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Polymer 43 (2002) 1139–1154

polymer

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The synthesis of oligomers related to poly(ethyleneglycol terephthalate)

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Received 23 August 2001

Abstract

Three end-capped oligomers **35**, **41** and **45** related to poly(ethyleneglycol terephthalate) have been prepared starting from *t*-butylthioterephthalic acid **21** and its ethyleneglycol monoterephthalate derivative **25** terminally protected on the glycol moiety (by the tetrahydropyranyl group) and on the carboxylic acid moiety [by the 2-(2-pyridyl)-group].

Keywords: Oligoesters; Oligo(ethyleneglycol terephthalate); Polymer

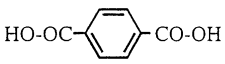
1. Introduction

Monodisperse polymers are a prerequisite for studying mechanisms of their crystallisation, a state of affairs which has not yet been realised. However, progress has been made using pure oligomers having a range of discrete lengths as models of a particular polymer to study the onset and detailed mechanisms of chain folding [1,2]. Previously, we have synthesised oligoalkanes in which van der Waals forces alone are responsible for the interactions between the chains [3,4], and a variety of oligoamides in which hydrogen bonds are the major intermolecular forces [5–7]. We now report syntheses of oligoesters related to poly(ethyleneglycol terephthalate) the study of which is expected to resolve some questions concerning mechanisms of polymer crystallisation in which there are only weak dipolar interactions between the chains in addition to van der Waals forces.

Pioneering synthetic work in this field was carried out over 30 years ago by Zahn [8] and by Wegner [9]. In the former work α,ω-dimethoxyester derivatives of oligomers containing up to nine terephthalate units (and therefore eight glycol units) were prepared and purified by chromatography on silica using dioxan/1,1,2,2-tetrachloroethane (TCE) (1:9) at room temperature, but temperatures of 40–50 °C and 80 °C were required to ensure solubility of the 10 and 11 terephthalate-containing compounds, respectively [10]. In our work with oligomers of alkanes and of various nylons, all the intermediates, either naturally or by design, were soluble in common organic solvents at room temperature and were purified by chromatography on silica, their purities being assessed by HPLC and by ^{1}H NMR. The *final* products in both series were soluble only at considerably high temperatures. In view of the high toxicity of TCE, in the present work we sought to incorporate a structural feature which would render the intermediates readily soluble at room temperature up to the ultimate stage in the synthesis. Furthermore, we have exploited the methodology of Whiting [11] based on a 'geometrical approach' to give the most rapid increase in the molecular weight of the growing chain and some 'arithmetical' chain extensions, illustrated in Scheme 1.

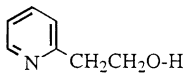
The following abbreviations will be used in this paper:

Terephthalic acid, is HO-T-OH



Tetrahydropyranyl is thp-

2-(2-Pyridyl)ethanol is Pet-H



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0032-3861/02/$ - see front matter
PII: S0032-3861(01)00694-2

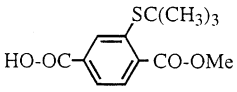
Ethylene glycol, H-OCH$_2$CH$_2$O-H
is H-G-H

t-Butyl, -C(CH$_3$)$_3$
is -Bu^t

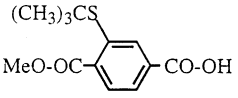
TMS is (CH$_3$)$_3$Si-

Benzyl, C$_6$H$_5$CH$_2$-
is Bzl-

NB



is HO-T^{SBut}-OMe



is MeO-^{tBuS}T-OH

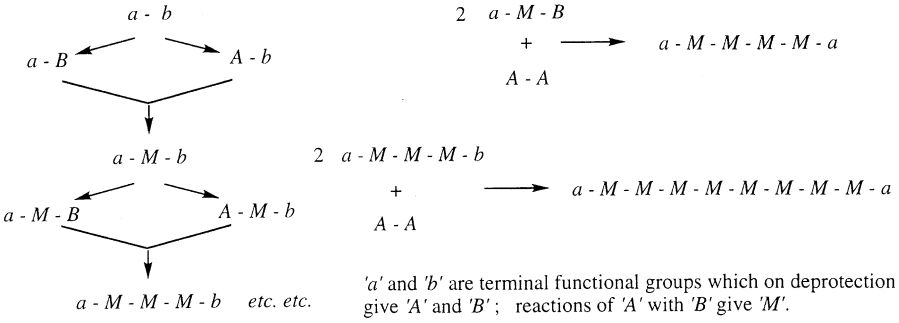
2. Synthetic work

Zahn synthesised a 'monomer' **1** [12] equivalent to *a–b* in Scheme 1 which was selectively deprotected to **2** and **3** and *could* have been used in the present work as shown in Scheme 2. However, in order to provide the desired solubility of all subsequent intermediates to enable chromatography on silica to be used for purification, the trimethylsilyl group (–TMS) was introduced as a substituent on the terephthalic acid moiety [13] but it was realised that on reaction with trifluoroacetic acid (TFA), the TMS group could also be cleaved, as for example in the TMS-analogue of **1** which could give compound **2** once again. Consequently the tetrahydropyranyl group (thp) which is very susceptible to removal by *mild* acid and had been used previously by Wegner [9], was chosen as the protecting group for the 2-monoester of ethylene glycol. In any *final* desilylation reaction in the *absence* of acid-sensitive protecting group, TFA was a possible reagent which needed to be examined.

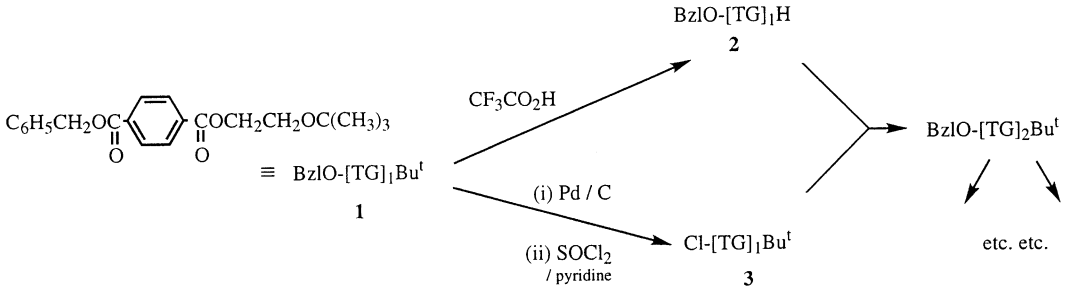
Preliminary experiments were necessary to find conditions for the selective removal of the trimethylsilyl group from a terephthalate diester. The diethyl ester **5**, prepared from the known compound **4** [13], gave desilylation *and* polar products with boiling TFA, thereby precluding its ultimate use (because of problems of purification), but with cesium fluoride in boiling CH$_3$CN [14] over 62 h gave diethyl terephthalate cleanly, in 97.5% yield (Scheme 3), which augured well for the final step in the synthesis of oligoesters from trimethylsilyl intermediates.

Conversion of **4** into the dibenzyl ester **6** followed by half hydrolysis gave **7**, the structure of which was determined by a ^{1}H NOESY experiment (Scheme 4).

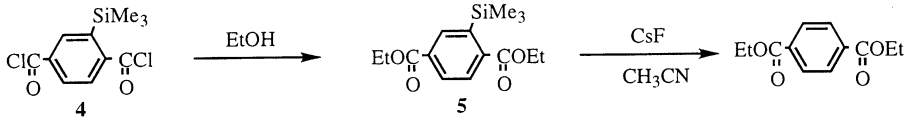
The mono-tetrahydropyranyl ether derivative of ethylene glycol (thp-G-H) **10** [15] was prepared by the acid catalysed reaction of bis (2-hydroxyethyl) terephthalate **8** [16] and dihydropyran to form **9**, followed by hydrolysis with sodium



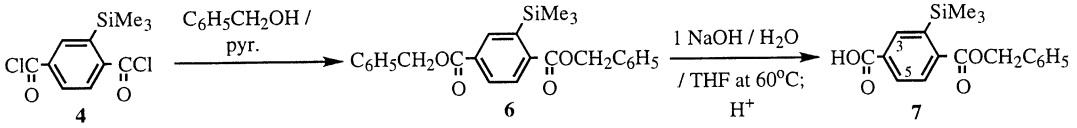
Scheme 1.



Scheme 2.



Scheme 3.

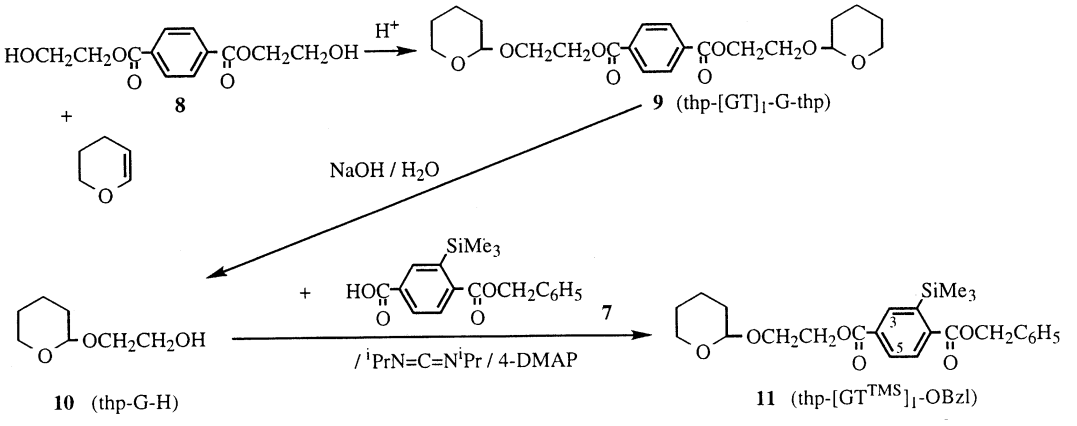


Scheme 4.

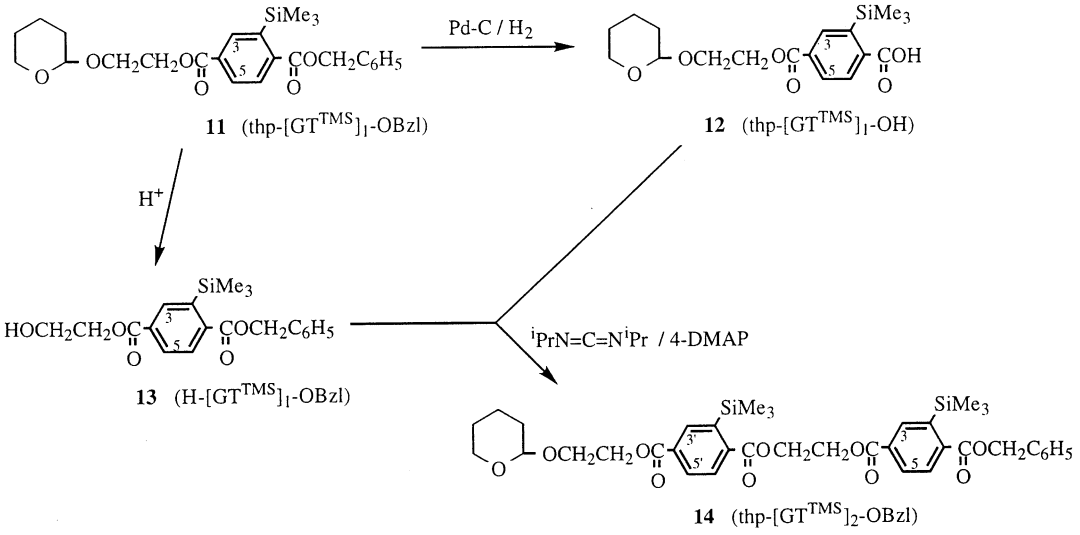
hydroxide. The carboxylic acid **7** was coupled with **10** using di-isopropylcarbodiimide /4-dimethylaminopyridine (4-DMAP) to give the fully protected monomer, thp-[GT^{TMS}]$_1$-OBz1 **11** (i.e. *a–b* in Scheme 1), Scheme 5.

Catalytic hydrogenolysis of the fully-protected monomer **11** removed the benzyl group slowly (5 days at room temperature) to yield the carboxylic acid **12**, while dilute acid cleaved the thp-group from **11** to give the alcohol **13**. Formation of the ester linkage between **12** and **13** was achieved as before (Scheme 6) to give the fully protected 'dimer' **14**. The thp end group of **14** was removed by acid and the exposed alcohol **15** converted into terminal ethanoate ester **16**; this in turn was subjected to hydrogenolysis of the terminal benzyl ester to the carboxylic acid **17** which was finally converted into the ethyl ester **18**. *All* attempts to replace the TMS-solubilising group by H using cesium fluoride or tetrabutylammonium fluoride [14] under a wide variety of conditions gave complex mixtures of products, Scheme 7, so this strategy was abandoned.

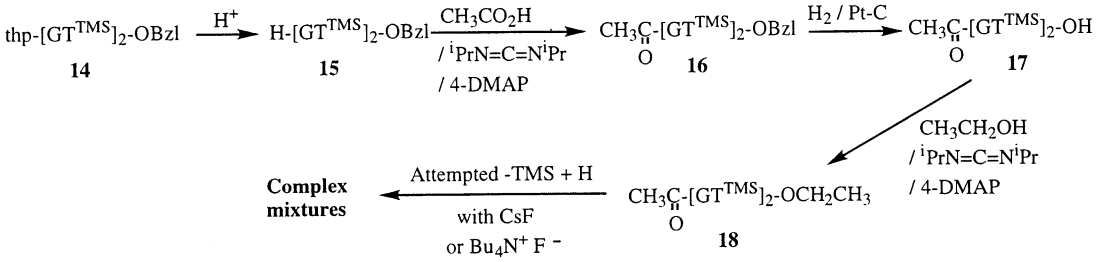
The *t*-butylthio group, $-SC(CH_3)_3$, was the next functionality examined to solubilise intermediates in the synthesis of oligoesters since replacement of thioethers by hydrogen using Raney nickel is well known. Commercially available dimethyl aminoterephthalate was converted into the iodoterephthalate ester **19** and reacted with copper (I) *t*-butylthiolate, prepared from copper (I) oxide and excess



Scheme 5.



Scheme 6.



Scheme 7.

thiol [17], to give the S-*t*-butyl diester **20** (69%). As a trial experiment, treatment of **20** with Raney nickel in dioxan overnight at room temperature gave dimethyl terephthalate quantitatively i.e. complete desulphurisation.

Saponification of **20** with excess aqueous sodium hydroxide followed by acidification gave the diacid **21**, while with one molar equivalent of base/acidification, a regioselective hydrolysis occurred at the site more remote to the bulky thiolate to give **22**, the structure of which was established by a NOESY NMR experiment, Scheme 8.

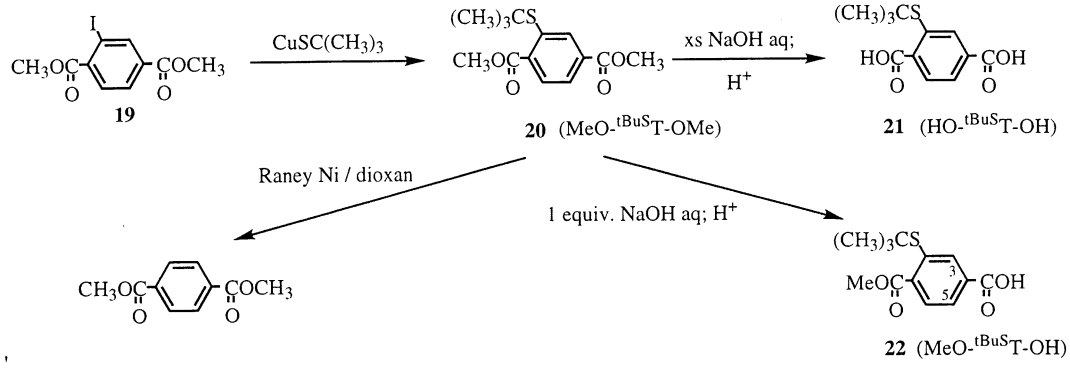
The presence of the *t*-butylthio functionality in intermediates ruled out the catalytic hydrogenolysis of benzyl group as the method for exposing the carboxylic acid from the half ester of phthalic acid moieties due to poisoning of the catalyst and cleavage of C–S bonds. The 2-(2-pyridyl)ethyl ester group (Pet) is an effective protecting group for carboxylic acids in peptide synthesis and is removed readily with excess methyl iodide followed by Et_2NH or morpholine [18,19]. Katritzky also found that the 2-(2-pyridyl)ethyl group could be used to protect aromatic thiols *without* concurrent *S*-methylation during the deprotection stage [20]. In the present work, it has been demonstrated that the *t*-butylthio ether group is similarly unaffected by methyl iodide during deprotection of Pet-carboxylates and as found before [20], added base is unnecessary: presumably the iodide anion was sufficiently basic to bring about the deprotection reaction.

Compound **21** was reacted with 2-(2-pyridyl)ethanol to give the diester **23**, which with one molar equivalent of base gave **24**, the structure of which was again determined by a ^{1}H NOESY experiment. Ester formation of **24** with the half protected glycol **10** (H-G-thp) gave the new fully protected monomer **25** (i.e. *a*–*b* in Scheme 1), Scheme 9.

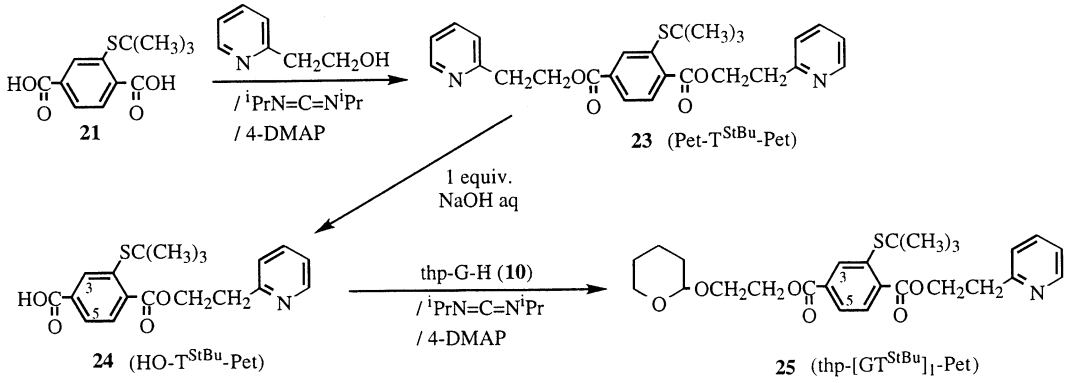
Removal of the 2-(2-pyridyl)ethyl group from **25** with methyl iodide gave the carboxylic acid **26** and acid hydrolysis of **25** gave the glycol monoester **27**. Formation of the ester bond using **26** and **27** gave the fully protected dimer **28**. Repetition of these reactions with **28** gave the dimer carboxylic acid **29** and the dimer alcohol **30**, respectively. The fully protected 'tetramer' **31** was formed from **29** and **30** (Scheme 10).

The preparation of the first oligoester in this work is shown in Scheme 11 and involved the terephthalic acid derivative **21** and its monomethyl ester **22**. Reaction of **21** with two equivalents of thp-G-H **10** gave the diester **32** which on treatment with acid to remove the pyranyl groups produced the α,ω-diol **33**, both end groups of which were converted with **22** to **34**. Replacement of the *t*-butylthio groups in **34** by hydrogen using Raney nickel under more vigorous conditions than were used in the model experiment with **20**, gave the oligoester **35** (MeO-[TG]$_2$T-OMe) (63%) containing three terephthalic acid units—the *trimer*, prepared earlier [10].

The α,ω-dicarboxylic acid **37** (HO-[$^{t\mathrm{BuS}}$TG]$_2$-T$^{S t\mathrm{Bu}}$-OH) which on terminal esterification with methanol *would* have given **34** was used as *A*–*A* (Scheme 1) for two 'arithmetical' chain extension reactions; its preparation is shown in Scheme 12. The terminal monoester of ethylene glycol **27** (H-[GT$^{S t\mathrm{Bu}}$]$_1$-Pet) was reacted with *t*-butylthioterephthalic acid **21** (HO-$^{t\mathrm{BuS}}$T-OH) to give **36** (Pet-[$^{t\mathrm{BuS}}$TG]$_2$-T$^{S t\mathrm{Bu}}$-Pet)



Scheme 8.

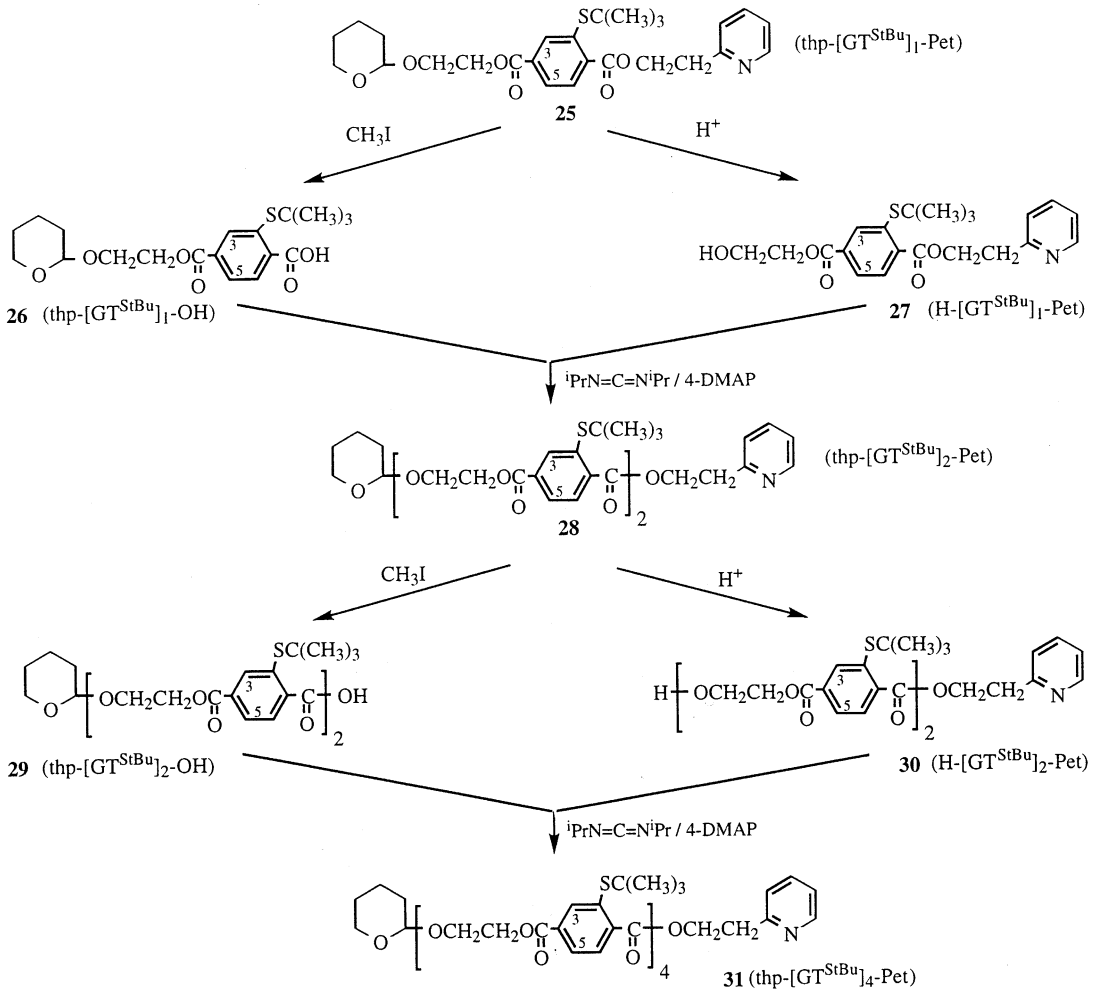


Scheme 9.

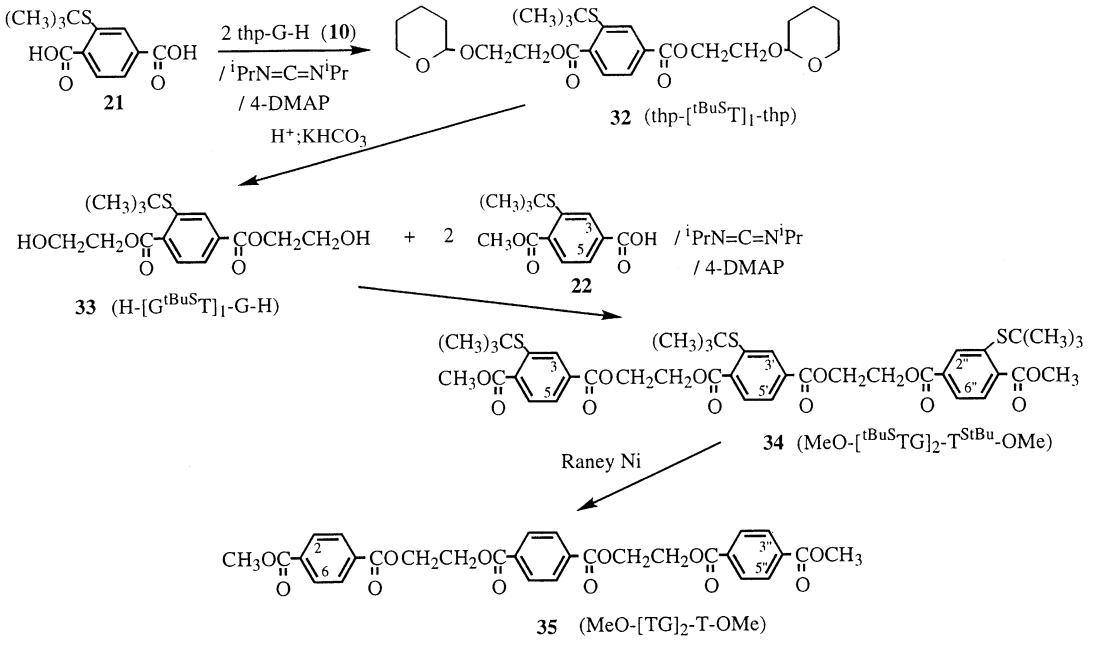
from which the terminal 2-(2-pyridyl)ethyl groups were removed with methyl iodide.

The *pentamer* **41** (MeO-[TG]$_4$T-OMe) was synthesised as follows from the α,ω-dicarboxylic acid **37** (HO-[$^{t\mathrm{BuS}}$TG]$_2$-T$^{S t\mathrm{Bu}}$-OH) (Scheme 13). Firstly, the monomethyl ester of *t*-butylthioterephthalic acid **22** was converted to the ester **38** (MeO-[$^{t\mathrm{BuS}}$TG]$_1$-thp) with thp-G-H **10** and the thp protecting group removed with acid to the terminal alcohol **39** (MeO-[$^{t\mathrm{BuS}}$TG]$_1$-H). Two molecular proportions of **39** to one of **37** gave **40** which was desulphurised with Raney nickel to the α,ω-dimethyl pentamer (MeO-[TG]$_4$-T-OMe) **41** (41% yield), prepared earlier [10].

The *elevenmer* **45** (MeO-[TG]$_{10}$-T-OMe) was obtained by a process analogous to the one used for the *pentamer*



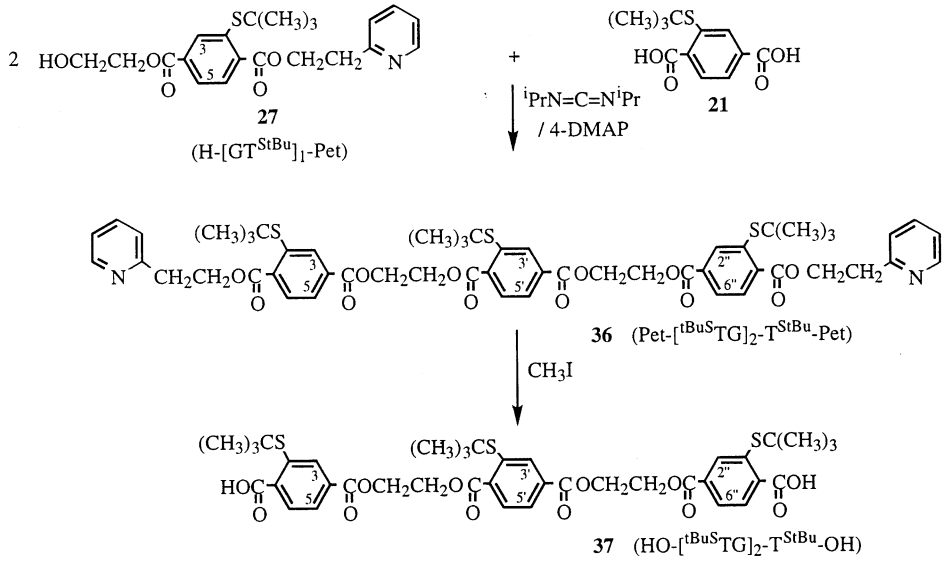
Scheme 10.



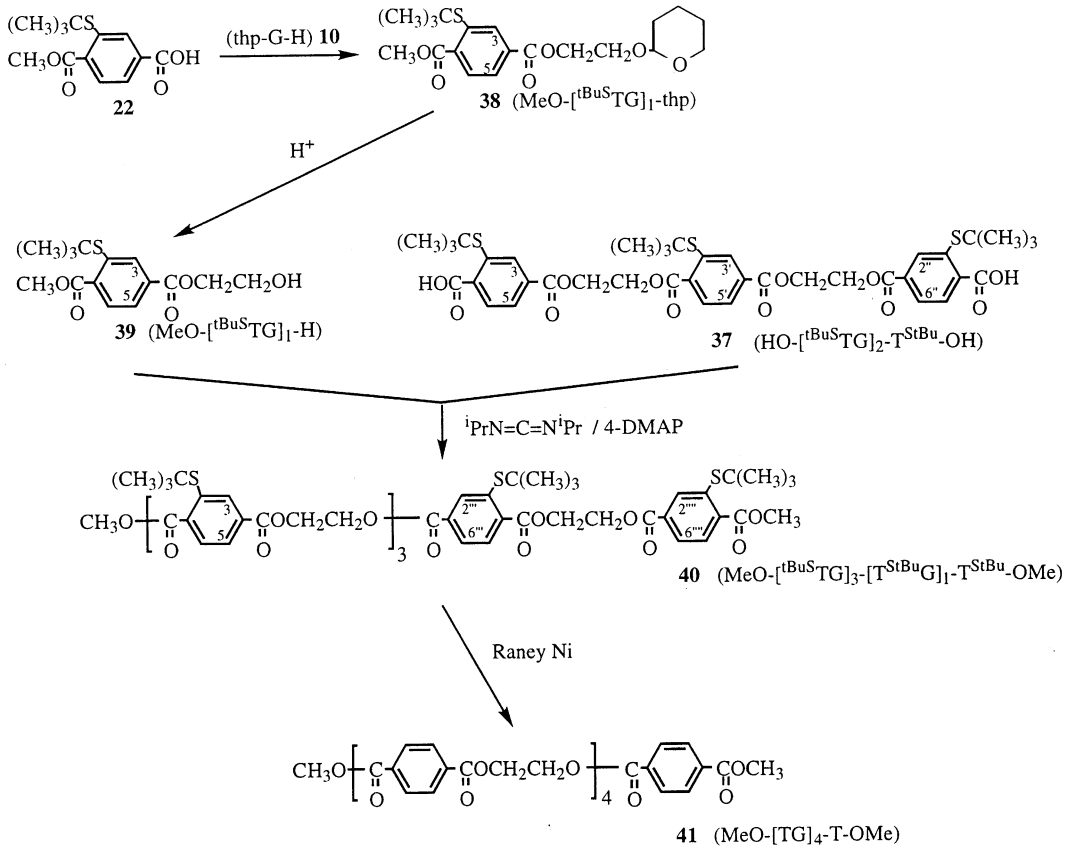
Scheme 11.

(described earlier). Removal of the thp group with acid from the fully protected tetramer **31** (thp-[GT$^{S\!t\!Bu}$]$_4$-Pet) gave **42** (H-[GT$^{S\!t\!Bu}$]$_4$-Pet) which was reacted with the α,ω-dicarboxylic acid **37** (HO-[$^{t\!Bu\!S}$TG]$_2$-T$^{S\!t\!Bu}$-OH) to give **43** (Pet-[$^{t\!Bu\!S}$TG]$_6$-[T$^{S\!t\!Bu}$G]$_4$-T$^{S\!t\!Bu}$-Pet).Treatment of compound **43** with *excess* methyl iodide/$KHCO_3$/acetonitrile conveniently gave the α,ω-dimethyl ester **44** (MeO-[$^{t\!Bu\!S}$TG]$_6$-[T$^{S\!t\!Bu}$G]$_4$-T$^{S\!t\!Bu}$-OMe) presumably via methylation of the intermediate dipotassium carboxylate salt, the Raney nickel desulphurisation of which gave the elevenmer **45** of ca. 95% purity by ^{1}H NMR, in 9% yield, a compound which had been prepared earlier [10], Scheme 14. However, pretreatment of the Raney nickel with *p*-toluenesulphonic acid and carrying out the experiment under milder conditions gave purer samples of **45**: 7% from the first extract (98% pure) plus 5% from the second extract (99.7% pure).

The solubilising influence of the *t*-butylthiolate intermediates in common organic solvents fulfilled all expectations in the present work and was considered of utmost priority, to avoid the use of the highly toxic 1,1,2,2-tetrachloroethane solvent. ^{1}H NMR spectroscopy was used to confirm the structure of each compound synthesised, in particular, the ratios of the terminal methyl groups to



Scheme 12.



Scheme 13.

internal aromatic protons in the penultimate *t*-butylthiolate intermediates and the final oligoesters confirmed the lengths of the molecules. However, the final desulphurisation reactions have proved, unexpectedly, to be the weakest link in our synthetic strategy, rapidly decreasing in efficiency as the chain length increased. This is obviously exceedingly disappointing, but that is often the case in research work. We have to acknowledge that Zahn and coworkers conducted a splendid piece of synthetic work over 30 years ago making the elevenmer **45**, at a time when the fear of health hazards did not loom so prominently in the minds of chemists as they do at the present time.

3. Experimental

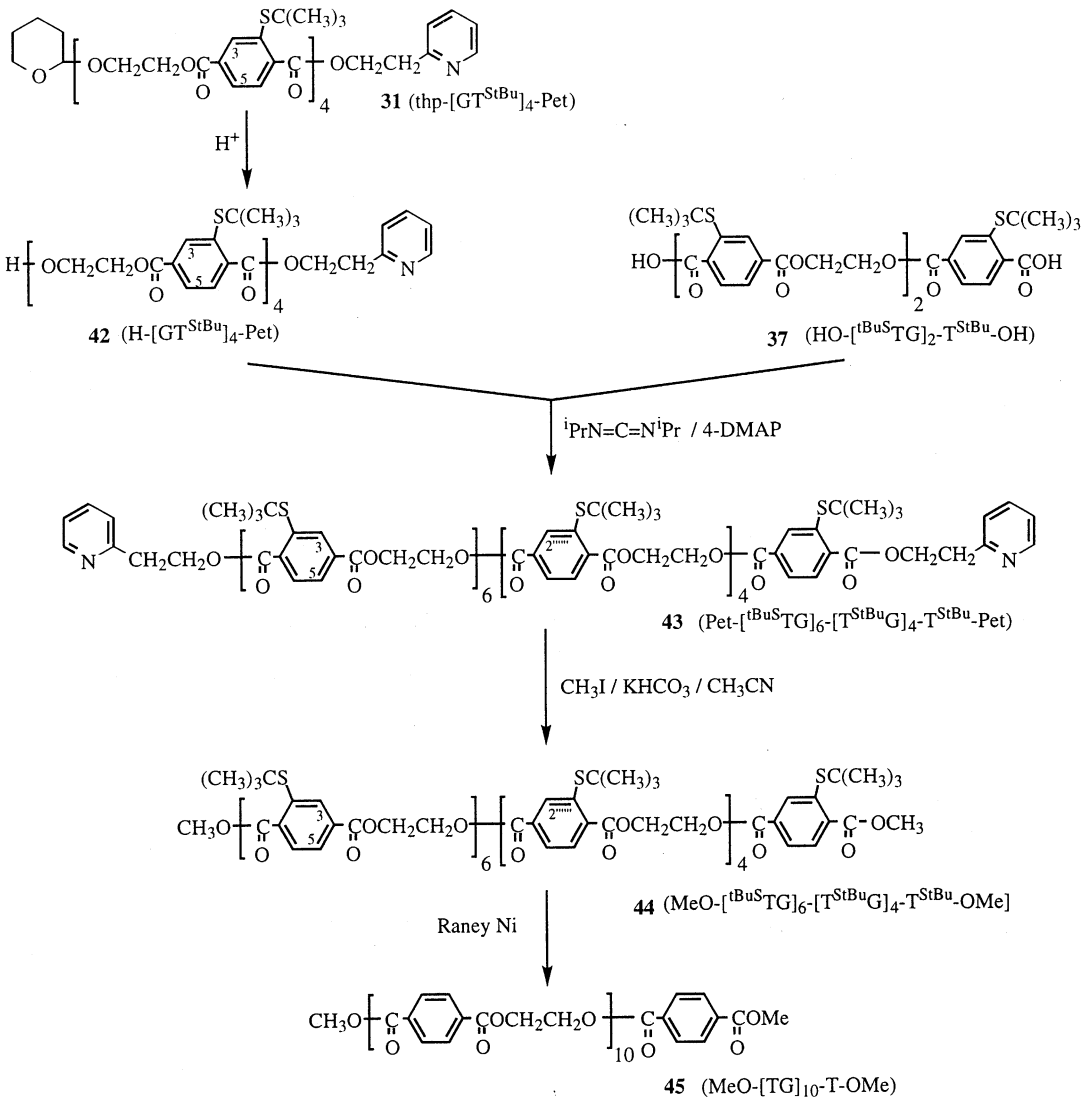
NMR spectra were recorded on the following instruments at the frequencies listed: Varian Mercury 200 (^{1}H, 199.991 MHz) and Varian Inova 500 (^{1}H, 499.782 MHz). Chemical shifts are reported using the high-frequency positive convention from TMS; *J* values are in Hz); NOESY experiments were carried out on compounds **7**, **20**, **22** and **24** to establish stereochemistry/assignments. Elemental analyses were performed on an Exeter Analytical Inc CE440 elemental analyser.

*3.1. Reaction of bis(2-hydroxyethyl)terephthalate **8** with 3,4-dihydro-2H-pyran to form **9** (thp-[GT]$_1$-G-thp)*

Compund **8** [15] (5.00 g) in THF (50 ml) and *p*-toluenesulphonic acid (42 mg) was treated dropwise with stirring with 3,4-dihydro-2H-pyran (5.4 ml, 5 g) in THF (10 ml) over 5 min and the mixture was kept at room temperature for 28 h. Saturated sodium bicarbonate solution (5 ml) was added, solvent (50 ml) was removed under vacuum at room temperature on a rotatory evaporator and the residue diluted with dichloromethane (60 ml) and washed with water (100 ml). The solution was dried over sodium sulphate mixed with potassium bicarbonate (ca. 100 mg) and the solvent removed in vacuo at 50–53 °C/5 × 10^{-2} mb for 20 h to give **9** (thp-[GT]$_1$-G-thp) (8.55 g, 100%) a liquid (Found: C, 62.76; H, 7.21. $C_{22}H_{30}O_8$ requires C, 62.55; H, 7.16%); δ_H($CDCl_3$) 8.122 (d, C_6H_4), 4.701 (t, chiral H* in thp), 4.551 (m, H_a in two thpOCH_AH$_B$CH_aH$_b$OC=O), 4.497 (m, H_b in two thpOCH_AH$_B$CH$_a$$H_b$OC=O), 4.054 (m, H_A in two thpOCH_AH$_B$CH$_a$H$_b$), 3.796 (m, H_B in two thpOCH$_A$$H_B$-CH$_aH_b$), 3.875 and 3.525 (m, unassigned in H in CH_2O of two thp), 1.88–1.47 (complex m $CH_2CH_2CH_2$ of two thp).

*3.2. Hydrolysis of **9** (thp-[GT]$_1$-G-thp) to give **10** (thp-G-H)*

The bis-ester **9** (122 g) in ethanol (350 ml) was stirred



Scheme 14.

vigorously during the addition of a warm (55 °C) solution of sodium hydroxide (32.7 g) in water (140 ml) giving a thick precipitate almost at once. After 17 h, the solid was separated and washed with ethanol and the filtrate evaporated until distillation was slow. The residue was dissolved in dichloromethane (400 ml), washed first with saturated brine (400 ml) and then with saturated sodium bicarbonate (50 ml) and the solution dried with $Na_2SO_4/KHCO_3$ as in Section 3.1. Evaporation of the solvent at 30 °C and distillation of the residue bp 65–67 °C/1 mm Hg (Ref. [15] 70–72 °C/1 mm Hg) gave **10** (thp-G-H) (72.4 g, 91% based on **8**.

3.3. Silicon derivatives

3.3.1. Diethyl trimethylsilylterephthalate 5

Trimethylsilyterephthaloyl chloride **4** [13] (2.01 g) in absolute ethanol (15 ml) was kept at room temperature for 4 h, then cooled to −18 °C in a freezer. After 2 h, the crystalline product was separated, washed with chilled ethanol and dried under high vacuum at room temperature to give **5** (EtO-T^{TMS}-OEt) (1.76 g, 82%) mp 53–54 °C unchanged by recrystallisation (Found: C, 60.95; H, 7.52. $C_{15}H_{22}O_4Si$ requires C, 61.19; H, 7.53%); $\delta_H(CDCl_3)$ 8.333 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.058 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 8.017 (d, 6-H), 4.402 and 4.392 (overlapping q, two CH_3CH_2O), 1.413 (overlapping t, two CH_3CH_2O), 0.352 [s, $Si(CH_3)]_3$.

3.3.2. Desilylation of diethyl trimethylsilylterephthalate 5

Compound **5** (2.00 g), anhydrous cesium flouride (10.65 g) and acetonitrile (40 ml) were refluxed with strong stirring under argon for 62 h. The mixture was cooled, diluted with water, the solution extracted with dichloromethane and the extracts dried with sodium sulphate. Evaporation of the solvent and drying under high vacuum gave a crystalline residue (1.47 g, 97.5%) identified by

NMR as pure diethyl terephthalate: $\delta_H(CDCl_3)$ 8.096 (s, C_6H_4), 4.401 (q, two CH_2CH_3), 1.410 (t, two CH_2CH_3).

3.3.3. Dibenzyl trimethylsilylterephthalate **6**

Trimethylsilylterephthaloyl chloride **4** (27.53 g) in THF (50 ml) was added dropwise for 25 min to a solution of benzyl alcohol (21.74 g) and pyridine (16.5 ml) in THF (100 ml) with ice cooling. After 3 h, the precipitate (pyr.HCl) was separated and washed with THF, and the filtrate was dissolved in ether (250 ml) and washed in turn with dil. HCl (1M, 200 ml), saturated $NaHCO_3$ (30 ml) and saturated brine (100 ml). The solution as dried with Na_2SO_4 and the solvent evaporated to leave a solid (43.8 g) which was crystallised from ethanol to give **6** (BzlO-T^{TMS}-OBzl) (35.5 g, 85%)mp 70–72 °C (Found: C, 71.57; H, 6.25. $C_{25}H_{26}O_4Si$ requires C, 71.74; H, 6.26%); $\delta_H(CDCl_3)$ 8.287 (d, 3-H; $J_{meta} = 1$ Hz), 8.079 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 8.054 (d, 6-H), 7.47–7.33 (complex m, two C_6H_5), 5.391 and 5.370 (both s, two $C_6H_5CH_2O$), 0.331 [broad s, $Si(CH_3)_3$].

3.3.4. Mono-benzyl 2-trimethylsilylterephthate **7** (HO-T^{TMS}OBzl)

Compound **6** (15.8 g) in THF (75 ml) was stirred during the addition of sodium hydroxide (1.69 g) in water (22.5 ml) and the two phase mixture was stirred at 60 °C for 4.5 h. Most of the THF was evaporated and the pasty residue was dissolved in water (90 ml) and washed with ether (2 × 50 ml). Dichloromethane was added followed by conc. HCl (10 ml). The mixture was stirred until most of the resulting precipitate had dissolved and filtered through Celite. The organic layer was separated, dried with Na_2SO_4, the solvent evaporated and the residue recrystallised from acetonitrile to give **7** (HO-T^{TMS}-OBzl) (9.59 g, 77%) mp 145.5–147 °C (Found: C, 65.71; H, 6.12. $C_{18}H_{20}O_4Si$ requires C, 65.83; H, 6.14%); $\delta_H(CDCl_3)$ 8.421 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.134 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 8.096 (d, 6-H), 7.480 to 7.344 (complex m, C_6H_5), 5.385 [s, 1-$C_6H_5CH_2OC(=O)$] 0.355 [s, $Si(CH_3)_3$].

3.3.5. Preparation of the fully protected monomer **11** (thp-[GT^{TMS}]$_1$-Obzl)

Compound **7** (HO-T^{TMS}-Obzl) (1.728 g) and diisopropylcarbodiimide (0.775 g) in dichloromethane (3 ml) was treated with a mixture of **10** (thp-G-H) (0.803 g) and 4-dimethylaminopyridine (0.057 g) washed in with DCM (7 ml) and the mixture stirred at room temperature for 16.5 h. The diisopropylurea which separated from the mixture was filtered off, the filtrate evaporated and the residue treated with cyclohexane from the solution of which was further urea biproduct filtered off. The filtrate was washed with saturated $NaHCO_3$ solution, the organic phase dried with Na_2SO_4 containing $NaHCO_3$ (ca. 200 mg) and the solvent evaporated to give an oil (2.76 g). Chromatography of the crude product on silica using ethyl acetate-light petroleum [bp 40–60 °C] (8.92 v/v) gave the fully protected monomer **11** (thp-[GT^{TMS}]$_1$-OBzl) (1.934 g, 81%) an oil (Found: C, 65.70; H, 7.11. $C_{25}H_{32}O_6Si$ requires C, 65.77; H, 7.05%); $\delta_H(CDCl_3)$ 8.359 (broad s, 3-H; J_{meta} unresolved), 8.066 (broad s, 5- and 6-H; J_{ortho} unresolved), 7.474–7.334 (complex m, C_6H_5), 5.370 [s, 1-$C_6H_5H_2O(C=O)$], 4.716 (t, chiral H* in thp), 4.543 (m, H_a in 4-thpOCH$_A$H$_B$CH_aH$_b$OC=O),4.491 (m, H_b in 4-thpOCH$_A$H$_B$CH_aH$_b$OC=O), 4.049 (m, H_A in 4-thpOCH_AH$_B$CH$_a$H$_b$), 3.780 (m, H_B in 4-thpOCH$_A$$H_BCH_aH_b$), 3.880 and 3.528 (m, unassigned H in CH_2O of thp), 1.88–1.48 (complex m, $CH_2CH_2CH_2$ of thp) 0.335 [s, $Si(CH_3)_3$].

3.3.6. Deprotection of 1-benzyl ester of **11** (thp-[GT^{TMS}]$_1$-OBzl) to **12** (thp-[GT^{TMS}]$_1$-OH)

Compound **11** (4.16 g) and 5% platinum–carbon (2.028 g) in dioxan (65 ml), initially under argon, was treated at room temperature with hydrogen at 40 psi for 114 h. The catalyst was filtered off through Hyflo and the solvent evaporated to give an oil (3.813 g) which was chromatographed on silica using dichloromethanemethanol (99:1 v/v) for a preliminary purification followed by a repeat separation under the same conditions to give **12** (thp-[GT^{TMS}]$_1$-OH) (1.09 g, 33%) mp 71–73 °C (Found: C, 59.25 H, 7.29. $C_{18}H_{26}O_6Si$ requires C, 58.99; H, 7.15%); $\delta_H(CHCl_3)$ 8.398 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.188 (d, 6-H; $J_{ortho} = 8.0$ Hz), 8.122 (dd, 5-H), 4.376 (t, chiral H* in thp), 4.564 (m, H_a in 4-thpOCH$_A$H$_B$CH_aH$_b$OC=O), 4.512 (m, H_b in 4-thpOCH$_A$H$_B$CH$_a$$H_b$OC=O), 4.070 (m, H_A in 4-thpOCH_AH$_B$CH$_a$H$_b$), 3.805 (m, H_B in 4-thpOCH$_A$$H_B$-CH$_aH_b$), 3.898 and 3.548 (m, unassigned H in CH_2O of thp), 1.94–1.46 (complex m $CH_2CH_2CH_2$ of thp), 0.374 [s, $Si(CH_3)_3$].

3.3.7. Deprotection of thp of **11** (thp-[GT^{TMS}]$_1$-OBzl) to **13** (H-[GT^{TMS}]$_1$-OBzl)

Compound **11** (4.165 g) in a mixture of ethanol (80 ml) and water (5 ml) was treated with *p*-toluenesulphonic acid (0.800 g for 50 h at room temperature. Dichloromethane (80 ml) was added to the solution which was then shaken with a mixture of water (750 ml) and saturated $NaHCO_3$ (50 ml), the organic phase separated and washed with water (800 ml) and finally dried with Na_2SO_4. The solvent was evaporated and the residual oil (3.61 g) was chromatographed on silica using dichloromethane–methanol (97:3 v/v) to give **13** (H-[GT^{StBu}]$_1$-OBzl), an oil after pumping under high vacuum, (2.93 g, 86%) (Found: C, 64.30; H, 6.58. $C_{20}H_{24}O_5Si$ requires C, 64.49; H, 6.49%); $\delta_H(CDCl_3)$ 8.349 (m, 3-H), 8.064 and 8.061 (components of AB spectrum, unassigned 5-H and 6-H), 7.472–7.338 (m, C_6H_5), 5.373 [s, 1-$C_6H_5CH_2O(C=O)$, 4.495 [m, 4-HOCH$_2$-CH_2O(C=O)], 3.978 [t, 4-HOCH_2CH$_2$O(C=O)], 2.006 [s, 4-*H*OCH$_2$CH$_2$O(C=O)], 0.338 [s, $Si(CH_3)_3$].

3.3.8. Preparation of the fully protected dimer **14** (thp-[GT^{TMS}]$_2$-OBzl) from **12** and **13**

Compounds **12** (1.126 g), **13** (1.114 g) and 4-dimethylaminopyridine (0.039 g) dissolved in dichloromethylene

were treated with diisopropylcarbodiimide in the same solvent (17 ml total volume) for 6 h and the crude product (1.981 g) isolated as in Section 3.3.5; chromatography on silica using ethyl acetate-light petroleum [bp 40–60 °C] (10:90 v/v) gave the fully protected dimer **14** (thp-[GT^{TMS}]$_2$-OBzl), an oil after pumping under high vacuum, (2.117 g, 81%) (Found: C, 63.06; H, 6.66. $C_{38}H_{48}O_{10}Si_2$ requires C, 63.31; H, 6.71%); $\delta_H(CDCl_3)$ 8.359 and 8.340 (both m, 3- and 3′-H), 8.09–8.04 (components of AB spectrum, unassigned 5-, 5′-, 6- and 6′-H), 7.462–7.332 (m, C_6H_5), 5.365 [s, 1-$C_6H_5CH_2O$(C=O)], 4.713 (t, chiral H* in thp), 4.689 (s, O=$COCH_2CH_2OC$=O), 4.544 (m, H_a in 4′-thp$OCH_AH_BCH_aH_bOC$=O), 4.492 (m, H_b in 4′-thp$OCH_AH_BCH_aH_bOC$=O), 4.049 (m, H_A in 4′-thp-$OCH_AH_BCH_aH_b$), 3.783 (m, HB in 4′-thp$OCH_AH_BCH_aH_b$) 3.878 and 3.528 (m, unassigned H in CH_2O of thp), 1.88–1.48 (complex m $CH_2CH_2CH_2$ of thp), 0.338 and 0.310 [both s, $Si(CH_3)_3$].

3.3.9. Deprotection of thp of **14** (thp-GT^{TMS}]$_2$-OBzl) to **15** (H-[GT^{TMS}]$_2$-OBzl)

Compound **14** (1.756 g) was dissolved in a mixture of water (1.4 ml) and ethanol (25 ml) and *p*-toluenesulphonic acid (0.250 g) was added. After 40 h at room temperature, water (250 ml) and saturated $NaHCO_3$ (50 ml) was added to the solution which was extracted with dichloromethane (40 ml) and the organic phase was separated, dried (Na_2SO_4) and the solvent evaporated. The crude product (1.80 g) was chromatographed on silica using dichloromethane–methanol (98:2 v/v) and the main component recrystallised from cyclohexane to give **15** (H-[GT^{TMS}]$_2$-OBzl) (1.38 g, 89%) mp 72–73 °C (Found: C, 62.09; H, 6.29. $C_{33}H_{40}O_9Si_2$ requires C, 62.24; H, 6.33%); $\delta_H(CDCl_3)$ 8.349 and 8.339 (both broad s, unassigned 3-, 3′-H), 8.059 and 8.049 (components of AB spectrum, unassigned 5-, 5′-, 6- and 6′-H), 7.46–7.33 (m, C_6H_5), 5.364 [s, 1-$C_6H_5CH_2O$(C=O)], 4.691 (s, O=$COCH_2CH_2OC$=O), 4.497 (m, 4′-$HOCH_2CH_2OC$=O), 3.979 [m, 4′-$HOCH_2CH_2O$(C=O)], 1.953 [t, 4′-*H*OCH_2CH_2O(C=O)], 0.342 and 0.310 [two unassigned s, $Si(CH_3)_3$].

3.3.10. Formation of terminal ester **16** by the acetylation of the terminal alcohol group in **15** (H-[GT^{TMS}]$_2$-OBzl)

Compound **15** (1.34 g), acetic acid (0.139 g) and dimethylaminopyridine (0.025 g) in dichloromethane (5 ml) was treated at room temperature with diisopropylcarbodiimide (0.292 g) in dichloromethane (8 ml) for 1.5 h. The mixture was filtered and the filtrate washed with hydrochloric acid (2M, 10 ml) and then with saturate brine/water (20 ml, 1:1 v/v) and the solvent evaporated. The residue was treated with cyclohexane as in Section 3.3.5 and the crude product was chromatographed on silica using ethyl acetate-light petroleum [bp 40–60 °C] (12:88 v/v) to give **16** {CH_3(C=O)-[GT^{TMS}]$_2$-OBzl} (1.355 g, 95%) an oil (Found: C, 62.09; H, 6.29. $C_{35}H_{42}O_{10}Si_2$ requires C, 61.92; H, 6.24%), $\delta_H(CDCl_3)$ 8.338 (broad s, 3-, 3′-H), 8.055 and 8.051 (components of AB spectrum, unassigned 5-, 5′-, 6- and 6′-H), 7.464–7.33 (m, C_6H_5), 5.364 [s, 1-$C_6H_5CH_2O$(C=O)], 4.690 (s, O=$COCH_2CH_2OC$=O), 4.539 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)]], 4.422 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)], 2.092 [s, CH_3(C=O)O], 0.341 and 0.309 [two unassigned s, $Si(CH_3)_3$].

3.3.11. Deprotection of 1-benzyl ester of **16** {CH_3(C=O)-[GT^{TMS}]$_2$-OBzl} to **17** {CH_3(C=O)-[GT^{TMS}]$_2$-OH}

Compound **16** (1.206 g) and 5% platinum–carbon (1.95 g) in dioxan (30 ml) was treated with hydrogen at 40 psi for 187 h and the product isolated as in Section 3.3.6 to give an oil (1.312 g) which was chromatographed on silica using dichloromethane–methanol (98:2 v/v) for a preliminary purification followed by a repeat using diethyl ether-light petroleum [bp 40–60 °C] (40:60 v/v) to give **17** {CH_3(C=O)-[GT^{TMS}]$_2$-OH} (0.484 g, 46%) an oil (Found: C, 57.25; H, 6.25. $C_{28}H_{36}O_{10}Si_2$ requires C, 57.12; H, 6.16%); $\delta_H(CDCl_3)$ 8.403 and 8.364 (broad d, unassigned 3-, 3′-H; $J_{meta} = 1.5$ Hz), 8.23–8.06 (components of AB spectrum, unassigned 5-, 5′-, 6- and 6′-H; $J_{ortho} = 8.0$ Hz), 4.729 (s, O=$COCH_2CH_2OC$=O), 4.563 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)], 4.446 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)], 2.116 [s, CH_3(C=O)O], 0.371 and 0.367 [two unassigned s, $Si(CH_3)_3$].

3.3.12. Formation of the ethyl ester **18** from the terminal carboxylic acid in **17** {CH_3(C=O)-[GT^{TMS}]$_2$-OH}

Compound **17** (0.470 g) was treated successively with ethanol (0.044 g) in dichloromethane (1.5 ml), 4-dimethylaminopyridine (0.010 g) in DCM (0.5 ml) and diisopropylcarbodiimide (0.121 g) in DCM (2 ml). After 4 h at room temperature, the crude product was isolated as in Section 3.3.10 and chromatographed on silica using diethyl ether-light petroleum [bp 40–60 °C] (25:75 v/v) to give **18** {CH_3(C=O)-[GT^{TMS}]$_2$-OCH_2CH_3} (0.363 g, 74%) an oil (Found: C, 58.44; H, 6.59. $C_{30}H_{40}O_{10}S_2$ requires C, 58.42; H, 6.54%); $\delta_H(CDCl_3)$ 8.336 (broad d, unassigned 3-, 3′-H), 8.085–8.00 (components of AB spectrum, unassigned 5-, 5′-, 6- and 6′-H; $J_{ortho} = 8.0$ Hz), 4.695 (s, O=$COCH_2$-CH_2OC=O), 4.540 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)], 4.423 [m, 4′-CH_3(C=O)OCH_2CH_2O(C=O)], 4.388 [q, CH_3CH_2O(C=O)], 2.094 CH_3CH_2O(C=O)], 1.407 [t, CH_3CH_2O(C=O)], 0.345 and 0.326 [two unassigned s, Si $(CH_3)_3$].

3.4. Sulphur derivatives

3.4.1. Dimethyl iodoterephthalate

Powdered dimethyl aminoterephthalate (251.6 g) was added over 30 min to a mixture of conc. sulphuric acid (210 ml) in water (950 ml) which was stirred mechanically with a teflon paddle. The stirred slurry was cooled to 2 °C with an ice/salt bath and a solution of sodium nitrite (90.0 g) in water (370 ml) was added over 40 min, the temperature being maintained at 2–6 °C. After a further 30 min at 2 °C,

solid material was removed from the mixture by rapid filtration through Celite, and the cold, clear solution was added in portions over 15 min to a stirred solution of potassium iodide (405 g) in water (300 ml) at room temperature. Solid sodium metabisulphite was added to the stirred mixture until the colour due to some free iodine was discharged, and diethyl ether (2 l) was added. After being stirred for a further 90 min, the ether layer was separated, washed with sodium bisulphite solution (20 g in 250 ml water), then with sodium bicarbonate solution (250 ml saturated solution +250 ml water), and finally with water (600 ml). The organic phase was dried (Na_2SO_4) and the solvent evaporated to give the crude product (330.7 g) which on recrystallisation from methanol gave dimethyl iodoterephthalate (282.2 g, 73%) mp 78–80 °C (Ref. [21] 80 °C).

3.4.2. Dimethyl tert-butylthioterephthalate **20** (*MeO-^{tBuS}T-OMe*)

Copper (I) oxide (89.2 g), methanol (800 ml) and *t*-buty thiol (128 ml) were vigorously stirred in an oil bath at 85 °C for 14.5 h under argon [16]. The mixture was filtered under argon through a glass sinter (90 mm) at room temperature, the solid washed with methanol (350 ml) and diethyl ether (350 ml), dried in vacuo and washed back into the reaction flash with monoglyme. Dimethyl iodoterephthalate **19** (301.2 g) was added to the mixture under argon along with pyridine (200 ml) and monoglyme (total amount used 1000 ml) which was then heated under reflux for 15 h. The cooled mixture was diluted with light-petroleum [bp 40–60 °C] (3 l), allowed to stand for 2 days and filtered, and the solid was washed with more solvent. The filtrate was washed with hydrochloric acid (4M, 400 ml) and water (2 × 4 l), dried (Na_2SO_4) and passed through a column of silica (100 g) which was washed with light petroleum [bp 40–60 °C] (600 ml) and diethyl ether-light petroleum [bp 40–60 °C] (20:80 v/v) The solvent was evaporated to give a pale yellow solid (251.8 g, 95%) suitable for use in the following experiment, though a small sample was chromatographed on silica using dichloromethane-light petroleum [bp 40–60 °C] (70:30 v/v) and recrystallised from light petroleum [bp 40–60 °C] to give a colourless sample of **20** (MeO-^{tBuS}T-OMe) mp 42–44 °C (Found: C, 59.50; H, 6.44. $C_{14}H_{18}O_4S$ requires C, 59.55; H, 6.42%); $\delta_H(CDCl_3)$ 8.276 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.024 (dd, 5-H; $J_{ortho} = 8.0$ Hz) 7.615 (d, 6-H), 3.943 (s, 4-CH_3OCO), 3.923 (s, 1-CH_3OCO), 1.302 [s, $(CH_3)_3$CS].

3.4.3. tert-Butylthioterephthalic acid **21** (*HO-^{tBuS}T-OH*)

Compound **20** (229.0 g) in ethanol (600 ml) was treated with sodium hydroxide (91.5 g) in water (350 ml) and the mixture was heated with stirring at 95 °C for 1 h. Volatile solvent (ca. 700 ml) was evaporated and the pasty residue was dissolved in water (400 ml) and dilute hydrochloric acid (200 ml 11 M in 2 l) was added with stirring. The thick precipitate was separated by gentle vacuum filtration and washed with water and then by resuspension in water (700 ml). This washing sequence was repeated and the product (199.6 g, 97%) dried under vacuum at ca. 50 °C. Recrystallisation of a small sample from acetonitrile gave a light yellow powder of **21** (HO-^{tBuS}T-OH) mp > 330 °C (decomp.) (Found: C, 56.39; H, 5.47. $C_{12}H_{14}O_4S$ requires C, 56.68; H, 5.55%); $\delta_H(CDCl_3)$ 8.511 (d, 6-H; $J_{ortho} = 8.0$ Hz), 8.324 (d, 3-H; $J_{meta} = 1.6$ Hz), 8.237 (dd, 5-H), 1.374 [s, $(CH_3)_3$CS].

3.4.4. Monomethyl 2-tert-butylthioterephthate **22** (*MeO-^{tBuS}T-OH*)

Compound **20** (1.00 g) in methanol (4 ml) was stirred in an ice bath and sodium hydroxide (0.157 g) in water (2 ml) was added dropwise for 4 min. After 20 h at room temperature, the solution was acidified with hydrochloric acid (0.5M, 15 ml) extracted with dichloromethane, the extracts dried (Na_2SO_4) and the solved evaporated. The residue was crystallised from cyclohexane to give **22** (MeO-^{tBuS}T-OH) (0.753 g, 79%) mp 131–134 °C (Found: C, 58.16; H, 6.01. $C_{13}H_{16}O_4S$ requires C, 58.19; H, 6.01%); $\delta_H(CDCl_3)$ 8.362 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.099 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.656 (d, 6-H), 3.940 (s, 4-CH_3OCO), 1.325 [s, $(CH_3)_3$CS].

3.4.5. Bis-[2-(2-pyridyl)ethyl]2-tert-butylthioterephthate **23** (*Pet-T^{StBu}-OPet*)

The diacid **21** (1.01 g) and 2-(2-pyridyl)ethanol (1.077 g) was stirred in dichloromethane (10 ml) with 4-dimethylaminopyridine (0.098 g) and diisopropylcarbodiimide (1.115 g) in DCM (15 ml) was added. After 17 h the solution was filtered, the solvent evaporated and cyclohexane/diethyl ether added to enable further diisopropylurea to be removed as in Section 3.3.5. The crude product (1.863 g) was chromatographed on silica using DCM–methanol (97:3 v/v) to give **23** (Pet-T^{StBu}-OPet) (1.164 g, 63%) an oil (Found: C, 66.88 H, 6.03. $C_{26}H_{28}N_2O_4S$ requires C, 67.22; H, 6.07%); $\delta_H(CDCl_3)$ 8.155 (d, 3-H; $J_{meta} = 1.5$ Hz), 7.920 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.497 (d, 6-H), 8.562, 7.617, 7.233 and 7.163 (unassigned H in 2-pyridyl rings), 4.728 [t, (2-pyridyl)CH_2CH_2O], 3.254 [t, (2-pyridyl)CH_2CH_2O], 1.226 [s, $(CH_3)_3$CS].

3.4.6. Mono-(2-pyridylethyl)-2-tert-butylthioterephthate **24** (*HO-T^{StBu}-Pet*)

Compound **23** (1.037 g) in monoglyme (5 ml) was stirred in an ice bath and 2.0 ml of a solution of sodium hydroxide (0.490 g) in water (10.0 ml) was added for 5 min. After 16 h at room temperature, the solution was diluted with water (30 ml), the pH adjusted to 3 with acetic acid and the organic material extracted with dichloromethane. The extracts were dried (Na_2SO_4) and the solvent evaporated to give **24** (HO-T^{StBu}-Pet) (0.720 g, 90%) mp 132.5–134 °C (from acetonitrile) (Found: C, 63.19; H, 5.87; N, 3.84. $C_{19}H_{21}NO_4S$ requires C, 63.49; H, 5.89; N, 3.90%); $\delta_H(CDCl_3)$ 8.228 (d, 3-H; $J_{meta} = 1.5$ Hz), 7.855 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.492 (d, 6H), 8.730, 7.746, 7.345 and

7.287 (unassigned H in 2-pyridyl rings), 4.696 {t, 1-[(2-pyridyl)CH_2CH_20]}, 3.343 {t, 1-[(2-pyridyl)CH_2CH_2O]}, 1.221[s, $(CH_3)_3CS$].

3.4.7. Preparation of the fully protected monomer **25** (thp-[GT^{StBu}]$_1$-Pet)

Compound **24** (1.911 g) in dichloromethane (15 ml) cooled in an ice baath was treated with 4-dimethylaminopyridine (0.065 g) and compound **10** (thp-G-H) (0.859 g) in DCM (5 ml) followed by diisopropylcarbodiimide (0.716 g) in DCM (5 ml). After 17.5 h at room temperature, diisopropylurea was filtered off, the solvent evaporated and the procedure given in Section 3.3.5 was carried out. The resulting product was chromatographed on silica using dichloromethane–methanol (98.5:1.5 v/v) to give the fully protected monomer **25** (thp-[GT^{StBu}]$_1$-Pet) (1.392 g, 54%) an oil (Found: C, 63.78; 6.84; N, 2.76. $C_{26}H_{33}NO_6S$ requires C, 64.04; H, 6.82;N, 2.87%); $\delta_H(CDCl_3)$ 8.267 (d, 3-H; J_{meta} unresolved), 8.008 (d, 5-H; $J_{ortho} = 8.0$ Hz), 7.528 (d, 6-H), 8.561, 7.614, 7.241 and 7.155 (unassigned H in 2-pyridyl rings), 4.735 {t, 1-[(2-pyridyl)CH_2CH_20]},4.690 (overlapping t, chiral H^* in thp), 4.532 (m, H_a in 4-thpOCH_AH_B-CH_aH_bOC=O), 4.482 (m, H_b in 4-thpO$CH_AH_BCH_aH_b$ OC=O), 4.035 (m, H_A in 4-thpO$CH_AH_BCH_aH_b$), 3.769 (m, H_B in 4-thpO$CH_AH_BCH_aH_b$) 3.259 {t, 1-[(2-pyridyl)CH_2 CH_20]} 3.860 and 3.519 (m, unassigned H in CH_2O of thp), 1.86–1.47 (complex m, $CH_2CH_2CH_2$ of thp) 1.256 [s, $(CH_3)_3CS$].

3.4.8. Deprotection of 1-[2-(2-pyridyl)ethyl)] ester of **25** (thp-[GT^{StBu}]$_1$-Pet) to **26** (thp-[GT^{StBu}]$_1$-OH)

Compound **25** (17.11 g) in acetonitrile (170 ml) was treated with iodomethane (17 ml) at room temperature for 144 h and all volatile materials evaporated at 30 °C. The residue was dissolved in ether (330 ml), washed with water (2 × 250 ml) and the organic layer was stirred with $KHCO_3$ (7.0 g) in water (250 ml) for 18 h. The aqueous layer was washed with ether (70 ml) and stirred with DCM (200 ml) while phosphoric acid (0.65M, ca. 125 ml) was added until the pH fell to 4 and no further precipitation was seen. The organic layer was dried (Na_2SO_4) and evaporated at 30 °C to give a pale yellow viscous oil (9.01 g). Re-extraction of the ether layer as before gave a further crop (0.45 g) and chromatography of the combined product on silica suing DCM–methanol (96.5: 3.5 v/v) gave **26** (thp-[GT^{StBu}]$_1$-OH) (9.00 g, 67%) a gum (Found: C, 59.38; H, 6.82. $C_{19}H_{26}O_6S$ requires C, 59.67; H, 6.85%); $\delta_H(CDCl_3)$ 8.464 (d, 6-H; $J_{ortho} = 8.0$ Hz, 8.276 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.192 (dd, 5-H), 4.702 (t, chiral H^* in thp), 4.567 (m, H_a in 4-thpO$CH_AH_BCH_aH_bOC$=O), 4.518 (m, H_b in 4-thpO$CH_AH_BCH_aH_b$CO=O),4.059 (m, H_A in 4-thpO$CH_AH_BCH_aH_b$), 3.797 m, H_B in 4-thpOCH_AH_B-CH_aH_b),3.871 and 3.534 (m, unassigned H in CH_2O of thp), 1.87–1.48 (complex m $CH_2CH_2CH_2$ of thp), 1.352 [s, $(CH_3)_3CS$].

3.4.9. Deprotection of thp of **25** (thp-[GT^{StBu}]$_1$-Pet) to **27** (H-[GT^{StBu}]$_1$-Pet)

Compound **25** (18.85 g) was stirred with hydrochloric acid (1M, 500 ml) at room temperature for 3.5 h and DCM (160 ml) and $KHCO_3$ added (56 g) then further $KHCO_3$ added in small portions until the pH was 7–8. The organic layer was separated, dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica using DCM–methanol (97:3, v/v) to give **27** (H-[GT^{StBu}]$_1$-Pet) (13.7 g, 88%) from which the solvent could not be completely removed; $\delta_H(CDCl_3)$ 8.258 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.005 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.527 (d, 6-H), 8.559, 7.615, 7.240 and 7.158 (unassigned H in 2-pyridyl rings), 4.735 {t, 1-[(2-pyridyl)CH_2CH_2CO=O]}, 4.481 (t, 4-$HOCH_2CH_2OC$=O), 3.969 (t, 4-$HOCH_2CH_2OC$=O), 3.259 {t, 1-[(2-pyridyl)CH_2CH_2O]}, 1.255 [s, $(CH_3)_3CS$].

3.4.10. Preparation of the fully protected dimer **28** (thp-[GT^{StBu}]$_2$-Pet) from **26** and **27**

A mixture of the monomer acid **26** (thp-[GT^{StBu}]$_1$-OH (5.18 g) and the monomer alcohol **27** (H-[GT^{StBu}]$_1$-Pet) (5.26 g) in DCM (100 ml) was treated with 4-dimethylaminopyridine (0.157 g) followed dropwise with diisopropylcarbodiimide (1.65 g) in DCM (20 ml). After 3.25 h at room temperature, diisopropylurea was filtered off, the solvent evaporated adn the procedure given in Section 3.3.5 was carried out. The resulting product was chromatographed on silica using dichloromethane–methanol (99:1 v/v) to give the fully protected dimer **28** (thp-[GT^{StBu}]$_2$-Pet) (8.46 g, 84%) an oil (Found: C, 62.28; H, 6.43; N, 1.62. $C_{40}H_{49}NO_{10}S_2$ requires C, 62.56; H, 6.43; N, 1.82%); $\delta_H(CDCl_3)$ 8.290 and 3.259 (both d, 3- and3′-H; $J_{meta} = 1.6$ H), 8.561, 7.612, 7.236 and 7.156 (unassigned H in 2-pyridyl rings), 4.734 {t, 1-[(2-pyridyl)CH_2CH_2O]}, 4.65–4.70 (overlapping m, chiral H^* in thp and O=$COCH_2$-CH_2OC=O), 4.541 (m, H_a in 4′-thpO$CH_AH_BCH_aH_bOC$=O), 4.491 (M, H_b in 4′-thpO$CH_AH_BCH_aH_b$OC=O), 4.04 (m, H_A in 4′-thpO$CH_AH_BCH_aH_b$), 3.77 (m, H_B in 4′-thpOCH_AH_B-CH_aH_b) 3.255 {t, 1-[(2-pyridyl)CH_2CH_2O]}, 3.860 and 3.519 (m, unassigned H in CH_2O of thp), 1.86–1.47 (complex m $CH_2CH_2CH_2$ of thp), 1.235 and 1.259 [both s, two $(CH_3)_3CS$].

3.4.11. Deprotection of 1-[2-(2-pyridyl)ethyl)] ester of **28** (thp-[GT^{StBu}]$_2$-Pet) to **29** (thp-[GT^{StBu}]$_2$-OH)

Compound **28** (4.93 g) in acetonitrile (50 ml) was treated with iodomethane (4.7 ml) and after 141 h at room temperature all volatile materials were evaporated at 30 °C and the residue dissolved in DCM (160 ml). The solution was washed with water (3 × 200 ml), dried (Na_2SO_4), the solvent evaporated and the residue (4.25 g) chromatographed on silica using DCM–methanol (96:4 v/v) gave pure product **29** (1.39 g). The impure fractions (2.44 g) were treated as in Section 3.4.8 but not chromatographed, to give more **29** (thp-[GT^{StBu}]$_2$-OH) (1.74 g, total yield 3.13 g, 74%) an oil from which slovent could not be completely removed;

$\delta_H(CDCl_3)$ 8.289 and 8.247 (unassigned d, 3-, 3′-H, J_{meta} unresolved), 8.206 and 8.044 (both d, unassigned 5-, 5′-H; $J_{ortho} = 8.0$ Hz), 8.463 (d, 6-H; $J_{ortho} = 8.0$ Hz), 7.625 (d, 6′-H; $J_{ortho} = 8.0$ Hz), 4.701 (overlapping s, OCH_2CH_2O), 4.692 (overlapping t, chiral H* in thp), 4.540 (m, H_a in 4′-thpOCH$_A$H$_B$CH_aH$_b$OC=O), 4.490 (m, H_b in 4′-thpOCH$_A$H$_B$CH$_a$$H_b$OC=O), 4.040 (m, H_A in 4′-thpOCH_AH$_B$CH$_a$H$_b$OC=O), 3.775 (m, H_B in 4′-thpOCH$_A$$H_BCH_aH_b$OC=O), 3.861 and 3.521 (m, unassigned H in CH_2O of thp), 1.87–1.47 (complex m $CH_2CH_2CH_2$ of thp), 1.262 and 1.333 [unassigned s, two $(CH_3)_3CS$].

3.4.12. Deprotection of thp **28** (thp-[GT^{StBu}]$_2$-Pet to **30** (H-[GT^{StBu}]$_2$-Pet)

Compound **28** (3.48 g) in hydrochloric acid (1M, 100 ml) and ethylene glycol (50 ml) was warmed to 35 °C for 5 min and stirred at room temperature for 3 h. Ether (80 ml) was added, the mixture stirred for a further 45 min and $KHCO_3$ (ca. 12.5 g) was added slowly until the pH was ca. 8. Water (200 ml) was added and the organic phase was separated, washed with water (2 × 250 ml), dried (Na_2SO_4) and the solvent evaporated. The residue (3.37 g) was chromatographed on silica using DCM–methanol (97:3 v/v) to give **30** (H-[GT^{StBu}]$_2$-Pet) (2.84 g, 92%) an oil (Found: C, 61.21; H, 6.10; N, 2.12. $C_{35}H_{41}NO_9S_2$ requires C, 61.47; H, 6.04; N, 2.05%); $\delta_H(CDCl_3)$ 8.261 and 8.286 (both broad s, unassigned 3-, 3′-H, J_{meta} unresolved), 8.038 and 8.018 (both d, unassigned 5-, 5′-H; $J_{ortho} = 8.0$ Hz), 7.623 and 7.525 (both d, 6-, 6′-H), 8.561, 7.608, 7.239 and 7.158 {unassigned aromatic H in 1-[(2-pyridyl)ethyl] ester rings}, 4.736 {t, 1-[(2-pyridyl)$CH_2C\mathit{H}_2O$]}, 4.679 (s, O=COCH_2-CH_2OC=O), 4.494 (t, 4′-HOCH$_2$CH_2OC=O), 3.980 (m, 4′-HOCH_2CH$_2$OC=O), 3.258 {t, 1-[(2-pyridy)CH_2CH$_2$O]}, 1.262 and 1.238 {unassigned s, two $(CH_3)_3CS$].

3.4.13. Preparation of the fully protected 'tetramer' **31** (thp-[GT^{StBu}]$_4$-Pet) from **29** and **30**

A mixture of the dimer acid **29** (thp-GT^{StBu}]$_2$-OH) (1.33 g) and the dimer alcohol **30** (H-[GT^{StBu}]$_2$-Pet) (1.39 g) in DCM (20 ml) cooled in an ice-bath, was stirred with 4-dimethylaminopyridine (0.025 g) followed dropwise with diisopropylcarbodiimide (0.262 g) in DCM (7 ml) over 3 min. After 4 h at room temperature, volatile material was evaporated at 30 °C, cyclohexane (30 ml) added followed by enough diethyl ether (ca. 30 ml) to dissolve the gummy residue, causing the precipitation of a granular white powder which was dissolved in ethanol (49 ml) at 60 °C and allowed to stand at room temperature for 16 h to give a white powder, the fully protected 'tetramer' **31** (thp-[GT^{StBu}]$_4$-Pet) (2.19 g, 82%) mp 90.5–92.5 °C (Found: C, 61.23; H, 6.11; N, 1.30. $C_{68}H_{81}NO_{18}S_4$ requires C, 61.47; H, 6.14; N, 1.01%); $\delta_H(CDCl_3)$ 8.279 and 3.256 (broad s in the ratio 3:1, respectively, unassigned, 3-, 3′-, 3″- and 3‴-H, J_{meta} unresolved), 8.00–8.07 (overlapping d, 5-, 5′-, 5″- and 5‴-H; $J_{ortho} = 8$ Hz), 7.619 and 7.52 (overlapping d in the ratio 3:1 unassigned 6-, 6′-, 6″- and 6‴-H), 8.560, 7.610, 7.234 and 7.155 (unassigned H in 2-pyridyl rings), 4.732 {t, 1-[(2-pyridyl)CH$_2$CH_2O]}, 4.71–4.63 (overlapping m, chiral H* in thp and three O=COCH_2CH_2OC=O), 4.537 (m, H_a in 4‴-thpOCH$_A$H$_B$CH_aH$_b$OC=O), 4.487 (m, H_b in 4‴-thpOCH$_A$H$_B$CH$_a$$H_b$OC=O), 4.038 (m, H_A in 4‴-thpOCH_AH$_B$CH$_a$H$_b$), 3.772 (m, H_B in 4‴-thpOCH$_A$$H_BCH_aH_b$), 3.253 {t, 1-[(2-pyridyl)CH_2CH$_2$OC=O]} 3.857 and 3.518 (m, unassigned H in CH_2O of thp), 1.86–1.47 (complex m $CH_2CH_2CH_2$ of thp), 1.257 and 1.233 [both s in the ratio 1:3, respectively, four $(CH_3)_3CS$].

3.4.14. Deprotection of thp of **31** (thp-[GT^{StBu}]$_4$-Pet) to **42** (H-[GT^{StBu}]$_4$-Pet)

Compound **31** (2.13 g) was stirred with 1,2-dimethoxyethane (50 ml) and hydrochloric acid (2M, 15 ml) at room temperature for 4 h after which DCM (150 ml) was added followed by dilute $NaHCO_3$ (40 ml saturated solution + 180 ml water) to bring the pH to 8. The organic phase was separated, washed with water (2 × 200 ml), dried (Na_2SO_4) and the solvent evaporated to an oil (2.4 g) which solidified on trituration with diethyl ether. Recrystallisation from methanol and chromatography of the solid (1.88 g) on silica using DCM–methanol (97:3 v/v) gave **42** (H-[GT^{StBu}]$_4$-Pet) (1.49 g, 75%) mp 92.6–93.6 °C (Found: C, 60.58; H, 5.91; N, 1.09. $C_{63}H_{73}NO_{17}S_4$ requires C, 60.80; H, 5.91; N, 1.13%); $\delta_H(CDCl_3)$ 8.275 and 8.253 (both broad s in the ratio 3:1, respectively, unassigned 3-, 3′-, 3″- and 3‴-H, J_{meta} unresolved), 8.07–7.99 (overlapping d, unassigned 5-, 5′-, 5″- and 5‴-H; $J_{ortho} = 8.0$ Hz), 7.617 and 7.519 (both d in the ratio 3:1, 6-, 6′-, 6″- and 6‴-H), 8.553, 7.610, 7.233 and 7.152 {unassigned aromatic H in 1-[(2-pyridyl)ethyl] ester rings}, 4.728 {t, 1-[(2-pyridyl)CH$_2$-CH_2O]}, 4.678 (s, three O=COCH_2CH_2OC=O), 4.486 (t, 4‴-HOCH$_2$CH_2OC=O), 3.968 (broad s, 4‴-HOCH_2CH$_2$O-C=O), 3.253 {t, 1-[(2-pyridyl)CH_2CH$_2$O]}, 1.253 and 1.230 (unassigned s, in the ratio 1:3, four $(CH_3)_3CS$).

3.4.15. Preparation of **32** (thp-[G^{tBuS}T]$_1$-G-thp) from t-butylthioterephthalic acid **21** and thp-G-H **10**

The diacid **21** (0.522 g), compound **10** (thp-G-H) (0.781 g) and 4-dimethylaminopyridine (0.050 g) were stirred in DCM (12 ml) and diisopropylcarbodiimide (0.547 g) in DCM (3 ml) was added. After 4 h, the diisopropylurea was filtered off, the solvent evaporated and the procedure given in Section 3.3.5 was carried out. The resulting product was chromatographed on silica using ethyl acetate-light petroleum [bp 40–60 °C] (20:80 v/v) to give **32** (thp-[G^{tBuS}T]$_1$-G-thp) 0.747 g, 71% an oil (Found: C, 61.01; H, 7.51. $C_{26}H_{38}O_8S$ requires C, 61.16; H, 7.50%); $\delta_H(CDCl_3)$ 8.297 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.042 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.642 (d, 6-H), 4.698 and 4.683 (overlapping t, chiral H* in thp), 4.544 (m, H_a in two thpOCH$_A$H$_B$CH_aH$_b$OC=O), 4.478 (m, H_b in two thpOCH$_A$H$_B$CH$_a$$H_b$OC=O), 4.037 (m, H_A in two thpOCH_AH$_B$-CH$_a$H$_b$), 3.780 (m, H_B in two thpOCH$_A$$H_BCH_aH_b$), 3.875 and 3.525 (m, unassigned H in CH_2O of two thp), 1.88–1.47 (complex m $CH_2CH_2CH_2$ of two thp), 1.305 [s, $CH_3)_3CS$].

3.4.16. Deprotection of thp of **32** *(thp-[G^{tBuS}T]$_1$-G-thp) to* **33** *(H-[G^{tBuS}T]$_1$-G-H)*

Compound **32** (0.740 g) in ethanol (20 ml) and water (1.2 ml) was stirred with *p*-toluenesulphonic acid (0.120 g) for 46 h. A solution of $KHCO_3$ (0.065 g) in water (10 ml) was added, the mixture stirred for 30 min and volatile solvent (20 ml) was evaporated at 40 °C in vacuo. Dichloromethane (20 ml) was added to the residue and the solution was washed with dilute $NaHOC_3$ (10 ml of saturated solution + 10 ml water) and dried (Na_2SO_4). Evaporation of the solvent and chromatography of the residue on silica gave **33** (H-[G^{tBuS}T]$_1$-G-H) (0.420 g, 87%) an oil (Found: C, 55.91; H, 6.53. $C_{16}H_{22}O_6S$ requires C, 56.12; H, 6.48%); $\delta_H(CDCl_3)$ 8.299 (d, 3-H; $J_{meta} = 1.5$ Hz) 8.092 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.692 (d, 6-H), 4.498 and 4.490 (overlapping t, two $HOCH_2CH_2OC{=}O$), 3.983 and 3.949 (overlapping t, two $HOCH_2CH_2OC{=}O$), 1.288 [s, $(CH_3)_3CS$].

3.4.17. Preparation of **38** *(MeO-[^{tBuS}TG]$_1$-thp) from* **22** *(MeO-^{tBuS}T-OH) and thp-G-H* **10**

The monomethyl ester **22** (7.92 g), compound **10** (thp-G-H) (4.52 g) and 4-dimethylaminopyridine (0.355 g) were stirred in DCM (60 ml) in an ice-bath and diisopropylcarbodiimide (3.92 g) in DCM (15 ml) was added dropwise over 5 min. After 20 h at room temperature, the diisopropylurea was filtered off the solvent evaporated and the procedure given in Section 3.2.5 was carried out to give **38** (MeO-[^{tBuS}TG]$_1$-thp) (11.82 g, 100%) an oil (Found: C, 60.08; H, 7.11. $C_{20}H_{28}O_6S$ requires C, 60.59; H, 7.12%); $\delta_H(CDCl_3)$ 8.294 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.038 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.614 (d, 6-H), 4.691 (t, chiral H* in thp), 4.536 (m, H_a in 4-thpOCH_AH$_B$CH_aH$_b$OC=O), 4.486 (m, H_b in 4-thpOCH$_A$H$_B$CH$_a$H$_b$OC=O), 4.039 (m, H_A in 4-thpOCH$_A$H$_B$CH$_a$H$_b$OC=O), 3.771 (m, H_B in 4-thpOCH$_A$H$_B$CH$_a$H$_b$ OC=O), 3.917 [s, 1-(C=O)OCH$_3$)], 1.87–1.47 (complex m, $CH_2CH_2CH_2$ of thp), 1.297 [s, $(CH_3)_3CS$].

3.4.18. Deprotection of thp of **38** *(MeO-[^{tBuS}TG]$_1$-thp) to* **39** *(MeO-[^{tBuS}TG]$_1$-H)*

Compound **38** (11.67 g) in ethanol (160 ml) and water (16 ml) was stirred with *p*-toluenesulphonic acid (1.62 g) at room temperature for 20 h. The pH of the solution was adjusted to 7 with $KHCO_3$ (ca. 0.9 g), the volatile solvent was evaporated and the aqueous residue extracted with DCM (110 ml). The extracts were washed with saturated brine (2 × 160 ml), dried (Na_2SO_4) and the solvent evaporated to give the crude product (9.04 g), purified by two chromatography separations using DCM–methanol (98:2 v/v) to give **39** (MeO-[^{tBuS}TG]$_1$-H) (7.43 g, 81%) an oil (Found: C, 57.39; H, 6.39. $C_{15}H_{20}O_5S$ requires C, 57.67; H, 6.45%); $\delta_H(CDCl_3)$ 8.296 (d, 3-H; $J_{meta} = 1.5$ Hz), 8.047 (dd, 5-H; $J_{ortho} = 8.0$ Hz), 7.627 (d, 6-H), 4.495 (m, 4-$HOCH_2CH_2OC{=}O$), 3.981 (q, 4-$HOCH_2CH_2OC{=}O$), 3.929 [s, 1-$CH_3O(C{=}O)$], 1.305 [s, $(CH_3)_3CS$].

3.4.19. Preparation of **36** *(Pet-[^{tBuS}TG]$_2$-T^{StBu}-Pet) from t-butylthioterephthalic acid* **21** *(HO-^{tBuS}T-OH) and* **27** *(H-[GT^{StBu}]$_1$-Pet*

The diacid **21** (5.85 g), the alcohol **27** (19.16 g) and 4-dimethylaminopyridine (0.564 g) in DCM (220 ml) were stirred in an ice-bath and diisopropylcarbodiimide (6.10 g) in DCM (25 ml) was added dropwise during 15 min. After 20 h, the mixture was filtered, the solution was evaporated and cyclohexane (100 ml) was added followed by enough ether (ca. 220 ml) to dissolve the oily residue. The solution was filtered and washed twice with dilute brine (50 ml of saturated brine + 250 ml water) with addition of more ether as necessary to maintain a clear organic phase. The organic phase was separated, dried (Na_2SO_4) and the solvent evaporated to give material containing cyclohexane by ^{1}H NMR (25.7 g) a sample of which was heated at 58 °C/ 2×10^{-2} mm Hg to give **36** (Pet-[^{tBuS}TG]$_2$-T^{StBu}-Pet) an oil (Found: C, 63.37; H, 6.27; N, 3.09. $C_{54}H_{60}N_2O_{12}S_3$ requires C, 63.26; H, 5.90; N, 2.73%); $\delta_H(CDCl_3)$ 8.262, 8.252 and 8.240 (all d, unassigned 3-, 3′- and 2″-H; $J_{meta} = 1.5$ Hz), 8.026–7.966 (ovarlaping dd, 5-, 5′- and 6″-H; $J_{ortho} = 8.0$ Hz), 7.64–7.58 and 7.54–7.50 (overlapping d, 6-, 6′- and 5″-H and two H from two 2-pyridyl moieties), 8.557, 8.547, 7.255–7.21 and 7.175–7.13 (overlapping m from six H from two 2-pyridyl moieties), 4.75–4.64 (overlapping m from two $O{=}COCH_2CH_2OC{=}O$ and two 2-pyridyl $CH_2CH_2OC{=}O$), 3.28–3.22 [overlapping m from two (2-pyridyl)CH_2CH_2O], 1.256, 1.227 and 1.221 [three $(CH_3)_3CS$].

3.4.20. Conversion of **36** *(Pet-[^{tBuS}TG]$_2$-T^{StBu}-Pet) to the α,ω-dicarboxylic acid* **37** *(HO-[^{tBuS}TG]$_2$-T^{StBu}-OH)*

Compound **36** (6.06 g) in acetonitrile (60 ml) was treated with iodomethane (6.0 ml) at room temperature for 107 h. Volatile material was evaporated, the residue dissolved in DCM (50 ml) and the solution washed with dilute hydrochloric acid (2 M, 100 ml) and saturated brine (50 ml) and then stirred with $KHCO_3$ (10.3 g) in water (450 ml) for 4 h. The aqueous layer was separated, washed with DCM (20 ml) and stirred with DCM (75 ml) while dilute hydrochloric acid (2 M) was added until the aqueous layer was strongly acid (and no further precipitation is seen at the point of mixing). The mixture was stirred overnight and the organic phase separated, dried (Na_2SO_4) and the solvent evaporated. The residue (3.43 g) was chromatographed on silica using DCM–methanol (98:2 v/v) to give **37** (HO-[^{tBuS}TG]$_2$-T^{StBu}-OH 0.5 H_2O) (2.00 g, 41%) a gum (Found; C, 58.12; H, 5.72. $C_{40}H_{46}O_{12}S_3$ 0.5 H_2O requires C, 58.31; H 5.75%); $\delta_H(CDCl_3)$ 8.461, 8.452 and 7.624 (all d, unassigned 6-, 6′- and 5″-H; $J_{ortho} = 8.0$ Hz), 8.268 and 8.249 (unresolved d and d in the ratio 2:1, respectively, 3-, 3′- and 2″-H, $J_{meta} = 1.5$ Hz), 8.197, 8.159 and 8.030 (all dd, unassigned 5-, 5′- and 6″-H), 4.714 and 4.698 [both s, two $O(O{=}C)CH_2CH_2O(C{=}O)$], 1.333, 1.327 and 1.238 [unassigned s, three $(CH_3)_3CS$].

*3.4.21. Reaction of **22** (MeO-^{tBuS}T-OH) with **33** (H-[G^{tBuS}T]$_1$-G-H) to form **34** (MeO-[^{tBuS}TG]$_2$-T^{StBu}-OMe)*

Compounds **22** (0.654 g), **33** (0.404 g) and 4-dimethylaminopyridine (0.029 g) were stirred in DCM (8 ml) and diisopropylcarbodiimide (0.329 g) in DCM (2 ml) was added at room temperature. After 3.5 h the mixture was filtered, the solvent evaporated and cyclohexane (20 ml) was added followed by ether (6 ml) in portions until the oily residue just redissolved. The solution was filtered, washed with dilute $NaHCO_3$ (10 ml saturated solution + 30 ml water), dried (Na_2SO_4) and the solvent evaporated. The product was twice chromatographed on silica using DCM–methanol (99:1 v/v) to give **34** (MeO-[^{tBuS}TG]$_2$-T^{StBu}-OMe) (0.385 g, 39%) a gum (Found: C, 59.66; H, 6.06. $C_{42}H_{50}O_{12}S_3$ requires C, 59.84; H, 5.98%); δH($CDCl_3$) 8.286, 8.274 and 8.269 (all d, unassigned 3-, 3′- and 2″-H; $J_{meta} = 1.7$ Hz), 8.045, 8.020 and 8.014 (all dd, unassigned 5-, 5′- and 6″-H; $J_{ortho} = 8.0$ Hz), 7.620, 7.609 and 7.605 (overlapping d, unassigned 6-, 6′- and 5″-), 4.691 and 4.667 (s and m accounting for two O=COCH$_2$CH$_2$OC=O), 3.919 and 3.918 (overlapping s, two OCH_3), 1.277, 1.271 and 1.234 [unassigned s, three $(CH_3)_3$CS].

*3.4.22. Reaction of **39** (MeO-[^{tBuS}TG]$_1$-H) with **37** (HO-[^{tBuS}TG]$_2$-T^{StBu}-OH) to form **40** (MeO-[^{tBuS}TG]$_3$-[T^{StBu}G]$_1$-T^{StBu}-OMe)*

Compounds **39** (1.82 g), **37** (2.33 g) and 4-dimethylaminopyridine (0.075 g) were stirred in DCM (34 ml) in an ice-bath and diisopropylcarbodiimide (0.736 g) in DCM (10 ml) was added dropwise over 5 min. After 22 h at room temperature the mixture was filtered, the solvent evaporated and cyclohexane (50 ml) was added followed by enough ether (62 ml) to dissolve the gummy residue. The solution was filtered, diluted with ether (20 ml) and washed in turn with dilute hydrochloric acid (1 M, 50 ml), water (25 ml), $KHCO_3$ solution (1 g in 40 ml water), and water (25 ml). More ether was added to remove cloudiness in the organic phase that was separated, dried (Na_2SO_4) and the solvent evaporated. The product was chromatographed on silica using DCM–methanol (99:1 v/v) to give **40** (MeO-[^{tBuS}TG]$_3$-[T^{StBu}G]$_1$-T^{StBu}-OMe) (1.62 g, 41%) a gum (Found: C, 59.90; H, 5.90. $C_{70}H_{82}O_{20}S_5$ requires C, 59.90 H, 5.89%); δ$_H$($CDCl_3$) 8.286, 8.275, 8.263 and 8.260 (all d in the ratio 2:1:1:1, unassigned 3-, 3′-, 3″-, 2‴- and 2⁗-H; $J_{meta} = 1.7$ Hz), 8.045 and 8.13 (overlapping dd in the ratio 3:2, unassigned 5-, 5′-, 5″-, 6‴- and 6⁗-H; $J_{ortho} = 8.0$ Hz), 7.617, 7.612 and 7.605 (overlapping d in the ratio 2:1:2, unassigned 6-, 6′-, 6″-, 5‴-, and 5⁗-H), 4.687 and 4.675 (s and m account for four O=COCH$_2$CH$_2$OC=O), 3.918 (s, two OCH_3), 1.277, 1.236 and 1.226 [unassigned s in the ratio 2:1:1:1, five $(CH_3)_3$CS].

*3.4.23. Reaction of **42** (H-GT^{StBu}]$_4$-Pet) with **37** (HO-^{tBuS}TG]$_2$-T^{StBu}-OH) to form **43** (Pet-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-Pet)*

Compounds **42** (1.44 g), **37** (0.047 g) and 4-dimethylaminopyridine (0.015 g) were stirred in DCM (16 ml) in an ice-bath and diisopropylcarbodiimide (0.159 g) in DCM (4 ml) was added dropwise over 3 min. After 22 h at room temperature the mixture was filtered, the solvent evaporated and the gummy residue stirred with ether (30 ml) to give a granular white powder which was washed with methanol, chromatography of which (1.56 g) on silica using DCM–methanol (97.5:2.5 v/v) gave **43** (Pet-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-Pet) (1.56 g, 84%) mp 98–98.5 °C (Found: C, 60.77; H, 5.82; N, 0.87. $C_{166}H_{188}N_2O_{44}S_{11}$ requires C, 61.01; H, 5.80; N, 0.86%); δ$_H$($CDCl_3$) 8.269 and 8.254 (unresolved d in the ratio 7:4 respectively, unassigned 3-, 3′-, 3″-, 3‴-, 3⁗-, 3⁗′- and five 2⁗″ etc. -H; $J_{meta} = 1.7$ Hz), 8.041 and 8.010 (overlapping dd in the ratio 8:3, unassigned 5-, 5′-, 5″-, 5‴-,5⁗-, 5⁗′- and five 6⁗″ etc. -H; $J_{ortho} = 8.0$ Hz), 7.611 and 7.520 [overlapping d in the ratio 11(including two H from two 2-pyridyl groups):2, unassigned 6-, 6′-, 6″-, 6‴-, 6⁗-, 6⁗′- and five 5⁗″ etc. -H], 8.560, 7.240 and 7.161 (unassigned m, 2 × 3 protons in two 2-pyridyl groups), 4.730 [t, two (2pyridyl)CH$_2$C*H*$_2$OC=O], 4.671 (m, accounting for ten O=COCH$_2$CH$_2$OC=O), 3.256 [t, two (2-pyridyl) C*H*$_2$CH$_2$OC=O], 1.228 [s, eleven $(CH_3)_3$CS].

*3.4.24. Conversion of **43** (Pet-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-Pet) to **44** (MeO-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-OMe)*

Compound **43** (1.55 g) and iodomethane (6.3 ml) in acetonitrile (31 ml) were stirred at room temperature with powered $KHCO_3$ (3.13 g) for 95 h. Dichloromethane (180 ml) was added and the solution was washed with water (400 ml; 2 × 250 ml), dried (Na_2SO_4) and the solvent evaporated. The residue (1.49 g) was chromatographed on silica using DCM–methanol (98.5:1.5 v/v) to give a pure sample of **44** (0.481 g); later fractions (0.920 g) were separated by preparative thick layer chromatography on silica using DCM–methanol (95:5 v/v) to give a further sample of **44** (MeO-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-OMe) (0.6 g; total yield 74%) a gum (Found: C,59.68; H,5.79. $C_{154}H_{178}O_{44}S_{11}$ requires C, 59.94 H, 5.81%); δH($CDCl_3$) 8.285, 8.276–8.269, 8.256 (all d in the ratio 2:7:2, unassigned 3-, 3′-, 3″-, 3‴-, 3⁗-, 3⁗′- and five 2⁗″ etc. -H; $J_{meta} = 1.7$ Hz), 8.041 and 8.010 (overlapping dd in the ratio 2:9, unassigned 5-, 5′-, 5″-, 5‴-, 5⁗-, 5⁗′- and five 6⁗″ etc. -H; $J_{ortho} = 8.0$ Hz), 7.619 and 7.613 (overlapping d in the ratio 2:9, unassigned 6-, 6′-, 6″-, 6‴-, 6⁗-, 6⁗′- and five 5⁗″ etc.-H], 4.674 (s accounting for ten O=COCH$_2$CH$_2$OC=O), 3.917 (s, two OCH_3), 1.275, 1.233, 1.228 and 1.223 [unassigned s in the ratio 2:2:5:2, eleven $(CH_3)_3$CS].

3.4.25. Desulphurisation reactions

*3.4.25.1. Formation of the trimer (MeO-[TG]$_2$-T-OMe) **35** from **34** (MeO-[^{tBuS}TG]$_2$-T^{StBu}-OMe).* Compound **34** (0.272 g) in dioxan (3 ml) was stirred under argon with raney nickel (ca. 1.5 g) and heated in an oil bath at 104–108 °C. More dioxan was added after 16 h and after 40 h the hot solution was filtered through Celite. After standing for a few hours at room temperature, the filtrate deposited small

white crystals (0.082 g); evaporation of the mother liquors to ca. 3 ml gave a second crop of **35** (MeO-[TG]$_2$-T-OMe) (0.035 g, total yield 63%) mp 199–199.5 °C, lit. [10] 194–198 °C (Found: C, 62.06; H, 4.63. $C_{30}H_{26}O_{12}$ requires C, 62.28; H, 4.53%); $\delta_H(CDCl_3)$ 8.112 and 8.100 (s in the ratio 4:8, respectively, due to 2-, 6-, 3″-, 5″-H and 3-, 5-, 2′-, 3′-, 5′-, 6′-, 2″- and 6″-H), 4.698 (s, two O=COCH_2-CH_2OC=O), 3.941 (s, two CH_3O).

*3.4.25.2. Formation of the pentamer (MeO-[TG]$_4$-T-OMe) **41** from **40** (MeO-[^{tBuS}TG]$_3$-[T^{StBu}G]$_1$-T^{StBu}-OMe).*
Compound **40** (0.682 g) in dioxan (16 ml) was stirred under argon with Raney nickel (ca. 12.6 g) at 90 °C for 22 h. The insoluble matter was transferred to the paper thimble of a continuous extraction apparatus and extracted with boiling dioxan for 16 h. After standing for 2 days the preciptate (0.201 g) was separated and the filtrate was evaporated to ca. 15 ml causing the precipitation of a second crop of product (0.022 g). The combined samples were recrystallised from dioxan (90 ml) and dried in vacuo at 55 °C to give **41** (MeO-[TG]$_4$-T-OMe) (0.190 g, 41%) mp 230.5–233 °C, lit. [10] 231–232 °C (Found:C, 62.18; H, 4.35. $C_{50}H_{42}O_{20}$ requires C, 62.37; H, 4.40%); δH(TCE-d$_2$) 8.020 and 8.007 (m, overlapping s due to 20H), 4.599 (s, four O=COCH_2CH_2OC=O), 3.842 (s, two CH_3O).

*3.4.25.3. Formation of the elevnmer (MeO-[TG]$_{10}$-T-OMe) **45** from **44** (MeO-[^{tBuS}TG]$_6$-[T^{StBu}G]$_4$-T^{StBu}-OMe).*
Compound **44** (0.469 g) in dioxan (10 ml) was stirred under argon with Raney nickel (ca. 8.3 g) at 81 °C for 16 h. The insoluble matter was extracted as in the previous experiment with dioxan for 22 h, the volume of the extracts reduced to ca. 15 ml and the solution left at room temperature for 5 days. The white solid which crystallised was filtered off (0.030 g, 9%) and recrystallised from 1,1,2,2-tetrachloroethane to give **45** (MeO-[TG]$_{10}$-T-OMe) (0.016 g) mp 240.5–242 ° C which on crystallising and reheating had mp 244–246 ° C, lit. [10] 254–256 °C; δ_H(TCE-d$_2$) 8.014 (overlapping s due to 44 H), 4.593 (s, 10 O=COCH_2CH_2OC=O), 3.840 (s, two CH_3O); minor impurities not due to retention of S*t*Bu-containing materials derived from **44**, were present at 7.048(t), 7.163(d), 7.395(m), 7.837(d) and 7.95(d) in the ratio 0.22:0.51:0.99:0.47:0.21 relative to the 44 overlapping protons in compound **45** at 8.014—which could be interpreted as approximately 5% impurity—responsible for the depressed melting point.

In a second experiment, the Raney nickel (ca. 10 g) was pre-treated with *p*-toluenesulphonic acid (0.100 g) in dioxane and then washed eight times by decantation from dioxan (50 ml). A solution of compound **44** (0.320 g) in dioxan (8 ml) and the pre-treated Raney nickel (ca. 4.3 g) was stirred under argon at 75 °C for 2.5 h, when all the starting materials was shown by TLC to have reacted. Insoluble matter was extracted with boiling point dioxan overnight and the extracts evaporated to dryness to give another batch of elevenmer **45** (0.015 g), mp 242–243 °C, the ^{1}H NMR of which again showed impurities not due to retention of S*t*Bu-containing materials derived from **44**, which were present at 6.767 (m), 7.158 (d), 7.704 (d) and 7.848 (m) in the ratio of 0.09:0.08:0.28:0.32 relative to the 44 overlapping protons in compound **45** at 8.010, which represents 2% impurity by the same criteria as above. Continued extraction for a further 72 h gave the purest batch of **45** isolated in this work: 0.012 g, mp 247–249 °C, the ^{1}H NMR showing only impurity at 7.846 (0.3%). The total amount of **45** (0.027 g) represented a yield of 12%.

Acknowledgements

The authors Dr A. Kenwright and Ian McKeag for NMR work, Mrs J. Dostal for elemental analyses and the EPSRC for funding (grant GR/M56692).

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