Highly Selective Route to Unsymmetrically Substituted 1-{2-[(Butylsulfanyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy}-3,7-dimethyloctane and Isomers toward Synthesis of Conjugated Polymer OC1C10 Used in LEDs: Synthesis and Optimization

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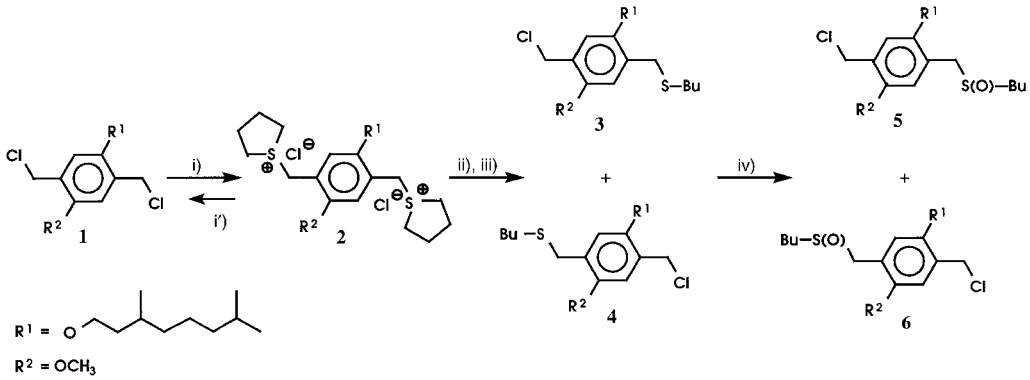
A new and convenient route to an unsymmetrically substituted sulfinyl monomer of precursor polymer toward poly[2-methyl-5-(3,7-dimethyloctyloxy)-*p*-phenylenevinylene] (OC1C10) is described. OC1C10 is a commercial polymer used as the active layer in LEDs. Therefore, the optimization of the reaction conditions of the monomer synthesis was of some importance for a possible commercialization of this new process. It was possible to increase the overall yield by a factor of 1.5, as compared to the route previously used to obtain these compounds.

1. Introduction. – The interest in light-emitting diodes (LEDs) based on thin π-conjugated polymer films as the active layer has increased since the first report by *Friend* and co-workers about poly(*p*-phenylene vinylene) (PPV) thin emission layer LEDs [1]. Organic polymer LEDs have many advantages in the manufacture of large-area visible-light-emitting displays because of the good processability, low operating voltage, fast response time, and the possibility to display the three primary colors [2]. Many conjugated polymers are insoluble in common solvents and are infusible at temperatures below the decomposition temperature of the polymer. Generally, polymeric precursors for conjugated polymers introduce solubility and processability, which is necessary for making a LED device. *Wessling* and *Zimmerman* introduced in the late 1960's a versatile precursor route in which poly(*p*-phenylene vinylene) and derivatives are obtained after thermal conversion from a polyelectrolyte precursor with good mechanical properties, high thermal stability and electrical conductivities [3]. However, *Wessling*'s method still shows some drawbacks, *e.g.*, instability of the precursor polymer and gelation. Furthermore, it is difficult to polymerize monomers with extended aromatic systems, *e.g.*, as poly(4,4′-biphenylenevinylene). Other precursor routes were developed by different groups [4]. An alternative precursor route was also developed by our group [5]. This method is particularly attractive because it avoids the use of ionic, polymeric intermediates, and a clear distinction is made between the three processing steps: formation of the active monomer, a *p*-quinodimethane system, the polymerization to the soluble precursor polymer, and the thermal conversion to conjugated polymer. To have control over the polymerization process, it is necessary to chemically differentiate in the structure of the monomer between the polarizer and the leaving group [6]. Different strategies have been developed to deal with the synthesis of this asymmetric monosubstituted monomer.

Many synthetic routes to sulfoxides are known from literature [7]. All of these approaches suffer from the use of excessive amounts of starting product, which necessitates subsequent purification by column chromatography. In this paper, a simple process for preparing such asymmetrically substituted monomers is described. We present the synthesis of 2-(chloromethyl)-5-[(butylthio)methyl]-1-[(3,7-dimethyloctyl)oxy]-4-methoxybenzene starting from 2,5-bis(chloromethyl)-1-[(3,7-dimethyloctyl)oxy]-4-methoxybenzene (BCDM; **1**) with an unexpectedly high selectivity. BCDM (**1**) is industrially applied as a monomer in dehydrohalogenation polymerizations toward the polymer abbreviated OC1C10, which is used in LEDs [8].

2. Results. – 2.1. *Asymmetric Monomer Synthesis.* 2.1.1. *Typical Procedure for the Synthesis of the Monomer Derived from BCDM*. In *Scheme 1*, the new synthetic approach is shown starting from BCDM (**1**). The first step is the synthesis of a bis(tetrahydrothiophenium) salt **2** of **1**. The salt **2** can be obtained in a yield of 70%. After the second reaction step, two different monosubstituted isomers **3** and **4** are obtained, besides unchanged BCDM (**1**) and bis(butylthio)-substituted product (not shown). The molar fraction of all these compounds in the reaction mixture were determined by ^{1}H-NMR.

Scheme 1. *Synthesis of the Isomeric Monomers* **3** *and* **4** *Derived from BCDM* (**1**)

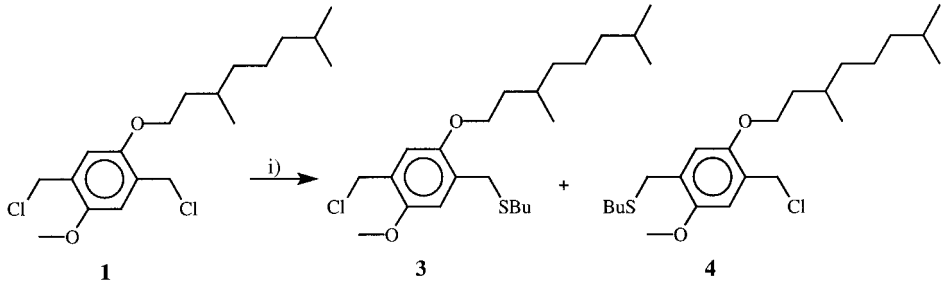


i) 4 equiv. tetrahydrothiopene (THT), MeOH, r.t., 60 H. ii) 0.98 equiv. *t*-BuONa, 1 equiv. BuSH, MeOH, r.t. iii) Octane, Δ. iv) H_2O_2, TeO_2, 1,4-dioxane, HCl (cat.), r.t., 3 h.

The key step of this method is the second step *ii*. This reaction is carried out in MeOH, which is a good solvent for the bis-sulfonium salt and the butanethiol. A high selectivity for the monosubstituted product was observed. The amount of remaining BCDM (**1**) (18%) was higher than the amount of 1,4-bis(chloromethyl)benzene (5%) in a comparable experiment for the synthesis of 4-[(butylthio)methyl]benzyl chloride, the intermediate for the unsubstituted PPV monomer [9]. Due to the electron-donating alkyloxy groups on the aromatic ring, the bis(tetrahydrothiophenium) salt **2** is less stable than the analogous bis-sulfonium derivative with $R^1 = R^2 = H$. Therefore, it is likely that the *retro*-reaction of **2** to BCDM (**1**) increases (*i'*; *Scheme 1*).

2.1.2. *Former Methods: Comparison of the Synthesis of the Intermediate Derived from BCDM* (**1**). If the reaction is performed with an equimolar amount of BCDM (**1**) (*Scheme 2*) instead of bis(tetrahydrothiophenium) derivative, the reaction mixture

Scheme 2. *Synthesis with BCDM* (**1**) *as Starting Material Used Formerly*



i) 1 equiv. BuSH, 1 equiv. *t*-BuONa, MeOH, 20°, 1 h.

consists of **1** (23%), (butylthio)methyl-chloromethyl derivatives **3** and **4** (52%), and bis[(alkylthio)methyl] derivative (25%). This product distribution is very close to the statistical distribution (25 : 50 : 25) and is similar to that found in experiments starting from the unsubstituted 1,4-bis(chloromethyl)benzene [9].

Addition of a phase-transfer catalyst increased the yield of the desired products **3** and **4**, comparable to the behavior of 1,4-bis(chloromethyl)benzene [9] (*Table 1*).

Table 1. *Product Yields* [%] *from Methods Formerly Applied to BCDM* (**1**)

Entry	Phase transfer?	Equiv. of thiol	Product yields [%]		
			1	**3** and **4** (ratio **3**/**4**)	Bis(butylthio) derivative
1	No	1.00	23	52	25
2	Yes	0.45	73	25 (41 : 59)	2
3	Yes	1.00	21	56 (43 : 57)	23

The use of excess of BCDM (**1**) as starting material decreases the amount of disubstitution, but excess **1** requires further purification by column chromatography.

2.2. *Optimum Reaction Conditions for the New Method.* BCDM (**1**) is applied industrially as a monomer. The polymers obtained serve as the active layer in LEDs [8]. With this industrial background in mind, we sought the optimal reaction conditions, including reaction time, ratio of thiol/monomer/base and reaction temperature.

2.2.1. *Reaction Time. Fig. 1* shows a graph of the change in pH as a function of time during the second step in the new process. The pH was measured in MeOH (instead of H_2O), and the reaction conditions are described in the *Exper. Part.* The pH rises sharply upon addition of the base, followed by a slower decrease, and approaches the initial value within *ca.* 40 min. This indicates a time scale of 40 min to run the reaction to completion.

2.2.2. *Ratio of Reactants (Alkanethiol/BCDM/Base). Table 2* shows the influence of different ratios of starting compounds on the product distribution with a reaction time of 40 min.

The ratio of these four compounds (**1**, **3**, **4**, and disubstituted product) can be determined by ^{1}H-NMR spectroscopy. The MeO resonance (3.84 – 3.77 ppm) of these products are sufficiently separated to allow a reliable determination of the product distribution by deconvolution of peaks as seen in *Fig. 2*. The highest yield of both

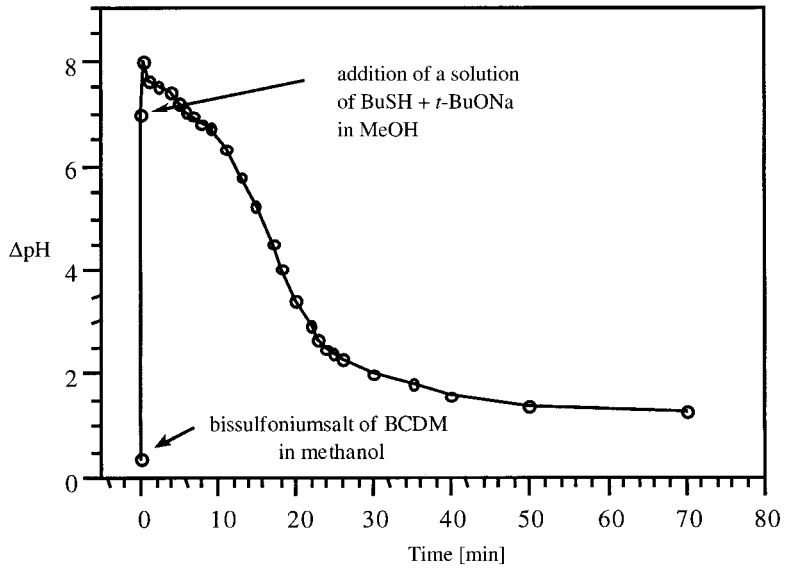


Fig. 1. *Change in pH as a function of time during the second step of the synthesis depicted in* Scheme 1

Table 2. *Effect of Ratio of Reagents on Product Distribution*

Entry	Ratio of BuSH/**1**/*t*-BuONa	Product yields [%]		
		1	**3** and **4** (ratio **3**/**4**)	Bis(butylthio) derivative
1	0.99 : 1.00 : 1.10	16	77 (49 : 51)	7
2	0.98 : 1.00 : 1.00	18	74 (50 : 50)	7
3	0.95 : 1.00 : 0.95	33	54 (49 : 51)	13

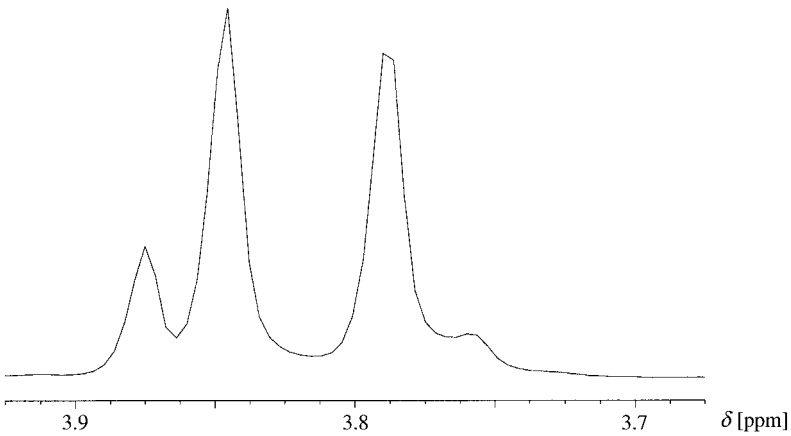


Fig. 2. *MeO Region in the* ^{1}*H-NMR spectrum analyzed during monomer synthesis*

monosubstituted isomers was obtained for BuSH/**1**/*t*-BuONa of 0.99 : 1.00 : 1.10. Under these conditions, however, a yellow color developed, presumably due to premature precursor polymer conversion caused by the excess base. This side reaction was suppressed at a ratio of 0.98 : 1.00 : 1.00, which gave a high enough selectivity (74%) for the monosubstituted thioether.

2.2.3. *Reaction Temperature. Table 3* shows the product distribution found in experiments conducted at three different tempertures at a constant ratio of bis(tetrahydrothiophenium) derivative/thiol/*t*-BuONa of 1.00 : 0.98 : 1.00. Low reaction temperatures favor monosubstitution. At the lowest temperature ($T = 0°$) 79% of monosubstituted compound and only 4% of disubstituted byproduct were found. However, the reaction carried out at room temperature still led to an acceptable yield of 74% of monosubstituted thioether.

Table 3. *Effect of Temperature on Product Distribution*

Temp. [°]	Product yields [%]		
	1	**3** and **4** (ratio **3**/**4**)	Bis(butylthio) derivative
20	18	74 (50 : 50)	7
10	19	77 (51 : 49)	4
0	17	79 (51 : 49)	4

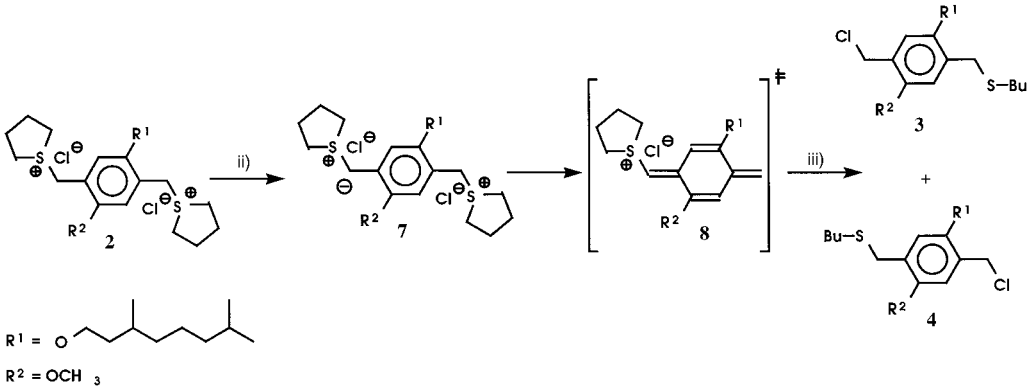
3. Discussion. – Sulfonium groups are good leaving groups. Thus, **2** can undergo a special kind of a nucleophilic substitution to predominantly yield the monosubstituted compounds **3** and **4**. As side-products, some disubstituted compound is formed, as well as some BCDM (**1**), originating either from a *retro*-reaction or from unreacted starting material. By selecting optimal reaction conditions (see above), the product distribution can be shifted in favor of the monosubstituted products **3** and **4** (74%), even if just 1 equiv. of bis-sulfonium salt of **1** is applied (see *Entry 2* in *Table 2*).

We suggest as the primary step a deprotonation of salt **2** by a thiolate anion, which is a strong enough base. The conjugated base **7** (*Scheme 3*) eliminates 1 equiv. of tetrahydrothiophene. This 1,6-elimination leads to a quinodimethane derivative, which is a notoriously reactive species and would usually polymerize immediately. Polymerization is obviously suppressed in presence of the thiol compound, which acts as an efficient trap or inhibitor[1]), leading to the monosubstituted thioether **3** and **4** with far higher yield than expected from simple statistics. Key to these findings is a balanced double function of the thiol derivative; it is a moderate base to generate smoothly with time the quinodimethane. In parallel, the thiol compound traps the quinodimethane efficiently and inhibits polymerization. The reaction sequence is completed by substitution of the remaining tetrahydrothiophenium group by a Cl^- ion, which is easily forced to full conversion by stripping off the tetrahydrothiophene by distillation.

This mechanism is in full agreement with the almost statistical product distribution found in the direct substitution of BCDM (**1**) with a thiolate, which was state-of-the-art formerly (*Entries 1* and *3* in *Table 1*). The weaker acid **1** would not be deprotonated

[1]) This resembles the S_N1cB-type substitution, where the active species is the conjugated base, as described in [10].

Scheme 3. *Proposed Mechanism of Step* ii.



ii) 0.98 equiv. *t*-BuONa, 1 equiv. BuSH, MeOH, r.t. 9iii) Octane, Δ.

under these conditions. A simple nucleophilic substitution occurs, with both reaction centers being independent and decoupled. Thus, the only way to disfavor the disubstituted product had been to use a huge excess of **1**, which, afterwards, required a tedious workup procedure including chromatographic processes.

4. Conclusion. – A new simple process for preparing asymmetrical thioether derivative of 2,5-bis(chloromethyl)-1-[(3,7-dimethyloctyl)oxy]-4-methoxybenzene (BCDM; **1**) with an unexpectedly high selectivity is reported. In comparison to the formerly applied nucleophilic substitutions, this method requires the synthesis of a bis(tetrahydrothiophenium) salt **2** of **1** as an intermediate, which then forms a quinodimethane system in presence of thiolate anion. As thiol derivatives can act as inhibitors of polymerization for quinodimethane and in parallel, as nucleophiles, these latter are trapped in a monosubstitution by the thiol derivate.

Optimal conditions lead to a reaction mixture of 18% of **1**, 74% of monosubstituted thioether, 7% of disubstituted compounds. As the fraction of side products is kept below 25% and as **1** and the disubstituted derivative do not interfere with the polymerization conditions chosen, this mixture can be used directly without any further purification in a polymerization process leading to a structurally pure, fully conjugated OC1C10 polymer with a very high yield [11]. This novel process could be used as a new tool in the synthesis of pure OC1C10 polymer in large scale as no time-consuming purification would be necessary.

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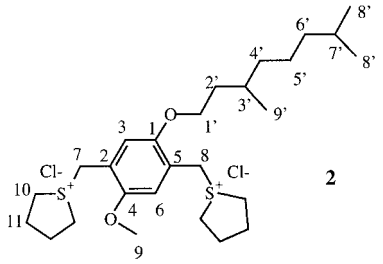
Experimental Part

General. 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 N_2. ^{1}H-NMR Spectra were obtained in a deuterated solvent ($CDCl_3$ or D_2O) at 200 or 400 MHz; chemical shifts (δ) in ppm relative to the residual non-deuterated solvent absorption (7.24 ppm for $CHCl_3$, 4.72 ppm for H_2O). The ^{13}C-NMR Spectra were recorded at 75 MHz; chemical shifts were referenced to the ^{13}C resonance of $CHCl_3$ (77.0 ppm).

H_2O Determination. A blank sample of D_2O with a known concentration of fumaronitrile as an internal reference was recorded, and the H_2O signal was integrated (*A*). A sample of product was introduced in the same tube and was recorded under the same conditions. The H_2O signal was integrated (*B*), after which subtraction of *B* from *A* gave the integration (*C*) corresponding to the amount of H_2O from the product.

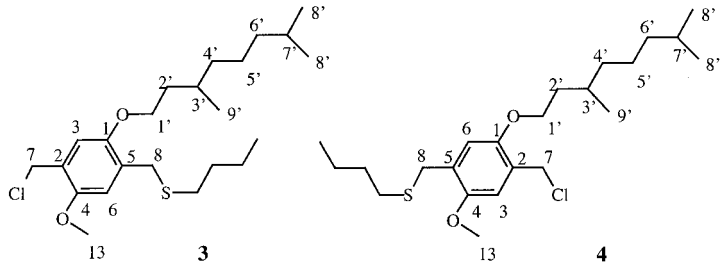
Bis(tetrahydrothiophenium) Salt **2** *of 1-[2,5-bis(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane* (BCDM; **1**). Compound **1** (10 g, 27.7 mmol) and 12.4 g of tetrahydrothiophene (141 mmol) in 20 ml of MeOH were stirred for 70 h at 30°. The excess tetrahydrothiophene was distilled off, the crude product was dissolved in a minimum amount of MeOH and precipitated in 100 ml of ice-cold acetone. The precipitate was washed with 40 ml of hexane and dried under vacuum for 4 h to give 11 g (75%) of **2**. M.p. 81–83° [11]. IR (NaCl): 3353, 3016, 2926, 2462, 1633, 1514, 1463, 1417, 1317, 1226, 920, 875, 786, 739, 699, 662. ^{1}H-NMR (D_2O, 400 MHz): 0.71–1.80 (*m*, 19 H, alkyl side chain); 2.24 (*m*, 4 SCH_2CH_2); 3.43 (*m*, 4 SCH_2); 3.82 (*s*, MeO); 4.11 (*m*, CH_2O); 4.33 (*s*, 2 $ArCH_2S$); 7.12 (*s*, 2 arom. H). ^{13}C-NMR (D_2O, 75 MHz): 19.10 (C(9′)); 22.07, 22.16 (C(8′)); 24.13 (C(5′)); 27.41 (C(7′)); 28.50, 28.55 (C(3′)); 29.06 (C(11)); 35.37 (C(2′)); 36.43 (C(4′)); 38.64 (C(6′)); 41.68 (C(7)); 43.22 (C(8)); 48.99 (C(10)); 56.37 (C(9)); 67.75 (C(1′)); 116.38, 115.55 (C(3), C(6)); 119.91, 119.86 (C(2), C(5)); 151.41, 152.03 (C(1), C(4)).



2

1-[2-[(Butylsulfanyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane (**3**) *and 1-[5-[(Butylsulfanyl)methyl]-2-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane* (**4**). A mixture of 0.1342 g (1 equiv.) of *t*-BuONa and 0.1234 g (0.98 equiv.) of BuSH in 10 ml of MeOH was stirred for 30 min at 20°. The clear soln. was added dropwise to a stirred soln. of 0.834 g of **2** in 40 ml of MeOH at 10°. After 40 min, the soln. was neutralized with 1M aq. HCl and evaporated on a rotary evaporator. The crude product was diluted with 20 ml of $CHCl_3$, and the precipitate was filtered off. The filtrate was concentrated *in vacuo*. The oil thus obtained was diluted with 20 ml of octane and concentrated to remove tetrahydrothiophene. This sequence was repeated three times to afford a mixture of **1** (18%), **3** and **4** (74%, in a 51:49 ratio), and the disubstituted product (7%) as a light yellow viscous oil (39.5 g), calculated from ^{1}H-NMR integral curve. IR (NaCl): 2954, 2927, 2869, 1507, 1465, 1409, 1212, 1036, 865, 739, 696. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.92–6.78 (br., 2 arom. H); 4.61 (*s*, CH_2Cl); 4.20–3.75 (br., CH_2O); 3.84–3.77 (4*s*, MeO, four compounds); 4.61 (*m*, $BuSCH_2$); 2.45 (*t*, CH_2S); 0.8–2.0 (br., 19 H, alkyl side chain). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.56 (C(12)); 19.55 (C(9′)); 21.91 (C(11)); 22.45, 22.55 (C(8′)); 24.53 (C(5′)); 27.81 (C(7′)); 29.64, 29.69 (C(3′), C(8)); 30.01 (C(9)); 31.39 (C(10)); 36.10, 36.17, 36.25 (C(2′)); 37.09, 37.14 (C(6′)); 41.12, 41.44 (C(7)); 55.94, 56.04 (C(13)); 67.09, 67.19 (C(1′)); 112.89, 113.12, 113.98, 114.24 (C(3), C(6)); 124.53, 124.86, 126.16, 126.58, 126.88, 128.46, 128.89 (C(2), C(5)); 150.47, 150.87 (C(1), C(4)).

Compounds **3** *and* **4** (*cf. Entry 3* in *Table 1*). A mixture of *t*-BuONa (0.86 g, 9 mmol) and BuSH (0.81 g, 9 mmol) in MeOH (20 g) was stirred for 30 min at 20°. The clear soln. was added dropwise to a stirred soln. of **1** (3.25 g, 9 mmol) in MeOH (70 g). After 1 h, the mixture was neutralized with 1M aq. HCl, diluted with $CHCl_3$ (250 ml), washed with H_2O (2 × 100 ml), dried ($MgSO_4$), and concentrated *in vacuo* to give 3.70 g of a yellow oil, which consists of a mixture of **1** (21%), **3** and **4** (56%, ratio 43:57), and disubstituted product (23%), calculated from ^{1}H-NMR integral curve. IR (NaCl): 2954, 2927, 2869, 1507, 1465, 1409, 1212, 1036, 865, 739, 696. ^{1}H-NMR

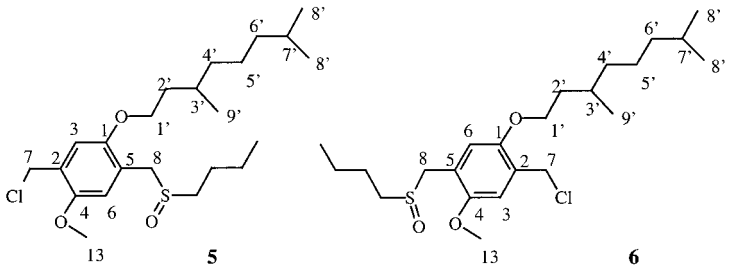


3 **4**

($CDCl_3$, 200 MHz): 6.92–6.78 (br., 2 arom. H); 4.61 (*s*, CH_2Cl); 4.20–3.75 (br., CH_2O); 3.84–3.77 (4*s*, MeO, 4 compounds); 4.61 (*m*, $BuSCH_2$); 2.45 (*t*, CH_2S); 0.8–2.0 (br., 19 H, alkyl side chain). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.56 (C(12)); 19.55 (C(9′)); 21.91 (C(11)); 22.45, 22.55 (C(8′)); 24.53 (C(5′)); 27.81 (C(7′)); 29.64, 29.69 (C(3′), C(8)); 30.01 (C(9)); 31.39 (C(10)); 36.10, 36.17, 36.25 (C(2′)); 37.09, 37.14 (C(6′)); 41.12, 41.44 (C(7)); 55.94, 56.04 (C(13)); 67.09, 67.19 (C(1′)); 112.89, 113.12, 113.98, 114.24 (C(3), C(6)); 124.53, 124.86, 126.16, 126.58, 126.88, 128.46, 128.89 (C(2), C(5)); 150.47, 150.87 (C(1), C(4)).

Compounds **3** *and* **4** (*cf. Entry 1* in *Table 1*). To a stirred mixture of **1** (36.1 g, 0.1 mol) in toluene (200 ml), NaOH (10.5 g, 0.26 mol) in H_2O, and *Aliquat 336* (0.44 g), a soln. of BuSH (4.01 g, 44.4 mmol) in toluene (50 ml) was added dropwise over a period of 24 h at r.t. The org. layer was washed with H_2O (3 × 100 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give 39.3 g of a light yellow solid, which is a mixture of **1** (23%), **3** and **4** (52%), and disubstituted product (25%), as calculated from ^{1}H-NMR integral curve. IR (NaCl): 2954, 2927, 2869, 1507, 1465, 1409, 1212, 1036, 865, 739, 696. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.92–6.78 (br., 2 arom. H); 4.61 (*s*, CH_2Cl); 4.20–3.75 (br., CH_2O); 3.84–3.77 (4*s*, MeO, 4 compounds); 4.61 (*m*, $BuSCH_2$); 2.45 (*t*, CH_2S); 0.8–2.0 (br., 19 H, alkyl side chain). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.56 (C(12)); 19.55 (C(9′)); 21.91 (C(11)); 22.45, 22.55 (C(8′)); 24.53 (C(5′)); 27.81 (C(7′)); 29.64, 29.69 (C(3′), C(8)); 30.01 (C(9)); 31.39 (C(10)); 36.10, 36.17, 36.25 (C(2′)); 37.09, 37.14 (C(6′)); 41.12, 41.44 (C(7)); 55.94, 56.04 (C(13)); 67.09, 67.19 (C(1′)); 112.89, 113.12, 113.98, 114.24 (C(3), C(6)); 124.53, 124.86, 126.16, 126.58, 126.88, 128.46, 128.89 (C(2), C(5)); 150.47, 150.87 (C(1), C(4)).

1-[2-[(Butylsulfinyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane (**5**) *and 1-[5-[(Butylsulfinyl)methyl]-2-(chloromethyl)-4-methoxyphenoxy]-3,7-dimethyloctane* (**6**). TeO_2 (0.038 g, 12 mol-%) was added to a soln. of the pale yellow oil (0.82 g), consisting of **1**, **3**, **4**, and disubstituted derivative (*Entry 3* in *Table 1*), in 40 ml of dioxane. Under vigorous stirring 0.39 g (4 mmol) of a H_2O_2 soln. (35 wt.-% soln. in H_2O) was added dropwise. The mixture was stirred vigorously at r.t. until a slight overoxidation was visible by TLC (*ca.* 3½ h). The reaction was quenched by pouring in ice-cold H_2O. The H_2O layer was extracted once with 50 ml of $CHCl_3$ and twice with 20 ml $CHCl_3$. The combined org. layers were dried ($MgSO_4$), filtered and evaporated on a rotary evaporator to give 0.6 g of product, consisting of 74% of **5** and **6**, 18% of **1**, and 7% of disubstituted product, as calculated from ^{1}H-NMR integral curve. This mixture was used without further purification in the following polymerization step [12]. Monsubstituted and disubstituted products do not polymerize under the reaction conditions as described in [11]. IR (KBr): 2960, 2930, 2868, 1506, 1462, 1409, 1221, 1037. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.90–6.80 (br., 2 arom. H); 4.61 (*s*, CH_2Cl); 4.20–3.75 (br. CH_2O); 3.84–3.77 (4*s*, MeO, 4 compounds); 4.61 (*s*, $BuS(O)CH_2$); 2.67 (*t*, $CH_2S(O)$); 0.8–2.0 (br., 19 H, alkyl side chain). ^{13}C-NMR ($CDCl_3$, 75 MHz): 13.51 (C(12)); 19.48 (C(9′)); 21.88 (C(11)); 22.39, 22.50 (C(8′)); 24.33 (C(10)); 24.47 (C(5′)); 27.75 (C(7′)); 29.57, 29.65 (C(3′)); 36.13 (C(2′)); 37.01 (C(4′)); 38.98 (C(6′)); 41.05, 41.12 (C(7)); 50.87, 50.98 (C(9));



5 **6**

52.45, 52.68 (C(8)); 55.78, 55.96 (C(13)); 66.83, 67.11 (C(1′)); 112.66–115.47 (C(3), C(6)); 119.26–119.64 (C(5)); 126.21–126.83 (C(2)); 150.40–150.97 (C(4), C(1)).

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