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Full Paper

Synthesis of Symmetrical, Substituted (alkane-α,ω-diyl) (bis[3,3′-allyl dithioethers]) Monomers for Photoplastic Polymer Networks

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Novel symmetrical (alkane-α,ω-diyl)(bis[3,3′-allyl dithioethers]) compounds and their ether analogues, have been synthesised from (alkane-α,ω-diyl)bis([2-{chloromethyl}allyl]sulfane) precursors, for use in crosslinked polymers which exhibit photoplastic behaviour. Facile synthesis and purification of these monomers was achieved if the alkane-α,ω-diyl moiety had at least one oxygen atom in this linker. The number of sulfur atoms in these monomers was varied from four to two to zero to produce monomers which can be used to evaluate their importance on the photoplasticity behaviour.

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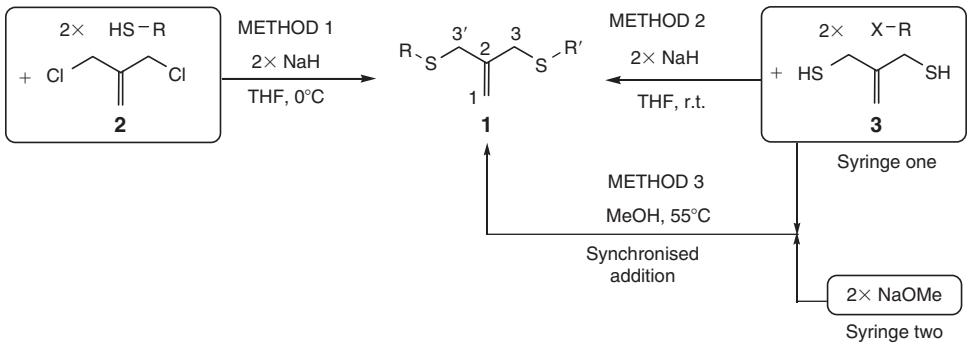
Introduction

In a recent communication[1] we described the synthesis of novel symmetrical 3,3′-allyl dithioethers **1** (R = R′) (Scheme 1). These compounds can function either as homopolymerizable monomers or can be copolymerized with other monomers (such as tri- or tetramercaptans) to form three-dimensional polymer networks with photoplastic behaviour.[2–4] Photoplasticity is the phenomenon whereby a solid crosslinked polymer can deform permanently on application of a load only when the polymer is irradiated. These polymers have important applications, e.g. for the re-adaptation of a dental filling material to the dental cavity to compensate for curing shrinkage.[5] We have previously noted[1] the importance of the choice of base for the preparation of compounds **1**. We developed methods whereby NaH can be used to furnish **1**, by either starting from a dichloride (METHOD 1) such as 3-chloro-2-chloromethyl-1-propene (**2**) or from a dimercaptan (METHOD 2) such as 3-mercapto-2-mercaptomethyl-1-propene (**3**, Scheme 1).[1] To illustrate this, when a mixture of 3-mercapto-2-mercaptomethyl-1-propene (**3**, 1 equiv.) and epichlorohydrin (**4**, 2 equiv.) was added to a suspension of NaH (2 equiv.) in tetrahydrofuran (METHOD 2), the bisepoxide, 2,2′-(2-methylenepropane-1,3-diyl)bis(sulfanediyl)bis(methylene) dioxirane (**5**) was obtained in a modest yield of 50 % after purification, whereas using potassium carbonate as a base, in either refluxing acetone or butanone, none of compound **5** could be isolated (Scheme 2).[1]

Although the method using NaH as a non-nucleophilic base worked very well for the preparation of **5**, this method did not work for vinyloxyethyl thioethers due to a very sluggish reaction leading to an incomplete alkylation and secondary reaction products. In this case we used 2-chloroethyl vinyl ether (**6**) with sodium methoxide as a base (Scheme 1) in a modification of the method employed by Evans and Rizzardo[6,7] and Scott and

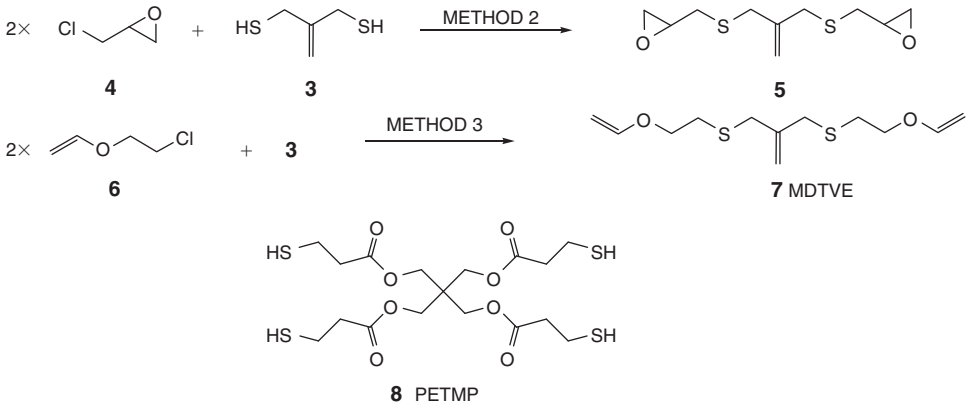


Scheme 1. Preparation of symmetrical 3,3′allyl dithioethers **1**.

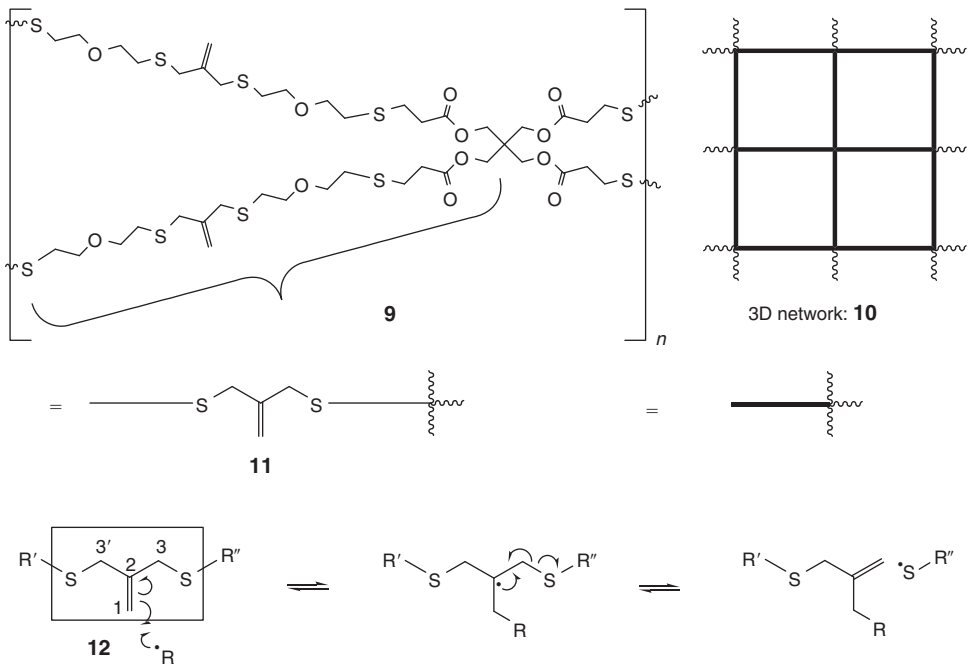
co-workers.[8,9] Thus, when a mixture of dimercaptan **3** (1 equiv.) and **6** (2 equiv.) in methanol and sodium methoxide (2 equiv.) in methanol was added together synchronously (METHOD 3, Scheme 1), 8-methylidene-3,13-dioxa-6,10-dithiapentadeca-1,14-diene (previously named 2-methylene-propane-1,3-di[thioethyl vinyl ether] and abbreviated as MDTVE, **7**) (Scheme 2) was obtained in 78 % yield.

The distinctive photoplastic behaviour of a cured, thiol-ene network,[2,3] in this case represented as the reaction product of MDTVE **7** (2 equiv.) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) **8** (1 equiv.) – shown in Scheme 3 as polymer network **9** schematically represented as **10** – is due to the (2-methylenepropane-1,3-diyl)bis(sulfandiyl) moiety **12** of the polymer strands **11**. These sub-units **12** have methylene groups which can be attacked by photogenerated carbon radicals, $R^{\bullet}$, at the least hindered carbon, C1 of the alkene, to form a bond with simultaneous β-cleavage to regenerate another alkene and a sulfanyl radical (Scheme 3). This sulfanyl radical is then able to attack another alkene in a neighbouring polymer strand, causing, once more, a β-scission and the formation of a new sulfanyl radical. Thus, network strands are broken and then reformed in new arrangements, continuously, and any stress that had been imposed on the strands can be relieved. In the end, the course of radical combination and loss of the photoinitiator depletes the concentration of radicals and that leads to the termination of the chain rearrangements thus restricting the extent of stress relaxation or shape change.

Our studies of the photoplastic behaviour of polymer networks of MDTVE **7** cured with PETMP **8**,[2,3] has led us to investigate polymer networks based on monomers having two 3,3′-allyl dithioether functionalities and even three 3,3′-allyl dithioether functionalities in the molecule. In this paper we disclose how we have applied the synthetic methods we have learned in our previous work,[1] and extended these syntheses for the preparation of novel (alkane-α,ω-diyl)bis([2-{2-(vinyloxy) ethylthiamethyl}allyl]sulfane) (abbreviated to: [alkane-α,ω-diyl]bis[3,3′-allyl dithioethers]) and analogous monomers **14** (Scheme 4) for the preparation of photoplastic polymer

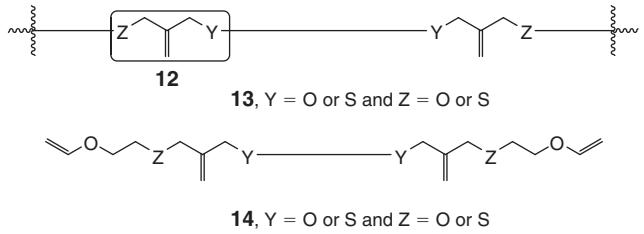


Scheme 2. Monomer compounds for photoplastic polymer networks.



Scheme 3. Identification of a 3D photoplastic polymer network.

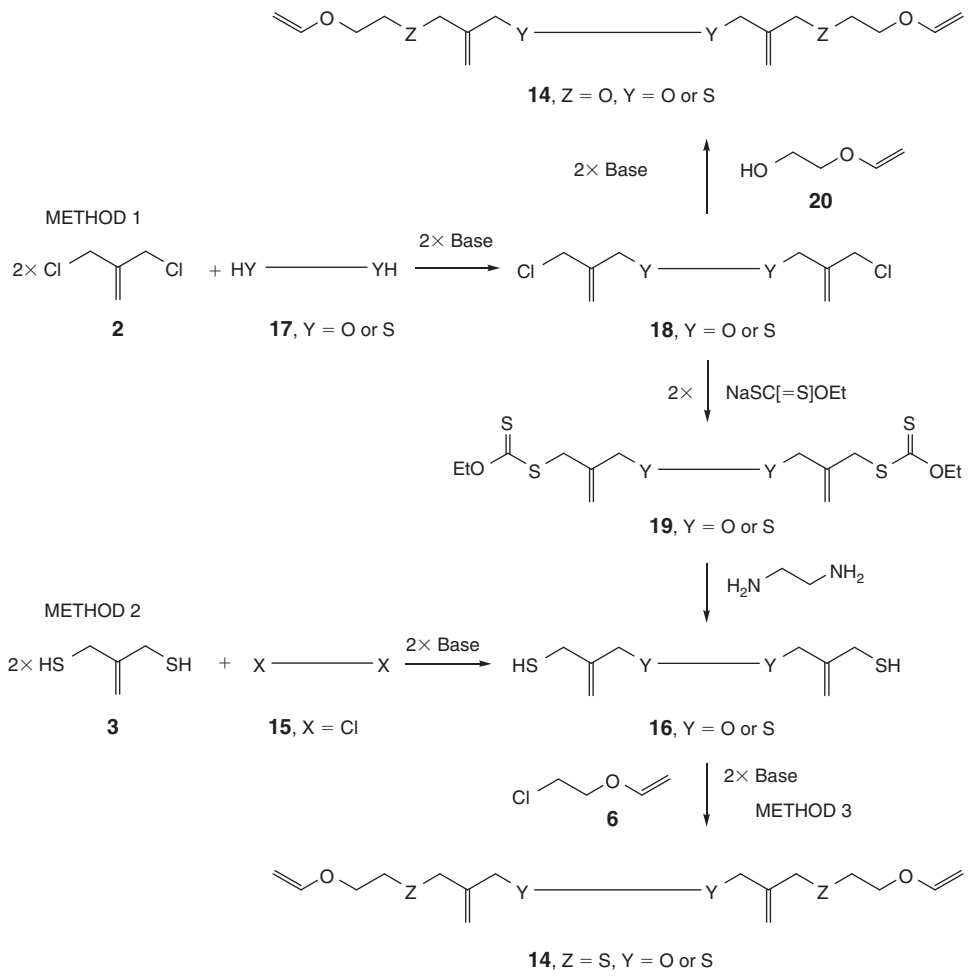
networks. Early in our investigations, we suspected that a three-dimensional network **10** having the essential 3,3′-allyl dithioether unit **12** *too close* to the cross-linkage, may actually diminish the rate and final extent of photoplasticity (Scheme 3). This could occur because, during the sulfanyl-radical attack and subsequent β-cleavage, the resulting new sulfanyl-radical arm may be too short and unable to attack another allylic dithio ether group in the nearest neighbouring polymer strand. To enable investigation of this hypothesis, we have designed monomers for the synthesis of photoplastic polymer networks where we modify the strands in **11** by increasing their length and by replacing the single 3,3′-allyl dithioether units **12** in the polymer strands with two or three 3,3′-allyl dithioether ether units, such as in polymer strand **13** (Scheme 4). To synthesise monomers with two 3,3′-allyl dithioether units, we specifically designed it with symmetry to have synthetic control.



Scheme 4. (Alkane-α,ω-diyl)bis([2-{2-(vinyloxy)ethylthiamethyl}allyl] sulfane) monomers.

Results and Discussion

The most direct route to synthesise monomers of the type **14** was to use either METHOD 1 or METHOD 2 as depicted in Scheme 5. Condensation of excess allylic dimercaptan **3** with dihalide **15** (METHOD **2**) in the presence of two molar equivalents of NaH should form the bis(allylic)dimercaptan **16** (Y = S), which would then be transformed, with one further reaction, into two final products **14** (Y = S, Z = O or S) (Scheme 5).[1] However, the lengthier route, METHOD **1**, reacting the allylic dichloride **2** with dimercaptan **17** was more attractive because with this superior approach we should be able to synthesise all four desired products **14** from **18** (Y = O or S).[1] For example, with in situ generated sodium ethyl xanthogenate, compound **18** (Y = O or S) should be transformed, into the bis(allylxanthates) **19** and then further reacted with ethylene diamine to release the bis(allylmercaptan) **16** (Y = O or S). Then the reaction of 2-chloroethyl vinyl ether (**6**) with **16**, using sodium methoxide as base (METHOD 3, Scheme 5), should furnish the desired photoplastic monomers **14** (Z = S, Y = O or S) (Scheme 5). Alternatively, the dichloride **18** (Y = O or S) should also react with 2-vinyloxyethanol (**20**) in the presence of a suitable base to obtain the monomers **14** (Z = O, Y = O or S) (Scheme 5) yielding a monomer with no allylic

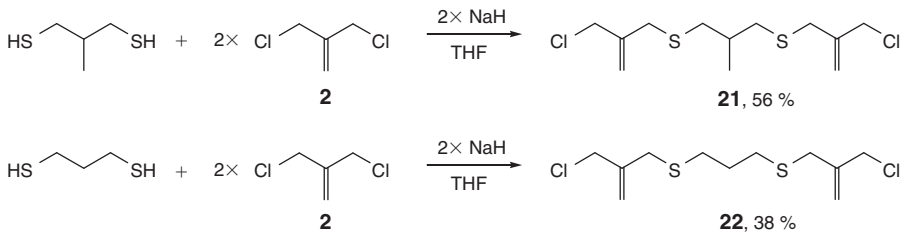


Scheme 5. Synthetic outline for (alkane-α,ω-diyl)bis([2-{2-(vinyloxy)ethylthiamethyl}allyl]sulfane) monomers **14**.

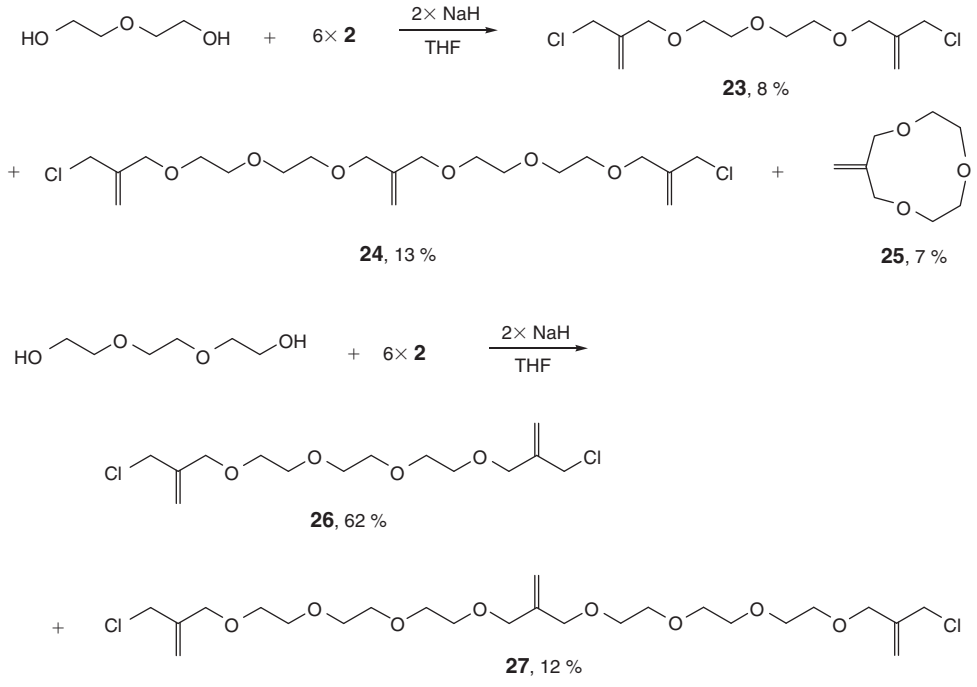
thioether units to act as a control in photoplasticity experiments. The unit **12** of **13** whereby the heteroatoms Z or Y could be oxygen, either near the cross-linkage (Z = O, Y = S) or distant to that (Y = O, Z = S), allow differentiation between longer and shorter sulfanyl radicals of photoplastic polymer systems **13** (Scheme 4).

In monomer **14** (Scheme 4), the selection of the linker group between the two allylic groups is expected to be very important to the photoplasticity of the final polymer because it affects the length of polymer strand terminated by the sulfanyl radical. In addition, this linker group cannot contain aromatic species because this would lead to inflexible polymer strands. We initiated this study using METHOD 1 (Scheme 5) by reacting either 2-methylpropane-1,3-dimercaptan or propane-1,3-dimercaptan with an excess of 2-chloro-2-chloromethyl-1-propene (**2**) in the presence of NaH (2 equiv.) to furnish dichlorides **21** and **22**, respectively, as oils (Scheme 6). However, analysis of the ^{1}H-NMR spectrum of each of the resulting reaction showed that the compounds had impurities of higher oligomers. Purification by distillation or crystallisation was not applicable. These mixtures could not easily be purified by silica gel chromatography as thin-layer chromatography (TLC) analysis revealed. Mixtures of similar sulfur oligomers with no oxygen in their structures are extremely difficult to separate because they have very similar R_f values. The reason for this is that the sulfane unit is not very polar and resembles the polarity of a methylene unit. A comparison of the Pauling electronegativities show that sulfur (2.58) is much closer to carbon (2.55) or hydrogen (2.20) but not oxygen (3.44).[10,11] for synthetic ease it is essential to have at least one oxygen in the linker between the allylic groups so that the desired product can be separated from its oligomers. In addition, the short aliphatic linker in **21** and **22** (Scheme 6) would limit the photoplasticity of the final polymer because the radical strands would be too short to reach neighbouring allylic dithioether groups (see Scheme 3). For example, the cured polymer network **9**, shows limited photoplasticity because the network strands are too short.[3] Therefore, we focussed on longer aliphatic linkers containing oxygen.

For example, allylic dichlorides **18** containing ether-based linkers such as diethylene glycol and triethylene glycol were found to be much easier to purify because each compound showed significant differences in their TLC R_f-values. Thus, the reaction of a 1 : 2 mixture of diethylene glycol, 3-chloro-2-chloromethyl-1-propene (**2**), and excess NaH in tetrahydrofuran at room temperature for 15 h produced the expected dichloride **23** (Scheme 7) which was purified by chromatography from other impurities but the yield was only 8 % and the major product was the triallyl dichloride **24** also in a low yield of 13 %. A little of the crown ether **25** was isolated. In contrast, when the reaction was performed with triethylene glycol, under



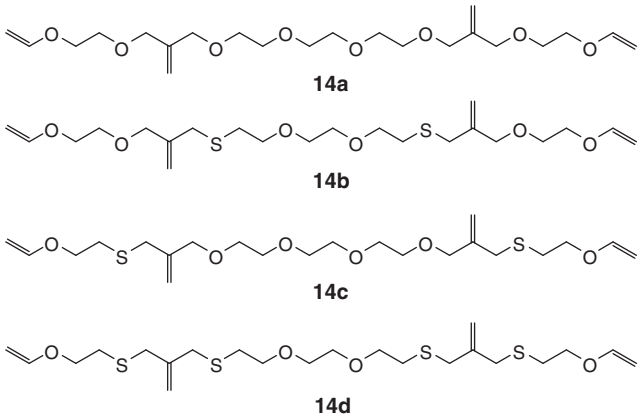
Scheme 6. Preparation of (alkane-α,ω-diyl)bis([2-{chloromethyl}allyl]sulfane with only sulfur in the backbone.



Scheme 7. Preparation of (alkane-α,ω-diyl)bis([2-{chloromethyl}allyl]ethers based on diethylene glycol and triethylene glycol.

exactly the same conditions, the outcome was dramatically different and a yield of 62 % was obtained of the required dichloride **26** along with 12 % of the triallyl dichloride **27**, but no cyclised product analogous to **25** was found (Scheme 7). All products **23** to **27** were simple to separate by chromatography on silica gel. For example, the dihalides **26** and **27** (Scheme 7), have R_f values of 0.39 and 0.13 (using 1 : 1 EtOAc : hexane). We cannot explain the considerable difference in yields between the alkylation reactions of diethylene glycol and triethylene glycol with excess **2**, but it determined our choice of derivatives to be based on triethylene glycol. The synthetic target molecules for compound **14** are outlined in Scheme 8.

In the synthesis of bis(allyl) di(vinyloxyethyl) monomer **14a**, the alkylation of bis(allyl) dichloride **26** and 2-vinyloxyethanol (**20**) was quite troublesome. Attempted alkylation of 2-vinyloxyethanol (**20**, 2 equiv.) and bis(allyl) dichloride **26** (1 equiv.), with NaOMe as base caused extensive methoxylation of **26**. Performing the reaction in anhydrous THF with slight excess NaH (>2 equiv.), gave the desired monomer **14a** (Scheme 9) as a colourless oil however, the optimum conditions for this reaction were rather narrow. For example, it was found that when the addition of **26** and **20** to NaH was carried out over a period of 5 min, this addition-rate was too slow and the alkylation reaction did not proceed to completion. However, fast addition (approx. 1 s) of a mixture **20** and **26** to NaH did yield the desired product **14a**. Unfortunately, this very rapid addition gave a strong exotherm that could not be controlled with larger scale reactions (>2 g). Alternatively, when 2-vinyloxyethanol (**20**) and bis(allyl) dichloride **26** were stirred in butanone for 15 h at 70°C under phase-transfer conditions using potassium carbonate as a base and benzyltriethylammonium chloride (BTEAC) as the catalyst, the product **14a** was obtained in a 43 % yield and this procedure could be repeated on a large scale (Scheme 9).

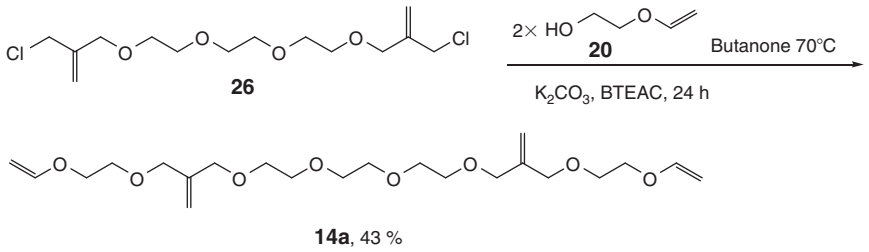


Scheme 8. Synthetic target molecules for 3D photoplastic monomer compounds.

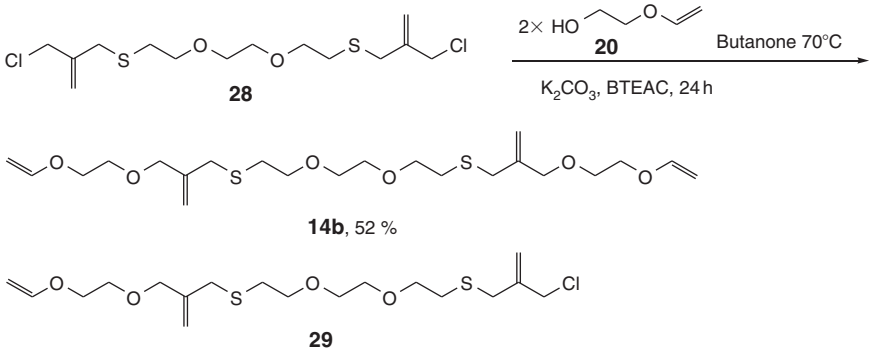
Using similar phase-transfer conditions, the product **14b**, a colourless oil, was obtained in a 52 % yield (Scheme 10) from 2-vinyloxyethanol (**20**) and bis(allyl) dichloride **28**[1]; the contaminating semi-alkylated product **29** was removed with difficulty by chromatography.

To synthesise **14c**, the dichloride **26** was treated with soluble sodium ethyl xanthogenate in ethanol to give the bis(xanthate) **30** (Scheme 11). Compound **30** then reacted with ethylene diamine to give the dimercaptan **31** as a colourless oil. After purification it was found to have little, if any, sulfurous smell, apparently due to the increase in chain length and decrease of its volatility, as explained in detail in the literature.[12] The dimercaptan **31** and chloride **6** was added synchronously with a solution of sodium methoxide to give **14c** as a colourless liquid in an unoptimised yield of 43 %.

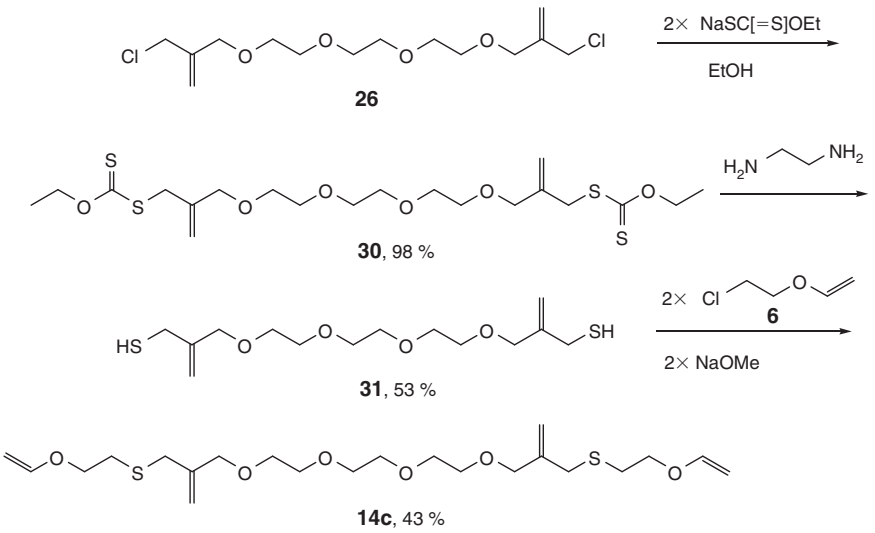
The monomer **14d** was synthesised in a similar fashion (Scheme 12). The dichloride **28**[1] was treated with sodium ethyl



Scheme 9. Synthesis of compound **14a**.



Scheme 10. Synthesis of compound **14b**.



Scheme 11. Synthesis of compound **14c**.

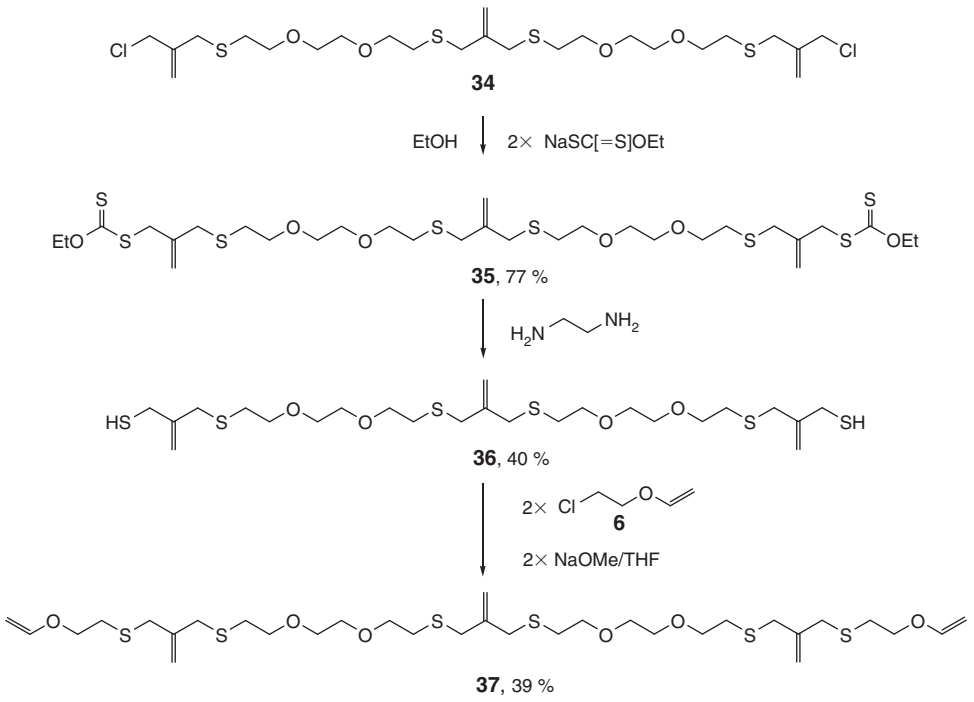
Scheme 12. Synthesis of compound **14d**.

xanthogenate in ethanol to give a pale yellow oil of the bis(xanthate) **32** (Scheme 12). Release of the dimercaptan **33** was accomplished with ethylene diamine and then purified by chromatography. Compound **33** also had little, if any, smell[12] and at room temperature was a colourless solid. The last step in this reaction sequence was carried out by treating the mixture of compound **33** and chloride **6** (2 equiv.) with sodium methoxide in methanol. The product **14d** was purified by chromatography to give a colourless oil in an unoptimised yield of 35 %. This oil crystallized slowly at room temperature.

The practical importance of having oxygen in the linker in-between the allyl groups of precursors **18** and final products **14** (Scheme 5) cannot be overstated. Monomers containing more sulfur atoms are less able to be chromatographically separated from their derivatives and impurities than monomers with fewer sulfur atoms. The differences of R_f values between the monomers **14** are quite dramatic. The polar, oxygenated monomer **14a** had an TLC R_f value of 0.14 (1 : 1 EtOAc : hexanes) whereas the mixed sulfur-oxygen analogues **14b** and **14c** had R_f values of 0.49 and 0.52 (1 : 1 EtOAc : hexanes), respectively, and the relatively non-polar tetrathia analogue **14d** with an R_f value at 0.63 (1 : 1 EtOAc : hexanes) compared with MDTVE **7** with an R_f value at 0.68 (1 : 1 EtOAc : hexanes).

The series of photoplasticity monomers was extended by synthesising compound **37**, having three 3,3′-allyl dithioether ether units, in a similar fashion as for the preparation of **14d** (Scheme 13). The tris(allyl) dichloride **34**[1] was treated with excess sodium ethyl xanthogenate in ethanol, and gave after workup a faint yellow oil of the bis(xanthate) **35**. The dimercaptan **36** was released from **35** with ethylene diamine at room temperature, and after chromatography over silica gel yielded an odourless, white solid of **36**. Synchronous combination of a mixture of dithiol **36** and **6** in a ratio of 1 : 2 with a solution of sodium methoxide (2 equiv.) in methanol at 50°C, gave compound **37** as a white solid in an unoptimised yield of 39 %.

The FT-IR spectra of the four diallylic monomers are shown in Fig. 1 and the peak assignments[13] are given below. The allylic peak at 1615 cm^{-1} is clearly obvious in all monomers but it overlapped with the vinyl ether peak at 1635 cm^{-1}. The vinyl ether (CH_2=CH-O-CH_2-) stretch at 1200 cm^{-1} is visible in



Scheme 13. Preparation of tris(allyl dithio) divinylethoxy monomer **37**.

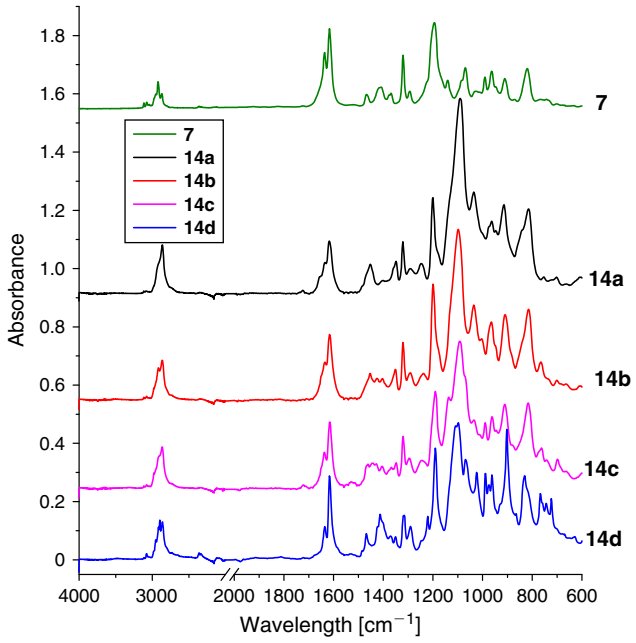


Fig. 1. FT-IR ATR spectra of monomer compounds **7**, **14a**, **14b**, **14c**, and **14d**.

these monomers and also in **7**. The aliphatic -CH_2-O-CH_2- asymmetric stretch is seen as a large peak near 1100 cm^{-1} in monomers **14** but not in **7**. The intensity of the aliphatic -CH_2-O-CH_2- asymmetric stretch in compounds **14** decrease in size as the allylic ether is substituted by the allylic thio-ether in these compounds. The aliphatic -CH_2-S-CH_2- sulfide is usually small and does not have a characteristic wavenumber and so is not identified in the spectra.

The mechanical properties, including photoplasticity, of the polymers derived from these new monomers and co-monomers, will be reported elsewhere.

Conclusions

According to a simple synthetic protocol, the preparation of a series of symmetrical (alkane-α,ω-diyl)bis([2-{2-(vinyloxy) ethylthiamethyl}allyl]sulfane) compounds and their analogous ethers **14** have been accomplished from (alkane-α,ω-diyl)bis ([2-{chloromethyl}allyl]sulfane) **18** and like compounds. Monomers **14** were designed for the preparation and the study of photoplastic three dimensional polymer networks. In purifying these compounds, it became apparent that the linker between the two allylic groups of the various (alkane-α,ω-diyl)bis ([2-{chloromethyl}allyl]sulfane) **18** compounds should have at least one oxygen in the back-bone to facilitate purification of these and all other derived compounds. Having derivatives of triethylene glycol as a linker proved both successful in yield and purity in this endeavour.

Experimental

General

All chemicals were used as received unless otherwise specified. 3-Chloro-2-chloromethyl-1-propene (**2**), was purchased from Secant Chemicals Inc. (MI, USA). 1,3-Propanedithiol, diethylene glycol, triethylene glycol and 60 % NaH in oil were purchased from Sigma Aldrich (Castle Hill, NSW, Australia). 60 % NaH in oil suspension was washed twice with a mixture of hexane isomers (termed ‘hexanes’ and supplied by Merck). All reactions were performed under nitrogen unless stated otherwise. Tetrahydrofuran was dried over NaH. The preparation of 3-mercapto-2-mercaptomethyl-1-propene (**3**), and compounds **28** and **34**, was carried out as described before.[1] 2-Methyl-1,3-propanedithiol was made according to Scott et al.[9] Some mass spectra experiments were carried out on a Waters Q-TOF II instrument, employing electrospray ionisation (ESI) with a 35 eV cone voltage and employing a Lockspray source and sodium iodide as a reference sample. Other mass spectra experiments were carried out on a ThermoQuest MAT95XP

instrument, employing electron impact (EI) at 70 eV and perfluorokerosene as a reference sample. NMR spectra were run on a Bruker Avance III 400 (9.4 Tesla magnet) with a 5 mm broadband inverse probe, ^{1}H at 400.13 MHz, or a Bruker DPX300 (7.05 Tesla magnet) with a 5 mm quad $^{1}H/^{13}C$ switchable probe, ^{1}H at 300.13 MHz, or a Bruker AV200 (4.7 Tesla magnet) with 5 mm $^{1}H/^{13}C$ probe with *Z*-gradients at 30°C in $CDCl_3$ using the residual chloroform peaks at 7.25 ppm as a reference in proton and 77.0 ppm in carbon spectra. Abbreviations for multiplets are 'sm' for a sharp multiplet and 'dm' for a doublet of multiplets and is caused by small coupling constants of the multiplets (<1 Hz). These multiplets cannot be accurately analysed but are clearly visible. A Nicolet 6700 FTIR was used to collect the ATR spectra. Silica gel on plastic TLC plates were obtained from Merck. Only some of the compounds on TLC could be observed clearly by UV (254 nm) fluorescence, however neutral aqueous potassium permanganate solution developed most of the sulfur- and alkene-based products on TLC very clearly - the excess potassium permanganate was then removed with gentle running water.

*(2-Methylpropane-1,3-diyl)bis([2-{chloromethyl}allyl] sulfane) (**21**)*

A neat mixture of 3-chloro-2-chloromethyl-1-propene (**2**) (12 g, 96.0 mmol, 5.9 equiv.) and 2-methyl-1,3-propanedithiol (2.00 g, 16.4 mmol, 1 equiv.) was added within 5 min to NaH (0.84 g, 35.0 mmol, 2 equiv.) in anhydrous THF (30 mL) at room temperature. A slow evolution of hydrogen gas occurred and the mixture was further stirred at room temperature for 4 days. The grey suspension had turned yellow-white. This mixture was diluted with THF (30 mL) and filtered over a bed of silica gel (3 cm diameter and 3 cm thick). The filter was further eluted with THF (40 mL) and the filtrate rotary evaporated dry on a hot waterbath (70°C) to give 2.98 g crude product as a pale-yellow oil. Chromatography on 60 g silica gel and elution with 5 : 95 EtOAc : hexanes gave product **21** (2.75 g, 56 %) with minor inseparable higher oligomers as impurities. δ_H (200 MHz, $CDCl_3$) 1.06 (d, 3H, *J* 6.8, $CHCH_3$), 1.87 (octet, 1H, *J* 6.8, $CHCH_3$), 2.34 (dd, 2H, *J* 12.8, 6.8, $CHCH_2S$), 2.52 (dd, 2H, *J* 12.8, 6.0, $CHCH_2S$), 3.27 (d, 4H, *J* 1.0, SCH_2), 4.19 (d, *J* 1.0, 4H, $ClCH_2$), 5.09 (dt, 2H, *J* 1.0, 1.0, HC=C), 5.23 (d, 2H, *J* 1.0, HC=C). δ_C (75 MHz, $CDCl_3$) 19.4 (Me), 33.2 (CH), 35.4 (2 × SCH_2-allyl), 37.6 (2 × CH_2S), 45.8 (2 × $ClCH_2$), 117.2 (2 × H_2C=), 141.2 (2 × =C) ppm.

*1,3-Bis(2-(chloromethyl)allylthio)propane (**22**)*

A mixture of 3-chloro-2-chloromethyl-1-propene (**2**) (13.39 g, 107 mmol, 5.4 equiv.) and 1,3-propanedithiol (2.16 g, 20 mmol, 1 equiv.) in anhydrous THF (1 mL) was added within 5 min to a stirred suspension of NaH (1.20 g, 50.0 mmol, 2.5 equiv.) in anhydrous THF (30 mL) at room temperature. A slow evolution of hydrogen gas occurred during the addition. After the addition, the mixture was stirred at room temperature for 24 h. The grey suspension-mixture had changed to a yellow-white colour. This mixture was diluted with a 1 : 1 mixture THF : hexanes (60 mL) and filtered over a bed of silica gel (3 cm diameter and 3 cm thick). The filter was further eluted with 1 : 1 THF : hexanes (100 mL) and the filtrate rotary evaporated dry over a waterbath (80°C) to give the crude product as a slightly pale-yellow oil. Chromatography on a 50 g silica gel column, and elution with 5 : 95 EtOAc : hexanes gave 2.66 g of an inseparable mixture of 82 % pure compound **22** (38 %) and other oligomers. δ_H (300 MHz, $CDCl_3$) 1.80 (p, 2H, *J* 6.9, CH_2), 2.48 (t, 4H, *J* 6.9, SCH_2), 3.26 (d, 4H, *J* 0.9, SCH_2C=), 4.18 (d, 4H, *J* 0.6, $ClCH_2$), 5.07 (d, 2H, *J* 0.9, HC=C), 5.21 (d, 2H, *J* 0.6, HC=C). δ_C (75 MHz, $CDCl_3$) 28.4 (CH_2), 30.0 (2 × SCH_2-allyl), 34.7 (2 × CH_2S), 45.8 (2 × $ClCH_2$-allyl), 117.1 (2 × H_2C=), 141.1 (2 × =C).

*2,12-Bis(chloromethyl)-4,7,10-trioxatrideca-1,12-diene (**23**) and 2,22-Bis(chloromethyl)-12-methylene-4,7,10,14,17,20-hexaoxatricosa-1,22-diene (**24**)*

A mixture of 3-chloro-2-chloromethyl-1-propene (**2**) (15 g, 120.0 mmol, 6 equiv.) and diethylene glycol (2.12 g, 20 mmol, 1 equiv.) in anhydrous THF (1 mL) was added within 5 min to a suspension of NaH (1.20 g, 50.0 mmol, 2.5 equiv.) in anhydrous tetrahydrofuran (30 mL) at room temperature. A vigorous exothermic reaction occurred with the simultaneous evolution of hydrogen gas. The mixture turned brown and was stirred for 15 h at room temperature. The suspension was diluted with 1 : 1 THF : hexanes (60 mL) and filtered over a bed of silica gel (3 cm diameter, 3 cm thick). The filter was further eluted with 1 : 1 THF : hexanes (100 mL) and the combined filtrate rotary evaporated dry on a hot waterbath (80°C) to give a crude oil. This product was then chromatographed on a 20 cm column with silica gel (50 g) and eluted with 95 : 5 hexanes : EtOAc to give cyclo-compound **25** (0.23g, 7 %). R_f (1 : 1 EtOAc : hexanes) = 0.68. δ_H (300 MHz, $CDCl_3$) 3.6–3.7 (m, 8H, OCH_2), 4.08 (t, 4H, *J* 0.3, CH_2-allyl), 5.16 (t, 2H, *J* 0.3, H_2C=). δ_C (75 MHz, $CDCl_3$) 69.9 (2 × O-CH_2), 70.9 (2 × O-CH_2), 72.0 (2 × O-CH_2), 114.0 (H_2C=), 143.5 (=C) ppm. The eluant was increased to 4 : 1 hexanes : EtOAc to give compound **23** (0.43 g, 8 %). R_f (1 : 1 EtOAc : hexanes) = 0.54. δ_H (300 MHz, $CDCl_3$) 3.58–3.62 (m, 4H, OCH_2), 3.63–3.64 (m, 4H, OCH_2), 4.10 (d, 4H, *J* 0.9, CH_2-allyl), 4.11 (s, 4H, CH_2-allyl), 5.23 (dt, 2H, *J* 1.2, 0.9, HC=), 5.28 (dm, 2H, *J* 0.9, HC=). δ_C (75 MHz, $CDCl_3$) 45.1 (2 × $ClCH_2$), 69.7 (2 × OCH_2), 70.6 (2 × OCH_2), 71.3 (2 × OCH_2), 116.7 (2 × H_2C=), 142.0 (2 × =C). *m/z* (EI) 247 ($[M-Cl]^+$, 5 %), 177 (38 %), 133 (22 %), 91 (35 %), 89 (100 %), 73 (45 %), 55 (31 %). *m/z* (HRMS) Anal. Calc. for $C_{12}H_{20}O_3{}^{35}Cl$ $[M-Cl]^+$: 247.1095. Found: 247.1093. The eluant was then further increased to 3 : 2 hexanes : EtOAc to give colourless compound **24** (0.58 g, 13 %). R_f (1 : 1 EtOAc : hexanes) = 0.27. δ_H (300 MHz, $CDCl_3$) 3.56–3.62 (m, 8H, OCH_2), 3.63–3.68 (m, 8H, OCH_2), 4.01 (dd, 4H, *J* 0.9, 0.9, CH_2-allyl), 4.09 (d, 4H, *J* 0.9, CH_2-allyl), 4.10 (s, 4H, CH_2-allyl), 5.17 (t, 2H, *J* 0.9, HC=), 5.22 (dt, 2H, *J* 1.2, 0.9, HC=), 5.28 (dm, 2H, *J* 1.2, HC=). δ_C (75 MHz, $CDCl_3$ 45.0 (2 × $ClCH_2$), 69.5 (2 × OCH_2), 69.6 (2 × OCH_2), 70.5 (2 × OCH_2), 70.6 (2 × OCH_2), 71.2 (2 × OCH_2), 71.7 (2 × OCH_2), 114.07 (H_2C=), 116.89 (2 × H_2C=), 142.12 (2 × =C), 142.62 (=C). *m/z* (EI) 405 ($[M-Cl]^+$, <1 %); 263 (<1 %); 247 (1 %), 187 (7 %), 177 (10 %), 159 (14 %), 135 (11 %), 133 (16 %), 97 (10 %), 91 (31 %), 89 (88 %), 73 (100 %), 55 (51 %). *m/z* (HRMS) Anal. Calc. for $C_{20}H_{34}O_6{}^{35}Cl$ $[M-Cl]^+$: 405.2038. Found: 405.2043.

*2,15-Bis(chloromethyl)-4,7,10,13-tetraoxahexadeca-1,15-diene (**26**) and 2,28-Bis(chloromethyl)-15-methylene-4,7,10,13,17,20,23,26-octaoxanonacosa-1,28-diene (**27**)*

A mixture of 3-chloro-2-chloromethyl-1-propene (**2**) (15 g, 120 mmol, 6 equiv.) and triethylene glycol (3.0 g, 20 mmol, 1 equiv.) was added all at once to a stirred suspension of NaH (1.02 g, 43 mmol, 2.1 equiv.) in anhydrous tetrahydrofuran (30 mL) at room temperature (vigorous evolution of H_2, and temperature increased immediately to 50°C). This mixture was stirred for 5 h at room temperature. The resulting yellowish-

white suspension was diluted with THF (30 mL) and filtered over a bed of silica gel (3 cm diameter and 3 cm thick). The filter was further eluted with THF (30 mL). This clear filtrate was rotary evaporated dry on a hot waterbath (80°C) to give a crude, pale-yellow oil. Chromatography of this oil on a 30 cm column, packed with silica gel (90 g), and elution with 3 : 2 hexanes : EtOAc gave colourless compound **26** (4.04 g, 62 %). R_f (1 : 1 EtOAc : hexanes) = 0.36. δ_H (300 MHz, $CDCl_3$) 3.58–3.61 (m, 4H, OCH_2), 3.64–3.68 (m, 4H, OCH_2), 3.65 (s, 4H, OCH_2), 4.10 (dm, 4H, *J* 1.2, CH_2-allyl), 4.11 (sm, 4H, CH_2-allyl), 5.23 (dt, 2H, *J* 0.9, 1.2, HC=), 5.29 (dm, 2H, *J* 0.9, HC=). δ_C (50 MHz, $CDCl_3$) 45.0 (2 × $ClCH_2$), 69.6 (2 × OCH_2), 70.5 (2 × OCH_2), 70.6 (2 × OCH_2), 71.2 (2 × OCH_2), 116.6 (2 × H_2C=), 142.0 (2 × =C) ppm. *m/z* (EI) 291 (<1 %, $[M - Cl]^+$); 221 (12 %); 133 (33 %), 97 (15 %), 91 (33 %), 89 (100 %), 73 (51 %), 55 (29 %). *m/z* (HRMS) Anal. Calc. for $C_{14}H_{24}O_4{}^{35}Cl$ $[M - Cl]^+$: 291.1359. Found: 291.1364. Increasing the eluent to 3 : 7 hexanes : EtOAc gave colourless compound **27** (0.62 g, 12 %). R_f (1 : 1 EtOAc : hexanes) = 0.13. δ_H (400 MHz, $CDCl_3$) 3.5–3.6 (m, 8H, OCH_2), 3.62–3.66 (m, 8H, OCH_2), 3.64 (s, 8H, OCH_2), 4.00 (dd, 4H, *J* 1.2, 1.2, CH_2-allyl), 4.08 (dm, 4H, *J* 1.2, CH_2-allyl), 4.09 (d, 4H, *J* 0.8, CH_2-allyl), 5.16 (dd, 2H, *J* 0.8, 0.8, HC=), 5.22 (dt, 2H, *J* 1.2, 1.2, HC=), 5.27 (dm, 2H, *J* 1.2, HC=). δ_C (75 MHz, $CDCl_3$) 45.1 (2 × $ClCH_2$), 69.5 (2 × OCH_2), 69.7 (2 × OCH_2), 70.5 (2 × OCH_2), 70.6 (2 × OCH_2), 70.7 (2 × OCH_2), 70.8 (2 × OCH_2), 71.2 (2 × OCH_2), 71.8 (2 × OCH_2), 113.9 (H_2C=), 116.7 (2 × H_2C=), 142.0 (2 × =C), 142.6 (=C). *m/z* (HRMS, ESI) Anal. Calc. for $C_{24}H_{42}O_8Cl_2Na$: 551.2154. Found: 551.2172.

*8,21-Dimethylene-3,6,10,13,16,19,23,26-octaoxaoctacosa-1,27-diene (**14a**)*

A solution of 2-(vinyloxy)ethanol (**20**) (0.7 g, 7.95 mmol, 2.6 equiv.) in butanone (1 mL) was added to a suspension of potassium carbonate (1.5 g, 10.85 mmol) and benzyltriethylammonium chloride as a phase transfer catalyst (0.1 g, 0.44 mmol) in butanone (2 mL). Then 2,15-bis(chloromethyl)-4,7,10,13-tetraoxahexadeca-1,15-diene (**26**) (1 g, 3.056 mmol, 1 equiv) was added and the mixture stirred for 18 h at 70°C. Butanone (40 mL) was added and the mixture filtered. The filtrate was rotary evaporated dry. The crude product was diluted with 1 : 1 THF : hexanes (20 mL) and filtered over a bed of silica gel (3 cm diameter and 2 cm thick). The filter was further eluted with 1 : 1 THF : hexanes (20 mL) and the clear filtrate rotary evaporated dry on a hot waterbath (90°C) to give 1.07 g crude product as a clear, but viscous oil (81 %). Chromatography on silica gel was carried out, and elution with 2 : 3 EtOAc : hexanes gave compound **14a** (0.56 g, 43 %). R_f (1 : 1 EtOAc : hexane) = 0.14. δ_H (300 MHz, $CDCl_3$) 3.54–3.61 (m, 4H), 3.62–3.67 (m, 8H), 3.62 (s, 4H), 3.81 (dd, 4H, *J* 6.1, 5.4), 3.97 (dd, 2H, *J* 6.9, 2.1), 4.00 (s, 4H), 4.01 (s, 4H), 4.16 (dd, 2H, *J* 14.4, 2.1), 5.17 (s, 4H), 6.46 (dd, 2H, *J* 14.4, 6.9). δ_C (75 MHz, $CDCl_3$) 67.3 (2 × OCH_2), 68.5 (2 × OCH_2), 69.5 (2 × OCH_2), 70.5 (2 × OCH_2), 70.6 (2 × OCH_2), 71.7 (2 × OCH_2), 71.8 (2 × OCH_2), 86.6 (2 × =CH_2), 114.2 (2 × =CH_2), 142.4 (=C), 151.8 (2 × =CH-O). *m/z* (HRMS, ESI) Anal. Calc. for $C_{22}H_{38}O_8Na$: 453.2464. Found: 453.2448.

*8,21-Dimethylene-3,6,10,13,16,19,23,26-octaoxaoctacosa-1,27-diene (**14a**)*

A mixture of 2,15-bis(chloromethyl)-4,7,10,13-tetraoxahexadeca-1,15-diene (**26**) (1 g, 3.056 mmol, 1 equiv.) and 2-(vinyloxy) ethanol (**20**) (0.7 g, 7.95 mmol, 2.6 equiv.) in anhydrous THF (1 mL) was added within 1 s to NaH (0.189 g, 7.9 mmol, ~2.6 equiv.) in anhydrous THF (10 mL). The reaction, under a vigorous evolution of hydrogen gas, was instantaneous, and the grey suspension had turned yellow-white. This mixture was stirred for 15 h at room temperature. This mixture was diluted with THF (10 mL) and filtered over a bed of silica gel (1 cm). The filter was further eluted with THF (20 mL) and the filtrate rotary evaporated dry on a hot waterbath (~90°C) to give crude product **14a** (1.05 g, 80 %) as a slightly pale-yellow oil.

*8,21-Dimethylene-3,6,13,16,23,26-hexaoxa-10,19-dithiaoctacosa-1,27-diene (**14b**)*

A solution of 2-(vinyloxy)ethanol (**20**) (1.07 g, 12.1 mmol, 4.0 equiv.) and 2,15-bis(chloromethyl)-7,10- dioxa-4,13-dithiahexadeca-1,15-diene (**28**) (1.1 g, 3.1 mmol, 1 equiv.) in butanone (1 mL) was added to a suspension of potassium carbonate (1.5 g, 10.9 mmol) and benzyltriethylammonium chloride (0.1 g, 0.4 mmol) in butanone (2 mL). The mixture was stirred at 70°C for 24 h. The reaction mixture was diluted with 1 : 1 THF : hexanes (20 mL) and filtered over a bed of silica gel (3 cm diameter and 2 cm thick). The filter was further eluted with 1 : 1 THF : hexanes (20 mL) and the clear filtrate rotary evaporated dry to give 1.46 g crude product as a clear, but viscous oil also containing some **20**. Chromatography on silica gel was carried out by gradient elution from 3 : 7 EtOAc : hexanes to 2 : 3 EtOAc : hexanes and gave the product **14b** (0.73 g, 52 %). R_f (1 : 1 EtOAc : hexane) = 0.49. δ_H (300 MHz, $CDCl_3$) 2.62 (t, 4H, *J* 6.9, CH_2S), 3.21 (d, 4H, *J* 0.6, SCH_2-allyl), 3.60 (s, 4H, OCH_2), 3.60 (t, 4H, *J* 6.9, OCH_2), 3.64–3.67 (m, 4H, OCH_2), 3.81–3.85 (m, 4H, OCH_2), 4.00 (dd, 2H, *J* 6.6, 2.1, H_2C=CH), 4.10 (s, 4H, OCH_2), 4.18 (dd, 2H, *J* 14.4, 2.1, H_2C=CH), 5.06 (d, 2H, *J* 0.9, H_2C=C), 5.14 (d, 2H, *J* 1.5, H_2C=C), 6.48 (dd, 2H, *J* 14.4, 6.6, H_2C=C*H*). δ_C (75 MHz, $CDCl_3$) 30.4 (2 × SCH_2), 34.9 (2 × SCH_2-allyl), 67.3 (2 × vinyl-OCH_2), 68.5 (2 × OCH_2), 70.3 (2 × OCH_2), 70.7 (2 × OCH_2), 71.9 (2 × OCH_2-allyl), 86.7 (2 × =CH_2), 115.1 (2 × =CH_2), 141.6 (2 × =C), 151.8 (2 × =CH-O). *m/z* (HRMS, ESI) Anal. Calc. for $C_{22}H_{38}O_6{}^{32}S_2Na$: 485.2008. Found: 485.1997. 'Semi'-alkylated product **29**. R_f (1 : 1 EtOAc : hexane) = 0.45. δ_H (300 MHz, $CDCl_3$) 2.57 (t, 2H, *J* 6.9, SCH_2), 2.60 (t, 2H, *J* 6.9, SCH_2), 3.19 (d, 2H, *J* 0.6, SCH_2-allyl), 3.30 (d, 2H, *J* 0.9, SCH_2-allyl), 3.57 (s, 4H, OCH_2), 3.57–3.64 (m, 6H, OCH_2), 3.81 (m, 2H, OCH_2), 3.97 (dd, 1H, *J* 6.9, 2.1, H_2C=CH), 4.07 (s, 2H, $ClCH_2$), 4.15 (dd, 1H, *J* 14.4, 2.1, H_2C=CH), 4.17 (dm, 2H, *J* 0.9, OCH_2-allyl), 5.03 (sm, 1H, H_2C=C), 5.07 (dm, 1H, *J* 0.9, H_2C=C), 5.12 (dm, 1H, *J* 1.5, H_2C=C), 5.20 (d, 1H, *J* 0.9, H_2C=C), 6.46 (dd, 1H, *J* 14.4, 6.9, H_2C=C*H*). δ_C (75 MHz, $CDCl_3$) 30.2 (2 × SCH_2), 34.7 (SCH_2-allyl), 34.9 (SCH_2-allyl), 45.6 (CH_2Cl), 67.3 (OCH_2), 68.3 (OCH_2), 70.1 (OCH_2), 70.2 (OCH_2), 70.5 (OCH_2), 70.6 (OCH_2), 71.7 (OCH_2), 86.5 (=CH_2), 115.0 (=CH_2), 117.3 (=CH_2), 140.9 (=C), 141.4 (=C), 151.6 (=CH). *m/z* (HRMS, ESI) Anal. Calc. for $C_{18}H_{31}O_4{}^{35}Cl{}^{32}S_2Na$: 433.1250. Found: 433.1228.

*S,S′-2,15-Dimethylene-4,7,10,13-tetraoxahexadecane-1,16-diyl O,O′-Diethyl Dicarbonodithioate (**30**)*

Sodium (1.20 g, 52.2 mmol, 2.1 equiv) was dissolved in anhydrous ethanol (40 mL) over 30 min. This solution was then reacted with carbon disulfide (4.1 g, 53.9 mmol, 2.2 equiv) to form an ethanolic solution of pale-yellow sodium ethyl xanthogenate. After 15 min, 2,15-bis(chloromethyl)-4,7,10,13-tetraoxahexadeca-1,15-diene (**26**) (7.9 g, 24.1 mmol) was added neat to this solution, within 1 min. The solution became slightly

warm (~35°C) and precipitation of white NaCl slowly occurred and the reaction mixture was kept stirring overnight at room temperature. EtOH was rotary evaporated off at 60°C to give a viscous yellow translucent oil. This residue was dissolved in ethyl acetate (40 mL) to precipitate sodium chloride, and this was filtered off over a layer of silica gel (2 cm). The filter was again treated with EtOAc (40 mL) and the combined yellow filtrate was rotary evaporated dry to give crude yellow oil. This oil was treated with dichloromethane (30 mL) which precipitated unreacted, excess sodium ethyl xanthogenate. This solution was filtered over *Celite* and the resulting filtrate was rotary evaporated dry to give the yellow xanthate **30** (11.75 g, 98 %). δ_H (400 MHz, $CDCl_3$) 1.40 (t, 6H, *J* 7.2, CH_3), 3.55–3.58 (m, 4H, OCH_2), 3.63–3.66 (m, 4H, OCH_2), 3.66 (s, 4H, OCH_2), 3.84 (dm, 4H, *J* 0.8, CH_2-allyl), 4.03 (s, 4H, SCH_2-allyl), 4.63 (q, 4H, *J* 7.2, OCH_2), 5.19 (dm, 2H, *J* 1.2, H_2C=), 5.23 (dm, 2H, *J* 0.8, H_2C=). δ_C (100 MHz, $CDCl_3$) 13.7 (2 × CH_3), 38.2 (2 × SCH_2-allyl), 69.5 (2 × OCH_2), 70.0 (2 × OCH_2), 70.7 (2 × OCH_2), 70.6 (2 × OCH_2), 72.8 (2 × OCH_2-allyl), 116.4 (2 × H_2C=), 140.1 (2 × =C), 214.1 (2 × C=S). *m/z* (HRMS, ESI) Anal. Calc. for $C_{20}H_{34}O_6{}^{32}S_4Na$: 521.1112. Found: 521.1136.

*2,15-Dimethylene-4,7,10,13-tetraoxahexadecane-1,16-dithiol (**31**)*

CAUTION: Workup of the reaction-mixture should be carried out in a fume-hood, since by-products may have a severe stench.

S,S′-2,15-Dimethylene-4,7,10,13-tetraoxahexadecane-1,16-diyl O,O′-diethyl dicarbonodithioate (**30**) (22.0 g, 44.1 mol) was added neat to ethylenediamine (6 mL, 5.4 g, 89.8 mmol, 2.04 equiv) over a period of 25 min at 0°C and then stirred for a further 35 min at 0°C and then subsequently allowed to come to room temperature and stirred for another 15 min. This reaction mixture was added to a premixed solution of conc. H_2SO_4 (10 mL, 18.4 g, 187.8 mmol) and 40 g crushed ice in a small beaker with fast magnetic stirring to neutralise ethylene diamine (followed by checking the pH). The yellow, opaque aqueous acidic layer was treated with dichloromethane (30 mL) and hexanes (10 mL). This mixture was transferred to a funnel and extracted. The organic layer was then isolated and treated with saturated $NaHCO_3$ solution (40 mL). All aqueous extractions were again extracted with dichloromethane (30 mL). The combined organic layer was dried (Na_2SO_4) for 15 min and filtered over silica gel and further eluted with dichloromethane. The filtrate was rotary evaporated at 40°C to give a crude oil (10.2 g, 72 %) of dimercaptan **31**. This oil was then chromatographed on silica gel (60 g) with 1 : 4 EtOAc : hexanes. After some minor amounts of very smelly sulfurous fractions, near odourless compound **31** (7.5 g, 53 %) was isolated pure. R_f (1 : 1 EtOAc : hexanes) = 0.36. δ_H (300 MHz, $CDCl_3$) 1.51 (t, 2H, *J* 8.1, SH), 3.20 (dd, 4H, *J* 8.1, 1.2, C*H*$_2$SH), 3.54–3.58 (m, 4H, OCH_2), 3.63–3.65 (m, 4H, OCH_2), 3.64 (s, 4H, OCH_2), 4.10 (s, 4H, OCH_2-allyl), 5.04 (d, 2H, *J* 1.2, =CH), 5.11 (d, 2H, *J* 0.6, =CH). δ_C (75 MHz, $CDCl_3$) 27.1 (2 × CH_2S), 69.4 (2 × CH_2O), 70.6 (2 × CH_2O), 70.7 (2 × CH_2O), 72.0 (2 × CH_2O), 113.8 (2 × CH_2=), 145.2 (2 × C=). *m/z* (HRMS, ESI). Anal. Calc. for $C_{14}H_{26}O_4{}^{32}S_2Na$: 345.1170. Found: 345.1170.

*8,21-Dimethylene-3,10,13,16,19,26-hexaoxa-6,23-dithiaoctacosa-1,27-diene (**14c**)*

A mixture of 2,15-dimethylene-4,7,10,13-tetraoxahexadecane-1,16-dithiol (**31**) (7.2 g, 22.2 mmol) and 2-chloroethyl vinyl ether (**6**) (5.50 g, 51.6 mmol, 2.3 equiv.) in anhydrous methanol (to fill a syringe to 25 mL) and a solution of pre-reacted sodium (1.1 g, 48 mmol, 2.2 equiv.) in anhydrous methanol (25 mL) were synchronously added to anhydrous methanol (20 mL) at 50°C within 40 min. After 10 min NaCl started to precipitate and the mixture was then further stirred for 40 min at 60°C. The reaction mixture was cooled to room temperature and further stirred for 15 h. Methanol was rotary evaporated off and the residue was suspended in dichloromethane (50 mL) and filtered over a bed of silica gel (3 cm) to remove impurities (including yellow colour) and sodium chloride. The clear solution was then rotary evaporated dry and gave a viscous, pale-yellow oil (10 g). This crude product was chromatographed on only 60 g silica gel and eluted fast with 1 : 5 EtOAc : hexanes and gave after removal of solvent compound **14c** (4.40 g, 43 %). R_f (1 : 1 EtOAc : hexane) = 0.52. δ_H (300 MHz, $CDCl_3$) 2.69 (t, 4H, *J* 6.9, SCH_2), 3.22 (d, 4H, *J* 0.9, SCH_2-allyl), 3.56–3.63 (m, 4H, CH_2O), 3.63–3.66 (m, 4H, CH_2O), 3.63 (s, 4H, CH_2O), 3.82 (t, 4H, *J* 6.9, vinyl-OCH_2), 4.01 (dd, 2H, *J* 6.9, 2.1, CH=C*H*$_2$), 4.08 (s, 4H, CH_2-allyl), 4.18 (dd, 2H, *J* 14.4, 2.1, CH=C*H*$_2$), 5.05 (dm, 2H, *J* 0.9, C=C*H*$_2$), 5.14 (dm, 2H, *J* 1.2, C=C*H*$_2$), 6.43 (dd, 2H, *J* 14.4, 6.9, C*H*=CH$_2$). δ_C (75 MHz, $CDCl_3$) 29.8 (2 × SCH_2), 34.9 (2 × SCH_2-allyl), 67.3 (2 × vinyl-OCH_2), 69.6 (2 × OCH_2), 70.6 (2 × OCH_2), 70.7 (2 × OCH_2), 71.7 (2 × OCH_2-allyl), 87.0 (2 × =CH_2), 115.0 (2 × =CH_2), 141.7 (2 × =C), 151.4 (2 × =CH-O). *m/z* (HRMS, ESI) Anal. Calc. for $C_{22}H_{38}O_6{}^{32}S_2Na$: 485.2008. Found: 485.2001.

*S,S′-2,15-Dimethylene-7,10-dioxa-4,13-dithiahexadecane-1,16-diyl O,O′-Diethyl Dicarbonodithioate (**32**)*

Sodium (1.65 g, 71.7 mmol, 2.2 equiv) was dissolved in anhydrous ethanol (40 mL) within 30 min, and this solution was then reacted with carbon disulfide (5.7 g, 75 mmol, 2.2 equiv) to form a solution of pale-yellow sodium ethyl xanthogenate. After 15 min, 2,15-bis(chloromethyl)-7,10-dioxa-4,13-dithiahexadeca-1,15-diene (**28**) (12 g, 33.4 mmol) in anhydrous THF (20 mL) was added to this solution within 3 min and the solution temperature increased slightly (~35°C). Precipitation of white NaCl slowly occurred and the reaction mixture was kept stirring overnight at room temperature. Ethanol and THF were rotary evaporated off at 60°C to give a viscous yellow translucent oil. This residue was dissolved in EtOAc (40 mL) and the precipitated NaCl was filtered off over a layer of silica gel (2 cm). The filter was again treated with EtOAc (40 mL) and the combined yellow filtrate was rotary evaporated dry to give crude yellow oil. This oil was treated with dichloromethane (30 mL) which precipitated unreacted, excess sodium ethyl xanthogenate. This solution was filtered over a layer of *Celite* (0.5 cm). The yellow filtrate was rotary evaporated dry to give compound **32** (17.1 g, 97 %). δ_H (300 MHz, $CDCl_3$) 1.42 (t, 6H, *J* 7.2, CH_3), 2.62 (t, 4H, *J* 6.9, SCH_2), 3.26 (dm, 4H, *J* 1.2, SCH_2-allyl), 3.60 (s, 4H, OCH_2), 3.63 (t, 4H, *J* 6.9, OCH_2), 3.95 (dm, 4H, *J* 1.2, CH_2-allyl), 4.64 (q, 4H, *J* 7.2, OCH_2), 5.07 (dm, 2H, *J* 1.2 Hz, H_2C=), 5.19 (dm, 2H, *J* 1.2, H_2C=). δ_C (75 MHz, $CDCl_3$) 13.8 (2 × CH_3), 30.4 (2 × SCH_2), 37.0 (2 × SCH_2-allyl), 39.1 (2 × SCH_2-allyl), 70.1 (2 × OCH_2), 70.3 (2 × OCH_2), 70.7 (2 × OCH_2), 117.3 (2 × H_2C=), 139.1 (2 × =C), 213.9 (2 × C=S). *m/z* (HRMS, ESI). Anal. Calc. for $C_{20}H_{34}O_4{}^{32}S_6Na$: 553.0679. Found: 553.0653.

*2,15-Dimethylene-7,10-dioxa-4,13-dithiahexadecane-1,16-dithiol (**33**)*

CAUTION: Workup of the reaction-mixture should be carried out in a fume-hood, since by-products may have a severe stench.

S,S′-2,15-dimethylene-7,10-dioxa-4,13-dithiahexadecane-1,16-diyl-O,O′-diethyl dicarbonodithioate (**32**) (17.0 g, 32.0 mol) was added neat to ethylenediamine (6 mL, 5.4 g, 90 mmol, 2.8 equiv) over a period of 20 min at 0°C and then further stirred for 30 min at 0°C and then allowed to come to room temperature and stirred for a further 15 min until the yellow xanthate colour had disappeared. This reaction mixture was added all at once to a premixed solution of conc. H_2SO_4 (10 mL, 18.4 g, 188 mmol) and 40 g crushed ice in a small beaker with rapid stirring to neutralise ethylene diamine (pH was checked). The yellow, opaque aqueous acidic layer was treated with dichloromethane (30 mL), followed by the addition of hexanes (10 mL) and stirred. This mixture was transferred to a funnel and extracted. The aqueous layer was once more extracted with 3 : 1 dichloromethane : hexanes (40 mL). The combined organic layer was then treated with a saturated $NaHCO_3$ solution (50 mL), separated and then dried (Na_2SO_4) for 15 min. Filtration over silica gel (4 cm layer) and further elution with dichloromethane (50 mL) gave a colourless filtrate. The filtrate was rotary evaporated to give a sulfurous smelling crude oil. This oil was then chromatographed on silica gel (60 g) and chromatographed as speedily as possible with 1 : 9 EtOAc : hexanes to curb decomposition of the wanted dimercaptan **33**. After some minor amounts of very smelly sulfurous fractions the colourless dimercaptan **33** (7.62 g, 72 %) was isolated. R_f (1 : 1 EtOAc : hexanes) = 0.54. δ_H (300 MHz, $CDCl_3$) 1.50 (t, 2H, *J* 8.4, SH), 2.59 (t, 4H, *J* 6.3, SCH_2), 3.29 (dd, 4H, *J* 8.4, 1.2, CH_2SH), 3.34 (d, 4H, *J* 1.2, SCH_2-allyl), 3.58 (s, 4H, CH_2O), 3.60 (t, 4H, *J* 6.3, OCH_2), 4.92 (d, 2H, *J* 1.2, =CH), 5.06 (dt, 2H, *J* 1.2, 1.2, =CH). δ_C (75 MHz, $CDCl_3$) 27.9 (2 × CH_2SH), 30.3 (2 × =CCH_2S), 35.9 (2 × SCH_2), 70.3 (2 × CH_2O), 70.6 (2 × CH_2O), 114.6 (2 × CH_2=), 144.1 (2 × C=). *m/z* (HRMS, ESI). Anal. Calc. for $C_{14}H_{26}O_2{}^{32}S_4Na$: 377.0713. Found: 377.0717.

*8,21-Dimethylene-3,13,16,26-tetraoxa-6,10,19,23-tetrathiaoctacosa-1,27-diene (**14d**)*

A mixture of 2,15-dimethylene-7,10-dioxa-4,13-dithiahexadecane-1,16-dithiol (**33**) (7.62 g, 21.5 mmol) and 2-chloroethyl vinyl ether (**6**) (5.45 g, 51.2 mmol, 2.4 equiv.) in anhydrous methanol (to fill a syringe to exactly 20 mL) and a solution of pre-reacted sodium (1.11 g, 48.3 mmol, 2.3 equiv.) in anhydrous methanol (20 mL) were synchronously added to anhydrous methanol (5 mL) at 50°C within 40 min. After 10 min sodium chloride started to precipitate. The reaction mixture was further stirred for 40 min at 60°C and then cooled to room temperature and stirred overnight for 15 h. Methanol was rotary evaporated off and the residue was suspended in dichloromethane (50 mL) and filtered over a bed of silica gel (3 cm) to remove impurities and sodium chloride. The clear solution was then rotary evaporated dry and gave a viscous, pale-yellow oil (8.5 g). This crude product was chromatographed on only 60 g silica gel and eluted fast with 1 : 9 EtOAc : hexanes to give after removal of solvent compound **14d** (4.40 g, 43 %). R_f (1 : 1 EtOAc : hexane) = 0.63. White solid, m. p. 35°C. δ_H (300 MHz, $CDCl_3$) 2.61 (t, 4H, *J* 6.9, SCH_2), 2.68 (t, 4H, *J* 6.6, SCH_2), 3.32 (s, 4H, SCH_2-allyl), 3.33 (d, 4H, *J* 0.6, SCH_2-allyl), 3.60 (s, 4H, OCH_2), 3.62 (t, 4H, *J* 6.9, OCH_2), 3.82 (t, 4H, *J* 6.6, OCH_2), 4.01 (dd, 2H, *J* 6.9, 2.1, CH=CH_2), 4.18 (dd, 2H, *J* 14.4, 2.1, CH=CH_2), 5.01 (sm, 2H, C=CH_2), 5.02 (sm, 2H, C=CH_2), 6.43 (dd, 2H, *J* 14.4, 6.9, CH=CH_2). δ_C (75 MHz, $CDCl_3$) 29.8 (2 × SCH_2-allyl), 30.4 (2 × SCH_2), 35.7 (2 × SCH_2-allyl), 35.8 (2 × SCH_2-allyl), 67.3 (2 × vinyl-OCH_2), 70.3 (2 × OCH_2), 70.7 (2 × OCH_2), 87.0 (2 × HC=CH_2), 116.1 (2 × =CH_2), 140.8 (2 × =C), 151.4 (2 × =CH-O). *m/z* (HRMS, ESI) Anal. Calc. for $C_{22}H_{38}O_4{}^{32}S_4Na$: 517.1551. Found: 517.1526.

*S,S′-2,15,28-Trimethylene-7,10,20,23-tetraoxa-4,13,17,26-tetrathianonacosane-1,29-diyl O,O′-Diethyldicarbonodithioate (**35**)*

Sodium (0.50 g, 21.7 mmol, 2.2 equiv.) was dissolved in anhydrous ethanol (20 mL) within 30 min, and this solution was then reacted with carbon disulfide (1.9 g, 25.0 mmol, 2.5 equiv) to form an ethanolic solution of pale-yellow sodium ethyl xanthogenate. Anhydrous THF (20 mL) was added. Then, after 20 min, 2,28-bis(chloromethyl)-15-methylene-7,10,20,23-tetraoxa-4,13,17,26-tetrathianonacosa-1,28-diene (**34**) (6.0 g, 10.11 mmol) in anhydrous THF (10 mL) was added neat to this solution within 1 min and the solution became slightly warm (35°C). Precipitation of white NaCl occurred slowly and the reaction mixture was kept stirring overnight at room temperature. The solvents were rotary evaporated off at 60°C to give a viscous, yellow translucent oil. This residue was dissolved in ethyl acetate (20 mL) and the precipitated NaCl was filtered off over a layer silica gel. The filter was again treated with ethyl acetate (20 mL) and the combined yellow filtrate was rotary evaporated dry to give a crude yellow oil. This oil was treated with dichloromethane (15 mL) which precipitated unreacted, excess sodium ethyl xanthogenate. This solution was filtered over a sintered glass funnel having a layer of *Celite* (0.5 cm). The filtrate was rotary evaporated dry and further evacuated to give yellow compound **35** (7.45 g, 96 %). δ_H (300 MHz, $CDCl_3$) 1.42 (t, 6H, *J* 7.2, CH_3), 2.61 (t, 4H, *J* 6.9, SCH_2), 2.62 (t, 4H, *J* 6.6, SCH_2), 3.26 (d, 4H, *J* 0.9, SCH_2-allyl), 3.31 (s, 4H, SCH_2-allyl), 3.60 (s, 8H, OCH_2), 3.62 (t, 4H, *J* 6.9, OCH_2), 3.63 (t, 4H, *J* 6.6, OCH_2), 3.95 (d, 4H, *J* 0.9, SCH_2), 4.64 (q, 4H, *J* 7.2, OCH_2), 5.00 (s, 2H, H_2C=) 5.07 (s, 2H, H_2C=), 5.19 (d, 2H, *J* 1.2, H_2C=). δ_C (100 MHz, $CDCl_3$) 13.8 (2 × CH_3), 30.3 (2 × SCH_2), 30.4 (2 × SCH_2), 35.7 (2 × SCH_2-allyl), 37.1 (2 × SCH_2-allyl), 39.1 (2 × SCH_2), 70.0 (2 × OCH_2), 70.3 (2 × OCH_2), 70.4 (2 × OCH_2), 70.6 (2 × OCH_2), 70.7 (2 × OCH_2), 116.0 (H_2C=), 117.3 (2 × H_2C=), 139.1 (2 × =C), 140.9 (=C), 213.8 (2 × C=S) ppm. *m/z* (HRMS, ESI) Anal. Calc. for $C_{30}H_{52}O_6{}^{32}S_8Na$: 787.1427. Found: 787.1415.

*2,15,28-Trimethylene-7,10,20,23-tetraoxa-4,13,17,26-tetrathianonacosane-1,29-dithiol (**36**)*

CAUTION: Workup of the reaction-mixture should be carried out in a fume-hood, since by-products may have a severe stench.

S,S′-2,15-dimethylene-4,7,10,13-tetraoxahexadecane-1,16-diyl-O,O′-diethyl dicarbonodithioate (**35**) (7.5 g, 9.80 mmol) was added neat to ethylenediamine (1.5 mL, 1.35 g, 22.5 mmol, 2.3 equiv) over a period of 7 min at 0°C and was then further stirred with a strong magnetic stirrer bar (viscous mixture) for 35 min at 0°C and then allowed to come to room temperature and stirred for another 30 min. This reaction mixture was added all at once to a premixed solution of conc. H_2SO_4 (2.5 mL, 4.6 g, 47 mmol) and 20 g crushed ice in a small beaker with fast magnetic stirring to neutralise ethylene diamine (checked by pH). The yellow, opaque aqueous acidic layer was treated with dichloromethane (40 mL) and vigorously stirred. This mixture was transferred to a funnel and extracted. The organic layer was then isolated and treated with saturated $NaHCO_3$ solution (40 mL). All aqueous extractions were again extracted with dichloromethane (30 mL). The combined organic layer was

dried (Na_2SO_4) for 15 min and filtered over silica gel and further eluted with dichloromethane (30 mL) and then ethyl acetate (50 mL). The combined filtrate was rotary evaporated at 40°C to give a crude oil. This oil was then chromatographed on silica gel (60 g) as speedily as possible with 1 : 4 EtOAc : hexanes to curb decomposition of the desired dimercaptan **36**. After some minor amounts of very smelly sulfurous fore-fractions, odourless compound **36** (2.33 g, 40 %) was isolated as a viscous oil at room temperature, but crystallizing below 10°C as a white solid. R_f (1 : 1 EtOAc : hexane) = 0.52. δ_H (300 MHz, $CDCl_3$) 1.50 (t, 2H, *J* 8.1, SH), 2.60 (t, 4H, *J* 6.6, CH_2S), 2.61 (t, 4H, *J* 6.9 Hz, CH_2S), 3.30 (dd, 4H, *J* 8.1, 1.2, C*H*$_2$SH), 3.31 (s, 4H, SCH_2-allyl), 3.35 (d, 4H, *J* 0.9, SCH_2-allyl), 3.59 (s, 8H, OCH_2), 3.61 (t, 4H, *J* 6.6, OCH_2), 3.62 (t, 4H, *J* 6.9, OCH_2), 4.93 (d, 2H, *J* 0.9, =CH), 4.99 (s, 2H, =CH), 5.06 (d, 2H, *J* 1.2 Hz, =CH). δ_C (50 MHz, $CDCl_3$) 27.9 (2 × CH_2SH), 30.3 (2 × SCH_2), 30.4 (2 × SCH_2), 35.7 (2 × SCH_2-allyl), 35.8 (2 × SCH_2-allyl), 70.3 (4 × OCH_2), 70.6 (2 × OCH_2), 70.7 (2 × OCH_2), 114.7 (2 × =CH_2), 115.9 (=CH_2), 140.9 (=C), 144.1 (2 × =C). *m/z* (HRMS, ESI). Anal. Calc. for $C_{24}H_{44}O_4{}^{32}S_6Na$: 611.1462. Found: 611.1433.

Note: This compound does not dissolve in methanol, but dissolves very well in THF.

*8,21,34-Trimethylene-3,13,16,26,29,39-hexaoxa-6,10,19,23,32,36-hexathia-hentetraconta-1,40-diene (**37**)*

A mixture of 2,15,28-trimethylene-7,10,20,23-tetraoxa-4,13,17,26-tetrathianonacosane-1,29-dithiol (**36**) (2.33 g, 4.0 mmol) and 2-chloroethyl vinyl ether (**6**) (1.00 g, 9.4 mmol, 2.4 equiv) in anhydrous methanol (2 mL) and anhydrous THF (3 mL) (total volume to 7 mL) and a solution of pre-reacted sodium (0.20 g, 8.7 mmol, 2.2equiv.) in anhydrous methanol (7 mL) were synchronously added to anhydrous THF (3 mL) at 50°C within 40 min and was then further stirred for 45 min at 60°C. The reaction mixture was cooled to room temperature and stirred overnight for 15 h. Methanol was rotary evaporated off and the residue was suspended in dichloromethane (50 mL) and filtered over a bed of silica gel (3 cm) to remove impurities and NaCl. The colourless solution was then rotary evaporated dry and gave a viscous, pale-yellow oil (3 g). This crude was chromatographed on 60 g silica gel and eluted with 1 : 5 EtOAc : hexanes to give after removal of solvent a colourless solid of compound **37** (1.07 g, 39 %). R_f (1 : 1 EtOAc : hexane) = 0.61. m.p. 42°C. δ_H (300 MHz, $CDCl_3$) 2.61 (t, 4H, *J* 6.9, SCH_2), 2.62 (t, 4H, *J* 6.9, SCH_2), 2.68 (t, 4H, *J* 6.9, SCH_2), 3.31 (s, 4H, SCH_2-allyl), 3.32 (d, 4H, *J* 0.3, SCH_2-allyl), 3.34 (d, 4H, *J* 0.6, SCH_2-allyl), 3.60 (s, 8H, OCH_2), 3.61 (t, 4H, *J* 6.9, OCH_2), 3.62 (t, 4H, *J* 6.9, OCH_2), 3.82 (t, 4H, *J* 6.9, OCH_2), 4.01 (dd, 2H, *J* 6.9, 2.1, CH=C*H*$_2$), 4.18 (dd, 2H, *J* 14.4, 2.1, CH=C*H*$_2$), 4.99 (sm, 2H, C=CH_2), 5.01 (s, 2H, C=C*H*$_2$), 5.02 (s, 2H, C=C*H*$_2$), 6.44 (dd, 2H, *J* 14.4, 6.9, C*H*=CH_2). δ_C (75 MHz, $CDCl_3$) 29.8 (2 × SCH_2), 30.3 (2 × SCH_2), 30.4 (2 × SCH_2), 35.6 (2 × SCH_2-allyl), 35.7 (2 × SCH_2-allyl), 35.8 (2 × SCH_2-allyl), 67.3 (2 × OCH_2), 70.3 (4 × OCH_2), 70.6 (2 × CH_2O), 70.7 (2 × CH_2O), 87.0 (2 × =CH_2), 116.0 (=CH_2), 116.1 (2 × =CH_2), 140.8 (2 × =C), 140.9 (=C), 151.4 (2 × =CH-O). *m/z* (HRMS, ESI). Anal. Calc. for $C_{32}H_{56}O_6{}^{32}S_6Na$: 751.2299. Found: 751.2277.

Supplementary Material

^1H and ^{13}C spectra and R_f chromatography values are available on the Journal's website.

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