

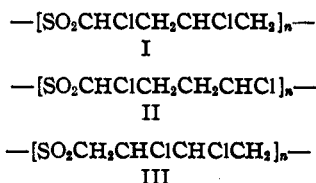
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Chloride Polysulfone<sup>1</sup>

BY C. S. MARVEL AND L. H. DUNLAP

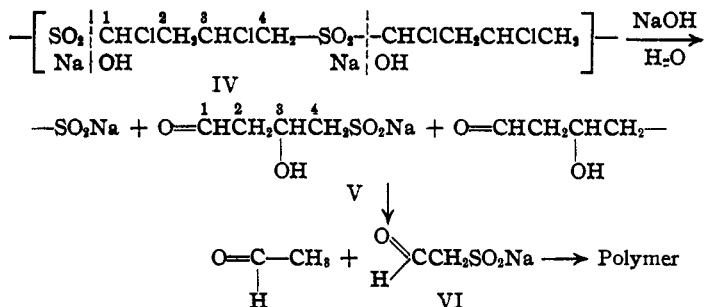
Vinyl chloride is unique among the olefins which have been found to combine with sulfur dioxide to give polysulfones since it yields a polymer having two olefin units to one sulfur dioxide unit.<sup>2</sup> In the work previously reported no evidence for the exact structure of the polymer was obtained. Hence a further study of this problem has been made.

When vinyl chloride polysulfone is hydrolyzed with 20% sodium hydroxide and volatile products are removed rapidly from the reaction flask in a current of steam, an aldehyde is produced.<sup>2</sup> This aldehyde has now been identified definitely as acetaldehyde. During the hydrolysis not only is the aldehyde formed but at the same time all of the chlorine is removed from the organic molecule as sodium chloride and practically all of the sulfur remains in organic combination. These facts make it possible to assign a definite structure (I) to vinyl chloride polysulfone.



The three most probable structures for the polymer are those represented by formulas I, II and III in which there are four carbon atoms between the sulfone groups. It is conceivable that vinyl chloride could dimerize to a butylene derivative which then would form a polysulfone. But all of the polysulfones which are derived from olefins are degraded by liquid ammonia and by dilute alkalis to yield cyclic disulfones.<sup>3</sup> Vinyl chloride polysulfone does not show this behavior.

Only structure I can account for the hydrolysis of the polymer to yield acetaldehyde and a sulfur-containing organic residue, according to the following scheme.



The  $\alpha$ -halogen sulfone linkage should break readily to yield the aldehyde on carbon 1 (IV and V). The hydrolysis of the chlorine atom on carbon 3 then gives a  $\beta$ -hydroxy aldehyde, which by a retrograde aldol reaction would give acetaldehyde and an aldehydo sulfinic acid (VI) which would be expected to polymerize in the alkaline reaction medium.

A polymer of structure II would be expected to yield succindialdehyde which would polymerize in the alkaline medium and no acetaldehyde could form. A polymer of structure III might hydrolyze to a glycol but the primary sulfone linkage would not break readily under the conditions used in our experiments.

Further experiments on the pyrolysis of vinyl chloride polysulfone in dioxane solution have shown that the reaction is very complex and both hydrogen chloride and sulfur dioxide are lost. No definite polymeric residue seems to be formed. Liquid ammonia removes the chlorine from the polymer forming ammonium chloride and considerable sulfur dioxide is also removed from the polymer. The reaction is not clean cut and definite polymeric products could not be isolated from the reaction mixture.

## Experimental

## Alkaline Hydrolysis of Vinyl Chloride Polysulfone.—

In a 1-liter distilling flask were placed 4.8 g. of powdered vinyl chloride polysulfone and 100 cc. of 20% aqueous sodium hydroxide. A current of steam was passed through this mixture, the distillate was cooled in a long condenser and collected below the surface of a solution containing 1 g. of 2,4-dinitrophenylhydrazine, 10 cc. of concentrated sulfuric acid and 75 cc. of ethanol. After about one hour of steam distillation the distillate was worked up to yield the aldehyde 2,4-dinitrophenylhydrazone. The yield was 0.35 g. (6.2% of the theoretical amount). In another run

(1) This is the tenth communication on polysulfones. For the ninth see, *THIS JOURNAL*, **60**, 1803 (1938).

(2) Marvel and Glavis, *ibid.*, **60**, 2622 (1938).

(3) Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935); Hunt and Marvel, *THIS JOURNAL*, **57**, 1691 (1935); Glavis, Ryden and Marvel, *ibid.*, **56**, 707 (1937).

2.8 g. of polymer gave 0.2 g. (6.1%) of the 2,4-dinitrophenylhydrazone derivative. The derivative was carefully recrystallized from alcohol and then melted at 160°. Acetaldehyde 2,4-dinitrophenylhydrazone melts at 164.5°<sup>4</sup> and a mixture of an authentic specimen with the derivative isolated from the above hydrolysis melted at 162°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O<sub>4</sub>: C, 42.8; H, 3.57. Found: C, 43.05; H, 3.68.

An authentic specimen of propionaldehyde 2,4-dinitrophenylhydrazone, m. p. 151° (lit. 155°<sup>5</sup>), was mixed with the derivative obtained in the above hydrolysis and the mixture melted at 140–144°.

The alkaline residue remaining in the distilling flask after the steam distillation was filtered to remove aldehyde resin and other insoluble material and analyzed for chloride, sulfite and sulfate. No sulfites were found. Precipitation of the sulfate with barium chloride showed that 3.72–4.22% out of the 16.9% of the sulfur originally present in the polymer had been converted to sulfate. Of the 37.6% of chlorine originally present in the polysulfone, 35.5% was present in this filtrate as chloride ion.

**Action of Liquid Ammonia on Vinyl Chloride Polysulfone.**—Many experiments were tried adding liquid ammonia to the polymer and vice versa. The liquid ammonia was then allowed to evaporate and the residue treated with

(4) Strain, *This Journal*, **57**, 758 (1935).

(5) Allen, *ibid.*, **52**, 2955 (1930).

water and filtered. Extensive analyses of the water solution and the insoluble part showed that the chlorine was entirely removed from the polymer as ammonium chloride. Considerable sulfur was removed as ammonium sulfite. The remaining polymeric products were not uniform in character and varied over a considerable range in their sulfur content.

**Pyrolysis in Dioxane.**—When small quantities of vinyl chloride polysulfone were suspended in dioxane and the mixture heated to boiling under a reflux condenser, gas was evolved. This gas consisted of a mixture of hydrogen chloride and sulfur dioxide. No vinyl chloride could be detected among the volatile products. In fact no organic material except dioxane was carried over through the reflux condenser. Analysis of the residual polymeric materials showed that they varied widely in sulfur content.

### Summary

1. Alkaline hydrolysis of vinyl chloride polysulfone produces acetaldehyde which is evidence that the polymeric unit in this material is —CHCl—CH<sub>2</sub>CHClCH<sub>2</sub>SO<sub>2</sub>—.

2. The polymer does not give a clean-cut reaction with liquid ammonia and pyrolysis causes loss of both hydrogen chloride and sulfur dioxide.

URBANA, ILLINOIS

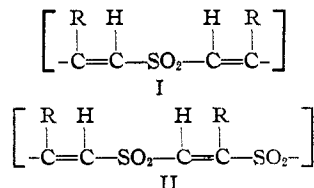
RECEIVED JULY 24, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Acetylene Polysulfones. XI.<sup>1</sup> The Compound C<sub>10</sub>H<sub>16</sub>SO<sub>2</sub> from 1-Pentynepolysulfone and Some Experiments on Other Acetylenepolysulfones

BY C. S. MARVEL AND W. W. WILLIAMS

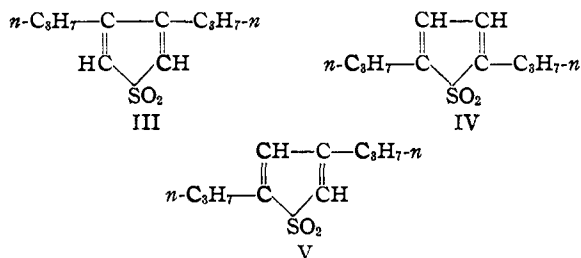
When acetylenes of the type RC≡CH combine with sulfur dioxide, the polysulfone formed has one remaining double union for each acetylene unit.<sup>2</sup> The arrangement of these units in the polymer may be either that shown in formula I or



that in formula II or the polymer may consist of a random mixture of these units. The present work was undertaken in order to add to our knowledge concerning these compounds.

It was found<sup>2</sup> that heating a solution of 1-pentynepolysulfone (C<sub>5</sub>H<sub>8</sub>SO<sub>2</sub>)<sub>n</sub> gave a crystalline solid of the composition C<sub>10</sub>H<sub>16</sub>SO<sub>2</sub> which tenta-

tively was considered to be a di-*n*-propylthiophene sulfone (III, IV or V). This product must



be formed by the loss of sulfur dioxide from two units of polymer and hence knowledge of its structure would make it possible to assign a definite formula for the polymer.

A more detailed study of the pyrolysis of 1-pentynepolysulfone in dioxane has been made. The reaction proceeds to some equilibrium stage. Isolation of the unchanged polymer and repetition of the pyrolysis in fresh dioxane gives more of the decomposition product. By using this stepwise

(1) For the tenth communication on polysulfones, see *This Journal*, **61**, 2709 (1939).

(2) Ryden and Marvel, *ibid.*, **66**, 2047 (1936).