

Linear Polythioesters. XIV. Products of Interfacial Polycondensation Isomeric Di(mercaptomethyl)trimethylbenzenes with Some Aliphatic Acid Dichlorides

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Synopsis

New polythioesters by interfacial polycondensation of 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene, 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene with adipoyl and sebacyl chlorides were obtained. Process of polycondensation was carried out under the same condition as established earlier as an optimal for synthesis of polythioester from 2,5-di(mercaptomethyl)-1,4-dimethylbenzene and sebacyl chloride. The conditions of polycondensation process were as follows: the organic phase benzene/hexane (1:1), ratio of aqueous to organic phase 1:1, the presence of 100% excess of NaOH as hydrogen chloride acceptor, temperature of reaction 15°C, little excess of acid dichloride with addition time 8.5 min. The structure of all polythioesters was determined by elementary analysis, infrared spectra, and X-ray analysis. Initial decomposition and initial intensive decomposition temperature were defined by the curves of thermogravimetric analysis. The molecular weights for these polymers were determined by gel chromatography.

INTRODUCTION

Continuing the studies on the synthesis, structure, and properties of polythioesters derivatives of di(mercaptomethyl)methylbenzenes with acid dichlorides in an earlier article,¹ the studies connected with optimization of synthesis process of polythioesters obtained by high- and low-temperature solution polycondensation as well as by interfacial polycondensation from di(mercaptomethyl)dimethylbenzenes and aliphatic acid dichlorides are described. It is stated that the best results were obtained by using of interfacial polycondensation.

The purpose of this article is to describe new polythioesters obtained from isomeric di(mercaptomethyl)trimethylbenzenes and adipoyl as well as sebacyl chlorides.

Di(mercaptomethyl)trimethylbenzenes are formed from suitable di(chloromethyl) compounds by thiouronic salts.²⁻⁴ The chloromethylation of isomeric trimethylbenzenes to difunctional compounds leads to obtaining the following products with the greatest yield: 4,6-di(chloromethyl)-1,2,3-trimethylbenzene, from hemimellitene,⁵ 3,5-di(chloromethyl)-1,2,4-trimethylbenzene from pseudocumene⁶, 2,4-di(chloromethyl)-1,3,5-trimethylbenzene from mezytylene.⁷ These di(chloromethyl)trimethylbenzenes were used to synthesis responsible di(mercaptomethyl)trimethylbenzenes.

Preparation of polythioesters from 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene, 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene, or 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene and adipoyl as well as sebacoyl chlorides was carried out under the same optimal conditions, established earlier for the interfacial polycondensation of 2,5-di(mercaptomethyl)-1,4-dimethylbenzene with sebacoyl chloride.¹

EXPERIMENTAL

Reagents

4,6-Di-(mercaptomethyl)-1,2,3,-trimethylbenzene [4,6-DMM-1,2,3-TMB], mp 60°C (after crystallization from methanol); 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene [3,5-DMM-1,2,4-TMB], bp 158°C/1.5 mm Hg; and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene [2,4-DMM-1,3,5-TMB], mp 68°C (after crystallization from ethanol) were obtained from the suitable di(chloromethyl)-compounds through the thiouronic salts.²⁻⁴

Adipoyl chloride with bp 126–128°C/18 mm Hg and sebacoyl chloride with bp 166–168°C/11 mm Hg were obtained by chlorination of the suitable acids with thionyl chloride.

Synthesis of Polythioesters

In a three-necked, round-bottomed flask of 250 cm³ volume, equipped with a mechanical stirrer (2000 rpm), thermometer and dropper, 2.12 g (0.01 mol) of dithiol, 50 mL benzene and sodium hydroxide solution (1.6 g NaOH in 100 mL water) were placed. After thorough mixing, the solution of 2.013 g (0.011 mol) adipoyl chloride or 2.629 g (0.011 mol) sebacoyl chloride in 50 mL hexane was added for a period 8.5 min and stirred in temperature of 15°C. After addition of acid chloride, stirring was continued for 0.5 h in this temperature, and then the mixture was acidified with hydrochloric acid (Congo Red). The isolated product of polycondensation was filtered and boiled in 100 mL water for 15 min. After cooling the polythioester was washed with acetone and dried under reduced pressure (15 mm Hg) at 60°C.

Measurement of Properties

Melting Point

Melting point determinations were made on a Boetius apparatus.

Viscosity

The reduced viscosity (dL/g) of a 1% solution of polythioesters in tetrachloroethane was measured in a Ubbelohde viscometer at 25°C.

Thermogravimetric Analysis

Measurement of weight loss was taken in a MOM derivatograph (Paulik, Paulik and Erdey, Budapest) at a heating rate of 10°C/min in air.

X-Ray Analysis

X-ray photographs were obtained by the Debye-Scherrer's powder method with a camera 64 mm in diameter and an X-ray tube Cu without filters. Exposure time was 8 h, tube voltage was 32 kV, and anodic intensity was 12 mA. The apparatus was an URS-60 type.

Molecular Weight

The average molecular weight (\bar{M}_w) of polythioesters was calculated on the basis of gel permeation chromatographic data.^{8,9} The chromatographic measurements were carried out applying Varian Aerograph liquid chromatograph type 4100 with RI detector and orlite pompe AF 10-4; tetrachloroethane was used as a mobile phase.

The investigated polythioesters as filtrated solution (0.5–1.0 g of polymer in 100 cm³ of tetrachloroethane) has been injected on the column system consisted of two chromatographic columns. The columns (300 mm long \times 7.8 mm i.d.) were filled with Lichrospher Si-100 and Si-500 (Merck, Darmstadt, FRG). The measurements were carried out at 18°C.

Glassy Temperature

Measurement of glassy temperature was taken in a DSC-IB Perkin-Elmer differential microcalorimeter, at a heating rate of 32°C/min, nitrogen flow rate of 30 cm³/min, sensibility of apparatus 4 mcal/s, and weight of sample of 16 mg.

Infrared Analysis

Infrared (IR) spectra were obtained with a UNICAM SP-200 spectrophotometer.

Chemical Resistance

In a flask of 200 cm³ volume, 1 g of polythioesters try to dissolve in a 50 cm³ of different several solvents at room temperature.

RESULTS AND DISCUSSION

The manner of obtaining of polythioesters by interfacial polycondensation of isomeric di(mercaptomethyl)trimethylbenzenes with adipoyl and sebacoyl chlorides presented in Experimental was stated in the basis of many studies for the polycondensation process of di(mercaptomethyl)dimethylbenzenes with aliphatic acid dichlorides.¹

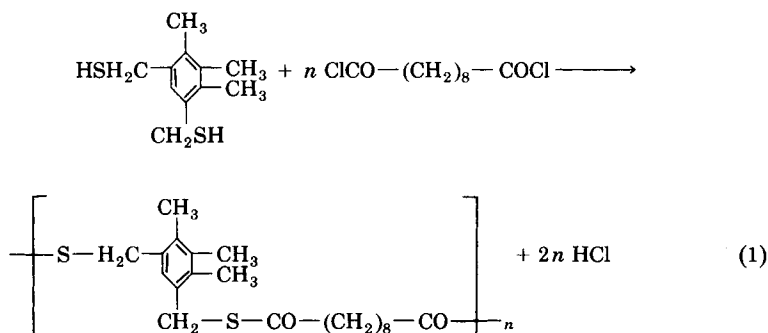
Using isomeric di(mercaptomethyl)trimethylbenzenes, i.e., 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene, 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene, 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene, and adipoyl as well as sebacoyl chloride six new aliphatic-aromatic polythioesters have been obtained. In Table I are presented some physicochemical properties of these polycondensates.

Infrared spectra of all polythioesters (Figs. 1 and 2) showed strong absorptions at 1680–1700 cm⁻¹ which are characteristic for carbonyl stretching, at

TABLE I
Some Physicochemical Properties of Polythioesters from Isomeric
Di(mercaptomethyl)trimethylbenzenes, Adipoyl, and Sebacoyl Chlorides

Polythioester		η_{red} (dL/g)	Intrinsic viscosity (dL/g)	Yield (%)	Glassy temp (°C)	Softening range (°C)	Molecular weight ($\bar{M}_w \times 10^3$)
Dithiol	Acid chloride						
4,6-DMM-1,2,3-TMB	Adipoyl	0.26	0.205	66	112.5	115-130	28
3,5-DMM-1,2,4-TMB	Adipoyl	0.24	0.125	65	111.5	120-130	14
2,4-DMM-1,3,5-TMB	Adipoyl	0.35	0.235	66	109.5	115-133	34
4,6-DMM-1,2,3-TMB	Sebacoyl	0.41	0.345	72	74	80-100	57
3,5-DMM-1,2,4-TMB	Sebacoyl	0.15	0.095	81	112	120-126	10
2,4-DMM-1,3,5-TMB	Sebacoyl	0.46	0.185	84	78	80-95	24

900–1000 cm^{-1} characteristic of $\text{C}=\text{S}$ stretching, and 1420–1440 cm^{-1} characteristic of the CH_2-S group. On the basis of good agreement of the calculated and found analytical data (Table II) and infrared spectra, the reaction scheme (1) for 4,6-DMM-1,2,3-TMB and sebacoyl chloride as an example was assumed:



Molecular Weight

Gel permeation chromatography system was calibrated in the range 2.1×10^3 – 3.1×10^6 by means of polystyrene standards (PS) from Water Associates. Eleven PS standards of a known average molecular weight characterized by an ultranarrow distribution of molecular weight were applied.

In order to calculate the molecular weights of polythioesters the universal calibration curve was used. According to Benoit et al.¹⁰ the elution volume of macromolecule depends on the hydrodynamic volume of macromolecule

$$\log [\eta] \cdot M = f(V_e)$$

where: $[\eta]$ = intrinsic viscosity and V_e = elution volume.

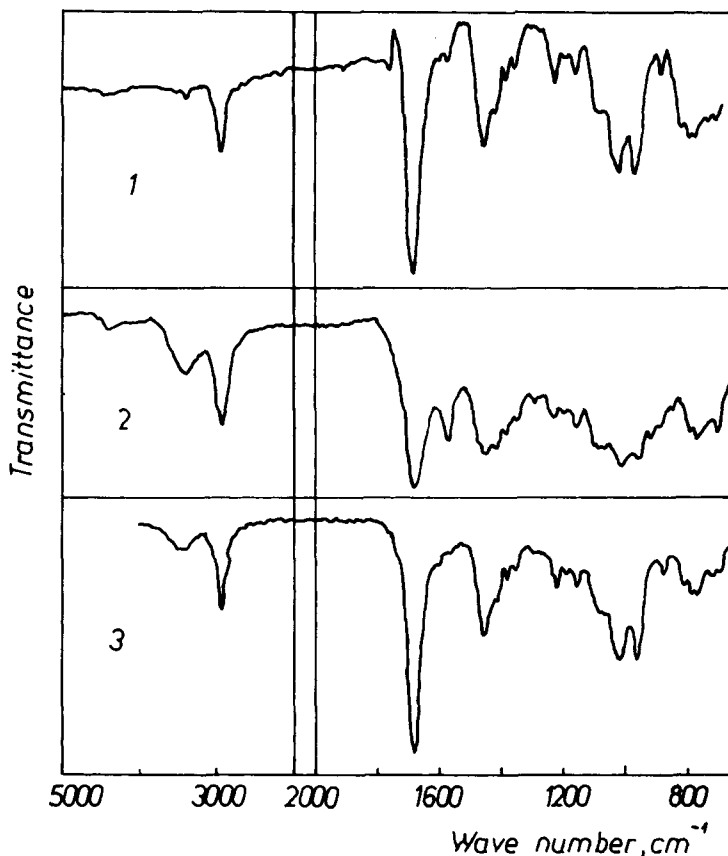


Fig. 1. Infrared spectra of polythioesters derivatives of adipoyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: (1) of 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene; (2) of 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene; (3) of 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene.

The $[\eta]$ values were calculated by extrapolation of $\eta_{sp}/c = f(c)$ functions. The measurements of $[\eta]$ were carried out for polythioester solutions of 0.2, 0.4, 0.6, 0.8, and 1 g/dL in tetrachloroethane (η_{sp} = specific viscosity).

Molecular weights (\bar{M}_w) polythioesters, derivatives of isomeric di(mercaptomethyl)trimethylbenzenes, and some aliphatic acid chlorides as well as the values of intrinsic viscosity are presented in Table I.

X-Ray Investigations

Polythioesters obtained by interfacial polycondensation of isomeric di(mercaptomethyl)trimethylbenzenes with adipoyl and sebacoyl chlorides were examined by means of X-ray analysis. The investigations were carried out for dithiols too.

On the basis of powder diffraction patterns the interplanar distances d_α and the relative intensities (I/I_0) have been obtained. Numerical data presented in Figure 3 indicate various crystallinity degrees of polycondensates. It

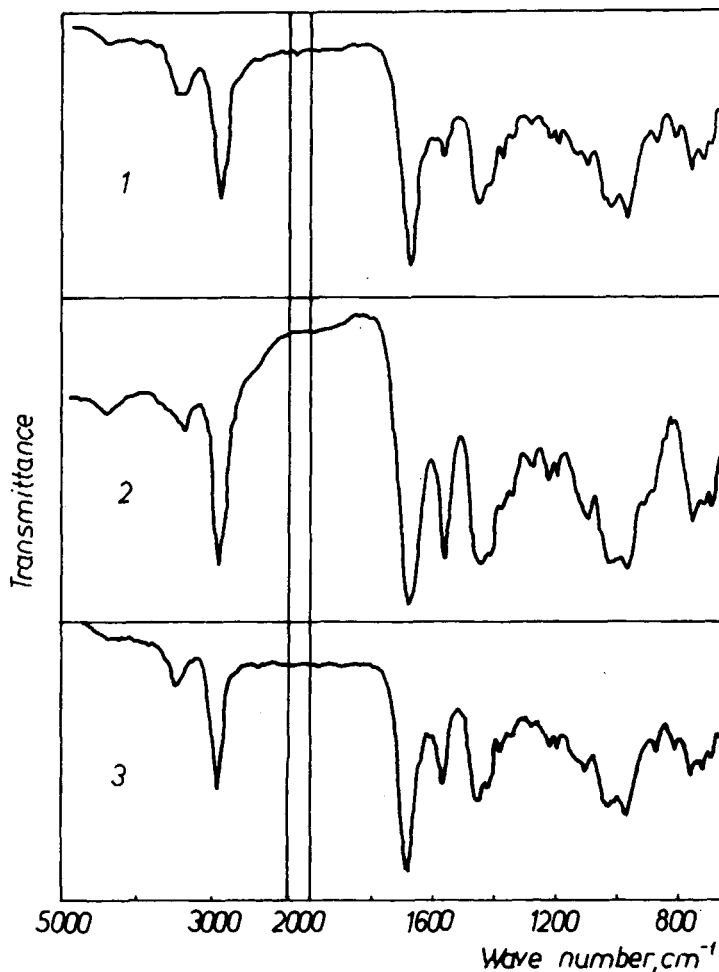


Fig. 2. Infrared spectra of polythioesters derivatives of sebacyl chloride and isomeric di(mercaptomethyl)trimethylbenzenes: (1) of 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene; (2) of 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene; (3) of 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene.

TABLE II
Results of Elementary Analysis of Polythioesters Derivatives of
Di(mercaptomethyl)trimethylbenzenes and Acid Chlorides

Polythioester		Analysis					
		% C		% H		% S	
Dithiol	Acid chloride	Calcd	Found	Calcd	Found	Calcd	Found
4,6-DMM-1,2,3-TMB	Adipoyl	63.32	63.20	6.88	6.60	19.89	19.60
3,5-DMM-1,2,4-TMB		63.10	6.73	19.50			
2,4-DMM-1,3,5-TMB		63.05	6.70	19.70			
4,6-DMM-1,2,3-TMB	Sebacyl	66.62	66.51	7.99	7.83	16.94	16.80
3,5-DMM-1,2,4-TMB		66.40	7.80	16.75			
2,4-DMM-1,3,5-TMB		66.35	7.75	16.60			

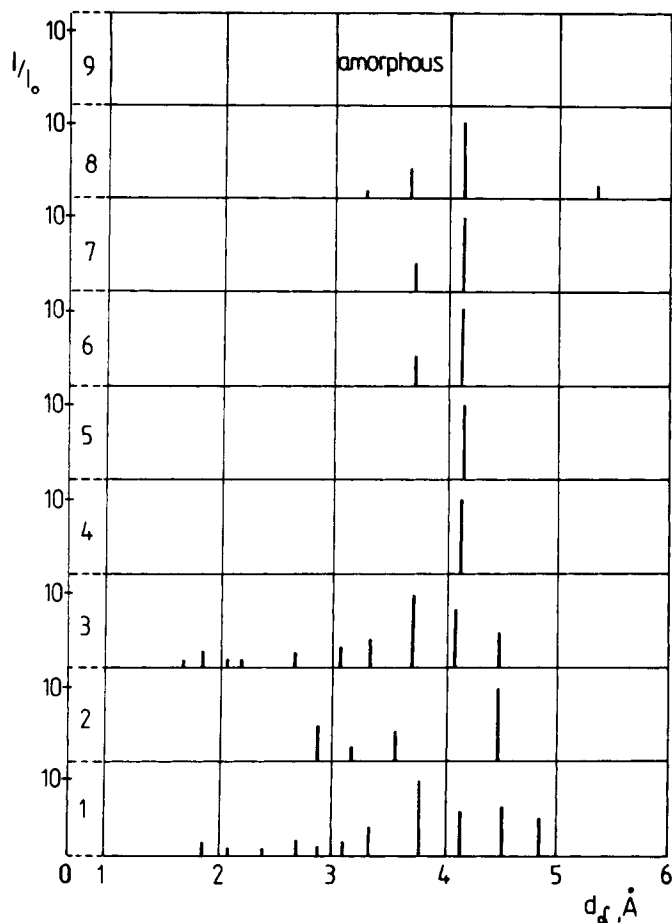


Fig. 3. X-ray diffraction patterns of: (1) 4,6-DMM-1,2,3-TMB; (2) 3,5-DMM-1,2,4-TMB; (3) 2,4-DMM-1,3,5-TMB; (4) polythioester 3,5-DMM-1,2,4-TMB and adipoyl chloride; (5) polythioester 3,5-DMM-1,2,4-TMB and sebacyl chloride; (6) polythioester 4,6-DMM-1,2,3-TMB and adipoyl chloride; (7) polythioester 4,6-DMM-1,2,3-TMB and sebacyl chloride; (8) polythioester 2,4-DMM-1,3,5-TMB and adipoyl chloride; (9) polythioester 2,4-DMM-1,3,5-TMB and sebacyl chloride.

may be supposed that polythioesters from 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene reveal a better ordered structure.

Thermal Properties

Polythioesters were also examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial decomposition, its mass loss in percent, and the temperature of the fastest decomposition process as well as mass loss percent for polythioesters at 250, 300, 350, 400, 500, and 600°C are listed in Table III. The results of the examination are shown only for polythioester of 4,6-DMM-1,2,3-TMB, and adipoyl chloride (Fig. 4).

TABLE III
Thermal Properties of Polythioester

Polythioester	Acid chloride	Thermal analysis ^a				Mass loss (%)					
		T_1 (°C)	K_1 (%)	T_2 (°C)	K_2 (%)	(°C)					
Dithiol						250	300	350	400	500	600
4,6-DMM-1,2,3-TMB	Adipoyl	290	1.5	360	40	1	2	39	67	71.5	82
3,5-DMM-1,2,4-TMB		210	0.5	330	35	3	17	45	56	62.5	74
2,4-DMM-1,3,5-TMB		290	1.5	350	35	0	1	35	68	73	82
4,6-DMM-1,2,3-TMB	Sebacoyl	310	0.2	350	25	0	0	25	56	63	73
3,5-DMM-1,2,4-TMB		280	2.5	360	33	2	3.5	29	57	70	80
2,4-DMM-1,3,5-TMB		300	1	360	35	1	1	24	60	72	81

^a T_1 = temperature of initial exothermic effect from the curve DTA (°C). K_1 = mass loss in the temperature T_1 (%). T_2 = temperature of initial intensive decomposition from the curve DTA (°C). K_2 = mass loss in the temperature T_2 (%).

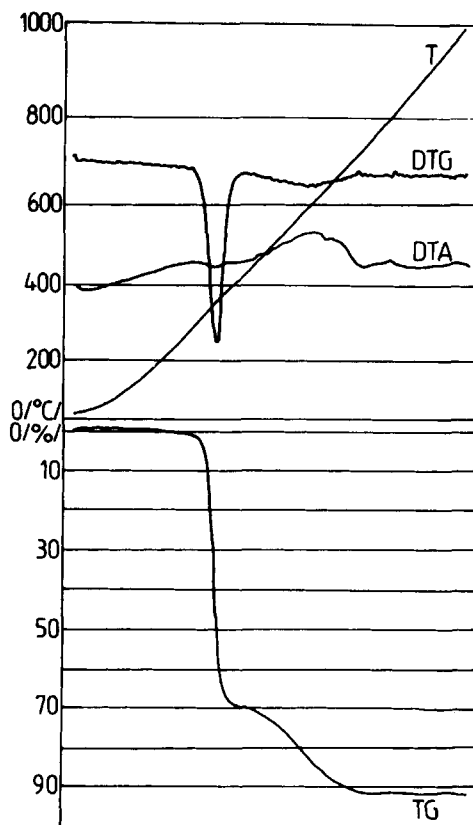


Fig. 4. TGA and DTA of polycondensation product of 4,6-DMM-1,2,3-TMB with adipoyl chloride. Heating time in air, 250 min; heating rate, 4°C/min; amount of polythioester 100 mg; measured relative to Al_2O_3 .

It can be seen from obtained data that decomposition of these compounds begins at 210–310°C and is fastest at 330–360°C.

Chemical Resistance

The polythioesters were treated with some organic solvents, i.e., acetone, benzene, chloroform, methylene chloride, dioxane, dimethylformamide, DMSO, nitrobenzene, phenol:tetrachloroethane (1:3), 10% and concentrated mineral acids as well as 10 and 50% sodium hydroxide. They are dissolved in chlorohydrocarbons but show good resistance to other organic solvents, diluted mineral acid and sodium hydroxide. They all react with concentrated nitric and sulphuric acids.

CONCLUSIONS

Six polythioesters by interfacial polycondensation of isomeric di(mercaptomethyl)trimethylbenzenes and adipoyl as well as sebacoyl chlorides were obtained. The best results of reduced viscosity, yield, molecular weight, and thermal resistance were obtained for polythioesters of 4,6-di(mercaptomethyl)-1,2,3-trimethylbenzene and 2,4-di(mercaptomethyl)-1,3,5-trimethylbenzene.

In contrast to these, polythioesters from 3,5-di(mercaptomethyl)-1,2,4-trimethylbenzene were obtained with good yield, but were characterized by smaller reduced viscosity, molecular weight, and lower thermal resistance.

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