

Polymer-Bound Ethylenediamine–Borane Reagent: A New Class of Polymeric Reducing Agent

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ABSTRACT: A polymer-supported ethylenediamine (EDA)–borane reagent was prepared under mild reaction conditions. The reagent was found to be efficient and selective in the reduction of aldehydes to the corresponding alcohols in high yields at room temperature. The polymeric reagent was prepared on a Merrifield resin and on a 1,6-hexanediol diacrylate-crosslinked polystyrene resin (HDODA–PS). HDODA–PS was prepared by suspension polymerization and chloromethylated by a Friedel–Crafts reaction. The preparation of the polymer-bound EDA–borane reagent involves a series of polymer analogous reactions, such as amination of the chloromethyl resin, conversion to amine hydrochloride, and, finally, complexation with sodium borohydride. The reagent exhibited good chemoselectivity in the reduction of aldehydes. The reduction reactions were carried out with a 2 molar excess of the polymeric reagent. In the competitive reduction of a 1:1 molar mixture of benzaldehyde and acetophenone, benzaldehyde was selectively reduced to benzyl alcohol. The spent resin could be recycled by treating with sodium borohydride. The recycled resin was used several times without much loss in chemical reactivity and mechanical stability. The HDODA–PS resin was found to be more efficient than was the Merrifield resin in the preparation of the reagent as well as in the reduction reactions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 593–600, 2001

Key words: polymer support; HDODA–PS; reducing agent; ethylenediamine –borane

INTRODUCTION

Insoluble polymeric reagents have acquired high popularity and have found wide applications in various fields, particularly in the fields of synthetic organic chemistry.^{1,2} Polymeric reagents have the physical properties of the macromolecular support and the chemical properties of the bound reagent function. The ease of the reaction workup, nontoxicity and recyclability are the intrinsic advantages of polymer-bound reagents

over the low molecular weight reagents.³ A number of synthetically important polymeric reagents have been reported so far, of which polymer-bound reducing agents have a significant contribution. Polymer-supported tin hydride⁴ and polyvinylpyridine–borane⁵ were reported to be good reducing agents. The low molecular weight borane reagents such as diborane, borane–tetrahydrofuran (THF), borane–dimethyl sulfide, and amine–borane are known to be effective reducing agents.^{6,7} Generally, the amine–borane complexes have many advantages as reducing agents due to their selectivity and stability.⁸ Itsuno et al. reported that a low molecular weight aminoalcohol–borane reagent reduces carbonyl compounds

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selectively in the presence of esters and polymer-bound aminoalcohol–borane has a significant selectivity in the reduction of aldehydes in the presence of ketones.⁹ The reagent was prepared by the reaction of aminoalcohol and borane–THF at an initial temperature of -78°C , elevating it to 30°C , and removal of unchanged borane by evaporation under reduced pressure. In the present work, we attempted to prepare a polymer-bound ethylenediamine (EDA)–borane reagent at room temperature under ordinary reaction conditions. The method that we adopted was similar to that of Hallensleben used in the preparation of polyvinylpyridine–borane from polyvinylpyridine hydrochloride by the reaction of sodium borohydride.¹⁰ Borch and Levitan reported the preparation of phenethylamine–borane by the reaction of sodium borohydride and phenethylamine hydrochloride.¹¹ Here, we report the preparation of polymer-bound EDA–borane and its utility in the reduction of aldehydes.

EXPERIMENTAL

Materials and Methods

Styrene was purchased from Fluka, AG (Buchs, Switzerland). Poly(vinyl alcohol) (PVA, molecular weight 70,000–1,00,000) and 1,4 hexanediol diacrylate (HDODA) were supplied by the Aldrich Chemical Co. (Milwaukee, WI). A Merrifield resin purchased sample was used. EDA from Merck, sodium borohydride from Spectrochem, and benzaldehyde, acetophenone, 2-nitrobenzaldehyde, 4-methoxybenzaldehyde, 4-cyanobenzaldehyde from Qualigens (Mumbai, India) were used. The Analar-grade solvents dichloromethane (DCM), THF, dimethylformamide (DMF), and *N*-methylpyrrolidone were purified according to the standard procedures. Chloromethyl methyl ether was prepared according to the literature procedure.¹² IR spectra were recorded on a Shimadzu IR 470 spectrophotometer. The ^{13}C -CP MAS NMR spectrum was recorded on a Bruker 300 MSL CP MAS instrument. Thermal stability was determined by TG using a NETZSCH-Geratebau GmbH. Elemental analysis for the determination of nitrogen was carried out on a Heraeus Carlo Erba 1108 instrument.

Preparation of 2% HDODA Crosslinked Polystyrene (2)

A mixture of styrene (11.3 mL, 98 mmol), HDODA (0.44 mL, 2 mmol), toluene (10 mL), and benzoyl

peroxide (500 mg) was suspended in a 1% aqueous solution of PVA (173 mL) and the suspension was stirred mechanically at a temperature of 85°C for 6 h. The polymer was filtered, washed with hot water to remove PVA, and purified by Soxhlet extraction with acetone followed by methanol. The yield of the polymer obtained was 90%.

Chloromethylation of HDODA–PS: Preparation of Resin 2a

The dry resin (5 g) was swollen in dichloromethane (50 mL) and refluxed with chloromethyl methyl ether (30 mL) in the presence of ZnCl_2 in dry THF (1 mL) as a catalyst, at 50°C for 12 h. After the reaction, the resin was filtered and washed with THF, THF–water (1:1), THF–HCl, and hot water until free from chloride ions. The resin was further purified by Soxhlet extraction in THF. The chlorine capacity of the resin was determined by Volhard's method¹³ and was found to be 4.1 mmol/g. The IR spectrum of the chloromethyl resin showed a characteristic C–Cl stretching band at 680 cm^{-1} .

Conversion of Chloromethyl Resins (1a, 2a) to Ethylenediaminomethyl Resins (1b, 2b)

The chloromethyl resin (5 g) was swollen in DMF (50 mL) and then shaken with EDA (6 mL, 5 molar excess) and pyridine (1.62 mL). After 15 h, the resin was filtered and washed with DMF ($3 \times 25\text{ mL}$), 1:1 DMF–methanol ($3 \times 25\text{ mL}$), methanol ($3 \times 25\text{ mL}$), and 1:1 methanol–water ($3 \times 25\text{ mL}$) and, finally, with water until free from excess EDA and free chloride ions. The amino capacities of resins (**1b**, **2b**) were estimated by the picric acid method¹⁴ and were found to be 6 and 4.98 mmol/g, respectively. The observed values were confirmed by elemental analysis (6.22 and 5.32 mmol/g for **1b** and **2b**, respectively). The aminated resin on reaction with the ninhydrin reagent showed blue-colored beads, indicating the presence of free amino groups. The IR spectra of the ethylenediaminomethyl resins showed a characteristic N–H band at 3240 cm^{-1} .

Preparation of Polymer-bound EDA–Borane (EDA–Borane) Reagents (1c, 2c)

The aminated resin (5 g) swollen in NMP (50 mL) for 12 h was shaken with concentrated HCl (10 mL) for 6 h. The resin was filtered and washed with water until free from acid and chloride ions. The resin was dried under a vacuum. The amine

Table I Reduction of Aldehydes by the EDA-Borane Reagent on HDODA-PS

Substrates	Product	Time for 100% Reduction (h)
Benzaldehyde	Benzyl alcohol	6
4-Methoxybenzaldehyde	4-Methoxybenzyl alcohol	10
4-Cyanobenzaldehyde	4-Cyanobenzyl alcohol	4
2-Nitrobenzaldehyde	2-Nitrobenzyl alcohol	3
Cinnamaldehyde	Cinnamyl alcohol	12

hydrochloride resin (5 g) suspended in DMF (50 mL) was shaken with sodium borohydride (2 g, 2 molar excess) for 5 h. After the reaction, the polymer was filtered and washed with DMF (3×25 mL), DMF-water (3×25 mL), and with water until excess sodium borohydride and free chloride ions were completely eliminated. Finally, the resin was washed with methanol and dried at 50°C. The IR spectra of the polymer-bound EDA-borane showed a B—H stretching band at 2390 cm^{-1} and a band at 1180 cm^{-1} , characteristic of B—N stretching.¹⁵ The extent of borane complexation was determined by estimating the free amino groups of the resins. The residual amino groups of the polymeric borane was estimated by the picric acid method and the values were found to be 3.18 and 1.65 mmol/g for the Merrifield resin and the HDODA-PS resin, respectively. The borane capacities of the resins were found to be 2.82 mmol/g for the Merrifield resin and 3.68 mmol/g for the HDODA-PS resin.

Reduction of Aldehydes with the Polymer-supported EDA-Borane Reagent

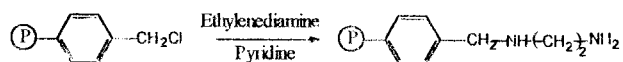
In a typical procedure, to a suspension of the polymer-bound EDA-borane (500 mg) in DCM (10 mL), benzaldehyde (0.1 mL, 1 mmol) was added and then shaken for 6 h. The extent of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, 1M HCl was added to the reaction mixture and shaken for 2 h (filtered off the spent resin and entracted the filtrate with ether, dried the extract over anhydrous sodium sulfate and evaporated the solvent). The product benzyl alcohol was confirmed by TLC, IR, and UV spectroscopic methods. The same procedure was adopted for the reduction of substituted aldehydes such as *o*-nitrobenzaldehyde, *p*-methoxybenzaldehyde, *p*-cyanobenzaldehyde, and cinnamaldehyde to their respective alcohols with 100% conversion.

Selective Reduction of Benzaldehyde in the Presence of Acetophenone

The polymer-bound reagent (1 g) was swollen in DCM (20 mL) and a mixture of benzaldehyde (0.1 mL, 1 mmol) and acetophenone (0.12 mL, 1 mmol) was added and then shaken in a waterbath shaker. The extent of the reaction was monitored by TLC. Complete reduction of benzaldehyde was observed within 6 h. The reaction was continued for another 5 h and acetophenone in the reaction mixture was found to remain unreacted. One molar HCl was added to the reaction mixture and the organic phase was extracted with ether. Only benzyl alcohol was obtained as the reduced product, which was confirmed by TLC, and the unreacted acetophenone was separated by column chromatography.

Regeneration and Recycling of the Resin

The spent resin after separation of the product alcohol and the unreacted carbonyl compound, if any, was washed with DCM and dried under a vacuum. The resin (1 g) was then swollen in NMP (10 mL) for 12 h and then shaken with concentrated HCl (2 mL) for 6 h. The polymer was washed with water thoroughly until free from excess acid. The amine hydrochloride resin (1 g) was swollen in DMF (10 mL) and the swollen resin was shaken with sodium borohydride (2 molar excess, 0.4 g) for 6 h. The polymer-bound EDA-borane thus obtained from the spent resin was washed and dried. The regenerated resin was characterized by an IR spectrum. B—H stretching and B—N stretching bands were observed at 2390 and at 1180 cm^{-1} , respectively. The utility of the regenerated resin was checked by the reduction of 2-nitrobenzaldehyde. The regenerated resin (100 mg) was swollen in DCM (5 mL), and to this suspension, 2-nitrobenzaldehyde (20 mg) was added and then shaken. The same reaction was



Scheme 1 Conversion of chloromethyl resin to ethylenediaminomethyl resin.

carried out with the fresh resin. The reactions were monitored by TLC. The time taken for a complete reduction of 2-nitrobenzaldehyde was the same (3 h) in both cases.

Determination of the Reagent Function in the Resin Available for Reduction

The reagent function available for reduction was estimated by the reaction of the polymeric reagent with excess 2-nitrobenzaldehyde. The polymer-bound borane reagent (58 mg) was swollen in DCM (10 mL) and then shaken with 2-nitrobenzaldehyde (40 mg) for 5 h. After the reaction, DCM (10 mL) was added to the reaction mixture. The concentration of 2-nitrobenzyl alcohol in the solution was determined spectrophotometrically. The

amount of 2-nitrobenzyl alcohol obtained was 22 mg (0.15 mmol). Then, the functional group equivalent of the resin used for reduction was found to be 2.59 mmol/g.

RESULTS AND DISCUSSION

The EDA–borane reagent was first prepared on a macroporous Merrifield resin. The Merrifield resin (**1a**), having a chlorine capacity of 3.9 mmol/g and beads of 800–1000 mesh size, was used. The chloromethyl resin was converted to ethylenediaminomethyl resin by treating with excess EDA in a DMF/pyridine mixture (Scheme 1).^{16,17}

The amino capacity of the resin estimated by the picric acid method was 6 mmol/g, which was confirmed by elemental analysis of nitrogen. The IR spectrum of the resin showed a characteristic N–H stretching band at 3240 cm^{-1} (Fig. 1). The aminated resin after overnight swelling in NMP

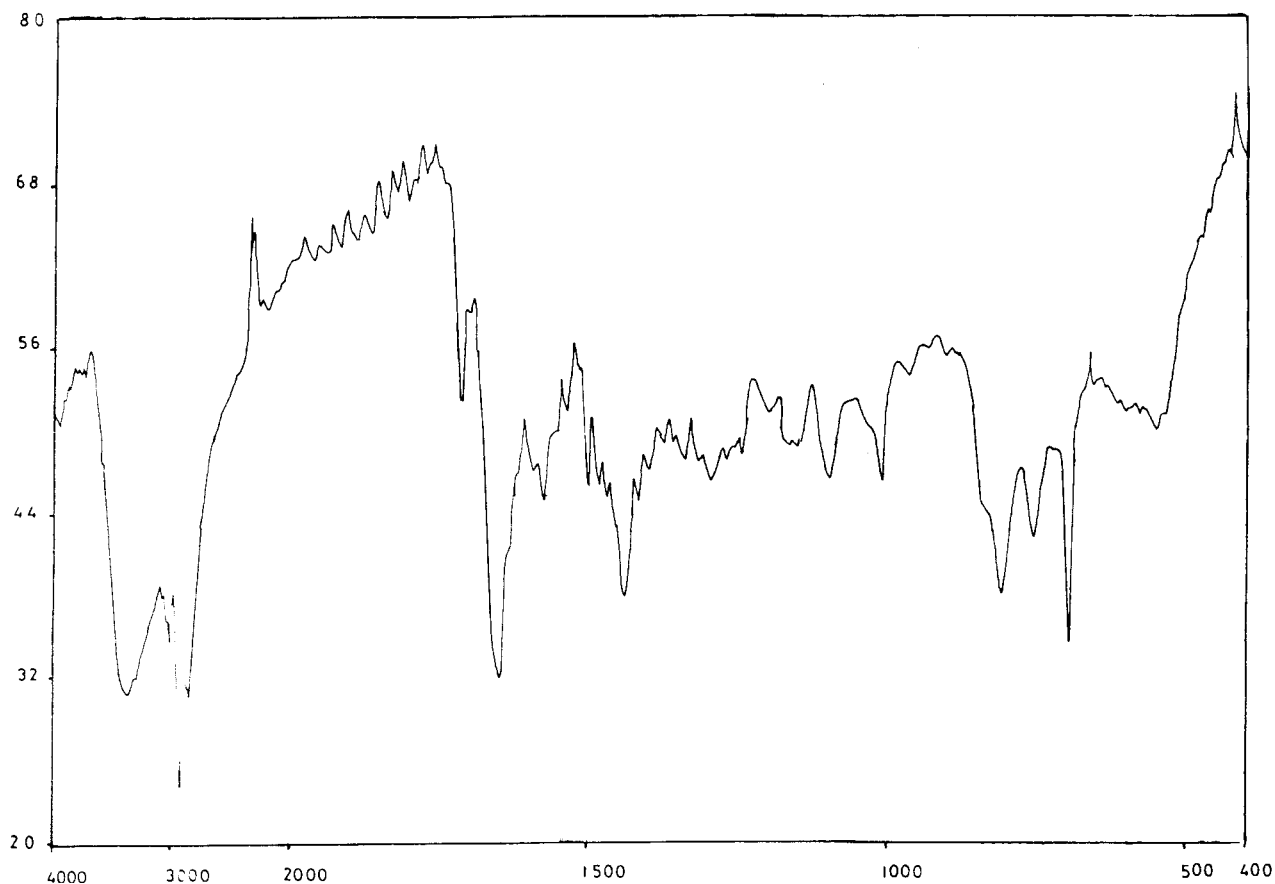
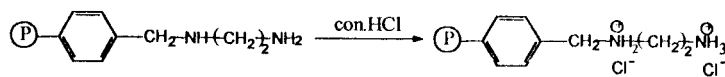


Figure 1 IR spectrum of ethylenediaminomethyl resin.



Scheme 2 Conversion of aminated resin to amine hydrochloride resin.

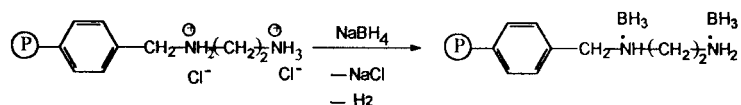
was treated with concentrated HCl to convert it to the corresponding hydrochloride (Scheme 2). In this step, 100% conversion did not take place, which may be due to the shrinking of the hydrophobic resin in the aqueous acid medium. The polymer-supported EDA hydrochloride was transformed to the polymer-bound EDA-borane complex (**1c**) by the reaction with sodium borohydride¹¹ (Scheme 3). The polymer-bound EDA-borane reagent (**1c**) was characterized by an IR spectrum, which showed a B—H stretching band at 2390 cm^{-1} and a B—N stretching band at 1180 cm^{-1} (Fig. 2). The borane content of the resin was calculated based on residual amino groups and was found to be 2.82 mmol/g. The reagent was found to reduce benzaldehyde to benzyl alcohol at room temperature. Complete reduction was achieved by stirring benzaldehyde with the polymeric reducing agent for 15 h.

Systematic studies of polymer supports in solid-phase synthesis have shown that the flexible polymer supports enhance the reactivity of bound functional groups due to high solvation and smooth diffusion of soluble reagents throughout the polymer matrix. The use of a polystyrene resin crosslinked with flexible, hydrophilic HDODA has already been reported in solid-phase peptide syntheses^{18–20} and other solid-phase reactions.²¹ We investigated the utility of the HDODA-PS resin in the preparation of the polymeric EDA-borane reagent. A 2% crosslinked HDODA-PS resin was found to be the optimum support for the preparation of the reagent.

The 2% HDODA crosslinked polystyrene resin (**2**) was prepared by suspension polymerization²² of the monomer styrene and HDODA in toluene with benzoyl peroxide as the initiator (Scheme 4). The resin was characterized by IR and solid-state BC-CP MAS NMR spectra. The IR spectrum of the resin showed the characteristic carbonyl

stretching band at 1720 cm^{-1} . The solid-state ¹³C-CP MAS NMR spectrum of the polymer (Fig. 3) showed an intense peak at 128.33 ppm, corresponding to aromatic carbons, and a small peak at 146.6 ppm, arising from styrene carbon. The carbon atoms of the polymer backbone gave peaks at 24.78 and at 40.83 ppm. The peak at 180.04 ppm corresponds to the ester carbonyl group. Polymer beads of 200–400-mesh size were chosen for the present study. The resin was functionalized with chloromethyl groups by a Friedel-Crafts reaction using chloromethyl methyl ether²³ (Scheme 5).

The functional-group capacity of the chloromethyl resin (**2a**) was estimated by Volhard's titrimetric method and the value was found to be 4.1 mmol/g. The C—Cl stretching band at 680 cm^{-1} observed in the IR spectrum confirmed the presence of chloromethyl groups. The chloromethyl resin was converted to ethylenediaminomethyl resin (**2b**) by treating it with EDA in a DMF/pyridine mixture. The amino capacity of the resin (**2b**) was evaluated by the picric acid method and the value was found to be 5.32 mmol/g, which was confirmed by elemental analysis. No residual chlorine was found in the resin. The estimated amino capacity of the resin was low compared to the theoretical value. The low value of the amino-group capacity in the absence of residual chlorine suggests the possibility of double binding of EDA. The primary amino group of the singly bound EDA moiety can interact with a second chloromethyl group, resulting in a crosslinked structure. It was already reported that the reaction of chloromethyl polystyrene and EDA proceeds with extensive site-site interactions and 80% of the reactive sites become involved in double binding.²⁴ The chance for double binding is higher in the case of the flexible HDODA-PS resin due to increased site-site interactions when compared to the DVB-PS resin.



Scheme 3 Preparation of polymer-bound EDA-borane from the corresponding amine hydrochloride resin by the reaction of sodium borohydride.

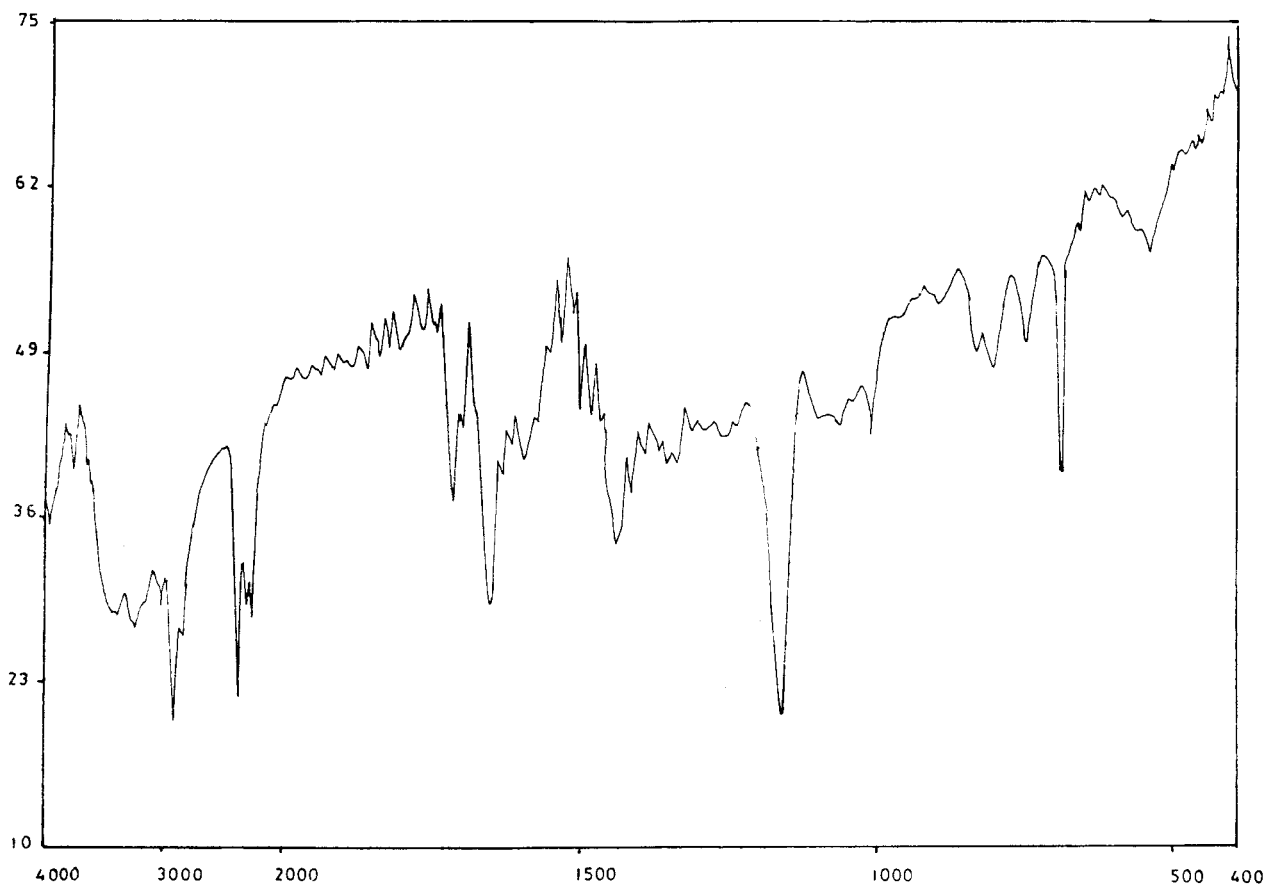
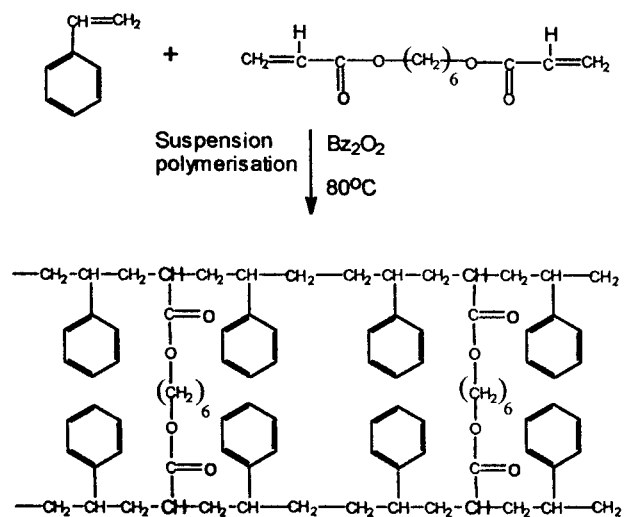


Figure 2 IR spectrum of polymer-bound EDA-borane.

The polymer-bound EDA-borane complex (**2c**) was prepared from the aminated resin (**2b**) according to the same procedure used in the case of

the Merrifield resin (**1c**) and was characterized by the IR spectrum. The borane capacity of the polymeric reagent was calculated by estimating the residual amino group present in the resin by the



Scheme 4 Suspension polymerization of 1,4 hexanediol diacrylate and styrene.

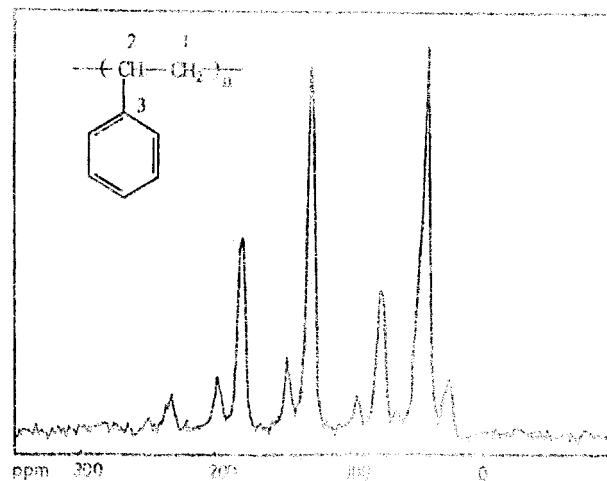
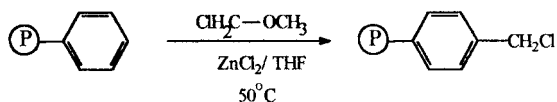


Figure 3 NMR spectrum of 2% HDODA-PS copolymer (**2**).



Scheme 5 Chloromethylation of HDODA-PS resin.

picric acid method. The borane capacity of the resin was found to be 3.68 mmol/g. The reagent function in the resin available for reduction was obtained by reacting the polymeric reagent with excess 2-nitrobenzaldehyde and determining the concentration of the product alcohol spectrophotometrically and the value was found to be 2.59 mmol/g. Since there is a chance of double binding of EDA groups, and also due to the macromolecular structure, we could not expect chelate formation in the case of polymer-bound EDA-borane, which was reported in the case of low molecular weight EDA-borane. The thermal stability of the polymeric reagent was studied by thermogravimetric analysis and the reagent was found to be stable up to 330°C.

The reduction reactions with the polymeric EDA-borane reagent were carried out at room temperature. Using this polymeric reagent, benzaldehyde was readily reduced to benzyl alcohol. The reduction reaction was done with a 2 molar excess of the polymeric reagent. To the suspension of the reagent resin in DCM, benzaldehyde was added and the reaction mixture was shaken. The extent of reaction was monitored by TLC. After completion of the reaction, 1M HCl was added to the reaction mixture and the filtrate was extracted with ether and dried over sodium sulfate and the solvent evaporated. The product benzyl alcohol was confirmed by TLC, IR, and UV spectroscopic methods. The polymer-bound EDA-borane reagent acted as a selective reducing agent for aldehyde in the reduction of a 1:1 molar mixture of benzaldehyde and acetophenone. An equimolar mixture of benzaldehyde and acetophenone was shaken with a 2 molar excess of the polymeric reagent suspended in DCM. The reaction was monitored by TLC. Complete reduction of benzaldehyde was observed within 6 h in the case of HDODA-PS resin (**2c**). The reaction was continued for another 5 h and 1 molar HCl was

Table II Reduction of 1 : 1 Molar Mixture of Benzaldehyde and Acetophenone by the Polymer-bound EDA-Borane

Reagent Resin	Reaction Time (h)	Percent of Benzaldehyde	Percent of Acetophenone
1c	0	100	100
	15	0	100
2c	0	100	100
	6	0	100

added to the reaction mixture and the organic phase was extracted with ether. Only benzyl alcohol was obtained as the product, leaving acetophenone unreacted. The results are summarized in Table I.

The reagent derived from the HDODA-PS resin reduces aldehydes in a shorter time interval than did the reagent from DVB-PS. This can be explained as a result of high solvation of the polymer support, which may be attributed to increased chain mobility of the polymer backbone by the hydrophilic, flexible HDODA crosslinks. This enhances the diffusion of soluble reagents through the macromolecular matrix. The reduction of benzaldehyde was completed within 6 h in the case of EDA-borane from the HDODA-PS resin, whereas, with the DVB-PS resin, the reaction period was increased to 15 h. We also attempted the reduction of substituted benzaldehydes by the EDA-borane reagent on HDODA-PS. The results obtained were quite positive and are summarized in Table II.

Several mechanisms were suggested for the carbonyl reductions involving the amine-borane reagents, either a direct attack of the amine-borane or prior dissociation to free BH_3 .²⁵ The mechanism suggested was the initial formation of an unstable intermediate of the carbonyl group with amine-borane and simultaneous hydride transfer, giving the product alcohol. This led us to follow a mechanism through observation of the reaction. The suggested reaction path in this case was as given in Scheme 6.

In the reduction of benzaldehyde, the product benzyl alcohol was obtained only after acid hydro-



Scheme 6 Mechanism of reduction of aldehyde with the polymer-bound amine-borane.

lysis of borate ester on the polymer beads. In the case of substituted aldehydes, the product was formed in the reaction mixture prior to hydrolysis. This may be due to the instability of the borate intermediate offered by the steric hindrance of the substituents, which facilitated the cleavage of the alcohol from the polymeric reagent. In the reduction of nitrobenzaldehyde and cyanobenzaldehyde, increased reaction rates were observed due to the effect of electron-withdrawing groups which increased the rate of hydride transfer.

The recyclability of the polymeric reagent was also tried. The polymeric reagent was regenerated by treating the spent resin with HCl followed by sodium borohydride and was characterized by an IR spectrum which showed the B—H stretching band at 2390 cm^{-1} and the B—N stretching band at 1180 cm^{-1} . The efficiency of the regenerated resin was checked by performing the reduction of aldehyde and comparing its reactivity with fresh resin. The time taken for 100% reduction of 2-nitrobenzaldehyde with the fresh resin and the recycled resin was the same.

CONCLUSIONS

A polymer-supported EDA–borane reagent was prepared using the Merrifield resin and the HDODA–PS resin. The reagent was prepared by treating the ethylenediaminomethyl polystyrene resin with HCl followed by sodium borohydride. The reagent was found to be an efficient reducing agent for aldehydes. Both preparation of the reagent and reduction of substrates were achieved at room temperature under mild reaction conditions. The EDA–borane prepared from 2% HDODA-crosslinked polystyrene showed a greater extent of reactivity than that of the reagent from the conventional Merrifield resin. The polymer-bound EDA–borane reagent selectively reduces aldehydes in the presence of ketones. The polymeric reagent could be regenerated easily and reused without loss in reactivity.

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