[COMMUNICATION NO. 1273 FROM THE KODAK RESEARCH LABORATORIES]

Preparation and Reactions of Sulfonic Esters. I. Preparation of Polyvinyl Sulfonates[1]

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

Introduction

The vinyl sulfonates should be useful intermediates for the synthesis of a variety of vinyl monomers and polymers thereof. Since the monomeric vinyl sulfonates are unknown, the work described herein was undertaken to obtain polyvinyl sulfonates, and to use them as intermediates for preparing a number of derived polymers. The term "polyvinyl sulfonate" is used in the papers of this series to describe those polymers prepared by the sulfonation of polyvinyl alcohol with an alkyl or aryl sulfonyl chloride in the presence of pyridine.

As far as the authors are aware, polyvinyl sulfonates which contain a high percentage of vinyl sulfonate units have not been described previously. After our investigation was completed, Izard and Morgan[2] described the preparation of a polyvinyl *p*-toluenesulfonate of relatively low vinyl *p*-toluenesulfonate content. Polyvinyl alcohol was treated with *p*-toluenesulfonyl chloride in pyridine at elevated temperature. Such conditions lead to polymers containing an appreciable amount of vinyl chloride units and a correspondingly low vinyl sulfonate content. Hess and Stenzel[3] made similar observations while studying the sulfonation of sugar derivatives. Benzenesulfonyl or methanesulfonyl derivatives prepared under analogous conditions, contain a higher percentage of combined vinyl chloride (see Tables III and IV). Such polymers are not desirable intermediates for preparing derived polymers.

It has now been found that polyvinyl sulfonates of high vinyl sulfonate and negligible vinyl chloride contents can be obtained by swelling polyvinyl alcohol, then treating it with a sulfonyl chloride in the presence of a tertiary amine, preferably pyridine, below 10°.

Experimental

Materials.—The polyvinyl alcohols were commercial products of negligible residual acetyl content. Hereinafter they are designated as pva-1 (high viscosity), and pva-2 (low viscosity). Anhydrous pyridine was prepared by distillation of Eastman Kodak Co. grade pyridine over calcium hydride. Sulfonyl chlorides were Eastman grade.

1. **Polyvinyl Benzenesulfonate.**—(A) Forty-four grams (1 mole) of pva-1 was heated on a steam-bath for two hours with 500 cc. of anhydrous pyridine. One liter of anhydrous pyridine was added, the reaction mixture was cooled to 5° and 265 g. (1.5 moles) of benzenesulfonyl chloride was added. Stirring was continued for twenty-four hours at 5–10°. An equal volume of acetone was added and a white, fibrous polymer was isolated by pouring the reaction mixture into water. This polymer was leached in water, dried, redissolved in acetone, filtered and reprecipitated in distilled water. After leaching in distilled water, it was air-dried at room temperature, then over phosphorus pentoxide in a vacuum at room temperature; yield 135 g. *Anal.* S, 16.3; Cl, trace; C, 52.9; H, 4.6. Analytically, the polymer contains 93.7 weight per cent. of vinyl benzenesulfonate units. Assuming that the remainder consists of unreacted vinyl alcohol units, this corresponds to 78 mole per cent. of combined vinyl benzenesulfonate units and 22 mole per cent. of combined vinyl alcohol units.

Fifty grams of this polymer was resulfonated in 500 cc. of pyridine containing 88.3 g. of benzenesulfonyl chloride by stirring for twenty-four hours at 5–10°. *Anal.* S, 15.5; Cl, 1.3, equivalent to 72.6 mole per cent. of vinyl benzenesulfonate, 21.8 of vinyl alcohol and 5.6 vinyl chloride units.

(B) Twenty-two grams of pva-2 was dissolved in 160 g. of benzenesulfonic acid monohydrate and then poured into 1500 cc. of cold pyridine. No precipitate was obtained. Pyridine and water were removed by distillation until the distillation temperature reached 112°. The remaining solution, cooled to 5–10°, was sulfonated with 200 g. of benzenesulfonyl chloride for twenty-four hours. White, fibrous polyvinyl benzenesulfonate was isolated and purified as in Experiment I-A. It contained 15.2% of sulfur.

II. **Polyvinyl *p*-Toluenesulfonate.**—(A) Experiment I-A was repeated using 234 g. (1.5 moles) of *p*-toluenesulfonyl chloride instead of the benzenesulfonyl chloride. The white, fibrous polyvinyl *p*-toluenesulfonate was isolated and purified according to the method of I-A; yield 187 g. *Anal.* S, 15.3; Cl, trace. This indicates a polymer containing 93.1 weight per cent. of vinyl *p*-toluenesulfonate units or 77.8 mole per cent. of vinyl *p*-toluenesulfonate units and 22.2 of vinyl alcohol units.

Fifty grams of the polymer was resulfonated in 500 cc. of pyridine containing 95 g. of *p*-toluenesulfonyl chloride for twenty-four hours at 5–10°. *Anal.* S, 14.8; Cl, < 1.

(B) Forty-four grams of pva-1 was dissolved by warming and stirring into 800 cc. of distilled water. Precipitation into 3 liters of a 1:1 acetone–pyridine mixture yielded a swollen polyvinyl alcohol which was centrifuged, leached in pyridine, centrifuged and suspended in 1500 cc. of anhydrous pyridine. Three hundred and eighty grams of *p*-toluenesulfonyl chloride was added and the reaction mixture stirred for twenty-four hours at 5–10°. One liter of acetone was added and a white, fibrous polyvinyl *p*-toluenesulfonate was isolated by precipitation in water. It was leached in water and dried. *Anal.* S, 15.5. This indicates a polymer composed of 96 weight per cent. of vinyl *p*-toluenesulfonate units or 84.3 mole per cent. of vinyl *p*-toluenesulfonate units and 15.7 of vinyl alcohol units.

III. **Polyvinyl Naphthalenesulfonate.**—Preparation I-A was repeated but using 341 g. (1.5 moles) of naphthalene-β-sulfonyl chloride. The white, fibrous polyvinyl naphthalenesulfonate was isolated as in I-A. It was then dissolved in pyridine, filtered and precipitated into water, again leached in water and dried; yield 150 g. *Anal.* S, 11.3; Cl, < 1. Neglecting the chlorine, this indicates a polymer composed of 47.2 mole per cent. of vinyl naphthalenesulfonate units and 52.8 of vinyl alcohol units. A 50-g. sample of the dry polymer was dissolved in anhydrous pyridine containing 113 g. of naphthalene β-sulfonyl chloride and stirred at 5–10° for twenty-four

---

[1] Presented before the High Polymer Forum of the American Chemical Society, Atlantic City, N. J., Meeting, September, 1949.

[2] E. F. Izard and P. W. Morgan, *Ind. Eng. Chem.*, **41**, 619 (1949).

[3] K. Hess and H. Stenzel, *Ber.*, **68**, 981 (1935).

hours. The polymer was isolated and purified as above. *Anal.* S, 12.5; Cl, 1.1.

IV. Polyvinyl Methanesulfonate.—(A) Preparation II-B was repeated but using 173 g. of methanesulfonyl chloride instead of *p*-toluenesulfonyl chloride. The reaction product was allowed to settle. The supernatant liquid was decanted and poured onto ice. A negligible amount of product separated. The main resinous mass was dissolved in moist acetone, filtered and precipitated in water as a white, fibrous product. It was leached in water, dried, redissolved in moist acetone, filtered, precipitated in water, leached in water and dried at room temperature; yield 54 g. *Anal.* S, 24.8; Cl, 1.2. This polymer contains 94.5 weight per cent. vinyl methanesulfonate, 2.3 of vinyl chloride and 3.2 of vinyl alcohol units. This corresponds to 87.6 mole per cent. vinyl methanesulfonate, 4.2 vinyl chloride and 8.2 of vinyl alcohol units. A 50-g. sample of the polymer in 500 cc. of anhydrous pyridine was resulfonated by the above procedure, using 58 g. of methanesulfonyl chloride and purified as above. *Anal.* S, 24.7; Cl, 1.3. The analysis indicated that no change had occurred during resulfonation.

(B) Twenty-two grams of pva-2 was dissolved by stirring into 150 cc. of methanesulfonic acid cooled in ice-water. The viscous dope was precipitated in cold pyridine. The pyridine salt of the acid was extracted with pyridine in a modified Soxhlet extractor. The swollen polyvinyl alcohol was sulfonated, isolated and purified as in the above experiment. Two hundred grams of methanesulfonyl chloride was used. *Anal.* S, 24.5; Cl, 1.8. This indicates a polymer consisting of 93.4 weight per cent. of vinyl methanesulfonate, 3.4 of vinyl chloride and 3.2 of vinyl alcohol units. On a molar basis, this represents 85.8 vinyl methanesulfonate, 6 vinyl chloride and 8.2 vinyl alcohol units.

V. Attempt to Prepare Polyvinyl Benzenesulfonate without the Use of Heat to Swell the Polyvinyl Alcohol.—Forty-four grams of pva-1 in 200 cc. of pyridine was placed at 25 to 30° for fourteen days. One liter of pyridine and 265 g. of benzenesulfonyl chloride were added and the solution was stirred at 5–10° for twenty-four hours. During this time there was no apparent change in the reaction mixture. The suspended product was removed. Analysis showed no combined sulfur, indicating no reaction under these conditions.

TABLE I

REACTION OF POLYVINYL ALCOHOL IN PYRIDINE WITH BENZENESULFONYL CHLORIDE AT 4 ± 1°

Reaction time in hours	S, %	Cl, %	Mole fraction vinyl benzenesulfonate	Mole fraction vinyl chloride	Mole fraction vinyl alcohol
4	10.0	...	0.245	...	0.755
8	11.5	...	.317	...	.683
12	14.1	...	.497	...	.503
24	15.9	...	.718	...	.282
48	16.4	...	.800	...	.200
60	15.2	1.0	.614	0.036	.350
72	15.9	1.2	.732	.050	.218
96	15.4	1.4	.668	.055	.277

TABLE II

REACTION OF POLYVINYL ALCOHOL IN PYRIDINE WITH *p*-TOLUENESULFONYL CHLORIDE AT 4 ± 1°

Reaction time in hours	S, %	Cl, %	Mole fraction vinyl *p*-toluenesulfonate	Mole fraction vinyl chloride	Mole fraction vinyl alcohol
4	7.3	...	0.155	...	0.845
8	9.6	...	.245	...	.755
12	11.5	...	.355	...	.645
24	13.8	...	.564	...	.436
48	14.5	...	.661	...	.339
60	14.6	..	.676	...	.324
72	14.5	...	.662	...	.338
120	15.1	0.7	.773	0.034	.193

VI. Sulfonation Reaction Rate.—Two separate 88-g. samples of pva-1 were swollen by heating in 500-cc. portions of pyridine on a steam-bath. Each was transferred to a 5-liter flask equipped for sulfonation under anhydrous conditions. The reaction mixtures were cooled to 4 ± 1°, and maintained at this temperature during the sulfonations. Three moles of benzenesulfonyl chloride (520.8 g.) was added to the first flask. Three moles of *p*-toluenesulfonyl chloride (571.8 g.) was added to the second flask. Samples were withdrawn periodically, purified by precipitation methods and analyzed. Analytical data are given in Tables I and II. These data indicate that the rate of sulfonation with benzenesulfonyl chloride is greater than that with *p*-toluenesulfonyl chloride. All samples gave negative tests for nitrogen. This study was not extended to polyvinyl methanesulfonate since its reaction mixture is heterogeneous, thus making it difficult to obtain truly representative samples.

TABLE III

REACTION OF POLYVINYL ALCOHOL IN PYRIDINE WITH BENZENESULFONYL CHLORIDE AT 26°

Nitrogen analysis by microanalytical methods gave values less than 1% for all samples

Reaction time in hours	S, %	Cl, %	Remarks
1	8.8	<1	Yellow powder
2	11.9	<1	Yellow powder
3	12.6	<1	Yellow powder
4	12.9	<1	Gray powder
6	14.0	<1	Gray powder
8	14.2	1.8	Gray powder
24	14.3	4.2	White, fibrous
32	15.0	5.0	White, fibrous
48	13.6	7.0	White, fibrous
72	11.6	9.3	White, fibrous
96	11.4	11.3	White, fibrous
144	10.9	12.0	White, fibrous
168	10.5	12.6	White, fibrous
192	10.2	12.9	White, fibrous
216	9.7	16.4	White, fibrous
264	9.6	17.1	White, fibrous

TABLE IV

REACTION OF POLYVINYL ALCOHOL IN PYRIDINE WITH BENZENESULFONYL CHLORIDE AT 50°

Reaction time in hours	N, %	S, %	Cl, %	Remarks
1.5	[a]	12.0	4.6	White; darkened with age
2	[a]	11.9	4.7	White; darkened with age
4	[a]	11.2	7.2	White
6	[a]	10.8	9.1	White
10	[a]	10.2	11.0	White
23	[a]	7.9	14.5	Yellow
32	[a]	7.3	18.6	Yellow
47	[a]	6.1	20.0	Yellow
71	2.1	5.2	21.9	Gray
145	2.4	2.2	24.2	Brown
192	2.6	<1	23.0	Dark brown
220	2.4	<1	23.9	Dark brown

[a] Nitrogen less than 1% by microanalytical analysis.

VII. The Effect of Temperature upon the Sulfonation Reactions.—(A) Eighty-eight grams of pva-1 was swollen for six hours in 500 cc. of anhydrous pyridine on a steam-bath. Three liters of pyridine was added. The mixture was cooled to 26°, and three moles of benzenesulfonyl chloride was added. The reaction mixture was stirred at 26°. Samples were withdrawn periodically, purified and analyzed. The analytical data are shown in Table III.

(B) A second experiment was performed exactly as the one just preceding, except that the temperature was maintained at 50°. Analytical results are shown in Table IV.

Discussion

Polyvinyl alcohol can be sulfonated satisfactorily only after pretreatment in such a manner that it is highly swollen or soluble in a reaction mixture. Two methods of pretreatment were used in this investigation, *i. e.*, (1) swelling of polyvinyl alcohol in pyridine at elevated temperature, and (2) dissolving polyvinyl alcohol, followed by transference of its solution to pyridine or to pyridine plus another non-solvent.

In the first method, the time of heating may be varied from ten minutes to fifteen hours at 80° with comparable results. The pyridine treatment is effective only at elevated temperatures. Experiment V shows that even after fourteen days in pyridine at room temperature, polyvinyl alcohol is not sufficiently swollen to be reactive at temperatures which prevent undesirable side reactions.

Although commercial grades of polyvinyl alcohol contain approximately 4% moisture, it has been found that anhydrous polyvinyl alcohol is equally satisfactory. No advantages were found when polyvinyl alcohol was swollen in 9:1 pyridine–water mixtures.

Water and sulfonic acids were used as solvents in the second method. Water is the preferred solvent since solution in sulfonic acids must be made at low temperature to prevent discoloration of the polyvinyl alcohol. Moreover, excess water can be removed more easily from the swollen polyvinyl alcohol than can the pyridine salts of the sulfonic acids which form when they are added to the pyridine.

The first method of pretreatment is not satisfactory for the preparation of polyvinyl methanesulfonate, as the product is only partially soluble in moist acetone or pyridine. The soluble portion is highly sulfonated, but the insoluble portion is very low in sulfur content. It is believed that this result is caused by a salting out of the reaction product by the pyridine–sulfonic acid salts. Whereas the polyvinyl arylsulfonates are soluble in the reaction mixture, the polyvinyl methanesulfonate is not. Because of the solubility of a polyvinyl arylsulfonate, it is continuously removed from the polyvinyl alcohol particles as it forms. On the other hand, the polyvinyl methanesulfonate is not removed from the polyvinyl alcohol particles, and thus prevents complete sulfonation. By obtaining the polyvinyl alcohol in a sufficiently highly swollen condition, as can be done by the second method of pretreatment, a substantially completely reacted polyvinyl methanesulfonate can be produced.

To avoid undesirable side reactions, the sulfonations must necessarily be performed at low temperatures, preferably below 10°. The rates of the side reactions which can take place decrease in the following order: (1) the reaction of vinyl sulfonate units with pyridine hydrochloride to form vinyl chloride units; (2) quaternization of vinyl sulfonate units by pyridine; (3) intramolecular reaction of vinyl sulfonate units with residual vinyl alcohol units to form intramolecular ethers. The first two reactions are evidenced by the data in Tables III and IV. The rate at which the sulfonoxy group is replaced by chlorine is in the following order: $CH_3SO_3- > C_6H_5SO_3- > CH_3-C_6H_4-SO_3-$. These reactions will be discussed more fully in subsequent papers of this series.

The degree of sulfonation which may be obtained is a function of the molecular size of the sulfonyl radical which is introduced. The highest degree of sulfonation is obtained with a methanesulfonyl group, the lowest with the naphthalenesulfonyl group, and an intermediate but approximately equal degree with the benzenesulfonyl and *p*-toluenesulfonyl groups. This qualitatively follows steric considerations.

Resulfonation experiments have shown that the degree of sulfonation cannot be increased appreciably after twenty-four hours at 5–10°. Experiment I-A indicates replacement of sulfonate groups by chlorine atoms.

The polyvinyl sulfonates show a certain instability upon remaining at room temperature. This instability is greatly increased at elevated temperatures. This property is being investigated more completely. The solubility characteristics of the polyvinyl sulfonates are shown in Table V.

TABLE V

SOLUBILITY OF POLYVINYL SULFONATES

− Insoluble; + soluble; ± insoluble anhydrous, but soluble if water is added. Polyvinyl methanesulfonate was insoluble in all the compounds except pyridine and moist acetone.

Solvent	Polyvinyl benzene-sulfonate	Polyvinyl *p*-toluene-sulfonate	Polyvinyl naphthalene-sulfonate
Acetone	+	+	−
Dioxane	±	±	−
Pyridine	+	+	+
2,6-Lutidine	±	+	±
Ethanol	−	−	−
Methanol	−	−	−
Water	−	−	−
Ethyl acetate	−	−	−
Acetic acid	−	−	−
Chloroform	+	+	+
Tetrahydropyran	−	+	−
Ethylene dichloride	+	+	+

Summary

1. Polyvinyl sulfonates of relatively high vinyl

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°.

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: $CH_3SO_3^- > C_6H_5SO_3^- > CH_3{-}C_6H_4SO_3^-$.

ROCHESTER 4, N. Y. RECEIVED JULY 16, 1949

[COMMUNICATION NO. 1277 FROM THE KODAK RESEARCH LABORATORIES]

Preparation and Reactions of Sulfonic Esters. II. The Reaction of Polyvinyl Sulfonates with Tertiary Amines[1]

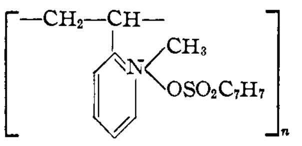
BY D. D. REYNOLDS AND W. O. KENYON

Introduction

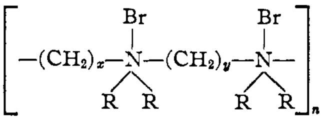
In the first paper of this series,[2] methods were given for the preparation of polyvinyl sulfonates which were shown to be copolymers consisting predominantly of vinyl sulfonate units combined with some residual vinyl alcohol units. The reaction of such polymers with tertiary amines is described in 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 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*-toluenesulfonate[3] and contains the unit



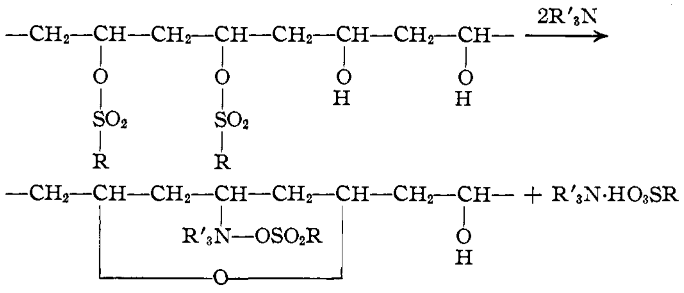
The other was formed by the reaction of an alkyl dibromide with a N,N,N′,N′-tetraalkyldiamine[4] to yield a linear polyquaternary salt having the structure



$$\left[-(\mathrm{CH_2})_x-\overset{\mathrm{Br}}{\underset{\mathrm{R\ \ R}}{\mathrm{N}}}-(\mathrm{CH_2})_y-\overset{\mathrm{Br}}{\underset{\mathrm{R\ \ R}}{\mathrm{N}}}-\right]_n$$

R = alkyl

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.



R = alkyl or aryl

Equation I

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

---

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

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

[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).