

Designing a Support for Borohydride Through Grafting onto Crosslinked Polyvinylpyrrolidone

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SYNOPSIS

Crosslinked polyvinylpyrrolidone (PVPy) was grafted with polyvinylpyridine by irradiating the polymer beads in air from a Co^{60} γ -radiation source and then heating with 4-vinylpyridine (4-VP) in water. The percentage of grafting was studied as a function of various reaction parameters and was determined from the increase in weight of PVPy and from the estimation of pyridine rings introduced into the polymer. PVPy-*g*-poly(4-VP) was treated with sodium in ethanol, which is known to reduce pyridine into piperidine together with small amounts of 1,2,5,6-tetrahydropyridine. On methylation with dimethyl sulfate and alkali, these are further converted into *N,N*-dimethylpiperidinium groups. The dimethylpiperidinium graft was used to support borohydride ions and the graft copolymer was shown to cleanly reduce several carbonyl compounds to the corresponding alcohols. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Crosslinked poly(*N*-vinylpyrrolidone) (PVPy) is an inert and strong polymer and is available in beaded form. It is prepared by suspension polymerization of *N*-vinylpyrrolidone along with a crosslinking agent. Common crosslinking agents used are the dimethacrylates of ethylene glycols and divinylbenzene.¹ PVPy has also been crosslinked with α,ω -diolefins such as 1,7-octadiene.² Under the action of light, PVPy has been crosslinked by diazo compounds or oxidizing agents such as dichromate.³⁻⁵ PVPy is one of the most nontoxic polymers known and crosslinked PVPy films have been suggested for desalination membranes and for membranes for artificial kidney dialysis. Crosslinked PVPy swells in both aqueous and alcoholic media, a property that makes it an excellent support for developing into a reagent for organic synthesis.

A polymer has to be functionalized for use as a polymeric reagent. We have chosen to introduce functional groups by free-radical-initiated grafting of the monomer. Beaded PVPy was exposed to γ -rays in air from a Co^{60} source and was heated with 4-vinylpyridine (4-VP) in water. Homopolymer was

removed by washing with warm aqueous methanol (1 : 1). The percentage of grafting was estimated from the increase in weight of PVPy and also from the intake of chloride by the grafted pyridine groups on PVPy, which were in close agreement. Conditions for maximum percentage of grafting were determined under various reaction parameters such as total dose, time, and temperature of heating and molar concentration of 4-VP used. The effect of the addition of methanol to the aqueous medium during grafting was also studied.

Pyridine rings are important functional groups on a polymer because these can be used in a variety of reactions. They are also amenable to further chemical transformations to give useful functionalities. We are exploring the applications of crosslinked PVPy-*g*-poly(4-VP) in chemical reactions. The present communication reports the transformation of pyridine to *N,N*-dimethylpiperidinium borohydride pendants and the use of polymer-supported borohydride for reducing several aldehydes and ketones in ethanolic medium.

EXPERIMENTAL

Materials and Methods

Crosslinked polyvinylpyrrolidone (PVPy) in beaded form was received from Polysciences Inc., Warring-

Table I Percentage of Grafting in Selected Samples

Total Dose (MR)	Percentage of Grafting	
	From the Increase in Weight of the Polymer	From the Uptake of the Chloride Ion
0.48	100	100
1.44	161	157
1.92	204	201
2.4	290	290

ton, PA, U.S.A. 4-Vinylpyridine, dioxane, aldehydes, and ketones were freshly distilled before use. Dimethyl sulfate was washed with an ice-cold saturated solution of sodium bicarbonate and dried over calcium oxide. The resin was irradiated in air from a 2100 Ci Co^{60} γ -radiation source at a constant dose rate (0.80 MR/h) for different periods of time.

Graft Copolymerization: General Procedure

Irradiated crosslinked PVPy beads were suspended in distilled water which was followed by the addition of 4-VP. The reaction mixture was heated in an oil bath. Similar experiments were run with dioxane as the reaction medium. After the reaction, the contents were filtered on a weighed sintered crucible and washed thoroughly with methanol : water (1 : 1) to ensure complete removal of the homopolymer, poly(4-VP). The grafted copolymer was dried at 50°C to a constant weight. Percentage of grafting was calculated from the increase in weight of the crosslinked PVPy. It was also estimated from the

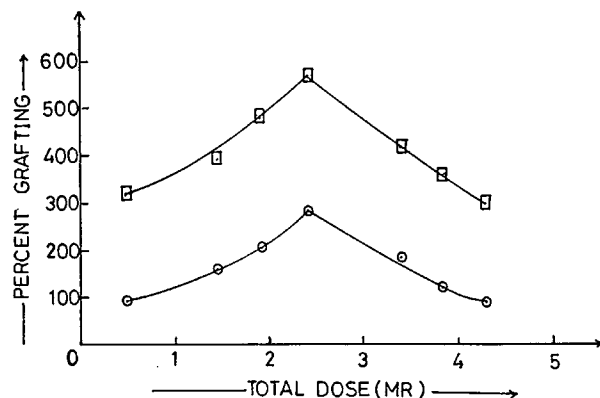


Figure 1 Effect of total dose on the percentage of grafting of 4-VP on PVPy. PVPy = 100 mg; water = 3 mL; temp = 118–121°C; (○—○) 4-VP = 0.009 mol; (□—□) 4-VP = 0.019 mol.

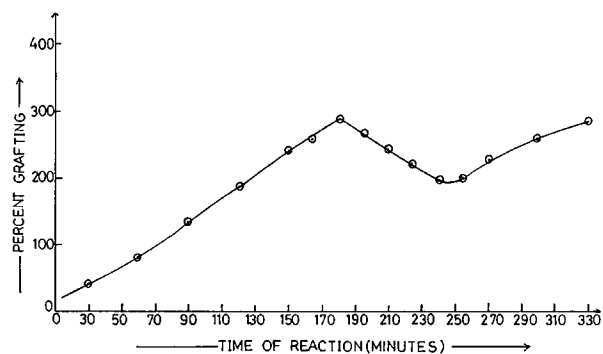


Figure 2 Effect of the time of reaction on the percentage of grafting of 4-VP on PVPy. PVPy = 100 mg; 4-VP = 0.009 mol; water = 3 mL; temp = 118–121°C; total dose = 2.4 MR.

intake of chloride ions by the grafted pyridine groups in selected samples of the graft copolymers having wide variations in the percentage of grafting (*vide infra*).

A weighed amount of grafted polymer was shaken with 0.5N HCl (20 mL) for 15 min and filtered and the filtrate (5 mL each time) was titrated against 0.5N AgNO_3 by Mohr's method. Percentage of grafting was calculated from the amount of HCl retained by the polymer. A blank run was made with PVPy in a similar manner. Table I presents the results.

Evidence of Grafting

The IR spectrum (KBr pellet) of the grafted copolymer showed peaks at 1580 cm^{-1} due to —C=N and at 2940 cm^{-1} caused by C—H stretching in —CH= of pyridine, indicating that 4-VP was grafted onto the crosslinked PVPy beads.

The percentage of grafting was determined as a function of the total dose, the time of reaction, the mol fraction of methanol in aqueous methanol as the reaction medium, and the temperature, media, and increasing dose. The results are recorded in Fig-

Table II Effect of Mol Fraction of MeOH in $\text{H}_2\text{O—MeOH}$ in Sealed Tubes at 118–121°C (Crosslinked PVPy, 100 mg; 4-VP, 0.009 mol; Total Dose, 2.4 MR)

Mol Fraction of MeOH	Percentage of Grafting
1.0	126
0.5	148
0.3	193
0.1	266

Table III Effect of Temperature on the Percentage of Grafting of 4-VP (0.009 mol) on Crosslinked PVPy (100 mg) in Different Reaction Media and with Increasing Total Dose

	Total Dose (MR)						
	0.48	1.44	1.92	2.4	3.36	3.84	4.32
Medium: water (3 mL); temp: 118–121°C							
% Grafting	100	161	204	290	197	123	93
Medium: Dioxane (3 mL); temp: 118–121°C							
% Grafting	22	66	77	84	62	59	31
Medium: Dioxane (3 mL); temp: 134–136°C							
% Grafting	128	225	301	377	246	193	132

ures 1 and 2 and Tables II and III, respectively. The effect of changing the molar concentration of 4-VP in water from 0.03 mol/100 mL to 0.38 mol/100 mL on the percentage of grafting was determined and the results are recorded in Figure 3. Keeping the amount of crosslinked PVPy, total dose, reaction time, and temperature of the reaction constant, four experiments were run using different volumes of a 2.3M aqueous solution of 4-VP. Table IV presents the results.

Preparation of Polymer-supported *N,N*-Dimethylpiperidinium Borohydride

Crosslinked PVPy-*g*-poly(4-VP) with 100% grafting (Resin I) was chosen for preparing the polymer-supported reducing agent.

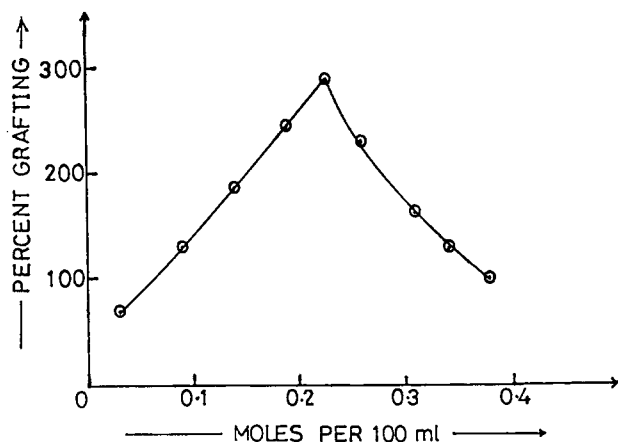


Figure 3 Effect of molar concentration of 4-VP on the percentage of grafting on PVPy. PVPy = 100 mg; temp = 118–121°C; total dose = 2.4 MR.

Preparation of Polymer-supported Piperidine (Resin II)

Resin I (1 g) dried in a vacuum over P_2O_5 was taken in anhydrous ethanol (30 mL) in a round-bottomed flask fitted with a condenser and protected from moisture. Pieces of sodium (3.5 g) were added to the flask and the contents were kept gently boiling over a water bath for 3 h. The resin was filtered and washed with dry ethanol. The process was repeated twice.

Preparation of Polymer-supported *N,N*-Dimethylpiperidinium Borohydride (Resin III)

Resin II was suspended in water (10 mL) and was treated with portions of 5% sodium hydroxide solution and purified dimethyl sulfate (30 mL) and stirred gently at 90°C for 3 h. Addition of dimethyl sulfate and sodium hydroxide solution was continued while maintaining the alkalinity of the mixture. The resin was filtered and washed with water. Methylation was repeated twice, and after the final wash-

Table IV Grafting with Different Amounts of 4-VP (Keeping the Molar Concentration Constant at 2.3M), Crosslinked PVPy, 100-mg; Total Dose, 2.4 MR; Temp 118–121°C; Reaction Time, 3 h

2.3M Aqueous 4-VP (mL)	Percentage of Grafting
3	290
6	291
9	289
12	292

Table V Bed Volumes of Resins (0.21 mL) on Swelling

Resin	Bed Volumes (mL)	
	In Water	In Ethanol
PVPy	0.58	0.51
Resin I [PVPy- <i>g</i> -poly(4-VP)]	0.56	0.50
Resin II (polymer-supported piperidine)	0.55	0.50
Resin III (polymer-supported <i>N,N</i> -Dimethylpiperidinium borohydride)	0.55	0.49

ings, the resin was treated with 1*N* HCl, filtered, and washed with water.

The resin in chloride form as obtained above was stirred with NaBH₄ solution (5 g in 20 mL), filtered, and washed with distilled water and ethanol. It was dried at 50°C and stored in a desiccator.

Study of Swelling Properties of PVPy and the Derived Resins

The swelling property of dry PVPy and Resins I, II, and III was studied in water and in ethanol. Each of the resins (0.21 mL) was left to swell for 6 h in ethanol or water and the bed volume was noted. Table V presents the results.

Reduction of Aldehydes/Ketones to Alcohols with Resin III

The following general method was used for the reactions: Resin III (1 g) was suspended in EtOH (20 mL) and was gently stirred and refluxed with the aldehyde/ketone (2 mmol). The reaction was monitored on a TLC. The resin was filtered and washed with ethanol and the combined filtrate and washings were concentrated and diluted with water. The product was extracted into ether and the IR spectra were compared with authentic samples of the products in each case.

The aldehydes/ketones reduced by this procedure were benzaldehyde, *p*-nitrobenzaldehyde, crotonaldehyde, cyclohexanone, 4-methylcyclohexanone, and cyclopentanone. Table VI presents the results.

Reuse of Resin III

The spent resin was washed successively with 5% NaOH, water, 0.5*N* HCl, and water and was treated with NaBH₄ solution. After washing with water and ethanol and drying, it was used again for reduction with the same efficiency as that of Resin III.

RESULTS AND DISCUSSION

Percentage of grafting was calculated from the increase in weight on grafting. It was also determined from the intake of the chloride ion by the graft copolymer when it was treated with HCl.

Irradiation of the backbone polymer in air followed by heating produces ©—O• radicals as well as HO•. The latter causes the homopolymerization of 4-VP inside and outside the polymer beads. Homopolymer radicals formed inside the beads can cause grafting by chain transfer but large homopolymer radicals cannot effectively enter the beads from outside through the pores because of their size. The result is that they mostly cause grafting on the outer

Table VI Reduction of Aldehydes/Ketones (Resin, 1 g; Aldehyde/Ketone, 2 mmol; Temp 74–75°C; Ethanol, 20 mL)

Aldehyde/Ketone	Product	Time (h)	Yield (Isolated) (%)
Benzaldehyde	Benzyl alcohol	18	68
<i>p</i> -Nitrobenzaldehyde	<i>p</i> -Nitrobenzyl alcohol	20	65
Crotonaldehyde	Crotyl alcohol	12	71
Cyclohexanone	Cyclohexanol	24	65
Cyclopentanone	Cyclopentanol	24	60
4-Methylcyclohexanone	4-Methylcyclohexanol	24	72

surface of the beads. Percentage of grafting increases progressively with increasing total dose (Fig. 1) because the number of hydroperoxide groups, the active sites for grafting, increases correspondingly. When a large number of homopolymer radicals are formed as on excessive irradiation, they terminate mutually or by combination with HO \cdot and the percentage of grafting falls.⁶

Percentage of grafting was studied as a function of total dose when the reaction was carried out in water and in dioxane at two different temperatures. Results are shown in Table III. At a reaction temperature of 118–121°C in water, the mixture gently keeps boiling. The percentages of grafting under this condition are uniformly higher than those observed when the reactions are done in dioxane. At 134–136°C in dioxane, at the boiling point of the reaction mixture, the percentage of grafting rises at all the doses of irradiation studied. These results show the positive role played by a low-chain transfer constant of the medium and a higher reaction temperature.

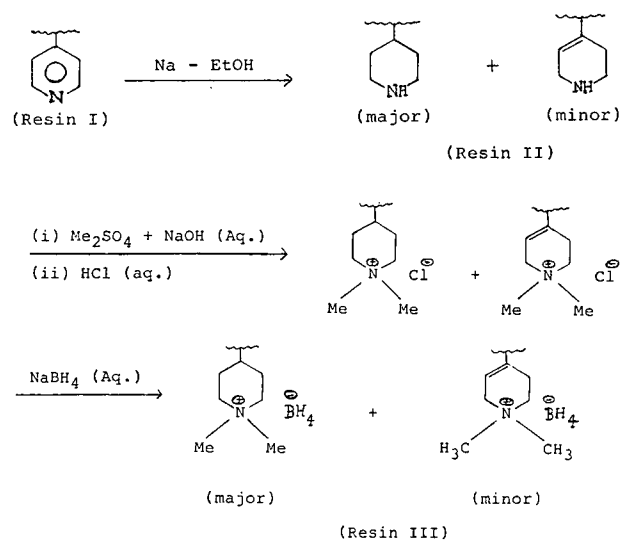
Figure 2 shows the percentage of grafting as a function of reaction time. Grafting seemed to increase linearly up to 180 min, after which it showed a regular decrease up to 240 min. Between 240 and 330 min of reaction, there was a regular increase in the percentage of grafting at a slightly lower rate. The decrease in grafting may be explained through a "back-biting" mechanism⁷ according to which a growing grafted chain is capable of attacking itself or a neighboring grafted chain, resulting in chain scission and the formation of a homopolymer species with a radical site or an olefinic bond. Further increase in the percentage of grafting may be due to the accumulation of bulky homopolymer species trapped inside the beads, some of which are grafted onto the polymer.

The effect of the concentration of 4-VP on grafting onto crosslinked PVPy is presented in Figure 3. It was observed that maximum grafting (290%) occurred at a 2.3M concentration of 4-VP, beyond which it decreases. Decrease in the percentage of grafting at higher monomer concentration may be because 4-VP has a high monomer transfer constant⁸ (C_M at 25°C = 6.7×10^{-4}) so that homopolymerization becomes a competing reaction.

Percentage of grafting is a function of the molar concentration of 4-VP under a set of reaction conditions. It remains essentially unchanged in larger volumes of the same monomer solution, although a quantitatively higher amount of the monomer is available for grafting. This is reflected in the results of experiments recorded in Table IV.

The effect of the addition of methanol in water as the reaction medium was studied at the optimum radiation dose in sealed tubes at 118–121°C (Table II). It was observed that the percentage of grafting increases as the mol fraction of MeOH in the reaction mixture decreases. These results are in accordance with the higher chain-transfer constant of methanol as compared to water. It also appears that there is a small contribution of pressure to the percentage of grafting when the reaction is done in closed tubes.

We intended to use the grafted polymer, cross-linked PVPy-*g*-poly(4-VP), as a support for the borohydride ion. The pendant pyridine rings of the grafted polymer could support the ion but the quarternized pyridine rings have a propensity of being reduced with borohydride. So, we decided to reduce the rings with sodium in ethanol. The major product of this reaction are piperidine pendants with small amounts of 1,2,5,6-tetrahydropyridine.⁹ On methylation with dimethyl sulfate and sodium hydroxide, the reduced rings are quarternized and are effective in supporting the borohydride ion:



During grafting and the subsequent reactions described here, the swelling characteristics and the physical form of the polymer beads remain unaltered. This indicates that the basic structure of the polymer has not changed substantially in these operations. A test with the Kaiser reagent¹⁰ shows the absence of free —NH₂ groups in each of the polymer derivatives, Resins I, II, and III, which shows that the reactions employed do not reduce the pyrrolidone rings of the backbone polymer. Crosslinked polyvinylpyrrolidone is inexpensive and grafting can easily and effectively introduce desired functionalities into it in a high yield. The present article has

described a use for the poly(4-vinylpyridine) graft. We are exploring other applications for the functionality introduced through this grafting.

Borohydride is a more selective hydride than are other reactive hydrides. Polymer-supported borohydride *does* not reduce the double bond of crotonaldehyde. Also, the aldehydes are more easily reduced than are the ketones. Spent resin can be recycled and used for reduction without any apparent loss in its effectiveness.

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