

# Synthesis of $\beta$ -amino alcohols catalyzed by poly(vinyl chloride)-supported Schiff base metal complexes

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**Abstract** Eight transition metal complexes of various Schiff bases supported on poly(vinyl chloride) (PVC) were prepared and characterized. These metal complexes were screened as heterogeneous catalysts in the synthesis of  $\beta$ -amino alcohols by ring opening of epoxides with amines. The best catalyst was identified as a Ni(II) complex of PVC-supported 2-[(2-aminoethylimino)methyl]phenol and it was used in the synthesis of a number of different  $\beta$ -amino alcohols. The catalyst was found to be reusable for up to five cycles.

**Keywords** Amines · Epoxides · Catalyst · Schiff bases · Polymer

## Introduction

$\beta$ -Amino alcohols are an important class of molecules in chemistry and biology because of their versatile properties and applications. These molecules constitute the backbones of a number of pharmaceutical entities, natural products, and ligands [1–9]. One of the most important synthetic procedures used to produce  $\beta$ -amino alcohols is the catalyzed ring opening of epoxides by primary amines. This procedure has found widespread application because of the simplicity of the procedure and the availability of a large number of substrates and catalysts that can be used in this reaction [10–25].

Here we describe the synthesis of some novel polymer-supported catalysts for ring opening of epoxides under mild conditions. The development of polymer-immobilized ligands and catalysts is a rapidly growing field, which has great importance in conventional and combinatorial organic synthesis mainly because of the easy separation and reusability of polymer-supported catalysts. The polymeric catalysts also represent one of the most powerful tools for ‘green’ sustainable chemistry, in the sense that they can be easily recovered and reused many times. Polymer-supported catalysts have many advantages over conventional homogeneous catalysts: (a) the ease of separation of the supported species from a reaction mixture by filtration and washing; (b) reuse of a catalyst after regeneration; (c) their adaptability to continuous flow processes and hence use in automated synthesis; (d) the reduced toxicity and odor of supported species compared with low molecular weight species; (e) chemical differences, such as prolonged activity or altered selectivity, of a catalyst in supported form compared with its soluble analogue [26–30].

But the problems associated with many of the commercially available polymer supports and polymer-supported catalysts are their high cost and low loading. These two drawbacks prevent their widespread use in industrial processes. In this article we describe the development of a high-loading polymer-supported catalyst from one of the cheapest polymers available, i.e., poly(vinyl chloride) (PVC). PVC is the most important of the vinyl thermoplastics considering the volume of production and field of applications [31]. Applications of PVC range from building materials to healthcare products [32, 33]. But examples showing the use of PVC as a support for catalysts in the literature are rare [34–36]. The catalyst developed here allows the reaction to be carried out under mild conditions and the catalyst is reusable.

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## Results and discussion

### Synthesis of the polymer-supported catalyst

The synthesis of the catalyst involves three steps. In the first step, PVC (**1**) was functionalized by replacing the labile chlorine atoms with ethylene diamine (**2**) to give a polymer carrying primary amino groups **3**. This reaction was performed with PVC and an excess amount of ethylene diamine. This excess can prevent the formation of cross-linking between different polymer chains as well as the formation of cyclic derivatives by condensation of the two primary amino groups of a single ethylene diamine molecule with neighboring chlorine atoms. The reaction was performed at room temperature to avoid any cross-linking as it was reported that cross-linking does occur when PVC was treated with ethylene diamine at elevated temperature for prolonged time [37]. After the reaction, the color of the polymer had changed from white to light yellow. The reaction is shown in Scheme 1.

The infrared spectrum of **3** had peaks at 3,350, 3,310, and 1,590  $\text{cm}^{-1}$  assigned to the stretching and bending vibrations of the primary amino groups. CHN analysis and estimation of the primary amino groups [38] showed that the polymer **3** contained 11 mmol of  $\text{NH}_2$  groups per gram of resin.

Polymer **3** was used as the amine component in the preparation of the Schiff base. Thus, **3** was allowed to react with salicylaldehyde (**4a**), vanillin (**4b**), veratraldehyde (**4c**), and camphor (**4d**) to give polymer-supported Schiff bases **5a–5d** as shown in Scheme 2.

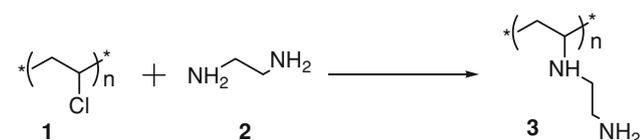
Infrared spectra of **5a–5d** showed that the bands due to the primary amino groups disappeared completely in all cases and new bands due to  $\text{C}=\text{N}$  stretching appeared at 1,682, 1,663, 1,631, and 1,617  $\text{cm}^{-1}$ , respectively. In the case of **5a** and **5b** broad peaks appeared at around 3,500  $\text{cm}^{-1}$  due to the  $-\text{OH}$  stretching vibrations.

Four complexes of  $\text{Cu}(\text{II})$  (**6a–6d**) and four complexes of  $\text{Ni}(\text{II})$  (**7a–7d**) were prepared using **5a–5d** as ligands. Detailed characterization of two representative complexes is given below.

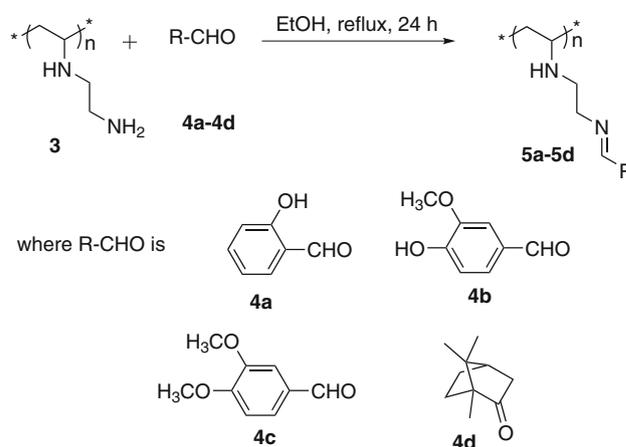
Comparison of the infrared spectra of **5a** and **6a** showed that the peaks due to the hydroxyl group disappeared and the peak due to  $\text{C}=\text{N}$  stretching at 1,680  $\text{cm}^{-1}$  shifted to 1,642  $\text{cm}^{-1}$  in the case of the

complex. In addition, a band due to the  $\text{Cu}-\text{N}$  bond appeared in the IR spectrum at 635  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra also showed the disappearance of  $-\text{OH}$  groups. Electronic spectra of the complex showed two bands at 422 and 543 nm and they are assigned to charge-transfer transitions and  $d-d$  transitions. Thermal analysis of the complex showed that the complex remained thermally stable up to 160  $^\circ\text{C}$  and first decomposition occurred between 160 and 175  $^\circ\text{C}$ . The thermal stability of the catalyst around 100  $^\circ\text{C}$  clearly indicates that there are no water molecules associated with the complex. From these analytical data, the structure of the complex is assigned to be square-planar as shown in Scheme 3. Square-planar complexes of copper(II) with similar ligands were reported previously [39–41].

Similarly on comparing the infrared spectra of **5a** and **7a**, it was observed that the band due to  $\text{C}=\text{N}$  stretching shifted to a lower frequency region as a result of complex formation and occupied a new position at 1,650  $\text{cm}^{-1}$ . There were no bands around 3,500  $\text{cm}^{-1}$  proving that there were no water molecules associated with this complex. The electronic spectrum of complex **7a** showed three distinct peaks at 262, 326, and 416 nm that could correspond to ligand-centered bands as well as electronic transitions involving metal/ligand exchange [42]. The  $^1\text{H}$  NMR spectrum of the complex also showed that there are no phenolic protons in this complex. Thermal analysis of the complex showed that the complex was stable up to 200  $^\circ\text{C}$  and this again proved the absence of coordinated water molecules. The first weight loss occurred between 200 and 300  $^\circ\text{C}$  followed by a second weight loss between 350 and 450  $^\circ\text{C}$  leaving a residue of 15% of initial weight of the sample. All these observations lead to the fact that the structure of the complex can be represented as in Scheme 4.

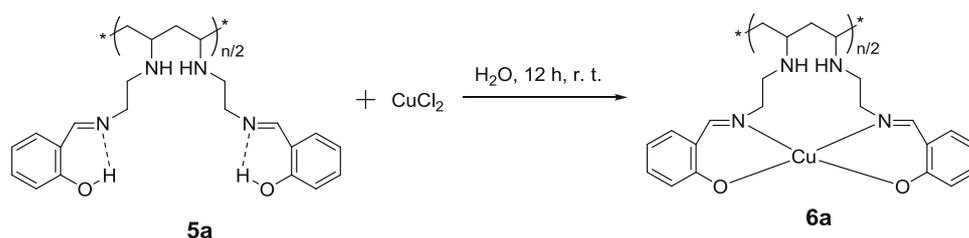


Scheme 1

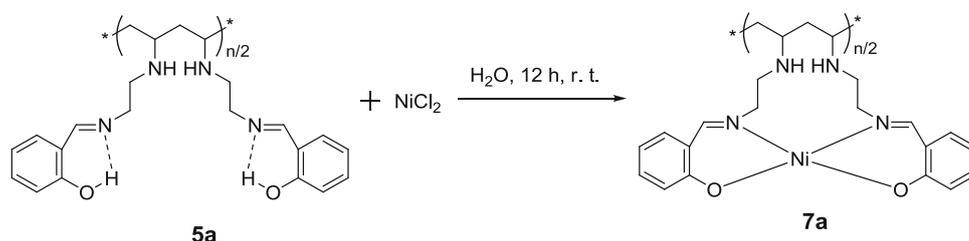


Scheme 2

Scheme 3



Scheme 4



### Synthesis of $\beta$ -amino alcohols catalyzed by polymer-supported nickel complexes

The polymer-supported metal complexes prepared were used as heterogeneous catalysts in the synthesis of  $\beta$ -amino alcohols **10** by nucleophilic ring opening of epoxides **8** by amines **9**. Initially, all eight complexes were screened in the ring opening of cyclohexene oxide by aniline under similar conditions. 1,4-Dioxane was selected as the solvent, because the complexes prepared were practically insoluble in dioxane and it allowed one to exploit the main advantage of heterogeneous catalysis, i.e., easy separation of the catalyst. Additionally, being a non-nucleophilic polar solvent, 1,4-dioxane does not compete with the reactant nucleophiles. After a fixed time, the percentage of formation of the product,  $\beta$ -(phenylamino)cyclohexanol, was determined using GC/MS. The results are summarized in Table 1.

As seen in Table 1, complex **7a** is the best catalyst among the eight screened. The percentage conversion given by the other complexes was poor in comparison. The

**Table 1** Reaction of cyclohexene oxide and aniline in the presence of different catalysts

Entry	Schiff base	Metal ion	Catalyst	Time/h	Yield/% <sup>a,b</sup>
1	Salicylaldehyde	Cu(II)	<b>6a</b>	6	70
2	Vanillin	Cu(II)	<b>6b</b>	6	63
3	Veratraldehyde	Cu(II)	<b>6c</b>	6	35
4	D-(+)-Camphor	Cu(II)	<b>6d</b>	12	–
5	Salicylaldehyde	Ni(II)	<b>7a</b>	6	94
6	Vanilin	Ni(II)	<b>7b</b>	6	85
7	Veratraldehyde	Ni(II)	<b>7c</b>	6	60
8	D-(+)-Camphor	Ni(II)	<b>7d</b>	12	–

<sup>a</sup> Reaction conditions: 5 mmol cyclohexene oxide, 5.1 mmol aniline, 0.25 mmol catalyst, 10 cm<sup>3</sup> 1,4-dioxane, 50 °C

<sup>b</sup> Yield by GC/MS

aim of the synthesis of the metal complexes based on D-camphor was to develop a chiral catalyst for the synthesis of 2-amino alcohols. But this catalyst failed miserably under the present reaction conditions.

After identifying **7a** as the most efficient catalyst, the conditions were optimized to exploit its maximum activity. Initially, the influence of catalyst concentration on the reaction was studied in detail. For this, the model reaction between cyclohexene oxide and aniline in 1,4-dioxane was carried out in the presence of various amounts of the catalyst under similar conditions. The results are summarized in Table 2. The reaction proceeded smoothly in the presence of 5 mol% of **7a** within a short period of time.

The temperature of the reaction has a significant effect on catalysis in the case of ring-opening reactions [25]. The reaction went to completion slowly at room temperature. But increasing the temperature to 50 °C had a remarkable impact on the speed of the reaction and the yield of the product was increased.

After optimizing the reaction conditions, a number of  $\beta$ -amino alcohols were prepared in the presence of the

**Table 2** Influence of the amount of catalyst on the ring-opening reaction

Entry	Amount of catalyst/mol%	Yield/% <sup>a,b,c</sup>
1	0	0
2	1	0
3	2	25
4	3	40
5	4	82
6	5	94
7	10	95

<sup>a</sup> Reaction conditions: 5 mmol cyclohexene oxide, 5.1 mmol aniline, 10 cm<sup>3</sup> 1,4-dioxane, 50 °C, 6 h

<sup>b</sup> Yield by GC/MS

<sup>c</sup> The catalyst is heterogeneous

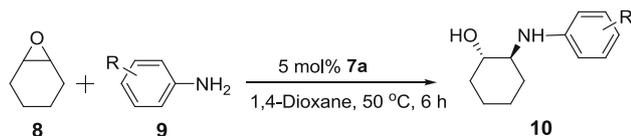
polymer-supported salicylaldehyde Schiff base–Ni(II) complex **7a**. The general reaction is shown in Scheme 5. In general, the reaction proceeded smoothly for all the substrates and the electronic effects of substituents have little or no influence on the reaction (Table 3). All  $\beta$ -amino alcohols were isolated in good to excellent yield within a short period of time. The *trans* configuration of the products in the case of cyclohexane derivatives was confirmed from the determination of the  $J_{\text{H-H}}$  coupling constants for CH–NH in the corresponding  $^1\text{H}$  NMR spectrum.

### Recycling of the catalyst

The possibility of reusing the catalyst was examined. The catalyst used in each run was washed well with copious amounts of water and methanol, dried, and reused in the subsequent runs. As seen in Table 4 the catalyst could be reused at least four times, without considerable loss of activity.

### Experimental

All solvents and salicylaldehyde were purified according to standard procedures. All other chemicals were used as received. PVC (high molecular weight,  $K$  value 69–71)



**Scheme 5**

**Table 3** Ring-opening reactions of epoxides with various amines

Entry	Epoxide	Amine	Time/h	Yield/% <sup>a,b,c</sup>
1	Cyclohexene oxide	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	6	93
2	Cyclohexene oxide	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	6	91
3	Cyclohexene oxide	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	6	91
4	Styrene oxide	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	8	88
5	Styrene oxide	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	85
6	Styrene oxide	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	82
7	2-Butene oxide	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	8	82
8	2-Butene oxide	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	83
9	2-Butene oxide	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	80
10	Epichlorohydrin	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	7	82
11	Epichlorohydrin	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	80
12	Epichlorohydrin	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	80

<sup>a</sup> Reaction conditions: 5 mmol epoxide, 5.1 mmol aniline, 0.25 mmol catalyst **7a**, 10 cm<sup>3</sup> 1,4-dioxane, 50 °C

<sup>b</sup> Isolated yield

<sup>c</sup> The catalyst is heterogeneous

**Table 4** Influence of recycling on catalyst's activity

Entry	No. of recycling steps	Yield/% <sup>a,b,c</sup>
1	1	93
2	2	93
3	3	93
4	4	92
5	5	89

<sup>a</sup> Reaction conditions: 5 mmol cyclohexene oxide, 5.2 mmol aniline, 0.25 mmol catalyst **7a**, 10 cm<sup>3</sup> 1,4-dioxane, 50 °C, 6 h

<sup>b</sup> Isolated yield

<sup>c</sup> The catalyst is heterogeneous

purchased from Fluka was used as received. Column chromatography was carried out on silica gel. Thin-layer chromatography (TLC) was done on silica-coated alumina plates (Merck, 60 F<sub>254</sub>). UV–Vis spectra were recorded on a Labomed Inc. Spectra 3500 D model UV–Vis spectrometer equipped with a solid-state accessory using MgSO<sub>4</sub> as standard. FTIR spectra were recorded on a Jasco model 4100 FTIR spectrometer from KBr pellets. Gas chromatography/mass spectrometry (GC/MS) was done on a Varian 1,200 L single quadrupole GC/MS with capillary column.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 300 or 400 MHz instruments with TMS as internal standard in CDCl<sub>3</sub> (from NMR Research Centre, IISc, Bangalore). The complexes were partially soluble in CDCl<sub>3</sub> and so it was possible to obtain their spectra in solution state. Thermogravimetric/differential thermogravimetric analysis (TG/DTA) was done on a Perkin-Elmer Diamond model TG/DTA system using platinum as the standard. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was recorded on a Thermo Electron IRIS Intrepid II XSP DUO model spectrometer (STIC, CUSAT, Cochin).

### Synthesis of amino-functionalized polymer **3**

PVC (2 g, 31 mmol Cl) was suspended in 10.7 cm<sup>3</sup> ethylene diamine (159.8 mmol) in a 50-cm<sup>3</sup> round-bottom flask. The reaction mixture was stirred at room temperature for 2 h. The light yellow colored polymer **3** was filtered, washed with water (20 cm<sup>3</sup> × 5) and water–methanol mixture (2:1 v/v, 20 cm<sup>3</sup> × 3), and dried under vacuum at room temperature. Yield 2.73 g; FTIR (KBr):  $\bar{\nu}$  = 3,350, 3,310 (NH<sub>2</sub> stretching), 2,900 (CH<sub>2</sub> stretching), 1,590 (N–H bending), 1,465 (CH<sub>2</sub> bending) cm<sup>-1</sup>.

### Preparation of polymer-supported Schiff bases **5a–5d**

Polymer **3** (2 g, 22 mmol NH<sub>2</sub> groups) was suspended in 20 cm<sup>3</sup> absolute ethanol in a 100-cm<sup>3</sup> round-bottom flask. The carbonyl compound (25 mmol) was added to it. The

reaction mixture was refluxed with stirring for 24 h. The polymer was filtered and washed with hexane ( $5 \text{ cm}^3 \times 5$ ), water–methanol (2:1 v/v,  $20 \text{ cm}^3 \times 3$ ), and water ( $20 \text{ cm}^3 \times 5$ ). The yellow solid was dried under vacuum at room temperature.

*PVC-supported 2-[(2-aminoethylimino)methyl]phenol (5a)*

FTIR (KBr):  $\bar{\nu} = 3,600$  (O–H), 3,064 (aromatic), 2,900 ( $\text{CH}_2$ ), 1,682 (C=N), 1,463 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 8.0$  (s, CH=N), 6.73–7.42 (m, aromatic), 5.5 (s, OH), 3.59 (t,  $\text{CH}_2$ ,  $\text{CH}_2\text{-N=CH}$ ), 3.00 (m,  $\text{CH}_2$ ,  $\text{CH}_2\text{-NH}$ ), 2.86–2.56 (m, CH, polymer), 2.02 (br, NH), 1.76–1.27 (m,  $\text{CH}_2$ , polymer chain) ppm;  $^{13}\text{C NMR}$ :  $\delta = 161.1, 132.5, 130.5, 124.5, 121.1, 115.7$  (aromatic), 160.8 (C=N), 55.4, 48.0 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 49.0, 35.8, 29.5, 24.9, 14.0 (polymer chain) ppm.

*PVC-supported 4-[(2-aminoethylimino)methyl]-2-methoxyphenol (5b)*

FTIR (KBr):  $\bar{\nu} = 3,600$  (O–H), 3,060 (aromatic), 2,910 ( $\text{CH}_2$ ), 1,663 (C=N), 1,460 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 8.1$  (s, CH=N), 6.62–7.00 (m, aromatic), 5.1 (s, OH), 3.9 (s,  $\text{OCH}_3$ ), 3.60 (t,  $\text{CH}_2$ ,  $\text{CH}_2\text{-N=CH}$ ), 3.01 (m,  $\text{CH}_2$ ,  $\text{CH}_2\text{-NH}$ ), 2.84–2.52 (m, CH, polymer), 2.00 (br, NH), 1.79–1.29 (m,  $\text{CH}_2$ , polymer chain) ppm;  $^{13}\text{C NMR}$ :  $\delta = 151.1, 148.0, 133.4, 122.8, 117.0$  (aromatic), 160.1 (C=N), 55.4, 48.3 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 56.0 ( $\text{OCH}_3$ ), 49.0, 35.4, 29.1, 24.3, 14.0 (polymer chain) ppm.

*PVC-supported  $N^1$ -(3,4-dimethoxybenzylidene)ethane-1,2-diamine (5c)*

FTIR (KBr):  $\bar{\nu} = 3,065$  (aromatic), 2,920 ( $\text{CH}_2$ ), 1,631 (C=N), 1,467 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 8.21$  (s, CH=N), 6.69–7.10 (m, aromatic), 3.73 (s,  $\text{OCH}_3$ ), 3.67 (t,  $\text{CH}_2$ ,  $\text{CH}_2\text{-N=CH}$ ), 3.00 (m,  $\text{CH}_2$ ,  $\text{CH}_2\text{-NH}$ ), 2.87–2.55 (m, CH, polymer), 2.10 (br, NH), 1.75–1.23 (m,  $\text{CH}_2$ , polymer chain) ppm;  $^{13}\text{C NMR}$ :  $\delta = 152.1, 149.9, 133.2, 122.5, 115.4$  (aromatic), 161.0 (C=N), 55.9, 48.9 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 56.4 ( $\text{OCH}_3$ ), 50.0, 35.8, 29.6, 22.9, 14.0 (polymer chain) ppm.

*PVC-supported  $N^1$ -methyl- $N^2$ -(1,7,7-trimethylbicyclo-[2.2.1]heptan-2-ylidene)ethane-1,2-diamine (5d)*

FTIR (KBr):  $\bar{\nu} = 1,617$  (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 2.87$ –2.60 (m, CH, polymer and camphor unit), 2.00 (br, NH), 1.99–1.10 (m,  $\text{CH}_2$ , polymer chain and camphor unit) ppm;  $^{13}\text{C NMR}$ :  $\delta = 174.1$  (C=N), 50.3, 48.9 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 50.0, 38.7, 35.4, 29.1, 24.3, 20.0, 14.0 (polymer chain and camphor) ppm.

*General procedure for the synthesis of metal complex of polymer-supported Schiff bases*

In a  $50\text{-cm}^3$  round-bottom flask 2 g of the polymer supported Schiff base (10 mmol), the metal salt ( $\text{NiCl}_2$  or

$\text{CuCl}_2$ , 5 mmol), and  $20 \text{ cm}^3$  water were mixed and the reaction mixture was stirred at room temperature for 24 h. The polymer was filtered, washed with water ( $20 \text{ cm}^3 \times 5$ ), water–methanol mixture (2:1 v/v,  $20 \text{ cm}^3 \times 3$ ), and methanol ( $20 \text{ cm}^3 \times 2$ ), and dried under vacuum at room temperature. Characterization data for Cu(II) complex **6a** and Ni(II) complex **7a** are given below. As the complexes with other polymer-supported Schiff bases showed inferior catalytic performance, they were not fully characterized.

*Cu(II) complex of PVC-supported 2-[(2-aminoethylimino)methyl]phenol (6a)*

FTIR (KBr):  $\bar{\nu} = 3,064$  (aromatic), 2,900 ( $\text{CH}_2$ ), 1,642 (C=N), 1,462 ( $\text{CH}_2$ ), 635 (Cu–N)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 8.0$  (s, CH=N), 6.73–7.42 (m, aromatic), 3.59 (t,  $\text{CH}_2$ ,  $\text{CH}_2\text{-N=CH}$ ), 3.00 (m,  $\text{CH}_2$ ,  $\text{CH}_2\text{-NH}$ ), 2.86–2.56 (m, CH, polymer), 2.02 (br, NH), 1.76–1.27 (m,  $\text{CH}_2$ , polymer chain) ppm;  $^{13}\text{C NMR}$ :  $\delta = 158.0, 133.0, 130.9, 124.8, 120.4, 115.9$  (aromatic), 163.0 (C=N), 49.0, 41.1 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 49.0, 35.4, 29.1, 24.0, 13.9 (polymer chain) ppm; UV–Vis (powder):  $\lambda_{\text{max}} = 422, 543 \text{ nm}$ . ICP–AES analysis of the complex showed that the loading of metal ion was 4.26 mmol/g polymer.

*Ni(II) complex of PVC-supported 2-[(2-aminoethylimino)methyl]phenol (7a)*

FTIR (KBr):  $\bar{\nu} = 3,400$  ( $\text{H}_2\text{O}$ ), 3,064 (aromatic), 2,900 ( $\text{CH}_2$ ), 1,650 (C=N), 1,462 ( $\text{CH}_2$ ), 540 (Ni–N)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta = 8.2$  (s, CH=N), 6.73–7.42 (m, aromatic), 3.59 (t,  $\text{CH}_2$ ,  $\text{CH}_2\text{-N=CH}$ ), 3.00 (m,  $\text{CH}_2$ ,  $\text{CH}_2\text{-NH}$ ), 2.86–2.56 (m, CH, polymer), 2.02 (br, NH), 1.76–1.27 (m,  $\text{CH}_2$ , polymer chain) ppm;  $^{13}\text{C NMR}$ :  $\delta = 157.3, 132.3, 130.1, 124.1, 120.4, 115.1$  (aromatic), 162.8 (C=N), 48.0, 40.0 ( $=\text{NCH}_2\text{CH}_2\text{NH}$ ), 49.5, 35.8, 29.5, 24.9, 14.0 (polymer chain) ppm; UV–Vis (powder):  $\lambda_{\text{max}} = 262, 326, 416 \text{ nm}$ . ICP–AES analysis of the complex showed that the loading of metal ion was 4.00 mmol/g polymer.

*General procedure for ring opening of epoxides*

In a round-bottom flask epoxide **8** (5 mmol) and amine **9** (5.1 mmol) were dissolved in  $10 \text{ cm}^3$  1,4-dioxane. Catalyst **7a** (62.5 mg, 5 mol% of Ni with respect to the epoxide) was added. The reaction mixture was stirred at  $50 \text{ }^\circ\text{C}$ . The progress of the reaction was monitored by TLC on silica-coated alumina plates with hexane–ethyl acetate (10:1) as eluent. After the completion of the reaction the catalyst was filtered and washed with methanol. The filtrate and washings were combined and evaporated. The final product **10** was isolated using column chromatography on a small silica column using hexane–ethyl acetate (10:1) as eluent. All products were previously reported [12–25] and were characterized by FTIR and  $^1\text{H NMR}$  spectroscopy.

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## References

1. Kokotou VC (2002) *Lett Pept Sci* 9:143
2. Shanks RG, Wood TM, Dornhost AC, Clark ML (1966) *Nature* 212:88
3. De Cree J, Geukens H, Leempoels J, Verhaegen H (1986) *Drug Dev Res* 8:109
4. Ager DJ, Prakash I, Schaad DR (1996) *Chem Rev* 96:835
5. Bergmeier SC (2000) *Tetrahedron* 56:2561
6. Fache F, Schulz E, Tommasino ML, Lemaire M (2000) *Chem Rev* 100:2159
7. Kobayashi J, Ishibashi M (1996) *Heterocycles* 42:943
8. Lee HS, Kang SH (2004) *Synlett* 15:1673
9. Meyers AI (2005) *J Org Chem* 70:6137
10. Hodgson DM, Gibbs AR, Lee GP (1996) *Tetrahedron* 52:14361
11. Pasor IM, Yus M (2005) *Curr Org Chem* 9:1
12. Fan RH, Hou XL (2003) *J Org Chem* 68:726
13. Azoulay S, Manabe K, Kobayashi S (2005) *Org Lett* 7:4593
14. Kleiner CM, Schreiner PR (2006) *Chem Commun* 4315
15. Shivani, Pujala B, Chakraborti AK (2007) *J Org Chem* 72:3713
16. Bhanushali MJ, Nandurkar NS, Bhor MD, Bhanage BM (2008) *Tetrahedron Lett* 49:3672
17. Reddy BM, Patil MK, Reddy BT, Park SE (2008) *Catal Commun* 9:950
18. Tabatabaeian K, Mamaghani M, Mahmoodi NO, Khorshidi A (2008) *Tetrahedron Lett* 49:1450
19. Bao W, Liu Y, Lv X, Qian W (2008) *Org Lett* 10:3899
20. Zhang C, Chen J, Yu X, Chen X, Wu H, Yu J (2008) *Synth Commun* 38:1875
21. Kureshy RI, Prathap KJ, Agrawal S, Khan NH, Abdi SHR, Jasra RV (2008) *Eur J Org Chem* 3118
22. Procopio A, Gaspari M, Nardi M, Oliverio M, Rosati O (2008) *Tetrahedron Lett* 49:2289
23. Ollevier T, Nadeau E (2008) *Tetrahedron Lett* 49:1546
24. Sarvari MH (2008) *Can J Chem* 86:65
25. Krishnan GR, Sreekumar K (2008) *Polymer* 49:5233
26. Frenzel T, Solodenko W, Kirschning A (2003) In: Buchmeiser MR (ed) *Polymeric materials in organic synthesis and catalysis*. Wiley-VCH, Weinheim, pp 201–240
27. Leadbeater NE, Marco M (2002) *Chem Rev* 102:3217
28. McNamara CA, Dixon MJ, Bradley M (2002) *Chem Rev* 102:3275
29. Bergbreiter DE (2002) *Chem Rev* 102:3345
30. Bergbreiter DE, Tian J, Hongfa C (2009) *Chem Rev* 109:530
31. Ghosh P (2001) *Polymer science and technology of plastics and rubbers*. Tata McGraw-Hill, New Delhi, p 267
32. Andrady AL (1999) *Polymer data handbook*. Oxford University Press, New York
33. Blass CR (2001) *The role of poly(vinyl chloride) in healthcare*. Rapra Technology, Shawbury
34. Dong F, Li YQ, Dai RF (2007) *Chin Chem Lett* 18:266
35. Wei R, Liang Y, Chen S, Jia C, Li F, Zhang T (2002) *J Appl Poly Sci* 84:1067
36. Gil-Llambías FJ, Gargallo L, Radic D, Román E (1983) *J Poly Sci Polym Lett Ed* 21:897
37. Balakrishnan B, Jayakrishnan A (2005) *Trends Biomater Artif Organs* 18:230
38. Krishnan GR, Sreekumar K (2008) *Eur J Org Chem* 4763
39. Chu Z, Ding LQ, Long Y, Chen LL, Lu XQ, Song JR, Fan DD, Bao F, Ma R (2010) *J Inorg Organomet Polym* 20:235
40. Karmakar R, Choudhary CR, Mitra S, Dahlenburg L (2005) *Struct Chem* 16:611
41. Yoshida N, Oshio H, Ito T (1998) *Chem Commun* 63
42. de Castro B, Ferreira R, Freire C, Garcia H, Palomares EJ, Sabater MJ (2002) *New J Chem* 26:405