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

Polythiolesters

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Polythioesters of the type $[SCORCOS–R']_x$ have been prepared from a variety of dibasic acid chlorides and aliphatic dithiols. They have also been prepared by the addition of dibasic thio acids to the non-conjugated diolefin biallyl. The polythiolesters thus far obtained are relatively low in molecular weight as judged by inherent viscosity, melt higher than oxygen analogs as a rule, show definite evidence of crystallinity in their X-ray patterns, and appear to be relatively stable to hydrolysis in distilled water.

The purpose of this study was to prepare polythiolesters, a class of polymers which had not been reported when this work was initiated. The removal of hydrogen chloride from a dithiol and a dibasic acid chloride, the elimination of water from a dithiol and a dicarboxylic acid, the splitting out of a metallic halide from a dimercaptide and a dibasic acid chloride and also from a dihalide and a dimetallic salt of a dibasic thio acid are methods analogous to those that have been used to produce simple thiol esters[2] and hence might be considered for polymer formation. During the course of the present investigation the preparation of a high molecular weight polymer from sebacyl chloride and hexamethylenedithiol was described in a patent.[3]

In the present study we have prepared polythiolesters from dibasic acid chlorides and dithiols under varying conditions. The best polymers were obtained by forming a pyridine complex of the dibasic acid chloride in benzene and then adding the dithiol at reflux temperatures. By this method adipyl chloride and a variety of dithiols gave the polythiolesters listed in Table I.

TABLE I

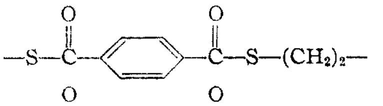
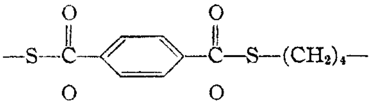
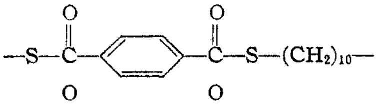
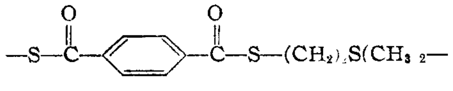
POLYTHIOLESTERS FROM ADIPYL CHLORIDE AND DITHIOLS

Dithioladipate	Formula	M. p., °C.	Inherent viscosity in $CHCl_3$	Yield, %	Analyses,[a] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Polyethylene	$—SCO(CH_2)_4—COS(CH_2)_2—$	111-125	0.13	62	47.03	47.78	5.92	6.13	31.39	31.08
Polytetramethylene	$—SCO(CH_2)_4COS(CH_2)_4—$	95-100	.13	50	51.69	51.52	6.94	7.00	27.60	27.82
Polyhexamethylene	$—SCO(CH_2)_4COS(CH_2)_6—$	97-104	.15	51	55.35	55.37	7.74	7.86	24.62	24.90
Polydecamethylene	$—SCO(CH_2)_4COS(CH_2)_{10}—$	70-75	.10	57	60.71	60.74	8.92	9.07	20.26	19.98
Polydiethylenesulfide	$—SCO(CH_2)_4COS(CH_2)_2S(CH_2)_2—$	67-70	.12	47	45.42	46.25	6.10	6.20	36.38	36.10

[a] Microanalyses reported in this paper were performed by Miss Emily Davis, Miss Rachel Kopel and by the Clark Microanalytical Laboratories, Urbana, Illinois.

TABLE II

POLYTHIOLESTERS FROM TEREPHTHALYL CHLORIDE AND DITHIOLS

Dithiolterephthalate	Formula	M. p., °C.	Yield, %	Analyses % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Polyethylene		335-340	68	53.55	53.62	3.59	3.74	29.59	28.83
Polytetramethylene		230-260	70	57.11	57.03	4.79	4.78	25.41	25.18
Polydecamethylene		136-144	71	64.24	63.43	7.19	7.34	19.06	18.77
Polydiethylenesulfide		140-146	73	50.67	50.73	4.25	4.21	33.82	33.53

Terephthalyl chloride also worked well in this reaction and the polythiolesters prepared from it and various dithiols are described in Table II.

Attempts to use fumaryl chloride, succinyl chloride and phthalyl chloride in this general reaction gave only dark colored oils and tars.

In view of the demonstration by Holmberg[4] that thio acids add to olefins in good yields to give thiol esters, it seemed reasonable that the reaction of a dibasic thio acid with a diolefin might provide a general method of preparing polythiolesters just as the addition of dithiols to diolefins has been found a good way to produce polyalkylene sulfides.[5] This seemed particularly attractive since Cunneen[6] has shown that in parallel cases the thio acids seem to add to olefins more readily than do thiols. Sunner and Nilson[7] developed a method of producing dithioladipic acid from adipyl chloride, pyridine and hydrogen sulfide. We were able to apply this method to pimelic, suberic, azelaic, sebacic, tere-

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[1] Monsanto Chemical Company Fellow in Chemistry, 1949-1950.

[2] H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., second edition, 1943, pp. 848, 932-933, 936.

[3] Wingfoot Corp., British Patent 630,625, Oct. 18, 1949; *C. A.*, **44**, 3741 (1950).

[4] B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **12B**, No. 47, 3 pp. (1938); *C. A.*, **32**, 4151 (1938).

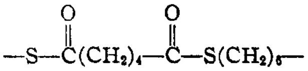
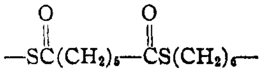
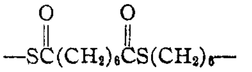
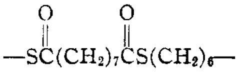
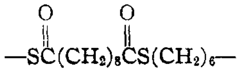
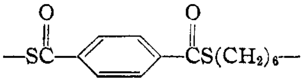
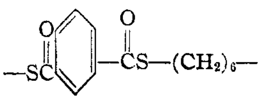
[5] (a) C. S. Marvel and R. R. Chambers, THIS JOURNAL, **70**, 993 (1948); (b) C. S. Marvel and P. H. Aldrich, *ibid.*, **72**, 1978 (1950); (c) C. S. Marvel and H. E. Baumgarten, *J. Poly. Sci.*, in press; (d) C. S. Marvel and G. Nowlin, THIS JOURNAL, **72**, 5026 (1950).

[6] J. P. Cunneen, *J. Chem. Soc.*, **134** (1947).

[7] S. Sunner and T. Nilson, *Svensk. Kem. Tid.*, **54**, 163 (1942); *C. A.*, **38**, 3249 (1944).

TABLE III

POLYTHIOLESTERS FROM DIBASIC THIO ACIDS AND BIALLYL

Polyhexamethylene polymer	Formula	M. p., °C.	Inherent viscosity in $CHCl_3$	Yield	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Dithioladipate	 $-S-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-S(CH_2)_6-$	99–102	0.16	72	55.35	55.37	7.74	7.86	24.62	24.90
Dithiolpimelate	 $-S\overset{O}{\overset{\|}{C}}(CH_2)_5-\overset{O}{\overset{\|}{C}}S(CH_2)_6-$	61–64	.19	61	56.89	56.62	8.08	7.94	23.37	23.63
Dithiolsuberate	 $-S\overset{O}{\overset{\|}{C}}(CH_2)_6\overset{O}{\overset{\|}{C}}S(CH_2)_6-$	82–85	.12	69	58.29	58.16	8.39	8.66	22.23	21.94
Dithiolazelate	 $-S\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}S(CH_2)_6-$	68–72	.21	75	59.56	59.79	8.66	8.83	21.20	20.95
Dithiolsebacate[a]	 $-S\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}S(CH_2)_6-$	68–80[a]	.17	65	60.71	60.58	8.92	8.89	20.26	19.92
Dithiolterephthalate		160–200	.07	92	59.97	60.14	5.75	5.94	22.87	22.98
Dithiolisophthalate		75–82	.07	22	59.97	60.23	5.75	6.00	22.87	22.59

[a] A recent British patent[3] describes a polymer prepared from sebacyl chloride and hexamethylenedithiol having a melting point of 107–109°.

phthalic and isophthalic acids in a fairly satisfactory way. The dibasic thio acids prepared in the aliphatic series are low melting (below 35°) and the adipic derivative has already been shown to decompose on distillation. Hence the compounds which were prepared were rather crude products with a disagreeable odor. They hydrolyzed in water and this made the use of emulsion techniques unsatisfactory for polymer formation. Their low purity also made the formation of high polymers impossible. Dithiolterephthalic acid (m.p. 123–125°) and dithiolisophthalic acid (m.p. 67–73°) were light tan and pink solids, respectively, but even these were not readily purified due to easy hydrolysis and oxidation.

By the use of benzene solutions of the crude dibasic thio acids and biallyl under the ultraviolet lamp, polymeric thiol esters were obtained in fair yield and with fair inherent viscosities (0.07–0.21) in chloroform solution. The aliphatic polythiolesters which were obtained had higher inherent viscosities. The aromatic polythiolesters were so slightly soluble in benzene that they precipitated out quickly before high polymers could form. Chloroform proved to be a good solvent for the polythiolesters but was unsatisfactory as a solvent for their formation since it is known that it may become involved in the radical reactions of formation to yield low molecular weight polymers containing chlorine.

The polythiolesters which have been obtained by the addition of dibasic thio acids to biallyl are listed in Table III.

The polythiolesters prepared from dibasic thio acids and biallyl were all light tan and none was obtained white, but those prepared from the acid chlorides and dithiols were white. The molecular weights are apparently low as indicated by the inherent viscosity figures and by the fact that none of our esters would cold draw to give fibers. In general a polythiolester melts higher than does the polyester from the corresponding dibasic acid and glycol. Thus polyhexamethylene dithioladipate, m.p. 97–104°, and polyhexamethylene adipate, m.p. 56°[8]; polyhexamethylene dithiolsebacate, m.p. 68–80°, and polyhexamethylene sebacate, m.p. 67°[8]; polyethylene dithiolterephthalate, m.p. 335–340°, and polyethylene terephthalate, m.p. 255–260°.[9]

The infrared pattern (Fig. 1) of the polyhexamethylene dithioladipate prepared from hexamethylenedithiol and adipyl chloride agreed in all respects with that from the ester prepared from dithioladipic acid and biallyl which shows this addition proceeded in a non-Markownikoff manner as was expected.[10] The X-ray patterns of polyhexamethylene dithioladipate showed sharp peaks indicating considerable crystallinity. The pattern for polyethylene dithiolterephthalate showed little sign of crystallinity.[11]

The polythiolesters were all soluble in chloroform and benzene, although the solubilities of the dithiolterephthalic esters were very low. None of the esters dissolved in water or showed evidence of hydrolysis when shaken with distilled water at 30° for four days. The esters were readily hydrolyzed with 5% alcoholic sodium hydroxide solution. The esters had little odor but it was difficult to remove the residual odors of the sulfur containing monomers.

Experimental

All melting points were taken on an Eimer–Amend block and are uncorrected.

Reaction of Adipyl Chloride–Pyridine Complex and Hexamethylenedithiol.—In a three-necked 250-ml. flask equipped

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[8] W. H. Carothers and J. A. Arvin, THIS JOURNAL, **51**, 2560 (1929).

[9] D. V. N. Hardy, *J. Soc. Chem. Ind.* (*London*), **67**, 426 (1948).

[10] We are indebted to Miss Elizabeth M. Petersen for the infrared analyses.

[11] We are indebted to Dr. J. Fuchs and Professor G. L. Clark for these X-ray studies.

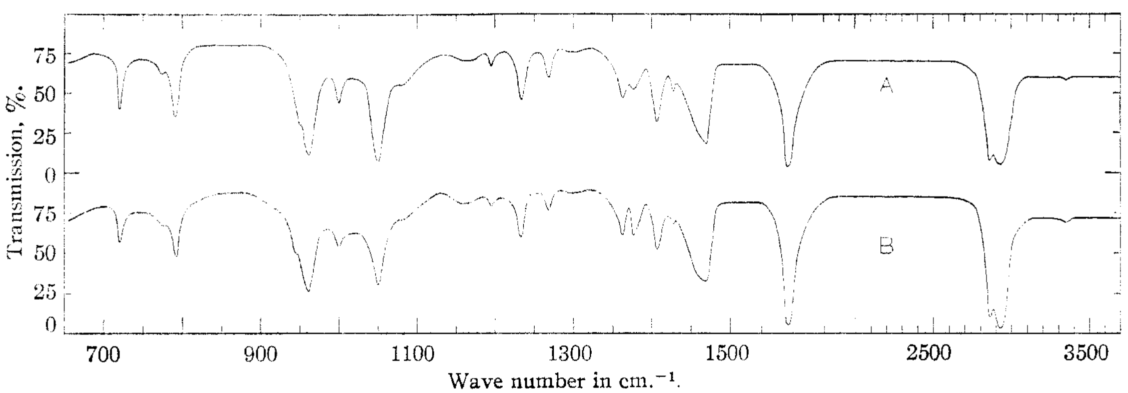

Fig. 1.—A, Polymer from adipyl chloride and hexamethylenedithiol; B, polymer from biallyl and dithioladipic acid.

with a mechanical stirrer, dropping funnel, and condenser were placed 5 ml. of reagent grade pyridine and about 50 ml. of dry, thiophene-free benzene. The mixture was stirred and cooled in an ice-water-bath and 3.66 g. of adipyl chloride in about 10 ml. of benzene was added dropwise to the cooled, well-stirred solution. The white solid complex formed immediately. To this reaction mixture was added 3.01 g. of hexamethylenedithiol dissolved in about 10 ml. of benzene. Since it appeared that no reaction was occurring, an additional 5 ml. of pyridine was added, and the mixture was heated to reflux and stirred at that temperature for about 24 hours. When the mixture was cool, the pyridine hydrochloride was filtered and dissolved in hot water. The small amount of insoluble material which remained, was filtered, dissolved in chloroform, reprecipitated with methanol, filtered and dried. The weight was 0.27 g.; the inherent viscosity was 0.15; and the m.p. was 97–104°.

The benzene filtrate was evaporated to a volume of about 25 ml., and this solution was added to about 100 ml. of methanol. The solid thus obtained was filtered, reprecipitated, and dried. It weighed 2.10 g., m.p. of 87–90°; inherent viscosity 0.08.

An additional 0.32 g. of polymer was isolated from the filtrate in the reprecipitation step. Thus, the total yield of solid polymer was 2.69 g. or 51.5%.

Other Dibasic Acid Chlorides and Dithiols.—Using essentially this technique the other polythiolesters listed in Tables I and II were prepared.

Dibasic Thio Acids.—The procedure of Sunner and Nilson[7] for dithioadipic acid was used with minor variations. The acids were very difficult to purify and in general were precipitated from alkaline solution by adding acid, cooled if necessary to solidify the dibasic thio acid, filtered and dried in a vacuum desiccator. The details of yields, analyses and properties of the impure dibasic thio acids are given in Table IV.

TABLE IV

PREPARATION AND PROPERTIES OF DIBASIC THIO ACIDS

Acid chlorides used	Amt., g.	Reagent grade pyridine, g.	Reacn. time after acid chloride was added, hr.	Yield of dibasic thio acid g.	Yield of dibasic thio acid %	M. p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
Adipyl	40	191.4	1	29	75.5	About 25						
Azelayl	19.8	100.1	0.5	17.6	91	20–25						
Suberyl	21.1	101.5	1	17	82.5	20–25	46.57	50.76	6.84	6.81	31.08	23.26
Pimelyl	20	100	1	17	85	About 5[a]	43.72	45.18	6.29	6.70	33.35	32.41
Sebacyl	20	100.5	1	20	98	30–35	51.24	52.82	7.74	7.51	27.36	22.82
Terephthalyl[b]	10.7	97.8	0.5	10.5	100	125–128	48.46	48.08	3.05	2.86	32.35	29.33
Isophthalyl[c]	20	101.1	0.75	18.2	93.5	67–73	48.46	50.79	3.05	3.11	32.35	24.35

[a] d^{20}_4, 1.158; n^{20}_D 1.5295. [b] Added as a solution in 35 ml. of benzene. [c] Added as a solution in 25 ml. of benzene.

Solution Polymerization of Dithioladipic Acid and Biallyl in Cyclohexane Solution.—In a 100-ml. quartz flask was placed 1.76 g. of crude dithioladipic acid, 0.82 g. of biallyl, and about 40 ml. of purified cyclohexane. All of the acid did not dissolve in the cyclohexane. The flask was stoppered with a cork and placed under the ultraviolet lamp (at a distance of about six inches from a polychromatic source of ultraviolet light, Hanovia Type 7420). After 3 hours of exposure, a solid began to form on the wall of the flask. The flask was removed after a total exposure time of 15 hours. When the solid was filtered and dried, it weighed 0.69 g., a yield of 26.8%. The solid was dissolved in chloroform, the solution was filtered, and the polymer was reprecipitated with methanol. The melting point was 91–95°, and the inherent viscosity was 0.13.

In Benzene Solution.—In a 50-ml. quartz flask was placed 3.08 g. of crude dithioladipic acid, 1.43 g. of biallyl, and 20 ml. of dry, thiophene-free benzene. After an exposure time of about 18 hours under the ultraviolet lamp, a solid weighing 1.74 g. was filtered from the solution. An additional 1.51 g. was obtained by diluting the filtrate with methanol. The total weight of solid polymer was 3.52 g., a yield of 72%. Both samples were reprecipitated by dissolving them in chloroform, filtering the chloroform solution, and pouring the solution into excess methanol. The first fraction had a melting point of 99–102° and an inherent viscosity of 0.16, while the second fraction had a melting point of 92–95° and an inherent viscosity of 0.12.

General Procedure for Solution Polymerization of Dibasic Thio Acids and Biallyl.—The other polymers from dibasic thio acids and biallyl were made and isolated according to the following general procedure. About 0.01 or 0.02 mole of each monomer and 200 ml. of dry, thiophene-free benzene were placed in a quartz flask under the ultraviolet lamp. Except in the case of dithiolterephthalic acid where some of the polymer came out of solution, the polymers remained in solution with that amount of benzene. After about a day of irradiation, the polymers were isolated by evaporating the benzene solution at the pressure of the water aspirator to a volume of about 50 ml. and then pouring the solution into about 200 ml. of methanol. The solid polymer thus obtained was filtered, dried and weighed. It was then dissolved in reagent-grade chloroform, and the solution was filtered through a sintered-glass funnel into about four volumes of methanol which had also been filtered. The reprecipitated polymer was filtered and dried. All inherent viscosities were taken in chloroform. The data on the polymers obtained by this method are recorded in Table III. The yields varied from 22 to 92% depending on the purity of the dibasic thio acid.

URBANA, ILLINOIS RECEIVED AUGUST 14, 1950