sulfonate content have been prepared by converting polyvinyl alcohol to a highly swollen condition and then treating it with an alkyl or aryl sulfonyl chloride in the presence of pyridine at $5-10^{\circ}$.

2. Polyvinyl methanesulfonate, polyvinyl benzenesulfonate, polyvinyl *p*-toluenesulfonate and polyvinyl naphthalenesulfonate have been prepared and isolated as white, fibrous polymers. Their solubility properties are listed.

3. It has been demonstrated that the sulfonation does not take place at low temperature if the polyvinyl alcohol is not pretreated. Polyvinyl alcohol can be sulfonated at elevated temperature without pretreatment, but the resulting product contains a relatively low degree of vinyl sulfonate units due to undesirable side reactions.

4. The degree of sulfonation is a function of the molecular size of the sulfonyl radical introduced.

5. Polyvinyl alcohol is sulfonated more rapidly by benzenesulfonyl chloride than by p-toluenesulfonyl chloride.

6. The rates at which the sulfonoxy groups are replaced by chlorine, by the reaction of polyvinyl sulfonate with pyridine hydrochloride, decrease in the following order: $CH_3SO_{3^-} > C_6H_5$ - $SO_{3^-} > CH_3-C_6H_4SO_3-$.

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Preparation and Reactions of Sulfonic Esters. II. The Reaction of Polyvinyl Sulfonates with Tertiary Amines¹

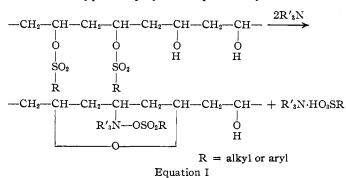
BY D. D. REYNOLDS AND W. O. KENYON

Introduction

In the first paper of this series,² methods were given for the preparation of polyvinyl sulfonates which were shown to be copolymers consisting predominantly of vinyl sulfonate units combined with some residual vinyl alcohol units. The reaction of such polymers with tertiary amines is described in this paper.

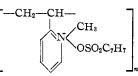
Two reactions occur when polyvinyl sulfonates are treated with tertiary amines: (1) quaternization of vinyl sulfonate units with the tertiary amine, and (2) an intramolecular condensation of vinyl sulfonate units with properly situated vinyl alcohol units to form cyclic ether units believed to be of the tetrahydropyran type. Equation I illustrates the reactions which produce the units of the resultant polymer. However, this formula should not be construed as indicating the ratio or arrangement of these units.

The two types of polymeric quaternary salts

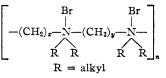


⁽¹⁾ Presented before the High Polymer Forum of the American Chemical Society at the Atlantic City, N. J. meeting, September, 1949.

prepared previously contain pentavalent nitrogen atoms which are a part of the parent polymer structure. One was formed by the reaction of polyvinylpyridine with methyl *p*-toluenesulfonate³ and contains the unit



The other was formed by the reaction of an alkyl dibromide with a N,N,N',N'-tetraalkyldiamine⁴ to yield a linear polyquaternary salt having the structure



The quaternary salts described in this paper differ from the above in that the nitrogen atom is not an integral part of the original polymer molecule, and by the fact that they contain cyclic ether units.

Experimental

Owing to similarities of the reaction conditions, a general procedure is given, and the experimental details are listed in Table I.

I. General Procedure.—One part of polyvinyl sulfonate in five parts of tertiary amine is

added to a flask which is then stoppered and placed at the desired temperature. After the allotted (3) R H Spectra and L C S Breaker U.S. Patert 2 484420

(3) R. H. Sprague and L. G. S. Brooker, U. S. Patent 2,484,430 (1949); L. M. Minsk and W. O. Kenyon, U. S. Patent 2,484,420 (1949).

(4) W. Kern and E. Brenneisen, J. prakt. Chem., 159, 193 (1941).

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

	QUATERNIZATION OF POLYVINYL SULFONATES								
No.	Amine	s, %	N, %	Moles N/ moles S	Quat., %	°C.	Time. days	Pptn. medium	Water solubility
IA	Pyridine ^{a,g}	10.7	3.9	0.28/0.33	84.8	50	8	Ethanol	Soluble
IB	Pyridine ^{a, e, g}	10.7	3.9	0.28/0.33	84.8	50	8	Ethanol	Soluble
IIA	α -Picoline ^{a, h}	11.5	1,8	0.13/0.36	36.1	60	7	Ethanol	Insoluble
IIB	α -Picoline ^{a, e, g}	5.8	2 , 4	0.17/0.18	94.5	95	29 hr.	Ether + ethanol	Soluble
III	β -Picoline ^{<i>a</i>,<i>e</i>,<i>g</i>}	9.0	4.0	0.28/0.28	100	60	7	Ether + ethanol	Soluble
IV	γ -Picoline ^{a, e, g}	9.6	4.3	0.30/0.30	100	60	7	Ether + ethanol	Soluble
V	2,4-Lutidine ^{a,e,h}	9.7	2.0	0.14/0.30	46.7	60	7	Ether + ethanol	Insoluble
VIA	2,6-Lutidine ^{a,e}	11.9	0.5	0.04/0.37	10.8	60	7	Ether + ethanol	Insoluble
VIB	2,6-Lutidine ^{a,e}	7.5	3.3	0.23/0.23	100	95	18 hr.	Ether + ethanol	Soluble
VII	N-Methylmorpholine ^{a.e,h}	11.6	1.4	0.10/0.36	27.8	50	21	Ethanol	Insoluble
\mathbf{VIII}	N-Ethylmorpholine ^{a, e, h}	10.8	1.0	0.07/0.34	20.5	50	21	Ethanol	Insoluble
\mathbf{IX}	Diethylaniline ^{a, /, h}	9.9	1.0	0.07/0.31	22.6	95	23 hr.	Ethanol	Insoluble
\mathbf{X}	Triethylamine ^{a, /}	5 . 5	1.0	0.07/0.17	41.0	95	24 hr.	Water	Insoluble
\mathbf{XI}	Pyridine ^{b,g}	18.2	3.0	0.21/0.57	36.8	50	7	Ether $+$ ethanol	Soluble
$\mathbf{X}\mathbf{I}\mathbf{I}$	Pyridine ^{c.h}	10.4	3.5	0.25/0.33	75.8	50	7	Water	Insoluble
$\mathbf{X}\mathbf{I}\mathbf{I}\mathbf{I}$	Pyridine ^{d,g} ·	8.6	3.8	0.27/0.27	100	50	7	Ether + ethanol	Insoluble

Table I

QUATERNIZATION OF POLYVINYL SULFONATES

"With polyvinyl benzenesulfonate. ^b With polyvinyl methanesulfonate. ^c With polyvinyl *p*-toluenesulfonate. ^d With polyvinyl naplithalenesulfonate. ^e Sufficient water added to keep reaction mixture homogeneous. ^f Moist dioxane added to effect solution. ^e Purified by dissolving in methanol, filtering and precipitating into an ether-ethanol mixture (1:1). ^h Purified by dissolving in an acetone-water mixture, filtering and precipitating into an ether-ethanol mixture (1:1).

period of time, the product is isolated by (a) pouring it into the precipitation medium if the reaction mixture is homogeneous, or (b) triturating the resin in the precipitation medium if it has separated as a second phase. If further purification is desired, it may be performed as indicated in Table I.

II. Rates of Liberation of Sulfonic Acids from Polyvinyl Sulfonates in Pyridine.—The experiments listed in Table I were directed toward formation of polymeric quaternary compounds but a simultaneous, competitive reaction liberating a sulfonic acid became evident. The rates of liberation of acid were measured under the following conditions and the results are given in Figs. 1 and 2.

A. A series of 2.0-g. samples of polyvinyl benzenesulfonate (S, 15.8; Cl, 0.5; C, 52.2; H, 4.8) was dried for three days over phosphorus pentoxide in a vacuum at room temperature to a moisture content of 0.03%, as determined by the Karl Fischer method. The samples, contained in glass-stoppered flasks previously dried at 100°, were each dissolved in 25 cc. of pyridine which had been refluxed and distilled over calcium hydride. The flasks were stoppered and maintained at 65°. At intervals a sample was diluted with water and titrated with 0.1 N sodium hydroxide, using phenolphthalein as indicator. The titrations were carried out rapidly because of fading end-points.

B. As in Experiment A, except that 1 cc. of distilled water was added to each sample.

C. As in Experiment A, except that the reaction temperature was 50° .

D. As in Experiment C, except that each sample contained 1 cc. of distilled water.

E. As in Experiment A, except that the reaction was run at room temperature, approximately 25°.

F. As in Experiment A, except that the reaction temperature was 2°.

G. Experiments II-C and II-D were repeated, except that the polyvinyl benzenesulfonate was replaced by polyvinyl p-toluenesulfonate (S, 14.8; Cl, 1.8; C, 54.6; H, 5.1).

H. Experiment II-C was repeated, except that an equal weight of polyvinyl methanesulfonate (S, 24.7; Cl, 1.8; C, 30.4; H, 4.9) replaced the polyvinyl benzenesulfonate.

III. Relative Rates of Quaternization of Polyvinyl Sulfonates with Pyridine.—The following polyvinyl sulfonates were used: polyvinyl benzenesulfonate (S, 15.8; C, 52.6; H, 4.2; Cl, 1.0); polyvinyl p-tolucnesulfonate (S, 14.6; C, 54.2; H, 6.0; Cl, 0.8); polyvinyl methanesulfonate (S, 24.2; C, 30.5; H, 5.1; Cl, 2.3). The polymers were dried over phosphorus pentoxide in a vacuum at room temperature for three days. The reaction flasks were dried at 110° and the pyridine was dried by distillation over calcium hydride.

Six separate 8-g. samples (0.039 mole of vinyl benzenesulfonate unit) of polyvinyl benzenesulfonate were heated in sealed flasks at 50° in 80 cc. of pyridine. Samples were withdrawn periodically, purified, and analyzed for sulfur and nitrogen, from which the percentage of quaternization was calculated.

This experiment was run simultaneously with one in which 8.65 g. of polyvinyl p-toluenesulfonate (0.039 mole of vinyl p-toluenesulfonate unit) and one in which 5.24 g. of polyvinyl methanesulfonate (0.039 mole of vinyl methanesulfonate unit) were used in place of the polyvinyl benzenesulfonate. The relative rates of quaternization are shown in Fig. 3.

Discussion

The formation of quaternary polymers from polyvinyl sulfonates is dependent upon the particular tertiary amine used. Tertiary amines having one or more alkyl groups, as exemplified by triethylamine, diethylaniline, N-methylmorpholine and N-ethylmorpholine, quaternized with polyvinyl benzenesulfonate to only a small extent under the reaction conditions employed (Table I, nos. VII to X inclusive). The products recovered when such reactions were run at elevated temperatures were much lower in sulfonic ester contents than the original sulfonates.

Pyridine and substituted pyridines quaternize the polymeric sulfonates much more readily to yield water-soluble polyvinyl pyridinium sulfonates. In this series of amines, the ease of quaternization depends upon the position of the substituent. β - and γ -picolines quaternize polyvinyl benzenesulfonate approximately as readily as does pyridine. α -Substituted pyridines, e. g., α -

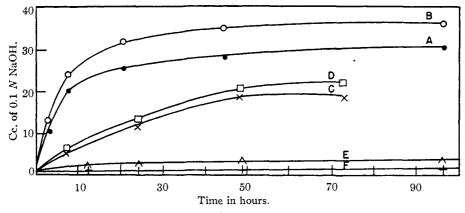


Fig. 1.—Rate of liberation of benzenesulfonic acid from polyvinyl benzenesulfonate: A \bullet , in anhydrous pyridine at 65°; B O, in aqueous pyridine at 65°; C \times , in anhydrous pyridine at 50°; D \Box , in aqueous pyridine at 50°; E \wedge , in anhydrous pyridine at 25°; F +, in anhydrous pyridine at 2°.

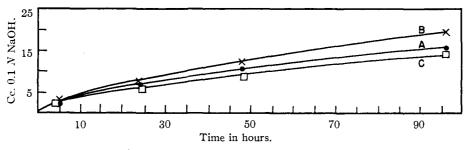


Fig. 2.—Rate of liberation of sulfonic acids from polyvinyl p-toluenesulfonate and polyvinyl methanesulfonate: A \bullet , polyvinyl p-toluenesulfonate in anhydrous pyridine at 50°; B \times , polyvinyl p-toluenesulfonate in aqueous pyridine at 50°; C \Box , polyvinyl methanesulfonate in anhydrous pyridine at 50°.

picoline and lutidines, quaternize more slowly (Table I, nos. II, V and VI). Quaternization by the α -substituted pyridines to the extent required to yield a water-soluble quaternary product requires elevated reaction temperatures (Table I, nos. II-B and VI-B). These observations are in qualitative agreement with quaternization experiments using glycol sulfonates.⁵

The apparent rates of quaternization of various polyvinyl sulfonates with a given tertiary amine vary with the sulfonate radical. The true quaternization rate must take into account the competing reaction of removal of sulfonate radicals and such studies are in progress. In particular, the apparent rates of quaternization by pyridine decreased in the order: polyvinyl benzenesulfonate > polyvinyl p-toluenesulfonate > polyvinyl methanesulfonate (Fig. 3).

Tertiary amines cause a cleavage of some sulfonic acid from the polymer molecules. The rate at which this takes place is appreciable at temperatures as low as 50° (Fig. 1). The liberation of this sulfonic acid might be brought about by one or more of three reactions: (1) hydrolysis of the vinyl sulfonate unit by moisture present in the reaction mixture, (2) intermolecular reaction of a vinyl sulfonate unit with a vinyl alcohol unit to

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

form a cross-linked polymer, and (3) an intramolecular reaction of a vinyl sulfonate unit with a vinyl alcohol unit to form a cyclic ether unit.

Certain factors affecting this reaction were investigated in Experiment II. In Experiments A, C, E and F, hydrolysis is ruled out because the

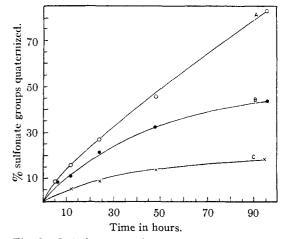


Fig. 3.—Relative rates of quaternization of polyvinyl sulfonates in anhydrous pyridine at 50° : A O, polyvinyl benzenesulfonate; B \bullet , polyvinyl *p*-toluenesulfonate; C \times , polyvinyl methanesulfonate,

polyvinyl benzenesulfonate used contained only 0.03% of moisture. A 2-g. sample of polymer would contain 0.0006 g., or 0.00003 mole of water, which would liberate 0.00003 mole of acid, which, in turn, would require 0.3 cc. 0.1 N sodium hydroxide. The data of Fig. 1 show that this would account for only an extremely small amount of the sulfonic acid liberated.

Comparison of Curves A and B or C and D (Fig. 1) shows that the presence of water causes a relatively small change in the amount of acid liberated. The difference between Curves A and B is greater than that between C and D, indicating that a higher temperature increases the degree of hydrolysis.

The analytical results shown in nos. I-A and I-B of Table I also show that hydrolysis does not take place to any appreciable extent under the reaction conditions even when water was deliberately added to the reaction mixture. If hydrolysis had taken place, the sulfur and nitrogen percentages would have been correspondingly low. Even in the presence of added water, some reaction other than hydrolysis occurs which liberates sulfonic acid.

Intermolecular reaction does not occur because the reaction products were soluble, indicating no cross-linking. This leaves only the possibility of an intramolecular reaction of a vinyl sulfonate group with a vinyl alcohol group to produce a cyclic ether unit. The introduction of cyclic ether structures into the sugar molecule by an intramolecular reaction of a sulfonate group with a properly situated hydroxyl group has been described by Ohle and Vargha.⁶ It is now one of the favored methods for preparing certain sugar anhydrides. Recently this method was used by Gardner and Purves⁷ to form anhydro-glucose units within the cellulose molecule.

Cyclic ethers can be formed in good yields⁵ by the reaction of alkali or a tertiary amine with compounds of the type

$RSO_2O-CH_2-(CH_2)_n-CH_2OH$ n = 2 or 3; R = alkyl or aryl

When n = 1, no cyclic ether was isolated. The presence of a cyclic ether structure in the quaternized polyvinyl sulfonates cannot be demonstrated by specific chemical reactions. Its pres-

(6) H. Ohle and L. Vargha, Ber., 62B, 2435 (1929).
(7) T. S. Gardner and C. B. Purves, THIS JOURNAL, 65, 444 (1943).

ence is postulated to explain formation of free sulfonic acid under anhydrous conditions. The extent of intramolecular cyclization will depend upon the relative rates of cyclization and quaternization which, in turn, depend upon the particular tertiary amine and polymeric sulfonic ester used. The cyclic ether may be four- or six-membered, but, by analogy with cyclization of monosulfonates of simple glycols, the formation of a tetrahydropyran type of structure is believed more probable.

The rates at which sulfonic acid is liberated to produce cyclic ether units is shown in Figs. 1 and 2 and the effect of temperature is shown in Fig. 1. The three curves which show the rate at which cyclization occurs in polyvinyl benzenesulfonate, polyvinyl p-toluenesulfonate and polyvinyl methanesulfonate at 50° in pyridine do not necessarily represent relative rates since equal weights rather than equal molar concentrations were used. These rates will be studied more thoroughly in subsequent work.

Summary

1. The polyvinyl sulfonates, which are composed predominantly of vinyl sulfonate units combined with some vinyl alcohol units, react with tertiary amines to form polymers having quaternized vinyl sulfonate units, cyclic ether units, residual vinyl alcohol units and possibly residual vinyl sulfonate units may be present.

2. The cyclic ether units are formed by an intramolecular reaction of vinyl sulfonate units and vinyl alcohol units, and are believed to be of the tetrahydropyran type. Data are given to show the rates of cyclization at various temperatures.

3. The vinyl sulfonate units quaternize most readily with pyridine and the β - or γ -substituted pyridines; less readily with the α -substituted pyridines; and only slightly with tertiary alkyl or alkylaryl amines.

4. The rate at which pyridine quaternizes polyvinyl sulfonates is in the order: polyvinyl benzenesulfonate > polyvinyl p-toluenesulfonate > polyvinyl methanesulfonate.

5. Quaternization of polyvinyl sulfonates at 50° in the presence of water is accompanied by a slight degree of hydrolysis which increases in amount as the reaction temperature is increased.

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