CHAPTER - III

RESULTS & DISCUSSION
III.1 Studies on MAP-MMA copolymers

The low-molecular weight aromatic ketones like acetophenone, hydroxyacetophenone, benzophenone, hydroxybenzophenone and their hydrazone derivatives have been extensively used as ligands for various metal ions. With a view to the complexing abilities of hydrazone derivatives of aromatic ketones incorporated into the polymer, the 4-methacryloxyacetophenone (MAP) cross-linked with methylmethacrylate (MMA) copolymer are selected. The hydrazone derivative of the cross-linked copolymer is used as insoluble polymeric ligand towards the metal ions like Cu (II) and Ni (II).

III.2 Characterisation of 4-methacryloxyacetophenone (MAP) monomer

The MAP monomer is characterized by the following techniques.

(i) IR spectroscopy

(ii) $^1$H NMR spectroscopy

(iii) Scanning electron microscopy (SEM)

(i) IR spectroscopy

The IR spectrum of MAP monomer is shown in Fig.III.2.1. The IR spectrum shows a broad band at 2977 cm$^{-1}$ due to alkene -CH stretching vibrations. The ester carbonyl of MAP appeared at 1718 cm$^{-1}$. The presence of strong absorption band at 1414 cm$^{-1}$ is attributed to the
Fig. III.2.1  IR spectrum of 4-methacryloxyacetophenone (MAP) monomer
(ii) **Proton NMR spectroscopy**

The $^1$H-NMR spectrum of MAP is presented in Fig.III.2.2. The signals between 7.0-8.2 ppm correspond to the protons of disubstituted phenyl ring. The signals at $\delta$ value 5.9-6.5 ppm correspond to Vinyl group protons. The peak at $\delta$ value 2.1 ppm are from the $-\text{C(CH}_3\text{)}$ protons. The peaks at $\delta$ value 2.5 ppm arise due to keto methyl group.

(iii) **Scanning electron microscopy**

The SEM photographs of MAP monomer is shown in Fig.III.2.3. The microphotograph indicate the crystalline nature of the particles.

III.3 **CHARACTERIZATION OF MAP–MMA COPOLYMER AND ITS ISONICOTINOYL HYDRAZONE FUNCTIONALIZED RESINS**

The MAP–MMA copolymer is prepared in ethylmethylketone at 70±2 °C using benzoyl peroxide as the initiator. The copolymer beads are characterized by the following techniques.

(i) Elemental analysis

(ii) FT–IR spectroscopy

(iii) $^1$H NMR spectroscopy

(iv) $^{13}$C NMR spectroscopy

(v) Thermogravimetric analysis

(vi) Scanning electron microscopy
Fig. III.2.2 \textsuperscript{1}H NMR spectrum of 4-methacryloyloxyacetophenone (MAP) monomer
Fig.III.2.3 SEM photograph of 4-methacryloxyacetophenone (MAP) monomer
The MAP–MMA copolymer is functionalized by treating with isonicotinoyl hydrazine to yield hydrazone derivative. The functionalized resins are characterized with appropriate instrumental techniques. These resins are used as polymeric ligands for complexing metal ions like Cu(II) and Ni(II). The cross-linked polymer metal complexes are characterized by EPR spectral studies in addition to the above techniques.

(i) Elemental analysis

The Elemental analysis of MAP–MMA copolymer and its functionalized polymers are carried out and the results are presented in Table III.3.1.

(ii) FT-IR spectroscopy

In the present investigation, FT-IR spectra are used for identifying the structural units in the copolymer and for monitoring the functionalization of the copolymer\(^{99,100}\). The FT–IR spectrum of MAP–MMA copolymer is shown in Fig.III.3.1. The selected IR characteristic frequencies are presented in Table III.3.2. The IR spectrum shows bands at 3010 and 2929 cm\(^{-1}\) because of aromatic –CH and backbone methylene stretching vibrations. The ester carbonyl of MAP appeared at 1737 cm\(^{-1}\) as a sharp intense band whereas the ketonic carbonyl of acetophenone appeared as sharp band at 1690 cm\(^{-1}\). The presence of strong absorption band at 1590 cm\(^{-1}\) is attributed to the C=C stretching vibrations of phenyl ring. Fig.III.3.2 shows the FT-IR spectrum of the isonicotinoyl hydrazone derivative of MAP-MMA copolymer. The
Table III. 3.1

Elemental analysis of MAP–MMA copolymer and its isonicotinoyl hydrazone functionalized resin

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Element</th>
<th>MAP–MMA</th>
<th>MAP–MMA–isonicotinoyl hydrazone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C</td>
<td>68.94</td>
<td>62.74</td>
</tr>
<tr>
<td>2.</td>
<td>H</td>
<td>5.98</td>
<td>5.71</td>
</tr>
<tr>
<td>3.</td>
<td>N</td>
<td>-</td>
<td>4.72</td>
</tr>
<tr>
<td>4.</td>
<td>-</td>
<td>-</td>
<td>*41</td>
</tr>
</tbody>
</table>

* indicates the percentage of conversion.
Fig. III. 3.1 FT-IR spectrum of methacryloxyacetophenone (MAP)-methylmethacrylate (MMA) copolymer.
Table III. 3.2

FT-IR (cm⁻¹) spectral data of copoly(MAP-MMA) and Copoly(MAP-MMA) isonicotinoyl hydrazone derivative

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Ester carbonyl</th>
<th>C=C &amp; C=N band</th>
<th>(C-O) stretching in ester</th>
<th>Carbonyl group</th>
<th>Back bone -CH stretching</th>
<th>C=C skeletal vibration band</th>
<th>-NH stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Copoly(MAP-MMA)</td>
<td>1737</td>
<td>1590</td>
<td>1210</td>
<td>1690</td>
<td>2929</td>
<td>1410</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Copoly(MAP-MMA) Isonicotinyol hydrazone derivative</td>
<td>1750</td>
<td>1630</td>
<td>1104</td>
<td>1658</td>
<td>2960</td>
<td>1440</td>
<td>3426</td>
</tr>
</tbody>
</table>
Fig.III.3.2 FT-IR spectrum of MAP- MMA-isonicotinoyl hydrazone(INH) derivative
disappearance of 1690 cm\(^{-1}\) indicates the absence of keto carbonyl of acetophenone unit and appearance of strong absorption band at 1660 cm\(^{-1}\) is attributed to C=N stretching vibrations. This clearly indicates formation of hydrazone derivative. The presence of sharp intense band around 1700 cm\(^{-1}\) clearly indicates the intactness of ester carbonyl of acrylate unit and also the participation of ketocarbonyl in the reactions.

iii) \(^1\)H NMR spectroscopy

The \(^1\)H NMR study (Fig.III.3.3 & Table III.3.3) helps in the confirmation of copolymer. The chemical shifts assignments for copoly(MAP-MMA) are based on chemical shifts observed for the respective monomer. The multiplet between \(\delta\) value 7.2-8.2 ppm correspond to the protons of disubstituted phenyl ring. The resonance signal at 3.6 ppm is due to the \(-\text{OCH}_3\) protons of MMA unit. The signals at \(\delta\) value 1.3 and 2.1 ppm are from the backbone \(-\text{C(CH}_3)\) and \(-\text{CH}_2\) protons respectively. The signal at \(\delta\) value 2.5 ppm corresponds to \(-\text{CO-CH}_3\) protons.

(iv) \(^{13}\)C NMR spectroscopy

The \(^{13}\)C NMR spectrum of copolymer is taken in CDCI\(_3\) solution. The \(^{13}\)C NMR spectrum of MAP-MMA of cross-linked copolymer is shown in Fig.III.3.4 and the data presented in Table III.3.4. The resonance signal lines at 39.0 ppm is due to the \(-\text{OCH}_3\) carbon of MMA unit. The backbone \(-\text{C(CH}_3)\) and \(-\text{CH}_2\) groups appeared as clear
Fig. III.3.3 $^1$H NMR spectrum of methacryloxyacetophenone (MAP)-methylmethacrylate (MMA) copolymer
### Table III. 3.3

$^1$H NMR (δ ppm) spectral data of MAP-MMA copolymer

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Aromatic protons</th>
<th>MMA unit -OCH$_3$ protons</th>
<th>-OC-CH$_3$ protons</th>
<th>Backbone -CH$_2$ protons</th>
<th>Backbone -(CH$_3$) protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MAP-MMA copolymer</td>
<td>7.2-8.2</td>
<td>3.6</td>
<td>2.5</td>
<td>2.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Fig. III.3.4: $^{13}$C NMR spectrum of MAP-MMA copolymer in CDCl$_3$ solution.
Table III. 3.4

$^{13}$C NMR (δ ppm) spectral data of MAP-MMA copolymer

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Ester carbonyl</th>
<th>Carbonyl group($^{13}$C)</th>
<th>Aromatic $^{5}$C/ $^{6}$C, $^{9}$C/ $^{7}$C, $^{8}$C/ $^{10}$C</th>
<th>$^{17}$C</th>
<th>$^{12}$C</th>
<th>$^{2}$C/$^{14}$C</th>
<th>$^{1}$C/$^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MAP-MMA copolymer</td>
<td>165.21</td>
<td>196.82</td>
<td>154.68</td>
<td>39</td>
<td>26.56</td>
<td>17.2</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>135.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
distinct lines at 17.2 and 18.3 ppm respectively. The ketonic carbonyl of MAP-MMA appeared at 196.82 ppm as sharp intense line in copolymer. The phenyl ester carbonyl gave sharp line at 165.21 ppm. The $^5$C of phenyl ring appeared at 154.68 ppm. The $^6$C & $^9$C, $^7$C & $^8$C aromatic carbons gave sharp lines at 134.64 and 129.92 ppm. The lines observed at 135.54 ppm are attributed to $^{10}$C of aromatic carbons. Due to residual brodening, a clear separation of the signals is not observed in the spectrum.

(v) Thermogravimetric analysis

In order to study the thermal stability and decomposition pattern of cross-linked copolymers, dynamic thermogravimetric analysis is undertaken and the data presented in the Table III.3.5. The thermograms of the copolymer and its functionalized resins are run in air atmosphere. The thermolysis curve of MAP–MMA copolymer and its derivatives are shown in Fig.III.3.5 & Fig.III.3.6. The degradation of MAP–MMA copolymer occurred in two stages. The first stage decomposition is observed from 176-372°C and the weight loss found is 50%. The second stage degradation of the copolymer resin is in the temperature range of 372-530°C. The weight loss involved in this stage is 46.7%.

The isonicotinoyl hydrazone derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 220°C and was completed at 413°C with a weight loss of 72%. The second stage of
Table III. 3.5

TG data of MAP-MMA copolymer, isonicotinoyl hydrazone functionalized copolymer and metal chelates

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Weight loss (%) at temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IDTs 250 300 350 400 450 500 550 600 650</td>
</tr>
<tr>
<td>1.</td>
<td>MAP-MMA copolymer</td>
<td>138  22  29  48  59  82.5  4.5  4  3 -</td>
</tr>
<tr>
<td>2.</td>
<td>Functionalized MAP-MMA copolymer</td>
<td>146  6  16  45  63.5  70  10  4.5  4 -</td>
</tr>
<tr>
<td>3.</td>
<td>Functionalized MAP-MMA-Cu(II) chelate</td>
<td>167  7.5  14  50  66.4  72.4  13.5  10.3  9  5</td>
</tr>
<tr>
<td>4.</td>
<td>Functionalized MAP-MMA-Ni(II) chelate</td>
<td>214  6.7  12  28.5  79  84  09.5  8  6  4</td>
</tr>
</tbody>
</table>
Fig. III. 3.5 Thermogram of Methacryloxyacetophenone (MAP)-methylmethacrylate (MMA) copolymer
Fig. III.3.6 Thermogram of Methacryloxyacetophenone (MAP)-methylmethacrylate (MMA)-isonicotinoyl hydrazone derivative
decomposition was between 413 and 558°C and the weight loss was 25.6%.

(vi) Scanning electron microscopy

The SEM has been employed for studying the shape, size and morphological features of the polymers\textsuperscript{102-107}. The SEM photographs of MAP-MMA cross-linked copolymer and its isonicotinoyl hydrazone derivative are shown in Fig.III.3.7 (b) & (c). It can be seen from the microphotographs that the surface of the monomer (cf. Fig.III.2.3) is smoother than the copolymer. The change in morphology of polymeric ligands with complexation has also been investigated in some cases\textsuperscript{108}.

III.4 Characterization of MAP-MMA-isonicotinoyl hydrazone functionalized resin metal complexes

The isonicotinoyl hydrazone derivatives of MAP-MMA copolymer and their metal complexes [Cu(II) and Ni(II)] are prepared and characterized by the following techniques.

(i) Elemental analysis
(ii) FT-IR spectroscopy
(iii) EPR spectroscopy
(iv) Thermogravimetric analysis
(v) Scanning electron microscopy
(i) Elemental analysis

The incorporation of metal ions into the cross-linked copolymer is monitored by elemental analysis. The C, H, N and M values are presented in Table III.4.1. The C, H and N elemental values of the resin complex decreased when compared to the functionalized resin. The amount of the metal incorporated in the copolymer is determined by estimating the metal ions.

(ii) FT-IR spectroscopy

The complexation of the metal ions with cross-linked MAP-MMA copolymer is monitored by observing the changes in the characteristic functional group absorption frequencies.

Cu(II) and Ni(II) complexes of isonicotinoyl hydrazone derivative

The Cu(II) and Ni(II) complexes of hydrazone derivative are shown in Fig.III.4.1 & Fig. III.4.2 and the data presented in the Table III.4.2. The FT-IR spectra of functionalized copolymer shows intense $\nu_{\text{C=O}}$ band at 1680 cm$^{-1}$ and its downward shift in Cu(II) complex suggest coordination of metal ion through oxygen atoms. There is a downward shift of $\nu_{\text{C=N}}$ band of azomethine group from 1630 cm$^{-1}$ to 1595 cm$^{-1}$ which indicates the coordination of azomethine nitrogen atom. Coordination through ketonic oxygen is supported by the appearance of band at 470 cm$^{-1}$ which may be assigned to $\nu_{\text{Cu-O}}$ and $\nu_{\text{Cu-N}}$ bands observed at 560 cm$^{-1}$ in copper complexes.
Table III.4.1

Elemental Analysis of MAP–MMA-isonicotinoyl hydrazone functionalized resin metal complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Element</th>
<th>Cu(II) complex</th>
<th>Ni(II) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C</td>
<td>52.29</td>
<td>52.58</td>
</tr>
<tr>
<td>2.</td>
<td>H</td>
<td>4.86</td>
<td>4.67</td>
</tr>
<tr>
<td>3.</td>
<td>N</td>
<td>2.53</td>
<td>2.47</td>
</tr>
<tr>
<td>4.</td>
<td>M</td>
<td>1.47</td>
<td>1.58</td>
</tr>
</tbody>
</table>
Fig. III.4.1 FT-IR spectrum of MAP-MMA-isonicotinoyl hydrazone functionalized Cu(II) metal chelate
Fig. III. 4.2 FT-IR spectrum of MAP-MMA-isonicotinoyl hydrazone functionalized Ni(II) metal chelate
Table III. 4.2

FT-IR (cm\(^{-1}\)) spectral data of copoly(MAP-MMA)Cu(II) and copoly(MAP-MMA)Ni(II) derivatives

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>C=N band</th>
<th>(C-O) stretching</th>
<th>Ester Carbonyl group</th>
<th>-CH stretching</th>
<th>-NH stretching</th>
<th>(\nu_{\text{M-O}})</th>
<th>(\nu_{\text{M-N}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copoly (MAP-MMA) Cu(II)</td>
<td>1595</td>
<td>1120</td>
<td>1696</td>
<td>2929</td>
<td>3361</td>
<td>470</td>
<td>560</td>
</tr>
<tr>
<td>2</td>
<td>Copoly (MAP-MMA) Ni(II)</td>
<td>1600</td>
<td>1148</td>
<td>1703</td>
<td>2977</td>
<td>3388</td>
<td>480</td>
<td>620</td>
</tr>
</tbody>
</table>

\(M = \text{Cu, Ni}\)
The C=N stretching frequency of the Ni(II) complex are lower than those of the hydrazone and noticed at 1605 cm\(^{-1}\). The coordination of the amide oxygen is also supported by the appearance of a band at 480 cm\(^{-1}\) which may be assigned to \(\nu_{\text{Ni-O}}\). The band observed at 620 cm\(^{-1}\) is assigned to \(\nu_{\text{N-N}}\) vibrations. It is therefore inferred that the ligands coordinate in bidentate fashion.

(iii) Electron Paramagnetic Resonance Spectroscopy

The EPR spectra of the hydrazone derivatives of Cu(II) and Ni(II) complexes are presented in Fig.III.4.3 & Fig.III.4.4. The EPR parameters give a measure of the nature of complexation with the metal ion and it is decided by the \(g_{||}\) values. The EPR parameters are calculated by kneubuhl\(^{109}\) method and are presented in the Table Table III.4.3. For the covalent complexes, \(g\) is less than 2.3 and for ionic environments, it is normally 2.3 or larger\(^{110}\). The \(g\) value of the Cu(II) and Ni(II) complexes are 2.17 and 2.10 respectively, thereby indicating the covalent nature of the complex.

The elemental analysis of polymer metal complexes indicated that the ligand to metal ratio is 2:1. From the elemental analysis, FT-IR and EPR data it may be assumed that the chelation is taking place between two polymeric chains through C=O and C=N groups.
Fig. III.4.3 ESR spectrum of MAP-MMA-isonicotinoyl hydrazone functionalized-Cu(II) metal complex
Fig. III.4.4 ESR spectrum of MAP-MMA-isonicotinoyl hydrazone functionalized-Ni(II) metal complex
Table III. 4.3
EPR parameters of metal complexes

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>$g_{\parallel}$</th>
<th>$g_{\perp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Copoly(MAP–MMA)Cu(II)</td>
<td>2.180</td>
<td>2.065</td>
</tr>
<tr>
<td>2.</td>
<td>Copoly(MAP–MMA)Ni(II)</td>
<td>2.109</td>
<td>2.006</td>
</tr>
</tbody>
</table>
(v) Thermogravimetric analysis

The thermograms of the isonicotinoyl hydrazone functionalized MAP-MMA copolymer Cu(II) and Ni(II) metal complexes are shown in Fig. III.4.5 and the data presented in the Table III.3.5. The IDTs of copoly (MAP-MMA)-Cu(II) and Ni(II) complexes are 167°C and 214°C respectively. The degradation occurred mainly in two stages and decomposition is fast up to 400°C. The first decomposition may be due to the rupture of weak linkages and volatilization of low molecular weight fragments. The second slow decomposition of chelates at higher temperatures may be due to the breakage of main chain accompanied by the volatilization of the cleaved products.

(vi) Scanning electron microscopy

The SEM photographs of isonicotinoyl hydrazone functionalized MAP-MMA are Cu(II) and Ni(II) metal complexes are shown in Fig.III.4.6 (d) & (e). It can be seen from the microphotographs that the rough appearance of the bound polymer stems from the doping of the metal.
Fig. III. 4.5 Thermograms of (---) functionalized MAP-MMA-Cu(II) and (---) functionalized AMP-MMA-Ni(II) isonicotinoyl hydrazone metal complexes.
Fig. III.3.7 SEM photographs of

(b) Methacryloxyacetophenone (MAP)-methylmethacrylate (MMA) copolymer and

(c) MAP-MMA-isonicotinoyl hydrazone (INH) derivative
Fig. III. 4.6  SEM photographs of
(d) MAP-MMA-INH-Cu(II) and
(e) MAP-MMA-INH-Ni(II) metal chelates