

## SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF *N,N'*-BIS(3-ALLYL SALICYLIDENE)ETHYLENEDIAMINE COBALT(II) SCHIFF BASE COMPLEX ANCHORED ON A NEW POLYMER SUPPORT

K.C. Gupta\*, H.K. Abdulkadir and S. Chand

Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee-247667, India

**Abstract** A new chelating polymer support has been prepared by suspension copolymerization of synthesized *N,N'*-bis(3-allyl salicylidene)ethylenediamine monomer Schiff base (*N,N'*-BSEDA) with styrene (St) and divinylbenzene (DVB) using azobisisobutyronitrile (AIBN) as initiator in the presence of poly(vinyl alcohol). The content and complexation ability of monomer Schiff base (*N,N'*-BSEDA) for cobalt(II) ions in prepared crosslinked polymer beads have shown dependence on the amount of DVB used in reaction mixture. The amount of monomer Schiff base (*N,N'*-BSEDA) in crosslinked beads showed a substantial decreasing trend at high concentration of DVB in the reaction mixture ( $> 1.5 \text{ mol dm}^{-3}$ ), hence the efficiency of complexation (EC%) and cobalt(II) ion loading (EL%) of polymer beads showed a decreasing trend. The structure of monomer Schiff base (*N,N'*-BSEDA) and its cobalt(II) complex on polymer support was elucidated by IR, UV and magnetic measurements. The catalytic activity of polymer bound cobalt(II) Schiff base complex was evaluated by analyzing kinetic data of decomposition of hydrogen peroxide in the presence of either supported cobalt (II) complex or free cobalt(II) complex. The activation energy for the decomposition of hydrogen peroxide by polymer supported cobalt(II) complex was found to be low ( $33.37 \text{ kJ mol}^{-1}$ ) in comparison with unsupported cobalt(II) complex ( $56.35 \text{ kJ mol}^{-1}$ ). On the basis of experimental observations, reaction steps are proposed and a suitable rate expression derived.

**Keywords** Cobalt(II) complex, Polymer support, Hydrogen peroxide, Catalysis

### INTRODUCTION

Although homogeneous catalysts have higher selectivity and act under mild experimental conditions in various reactions they have problems of separation and recovery from reaction products. Hence current research activities are aimed at developing catalysts of coordination compounds anchored on suitable supports<sup>[1, 2]</sup>. This technique of immobilization of catalyst on an inert support increases the catalytic activity, selectivity, efficiency<sup>[3]</sup>, operational flexibility and stability. The decrease in efficiency of catalyst at high concentration in homogeneous and unsupported conditions was considered to be due to aggregation and insolubilization of catalyst in the reaction mixture. But in polymer bound conditions, the aggregation of catalyst is physically prevented by the polymer matrix. The most challenging problems in supported catalysts are their characterization by commonly used physico-chemical techniques; hence they are characterized indirectly by evaluating their catalytic activity in comparison with the unsupported analogues. The unsupported catalysts are more sensitive to poisoning by impurities in comparison with the supported catalysts. Insoluble polymer supports are most frequently used as inert support for immobilizing the transition metal catalysts over cross-linked chloromethylated polystyrene<sup>[4]</sup>, poly(methyl methacrylate), poly(glycidyl methacrylate), poly(hydroxy ethyl methacrylate)<sup>[5, 6]</sup> and silica<sup>[7]</sup>. The metal complexes on polymeric supports have shown excellent catalytic activity for the hydrogenation of unsaturated substrates<sup>[8–10]</sup> compared to homogeneous catalysts<sup>[11]</sup>. Polymer supported catalysts have been used

\* Corresponding author: K.C. Gupta, E-mail: kcgptfcy@iitr.ernet.in

Received October 8, 2002; Revised January 8, 2003; Accepted January 10, 2003

for enantioselective epoxidation of *cis*-alkenes analogous to Jacobson catalysts<sup>[12–14]</sup>. The synthesized new polymer support keeps metal complex far away and provides access to the substrate and improves its catalytic efficiency as compared with Merrifield resins routinely used for supporting the catalysts. Many researches have been reported on linker groups for attachment of reagent to resins<sup>[15–17]</sup>. This area of polymer supported catalysts is expanding enormously because of their high efficiency, thermal stability<sup>[18, 19]</sup>, ease of handling and economy in various industrial processes<sup>[20, 21]</sup>. Cobalt(II) complexes supported on cross-linked polystyrene through phosphine ligands have been reported<sup>[22, 23]</sup> but they have not shown significant increase in their catalytic activity due to high percentage of non-coordinated polymer bound phosphine ligands. The Schiff base complexes of transition metal ions have been anchored on chloromethylated polystyrene and their structural information discussed<sup>[24]</sup>. In these reported catalysts, the ligands or transition metal complexes are anchored on insoluble polymer supports but the synthesis of supported catalysts by copolymerizing monomer Schiff base with other monomers using cross-linking agent has not been reported sufficiently, hence the present investigations aim to synthesize chelating support by polymerizing monomer Schiff base and loading of cobalt(II) ions was carried out to prepare polymer supported catalyst. The activity of prepared catalyst was evaluated by studying the rate of decomposition of hydrogen peroxide under various experimental conditions.

## EXPERIMENTAL

### Material and Methods

Salicylaldehyde and ethylenediamine (A.R. grades, B.D.H., UK) were purified by standard methods before using them in synthesis of salicylidene ethylenediamine (salen). Allyl chloride, divinyl benzene (DVB) and poly(vinyl alcohol) ( $M_w = 50 \times 10^3 \text{ g mol}^{-1}$ ) were procured from Aldrich Chemical Company, USA and vacuum distilled for synthesis of polymer support. The stabilizer in styrene was removed by washing with aqueous NaOH solution and water and finally dried with anhydrous calcium chloride.

### FTIR-Spectra

The FTIR spectra of free ligand (*N,N'*-BSEDA), polymer anchored ligand and their cobalt(II) complexes were recorded with KBr pellets using a Perkin-Elmer 1600 FTIR spectrophotometer.

### Electronic Spectra

The electronic spectra of the catalyst were recorded with an UV-VIS 1601 PC Shimadzu spectrophotometer in DMF.

### Magnetic Measurements

The magnetic moment ( $\mu$ ) of free and polymer supported *N,N'*-bis(3-allyl salicylidene) ethylenediamine cobalt(II) complex was measured with a Gouy balance at 297 K.

### Thermal Studies

The thermal stability of polymer anchored monomer Schiff base and its cobalt(II) complex was evaluated using a Stanton Redcroft STA-780 Thermal Analyzer (UK).

### Molecular Weight Measurements

The molecular weight of the monomer Schiff base (*N,N'*-BSEDA) and its cobalt(II) complex was determined with a vapor pressure osmometer (Knauer K-700, Germany) using benzil as the standard.

### SEM Studies

The beads size and their degree of swelling (%S) in DMF was measured with a scanning electron microscope (Leo-435 VP-England) by mounting beads on metal stubs and vacuum coating with gold.

### Synthesis of Monomer Schiff Base *N,N'*-bis(3-allyl salicylidene)ethylenediamine (*N,N'*-BSEDA)

First of all, quadridentate Schiff base, *N,N'*-bis(salicylidene)ethylenediamine (salen), was prepared by refluxing an ethanolic mixture of salicylaldehyde (2 mmol, 0.244 g) and ethylenediamine (1 mmol, 0.06 g) for 45 min at 70 °C. On cooling the reaction mixture, a bright yellow product was obtained which was filtered off and purified by

washing repeatedly with ethanol. The recrystallized yellow colored product was finally vacuum dried on calcium chloride (Yield: 71%, m.p. 128°C, (Lit. 126°C)). The potassium salt of salen was obtained by mixing 10 mmol (2.68 g) of salen and 20 mmol (1.14 g) of KOH in 20 mL of methanol and evaporating methanol under vacuum after stirring for 10 min. To obtain *N,N'*-bis(2-allyloxy salen), a calculated amount of potassium salt of salen (10 mmol, 3.4 g) was mixed with allyl chloride (10 mmol, 0.765 g) in DMF (20 mL) and refluxed for 15 min. The precipitated potassium chloride was filtered and *N,N'*-bis(2-allyloxy salen) was obtained from the filtrate by evaporating solvent in a Buchi vacuum evaporator. After washing the residue with water and recrystallizing in ethyl acetate, yellow colored crystals of *N,N'*-bis(2-allyloxy salen) were obtained (Yield: 75%, m.p. 148°C). The IR spectrum of prepared *N,N'*-bis(2-allyloxy salen) was recorded with KBr pellets. The nitrogen estimation of *N,N'*-bis(2-allyloxy salen) has been used to verify the molecular weight determined by vapor pressure osmometry. To prepare functionalized monomer *N,N'*-BSEDA, 10 mmol (3.48 g) of *N,N'*-bis(2-allyloxy salen) was dissolved in 50 mL of DMF and refluxed for 2 h between 170–180°C, which produced yellow colored residue after evaporating the solvent. During refluxing, the *N,N'*-bis(2-allyloxy salen) was converted into *N,N'*-BSEDA which on recrystallization in toluene/petroleum ether (2:1) mixture (b.p. 60°C–80°C) produced yellow colored crystal (Yield: 56%, m.p. 176°C). Finally, the IR spectrum and molecular weight of *N,N'*-BSEDA were recorded.

#### **Synthesis of *N,N'*-BSEDA Anchored Beads and Loading of Cobalt(II) Ions**

To prepare ligand anchored cross-linked beads, the suspension copolymerization of *N,N'*-BSEDA was carried out with styrene and DVB in the presence of AIBN. A calculated amount of styrene (48.97 mmol, 5.1 g), functionalized monomer *N,N'*-BSEDA (48.97 mmol 17.64 g) and DVB (1.5 mmol, 0.188 g) were dissolved in 50 mL of toluene and deaerated for about 30 min with N<sub>2</sub> gas. The deaerated solution of AIBN (0.3 g in 10 mL toluene) and monomers were added dropwise in a three-necked round bottom flask containing gelatin (0.75 g), bentonite (2.0 g), boric acid (2.5 g) and poly(vinyl alcohol) (1.5 g) in 500 mL of water. The aqueous phase containing suspended droplets of organic phase was stirred vigorously to control the size of the beads and to dissipate the heat released during polymerization and cross-linking reactions during bead formation. At the end of reaction, the mixture was allowed to cool to room temperature and the beads were washed with hot water and dried in vacuum oven at 70°C for about 2 h (Yield: 70%, 18.85 g). The measurements of bead size were carried out with a scanning electron microscope. The IR and elemental analysis (Perkin-Elmer 240C Elemental Analyzer) were carried out for the identification and estimation of *N,N'*-BSEDA in the prepared beads (Table 1a). To obtain beads (Types I-V) of different crosslink densities, the amount of DVB used was varied from 0.8 mmol to 2.0 mmol in the reaction mixture. The complexation of cobalt(II) ions on ligand anchored polymer beads was carried out by keeping known amount of beads swelled by DMF in 40 mL (5 mmol, 1.189 g) solution of cobalt chloride (CoCl<sub>2</sub> • 6H<sub>2</sub>O) and heating to reflux in an oil bath at 120°C for 8 h under magnetic stirring. At the end of refluxing, the brownish-red colored beads were filtered, washed repeatedly with methanol and dried at 80°C. (Yield: 73.9%). IR spectrum of cobalt(II) ion-loaded beads was recorded to ascertain the loading of cobalt(II) ions on polymer anchored monomer Schiff base. The complexation of cobalt(II) ions has also been studied by taking beads of different crosslink densities. The amount of cobalt(II) ions loaded on crosslink beads was estimated by putting 1.0 g of cobalt(II) ion-loaded beads in a conical flask, which contains 20 mL 4.0 mol/L acetic acid, and refluxing on a heating mantle at 105°C. After 2 h, the beads were washed and filtered. The amount of cobalt(II) ions was estimated by analyzing the filtrate with an atomic absorption spectrophotometer (Perkin-Elmer 2100) at  $\lambda_{\max} = 240.7$  nm. The loading of cobalt(II) ions was expressed as efficiency of complexation (EC%) and loading (EL%) using the following equations. It was found that 1.0 g beads of optimum crosslink density (Type-III) can load 1.70 mmol of cobalt(II) ions (Table 1b).

$$\text{EC \%} = \frac{\text{Amount of Co (II) ions loaded g}^{-1} \text{ of beads}}{\text{Amount of ligand available for complexation g}^{-1} \text{ of beads}} \times 100$$

$$\text{EL\%} = \frac{\text{Amount of Co (II) ions loaded g}^{-1} \text{ of beads}}{\text{Amount of Co (II) ions taken initially}} \times 100$$

### Evaluation of Catalytic Activity of Polymer Anchored *N,N'*-BSEDA Co(II) Complex

In order to evaluate the catalytic activity of cobalt(II) ions loaded beads, the rate of decomposition of hydrogen peroxide was evaluated by placing known amount of cobalt(II) ion-loaded beads (Type-III) in 100 mL solution of  $\text{H}_2\text{O}_2$  of known molarity which was obtained from a stock solution of  $\text{H}_2\text{O}_2$  (2 volume, 0.6 W/W%) and thermostated to  $25^\circ\text{C}$  under constant stirring. The amount of undecomposed hydrogen peroxide at different intervals of time was estimated by taking a 5 mL aliquot of the reaction mixture and titrating it with  $0.01 \text{ mol L}^{-1}$   $\text{KMnO}_4$  in the presence of  $0.02 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$ . The procedure was repeated at different initial concentrations of hydrogen peroxide and taking different amount of beads to vary the concentration of cobalt(II) ions in the reaction mixture. To compare the catalytic activity of polymer supported cobalt(II) complex, the decomposition of  $\text{H}_2\text{O}_2$  was also estimated by taking known amount of unsupported cobalt(II) complex in the reaction mixture and determining the rate of decomposition of  $\text{H}_2\text{O}_2$  by a similar procedure to that used for polymer supported cobalt(II) complex.

**Table 1a.** Composition and characteristics of *N,N'*-BSDEA Schiff base anchored crosslinked beads

| Types of beads | DVB* in reaction mixture (mmol) | N%   |      | Amount of <i>N,N'</i> -BSEDA (mmol $\text{g}^{-1}$ ) beads | Beads size ( $\mu\text{m}$ ) | $\rho$ ( $\text{g cm}^{-3}$ ) |
|----------------|---------------------------------|------|------|------------------------------------------------------------|------------------------------|-------------------------------|
|                |                                 | Obs. | Cal. |                                                            |                              |                               |
| I              | 0.80                            | 4.35 | 4.39 | 1.60                                                       | 188.60                       | 0.41                          |
| II             | 1.15                            | 5.69 | 5.68 | 1.96                                                       | 180.00                       | 0.43                          |
| III            | 1.50                            | 6.31 | 6.63 | 2.20                                                       | 178.10                       | 0.46                          |
| IV             | 1.75                            | 4.74 | 4.75 | 1.80                                                       | 160.10                       | 0.49                          |
| V              | 2.00                            | 4.43 | 4.44 | 1.50                                                       | 156.00                       | 0.52                          |

[Styrene]<sub>i</sub> = 48.97 mmol, [*N,N'*-BSEDA]<sub>i</sub> = 48.97 mmol; \* Divinyl benzene

**Table 1b.** Composition and characteristics of *N,N'*-BSDEA Schiff base anchored crosslinked beads

| Type of beads | Percent swelling (%) | Weight of Co (II) ions (mmol $\text{g}^{-1}$ ) of beads | EL (%) | EC (%) |
|---------------|----------------------|---------------------------------------------------------|--------|--------|
| I             | 14.10                | 0.88                                                    | 17.60  | 55.00  |
| II            | 12.60                | 1.25                                                    | 25.00  | 64.00  |
| III           | 9.09                 | 1.70                                                    | 34.00  | 77.00  |
| IV            | 6.80                 | 1.08                                                    | 21.60  | 60.00  |
| V             | 5.20                 | 0.75                                                    | 15.00  | 50.00  |

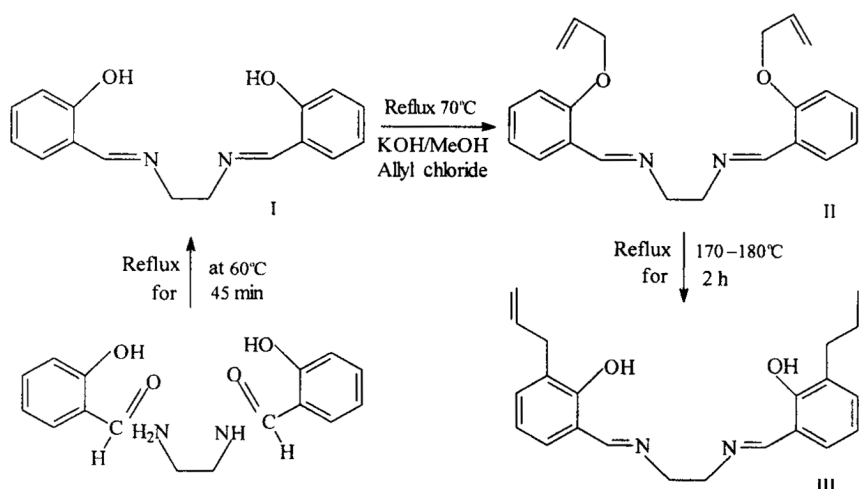
[Co (II)]<sub>i</sub> = 5.0 mmol, EL (Efficiency of loading), EC (Efficiency of complexation)

## RESULTS AND DISCUSSION

The reaction of salicylaldehyde with ethylenediamine can produce salen (Structure-I in Scheme 1) which will produce *N,N'*-bis(2-alkoxy salen) (Structure-II in Scheme 1) on reacting the potassium salt of salen with allyl chloride. The absorption band at  $1150 \text{ cm}^{-1}$  in the IR spectrum has confirmed the presence of the ether group in *N,N'*-bis(2-alkoxy salen). The determined molecular weight ( $348 \text{ g mol}^{-1}$ ) and nitrogen content (8.34%) correspond to  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$  for *N,N'*-bis(2-alkoxy salen). The *N,N'*-BSEDA was obtained by refluxing *N,N'*-bis(2-alkoxy salen) at high temperature ( $170$ – $180^\circ\text{C}$ ) for about 2 h as shown in Scheme 1.

The disappearance of  $\nu(\text{C}=\text{O}=\text{C})$  absorption peak at  $1150 \text{ cm}^{-1}$  in the IR spectrum of *N,N'*-bis(2-alkoxy salen) on heating around  $170^\circ\text{C}$  indicates the shifting<sup>[25]</sup> of allyl group to 3-position of salen to form *N,N'*-BSEDA (Structure-III in Scheme 1). The appearance of  $\nu(\text{OH})$  absorption band between  $2956$ – $3396 \text{ cm}^{-1}$  further confirms the shift of allyl group and regeneration of OH group which is changed to ether group ( $\text{C}=\text{O}=\text{C}$ ) during the reaction of salen with allyl chloride (Scheme 1). The observed molecular weight ( $348 \text{ g mol}^{-1}$ ) of *N,N'*-BSEDA corresponds to  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$ , which agrees with the measured nitrogen content (Obs. 7.99%, Calcd. 8.04%). To prepare unsupported complex, the synthesized monomer Schiff base (*N,N'*-BSEDA) was reacted with

cobalt(II) ions. The IR spectrum of monomer Schiff base (*N,N'*-BSDEA) on complexation with cobalt(II) ions has shown a shift of the  $\nu(\text{C}=\text{N})$  absorption band of azomethine from  $1639\text{ cm}^{-1}$  to  $1621\text{ cm}^{-1}$  (Table 2a) and the band corresponding to phenolic  $\nu(\text{C}=\text{O})$  is shifted from  $1287\text{ cm}^{-1}$  to  $1316\text{ cm}^{-1}$  which gives evidence for coordination of cobalt(II) ions through phenolic oxygen and azomethine nitrogen of monomer Schiff base. The disappearance of original phenolic  $\nu(\text{O}-\text{H})$  band between  $2956\text{--}3396\text{ cm}^{-1}$  on complexation with cobalt(II) ions (Table 2a) also gives evidence for complexation of cobalt(II) ions with monomer Schiff base. The appearance of two new bands at  $576\text{ cm}^{-1}$  and  $426\text{ cm}^{-1}$  is due to the coordination of cobalt(II) ions with phenolic oxygen ( $\text{M}-\text{O}$ ) and nitrogen of azomethine ( $\text{M}-\text{N}$ ) of monomer Schiff base. The electronic spectra of monomer Schiff base on coordination with cobalt (II) ions have shown a shift in  $\pi-\pi^*$  and  $n-\pi^*$  transitions (Table 2b). The appearance of new band at  $388\text{ nm}$  on coordination with cobalt(II) ions is an indication of a charge transfer process (CT) between ligand and metal ( $\text{L}\rightarrow\text{M}$ ). The cobalt(II) ions complex prepared with monomer Schiff base has a magnetic moment ( $\mu$ ) of  $2.31\text{ BM}$  at  $297\text{ K}$ , which corresponds to one unpaired electron in the complex, hence providing an indication of square planar geometry of the complex<sup>[24]</sup> (Table 2b).



Scheme 1

Table 2a. IR Frequencies of *N,N'*-BSDEA Schiff base and its cobalt(II) complex

| Metal ion | Functional groups        | Frequencies of unsupported  |                              | Frequencies of polymer supported |                              |
|-----------|--------------------------|-----------------------------|------------------------------|----------------------------------|------------------------------|
|           |                          | Ligand ( $\text{cm}^{-1}$ ) | Complex ( $\text{cm}^{-1}$ ) | Ligand ( $\text{cm}^{-1}$ )      | Complex ( $\text{cm}^{-1}$ ) |
| Co (II)   | $\nu(\text{OH})$         | 2956–3396                   | -                            | 2907–3432                        | -                            |
|           | $\nu(\text{C}-\text{O})$ | 1287                        | 1316                         | 1283                             | 1312                         |
|           | $\nu(\text{C}=\text{N})$ | 1639                        | 1621                         | 1636                             | 1615                         |
|           | $\nu(\text{M}-\text{O})$ | -                           | 576                          | -                                | 572                          |
|           | $\nu(\text{M}-\text{N})$ | -                           | 426                          | -                                | 423                          |

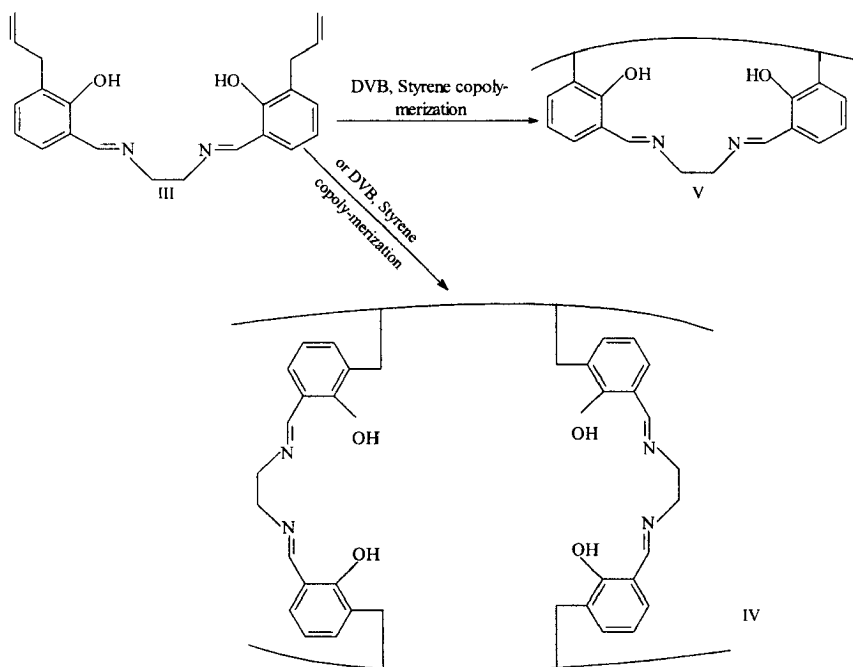
Table 2b. Electronic transitions and magnetic moment of *N,N'*-BSDEA cobalt(II) complex

| Metal ion | Electronic transitions  | Transition frequencies of unsupported |                             | Transition frequencies of polymer supported |                             | $\mu_{\text{eff}}$ (B.M) | Structure     |
|-----------|-------------------------|---------------------------------------|-----------------------------|---------------------------------------------|-----------------------------|--------------------------|---------------|
|           |                         | Ligand                                | Complex                     | Ligand                                      | Complex                     |                          |               |
|           |                         | $\lambda_{\text{max}}$ (nm)           | $\lambda_{\text{max}}$ (nm) | $\lambda_{\text{max}}$ (nm)                 | $\lambda_{\text{max}}$ (nm) |                          |               |
| Co (II)   | $\pi \rightarrow \pi^*$ | 256                                   | 208                         | 254                                         | 205                         | 2.31 (2.05)*<br>at 297 K | Square planar |
|           | $n \rightarrow \pi^*$   | 320                                   | 274                         | 317                                         | 271                         |                          |               |
|           | C $\rightarrow$ T       | -                                     | 388                         | -                                           | 385                         |                          |               |
|           | d $\rightarrow$ d       | -                                     | -                           | -                                           | -                           |                          |               |

\*  $\mu_{\text{eff}}$  of supported catalyst

### Characteristics of *N,N'*-Bis(3-allyl salicylidene)ethylenediamine Anchored Crosslinked Beads

The catalytic activity of polymer anchored metal complex depends upon the nature of polymer support<sup>[26]</sup> and the amount of metal complex anchored on it. The synthesis of polymer supported cobalt(II) complex by anchoring ligands on polymer was well reported<sup>[24, 27, 28]</sup> but the synthesis of polymer anchored cobalt(II) complex by ligand anchored polymer was rarely reported. In order to synthesize polymer supported cobalt(II) complex by this technique, the monomer Schiff base (*N,N'*-BSEDA) was copolymerized with styrene and DVB which can produce polymer support with sufficient chelating sites for complexation of cobalt(II) ions (Structure-IV in Scheme 2). The suspension copolymerization at different concentrations of DVB has produced beads of different size (Table 1a) which was determined by SEM measurements. On increasing the amount of DVB from 0.8 mmol to 2.0 mmol in the reaction mixture, the size of beads decreased from 188  $\mu\text{m}$  to 156  $\mu\text{m}$  (Table 1a) while the degree of swelling was decreased from 14.1% to 5.2% (Table 1b). The density of the prepared beads increased from 0.41  $\text{g cm}^{-3}$  to 0.52  $\text{g cm}^{-3}$  on increasing the amount of DVB from 0.8 mmol to 2.0 mmol in the reaction mixture (Table 1a), indicating that the beads prepared with high amount of DVB were compact with low porosity. The content of monomer Schiff base *N,N'*-BSEDA in the beads (Structure-IV & V in Scheme 2) was found to increase upto 1.5 mmol of DVB in the reaction mixture as verified from the percentage of content (8.34%) nitrogen content (Table 1a). This variation in content of *N,N'*-BSEDA in the polymer beads is due to the competitive reaction of DVB and *N,N'*-BSEDA with styrene taken in the reaction mixture (Structure-IV & V in Scheme 2). With high amount of DVB (> 1.5 mmol) in reaction mixture, the *N,N'*-BSEDA participates exclusively in the formation of linear portion of polymer chains than in the formation of crosslinks between the polymer chains, which has substantially decrease the content of *N,N'*-BSEDA in the polymer beads (Structure-V in Scheme 2).

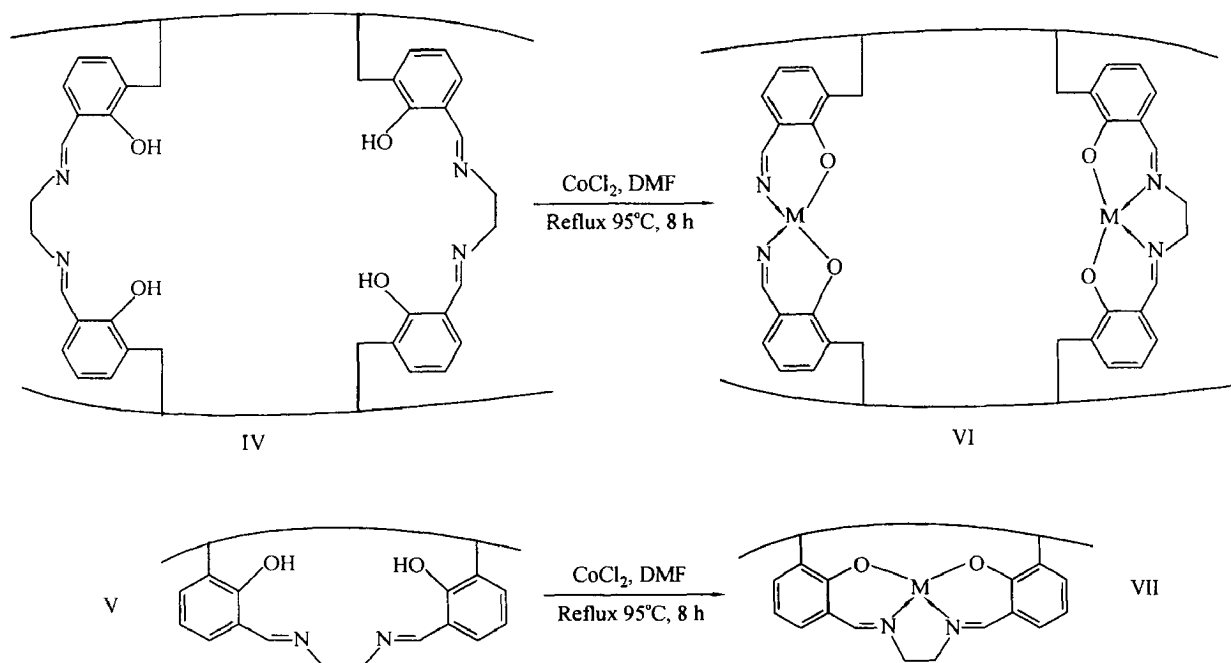


Scheme 2

### Loading of Cobalt (II) Ions on Crosslinked Beads and Their Characterization

The extent of cobalt(II) ions loading on crosslinked beads has shown variation on using different amount of DVB in the reaction mixture. This is evidenced from the decreasing trend (Table 1b) in the efficiency of loading (EL) and complexation (EC) for cobalt(II) ions on polymer beads prepared with high amount of DVB (> 1.5 mmol). This decreasing trend in percent loading (EL) and complexation (EC) for cobalt(II) ions at high concentration of DVB (> 1.5 mmol) is due to the high degree of crosslinking in the beads, which reduces the complexation of

cobalt(II) ions (Table 1b) with polymer anchored monomer Schiff base *N,N'*-BSEDA (Structure-VII in Scheme 3). The decrease in cobalt(II) ions loading at high amount of DVB ( $> 1.5$  mmol) has been attributed to the variation in flexibility<sup>[29]</sup> and configuration<sup>[30]</sup> of monomer Schiff base on polymer beads. The beads obtained at low concentration of DVB ( $\leq 1.5$  mmol) and with *N,N'*-BSEDA as cross-linker between two chains will provide better orientation for *N,N'*-BSEDA on polymer backbone for coordinating easily with cobalt(II) ions (Structure-VI in Scheme 3) than beads obtained at high concentration of DVB ( $> 1.5$  mmol). At high concentration of DVB ( $> 1.5$  mmol), *N,N'*-BSEDA becomes a part of a polymer chain in which coordination of cobalt(II) ions becomes difficult (Structure-VII in Scheme 3) due to high crosslink density in the beads.



Scheme 3

The complexation of cobalt(II) ions on polymer anchored *N,N'*-BSEDA showed a substantial increase in decomposition temperature from  $350^\circ\text{C}$  to  $375^\circ\text{C}$  and a significant reduction in weight loss from 58% to 34% as observed from thermogravimetric analysis (Fig. 1), which suggests that polymer supported cobalt(II) complex can be used as catalyst in reactions operating at high temperature. The structure of polymer anchored cobalt(II) ions complex was proposed on the basis of the magnetic moment ( $\mu$ ), IR and UV measurements. The IR spectrum of *N,N'*-BSEDA anchored polymer (Structure IV&V in Scheme 2 and Table 2a) exhibits a broad and weak absorption band at  $2907\text{--}3432\text{ cm}^{-1}$  attributed to intramolecular hydrogen bonded<sup>[31]</sup> OH stretching vibration (Fig. 2a). The disappearance of the  $2907\text{--}3432\text{ cm}^{-1}$  band on complexation of the polymer with cobalt(II) ions (Fig. 2b and Table 2a) clearly suggest the coordination of cobalt(II) ions with oxygen of phenolate ions of polymer anchored *N,N'*-BSEDA (Structures VI & VII in Scheme 3). The phenolic  $\nu(\text{C}\text{--}\text{O})$  band of polymer anchored *N,N'*-BSEDA on complexation with cobalt(II) ions was shifted from its original frequency at  $1283\text{ cm}^{-1}$  to  $1312\text{ cm}^{-1}$  which again confirms the participation of phenolic oxygen in the formation of metal-oxygen linkage with cobalt(II) ions. The  $\nu(\text{C}\text{--}\text{N})$  band of azomethine at  $1636\text{ cm}^{-1}$  of polymer anchored *N,N'*-BSEDA was shifted to  $1615\text{ cm}^{-1}$  on complexation with cobalt(II) ions, (Fig. 2 and Table 2a). The appearance of new bands at  $572\text{ cm}^{-1}$  and  $423\text{ cm}^{-1}$  on complexation of polymer anchored *N,N'*-BSEDA with cobalt(II) ions was assigned to  $\nu(\text{Co}\text{--}\text{O})$  and  $(\text{Co}\text{--}\text{N})$  stretching vibrations, which further proves the coordination of cobalt(II) ions with nitrogen of azomethine and oxygen of phenolate ion of polymer bound *N,N'*-BSEDA. These IR data further verify the square planar geometry of polymer anchored cobalt(II) ions Schiff base complex as reported in

the literature<sup>[24]</sup>. The reported flexibility<sup>[29]</sup> and preferred *cis*-configuration<sup>[30]</sup> of salen are significant factors responsible for high loading capacity and catalytic activity in comparison with other cobalt(II) Schiff base complexes. The electronic spectra of polymer anchored Schiff base and its cobalt(II) complex provided significant evidence for the complexation of cobalt(II) ions with various coordination sites of monomer Schiff base (*N,N'*-BSEDA). The electronic spectra of polymer anchored Schiff base on complexation with cobalt(II) ions (Structures VI & VII in Scheme 3) show some frequency shifts in their bands (Table 2b) which indicates the coordination of cobalt(II) ions with azomethine nitrogen of Schiff base. The observed bands are assigned to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions. The appearance of transition band at 385 nm in polymer bound cobalt(II) Schiff base complex (Table 2b) implies that the cobalt(II) complex on polymer support has square planar geometry. In order to ascertain the structure of cobalt(II) Schiff base complex, the magnetic moment ( $\mu$ ) of polymer anchored cobalt(II) complex (Structures-VI & VII in Scheme 3) was evaluated and was found to be 2.05 B.M at 297 K (Table 2b) indicating low spin square planar geometry for cobalt(II) complex. The high spin 4-dentate cobalt(II) complexes show tetrahedral structure with magnetic moment ( $\mu$ ) in the range of 4.2 to 4.9 B.M, hence the observed low value of magnetic moment ( $\mu$ ) clearly suggests a square planar geometry for polymer supported cobalt(II) Schiff base complex. But the extent of complexation of cobalt(II) ions depends on the flexibility<sup>[29]</sup> and configuration<sup>[30]</sup> of polymer anchored ligand.

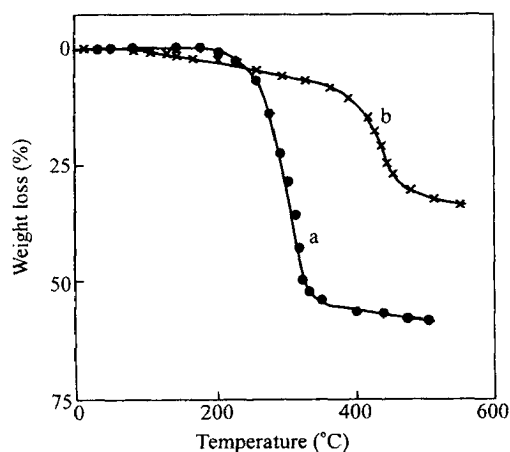


**Fig. 1** TG curves of functionalized (a) and cobalt(II) ion complexed polymer (b)  
Heating rate 10 K/min

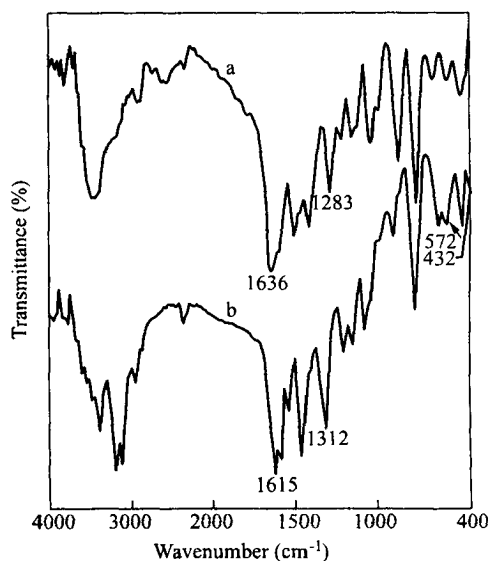


**Fig. 2** FTIR-spectra of *N,N'*-bis(3-allyl salicylidine) ethylenediamine anchored polymer beads (a) and loaded with cobalt(II) ions (b)

### Catalytic Activity of Polymer Anchored *N,N'*-BSEDA Co(II) Complex

The catalytic activity of polymer supported cobalt(II) complex was evaluated by using beads (Type-III) with optimum cobalt(II) ion loading and crosslink density (Structure-VI in Scheme 3). The rate of decomposition of hydrogen peroxide was evaluated at different concentrations of hydrogen peroxide and supported cobalt(II) ions. To avoid structural effects of polymer support on the catalytic activity of cobalt(II) ions, the concentration of supported cobalt(II) ions was varied by using different amount of beads in the reaction mixture of fixed loading capacity (Type-III). The kinetic data were compared with those of unsupported cobalt(II) complex. The rate of decomposition of hydrogen peroxide found to be high ( $k = 8.19 \times 10^{-2} \text{ min}^{-1}$ ) with supported catalyst in comparison with the unsupported catalyst ( $k = 7.68 \times 10^{-3} \text{ min}^{-1}$ ) as illustrated clearly in the plots of  $\lg(a-x)$  versus time (Fig. 3). The turnover number for supported catalyst was high ( $13.52 \times 10^{21} \text{ molecules s}^{-1} \text{ mol}^{-1}$  of cobalt(II) ions) in comparison with the unsupported catalyst ( $1.7 \times 10^{21} \text{ molecules s}^{-1} \text{ mol}^{-1}$  of cobalt(II) ions). The reaction rate ( $R_p$ ) was also studied at different concentrations of hydrogen peroxide and log-log plots (Fig. 4)

were drawn to evaluate the dependence of reaction rate ( $R_p$ ) on the concentration of hydrogen peroxide, which was found to be first order with respect to the concentration of hydrogen peroxide. The reaction rate ( $R_p$ ) also showed first order dependence on concentration of cobalt(II) ions as it is clearly evident from the slope values of plots drawn between  $\lg R_p$  versus concentration of the cobalt(II) ions (Fig. 5). Similar trends in reaction rate ( $R_p$ ) with supported and unsupported catalyst indicate the existence of a similar reaction mechanism for supported and unsupported catalyst. The polymer support played a significant role in decreasing the energy of activation for the decomposition of hydrogen peroxide as can be seen from the energy of activation determined with Arrhenius plot (Fig. 6) drawn between  $\lg k$  versus  $1/T$  for supported catalyst ( $33.37 \text{ kJ mol}^{-1}$ ) and unsupported catalyst ( $56.35 \text{ kJ mol}^{-1}$ ). The rate of decomposition of hydrogen peroxide was also studied at different solution pH maintained with sodium hydroxide or perchloric acid (Fig. 7). The rate of reaction showed inverse dependence on hydrogen ion concentrations in the pH range from 2.0–8.0. The variation in reaction rate on varying the ionic strength ( $\mu$ ) of the medium indicates the involvement of ionic intermediates in the decomposition of hydrogen peroxide in the presence of cobalt(II) complex.

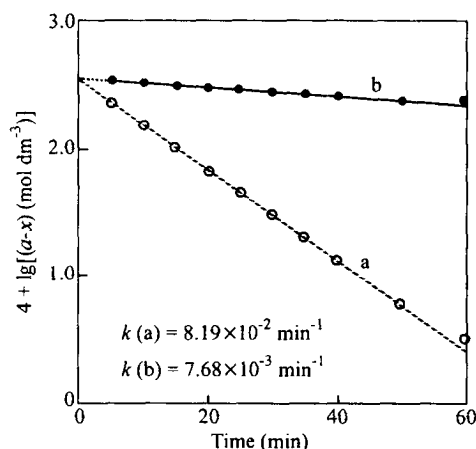
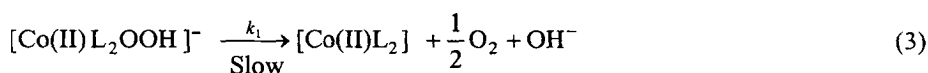


**Fig. 3** Effect of reaction time on the decomposition of  $\text{H}_2\text{O}_2$  with supported (a) and unsupported catalyst (b).  $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Co}^{2+}] = 17.0 \times 10^{-4} \text{ mol dm}^{-3}$  (a) and  $16.0 \times 10^{-4} \text{ mol dm}^{-3}$  (b) pH = 8.0,  $\mu = 0.5 \text{ mol dm}^{-3}$ , Temperature =  $25^\circ\text{C}$

Thus on the basis of experimental observations, the following reaction steps are proposed for the decomposition of hydrogen peroxide using supported and unsupported cobalt (II) Schiff base complex.

#### Reaction Scheme



Reaction step-3 is slow and taken as the rate determining step for the decomposition of the hydrogen peroxide. Considering steps 1–4, the rate expression for decomposition of hydrogen peroxide is given as:

$$\frac{d[H_2O_2]}{dt} = \frac{k_d K k_1 [Co(II)L_2][H_2O_2]}{[H^+]} \quad (5)$$

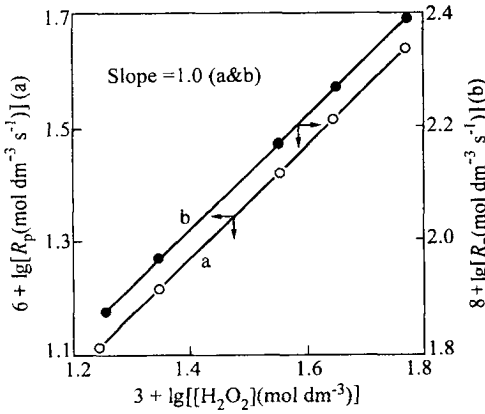


**Fig. 4** lg-lg plot between rate of decomposition of  $H_2O_2$  ( $R_p$ ) versus  $[H_2O_2]$  with supported (a) and unsupported catalyst (b)  $[Co^{2+}] = 17.0 \times 10^{-4}$  mol  $dm^{-3}$  (a) and  $16.0 \times 10^{-4}$  mol  $dm^{-3}$  (b), pH = 8.0,  $\mu = 0.5$  mol  $dm^{-3}$ , Temperature =  $25^\circ C$

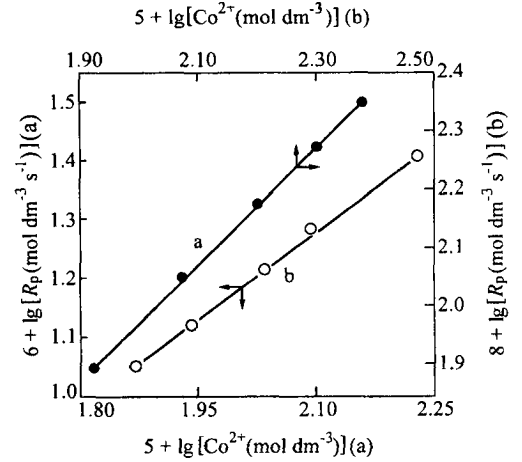


**Fig. 5** lg-lg plot between rate of decomposition of  $H_2O_2$  ( $R_p$ ) versus  $[Co^{2+}]$  with supported (a) and unsupported catalyst (b)  $[H_2O_2] = 3.57 \times 10^{-2}$  mol  $dm^{-3}$ , pH = 8.0,  $\mu = 0.5$  mol  $dm^{-3}$ , Temperature =  $25^\circ C$

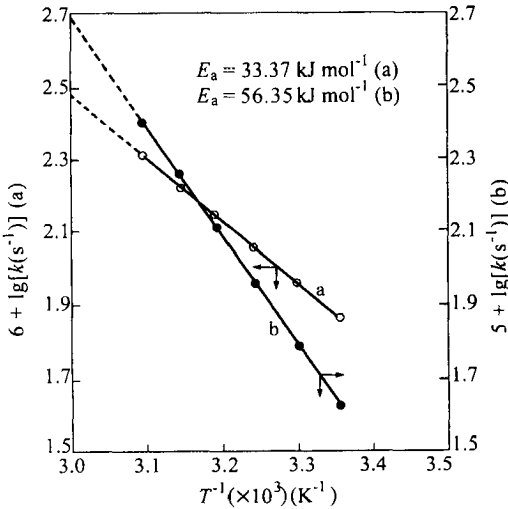


**Fig. 6** Arrhenius plot for the decomposition of  $H_2O_2$  with supported (a) and unsupported catalyst (b).  $[H_2O_2] = 3.57 \times 10^{-2}$  mol  $dm^{-3}$   $[Co^{2+}] = 17.0 \times 10^{-4}$  mol  $dm^{-3}$  (a) and  $16.0 \times 10^{-4}$  mol  $dm^{-3}$  (b), pH = 8.0,  $\mu = 0.5$  mol  $dm^{-3}$ , Temperature =  $25^\circ C$

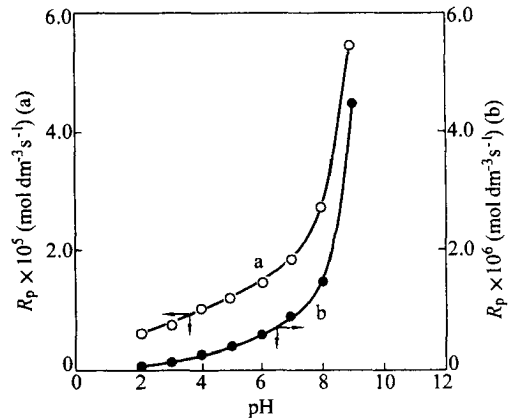


**Fig. 7** Effect of pH on the rate of decomposition of  $H_2O_2$  with supported (a) and unsupported catalyst (b)  $[H_2O_2] = 3.57 \times 10^{-2}$  mol  $dm^{-3}$   $[Co^{2+}] = 17.0 \times 10^{-4}$  mol  $dm^{-3}$  (a) and  $16.0 \times 10^{-4}$  mol  $dm^{-3}$  (b)  $\mu = 0.5$  mol  $dm^{-3}$ , Temperature =  $25^\circ C$

Where,  $k_d$ ,  $K$  and  $k_1$  are the rate constants for the dissociation of hydrogen peroxide and equilibrium constant for intermediate complex formed between  $\bar{O}OH$  and cobalt(II) Schiff base complex. The rate of decomposition is directly proportional to the concentration of hydrogen peroxide and cobalt(II) complex. The rate of decomposition also shows inverse dependence on the concentration of  $H^+$  ions. The rate equation [Eq.(5)] explains the experimental observations, hence proposed steps 1–4 are assumed to be correct.

## CONCLUSION

The monomer Schiff base anchored polymer shows a high degree of complexation and loading for cobalt(II) ions due to the presence of a sufficient amount of functionalized monomer *N,N'*-BSEDA on the polymer support. The amount of ligand on the polymer has shown a dependence on the concentration of DVB in the reaction mixture and reached its maximum at 1.5 mmol of DVB in the reaction mixture. Although the mechanism suggested for the decomposition of hydrogen peroxide both for supported and unsupported cobalt(II) complex is the same, the rate of decomposition is higher for supported catalyst due to the reduction in energy of activation for decomposition of hydrogen peroxide. The order of reaction is unity with respect to the concentration of hydrogen peroxide and cobalt(II) complex. The experimental results clearly indicate that the amount of DVB in the reaction mixture plays a significant role in controlling the composition and size of crosslinked beads and their degree of swelling.

## ACKNOWLEDGEMENT

The authors are thankful to Indian Institute of Technology, Roorkee, for providing facilities to carry out these investigations. One of the authors, Mr. H. K. Abdulkadir is thankful to ICCR, New Delhi India for the award of a fellowship.

## REFERENCES

- Hartley, F.R., "Supported Metal Complexes", Dordrecht Riedel Publishing Co., Amsterdam, 1985
- Sherrington, D.C., "Polymer-supported synthesis", in: "Chemistry of Waste Minimization Clark", ed. by Clark, J.H., Blackie, 1995, Chap. 6, p.141
- Neuse, E.W., "Encyclopedia of Polymer Science and Technology", Interscience, New York, 1968, Vol. 8
- Merrifield, R.B., J. Am. Chem. Soc., 1963, 85: 2149
- Kapanchan, A.T., Pshezhetskii, V.S. and Kabanov, V.A., Vysokomol, Soed. A., 1969, 11: 5
- SaSaki, T. and Matsunaga, F., Bull. Chem. Soc., Jpn., 1968, 41: 2440
- Liu, C., Tang, T. and Huang, B., J. Polym. Sci. Part-A: Polym. Chem., 2001, 39: 2085
- Rampino, L.D. and Nord, F.F., J. Am. Chem. Soc., 1941, 63: 2745
- Hernandez, L. and Nord, F.F., J. Colloid, Sci., 1948, 3: 363
- Dunworth, W.P. and Nord, F.F., Advances in Catalysis, 1954, 6: 125
- James, B.R., Homogeneous Hydrogenation, Wiley, N.Y., 1973
- Minutolo, F., Pini, D., Petri, A. and Salvadori, P., Tetrahedron Asym., 1996, 7: 2293
- Minutolo, F., Pini, D. and Salvadori, P., Tetrahedron Lett., 1996, 37: 3375
- Kureshy, R.I., Khan, N.H., Abdi, S.H.R. and Iyer, P., React. Funct. Polym., 1997, 34: 153
- Guilier, F., Orain, D. and Bradley, M., Chem. Rev, 2000, 100: 2091
- James, I.W., Tetrahedron, 1999, 55: 4855
- Barrett, A.G.M., Cramp, S.M., Roberts, R.S. and Zecri, F., J. Org. Lett., 2000, 2: 261
- Akelah, A., Abbasi, M.M. and Awad, M.K.H., Indian, J. Chem., 1986, 25A: 923
- Akelah, A. and Sherrington, D.C., Chem. Rev., 1981, 81: 557
- Drake, R., Dunn, R., Sherrington, D.C. and Thomson, S., J. Chem. Commun., 2000, 1931
- Jung, G., "Combinatorial Peptide and Non-Peptide", ed. by Libraries, VCH, Weinheim, German, 1996
- Masuda, T. and Stille, J.K., J. Am. Chem. Soc., 1978, 100: 268
- Montelatici, S., Van der Ent, A., Osborn, J.A. and Wilkinson, G., J. Chem. Soc. A., 1968, 1054
- Syamal, A. and Singh, M.M., Indian J. Chem., 1993, 32A: 431
- Ibrahim, Y.A., Elwahy, A.H.M., Abbas, A.A. and Kassab, R.M., J. Chem. Res. (M), 1999, 2201

- 26 Allum, K.G., Hancock, R.D., Howell, I.V., McKenzie, S., Pitkethly, R.C. and Robinson, P.J., *J. Organomet. Chem.*, 1975, 87: 203
- 27 Kurimura, Y., Takagi, Y. and Saito, M., *J. Chem. Soc. Faraday Trans. I*, 1988, 84: 1025
- 28 Kurimura, Y., Kikuchi, T. and Tsuchida, E., *Macromolecules*, 1989, 22: 1645
- 29 Dwyer, F.P. and Mellor, D.P., "Chelating Agents and Metal Chelates", Academic Press, N.Y., 1964
- 30 Martell, A.E. and Calvin, M., "Chemistry of Metal Chelate Compounds", Prentice Hall, N. Jersey, 1962
- 31 Ueno, K. and Martell, A.E., *J. Phys. Chem.*, 1956, 60: 1270