Heavy metal ion uptake by homo and copolymers—A comparative study

K Hussain Reddy* & A Ravikumar Reddy
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, India

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Homo and copolymers of 2-hydroxy ethyl methacrylate and chloromethylated styrene-anthranilic acid have been prepared by free radical polymerization technique. The chelating polymers have been characterized by IR and solid state $^{13}$C NMR spectroscopic techniques. Thermal stabilities of these polymers are investigated using thermogravimetric and differential thermal analyses. Heavy metal ions viz., Pb(II), Hg(II), Cd(II) and Cr(VI) have been removed by employing the present chelating polymers. Metal ion uptake efficiency, effect of pH and time on the metal removal have also been studied. The metal removal properties are also tested under competitive conditions and found to depend strongly on pH. The polymers possess appreciable selectivity for Pb(II) and Hg(II) over Cd(II) and Cr(VI). The amount of metal uptake by the polymer has been determined using atomic absorption spectrophotometer. The polymers have been reused after desorbing the metal ion from the polymer metal complex by HCl.

In recent years, there has been growing attention to the removal of toxic materials from industrial waste waters, not only for pollution control but also to enable to reuse the water$^{1,2}$. Most of the waste water results from cooling, rinsing, finishing, tanning, plating operations in the industry and is contaminated with heavy metals$^3$. Heavy metals are not biodegradable, hence their concentration continuously increases in the environment. These metals besides being carcinogenic, pose serious threat to aquatic biota and environment.

Adsorption techniques employing activated carbon$^4$, starch xanthate$^5$, fly ash$^6$, serpentine minerals$^7$ have been used for the treatment of industrial waste water. Alkaline precipitation$^7$ and ion exchange$^8$ methods have also been used for the removal of toxic metals. Recently bioprecipitation of some toxic metal ions by sewage bacteria has been reported$^9$. However, conventional methods are generally non-selective and less efficient.

The use of complexing agents for the separation of metal ions are well established. An alternative mode of application of complex formation is however, the use of chelating resins in which various chelating groups have been incorporated and are attached to the resin matrix. Syntheses of chelating polymers have been accomplished using either polymerization or simple functionalization principles$^{10}$. The former involves the polymerization of monomers containing the desired ligands.

The functionalized polymers have been recently used$^{11,12}$ for the removal of heavy metal ions. In the light of the above, we report herein, the synthesis and characterization of the chelating homo and copolymers of 2-hydroxy ethyl methacrylate and chloromethylated styrene – anthranilic acid and their applications in the removal of heavy metal ions.

Materials and Methods

Chloromethylated styrene (Fluka) and 2-hydroxy ethylmethacrylate (Merck) were freed from inhibitor by washing with 5% NaOH solution. Anthranilic acid (Merck) was purified before use. The polymerizations were initiated with benzoyl peroxide (BPO, 97% active compound; BDH Chemicals Limited). Stock solutions of metal ions were prepared using AR grade lead nitrate, mercuric chloride, cadmium nitrate and dichromate salts.

Elemental analyses of the chelating polymers were carried out on an Hareaus Carlo Erba DP-200; CDRI, Lucknow. Fourier transform infrared (FTIR) spectra were recorded on a Brucker IFS 66 V model using potassium bromide pellets. Solid state $^{13}$C NMR spectra of the samples were recorded on a Brucker DEX 300 MHz instrument. NETZSCH-Geratebau-GmbH thermal analysing system(TAS) was used to evaluate the thermal stability, decomposition temperature and kinetic parameters of the polymers at a heating rate of 10°C min$^{-1}$. The metal removal was determined using a UNICAM UK Model 839 atomic absorption spectrophotometer.

Preparation of poly(2-hydroxy ethyl methacrylate) (PHEM)

2-hydroxy ethyl methacrylate(12 ml, 0.095 mol), methylethylketone (MEK) (30 ml) and benzoyl
peroxide (BPO) (0.2 g) were taken in a polymerization tube (100 ml) and deaerated by passing oxygen free nitrogen gas for half an hour. The reaction tube was closed and kept in a thermostat at 70 ± 1°C for 17 h. At the end, contents were added to large excess of methanol. The precipitated poly(2-hydroxy ethyl methacrylate) (PHEM) was filtered, washed with methanol and purified by dissolving in DMF and reprecipitating by the addition of excess methanol. The purified polymer was dried under reduced pressure at 60°C for constant weight.

Preparation of chloromethylated polystyrene-anthranilic acid (CMPS-AA)

Chloromethylated polystyrene (CMPS) was achieved by subjecting chloromethylated styrene to solution polymerization technique using free radical initiator (BPO). Chloromethylated styrene (7.25 g, 0.0475 mol), BPO (0.2 g) and EMK (30 ml) were taken into a polymerization tube and purged with nitrogen gas for 30 min. The reaction tube was closed, kept in a thermostat at 70 ± 1°C for 17 h. The contents were poured to excess methanol. The precipitated chloromethylated polystyrene was filtered, washed with methanol, purified by dissolving in DMF and reprecipitating by the addition of excess methanol. The CMPS was dried under reduced pressure at 60°C for constant weight. The CMPS obtained was used for the preparation of CMPS-AA. 1.0 g of CMPS was allowed to swell in DMF (15 ml) for 45 min. The anthranilic acid (0.0036 mol) was dissolved in hot DMF (30 ml) and was added to the polymer suspension. Ethylacetate (100 ml) and triethylamine (0.015 mol, 1.5 g) were added to the above mixture, while stirring magnetically. The reaction mixture was refluxed for 8 h. On cooling to room temperature, the resin was collected by filtration, washed several times with DMF, ethylacetate and absolute alcohol and dried in a vacuum desiccator.

Preparation of copoly(chloromethylated styrene-anthranilic acid-2-hydroxy ethyl methacrylate) P(CMS-AA-HEM)

The copoly(chloromethylated styrene-2-hydroxy ethyl methacrylate) P(CMS-HEM) was prepared by solution polymerization technique using free radical initiator (BPO). Chloromethylated styrene (7.25 g, 0.0475 mol), 2-hydroxy ethyl methacrylate (6 ml, 0.0475 mol) and BPO (0.2 g) were taken into a polymerization tube. The contents were dissolved in (40 ml) ethylmethylketone and purged with nitrogen gas for 30 min. The reaction tube was closed and kept in a thermostat at 70 ± 1°C for 17 h. At the end, contents were added to large excess of methanol. The precipitated copoly(chloromethylated styrene-2-hydroxy ethyl methacrylate) was filtered, washed with methanol purified by dissolving in DMF and reprecipitating by the addition of excess methanol. The purified polymer was washed with chloroform to remove the traces of CMPS and PHEM formed during the reaction and finally with methanol. The pure copolymer was dried under reduced pressure at 60°C for constant weight. The procedure involved in the preparation of P(CMS-AA-HEM) is similar to that of (CMPS-AA). 1.0 g of copoly(chloromethylated styrene-2-hydroxy ethyl methacrylate) was allowed to swell in DMF (15 ml) for 45 min. Anthranilic acid (0.0036 mol, 0.5 g) was dissolved in DMF (30 ml) and was added to the polymer suspension. Ethylacetate (100 ml) and triethylamine (0.015 mol, 1.5 g) were added to the above mixture, while stirring magnetically. The reaction mixture was refluxed for 8 h. The P(CMS-AA-HEM) obtained was filtered after cooling to room temperature, washed several times with DMF, ethylacetate and absolute alcohol and dried in a vacuum desiccator at room temperature.

Recommended procedure for the removal of metal ion at different pH values

A 2.5 ml of 1×10⁻² M metal ion (Pb(II), Hg(II), Cd(II) or Cr(VI)) solution, 7.5 ml of buffer (pH 2-10) solution and resin (0.2 g) were combined in a 100 ml beaker and maintained under stirring for 1 h. The metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively into a 25 ml standard flask and diluted to the mark. The amount of metal ion present in the filtrate was estimated using atomic absorption spectroscopy [Pb, 283.3; Cd, 228.8 and Cr, 357.9 nm] and Hg(II) was determined (470 nm) spectrophotometrically using 1,10-phenanthroline. The amount of metal ion was deduced from the predetermined calibration curve.

Recommended procedure for the removal of Hg(II) at different time intervals

A 2.5 ml of 1×10⁻² M Hg(II) solution, 7.5 ml of buffer (pH 10) solution and resin (0.2 g) were mixed in a 100 ml beaker, the mixture was maintained under stirring for different periods of time (15, 30, 45, 60 and 120 min). The metallated resin was filtered and washed thoroughly with distilled water. The filtrate
was collected quantitatively into a 25 ml standard flask and diluted to the mark. The amount of Hg(II) present in the filtrate was estimated using 1,10-phenanthroline spectrophotometrically. The amount of Hg(II) was estimated from the predetermined calibration plot.

**Recommended procedure to determine the metal ion selectivity on various chelating polymers**

An aliquot [containing 0.1 M Pb(II) (0.5 ml), Hg(II) (0.5 ml), Cd(II) (1 ml) and Cr(VI) (2 ml)] was taken in a 100 ml beaker containing 1 g of the resin and 7.5 ml of buffer (pH 10) solution. The mixture was maintained under stirring for 1 h. The metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively in 100 ml standard flask and diluted to volume. The amounts of metal ions were determined by AAS and spectrophotometric [for Hg(II)] methods.

**Results and Discussion**

2-Hydroxy ethyl methacrylate, chloromethylated styrene and anthranilic acid were used to get the homo and copolymers. The preparative scheme for the chelating polymers is given in Scheme I. The reactions were carried out in DMF, which causes considerable swelling of the polymer. The CMPS was colourless, however CMPS-AA and P(CMS-AA-HEM) are yellow and pale yellow in colour. The analytical data are given. PHEM: 80% yield, Anal. Found: C, 54.5%; H, 7.9%. Calcd: C, 55.3%; H, 7.89%. CMPS-AA: 70% yield. Anal. Found: C, 73.2%; H, 6.01%; N, 5.50%. Calcd: C, 75.8%; H, 5.92%; N, 5.53%. P(CMS-AA-HEM): 63% yield. Anal. Found: C, 63.9%; H, 7.4%; N, 3.01%. Calcd: C, 65.5%; H, 7.5%; N, 3.2%. The data suggest that yields of the resins are moderate to high. The analytical data are in agreement with the calculated values.

The chelating polymers are insoluble in organic solvents. The typical CP/MAS solid state $^{13}$C NMR spectrum was recorded. The backbone of methylene carbon appeared as a sharp peak at 48.33, 47.52 and 48.05 ppm respectively for PHEM, CMPS-AA and P(CMS-AA-HEM). 40.48 ppm peak was also observed in P(CMS-AA-HEM), it is due to the (-CH$_2$-) methylene group of HEM. Ester carbonyl carbon (C=O) appeared at 180.50, 170.72 and 179.28 ppm respectively for PHEM, CMPS-AA and P(CMS-AA-HEM). 164.31 peak observed in case of P(CMS-AA-HEM), this is due to the carbonyl carbon of HEM.

The lower value when compared to PHEM may be due to the presence of adjacent (CMS-AA) group. The assignment of the peaks are given in Table I.

Infrared spectra of the chelating polymers were recorded in the range 4000-500 cm$^{-1}$, using KBr discs. A comparison of IR spectra of CMPS to that of CMPS-AA and P(CMS-AA-HEM) shows the absence of $v$$_{C=O}$ (672 cm$^{-1}$) and the presence of C-O-C (~1095 cm$^{-1}$). IR: CMPS; v 2958 (C-H), 672 (C-Cl) cm$^{-1}$. PHEM; v 3600 (O-H), 2992 (C-H), 1740 (C=O), 1120 (C-O-C) cm$^{-1}$, CMPS-AA: v 3320 (N-H), 2902 (C-H), 1690 (C=O), 1085 (C-O-C) cm$^{-1}$. P(CMS-AA-HEM); v 3500 (O-H), 2520 (N-H), 2550 (C-H), 1730 (C=O), 1133 (C-O-C) cm$^{-1}$. The lower OH and NH stretching frequencies (~3300 cm$^{-1}$) were due to hydrogen bonding in polymeric association. Thus the above data support the formation of the chelating polymers.

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**Scheme I**

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Thermograms of the chelating polymers are shown in Fig. 1. A mathematical interpretation of thermogravimetric curves enables one to determine kinetic parameters of pyrolysis reactions. Horowitz and Metger have demonstrated the method of calculation of energy of activation of polymeric substances. The equation used for the calculation of energy of activation \( E \) was,

\[
\ln \left( \frac{W_o}{W_t} \right) = \frac{E\theta}{RT_s^2} \tag{1}
\]

where \( \theta = T - T_i \).

\( W_o \) is the initial weight, \( W_t \) is the weight at any time \( t \), \( T_i \) is the peak temperature and \( T \) is the temperature at particular weight loss. A plot of \( \ln \left( \frac{W_o}{W_t} \right) \) versus \( \theta \) gives an excellent approximation to a straight line. The slope is related to the activation energy, i.e.,

\[
\text{Slope} = \frac{E}{RT_s^2} \tag{2}
\]

Representative plots are shown in Fig. 2. The calculated values for the activation energy of decomposition are listed in Table 2. The activation energy associated with each stage of decomposition was also evaluated by the well known Broido method. The equation used for the calculation of activation energy \( E \) was,

\[
\ln \left( \frac{1}{Y''} \right) = \left( \frac{-E}{R} \right) \frac{1}{T} + \text{Constant} \tag{3}
\]

where \( Y'' = \frac{W_i - W_t}{W_o - W_i} \).

| Table 1 — Solid state \(^1^H\text{C}-\text{CP/MAS NMR spectral data of the chelating polymers} |
| \( \delta_{ppm} \) of | \( \delta_{ppm} \) of | \( \delta_{ppm} \) of | Assignment |
| PHEM | CMPS-AA | P(CMPS-AA-HEM) |
| 23.23 | 20.65 | | \( \delta_1 \) |
| 48.33 | 47.52 | 48.05 | H/C group present in the polymer backbone |
| 62.87 | 68.47 | 66.05 | Methylene (-CH₂-) backbone |
| 128.27 | 132.65 | | (C-) of the main chain and 68.47 is chain CH of the main chain |
| 180.50 | 170.72 | 179.28 | Ester carbonyl |
| 164.31 | |

Fig. 1 — Thermograms of the polymers PHEM (--), CMPS-AA (---) and P(CMPS-AA-HEM) (- - - -)
Table 2—Activation energy of decomposition for various chelating polymers by thermogravimetric analyses

<table>
<thead>
<tr>
<th>Polymer samples</th>
<th>Peak temperature (T, °C)</th>
<th>Decomposition temperature range (°C)</th>
<th>Weight loss (%)</th>
<th>Method</th>
<th>Activation energy (kJ mol⁻¹)</th>
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</thead>
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<tr>
<td>PHEM</td>
<td>244</td>
<td>200-380</td>
<td>76</td>
<td>HM</td>
<td>42.05</td>
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<tr>
<td></td>
<td>418</td>
<td>380-600</td>
<td>12</td>
<td>HM</td>
<td>65.32</td>
</tr>
<tr>
<td>CMPS-AA</td>
<td>180</td>
<td>115-335</td>
<td>21</td>
<td>HM</td>
<td>34.52</td>
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<tr>
<td></td>
<td>430</td>
<td>335-500</td>
<td>42</td>
<td>BR</td>
<td>39.55</td>
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<tr>
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<td>580</td>
<td>500-700</td>
<td>20</td>
<td>BR</td>
<td>50.64</td>
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<tr>
<td>P(CMS-AA-HEM)</td>
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<td>200-274</td>
<td>8</td>
<td>HM</td>
<td>45.2</td>
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<tr>
<td></td>
<td>343</td>
<td>274-400</td>
<td>32</td>
<td>BR</td>
<td>50.05</td>
</tr>
<tr>
<td></td>
<td>565</td>
<td>400-780</td>
<td>40</td>
<td>BR</td>
<td>78.60</td>
</tr>
</tbody>
</table>

HM  Horowitz & Metger 
BR  Broido

Fig. 4 — DTA plots of the polymers PHEM(---), CMPS-AA (---) and P(CMS-AA-HEM) (+++--+)

time 't', \( W_o \) the weight at infinite time (= zero); and \( W \), the initial weight. A plot of \( \ln \ln \left(1/Y''\right) \) versus \( 1/T \) gives an excellent approximation to a straight line over a range of 0.999 > \( Y'' \) > 0.001. The slope is related to the activation energy. Representative plots are shown in Fig. 3. The calculated values for the activation energy of decomposition are listed in Table 2.

The DTA plots of the polymers are given in Fig. 4. Kissinger\(^{18,19}\) method was used for the determination of activation energy. The equation used for the calculation of activation energy (\( E \)) was,

\[
\frac{d}{dT} \left( \ln \left( \frac{\phi}{T_m^2} \right) \right) = -\frac{E}{R}
\]

where \( \phi \), a constant rate of temperature rise, \( T_m \) the temperature at which the peak differential thermal analyses deflection occurs; and \( T \), the temperature.

The plot of \( \ln \left( \frac{\phi}{T_m^2} \right) \) against the reciprocal of the
absolute temperature \((1/T)\) gives the energy of activation \((E)\) of the decomposition using the equation,

\[
\text{Slope} = \frac{E}{R} \quad \ldots (5)
\]

Representative plots are shown in Fig. 5. The calculated values for the activation energy of decomposition are 9.21, 10.23 and 11.46 kJ mol\(^{-1}\) for PHEM, CMPS-AA and P(CMS-AA-HEM) respectively. It has been found that all the chelating polymers are stable and shows maximum peak differential thermal analyses deflection in the temperature range 350-580 °C.

**Removal of heavy metal ions**

**Effect of pH on the removal of metal ions**

The effect of pH on metal ion uptake was studied at different pH values by following the recommended procedure. The effect of pH on the removal of heavy metal ion by the present chelating polymers are given in Fig. 6. Uptake efficiencies of the polymers depended strongly on the pH. It increased from pH 2 to pH 10. As the pH increases, uptake of metal ion by polymer also increases. As the uptake of metal ions is maximum at pH 10, an NH\(_4\)Cl-NH\(_4\)OH buffer solution of this pH is selected for further studies. At higher pH values (∼10), the alcoholic OH [present in PHEM, P(CMS-AA-HEM)] is presumably deprotonated and binds with metal ions to give metal chelate. The time required for full metal ion uptake is found to be about 1h. Affinity order at pH 10 is Pb(II) > Hg(II) > Cd(II) > Cr(VI) for CMPS AA and P(CMS-AA-HEM) and Pb(II) > Hg(II) > Cd(II) > Cr(VI) for PHEM. At pH 6, Hg(II) > Pb(II) > Cd(II) > Cr(VI) for PHEM, Hg(II) > Cr(VI) > Pb(II) > Cd(II) for CMPS-AA and Hg(II) > Cr(VI) > Cd(II) > Pb(II) for P(CMS-AA-HEM). At pH 2 appreciable metal ion removal was not observed. Therefore, the present chelating polymers are Pb(II) selective at pH 10 and Hg(II) selective at pH 6. Thus, selectivity of chelating polymers depends on pH.

**Effect of time on the metal ion uptake**

The effect of time on metal ion uptake was studied at pH 10 by following the recommended procedure. It was found that 1h time was required for maximum and constant metal ion uptake. The data are presented in Fig. 7.

**Selectivity studies**

The selectivity studies were carried out by following the recommended procedure. In this case, 100 ppm of each metal ion in the solution was
allowed to react with the polymer at pH 10. The overall metal uptake capacity of the polymers at pH 10 under competitive conditions are in good agreement with the results obtained in the noncompetitive experiments. The chelating efficiencies of the present polymers increased from PHEM, CMPS-AA and P(CMS-AA-HEM). This is probably due to the increase in the stability of the complex in the above order. The selectivity order is P(CMS-AA-HEM) > CMPS-AA > PHEM and the data are presented in Fig. 8.

Effect of recyclability on the removal of metal ions

The most important advantage of chelating polymers is their reuse after a particular process. The desorbing the metal from metallated polymers using 6M HCl in tetrahydrofuran. The metal free polymers can be reused after neutralization. In acidic medium, the metallated chelating resins are protonated and releases the metal into the solution. The metal ion uptake was found to be almost same even after 4 cycles. For every cycle, the % metal ion desorption and uptake was estimated. The data are given in Table 3.

Conclusion

Heavy metal ions [viz., Pb(II), Hg(II) and Cd(II)] are known inorganic pollutants. The presence of these metal ions in aquatic systems pose heavy risk to human health. Therefore, removal of metal ion from water bodies may be considered as an interesting research activity.

Chelating polymers have been synthesized by employing free radical polymerization and subsequent modifications. These resins have been characterized based on elemental analyses, infrared and solid state ^1^C NMR spectra. Kinetic data suggest that the resins are highly stable and may be used for the removal of metal ions at room temperature. The metal uptake efficiency increases with pH and reaches plateau value around pH 10. The favourable characteristic of present chelating polymers is the time required for the maximum and constant uptake of metal ion from aqueous media. Just 1h time is sufficient in the present methods, while recently reported methods require longer period of time. The metal ion selectivity of present chelating polymers (at pH 10) is found to be in the order Pb(II) > H(II) > Cr(VI) > Cd(II). The metal ion uptake efficiency of the resin is not altered much even after four cycles.

Table 3 — Recyclability of the resins on the uptake of metal ions at recommended pH from 207.2 ppm of Pb(II), 200.6 ppm of Hg(II), 112.4 ppm of Cd(II) and 52.0 ppm of Cr(VI)

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Polymer</th>
<th>Pb(II) Uptake (ppm)</th>
<th>Pb(II) desorption (%)</th>
<th>Hg(II) Uptake (ppm)</th>
<th>Hg(II) desorption (%)</th>
<th>Cd(II) Uptake (ppm)</th>
<th>Cd(II) desorption (%)</th>
<th>Cr(VI) Uptake (ppm)</th>
<th>Cr(VI) desorption (%)</th>
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</thead>
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<tr>
<td>1</td>
<td>PHEM</td>
<td>175.2</td>
<td>98.5</td>
<td>179.7</td>
<td>97.5</td>
<td>56.7</td>
<td>98.0</td>
<td>19.2</td>
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<tr>
<td>2</td>
<td>PHEM</td>
<td>174.8</td>
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<td>175.4</td>
<td>96.4</td>
<td>56.3</td>
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<td>3</td>
<td>PHEM</td>
<td>174.1</td>
<td>96.5</td>
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<td>18.5</td>
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The metal ion uptake efficiency of the polymers is in the order P(CMS-AA-HEM) > CMPS-AA > PHEM. Thus, the copolymer containing functional groups of both the homo polymers is more efficient in the removal of metal ions.

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The authors thank the CSIR, New Delhi, India (Grant No. 01(1558)/98/EMR-II) for financial support. Further, we acknowledge RSIC Chennai; SIF, Bangalore and NMDC, Hyderabad for providing thermal and solid state $^{13}$C NMR and AAS data respectively.

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