

Polymer-Immobilized *N,N'*-Bis(acetylaceton)ethylenediamine Cobalt(II) Schiff Base Complex and Its Catalytic Activity in Comparison with That of Its Homogenized Analogue

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ABSTRACT: For the preparation of a heterogenized *N,N'*-bis(acetylaceton)ethylenediamine cobalt(II) Schiff base complex, first crosslinked polymer beads were prepared by the suspension copolymerization of styrene (48.97 mmol, 5.1 g), allyl chloride (48.97 mmol, 3.746 g), and divinyl benzene (DVB; 1.75 mmol, 0.228 g) in the presence of azobisisobutyronitrile (0.9×10^{-3} mmol, 0.15 g) as an initiator at $23 \pm 0.1^\circ\text{C}$ under an inert atmosphere. The copolymerization of styrene, allyl chloride in the presence of gelatin (0.75 g), bentonite (2.0 g), and boric acid (2.5 g) produced beads of different crosslinked densities corresponding to the concentration of DVB in the reaction mixture. The amount of allyl chloride in the prepared beads varied from 5.40 to 7.40 mmol g^{-1} of beads with the amount of DVB varying from 2.0 to 0.8 mmol in the reaction mixture. A quadridentate Schiff base (acen) was prepared with ethylenediamine (5.0 mmol, 0.3 g) and acetylaceton (10.0 mmol, 1.0 g), and it was used to obtain a homogenized and heterogenized Co(II)(acen)_2 complex. The extent and arrangement of the Schiff base (acen) in the crosslinked beads depended on the availability of DVB in the reaction mixture. The amount of DVB in the reaction mixture influenced the extent of cobalt(II) ion loading, the degree of swelling, the porosity, and the pore size in the prepared beads. The beads (type IV) prepared with 1.75 mmol (0.228 g) of DVB in the reaction mixture showed a degree of

swelling of 9.65% and efficiencies of loading and complexation for cobalt(II) ions of 49.4 and 85%, respectively, in comparison with beads obtained at other concentrations of DVB in the reaction mixture. The structure of free and polymer-supported Co(II)(acen)_2 complexes was verified with IR, UV, and magnetic measurements, which suggested a square planar geometry for the complexes under both conditions. The catalytic activities of the homogenized and heterogenized Co(II)(acen)_2 complexes were compared by the evaluation of the rate constant (k) for the decomposition of hydrogen peroxide. The heterogenized Co(II)(acen)_2 complex showed a high catalytic activity for the decomposition of hydrogen peroxide ($k = 2.02 \times 10^{-4} \text{ s}^{-1}$) in comparison with the homogenized Co(II)(acen)_2 complex ($k = 4.32 \times 10^{-6} \text{ s}^{-1}$). The energy of activation for the decomposition of hydrogen peroxide with the heterogenized Co(II)(acen)_2 complex was low (38.52 kJ mol^{-1}) in comparison with that for the homogenized complex (73.44 kJ mol^{-1}). In both cases, the rate of decomposition of hydrogen peroxide was directly proportional to the concentration of hydrogen peroxide and cobalt(II) ions. On the basis of experimental observations, a rate expression for the decomposition of hydrogen peroxide was derived. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1398–1411, 2003

Key words: catalysis; crosslinking; swelling; supports

INTRODUCTION

Polymer-bound catalysts are remarkably efficient and selective for various reactions that otherwise scarcely take place.¹ Supported catalysts lower the energy of activation by providing active sites to the reactants. Active polymer support increases the fraction of the catalyst at the surface more than at the inner side of impenetrable bundles of polymeric chains. Supported catalysts are separated easily from reaction mixtures and show high turnover numbers.² There has been

considerable interest in the synthesis of polymer-supported metal complexes because of their potential applications in electrical, electrochemical, and photochemical processes.³ Catalysts supported on insoluble crosslinked polymers are more convenient agents⁴ for organic synthesis than those supported on linear soluble polymers.⁵ Soluble supports lack an advantage of solid catalysts, that is, easy separation from reactants and products. Insoluble linear polymer supports⁶ are also not suitable as they are not able to increase the efficiency of active sites,² as observed with insoluble crosslinked polymers.⁴ The uniform distribution of active sites on polymer supports is also a significant factor in the higher efficiency² of supported catalysts in comparison with that of homogenized catalysts, in which reduced efficiency is due to the aggregation of the catalyst.^{7,8} Although numerous inorganic sup-

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ports^{9–12} have been used for anchoring catalysts, polymer supports are attractive because of their flexibility in providing stereoselectivity between the catalyst and reactants in the presence of the solvent. Zeolites are shape-selective supports, but the slow diffusion of reacting molecules from the liquid phase through the molecular channels of zeolites has resulted in very slow reaction rates;¹³ therefore, they are not suitable catalytic supports for reactions occurring in liquid phases. Crosslinked polymers are able to show enhanced activity through increased concentrations of the reactants around active sites, as observed with mesoporous silica and clays.¹⁴ The degree of crosslinking in polymers plays an important role in controlling the activity,^{15–17} selectivity,^{18–20} and regioselectivity.²¹ Polymer-anchored complexes are also useful for the treatment of water,²² the immobilization of enzymes,²³ affinity chromatography,²⁴ substrate carriers,²⁵ and the development of fine chemicals.²⁶ The 1,3-diketono complexes of transition metals have been reported to be homogeneous catalysts for various reactions^{27,28} because of the excellent coordination capacity of the 1,3-diketo group with transition metals. The 1,3-diketonatotitanium complexes have been used as efficient catalysts in the polymerization of olefins.^{29,30} The 1,3-diketonato complexes of titanium³¹ and zirconium³² have been used in the preparation of syndiotactic polystyrene, but 1,3-diketonato complexes of transition metals supported on polymers have scarcely been reported.³³ Acetylacetonate cobalt(II) complexes with various alkyldiamines were reported by Morgan and Smith,^{34,35} but no reports are available for the synthesis of the polymer-supported Co(II)(acen)₂ complex [where acen is the quadridentate Schiff base *N,N'*-bis(acetylacetonate)ethylenediamine] and the evaluation of its catalytic activity. Therefore, we have attempted to develop the polymer-anchored Co(II)(acen)₂ complex and to compare its catalytic activity with that of its homogeneous counterpart with the decomposition of hydrogen peroxide as a model reaction.

EXPERIMENTAL

Chemicals

Ethylenediamine (Loba Chemie, Mumbai, India) was vacuum-distilled and vacuum-dried over solid potassium hydroxide. The distilled fraction of ethylenediamine from 116 to 118°C was used for the synthesis of the Schiff base. Acetylacetonate (Loba Chemie, Mumbai, India), with a boiling range of 133–135°C, was used as received. Styrene, allyl chloride, and divinyl benzene (DVB) were reagent-grade chemicals (Aldrich Chemical Co., Inc., Milwaukee, WI); they were vacuum-distilled before being used for the synthesis of the crosslinked polymers. Azobisisobutyronitrile (Aldrich

Chemical Co., Inc.) was used directly without further purification.

Fourier transform infrared spectra

The IR spectra of the Schiff base (acen) and its cobalt(II) complex were recorded on KBr pellets with a PerkinElmer (Norwalk, CT) 1600 Fourier transform spectrophotometer.

Electronic spectra

The electronic spectra of the Schiff base and its cobalt(II) complex were recorded in dimethylformamide (DMF) with a Shimadzu (Japan) 1601 PC ultraviolet-visible spectrophotometer.

Magnetic measurements

The dipole moment (μ) and magnetic susceptibility (χ) of homogeneous and polymer-supported Co(II)(acen)₂ complexes were determined with a Gouy balance at 294 K, and diamagnetic corrections were made.

Thermal studies

The thermal behavior of the Schiff base (acen) and its cobalt(II) complex was determined by the recording of thermograms with a Stanton Red Croft STA-780 thermal analyzer (United Kingdom) at a heating rate of 10°C/min under a nitrogen atmosphere. The Stanton Red Croft DSC-1500 was used to determine the glass-transition temperature and melting point of the polymer support.

Elemental analysis

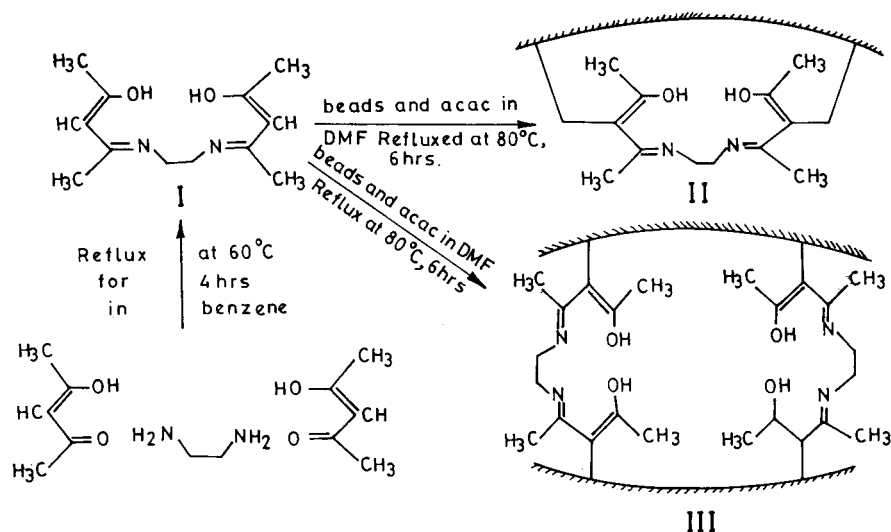
The elemental analysis of the free Schiff base (acen) and polymer-anchored Schiff base [polymer-anchored *N,N*-bis(acetylacetonate)ethylenediamine (p-acen)] was carried with a PerkinElmer 240C elemental analyzer to determine the composition of the Schiff base and its amount on the polymer support.

Estimation of the cobalt(II) ion loading

The loading capacity of the polymer-anchored Schiff base (p-acen) was determined by the leaching of cobalt(II) ions forming the polymer-supported complex and by the estimation of its amount with a PerkinElmer 2100 atomic absorption spectrophotometer at $\lambda_{\text{max}} = 240.7$ nm.

Polymer bead size measurements

The size of the crosslinked polymer beads prepared by suspension copolymerization was measured with



Scheme 1

scanning electron microscopy (SEM; Leo-435 VP, England) by the mounting of beads on metal stubs and vacuum coating with gold.

Molecular weight of the Schiff base (acen) and its cobalt(II) complex

The molecular weights of the synthesized Schiff base (acen) and its cobalt(II) complex were determined by vapor pressure osmometry (Knauer K-700, Berlin, Germany) with bezil as a calibrant.

Swelling studies

The degree of swelling (S) of crosslinked polymer beads obtained at different concentrations of DVB was determined by the soaking of the beads for 24 h in DMF and the recording of the variations in their sizes with SEM and also by the recording of the increases in the weight with respect to the initial weight.

Porosity

The porosity of the beads was calculated from the initial weight of the dried beads (W_0) and the weight after swelling (W_t) for 24 h in DMF. The density (d_s) of DMF was used to determine the porosity as follows:

$$\text{Porosity} = \frac{W_t - W_0}{W_0 d_s}$$

Bead density (ρ) and surface area (S_{BET}) of the beads

ρ was measured by a liquid displacement technique with the ASTM D 792 test method. S_{BET} was deter-

mined by the nitrogen adsorption isotherm using Brunauer, Emmett, and Teller (BET) method.

Synthesis of the Schiff base (acen) and its cobalt(II) complex

For the preparation of the quadridentate Schiff base (acen), 5 mmol (0.3 g) of anhydrous ethylenediamine was mixed with 10 mmol (1.0 g) of acetylacetone and refluxed at 60°C for 4 h. With the cooling of the reaction mixture, a dark purple product (acen) was obtained (Structure I in Scheme 1), which was recrystallized in water and vacuum-dried over calcium chloride (yield = 68% or 0.884 g, mp = 111–112°C). The nitrogen percentage calculated for $C_{12}H_{20}N_2O_2$ was 12.5%, and the experimentally determined percentage was 12.8%; the calculated molecular weight was 224.0 g, and the experimentally determined weight was 224.0 g. The IR spectrum of the Schiff base (acen; Structure I in Scheme 1) was recorded, and the observed absorption bands were analyzed for structural information. The electronic spectrum of the Schiff base (acen) was also recorded in support of possible electronic transitions and bonding of the Schiff base (acen) with cobalt(II) ions. The cobalt(II) complex of the Schiff base (acen) was prepared by the reaction of 5.0 mmol (1.12 g) of the Schiff base (acen) with 5.0 mmol (1.19 g) of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in DMF under reflux at 95°C for 8 h, which, on cooling, produced a dark blue product. The recrystallization of the product gave fine crystals of the Co(II)(acen)_2 complex (yield = 66%, mp = 186°C). The IR and UV spectra of the prepared Co(II)(acen)_2 complex were recorded for the presence of functional groups and coordination sites of the Schiff base (acen).

TABLE I
Composition and Characteristics of Synthesized Crosslinked Beads

Type of beads	DVB in the reaction mixture (mmol)	Amount of allylchloride (mmol g ⁻¹ beads)	% Cl in beads	Beads size (μm)	ρ (g cm ⁻³)	S (%)
I	0.80	7.40	26.26	182.0	0.46	16.20
II	1.15	6.60	23.48	161.0	0.49	12.60
III	1.50	6.20	21.94	138.0	0.51	11.40
IV	1.75	6.00	21.34	124.2	0.52	9.65
V	2.00	5.40	19.20	111.5	0.53	6.32

[Styrene]₁ = 48.97 mmol; [Allyl chloride]₁ = 48.97 mmol.

Preparation of the functionalized crosslinked polymer beads

For the preparation of the heterogenized cobalt(II) complex, the functionalized crosslinked polymer beads were prepared by the copolymerization of styrene and allyl chloride in the presence of DVB as a crosslinking agent. For the preparation of the crosslinked beads (type IV), the reactants were placed separately in DMF. First, the organic phase (40 mL of DMF) contained styrene (48.97 mmol, 5.1 g), DVB (1.75 mmol, 0.228 g), and allyl chloride (48.97 mmol, 3.746 g), and the other organic phase (10 mL of DMF) contained azobisisobutyronitrile (0.9 × 10⁻³ mmol, 0.15 g) were prepared. Both phases were deaerated separately with nitrogen gas and added dropwise to 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) dissolved in 500 mL of water. The flask was equipped with a mechanical stirrer and a condenser and was heated at 70°C. After 6 h, the heating was stopped, and stirring was continued for another 30 min to cool the solution. The beads were separated and washed with methanol (4 × 50 mL) for the removal of unreacted monomers and initiator. Finally, the beads were washed with distilled water on a mesh for the removal of bentonite and dried in a vacuum oven at 70°C for 24 h. This produced yellow beads (yield = 65% or 5.89 g, mp = 450°C). The IR spectrum of the beads showed an absorption band at 1260 cm⁻¹, which was ascribed to the C—Cl bond in the polymer beads.³⁶ The amount of allyl chloride was

3.0 mmol g⁻¹ of beads, as calculated from the chlorine content (21.34%). The beads of other compositions (Table I) were prepared with a similar procedure. The amount of allyl chloride in beads of different crosslinked densities varied from 5.40 to 7.40 mmol g⁻¹ of bead with the content of DVB varying from 2.0 to 0.8 mmol in the reaction mixture (Table I).

Synthesis of the polymer-anchored Schiff base (p-acen)

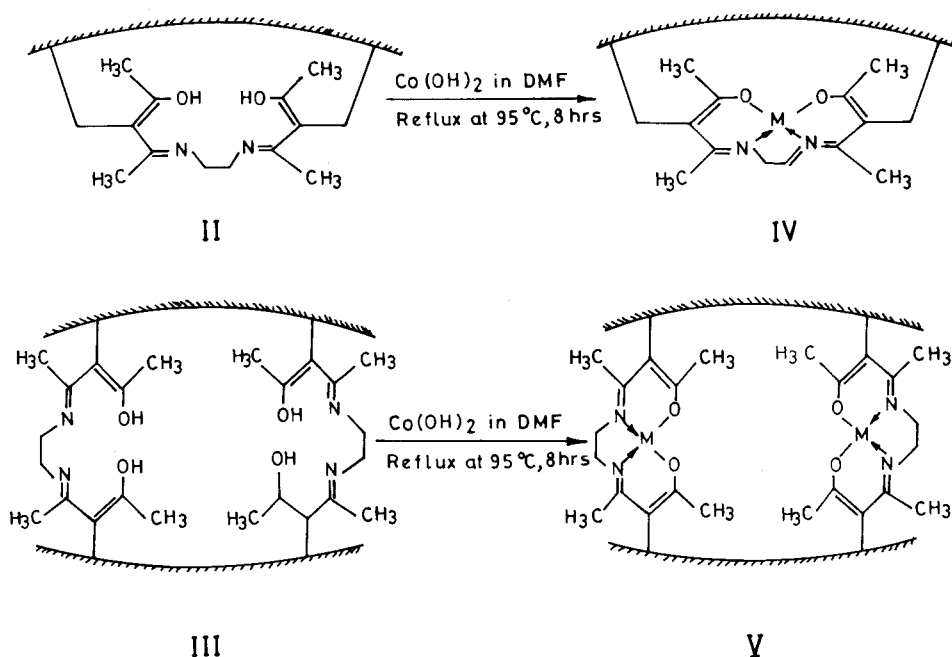
We performed the anchoring of the Schiff base (acen) onto synthesized crosslinked polymer beads by taking DMF swollen beads (1.0 g) in a 20-mL DMF solution containing the Schiff base (acen; 5.0 mmol, 1.12 g; structure I in Scheme 1) and refluxing them for 6 h at 80°C in an oil bath. After cooling to room temperature, the Schiff base (acen) anchored beads (Structure II or III in Scheme 1) were washed with methanol and dried in a vacuum oven. The beads (type I) with network structure II (Scheme 1) showed 1.85 mmol g⁻¹ (0.414 g) of Schiff base (acen), and beads (type IV) with network structure III (Scheme 1) showed 2.90 mmol (0.65 g) of Schiff base (acen) on 1.0 g of beads (Table II). The amount of the Schiff base (acen) loaded onto the beads was determined from the nitrogen content, which was estimated with elemental analysis (Table II).

The beads (type V) prepared with a large amount of DVB (2.00 mmol) in the reaction mixture also have network structure III (Scheme 1) but showed a low

TABLE II
Characteristics of Schiff Base (acen) Anchored Cross-Linked Beads

Types of beads	Allylchloride consumed in the anchoring of the Schiff base (%)	Nitrogen in anchored Schiff base beads (%)	Weight of anchored Schiff base (mmol g ⁻¹ of beads)	Weight of Co(II) ions loaded (mmol g ⁻¹ of beads)	EL (%)	EC (%)
I	50.00	5.25	1.85	1.15	23.00	62.0
II	66.60	5.72	2.20	1.51	30.20	72.0
III	92.22	8.16	2.86	2.35	47.00	82.0
IV	96.70	8.37	2.90	2.47	49.40	85.0
V	70.37	5.63	1.90	1.44	28.80	76.0

[Schiff base]₁ = 5.0 mmol; [Co(II)]₁ = 5.0 mmol.



Scheme 2

anchoring capacity for the Schiff base (1.90 mmol, 0.426 g g⁻¹ of beads), as shown in Table II. The IR spectrum of Schiff base (p-acen) anchored beads was recorded to support the anchoring of the Schiff base (acn) on the beads. The appearance of characteristic peaks of the Schiff base (acn) in the spectrum was used as supporting evidence for Schiff base (acn) anchoring.

Loading of cobalt(II) ions onto the polymer-anchored Schiff base (p-acen)

The complexation of cobalt(II) ions was carried out by 1.0 g of DMF-swollen Schiff base (p-acen) anchored beads (Structures II and III in Scheme 1) being kept in 30 mL of DMF containing 5 mmol of cobalt(II) hydroxide. The cobalt(II) hydroxide solution was prepared by the mixing of 5 mmol (1.189 g) of CoCl₂ · 6H₂O with 10 mmol (10.56 g) of KOH in distilled water. Then, previously weighed beads were refluxed at 95°C for 8 h in an oil bath. After cooling, the beads were washed with water and dried at 100°C in a vacuum oven, and this produced dark blue beads (Structures IV and V in Scheme 2). For the confirmation of cobalt(II) ion complexation with polymer-anchored Schiff base (p-acen), the IR spectra of cobalt(II) ion loaded beads were also recorded and compared with IR spectra of Schiff base anchored beads (p-acen). For the evaluation of cobalt(II) ion loading, 1.0 g of cobalt(II) ion loaded beads of a particular composition was placed in a conical flask containing a 20-mL solution of 4N acetic acid and was refluxed for 2 h on a heating mantle at 110°C. On cooling, the beads were separated and washed care-

fully for the removal of the leached cobalt(II) ions from the beads. The filtrate and washing of the beads were mixed carefully and analyzed for the cobalt(II) ion concentration with atomic absorption spectrometry at λ_{max} = 240.7 nm. The loading of cobalt(II) ions onto polymer beads was calculated as the efficiency of complexation [EC (%)] and efficiency of loading [EL (%)] with the following equations:

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

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

The extent of the cobalt(II) ion loading was dependent on the degree of crosslinking and the amount of the polymer-anchored Schiff base (p-acen). The beads with a low degree of crosslinking (type I) had a different structure (Structure IV in Scheme 2) than the beads (types IV and V) with a high degree of crosslinking (Structure V in Scheme 2); this resulted in variations in EC and EL for cobalt(II) ions, as shown in Table II.

TABLE III
Effect of Bead Parameters on Rate Constant (k) for of Decomposition of Hydrogen Peroxide

Bead type	DVB in reaction mixture (mmol)	Porosity ($\text{cm}^3 \text{g}^{-1}$)	\bar{D} (\AA)	$S_{\text{BET}}/(\text{m}^2\text{g}^{-1})$	$k/(10^{-2} \text{min}^{-1})$
I	0.80	0.62	620	40	0.98
II	1.15	0.56	345	65	1.10
III	1.50	0.48	240	80	1.16
IV	1.75	0.42	147	114	1.21
V	2.00	0.21	27	310	0.80

$[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{mol dm}^{-3}$; [beads] = 1.0g dm^{-3} ; pH = 7.5; temperature = 25°C ; \bar{D} = average pore diameter; S_{BET} = surface area.

Evaluation of the catalytic activity of the polymer-anchored Schiff base (p-acen) cobalt(II) complex

To evaluate the catalytic activity of the polymer-anchored Co(II)(acen)_2 complex, we evaluated the rate of decomposition (R_p) of hydrogen peroxide with this catalyst. R_p of hydrogen peroxide was determined at $25^\circ\text{C} \pm 0.1^\circ\text{C}$ with Co(II)(acen)_2 complex anchored beads in a 100-mL solution of hydrogen peroxide of known molarity prepared with 2.0 volumes of H_2O_2 (0.6% w/w). We estimated the amount of hydrogen peroxide that decomposed at different intervals of time by taking out a 5.0-mL aliquot of the reaction mixture and titrating it with a 0.01M KMnO_4 solution in the presence of 0.01M sulfuric acid. The procedure was repeated at different concentrations of hydrogen peroxide, at different reaction temperatures, and with beads of different cobalt(II) ion loading capacities. R_p of hydrogen peroxide was also recorded with the homogenized Co(II)(acen)_2 complex so that we could compare the effect of the polymer support on the catalytic activity of the cobalt(II) complex.

RESULTS AND DISCUSSION

The attachment of the homogeneous catalyst onto chloromethylated styrene divinyl benzene and silica has been reported frequently, but chloromethylated styrene and silica are not able to provide sufficient flexibility to anchored ligands to complex with metal ions. It also reduces reactant accessibility to polymer-bound metal complexes for catalysis, and so supports with flexible arms have been thought to be more useful than supports with rigid ligands.⁹⁻¹² The hydrophobic nature of polystyrene has also shown an adverse effect on the reaction rates of substrates that are soluble in polar solvents. Supports with sufficient amounts of DVB have shown physicochemical incompatibility in polar solvents and have been found to be responsible for reduced reaction rates in comparison with those of other crosslinking agents such as N,N' -methylenebisacrylamide and ethylene glycol dimethacrylate. The copolymerization of allyl chloride and styrene with DVB has produced a solvent-com-

patible polymer support with suitable flexibility. The prepared polymer support shown enhanced loading for the Schiff base (acen) and cobalt(II) ions. The polystyrene-bound acetylacetone was reported as an O—O chelating agent for transition-metal ions,³⁷ and so the synthesized polymer-supported Schiff base (acen) showed high efficiency for cobalt(II) ion loading because of the increased flexibility of this Schiff base (acen) for coordinating with cobalt(II) ions through O—N donor atoms in comparison with polymer-anchored acetylacetone as a coordinating ligand. The amount of the Schiff base (acen) anchored onto the polymer support showed significant variations with the types of polymer supports (types I–V) obtained with different amounts of DVB in the reaction mixture. The amount of allyl chloride in the prepared polymer beads (types I–V) varied from 7.40 to 5.50 mmol g^{-1} of beads with the amount of DVB varying from 0.8 to 2.0 mmol in the reaction mixture (Table I). The amount of allyl chloride was calculated with the chlorine contents in the prepared beads. The beads prepared with different amounts of DVB also showed variations in the extent and arrangement of the Schiff base because of the variations in the degree of crosslinking and the arrangement of the allyl chloride in the polymer backbone (Structures II and III in Scheme 1). The variations in the arrangement of the Schiff base with a varying degree of crosslinking were evident from the variations in the average pore diameter (\bar{D}) from 20 to 27 \AA (Table III) and the variation in the porosity of the beads. At high concentrations of DVB ($>1.75 \text{mmol}$), \bar{D} suddenly decreased from 147 to 27 \AA , and the pore volume also decreased from 0.42 to 0.21 $\text{cm}^3 \text{g}^{-1}$ (Table III). This was a clear indication that at high concentrations of DVB ($>1.75 \text{mmol}$), the arrangement of the Schiff base was different than that at low concentrations of DVB ($<1.75 \text{mmol}$). The beads prepared with different amounts of DVB had different physicochemical properties, such as porosity, S_{BET} , and D values. The bead size and S values showed a decreasing trend with an increasing amount of DVB in the reaction mixture (Table I). The beads prepared with 1.75 mmol of DVB (type IV) had the maximum

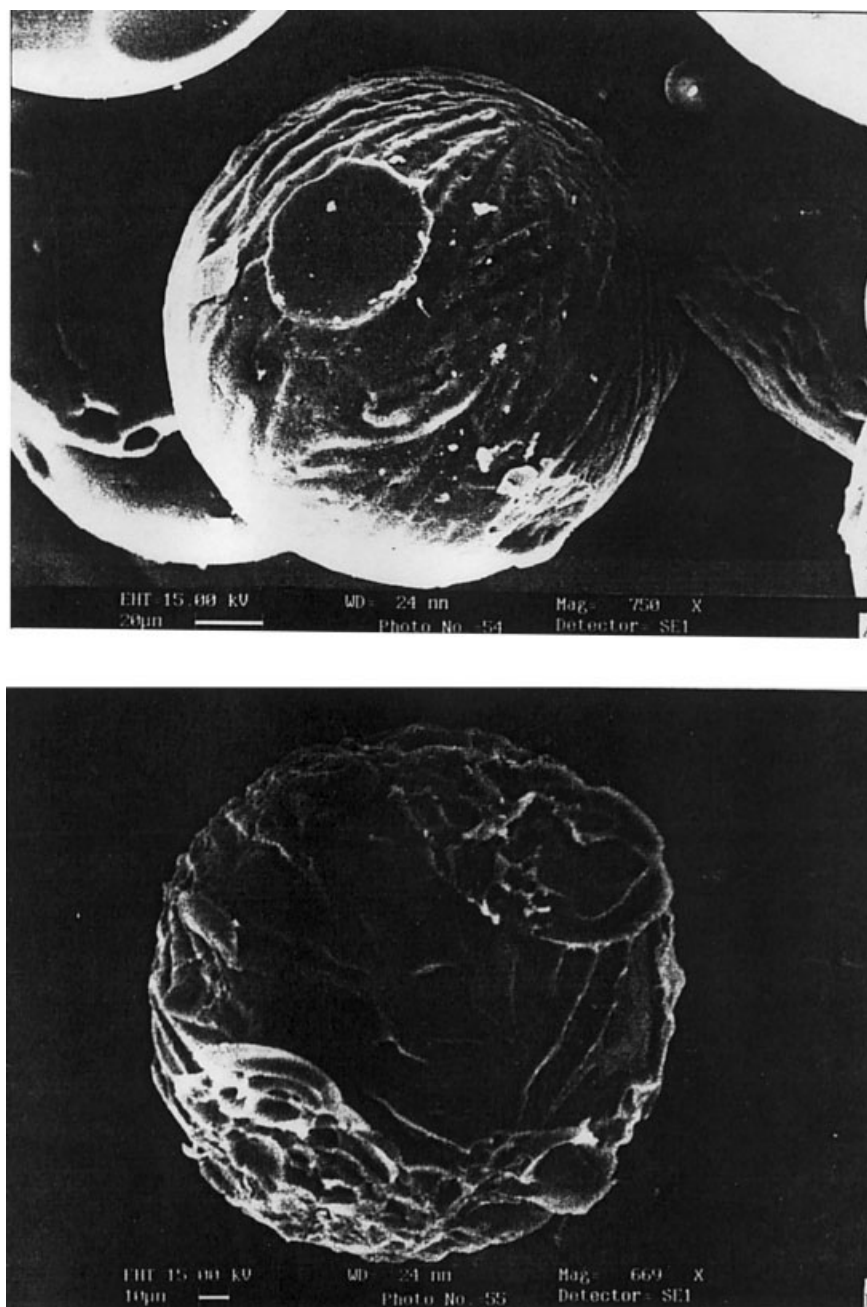


Figure 1 SEM micrographs of crosslinked polymer beads (A) before and (B) after swelling.

amount of the Schiff base (acen; 2.90 mmol g^{-1} of beads) and also showed the highest EL value (49.40%) and EC value (85.0%) for cobalt(II) ions (Table II). The S values for beads prepared with different amounts of DVB were determined by SEM studies (Table I) and with weight variations of the beads in DMF. The beads with an optimum amount of DVB (1.75 mmol) showed $S = 9.65\%$ (type IV) in DMF, as evident from their size variation on swelling [Fig. 1(A,B)]. The complexation of cobalt(II) ions with the polymer-anchored Schiff base (p-acen) showed a substantial increase in the thermal stability, as shown by thermogravimetry (TG)

curves recorded for the polymer-anchored Schiff base [Fig. 2(A)] and its cobalt(II) complex [Fig. 2(B)]. The increase in the thermal stability was an indication of the complexation of the cobalt(II) ions with the polymer-anchored Schiff base. This also indicated that the beads could be used as catalysts for reactions occurring at and above 300°C . The structure of the Co(II) (acen)₂ complex on the polymer support controlled the catalytic activity, and so the analysis and characterization of the supported catalyst were very important steps for evaluating its properties in comparison with the unbound catalyst.

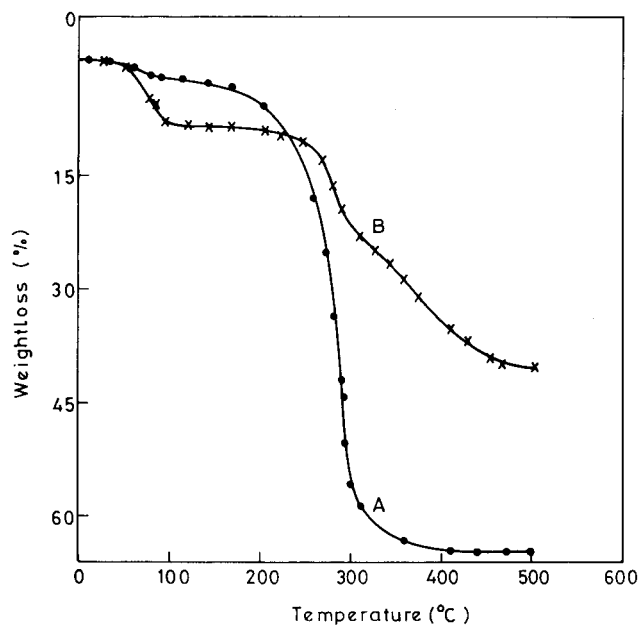


Figure 2 TG curves for (A) the polymer-anchored Schiff base and (B) its cobalt(II) complex.

Synthesis and characterization of the homogenized Co(II)(acen)₂ complex

The IR spectra of the synthesized Schiff base (acen; structure I in Scheme 1) showed a broad band between 2852 and 3396 cm^{-1} due to intermolecular hydrogen-bonding $\nu(\text{N}-\text{H})$ and $\nu(\text{OH})$ enolic vibrations (Table IV). The disappearance of the absorption band at 1700 cm^{-1} was an indication of the absence of free carbonyl groups in the prepared Schiff base. A strong absorption band at 1609 cm^{-1} was assigned to the $\nu(\text{C}=\text{N})$ azomethine group, and the absorption band between 1098 and 1108 cm^{-1} was attributed to $\nu(\text{C}-\text{O})$ vibrations. The Schiff base (structure I in Scheme 1) showed a band at 1570 cm^{-1} that corresponded to the $\nu(\text{C}=\text{C})$ group (Table IV). The electronic spectra (Table V) of the Schiff base (acen) in DMF showed two absorption bands at 258 and 319 nm for $\Pi-\Pi^*$ and $n-\Pi^*$ transitions in the Schiff base (acen). The IR spectra of the homogeneous Co(II)(acen)₂ complex showed absorp-

tion bands at 1062 and 1612 cm^{-1} corresponding to $\nu(\text{C}-\text{O})$ enolic and $\nu(\text{C}=\text{N})$ azomethine groups of the complex (Table IV). The shift in the absorption bands in the IR spectra of the Schiff base (acen) provided evidence for its complexation with cobalt(II) ions. The absorption band at 1570 cm^{-1} , corresponding to $\nu(\text{C}=\text{C})$, shifted to 1576 cm^{-1} , which was also an indication for the complexation of cobalt(II) ions with the Schiff base (acen). The absorption band of $\nu(\text{C}=\text{N})$ azomethine in the free Schiff base (acen) shifted from 1609 to 1612 cm^{-1} on complexation with cobalt(II) ions (Table IV). There was a complete absence of the absorption band corresponding to enolic OH, which was present in the free Schiff base (acen) between 2852 and 3396 cm^{-1} , and the absorption band between 1098 and 1108 cm^{-1} of the $\nu(\text{C}-\text{O})$ group of the free Schiff base (acen) shifted to 1062 cm^{-1} . On complexation, two new bands at 563 and 474 cm^{-1} appeared that corresponded to vibration frequencies of bonds formed between cobalt(II) ions with the enolic oxygen and nitrogen atoms of the azomethine of the Schiff base (Table IV). The absorption band at 1570 cm^{-1} due to $\nu(\text{C}=\text{C})$ also shifted to 1576 cm^{-1} , and this was an indication for the complexation of the cobalt(II) ions with the Schiff base (p-acen). These IR data supported the tetradentate coordination of the cobalt(II) ions with the polymer-anchored Schiff base. The electronic spectra of the ligand on complexation also showed variations in the absorption bands corresponding to $\Pi-\Pi^*$ and $n-\Pi^*$ transitions (Table V). The original absorption band at 258 nm ($\Pi-\Pi^*$) shifted to 241 nm ($\Pi-\Pi^*$), and the band at 319 nm ($n-\Pi^*$) shifted to 270 nm ($n-\Pi^*$). This shift in the absorption bands provided evidence for the complexation of the cobalt(II) ions with the nitrogen atom of the Schiff base (acen). Two new absorption bands at 301 and 395 nm in the electronic spectrum of the cobalt(II) complex were attributed to charge-transfer (CT) and $d-d$ transitions in the cobalt metal. These transitions were suggestive of a square planar structure of the cobalt(II) ions with the Schiff base (acen), as reported for other quadridentate chromophores (N_2O_2).³⁸ The magnetic moment (μ_{eff}) of the Co(II)(acen)₂ complex was 2.42 BM at 294

TABLE IV
IR Frequencies of the Schiff Base (acen) and Its Cobalt(II) Complex

Metal ion	Functional group	Frequency of unsupported		Frequency of polymer supported	
		Schiff base (cm^{-1})	Complex (cm^{-1})	Schiff base (cm^{-1})	Complex (cm^{-1})
Co (II)	$\nu(\text{OH})$	2852–3396	—	2847–3398	—
	$\nu(\text{C}=\text{O})$ (Enolic)	1098–1108	1062	1085–1164	1056
	$\nu(\text{C}=\text{N})$	1609	1612	1607	1610
	$\nu(\text{C}=\text{C})$	1570	1576	1563	1567
	$\nu(\text{M}=\text{O})$	—	563	—	559
	$\nu(\text{M}=\text{N})$	—	474	—	469
	$\nu(\text{C}=\text{Cl})$	—	—	1260	1262

TABLE V
Electronic and Magnetic Properties of the Schiff Base (acen) and Its Co(II) Complex

Metal ion	Electronic transition	Transition frequency of unsupported		Transition frequency of supported		μ_{eff} (BM)	Structure
		Schiff base ($\lambda_{\text{max}}/\text{nm}$)	Complex ($\lambda_{\text{max}}/\text{nm}$)	Schiff base ($\lambda_{\text{max}}/\text{nm}$)	Complex ($\lambda_{\text{max}}/\text{nm}$)		
Co(II)	$\pi \rightarrow \pi^*$	258	241	256	254	2.42	Square planar
	$n \rightarrow \pi^*$	319	270	316	267	(2.41) ^a	
	C \rightarrow T	—	301	—	326	at 294 K	
	d \rightarrow d	—	395	—	466		

^a μ_{eff} of the supported complex.

K, which further supported the square planar structure³⁹ with the Schiff base (acen).

Synthesis and characterization of the heterogenized Co(II)(acen)₂ complex

The activity of the catalyst on the polymer support increased if the structure of the complex was not distorted on heterogenization. The activity enhancement of the catalyst on the polymer support was due to a substantial increase in the interactions of the catalyst with the reacting molecules. The heterogenized Co(II)(acen)₂ complex on the crosslinked polymer support was synthesized by the anchoring of the Schiff base (acen) onto the crosslinked polymer beads and the subsequent complexation of cobalt(II) ions. The anchoring of the Schiff base (acen) on the crosslinked polymer beads depended on the amount of allyl chloride in the polymer chains and the degree of crosslinking in the beads. The amount of allyl chloride in the polymer and its reaction with the Schiff base (acen) through chlorine depended on the degree of crosslinking in the polymer matrix (Table I). At a low concentration of DVB (0.8 mmol) in the reaction mixture, the amount of allyl chloride in the polymer chains was high (7.40 mmol g⁻¹ of beads, type I), but its complexation (Table II) with the Schiff base (acen) was low (50%). The beads obtained at this concentration of DVB (type I) were highly porous (0.62 cm³ g⁻¹) network structures (structure II in Scheme 1) with the Schiff base (acen) on a single polymer chain. The porosity and \bar{D} values of such beads (type I) were 0.62 cm³ g⁻¹ and 620 Å, respectively (Table III). With an increasing amount of DVB (>0.8 mmol), the amount of allyl chloride in the polymer beads (Table I) showed a decreasing trend (6.0 mmol g⁻¹ of beads, type IV), but its complexation with the Schiff base (acen) increased (96.7%). These beads (type IV) had a different network structure (Structure III in Scheme 1) with a low porosity (0.42 cm³ g⁻¹) and a low average diameter (147 Å; Table III). This clearly indicated that with large amounts of DVB (≥ 1.75 mmol), the amount of allyl chloride in the polymer chains decreased, but its complexation with the Schiff base (acen) increased

(Table II) because of the anchoring of the Schiff base between two polymeric chains (structure III in Scheme 1 for bead type IV). The extent of complexation of the Schiff base (acen) on the crosslinked beads was determined by the estimation of the content of chlorine (Table I) before and after the anchoring of the Schiff base (acen) onto the crosslinked beads. The amount of the Schiff base (acen) on the polymer support was also evaluated by the estimation of the nitrogen content in the ligand-anchored beads (Table II). The amount of the Schiff base varied from 1.85 to 1.90 mmol g⁻¹ of crosslinked beads with DVB varying from 0.8 to 2.0 mmol (Tables I–III). The data shown in Table II clearly indicated that the extent of the anchoring of the Schiff base (acen) increased up to 1.75 mmol of DVB (bead type IV) and decreased with a further increase in the concentration of DVB beyond 1.75 mmol (bead type V). The IR spectra of the polymer-anchored Schiff base (p-acen) showed absorption bands at 1563 cm⁻¹ for $\nu(\text{C}=\text{C})$, at 1607 cm⁻¹ for $\nu(\text{C}=\text{N})$, and at 1085–1164 cm⁻¹ for $\nu(\text{C}-\text{O})$ enolic and a band between 2847 and 3398 cm⁻¹ for $\nu(\text{OH})$, which provided sufficient evidence for the anchoring of the Schiff base (acen) onto the polymer support (Table IV). The band at 1262 cm⁻¹ corresponding to $\nu(\text{C}-\text{C})$ had not completely disappeared with the anchoring of the Schiff base (acen) onto the crosslinked beads. This was an indication that the polymer beads still had unreacted methylene chloride groups. The electronic spectra also showed absorption bands at 256 and 316 nm corresponding to $\pi-\pi^*$ and $n-\pi^*$ transitions of the polymer-anchored Schiff base (p-acen) (Table V). The complexation of the cobalt(II) ions with the polymer-anchored Schiff base (p-acen) showed variations in the characteristic IR bands of the uncomplexed Schiff base (acen) and also showed new bands that provided sufficient evidence for the complexation of cobalt(II) ions with the polymer-anchored Schiff base (p-acen). The absorption band of $\nu(\text{C}=\text{C})$ shifted to 1567 cm⁻¹, and that of azomethine $\nu(\text{C}=\text{N})$ shifted to 1610 cm⁻¹. On complexation, the original band between 2847 and 3398 cm⁻¹ for $\nu(\text{OH})$ disappeared completely, and this was an indication of the complexation of cobalt(II)

ions through enolic oxygen of the Schiff base (acen) (Table IV). The appearance of two new absorption bands at 559 and 469 cm^{-1} , corresponding to M—O and M—N bonds, provided further support for the complexation of cobalt(II) ions with the polymer-supported Schiff base (p-acen). In electronic spectra, the variations in the absorption band from 256 to 254 nm for the II—II* transition and from 316 to 267 nm for the n —II* transition were ascribed to the coordination of cobalt(II) ions with the nitrogen atom of the polymer-anchored Schiff base (Table V). On the complexation of cobalt(II) ions, the electronic spectra showed two new absorption bands at 326 (CT) and 466 nm ($d-d$), which provided further evidence for the complexation of cobalt(II) ions with the Schiff base (p-acen) and for the existence of a square planar geometry of the Co(II)(acen)₂ complex on the polymer support, as shown by the homogeneous Co(II)(acen)₂ complex. The magnetic moment of the polymer-supported Co(II)(acen)₂ complex was 2.41 BM at 294 K, which corresponded to one unpaired electron in the cobalt(II) ion of the complex, which again supported a square planar geometry of the Co(II)(acen)₂ complex on the polymer support (Table V). These investigations clearly indicated that the extent of the immobilization of the Schiff base (acen) and its complexation with cobalt(II) ions varied with the degree of crosslinking, but the structure of the complex remained the same as that observed with the homogenized complex, and so the enhancement in the catalytic activity was purely due to the increase in the concentration of reactants at active sites on the polymer support.

Swelling and complexation behavior of the polymer beads

The S value of the crosslinked beads was a significant property of the polymer, which depended on the hydrophilic nature of the polymer matrix and the extent of crosslinking between the polymeric chains. The catalytic sites at the inner surfaces of the beads were able to show their activity if the polymer matrix was swollen sufficiently to facilitate the solvent-mediated diffusion of reacting molecules to the center of the beads and the diffusion of products from center to the periphery. The distribution of the reactants, the product, and the catalytic activity ultimately depended on the degree of crosslinking and the swelling of the beads. The prepared beads (Type IV) showed substantial variations in their S values (9.65%) in DMF, as shown in Table I. The beads prepared with 0.8 mmol of DVB (type I) showed the highest S value (16.2%) in DMF in comparison with the beads prepared with large amounts of DVB (>0.8 mmol) in the reaction mixture, but the catalytic activity of the beads prepared with 0.8

mmol of DVB was the lowest because of the lower amount of polymer-anchored cobalt(II) ions. The beads (types I–III) prepared with low amounts of DVB (<1.75 mmol) had a different network structure (structure II in Scheme 1) and composition than the beads (types IV and V) prepared with large amounts of DVB (≥ 1.75 mmol). The structure of the beads with large amounts of DVB (≥ 1.75 mmol) was different (structure III in Scheme 1). At low concentrations of DVB (<1.75 mmol), the crosslinked density was low, and the Schiff base (acen) was anchored by its reaction with two adjacent allylic chlorides on the same polymer chain (structure II in Scheme 1). The anchoring of the Schiff base (acen) in this fashion was due to a sufficient number of allylic repeat units between the crosslinks formed by DVB, but the overall amount of the Schiff base (1.85 mmol g^{-1} of beads) and the efficiency of the cobalt(II) ion loading (23.0%) were low (Table II). These beads (types I–III) with network structure II (Scheme 1) had high porosities ranging from 0.62 to 0.48 $\text{cm}^3 \text{g}^{-1}$ (Table III) and high S values ranging from 16.2 to 11.40% (Table I). The beads (type IV) with an optimum amount of DVB (1.75 mmol) had a sufficient amount of the Schiff base (2.90 mmol g^{-1} beads) because of the facile reaction of the Schiff base (acen) with allylic chloride of two adjacent polymer chains (structure III in Scheme 1). These beads had an optimum porosity (0.42 $\text{cm}^3 \text{g}^{-1}$) and optimum \bar{D} value (147 Å). The anchoring of the Schiff base (acen) in this fashion in these beads (type IV) was due to the lower number of allylic groups on the same chains between two crosslinks formed by DVB in the polymer networks. In these beads, (type IV; structure III in Scheme 1), the maximum amount of allyl chloride (96.70%) was consumed in the anchoring of the Schiff base (acen), unlike in beads with low amounts of DVB (type I), in which 50% of allyl chloride was consumed in the anchoring of the Schiff base (Table I). At further high concentrations of DVB (> 1.75 mmol), the crosslinked density in the beads was increased further, but the amount of allyl chloride decreased to 5.40 mmol g^{-1} of beads (Table I). The Schiff base anchoring capacity also decreased to 70.37% (Table II). The S value of these beads was reduced to the minimum (6.32%), as shown in Table I. The presence of excess crosslinks in the network structure reduced the EL (28.8%) and EC (76.0%) of cobalt(II) ions to a minimum, as clearly shown by the data in Table II. The beads (type V) prepared at a high concentration of DVB (2.0 mmol) showed a low porosity (0.21 $\text{cm}^3 \text{g}^{-1}$) and a low catalytic activity. The size of the beads decreased (111.5 μm) with an increasing degree of crosslinking, but their catalytic activity did not increase inversely to the size of the beads⁴⁰ because the amount of the Schiff base (acen)

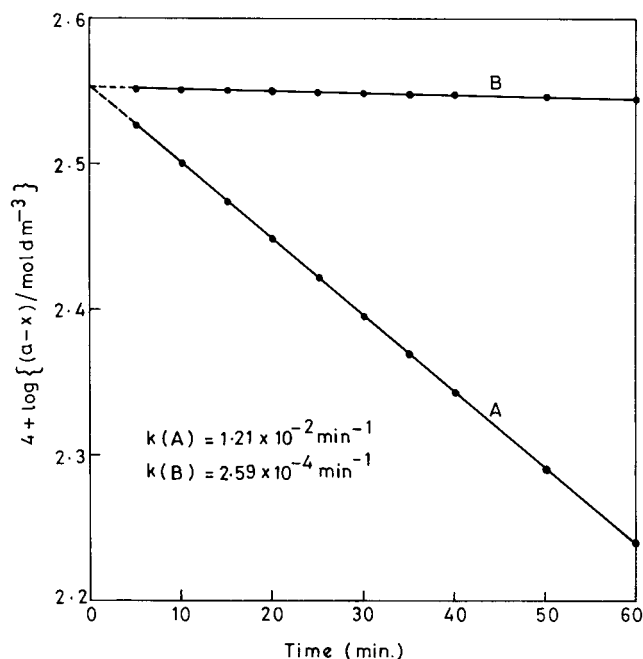


Figure 3 Effect of the reaction time on the decomposition of H_2O_2 with (A) supported and (B) unsupported cobalt(II) Schiff base complexes. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Co(II)}] = \text{(A)} 2.47 \times 10^{-3}$ or $\text{(B)} 3.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 7.5$; $\mu = 0.1 \text{ mol dm}^{-3}$; temperature = 25°C .

and cobalt(II) ions also decreased after the optimum degree of crosslinking. \bar{D} decreased to a minimum (27 Å) at a high concentration of DVB (Table II). These investigations clearly indicated that beads prepared with 1.75 mmol of DVB had optimum S , porosity, \bar{D} , and complexation values for cobalt(II) ions and were, therefore, suitable for evaluating the catalytic activity under different experimental conditions.

Evaluation of the catalytic activity of the polymer-supported Schiff base (acen) cobalt(II) complex

The catalytic activity of the polymer-supported and free Co(II)(acen)_2 complex was evaluated by the study of R_p of hydrogen peroxide under identical conditions. R_p of hydrogen peroxide was determined with different concentrations of hydrogen peroxide, with different catalysts, and at different reaction temperatures at a constant ionic strength (μ) and pH of the medium. To vary the amount of the supported catalyst, we took the beads of optimum loading capacity (bead type IV) to avoid structural effects of the beads on the catalytic behavior of the loaded cobalt(II) ions. The cobalt(II) ion supported beads were initially swelled for 24 h in DMF before being added to a reaction mixture for catalyzing the decomposition of hydrogen peroxide. The catalytic activity of polymer-supported cobalt(II) ions in the decomposition of hydrogen peroxide was studied as a function of the

concentration of hydrogen peroxide, the concentration of cobalt(II) ions, and the reaction temperature. The pH of the medium was maintained by hydrochloric acid and sodium hydroxide. μ of the medium was maintained by the addition of sodium perchlorate (0.1M) in the reaction mixture. The logarithmic value of the remaining concentration of hydrogen peroxide ($a-x$) as a function of the reaction time showed a linear decreasing trend [Fig. 3(A)] at $3.57 \times 10^{-2} \text{ mol dm}^{-3}$ hydrogen peroxide and $2.47 \times 10^{-3} \text{ mol dm}^{-3}$ polymer-supported cobalt(II) ions at 25°C . A similar trend was shown by homogenized cobalt(II) ions ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$) with $3.57 \times 10^{-2} \text{ mol dm}^{-3}$ hydrogen peroxide [Fig. 3(B)]. However, R_p of hydrogen peroxide was high in the presence of heterogenized cobalt(II) ions in comparison with homogenized cobalt(II) ions. The rate constant (k) for the decomposition of hydrogen peroxide in the presence of heterogenized cobalt(II) ions was high ($k = 1.21 \times 10^{-2} \text{ min}^{-1}$) in comparison with that in the presence of homogenized cobalt(II) ions ($k = 2.59 \times 10^{-4} \text{ min}^{-1}$; Fig. 3). The decomposition trend of hydrogen peroxide in both supported and free Co(II)(acen)_2 complexes was the same, and so it was clear that mechanism of decomposition was also the same in both cases. The turnover number for heterogenized cobalt(II) ions was very high ($17.54 \times 10^{19} \text{ molecules s}^{-1} \text{ mol}^{-1}$ of catalyst) in comparison with that of the homogenized catalyst ($30.92 \times 10^{17} \text{ molecules s}^{-1} \text{ mol}^{-1}$ of catalyst). To ascertain the kinetics of decomposition of hydrogen peroxide, we drew the logarithmic plots of R_p versus the concentration of hydrogen peroxide for both heterogenized [Fig. 4(A)] and homogenized cobalt(II) catalysts [Fig. 4(B)]. The slopes of these plots were almost

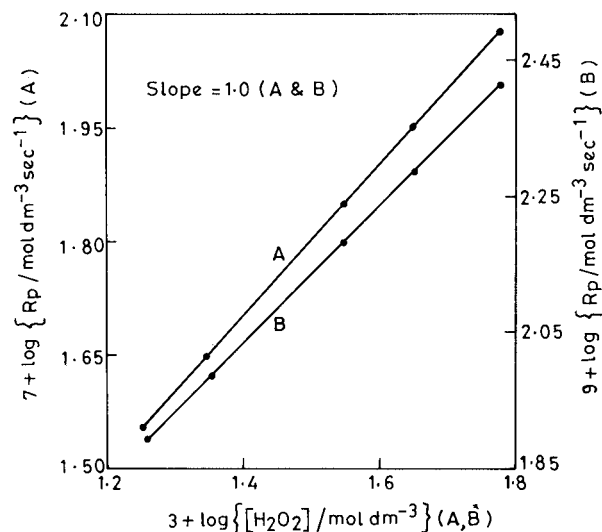


Figure 4 Log-log plot of R_p versus $[\text{H}_2\text{O}_2]$ for (A) supported and (B) unsupported cobalt(II) Schiff base complexes. $[\text{Co(II)}] = \text{(A)} 2.47 \times 10^{-3}$ or $\text{(B)} 3.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 7.5$; $\mu = 0.1 \text{ mol dm}^{-3}$; temperature = 25°C .

unity, indicating a first-order dependence of the reaction rate on the concentration of hydrogen peroxide. This was also an indication for a similar mechanism under both homogeneous and heterogeneous conditions. The high R_p under heterogenized conditions was attributed to substantial interactions between cobalt(II) ions and reactants in comparison with the homogenized catalyst. R_p at different concentrations of cobalt(II) ions at a fixed concentration of hydrogen peroxide ($3.57 \times 10^{-2} \text{ mol dm}^{-3}$) in both supported and free cobalt(II) ions showed a linear dependence on the concentration of cobalt(II) ions (Fig. 5). The concentration of polymer-supported cobalt(II) ions varied from 1.15×10^{-3} to $2.47 \times 10^{-3} \text{ mol dm}^{-3}$ with beads of similar loading capacities (type IV). The unit slope of the log-log plot between R_p and the cobalt(II) ion concentration suggested a first-order dependence of the reaction rate on the concentration of cobalt(II) ions in both cases (Fig. 5). R_p of hydrogen peroxide was also studied with beads of different loading capacities for cobalt(II) ions, which showed a variation in R_p of hydrogen peroxide due to variations in the cobalt(II) ion loading and differences in the bead structures. The effect of the bead structure on the catalytic activity was compared by the estimation of k for the decomposition of hydrogen peroxide, as given in Table III. k was highest with beads (type IV) having optimum porosity, D , and S values. The effect of the temperature on the decomposition of hydrogen peroxide with supported and free cobalt(II) complexes was investi-

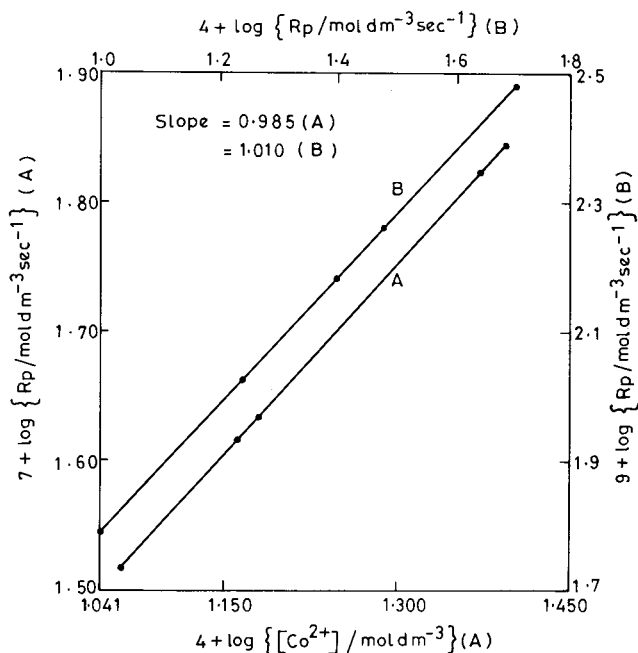


Figure 5 Log-log plot of R_p versus $[\text{Co(II)}]$ for (A) supported and (B) unsupported cobalt(II) Schiff base complexes. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{pH} = 7.5$, $\mu = 0.1 \text{ mol dm}^{-3}$; temperature = 25°C .

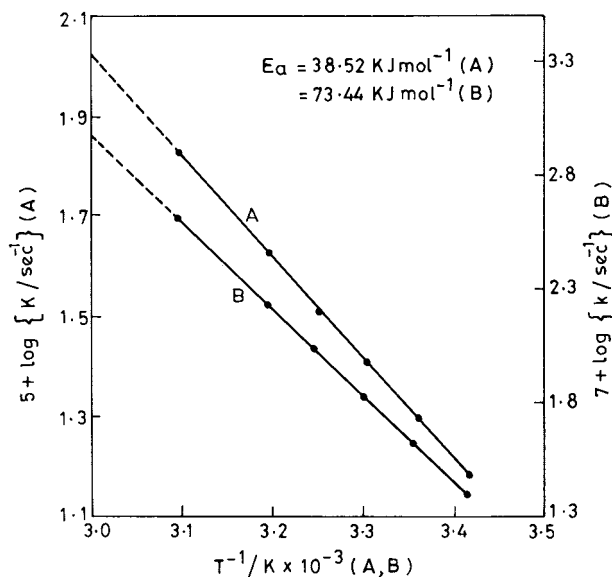


Figure 6 Arrhenius plot for the energy of decomposition of H_2O_2 for (A) supported and (B) unsupported cobalt(II) Schiff base complexes. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Co(II)}] = (\text{A}) 2.47 \times 10^{-3}$ or (B) $3.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 7.5$; $\mu = 0.1 \text{ mol dm}^{-3}$.

gated by the study of R_p of hydrogen peroxide at different temperatures ranging from 25 to 50°C , and the energy of activation was calculated [Fig. 6(A,B)]. During temperature variations, the concentration of hydrogen peroxide ($3.57 \times 10^{-2} \text{ mol dm}^{-3}$) and cobalt(II) ions on supported ($2.47 \times 10^{-3} \text{ mol dm}^{-3}$) and unsupported ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$) complexes was also kept constant. The energy of activation for the decomposition of hydrogen peroxide in heterogenized cobalt(II) ions was low ($38.52 \text{ kJ mol}^{-1}$) in comparison with that for homogenized cobalt(II) ions ($73.44 \text{ kJ mol}^{-1}$) within temperature variation from 25 to 50°C . This clearly indicated that the activity of cobalt(II) ions on the polymer support increased and contributed significantly in reducing the energy of activation of decomposition because of the facile orientation of reacting molecules on the polymer support during their transformation. The catalyst under homogeneous conditions was not able to provide suitable interactions with reactants, and so sufficient energy was needed to decompose hydrogen peroxide. R_p of hydrogen peroxide depended on μ and pH of the medium. The variation of R_p of hydrogen peroxide with μ varying from 0.1 to 0.5 mol dm^{-3} was an indication of the formation of ionic species in one or more reaction steps during the decomposition of hydrogen peroxide. R_p of hydrogen peroxide also showed significant variations with an increasing concentration of the hydrogen ions (Fig. 7). R_p of hydrogen peroxide was higher at high pH s (>7.5) of the medium.

The trends and orders of the reaction rate in both heterogenized and homogenized states of cobalt(II)

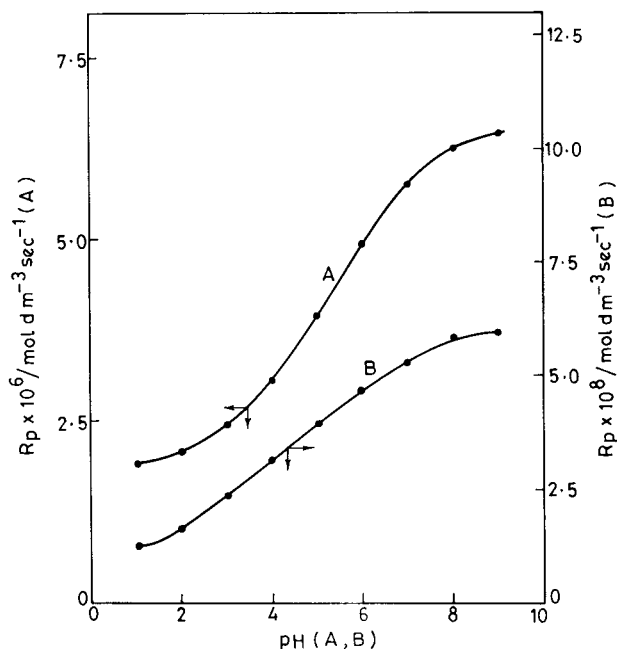
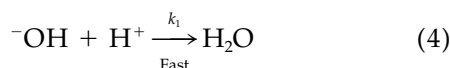
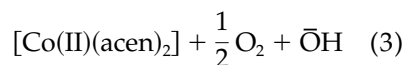
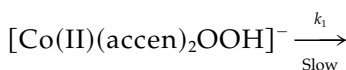
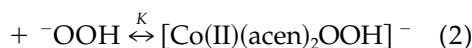


Figure 7 Effect of pH on R_p of H_2O_2 for (A) supported and (B) unsupported cobalt(II) Schiff base complexes. $[H_2O_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$; $[Co(II)] = (A) 2.47 \times 10^{-3}$ or (B) $3.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 0.1 \text{ mol dm}^{-3}$; temperature = 25°C .

ions were found to be the same, and so the mechanism and reactions steps for the decomposition of hydrogen peroxide under homogenized and heterogenized conditions were assumed to be the same:



$[Co(II)(acen)_2]$



On the basis of reaction steps 1–4, the rate expression for the decomposition of hydrogen peroxide was derived as follows:

$$\frac{-d[H_2O_2]}{dt} = \frac{k_d K k_1 [Co(II)(acen)_2] [H_2O_2]}{[H^+]} \quad (5)$$

where k_d and k_1 are the rate constants for the dissociation of hydrogen peroxide and the intermediate com-

plex formed in step 2. K is the equilibrium constant for the intermediate complex formed between HOO^- ions and the $Co(II)(acen)_2$ complex.

The derived rate expression agreed with the dependence of the reaction rate on the concentration of hydrogen peroxide, the cobalt(II) complex, and the hydrogen ion concentration in the reaction mixture and so provided strong support for proposed steps 1–4 for the decomposition of hydrogen peroxide in the presence of the cobalt(II) catalyst prepared with the new polymer-anchored Schiff base.

CONCLUSIONS

The polymer-supported Schiff base (p-acen) showed a strong affinity to complex with cobalt(II) ions, similarly to the free Schiff base. The polymer-supported $Co(II)(acen)_2$ complex so obtained was characterized for its structure by IR, UV, and magnetic measurements, which suggested a square planar geometry similar to that observed with the homogenized $Co(II)(acen)_2$ complex. The EC and EL for cobalt(II) ions by the polymer-anchored Schiff base (p-acen) depended on the degree of crosslinking in the polymer network. The bead size, ρ , S , porosity, S_{BET} , and \bar{D} values also depended on the degree of crosslinking. The catalytic activity of the polymer-supported $Co(II)(acen)_2$ complex was evaluated by the study of R_p of hydrogen peroxide and compared with that of the homogenized $Co(II)(acen)_2$ complex. This clearly indicated a significant increase in the catalytic activity of the cobalt(II) complex with the anchoring of the polymer support. The kinetic parameters suggested similar mechanisms for the decomposition of hydrogen peroxide under homogenized and heterogenized conditions for the cobalt(II) complex.

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