

Synthesis of a Cellulose-Grafted Polymeric Support and Its Application in the Reductions of Some Carbonyl Compounds

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ABSTRACT: The reduction of carbonyl compounds by borohydride supported on a cellulose-anion exchange resin is known. The synthesis of a graft copolymer of cellulose and poly(4-vinyl pyridine) [CellO-g-poly(4-VP)] has been carried out with ceric ions as a redox initiator. A postgrafting treatment of CellO-g-poly(4-VP) with sodium borohydride has produced CellO-g-poly(4-VP) borane, a polymer-supported reducing agent. Optimum conditions pertaining to the maximum percentage of grafting have been evaluated as a function of the concentrations of the initiator, monomer, and nitric acid, amount of water, time, and temperature. The maximum percentage of grafting (585%) has been obtained with 0.927 mol/L of 4-vinyl pyridine and 0.018 mol/L of ceric ammonium nitrate in 120 min at 45°C. The polymeric support, CellO-g-poly

(4-VP) borane, has been used for reduction reactions of different carbonyl compounds such as benzaldehyde, cyclohexanone, crotonaldehyde, acetone, and furfural. The graft copolymer has been characterized with IR and thermogravimetric analysis. The grafted cellulose has been found to be thermally stable. The reduced products have been characterized with IR and NMR spectral methods. The reagent has been reused for the reduction of a fresh carbonyl compound, and it has been observed that the polymeric reagent reduces the compounds successfully but with a little lower product yield. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 99–111, 2008

Key words: FTIR; graft copolymers; radical polymerization; synthesis; thermogravimetric analysis (TGA)

INTRODUCTION

The study of polymer-supported (PS) reactions has been an area of considerable interest in the field of organic synthesis. The supports have been designed and functionalized in various ways depending on their applications; they are quite selective and can be reused more efficiently than their nonsupported analogues. The isolation of the products by simple processes is another interesting feature of these reactions. Qin et al.¹ prepared a new crosslinked resin by an inverse emulsion method under the protection of an amino group. The resin reacted with glycidyl trimethyl ammonium chloride to form the quaternary ammonium ion resin, whose chloride was exchanged with potassium borohydride to get the borohydride exchange resin (crosslinked borohydride exchange resin) (CBER). CBER was used as a new PS reducing agent for the reduction of carbonyl compounds to the corresponding alcohols and exhibited relatively high chemoselectivity and possessed the advantage of easy workup. Kaneda et al.² developed high-performance polymer-bound metal complex catalysts

for the chemoselective reduction of organic compounds with various hydrogen sources such as H₂O, H₂, and HCOOH. The vapor phase hydrogenation of toluene on resin poly(4-vinyl pyridine-co-styrene) supported Pd catalysts was studied by Reyes et al.³ Hutchins et al.⁴ prepared ion-exchange resin-bound cyanoborohydride, which provided a successful and convenient reagent for a variety of reductions with the added advantage of ease of workup and retention of cyanide on the resin. The polymeric resin offers important advantages over NaBH₃CN because the toxic cyanide residues are retained on the polymer and not extracted into an organic or aqueous phase. Young et al.⁵ observed that the borohydride exchange resin exhibited high chemoselectivity not only between aldehydes and ketones but also between aldehydes and between ketones. Sande et al.⁶ reported borohydride exchange resin selectivity in the reduction of α,β -unsaturated carbonyl compounds to corresponding unsaturated alcohols in high yields. Asymmetric borane reduction of prochiral ketones by PS chiral sulfonamides has been reported.⁷ The enantioselective reduction of prochiral ketones by chiral catalysts and reagents has attracted intense interest in the past 20 years.⁸ Chiral 1,3,2-oxazaborolidines has been applied in asymmetric organic synthesis, including enantioselective reduction of ketones, imines, and

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oxime esters, asymmetric Diels–Alder reactions, aldol condensation, and atropo-enantioselective reduction of lactones.⁹ A new PS reagent for the synthesis of β -lactams in solution was studied by Donati et al.¹⁰ Recently, it has been shown that conducting polymer films can be used to reduce Cr(VI). Rajeshwar and coworkers^{11–13} observed the reduction of hexavalent chromium at a polypyrrole electrode with 100% efficiency. The reversibility of the polymer redox process enabled the electrochemical recycling of the polypyrrole for repeated treatment of Cr(VI). Malinauskas and Holze¹⁴ observed the reduction of Cr(VI) on a polyaniline film. The bis(cyclopentadienyl) titanium(IV)dichloride indium ($\text{Cp}_2\text{TiCl}_2/\text{In}$) system is a new reagent for reducing various aromatic nitro compounds to the corresponding aromatic amines in good yields under mild and neutral conditions.¹⁵ In this article, we report on the use of a PS reducing reagent, Cello-g-poly(4-VP)· BH_3 , for different reduction reactions of carbonyl compounds.

EXPERIMENTAL

Materials and methods

Cellulose (CDH, New Delhi, Delhi) in a powder form was dried before use. Ceric ammonium nitrate (CAN; Qualigens Fine Chemicals Glaxo India, Ltd., Mumbai, India) and nitric acid were used as redox initiators. Deaerated water was used as the reaction medium. 4-Vinyl pyridine (4-VP; Merck, Munchen, Germany) was distilled before use.

Preparation of Cello-g-poly(4-VP)

Dried cellulose (200 mg) was suspended in a known amount of water in a three-necked, round-bottom flask. To it were added a known amount of CAN and a definite amount of concentrated HNO_3 . The reaction mixture was purged with nitrogen gas, free of oxygen, for 30 min before the addition of the monomer. The reaction was carried out at a definite temperature for a stipulated time period. 4-VP was added in small installments from the separating funnel, and the flow of nitrogen was maintained continuously through the reaction mixture until the reaction was complete. After the specified time, the reaction mixture was filtered through dried and weighed Whatman filter paper. The residue was thoroughly washed with a 1 : 1 (v/v) acetone–water mixture that formed. The product was dried to a constant weight.

The percentage of grafting was calculated from the increase in the initial weight of the cellulose powder as follows:

$$\text{Percentage of grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 and W_0 are the weight of the grafted cellulose powder after complete removal of the homopolymer and the weight of the original cellulose powder, respectively.

The grafting of ethyl acrylate onto cellulose was expressed as the apparent graft yield and as the true graft yield by calculation of the weight percentage of grafted poly(ethyl acrylate) with respect to the amount of cellulose taken initially in the reaction mixture for grafting and the amount of cellulose on which grafting of poly(ethyl acrylate) actually took place after graft copolymerization.¹⁶

The percentage of grafting was determined as a function of different grafting parameters such as the concentrations of the initiator, CAN, nitric acid, and monomer, amount of water, and temperature and time of the reaction. Optimum conditions pertaining to the maximum percentage of grafting were evaluated as a function of these reaction variables.

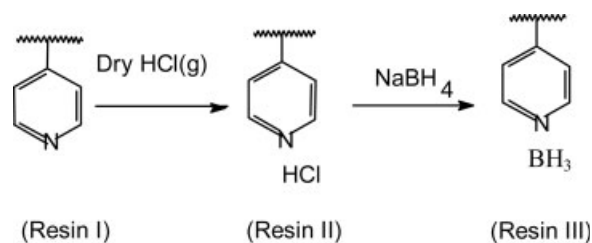
Preparation of the polymeric reagent Cello-g-poly(4-VP) borane

Quaternization of Cello-g-poly(4-VP)

Cello-g-poly(4-VP) (resin I; 2 g) was suspended in 40 mL of benzene. Dry HCl gas was passed through it under stirring for 2 h. The reaction mixture was filtered through dried and weighed Whatman filter paper. The residue, Cello-g-poly(4-VP) hydrochloride (resin II), was washed with benzene and dried.

Conversion of Cello-g-poly(4-VP) pyridinium chloride to Cello-g-poly(4-VP) borane

Cello-g-poly(4-VP) hydrochloride (resin II) was suspended in 100 mL of water and added slowly to an aqueous solution of sodium borohydride (1 g in 20 mL) under stirring at room temperature. Evolution of hydrogen gas was observed during the addition. After the stipulated time period, the reaction was stopped, and the solid product, Cello-g-poly(4-VP) borane (resin III), was filtered, washed with water, and dried to a constant weight:



Reduction of carbonyl compounds

The following general method was followed for the reductions. Resin III (0.74 g) was suspended in 20 mL

TABLE I
Reduction of Aldehydes/Ketones with CellO-g-Poly(4-VP)-BH₃ as the PS Reducing Reagent

Reactant	Product	Time (h)	R_f		Yield (%)
			Reactant	Product	
Benzaldehyde	Benzyl alcohol	14	0.75	0.66	29.60
Cyclohexanone	Cyclohexanol	9	0.88	0.83	25.00
Crotonaldehyde	Crotyl alcohol	12	—	—	23.98
Acetone	Isopropyl alcohol	3	—	—	67.56
Furfural	Furfuryl alcohol	4	0.82	0.63	71.00

of benzene (hexane in the case of acetone). To it was added 0.05 mol of aldehyde/ketone. The mixture was refluxed for different time periods. The course of the reaction was monitored by thin-layer chromatography at regular intervals. After the completion of the reaction, the resin was filtered off, and the product was extracted by fractional distillation at the boiling point of the respective alcohols.

Reduction of aldehydes/ketones such as benzaldehyde, crotonaldehyde, furfural, cyclohexanone, and acetone was carried out with resin III as the PS reducing reagent. The time taken for oxidation, the R_f values for the reactants and products, and the percentage yields of the products are presented in Table I.

Characterization

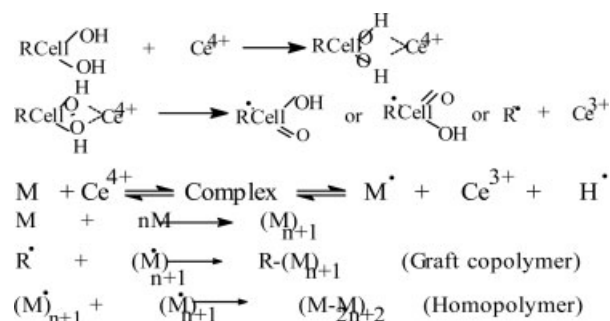
The characterization of cellulose, Cell-g-poly(4-VP), Cell-g-poly(4-VP)·HCl and the polymeric support that is Cell-g-poly(4-VP)·BH₃, was carried out with FTIR spectroscopy and thermogravimetric analysis (TGA). FTIR spectra were obtained on a Beckman spectrophotometer, whereas TGA was performed on a Shimadzu simultaneous thermal analyzer in air at a heating rate of 10°C/min, except for TGA of CellO-g-poly(4-VP)·HCl, which was performed on a Linseis (Germany) L 81-11.

RESULTS AND DISCUSSION

The synthesis of a graft copolymer of cellulose essentially involves the generation of active sites on the cellulose backbone upon which a suitable monomer is polymerized. In this work, grafting onto cellulose has been carried out in the presence of 4-VP with CAN as a redox initiator. Ceric ions are known to form complexes with various functional groups^{17,18} that undergo decomposition by one electron-transfer mechanism to produce free radicals, by which the grafting of the appropriate monomer takes place. The presence of radicals on the cellulose backbone has been confirmed by electron spin resonance measurements.¹⁹ A monomer is also known to form a complex with ions that dissociates to give a mono-

mer radical, which further propagates to give polymeric chains. These growing polymeric chains attach to the radical site on cellulose to produce the graft copolymer or terminate to give the homopolymer.

In general, the mechanism of the transition-metal-ion-induced grafting process, in which glycol groups are involved, with Ce(IV) salt can be represented as follows:



The effects of different reaction parameters such as the CAN concentration, HNO₃ concentration, amount of water, temperature, reaction time, and 4-VP concentration on the percentage of grafting of 4-VP onto cellulose have been studied, and the results are explained in light of the aforementioned mechanism.

Effect of the CAN concentration

The generation of active sites on cellulose via complex formation depends on the concentration of the initiator, and because of this, the graft copolymerization of 4-VP onto cellulose has been studied as a function of the concentration of CAN. The results are presented in Figure 1. With an increase in the Ce⁴⁺ concentration, the formation of the complex is facilitated, and it dissociates to generate radical sites on the backbone. This leads to an increase in the percentage of grafting, giving the maximum (392.5%) at [CAN] = 0.018 mol/L. A further increase in the Ce⁴⁺ concentration leads to a decrease in the percentage of grafting. This is explained by the fact that at a higher Ce⁴⁺ concentration, preferential homopolymer formation takes place at the expense of the graft copolymer. The formation of the complex with

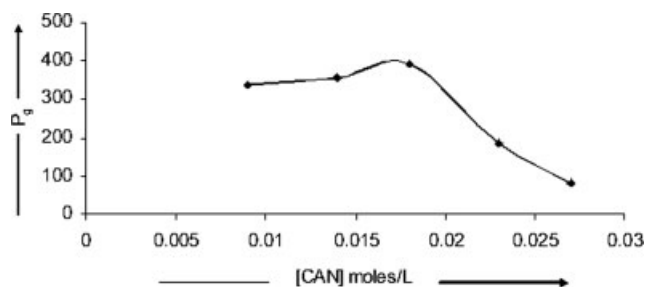


Figure 1 Effect of the CAN concentration on the percentage of grafting (P^g) of 4-VP onto cellulose.

cellulose and Ce^{4+} is preferred over the complex with the monomer. However, with an increasing concentration of the initiator, the formation of the complex with the monomer also takes place and leads to the formation of the homopolymer in preference to graft copolymer formation. Termination of growing polymeric chains is also accelerated at a higher concentration of Ce^{4+} , leading to a decrease in the percentage of grafting.

Effect of the HNO_3 concentration

The percentage of grafting of 4-VP onto cellulose was studied as a function of the nitric acid concentration, and the results are presented in Figure 2. There exists an optimum concentration of nitric acid (0.797 mol/L) at which the maximum percentage of grafting (392.5%) is obtained. A further increase in the HNO_3 concentration decreases the percentage of grafting. The increase in the percentage of grafting with an increasing HNO_3 concentration is due to the fact that the concentration of Ce^{4+} increases with an increasing concentration of acid, which forms a complex with the substrate, that is, cellulose, and hence facilitates grafting:

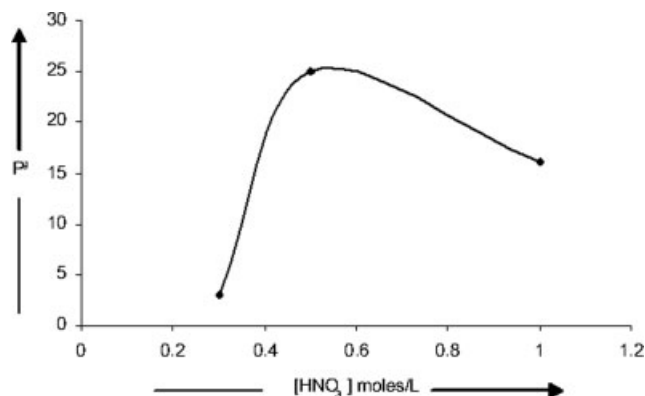
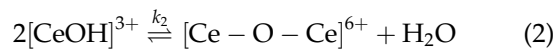


Figure 2 Effect of the HNO_3 concentration on the percentage of grafting (P^g) of 4-VP onto cellulose.



From eq. (1), we obtain

$$[CeOH]^{3+} = \frac{k_1 [Ce]^{4+}}{[H^+]} \quad (3)$$

The total concentration of ceric ions, $[Ce]_T^{4+}$, is thus given by

$$\begin{aligned} [Ce]_T^{4+} &= [Ce]^{4+} + [Ce-O-H]^{3+} \\ &= (1 + K_1/[H^+])[Ce]^{4+} \end{aligned} \quad (4)$$

$$\frac{1}{[Ce]^{4+}} = \frac{1}{[Ce]_T^{4+}} + \frac{K_1}{[Ce]_T^{4+}[H^+]} \quad (5)$$

The decrease in the percentage of grafting beyond the HNO_3 concentration is attributed to the fact that with an increasing concentration of HNO_3 , the equilibrium (I) shifts progressively toward $[Ce]^{4+}$. At a higher concentration, $[Ce]^{4+}$ is known to accelerate the termination of growing polymeric grafting chains, resulting in the decrease in the percentage of grafting. Termination of a growing chain by ceric ions was reported by Saha and Chaudhari²⁰ during the polymerization of acrylonitrile and by Kantouch et al.²¹ during the grafting of methyl methacrylate onto wool. An initial increase in the extent of grafting may be associated with the fact that the acid catalyzes the grafting reaction and enhances the oxidizing capacity of the initiator. The subsequent decrease in the grafting may be related to the abundance of H^+ , which may act as a free-radical terminator.

Effect of the liquor ratio

The effect of the amount of water on the percentage of grafting of 4-VP onto cellulose was studied, and the results are presented in Figure 3. The percentage

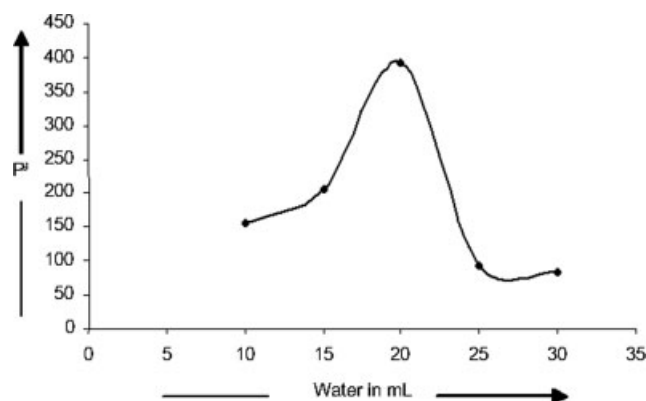


Figure 3 Effect of water on the percentage of grafting (P^g) of 4-VP onto cellulose.

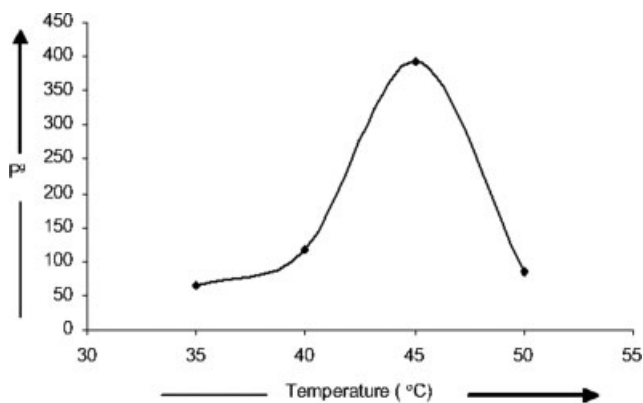
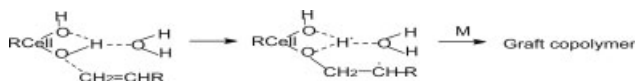


Figure 4 Effect of temperature on the percentage of grafting (P^g) of 4-VP onto cellulose.

of grafting increases with an increasing amount of water and reaches a maximum (392.5%) when 20 mL of water is used. A further increase in the amount of water results in a decrease in the percentage of grafting. An increase in the amount of water helps in exposing the active sites because of increased swelling, and hence a rise in the percentage of grafting can be observed. The decrease in the percentage of grafting beyond the optimum amount of water may be due to the fact that a three-component complex between the substrate, water, and monomer is formed that, in addition to the formation of free-radical sites on the backbone, liberates atomic hydrogen,²²⁻²⁴ which initiates homopolymerization. This leads to a decrease in the percentage of grafting:



In addition, on dilution, a decrease in the concentration of the ceric ion as well as the monomer takes place, resulting in the reduction of the formation of the cellulose-ceric complex and the accessibility of

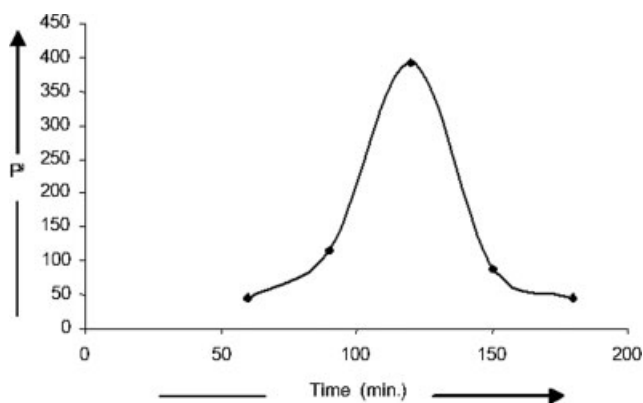


Figure 5 Effect of time on the percentage of grafting (P^g) of 4-VP onto cellulose.

the monomer to the active sites, thus leading to a decrease in the percentage of grafting.

Effect of temperature

The percentage of grafting of 4-VP onto cellulose was studied as a function of temperature, and the results are presented in Figure 4. The percentage of grafting of 4-VP onto cellulose increases steadily with the increase in temperature and affords maximum grafting (392.5%) at 45°C. The increase in the percentage of grafting with increasing temperature is due to the increased decomposition of the complex generating free-radical sites and the increased rate of diffusion of the monomer to the active sites. Beyond the optimum temperature, the decrease in the percentage of grafting is attributed to the increase in the various chain-transfer reactions leading to the termination of growing grafted chains. Increased molecular motion with increasing temperature results in decay of the free radicals, leading to a decrease in the percentage of grafting. At a higher temperature, thermal polymerization is also accelerated, and this leads to a decrease in the grafting percentage.

Effect of time

The percentage of grafting of 4-VP onto cellulose was studied as a function of time, and the results are presented in Figure 5. The percentage of grafting of 4-VP increases first with an increase in time, with maximum grafting (392.5%) obtained in 120 min. A further increase in time leads to a decrease in the percentage of grafting. This may be due to the back-biting of the growing grafted polymeric chains²⁵ and hence decrease in the percentage of grafting:

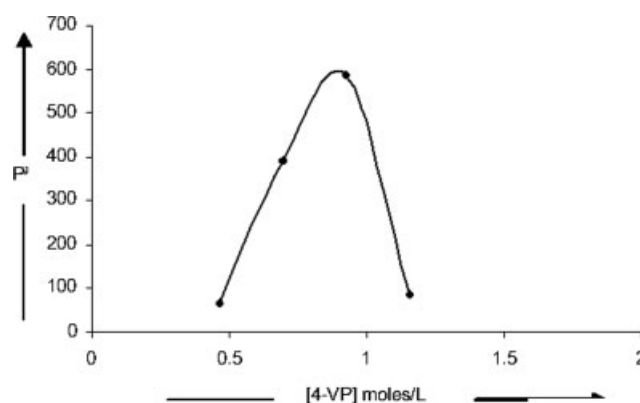


Figure 6 Effect of the monomer on the percentage of grafting (P^g) of 4-VP onto cellulose.

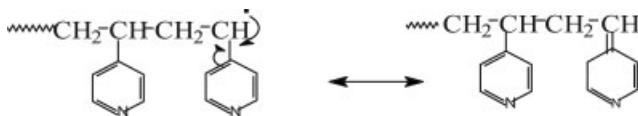
TABLE II
Optimum Conditions Obtained for Maximum Percentage of Grafting (585%)

Cellulose (g)	[CAN] (mol/L)	[HNO ₃] (mol/L)	H ₂ O (mL)	Temperature (°C)	Time (min)	[4-VP] (mol/L)
0.200	0.018	0.797	20	45	120	0.927

Effect of the monomer concentration

Figure 6 presents the effect of the concentration of 4-VP on the percentage of grafting. The percentage of grafting of 4-VP increases with an increase in the 4-VP concentration and affords maximum grafting (585%) at [4-VP] = 0.927 mol/L, beyond which it decreases. These observations are explained by the fact that at a lower concentration of 4-VP, the complex of cellulose and Ce⁴⁺ slowly decomposes, and the monomer reacts selectively with the active sites to produce the graft. At a higher concentration of 4-VP, homopolymerization becomes the preferred process. As the amount of the homopolymer increases, the viscosity of the reaction medium increases [poly(4-VP) being soluble in water], and this inhibits the diffusion of the growing polymeric chains to the active sites, leading to a decrease in the percentage of grafting.

With increasing monomer concentration, the resonance-stabilized growing polymeric chain interacts with the monomer unit lying in close vicinity, leading to more of the homopolymer in preference to grafting:



Monomer transfer reactions (monomer chain transfer constant (C_M) for 4-VP at 70°C = $7.0 \pm 3.2 \times 10^{-5}$)²⁶ are also accelerated there by the spending of the monomer in a wasteful reaction and the killing of the growing polymeric chains, leading to a decrease in the percentage of grafting.

Cellulose is thus successfully grafted with 4-VP with 585% as the maximum percentage of grafting.

Table II gives the optimum conditions obtained for the maximum percentage of grafting.

FTIR spectroscopic studies of ungrafted and grafted cellulose

On comparison of the IR spectra of cellulose and CellO-g-poly(4-VP), it can be observed that in addition to the absorption peaks of cellulose at 2902.57 cm⁻¹ due to C—H stretching, at 1430.77–1376.02 cm⁻¹ due to C—H def., and between 1341 and 1029 cm⁻¹ due to C—O stretching, additional peaks at 3043.26 cm⁻¹ of a heteroaromatic group due to =C—H stretching and at 1644.72, 1521.47, and 1352.66 cm⁻¹ of a pyridine group due to combination bands of C=C and C=N stretching in the FTIR spectrum of the grafted cellulose can be observed. This confirms the formation of the graft copolymer. The values of different peaks are presented in Table III.

The IR spectra of CellO-g-poly(4-VP) hydrochloride and CellO-g-poly(4-VP) borane (Fig. 7), in addition to the regular peaks of cellulose (2903.7 cm⁻¹ due to C—H stretching and 1375–1030 cm⁻¹ due to C—O stretching) and a pyridine ring, show peaks at 2393.5 and 2364.4 cm⁻¹, respectively. These peaks are attributed to the pyridinium salt formation in hydrochloride and borane resins.

TGA of ungrafted and grafted cellulose

The primary thermograms of cellulose and CellO-g-poly(4-VP) are presented in Figures 8 and 9, respectively. The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperature (DT) at every 10% weight loss are presented in Table IV. It can be observed from

TABLE III
FTIR Spectral Peaks of Cellulose and CellO-g-Poly(4-VP)

Sample	Structure	C—H (v, cm ⁻¹)	=C—H (v, cm ⁻¹)	C=C (v, cm ⁻¹)	C=N (v, cm ⁻¹)	C—O (v, cm ⁻¹)
Cellulose		2902.5 1430.7 (def.) 1376.0 (def.)				1341–1029
CellO-g-poly(4-VP)			3043.2	1644.7 1521.4 1352.6	1644.7 1521.4 1352.6	1176–1031

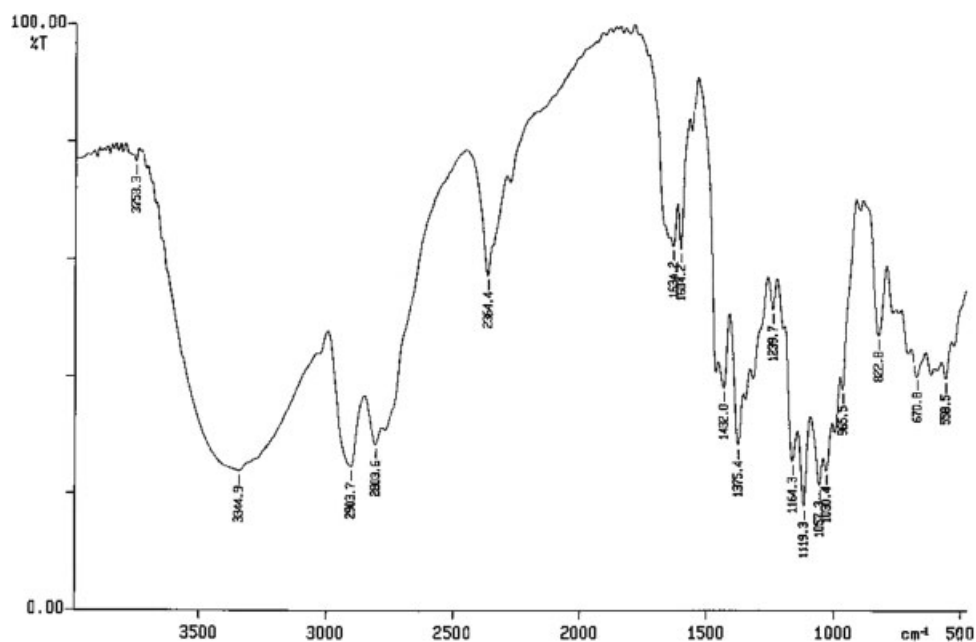


Figure 7 FTIR spectrum of Cello-g-poly(4-VP) borane.

the thermograms that unmodified cellulose shows a single stage of decomposition, whereas the grafted cellulose shows a double stage of decomposition. It is known that the thermal degradation of cellulose proceeds essentially through two types of reactions. At lower temperatures, that is, between 120 and 250°C, there is a gradual degradation that includes depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation. At higher temperatures (250–397°C), rapid volatilization occurs, causing the loss of H₂O, CO₂, and CO molecules with the formation of glucosan. The residue percentage is 13.08%.

The first stage of decomposition of Cello-g-poly(4-VP) lies between 170 and 205°C, during which the pendant grafted chains of poly(4-VP) are degraded up to 35% weight loss, beyond which the second stage of decomposition starts, goes up to 375°C, and continues up to 584.5°C with 45% weight loss. A

high percentage (26.67%) of residue is left after the degradation.

It can be observed from the table that the IDT (177.5°C) of the grafted polymer is much lower than that of the unmodified cellulose (319.35°C), and the FDT (375°C) of Cello-g-poly(4-VP) is higher than that of cellulose (360°C). DT of the grafted polymer is also lower than that of cellulose up to 50% weight loss, beyond which the DT values are much higher for 60% weight loss (440–366.77°C for cellulose) and 70% weight loss (545–393.87°C for cellulose). The lower IDT and DT values of the grafted cellulose up to 50% weight loss are due to the early decomposi-

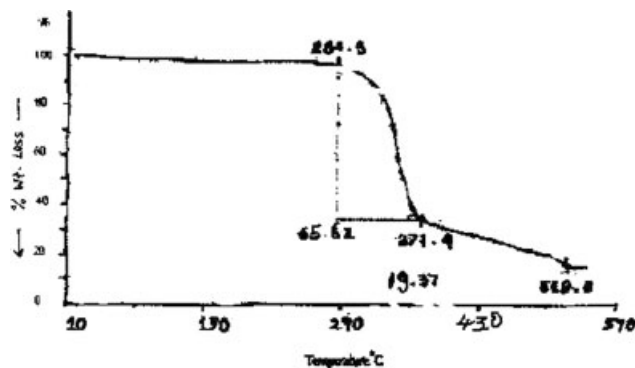


Figure 8 Primary thermogram of cellulose.

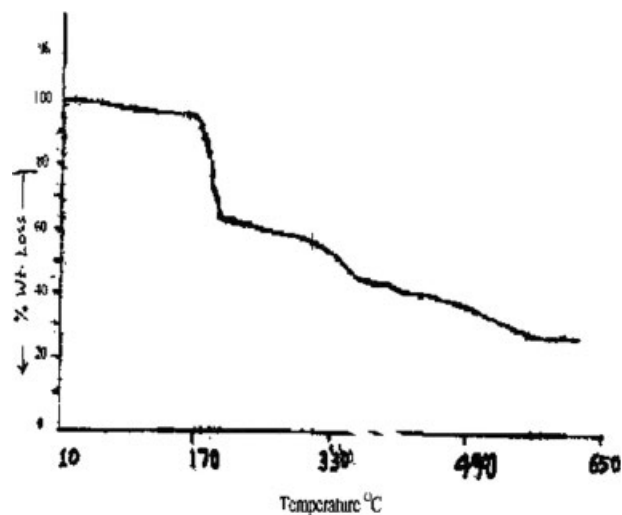


Figure 9 Primary thermogram of Cello-g-poly(4-VP).

TABLE IV
Primary Thermograms of Cellulose, Cello-g-Poly(4-VP)·HCl, and Cello-g-Poly(4-VP)·BH₃

Sample	IDT (°C)/ weight loss (%)	FDT (°C)/ weight loss (%)	DT at every 10% weight loss (°C)							Residue (%)		
			10%	20%	30%	40%	50%	60%	70%		80%	90%
Unmodified cellulose	319.35/4.28	360/65.62	330.65	339.68	346.45	350.97	353.23	366.77	393.87	500	—	13.08
Cello-g-poly(4-VP)	177.5/5	375/58.3	190	192.5	202.5	250	342.5	440	545	—	—	26.67
Cello-g-poly(4-VP)·HCl	192.5/11.07	200/51.43	170	191.25	192.50	195	197.5	231.25	307.5	—	—	23
Cello-g-poly(4-VP)·BH ₃	223.33/0.89	570/28.68	351.33	495.33	618	—	—	—	—	—	—	70.22

tion of the grafted poly(4-VP) chains. Similar observations were made during TGA of Teflon-FEP grafted with 4-VP.²⁷ It is further observed that the temperature difference between each 10% weight loss of cellulose up to 70% is very low, lying between 2.26 and 27.10°C, and from 70% weight loss to 80% weight loss, this difference increases to 106.13°C, indicating the formation of stable glucosan. In the case of the grafted sample, although the decomposition values are very low compared to that for unmodified cellulose, the temperature difference between each 10% weight loss is very high; beyond 30% weight loss, the difference lies between 47.5 and 105°C. These observations indicate that cellulose upon grafting attains stability toward increasing temperature. The higher residue percentage in the case of grafted cellulose also confirms the formation of the graft copolymer and its thermal stability.

The primary thermograms of Cello-g-poly(4-VP)·HCl and Cello-g-poly(4-VP)·BH₃ are presented in Figures 10 and 11, respectively. IDT, FDT, and DT at every 10% weight loss are presented in Table IV.

The primary thermogram of Cello-g-poly(4-VP)·HCl (Fig. 10) reveals that water desorption occurs between 75 and 120°C, beyond which it remains stable up to 190°C and then begins the initial decomposition (192.5°C). The loss of weight during this stage is very fast; the temperature difference between each 10% weight loss (from 20 to 50%) is only 1–2°C. After 50% weight loss, the final decomposition begins at 200°C, and the loss of weight is slow. The temperature difference between 50% weight loss and 60% weight loss increases to 33.75°C, and from 60 to 70% weight loss, the difference is quite high (75.25°C). It can be observed from the table that the IDT, FDT, and DT values of Cello-g-poly(4-VP)·HCl at every 10% weight loss are much lower than those observed for unmodified cellulose and 4-VP grafted cellulose. However, the residue percentage is much higher (23%) than that of the unmodified cellulose (13.08%) and is a little less than that of the grafted cellulose, that is, Cello-g-poly(4-VP) (26.67%).

A careful examination of the primary thermogram of Cello-g-poly(4-VP)·BH₃ (Fig. 11) reveals that the initial decomposition of the PS borane begins at a much lower temperature (223.33°C). However, further degradation with increasing temperature occurs at a very slow rate and low weight loss. The temperature difference between 10 and 20% weight loss and 20 and 30% weight loss is very large (144 and 122.67°C, respectively). With only 28.68% weight loss during the initial degradation, final decomposition begins at 570°C and continues up to 650°C, at which 70.22% residue is left.

From the thermal data, it is thus evident that the Cello-g-poly(4-VP)-supported borane is thermally

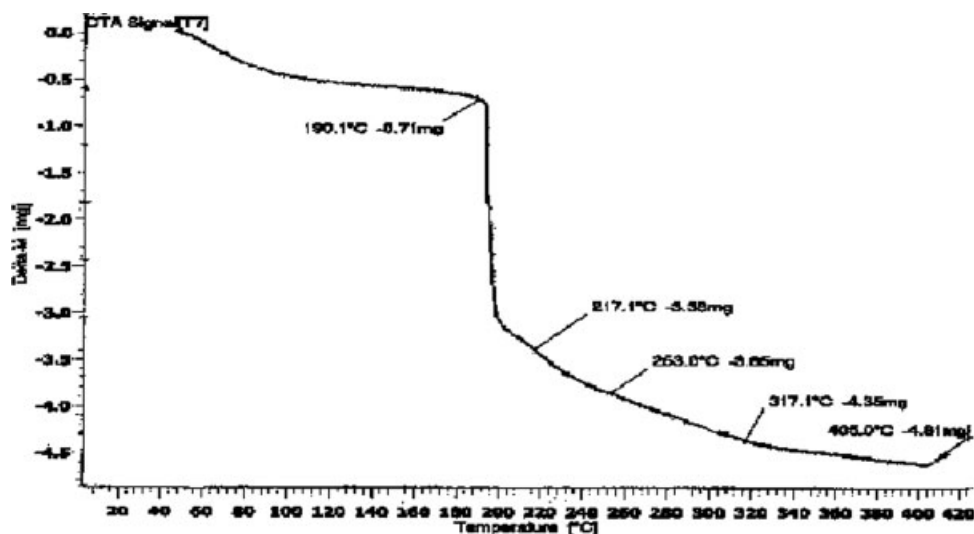


Figure 10 Primary thermogram of Cello-g-poly(4-VP)-HCl.

more stable than either the cellulose or the simple grafted cellulose, that is, Cello-g-poly(4-VP).

FTIR spectroscopic studies of reductions

The FTIR spectral data of the products obtained by the reduction of benzaldehyde (i.e., benzyl alcohol), cyclohexanone (i.e., cyclohexanol), crotonaldehyde (i.e., crotyl alcohol), acetone (i.e., 2-propanol), and furfural (i.e., furfuryl alcohol) are shown in Table V.

The IR spectra of benzyl alcohol, a product of benzaldehyde, shows distinct peaks for ν_{C-H} stretching ($3030\text{--}3060\text{ cm}^{-1}$), $\nu_{C=C}$ stretching (1591.7 cm^{-1}), and ν_{C-O} stretching (1207.6 cm^{-1}) and a broad band at 3344.5 cm^{-1} due to associated ν_{O-H} stretching. A characteristic peak for the benzaldehyde ν_{C-H} stretching at 2800 cm^{-1} is absent, and this confirms the successful reduction.

The ν_{C-O} stretching absorption in cyclohexanol, a product of cyclohexanone, occurs between 1139 and 1363 cm^{-1} . The ν_{O-H} stretching frequency can be observed at 3306.9 cm^{-1} .

The selectivity of this reagent in reducing aldehyde/ketone in the presence of a double bond was observed during the reduction of crotonaldehyde. The product, crotyl alcohol (Fig. 12), shows distinct peaks for ν_{C-H} stretching (2933.6 cm^{-1}) and $\nu_{C=C}$ stretching (1654.6 cm^{-1}) indicative of the presence of a double bond. Two peaks at $1215.6\text{--}1379$ and 1043.9 cm^{-1} due to ν_{C-O} stretching can be observed in addition to the peak at 3350 cm^{-1} due to ν_{O-H} stretching.

Reduction of acetone to 2-propanol shows ν_{C-O} stretching absorptions at 1186 cm^{-1} and ν_{O-H} stretching absorption at 3411 cm^{-1} .

The reduction of furfural also involves selective reduction of the aldehyde group to $-\text{CH}_2\text{OH}$, a pri-

mary alcoholic group, without disturbing the ring structure. Figure 13 shows that the peak due to the ν_{C-O} stretching of primary alcohol appears at 1278.2 cm^{-1} and the ν_{O-H} stretching absorption can be observed at 3527.9 cm^{-1} . The peaks at 3133.5 cm^{-1} due to ν_{C-H} stretching and characteristic peaks at 1567.9 , 1466.1 , and 1393.4 cm^{-1} due to the heteroaromatic ring structure of furan can be observed.

$^1\text{H-NMR}$ spectral studies of reductions

The $^1\text{H-NMR}$ spectra of the products (benzyl alcohol, cyclohexanol, 2-propanol, crotyl alcohol, and furfuryl alcohol) obtained by the reduction of corresponding aldehydes/ketones with Cello-g-poly(4-VP) $\cdot\text{BH}_3$ as a PS reducing agent were also obtained, and the respective spectra are presented in Figures 14 and 15.

The NMR spectra of benzyl alcohol (Fig. 14) obtained by the reduction of benzaldehyde shows a

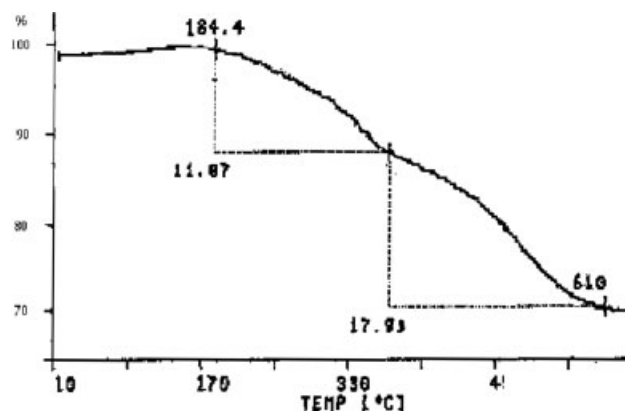


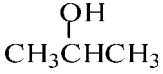
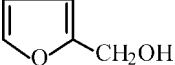


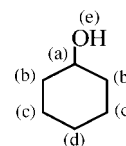
Figure 11 Primary thermogram of Cello-g-poly(4-VP) $\cdot\text{BH}_3$.

TABLE V
FTIR Spectral Data of Reduction Reactions

Product	C—H (ν , cm^{-1})	C=C (ν , cm^{-1})	C—O (ν , cm^{-1})	O—H (ν , cm^{-1})
	3030–3063	1591.7 (aromatic)	1207.6	3344.5
	2933.7		1139–1363	3306.9
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$	2933.6	1654.6	1215.6–1379, 1043.9	3350.0
	2978.3, 1375.6 (def.)		1186	3411
	3133.5		1278.2 (1° alcohol)	3527.9

characteristic singlet for the O—H proton at 4.68 δ , a multiplet for phenyl protons at 7.42 δ , and a singlet for methylene (CH_2) protons at 2.15 δ .

The NMR spectra of cyclohexanol (Fig. 15) show five characteristic peaks for the protons marked a to e in the diagram shown below. O—H (e) appears at 3.56 δ , the C—H proton (a) shows a quintet at 1.88 δ , the methylene protons (b) show a quartet at 1.72 δ , the CH_2 protons (c) show a quintet near 1.58 δ and the protons of CH_2 protons (d) show a quintet near 1.25 δ . All these peaks confirm the formation of cyclohexanol:



The NMR spectrum of 2-propanol shows three distinct signals due to three types of protons (a, b, and c in the diagram). The methyl protons (a) show a doublet at 1.20 δ . A septet appears at 2.65 δ due to the C—H proton, which is attached to a more electronegative oxygen atom and is therefore deshielded.

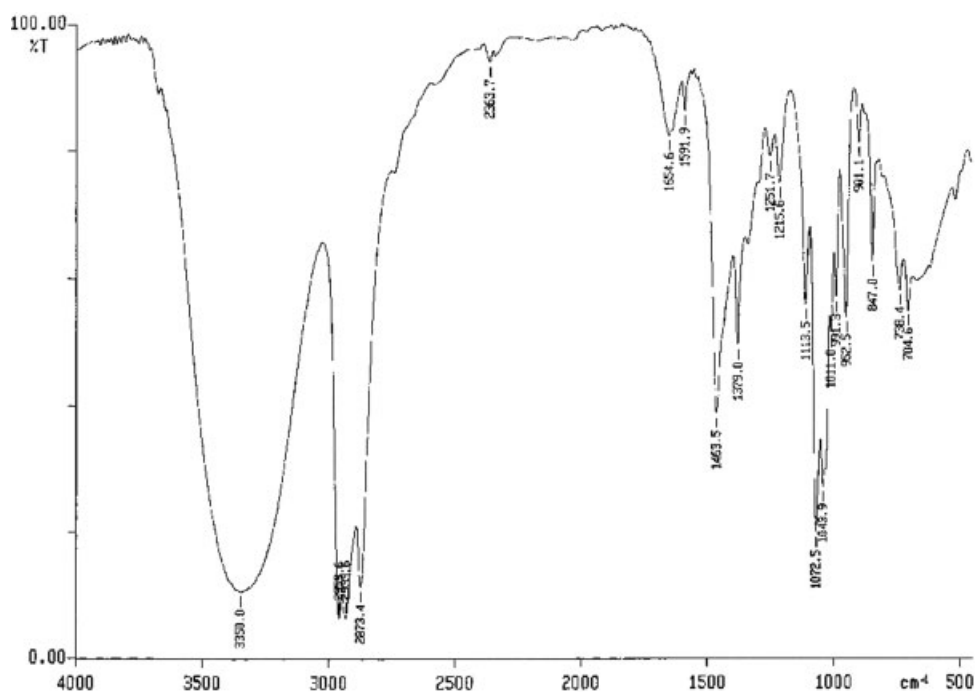


Figure 12 FTIR spectrum of crotyl alcohol.

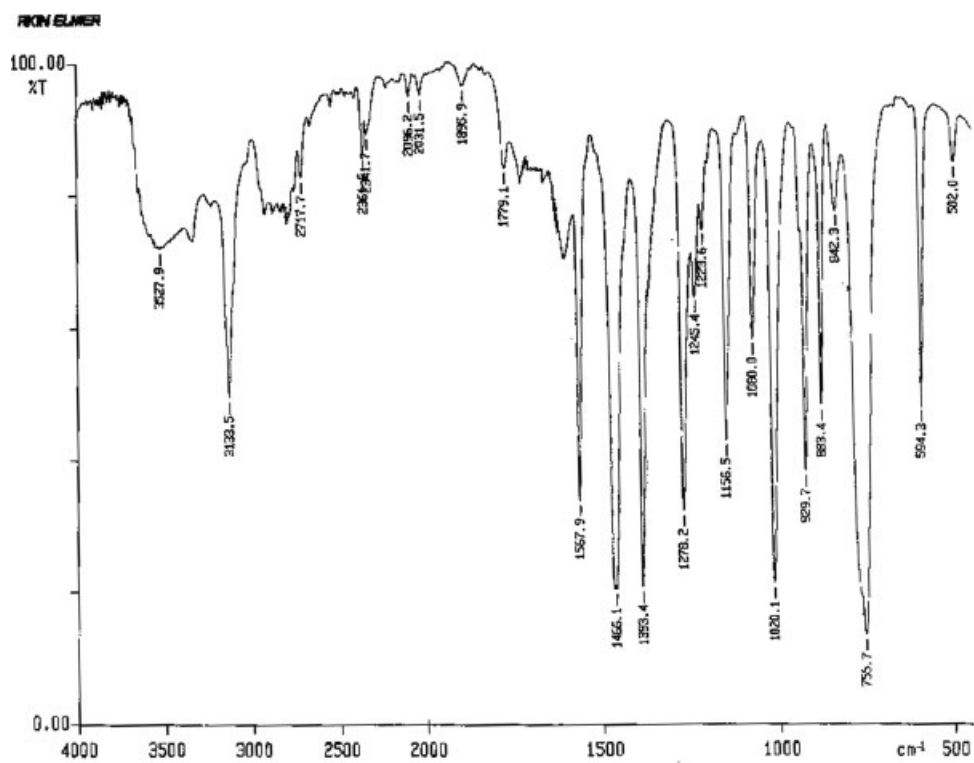


Figure 13 FTIR spectrum of furfuryl alcohol.

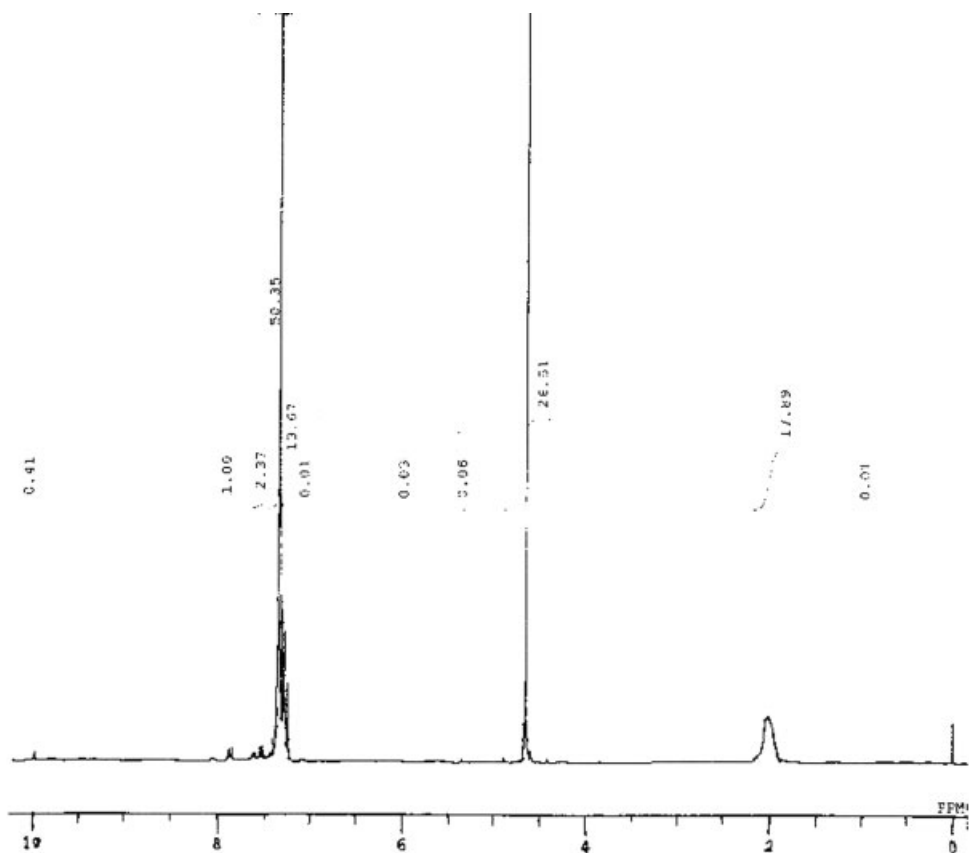


Figure 14 ¹H-NMR spectrum of benzyl alcohol.

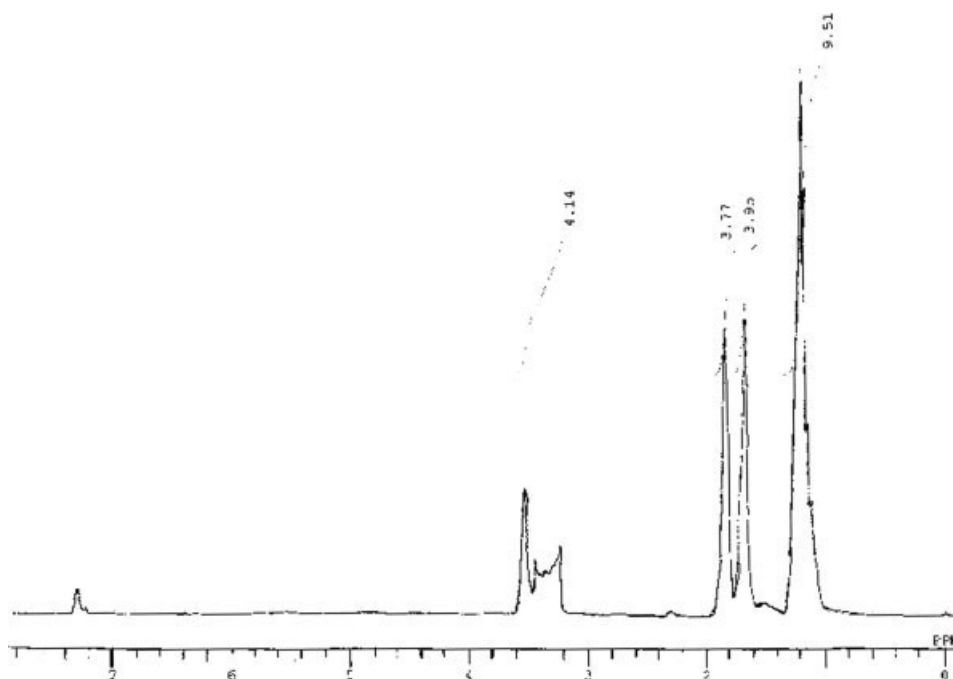


Figure 15 $^1\text{H-NMR}$ spectrum of cyclohexanol.

The proton of the hydroxyl group (c) appears as a singlet at 3.97 δ :

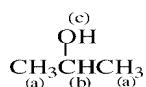


Table I shows that the reductions of benzaldehyde, cyclohexanone, acetone, crotonaldehyde, and furfural, carried out with Cello-g-poly(4-VP) $\cdot\text{BH}_3$, gave yields ranging from 24 to 71%. Acetone and furfural gave maximum yields (67.56 and 71%, respectively) in short reaction times of 3 and 4 h. However, the reduction of benzaldehyde gave only a 29.60% yield after 14 h. The reduction of benzaldehyde with poly(2-vinyl pyridine) borane and poly(4-VP) borane as the reducing reagents was successfully attempted by Menger et al.²⁸ and Hallensleben,²⁹ who obtained 65 and 14% yields in 3 and 4 h, respectively. The reduction of cyclohexanone by poly(2-vinyl pyridine) borane gave a 94% yield in 3 h, whereas with Cello-g-poly(4-VP) borane, the yield of cyclohexanol was 25% in 9 h.

The difference in the yields and reduction times observed during reductions can be attributed to the difference in the polymer carrying the reducing functionalities. Menger et al.²⁸ used poly(2-vinyl pyridine), whereas in this case, the reagent is based on cellulose grafted with poly(4-VP). As discussed earlier, the poly(4-VP) backbone shows sluggish behavior toward reactions with carbonyl groups and as such would have given lower yields in longer time periods.

The foregoing discussion of FTIR and $^1\text{H-NMR}$ of the different reduced products confirms that the reductions of aldehydes/ketones take place successfully with Cello-g-poly(4-VP) $\cdot\text{BH}_3$, and its selectivity is also confirmed by crotonaldehyde and furfural reductions.

Reusability/regeneration of Cello-g-poly(4-VP) $\cdot\text{BH}_3$

The PS reducing agent after drying was reused for the same reduction reactions without any treatment, and it was observed that it efficiently reduced the reactant, although the yield was a little low; for example, in the case of benzaldehyde reduction, the yield of benzyl alcohol obtained was only 23%, lower than that obtained with the fresh reagent (29.60%). The reagent, however, can be regenerated by washing with a very dilute HCl solution followed by washing with a very dilute NaOH solution and finally rinsing with distilled water. The washed polymer is treated with fresh NaBH_4 to give the regenerated PS reagent. This can be used as efficiently and effectively for the reduction reactions as the fresh resin.

CONCLUSIONS

The synthesis of a simple polymeric support from cellulose graft-copolymerized with 4-VP, that is, Cello-g-poly(4-VP), by a postgrafting reaction has been discussed. The respective polymeric reagent, Cello-g-poly(4-VP) $\cdot\text{BH}_3$, is used for the reduction of

some aldehydes/ketones such as benzaldehyde, crotonaldehyde, furfural, cyclohexanone, and acetone. This work comprises the synthesis and characterization of CellO-g-poly(4-VP) hydrochloride and CellO-g-poly(4-VP) borane from CellO-g-poly(4-VP) and the use of CellO-g-poly(4-VP) borane in different reduction reactions. The support can be still operative after its use and can also be easily regenerated for further reductions. The polymeric support also shows its selectivity by reducing crotonaldehyde and furfural to respective alcohols without disturbing the double bond and furan ring. Hence, we can conclude that this support is highly selective, can be reused efficiently, and can be regenerated for other reduction reactions.

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