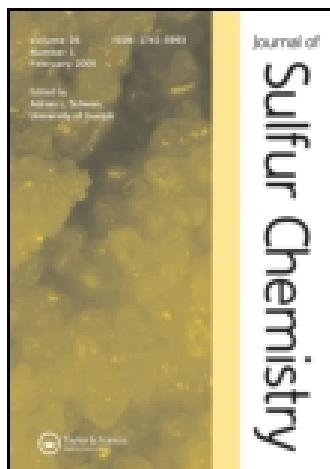


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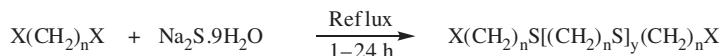
The synthesis of polymeric sulfides by reaction of dihaloalkanes with sodium sulfide

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Several poly(alkylene sulfide)s have been synthesized in excellent yields from reactions of α,ω -dibromo- and/or α,ω -dichloroalkanes with sodium sulfide nonahydrate under reflux conditions. The procedure is general, simple and convenient for the production of various poly(alkylene sulfide)s and the way reaction parameters influence the properties of the polymers formed has been examined.



X = Br, Cl; n = 1–10; y = 1–42

Keywords: polymeric sulfides; polycondensation; dihaloalkanes; sodium sulfide; synthesis

1. Introduction

Poly(alkylene sulfide)s are important polymers and their applications have been reviewed recently (1). They possess excellent thermal stability, weatherability, solvent resistance and oil resistance (2–4) and hence are widely used in coatings, adhesives, sealants, insulators and other applications (5–8). Also, poly(alkylene sulfide)s find application in vulcanizing rubbers (9). Moreover, poly(alkylene sulfide)–AgNO₃ electrolytes show interesting conductivities (10). Therefore, the syntheses of such polymers are always of interest.

Poly(alkylene sulfide)s are usually prepared by one of four major methods: polymerization of episulfides; reactions of dithiols with carbonyl compounds; addition of dithiols to diolefins; and reactions of dithiols with dihalides. The first two obviously apply to only very specific types of polymeric sulfides (containing a two-carbon or one-carbon spacer group, respectively), while the other two methods are not simple to operate and require the availability of appropriate dithiols. Other problems may also arise. For example, in the episulfide polymerization, the presence of disulfide impurities results in the poor control over molecular weight distribution; therefore, work

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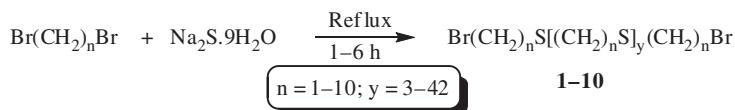
carried out by Wang *et al.* (11) was aimed at minimizing the presence of disulfides and optimizing synthesis procedures.

In the view of the above problems and also on grounds of convenience and cheapness, a method involving a direct reaction of a metal sulfide with a dihaloalkane would have obvious attractions. Early workers prepared poly(alkylene sulfide)s from dihaloalkanes and potassium sulfide; however, they used only 1,2-dihaloethenes and the polymeric materials obtained were poorly characterized (12). Later, the reaction of dichloromethane (DCM) with sodium sulfide nonahydrate was shown to form tetrathiocane first, but treatment of this with BF_3 gave poly(methylene sulfide), which was obtained as an insoluble polymer (13). In 1974, Landini and Rolla (14) demonstrated that excellent yields of simple dialkyl sulfides can be obtained from sodium sulfide and monohaloalkanes using a phase-transfer catalysis technique. Related reactions of sodium dithiolates with their corresponding dihalides gave polymers, with some cyclic oligomers also formed (15), and Imai *et al.* (16) reported that a phase-transfer catalyst could be used to assist in the synthesis of such poly(alkylene sulfide)s. Subsequently, the same group reported the preparation of higher molecular weight poly(alkylene sulfide)s from dibromoalkanes having relatively long spacer groups (8–11 carbon atoms) by reaction with 1 M aqueous sodium sulfide solution in the presence of quaternary ammonium or phosphonium salts (4 mol %) under a nitrogen atmosphere at 100°C for 24 h (17). The yields of polymers were good (86–99% depending on the type of catalyst used). However, application of the process on only a small scale (1–2 g) and with a restricted range of dibromoalkanes, together with the need for a catalyst, a long reaction time and use of an inert atmosphere, limits the attractiveness of the process; also the factors that influence the process are not clear.

As a part of our own interest in the synthesis of sulfur-containing compounds (18), we have examined the reaction of dibromoalkanes and dichloroalkanes with sodium sulfide in more detail. We have been able to produce a range of polymers simply from reactions of dihaloalkanes with cheap sodium sulfide nonahydrate by use of reflux conditions in the absence of a catalyst or additional solvent. The process has been applied to dihaloalkanes with spacer lengths from 1 to 10 carbons and generally gives excellent yields. In this paper, we report the high-yielding syntheses of a range of such poly(alkylene sulfide)s. Very recently, we have synthesized a range of borane adducts derived from such polymeric sulfides as new hydroborating and reducing reagents, which might well be suitable for large scale industrial application (19).

2. Results and discussion

Initial experiments were conducted in which mixtures of dibromomethane and various quantities of sodium sulfide nonahydrate (1.0–1.5 mole equivalents) were heated under reflux for various times with efficient stirring (Scheme 1; $n = 1$). The mixtures became very viscous and on cooling to room temperature produced solids, which were filtered, washed with water and dried to give the polymeric material **1** in high yield. The yield of **1** was 95% when the reaction time was 4 h and the molar ratio of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ to dibromomethane was 1.5:1.



Scheme 1. Synthesis of poly(alkylene sulfide)s **1–10** from polycondensation of dibromoalkanes with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$.

The solubility of polymeric material **1** was poor in organic solvents and we were unable to run the ^1H NMR spectrum or gel permeation chromatography (GPC) analysis for such material. Therefore, our attention was next turned to the investigation of the synthesis of other polymeric materials in which various α,ω -dibromoalkanes having different spacer group chain lengths from 2 to 10 carbons were used (Scheme 1). The molar ratio of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$:dibromoalkane was kept at 1.5:1 but the reaction time was varied for each dibromoalkane in order to provide high yields of polymeric material. Table 1 gives the reaction times, yields, melting points, average molecular weights calculated by GPC and the average number of repeating units calculated from the ^1H NMR spectrum for poly(alkylene sulfide)s **1–10**. No NMR spectroscopy or GPC analysis was carried out for **2** since that material, like **1**, was highly insoluble in organic solvents.

The average molecular weights calculated by GPC were usually higher than those calculated based on the number of repeating units calculated from the ratio of end-groups CH_2Br to internal CH_2SCH_2 units in the ^1H NMR spectra. In some cases, this may be because of the presence of significant quantities of disulfide impurities, which lead to additional NMR signals that are not taken into account in the calculations. Another factor may be because polystyrene was used as the GPC standard rather than a polymeric sulfide. However, the trends in molecular weights derived from GPC analysis were consistent with the trends in the number of repeating units calculated based on ^1H NMR spectra.

As can be seen from Table 1, the reaction is simple, general, accommodates various spacer chain lengths varying from 1 to 10 and usually provides high yields (90–100%) of the polymeric sulfides. The reaction involves no solvent and employs inexpensive starting materials. This therefore represents a very useful general method for the synthesis of poly(alkylene sulfide)s.

However, the yield of polymeric sulfide **4** was very low (11%) under the conditions tried. In this case, tetrahydrothiophene (**11**; Figure 1) was obtained in 78% yield due to the rapid cyclization on reaction of 1,4-dibromobutane with sodium sulfide. No attempts were made to try to find conditions under which the yield of **4** could be increased. It has been reported previously that the reaction of 1,4-dibromobutane in chloroform with sodium sulfide nonahydrate in water in the presence of a phase-transfer catalyst under nitrogen gave **11** in 42% yield, but no polymeric material of the structure **4** was reported in that case (20). In contrast, 1,2-dithiane (**12**) was produced in 80% yield from the reaction of 1,4-dibromobutane with sodium sulfide in the presence of sulfur and

Table 1. Synthesis of poly(alkylene sulfide)s **1–10** from reactions of 1,*n*-dibromoalkanes and sodium sulfide nonahydrate according to Scheme 1.^a

Polymer	<i>n</i>	Time (h)	Melting point (°C)	Yield (%) ^b	Mn ^c	Approximate number of repeating units (\bar{y}) ^d
1 ^e	1	4	225–230	95	Not known	Notknown
2 ^e	2	1	185–186	100	Not known	Notknown
3	3	4	55–57	100	4546	24
4	4	6	65–68	15 ^f	5939	43
5	5	4	70–75	94	3921	33
6	6	4	70–77	100	4068	33
7	7	5	78–85	90	4308	33
8	8	5	58–64	97	1201	3
9	9	5	70–76	92	2082	5
10	10	5	70–78	95	1700	5

Notes: ^aA mixture of dibromoalkane (0.10 mmol) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (36.0 g, 0.15 mmol) was heated under reflux in an oil bath set at 140–160°C for the indicated reaction time.

^bYield based on an assumed empirical formula for the product of $(\text{CH}_2)_n\text{S}$.

^cThe average molecular weight calculated by GPC.

^dCalculated from the ^1H NMR spectrum by comparison of the integrations of the CH_2Br and CH_2SCH_2 signals.

^eThe polymeric material was highly insoluble in solvents.

^fTetrahydrothiophene (**11**; Figure 1) was produced in 78% yield.



Figure 1. Structures of tetrahydrothiophene (**11**) and 1,2-dithiane (**12**).

didecyldimethylammonium bromide, as a phase-transfer catalyst, at 30°C for 4 h in a mixture of water and chloroform (21). In our current reaction, the preferential formation of **11** accounts for the low yield of **4**. No evidence was found to suggest the formation of a significant amount of **12** during the reaction.

The NMR spectra of polymeric sulfides **8–10** ($n = 8–10$) showed the prevalence of short-chain polymers in which the calculated average numbers of repeating units were in the range of 3–5, compared with averages of 24–43 repeating units in cases where n was less than 8. We therefore varied the reaction time and the quantity of sodium sulfide in an attempt to increase the chain length of polymeric sulfide **8** and to see what effect these parameters have on the chain length and physical properties (*e.g.* melting point) of the polymer. Initially, the reaction of 1,8-dibromooctane (1 mole equivalent) with sodium sulfide nonahydrate (1.5 mole equivalents) was conducted under reflux conditions and the reaction time was varied (2–24 h). The results obtained are recorded in Table 2.

The results (Table 2) show that the chain length (y) increases with increasing reaction time up to a reaction period of around 16 h, by which time the average number of repeating units (y) was ca. 20. Also, the yield and the melting point of the polymeric material **8** increased in line with the chain length as the reaction period increased. The reaction conducted for the shortest period (2 h) produced a low yield (30%) of the material that contained a calculated average of only two sulfur atoms per molecule (Scheme 1; $y = 1$). It is likely that the low cross-solubility of water with both the longer-chain dibromides and with the corresponding intermediate thiolates is responsible for the longer time taken in these cases for the polymer chain length to reach the higher values.

We also investigated reactions of 1,8-dibromooctane with various quantities of sodium sulfide (1.0–2.5 mole equivalents) under reflux conditions for a fixed period of 5 h and the results obtained are shown in Table 3.

Increasing the quantity of sodium sulfide resulted in a longer chain length over the fixed 5 h reaction period, but there were still only approximately eight repeating units when 2.5 mole equivalents of sodium sulfide were used. Also, the use of 1.2 mole equivalents for a longer period (24 h) provided polymeric sulfide **8** with only approximately six repeating units. Clearly, at least 1.5 mole equivalents of sodium sulfide and a prolonged reaction time are important for obtaining a longer-chain polymer.

Table 2. Effect of reaction time on the chain length of **8** according to Scheme 1.^a

Time (h)	Melting point (°C)	Yield (%) ^b	Approximate number of repeating units (y) ^c
2	Slurry	30	1
5	58–64	97	3
8	80–85	96	13
16	110–118	100	20
24	110–118	100	20

Notes: ^aA mixture of 1,8-dibromooctane (27.0 g, 0.10 mol) and Na₂S·9H₂O (36.0 g, 0.15 mmol) was heated under reflux in an oil bath set at 140–160°C for the indicated reaction time.

^bYield based on an assumed empirical formula for the product of (CH₂) _{n} S.

^cCalculated from the ¹H NMR spectrum by comparison of the integrations of the CH₂Br and CH₂SCH₂ signals.

Table 3. Effect of quantities of Na₂S·9H₂O on the average chain length of **8**.^a

Na ₂ S·9H ₂ O (mole equivalent)	Melting point (°C)	Yield (%) ^b	Approximate number of repeating units (y) ^c
1.0	Slurry	25	1 ^d
1.2	52–60	57	2 ^d
1.5	58–64	97	3
1.7	75–79	92	6
2.0	75–79	92	6
2.5	78–85	98	8

Notes: ^aA mixture of 1,8-dibromooctane (27.0 g, 0.10 mmol) and Na₂S·9H₂O was heated under reflux in an oil bath set at 140–160°C for 5 h.

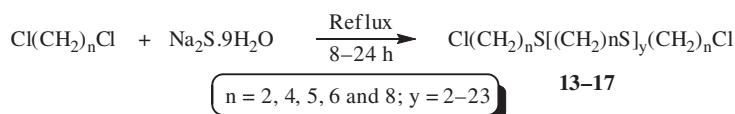
^bYield based on an assumed empirical formula for the product of (CH₂)_nS.

^cCalculated from the ¹H NMR spectrum by comparison of the integrations of the CH₂Br and CH₂SCH₂ signals.

^dThe number of repeating units (y) may be a little higher than reported due to the presence of a significant proportion of disulfide.

Attention was next turned to the use of various dichloroalkanes with sodium sulfide nonahydrate to produce the polymeric sulfides **13–17** (Scheme 2). These reactions were significantly slower than those using dibromides and therefore required longer reaction times to provide good yields of polymers. In the early experiments, the NMR peaks assumed to arise from disulfides were more prominent in the products than had been observed with the dibromides. In the case of reaction of 1,6-dichlorohexane with sodium sulfide nonahydrate (1.5 mole equivalents) for 48 h, the product mixture was treated with methanol and most of the polymeric material (**16**) precipitated and was collected by filtration. The filtrate was then cooled to 0°C and more **16** separated out. The total yield of **16** was around 60%. The filtrate was then concentrated under reduced pressure to give a 40% yield of the material that was mainly the cyclic disulfide 1,2-dithiocane (**18**; Figure 2), identical in all respects to the authentic material produced from the oxidation of 1,6-hexanedithiol with bromine (**22**). It is believed that compound **18** resulted from oxidation in air of 1,6-hexanedithiol formed *in situ* from 1,6-dichlorohexane under the conditions used.

The yield of **16** was higher when the quantity of sodium sulfide nonahydrate was increased to 2.5 mole equivalents, but **18** was still evident in the ¹H NMR spectrum of the product mixture, albeit in low proportion. Several attempts were made in order to find conditions under which **18**



Scheme 2. Synthesis of poly(alkylene sulfide)s **13–17** from polycondensation of dichloroalkanes and Na₂S·9H₂O.

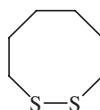


Figure 2. Structure of 1,2-dithiocane (**18**).

could be eliminated. However, carrying out the reaction under an inert atmosphere or the use of KI as a catalyst for the nucleophilic substitution reaction had little effect on the yield of **16** or the proportion of **18** formed. In the course of these investigations, it was noticed that a volatile material, believed to contain 1,6-hexanedithiol, evaporated from the reaction mixture and after condensation ran down the wall of the flask rather than dripping back directly into the reaction mixture. It was felt that the liquid dithiol might be re-evaporating on contact with the hot walls of the flask before it got back into the reaction mixture, thereby preventing its reaction with further chloroalkyl-terminated polymer in the flask and also increasing the likelihood of its oxidation to **18**. In order to minimize this problem, a condenser with a long drip-tip, which would allow the condensed material back into the reaction mixture more efficiently, was employed. The use of such a condenser improved the yield of **16** and also reduced the amount of **18** to a trace. Such a condenser was therefore used for further investigations.

A series of experiments was conducted in which the conditions of the reaction were varied in an attempt to produce the corresponding polymeric sulfides **13–17** in high yields. The optimum yields were obtained when a larger quantity of sodium sulfide nonahydrate (2.5 mole equivalents) was used for a longer reaction time (8–24 h, Table 4) than was the case for the corresponding dibromoalkanes (1–6 h). The NMR spectra of **14–17** showed the presence of only very low proportions of peaks thought to be due to disulfides.

As can be seen from Table 4, the reaction is general and usually provides high yields of the polymeric sulfides. However, the reactions were slower than those involving the use of dibromoalkanes (Table 1) and gave shorter-chain polymers. Again, the yield of polymeric sulfide **14** was low (19%) due to the formation of tetrahydrothiophene (**11**; Figure 1) in high yield (75%). It is clear that poly(alkylene sulfide)s can generally be synthesized efficiently in high yields from either dibromo- or dichloroalkanes by reactions with sodium sulfide. However, longer reaction times and/or greater quantities of sodium sulfide are required with dichloroalkanes in order to achieve comparable chain lengths.

For the polymers with the very short spacer groups (one or two methylene units), there was an issue of lack of solubility of the polymers produced under all the conditions tried. Several attempts were therefore made to synthesize a soluble polymeric material of structure similar to **2** or **13** to widen the scope of application for such polymeric materials. It was thought that the low solubility might be caused by longer chain lengths and that shorter chain lengths could be encouraged by the addition of a monohaloalkane to terminate the polymeric chains. Therefore, mixtures of 1,2-dichloroethane (0.6 mole equivalents), a haloalkane (1-bromobutane, 2-bromopropane, 1-chlorobutane or 2-chlorobutane; 0.4 mole equivalent) and sodium sulfide nonahydrate (1.5 mole

Table 4. Synthesis of polymers **13–17** from dichloroalkanes according to Scheme 2.^a

Polymer	<i>n</i>	Time (h)	Melting point (°C) ^d	Yield (%) ^b	Mn ^c	Approximate number of repeating units (<i>y</i>) ^d
13 ^e	2	8	185–186	91	Not known	Not known
14	4	24	68–70	19 ^f	5243	47
15	5	14	70–75	85	2726	25
16	6	14	72–76	97	2727	13
17	8	14	60–66	90	1229	3 ^g

Notes: ^aA mixture of dichloroalkane (0.10 mol) and Na₂S·9H₂O (60.0 g, 0.25 mol) was heated under reflux in an oil bath set at 140–160°C for the indicated reaction time.

^bYield based on an assumed empirical formula for the product of (CH₂)_{*n*}S.

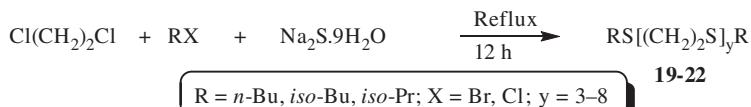
^cThe average molecular weight calculated by GPC.

^dCalculated from the ¹H NMR spectrum by comparison of the integrations of the CH₂Br and CH₂SCH₂ signals.

^eThe polymeric material is highly insoluble in most solvents.

^fTetrahydrothiophene (**11**; Figure 1) was produced in 75% yield.

^gThe calculated number of repeating units is less accurate due to the presence of a significant quantity of disulfide.



Scheme 3. Synthesis of poly(alkylene sulfide)s **19–22** from polycondensation of 1,2-dichloroethane and Na₂S·9H₂O in the presence of haloalkanes.

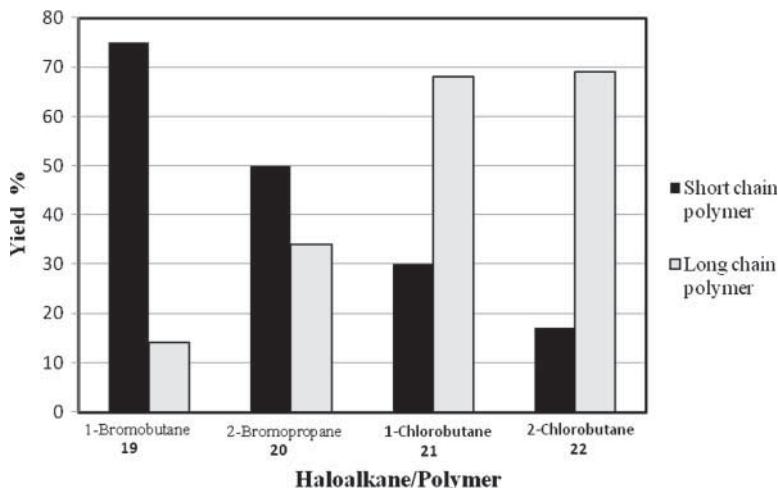


Figure 3. Total yields of polymeric materials **19–22** obtained from polycondensation of 1,2-dichloroethane and Na₂S·9H₂O in the presence of haloalkanes under reflux conditions.

equivalents) was refluxed for 12 h (Scheme 3). The polymeric materials produced (**19–22**) were treated with DCM and the residual solids (longer-chain polymers) were removed by filtration. The DCM was removed under reduced pressure from the filtrate to give the shorter-chain polymers as white solids. The total yield of the polymeric materials **19–22** are shown in Figure 3. The ¹H NMR spectra of the shorter-chain polymers indicated that the number of repeating units (*y*) was in the range of 3–8. The low solubility of the residual solid polymers meant that it was difficult to obtain molecular weight data, but it is assumed that the average chain lengths of such materials were significantly greater.

It is clear from Figure 3 that the total yields of polymeric materials **19–22** were high. In general, the yields of the short-chain polymeric materials using monobromoalkanes to terminate the chains were higher than those obtained with monochloroalkanes. Alkyl bromides tend to terminate the polymerization reaction faster than alkyl chlorides, and as a result, the proportions of short-chain oligomers are higher and the average chain lengths of such oligomers are lower (*y* = 3–5 with the bromides compared with *y* = 5–8 with the chlorides). Also, the yield of short-chain polymeric materials using 1-bromobutane was higher than that obtained with 2-bromopropane (Figure 3). This arises because the rate of nucleophilic substitution of primary alkyl halides is higher than that of secondary ones in these reactions (23).

The melting points of the short-chain polymeric materials prepared using primary alkyl halides were in the range of 70–72°C, while, the melting points of the corresponding ones obtained with secondary alkyl halides were a bit lower (64–68°C).

3. Conclusions

A general method for the synthesis of symmetrical poly(alkylene sulfide)s has been developed based on reactions of α,ω -dihaloalkanes of different spacer lengths with cheap sodium sulfide nonahydrate, in the absence of any added solvent, base or catalyst. The process is simple, general and convenient and provides excellent yields of polymer sulfides. Dibromoalkanes react faster than dichloroalkanes and under comparable conditions provide polymers with greater average chain lengths and molecular weights. The chain lengths of the polymeric materials can be increased by increasing the reaction time and/or the quantity of sodium sulfide. On the other hand, chain lengths are reduced by the addition of monohaloalkanes. Consequently, the properties of the polymeric materials obtained can be controlled to a large extent by judicious choice of dihaloalkane, haloalkane terminating agent (if any), reactant proportions and reaction time.

4. Experimental

4.1. General

Melting point determinations were performed by the open capillary method using a Gallenkamp melting point apparatus and are reported uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C measurements. Chemical shifts are reported relative to TMS and coupling constants J are in Hz and have been rounded to the nearest whole number. Assignments of signals are based on coupling patterns and expected chemical shift values and have not been rigorously confirmed. Signals with similar characteristics might be interchanged. GPC was carried out using a GPC MAX variable loop equipped with two KF-805L SHODEX columns in CHCl_3 , with a RI (VE3580) detector using a GPC MAX pump operating at a flow rate of 1 ml/min. Calibration was achieved using a series of Viscotek polystyrene standards up to $M_w = 9.4 \times 10^5$. Microanalyses were performed by Warwick analytical service at the University of Warwick. Chemicals were obtained from Aldrich Chemical Company and used without further purification.

4.2. Typical experimental procedure for the synthesis of polymeric sulfides 1–10

Dibromoalkane (100 mmol) and sodium sulfide nonahydrate (36.0 g, 150 mmol) were placed in a 1 l round-bottom flask that contained a magnetic bar. The flask was equipped with a water condenser and placed in an oil bath set at 140–160°C. The mixture was heated under reflux for 1–6 h with vigorous stirring, by which time a very viscous material resulted. Water (ca. 30 ml) was added to the hot reaction mixture, which was then poured into a clean beaker and vigorously stirred before being left to cool to room temperature. The solid mass was then collected by filtration, washed thoroughly with water (3×30 ml) and dried at 50°C under reduced pressure to give a white powdery solid. The physical properties and NMR spectroscopic data of **1–10** are presented in Tables 1 and 5, respectively.

4.3. Typical experimental procedure for the synthesis of polymeric sulfides 13–17

The procedure was similar to that described for the formation of polymers **1–10** but using a mixture of dichloroalkane (0.10 mol) and sodium sulfide nonahydrate (60.0 g, 0.25 mol) heated under reflux for 8–24 h in a bath set at 140–160°C. Also, a condenser with a long drip-tip was used to minimize disulfide formation. The physical properties and NMR spectroscopic data of **13–17** are presented in Tables 4 and 5, respectively.

Table 5. NMR spectra for polymeric sulfides **3–10**, **14–17** and **19–22**.^a

Polymer	NMR (δ , ppm; CDCl ₃) ^b	
	¹ H NMR (500 MHz)	¹³ C NMR (125 MHz) ^c
3	1.90 (m, 2H, CH ₂ CH ₂ S), 2.65 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.80 (t, $J = 7$ Hz, 0.166H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.166H, CH ₂ Br)	29.5 (CH ₂ CH ₂ S), 32.6 (CH ₂ S), 37.6 (CH ₂ SS)
4	1.70 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.65 (t, $J = 7$ Hz, 0.372H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.093H, CH ₂ Br)	28.4 (CH ₂ CH ₂ S), 32.4 (CH ₂ S)
5	1.40 (m, 2H, CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.24H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.12H, CH ₂ Br)	28.4 (CH ₂ CH ₂ CH ₂ S), 29.5 (CH ₂ CH ₂ S), 32.4 (CH ₂ S), 38.8 (CH ₂ SS)
6	1.35 (m, 4H, CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 3.35 (t, $J = 7$ Hz, 0.12H, CH ₂ Br)	28.4 (CH ₂ CH ₂ CH ₂ S), 29.5 (CH ₂ CH ₂ S), 32.4 (CH ₂ S)
7	1.20–1.35 (m, 6H, CH ₂ CH ₂ CH ₂ CH ₂ S and CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.89H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.12H, CH ₂ Br)	28.1 (CH ₂ CH ₂ CH ₂ CH ₂ S), 29.1 (CH ₂ CH ₂ CH ₂ S), 29.6 (CH ₂ CH ₂ S), 32.1 (CH ₂ S), 39.0 (CH ₂ SS)
8 ^d	1.27–1.45 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.65 (t, $J = 7$ Hz, 0.42H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.20H, CH ₂ Br)	28.6 (CH ₂ CH ₂ CH ₂ CH ₂ S), 29.4 (CH ₂ CH ₂ CH ₂ S), 29.7 (CH ₂ CH ₂ S), 32.2 (CH ₂ S)
9	1.16–1.40 (m, 10H, CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ S and CH ₂ CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.8H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.8H, CH ₂ Br)	28.9 (CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ S), 29.2 (CH ₂ CH ₂ CH ₂ CH ₂ S), 29.4 (CH ₂ CH ₂ CH ₂ S), 29.7 (CH ₂ CH ₂ S), 32.2 (CH ₂ S), 34.0 (CH ₂ Br), 39.5 (CH ₂ SS)
10	1.17–1.25 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ S), 1.27–1.40 (m, 4H, CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.61 (t, $J = 7$ Hz, 0.27H, CH ₂ SS), 3.35 (t, $J = 7$ Hz, 0.86H, CH ₂ Br)	28.9 (CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ S), 29.2 (CH ₂ CH ₂ CH ₂ CH ₂ S), 29.5 (CH ₂ CH ₂ CH ₂ S), 29.7 (CH ₂ CH ₂ S), 32.2 (CH ₂ S), 34.2 (CH ₂ Br), 39.5 (CH ₂ SS)
14	1.90 (m, 4H, CH ₂ CH ₂ S), 2.65 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.65 (t, $J = 7$ Hz, 0.344H, CH ₂ SS), 3.50 (t, $J = 7$ Hz, 0.086H, CH ₂ Cl)	28.4 (CH ₂ CH ₂ S), 32.4 (CH ₂ S), 38.5 (CH ₂ SS)
15	1.40 (m, 2H, CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.416H, CH ₂ SS), 3.50 (t, $J = 7$ Hz, 0.157H, CH ₂ Cl)	28.4 (CH ₂ CH ₂ CH ₂ S), 29.5 (CH ₂ CH ₂ S), 32.4 (CH ₂ S)
16	1.35 (m, 4H, CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.393H, CH ₂ SS), 3.50 (t, $J = 7$ Hz, 0.304H, CH ₂ Cl)	28.4 (CH ₂ CH ₂ CH ₂ S), 29.5 (CH ₂ CH ₂ S), 32.4 (CH ₂ S), 38.5 (CH ₂ SS), 44.5 (CH ₂ Cl)
17	1.20–1.42 (m, 8H, CH ₂ CH ₂ CH ₂ CH ₂ S), 1.50 (m, 4H, CH ₂ CH ₂ CH ₂ S), 2.45 (t, $J = 7$ Hz, 4H, CH ₂ S), 2.60 (t, $J = 7$ Hz, 0.834H, CH ₂ SS), 3.50 (t, $J = 7$ Hz, 1.57H, CH ₂ Cl)	28.6 (CH ₂ CH ₂ CH ₂ CH ₂ S), 29.4 (CH ₂ CH ₂ CH ₂ S), 29.7 (CH ₂ CH ₂ S), 32.2 (CH ₂ S), 39.0 (CH ₂ SS), 45.0 (CH ₂ Cl)
19	0.95 (t, $J = 7$ Hz, 1.27H, CH ₃ CH ₂ CH ₂ CH ₂ S), 1.45 (m, 0.85H, CH ₃ CH ₂ CH ₂ CH ₂ S), 1.61 (m, 0.85H, CH ₃ CH ₂ CH ₂ CH ₂ S), 2.55 (t, 0.85H, $J = 7$ Hz, CH ₃ CH ₂ CH ₂ CH ₂ S), 2.80 (s, 4H, CH ₂ S)	13.6 (CH ₃ CH ₂ CH ₂ CH ₂ S), 22.1 (CH ₃ CH ₂ CH ₂ CH ₂ S), 29.3 (CH ₃ CH ₂ CH ₂ CH ₂ S), 31.0 (CH ₃ CH ₂ CH ₂ CH ₂ S), 32.4 (CH ₂ S).
20	1.20 [d, $J = 7$ Hz, 4H, CH(CH ₃) ₂ S], 2.71 (s, 4H, CH ₂ S), 2.90 [m, 0.67H, CH(CH ₃) ₂ S]	23.5 [CH(CH ₃) ₂ S], 32.4 [CH(CH ₃) ₂ S], 35.1 (CH ₂ S)
21	0.95 (t, $J = 7$ Hz, 1.27H, CH ₃ CH ₂ CH ₂ CH ₂ S), 1.45 (m, 0.85H, CH ₃ CH ₂ CH ₂ CH ₂ S), 1.61 (m, 0.85H, CH ₃ CH ₂ CH ₂ CH ₂ S), 2.55 (t, $J = 7$ Hz, 0.85H, CH ₃ CH ₂ CH ₂ CH ₂ S), 2.80 (s, 4H, CH ₂ S)	13.6 (CH ₃ CH ₂ CH ₂ CH ₂ S), 22.1 (CH ₃ CH ₂ CH ₂ CH ₂ S), 29.3 (CH ₃ CH ₂ CH ₂ CH ₂ S), 31.0 (CH ₃ CH ₂ CH ₂ CH ₂ S), 32.4 (CH ₂ S)
22	0.95 (t, $J = 7$ Hz, 0.70H, CH ₃ CH ₂), 1.22 (d, $J = 7$ Hz, 0.70H, CH ₃ CHS), 1.50 (m, 0.47H, CH ₃ CH ₂), 2.70 (m, 0.23H, CH ₃ CHS), 2.85 (s, 4H, CH ₂ S)	22.9 (CH ₃ CH ₂), 30.8 [CH ₂ CH(CH ₃)S], 32.4 (CH ₃ CHS), 35.1 (CH ₂ S)

Notes: ^aPolymeric sulfides **1**, **2** and **13** were highly insoluble in most solvents and no NMR spectra were recorded.

^bCH₂X (X = Br, Cl) represents the terminal CH₂ of the polymer and the CH₂SS represents the disulfide. The term CH₂S refers to signals next to sulfide sulfur, CH₂SCH₂.

^cIn some cases, the signals for the CH₂X and the CH₂SS were not noticeable.

^dNMR for the polymeric material **8** obtained when the reaction time was 16 h.

4.4. Typical experimental procedure for the synthesis of short-chain polymeric sulfides 18–21

A mixture of 1,2-dichloroethane (5.8 g, 60 mmol), haloalkane (40 mmol) and sodium sulfide nonahydrate (36.0 g, 150 mmol) was heated under reflux with efficient stirring for 12 h in a silicon oil bath set at 140–160°C. The reaction mixture was allowed to cool and then water (30 ml) was added. The solid was removed by filtration and washed thoroughly with water (3 × 30 ml) and dried to give a white solid. The solid was treated with DCM (30 ml) and the insoluble solid was removed by filtration to give the longer-chain polymers. The DCM was removed under reduced pressure from the filtrate to give the shorter-chain polymers as white solids. The NMR spectroscopic data of the short-chain polymers **19–22** are presented in Table 5.

4.5. Tetrahydrothiophene (11)

A mixture of 1,4-dibromobutane or 1,4-dichlorobutane (100 mmol) and sodium sulfide nonahydrate (150–250 mmol) was heated under reflux for 6–24 h. The mixture was cooled and DCM (50 ml) was added. The layers were separated and the organic layer was dried (MgSO₄) and concentrated under reduced pressure. Diethyl ether (30 ml) was added to precipitate the polymeric material **4** or **14**. The solid was filtered and washed with diethyl ether (30 ml). The filtrates were combined and the solvent was removed under reduced pressure to give tetrahydrothiophene (**11**) in 75–78% yield. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 2.76 (t, *J* = 6 Hz, 4 H, CH₂S), 1.87 (t, *J* = 6 Hz, 4 H, CH₂CH₂S); ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 31.8 (CH₂S), 31.0 (CH₂CH₂S); EI-MS (*m/z*, %): 88 (M⁺, 88), 60 ([M – S]⁺, 100); HRMS (EI): calcd for C₄H₈S (M), 88.0347; found, 88.0343.

4.6. 1,2-Dithiocane (18)

Compound **18** was produced in around 40% yield as a side product from the reaction of 1,6-dichlorohexane with sodium sulfide nonahydrate along with the polymeric material **16**. Also, it was produced in 87% yield by oxidation of 1,6hexanedithiol with bromine according to the literature procedure (22). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 3.35 (t, *J* = 7 Hz, 4 H, CH₂SS), 1.65 (m, 4 H, CH₂CH₂SS), 1.30 (m, 4 H, CH₂CH₂CH₂SS); ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 38.9 (CH₂SS), 29.1 (CH₂CH₂SS), 27.5 (CH₂CH₂CH₂SS); EI-MS (*m/z*, %): 148 (M⁺, 37), 116 ([M – S]⁺, 25), 101 (20), 87 (100), 84 ([M – 2 S]⁺, 25); HRMS (EI): calcd for C₆H₁₂S₂ (M), 148.0380; found, 148.0376.

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