Polymerization Mechanism of 1-[(Butylsulfi(o)nyl)methyl]-4-(halomethyl)benzene: The Effect of Polarizer and Leaving Group

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ABSTRACT: A synthesis route to soluble high molecular weight poly(*p*-xylylene) derivatives has been investigated. This method provides a versatile route to poly(phenylenevinylene) (PPV) from a precursor polymer that is amenable to the conventional nonaqueous processing techniques. To investigate the mechanism in the solvent mixture, monomethylformamide (MMF)/CH_2Cl_2 (60/40), the influence of the leaving group and polarizer of the monomer was studied. The evaluation of the molecular weight of the polymer, the polymer yield, and the residual low molecular weight fraction indicates that only the kind of polarizer has an effect on the reaction in contrast with the leaving group, having no observable effect.

Introduction

Since the discovery of electroluminescence in poly(*p*-phenylenevinylene) (PPV), a wide range of conjugated and semiconjugated polymers have been used as the active layer in devices.[1] Light emission is thought to arise from the combination of a hole with an electron within the polymer. Unfortunately, the conjugated nature of this kind of polymer results in highly crystalline, insoluble and infusible materials, which are thereby difficult to process.

There are two important approaches to the preparation of conjugated polymers, 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. They can then be transformed to the final conjugated polymer through solid-state thermoconversion. The side chain approach involves the polymerization of a highly substituted monomer[2] to a soluble conjugated polymer that can be cast into thin films directly without any conversion. The precursor route often used is the Wessling route.[3] This method involves the heating of a high molecular weight water soluble precursor polyelectrolyte, which is the result of the treatment of α,α′-bis(tetrahydrothiophenium chloride)-*p*-xylene with sodium hydroxide. Unfortunately, this method has a number of disadvantages[4,5] inherent in this route.

The mechanism of the Wessling and analogous precursor routes to PPV derivatives has been under discussion for several years[3,6,7] but is still somewhat unclear. The monomer in this polymerization reaction is a *p*-xylylene derivative. Whether the reaction follows a radical or an anionic reaction path is still indefinite. Research on this mechanism is rather difficult because of the insolubility of the ionic precursor in common organic solvents. Another difficulty is the instability of the precursor due to the good leaving capacity of the sulfonium groups. And, last but not least, molecular weight determinations are hard to perform due to the irreversible interactions between the precursor and the packing material of the size exclusion chromatography (SEC) columns.[7]

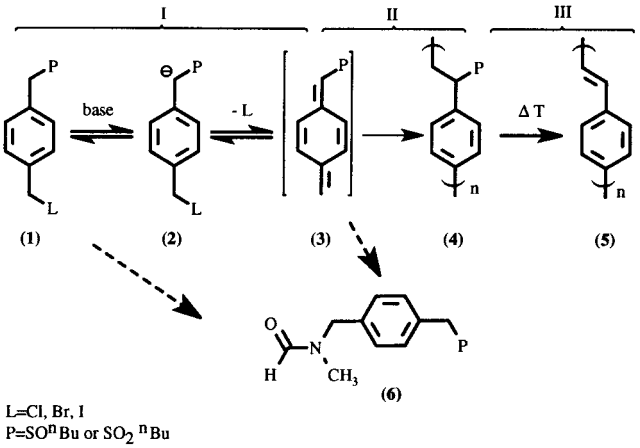

Figure 1. General scheme of the polymerization in MMF.

In our work we have tried to define the prerequisites[5] of such polymerization routes. To that end we have introduced a generalized scheme (Figure 1) in which a clear distinction is made between the three steps of the process. First, the in situ formation of the actual monomer, the *p*-quinodimethane system **(3)**. Second, the polymerization reaction that has been described in our group[8] as a self-initiating radical chain polymerization, and third, the conversion to the fully conjugated system.

In this general scheme the first step is defined as a base-induced elimination reaction of a *p*-xylene derivative, 1-[(butylsulfi(o)nyl)methyl]-4-(halomethyl)benzene **(1)** (Figure 1), which has to fulfill two requirements: (i) in the α-position of the *p*-xylene **(1)** a polarizer is necessary because the anion **(2)** formed in the acid−base equilibrium has to be stabilized, and (ii) in the α′-position of the *p*-xylene a leaving group is required to obtain the *p*-quinodimethane intermediate **(3)**. The latter is the actual monomer in the polymerization reaction. Notice that the polarizer and leaving group are not inevitably chemically identical as it is in the Wessling and other precursor routes. The mechanism for the first step depicted in Figure 1 implies an E_{1cb} mechanism for the formation of the *p*-quinodimethane system **(3)**.

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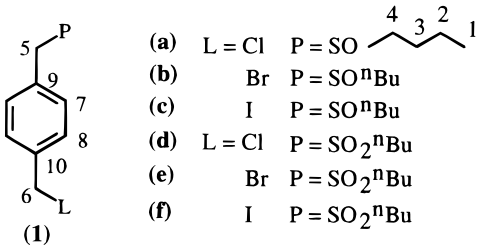


Figure 2. 1-[(butylsulfi(o)nyl)methyl]-4-(halo-methyl)benzene or α-leaving group-α′-polarizer-*p*-xylene.

In this contribution we describe the effect of leaving group and polarizer on the overall reaction by comparing molecular weights, polymer yields, and the composition of the residual fraction. In addition, the synthesis and characterization of the used *p*-xylylene derivatives **(1)** (Figure 2) with different polarizers and leaving groups will be reported.

Experimental Section

(1) Monomers. Materials. All materials used for the synthesis of α-leaving group-α′-polarizer-*p*-xylene were purchased from Acros Chimica and used as received.

Synthesis of 1-[(Butylsulfinyl)methyl]-4-(chloromethyl)benzene (1a).[5] A mixture of 99.7 g (0.5695 mol) of 1,4-bis(chloromethyl)benzene in 1000 mL of toluene, 60 g of NaOH (1.5 mol) in 1000 mL of H_2O, and 2.5 g of a phase transfer catalyst Aliquat 336 is stirred vigorously at ambient temperature. A solution of 30.5 mL of butanethiol (0.2848 mol = 0.5 equiv) in 300 mL of toluene is added drop by drop to this mixture over a period of 24 h. The organic layer is separated, washed with water, dried over magnesium sulfate, and evaporated on a rotary evaporator to give white-yellow crystals. The mixture of 1,4-bis(chloromethyl)benzene and 1-[(butylthio)methyl]-4-(chloromethyl)benzene is further dried as much as possible under vacuum. Via a recrystallization in 500 mL of hexane, most of the 1,4-bis(chloromethyl)benzene can be removed by filtration. The resulting hexane solution is evaporated under reduced pressure and dried under vacuum.

A catalyst TeO_2 (4.614 g, 2.891×10^{-2} mol), is added to a solution of these crystals in 1200 mL of MeOH. Under nitrogen protection and vigorously stirring, 64.66 mL (0.5702 mol) of a hydrogen peroxide solution (35 wt % solution in water) is added slowly. The reaction is stirred vigorously at room temperature until a slight overoxidation is visible on TLC. The reaction is quenched by adding 800 mL of a saturated NaCl solution. The water layer is once extracted with 600 mL of $CHCl_3$ and twice with 400 mL of $CHCl_3$. The combined $CHCl_3$ layers are dried over magnesium sulfate and evaporated on a rotary evaporator to give white crystals (a mixture of 1,4-bis(chloromethyl)benzene [A] and **1a**). These two products are separated by column filtration ($R_{f[A]} = 0.67$, $R_{f[\mathbf{1a}]} = 0.17$ on silica) in $CHCl_3$. 1,4-Bis(chloromethyl)benzene can be reused after recrystallization from toluene. 1-[(Butylsulfinyl)methyl]-4-(chloromethyl)benzene is recrystallized from a mixture of hexane/CH_2Cl_2, washed with ice cold diethyl ether, and dried under vacuum, giving a yield of 77%: mp 111−112 °C; IR (KBr, cm^{-1}) 3060 (ν_{C-H} arom), 2970−2870 (ν_{C-H} aliph), 1450−1410 (ν_{C-H} CH_3, CH_2, Cl−C−H), 1010 (ν_{S-O}), 850 (1,4-subst arom), 660 (ν_{C-S}), 520−730 (ν_{C-Cl}); MS (EI, *m*/*e*) 244 (M^+), 209 ($M^+ - Cl$), 139 ($M^+ - SO^nBu$), 104 ($M^+ - Cl - SO^nBu$); ^1H NMR δ 0.90 (t), 1.41 (m), 1.70 (m), 2.56 (t), 3.93 (dd), 4.55 (s), 7.27 (d), 7.38 (d); ^{13}C NMR δ 13.1 (C_1), 21.3 (C_2), 23.8 (C_3), 45.1 (C_6), 50.2 (C_4), 56.9 (C_5), 129.9 (C_9), 129.8 (C_7), 128.4 (C_8), 136.8 (C_{10}).

Synthesis of 1-[(Butylsulfonyl)methyl]-4-(chloromethyl)benzene (1d).[5] A mixture of 42 g of 3-chloroperoxybenzoic acid (0.1339 mol; 50−60%, stabilized with 3-chlorobenzoic acid and water) in 500 mL of CH_2Cl_2 and 50.25 g of $NaHCO_3$ (0.5982 mol) in 300 mL of H_2O is stirred vigorously and cooled to 0 °C. A solution of 25 g of 1-[(butylsulfinyl)methyl]-4-(chloromethyl)benzene **(1a)** is added dropwize. The mixture is allowed to warm to room temperature and to react for another 3 h. The organic layer is separated, washed with 1250 mL of 5% $NaHCO_3$ (aq), treated with 1250 mL of 5% Na_2CO_3 (aq), and washed again with 1250 mL of 5% Na_2CO_3 (aq). The organic layer is dried over magnesium sulfate and evaporated on a rotary evaporator to give white-yellow crystals. The crystals are recrystallized from a mixture of hexane/CH_2Cl_2, washed with ice cold diethyl ether, and dried under vacuum, giving a yield of 88%: mp 121−122 °C; IR (KBr, cm^{-1}) 2940, 2910, 2850 (ν_{C-H}), 1450−1410 (ν_{C-H} CH_3, CH_2, Cl−C−H), 1300−1160 (ν_{SO_2}), 840 (1,4-subst arom); MS (EI, *m*/*e*) 260 (M^+), 225 ($M^+ - Cl$), 139 ($M^+ - SO_2{}^nBu$), 104 ($M^+ - Cl - SO_2{}^nBu$); ^1H NMR δ 0.91 (t), 1.40 (m), 1.78 (m), 2.81 (t), 4.19 (s), 4.57 (s), 7.38 (d), 7.42 (d); ^{13}C NMR δ 13.4 (C_1), 21.5 (C_2), 23.6 (C_3), 45.4 (C_6), 50.9 (C_4), 58.8 (C_5), 128.1 (C_9), 130.8 (C_7), 129.1 (C_8), 138.3 (C_{10}).

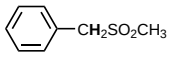
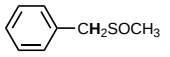
Synthesis of 1-[(Butylsulfinyl)methyl]-4-(bromomethyl)benzene (1b).[9] A mixture containing 0.974 g of 1-[(butylsulfinyl)methyl]-4-(chloromethyl)benzene **(1a)** and 3.48 g (10 equiv) of lithium bromide in 170 mL of 3-pentanone was heated at 120 °C for 2 h. The reaction mixture was then cooled to room temperature, and the solvent was removed by a flash-rotary evaporator under water aspiration at 50 °C. The residue in ethyl acetate (200 mL) was washed with 200 mL of water. The organic phase was then evaporated to give a mixture of RCH_2Br and RCH_2Cl, which was once more treated with lithium bromide (10 equiv) in 100 mL of 3-pentanone. The mixture was subsequently refluxed for 3 h at 120 °C, after which the aqueous workup described above, drying ($MgSO_4$), removal of the solvent, and recrystallization in *n*-hexane afforded the 1-[(butylsulfinyl)methyl]-4-(bromomethyl)benzene **(1b)** with high chemical purity, giving a yield of 75%: mp 120 °C; IR (KBr, cm^{-1}) 3040 (ν_{C-H} arom), 2930−2840 (ν_{C-H} aliph), 1460−1420 (ν_{C-H} CH_3, CH_2), 1020 (ν_{S-O}), 840 (1,4-subst arom), 660 (ν_{C-S}); MS (EI, *m*/*e*) 288 (M^+), 209 ($M^+ - Br$), 184 ($M^+ - SO^nBu$), 104 ($M^+ - Br - SO^nBu$); ^1H NMR δ 0.90 (t), 1.41 (m), 1.70 (m), 2.56 (t), 3.92 (dd), 4.46 (s), 7.25 (d), 7.38 (d); ^{13}C NMR δ 13.5 (C_1), 21.9 (C_2), 24.3 (C_3), 32.7 (C_6), 50.8 (C_4), 57.7 (C_5), 129.7 (C_8), 130.3 (C_9), 130.5 (C_7), 138.0 (C_{10}).

Synthesis of 1-[(Butylsulfonyl)methyl]-4-(bromomethyl)benzene (1e).[9] The synthesis of this *p*-xylene derivative is completely analogous to the synthesis described above, using 1-[(butylsulfonyl)methyl]-4-(chloromethyl)benzene **(1d)** as starting product. Recrystallization in a toluene/hexane mixture afforded the 1-[(butylsulfonyl)methyl]-4-(bromomethyl)benzene with high chemical purity giving a yield of 70%: mp 141−142 °C; IR (KBr, cm^{-1}) 2940, 2910, 2850 (ν_{C-H}), 1450−1410 (ν_{C-H} CH_3, CH_2, Br−C−H), 1300−1100 (ν_{SO_2}), 840 (1,4-subst arom); MS (EI, *m*/*e*) 304 (M^+), 225 ($M^+ - Br$), 184 ($M^+ - SO_2{}^nBu$), 104 ($M^+ - Br - SO_2{}^nBu$); ^1H NMR δ 0.89 (t), 1.39 (m), 1.76 (m), 2.81 (t), 4.18 (s), 4.46 (s), 7.36 (d), 7.42 (d); ^{13}C NMR δ 13.4 (C_1), 21.6 (C_2), 23.6 (C_3), 32.4 (C_6), 51.0 (C_4), 58.9 (C_5), 128.3 (C_9), 129.8 (C_8), 131.0 (C_7), 138.8 (C_{10}).

Synthesis of 1-[(Butylsulfinyl)methyl]-4-(iodomethyl)-benzene (1c).[5] A mixture of 1.85 g of 1-[(butylsulfinyl)-methyl]-4-(chloromethyl)benzene **(1a)** and 12.25 g of sodium iodide in 150 mL of acetone was refluxed for 24 h. The reaction mixture was then cooled to room temperature and put in the freezer for 3 h. The precipitated sodium chloride was filtered out and washed with diethyl ether. The filtrate was slightly evaporated at 60 °C and again put in the freezer for 3 h. After filtration and washing of the salt formed, the reaction mixture was evaporated under reduced pressure and the resulting crystals were recrystallized in a mixture of ethyl acetate/hexane giving a yield of 70%: mp 133.5 °C; IR (KBr, cm^{-1}) 3050 (ν_{C-H} arom), 2960−2860 (ν_{C-H} aliph), 1400−1500 (ν_{C-H} CH_3, CH_2), 1010 (ν_{S-O}), 850 (1,4-subst arom), 500 (ν_{C-I}); MS (EI, *m*/*e*) 336 (M^+), 209 ($M^+ - I$), 231 ($M^+ - SO^nBu$), 104 ($M^+ - I - SO^nBu$); ^1H NMR δ 0.90 (t), 1.42 (m), 1.70 (m), 2.55 (t), 3.90 (dd), 4.42 (s), 7.20 (d), 7.36 (d); ^{13}C NMR δ 4.7 (C_6), 13.6 (C_1), 22.0 (C_2), 24.4 (C_3), 50.8 (C_4), 57.7 (C_5), 129.3 (C_8), 129.6 (C_9), 130.4 (C_7), 139.5 (C_{10}).

Synthesis of 1-[(Butylsulfonyl)methyl]-4-(iodomethyl)-benzene (1f)[5]. The preparation of this monomer is analogous

Table 1. pK_a of Hydrogen Next to Sulfoxide and Sulfone

structure	pK_a (Solvent)[15]
	25.4 (DMSO)
	29.0 (DMSO)

to the latter synthesis using 1-[(butylsulfonyl)methyl]-4-(chloromethyl)benzene **(1d)** as starting material. The resulting crystals are recrystallized in a mixture of chloroform/hexane giving a yield of 70%: mp 142−145 °C; IR (KBr, cm^{-1}) 3050 (ν_{C-H} arom), 2960−2860 (ν_{C-H} aliph), 1400−1500 (ν_{C-H} CH_3, CH_2), 1300−1100 (ν_{SO_2}), 850 (1,4-subst arom), 500 (ν_{C-I}); MS (EI, *m/e*) (M^+) not detected, 225 ($M^+ - I$), 231 ($M^+ - SO_2{}^nBu$), 104 ($M^+ - I - SO_2{}^nBu$); ^1H NMR δ 0.90 (t), 1.40 (m), 1.77 (m), 2.81 (t), 4.16 (s), 4.43 (s), 7.31 (d), 7.39 (d); ^{13}C NMR δ 4.3 (C_6), 13.5 (C_1), 21.7 (C_2), 23.7 (C_3), 51.0 (C_4), 58.9 (C_5), 127.6 (C_9), 129.4 (C_8), 131.0 (C_7), 140.3 (C_{10}).

(2) Polymerization. Materials. To ensure a reproducible polymerization, all solutions are freshly made and nitrogen flushed for 1 h while the reaction system was thermostatically controlled (30 °C). Monomethylformamide (MMF) p.a. was dried over 4 Å molecular sieves for 2 days followed by a distillation at reduced pressure. Sodium *tert*-butoxide was purchased from Acros Chimica and used as received. A 40/60 CH_2Cl_2/MMF mixture was used as the polymerization medium, as the solubility of the six monomers had to be assured. MMF-*d* was prepared from MMF treated with D_2O and KOtBu several times, while a mixture of D_2O/H_2O is removed by distillation.

Standard Polymerization of 1-[(Butylsulfi(o)nyl)-methyl]-4-(halomethyl)benzene (1). A solution of 1.3 mmol of sodium *tert*-butoxide in 6 mL of a 40/60 CH_2Cl_2/MMF mixture was added all at one time to 1 mmol of monomer **1a**−**f** in 14 mL of a 40/60 CH_2Cl_2/MMF mixture. After 1 h the reaction mixture was poured into 200 mL of ice water and neutralized with a 0.1 N HCl solution. The organic part (polymer and a low molecular weight part) was extracted with 150 mL of CH_2Cl_2 and washed with water. The CH_2Cl_2 layer was partly (15−20 mL) evaporated on a rotary evaporator and precipitated in cold diethyl ether. The latter was decanted after a while, and the resulting white, precursor polymer **(4)** poly[(butylsulfi(o)nyl)ethylene-1,4-phenylene] was dried under vacuum.

Molecular weights were determined with gel permeation chromatography (see Table 2). Every polymerization was performed twice to ensure reproducibility. The corresponding data are in paretheses in Table 2. The low molecular weight fraction soluble in diethyl ether was characterized with ^1H NMR. In all cases two products were found−unreacted monomer **(1)** and a side product **(6)** (Figure 1)−with their yields depicted in Table 2.

For **(6)** P═SO^nBu: mp 68−69 °C; IR (KBr, cm^{-1}) 3020−3010 (ν_{C-H} arom), 2915−2900 (ν_{C-H} aliph), 2840 (ν_{C-H} N−CH_3), 2735 (ν_{C-H} CHO), 1640 ($\nu_{C=O}$), 1470−1430 (ν_{C-H} CH_3, CH_2), 1010 (ν_{S-O}), 815 (1,4-subst arom); MS (EI, *m/e*) 268 (M^+), 209 ($M^+ - HCONCH_3$), 162 ($M^+ - SO^nBu$), 105 ($M^+ - HCONCH_3 - SO^nBu$); ^1H NMR δ 0.90 (t), 1.42 (m), 1.66 (m), 2.56 (t), 2.79 (d), 3.90 (dd), 4.43 (d), 7.20 (d), 7.28 (d), 8.20 (d). For **(6)** P═SO_2: mp 82.7−82.9 °C; IR (KBr, cm^{-1}) 2960 (ν_{C-H}), 2874 (ν_{C-H} N−CH_3), 1660 ($\nu_{C=O}$), 1453−1422 (ν_{C-H} CH_3, CH_2), 1280−1129 (ν_{SO_2}); MS (EI, *m/e*) 284 (M^+), 225 ($M^+ - HCONCH_3$), 162 ($M^+ - SO_2{}^nBu$), 105 ($M^+ - HCONCH_3 - SO_2{}^nBu$); ^1H NMR δ 0.82 (t, d), 1.33 (m), 1.70 (m), 2.76 (t), 2.73 (d), 4.13 (d), 4.38 (d), 7.17 (q), 7.3 (q), 8.18 (d).

$^1H-^2H$ Exchange Experiment. Monomer **1a** was treated as in the standard polymerization with the following adaptions: (1) reaction temperature of −45, −40, and −35 °C, (2) a 40/60 mixture of CH_2Cl_2/MMF-*d* as medium, (3) neutralization with a D_2O/DCl mixture.

(3) Characterization. SEC analyses of polymers were performed at 70 °C with flow rates of 1.0 mL min^{-1} in 1-methyl-2-pyrrolidinone (NMP) using a differential refractometer (RI) detector (Shodex) and MIXED-B (10μ, 2 × 30 cm) columns (Polymer Laboratories) after calibration with polystyrene standards (Polymer Laboratories). Since polysulfoxides and polysulfones have a different hydrodynamic volumes, the relative molecular weights, determined by SEC, cannot be compared. To circumvent this difficulty, the polysulfoxides were fully oxidized into polysulfones before analysis using a procedure developed in our group.[10]

There is a second difficulty concerning SEC analyses of these polymers. Such polymers have a certain irreversible interaction with the column material, resulting in a silting up of the columns. Therefore every series of SEC measurements has to be done at one time using a reference sample of polymer **4a** to allow any comparison.

IR spectra were recorded on a Philips Pye Unicam SP-300, and mass spectra, on a Finigan 1020 or a TSQ70. Both ^1H NMR and ^{13}C NMR spectra (Varian Unity 400) of the monomers were measured in $CDCl_3$ at 20 °C. To obtain an unambiguous assignment, we made use of APT (attached proton test) and 2D heteronuclear correlation techniques (direct $^1H-^{13}C$ heteronuclear correlations and long range $^1H-^{13}C$ heteronuclear correlations) as described in detail elsewhere.[11]

Elemental Analysis in Table 3. The elemental analysis for the polysulfoxides and the polysulfones should be corrigated for the water bond on the polymer. The removal of water needs a temperature of 80 °C, which results in the elimination of the precursor polymer. The amount of water present in the sample is determined with ^1H NMR and used to corrigate the elemental analysis.

Results and Discussion

Using the same functional groups as polarizer as well as leaving group like in Wessling and other precursor routes leads to disadvantages that are intrinsic to such routes. The chemistry desired for either polarizer or leaving group will also apply to leaving group or polarizer, respectively. Due to this, an unstable precursor polymer is inevitably obtained when good leaving group properties are desired. Moreover, introducing a functional group, as in the Wessling route, with good leaving group properties, lowering the pK_a of the benzylic hydrogens, will lead to the loss of control (regioregularity) on the polymerization reaction in the case of monomers that are asymmetrically substituted.

Taking this in consideration, it became obvious to us that when stable precursors and an enforced control on the polymerization process are desired, a chemical differentiation on the stage of polarizer and leaving group is essential. As a consequence, halogens were chosen as the leaving group because of their good leaving group properties and also because they do not really lower the pK_a of the nearby benzylic protons. As polarizer, sulfoxide and sulfone functional groups were chosen, as they have no leaving group properties in nucleophilic substitution reactions. The sulfoxide group is a good precursor for a double bond via a thermal elimination reaction.[12]

Furthermore, the alkyl (aryl) group on the sulfur functional group in the *p*-xylene derivative gives us control on the solubility characteristics of the precursor polymer. This nonionic polarizer is responsible for the solubility of monomer and precursor polymer in common organic solvents. Because of the latter, characterization of the polymer and the determination of molecular weight and molecular weight distribution can be performed in a straightforward way. This opens new perspectives to the study of the mechanism of the polymerization reaction of this type of *p*-xylene derivatives.

Table 2. Polymer Characteristics and Composition of the Residual Fraction Converted to the 100% sulfone derivative

	polymer **(4)** characteristics			residual fraction	
monomer **1**	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	yield (%)	yield (**6**) (%)	yield (**1**) (%)
a[a]	0.23 (0.17)	2.74 (2.47)	24 (24)	20 (13)	46 (55)
b[a]	0.08 (0.13)	2.42 (2.16)	27 (33)	20 (25)	30 (26)
c[a]	0.14 (0.20)	2.24 (2.27)	26 (34)	19 (20)	55 (45)
d	6.33 (5.68)	1.70 (1.83)	13 (22)	45 (48)	10 (8)
e	5.86 (5.86)	3.17 (2.51)	11 (16)	35 (37)	17 (17)
f	6.76 (5.43)	2.28 (2.19)	27 (27)	45 (45)	28 (20)

[a] Converted to the 100% sulphone derivative.

Table 3. Elemental Analysis of the Precursor Polymers

		calcd values	corrigated values	exptl values
polysulfoxide	% C	69.19	66.76	66.86
	% H	7.74	7.86	7.57
	% S	15.39	14.85	14.33
polysulfone	% C	64.25	63.40	61.00
	% H	7.19	7.24	7.06
	% S	14.29	14.11	13.05

Monomer Synthesis. The synthesis of 1-[(butylsulfinyl)methyl]-4-(chloromethyl)benzene (**1a**) is performed in two steps (Figure 3): the preparation of the sulfide and next the oxidation to the sulfoxide.

The synthesis of the asymmetric substituted sulfide is possible via a nucleophilic substitution of the butanethiol anion at 1,4-bis(chloromethyl)benzene. In 1975[13] Herriot et al. described a method to prepare sulfides without using Na or NaH in dry conditions and which shortens the reaction time and results in better yields. This synthesis is based on the use of a phase transfer catalyst like methyltrioctylammonium chloride (Aliquat 336). The most important difficulty is to prevent disubstitution of the dichloro derivative resulting in the disulfide. We can avoid[5] this by adding a dilute thiol solution dropwise over a period of 24 h to a solution of a 2− to 3-fold excess of 1,4-bis(chloromethyl)benzene in toluene and sodium hydroxide in water. A first purification is made by a recrystallization in *n*-hexane after which the 1,4-bis(chloromethyl)benzene can be partially removed by filtration.

A multitude of oxidizing reagents are available for the oxidation of a sulfide to a sulfoxide. Nevertheless, only a few of these guarantee a selective oxidation of the sulfide to the sulfoxide like sodium periodate,[5] dichloroiodobenzene, and *tert*-butyl hypochlorite. To prevent overoxidation, these reagents should be used in equivalent amounts. In our hands[5] it was found that the best procedure consisted of using $H_2O_2-TeO_2$ in methanol. Adding tellurium oxide in catalytic amounts to the sulfide solution while hydrogen peroxide is added dropwize almost excludes overoxidation. After oxidation, the sulfoxide **1a** can be isolated by liquid chromatography in chloroform and recrystallized in a mixture of CH_2Cl_2/hexane.

For the oxidation of the sulfoxide **1a** to the sulfone[5] **1d** we used *m*-chloroperbenzoic acid in CH_2Cl_2.

The preparation of both 1-[(butylsulfinyl)methyl]-4-(bromomethyl)benzene **(1b)** and 1-[(butylsulfonyl)-methyl]-4-(bromomethyl)benzene **(1e)** was based on a convenient and practical method for the conversion of a primary alkyl chloride to highly pure bromides using LiBr in 3-pentanone as the reagent.[9]

The synthesis of sulfoxide **1c** and sulfone **1f** was established[5] by the Finkelstein reaction. The corresponding chlorides were dissolved in acetone and a 15% sodium iodide solution was added. After a short time sodium chloride precipitated and was filtered from the solution. **1c** and **1f** were recrystallized from acetone.

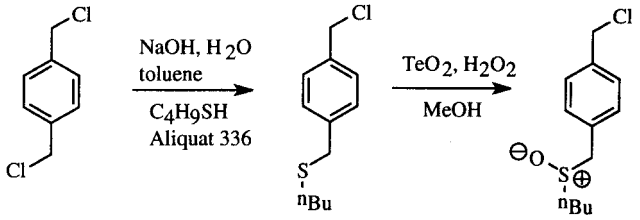


Figure 3. The synthesis of 1-[(butylsulfinyl)methyl]-4-(chloromethyl)benzene.

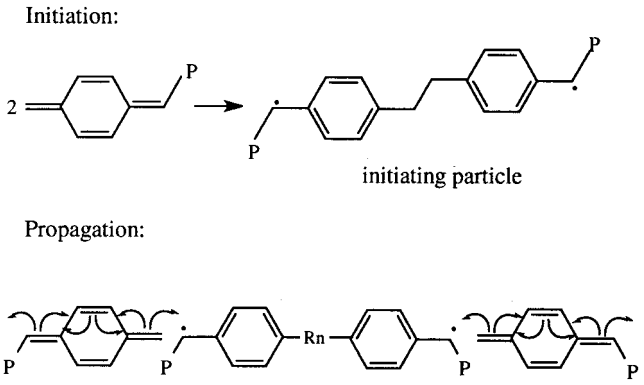


Figure 4. A self-initiating radical chain polymerization.

Polymerization. As stated before, the *p*-xylene derivative **1** needs a polarizer at the α-position and a leaving group at the α′-position. Then the quinoid structure **3** is formed, which will polymerize into the precursor polymer via a self-initiating radical pathway[8] (Figure 4). The polymerization of **1** is possible in polar protic solvents such as *N*-methylformamide (MMF).[8] This solvent allows us to avoid the formation of a bimodal molecular weight distribution, as found typically in aprotic solvents such as DMF.[8] As a result of the low pK_s of MMF (autoprotolyse constant $K_s = 10^{-10.5}$),[14] the used base (sodium *tert*-butoxide) will dissociate and form *tert*-butyl alcohol and the MMF-anion. The latter will act as the actual base finally resulting in the quinoid-structure **(3)** (Figure 1).

One should make a clear distinction between the two first parts in the process (Figure 1: I, II): first, the formation of the *p*-quinodimethane system **3** and then the polymerization itself. But in practice it is difficult to investigate these two steps separately because the *p*-quinodimethane system **3** is not stable and thus cannot be isolated. So, the information available for discussion and interpretation is the polymer yield, the molecular weight of the polymer, and the composition of the low molecular weight fraction.

When the benzylic hydrogen next to the polarizer is captured by a base, the quinoid structure **3** is formed immediately. There seems to be no anionic intermedi-

ate. This is indicated by a $^1H-^2H$-exchange experiment. Earlier it was found that the polymerization reaction starts to takes place at temperatures higher than −40 °C. Since we wondered if the formation of quinoid structure **3** from monomer **1** happened via anion **2**, monomer **1** was treated with sodium *tert*-butoxide for 1 h in deuterated *N*-methylformamide (MMF-*d*) at −45, −40, and −35 °C. The presence of an anion in a deuterated solvent should result in exchange of ^1H into ^2H at the acidic benzylic position. But in this case no exchange was noticed with ^2H NMR, even at −35 °C, where the polymerization already started. This indicates that proton abstraction is a much slower process than the elimination of the leaving group.

To learn something about the effect of the leaving group and polarizer on the overall reaction, both functional groups were varied. Monomers with Cl, Br, or I as leaving group are used because of their different leaving group properties, which improves going from chloride to iodide. The polarizers used were *n*-butyl sulfoxide and *n*-butylsulfone.

The acidity of the benzylic proton abstracted in the first step (Figure 1) is dependent on the acceptor properties of the polarizer (Table 1). In literature it is known[15] that an anion next to a sulfone group is thermodynamically more stabilized than an anion next to a sulfoxide group. In other words, the hydrogen next to the sulfone has the greatest acidity.

As stated before, the low molecular weight fraction soluble in diethyl ether was characterized with ^1H NMR. Each time two products were found, unreacted monomer **1** and a side product **6** (Figure 1). Compound **6** is the result of a reaction with the solvent (MMF) and is called from now on the "solvent-substituted product".

An overview of the experimental results is shown in Table 2.

Without making any assumptions, we observe that the yield of the precursor polymer is in each case approximately the same. The small variations can be attributed to the experimental error. There is no observable relationship between the leaving group and the yield or molecular weight of the precursor polymer **4**. There is a very strong increase of $\bar{M}_w$ (>10 times) for the polysulfones **(d, e, f)**, while the polymer yield stays the same. Looking at the ratios of **1** and **6** in the residual fraction, it is clear that for the sulfones **1d−f** the low molecular weight fraction consists mainly of solvent-substituted product **6** and less of monomer **1**. In front of that, for the reaction of the sulfoxides **1a−c** in MMF, the residual fraction consists mainly of monomer **1** and less of solvent-substituted product **6**. No significant tendency is found toward the leaving group.

Because solvent substitution seems on one hand independent of the leaving properties of the halogen and on the other hand strongly dependent on the kind of polarizer, compound **6** appears to be mainly the product of addition of MMF to the quinoid structure **3**, though partial nucleophilic substitution of the halogen by the solvent anion is not excluded. But the latter seems not to occur to the extent that the effect of the leaving group can be observed.

Then solvent substitution can be considered as a competitive reaction of the polymerization. The quinoid structure **3** will either polymerize or react with the solvent anion. Once compound **6** is formed, no 1,6-elimination to form **3** seems to take place under these circumstances, so it is not able to participate in the polymerization reaction.

Assuming solvent substitution takes place at the stage of the QM **3**, then the sum of the polymer yield and the amount of **6** is a measure of the amount of quinoid structure **3**. This means that under the same conditions sulfones would form more **3** compared to the sulfoxides. The difference between sulfoxides and sulfones is the acidity of the benzylic proton (Table 1). Thus the pK_a of the benzylic proton next to the polarizer seems to determine the ease of quinoid formation.

As stated in an earlier paper,[8] the polymerization starts with the head-to-head dimerization of two quinoid structures, leading to a diradical (Figure 4). The propagation step is a diradical growth of a polymer chain.

The molecular weight of the polysulfones is substantially larger than the polysulfoxides, but their yield is not different. This means that, in the case of sulfone quinoids, fewer polymer chains grow during the polymerization or, in other words, there is less initiation. There are several possible explanations for this phenomenon. Since the initiation has to be slower, once the diradical is formed the chain will grow with the same rate as for sulfoxides. Or the propagation rate is much faster for sulfone quinoids. Different rates of chain transfer might also account for (part of) the difference, although the polymerization reactions of quinodimethane systems are quite insensible toward chain transfer reagens.[8]

In preliminary UV−vis measurements in the solvent system MMF/CH_2Cl_2, the formation and diminishing of the quinoid structure **3** is observed at room temperature. One can see a very fast increase and subsequently a decrease of **3** at 316 nm. Within 1 or 2 min the majority of **3** has disappeared. Further research should be done to investigate the kinetic aspects of the studied reaction sequence.

Note: The above argumentions are all based on the statement that the solvent-substituted product does not participate in the polymerization reaction. The amide functional group is a bad leaving group, so quinoid formation is not probable. But as this statement is quite important for the interpretation of the data, it was checked experimentally. Therefore product **6** was treated like monomer **1**, as described in the standard polymerization procedure, but no polymer could be detected.

Conclusion

Although it is difficult to investigate this polymerization reaction as a consequence of the in situ formation of the actual monomer, we made a first attempt to learn something about the reaction mechanism in the polar protic solvent system MMF/CH_2Cl_2. It seems that the pK_a of the benzylic proton next to the polarizer determines the ease of quinoid formation. An important side reaction of the polymerization in MMF is investigated, namely the solvent substitution. The results can be interpreted in terms of a side reaction happening mainly after the formation of quinoid structure, resulting in a decrease of the polymer yield. In future work, the study of the mechanism will be continued in other solvents (polar aprotic and apolar protic) while these results will be further elaborated.

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