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Synthesis Of Nanoporous Terpolymer Resin (8-Hydroxyquinoline-Ethylene Diamine-Formaldehyde) And Its Characterization

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ABSTRACT

The condensation of 8-hydroxyquinoline and ethylene-diamine with formaldehyde in the presence of acid catalyst in 1:1:2 molar proportions respectively, enabled the formation of the nanoporous tercopolymer resin 8-Hydroxyquinoline-EthyleneDiamine-Formaldehyde(8-HQEDF). It was characterized by elemental analysis, UV, IR and ¹H-NMR. Surface morphology analysis by SEM of the sample revealed presence of nanoporous structures. The number average molecular weight of the resin was determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethyl formamide(DMF) have been carried out with a view to ascertain the characteristic functions and constants. The nanoporous 50nm, of the terpolymer can find its application in catalysis and adsorption phenomena.

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KEYWORDS

Hydroxyquinoline;
Nanoporous structure;
Terpolymers.

INTRODUCTION

Synthesis and characterization of polymeric resins deserves to be investigated because of their varied characteristics and beneficial properties. So far, several copolymers of phenol or 8-Hydroxyquinoline derivatives like o-aminophenol, resorcinol and p-hydroxybenzoic acid with formaldehyde have been reported^[1-3]. Extensive studies on the copolymers, reported in the literature, are synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid, various amines and formaldehyde^[4,5]. The salicylic acid/p-chloro(-bromo)-formaldehyde polymer

show chelation ion exchange capacities^[6,7]. Poly (oxine-alkaline) polymers have been reported as ion exchangers^[8] as well. After loosing a proton, 8-Hq and its derivatives are capable of forming complexes with a large number of both main group and transition metal ions^[6]. The complexes of Mg, Al, Zn and B have attracted particular attentions in recent years because of their application in organic electro luminescence (OEL) devices^[7-9]. Recently, the groups of Pierre, Serratrice, Bradshaw and Hiratani developed di and tritopic 8- HQ derivatives for the selective extraction or sensitizing of Metal ions^[10-12]. The present paper deals with the synthesis and detailed characterization

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of a new tercopolymer resin derived from 8-hydroxyquinoline, ethylenediamine and formaldehyde.

EXPERIMENTAL

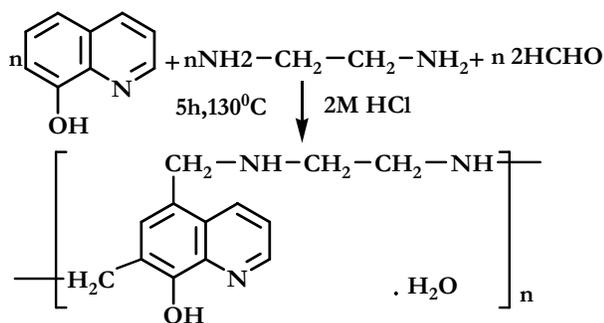
Preparation of 8-HQEDF tercopolymer resin

A mixture of 8-hydroxyquinoline (0.1mol), ethylene diamine (0.1mol) and formaldehyde (0.2mol) in the presence of 2 M HCl was heated in an oil bath at 130°C for 5h. The reaction process is shown in the SCHEME 1.

The solid product obtained was immediately removed and washed with cold water, dried and powdered. The powder was repeatedly washed with hot water and ethanol to remove unreacted monomers. It was then dried and powdered. The air-dried tercopolymer was extracted with chloroform to remove excess of 8-HQ-formaldehyde copolymer, which might be present along with the tercopolymer. It was then purified by dissolving in 1:1(v/v)dil. HCl and then reprecipitating by drop wise addition of 8% NaOH with constant stirring. The resulting polymer was washed with boiling water and dried in vacuum at room temperature.

Characterization

The tercopolymer resin was subjected to elemental analysis for C, H and N on a Perkin-Elmer C, H, N and S Analyzer. The number average molecular weight of the tercopolymer was determined from the conductometric titration carried out in non aqueous medium. Electronic absorption spectrum of the tercopolymer dissolved in spec-pure DMF was recorded in the range of 200-850nm using GBC Cintra 10e(Australia) UV-Visible spectrophotometer. The



structural characterization was carried out FTIR(Perkin-Elmer Infra Red Spectrum RX1) and proton NMR(Bruker DRX-300 NMR spectrometer). SEM images were obtained using FEI Quanta 200, Netherland, of the polished and gold coated sample pellets. The non-isothermal thermogravimetric measurement of the tercopolymer was carried out using Mettler Toledo Stare System, with in the temperature range 40–800°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Elemental analysis and Molecular weight

The tercopolymer resin prepared was pale orange in color with the decomposition temperature of 230°C. It was found to be soluble in solvents such as DMF and DMSO. The results obtained from the elemental analysis for C, H and N were in agreement with the theoretical values.

[Empirical formula of the repeating unit: $C_{13}H_{15}N_3O.H_2O$, Theoretical(Observed)%: C=63.15 (63.09); H=6.07(6.02); N=17.00(16.85)].

The degree of polymerization(D_p) was calculated using the relation, $D_p = V_{bn}/V_{bs}$ where, V_{bn} = mEquivalents of base required for complete neutralization; V_{bs} = meq of base required for smallest interval. The value for number average molecular weight(M_n) is found to be 22520 calculated on the basis of the given relation, $M_n = D_p \times$ repeat unit weight.

UV-Visible spectral studies

The electronic spectrum of the tercopolymer resin is shown in the figure 1. A characteristic band ob-

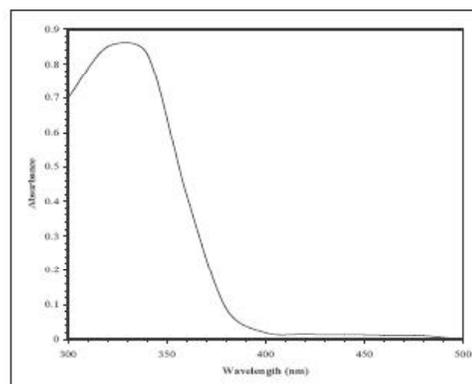


Figure 1: UV-visible spectra of the terpolymer

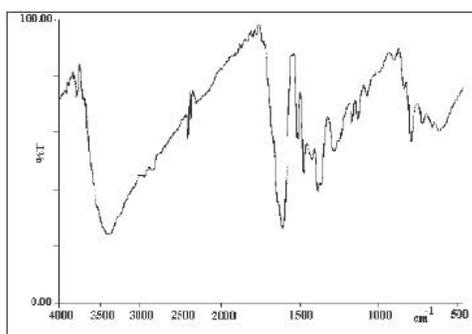


Figure 2 : IR spectra of the terpolymer

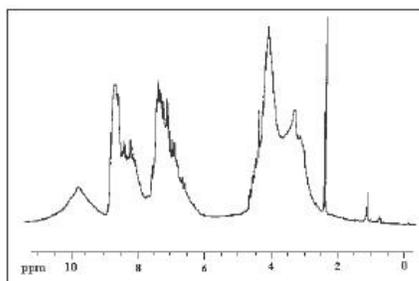
Figure 3 : ¹H-NMR spectra of the terpolymer

TABLE 1: IR frequencies assignment for the tercopolymer

Assignment	Expected band frequency (cm ⁻¹)	Observed band frequency (cm ⁻¹)
Phenolic-OH stretching	3500 - 3000	3371
-NH stretching	3320 - 3140	2950 - 3150
N-H bend wagging	800 - 666	830 - 604
Methylene bridge (-CH₂) modes		
-bend	1460	1463
-rock	775	785
-wagging	1300 - 1200	1270
Aromatic ring vibrations	1600 - 1450	1502
Phenolic C-Ostr	1410 - 1310	1372
>C=N str	1690 - 1640	1593

TABLE 2: ¹H-NMR Data for the terpolymer

Nature of proton assigned in the ¹ H-NMR spectrum	Chemical shift (δ) ppm	
	Expected	Observed
Phenolic proton(-OH)	8-12	8.6
Aryl proton(Ar-H)	7.5-8.8	8.45
Ethylene proton	4 - 5	4.3-4.5
Amido proton	5-8.5	9.6

served at 330nm is due to $\pi \rightarrow \pi^*$ allowed transition of the benzenoid system of heteroaromatic compounds such as quinolines^[13]. The bathochromic shift from 310nm may be due to the combined effect of conjugation and presence of phenolic hydroxyl group(an auxochrome).

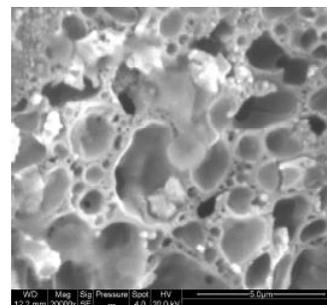


Figure 4 : SEM of the terpolymer pellet

Infra-Red spectral studies

The various infra-red frequencies observed in the infra-red spectrum(Figure 2) of the tercopolymer resin are assigned in the TABLE 1.

The IR frequency assignments clearly show the presence of phenolic hydroxyl (-OH) groups^[13-15], which is lowered due to intra and intermolecular hydrogen bonding^[16] and the band in the range 3150-2950 cm⁻¹ is attributed to -NH stretching vibration^[17]. The medium band (1593cm⁻¹) may be due to >C=N-stretch of 8-hydroxyquinoline. Thus the presence of quinoline ring with side chain of -CH₂-NH-CH₂-CH₂-NH- can be ascertained from the IR analysis.

¹H-NMR spectral analysis

¹H-NMR spectral data of the tercopolymer resin is given in the TABLE 2. NMR spectra shown in the figure 3 depicts an intense signal arising at 8.6(δ) ppm which is ascribed to hydroxyl proton of phenolic -OH group involved in the intermolecular hydrogen bonding^[17-19]. A sharp intense peak at 8.45(δ) ppm may be assigned to aromatic proton^[28]. A single broad peak around 9.6(δ) ppm indicates the presence of amido protons^[13,17,18]. The presence of ethylenic protons is supported by the doublet in the range 4.3 to 4.5(δ) ppm^[17,18].

On the basis of the nature, characterization and the reactive positions of the monomers, as well as considering the linear structure of some other substituted phenol-formaldehyde polymers^[20], including the linear branched nature of urea-formaldehyde polymers^[21], the structure proposed for the newly synthesized terpolymer resin may be a linear structure as shown in the SCHEME 1.

SEM analysis

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The SEM image shown in the figure 4 clearly indicates porous structure morphology of the terpolymer prepared. Apart from pores of bigger size 1-2 μ , large numbers of nanopores in the range of 50-40nm size can be seen. These nanoporous structures may be useful in catalytic activities.

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