

[COMMUNICATION NO. 1278 FROM THE KODAK RESEARCH LABORATORIES]

Preparation and Reactions of Sulfonic Esters. III. Reaction of Polyvinyl Sulfonates with Primary and Secondary Amines<sup>1</sup>

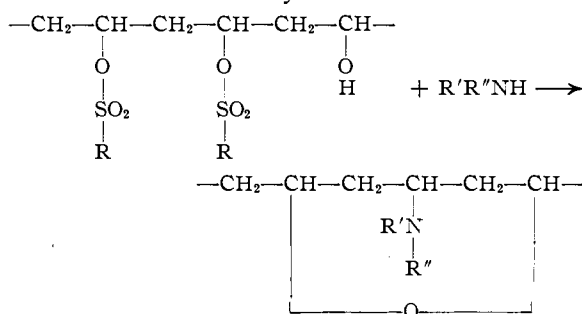
BY D. D. REYNOLDS AND W. O. KENYON

## Introduction

Polyvinyl alcohol reacts with alkyl or aryl sulfonyl chlorides in the presence of pyridine to yield polyvinyl sulfonates.<sup>2</sup> Such sulfonation reactions do not go to completion and the polyvinyl sulfonates obtained are binary copolymers consisting predominantly of vinyl sulfonate units combined with some residual vinyl alcohol units.

The reaction of these sulfonated polymers with tertiary amines has been described.<sup>3</sup>

The investigation has now been extended to a study of the reactions of the polyvinyl sulfonates with primary and secondary amines. The two reactions found to take place with the primary and secondary amines are (1) the reaction of vinyl sulfonate units with the amine to yield N-substituted vinylamine units, and (2) the intramolecular reaction between a vinyl sulfonate unit and a vinyl alcohol unit to form a cyclic ether unit.



R', R'' = hydrogen, alkyl and/or aryl  
R = alkyl, aryl

To the authors' knowledge, the only instance in polymer chemistry<sup>4</sup> wherein a sulfonyl group was replaced by an amino group involved the reaction of a copolymer of ethylene and vinyl *p*-toluenesulfonate with aniline to yield a nitrogen-containing polymer. Owing to the limited knowledge of amine polymers, it was believed desirable to investigate the reaction more thoroughly.

## Experimental

Since the experimental conditions under which the polyvinyl sulfonates reacted with primary and secondary amines were similar in all cases, a general procedure is given below. The experimental details are listed in Table I.

**General Procedure.**—One part of polyvinyl sulfonate, thoroughly dried in a vacuum over phosphorus pentoxide

(1) Presented before the High Polymer Forum of the American Chemical Society at the Atlantic City meeting, September, 1949.

(2) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **72**, 1584 (1950).

(3) D. D. Reynolds and W. O. Kenyon, *ibid.*, **72**, 1587 (1950).

(4) W. H. Sharkey, U. S. Patent 2,395,347 (February 19, 1946).

TABLE I

N-SUBSTITUTED VINYLAMINE POLYMERS						
Polyvinyl	Amine	Time, days	Temp., °C.	N, %	S, %	Soly. in dilute acid
Benzene sulfonate	Piperidine <sup>a</sup>	6	50	8.1	0.0	Soluble
	Morpholine <sup>a</sup>	6	50	7.8	0.0	Soluble
	Cyclohexyl <sup>a</sup>	6	50	8.2	1.0	Soluble
	<i>n</i> -Butyl <sup>a</sup>	6	50	8.0	0.0	Soluble
	Ethyl <sup>a</sup>	10	25	8.1	2.9	Soluble
Methane sulfonate	N-Methylaniline <sup>b</sup>	16 hr.	95	6.5	2.2	Insol.
	Diethyl <sup>b</sup>	7	60	4.2	3.6	Soluble
Methane sulfonate	Morpholine <sup>a</sup>	2	50	7.0	6.6	Soluble
	Aniline <sup>b</sup>	18 hr.	95	8.9	0.0	Insol.
	<i>n</i> -Butyl <sup>a</sup>	2	50	8.3	2.3	Soluble
	Piperidine <sup>a</sup>	2	50	8.7	5.7	Soluble

<sup>a</sup> Precipitation medium is water. <sup>b</sup> Precipitation medium is ethanol.

at room temperature, is mixed with 5 to 10 parts of anhydrous amine. The reaction flask is evacuated and nitrogen added. The stoppered flask is then placed at the desired temperature for the allotted time. The resulting solution is filtered and poured into a precipitation medium. The aminated polymer is separated, washed with fresh precipitation medium, and dried.

## Discussion

Analysis of the aminated polyvinyl sulfonates shows that the molar loss of sulfur during the reaction is greater than the molar gain in nitrogen, which indicates that some sulfonyl groups are removed by means other than amination. One or more of four possible reactions can account for the removal of additional sulfonyl groups: (1) hydrolysis of the vinyl sulfonate units to yield vinyl alcohol units and a sulfonic acid; (2) aminolysis of vinyl sulfonate units to yield vinyl alcohol units and a sulfonamide; (3) intramolecular reaction between a vinyl sulfonate unit and a preformed N-monosubstituted vinylamine unit to yield a cyclic tertiary amine unit and a sulfonic acid; and (4) an intramolecular reaction between a vinyl sulfonate unit and a vinyl alcohol unit to form a cyclic ether unit. The hydrolysis reaction was eliminated by keeping the reaction conditions strictly anhydrous.

The aminolysis reaction is unlikely, and is believed to take place to a very small extent, if at all, since numerous attempts to isolate the sulfonamide reaction product were unsuccessful.

The intramolecular reaction of a vinyl sulfonate unit with a preformed N-monosubstituted vinylamine unit is possible only when the amination is produced by a primary amine. This type of cyclization is possible, as has been demonstrated by its use in the preparation of non-polymeric cyclic tertiary amines.<sup>5</sup> A study of this type of cyclization in polymers will be the subject of a

(5) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **72**, 1597 (1950).

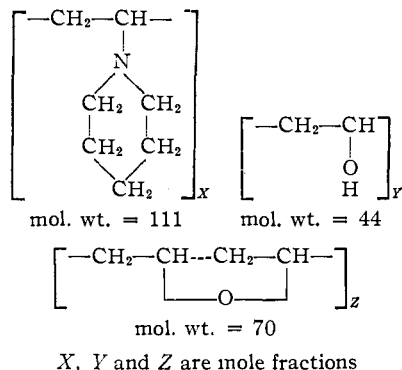
later investigation. Cyclic quaternary polymers involving vinyl sulfonate and vinylamine units in the same chain do not appear to form, as all of the sulfonyl units can be replaced by amine groups.

Aminations were run in the presence of a large excess of amine. For this reason, and because of the comparable cleavage of sulfonyl groups observed when secondary and tertiary amines were used, it is believed that the intramolecular reaction of the vinyl sulfonate unit with a vinyl alcohol unit to form a cyclic ether unit is the one which accounts for the loss of sulfur, beyond that removed by amination. This type of cyclization has been used for the preparation of non-polymeric cyclic ethers.<sup>6</sup>

The non-cyclic amination reaction is evidenced in the polymer reactions by the water-insolubility and dilute-acid-solubility.

On the basis of the amination and cyclization reactions, the molar ratios of vinyl alcohol, N-substituted vinylamine, cyclic ether, and any residual vinyl sulfonate units may be calculated. Such calculations are based on elemental analyses, and are therefore accurate only within the limits of accuracy of such analyses, and the errors may be additive.

The product of the reaction of piperidine and polyvinyl benzenesulfonate has the analysis: N, 8.1; S, 0.0; C, 72.5; H, 10.4; O, 9.0 (by difference). The polymer contains the following units:



Therefore

$$8.1/14 \times 111 = 64.2 \text{ g. per 100 g. polymer or 64.2 weight per cent. vinyl piperidine units}$$

and

$$84/111 \times 64.2 = 48.6 \text{ g. of carbon in vinyl piperidine units per 100 g. polymer}$$

Hence

$$72.5 - 48.6 = 23.9 \text{ g. of carbon in vinyl alcohol plus ring structure}$$

Let  $V$  = grams of vinyl alcohol units and  $R$  = grams of ring unit per 100 g. of aminated product, then

$$\begin{array}{l}
 24/44 V + 48/70 R = 23.9 \text{ (carbon difference)} \\
 16/44 V + 16/70 R = 9.0 \text{ (oxygen content)}
 \end{array}$$

(6) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **72**, 1593 (1950).

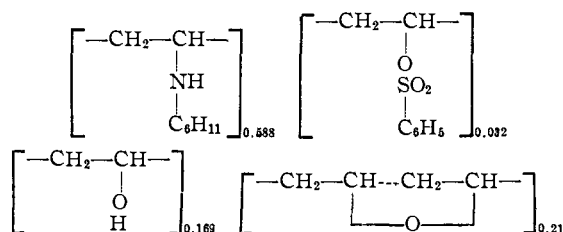
Solving, we have  $V = 5.7$  g. vinyl alcohol per 100 g., or 5.7% vinyl alcohol.

$R = 30.1$  g. ring structure per 100 g., or 30.1% ring structure

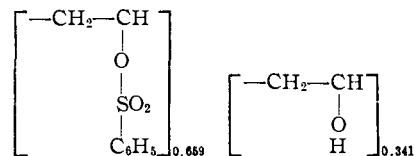
Solving for  $X$ ,  $Y$  and  $Z$ , we obtain

$$\begin{array}{l}
 X = 0.508 \\
 Y = 0.113 \\
 Z = 0.378
 \end{array}$$

The action of cyclohexylamine on polyvinyl sulfonate gave a product having the analysis: N, 8.2; S, 1.0; C, 73.4; H, 9.9, O, 7.5 (by difference). This method of calculation indicates the following structure for the aminated polymer



Both of these copolymers were prepared from a polyvinyl benzenesulfonate of the composition



By reverting the units of the aminated polymer into terms of vinyl benzenesulfonate and vinyl alcohol from which it was formed, the ratio of the vinyl benzenesulfonate units to vinyl alcohol units should be the same as the corresponding ratio in the starting material, provided there has been no conversion of vinyl sulfonate to vinyl alcohol during the amination reaction. Application of this procedure to the vinylpiperidine copolymer indicates that

$$\begin{array}{rcl}
 0.508 \text{ mole vinyl piperidine} & \equiv & 0.508 \text{ mole vinyl benzenesulfonate} \\
 0.378 \text{ mole cyclic ether} & \equiv & 0.378 \text{ mole vinyl benzenesulfonate} \\
 \text{Total} & = & 0.886 \text{ mole vinyl benzenesulfonate} \\
 0.113 \text{ mole vinyl alcohol} & \equiv & 0.113 \text{ mole vinyl alcohol} \\
 0.378 \text{ mole cyclic ether} & \equiv & 0.378 \text{ mole vinyl alcohol} \\
 \text{Total} & = & 0.491 \text{ mole vinyl alcohol}
 \end{array}$$

$$0.886/0.491 = 1.8$$

compared to the original ratio of

$$0.659/0.341 = 1.9$$

Reverting the polymeric units of the N-vinyl-cyclohexylamine copolymer to vinyl benzenesulfonate and vinyl alcohol units by the same method yields a ratio of

$$0.831/0.380 \text{ or } 1.8$$

These calculations substantiate the proposed structures for the polymers. The relative amounts of amine and cyclic structures will depend upon the relative amination and cyclization rates. The

positions of the sulfonate and hydroxyl units along the chain will determine whether or not cyclization will occur. Probably the residual vinyl alcohol units represent isolated hydroxyl groups.

### Summary

1. Polyvinyl sulfonates have been treated with primary and secondary amines to yield polymers composed of N-substituted vinylamine units and cyclic ether units. Unreacted vinyl al-

cohol and vinyl sulfonate units may be present.

2. Evidence has been presented which substantiates the structures proposed for the polymers.

3. The aminated polymers prepared from alkyl primary or secondary amines are insoluble in water but soluble in dilute acid. Those prepared from primary or secondary amines containing aryl groups are insoluble in water and in dilute acid.

ROCHESTER 4, NEW YORK

RECEIVED JULY 16, 1949

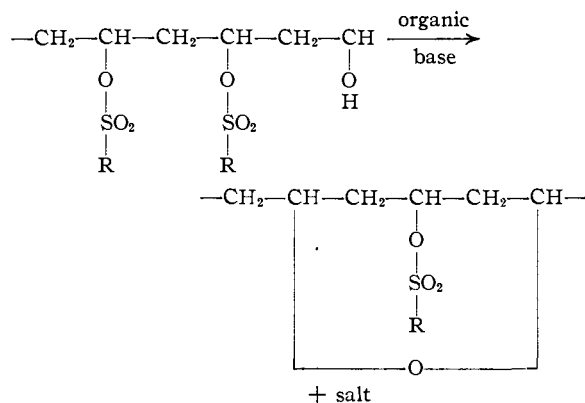
[COMMUNICATION NO. 1279 FROM THE KODAK RESEARCH LABORATORIES]

## Preparation and Reactions of Sulfonic Esters. IV. Preparation of Cyclic Ethers<sup>1</sup>

BY D. D. REYNOLDS AND W. O. KENYON

### Introduction

In a previous publication<sup>2</sup> polymers have been described for which a structure containing cyclic ether units was postulated. The cyclic ether is believed to be of the tetrahydropyran type. Evidence was reported which substantiated the structures assigned. Such ether structures were formed by an intramolecular reaction involving the hydroxyl group of a vinyl alcohol unit and the alkylsulfonyl or arylsulfonyl radical of a suitably situated vinyl sulfonate unit, as illustrated in the equation



In order to elucidate the reactions leading to such compounds, a study was made of the preparation of non-polymeric cyclic ethers of the tetrahydropyran and tetrahydrofuran types. During its course a method for the preparation of cyclic ethers was developed which involves the reaction of a glycol with one mole of a sulfonyl chloride in the presence of a suitable tertiary amine. The products obtained are listed in Table I.

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J. meeting, September, 1949.

(2) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **72**, 1587 (1950).

### Experimental

**Materials.** 2,6-Heptanediol was prepared by the method of Perkins<sup>3</sup> from heptane-2-ol-6-one but using hydrogen and Raney nickel at 50 to 80° and 3500 p. s. i. instead of sodium amalgam in alcohol as the reductant.

1,5-Pentanediol was purchased from E. I. du Pont de Nemours and Co., Inc.

2,5-Hexanediol and 2,4-pentanediol were prepared by the reduction of the corresponding ketones with hydrogen over Raney nickel at 100° and 4000 p. s. i.

1,4-Butanediol was prepared by the reduction of butyne-diol by hydrogen over Raney nickel at 3000 p. s. i. at 50 to 100°.

1,3-Propanediol was Eastman Kodak Co. white label grade.

Sulfonyl chlorides were Eastman white label grade.

Anhydrous pyridine and anhydrous 2,6-lutidine were obtained by distillation of Eastman white label grade products over calcium hydride.

**I. Procedure.**—One mole of a glycol was refluxed with four moles of a tertiary amine while one mole of an alkyl- or arylsulfonyl chloride was added dropwise. The cyclic ether which formed was separated, and purified by distillation.

The sulfur oxide-tertiary amine complex formed when methanesulfonyl chloride is used can be removed from the cyclic ether by washing with water.

**II. Preparation of Monobenzenesulfonate of 1,5-Pentanediol.**—Two liters of anhydrous ether, 600 g. of 1,5-pentanediol and 500 cc. of anhydrous pyridine were stirred in a 5-liter, 3-necked flask equipped with a thermometer and a dropping funnel. The temperature was maintained at 5°, and 300 g. of benzenesulfonyl chloride was added dropwise over a three-hour period. Stirring was continued for an hour. The product was washed three times with water, once with dilute hydrochloric acid, and twice more with water. The ether layer was dried over calcium chloride, then over magnesium sulfate, and the ether was removed *in vacuo*; yield 300 g. of viscous product.

**III. Treatment of Monobenzenesulfonate of 1,5-Pentanediol with 2,6-Lutidine.**—One hundred and fifty grams of the product prepared in Experiment II was mixed with 300 g. of 2,6-lutidine and fractionally distilled. After removal of a small amount of residual ether, 32.4 g. of tetrahydropyran fraction, b. p. 70 to 90°, was collected. Redistillation of this fraction yielded 21 g. of pure tetrahydropyran. The residue which remained from the first distillation after removal of the tetrahydropyran separated at room temperature into two layers of approxi-

(3) W. H. Perkin, *J. Chem. Soc.*, **105**, 1360 (1914).