Aminothiol Polyalkylene Sulfide Oligomers

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Synopsis

The carbonates and oxides of zinc and cadmium polymerize propylene sulfide to elastomeric materials, but with the addition of ammonia low molecular weight polymers are produced. The effect of the ammonia is to react with some of the propylene sulfide to give aminopropanethiol, which will itself polymerize monomer by a stepwise reaction or, after reaction with the metal carbonate, form a metal bis(aminopropanethiolate) which is an active initiator. Chemical and spectroscopic examination of these polymers shows them to be essentially bifunctional, with one NH_2 and one SH terminal group. There is, however, evidence to suggest that further reaction of monomer occurs with the terminal amine groupings to give polyfunctional compounds. From the relative proportions of ammonia, zinc carbonate, and monomer, the rate of polymerization, molecular weight, and degree of endgroup coordination with catalyst residue can be controlled as desired. Due to the highly reactive endgroups, the polymers are readily crosslinked with epoxy resins, aziridinyl compounds, and hexamethoxymethylene melamine to give useful products exhibiting high solvent resistance.

INTRODUCTION

In a previous publication[1] it was shown that propylene sulfide could be polymerized to high molecular weight using zinc diethyl and water as catalyst. Copolymers of propylene sulfide with allyloxymethyl thiirane produced unsaturated elastomers which could be vulcanized in the usual manner with sulfur plus an accelerator to yield solvent-resistant elastomers comparable to the well-known Thiokol rubbers.[2] The introduction of ethylene sulfide into the polymer further increased the solvent resistance. In this study, an alternative method of vulcanization is described, in which low molecular weight oligomers of propylene sulfide with terminally reactive substituents are chain extended and crosslinked using epoxy resins, aziridinyl compounds, or hexamethoxymethylene melamine.

The low molecular weight polymers used in this investigation were prepared in aqueous ammonia using zinc or cadmium salts, especially technical-grade zinc carbonate. Polymerizations were usually rapid and reached complete conversion after several hours at room temperature with moderate agitation. An unusual feature of this polymerization system is the coordination of the polymer endgroups with the catalyst

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residue so that the resulting polymer, as recovered, is not liquid as might be expected from the low molecular weight, but has the appearance of a tough, resilient rubber. This gum behaves like a crosslinked gel and quickly crumbles to a powder on a cold mill. On a hot mill, however, the weak coordination is overcome and the crude polymer becomes very soft and somewhat paste-like. On recooling, it reverts once again to its original nonprocessible form.

Although the catalyst residues can be extracted with strong acids, thiols, or cyanide solutions, it is found beneficial to leave them in, since they apparently do no harm and possibly contribute to the physical properties after vulcanization. Also, in the solid-complexed form, the material is much easier to handle, exhibits a less objectionable odor, and appears to remain unchanged for long periods in storage. When treated with special plasticizers, good processibility is achieved and the polymer can be reinforced with carbon black in the usual manner. The cured physical properties are comparable to those obtained with the high molecular weight unsaturated polymers, with a slight loss of elongation but moderately improved compression-set values at 70°C. However, the polymers are still subject to rapid stress decay at temperatures above 100°C. Similar swelling behavior was obtained and appears to be independent of the method of curing.
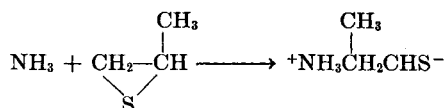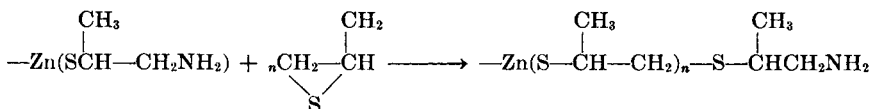
EXPERIMENTAL

Polymerization

The mechanism of aqueous polymerization of propylene sulfide with zinc or cadmium salts has been described in recent publications. From a detailed examination of the kinetics of polymerization, it is assumed that the initial step is the reaction of ammonia with propylene sulfide to form 2-aminopropanethiol. In the presence of zinc carbonate, the thiolate is formed and thereby becomes the principal initiator species. Initiation by ammonia, hydroxyl ions, or zinc carbonate itself is not ruled out, but is believed to constitute a minor part of the reaction. Evidence based on the analysis of the liquid, noncoordinated oligomers prepared by the polymerization of propylene sulfide in the presence of high ammonia to zinc carbonate charge ratios indicates that the thiol content is generally greater than the one per polymer chain that would be expected. Kjeldahl determination of the nitrogen content and molecular weight measurements in carbon tetrachloride solvent at 37°C using a vapor pressure osmometer (Mechrolab Model 201A) confirmed the presence of approximately one nitrogen atom per polymer molecule.[5] From infrared analysis of the polymers it was concluded that some of the primary endgroups gave rise to further substitution and resultant secondary or even tertiary amine groups. Substitution was apparently greater in zinc-initiated systems since the NH absorbances at 2.96 μ and 6.3 μ were generally lower than when ammonia alone or cadmium-containing initiators were used; the ratio of 2.96 μ to

3.92 μ (thiol absorption) peaks was usually in the region of 2 for cadmium initiators and below 0.5 for zinc polymers.[6] Confirmation of thiol concentration was also obtained using an argentimetric procedure[7] and iodine monochloride titration. This multiple substitution would account for the greater number of thiol endgroups and is consistent with the following general mechanism:
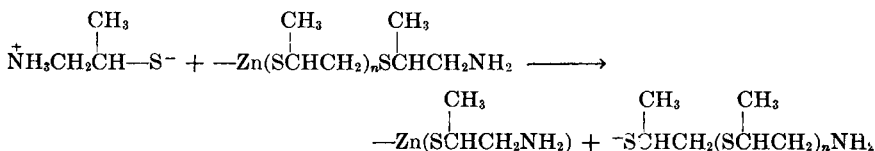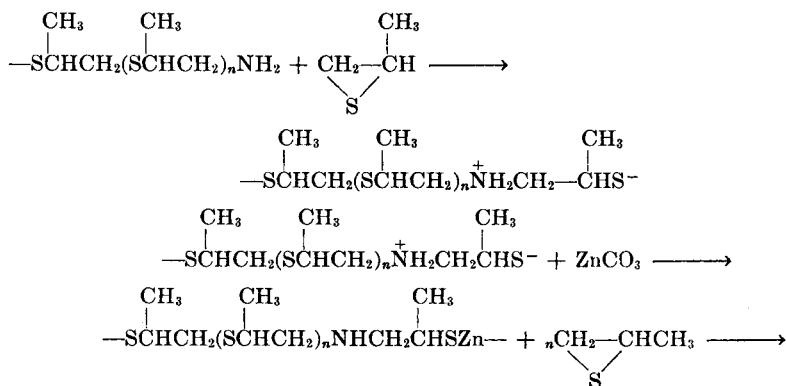
I. Initiation

$$NH_3 + CH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH} \xrightarrow{} {}^+NH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HS^-$$

$$\underset{S}{\diagdown\diagup}$$

$$\overset{\overset{\displaystyle CH_3}{|}}{}^+NH_3CH_2\text{—}S^- + ZnCO_3 \xrightarrow{} Zn(S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2)_2 + H_2O + CO_2$$

II. Propagation

$$\text{—}Zn(S\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}CH_2NH_2) + {}_nCH_2\text{—}\overset{\overset{\displaystyle CH_2}{|}}{CH} \xrightarrow{} \text{—}Zn(S\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}CH_2)_n\text{—}S\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2NH_2$$

$$\underset{S}{\diagdown\diagup}$$

III. Transfer

$$\overset{+}{N}H_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}S^- + \text{—}Zn(S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2)_n S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2NH_2 \xrightarrow{}$$

$$\text{—}Zn(S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2NH_2) + {}^-S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2(S\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2)_nNH_4$$

IV. Substitution or Branching

$$\text{—}\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2(\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2)_nNH_2 + CH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{CH} \xrightarrow{}$$

$$\underset{S}{\diagdown\diagup}$$

$$\text{—}\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2(\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2)_n\overset{+}{N}H_2CH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}HS^-$$

$$\text{—}\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2(\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2)_n\overset{+}{N}H_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HS^- + ZnCO_3 \xrightarrow{}$$

$$\text{—}\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2(\overset{\overset{\displaystyle CH_3}{|}}{S}HCH_2)_nNHCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HSZn\text{—} + {}_nCH_2\text{—}CHCH_3 \xrightarrow{}$$

$$\underset{S}{\diagdown\diagup}$$

Further propagation as in step II and succeeding steps

The molecular weight is dependent upon the ammonia concentration, decreasing as the concentration of ammonia increases. Zinc salts will weakly coordinate with thioethers and it is likely that coordination with the monomer takes place before insertion into the growing polymer chain occurs. In the case of cadmium, coordination is much stronger and leads to a more regular placement of the methyl groups along the chain to form

a polymer showing some tacticity.[1] The dried polymer, which is coordinated with the residual zinc catalyst, exhibits a long shelf life at room temperature, illustrating the protective influence of the coordination against the effect of air oxidation.

Zinc carbonate and zinc oxide are preferred as catalysts, with ammonia as cocatalyst or chain-transfer agent. Other amines were investigated and apparently all undergo similar reactions, becoming incorporated into the polymer chain end. The following amines were successfully employed[8]: hydrazine, ethylenediamine, ethyleneimine, 2-aminoethanol, methylamine, 1,6-hexanediamine, 2-propylamine, glycine, ethylenetriamine, 3-methoxypropylamine, 3,3-amino-bis(propylamine).

However, all the polymers reported in this study were prepared using ammonia as the chain-transfer modifier, according to the polymerization recipe shown in Table I. The polymer was recovered as a coarse suspension of solid particles, easily filtered and dried in air. The dried crumb formed a compact, tough elastomer which could not be processed except at very high temperatures, approximately 141°C (40 psi steam).

TABLE I
Polymerization Recipe for Propylene Sulfide

Propylene sulfide	100 g
Water (distilled)	200 g
Zinc carbonate	4 g
Ammonia (29 wt-% aqueous)	4 g
Polymerization temperature	ambient
Polymerization time	16 hr
Conversion, %	95+

The polymer had a mildly disagreeable odor and was white and opaque.

Compounding and Vulcanization

Vulcanization of the aminothiol oligomers is achieved through chain extension and crosslinking via the reactive endgroups. The oxides and peroxides of metals commonly employed in the vulcanization of dithiol polymers[2] were found to be effective curing agents, particularly the oxides of zinc, lead, arsenic, magnesium, manganese, cadmium, iron, and antimony. Some inorganic oxidizing agents such as zinc and lead chromate were examined and also organic oxidizing agents such as quinone and p-quinone dioxime. Zinc peroxide is typical for this class of compounds and the results are shown in Table II. High-abrasion furnace (HAF) black was used as the reinforcing filler, 50 parts usually required for optimum properties. Since the raw polymer does not process at low temperatures, compounding must be done at elevated temperatures on a rubber mill. These cures were subject to considerable reversion, especially at the higher levels of curing agent. Since the polymers are readily degraded by oxygen at elevated temperatures, this is not surprising.

TABLE II
Typical Zinc Peroxide Cures[a]

Polymer, parts	100	100	100	100	100	100	100	100
HAF Black, parts	50	50	50	50	50	50	50	50
Zinc peroxide, parts	—	10	10	20	30	30	30	30
Cure time, min	10	15	90	10	10	20	45	60
100% Modulus, psi	100	350	360	400	550	420	80	60
Tensile strength, psi	300	950	1000	1100	1250	910	180	110
Elongation, %	280	270	260	330	255	230	370	370
Hardness, Shore A	44–34	66–62	66–63	67–63	69–63	67–58	50–23	30–12
% Set at break	High	15	10	20	10	10	60	60
Compression set, % (after 22 hr at 70°C)	—	93	—	90	85	70	—	—

[a] Cure temperature 307°F.

Due to the highly reactive endgroups, a number of other curing agents were successfully employed, including epoxy resins, tris-methylaziridinyl phosphine oxide (MAPO), and hexamethoxymethylene melamine (Cymel 300). Typical recipes and vulcanizate properties are shown in Table III for these three types. Processability could be obtained at lower temperatures through the addition of special plasticizing agents. The most effective plasticizing agents include high molecular weight thiols and 8-hydroxyquinoline. The addition of a few parts of the plasticizing agent (1–5 parts) was usually sufficient to reduce the polymer to a plastic state so that it could be processed in a normal fashion without impairing the
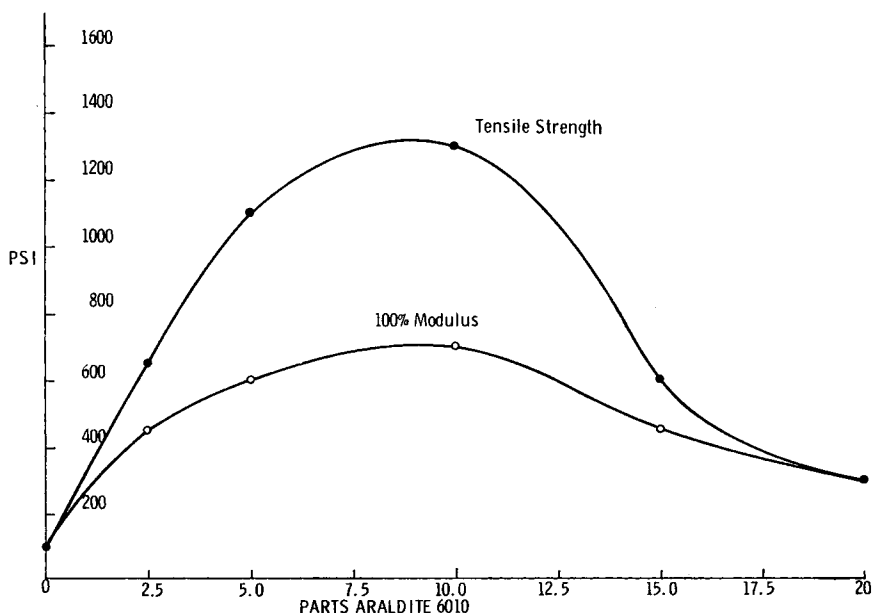

Fig. 1. Effect of Araldite 6010 concentration on cured tensile and modulus.

TABLE III
Comparison of Typical Curing Systems[a]

Compound Recipe, parts			
Polymer	100	100	100
PMP	1.5	1.5	1.5
Stearic acid	1	1	1
HAF Black	50	50	50
MAPO	3	—	—
Araldite 6010	—	5	—
Cymel 300	—	—	2
p-Toluenesulfonic acid	—	—	1
Unaged Properties			
100% Modulus, psi	835	460	770
300% Modulus, psi	—	1345	—
Tensile strength, psi	1870	1575	1420
Elongation, %	205	405	180
Hardness, Shore A	76–70	68–62	76–71
% Set at break	10	25	10
Angle tear, pi	215	230	155
Compression set, %			
22 hr at 70°C	17	52	31.5
70 hr at 100°C	94	100	100
Rebound (Tripsometer), %	54	—	—
Aged 70 hr at 100°C			
100% Modulus, psi	415	280	480
300% Modulus, psi	—	755	—
Tensile strength, psi	1095	985	920
Elongation, %	295	460	200
Hardness, Shore A	72–64	66–55	71–63
% Set at break	20	50	10
Compression set, %			
22 hr at 70°C	13	39	19.5
70 hr at 100°C	90	100	97.5
Unaged—Tested at 100°C			
100% Modulus, psi	685	300	720
Tensile strength, psi	930	1020	720
Elongation, %	120	300	100
Angle tear, pi	130	155	95

[a] Cures 20 min. at 150°C. PMP, a sulfur plasticizer of unknown structure from Carlisle Chemical Co.; MAPO, tris-(1)-2-methylaziridinyl phosphine oxide from Interchemical Corp.; Araldite 6010, a bisphenol A-type diepoxide (mol wt 370–392) from Ciba; Cymel 300, hexamethoxymethylene melamine from American Cyanamid Co.

subsequent cure. These plasticizing agents apparently reduce the polymer–catalyst coordination through preferential competition for the coordinating sites. 8-Hydroxyquinoline is well known to be a strong complexing agent for zinc ions.

As would be expected, the level of curing agent is very specific for a given molecular weight, since the stoichiometry between the number of endgroups and the curing agent must be approximately equivalent. Either too much or too little of the epoxy resin will result in an undercure, as is

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TABLE IV
Comparison of Swelling Resistance[a]

	A	B	B	C	Thiokol ST	Neoprene WRT	Krynac 801
Polymer Composition							
Propylene sulfide, mole-%	90	51	100	100			
Ethylene sulfide, mole-%	—	46	—	—			
Allyl oxymethyl thiirane, mole-%	10	3	—	—			
Cure system	sulfur	sulfur	ZnO_2	Araldite X33/1189	Dibenzo–GMF	sulfur	sulfur
Fluid Resistance, % Volume Swell							
14 days at 70°C							
Water	11	8	3	2	24	10	4
Petrol	76	15	36	42	16	72	18
Mineral oil	8	1	10	23	−5	36	−3
Ester Oil DTD 2487	35	1	44	39	−6	76	0.3
Girling brake fluid	10	5	8	32	12	13	49
E thylene glycol	−6	2	−1	1	2	4	1
Skydrol 500	++	50	310	191	107	179	188
Toluene	++	156	++	152	174	179	96
14 days at 21°C							
Carbon tetrachloride	149	71	—	++	36	138	38
Acetone	35	18	37	45	34	33	—

[a] Reinforcing agent 50 parts FEF carbon black. Araldite X33/1189, a solid tetrafunctional epoxy from Ciba; ++, too high to measure.

evident from Figure 1. The maximum modulus and tensile strength for this particular epoxy resin (Araldite 6010) is reached when 8.5 parts have been added per 100 parts of the polymer. The plasticizer would also be expected to consume some of the epoxy resin. The higher the molecular weight of the polymer, the less curing agent is required to reach the optimum cure.

DISCUSSION OF RESULTS

Of the several curing systems examined, polymers cured with tris-aziridinyl phosphine oxide (MAPO) gave the lowest compression set values at 70°C (Table III). However, all cures failed to give acceptable compression set values at 100°C, including the unsaturated cures reported in the earlier publication.[1] It was concluded that at temperatures above 70°C, some of the crosslinks must become liable, as would be the case if disulfide or polysulfide linkages were present. The exceptionally good compatibility of these polymers with epoxy resins has been extended to their use in coating formulations, giving unusually hard, tough, and chemically resistant enamels with excellent adhesion to metals. This work will be reported separately.

The solvent resistance of the cured oligomers is comparable to that of the high molecular weight elastomers as seen from some typical values tabulated in Table IV. In general, the polyalkylene sulfide rubbers are more resistant to alcohols and water than Thiokol St but less resistant to esters, toluene, and carbon tetrachloride. They generally approach the solvent resistance of low acrylonitrile NBR elastomer.

Resistance of the white compounds to ultraviolet light exposure and weathering in the weatherometer appears to be excellent and is comparable to that obtained for the unsaturated high molecular weight polymers and neoprene WRT. No additional protection appears to be given by the addition of a nonstaining antioxidant such as Santowhite Crystals, 4,4'-thiobis(6-tert-butylcresol). However, the lower initial strength of these polyalkylene sulfides compared to Neoprene WRT may be a possible disadvantage. They are also somewhat inferior in resistance to ozone cracking compared to Neoprene WRT but better than Krynac 801.

Other general observations concerning these polymers might be summarized as follows. Processability in the presence of a suitable processing aid is usually outstanding and compares well with other elastomers, handling like Neoprene WRT and Krynac 801. However, the compounded polyalkylene sulfide rubber has a relatively short shelf life, under 20 hr in many cases, making it necessary to use the material shortly after compounding. Although the original processing characteristics can be restored by further addition of plasticizer, the cured properties are inferior. In most properties, these polymers are similar to Thiokol ST, although the low-temperature torsional stiffening (temperature at which the rigidity modulus equals 1000 kg/cm² per radian) is 20°C higher, viz., −48.5°C for

Thiokol ST and $-31.5°C$ for a typical, cured polyalkylene sulfide. The similarities include tensile strength, tear resistance, permeability, heat aging, rate of cure, and solvent resistance.

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