Experimental

***p*-Sulfonamidostyrene (Free of Sulfone).**—*p*-(β-Bromoethyl)-benzenesulfonamide was prepared by the following modification of the procedure described previously.[1c] 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 C_8H_9ONS: mol. wt., 183.22. Found: mol. wt., 186.96 (by bromine titration[8]).

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 methanol[5] 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 undertaken. The crude sulfone was recrystallized twice from methanol to give a product melting at 163.5–164°.

Anal. Calcd. for $C_{16}H_{16}SO_2Br_2$: 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 $C_{16}H_{14}O_2S$: 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 described[1c] 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.[1c] 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.[1c]

Swelling Characteristics.—The swelling ratios were determined by the procedure previously described.[1c] 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.

LOUISVILLE 8, KY.

---

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

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

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

BY RICHARD H. WILEY AND S. F. REED, JR.

RECEIVED NOVEMBER 21, 1955

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 viscosites than polymers previously prepared in aqueous solution.

In a previous paper[2] 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).

groups eliminates some of the heterogeneity thought to contribute to the unusual reversal of selectivity observed in partially desulfonated sulfonated polystyrenes[3] and in highly cross-linked sulfonated polystyrenes.[4] In polymers prepared from potassium *p*-vinylbenzenesulfonate there can be no *ortho, meta,* or di-sulfonated benzene rings, no side chain sulfonation, and no sulfonation in the nucleus of the cross-linking divinylbenzene. Furthermore, the distribution of the sulfo groups along the chain in the copolymers of variable capacity will be in accord with a recognized and determinable copolymerization phenomenon rather than by the statistical factors involved in the access of a reagent to the polymer chain involved in a reaction designed to reduce or increase the capacity of an ion exchange resin. A thermodynamic calculation of cation-exchange selectivities[5] has further emphasized the desirability of additional studies with homogeneous exchange resins.

The monomeric potassium *p*-vinylbenzenesulfonate used in these studies was prepared by the combined alcoholic potassium hydroxide dehydrohalogenation and hydrolysis of *p*-(β-bromoethyl)-benzenesulfonyl chloride and purified by recrystallization from ethanol at −20°. Polymerization of this monomer in dimethylformamide at 109° with 0.01–1.0% *t*-butyl peracetate as initiator resulted in the precipitation of a white, solid, hygroscopic polymer soluble in water and alcohol. The viscosity data for these polymers are given in Fig. 1. As with other polyelectrolytes[6] these data show marked increase of reduced viscosity (n_{sp}/c) in dilute solutions. The curves for these polymers are similar in shape to those observed previously[1] with polymers prepared in aqueous solution but reflect a distinct increase in molecular weight. Thus, although the highest viscosity polymer previously reported had a reduced viscosity of 2.62 at 1.0 g./100 ml., the polymers prepared in dimethylformamide with 1.0, 0.1 and 0.01% initiator had reduced viscosities of 2.84, 3.70 and 3.99, respectively. At lower concentrations the contrast in reduced viscosity values is even greater

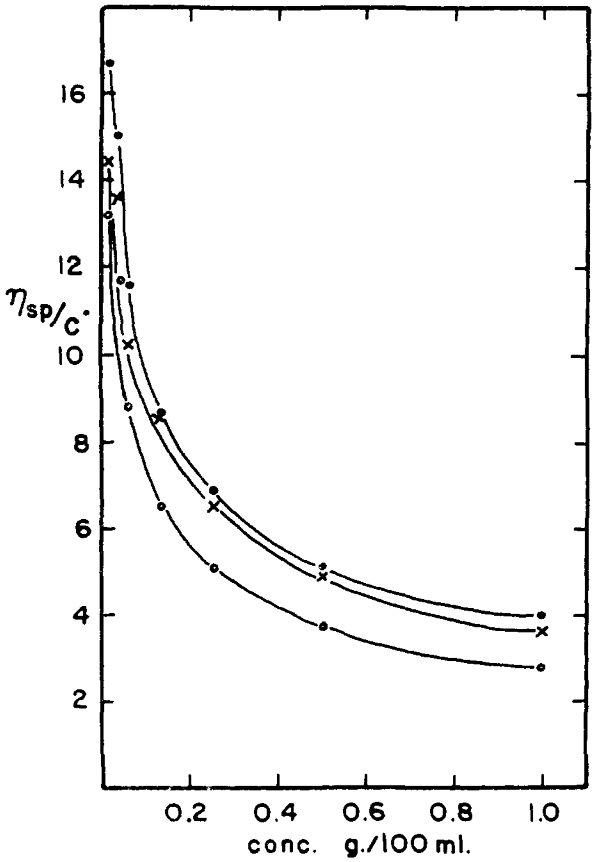

Fig. 1.—Plot of the reduced viscosity against the concentration for potassium *p*-vinylbenzenesulfonate polymers.

Cross-linked copolymers were prepared from potassium *p*-vinylbenzenesulfonate, styrene and divinylbenzene in dimethylformamide using *tert*-butyl peracetate as a catalyst at temperatures of 89 and 109°. The swelling properties, capacity data and sulfur analyses for typical polymers prepared at 89° are given in Table I. The capacity and sulfur content of the copolymers prepared from monomer mixtures containing 50 and 25% of salt indicated that the copolymers had nearly the same composition as that of the monomer mixture from which they were prepared. This is not surprising in view of the fact that the polymerizations were carried to over 90% of yields. With 75% salt in the monomer mixture, however, and also with several copolymers prepared at 109°, the copolymer had a lower sulfur content and a lower capacity than predicted for the composition of the polymer to be obtained if the two monomers were incorporated in the copolymer at the same ratio as that of the monomer mixture used. This is not in accord with previously recorded data for the copolymerization of other substituted styrenes with styrene in which it has been shown that electron attracting substituents in the styrene nucleus increase the rate at which the substituted styrene enters the polymer chain relative to styrene.[7] The monomer reactivity ratios for the *p*-nitrostyrene/styrene copolymerization are: r_1 = 0.19; r_2 = 1.15; r_1r_2 = 0.22. For the *p*-cyanostyrene/styrene copolymerization: r_1 = 0.28; r_2 = 1.16; r_1r_2 = 0.33. It may be noted that these are not extreme examples of non-azeotropic copolymerization. Our data on 75/25 copolymer compositions indicate that the salt enters the chain less rapidly and by analogy one would not predict monomer reactivity ratios of the same order of magnitude as for the nitro- and cyanostyrenes. A determination of the monomer reactivity ratios, which is in process in our laboratories, will provide a basis for establishing the kind of charge distribution in the resulting copolymer.

Experimental

Potassium Vinylbenzenesulfonate.—To 326 ml. of chlorosulfonic acid at 0–5° was added dropwise 138 ml. (1.0 mole)

---

(3) G. E. Boyd, B. A. Soldano and O. D. Bonner, *J. Phys. Chem.*, **58**, 456 (1954).

(4) O. D. Bonner, *ibid.*, **58**, 318 (1954).

(5) G. E. Myers and G. E. Boyd, Symposium on Ion-Exchange, Southeastern Regional Meeting, American Chemical Society, Columbia, South Carolina, November 3–5, 1955.

(6) R. H. Wiley and C. C. Ketterer, *Trans. Kentucky Acad. Sci.*, **16** (1955).

(7) C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, THIS JOURNAL, **70**, 1537 (1948).

of β-bromoethylbenzene. During the addition the temperature rose to, but not over, 20°. After one hour the reaction mixture was poured onto ice with stirring to precipitate the sulfonyl chloride which was washed with ice-water and taken up in ether. The ether solution was washed with dilute sodium bicarbonate and dried. The residue remaining on evaporation of the ether was dissolved in 350 ml. of cold 95% ethanol. To this solution was added slowly a solution of 224 g. of potassium hydroxide in one l. of 95% ethanol. This reaction mixture was refluxed one hour and filtered. The solid thus collected was washed with an additional 500 ml. of hot ethanol and filtered. The combined filtrates were cooled to −20° to precipitate the crude product. This crude product was taken up in the minimum quantity of hot water and filtered. The filtrate was extracted with benzene and cooled to precipitate the product. A final recrystallization from 95% ethanol gave 66.5 g. (30%) of potassium p-vinylbenzenesulfonate.

Anal. Calcd. for $C_8H_7KO_3S$: S, 14.42. Found: S, 14.37.

The monomer was stored at −20° and recrystallized from ethanol just prior to use. It was free from halide ion and was converted to its toluidine salt, m.p. 189–190°.

Anal. Calcd. for $C_{15}H_{17}NO_3S$: neut. equiv., 291.35. Found: neut. equiv., 290.8.

Polymerization of Potassium *p*-Vinylbenzenesulfonate in Dimethylformamide Solution.—A solution of 1.56 g. of potassium p-vinylbenzenesulfonate and 0.156 mg. (0.01%) of t-butyl peracetate in 15 ml. of dimethylformamide was heated under an oxygen-free nitrogen atmosphere at 109° for 22 hours. The polymer began to precipitate from the solution within 10 minutes at reaction temperature. The precipitated polymer, along with an additional amount of polymer precipitated by the addition of an equal volume of ether, was washed with ether and vacuum dried to give 1.5 g. of polymer. This procedure was repeated using 1.56 mg. (0.1%) and 15.6 mg. (1.0%) of t-butyl peracetate initiator.

All of these polymers were hygroscopic solids soluble in water and alcohol. Viscosities were determined on samples vacuum dried at 56° to constant weight. The viscosity data are given in Fig. 1. The addition of 9–17% of divinylbenzene to this polymerization procedure gave cross-linked, insoluble polymers.

Cross-linked Copolymers of Styrene and Potassium *p*-Vinylbenzenesulfonate.—A mixture of 6.66 g. (0.03 mole) of potassium p-vinylbenzenesulfonate, 0.77 g. (0.00592 mole 10%) of divinylbenzene, 0.43 g. (0.00408 mole) of styrene, 100 ml. of dimethylformamide and 0.78 mg. (0.01%) of t-butyl peracetate was heated at 89° with stirring under oxygen-free nitrogen for 22 hours. All ingredients had dissolved within 5–10 minutes and the copolymer began to precipitate in 25–30 minutes. The precipitate, along with an additional quantity of polymer precipitated by the addition of ether, was washed with ether and dried to give 7.15 g. of the 75/25 copolymer.

Using a similar procedure but with varying quantities of monomers 6.41 g. of 50/50 copolymer and 10.03 g. of 25/75 copolymer were obtained. The 50/50 copolymer was also prepared without addition of the ether-precipitated copolymer in 6.07 g. yield.

The capacities and swelling ratios of these copolymers were determined as previously described.[1] Difficulties were encountered in converting these resins to the acid form because they were too fine to wash in a column. The degree of swelling was also determined by weighing the resins before and after swelling with water to determine the weight of water absorbed.

TABLE I

Copolymer composition[a]	Yield, %	Swelling ratio	Capacity Calcd.	Capacity Obsd.	Sulfur Calcd.	Sulfur Found
75/25	91	6.3	4.56	4.18	14.63	14.22, 14.08
50/50	94	4.1	3.47	3.53	11.11	11.35, 11.40
50/50[b]	91	..	3.47	3.49	11.11	11.45, 11.63
25/75	92	3.3	2.02	2.03	6.67	6.69, 6.84

[a] The ratio is that of the moles of potassium p-vinylbenzenesulfonate to moles of styrene plus moles of divinylbenzene. [b] Without added ether precipitated copolymer.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Heats of Reaction of Pyridine and Nitrobenzene with Boron Trifluoride, Trichloride and Tribromide; the Relative Acceptor Properties of the Boron Halides[1,2]

BY HERBERT C. BROWN AND ROBERT R. HOLMES[3]

RECEIVED OCTOBER 27, 1955

The 1:1 molecular addition compounds of boron trifluoride, trichloride and tribromide with pyridine and of the trichloride and tribromide with nitrobenzene were prepared and characterized. The molar heats of reaction of the three boron halides with nitrobenzene were determined, calorimetrically in the case of the chloride and bromide, and from Henry's law constants in the case of the fluoride. The molar heats of reaction of pyridine with these boron halides in nitrobenzene solution were also determined calorimetrically. From the resulting data, the relative bond dissociation energies of the pyridine–boron trihalides addition compounds were calculated, providing a measure of the relative strengths of the boron trihalides as Lewis acids. The results reveal that the acceptor properties increase in the order: $BF_3 < BCl_3 < BBr_3$. The order is opposite to that which would be predicted on the basis of the relative electronegativities of the halogens and suggests that resonance contributions must play a dominant role in determining the relative acceptor properties of the boron halides.

The boron trihalides are typical Lewis acids or electron-pair acceptors. Numerous 1:1 molecular addition compounds formed by the reaction of these halides with organic bases have been described.[4,5]

An examination of the available data suggests that the coördinating ability of the boron halides must increase with increasing atomic weight of the halogen, $BF_3 < BCl_3 < BBr_3 < [BI_3]$. For example, no evidence could be found for the existence of a compound between boron trifluoride and arsine, even at temperatures as low as −120°,[6] whereas addition compounds of arsine with boron trichloride[7] and boron tribromide[8] are stable with respect to dissociation at temperatures near 0°. Similarly, phosphorus trichloride forms a 1:1 addition com-

---

[1] The Catalytic Halides. XIV.

[2] Based upon a thesis submitted by Robert R. Holmes in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Research assistant (1951–1953) on a grant from the Atomic Energy Commission for the study of "Chemistry of Polyvalent Metal Halides."

[4] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

[5] D. R. Martin, *Chem. Revs.*, **34**, 461 (1944).

[6] D. R. Martin and R. Dial, THIS JOURNAL, **72**, 852 (1950).

[7] A. Stieber, *Compt. rend.*, **195**, 610 (1932).

[8] A. Stock, *Ber.*, **34**, 949 (1901).