

**THE SYNTHESIS OF A POLYTHIOESTER FROM
ADIPIC ACID AND 1,2-ETHANEDITHIOL**

by

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I. INTRODUCTION

Since the development of nylon, the first high polymer to be synthesized commercially, the field of high polymers has expanded rapidly. The use of high polymers for fibers has developed to a point where the synthetic fibers are excelling the natural ones in texture appeal as well as durability.

High polymers are of many types: polyamides such as nylon, polyesters such as dacron, and polyvinyl types such as chemstrand. The preceding are all used for the production of fiber. Many of the polymers for the production of rubber-like material employ the use of non-organic monomers. A noted example of a copolymer of organic and inorganic compounds is silicone.

Sulfide compounds can be used as copolymers. Ethylene dichloride is reacted with sodium tetrasulfide to produce a polymer known commercially as thiokol. The disadvantage of polysulfide polymers is their mercatan-like odor.

The purpose of this investigation was to determine if adipic acid and 1,2-ethanedithiol could at atmospheric pressure and using an acid catalyst be polymerized, and if the polymer formed has properties that might indicate its suitability for fiber.

II. LITERATURE REVIEW

The following is a review of the literature on the synthesis of polythioesters.

History

The realization that the physical structure of high polymer compounds has a controlling effect on their physical properties lead to the development of the synthetic fibers of today. The first synthetic fiber produced from simple chemical units was nylon. There are several types of nylon ; the ordinary type is synthesized from adipic acid and hexamethylene diamine.

There are high polymers of many types: polyamides such as nylon, polyesters such as dacron, and polyvinyl types such as chemstrand. All of the preceding polymers are used for fiber.⁽¹⁾

Sulfide compounds can be used as copolymers. Ethylene dichloride is reacted with sodium tetrasulfide to produce a polymer known commercially as thiokol. Thiokol is not suited for fiber but is a rubber-like compound especially inert to organic solvents.⁽¹⁶⁾

Polythioesters have been investigated for use as fiber and two methods of synthesis have been patented. One process reacts a dimercaptan with dicarboxylic acid ⁽¹⁴⁾ and the other reacts a dimercaptan with diacyl chloride. ⁽⁶⁾

Polythioesters

Mercaptans, from which polythioesters are made, and the preparation, properties, and uses of polythioesters are reviewed in the following paragraphs:

Mercaptans. Mercaptans or thioalcohols are analogous to alcohols, there being a sulfur atom in the mercaptan where oxygen is in alcohols. They have a pungent and disagreeable odor, especially the low molecular weight ones. The odor decreases with increased molecular weight.

Mercaptans are more acidic than alcohols and will form insoluble salts with heavy metals. Where as alcohols are not readily oxidized, mercaptans are, and can be oxidized to disulfides by such oxidizing agents as ⁽³⁾ hydrogen peroxide.

The mercaptans are easily prepared from alkali hydrogen sulfides and alkylating agents. Usable alkylating agents are alkyl halides, alkyl hydrogen sulfates, and dialkyl sulfates. ⁽¹²⁾ The reaction is usually performed in a solvent such as alcohol and under an inert atmosphere.

Polythioester Preparation. There are several methods for the preparation of thioesters all of which are analogous to the methods of preparation with the corresponding alcohols. To prepare thioesters mercaptans can be reacted with carboxylic acids, ⁽²⁾ acyl halides, ⁽⁷⁾ nitriles, ⁽¹¹⁾ ketene, and anhydrides. ⁽⁴⁾

All of the preceding methods are not applicable to the preparation of polythioesters, but only the methods which employ reagents that can have at least two of the reactive groups will polymerize.

⁽⁵⁾ Flory has patented a process whereby polythioesters are synthesized from dimercaptans and the acyl chlorides of dibasic acids. The method is said to be more satisfactory than the reaction between the corresponding acid and mercaptan. The reaction is also faster than the reaction between the acid and mercaptan, it going to completion in about ten minutes.

A process for the esterification of dimercaptans and dibasic acids has been patented by Patrick ⁽¹³⁾ and Ferguson. The specific claim of the patent is the synthesis of a polythioester from dimercapto ethane and maleic acid mixed in a mol ratio of one to one and dissolved in benzene.

The reaction is catalyzed by hydrochloric acid. Other catalyst are strong acids or acid salts and Lewis acids such as sulfuric acid, phosphoric acid, chlorosulfonic acid, $AlCl_3$, SO_2Cl_2 , and S_2Cl_2 .

Properties of Polythioesters. A basic investigation of the equilibrium compositions of systems of benzoic acid, water, various mercaptans, and the corresponding esters was conducted by Pratt⁽¹⁷⁾ and Reid. It was found that the limits of esterification of mercaptans are similar to those of alcohols, but much lower. The thioesters tested exhibited a marked resistance to hydrolysis; the hydrolysis of ethyl thio benzoate was negligible at $193^\circ C$. However, at $220^\circ C$ the expected equilibrium was obtained. The stability of thioesters decreases as the molecular weight of the mercaptan increases.

Polythioesters of dimercaptans usually melt sharply and at most over a range of a few degrees. The melting point of some polythioesters exceeds $200^\circ C$. Generally polythioesters melt at temperatures from 25 to $100^\circ C$ higher than the corresponding polyester.⁽⁸⁾

The polythioester polymers are opaque and can vary in color from white through yellow to a dark brown.

The viscosity can be as low as 1.57 poises and can exceed 19,000 poises. ⁽⁹⁾ A polythioester of maleic acid and dimercapto ethane synthesised by Patrick ⁽¹⁵⁾ and Ferguson is described as wax-like and resembling paraffin in appearance.

Use of Polythioesters. The polymers of simple acids and mercaptans have typical fiber molecular patterns as evidenced by x-ray studies and can be extruded into fiber. The fibers upon cold drawing increase in tensile strength; thus the polymers are suited for textile fibers. More complicated polythioesters are more suited to molding and sheet formation. ⁽¹⁰⁾

III. EXPERIMENTAL

The following sections give the purpose, plan of investigation, material and apparatus, method of procedure, and data and results for this investigation.

Purpose of Investigation

The purpose of this investigation was to determine if adipic acid and 1,2-ethanedithiol can be polymerized using methanesulfonic acid as catalyst and if the polymer formed has properties that indicate its suitability for fiber.

Plan of Investigation

Three series of tests, five test per series, will be performed in an effort to find the optimum conditions for synthesis to give a polythioester.

The general procedure for all the test will be the same. Adipic acid, 1,2-ethanedithiol, and methanesulfonic acid catalyst will be mixed in a round bottomed triple necked flask equipped with a distillation column and thermometers and containing 250 grams of n-butyl ether as a solvent. The mixture will be boiled at a rate such that the temperature of the distillation column outlet will be 100°C. The water formed during the reaction will be distilled off, collected and weighed. The water will give a measure of the rate and extent of the reaction. The test will be continued until equilibrium is reached as indicated by no water distilling off.

Air will be excluded from the reaction by nitrogen.

Series One. The first series is designed to determine the effect of concentration on the reaction. The adipic acid and 1,2-ethanedithiol will be mixed in a mol ratio of one and test performed at concentrations of 2.0, 1.0, 0.5, 0.25, and 0.1 molal. One gram of methanesulfonic acid catalyst will be used in each test.

Series Two. Series two will use the optimum concentration from series one and the same ratio fo adipic acid to 1,2-ethanedithiol. Test will be performed using 2.0, 1.5, 1.0, 0.5, and 0.2 grams of methanesulfonic acid catalyst.

Series Three. Series three will be performed at the optimum conditions from series one and two. Test will be performed using mol ratios of adipic acid to 1,2-ethanedithiol of 1.5, 1.25, 1.0, 0.75, and 0.5.

Molecular Weight. The molecular weight of the polythioester will be determined by the viscosity method as described by Schmidt⁽¹⁹⁾ and Marlies.

Method of Procedure

The procedure used in the investigation was the preparation of sodium hydrosulfide, the preparation of 1,2-ethanedithiol from the sodium hydrosulfide, and the synthesis of a polythioester from the 1,2-ethanedithiol.

Sodium Hydrosulfide Preparation. Sodium hydrosulfide was prepared from sodium sulfide and hydrogen sulfide in isopropyl alcohol. Sodium sulfide was broken into pieces no larger than 1/4 inch and put into a 500 milliliter flask 1/3 full of isopropyl alcohol. Enough sodium sulfide was added to the flask to make a layer 1/4 inch thick on the bottom. Hydrogen sulfide was added until all of the sodium sulfide had dissolved. The flask was shaken as the hydrogen sulfide was added.

1,2-Ethanedithiol Preparation. Two methods were used to prepare 1,2-ethanedithiol; both of which were unsuccessful.

The first method was to mix 81 grams of sodium hydrosulfide and 200 milliliters of isopropyl alcohol, used in producing the sodium sulfide, with 60 grams of ethylene chloride. The mixture was refluxed for two hours and allowed to sit at room temperature for four days before distillation.

The second method of preparing 1,2-ethanedithiol was the same as the first except that absolute alcohol was used and the sodium hydrosulfide was dried. The sodium hydrosulfide was dried at 30 °C by passing a current of air over it for five hours.

Materials

The following is a list of materials used in the investigation of the synthesis of a polythioester.

Acid, Adipic. Reagent grade. Obtained from Fisher Chemical Co., 7722 Woodbury Drive, Silver Spring, Md. Used for synthesis of polythioester.

Acid, Methanesulfonic. Practical. Obtained from Fisher Chemical Co., 7722 Woodbury Drive, Silver Spring, Md. Used as catalyst in esterification.

Alcohol, Absolute. Reagent grade. Obtained from Fisher Chemical Co., 7722 Woodbury Drive, Silver Spring, Md. Used as solvent.

Alcohol, Isopropyl. Purified, lot No. 6252. Obtained from the J. J. Baker Chemical Co., Phillipsburg, N. J.. Used for solvent.

1,2-Ethanedithiol. Water free, distillation range 144 to 147 C. Prepared from sodium hydrosulfide and ethylene chloride. Used as reagent in synthesis of polythioester.

Ether, n-Butyl. Practical. Obtained from Fisher Chemical Co., 7722 Woodbury Drive, Silver Spring, Md. Used as solvent for adipic acid and 1,2-ethanedithiol.

Ethylene Chloride. Purified. Obtained from Fisher Chemical Co., 7722 Woodbury Drive, Silver Spring, Md. Used for the preparation of 1,2-ethanedithiol.

Sodium Hydrosulfide. Unpurified. Prepared from sodium sulfide and hydrogen sulfide. Used for the preparation of 1,2-ethanedithiol.

Sodium Sulfide. Fused chips, 60 per cent, code 2299, lot No. C136. Obtained from General Chemical Co., 40 Rector Street, New York 6, N. Y. Used to prepare sodium hydrosulfide.

Apparatus

The following apparatus was used to perform the investigating.

Balance, Analytical. Notched-beam, chain type, subdivisions 0.0001 gram. Manufactured by Seederer-Kohlbusch Inc., Jersey City, N. J. Used to weigh reactants.

Condenser. Liebig, glass, sealed, jacket length 300 millimeters, catalog No 7-715. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to condense water vapor distilled from the reaction.

Distilling Column. Glass, bulb form, one bulb, catalog No 9-160. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to effect a separation of water from the reaction.

Flask, Distilling. Three necks, 1000 milliliter, pyrex brand glass, catalog No 10-163. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as reaction vessel.

Glassware, Assorted. Beakers and flasks, pyrex brand glass. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to contain reagents.

Graduated Cylinder. Glass, pyrex brand, 50 milliliter, subdivisions 5 milliliters. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure reagents.

Heater, Electric. Serial No 4254, 465 watts, 110 volt maximum, Manufactured by Glas-Col Apparatus Co., Terre Haute, Ind. Used to Heat the reaction.

Thermometer. Mercury filled, range -5 to 360°C, subdivisions 1°C, catalog No 15-005. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to Measure the temperature of reaction and distillation.

Viscosimeter, Ostwald. No 300. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine the molecular weight of the polythioester.

Data and Results

The data and results of the experiment are given in the following tables.

Preparation of Sodium Hydrosulfide. The data for the preparation of sodium hydrosulfide are given in table I, page 17.

Drying of Sodium Hydrosulfide. The data for the drying of sodium hydrosulfide with air are given in table II, page 18.

Preparation of 1,2-Ethanedithiol. The data and results for the attempted preparation of 1,2-ethanedithiol are given in tables III and IV, pages 19 and 20 . Table III gives the results obtained when the alcohol used as solvent was that used to prepare the sodium hydrosulfide. Table IV give the results obtained when absolute alcohol was used as solvent.

TABLE I

Preparation of Sodium Hydrosulfide

Isopropyl alcohol, ml	1000
Sodium sulfide, gm	203
Hydrogen sulfide	saturated
Pressure in flask, inches H ₂ O	12
Temperature, °C	20
Sodium hydrosulfide formed, gm	126

TABLE II

Evaporation of Isopropyl Alcohol from Alcohol-
Hydrosulfide Mixture

Temperature of mixture, °C	28 - 32
Air temperature, °C	25
Time of drying, hr	5
Weight of solid recovered, gm	45

TABLE III

First Preparation of 1,2-Ethanedithiol

Sodium hydrosulfide, gm	81
Ethylene chloride, gm	60
Isopropyl alcohol, ml	200
Reflux time, hr	2
Reflux temperature, °C	70
Contact time at 25°C, days	4
Yield	none

TABLE IV

Second Preparation of 1,2-Ethanedithiol

Sodium hydrosulfide, gm	45
Ethylene chloride, gm	30
Absolute alcohol, ml	200
Reflux time, hr	2
Reflux temperature, °C	68 - 73
1,2-Ethanedithiol yield	none
Unknown product, gm	3.6
Physical stateamorphous solid
Solubility at 25 °C	
Water	insoluble
Benzene	insoluble
Absolute alcohol	insoluble
Dilute NH ₄ OH	insoluble
n-Butyl ether	insoluble
Ethylene chloride	insoluble

IV. DISCUSSION

In the following paragraphs the results obtained from the experiment are discussed and recommendations made concerning future investigations.

Discussion of Results

The paragraphs which follow are a discussion of the technique used and results obtained from the experiment. There is also a discussion of the possible reaction mechanism of mercaptan formation from sodium hydrosulfide.

Reactant Impurities. The sodium hydrosulfide that was produced was not analyzed and therefore the exact composition was not known. The sodium sulfide used for preparing the hydrosulfide when melted was completely fluid except for a few small lumps that did not melt. The lumps that did not melt were probably sodium polysulfide impurity. Another indication that sodium polysulfide was present as an impurity was the appearance, in the second attempt to prepare 1,2-ethanedithiol, of a dark gray rubber-like polymeric substance. The first attempt to prepare 1,2-ethanedithiol did not result in the formation of the rubber-like substance.

Comparing the polymeric substance that was formed in the second test with the properties of thiokol it is seen that they are quite similar. Neither the polymeric substance formed in the experiment nor thiokol dissolve in water or hydrocarbon solvents. It is reasonable to assume that the polymeric substance formed was thiokol since the required reactants were present; sodium polysulfide was present as an impurity and ethylene chloride was present as one of the primary reactants.

Method of Preparing Sodium Hydrosulfide. Difficulty was encountered in producing sodium hydrosulfide from sodium sulfide and hydrogen sulfide. The sodium sulfide was melted and attempts made to saturate it with hydrogen sulfide. The rate of absorption of the hydrogen sulfide in the molten sodium sulfide was very low, so low that there was no visible evidence that the hydrogen sulfide was being absorbed. It was also difficult to keep the molten salt from backing up the gas delivery tube and there solidifying. This, of course, would plug the tube. The flask of molten sodium sulfide was shaken, but the action had little effect on the absorption rate of the hydrogen sulfide. The shaking caused the gas delivery tube to become plugged more rapidly. Due to these difficulties the method was abandoned.

The method finally used was to saturate alcohol with hydrogen sulfide and mix it with sodium sulfide. This method presented the problem of drying the sodium hydrosulfide. The sodium hydrosulfide was difficult to dry because as it dried the original color of the sodium sulfide returned. This was probably due to the evolution of hydrogen sulfide. A sample of pure sodium hydrosulfide was therefore not prepared. It is evident that there must be an equilibrium between sodium sulfide, sodium hydrosulfide, and hydrogen sulfide. The evolution of hydrogen sulfide is probably favored by high temperatures. Any sodium sulfide that was present in the reaction mixture should have been converted to the hydrosulfide when the reaction mixture was saturated with hydrogen sulfide.

Reaction Mechanism. The method used to attempt to prepare 1,2-ethanedithiol used sodium hydrosulfide in its ionic state. Sodium hydrosulfide was added to the alcohol and then the mixture saturated with hydrogen sulfide to insure that no sodium sulfide was present and to eliminate oxygen from the reaction. However, as can be seen from the results the sodium hydrosulfide present in the ionic form did not result in the production of any mercaptan.

It is possible that for the hydrosulfide to be reactive it must be in a form other than ionic.

The method of preparing mercaptan with sodium hydrosulfide and a chloro hydrocarbon as described by Hall and Reid (18) is an example where so-called sodium hydrosulfide was used. They reacted metallic sodium with absolute alcohol then saturated the solution with hydrogen sulfide. To the alcohol mixture was added the chloro hydrocarbon dissolved in absolute alcohol. In saying that the reaction that occurred was between sodium hydrosulfide and the chloro hydrocarbon it must have been assumed that the hydrogen sulfide reacted with the sodium ethoxide, formed by the solution of sodium, reacted to give ethanol and sodium hydrosulfide in solution as ions.

It is thought that there is a difference in the so-called sodium hydrosulfide produced by the method described by Hall and ionic sodium hydrosulfide. There is a possibility that the reaction between sodium ethoxide and hydrogen sulfide does not produce ionic sodium hydrosulfide, but instead a complex is formed between the sodium ethoxide and hydrogen sulfide. It would then be the complex molecule that reacts with the chlor hydrocarbon to produce mercaptans. It is possible that the mechanism of a complex molecule is a plausible assumption.

The correctness of this assumption is not known. If the reaction proceeded by means of sodium hydrosulfide as ions then it would make little difference what the origin of the hydrosulfide ion was. It would even seem possible to produce it in the reaction vessel by such a process as dissolving a sodium salt in the alcohol and then saturate it with hydrogen sulfide.

There is also the question that if a complex is assumed then why won't the same complex be formed by the reaction between alcohol and sodium hydrosulfide as well as sodium ethoxide and hydrogen sulfide. The result of the experiment can be interpreted as showing that a complex is not formed between alcohol and sodium hydrosulfide.

Recommendations

The recommendations for further study are presented in the following paragraphs.

Sulfide Equilibria. It is recommended, in view of the difficulty encountered in drying the sodium hydrosulfide, that an investigation be made of the equilibrium between sodium sulfide, sodium hydrosulfide, and hydrogen sulfide by determining the partial pressure of hydrogen sulfide over sodium hydrosulfide at temperatures varying from 0°C to 80°C.

Concentration of Hydrosulfide. It is recommended that further tests be performed to prepare 1,2-ethanedithiol using varying concentrations of sodium hydrosulfide. A test should be performed using only hydrogen sulfide saturated alcohol and ethylene chloride. Tests should also be performed using sodium hydrosulfide concentrations ranging from 0.01 molar to saturation. In future test it is recommended that the reaction mixture be refluxed for at least ten hours instead of the two hours used in this experiment.

Limitations

The experiments which were an attempt to prepare 1,2-ethanedithiol were performed at the following conditions.

Concentration. In each test the ethylene chloride and sodium hydrosulfide were used in stoichiometric amounts. The quantity of sodium hydrosulfide, 81 and 45 grams in the first and second test respectively, was such that it did not all dissolve in the 200 milliliters of alcohol.

Temperature. The reactants were mixed and refluxed at a temperature varying from 68 to 73°C.

Time. The reactants were mixed and refluxed for two hours.

Pressure. The experiment was performed at atmospheric pressure.

V. CONCLUSIONS

The attempt to prepare 1,2-ethanedithiol from stoichiometric amounts of sodium hydrosulfide and ethylene chloride, where 81 and 45 grams of sodium hydrosulfide were used in the first and second test respectively in 200 milliliters of alcohol and the mixture refluxed for two hours at 68 to 73°C, led to the conclusion that 1,2-ethanedithiol cannot be prepared under such conditions.

VI. SUMMARY

The purpose of this investigation was to synthesize a polythioester from adipic acid and 1,2-ethanedithiol. Due to the commercial unavailability of 1,2-ethanedithiol it was decided to synthesize it from sodium hydrosulfide and ethylene chloride.

Sodium hydrosulfide was prepared by reacting hydrogen sulfide with sodium sulfide in alcohol. In the first test 81 grams of sodium hydrosulfide were mixed with a stoichiometric amount of ethylene chloride and 200 milliliters of isopropyl alcohol, and for the second test 45 grams of sodium hydrosulfide were mixed with a stoichiometric amount of ethylene chloride in 200 milliliters of absolute alcohol. Each test was performed at atmospheric pressure in a three-necked, round bottomed, liter flask. The reaction mixture was refluxed for two hours.

The result of the experiment was that no 1,2-ethanedithiol was formed.

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