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Synthesis and Characterization of 8-Hydroxyquinoline-Melamine-Formaldehyde Terpolymers

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The terpolymer resins have been synthesized by the condensation of 8-hydroxyquinoline (Q) with melamine (M) and formaldehyde (F) in the presence of 2M HCl as catalyst. Four different types of 8-HQMF terpolymer resins with different stoichiometry have been synthesized by taking different molar ratios of 8-hydroxyquinoline : melamine : formaldehyde as (1 : 1 : 3), (2 : 1 : 3), (3 : 1 : 5) and (4 : 2 : 7). The terpolymer resins were purified by suitable method. The terpolymers were characterized by elemental analysis, UV-visible, infrared and ^{1}H NMR spectral studies. The number average molecular weights of terpolymers resins have been determined by conductometric titrations in non-aqueous medium and vapour pressure osmometry (VPO). Viscometric measurements in dimethylformamide (DMF) have been carried out in order to ascertain the characteristic functions and constants of terpolymer resins. The structures of the terpolymer resins have been established by analytical and spectral data.

INTRODUCTION

Various hydroxybenzoic acid-formaldehyde copolymers have been reported to find use as ion exchangers[1–3]. Copolymers can also be synthesized by the condensation of a mixture of phenols or hydroxybenzoic acid, various amines and formaldehyde[4–7]. Chelating ion-exchange resins prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like *o*-aminophenol or resorcinol with formaldehyde have been reported by Pennington and Williams[8] and by Aristov and Kostantinov[9]. Ion-exchange resins incorporating 8-hydroxyquinoline (oxine) have been known but their properties have not been completely investigated. However, in further work Vernon and Nyo[10] claimed to have optimized the synthesis of condensation resins from oxime. Patel and Patel[11] have synthesized and characterized 2-hydroxy-4-methoxy-acetophenoxime-urea-formaldehyde resins. Manavalan and Patel[12] have synthesized salicylic acid-thiourea-trioxane terpolymer resins in acidic medium and characterize these resins. The present work reports on the composition of these newly synthesized terpolymer resins and their characterization by elemental analysis, molecular weight ($\overline{Mn}$), intrinsic viscosity in DMF, IR spectra, absorption spectra and ^{1}H NMR spectra.

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EXPERIMENTAL

All chemicals used were of analytical grade or chemically pure grade. DMF was used after distillation.

Synthesis of 8-HQMF Terpolymers: The 8-HQMF terpolymer resins were prepared by condensing 8-hydroxyquinoline (8-HQ) and melamine (M) with formaldehyde (F) in the mole ratios of 1 : 1 : 3, 2 : 1 : 3, 3 : 1 : 5 and 4 : 2 : 7 respectively, in the presence of 2M HCl (200 mL). The mixture was heated at 130 ± 2°C in an oil bath for 6 h[13–15]. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air-dried terpolymer resin was extracted with ether to remove excess of 8-hydroxyquinoline-formaldehyde copolymer which might be present along with 8-HQMF terpolymer. It was further purified by dissolving in 8% NaOH and filtered. It was then precipitated by dropwise addition of 1 : 1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified terpolymers were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel.

Characterization of the terpolymers

The carbon, hydrogen, nitrogen analyses were made on the Carlo-Erba Elemental Analyzer. Molecular weight of the terpolymers were determined by non-aqueous conductometric titrations in DMF against standard ethanolic KOH solution[13–17]. Number average molecular weight ($\overline{Mn}$) of all the terpolymers has been estimated by vapour pressure osmometry (VPO) method using DMF as solvent and benzil as calibrant. The Wescan Model 233 vapour pressure osmometer has been used for this purpose. The viscosities were determined using a Tuan-Fuoss[18] viscometer at six different concentrations ranging from 3.0 to 0.5 wt. % of resin in DMF at 30°C. Infrared spectra of 8-HQMF terpolymers were scanned in the solid state (KBr pellets) on Magna 550, series II Nicolet USA FTIR Spectrophotometer in the range 4000–400 cm^{-1}. Electronic absorption spectra of the terpolymers in DMF were recorded at room temperature in 190 to 700 nm range by using UV-240 Shimadzu automatic recording double beam spectrophotometer. ^1H NMR spectra were scanned on 90 MHz for ^1H proton using Perkin-Elmer Model R-32 NMR spectrophotometer in DMSO-d_6 solvent.

RESULTS AND DISCUSSION

The terpolymer sample was yellow in colour, insoluble in commonly used organic solvents, but was soluble in DMF, DMSO, THF, aq. NaOH and concentrated sulphuric acid. Melting points of terpolymers were found in the range 233–285°C.The tentative structure of the terpolymers have been determined on the basis of elemental analysis and spectral data (Table-1). The details of synthesis of terpolymers along with colour are incorporated in Table-1.

TABLE-1
CHARATERIZATION OF TERPOLYMERS

Terpolymer	Reactants			Catalyst (2 M)	Colour	Yield (%)	Elemental Analysis (%)		
	8-hydroxyquinoline (mol)	Melamine (mol)	37% Formaldehyde (mol)				C	H	N
							Calcd. (Found)		
8-HQMF-1	0.1	0.1	0.3	HCl	Yellow	68.5	57.65 (58.44)	4.21 (4.54)	32.16 (31.81)
8-HQMF-2	0.2	0.1	0.3	HCl	Yellow	52.4	62.77 (63.85)	4.39 (4.21)	25.77 (24.83)
8-HQMF-3	0.3	0.1	0.5	HCl	Yellow	44.2	65.15 (66.77)	4.63 (4.74)	20.02 (20.62)
8-HQMF-4	0.4	0.2	0.7	HCl	Yellow	39.5	62.82 (64.19)	4.52 (4.36)	25.37 (24.45)

The molecular weight ($\overline{Mn}$) of the resins was determined by non-aqueous conductometric titration in DMF against ethanolic potassium hydroxide by taking 50 mg of sample. A plot of the 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 were many breaks in the plot. From this plot the first and last break were noted. The calculation of $\overline{Mn}$ by this method is based on the following considerations[16, 19]: (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 is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized. On this basis, the average degree of polymerization $\overline{DP}$ is given by the following relation:

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

The number average molecular weight ($\overline{Mn}$) could be obtained by multiplying the formula weight of the repeating unit[16, 20]

Molecular weights of terpolymers were also estimated by vapour pressure osmometry[14, 15] (Table-2). The molecular weights of terpolymer samples estimated by conductometric titration and VPO method are comparable within limits of experimental errors. The results of the molecular weight of terpolymer samples prepared using higher proportion of the two monomers (8-HQ and M) has the highest molecular weight in the series.

Viscosity measurements were carried out in DMF at 30 ± 0.1 K. The terpolymer showed normal behaviour. The intrinsic viscosity was determined by the Huggin[21] equation:

$$\eta sp/c = [\eta] + k_1[\eta]^2C$$

and the Kraemer[22] equation:

$$\ln \eta r/c = [\eta] - k_2[\eta]^2C$$

TABLE-2
MOLECULAR WEIGHT DETERMINATION, VISCOMETRIC DATA AND IR FREQUENCIES OF TERPOLYMERS

Polymers	$\overline{Mn}$		Intrinsic viscosity $[\eta] \times 10^2$ (dl/g)	Huggin's constant k_1	Kraemer's constant k_2	$k_1 + k_2$	Important IR frequencies	
	By conductometric titration	By VPO					Wave number (cm^{-1})	Assignments
8-HQMF-1	2771	2820	0.144	2.60	–2.12	0.480	3300–3400 (br)	—OH stretching (Phenolic)
8-HQMF-2	3896	3785	0.182	2.50	–2.00	0.500	3100–3190 (w)	>NH stretching (imido)
8-HQMF-3	4935	4876	0.217	2.22	–1.70	0.470	1628 (m)	>C=N stretching (melamine moeity)
8-HQMF-4	6622	6690	0.249	2.00	–1.48	0.520	1528–1552 (s)	Aromatic ring
							2950 (m), 800 (s)	>CH_2 (methylene) bridges
							1371–1395 (s)	5,7,8-Trisubstituted aromatic oxine ring
							1156 (m)	—C=C stretching (aromatic)
							1033 (s)	—C—H in-plane bending (aromatic)

In accordance with the above relations the plots of $\eta sp/c$ and $\ln \eta r/c$ against C were linear giving as a slope k_1 and k_2, respectively. Intercepts on the axis of viscosity functions gave the $[\eta]$ value in both the plots. The values of $[\eta]$ obtained from both relations were in agreement with each other. The values of Huggins and Kraemer's constants k_1 and k_2 were determined from the slope of the graph and satisfy the condition of the relation $k_1 + k_2 = 0.5$ favourably[23].

UV-Visible spectra of all purified 8-HQMF terpolymers have been recorded in pure DMF. The perusal of the UV-visible spectra of 8-HQMF terpolymers showed almost similar nature. The spectra of these terpolymers exhibit two absorption maxima in the regions 260–280 nm and 320–330 nm. A broad band at 260–280 nm indicates the presence of carbonyl (>C=O) group containing carbon-oxygen double bond in conjugation with aromatic nucleus and is ascribed to $\pi \rightarrow \pi^*$ transition[24]. The absorption band at 320–330 nm indicates the presence of >C=N— (endocyclic double bond) group which is in conjugation with the aromatic nucleus of melamine and is assigned to n → π* transition[25].

The shift towards longer wavelength, *i.e.*, bathochromic shift from the basic values, *viz.*, 240 and 310 nm respectively may be due to conjugation effect and presence of phenolic hydroxy group (auxochrome) is responsible for hyperchromic effect, *i.e.*, higher ε_{max} values[25, 27]. From the spectra of 8-HQMF terpolymers it is observed that ε_{max} value gradually increases in the order given below:

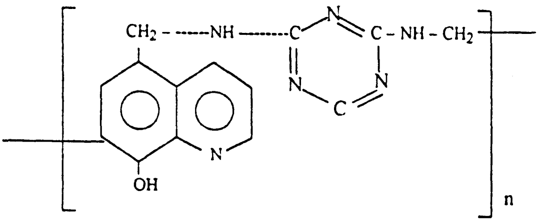
8-HQMF-1 < 8-HQMF-2 < 8-HQMF-3 < 8-HQMF-4

The increasing order of ε_{max} values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic —OH group) in the repeat unit of the terpolymers[26, 27].

From IR spectral studies it is found that all the terpolymer resins give rise to similar spectra. A broad band containing several inflections appearing in the region 3400–3300 cm^{-1} may be assigned to the stretching vibration of phenolic —OH group, which is known to be the lower side due to intermolecular hydrogen bonding[25, 28, 29]. The presence of —NH— stretch in melamine moiety may be assigned because of broad band in the region 3190–3100 cm^{-1}. The sharp band at 1628 cm^{-1} is due to —C=N— sretching of melamine moiety[30] and the bands obtained at 1552, 1528 cm^{-1} may be ascribed to aromatic skeletal ring[13, 15]. The bands obtained at 2950 cm^{-1} and 811 cm^{-1} are due to stretching vibration of —CH_2 group which suggest the presence of methylene bridges in the polymeric chain[1, 20]. The presence of a very small but distinct band in the region 1395–1371 cm^{-1} may be attributed to the presence of 5,7,8-trisubstituted aromatic quinoline ring of the repeating unit. A band around 1156 cm^{-1} is due to —C=C— stretching vibration (aromatic) and band at 1033 cm^{-1} may be due to C—H in-plane bending[25, 31].

^{1}H NMR spectra of all terpolymers are scanned in DMSO-d_6 solvent. The NMR spectral data are incorporated in Table-3. The NMR spectra show that the intense signal arising in the region 8.7 to 9.0 δ(ppm) may occur on account of hydroxyl proton of phenolic —OH group involved in intermolecular hydrogen bonding[24, 25, 32]. A sharp intense peak in the region 7.5 to 7.8 δ(ppm) may be assigned to aromatic protons[24]. A weak signal which appeared in the range 4.1 to 4.6 δ(ppm) may be ascribed as proton of —NH— bridges[25]. The methylenic protons of Ar—CH_2—N moiety may be recognized from signals which appeared in the region 2.36 to 2.56 δ(ppm).

The terpolymers in the present study contain three monomers and hence it is rather difficult to assign exact structure to them. However, taking into account the above evidence and reactive positions of monomers and taking into consideration the linear structure of other substituted phenol-formaldehyde polymers[1, 6] and linear branched nature of urea-formaldehyde polymers, the most probable structure for 8-HQMF terpolymer may be a linear branched structure (I) as shown below.



(I)

TABLE-3

^{1}H NMR SPECTRAL DATA OF 8-HQMF TERPOLYMERS IN (DMSO-d_6)

Nature of proton assigned	Observed chemical shift δ(ppm)				Expected chemical shift δ(ppm)
	8-HQMF-1	8-HQMF-2	8-HQMF-3	8-HQMF-4	
Proton of phenolic —OH (involved in hydrogen bonding)	8.78	9.02	8.78	8.81	8–12
Aromatic proton (Ar—H) (unsymmetric pattern)	7.65	7.53	7.46	7.80	6–8
Proton of —NH— bridges	4.45	4.61	4.07	4.64	5.16
Methylene proton Ar—CH_2—N moiety	2.36	2.52	2.52	2.56	2.0–3.0

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