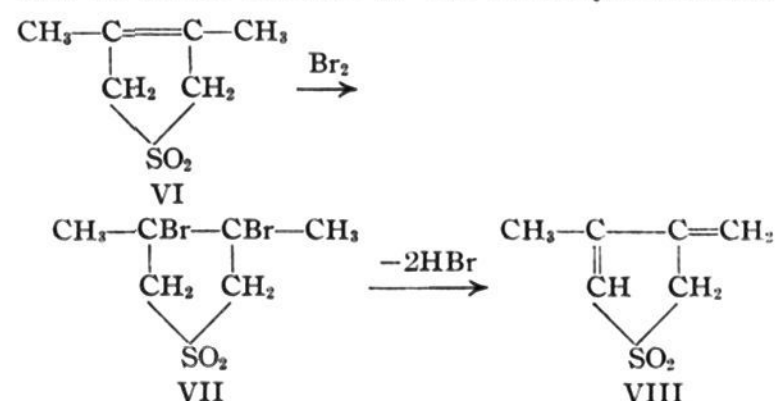


procedure it has been possible to increase the yield of the crystalline sulfone to 22% on the basis of the polysulfone which is used up in the process. It has not been possible to obtain other crystalline products from 1-pentynepolysulfone. Neither has it been possible to pyrolyze other acetylene-polysulfones to give a product similar to the C₁₀H₁₆SO₂ compound.

Evidence that this crystalline degradation product has an α,β -unsaturated sulfone linkage has been obtained by a study of its addition reactions. Sodimalonic ester adds readily to give a product of the expected composition.³ Reduction of the cyclic sulfone with zinc and acetic acid yields a dihydro compound. This reaction must proceed by a 1,4-addition of hydrogen with a resulting shift of the double union to the 3,4-position in the ring (III, IV or V) as otherwise this reduction would be expected to give a tetrahydro compound.

Catalytic reduction of the cyclic sulfone using hydrogen at three atmospheres and a platinum oxide-platinum black catalyst⁴ gave another dihydro compound. The catalyst was poisoned rather quickly during this reaction. Since this dihydro compound is isomeric with the one formed by a 1,4-addition of hydrogen, it must be the 1,2-addition product. However, if it is the result of 1,2-addition of hydrogen to one of the structures III, IV or V, the resulting molecule would still be an α,β -unsaturated compound and would be expected to reduce with zinc and acetic acid. This could not be accomplished.

One or the other of these reduction products may be derived from a rearranged form of the cyclic sulfone. Backer and Strating⁵ have shown that the cyclic sulfone (VIII) obtained by the addition of sulfur dioxide to 2,3-dimethylbutadiene



(3) Kohler and Potter, *THIS JOURNAL*, **57**, 1316 (1935), have shown this reaction is characteristic of α,β -unsaturated sulfones.

(4) Adams, Vorhees and Shriner, "Org. Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(5) Backer and Strating, *Rec. trav. chim.*, **53**, 525 (1934); **54**, 170 (1935).

followed by bromination and removal of two molecules of hydrogen bromide has only one double bond in the ring.

The sulfone (III, IV or V) obtained by the pyrolysis of 1-pentynepolysulfone might have a similar structure but the fact that Backer and Strating's compound (VIII) adds bromine, whereas our compound does not, seems to cast doubt on this possibility.

The polysulfones derived from acetylenes have an α,β -unsaturated sulfone linkage⁶ (I or II) and therefore would be expected to show the characteristics of simpler molecules containing this system.³ Attempts to add sodimalonic ester, the Grignard reagent and hydrogen from zinc and acetic acid all resulted in degradation of the polymers without the formation of products which could be characterized.

X-Ray diffraction patterns of the polysulfones from 1-pentyne, 1-hexyne, 1-heptyne, 1-nonyne and 1-pentadecyne have been furnished us by Dr. S. T. Gross. Fibered samples obtained by extruding the hot sample through a conical orifice were used. The patterns were prepared at 5 cm. using radiation from a copper target Phillips metallix diffraction X-ray tube. A nickel filter furnishing approximately monochromatic K-radiation was used. An analysis of the patterns will be reported later by Dr. Gross. It is of interest to note that the patterns are much better defined than any which have been obtained with olefin polysulfones. It is possible that the many asymmet-

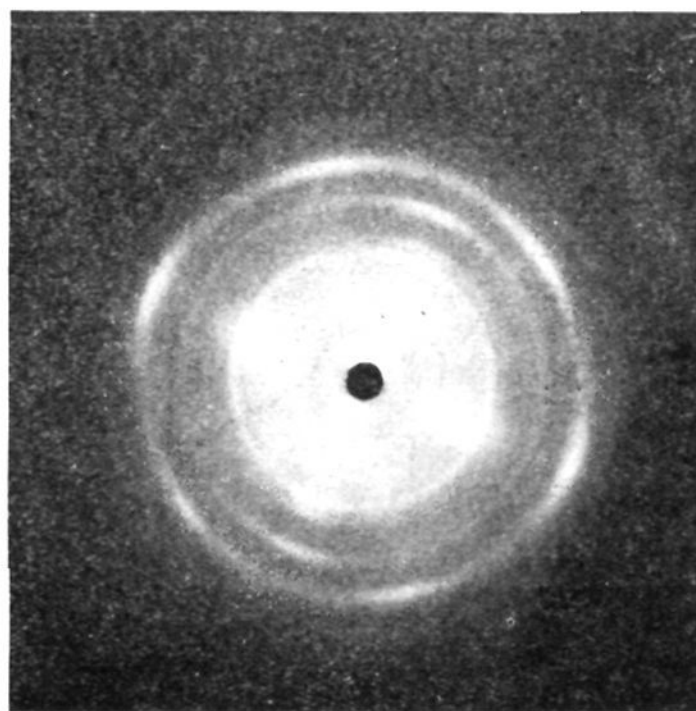


Fig. 1.—Pentyne polysulfone.

(6) This fact was called to our attention by Dr. H. R. Turner.

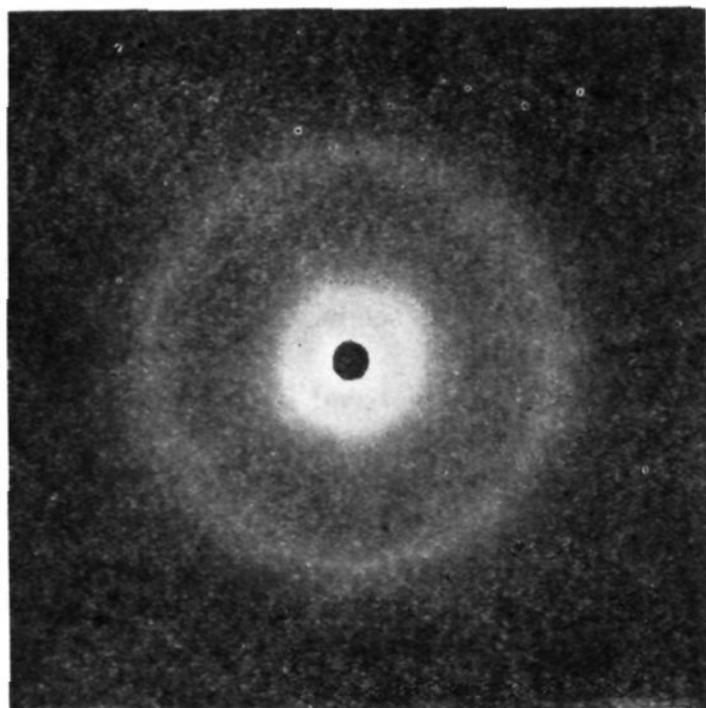


Fig. 2.—Hexyne polysulfone.

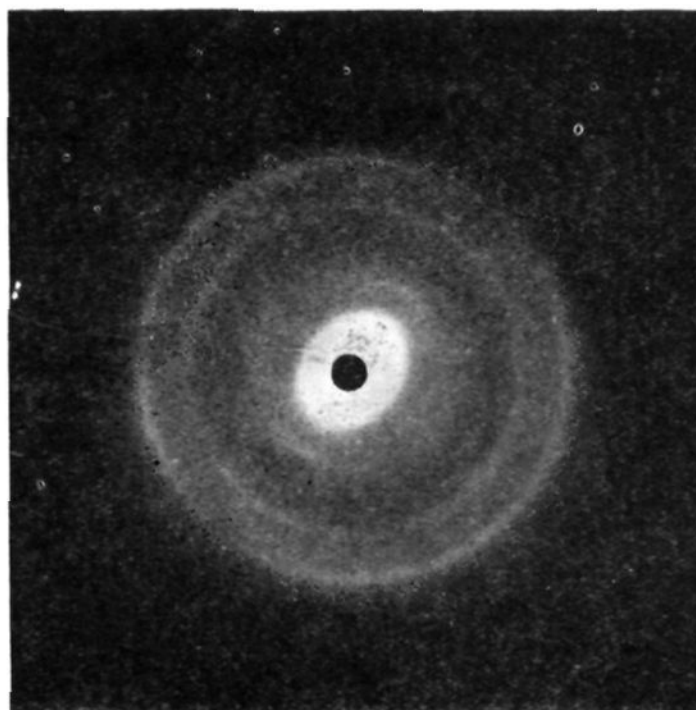


Fig. 4.—Nonyne polysulfone.

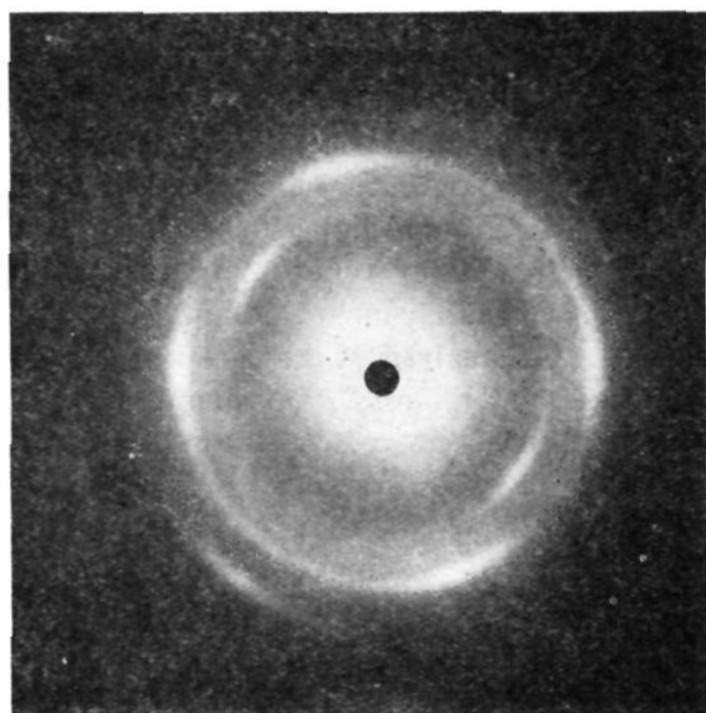


Fig. 3.—Heptyne polysulfone.

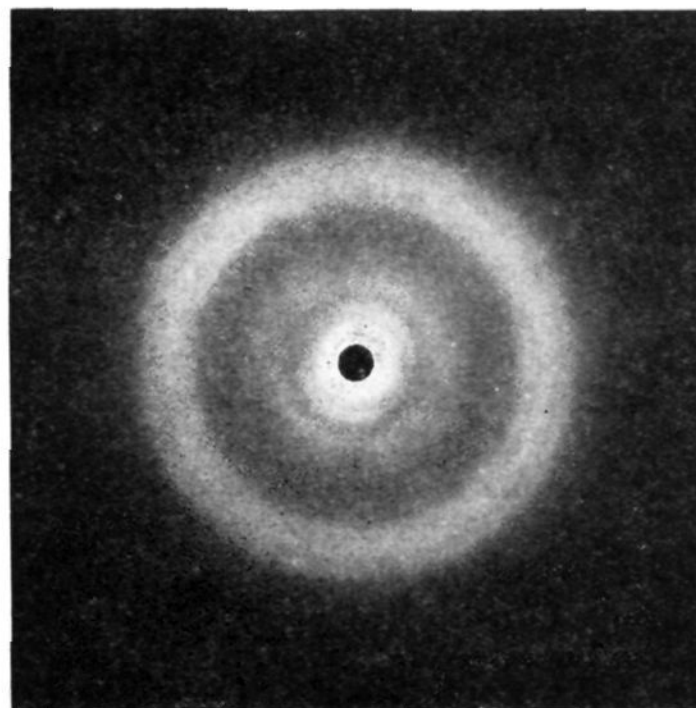


Fig. 5.—Pentadecyne polysulfone.

ric centers in the latter are responsible for their less sharp patterns.

Attempts to prepare a polysulfone from acetylene itself proved futile.

Experimental

Heat Degradation of 1-Pentyne polysulfone.—In general the polymer was decomposed by boiling its dioxane solution as previously described.² The yields have been improved and the details of a typical experiment follow.

A solution of 10 g. of 1-pentyne polysulfone in 500 cc. of dioxane was heated under reflux condenser for about fifty hours. The evolution of sulfur dioxide had nearly stopped at this time. The dioxane was removed by boiling under reduced pressure and ether was added to the brownish residue. The ether solution was filtered and the residue

again extracted with ether. The ether extracts were combined, washed with 5% sodium hydroxide solution and then with water. The alkaline extract turned orange-red during the extraction. The ether layer was dried over anhydrous sodium sulfate, filtered and most of the ether removed by distillation on a steam cone. The last of the ether was removed in a desiccator under reduced pressure. The brownish residue containing some crystals was allowed to stand for about a day in the refrigerator to permit as much crystallization as would occur. This residue, which resembled apple butter, was spread on a clay plate and allowed to stand about a day. The residual material was scraped off and crystallized from dilute alcohol. Norite was used to remove the color. The material thus obtained amounted to 0.3 to 0.4 g. (3.5–5.3%) of product melting at 88°.

In one run 10 g. of polysulfone in 400 cc. of purified

dioxane was heated under a reflux condenser in a current of nitrogen for about one hundred twenty-five hours. The evolved sulfur dioxide was led into standard alkali and titration showed that 8.5% of the total sulfur dioxide in the polymer came off in this time. Evaporation of the dioxane and extraction of the residue with ether left 6.6 g. of polymer which sulfur analysis showed to be essentially unchanged. The yield of crystalline monosulfone in this run was 0.3 g. (3.48% on total polymer or 11.5% on polymer destroyed).

In another set of experiments 30-g. samples of the polymer in 500 cc. of dioxane were heated for about twenty-four hours, then the unchanged polymer was isolated, put in fresh dioxane and heated again for twenty-four hours. This was repeated until practically no unchanged polymer was left. Only one such experiment is recorded for illustration.

	Heating				
	First	Second	Third	Fourth	Fifth
G. polymer	30	24	18.3	14.0	10.7
Cc. dioxane	500	300	250	200	200
Hours refluxing	24	25	26	25	35
G. polymer lost	6	5.7	4.3	3.3	2.7
G. crystalline C ₁₀ H ₁₆ SO ₂	0.88	0.8	0.71	0.43	0.28
% yield based on polymer used	19.4	18.5	21.8	17.1	13.7

Careful fractional distillation of the dioxane from one of the decomposition experiments showed a low boiling fraction which contained a small amount of 1-pentyne. This was identified as the mercury derivative by means of Johnson and McEwen's reagent.⁷ Known 1-pentyne gave a derivative melting at 117–118°, the alkyne from the pyrolysis gave a derivative melting at 116–119°; the mixture of the two melted at 116–119°.

An acidic substance was always present in the dioxane after the heating period but no definite acidic product could be separated.

Reactions of C₁₀H₁₆SO₂.—As noted previously² the sulfone would not add bromine but did decolorize alkaline potassium permanganate solution.

The addition of sodiomalonic ester was accomplished by treating 0.7 g. of ethyl malonate in about 5 cc. of benzene with sodium until the salt was formed. The excess sodium was removed and 60 cc. of benzene added. To the suspension thus obtained was added 0.44 g. of the sulfone. The reaction mixture was heated for three hours on a steam-bath, cooled, washed with water until the washings were neutral, and the benzene removed. The excess malonic ester was removed by distillation under reduced pressure. When the residue was cooled and dried on a clay plate, 0.56 g. of white crystals remained. Crystallization from alcohol gave a product melting at 104.5–105°.

Anal. Calcd. for C₁₇H₂₈O₆S: S, 8.9. Found: S, 8.6.

Attempts to add a second mole of malonic ester to this product were ineffective and the starting material was recovered.

Reduction with zinc and acetic acid was carried out by dissolving 0.41 g. of the sulfone in 50 cc. of glacial acetic acid and boiling the mixture for seven hours with 10 g. of zinc. The hot mixture was then filtered from undissolved zinc, the zinc washed with hot acetic acid, and then the

combined acetic acid solutions diluted with water. The solution turned cloudy but no crystals separated. The solvent was then removed through a Widmer column and the residue was dissolved in ether. After removal of the ether the residue was finally induced to crystallize from low-boiling petroleum ether. The product thus obtained melted at 49–50° on a hot-stage microscope. Analysis showed it to be a dihydro derivative of the sulfone.

Anal. Calcd. for C₁₀H₁₈SO₂: C, 59.35; H, 8.97. Calcd. for C₁₀H₂₀SO₂: C, 58.76; H, 9.87. Found: C, 59.43; H, 9.06.

Catalytic reduction of 2.86 g. of the sulfone in 50 cc. of absolute alcohol with hydrogen in the presence of 0.1 g. of platinum oxide-platinum black⁴ in a low pressure reduction apparatus⁸ for twenty hours gave a solution with a faint odor of hydrogen sulfide. The platinum catalyst was removed by filtration. The solution was cooled in a dry ice-acetone bath and the solid collected in a filter. The solid thus obtained was twice recrystallized from ether by cooling the solution in a dry ice-acetone bath. This product melted at 56.5–57° on a hot-stage microscope.

Anal. Calcd. for C₁₀H₁₈SO₂: C, 59.35; H, 8.97. Found: C, 59.55, 59.43; H, 8.88, 8.90.

A mixture of this compound with the dihydro derivative which melted at 49–50° melted below 44°. This dihydro compound could not be further reduced with zinc and acetic acid.

Attempts to Add Reagents to the Acetylene Polysulfones.—When 5 g. of 1-pentynepolysulfone in 225 cc. of glacial acetic acid was boiled under a reflux condenser with 15 g. of powdered zinc for thirteen hours, some hydrogen sulfide was liberated. After isolating the polymer it was found to have the melting point (200–208°) characteristic of the original 1-pentynepolysulfone.² Attempts to reduce 1-nonynepolysulfone with zinc and acetic acid were also unsuccessful. Similarly attempts to reduce dioxane solutions of 1-nonynepolysulfone, propynepolysulfone and 1-pentynepolysulfone with hydrogen in the presence of platinum oxide-platinum black^{4,8} were unsuccessful.

The carefully dried polysulfones from 1-pentyne, 1-hexyne, 1-heptyne, 1-nonyne and phenylacetylene dissolved in an ether solution of ethylmagnesium bromide with the evolution of gas and the formation of amber to red colored solutions. Attempts to follow the gas liberation quantitatively gave unreplicable results. Recovery of the polymers from the solution showed that considerable degradation had taken place in this reaction. No evidence for a simple addition was obtained.

Sodium malonic ester in dry benzene did not add to 1-pentynepolysulfone in the cold and when the mixture was warmed the polymer was degraded.

Attempts to Obtain Acetylene Polysulfone.—Various attempts to bring about the combination of acetylene and sulfur dioxide at atmospheric pressure and under the pressure of a solution of acetylene in acetone and sulfur dioxide were made. Ascaridole was used as a catalyst. Ethyl alcohol was also added to some of the mixtures. In the experiments at atmospheric pressure acetylene was bubbled through the cold reaction mixture. No evidence of polymer formation was ever obtained.

(7) Johnson and McEwen, *THIS JOURNAL*, **48**, 469 (1926).

(8) Adams and Vorhees, *ref. 4*, p. 53.

