gives an immediate wine colored reaction. In this solvent system, excess or unreacted hydrazine appears as a bright yellow spot superimposed upon the isoasparagine spot following ninhydrin treatment.

TABLE I

R_f VALUES AND COLOR REACTIONS OF ASPARAGINE AND ISOASPARAGINE IN BUTANOL–WATER–ACETIC ACID (40: 50:10) AND IN WATER-SATURATED PHENOL

18 hour ascending chromatograms; spray reagent 0.25% ninhydrin in butanol

	Phenol		Butanol-water-acetic acid	
	R_f	Color	R_f	Color
Isoasparagine	0.39	Wine[a]	0.14	Wine
Asparagine	.40	Yellow-tan	.095	Yellow-tan

[a] Unless the phenol is allowed to air dry for 24 hours, even pure samples of isoasparagine will show a tan-colored halo around the wine spot due to interaction with the residual phenol at 100°.

Biological Assay.—Since only asparagine is active in supporting growth of *Neurospora* mutant S1007, the auxanographic plate technique[10] is applicable for differentiating between asparagine and isoasparagine on a semi-micro scale. Here, the addition of a crystal of test substance to a minimal agar plate heavily seeded with the microörganism followed by incubation at 30° for eighteen hours indicates the presence of asparagine by a zone of growth. Both D- and L-isomers can serve to fulfill this nutritional requirement. The quantitative determination of asparagine by means of measuring growth of the organism in liquid cultures will be described elsewhere.

(10) M. J. Beijerinck, *Arch. Neerl. Sci.*, **23**, 367 (1889).

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Copolymerization of Vinyl Acetate with a Cyclic Disulfide

BY W. H. STOCKMAYER, R. O. HOWARD AND J. T. CLARKE

In the course of an extensive study of chain transfer in the free-radical polymerization of vinyl acetate, the high reactivity of disulfides as compared with monosulfides was observed. For example, the following transfer constants C were obtained at 60°: di-n-butyl sulfide, 0.026; di-n-butyl disulfide, 1.0; diethyl dithioglycolate, 1.5. These figures are the slopes of plots[1] of reciprocal number-average polymerization degree $P_n{}^{-1}$ against the mole ratio S/M of transfer agent to monomer, for low-conversion polymers initiated by benzoyl peroxide or azo-bis-isobutyronitrile. The values of P_n were obtained viscometrically with the aid of a viscosity–molecular weight relation to be described elsewhere.

It should be mentioned that the disulfides caused considerable retardation of the polymerization of vinyl acetate; for example, at a benzoyl peroxide concentration of 10^{-2} M the addition of 5.5×10^{-3} M and 2.7×10^{-2} M dibutyl disulfide reduced the polymerization rate to about 40 and 1.5%, respectively, of the value for pure vinyl acetate. Under such conditions, the true transfer constant C may be less than the slope of $P_n{}^{-1}$ against S/M. At worst, however, this slope becomes $2C$, so that the values given above still display the high reactivity of the disulfides.

The above figures suggest that the transfer reac-

(1) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

tion in disulfides involves the scission of the disulfide link (compare the "induced decomposition" of benzoyl peroxide[2])

$$\text{R}'\text{M}_n\cdot + \text{RSSR} \longrightarrow \text{R}'\text{M}_n\text{SR} + \text{RS}\cdot \qquad (1)$$
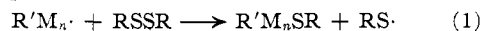
The lability of this bond under more extreme conditions is of course well known. If reaction (1) correctly depicts the transfer process, a *cyclic* disulfide would be capable of copolymerization with vinyl monomers

$$\text{R}'\text{M}_n\cdot + \underset{\text{S}\overline{}\text{S}}{\overset{\diagup\text{R}\diagdown}{}} \longrightarrow \text{R}'\text{M}_n\text{SRS}\cdot \qquad (2)$$
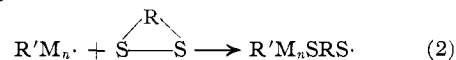
provided the resulting radical were sufficiently reactive to propagate the chain

$$\text{R}'\text{M}_n\text{SRS}\cdot + \text{M} \longrightarrow \text{R}'\text{M}_n\text{SRSM}\cdot, \text{ etc.} \qquad (3)$$
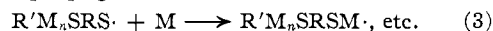
If this scheme holds, a cyclic disulfide would give an apparently *low* transfer constant by the molecular-weight method, but the polymer would contain a large amount of combined sulfur.

We have demonstrated that the reaction actually follows this course to a considerable extent, using for this purpose the cyclic disulfide 1-oxa-4,5-dithia-cycloheptane,[3] $\overline{\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}}$. An impure but adequate sample of this material was prepared[3] by cracking of the related disulfide polymer; from its properties (45.1% S, $n^{25}\text{D}$ 1.5711, d_{25}^{25} 1.261) the purity of the product is about 90% if the sole contaminant is the related monosulfide, p-oxathiane. The properties of a series of low-conversion vinyl acetate polymers prepared at 60° in the presence of various concentrations of the cyclic disulfide are given in Table I. The values of $P_n{}^{-1}$ fall on a fair straight line against S/M, yielding an apparent transfer constant of about 0.25. However the high sulfur content (7.07% S) of the last polymer corresponds to a mole ratio 0.11 of disulfide to vinyl acetate in the polymer, and therefore to an actual transfer constant of about 2.5. Since P_n for this sample is about 90, there are on the average about nine disulfide units per polymer molecule, so that the predicted copolymerization is clearly substantiated. We may remark, in view of the impurity of our disulfide and of a retardation comparable to that found with dibutyl disulfide, that the transfer constants given above are only approximate.

TABLE I

POLYMERIZATION[a] OF VINYL ACETATE IN PRESENCE OF A CYCLIC DISULFIDE, $\overline{\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}}$, AT 60°

S/M	$[\eta]$[b]	P_n	% S[c]
0	1.24	2200	
0.010	0.31	310	
.023	.26	250	
.035	.15	110	
.045	.12	90	7.07

[a] Initiator, 5×10^{-3} M azo-bis-isobutyronitrile. [b] Limiting viscosity number of low-conversion polymer in acetone, 25°. [c] Weight per cent. of sulfur in the polymer.

Obviously this reaction could in principle be used to prepare certain "block" copolymers by polymerizing vinyl monomers in the presence of polymeric disulfides. However, retardation such as that evi-

(2) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).
(3) F. O. Davis and E. M. Fettes, *ibid.*, **70**, 2611 (1948).

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.

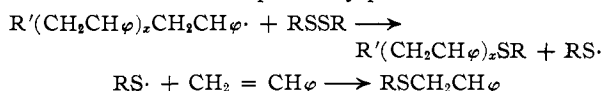(5) A. V. Tobolsky and B. Baysal, This Journal, **75**, 1757 (1953).

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The Reaction between Styrene and Ring Disulfides: Copolymerization Effected by the Chain Transfer Reaction
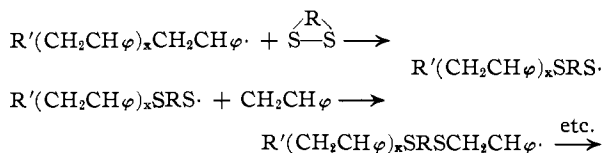
By A. V. Tobolsky and B. Baysal

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.

$$R'(CH_2CH\varphi)_xCH_2CH\varphi\cdot + \overset{R}{\underset{S-S}{\diagdown}} \longrightarrow$$
$$R'(CH_2CH\varphi)_xSRS\cdot$$
$$R'(CH_2CH\varphi)_xSRS\cdot + CH_2CH\varphi \longrightarrow$$
$$R'(CH_2CH\varphi)_xSRSCH_2CH\varphi\cdot \overset{etc.}{\longrightarrow}$$

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

(1) E. Fettes and F. O. Davis, This Journal, **70**, 2611 (1948).

(2) A. V. Tobolsky, F. Leonard and G. P. Roeser, J. Polymer Sci., **3**, 604 (1948).

(3) F. R. Mayo, R. A. Gregg and M. S. Matheson, This Journal, **73**, 1691 (1951).

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	$\bar{M}n$[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.

(4) D. C. Pepper, J. Polymer Sci., **7**, 347 (1951).

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Synthesis of Radioactive Noradrenaline

By Richard W. Schayer[1]

The synthesis of α-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-

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