A New Precursor Polymer via a New 1,6-Polymerization Reaction. A New Route to Cyano Poly(*p*-phenylene vinylenes)

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The derivatives of α,α′-dichloro-*p*-xylene and α,α′-dibromo-*p*-xylene represent an important class of monomers for the synthesis of poly(*p*-phenylene vinylenes) (PPV), which are emerging as one of the most important classes of electroactive polymers for semiconductor device application.[1] The dihalides have been converted into other PPV monomers, such as *p*-xylylene bis(dialkylsulfonium halide)s,[2] *p*-xylylene bis(ethyl-xanthate),[3] 1-halo-4-alkylsulfonyl-*p*-xylenes,[4] *p*-xylylene dithiocyanate,[5] or *p*-xylylene bis(*N*,*N*-diethyldithiocarbamate).[5] All the above-mentioned *p*-xylene monomers have been used for the synthesis of PPVs via 1,6-polymerization of *p*-xylylene [**X**] as shown in Scheme 1. The *p*-xylylene [**X**] can undergo radical and/or anionic 1,6-polymerization along with 1,2-elimination of HL to give a PPV derivative in the presence of a large excess of a base. This direct approach is widely used for the preparation of PPVs with solubilizing side chain groups.[6] One can carry out the 1,6-polymerization and the 1,2-elimination separately so that a precursor polymer is first obtained, which is then converted to the corresponding PPV. This precursor approach has been extensively used for the fabrication of insoluble PPV thin films from a soluble precursor material.[7]

The derivatives of α,α′-dihalo-*p*-xylenes have also been converted to terephthalaldehydes and α,α′-dicyano-*p*-xylenes. These two types of monomers can undergo condensation polymerization via the Knoevenagel reaction to give a PPV with a cyano group attached to the vinylene group. Such cyano-PPV polymers showed a very high photoluminescence (PL) efficiency of 60% as well as 4% external efficiencies in a single-layer electroluminescent (EL) device.[8] This improved device property has been attributed to the electron-withdrawing cyano groups that can facilitate electron injection.[8]

As shown in Scheme 2, in an attempt to prepare α,α′-dicyano-*p*-xylene (**2**), which is one of the monomers needed for the synthesis of Knoevenagel type MEH-2CN-PPV, by cyanation of 2-methoxy-5-(2-ethylhexyloxy)-1,4-bis(chloromethyl)benzene (**1**) in the presence of NaCN in dioxane−water solution, we found an unexpected polymer. In this communication, we report the identification and characterization of this polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-α-cyano-p-xylylene] (MEH-CN-PX), by NMR, IR, elemental analysis, and GPC. The bulky 2-ethylhexyloxy group plays a unique role in this unexpected polymerization by providing adequate steric interaction. A 1,6-polymerization mechanism is proposed. It is conceivable that MEH-CN-PX can serve as a precursor polymer to a wide range of nonconjugated functional polymers through conversion of the cyano groups. In addition, we have demonstrated that MEH-PX-CN can be used as a precursor polymer to give conjugated poly[2-methoxy-5-(2-ethylhexyloxy)-α-cyano-*p*-phenylene vinylene] (MEH-CN-PPV) via an oxidative conversion with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[9]

The cyanation of **1** in the presence of 10 equiv of NaCN in dioxane and water (1:1) mixed solvent at reflux did not give the expected dicyano compound **2**; instead, an unexpected polymer was formed as shown in Scheme 2 in about 30% yield. When the same mixture was stirred for 50 h at room temperature, no reaction occurred. We were able to obtain **2** by treating **1** with NaCN in DMSO at 50 °C. The polymer has been identified as poly[2-methoxy-5-(2-ethylhexyloxy)-α-cyano-*p*-xylylene] (MEH-CN-PX) according to the following analytical results. The IR spectrum showed a moderate peak at 2239 cm^{-1}, which corresponds to cyano groups. The ^{13}C NMR spectrum shows a peak at 120.8 ppm, which represents CN−*C*. There were two broad peaks at 4.52 and 3.19 ppm in the ^{1}H NMR spectrum corresponding to the C*H*−CN and C*H*$_2$, respectively. Elemental analysis data agree well with the assigned structure. Anal. Calcd for $(C_{18}H_{25}NO_2)_n$: C, 75.23; H, 8.77; N, 4.87. Found: C, 75.09; H, 8.71; N, 4.88. GPC analysis shows high molecular weights (M_w = 293K; M_n = 116K; polydispersity = 2.54; work done in tetrahydrofuran using polystyrene standards). MEH-CN-PX is soluble in many organic solvents, for example, methylene chloride, chloroform, THF, and toluene.

A 1,6-polymerization reaction via *p*-xylylene shown in Scheme 3 is proposed to account for the formation of MEH-CN-PX. Nucleophilic substitution of Cl by CN takes place at the less hindered chloromethyl group in **1** to form a chloromethyl−cyanomethylbenzene, **3**. This sequence is followed by deprotonation of the less hindered and more acidic cyanomethyl proton in **3** and then a spontaneous 1,6-elimination reaction to give the reactive *p*-xylylene **4**. This reactive species polymerizes via a radical or/and anionic 1,6-polymerization to give MEH-CN-PX.[6−7]

To support the proposed mechanism, two similar monomers, 2,5-dimethoxy-α,α′-dichloro-*p*-xylene and 2,5-bis(2-ethylhexyloxy)-α,α′-dichloro-*p*-xylene, were prepared and reacted with NaCN under the same conditions. For the former, substitution of both Cl atoms takes place to give the corresponding dicyano compound, namely, 2,5-dimethoxy-α,α′-dicyano-*p*-xylene. Thus both Cl atoms were readily available for nucleophilic substitution by CN ions. There was no reaction in 2,5-bis(2-ethylhexyloxy)-α,α′-dichloro-*p*-xylene, and the starting material was recovered. The steric effect of the 2-ethylhexyloxy groups is readily apparent. The above results show that under this reaction condition nucleophilic substitution by cyanide ions is sensitive to steric effects, and the results support the first step of our proposed mechanism.

It is obvious that MEH-CN-PX is a versatile precursor polymer suitable for a wide range of transformations through the CN groups to various functional polymers with a wide range of properties. Further work will be directed to converting the CN groups into functional

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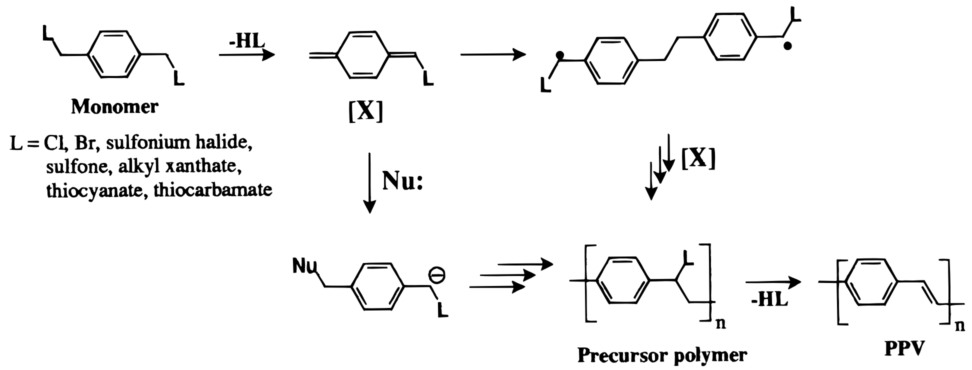
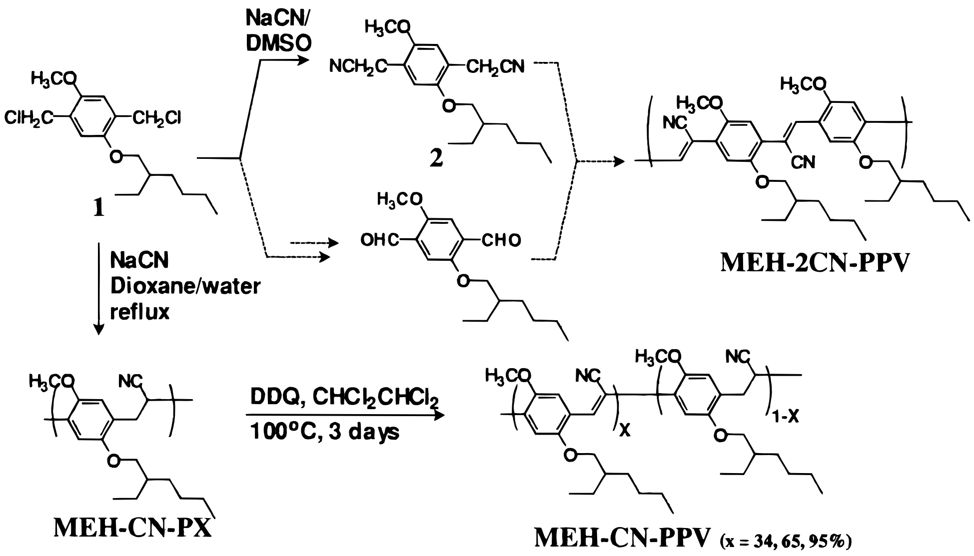
Scheme 1

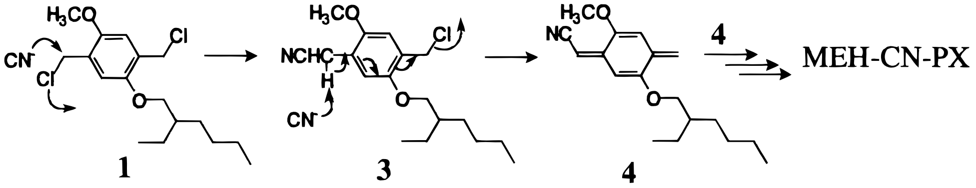


Scheme 2



a. NaCN. Water/dioxane, 110°C; b. NaCN, DMSO at 50°C.

Scheme 3



groups such as COOH, COONa, CONH$_2$, CH$_2$NH$_2$, and oxazoline, among others. As shown in Scheme 1, we have attempted the conversion of MEH-CN-PX into a PPV derivative using DDQ.[9] In the presence of one equivalent DDQ, MEH-CN-PX was partially converted to MEH-CN-PPV with 64% of phenylene cyano–vinylene segments, as estimated from the respective ^{1}H NMR spectra.[9] The molecular weight of MEH-CN-PPV (M_w = 24K; M_n = 10K; polydispersity = 2.4; work done in THF using polystyrene standards) is lower than that of the precursor MEH-CN-PX. We tentatively attribute the molecular weight reduction to oxidative cleavage of head-to-head moieties in the precursor polymer by DDQ.[9] Nevertheless, the molecular weight of MEH-CN-PPV is still comparable with that of the cyano PPV synthesized by the Knoevenagel reaction.[8c] By varying the amount of DDQ, we were able to control the degree of conversion.[9] For example, when MEH-CN-PX was oxidized with $^1/_2$ and 2 equiv of DDQ, MEH-CN-PPVs with 34% and 95% conversion, respectively, were obtained.

Figure 1 shows the UV–vis and PL spectra of MEH-CN-PPV at different degrees of conversion. The absorption maxima shift to longer wavelength as the degree of conversion increases, while the emission spectra remain relatively unchanged. The PL result indicates that the longest conjugation segments in MEH-CN-PPV were achieved even at a low conversion of 34%. This is supported by the fact that the absorption band edges, which can be associated with the longest conjugated segments in the polymer, remain relatively unchanged in all cases. The longest conjugated segments in a polymer are known to be responsible to its steady-state PL spectra because of exciton diffusion to the lowest energy segments.[10] It should be noted that partially converted PPVs showed improved transport properties as well as device performance.[11] Some of the current state-of-the-art PPV devices are based on partially

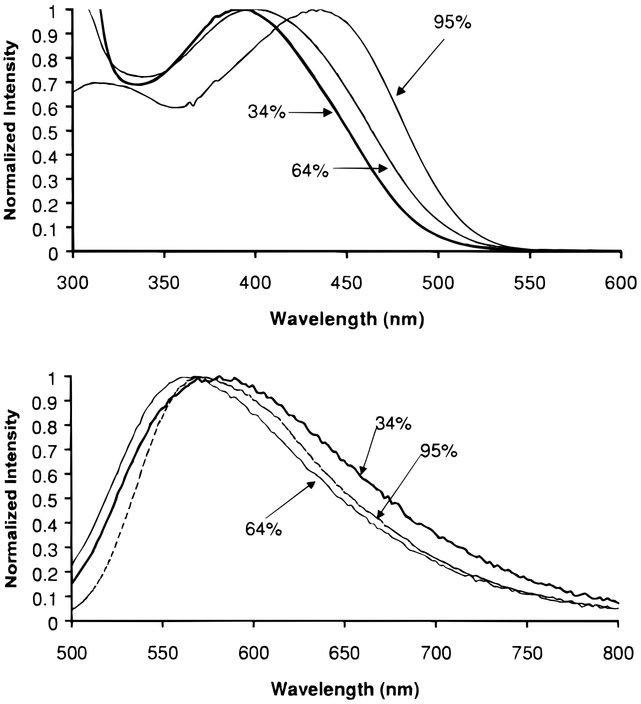


Figure 1. UV−vis spectra (top) and PL spectra (bottom) of MEH-CN-PPV with 34%, 64%, and 95% conversion. The PL spectra were obtained by excitation at 415 nm.

converted PPVs.[12] Fully converted PPV is prone to self-quenching because of the formation of exciplexes, excimers, or polaron pairs among the adjacent emission segments.[10] The detailed photophysical properties and device properties of MEH-CN-PPV are being investigated.

In conclusion, we have expanded the scope of 1,6-polymerization to the preparation of a new, partially conjugated polymer containing electron-withdrawing cyano groups. MEH-CN-PX is a versatile precursor polymer, which can be converted into both nonconjugated and conjugated polymers. We have converted MEH-CN-PX to new, partially conjugated MEH-CN-PPVs with different degrees of conversion using DDQ. Controlling the degree of conversion in the soluble, partially conjugated MEH-CN-PPV may offer an excellent approach to optimizing device properties.

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