ductance of 377 (cm.²/ohm equivalent). Table II summarizes our findings.

TABLE II

CONDUCTANCE OF DIBENZOFURAN-2-SULFONIC ACID AT 25°

Equivs./liter	Specific conductance $\times 10^3$ ($\text{ohm}^{-1} \times \text{cm.}^{-1}$)	Equivalent conductance (cm.²/ohm equiv.)
0.020	5.9	29_0
.010	3.4	34_0
.005	1.8	37_0
.0025	0.88	35_0
.0012	.48	40_0
.00062	.23	38_0

The *p*H of a 0.20 *N* (5%) solution of the sulfonic acid was determined and found to be 0.80. A corresponding hydrogen ion activity of 0.2 of unity would give a *p*H of 0.7. The calculated dissociation of the acid at 0.2 *N* = $(10^{-0.8}/10^{-0.7})100 = 79\%$.

(c) **Solubility.**—The water solubility of the sulfonic acid was determined at 0 and 25°. Concentrated solutions of the acid were prepared at 50–60°, then chilled in tall cylinders for twenty-four hours. Titration of the clear liquid above the precipitated acid gave the following results: solubility at 25° = 0.34 *N* = 8.5 g./100 ml.; at 0° = 0.0887 *N* = 2.2 g./100 ml.

3. **Precipitation of Sodium and Potassium, and Various Other Cations by Dibenzofuran-2-sulfonic Acid.**—The recrystallized acid was dissolved in water at various concentrations ranging downward from 2.0%. Such solutions were neutralized by the addition of sodium, potassium, ammonium and barium hydroxides, after which the resulting solutions were diluted to a standard volume and chilled in ice. The appearance of a precipitate immediately indicated the point at which saturation had been reached. By determining the amount of precipitated salt, and knowledge of the original amount produced, one can calculate the solubilities of these salts. The solubility of the lithium salt was determined by addition of the acid to dilute lithium chloride solutions.

A great many other metal ions were precipitated from their dilute aqueous solutions by addition of the 2-sulfonic acid. The results of these various determinations are summarized in Tables III and IV.

TABLE III

SOLUBILITIES OF VARIOUS SALTS OF DIBENZOFURANSULFONIC ACID AT 0°

Cation	Solubility (g./100 ml.)	Solubility product
Na	0.300	1.23×10^{-4}
K	0.520	3.31×10^{-4}
Ba	0.094	1.29×10^{-8}
Li	0.74	8.5×10^{-4}
NH_4	1.87	49.7×10^{-4}

Ag, Cu^{+2}, Hg^{+2}, Mg, Ca, Zn, Al, Pb^{+2}, Sb^{+3}, Bi^{+3}, Cr^{+3}, Mn^{+2}, Ni, Fe^{+3}, Co^{+2}-chloride and sulfate salt solutions of all these metals in 1% concentration, gave abundant precipitation when the acid solution was added.

TABLE IV

ANALYSIS OF SODIUM, POTASSIUM, AND BARIUM SALTS OF DIBENZOFURAN-2-SULFONIC ACID (DRIED IN VACUUM OVEN TWO HOURS AT 110°)

Salt	Molecular formula	Per cent. sulfur Calcd.	Per cent. sulfur Found	Per cent. metal Calcd.	Per cent. metal Found
Na	$(C_{12}H_7SO_4)Na$	11.85	11.76	8.51	8.19
K	$(C_{12}H_7SO_4)K$	11.20	11.05	13.63	13.27
Ba	$(C_{12}H_7SO_4)_2Ba$	10.15	10.10	21.75	21.34

The sodium and potassium salts were analyzed by combustion in a platinum crucible with sulfuric acid to form metal sulfates.

The very low water-solubility of the sodium, potassium, and lithium salts is noteworthy—a phenomenon that augurs a new technique in the determination of these metals.

Summary

Dibenzofuran-2-sulfonic acid has been prepared and crystallized from water. The acid appears to be a general metal ion precipitant, even for lithium, sodium and potassium, and for these metals offers promise as an analytical reagent.

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[7] Original manuscript received June 1, 1948.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

Base Catalyzed Polymerization of Styrene

BY JAMES J. SANDERSON[1] AND CHARLES R. HAUSER

A study of the base catalyzed polymerization of styrene has been in progress in this Laboratory for some time. In view of the recent paper by Beaman[2] on the base catalyzed polymerization of methacrylonitrile it seems desirable to publish our results.

We have found that styrene is polymerized by sodium amide in liquid ammonia to give an easily pulverized white solid, melting at 130–170°, and having an average molecular weight of about 3000. On fusion this polymer is transformed to a brittle, glassy solid. The properties of this material are those reported for polystyrene of the same average molecular weight prepared by heating styrene at 240°.[3] Results obtained under varying conditions are summarized in Table I. It can be seen that the yields and average molecular weights are approximately the same using 5, 10 and 100 mole

TABLE I

POLYMERIZATION OF STYRENE BY SODIUM AMIDE IN LIQUID AMMONIA

Mole % of $NaNH_2$	Reaction time, min.	Yield, %	Average mol. weight
5	240	71	2900
10	240	72	3200
100	240	68	3100
100	120	64	..
100	20	40	4300

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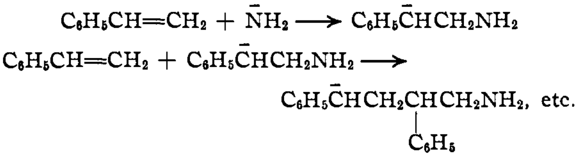
[1] Carbide and Carbon Chemicals Corporation Fellow, 1946–1948.

[2] Beaman, THIS JOURNAL, **70**, 3115 (1948).

[3] Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli, *Ber.*, **62**, 241 (1929).

per cent. of sodium amide. In these experiments, the reaction time was two hundred and forty minutes but approximately the same yield of polymer was obtained (using 100 mole per cent. of sodium amide) when the reaction time was only one hundred and twenty minutes. It is to be noted that the average molecular weight was somewhat higher when the reaction time was shortened to twenty minutes. These polymers, which were isolated by precipitation from ether solution by methanol, failed to give a positive test for nitrogen by the sodium fusion method,[4] but their pyrolysis products yielded a small amount of acid soluble material which gave a strong positive test for nitrogen. A positive test was given directly by the lower molecular weight polymers remaining in the ether–methanol solution. Since polymerization does not occur in the presence of liquid ammonia alone with a trace of ferric nitrate (used in the conversion of sodium to sodium amide) the polymerization must be initiated by the sodium amide. Because the polymerization by sodium amide has occurred in the presence of *t*-butylcatechol (sodium salt) a free radical mechanism appears not to be involved. It is suggested that the polymerization is initiated by the addition of the amide ion to the vinyl double bond of styrene to form a carbanion which starts a chain reaction. One mode of addition might be represented as



$$C_6H_5CH{=}CH_2 + \bar{N}H_2 \longrightarrow C_6H_5\bar{C}HCH_2NH_2$$

$$C_6H_5CH{=}CH_2 + C_6H_5\bar{C}HCH_2NH_2 \longrightarrow$$

$$C_6H_5\bar{C}HCH_2\underset{\underset{\displaystyle C_6H_5}{|}}{C}HCH_2NH_2,\ \text{etc.}$$

Similar ionic mechanisms have been postulated by Morton[5] for the polymerization of butadiene by sodium alkyls and by Beaman[2] for the polymerization of methacrylonitrile by triphenylmethylsodium or Grignard reagents in ether. It seems likely that the reported polymerization of styrene by sodiomalonic ester[6] or triphenylmethylsodium[7] involves a similar mechanism.

We have been unable to effect the polymerization of styrene by sodium amide in ether. Apparently a more polar medium such as liquid ammonia is required. Also, styrene failed to be polymerized by sodioacetophenone or diethylaminomagnesium bromide in ether. Gilman and McGlumphy[8] have reported that styrene fails to be polymerized by benzylmagnesium chloride or triphenylmethylmagnesium chloride.

α-Methylstyrene and butadiene were not polymerized by sodium amide in liquid ammonia. An attempt to co-polymerize styrene and α-methylstyrene resulted in a low yield of polymer (m. p. 95–110°) having an average molecular weight of 1300, while a similar experiment with styrene and butadiene gave no polymer. These compounds apparently not only failed to enter into the polymerization but tended to inhibit polymerization of the styrene.

Experimental

Polymerization of Styrene by Sodium Amide.—In a typical experiment, sodium amide was prepared in the usual way by adding 8.9 g. (0.39 gram-atom) of sodium to 300 ml. of anhydrous ammonia in the presence of one or two crystals of ferric nitrate. When the amide formation was complete, as evidenced by the disappearance of the blue color and formation of a gray suspension, 40 g. (0.39 mole) of redistilled styrene was added rapidly. The reaction mixture was stirred four hours and the sodium amide neutralized by the careful addition of 25 g. of ammonium chloride. Then 200 ml. of ether was added and the reaction mixture poured carefully into 1 liter of water. The ether layer was separated and washed with two 100 ml. portions of water. On addition of an equal volume of methanol to the ether solution, the polystyrene precipitated as a sticky, white mass. The supernatant liquid cleared in about thirty minutes and was decanted and replaced by methanol. The tacky mass gradually changed to a white granular solid when stirred under the methanol and, after standing overnight, it was collected on a Buchner funnel, washed twice with methanol, and allowed to dry in air. The yield of polystyrene, melting over the range 130–170°, was 27 g. (68%). It gave a negative test for nitrogen by the sodium fusion method. The average molecular weight, estimated by the Staudinger viscosity method, as revised by Kemp and Peters,[9] was 3100.

The ether-methanol solution, decanted from the precipitated polystyrene, was distilled and the residue heated at 120° at 45 mm. for forty-five minutes to remove styrene and any traces of ammonia. The polymer was dissolved in a little ether and the solution evaporated on a watch glass. The low molecular weight polystyrene residue was a brownish, tacky material giving a strong positive test for nitrogen by the sodium fusion method.

Pyrolysis of Polymer.—Polystyrene (63 g., average molecular weight, 2900–3200), prepared using 5–10 mole per cent. of sodium amide, was heated above 360° for four hours in a flask equipped with a downward condenser leading to a receiver to which was attached a tube leading into a dilute hydrochloric acid trap. The main pyrolysis product (46 g.), which smelled strongly of amines, the vapors of which reacted basic toward moist litmus paper, was extracted with the dilute hydrochloric acid from the trap. The acid solution was evaporated to dryness on a steam-bath, yielding about 0.1 g. of flaky hydrochloride salt. The salt gave a strong positive test for nitrogen on sodium fusion and reacted with benzoyl chloride in alkaline solution to form an oily product which appeared to be a mixture.

The main pyrolysis products, on redistillation, boiled over the range of 40–150°, mostly at 140–150°, consisting mainly of styrene.

Summary

Styrene has been polymerized by sodium amide in liquid ammonia. The reaction was shown to be catalytic. An ionic mechanism is suggested. The polymerization failed in ether with sodium amide, sodioacetophenone and diethylaminomagnesium bromide. α-Methylstyrene and butadiene were not polymerized by sodium amide in liquid ammonia.

DURHAM, N. C. RECEIVED OCTOBER 30, 1948

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(4) The sodium fusion test apparently is not sensitive enough to detect the amount of nitrogen that would be present in polymer having a molecular weight of 3000. In this connection see Viehoever and Johns, THIS JOURNAL, **37**, 606 (1915).

(5) Morton, Patterson, Donovan and Little, *ibid.*, **68**, 93 (1946).

(6) Hermann and Vorlander, *Chem. Zentr.*, **70**, I, 730 (1899).

(7) Ziegler and Jakob, *Ann.*, **511**, 45 (1934).

(8) Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 421 (1928).

(9) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).