

A comparison of 1,4-bis(halomethyl)benzenes as monomers for the modified Gilch route to poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene]

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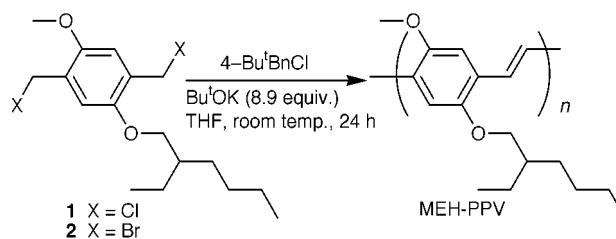
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A comparison of 1,4-bis(bromomethyl)- and 1,4-bis(chloromethyl)-2-(2'-ethylhexyloxy)-5-methoxybenzene as monomers for the modified Gilch route to poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] was made; the bis(bromomethyl) monomer was found to give substantially higher yields of MEH-PPV with consistently higher molecular weights and narrower polydispersities than the corresponding bis(chloromethyl) monomer.

There is currently renewed interest in poly(*p*-phenylenevinylene) (PPV) and its derivatives due to the potential these polymers have for application in organic light-emitting diodes.^{1–3} The two main routes to these polymers, the precursor route and the side chain approach, were developed to address the processability problems of PPV due to low solubility. The precursor approach involves the formation of a soluble precursor polymer that after fabrication can be converted to the final conjugated polymer using solid state thermal or photochemical processes. Both the sulfonium precursor route^{4,5} and the halogen precursor route^{6,7} have successfully addressed the lack of processability of insoluble PPV and led to the production of electroluminescent devices from PPV films. The precursor approach, however, has some inherent problems.^{2,8,9} The precursor polymers themselves can contain segments where elimination has occurred in 5–50% of polymer. The ill-defined nature of the precursor polymers due to such premature elimination makes their synthesis, storage and subsequent processing difficult. The lack of stability of the sulfonium precursor to PPV has caused problems such as gelation of the precursor polymer and difficulties in processing. Conversion of the precursor polymer to the conjugated form is also expensive and prone to the formation of defects in the resulting polymer due to incomplete elimination and side reactions with the eliminated species. The side chain approach addresses the solubility problems of PPVs by using monomers substituted with solubilizing groups. Ideally, the monomers are then converted directly into the corresponding soluble conjugated polymer that is processible by standard procedures. In 1966 Gilch reported a route to PPVs using the direct polymerization of bis(halomethyl)benzenes in the presence of excess base.¹⁰

Although the polymerization *via* the Gilch route of bis(halomethyl)benzenes substituted with solubilizing groups should lead to soluble PPVs, in practice the preparation of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and poly(2,5-dihexyloxy-*p*-phenylenevinylene) *via* this route led to the gelation and precipitation of the products.^{6,11,12} Hsieh *et al.* report that they were able to minimize gelation in the preparation of MEH-PPV by following the procedure of Wudl *et al.*, in which the Bu^tOK is added slowly and intermittently.^{13,14} The MEH-PPV obtained by Hsieh in this manner, however, could not be filtered through a 0.5–1.0 μm filter indicating microgel formation.¹⁴ Hsieh reports that microgel formation in the production of MEH-PPV has been an under-reported but significant problem in its synthesis. In our laboratory we had indeed encountered a similar problem when exploring a side chain route to MEH-PPV using a modified McMurry reaction of the corresponding dialdehyde. The polymer produced in the reaction appeared to be soluble, but was unfilterable through 0.45 μm filters. Hsieh's report was the first we encountered that addressed the problem of microgel formation in the preparation of MEH-PPV. Hsieh solved this problem in the preparation of MEH-PPV with the development of a modified Gilch route that uses the non-polymerizable additive 4-*tert*-butylbenzyl chloride **3** to control molecular weight and prevent microgel formation.¹⁴ Having 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-methoxybenzene **2** in hand, we were curious whether replacing bromine for chlorine would affect polymerization using the modified Gilch route. We found that the polymerization of **2** *via* the modified



Scheme 1

Table 1 Conditions and results of the polymerization of **1** and **2**

Monomer	[Monomer] ^a / mol l ⁻¹	Molar ratio 3 :monomer	<i>M</i> _w ^b /10 ⁻³	<i>M</i> _n ^b /10 ⁻³	Polydispersity	Yield (%)
1 ^c	0.03	0.06	331	66.5	5.0	35
1 ^c	0.04	0.06	199	39.1	5.1	39
1 ^c	0.06	0.06	164	26.9	6.1	56
1	0.03	0.06	125	16.7	7.5	30
1	0.04	0.06	110	23.8	4.6	46
1	0.06	0.06	99	18.9	5.2	14
2	0.03	0.06	274	84.6	3.2	77
2	0.04	0.06	200	70.3	2.8	79
2	0.06	0.06	146	39.7	3.7	86

^a 8.9 equiv. of Bu^tOK (1.0 mol l⁻¹ in THF) was added all at once to an ice-water cooled solution of monomer in THF. ^b Relative to polystyrene in THF. ^c Hsieh *et al.* results for **1** (ref. 14).

Gilch route produced significantly different results than those reported by Hsieh for 1,4-bis(chloromethyl)-2-(2'-ethyl-hexyloxy)-5-methoxybenzene **1**.†

The polymerizations of both **1** and **2** (Scheme 1) were repeated under the reaction conditions that gave the highest molecular weight and the highest yield of MEH-PPV reported by Hsieh for the modified Gilch route (Table 1).¹⁴ Products were isolated after a single precipitation of the reaction mixtures in methanol. We obtained results similar, but not identical, to those of Hsieh for **1** (Table 1). Overall, our molecular weights were lower, but followed the same trend of decreasing with increasing concentration of **1** in THF. The decrease, however, was less dramatic in our hands. We observed a wider range of polydispersities and obtained yields both slightly better and significantly worse than those reported by Hsieh. All the products were readily soluble in THF, CHCl₃ and CH₂Cl₂ and easily filterable through 0.45 µm filters. When 4-*tert*-butylbenzyl chloride was not added to the polymerization of **1**, we did encounter problems in filtering solutions of the polymer through 0.45 µm filters, indicating microgel formation, and obtained extremely low yields. The same procedures were then repeated for **2**. Under all three reaction conditions higher molecular weight material was obtained in significantly higher yield than we observed with **1**, Table 1. The molecular weights that we observed for the polymerization of **2** were similar to those reported by Hsieh for **1** and significantly higher than we observed for **1**. Polydispersities were narrower than those both Hsieh reported and we observed with **1**. Typical data for the elemental analysis of MEH-PPV produced from **2** (C, 77.61; H, 9.23; Br, 0.01%) shows very good agreement with that calculated for [C₁₇H₂₄O₂]_n (C, 78.42; H, 9.29%) and very low bromine content. When no 4-*tert*-butylbenzyl chloride was added to the polymerization of **2**, both the yield and the molecular weight decreased but neither insoluble product nor microgel formation was observed, suggesting that the leaving group helps to prevent microgel formation but does not give as good results as the use of **2** with 4-*tert*-butylbenzyl chloride. ¹H NMR, UV, fluorescence and IR spectra of MEH-PPV produced from **1** and **2** are essentially the same and do not vary more than different polymerization runs using **1**. Relative quantum yields, as measured by a ratio of absorbance at 337 nm to integrated fluorescence intensity, did not vary as a function of method of preparation.

In conclusion, the modified Gilch route using the bis(chloromethyl)benzene **1** does indeed give soluble MEH-PPV in poor to moderate yields. Moderate to excellent yields of soluble MEH-PPV were obtained using the bis(bromomethyl)benzene **2**. Both **1** and **2** gave similar products. Elemental analysis data show products from **1** had slightly higher purity (99.5% compared to 99.0%) compared to **2** and had similar halogen content. Products from **2** consistently had higher molecular weights, narrower polydispersities and higher yields than the corresponding reactions with **1** in our hands. We conclude that

the bromo monomer **2** gives significantly better yields with consistently higher molecular weights and narrower polydispersities of a comparable quality MEH-PPV than monomer **1** using the modified Gilch route and is recommended when the use of benzyl bromides is convenient.

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Notes and references

† Monomer **2** was prepared from the alkylation of 4-methoxyphenol in the presence of base followed by bromomethylation with paraformaldehyde in HBr and acetic acid (ref. 15) Monomer **1** was prepared by Hsieh in a similar manner (ref. 12). We prepared monomer **1** from **2** using a halogen exchange reaction.

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