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The Preparation and Properties of Polyamines Prepared by the Reduction of Poly(4-vinylpyridine)

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ABSTRACT

Poly(4-vinylpyridine), both as a linear polymer and as a cross-linked resin was quaternized with methyl iodide (I, II) and reduced with sodium borohydride to poly(4-vinyltetrahydropyridine) (III, IV). The remaining double bonds in III or IV were inert to catalytic hydrogenation and to reduction with diborane or diimide. Catalytic hydrogenation of linear poly(4-vinylpyridine), quaternized with methyl iodide (I), gave irreproducible results; however, the fully saturated linear poly(4-vinylpiperidine) (V) was obtained in one experiment. Polyamine resins were also prepared by reacting dibromohexane with tetramethylene diamine (VI) and by reacting epichlorohydrin with tetramethylenediamine (VII). The suitability of all these polyamines as the amine component in thermally regenerable resin systems was examined. The polyamines III, IV, VI, and VII oxidized faster than polystyrene-based polyamines whereas V oxidized much more slowly. The amine capacities were all greater than polystyrene-based polyamines and were at least equal to those of poly(alkyldiallylamine)s.

INTRODUCTION

The polyamine is the major partner in the composite of basic and acidic polymers which make up thermally regenerable (Sirotherm) resins, in that it dictates the magnitude of the salt uptake after thermal regeneration [1]. ("Sirotherm" is an ICI Australia Limited trademark for thermally regenerable ion-exchange resins and associated plant.) In the early Sirotherm resins the polyamine half of the resins was based on polystyrene. Greater thermally regenerable capacities were achieved by changing to poly(alkyldiallylamine) resins since such resins have higher amine capacities.

The preferred polyamine is one which has a high concentration of amino groups (high amine capacity), gives a flat titration curve (i.e., exhibits a plateau), and is resistant to oxidation. Several factors contribute to the shape of the titration curve. For a plateau, the polyamine should be homofunctional, preferably a tertiary amine, and the polymer backbone should be nonpolar. The best polyamines which have been found so far to meet these requirements are poly(alkyldiallylamine)s [2]. There are other polyamines which could be suitable for use in the Sirotherm resin systems, and those derived from the reduction of poly(vinylpyridine) are discussed in this paper. Resins formed by the reaction of dibromohexane and tetramethylenediamine, and epichlorohydrin and tetramethylenediamine, are also discussed.

RESULTS AND DISCUSSION

Preparation of Polyamines from Poly(4-vinylpyridine) by Catalytic Hydrogenation

Poly(4-vinylpyridine) (PVP) was prepared from 4-vinylpyridine using 2,2'-azobisisobutyronitrile as initiator in toluene. The polymer was purified by Soxhlet extraction with hexane. The molecular weight in ethanol at 25°C was about 220,000 as measured viscometrically and calculated from the expression:

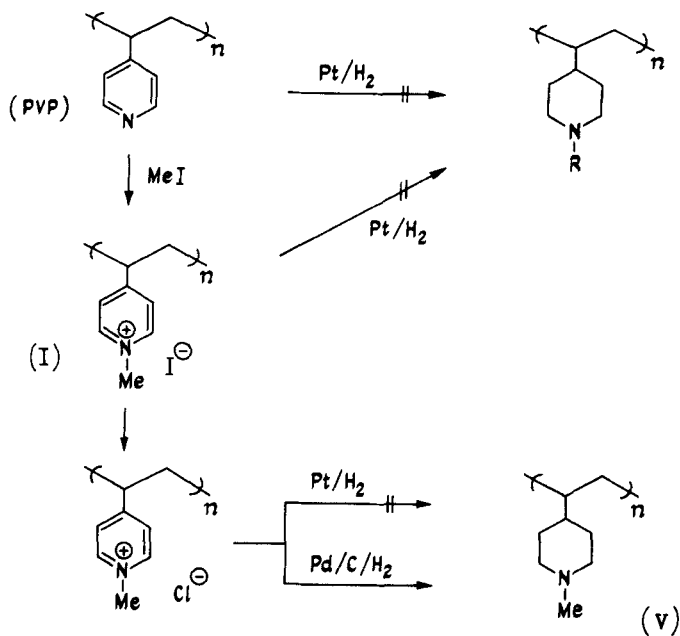
$$[\eta] = 25 \times 10^{-3} \underline{M}^{0.68} \quad [3]$$

The molecular weight distribution is probably quite large since about 20% of the PVP passed through dialysis tubing. Normally, dialysis tubing is not permeable to polymers of molecular weight greater than about 10^4 .

Although pyridine poisons most hydrogenation catalysts, hydrogenation of pyridine in acid media occurs readily [4, 5]. However, attempts to reduce PVP in hydrochloric acid or glacial acetic acid

over platinum at 3100 kPa and 20°C failed. PVP has been reduced in glacial acetic acid under the much more vigorous conditions of 24,100 kPa at 250°C for 20 h over Pd/C but under such conditions the molecular weight is reduced to about one-third of the parent PVP [6]. Similarly, although pyridine is readily reduced with sodium and ethanol [7], attempts to reduce PVP using similar conditions were unsuccessful and the PVP was recovered unchanged.

The final preferred polymer is a tertiary amine, and quaternized pyridines are usually easy to reduce to tertiary amines [5]. Thus PVP was quaternized with methyl iodide in ethanol or nitromethane [8, 9]. The best degree of quaternization of PVP was about 90% when nitromethane was used as the solvent. No reduction occurred when this quaternized sample I (Scheme 1) in HCl was shaken over Pt



SCHEME 1. Catalytic reduction of poly(4-vinylpyridine).

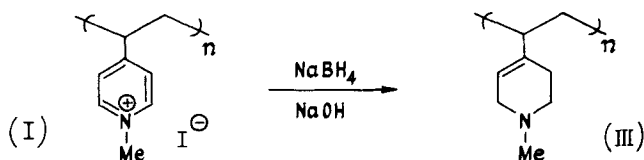
at a hydrogen pressure of 4000 kPa and 70°C. The iodide ion is not responsible for this failure since no hydrogenation occurred after I was converted to the chloride form and then heated at 110°C and 4100 kPa over Pt.

In one experiment I in the chloride form was successfully hydrogenated to give V (Scheme 1) by shaking with a large amount of 5% Pd on carbon and heating at 150°C and 3400 kPa for 15 h. The ¹³C NMR,

proton NMR, and IR spectrum confirmed that full reduction had been achieved. However, many attempts to repeat this experiment failed. In all subsequent experiments at least one of several undesired things occurred. Sometimes a product was obtained in which about 60% of the pyridine rings had been reduced and the remainder were unchanged. On other occasions some of the Pd remained strongly complexed to the polymer, and since it could not be removed, it was not possible to obtain satisfactory NMR spectra. In one case NMR spectra suggested that although hydrogenation appeared complete, it had been accompanied by demethylation of the N-methyl groups. This approach is therefore not straightforward and would require more work in order to achieve consistent reduction without other undesired reactions.

Preparation of Polyamines from Poly(4-vinylpyridine) by Sodium Borohydride Reduction

When I was heated at 50°C for several hours with an alkaline sodium borohydride solution a polymer III (Scheme 2) was obtained



SCHEME 2. Sodium borohydride reduction of quaternized poly(4-vinylpyridine).

which was soluble in chloroform, ethanol, methanol, and dilute hydrochloric acid. NMR spectral and titration data, which are discussed below, indicated that III is the tetrahydro compound shown in Scheme 2. This is directly analogous to the results obtained on the sodium borohydride reduction of quaternized pyridine derivatives [10].

Surprisingly, attempts to reduce the double bonds in III by catalytic hydrogenation in acetic acid or HCl over Pt/H₂ at atmospheric pressure failed. Attempted reduction over Pd/carbon under the more vigorous conditions of 135°C and 4100 kPa for 10 h on one occasion gave a product for which no NMR spectrum could be obtained, due presumably to complexing of the polyamine with Pd. On another occasion only a poor spectrum could be obtained, and this indicated that both hydrogenation of the double bond and also demethylation of the N-methyl group had occurred. The titration curve (Fig. 1) for the product from one reaction indicated that it had a capacity of 4.2 meq/g and a pH at half-neutralization (pH_{1/2}) of 4.2. No satisfactory structure can be proposed for a product with these properties.

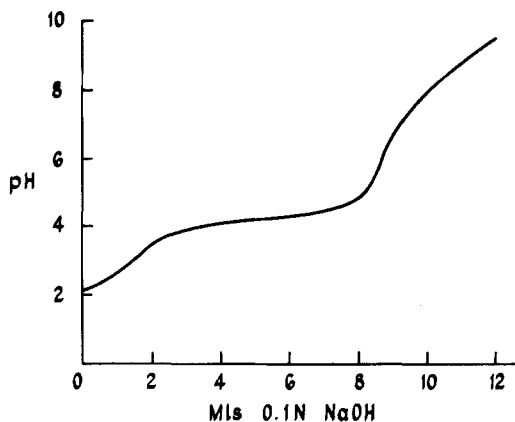


FIG. 1. Titration curve of the product (0.2 g) from an attempted hydrogenation of III over Pd/C.

An attempt to reduce the residual double bonds in III using diimide in methanol at 90°C for 1 d also failed [11].

Poly(vinylpyridine) cross-linked with 2.5 wt% divinylbenzene was prepared using methods described in the literature [12] and was freed of monomers by extraction with ethanol. It was then quaternized with methyl iodide to form II which is the cross-linked version of I. Since difficulty was experienced in attempting catalytic hydrogenation of the linear versions of these polymers (both quaternized and non-quaternized), catalytic methods of reduction for the cross-linked polymer were not tried.

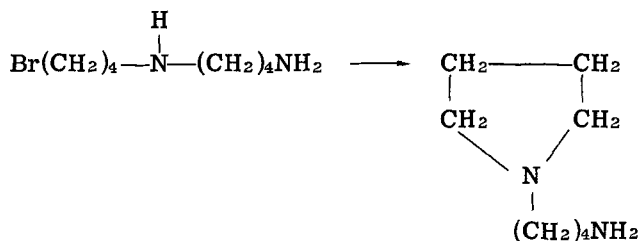
The sodium borohydride reduction of II proceeded readily to give the tetrahydropyridine derivative IV (which is the cross-linked version of III).

Attempts to remove the residual double bond in the sodium borohydride reduced product IV using diborane were unsuccessful with some unsaturation always remaining. Furthermore, the amine capacity (Fig. 4) was always less than that of the starting material because of the strong complex formed between the amine and diborane.

Preparation of Other Polyamines

Two other polyamines were prepared by the following procedures.

The reaction between dibromobutane (0.1 mol) and tetramethylenediamine (0.1 mol) in dimethylsulfoxide at 80°C failed to yield any cross-linked polymer which may be explained by assuming that five-membered rings are formed [13] rather than cross-links:



On the other hand, dibromohexane (0.1 mol) reacted vigorously with tetramethylenediamine (0.1 mol) in water at 100°C to give a 25% yield of a cross-linked resin VI. In this case cyclization is less favorable and therefore some cross-linking can occur. The resin contained primary, secondary, tertiary, and quaternary amino groups.

Another lightly cross-linked polyamine VII was prepared by reacting tetramethylenediamine (0.1 mol) with epichlorohydrin (0.1 mol) in water at room temperature with cooling for 1 h and then heating at 80°C overnight. The yield of cross-linked resin was 60%.

Properties of Polyamines

The titration curves for VI and VII are shown in Fig. 2 and their properties summarized in Table 1. The titration curves for both of these resins are too sloping to be suitable as Sirotherm resins although the amine capacities of 11.2 meq/g for VII and 7.0 meq/g for VI are good. The rate of oxidation of VI is almost twice as fast as that of cross-linked poly(propyldiallylamine) (PPrDAA).

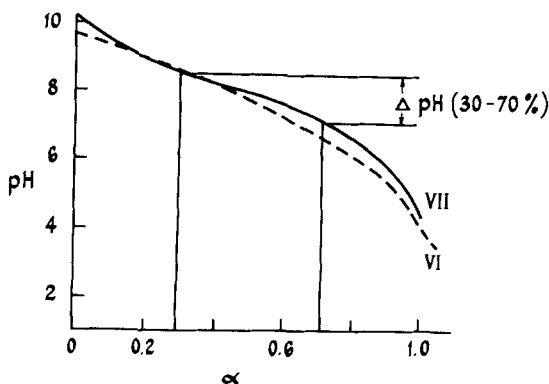


FIG. 2. Titration curves for resins prepared by the reaction between dibromohexane and tetramethylenediamine (VI) and epichlorohydrin and tetramethylenediamine (VII).

TABLE 1. Properties of Some Polyamines

Polyamine	pH _{1/2} ^a	pH (30-70%)	Capacity (meq/g)	Capacity loss (%/d) ^d (α)
Polystyrene 1 ^b	6.1	0.4	4.10	0.2
Polystyrene 2 ^c	5.3	2.0	6.20	2.2
Cross-linked poly- (propyldiallylamine)	8.2	0.1	6.75	4.0 (0 or 0.2)
VI	7.8	2.0	7.0	7.5
VII	7.9	1.6	11.2	1.0
III	8.5	0.8	6.5	0.0 (0.4) 1.2 (0.2)
IV	7.4	0.9	6.5	4.0
V	8.8	1.1	7.4	0.0

^apH_{1/2} = pH at half neutralization. Polyamines were titrated in water; titration curves for cross-linked resins were measured in 1100 mg NaCl/L.

^bPolystyrene 1 contained all -NEt₂ groups.

^cPolystyrene 2 contained a mixture of primary, secondary, and tertiary amino groups.

^dOxidized at 80° in a stream of oxygen. α = degree of protonation of the sample during the oxidation. α was always 0.0 unless otherwise indicated.

The titration curves for the soluble polymers III and V are shown in Fig. 3 and the properties summarized in Table 1. Titration curves for cross-linked resins are shown in Fig. 4 and some of their properties are also summarized in Table 1. The pH_{1/2} values for all the polyamines are in accord with the proposed structures. The amine capacities of all of these polyamines or resins are as good as, or better than, PPrDAA and better than aminated polystyrene. However, the slopes (Δ pH) are generally higher than required for good performance in a Sirotherm system. Although the linear tetrahydro polymer III oxidizes less readily than poly(propyldiallylamine), the cross-linked tetrahydro polymer IV oxidizes just as readily as cross-linked poly(propyldiallylamine). This still contains a double bond which may facilitate the oxidation. The double bond in IV is much less reactive with bisulfite than is the double bond in poly(triallylamine). Under conditions which result in 100% reaction with poly(triallylamine) [14], only 15% reaction occurred with IV. Polymer III when left in the free base form gelled after several weeks, as does poly(methyldiallylamine) [15].

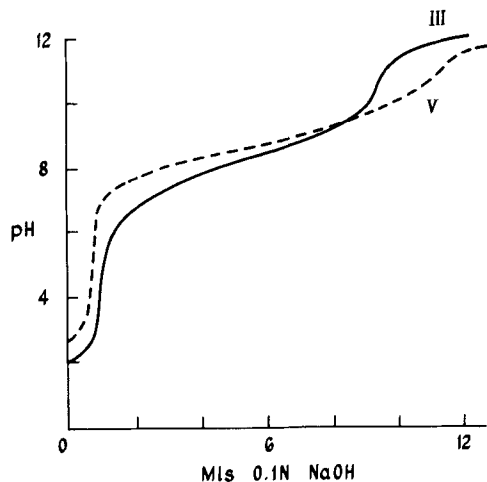


FIG. 3. Titration curves for the polyamines III (0.15 g) and V (0.20 g).

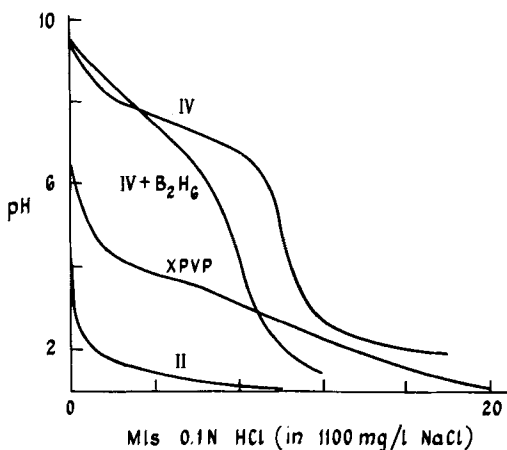


FIG. 4. Titration curves for cross-linked poly(vinylpyridine) (XPVP), quaternized XPVP (II), IV, and IV after treatment with diborane (IV + B₂H₆). 0.16 g of sample was used for each point.

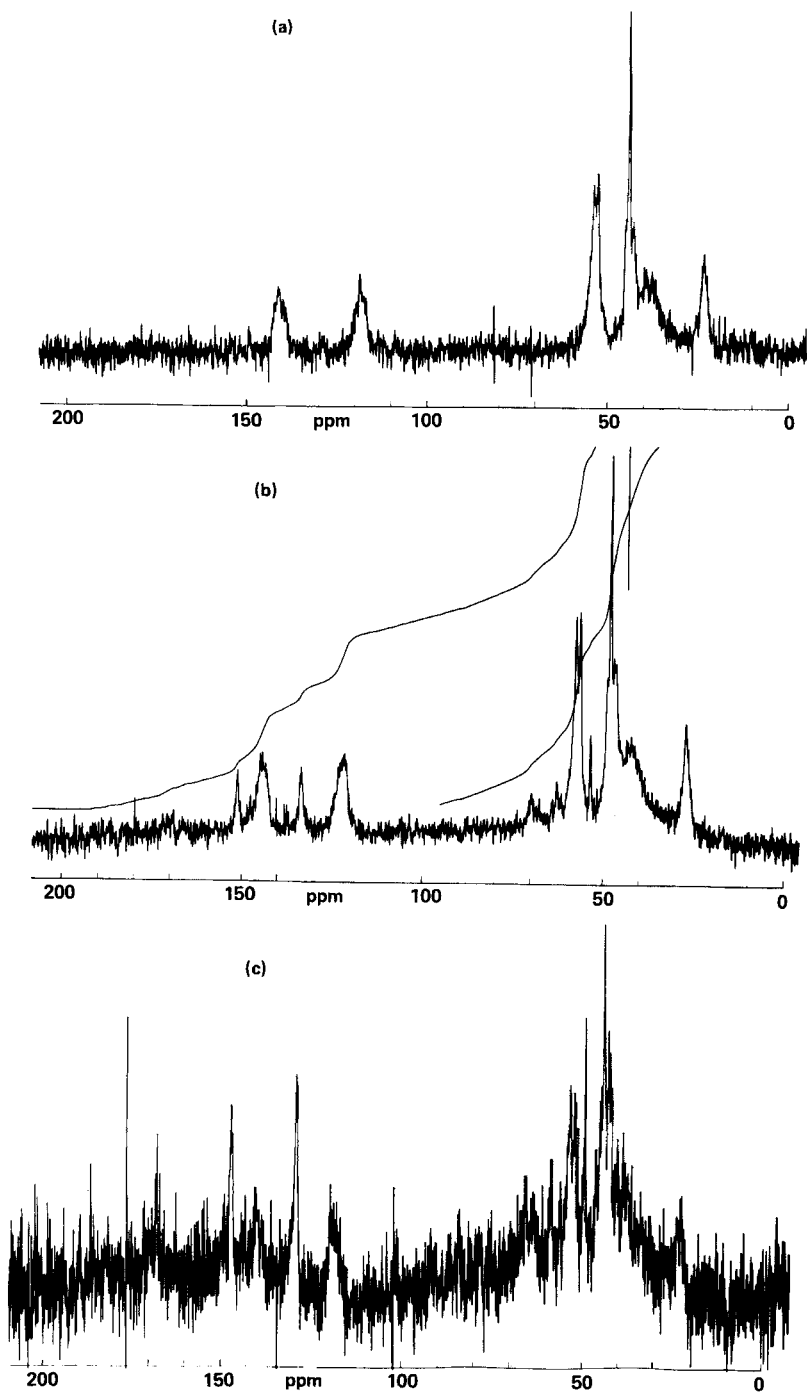


FIG. 5. ^{13}C NMR spectra of III as the hydrochloride in D_2O : (a) before oxidation; (b) after oxidation at 80°C for 5 d with the degree of protonation $\alpha = 0.4$; (c) after oxidation at 80° for an extended time with $\alpha = 0.2$ (the polyamine was now a solid gel).

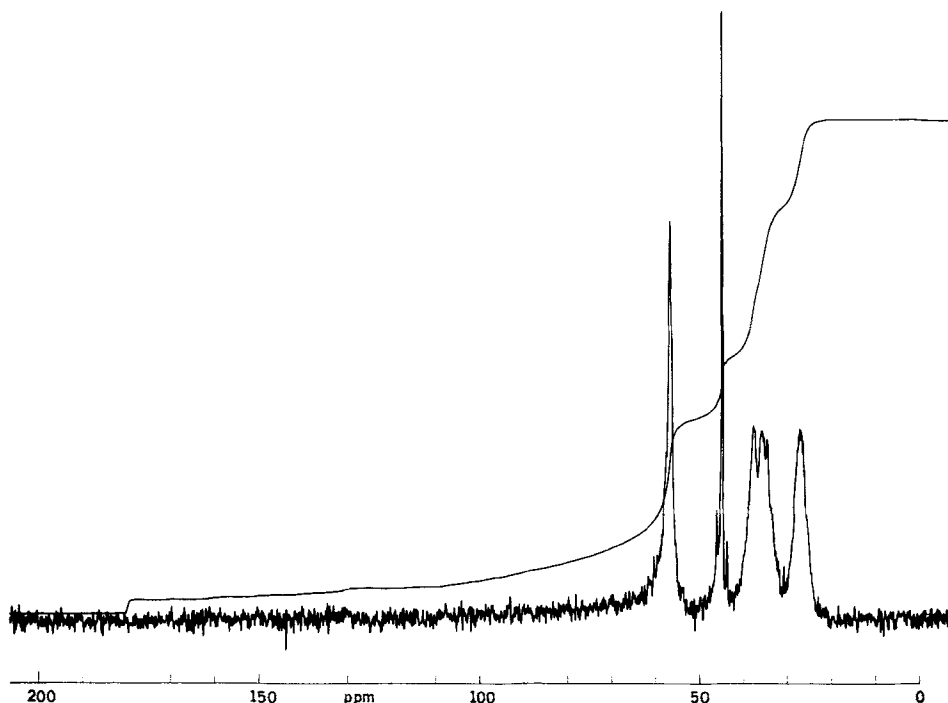


FIG. 6. ^{13}C NMR spectra of V as the hydrochloride in D_2O both before oxidation and after oxidation at 80°C for 10 d with the degree of protonation $\alpha = 0.2$.

Figure 5(a) shows the ^{13}C NMR spectrum of the linear polymer III before oxidation. The signals at 119 and 143 ppm are those due to the double bond. After oxidation for 5 d with 40% of the amino groups protonated (i.e., the degree of protonation $\alpha = 0.4$), two new peaks appeared in the olefinic region. No change in the amine capacity was found after this amount of oxidation. These peaks increased still further by the time the resin had oxidized sufficiently, at $\alpha = 0.2$, to form a gel. More work would be needed to interpret further these results but it seems that the ^{13}C NMR spectra are detecting changes in the polymer structure before changes in base capacity become evident.

The poly(vinylpyridine) V is not oxidized even after 10 d as judged by no change in amine capacity and no change in the ^{13}C NMR spectra (Fig. 6). The ^{13}C NMR spectrum shown in Fig. 6 confirms the fully saturated structure of V.

ACKNOWLEDGMENTS

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