



Research Article

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Polymer-supported benzyltributylammonium borohydrides: Effect of nature of crosslinking and spacer group in reduction reactions

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ABSTRACT

Polystyrene-supported benzyltributylammonium borohydrides were prepared and the reducing properties of the reagents were studied in the reduction of aldehydes, ketones, esters and imines. The reagent exhibited chemoselectivity towards reduction of aldehydes in presence of ketones. The reducing efficiency of the reagent was optimized by investigating the effect of macromolecular characteristics of the polymer support like nature and extent of crosslinking, presence of spacer groups etc. on the reduction of 4-nitrobenzaldehyde to 4-nitrobenzyl alcohol. The progress of the reaction was monitored spectrophotometrically at λ_{max} 252 nm. The effect of the reaction conditions like temp, solvent used and the concentration of the polymeric reducing agent were also analyzed. The reducing agent derived from 2 % butanediol dimethacrylate crosslinked polystyrene resin with a PEG (600) chain spacer between the polymer backbone and the borohydride moiety, was found to be the optimum reagent. DCM and THF were found to be ideal solvents for reduction and maximum rate was found at 55°C in THF. The substrates were reduced at faster rates by the polymer bound borohydride reagents in presence of acid catalysts.

Key words: Polymer supported reducing agents, borohydride and aldehyde.

INTRODUCTION

Polymer supported quaternary ammonium borohydride reagents form an important class of polymeric reducing agent and play a significant role in organic synthetic reactions. Polymer-bound quaternary ammonium borohydride was first developed by Gibson *et al.* for the reduction of aldehydes to primary alcohols [1]. There are many reports on polymer bound borohydride reagents for the reduction of various functional groups viz. reduction of aryl azides and aryl sulfonyl azides [2]. The resin bound analogue of borohydride has also been used in the rapid reduction of conjugated olefinic bonds in high yield and in the conversion of nitroalkenes to nitroalkanes [3-5]. Coordination polymer of zinc borohydride with pyrazine was reported as a stable and reliable reducing agent [6]. Janda and coworkers have reported the use of soluble polymer-bound borohydride reagents in ozonide reduction [7]. Crosslinked chitosan supported borohydride developed by Caiquin and was found to be effective in the reduction of aldehydes and ketones to the corresponding alcohols [8]. Polymer bound crown ether/tin hydride complex is used in the reduction of alkyl halides [9]. Carboxylic acids were reduced to alcohols using borohydride exchange resin in the presence of cyanuric acid [10]. Bhattacharya *et al.* have developed a polymer supported triacetoxyborohydride for the reductive amination of aldehydes and ketones [11]. Reduction reactions with quaternary ammonium borohydrides in presence of several transition metal ions have also been reported [12-20]. We have reported the synthesis of quaternary ammonium chloride resins and their phase transfer catalytic activity in halogen exchange reactions [21]. In this paper we discuss the synthesis and optimization studies of polystyrene supported benzyltributylammonium borohydrides for the reduction of carbonyl compounds especially aldehydes to primary alcohols.

EXPERIMENTAL SECTION

Poly(vinyl alcohol) (PVA; molecular weight = 72,000–1, 00,000) and 1, 4-butanediol dimethacrylate (BDDMA) were supplied by Aldrich Co. (USA). Styrene was provided by Fluka AG (Switzerland). Sodium borohydride, N, N-dimethylformamide (DMF), and tributylamine (TBA) were purchased from E-Merck (Germany). AR grade solvents were used after distillation and purification according to literature procedures.

Fourier transform infrared spectra were recorded on a Shimadzu IR 470 spectrophotometer with KBr pellets. Spectrophotometric studies were carried out using Shimadzu UV-170 H spectrophotometer. Thermo-gravimetric analysis was carried out on a Delta series TGA-7 and on a Shimadzu D-40 thermal analyzer.

Preparation of DVB- and BDDMA-crosslinked styrene copolymers

A mixture of styrene (11.2 mL, 98 mmol), DVB (0.476 mL, 2 mmol), toluene (20 mL) and benzoyl peroxide (500 mg) was suspended in a 1% aqueous solution of PVA (350 mL) and kept mechanically stirred at 600 rpm under a nitrogen atmosphere at 85°C. After 6 h, the beaded resin was filtered and washed with hot water to remove PVA. The polymer was then subjected to Soxhlet extraction with acetone followed by methanol to remove linear polymers and low-molecular-weight products. The polymer beads were dried and meshed to the 200–400 range. For the preparation of BDDMA-PS, BDDMA (0.44 mL) was added instead of DVB and the same procedure was employed.

Chloromethylation of DVB- and BDDMA-crosslinked styrene copolymers

The dry resin (5 g) was swollen in dichloromethane (DCM; 25 mL) and to the swollen resin chloromethyl methyl ether (25 mL) and freshly prepared ZnCl₂ in THF (0.1M, 0.3 mL) were added. The mixture was refluxed at 60 °C for 8 h. After the reaction the resin was filtered, washed with THF, THF/H₂O (1: 1), THF/HCl (1: 1) and hot water until it was free from chloride and finally washed with methanol. The resulting resin was further purified by Soxhlet extraction with THF. The chlorine capacities of the resins were determined by Volhard's titrimetric method.

Preparation of PEG grafted polystyrene

To a suspension of chloromethylpolystyrene (BDDMA-PS-CH₂Cl, 5g, 2.40mmol Cl/g) swelled in THF (30 mL) monosodium derivative of PEG₆₀₀ (5 g) in dried THF (25mL) was added. The mixture was heated under reflux for 42 h. The resin was filtered, washed with water, (5×10 mL) dioxane, methanol and acetone and dried under vacuum to constant weight. The hydroxyl capacity was estimated by acetylation method. Following the same procedure PEG grafted DVB-PS polymer was prepared.

Preparation of PS-PEG –CH₂Cl resin

PS-PEG resin (5g) was refluxed with thionyl chloride (15 mL) on a water bath for 3h in a fume- hood until the evolution of HCl vapors ceased. The reaction mixture was cooled, filtered at the pump, washed with DCM and acetone and dried under vacuum. The chlorine capacity of the resin was determined by the Volhard's method.

Preparation of polymer-supported benzyltributylammonium chloride

To a suspension of chloromethylated DVB-PS resin (1 g, 2.40 mmol Cl) in DMF (15 mL), TBA (3.85 mL, 5 molar excess) was added and the reaction mixture was stirred at 80°C. The quaternization reaction was followed by determining the free chloride liberated. The reaction was found to be completed after 24 h (**Table 1**). The polymer beads were filtered and washed with DMF (5 -15 mL), DMF/water (1: 1 v/v, 5-15 mL), water and finally with methanol (5 -10 mL). The polymer-bound catalysts derived from other chloromethyl resins were carried out by the same procedure.

Preparation of polymer bound quaternary ammonium borohydride reagent P1-P4

Benzyltributylammonium chloride resin (1g) was swelled in DMF (10mL) and NaBH₄ (100 mg) in DMF (10mL) was added to the swollen resin. The reaction mixture was stirred at room temperature till the reaction was complete. Polymer bound borohydride reagent formed was filtered, washed with DMF (5 x 15 mL), DMF: H₂O (5 x 15mL; 1:1, V/V), H₂O (5 x 15 mL), acetone (5 x 15 mL) and methanol (5 x 15mL) and dried.

Estimation of BH₄⁻ capacity

Borohydride resin (50mg) was suspended in THF (5mL) and iodine in KI solution (5mL) was added. The mixture was shaken well and titrated against standard sodium thiosulphate solution using starch solution indicator. A blank was also performed and the BH₄⁻ capacity was calculated. Results are given in **Table 1**.

Reduction reactions using borohydride reagent: General procedure

To a suspension of the polymer bound borohydride reagent (1g) in DCM (15mL), the substrate (1 mmol) was added and shaken at room temperature. The progress of the reaction was followed by TLC. After the completion of the reaction, the reaction mixture was filtered and washed with DCM (3x5mL) to remove the spent polymer. The combined filtrate and washings on evaporation afforded the product alcohol. The same procedure was adopted for the reduction of various aldehydes, ketones, imines and esters using the polymer bound reagents, **P1 -P4**. Details are given in **Table 3**.

Selective reduction of benzaldehyde in the presence of acetophenone

The polymer bound borohydride reagent (1g) was swelled in DCM(15mL) and a mixture of benzaldehyde (0.1mL, 1mmol) and acetophenone (0.12 mL, 1mmol) was added and the reaction mixture was shaken at room temperature. The extent of reaction was followed by TLC. Details are given in **Table 4**.

Kinetics of reduction of 4-nitrobenzaldehyde with polymer supported borohydride reagent

To a suspension of borohydride resin (**P1**, 0.1g) in DCM (10 mL), 4-nitrobenzaldehyde (0.015g, 0.1mmol) in DCM (5 mL) was added and shaken. The reaction mixture (0.1 mL) was withdrawn at different time intervals. The solutions were diluted to 5mL and optical densities at λ_{\max} 252nm were measured spectrophotometrically. A standard curve was obtained and the percentage conversion at each time interval was calculated from the standard curve. The experiment was repeated with reagents **P2**, **P3** and **P4**. **Fig. 3** shows percentage conversion of 4-nitrobenzaldehyde to 4-nitrobenzyl alcohol at different time intervals.

Effect of various parameters on the reactivity of polymer bound borohydride reagent**Temperature**

Polymer bound borohydride reagent (**P4**, 500mg) was swelled in toluene (15mL) and was shaken with 4-nitrobenzaldehyde (10mg) in DCM (10 mL) at room temperature (27°C). The reaction was followed by TLC. Time taken for the complete reaction was noted. The reaction was repeated at different temperatures and at refluxing temperature. The results are depicted in **Fig 4**.

Effect of acid catalyst on the reactivity of polymer bound reagent

To a solution of 4-nitrobenzaldehyde (20 mg) in DCM (10mL), 10% glacial acetic acid (0.1mL) was added and the reaction mixture was added to the polymer bound borohydride reagent (500mg) swollen in DCM (15mL). Stirred at room temperature and the reaction was followed by TLC. Time for complete reduction was noted. Other aldehydes were also reduced in the presence of acid by polymeric borohydride reagent and the details are given in **Table 6**.

Recycling

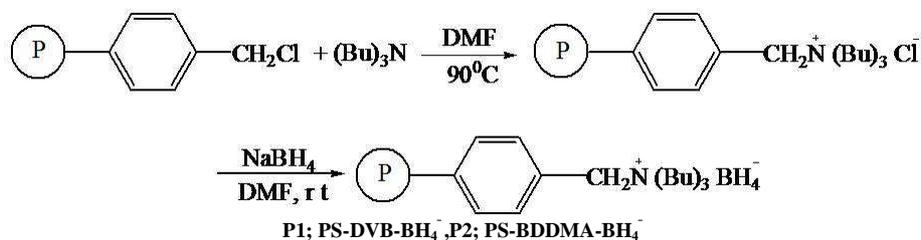
The spent resin after the separation of product was washed thoroughly with DCM (3x5mL) followed by acetone (3x5mL) and methanol (3x5mL) and dried in vacuum. The spent resin (1g) was swelled in DMF (15mL), added NaBH₄ (1g) in DMF (15mL) and shaken well for 5h. Filtered, washed with DMF (3x5mL), DMF-water, water, methanol and acetone and dried. The borohydride capacities of the resins were estimated by iodometric titration. The recycled resin (1g) was swelled in DCM (15mL) and added 4-nitrobenzaldehyde and stirred at room temperature. Time for reduction was almost same as that of fresh resin. Results are summarized in **Table 7**.

RESULTS AND DISCUSSION

Polymer supported quaternary ammonium salts are used widely as reagents and catalysts in a number of organic reactions. We have synthesized polystyrene supported benzyltrialkylammonium chlorides with different structural characteristics and investigated their phase transfer catalytic activity in halogen exchange reactions. Optimization studies were carried out by investigating the macromolecular characteristics of the polymer support like nature and extent of crosslinking, presence of spacer groups, nature of the trialkylamine etc. and the reaction conditions like temperature, nature of the solvent, concentration of the catalyst etc. to develop an efficient polymeric phase transfer catalyst. These polymer bound benzyltrialkylammonium chlorides on treatment with sodium borohydride at room temperature afforded the corresponding polymer bound benzyltrialkylammonium borohydrides which were found to reduce aldehydes and ketones effectively under mild conditions.

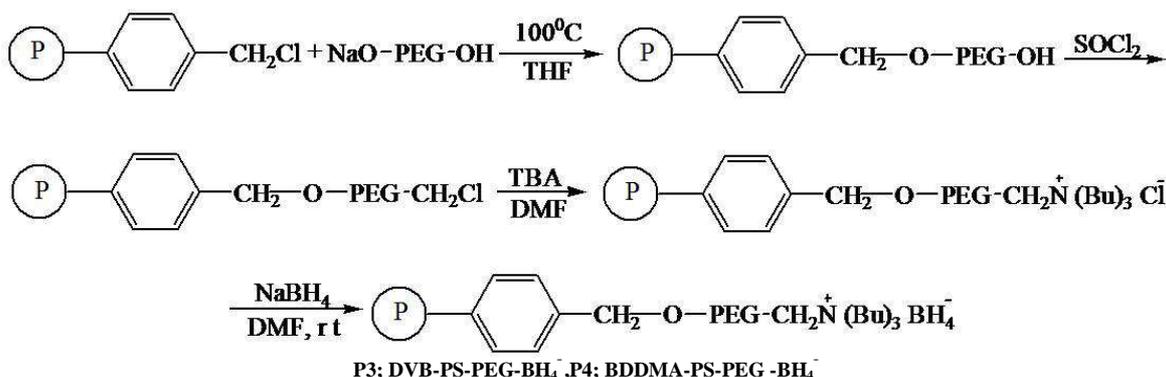
Preparation and characterization of polymer bound borohydride reagents P1 - P4

The polymeric reagents were prepared starting with chloromethylpolystyrenes (2% BDDMA-PS&2% DVB-PS) which were converted to polymer bound benzyltributylammonium chlorides by treating with tributylamine in DMF solvent at 90 °C. A suspension of the quaternary ammonium chloride resin in DMF was treated with sodium borohydride at room temperature to form the corresponding quaternary ammonium borohydride (Scheme 1).



Scheme 1. Preparation of polymer supported borohydride reagent

Polystyrene-polyethylene glycol graft copolymers (BDDMA-PS-PEG & DVB-PS-PEG) were used as the supports for the preparation of the polymer bound reducing agent. Preparation of PEG-grafted polystyrene supported reagents P3 and P4 are given in Scheme 2.



Scheme 2. Preparation of PS-PEG graft quaternary ammonium borohydride

The progress of the formation of the borohydride reagent was followed by estimating the liberated chloride ions titrimetrically. The results obtained revealed complete replacement of Cl⁻ ions with BH₄⁻ ions. The borohydride capacity of the resin was determined by iodometric method and the values are in good agreement with the quantity of Cl⁻ liberated. Details of the reagents are given in Table 1. From the table it is clear that the time for the complete exchange of Cl⁻ with BH₄⁻ is maximum for the DVB-PS resin supported reagent P1 (10 h). For the polymer P2, the exchange time is 5 h. The rigidity and hydrophobicity imparted to the polymer by DVB crosslinks reduce the diffusion of the polar BH₄⁻ ions into polymer matrix for the exchange reaction.

Table 1: Preparation of PS & PS -PEG bound borohydride reagents

Polymeric reagent	Time for complete exchange (h)	Cl ⁻ capacity mmol/g	BH ₄ ⁻ capacity mmol/g
P1, PS-DVB-BH ₄ ⁻	10	2.41	2.52
P2, PS-BDDMA-BH ₄ ⁻	5	2.82	2.95
P3, PS-PEG-DVB-BH ₄ ⁻	6	1.98	1.99
P4, PS-PEG-BDDMA-BH ₄ ⁻	3	2.15	2.18

The BDDMA crosslinks are comparatively polar and flexible and enhance the accessibility of the reactive sites thereby reducing the exchange time. In the case of spacer modified polymers also reaction period is more for the DVB crosslinked polymer P3 than BDDMA crosslinked polymer P4. Further P3 is less reactive than P2 (BDDMA-PS) but less than P1, DVB-PS polymer without PEG spacer. The spacer group keeps the reactive sites distant from the polymer network and make more accessible to the soluble reagents. Polymer P4 with BDDMA crosslinks and PEG spacer exhibited lowest exchange time.

Characterization of polymer bound borohydride reagents

The polymeric borohydride reagents were characterized by IR spectroscopy (Fig. 1). The spectrum showed characteristic B-H stretching band at 2345 cm^{-1} and B-H in-plane deformation at 1178 cm^{-1} . The borohydride capacities of the polymers were determined by iodometric method.

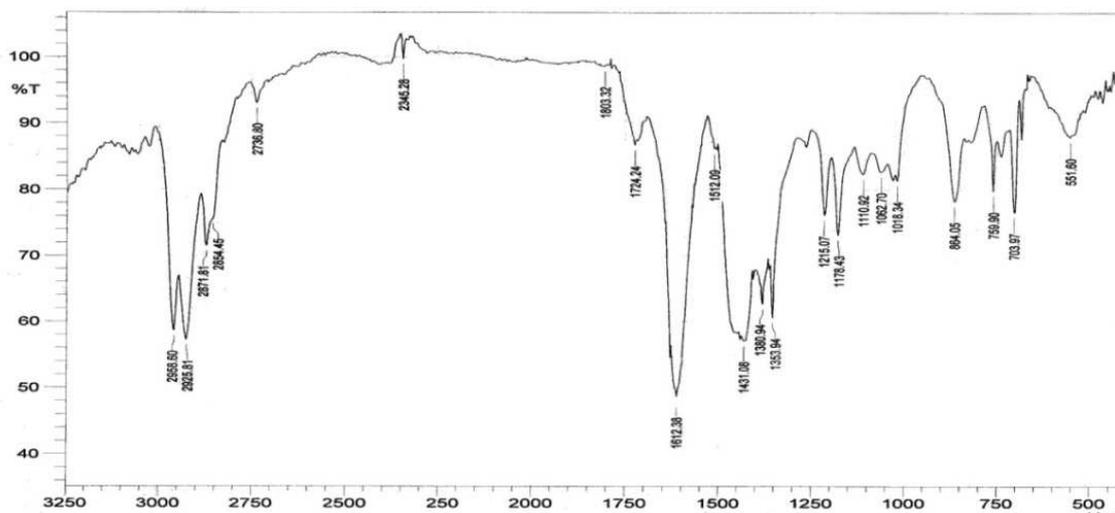


Fig. 1. IR spectrum of 2% BDDMA-PS- $\text{N}^+\text{Bu}_3\text{BH}_4^-$

Stability of the borohydride reagent

The stability of the BDDMA-PS supported benzyltributylammonium borohydride reagent was studied using thermogravimetric analysis.

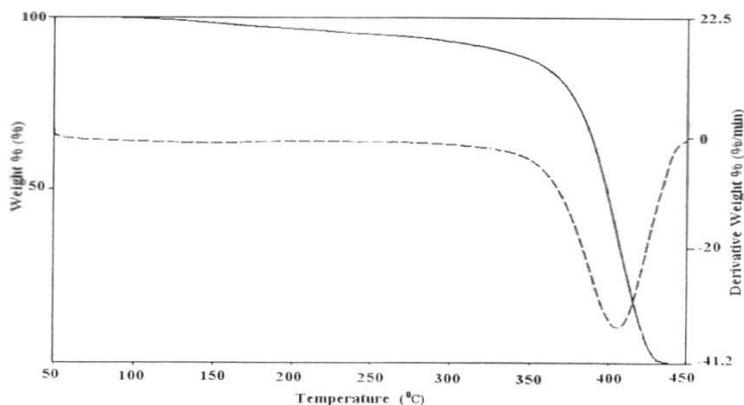


Fig. 2. Thermogram of 2% BDDMA-PS- $\text{N}^+\text{Bu}_3\text{BH}_4^-$

Initially there was a small weight loss which may be due to removal of absorbed water. The thermogram shows that the decomposition of the borohydride reagent starts at 370°C (Fig. 2). After that there is gradual decomposition of the reagent.

Swelling Studies

The immobilized functional groups on the polymeric supports can significantly affect the swelling properties of the polymer matrix. The swelling properties of polymer supported reagents may change considerably as one functional group is transformed into another. Thus the choice of the reaction solvents is crucial in polymer supported reaction and optimum solvent may not be the same one as that commonly used in analogous reactions using low molecular mass reactants.

Table 2: Swelling capacities of polymer bound borohydride reagents P1-P4

Solvents	Swelling capacity (mL/g)			
	P1	P2	P3	P4
THF	5.15	7.66	7.72	8.71
DCM	5.17	7.70	7.81	8.23
DMF	5.12	8.39	8.47	8.58
Toluene	4.92	7.52	7.65	7.78
Methanol	2.14	3.72	3.86	3.98
Water	2.02	3.42	3.56	3.67

The solvation properties of the polymer bound borohydride reagents were investigated in a number of solvents. The reagents exhibit increased swelling capacities in THF, DMF, methanol and water compared to the corresponding chloromethyl and the quaternary ammonium chloride resins due to increased polarity of the borohydride moiety. DCM was used as the reaction medium in all cases due to good swelling of the polymeric reagent in the solvent and easy recovery of the products after reaction. The swelling capacities of the borohydride reagents are given in **Table 2**.

Reduction studies using polymer bound borohydride reagent

The reduction reactions of carbonyl compounds and imines with polymer bound borohydride reagent were carried out at room temperature. In all cases, substrate and polymeric reducing agent were taken in 1:2 molar ratio.

A suspension of the polymer bound reagent in DCM was shaken with the substrate. The progress of the reaction was followed by TLC. After the completion of the reaction the spent polymer was removed by filtration and washed with suitable solvents and the combined filtrate and washings on evaporation yielded the product alcohol. Imino compounds were reduced to amines using the polymeric reducing agent. The results are summarized in **Table 3**. Aldehydes were reduced in shorter reaction periods compared to ketones and esters, but reduction of imines took minimum reaction periods. In the reduction of substituted aldehydes with polymer bound borohydride reagent, as expected, substrates with electron withdrawing substituents like $-\text{NO}_2$, $-\text{CN}$ etc. were found to be reduced at faster rates. Similarly decreased reaction rate was observed in the case of aldehydes having electron donating substituent such as methoxy group.

Cinnamaldehyde was reduced to cinnamyl alcohol without affecting the double bond. In cinnamaldehyde increased reaction period was observed due to reduced reactivity of the conjugated carbonyl group. The reduction of esters required prolonged reaction periods and traces of the starting esters found in TLC after 40 h in the case polymer reagent **P1**.

Table 3: Reduction reactions using polymer bound borohydride reagents

Substrate	Product	Time for reduction (h)			
		P1	P2	P3	P4
Benzaldehyde	Benzyl alcohol	18	11	6	4
4-Nitrobenzaldehyde	2-Nitrobenzyl alcohol	14	8	5	3
4-Cyanobenzaldehyde	4-Cyanobenzyl alcohol	14	8	5	3
4-Methoxybenzaldehyde	4-Methoxybenzyl alcohol	24	17	14	10
Cinnamaldehyde	Cinnamyl alcohol	25	18	15	12
Acetophenone	1-Phenylethanol	30	20	18	15
Benzophenone	Benzhydrol	29	19	16	12
Methyl salicylate	o-Hydroxybenzyl alcohol	40*	29	22	18
Ethyl benzoate	Benzyl alcohol	35	25	21	16
N-benzylideneaniline	Aniline	10	5	4	2
N-(4-methylphenyl)-N-(phenylmethylidene)amine	p-Toluidine	15	9	6	4
N-(4-methoxyphenylmethylidene)-N-(4-methylphenyl)amine	p-Toluidine	22	14	10	8
Phenyl benzoate	Phenol	40*	33	30	28
Naphthyl benzoate	2-Naphthol	40*	34	32	30

*Complete reaction was not observed, traces of starting esters found in TLC after 40 h.

Chemoselectivity in the reduction of carbonyl compound

The selectivity of the polymer bound borohydride reagent was investigated in the reduction of 1:1 molar mixture of benzaldehyde and acetophenone with a two molar excess of the polymeric reducing agents in dichloromethane. In the case of polymer **P1**, benzaldehyde was reduced completely in 18 h and no

acetophenone was reduced even after 22 h. With reagents **P2** and **P4** complete reduction of benzaldehyde was observed within 11 h and no reduction of acetophenone was observed before the reduction of benzaldehyde. With **P4** benzaldehyde was first reduced (4 h) but reduction of acetophenone was also observed after 15 h when a 2 molar excess of the reagent was used. Results are summarized in **Table 4**.

Table 4: Chemoselectivity in the reduction of carbonyl compound

Reagent resin	Reaction time (h)	Percentage of benzaldehyde	Percentage of acetophenone
DVB-PS-BH ₄ ⁻	0	100	100
	18	0	100
DVB-PS-PEG-BH ₄ ⁻	0	100	100
	11	0	100
BDDMA-PS-BH ₄ ⁻	0	100	100
	11	0	100
BDDMA-PS-PEG-BH ₄ ⁻	0	100	100
	4	0	100

Kinetics of reduction of 4-nitrobenzaldehyde

The reduction studies of polymer bound borohydride reagent was done in a quantitative way by following the reduction of 4-nitrobenzaldehyde spectrophotometrically. The extent of conversion of 4-nitrobenzaldehyde with polymer bound borohydride reagent at different time intervals was determined by measuring the optical density at λ_{max} 252nm. The concentration of the product 4-nitrobenzyl alcohol at each time interval was noted from the working curve and the percentage conversion at each time interval was calculated. The reduction reaction was followed with polymer bound borohydride reagents **P1-P4**. The results are depicted in **Fig. 3**.

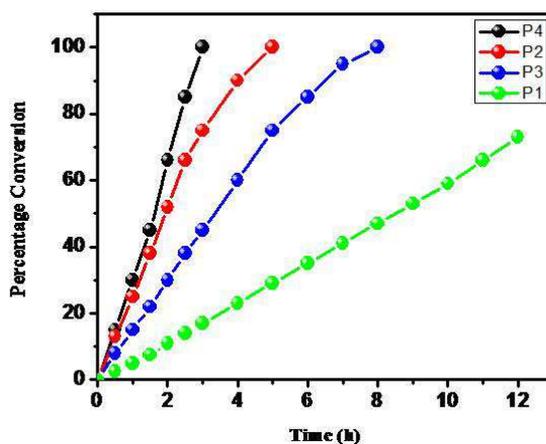


Fig. 3. Conversion of reduction of 4-nitrobenzaldehyde

Effect of temperature

Temperature is a crucial factor which affects the rate and yield of reactions. The effect of temperature on the reduction of aldehyde with the polymer bound borohydride reagent was studied by carrying out the reduction of 4-nitrobenzaldehyde with 2% BDDMA-PS-PEG-BH₄⁻ (**P4**) at different temperatures in DCM solvent. The reaction was carried out with two molar excess of polymeric reagent and the time taken for complete reduction of 4-nitrobenzaldehyde was noted by TLC. The rate of reaction was found to increase as the temperature was increased. At 27 °C reaction was completed in 3 h. As the temperature was increased to 42 °C completion of the reaction was observed within 1.5 h. At the refluxing temperature the reaction time was found to be 1 h. The effect of temperature on the reactivity is depicted in **Fig. 4**.

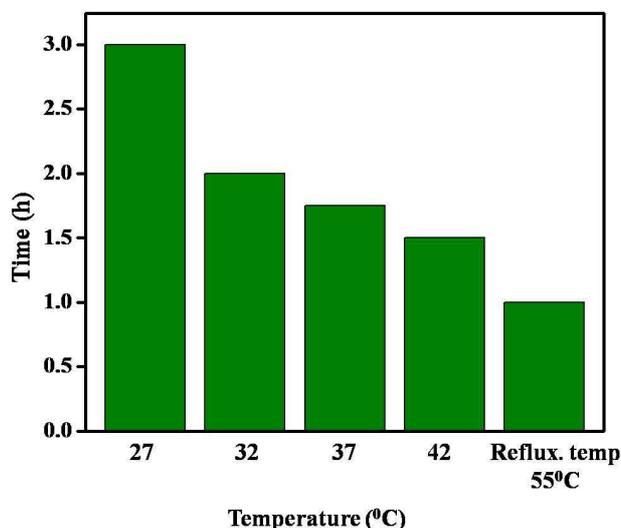


Fig. 4. Effect of temperature on the reduction of 4-nitrobenzaldehyde

Effect of solvent

The effect of solvent on the reduction reaction was investigated by following the reduction of 4-nitrobenzaldehyde using different solvents with the aid of polymeric borohydride reagent 2% BDDMA-PS-PEG-BH₄⁻ (**P4**).

Table 5: Effect of solvents on the reduction of 4-nitrobenzaldehyde

Solvent	Time of 100% Conversion (h)
DCM	3
THF	3
DMF	5
Toluene	12
Hexane	15
Nitrobenzene	20

The reaction was carried out at room temperature (27 °C) under identical conditions in the solvents DCM, THF, DMF, toluene, hexane and nitrobenzene. The reaction was followed by TLC analysis. The details are given in **Table 5**. Among these solvents, maximum rate was observed in THF and DCM, the solvents in which the polymer bound borohydrides exhibit maximum swelling proving the importance of solvation or swelling of the polymeric reagents in the solvent medium used.

Effect of molar excess of the reagent

One of the pioneering advantages of the polymer supported reaction is the use of excess of either the polymer bound or the soluble reagents for lower reaction periods and higher yields of the products without separation problems. The effect of concentration of the polymeric reducing reagent on the reduction reaction was investigated. The effect of molar excess of the reagent **P4** on the reduction of 4-nitrobenzaldehyde was studied. Initially the reaction was conducted with equimolar amounts of the reagent and the substrate at room temperature and the time of reduction was noted. Even after 4.5 h the reaction was not complete and traces of 4-nitrobenzaldehyde was noted. The reaction was repeated with 2, 3 and 4 molar excess of the reagent. In all the cases the time for complete reduction was noted to be 3 h.

Effect of acid catalyst

To study the effect of acid catalyst on the reduction of aldehydes with polymer bound borohydride reagent the reduction of p-nitrobenzaldehyde was carried out in the presence of acetic acid using the reagent resin in THF. The progress of the reaction was followed by TLC. The time for complete reduction of aldehyde was noted. In the

presence of acetic acid the time for reduction of benzaldehyde was reduced from 4 h to 1.5 h. Several aldehydes were reduced in the presence of acid with polymeric borohydride reagents. The results are given in **Table 6**.

Table 6: Comparison of reduction of aldehydes in the presence and absence of acid with borohydride reagent P4

Substrates	Reaction period in presence of acid catalyst (h)	Reaction period in the absence of acid catalyst (h)
Benzaldehyde	1.5	4
2-Nitrobenzaldehyde	1.0	3
4-Cyanobenzaldehyde	1.0	3
Acetophenone	6.5	15
Benzophenone	6.0	14
Methyl salicylate	10.0	18
Ethyl benzoate	8.0	16

Recycling of the spent polymer

The spent resin after the separation of the product was washed thoroughly with DCM followed by methanol and dried under vacuum. The dried polymer was converted to the original borohydride reagent according to the same procedure described in the original preparation. IR spectrum of the regenerated resin shows the B-H stretching at 2388 cm^{-1} . The capacity of the regenerated resin was almost same as that of the fresh resin and not varied much even after recycling five times. It was observed that even though a slight decrease in the borohydride capacity after recycling the efficiency of the reagent remains more or less same even after 4 cycles of regeneration. The efficiency of the regenerated reagent was checked in the reduction of 4-nitrobenzaldehyde comparing its reactivity with that of the fresh reagent resin. The time for 100% reduction with the fresh resin and the recycled resin was comparable. The results are summarized in **Table 7**.

Table 7: Capacity of the polymeric reagent P4 after recycling

No. of recycling	Capacity (mmol/g)	Time for reduction (h)
1	1.10	3.0
2	1.05	3.0
3	0.96	3.0
4	0.84	3.0
5	0.72	4.0

CONCLUSION

Polymer-bound benzyltributylammonium borohydride reagents were found to be good reducing agents for the reduction of aldehydes, ketones, esters and imines. The reagents reduce aldehydes selectively in the presence of ketones. Reagents having a PEG spacer between the polymer matrix and the borohydride moiety were found to be more efficient in reduction reactions.

Acknowledgements

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