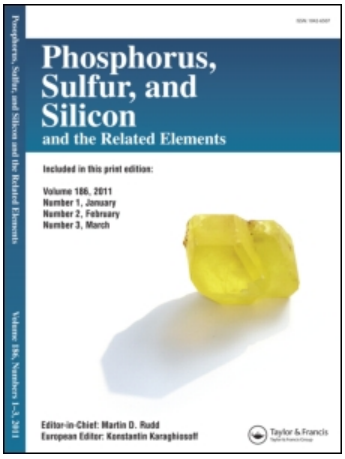

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SYNTHESIS OF AROMATIC MONODISPERSED TELECHELIC DITHIOLS

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SYNTHESIS OF AROMATIC MONODISPERSED TELECHELIC DITHIOLS

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The synthesis of aromatic monodispersed telechelic dithiols performed from the esterification of thioglycolic acid with aromatic monodispersed telechelic diols is presented. The diols were prepared from the transesterification of ethylene glycol with the dimethyl terephthalate. In all cases the yields are high and the products are carefully characterized by ^1H and ^{13}C-NMR.

Key words: Dithiol; telechelic oligomers; ethylene terephthalate derivatives; monodispersity; aromatic compounds.

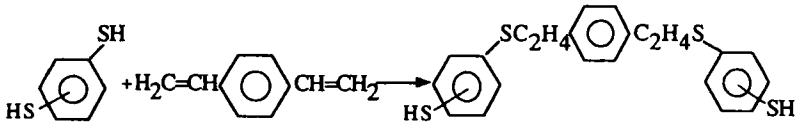
INTRODUCTION

Telechelic dithiols are very interesting intermediates for the synthesis of elastomers,[1] prepolymers,[2] multiblock copolymers,[3] diols[4] and their final products can find applications in various fields: textile,[5] photocuring coatings produced by the thiol-ene process,[6] optical material,[7] and liquid rubber.[8]

These dithiols may exhibit special groups which lead to specific applications: triazine for acrylic elastomers[1]; amino groups for prepolymer used in the synthesis of polythiazoles[2]; dimethyl siloxane,[9] ammonium, ester or anhydride for textiles,[5] ether or thioether[10–14] phosphonic derivatives,[13] or fluorinated aromatic rings.[15]

However, if the literature concerning the synthesis of aliphatic dithiols is abundant, the articles about the aromatic telechelic dithiols are less numerous, and most of them deal with the preparation of polydispersed aromatic dithiols.[16–22]

Vögtle,[23] Kobayashi[18] and Corbellini[24–25] synthesized metadimercaptobenzene, paradimercaptobenzene and dimercaptonaphthalene, respectively. Interestingly, the former two were used in polyaddition reactions with 1,4-divinyl benzene[26–27] or 1,4-diethynyl benzene[18,28–30] to obtain new aromatic α,ω-dithiols as follows:



(excess)

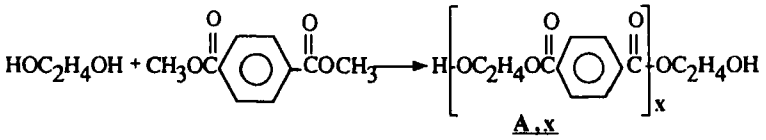
Nuyken *et al.*[26] showed that the end-group titration can be used to determine the molecular weights below 5,000. However, it was observed that most oligomers and polymers produced from the above dithiols were rather insoluble in organic common solvents. But, the improvement of the solubility can be achieved by introducing polar groups, e.g., amido[31] or ester[32,33] groups.

The article presents an effective synthesis of new aromatic telechelic monodispersed dithiols obtained from esterification of thioglycolic acid with α,ω-dithiols.

RESULTS AND DISCUSSION

a) Synthesis of Aromatic Diols

Ethylene terephthalate oligomers were prepared by transesterification of dimethyl terephthalate and ethylene glycol as follows:



A,x

The different low molecular weight oligomers can be separated by fractioned precipitation and the first two adducts were obtained owing to their solubility into boiling water and THF, respectively.

Both of them were easily identified by size exclusion chromatography (Figure 1) and were characterized by IR and NMR.

The IR spectra show broad bands at 3400–3600 cm^{-1} assigned to the hydroxyl groups. The ^{1}H-NMR spectra exhibit a singlet at $8.15 \cdot 10^{-6}$ characteristic of the aromatic ring whereas both methylene groups in α and β positions about the hydroxy end-groups give triplets at 3.75 and $4.35 \cdot 10^{-6}$, respectively. The singlet at $4.7 \cdot 10^{-6}$ corresponds to both methylene groups located between the terephthalic groups.

b) Synthesis of Aromatic Telechelic Monodispersed Dithiols

Two pathways were chosen to introduce mercapto functions: the α,ω-dithiols can be prepared either by direct thiolation from the diol or by esterification of the thioglycolic acid with the above mentioned aromatic diols.

1) *Direct thiolation.* Direct thiolation consists in the selective chemical change of the hydroxy functions into the mercaptan ones as described by Cossar[34] or Klemm.[14]

Such a reaction was carried out in the same conditions as those used by these authors but it was observed that the aromatic diols are insoluble in the acidic thiourea medium even in the case of diol **A,1** (which is regarded as the more soluble), at higher temperatures and in harder conditions.

The yields are poor and because of the insolubility of the diols such a method is not valid to prepare new α,ω-dithiols.

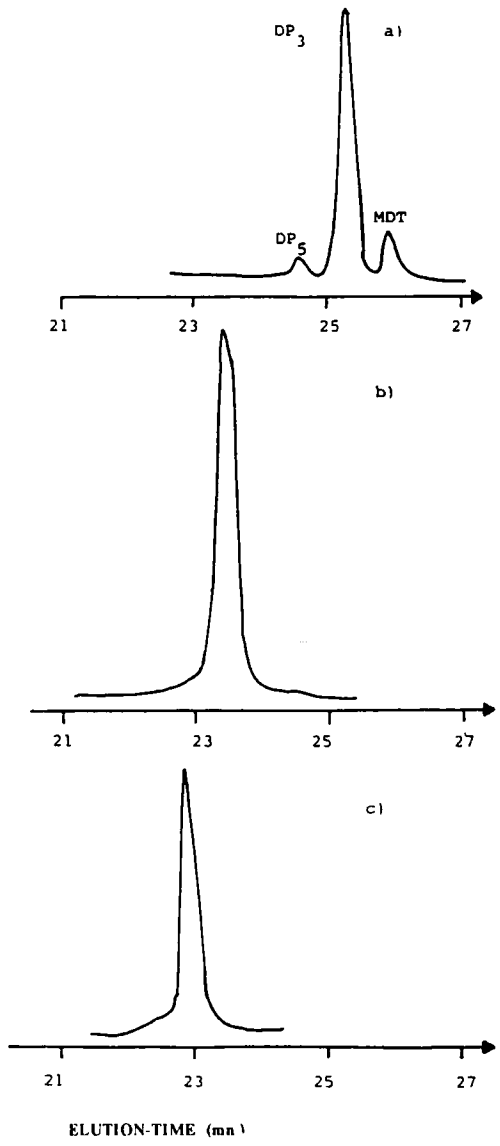
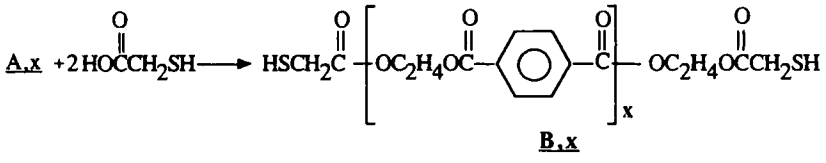


FIGURE 1 SEC chromatogram of the ethylene terephthalate oligomers (a), of the dithiol **B,1** (b), and of the dithiol **B,2** (c).

2) *Esterification of the thioglycolic acid with the aromatic α,ω-diols.* The esterification was performed at reflux of benzene in a THF/DMSO mixture in order to increase the solubility of the diol, as follows:



Such a mild method does not produce any by-product, e.g., polymer with thioester groups as was the case previously.[33]

After reaction, the dithiols were precipitated and recrystallized from hexane and the yields were quantitative. These dithiols are more soluble—and in most organic solvents—than the corresponding diols. The polar ester groups in the β position about the mercaptan groups improve the solubility. It is observed that the α,ω-mercapto alcohol resulting from the 1:1 esterification was not produced.

Both the IR spectra of the dithiols **B,1** and **B,2** show the presence of a band at 2320 cm^{-1} assigned to the vibration of the —SH group, and the absence of broad band in the 3400–3600 cm^{-1} range.

The dithiols were characterized by both ^1H and ^{13}C-NMR.

The ^1H-NMR spectrum (Figure 2) of dithiol **B,1** shows:

- the absence of the signals corresponding to the hydroxyl protons of the thioglycolic acid and diol;
- the presence of a triplet at $\delta = 1.95 \cdot 10^{-6}$ characteristic of the SH group;
- the singlet at $8.00 \cdot 10^{-6}$ assigned to the aromatic ring;
- the doublet at $3.20 \cdot 10^{-6}$ which corresponds to the methylene adjacent to the SH group;
- an A_2B_2 system at $4.45 \cdot 10^{-6}$ assigned to the methylenes adjacent to the carbonyl group.

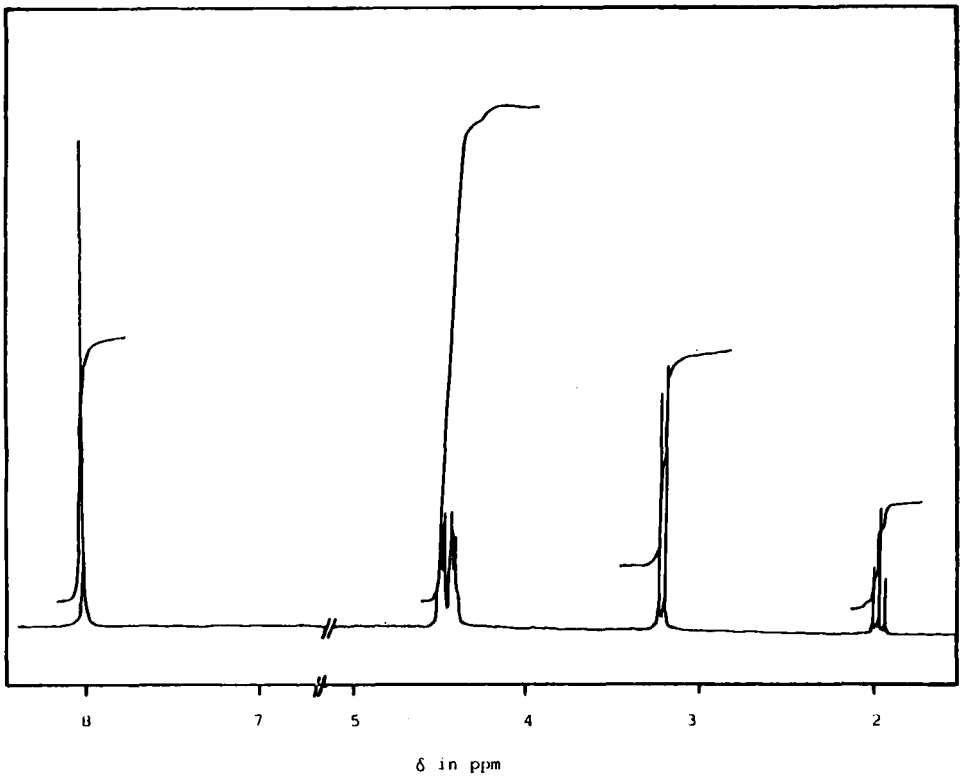


FIGURE 2 ^1H-NMR spectrum of the dithiol **B,1**.

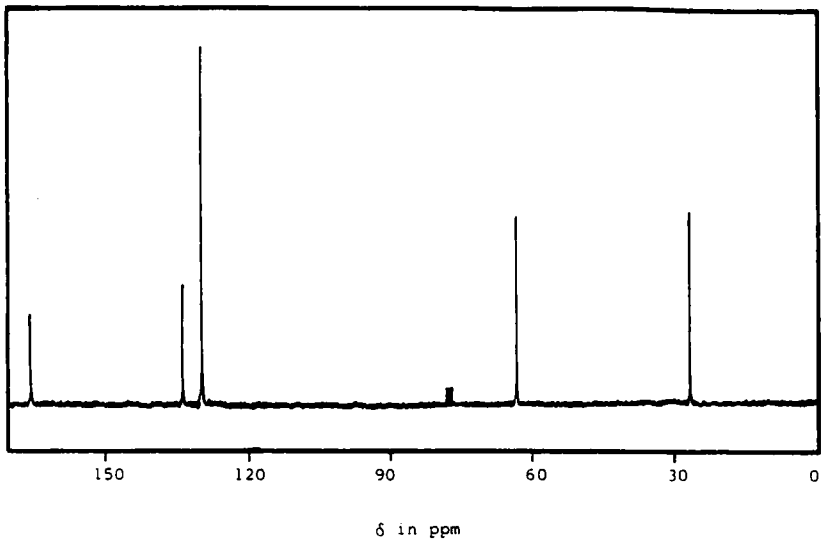


FIGURE 3 ^{13}C-NMR spectrum of the dithiol **B,2**.

Similar chemical shifts are observed on the ^{1}H-NMR spectrum of dithiol **B,2** with in addition, the presence of a singlet at $4.65 \cdot 10^{-6}$ characteristic of both methylenes located between the terephthalate groups.

On the ^{13}C-NMR spectra (Figure 3), the following observations were made:

- presence of a signal at $26.09 \cdot 10^{-6}$ characteristic of the methylene group adjacent to mercaptan;
- presence of two close singlets at about $62.8 \cdot 10^{-6}$ assigned to the methylene groups adjacent to ester;
- presence of a peak at about $165.1 \cdot 10^{-6}$ corresponding to the carbonyl group.
- the aromatic carbons were representated by signals at 133.4 and $129.4 \cdot 10^{-6}$.

CONCLUSION

The synthesis of telechelic aromatic monodispersed dithiols of 400–600 molecular weight can be achieved by a simple esterification of the thioglycolic acid with monodispersed aromatic α,ω-diols produced by transesterification of dimethyl terephthalate and ethylene glycol. The yields are quantitative. Such dithiols, soluble in most common organic solvents are interesting new intermediates for the synthesis of further products such as the aromatic telechelic diols which are under investigations.

EXPERIMENTAL

a) Apparatus

The starting materials were supplied by Aldrich and did not require further purification prior to use.

FTIR spectra were conducted with a Nicolet 510 P spectrometer. The accuracy of the bands was given with an error of ± 2.0 cm^{-1} and the letters FF, F, m, f indicate a very strong, strong, medium or weak intensity, respectively.

Size Exclusion Chromatography (SEC) investigations were monitored with a Waters Associates Apparatus equipped with microstyrogel columns, whose pore diameters were 10,000, 1000, 500 and 100 Å. The detection was performed with a BD40 model refractometer.

THF was used as an eluent (flow 1.5 ml·mm^{-1} at T = 25°C).

The different pure telomers were characterized by ^{1}H and ^{13}C-NMR at room temperature. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AC 250 or Bruker AC 200 by using deuterated chloroform or dimethylsulfoxide as internal reference and solvent, respectively. The letters *s*, *d*, *t*, *q* and *m* designate singlet, doublet, triplet, quartet and multiplet, respectively.

Melting (T_m) and glass transition (T_g) temperatures were determined with a Perkin Elmer DSC 4 calibrated with indium which has a melting point of 156·5°C and an enthalpy of fusion of 28·5 $J \cdot g^{-1}$. After its insertion in the DSC apparatus, the sample was first cooled to −100°C for 15 min. A first scan was made at a heating-rate of 80°C·min^{-1} up to 200°C where it stayed for 30 sec. Then, it was quenched to −100°C at a cooling-rate of 320°C·min^{-1}. It was left for 10 min at that temperature before a second scan was made at a heating-rate of 20°C·min^{-1}. The values of T_g and T_m reported in this paper were taken at half-height of the heat capacity jump of the glass transition and at the maximum of the endotherm peak of the melting, respectively.

The determination of the SH content was performed by titration with iodine.

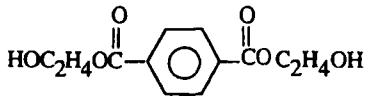
b) Synthesis of the Telechelic Monodispersed Diols

In a two necked round bottom flask equipped with a condenser and a distillation device, dimethyl terephthalate and an excess of ethylene glycol in a 1:12 molar ratio were introduced. Zinc acetate (0.4 mmol for 100 ml of ethylene glycol) was added as a catalyst and chloroacetic acid (1 mmol for 100 ml of ethylene glycol) was added to prevent the catalyst from being inhibited.

Methanol was recovered by distillation. The mixture was cooled, then dropwise added into demineralised water and the precipitate was heated up to 70°C for 24 hours under pressure.

The mixture was heated up to 100°C and quickly filtered to separate the diol DP_3, soluble in boiling water. Then, this filtrate was cooled down to 10°C and the crystals were dried under pressure at 80°C.

DP_3: bis(2-hydroxy ethylene) terephthalate (**A,1**).



T_m = 109°C. No T_g was observed by DSC.

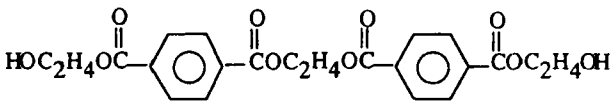
IR (KBr, cm^{-1}): 3600–3200 (F, broad); 2950 (F); 2890 (m); 1950 (f); 1700 (FF); 1500 (f), 1450 (m); 1400 (F); 1270 (FF); 1140 (F); 1070 (F); 1020 (F); 900 (F); 870 (m); 840 (m); 730 (F); 500 (m).

^{1}H-NMR (DMSO d_6): δ = 3.75 (m, 4 H); 4.50 (t, 4 H, J = 6.9 Hz): 5.00 (t, 2 H, J = 7.0 Hz); 8.15 (s, 4 H).

^{13}C-NMR (DMSO d_6): δ = 59.17; 67.11; 129.56; 133.80; 165.27.

$C_{12}H_{14}O_6$ (FW = 254.24 g.mol^{-1})	Calc.	C 56.69	H 5.55
	Found	57.08	5.28

Diol DP_5 is soluble in boiling THF. Hence it can be separated from the higher molecular weight diols. A white powder is obtained.



bis(2-hydroxy ethyl terephthaloyl) ethylene (A,2).

T_m = 169°C. No T_g was observed by DSC.

IR (KBr, cm^{-1}): 3600–3200 (F, broad); 2950 (F); 2890 (m); 1960 (f); 1700 (FF); 1500 (f); 1450 (f); 1410 (m); 1340 (m); 1270 (FF); 1130 (F); 1070 (F); 1020 (m); 900 (m); 870 (m); 830 (f); 730 (FF); 500 (m).

^{1}H-NMR (DMSO d_6): δ = 3.75 (q, 4 H, J = 6.9 Hz); 4.35 (t, 4 H, J = 7.0 Hz); 4.70 (s, 4 H); 5.00 (t, 2 H, J = 6.9 Hz); 8.15 (s, 8 H).

^{13}C-NMR (DMSO d_6): δ = 56.25; 59.11; 63.27; 67.15; 129.60; 129.72, 133.41; 134.00; 165.12; 165.22.

$C_{22}H_{22}O_{10}$ (FW = 446.41)	Calc.	C 59.19	H 4.97
	Found	59.93	4.71

c) Synthesis of the Aromatic Telechelic Monodispersed Dithiols

bis(5-mercapto-4-keto-3-oxa pentyl) terephthalate (B,1).

In a two necked round bottom flask equipped with a distillation device, diol DP_3 dissolved in THF and the thioglycolic acid in an initial molar ratio of 1:2, and benzene were placed. Paratoluene sulfonic acid was introduced as a catalyst. The reaction was then carried out in boiling benzene for 24 hours and the reaction equilibrium was shifted by elimination of water produced by azeotropy. Then, the mixture was washed several times with demineralised water and the α,ω-dithiol was extracted with chloroform, then precipitated and recrystallized from hexane. The yield was quantitative.

$$T_m = 32°C \qquad T_g = -11°C$$

IR (KBr, cm^{-1}): 3400 (broad, f); 2980 (F); 2850 (F); 2320 (f); 1740 (FF); 1410 (f); 1270 (FF); 1160 (f); 1130 (m); 1100 (m) 1050 (f); 1020 (f); 870 (f); 730 (m).

^{1}H-NMR ($CDCl_3$): δ = 1.95 (t, 2 H, J = 7.0 Hz); 3.25 (d, 4 H, J = 7.0 Hz); 4.45 (m, 8 H): 8.05 (s, 4 H).

^{13}C-NMR ($CDCl_3$): δ = 26.08; 62.80; 62.90; 129.43; 133.38; 165.04.

$C_{16}H_{18}O_8S_2$ (FW = 402.44 g.mol^{-1})	Calc.	C 47.75	H 4.51	S 15.93
	Found	48.09	4.39	16.11

%SH = 16.92 (Calc. 16.44).

bis(5-mercapto-4-keto-3-oxa pentyl terephthaloyl) ethylene (B,2)

The preparation of the dithiol **B,2** was similar to that of the previous one but it requires a longer reaction-time, a higher catalyst amount and also DMSO for increasing the solubility of the diol (yield = 92%).

$$T_m = 44°C \qquad T_g = -7°C$$

IR (KBr, cm^{-1}): 3400 (f, broad); 2980 (F); 2850 (F); 2320 (f); 1740 (FF); 1410 (f); 1270 (FF); 1160 (f); 1140 (m); 1100 (m), 1020 (f); 870 (f); 730 (m); 600 (m).

^{1}H-NMR ($CDCl_3$): δ = 1.95 (t, 2 H, J = 7.0 Hz); 3.25 (d, 4 H, J = 7.0 Hz); 4.45 (m, 8 H); 4.65 (s, 4 H); 8.05 (s, 8 H).

^{13}C-NMR ($CDCl_3$): δ = 29.09; 62.81; 62.92; 129.46; 133.42; 133.45; 165.10; 165.16.

$C_{26}H_{26}O_{12}S_2$ (FW = 594.61 g.mol^{-1})	Calc.	C 52.52	H 4.41	S 10.78
	Found	53.15	4.27	10.93

%SH = 11.58 (Calc. 11.12).

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