General Methodology toward Soluble Poly(*p*-phenylenevinylene) Derivatives

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Poly(*p*-phenylenevinylene) (PPV) and derivatives are an important class of light-emitting polymers for electroluminescent (EL) device applications.[1,2] There are two principal approaches to the fabrication of PPV thin films, namely, the precursor approach and the side chain approach. The former relies on the preparation of a soluble precursor polymer that can be cast into thin films. The precursor polymer films can then be converted to the final conjugated polymer films through solid state thermo- or photoconversion. EL devices based on PPV thin films derived from a sulfonium precursor route[2] and a halogen precursor route[3] have been reported. However, there are several problems associated with the precursor approach. First, the precursor polymers derived from these precursor routes have ill-defined molecular structures because they are typically random copolymers containing 5−50% of converted segments. Second, relatively expensive and potentially environmentally harmful photo- or thermoconversion is required. Third, structural defects arising from incomplete thermoconversion and side reactions with volatile organic species generated during the thermal conversion are presented. These aspects can lead to poor device properties and poor manufacturing reproducibility.[4]

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 film directly without conversion. The polymerization of bis(halomethyl)benzenes in the presence of large excess of a base to give PPV products was first reported by Gilch et al. in 1966.[5] In principle, the adaptation of the Gilch route to the polymerization of a 1,4-bis(halomethyl)benzene containing solubilizing groups should give a soluble PPV derivative. Unfortunately, this is not the case in practice because of gelation and precipitation of polymer products during the polymerization. This problem was encountered during the synthesis of poly[2-methoxy-5-((2′-ethylhexyl)-oxy)-*p*-phenylenevinylene] (MEH−PPV),[6,7] the most widely investigated PPV derivative, and poly(2,5-dihexyloxyl-*p*-phenylenevinylene).[3b] For example, when we carried out the standard Gilch polymerization with excess potassium *tert*-butoxide (t-BuOK) as the base, an insoluble MEH−PPV gel was formed. We were able to minimize the degree of gelation by slow intermittent addition of the base, according to the procedure described by Wudl et al in a 1993 patent.[8] The resulting MEH−PPV appeared to be soluble in chloroform and in *p*-xylene; however, the solutions, even after heating, could not be readily filtered through 0.5−1.0 μm filters, indicating microgel formation. In our opinion, this is one of the most unpublicized but yet the biggest problems associated with MEH−PPV.

In this communication we report the synthesis of soluble high molecular weight MEH−PPV through a modified Gilch route involving the use of a non-polymerizable acidic additive, such as 4-*tert*-butylbenzyl chloride (**2**), as shown in Scheme 1. The molecular weight of MEH−PPV can be controlled by varying the molar ratio of **2**:**1** or by changing the concentration of **2**. Discussion on the polymerization mechanism of this modified Gilch route is also presented.

Scheme 1

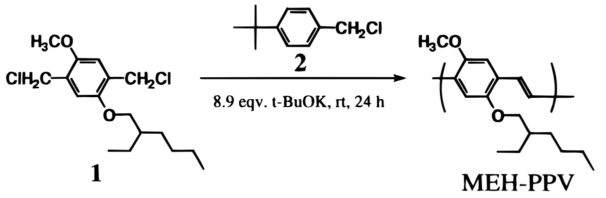

Table 1. Polymerization Parameters and the Molecular Weights of MEH−PPV

entry	**2**/**1**//THF (g/g//mL)	molar ratio **2**:**1**	amount of 1.0 M *t*-BuOK in THF (mL)[a]	M_w/M_n ($\times 10^3$)[b]	poly-dispersity	% yield
1	0.0/3.0//300	0	80	gel		
2	0.0/3.0//300	0	80[c]	microgel		
3	0.01/3.0//300	0.006	80	gel		
4	0.1/3.0//300	0.06	80	331/66.5	5.0	35
5	0.2/3.0//300	0.12	80	172/15.1	11.4	20
6	1.0/3.0//300	0.61	80	85/11.3	7.5	17
7	0.1/3.0//200	0.06	80	199/39.1	5.1	39
8	0.1/3.0//150	0.06	80	164/26.9	6.1	56

[a] The base was added all at once into an ice−water cooled and mechanically stirred solution of **2**/**1**/THF. [b] Relative to polystyrene in THF. [c] The base was added in small portions over a period of 5 h.

As shown in Table 1, insoluble MEH−PPV gel is obtained in the absence of or with an insufficient amount of **2** (entries 1, 2, and 3) and soluble products are obtained by adding larger amount of **2**. Entries 4, 5, and 6 show that the molecular weight of MEH−PPV decreases as the molar ratio of **2**:**1** increases. Entries 4, 7, and 8 show that the molecular weight of MEH−PPV decreases as the volume of THF decreases. This suggests that the molecular weights of MEH−PPV products are inversely proportional to the concentration of **2**. The molar ratio of **2**:**1** and the concentration of **2** are therefore two important factors in controlling the molecular weights of the polymer.

Although the soluble MEH−PPVs shown in Table 1 were isolated by a single precipitation of the reaction mixtures into methanol, they still showed very high purity according to the elemental analysis data. The typical elemental analysis data (C, 78.13; H, 9.17; Cl, < 0.05) are in excellent agreement with that (C, 78.42; H, 9.29) calculated for $[C_{17}H_{24}O_2]_n$. This result indicates that the soluble MEH−PPVs obtained from the modified Gilch route have very high purity and very low chlorine content which implies a high degree of conversion or purity (>99.5%). To the best of our knowledge this is the first report on the elemental analysis of chlorine content in MEH−PPV. All the polymer products in table entries 4−8 are readily soluble in THF and chloroform, and the polymer solutions can smoothly filter through 0.5 μm filters for GPC analysis.

The fact that the molecular weight of MEH−PPV products is inversely proportional to the amount and the concentration of **2** indicates the involvement of the anionic polymerization process. Scheme 2 demonstrates one of the possible anionic mechanisms. Deprotonation of a chloromethyl proton in **1** gives an anionic intermediate **3**, which undergoes a 1,6-dehydrochlorination to

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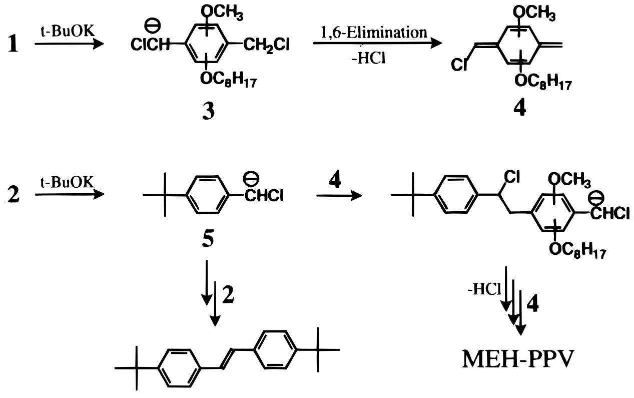
Scheme 2



give *p*-xylylene **4**. Deprotonation of **2** produces **5**, which can nucleophilically attack **4** to initiate anionic polymerization to give MEH−PPV with *tert*-butyl chain ends or attack **2** followed by 1,2-dehydrochlorination to give 4,4′-di-*tert*-butylstilbene as a side product.[5] Similarly, propagating anionic chains may nucleophilically attack **2** to terminate the polymerization. The formation of the stilbene is one possible reason for the formation of high polymers even in the presence of a large amount of **2**. The other possibility is the involvement of radical polymerization as reported for the analogous sulfonium precursor routes and sulfone precursor routes where the formation and the 1,6-radical polymerization of xylylene intermediates have been proposed.[9,10]

The formation of *p*-xylylene (such as **4**) is an important step in the 1,6−polymerization. Electron-rich groups in a monomer may favor the formation of the *p*-xylylene intermediate and give rise to a very high molecular weight material that is prone to precipitation.[1] Electron-withdrawing groups may result in the formation of stable anionic species similar to **3** and suppress the formation of the *p*-xylylene intermediate needed for the polymerization. This in turn will result in low molecular weight materials.[1,11] The substituent groups on the phenyl ring of a monomer may also dictate the preference of the anionic or radical mechanisms.

The scope of this modified Gilch route is being expanded to the synthesis of other soluble new PPV derivatives such as poly(2,3-diphenyl-5-hexyl-*p*-phenylene vinylene) (DP6-PPV) and its analogues.[12] One may control the polymer chain ends by varying the types of mono-functional additives, similar to the modified sulfonium precursor route reported by Ohnishi et al.[13]

In conclusion, soluble MEH−PPV with controlled molecular weight has been prepared in high yields via a modified Gilch route in the presence of a nonpolymerizable acidic additive. An anionic polymerization mechanism is proposed to account for the fact that the molecular weight of MEH−PPV is inversely proportional to the amount and the concentration of the additive. This approach provides a new way of investigating the mechanism of the 1,6-polymerization of *p*-xylylenes. With a better understanding of the additive effects on the polymerization mechanism, the synthesis of PPVs with controlled molecular weight, molecular weight distribution, and end groups may be possible.

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