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# Synthesis of polymers bearing sulfoxide groups by oxidation of monothio-orthoesters and their rearrangement into carboxylic ester-containing monomers and polymers

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**Abstract**—Reaction of monomers, polymers and copolymers containing monothio-orthoester groups with *meta*-chloroperoxybenzoic acid in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  affords the corresponding *S*-oxides. The chemoselective conversion of alkythio group into a sulfoxide moiety was achieved with monomers, polymers and copolymers bearing monothio-orthoester functionality to yield the first examples of sulfoxide monothio-orthoesters. These compounds are rather unstable and undergo a novel rearrangement to carboxylic esters and (co)polyesters at room temperature. The process is proposed as a convenient synthetic route for preparing (co)polymers bearing carboxylic ester functions in the side-chains. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Sulfur plays a major role in heteroatom chemistry.<sup>1</sup> The oxidation of sulfur groups has been studied successfully by Zwanenburg et al.,<sup>2–4</sup> Bonini–Mazzanti,<sup>5–9</sup> Block<sup>10</sup> and Metzner et al.<sup>11–15</sup> Madesclaire<sup>16</sup> has shown that the oxidation of thioether **A** ( $\text{R}^1\text{SR}^2$ ) can yield either the corresponding sulfoxide **B** ( $\text{R}^1\text{SOR}^2$ ) or the corresponding sulfone **C** ( $\text{R}^1\text{SO}_2\text{R}^2$ ) or both, depending on the method used. A gentle oxidation to the sulfoxide alone requires highly selective methods that cannot usually be applied generally, whereas complete oxidation to the sulfone is much easier to achieve.

The oxidation of thioether **A** to sulfoxides **B** by using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) either alone or associated with various solvents or catalysts is the most widely used oxidizing agent for oxidizing organic sulfides.<sup>16</sup> However, oxidation can proceed further to give the corresponding sulfone **C** as was reported previously<sup>16</sup> for thioethers **A**. Moreover Lewin<sup>17–20</sup> and Madesclaire<sup>16</sup> have described that *meta*-chloroperoxybenzoic acid (*m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>3</sub>H) is one of the best selective oxidizing agents for transformation of sulfide **A** to sulfoxide **B**. In a few cases, the Meisenheimer rearrangement of a sulfoxide to sulfenate has been reported.<sup>21</sup>

Our aim was the formation of new polymer and copolymer surfactants by chemical modification of the pendent monothio-orthoester group and if possible the evaluation of their stabilities and wetting properties.

Recently we reported a very convenient method for the preparation, in good yield, of monothio-orthoesters<sup>22</sup> including monomers and (co)polymers starting from aromatic dithioester monomers and (co)polymers. This process was realized by reaction of excess sodium alkoxides with aromatic (non-enethiolizable) dithioesters followed by in situ alkylation of the resulting monothiolate-orthoester sodium salts (Scheme 1). An association of these methods<sup>17–22</sup> that use the *meta*-chloroperoxybenzoic acid (*m*-CPBA) seemed an interesting way for the one-pot oxidation of a variety of monothio-orthoesters **1** to attempt the preparation of their sulfoxides **2** (Scheme 1).

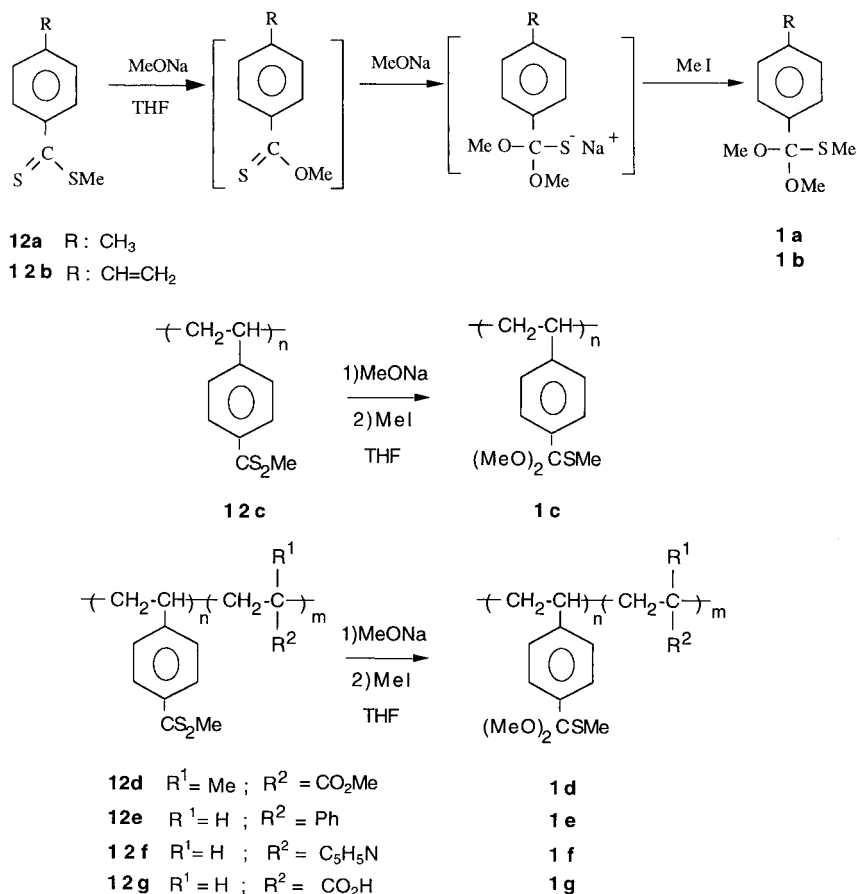
However, the stabilities of the obtained monothio-orthoesters sulfoxides **2** have not been studied yet. Here we demonstrate that they rapidly rearrange into carboxylic esters **9**.

## 2. Results and discussion

Monothio-orthoesters including monomers and (co)polymers used for the oxidation were prepared from aromatic dithioester monomers and (co)polymers.<sup>22</sup> This process was performed by reaction of excess sodium alkoxides with aromatic (non-enethiolizable) dithioesters followed by in situ alkylation of the resulting monothiolate-orthoester

**Keywords:** monothio-orthoesters containing monomers and polymers; oxidation; sulfoxides; carboxylic esters; (co)polyesters; free radical polymerization and copolymerization.

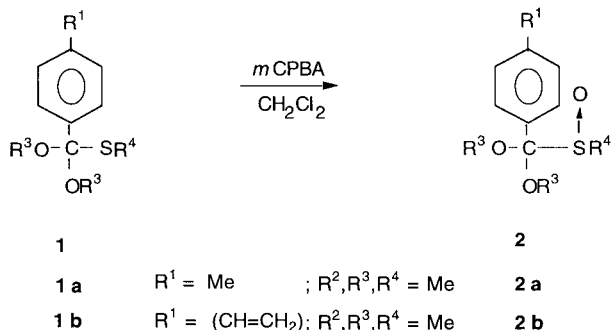
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**Scheme 1.** Synthesis of monothio-orthoester monomers and (co)polymers **1a–g**.

sodium salts, according to the synthetic route reported previously<sup>22</sup> (Scheme 1).

A preliminary investigation was carried out with 4-methyl-1-(dimethoxy methylthio methyl) benzene **1a** as a model compound. The oxidation reaction of monothio-orthoesters **1a** was performed at first with a slight excess of *m*-CPBA in dichloromethane at 20°C during 1 h. After work-up and base elimination of excess *m*-CPBA and *meta*-chlorobenzoic acid, purification was avoided with immediate NMR analysis of the crude material. To our surprise, the products exhibit NMR signals that are characteristic of a mixture of the sulfoxide **2a** (5%) (Scheme 2), the carboxylic ester **9a** (88%) (Table 1, Scheme 3), and some eventually remaining



**Scheme 2.** Preparation of sulfoxides **2** by oxidation of monothio-orthoesters **1**.

monothio-orthoester **1a** (7%) [<sup>1</sup>H NMR: 1.60 ppm (SCH<sub>3</sub>) and <sup>13</sup>C NMR: 7.00 ppm (SCH<sub>3</sub>)]. The <sup>1</sup>H NMR signal for the methoxy group of carboxylic ester **9a** is observed at 3.91 ppm and a minor signal at 2.90 and 2.60 ppm can be assigned to the methoxy and methyl sulfoxide group of the sulfoxide **2a**.

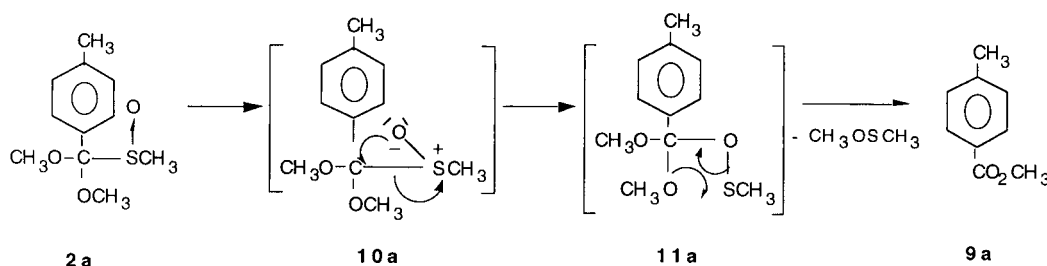
The structure of sulfoxide **2a** is confirmed by <sup>13</sup>C NMR shifts at 47.00 and 44.00 ppm related, respectively, to the methoxy and methylsulfoxide groups. <sup>13</sup>C NMR signal for the carbonyl group C=O of carboxylic ester **9a** is observed at 167.30 ppm.

The thermal stability of the sulfoxide **2a** was examined at various conditions. A set of experiments was performed. The reaction was followed easily by monitoring IR and NMR spectra. The results are listed in Table 1. From these data, the following observations can be drawn.

Although a low percentage of sulfoxide was observed always (even at –78°C), the ratio of sulfoxide **2a** and monothio-orthoester remaining **1a** decreased with increasing temperatures while the proportion of carboxylic ester **9a** increased. The major product was always the carboxylic ester **9a**, together with some sulfoxide **2a** and unreacted monothio-orthoester **1a** (at lower temperatures). At 20°C, after 3 h of reaction the conversion was complete; in the crude reaction mixture carboxylic ester **9a** was always the major product.

**Table 1.** Oxidation of monothio-orthoester **1a**

Temperatures (°C)	Time (h)	Ester <b>9a</b> (%)	Monothio-orthoester <b>1a</b> (%)	Sulfoxide <b>2a</b> (%)
-78	1	49	42	9
-78	3	60	32	8
-30	1	70	25	5
-30	3	82	11	7
-15	1	90	7	3
+20	1	88	7	5
+20	3	95	0	5

**Scheme 3.** Rearrangement of sulfoxide **2a** into carboxylic ester **9a**.

Sulfoxide **2a** is unstable, the formation of carboxylic ester **9a** can be explained by the Meisenheimer rearrangement<sup>21</sup> and Metzner et al.<sup>12,23,24</sup> We suggested that ester **9a** formation can be interpreted through the following intramolecular rearrangement: electrocyclization to an intermediate **10a** with migration of the ‘alkylthio group’ to afford **11a** and the latter compound decomposing according to Scheme 3 to furnish carboxylic ester **9a** and 2-oxa-3-thiabutane.

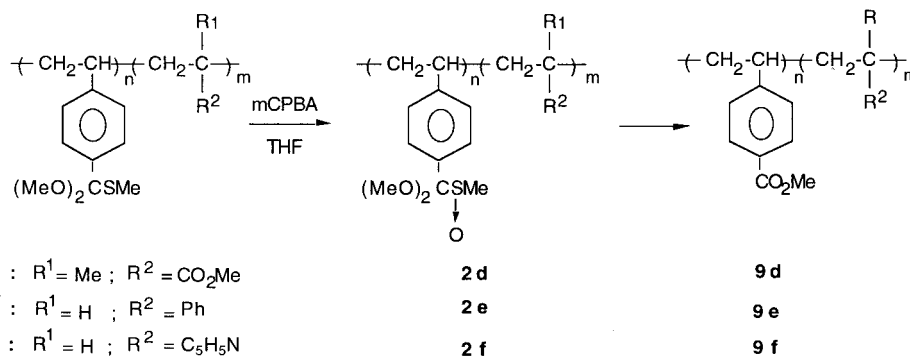
Similar rearrangements were observed from oxidation of monomer **1b**, homopolymer **1c** and (co)polymers **1d–f** (Table 2) containing monothio-orthoesters. Each sulfoxide **2b–f** was converted into corresponding carboxylic ester **9b–f** (Schemes 1 and 4). They were characterized by their

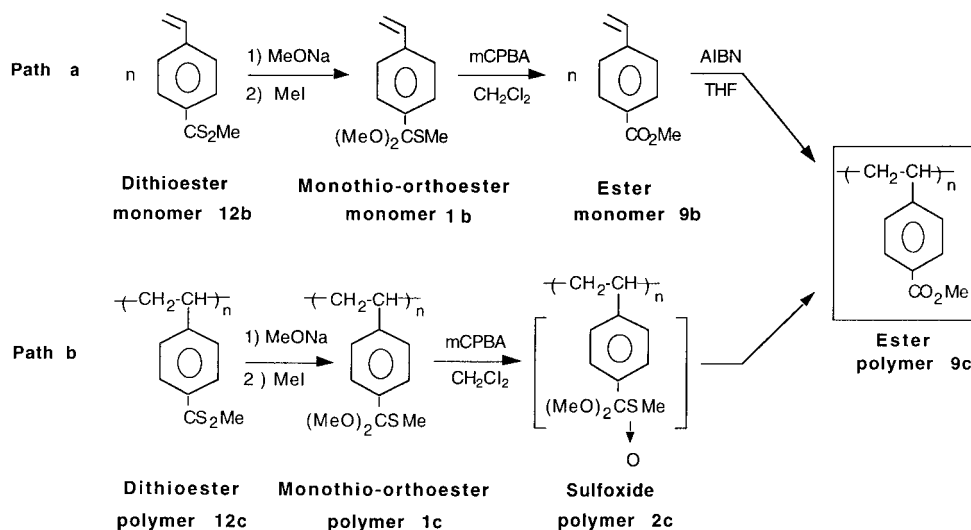
IR data [ $\nu_{\text{C=O}}$  (KBr pellets) at 1610–1770  $\text{cm}^{-1}$ ] and NMR spectra ( $\text{CDCl}_3$ ) [ $^{13}\text{C}(\text{C=O})$  at 165.00–173.00 ppm and proton signal for  $\text{OCH}_3$  at 3.93–4.02 ppm].

To our knowledge, the oxidation of monothio-orthoesters into sulfoxides and their rearrangement into carboxylic ester are still unknown. A number of (co)polymers containing carboxylic ester groups in the side chains could be isolated in good yields (Table 2) and characterized. Although there exist numerous methods for the preparation of water-soluble polyesters, they are almost exclusively limited to condensation of different dicarboxylic acids or anhydrides and polyoxyethylene<sup>35</sup> or esterification of polyoxyethyleneglycol with carboxylic acids.<sup>36</sup> This method, even though longer than the classical methods, offers a

**Table 2.** Synthesis of sulfoxides **2a–f** and carboxylic esters **9a–f** from monothio-orthoesters **1a–f**

Used dithioesters <b>12</b>	R <sup>1</sup>	R <sup>2</sup> R <sup>3</sup> R <sup>4</sup>	Monothio-orthoesters <b>1</b>	Sulfoxides <b>2</b>	Carboxylic ester <b>9</b>	Yield (%)
<b>12a</b>	$\text{CH}_3$	$\text{CH}_3$	<b>1a</b>	<b>2a</b>	<b>9a</b>	88
<b>12b</b>	$\text{CH}=\text{CH}_2$	$\text{CH}_3$	<b>1b</b>	<b>2b</b>	<b>9b</b>	78
<b>12c</b>	$(\text{CHCH}_2)_n$	$\text{CH}_3$	<b>1c</b>	<b>2c</b>	<b>9c</b>	75
<b>12d</b>	$(\text{CHCH}_2)_m[\text{CH}(\text{Me})(\text{CO}_2\text{Me})]_m$	$\text{CH}_3$	<b>1d</b>	<b>2d</b>	<b>9d</b>	70
<b>12e</b>	$(\text{CHCH}_2)_n(\text{CH}_2\text{CHPh})_m$	$\text{CH}_3$	<b>1e</b>	<b>2e</b>	<b>9e</b>	78
<b>12f</b>	$(\text{CHCH}_2)_m[\text{CH}_2-\text{CH}(\text{C}_5\text{H}_5\text{N})]_m$	$\text{CH}_3$	<b>1f</b>	<b>2f</b>	<b>9f</b>	80

**Scheme 4.** Oxidation of (co)polymers **1d–f** containing monothio-orthoesters into corresponding carboxylic esters **9d–f**.



Scheme 5. Independent synthesis of homopolymer carboxylic ester **9c**.

more efficient synthetic route to amorphous (co)polymers bearing long-chain carboxylic ester groups.<sup>37</sup>

The structure of **9c** obtained from path **a** (Scheme 5) was confirmed by independent synthesis of homopolymer carboxylic ester **9c** through path **b**, at first reaction of monomer dithioester **12b** with excess sodium methoxide and methyl iodide followed by in situ oxidation of **1b**, then free radical polymerization or (co)polymerization using AIBN, of the resulting mixture sulfoxide **2b**–carboxylic ester **9b**, according to our previously described method<sup>22</sup> (Scheme 5).

### 3. Conclusions

We have described for the first time the oxidation of polymers bearing monothio-orthoester groups. Reaction of model, monomer and (co)polymer containing monothio-orthoester groups with the standard oxidizing agent *m*-CPBA provides the corresponding sulfoxides. However, their stabilities are very moderate. These compounds undergo a novel rearrangement into carboxylic esters and (co)polyesters. So, the synthesis of a variety of amorphous (co)polymers containing carboxylic ester groups in the side chains have been carried out in a good yield by this way. Such a chemical modification of a reactive functional group opens a new way for chemically grafting the polyoxyethylene glycol onto the side chain of polymers containing esters. This preliminary work has stimulated us to carry out further studies on polyester and poly(monothio-orthoester) surfactants.<sup>37</sup>

## 4. Experimental

### 4.1. General

All reactions were run under a positive nitrogen pressure. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. Monomers and model compound were purified by flash chromatographies (silica gel or alumina).

Eluent is cyclohexane or cyclohexane–ethyl acetate or cyclohexane–dichloromethane mixture in the ratio indicated below.

<sup>1</sup>H NMR 60 and 250 MHz spectra were run on Varian EM 360 and Bruker AC 25 spectrometers with TMS as an internal reference. The products were dissolved in the mentioned solvent. Data are given in the following order: chemical shift in ppm, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; hept, heptuplet; m, multiplet), coupling constant in hertz, assignment. <sup>13</sup>C NMR spectra were determined at 20.15 MHz with a Bruker WP 80 spectrometer operating with broad band <sup>1</sup>H decoupling. The solvent used is indicated below.

*IR absorption spectra* were recorded as liquid thin films between NaCl plates or as solids in KBr pellets, or dissolved in CDCl<sub>3</sub> on a Perkin–Elmer 257 IR spectrophotometer and a Pye–Unicam SP3 100 or a Perkin–Elmer 16 PC Fourier transform spectrometer. The mentioned IR-absorptions were observed as strong bands in cm<sup>-1</sup>.

*UV–Vis spectra* were executed on a Perkin–Elmer λ 15 or Beckman DU-7. The products were dissolved in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> or THF.

*Elemental analyses* were performed by ‘Service Central d’Analyse’ of CNRS at Vernaison. The results are described in percentages.

*Molecular weights* were determined by Gel Permeation Chromatography (GPC) on Styragel columns calibrated with standard polystyrene samples using THF at 30°C as the mobile phase at a flow rate of 1.0 ml min<sup>-1</sup>.

*Intrinsic viscosity* measurements were carried out by using an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 15 cm. The flow times were measured by using viscotimer Schott Gerate AVS 400. As the flow times were relatively long (*t*<sub>0</sub> > 100 s), the correction for kinetic energy could be ignored. The samples were dissolved by adding fresh solvent and the solutions

were then introduced into the viscosimeter reservoir at 30°C.

*Thermal properties* of the (co)polymonothio-orthoesters and (co)polyesters were studied by differential scanning calorimetry (DSC) on a Perkin–Elmer DSC-7 calibrated with an indium standard. The values of glass transition temperatures ( $T_g$ ) are obtained from the second heating run, at 10°C min<sup>-1</sup> under a nitrogen atmosphere, and at least 10 mg of the sample used for DSC measurement.

## 4.2. Aromatic dithioesters

Aromatic dithioesters **12a,b** were synthesized by reaction of carbon disulfide with a Grignard solution, prepared under nitrogen from magnesium and alkyl halides, followed by alkylation with methyl iodide, according to the procedures described earlier.<sup>22,25–30</sup>

## 4.3. Preparation of homopolymers **12c**, **1c** and copolymers **12d–f**, **1d–f**

All polymerizations were performed in THF with *N,N'*-azobisisobutyronitrile (AIBN) as an initiator under nitrogen atmosphere. The radical polymerization of dithioester monomers was conducted at 66°C under conditions described previously (according to Refs. 22, 31–34). The polymers were isolated by precipitation in cyclohexane and fully characterized by spectroscopy, GPC and DCS analysis.

**4.3.1. Synthesis of poly[methyl (4-vinylbenzene) dithiocarboxylate-(co)-2-vinylpyridine] **12f**.** Methyl (4-vinylbenzene) dithiocarboxylate **12b** (1 g, 5 mmol), 2-vinylpyridine (2.6 g, 25 mmol) and AIBN (0.17 g, 1 mmol) in 50 ml of anhydrous freshly distilled THF were placed in a septum-sealed, 100 ml round-bottomed, three-necked flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer. The flask was then immersed in an oil bath at 70°C and the polymerization allowed to proceed during 28 h before cooling. The red mixture was concentrated, then diluted with chloroform and precipitated from solution by dropwise addition to petroleum ether. The red powder was filtered, washed repeatedly with diethylether and dried. The recovery procedure was repeated twice before the polymer was dried under vacuum to furnish 0.9 g of red powder. Yield=25%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.1–2.6 (6H, m, CH–CH<sub>2</sub>), 2.8 (3H, s, SCH<sub>3</sub>), 6.0–8.7 (8H, 2 m, 2 systems H<sub>arom</sub>); GPC:  $M_n$ =5173;  $M_w$ =6472,  $T_g$ =106°C.

## 4.4. Preparation of monothio-orthoesters **1a–f**

The starting monothio-orthoesters **1a–f** including monomers and (co)polymers were synthesized by reaction of excess sodium alkoxides with aromatic (non-enethiolizable) dithioesters followed by in situ alkylation of the resulting monothiolate, according to the methods described previously.<sup>22</sup>

**4.4.1. General methods.** A mixture of sodium hydride, 3 equiv. (60%, 0.12 g, 5 mmol), in dry freshly distilled THF was placed in a septum-sealed, 100 ml round-bottomed, three-necked flask equipped with a condenser, a

nitrogen inlet and a magnetic stirrer; methanol (3 equiv., 0.16 g, 5 mmol) was added over a period of 1 h 30 min at room temperature. A solution of dithioesters monomer or (co)polymer (1 equiv.) diluted in THF (20 ml) was added into the mixture of sodium methylate. After 2 h stirring at room temperature, methyl iodide (3 equiv., 0.7 g, 5 mmol) diluted in THF (20 ml) was added (the pink color disappears). The mixture was stirred at room temperature overnight, and NaI was eliminated by filtration of the orange- or beige-colored solution.

For monomers **1a,b**, the work-up involved addition of a cyclohexane/water solution (2×50 ml), extraction of the aqueous phase with cyclohexane (2×30 ml), drying over MgSO<sub>4</sub>, filtration and then concentration under vacuum. The monothio-orthoesters were isolated and purified by flash chromatography on alumina with cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (**1a**: 99/1; **1b**: 95/5) as eluent.

For (co)polymers **12d–f**, after evaporation of THF, the residue was dissolved in dichloromethane and precipitated from the solution by dropwise addition to cyclohexane. The (co)polymers were filtered and dried in vacuo.

**4.4.2. Poly[(dimethoxymethylmethylthio)-4-vinylbenzene]-(co)-2-vinylpyridine **1f**.** Yield=55%, beige color powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.1–2.5 (6H, m, CH–CH<sub>2</sub>), 3.2 (6H, s, OCH<sub>3</sub>), 6.1–8.6 (8H, 2m, 2 systems, H<sub>arom</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 10.0, 14.0, 18.0 (SCH<sub>3</sub>), 25.0, 30.0 (CH, CH<sub>2</sub>), 42.0, 44.0, 50.0 (OCH<sub>3</sub>), 122.0–137.0 (C<sub>arom</sub>); IR (KBr pellets): (C–O); GPC:  $M_n$ =4764;  $M_w$ =6593.  $T_g$ =167°C.

## 4.5. Oxidation of monothio-orthoesters **1a–f**

**4.5.1. Model and monomer. General procedure.** In a round-bottomed, three-necked flask equipped with a nitrogen inlet and a magnetic stirrer were placed monothio-orthoester (1 equiv.) in 25 ml of dry dichloromethane. A solution of dry *m*-CPBA (70%; 1.2 equiv.) diluted in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was added dropwise to the stirred monothio-orthoester solution previously cooled to 0°C (–15, –30, –78°C or at room temperature). The stirred mixture was allowed to react during about 3 h at room temperature and the dichloromethane solution was washed successively with saturated aqueous NaHCO<sub>3</sub> (3×20 ml) and saturated brine (30 ml). The organic layer was dried with MgSO<sub>4</sub>, filtered and then concentrated under reduced pressure without heating to leave the sulfoxide **2**. NMR analysis was carried out right away, i.e. approximately one hour after the oxidation step. No dithioester signal, or some eventually remaining dithioester, could be observed.

**4.5.2. Oxidation of monothio-orthoester **1a**. Synthesis of methyl (4-methylbenzoate) **9a**.** **9a** was obtained by reaction of monothio-orthoester **1a** (0.5 g, 2.5 mmol) with *m*-CPBA (70%, 0.75 g, 3 mmol) in dichloromethane. The purification by flash chromatography in aluminum oxide and cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (98/2) furnishes the pure ester **9a**. Yield=88%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.44 (3H, s, CH<sub>3</sub>–Ph), 3.91 (3H, s, CH<sub>3</sub>), 7.18–7.82 (4H, 2d, AB system,  $J_{AB}$ =6 Hz, H<sub>arom</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 20.0, 21.6 (CH<sub>3</sub>–Ph), 49.9, 51.0,

52.0 (OCH<sub>3</sub>), 127.3, 127.9, 128.7, 133.5, 138.2, 143.7 (C<sub>arom</sub>), 167.3 (C=O); IR (KBr pellets): 1145 (C–O), 1600 (C=C<sub>arom</sub>), 1723 (C=O).

**4.5.3. Oxidation of monothio-orthoester 1b. Synthesis of methyl (4-vinylbenzoate) 9b.** Reaction was carried out on monothio-orthoester **1b** (0.25 g, 1.1 mmol) and *m*-CPBA (0.32 g, 1.3 mmol). Ester **9b** was purified by flash chromatography in aluminum oxide and cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> mixture (95/5). Yield=78%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.93 (3H, s, OCH<sub>3</sub>), 5.46–5.96–6.81 (3H, m, ABX system, J<sub>AB</sub>=1.2 Hz, J<sub>BX</sub>=9.8 Hz, J<sub>AX</sub>=17 Hz, CH=CH<sub>2</sub>), 7.42–8.05 (4H, 2d, AB system, J<sub>AB</sub>=8.4 Hz, H<sub>arom</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 25.3, 42.6 (OCH<sub>3</sub>), 118.4 (=CH<sub>2</sub>), 132.8, 135.9, 136.0 (HC=), 125.9–143.2 (C<sub>arom</sub>), 169.2 (C=O); IR (KBr pellets): 1098, 1260 (C–O), 1400, 1610 (C=C), 1720 (C=O), 1818 (vinyl).

**4.5.4. (Co)polymers. General procedure.** To a stirred solution of monothio-orthoester (co)polymers (1 equiv.) in anhydrous freshly distilled THF (25 ml), under an inert atmosphere of nitrogen, a solution of dry *m*-CPBA (70%; 1.2 equiv.) diluted in CH<sub>2</sub>Cl<sub>2</sub> (25 ml) was added dropwise, and the mixture was stirred at room temperature for 10 h. After evaporation of THF under reduced pressure, the residue was dissolved in chloroform. The work-up involved washing the organic layer with saturated aqueous NaHCO<sub>3</sub>, then saturated brine (30 ml), drying of the organic phase over MgSO<sub>4</sub>, filtration and concentration under vacuum. The product was diluted with chloroform and precipitated by adding slowly to 100 ml of petroleum ether. The purified polymer was then dried in vacuo for 3 h to furnish carboxylic esters (co)polymers **9**.

**4.5.5. Oxidation of poly[(dimethoxymethylthio) methyl-4-vinylbenzene] 1c. Synthesis of poly [methyl (4-vinylbenzoate)] 9c.** Reaction of homopolymer **1c** (0.1 g, 0.4 mmol) with *m*-CPBA (70%, 0.2 g, 1.2 mmol) diluted in THF (50 ml) affords **9c**. Yield=75%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.77–2.32 (3H, m, CH–CH<sub>2</sub>); 3.95 (3H, s, OCH<sub>3</sub>), 6.52–7.78 (4H, AB system, 2m, H<sub>arom</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 25.6, 29.5, 34.7 (CH–CH<sub>2</sub>), 52.3 (OCH<sub>3</sub>), 127.2, 128.0, 129.9, 130.4, 134.0, 134.6, 135.3 (C<sub>arom</sub>), 161.9, 163.0, 163.6, 165.4 (C=O); IR (KBr pellets): 1049–1203 (C–O), 1418–1610 (Ph), 1710 (C=O); GPC: M<sub>n</sub>=2881, M<sub>w</sub>=5200, T<sub>g</sub>=105°C.

**4.5.6. Oxidation of (co)poly[methylmethacrylate-(dimethoxymethylthio) methyl-4-vinyl benzene] 1d. Synthesis of (co)polymethylmethacrylate [methyl (4-vinylbenzoate)] 9d.** The reaction was performed with monothio-orthoester copolymer **1d** ((0.11 g, 0.3 mmol) and *m*-CPBA (70%, 0.15 g, 0.9 mmol) diluted in THF. Purification of the resulting (co)polyester **9d** was accomplished by re-precipitation from chloroform using petroleum ether as the non-solvent. Yield=70%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.54–2.24 (5H, m, CH–CH<sub>2</sub>), 3.63 (3H, s, OCH<sub>3</sub> non-arom), 4.02 (3H, s, OCH<sub>3</sub> arom), 6.66–8.26 (4H, AB system, 2m, H<sub>arom</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 19.4, 21.4, 25.9, 28.6, 29.4 (CH, CH<sub>2</sub>), 44.7, 50.3, 51.2, 53.9, 55.1 [MeC(COOMe)], 125.7, 126.8, 127.6, 129.1, 138.2 (C<sub>arom</sub>), 173.2 (C=O); IR (KBr pellets): 1090, 1150 (C–O), 1315, 1592 (C=C<sub>arom</sub>), 1710, 1729 (C=O); GPC: M<sub>n</sub>=2003, M<sub>w</sub>=3174, T<sub>g</sub>=122°C.

**4.5.7. Oxidation of poly[(dimethoxymethylthio) methyl-4-vinylbenzene-(co)-styrene] 1e. Synthesis of poly[methyl (4-vinylbenzoate)-(co)-styrene] 9e.** Reaction of monothio-orthoester copolymer **1e** (50 mg, 0.1 mmol) with *m*-CPBA (70%, 0.05 g, 0.3 mmol) diluted in dry dichloromethane affords (co)polyester **9e**. Yield=78%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.74, 2.57 (6H, m, CH–CH<sub>2</sub>), 3.92 (3H, s, OCH<sub>3</sub>), 6.26–8.18 (9H, m, 2 arom. systems); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 22.5, 22.9, 23.4, 25.0, 25.9, 32.4 (CH, CH<sub>2</sub>), 127.0, 127.8, 128.0, 128.4, 130.4, 132.4, 133.9, 134.6 (C<sub>arom</sub>), 170.5 (C=O); IR (KBr pellets): 1086, 1195 (C–O), 1418, 1602 (Ph), 1698, 1772 (C=O); GPC: M<sub>n</sub>=1996, M<sub>w</sub>=3858, T<sub>g</sub>=68°C.

**4.5.8. Oxidation of poly[(dimethoxymethylthio) methyl-4-vinylbenzene-(co)-2-vinylpyridine] 1f. Synthesis of poly[methyl (4-vinylbenzoate)-(co)-styrene] 9f.** Reaction was carried out on monothio-orthoester copolymer **1f** (0.20 g, 0.6 mmol) and *m*-CPBA (70%, 0.2 g, 1.3 mmol) diluted in dry dichloromethane. Purification of the resulting (co)polyester **9f** was accomplished by re-precipitation from dichloromethane using petroleum ether as the non-solvent. Yield=80%, white powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.70–2.70 (6H, m, CH–CH<sub>2</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 6.10–7.90 (8H, m, 2 arom. systems); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 12.0, 15.0, 23.0 (CH, CH<sub>2</sub>), 115.0, 120.0, 128.0, 133.0, 138.0 (C<sub>arom</sub>), 167.0, 175.0 (C=O); IR (KBr pellets): 1086, 1195 (C–O), 1418, 1602 (Ph), 1698, 1772 (C=O); T<sub>g</sub>=121°C.

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### References

- Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Academic: London, 1994.
- Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1.
- Zwanenburg, B. *Phosphorus Sulfur Silicon Relat. Elem.* **1989**, *43*, 1.
- Zwanenburg, B.; Lenz, B. G. *Houben-Weyl Methoden der Organischen Chemie*; Academic, 1985 (Band E 11, Teil 1; 911 pp).
- Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Rosini, G.; Foresti, E. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2322.
- Barbaro, G.; Battaglia, A.; Giorgianni, P.; Bonini, B. F.; Maccagnani, G.; Zani, P. *J. Org. Chem.* **1990**, *55*, 3744.
- Mazzanti, G.; Ruinaard, R.; Van Vliet, L. A.; Zani, P.; Bonini, B. F.; Zwanenburg, B. *Tetrahedron Lett.* **1992**, *23*, 6383.
- Bonini, B. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *74*, 31.
- Bonini, B. F.; Busi, F.; de Laet, R. C.; Mazzanti, C.; Thuring, J. W. J. F.; Zani, P.; Zwanenburg, B. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1011.
- Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135.
- Metzner, P.; Pham, T.-N. *J. Chem. Soc., Chem. Commun.* **1988**, 390.
- Cerreta, F.; Le Nocher, A.-M.; Leriverend, C.; Metzner, P.; Pham, T.-N. *Bull. Soc. Chim. Fr.* **1995**, *132*, 67.

13. Le Nocher, A.-M.; Metzner, P. *Tetrahedron Lett.* **1991**, 32, 747.
14. Lemarié, M.; Metzner, P.; Pham, T.-N. *Tetrahedron Lett.* **1991**, 32, 7411.
15. Chevrier, D.; Metzner, P. *Tetrahedron Lett.* **1998**, 39, 8983.
16. Madesclair, M. *Tetrahedron* **1986**, 42 (20), 5459.
17. Lewin, L.-N. *J. Prakt. Chem.* **1928**, 118, 282.
18. Lewin, L.-N. *J. Prakt. Chem.* **1928**, 119, 211.
19. Lewin, L.-N. *J. Prakt. Chem.* **1930**, 127, 77.
20. Lewin, L.-N.; Tschulkoff, J. *J. Prakt. Chem.* **1930**, 128, 171.
21. Maricich, T.-J.; Harrington, C. K. *J. Am. Chem. Soc.* **1972**, 94, 5115.
22. Hadjout, S.; Levesque, G.; Pham, T.-N.; Tran, H.-N. *Polymer* **1997**, 38 (14), 3691.
23. Leriverend, C.; Metzner, P. *Tetrahedron Lett.* **1994**, 35 (29), 5229.
24. Leriverend, C.; Metzner, P.; Capperucci, A.; Degl'Innocenti, A. *Tetrahedron Lett.* **1997**, 53 (4), 1323.
25. Meijer, J.; Vermeer, P.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1973**, 92, 601.
26. Westmijze, H.; Klein, H.; Meijer, J.; Vermeer, P. *Synthesis* **1979**, 432.
27. Beiner, J. M.; Thuillier, A. *C. R. Acad. Sci., Ser. C.* **1972**, 274, 642.
28. Ramadas, S. R.; Srinivasan, P. S.; Ramachandran, J.; Sastry, V. V. V. K. *Synthesis* **1983**, 605.
29. Cazes, B.; Julia, S. *Tetrahedron Lett.* **1978**, 4065.
30. Kjaer, A. *Acta Chem. Scand.* **1952**, 6, 327.
31. Haraoubia, R.; Bonnans-Plaisance, C.; Levesque, G. *Makromol. Chem.* **1981**, 182, 2409.
32. Haraoubia, R.; Gressier, J. C.; Levesque, G. *Makromol. Chem.* **1982**, 183, 2367.
33. Haraoubia, R.; Levesque, G.; Bonnans-Plaisance, C.; Gressier, J. C. *Makromol. Chem.* **1981**, 183, 2383.
34. Bonnans-Plaisance, C.; Levesque, G. *Makromol. Chem., Rapid Commun.* **1985**, 6, 145.
35. Piirma, I. *Polymeric Surfactants*; Marcel Dekker: New York, 1992 (p 87).
36. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1989 (p. 25).
37. Lê, N. U. P.; Hadjout, S.; Pham, T.-N.; Madec, P.-J.; Levesque, G. In preparation.