[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

POLYTHIOLESTERS. III. FURTHER STUDIES ON PREPARATION IN EMULSIONS

C. S. MARVEL AND EUGENE A. KRAIMAN[1]

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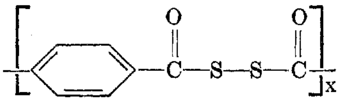
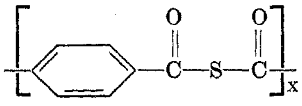
Further investigation of the preparation of polythiolesters has been carried on in order to establish the limits of the polymerization reaction and to clear up uncertainties relating to the work previously reported (1).

In the aliphatic series, polythiolesters were obtained from biallyl and both *cis*- and *trans*-hexahydrodithiolterephthalic acids in emulsion. These polymers were insoluble in both chloroform and *m*-cresol, indicating the probability of some form of cross-linking. The fact that these hydroaromatic dithiol acids polymerized suggests that the failure of dithiolterephthalic and dithioliso-phthalic acids to polymerize may be attributed to the aromatic system.

The decomposition product from the attempted solution polymerization of dithiolterephthalic acid and biallyl (1) has been identified as polyterephthalyl disulfide (I), the oxidation product, rather than polythioterephthalic anhydride (II).



I



II

The infrared spectra (Nujol mull) of the decomposition product and of a sample of I prepared by an unequivocal method were identical, with a strong carbonyl absorption at 1692 cm.$^{-1}$. Polymer II has carbonyl absorption peaks at 1723 cm.$^{-1}$ (strong) and 1670 cm.$^{-1}$ (medium). The soluble polymer obtained in low yield from the same reaction has a less definite spectrum (probably due to a mixture of carbonyl-containing groups) and might contain some thiolester groups. In any case, the oxidation by air is much more rapid than the addition to biallyl.

An attempt was made to establish by further experiment the inverse correlation between water-solubility of the dithiol acid and the molecular weight of its polythiolester by the preparation and polymerization of hexamethylene *bis*(dithiol hydrogen adipate) (III). This compound, which represents about 1½ units of polyhexamethylene dithioladipate, was obtained from the corresponding dicarboxylic acid (IV). It should show the same reactivity as dithioladipic acid in the polymerization with biallyl, since it can be thought of as an intermediate in the polymer formation. However, the larger molecule (III) should be much less water-soluble than dithioladipic acid. Under the same conditions, this ester dithiol acid gave a polymer with an inherent viscosity of 0.48 compared to 0.33 for dithioladipic acid. This difference would of itself be sufficient to support the above correlation, and it is particularly significant in view

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[1] Visking Corporation Fellow in Chemistry 1952–1953.

of the difficulty in purifying so large a molecule. A small percentage of a chain-terminating impurity such as the thiol acid (V), resulting from the incomplete conversion of the diacid to the dithiol acid, would sharply lower the molecular weight of the polymer but not greatly affect the elemental analysis:

$$ACO(CH_2)_4COS(CH_2)_6SCO(CH_2)_4COB$$

III: $A = B = SH$
IV: $A = B = OH$
V: $A = SH; B = OH$

Compounds corresponding to the dithiol ester diacid (IV) were prepared in the succinate, glutarate, and phthalate series in an attempt to obtain polythiolesters based on dithiol acids which do not exist or are very unstable. However, the conversions from the intermediate diacids to the dithiol acids resulted in mixtures from which no definite products could be obtained. The new intermediates in these series are included in the experimental section. Another indication of the unreactivity of aromatic thiol acid groups in the addition to double-bond reaction was the failure to obtain the isophthalate and terephthalate intermediates corresponding to IV by the addition of monothiolisophthalic and monothiolterephthalic acids to biallyl under the influence of ultraviolet light.

The use of ultraviolet light to initiate emulsion polymerizations of this type was not successful since the polymers obtained were only comparable to those which could be obtained by merely allowing air to act as the initiator. 1-Hexyne was employed as the unsaturated component in this polymerization, but the results were far inferior to those obtained with biallyl. Possibly the second addition to the acetylenic bond is much slower than the first. An attempt to prepare and polymerize thiolundecylenic acid was unsuccessful in that the crude monomer polymerized before it could be purified. For this reason, the polymers had low molecular weights.

EXPERIMENTAL

We are indebted to Mrs. Katherine Pih, Mr. Joseph Nemeth, and Mrs. L. Chang for the microanalyses and to Miss Helen Miklas for the determination and interpretation of the infrared spectra. All melting points are uncorrected.

Phenyl hydrogen adipate. To 100 g. of adipyl chloride heated to about 100° was added 55 g. of phenol. After brief stirring, the mixture was heated until the reaction was complete. When cool, the reaction mixture was allowed to react with excess sodium bicarbonate solution. The insoluble diphenyl adipate was removed by filtration, and the filtrate was acidified. The precipitate was separated by filtration, dried, and recrystallized from petroleum ether to give 39 g. (32%) of product, m.p. 93–94°. About the same yield was obtained irrespective of the order of mixing of the reactants.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35.
Found: C, 64.90; H, 6.28.

p-(Chloroformyl)benzoic acid. A mixture of 150 g. of terephthalyl chloride, 15 ml. of water, and 1½ liters of absolute ether was refluxed for 45 hours. The solid material was separated by filtration, and more solid was obtained by evaporation of the filtrate to dryness. The combined solid material was recrystallized to give 98 g. (72%) of product which did not melt but appeared to decompose at about 200°.

Anal. Calc'd for $C_8H_5ClO_3$: C, 52.05; H, 2.73.
Found: C, 52.12; H, 2.91.

m-(Chloroformyl)benzoic acid. In the same manner as above, 90 g. of isophthalyl chloride and 8.5 ml. of water refluxed in 1 liter of absolute ether afforded 32 g. (39%) of product, m.p. 130°d., after precipitation from benzene solution with petroleum ether.

Anal. Calc'd for $C_8H_5ClO_3$: C, 52.05; H, 2.73.

Found: C, 52.47; H, 2.95.

Attempted preparation of o-(chloroformyl)benzoic acid. When a partial hydrolysis of phthalyl chloride was carried out in the same manner as above, the major product was phthalic anhydride.

Monothioladipic acid. (a) A solution of 39 g. of phenyl hydrogen adipate in 200 ml. of absolute ethanol was added to a stirred, refluxing solution of sodium hydrosulfide prepared by dissolving 25 g. of sodium in 500 ml. of absolute ethanol and saturating with hydrogen sulfide. The mixture was refluxed with stirring for six hours, after which the alcohol was distilled under reduced pressure. The residue was dissolved in ice-water, acidified, and extracted with ether. The dried ether extract was evaporated under reduced pressure, and the residue was recrystallized by chilling (acetone-Dry Ice bath) from petroleum ether containing a little absolute ether. The yield was 9 g. (33%), m.p. 40–41°.

Anal. Calc'd for $C_6H_{10}O_3S$: C, 44.42; H, 6.21.

Found: C, 44.60; H, 6.27.

(b) To a mixture of 100 g. of adipic acid, 70 g. of triethylamine, and 500 ml. of methylene chloride cooled by a Dry Ice-carbon tetrachloride bath was added 40 g. of ethyl chloroformate over a period of one hour. Another 70 g. of triethylamine was introduced, and the mixture was saturated with hydrogen sulfide. The temperature of the reaction mixture was kept between −10 and −20° at all times up to this point when the cooling bath was removed and the mixture allowed to come to room temperature. After acidification, the methylene chloride layer was separated, dried, and evaporated under reduced pressure. The crude product was purified as above to give 21 g. (35%) of product, m.p. 38–39°.

Monothiolglutaric acid. To a stirred, cooled solution of 100 g. of sodium sulfide (nonahydrate) in 200 ml. of water, saturated with hydrogen sulfide before and during the reaction, was added 19.5 g. of glutaric anhydride (2) over a period of one hour. The resulting solution was acidified, and the crude product was obtained by ether extraction and purified by dissolving in petroleum ether, filtering, and chilling the solution with an acetone-Dry Ice bath. The yield was 10.5 g. (42%) m.p. 30–31°.

Anal. Calc'd for $C_5H_8O_3S$: C, 40.52; H, 5.44.

Found: C, 40.91; H, 5.44.

Monothiolsuccinic acid. This compound was obtained by the reaction of 25 g. of succinic anhydride with a solution of 150 g. of sodium sulfide (nonahydrate) in 250 ml. of water saturated with hydrogen sulfide in the same manner as above. Purification was by precipitation from a benzene solution with excess petroleum ether. The yield was 14.5 g. (43%), m.p. 60–61°.

Anal. Calc'd for $C_4H_6O_3S$: C, 35.81; H, 4.51.

Found: C, 36.06; H, 4.46.

Attempted preparation of monothiolphthalic acid. The reaction of phthalic anhydride in the same manner as above yielded a mixture of phthalic anhydride and phthalic acid. It is believed that the phthalic anhydride resulted from the decomposition of the desired product upon acidification.

Monothiolterephthalic acid. *p*-(Chloroformyl)benzoic acid (30 g.) was converted to the desired product by the method of Sunner and Nilson (3). The crude product was separated from the acidified reaction mixture by filtration, dried, and sublimed under reduced pressure. The yield was 20 g. (68%) of product which did not melt up to 330° (probably decomposed).

Anal. Calc'd for $C_8H_6O_3S$: C, 52.73; H, 3.32.

Found: C, 52.51; H, 3.60.

Monothiolisophthalic acid. In the same manner, 20 g. of *m*-(chloroformyl)benzoic acid yielded 10 g. (51%) of product after vacuum sublimation; m.p. 185°d.

Anal. Calc'd for $C_8H_6O_3S$: C, 52.73; H, 3.32.

Found: C, 52.52; H, 3.37.

Hexamethylene bis(monothiol-O-hydrogen dicarboxylates) (a) Addition of monothioldicarboxylic acids to biallyl. A benzene solution of biallyl and slightly more than two molar equivalents of the monothioldicarboxylic acid was irradiated with ultraviolet light for the indicated time. The resulting solid was separated by filtration and recrystallized from benzene. Table I contains the experimental data.

(*b*) *Reaction of hexamethylenedithiol with anhydrides.* A mixture of hexamethylenedithiol and slightly more than two molar equivalents of the anhydride was refluxed for the indicated time in pyridine containing a trace of sodium hydroxide. The mixture was allowed to cool before being taken up in water and acidified. The resulting solid was separated by filtration and dried. The succinic and glutaric derivatives were recrystallized from benzene while petroleum ether was used for the phthalic derivative. In those cases where the same compound had been prepared by method *a*, a mixed melting point was found to be undepressed. Table II contains the experimental data.

TABLE I

HEXAMETHYLENE BIS(MONOTHIOL-O-HYDROGEN DICARBOXYLATES)

MONOTHIOL ACID	ACID, g.	BIALLYL, g.	BENZENE, ml.	TIME, hrs.	YIELD		M.P., °C.	ANALYSES			
								C		H	
					g.	%		Calc'd	Found	Calc'd	Found
Succinic	13	3.50	200	65	10	67	122–123	47.98	48.04	6.33	6.45
Glutaric	10	2.80	100	65	75	58	106–107	50.77	51.02	6.92	6.85
Adipic	6.5	1.50	50	12	6	80	123–124	53.18	53.08	7.44	7.44
	19	4.50	50	14	16	73	122–123	—	—	—	—
Terephthalic	15	3.00	150[a]	65	polymeric			—	—	—	—
Isophthalic	9	1.80	150[a]	65	polymeric			—	—	—	—

[a] These reactions were carried out in dioxane solution.

TABLE II

HEXAMETHYLENE BIS(MONOTHIOL-O-HYDROGEN DICARBOXYLATES)

ANHYDRIDE	ANHYDRIDE, g.	DITHIOL, g.	PYRIDINE, ml.	TIME, hrs.	YIELD		M.P., °C.
					g.	%	
Succinic	21	15	200	3	18	51	123–124
	15	10	50	5	9	39	121–122
Glutaric (2)	15	9.5	100	3	12	50	103–104
Phthalic	21	10	200	72	9	30	137.5–138[a]
	17	8	200	120	2.5	11	136–138

[a] *Anal.* Calc'd for $C_{22}H_{22}O_6S_2$: C, 59.17; H, 4.97. Found: C, 59.31; H, 5.21.

(*c*) The reaction of *m*- and of *p*-(chloroformyl)benzoic acids with hexamethylenedithiol in refluxing dioxane or benzene resulted in polymeric material.

Dithiol acids. These were prepared by the method of Sunner and Nilson (3), with the modifications described previously (1). Two new compounds of this type were obtained from 10 g. of each of the acid chlorides (4) and were purified by chilling (acetone-Dry Ice bath) from petroleum ether solution.

trans-Hexahydrodithiolterephthalic acid. Yield: 7 g. (72%); m.p. 80–80.5°.

Anal. Calc'd for $C_8H_{12}O_2S_2$: C, 47.03; H, 5.92.

Found: C, 47.47; H, 6.06.

cis-Hexahydrodithiolterephthalic acid. Yield: 5 g. (51%); m.p. 37.5–38°.

Anal. Calc'd for $C_8H_{12}O_2S_2$: C, 47.03; H, 5.92.
Found: C, 47.58; H, 6.07.

Hexamethylene bis(dithiol hydrogen dicarboxylates). (*a*) *Hexamethylene bis(dithiol hydrogen adipate).* To a solution of 10 g. of hexamethylene bis(monothiol-O-hydrogen adipate) and 2.5 g. of triethylamine in 100 ml. of methylene chloride, cooled by a Dry Ice-carbon tetrachloride bath, was added 3 g. of ethyl chloroformate during 15 minutes with stirring. Another 2.5 g. of triethylamine was introduced, and the addition of 3 g. of ethyl chloroformate was repeated. After the addition of 5 g. more of triethylamine, the mixture was saturated with hydrogen sulfide, the temperature of the mixture being kept between −10 and −20° up to this point. Upon completion of the hydrogen sulfide saturation the cooling bath was removed, and the mixture was allowed to come to room temperature. Excess cold, dilute hydrochloric acid was used to acidify the mixture. The organic layer was separated, dried, and evaporated under reduced pressure. The residue was purified by chilling from petroleum ether with an acetone-Dry Ice bath. The yield was 4 g. (37%), m.p. 44–45°.

Anal. Calc'd for $C_{18}H_{30}O_4S_4$: C, 49.28; H, 6.89.
Found: C, 49.13; H, 6.95.

TABLE III

EMULSION POLYMERIZATIONS

DITHIOL ACID	UNSATURATED MONOMER	INITIAL pH	YIELD, %	INHERENT VISCOSITY[a]
trans - Hexahydrodithiolterephthalic	Biallyl	4.2	[b]	[c]
cis-Hexahydrodithiolterephthalic	Biallyl	4.2	99	[d]
Hexamethylene bis(dithiol hydrogen adipate)	Biallyl	4.2	85	0.48
Dithioladipic (1)	Biallyl	4.1	87	.33
Dithiolsebacic	1-Hexyne	4.2	61	.29
	1-Hexyne	4.2	60	.33
	Biallyl[e]	4.2	90	.27
	1-Hexyne[e]	4.2	49	.15

[a] In chloroform at 25°. [b] Insoluble in chloroform; not precipitated; crude material in excess of theoretical yield. [c] Insoluble in both chloroform and *m*-cresol. [d] Precipitated polymer no longer soluble in chloroform; insoluble in *m*-cresol. [e] Ultraviolet light-initiated.

(*b*) When the above reaction was carried out with the corresponding succinate, glutarate, and phthalate, no definite product could be isolated.

Polythiolundecylenic acid. (*a*) The conversion of 21 g. of freshly distilled undecylenyl chloride to thiolundecylenic acid was carried out in the usual manner according to the method of Sunner and Nilson (3). Upon acidification of the reaction mixture, the clear organic layer separated on top but became cloudy and solidified within a very short time. This solid was separated by filtration, dissolved in chloroform, and precipitated by filtering into methanol. After drying under reduced pressure, it amounted to 20 g. (97%), inherent viscosity 0.24.

(*b*) Undecylenic acid (10 g.) was converted to the thiol acid with triethylamine, ethyl chloroformate, and hydrogen sulfide (5) as described for hexamethylene bis(dithiol hydrogen adipate), except that ether was used as the solvent. The reaction mixture was filtered and evaporated under reduced pressure. The residue was taken up in 50 ml. of distilled water, placed in a 4-oz. polymerization bottle with 10 ml. of 50% MP-635-S[2] solution and 30

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[2] We are indebted to Dr. Stanley Detrick, Jackson Laboratory, E. I. du Pont de Nemours and Company, Inc., for a supply of this emulsifier and for the following analysis of it:

ml. of 2 *N* sulfuric acid. After shaking, 1 ml. of 3% hydrogen peroxide solution was added, the bottle was capped, and then tumbled in the 30°-bath for one day. The polymer was coagulated and recovered in the usual manner (1). The yield was 7 g. (64%), inherent viscosity 0.26.

Polyterephthalyl disulfide. A solution of 2 g. of dithiolterephthalic acid in methanol was treated with methanolic iodine solution until the iodine color persisted. The precipitate was separated by filtration, thoroughly washed with methanol, and dried under reduced pressure. About 2 g. of polymer was obtained.

Polythioterephthalic anhydride. A solution of 2 g. of dithiolterephthalic acid and 2 g. of pyridine in 250 ml. of chloroform was treated with 2 g. of terephthalyl chloride, added in small portions with stirring. A precipitate formed during the addition. The mixture was poured into methanol, and the solid material was separated by filtration, washed with methanol, and dried under reduced pressure. About 3.5 g. of polymer was obtained.

Emulsion polymerization. The procedure was the same as that described previously (1). Quartz flasks were used for the ultraviolet light-initiated polymerizations. These were mechanically shaken at room temperature. Table III contains the data for these polymerizations for which the following standard conditions had been adopted:

1. Initiator: 0.5 ml. of 3% hydrogen peroxide solution (except where ultraviolet light was employed).
2. Time: one day.
3. Monomers balanced.
4. Initial *p*H: 4.0 to 4.6.
5. Emulsifier concentration: 10 ml. of 50% MP-635-S solution per 100 ml. of distilled water.

SUMMARY

New polythiolesters have been prepared in emulsion from aliphatic dithiol acids and both biallyl and 1-hexyne. The product of the attempted solution polymerization of dithiolterephthalic acid and biallyl has been identified as the oxidation product of the acid. The effect of water solubility of the dithiol acid on the results of an emulsion polymerization has been demonstrated. A polymer has been obtained from an unsaturated thiol acid (thiolundecylenic acid) which was found to be too unstable to isolate and purify.

URBANA, ILLINOIS

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C_{16}-sodium alkanesulfonate, 49.5%; unreacted hydrocarbon, 10.3%; sodium chloride, 0.80%; sodium sulfate, 0.4%; isopropyl alcohol, about 3% to maintain a homogeneous aqueous solution.