reduced pressure. The fraction of b.p. 153–163° (1 mm.) (12.1 g., 14% yield) was purified by three recrystallizations from ligroin (b.p. 60–90°). The almost colorless lath-like crystals had m.p. 101–102°; yield 7%.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.3; H, 6.4. Found: C, 76.6; H, 6.3.

Gabriel and Neumann[10] who prepared this compound by another method give m.p. 103°. It was obtained as an oil by Erlenmeyer, Baumann and Sorkin.[2]

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(10) Gabriel and Neumann, *Ber.*, **25**, 3563 (1892).

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

Polyarylene-alkylene Sulfides[1]

BY C. S. MARVEL AND P. D. CAESAR[2]

Aryl dithiols and biallyl react in emulsion polymerization systems to produce polyarylene-alkylene sulfides of high molecular weight and high melting point. Some of these polymers give orientable fibers on cold drawing. The introduction into the emulsion of an inert organic solvent such as benzene or methanol and an increase in polymerization temperature improves the yields when high melting dithiols are used in these polymerizations. Methods for the preparation and purification of some aryl dithiols have been evaluated and developed.

The present work was undertaken to see if aryl dithiols would copolymerize with non-conjugate aliphatic diolefins to form linear, high molecular weight polymers similar to the polyalkylene sulfides obtained in the earlier work in this Laboratory.[3] It was found that the resultant polyarylene-alkylene sulfides were crystalline fibrous polymers of higher melting point than the polyalkylene sulfides, and an investigation of the effect of the structure of the aryl dithiol monomer on the properties of the polymer was carried out with the particular purpose of increasing the melting point as much as possible. Biallyl was used as the aliphatic diolefin throughout this work.

An emulsion polymerization technique similar to that described by Marvel and Aldrich[3b] was found to be the most satisfactory method of polymerization. However, the presence of a solid insoluble monomer presented features which were novel to such systems. When an initiator system consisting of ammonium persulfate, sodium hydrogen sulfite and cupric sulfate[4] was used at 30° with the emulsifier, MP-189-EF,[5] buffered with sodium acetate and adjusted to a *p*H of 3.35,[6] it was found that a small amount of an organic solvent, such as benzene or methanol, in the system increased the yield of higher molecular weight polyarylene-alkylene sulfides. It was necessary, of course, to use a solvent which was inert to the monomers. Although a small amount of solvent solubilized the solid monomer sufficiently to facilitate polymerization, larger amounts had a deleterious effect as shown in Tables I and II. It was found, too, that the yield and molecular weight of polyarylene-alkylene sulfides of higher melting point and lower solubility could be increased by employing a polymerization temperature of 50° and higher (see Table III). At these temperatures no reducing agent could be tolerated in the system.

The polymers from aryl dithiols with biallyl showed an increase in melting point from the maximum of 86° for polyalkylene sulfides thus far obtained[3a] to 225–235° for the polyarylene-alkylene sulfide prepared from biphenyl-4,4′-dithiol and biallyl. This effect on the melting point was more noticeable when such a polynuclear group was introduced into the polymer than when the various isomeric forms of a condensed nucleus like naphthalene were incorporated therein. The polyarylene-alkylene sulfides of high melting point had very low solubilities in organic solvents.

With the exception of melting point and solubility in organic solvents, however, the polyarylene-alkylene sulfides were similar in properties to the polyalkylene sulfides. The polymers with inherent viscosities of the order of 0.4 and higher melted sharply and yielded fibers from a melt. These fibers could be cold-drawn. X-Ray diffraction patterns showed crystallinity in the original polymer and orientation in the stretched fiber.[7] The strength of these polymers seemed to be as much a function of the type of monomeric dithiol as of the molecular weight. For example, two polymers obtained by the polymerization of diphenylmethane-4,4′-dithiol and phenoxybenzene-4,4′-dithiol with biallyl, although of similar melting point and inherent viscosity, gave very strong and weak fibers, respectively.

Two methods for the preparation of aryl dithiols were utilized. The first was the reduction of aryl sulfonyl chlorides with zinc dust and acid.[8] It was found that more reproducible results could be obtained by amalgamation of the zinc dust prior to its use as a reducing agent. This process seemed to be limited, however, to the reduction of those aryl disulfonyl chlorides that gave aryl dithiols of relatively low melting point and high solubility. For the preparation of the less soluble aryl dithiols of higher melting point it was necessary to use a second, less familiar reduction technique. In this

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(1) This is the ninth communication on polyalkylene sulfides. For the eighth see C. S. Marvel and C. W. Roberts, *J. Poly. Sci.*, in press.

(2) Recipient of Socony–Vacuum Oil Company Scholarship in Chemistry 1947–1950.

(3) (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).

(4) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); L. B. Morgan, *ibid.*, **42**, 169 (1946).

(5) MP-189-EF is an electrolyte-free emulsifier which consists essentially of mixed alkanesulfonic acids. We are indebted to Dr. Stanley Detrick of Jackson Laboratory, E. I. du Pont de Nemours and Company, for this material.

(6) C. S. Marvel and G. Nowlin, THIS JOURNAL, **72**, 5026 (1950).

(7) We are indebted to Dr. J. Fuchs and Professor G. L. Clark for these X-ray studies.

(8) R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 504.

process the aryl disulfonyl chloride was reduced at 80–90° by a solution of stannous chloride dihydrate dissolved in glacial acetic acid saturated with hydrogen chloride.[9]

The high degree of purification of the aryl dithiols requisite for polymerization was realized in most cases by first purifying the original aryl disulfonyl chloride to eliminate those impurities which might reduce to thiols with properties similar to those of the desired product; by subliming the dithiol in a molecular still under high vacuum; and finally by dissolving the aryl dithiol sublimate in dilute alkali and immediately filtering the alkaline solution into excess acid.

Experimental

Preparation of Aryl Disulfonyl Chlorides.—Phenoxybenzene-4,4′-disulfonyl chloride and diphenylmethane-4,4′-disulfonyl chloride were prepared by chlorosulfonylation of diphenyl ether and diphenylmethane, respectively.[10] It was found advisable, however, to prepare biphenyl-4,4′-disulfonyl chloride by the reaction of phosphorus pentachloride with the dipotassium salt of biphenyl-4,4′-disulfonic acid.[11] The product melted at 209–210°; reported m.p. 203°.[11] This method was used, too, for the preparation of naphthalene-1,5-disulfonyl chloride from the disodium salt of naphthalene-1,5-disulfonic acid (The Matheson Company, Inc., technical grade) and for the synthesis of naphthalene-2,6-disulfonyl and naphthalene-2,7-disulfonyl chlorides from naphthalene-2,7-disulfonic acid (E. I. du Pont de Nemours and Company, Inc., 46.4% purity). The 2,7-derivative melted at 227.5–228.5° and the 2,6-derivative at 158.5–159.5°; reported m.p. 226° and 157–158°, respectively. Purification of these two sulfonyl chlorides was very difficult because the starting material was a mixture. Approximately 10% of the over-all yield was the 2,6-isomer which could be isolated readily because of its lower solubility in organic solvents. The remainder consisted of a mixture of the 2,7-isomer and contaminants which melted over a 10° range. Although the melting point was brought within a 1° range by fractional crystallization with careful seeding, it is quite possible that a small amount of impurity still remained which was reflected later in the low molecular weight of the copolymer with biallyl.

Naphthalene-1,5-dithiol.—A mixture of 8 g. (0.024 mole) of naphthalene-1,5-disulfonyl chloride and 300 g. of 33% sulfuric acid was stirred with a Hershberg stirrer at room temperature and 50 g. of zinc dust amalgam (Schaar Chemicals, 95% purity) added quickly. The zinc dust amalgam was prepared by the addition of 50 g. of zinc dust[12] to a solution of 10 g. of mercuric chloride and 5 ml. of hydrochloric acid in 150 ml. of water. All lumps were broken up and the mixture stirred for 10 to 15 minutes. The zinc dust amalgam was then isolated by filtration, washed well with water and dried by removing the water with alcohol, the alcohol with ether and most of the ether with air. It was used immediately. After the addition of the zinc dust amalgam, the mixture was immediately brought to the boiling point, held there for 6 hours and left at room temperature overnight. The product was filtered and the naphthalene-1,5-dithiol extracted with 300 ml. of warm ether. Most of the ether was removed by evaporation leaving 4.0 g. (85% of product, m.p. 118–121°; reported m.p. 119°.[13]

The reduction of phenoxybenzene-4,4′-disulfonyl chloride and diphenylmethane-4,4′-disulfonyl chloride to the corresponding dithiols occurred in yields of 85–90% using this reduction technique.

Biphenyl-4,4′-dithiol.—A mixture of 100 g. (0.45 mole) of stannous chloride dihydrate and 400 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride.[9] When all the stannous chloride had dissolved, the solution was heated to 80–90° on a steam-cone and 8 g. (0.02 mole) of biphenyl-4,4′-disulfonyl chloride added quickly with shaking. The temperature was kept at 80–90° for one-half hour and the solution was then allowed to cool to room temperature, poured into 300 ml. of concentrated hydrochloric acid and filtered. The precipitate was added to 200 ml. of 5% sodium hydroxide, shaken well and filtered through a sintered-glass funnel into 100 ml. of concentrated hydrochloric acid. This procedure was repeated and the solid product dried. It was then sublimed at 160–165° at 0.05 mm. in a molecular still. The sublimate weighed 2.8 g. (58%) and melted at 179–181°; reported m.p. 175–176°.[14]

This method proved useful for the preparation of naphthalene-2,6-dithiol and naphthalene-2,7-dithiol in yields of 65 and 55%, respectively. The former melted at 196–196.5°; reported m.p. 178,[15] and the latter at 185–187°; reported m.p. 173–174°[16] and 180–181°.[17]

Dithiohydroquinone.—Dithiohydroquinone was prepared by the chlorosulfonylation of thiophenol followed by a zinc dust amalgam–sulfuric acid reduction of the crude product. The product consisted of a mixture of base-soluble, acid-insoluble, sublimable materials, only a small part of which was the desired dithiohydroquinone. From 13 g. of thiophenol there was obtained 0.4 g. of dithiohydroquinone which melted at 97–98°; reported m.p. 97–98°.[18] The pure product was obtained by sublimation in a molecular still at 70–80° at 0.1 mm. followed by two recrystallizations of the sublimate from ethanol.

Purification of Aryl Dithiols for Polymerization.—The purification of biphenyl-4,4′-dithiol typifies the procedure used throughout this investigation. The crude material which melted at 179–181° was resublimed at 150–160° at 0.05 mm. The sublimate was dissolved in 5% sodium hydroxide and filtered through a sintered-glass funnel into excess hydrochloric acid. This procedure was repeated if the original material was very impure. The precipitate was isolated by filtration, washed well with distilled water, and dried overnight at 60–70° at 0.05 mm. It was then used immediately.

Emulsion Polymerizations of Phenoxybenzene-4,4′-dithiol and Naphthalene-1,5-dithiol and Biallyl—Effect of Solvent.—The polymerizations were run in 4-oz. screw-capped bottles which were tumbled end-over-end in a constant temperature bath during the polymerization period. The phenoxybenzene-4,4′-dithiol and naphthalene-1,5-dithiol were purified and the emulsifier and activator solutions prepared just before use. The thiophene-free benzene used as a solvent in these polymerizations was distilled through a two-foot, helix-packed column. After a fore-fraction of 400 ml. had been distilled over, potassium permanganate was added to the contents of the distilling flask and the next 2 l. of distilled collected and stored over sodium ribbon. A residue of 200 ml. was discarded. Distilled water, redistilled in an all-glass system, was used in these reactions. The emulsifier solution was prepared by acidifying 200 ml. of 0.015 *M* sodium acetate with acetic acid to a *p*H of 3.35, and adding 2.0 g. of MP-189-EF. The initiator system consisted of 2.150 g. of ammonium persulfate, 1.108 g. of sodium hydrogen sulfite and 0.110 g. of cupric sulfate in 200 ml. of distilled water.

To a mixture of 2.000 g. (0.0085 mole) of phenoxybenzene-4,4′-dithiol and 0.701 g. (0.0085 mole) of biallyl (plus an additional 2 mg. to allow for evaporation losses) carefully weighed into a 4-oz. bottle were added varying amounts of benzene, 50 ml. of emulsifier solution and 1 ml. of initiator solution in that order and as rapidly as possible. The bottle was capped and placed on the tumbler in the 30° constant temperature bath. Each bottle was charged, capped and put into the bath independently.

At the end of the polymerization period of 5 days the polymers were coagulated by adding each emulsion to 15 ml. of a coagulating solution prepared by dissolving 100 g. of potassium aluminum sulfate in 100 ml. of concentrated hydrochloric acid and 1 l. of distilled water. The polymers were isolated by filtration and each was dissolved in 40 ml.

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(9) M. T. Bogert and J. H. Bartlett, This Journal, **53**, 4046 (1931).

(10) C. M. Suter, *ibid.*, **53**, 1112 (1931).

(11) J. Feldmann, *Helv. Chim. Acta*, **14**, 751 (1931).

(12) An occasional batch of zinc dust was found which gave poor yields of the desired dithiol. It is believed that this was due to excessive oxide deposits on the surface of the zinc. It is recommended, therefore, that the zinc dust be pretreated with dilute hydrochloric acid before amalgamation.

(13) A. Corbellini and L. Albenga, *Gazz. chim. ital.*, **61**, 111 (1931).

(14) S. Gabriel and A. Deutsch, *Ber.*, **13**, 386 (1880).

(15) L. Braun and R. Ebert, *ibid.*, **25**, 2735 (1892).

(16) R. Ebert and E. Kleiner, *ibid.*, **24**, 144 (1891).

(17) L. Grosjean, *ibid.*, **23**, 2370 (1890).

(18) T. Zincke and W. Frohneberg, *ibid.*, **42**, 2721 (1909).

of benzene and filtered into 100 ml. of methanol. The precipitated polymer was separated by filtration, dried and weighed. The yields and inherent viscosities are recorded in Table I.

TABLE I

EMULSION POLYMERIZATION OF PHENOXYBENZENE-4,4'-DITHIOL AND BIALLYL—EFFECT OF BENZENE IN SYSTEM

Sample number	Vol. of benzene, ml.	Yield, g.	Yield, %	Inherent[a] viscosity
1	10	1.5	56	0.15
2	5	2.0	74	.15
3	5	2.1	78	.25
4	1	2.3[b]	85	.47
5	1	2.5	93	.34
6	0.25	2.5	93	.34
7	None	2.0	74	.15

[a] A 0.2% solution of polymer in chloroform at 25° was used for all inherent viscosity determinations. [b] This polymer was recrystallized a second time from benzene. M.p. 118–119°.

Anal.[19] Calcd. for $C_{18}H_{20}OS_2$: C, 68.35; H, 6.3; S, 20.25. Found: C, 68.2; H, 6.6; S, 20.6.

This procedure was repeated exactly for the polymerization of naphthalene-1,5-dithiol and biallyl, using a monomer mixture of 2.000 g. (0.014 mole) of naphthalene-1,5-dithiol and 0.854 g. (0.014 mole) of biallyl. Redistilled methanol was used as the solvent in some of these runs.

After coagulation and isolation of these polymers in the usual manner, they were washed well with water, dried and leached with 100 ml. of hot benzene. The benzene insoluble, high molecular weight polymer was isolated by filtering the hot mixture into 100 ml. of methanol. Filtration of this filtrate served to isolate the benzene soluble, lower molecular weight polymer. Both were dried and weighed. The results are summarized in Table II.

TABLE II

EMULSION POLYMERIZATION OF NAPHTHALENE-1,5-DITHIOL AND BIALLYL—EFFECT OF SOLVENT IN SYSTEM

Sample number	Organic solvent		Low mol. wt. polymer		High mol. wt. polymer	
	Solvent	Vol., ml.	Yield, %	M.p., °C.	Yield, %	M.p., °C.
1	Benzene	0.5	46	120–130	42	145–148
2	Benzene	1.0	46	105–110	42	140–148
3	Benzene	5.0	60	<110	None	.....
4	Methanol	1.0	32	105–110	51	135–145
5	Methanol	5.0	46	110–125	28	145–148

Emulsion Polymerizations of Naphthalene-1,5-dithiol and Naphthalene-2,6-dithiol and Biallyl—Effect of Temperature.—The emulsion polymerization technique described above was repeated for the investigation of the effect of temperature on the polymerization of naphthalene-1,5-dithiol. A monomer mixture of 2.000 g. (0.014 mole) of naphthalene-1,5-dithiol and 0.854 g. (0.014 mole) of biallyl was used and 0.5 ml. of benzene or methanol added to the system. One important variation in the initiator solution for the reactions carried out at 50° was the omission of the reducing agent, sodium hydrogen sulfite. It had previously been found that it affected the yields adversely at temperatures above 30°. The results are shown in Table III. A fiber could be drawn only from the high molecular weight polymers obtained at 50°.

TABLE III

EMULSION POLYMERIZATION OF NAPHTHALENE-1,5-DITHIOL AND BIALLYL—EFFECT OF TEMPERATURE

Polym. temp., °C.	Organic solvent	Low mol. wt. polymer		High mol. wt. polymer	
		Yield, %	M.p., °C.	Yield, %	M.p., °C.
30	Benzene	46	120–130	42	145–150
50	Benzene	23	120–130	70	148–151[a]
50	Methanol	19	120–130	75	148–151

[a] *Anal.* Calcd. for $C_{18}H_{18}S_2$: C, 70.1; H, 6.6; S, 23.3. Found: C, 70.1; H, 6.8; S, 23.4.

The technique used for the polymerization of naphthalene-2,6-dithiol and biallyl was similar to that described above. A 2% solution of MP-189-EF was used instead of the usual 1% solution, and sodium hydrogen sulfite was omitted from the initiator solution. The monomer mixture consisted of 1.477 g. (0.0077 mole) of naphthalene-2,6-dithiol and 0.631 g. (0.0077 mole) of biallyl, and 0.5 ml. of benzene was added to the system. The polymerization was run at 50° for 5 days. Throughout this period there was a considerable amount of unemulsified solid present.

The polymer was coagulated and isolated in the customary manner and dried. It was leached with 400 ml. of hot chloroform and then with 400 ml. of hot benzene. There was obtained in this manner 0.7 g. (33%) of solvent insoluble polymer which melted at 175–183°. A fiber could not be drawn from this polymer.

Anal. Calcd. for $C_{16}H_{18}S_2$: C, 70.1; H, 6.6; S, 23.3. Found: C, 69.9; H, 6.9; S, 23.7.

A second polymerization of naphthalene-2,6-dithiol and biallyl was run at 72° but for only 12 hours. A 3% solution of MP-189-EF was used and again no sodium hydrogen sulfite. The polymer was coagulated and leached with hot chloroform and benzene as before. There was obtained 2.2 g. (78%) of solvent-insoluble polymer which melted at 187.5–189.5°. Although the molecular weight of this polymer was probably considerably higher than the one obtained at 50°, it was still not possible to draw a fiber from its melt.

Emulsion Polymerizations of Other Aryl Dithiols and Biallyl.—From a monomer mixture of 0.988 g. (0.0042 mole) of diphenylmethane-4,4'-dithiol and 0.349 g. (0.0042 mole) of biallyl there was obtained by the usual emulsion polymerization technique 1.1 g. (82%) of benzene-soluble polymer, which melted at 120–121°. It had an inherent viscosity of 0.45, and a strong fiber could be drawn from its melt.

Anal. Calcd. for $C_{19}H_{22}S_2$: C, 72.6; H, 7.05; S, 20.4. Found: C, 72.45; H, 7.0; S, 20.6.

The polymerization temperature used in this run was 30°, the solvent was 0.5 ml. of benzene, a 2% buffered solution of MP-189-EF was used as the emulsifier and the initiator system was made up at half strength because of the smaller amount of monomers used.

From a monomer mixture of 0.395 g. (0.0028 mole) of dithiohydroquinone and 0.228 g. (0.0028 mole) of biallyl there was obtained 0.45 g. (75%) of benzene insoluble polymer which melted at 155–159°. From appearance and analysis it seemed to be a low molecular weight polymer having thiol end groups.

Anal. Calcd. for $C_{12}H_{16}S_2$: C, 64.3; H, 7.14; S, 28.56. Found: C, 62.7; H, 7.1; S, 29.9.

With the exception that 0.3 ml. of benzene was used all factors were identical to those described for the preceding experiment.

The emulsion polymerization of a monomer mixture of 2.000 g. (0.0092 mole) of biphenyl-4,4'-dithiol and 0.752 g. (0.0092 mole) of biallyl was carried out at 30° using 0.5 ml. of benzene as the solvent and following the general procedure used for the polymerization of naphthalene-1,5-dithiol and biallyl. There was obtained 2.0 g. (73%) of solvent-insoluble polymer, which melted at 225–235°. A fiber could not be drawn from this polymer.

Anal. Calcd. for $C_{18}H_{20}S_2$: C, 72.0; H, 6.7; S, 21.3. Found: C, 72.2; H, 6.9; S, 21.0.

The emulsion polymerization of a monomer mixture of 1.394 g. (0.0075 mole) of naphthalene-2,7-dithiol and 0.595 g. (0.0075 mole) of biallyl was carried out at 50° using 0.5 ml. of benzene as the solvent, a 2% buffered solution of MP-189-EF as the emulsifier and no sodium hydrogen sulfite in the initiator solution. Unemulsified solids were present throughout the run. There was obtained 1.7 g. (85%) of low molecular weight polymer which melted at 70–90° and was soluble in hot benzene. This, too, appeared to have thiol end groups.

Anal. Calcd. for $C_{16}H_{18}S_2$: C, 70.1; H, 6.6; S, 23.3. Found: C, 69.0; H, 6.5; S, 23.9.

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(19) We are indebted to Miss Emily Davis and Miss Rachel Kopel for the microanalyses reported in this manuscript.