

SYNTHESIS AND CHARACTERIZATION OF COPOLYMER RESIN DERIVED FROM PHTHALLIC ACID AND MELAMINE

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ABSTRACT

Copolymer resin (PTMF) was synthesized by the condensation of phthallic acid (PT) and melamine (M) with formaldehyde (F) in the presence of acid catalyst and using varied molar ratios of reacting monomers. Copolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weights of resin were 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 UV-visible, FTIR and proton nuclear magnetic resonance (H^+ NMR) spectra were studied to elucidate the structure. The surface features and crystalline behavior of the ligand and its complexes were analyzed by scanning electron microscope (SEM).

Keywords: Synthesis, polycondensation, resin, structure, degree of polymerization, Characterization.

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INTRODUCTION

Much of research work has been carried out on the synthesis and characterization of thiourea containing copolymer. A literature survey reveals that copolymer derived from substituted hydroxy or dihydroxy-dithioamide-formaldehyde resin shows improved ion-exchange properties, thermal resistance property, coordinating property and good storage stability etc.¹ Copolymer derived from itaconic acid-acrylamide-2-acryl amido-2-methyl-propane sulphonic acid by free radical polymerization have been reported in literature². 8-Hydroxyquinoline (8-HQ) and its derivatives are widely used as complexing agents in various applications due to their good complex forming ability³. Anupriya and co-workers⁴ 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.

Shah and coworkers⁵ have prepared chelating ion-exchange resin from salicylic acid-formaldehyde-resorcinol (SFR) using DMF as solvent at $80 \pm 2^\circ\text{C}$. 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 coefficient values.

Terpolymers of 8-hydroxyquinoline-formaldehyde-resorcinol/catechol were reported⁶⁻⁸, 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 copolymer derived from phthallic acid, melamine and formaldehyde.

EXPERIMENTAL

Materials

Pthallic acid (Ranbaxy Fine Chemicals, Mumbai) purified by rectified spirit. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai) was used as received. Melamine (Loba, Mumbai, extra pure) was used as received. The solvents and monomers were purified by the conventional methods⁹.

Preparation of PTMF copolymer resin

A mixture of pthallic acid [0.1mol], melamine [0.1mol] and formaldehyde [0.3 mol] in the presence of 2M hydrochloric acid (200 ml) was heated in an oil bath at $124^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 5 h with occasional shaking¹⁰⁻¹². The separated resinous product (PTMF) 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 (v/v) 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 copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of the copolymer resin was found to be 88%. The reaction taking place is as shown in Fig.-1.

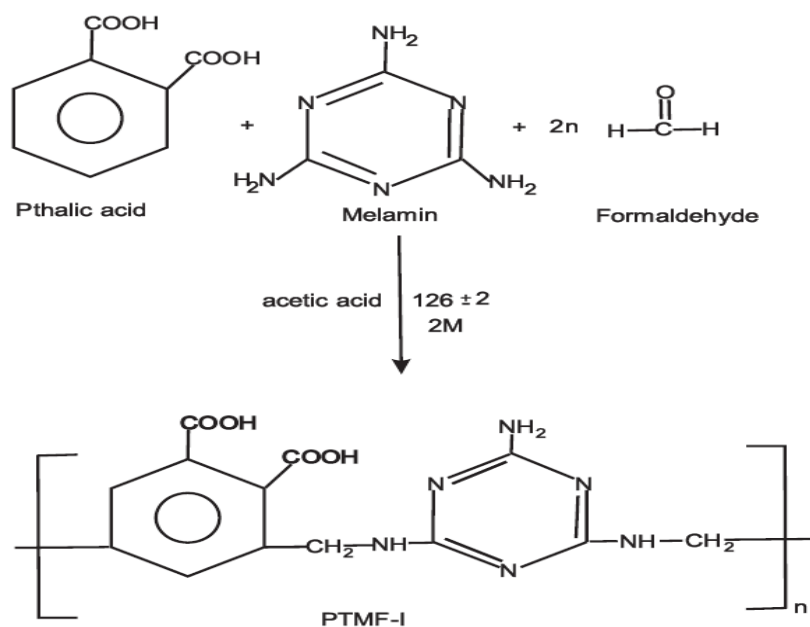


Fig.-1: Synthesis of PTMF copolymer resin

Characterization of copolymer resin

The copolymer resin was subjected to microanalysis for carbon, hydrogen and nitrogen on Perkin Elmer C, H, N, S analyzer. The number average molecular weights (M_n) were determined by conductometric titration in DMF using KOH in a 50% (v/v) DMF/alcohol mixture as a titrant. The viscosities were determined using Tuan-Fuoss viscometer at six different (concentration ranging from 3.0 wt % to 0.5 wt % of resin in DMF at 33°C). The intrinsic viscosity η was calculated by the Huggins equation (1) and Kramer equation (2).

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

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

Electronic absorption spectra of the copolymer in DMF were also recorded on Shimadzu UV-1800 double beam spectrophotometer in the range of 200-800 nm. Infrared spectra of PTMF copolymer resin was recorded, using a Shimadzu PR-Affinity spectrophotometer in KBr pellets in the number region of 4000-400 cm^{-1} at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. Proton NMR spectra of PTMF copolymer was recorded on Varian VXR – 300s 300 MHz proton NMR spectrophotometer using DMSO- d_6 as a solvent at STIC, Kochi. The surface analysis of the PTMF copolymer was examined at different magnifications at STIC analysis centre, Kochi.

RESULTS AND DISCUSSION

The copolymer resin(PTMF) sample was brown in color, insoluble in commonly used organic solvents but were soluble in DMF, THF, DMSO and aq. NaOH. The resin was analyzed for carbon, hydrogen and nitrogen content. The resin synthesized do not show sharp melting point but undergo decomposition above 238°C . This resin was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value, as-

Calculated for $\text{C}_{13}\text{H}_{11}\text{N}_6\text{O}_4$: C: 49.52 %; H: 3.49 %; N: 26.66 %, O: 20.31%,

Found for $\text{C}_{13}\text{H}_{11}\text{N}_6\text{O}_4$: C: 49.90 %; H: 3.03 %; N: 26.17 %. O: 20.45%,

The molecular weight ($\overline{\text{Mn}}$) of the copolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in 50% (v/v) 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 copolymers 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 (Fig.-2). The calculation of ($\overline{\text{Mn}}$) by this method is based on the following considerations¹³.

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

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

The number average molecular weight ($\overline{\text{Mn}}$) could be obtained by multiplying the $\overline{\text{Dp}}$ by the formula weight of the repeating unit¹³. The results are incorporated in Table-1.

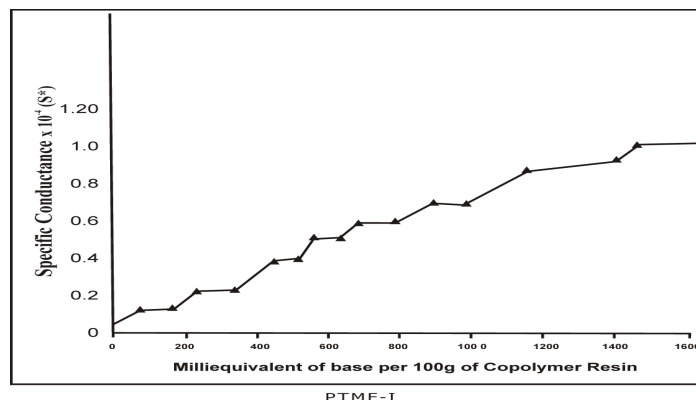


Fig.-2: Non-aqueous conductometric titration curve of PTMF copolymer

Viscometric measurements were carried out in DMF at 30°C. The resin showed normal behaviour. The intrinsic viscosity was determined by the Huggin¹⁴ equation and Kraemers²¹ equation :

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

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

The viscometric plots are shown in Fig.-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-1] in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favourably¹⁴. The values of $[\eta]$ obtained from equation (1) and equation (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of copolymer.

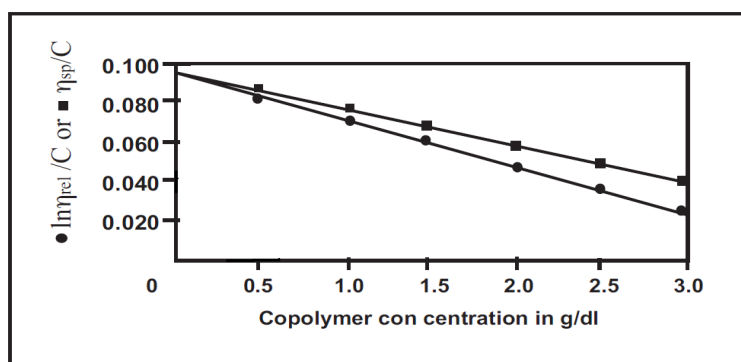


Fig.-3: Viscometric plots of PTMFCopolymer

The electronic spectra of the PTMF copolymer resin is depicted in Fig.3. The spectra of the copolymer exhibit two absorption maxima in the region 260 to 290 nm and 320 to 330 nm. The intense band at 280 nm is due to $(\pi - \pi^*)$ allowed transition of phthalic acid 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 compounds¹⁵. The bathochromic 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)¹⁵.

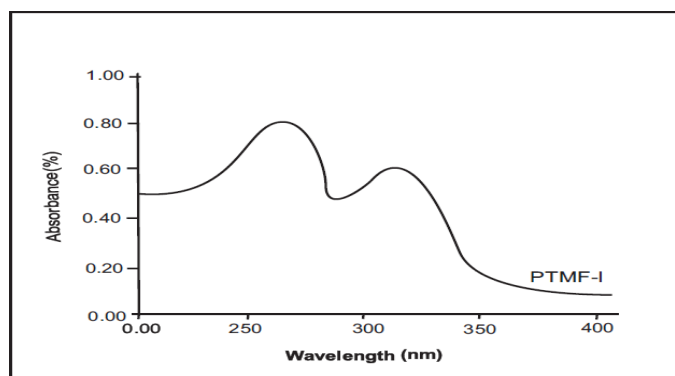


Fig.-4: Electronic spectra of PTMF copolymer

The IR spectra of copolymer resin is presented in Fig.-4. The IR spectra revealed that the resin give rise to a broad band appearing in the region 3400-3800 cm^{-1} may be assigned to the stretching vibration of

carboxylic acid groups exhibiting intermolecular hydrogen bonding¹⁶. The band at 2900 cm^{-1} assignable to -NH- stretching, bending and deformation out of plane vibrations of melamine moiety in copolymers respectively. The band at 1502 cm^{-1} may be ascribed to aromatic skeletal ring¹⁶. The presence of methylene bridges ($\text{-CH}_2\text{-}$) in the polymeric chain may be assigned due to presence of band at $1460\text{-}1470\text{ cm}^{-1}$, $1375\text{-}1360\text{ cm}^{-1}$ and $788\text{-}753\text{ cm}^{-1}$ [$\text{-CH}_2\text{-}$ rocking]¹⁶.

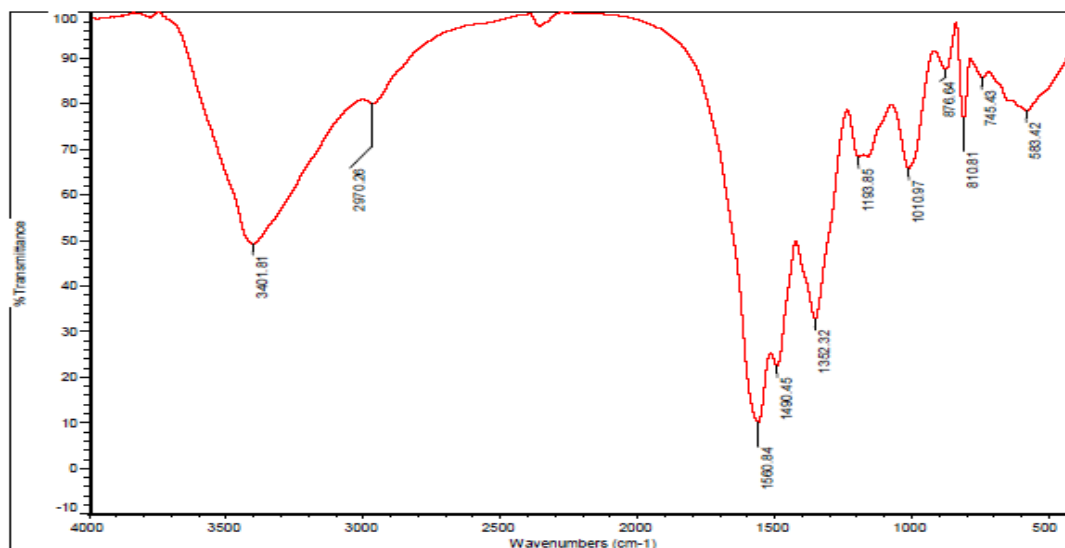


Fig.-5: Infrared spectra of PTMF copolymer

Proton NMR spectra of copolymer resin is presented in Fig.-6. Proton NMR spectra of copolymer resin show the intense signal arising in the region $7.80(\delta)$ ppm which may occur on account of hydroxyl proton of -COOH group involved in the intermolecular hydrogen bonding¹⁶. The sharp intense peak at $6.80(\delta)$ ppm may be assigned to aromatic proton. A weak signal made its appearance at $3.90(\delta)$ ppm which may be due to amido protons of -NH bridge in the chain¹⁷. An intense signal appearing at $2.60(\delta)$ ppm may be due to methylene proton ($\text{-CH}_2\text{-}$). Copolymer show signal around $3.62(\delta)$ ppm suggesting the presence of methylene bridges of $\text{Ar-CH}_2\text{-N}$ linkage¹⁷.

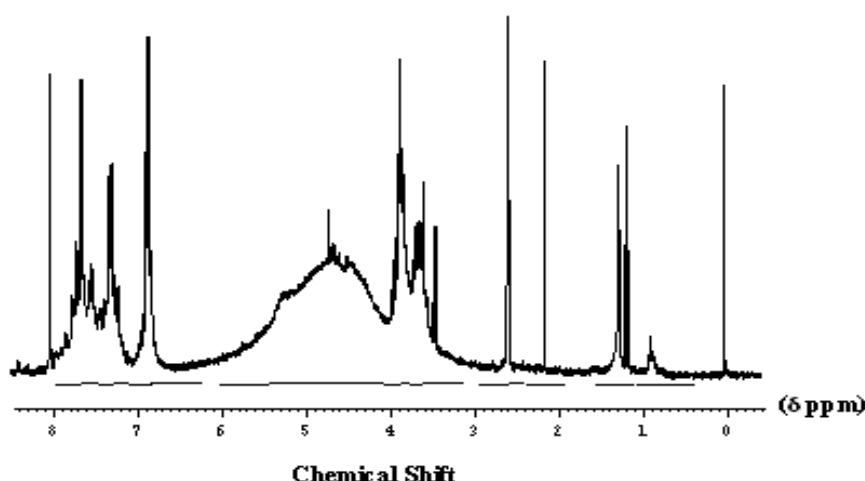


Fig.-6: Proton NMR spectra of PTMF polymer

The SEM photographs obtained in different magnifications for the PTMF copolymer resin are shown in Fig.-7. It indicates that the PTMF copolymer has a net-like appearance and the surface features of the copolymer shows a fringed, scattered, and miscellaneous model of the crystalline–amorphous structure. Scanning electron microscopy of copolymer was carried out to understand the inner morphology and pore structure. The morphology of fracture surfaces of the copolymer is quite different from that of polymer–metal complexes. It is clear from SEM that the copolymer is porous in nature. The morphology of the copolymer shows a fringed model of the semicrystalline nature. The fringes represent the transition between the crystalline and the amorphous phases. The copolymer exhibits a more amorphous character with a close-packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The presence of few holes and cracks are noted which may be due to air voids¹⁷.

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 copolymer resin as shown in Fig.-1.

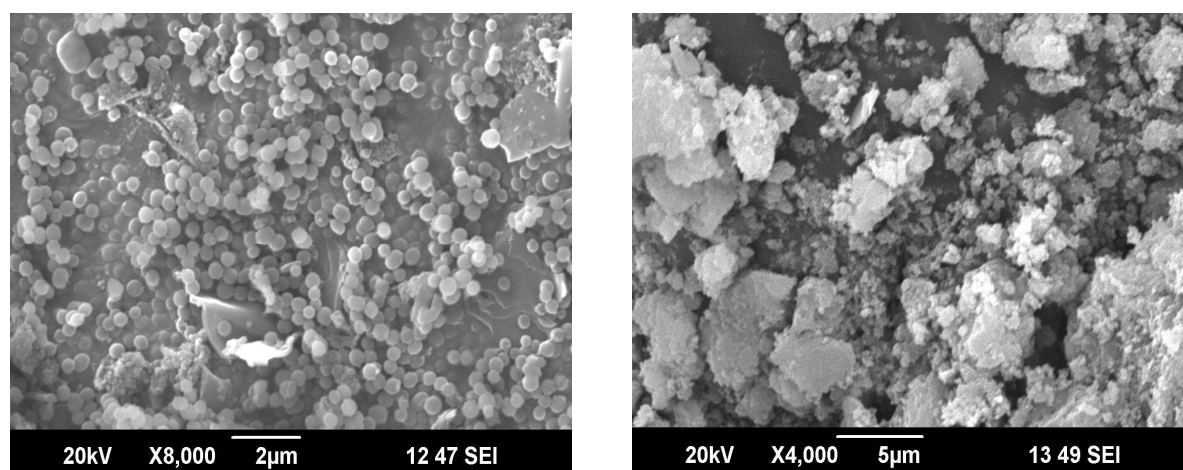


Fig.-7: SEM Images of PTMF copolymer resin

Table-1: Molecular Weight Determination and Viscometric Data of copolymer

Copolymer	Expirical formula of repeating unit	Empirical formula weight	$\overline{Dp}$	$\overline{Mn}$	Intrinsic viscosity $dl\ g^{-1}$	Huggin's constant (K_1)	Kraemer constant (K_2)	K_1+K_2
PTMF	$C_{13}H_{11}N_6O$ 4	315	14.37	5104	0.144	-0.320	0.2448	0.56

CONCLUSIONS

A copolymer resin PTMF based on polycondensation reaction of pthallic acid and melamine with formaldehyde in the presence of acid catalyst have been prepared. On the basis of elemental analysis, UV-Visible spectra, FTIR, NMR spectra and conductometric titration in non-aqueous medium, the proposed structure of the copolymer resin is as shown in the Fig. 1. The copolymer resin can be used as ion-exchanger and can also be used for the preparation of polychelates with transition metal ions.

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