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### ***cis,trans*-1,5-Cyclodecadiene—Sulfur Dioxide Copolymer**

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## *cis,trans*-1,5-Cyclodecadiene-Sulfur Dioxide Copolymer

FLOYD L. RAMP

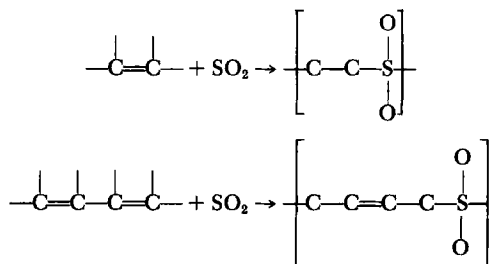
B. F. GOODRICH RESEARCH CENTER  
BRECKSVILLE, OHIO

### Summary

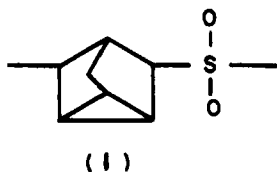
An alternating linear copolymer of *cis,trans*-1,5-cyclodecadiene and sulfur dioxide has been prepared in quantitative yield. Transannular carbon-carbon bond formation gives four saturated carbon atoms between the sulfone groups. The polymer is resistant to alkali but degrades thermally above 150°C with random chain cleavage.

### INTRODUCTION

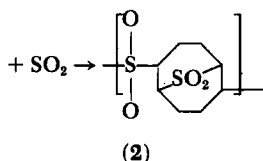
The reaction of sulfur dioxide with mono- or dienes to give polysulfones is well known. The process is free radical in character and normally results in an alternating copolymer (1).



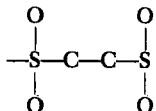
Styrene and vinyl chloride may vary to some extent from the alternating structure, (2,3). The only exception to normal polymerization of dienes has been found with norbornadiene (4-6), which yields at least partially, structure (1).



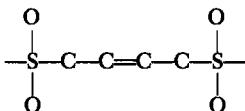
Transannular bond formation in 1,5-cyclooctadiene might also lead to sulfur dioxide separated by more than two saturated carbon atoms. However, it has been shown that two moles of sulfur dioxide are incorporated per mole of 1,5-cyclooctadiene, giving a polymer with a repeating unit (2) (6,7).



All these polymers except that from norbornadiene are made up of the units



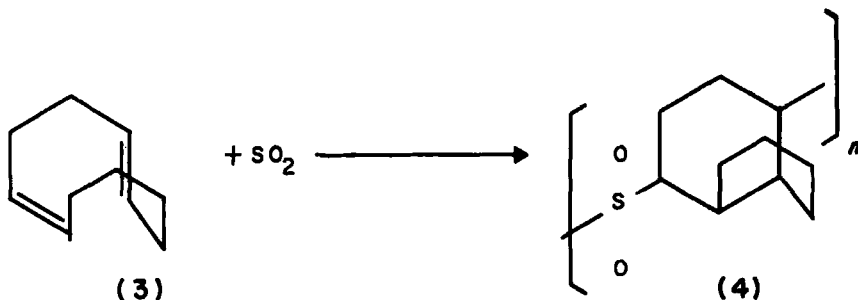
or the vinylog



They possess alkali sensitivity and thermal instability which is known to be associated with monomeric materials containing this structural feature (8,9). Separation of the sulfone groups by more than two saturated carbon atoms in small molecules which carry no electron-withdrawing groups results in a marked increase in alkali resistance (10). Polysulfones with four or more carbon atoms between the sulfone groups have been obtained by condensation of dihalides and dimercaptans (11-13), or by free radical-catalyzed addition of dimercaptans to diolefins (14,15). Oxidation converts the intermediate sulfides to sulfones. Little information is available

concerning their thermal properties. The polysulfones prepared by sulfide oxidation showed increased alkali resistance. Thermal properties of these polymers reported recently by Wellisch et al. (11) will be discussed later.

This paper described a polysulfone prepared from sulfur dioxide in which the sulfone linkages are separated by four saturated carbon atoms. *cis,trans*-1,5-Cyclodecadiene, (3), gives a one-to-one soluble copolymer with sulfur dioxide with transannular bond formation in the carbocyclic ring, (4).



## DISCUSSION AND RESULTS

### Polymerization

Although sulfur dioxide copolymerization is agreed to be free radical in character (12), there is wide variation in effectiveness of various free-radical initiators. Hill and Caldwell obtained excellent yields in the norbornene system with *t*-butyl hydroperoxide as an initiator (13). Zutty et al. found extremely rapid copolymerization with the parent hydrocarbon in the absence of initiator (14-16). Similar studies by Vanhaeren and Butler with bicycloheptadiene suggest that traces of oxygen or peroxy materials act as initiators (17). On the other hand, Frazer and O'Neill report that cumene hydroperoxide, benzoyl peroxide, and ammonium nitrate are ineffective in sulfur dioxide-cyclooctadiene copolymerization but that methyl ethyl ketone peroxide was quite effective (7).

In our studies with *cis*-1,5-cyclodecadiene, ammonium nitrate was found to be the initiator of choice giving in sustained polymerization a nearly quantitative yield of polymer. Other initiators may be used. For example, *t*-butyl hydroperoxide or methyl ethyl

ketone peroxide in acetone or *t*-butanol resulted in yields >90% when large amounts of initiator were used.

Some "flash" copolymerization (17) occurred when the reactants were mixed in the absence of solvent or in media such as methanol, acetone, or *t*-butanol. However, in the absence of added initiator the reaction stopped after an initial period of rapid polymerization.

In inert solvents such as chloroform or cyclohexane a brown oil was obtained in the absence of initiator but quantitative yields of polymer were obtained if aqueous or methanolic ammonium nitrate was added immediately after mixing.

The polymerization catalyzed by ammonium nitrate is not sensitive to olefin/SO<sub>2</sub> ratio or to the order of addition of reagents. The polymerization is inhibited by thioacetamide. The thermally stable *cis,cis*-1,6-cyclododecadiene does not polymerize under conditions which give quantitative yield from the 1,5-isomer nor does its presence appear to influence the polymerization of the 1,5 isomer.

The flash polymerization frequently observed invariably gave low conversion. This is probably due to traces of peroxidic material (12) which is rapidly consumed. No rationalization of the wide variation in initiator effectiveness with various olefins is immediately apparent.

A wide variety of solvents may be used with the nitrate catalyst system. In nonsolvents such as acetone, methanol, acetonitrile, and *t*-butanol the polymer separated as a white precipitate. Solvents such as chloroform, 1,2-dichloroethane, and  $\gamma$ -butyrolactone gave clear, colorless solutions with increasing viscosity as polymerization progressed. The polymerization proceeded slowly in pure dimethyl sulfoxide (a polymer solvent) but 16 hr after addition of methanol a high yield of polymer was obtained. Representative polymerization data are shown in Table 1.

### Polymer

The polymer was in every instance soluble in suitable solvents—chloroform, 1,2-dichloroethane,  $\gamma$ -butyrolactone, dimethyl sulfoxide, *m*-cresol. The polysulfone was insoluble in acetonitrile, acetone, tetrahydrofuran, ethyl acetate, toluene, 1,2,4-trichlorobenzene, and carbon tetrachloride but partially soluble in dimethyl formamide and methylene chloride.

Inherent viscosity was normally determined in chloroform (0.4

TABLE 1<sup>a</sup>  
Copolymerization of Sulfur Dioxide and 1,5-Cyclodecadiene

Reaction medium	Time, hr	Yield, %	$\eta_{inh}^b$	$\eta_{inh}^b$ (after 5% alc. KOH, 24 hr)
<i>t</i> -Butanol	20	97	0.52	0.47
Acetonitrile	3	90	0.66	0.50
Acetone	70	92	0.55	—
Methanol	24	95	0.60	0.51
Dimethyl sulfoxide	20	94	0.49	0.52
$\gamma$ -Butyrolactone	70	93	0.61	0.58
	23	84	0.44	0.36
Chloroform	70	96	1.03	0.60
	19	95		
1,2-Dichloroethane	20	93	0.80	0.52
Chloroform- <i>t</i> -butanol	18	93	0.73	0.51
1,2,3-Trichloropropane	21	94	0.79	0.51
Chloroform	18	93	0.95	0.62 <sup>c</sup>
$\gamma$ -Butyrolactone	16	85	0.77	0.54 <sup>d</sup>
Purified chloroform	70	94	0.83	0.53
Methanol- $\gamma$ -butyrolactone	24	88	0.59	0.49
Chloroform	24	91	0.83	0.53 <sup>e</sup>
Methanol-chloroform	20	92	0.60	0.45
Chloroform	20	92	0.79	0.55 <sup>f</sup>
	21	96	0.55	0.48 <sup>f</sup>
Chloroform	65	97	0.86	0.53
Chloroform	21	45	0.84	0.71 <sup>g</sup>

<sup>a</sup> All reactions carried out with 8.3% diene in the solvent and SO<sub>2</sub>/diene mole ratio 2:1 at 25°C. Catalyst aqueous ammonium nitrate.

<sup>b</sup>  $\eta_{inh}$ , inherent viscosity ( $\ln \eta_{rel(c)}$ ) for 0.4 g polymer/100 ml of chloroform solution.

<sup>c</sup> No excess sulfur dioxide.

<sup>d</sup> 30% normal initiator level.

<sup>e</sup> Diene purified by diborane treatment.

<sup>f</sup> Methanolic ammonium nitrate catalysis.

<sup>g</sup> Diene—a mixture of 1,5- and 1,6-cyclodecadiene.

g/100 ml). Polymers prepared in solution typically have an inherent viscosity from 0.8 to 1.0. Polymers precipitating as formed generally ranged from 0.5 to 0.6. The osmotic molecular weight was determined in  $\gamma$ -butyrolactone at 37°C using an SS-08 membrane. Table 2 shows a comparison of molecular weight and inherent viscosity data.

Representative polymers prepared in solvents and nonsolvents

TABLE 2  
Molecular Weight vs. Inherent Viscosity

Polymerization medium	$\eta_{inh}$	$M_n$	Polymer
Acetone	0.61	25,000	—
Chloroform	1.03	60,000	—

contained 16.08 and 15.94% sulfur, respectively. Theory for  $C_{10}H_{16}SO_2$ , 16.03.

Both infrared (Fig. 1) and NMR confirmed the absence of carbon-carbon double bonds. The very ready thermal isomerization of *cis,trans*-1,5-cyclodecadiene to 1,2-divinyl cyclohexane establishes the ease of 1,6 bond formation.

These facts are consistent with a 1,4-perhydronaphthalene structure in the polymer (4). The polymer can be cast from  $\gamma$ -butyrolactone into clear, colorless amorphous films. The films are brittle but can be creased without breaking. Satisfactory specimens for stress-strain measurement were not obtained although the tensile strength is at least 8000 psi at very low elongation.

### Polymer Degradation

**Thermal.** Differential thermal analysis shows no change up to 235°C in air and no change to 250°C in nitrogen or vacuum. Hence oxidative attack must start about 235°C. No decomposition products

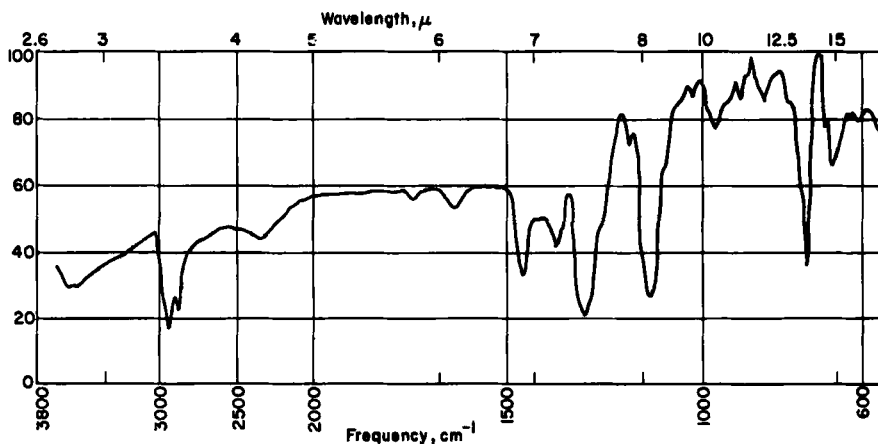


FIG. 1. Infrared spectrum of *cis,trans*-1,5-cyclodecadiene-sulfur dioxide copolymer.

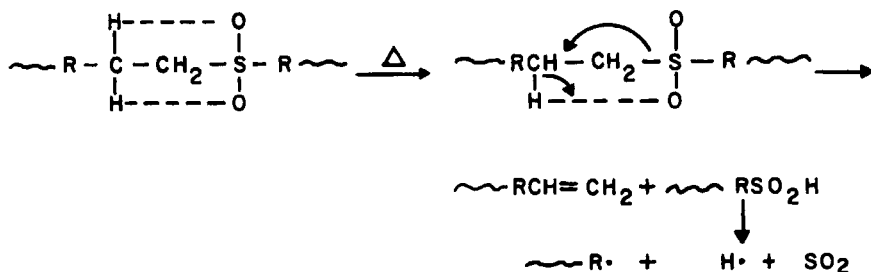
TABLE 3  
Mass Spectrograph Analysis of Thermal Decomposition Products

Hydrocarbon	Relative mole %
C <sub>10</sub> H <sub>8</sub>	6.9
C <sub>10</sub> H <sub>10</sub>	3.4
C <sub>10</sub> H <sub>12</sub>	29.7
[presumably  ]	
C <sub>10</sub> H <sub>14</sub>	54.6
[presumably  ]	
C <sub>10</sub> H <sub>16</sub>	5.4

were noted in the mass spectrometer at 247°C but at 300°C the polymer became black and hydrocarbons were found as indicated in Table 3.

The thermal decomposition of polysulfones prepared from sulfur dioxide and olefins at or near their melting points give high yields of olefin and sulfur dioxide (18). Random degradation with a large decrease in molecular weight at much lower temperatures has also been noted. Poly-1-butene sulfone degrades with no appreciable loss in weight (19) when heated, alone or in solution, at 70°C.

Polysulfones with four or more saturated carbon atoms between the sulfone groups have been prepared (20-24). The thermal characterization of this class of polysulfones was reported very recently by Wellisch et al. (11). They noted some decomposition at 200°C and rapid decomposition at 275°C. The study was made primarily upon the decomposition products. No evidence related to molecular weight drop at lower temperatures was reported. However, the mechanism proposed to account for their results would give in random cleavage and hence large decreases in molecular weight with little weight loss.





The thermal characteristics of cyclodecadiene-sulfur dioxide copolymers are consistent with this mechanism—a large decrease in molecular weight with only a slight change in weight (Table 4).

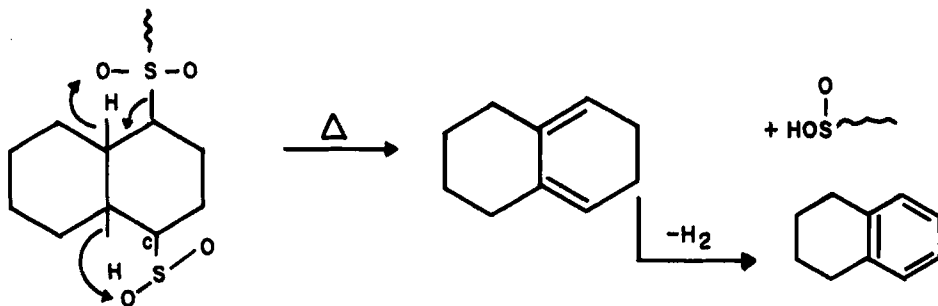
**TABLE 4**  
Thermal Degradation of Copolymer After 1 Hour

Temp., °C	Weight loss, %		Inherent viscosity	
	Air	Nitrogen	Air	Nitrogen
—	—	—	0.94	0.94
100	0	0	0.92	0.93
150	1	1	0.83	0.84
200	1	2	0.40	0.63 <sup>a</sup>
250	9	3	0.10	0.20 <sup>b</sup>
275	12	9	0.12	0.17 <sup>b</sup>

<sup>a</sup> Copolymer light tan.

<sup>b</sup> Polymer black—some insoluble material present.

The extent of this reaction is small enough that it is not apparent in the differential thermal analysis run on the polymer.



The hydrocarbons observed by mass spectrometry are those expected from this mode of decomposition.

The density of the polymer was found to be 1.4. X-ray analysis indicated no crystallinity. The infrared spectrum of the polymer is attached.

**Alkaline.** One of the chief characteristics of olefin polysulfones is their sensitivity to alkali. The cyclodecadiene-sulfur dioxide copolymer is much more stable toward alkali (Table 5), remaining

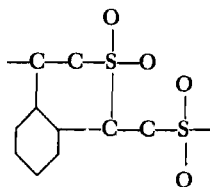
TABLE 5  
Stability of Copolymer to Alkali

Base	Temp., °C	Time, hr	Orig. $\eta_{inh}^a$	Final $\eta_{inh}^a$
5% Alc. KOH	25	24	0.83	0.53 <sup>b</sup>
5% Alc. KOH	78	3	0.83	0.47 <sup>b</sup>
5% Alc. KOH	25	168	0.83	0.47 <sup>b</sup>

<sup>a</sup>  $\eta_{inh}$ , inherent viscosity, 0.4 g/100 ml chloroform.

<sup>b</sup> The polymers remained insoluble and were recovered nearly quantitatively. The copolymer of sulfur dioxide and butadiene degraded and dissolved in ½ hr under these conditions.

insoluble is 5% alcoholic potassium hydroxide. The polymer may be recovered without loss after several days. Butadiene-sulfur dioxide copolymer dissolves in ½ hr under these conditions. The inherent viscosity of a large number of preparations dropped to a range of 0.47 to 0.55 even though the initial value ranged from 0.5 to 1.1. This suggests the presence of a unit from monoolefin in the polymer. Such material could come from the thermal isomerization to 1,2-divinyl cyclohexane prior to polymerization.



1,2-Divinyl hexane copolymerized with sulfur dioxide in chloroform to give an insoluble polymer. Both intra(linear)- and inter-(cross-linking)-molecular copolymerization should be possible (25). The structure of this polymer was not established. However, assuming one sulfur dioxide per double bond, the yield was 84%.

An inherent viscosity of 0.5 was shown by osmotic molecular weight to correspond to an  $M_n$  of ~20,000 or a  $D_p$  of ~100. Hence 1% of rearranged hydrocarbon in the 1,5-cyclodecadiene could account for the observed drop. Because of the great thermal sensitivity of the diene, satisfactory analysis by VPC were not obtained. Normal analysis by NMR gave no indication of the divinyl isomer

**TABLE 6**  
Relative Solvent Power for the Copolymer

Solvent	Inherent viscosity
Dimethyl sulfoxide	0.97
$\gamma$ -Butyrolactone	1.05
Sulfuric acid	1.11
Chloroform	0.74
1,2-Dichloroethane	0.96

in the diene. Analysis by NMR with computer attachment indicated less than 0.5% divinyl content.

Alternative explanations are that ~1% of the 1,5-cyclodecadiene polymerizes without formation of a transannular carbon-carbon bond or that sulfur dioxide causes some acid-catalyzed rearrangement of the diene. Data are not available to distinguish between these possibilities.

A comparison (Table 6) of inherent viscosities of a given sample of polymer in different solvents indicates the relative solvent power.

The resistance of the polymer in air to ultraviolet light is shown in Table 7.

**Polymer Stabilization.** The exotherm starting at 235°C with DTA samples in air was not observed with samples under nitrogen. Similarly, no change in the polymer was noted in samples heated to 250°C under vacuum. The exotherm was attributed to oxidation and various antioxidants were evaluated. Ionox (R) 330 or phenyl- $\beta$ -naphthylamine gave very slight if any change in the melting char-

**TABLE 7**  
Influence of Ultraviolet Light on Copolymer<sup>a</sup>

Exposure time, hr	$\eta_{inh}$
0	0.86
0.5	0.85
1.0	0.85
2.0	0.82
4.0	0.80

<sup>a</sup> Illuminated as a film between  $\frac{1}{8}$ -in. Vycor glass plates mounted 5 in. from a 275W GE sunlamp.

acteristics. Similarly, stannous oxide and thioacetamide, reported to be stabilizers for polysulfones (28), gave no obvious change in melt characteristics.

## EXPERIMENTAL

### *cis,trans*-1,5-Cyclodecadiene (26)

*cis,trans*-1,5-Cyclodecadiene is formed in a yield of 80% when butadiene and ethylene react together at a total pressure of 20 to 38 atm and 20°C in the presence of "bare" nickel, i.e., a nickel catalyst whose ligands can all be displaced by butadiene. Cyclooctadiene or cyclododecatriene complexes of nickel are particularly suitable. The reaction mixture may contain some *n*-1,4,9-decatriene, cyclooctene, or 1,2-divinyl cyclohexane. The last component arises from thermal rearrangement of *cis-trans*-1,5-cyclodecadiene. The thermal rearrangement proceeds slowly but quantitatively at about 80°C and at a preparative rate at 150°C.

The diene was separated from catalyst and high-boiling to residue by distillation through a rotofilm still at 34 to 35°C/2 mm. The crude diene was fractionated through a 14- × 1½-in. glass helix packed column. The pot temperature was maintained at 66°C. *cis,trans*-1,5-Cyclodecadiene distilled at 37°C/mm  $n_D^{25}$  1.4939.

Analysis of the 1,5 isomer for purity by vapor-phase chromatography was not satisfactory. The ease of thermal rearrangement led to erroneously low figures for the purity of this material. NMR gave the most reliable results. The sample of *cis,trans*-1,5-cyclodecadiene distilled at 33°C/1.4 mm,  $\eta_D^{25}$  1.4938 showed <0.5% divinyl content.

### *cis,cis*-1,6-Cyclodecadiene

*cis,trans*-1,5-Cyclodecadiene may also be isomerized to *cis*-1,6-cyclodecadiene by heating in the presence of "bare nickel," Raney nickel, or palladium (27).

*cis,cis*-1,6-Cyclodecadiene is a thermally stable compound reported to melt at 28°C. A sample with a clear point of 24°C had  $\eta_D^{25}$  1.4977 and b.p. 39 to 40°C/1.6 to 1.9 mm.

### Preparation of *cis,trans*-1,5-Cyclodecadiene-Sulfur Dioxide Copolymer

*cis,trans*-1,5-Cyclodecadiene (36 g), chloroform (480 g), and a 20% aqueous solution of ammonium nitrate (6 ml) were charged into a 1-liter flask equipped with a stirrer. Sulfur dioxide (36 g) was added over the surface. Slight turbidity developed in 10 min. The mixture was stirred at room temperature for 17 hr. The viscous mass was diluted with 400 ml chloroform and transferred to a large beaker with 200 ml chloroform. The polymer was precipitated by addition of 1.5 liters of methanol with vigorous stirring. The polymer was rinsed with methanol and dried under vacuum at 50°C. Yield 50.6 g—94%  $\eta_{inh} = 1.1$ .

The same procedure with a nonsolvent such as acetone gave a 92% yield of polymer ( $\eta_{inh}$  0.55) which was isolated by filtration from the reaction mixture.

### Acknowledgment

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### Zusammenfassung

Ein Copolymerisat bestehend aus *cis,trans*-1,5-Cyclohexadien und Schwefeldioxid in alternierender Anordnung wurde in quantitativer Ausbeute dargestellt. Durch transannulare Kohlenstoff-Kohlenstoffbindung ergibt sich eine Anordnung von vier Kohlenstoffatomen zwischen den Sulfongruppen. Das Polymerisat ist beständig gegenüber Alkalien, zerfällt jedoch thermisch bei Temperaturen von oberhalb 150°C unter statistisch erfolgreicher Kettenspaltung.

### Résumé

On a préparé avec un rendement quantitatif un polymère linéaire alternant du *cis,trans*-1,5-cyclodécadiène avec l'anhydride sulfureux. La formation transannulaire de liaisons carbone-carbone donne quatre atomes de carbones saturés entre les groupes sulfones. Le polymère résiste aux alcalis, mais audessus de 150°C subit une décomposition thermique avec ouverture des chaînes au hasard.