^{13}C NMR of Polysulfide Prepolymers

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ABSTRACT: The ^{13}C NMR analysis of commercial polysulfide prepolymers has revealed the presence of a number of minor components that arise from the manufacturing process. Those identified include monosulfides, diformyl ethers, and terminal thiols and alcohols. Trithiopropane cross-links are difficult to detect and in some prepolymers they do not appear to exist in the quantities expected.

Introduction

The development of polysulfide elastomers based on 1,7-dithio-3,5-dioxaheptane took place during the 1940s.[1] They became noted for their solvent and fuel resistance, good aging properties, and excellent weatherability. As a result they continue to be extensively used in the construction industry as well as in the sealing of aircraft integral fuel tanks.[1,2]

Despite this long history of commercial use, the detailed composition of the polymers has not been published in the open literature. This may be attributable to the difficulty of identifying the presence of low concentrations of chemically related species that do not significantly differ from the dominant monomer unit. Such components are difficult to characterize by commonly accessible analytical techniques such as electrochemistry,[3] IR,[4] and ^1H NMR.[5]

^{13}C NMR appears to offer the best prospect of comprehensive qualitative analysis of these components. The lack of data on this subject and the recent publication of a preliminary ^{13}C NMR analysis of these prepolymers that contained a number of incorrect assignments[6] prompted us to report our studies based on comparisons with the chemical shifts of model compounds.

The approach reported here relies upon, and is limited to, the prediction of likely products arising from the manufacturing processes previously described.[1] The initial process involves the preparation of 1,7-dichloro-3,5-dioxaheptane from 2-chloroethanol and paraformaldehyde.

$$ClCH_2CH_2OH + (HCHO)_n \xrightarrow{H^+} ClCH_2CH_2OCH_2OCH_2CH_2Cl \quad (1)$$

A suspension of the product together with a cross-linking agent such as 1,2,3-trichloropropane is then reacted with sodium polysulfide to produce a mixture of sulfides of various ranks.

$$ClCH_2CH_2OCH_2OCH_2CH_2Cl + Na_2S_x \rightarrow -S_yCH_2CH_2OCH_2OCH_2CH_2S_y- \quad (2)$$

The polysulfide linkages are subsequently reduced with sodium sulfite and sodium hydrosulfide to form the disulfide and thiol, respectively. On acidification the suspension coagulates to give a prepolymer containing disulfide linkages with thiol terminal groups and a molecular weight in the range 1000–8000.

Experimental Section

Model compounds were synthesized by standard procedures. 1,2,3-Propanetrithiol was prepared according to Wragg.[7]

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Petroleum Ether Extraction of Polysulfide Prepolymer LP-3. Polysulfide prepolymer LP-3 (29.64 g) was stirred with petroleum ether (40–60 °C) (180 mL) for 2 h. The organic layer was decanted and the solvent evaporated on a rotary evaporator; residue, 0.38 g (1.3%).

Reduction of Polysulfide Prepolymer LP-3. Polysulfide prepolymer LP-3 (17 g, 0.1 mol) was dissolved in dried THF (20 mL) and added to $LiAlH_4$ (5 g, 0.13 mol) in dried diethyl ether (250 mL). The mixture was stirred overnight at room temperature. Unreacted $LiAlH_4$ was destroyed with the dropwise addition of water until the evolution of hydrogen ceased. The aqueous layer was separated, acidified, and extracted with ether (3 × 50 mL), the combined extracts were washed with water (3 × 100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed on a rotary evaporator; residue, 2.2 g.

1,7-Dichloro-3,5-dioxaheptane and 1,9-Dichloro-3,5,7-trioxanonane. A mixture of 2-chloroethanol (400 mL, 3 mol), paraformaldehyde (90 g, 1.5 mol), and toluene (100 mL) was refluxed in the presence of concentrated sulfuric acid (3 drops). Water from the condensation reaction was collected in a Dean and Starke apparatus. The reaction mixture was cooled when the stoichiometric amount of water was removed (approximately 3 h). The mixture was dried over $MgSO_4$ and the solvent removed by distillation. The residue was distilled under vacuum, using a 100-cm-long, 1.7-cm-diameter, heated fractionation column, packed with Fenske rings. Fraction 1: bp 40 °C (6 mmHg); 19.5 g; ^{13}C NMR ($CDCl_3$) δ (relative intensity) 43.2 (100), 46.9 (6.4), 63.0 (7.2), 68.2 (98.3), 90.0 (7.2), 95.6 (85.0). Fraction 2: bp 86 °C (6 mmHg); 278 g; ^{13}C NMR ($CDCl_3$) δ (relative intensity) 43.2 (100), 68.2 (99.4), 95.6 (37.4). Fraction 3: bp 60–64 °C (0.01 mmHg); 36 g; ^{13}C NMR ($CDCl_3$) δ (relative intensity) 43.0 (41.7), 68.6 (60.8), 92.1 (100).

1,9-Dichloro-4,6-dioxanonane. This compound was prepared from 3-chloropropanol in a manner similar to that described above. The reaction product was washed with water (3 × 70 mL), dried over $MgSO_4$, and filtered. The solvent was removed by distillation and the residue distilled under vacuum. Fraction 1, bp 68 °C (0.1 mmHg), 3.6 g; fraction 2, bp 68–72 °C, (0.1 mmHg), 43.7 g; fraction 3, bp 72 °C (0.1 mmHg), 2.3 g. Theoretical yield, 60.3 g; ^{13}C NMR ($CDCl_3$) δ 32.7, 41.8, 64.2, 95.4.

1,7-Dimercapto-3,5-dioxaheptane, 1,9-Dimercapto-3,5,7-trioxanonane, and 1,9-Dimercapto-4,6-dioxanonane. These thiols were prepared from the corresponding chloro derivatives by the method of Martin and Greco[8] and were distilled from the reaction mixture, bp 80–90 °C (0.5 mmHg), 83–100 °C (0.3 mmHg), and 92–104 °C (0.1 mmHg), respectively. 1,9-Dimercapto-4,6-dioxanonane, ^{13}C NMR ($CDCl_3$) δ 21.4, 33.8, 65.7, 95.5.

5-Mercapto-3-oxapentane. This thiol was prepared from the reaction of 5-bromo-3-oxapentane and thiourea by a standard literature method;[9] yield, 33.5 g (63%).

3,10-Dioxa-6,7-dithiododecane. 5-Mercapto-3-oxapentane (6.36 g, 0.06 mol) was added to KOH (3.36 g, 0.06 mol) in water (200 mL). The solution was heated to 75 °C, H_2O_2 (3.1 mL, 37%, 0.04 mol) in water (30 mL) was added dropwise to the stirred thiolate, and the reaction mixture was maintained at this temperature for another hour. After cooling, the mixture was extracted with petroleum ether (3 × 20 mL), the combined

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extracts were washed with water, dried over $MgSO_4$, and filtered, and the solvent was removed by distillation; yield, 5 g (79%).

3,4-Dithio-7-oxanonanol. 2-Mercaptoethanol (4.3 g, 0.05 mol) and 5-mercapto-3-oxapentane (5.3 g, 0.05 mol) were dissolved in a solution of NaOH (4.0 g, 0.1 mol) in water (50 mL). Hydrogen peroxide (7.5 mL, 34%, 0.09 mol) in water (20 mL) was added dropwise to the stirred thiolate solution. The reaction mixture was acidified after 3 h and extracted with $CHCl_3$ (3 × 20 mL), the combined extracts were washed with water (3 × 50 mL), dried over $MgSO_4$, and filtered, and the solvent was removed by distillation; yield, 5.5 g (60%). ^{13}C NMR ($CDCl_3$) δ 15.10, 15.14*, 38.74, 38.80*, 41.56, 60.32, 66.42*, 68.87, 68.92* (* denotes 3,-10-dioxa-6,7-dithiododecane).

1,5-Dimercapto-3-oxapentane. This compound was obtained from Aldrich Chemical Co. and converted to the corresponding disulfide polymer by oxidation with iodine in dimethyl sulfoxide.

Disulfide Polymers. The dithiols were polymerized by oxidation with iodine in dimethyl sulfoxide solution. Typically, the dithiol (0.01 mol) was dissolved in KOH (0.021 mol) and a minimum amount of water. DMSO (20 mL) was added to the solution and the mixture cooled in an ice bath. A solution of iodine (0.02 mol) and DMSO (20 mL) was added dropwise to the stirred thiolate solution. Addition of iodine was continued until a permanent coloration persisted. The reaction mixture was poured into water (500 mL) and stirred for 20 min, after which it was acidified with HCl. The aqueous layer was then decanted and fresh water added to the residue with stirring. This was repeated twice. The residue was then washed with methanol, dissolved in toluene (50 mL), and precipitated with methanol. The tarlike residue was then dried in vacuo.

Poly(3,5-dioxa-1-thioheptane). 1,7-Dibromo-3,5-dioxaheptane was prepared from 2-bromoethanol in a similar manner to the chloro analogue; ^{13}C NMR ($CDCl_3$) δ 30.5, 68.0, 95.2. The dibromide (6.5 g, 0.05 mol) was added dropwise under nitrogen, to a solution of 1,7-dimercapto-3,5-dioxaheptane (4.2 g, 0.05 mol) and KOH (2.8 g, 0.05 mol) in methanol (30 mL) over a period of 15 min and stirred overnight at room temperature. The methanol was then decanted and water (100 mL) was added to the residue. The polymer was extracted with dichloromethane (3 × 20 mL) and the extracts were washed with water and then dried over $MgSO_4$. The filtered solution was distilled to remove the solvent and the residue dried in vacuo; yield, 4 g.

Propanetrithiol *S*-Ethyl Ether. 1,2,3-Propanetrithiol (2.8 g, 0.02 mol) was dissolved in a solution of KOH (0.4 g, 0.007 mol) in water (30 mL). Ethyl iodide was added dropwise to the stirred solution over a period of 0.3 h and stirring was maintained for a further 1.5 h, after which water (100 mL) was added. The products were extracted with dichloromethane (3 × 20 mL) and the combined extracts were washed (Na_2SO_3 solution), dried over $MgSO_4$, and filtered and the solvent was distilled; yield, 2.7 g. ^{13}C NMR ($CDCl_3$) δ 14.9, 25.3, 26.6, 28.3, 30.9*, 31.6, 38.4, 42.6, 45.1*, 50.6 (* denotes 1,2,3-propanetrithiol).

3,9-Dioxa-6-thioundecane. 3-Oxa-1-mercaptopentane (1 g, 0.01 mol) was dissolved in KOH (0.5 g, 0.05 mol) and methanol (20 mL), 1-bromo-3-oxapentane (1.5 g, 0.05 mol) was added dropwise with stirring, and the mixture was allowed to stand overnight at room temperature. Water (50 mL) was added to the reaction mixture, which was then extracted with petroleum ether (3 × 30 mL). The extracts were combined, washed with water (3 × 60 mL), dried over $MgSO_4$, and filtered and the solvent was distilled; residue, 1.1 g.

Thiol–Disulfide Interchange Reactions. Typically, 1 g of disulfide or prepolymer was added to 0.3 g of thiol and 2 drops of triethylamine. The reaction was carried out in $CDCl_3$ solution (3 mL) at room temperature at least 48 h prior to measurement of the spectrum.

Measurements. NMR measurements were carried out on a Bruker AM 300 spectrometer. Spectra were proton-decoupled with sample concentrations 5–10% in $CDCl_3$. The spectrometer was locked to ^2H and all chemical shifts were measured relative to TMS. Typically, chemical shifts were determined by using a 90° pulse with a pulse delay of 1 s with 16 000 data points accumulated over a spectral bandwidth of 20 kHz. The DEPT experiments were conducted with a pulse length of 10.8 μs (90°) and 21.5 μs (180°) for ^{13}C and 19.0 μs (90°) and 23.8 μs (180°) for ^1H. A recovery delay of 1 s and $\tau(1/2J)$ of 3.8 ms was used. The spectral bandwidth was set to 20 kHz involving 16,000 data points. Solutions of approximately 40% in $CDCl_3$ were used and required approximately 30 000–160 000 scans. The spectra were plotted with 5-Hz line broadening. The inverse gated decoupled spectra were obtained using a 90° pulse, a recovery delay of 3 s, and a spectral bandwidth of 15 kHz, with the accumulation of 16 000 data points. Between 80 000 and 100 000 scans were used to obtain spectra of approximately 40% solutions in $CDCl_3$. No line broadening was used. In all cases the free induction decays were zero filled to 32K.

GC–MS measurements were made by using a Varian Model 3700 gas chromatograph fitted with a BP 10 capillary column and coupled to a VG 7035 mass spectrometer.

Results and Discussion

Repeating Units. The ^{13}C NMR of polysulfide prepolymers is dominated by three resonances at 38.9, 66.2, and 95.4 ppm with variations in the intensities of a multitude of minor signals being dependent on the grade of prepolymer (Figure 1). The idealized disulfide monomer unit **1** is analogous to model compound **2** and the chemical shifts obtained from this compound confirm the identity of the first two major peaks as being due to the ethylene carbon atoms of the disulfide monomer unit. The discrepancy between the peak at 66.2 ppm and its equivalent at 68.9 ppm is obviously due to the imperfect model compound. However, the chemical shifts of compound **3**, prepared from 1,7-dichloro-3,5-dioxaheptane, are in excellent agreement with the assignments made to the prepolymer (**1**). The formal carbon chemical shift in the prepolymer (**1**) at 95.4 ppm is conserved in the precursor compound **4**.

Polym-SS$\underset{95.4}{CH_2}\underset{}{CH_2}O\underset{95.4}{CH_2}O\overset{66.2}{\underset{}{CH_2}}\underset{38.9}{CH_2}SS$-Polym

1

$CH_3\underset{66.4}{CH_2}O\underset{}{CH_2}\underset{38.8}{CH_2}SS\overset{68.9}{\underset{}{CH_2}}\overset{15.1}{\underset{}{CH_2}}O\underset{66.4}{CH_2}CH_3$

2

$[SCH_2CH_2O\underset{95.5}{CH_2}O\overset{66.2}{\underset{}{CH_2}}\underset{38.9}{CH_2}S]_n$ **3**

$ClCH_2CH_2O\underset{95.6}{CH_2}O\overset{68.3}{\underset{}{CH_2}}\underset{43.2}{CH_2}Cl$ **4**

Comparisons of the chemical shifts of poly(1,9-dithio-4,6-dioxanonane) (**5**) with those of the polysulfide prepolymers indicated the absence of detectable quantities of this homologue of 1,7-dithio-3,5-dioxaheptane (**3**), which was suspected of contributing to some of the minor peaks in the ^{13}C NMR spectrum of the polysulfides (Figure 1). During the manufacture of 1,7-dichloro-3,5-dioxaheptane

$[-SCH_2CH_2CH_2O\underset{95.3}{CH_2}O\overset{65.9}{\underset{}{CH_2}}\underset{35.4}{CH_2}\overset{29.2}{\underset{}{CH_2}}CH_2S-]_n$

5

(1) it is conceivable that some 1,5-dichloro-3-oxapentane (**6**) may be produced by dehydration of 2-chloroethanol.[10]

$$2ClCH_2CH_2OH \xrightarrow{-H_2O} ClCH_2CH_2OCH_2CH_2Cl \quad (3)$$

6

This would then form the corresponding disulfide on subsequent processing.

The chemical shifts of this disulfide (**7**) prepared by the oxidation of 1,5-dimercapto-3-oxapentane occurred at 38.4 and 69.2 ppm. When the thiol was incorporated into the

$[-SCH_2CH_2O\overset{69.2}{\underset{38.4}{CH_2}}CH_2S-]_n$

7

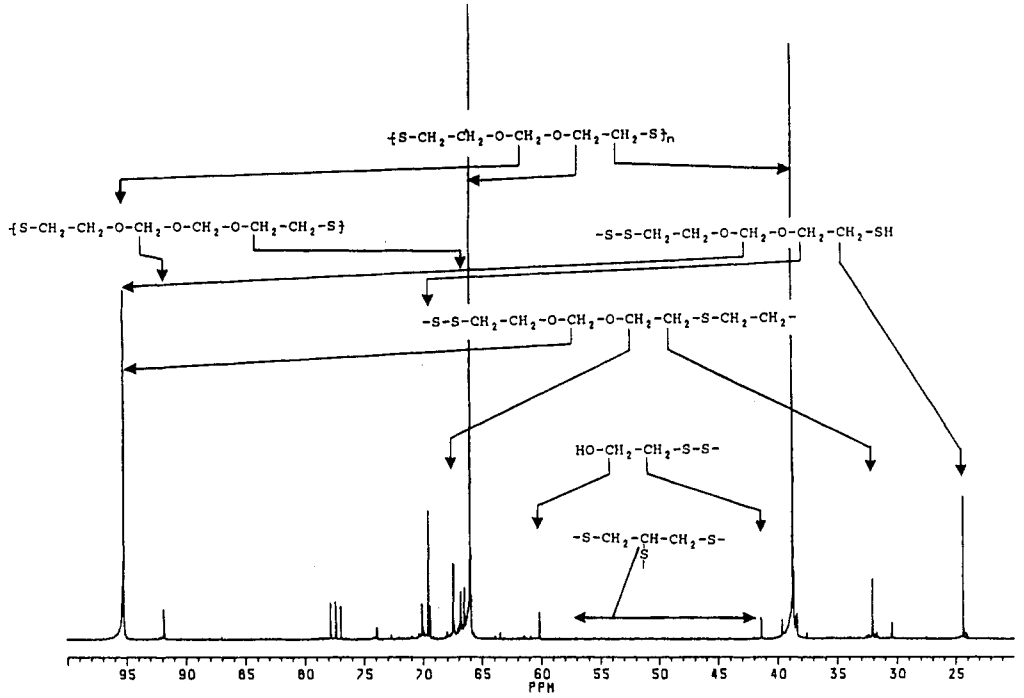


Figure 1. ^{13}C NMR spectrum of a polysulfide prepolymer (LP-3) claimed to have an average molecular weight of 1000, a thiol content of 6–8%, and 2% of added cross-linking agent.

polymer (LP-12) as the disulfide via a *thiol–disulfide* interchange reaction, the prepolymer peak at 38.3 ppm increased in intensity but a new peak appeared at 69.1 ppm, suggesting that this species was not present in the prepolymer to any significant extent.

Resonances at 32.2 and 67.9 ppm in the prepolymer spectrum were assigned from model compound **8** to a monosulfide component in the prepolymer **9**. These assignments were confirmed by the spectrum of the polythioether **10**.

$$\underset{15.1}{CH_3}\underset{58.3}{CH_2}\underset{70.4}{OCH_2}\underset{32.1}{CH_2}\underset{67.6}{SCH_2}\underset{32.2}{CH_2}\underset{70.4}{OCH_2}\underset{66.4}{CH_2}\underset{15.2}{CH_3}$$

8

$$\text{Polym-}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{32.1}{SCH_2}\underset{67.6}{CH_2}\underset{70.4}{OCH_2}\underset{32.2}{CH_2}\underset{95.4}{OCH_2}\text{-Polym}$$

9

$$[\text{-}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{32.1}{SCH_2}\underset{67.5}{CH_2}\underset{70.4}{OCH_2}\underset{32.3}{CH_2}\underset{95.4}{OCH_2}\text{-}]_n$$

10

A minor peak at 92.0 ppm was assigned to a diformal ether group (**11**) based on the spectrum of 1,9-dichloro-3,5,7-trioxanonane (**12**), which appears as an impurity in the preparation of 1,7-dichloro-3,5-dioxaheptane. GC–MS of 1,7-dichloro-3,5-dioxaheptane indicated the presence of small quantities of diformal ether (**12**) and lesser amounts of the triformal ether, which was also detected by NMR. The formation of these impurities was found to be facilitated by subjecting 1,7-dichloro-3,5-dioxaheptane to elevated temperatures (170 °C) in the presence of mineral acid. The chemical shifts of the disulfide polymer (**13**) prepared from **12** confirmed the assignment and allowed the identification of a minor peak at 66.7 ppm in the spectra of the prepolymers.

End Groups. The polysulfide prepolymers are cured by oxidation of the terminal thiol groups, which, in the case of the prepolymer in Figure 1, are specified as being present in the concentration range 6–8%. The chemical shifts obtained for **14** allow assignments to be made to the carbon atom adjacent to the terminal thiol group in the prepolymer (**15**).

$$\text{Polym-}\underset{58.3}{SCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{32.1}{S}\text{-Polym}$$
$$\underset{92.0}{}$$

11

$$\underset{58.3}{ClCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{68.7}{CH_2}\underset{70.4}{OCH_2}\underset{43.2}{CH_2}Cl$$
$$\underset{92.2}{}$$

12

$$[\text{-}\underset{58.3}{SCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{66.7}{CH_2}\underset{70.4}{OCH_2}\underset{38.8}{CH_2}\underset{32.1}{S}\text{-}]_n$$
$$\underset{92.0}{}$$

13

$$\underset{15.1}{CH_3}\underset{58.3}{CH_2}\underset{70.4}{OCH_2}\underset{66.3}{CH_2}\underset{70.4}{OCH_2}\underset{24.4}{CH_2}\underset{72.2}{SH}$$

14

$$\text{Polym-}\underset{58.3}{SCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{95.4}{CH_2}\underset{70.4}{OCH_2}\underset{24.5}{CH_2}\underset{69.7}{SH}$$

15

When the prepolymer is reduced with lithium aluminum hydride, the spectrum of the product is dominated by peaks at 24.5, 69.7, and 95.3 ppm corresponding to the dithiol **16**. A petroleum ether (40–60 °C) extract of the prepolymer resulted in the isolation of a small quantity of product (1.3%) rich in thiol content as indicated by three intense peaks at 24.5, 69.8, and 95.4 ppm. The spectrum of the dithiol **17** prepared from 1,7-dichloro-3,5-dioxaheptane confirms these assignments, while that of the homologous dithiol **18** enables a minor peak at 70.2 ppm, in a high thiol content prepolymer, to be identified.

$$\underset{58.3}{HSCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{95.3}{CH_2}\underset{70.4}{OCH_2}\underset{24.5}{CH_2}\underset{69.7}{SH}$$

16

$$\underset{58.3}{HSCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{95.4}{CH_2}\underset{70.4}{OCH_2}\underset{24.6}{CH_2}\underset{69.7}{SH}$$

17

$$\underset{58.3}{HSCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{70.4}{CH_2}\underset{58.3}{OCH_2}\underset{92.1}{CH_2}\underset{70.4}{OCH_2}\underset{24.5}{CH_2}\underset{70.2}{SH}$$

18

The possible formation of terminal hydroxy groups from the hydrolysis of one of the chloro groups of the precursor, 1,7-dichloro-3,5-dioxaheptane, was also considered. The hydrolysis of both chloro groups, on the other hand, would produce a water-soluble dihydroxy alcohol, which could not be incorporated into the prepolymer and would stay in the aqueous phase after coagulation of the prepolymer during the manufacturing process. Oxidation of a mixture

Table I
Trichloropropane Cross-Linker Content of Polysulfide Prepolymers

polysulfide prepolymer	trichloropropane, wt % reacted, determined by ^{13}C NMR[a] derivs as identified by shifts of CH signals, ppm[b] 56.9	53.2	50.7	49.6	41.8	total		added during manufacture[c]
LP-2	0.20	0.10	0.20	0.46	0.80	1.76	1.46[d]	2.0
LP-3	0.20	0.10	0.62	0.24	0.69	1.85	1.55[d]	2.0
LP-31	0.32	0.06	0.06	0.18	0.30	0.92	0.54[d]	0.5
LP-32	0.26	0.08	0.08	0.18	0.30	0.92	0.58[d]	0.5
LP-12	0.26	0.06		0.09	0.11	0.52	0.22[d]	0.2

[a] Concentrations determined by peak heights of the CH signals of the cross-linker relative to the combined disulfide, thioether, and thiol C-1 peaks at 38.7, 32.2, and 24.5 ppm, respectively, in the inverse-gated spectra of the prepolymers. [b] CH peaks of the cross-linking moiety $-CH_2C(-)HCH_2-$ identified by DEPT experiments at prepolymer concentrations of approximately 40%. [c] As specified by the manufacturer. [d] Excluding contributions from peaks at 56.9 and 53.2 ppm.

of $HOCH_2CH_2SH$ and $CH_3CH_2OCH_2CH_2SH$ allowed the identification of **19** in the resultant mixture, which led to the detection of **20** in the prepolymer.

$$\overset{60.3}{HO}\overset{41.5}{CH_2}\overset{38.7}{CH_2}SSCH_2\overset{68.9}{CH_2}O\overset{66.5}{CH_2}\overset{15.1}{CH_3} \qquad \overset{60.3}{HO}\overset{41.5}{CH_2}CH_2SSCH_2CH_2OCH_2O\text{-Polym}$$

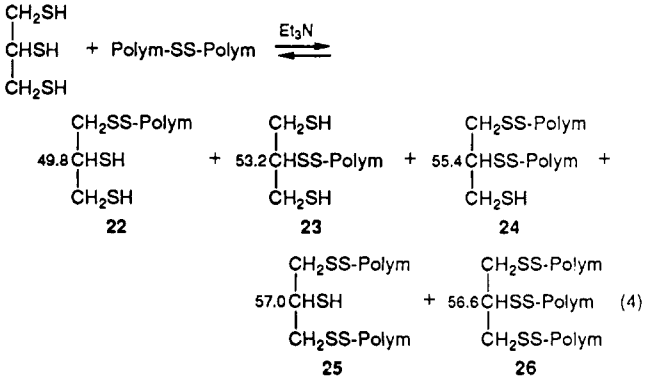
19 **20**

Cross-Linking. Cross-linking is allegedly introduced into the prepolymer by way of 1,2,3-trichloropropane, which would most likely be incorporated as a trifunctional disulfide (**12**), although some monosulfide linkages will inevitably occur. The amount of cross-linker added to some commercial prepolymers lies in the range 0.2–2.0%, depending on the grade of product. However, there is no report of this being measured in the prepolymer. DEPT

$$\text{Polym-O}CH_2CH_2SSCH_2\underset{\displaystyle SSCH_2CH_2O\text{-Polym}}{\overset{|}{C}}HCH_2SSCH_2CH_2O\text{-Polym}$$

21

experiments, carried out on concentrated solutions of the prepolymers, identified the presence of six CH signals in the region 40.4–56.9 ppm (Table I), although there was some concern about the authenticity of the signals at 41.8 and 40.4 ppm due to the presence of overlapping CH_2 resonances (Figure 2). However, the authenticity of some of these peaks was confirmed when 1,2,3-propanetrithiol was interchanged with a prepolymer (LP-12) and a DEPT experiment revealed the presence of five CH resonances (49.7, 53.1, 55.4, 56.6, and 57.0 ppm), corresponding to the five possible derivatives produced by this reaction (4). Similar results were obtained from the interchange of the trithiol with dibutyl disulfide. In both cases the intensities of the CH peaks in the inverse-gated decoupled ^{13}C NMR spectra decreased with the increase in the chemical shifts with the exception of the resonances of 56.6 and 57.0 ppm (Figure 3).



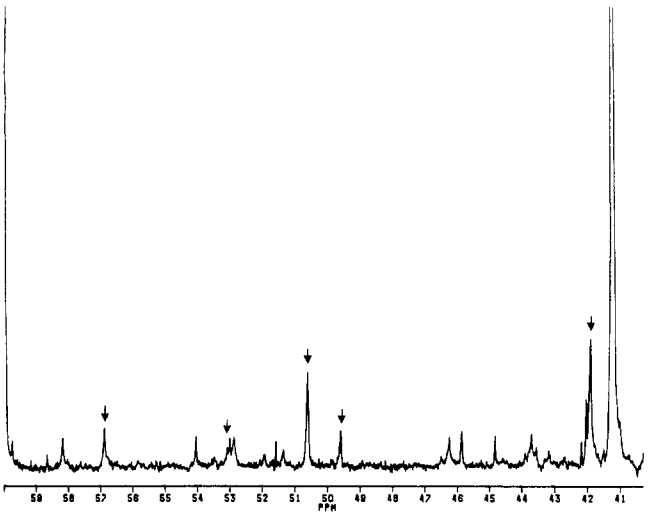
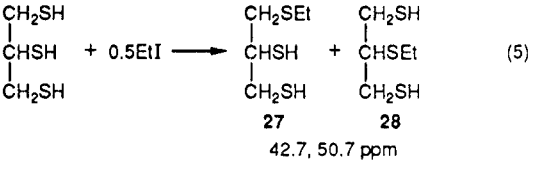


Figure 2. Inverse-gated decoupled ^{13}C NMR spectrum of a polysulfide prepolymer (LP-2) showing CH carbon resonances identified by a DEPT experiment.

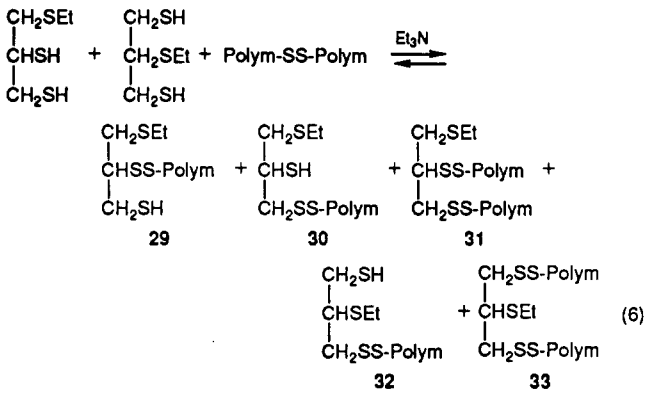
The relative probabilities of forming these derivatives are 16 (**22**), 8 (**23**), 4 (**24**), 2 (**25**), and 1 (**26**), assuming equal interchange equilibrium constants for both the primary and secondary thiol groups.[11] This assumption was supported by an experiment that, under similar conditions, using 1-butanethiol and 2-butanethiol, showed no discernible selectivity in the interchange of these two thiols with LP-12. Thus it is tempting to assign the five CH peaks in Figure 3 to the structures **22**–**26**.

The identification of the thioether-containing cross-links in the prepolymers was carried out by preparing



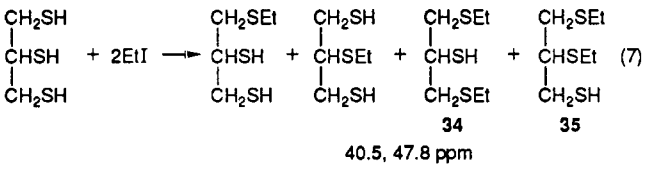
monothioethers from 1,2,3-propanetrithiol (eq 5). The ^{13}C NMR of the reaction mixture showed two CH resonances at 42.7 and 50.7 ppm (in addition to the unreacted trithiol), one of which corresponds to a peak identified with a cross-linker in the prepolymers (Table I). The two derivatives could not be separated either by gas chromatography or thin-layer chromatography and therefore individual chemical shift assignments could not be made.

When this mixture was interchanged with the prepolymer LP-12 (eq 6), the products gave rise to a new CH peak at 41.8 ppm, coinciding with that observed in the prepolymers (Table I). It is difficult to assign a structure to



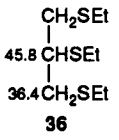
this peak on the basis of data available but clearly the scope is limited to structures **29–33**, with either structure **29** or **30** being most likely on the basis that they would predominate as products of the first step in the *thiol–disulfide* interchange reaction.

On repeating the reaction outlined in eq 5, using larger amounts of ethyl iodide, a mixture containing mono- and dithioethers was produced (eq 7) as indicated by the



appearance of two additional CH signals in the ^{13}C NMR of the products (40.5 and 47.8 ppm), none of which coincided with the signals identified as a cross-linking CH carbon atoms in the spectra of the prepolymers (Table I).

The presence of the trithioether (**36**), prepared by similar means, could not be identified in the ^{13}C NMR spectra of the prepolymers.



It is likely that most of the thiols, thioethers, and disulfides canvassed as possible cross-linkers are present in the polysulfide prepolymers, but because of their low concentration they may have escaped detection. The experiments carried out with the model compounds support the assignment of the peaks identified in Table I as being attributable to cross-linkers in the prepolymers.

Table I shows that in the case of two of the prepolymers with relatively high cross-linker contents (LP-2 and LP-3), the total amount of cross-linkers estimated from the NMR is less than the amount of trichloropropane cross-linking agent added in the manufacturing process, indicating incomplete reaction. However, three of the prepolymers with relatively low cross-linker content (LP-31, LP-32, and LP-12) have estimated trichloropropane contents greater than the quantities allegedly added. The contributions of cross-linkers determined at 56.9 and 53.2 ppm in all the prepolymers appears to show little variation from one prepolymer to another, suggesting that these signals may not be due to species formed from the addition

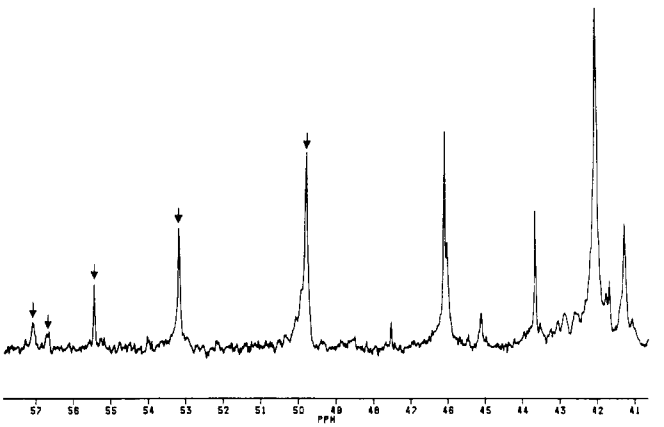


Figure 3. Reaction products from the interchange of 1,2,3-propanetrithiol and a polysulfide prepolymer (LP-12).

of trichloropropane although it is difficult to envisage an alternate source for these assignments. When these contributions are excluded, the total amount of cross-linkers calculated is significantly reduced and no longer exceeds the amount of trichloropropane added. Two of the prepolymers (LP-2 and LP-3) now have estimated cross-linker contents well below the level expected for complete incorporation of trichloropropane, while the remainder (LP-31, LP-32, and LP-12) seem to have complete incorporation of the reagent.

Conclusions

The ^{13}C NMR of commercial polysulfide prepolymers reveals the presence of a number of minor components incorporated into the polymer. The most obvious are the monosulfide and diformal ether analogues of the idealized monomer unit. End groups detected include SH and OH. Other species are also present but these are difficult to identify without access to the details of the manufacturing process.

The presence of a trifunctional propyl cross-linking agent is difficult to detect, and, in the prepolymers examined in this work, there appears to be incomplete incorporation of the cross-linking agent in some of the prepolymers. The cross-linkers were identified as CH carbon resonances and were assigned on the basis of thioether and disulfide derivatives of 1,2,3-propanetrithiol. Because of the diversity of possible products that may be attributed to these resonances, unequivocal assignments could not be made, but the identities of the signals were confined to a limited number of compounds.

References and Notes

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