Experimental

7.1. Materials

Divinylbenzene (DVB), 1,4-butanediol dimethacrylate (BDDMA), 1,6-hexanediol diacrylate (HDODA) and N,N-methylebisacrylamide (NNMBA) were purchased from Aldrich Chemical Company, USA. Styrene, acrylamide, ethylenediamine and benzoyl peroxide were purchased from Merck, Germany. All other chemicals and solvents were commercially available samples and were purified by distillation or recrystallization as per the standard procedures.

7.2. Instrumental

- IR spectra were recorded on a Shimadzu FT-IR-8400 S spectrophotometer.

- Thermal stability was determined by Shimadzu Simultaneous DTA-TG

- Scanning electron microscopic studies were carried out using JEOL-JSM840A.

- 1H NMR spectra recorded using BRUKER BZH 500MHz NMR spectrometer.

- UV spectra were recorded using Shimadzu UV-2450 spectrophotometer.

- Elemental analysis using Perkin Elmer PE: 2400 CHN analyser.

- Melting points were measured using Buchi-530 melting point apparatus.

- Mass spectral analysis was carried out by Thermo Scientific™ TSQ™ 8000 Evo Triple Quadrupole GC-MS/MS with Autosampler.
7.3. Preparation of various crosslinked polystyrenes

Styrene (100 mL) washed with 1% NaOH solution (3 × 40 mL) and water (3 × 40 mL) to remove the stabilizers. The final clear solution was then dried over anhydrous sodium sulphate.\textsuperscript{189}

Benzoyl peroxide (50 mg) was purified by dissolving in CHCl\(_3\) (15 mL) at room temperature and precipitating by the addition of an equal volume of methanol (15 mL). Dried under vacuum at room temperature for 24 h and stored in a desiccators.

7.3.1. Preparation of DVB-crosslinked polystyrene supports with varying crosslink density(1a\textsubscript{1}-1a\textsubscript{5})

Radical initiated suspension polymerization technique was employed for the preparation of crosslinked polystyrene resins.\textsuperscript{190}

A mixture of styrene (22.4 mL, 98 mmol) and DVB (1.04 mL, 2 mmol) in toluene (10 mL) and benzoyl peroxide (500 mg) was suspended in 1% solution of polyvinyl alcohol (2.2 g, 350 mL water). This suspension was stirred mechanically at 85 °C under 600 rpm. The polymerization was allowed to proceed for 6 h. The white shiny beads obtained were collected by simple filtration, washed with hot water to remove PVA and purified by Soxhlet extraction with acetone, chloroform and finally with methanol to remove all low molecular weight impurities. The polymer beads were dried under vacuum at 50 °C and sieved into 200-400 mesh size. The yield of the polymer obtained was 87%.

DVB-crosslinked polystyrene with 4,8,12 and 20 mol% DVB crosslinking (1a\textsubscript{2}-1a\textsubscript{5}) were also prepared using the same procedure by varying the composition of the monomer and crosslinker (Table 3.1).\textsuperscript{191}
7.3.2. Preparation of BDDMA-crosslinked polystyrene supports with varying crosslink density (2a\textsubscript{1}-2a\textsubscript{5})\textsuperscript{192}

BDDMA-crosslinked polystyrene supports with varying crosslink density were prepared as per the radical initiated suspension polymerization of styrene and BDDMA (Table 3.2). FTIR: 1721 cm\textsuperscript{-1}.

7.3.3. Preparation of HDODA-crosslinked polystyrene supports with varying crosslink density (3a\textsubscript{1}-3a\textsubscript{5})

Polystyrene supports with varying HDODA crosslink density were also prepared as per the radical initiated suspension polymerization of styrene and HDODA. The details of polymer synthesis of polymer synthesis are given in Table 3.3. FTIR: 1721 cm\textsuperscript{-1}.

7.4. Functionalization of crosslinked polystyrene resins

7.4.1. Preparation of chloromethyl methyl ether, CMME\textsuperscript{193}

A mixture of formaldehyde (132 mL) and methanol (66 mL) were kept at 0 °C and dry HCl was passed through the reaction mixture till an oily layer of CMME was formed. The oily layer was separated and dried over CaCl\textsubscript{2}. The reaction was carried out in fumehood.

7.4.2. Preparation of 1M ZnCl\textsubscript{2} in THF

Anhydrous ZnCl\textsubscript{2} (0.5 g) was taken in an Erlenmeyer flask and conc. HCl (3 drops) and water (5 drops) were added to it; the solution was heated till complete dissolution of the solid. Heating was continued till a solid mass of ZnCl\textsubscript{2} was left which melts on further heating. The mobile liquid mass was kept in a desiccator and allowed to cool. The solid obtained was dissolved in freshly distilled anhydrous THF (10 mL) and kept sealed.
7.4.3. Synthesis of chloromethylated resins (1b₁-1b₅, 2b₁-2b₅ & 3b₁-3b₅): General procedure

Pre-swelled dry resin (1 g) in dichloromethane (10 mL) was refluxed with chloromethyl methyl ether (6 mL) and anhydrous ZnCl₂ in THF (0.4 mL) at 50 °C for 6 h keeping in an oil bath. The polymer was filtered, washed with THF, THF: HCl (1:1), THF: HCl: H₂O (1:1:1) and hot water until free from chloride ions. Then Soxhlet extracted using DCM and finally with methanol. The resin was further purified by Soxhlet extraction using THF and dried in vacuum at 50 °C. FTIR: 681, 1258 cm⁻¹.

All the polystyrene resins (1a₁-1a₅, 2a₁-2a₅ and 3a₁-3a₅) were functionalized in this manner.

7.4.4. Estimation of chlorine capacity - Volhardt’s method

The dry chloromethylated resin (50 mg) was agitated with pyridine (4 mL) at 100 °C for 6 h. To the suspension con. HNO₃ (5 mL), acetic acid-water mixture (1:1v/v, 30 mL) and silver nitrate (0.05 M, 5 mL) were added and titrated against standard ammonium thiocyanate solution (0.1 N) using ferric alum as indicator. A blank titration was also conducted. The estimated of chlorine capacity values of each polymers were included in the corresponding Table 3.5.

7.5. Functional modification of chloromethylated resins

7.5.1. Quaternization of chloromethylated resins: General procedure

To the chloromethylated polymer 1b₁ (1 g, 2.16 mmol Cl) swelled in DMF (15 mL) for 12 h, five molar excess of trimethylamine TMA (0.8 mL, 9 mmol) was added and heated to 80 °C for 6 h. The extent of quaternization was followed by estimating free chloride ion capacity by Volhardt’s titrimetric method. The reaction was found to be completed
after 18 h. The quaternized polymer $1c_1$ was washed with DMF ($5 \times 5 \text{ mL}$), DMF: $\text{H}_2\text{O}$ ($5 \times 15 \text{ mL}, 1:1, \text{ V/V}$) and finally with methanol ($5 \times 10 \text{ mL}$). The chloride ion capacity was found to be $1.82 \text{ mmol} \ \text{Cl}/\text{g}$. \textbf{FTIR}: $1379 \text{ cm}^{-1}$.

Same procedure was adopted for the preparation of all the other quaternized resins and chloride ion capacities were estimated (\textbf{Table 3.7, 3.9 & 3.10}).

7.5.2. Preparation of crosslinked polystyrene based quaternary ammonium dichromate reagents

The polymer beads after quaternization ($1 \text{ g}, 1.82 \text{ mmol}$) was swelled in THF ($5 \text{ mL}$) and shaken with a saturated solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in ACN at room temperature for 12 h. The polymer was filtered and washed with water until the filtrate was completely free from any dichromate ions. The polymer was then washed with methanol and acetone and dried in vacuum to afford orange crystalline polymer beads.

7.5.3. Determination of dichromate capacity

The polymeric dichromate reagent ($100 \text{ mg}$) was suspended in KOH solution ($2 \text{ N}, 10 \text{ mL}$) overnight with occasional stirring. Con. $\text{HCl}$ ($3 \text{ mL}$) and 10% KI ($5 \text{ mL}$) were added to the suspension. Then $50 \text{ mL}$ water was added and titrated against standard sodium thiosulphate using starch as indicator. The details are given in \textbf{Table 3.12}.

7.6. Preparation of polymeric dichromate reagents with spacer arms

7.6.1. Preparation of polymeric dichromate reagents with dimethylene spacer

To a suspension of the BDDMA-PS resin $2a_1$ ($1 \text{ g}$) swollen in DCM ($15 \text{ mL}$) added previously prepared suspension of anhydrous $\text{AlCl}_3$
(3 g) in 1,2-dichloroethane (3 mL) in an ice bath. The mixture was stirred well for half an hour at room temperature and then refluxed for 10 h. After cooling, distilled water (20 mL) was added and the resin particles were filtered at the pump, washed with water, methanol, chloroform and acetone. The polymer was dried and the chlorine capacity of the resin was estimated (2.17 mmol Cl/g).

7.6.2. Preparation of polymeric dichromate reagents with tetramethylene spacer

Preparation of polymeric keto acid

Pre-swelled BDDMA-PS resin (1 g) in DCM (15 mL) and a suspension of succinic anhydride (1.5 g) in anhydrous AlCl₃ (3 g) in DCM (3 mL) was stirred well for 30 minutes and then refluxed for 12 h at 50 °C. After cooling and washing, the resin particles were filtered and subjected to further washing as in the case of reagent with dimethylene spacers. The presence of the acid function was estimated by treating with sodium bicarbonate in aqueous THF and keto group by the formation of phenylhydrazone derivative. The carbonyl capacity of the resin was estimated by titrimetric method using standard NaOH. FTIR: 1655, 1722 cm⁻¹.

Clemensen reduction of keto acid

The polymeric keto acid was then reduced by Clemmenson reduction using Zn-Hg and HCl. Amalgamated zinc was prepared by shaking a mixture of zinc (6 g), mercuric chloride 90.6 g), water (10 mL) and conc. HCl (0.5 mL) for 5 minutes. The supernatant solution was decanted, washed with water and this freshly prepared zinc amalgam was used immediately. A mixture of pre-swelled polymeric keto acid (1 g, 2.25 mmol carboxyl group capacity) in toluene (10 mL), water (7 mL)
and conc. HCl (15 mL) were added to the freshly prepared zinc amalgam. After refluxing for 24 h, the polymeric reagent was cooled, filtered and washed with water, methanol, chloroform and acetone and then dried under vacuum. Negative Borsche’s reagent test confirms the absence of keto group. \textbf{FTIR:} 1450, 1720 cm\textsuperscript{-1}. The carboxyl capacity of the resin was estimated to be 2.21 mmol/g.

\textit{Conversion of acid resin to alcoholic resin}

The acid resin was then converted to alcoholic resin as per the following procedure. To the acid resin (1 g, 2.21 mmol), pre-swelled in dry THF (15 mL) for 12 h, BH\textsubscript{3}-THF (10 mL) was added. The mixture was stirred for 24 h at 0 °C. The polymer was then filtered, washed with THF, acetone and methanol and dried. The hydroxyl capacity of the resin was estimated by acetylation method. To the resin (50 mg) swelled in toluene for 12 h, acetylating mixture (acetic anhydride/pyridine 1:10 by volume, 1 mL) was added and refluxed for 10 h. Distilled water (20 mL) was added to the mixture and refluxed for another 3 h. The unreacted acetic anhydride was hydrolyzed to acetic acid and titrated against standard NaOH solution. A blank reaction was also conducted. The hydroxyl capacity was calculated to be 2.03 mmol.

\textit{Conversion of alcohol resin to chlororesin}

The alcohol resin was then functionally modified to chlororesin by treating with thionyl chloride. The alcoholic resin (1 g, 2.03 mmol) was refluxed with thionyl chloride (6 mL) on a water bath for 3 h in a fume hood until the evolution of HCl vapours was ceased. The reaction mixture was cooled, filtered and washed with chloroform and acetone. The spacer
modified resin was then dried under vacuum. The chloride capacity was estimated to be 1.98 mmol/g.

Quaternization of chlororesin

The spacer modified chlororesin was swelled in THF and quaternized using TBA according to the procedure discussed earlier. The chloride ion capacity was calculated to be 1.92 mmol/g. The quaternized resin was swelled in THF and treated with K$_2$Cr$_2$O$_7$ as per the reported procedures.

7.7. Preparation of PS-PEG dichromate reagents$^{197}$

Monosodium derivative of PEG$_{600}$ was prepared by heating PEG$_{600}$ (20 mL) in dry THF (50 mL) with metallic sodium (5 g) at 80°C. Chloromethylated polystyrene $1b_1$ (10 g, 3.23 mmol Cl/g) swelled in THF (60 mL) and the PEG$_{600}$ derivative was refluxed at 100°C for 42 h. The resin was filtered, washed with water (5×10 mL), dioxane, methanol and acetone and dried under vacuum. The hydroxyl capacity was estimated to be 2.51 mmol/g. Spacer modification of $2b_1$ and $3b_1$ were also carried out as per the same procedure.$^{198}$

The PS-PEG-CH$_2$-OH resin was converted to PS-PEG-CH$_2$-Cl resin by treating with thionyl chloride as per the same procedure discussed earlier. The chlorine capacity of the resin was estimated and was calculated to be 2.34 mmol/g. PEG grafted chlororesin swelled in THF was quaternized using TBA as discussed earlier. The quaternized PS-PEG resins were then treated with potassium dichromate in acetonitrile as per the same methodology reported earlier.
7.8. Preparation of polyacrylamide supported dichromate reagents

7.8.1. Preparation of 5% NNMBA crosslinked polyacrylamide 4a

The monomer acrylamide (13.6 g) and the crosslinker NNMBA (1.5 g) were dissolved in water. The radical initiator potassium persulfate (500 mg) was added to the mixture and heated with stirring at 80 °C for 2 h. Heating and stirring was continued for 3 h to ensure the completion of the polymerization reaction. The polymer formed was collected by filtration and washed with water, methanol and acetone. The polymer lumps were powdered and dried at 60 °C.

7.8.2. Preparation of 5% BDDMA crosslinked polyacrylamide 5a

The mixture of acrylamide monomer (13.5 g) in water and BDDMA (0.25 mL) dissolved in ethanol (70 mL) was stirred well with the radical initiator benzoyl peroxide (250 mg) till the polymer got precipitated. The polymer formed was filtrated and washed with water, methanol and acetone and dried at 60 °C.

7.8.3. Transamidation of crosslinked polyacrylamide resins

A mixture of polyacrylamide resin 4a (5 g) and excess of ethylenediamine (50 mL) was refluxed at 90 °C for 20 h. The reaction mixture was poured into ice cold water, filtered, washed with aqueous NaCl (0.1 M) solution until the washings were free from ethylenediamine. The transamidated resin washed thoroughly with water to remove chloride ions. Finally, the aminated resin 4b was washed with methanol and acetone and dried under vacuum. The presence of primary amine groups were confirmed from the blue colouration obtained with alcoholic solution of ninhydrin. Aminated resin 5b was also prepared in the same manner.

Estimation of amino capacity of the resin was also conducted. For this, the aminated resin 4b (100 mg) was treated with excess HCl (0.02 N,
20 mL) and kept for 6 h. The resin sample was filtered and washed with distilled water (6 × 10 mL) to remove the unreacted HCl and the filtrate was back titrated against NaOH (0.02 N). A blank reaction was also conducted. The amino capacity estimated was 2.40 mmol/g. Similarly amino capacity estimated for 5b was 2.92 mmol/g.

7.8.4. Quaternization of the amino functionalized acrylamide resin

The quaternization reaction was carried out by stirring pre-swelled NN MBA crosslinked polymeric amino resin 4b (1 g) with excess methyl iodide and saturated solution Na₂CO₃ (1 mL) at room temperature for 24 h. The resin was filtered and washed with acetone, ethyl acetate and then with ether to afford quaternized product 4c. Similar method was adopted to prepare 5c from BDDMA crosslinked resin 5b. The iodide ion capacity was estimated by titrimetric method using AgNO₃.

7.8.5. Quaternization of the amino functionalized resins

The quaternized resin was then converted to the polymeric dichromate reagent by treating with potassium dichromate solution as per the procedure discussed earlier. The dichromate capacity was also estimated and was found to be 0.35 and 0.43 mmol/g for the polymeric reagents 4d and 5d.

7.9. Swelling studies

The dry polymers were equilibrated with the solvents (chloroform, DCM, THF, Toluene, methanol, water and hexane) in dry previously weighed sintered crucibles for 24 h. The excess solvent was drained. Adhering traces of solvents were removed by pressing with filter paper. The weight of the swollen polymer was noted. From the difference in weights the equilibrium swelling ratio was calculated.
7.10. Oxidation reactions using crosslinked polymeric dichromate reagents

7.10.1. Oxidation of benzoin using polystyrene based dichromate reagent 1d₁

In a typical reaction, the substrate benzoin (27.56 mg, 0.12 mmol) was dissolved in chloroform (5 mL) and 2 molar excess of the polymeric dichromate reagent 1d₁ swelled in CHCl₃ was added. Five drops of glacial acetic acid was added to the reaction mixture and refluxed for 6-12 h in a water bath shaker. The progress of the reaction was followed by TLC and the time for complete conversion was noted.

The same procedure was adopted for other alcohols and polystyrene based reagents.

7.10.2. Kinetics of oxidation of benzoin to benzil

The kinetics of the conversion of benzoin to benzil was monitored spectrophotometrically at 283 nm. Aliquots were taken in regular intervals of time and the absorbance values were noted and the percentage conversion was evaluated using standard calibration curves. The rate constant was also evaluated as per pseudo first order kinetics. After the complete conversion, the spent polymer was filtered and washed with solvent. The filtrate was dried over anhydrous sodium sulphate and the product was isolated by evaporating the solvent.

7.10.3. Oxidation of benzoin using NN MBA crosslinked polyacrylamide bound dichromate reagent 4d

To the pre-swollen polyacrylamide derived dichromate reagent 4d (2 mmol) in water, the substrate benzoin (1 mmol) dissolved in minimum quantity of THF was added. The reaction mixture was stirred at 70 °C. The reaction was monitored by TLC and UV spectrophotometry.
Oxidation of benzoin was repeated with BDDMA-PA dichromate reagent 5d too. The same procedure was adopted for the oxidation of other alcohols.

**7.10.4. Oxidation of metal ions: General procedure**

The substrate ferrous sulphate (152 mg, 0.1 mmol) was dissolved in water (5 mL) and reacted with 2 molar excess of the polyacrylamide bound dichromate reagent 4d in aqueous medium at room temperature. The progress of the reaction was followed by TLC and the time for complete conversion was noted.

The reaction was repeated with 5d derived from PA-BDDMA. In the case of 2g, the reaction was carried out with the reagent swelled in THF. The same procedure was adopted for the oxidation of Co(NO\(_3\))\(_2\)·6H\(_2\)O, CuCl\(_2\) and Hg\(_2\)Cl\(_2\).

**7.10.5. Oxidation of amino acids: General procedure**

To the substrate phenylalanine (165 mg, 1 mmol) dissolved in minimum quantity of CHCl\(_3\), 2 molar excess of the dichromate reagent 2g\(_1\) pre-swelled in CHCl\(_3\) and refluxed in a typical reaction.

In aqueous medium, the reaction was carried with 4d, the polyacrylamide bound dichromate reagent by dissolving the substrate phenylalanine in minimum amount of THF. Oxidation of all the other amino acids was carried out using these procedures.

**7.10.6. Oxidation of pyrrole**

The substrate pyrrole (67 mg, 1 mmol) dissolved in minimum quantity of CHCl\(_3\) was refluxed with 2 molar excess of the polystyrene supported dichromate reagent 2g\(_1\) swelled in chloroform. The reaction was repeated with 4d, the NNMBPA-PA reagent in aqueous medium by
dissolving pyrrole in minimum quantity of THF. The oxidation of porphyrin was also carried out as per the same methodology.

**7.10.7. Oxidation of nicotine**

Nicotine (162 mg, 1 mmol) was dissolved in CHCl\textsubscript{3} and refluxed with 2g\textsubscript{1} swelled in CHCl\textsubscript{3}. The progress of the reaction was monitored by TLC. The oxidation was repeated with the polymeric reagent 4d/5d in aqueous medium by dissolving nicotine in minimum quantity of THF.

**7.10.8. Oxidation of indole**

The substrate indole (117 mg, 1 mmol) was taken in a stoppered bottle and dissolved in hot water (5 mL). To this solution, 2 molar excess of dichromate reagent 4d (PA-NNMBA resin) swelled in water was added and the reaction was carried out at 90 °C.

**7.10.9. Oxidation of sulfides: General procedure**

In a typical reaction, thioanisole (124 mg, 1 mmol) was dissolved in CHCl\textsubscript{3} was refluxed with 2g\textsubscript{1}, the dichromate reagent bound on 2% BDDMA-PS-PEG resin for 2 h.

In aqueous medium, the reaction was carried out with 2 molar excess of PA-NNMBA derived reagent 4d and PA-NNMBA supported reagent 5d by dissolving the substrate in THF.

The same procedures were adopted for the oxidation of all the other sulfides.

**7.11. Recycling and reuse of the spent reagent**

The spent resin was washed thoroughly with chloroform (3 × 5 mL) followed by acetone (3 × 5 mL) and methanol (3 × 5 mL) to remove any
residual soluble organic substrate or product. The dried polymer was treated with HCl (2N, 4× 5 mL), NaOH (2N, 4× 5 mL), and washed with distilled water several times and finally with acetone. The polymer was then treated with K$_2$Cr$_2$O$_7$ in acetonitrile at room temperature. Filtered, washed with water till the filtrate becomes colourless.