

Synthesis and Characterization of p-Amino Phenol (p-AP)-Dithiooxamide(D) Formaldehyde (F) Terpolymer Resins.

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ABSTRACT

Terpolymer resins p-APDF were synthesized by condensing paraamino phenol and dithiooxamide with formaldehyde in varied molar ratio in the presence of acid catalyst. Terpolymer resins compositions have been determined on the basis of elemental analysis and number average molecular weights of these resins were determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethylformamide (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.

Keywords: synthesis; polycondensation, resin, polymerisation.

INTRODUCTION

Polymers are high molecular weight compound containing covalent bonds as the force holding together atoms or smaller molecular fragments. Research on polymers or giant molecules has been carried out due to their importance, currently attached to the problem of producing material with high temperature resistance. Thermally stable materials are used as high temperature lubricants, surface coatings, adhesives, fibres, elastomers, construction materials required in high speed aircrafts and space vehicles. The high molecular weight compounds like, rubber, silk cellulose, proteins, resins and gums were known to the chemists since long and were believed to be made of colloidal aggregates of small molecules which were held together by some undefined binding force.

Macromolecular science deals with compounds whose characteristic properties depend mainly on the extraordinary large size of the molecules and synthetic polymeric or macromolecular compounds lies between 10^4 and 10^7 polymeric materials received attention and importance only in the recent years.

Polymer whether synthetic or man-made are used in daily life in the form of plastics, fibres, rubber, paints and coatings. Condensation of phenol or hydroxybenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydroxybenzoic acid and urea/thiourea with formaldehyde /trioxane in presence of acid yields a terpolymer. These terpolymers are reported to have better acid resistance, better thermal stability and electrical properties than those of phenol-formaldehyde type copolymers.

The terpolymers can be used as adhesives, abrasives, binders, fibers, chemical resistant, insulators, surface coatings, flocculent, ion-exchangers, antioxidants, semiconductors, dyes, rectifiers, fungicides in plants and living tissues, hair fixatives, hardening agents, molding materials, fire resistant, thermal and thermo oxidative stable products etc. Metal containing conducting polymers are a new and interesting class of materials that combine some of the redox properties of the conducting polymer and some of those of the metal ions.

A large number of such polymers have been synthesized and studied and have been found to be of interest because the electronic, optical and catalytic properties of the complexes produced are combined in a processable form. The conventional polymers with an organic backbone are characterized by high viscosity and long range elasticity, useful for their applications in technology but they suffer from a disadvantage that most of them break down on heating in air below 250°C commercial products, like polyethylene, polyamide, polyester, fiber etc. are well known examples of organic polymers.

The high density polyethylene so formed is relatively hard, stiff and consists of mainly straight chains. Terpolymer are macromolecular entities which form an integral part of the backbone.

Terpolymers are found to be amorphous powder or crystalline resinous in nature and form special class of polymers which are widely known for their uses. Condensation of phenol or hydrobenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydrobenzoic acid and biuret with formaldehyde or trioxane in presence of acid as catalyst yields a Terpolymer. This terpolymers in general are found to be insoluble in most of the common organic solvent and are fuseable to clear melts. These Terpolymer have better thermal stability and electrical properties than those of phenol - formaldehyde type copolymers. The terpolymers can be used as ion-exchangers, semi-conductors, antioxidants, hardening agents, molding materials, rectifiers, dyes, fungicides in plants and living tissues.

The rapidly expanding field of terpolymers are interestingly attracting attention by scientists and has undergone spectacular growth during the last few years. Terpolymer are thermally more stable and therefore suitable for withstanding high temperature.

The p-APDF terpolymer resins which are synthesized taking various molar ratios of monomers in 4 different ratios. They are found to be in green colour and are soluble in DMF, DMSO, aqueous KOH, NaOH and are insoluble almost in all other organic and inorganic solvents.

METHODOLOGY

Synthesis of p-Aminophenol(p-A)Dithiooxamide (D)-Formaldehyde (F) Terpolymer Resin

The four different types of p-APDF terpolymer resins have been successfully synthesized and abbreviated as given in Table 2.3.

Synthesis of p-APDF-I terpolymer resin

A mixture of p-aminophenol (1.09 g, 0.1 mol) and dithiooxamide (1.20g, 0.1 mol) with formaldehyde (7.50 ml, 0.2 mol) was carried out in the presence of 2M (200 ml) HCl as catalyst by molar ratio of 1:1:2 of reacting monomers, was taken in a round bottom flask fitted with water condenser and heated in an oil bath at $122^\circ\text{C} \pm 2^\circ\text{C}$ for 5 hrs with occasional shaking to ensure thorough mixing. The temperature of electrically heated oil bath was controlled with the help of

dimmerstat. The brown coloured resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction is shown as follows in Fig. 1.

Purification of Resins :

The solid product was repeatedly washed with cold distilled water, dried in air and powdered with the help of agate mortar and pestle. The powder was washed many times with hot water followed by methanol to remove the unreacted starting materials, if any. The properly washed powder was dried in vacuum desiccator over anhydrous calcium chloride. The resin was further purified by reprecipitation technique. The terpolymer was dissolved in 8% NaOH, filtered and reprecipitated by dropwise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with rapid stirring to avoid the lump formation. The process of reprecipitation was repeated twice. The terpolymer resin p-APDF-I so obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over unhydrous calcium chloride.

p-APDF Terpolymer

Similarly other terpolymer resins p-APDF-II, p-APDF-III and p-APDF-IV were synthesized by varying molar proportions of starting materials viz. (2:1:3), (3:1:4) and (4:1:5) with the little variation of experimental conditions.

MOLECULAR WEIGHT DETERMINATION BY NON-AQUEOUS CONDUCTOMETRIC TITRATION

Measurement of polymer molecular weights is a matter of fundamental importance for the characterization of polymeric materials. It has been done by conductometric titration method in non-aqueous medium i.e. in double distilled dimethyl sulphoxide. The conductometric titrations were carried out in DMSO using standard potassium hydroxide (0.5N) in absolute ethanol as a titrant. The results are presented in Table 1. The specific conductance was plotted against milli equivalents of ethanolic KOH required for neutralization of 100 gm of each terpolymer resins. The titration curves are shown in Fig. 2. The plots obviously indicates that

there are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot corresponds to a stage in titrations when an average one phenolic hydroxyl group of each chain was neutralized. The curves reveal that size of the most of the break was nearly equal or was a whole number multiple of the size of the first break. The conductometric curve indicates a sharp stepwise increase in conductance till the stage of complete neutralization of all the phenolic hydroxyl groups. It has been observed that there is continuous steady increase in the value of conductance after neutralization stage [1, 2, 3, 4]. The amount of standard KOH was transferred into milliequivalents for 100gm of terpolymer resins and plotted against specific conductance. From the plot, the first and the last breaks were noted. Average degree of polymerization (\overline{DP}) and hence the number average molecular weight (\overline{Mn}) of all terpolymer resins have been determined using the formula.

$$\overline{DP} = \frac{\text{Total milliequivalents of base for complete neutralisation}}{\text{Milliequivalents of base required for smaller intervals}}$$

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight}$$

Thus the degree of polymerization (\overline{DP}) and the average molecular weight (\overline{Mn}) were evaluated from the conductometric titration curves are presented.

INTRINSIC VISCOSITY

The most evident distinguishing property of polymer solution is its viscosity. The viscosity measurements were carried out at 300K in freshly triple distilled DMSO using Tuan-Fuoss viscometer [5] at six different concentrations ranging from 1.00% to 0.031%. The plot of reduced viscosity η_{sp}/C and inherent viscosity $\ln \eta_{rel}/C$ against concentrations were linear with slopes K_1 (Huggins' constant) and K_2 (Kraemer's constant) respectively. By extrapolating linear plot (Fig. 3) to zero concentration intercept on the viscosity function axis gives the value of intrinsic viscosity (η) in both the plots. The calculated value of the constants K_1 and K_2 in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably [6,7,8]. It was observed that terpolymer resins having higher \overline{Mn} shows

higher value of intrinsic viscosity (η) which is in good agreement with earlier co-workers [9,10,11].

UV-VISIBLE SPECTRA

The UV-visible spectra (Fig. 4) of all p-APDF terpolymer resins in pure DMSO were recorded in the region 200-800 nm. All p-APDF terpolymer samples gave two characteristics bands at 200-290 nm and 290-390 nm. These observed positions for the absorption bands have different intensities. The more intense band 200-290 nm is due to ($\pi \rightarrow \pi^*$) allowed transition of a C=S group containing a carbon sulphur double bond in with the aromatic. The less intense band 290-390 nm may be due to ($n \rightarrow \pi^*$) forbidden transition of -OH and -NH groups. Thus $\pi \rightarrow \pi^*$ transition indicates the presence of aromatic nuclei and to $n \rightarrow \pi^*$ transition indicates the presence of -NH and OH groups the later band indicates ($n \rightarrow \pi^*$) transition due to bathochromic shift (the shift toward a longer wave length) from the basic values (257nm and 320 nm) may be due to the combined effect of conjugation and the phenolic hydroxyl group (ausco chrome) [12,13,14,15,16,17].

INFRA-RED SPECTRA

The IR spectral data of p-APDF terpolymer resins are depicted in Fig. 5. The IR spectral studies revealed that all these terpolymer resins give rise to nearly similar pattern of spectra. A broad absorption band appeared in the region 3602-3608 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [18,19,20]. The peak, at 3345-3357 cm^{-1} and indicate the presence of <NH stretching (amide/imides) [21,22]. The peak at 31.06-3135 cm^{-1} (-CH stretching), 2512-2514 cm^{-1} (-CH stretching of -CH₂ group), 1367-1369 cm^{-1} (-CH₂ bending wagging and twisting), 1220-1221 cm^{-1} (-CH₂ plane bending), indicate the presence of methylene (-CH₂) group and 1367-1369 cm^{-1} methylene bridge in terpolymer chain. The bands appeared at 3203-3209 cm^{-1} (Aryl C-H stretching) and 1609-1612 cm^{-1} (substituted aromatic ring) may be ascribed to aromatic ring [23,24]. The band at 824-827 cm^{-1} indicates the presence of tetra substituted aromatic ring. 1,2,3,5 substitution in aromatic ring was confirmed by the bands appeared at 906-909 cm^{-1} , 1067-1071 cm^{-1} , 1128-1130 cm^{-1} . The band of -NH stretching (3345-3357 cm^{-1}) seems to be

merged with very broad band of phenolic hydroxyl group [25,26,27].

¹H NMR SPECTRA

Proton NMR spectra of p-APDF terpolymer resins were scanned in DMSO-d₆ solvent. The spectra are given in Fig. 5. From the spectra it is revealed that p-APDF terpolymer resins give rise to different pattern of ¹H NMR spectra, since each of p-APDF terpolymer possesses set of proton having different electronics environment. The chemical shift (δ) ppm observed is assigned on the basis of data available in the literature [28]. The singlet obtained in the region 3.47-3.67 (δ) ppm may be due to proton of Ar-NH₂ group. The singlet obtained in the region of 3.62-3.72 (δ) ppm may be due to the methylene proton of Ar-CH-N moiety. The signal in the region 7.21-7.35 (δ) ppm are attributed to protons of -NH bridge. The weak multiplet signal (unsymmetrical pattern) in the region of 8.76-8.81 (δ) ppm may be attributed to aromatic proton (Ar-H) [29,30,31]. The signal appeared at 9.13 to 9.18 (δ) ppm may be due to phenolic hydroxyl group protons [32]. The much downfield chemical shift for phenolic -OH indicate clearly the intramolecular hydrogen bonding of -OH group [33,34,35].

On the basis of all the physico-chemical and spectral evidences and foregoing results and discussion the most probable structures have been proposed for p-APDF terpolymer resins under investigations as shown in Fig. 7.

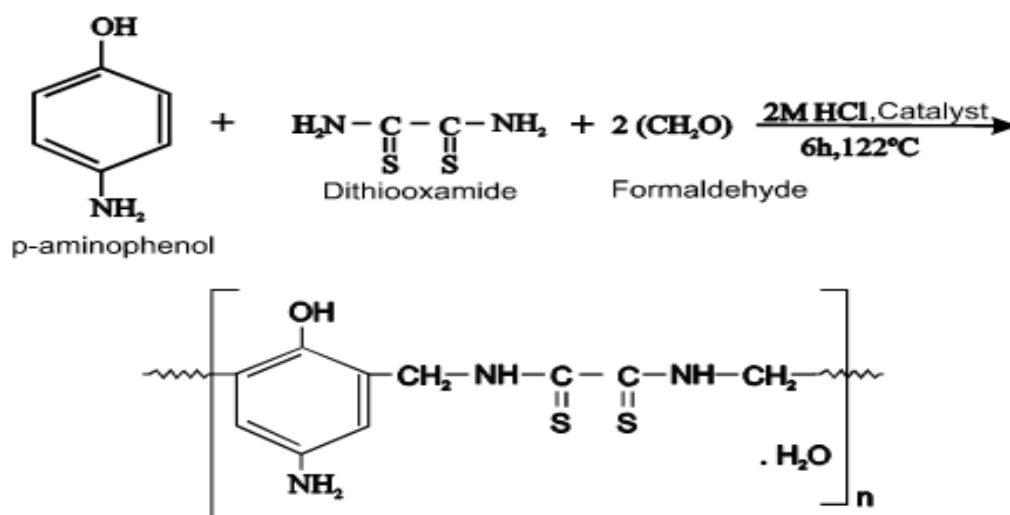
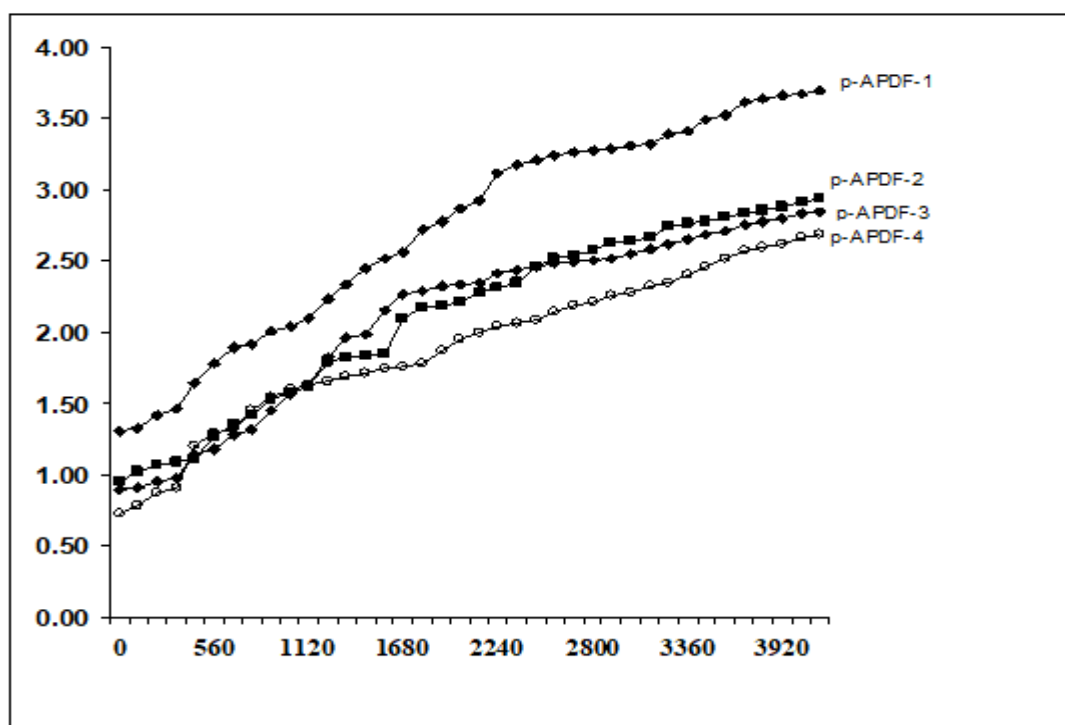
RESULTS AND DISCUSSION

The resin samples were green in colour, insoluble in commonly used organic samples but 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.

The molecular weight (\bar{M}_n) of the terpolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in 50%(vol/vol) DMF/alcohol mixture using 100 mg of resin sample .

Table 1: Synthesis and Physical Data of p-APDF Terpolymer Resins

Terpolymer Resin Abbreviation	Reactants			Molar ratio	Catalyst 2M/Cl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	Para amino phenol p-AP (mol)	Dithiooxamide D (mol)	Formaldehyde F (mol)						
p-APDF-I	0.1	0.1	0.3	1:1:3	200	393	5	75	374
p-APDF-II	0.2	0.1	0.4	2:1:4	200	393	5	80	386
p-APDF-III	0.3	0.1	0.5	3:1:5	200	393	5	75	389
p-APDF-IV	0.4	0.2	0.7	4:2:7	200	393	5	80	393

**Fig. 1 Reaction and Suggested Structure of Representative p-APDF-I Terpolymer Resin****Fig. 2 Conductometric Titration Curves of p-APDF Terpolymer Resins**

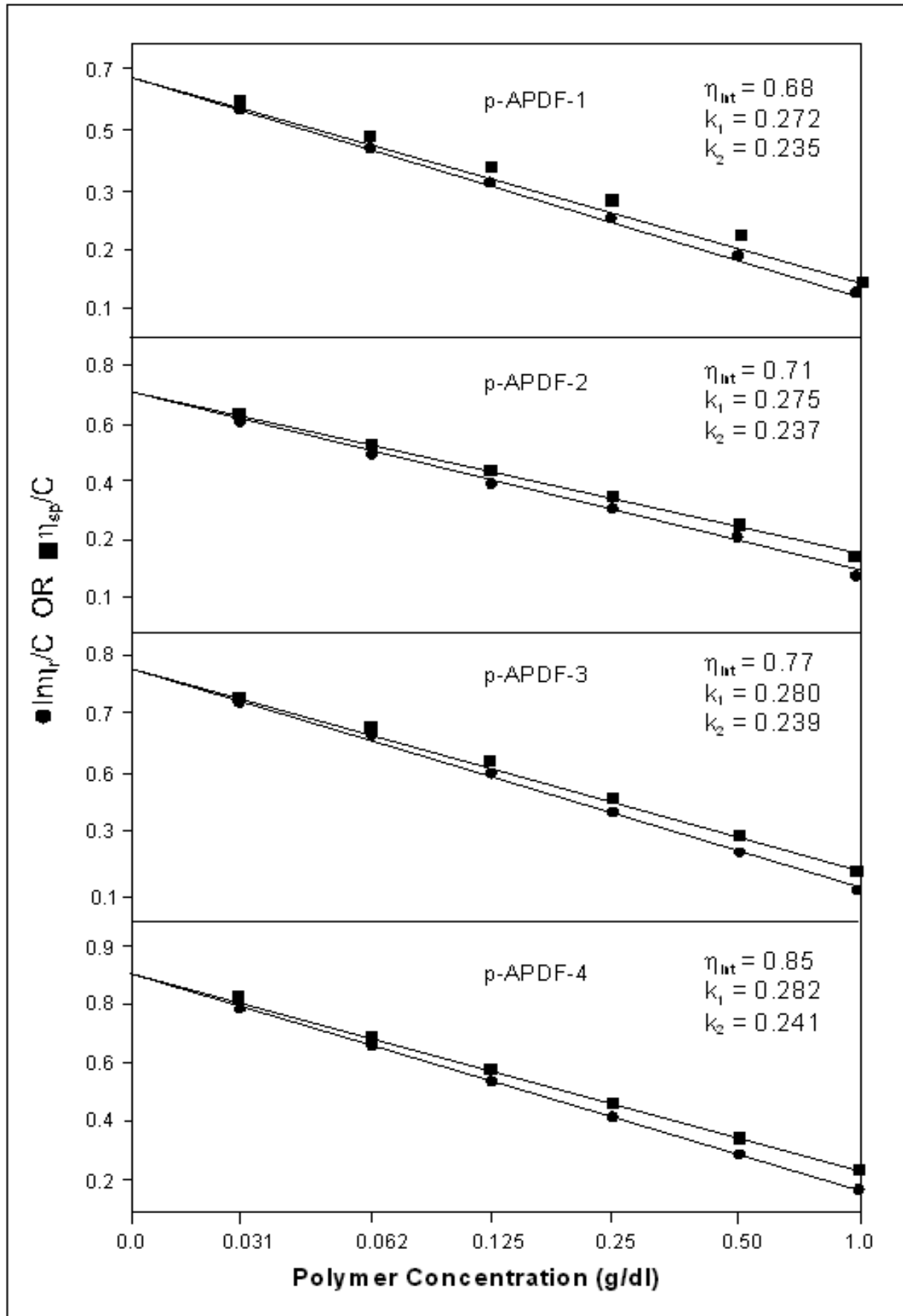


Fig. 3 : Viscometric Plots of p-APDF Terpolymer Resins

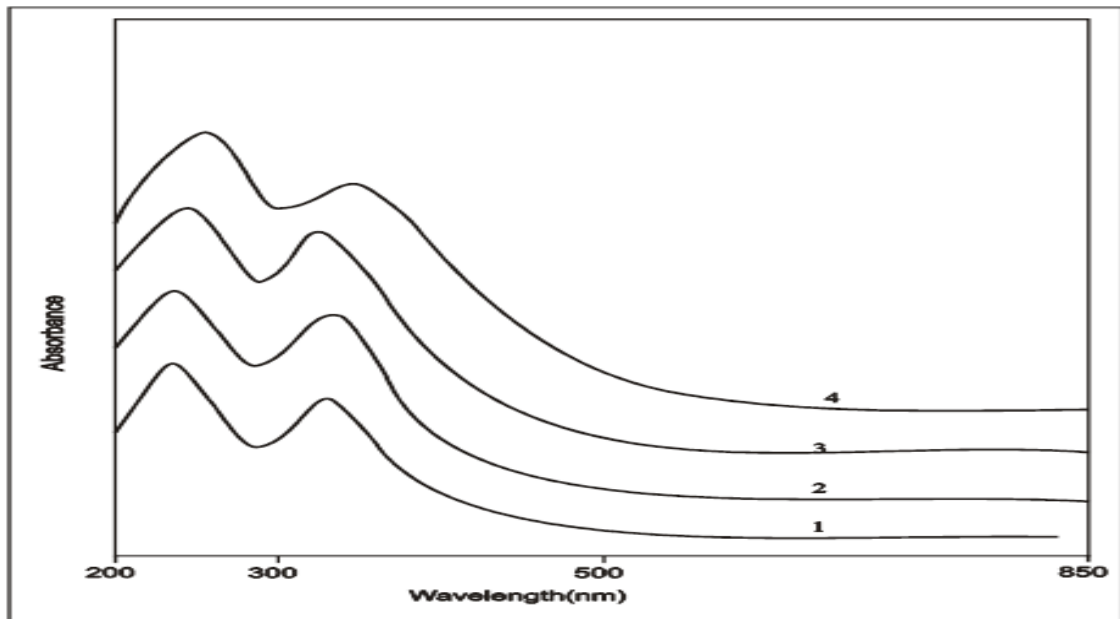


Fig. 4 UV-Visible Spectra of p-APDF Terpolymer Resins

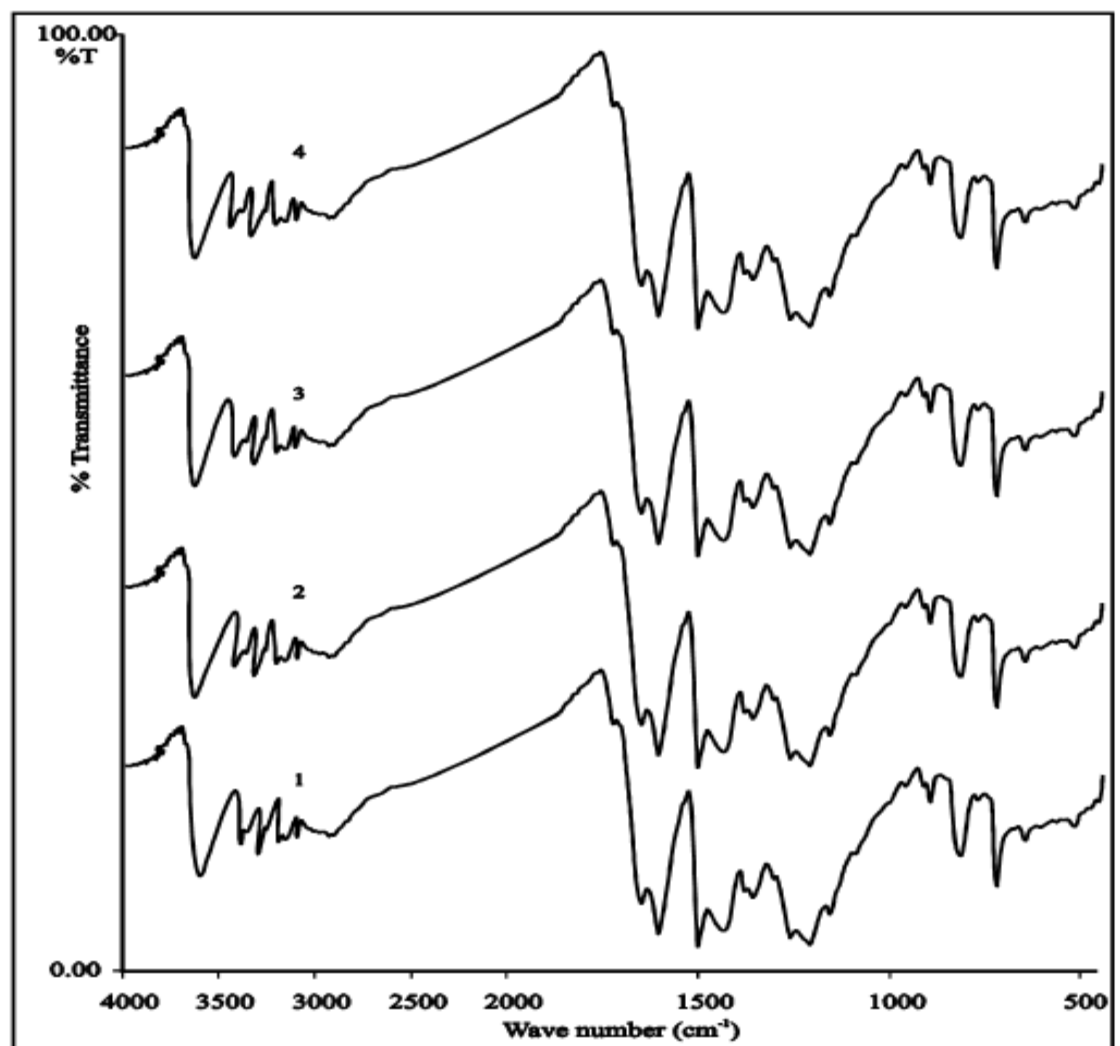


Fig. 5 : Infra Red Spectra of p-APDF Terpolymer Resins

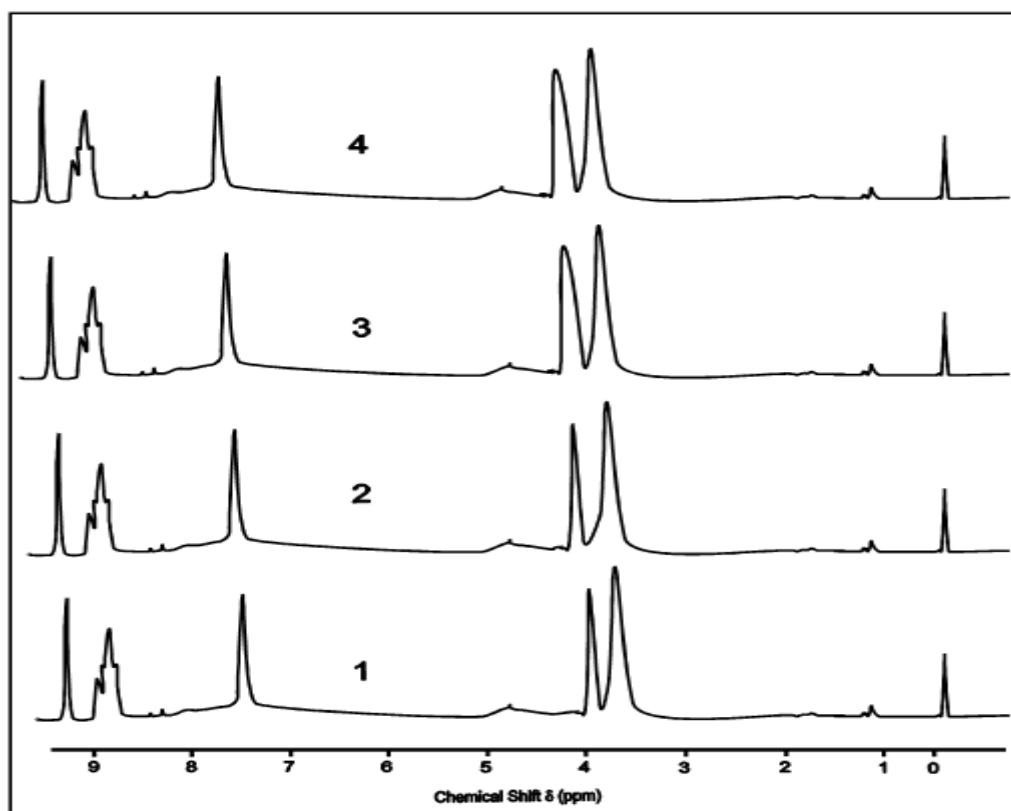


Fig. 6 :¹H NMR Spectra of p-APDF Terpolymer Resins

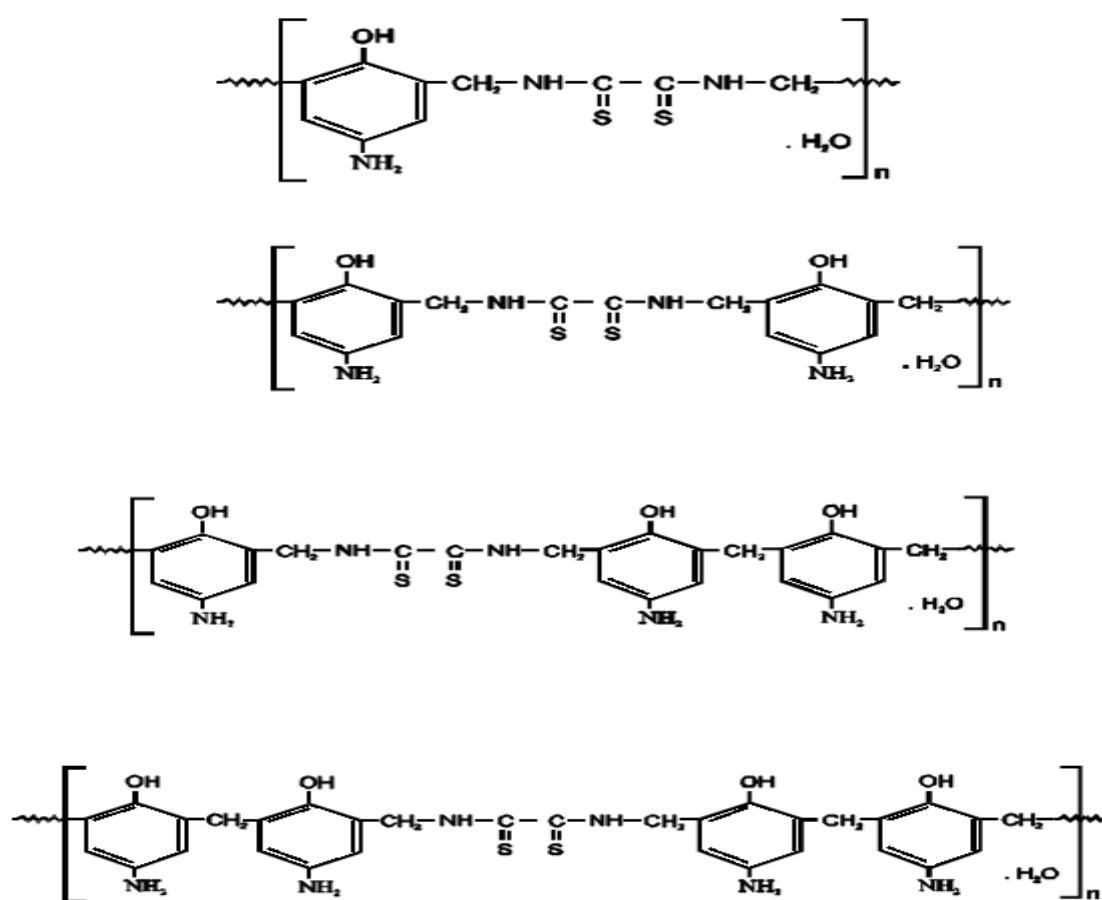


Fig. 7. Structures of p-APDF Terpolymer Resins

A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100g of terpolymers was made. Inspection of such a plot revealed that there are many breaks in plot. From these plot the first break and the last break were noted. The calculation of (\bar{M}_n) by this method is based on the following considerations[36].

1. The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all repeating units and
2. The break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxyl group of all repeating units are neutralized.

Viscometric measurements were carried out in DMF at 300C. All the resins showed normal behavior. The intrinsic viscosity was determined by the Huggins equation[36].

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

And Kraemers equation[37].

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

The viscometric plots are shown in Fig.3. In accordance with the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ 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 in most of cases satisfy the relation $K_1 + K_2 = 0.5$ favourably. The values of $[\eta]$ obtained from eq. (1) and eq. (2) were in close agreement with each other.

The UV-visible spectra of all the p-APDFterpolymer resins are depicted in Fig. 4. The IR spectra of all the p-APDFterpolymer resins are presented in Fig. 5 and proton NMR spectra in Fig. 5.

On the basis of the nature and reactive positions of the monomers, elemental analysis, UV-visible spectra, IR spectra, NMR spectra and molecular weight, the most

probable structures have been proposed for terpolymer resins as shown in Fig. 7.

CONCLUSION

The terpolymer resins p-APDF were prepared in four molecular proportions based on condensation reaction of p-Amino Phenol and dithiooxamide with formaldehyde in the presence of acid catalyst. Elemental analysis, UV-Visible spectra, IR, NMR spectra, conductometric titration in non-aqueous medium and viscometric measurements, the proposed structures of the terpolymer resins are shown in Fig. 7. These terpolymer resins can be used as ion-exchangers.

Conflicts of interest: The authors stated that no conflicts of interest.

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