Research Article

Synthesis and Characterization of Newly Synthesis Polymer Resin 1-N-4-SAHDF-I

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ABSTRACT

A new terpolymer resin was synthesized from 1-Naphthol-4-sulphonic acid and Hexamethylene diamine with formaldehyde by polycondensation method in an acidic medium with molar proportion of reactants (1:1:2). To reveal the structure of the resin, the resin was characterized by elemental analysis and spectral methods, i.e. composition of terpolymer has been determined in the basis of their elemental analysis. The terpolymer resin has been characterized by UV-Visible, FT-IR and NMR (^{1}H & ^{13}C) spectra. The number average molecular weight has been determined by conductometric titration in non-aqueous medium. The structure of the terpolymer resin was confirmed on the basis of spectral data.

Keywords: Resin, Synthesis, Terpolymer, NMR, polycondensation.

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-hydroxyacetophenone-formaldehyde resin[4], and oximes of 2-hydroxyacetophenone substituted benzoic acid-formaldehyde resin[5] for different metal ions. Thermogravimetric analysis of urea formaldehyde polycondensate (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-thiourea-paraformaldehyde and anthranilic acid-thioureapara formaldehyde resins were synthesized and reported for its excellent ion-exchange capacity[7]. In an earlier communication from this department numbers of studies on such terpolymers have been reported[8-11]. However no work seems to have been carried out on synthesis, characterization of the terpolymer resin from 1-Napthol-4-sulphonic acid-Hexamethylene diamine 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 Hexamethylene diamine (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 in 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

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reprecipitation was repeated twice. The terpolymer sample 1-N-4-SAHDF-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%.
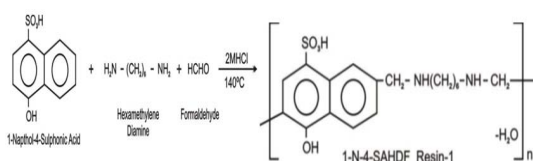

Figure 1: Reaction and suggested structure of representative 1-N-4-SAHDF-Resin-I terpolymer

Characterization

1-N-4-SAHDF-Resin-II terpolymer resins 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 dimethylsulphoxide (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-SAHDF-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 ^{1}H & ^{13}C 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-SAHDF-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 synthesize 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.

$$DP = \frac{\text{Total meq. of base required for complete neutralization}}{\text{Meq. of base required for smallest interval}}$$

$$(Mn) = (DP) \times \text{Repeat unit weight}$$

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.

Table 1: Details of Elemental analysis and molecular weight

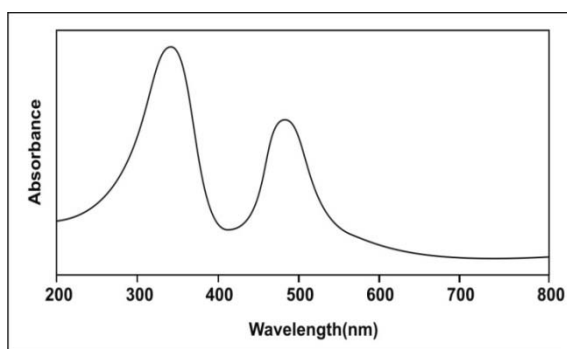| Empirical Formula of Repeat unit	Carbon%	Hydrogen%	Nitrogen%	Sulphur%	Empirical Weight of Repeat unit, g	Average Degree of Polymerization (DP)	Average Molecular Weight (Mn)
$C_{40}H_{40}O_{12}S_3N_2$	59.34(Cal)	6.59(Cal)	7.69(Cal)	8.79(Cal)	364	18.00	6552
	59.64 (F)	6.33 (F)	7.99 (F)	8.98 (F)			

UV-Visible Spectra

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

The UV-Visible spectra of 1-N-4-SAHDF-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-SAHDF-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 $\pi\text{-}\pi$* transition and the less intense is due to n π* transition.

$\pi\text{-}\pi$* transition indicates the presence of aromatic nuclei and n π* transition indicates the presence of –NH and –OH group. The hyperchromic effect is due to the presence of –OH and –NH groups, which act as

auxochrome[12]. 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 λ max values. The observation is in good agreement with proposed structures of above terpolymer resins.

FT-IR Spectra

The IR spectra 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 (-CH2) 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.
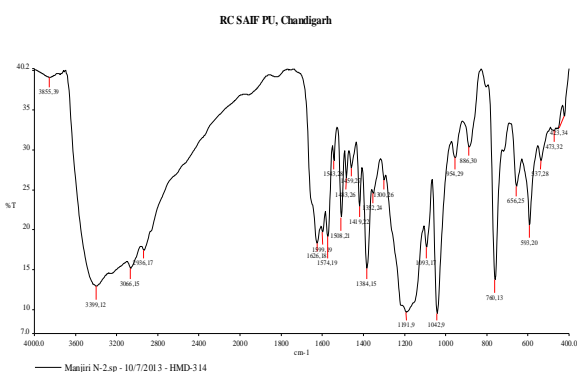

Figure 3: IR Spectrum of 1-N-4-SAHDF-Resin-I

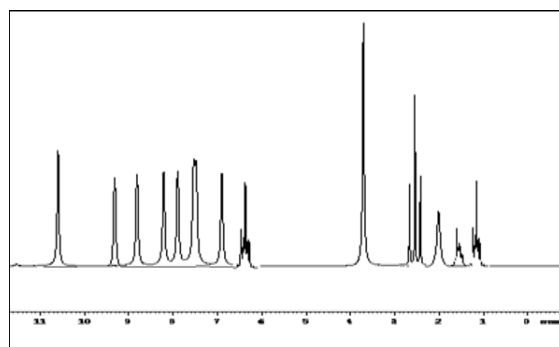### H[1] Nuclear Magnetic Resonance Spectra

Figure 4: NMR spectrum of 1-N-4-SAHDF-Resin-I

The H[1] NMR spectrum of 1-N-4-SAHDF-Resin-I terpolymer was scanned in DMSO-d[6] and has been shown in Figure 3. 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 an multiplate signals at δ 2.56 ppm which may be attributed to methyl proton of Ar-CH3group. The singlet obtained in the region of δ 3.46 ppm may be due to the methylene proton of Ar-CH2-N

moiety. The signal in the region of δ 6.2 ppm is attributed to protons of bridge –NH. The weak multiplate 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 multiplates at δ 1.29 ppm and 1.55 ppm may due to -CH2-CH2- moiety of amine. The signal at δ 7.52 ppm may due to aromatic proton (Ar-H). The singlet obtained at 9.41ppm may be assigned to sulphonic group.

13C Nuclear Magnetic Resonance Spectra

13C NMR spectrum of 1-N-4-SAHDF-Resin-I has been recorded as shown in Figure 5. 13C NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton of the terpolymer. The 13C NMR spectrum of 1-N-4-SAHDF-Resin-I 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_{10} 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, deshielding shifts increases[16]. Thus, the peak of C_1 at 155.56 ppm may be because of deshielding effect by –OH grp. The signal at 42.1 ppm may be assigned to -C-NH-group 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-group. 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.
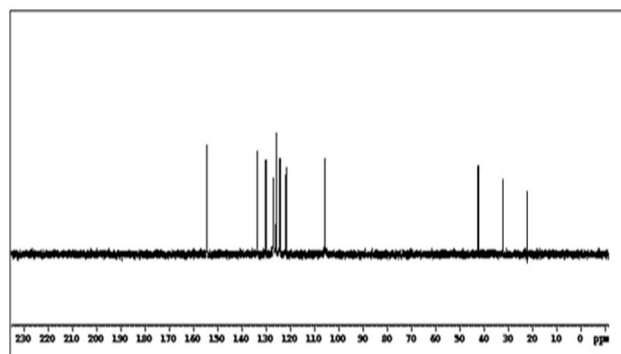

Figure 5: 13C Nuclear Magnetic Resonance Spectra of 1-N-4-SAHDF-Resin-I

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the 1-N-4-SAHDF-Resin-I has been recorded as shown in Figure 6. The SEM micrographs of 1-N-4-SAHDF-Resin-I sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the

spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions[17]. Thus SEM study shows that the 1-N-4-SAHDF-Resin-I has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.
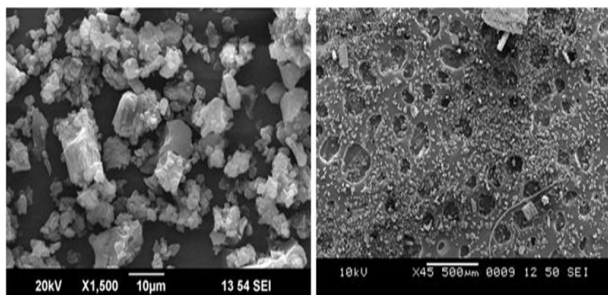

Figure 6: SEM micrographs of 1-N-4-SAHDF-Resin-I

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.

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