6.1 Materials

Styrene was purchased from Fluka, A.G (Switzerland) Polyvinyl alcohol (PVA, molecular weight, 72,000-1,00,000) 1,6-hexanediol diacrylate (HDODA), 1,4-butane diol dimethacrylate (BDDMA) and divinyl benzene (DVB) were supplied by the Aldrich Chemical company (Milwaukee, WI) Ethylenediamine, potassium phthalimide, 2-nitrobenzaldehyde, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-nitroacetophenone and salicylaldehyde were purchased from Merck (India). Sodium borohydride was supplied by Spetrochem (India). Diethylamine, benzaldehyde acetophenone and p-chlorobenzaldehyde were purchased from Qualigens (India). Acrylamide, N, N'-methylene-bis-acrylamide (NNMBA) and 4-methoxybenzaldehyde were supplied by SRL (India). Chloromethyl methyl ether was prepared according to the literature procedure. Analar grade solvents dichloromethane (DCM), tetrahydrofuran (THF), N, N dimethylformamide (DMF),
toluene, chloroform and N-methylpyrrolidone were purified according to the standard procedures.

6.2 Instrumental

- IR spectra were recorded on a Shimadzu IR-470 spectrophotometer.
- Photometric analyses were done by Shimadzu UV-160A spectrophotometer.
- $^{13}$C CP MAS NMR spectra were recorded on a Bruker 300 MSL CP instrument.
- Thermal stability was determined by TG using a NETZCH-geratebau GmbH.
- Elemental analyses were carried out on a Heracus Carlo Erba 1108 instrument.

6.3 Preparation of Crosslinked Polystyrene Resins

Styrene (100 mL) was destabilised by washing with 1% sodium hydroxide solution (3 times), and washed with water (3 times) and dried over sodium sulfate.

6.3.1 Preparation of 2% DVB crosslinked polystyrene (1a)

A mixture of styrene (22 mL, 98 mmol), divinylbenzene (55% DVB, 1.04 mL, 2 mmol), toluene (10 mL) and benzoyl peroxide (500 mg) was suspended in 1% aqueous solution of PVA (350 mL) and the suspension was stirred mechanically at a temperature of 85°C for 6 h. The polymer was filtered, washed
Experimental

with hot water to remove PVA and purified by Soxhlet extraction with acetone followed by methanol. The details of polymerisation are given in Table 3.1.

6.3.2 Preparation of HDODA crosslinked polystyrene resins

A mixture of styrene (22 mL, 98 mmol), HDODA (0.88 mL, 2 mmol) toluene (10 mL) and benzoyl peroxide (500 mg) was suspended in 1% aqueous solution of PVA (350 mL) and the suspension was stirred mechanically at a temperature of 85°C for 6 h. The polymer obtained was filtered, washed with hot water to remove PVA and purified by Soxhlet extraction with acetone followed by methanol. The IR spectrum of the resin showed carbonyl stretching band at 1720 cm⁻¹.

The polymers with different crosslink densities 4, 6, 8, 12 and 20 mole percentages of HDODA were prepared by the same procedures by adjusting the compositions of monomers. The preparative details of the polymers were given in Table 3.2.

6.3.3 Preparation of 2% BDDMA crosslinked polystyrene (3a)

A mixture of styrene (22 mL, 98 mmol) BDDMA (0.88 mL, 2 mmol) toluene (10 mL) and benzoyl peroxide (500 mg) was suspended in 1% aqueous solution of PVA (350 mL) and the solution 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
Experimental

The yield of the polymer obtained was 85%. The resin was characterised by IR spectrum, which shows carbonyl stretching band at 1720 cm⁻¹.

6.4 Functionalisation of the Crosslinked Polymers (DVB-PS, BDDMA-PS, HDODA-PS)

6.4.1 Preparation of chloromethyl methyl ether (CMME)

A mixture of formaldehyde (132 mL) and methanol (66 mL) were kept at 0°C and dry HCl gas was passed through the reaction mixture till an oily layer of CMME was formed. The oily layer was separated and dried over calcium chloride. The reaction was carried out in a fumehood.

6.4.2 Preparation of 1M ZnCl₂ in THF

To anhydrous ZnCl₂ (1.5 g) taken in an Erlenmayer flask, conc. HCl (3 drops) and water (5 drops) were added. The solution was heated till the solid was dissolved completely. Heating was continued till a solid mass of ZnCl₂ was left which melted on further heating. When it became a mobile liquid, the flask was kept in a desiccator and allowed to cool. The solid was dissolved in freshly distilled anhydrous THF (10 mL) and kept sealed.

6.4.3 Chloromethylation of crosslinked polystyrene resins: Preparation of resins (1b, 2b₁-2b₆ and 3b)

General Procedure

The dry resin (5 g) was swollen in dichloromethane (50 mL) and refluxed with chloromethyl methyl ether (30 mL) in the presence of 1 M ZnCl₂ in dry MeOH.
Experimental

THF (1 mL) 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 using THF.

6.5 Estimation of Chlorine Capacity

Volhard’s Method: The dry resin (50 mg) was agitated with pyridine (4 mL) for 6 h. To the suspension con HNO₃ (5 mL), acetic acid-water mixture (1:1 v/v, 30 mL) and silver nitrate solution (0.05 N, 5 mL) were added and titrated against ammonium thiosulphate solution (0.1N), using ferric alum as the indicator. A blank titration was also done. The values obtained were given in Table 3.3. The IR spectra (Fig. 3.4) of the chloromethyl resins showed characteristic C-Cl stretching band at 680 cm⁻¹.

6.6 Conversion of Chloromethyl Resins to Ethylenediaminomethyl Resins (1c, 2c₁-2c₆ and 3c)

General Procedure

The chloromethyl resin (5 g) was swollen in DMF (50 mL) and then shaken with ethylenediamine (6 mL, 5 molar excess) and pyridine (1.62 mL). After 15 h, the resin was filtered and washed with DMF (3 × 25 mL), DMF-methanol (1:1, 3 × 25 mL) and finally, with water until free from excess amine and free chloride ions. The resin was washed with methanol and dried under vacuum. The amino group capacities of the resins were estimated by picric acid method and the values were given in Table 3.4. The observed values were confirmed by elemental analyses. The aminated resins on reaction with the ethanolic solution of ninhydrin
showed blue colour of the beads, indicating the presence of primary amino groups. The IR spectra (Fig. 3.5) of the ethylenediaminomethyl resins showed characteristic N-H band at 3240 cm\(^{-1}\) and complete disappearance of the C-Cl band at 680 cm\(^{-1}\).

6.7 Estimation of Amino Group Capacity: Gisin's method

The aminated resin (2 mg) was weighed out, accurately into a Gisin's tube. The resin was washed with DCM (2 mL \(\times\) 3) and then treated with picric acid (0.1N, 2 mL, \(3 \times 5\) min) and the excess picric acid was thoroughly washed off with DCM (5 \(\times\) 2 mL). The quantity of picric acid complexed with the amino groups of the resin was quantitatively eluted with 10% TEA in DCM (7 \(\times\) 2 mL) and then washed with DCM (6 \(\times\) 1 mL). The solution was made up to 15 mL, using ethanol. About 0.5 mL of the solution was pipetted out and made upto 5 mL using ethanol. The absorbance of the solution was measured at \(\lambda 358\) nm. A blank was also conducted for the final correction of the value obtained. The molar absorption coefficient (\(\varepsilon\) max) of picrate in 14,500. The amino capacity of the resin was then calculated using the formula.

\[
\text{Amino group capacity} = \frac{(\text{Absorbance} \times 5 \times 15)}{(14.5 \times 0.5 \times \text{weight of resin in mg})}
\]

6.8 Conversion of Ethylenediaminomethyl Resins to the Corresponding Amine hydrochloride Resins (1d, 2d\(_1\)-2d\(_6\) and 3d)

The aminated resins (5 g) swollen in NMP (50 mL) for 12 h was shaken with HCl (10 mL) for 6 h. The resin was filtered and washed with water until free
from acid and chloride ions. The chloride capacities of the amine hydrochloride resins were estimated by argentometric titrations. The values obtained were given in Table 3.5.

6.9 Preparation of Polymer Supported EDA-borane Reagents (1e, 2e₁-2e₆, and 3e)

The amine 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 under vacuum. The IR spectra (Fig. 3.6) of the polymer bound EDA-borane showed a B-H stretching band at 2390 cm⁻¹ and B-N stretching band at 1150 cm⁻¹. The extent of borane complexation was determined by estimating the free amino groups of the resins. The residual amino groups of the polymer bound EDA-borane were estimated by the picric acid method and the values were given in Table 3.6.

6.10 Determination of the Borane Reagent Function Available for Reduction

The borane 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 was shaken with 2-nitrobenzaldehyde (40 mg) for 5 h. After the reaction, DCM (10 mL) was added to the reaction mixture. The amount of unreacted 2-nitrobenzaldehyde in the solution
Experimental

was determined spectrophotometrically. Then functional group equivalent of the resin used for reduction was calculated. The values obtained were given in Table 3.7.

6.11 Reduction of Aldehydes with the Polymer Supported EDA-Borane Reagent

General Procedure

To the suspension of the polymer bound EDA-borane (1e) (500 mg) in DCM (10 mL), benzaldehyde (0.1 mL, 1 mmol) was added and shaken for 10 h. The extent of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, solvent DCM was evaporated and the polymer was allowed to swell in THF. 1 M HCl (2mL) was added to the reaction mixture and shaken for 2 h. The spent resin was filtered off and extracted the filtrate with ether, dried over anhydrous sodium sulfate and evaporated the solvent. The formation of the product benzyl alcohol was confirmed by TLC, IR and UV spectroscopic methods. The same procedure was adopted for the reduction of various aldehydes and ketones to their respective alcohols by the EDA-borane reagent from DVB-PS, HDODA-PS and BDDMA-PS resins. The results are given in Tables 4.1a, 4.1b and 4.1c.

6.12 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 shaken the mixture in a waterbath shaker. The extent of the
reaction was monitored by TLC. Complete reduction of benzaldehyde was observed within 10 h. The reaction was continued for another 5 h and the acetophenone in the reaction mixture was found to remain unreacted. 1N HCl (5 mL) was added to the reaction mixture and shaken for another 2 h. The organic phase was extracted with ether. Only benzyl alcohol was obtained as the reduced product, which was confirmed by TLC. The unreacted acetophenone was separated. The results are given in Table 4.2.

6.13 Quantitative Study of the Extent of Reduction of 2-nitrobenzaldehyde

Quantitative study of reduction of aldehydes with the polymeric reagent was studied by following the reduction of 2-nitrobenzaldehyde spectrophotometrically. Standard solutions of 2-nitrobenzaldehyde and 2-nitrobenzyl alcohol were prepared. 2-nitrobenzaldehyde (20 mg) was weighed accurately and dissolved in DCM (10 mL). 0.5 mL of the solution was diluted with methanol in a 50 mL standard flask. The concentration of the solution was 0.04 mg/mL. A solution of 2-nitrobenzyl alcohol of the same concentration was also prepared. The mixture of these solutions at different concentrations of 2-nitrobenzaldehyde and 2-nitrobenzyl alcohol were prepared. The optical densities of the solutions at $\lambda_{max}$ 253 nm were measured spectrophotometrically. A standard curve is drawn by plotting optical densities against concentrations. A straight line graph was obtained. From the graph, the concentration of 2-nitrobenzaldehyde reacted at different time intervals was determined.
6.14 The Extent of Reduction of 2-nitrobenzaldehyde with Polymer Bound EDA-borane Reagents (1e and 2e₁)

General Procedure

Polymer bound EDA-borane reagent (100 mg) was swelled in DCM (5 mL). 2-nitrobenzaldehyde solution of concentration 2 mg/mL was prepared in DCM in a 50 mL flask. To the swollen polymer 2-nitrobenzaldehyde solution (10 mL) was added and shaken. 0.1 mL of the solution was withdrawn at time intervals 30, 40, 60, 80, 100 and 120 min. The solutions were diluted to 5 mL and optical densities were measured spectrophotometrically. At each time interval the percentage conversion was calculated from the standard curve. Fig 4.1 shows percentage conversion of 2-nitrobenzaldehyde at different time intervals.

6.15 Effect of Various Parameters on the Reactivity of the Polymer Bound EDA-borane

6.15.1 Effect of degree of crosslinking

The polymer bound EDA-borane reagents (2e₁-2e₆) derived from 2%, 4%, 6%, 8%, 12% and 20% HDODA crosslinked polystyrene resins (100 mg each) were suspended in DCM (5 mL). 2-nitrobenzaldehyde solution in DCM (10 mL, concentration 2 mg/mL) was added to each resin sample and were shaken in a waterbath shaker. After 3 h, 0.1 mL of solution was withdrawn from each bottle and diluted to 5 mL with methanol. The optical densities of these solutions were measured spectrophotometrically. Concentrations of solutions corresponding to optical densities were noted from the standard curve.
Percentages of reduction with each resin was calculated. Fig. 4.2 shows the extent of reduction with degree of crosslinking.

6.15.2 Effect of solvent

Polymer bound EDA-borane reagent (2e₁) (100 mg) was suspended in DCM (5 mL). To the suspension 2-nitrobenzaldehyde (20 mg) was added and shaken. After 3h, 0.1 mL of solution was withdrawn and diluted to 5 mL with methanol. The optical density at 253 nm was measured spectrophotometrically. The percentage conversion was calculated from the standard curve. The reaction was repeated with different solvents such as THF, CHCl₃, toluene, DMF and NMP under identical conditions. The percentage conversion in each solvent was calculated from the standard curve. The results are depicted in Fig. 4.3. The reaction in each solvent was also monitored by TLC. The time taken for complete reduction of 2-nitrobenzaldehyde in each solvent was noted. The results are given in Table 4.3.

6.15.3 Effect of temperature

Polymer bound EDA-borane reagent (2e₁) (100 mg) was swollen in toluene (10 mL) and was shaken with 2-nitrobenzaldehyde (20 mg) at room temperature. The reaction was followed by TLC. Time taken for complete reduction was noted. The time for complete conversion of 2-nitrobenzaldehyde was found to be 3 h. The reaction was repeated at different temperatures i.e., 37°C, 47°C, 57°C and 67°C and time for 100% conversion was noted in each case by TLC. Fig. 4.4 shows the effect of temperature on the reaction.
6.15.4 Effect of acid catalyst on the reactivity of polymer bound EDA-borane

General Procedure

To 2-nitrobenzaldehyde (20 mg), 10% glacial acetic acid in DCM (0.1 mL) was added and the reaction mixture was added to polymer bound EDA-borane reagent (100 mg), swollen in DCM (10 mL). The reaction was followed by TLC. Time for complete reduction was noted as 1 h and 50 min. Benzaldehyde, 4-cyanobenzaldehyde and p-methoxybenzaldehyde were reduced with the polymeric EDA-borane reagents in the presence of acetic acid and the time for complete reduction was noted. The results were summarised in Table 4.4. The same experiment was repeated with polymeric reagent 1e. Results are given in Table 4.5. After completion of reaction, the polymer was filtered off and the solvent was evaporated. The product alcohol was isolated and characterised.

6.15.5 Effect of concentration of polymeric reagent

Polymer bound EDA-borane reagents (2e1), (50 mg) was swollen in toluene (10 mL) and was shaken with 2-nitrobenzaldehyde (20 mg). The concentrations of the reagent and the substrate were taken in the 1:1 molar ratio. The percentage of conversion was determined spectrophotometrically after 1 h. The reaction was repeated with reagent and substrate in different molar concentrations (1:2, 1:3, 1:4 and 1:5). The percentage conversion of 2-nitrobenzaldehyde was determined in each case. The results are summarised in Table 4.6.
6.16 Regeneration and Recycling of the Resin

The spent resin after separation of the product alcohol and the unreacted carbonyl compound if any, was washed thoroughly with DCM followed by methanol and dried under vacuum. The purified resin (1 g) was swollen in NMP (10 mL) for 12 h and shaken with HCl (2 mL) for 6 h. The polymer was washed with water thoroughly. The amine hydrochloride resin (1 g) was swollen in DMF (10 mL) and was shaken with sodium borohydrate (2 molar excess, 0.5 g) for 6 h. The polymer bound EDA-borane thus obtained from the spent resin was washed with DMF, water and MeOH and dried under vacuum. The regenerated resin was characterised by IR spectrum. The B-H stretching and B-N stretching bands were observed at 2390 cm$^{-1}$ and 1150 cm$^{-1}$ respectively. The borane reagent function available for reduction was determined spectrophotometrically. The value obtained even after recycling the reagent resin for 5 times was almost the same as that of fresh resin. The results are summarised in Table 4.7. The utility of the regenerated resin was checked by the reaction with 2-nitrobenzaldehyde. The resin (100 mg) was swollen in DCM (10 mL) and to this suspension 2-nitrobenzaldehyde (20 mg) was added and shaken. The same reaction was carried out with the fresh resin (2e$_1$). The reactions were monitored by TLC. The time taken for complete reduction of 2-nitrobenzaldehyde was the same (3 h) in both the cases.
6.17 Preparation of Polymer Bound Monofunctional Amines

6.17.1 Preparation of aminomethyl polystyrene

The chloromethyl polystyrene resin (2b₁, 1 g, 4 mmol) was allowed to swell in DMF (20 mL) for half an hour. Potassium phthalimide (3.1 g, 4 molar excess) was added to the suspension and the reaction mixture was heated at 110-120°C for 12 h. The phthalimidomethyl resin obtained was filtered and washed with DMF, DMF-water and finally washed with methanol and dried under vacuum. The phthalimidomethyl resin (1 g) swollen in THF (20 mL) was refluxed with ethanol (10 mL) and hydrazine hydrate (1.5 mL, 2 molar excess) for 3 h. The resin was filtered and washed with ethanol, THF, THF-water, water and finally with methanol. The resin was dried under vacuum. The resin on heating with alcoholic solution of ninhydrin showed blue colour. The amino capacity of the resin was determined by picric acid method and the value obtained was 3.95 mmol/g. The aminomethyl resin was characterised by IR spectrum which showed the characteristic band of N-H stretching at 3240 cm⁻¹.

6.17.2 Preparation of polymer-bound ethylamine

Chloromethyl resin (2b₁) (2g, Cl capacity 4 mmol/g) was swollen in DMF (20 mL) and shaken with ethylamine (4 mL, 5 molar excess). After 15 h, the resin was filtered and washed with DMF (3 × 10 mL), 1:1 DMF-MeOH (3 × 10 mL), 1:1 methanol-water (3 × 10 mL) and finally with water until free from excess ethylamine and free chloride ions. The amino capacity of the resin was estimated by picric acid method and the value obtained was 3.6 mmol/g. The residual chlorine in
the resin was checked by Volhard’s titration. No residual chlorine was found in the resin. The IR spectrum of the aminated resin showed a characteristic N-H stretching band at 3280 cm\(^{-1}\) and disappearance of C-Cl band at 680 cm\(^{-1}\).

6.17.3 Preparation of diethylaminomethyl polystyrene resin

Chloromethyl resin (2b\(_1\), 2 g, 4 mmol-Cl/g) was swollen in DMF (20 mL) and shaken with diethylamine (4.2 mL, 5 molar excess). After 15 h the resin was filtered and washed with DMF (3 \(\times\) 10 mL), 1:1 DMF-MeOH (3 \(\times\) 10 mL), 1:1 methanol-water (3 \(\times\) 10 mL) and finally with water until free from excess diethylamine and free chloride ions. The residual chlorine in the aminated resin was checked by Volhard’s titrimetric method. Complete conversion was not observed in this case. The residual chlorine capacity of the resin was found to be 0.5 mmol/g.

6.18 Preparation of Polymer Bound Amine-borane Reagents Using Monofunctional Amines

6.18.1 Preparation of Polymer bound methylamine-borane (\(1^0\) amine-borane reagent (2e) from aminomethyl polystyrene)

The aminomethyl polystyrene resin was converted to the amine hydrochloride resin according to the procedure previously described. The resin (1 g) after overnight swelling in NMP was shaken with HCl (4 mL). The amine hydrochloride resin was washed and dried under vacuum. The resin (1 g) was swollen in DMF (15 mL) and was shaken with sodium borohydride (0.5 g, 2 molar excess) for 5 h. The resin was filtered and washed with DMF (3 \(\times\) 10 mL) DMF-water
(3 × 10 mL) and with water, until excess sodium borohydride and free chloride ions were completely removed. Finally the resin was washed with methanol and dried under vacuum. The polymer bound methylamine-borane was characterised by IR spectrum (Fig. 4.6). The IR spectrum shows the B-H and B-N stretching bands at 2392 cm⁻¹ and 1170 cm⁻¹ respectively. The borane function of the polymeric reagent available for reduction was determined spectrophotometrically and the value was found to be 2.92 mmol/g.

6.18.2 Preparation of polymer bound secondary amine-borane (2e") from ethylaminomethyl resin

The ethylaminomethyl resin (2 g) was swollen in NMP (20 mL) for 12 h and was shaken with HCl (4 mL) for 10 h. The resin was filtered and washed with water until free from acid and chloride ions. Finally the resin was washed with methanol and dried under vacuum. The amine hydrochloride resin (2 g) was suspended in DMF (20 mL) and shaken with sodium borohydride (0.545 g, 2 molar excess) for 5 h. After the reaction, the polymer was washed with DMF (3 × 10 mL), DMF-water (3 × 10 mL) and with water, until excess sodium borohydride and free chloride ions were completely eliminated. Finally, the resin was washed with methanol and dried under vacuum. The IR spectrum (Fig. 4.7) of polymer bound ethylamine-borane, showed a B-H stretching band at 2365 cm⁻¹ and B-N stretching band at 1167 cm⁻¹. The borane reagent function of the polymeric reagent, available for reduction was determined spectrophotometrically. The value was found to be 2.84 mmol/g.
6.18.3 Preparation of polymer bound diethylamine-borane (2e'"")

The diethylaminomethyl resin (2 g) was swollen in NMP for 12 hrs and was shaken with HCl (4 mL) for 10 hrs. The resin was washed with water and methanol. The resin was dried under vacuum. The amine hydrochloride resin (2 g) was suspended in DMF (20 mL) and shaken with sodium borohydride (0.5 g, 2 molar excess) for 5 h. After the reaction, the polymer was washed with DMF (3 x 10 mL), DMF-water (3 x 10 mL) and water, until excess sodium borohydride and free chloride ions were completely eliminated. Finally, the resin was washed with methanol and dried under vacuum. The IR spectrum (Fig. 4.8) of the resin showed the B-H and B-N stretching bands at 2370 cm\(^{-1}\), 2310 cm\(^{-1}\) and 1164.5 cm\(^{-1}\).

6.19 Reduction of Aldehydes Using Polymer Bound Amine-Borane Reagents (2e', 2e'', 2e'''"")

The polymer bound amine-borane reagent (100 mg) was suspended in DCM (10 mL) and was shaken with 2-nitrobenzaldehyde (20 mg). The reaction was followed by TLC. The time taken for 100% conversion of 2-nitrobenzaldehyde was noted. 4-Cyanobenzaldehyde, benzaldehyde and p-methoxybenzaldehyde were reduced by the polymeric amine-borane reagents (2e', 2e'', 2e'''). The results are summarized in Table 4.9.

6.20 Swelling Studies

The dry resin (500 mg) was weighed accurately in a sintered crucible. The resin was equilibrated with solvent for 24 h. The weight of swollen resin
was noted. A control was done with the empty crucible. The swelling capacity of the resin was calculated using the equation,

\[
\text{Swelling capacity} = \frac{\text{weight of swollen resin}}{\text{weight of dry resin}}
\]

Swelling capacity of resin in mg/mL = \(\frac{\text{weight of swollen resin}}{\text{weight of dry resin} \times \text{density of solvent}}\)

The swelling studies of DVB-PS, HDODA-PS and BDDMA-PS resins were carried out in different solvents. The results are given in Table 3.8. Swelling properties of HDODA-PS resins of different crosslink densities were also studied (Table 3.9). Solvation properties of the HDODA-PS resin (2b1) at various stages of functionalisation are studied and the results are shown in Fig. 3.11. Swelling capacities of EDA-borane reagents prepared from DVB-PS and HDODA-PS resins were determined in different solvents (Table 3.10).

6.21 Preparation of Amine-borane Reagents on Crosslinked Polyacrylamide Resins

6.21.1 Preparation of 5% NNMBA crosslinked polyacrylamide

NNMBA crosslinked polyacrylamides were prepared by free radical initiated solution polymerisation. For the preparation of 5% NNMBA crosslinked polyacrylamide, the monomer acrylamide (13.6 g) and the crosslinking agent, NNMBA (1.5 g) were dissolved in water. The initiator potassium persulphate (500 mg) was added and the reaction mixture was heated with stirring at 80°C
for 5 h. The polymer was collected by filtration and washed with water, methanol and acetone. The lumps were powdered and dried at 60°C.

6.21.2 Preparation of 5% HDODA crosslinked polyacrylamide

HDODA crosslinked polyacrylamides were prepared by free radical solution polymerisation. The mixture of monomers acrylamide (13.49 g) and 1,6 hexanediol diacrylate were dissolved in ethanol (70 mL). Benzoyl peroxide (250 mg) was added to it and the contents were heated on a water bath. The reaction mixture was stirred until the polymer was precipitated. Heating was continued for 30 min and the polymer was filtered, washed with water and methanol and dried at 60°C.

6.21.3 Incorporation of amino groups on crosslinked polyacrylamide resin by transamidation

Ethylenediamine (50 mL) was added to polyacrylamide resin (5 g). The reaction mixture was refluxed at 90°C for 20 h (Scheme 5.3). The reaction mixture was poured into ice cold water. The resin was filtered, washed with aqueous NaCl (0.1 M) solution until the washings were free from ethylenediamine. The resin was washed with water several times to remove chloride ions. Finally, the resin was washed with methanol, acetone and dried under vacuum. The resin on heating with alcoholic solution of ninhydrin showed blue colour indicating the presence of primary amine groups.
6.21.4 Estimation of amino capacity

Each aminated resin (100 mg) was neutralised by equilibration with 0.02 N HCl (20 mL) for 24 h. The resin samples were filtered and washed with distilled water to remove unreacted HCl and the filtrate was titrated against NaOH (0.02 N). A blank titration was also carried out. The amino group capacities of the NNMB and HDODA crosslinked resins were found to be 2.5 and 3 mmol/g respectively.

6.21.5 Conversion of the amino functionalised resins to the corresponding amine-hydrochloride

The aminated resin (5 g) was equilibrated with 0.02N HCl and shaken for 10 h. The resin was washed with water and methanol and dried under vacuum.

6.21.6 Preparation of amine-borane reagent on polyacrylamide resins

The protonated aminopolyacrylamide resin (5 g) was suspended in water. To this sodium borohydride (1.14 g, 2 molar excess) dissolved in DMF was added and shaken for 10 h. After reaction the resin was washed with water thoroughly to remove excess sodium borohydride and free chloride ions completely. The resin was washed with methanol and acetone and dried under vacuum. The reagent on treatment with HCl showed evolution of hydrogen. The capacity calculated from residual amino groups showed very low borane content.

6.22 Reduction of Aldehydes

The polyacrylamide supported amine-borane (250 mg) was allowed to swell in water (10 mL) for 1 h. To the suspension, 2-nitrobenzaldehyde (20 mg)
dissolved in minimum volume of THF (5 mL) was added and the reaction mixture was shaken. The reaction was monitored by TLC. No noticeable conversion was observed by TLC. The reduction was continued for 20 h and very low conversion was observed. The reaction was repeated with excess of polymeric reagent (500 mg and 1 g). No considerable change in reaction was observed.

6.22.1 Reduction of aldehyde at high temperature

The reduction of aldehydes with polyacrylamide bound amine-borane reagent was carried out at high temperature. The reagent (1 g) was swollen in water. To the reaction mixture 2-nitrobenzaldehyde (20 mg) dissolved in THF was added and the reaction mixture was stirred at 70°C. The reaction was monitored by TLC. Even after 20 h very low conversion was obtained. The reaction was repeated with other substrates, 4-cyanobenzaldehyde and benzaldehyde and similar results were observed.

6.22.2 Reduction in the presence of acid catalyst

The polyacrylamide supported amine-borane reagent (50 mg) was swollen in water. To the suspension, 2-nitrobenzaldehyde (20 mg) dissolved in THF was added. Glacial acetic acid (0.1 mL) was added to the reaction mixture and shaken. The reaction was monitored by TLC. After 20 h the mixture was filtered and unreacted aldehyde was washed off. The resin was hydrolysed with HCl and the product alcohol was isolated. Only 8% conversion was obtained.