Polysulfide Sealant Compositions. II. Interactions Between Elemental Sulfur and Organosulfur Compounds

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SYNOPSIS

Added sulfur in polysulfide aircraft sealants can become chemically bound to the polymer backbone. The chemical processes involved, and their effect on thermal performance of the resulting sealants, have been examined. Reactions of aliphatic thiols with sulfur and amine catalysts have been reinterpreted to include possible involvement of hydropolysulfide intermediates. When the procedure was applied to polysulfide liquid polymers, products with substantial levels of tri- and tetra-sulfide links were formed. ^{13}C-NMR spectroscopy of model compounds enabled the assignment of chemical shifts associated with S_3 to S_5 links in the sulfur enriched polymers. Spectroscopic examination afforded no evidence for the presence of such species in commercial polysulfide liquid polymers.
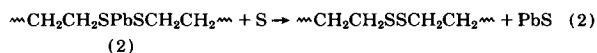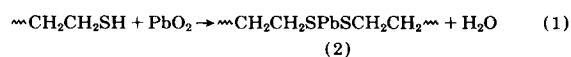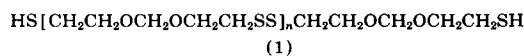
No obvious detrimental effects on elevated temperature performance of polysulfide sealants resulted from the incorporation of up to 1% sulfur into the polymer backbone. A higher degree of cure is achieved and this is associated with increased hardness and modulus, together with reduced extension as compared with untreated sealants. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polysulfide[†] sealant formulations are generally composed of two parts, one containing the curing agent in paste form and the other the liquid prepolymer (1). Numerous additional components are introduced into the formulated product and these may include viscosity modifiers, cure retarders or accelerators, dispersing agents or solvents for the curative, and adhesion additives.[1,2] In order to rationalize the chemical processes which lead to degradation upon storage or exposure to environmental influences, it is essential to determine the composition of the sealant. A general procedure to achieve this has been developed for the cases of two part manganese dioxide or dichromate-cured polysulfide aircraft sealants.[3]

One common practice, considered to improve the thermal stability of cured polysulfides, has been the introduction of sulfur into the sealant formulation.[1,4,5] For the specific case of lead dioxide cures it is recognized that lead thiolates (2) can be produced [eq. (1)] and these species have been considered to be responsible for degradation of the polymer at elevated temperatures. In the presence of sulfur, however, the thiolate reacts as in eq. (2) to produce a polymer that is more thermally resistant.[1,4]

$$HS[CH_2CH_2OCH_2OCH_2CH_2SS]_nCH_2CH_2OCH_2OCH_2CH_2SH$$
$$(1)$$

$$\sim\!CH_2CH_2SH + PbO_2 \rightarrow \sim\!CH_2CH_2SPbSCH_2CH_2\!\sim + H_2O \qquad (1)$$
$$(2)$$

$$\sim\!CH_2CH_2SPbSCH_2CH_2\!\sim + S \rightarrow \sim\!CH_2CH_2SSCH_2CH_2\!\sim + PbS \quad (2)$$
$$(2)$$

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† It is unavoidable that the term polysulfide must be used throughout this article to indicate two different types of materials. This descriptor is appropriate for organic compounds which incorporate several sulfur atoms in a continuous sequence (RS_xR^1). The class of sealants of general structure (1), however, has also been named polysulfide, despite the fact that the recurring links involve disulfides. Care has been taken in the text to avoid confusion and, in particular, the sealants or their components are either referred to as such or termed liquid polymers.

A ready means of evaluating whether sulfur has been incorporated into polysulfide formulations is desirable, since its presence may influence both the mechanical performance and the chemical behavior of the sealant. Moreover, the detection procedure will depend upon whether the sulfur remains present in elemental form or becomes bound into the structure of the liquid polymer. The latter possibility is particularly relevant for the case of manganese dioxide-cured polysulfides, in which amines are used as cure accelerators. Under these circumstances, a fast reaction to produce polymers of higher sulfur rank could be expected to occur in a fashion similar to the formation of polysulfides from thiols[6-10] [eq. (3)]. The presence of tri- and tetra-sulfide links in the polysulfide backbone has been viewed as potentially detrimental to the thermal stability of sealants, since disproportionation of such species at elevated temperatures is recorded.[11]

$$RSH + S \xrightarrow{R_2'NH} RS_2R + RS_3R + RS_4R \cdots \quad (3)$$

This study addresses these aspects, using spectroscopic procedures to follow the incorporation of sulfur into model compounds and polysulfide liquid polymers. A methodology to determine the presence of higher rank species in commercial blends has been developed and the effect of introduced tri- and tetrasulfide links on the thermal resistance of polysulfide sealants also has been evaluated.

EXPERIMENTAL

Analytical Methods

[1]H and ^{13}C magnetic resonance spectra were determined in $CDCl_3$ using a Bruker AM 300 instrument, and all chemical shifts are reported in ppm relative to tetramethylsilane as internal standard. For those cases where low levels of sulfur were incorporated, multiple scans (up to 4000) were necessary to enable interpretation. Infrared spectra were obtained with a Perkin–Elmer 580B double beam ratio recording infrared spectrophotometer, equipped with a Model 3600 data station, and GC-MS analyses were carried out using a Vacuum Generators Model 7035 instrument interfaced with a Varian 3700 gas chromatograph operated with a 15 m × 0.2 mm bonded phase (BP10)-fused silica column and SGE universal injector. Where appropriate a splitless injection was used. The initial column temperature was 50°C and

a programmed increase of 10°C per minute was employed to give a final temperature of 270°C.

Materials

The polysulfide liquid polymers LP-2, LP-3, and LP-32 were obtained from Toray Thiokol. The two part polysulfide aircraft sealants, PR-1422 B-2 and PR-1750 B-2, were acquired respectively from Selleys Australia Pty. Ltd., Bankstown, NSW and Products Research and Chemical Corporation, Glendale, California. The polysulfide polymers of these sealants were separated from the fillers of the polymer base component as described previously.[3]

Di-n-butyl disulfide, diethyl disulfide, (^{13}C–NMR δ 14.4, 32.9) diethyl sulfide (^{13}C–NMR δ 14.8, 25.5), and n-butanethiol (^{13}C–NMR δ 13.3, 21.3, 24.1, 36.0) were all procured from Aldrich and were distilled prior to use to remove trace quantities of impurities (mainly propyl and butyl isomers), which otherwise complicated interpretation of spectra resulting from low levels of sulfur incorporation. Diethyl trisulfide, diethyl tetrasulfide, di-n-butyl trisulfide, and di-n-butyl tetrasulfide were obtained by the method of Decker and Post[12] and were separated by repeated distillations. Diethyl trisulfide and diethyl tetrasulfide were prepared similarly. Di(2-ethoxyethyl) disulfide (5), 1,7-dichloro-3,5-dioxaheptane (3), and 1,9-dichloro-3,5,7-trioxanonane (4) were synthesized as described by Mazurek and Moritz.[13] The reference compounds had the following mass spectral data: di(2-ethoxyethyl) disulfide, m/z 210 (M, 71%), 164 (4), 138 (13), 105 (14), 105 (50), 93 (31), 92 (48), 79 (27), 76 (19), 73 (83), 64 (34), 61 (64), 60 (59), 59 (92), 47 (17), 46 (15), 45 (100), 44 (22), and 43 (41); di-n-butyl trisulfide, m/z 210 (M, 46%), 178 (5), 154 (7), 122 (8), 89 (76), 87 (16), 79 (8), 64 (8), 57 (100), 56 (11), and 55 (40); di-n-butyl tetrasulfide, m/z 242 (M, 13%), 210 (24), 178 (8), 122 (17), 89 (41), 87 (34), 79 (15), 64 (41), 57 (100), 56 (19), and 55 (44); diethyl trisulfide, m/z 154 (M, 96%), 125 (6), 97 (10), 94 (11), 93 (19), 92 (11), 91 (15), 89 (13), 75 (7), 66 (11), 64 (25), 62 (15), 61 (100), and 59 (23); diethyl tetrasulfide, m/z 186 (M, 71%), 154 (6), 122 (10), 97 (12), 94 (35), 93 (100), 91 (16), 66 (36), 65 (14), 64 (55), 61 (40), 59 (44), and 58 (15).

Tetrabutylammonium n-butylthiolate was prepared as follows: a mixture of tetrabutylammonium hydroxide (0.685 g of 42% aqueous solution, 1.1 mmole) and n-butanethiol (0.15 g, 1.7 mmole) was stirred at room temperature for 16 h. Water and excess thiol were then removed under reduced pres-

sure to give the thiolate as a solid (0.36 g) which was used without further purification.

Interactions with Sulfur

Monosulfides and Methylenedioxy Compounds

Mixtures of equimolar quantities of sulfur and (a) diethyl sulfide (b) di(2-ethoxyethyl) sulfide (c) 1,7-dichloro-3,5-dioxaheptane (3), and (d) 1,9-dichloro-3,5,7-trioxanonane (4) were heated at 70°C for 3 h, both with and without the addition of catalytic quantities of triethylamine (generally 0.05 g for each gram of sulfur). The cooled liquid products were filtered from unreacted sulfur and were analyzed spectroscopically.

Disulfides

Di-n-butyl disulfide, diethyl disulfide, and di(2-ethoxyethyl) disulfide (0.02 mole) were each heated with sulfur (0.04 mole) at 70–80°C for 3 h, both with and without triethylamine (0.01 g).

The amine catalyzed reaction of di-n-butyl disulfide yielded a clear brown solution, which deposited crystals of sulfur on cooling. A catalyzed reaction, using equimolar quantities of di-n-butyl disulfide and sulfur, was also carried out. These reagents were also heated at 130°C for 3 h in the absence of catalyst and were reacted at ambient temperature for 2 days in the presence of triethylamine. Products of these reactions, and those of n-butanethiol below, were examined using GC-MS and NMR spectroscopy.

n-Butanethiol

The thiol (0.03 mole) and sulfur (0.06 mole) were heated as above at 70°C for 3 h. With added triethylamine catalyst, a series of reactions was conducted at room temperature with the stoichiometric ratio of thiol to sulfur varying from 2 : 1 to 2 : 3.

A further ambient temperature reaction was carried out by adding sublimed sulfur (0.29 g) to a solution of the thiol (1.0 g) and tetrabutylammonium n-butanethiolate (0.36 g). An immediate, vigorous gas evolution resulted and the pale yellow solution darkened to a red-brown color. This mixture was allowed to stand for 1 h and was then analyzed spectroscopically.

Liquid Polymers and Commercial Polysulfides

LP-2, LP-3, and the filler-free liquid polysulfides from PR-1422 B-2 and PR-1750 B-2 (each 10 g)

were separately heated with sulfur (1 g) at 70°C for 3 days and the resulting mixture was decanted from undissolved solid and compared spectroscopically with liquid polymer samples, which had been maintained under similar conditions in the absence of sulfur. In addition, LP-2 (10 g) was heated with sulfur (3 g) for 3 days at 70°C. This molar ratio would equate to a sulfur rank of 3.6 if total reaction occurred, whereas for the other reactions a rank of around 2.5 would result. All amine catalyzed reactions used a 10 to 1 w/w ratio of polysulfide and sulfur and were carried out at 70–90°C for 45 min. Various amines, including di-n-butylamine, diisopropylamine, and triethylamine, were used with similar results. Thiol contents of the liquid polymers were determined mainly by gated-decoupled ^{13}C–NMR spectroscopy, using the peak intensity of the CH_2SH signal at 24 ppm relative to the summed intensities of the rest of the polysulfide spectrum.[3] These results were occasionally compared with those of the infrared technique[14] and good correlation was observed.

Preparation of Sealants Containing Tri- and Tetra-Sulfide Links

Sulfur addition into the liquid polymer LP-2 and the filler-free polymer from PR-1750 was carried out as follows. Diisopropylamine (0.5 mL) was added to mixtures of the liquid polymers (200 g) with introduced sulfur at levels of 0%, 0.5%, and 1%. The mixtures were heated at 60–70°C for 2 h and were then allowed to stand at ambient temperature for 4 days before curing. The LP-2-based sealants were cured by reacting the polysulfide polymer (60 g) with a reagent consisting of manganese dioxide (Riedel-de Haën, type C, 3.6 g), Cerechlor AS52 (3.6 g), and m-dinitrobenzene (0.12 g) which had been dissolved in the minimum amount of toluene. The components were first mixed by hand and then with a spindle driven by an electric drill. The mixed sealant was transferred to a steel mold (152 × 152 × 2 mm) which had been coated with mold release agent, then covered with a Teflon sheet and the backing plate. The completed mold was then placed on a press platen which had been preheated to 50°C. The press was operated at a pressure of 7000 kPa, which was applied and removed six times in order to eliminate voids. The mold was kept under pressure overnight, the sheet of sealant then removed and maintained in an oven at 50°C for 4 days to complete the curing process.

Thermal Stability Studies

Measurement of sealant properties was undertaken immediately after curing and thereafter at various intervals over 25 days, during which time the sealants were continuously subjected to a temperature of 125°C. Hardness changes, weight loss, tensile strength, modulus, and extension at break were monitored. Hardness readings were taken on cooled samples and were measured in a multilayer stack, using a Shore Conveloader fitted with a type A2 durometer. Tensile, modulus, and elongation measurements were determined with an Amsler Type Dkf tensiometer. Test specimens were cooled and were equilibrated overnight before testing.

Polythiopolymercaptan Polymers

LP-3, LP-2, and LP-32 (each 20 g) were separately treated with a mixture of sulfur (5 g), water (0.05 g), and diisopropylamine (0.2 g) using the method of Bertozzi.[15] Each mixture was stirred by hand at ambient temperature and samples were periodically removed for NMR analysis.
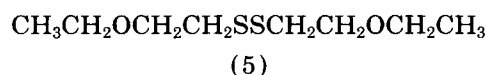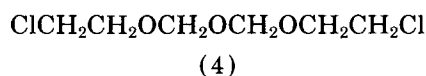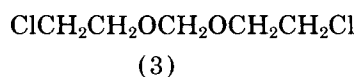
RESULTS AND DISCUSSION

Previous work[3] has shown that most analytical techniques are insensitive to minor changes in polysulfide structure. ^{13}C–NMR spectroscopy, however, can be a powerful probe and, when combined with synthesis of appropriate model compounds, the great majority of signals in the spectrum can be assigned with confidence.[13] In order to establish the presence of minor amounts of trisulfide species a similar approach was undertaken. The extent of interactions between sulfur and key functional groups in polysulfide liquid polymers was established by examining spectra after the addition of sulfur and an amine catalyst to representative compounds that contained sulfide, disulfide, thiol, and methylenedioxy groups. These exploratory experiments gave a guide to likely chemical shifts and also identified groups which were inert in the presence of sulfur.

$$RS_2R + S \xrightarrow{R_2'NH} RS_3R + RS_4R + RS_5R \cdots \quad (4)$$
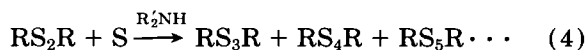
The formation of tri- and tetra-sulfides by reaction of thiols with sulfur[6–10] [eq. (3)] or by reacting disulfides with sulfur in the presence of ammonia,[7,16] or an amine catalyst[17–19] [eq. (4)] is well documented. Monosulfides require extreme forcing conditions before they undergo the addition of sulfur

and it would seem that the process occurs more readily with higher members of the dialkyl sulfide series.[20–25] For example, dimethyl sulfide undergoes only a slight reaction after 2.5 months in a sealed tube at 190°C, whereas diethyl sulfide generates some disulfide and trisulfide after being heated with sulfur at 180°C for 24 h.[20,21] In the present study, it was found that when diethyl sulfide or di(2-ethoxyethyl) sulfide was heated with sulfur for 3 days at 70°C in the absence of amine, traces of disulfide could be identified by GC-MS but the conversion level was < 0.5%. The extent to which this insertion proceeds under more mild conditions is of relevance to polysulfide sealant chemistry, since monosulfide groups are present in a minor but significant quantity in the commercial liquid polymer.[13] The ^{13}C–NMR spectra of the products from treatment of the above sulfides with sulfur and a catalytic quantity of amine for 3 h at either ambient temperature or 70°C, however, indicated that no disulfide species were produced. The susceptibility of the methylenedioxy links, together with that of the chloro end group, were similarly examined using compounds (3) and (4). These groups were also inactive towards sulfur in the presence of traces of triethylamine. It was concluded that the only interactions which would be expected with the liquid polysulfides would involve disulfide links and thiol end groups.

$$ClCH_2CH_2OCH_2OCH_2CH_2Cl$$

(3)

$$ClCH_2CH_2OCH_2OCH_2OCH_2CH_2Cl$$

(4)

$$CH_3CH_2OCH_2CH_2SSCH_2CH_2OCH_2CH_3$$

(5)

In order to establish the indicative chemical shifts of newly formed species, the spectra of mixtures produced from sulfur and triethylamine catalyst with dibutyl disulfide, di(2-ethoxyethyl) disulfide (5), and n-butanethiol, were examined. Amine-catalyzed reactions between alkyl disulfides and sulfur are recognized to generate polysulfide mixtures with trisulfide generally being the most abundant product. The sulfur–sulfur bonds in the polysulfides are, however, labile and thermal treatment results in an equilibrium mixture, while distillation of higher homologues, even under high vacuum, often results in collection of lower members of the series.[11] Reactions of dibutyl disulfide were therefore examined at both ambient and elevated temperatures. The ^{13}C–NMR spectra of the reacted disulfides revealed a series of new lines that were adjacent to the signals from the

starting materials and these were attributed to higher homologues of the polysulfide series (Table I). The most diagnostic atoms are those adjacent to sulfur with the effect of inserted sulfur on chemical shift diminishing greatly after C-2. Peak assignments for BuS_3Bu and BuS_4Bu were confirmed through authentic specimens. From this data, and that for the diethyl series, it was established that relative to the disulfide, the chemical shift of C-1 moves to a slightly higher field in trisulfides (0.3–0.4 ppm) and a somewhat lower field for tetrasulfides (0.3 ppm). It was therefore feasible to show that, at ambient temperature, only 3% conversion of dibutyl disulfide to the trisulfide occurred. Reactions at 80°C proceeded more effectively and with a mole ratio of disulfide to sulfur of 2 : 1, a polysulfide mixture containing 58% S_2, 33% S_3, and 9% S_4 was formed, whereas with an equimolar ratio of reactants the product was comprised of 45% S_2, 12% S_3, 16% S_4, 13% S_5, and 14% S_6. The proton NMR spectra of these mixtures also can be readily interpreted[9,26] with a series of triplets, corresponding to the α-methylene groups of the polysulfide, occurring in a regular downfield progression. A more appropriate model compound for polysulfide liquid polymers is di(2-ethoxyethyl) disulfide (5) and products of the amine-catalyzed reaction of sulfur with this compound at 80°C, were analyzed in a similar fashion. The proton NMR spectrum exhibited the expected triplets with only those of S_5 and S_6 overlapping (Table I). From peak areas, the relative proportions

of the homologues were S_2, 18%; S_3 27%; S_4, 29%; S_5, 16%, and S_6, 10%. Given the expected direction of chemical shifts, supported by the above proportional distribution, the C-1 peaks of the ^{13}C–NMR spectrum (Fig. 1) were assigned as shown in Table I. Additional signals at 39.31 and 39.43 ppm, due to S_5 and S_6 species were not able to be differentiated. Multiple peaks, centered at 68 ppm and 66 ppm, arising from C-2 and C-3 carbons were not as informative and, as some appeared coincident, were not analyzed. In general, however, all new lines for C-2 appeared slightly upfield (0.2–0.4 ppm) whereas those for C-3 moved downfield (0.07–0.15 ppm).

When the disulfides were heated with sulfur at 70°C for 3 days in the absence of amine catalyst, incorporation of sulfur was minimal. No insertion of sulfur could be detected with the disulfide (5) while in the case of dibutyl disulfide, GC/MS indicated that approximately 4 to 5% of the trisulfide was formed. This was confirmed by ^{13}C–NMR analysis of the product mixture.

The amine-catalyzed interactions between thiols and sulfur are particularly interesting in relation to polysulfide sealant chemistry. In the absence of the catalyst, production of disulfides and polysulfides (RS_xR) is not extensive. GC analysis showed that for ethanethiol only 4% conversion occurred after 3 days at 70°C, whereas for n-butanethiol this increased to 8% with species up to S_5 present. The amine-catalyzed reactions, however, proceed rapidly at room temperature with the evolution of hydrogen

Table I   NMR Chemical Shifts[a] for Aliphatic Polysulfides[b]

Polysulfide	x	^{13}C–NMR[c]				^{1}H–NMR
		C-1	C-2	C-3	C-4	CH_2S_x
Bu_2S_x	2	38.86	31.29	21.64	13.67	2.68
	3	38.56	30.89	21.59	13.61	2.87
	4	39.14	31.07	21.66	13.61	2.95
	5	39.58	31.07	21.66	13.61	2.98
$(C_2H_5OCH_2CH_2)_2S_x$	2	38.69	68.76	66.30	15.12	2.88
	3	38.28	68.39	66.37	15.12	3.07
	4	38.98	68.55	66.40	15.12	3.14
	5	(39.31)	(68.32)	(66.43)	15.12	3.17
$(C_2H_5)_2S_2$	2	32.90	14.40			2.71
	3	32.59	14.40			2.88
	4	33.21	14.41			2.95
	5	33.67	14.41			2.98

[a] In ppm relative to tetramethylsilane; spectra obtained in $CDCl_3$.

[b] Chemical shifts shown in parentheses are tentative assignments.

[c] The carbon atoms are numbered from S_x: C-1 is α to the sulfur atoms, C-2 is β, etc. In the case of the ethoxyethyl compounds, C-3 and C-4 represent the ethyl methylene and methyl carbons, respectively.
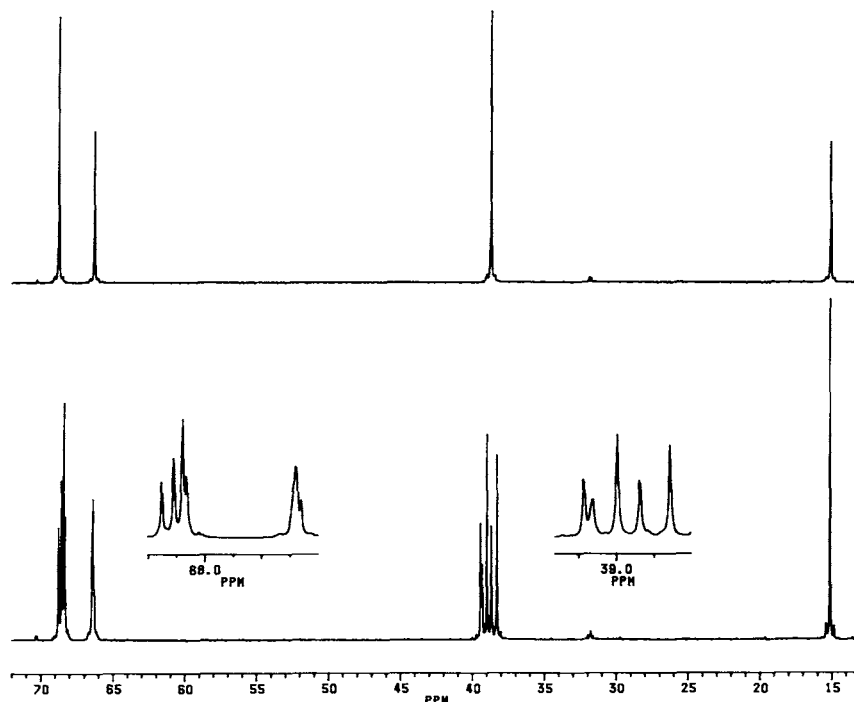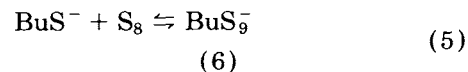
Figure 1 (Top) ^{13}C–NMR spectrum of di(2-ethoxyethyl) disulfide; (bottom) spectrum of the product following treatment with sulfur and di-n-butylamine. Each scale division of the expanded sections of the spectrum corresponds to 0.5 ppm.
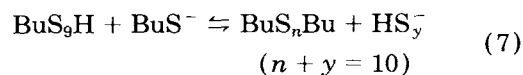
sulfide and all sulfur passing into solution in around a minute. ^{13}C–NMR spectroscopy enabled the product distributions to be examined without subjecting the mixtures to elevated temperatures. The stoichiometric proportions used are useful in the context of mechanistic interpretation (Table II). The use of a two-to-one molar ratio of n-butanethiol to sulfur yielded a product that was comprised of dibutyl disulfide (90%), dibutyl trisulfide (5%), and n-butanethiol (5%). The addition of further sulfur to this mixture, to the level that would have represented a 1.33 to 1 molar ratio relative to the original thiol, did not immediately lead to any observable reaction, but over 90 min all sulfur was gradually taken into the solution. Substantial amounts of S_3 to S_5 polysulfides were present in the resulting mixture and the proportion of disulfide was reduced to 40%.

These observations can be interpreted in terms of the mechanism proposed by Vineyard.[27] The role of the amine is to produce thiolate anion, which interacts with the cyclic S_8 molecule [eq. (5)] to form a linear hydropolysulfide BuS_9^- (6). Further reaction of (6) with thiol will then lead to a mixture of polysulfides (Scheme 1). By use of NMR spectroscopy, Vineyard showed that the polysulfide composition changed with time as the interchange processes

continued. An equilibrium was eventually reached in which lower members of the series predominated at the expense of initially formed S_6 and S_7 species.

$$BuS^- + S_8 \rightleftharpoons BuS_9^- \quad (5)$$
$$(6)$$

$$BuS_9^- + BuSH \rightleftharpoons BuS_9H + BuS^- \quad (6)$$

$$BuS_9H + BuS^- \rightleftharpoons BuS_nBu + HS_y^- \quad (7)$$
$$(n + y = 10)$$

Scheme 1

The critical involvement of thiolate anion [eqs. (5)–(7)] has now been demonstrated by conducting the reaction between n-butanethiol and sulfur with tetrabutylammonium n-butanethiolate replacing the amine. A vigorous reaction ensued at ambient temperature and the product mixture was identical to that from the amine-catalyzed process with the same mole ratio (1.33 : 1) of thiol to sulfur.

Since, in the absence of amine, sulfur and dibutyl disulfide are virtually unreactive at ambient temperature, the continuing reaction following the addition of further sulfur to the 2 : 1 molar ratio mixture must be due to the residual n-butanethiol. This will participate in reactions with sulfur as in Scheme

Table II Composition of Products[a] from Catalyzed Reactions of Sulfur with Butanethiol

Mole Ratio BuSH : S	Bu_2S_x Composition (%)				
	S_2	S_3	S_4	S_5	S_6
2 : 1	94	6			
1.33 : 1[b]	40	38	17	5	
1.33 : 1[c,d]	58	33	9		
1 : 1	34	39	20	7	
2 : 3	19	29	31	15	(6)

[a] Determined using peak intensities of gated-decoupled ^{13}C–NMR spectra; data in parentheses based on tentative assignment.
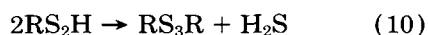
[b] Addition of further sulfur after 2 : 1 mole ratio reaction complete.

[c] Addition of total sulfur in one step.

[d] Replacement of amine by tetrabutylammonium n-butane-thiolate.

1 and the sequence will proceed until all sulfur is consumed, or production of polysulfane (HS_y^-) or hydrogen sulfide (reaction 7) terminates the process.

Further complexity is implicit from a study by Langer and Hyne[28] of the reaction of thiophenol and liquid sulfur. These authors obtained spectroscopic evidence for the formation of a series of hydropolysulfides, ArS_xH, (x = 2 to 7) and polysulfanes, and suggested that lower homologues of these series were formed through disproportionation processes involving the loss of sulfur. Moreover, the possibility of interchange reactions between a hydropolysulfide and the polysulfide mixture is an additional complication that is not considered by Vineyard[27] or Langer and Hyne.[28] In its simplest form this process can be represented by eq. (8) and related interactions have been advanced to rationalize the formation of trisulfides from disulfides.[29,30] Given the presence of hydrodisulfides, eq. (9), which is a modification of eq. (7), is of importance since it is responsible for the consumption of thiol, while processes, such as is shown in eq. (10) offer a further route to tri- and polysulfides.

$$RS_2H + RS_nR \rightarrow RS_{n+1}R + RSH \quad (8)$$

$$RS_2H + RSH \rightarrow RS_2R + H_2S \quad (9)$$

$$2RS_2H \rightarrow RS_3R + H_2S \quad (10)$$

Product analysis of reactions with mole ratios of n-butanethiol to sulfur varying from 2 : 1 to 2 : 3 (Table II), indicates that the method cannot be manipulated to generate a preponderance of any given member of the polysulfide series. While this is consistent with Vineyard's proposal, processes such as

that of eq. (8) which involve hydropolysulfide interchanges, will also influence the outcome. The likelihood that such additional mechanistic pathways may be operating is supported by product compositions of the two reactions using 1.33 : 1 ratios of thiol to sulfur. Here the polysulfide mixtures from the one-step and two-step sulfur additions differ considerably.

Interpretation of the reactions between polysulfide polymers and sulfur followed in a straightforward manner from the results obtained with model compounds. Catalyzed reactions of the filler-free polymers from PR-1422 B-2 and PR-1750 B-2, together with the liquid polymers LP-2 and LP-32, all afforded products that were shown by ^{13}C–NMR spectroscopy to contain between 40 and 50% of tri- and tetrasulfide linkages. This corresponds to a sulfur rank of close to 2.5, which would represent virtual total incorporation of the available sulfur.

Most reactions were carried out at 70–90°C to reduce the viscosity of the polymer and to assist in obtaining a homogeneous mixture. It was shown, however, that significant interaction (35–40%) also occurs at ambient temperature; this is relevant to the situation that occurs when two part sealant formulations are mixed. Chemical shifts of carbon atoms proximate to the introduced groups coincided in position and direction with those for the model compounds, and assignments are collated in Table III. All peaks in the 38 ppm region were clearly resolved, whereas the tetrasulfide signals arising from $OCH_2CH_2S_4$ in the 65 ppm region were often poorly separated from those of the disulfides. This is exemplified in Figure 2 for the case of LP-2. Indications of the presence of pentasulfide species were noted in the spectra of all polymeric products. In each case a new signal was noted 0.83–0.85 ppm downfield from the $OCH_2 \underline{CH_2} S_2$ peak, but any assignment is considered to be tentative. As expected, the signals associated with the diformal and monosulfide groups remained in constant proportion in both starting materials and products. The ^1H–NMR spectra of the sulfur-enriched polysulfide polymers all showed the expected triplets arising from $—CH_2S_x—$ (Table III). The possible presence of pentasulfide species could not be determined reliably by this technique.

In general these reactions resulted in a lowering of the thiol content in the sulfur-enriched polymer. Aging polysulfide polymers at 70°C in air for equivalent periods has a negligible effect on thiol levels and consequently oxidation is not significant. There is, therefore, a presumption that the sulfur insertion reactions involve hydropolysulfide intermediates

Table III   NMR Chemical Shifts[a] for Sulfur-Enriched Polysulfide Polymers

| Polysulfide | ^{13}C-NMR | | | | | | ^{1}H-NMR | | | %[SH][b] | |
| | —OCH$_2$CH$_2$S$_x$— | | | —OCH$_2$CH$_2$S$_x$— | | | —OCH$_2$CH$_2$S$_x$— | | | | |
	S$_2$	S$_3$	S$_4$	S$_2$	S$_3$	S$_4$	S$_2$	S$_3$	S$_4$	Initial	Final
LP-3	38.64	38.30	38.99	66.00	65.68	65.85	2.92	3.10	3.18	6.01	3.60
LP-32	38.33	38.01	38.68	65.64	65.33	65.42	2.92	3.10	3.18	1.44	1.17
LP-2	38.63	38.32	38.98	65.93	65.62	65.80	2.90	3.11	3.18	1.90	1.78
PR-1422[c]	38.49	38.16	38.84	65.82	65.50	65.69	2.91	3.10	3.17	0.93	[d]
PR-1750[c]	38.62	38.28	38.96	65.94	65.62	65.78	2.92	3.10	3.18	1.68	0.87

[a] In ppm relative to tetramethylsilane; spectra obtained in CDCl$_3$.

[b] Initial and final refer to thiol content at start and conclusion of amine-catalyzed reaction with sulfur.

[c] Filler-free liquid polymer from commercial product.

[d] Too low to measure.

which polymerize rapidly by processes similar to those shown in eqs. (9) and (10), a sequence that would ultimately lead to depletion of the original thiol content. The inability to identify hydropolysulfides in reactions of n-butanethiol, with sulfur and triethylamine also supports this conclusion. It would be anticipated that the α-carbon of a hydrodisulfide would possess a chemical shift on the order of 30 ppm. In this context it was of interest to ex-

amine spectra of the polythiopolymercaptan polymers (7), prepared by the method of Bertozzi[15] using sufficient quantities of sulfur to generate a sulfur rank of 3.3. These polymers, which were considered to possess hydrodisulfide terminal groups, were converted into sealants using conventional polysulfide curing agents, but Bertozzi found that exposure to the air also led to elastomer formation and a process akin to reaction (10) was proposed to explain
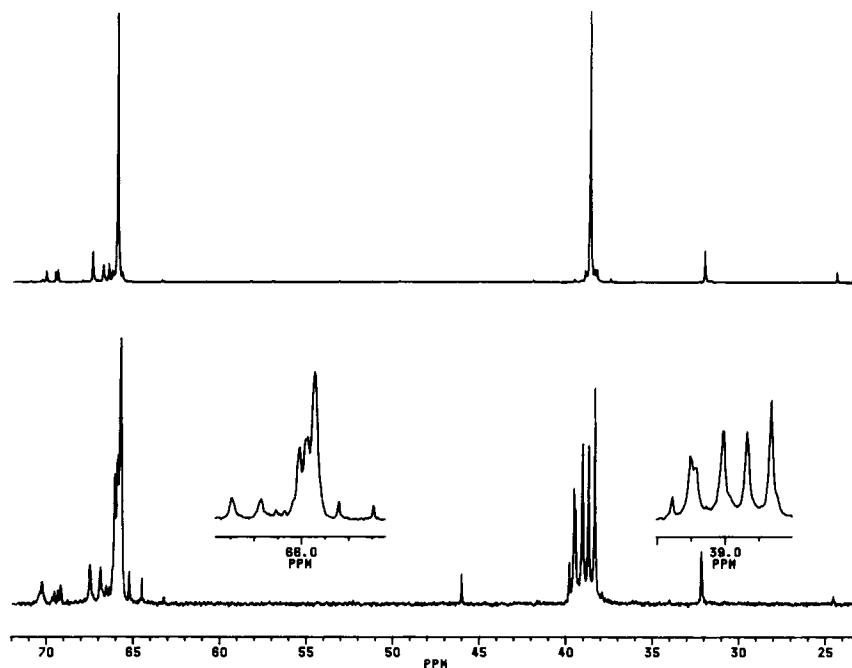

Figure 2   (Top) Relevant portion of the ^{13}C-NMR spectrum of LP-2; (bottom) spectrum of the product formed by treatment of LP-2 with sulfur and triethylamine according to the procedure of Bertozzi.[15] Each scale division of the expanded sections of the spectrum corresponds to 0.5 ppm.

Table IV Weight Loss (%) from Sulfur-Enriched Sealants during Exposure at 125°C

Sealant	Exposure Time (Days)								
	2	3	6	8	13	16	20	22	25
LP-2	3.1	3.8	5.8	6.6	8.6	9.9	10.9	11.6	12.3
LP-2 + 0.5% S	2.4	2.7	4.1	4.5	5.9	6.6	7.8	8.3	8.9
LP-2 + 1% S	2.8	3.0	4.5	5.0	6.4	7.2	8.5	8.5	10.0
PR-1750	3.9	4.5	5.8	6.4	7.8	8.5	9.6	10.1	10.9
PR-1750 + 0.5% S	3.5	4.0	5.2	5.7	6.9	7.7	8.6	9.2	9.9
PR-1750 + 1% S	3.2	3.6	5.2	5.8	7.5	8.5	9.8	10.7	11.7

this effect.[15] It was advocated that the polymer (7) was preferably produced under an inert atmosphere which would suppress the development of cure.

$$HSS(RS_x)_nRSSH$$

$$(7)$$
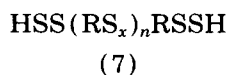
In an endeavor to establish that hydrodisulfide terminals are formed in these reactions, the Bertozzi procedure was applied to the liquid polymers L-2, LP-32, and LP-3, the latter being selected since its high thiol content (6%) offered the best potential to observe changes in the end groups. The reactions were conducted both in air and under nitrogen and were monitored by NMR spectroscopy after the bulk of the sulfur had passed into solution (approx. 1 h). New resonances that formed were associated with the presence of S_3 to S_6 or S_7 species in the polymer chains. Peaks in the ^{13}C–NMR spectra, at +0.83 and +1.11 ppm relative to that from $CH_2\underline{CH_2}S_2$— are probably associated with species such as S_5 and above. Further manipulation of the reaction product, whether by heat or increased reaction time, had es-

sentially no effect on the relative proportions of these groups. It was also established that the reactions followed an identical course regardless of the presence or absence of air. On mechanistic grounds it is difficult to rationalize the role of air in the polymerization of (7) by a process such as reaction (10). The present observation, that hydrogen sulfide is generated even under nitrogen, supports this view. The proton spectra were difficult to interpret beyond the tetrasulfide units, since chemical shift differences of the triplets contract to 0.02 ppm or less and the overlapping of peaks is considerable. The development of higher sulfur rank units at ambient temperature is consistent with our proposal for the formation of hydropolysulfide groups which then participate in a fast interchange process that regenerates thiol [eq. (8)]. As hydropolysulfides were not able to be detected such reactions are probably irreversible, in contrast to the recognized thiol–disulfide exchange reactions.[1,2] The proposed structure (7) for the sulfur-enriched polymers should, therefore, be revised to denote thiol rather than hydrodisulfide end groups.

**Table V Changes in Hardness of Sulfur-Enriched Sealants during Exposure at 125°C**

Sealant	Exposure Time (Days)									
	0	2	3	6	8	13	16	20	22	25
LP-2	35	33	33	34	34	36	35	36	36	36
LP-2 + 0.5% S	42	38	36	38	38	38	39	39	39	39
LP-2 + 1% S	38	37	36	40	42	42	43	46	47	45
PR-1750	59	59	61	65	67	71	73	75	77	78
PR-1750 + 0.5% S	57	57	61	66	68	73	75	76	78	70
PR-1750 + 1% S	57	70	74	78	81	85	86	87	89	89

Table VI   Changes in Modulus (MPa) at 70% Extension of Sulfur-Enriched Sealants during Exposure at 125°C

Sealant	Exposure Time (Days)						
	0	1	2	3	6	14	20
LP-2	0.73	0.84	0.52	0.56	0.64	0.64	0.31
LP-2 + 0.5% S	0.67	0.65	0.56	0.56	0.71	0.83	0.45
LP-2 + 1% S	0.66	0.69	0.52	0.57	0.65	0.98	0.56
PR-1750	1.47	1.69	1.75	2.26	2.56	3.54	3.18
PR-1750 + 0.5% S	1.34	1.78	1.89	2.52	3.63		
PR-1750 + 1% S	1.38	1.66		2.9	3.19		

From the data in Table III it was established that, for the original liquid polysulfide polymers and those heated with sulfur at 70°C for 3 days, tri- and tetrasulfide species were either absent or were present at undetectable levels. The various precursors and partially reacted species which are present in the polysulfides in small amounts are responsible for some small, often overlapping peaks in the 38 ppm region. By use of expanded scales, however, identification of higher sulfide species was considered to be possible down to at least 0.2%. In the case of LP-2, heating with sulfur at 70°C introduced two small peaks at 41.2 and 60.1 ppm which had previously been assigned[13] to the molecular unit (8) and presumably arose through the hydrolysis of methylenedioxy groups by adventitious water. An uncatalyzed reaction between LP-2 and sufficient sulfur to afford a rank of 3.6 if total incorporation occurred, resulted in almost complete consumption of the thiol and no trisulfide was formed. This is explicable if any hydrodisulfide that forms reacts with thiol end groups to produce disulfide links and hydrogen sulfide. The absence of free sulfur in any of the poly-sulfide starting materials was also demonstrated readily, since the addition of amine catalysts did not alter the spectra.

$$HOCH_2CH_2SS—$$

(8)
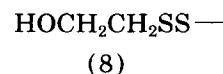
Sealants based on LP-2 and the PR-1750 polymer blend, in which 0.5% and 1% sulfur had been incorporated into the backbone, were prepared in order to determine susceptibility to thermal degradation. On the basis of the above spectroscopic studies, these reactions were assumed to proceed with total incorporation of sulfur. The resulting sealants were maintained at 125°C for 25 days and the thermal resistance was assessed by monitoring changes in hardness, weight loss, modulus, tensile strength, and elongation during the exposure period. Results are shown in Tables IV–VIII, which, for comparative purposes, include data from sealants without added sulfur. A consistent picture is revealed by these data. Weight loss differences in the presence or absence of reacted sulfur are negligible and do not suggest

Table VII   Change in Tensile Strength at Break (MPa) of Sulfur-Enriched Sealants during Exposure at 125°C

Sealant	Exposure Time (Days)						
	0	1	2	3	6	14	20
LP-2	0.95	1.04	0.74	0.85	0.80	0.81	0.84
LP-2 + 0.5% S	0.90	0.83	0.81	0.91	0.95	0.79	0.63
LP-2 + 1% S	0.91	0.87	0.71	0.75	0.95	0.98	0.80
PR-1750	2.93	3.62	3.43	3.40	3.46	3.96	3.46
PR-1750 + 0.5% S	3.55	3.85	3.77	4.01	3.85	3.91	4.33
PR-1750 + 1% S	3.36	4.07		3.90	3.60	3.23	3.57

Table VIII   Changes in Extension at Break (%) of Sulfur-Enriched Sealants during Exposure at 125°C

	Exposure Time (Days)						
Sealant	0	1	2	3	6	14	20
LP-2	127	136	172	224	172	177	172
LP-2 + 0.5% S	156	120	167	183	168	125	100
LP-2 + 1% S	170	156	142	138	138	97	89
PR-1750	186	231	187	141	127	94	70
PR-1750 + 0.5% S	239	250	166	143	93	66	68
PR-1750 + 1% S	262	272	170	139	98	67	47

that sulfur facilitates thermal breakdown. The hardness results indicate that the sulfur-enriched polymers cure more effectively than those formed without added sulfur, while the mechanical property data imply that the introduction of sulfur produces a tougher, stiffer sealant. The elongation measurements are of interest, since they indicate that the cure of the sulfur-enriched sealants takes some days to develop fully, even at elevated temperatures. With the increased network formation, elongation of the sealants is significantly diminished. This would also be consistent with the hardness results, particularly those of the PR-1750 sealants, for which the continuous increase in hardness with time appears to be related more to a slow cure rather than to degradation.

CONCLUSIONS

Reactions of sulfur with model compounds have been examined and mechanistic interpretations of amine-catalyzed processes involving thiols and disulfides have been proposed. The role of hydropolysulfide intermediates has also been considered.

Nuclear magnetic resonance spectroscopy can be used to determine the presence of tri- and tetrasulfide links in polysulfide liquid polymers and ^{13}C chemical shifts for these groups have been assigned. For the commercial liquid polymers studied, S_3 or S_4 links were absent, at least down to the 0.2% level.

No obvious deleterious effects on the elevated temperature performance of polysulfides result from the incorporation of modest levels of tri- and tetrasulfides in the sealant structure. It seems likely that the development of hydropolysulfide terminals drives the degree of cure to higher levels than is achieved with thiol end groups and this is manifested

in increased hardness and modulus and reduced extension at break, relative to those of untreated sealants.

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