Synthesis and characterization of an acetophenone derived resin and its lanthanide (III) polychelates

Patel Vijay R¹, Shrivastav Pranav S², Patel Vasant M³, Joshi Jayantilal D⁴

1. Research Scholar, Chemistry Department, Shri R K Parikh Arts & Science College, Patdi-388450, India
2. Associate Professor, Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad- 380009, India
3. Associate Professor, Shri Natvarsinhji Arts & Science & S G Patel Commerce College, Chhota Udepur, Vadodara- 391165, India
4. Former Professor, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar- 388120, India

Corresponding author: Associate Professor, Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad- 380009, India. Mail: pranav_shrivastav@yahoo.com

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ABSTRACT

The study describes the synthesis and characterization of a poly [(2,4-dihydroxyacetophenone) ethylene] resin and its lanthanide (III) polychelates. The resin was synthesised by condensation reaction of 2,4-dihydroxyacetophenone with ethanediol in presence of polyphosphoric acid in 80.41 % yield. Number average molecular weight (Mn) of the resin was found to be 1029 g/mol by vapour pressure osmometry method. It was characterized by elemental analysis, UV-Visible, IR and ¹H NMR spectroscopy. The UV spectrum of 2,4-dihydroxyacetophenone and its resin showed two peaks at 281.0 and 395.0 nm. The resin was used to prepare polychelates of seven lanthanide ions viz. La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III). The polychelates were characterized NMR spectroscopy, electronic spectra and magnetic measurements.

Keywords: Phenolic Resin; Polychelates; Lanthanides; 2,4-dihydroxyacetophenone

1. INTRODUCTION

Polymer-metal complexes have been attracting interest in many scientific and technological fields in recent years. In general, organic polymers have some limitations; therefore, their applications are also limited to some extent. These problems can be solved by the addition of metal ions in the polymeric system (Jayakumar et al., 2002), which changes the physicochemical, as well as, biological properties of the polymers (Belfiore et al., 2001). Transition and inner transition metal ions form coordination polymers which are thermally stable and impart both high flexibility due to presence of the organic moiety and thermal stability due to the presence of the inorganic elements in the same polymeric skeleton. Therefore, coordination polymers are widely used in scientific and industrial applications compared to organic polymers. Polymeric coordinating reagents are the novel types of substances possessing a combination of physical properties of a polymer and chemical properties of the attached element.

Metal containing polymers show many potential applications as functional materials with desirable chemical and physical properties, catalytic activities (Winterton, 2000; Islam et al., 2007), and models for bioinorganic systems (Shulman and Dwyer, 1964). Metal complexes have been explored for their catalytic and biological activities (Shulman and Dwyer, 1964) and polymer metal complexes are developed as interdisciplinary involving chemistry, electrochemistry, metallurgy, environmental protection, and material science (Kaminski and Modrzejewksa, 1997; Kaliyappan and Kannan, 2000). Chelate-forming polymers (Fender and Drian, 1998; Mizuta et al., 2000; Orazhanova et al., 2003) have found wide applications in the separation and monitoring of heavy metals, including lanthanides (Varvara et al., 2004), from aqueous solutions; they show significant applications in pollution control (Ro et al., 2003); bioinorganic industry, water purification and selective removal of waste materials in nuclear plants (Varghese et al., 2001; Patel et al., 2007), pre-concentration (Stanier, 1986) and hydrometallurgy (Jeffery et al., 1989). Thus, study on the characterization and properties of chelating polymers are of great importance. Among others, coordination compounds containing phenolic resin have received attention due to their interesting properties and possible uses.
In the present work lanthanide (III)-coordination polymers were synthesized using phenolic resin, poly [(2,4-dihydroxyacetophenone)ethylene]. It is found that polymeric ligand possess good thermal stability, while coordination polymers are thermally less stable. Further VPO, IR, NMR and UV spectrophotometry was used for the characterization of the resin and the polychelates of lanthanides.

2. EXPERIMENTAL

2.1. Material and reagents

All the chemicals used namely resorcinol, zinc chloride, potassium bromide, ethylenediamine tetraacetic acid, were of AR grade procured from E. Merck (Mumbai, India). During the entire synthesis and characterization study, analytical grade solvents and reagents were used namely tetrahydrofuran, dimethyl sulfoxide, dimethyl formamide, hydrochloric acid, sulphuric acid, perchloric acid, acetic acid glacial, ethanedio and polyphosphoric acid from Central Drug House Pvt. Ltd. (New Delhi, India), and Hydrated acetate salts of lanthanide elements viz. Pr(III), Nd(III), Sm(III), Tb(III) and Dy(III) were procured from Otto Chemie Pvt. Ltd. (Mumbai, India), while the acetate salts of La(III) and Gd(III) were procured from Alpha Chemica (Mumbai, India); all the rare earth acetate salts were obtained with ≥ 99.9 % purity.

2.2. Instruments and analysis conditions

Melting points were taken in a single capillary tube using a Toshinwal melting point apparatus and were uncorrected.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula weight of Repeating unit</th>
<th>Yield gm (%)</th>
<th>% Found (Calculated)</th>
<th>Keff (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DHAP-ED]p</td>
<td>240</td>
<td>7.33 (80.41)</td>
<td>...</td>
<td>74.88 (74.99)</td>
</tr>
<tr>
<td>([La(DHAP-ED])3(H2O)2]OH)n</td>
<td>670</td>
<td>0.91 (75.12)</td>
<td>20.10 (20.71)</td>
<td>53.64 (53.74)</td>
</tr>
<tr>
<td>([Pr(DHAP-ED])3(H2O)2]OH)n</td>
<td>672</td>
<td>0.88 (73.43)</td>
<td>20.35 (20.95)</td>
<td>53.51 (53.58)</td>
</tr>
<tr>
<td>([Nd(DHAP-ED])3(H2O)2]OH)n</td>
<td>676</td>
<td>0.89 (74.92)</td>
<td>21.14 (21.34)</td>
<td>53.22 (53.32)</td>
</tr>
<tr>
<td>([Sm(DHAP-ED])3(H2O)2]OH)n</td>
<td>682</td>
<td>0.88 (73.29)</td>
<td>21.95 (22.05)</td>
<td>53.69 (53.84)</td>
</tr>
<tr>
<td>([Gd(DHAP-ED])3(H2O)2]OH)n</td>
<td>689</td>
<td>0.91 (75.59)</td>
<td>22.71 (22.83)</td>
<td>52.23 (52.31)</td>
</tr>
<tr>
<td>([Tb(DHAP-ED])3(H2O)2]OH)n</td>
<td>690</td>
<td>0.89 (74.32)</td>
<td>22.91 (23.02)</td>
<td>52.14 (52.19)</td>
</tr>
<tr>
<td>([Dy(DHAP-ED]3(H2O)2]OH)n</td>
<td>694</td>
<td>0.92 (76.21)</td>
<td>23.32 (24.41)</td>
<td>51.84 (51.91)</td>
</tr>
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</table>

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (ppm)</th>
<th>-OH (para to COCH3)</th>
<th>-OH (ortho to COCH3)</th>
<th>Aromatic protons</th>
<th>CO-CH3</th>
<th>-[CH2-CH2]- bridge</th>
<th>δ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>DHAP</td>
<td>12.75</td>
<td>6.55</td>
<td>6.44-7.62</td>
<td>2.57</td>
<td>-</td>
<td>2.55-3.29</td>
<td>-</td>
</tr>
<tr>
<td>Polymer resin [DHAP-ED]p</td>
<td>12.85</td>
<td>5.55</td>
<td>6.51</td>
<td>5.39</td>
<td>2.55-3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([La(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([Pr(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
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<tr>
<td>([Nd(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([Sm(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
<td></td>
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<tr>
<td>([Gd(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
<td></td>
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<tr>
<td>([Tb(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
<td></td>
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<tr>
<td>([Dy(DHAP-ED])3(H2O)2]OH)n</td>
<td>-</td>
<td>5.55</td>
<td>6.67</td>
<td>3.56</td>
<td>2.55-3.29</td>
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</table>

Table 3

<table>
<thead>
<tr>
<th>Resins</th>
<th>Concentration gm/kg</th>
<th>Millivolts (mV)</th>
<th>Slope of Plot</th>
<th>K/Slope gm/mole</th>
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</thead>
<tbody>
<tr>
<td>DHAP-ED</td>
<td>2.21</td>
<td>24.0</td>
<td>11.17</td>
<td>1029</td>
</tr>
<tr>
<td></td>
<td>4.42</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.83</td>
<td>74.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.84</td>
<td>99.0</td>
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</table>

K = polystyrene constant = 1.15 × 10^3
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Magnetic susceptibilities were measured by the Gouy method at room temperature. The number average molecular weight (Mn) of polymeric resin sample was measured by a VPO (Knaur, Germany) using DMF as a solvent at 90 °C and polystyrene as a calibrant.

2.3. Synthesis of monomer 2,4-dihydroxyacetophenone (DHAP)

Freshly fused and powdered zinc chloride (16.5 g, 0.27 mol) was dissolved in glacial acetic acid (16 mL) by heating in a beaker on a sand bath. Dry resorcinol (11 g, 0.1 mol) was added with stirring to the mixture at 140 °C. The solution was heated until it just begins to boil and kept for 20 min at 150 °C. Dilute hydrochloric acid (1:1, 50 mL) was added to the mixture and then the solution was cooled to 5 °C. The separated yellow product was filtered, washed with dilute hydrochloric acid (1:3) and crystallized from hot water containing a little hydrochloric acid, the yield is 14 g (93 %) and melting point is 142-144 °C.

2.4. Synthesis of resin poly[(2,4-dihydroxyacetophenone)ethylene] (DHAP-ED)

To a well stirred ice-cooled mixture of 2,4-dihydroxyacetophenone (9.12 g, 0.06 mol) and ethanediol (3.35 mL, 0.06 mol), polyphosphoric acid (20.0 g) was added slowly with stirring as a catalyst in 500 mL in a round bottom flask. The reaction mixture was left at room temperature for half an hour and condensed on an oil bath at 145 °C for 10 h. The reaction mixture was then cooled, poured on crushed ice and left overnight. The product was collected by filtration and washed with cold water and methanol to remove unreacted acid and monomer. The synthesized resin was soluble in DMF, DMSO and THF. The obtained polymer is brown in colour, decomposition point is greater than 270 °C and yield is about 7.33 g (80.41%).

2.5. Synthesis of polychelates

Hydrated acetate salts of lanthanides viz. lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium and dysprosium, with a minimum purity of 99.9 % were used in the preparation of the polychelates. The hot and clear solution of the lanthanum acetate (1.72 g, 0.005 mol) was added with constant stirring to the hot and clear solution of polymeric ligand (0.01 mol). A blackish colored product separated out immediately. The suspension was digested on a water bath for two hours and then filtered. The solid was washed with cold DMSO to remove unreacted metal acetate. Finally, the polychelate formed was washed with acetone and dried at 80 °C for 24 h. A similar procedure was applied for the synthesis of Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) polychelates. All the polychelates are found soluble in DMF and DMSO.

3. RESULTS AND DISCUSSION

Under the established conditions, the % yield for the resin [DHAP-ED], and their polychelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) was within 73-81 %. The magnetic susceptibility as determined by Gouy’s method is depicted in Table 1, along with other analytical data.

3.1. IR Spectral characteristics

The IR spectra (Figure 1) of monomer showed a broad band appearing in the range 3200-3400 cm⁻¹ due to O-H stretching. The strong band around 1589 cm⁻¹ suggests the presence of O=C-O and a weak band of O-H at 2734 cm⁻¹ indicates an intramolecular hydrogen bonding. The bands observed around the 1492-1563 cm⁻¹ region can be attributed to C=C stretching (aromatic) vibrations. The strong band observed around the 1266±10 cm⁻¹ region is associated with the Ph-O-CH₃ ether linkage. FTIR spectra of polychelates showed the C=O stretching frequency around 1635±10 cm⁻¹, appearing at a lower frequency of 20 to 40 cm⁻¹, which suggests -C=O-M coordination [17] as shown in Figure 2. In the polychelates, the bands observed around 459-480 cm⁻¹ indicate the M-O bond, suggesting that phenolic and

Scheme 1
Synthesis of 2,4-dihydroxyacetophenone (DHAP)

Scheme 2
Synthesis of resin DHAP-ED

Scheme 3
Proposed structure of polychelate (M=La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III); X=H)

Figure 1
IR spectra of 2,4 dihydroxyacetophenone (DHAP)
carbonyl groups are involved in bond formation with the metal ion. The other bands observed in the spectra of all polychelates were at 3200-3400 cm\(^{-1}\) (\(\text{-OH}\) stretching), 2950-2880 cm\(^{-1}\) (\(\text{-CH}_2\) stretching), 2730 cm\(^{-1}\) (intra molecular H-bond), 1615 cm\(^{-1}\) (\(\text{-C=O}\)), 1560, 1525 and 1490 cm\(^{-1}\) (\(\text{-C=C-}\)), 1375 cm\(^{-1}\) (\(\text{-OH}\)), 1230 ± 10 cm\(^{-1}\) (Ar-O-R), 1115, 890 and 690 cm\(^{-1}\) (phenyl ring).

### 3.2. NMR Spectral characteristics

The \(^1\text{H}\) NMR data of DHAP, resin \([\text{DHAP-ED}]_n\), and polychelates \([\text{M(DHAP-ED)}_2(\text{H}_2\text{O})_2\text{OH}]_n\) are presented in Table 2. From the general observation, it was concluded that the signal of the \(-\text{OH}\) group completely disappears in all the polychelates which suggests that the bond formation takes place through the \(-\text{OH}\) group ortho to \(-\text{COCH}_3\). Further, the deshielding effect of the metal ion on the ligand protons resulted in downfield shift of 0.12-0.81 ppm for aromatic protons and 0.11-0.43 ppm for \(-\text{COCH}_3\) protons in the NMR spectra of the polychelates. A representative NMR spectra of the polymer \([\text{DHAP-ED}]_n\) is shown in Figure 3. From the obtained spectral information, the possible structure of the polychelate was proposed as represented in Scheme 3.

### 3.3. Vapor Pressure Osmometry

The following procedure was used to estimate the average molecular weight of the resin. Dilute solutions of the resin having 2.21, 4.42, 6.63, 8.84 g/kg in DMF were prepared. VPO experiment was carried out with each concentration and the corresponding bridge output reading in mV was noted and a plot of mV versus concentration was drawn. It was found linear and the value \(M_n\) of the polymer was estimated from the value of the slope and the VPO constant \(K\). The molecular weights of the resins determined by VPO method are presented in Table 3.

### 3.4. UV-Visible spectra of resins

Polymers carrying the reactive functional groups are of value in a variety of uses, which have ultraviolet absorbing groups attached to the polymer chain. In recent years polyolefin films have been made more stable to atmospheric degradation by incorporating polymerizable 2-hydroxy benzophenone in the main chain. The UV spectra of DHAP and its resins \([\text{DHAP-ED}]_n\) showed one band each at 281.0 and 395.0 nm, due to the n-\(\pi^*\) and \(\pi-\pi^*\) transitions, respectively. By proper selection of co-monomer, useful UV-absorbing polymers with varying amount of UV-absorbing groups (DHAP) can be prepared. DHAP has intermediate thermal properties and hence can remain in a blend resin during various applications and can also protect the resin from UV light.

### 3.5. Electronic spectra and magnetic measurements of polychelates
The data indicates the energy of f-H transitions in the polychelates is slightly reduced compared to the corresponding aquo ions. This may be either because of the slight covalent interaction of the f orbitals with vacant ligand orbitals, leading to some delocalization with consequent reduction in inter-electronic repulsion or by increased nuclear shielding of the orbitals due to a slight covalent ligand-metal electron drift compared to the aquo ions of the lanthanides. The f-H transition bands of the polychelates showed weak perturbation and increased intensity as a result of complex formation, presumably due to the nephelauxetic effect.

The electronic spectra of all the polychelates exhibit the additional two spectral bands in the resin at 278 - 293 nm and 449 - 460 nm. The first band occurs in the spectra of polymeric ligand (resin). The band is assigned to the transition of the type π→τ1, and π→τ2 (Gudasi et al., 2007). The second band is assigned to the polymeric ligand (resins) Ln(III) transitions of all the polychelates. The Ln(III) polychelates were found diamagnetic in nature as expected for six coordinated octahedral geometry. The electronic spectra of Pr(III), Tb(III), polychelates exhibited absorption at 21324, 20865, 19458 and 17715 cm⁻¹, assigned to H₄P²→H₄P², H₄P²→H₆P², H₄P²→H₆P² and H₄P²→D₂ transitions of Pr(III) in a octahedral environment, due to large crystal field with magnetic moment 3.71 B.M. The Nd(III) polychelates were paramagnetic as expected for f⁴ system. Bands were obtained at 18970, 17645, 14273 and 9885 cm⁻¹ for H₂P⁶→H₂P⁶, H₂P⁶→H₆P⁶, H₂P⁶→H₆P⁶ and H₂P⁶→H₆P⁶ transitions of Nd(III) in octahedral geometry. In addition the bands at 23168, 22920 and 23880 cm⁻¹ for polychelates were assigned to H₂P⁶→F₃P₃, H₂P⁶→F₃P₃ and H₂P⁶→F₃P₃ transitions of Sm(III) in octahedral geometry due to large crystal field splitting and all the polychelates were paramagnetic in nature. The magnetic moment 1.73 B.M. is obtained as expected. The Gd(III) and Tb(III) polychelates were found paramagnetic in nature giving 7.89 B.M. and 9.50 B.M. respectively for six coordinated octahedra.

4. CONCLUSION

In the present work, a monomer 2,4-dihydroxyacetophenone (DHAP) was synthesized from resorcinol. It was utilized to synthesize polymeric resin poly[(2,4-dihydroxyacetophenone) ethylene] (DHAP-ED₄) by reacting DHAP with ethanolol. Synthesized resin was used to prepare polychelates of lanthanide metal ions viz. La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III). For descriptive characterization of synthesized monomer, resin and polychelates, several analytical techniques were employed namely ¹H NMR, IR, VPO and UV-Visible spectrophotometric techniques to define some of their properties.

SUMMARY OF RESEARCH

1. A novel phenolic polymeric resin was prepared from 2,4-dihydroxyacetophenone, an acetophenone derived monomer, which was used to synthesize polychelates of lanthanide(III) elements.

2. The resultant polychelates were characterized using IR, NMR, VPO and UV-Visible spectrophotometric techniques to define some of their properties.

FUTURE ISSUES

It would be definitely beneficial to investigate the physicochemical and antimicrobial activities of the prepared polychelates, which may help to explore their potential for a variety of fields in chemistry.

DISCLOSURE STATEMENT

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