Picric Acid (by R. M.).—Phenylmercuric nitrate (5 g.) was added to 25 ml. of concentrated nitric acid and 12.5 ml. of water. The mixture was heated on a steam-bath for five hours, after which it was diluted, cooled and extracted with ether. Evaporation of the ether extract left crude yellow crystals, which were dissolved in water and recovered by a second extraction with ether. Evaporation of this extract and three recrystallizations from benzene gave crystals that melted at 120°, a little low, but otherwise were identical with a known sample. Tarry products, similar to those observed in the preparation of phenylmercuric nitrate, were present in the nitrating mixture.

Summary

Mercuric nitrate reacts readily with benzene, and if mercuric oxide and Drierite (calcium sulfate) are used in the mixture to prevent the secondary effects from nitric acid and water, and if air is excluded, the yields and quality of the phenylmercuric nitrate produced are very high.

Phenylmercuric nitrate is probably the intermediate when mercuric nitrate is used as a catalyst in nitration.

Mercuration appears to be a very rapid and easy reaction, probably faster under certain conditions than nitration.

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The Preparation of Polyvinylamine, Polyvinylamine Salts, and Related Nitrogenous Resins

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

Introduction

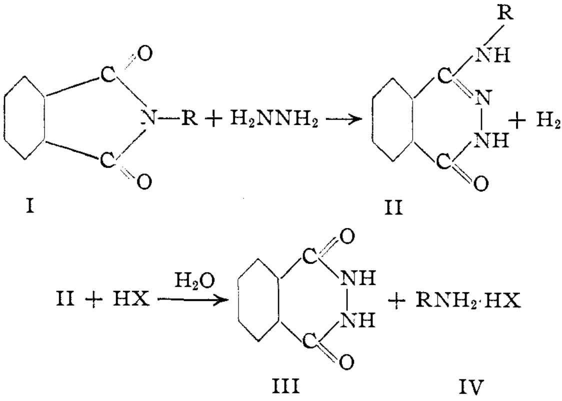
Polyvinylamine is not only of theoretical importance, but also of practical value, since it may be used as the starting material for the preparation of a variety of derived resins. Prior to the present work, a substantially pure polyvinylamine or its salts had not been prepared, though Hanford and Stevenson[1] isolated a polymer containing approximately 75% free amino groups and 25% incompletely hydrolyzed imide groups by hydrolysis of polyvinyl succinimide with concentrated hydrochloric acid at 700 pounds pressure and 180° for six hours.

After the work reported here had been completed, Jones, Zomlefer and Hawkins[2] published an account of their attempts to prepare polyvinylamine by a number of different methods. They state that "attempts at the hydrazine hydrolysis of polyvinyl phthalimide, hypobromite degradation of polyacrylamide and Beckmann rearrangement of polyvinyl methyl ketoxime did not meet with success." Their attempt to reduce polynitroethylene was also reported as unsuccessful.

The Gabriel synthesis[3] is often employed to produce primary amines but the conditions used are usually drastic, consisting in treating a substituted phthalimide with strong mineral acids or bases at relatively high temperatures, and often under pressure. These reaction conditions are not easy to carry out, especially on polymeric materials, and since the reactions are attended by side reactions, there is little hope of obtaining a pure polymeric product. In simple organic reactions, if even a small yield of the desired product is obtained it can be isolated and purified by distillation or crystallization. In polymer chemistry, these manipulations are not possible. To obtain a pure resin on a structural basis, the reaction must go to completion along the desired path; otherwise, residual or partially reacted groups will be a part of the molecule and cannot be physically removed therefrom. A number of attempts by us to prepare polyvinylamine by the usual technique of the Gabriel synthesis as well as the reported work of Hanford and Stevenson[1] have borne out these facts.

Such consideration led to the adoption of the hydrazine hydrolysis of polyvinyl phthalimide. Polyvinyl phthalimide was first treated with hydrazine hydrate to form a phthalhydrazide salt of polyvinylamine, as shown by VIII, from which phthalhydrazide and polyvinylamine hydrohalide were liberated. The latter was converted to polyvinylamine by treatment with alkali or to derived resins by reaction with the appropriate reagent. This method was used by Ing and Manske[4] for obtaining amines from simple non-polymeric nitrogen-substituted phthalimides. They often obtained nearly quantitative yields of the desired amine.

The supposed mechanism of the reaction is



$$\mathrm{IV} + \mathrm{NaOH} \longrightarrow \mathrm{RNH_2} + \mathrm{NaX} + \mathrm{H_2O}$$

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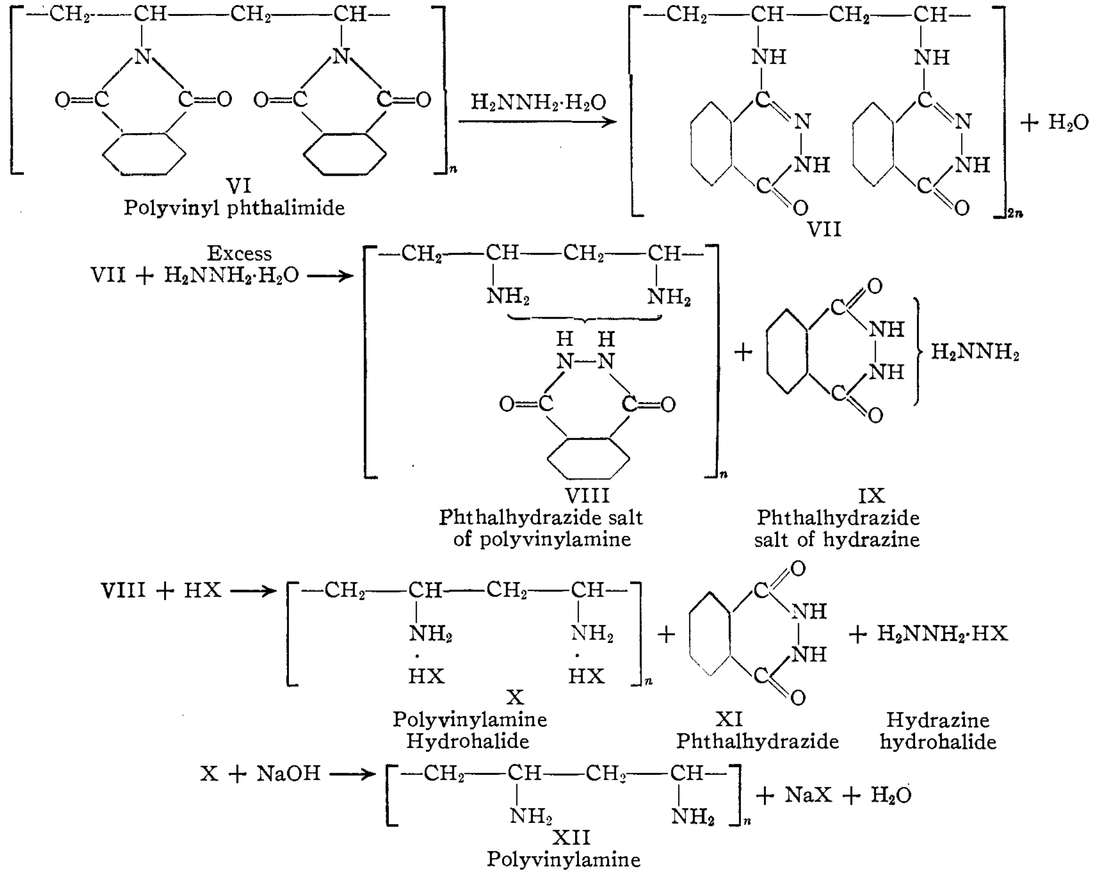
(1) Hanford and Stevenson, U. S. Patent 2,365,340.

(2) Jones, Zomlefer and Hawkins, *J. Org. Chem.*, **9**, 500 (1944).

(3) Gabriel, *Ber.*, **20**, 2224 (1887); **24**, 3104 (1891).

(4) Ing and Manske, *J. Chem. Soc.*, 2348 (1926).

The simple amines are prepared by treating compound I with a molal quantity of hydrazine hydrate in ethanol. Compound II, which separates as a crystalline product, can be hydrolyzed to yield the free amine. The reaction products are analogous with polymeric phthalimides. An excess of hydrazine was always used with the latter and the following differences in the intermediate reaction mechanism were encountered



VI
Polyvinyl phthalimide

VII

VIII
Phthalhydrazide salt of polyvinylamine

IX
Phthalhydrazide salt of hydrazine

X
Polyvinylamine Hydrohalide

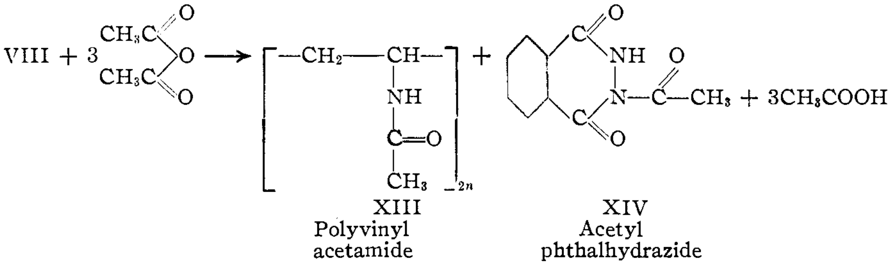
XI
Phthalhydrazide

Hydrazine hydrohalide

XII
Polyvinylamine

Phthalhydrazide (XI) has one active hydrogen, as illustrated by earlier investigators,[5] and thus may form salts. No attempts were made to isolate compound VII, but the phthalhydrazide salts of polyvinylamine (VIII) and of hydrazine (IX) were isolated and identified.

This reaction affords a direct method for preparing polyvinyl acetamide or other similar polyamide resins. The phthalhydrazide salt of polyvinylamine (VIII) reacts smoothly with acetic anhydride according to the equation (A) below. A very pure polyvinyl acetamide is obtained since the by-products of the reaction can easily be removed by solvent extraction. By using a mixture of acyl anhydrides copolymers containing different vinyl amide units are produced. These amide resins can also be prepared from polyvinylamine or from polyvinylamine salts in the presence of a base stronger than polyvinylamine.



(A)

XIII
Polyvinyl acetamide

XIV
Acetyl phthalhydrazide

During this investigation an improved method for preparing polyvinyl phthalamic acid was developed and is described here.

A number of resins derived from polyvinylamine are shown in the following structural formulas and their properties are described in the experimental section

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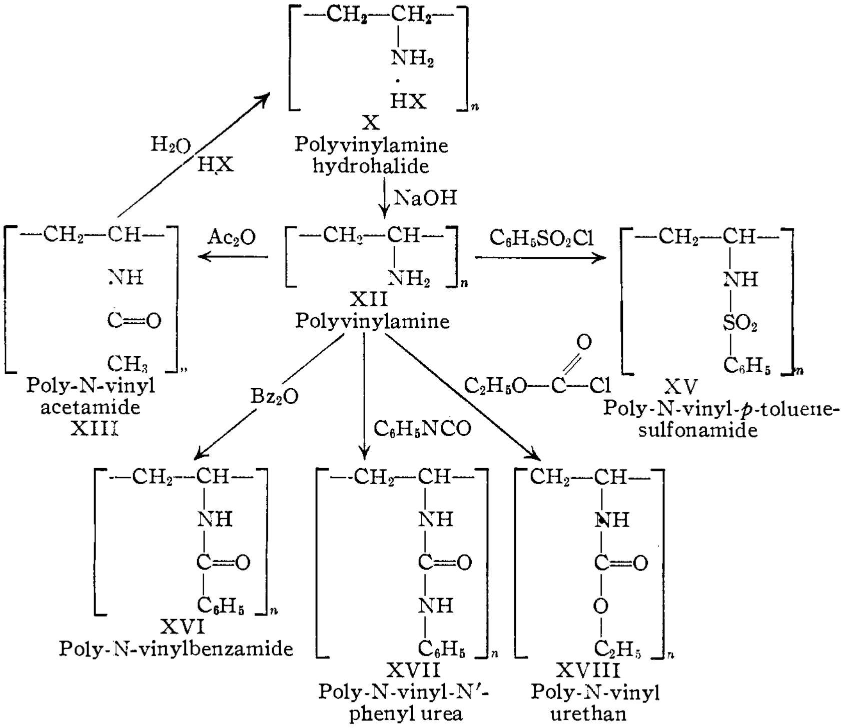
(5) Foersterling, *J. prakt. Chem.*, **51**, 371 (1895).



Experimental

N-Vinyl Phthalimide.—β-Acetoxyethyl phthalimide was pyrolyzed as described by Hanford and Stevenson.[1] In the present work a stainless steel pyrolysis tube packed with copper helices was used.

Polyvinyl Phthalimide (VI).—Three hundred grams of N-vinyl phthalimide and 1.5 g. of benzoyl peroxide were refluxed for forty hours in two liters of ethylene chloride–methanol (85/15 by volume). The clear viscous dope, diluted with additional ethylene chloride, was poured into ethanol, precipitating polyvinyl phthalimide as a white, brittle, fibrous material.

Anal. Calcd. for $C_{10}H_7O_2N$: N, 8.1. Found: N, 7.91.

Phthalhydrazide Salt of Polyvinylamine (VIII).—Polyvinyl phthalimide (100 g.) was refluxed for one hour with 150 cc. of 85% hydrazine hydrate. The mixture was cooled and poured into ethanol. The precipitated white fibrous resin was leached in ethanol and dried at 60°; yield, 69 g.

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: N, 22.58. Found: N, 22.15.

Isolation of Polyvinylamine Hydrohalides.—The isolation of polyvinylamine hydrochloride or hydrobromide can be performed by several methods, the essential difference lying in the methods used to remove excess hydrazine, the hydrazine resulting from compound IX and the phthalhydrazide liberated from compounds VIII and IX.

Polyvinylamine Hydrochloride.—The following separation is based on (a) the insolubility of the phthalhydrazide salt of polyvinylamine (VIII) in ethanol, (b) the salting-out of polyvinylamine hydrochloride by an excess of hydrochloric acid, (c) the low solubility of phthalhydrazide (XI) in water, and (d) the insolubility of polyvinylamine hydrochloride in methanol or ethanol as compared with the soluble hydrazine hydrochloride.

Forty-seven grams of VIII was refluxed with excess concentrated hydrochloric acid, and filtered. The residual mixture of polyvinylamine hydrochloride and phthalhydrazide was stirred with water and centrifuged to remove the latter. The supernatant liquid was poured into ethanol and the polyvinylamine hydrochloride which precipitated was purified by repeated extractions with methanol; yield, 18 g.

Anal. Calcd. for C_2H_6NCl: N, 17.6; Cl, 44.6. Found: N, 17.09; Cl, 41.53.

The proportion of amino nitrogen was calculated on the assumption that each amino group is present as a vinyl amine hydrohalide unit and hence each mole of halogen represents a mole of amino group. Application of this calculation to the sample indicated 16.38% by weight of amino nitrogen or approximately 95.8% of the nitrogen present as free amino groups and 4.2% present as incompletely hydrolyzed imide groups. The product appeared to be substantially polyvinylamine hydrochloride.

Polyvinylamine Hydrobromide.—Method A: The following preparation is similar to that for polyvinylamine hydrochloride, with the exception that most of the excess hydrazine was removed by steam-distillation.

Polyvinyl phthalimide (45 g.) was refluxed for eighteen hours with a mixture of water (100 cc.) and 85% hydrazine hydrate (100 cc.) and then steam-distilled, collecting four liters of distillate. Upon cooling, a resinous mass separated from the reaction mixture. The supernatant liquid was decanted, the resin dissolved in warm water, and poured into 48% hydrobromic acid. The precipitated solid obtained was separated and dispersed in water. The polyvinylamine hydrobromide and hydrazine hydrobromide dissolved, leaving phthalhydrazide which was removed by centrifuging and filtering. After concentration, the liquid was filtered and poured into methanol. The precipitated polyvinylamine hydrobromide was extracted with methanol to remove hydrazine hydrobromide.

Anal. Calcd. for C_2H_6NBr: N, 11.28; Br, 64.5. Found: N, 10.73; Br, 61.33.

Assuming that each bromine atom was combined with one free amino group, the bromine content was equivalent to 10.74% nitrogen. All the nitrogen in the polymer appeared as amino nitrogen and the product was substantially polyvinylamine hydrobromide. No nitrogenous impurity was present, because the nitrogen and bromine deviated from theory by the same amount, indicating residual methanol or moisture.

Method B: This separation is based on (a) the solubility of polyvinylamine and its phthalhydrazide salt in methanol, (b) the insolubility of the phthalhydrazide salt of hydrazine in methanol, and (c) the insolubility of the barium salt of phthalhydrazide in water.

Polyvinyl phthalimide (40 g.) was refluxed in a mixture of 85% hydrazine hydrate (80 cc.) and water (80 cc.), then concentrated under reduced pressure until the crystalline hydrazine salt of phthalhydrazide began to separate from solution. The mixture was cooled and methanol was added. The resin at this stage was subtantially polyvinylamine, which is soluble in methanol. The methanol-insoluble phthalhydrazide salt of hydrazine was removed by filtration and the filtrate distilled in a vacuum to remove the methanol. The residue was poured into a solution of 30 g. of barium hydroxide dissolved in warm water. Barium phthalhydrazide separated immediately and was removed by filtration. Upon cooling the filtrate, more barium phthalhydrazide crystallized. After filtration, carbon dioxide was passed into the filtrate to remove excess barium ion. Barium carbonate was separated, and, upon concentration of the filtrate in a vacuum, more barium carbonate separated and was removed by filtering. It was discovered at this point that a carbonic acid salt of polyvinylamine had formed which is stable even in boiling water. The filtrate containing the polyvinylamine salt was poured into concentrated hydrobromic acid. The precipitated polyvinylamine hydrobromide was separated, washed with methanol, and dried at 70°.

Anal. Calcd. for C_2H_6NBr: N, 11.28; Br, 64.5. Found: N, 11.42; Br, 61.12.

This indicates that 93.8% of the nitrogen is present in the form of amino nitrogen.

Polyvinylamine (XII).—Owing to the rapid absorption of carbon dioxide from the air, it is difficult to prepare a polyvinylamine free from its carbonic acid salt.

Thirty grams of polyvinylamine hydrochloride, dissolved in a solution containing 15 g. of sodium hydroxide in freshly distilled ethanol, was shaken in a glass-stoppered flask for twelve hours and the sodium chloride separated by filtration. The filtrate was concentrated by vacuum-distillation and precipitated in ether. The polyvinylamine thus obtained was dried in a vacuum over sodium hydroxide pellets.

Anal. Calcd. for C_2H_5N: N, 32.25. Found: N, 27.42; Cl, <1.

Qualitative tests showed the presence of some carbonate salt.

Poly-N-vinyl Acetamide (XIII).—Polyvinyl phthalimide (100 g.) was refluxed in 150 cc. of 85% hydrazine hydrate. The phthalimide dissolved completely and crystalline phthalhydrazide salt of hydrazine separated. Water was added and solution was completed by heating. The white, fibrous phthalhydrazide salt of polyvinylamine (VIII) was obtained by precipitation in ethanol. This polymer was leached in fresh ethanol and dried at 60°. The yield was 69 g. After this polymer had been ground to 40-mesh size, it was refluxed for forty-five minutes with acetic anhydride (180 cc.). Upon cooling, crystalline acetyl phthalhydrazide (XIV) separated from the solution. The mixture was poured into an excess of acetone. The acetyl phthalhydrazide dissolved and the precipitated polyvinyl acetamide was again extracted with acetone.

Anal. Calcd. for C_4H_7NO: N, 16.5; H, 8.24; C, 56.5. Found: N, 15.62; H, 8.12; C, 55.10.

Poly-N-vinyl Benzamide (XVI).—Polyvinylamine hydrobromide (20 g.) was dissolved in water (250 cc.) and mixed with sodium hydroxide (13 g.) dissolved in water (100 cc.). This solution was stirred while benzoyl chloride (25 g.) was slowly added. Polyvinyl benzamide separated from the solution. The reaction mixture was stirred for a total of three hours. The polyvinyl benzamide was separated from the solution, washed well with water, and dried. It was dissolved in methanol and precipitated in water. After drying at 60°, the resin was leached in dry acetone, and dried at 70°.

Anal. Calcd. for C_9H_9NO: N, 9.52. Found: N, 9.41.

Poly-N-vinyl *p*-Toluenesulfonamide (XV).—Polyvinylamine hydrochloride (25 g.) was stirred in dioxane (250 cc.) and *p*-toluenesulfonyl chloride (80 g.) was added while the reaction temperature was maintained below 25°. While this temperature was maintained, 4 *N* sodium hydroxide (250 cc.) was added drop-wise. The polyvinyl *p*-toluenesulfonamide which separated as a sticky mass was dissolved in an acetone-water mixture and precipitated in dilute hydrochloric acid. It was filtered, washed well with water, and finally extracted in a Soxhlet extractor with ethanol. The resin, dissolved in acetone containing a small amount of water, was precipitated in ethanol and dried at 70° in a vacuum.

Anal. Calcd. for $C_9H_{11}NSO_2$: N, 7.65; S, 17.4. Found: N, 7.74; S, 15.20.

Polyvinylamine Hydrochloride from Polyvinyl Acetamide.—Polyvinyl acetamide (6 g.) was refluxed with 6 *N* hydrochloric acid (100 cc.) for three hours. Polyvinylamine hydrochloride precipitated. It was separated, dissolved in water, and precipitated in ethanol to give a brittle, fibrous, straw-colored material which was leached in ethanol. It was redissolved in water, filtered and precipitated in acetone. This product was identical with the polyvinylamine hydrochloride obtained directly by the hydrazine reaction.

Polyvinylamine Hydrobromide from Polyvinyl Acetamide.—Polyvinyl acetamide (20 g.) was refluxed with 48% hydrobromic acid. The polyvinyl acetamide dissolved and then polyvinylamine hydrobromide separated. The reaction mixture was cooled, the supernatant liquid decanted, and the polyvinylamine hydrobromide was dissolved in water, filtered, precipitated in methanol, extracted with methanol and dried.

Anal. Calcd. for C_2H_6NBr: N, 11.28; Br, 64.5. Found: N, 11.42; Br, 57.10.

Poly-N-vinyl Urethan (XVIII).—Polyvinylamine hydrochloride (16 g.) was stirred in dioxane (150 cc.), while the temperature was maintained at 20°. Ethyl chlorocarbonate (48 g.) was added and 4 *N* sodium hydroxide (150 cc.) was added dropwise. After the sodium hydroxide had been added, stirring was discontinued. The soft gel of polyvinyl urethan which separated was stirred rapidly in water. It was dissolved in acetone and precipitated in water as a fibrous resin. After the resin had been leached in water, it was redissolved in acetone, again precipitated in water, and then dried at 70° in a vacuum.

Anal. Calcd. for $C_5H_9NO_2$: N, 12.1. Found: N, 12.2.

Poly-N-vinyl-N′-Phenyl Urea (XVII).—Polyvinylamine hydrobromide (12.4 g.) was dissolved in methanol (100 cc.) containing 4 g. of sodium hydroxide. Phenyl isocyanate (15 g.) was added. The reaction mixture became cloudy and heat was evolved. After the reaction mixture had been stirred for about ten minutes, the resin was separated by pouring the mixture into ether. It was then leached in ether and filtered. After the resin was leached for two days in distilled water, it was separated and dried, ground to a powder, extracted with methanol, and dried at 70°.

Anal. Calcd. for $C_9H_{10}NO_2$: N, 17.28. Found: N, 17.36.

Polyvinyl Phthalamic Acid.—Polyvinyl phthalimide was refluxed with 50 cc. of trimethylbenzylammonium hydroxide (*ca.* 40% aqueous solution) for twenty-three hours. This solution was poured into dilute hydrochloric acid and the precipitated polyvinyl phthalamic acid was

TABLE I

ANALYSIS OF POLYVINYLAMINE HYDROCHLORIDE AND HYDROBROMIDE

Calculated for C_2H_6NCl: Cl = 44.6% by weight, N = 17.6% by weight. Calculated for C_2H_6NBr: Br = 64.5% by weight; N = 11.28% by weight.

Found by analysis, %		Calculated, %	
Halogen	Nitrogen	Nitrogen from halogen analysis	% of total nitrogen combined as —NH_2
41.53[a]	17.09	16.38	95.8
40.80[a]	16.53	16.09	97.2
56.91[b]	10.90	9.97	91.4
61.33[b]	10.73	10.74	100.0
60.40[b]	11.30	10.58	93.7
59.64[b]	11.38	10.45	91.9
60.27[b]	11.34	10.57	93.2
62.79[b]	11.20	11.00	98.2
61.12[b]	11.42	10.71	93.8

[a] Halogen = chlorine. [b] Halogen = bromine.

washed free of chloride ion. It was further purified by dissolving in an acetone–water mixture, filtering, precipitating in water, drying at 70° and finally at 116°.

Anal. Calcd. for $C_{10}H_9NO_3$: 5.23 cc. N sodium hydroxide per gram; N, 7.32. 0.5310 g. dissolved in 50 cc. of pyridine plus 50 cc. of water required 4.8 cc. of 0.5501 N sodium hydroxide, *i. e.*, 4.98 cc. of N sodium hydroxide per gram. Found: N, 7.28.

Analysis of Polyvinylamine Salts.—Table I presents the analyses of a few samples of polyvinylamine hydrochloride and polyvinylamine hydrobromide. It illustrates the degree of hydrolysis of the cyclic imide group to amino group. Column 3 shows the percentage by weight of amino nitrogen calculated from the halogen values of Column 1. Column 4 represents the percentage of the total nitrogen content which was present in the form of amino groups.

TABLE II

	Water	Methanol	Ethanol	Acetone	Dioxane	Acetic acid	Pyridine	Dioxane + H_2O	Acetone + H_2O	10% NaOH
Polyvinylamine	+	+	+	−	0	+	0	0	0	0
Polyvinylamine hydrochloride	+	−	−	−	−	−	−	+	+	+
Polyvinylamine hydrobromide	+	−	−	−	−	−	−	+	+	+
Polyvinyl acetamide	+	+	+	−	−	+	±	+	+	+
Polyvinyl benzamide	−	+	+	−	−	+	+	+	+	−
Poly-N-vinyl urethan	−	+	+	+	−	+	+	+	+	−
Poly-N-vinyl-N′-phenylurea	−	−	−	−	−	+	±	+	+	−
Poly-N-vinyl-*p*-toluenesulfonamide	−	−	−	−	±	−	+	+	+	−
Polyvinyl phthalamic acid	−	−	−	−	−	−	−	−	−	+

Legend: +, soluble; −, insoluble; ±, swells; 0, not tested.

Solubility Table.—Table II lists some of the solubility properties at room temperature of the polymers described in this paper.

Summary

1. Polyvinyl phthalimide was treated with hydrazine to yield a polymer which is believed to be the hydrazine salt of polyvinylamine.

2. Reaction of the latter with acetic anhydride produced polyvinyl acetamide, whereas treatment with hydrohalide acids yielded polyvinylamine salts which were converted by alkalies to the free polymeric base.

3. The following related nitrogenous resins were prepared and characterized: polyvinylamine hydrochloride, polyvinylamine hydrobromide, poly-N-vinyl benzamide, poly-N-phenyl-*p*-toluenesulfonamide, poly-N-vinyl urethan, poly-N-vinylurea.

4. Polyvinylamine was found to be a relatively strong base forming stable carbonic acid salts.

ROCHESTER, N. Y.

RECEIVED JANUARY 2, 1947

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY OF THE UNIVERSITY OF MINNESOTA AND THE ABBOTT LABORATORIES]

The Controlled Sodium Amalgam Reduction of Aldonolactones and their Esters to Aldoses and an Improved Synthesis of D-Arabinose[1]

BY NATHAN SPERBER,[2,3] HAROLD E. ZAUGG[4] AND W. M. SANDSTROM

The sodium amalgam reduction of aldonolactones to aldoses, one of the most important reactions in carbohydrate chemistry, was discovered by Emil Fischer[5] in the course of his studies on the synthesis and structure proof of the aldoses. Fischer and Piloty[6] synthesized aldoses from the corresponding lactones by reduction with sodium amalgam and dilute sulfuric acid, for example, L-ribose from L-ribonolactone. Fischer[5,7] applied the cyanohydrin reaction to an aldose, obtained the next higher pair of epimeric acids which as lactones were reduced to the aldoses with sodium amalgam. Nef and co-workers[8] described a method whereby an aldose in the presence of air and a strong base could be degraded one carbon atom to the salt of the lower aldonic acid. Hudson and Chernoff[9] employed the Nef procedure to prepare rhamnotetronic lactone from rhamnose. Spengler and Pfannenstiehl,[10] substituted oxygen for air in the Nef degradation and secured a 75% yield of potassium arabonate in the oxidation of glucose, as compared with the published yield of 36%. Isbell[11] prepared a number of aldonolactones by this method and Richtmyer, Hann and Hudson[12] have used this procedure in the degradation of perseulose and sedoheptulose.

A survey of the literature revealed that, although the procedure for the sodium amalgam reduction has been indicated broadly by Fischer and subsequent investigators, the conditions for securing maximum and reproducible yields are not as precise as is possible from modern methods of study. For example, Fischer[5] described the reduction of a lactone with a 10–15-fold quantity

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(1) Paper No. 2297, Scientific Journal Series, Minnesota Agricultural Experiment Station.

(2) Abstracted from a thesis by Nathan Sperber, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, March, 1945.

(3) Present address: Schering Corporation, Bloomfield, New Jersey.

(4) Abbott Laboratories, North Chicago, Illinois.

(5) Fischer, *Ber.*, **22**, 2204 (1889); *ibid.*, **23**, 930 (1890).

(6) Fischer and Piloty, *ibid.*, **24**, 4214 (1891).

(7) Fischer, *ibid.*, **23**, 2611 (1890).

(8) Nef, Hedenburg and Glattfeld, THIS JOURNAL, **39**, 1638 (1917); Glattfeld, *Am. Chem. J.*, **50**, 135 (1913).

(9) Hudson and Chernoff, THIS JOURNAL, **40**, 1005 (1918).

(10) Spengler and Pfannenstiehl, *Z. Wirtschaftsgruppe Zuckerind, Tech. Tl.*, **85**, 546 (1935); German Patent 618,164 (1935).

(11) Isbell, *J. Research Natl. Bur. Standards*, **29**, 227 (1942).

(12) Richtmyer, Hann and Hudson, THIS JOURNAL, **61**, 340, 343 (1939).