

extraction with 50 ml. of 6 *N* sodium hydroxide. The sodium carbonate wash liquors were neutralized with dilute hydrochloric acid to yield 0.5 g. of crude product having m.p. 158°. Further acidification caused precipitation of benzoic acid. Acidification of the alkali extract produced 3 g. of crude product, m.p. 158°. Evaporation of the tetrahydrofuran-ether phase produced 0.2 g. of product, m.p. 158° (total 3.7 g., 61.5% yield). The crude material was crystallized from ethanol to yield V, m.p. and mixed m.p. 160–161°.

Attempted Reduction of 2-Benzimidazolethiol (VI).—An attempt to reduce VI with LAH in a refluxing tetrahydrofuran solution for three hours resulted in a 64% recovery of unreacted VI. No reduction product was isolated.

Reduction of 2,5-Diphenyloxazole (VIII).—A straw yellow solution of 10 g. (0.45 mole) of VIII in 50 ml. of tetrahydrofuran was added over 40 minutes to a solution of 4 g. of LAH in 200 ml. of tetrahydrofuran. The brick red reaction mixture was refluxed for 3 hours and then decomposed with 4 ml. of water, 4 ml. of 15% sodium hydroxide and 12 ml. of water, in that order. The resultant canary

yellow mixture was filtered and the filter cake was washed with tetrahydrofuran. After drying over magnesium sulfate the orange filtrate was treated with gaseous hydrogen chloride for 30 minutes until the solution became light yellow and no further evidence of solid formation was observed. The solid was filtered and washed with ether to yield 5.3 g. (44.5% yield) of the hydrochloride of 2-benzylamino-1-phenylethanol, m.p. 221–223° (reported¹⁰ m.p. 219.5–221.5°).

Several drops of 6 *N* sodium hydroxide were added to a solution of the hydrochloride in hot water. The resultant white solid was filtered, washed with water and air dried. Several recrystallizations from petroleum ether gave the free base, m.p. 102° (reported¹⁰ m.p. 103°).

A portion of the free base was treated with a saturated alcohol solution of picric acid to yield the picrate, recrystallized from alcohol; m.p. 150–151°.

Anal. Calcd. for C₂₁H₂₀N₄O₈: C, 55.32; H, 4.39. Found: C, 55.66; H, 4.76.

(10) C. L. Browne and R. E. Lutz, *J. Org. Chem.*, **17**, 1187 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

Sulfostyrenes.¹ Variable Capacity Di-(*p*-vinylphenyl)-sulfone Cross-linked Sulfostyrene Cation Exchange Polymers from Styrene/Sulfonamidostyrene Copolymers

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Di-(*p*-vinylphenyl)-sulfone has been obtained from di-(*p*-bromoethylphenyl)-sulfone which occurs as a by-product in the previously described *p*-sulfonamidostyrene. Sulfone-free *p*-sulfonamidostyrene has been polymerized and copolymerized with and without added di-(*p*-vinylphenyl)-sulfone as a cross-linking co-monomer. These polymers have been hydrolyzed to a series of cation-exchange sulfostyrene polymers and copolymers with uniformly varied distribution of exchange groups and varying degrees of cross-linkages.

The variable capacity sulfostyrene cation-exchange polymers prepared previously¹ by the nitrous acid hydrolysis of styrene/sulfonamidostyrene copolymers were either cross-linked or highly branched as evidenced by their solvent and alkali insolubility. Because these copolymers are the only available cation-exchange polymers in which the distribution of the exchange units along the chain can be controlled with some degree of predictability and conformity, precise knowledge about their composition is a critical factor in determining the extent of their utility in theoretical studies of selectivity coefficients.² The nature and extent of the cross-linking involved in their structure is particularly significant because it is known³ that the degree of cross-linking is intimately connected with selectivity behavior to the extent that at very low levels of cross-linking selectivity is almost completely lost and that under other conditions reversals of the selectivity coefficients may take place. It is, therefore, highly desirable to have additional data about the character of the cross-linkage or chain branching in the polymers and copolymers of *p*-sulfonamidostyrene and, if possible,

to have available a series of variable capacity copolymers with a controlled degree of cross-linkage.

Previously the cross-linkage or branching in these copolymers was attributed to chain transfer reactions involving the N–H linkage of the sulfonamide. Consistent with this was the observation that the hydrolysis of the copolymers did not usually go to completion from which it was inferred that some nitrogen remained in the polymer in linkages other than amino, presumably imino. It has been reported⁴ that under some conditions the nitrous acid treatment of sulfonamides leads to the formation of di-(arylsulfonyl)-hydroxylamine, (Ar-SO₂)₂NOH, as a minor by-product. Although this reaction could conceivably lead to cross-linking during hydrolysis of the polymer this possibility seems unlikely since the cross-linking or chain-branching phenomena appear during polymerization as is evidenced by the insolubility of polymers produced under some but not other conditions.

A third possibility leading to cross-linkage in these polymers is that of the presence of traces of di-(*p*-vinylphenyl)-sulfone. This divinyl sulfone would presumably be present as a result of sulfone formation in the preparation of *p*-bromoethylbenzenesulfonyl chloride. The procedure used previously in the preparation of the monomeric *p*-sulfonamidostyrene is not absolutely certain to remove traces of this sulfone. The simple expedient of dissolving the sulfonamide in alkali will, however, per-

(1) Previous papers in this series: (a) R. H. Wiley and S. F. Reed, *J. Phys. Chem.*, **60**, 533 (1956); (b) R. H. Wiley, N. R. Smith and C. C. Ketterer, *THIS JOURNAL*, **76**, 720 (1954); (c) R. H. Wiley and C. C. Ketterer, *ibid.*, **75**, 4519 (1953).

(2) G. E. Boyd, B. A. Soldano and O. D. Bonner, *J. Phys. Chem.*, **58**, 456 (1954); G. E. Myers and G. E. Boyd, *ibid.*, **60**, 521 (1956).

(3) O. D. Bonner, *ibid.*, **58**, 318 (1954); H. P. Gregor and J. Bregman, *J. Colloid Sci.*, **6**, 323 (1951); D. Reichenberg, K. W. Pepper and D. J. McCawley, *J. Chem. Soc.*, 493 (1951).

(4) O. Hinsberg, *Ber.*, **27**, 598 (1894).

mit easy and complete separation from the alkali-insoluble sulfone and simultaneously a means of obtaining some of the sulfone. We have demonstrated that the sulfone is actually present in such preparations of the amide and that the amide thus purified is not less than 98% pure on the basis of bromine titration.

A study of the conditions used in the chlorosulfonation of bromoethylbenzene in terms of maximum obtainable yields of sulfone established that only 1.36 to 4.27% of recrystallized sulfone was formed at temperatures ranging from 22 to 45° during chlorosulfonation even when deliberate alterations in procedure were made to achieve sulfone formation. This establishes a maximum limit for the amount of sulfone in the sulfonamidostyrene previously used of not over 4% since undoubtedly a portion of the sulfone was removed in the previously described purification of the monomer. Furthermore, although it established the unattractive nature of this procedure for the synthesis of the sulfone in any quantity, no more satisfactory method for its synthesis has been devised. The only even remotely satisfactory synthesis for this sulfone appears to be the partial conversion of β -bromoethylbenzene to di-(β -bromoethylphenyl)-sulfone during the preparation of β -bromoethylbenzenesulfonyl chloride. This is understandable when it is realized that any of the usual procedures designed to favor or achieve sulfone formation will also increase the probability of Friedel-Crafts type reactions of the halide. The di-(bromoethylphenyl)-sulfone which was previously reported⁵ has now been obtained analytically pure and has been dehydrohalogenated to the bi-(*p*-vinylphenyl)-sulfone.

With the sulfone-free sulfonamidostyrene and di-(*p*-vinylphenyl)-sulfone now available we have prepared a series of polymers and copolymers of styrene and sulfone-free sulfonamidostyrene without any added cross-linking agent and with 5 and 10% mole per cent. of di-(*p*-vinylphenyl)-sulfone as cross-linking agent. The amide polymers and copoly-

mers were prepared and hydrolyzed as previously described and data on their capacities and swelling ratios are given in the Table I.

The polymer obtained from sulfone-free sulfonamidostyrene by polymerization for 10 minutes at 150° with no added initiator was soluble in boiling pyridine. If the monomer is not freed of sulfone, polymers prepared under these conditions are not soluble in pyridine. If, however, the heating period is extended the sulfone-free monomer is also converted to an insoluble polymer. Data on a series of polymers prepared under controlled conditions at 110° with initiator indicate that this transition from solubility to insolubility goes through steps as the time of polymerization is extended in which solubility in pyridine is first lost, then solubility in sodium hydroxide is lost. A comparison of the swelling ratios for the polymer obtained from sulfone-free monomer shows that this polymer swells considerably more than does the hydrolyzed polymer prepared from monomer that has not been freed of sulfone. The hydrolyzed copolymers show less difference in swelling ratios. The addition of 5 or 10% of the sulfone produces hydrolyzed copolymers with very definitely decreased swelling ratios. A comparison of the swelling data for these polymers with swelling data previously reported⁶ for sulfonated polystyrene cross-linked with varying amounts of divinylbenzene indicates that the polymers cross-linked with 5% of the sulfone swell to about the same degree as sulfonated polystyrenes cross-linked with about 3% divinylbenzene. This is in the range to be expected on the basis of the comparative molecular weights of the two cross-linking monomers. The swelling ratios on the polymer containing no added sulfone (22.2) and on the previously reported polymer (14.1) are both comparable to those observed with about 1% divinylbenzene cross-linked sulfonated polystyrene.

Although two types of cross-linking are present in these hydrolyzed sulfonamide polymers and copolymers, they are probably no less, and may be considerably more, uniform in their composition than the divinylbenzene cross-linked, sulfonated polystyrene resins since the latter have been reported to contain either 1-2% or 6%⁷ of sulfone cross-links in addition to the divinylbenzene cross-links. It is believed that further refinements in the copolymerization of *p*-sulfonamidostyrene and of potassium *p*-styrenesulfonate, both of which are under study in our laboratories and will be reported in subsequent papers, will provide materials of more precisely defined composition desirable for theoretical studies of selectivity coefficients and diffusion coefficients of ion-exchange resins.

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(6) H. P. Gregor, F. Guttoff and J. Bregman, *J. Colloid Sci.*, **6**, 245 (1951).

(7) W. C. Bahman and J. Eichhorn, *This Journal*, **69**, 2830 (1917).

TABLE I
SULFOSTYRENE POLYMERS AND COPOLYMERS^a

Mono- mer ratio ^b	SAS ^c (g.)	Sty- rene (g.)	Sul- foned ^d	Capacities, meq./g.		Swelling Ratio
				Calcd.	Obsd.	
100/0	13.00	5.43	5.45	22.25
75/25	11.50	2.18	...	4.57	4.29	18.86
50/50	9.00	5.11	...	3.46	3.45	6.09
25/75	4.62	7.88	...	2.01	2.02	1.69
100/0	12.00	..	0.89 ^e	5.06	4.90	3.46
75/25	10.48	1.99	1.03 ^e	4.22	4.24	2.60
50/50	7.96	4.52	1.17 ^e	3.17	3.12	2.36
25/75	4.62	7.88	1.36 ^e	1.82	1.80	1.40
100/0	12.00	..	1.78 ^f	4.74	4.70	2.36
75/25	11.50	2.18	2.26 ^f	3.92	3.75	1.82
50/50	7.96	4.52	2.34 ^f	2.92	2.92	1.74
25/75	4.62	7.88	2.72 ^f	1.65	1.46	1.25

^a Prepared by hydrolysis of sulfonamidostyrene polymers polymerized at 110°. ^b Mole per cent. *p*-sulfonamidostyrene to styrene. ^c *p*-Sulfonamidostyrene. ^d Bis-(*p*-vinylphenyl)-sulfone. ^e 5 mole per cent. of sulfone. ^f 10 mole per cent. of sulfone.

(5) G. E. Inskip and R. Deakin, *This Journal*, **69**, 2237 (1917).

Experimental

***p*-Sulfonamidostyrene (Free of Sulfone).**—*p*-(β -Bromoethyl)-benzenesulfonamide was prepared by the following modification of the procedure described previously.¹⁰ Five hundred grams (2.7 moles) of β -bromoethylbenzene was chlorosulfonated with 1566 g. (13.56 moles) of chlorosulfonic acid at 22°. The addition required five hours. The sulfonyl chloride was converted to the sulfonamide by treating with an excess of ammonium hydroxide. The crude *p*-(β -bromoethyl)-benzenesulfonamide was dissolved in 9 liters of 5% sodium hydroxide and filtered. The residue was washed with 300 ml. of hot 5% sodium hydroxide and 300 ml. of water and dried to give 30 g. (5.1%) of crude bis-*p*-(β -bromoethyl)-phenylsulfone. Recrystallization from methanol gave 10 g. (1.7%) of pure sulfone, m.p. 163.5–164°. The alkaline solution was extracted with 3 liters of benzene to remove sulfone possibly not separated by the alkali treatment. After standing at room temperature for five hours to complete dehydrohalogenation the alkaline solution was acidified with 2 liters of 6 *N* hydrochloric acid. The precipitate was washed with 1 liter of water and dried under vacuum. The yield of crude *p*-sulfonamidostyrene, m.p. 130–140°, was 300 g. or 60%. The amide after recrystallization from benzene and then ethanol, melted at 138–139°. If the *p*-(β -bromoethyl)-benzenesulfonamide was recrystallized from an ethanol-water mixture of equal proportions before treatment with sodium hydroxide, the yield of *p*-sulfonamidostyrene, m.p. 138–139°, was 27% lower.

Anal. Calcd. for C₈H₉ONS: mol. wt., 183.22. Found: mol. wt., 186.96 (by bromine titration⁸).

Bis-*[p*-(β -bromoethyl)-phenyl]-sulfone.—The possibility of separating the sulfone from the sulfonyl chloride by the precipitation of the sulfone from the sulfonyl chloride by the addition of methanol⁹ was abandoned because of the loss of sulfonamidostyrene resulting from methanolysis of the halide. During studies of this method of isolation, it was demonstrated that alterations in the temperature from 22–45° and in the time of reaction from 5 minutes to 5 hours gave variations in yield of only 1.36–4.27% of the recrystallized sulfone. Higher yields (3.25%, 4.2%) were obtained at higher temperatures (45°, 35°) and shorter addition times (5 minutes, 30 minutes). Since sufficient amounts of the sulfone for our studies were available as a by-product from the preparation of sulfone-free monomer as described in the preceding paragraph no further study of improved methods of synthesis of this monomer has been under-

(8) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, New York, N. Y., 1954, p. 69.

taken. The crude sulfone was recrystallized twice from methanol to give a product melting at 163.5–164°.

Anal. Calcd. for C₁₆H₁₆SO₂Br₂: C, 44.46; H, 3.73. Found: C, 44.23; H, 3.85.

Bis-*(p*-vinylphenyl)-sulfone.—To 150 ml. of ethanol containing 7.5 g. of potassium hydroxide in a three-necked round bottom flask equipped with a stirrer, reflux condenser and heating mantle was added 10 g. of bis-*p*-(β -bromoethyl)-phenylsulfone and a trace of hydroquinone. The solution was refluxed for 1 hour, cooled to room temperature and 300 ml. of water added. The precipitate was washed with water, filtered, allowing no air to pass through the precipitate, and dried under vacuum. The precipitate was recrystallized twice from petroleum ether to give 2.9 g. or 47% of product, 125°.

Anal. Calcd. for C₁₆H₁₄O₂S: C, 71.09; H, 5.22. Found: C, 71.07; H, 5.47.

Polymerization of *p*-Sulfonamidostyrene with Styrene with and without Cross-linking Agents.—This polymerization was carried out as previously described¹⁰ with the exceptions that 0.5 ml. of dimethylformamide was used per 1.5 g. of monomer instead of 0.5 ml. per 1.56 g. of monomer and that bis-*(p*-vinylphenyl)-sulfone was added as cross-linking agent in 0, 5 and 10 mole per cent. to prepare the three series of resins. The polymer and copolymers are described in the table. Vacuum treatment at 2 mm. for one week to remove the dimethylformamide gave a weight loss of 31–50% with the exception of the 75/25 uncross-linked copolymer and the 5% cross-linked polymer which lost only 17–18% by weight.

Hydrolysis of the Polymers.—The hydrolysis was carried out as previously described.¹⁰ Four repetitions of the hydrolysis rather than three were used. After the hydrolysis the resin was placed in a glass column and washed with distilled water until a negative test was obtained for nitrite ion, with 3 liters of 1 *N* hydrochloric acid, and finally with distilled water until the effluent was free of acid. The polymer was dried under vacuum (2 mm.) over phosphorus pentoxide at room temperature to constant weight prior to titration. This dried polymer gave no residue on combustion.

Capacity Measurements.—These measurements were total capacity measurements made as previously described.¹⁰

Swelling Characteristics.—The swelling ratios were determined by the procedure previously described.¹⁰ To check the assumption that the ratio of the true volume to bulk volume was the same in water as in hexane, the volume of the swollen particles was measured in hexane. The difference in the calculated value and the measured value for the swollen particles was well within experimental error.

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Sulfostyrenes.¹ Polymers and Copolymers of Potassium *p*-Vinylbenzenesulfonate

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Divinylbenzene cross-linked insoluble copolymers have been prepared by the copolymerization of potassium *p*-vinylbenzenesulfonate, prepared and purified by a new procedure, with styrene. The copolymers precipitate during polymerization of the monomer mixture in dimethylformamide solution. Prepared at high conversions, they have capacities of 2.03–4.18 meq. per gram. Sulfur analyses establish copolymer compositions in agreement with the composition of monomers copolymerized. Water-soluble polymers of potassium *p*-vinylbenzenesulfonate prepared by polymerization of dimethylformamide solutions of the monomer from which the polymer precipitates have higher viscosities than polymers previously prepared in aqueous solution.

In a previous paper² we described the preparation and polymerization of potassium *p*-vinylbenzenesulfonate. The monomer was purified *via* its toluidine salt and polymerized in aqueous solution to a water-soluble polyelectrolyte. In continuing

these studies we have developed a more direct synthesis of the monomer and a procedure for the preparation of polymers and copolymers which are of higher viscosity. Furthermore, the copolymerization procedure can be adapted to the preparation of cross-linked copolymers in a form suitable for ion-exchange studies.

In these polymers and copolymers the uniformity of distribution and certainty of location of the ionic

(1) Previous paper in this series: R. H. Wiley and J. E. Schmitt, *This Journal*, **78**, 2169 (1956).

(2) R. H. Wiley, N. R. Smith and C. C. Ketterer, *ibid.*, **76**, 720 (1954).