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

Polyalkylene Sulfides from Diolefins and Dimercaptans

BY C. S. MARVEL AND R. R. CHAMBERS[1a]

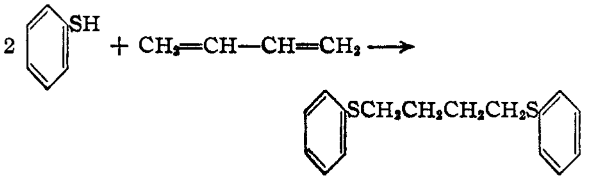
The addition of a thiol to an olefin in the presence of a peroxide catalyst[1b] or under the influence of ultraviolet light[2] has been demonstrated to be a general reaction which proceeds smoothly to give high yields of a product of definite composition. Thus, the reaction meets the requirements for a suitable polymer-forming reaction.

$$n\text{HS(CH}_2)_x\text{SH} + n\text{CH}_2\text{=CH—(CH}_2)_x\text{—CH=CH}_2 \longrightarrow \text{H[S(CH}_2)_x\text{—SCH}_2\text{CH}_2\text{(CH}_2)_x]_n\text{—CH=CH}_2$$

$$n\text{CH}_2\text{=CH—(CH}_2)_x\text{SH} \longrightarrow \text{CH}_2\text{=CH(CH}_2)_x\text{—S[CH}_2\text{CH}_2\text{(CH}_2)_x\text{—S]}_{n-1}\text{H}$$

Cahours and Hoffman,[3] who first made allyl mercaptan, did not mention any loss due to polymer formation, but Braun and Hahn[4] did report a loss of product in non-distillable residue each time they distilled their product. Braun and Plate[5] also found that several other unsaturated mercaptans gave liquid polymers. Vaughan and Rust[2a] obtained low molecular weight (less than 300) polyalkylene sulfides from hydrogen sulfide and diallyl or diallyl ether. Coffman,[6] using dithiols and diolefins without a solvent, obtained a wide variety of liquid polymeric alkylene sulfides with molecular weights up to about 1300.

In the present work we have tried to extend the reaction described by Coffman[6] and to obtain larger polymers which might have more interesting properties. Some experiments using 1,3-butadiene showed that an aromatic thiol would add readily to give the expected sulfide. However, with an aliphatic mercaptan the addition reaction was accompanied by some diene polymerization and the nature of the product was not immediately evident. Hence, in further studies non-conjugated diolefins were selected for study so that this side reaction might be avoided.



The preliminary search for conditions which favor formation of large molecules was made using hexamethylenedithiol and 1,5-hexadiene (diallyl). When these two reagents were mixed in Pyrex test-tubes and exposed to a source of ultraviolet light only a little solid polymer was formed. When the reaction was carried out in an open beaker with an excess of 1,5-hexadiene, polymerization took place quickly and a white waxy product was formed in about five minutes. However, the product was of low molecular weight (about 1100) due to loss of much butadiene by evaporation. By use of cyclohexane as a solvent a polymer with a molecular weight of about 1700 was obtained by the open-beaker method. These experiments indicated that if large molecules were to be obtained it would be necessary to balance closely the quantities of the two reacting species so that one would not be in excess and thus stop the growth of the polymer chain.

A series of reactions was run with one-hundredth molar quantities of hexamethylenedithiol and 1,5-hexadiene in cyclohexane solution in closed quartz test-tubes. The monomers were weighed out with an accuracy of somewhat better than one-half of one per cent. Cyclohexane proved to be a fairly satisfactory solvent since it does not absorb ultraviolet light nor react with the free radical intermediates produced during polymerization. Chloroform is a better solvent for the polymers but gave lower-molecular-weight products and yellow-colored by-products which makes it seem probable that it reacts with free radical intermediates formed in the polymerization reaction.[7] The polymers were separated as solids from cyclohexane and were isolated by filtration. The reaction time was varied from two to three hours to forty-eight hours. Usually the shorter period of time was sufficient, and the time factor did not seem to affect the type of polymer obtained. These polymers were white solids soluble in benzene or cold chloroform. The low-molecular-weight materials (mol. wt. about 1400) were waxy and the higher-molecular-weight materials (about 8000 to 14000) were solids. They were insoluble in ethanol, acetone and low-boiling petroleum ether.

In order to determine whether these polymers had the expected structure resulting from a non-Markownikoff type of addition the infrared absorption of an addition polymer ($[\eta] = 0.206$) was compared with those of two synthetic polymers made from alkali, hexamethylenedithiol and 1,6-dibromohexane and 2,5-dibromohexane, respectively.[8] The two polymers made from the bro-

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[1a] Allied Chemical and Dye Corporation Fellow, 1944 to 1945; Monsanto Fellow, 1946 to 1947. Present address: Sinclair Refining Co., East Chicago, Ind.

[1b] See Mayo and Walling, *Chem. Rev.*, **27**, 387 (1940).

(2) (a) Vaughan and Rust, *J. Org. Chem.*, **7**, 473 (1942); (b) Rust and Vaughan, U. S. Patents 2,392,294, 2,392,295 (*C. A.*, **40**, 2453 (1946)); (c) Vaughan and Rust, U. S. Patents 2,398,429, 2,398,480 (*C. A.*, **40**, 3765 (1946)).

(3) Cahours and Hoffmann, *Ann.*, **102**, 291 (1857).

(4) Braun and Hahn, *Ber.*, **59**, 1202 (1926).

(5) Braun and Plate, *Ber.*, **67B**, 281 (1934).

(6) Coffman, U. S. Patent 2,347,182; *C. A.*, **39**, 226 (1945).

(7) Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

(8) In U. S. Patent 2,201,884 Carothers mentions that polyhexamethylene sulfide can be made by this reaction but no details are given.

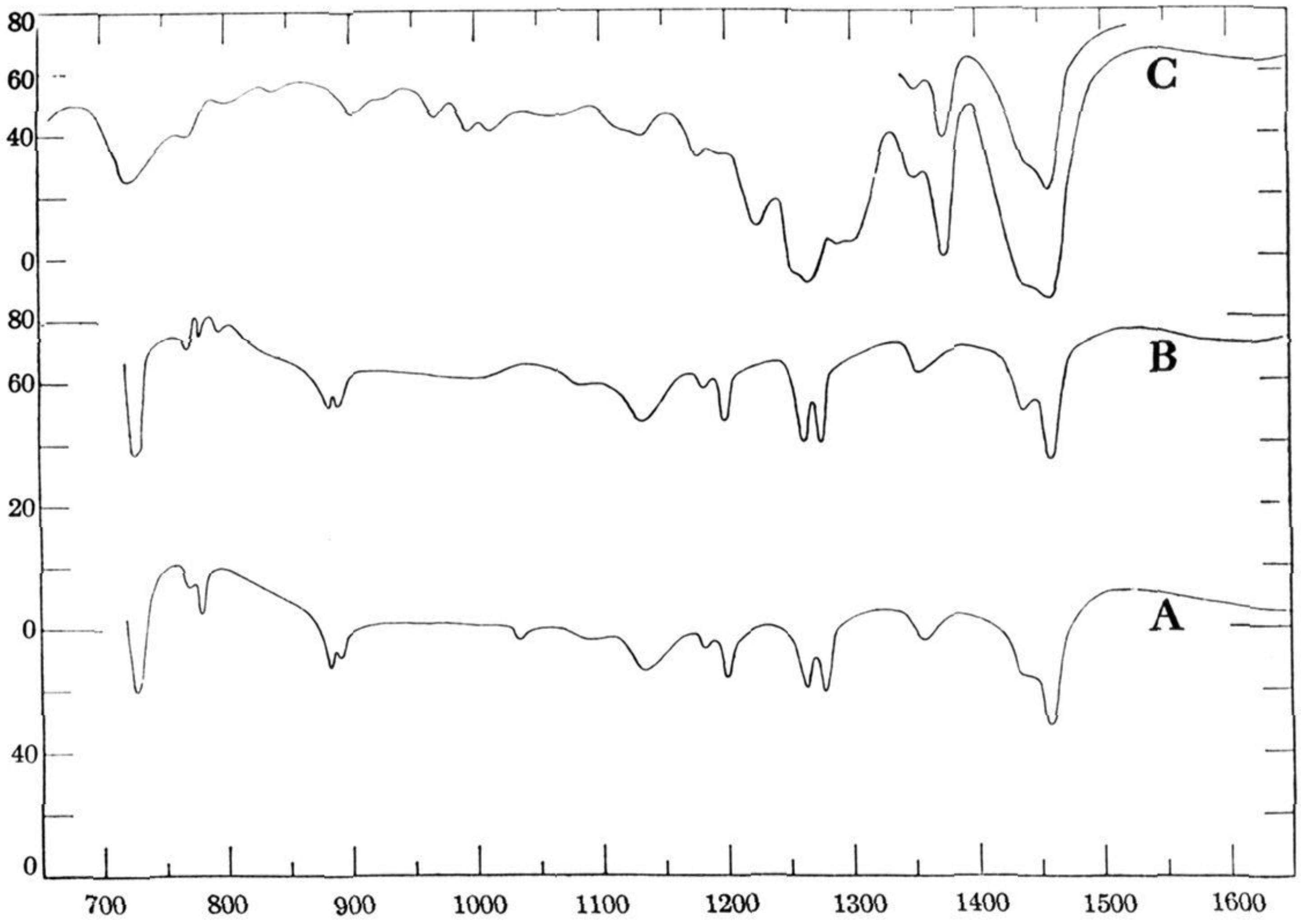
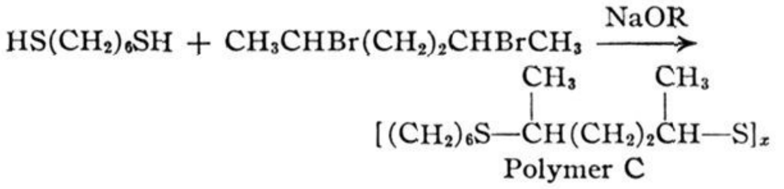


Fig. 1.

mides were of low molecular weight and analysis indicated that they had bromine end-groups.

$$HS(CH_2)_6SH + CH_2{=}CH(CH_2)_2CH{=}CH_2 \longrightarrow \text{Polymer A}$$

$$HS(CH_2)_6SH + Br(CH_2)_6Br \xrightarrow{NaOR} [(CH_2)_6S{-}(CH_2)_6{-}S]_x \quad \text{Polymer B}$$



$$HS(CH_2)_6SH + CH_3CHBr(CH_2)_2CHBrCH_3 \xrightarrow{NaOR} [(CH_2)_6S{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H(CH_2)_2\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}S]_x \quad \text{Polymer C}$$

Figure 1 contains the infrared absorption patterns[9] of polymer Samples A, B and C. It is evident that A and B are very similar and C is markedly different. Polymer C shows the typical methyl group deformational frequency at 1375 cm.$^{-1}$ and bands at 1225 and 1300 cm.$^{-1}$ which are not present in the spectrum of B and A. This seems fairly conclusive evidence that the expected linear non-Markownikoff polymers result from the addition reaction. The differences in the spectra of A and B samples can probably be attributed to the different end-groups present.

Other polymers were obtained from a variety of dithiols and diolefins. Where the monomers were unbranched, solid products resulted. Where there were side groups in the monomers which would be responsible for optical isomerism in the polymer, only liquid products were obtained. In Table I the various polymers which have been obtained in this work are listed. All were prepared by the procedure described for hexamethylenedithiol and 1,5-hexadiene. All had essentially the same solubility in benzene and chloroform as reported for that polymer.

Since the solid polymers had sharp melting points, some X-ray diffraction patterns were taken

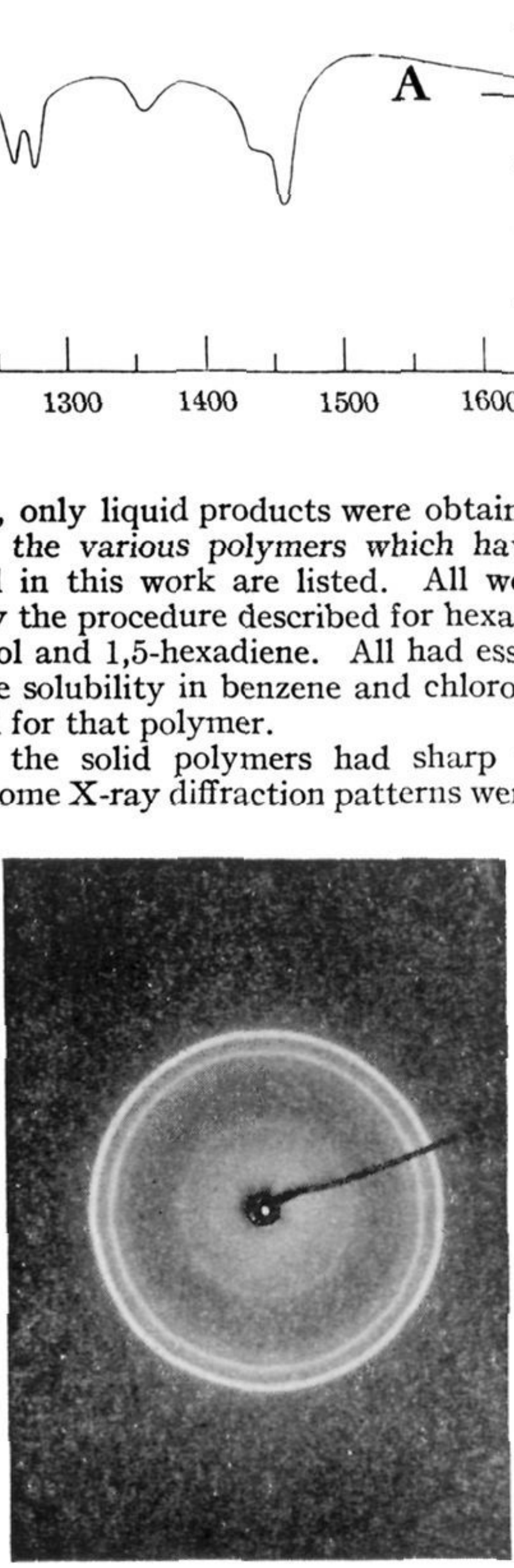


Fig. 2.—Hexamethylenedithiol–1,5-hexadiene polymer.

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[9] We are indebted to Dr. F. A. Miller and Mrs. J. L. Johnson for the infrared measurements and their interpretation.

TABLE I

Monomers Dithiol	Monomers Diolefin	M. p., °C.	(η)	Calculated, % C	Calculated, % H	Calculated, % S	Found, % C	Found, % H	Found, % S
Ethanedithiol	1,5-Hexadiene	82–86		54.49	9.15	36.36	54.65	9.06	36.56
Tetramethylenedithiol	1,5-Hexadiene	65–67		58.76	9.86	31.37	58.91	10.05	31.28
Pentamethylenedithiol	1,5-Hexadiene	64–65	0.256	60.49	10.15	29.36	60.32	10.10	29.30
Hexamethylenedithiol	1,5-Hexadiene	71–76	.206	62.00	10.41	27.59	62.29	9.98	27.88
Decamethylenedithiol	1,5-Hexadiene	76–78	.238	66.60	11.18	22.22	66.76	11.41	21.99
Hexamethylenedithiol	1,10-Undecadiene	72–78	.217	67.48	11.33	21.19	65.91	11.03	22.89
Decamethylenedithiol	1,10-Undecadiene	74–78	.143	70.32	11.80	17.88	69.58	11.69	18.31
bis-(*p*-β-Mercaptoethylphenyl)-methane	1,5-Hexadiene	84–88		74.54	8.16	17.30	74.05	7.96	17.85
Hexamethylene dithiol	bis-(*p*-Vinylphenyl)-methane	gel[a]		74.54	8.16	17.30	74.19	8.10	16.27 16.05
bis-(*p*-β-Mercaptoethylphenyl)-methane	bis-(*p*-Vinylphenyl)-methane	105–108		80.26	7.13	12.60	80.40	7.22	12.66
Hexamethylenedithiol	3,4-Dimethyl-1,5-hexadiene	Liquid	.097	64.55	10.83	24.62	63.62	10.68	25.46
Hexamethylenedithiol	Vinyl-3-cyclohexene	Liquid	.072	65.05	10.14	24.81	63.86	9.75	...
2-Methyl-1,4-butanedithiol	1,5-Hexadiene	Liquid		60.49	10.15	29.36	59.99	10.16	29.75

[a] This gel did not melt or otherwise change at 220°.

to see if they would furnish evidence of crystallinity.[10] Figures 2, 3 and 4 are the patterns for the hexamethylenedithiol–1,5-hexadiene polymer, ethanedithiol–1,5-hexadiene polymer and decamethylenedithiol–1,10-undecadiene polymer, respectively. These diagrams indicate that the polymers are crystalline and that the spacings that can be calculated from their measurement show the roughly paraffinic packing of the chains that might be expected.

The various liquid polymers described in Table I did not tend to crystallize even when cooled, whereas the solids were crystalline as shown for the above samples by X-ray methods. It was thought that some interesting products might be attained by making polymers from the three components hexamethylenedithiol, 1,5-hexadiene and 3,4-dimethyl-1,5-hexadiene. Table II gives the results of three such experiments.

TABLE II

Expt.	Hexamethylenedithiol mole	1,5-Hexadiene, mole	3,4-Dimethyl-1,5-hexadiene, mole	Softening point of product, °C.
1	0.005	0.004	0.001	62.5–65
2	.005	.003	.002	56–60
3	.005	.002	.003	Greasy

No analysis of these polymers is reported since the results do not indicate whether the two olefins are both present in the chain.

Attempts have been made to oxidize the polymer from hexamethylenedithiol and 1,5-hexadi-

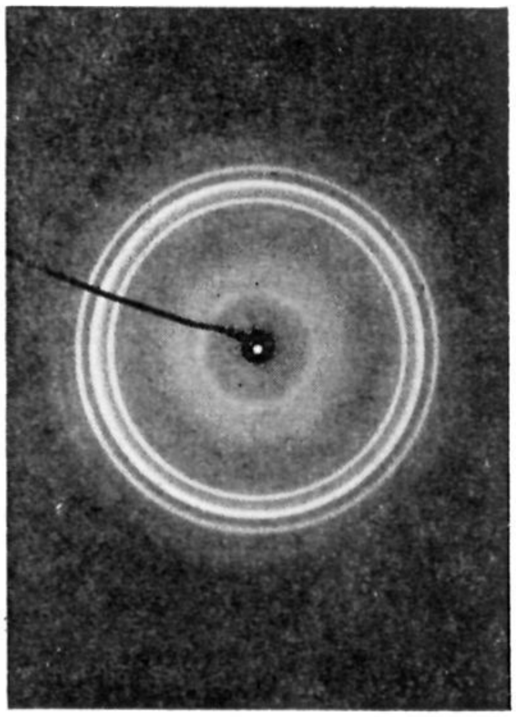

Fig. 3.—Ethanedithiol–1,5-hexadiene polymer.

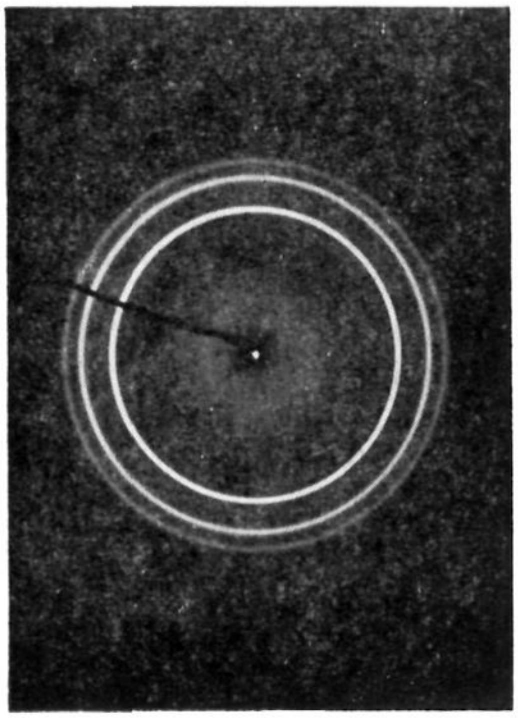

Fig. 4.—Decamethylenedithiol–1,10-undecadiene polymer.

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[10] We are indebted to Professor G. L. Clark and Mr. D. L. Leussing for these X-ray diffraction measurements and their interpretation.

ene with bromine, potassium permanganate solution, perbenzoic acid and hydrogen peroxide. The polymer took up a large amount of bromine and liberated hydrogen bromide, giving a heavy liquid product which solidified on standing but was intractable. The other three oxidizing agents gave a white solid polymer insoluble in benzene and chloroform as well as other common solvents. It could be dissolved in hot *m*-cresol.

Some attempts were made to determine the end-groups in the polyhexamethylene sulfide but they were not very satisfactory. As indicated above, bromine appears to react with the sulfide sulfur atoms. Using traces of perbenzoic acid or iodine as oxidizing agents did produce polymers with increased intrinsic viscosities which would indicate mercaptan end-groups. These experiments, however, are somewhat inconclusive.

The authors are glad to acknowledge their indebtedness to Professor H. A. Laitinen and Mrs. H. E. Fritz for amperometric titration of the mercaptans used.

Experimental

1,4-bis-(Phenylmercapto)-butane.[11]—In a Pyrex tube were placed 11 g. of thiophenol and 5 g. of liquid butadiene. The tube was cooled and sealed and exposed to a source of ultraviolet light for sixteen hours and then allowed to stand about two weeks. It was then cooled and opened, the unreacted butadiene evaporated and the residue cooled in an ice-bath. From the unreacted thiophenol, a small amount of crystalline material separated and it was collected on a filter and recrystallized. The yield was 0.47 g. of 1,4-bis-(phenylmercapto)-butane, m. p. 84–84.5°. Bennett and Mosses[12] report a melting point of 85° for a sample of this material prepared in a different manner.

1,4-bis-(*p*-Tolylmercapto)-butane.[11]—In a similar manner 4.6 g. of butadiene and 13.8 g. of *p*-thiocresol were exposed to ultraviolet light for eighteen hours and allowed to stand fifteen days. The butadiene was evaporated and the thiocresol removed by distillation under 6 mm. pressure. The residue solidified and on recrystallization from 90% alcohol there was obtained 6.4 g. of bis-1,4-(*p*-tolylmercapto)-butane, m. p. 65–65.5°.

Anal. Calcd. for $C_{18}H_{22}S_2$: C, 71.45; H, 7.33. Found: C, 71.49; H, 7.50.

Butadiene and *n*-Butyl Mercaptan.[11]—Three grams of butadiene and 10 g. of *n*-butyl mercaptan were sealed in a Pyrex tube and exposed to ultraviolet light for eighteen hours and then allowed to stand for about two weeks. The tube was opened and the contents distilled. A 0.97-g. fraction of material boiling at 53–55° at 3 mm. was obtained; $n^{20}D$ 1.4749; d^{20}_4 0.9002. Analysis indicated the ratio of butadiene to mercaptan was approximately 1 mole to 1 mole, yet the boiling point is too high for such a molecule. It was not further identified.

Anal. Calcd. for $C_4H_8 \cdot C_4H_9SH$: C, 64.6; H, 12.7; S, 21.25. Calcd. for $C_4H_8 \cdot 2C_4H_9SH$: C, 60.9; H, 11.85; S, 27.00. Found: C, 66.93; H, 10.39; S, 22.71.

Addition of Hexamethylenedithiol and 1,5-Hexadiene.—In a typical polymerization a solution of 1.5 g. of hexamethylenedithiol and 0.82 g. of 1,5-hexadiene in 10 cc. of cyclohexane was placed in a tightly stoppered quartz test-tube under an ultraviolet lamp. After twelve hours the white solid was filtered off and dried. The yield was 1.69 g. This polymer softened in a melting point tube at 70° and was liquid at 74°. A solution of 0.4188 g. in 100 cc. of benzene showed an intrinsic viscosity of 0.156.

Anal. Calcd. for $(C_6H_{12}S)_x$: C, 62.00; H, 10.41; S, 27.59. Found: C, 62.19; H, 9.98; S, 27.88.

To the mother liquor from which this product had been isolated was added 1 cc. of absolute alcohol. A second crop of solid material weighing 0.13 g. was obtained. This polymer melted at 63–67° and had an intrinsic viscosity of only 0.082.

In other similar experiments the various polymers of hexamethylenedithiol and 1,5-hexadiene listed in Table III were isolated. One polymer isolated from cyclohexane solution by the open vessel method melted at 63–67° and had a molecular weight of 1700 as determined ebullioscopically in benzene. Another polymer made in an open vessel without solvent melted at 60–65° and had a molecular weight of 1100.

TABLE III

Expt.	[η]	Melting range, °C.	Cryoscopic mol. wt.	Approximate molecular weights
57	0.139	70–72	..	4500– 5600
55	.271	73–76	..	9000–11000
58	.293	74–76	..	12000–14000
3B1[a]	.05	50–56	1400	....
5B2[a]	.07	62–64	2100	....

[a] These low molecular weight polymers were characterized by Paul H. Aldrich and used as a basis for approximating the molecular weights of those products with a greater intrinsic viscosity.

Hexamethylenedithiol and 1,6-Dibromohexane.—To a solution of 0.26 g. of sodium in 20 cc. of absolute alcohol in a 50-cc. Erlenmeyer flask was added 1.5 g. of hexamethylenedithiol and then dropwise 2.44 g. of hexamethylene dibromide. The reaction proceeded rapidly and the product separated. It was filtered off and the alcohol diluted with water and filtered again. The two precipitates were taken up in benzene and the polymer precipitated with methanol. This process was repeated. There was obtained about 0.26 g. of product.

Anal. Calcd. for $(C_6H_{12}S)_x$: C, 62.00; H, 10.41; S, 27.59. Found: C, 58.57; H, 9.65; S, 29.07; Br, 3.19. This is Polymer B used in the infrared study.

Hexamethylenedithiol and *meso*-2,5-Dibromohexane.—To a solution of sodium ethylate prepared from 15 cc. of absolute alcohol and 0.24 g. of sodium hydride was added 1.5 g. of hexamethylenedithiol and 2.44 g. of *meso*-2,5-dibromohexane[13] (m. p. 37–39°) dissolved in 15 cc. of absolute alcohol. This solution was refluxed for about four hours. To the mixture was added 50 cc. of water and 20 cc. of ether. The ether solution was separated and the solvent evaporated. The remaining liquid was treated with sufficient methanol to dissolve about half of it and the methanol solution was decanted. The undissolved liquid was taken up in low-boiling petroleum ether. The solution was decolorized with Norite and filtered. The solvent was evaporated and the residue heated to 100° for two hours to remove traces of solvent. The product was a yellow, fairly mobile liquid containing some halogen.

Anal. Calcd. for $(C_6H_{12}S)_x$: C, 62.00; H, 10.41; S, 27.59. Found: C, 54.83; H, 9.60; Br, 6.45. It is perhaps significant to note that a polymer of the expected type with a molecular weight of 2500 having bromine end group would have the following analysis: C, 58.01; H, 9.74; Br, 6.43. This liquid product was used as sample C in the infrared work.

Oxidation of Polyhexamethylene Sulfide.—In a 500-cc. Erlenmeyer flask was placed a solution of 1.16 g. of polyhexamethylene sulfide in 150 cc. of chloroform and to it was added 150 cc. of a chloroform solution containing

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(11) This experiment was performed by Robert J. Buswell and submitted in his M. A. thesis, University of Illinois, 1937.

(12) Bennett and Mosses, *J. Chem. Soc.*, 2364 (1930).

(13) Wislicenus, *Ber.*, **34**, 2580 (1901).

0.0287 mole of perbenzoic acid.[14] The mixture was shaken on a shaking machine for twenty four hours. Titration of an aliquot portion indicated that about 0.01 mole of perbenzoic acid had been used up. To the original reaction mixture was added 150 cc. of methanol and the precipitate was collected on a filter. The precipitate was extracted in a Soxhlet extractor for five hours with hot benzene. The undissolved material melted at 189–194°. Another similar oxidation carried out at −10° for two and a half hours, at 0° eleven hours and at room temperatures for five hours showed that the oxidation was complete in the first hour and a half at −10° since after that no more perbenzoic acid was used up. This gave a 66% yield of solid melting at 190–194°. This polymer was slightly brown after purifying by solution in hot *m*-cresol and precipitation with benzene.

Anal. Calcd. for $C_6H_{12}SO$: C, 54.50; H, 9.15. Calcd. for $C_6H_{12}SO_2$: C, 48.62; H, 8.16. Found: C, 49.16; H, 8.38.

It therefore appears that a polysulfone is the oxidation product. A similar product was obtained using aqueous potassium permanganate as the oxidizing agent.[15] Carothers[15] has oxidized the polyhexamethylene sulfide made from hexamethylene bromide and sodium hexanedithiol to a polysulfone which melted at 196–198°. Our product is apparently similar if not identical with his.

End Group Oxidation.—A one-tenth gram sample of polyhexamethylene sulfide (intrinsic viscosity of 0.293, m. p. 74–76°) in 25 cc. of benzene was treated with 3 drops of dilute perbenzoic acid solution in chloroform (0.186 millimoles of perbenzoic per cc. solution) and shaken ten minutes. Then an additional 3 drops of oxidizing solution was added and the mixture shaken again for two minutes. The polymer was precipitated with methanol. In benzene solution the oxidation product had an intrinsic viscosity of 0.326. It melted at 75–77°.

A similar experiment using 0.1 g. of polymer in 20 cc. of benzene, 0.01 g. of iodine and 10 cc. of very dilute sodium hydroxide solution changed the intrinsic viscosity of the polymer from 0.293 to 0.443 and the melting point increased from 74–76° to 75–77°.

Pentamethylenediisothiouronium Bromide.—In a 500-cc. Erlenmeyer flask was placed 82 g. ($^1/_3$ mole) of pentamethylene dibromide, 54 g. ($^2/_3$ mole) of thiourea and 200 cc. of 95% ethanol. The mixture was refluxed on a steam cone for six hours, and then cooled in an ice-bath. When scratching the side of the beaker did not induce crystallization, the solvent was removed from a small sample of solution on a metal spatula and the mixture seeded with the residue. The crystals were filtered and dried in a vacuum desiccator over calcium chloride. There was obtained 124.5 g. (91% of the theoretical amount). After recrystallization from a concentrated water solution, the compound melted at 160–160.5°. This intermediate does not appear to have been isolated before.

Anal. Calcd. for $C_7H_{18}S_2N_4Br_2$: C, 22.00; H, 4.75. Found: C, 22.16; H, 4.75.

bis-(*p*-β-Mercaptoethylphenyl)-methane Diacetate.—A mixture of 10 g. of crude bis-(*p*-vinylphenyl)-methane[16] containing about 1 g. of water, and 16 g. of thiolacetic acid were placed in a quartz flask and irradiated with ultraviolet light. In a half hour the mixture became quite hot, but in another half hour it had cooled and solidified. The compound was recrystallized twice from methanol and once from low petroleum ether. There was obtained 6.5 g., melting point 75–77°. Upon further recrystallization from low petroleum ether small shiny flakes were obtained which melted at 75.5–77.5°.

Anal. Calcd. for $C_{21}H_{24}S_2O_2$: C, 67.70; H, 6.50; S, 17.21. Found: C, 67.74; H, 6.70; S, 17.06.

bis-(*p*-β-Mercaptoethylphenyl)-methane.—To a hot solution of 5 g. of bis-(*p*-β-mercaptoethylphenyl)-methane diacetate in 50 cc. of ethanol was added 10 cc. of 10% sodium hydroxide solution, and the mixture heated on the steam cone for twenty minutes. Then the solution was poured into 100 cc. of water containing 25 cc. of concentrated hydrochloric acid. The milky solution was extracted with ether, and the ether solution dried over magnesium sulfate. Removal of the ether left an oil which crystallized from low petroleum ether. A further small amount of the product was recovered from the aqueous solution by allowing it to remain in the refrigerator for several days. Further recrystallization of a sample of this compound from low petroleum ether gave white flakes melting at 34.5°. There was obtained 1.5 g. which is 39% of the theoretical yield.

Anal. Calcd. for $C_{17}H_{20}S_2$: C, 70.78; H, 6.99; S, 22.23. Found: C, 70.80; H, 6.97; S, 22.23.

2-Methylbutenethiol Acetate.—The method of adding thiolacetic acid used here was that of Frank and Hein.[17] A mixture of 22.6 g. of isoprene and 55 g. of thiolacetic acid was placed in a quartz flask cooled by an ice-bath and irradiated by ultraviolet light for fifteen minutes. On distillation fractions came over at 34–75° (12.2 g.); 85–90° (37.2 g.); and 40° (2 mm.) (12.8 g.). Apparently the first fraction is unchanged isoprene and the second unchanged thiolacetic acid. On redistillation, the third fraction, a colorless liquid, distilled at 49–51° (2 mm.), $n^{20}D$ 1.4916. This appeared to be an addition product of one mole of thiolacetic acid to one mole of isoprene.

Anal. Calcd. for $C_7H_{12}SO$: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.52, 58.66; H, 8.74, 8.55; S, 22.64.

2-Methyl-1,4-butanedithiol Diacetate.—The thirty-seven grams of thiolacetic acid recovered from the previous experiment, and 16.5 g. of isoprene were placed in a quartz flask under the ultraviolet light for thirty minutes while in an ice-bath. Then the flask was removed from the ice-bath, and irradiated for an hour, during which time it heated up considerably. On distillation 3.9 g. of material was obtained which distilled at 38–75°, while the remainder distilled at 75–100° (1 mm.). On redistillation of the latter through a six-inch helices packed column, there was obtained 36.3 g. (a quantitative yield) of material distilling at 97–99° (1 mm.); $n^{20}D$ 1.5137. A sample from the middle of this fraction was analyzed.

Anal. Calcd. for $C_9H_{16}S_2O_2$: C, 49.06; H, 7.32; S, 29.10. Found: C, 49.65; H, 7.26; S, 29.46.

2-Methyl-1,4-butanedithiol.—A mixture of 36 g. of 2-methyl-1,4-butanedithiol diacetate, 40 g. of potassium hydroxide, 180 cc. of water and 200 cc. of 95% ethanol was refluxed for a half hour. The solution was then neutralized with acetic acid, and extracted with ether. The ether solution was dried over sodium sulfate, and then the ether removed. The residue, which existed in two layers, was distilled. The first fraction which distilled at 30° (80 mm.) was colorless, but the second fraction which distilled at 47–49° (3 mm.) was yellow and had an unpleasant odor. The second fraction which contained 8.3 g. of material was redistilled through a six-inch helices packed column at 46–48° (1 mm.), $n^{20}D$ 1.5202. There was obtained 6.4 g. (35% of the theoretical amount).

Anal. Calcd. for $C_5H_{12}S_2$: C, 44.07; H, 8.88; S, 47.05. Found: C, 44.61; H, 8.87; S, 47.22.

Summary

Hexamethylenedithiol and 1,5-hexadiene react in cyclohexane solution under the influence of ultraviolet light to produce polymers having molecular weights varying upward from 1000. The addition gives a linear polyhexamethylene sulfide.

The reaction is general for other dimercaptans and unconjugated diolefins. The polyalkylene

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[14] This preparation of the perbenzoic acid solution was carried out by the procedure of Braun, "Organic Syntheses," Col. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431, as modified by Kolthoff, Lee and Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

[15] The procedure of Carothers, U. S. Patent 2,201,884, was followed.

[16] We are indebted to Dr. D. W. Hein for this sample.

[17] R. L. Frank and D. W. Hein, private communication.

sulfides from unbranched dienes and dimercaptans are solids showing definite crystallinity in their X-ray patterns. Attempts at end group determination by oxidation gave increased molecular weights as measured by intrinsic viscosity but conclusive evidence of thiol end groups was not obtained.

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[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

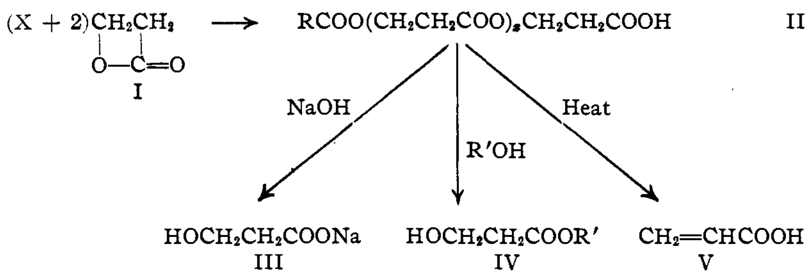
β-Propiolactone. I. Polymerization Reactions

BY T. L. GRESHAM, J. E. JANSEN AND F. W. SHAVER

β-Propiolactone (I) was first prepared[1] from the silver salt of β-iodopropionic acid. Only a few reactions such as its hydrolysis with acids and bases were described. Apparently no further investigations of this interesting β-lactone have been made.

The availability of I, by the practical synthesis from ketene and formaldehyde discovered by Küng,[2] has made possible an extensive study of its many reactions. This has revealed that β-propiolactone is a highly reactive and synthetically useful chemical.

Pure I polymerizes slowly when heated, and several hours at 150° are required for complete reaction. This polymerization is markedly catalyzed by acids, bases or salts. The most effective catalysts, such as ferric chloride, stannic chloride, sulfuric acid and sodium hydroxide, are moderately soluble in the lactone. Such catalyzed reactions are extremely vigorous and explosive in nature and are highly exothermic. Less effective catalysts are sodium chloride, calcium hydroxide, anhydrous hydrogen chloride and acetic acid. Solutions of polymerization catalysts in I at 0° are relatively stable. The polymerization reaction may be controlled by adding I slowly to a solution of the catalyst in an inert solvent. It is of interest to note that polymerization does not occur with sulfuric acid in ether solution even at the reflux temperature.



R represents $CH_2{=}CH{-}$(IIa) or $HOCH_2CH_2{-}$(IIb)

The polymers of I, prepared with or without added catalysts, are similar and are poly-ester acids (II). They vary from colorless viscous oils to white solids depending on the degree of polymerization and their alkali metal salts are soluble in water. Precipitation of the higher molecular weight fractions by dilution of hot acetone solutions with water yields solid polymers melting about 86°, with an average molecular weight in the range of 800–1000 as determined ebullioscopically in chloroform. Titration with base indicates a similar molecular weight range and thus shows that the polymers contain one carboxyl group per molecule. The other end group is either vinyl or a β-hydroxyethyl. The analysis for carbon and hydrogen and iodine number indicate that there are more vinyl than β-hydroxyethyl groups present in the mixture. These analyses are characteristic of a certain polymer since less unsaturation but similar molecular weights are sometimes obtained without known variants in the preparation. This could be due to variations in traces of moisture.

In boiling aqueous caustic, the polymers are saponified to salts of hydracrylic acid (III) and saponification equivalents are in close agreement with those expected for the basic unit of 72. Prolonged treatment of the polymers with alcohols when catalyzed by acids results in almost complete conversion to hydracrylate esters (IV). Basic catalysts are unsatisfactory for this alcoholysis due to the sensitivity of the hydracrylate esters to alkali. Pyrolysis[3] of the poly-ester acids to acrylic acid (V) is rapid and complete at 150°.

Other reactions of β-propiolactone to be reported in later papers include reactions with salts of inorganic acids, salts of dithiocarbamic acids, salts of carboxylic acids, alcohols, phenols and thiophenols, amines, organic and inorganic acid chlorides, metal organic compounds, inorganic acids and compounds with labile hydrogen or active methylene groups. Further work is now being undertaken to determine the mechanisms of these reactions.

Experimental

β-Propiolactone (I).—Physical constants: b. p. 51° at 10 mm., 150° at 750 mm., (with extensive decomposition); m. p. −33.4°; d^{20}_4 1.1460; n^{20}_D 1.4131; dipole moment 3.8 ± 0.1 *D*.

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(1) Johannson, Lund University Annual, New Series, Div. 2, Vol. 12, No. 8 (1915).

(2) Küng, U. S. Patent 2,356,459 (1941).

(3) Küng, U. S. Patent 2,361,036 (1944).