Terpolymer Resin–III: Synthesis and Characterization of 8-Hydroxyquinoline–Dithiooxamide–Formaldehyde Terpolymer Resins

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ABSTRACT: Terpolymer resins (8-HQDF) were synthesized by the condensation of 8-hydroxyquinoline (8-HQ) and dithiooxamide (D) with formaldehyde (F) in the presence of acid catalyst and using varied molar ratios of reacting monomers. Terpolymer resins compositions have been determined on the basis of their elemental analysis and the number average molecular weights of these resins were determined by conductometric titration in non-aqueous medium. Viscometric measurements in di-methyl formamide (DMF) have been carried out with a view to ascertain the characteristic functions and constants. The UV-visible, FTIR, and proton nuclear magnetic resonance (H$^+$ NMR) spectra were studied to elucidate the structure. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3330–3335, 2009

Key words: synthesis; polycondensation; resins; structure; degree of polymerization

INTRODUCTION

Much of research work has being carried out on the synthesis and characterization of thiourea containing terpolymer. A literature survey reveals that terpolymer derived from substituted hydroxy or dihydroxy–dithioxamide–formaldehyde resin shows improved ion-exchange properties, thermal resistance property, coordinating property, and good storage stability etc.[1–5]. Terpolymer derived from itaconic acid–acrylamide-2-acryl amido-2-methyl-propane sulphonic acid by free radical polymerization have been reported in literature.[6] 8-Hydroxyquinoline (8-HQ) and its derivatives are widely used as complexing agents in various applications due to their good complex forming ability.[7,8] Anupriya and Kannam[9] have synthesized 8-acryloyloxyquinoline (8-AQ) and polymerized it in MEK at 70°C using BPO initiator. Polychelates were obtained from an aqueous solution of Th(II), Cd(II), Zn(II), and Mg(II) ions when added to the polymer in aqueous NaOH. The IR spectra of these polychelates suggest that metals are coordinated through oxygen atom of the ester carbonyl and with the nitrogen atom.

Liu et al.[10] studied the interaction of heavy metal ions and chelating ion exchange resin containing 8-HQ. The resin has good selectivity to exchangeable adsorption of heavy metal ions including Cu(II), Hg(II), Pb(II), and Mg(II) under pH 5.0 and also suggested that the chelating ion-exchange resin containing 8-HQ could be used to enrich heavy metals in water and their analysis.

Shah et al.[11] have prepared chelating ion-exchange resin from salicylic acid–formaldehyde–resorcinol (SFR) using DMF as solvent at 80 ± 2°C. The resin was characterized by FTIR and elemental analysis. The physico-chemical properties of this ion-exchange resin were studied. The effect of pH, metal ion concentration, and rate of exchange of metal ions were also studied by employing batch equilibrium method. The constituents of brass were also analysed by selective sorption on column at optimized distribution cofficient values. Terpolymers of 8-hydroxyquinoline-formaldehyde-resorcinol/catechol were reported by Shah et al.,[12,13] and chromatographic column separation for various metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} have carried out using the quinoline base resins. The present work describes the synthesis and characterization of terpolymers derived from 8-hydroxyquinoline, dithioxamide, and formaldehyde.

EXPERIMENTAL

Materials

8-Hydroxyquinoline (Ranbaxy Fine Chemicals, Mumbai) purified by rectified spirit. Formaldehyde
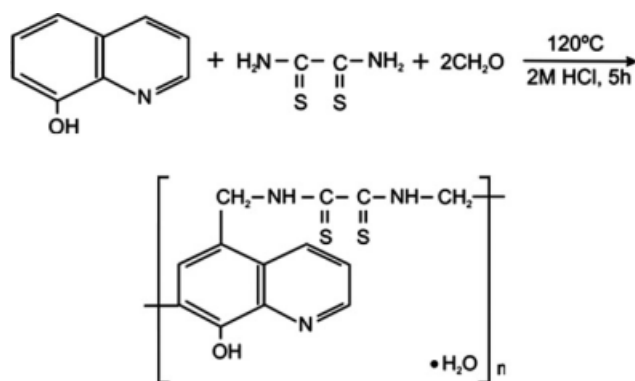
Figure 1 Synthesis of terpolymer resin.

(37%) (Qualigens Fine Chemicals, Mumbai) was used as received. Dithiooxamide (Loba, Mumbai, extra pure) was used as received. The solvents and monomers were purified by the conventional methods.[14]

Preparation of 8-HQDF terpolymer resin [8-HQDF-1]

A mixture of 8-hydroxyquinoline [1.45g, 0.1 mol], dithioxamide [1.20 g, 0.1 mol], and formaldehyde [7.50ml of 37% solution, 0.2 mol] in the presence of 2M hydrochloric acid (200 mL) was heated in an oil bath at 120°C ± 2°C for 5 h with occasional shaking.[15,16] The separated resinous product (8-HQDF-1) was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1 : 1 (vol/vol) HCl/water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions. The purified terpolymer resins were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of these terpolymer resins were found to be 73–88%. The reaction taking place is as shown in Figure 1.

Similarly, other terpolymer resins viz. 8-HQDF-2, 8-HQDF-3, and 8-HQDF-4 were synthesized by varying the molar proportion of the starting materials, i.e., 8-hydroxyquinoline, dithiooxamide, and formaldehyde in a ratio of 2 : 1 : 3, 3 : 1 : 4, and 4 : 1 : 5 (Table I).

Characterization of terpolymer resins

The terpolymer resins were subjected to microanalysis for carbon, hydrogen, and nitrogen on Perkin Elmer C, H, N, S analyzer. The number average molecular weights (Mn) were determined by conductometric titration in DMF using KOH in a 50% (vol/vol) DMF/alcohol mixture as a titrant. The viscosities were determined using Tuan-Fuoss viscometer at six different (concentration ranging from 3.0 wt %

TABLE I
Synthesis and Physical Data of Terpolymers

Terpolymer	Reactants					Elemental Analysis (%)								Decomposition temperature (K)
	8-Hydroxy quinoline (8-HQ) mol	Dithiooxamide [D] mol	Formaldehyde [F] mol	% yield	Color	% of C		% of H		% of N		% of S		
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
8-HQDF-1	0.1	0.1	0.2	73	Cream	50.81	49.72	4.23	3.32	13.68	4.72	20.8	19.2	392
8-HQDF-2	0.1	0.1	0.3	78	Cream	61.60	62.16	4.46	4.42	12.5	7.62	20.8	18.6	402
8-HQDF-3	0.1	0.1	0.4	82	Cream	64.15	63.36	4.71	4.58	11.00	8.12	20.8	18.4	421
8-HQDF-4	0.1	0.1	0.5	88	Cream	63.32	62.18	4.37	4.36	10.78	8.14	20.8	21.3	430

Terpolymer	Expirical formula of repeating unit	Empirical formula weight	$\overline{Dp}$	$\overline{Mn}$	Intrinsic viscosity $[\eta]$ dl g^{-1}	Huggin's constant (K_1)	Kraemer constant (K_2)	$K_1 + K_2$
8-HQDF-1	$C_{13}H_{11}N_3S_2O.H_2O$	307	13.37	4104	0.144	−0.320	−0.2448	0.5648
8-HQDF-2	$C_{23}H_{18}N_4S_2O_2.H_2O$	464	15.7	7284	0.147	−0.270	−0.292	0.5620
8-HQDF-3	$C_{34}H_{28}N_5S_2O_3.H_2O$	636	17.71	11263	0.149	−0.260	−0.030	0.5600
8-HQDF-4	$C_{43}H_{32}N_6S_2O_4.H_2O$	778	18.75	14587	0.158	−0.305	−0.354	0.6590

to 0.5 wt % of resin in DMF at 33°C. The intrinsic viscosity η was calculated by the Huggins eq. (1) and Kramer eq. (2).

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

$$\ln \eta_{rel}/C = [\eta] - K_2[\eta]^2 C \qquad (2)$$

Electronic absorption spectra of the terpolymers in DMF were also recorded on Shimadzu double beam spectrophotomer in the range of 190–700 nm. Infrared spectra of 8-HQDF terpolymer resins were recorded, using a Nicolet Magna 550 IR spectrophotometer in KBr pellets in the number region of 4000–400 cm^{-1}. Proton NMR spectra of 8-HQDF terpolymers were recorded on Varian VXR–300s 300 MHz proton NMR spectrophotometer using DMSO-d_6 as a solvent at Sophisticated Analytical Instrumentation facility, Punjab University, Chandigarh.

RESULTS AND DISCUSSION

The resin samples were cream in colour, insoluble in commonly used organic solvents but were soluble in DMF, THF, DMSO, and aq. NaOH. These resins were analysed for carbon, hydrogen, nitrogen, and sulphur content. The resin synthesized do not show sharp melting point but undergo decomposition above 228°C (Table I).

The molecular weight ($\overline{Mn}$) of the terpolymer resin was determined by non-aqueous coductometric titration in DMF against KOH in 50% (vol/vol) DMF/alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymers 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 ($\overline{Mn}$) by this method is based on the following considerations.[17,18]

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 ($\overline{Dp}$) is given by the following relation.

$$\overline{Dp} = \frac{\text{Total Meq. of base required for complete neutralization, i.e., last break}}{\text{Meq. of base required for smallest interval, i.e., first break}}$$
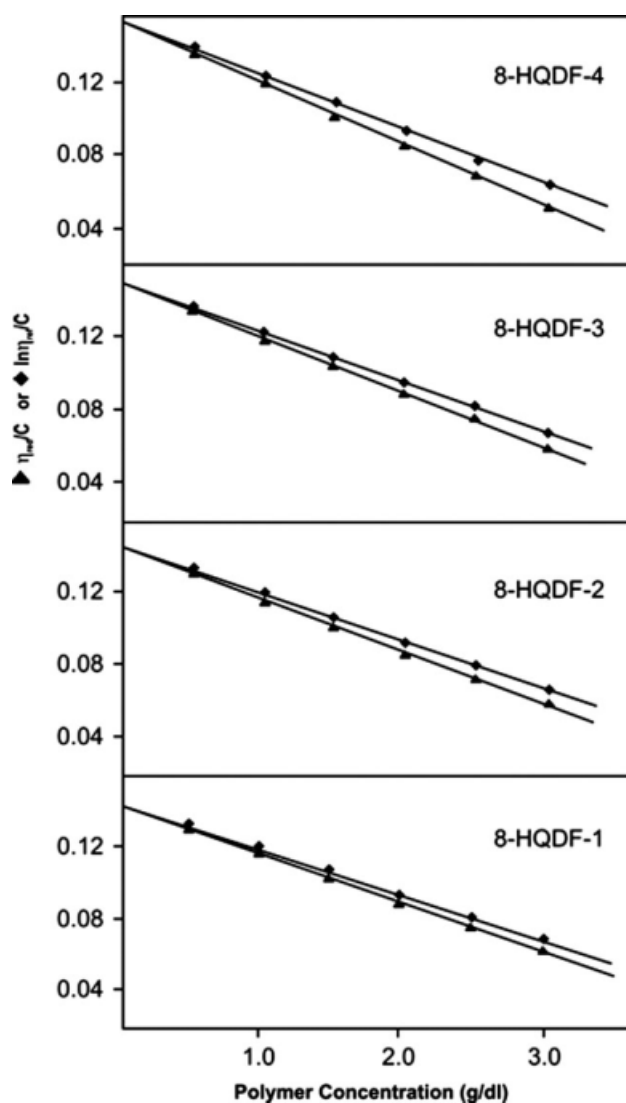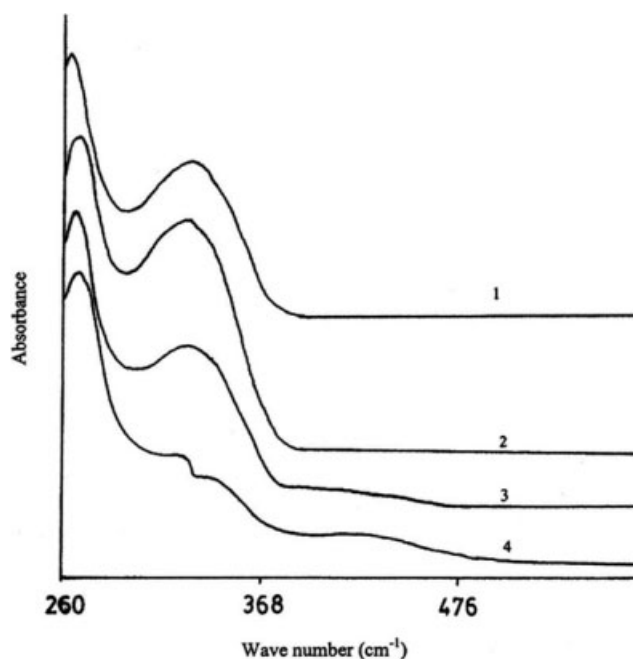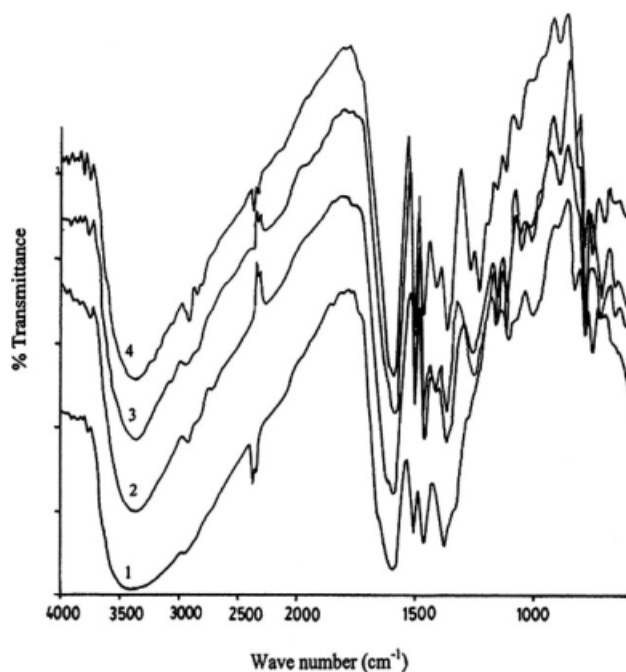

Figure 2 Viscometric plots of terpolymers.

Figure 3 Electronic spectra of terpolymers (1) 8-HQDF-1; (2) 8-HQDF-2; (3) 8-HQDF-3; and (4) 8-HQDF-4.

Figure 4 Infrared spectra of terpolymers (1) 8-HQDF-1; (2) 8-HQDF-2; (3) 8-HQDF-3; and (4) 8-HQDF-4.

The number average molecular weight ($\overline{Mn}$) could be obtained by multiplying the $\overline{Dp}$ by the formula weight of the repeating unit.[19] The results are incorporated in Table II.

Viscometric measurements were carried out in DMF at 30°C. All the resins showed normal behaviour. The intrinsic viscosity was determined by the Huggin[20] equation.

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C$$

and Kraemers[21] equation:

$$\ln \eta_{rel}/C = [\eta] - K_2[\eta]^2 C$$

The viscometric plots are shown in Figure 2. In accordance with the above relations, the plots of η_{sp}/C and η_{rel}/C against C were found to be linear giving as slopes K_1 and K_2, respectively. The intercept on the axis of viscosity function gave the $[\eta]$ value in both the plots. The calculated values of constants K_1 and K_2 (Table II) in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favourably.[22] The values of $[\eta]$ obtained from eq. (1) and eq. (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of terpolymer.

The electronic spectra of all the 8-HQDF terpolymer resins give rise to a similar pattern and are

TABLE III
Ir Spectral Data of 8-HQDF Terpolymers

| Observed band frequency (cm^{-1})				Assignment	Expected band frequency
8-HQDF-1	8-HQDF-2	8-HQDF-3	8-HQDF-4		
3990	3370	3372	3368 (b, St)	—OH phenolic intermolecular hydrogen bonding	3750–3200
2900	2900	2900	2926 (Sh, St)	>NH stretching	2800–3500
1590	1593	1585	1592 (m)	>C=S stretching	1600–1400
1502.8	1503.1	1502.3	1504.6 (Sh, b)	Aromatic ring	1600–1500
1460	1462	1461	1467 (m)	—CH$_2$— bending	1460
1374.7	1373.6	1372.8	1373.7 (Sh,b)	—CH$_2$— wagging	1280–1370
788	787.7	787.3	786.4 (m)	—CH$_2$— rocking	710–800
1164	1158	1158	1161 (m)	⎫	
1111	1119	1118	1122 (m)	⎬ 3,4,8 substitution	1000–1200
1009	1014	1012	1069 (m)	⎭	

Sh, sharp; b, broad; St, strong; m, medium; w, weak.
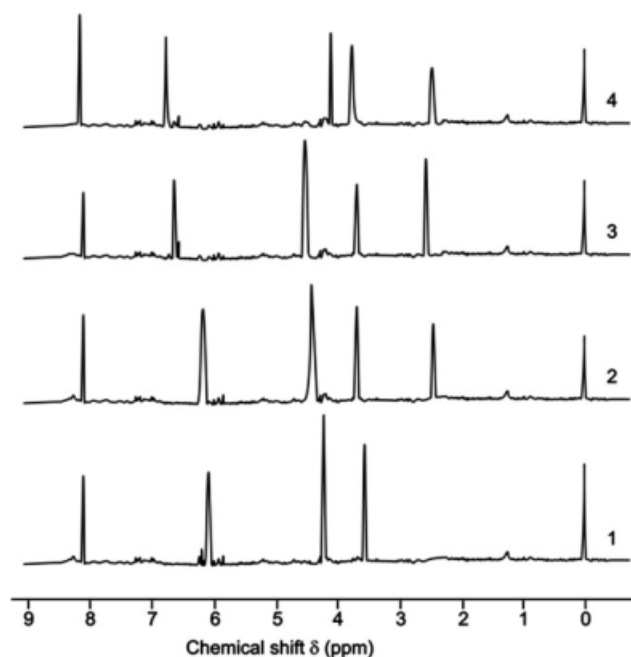
Figure 5 Proton NMR spectra of terpolymers (1) 8-HQDF-1; (2) 8-HQDF-2; (3) 8-HQDF-3; and (4) 8-HQDF-4.

depicted in Figure 3. The spectra of these terpolymers exhibit two absorption maxima in the region 260 to 290 nm and 315 to 330 nm. The intense band at 270 nm is due to ($\pi-\pi^*$) allowed transition of quinoline moiety which readily attains coplanarity and the shoulders merging (loss of fine structure) band at 324 nm may be due to ($n - \pi^*$) forbidden transition in saturated aliphatic carbonyl compounds.[23,24] The bathocromic shift from the basic values viz. 260 nm and 270 nm, respectively, may be due to combined effect of conjugation and phenolic hydroxy group (auxochrome).[23,24]

The IR spectra of all four terpolymer resins are presented in Figure 4 and IR spectral data are incorporated in Table III. The IR spectra revealed that all these resins give rise to a nearly similar pattern of spectra. A broad band appearing in the region 3400–3800 cm^{-1} may be assigned to the stretching vibration of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding with the thionyl group of a differ-
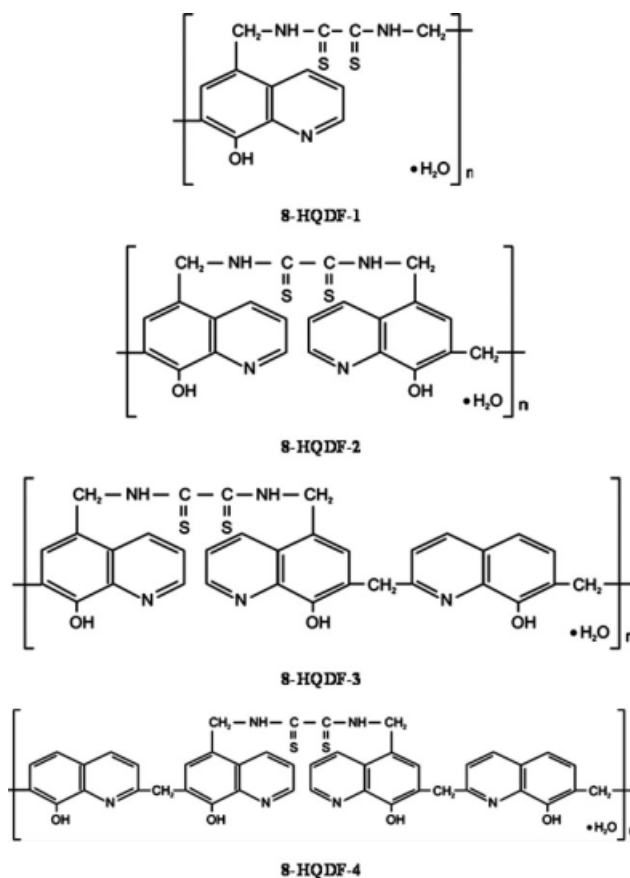
Figure 6 Suggested structure of 8-HQDF terpolymer resins.

ent polymeric chain, i.e., —OH phenolic intermolecular polymeric association.[25,26] The band at 1750–1600 cm^{-1} may be due to the stretching vibrations of >C=S group of amide moiety.[27,28] The band at 2900 cm^{-1} assignable to —NH— stretching, bending, and deformation out of plane vibrations of dithiooxamide moiety in terpolymers, respectively. The band at 1502 cm^{-1} may be ascribed to aromatic skeletal ring.[29,30] The presence of methylene bridges (—CH$_2$—) in the polymeric chain may be assigned due to presence of band at 1460–1470 cm^{-1}, 1375–1360 cm^{-1}, and 788–753 cm^{-1} [—CH$_2$— rocking].[29,30] The band obtained at 1009 cm^{-1}, 1111 cm^{-1}, and 1161 cm^{-1} suggest that the aromatic ring is 3,4,8 substituted.

TABLE IV
Nuclear Magnetic Resonance Spectral Data of 8-HQDF Terpolymers

| Sr. No.	Nature of proton assigned	8-HQDF-1	8-HQDF-2	8-HQDF-3	8-HQDF-4	Expected chemical shift (ppm)
1	Proton of phenolic —OH involved in hydrogen bonding	8.12	8.15	8.13	8.20	8.0–12
2	Aromatic proton (Ar—H) (unsymmetric pattern)	6.10	6.25	6.75	6.80	6.2–8.5
3	Thioimide proton of —NH linkage	4.27	4.44	4.65	4.16	5.0–8.5
4	Methylene proton of Ar—CH$_2$—N	3.61	3.65	3.62	3.81	3.5–6.0
5	Methylene proton of Ar—CH$_2$—Ar moiety	–	2.51	2.60	2.52	2.0–3.0
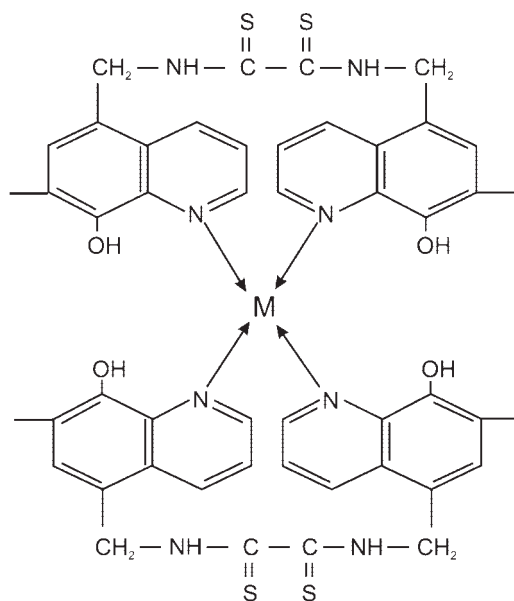
Figure 7 Proposed geometry of the polymeric chelate.

Proton NMR spectra of all four terpolymer resins are presented in Figure 5. NMR spectral data are shown in Table IV. Proton NMR spectra of all terpolymer resins show the intense signal arising in the region 8.12 to 8.20 (δ) ppm which may occur on account of hydroxyl proton of phenolic —OH group involved in the intermolecular hydrogen bonding.[31] The sharp intense peak at 6.10–6.80 (δ) ppm may be assigned to aromatic proton. A weak signal made its appearance at 4.16–4.46 (δ) ppm which may be due to amido protons of —NH bridge in the chain.[32] An intense signal appearing at 2.51–2.60 (δ) ppm may be due to methylene proton of Ar—CH$_2$—Ar moiety. Except 8-HQDF-1 terpolymer, the remaining three terpolymer which are 8-HQDF-2, 8-HQDF-3, and 8-HQDF-4 show signal around 3.62 (δ) ppm suggesting the presence of methylene bridges of Ar—CH$_2$—N linkage.[33]

On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, NMR spectra, and molecular weight, the most probable structures have been proposed for terpolymer resins as shown in Figure 6.

From the above data, the following structure (Fig. 7) has been proposed for the polychelates.

CONCLUSIONS

A terpolymer resin 8-HQDF based on condensation reaction of 8-hydroxyquinoline and dithiooxamide with formaldehyde in the presence of acid catalyst have been prepared. Elemental analysis, UV-Visible spectra, IR, NMR spectra and conductometric titration in non-aqueous medium, the proposed structure of the terpolymer resins are as shown in the Figure 6. These terpolymer resins can be used as ion-exchanger and can also be used for the preparation of polychelates with transition metal ions.

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