



Synthesis of polymer anchored N,N' -bis(3-allyl salicylidene) o -phenylenediamine cobalt(II) Schiff base complex and its catalytic activity for decomposition of hydrogen peroxide

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Abstract

The anchoring of N,N' -bis(3-allyl salicylidene) o -phenylenediamine cobalt(II) Schiff base complex on polymer support has been carried out by suspension copolymerization of synthesized N,N' -bis(3-allyl salicylidene) o -phenylenediamine monomer Schiff base (N,N' -BSPDA) with styrene (St) and divinylbenzene (DVB) using azobisisobutyronitrile (AIBN) as initiator in presence of poly(vinyl alcohol). The polymer anchored Schiff base (N,N' -BSPDA) was subsequently loaded with cobalt(II) ions. The cobalt(II) ions loading, degree of cross-linking and swelling in prepared beads have shown dependence on the amount of DVB taken in the reaction mixture. The amount of N,N' -BSPDA monomer Schiff base and its arrangement in cross-linked beads have also shown dependence on the amount of DVB taken in the reaction mixture. The cross-linked beads (Type-III) obtained at 1.50 mmol of DVB have shown highest loading for cobalt(II) ions (1.18 mmol g^{-1} of beads) due to maximum amount of N,N' -BSPDA monomer Schiff base on these beads (1.74 mmol g^{-1} of beads). The amount of DVB taken in the reaction mixture has shown significant effect on porosity, internal surface area (S_{BET}), average pore diameter (\bar{D}) and degree of swelling in prepared beads. The IR, UV and magnetic measurements have provided sufficient evidences for square planar geometry of N,N' -BSPDA cobalt(II) complex both in homogeneous and heterogeneous conditions. The complexation of cobalt(II) ions on polymer anchored N,N' -BSPDA monomer Schiff base has shown a significant increase in its thermal stability. The catalytic activity of polymer supported N,N' -BSPDA cobalt(II) complex was evaluated under different experimental conditions and its activity was compared with unsupported analogue. The energy of activation for decomposition of hydrogen peroxide with supported N,N' -BSPDA cobalt(II) complex has been found to be low ($36.04 \text{ kJ mol}^{-1}$) in comparison to unsupported one ($61.27 \text{ kJ mol}^{-1}$). To explain experimental results, a suitable rate expression has been derived.

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1. Introduction

Heterogenization of catalyst on inert support prolongs the life of the catalyst and makes its separation

easy from reaction mixture. The various advantages of supported catalysts have attracted organic and industrial chemists to develop heterogenized catalysts using suitable supports [1]. The catalysts on cross-linked supports with pores of molecular dimension have shown significant increase in their selectivity [2–4] and activity due to high concentration of active sites within the small pores [5–8]. The

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efficiency of catalyst on inert support has been found to be high [9] in comparison to unsupported state of catalyst [10,11] because in unsupported state, the aggregation of catalyst reduces its efficiency. The insoluble cross-linked polymers are used widely as they are inert, non-toxic, thermally stable and easy to be recycled [12], whereas, linear soluble polymers [13] are of limited value because their separation from reaction mixture is difficult. Similarly, linear insoluble polymer supports [14] are also of limited use as they are not able to increase the turnover number [15] in comparison to cross-linked polymers [5]. Although various inorganic supports such as silica [16–18] have been used for anchoring catalysts but polymer supports have been found to be more useful as they are able to provide preferential stereochemistry for catalysts and reactants [19] in presence of solvent in comparison to rigid inorganic supports. The unsupported metals and their oxides have shown poor catalytic efficiency in comparison to supported catalysts because in such catalysts only atoms at the surface participate in catalysis and other remain inactive. The reported high oxygen binding efficiency [20,21] of cobalt(II) complex and its enhanced catalytic activity on polymer support [22,23] have clearly indicated that supports play an important role in property modification of active species. The metal complexes supported on polymers have shown excellent catalytic activity for hydrogenation [24], enantiomeric epoxidation of alkenes [25–28] in comparison to homogenized catalyst [29]. Various catalysts have been anchored on cross-linked chloromethylated polystyrene [14], poly(methylmethacrylate), poly(glycidylmethacrylate) and poly(hydroxyethylmethacrylate) [30,31]. The spacer between support and metal complex has played important role in epoxidation of olefins [29,32,33], hence synthesis of polymer support in current investigations by copolymerization of *N,N'*-BSPDA monomer Schiff base with styrene (St) and DVB has been considered an useful step to obtain polymer anchored *N,N'*-BSPDA cobalt(II) complex with a spacer between complex and support. The cross-linked phosphinated polystyrene has shown low catalytic activity due to low complexation efficiency of phosphine ligand [34,35] for cobalt(II) ions. The anchoring of Schiff bases and their metal complexes on polymer supports usually occurs very poorly [34,35], hence in these investigations an ef-

fort has been made to prepare polymer supported *N,N'*-BSPDA monomer Schiff base by copolymerization of *N,N'*-BSPDA monomer Schiff base with styrene and DVB. Although polymer supported salen complexes of cobalt(II) and other transition metal ions are reported by Canali et al. [36], Canali and Sherrington [37] and Sherrington et al. [38], and unsupported transition metal complexes of *N,N'*-BSPDA Schiff base are also reported [39] but studies on catalytic activity of polymer supported *N,N'*-BSPDA cobalt(II) complex are not available in the literature, hence efforts have been made to prepare polymer anchored *N,N'*-BSPDA cobalt(II) complex and to evaluate its catalytic activity using hydrogen peroxide decomposition as model reaction.

2. Experimental

2.1. Chemicals used

Salicylaldehyde (A.R. Grade, BDH, UK) used directly without further purification. Styrene and allylchloride (Aldrich Chemical Company, USA) monomers were vacuum distilled before using them in synthesis of cross-linked polymer. The *o*-phenylene diamine, poly(vinyl alcohol) ($M_w = 50 \times 10^3 \text{ g mol}^{-1}$) and divinylbenzene (DVB) (Aldrich Chemical Company, USA) were used as received.

2.2. FT-IR spectra

The spectra of *N,N'*-BSPDA monomer Schiff base and its cobalt(II) complex were recorded on KBr pellets using Perkin-Elmer 1600 Fourier transform spectrophotometer.

2.3. Electronic spectra

The electronic spectra of free and polymer supported monomer Schiff base (*N,N'*-BSPDA) and its cobalt(II) complex were recorded in dimethylformamide (DMF) using UV-Vis spectrophotometer (1601-PC, Shimadzu, Japan).

2.4. Magnetic measurements

The dipole moment (μ) of free and polymer supported *N,N'*-BSPDA cobalt(II) complexes was

estimated with Gouy balance at 296 K and diamagnetic corrections were made.

2.5. Thermal studies

Thermal stability of polymer supported *N,N'*-BSPDA monomer Schiff base and its cobalt(II) complex was estimated by recording thermograms with Stanton Red Croft STA-780 Thermal Analyzer (UK) at a heating rate of 10 °C min⁻¹ under inert atmosphere.

2.6. Elemental analysis

The amount of *N,N'*-BSPDA monomer Schiff base supported on cross-linked polymer beads was calculated by estimating nitrogen content by Perkin-Elmer 24 Elemental Analyzer.

2.7. Molecular weight measurements

The molecular weights of *N,N'*-BSPDA monomer Schiff base and its cobalt(II) complex were estimated with vapor pressure osmometer (Knauer K-700, Germany).

2.8. SEM studies

The size of cross-linked beads obtained at different amount of DVB and after swelling in organic solvent was measured with scanning electron microscope (Leo-435 VP, England) by mounting beads on metal studs and vacuum coating with gold. The variation in bead size after swelling as determined by SEM studies has been used to calculate the degree of swelling.

2.9. Degree of swelling and pore volume

In addition to SEM studies, the degree of swelling has also been measured as percent weight variation of cross-linked beads after keeping them for 24 h in dimethylformamide. The pore volume of cross-linked beads was determined by recording variation in weight (W_t) in comparison to their initial weight (W_0) on keeping beads for 24 h in DMF and using density (ρ) of DMF in following equation:

$$\text{Pore volume} = \frac{W_t - W_0}{W_0 \rho}$$

2.10. Synthesis of *N,N'*-bis(3-allyl salicylidene)-*o*-phenylenediamine monomer Schiff base (*N,N'*-BSPDA) and its cobalt(II) complex

First of all *N,N'*-bis(salicylidene)-*o*-phenylenediamine (salphen) was synthesized by refluxing ethanolic mixture of salicylaldehyde (20 mmol, 2.44 g) and *o*-phenylenediamine (10 mmol, 1.089 g) for 45 min at 60 °C. On cooling, the crystalline product was separated, which on recrystallization from ethanol has produced bright yellow colored crystals after drying on calcium chloride in vacuum desiccator (yield: 73%, 2.57 g, mp 166 °C). The elemental analysis of salphen was carried out and its IR spectrum was recorded on KBr pallets. To prepare *N,N'*-bis(3-allyl salicylidene)-*o*-phenylenediamine (*N,N'*-BSPDA), the potassium salt of salphen was prepared by mixing 20 mmol (4.8 g) of salphen with 40 mmol (2.28 g) of potassium hydroxide in 40 ml of methanol at room temperature under vigorous stirring for about 30 min. The potassium salt of salphen was obtained by removing methanol in vacuum evaporator. Subsequently, *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine was prepared by reacting 10 mmol (3.94 g) of potassium salt of *N,N'*-bis(salicylidene)-*o*-phenylenediamine with 10 mmol (0.765 g) of allylchloride in dimethylformamide (20 ml) under reflux at 70 °C for about 15 min. The precipitated potassium chloride was separated and *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine was obtained by evaporating the dimethylformamide from the filtrate. Finally, *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine was washed repeatedly with cold water and recrystallized with ethylacetate (yield: 71%, mp 198 °C). The IR spectrum of *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine was recorded on KBr pallets. To produce *N,N'*-BSPDA monomer Schiff base, 10.0 mmol (3.96 g) of *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine was heated at a temperature range of 170–180 °C in 50 ml of dimethylformamide for 2 h on oil bath which on cooling has produced [40] a brown colored product (*N,N'*-BSPDA). This brown colored product (*N,N'*-BSPDA) was recrystallized from 2:1 mixture of toluene and petroleum ether (60:50) (yield: 50%, mp 174 °C). The IR spectrum of *N,N'*-BSPDA was recorded on KBr pallets. The *N,N'*-BSPDA cobalt(II) complex was prepared by reacting 2.0 mmol (0.792 g) of *N,N'*-BSPDA monomer Schiff base with 2.0 mmol

(0.476 g) of cobalt(II) chloride under reflux at 95 °C for about 2 h, which produced brown colored crystalline *N,N'*-BSPDA cobalt(II) complex (yield: 73%, 0.81 g, mp 253 °C). The IR spectrum of *N,N'*-BSPDA cobalt(II) complex was recorded on KBr pallets.

2.11. Synthesis of polymer anchored *N,N'*-bis(3-allyl salicylidene)-*o*-phenylenediamine monomer Schiff base (*N,N'*-BSPDA) and its cobalt(II) complex

To obtain polymer anchored monomer Schiff base (*N,N'*-BSPDA), the suspension copolymerization was carried out taking 80 ml deaerated solution of toluene containing styrene (48.97 mmol, 5.1 g), DVB (1.50 mmol, 0.188 g) and *N,N'*-BSPDA (48.97 mmol, 19.39 g) and 20 ml deaerated solution of azobisisobutyronitrile (0.9×10^{-3} mmol, 0.15 g) in toluene and adding these solutions 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 water. The reaction flask was heated to 70 °C under vigorous stirring to prevent the agglomeration of polymer beads and to dissipate heat generated during copolymerization and cross-linking reactions taken place between polymeric chains. To obtain beads of uniform size, the rate of stirring was kept almost constant. At the end of 2 h, the heating was discontinued and reaction mixture was allowed to cool under constant stirring and suspension of beads thus obtained was transferred to a flask. The brown colored beads were allowed to settle and separated from the supernatant liquid. The resultant beads were washed with methanol (four times 50 ml) and hot

N,N'-BSPDA monomer Schiff base. The scanning electron microscope has been used to record the beads size and degree of swelling in DMF. The degree of swelling of beads was also verified by recording the percent weight variation of beads after swelling for 24 h in DMF. The amount of monomer Schiff base (*N,N'*-BSPDA) in the cross-linked beads was estimated with percent nitrogen content. The IR spectrum of the beads was recorded on KBr pallets. After synthesis of *N,N'*-BSPDA anchored beads, the loading of cobalt(II) ions was carried out reacting DMF swollen beads with cobalt(II) chloride. To obtain sufficient loading of cobalt(II) ions on polymer anchored *N,N'*-BSPDA monomer Schiff base, the beads (1.0 g) were allowed to swell in DMF (20 ml) for 24 h and after washing with water these beads were kept in 40 ml solution of cobalt(II) chloride (5.0 mmol, 1.1896 g) for about 8 h under reflux on oil bath at 95 °C. On cooling to room temperature, the beads were washed repeatedly with methanol and deionized water and dried in vacuum oven at 60 °C under inert atmosphere to prevent oxidation of cobalt(II) ions (yield: 75%, 11.65 g, mp 380 °C). The IR spectrum of beads was recorded on KBr pallets to ensure the complexation of cobalt(II) ions. The loading capacity of prepared beads was determined by leaching cobalt(II) ions with 4N acetic acid under reflux for 2 h at 110 °C and leached amount of cobalt(II) ions was estimated with atomic absorption spectrophotometer (Perkin-Elmer 2100) at $\lambda_{\max} = 240.7$ nm. The efficiency of complexation (%EC) and loading (%EL) of cobalt(II) ions on cross-linked beads are calculated using following equations:

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

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

water on a sieve to remove impurities and bentonite. Finally, beads were dried in a vacuum oven at 70 °C for 24 h (yield: 72%, 17.88 g). To obtain beads of different cross-linked densities, the copolymerization was carried out taking different amount of DVB in reaction mixture ranging from 0.8 to 2.0 mmol at constant concentration of styrene, allylchloride and

2.12. Decomposition kinetics of hydrogen peroxide

The catalytic activity of polymer supported *N,N'*-BSPDA cobalt(II) complex has been evaluated by recording the rate of decomposition (R_p) of hydrogen peroxide of known molarity prepared with 0.6% (w/v) solution of hydrogen peroxide. The content

of hydrogen peroxide at different intervals of time was estimated by titrating 5.0 ml aliquot of reaction mixture with 0.01 M KMnO_4 solution in presence of 0.01 M H_2SO_4 . The catalytic activity of supported N,N' -BSPDA cobalt(II) complex was also evaluated at different concentrations of hydrogen peroxide, reaction temperature and using beads of different loading capacities and cross-linked densities. To compare the catalytic activity of polymer supported N,N' -BSPDA cobalt(II) complex, the kinetic data for decomposition of hydrogen peroxide were also recorded using unsupported N,N' -BSPDA cobalt(II) complex under similar experimental conditions.

3. Results and discussion

The high catalytic activity of heterogenized catalyst is due to the sufficient number of metal ions on polymer surface and due to increased concentration of reactants nearby to active sites on polymer support, which accelerate reaction rate in comparison to unsupported catalyst. The extent of cross-linking plays an important role in increasing the number of active sites and turnover number of metal ions due to the increased internal surface of polymer support. The heterogenized metal complexes on polymer support usually have similar geometry if coordinating sites of polymer anchored ligands and oxidation state of metal ions remain same as with unsupported catalyst. The activity of metal ions on cross-linked support increases upto a certain degree of cross-linking and beyond which no significant change is observed due to the decrease in accessibility of reactants to supported metal ions and due to decrease in pore size

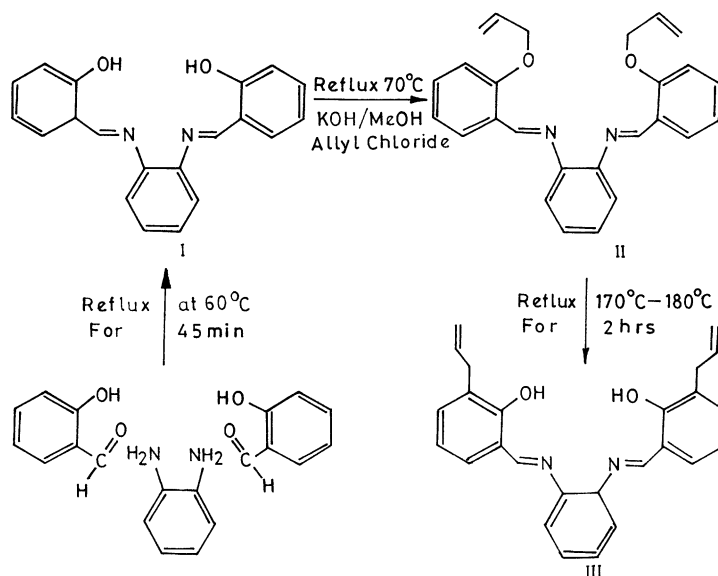
in polymer support. The highly cross-linked polymer supports show poor tendency to swell in solvents and movement of reactants in polymer matrixes becomes diffusion controlled. On other hand, the low degree cross-linked polymer supports are fragile and undergo degradation even with magnetic stirring, hence such polymer supports are not suitable for immobilization catalysts [41]. To obtain an efficient heterogenized catalyst, the polymer matrix must have struck a balance between porosity and its mechanical strength. The heterogenization of cobalt(II) ions through their complexes on functional polymer support is well reported [34,35] but this technique has shown low degree of heterogenization. The heterogenization of cobalt(II) ions on polymer support prepared with copolymerization of N,N' -BSPDA monomer Schiff base with styrene and DVB has been found to be attractive due to availability of synthetic opportunities to control the number and distribution of chelating sites on polymer support. This is evident from the observed variations in composition and loading capacity of cross-linked beads obtained at different amount of DVB taken in the reaction mixture (Table 1). To heterogenize the cobalt(II) ions, the polymer support has been synthesized through copolymerization of N,N' -BSPDA monomer Schiff base. Therefore, N,N' -BSPDA monomer Schiff base was synthesized reacting allylchloride with salphen. The reaction of salicylaldehyde and *o*-phenylenediamine has produced a yellow colored salphen (yield: 73%, 2.57 g, mp 166 °C). The elemental analysis (found: in % C, 75.92; H, 5.2; N, 8.82; calcd.: in % C, 75.95; H, 5.1; N, 8.86) and molecular weight (316.2 g mol^{-1}) correspond to $\text{C}_{20}\text{H}_{16}\text{N}_{22}$ for synthesized salphen (Structure I in Scheme 1). The IR spectrum of the

Table 1
Physical characteristics of synthesized cross-linked beads

Beads at different concentrations of DVB ^a	Beads size (μm)	ρ (g cm^{-3})	Percent swelling (%S)	Porosity ($\text{cm}^3 \text{g}^{-1}$)	Surface area (S_{BET}) ($\text{m}^2 \text{g}^{-1}$)	Pores diameter (\bar{D}) (\AA)
Type-I (0.8 mmol DVB)	176	0.38	13.15	0.76	56	542.86
Type-II (1.15 mmol DVB)	152	0.40	10.90	0.64	72	355.56
Type-III (1.50 mmol DVB)	124	0.44	7.21	0.52	94	221.60
Type-IV (1.75 mmol DVB)	118	0.45	5.45	0.36	132	109.10
Type-V (2.00 mmol DVB)	110	0.48	4.32	0.28	380	29.47

[Styrene]_I = 48.97 mmol, [N,N' -BSPDA]_I = 48.97 mmol.

^a Divinyl benzene.



Scheme 1.

salphen has shown absorption bands as reported in the literature [34]. The reaction of potassium salt of salphen with allylchloride has produced *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine (Structure II in Scheme 1). The observed molecular weight (396 g mol^{-1}) and elemental analysis (found: in % C, 78.79; H, 6.25; N, 7.22; calcd.: in % C, 78.78; H, 6.06; N, 7.07) correspond to $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$. The IR spectrum of *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine has shown absorption bands at 1614 cm^{-1} $\nu(\text{C}=\text{N})$ and at 1156 cm^{-1} $\nu(\text{C}-\text{O}-\text{C})$ for the presence of azomethine and ether group. The spectrum has also shown band corresponding to the presence allyl group. On heating *N,N'*-bis(2-allyloxy salicylidene)-*o*-phenylenediamine at $170\text{--}180^\circ\text{C}$, the shifting of allyl group has taken place [40] to produce *N,N'*-BSPDA (Structure III in Scheme 1). The observed molecular weight (396 g mol^{-1}) and elemental analysis (found: in % C, 78.76; H, 6.16; N, 7.20; calcd.: in % C, 78.78; H, 6.06; N, 7.07) correspond to $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$. The IR spectrum of *N,N'*-BSPDA has shown absorption bands at 1614 and 1278 cm^{-1} for the presence of azomethine $\nu(\text{C}=\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ groups. The presence of broad band in the frequency range from 2928 to 3419 cm^{-1} corresponds to stretching vibration of phenolic OH group (Table 3) [34]. The electronic spectrum of free *N,N'*-BSPDA has shown

absorption bands at 274 and 337 nm correspond to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine group in *N,N'*-BSPDA monomer Schiff base (Table 4). These IR and UV data have supported the formation of *N,N'*-BSPDA monomer Schiff base (Structure III in Scheme 1). To prepare cobalt(II) ions complex, the *N,N'*-BSPDA was reacted with cobalt(II) chloride, which produced yellow colored crystal of *N,N'*-BSPDA cobalt(II) complex. The IR spectrum of *N,N'*-BSPDA cobalt(II) complex has shown absorption band at 1609 cm^{-1} for azomethine $\nu(\text{C}=\text{N})$ in place of 1614 cm^{-1} of free Schiff base (Table 3). The phenolic band $\nu(\text{C}-\text{O})$ on complexation with cobalt(II) ions has also shown a shift from 1278 to 1332 cm^{-1} indicating the coordination of cobalt(II) ions through phenolic oxygen of the Schiff base (Table 3).

The OH stretching band within a frequency range of $2928\text{--}3419 \text{ cm}^{-1}$ was missing on complexation with cobalt(II) ions, which is an evidence for the coordination of cobalt(II) ions through phenolic oxygen (Table 3). The appearance of two new bands at 550 cm^{-1} $\nu(\text{M}-\text{O})$ and 447 cm^{-1} $\nu(\text{M}-\text{N})$ in IR spectrum of cobalt(II) complex correspond to the stretching frequency of bond formed between cobalt(II) ions with phenolic oxygen (M–O) and nitrogen atom (M–N) of azomethine group of *N,N'*-BSPDA monomer Schiff base. The electronic spectrum of

N,N'-BSPDA cobalt(II) complex was also recorded to obtain information about the structure of *N,N'*-BSPDA cobalt(II) complex. The bands correspond to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions have shifted to 263 and 270 nm on complexation with cobalt(II) ions (Table 4). A new absorption band at 383 nm in cobalt(II) complex has been assigned to charge transfer transitions ($L \rightarrow M$). These spectral transitions are indicative of square planar geometry for cobalt(II) complex with *N,N'*-BSPDA monomer Schiff base as similar to reported quadridentate chromophore (N_2O_2) [42]. The magnetic moment (μ_{eff}) of the complex was 2.25 B.M. at 296 K which correspond to the presence of one unpaired electron, hence attributed to low spin square planar structure [43] for cobalt(II) complex.

3.1. Characterization of polymer anchored *N,N'*-bis(3-allyl salicylidene)*o*-phenylenediamine monomer Schiff base (*N,N'*-BSPDA) and its cobalt(II) complex

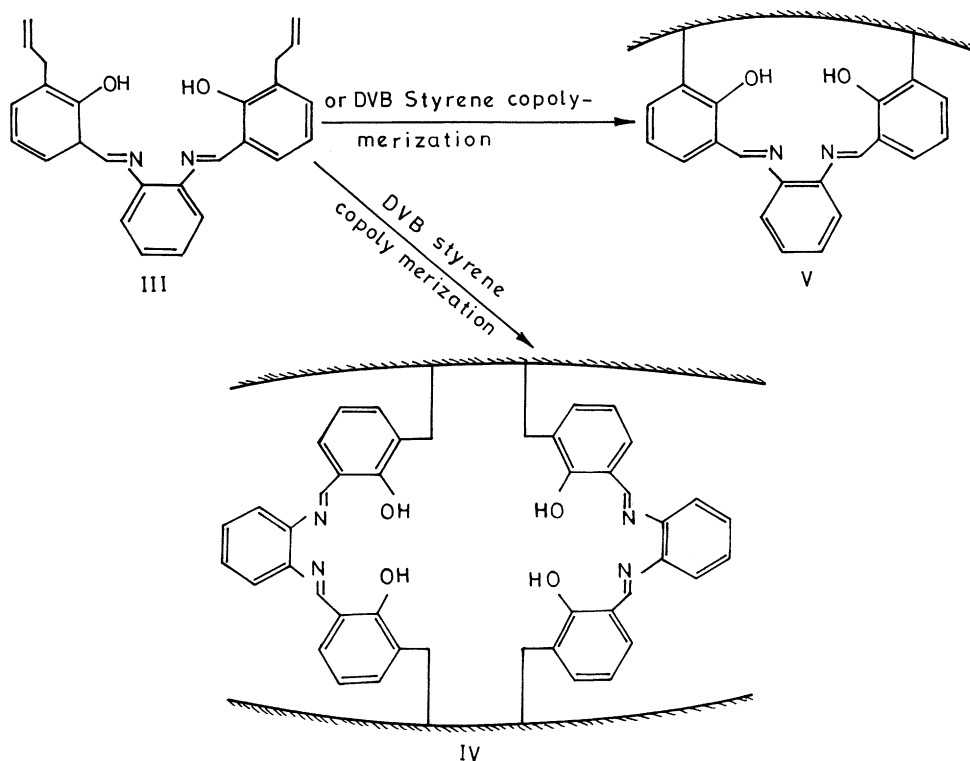
The polymer heterogenized *N,N'*-bis(3-allyl salicylidene)*o*-phenylenediamine monomer Schiff base (*N,N'*-BSPDA) was prepared by copolymerization of *N,N'*-BSPDA (Structure III in Scheme 1) with styrene in presence of DVB using AIBN as initiator, which produced brown colored cross-linked beads (yield: 72%, 17.88 g). The amount of *N,N'*-BSPDA in the prepared cross-linked beads has shown dependence on the amount of DVB taken in the reaction mixture, as verified with nitrogen content in the prepared beads (Tables 1 and 2). The amount of *N,N'*-BSPDA in cross-linked beads has varied from 1.46 to 1.32 mmol g⁻¹ of beads on varying the amount of DVB from 0.80 to 2.00 mmol in the reaction mixture. The beads obtained with 1.5 mmol of

DVB have shown maximum amount of *N,N'*-BSPDA (Table 2). The amount of *N,N'*-BSPDA in cross-linked beads has shown variation due to competitive reaction between *N,N'*-BSPDA and DVB with styrene to form polymeric chains. At low concentration of DVB (≤ 1.50 mmol), the *N,N'*-BSPDA monomer Schiff base has participated in the formation of cross-links between polymer chains (Structure IV in Scheme 2) but at higher concentration of DVB (> 1.5 mmol), the *N,N'*-BSPDA was able to form cyclic close structure on single polymer chain (Structure V in Scheme 2). The concentration variation of DVB in the reaction mixture has changed pore volume, beads density, average pore diameter (\bar{D}), internal surface area (S_{BET}) and size of beads (Table 1), hence controlled the catalytic behavior of the beads. At low concentration of DVB, the beads with high pore volume were formed (Structure IV in Scheme 2). The cross-linked beads formed at different concentrations of DVB have also shown variation in their degree of swelling (Table 1). The beads prepared with 1.5 mmol of DVB in the reaction mixture have shown a degree of swelling of 7.21% as determined by SEM measurements (Fig. 1A and B). The thermal data of polymer supported *N,N'*-BSPDA monomer Schiff base have shown a weight loss of about 54.64% as determined with TG analysis of the cross-linked beads (Fig. 2A). The IR spectrum of polymer anchored *N,N'*-BSPDA monomer Schiff base (Structures-IV and V in Scheme 2) has shown absorption bands at 1275 and 1611 cm⁻¹ corresponding to phenolic $\nu(\text{C}-\text{O})$ and azomethine $\nu(\text{C}=\text{N})$ functional groups (Table 3). A broad absorption band between 2942 and 3415 cm⁻¹ corresponds to stretching frequency of phenolic group OH. These IR bands have shown slight variation in comparison to unsupported *N,N'*-BSPDA monomer Schiff base (Table 3). The

Table 2
Compositional characteristics of synthesized cross-linked beads

Beads at different concentrations of DVB	N ₂ (%)	Amount of <i>N,N'</i> -BSPDA (mmol g ⁻¹ beads)	Amount of cobalt(II) ions (mmol g ⁻¹ of beads)	EL (%)	EC (%)
Type-I (0.8 mmol DVB)	4.08	1.46	0.66	13.18	52
Type-II (1.15 mmol DVB)	4.12	1.60	1.04	20.80	65
Type-III (1.50 mmol DVB)	5.18	1.74	1.18	23.66	68
Type-IV (1.75 mmol DVB)	4.77	1.52	0.79	15.80	52
Type-V (2.00 mmol DVB)	4.31	1.32	0.61	12.14	46

[Co(II)]_i = 5.0 mmol, [*N,N'*-BSPDA]_i = 48.97 mmol; %S (percent swelling), EL (efficiency of loading), EC (efficiency of complexation).



Scheme 2.

electronic spectra of polymer anchored N,N' -BSPDA (Structures-IV and V in Scheme 2) have shown bands at 272 and 334 nm correspond to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions as shown by unsupported N,N' -BSPDA monomer Schiff base (Table 4).

The N,N' -BSPDA anchored beads were loaded with cobalt(II) ions by reacting with cobalt chloride under reflux (yield: 75%, 11.65 g, mp 380 °C). On complexation with cobalt(II) ions, the thermal stabil-

ity of N,N' -BSPDA anchored beads was increased as was evident from significant reduction in weight loss of 16.80% at 378 °C (Fig. 2B). The efficiency of complexation (%EC) and loading (%EL) of cross-linked beads for cobalt(II) ions have shown dependence on the degree of cross-linking and the amount of supported N,N' -BSPDA monomer Schiff base (Table 2). The loading of cobalt(II) ions has increased upto 1.5 mmol of DVB in the reaction mixture and after that a

Table 3

IR Frequencies of N,N' -bis(3-allylsalicylidene)-*o*-phenylenediamine Schiff base (N,N' -BSPDA) and its cobalt(II) complex

Metal ion	Functional groups	Unsupported		Polymer supported	
		Ligand (cm ⁻¹)	Complex (cm ⁻¹)	Ligand (cm ⁻¹)	Complex (cm ⁻¹)
Co(II)	$\nu(\text{OH})$	2928–3419	–	2924–3415	–
	$\nu(\text{C–O})$	1278	1332	1275	1329
	$\nu(\text{C=N})$	1614	1609	1611	1606
	$\nu(\text{M–O})$	–	550	–	546
	$\nu(\text{M–N})$	–	447	–	443

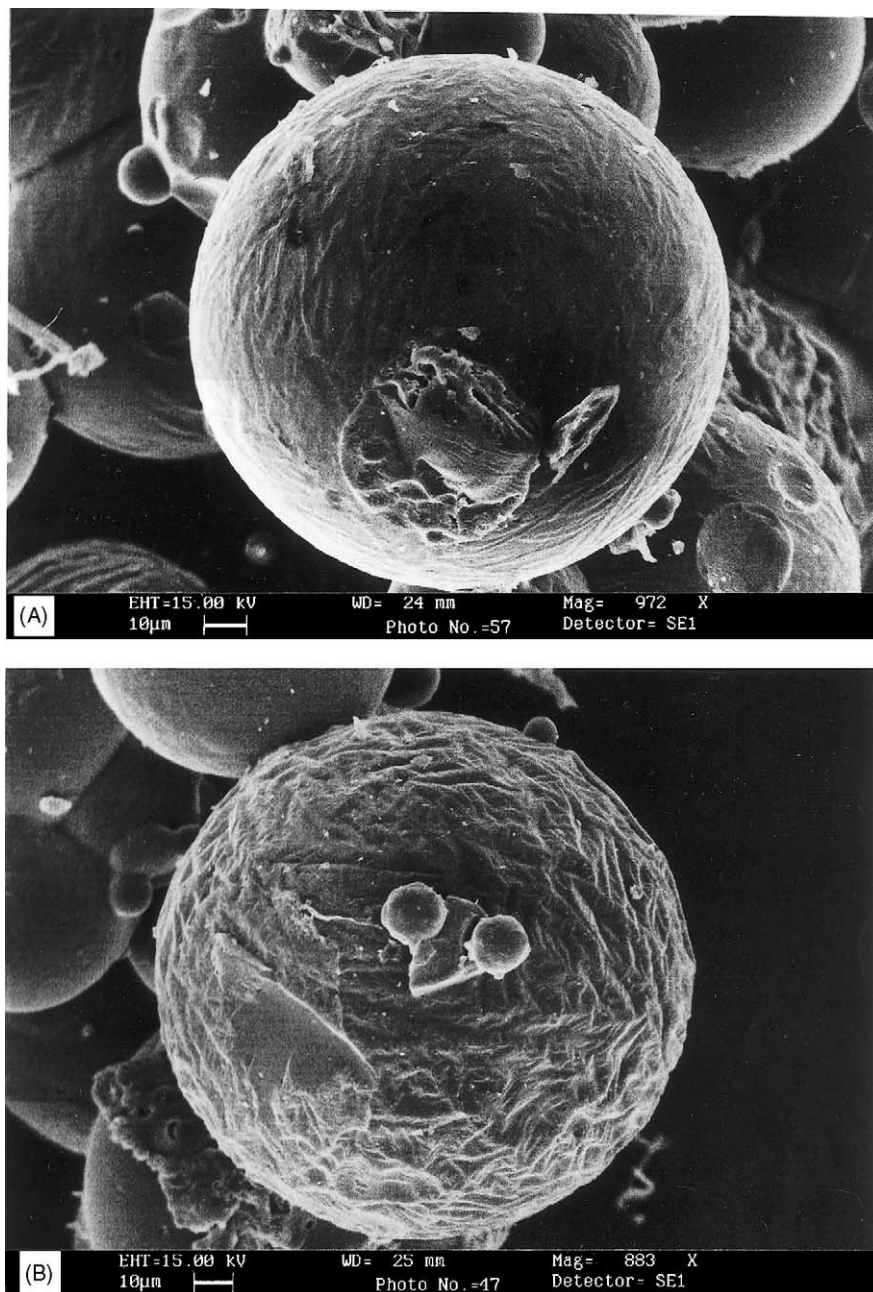


Fig. 1. Scanning electron micrographs of cross-linked polymer beads before (A) and after swelling (B).

decreasing trend was observed. The beads with optimum cross-linked density have shown a loading capacity of 1.18 mmol of cobalt(II) ions g^{-1} of beads (Scheme 3).

The IR spectra of cross-linked beads before and after cobalt(II) ions loading have shown a shift in frequency from 1611 to 1606 cm^{-1} for $\nu(\text{C}=\text{N})$ and shown two new absorption bands at 443 and

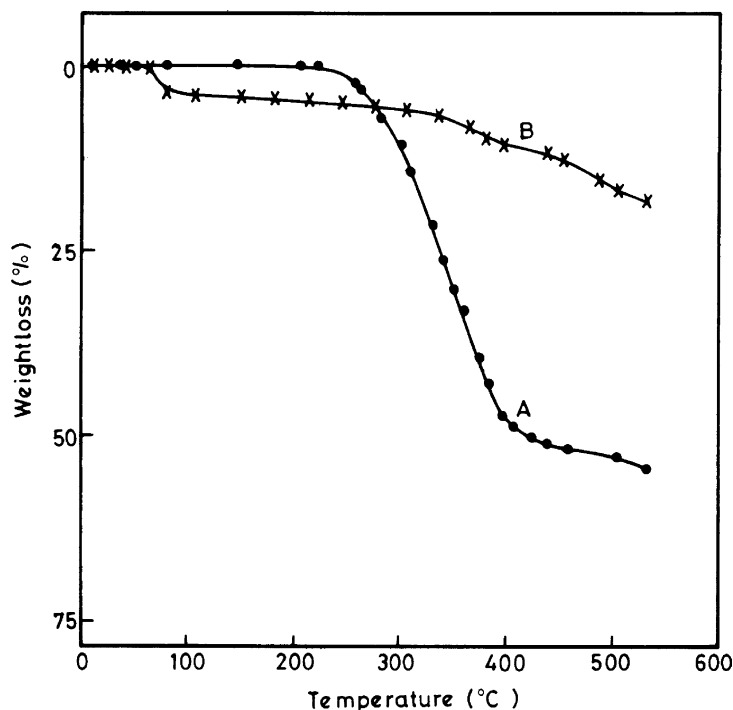


Fig. 2. TG curves for polymer anchored *N,N'*-BSPDA monomer Schiff base (A) and its cobalt(II) complex (B).

Table 4

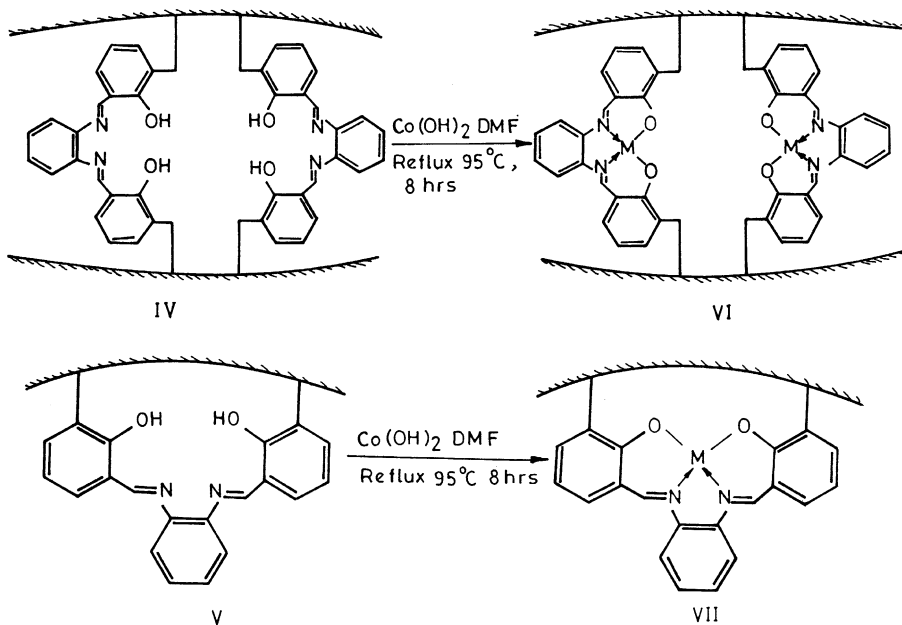
Electronic transitions and magnetic moment of *N,N'*-bis(3-allyl salicylidene)-*o*-phenylenediamine cobalt(II) complex

Metal ion	Electronic transitions	Transitions frequencies of unsupported		Transitions frequencies of polymer supported		μ_{eff} (B.M.)	Structure
		Ligand (λ_{max}) (nm)	Complex (λ_{max}) (nm)	Ligand (λ_{max}) (nm)	Complex (λ_{max}) (nm)		
Co(II)	$\pi \rightarrow \pi^*$	274	263	272	260	2.25 (2.23) ^a at 296 K	Square planar
	$n \rightarrow \pi^*$	337	270	334	268		
	C \rightarrow T	–	386	–	380		
	d \rightarrow d	–	–	–	–		

^a μ_{eff} of polymer supported complex.

546 cm^{-1} for $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ groups, respectively. These variations have confirmed the coordination of cobalt(II) ions with the azomethine nitrogen and phenolic oxygen of polymer anchored *N,N'*-BSPDA monomer Schiff base (Table 3). The disappearance of absorption band between 2924 and 3415 cm^{-1} of phenolic OH and shift in frequency from 1275 to 1329 cm^{-1} for $\nu(\text{C}-\text{O})$ band have supported the coordination of cobalt(II) ions with polymer anchored *N,N'*-BSPDA monomer Schiff

base. The electronic spectra of polymer anchored *N,N'*-BSPDA cobalt(II) complex have shown shift in $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions from 272 to 260 nm and from 334 to 268 nm which further provided evidence for the coordination of cobalt(II) ions through nitrogen atom of azomethine of polymer anchored *N,N'*-BSPDA monomer Schiff base. The appearance of new band at 380 nm has been attributed to charge transfer process (L \rightarrow M) from ligand to cobalt(II) ions (Table 3). The magnetic moment (μ_{eff}) of poly-



Scheme 3.

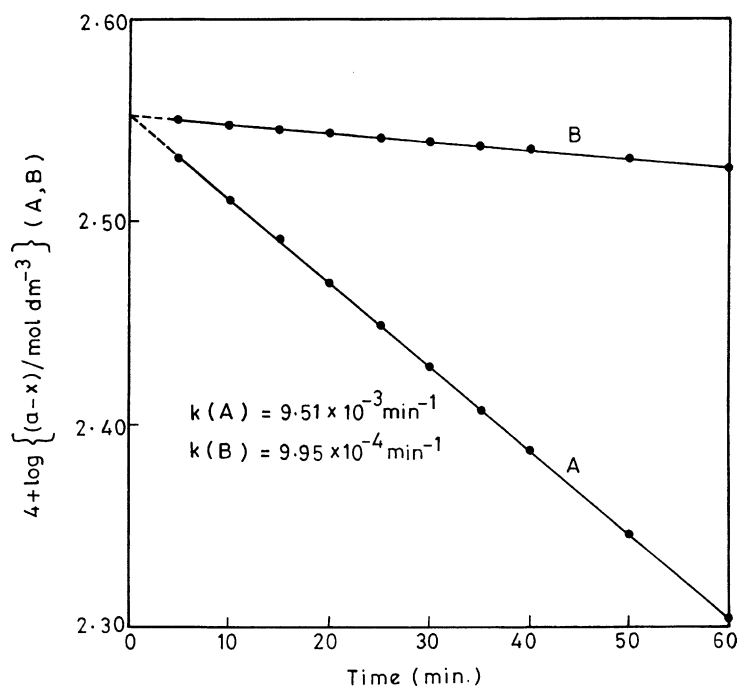


Fig. 3. Effect of reaction time on decomposition of H_2O_2 with supported (A) and unsupported (B) N,N' -BSPDA cobalt(II) complex. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Co(II)}]$ (A) $11.83 \times 10^{-4} \text{ mol dm}^{-3}$; (B) $12.0 \times 10^{-4} \text{ mol dm}^{-3}$, pH 8.0, $\mu = 0.1 \text{ mol dm}^{-3}$, temperature = 25°C .

mer anchored N,N' -BSPDA cobalt(II) complex was 2.23 B.M. at 296 K, which correspond to one unpaired electron in cobalt(II) complex. The IR, UV and magnetic measurements have clearly supported a square planar geometry for both unsupported and polymer supported N,N' -BSPDA cobalt(II) complex. The comparison of spectral data has clearly indicated that N,N' -BSPDA cobalt(II) complex has not shown variation in its geometry on anchoring at polymer support.

3.2. Swelling and complexation behavior of cross-linked beads

The swelling in cross-linked beads is an useful property to show enhanced catalytic activity by polymer anchored metal complexes. The swollen beads facilitate the interactions of reactants with active sites through solvent mediated diffusion and also help in diffusing out the product from the beads. The inward

and outward diffusion of reactants and products depend upon the degree of swelling, which ultimately depends upon the cross-linked density. The degree of swelling determined by size variation with SEM measurements (Fig. 1) and weight percent variation (W_t) on swelling in DMF have shown a decreasing trend in degree of swelling (%S) from 13.15 to 4.32% on increasing the concentration of the DVB from 0.80 to 2.0 mmol (Table 1). The beads prepared with 1.50 mmol of DVB have shown optimum degree of swelling of 7.21% (Table 1). On further increasing the amount of DVB beyond 1.5 mmol, the degree of swelling was decreased (Table 1). The variation in degree of swelling in beads prepared with different amount of DVB has been due to the variation in their network structure. At low concentration of DVB (≤ 1.50 mmol), the N,N' -BSPDA monomer Schiff base has formed cross-links between two polymeric chains, which produced beads with high pore volume (Structure IV in Scheme 2). These beads were having

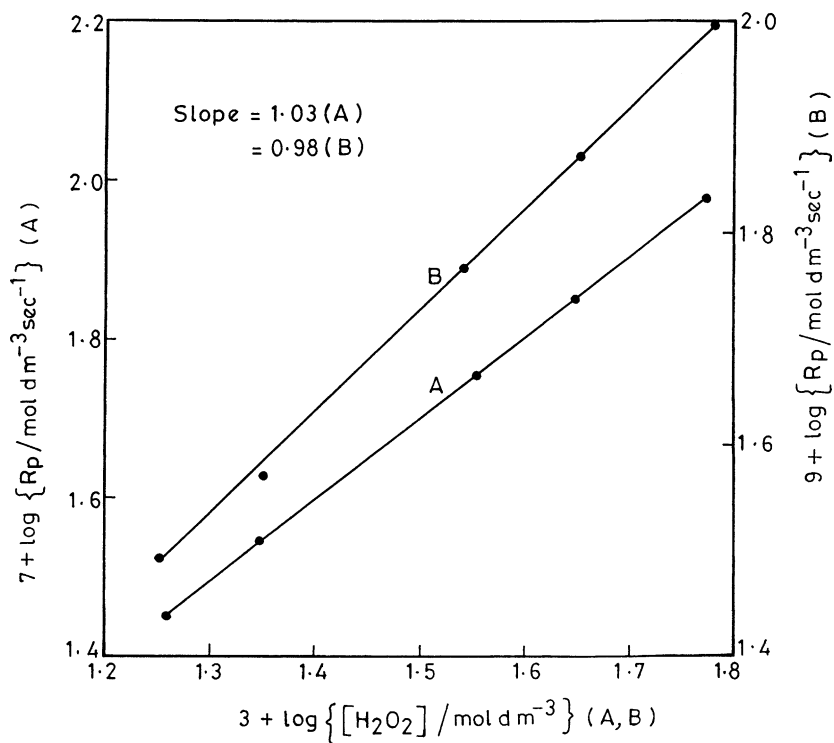


Fig. 4. Log-log plot between R_p vs. $[H_2O_2]$ for supported (A) and unsupported (B) N,N' -BSPDA cobalt(II) complex. $[Co(II)]$ (A) $11.83 \times 10^{-4} \text{ mol dm}^{-3}$; (B) $12.0 \times 10^{-4} \text{ mol dm}^{-3}$, pH 8.0, $\mu = 0.1 \text{ mol dm}^{-3}$, temperature = 25°C .

high pore diameter, low surface area (Table 1) and low capacity for cobalt(II) ions (Table 2). The beads obtained at 1.5 mmol of DVB were having maximum loading capacity for cobalt(II) ions (Table 2), but had shown decreasing trends on further increasing the amount of DVB beyond 1.5 mmol in the reaction mixture (Table 2). At high concentration of DVB (>1.5 mmol), the degree of cross-linking was increased, hence pore volume, average pore diameter of the prepared beads have shown decreasing trends and beads become compact (Table 1). Although surface area of beads was increased (Table 1), loading capacity for cobalt(II) ions was decreased (Table 2). The beads prepared with 1.5 mmol of DVB have shown highest loading for cobalt(II) ions, optimum swelling, pore diameter and pore volume, hence these beads were subsequently used to evaluate their catalytic activity in comparison to unsupported *N,N'*-BSPDA cobalt(II) complex.

3.3. Evaluation of catalytic activity of polymer supported *N,N'*-bis(3-allyl salicylidene)-*o*-phenylenediamine cobalt(II) complex

To investigate the effect of polymer support on catalytic activity of *N,N'*-BSPDA cobalt(II) complex, the rate of decomposition of hydrogen peroxide has been evaluated using polymer supported and unsupported *N,N'*-BSPDA cobalt(II) complex. The beads (Type-III) with optimum cobalt(II) ions loading capacity (1.18 mmol g⁻¹ of beads) and swelling degree (7.21%) were used to evaluate catalytic activity. The decomposition rate of hydrogen peroxide was determined as a function of concentration of hydrogen peroxide and cobalt(II) ions at constant temperature and pH of the medium. A linear variation between log(*a*-*x*) versus reaction time (Fig. 3) at constant concentration of hydrogen peroxide (3.57 × 10⁻² mol dm⁻³) and heterogenized cobalt(II)

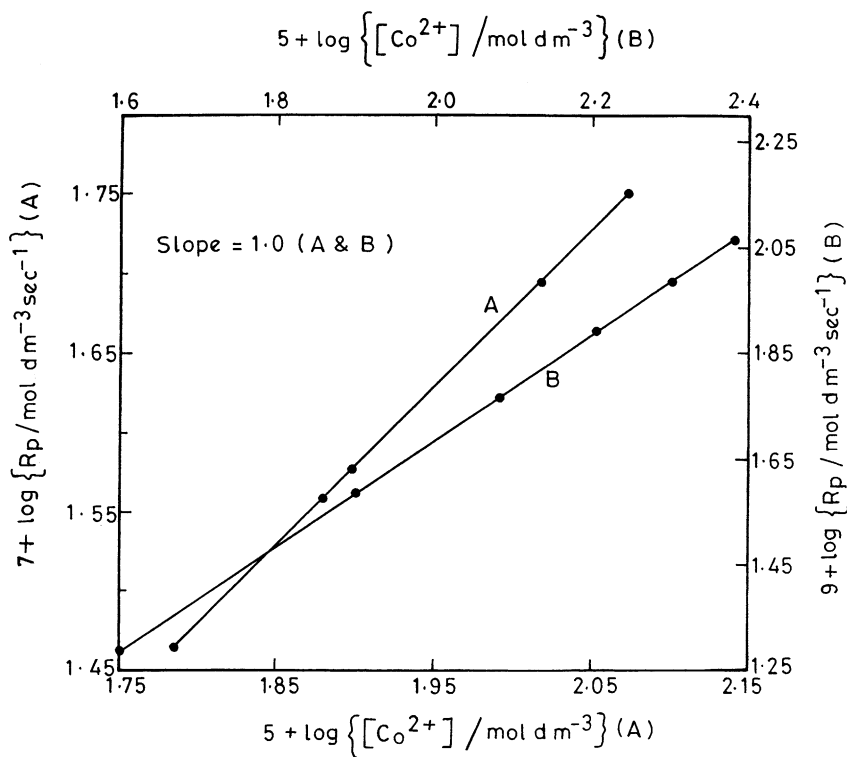


Fig. 5. Log–log plot between R_p vs. $[Co(II)]$ with supported (A) and unsupported (B) *N,N'*-BSPDA cobalt(II) complex. $[H_2O_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, pH 8.0, $\mu = 0.1 \text{ mol dm}^{-3}$, temperature = 25 °C.

ions ($11.83 \times 10^{-4} \text{ mol dm}^{-3}$) at 25°C (Fig. 3A) has clearly indicated that the rate of decomposition of hydrogen peroxide is first order with respect to the concentration of hydrogen peroxide. The decomposition of hydrogen peroxide with homogenized cobalt(II) ions ($12.0 \times 10^{-4} \text{ mol dm}^{-3}$) has shown similar trends, which suggested for similar mechanism for decomposition of hydrogen peroxide with free and polymer supported cobalt(II) complex. The rate constant (k) for decomposition of hydrogen peroxide in heterogenized cobalt(II) ions has been found to be high ($1.59 \times 10^{-4} \text{ s}^{-1}$) in comparison to homogenized cobalt(II) ions ($1.66 \times 10^{-5} \text{ s}^{-1}$). The high turnover number ($3.18 \times 10^{23} \text{ mol s}^{-1} \text{ mol}^{-1}$) with heterogenized cobalt(II) ions in comparison to homogenized cobalt(II) ions ($3.27 \times 10^{22} \text{ mol s}^{-1} \text{ mol}^{-1}$) has further indicated that polymer support has increased the efficiency of the catalyst in comparison to free complex. The log–log plots (Fig. 4) drawn between R_p versus concentration of hydrogen peroxide using heterogenized (Fig. 4A) and homogenized (Fig. 4B) cobalt(II) ions have given unit value of their slope, which anticipated for considering first order dependence of reaction rate on concentration of the hydrogen peroxide. The concentration of polymer supported cobalt(II) ions varied from 6.1×10^{-4} to $11.83 \times 10^{-4} \text{ mol dm}^{-3}$ taking different amount of beads of same loading capacity (Type-III) and rate of decomposition of hydrogen peroxide was evaluated. The rate of decomposition of hydrogen peroxide recorded at different concentrations of polymer supported cobalt(II) ions was also compared at different concentrations of homogenized cobalt(II) ions ranging from 4.0×10^{-4} to $24.0 \times 10^{-4} \text{ mol dm}^{-3}$. The log–log plots (Fig. 5) drawn between R_p versus concentration of cobalt(II) ions both for supported (Fig. 5A) and free cobalt(II) ions (Fig. 5B) have given slope value almost unity indicating first order dependence of reaction rate on concentration of cobalt(II) ions. This has provided evidence for similar mechanism with supported and unsupported cobalt(II) ions. However, the rate of decomposition of hydrogen peroxide was higher with supported catalyst (Fig. 5A). The rate of decomposition of hydrogen peroxide was also studied by taking beads of different loading capacity (beads Type I–V) to evaluate the effect of matrix structure. The variation in reaction rate with beads of different structures has clearly indicated that matrix structure plays an impor-

tant role in controlling the reaction rate. The energy of activation for decomposition of hydrogen peroxide with homogenized and heterogenized cobalt(II) ions was determined within a temperature range of $20\text{--}50^\circ\text{C}$ at constant concentration of hydrogen peroxide ($3.57 \times 10^{-2} \text{ mol dm}^{-3}$) and cobalt(II) ions. The Arrhenius plot (Fig. 6) has shown low energy of activation for decomposition of hydrogen peroxide with supported cobalt(II) ions ($30.04 \text{ kJ mol}^{-1}$) than free cobalt(II) ions ($61.27 \text{ kJ mol}^{-1}$). This has further indicated that polymer support has played significant role in lowering the energy barrier between reactants and products. The rate of decomposition of hydrogen peroxide has also shown dependence on pH of the medium and found to be maximum at and above pH 7.8 (Fig. 7). The variation in rate of decomposition (R_p) on varying the ionic strength of the medium (μ), has indicated the involvement of ionic species (HOO^-) during decomposition of hydrogen peroxide in presence of the cobalt(II) ions. Thus, on the basis of experimental observations, the following reaction steps are proposed for decomposition of hydrogen

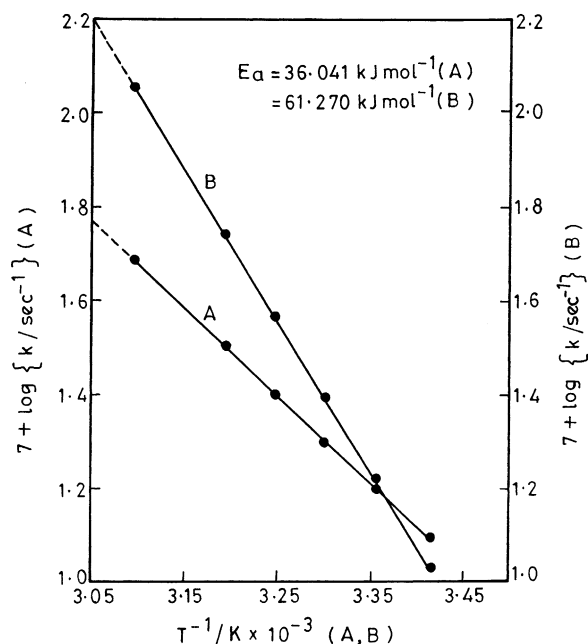


Fig. 6. Arrhenius plots for the energy of decomposition of H_2O_2 with supported (A) and unsupported (B) N,N' -BSPDA cobalt(II) complex. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Co(II)}]$ (A) $11.83 \times 10^{-4} \text{ mol dm}^{-3}$; (B) $12.0 \times 10^{-4} \text{ mol dm}^{-3}$, pH 8.0, $\mu = 0.1 \text{ mol dm}^{-3}$.

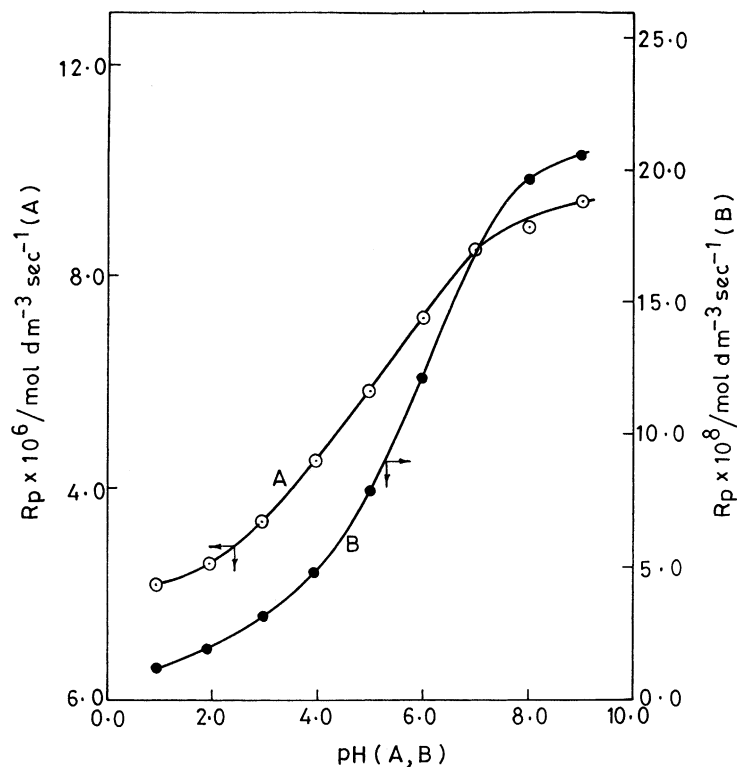
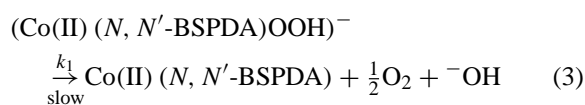
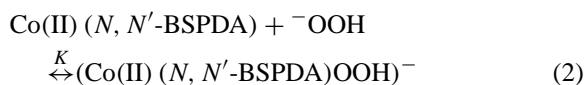


Fig. 7. Effect of pH on rate of decomposition (R_p) of H_2O_2 with supported (A) and unsupported (B) N,N' -BSPDA cobalt(II) complex $[H_2O_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[Co(II)]$ (A) $11.83 \times 10^{-4} \text{ mol dm}^{-3}$; (B) $12.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, temperature = 25°C .

peroxide with heterogenized and homogenized N,N' -BSPDA cobalt(II) complex:



Considering steps 1–4, the rate expression for decomposition of hydrogen peroxide is derived as below:

$$\frac{-d[H_2O_2]}{dt} = \frac{k_d K k_1 [Co(II) (N, N'-BSPDA)][H_2O_2]}{[H^+]} \quad (5)$$

where, k_d and k_1 are the rate constants for the dissociation of hydrogen peroxide and intermediate complex formed in step 2. The K is equilibrium constant for the formation of intermediate complex between HOO^- ions and N,N' -BSPDA cobalt(II) complex.

The agreement between experimental observations and rate expression (Eq. (5)) has provided strong support for the proposed steps 1–4 for the decomposition of the hydrogen peroxide in presence of homogenized and heterogenized cobalt(II) ions.

4. Conclusion

The copolymerization of N,N' -BSPDA monomer Schiff base with styrene and DVB has produced polymer support with high amount of N,N' -BSPDA monomer Schiff base for complexation with cobalt(II) ions in comparison to direct anchoring of Schiff base on functional polymer. The allyl group on

N,N'-BSPDA monomer Schiff base has enabled cobalt(II) complex to show high flexibility while attached to polymer support. The catalytic activity, degree of swelling, and loading capacity have shown dependence on network structure of polymer support obtained at different concentrations of the DVB used during copolymerization reaction.

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