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Der Pharma Chemica, 2011, 3 (6):235-242
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ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis and Characterization of High Performance Terpolymer Resin Derived from 8-Hydroxyquinoline and Adipamide

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ABSTRACT

A new terpolymer resin was synthesized from 8-Hydroxyquinoline and adipamide with formaldehyde by polycondensation method in the presence of 2M HCl as catalyst. 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, I.R. and NMR spectra. The number average molecular weight has been determined by conductometric titration in non-aqueous medium. Intrinsic viscosities of the solution of the terpolymer has been determined in dimethyl formamide. The structure of the terpolymer resin was confirmed on the basis of spectral data.

Key words: Resin, Terpolymer, NMR, FT-IR, Degree of polymerization, viscosity.

INTRODUCTION

Extensive research work has been carried out on synthesis and characterization of terpolymers in our laboratory [1-3]. The terpolymers offered, novelty and versatility, hence they occupy the pivotal position in the field of material science. The progress in the field, terpolymer have been extensively rapid, as they useful in packaging, adhesive, coating in electrical sensors and organometalic semiconductors [4-6]. Ion-exchange process is a powerful and eco-friendly extraction technique for the reparation of metal ions and recovery of toxic heavy metal ions from the industrial wastes, sewages etc. [7-8]. In the recent past, there were several incidents of metal ion toxicity to human through the contamination of ecosystem. Increasing environmental concern has lead us organic ligands anchored to solid supports in order to remove and recover important as well as toxic metal ions from aqueous solutions. Ion-exchange resin plays a vital role in these types of environmental issues. Chelation ion-exchange behavior of a copolymer was reported for Cu(II), Ni(II) and Fe(III) metal ions among the other metal ions under study [9]. Water soluble

polymer containing carboxylic acid and sulphonic acid groups were synthesized and reported as polychelators for Ag(I), Cu(II), Ni(II), Co(II) and Cr(III) metal ions [10]. A heteropolyacid-based cation exchanger such as zirconium(IV) selenomolybdate has been synthesized and it was employed for the separation of sixteen selected metal ions using column technique [11]. Terpolymer involving *o*-nitrophenol-thiourea-paraformaldehyde and anthranilic acid-thiourea-paraformaldehyde resins were synthesized and reported for its excellent ion-exchange capacity [12-13]. In this article, synthesis and characterization of terpolymer resin prepared from 8-Hydroxyquinoline, adipamide and formaldehyde is incorporated.

MATERIALS AND METHODS

Materials

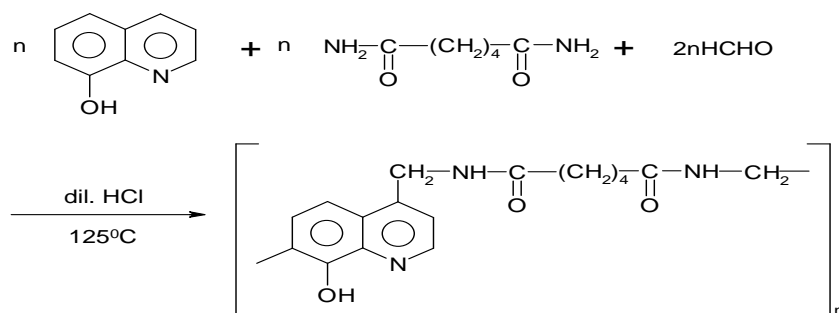
The chemicals used were all of AR or chemically pure grade. 8-Hydroxyquinoline (Merck, 99%); Formaldehyde solution (Merck, 37%) and adipamide (Merck, 99%).

Preparation of 8-HQAF terpolymer resin

A mixture of 8-Hydroxyquinoline(0.1mol), adipamide (0.1mol) and formaldehyde (7.5ml of 37% solution, 0.2mol) in the presence of 200ml 2M HCl as a catalyst was taken in 500ml round bottom flask with water condenser and heated in an electrically operated oil bath at $125 \pm 2^\circ\text{C}$ for 5hr. with occasional shaking. The temperature of the oil bath was controlled with the help of dimmer stat. The resinous mass obtained is removed immediately as reaction process was over (Table 1). The separated resinous product (8-HQAF) was purified as follows:

Purification of resin

The solid product was repeatedly washed with hot water followed by methanol to remove unreacted monomers. The resinous product was air dried and powdered. The powder was washed many times with ether in order to remove hydroxyquinoline-formaldehyde copolymer which may present with the terpolymer. The product so obtained was further purified by reprecipitation technique. The terpolymer was dissolved in 8% aqueous NaOH, filtered and reprecipitated by drop wise addition of ice cold 1:1 (v/v) conc. HCl / distilled water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered. The purified polymer sample was dried in vacuum at room temperature. The finely ground resin was passed through a 300 mesh size sieve. The yield of terpolymer resin was found to be 83%. The reaction taking place is shown in scheme 1.



Scheme 1. Reaction scheme for 8-HQAF terpolymer resin.

Table 1 Experimental Details of 8-HQAF Terpolymer Resins

Resin Abbreviation (Decomp Temp) (°C)	Reactants			Molar ratio	Catalyst 2M HCl (ml)	Reflux Temp ±2K	Yield (%)	Time (h)
	8-Hydroxy Quinoline 8-HQ (mol)	Adipamide A (mol)	CH ₂ O F(mol)					
8-HQAF	0.05	0.05	0.1	1:1:2	200ml	398	76	5

Characterization of terpolmer

These terpolymer resin was subject to microanalysis for C, H, and N on Perkin Elmer 2400 series II CHNS/O analyzer at Sophisticated Instrumentation Center for Applied Research and Testing (Sicart), Vallabh Vidyanager, Gujarat, India. The number average molecular weight (Mn) was determined by conductometric titration in DMF using KOH in 50% (v/v) DMF/Alcohol mixture as the titrant using Equiptronics conductivity meter within built magnetic stirrer (model No EQ-664). The viscosity were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.5 to 3.0% of terpolymer in DMSO at 30⁰C. The intrinsic viscosity was calculated using the Huggins equation (1) and the Kramer equation (2).

$$\eta_{sp} / C = [\eta] + k_1 [\eta]^2 C \text{ ----- (1)}$$

$$\ln \eta_{rel} / C = [\eta] + k_2 [\eta]^2 C \text{ ----- (2)}$$

Electronic absorption spectra of the terpolymers in DMSO was recorded with a Shimadzu UV-visible double beam spectrophotometer tied with an automatic pen chart recorder on thermosensitive paper in the range of 200–800 nm. Infrared spectra of 8-HQAF terpolymer resins were recorded in nujol mull with Perkin–Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm⁻¹. Proton NMR spectra were recorded with Bruker Advance-II 400 MHz proton NMR spectrophotometer and DMSO-d₆ was used as a solvent.

RESULTS AND DISCUSSION

The terpolymer resin is found to be amorphous and pale yellow in color. This purified resin is found to be soluble in DMF, DMSO, aqueous NAOH and KOH solution. The 8-HQAF terpolymer resin was analyzed for the percentage of carbon, hydrogen and nitrogen. The results are incorporated in Table 2. The resin synthesized do not show sharp melting point but undergo decomposition above 200⁰C.

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.

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

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 results are incorporated in Table 2.

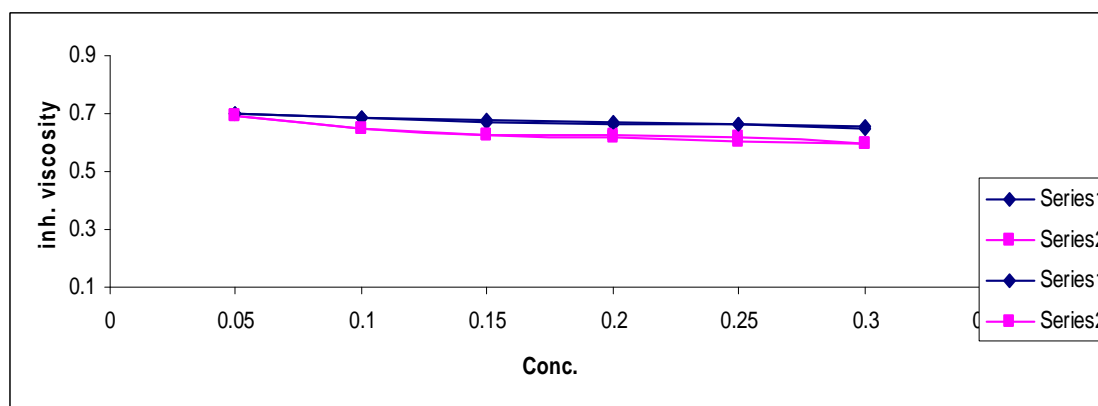


Fig. 1. Viscometric plot of 8-HQAF terpolymer resin

Viscometric measurements were carried out in DMSO at 30°C. The resin showed normal behavior. The intrinsic viscosity $[\eta]$ was determined by the Huggins equation (1) and Kraemers equation (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 slopes K_1 and K_2 , respectively. The intercept on the axis of viscosity function gave the $[\eta]$ value in both plots. The calculated values of constants K_1 and K_2 (Table II) in weight of the terpolymer in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably. The values of $[\eta]$ obtained from equations. (1) and (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of the terpolymer.

Table 2 Molecular weight determination and viscometric data of terpolymer

Terpolymer	Empirical Formula of repeating unit	Empirical formula weight	DP	Mn	Intrinsic viscosity $[\eta]$ dl g ⁻¹	(K1) Huggin's constant	(K2) Kraemer constant	K1+K2
8-HQAF	C ₁₇ H ₁₉ O ₃ N ₃	313	2.16	3144	0.72	0.6132	-0.08352	0.5296

The elemental analysis of terpolymer resin has been given in the Table 3. The observed value was found to be agreement with theoretical value.

Table 3 Elemental Analysis

Terpolymer Resin	%C Obs (Calc)	%H Obs (Calc)	%N Obs (Calc)	Empirical Formula
8-HQAF	65.23 (65.17)	6.13 (6.07)	13.55 (13.41)	C ₁₇ H ₁₉ O ₃ N ₃

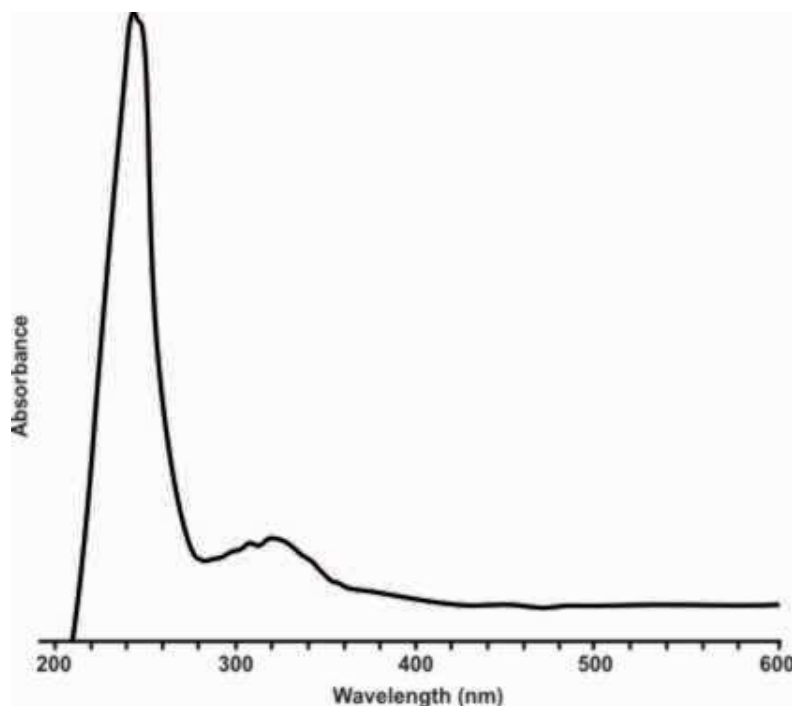


Fig. 2. UV-Visible spectrum of 8-HQAF terpolymer resin

The electronic spectra of the 8-HQAF terpolymer resin gave rise to similar pattern and are depicted in Fig. 2. Electronic spectra of 8-HQAF terpolymer resin was scanned in HPLC grade DMSO. The terpolymer exhibit two Characteristic bands at 293-296nm and 328-336nm. The intense band at 293-296nm may be due to the ($\pi-\pi^*$) allowed transition of quinoline ring, which readily attains coplanarity and the shoulder merging (loss of fine structure) band at 328-336 nm may be due to ($n-\pi^*$) forbidden transition in $>C=S$ or $>C=N$ group. The bathochromic shift from the basic value, viz., 252 - 320 nm, ($\pi-\pi^*$) and 291($>C=S$) or 270-300nm ($>C=N$) may be due to combined effect of conjugation (due to chromophore) and phenolic hydroxy group (auxochrome).

The IR spectra of all four terpolymer resin is depicted in Fig. 3 and spectral data incorporated in Table 4. The IR spectra revealed that the resin give rise to a nearly similar pattern of spectra. A broad band appeared in the region $3380-3370\text{ cm}^{-1}$ may be due to the stretching vibrations of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding which exists between $-OH$ and $>NH$ group of different polymer chains. The carbonyl group of a different polymeric chain. The bands observed at $2915-2926\text{ cm}^{-1}$, $1418-1434\text{ cm}^{-1}$, 1347 cm^{-1} and $1280-1296\text{ cm}^{-1}$ suggest the presence of methylene bridges in polymeric chains. The medium broad band at $1546-$

1566 cm^{-1} may be ascribed to aromatic skeletal ring. The band at 1610-1642 cm^{-1} may be due to the stretching vibrations of $>\text{C}=\text{N}$ -. The bands appeared at 1495-1500 cm^{-1} and 498-527 cm^{-1} are due to $-\text{NH}$ - bending and deformation out of plane vibrations of the adipamide moiety in terpolymer resins respectively. The band at 1220-1240 cm^{-1} may be due to $>\text{C}=\text{O}$ stretch in phenol. The presence of band at 955-960 cm^{-1} , 1017-1058 cm^{-1} and 1125-1133 cm^{-1} suggest that the aromatic ring is 1,2,4-substituted. This fact is further supported by presence of band at 823-833 cm^{-1} for tetra substituted benzene ring and band at 895-955 cm^{-1} for one isolated H-atom situated between two substituents.

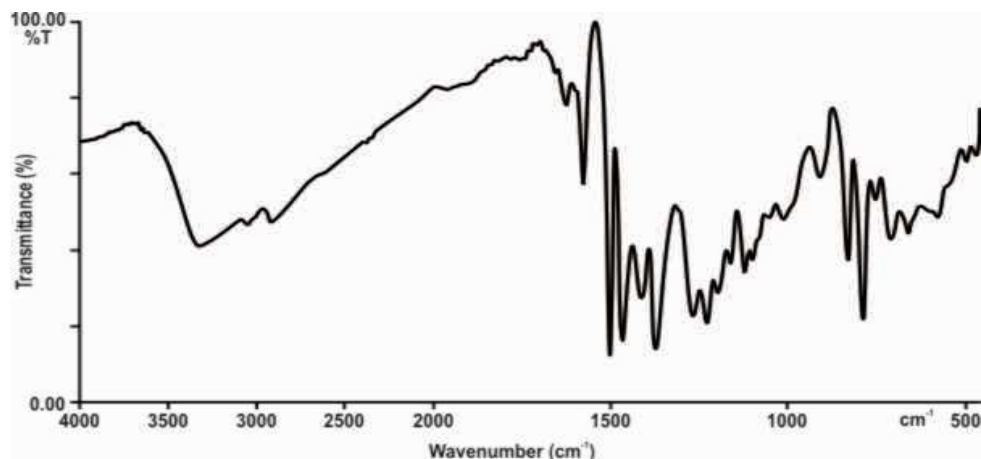


Fig. 3. IR Spectrum of 8-HQAF Terpolymer Resin

Table 4 IR Spectral Data of 8-HQAF Terpolymer Resin

Observed band frequency (cm ⁻¹) 8-HQAF	Assignment	Expected band frequency (cm ⁻¹)
2921.7	-OH stretching vibrations (phenolic)	2900-3700
3110.0	Intramolecular H-bending	2600-3100
1623.1	$>\text{C}=\text{O}$ stretching	1666-1750
3323.4	-NH stretching	3200-3400
1576.8	-C=N stretching	1550-1750
1465.1	-Aromatic skeletal ring	1450
827.5	-CH ₂ Bridge	800-1300
1503.2	-C=C- stretching (Aromatic vibration)	1300-1500
1007.5	-C-H in plan bend (Aromatic)	1000-1150
710.7	-CH ₂ - rocking	716

Proton NMR spectrum terpolymer resin is presented in Fig. 4 and NMR spectral data are shown in Table 5. Peak at 4-4.5 (δ) ppm may be due to presence of Ar-CH₂-NH- moiety. The proton of the -NH- bridge can be identified from the peaks at 4.6 (δ) ppm. Signals appeared at (δ) ppm values 6.8-7.2 can be assigned to aromatic protons. The protons of Ar-OH group involved in proton exchange reaction gives peak at 7.8-8.0 (δ) ppm.

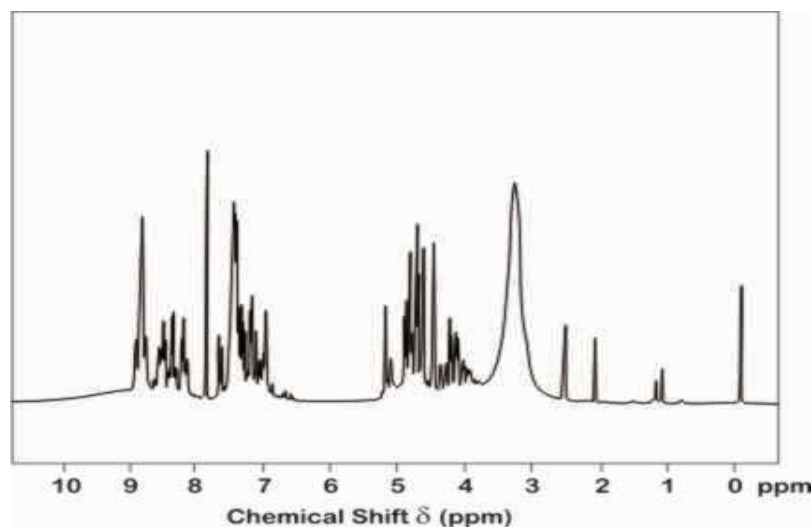


Fig. 4. NMR spectrum of 8-HQAF Terpolymer Resin

Table 5 Proton NMR Spectral Data of 8-HQAF Terpolymer Resin

Observed chemical shift, δ (ppm) 8-HQAF-I	Nature of proton assigned	Expected chemical shift, δ (ppm)
8.84	Proton of phenolic -OH (hydrogen bonding)	8.0-12
7.35	Aromatic proton (Ar-H)	6.2-8.5
4.65	Methylene proton of Ar-CH ₂ -Ar	3.5-6.0
4.54	Amido proton of Ar-CH ₂ -NH-CO	3.5-6.0
2.59	Methylene proton Ar-CH ₂ -NH moiety	2.0-3.0
7.45	-CH ₂ -CH ₂ -CO-NH-	7.0-7.7

On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, and NMR spectra, and molecular weight, the most probable structures have been proposed for terpolymer resin.

CONCLUSION

The new 8-HQAF terpolymer resin based on the condensation polymerization of 8-hydroxyquinoline and adipamide with formaldehyde in the presence of acid catalyst has been prepared. The newly synthesized terpolymer resin is soluble in DMF, DMSO and aqueous NaOH and insoluble in common organic solvents. From the elemental analysis, UV-visible, FT-IR and ¹H NMR spectral studies the proposed structure of the 8-HQAF terpolymer has been determined.

Acknowledgement

Authors are thankful to Director of the LIT, RTM Nagpur University and also thankful to Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh for carrying out spectral analysis. One of the author (W. B. Gurnule) thanks to University Grant Commission, New Delhi for financial assistance.

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