Synthesis of new terpolymer resin-II derived from 8-hydroxyquinoline 5-sulphonic acid and oxamide with formaldehyde and its characterization

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ABSTRACT

Terpolymer (8-HQ5-SAOF-II) was synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and oxamide (O) with formaldehyde (F) in the presence of acid catalyst. The terpolymer resin was synthesized by (2:1:3) molar proportion of the reacting monomers. The terpolymer resin composition has been determined on the basis of elemental analysis. The number average molecular weight of this resin was determined by conductometric titration in non-aqueous medium. Viscometric measurement in dimethylsulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. Uv-Visible spectra, FTIR, ^1H NMR and ^{13}C NMR spectra were studied to elucidate the structure. The morphology of terpolymer was studied by SEM.

Keywords*: Synthesis, polycondensation, resins, spectra, morphology.*

INTRODUCTION

The synthesis of new terpolymers attracted the attention of researcher because of versatile utility in our day-to-day life. Resins as terpolymers which form special class of polymers are widely known for their uses. Various modified phenol-formaldehyde resins have large number of practical applications [1-3] viz. high thermal conducting material, excellent abrasive, ion exchangers and many more other renowned applications are reported in the literature. Synthesis of various kinds of terpolymers using varied organic compounds, their physico-chemical properties and applications were studied by various co-workers [4, 5]. M.M.Jadhao et al [6] have synthesized and studied the ion-exchange properties of 2, 2'-dihydroxy biphenyl, urea and formaldehyde terpolymer resins. Extensive research work has been reported on terpolymer resins derived from phenolic compounds-amine /amide-trioxane/ formaldehyde from this department [7, 8]. However no work seems to have been carried out on synthesis and physico-chemical technique used for the characterization of newly synthesized terpolymer resin-II derived from 8-hydroxyquinoline 5-sulphonic acid and oxamide with formaldehyde. The present paper includes the synthesis of this new terpolymer resin and its systematic structural study with the help of elemental, spectral studies and other various physico-chemical techniques.

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MATERIALS AND METHODS

Materials

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

Synthesis of 8-HQ5-SAOF-II terpolymer resin

The new terpolymer resin 8-HQ5-SAOF-II was synthesized by condensing 8-hydroxyquinoline 5-sulphonic acid (4.86g, 0.2 mol) and oxamide (0.88g, 0.1 mol) with 37% formaldehyde (11.1 ml, 0.3 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at $130^0C \pm 2^0C$ for 6h 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 8-hydroxyquinoline 5-sulphonic acid- formaldehyde copolymer which might be present along with 8-HQ5-SAOF-II terpolymer. The yellow colour resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 8-HQ5-SAOF-II is shown in Fig. 1.

The terpolymer was purified by dissolving in 8% 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 8-HQ5-SAOF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the terpolymer resin was found to be 80%.The sample yield (%) and reaction details are tabulated in Table 1.
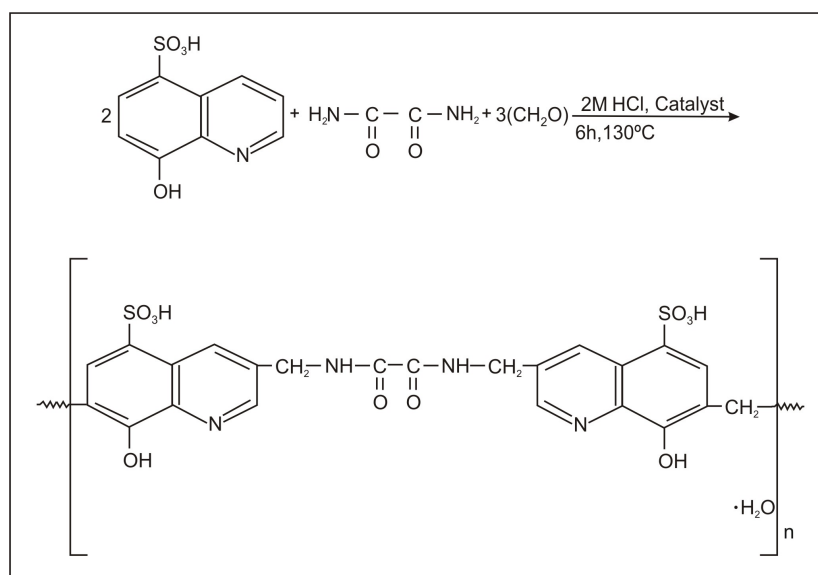

Fig. 1 Reaction and suggested structure of 8-HQ5-SAOF-II terpolymer resin

Characterization

The viscosity was determined using Taun-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.031% of terpolymer in DMSO at 30°C. the intrinsic viscosity (η) was calculated by relevant plots of the Huggins' equation and Kraemmer's equation.

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$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \quad \ldots\ldots\ldots(1)$$

$$\ln \eta_{rel}/C = [\eta] + K_2 [\eta]^2 C \quad \ldots\ldots\ldots(2)$$

The number average molecular weight $(\overline{Mn})$ 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 $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ has been calculated for the terpolymer resin.

Uv-Visible spectrum of terpolymer resin was recorded in DMSO (spectroscopic grade) on shimadzu double beam spectrophotometer in the range of 200 to 850. An infra-red spectrum of 8-HQ5-SAOF-II terpolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000 - 400 cm^{-1}. A Nuclear Magnetic Resonance (NMR) spectrum of newly synthesized terpolymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d$_6$. The ^{13}C NMR spectrum was also recorded using Bruker 400 MHz to identify the carbon linkage.

RESULTS AND DISCUSSION

The newly synthesized purified 8-HQ5-SAOF-II terpolymer resin was found to be yellow in colour. The terpolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of the terpolymer was determined by using electrically heated melting point apparatus and is found to be of 422 K. This resin was analyzed for carbon, hydrogen and nitrogen content. The details of synthesis of terpolymer along with colour, melting point, yield and elemental analysis are incorporated in Table 1. The terpolymer which has been used in the present investigation was prepared by the reaction given in Fig. 1.

Table 1 Synthesis and physical data of 8-HQ5-SAOF-II terpolymer resin

Terpolymer	Reactants			Catalyst 2M HCL (ml)	Yield (%)	Color	Melting point (K)	Elemental Analysis			
	8-hydroxyquinoline 5-sulphonic acid (mol)	oxamide (mol)	Formaldehyde (mol)					% of C Found (Cal.)	% of H Found (Cal.)	% of N Found (Cal.)	% of S Found (Cal.)
8-HQ5-SAOF-II	0.2	0.1	0.3	200	80	Yellow	422	45.98 (45.4)	3.15 (3.2)	8.97 (8.4)	10.23 (10.8)

Viscosity measurements were carried out at 300 K in freshly triple distilled Dimethyl Sulphoxide (DMSO) using Tuan-Fuoss Viscomer, at six different concentrations ranging from 1.00% to 0.031%. Reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity [η] was determined by the corresponding linear plot (Fig. 2). Huggins' and Kraemer's constants were determined by an expression 1 and 2.

According to the above relations, the plots of η_{sp}/C and $\ln\eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give [η] value in both plots. The values of intrinsic viscosity obtained from both plots have been found to be closed agreement with each other. The calculated values of the constants K_1 and K_2 (Table 2) in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably [9].

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Table 2 Molecular weight determination and Viscometric data of the 8-HQ5-SAOF-II terpolymer resin

Copolymer	Empirical formula of repeat unit	Empirical weight of repeat unit (gm)	Average degree of polymerization $(\overline{DP})$	Average molecular weight $(\overline{Mn})$	Intrinsic viscosity $[\eta]$ (dl/g)	Huggins' constant K_1	Kraemmer's constant K_2	$K_1 + K_2$
8-HQ5-SAMF-II	$C_{23}H_{21}N_4O_{11}S_2$	592	17.00	10064	1.12	0.253	0.251	0.504
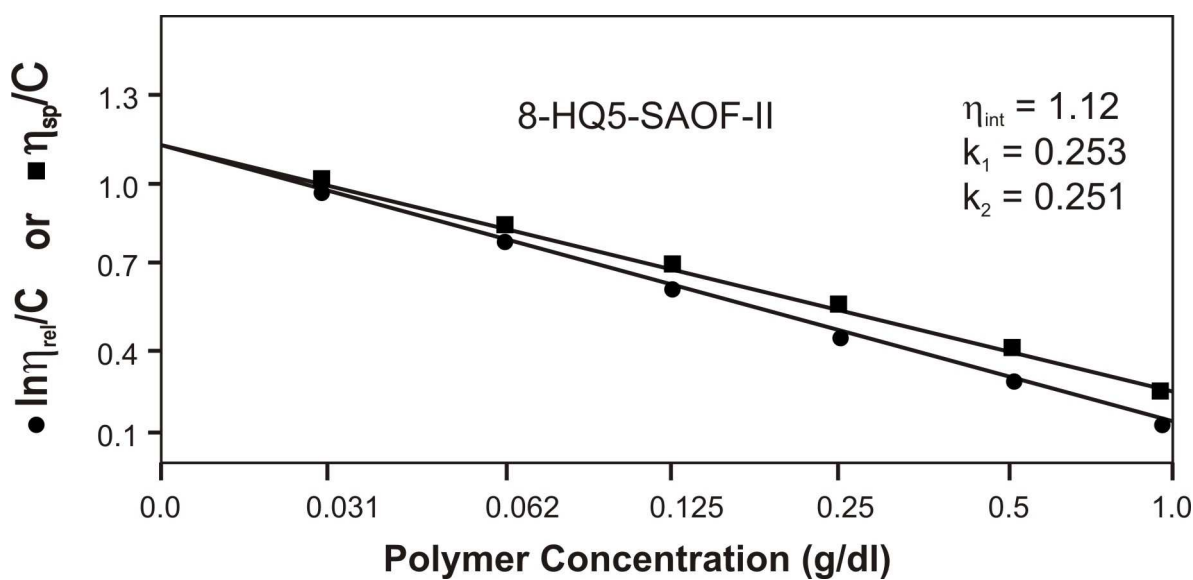
Fig. 2. Viscometric plots of terpolymer resin 8-HQ5-SAOF-II

The number average molecular weight $(\overline{Mn})$ of this terpolymer has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.05 M) in absolute ethanol as a titrant. The results are presented in Table 2. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of terpolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized.

From the plot (Fig.3) the first and final breaks were noted. The average degree of polymerization $(\overline{DP})$ and hence the number average molecular weight $(\overline{Mn})$ of the terpolymer has been determined using the formula. This observation is in agreement with the trend observed by earlier workers [10].

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequivalents of base required for smallest interval}}$$

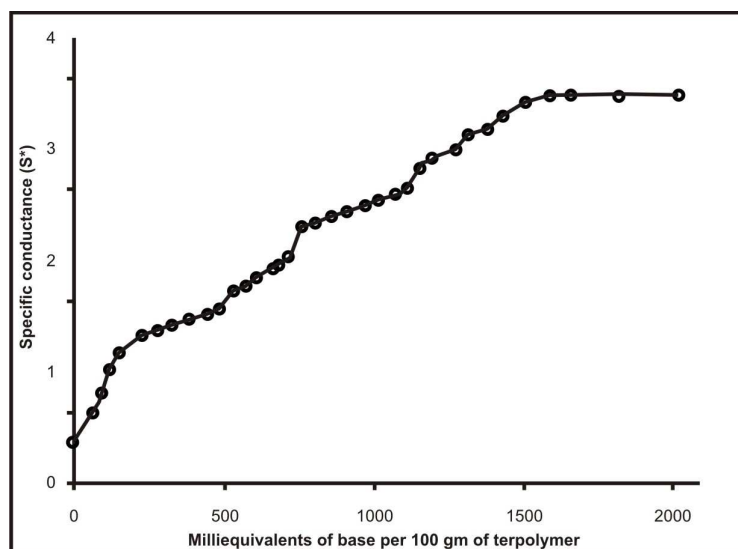$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight}$$

Fig. 3: Conductometric plot of terpolymer resin 8-HQ5-SAMF-II

The Uv-Visible spectra (Fig. 4) of the 8-HQ5-SAOF-II terpolymer sample in pure DMSO was recorded in the region 200-850 nm at a scanning rate of 100 nm min^{-1} and a chart speed of 5 cm min^{-1}. The 8-HQ5-SAOF-II terpolymer sample gave two characteristics bands at 320 nm and 250 nm. These observed positions for the absorption bands have different intensities. The more intense band 2580 nm is due to $(\pi \rightarrow \pi *)$ allowed transition of quinoline ring , which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromophore groups like >C=C, >C=N and –SO_3H groups and the less intense 320 nm   may be due to $(n \rightarrow \pi *)$ forbidden transition in >C=N and –SO_3H groups .Thus $\pi \rightarrow \pi *$ transition indicates the presence of aromatic nuclei and $n \rightarrow \pi *$ transition indicates the presence of –NH and –OH group. The bathochromic shift from the basic value viz. 210 nm and 300 nm may be due to combined effect of conjugation (due to chromophore) and phenolic hydroxyl groups as well as –NH groups (auxochrome). The hyperchromic effect is due to the presence of –OH and -NH groups, which act as auxochrome [11].
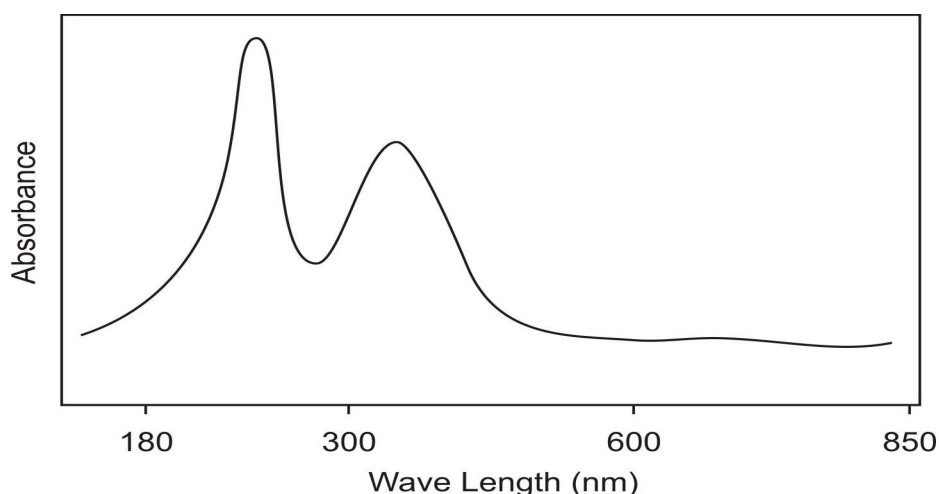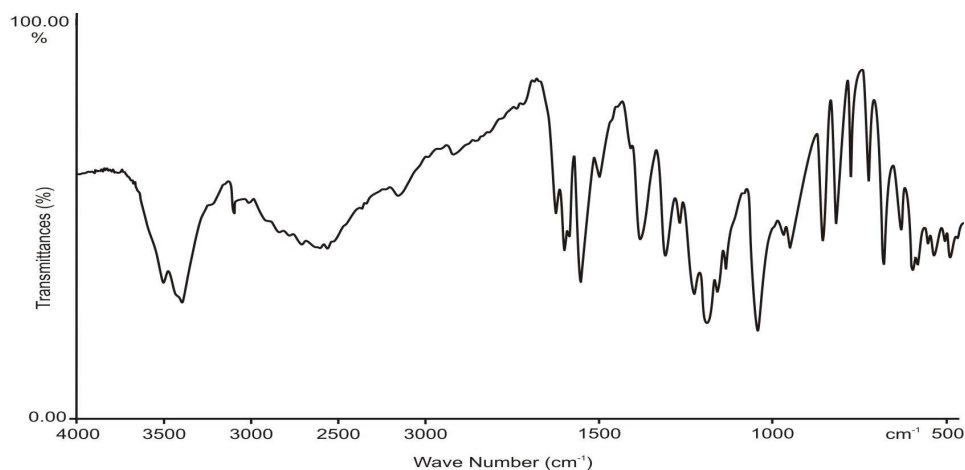

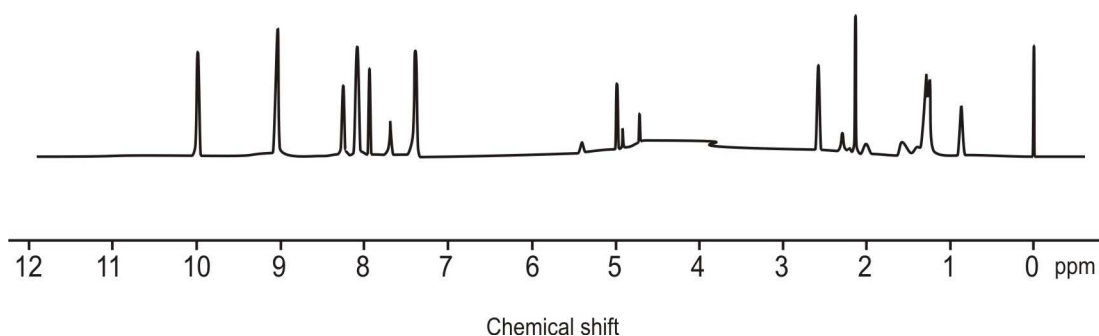**Fig. 4: Uv-Visible Spectra of terpolymer resin 8-HQ5-SAOF-II**

The IR spectrum is depicted in Fig. 5. A broad absorption band appeared in the region 3507 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding.[12] A sharp strong peak at 1551 cm^{-1} may be ascribed to

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aromatic skeletal ring. The bands obtained at 1303 cm^{-1} suggest the presence of methylene (-CH$_2$) bridge [13]. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 957, 1071and 1141 cm^{-1} respectively. The presence of sharp and strong band at 3398 cm^{-1} indicates the presence of –NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

Fig. 5: Infrared Spectra of terpolymer resin 8-HQ5-SAOF-II

The NMR Spectra of the 8-HQ5-SAOF terpolymer was scanned in DMSO-d$_6$ solvent. The spectrum has been given in Fig. 6. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [14]. The singlet obtained in the region 4.67 (δ) ppm may be due to the methylene proton of Ar-CH$_2$-N moiety. The signals in the region 7.44 (δ) ppm are attributed to protons of –NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region of 8.97 (δ) ppm may be attributed to aromatic proton (Ar-H). The signals in the range at 9.04 (δ) 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, 16]. The signals in the range of 9.99(δ) ppm are attributed to proton of -SO$_3$H groups.

Chemical shift
Fig. 6: NMR Spectra of terpolymer resin 8-HQ5-SAMF-II

A ^{13}C NMR spectrum of 8-HQ5-SAOF-II terpolymer resin has been shown in Fig. 7. The assignment of the position of the peaks in the ^{13}C NMR spectra has been studied according to the literature [17]. The Carbon NMR spectrum of 8-HQ5-SAOF-II terpolymer resin shows different signals for each carbon atom. The peaks appeared at 155.2, 123.3, 137.8 130.6, 129.5, 128.2, 127.3, 130.3 and 147.4 ppm may be corresponded to carbon number one to nine (1-9) of the aromatic quinoline ring. The peak appeared at 178.2 and 179.3 ppm of may be corresponded to carbon of carbonyl group (C$_1$ and C$_2$) of oxamide moiety. The peak appeared at 118.3 ppm may be confirmed the presence of -C-NH group in the terpolymer resin. The peak appeared at 60.5

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ppm may be due to the presence of -C-OH group. The peak appeared at 39.8 ppm may be due to the -CH$_2$- bridge in terpolymer molecular. All these peaks and their minute and proper study confirmed that the 8-HQ5-SAOF-II terpolymer resin must have linear structure. Thus the linear structure of 8-HQ5-SAOF-II terpolymer resin can be confirmed by Carbon NMR spectra.
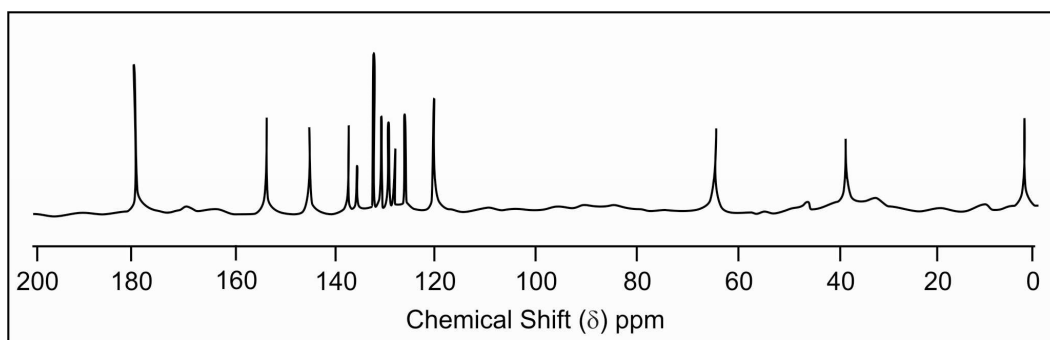

Fig 7 ^{13}C NMR spectra of 8-HQ5-SAOF-II terpolymer resin

The SEM micrographs (Fig.8, A & B) of 8-HQ5-SAOF-II terpolymer resin sample exhibits spherulites with deep corrugation [18]. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline formation composed of simplest structural formula having smoothest surface free from defects of growth. The crystals are smaller in surface area with less closely packed structure. Thus the spherulites morphology of resin exhibit crystalline structure of resin 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. Thus SEM study shows that the 8-HQ5-SAOF-II terpolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.
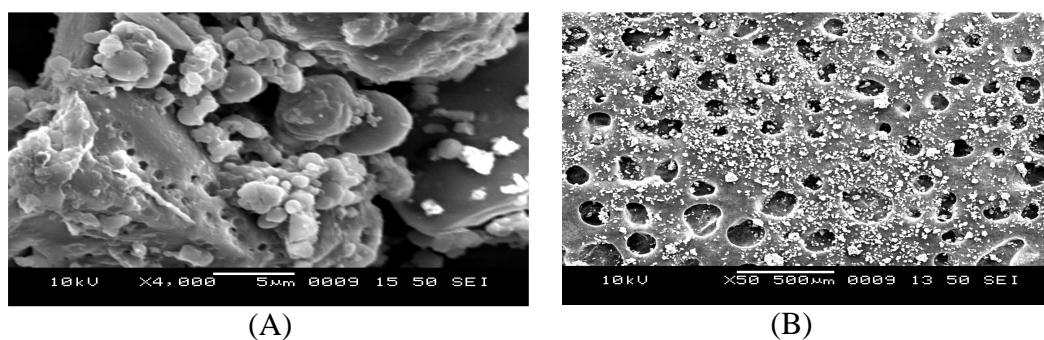

(A)   (B)

Fig 8 SEM micrographs of 8-HQ5-SAOF-II terpolymer resin

The polymer under study is terpolymer and hence, it is very difficult to assign their exact structure. However, on the basis of the nature and reactive site of the monomers and taking into consideration the linear structure of other substituted phenol formaldehyde polymers and the linear branched nature of urea-formaldehyde polymers the most probable structures of proposed for 8-HQ5-SAOF-II terpolymer has been shown in Fig. 1.

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CONCLUSION

Terpolymer 8-HQ5-SAOF-II, based on the condensation reaction of 8-hydroxyquinoline 5-sulphonic acid, oxamide and formaldehyde in the presence of acid catalyst, was prepared by using varied molar proportion for the reacting monomers. Terpolymer 8-HQ5-SAOF-II is yellow in color, partly soluble in methanol and completely soluble in DMF and DMSO and insoluble in almost all other common solvents. From the elemental analysis, Uv-Visible, FTIR, NMR spectral studies, the proposed structure of the 8-HQ5-SAOF-II terpolymer was determined.

The morphological study by SEM indicates that the terpolymer resin can be used as cation ion-exchanger for the separation of transition metal ions. The resins can also be used for removal of toxic metals. The resins can form polychelates with certain metal ions. Therefore it can be used for the separation of metal ions from the mixture.

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