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Polymers Containing Disulfide Bonds. I. Derivatives of *p*-Benzene-bis(*ω*-*S*-alkylthiosulfate)[1]

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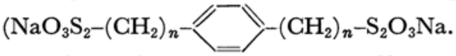
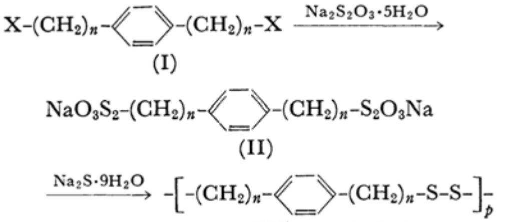
Highly crystalline polymers were synthesized by the polymerization of *p*-benzene-bis(*ω*-*S*-alkylthiosulfate)  Sodium sulfide was effective as a catalyst, but polymers obtained showed much more sulfur content than the theoretical value. The polymers ($n \geqq 2$) possessed rubber-like characteristics.

Polymers containing disulfide bonds in the main chain have been reported only in the series of aliphatic compounds. Patrick has reported that the disulfide polymers are usually not rubber-like unless the spacing between the –S–S– group is equal to four or more carbon atoms in the chain.[2]

The present paper is concerned with the polymerization of *p*-benzene-bis(*ω*-*S*-alkylthiosulfate) (II), by reaction with sodium sulfide.



In connection with the polymerization, the influences of the benzene ring and the length of the polymethylenic chains of the monomeric compound (n) on the physical properties have been studied. The relation between the initial catalyst concentration and the sulfur content in the polymer has also been investigated.

Results and Discussion

Syntheses of the Polymers. α, ω-Dihalides (I) were treated with sodium thiosulfate pentahydrate in water-ethanol mixture to produce the di-Bunte salts (II) in quantitative yields. The polymerization of the di-Bunte salts by reaction with sodium sulfide nonahydrate in water afforded the corresponding polymers, which were insoluble in common organic solvents except 1, 1, 2, 2-tetrachloroethane.

Polymers could also be obtained by using of other catalysts, *e. g.* dimethylsulfoxide. The high crystallinity of the polymers (III) was shown by the sharp X-ray diagrams.

The Structure of the Polymers. In the polymerization of the di-Bunte salts (II), there may be the following three possibilities as an end group.

1. thiosulfuric group:

$$R\text{-}SSO_3^- \xrightarrow{H^+} R\text{-}SSO_3H$$

2. thiol group:

$$R\text{-}SSO_3^- \xrightarrow{H_2O} R\text{-}SH + H^+ + HSO_4^-$$

3. aldehyde group:

$$R\text{-}CH_2\text{-}SSO_3^- \xrightarrow{(O)} R\text{-}CHO$$

From the infrared spectra of polymers, thiosulfuric group may be most possible (Fig. 1).

All of the resulting polymers showed much more sulfur content than the theoretical values (Tables 1, 2, 3 and 4). The sulfur content in the polymers was further increased with the increasing of the initial catalyst concentration. On the other hand, sulfur content, 29.17%, of the polymer (III: n=3), which obtained by reaction with dimethylsulfoxide, was almost near to the theoretical value, 28.68%.

From these results, when sodium sulfide nonahydrate is used as a catalyst, its sulfur atom may enter into polymer chains.[3] Therefore, the polymer obtained may be considered to contain polysulfide linkage partially.

Dimethylsulfoxide. The catalytic action of dimethylsulfoxide was very specific as in the case of the coupling of thiols.[4] II (n=3) gave polymer as soon as it mixed with dimethylsulfoxide at the room temperature, while II (n=1, 2) gave no polymer. On the other hand, a mixture of benzyl-

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[1] Preliminary report, *Chem. & Ind.*, **1967**, 402.

[2] J. C. Patrick, *Trans. Faraday Soc.*, **32**, 347 (1936); S. M. Martin and J. C. Patrick, *Ind. Eng. Chem.*, **28**, 1144 (1936).

[3] K. Schimmelschmidt, *Angew. Chem.*, **74**, 975 (1962).

[4] T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).

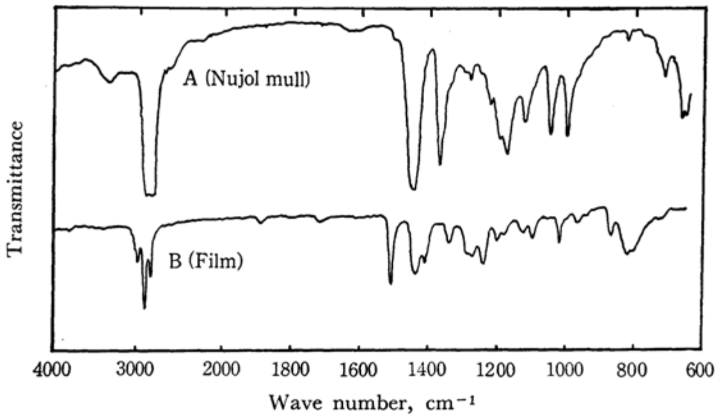


Fig. 1. Infrared spectra of *p*-benzene-bis(3-*S*-propylthiosulfate) (II, n=3), (A) and polymer of II, n=3, (B).

TABLE 1. POLYMERIZATION OF *p*-BENZENE-BIS(ω-*S*-ALKYLTHIOSULFATE) (II)
All reactions were carried out at 50°C under atmosphere of air.

II n	g	$Na_2S \cdot 9H_2O$ g	Water ml	Time min	Polymer g	Softening point °C	η_{sp}/c*	Anal S%
1	3.92	2.40	100	120	1.7	165	0.24	Found 42.19 Calcd 38.09
2	5.03	3.00	100	120	2.3	85	1.38	Found 38.62 Calcd 32.68
3	4.48	2.40	100	300	2.3	60	0.87	Found 36.55 Calcd 28.68

* In 1, 1, 2, 2-tetrachloroethane, c=0.5; n=1, at 70°C; n=2, 3, at 30°C.

TABLE 2. EFFECT OF TIME ON THE POLYMERIZATION OF II (n=1)
(Na_2S)/(II) molar ratio: 1.0, at 50°C

Time, min	10	30	60	90	120	180	240
η_{sp}/c*	0.05	0.09	0.18	0.23	0.24	insol.	insol.
S%	40.23	43.77	44.45	42.21	43.64	41.57	42.70

* In 1, 1, 2, 2-tetrachloroethane, c=0.5, at 70°C.

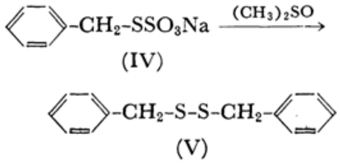
TABLE 3. EFFECT OF TIME ON THE POLYMERIZATION OF II (n=3)
(Na_2S)/(II) molar ratio: 1.0, at 50°C

Time, min	30	60	90	120	180	300
η_{sp}/c*	0.06	0.14	0.20	0.36	0.49	0.87
S%	36.86	35.52	38.20	36.55	36.39	36.52

* In 1, 1, 2, 2-tetrachloroethane, c=0.5, at 30°C.

TABLE 4. EFFECT OF CATALYST CONCENTRATION ON THE SULFUR CONTENT IN THE POLYMER II (n=1)
All reactions were carried out at 50°C for 120 min.

(Na_2S)/(II) molar ratio	0.5	1.0	1.5	2.0	3.0
S%	37.80	43.69	43.92	50.73	58.27



(IV)

(V)

thiosulfate and dimethylsulfoxide was heated at 85°C for several minutes to afford benzyldisulfide.

Experimental*[1]

α, α'-Dichloro-*p*-xylene was prepared by the procedure in the literature.[5] *p*-Bis(2-chloroethyl)benzene was prepared by the chlorination of *p*-bis(2-hydroxyethyl)benzene with thionyl chloride.

***p*-Bis(3-hydroxypropyl)benzene.** To a mixture of sodium borohydride (41 g), diglyme (1000 m*l*) and *p*-diallylbenzene (237 g), boron trifluoride etherate (210 g) was dripped under stirring for 2.5 hr in an ice-water bath. The stirring was continued for further 1 hr. The reaction mixture was then treated with 3 N sodium hydroxide (320 m*l*) and 30% hydrogen peroxide (320 m*l*), decomposed with water, and extracted with ether. The ethereal layer was dried over magnesium sulfate. The removal of the solvent and the distillation of the crude product under a reduced pressure afforded the diol (90%), bp 175—178°C/1 mmHg, mp 61°C.

Found: C, 74.20; H, 9.30%. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28%.

The Bromination of *p*-Bis(3-hydroxypropyl)benzene. To a mixture of *p*-bis(3-hydroxypropyl)benzene (77 g) and pyridine (30 m*l*), phosphorus tribromide (87 g) was dropped under stirring for 50 min in an ice-water bath. The mixture was allowed to the room temperature for 1 hr, and then heated at 80°C for 20 hr. The removal of the solvent and the distillation of the crude product under a reduced pressure afforded the dibromide (55%), bp 151—153°C/0.6 mmHg, n_D^{20} 1.5632.

Found: C, 45.09; H, 5.05; Br, 49.93%. Calcd for $C_{12}H_{16}Br_2$: C, 45.00; H, 5.00; Br, 50.00%.

Sodium *S*-Benzylthiosulfate (IV). IV was prepared by the reaction of benzyl chloride with sodium thiosulfate pentahydrate, colorless leaflets, and used without purification.

Found: C, 35.65; H, 3.50%. Calcd for $C_7H_7O_3S_2\cdot\frac{1}{2}H_2O$: C, 35.75; H, 3.40%.

The Reaction of IV with Dimethylsulfoxide. A mixture of IV (9.1 g) and dimethylsulfoxide (40 m*l*) was heated at 85°C for 10 min, poured into ice-water, and the solid which deposited was collected by filtration, washed with water to afford V (10%), mp 69°C (lit. value, 69—70°C).

***p*-Benzene-bis(ω-*S*-alkylthiosulfate) (II).** To a solution of α, α'-dichloro-*p*-xylene (18 g) in ethanol (200 m*l*), sodium thiosulfate pentahydrate (55 g) in water (85 m*l*) was added at 80°C under the stirring. The stirring was continued for 1 hr to yield white precipitate, which was collected by filtration, washed with ethanol and then dried at 60°C for 48 hr *in vacuo* to afford quantitatively II, $n=1$, as monohydrate, decomposed above 250°C. IR: Nujol mull, 3400 (hydrate), 1165, 1050 ($-SO_3$), 855 cm^{-1} (*p*-substituted benzene).

Found: C, 24.36; H, 2.74%. Calcd for $C_8H_8O_6S_4Na_2\cdot H_2O$: C, 24.49; H, 2.55%.

A similar treatment of I ($n=2$, X=Cl; $n=3$, X=Br) with sodium thiosulfate pentahydrate yielded the following di-Bunte salts.

II, $n=2$, white powders (quantitatively), decomposed above 250°C.

Found: C, 26.90; H, 3.21%. Calcd for $C_{10}H_{12}O_6S_4Na_2\cdot H_2O$: C, 27.37; H, 3.19%.

II, $n=3$, white powders (quantitatively), decomposed above 250°C.

Found: C, 29.95; H, 3.83%. Calcd for $C_{12}H_{16}O_6S_4Na_2\cdot H_2O$: C, 30.90; H, 3.86%.

The General Procedure for the Polymerization of II. A mixture of II, sodium sulfide nonahydrate and water was stirred under the conditions summarized in Table 1. The precipitate formed was treated with dilute hydrochloric acid, collected by filtration, washed successively with water and methanol, and then dried *in vacuo*. Although III ($n=2, 3$) were soluble only in 1, 1, 2, 2-tetrachloroethane at room temperature, III ($n=1$) above 70°C.

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*[1] All melting points are uncorrected.

[5] M. Wakae and K. Konishi, *Yuki Gosei Kagaku Kyokaishi (J. Synthetic Org. Chem. Japan)*, **14**, 615 (1956).