A New Synthetic Route to a Soluble High Molecular Weight Precursor for Poly(*p*-phenylenevinylene) Derivatives

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Mostly highly conjugated polymers are insoluble and infusible and therefore difficult to process. A methodology that avoids this problem is to develop a synthetic route that involves a soluble precursor polymer. Poly(*p*-phenylenevinylene) (PPV) is a conjugated polymer that is accessible via the Wessling precursor route.[1] The Wessling polymerization involves the treatment of bis(sulfonium halide) salts of *p*-xylene with base in water or alcohol as a solvent. PPV and some of its derivatives have generated interest because of their high conductivities upon oxidation[2] and recently their incorporation into light-emitting diodes (LED).[3] The mechanism is believed to proceed according to a chain growth polymerization process via the *in situ* generation of the monomer, a *p*-quinodimethane-like intermediate. It is still under discussion as to whether the polymerization is ionic[4] or free radical.[5]

Some questions arise: Can the Wessling route be viewed as a typical example of the polymerization of *p*-quinodimethane systems? Is it therefore possible to generalize the Wessling route in order to obtain many types of poly(arylenevinylene)s?

Generalizing this polymerization route, one should make a clear distinction between the two steps in the process: first, the formation of the *p*-quinodimethane system **3** and, second, the polymerization reaction itself. As a first step in such a generalization we want to address the question of the prerequisites for the formation of the monomer (Scheme 1).

To generate the *p*-quinodimethane **3**, substitution of a *p*-xylene derivative in the α position with a polarizer (Pol) and in the α′ position with a leaving group (L) is required. After the proton is abstracted by base, the polarizer stabilizes the anionic center in the intermediate **2**. The next step is 1,6-elimination of the leaving group which yields intermediate **3**. An ionic or free-radical polymerization would yield polymer **4**. If the polarizer can be thermally eliminated, then polymer **4** would be converted to PPV.

The monomers used in this study were the α-chloro-α′-alkyl(aryl)sulfinyl- (**1a** and **1b**) and α-chloro-α′-alkyl(aryl)sulfonyl-*p*-xylenes (**1c** and **1d**). The monomers were synthesized in two successive steps. In the first step the sulfide was formed by nucleophilic attack of the respective thiolate anion on an excess of α,α′-dichloro-*p*-xylene. The sulfinyl derivatives were formed by the oxidation of the sulfide with hydrogen peroxide and TeO_2 as a catalyst.[6] The sulfonyl derivatives were formed with *m*-chloroperbenzoic acid.

Scheme 1

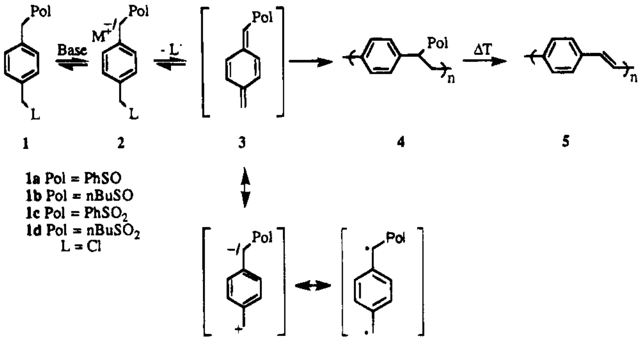

Table 1. Molecular Weight Values[a] for the Polymerization of Monomers with Different Polarizers in NMP

polarizer	M_p (×10^5)[b]	M_n (×10^5)	M_w (×10^5)	yield[c] (%)
PhSO	0.5	0.24	0.64	47
nBuSO	3.0	0.69	3.0	37
$PhSO_2$	5.0	2.40	4.30	71
$nBuSO_2$	2.0	0.91	4.20	46
$nBuSO_2$[d]	21.5	4.84	29.30	53

[a] Molecular weight values were measured with GPC in NMP against polystyrene standards. [b] M_p = molecular weight at peak maximum. [c] Yield of the high molecular weight fraction. [d] DMF was used as solvent instead of NMP.

Polymerizations were conducted at −20 °C in *N*-methylpyrrolidinone (NMP) or dimethylformamide (DMF) with sodium hydride as a base. The reaction was terminated by pouring the polymerization mixture in water and then acidifying with aqueous hydrochloric acid to pH = 7. The precipitate was filtered, and the residue was redissolved in $CHCl_3$ and reprecipitated in ether. The weight-average molecular weights of polymer **4d** after 1 h of polymerization in NMP or DMF were found to be 420 000 and 2 930 000, respectively. Polymer yields ranged from 30 to 70%. The polymer **4d** could be characterized with ^1H and ^{13}C NMR spectroscopy. Table 1 lists the molecular weights and yields of polymers with different polarizers. A detailed analysis of the NMR data will be published in a subsequent paper.

All polymers can be cast into flexible films from $CHCl_3$ solutions; other solvents in which the polymers are soluble are DMF, DMSO, and NMP. The thermal properties of the polymers were analyzed using thermogravimetric analysis under a constant N_2 stream (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The sulfonyl derivatives (**4c** and **d**) were found to be stable up to 270 °C, after which severe degradation occurs. The sulfinyl polymers (**4a** and **4b**) exhibited a region of weight loss from 100 to 150 °C, consistent with the elimination of the theoretical amount of the respective sulfinic acid. This was confirmed using a coupled technique, TGA–mass spectroscopy. A second weight loss was observed at 550 °C, consistent with the decomposition of the final polymer PPV (**5**). Thermal treatment of a free-standing film of **4b** in vacuo at 200 °C for 4 h yielded a polymer film. Elemental analysis (Anal. Calcd for C_8H_6: C, 94.08; H, 5.92. Found: C, 90.31; H, 5.91; S, 0.89) is consistent with a PPV structure with 3 mol % *n*-butylsulfinyl groups remaining. An FT-IR study in film of polymer **4b** subjected to 200 °C *in vacuo* showed that the S=O absorption (1030 cm^{-1}) had disappeared and that the IR bands for PPV were present at 3024, 1518, 1423, 1335, 964, 837, and 555 cm^{-1}. The UV/vis spectrum of the thermally eliminated polymer **4b**, shown in Figure 1, is very similar to PPV.[7] The ^{13}C CP/MAS NMR spectrum of

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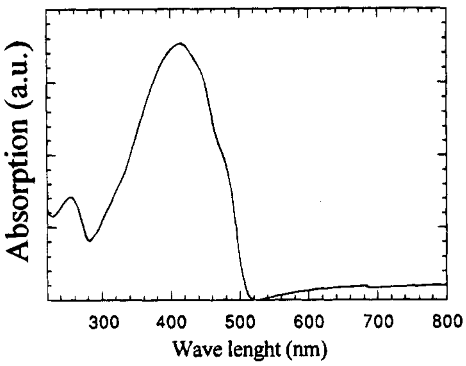

Figure 1. UV/vis spectrum of a film of thermally eliminated polymer **4b**.

these films showed two resonances at 136 (aromatic quaternary carbons) and 128 ppm (vinylene and aromatic C–H carbons) in agreement with literature values.[8] The absence of carbonyl and aliphatic carbon resonances in the spectrum provides further supporting evidence of the conjugated structure in polymer **5**.

In this work a general route to a high molecular weight precursor for poly(*p*-phenylenevinylene)s has been described. Other poly(xylylene) derivatives could be synthesized using this general method. The poor stability of some of the sulfonium salt precursors of 2,5-dialkoxypoly(*p*-phenylenevinylene)[9] or poly(2,5-thienylenevinylene) (PTV)[10] would be avoided using this synthetic route. A nonionic polymer, thermally-stable at ambient temperature and soluble in organic solvents, would be easier to characterize. Indeed the molecular weight and molecular weight distribution determination of the polyelectrolyte precursor of PPV is very difficult due to irreversible interactions between the precursor and GPC columns.[5] A soluble nonionic polymer would be much more amenable to GPC analysis. Scheme 1 defines the essential prerequisites of the formation of the *p*-quinodimethane intermediate **3**. Whether the polymerization reaction of **3** occurs via a free-radical or ionic pathway is beyond the scope of the present work. However, because of the stability of the monomers and the resulting polymers, this synthetic route may provide a new tool to study in detail the polymerization reaction or lead to a clearer distinction between the two steps in the polymerization process.

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