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Polymer Modification and Synthesis Using Sulphenyl Derivatives, 2*)

Preparation of Poly(β-chlorothioether)s, Poly(sulphone)s and Poly(disulphide)s

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SUMMARY:

The preparation of a further series of poly(β-chlorothioether)s, from reaction of 4,4′-methylenedisulphenyl chloride (**2**) with diolefins, is described. Poly(sulphone)s were prepared by controlled oxidation of the poly(β-chlorothioether)s from **2** and from 4,4′-biphenyldisulphenyl chloride (**1**). Poly(disulphide)s were prepared by reaction of **1** or **2** with dithiols or lithium metal. All the above polymers were characterized by NMR, IR, elemental analysis, and rel. mol. mass determinations.

ZUSAMMENFASSUNG:

Die Darstellung einer weiteren Reihe Poly(β-chlorthioäther) aus der Reaktion von 4,4′-Methylendisulfenylchlorid (**2**) mit Diolefinen wird beschrieben. Poly(sulfon)e wurden durch kontrollierte Oxidation der Poly(β-chlorthioäther) aus **2** und aus 4,4′-Biphenyldisulfenylchlorid (**1**), Poly(disulfid)e durch die Reaktion von **1** oder **2** mit Dithiolen oder metallischem Lithium dargestellt. Sämtliche Polymere wurden durch ihre IR-, NMR-Spektren bzw. Elementaranalysen und durch Molekulargewichtsbestimmungen charakterisiert.

Introduction

In a previous paper the preparation and characterization of a series of poly(β-chlorothioether)s from 4,4′-biphenyldisulphenyl chloride (**1**) with diolefins was reported[1]. A second series of these polymers has now been prepared

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*) Part 1, cf.[1].

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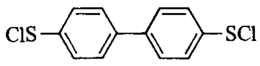
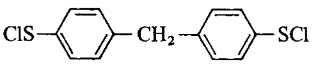
from 4,4′-methylenediphenylsulphenyl chloride (**2**). In addition, poly(disulphide)s from **1** and from **2** have been prepared, and poly(sulphone)s from the poly(β-chlorothioether)s.



1



2

The new poly(β-chlorothioether)s are the polyaddition products of **2** with 1,7-octadiene, 2,5-dimethyl-1,5-hexadiene and 1,4-cyclohexadiene. The poly(disulphide)s were prepared by reacting **1** and **2** with dithiols or with metallic lithium. The poly(sulphone)s are the oxidation products of the appropriate poly(β-chlorothioether)s with *m*-chloroperbenzoic acid.

Experimental Part

4,4′-Methylenediphenylsulphenyl chloride (**2**)[2]: 4,4′-methylenediphenylsulphonyl chloride (from chlorosulphonation of diphenylmethane) was reduced to 4,4′-methylenediphenylthiol using zinc dust[3]. Chlorination of this dithiol in CCl_4 gave **2** as orange-yellow crystals, mp 61–62 °C from light petroleum.

Diolefins: 1,7-octadiene (Ralph Emanuel Ltd.), 2,5-dimethyl-1,5-hexadiene (Pfaltz and Bauer Ltd.), 1,4-cyclohexadiene (Koch-Light Ltd.) were purified by refluxing over sodium wire followed by fractional distillation. THF was dried and purified by the same means.

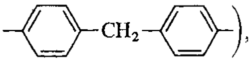
Polymerisation procedure for poly(β-chlorothioether)s: An amount of fresh **2** ($\approx$0,01 mol) was added to a flask (fitted with a stopcock) into which the required amount of dry, degassed THF ($\approx$25 cm^3) was distilled on a vacuum line. The THF was stored in and distilled from a vessel on the vacuum line containing green sodium dihydronaphthylide. The reaction flask was then transferred, still under vacuum, to a dry nitrogen glove box where the required (stoichiometric) amount of diolefin was added by means of a syringe. The flask was then replaced on the vacuum line and sealed off i. vac. The polyaddition was allowed to continue at room temp. for two days. Then, the polymer was precipitated from light petroleum or acidified methanol and was purified by reprecipitation from the same solvent.

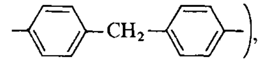
Oxidation of poly(β-chlorothioether)s to poly(sulphone)s: About 0,25 g poly(β-chlorothioether) was dissolved in chloroform ($\approx$15 cm^3) (Analar grade). Then the theoretical amount of *m*-chloroperbenzoic acid (Ralph Emanuel Ltd.), dissolved in chloroform ($\approx$10 cm^3), was poured into the polymer solution. The mixture was left overnight, and the resulting oxidized polymer precipitated from light petroleum or acidified methanol.

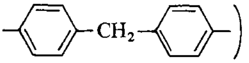
Preparation of poly(disulphide)s: Equimolar amounts of **1** or **2** and 4,4′-biphenyldithiol, 4,4′-methylenediphenylthiol or 1,3-benzenedithiol were placed in a flask into which the required amount of dry, degassed THF ($\approx$25 cm^3) was distilled on the vacuum line. The flask was then sealed off i. vac. The disulphide polymer which precipitated overnight was filtered off and dried. Poly(disulphide)s **9b** and **9d** were soluble in THF and were recovered by precipitation from light petroleum.

Characterization of the polymers: The rel. mol. masses of the polymers were determined by vapour pressure osmometry (Perkin-Elmer Molecular Apparatus 115). Gel permeation chromatography showed a single product peak for each polymer, except in the case of poly(disulphide)s which appeared to contain several broad overlapping peaks. The structure of the polymers was confirmed by elemental analysis, IR and NMR spectrometry. IR spectra were recorded on a Perkin-Elmer 237 Grating Spectrophotometer using KBr discs or polymer solutions in chloroform. NMR spectra were recorded on a Varian HA 100D MHz instrument using $DCCl_3$ solutions with TMS as internal reference. The yields of the polymers from all the reactions, were at least 90%.

Properties of poly(β-chlorothioether)s: All polymers were soluble in THF and chloroform. IR spectra were similar to those previously described[1]. Elemental analyses are shown in Tab. 1.

Polymers **3b/4b**: Colourless rubbery solids; rel. mol. masses: 6000–20000; NMR ($DCCl_3$): $\tau = 2{,}70$, 2,78, 2,95, 3,03 (arom. protons), 6,16 (methylene in , 6,54 (—CH_2Cl), 6,76 (—CH_2S—), 8,08 (—CH_2—), 8,48 (CH_3—C—Cl), and 8,64 or 8,84 ppm (CH_3—C=C— or CH_3—C—S—).

Polymers **7b/8b**: Colourless rubbery solids; rel. mol. masses: 5000; NMR ($DCCl_3$): $\tau = 2{,}63$, 2,71, 2,88, 2,96 (arom. protons), 6,09 (methylene in , 6,2–6,9 (—CH_2S—, —CH_2Cl, >CHS—, >CHCl), and 8,0–8,5 ppm (—CH_2—).

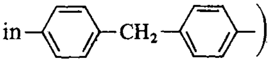
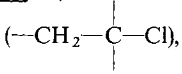
Polymers **5b/6b**: Colourless powders; rel. mol. masses: 10000; NMR ($DCCl_3$): $\tau = 2{,}63$, 2,72, 2,89, 2,96 (arom. protons), 5,8–5,9 (>CHCl), 6,08 (methylene in , 6,4–6,6 (>CHS—), and 7,0–7,8 ppm (—CH_2—).

Tab. 1. Elemental analyses of copolymers of 4,4′-methylenediphenylsulphenyl chloride (**2**) and diolefins

Copolymer	Brutto formula	Rel. mol. mass	Calc.	Found
3b/4b	$(C_{21}H_{24}Cl_2S_2)_n$	$(411{,}5)_n$	C 61,3	C 62,3
			H 5,8	H 5,7
			Cl 17,3	Cl 15,1
			S 15,6	S 16,7
5b/6b	$(C_{19}H_{18}Cl_2S_2)_n$	$(381{,}4)_n$	C 59,8	C 61,4
			H 4,7	H 5,0
			Cl 18,6	Cl 15,7
			S 16,8	S 16,8
7b/8b	$(C_{21}H_{24}Cl_2S_2)_n$	$(411{,}5)_n$	C 61,3	C 61,0
			H 5,8	H 6,0
			Cl 17,3	Cl 17,0
			S 15,6	S 15,8

Properties of poly(sulphone)s

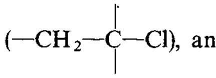
All were colourless powders, soluble in THF and chloroform except the polymers **5d/6d** and **5c/6c** which were insoluble. Rel. mol. masses and elemental analyses are shown in Tab. 2. The (typical) IR spectrum of **7d/8d** is shown in Fig. 1.

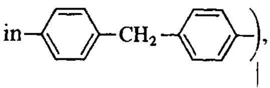
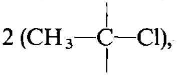
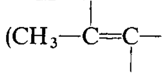
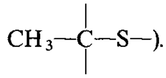
Polymer **7d/8d**: NMR ($CDCl_3$): $\tau = 2{,}16, 2{,}25, 2{,}62, 2{,}70$ (arom. protons), 5,85 (methylene in ), 5,7, 6,3, 6,5 or 6,8 ($>$CHCl, —CH_2Cl, $>$CHSO$_2$— or —CH_2SO_2—), 8,14 ( $-CH_2-\overset{|}{\underset{|}{C}}-Cl$), and 8,56 ppm (—$CH_2$—). IR ($CHCl_3$): 3020 (CH-stretch arom. or olefinic), 2950, 2920 and 2860 (CH-stretches of CH_2), 1730 (C=O-stretch), 1600 (C=C-stretch, arom.), 1410 (CH_2, bend), 1310 (SO_2, asym. stretch), 1150 (SO_2, sym. stretch and solvent), and 1090 cm^{-1} (—CH=CH—, bend).

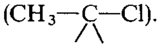
Tab. 2. Characterization of poly(sulphone)s prepared from the oxidation of some poly(β-chlorothioether)s

Poly(sulphone)	Rel. mol. mass. expected[a]	observed	theoretical	Elemental analysis calc.	found
7d/8d	5000	3000	$(475{,}4)_n$	C 53,1	C 53,3
				H 5,1	H 5,5
				Cl 14,9	Cl 13,6
				S 13,5	S 13,5
7c/8c	10000	10000	$(461{,}4)_n$	C 52,1	C 52,2
				H 4,8	H 4,5
				Cl 15,4	Cl 14,6
				S 13,9	S 13,9
3d/4d	6000–10000	3000–6000	$(475{,}4)_n$	C 53,1	C 53,1
				H 5,1	H 5,4
				Cl 14,9	Cl 14,3
				S 13,5	S 13,3
3c/4c	5000–10000	5000–10000	$(461{,}4)_n$	C 52,1	C 51,9
				H 4,8	H 4,5
				Cl 15,4	Cl 14,3
				S 13,9	S 13,9
5d/6d	—	Insoluble	—	C 51,2	C 51,9
				H 4,0	H 4,1
				Cl 16,0	Cl 13,9
				S 14,4	S 12,6
5c/6c	—	Insoluble	—	C 50,1	C 52,2
				H 3,7	H 3,9
				Cl 16,5	Cl 15,6
				S 14,8	S 13,7

[a] Based on the rel. mol. mass of the parent poly(β-chlorothioether).

Polymer **7c/8c**: NMR ($CDCl_3$): $\tau = 1{,}96$, 2,04, 2,16, 2,24 (arom. protons), 5,7, 6,2, 6,4 or 6,7 (>CHCl, $-CH_2Cl$, $>CHSO_2-$ or $-CH_2SO_2-$), 8,02  $(-CH_2-\overset{|}{\underset{|}{C}}-Cl)$, and 8,48 ppm ($-CH_2-$).

Polymer **3d/4d**: NMR ($CDCl_3$): $\tau = 2{,}10$, 2,16, 2,62, 2,69 (arom. protons), 5,87 (methylene in ), 6,39 ($-CH_2SO_2-$), 7,64 ($-CH_2-$), 8,12  $(CH_3-\overset{|}{\underset{|}{C}}-Cl)$, and 8,60 or 8,72 ppm  $(CH_3-\overset{|}{C}=\underset{|}{C}-$ or  $CH_3-\overset{|}{\underset{|}{C}}-S-)$.

Polymer **3c/4c**: NMR ($DCCl_3$): $\tau = 1{,}90$, 1,98, 2,19, 2,27 (arom. protons), 6,30 ($-CH_2SO_2-$), 7,58 ($-CH_2-$), and 8,06 ppm  $(CH_3-\underset{/\backslash}{C}-Cl)$.

Properties of *Poly(disulphide)s*

All were yellow powders. The polymers **9b** and **9d** were soluble in THF and chloroform, the other ones were insoluble in all common solvents. Elemental analyses and rel. mol. masses are recorded in Tab. 3. The (typical) IR spectrum of **9a** is shown in Fig. 3.

Polymer **9b**: NMR ($DCCl_3$): $\tau = 2{,}57$, 2,71, 2,93, 3,06 (arom. protons), and 6,16 ppm ($-CH_2-$).

Polymer **9d**: NMR ($DCCl_3$): $\tau = 2{,}3$–3,1 (arom. protons), and 6,17 ppm ($-CH_2-$).

Polymer **9a**: IR(KBr): 3010 (CH-stretch, arom.), 1590 (C=C-stretch, arom.), 1475, 1390, 1080, 1000, and 805 cm^{-1} (CH, bends).

Tab. 3. Characterization of Poly(disulphide)s prepared from disulphenyl chlorides and dithiols

Poly(disulphide)	Rel. mol. mass		Elemental analysis	
	observed	theoretical	calc.	found
9a[a]	Insoluble	$(216{,}3)_n$	C 66,7 H 3,7 S 29,6	C 66,8 H 3,9 S 29,3
9b	2000–4000	$(230{,}3)_n$	C 67,8 H 4,4 S 27,8	C 67,6 H 4,4 S 27,6
9c	Insoluble	$(446{,}7)_n$	C 67,3 H 4,0 S 28,7	C 67,0 H 4,0 S 28,5
9d	2000–4000	$(370{,}6)_n$	C 61,6 H 3,8 S 34,6	C 63,7 H 4,5 S 31,2
9e	Insoluble	$(356{,}5)_n$	C 60,7 H 3,4 S 36,0	C 61,7 H 3,1 S 35,1

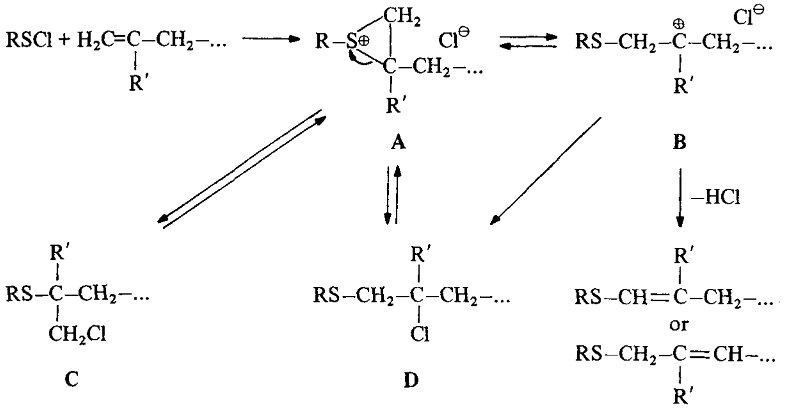
[a] Also prepared by reaction of metallic Li with **1**.

Results and Discussion

Poly(β-chlorothioether)s

We were unable to obtain polymers **3b/4b** and **5b/6b** giving elemental analyses which correspond to the theoretical values. The experimental values were always lower in chlorine and generally higher in carbon and sulphur than the calculated ones (Tab. 1). This indicates an elimination of HCl during the polymerisation. The presence of chloride in the THF at the end of the synthesis of these polymers was confirmed. It was also noted previously that the polymers **3a/4a** had a slight tendency to be too low in chlorine, and several samples were prepared before an acceptable chlorine analysis was obtained. The significance of this observation was not appreciated at that time but it may have some importance in the present context.

The addition of a sulphenyl chloride to a double bond is believed to involve the intermediate formation of an episulphonium ion **A**[4] which is in equilibrium with the corresponding carbonium ion **B**[5] as shown below:



Our observations indicate that the stronger the electronreleasing powers[*] of the substituents R' and R the greater is the tendency of the polymer to be deficient in chlorine. Thus, for example, with **2** and 2,5-dimethyl-1,5-hexadiene ($R'=CH_3$) HCl loss is considerable, whereas with **1** and 1,7-octadiene ($R'=H$) the HCl loss is negligible. In the case of R' these results can be readily rationalized if it is postulated that **B**, rather than **A**, is the reactive intermediate which eliminates HCl, because **B** becomes relatively more stable

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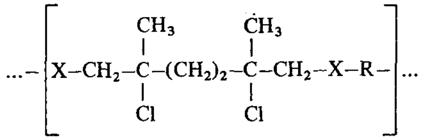
[*] The electron-releasing effect of R in **2** is considered to be slightly greater than that of R in **1**, on the basis of the σ^+ values for *p*-benzyl(−0,197)[6] and *p*-phenyl (−0,17)[7].

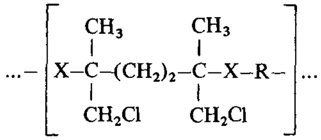
as the electron release from R′ increases. This explanation is certainly oversimplified since it does not consider kinetic effects and does not account adequately for the rôle of R in the elimination reaction. We hope to shed more light on this side reaction in future studies of this polymerisation.

The expected structures of the polymers from **2** with the three diolefins are identical to the corresponding ones from **1** with the same diolefins shown



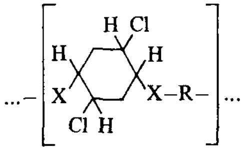
$\cdots-\left[X-CH_2-\underset{Cl}{\overset{CH_3}{C}}-(CH_2)_2-\underset{Cl}{\overset{CH_3}{C}}-CH_2-X-R-\right]\cdots$

3



$\cdots-\left[X-\underset{CH_2Cl}{\overset{CH_3}{C}}-(CH_2)_2-\underset{CH_2Cl}{\overset{CH_3}{C}}-X-R-\right]\cdots$

4



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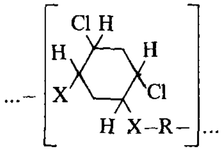

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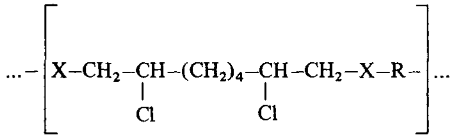
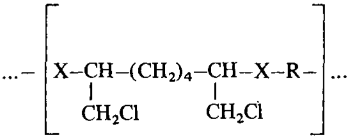


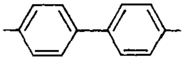
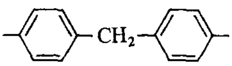
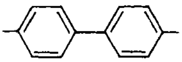
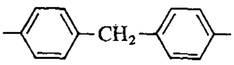
$\cdots-\left[X-CH_2-\underset{Cl}{CH}-(CH_2)_4-\underset{Cl}{CH}-CH_2-X-R-\right]\cdots$

7



$\cdots-\left[X-\underset{CH_2Cl}{CH}-(CH_2)_4-\underset{CH_2Cl}{CH}-X-R-\right]\cdots$

8

3–8	–X–	–R–
a	–S–	
b	–S–	
c	$-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-$	
d	$-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-$	

in Part 1[1], except that the aromatic rings are now separated by a methylene bridge. For example poly[thio-(2,5-dichloro-2,5-dimethyl)-hexamethylenethio-1,4-phenylenemethylene-1,4-phenylene][*] (**3b**) and poly[thio(1,4-dichloromethyl-1,4-dimethyl)-tetramethylenethio-1,4-phenylenemethylene-1,4-phenylene] (**4b**) result from the Markownikoff and *anti*-Markownikoff addition (type **D** and **C**), respectively, of **2** with 2,5-dimethyl-1,5-hexadiene and correspond with **3a** and **4a** described in Part 1[**].

The NMR spectrum of **3b**/**4b** shows that the former accounts for more than 90% of the product. This is similar to the situation with **3a**/**4a**[1]. The absorptions of $CH_3{-}C{=}C$ in **3b**/**4b** could be due to HCl elimination or to unsaturated end groups.

The polymers **7b**/**8b** obtained from the additions of **2** to 1,7-octadiene correspond with **7a**/**8a** of Part 1. In this case it is not possible to distinguish **7b** (Markownikoff, type **D**) from **8b** (*anti*-Markownikoff, type **C**) because of the overlap of the relevant proton absorption bands in the region $\tau = 6{,}2$–6,9 ppm.

The expected repeating units in the polymers obtained from **2** with 1,4-cyclohexadiene are [thio-(2,5-dichloro-1,4-cyclohexenylene)thio-1,4-phenylenemethylene-1,4-phenylene] (**5b**) and [thio-(2,4-dichloro-1,5-cyclohexylene)thio-1,4-phenylenemethylene-1,4-phenylene] (**6b**). In this case the two possible isomers arise from the different modes of incorporation of diene into the polymer chain. Although the NMR spectra are consistent with the structures of both isomers, it is not possible to distinguish their signals. This contrasts with our earlier observations on polymers **5a**/**6a**[1]. The IR spectra of all three polymers are in accord with the above structures[8].

Poly(sulphone)s

The sulphur atoms in the above poly(β-chlorothioether)s are the most sensitive parts of the polymer chains towards oxidation, and by controlled oxidation these polymers should be transformed to poly(sulphone)s. The elemental analyses and rel. mol. masses of some poly(sulphone)s prepared by this means are shown in Tab. 2. The elemental analyses are in general agreement with the proposed structures (Tab. 2), although some unsaturation (from

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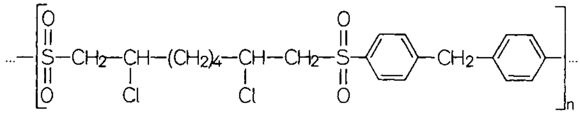
[*] Nomenclature according to IUPAC Information Bull., No. 29, 1972; J. Polymer Sci. Part B **11**, 389 (1973).

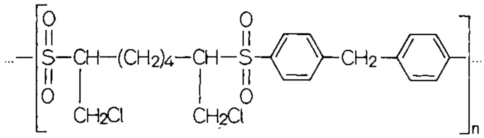
[**] The polymers **3a**–**8a** are identical with the polymers 3–8 in Part 1.

HCl elimination) was present in some of the parent poly(β-chlorothioether)s, notably in **3b/4b**. The sulphur and hydrogen analyses usually agreed well with the theoretical values, but the carbon value was often too high and the chlorine value too low. Discrepancies of the same order were recorded by *Stille* and *Empen*[9] on the oxidation of poly(thioether)s to poly(sulphone)s. The oxidation is very sensitive to the amount of *m*-chloroperbenzoic acid used, an excess of this reagent producing oxidations at other parts of the molecule.

The IR spectra are also consistent with the proposed structures[8] (see Exp. Part). The strong absorption bands near 1315 and 1145 cm^{-1} are due to the SO$_2$-stretching. Poly(sulphone)s prepared from **2** all show some carbonyl absorption at $\approx$1730 cm^{-1} in the IR spectrum (Fig. 1). This is attributed to an oxidation of the methylene bridge between the benzene rings. It is also interesting to note that these poly(β-chlorothioether)s show a pronounced decrease in rel. mol. mass on oxidation (**7d/8d** and **3d/4d** in Tab. 2). Again the methylene bridge is the likely vulnerable point in the chain.



7d



8d

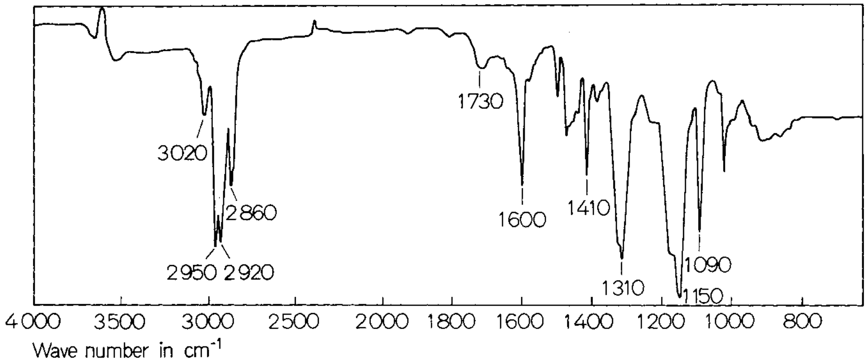
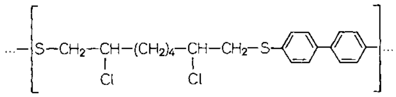
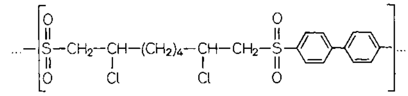


Fig. 1. IR spectrum of the poly(sulphone) **7d/8d**

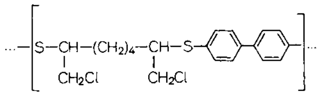
The NMR spectra of the poly(sulphone)s are also in agreement with the expected structures. The proton resonances in the poly(sulphone)s are usually downfield compared with the corresponding signals in the parent poly(β-chlorothioether)s and the aromatic peak in **3a**/**4a** and **7a**/**8a** is split into a quartet in the oxidized polymers. In poly(β-chlorothioether)s from 1,7-octadiene it was not possible to estimate the relative proportions of Markownikoff and *anti*-Markownikoff structures **D** and **C**, because of the poor resolution in the relevant part of the NMR spectrum. Oxidation to the corresponding poly(sulphone)s, however, improves the resolution in this region (Fig. 2) and an estimate of the relative proportions of the two types of adduct is now possible.



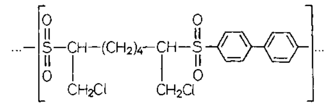
7a



7c



8a



8c

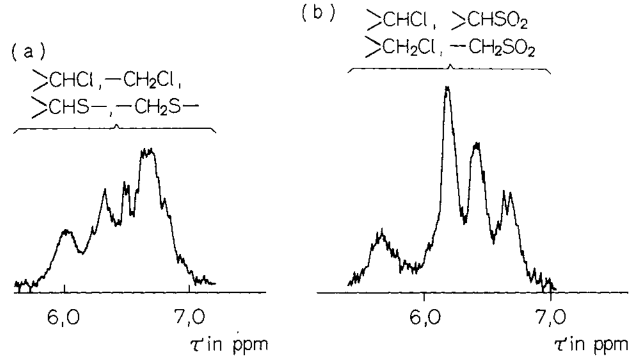


Fig. 2. Parts of the NMR spectra of (b): the poly(sulphone) **7c**/**8c**, and (a): of the corresponding parent poly(β-chlorothioether) **7a**/**8a**

Surprisingly, it appears that the *anti*-Markownikoff adduct, which is responsible for two of the peaks of **7c**/**8c** in Fig. 2 (spectrum (b)) is present in about the same amount as the Markownikoff adduct. This is in contrast to the much higher proportion ($\approx 90\%$) of Markownikoff adduct which is formed with 2,5-dimethyl-1,5-hexadiene. The *anti*-Markownikoff adduct in alkyl-substituted olefins is kinetically favoured but the thermodynamically favoured Markownikoff adduct tends to be formed in a subsequent isomerisation[4]. It seems that either there is initially a greater percentage of Markownikoff adduct formed with substituted alkenes or that this isomerisation occurs less readily with 1,7-octadiene than with 2,5-dimethyl-1,5-hexadiene. This could be a consequence of the methyl group in the latter which stabilizes the intermediate episulphonium ion. Little additional detailed information is available from the NMR spectra of **3d**/**4d** and **3c**/**4c** because of the complications arising from the unsaturation in the parent poly(β-chlorothioether)s. **5d**/**6d** and **5c**/**6c** are insoluble and NMR spectra were not recorded.

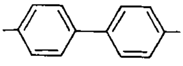
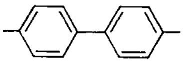
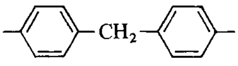
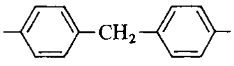
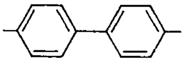
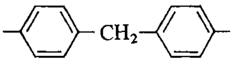
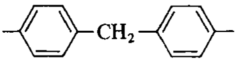
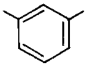
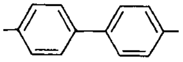
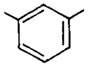
Poly(disulphide)s

Polymeric disulphides are readily formed from difunctional sulphenyl chlorides and dithiols.

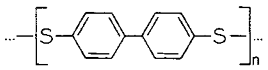
$$\text{ClS—R—SCl} + \text{HS—R—SH} \xrightarrow[-\text{HCl}]{} \ldots\text{—[S—R—SS—R}'\text{—S—]}_n\ldots$$

9

This reaction, therefore, offers a new route to regularly alternating disulphide copolymers, e.g., poly(dithio-1,4′-biphenylenedithio-1,4-phenylenemethylene-1,4-phenylene) (**9c**), poly(dithio-1,4-phenylenemethylene-1,4-phenylenedithio-1,3-phenylene) (**9d**), and poly(dithio-1,4′-biphenylenedithio-1,3-phenylene) (**9e**). Disulphide homopolymers, e.g., poly(dithio-1,4′-biphenylene) (**9a**) and poly(dithio-1,4-phenylenemethylene-1,4-phenylene) (**9b**), however, can also be pre-

9	R	R′
a		
b		
c		
d		
e		

pared by the reaction of disulphenyl chloride with lithium metal. The elemental analyses of the synthesized poly(disulphide)s (Tab. 3) are in good accord with the expected structures (with the possible exception of **9d**). The IR spectra are also consistent with the proposed structures and a typical spectrum is shown in Fig. 3.



9a

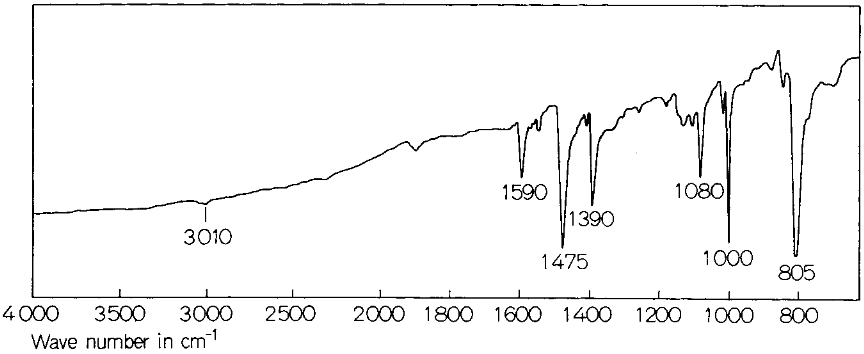


Fig. 3. IR spectrum of the poly(disulphide) **9a** obtained from 4,4′-biphenyldisulphenyl chloride (**1**) and 4,4′-biphenyldithiol

Most of these polymers proved to be insoluble in the common solvents so that NMR and rel. mol. mass data are limited. Nevertheless, the available NMR data confirm the assigned structures.

The facility of the reaction between dithiols and disulphenyl chlorides may offer an attractive alternative to previously published routes to regularly alternating disulphide polymers[10]. We hope to publish a more exhaustive account of this synthesis in the future.

One of us (S.A.S.) thanks the *Science Research Council* for the award of a studentship.

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