Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Lautenschlaeger, F.(1972) 'Alkylene Sulfide Polymerizations', Journal of Macromolecular Science, Part A, 6: 6, 1089 — 1108

To link to this Article: DOI: 10.1080/10601327208056887

URL: http://dx.doi.org/10.1080/10601327208056887

J. MACROMOL. SCI.—CHEM., A6(6), pp. 1089-1108 (1972)

Alkylene Sulfide Polymerizations

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ABSTRACT

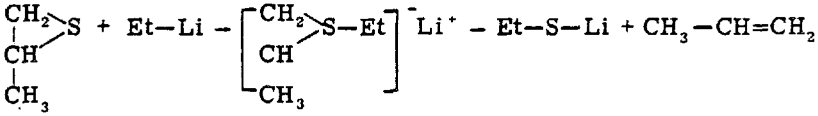
A review of the most recent published and unpublished observations on the polymerization of alkylene sulfides is presented.

This review concentrates on developments which are either unpublished or reported subsequent to the most recent review by Sigwalt [1].

Another author's summary [2] reviews synthetic aspects and polymer evaluation in that author's laboratories. In this review, a wider approach is chosen. Recent developments are separated into sections based on the various modes of initiation of the polymerization of alkylene sulfides.

ANIONIC POLYMERIZATION

Side reactions in anionically initiated polymerizations were investigated in greater detail. The formation of propylene in conjunction with sodium sulfide(s) in sodium naphthalene-initiated polymerizations was further supported by desulfurization using zinc carbonate [2] or tertiary amines [3]. The reaction was now shown to be very rapid in tetrahydrofuran, even at -78°C. Propylene sulfide and ethyllithium in equimolar proportions lead, after acid treatment, to ethyl mercaptan and propylene without evidence for the formation of ethane [4]. A sulfurane intermediate may be suggested for this reaction. The conversion of the sulfur decet to the octet would provide the driving force for this elimination. The absence of

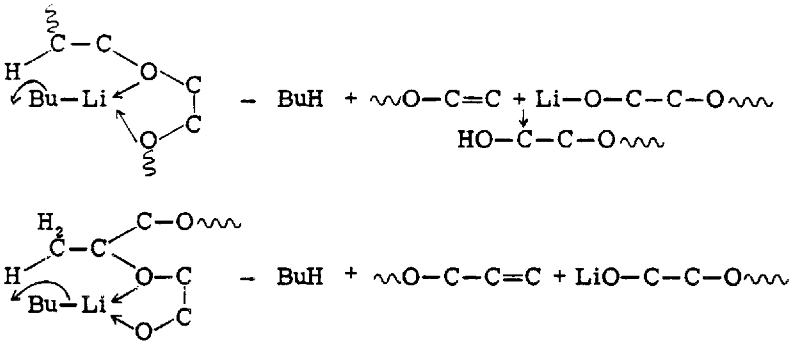


ethylene indicates that the lithium ion does not approach the sulfur atom of the three-membered ring. Lithium ethyl mercaptide would then be the initiating species when excess alkylene sulfide is present.

An additional complicating factor when using organolithium compounds [5] is cleavage of several polyethers as well as poly(propylene sulfide) to give alkoxide or mercaptide end groups, respectively (Scheme I). The β-hydrogen on the main chain, which is also in the α-position to either oxygen or sulfur, is the site of the attack. Activation of the lithium by chelation with the oxygen was assumed. After acidification, bifunctionality of the fragments can be demonstrated by reaction with diisocyanates.

When desulfurization of alkylene sulfides occurs, as during the polymerization of propylene sulfide with zinc thiolates, propylene is eliminated and incorporation of the sulfur as di- or polysulfide links into the polymer chain occurs [6]. Desulfurization of these polymers can be achieved with n-mercaptan/piperidine or by tributylphosphine.

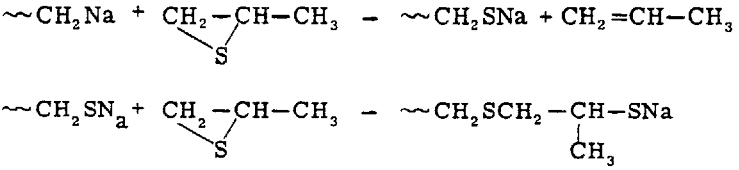
Anionic initiation systems have found synthetic usefulness in the preparation of polydiene-poly(episulfide) block polymers. Block polymerizatinn of isoprene and propylene sulfide was achieved [7] under the following conditions: To the solution in hexane of the block of living polyisoprene ($\overline{M}_n = 175 \times 10^3$) was added a solution of episulfide in tetrahydrofuran at -78°C. After 10 days at room temperature and 20 hr at 50°C, complete polymerization of propylene sulfide was obtained and a polymer of $\overline{M}_n = 350 \times 10^3$ was isolated. This indicates that the reaction of ring opening prevails on the deactivation reactions and that the mercaptide groups—the living ends—are stable in tetrahydrofuran at ambient temperature. Similarly,



	BuLi (meq/g)	hr	°C	Yield (%)	(meq/g)sh	$\overline{M}_n$ Calc	$\overline{M}_n$ Found
$\sim H_2C-CH(CH_3)-S\sim$	3.0	2	30	99	1.7	1180	1316

SCHEME 1.

carbanions of polybutadiene can initiate propylene sulfide at -40° C, but room temperature is required for the anion of poly-2-vinylpyridine. By this procedure, block polymers with well-defined end groups and narrow molecular weight distributions were obtained. Desulfurization and mercaptide formation are again considered to be the basic initiation reactions.



Attempts to produce block polymers containing an amorphous plastic and a rubbery block led to the preparation of poly(α-methylstyrene)–poly(propylene sulfide)–poly(α-methylstyrene). Using ethyllithium as initiator and phosgene to couple the active lithium thiolate end groups [8], block polymers of predictable molecular weight were obtained. The coupling is necessary since the active chain end of poly(propylene sulfide) will not react with α-methylstyrene.

Since the reaction between propylene sulfide and ethyllithium at -78° C in tetrahydrofuran leads exclusively to elimination of propene, the crossover reaction between poly (α-methylstyryl)lithium species and propylene sulfide must be carried out at -78° C and the remaining slow propagation at +25° C. The polymers showed narrow molecular weight distribution, which indicates fast crossover reactions from active poly(α-methylstyrene) to propylene sulfide.

The results confirmed that polymerization proceeds without termination or chain transfer reaction. It is of interest that the use of dilithium initiators (1,1-dilithio-1,1,4,4-tetraphenylbutane) leads to temporary gel formation. This is attributed to association of lithium alkylthiolate with itself or the bivalent sulfur atoms. Addition of tetrahydrothiophene disrupted the gel partially.

Tensile strength values were found to be very much lower than for styrene-butadiene-styrene or styrene-isoprene-styrene block polymers, although the strain at break compares favorably with these polymers.

Potassium ethanedimercaptide was used for the formation of ABA block polymers by reaction first with propylene sulfide and then with ethylene sulfide [9]. Softening temperatures from 70-78 to 117-125° C were obtained for poly(ethylene sulfide) contents of 9 to 29%. Low physical properties were obtained for the center block, presumably as the result of insufficient purity of solvents, initiator, and monomer.

Since metal alkyl initiated polymerization actually proceeds via alkyl mercaptides, arising from the desulfurization of episulfides [10], it is not surprising that similar living polymerization systems were obtained from both initiators. The nature of the mercaptide ion RS^- is of little importance provided the mercaptide ion is soluble [10]. Since high dielectric constants promote ionization, polymerization is slow in heptane, moderate in tetrahydrofuran, and rapid in dimethyl sulfoxide. The rate of propagation is increased in the order $Na < K \cong Ca < Ba$.

The observation that thiolates of unsaturated mercaptans or of dialkylamino-alkylmercaptans dissolve in propylene sulfide has led to kinetic studies which further supported earlier conclusions that mercaptide initiated polymerizations are nonterminating [9a]. An induction period was observed, which can be attributed either to

$X\,[SCHMe\ CH_2N\ (n{-}Bu)_2]_2$

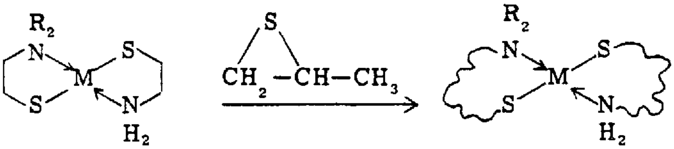
$X\,[SCHMe\ CH_2SCHMe\ CH_2(n{-}Bu)_2]$

$X\,(SCH_2\ CH{=}CH_2)_2$

$X = Zn, Cd$

impurities or to a slow initiation reaction. In monomer and initiator, polymerization by cadmium salts is of first order. Propagation reaction velocity constants were very similar whether cadmium alkylmercaptide or cadmium dialkylamino-alkylmercaptide were used. Zinc mercaptide showed a more marked induction period. The observation that cadmium mercaptides give crystalline polymers and that primary amines retard polymerization was taken as evidence that coordination of monomer to metal occurs, which was independently confirmed with magnesium perchlorate [21]. High molecular weight polymers obtained from cadmium catalysts showed stereoregularity (mp 52°C, x-ray diffraction peaks at $2\theta = 18$ and 20.4°).

Mercaptans were found to be effective chain transfer agents, and by choice of their functionality, the number of mercaptan groups could be increased. Solubility of mercaptides in reaction systems can also be achieved by using mercaptides having β-substituents capable of coordinating to the metal atom [9b]. Such complexes of zinc and primary or tertiary amino mercaptans can be separated. Polymerization of propylene sulfide initiated by these catalysts was suggested to proceed by formation of loops with the end groups remaining attached to the catalyst. The mercaptide bond can be broken by such mercaptans which form insoluble mercaptides.



The polymerization of ethylene sulfide toward high molecular weight is best achieved with zinc diethyl/water [10a] in a two-step procedure. The insoluble crystalline polymer is formed initially at 25°C with a high catalyst-monomer ratio. The resulting polymer, which contains all the catalyst, can then be used as the seed for further polymerization. Compacted seed permits the preparation of polymer of increased bulk density in the second polymerization step. When this polymer was molded, the physical properties shown in Table 1 were obtained.

Due to the insolubility of the polymer in common solvents or to thermal degradation in solutions above 140° C, solution properties could not be obtained. Melt viscosity measurements indicated apparent molecular weights of 600,000 to 900,000 for conversions of 15 or 20%, respectively.

Furukawa has reported an asymetric selection polymerization of diethyl zinc-d-t-borneol and diethyl zinc-L-(-)leucine [11]. Polymers were found to be levorotatory both in benzene and chloroform, and both catalysts select the same enantiomer, (-) propylene sulfide,

TABLE 1. Physical Properties of Poly(ethylene Sulfide) [10a]

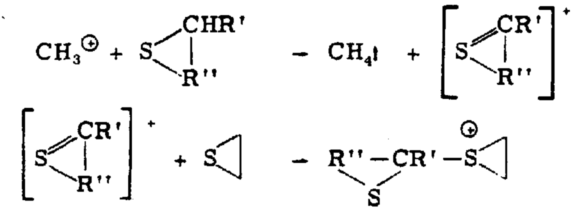
Tensile strength (psi)	10,500
Elongation (%)	10
Modulus of elasticity (psi)	320,000
Heat-distortion temp (264 psi), (°C)	159
Creep (room temp, 5000 psi, 500 hr), (%)	1

during polymerization, in contrast to the observations on the polymerization of propylene oxide.

A catalyst obtained from the reaction of diethyl zinc and R(-)-3,3-dimethyl-1,2-butanediol produces a dextrorotatory polymer [12], leaving unreacted levorotatory monomer [13]. The preferential consumption of R-monomer from a racemic mixture leads to an increasing optical activity with increasing conversion. An optical purity of the residual monomer of 90% was achieved. The optical activity of monomer for high yields of polymerization was higher than the activity for the purest enantiomer obtained synthetically, which suggested some racemization during a synthesis based on optically pure 1,2-propylene glycol. A surprising observation was that the optical activity of the resulting polymer depended on the conversion, with a maximum at ~20%.

CATIONIC POLYMERIZATIONS

Basic studies on the cationic polymerization of several cyclic sulfides [14, 15] suggest sulfonium ions as the propagating species. The sulfonium ion could be formed either by an approach of the catalyst's electron accepting site or, with trimethyloxonium borofluoride, via hydride abstraction by the methyl carbonium ion [14].



Diisobutyl aluminum chloride as initiator for propylene sulfide was used for the study of the reaction order of polymerizations [16]. Fluctuations from 0.47 to 0.93 were obtained over a temperature range from +20 to -15°C (Table 2). The small values for the tentative reaction order were taken to suggest the presence of associated propylene sulfide molecules.

TABLE 2. The Reaction Order of Polymerizations of Propylene Sulfide Initiated by Diisobutyl Aluminum Chloride

Polymerization temp (°C)	Rate of reaction constant ($\text{mole}^{0.5}/\text{liter}^{0.5} \times 10^3$ sec)	Reaction order according to monomer (tentative)
+20	3.20	0.51
+5	-0.32	0.50
0	0.25	0.47
-10	0.015	0.67
-15	-	0.93
-20	-	0.85
+5 in Et_2O		1.00

The speculation that increasing the polarity of the medium would break down the association was confirmed. When benzene (ϵ = 2.28) was replaced by ethyl ether (ϵ = 4.3), a reaction order of unity was observed. However, in conflict with this interpretation is that the order in benzene was highest at lower temperatures. One would anticipate association to be more pronounced at low temperatures.

Although an increase in catalyst concentration (Fig. 1) causes an increase in poly(propylene sulfide) yield, only a maximum yield of 74% was obtained. The expected decrease of $\overline{M}_n$ with increased catalyst concentration was observed. The estimated activation energy of 11.4 kcal/mole compares favorably with 11.8 kcal/mole obtained from polymerization with butyllithium.

The mechanism of borontrifluoride/diethyl ether catalyzed polymerization of propylene sulfide [17] indicated a "living" chain mechanism in ethyl chloride solution (Fig. 2). In the early stages of conversion, the experimental molecular weight corresponds to that calculated from $S = \alpha[M]/[C]$ typical for "living" polymers. The activation energy was found to be 18 ± 2 kcal/mole for early stages of conversion (5-20%).

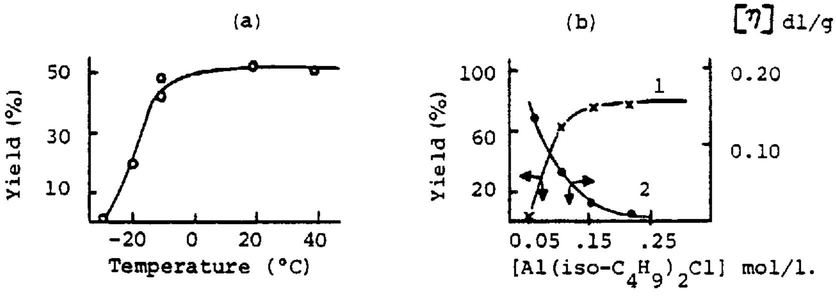


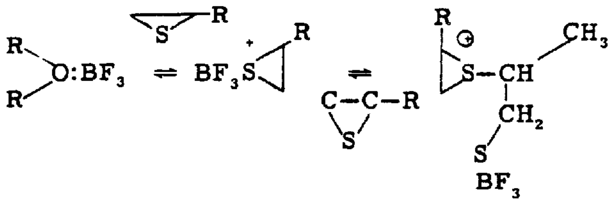
FIG. 1. The dependence of PPS yield on (a) polymerization temperature and (b) catalyst concentration. (a) [Al(iso-C_4H_9)$_2$Cl] concentration of 0.108 mole/liter for the duration of polymerization, 5 hr. (b) Polymerization temperature 20°C. 1: Per cent yield. 2: [η].

In studying the relationship of the initial process rate to monomer and initiator concentration, the rate of reaction is first order (in both components) in the monomer concentration range of 3.5 to 6.4 and 0.0015 to 0.09 moles/l ($BF_3.Et_2O$) (at 20°C) and follows the equation:

$$-d[m]/d_t = K_p[m]\,(BF_3.Et_2O] \qquad K_p = 3.53 \text{ liters/mole min}$$

Solvent polarity exhibits a marked influence on the rate. A decrease from ethyl chloride (ϵ = 6.3) to diethyl ether (ϵ = 4.35) is observed.

A stable sulfonium ion, generated from the catalyst's electron accepting site with the sulfur atom, was postulated as shown.



As in cyclic oxide cationic polymerizations, the reaction proceeds with chain scission transfer which is indicated at various stages of conversion by a change in molecular weight distribution, its bimodal character, and a marked decrease in the average molecular weight of the polymer on completion of the polymerization (Fig. 3).

A direct indication that episulfide polymerization follows a chain

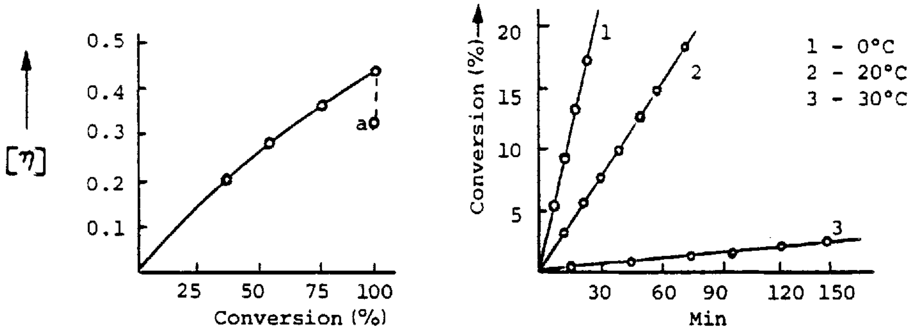


FIG. 2. Left: $[\eta]$ vs. per cent conversion for polypropylene sulfide with $[BF_3.O(Et)_2]$ = 0.003 mole/liter and [M] = 3.5 moles/liter; 20°C; 48 hr to complete polymerization. Right: The effect of temperature on the rate of polymerization of propylene sulfide with $[BF_3.O(Et)_2]$ = 0.003 moles/liter and [M] = 3.4 moles/liter.

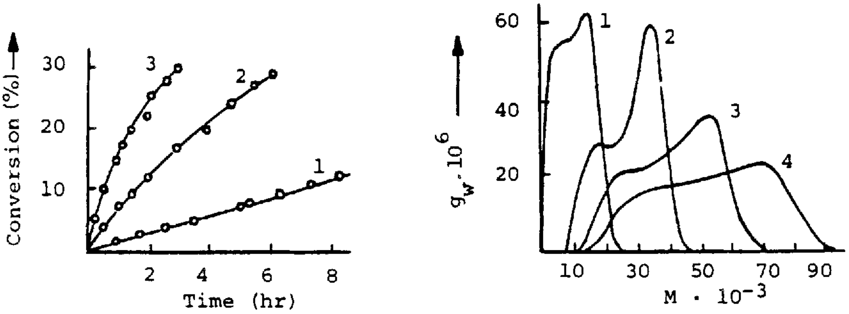


FIG. 3. Left: Effect of solvent polarity on the rate of polymerization. [M] = 3.5 moles/liter; [BF$_3$.O(Et)2] = 0.003%; 20°C; (1) diethyl ether; (2) ethyl chloride; (3) nitroethane. Right: Molecular weight distribution (as viscosity average). [M] = 3.5 moles/liter; $[BF_3.O(Et)_2]$ = 0.003 mole/liter; 20°C; (1) 38% conversion after 4.5 hr; (2) 77% conversion after 16 hr; (3) 100% conversion after 22 hr; (4) 48 hr after complete polymerization.

scission transfer mechanism under the influence of $BF_3.Et_2O$ is the formation of block copolymers from homopolymers of PS and ES for which, however, no details were reported.

Few direct comparisons of polymerization of epoxides and episulfides are available. cis- and trans-2-Butene-episulfide with cationic catalysts such as $ZnEt_2.H_2O$, $i\text{-}Bu_3Al.H_2O$, and BF_3 were shown to give a different stereoregularity [18] than the corresponding epoxides [19]. The cis-sulfide gives crystalline polymer, in contrast to the amorphous disyndiotactic poly(isobutylene oxide). The trans-sulfide gives mainly amorphous polymer, again in contrast to the crystalline, meso-diisotactic poly(isobutylene oxide). Isobutylene sulfide leads to crystalline polymers of widely ranging melting points (125-178°C) with cationic catalysts. The highest melting point (187°C) was obtained with $Et_2Mg—NH_3$. Partially amorphous polymer was obtained with $i\text{-}Bu_3Al.0.5H_2O$.

Mechanical properties of poly(isobutylene sulfide) were reported as in Table 3.

TABLE 3. Mechanical Properties of Poly(isobutylene Sulfide)

	Unoriented[a]
Tensile strength, (psi)	2100
Elongation, %	2
Modulus of elasticity (psi)	270,000
T_g (°C)	-12[b]

[a] Obtained using 8 mmoles $Et_2Mg.0.8\ NH_3$ after 19 hr at 0°C; η_{inh} 1.20; mp 187°C.

[b] By differential thermal analysis.

Poly(propylene sulfide) deuterated in the tertiary position when polymerized with zinc or cadmium carbonate gives rise to a soft rubbery or hard polymer, respectively. In the NMR spectrum [20] the methylene protons show two overlapping AB quartets. The lower field quartet was assigned to the isotactic dyad since it is of higher proportion in the polymer initiated by cadmium carbonate (65:35 vs 52:48).

In a qualitative approach, polymerizations initiated by organic and inorganic salts were studied. The observation that saturated solutions of magnesium perchlorate in propylene oxide or propylene sulfide show strong uv absorptions (at 285 mμ for the former) suggests a coordination mechanism for the initiation by this inorganic salt [21].

The following conclusions can be derived from the initiation by salts other than thiolates [10]:

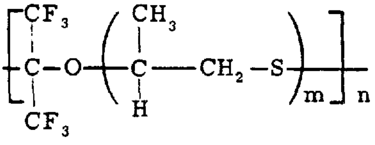
(1) Induction periods are observed even when very basic salts are used.

(2) Potassium-tert-butoxide is an excellent initiator—even in hydrocarbons—presumably because of its solubility.

(3) The use of the sodium ethylene-diamino tetraacetate leads to molecular weights (M_n) from 30 to 130% higher than expected, presumably as the result of end group association.

The efficiency of quarternary ammonium and phosphonium compounds depends on the basicity of the anion and is relatively independent of solvent; e.g. polymerization in media of average dielectric constant is almost as fast as in dimethyl sulfoxide [10]. As expected, increasing the steric requirements decreases the rate of polymerization ($N^+(CH_3)_4 > N^+R_4$); phenyl substitution has a similar effect. A similar rate of initiation by tetraethyl phosphonium and tetrabutyl ammonium ions was observed.

Copolymers of undefined molecular weight were obtained from propylene sulfide and perfluoroacetone [21a]. Using cesium fluoride as initiator and equimolar proportions of monomers, a copolymer of the proportion perfluoroacetone:propylene sulfide 1:4.8 could be obtained, based on elemental analysis. Although the general formula shown was suggested for the product, purification and characterization were not reported.



$$\left[-\overset{CF_3}{\underset{CF_3}{C}}-O-\left(\overset{CH_3}{\underset{H}{C}}-CH_2-S- \right)_m \right]_n$$

INITIATION BY AMINES

Of the various amino compounds, tertiary amines have been shown to be the most effective initiators for the initiation of ethylene sulfide [22, 23, 10], propylene sulfide [10], and vinyl thiirane [3]. The rate of initiation is affected by the dielectric constant of the solvent, is instantaneous in dimethyl sulfoxide, and slow in tetrahydrofuran or monomer [10]. Triphenyl amine or dimethylaniline do not initiate ethylene sulfide polymerization even in dimethyl sulfoxide solution. The speed of initiation of ethylene sulfide is approximately 2000 times slower than its propagation. For propylene sulfide, this factor is ~800,000. In general, it is not necessary that the initiator be more basic than the active polymer, but there is a basic minimum, depending on the solvent, below which no initiation occurs [10].

Of interest is the observation that initiation of the polymerization of propylene sulfide with tributyl phosphine in ethyl bromide leads to a blue-green color at 0-5°. Decolorization occurs at ambient temperature [10]. A similar polar mechanism for the initiation by tertiary amine and tertiary phosphine is assumed. In contrast to tertiary amines, twice the molecular weight (M_n) of the calculated M_n is observed, although only one phosphorous atom is incorporated into the macromolecule. It was assumed that decomposition of the phosphonium salt to phosphine would lead to coupling of two polymer chains.

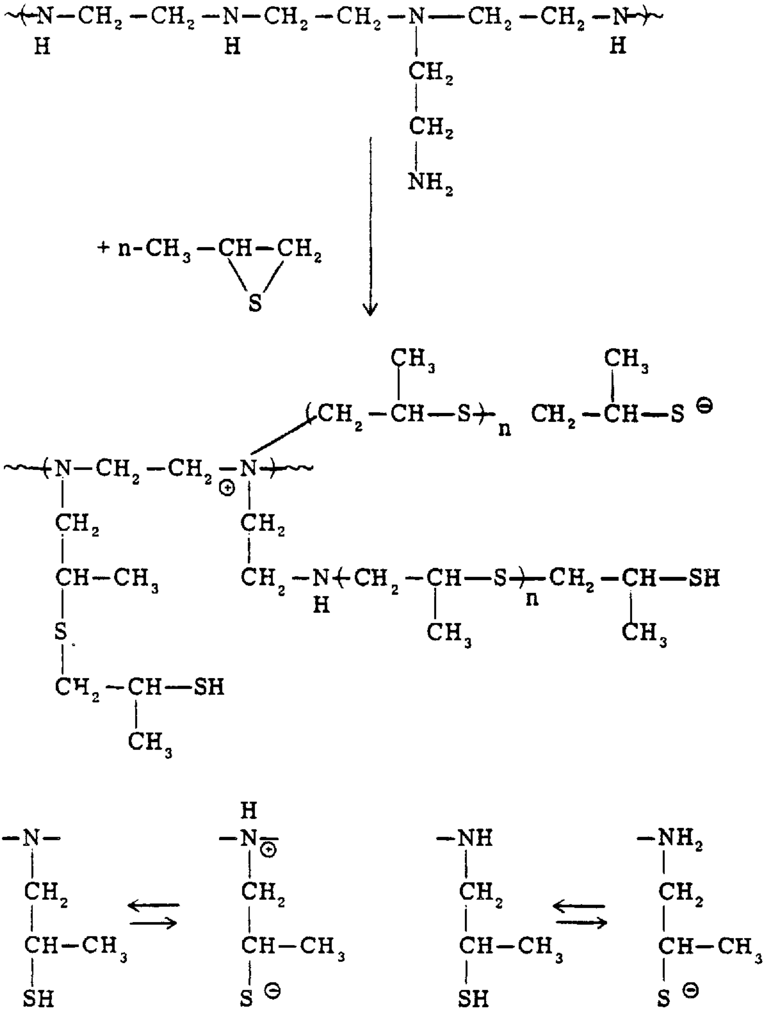
Especially effective is 1,4-diazobicyclo(2.2.2)octane [23], which leads to high conversion of ethylene sulfide and high molecular weights at room temperature as well as to a poly(ethylenesulfide) of a thermal stability improved over other amine-initiated polymers, although not better than a polymer obtained with $ZnEt_2.H_2O$ [24]. In contrast to the polymerization of ethylene oxide, initiation was carried out in the absence of water. There is evidence that the mode of initiation by 1,4-diazobicyclo(2.2.2)octane depends on the presence of water [3], as demonstrated by yields and structure of the polymers of vinylthiirane. Slow propagation compared with the rate of polymerization leads to residues of unreacted amines [10, 23].

Liquid poly(alkylene sulfides) can be obtained when secondary amines are used as initiators. An addition product of ethylene diamine and propylene sulfide (1:4 molar proportion) was found to be of very low molecular weight. On curing with lead dioxide the polymer compared favorably with a Thiokol LP 32 polymer in acid resistance [23a].

In secondary amines, increased N-methylation results in the formation of more active amines [23]. However, poly(ethylenimine) and various polyamides satisfactorily initiate polymerization of propylene sulfide [25].

For the mechanism of reaction with propylene sulfide, the complex structure of poly(ethylenimine) has to be considered [26]. A branched structure with a degree of branching of one branch per 3 to 3.5 nitrogen atoms was suggested. The presence of one primary amino group as end group for each tertiary amino group at the point of branching leads to a polymer with distinctly different reactive sites.

Since primary, secondary, and tertiary amino groups would compete in the initiation of propylene sulfide grafting, the resulting polymer would contain structures (Scheme 2) consisting of both mercapto and mercaptide groups, the latter arising from ring opening



SCHEME 2. Possible structure of propylene sulfide grafted poly(ethylenimine).

by tertiary amino groups and proton transfer from the mercaptan to the tertiary amino groups. Initial attachment of the grafted chain is assumed to occur exclusively via a CH_2- in preference to a CH-group since ring opening reactions of episulfides by secondary amines were shown to involve approach from the least hindered site.

In case of complete grafting, the proportion of the number of 1) terminal—SH-groups vs unreacted NH-groups, and 2) CH_3-groups vs remaining NH-groups is an expression for the number of grafted sites as well as a measure for the average chain length of the branch for each given proportion of poly(ethylenimine) and propylene sulfide. Complete reaction or grafting on all amino groups would lead to a proportion of

$$A = n_{CH_3}/n_{NH} = n_{CH_3}/0 = \infty$$

[n_{CH_3} = number of propylene sulfide units per repeating unit in poly(ethylenimine)], resulting in a multifunctional polymercaptan.

On the other hand, attachment of all propylene sulfide units to only one amino group would give a proportion of

$$A' = n_{CH_3}/n_{NH-1} = n_{CH_3}/n-1 \approx n_x$$

whereby $n_x = 1$ if the degree of polymerization of ethylenimine corresponds to the molar equivalents of propylene sulfide added. In case of a high degree of polymerization, $n_{NH-1} \approx n$. The observed proportion reflects the reactivity ratio of amine-initiated ring opening vs propagation of the growing chain. The upper limit for the number of grafting sites is not only a function of the proportion of early initiation rate and propagation rate, since it must be assumed that increasing steric hindrance of the bulky backbone and decreasing basicity of the remaining unreacted amino-groups as a result of neighboring groups would make further initiations on the backbone increasingly difficult.

Table 4 summarizes the results using poly(ethylenimine) of $\overline{DP}$ = 41 and shows an expected increase of M_n of the resulting polymer with increasing amount of propylene sulfide. In the region of low concentration of propylene sulfide, the deviation of observed $\overline{M}_n$ from calculated values is in the order of 15%, indicating a contribution of nongrafted homopolymer of propylene sulfide. This deviation approaches 50% if an excess of propylene sulfide is used (ratio 4:1). Separation of the grafted polymer from the homopolymer was unsuccessful because of its rapid oxidative cross-linking when exposed to the atmosphere.

Table 4 also shows the increase of the mercaptan functionality with increasing grafting of propylene sulfide. A rapid initial increase of the number of mercaptan groups is observed, reflecting the expected

TABLE 4. The Reaction of Propylene Sulfide with Poly(ethylenimine)

Reaction	Ratio of reactants[a]	$\overline{M}_n$				Mercapto functionality[d]
		Observed	Calc max[b]	M_n calc - M_n obs[c]		
1	0.2	2,100	2,400	300	(12.5)	1.2
2	0.5	2,860	3,300	440	(13)	7.3
3	0.5	2,900	3,300	400	(12)	-
4	0.6 (0.5)	2,900	3,600	700	(19.5)	6.5
5	1.0 (0.95)	4,000	4,800	800	(17)	7.6
6	1.0	3,850	4,800	950	(19)	8.5
7	1.0 (0.95)	4,500	4,800	300	(6)	8.0
8	1.5	5,300	6,400	1,100	(17)	-
9	2.0 (1.4)	7,700	7,900	200	(2)	8.2
10	4.0	6,750	14,000	7,050	(51)	10.6
11	4.0 (2.8)	8,000	14,000	6,000	(43)	-

[a] Expressed in number of molecules of propylene sulfide per repeating unit in the polyamine. In parenthesis, the observed value n_{CH_3}/n_{NH} is shown.

[b] Assuming complete grafting reaction.

[c] Deviation from calculated $\overline{M}_n$ in both absolute values and percentages (in parenthesis).

[d] Number of SH groups per molecule.

higher tendency for initiation (the attachment of branches and thus the formation of new SH-groups) vs propagation at this early stage.

Structure elucidation of the polymers by NMR spectroscopy was only partially successful. A single peak for the NH-proton at 1.57 ppm is observed in poly(ethylenimine). Grafting of propylene sulfide leads to a downfield shift of the NH-signal to between 1.7 and 2.1 ppm in deuterochloroform. A limitation of NMR spectroscopy on these polymers arises from proton transfer between mercapto groups and amino groups, affecting the ratio n_{CH_3}/n_{NH}, which would provide a measure of grafting efficiency. This proton transfer is significant; the ratio of n_{CH_3}/n_{NH} for each polymer is smaller than calculated from the experimental proportions of propylene sulfide and polyamine, which is the result of an increase of the NH-signal. This can further be demonstrated by observing the spectrum of a solution containing poly(ethylenimine) and ethyl mercaptan corresponding to theoretical value of $n_{CH_3}/n_{NH} = 1$. A value of 0.25 was observed for that solution, demonstrating the efficiency of amino-mercaptan interaction.

The NMR spectrum of a poly(ethylenimine) treated with one molecule of propylene oxide per amino group was recorded for comparison. The spectrum in pyridine shows a n_{CH_3}/n_{CH} value of 1. Thus homopolymer or grafted branches of more than one repeating unit of propylene oxide, if present, remain undetectable. The observation of only one proton in the α-position to oxygen suggests exclusive opening of the epoxide ring by the amino group at the least hindered site, in agreement with earlier observed base-catalyzed ring openings of epoxides.

Propylene sulfide was found to react readily with amides [24]. The commercially available Versamid 140, a liquid polyamide of approximate $\overline{M}_n$ 750, containing, on the average, five amino groups per molecule, reacts with propylene sulfide at a slightly elevated temperature (~ 60°C). The results are summarized in Table 5. A linear increase of $\overline{M}_n$ of the resulting product with increasing amount of added monomer up to a proportion of Versamid/propylene sulfide of 1:10, or up to a molecular weight of 11×10^3 was observed. Higher proportions were not investigated. A linear increase in the mercaptan functionality is observed which suggests continuous initiation of grafting.

TABLE 5. The Reaction of Propylene Sulfide with Versamid 140

Example	Ratio of reactants[a]	Mol wt, $\overline{M}_n$	Mercapto functionality[b]
1	0.3	950	0.5
2	1	1,900	1.2
3	4	4,800	2.0
4	10	11,000	3.4

[a] Expressed in weight of propylene sulfide per weight of Versamid.
[b] Number of SH groups per molecule.

Similarly, rapid reaction of propylene sulfide with nylon-11 was observed at the reflux temperature of the sulfide [25]. The reaction is accompanied by extensive swelling of the polyamide. An average grafting of < 1 molecule of propylene sulfide per amide group of the polymer is achieved, corresponding to a final poly(propylene sulfide) content of 44%, which represents the maximum value achievable under the reaction conditions. Due to the insolubility of the product, no further structure evaluation was carried out.

Differential thermal analysis (DTA) indicates that in all samples an endotherm near 180°C can be observed which is indicative for residual nylon-11 segments. At a heating rate of 10°C/min an exotherm is evident near 305°C, which is attributed to the rapid decomposition of the poly(propylene sulfide) segments. This decomposition is quantitative and provides a measure for the poly(alkylene sulfide) content.

POLYMERIZATION OF VINYLTHIIRANE

Polymerization of episulfides containing additional unsaturation may lead to isomeric structures resulting from the participation of both olefinic and episulfide group [3].

A more carefully studied example was vinyl thiirane (butadiene episulfide) in which the episulfide group is in "conjugation" with the double bond. Varying ratios of 1,3- and 1,5-repeating units in the polymer were obtained.

The results can be summarized as follows:

(1) Both cationic and anionic catalysts produce 1,3-polymers.

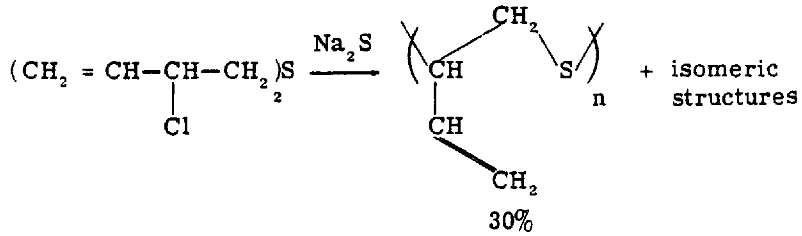
(2) At higher temperature, increasing proportions of 1,5-polymer are formed.

(3) A linear decrease of 1,3-polymer with temperature is observed.

(4) In $BF_3 \cdot Et_2O$-catalyzed polymerization, the reaction temperature has a more pronounced effect than the polarity of the medium.

(5) Triethylenediamine in benzene is not very efficient but 1,5-polymer is almost exclusively formed. On shorter reaction time at lower temperature, a higher amount of 1,3-structure is detected, the proportion of which increases somewhat when equimolar amounts of catalyst and water are present.

Azobisisobutyronitrile is the only catalyst which leads to polymer in which cis-unsaturation was detected in a relatively high proportion of 1,5-polymer. By spectroscopic analysis, the structure of this polymer is identical with the polymer obtained from sulfur dichloride and butadiene-1,3, after treatment with Na_2S/EtOH. Cis-, trans-, as well as vinyl-unsaturation in a proportion corresponding to that of AIBN polymer of butadiene episulfide was observed. This surprising result is not easily rationalized. However, a common feature in both reactions is that the primary C—S bond is not attacked, giving the allylic radical or allylic carbonium ion the opportunity to undergo allylic rearrangement with formation of both trans- and cis-double bonds.



In addition to vinylthiirane, the monoepisulfides of 1,5-cyclooctadiene and bicyclo(2.2.1)heptadiene-2,5 (endo-isomer) were investigated. The exo-isomer of the latter has now been synthesized by the reaction of arylthiosulfenyl chlorides with bicyclo(2.2.1)heptadiene [27]. Its polymerization studies could provide an interesting comparison with the endo-isomer.

A structural change occurs on the isolated crude polymers on subsequent heating with $BF_3.Et_2O$. A reduction in 1,3-structure in favor of isomeric units is evident.

In the case of poly(vinylthiirane) this can be verified if $BF_3.Et_2O$ is added to a 100% 1,3-polymer prepared using $ZnEt_2.H_2O$ as initiator. The rearrangement is drastic in the case of the polymer obtained from cyclooctadiene episulfide. After heating, major spectroscopic changes in the polymer are observed, consisting of a virtual disappearance of ir bands arising from olefinic unsaturation, supported by the detection of only 10% of unsaturation in the NMR spectrum.

The postulated rearrangement of these polymers was considered in analogy to 1,2-addition products of butadiene-1,3 where isomerization to 1,4-structures is known to proceed at elevated temperature and where 1,4-structures are known to make an increased contribution at higher temperature, reflecting the fact that 1,4-products are thermodynamically more stable.

DEGRADATION OF POLY(ALKYLENE SULFIDES)

The thermal degradation and partial stabilization of poly(ethylene sulfide) was thoroughly studied [24]. For details, the study of the original article is suggested. Severe degradation above 220° C can be reduced by small concentrations of 1,2-polyamines. The best amine found was bis[p-(2,5-diazapentyl)phenyl] oxide in combination with zinc hydroxychloride or colloidal zinc oxide. Decomposition leads to ethylene, hydrogen sulfide, acetaldehyde, and ethanethiol. ΔE^* values of 58 ± 2 kcal/mole correspond to the energy requirement expected for the homolytic cleavage of a carbon—sulfur bond. An effect of molecular weight, end groups, or inorganic fragments on the rate of gas evolution was not observed. There is evidence that, depending on the initiator, chain scission as observed by melt viscosity can occur without gas evolution. This decomposition was not further investigated.

For the mechanism of the degradation, based on the rate of gas evolution, the decomposition of model compounds and the activation energy for evolution of gas, a random homolytic scission is suggested, leading to ethylene; ethanethiol was assumed to arise from the addition of hydrogen sulfide to ethylene.

For zinc mercaptide initiated polymers, model compounds of the type $Bu{-}S{-}CH_2CH_2{-}S{-}Zn{-}S{-}CH_2CH_2{-}S{-}Bu$ evolved ethylene and hydrogen sulfide at 220°C and above [28]. The cleavage of the mercaptide bond at this temperature is not unanticipated.

Oxidative degradation assumed to result from hydrogen abstraction or thermal scission of the C—S bond prior to attack by oxygen can be retarded with some success by using dithiocarbonate salts and selenocyanates [29]. Oxidation products are acetaldehyde, carbon dioxide, carbon monoxide, ethylene, and carbonyl sulfide.

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Accepted by editor October 7, 1971
Received for publication October 28, 1971