Some Thiol-Terminated Polyethers*

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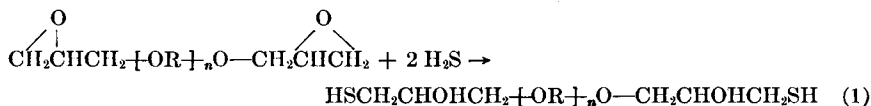Minneapolis, Minnesota 55413*

Synopsis

Thiol-terminated polyethers were prepared by two different routes, the starting materials being commercially available polyether polyols and epoxy resins. The products were pale colored liquids and were found to be very stable on storage at room temperature. Thiol-terminated polyethers of functionality from 2 to 4 were prepared. They are interesting building blocks for polymers through oxidation of the terminal SH groups or through coreaction with epoxy resins.
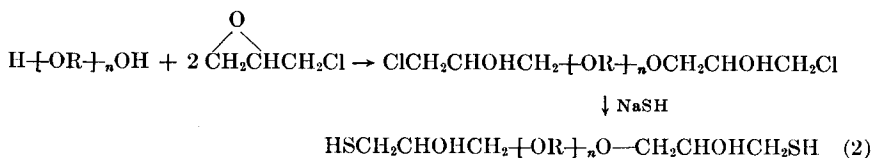
INTRODUCTION

Thiol-terminated polysulfides of varying molecular weights are well known and have been of interest for several years for polymers.[1,2] They have been prepared by reduction of polysulfides,[1,3] addition of hydrogen sulfide to divinylacetylene,[4] and interaction of dichlorides with sodium polysulfide and sodium hydrosulfide.[5] The thiol-terminated polysulfides are frequently cured to elastomers through the use of oxidizing agents and may coreact with epoxy resins to give flexible thermosetting products.[6]

In this paper are described some new thiol-terminated polyethers. The new products may be obtained as clear low-viscosity liquids that show excellent stability on storage. In the uncured form the linear chain or backbone contains only carbon-to-carbon and carbon-to-oxygen bonds, both noted for stability. The thiol-terminated polyethers may serve as interesting building blocks for higher polymers. They will undergo the oxidation reactions typical of the thiol group and are also capable of interaction with epoxy resins.

Thiol-terminated polyethers of functionalities 2, 3, and 4 were prepared by two different routes. These routes were (1) interaction of hydrogen sulfide with diepoxides and polyepoxides and (2) interaction of epichlorohydrin with a polyether polyol, followed by replacement of chlorine with the thiol group. The two routes may be illustrated as follows:

$$CH_2CHCH_2 \left[OR \right]_n O-CH_2CHCH_2 + 2 H_2S \rightarrow$$

$$HSCH_2CHOHCH_2 \left[OR \right]_n O-CH_2CHOHCH_2SH \quad (1)$$

$$H\text{-}[\text{-OR-}]_n OH + 2\ CH_2CHCH_2Cl \rightarrow ClCH_2CHOHCH_2\text{-}[\text{-OR-}]_n OCH_2CHOHCH_2Cl$$

$$\downarrow NaSH$$

$$HSCH_2CHOHCH_2\text{-}[\text{-OR-}]_n O\text{---}CH_2CHOHCH_2SH \quad (2)$$

In addition, the chlorohydrin intermediates illustrated in route (2) can be dehydrohalogenated to form di- or polyepoxide compounds.[7] These in turn can react with hydrogen sulfide, as illustrated in route (1), to form thiol-terminated compounds.

DISCUSSION

It is well known that the three-membered epoxy ring is strained and that a variety of compounds containing active hydrogen can open this ring.[8] It is, therefore, possible to open this ring with hydrogen sulfide, to form a compound containing thiol groups. This has been done with several types of commercial epoxy resin. The following epoxy resins were included in this study: diglycidyl ether of bisphenol A (GenEpoxy 190, General Mills, Inc.), poly(oxypropylene diepoxide), and the glycidyl ether of a novolac resin (DEN 438, Dow Chemical Co.).

These were converted to the corresponding thiol compounds by reaction with an excess of hydrogen sulfide at low pressures and ambient room temperature and with sodium methoxide as catalyst. The reaction proceeded equally well with or without solvent, since the epoxy resins used, with the exception of the DEN 438, were liquids. The reaction, generally carried out for 24 hr., produced a slight exotherm, and a slight drop in pressure was observed. The resulting thiol compounds were light colored liquids, with the exception of the novolac compound, which was a solid at room temperature.

According to the oxirane oxygen content of the epoxy resins, conversion to the corresponding thiol compounds by the procedure just described was nearly quantitative. The presence of sulfur or thiol and of the hydroxyl group formed in the reaction was confirmed by infrared analysis.

The second route, involving preparation of chlorohydrin ethers and reaction of these intermediates with sodium sulfhydrate, was used for synthesizing thiol compounds from a variety of commercially available diols and polyols. Preparation of the chlorohydrin intermediates involved addition of epichlorohydrin to the polyol, following essentially the method used by Price and Belanger.[7] Our results confirmed their observation that the secondary hydroxyl group formed by addition of epichlorohydrin to the alcohol group can further react with epichlorohydrin to form a compound containing inactive chlorine. This is defined as chlorine not readily removed by alkaline hydrolysis. By analysis, the chlorohydrin ethers in all instances contained from 1 to 2% more total chlorine than active chlorine.[9] These compounds are quite stable, as is indicated by the results of analysis for chlorine content after several months of storage.

Conversion of the chlorohydrin ethers to the corresponding thiol compounds was accomplished in good yields by reaction with sodium sulfhydrate in an atmosphere of hydrogen sulfide at moderate pressure in a rocking autoclave. The hydrogen sulfide gas was used for excluding air and minimizing formation of sulfides. According to the thiol content of the products, conversion averaged about 90%.

EXPERIMENTAL

Reaction of Epoxy Resins with Hydrogen Sulfide

A typical preparation, involving addition of hydrogen sulfide to an epoxy resin, is as follows.

A solution of 300 g. of a glycidyl ether of poly(oxypropylene glycol) (5.02% oxirane oxygen) in 250 g. of cyclohexane was placed in a stainless-steel rocking autoclave equipped with a gas inlet and thermocouple well. The catalyst (1.0 g. sodium methoxide) was then added and 100 g. of H_2S introduced, resulting in a pressure reading of 100 psig. The autoclave was then sealed and rocked for 24 hr. A slight exotherm was noted (to 30°C.), and at the end of 24 hr. the pressure reading was about 60 psig. Excess H_2S was vented through aqueous alkali, and after thorough degassing and filtering, to remove catalyst, the product was isolated by removing the solvent at reduced pressure at 50°C. by means of a rotary evaporator. The product, 325 g., 0.04% oxirane oxygen and 9.1% sulfur, and had a viscosity of 4 poise at 26°C. This result and others obtained with essentially the same procedure are shown in Table I.

As might be expected, incomplete addition of hydrogen sulfide resulted in the formation of products that gradually increased in viscosity on storage. This can be attributed to inter- and intramolecular reaction of the thiol with residual oxirane oxygen. None of the products described in Table I changed in viscosity over a period of several months, demonstrating the good stability of the compounds.

Preparation of Chlorohydrin Ethers

Preparation of the chlorohydrin ether derivative of various polyols followed the general procedure described below.

To 544 g. (1.0 mole) of a polyoxybutylene diol (Polyglycol B-500, Dow Chemical Co.) was added 1 ml. of boron trifluoride etherate with stirring. Then 203.5 g. (2.2 moles) of epichlorohydrin were added slowly dropwise over a period of 80 min. The temperature of the reaction mixture rose slowly to 60°C. and was held there with intermittent cooling, until the exotherm was spent. The product, after cooling to 25°C., was 8.47% active chlorine and 9.75% total chlorine (theory, 9.4%).

Taking into account the purity of the epichlorohydrin (chlorine found, 32.8%; theory, 38.3%) a 10% excess was used in all preparations, to insure complete reaction. A number of typical runs are illustrated in Table II.

TABLE I

Reaction of Glycidyl Ethers with Hydrogen Sulfide[a]

No.	Glycidyl ether of:	Oxirane oxygen, %	Solvent	Product		
				Oxirane oxygen,[b] %	Sulfur,[c] %	Visc., poise, and temp., °C.
1	Poly(oxypropylene glycol)	5.02	Cyclohexane	0.04	9.1 (9.1)	4, 26
2	Poly(oxypropylene glycol)	5.02	None	0.05	9.2 (9.1)	3.3, 27
3	Bisphenol A (GenEpoxy 190, Gen. Mills, Inc.)	8.54	Chloroform	0.015	13.6 (13.8)	6900, 26
4	Novolac resin (DEN 438, Dow Chem. Co.)	8.55	Chloroform	0.05	13.87 (13.8)	Solid

[a] All reactions carried out for 24 hr. at 25°C. and hydrogen sulfide pressure of 100 psig.

[b] By method of A. G. Durbetaki (*Anal. Chem.*, **28**, 2000, 1956).

[c] By Parr bomb procedure; theoretical values in parentheses.

TABLE II
Preparation of Chlorohydrin Ether Compounds

No.	Polyol type	Composition of polyol	Approx. mol. wt.	Active chlorine of chlorohydrin ether,[a] %	Total chlorine of chlorohydrin ether,[b] %
1	Diol	Poly(1,2-oxybutylene glycol)	500	8.46	9.75 (9.4)
2	Diol	Poly(1,2-oxybutylene glycol)	500	8.41	9.6 (9.4)
3	Triol	Hexanetriol–propylene oxide adduct	700	9.14	10.8 (10.7)
4	Triol	Hexanetriol–propylene oxide adduct	1500	5.06	6.1 (5.87)
5	Triol	Hexanetriol–propylene oxide adduct	2500	3.5	4.1 (3.96)
6	Triol	Hexanetriol–propylene oxide adduct	4400	2.11	2.5 (2.32)
7	Triol	Glycerol–propylene oxide adduct	3000	2.98	3.32 (3.38)
8	Tetrol	Pentaerythritol–propylene oxide adduct	650	12.13	15.3 (14.4)

[a] See ASTM method.[9]
[b] By x-ray fluorescence analysis; theoretical values in parentheses.

Conversion of the Chlorohydrin Ethers to Corresponding Thiol Compounds

Replacement of chlorine in the chlorohydrin ethers with the thiol group was generally conducted as follows.

To 160 g. (0.22 moles) of a polyoxybutylene chlorohydrin ether (product 1, Table II) was added 50 g. of powdered sodium sulfhydrate in an autoclave. Then a total of 53 g. of hydrogen sulfide gas was added under pressure, to give an initial reading of 180 psig. The autoclave was then sealed and heat was applied, to raise the temperature of the reaction mixture to about 85°C. (pressure of 340 psig) with agitation. After 2 hr. heating was discontinued and the rocking autoclave allowed to cool slowly to ambient room temperature. After venting of excess H_2S through a scrubber, the reaction mixture was taken up in cyclohexane and pressure-filtered to remove salts and the filtrate was dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure in a rotary evaporator, until a product of constant weight was obtained. The product, a clear, nearly colorless liquid, was 7.93% SH, 8.3% S, and 0.32% Cl.

The commercial grade of sodium sulfhydrate used in all reactions of this type contained from 25 to 30% water. A molar excess of 50–75% was used in most laboratory preparations, although later experiments showed that equally good results could be obtained with an excess of only 30%.

Additional preparations are shown in Table III. The thiol compounds described were prepared from the corresponding chlorohydrin intermediates listed in Table II.

TABLE III
Thiol Compounds

Thiol compound prepared from chlorohydrin ether derivative of polyol, no.[a]	SH,[b] %	S,[c] %	Cl,[d] %
1	7.93 (9.36)	8.3 (9.1)	0.36
2	7.93 (9.36)	8.2 (9.1)	0.37
3	9.12 (10.03)	9.5 (9.73)	0.2
4	4.85 (5.49)	5.28 (5.33)	0.6
5	3.03 (3.69)	3.65 (3.58)	0.0
6	1.83 (2.16)	2.3 (2.09)	0.02
7	2.77 (3.16)	3.23 (3.06)	0.2
8	11.8 (13.5)	13.0 (13.13)	0.1

[a] All listed in Table II.

[b] By oxidation with iodine and back titration with thiosulfate; theoretical values in, parentheses.

[c] By Parr bomb method; theoretical values in parentheses.

[d] By x-ray fluorescence analysis.

CONCLUSIONS

The preparation of thiol-terminated polyethers via two different routes has been described. These routes utilize as starting materials commercially available polyether polyols and epoxy resins. The new thiol substances are pale colored liquids, with one exception. The sulfur contents of the thiol-terminated polyethers described in this paper are generally very close to the calculated values, while thiol contents are only slightly lower than the calculated values in most instances.

References

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Résumé

Des polyéthers à groupes thiols terminal ont été préparés par deux méthodes différentes utilisant comme matériaux de départ, des polyols polyéthers commercialement disponibles et des résines époxy. Les produits sont des liquides faiblement colorés et étaient très stables au stockage à température de chambre. On a pu préparèr des polyéthers à groupe thiol terminal de fonctionnalité variant de 2 à 4. Ce sont des blocs intéressants pour l'édification de polymères par oxydation des groupes SH terminaux et par coréaction avec des résines époxy.

Zusammenfassung

Polyäther mit Thiol-Endgruppen wurden auf zwei verschiedenen Wegen hergestellt, wobei man als Ausgangsmaterialien käuflich erhältliche Polyäther-Polyole und Epoxyharze verwendete. Die Produkte waren schwach gefärbte Flüssigkeiten und erwiesen sich bei Lagerung bei Raumtemperatur als sehr stabil. Die hergestellten Polyäther mit Thiol-Endgruppen besassen eine Funktionalität von zwei bis vier. Durch Oxydation der SH-Endgruppen oder durch Coreaktion mit Epoxyharzen können sie zu interessanten blockartigen Bausteinen für Polymere werden.