INTRODUCTION

The synthesized terpolymer resins, showing versatile applications and properties, attracted the attention of scientist and introduce the recent innovations in the polymer chemistry. These terpolymers can be used as high energy material\(^1\), ion-exchanger\(^2\), semiconductors\(^3\), antioxidants, fire proofing agent, optical storage data, binders, molding materials etc. Literature survey reveals the chelation ion-exchange properties of 2, 4 dinitrophenylhydrazone of 2-hydroxyacetoephonone-formaldehyde resin\(^4\), and oximes of 2-hydroxyacetophenone substituted benzoic acid-formaldehyde resin\(^5\) for different metal ions. Thermogravimetric analysis of urea-formaldehyde polycrystalline (UFPS) has been reported by Zeman and Tokarova\(^6\). Some terpolymers have been proved to have excellent ion exchange capacity for many transition metals. Terpolymer involving o-nitrophenol-thioureaparaformaldehyde and antranilic acid-thioureaparaformaldehyde resins were synthesized and reported for its excellent ion-exchange capacity\(^7\). In an earlier communication\(^8\) from this department numbers of studies on such terpolymers have been reported. However no work seems to have been carried out on synthesis, characterization of the terpolymer resin from 1-Naphthol-4-sulphonic acid-Hexamethylenediamine and formaldehyde. Looking the scope of high performing terpolymer resins, in the present paper, synthesis of 1-N-4-SAHDF-Resin-I; its spectral characterization by UV-Visible absorption spectra, NMR spectra have been described and morphology was studied by SEM micrographs.

MATERIALS AND METHODS

Materials

The chemicals used in the synthesis of new terpolymer resin were procured from the market and were Sigma-Aldrich or chemically pure grade. Whenever required they were further purified by standard procedure.

Synthesis of 1-N-4-SAHDF-Resin-I terpolymer

The new terpolymer 1-N-4-SAHDF-Resin-I was synthesized by condensing 1-Naphthol-4-sulphonic acid (0.1 mol) and Hexamethylenediamine (0.1 mol) with 37% formaldehyde (0.2 mol) in a mol ratio of 1:1:2 in the presence of 2M 200 ml HCl as a catalyst at 140°C ± 20°C for 6hr in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 1Naphthol-4-sulphonic acid formaldehyde copolymer which might be present along with 1-N-4-SAHDF-Resin-I terpolymer. The coffee brown colored powdery product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 1-N-4-SAHDF-Resin-I is shown in Figure 1.

Purification of Resin

The separated terpolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 1-Naphthol-4-sulphonic acid - formaldehyde copolymer which might be present along with 1-N-4-SAHDF-Resin terpolymer. The product so obtained was further purified by reprecipitation technique. For this purpose the terpolymer resin was dissolved in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated
hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation.

The process of reprecipitation was repeated twice.

The terpolymer sample 1-N-4-SA HDF-Resin-I thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The yield of the terpolymer resin was found to be 77%.

![Reaction scheme](image)

**Figure 1**: Reaction and suggested structure of representative 1-N-4-SA HDF-Resin-I terpolymer

**Characterization**

A 1-N-4-SA HDF-Resin-II terpolymer resin was subjected to microanalysis for C, H, S and N at STIC, Cochin.

The number average molecular weight (Mn) was determined by conductometric titration in non-aqueous medium such as dimethyl sulphoxide (DMSO) using ethanolic KOH as a titrant.

From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (Mn) has been calculated for terpolymer resin under investigation.

An infra-red spectrum of 1-N-4-SA HDF-Resin-II was recorded on Perkin-Elmer-R-XR Spectrophotometer in KBr pallets in the wave number region of 4000-400 cm⁻¹ at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University; Chandigarh.

Both ¹H & ¹³C NMR spectrum of newly synthesized terpolymer resin has been scanned on Bruker Avance II 400 MHz NMR spectrometer using DMSO-d₆ at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.

SEM has been scanned by FEI-Philips XL-30 electron microscope at STIC, Cochin.

**RESULTS AND DISCUSSION**

Newly synthesized, purified 1-N-4-SA HDF-Resin-I was found to be amorphous and coffee brown in colour. The terpolymers are soluble in solvents such as DMF, DMSO, THF and aq. NaOH while insoluble in almost all other organic solvents. The resin synthesized did not show sharp melting point but undergo decomposition above 240°C. These resins were analyzed for carbon, hydrogen, nitrogen and sulphur content. The Mn of the terpolymer resin was determined by non-aqueous conductometric titration in DMSO against KOH in 50% (v/v) DMSO-Alcohol mixture using 100mg of resin sample.

A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break were noted.

The calculation of (Mn) by this method is based on the following considerations. (1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all repeating units are neutralized. On the basis of the average, degree of polymerization (DP) is given by the following relation.

\[
DP = \frac{\text{Total m.eq. of base required for complete neutralization}}{\text{M eq. of base required for smallest interval}}
\]

(Mn) = (DP) X Repeat unit weight

On the basis of degree of polymerization (DP), the average number molecular weight (Mn) is calculated by multiplying the (DP) by the formula weight of repeating unit.

The details of Elemental analysis, molecular weight determination are incorporated in Table 1.

**UV-Visible Spectra**

The UV-Visible spectra of 1-N-4-SA HDF-Resin-I is incorporated in Figure 2.

It is recorded in pure DMSO in the region 200-850 nm at a scanning rate of 100 nm min⁻¹ and a chart speed of 5 cm min⁻¹. 1-N-4-SA HDF-Resin-I gave two characteristics bands at 330 nm and 480 nm. These observed positions for the absorption bands have different intensities.

The more intense band is due to \(\pi\rightarrow\pi^*\) transition and the less intense is due to \(n\rightarrow\pi^*\) transition. 

\(\pi\rightarrow\pi^*\) transition indicates the presence of aromatic nuclei and \(n\rightarrow\pi^*\) transition indicates the presence of –NH and –OH group.

The hyper chromic effect is due to the presence of –OH and –NH groups, which act as auxochrome. It is found that, as no. of aromatic ring and auxochrome phenolic - OH and -NH groups in the repeated unit increases, there will be increase in \(\varepsilon_{max}\) values. The observation is in good agreement with proposed structures of above terpolymer resins.
Table 1: Elemental Analysis

<table>
<thead>
<tr>
<th>Empirical formula of repeat unit</th>
<th>Carbon%</th>
<th>Hydrogen%</th>
<th>Nitrogen%</th>
<th>Sulphur%</th>
<th>Empirical weight of repeat unit, g</th>
<th>Average degree of polymerization (DP)</th>
<th>Average molecular weight (Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}H_{42}O_{12}S_{7}N_{2}</td>
<td>59.34(Cal)</td>
<td>6.59(Cal)</td>
<td>7.69(Cal)</td>
<td>8.79(Cal)</td>
<td>364</td>
<td>18.00</td>
<td>6552</td>
</tr>
<tr>
<td></td>
<td>59.64(F)</td>
<td>6.33(F)</td>
<td>7.99(F)</td>
<td>8.98(F)</td>
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</tbody>
</table>

**FT-IR Spectra**

The IR spectrum of 1-N-4-SAHDF-Resin-I is incorporated in Figure 3 and the studies revealed that terpolymers give rise to nearly similar pattern of IR spectra. A broad absorption band appeared in the region 3500-3510 cm\(^{-1}\) may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding\(^{13,14}\).

A sharp strong peak at 1500-1650 cm\(^{-1}\) may be ascribed to aromatic skeletal ring. The bands obtained at 1150-1250 cm\(^{-1}\) suggest the presence of methylene (-CH\(_2\)) bridge. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 960-980, 1120-1055, 1210-1182 and 1320-1280 cm\(^{-1}\) respectively. The presence of sharp and strong band at 3390-3410 cm\(^{-1}\) indicates the presence of -NH Bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

**\(^1H\) Nuclear Magnetic Resonance Spectra**

The \(^1H\) NMR spectrum of 1-N-4-SAHDF-Resin-I terpolymer was scanned in DMSO-d\(_6\) and has been shown in Figure 4. The chemical shift (δ) in ppm has been assigned on the basis of data available in literature. The 1-N-4-SAHDF-Resin-II terpolymer resin shows a multiplet signal at δ 2.56 ppm which may be attributed to methyl proton of Ar-CH\(_2\) group. The signal obtained in the region of δ 3.46 ppm may be due to the methylene proton of Ar-CH\(_2\)-N moiety. The signal in the region of δ 6.2 ppm is attributed to protons of bridge –NH. The weak multiplet signal (unsymmetrical pattern) in the region of δ 6.62 ppm may be due to terminal methylene group. The signals in the range at δ 10.21 ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding of -OH group\(^15\). The multiplets at δ 1.29 ppm and 1.55 ppm may due to -CH\(_2\)-CH\(_2\) moiety of amine. The signal at δ 7.52 ppm may due to aromatic proton (Ar-H). The signal obtained at 9.41 ppm may assigned to sulphonic group.

**\(^{13}C\) Nuclear Magnetic Resonance Spectra**

\(^{13}C\) NMR spectrum of 1-N-4-SAHDF-Resin-I has been recorded as shown in Figure 4. \(^{13}C\) NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton of the terpolymer. The \(^{13}C\) NMR spectrum of 1-N-4-SAHDF-Resin-II shows the corresponding peaks at 155.56, 107.8, 126.1, 133.89, 130.2, 126.6, 127.4, 126.32, 122.45, 126.21 ppm with respect to C\(_1\) to C\(_{26}\) of the aromatic napthalene ring. The shifting of signals is due to the substitution in napthalene ring. More electronegative group is bonded to Carbon atom, de-shielding shifts increases\(^{16}\). Thus, the peak of C\(_1\) at 155.56 ppm may be

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**Figure 2:** UV-visible spectrum of 1-N-4-SAHDF-Resin-I

**Figure 3:** IR Spectrum of 1-N-4-SAHDF-Resin-I

**Figure 4:** NMR spectrum of 1-N-4-SAHDF-Resin-I
because of deshielding effect by –OH grp. The signal at 42.1 ppm may be assigned to –C-NH- grp. Of hexamethylene diamine moiety. Two peaks more are obtained for hexamethylene diamine, out of which peak at 26.5 ppm may be because of methylene -CH₂- grp. The 13C NMR spectrum after analysis minutely confirmed that the monomers are arranged in a straight manner, giving the linear structure for terpolymer, which we have proposed is obviously correct given in Figure 1.

CONCLUSION

The new terpolymer 1-N-4-SAHDF-Resin-I has been synthesized by condensation polymerization of 1-Naphthol-4-sulphonic acid and Hexamethylene diamine with formaldehyde in the presence of acid catalyst.

This brown coloured newly synthesized terpolymer resin is soluble in DMF, DMSO, THF and aq. NaOH and insoluble in common organic solvents.

On the basis of nature and reactive positions of the monomers, molecular weight, elemental analysis, electronic, IR, and NMR spectra, the structure of 1-N-4-SAHDF-Resin-I terpolymer has been determined.

The synthesized terpolymer may find variety of applications in the field of material science.

REFERENCES


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