Polymer Vol. 38 No. 14, pp. 3691–3696, 1997

0032-3861/97/\$17.00 + 0.00

PII: S0032-3861(96)00933-0

Synthesis of polymers bearing monothio-orthoester groups using a direct route from dithioester-containing monomers and polymers

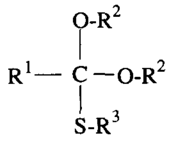
Slimane Hadjout, Guy Levesque, Thi-Nhàn Pham* and Huu-Nhân Trân
Laboratoire de Chimie Moléculaire et Thio-organique, groupe Polymères et Interfaces (URA CNRS 480), Université de Caen – Institut des Sciences de la Matière et du Rayonnement (ISMRA), 6 Boulevard du Maréchal Juin, F-14050 Caen, France
(Received 24 June 1996; revised 10 October 1996)

Reaction of excess sodium alkoxides with aromatic (non-enethiolisable) dithioesters followed by *in situ* alkylation offers a high-yield direct synthetic route to monothio-orthoesters. When applied to previously described monomers, polymers and copolymers containing dithioester groups, this method provides a direct access to the corresponding monomers, polymers and copolymers in which monothio-orthoesters are present. [(Methylthio) dimethoxymethyl]-4-vinyl benzene [obtained from methyl (4-vinyl benzene) dithiocarboxylate] undergoes convenient free radical homo- and co-polymerizations. © 1997 Elsevier Science Ltd.

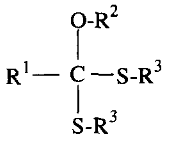
(Keywords: monothio-orthoester containing monomers and polymers; aromatic dithioesters; free radical polymerization and copolymerization)

INTRODUCTION

Monothio-orthoesters (**A**) have been the subject of a few papers[1–6] as their synthesis is usually obtained through an acid-catalysed transesterification of an orthoester $R^1-C(O-R^2)_3$ using a thiol[4,5,7,8]. This method yields mainly a mixture of monothio-orthoester (**A**) and dithio-orthoester (**B**) from which the isolation of pure compounds is not obvious.


$$R^1-\underset{\underset{S-R^3}{|}}{\overset{\overset{O-R^2}{|}}{C}}-O-R^2$$

A


$$R^1-\underset{\underset{S-R^3}{|}}{\overset{\overset{O-R^2}{|}}{C}}-S-R^3$$

B

The reaction of an excess of sodium alkoxide onto O-alkyl arenecarbothioates (thiono-esters) $R-C(=S)-OR^2$ (**C**) was described a few years ago[1] as leading to monothio-orthoesters in good to high yields.

Moreover, one example of the conversion of an aromatic dithioester into the corresponding thiono-esters using an alkoxide was described some years ago by Brandsma *et al.*[9,10].

An association of these two independent reactions which use the same reagent seemed to us an interesting way for the one-pot synthesis of pure aromatic monothio-orthoesters from the corresponding dithioesters. The latter compounds are readily available from either nitriles[11] or Grignard reagents[9,10,12–14] and they are more stable than thiono-esters which can undergo a thiono–thiolo rearrangement. The whole synthetic process is shown in *Scheme 1*.

This synthetic scheme was applied with full success to benzenic dithioesters and particularly methyl (4-vinyl benzene) dithiocarboxylate, their polymers and some copolymers as well as to a model compound [methyl (4-methyl benzene) dithiocarboxylate] (*Scheme 2*).

Such a chemical modification of a reactive functional group opens a new way for chemical grafting onto the main chain of polymers containing the group, for which one of us has previously established several synthetic paths[16–19]. Our aim was the formation of new polymers and copolymers with the pendent monothio-orthoester group.

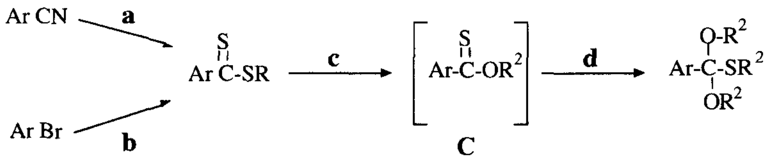
EXPERIMENTAL

All reactions were run under a positive nitrogen pressure. THF was distilled just before use over sodium benzophenone ketyl. Monomers and model compound were purified by flash chromatographies (silica gel or alumina). Eluent was cyclohexane or cyclohexane/ethyl acetate mixture in the ratios indicated below.

^1H n.m.r. 60 and 250 MHz spectra were run on Varian EM 360 and Bruker AC 250 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, coupling constant in Hz, assignment. ^{13}C n.m.r. spectra were determined at 20.15 MHz with a Bruker WP 80 SY spectrometer operating with broad band ^1H decoupling or a Bruker AC 250 spectrometer at 62.89 MHz, with

---

* To whom correspondence should be addressed



a : RSH, HCl then H_2S, pyridine ; **b** : Mg, THF, then CS_2, then RX ;
c and **d** : sodium alkoxide (R^2ONa) in excess, then CH_3I

Scheme 1 General synthetic scheme to benzenic monothio-orthoesters

TMS as an internal standard. The solvents used are indicated.

I.r. absorption spectra were recorded as liquid thin films or dissolved in $CDCl_3$ between NaCl plates or as solids in KBr pellets, on a Perkin Elmer 257 i.r. spectrophotometer and a Pye-Unicam SP 3-100 or a Perkin Elmer 16 PC FT-spectrometer. U.v.-vis spectra were executed on Perkin-Elmer λ 15 or Beckman DU-7. The products were dissolved in $CHCl_3$, CH_2Cl_2 or THF.

Elemental analyses were performed by 'Service Central d'Analyse' of CNRS at Vernaison. The results are described as percentages.

Mass spectra were recorded with a Nermag R 10 10 H spectrometer, electronic impact at 70 eV (the molecular ion and the most abundant ion are reported).

Molecular weights were determined by g.p.c. on Styragel columns calibrated with standard polystyrene samples using THF at 30°C as the mobile phase at a flow rate of $1.0\,ml\,min^{-1}$.

Aromatic dithioesters

General procedure. Aromatic dithioesters **1** were prepared by reaction of carbon disulfide according to the procedures described earlier[9,10,12–15].

A Grignard solution, prepared under nitrogen from magnesium (1.1 equiv) (0.8 g, 33 mmol) and aromatic halides (amount: see below) (1 equiv) in 50 ml dry THF at reflux for 2 h. A solution of dry CS_2 (1 equiv) in 20 ml dry THF was added to a well stirred and ice-cooled Grignard solution. The mixture was stirred over a period of 1 h at room temperature then cooled, and iodomethane (1.1 equiv) or sodium chloroacetate (1.1 equiv) was added. The reaction mixture was stirred for the time indicated below. After quenching by aqueous ammonium chloride for **1a**, **c** or an ice-cooled solution of 20% HCl for **1b**, **d** they were extracted with ethyl ether and brine. The organic layer was dried over magnesium sulfate and concentrated *in vacuo*. The residue is chromatographed on silica gel with cyclohexane as the eluting solvent.

Methyl (4-methyl benzene) dithiocarboxylate (**1a**). From the reaction of 4-bromotoluene (10 g, 58 mmol) with magnesium (1.4 g, 28 mmol), CS_2 (4.5 g, 59 mmol) and iodomethane (9.95 g, 70 mmol) for 4 h. Yield = 75%, red liquid. ^1H n.m.r. ($CDCl_3$): 2.4 (3H, *s*, CH_3-Ph); 2.8 (3H, *s*, CH_3), 7.1–7.9 (4H, 2*d*, AB syst $J_{AB} = 8\,Hz$, H arom); ^{13}C n.m.r. ($CDCl_3$): 20.5 (CH_3-Ph), 21.5 (SCH_3), 129.0–143.2 (C arom), 228.5 (C=S); i.r. (film NaCl plates): 1050, 1178, 1400, 1600; u.v.-vis ($CHCl_3$): 313 (log $\epsilon = 4.28$), 491 (log $\epsilon = 2.25$); Anal. Calcd. for $C_9H_{10}S_2$: C, 59.3; H, 5.53; S, 35.17. Found: C, 59.35; H, 5.38; S, 35.15.

Carboxymethyl (4-methyl benzene) dithiocarboxylate (**1b**). Obtained by the reaction of 4-bromotoluene (5 g, 30 mmol) with magnesium (0.8 g, 33 mmol), carbon disulfide (2.3 g, 30 mmol) and sodium chloroacetate (4.6 g, 40 mmol) for 18 h. Yield = 60%, red liquid (pink powder at room temperature). ^1H n.m.r. ($CDCl_3$): 2.4 (3H, *s*, CH_3-Ph); 4.3 (2H, *s*, CH_2), 6.46 (1H, *s*, COOH), 7.1–8.1 (4H, 2d, AB syst $J_{AB} = 8.4\,Hz$, H arom); ^{13}C n.m.r. ($CDCl_3$): 21.7 (CH_3-Ph), 38.7 (SCH_2), 127.0–144.0 (C arom), 173.0 (COOH), 225.0 (C=S); i.r. (KBr pellets): 1050, 1178, 1400, 1599 (Ph), 1700 (C=O), 3100 (OH); u.v.-vis ($CHCl_3$): 315 (log $\epsilon = 4.28$), 490 (log $\epsilon = 2.21$); Anal. Calcd. for $C_{10}H_{10}O_2S_2$: C, 53.07; H, 4.45; O, 14.24; S, 28.33. Found: C, 52.67; H, 4.45; O, 14.52; S, 28.69.

Methyl (4-vinyl benzene) dithiocarboxylate (**1c**). From the reaction of 4-bromostyrene (5.5 g, 30 mmol) with magnesium (0.8 g, 33 mmol), CS_2 (2.3, 30 mmol) and iodomethane (5.8 g, 40 mmol) for 4 h. Yield = 65%, red liquid (red powder at room temperature). ^1H n.m.r. ($CDCl_3$): 2.7 (3H, *s*, SCH_3), 5.4–6.8 (3H, m, ABX syst $J_{AB} = 1.4\,Hz$, $J_{BX} = 10\,Hz$, $J_{AX} = 17\,Hz$, CH=CH_2), 7.4–8.0 (4H, 2*d*, AB syst $J_{AB} = 8.3\,Hz$, H arom); ^{13}C n.m.r. ($CDCl_3$): 20.4 (SCH_3), 116.2 (=CH_2), 136.5 (HC=), 126.1, 144.2 (C arom), 227.8 (C=S); i.r. (KBr pellets): 1055, 1178, 1400, 1595 (Ph), 1625, 1820 (vinyl); u.v.-vis ($CHCl_3$): 353 (log $\epsilon = 4.1$), 496 (log $\epsilon = 2.29$); Anal. Calcd. for $C_{10}H_{10}O_2S_2$: C, 61.8; H, 5.2; S, 33. Found: C, 61.4; H, 5.15; S, 32.9.

Carboxymethyl (4-vinyl benzene) dithiocarboxylate (**1d**). Obtained by the reaction of 4-bromostyrene (5.5 g, 30 mmol) with magnesium (0.8 g, 33 mmol), CS_2 (2.3 g, 30 mmol) and sodium chloroacetate (4.6 g, 40 mmol) for 18 h. Yield = 80%, pink powder. ^1H n.m.r. ($CDCl_3$): 4.3 (2H, *s*, SCH_2), 5.3–6.9 (3H, *m*, ABX syst $J_{AB} = 1.4\,Hz$; $J_{BX} = 10\,Hz$; $J_{AX} = 17\,Hz$, CH=CH_2), 7.3–8.1 (4H, 2*d*, AB syst $J_{AB} = 8.4\,Hz$, H arom); ^{13}C n.m.r. ($CDCl_3$): 38.6 (SCH_2), 116.7 (=CH_2), 135.9 (HC=), 126.3, 143.2 (C arom), 172.7 (COOH), 224.3 (C=S); i.r. (KBr pellets): 1047, 1178, 1400 (vinyl), 1595 (Ph), 1705 (C=O), 3100 (OH); u.v.-vis ($CHCl_3$): 353 (log $\epsilon = 4.13$), 496 (log $\epsilon = 2.31$); Anal. Calcd. for $C_{11}H_{10}O_2S_2$: C, 54.44; H, 4.23; O, 13.43; S, 26.90. Found: C, 54.83; H, 4.03; O, 14.19; S, 25.90.

Preparation of homopolymers and copolymers (according to refs 16–19)

General procedure. 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 below. The polymers were isolated by precipitation in cyclohexane and fully characterized by spectroscopy, g.p.c. and d.c.s. analysis.

Polymerization of methyl (4-vinyl benzene) dithiocarboxylate (**1c**). In a 100 ml round-bottom, three-necked flask equipped with a condenser, a nitrogen gas inlet and a magnetic stirrer were placed dithioester **1c** (1 g, 5 mmol) and 5 mg AIBN (0.3 mmol, 5.0 wt%) in 20 ml of freshly distilled THF. The mixture was heated for 20 h at 66°C. The red polymerization mixture was allowed to cool, then concentrated. The product was diluted with dichloromethane and precipitated by adding slowly to 500 ml of cyclohexane. The pink powder **1e** was dried *in vacuo* for 3 h to furnish 0.42 g of homopolymer **1e**. Yield = 42%. ^{1}H n.m.r. ($CDCl_3$): 0.9–2.4 (3H, *m*, $CH-CH_2$), 2.7 (3H, *s*, SCH_3), 6.4–7.8 (4H, 2*m*, H arom); ^{13}C n.m.r. ($CDCl_3$): 13.0, 15.0, 32.0, 41.0 ($CH-CH_2$), 20.7 (SCH_3), 110.0, 125.0, 126.9, 135.5, 145.0 (C arom), 207.2 (C=S); i.r. (KBr pellets): 1180–1605 (Ph), 1049–1418 (C=S), 1260 ($CSCH_3$), 3000 (CH, CH_2); u.v.-vis ($CHCl_3$): 313 (log $\epsilon = 4.13$, 494 (log $\epsilon = 2.11$); g.p.c.: $M_n = 43\,510$, $M_w = 49\,800$. $T_g = 104$°C.

Polymerization of carboxymethyl (4-vinyl benzene) dithiocarboxylate (**1b**). Polymer **1f** was obtained by the reaction of dithioester **1b** (4 g, 17 mmol) with 5 wt% AIBN (0.2 g, 1.2 mmol). The pink powder was dissolved in acetone and precipitated by dropwise addition to cyclohexane and dried. Yield = 40%. ^{1}H n.m.r. ($CDCl_3$): 0.6–2.8 (3H, 2*m*, $CH-CH_2$), 4.2 (2H, *s*, SCH_2), 5.6 (1H, *s*, OH), 6.2–7.7 (4H, 2*m*, AB syst, H arom); i.r. (KBr pellets): 1180, 1595 (Ph), 1050–1410 (CO), 1710 (C=O), 3100 (OH); u.v.-vis ($CHCl_3$): 313 (log $\epsilon = 4.09$), 495 (log $\epsilon = 2.08$); g.p.c.: $M_n = 12\,420$, $M_w = 24\,450$.

Preparation of copolymer **1g** *from* **1c** *and methyl methacrylate.* In order to evaluate quantitatively the stoechiometric ratio we performed a set of experiments in which we changed the composition in dithioester **1c**/MMA mixture from 2/98, 10/90, 20/80 and 30/70 mol ratio. The copolymerization was carried out in a 100 ml round-bottom, three-necked flask equipped with a condenser, a nitrogen gas inlet and a magnetic stirrer. After the required amounts of the two monomers, **1c** methyl (4-vinyl benzene) dithiocarboxylate (1.0 g, 5 mmol) and methyl methacrylate (2.0 g, 20 mmol) in 50 ml freshly distilled THF and 5.0 wt% (0.05 g, 0.3 mmol) AIBN had been added, the mixture was left stirring for 30 min prior to being refluxed for 40 h. The polymerization mixture was allowed to cool, then concentrated and poured dropwise into an excess of cyclohexane to precipitate the copolymer. The polymer was dried for 2 h *in vacuo*. Purification of the resulting copolymer was accomplished by two reprecipitations from dichloromethane using cyclohexane as the non-solvent. The polymer was then dried *in vacuo* for 3 h to afford 1.65 g of purified copolymer.

The red powder alternating copolymer **1g** was obtained in a conversion of 65, 29, 42 and 15%. ^{1}H n.m.r. ($CDCl_3$): 0.6–2.6 (5H, 3*m*, $CH-CH_2$), 2.8 (3H, *s*, SCH_3), 3.6 (3H, *s*, OCH_3), 6.4–8.1 (4H, 2*m*, H arom); ^{13}C n.m.r. ($CDCl_3$): 19.4, 20.7, 27.0, 30.4 (SCH_3, CH, CH_2), 44.5, 45.7, 51.2, 51.9 [MeC(COOMe)], 126.7, 127.1, 128.0, 143.2 (C arom), 176.4 (C=O), 228.2 (C=S); i.r. (KBr pellets): 1150, 1180, 1242, 1271, 1595 (Ph), 1067–1448 (C=S), 1710 (C=O); u.v.-vis ($CHCl_3$): 314, 494; GPC: $M_n = 54\,170$; $M_w = 176\,000$; $M_n = 185$, $M_w = 270$; $M_n = 2399$, $M_w = 4217$. $T_g = 108.8$°C.

Preparation of copolymer **1h** *from* **1d** *and methyl methacrylate.* The copolymer **1h** was obtained by the reaction of carboxymethyl (4-vinyl benzene) dithiocarboxylate **1d** with methyl methacrylate in the mol% ratio of 2/98 and 10/90, in the presence of AIBN 1 mol% as initiator under nitrogen atmosphere. The copolymer **1h** was purified by reprecipitation from chloroform using heptane as the non-solvent and dried *in vacuo* for 3 h. Yield = 27% (pink powder). ^{1}H n.m.r. ($CDCl_3$): 0.7–2.8 (5H, 3*m*, $CH-CH_2$), 4.2 (2H, *s*, SCH_2), 3.8 (3H, *s*, OCH_3), 5.8 (1H, *s*, OH), 6.9–8.2 (4H, 2*m*, AB syst, H arom); i.r. (KBr pellets): 1190, 1600 (Ph), 1145, 1275 (C–O), 1059–1445 (C=S), 1725 (C=O), 3150 (OH); u.v.-vis ($CHCl_3$): 314 (log $\epsilon = 4.11$), 494 (log $\epsilon = 2.09$); g.p.c.: $M_n = 11\,670$; $M_w = 43\,160$ (**1h** mol% = 10).

Synthesis of monothio-orthoester polymer **4e** *from [(methylthio) dimethoxymethyl]-4-vinyl benzene* **4c**. Monothio-orthoester **4c** (4 g, 17.8 mmol) and 10 wt% AIBN (0.04 g, 0.2 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 for 30 h before cooling. The mixture was concentrated then diluted with dichloromethane and precipitated from solution by dropwise addition to cyclohexane, filtered washed repeatedly with cyclohexane and dried. The recovery procedure was repeated twice before polymer was dried *in vacuo* at 40°C for 3 h to furnish 2 g of yellow colourless powder. Yield 50%. ^{1}H n.m.r. ($CDCl_3$): 0.8–2.1 (3H, *m*, $CH-CH_2$), 1.6 (3H, *s*, SCH_3), 3.2 (6H, *s*, OCH_3), 6.2–8.0 (4H, 2*m*, AB syst, H arom); ^{13}C n.m.r. ($CDCl_3$): 12.0, 13.0 (SCH_3), 15.0, 27.0, 31.1, 37.0 (CH, CH_2), 44.0 [$CH_3SC(OCH_3)$], 51.0 (OCH_3), 128.0, 135.0, 140.0, 153.0 (C arom); i.r. (KBr pellets): 1070, 1090, 1245 (C–O), 1630 (C=C arom), 2900 ($CH-CH_2$); u.v.-vis ($CHCl_3$): 244 (log $\epsilon = 3.25$).

Synthesis of monothio-orthoester copolymer **4f** *from [(methylthio) dimethoxymethyl]-4-vinyl benzene* **4c** *and methyl methacrylate.* Monothio-orthoester **4c** monomer (0.7 g, 3.13 mmol), MMA (2.83 g, 28.3 mmol) and 1 mol% AIBN (5.14 mg, 0.031 mmol) were used to furnish the copolymer methyl methacrylate [(methylthio) dimethoxymethyl] 4-vinyl benzene **4f**. The reaction was performed during 14 h at 65°C. The copolymer was purified by reprecipitation from CH_2Cl_2 using cyclohexane as non-solvent, and dried *in vacuo*. Yield 96%. ^{1}H n.m.r. ($CDCl_3$): 0.5–2.5 (5H, 3*m*, $CH-CH_2$), 1.6 (3H, *s*, SCH_3), 3.2 (6H, *s*, OCH_3), 3.6 (3H, *s*, $O=COCH_3$), 6.9–7.9 (4H, 2*m*, AB syst, H arom); ^{13}C n.m.r. ($CDCl_3$): 12.0, 17.0 (SCH_3), 25.0, 27.0, 31.1, 37.0 (CH, CH_2), 44.0 [$CH_3SC(OCH_3)$], 50.0, 51.3 (OCH_3), 125.0, 127.0, 130.0, 140.0, 145.0, 163.0 (C arom), 173.0, 186.0, 192.0 (C=O); i.r. (KBr pellets): 1050, 1080, 1245 (C–O), 1730 (C=O); u.v.-vis (CH_2Cl_2): 345 (log $\epsilon = 3.21$); g.p.c.: $M_n = 9940$, $M_w = 19\,910$ (PI = 2.003).

*Preparation of monothio-orthoesters (*Scheme 2, Table 1*)*

Monomers. General procedure. To a stirred solution of sodium methylate (2.5 equivalents) in anhydrous freshly distilled THF (25 ml), under an inert atmosphere of nitrogen, dithioesters (1 equiv) were added, and the mixture was stirred at room temperature for 1 h 30 min. A solution of methyl iodide (2.5 equiv) in THF (15 ml) was then added dropwise (the red or pink colour disappears). After 1 h stirring at room temperature, NaI was filtered, and then the reaction mixture was concentrated under reduced pressure. Work-up involved addition of a cyclohexane/water solution (100 ml), extraction of the aqueous phase with 3 × 30 ml portions of cyclohexane, drying of the organic phase over $MgSO_4$, filtration then concentration *in vacuo*, to give the crude product. The monothio-orthoester was isolated and purified by flash chromatography on alumina with cyclohexane/ CH_2Cl_2 (95/5) as eluent.

4-Methyl [(methylthio) dimethoxymethyl] benzene (**4a**). Compound **4a** was obtained from the reaction of methyl (4-methyl benzene) dithiocarboxylate **1a** (2.73 g, 15 mmol) in THF (10 ml) with sodium methylate (2.03 g, 37.5 mmol) in THF (25 ml) and methyl iodide (5.33 g, 37.5 mmol) in THF (15 ml). Yield = 72%, yellow colourless liquid. Compound **4a** was also furnished by the reaction of carboxymethyl (4-methyl benzene) dithiocarboxylate **1b** (3.39 g, 15 mmol), sodium methylate 4.4 equiv (3.56 g; 66 mmol) and methyl iodide 4.4 equiv (9.37 g, 66 mmol). Yield = 83%. ^1H n.m.r. ($CDCl_3$): 1.66 (3H, *s*, SCH_3), 2.35 (3H, *s*, CH_3Ph), 3.29 (6H, *s*, OCH_3), 7.13–7.50 (4H, 2*d*, AB syst $J_{AB} = 8\,Hz$, H arom); ^{13}C n.m.r. ($CDCl_3$): 7.1 (SCH_3), 16.1 (CH_3Ph), 44.9 (OCH_3), 107.7 ($(MeO)_2$-C-SMe), 122.2, 123.4, 131.4, 132.7 (C arom); i.r. (film NaCl plates): 1060, 1080, 1240 (C–O), 1600 (C=C arom); u.v.-vis (CH_2Cl_2): 246 ($\log \epsilon = 3.4$); Anal. Calcd. for $C_{11}H_{16}O_2S$: C, 62.22; H, 7.59; O, 15.07; S, 15.1. Found: C, 61.93; H, 7.65; O, 15.12, S, 14.82. Mass: 212 (4) M^+; 166 (21); 165 (100); 123 (23); 119 (52); 91 (17).

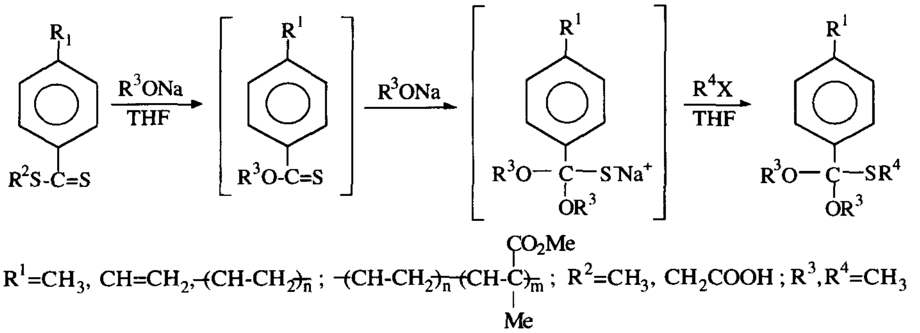
[(Methylthio) dimethoxymethyl]-4-vinyl benzene (**4c**). Compound **4c** was obtained by the reaction of methyl (4-vinyl benzene) dithiocarboxylate **1c** (1.94 g, 10 mmol) in THF (15 ml) and sodium methylate (1.25 g, 25 mmol) in THF (25 ml) followed by alkylation with methyl iodide (3.55 g, 25 mmol) in THF (10 ml). Yield = 61% (from **1c**) and 75% (from **1b**), yellow colourless viscous liquid. ^1H n.m.r. ($CDCl_3$): 1.65 (3H, *s*, SCH_3), 3.20 (6H, *s*, OCH_3), 5.15, 5.70, 6.65 (3H, *m*, ABX syst, $J_{AB} = 1.2\,Hz$, $J_{AX} = 17\,Hz$, $J_{BX} = 9.8\,Hz$, $CH{=}CH_2$), 7.30–7.50 (4H, 2*d*, AB syst $J_{AB} = 7.8\,Hz$, H arom). ^{13}C n.m.r. ($CDCl_3$): 9.5 (SCH_3), 29.6, 45.5 (OCH_3), 106.6 $(MeO)_2$-C-SMe), 108.1, 122.5, 125.0, 123.5, 131.4, 134.4 ($CH{=}CH_2$, C arom); i.r. (film NaCl plates): 1055, 1080, 1235 (C–O), 1630 ($CH{=}CH_2$); u.v.-vis (CH_2Cl_2): 259 ($\log \epsilon = 3.14$); Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.23; H, 7.19; O, 14.26; S, 14.29. Found: C, 64.24; H, 7.44; O, 14.67, S, 14.01. Mass: 224 (40) M^+; 177 (16); 176 (45); 175 (19); 150 (13); 149 (94); 148 (100).

(Co)polymers. General methods. Monothioorthoester (co)polymers were prepared according to the methods described previously. Into a mixture of sodium methylate (3 equiv) in dry freshly distilled THF (15 ml), a mixture of (co)poly [methyl (4-vinyl benzene) dithiocarboxylate] **1e–h** (1 equiv) in THF (25 ml) was added dropwise over a period of 15 min under N_2 atmosphere at room temperature.

After 2 h stirring, most of (co)poly dithioester was consumed, methyl iodide (3.5 equiv) diluted in THF (10 ml) was then added (the pink colour disappears). The mixture was stirred at room temperature for 2 h, and NaI eliminated by filtration of the orange-coloured solution. 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*.

Poly [(methylthio) dimethoxymethyl]-4-vinyl benzene (**4e**). Reaction of poly [methyl (4-vinyl benzene) dithiocarboxylate] **1e** (0.2 g, 1.03 mmol) with sodium methylate (0.167 g, 3.09 mmol) followed by alkylation with methyl iodide (0.512 g, 3.6 mmol) affords **4e** (12 g). Yield = 54%, yellow powder. ^1H n.m.r. ($CDCl_3$): 0.8–2.1 (3H, 2*m*, $CH{-}CH_2$), 1.6 (3H, *s*, SCH_3), 3.2 (6H, *s*, OCH_3), 6.1–8.1 (4H, 2*m*, AB syst, H arom); ^{13}C n.m.r. ($CDCl_3$): 12.0 (SCH_3), 25.0, 30.0 (CH, CH_2), 50.0 (OCH_3), 125.0–140.0 (C. arom); i.r. (KBr pellets): 1050, 1080, 1245 (C–O); u.v.-vis ($CHCl_3$): 244 ($\log \epsilon = 3.25$). $T_g = 107°C$.

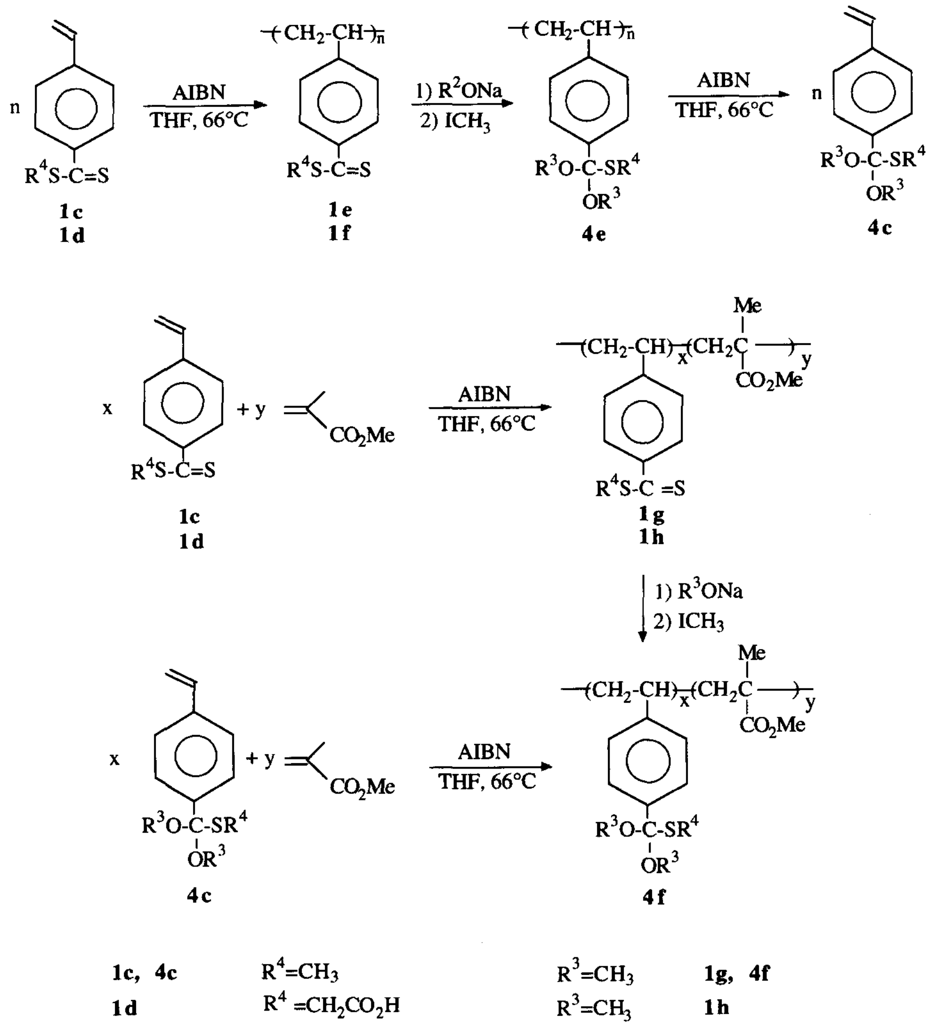
(Co)poly methyl methacrylate-[(methylthio) dimethoxymethyl]-4-vinyl benzene **4f**. Obtained by addition of copoly[methyl (4-vinyl benzene) dithiocarboxylate] **1g** (1 g) in THF to a mixture of sodium methylate (0.73 g, 13.6 mmol) in THF followed by reaction with methyl iodide (2.17 g, 15.3 mmol). Purification of the resulting copolymer by reprecipitation from CH_2Cl_2/ cyclohexane furnished 0.85 g of yellow colourless powder. Yield = 77%. ^1H n.m.r. ($CDCl_3$): 0.5–2.5 (5H, 3*m*, $CH{-}CH_2$), 1.6 (3H, *s*, SCH_3), 3.2 (6H, *s*, OCH_3), 3.6 (3H, *s*, CO_2CH_3), 6.9–7.9 (4H, 2*m*, AB syst, H arom); ^{13}C n.m.r. ($CDCl_3$): 11.6, 16.9, 19.0 (SCH_3),



Scheme 2

Table 1 Synthesis of aromatic monothio-orthoesters **4** from dithioesters **1** in the presence of excess sodium methylate followed by methyl iodide alkylation

Entry	R^1	R^2	R^3	R^4	Aromatic dithioesters	Yield (%)		Monothio-orthoester	Yield (%)
a	CH_3	CH_3	CH_3	CH_3	**1a**	75	red liquid	**4a**	72
b	CH_3	CH_2CO_2H	CH_3	CH_3	**1b**	60	pink powder	**4a**	83
c	$CH=CH_2$	CH_3	CH_3	CH_3	**1c**	65	red powder	**4c**	61
d	$CH=CH_2$	CH_2CO_2H	CH_3	CH_3	**1d**	80	pink powder	**4c**	75
e	$-\!(CH-CH_2)\!-_n$	CH_3	CH_3	CH_3	**1e**		pink powder	**4e**	54
f	$-\!(CH-CH_2)\!-_n$	CH_2CO_2H	CH_3	CH_3	**1f**		pink powder	**4e**	
g	$-\!(CH-CH_2)\!-_x(CH-\overset{Me}{\underset{CO_2Me}{C}})\!-_y$	CH_3	CH_3	CH_3	**1g**		pink powder	**4f**	
h	$-\!(CH-CH_2)\!-_x(CH-\overset{Me}{\underset{CO_2Me}{C}})\!-_y$	CH_2CO_2H	CH_3	CH_3	**1h**		pink powder	**4f**	



Scheme 3

27.0, 44.8, 45.1, 46.0, 51.0, 51.7, 52.6, 52.8, 53.0, 54.4, 54.6 (OCH_3, CO_2CH_3), 128.5, 129.3, 129.5, 135.5, 166.9, 176.2, 177.0, 177.8, 178.0 (C arom), 191.8 (C=O); i.r. (KBr pellets): 1050, 1080, 1245 (C=O), 1730 (C=O); u.v.-vis (CH_2Cl_2): 345 (log $\epsilon = 3.21$; g.p.c.: $M_m = 9940$, $M_w = 19910$. $T_g = 160.5$°C.

RESULTS AND DISCUSSION

Starting dithioesters **1a**–**d** were synthesized, respectively, by reaction of the 4-methyl and 4-vinyl benzene magnesium bromides with carbon disulfide followed by addition with methyl iodide or sodium chloroacetate (*Scheme 1*).

Polymers **1e**, **f** were prepared by free-radical polymerization of **1c**, **d** using *N,N'*-azo-bisisobutyronitrile (AIBN) in tetrahydrofuran (THF) (*Scheme 3*). The number average molecular weight of the polymers **1e**, **f** by g.p.c. in THF was found to be 43 500 and 12 400, respectively [according to polystyrene (PS) standards] with a polydispersity index of 1.7. These polymers present glass transition temperatures (T_g), respectively, at 104°C (**1e**) and 107°C (**1f**) and do not crystallize.

Under the same conditions, copolymerization of **1c**, **d** with methyl methacrylate gave the copolymers **1g**, **h** ($T_g \approx 109°C$) (*Scheme 3*).

The conversion of monomers **1a**–**d** and (co)polymers **1e**–**h** into monothio-orthoesters **4a**–**f** was performed in tetrahydrofuran (THF) at room temperature using 2.5 molar excess of sodium methylate (*Scheme 2*). The products formed were isolated in good yields by column chromatography (monomers) or by precipitation in cyclohexane (polymers) (*Table 1*). The structure and purity of the monothio-orthoesters **4** were confirmed in each case by ^{1}H, ^{13}C n.m.r., i.r. and u.v. spectroscopy and elemental analysis. Yields are slightly better starting from carboxymethyl dithioester, the carboxymethylthiolate ions being better leaving groups than methylthiolate ones.

The absence of the methylthio singlet at 2.8 ppm (or of the carboxymethylthio group at 4.3 ppm) indicates the reaction is complete. Compounds **4a**–**f** exhibit characteristic n.m.r. signals of monothio-orthoesters. For example, the ^{1}H n.m.r. signal for the methylthio group of **4a** is observed at 1.66 ppm and methoxy signals around 3.20 ppm, respectively[1,5]. The monothio-orthoester **4a** structure is confirmed by ^{13}C n.m.r. shifts at 49.0 and 11.2 ppm related, respectively, to the methoxy and methylthio groups. No thiocarbonyl signal (from some eventually remaining dithioester) could be observed near 227.8 ppm. All monothio-orthoesters show characteristic i.r. absorption for the methoxy group: ν (film) = 1235 and 825 cm^{-1} for the methylthio group according to the literature[1]. U.v.-vis spectra (dichloromethane) exibit a maximum at *ca* 246 nm ($\log \epsilon = 3.4$) and again the absence of absorptions at *ca* 500 nm and *ca* 310 nm confirms the complete dithioester conversion into monothio-orthoester **4**.

To our knowledge, nucleophilic reactions of sodium methylate with dithioester polymer are still unknown. It was of interest to prepare similar structures obtained as homopolymers **1e**, **f** and copolymers **1g**, **f** from monomeric structures, monothio-orthoesters **1c**, **d**.

The ^{1}H n.m.r. spectrum of **4e** shows broad signal for aromatic protons at 6.1–8.1 ppm, multiple peaks for methylthio group at 1.6 ppm (in monomer **4c** the methylthio signal was a sharp singlet) and a broad signal for aliphatic methylene protons at 0.8–2.1 ppm [compared with the starting dithioester polymer **1e** bearing a methylthio group (recorded at 2.7 ppm)]. Characteristic i.r. spectroscopic absorption for the methoxy group was observed at ν (KBr) 1245 cm^{-1} (ref. 1) and u.v.-vis spectra (chloroform) show a maximum at 244 nm ($\log \epsilon = 3.25$) and no signal of remaining dithioester in the polymer at 494 and 313 nm. Except for the u.v.-vis signal at 245 nm masked by the broad carbonyl group absorption, the same characteristic signals were observed on copolymer **4f**. In both cases, it is possible to confirm that the reactions were complete by u.v.-vis and n.m.r. spectroscopies.

It seemed interesting to explore similar structures from homopolymers **4e** and copolymers **4f** obtained through free radical polymerization of the monomeric monothio-orthoester **4c** (*Scheme 3*). The absence of ABX system at 5.25, 5.70 and 6.65 ppm in ^{1}H n.m.r. spectra of **4e**, **f** shows that the precipitated polymers were monomer-free.

CONCLUSION

We have developed a very convenient method for the preparation in good yield of monothio-orthoesters including monomers and (co)polymers starting from aromatic dithioesters monomers and (co)polymers. This route (which can be extended to a large variety of alcoolates) avoids the difficulties encountered in other methods using boron trifluoride and thiols[1,4,5].

ACKNOWLEDGEMENT

We wish to acknowledge Dr S. Masson for helpful discussions.

REFERENCES

1. Voss, J. and Wollny, B., *J. Chem. Soc., Chem. Commun.*, 1989, 684.
2. Shimchen, G., *Houben-Weyl*, 4th edn, Vol. E5. Georg Thieme, Stuttgart, 1985, p.123.
3. Feugeas, C. and Olschwang, D., *C.R. Acad. Sci., Ser. C.*, 1968, **266**, 1506.
4. Feugeas, C. and Olschwang, D., *Bull. Soc. Chim. Fr.*, 1969, 325.
5. Okuyama, T., Kitano, M. and Fueno, T., *J. Org. Chem.*, 1987, **52**, 2657.
6. Khouri, F. F. and Kaloustian, M. K., *J. Am. Chem. Soc.*, 1986, **108**, 6683.
7. De Wolfe, R. H., *Carboxylic Ortho Acid Derivatives*. Academic Press, New York, 1970, Chap. 6.
8. Narasimhan, L., Sanitra, R. and Swenton, J., *J. Chem. Soc., Chem Commun.*, 1978, 719.
9. Meijer, J., Vermeer, P. and Brandsma, L., *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 601.
10. Westmijze, H., Klein, H., Meijer, J. and Vermeer, P., *Synthesis*, 1979, 432.
11. Marvel, C. S., Radzitzky, P. de and Bader, J. J., *J. Am. Chem. Soc.*, 1955, **77**, 5997.
12. Beiner, J. M. and Thuillier, A., *C.R. Acad. Sci., Ser. C.*, 1972, **274**, 642.
13. Ramadas, S. R., Srinivasan, P. S., Ramachandran, J. and Sastry, V. V. S. K., *Synthesis*, 1983, 605.
14. Cazes, B. and Julia, S., *Tetrahedron Lett.*, 1978, 4065.
15. Kjaer, A., *Acta Chem. Scan.*, 1952, **6**, 327.
16. Haraoubia, R., Bonnans-Plaisance, C. and Levesque, G., *Makromol. Chem.*, 1981, **182**, 2409.
17. Haraoubia, R., Gressier, J. C. and Levesque, G., *Makromol. Chem.*, 1982, **183**, 2367.
18. Haraoubia, R., Levesque, G., Bonnans-Plaisance, C. and Gressier, J. C., *Makromol. Chem.*, 1981, **183**, 2383.
19. Bonnans-Plaisance, C. and Levesque, G., *Makromol. Chem., Rapid Commun.*, 1985, **6**, 145.