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## Preparation and Hydrolytic Stability of Cross-Linked Poly(4-vinylpyridine)-Borane

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### ABSTRACT

Cross-linked poly(4-vinylpyridine) was converted to its borane complex by different methods. The exchange reaction with  $\text{BH}_3$ -THF; the reaction of boron trifluoride iodine, and bromine polymer complexes; as well as the hydrochloride derivative with sodium borohydride were investigated. Polymers with a high borane content were obtained. The borane content was dependent on the cross-linking level and on the method of preparation. The hydrolytic stability of the borane-bound polymer was higher than that of pyridine-borane. The cross-linked poly(4-vinylpyridine)-borane showed a high degree of stability toward hydrolysis under acidic conditions. Hydrolysis in acidic media was found to be an autoaccelerated reaction.

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## INTRODUCTION

In the last decade there is a growing interest in the preparation and use of polymeric amine boranes as polymeric reagents. Poly-ethylenimine borane was suggested by Wade [1] as a reductive bleaching and stabilizing agent for cellulose and clay. Commercially available polymer-bound amine boranes are available under the name of Amborane. These polymers are recommended for recovery of precious metals [2] and can also be used for the reduction of aldehydes, ketones, and olefines [3]. Attempts to use chiral polymeric amine borane, poly(imino-1-isobutylene)-borane and poly[1,2-bis(4-vinylphenyl ethyl amine)]-borane, for asymmetric reduction of ketones was reported in the literature [4]. The use of poly(vinylpyridine)-borane for reduction of carbonyl compounds was investigated in different laboratories [5-7]. Linear and cross-linked copolymers of 4-vinylpyridine-borane were prepared and used as reducing reagents toward various aldehydes and ketones. Poly(2-vinylpyridine)-borane and partially quaternized poly(4-vinylpyridine)-borane were used successfully by Menger et al. [7] for the reduction of carbonyl compounds.

Poly(vinylpyridine)-borane can be prepared by an exchange reaction with the borane complex of tetrahydrofuran [6] or dimethyl sulfide [7]. The use of these water-sensitive and highly reactive borane complexes can be avoided. Poly(4-vinylpyridine)-borane was prepared by reaction of its hydrochloride derivative with sodium borohydride in water or in DMF [5].

Borane complexes can be prepared from diborane which is conveniently generated by reaction of boron trifluoride etherate with sodium borohydride [8]. Similarly, generation of borane by the reaction of sodium borohydride with iodine in the presence of amine was used for the preparation of low molecular weight amine boranes [9]. The use of halogen as well as boron trifluoride complexes of polymeric amines such as poly(4-vinylpyridine) for the preparation of the corresponding polymer-borane complex by reaction with sodium borohydride was not reported in the literature.

Polymeric amine boranes are relatively stable and are sometimes more stable than their low molecular weight analog [4]. Such polymers show a high degree of stability toward hydrolysis under strong acidic conditions [2]. Cross-linking of poly(vinylpyridine) is essential for its use as a polymeric reagent. Electron donor properties and complexing characteristics of poly(4-vinylpyridine) are affected by the extent of cross-linking [10, 11]. In the present work, complexation of borane by poly(4-vinylpyridine) of different cross-linking levels was investigated. Poly(4-vinylpyridine)-borane was prepared by the already-reported methods as well as by reaction of iodine, bromine, and boron trifluoride poly(4-vinylpyridine) complexes with sodium borohydride.

Hydrolytic stability of poly(4-vinylpyridine)-borane is important when such a polymer is used in aqueous and acidic media. The influence of the cross-linking level on its hydrolytic stability was also investigated.

## EXPERIMENTAL

Materials

Divinylbenzene (technical, 55%) in ethylvinylbenzene and 4-vinylpyridine (Fluka) were distilled before use. Borane-tetrahydrofuran complex in a 1 M solution in tetrahydrofuran (Aldrich), sodium borohydride (Bayer), and boron trifluoride etherate (Aldrich) were used. Dimethylformamide (BDH) was dried over molecular sieve type 4A. Tetrahydrofuran (Frutarom) was dried by distillation from sodium benzophenone solution. Pyridine-borane was prepared according to a known procedure [12]. Buffer solutions were prepared according to the literature [13].

Cross-Linked Poly(4-vinylpyridine)

4-Vinylpyridine (20.0 g, 0.190 mol) and divinylbenzene (2.5 g, 0.019 mol) were polymerized by azobisisobutyronitrile (0.2 g) in toluene at 80°C for 18 h. The cross-linked polymer was isolated by filtration. In order to remove any homopolymer formed and unreacted monomer, the polymer was washed with methanol and water, slurried in 2 N hydrochloric acid (100 mL), and washed again with water. The polymer was neutralized by 2 N sodium hydroxide solution and was dried in vacuum at 80°C for 18 h over P<sub>2</sub>O<sub>5</sub>; 19.0 g of cross-linked polymer was obtained. Cross-linked polymer analysis: C, 81.40; H, 6.93; N, 11.67% corresponds to a 12.5% cross-linking level as calculated from nitrogen analysis.

When different amounts of divinylbenzene (5.0 and 7.5 g) were used, cross-linked polymer analysis was C, 82.66; H, 7.00; N, 10.34% and C, 84.10; H, 7.27; N, 8.63%, corresponding to 22.5 and 35.0% cross-linking levels, respectively.

Determination of Borane Content

Borane content was determined according to a known procedure [14] by volumetric determination of the hydrogen released on hydrolysis of the borane-bound polymer in concentrated hydrochloric acid.

Reaction of Cross-Linked Poly(4-vinylpyridine) with BH<sub>3</sub> - THF

In a typical procedure, 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) previously dried in vacuum over P<sub>2</sub>O<sub>5</sub> at 50°C for 24 h was allowed to react under nitrogen at room temperature with 1 M BH<sub>3</sub> -

THF solution in THF (17 mL). The polymer was kept under constant stirring for 30 min, filtered, and washed with hexane and methanol. The polymer was dried at 50°C in vacuum for 1 h. Homopoly(4-vinylpyridine)-borane was prepared similarly using poly(4-vinylpyridine) (1.0 g) solution in THF (10 mL).

#### Cross-Linked Poly(4-vinylpyridine)-Boron Trifluoride

In a typical procedure, 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) which was previously dried as described above was allowed to react with 2 N boron trifluoride etherate solution in ether (7 mL). The reaction was carried out at room temperature under constant stirring. After 20 h the polymer was filtered under dry atmosphere, washed with dry ether, and dried in vacuum at room temperature for 24 h. Boron trifluoride content (5.21 mmol/g) was determined after hydrolysis by titration according to a known procedure [15].

#### Cross-Linked Poly(4-vinylpyridine)-Halogen

In a typical procedure, 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with 0.1 N solution of iodine or bromine (100 mL). After 1 h under constant stirring at room temperature, the polymer was filtered, washed with water, and dried over P<sub>2</sub>O<sub>5</sub> at room temperature for 20 h. The iodine content (2.87 mmol/g) was determined by titration with sodium thiosulfate solution. The bromine content (3.50 mmol/g) was determined similarly after addition of an excess of potassium iodide.

#### Cross-Linked Poly(4-vinylpyridine) Hydrochloride

In a typical procedure, 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react at room temperature with 3 N HCl solution (10 mL) under constant stirring for 1 h. The polymer was filtered, washed with water and acetone, and dried over P<sub>2</sub>O<sub>5</sub>. The polymer hydrochloride content 6.14 mmol/g was determined by titration with 0.1 N sodium hydroxide solution.

#### Reaction of Cross-Linked Poly(4-vinylpyridine)-Halogen, Boron Trifluoride, and Hydrochloride with Sodium Borohydride

Cross-linked poly(4-vinylpyridine)-halogen, boron trifluoride, and hydrochloride derivatives (5 mmol) were allowed to react with 2.5 M sodium borohydride solution in water or in DMF (6 mL) at room tem-

perature. The reaction mixture was kept for 1 h under constant stirring. The polymer was filtered, slurried, washed with methanol, and dried in vacuum at 50°C for 1 h. The reaction with cross-linked poly(4-vinylpyridine)-BF<sub>3</sub> with sodium borohydride was carried out in dry DMF.

When uncross-linked polymer hydrochloride derivative was prepared, poly(4-vinylpyridine) was allowed to react in water at 5°C. The polymer-borane was isolated by filtration after 3 h.

## RESULTS AND DISCUSSION

Cross-linked poly(4-vinylpyridine) was prepared by copolymerization of 4-vinylpyridine and divinylbenzene. Copolymers of different divinylbenzene content were prepared. The cross-linking level was determined from nitrogen analysis of the polymers.

### Reaction of Cross-Linked Poly(4-vinylpyridine) with BH<sub>3</sub>-THF

The exchange reaction between BH<sub>3</sub>-THF and cross-linked polymer is a fast reaction. Complexation of 12.5% cross-linked polymer at 0°C in the presence of a molar excess of 1 M BH<sub>3</sub>-THF solution was completed within 1 min. Cross-linked poly(4-vinylpyridine)-borane of 7.2 mmol/g borane content was obtained. This value corresponds to complexation of 95% of the pyridine groups in the polymer. The borane content of the cross-linked polymer can be controlled by varying the BH<sub>3</sub>-THF concentration (Fig. 1) or by controlling the BH<sub>3</sub>-THF/pyridine molar ratio at a constant BH<sub>3</sub>-THF concentration (Fig. 2). An increase in BH<sub>3</sub>-THF concentration up to 0.6 M led to an increase in the borane content of the cross-linked polymer. The linear dependence of the borane content of the polymer on BH<sub>3</sub>-THF/pyridine up to a 1:1 molar ratio was found.

The influence of the cross-linking level of poly(4-vinylpyridine) on the extent of borane complexation is described in Table 1. At a low cross-linking level (12.5%) there is no difference in the extent of complexation by the pyridine groups in homo and cross-linked polymer. The small decrease in borane content at that cross-linking level is due to the presence of divinylbenzene residues which do not participate in complexation. At higher cross-linking levels a marked decrease in borane content was found. At these levels the complexation characteristics of the pyridine groups are affected, and a decrease in their participation in complex formation was found.

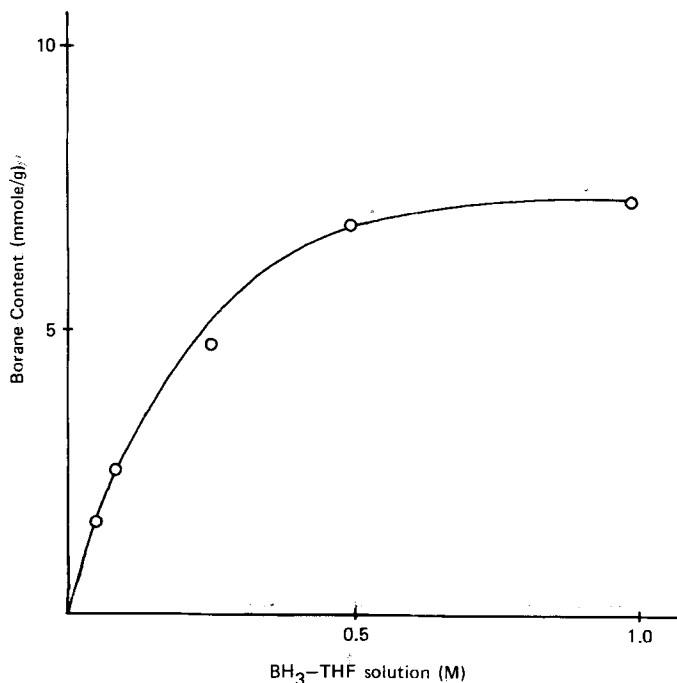


FIG. 1. Borane exchange between  $\text{BH}_3$ -THF and cross-linked poly(4-vinylpyridine)-concentration dependence: 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with molar excess (2.0) of  $\text{BH}_3$ -THF in THF. Reaction was carried out for 30 min at  $25^\circ\text{C}$ .

TABLE 1. Reaction of Cross-Linked Poly(4-vinylpyridine) with Borane-THF<sup>a</sup>

Cross-linking level (%)	Borane in polymer	
	mmol/g	$\frac{\text{BH}_3}{\text{N}}$ <sup>b</sup>
0.0	7.8	0.91
12.5	7.2	0.95
22.5	4.8	0.69
35.0	2.7	0.45

<sup>a</sup>Polymer (1.0 g) was allowed to react with  $\text{BH}_3$ -THF 1 M solution in THF (17 mL) at room temperature for 30 min.

<sup>b</sup>Molar ratio.

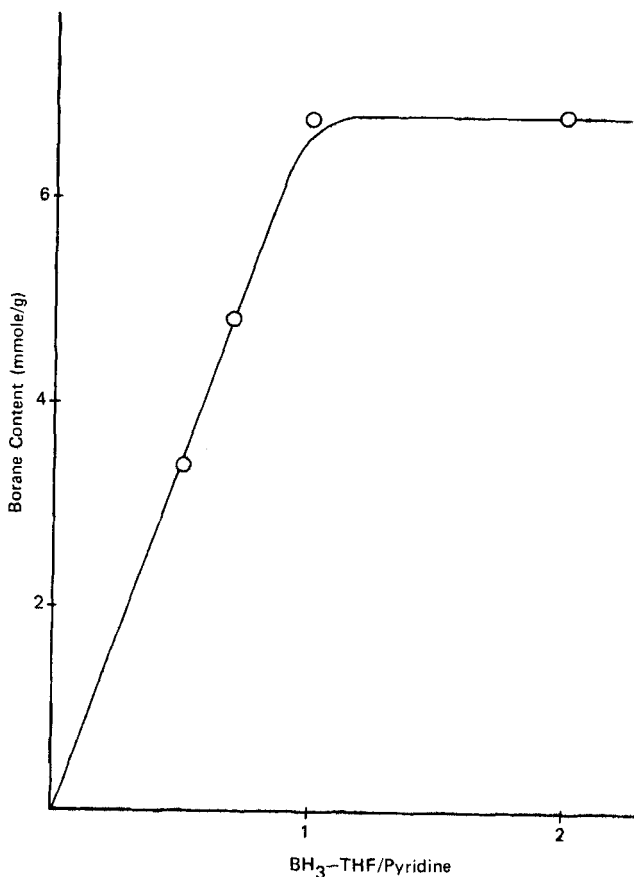


FIG. 2. Borane complexation by cross-linked poly(4-vinylpyridine) at different BH<sub>3</sub>-THF/pyridine molar ratio: 12.5% cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with 0.5 M BH<sub>3</sub>-THF solution in THF for 30 min at 25°C.

#### Reaction of Cross-Linked Poly(4-vinylpyridine)-Boron Trifluoride with Sodium Borohydride

Cross-linked poly(4-vinylpyridine)-boron trifluoride can be used for the preparation of the corresponding borane complex. The reaction of polymer-boron trifluoride with sodium borohydride in DMF led to the formation of the polymer-borane complex (Table 2). Cross-linked polymer(4-vinylpyridine)-BF<sub>3</sub> was prepared by reaction of BF<sub>3</sub>-OEt<sub>2</sub> with the cross-linked polymer. The extent of boron trifluoride



TABLE 2. Reaction of Cross-Linked Poly(4-vinylpyridine)-Boron Trifluoride with Sodium Borohydride<sup>a</sup>

Cross-linking level (%)	Boron trifluoride in polymer		Borane in polymer		
	mmol/g	$\frac{\text{BF}_3^b}{\text{N}}$	mmol/g	$\frac{\text{BH}_3^b}{\text{N}}$	Yield <sup>c</sup> (%)
12.5	5.21	0.97	4.1	0.52	54
22.5	4.21	0.80	2.9	0.41	51
35.0	3.53	0.75	2.1	0.35	47

<sup>a</sup>Cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with 2 N  $\text{BF}_3(\text{OC}_2\text{H}_5)_2$  ether solution (7 mL) at room temperature for 18 h. Boron trifluoride bound polymer (5.0 mmol) was reacted with 2.5 M sodium borohydride solution in DMF (6 mL) at room temperature for 1 h.

<sup>b</sup>Molar ratio.

<sup>c</sup>Corresponds to conversion of boron trifluoride complex to borane complex.

complexation varied with the level of cross-linking. Only at the lowest cross-linking level (12.5%) did almost all pyridine groups (97%) participate in complexation. The boron trifluoride complex was converted to the borane complex by reaction with sodium borohydride. Conversion of the boron trifluoride complex into the borane complex was achieved in moderate yields. The unreacted boron trifluoride was hydrolyzed during isolation of the polymer-borane complex. An increase in the cross-linking level led to a small decrease in reaction yield.

Preparation of the polymer-borane by this method as well as by exchange reaction with  $\text{BH}_3$ -THF requires anhydrous conditions.

#### Reaction of Cross-Linked Poly(4-vinylpyridine)-Halogen Complexes with Sodium Borohydride

Halogen complexes of the cross-linked polymers were prepared by reaction with halogen aqueous solution (Table 3). A high degree of complexation was achieved. The effect of cross-linking level on the extent of complexation was minimal. The high molar ratio (1.27) of complexed  $\text{I}_2/\text{N}$  found for 12.5% cross-linked polymer can result from complexation of iodine molecules by already complexed pyridine groups. Such a complexation will lead to the presence of  $\text{I}_3^-$  in the polymer. The reaction with sodium borohydride was carried in DMF and water solution. The reaction in DMF was completed after 10 min. The use

TABLE 3. Reaction of Cross-Linked Poly(4-vinylpyridine)-Halogen Complexes with Sodium Borohydride<sup>a</sup>

Cross-linking level (%)	Halogen	Halogen in polymer		Borane in polymer					
		mmol/g	$\frac{X_2}{N}$ <sup>b</sup>	Reaction in DMF		Reaction in water			
				mmol/g	$\frac{BH_3}{N}$ <sup>b</sup>	Yield <sup>c</sup> (%)	mmol/g	$\frac{BH_3}{N}$ <sup>b</sup>	Yield <sup>c</sup> (%)
12.5	Iodine	2.87	1.27	5.1	0.66	52	2.3	0.29	22
22.5	"	2.50	0.93	4.3	0.62	66	1.9	0.26	28
35.0	"	2.20	0.81	3.9	0.67	83	1.6	0.26	33
12.5	Bromine	3.50	0.96	6.0	0.78	81	3.5	0.44	46
22.5	"	3.27	0.93	4.4	0.63	68	2.5	0.35	38
35.0	"	3.03	0.95	3.5	0.59	62	2.1	0.35	37

<sup>a</sup>Cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with 0.1 N halogen solution (100 mL) at room temperature for 1 h. Halogen-bound polymer (5.0 mmol) was reacted with 2.5 M sodium borohydride solution in DMF or water (6 mL) at room temperature for 1 h.

<sup>b</sup>Molar ratio.

<sup>c</sup>Corresponds to conversion of halogen complex to borane complex.

TABLE 4. Reaction of Cross-Linked Poly(4-vinylpyridine) Hydrochloride Derivative with Sodium Borohydride<sup>a</sup>

Cross-linking level (%)	Borane in polymer					
	HCl in polymer			Reaction in DMF		
	mmol/g	$\frac{\text{HCl}^b}{\text{N}}$	Yield <sup>c</sup> (%)	mmol/g	$\frac{\text{BH}_3^b}{\text{N}}$	Yield <sup>c</sup> (%)
12.5	6.14	0.95	97	7.0	0.92	97
22.5	4.19	0.68	88	4.2	0.60	88
35.0	3.51	0.65	64	2.5	0.42	64
				mmol/g		
					$\frac{\text{BH}_3^b}{\text{N}}$	Yield <sup>c</sup> (%)
				1.5	0.18	19
				2.0	0.28	41
				1.5	0.25	38

<sup>a</sup> Cross-linked poly(4-vinylpyridine) (1.0 g) was allowed to react with 3 N hydrochloric acid solution (10 mL) at room temperature for 1 h. Hydrochloride bound polymer (5.0 mmol) was reacted with 2.5 M sodium borohydride solution in DMF or in water (6 mL) at room temperature for 1 h.

<sup>b</sup> Molar ratio.

<sup>c</sup> Corresponds to conversion of hydrochloride derivative to borane complex.

of a molar excess of sodium borohydride in the reaction with iodine complex (2.5) and with bromine complex (2.0) is sufficient for obtaining a maximum borane content under these experimental conditions. The reaction in water is faster. The maximum borane content was reached after 7 min using a sodium borohydride (2.8 and 2.3) molar excess for the reaction with iodine and bromine complexes, respectively.

Conversion of the halogen complex into the corresponding borane complex by reaction with sodium borohydride in DMF was achieved in good yields. Full conversion was prevented by a possible side reaction between the already formed borane and unreacted iodine or bromine. The polymer-halogen complex partially dissociates in DMF solution. Under the experimental conditions used, 22% of the iodine and 5% of the bromine were found in solution within 10 min. A partial loss of borane formed in solution will also contribute to a decrease in polymer-borane complex formation. The halogen complexed pyridine groups were found to be less sensitive to the presence of the cross-linking agent and were converted to the borane complex in good yields. As a result, a much higher borane content was reached at the 35% cross-linking level. When borane-complexed polymer was prepared by reaction in water, a much lower borane content was reached. Hydrolysis during borane formation as well as the reaction between iodine and borane are responsible for the lower borane content of these polymers.

#### Reaction of Cross-Linked Poly(4-vinylpyridine) Hydrochloride with Sodium Borohydride

Cross-linked poly(4-vinylpyridine) hydrochloride was prepared by reaction of the polymer with hydrochloric acid (Table 4). At the 12.5% cross-linking level, most of the pyridine groups were converted into the hydrochloride derivative. A decrease in the extent of reaction occurred at higher cross-linking levels. Conversion of the hydrochloride derivative into the corresponding borane complex was carried out in DMF and water. The reaction in DMF was completed within 60 min; after 5 min, 70% of the final borane content was reached. The maximum borane content (7.0 mmol/g) was reached when a molar excess (1.45) of sodium borohydride was used. When stoichiometric amounts of the reactants were used, 91% of the final borane content was obtained. Practically all hydrochloride was removed from the polymer during borane-complex formation. Chlorine analysis of these polymers was less than 1.12%. The borane content of the polymer varied with the cross-linking level. Full conversion of the hydrochloride to the borane complex occurred only in DMF at a low cross-linking level. The reaction of hydrochloride derivative in water was accompanied by partial hydrolysis of the borane, leading to a much lower borane content.

Of the five different methods for the preparation of cross-linked poly(4-vinylpyridine)-borane investigated, the exchange reaction with

$\text{BH}_3$ -THF and the reaction of the cross-linked polymer hydrochloride with sodium borohydride in DMF led to the highest borane content. Good results were also obtained when the halogen complex of the cross-linked polymer was reacted in DMF. If highly cross-linked polymer-borane is required, the use of a halogen complex is preferred. The preparation of cross-linked poly(4-vinylpyridine)-borane in water instead of DMF led to polymers with a much lower borane content. Better results were obtained when halogen-complexed polymers were used. The degree of borane incorporation in cross-linked poly(4-vinylpyridine) prepared in water is not lower than the degree of functionalization commonly encountered in many polymeric reagents [16].

Recycling of cross-linked polymer-borane is important when it is used as a polymeric reagent. 12.5% Cross-linked poly(4-vinylpyridine)-borane practically did not change its borane content (7.0 mmol/g) after 10 cycles of borane-complex formation and hydrolysis. The polymer-borane complex used in these experiments was prepared by an exchange reaction with  $\text{BH}_3$ -THF and by the use of the polymer hydrochloride derivative.

#### Hydrolytic Stability of Cross-Linked Poly(4-vinylpyridine)-Borane

Hydrolytic stability of the cross-linked polymer-borane is of utmost importance when used as a polymeric reagent. Storing of the polymer, as well as its use in aqueous solution and acidic media, over a long period of time is highly dependent on its hydrolytic stability.

Cross-linked poly(4-vinylpyridine)-borane stored over 2 years maintained its borane content (7.0 mmol/g) unchanged. The time to a 50% decrease in borane content of 12.5% cross-linked polymer in aqueous media at different pH values is reported in Table 5. It can be seen that even in acidic media the polymer maintains its activity over reasonably long time periods. In a separate hydrolysis experiment carried out in buffer pH 1 solution under the same experimental conditions, it was found that no hydrolysis was detected up to 5 h at room temperature. After 24 h, 88% of the borane-bound polymer remained active. Pyridine-borane hydrolyzed completely after 120 min under these experimental conditions.

The cross-linked polymer borane is much more stable toward hydrolysis than its low molecular weight analog pyridine-borane.

The hydrolytic stability of cross-linked poly(4-vinylpyridine)-borane at different cross-linking levels in 1 N HCl solution is described in Fig. 3. The extent of hydrolysis was determined volumetrically by measuring the hydrogen released during borane hydrolysis. The hydrolysis rate is higher than that which occurred at pH 1 buffer solution. Here, too, the borane-bound polymer showed a higher hydrolytic stability than

TABLE 5. Hydrolytic Stability of Cross-Linked Poly(4-vinylpyridine)-Borane<sup>a</sup>

Hydrolysis solution	Time to 50% decrease in borane content
1 <u>N</u> HCl/H <sub>2</sub> O	52 min <sup>b</sup>
0.5 <u>N</u> HCl/H <sub>2</sub> O	11 h <sup>b</sup>
Buffer pH 1	8 d
Buffer pH 2	48 d
Buffer pH 3	136 d
Buffer pH 7	>360 d
Buffer pH 9.2	>360 d
Acetic acid	>10 d

<sup>a</sup> 12.5% Cross-linked poly(4-vinylpyridine)-borane (0.1 g, 7.2 mmol/g) was allowed to react with hydrolysis solution (10 mL). Borane content was determined by hydrolysis of the remaining borane-bound polymer.

<sup>b</sup> Borane content was determined volumetrically by measuring the hydrogen released during hydrolysis.

pyridine-borane, which hydrolyzed completely within 2 min under the same experimental conditions. The hydrolysis of the cross-linked polymers is characterized by a short induction period which increases with an increase in the cross-linking level. The hydrolysis rate is strongly dependent on the cross-linking level. An increase in the cross-linking level leads to a decrease in the hydrolysis rate. The relative hydrolytic stability of highly cross-linked polymer-borane may be advantageous when used in acidic media. The hydrolysis of borane-bound homo and cross-linked polymer is an autoaccelerated reaction. Autoacceleration results from progressive protonation of the polymer as complexed borane is removed by hydrolysis. An increase in protonation of the polymer leads to swelling and conformational changes which enhance polymer-borane reactivity. Kinetic studies of low molecular weight amine borane hydrolysis were reported in literature [17-20]. Autoacceleration was not detected in these studies. It seems that it is unique to the borane-bound polymer.

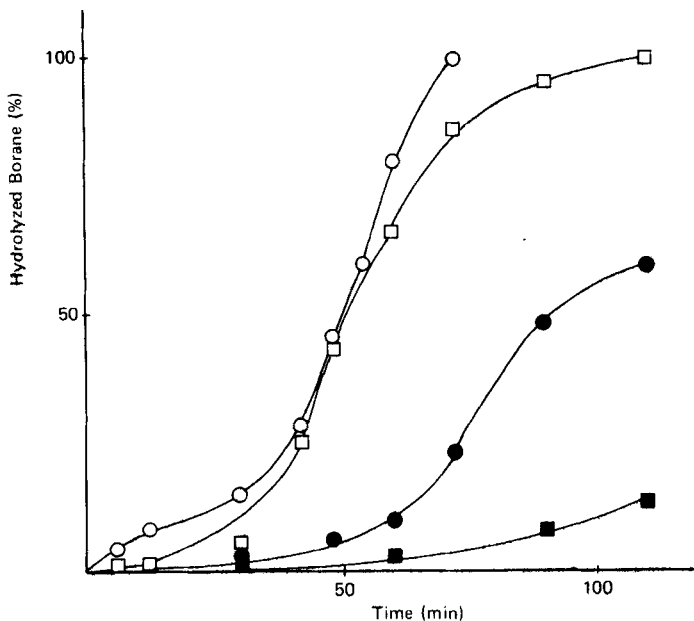


FIG. 3. Hydrolytic stability of cross-linked poly(4-vinylpyridine)-borane in 1.0 N hydrochloric acid solution: (○) uncross-linked polymer borane 7.8 mmol/g, (□) 12.5% cross-linked polymer-borane 7.2 mmol/g, (●) 22.5% cross-linked polymer-borane 4.8 mmol/g, (■) 35.0% cross-linked polymer-borane 2.7 mmol/g. Borane-bound polymer (1.0 mmol) was hydrolyzed in 1 N HCl solution (5.0 mL) at 25°C.

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