films and thermally converted for 2 hours at 250 °C to **6c** (DPBP-PPV). DPBP-PPV showed a number and weight average molecular weights of 295,709 and 998,557 respectively. Elemental analysis showed 86.06 % carbon, 5.21 % hydrogen and 7.65 % chlorine, indicating 4 % conversion had occurred.

Scheme 1. Synthetic route to HP-PPV.



a, R = phenyl
b, R = 4-fluorophenyl
c, R = 4-biphenyl

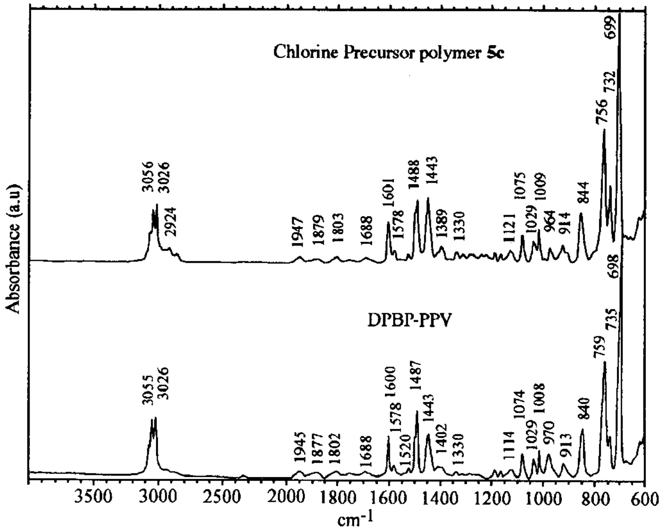


Figure 1. Infrared spectra of the polymer precursor 5c (Top) and DPBP-PPV, which was converted at 250 °C (bottom) for 2 hours.

The infrared spectra of 5c and DPBP-PPV are shown in Figure 1. They are both very similar to each other except for an additional peak at 970 cm^{-1} for DPBP-PPV, which is attributed to the vinylic out of plane deformation of trans C-H. A small shoulder is still present at 735 cm^{-1} for DPBP-PPV which is assigned to the C-Cl absorption band, indicating that thermal conversion of the precursor polymer (5c) was not completed. This may be attributed to the bulky phenyl substituents which may have interfered with the dehydrochlorination process during thermal conversion, and may be a possible reason why we were unable to characterize the electroluminescent properties of DPBP-PPV.

Figure 2 shows the absorption and emission spectra of DPBP-PPV thermally converted under different conversion temperatures. The absorption λ_{max} is at 370 nm and the emission λ_{max} is between 490 nm and 510 nm. Therefore, DPBP-PPV is a green emission polymer. A new shoulder appears in the absorption spectra of DPBP-PPV at 350 nm for samples thermally converted above 200 °C. There is also a slight red shift (~10 nm) in the PL spectra occuring between 150 to 200 °C. The new absorption peak and the red shift in the PL spectra of DPBP-PPV both correlate with the onset of conversion from precursor polymer, 5c to DPBP-PPV which occurs at 200 °C. We were unable to discern any further trends in the observed absorption and emission spectra of DPBP-PPV. This may be due to the different morphology for these samples under different conversion temperatures, thus making direct comparison of these spectra difficult.

The current vs. voltage characteristic of ITO/DPBP-PPV/Al and ITO/PPV/Al devices are shown in Figure 3 for comparison. A turn-on voltage of about 15 V is evident for DPBP-PPV (Figure 3; bottom) which is higher than the turn-on voltage for ITO/PPV/Al which is 5 V (Figure 3; top), and is significantly higher than the turn-on voltages for PPV monolayer devices which have been reported to be as low as 2 V [11,12]. The brightness of DPBP-PPV reaches a maximum at 18 V, which then begins to drop as higher voltage is applied across the thin film, indicating degradation of the device [13].

Batch to batch variations in the properties of PPV and its derivatives in terms of solubility, gel particle contents, molecular weights, absorption, and emission properties are well known problems and have resulted in a wide range of device properties which have created a lot of confusion amongst different laboratories. Our results for DPBP-PPV show that it is not an exception. Irreproducible data and a wide scattering of device properties for an ITO/DP-PPV/Al monolayer device we prepared has also been reported [14]. The external quantumn efficiency ranged from an amazingly high external quantum efficiency of 1.2 % to as low as 5.4 x 10^{-4} % demonstrating the irreproducibility of the precursor route approach in general.

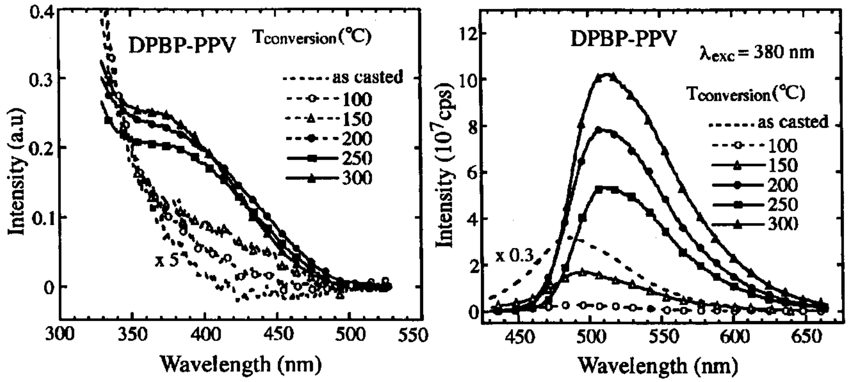


Figure 2. Absorption (left) and photoluminescence (right) spectra of DPBP-PPV thin films thermally converted at the indicated temperatures for 2 hours.

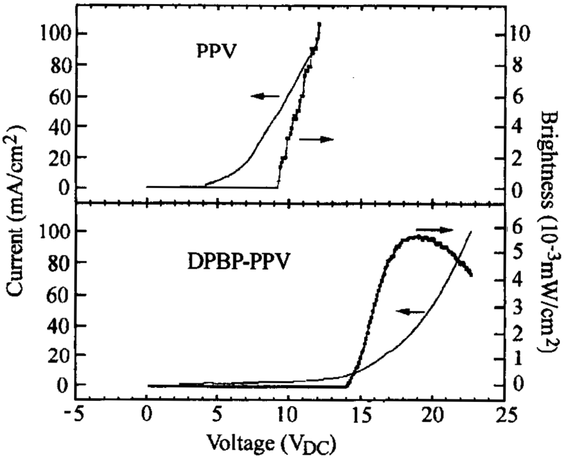


Figure 3. Current vs. voltage and brightness vs. voltage measurements of PPV and DPBP-PPV.

Summary

We have developed a simple and versatile synthetic route to highly phenylated poly(phenylene vinylenes) (HP-PPV). The bis(halomethyl)benzene monomers are prepared by a robust and simple procedure involving the Diels-Alder reaction. The three bis(halomethyl)benzene monomers are then polymerized to the precursor polymer using the CPR route. Only **5c** gave a soluble precursor polymer. Compound **5c** was deposited as thin films and converted to DPBP-PPV. The photoluminescence spectra show that DPBP-PPV is a green emission polymer.

Our results indicate that the CPR approach to HP-PPV is limited and that insoluble precursor polymers may result. The insolubility of the precursor polymer can be overcome by selectively choosing a phenyl subsituent that will result in a soluble precursor polymer. We are continuing to explore the scope of CPR with new phenyl substituents. In addition, we plan to pursue new HP-PPV derivatives with solubilizing substituents, such as alkyl chains which will be reported in due course.

Acknowledgement

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