Highly Selective Route for Producing Unsymmetrically Substituted Monomers toward Synthesis of Conjugated Polymers Derived from Poly(*p*-phenylene vinylene)

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A new convenient route for producing unsymmetrically substituted sulfinyl monomers of precursor polymers toward poly(*p*-phenylene vinylene) is described. Upon treating a symmetrical bissulfonium salt with a thiolate anion, an unexpected high selectivity for the monosubstituted thioethers (90%) is obtained. Optimization of the reaction conditions showed that the stoichiometry of the reactants in this reaction is important to ensure the high selectivity and to prevent unwanted side reactions. Reaction of equimolar amounts of reagents at ambient temperature gave the best results. A mechanism consistent with these results, supported by UV−vis experiments, is presented. Selective oxidation of the thioethers yielded the sulfinyl monomers. By using this new route, it was possible to increase the overall yield by a factor of 2, as compared to the route previously used to obtain these compounds.

Introduction

Light-emitting diodes (LEDs), in which thin films of conjugated polymers constitute the active layer, were first reported in 1990 by Friend et al.[1] They succeeded in fabricating a LED with poly(*p*-phenylene vinylene), PPV, as the emission layer. Interest in this field then grew rapidly, and extensive research was performed in order to improve the synthesis of the active materials and the performance of these devices.[2]

Precursor routes for conjugated materials are of major importance for the development of optical and electronic applications for organic semiconductors. They introduce processability, which makes the incorporation of these materials into devices feasible. A precursor route that has shown to be very versatile is the one introduced by Wessling and Zimmerman.[3,4] Their sulfonium precursor polymer leads, after thermal conversion, to PPV derivatives with good mechanical properties, high thermal stability, and large conductivities. Still there are some drawbacks, which are inherent to this route, e.g., instability of the precursor polymer and gel formation. Furthermore, it is difficult to polymerize monomers with extended aromatic systems such as 4,4′-biphenylene[5] or 2,6-naphthalene.[6]

To solve these problems we have evaluated a general scheme,[7−10] in which a clear distinction is made in three steps of the process: formation of the actual monomer, viz., *p*-xylylene derivative **2**, polymerization to precursor polymer **3**, and thermal conversion[11] to the conjugated polymer **4** (Scheme 1).

To have control over the polymerization process[7,12] and the stability of the precursor polymers,[13] a chemical differentiation of the polarizer (S(O)R) and leaving group (Cl) is needed. A consequence of this approach is the use of an unsymmetrically substituted monomer like **1**.

For a convenient, large-scale synthesis of these unsymmetrically monosubstituted monomers starting from symmetrical starting products, a high selectivity of the monosubstituted product is desired. This high selectivity can be achieved in several ways. Precipitation of a monosubstituted derivative from a reaction medium can give good results. However, this method is often only applicable for a small number of well-defined starting products.[14] Another possibility is the use of an excess of symmetrical starting product to shift the product distribution to the side of the unsymmetrically monosubstituted product. The disadvantage of this approach is often a cumbersome recuperation of (expensive) starting product. The drawbacks mentioned above demand for a new synthesis route in which, starting from a commercially available symmetrical starting product, unsymmetrically substituted monomers can be made using equimolar amounts of reagents.

In this paper we present such a simple process for producing unsymmetrically substituted sulfinyl monomers toward PPV with an unexpected high selectivity.

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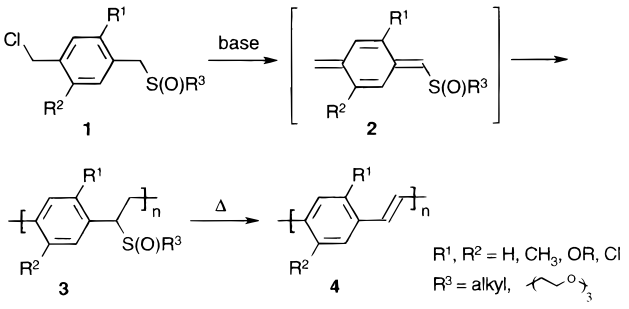
Scheme 1



Results

Many synthetic routes to obtain sulfoxides are known from literature.[15−17] The most versatile one is the oxidation of thioethers. In this approach the first step to these sulfoxides is synthesis of thioethers.

Synthesis of Thioethers. The reaction of alkyl halides with various nucleophilic sulfur species is one of the classic methods of thioether synthesis.[16] In Scheme 2 such a method using phase-transfer conditions[18] (route A) is applied for producing monosubstituted thioethers **6a**−**g**, which can be later converted to sulfinyl monomers **1**.

After workup the reaction mixture consists of three products, α,α′-dichloro-*p*-xylene **5**, α-chloro,α′-alkylthio-*p*-xylene **6a**−**g**, and α,α′-dialkylthio-*p*-xylene **7a**−**g**. The product distribution of the crude reaction mixture was determined with ^{1}H NMR. The aromatic part of the ^{1}H NMR spectra of the pure compounds **5** and **7f** and the ^{1}H NMR spectrum of a reaction mixture resulting from method A (starting from equimolar amounts of reagents) are presented in Figure 1a−c. The aromatic signals of **5**, **6a**−**g**, and **7a**−**g** are sufficiently separated to allow a reliable determination of the product distribution.

To avoid the unwanted disubstituted products **7a**−**g**, a large excess (2.2 equiv) of **5** has to be used. The results are collected in Table 1. In all cases the amount of disubstituted product is in the range 2−6%. Thus via this route it is possible to minimize the amount of disubstituted product by using a large excess of **5**, but the selectivity for the monosubstituted product is poor.

To obtain a higher selectivity for the monosubstituted product, a new route (Scheme 2, route B) using equimolar amounts of reagents was explored starting from α,α′-bissulfonium-*p*-xylene (**8**). Bissulfonium salts such as **8** give upon reaction with base a very reactive unsymmetric compound, viz., a *p*-xylylene derivative.[19−21] If these *p*-xylylene derivatives can be trapped by, for example, a thiol, this would lead to the unsymmetric substituted compound **9**. Moreover, the easily occurring substitution of the sulfonium group by chlorine, an unwanted side reaction of sulfonium precursor polymers,[22] could be exploited to yield thioethers such as **6**.

The first step in this new route is synthesis of a bissulfonium salt like **8**. This reaction is very well documented in literature.[22,23] Starting from **5** reaction with tetrahydrothiophene gives the corresponding bissulfonium salt **8** in a yield of 91%. Bissulfonium salts are very hygroscopic and therefore contain a certain amount of water. This amount of water can be determined by ^{1}H NMR in D_2O (see Experimental Section). Different batches of **8** contained 2−5 wt % H_2O.

In a first experiment via route B, reaction of equimolar amounts of **8**, *n*-octanethiol, and NaOtBu gave, after azeotropic distillation of tetrahydrothiophene,[24] again a mixture of three products, α,α′-dichloro-*p*-xylene (**5**) (5%), α-chloro,α′-*n*-octylthio-*p*-xylene (**6f**) (90%), and α,α′-*n*-octylthio-*p*-xylene (**7f**) (5%) according to ^{1}H NMR. Remarkably we obtained a very high selectivity for monosubstituted thioether **6f**. It should be emphasized that precipitation of monosubstituted thioethers **6** or **9** from the reaction medium was not observed. As a counter example, the reaction was repeated in the same manner via route C, starting from **5**. In this way a statistical distribution (25% **5**, 50% **6f**, 25% **7f**) of products was obtained.

Tuning of Reaction Conditions. To tune the reaction conditions, the influence of the amount of NaOtBu, amount and type of thiol, and temperature on the product distribution was investigated.

Optimization of Relative Amount of NaOtBu. All reactions were carried out with 1 equiv of *n*-octanethiol and equimolar amounts of **8** and NaOtBu at 20 °C. The results are collected in Table 2.

Reaction conditions for route B resemble those of the polymerization of bissulfonium salts to Wessling precursor polymers.[3] Hence this could be an important, unwanted side reaction of route B. If polymerization and subsequent elimination to PPV occurs during the reaction, it can be detected by the appearance of a characteristic yellow fluorescent color caused by the conjugated system of PPV. No efforts were made to determine the exact amount of polymer, because we were only interested in avoiding this side reaction. As can be deduced from Table 2, polymerization and subsequent elimination to PPV becomes a side reaction if an excess of NaOtBu and bissulfonium salt is used relative to the amount of thiol. From these experiments it became clear that the ratio of thiol and NaOtBu should be higher than 1 to avoid polymerization.

Optimization of Relative Amount of Thiol. All reactions were carried out at 20 °C with a ratio *n*-octanethiol:NaOtBu of 1:1 in order to prevent polymerization. The results are collected in Table 3.

The experiments showed that no polymerization occurred using equimolar amounts of thiol and NaOtBu. In addition, the amount of α,α′-dichloro-*p*-xylene (**5**) increased at the expense of monosubstituted α-chloro,α′-*n*-octylthio-*p*-xylene (**6f**) when less than 1 equiv of thiol was used. Combining these data with those of Table 2,

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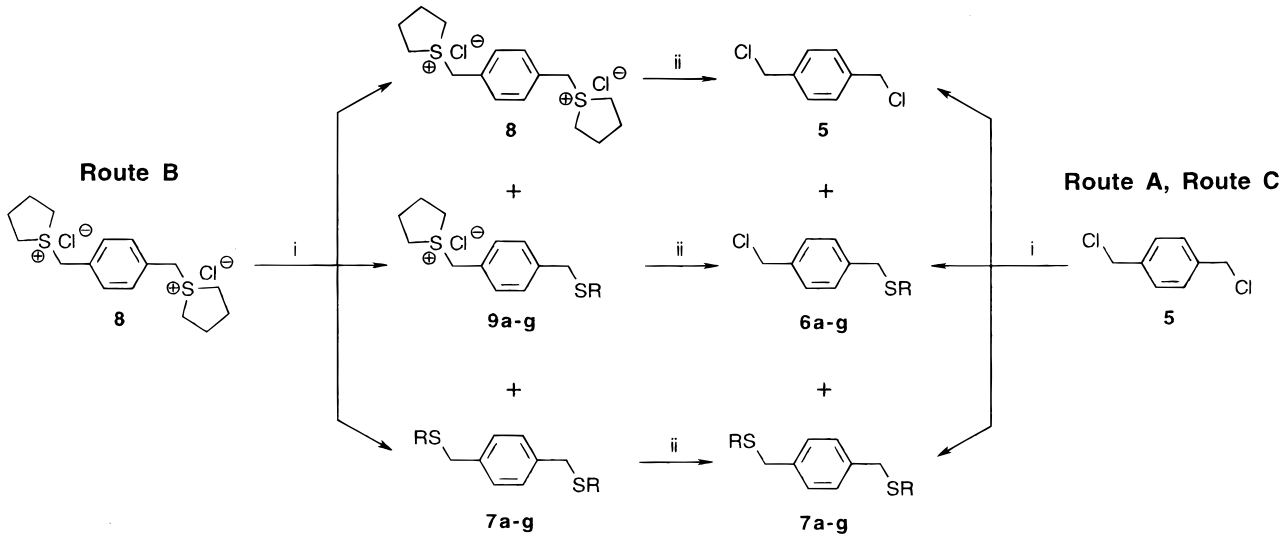
Scheme 2



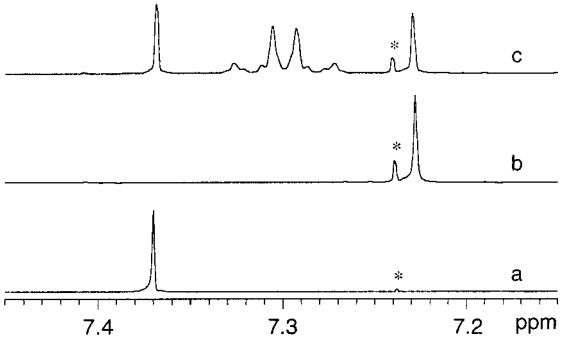


Figure 1. ^{1}H NMR spectra of (a) α,α′-dichloro-*p*-xylene **5**, (b) α,α′-dioctylthio-*p*-xylene **7f**, (c) reaction mixture obtained from route A (equimolar amounts of reagents). The resonance marked with an asterisk results from chloroform.

Table 1. Product Distribution of Crude Reaction Mixtures of Thioether Synthesis and Overall Yields of 1 by Applying Routes A and B

		route A				route B			
		product distribution (%)[a]			yield (%)[b]	product distribution (%)[a]			yield (%)[b]
entry	thiol (R)	**5**	**6**	**7**	**1**	**5**	**6**	**7**	**1**
1	**a**: *n*-butyl	58	40	2	33	5	90	5	68
2	**b**: *i*-butyl	59	38	3	30	6	89	5	66
3	**c**: *s*-butyl	58	39	3	30	7	87	6	65
4	**d**: *t*-butyl	60	35	5	29	8	85	7	64
5	**e**: *i*-pentyl	59	38	3	32	6	89	5	67
6	**f**: *n*-octyl	59	39	2	31	5	90	5	68
7	**g**: 	61	33	6	27	7	86	7	64

[a] Crude reaction mixture (determined by ^{1}H NMR). [b] Overall yield after column chromatography.

it is clear that the stoichiometry in route B is important to achieve a high selectivity and to suppress polymerization.

Table 2. Tuning of Relative Amount of NaOtBu

		product distribution (%)[a]		
entry	equiv of NaOtBu	**5**	**6f**	**7f**
1	0.95	14	78	8
2	1.00	5	90	5
3	1.05[b]	7	87	6
4	1.10[b]	6	89	5

[a] Crude reaction mixture (determined by ^{1}H NMR). [b] Polymerization could not be avoided; amount of polymer is not determined.

Table 3. Tuning of Relative Amount of *n*-Octanethiol

		product distribution (%)[b]		
entry	equiv of thiol[a]	**5**	**6f**	**7f**
1	0.95	14	78	8
2	0.98	8	84	8
3	1.00	5	90	5

[a] One equivalent of **8** is used; ratio thiol:NaOtBu was 1:1. [b] Crude reaction mixture (determined by ^{1}H NMR).

Table 4. Tuning of Reaction Temperature

		product distribution (%)[a]		
entry	temp (°C)	**5**	**6f**	**7f**
1	−20	8	84	8
2	0	6	87	7
3	20	5	90	5
4	40	6	87	7

[a] Crude reaction mixture (determined by ^{1}H NMR).

Optimization of Reaction Temperature. Four different temperatures were examined, while the optimized ratio of reagents was used (ratio of **8**:*n*-octanethiol: NaOtBu is 1:1:1). The results are collected in Table 4.

The data in Table 4 show that a change in reaction temperature does not affect the product distribution in a significant way. This means that the reaction can be performed at ambient temperature.

Table 5. Product Distribution Applying Different Routes for Thioether Synthesis

			product distribution (%)[a]		
entry	route[b]	equiv of thiol	**5**	**6f**	**7f**
1	A	0.45	59	39	2
2	A	1.00	19	63	18
3	B	1.00	5	90	5
4	C	1.00	25	50	25

[a] Crude reaction mixture (determined by ^{1}H NMR). [b] See Scheme 2.

Use of Different Thiols. Different thiols were used in order to investigate the scope of this route starting from **8**. The optimized conditions, ratio **8**:thiol:NaOtBu of 1:1:1, were used. The results are collected in Table 1. It is evident that this route is applicable for other types of thiols as well with a comparable selectivity.

Oxidation of Thioethers. The oxidation of a thioether can yield either the corresponding sulfoxide or the corresponding sulfone or both, depending on the method used.[14−16,25] Overoxidation to sulfones can be avoided by using a tellurium dioxide (TeO_2)-catalyzed selective oxidation with H_2O_2 as the oxidant.[26] Oxidation of the crude mixtures of **6a**−**g** from routes A and B afforded the corresponding sulfoxides **1a**−**g** in a 90% yield. The overall yields of synthesis of sulfinyl monomers **1a**−**g** via routes A and B are collected in Table 1. The data reveal that the overall yield is increased by a factor of 2 using route B instead of route A.

Discussion

The products obtained in the synthesis of thioethers by the routes described above are the same. In all cases a mixture of starting compound **5**, monosubstituted compound **6**, and disubstituted compound **7** is obtained. This allows a comparison of the mechanisms operating in these different routes. A spectacular improvement in selectivity for monosubstituted thioether **6** is obtained when route B is compared with routes A and C (Table 5). Introduction of the thioether group in the latter two routes occurs via a simple nucleophilic substitution of chlorine by a thiolate anion. In this way there is no selectivity at all (route C), or just a small preference for compound **6** if phase transfer conditions are used (Table 5, entry 2).

Since a sulfonium group is also a good leaving group, nucleophilic substitution by a thiolate anion can be envisaged (pathway II, Scheme 3). However, this cannot explain the high selectivity for **9** and **6**, if no precipation of **9** from the reaction medium occurs. In all experiments via route B precipitation was never observed; therefore another mechanism should be operative here.

Recently, Pierce et al.[27] described a high selectivity for the synthesis of the unsymmetrically substituted compound (4-(chloromethyl)phenyl)methan-1-ol starting from the symmetrical (4-(hydroxymethyl)phenyl)methan-1-ol. They proposed a mechanism in which the reaction proceeds via a *p*-xylylene oxide derivative. However, no further evidence for the existence of this intermediate was presented.

The polymerization reaction of bissulfonium salts proceeds via a *p*-xylylene intermediate like **11**, which undergoes polymerization either by an anionic or a free radical mechanism.[3,18−20,28] It is accepted that this *p*-xylylene derivative is produced via the ylide intermediate. The mechanism of this step was assessed by H−D exchange experiments.[29] Furthermore, the increase and decrease of *p*-xylylene derivatives can be visualized by UV−vis measurements.[20] Control comparison studies on nonpolymerizable monobenzylic sulfonium salts established that the absorbances are not due to ylides formed by simple deprotonation.[21] To verify whether such a *p*-xylylene intermediate plays a role in the mechanism of thioether synthesis via route B, similar UV−vis experiments were performed. The results are depicted in Figure 2a,b. Polymerization and thioether synthesis can also be examined by monitoring the change in absorbance (at the absorption maximum of 316 nm) with time (Figure 3), as described in the Experimental Section.

From Figure 2a,b it is evident that during thioether synthesis via route B the same *p*-xylylene intermediate is formed. Although in both experiments the same concentrations were used, one can see that the maximum of absorption is lower in thioether synthesis and the decrease of absorption is faster than for polymerization (curves a and b Figure 3). Upon reaction of **11** with a thiol, the *p*-xylylene intermediate is consumed with formation of thioether **9**, thereby leading to a decrease in absorption. The thiol addition to **11** thus inhibits polyaddition of **11**, viz., polymerization. However, if the ratio of NaOtBu to thiol is higher than 1, polymerization can of course still occur. Curve c represents thioether synthesis by route C in which no *p*-xylylene intermediate is involved. Curve d represents thioether synthesis starting from α,α′-bis(triethylammonium)-*p*-xylene instead of **8**. Under the conditions used for route B the ammonium derivative gives no reaction at all. From curve d it is evident that no *p*-xylylene intermediate is formed, probably because of the higher pK_a of this compound or the poor leaving group capacity of an ammonium group compared to a sulfonium group.[30]

Combining the above-mentioned observations, we propose that thioether synthesis via route B occurs by pathway I of the mechanism depicted in Scheme 3.

The first two steps are similar to the mechanism proposed for the polymerization reaction. The only difference is that deprotonation in thioether synthesis will take place by a thiolate anion since a thiol has a lower pK_a value than an alcohol.[31] Overall addition of a thiol to the unsymmetrical *p*-xylylene **11** gives the unsymmetrically substituted thioether **9**. Substitution of the sulfonium group by chlorine, induced by azeotropical removal of tetrahydrothiophene, leads to monosubstituted thioether **6**. Apparently, the rate of introduction of a thioether via an elimination−addition reaction (pathway I) exceeds the rate of introduction via a nucleophilic substitution (pathway II). Since **9** will not give a *p*-

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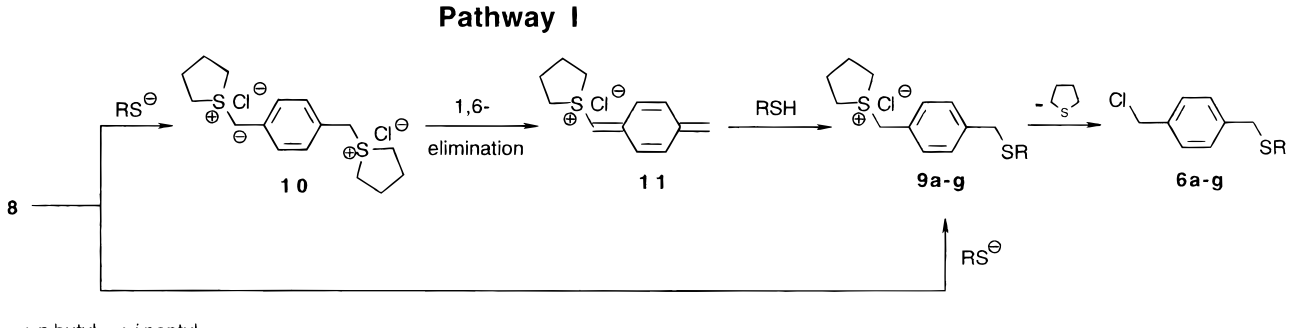
Scheme 3



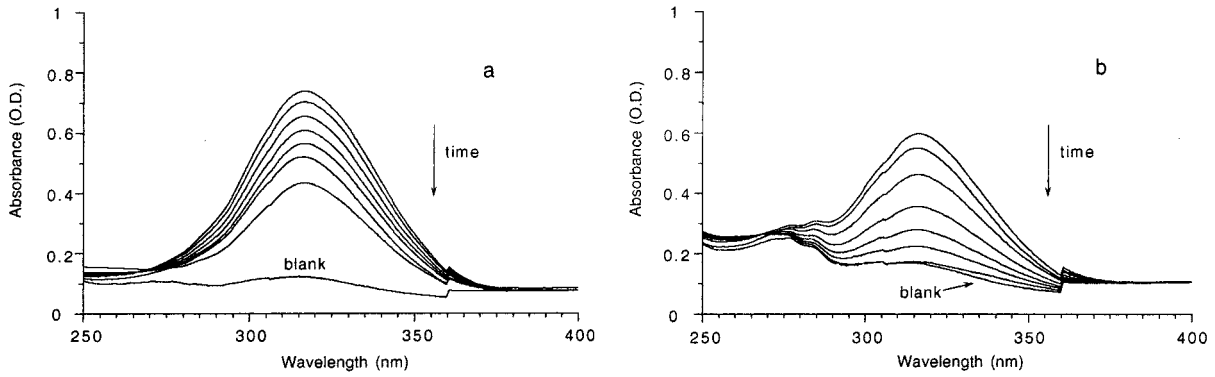


Figure 2. UV−vis spectra for QM **11**: (a) polymerization of **8** at different time intervals, (b) thioether synthesis via route B at different time intervals. Both spectra were obtained in MeOH at room temperature under the conditions described in the Experimental Section.

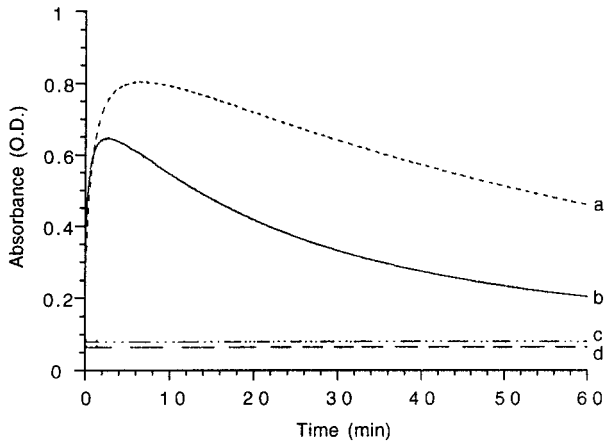


Figure 3. Change of absorbance (316 nm) of **11** with time: (a) polymerization, (b) thioether synthesis via route B, (c) thioether synthesis via route C, (d): thioether synthesis starting from bisammonium-*p*-xylene.

xylylene derivative under the reaction conditions used, disubstitution is suppressed if 1 equiv of thiol is used.

Conclusions

The novel route described herein is a highly selective one in which, starting from a symmetrical bissulfonium salt **8**, unsymmetrically substituted thioethers **6a**−**g** are obtained with selectivities of 90%. Stoichiometry of the reactants used is very important to ensure this high selectivity and to prevent side reactions from taking place. Exploration of the scope and limitations of this route starting from other bissulfonium salts is currently under way. Results of UV−vis and product studies reveal that thioether synthesis via this route proceed via the unsymmetrical *p*-xylylene intermediate **11**. Selective oxidation of the thioethers obtained from this new route affords sulfinyl monomers for PPV precursors, with a 2-fold increase in overall yield compared to route A, which was used previously to synthesize these compounds.

Experimental Section

Reagents and Methods. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. All reactions were conducted under an inert atmosphere of nitrogen.

^{1}H NMR spectra were obtained in a deuterated solvent ($CDCl_3$ or D_2O) at 400 MHz. Chemical shifts (δ) in ppm were determined relative to the residual nondeuterated solvent absorption (7.24 ppm for $CHCl_3$, 4.72 ppm for H_2O). The ^{13}C NMR experiments were recorded at 100 MHz on the same spectrometer. Chemical shifts were defined relative to the ^{13}C resonance shift of $CHCl_3$ (77.0 ppm). Resonance assignments were achieved by the use of one- and two-dimensional NMR techniques such as ^{1}H, ^{13}C, attached proton test (APT), 2D HETCOR (J = 8 Hz, J = 140 Hz), 2D COSY, and 2D INADEQUATE and will be desribed elsewhere.[32] For direct insert probe mass spectra electron impact (EI) was used as ionization mode. Ionization energy was 70 eV. Melting points are uncorrected.

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Water Determination by ^{1}H NMR. A blank sample of D_2O (750 μL) was recorded quantitatively using a delay time of 60 s, and the H_2O signal was integrated (A). A 15 mg sample of product was introduced in the same tube, and the sample was recorded under the same conditions. The H_2O signal was again integrated (B), after which subtraction of B from A gave the integration (C) corresponding to the amount of water from the product. C can be correlated to another known proton signal of the product leading to a formula of the type: product·$x$$H_2O$.

UV−Vis Spectroscopy. All MeOH used in preparation of the solutions was thoroughly purged with nitrogen before use. A magnetic stirrer was incorporated in the sample holder of the UV−vis spectrometer to achieve efficient mixing of the reagents.

A stock solution of **8** was made by dissolving 18.3 mg (52.1 μmol) in MeOH (100 mL) to generate a 0.52 mM solution. The same concentration range was used for all other compounds. Stock solution NaOtBu: 12.5 mg (130.3 μmol) in MeOH (250 mL). Stock solution NaOtBu + *n*-octanethiol: 12.5 mg of NaOtBu (130.3 μmol) + 19.1 mg of *n*-octanethiol (130.3 μmol) in MeOH (250 mL). Stock solution α,α′-bis(triethylammonium)-*p*-xylene: 25.5 mg (52.1 μmol) in MeOH (100 mL). Stock solution **5**: 18.2 mg (104.0 μmol) in MeOH (200 mL).

Monitoring Polymerization. Stock solution of **8** (100 μL) was transferred by syringe to a quartz cuvette and diluted with MeOH (1.5 mL). A blank spectrum was recorded at ambient temperature against a MeOH reference. Next, NaOtBu solution (100 μL) was injected in the cuvette, and spectra were acquired from 200 to 400 nm (scan rate "fast") at different programmed time intervals, or the change in absorbance at λ_{max} (316 nm) was monitored in time (sampling interval 0.2 nm).

Monitoring Monomer Synthesis via Route B. The same procedure was followed as for polymerization starting from **8** now using the NaOtBu/*n*-octanethiol stock solution.

Monitoring Monomer Synthesis via Route C. The same procedure was followed as for route B now starting from **5**.

Monitoring Monomer Synthesis Starting from α,α′-Bis(triethylammonium)-*p*-xylene. The same procedure was followed as for route B now starting from α,α′-bis(triethylammonium)-*p*-xylene.

Synthesis. 1,4-Bis(tetrahydrothiopheniomethyl)xylene Dichloride (8). A solution of **5** (52.5 g, 0.3 mol) and tetrahydrothiophene (105 mL, 1.19 mol) in MeOH (105 mL) was stirred for 60 h at ambient temperature. The reaction mixture was precipitated in acetone (420 mL) at −10 °C. The precipitate was collected and washed with cold acetone (600 mL). Evaporation of the solvent gave a white hygroscopic solid (95.9 g, 91%): ^{1}H NMR (D_2O, 400 MHz) δ 2.12−2.30 (m, 8H), 3.31−3.50 (m, 8H), 4.48 (s, 4H), 7.53 (s, 4H) ppm.

α,α′-Bis(triethylammonium)-*p*-xylene. A well-stirred amount of dibromo-*p*-xylene (11.8 g, 45 mmol), Et_3N (25 mL, 180 mmol), and EtOH (250 mL) was refluxed for 72 h. After cooling the reaction mixture, the precipitate was filtered off, washed with Et_2O (2 × 100 mL), and dried under vacuum to give a white solid (19.9 g, 95%): ^{1}H NMR (D_2O, 400 MHz) δ 1.32 (t, J = 9.6 Hz, 18H), 3.17 (q, J = 9.6 Hz, 12H), 4.39 (s, 4H), 7.56 (s, 4H) ppm.

1-(Chloromethyl)-4-[(alkylsulfanyl)methyl]benzenes (6a−g) via Route A. General Procedure. To a stirred mixture of **5** (39.4 g, 0.225 mol) in toluene (400 mL), NaOH (23.7 g, 0.59 mol) in H_2O (400 mL) and Aliquat 336 (1 g) was added a solution of thiol (0.10 mol, 0.45 equiv) in toluene (100 mL) dropwise over a period of 24 h at room temperature. The organic layer was washed with H_2O (3 × 200 mL), dried over $MgSO_4$, and concentrated in vacuo.

1-(Chloromethyl)-4-[(alkylsulfanyl)methyl]benzenes (6a−g) via Route B. General Procedure. A mixture of NaOtBu (1.83 g, 19 mmol) and thiol (19 mmol) in MeOH (40 g) was stirred for 30 min at the temperatures indicated in the text. The temperature was maintained by a thermostated experimental setup. The clear solution was added in one portion to a stirred solution of **8** (6.68 g, 19 mmol) in MeOH (100 g) at the temperatures indicated in the text. After 1 h the reaction mixture was neutralized with aqueous HCl (1 M), if necessary, and concentrated in vacuo. The crude product was diluted with $CHCl_3$ (200 mL), and the precipitate was filtered off. The filtrate was concentrated in vacuo. The oil thus obtained was diluted with *n*-octane or petroleum ether (boiling range 100−130 °C) and concentrated to remove tetrahydrothiophene. This sequence was repeated three times.

1-(Chloromethyl)-4-[(*n*-butylsulfanyl)methyl]benzene (6a). This compound was synthesized according to the general procedure for route A or route B, starting from *n*-butanethiol (9.02 g, 0.1 mol (route A); 1.71 g, 19 mmol (route B)) to give a crude mixture of **5**, **6a**, and **7a** as a light yellow solid (yield 44.24 g; 4.30 g).

1-(Chloromethyl)-4-[(isobutylsulfanyl)methyl]benzene (6b). This compound was synthesized according to the general procedure for route A or route B, starting from isobutanethiol (9.02 g, 0.1 mol (route A); 1.71 g, 19 mmol (route B)) to give a crude mixture of **5**, **6b**, and **7b** as a light yellow solid (yield 44.00 g; 4.25 g).

1-(Chloromethyl)-4-[(*sec*-butylsulfanyl)methyl]benzene (6c). This compound was synthesized according to the general procedure for route A or route B, starting from *sec*-butanethiol (9.02 g, 0.1 mol (route A); 1.71 g, 19 mmol (route B)) to give a crude mixture of **5**, **6c**, and **7c** as a light yellow solid (yield 44.32 g; 4.32 g).

1-(Chloromethyl)-4-[(*tert*-butylsulfanyl)methyl]benzene (6d). This compound was synthesized according to the general procedure for route A or route B, starting from *tert*-butanethiol (9.02 g, 0.1 mol (route A); 1.71 g, 19 mmol (route B)) to give a crude mixture of **5**, **6d**, and **7d** as a light yellow solid (yield 43.79 g; 4.22 g).

1-(Chloromethyl)-4-[(isopentylsulfanyl)methyl]benzene (6e). This compound was synthesized according to the general procedure for route A or route B, starting from isopentanethiol (10.42 g, 0.1 mol (route A); 1.98 g, 19 mmol (route B)) to give a crude mixture of **5**, **6e**, and **7e** as a light yellow solid (yield 44.95 g; 4.51 g).

1-(Chloromethyl)-4-[(*n*-octylsulfanyl)methyl]benzene (6f). This compound was synthesized according to the general procedure for route A or route B, starting from *n*-octanethiol (14.63 g, 0.1 mol (route A); 2.78 g, 19 mmol (route B)) to give a crude mixture of **5**, **6f**, and **7f** as a light yellow solid (yield 49.21 g; 5.30 g).

1-(Chloromethyl)-4-[({2-[2-(2-methoxyethoxy)ethoxy]-ethyl}sulfanyl)methyl]benzene (6g). This compound was synthesized according to the general procedure for route A or route B, starting from 2-[2-(2-methoxyethoxy)ethoxy]ethylthiol (18.03 g, 0.1 mol (route A); 3.42 g, 19 mmol (route B)) to give a crude mixture of **5**, **6g**, and **7g** as a light yellow solid (yield 52.30 g; 5.90 g).

1-(Chloromethyl)-4-[(*n*-octylsulfanyl)methyl]benzene (6f) via Route C. A mixture of NaOtBu (1.83 g, 19 mmol) and *n*-octanethiol (2.78 g, 19 mmol) in MeOH (40 g) was stirred for 30 min at 20 °C. The clear solution was added dropwise to a stirred solution of **5** (3.33 g, 19 mmol) in MeOH (100 g). After 1 h the reaction mixture was neutralized with aqueous HCl (1 M), diluted with $CHCl_3$ (250 mL), washed with H_2O (2 × 100 mL), dried over $MgSO_4$, and concentrated in vacuo to give a yellow oil (yield 5.29 g).

1-(Bromomethyl)-4-[(*n*-butylsulfanyl)methyl]benzene. A mixture of NaOtBu (0.97 g, 10 mmol) and *n*-butanethiol (0.88 g, 9.8 mmol) in MeOH (20 g) was stirred for 30 min at 20 °C. The clear solution was added in one portion to a stirred solution of α,α′-bis(triethylammonium)-*p*-xylene (4.66 g, 10 mmol) in MeOH (50 g). After 1 h the reaction mixture was neutralized with aqueous HCl (1 M) and concentrated in vacuo to give a white solid identified as α,α′-bis-(triethylammonium)-*p*-xylene (yield 4.60 g, 99%).

General Procedure for the Oxidation of Thioethers from Route A; Route B. An aqueous (35 wt %) solution of H_2O_2 (11.7 g, 0.12 mol; 3.4 g, 35 mmol) was added dropwise to a solution of crude thioether (∼0.06 mol; ∼17 mmol) in MeOH (400 mL; 125 mL) and TeO_2 (1.44 g, 5 mol %; 0.28 g). After 6 h the reaction was quenched by adding a saturated aqueous NaCl solution (200 mL; 75 mL). The reaction mixture was extracted with $CHCl_3$ (3 × 150 mL; 3 × 50 mL), and the

combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The reaction mixture was purified by column chromatography (SiO_2, eluent $CHCl_3$) and subsequent crystallization from CH_2Cl_2/hexane. The yields given below (route A; route B) are referred to starting compound **5**.

1-(Chloromethyl)-4-[(*n*-butylsulfinyl)methyl]benzene (1a). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6a**, and **7a** to give **1a** as a white solid (18.16 g, 33%; 3.46 g, 68%): mp 111.5−112.5 °C. R_f = 0.43 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.90 (t, J = 7.2 Hz, 3H), 1.41 (m, 2H), 1.70 (m, 2H), 2.56 (t, J = 8.0 Hz, 2H), 3.92 + 3.95 (dd, J_{AB} = 13.2 Hz, 2H), 4.55 (s, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.1, 21.3, 23.8, 45.1, 50.2, 56.9, 128.4, 129.8, 129.9, 136.8 ppm. IR (KBr): ν 2965, 2902, 2870, 1025 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 244 ([M]$^+$, 9), 209 ([$C_{12}H_{17}OS$]$^+$, 5), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 19), 77 ([C_6H_5]$^+$, 5). Anal. Calcd for $C_{12}H_{17}ClOS$: C, 58.88; H, 7.00; S, 13.10. Found: C, 59.26; H, 7.09; S, 12.89.

1-(Chloromethyl)-4-[(isobutylsulfinyl)methyl]benzene (1b). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6b**, and **7b** to give **1b** as a white solid (16.45 g, 30%, 3.39 g, 66%): mp 116.0−117.0 °C. R_f = 0.41 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.02 (d, J = 6.8 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 2.17 (m, 1H), 2.29 + 2.32 (d, J = 12.4 Hz, 1H), 2.54 + 2.57 (d, J = 12.4 Hz, 1H), 3.92 + 3.95 (dd, J_{AB} = 12.8 Hz, 2H), 4.57 (s, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 22.8, 23.6, 45.6, 58.2, 60.4, 129.0, 130.1, 130.3, 137.4 ppm. IR (KBr): ν 2964, 2911, 2894, 2870, 1019 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 244 ([M]$^+$, 16), 209 ([$C_{12}H_{17}OS$]$^+$, 39), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 21), 77 ([C_6H_5]$^+$, 7). Anal. Calcd for $C_{12}H_{17}ClOS$: C, 58.88; H, 7.00; S, 13.10. Found: C, 59.41; H, 7.15; S, 12.82.

1-(Chloromethyl)-4-[(*sec*-butylsulfinyl)methyl]benzene (1c). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6c**, and **7c** to give **1c** as a white solid (16.52 g, 30%, 3.34 g, 65%): mp 105.0−107.0 °C. R_f = 0.40 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.99 + 1.02 (t, J = 7.2 Hz, 3H), 1.24 + 1.29 (d, J = 6.8 Hz, 3H), 1.56 (m, 1H), 1.81 + 1.92 (m, 1H), 2.41 + 2.58 (m, 1H), 3.78 + 3.95 (dd, J_{AB} = 12.8 Hz, 1H), 3.86 + 3.92 (dd, J_{AB} = 12.8 Hz, 1H), 4.57 (s, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.1, 10.5, 11.2, 12.2, 22.0, 24.1, 45.5, 45.6, 53.6, 54.3, 54.4, 55.5, 128.8, 128.9, 130.0, 130.2, 130.8, 137.2 ppm. IR (KBr): ν 2966, 2917, 2876, 1020 cm^{-1}; MS (EI, *m*/*z*, rel int (%)): 244 ([M]$^+$, 4), 209 ([$C_{12}H_{17}OS$]$^+$, 5), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 19), 77 ([C_6H_5]$^+$, 5). Anal. Calcd for $C_{12}H_{17}ClOS$: C, 58.88; H, 7.00; S, 13.10. Found: C, 59.08; H, 6.72; S, 12.86.

1-(Chloromethyl)-4-[(*tert*-butylsulfinyl)methyl]benzene (1d). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6d**, and **7d** from route A to give **1d** as a white solid (15.97 g, 29%, 3.25 g, 64%): mp 101.0−103.0 °C. R_f = 0.38 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30 (s, 9H), 3.59 + 3.79 (dd, J_{AB} = 12.4 Hz, 2H), 4.56 (s, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 45.8, 52.3, 53.7, 129.0, 130.4, 132.3, 137.1 ppm. IR (KBr): ν 2962, 1384, 1037 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 244 ([M]$^+$, 5), 209 ([$C_{12}H_{17}OS$]$^+$, 27), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 34), 77 ([C_6H_5]$^+$, 11), 57 ([C_4H_9]$^+$, 80). Anal. Calcd for $C_{12}H_{17}ClOS$: C, 58.88; H, 7.00; S, 13.10. Found: C, 58.97; H, 6.85; S, 12.96.

1-(Chloromethyl)-4-[(isopentylsulfinyl)methyl]benzene (1e). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6e**, and **7e** from route A to give **1e** as a white solid (18.63 g, 32%, 3.61 g, 67%): mp 90.0−91.0 °C. R_f = 0.47 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (d, J = 6.4 Hz, 3H), 0.90 (d, J = 6.4 Hz, 3H), 1.50−1.70 (m, 1H), 1.50−1.70 (m, 2H), 2.56 (m, 2H), 3.93 + 3.94 (dd, J_{AB} = 13.2 Hz, 2H), 4.56 (s, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.0, 22.2, 27.5, 30.8, 45.6, 49.0, 57.4, 129.0, 130.1, 130.3, 137.5 ppm. IR (KBr): ν 2959, 2912, 2872, 1025 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 258 ([M]$^+$, 20), 223 ([$C_{13}H_{19}OS$]$^+$, 32), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 20), 77 ([C_6H_5]$^+$, 7). Anal. Calcd for $C_{13}H_{19}ClOS$: C, 60.33; H, 7.40;S, 12.39. Found: C, 60.65; H, 7.67; S, 12.13.

1-(Chloromethyl)-4-[(*n*-octylsulfinyl)methyl]benzene (1f). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6f**, and **7f** to give **1f** as a white solid (20.99 g, 31%, 4.25 g, 68%): mp 109.5−110.5 °C. R_f = 0.52 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.84 (t, J = 6.8 Hz, 3H), 1.23 (m, 8H), 1.36 (m, 2H), 1.70 (m, 2H), 2.53 (t, J = 7.8 Hz, 2H), 3.91 + 3.93 (dd, J_{AB} = 13.0 Hz, 2H), 4.55 (s, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 22.4, 22.5, 28.7, 28.9, 29.1, 31.6, 45.6, 51.0, 57.6, 129.1, 130.2, 130.3, 137.5 ppm. IR (KBr): ν 2959, 2918, 2847, 1024 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 300 ([M]$^+$, 5), 265 ([$C_{16}H_{25}OS$]$^+$, 82), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 45), 77 ([C_6H_5]$^+$, 5). Anal. Calcd for $C_{16}H_{25}ClOS$: C, 63.87; H, 8.37; S, 10.66. Found: C, 64.15; H, 8.69; S, 10.32.

1-(Chloromethyl)-4-[({2-[2-(2-methoxyethoxy)ethoxy]ethyl}sulfinyl)methyl]benzene (1g). This compound was synthesized according to the general procedure starting from the crude mixture of **5**, **6g**, and **7g** to give **1g** as a white solid (20.34 g, 27%, 4.50 g, 64%): mp 51.0−53.0 °C. R_f = 0.17 ($CHCl_3$/MeOH 99:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.70 (m, 1H), 2.90 (m, 1H), 3.33 (s, 3H), 3.51 (m, 2H), 3.61 (m, 2H), 3.64 (m, 4H), 3.84 + 3.92 (m, 2H), 3.98 + 4.11 (dd, J_{AB} = 12.8 Hz, 2H), 4.57 (s, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 45.5, 50.3, 57.4, 58.7, 63.0, 70.1, 70.2, 70.2, 71.6, 128.7, 130.0, 130.4, 137.2 ppm. IR (KBr): ν 2883, 1384, 1135, 1116, 1032 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 334 ([M]$^+$, 8), 299 ([$C_{15}H_{23}O_4S$]$^+$, 8), 139 ([C_8H_8Cl]$^+$, 100), 104 ([C_8H_8]$^+$, 16), 77 ([C_6H_5]$^+$, 5). Anal. Calcd for $C_{15}H_{23}ClO_4S$: C, 53.80; H, 6.92; S, 9.58. Found: C, 53.71; H, 7.05; S, 9.19.

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Supporting Information Available: Spectral characterization of sulfinyl monomers **1a**−**g** (^{1}H and ^{13}C spectra), analysis by means of ^{1}H NMR of crude reaction mixtures of routes A, B, and C using 1 equiv of *n*-octanethiol, and ^{1}H NMR spectra of **5** and **7f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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