dent in our work would present a practical limitation.

Since completing these experiments, we learned[4] that Tobolsky and Baysal[5] have demonstrated this reaction in the case of styrene. We thank the American Chicle Company for a grant in aid of this investigation, Dr. D. H. Johnson for details of the cyclic disulfide preparation, and S. M. Nagy for the sulfur analysis.

(4) A. V. Tobolsky, private communication, July 7, 1952.

(5) A. V. Tobolsky and B. Baysal, THIS JOURNAL, **75**, 1757 (1953).

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## The Reaction between Styrene and Ring Disulfides: Copolymerization Effected by the Chain Transfer Reaction

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Disulfides such as dibutyl disulfide are active chain transfer agents in the polymerization of vinyl and diene monomers such as styrene and butadiene. The transfer reaction probably proceeds as

$$R'(CH_2CH\varphi)_xCH_2CH\varphi\cdot + RSSR \longrightarrow R'(CH_2CH\varphi)_xSR + RS\cdot$$

$$RS\cdot + CH_2 = CH\varphi \longrightarrow RSCH_2CH\varphi$$

It was therefore conceived that if a ring disulfide was present in a vinyl polymerization, the chain transfer process would result in the incorporation of the ring disulfide molecule in the growing polymer chain; *i.e.*, a copolymerization would be effected by the elementary reaction of chain transfer.

$$R'(CH_2CH\varphi)_xCH_2CH\varphi\cdot + \overset{\diagup R \diagdown}{S\text{—}S} \longrightarrow R'(CH_2CH\varphi)_xSRS\cdot$$

$$R'(CH_2CH\varphi)_xSRS\cdot + CH_2CH\varphi \longrightarrow \text{etc.} \longrightarrow R'(CH_2CH\varphi)_xSRSCH_2CH\varphi\cdot$$

The direct consequence of these considerations is that if a vinyl monomer is polymerized in the presence of a large amount of an open chain disulfide such as dibutyl disulfide, two sulfur atoms should be incorporated in every polymer chain. On the other hand, polymerization of a vinyl monomer in the presence of a ring disulfide such as diethyl ether disulfide,[1,2] should produce polymers with more than two sulfur atoms per polymer chain.

To test this hypothesis we polymerized styrene in the presence of varying amounts of dibutyl disulfide and diethyl ether disulfide. The polymerizations were carried out for 48 hours at 130° followed by 48 hours at 150° in the absence of catalysts. Oxygen was rigorously excluded from the system. The polymers were then twice precipitated in methanol and weighed. Sulfur analyses of the polymers were carried out, and the molecular weights of the polymers determined by measurement of the intrinsic viscosities, using the relation of Mayo, *et al.*[3] This relation was also verified by Pepper[4] for low molecular weight polymers. The use of this relation is only approximate for styrene polymers prepared in the presence of large amounts of disulfide, particularly if the ring disulfide is incorporated in the polymer chain.

The results of these experiments are shown in Table I. Two facts are especially noteworthy. The polymerizations effected in the presence of large amounts of ring disulfide gave a larger weight of polymer than the weight of styrene incorporated in the charge. Also, the number of sulfur atoms per chain in the case of these polymers was much larger than two, whereas in the case of polymers prepared in the presence of dibutyl disulfide the number of S atoms per chain was approximately two.

The results shown in Table I provide a clear indication that a significant difference results in the polymerizations carried out in the presence of chain and ring disulfides, which can only be accounted for by an effective copolymerization in the case of the ring disulfides.

TABLE I

| Chain transfer agent (A) | Charge ratio, c.c.A:c.c. styrene | Total weight charge,[a] g. | Total weight polymer, g. | $[\eta]$ |
|---|---|---|---|---|
| Dibutyl disulfide | 1:3 | 3.64 | 2.64 | 0.239 |
| Dibutyl disulfide | 2:3 | 4.56 | 2.11 | .145 |
| Diethyl ether disulfide | 2:3 | 5.26 | 4.37 | .048 |
| Diethyl ether disulfide | 1:3 | 3.99 | 3.25 | .094 |
| Diethyl ether disulfide | 0.5:3 | 3.35 | 2.86 | .109 |
| Diethyl ether disulfide | 0.3:3 | 3.10 | 2.53 | .175 |
| Diethyl ether disulfide | 0.1:1 | 2.85 | 2.56 | .492 |

| Chain transfer agent (A) | Charge ratio c.c.A:c.c. styrene | $\overline{M}n$[b] | % S in polymer | % S in polymer/ % S in charge | S atom per chain |
|---|---|---|---|---|---|
| Dibutyl disulfide | 1:3 | 24600 | 0.35 | 0.038 | 2.69 |
| Dibutyl disulfide | 2:3 | 11800 | 1.04 | .072 | 3.84 |
| Diethyl ether disulfide | 2:3 | 2570 | 9.20 | .410 | 7.34 |
| Diethyl ether disulfide | 1:3 | 6560 | 5.43 | .369 | 11.1 |
| Diethyl ether disulfide | 0.5:3 | 7950 | 2.72 | .310 | 6.75 |
| Diethyl ether disulfide | 0.3:3 | 15200 | 0.96 | .168 | 4.56 |
| Diethyl ether disulfide | 0.1:1 | 52500 | 1.05 | .495 | 17.2 |

[a] Density of styrene at 20° = 0.905; density of dibutyl disulfide at 20° = 0.919; density of diethyl ether disulfide at 20° = 1.274. [b] Number average molecular weight.

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## Synthesis of Radioactive Noradrenaline

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The synthesis of $\alpha$-$C^{14}$-*dl*-noradrenaline (norepinephrine, arterenol) was accomplished by known procedures[2] modified for small scale use suitable for the preparation of high activity material.

Chloroacetylcatechol, 210 mg., was converted successively to noradrenalone, 93 mg., noradren-

(1) Supported in part by a research grant from the U. S. Public Health Service.

(2) W. Langenbeck and F. Fischer, *Pharmazie*, **5**, 56 (1950).