Scientific Research

Synthesis, Characterization of Cellulose Grafted N-Oxide Reagent and Its Application in Oxidation of Alkyl/Aryl Halides

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Abstract

Oxidation of aliphatic and aromatic halides by N-oxide functionalities supported on 4-vinyl pyridine, (4-VP), grafted cellulose is reported in the present manuscript. Synthesis of graft copolymer of cellulose and poly 4-vinyl pyridine, poly(4-VP), has been carried out using ceric ions as redox initiator. Post-grafting treatment of CellO-g-poly(4-VP) with 30% H_2O_2 in acetic acid gives Cellulose-g-poly(4-VP) N-oxide, the polymeric supported oxidizing reagent. The polymeric support, CellO-g-poly(4-VP) N-oxide, has been used for oxidation of different alkyl/aryl halide such as 1-bromo-3-methyl butane, 2-bromo propane, 1-bromo heptane and benzyl chloride. The polymeric reagent was characterized by IR and thermo-gravimetric analysis. The oxidized products were characterized by FTIR and H^1NMR spectral methods. The reagent was reused for the oxidation of a fresh alkyl/aryl halides and it was observed that the polymeric reagent oxidizes the compounds successfully but with little lower product yield.

1. Introduction

Preparation of chemically modified polymer surfaces with controllable structures is an area of current research, having both theoretical and practical interest [1]. The objective is to devise mild techniques of primary surface functionalization with a high degree of chemo- and topological selectivity. The primary functional groups on the surface should be capable of undergoing a variety of organic chemical transformations under mild conditions, thus enabling creation of novel secondary surface functionalities.

Efficient methods for the conversion of alcohols to aldehydes, ketones or carboxylic acids under mild conditions have been developed, using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), (I), as a catalyst and

（I）
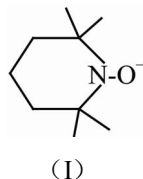
stoichiometric amounts of inexpensive, safe and easy to handle oxidants such as bleach [2], [bis(acetoxy) iodo] benzene (BAIB) [3], trichloroisocyanuricacid (TCCA) [4], oxone [5] or iodine [6].

However, separation of the products from TEMPO could require lengthy workup procedures, especially when reactions are run on large scale [7]. To solve this problem, TEMPO residue has been successfully immobilized to polymeric supports both inorganic [8] and organic polymers [9], affording heterogeneous catalysts which are readily separated from the reaction mixtures but are usually far less versatile than the homogeneous TEMPO [10]. The use of heterogeneous catalysts in the liquid phase, however, offers several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility and enhanced stability [11]. TEMPO anchored to poly (ethylene glycol) (PEG) has been prepared by Pozzi *et al.* [12] and its catalytic activity in the chemoselective oxidation of alcohols with stoichiometric amounts of organic or inorganic oxidants has been investigated. The PEG-TEMPO is a new metal free catalyst and exhibits high activity. It can be easily removed from

the reaction mixture and can be reutilized number of times.

Miyazawa and Endo [13] reported the synthesis of soluble and insoluble polystyrene type polymers featuring TEMPO residue and used it in combination with potassium ferricyanide in alkaline water/acetonitrile as solvent for the oxidation of benzyl alcohol to benzaldehyde at room temperature. Leadbeater and Scott [14] prepared a resin-bound cobalt phosphine complex and assessed its use in catalytic oxidation and acid anhydride synthesis. Gopinathan *et al.* [15] described a simple, mild and high yielding procedure for the iodination of allylic, benzylic and other primary alcohols using a combination of iodine imidazole on polymer supported triphenylphosphine. Poly(ethylene glycol) based aqueous biphasic systems (PEG-ABSs) have been investigated as tunable reaction media to control the oxidation of cyclohexene to adipic acid with hydrogen peroxide [16].

Divinyl benzene cross-linked polystyrene supported β-diketone linked complexes of Mn (II) have been prepared, characterized and their role as catalysts in the oxidation of alcohols by Cr (VI) has been invesitigated [17]. New reagents and polymer supported versions are highlighted which facilitate the use of hypervalent iodine compounds in oxidation and rearrangement reactions [18]. A three-step preparation of a polymer-supported iodoxybenzoic acid (PSIBX) reagent from poly(p-methyl styrene) has been reported and it was used for the efficient oxidation of a series of alcohols to the corresponding aldehydes [19]. An efficient procedure for the highly selective oxidation of leucomycines to the corresponding 16-membered 9- and 13-oxomacrolides using hypervalent iodine reagents in solution and on solid support has been reported [20].

A polymer support, (1-hydroxy-1,2-benziodoxol-3(1H)-one-1-oxide), was synthesized and used to oxidize alcohols selectively to the corresponding ketones and aldehydes [21].

It is well known that pyridine has wide applicability in organic synthesis by itself or in conjunction with other reagents. Both poly(2-vinyl pyridine) and poly(4-vinyl pyridine) form complexes with various transition metal ions [22,23]. Therefore, it seems that in case of grafted pyridines, the presence of pendant reactive pyridyl group nitrogen on the repeating unit of polyvinyl pyridine will make the grafted polymer useful as a reagent. Recently we reported on the oxidation and reduction reactions using polymer supported reagents developed from cellulose grafted with 4-vinyl pyridine [24].

Thus, it is evident from literature that different polymeric supports carrying specific functional groups are used for specific reactions. In view of this, in the present manuscript, synthesis of simple polymeric support from cellulose graft copolymerized with 4-vinyl pyridine *i.e.* Cellulose-g-poly (4-vinyl pyridine) carried out by post grafting reaction is discussed. The respective polymeric reagent was utilized for oxidation of some alkyl halides such as 1-bromo-3-methyl butane, 2-bromo propane and 1-bromo heptane and aryl halide such as benzyl chloride. Structure – reactivity relationship between the reactant and the reagent has been evaluated and discussed.

2. Experimental

2.1 Synthesis of Cellulose Based Poly(4-VP)

The details of the synthesis of 4-vinyl pyridine grafted cellulose has been discussed in our previous papers [24,25].

Optimum conditions pertaining to maximum percentage of grafting have been evaluated as a function of concentration of the initiator, monomer, and nitric acid, amount of water, time and temperature. Maximum percentage of grafting (585%) was obtained using 0.927 moles/L of 4-VP and 0.018 moles/L of ceric ammonium nitrate (CAN) in 120 min. at 45°C.

2.2 Synthesis of Cellulose Based N-oxide Reagent

1) Materials and Method

CellO-g-poly (4-VP), referred to as Resin I, was used as the base polymer. Acetic acid (Reagent Grade) and 30% H_2O_2 (S.D. Fine Chem. Ltd.) were used as received. Benzene-Methanol in different proportions was used as the solvent for TLC.

2) Procedure

A suspension of 1 gm of Resin I in 8 mL acetic acid was treated with 5.3 mL of H_2O_2 (30%) and kept at room temperature under stirring for 4h. After the stipulated time, the reagent, CellO-g-poly(4-VP) N-oxide, referred to as Resin II, was collected and dried.

2.3 Oxidation of Alkyl/Aryl Halides

The following general method was followed for the oxidation reactions:

Freshly prepared CellO-g-poly(4-VP) N-oxide, Resin II, 0.500 g in 10 mL of benzene was placed in a round bottomed flask and to this was added 5 mL of the reactant *i.e.* alkyl/aryl halide. The reaction mixture was heated under reflux and continuous stirring. The progress of the reaction was monitored on TLC. After the completion of the reaction, the resin was filtered off and the products were separated by fractional distillation.

3. Characterization

The characterization of CellO-g-poly(4-VP) N-oxide was carried out by FTIR spectroscopy and thermo gravimetric analysis (TGA) and was compared to that of cellulose and CellO-g-poly(4-VP). FTIR spectra have been obtained on Beckman spectrophotometer. TGA have been taken on LINSEIS, L 81-11 Germany made, in air at the heating rate of 10 ˚C/min. The oxidation products of alkyl/aryl halides to respective aldehydes/ketones have been characterized by IR and NMR spectroscopic methods. H^1NMR was obtained on JEOL FT-NMR AL 300 MHz Spectrophotometer.

3.1 FTIR Spectroscopy

The FTIR data of CellO-g-poly(4-VP) N-oxide (**Figure 1**), in addition to the regular bands due to v_{C-H} str. at 2952.3 cm^{-1} and v_{C-O} str. at 1352 - 1032 cm^{-1} of cellulose and $v_{C=C}$ and $v_{C=N}$ str. at 1644 - 1381 cm^{-1} of pyridine ring of grafted poly(4-VP) (**Table 1**), shows a characteristic peak for the ammonium salt *i.e.* at 2392.3 cm^{-1} which confirms that CellO-g-poly(4-VP) is converted into ammonium salt with oxide anion attached to it. In case of quaternization, the signal for $v_{C=N}$ is shifted from 1575.1 cm^{-1} to 1644.3 cm^{-1} and a new strong signal at 1209.2 cm^{-1} due to N-oxide has appeared, thus proving the chemical transformation. Similar observations were made by Zupan, Sket and Johar [25] during the studies on synthesis and preparation of cross-linked 4-vinyl pyridine-styrene-halogen complexes.

3.2 Thermo-gravimetric Analysis

The primary thermograms of cellulose, CellO-g-poly (4-VP) and CellO-g-poly(4-VP) N-oxide are compared. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10% weight loss are presented in **Table 2**. It is observed from the thermo grams that unmodified cellulose shows a single stage of decomposition
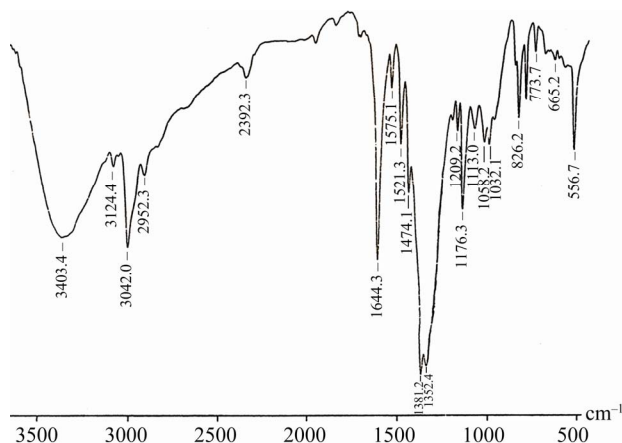

Figure 1. FTIR spectrum of CellO-g-poly(4-VP)N-oxide.

while the 4-VP grafted cellulose shows double stage of decomposition.

In case of the primary thermogram of cellulose the thermal degradation of cellulose proceeds essentially through two types of reactions. At lower temperatures *i.e.* between 120˚C - 250˚C, there is a gradual degradation, which includes depolymerization, hydrolysis, oxidation, dehydration and decarboxylation. At higher temperatures (250˚C - 397˚C), a rapid volatilization occurs losing H_2O, CO_2 and CO molecules with the formation of glucosan. The percent residue is 13.08%.

Thermal decomposition of grafted cellulose *i.e.* CellO-g-poly(4-VP) proceeds in two stages. The first stage of decomposition lying between 170˚C - 205˚C during which the pendant grafted chains of poly(4-VP) are degraded with up to 35% weight loss beyond which the second stage of decomposition starts and goes upto 375˚C and continues up to 584.5˚C with further loss of 45% weight. High percentage (26.67%) of residue is left after the decomposition.

In case of CellO-g-poly(4-VP) N-oxide (**Figure 2**), it is observed from the primary thermogram that the cellulose graft N-oxide shows a single stage decomposition as observed for cellulose. During the initial rise in temperature from 80˚C to 283.3˚C, from where the initial

Table 1. FTIR spectroscopy of CellO-g-poly(4-VP).

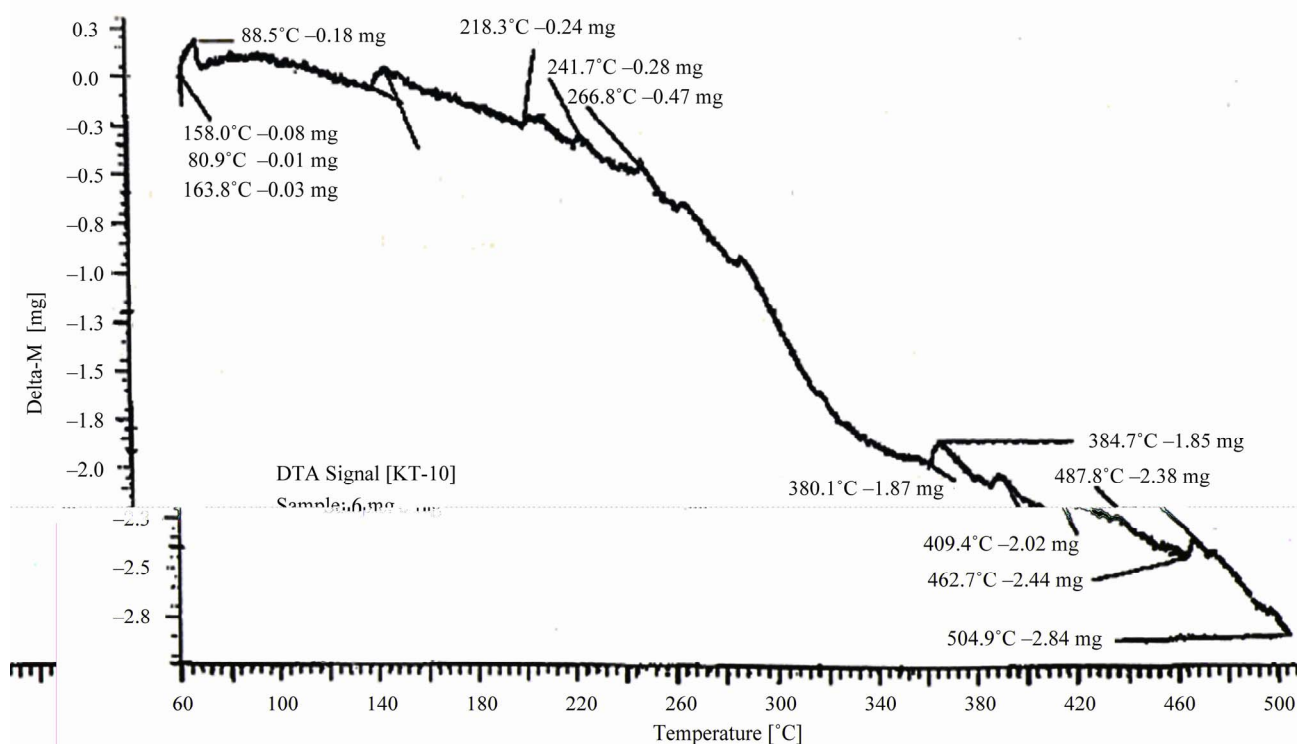| Sample	Structure	C-H v, cm^{-1}	=C-H v, cm^{-1}	C=C v, cm^{-1}	C=N v, cm^{-1}	C-O v, cm^{-1}
Cellulose		2902.5 1430.7 (def.) 1376.0 (def.)				1341-1029
CellO-g-poly(4-VP)			3043.2	1644.7 1521.4 1352.6	1644.7 1521.4 1352.6	1176-1031

Figure 2. Primay thermogram of CellO-g-poly(4-VP) N-oxide.

Table 2. Thermogravimetric data of cellulose and cellulose g-poly (4-VP) N-Oxide.

Sample	IDT (˚C) (%wt. Loss)	FDT (˚C) (%wt. Loss)	DT at every 10% wt. Loss (˚C)									Percent 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	500.00	-	13.08%
CellO-g-poly (4-VP) N-Oxide	283.3 (10.53%)	354.3 (32.11%)	271.43	315.7	348.57	462.85	-	-	-	-	-	52.66%

decomposition begins, the decomposition is very slow with a small loss in weight (10%). There may be some loss due to moisture desorption during this phase. Beyond the initial decomposition, (283.3˚C), the degradation is fast with a large temperature difference between each 10% wt, loss (44.27˚C between 10% to 20%, 32.87˚C between 20 to 30% and 117.28˚C between 30% to 40% wt. loss). The temperature difference between each 10% weight loss of cellulose up to 70% is very low, lying between 2.26˚C to 27.10˚C and moving from 70% weight loss to 80% weight loss this difference increases to 106.13˚C indicating the formation of stable glucosan. In case of the grafted sample, although the decomposition values are very low as compared to that for unmodified cellulose, the temperature difference between each 10% weight loss is very high, beyond 30% wt. loss the value difference lies between 47.5˚C to 105˚C.

Final decomposition begins at 354.3˚C with only 32.11% wt. loss. The percent residue left is very high (52.66%).
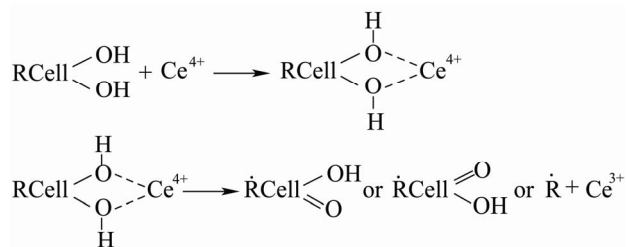
Higher DT values, large temperature difference between each 10% wt. loss and high percent residue indicate a very good thermal stability of CellO-g-poly(4-VP) N-oxide as compared to cellulose and CellO-g-poly (4-VP).
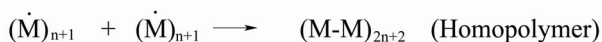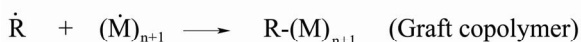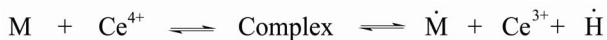
4. Results and Discussion

4.1 Synthesis of Polymeric Support

Synthesis of graft co-polymer of cellulose essentially involves generation of active sites on the cellulose backbone upon which a suitable monomer is polymerized. In

the present work grafting onto cellulose is carried out in the presence of 4-VP, by chemical method using CAN as redox initiator. The detailed mechanism has been discussed elsewhere [24]. In general the mechanism of the transition metal ion induced grafting process, where glycol groups are involved, using Ce(IV) salt, can be represented as follows:

$$RCell \overset{OH}{\underset{OH}{\diagdown}} + Ce^{4+} \longrightarrow RCell \overset{O}{\underset{O}{\diagdown}} \overset{H}{\underset{H}{\diagup}} Ce^{4+}$$

$$RCell \overset{O}{\underset{O}{\diagdown}} \overset{H}{\underset{H}{\diagdown}} Ce^{4+} \longrightarrow \dot{R}Cell \overset{OH}{\underset{O}{\diagdown}} \text{ or } \dot{R}Cell \overset{O}{\underset{OH}{\diagdown}} \text{ or } \dot{R} + Ce^{3+}$$

$$\dot{R} + M \longrightarrow \text{Graft copolymer}$$

The presence of radicals on the cellulose backbone has been confirmed by ESR measurements [26]. Monomer is also known to form complex with ions, which dissociate to give monomer radical that propagates to give polymeric chains. These growing polymeric chains attach to the radical site on cellulose to give graft copolymer or terminate to give homopolymer.

$$M + Ce^{4+} \rightleftharpoons \text{Complex} \rightleftharpoons \dot{M} + Ce^{3+} + \dot{H}$$

$$\dot{M} + nM \longrightarrow (\dot{M})_{n+1}$$

$$\dot{R} + (\dot{M})_{n+1} \longrightarrow R\text{-}(M)_{n+1} \quad \text{(Graft copolymer)}$$

$$(\dot{M})_{n+1} + (\dot{M})_{n+1} \longrightarrow (M\text{-}M)_{2n+2} \quad \text{(Homopolymer)}$$

The effect of different reaction parameters such as [CAN], [HNO$_3$], [4-VP], amount of water, temperature, and reaction time on percentage of grafting of 4-VP onto cellulose has been studied and maximum percentage of grafting (585%) was obtained at the following reaction conditions.
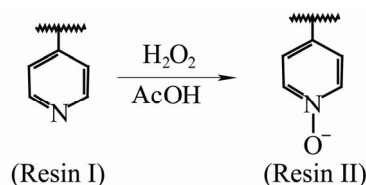
Table 3. Optimum conditions for grafting 4-vinyl pyridine onto cellulose.

Cellulose (g)	[CAN] (mol/L)	[HNO$_3$] (mol/L)	H$_2$O (mL)	Temp. (^{o}C)	Time (min.)	[4-VP] (mol/L)
0.200	0.018	0.797	20	45	120	0.927

On treatment 4-vinyl pyridine grafted cellulose, CellO-g-poly(4-VP), with H$_2$O$_2$/AcOH polymeric reagent, CellO-g-poly(4-VP) N-oxide was obtained and was used for the oxidation reactions.
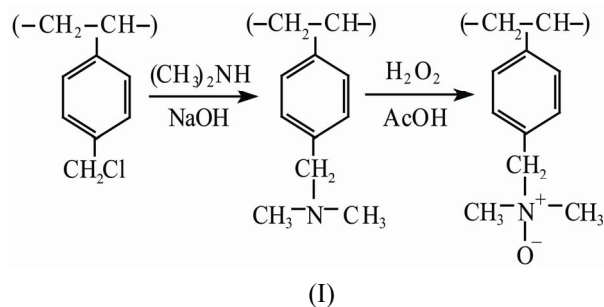

(Resin I)   (Resin II)

4.2 Oxidation Reactions

Oxidations of alkyl/aryl halides were carried out by CellO-g-poly(4-VP) N-oxide. The time of reaction, percent yield and Rf values for reactants and products are presented in **Table 4**.

Few reagents are available for the direct oxidation of alkyl halides into carbonyl compounds. Perhaps the best known reagent for this transformation is DMSO. Johnson and Pelter [27] showed that DMSO at 150˚C oxidized 1-iodooctane rapidly to aldehyde in 74% yield. Lower yields were obtained with secondary iodides or primary chlorides. By adding silver tetrafluoroborate to the reaction mixture Ganem and Boeckman [28] obtained 83% yield of octanal from 1-bromooctane. Another reagent which is available but is seldom used for this type of transformation is trimethylamine oxide [29]. This reagent is potentially very interesting but it affords only 30% - 50% yields of highly contaminated aldehydes from corresponding primary alkyl iodides. It also requires scrupulously anhydrous conditions.

Significant improvements in oxidation were achieved by using insoluble polymer, cross-linked polystyrene containing amine oxide group (I).

(I)

Table 4. Oxidation of alkyl/aryl halides using CellO-g-poly (4-VP) N-oxide, Resin II, as PS-oxidizing reagent: (Resin II = 500 mg, Solvent = 10 mL, Reactant = 5 mL).

Reactant	Product	Time (hrs.)	Rf values		Yield
			Reactant	Product	
Benzyl chloride	Benzaldehyde	18	------	0.75	53.4%
1-Br-3-methyl butane	3-Methyl butanal	24	0.47	0.22	30%
2-Bromopropane	Acetone	16	------	------	40%
1-Br-heptane	Heptanal	38	0.90	0.40	60%

Frechet and co-workers [30] used five fold excess of the polymeric N-oxide (I) for the oxidation of 1-bromoheptane and benzyl chloride to yield 87% and 95% of corresponding aldehydes at 70˚C. In the present work, N-oxide functionality supported on a polymeric backbone, CellO-g-poly(4-VP), to carry out oxidation of alkyl/aryl halides has been used. The percent yield of the corresponding aldehydes from 1-bromoheptane and benzyl chloride using CellO-g-poly(4-VP) N-oxide was 60% and 53.4% obtained in 38 h and 18 h respectively which was less than that obtained by using polymeric N-oxide (I). The low yield may be due to the reason that nitrogen carrying the oxygen is a part of the aromatic ring and thus behaves differently from its alkyl N-oxide (I) counterpart.

4.3 FTIR Spectroscopy of Oxidized Products

The FTIR spectra of benzaldehyde (**Figure 3**) obtained upon oxidation of benzyl chloride, 3-methyl butyraldehyde (**Figure 4**) from 1-bromo-3-methyl butane, acetone from 2-bromopropane and heptanal from 1-bromoheptane show characteristic peaks for aldehydes/ketones between 1637.2 - 1733.3 cm^{-1} due to $\nu_{C=O}$ str.. The aldehydic function of 3-methyl butyraldehyde and heptanal show a doublet for ν_{C-H} str. in the region between 2859 - 2962 cm^{-1}. Several bands in the range 1023 - 1386 cm^{-1} due to C-CHO skeletal structure are also observed.

4.4. H^{1}NMR Studies

In the H^{1}NMR spectrum of the benzaldehyde obtained by the oxidation of benzyl chloride, a characteristic singlet at 10.00 δ for aldehydic protons is observed in addition to the aromatic protons.

3-Methyl butyraldehyde obtained by the oxidation of 1-bromo-3-methyl butane, have four types of equivalent protons (marked as a, b, c and d).

$$\begin{array}{c} (a) \\ CH_3 \\ | \\ CH_3CHCH_2CHO \\ (a)\ (b)\ (c)\ \ (d) \end{array}$$
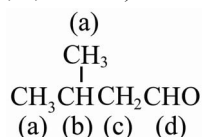
The H^{1}NMR spectrum accordingly reveals a doublet at 0.97 δ due to CH$_3$ (a) protons, a multiplet at 1.35 δ due to CH (b) proton and CH$_2$ (c) protons (not splitted) and a triplet at 10.00 δ for aldehydic proton (d).
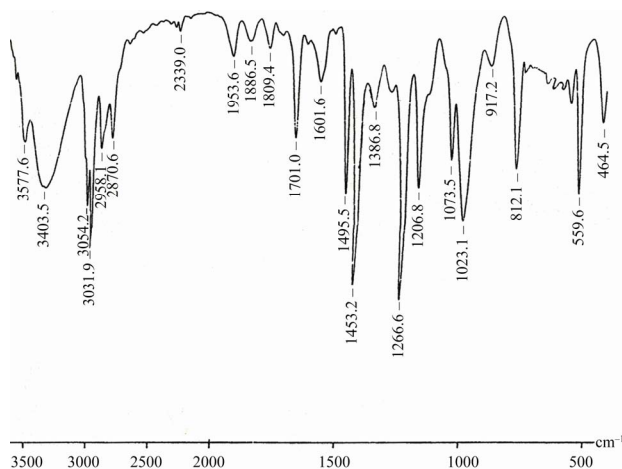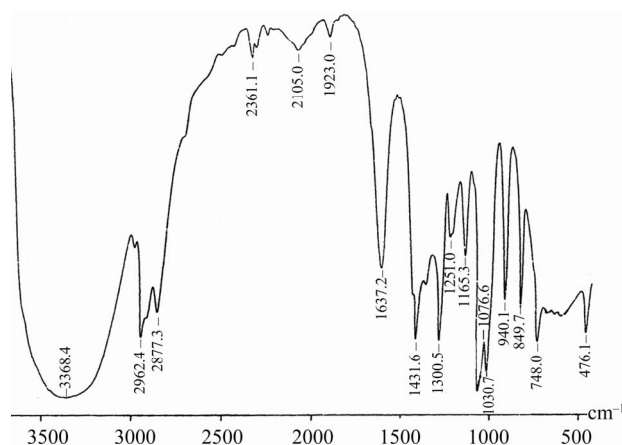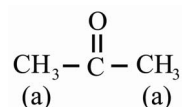

Figure 3. FTIR spectrum of benzaldehyde.

Figure 4. FTIR spectrum of 3-methyl butyraldehyde.

The H^{1}NMR spectrum of acetone, (**Figure 5**), obtained upon oxidation of 2-bromo propane shows a singlet at 1.20 δ, equivalent to 6H due to the methyl protons (a) attached to the carbonyl group.

$$\begin{array}{c} O \\ || \\ CH_3 - C - CH_3 \\ (a)\ \ \ \ \ \ \ \ (a) \end{array}$$

The H^{1}NMR spectra of heptanal obtained by the oxidation of 1-bromo heptane is shown in **Figure 6**. Characteristic triplet at 10.00 δ for aldehydic proton and peaks between 0.90 δ to 2.47 δ for alkyl chain of heptanal are observed. The splitting of the peaks is not so clear due to the overlapping of the peaks.

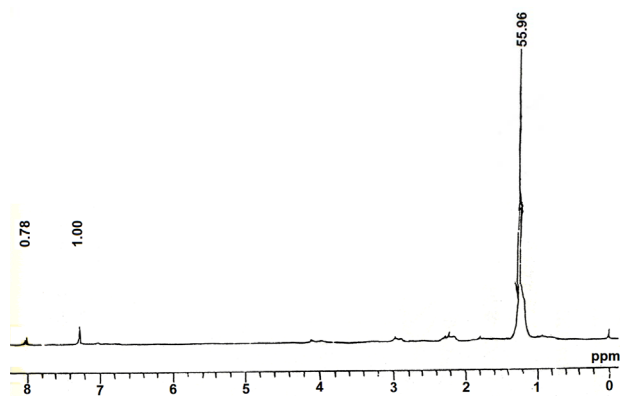From the above studies it is, thus, clear that successful
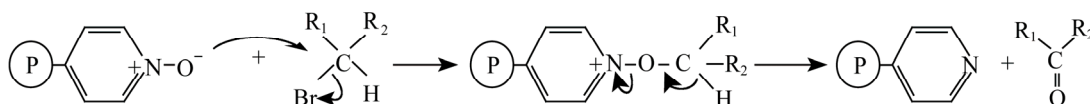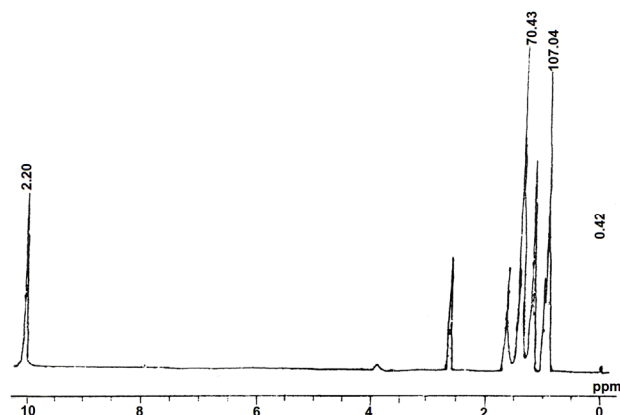
Figure 5. H1 NMR spectrum of acetone.

Figure 6. H1 NMR spectrum of heptanal.

oxidations of alkyl/aryl halides using CellO-g-poly(4-VP) N-oxide as PS-oxidizing reagent has been achieved.

5. Reusability of PS-oxidizing Reagents

In order to check that whether the polymeric support is reusable after the reaction, the PS-oxidizing reagents were reused after drying for the oxidation of benzyl chloride. It was observed that the reagent efficiently oxidized the reactant although the yield of the oxidation product was little low (46%) as compared to the yield (53.4%) obtained from freshly prepared polymeric reagent.

The PS-oxidizing reagent could also be easily regenerated by washing with very dilute HCl solution, fol-

lowed by very dilute NaOH solution and rinsing with water. The washed polymers were treated with subsequent simple organic reagents to introduce respective functional moieties such as N-oxide and then used for further oxidation reactions. **Table 5** shows the % yield of the products obtained by oxidation of benzyl chloride using the used CellO-g-poly(4-VP) N-oxide reagent and the regenerated CellO-g-poly(4-VP) N-oxide polymeric support. The data shows that the percent yield is less with the used PS-oxidizing reagent but it is almost regained after regenerating the polymeric support with respective oxidizing groups.

6. Conclusion

The synthesis of simple polymeric support from cellulose graft copolymerized with 4-vinyl pyridine *i.e.* cellulose-g-poly(4-vinyl pyridine) by carrying out post grafting reaction is discussed. The respective polymeric reagent *i.e.* CellO-g-poly(4-VP) N-oxide is utilized for oxidation of different alkyl/aryl halide such as 1-bromo-3-methyl butane, 2-bromo propane, 1-bromo heptane and benzyl chloride. The support can be reused and can also be easily regenerated for further oxidations.

7. References

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Table 5. Oxidation of benzyl chloride using used and regenerated CellO-g-poly(4-VP) N-oxide, Resin II, as PS-oxidizing reagent: (Resin II = 500 mg, Solvent = 10 mL, Reactant = 5 mL).

PS-oxidizing reagent	Reactant	Product	Time (hrs.)	Yield
CellO-g-poly(4-VP)N-oxide (untreated)	Benzyl chloride	Benzaldehyde	18	46%
CellO-g-poly(4-VP)N-oxide (treated)	Benzyl chloride	Benzaldehyde	18	52%

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