[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

POLYTHIOLESTERS. II. PREPARATION IN EMULSIONS

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Recent work (1) has demonstrated that polythiolesters can be obtained by the ultraviolet light-catalyzed addition of dithiol acids to unconjugated diolefins in hydrocarbon solvents. The polymers thus prepared had low molecular weights as measured by their inherent viscosity. The work on emulsion polymerization described here was undertaken to obtain higher molecular weight polymers.

When tetrahydrofuran was used as the solvent instead of cyclohexane or benzene, a polythiolester was obtained from dithioladipic acid and biallyl (1,5-hexadiene) which had an inherent viscosity of 0.36 instead of 0.16 as obtained before. But at this molecular weight the polymer separated from solution and further growth was prevented. Polymerization without a solvent produced polyhexamethylene dithioladipates of inherent viscosity of only 0.17 to 0.22, and hence this type of polymerization was not further investigated.

It was found that emulsion polymerization yielded high molecular weight polymers from biallyl and those aliphatic dithiol dibasic acids which are not too soluble in water. Thus dithiolsebacic acid gave high polymers (inherent viscosity 1.2–2.0) while dithioladipic acid gave polymers which were higher in molecular weight than those obtained in solution or bulk (inherent viscosity up to 0.5) but were much lower in molecular weight than the sebacic acid derivatives. The water solubility is in the reverse order, 3.3 g. per l. for dithioladipic acid, as against 0.2 g. per l. for dithiolsebacic acid. A few preliminary experiments designed to reduce the solubility of the dithiol acid in the aqueous phase by the addition of salt were unsuccessful, since the emulsions broke when salt was added.

Two different oxidation initiators, hydrogen peroxide and ammonium persulfate-sodium metabisulfite, have been used. Hydrogen peroxide gave the best results when used in the *p*H range of 4.0 to 4.6, and the persulfate initiation was best at about *p*H 2.0. The emulsifier used was a mixture of alkanesulfonic acids designated as MP-635-S.[1] As in similar reactions the amount of initiator used was an important factor in determining polymer size; an increase in the emulsifier concentration also resulted in increased polymer size.

The aromatic dithiol acids (dithiolterephthalic and dithiolisophthalic acid) which were tried in solution polymerization in tetrahydrofuran did not yield polythiolesters but appeared to lose hydrogen sulfide. The same material was obtained from these acids whether the biallyl was added or not, and its formation was inhibited by hydrogen sulfide but not by hydroquinone. This reaction is

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[1] We are indebted to Dr. Stanley Detrick of the Jackson Laboratory, E. I. du Pont de Nemours and Company, for this product. Analysis indicates that it contains 49.5% of 16-carbon sodium alkanesulfonate, 10.3% of unreacted hydrocarbon, 0.86% of sodium chloride, 0.4% of sodium sulfate, and 3% of isopropyl alcohol.

being studied further. A low molecular weight polythiolester was obtained from the mixed aliphatic aromatic dithiolhomoterephthalic acid.

Dithiolisophthalic acid crystallized in two forms, one white and the other yellow. It appeared that the white form came out of ether-petroleum ether solution at a lower temperature. Infrared spectra on the solids (in Nujol) showed a striking difference in carbonyl absorption. The white crystals absorbed strongly at 1659 cm.$^{-1}$ while the yellow solid showed weak absorption at 1677 and 1662 cm.$^{-1}$ (possibly due to the presence of thioanhydride impurities, since thiophthalic anhydride absorbs at 1695 and 1657 cm.$^{-1}$). In addition, the SH absorption of the white form at 2503 cm.$^{-1}$ was exceptionally broad, while the yellow form had a normal SH absorption at 2512 cm.$^{-1}$ and a trace of OH absorption. The white solid gave yellow solutions in ether, benzene and chloroform. Both forms gave identical spectra in chloroform solution (carbonyl, very strong at 1677 cm.$^{-1}$ and—SH at 2577 cm.$^{-1}$). A possible explanation for these data would be the presence of one thion acid group in the yellow form.

The preparations of some known dicarboxylic acids have been improved by minor changes in procedures, and these are recorded in the experimental part. The dithiol dibasic acids were prepared by the method of Sunner and Nilson (2) with minor variations in purification. Since these products are relatively unstable we are recording the properties and often the analyses of the products used in this work.

ENPERIMENTAL

We are indebted to Miss Emily Davis, Mrs. Jean Fortney, and Mrs. Katherine Pih for the carbon and hydrogen analyses; to Clark Microanalytical Laboratories, Urbana, Illinois, for the sulfur analyses; to Mrs. Elizabeth Peterson Leighly and Miss Helen Miklas for the infrared data and their interpretation; and to Miss Ella Richards for the ultraviolet and visible spectra which were determined on a Model 11 Cary recording spectrophotometer. Because the thiol acids are relatively unstable, carbon and hydrogen analyses were in accord with theory only if determined within a day of their preparation and purification. The sulfur analyses reported are in general on samples which are not more than a week or two old.

Homoterephthalic acid. A mixture of 100 g. of *p*-toluic acid, 200 g. of N-bromosuccinimide, a trace of benzoyl peroxide, and 250 ml. of carbon tetrachloride was refluxed for 12 hours on a steam cone. The reaction mixture was taken up in water, and the solid material was separated by filtration. More solid was obtained from the carbon tetrachloride layer. Recrystallization of the combined solids from 95% ethanol resulted in 80 g. (51%) of α-bromo-*p*-toluic acid, m.p. 219–220°.

This was converted to α-cyano-*p*-toluic acid by treatment with aqueous-alcoholic potassium cyanide. After recrystallization from water the yield was 31 g. (52%) m.p. 191–192°. Stirring with 500 ml. of hot concentrated hydrochloric acid for four hours (3) followed by recrystallization from water resulted in 28 g. (81%) of homoterephthalic acid, m.p. 233–234°.

p-Benzenediacetic acid. Dimethyl terephthalate (97 g.) was extracted by refluxing ether into a stirred solution of 40 g. of lithium aluminum hydride in 1½ liters of absolute ether. Water was carefully added to decompose the excess reducing agent. After removal of the ether under reduced pressure, the reaction mixture was stirred with 750 ml. of hot concentrated hydrochloric acid for one hour. The solid obtained after cooling was separated by filtration and recrystallized from 95% ethanol. The yield of α,α'-dichloro-*p*-xylene, m.p. 97–98°, was 51 g. (58%).

TABLE I

DITHIOL DIBASIC ACIDS

ACID	METHOD OF PURIFICATION	YIELD, %	M.P., °C.	FORMULA	ANALYSES					
					Carbon		Hydrogen		Sulfur	
					Calc'd	Found	Calc'd	Found	Calc'd	Found
Dithioladipic[a]	A	79	26–26.5							
Dithiolpimelic[a]	A	79	13–13.5	$C_7H_{12}O_2S_2$	43.72	44.19	6.29	6.39		
Dithiolsuberic[a]	A	76	15–15.5	$C_8H_{14}O_2S_2$	46.57	46.78	6.84	6.72		
Dithiolazelaic[a]	A	86	22.5–23							
Dithiolsebacic[a]	A	75	30–30.5	$C_{10}H_{18}O_2S_2$	51.24	51.16	7.74	7.83		
Dithiol-*p*-benzenediacetic	A	59	73–73.5	$C_{10}H_{10}O_2S_2$	53.07	53.61	4.45	4.78		
Dithiolhomoterephthalic	A	47	48.5–49[b]	$C_9H_8O_2S_2$	50.92	51.39	3.80	4.02		
2,5-Dimethoxydithiolterephthalic	[c]	41	138–139[c,d]	$C_{10}H_{10}O_2S_2$	46.49	47.07	3.90	4.35	24.82	25.30
Dithiolterephthalic[a,e]	B		125–126	$C_8H_6O_2S_2$	48.46	45.80	3.05	2.85	32.35	30.23
	C	49	129–130			49.17		3.27		32.15
	D	68	127–127.5			49.19		3.11		32.53
						49.07		3.48		
Dithiolisophthalic[a,e]	B		75–76		48.46		3.05		32.35	
	C		77–79			49.12		3.04		33.83
	D	Decomposed				48.98		3.22		33.62

[a] These compounds have been described; see references 1, 2, and 5. [b] Light yellow solid. [c] Precipitated from cold benzene solution with excess cold purified petroleum ether. [d] Yellow solid. [e] Because of the yellow color of these compounds ultraviolet and visible spectra were obtained in 95% ethanol solution. There was small absorption at the ultraviolet end of the visible region and peaks in the ultraviolet region as follows:

	λ max (Å)	log ε max
Dithiolterephthalic acid	3125–3150	4.05
	2525	4.03
	2025	4.26
Dithiolisophthalic acid	2930	4.03
	2430	4.05
	2230	4.11

TABLE II

Emulsion Polymerization of Dithiol Acids and Biallyl: Persulfate-Bisulfite Initiated

DITHIOL ACID	EMULSIFIER CONCENTRATION[a]	INITIAL *p*H	VOLUME OF INITIATOR, ML[b].	TEMP., °C.	TIME, DAYS	YIELD, %	INHERENT VISCOSITY
Terephthalic	5	2.0	1.0	30	5	3.5	0.01
	5[c]	2.0	1.0	30	5	8.4	0.01
	4[d]	5[n]	1.0	30	5	0	—
	4[d]	5	1.0	50	5	26	—[e]
Adipic[o]	5	1.0	1.0	30	4	88	0.19
	5	1.5	1.0	30	4	97	0.28
	5	2.0	1.0	30	4	92	0.32
	5	2.5	1.0	30	4	94	0.30
	5	3.0	1.0	30	4	87	0.21
	5	4.0	1.0	30	4	90	0.16
	5	5.0	1.0	30	4	78	0.10
	5	6.0	1.0	30	4	74	0.10
	5	7.0	1.0	30	4	58	0.07
	10	~4	1.0	30	5	86	0.15
	5[f]	~5	1.0	30	4	81	0.22
	5[g]	~5	1.0	30	5	84	0.16
	5	2.0	0.5	30	5	100	0.32
	10	2.0	1.0	30	5	94	0.28
	20[h]	2.0	1.0	30	4	98	0.17
	4[i]	~5	1.0	30	3	99	0.21
	4[j]	~5	1.0	30	5	65	0.07
	4[k]	~5	1.0	30	5	77	0.08
	4[l]	~5	1.0	30	5	62	0.07
	4[m]	~5	1.0	30	5	62	0.07
Pimelic	10	2.0	1.0	30	5	89	0.24
	20	2.0	1.0	30	4	84	0.35
Suberic	10	2.0	1.0	30	5	89	0.29
	20	2.0	1.0	30	4	93	0.33
Azelaic	10	2.0	1.0	30	5	90	0.43
	20	2.0	1.0	30	4	99	0.52
Sebacic	10	~4	1.0	30	5	100	0.44
	10	2.0	1.0	30	5	96	0.52
	20	2.0	1.0	30	4	99	0.49

[a] Number of ml. of 50% MP-635-S solution per 100 ml. of distilled water. [b] Number of ml. each of ammonium persulfate solution (1.46 g./20 ml. of water) and sodium metabisulfite solution (0.37 g./10 ml. of water). [c] 5 ml. of benzene added. [d] 10 ml. of benzene added. [e] Dried polymer no longer soluble in chloroform. [f] 1.0 g. of (anal. reagent) sodium chloride added. [g] 2.0 g. of (anal. reagent) sodium chloride added. [h] 15 g. of dithiol acid used. [i] 5% excess dithiol acid used. [j] 2% excess dithiol acid used. [k] 2.5% excess dithiol acid used. [l] 3% excess dithiol acid used. [m] 4% excess dithiol acid used. [n] Where an approximate *p*H is indicated, it is that of the emulsifier solution without anything added. [o] The infrared spectrum of this emulsion polymer was the same as that found previously (1) for the corresponding solution polymer.

TABLE III

EMULSION POLYMERIZATION OF DITHIOL ACIDS AND BIALLYL: HYDROGEN PEROXIDE INITIATED

DITHIOL ACID	EMULSIFIER CONCENTRATION[a]	INITIAL pH	VOLUME OF 3% H_2O_2, ML.	TEMP., °C.	TIME, DAYS	YIELD, %	INHERENT VISCOSITY
Sebacic	10	$\sim$4[g]	1.0	30	4	91	0.97
	10	2.0	1.0	30	4	89	.46
	10	$\sim$4	0	30	4	90	.51
	10	2.0	1.0	0	4	78	.25
	10	$\sim$4	1.0	0	4	66	.08
	10	$\sim$4	1.0	50	4	86	.34
	10	$\sim$4	10	30	4	78	.37
	10	$\sim$4	0.1	30	4	87	.45
Adipic	10	3.6	.1	30	4	91	.33
	10	3.6	.5	30	4	87	.33
	10	3.6	1.0	30	4	89	.36
	10	3.6	5.0	30	4	87	.50
	10	3.6	10.0	30	4	72	.25
	10	4.1	.5	30	1	87	.33
Sebacic	10	3.6	.1	30	4	82	.94
	10	3.6	.5	30	4	80	1.6
	10	3.6	1.0	30	4	77	1.3
	10	3.6	5.0	30	4	79	.28
	10	3.6	10	30	4	73	.36
	10	3.6	.5	30	0.5	87	1.2
	10	3.6	.5	30	1	88	1.2
	10	3.6	.5	30	1.5	91	1.2
	10	3.6	.5	30	2	89	1.3
	10	3.6	.5	30	3	91	1.2
	10[b]	3.6	.5	30	1	88	1.6
	10[c]	3.6	.5	30	1	84	1.6
	10[d]	3.6	.5	30	1	85	1.7
	10[e]	3.6	.5	30	1	87	1.6
	10[f]	3.6	.5	30	1	88	1.5
	10	2.0	.5	30	1	90	.68
	10	3.0	.5	30	1	85	1.1
	10	3.3	.5	30	1	86	1.4
	10	3.6	.5	30	1	85	1.4
	10	4.0	.5	30	1	88	1.9
	10	4.3	.5	30	1	86	1.9
	10	4.6	.5	30	1	85	2.0
	10	5.0	.5	30	1	86	1.4
	10	6.0	.5	30	1	89	1.3
	10	7.0	.5	30	1	91	1.3
	1	4.4	.5	30	1	82	.55
	2.5	4.4	.5	30	1	73	.65
	5	4.4	.5	30	1	61	1.2
	7.5	4.4	.5	30	1	81	1.3
	10	4.4	.5	30	1	90	1.2

TABLE III—*Concluded*

DITHIOL ACID	EMULSIFIER CONCENTRATION[a]	INITIAL pH	VOLUME OF 3% H_2O_2, ML.	TEMP., C°.	TIME, DAYS	YIELD, %	INHERENT VISCOSITY
Azelaic	10	4.2	0.5	30	1	79	1.0
	10	4.4	.5	30	1	79	1.0
	10	4.6	.5	30	1	85	.70
Suberic	10	4.2	.5	30	1	91	.92
	10	4.4	.5	30	1	94	.62
Pimelic	10	4.2	.5	30	1	74	.31
p-Benzenediacetic	10	4.4	.5	30	1	96	.71
Homoterephthalic	10	4.4	.5	30	1	38	.16
2,5-Dimethoxyterephthalic	10	4.4	.5	30	1	0	—

[a] Number of ml. of 50% MP-635-S solution per 100 ml. of distilled water. [b] 99.50% of required dithiol acid used. [c] 99.75% of required dithiol acid used. [d] 100.00% of required dithiol acid used. [e] 100.25% of required dithiol acid used. [f] 100.50% of required dithiol acid used. [g] Where an approximate *p*H is indicated, it is that of the emulsifier solution without anything added.

Other similar compounds prepared in this manner with the indicated yields were α,α'-dichloro-*m*-xylene (56%), α,α'-dichloro-*o*-xylene (66%), and α,α'-dibromo-*p*-xylene (73%).

Treatment with aqueous-alcoholic potassium cyanide converted the α,α'-dichloro-*p*-xylene to *p*-benzenediacetonitrile. The yield after recrystallization from aqueous-alcohol was 32 g. (64%), m.p. 95–96°. Stirring with 500 ml. of hot concentrated hydrochloric acid for four hours (3) followed by recrystallization of the crude solid from water-ethanol yielded 34 g. (85%) of *p*-benzenediacetic acid, m.p. 238–239°.

Homoterephthalyl chloride. Homoterephthalic acid (27 g.) and 100 ml. of purified thionyl chloride (4) were refluxed, and after the reaction was complete the excess thionyl chloride was removed under reduced pressure. The crude product was purified by cooling petroleum ether solutions made at room temperature. The yield was 13.5 g. (42%), m.p. 35–35.5°. The analytical sample was prepared by molecular distillation under reduced pressure.

Anal. Calc'd for $C_9H_6Cl_2O_2$: C, 49.80; H, 2.79.
Found: C, 49.66; H, 3.02.

p-Benzenediacetyl chloride. By the same procedure as above this compound was obtained in 51% yield, m.p. 66–66.5°.

Anal. Calc'd for $C_{10}H_8Cl_2O_2$: C, 51.97; H, 3.49.
Found: C, 52.04; H, 3.71.

2,5-Dimethoxyterephthalyl chloride. The yield of yellow solid, m.p. 106–107°, was 59%.

Anal. Calc'd for $C_{10}H_8Cl_2O_4$: C, 45.65; H, 3.07.
Found: C, 47.71; H, 3.17.

Preparation of dithiolacids. The reaction of the acid chlorides with pyridine saturated with hydrogen sulfide was carried out essentially as described in the literature (2 5,), but some modifications were made in the method of purification of the crude products.

Method A. The crude product was dissolved in olefin-free petroleum ether at room temperature, the solution was filtered, and then chilled in a Dry Ice-acetone bath. The resulting solid was separated by filtration and dried under reduced pressure.

Method B. The solutions of the crude dithiol acids from terephthalic and isophthalic acids in chloroform were cooled in Dry Ice-acetone baths until crystallization occurred.

Method C. The crude thiol acid was dissolved in absolute ether and precipitated with about four volumes of petroleum ether. Dithiolisophthalic acid was partly decomposed each time it was purified by this method.

Method D. Here the crude solids were sublimed under reduced pressure. A temperature of about 100° at 0.05–0.10 mm. was required for dithiolterephthalic acid, while dithiolisophthalic acid decomposed completely at 60–70°.

POLYTHIOLESTERS

Solution polymerization. Equimolecular amounts of dithioladipic acid and biallyl were placed in a quartz flask with freshly distilled tetrahydrofuran (purified with sodium). The flask was stoppered and placed under an ultraviolet lamp (Hanovia type 7420). After 50 hours, the solid which separated was filtered, washed with tetrahydrofuran, and dried. The yield was 24% of the theoretical amount of polymer, with an inherent viscosity of 0.36 in chloroform at 25°. From the filtrate and washings 52% of the theoretical amount of low molecular weight product (inherent viscosity 0.07 in chloroform) was also obtained after evaporation and precipitation from chloroform solution with methanol.

TABLE IV

CAPILLARY MELTING POINTS OF SOME POLYTHIOLESTERS

HEXAMETHYLENEDITHIOL ESTER OF	INHERENT VISCOSITY[a]	M.P., °C.	REFERENCE
Adipic acid	0.16	99–102	1
Adipic acid	.50	100	
Pimelic acid	.19	61–64	1
Pimelic acid	.31	70	
Suberic acid	.12	82–85	1
Suberic acid	.92	110	
Azelaic acid	.21	68–72	1
Azelaic acid	1.00	105	
Sebacic acid	.17	68–80	1
Sebacic acid	.65	95	
Sebacic acid	1.3	140	
Sebacic acid	2.0	250 d.	
p-Benzenediacetic acid	.71	105	
Homoterephthalic acid	.11	Gummy	

[a] The polythiolesters with inherent viscosities above 0.5 were fibrous in character as they were precipitated from chloroform solution.

When solution polymerization experiments of this type were conducted with dithiolterephthalic acid and dithiolisophthalic acid only degradation products of the dithiol acids were obtained. The nature of these products is under investigation.

Bulk polymerization. Dithioladipic acid and an equimolecular amount of biallyl were placed in a quartz test tube which was then stoppered, agitated and placed under the ultraviolet lamp. After several hours, the material had solidified. It was dissolved in chloroform, and this solution was filtered into methanol. The precipitated polymer was collected, washed, and dried under reduced pressure. Two experiments yielded polymers with inherent viscosities (in chloroform at 25°) of 0.22 and 0.17 in yields of 63 and 79% respectively.

Emulsion polymerization. The freshly prepared dithiol acid was weighed into a four-ounce screw cap polyethylene bottle (used for its light weight) on an analytical balance. The corresponding weight of biallyl was accurately weighed into a glass stoppered weighing bottle which could fit through the neck of the polyethylene polymerization bottle. An emulsifier solution was prepared by diluting a 50% MP-635-S solution and adjusting the *p*H with acid or base using a Beckman *p*H meter. Then 50 ml. of this solution was added to the bottle followed by the initiator. In rapid succession, the glass stopper of the weighing bottle was loosened, and the weighing bottle followed by the stopper was dropped into the polyethylene bottle which was then tightly capped, thoroughly shaken, and placed in a constant temperature bath to be tumbled end over end.

After the indicated length of time, the polymerization was stopped by pouring the contents of the bottle into 100 ml. of a coagulant solution (100 g. of hydrated aluminum potassium sulfate and 100 ml. of glacial acetic acid diluted to 2.5 liters with distilled water). The coagulated polymer was collected, washed with water, and dissolved in 150 ml. of chloroform. Filtering this solution into 300 ml. of methanol precipitated the polymer which was then separated by filtration, washed with methanol, and dried under reduced pressure. Inherent viscosities were determined in chloroform at 25°. Tables II and III contain the experimental data.

Approximate water solubility of aliphatic dithiol acids. The approximate water solubilities of the dithiol acids were determined by titrating their saturated solutions with standard sodium hydroxide. The solutions were prepared by shaking excess dithiol acid with water for several hours. The results at 26° are as follows:

DITHIOL ACID	SOLUBILITY, g./liter
Adipic	3.3
Pimelic	1.6
Suberic	1.2
Azelaic	0.9
Sebacic	.2

Physical properties of polythiolesters. The approximate melting points of the higher molecular weight polythiolesters are compared with those of the lower molecular weight esters previously prepared (1) in Table IV. These melting points were taken by the capillary tube method and are only approximate values since these materials do not melt sharply.

SUMMARY

The reaction of aliphatic dithiol dibasic acids with biallyl in emulsions affords polythiolesters having much higher molecular weights than the products of either bulk or solution polymerization. The less water-soluble acids tend to give the higher molecular weight products. Aromatic dithiol dibasic acids seem to undergo self-condensation rather than polythiolester formation.

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REFERENCES

(1) Marvel and Kotch, *J. Am. Chem. Soc.*, **73**, 1100 (1951).
(2) Sunner and Nilson, *Svensk Kem. Tidskr.*, **54**, 163 (1942).
(3) Wenner, *J. Org. Chem.*, **15**, 548 (1950).
(4) Cottle, *J. Am. Chem. Soc.*, **68**, 1380 (1946).
(5) Sunner, *Svensk Kem. Tidskr.*, **58**, 77 (1946); **62**, 204 (1950).