

Full Paper

Studies on Semiconducting, Chelating and Thermal Properties of P-Cresol–Oxamide-Formaldehyde Terpolymer Resin

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Abstract- The title terpolymer (p-COF-II) synthesized by the condensation of p-Cresol (p-C) and Oxamide (O) with Formaldehyde (F) in the presence of acid catalyst and using 2:1:3 molar proportions of the reacting monomers. The synthesized terpolymer resin then characterized by elemental analysis and spectral studies like IR, ¹H NMR, ¹³C NMR and XRD. The morphology of synthesized terpolymer was studied by scanning electron microscopy (SEM). The electrical property was measured over a wide range of temperature (313-403K). The plot of log σ vs. $10^3/T$ of the resin is linear over a wide range of temperature showing its semiconducting nature. The chelating ion-exchange study was carried out over a wide pH range, shaking time and in media of various ionic strengths for seven metal ions Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) in the form of their metal nitrate solutions. The terpolymer showed a higher selectivity for Fe (III), Cu (II), and Ni (II) ions. Thermal study of the resin was carried out to determine its mode of decomposition and thermal stability. By using data of thermogravimetry various kinetic parameter like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S^*) have been determined using Freeman-Carroll method.

Keywords- Semiconductor, Ion-exchanger, Adsorption, Thermogravimetric Analysis, Synthesis

1. INTRODUCTION

The synthesized terpolymer resins with highly conjugated chains have attracted much attention of scientist and introduce the recent innovations in the polymer chemistry in the last few years because they show versatile applications and properties. The terpolymer resins can be used as high energy material: ion-exchanger, semiconductors, antioxidants, fire proofing agent, optical storage data, binders, molding materials etc [1,2,3].

The semiconducting properties of terpolymer resins have gained sufficient ground in recent years. Electrically conducting polymer resins are undoubtedly one of the focal points of current interest in solid-state physics and chemistry. Their discovery has led to the emergency of not only new types of materials capable of replacing metals but also new concepts to explain their high conductivity. Work on organic conducting polymers is carried out extensively due to their wide applications in areas such as corrosion protection and antistatic coatings [4], in biosensors for coupling of electron transfer [5], fabrication of electrochemical windows and gas sensors [6], development of individual electronic devices and whole integrated circuits [7,8] etc. Delocalized electrons and conjugation impart semiconducting properties to the polymer resins.

Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture, and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, precipitation, and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacity and selectivity having physical and chemical stabilities [9, 10]. Chelating ion-exchange properties of the resin involving poly [(2, 4-dihydroxybenzophenone) butylenes] V and its polychelates with transition metals are reported [11]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [12].

The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Terpolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials. Michael EP, et al. studied the thermal decomposition behavior of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer [13].

The present paper explored the synthesis and characterizations of p-Cresol-Oxamide-Formaldehyde (p-COF-II) terpolymer resin which exhibits a unique combination of properties: chelating and thermal properties along with the semiconducting nature.

2. EXPERIMENTAL

2.1. Starting materials

The chemicals (starting materials) were of Analar or Chemically pure grade and wherever necessary the purity was tested and confirmed by TLC.

2.2. Synthesis of p-COF-II terpolymer resin

The new terpolymer resin p-COF-II was synthesized by condensing p-cresol (2.16 g, 0.2 mol) and oxamide (0.88 g, 0.1 mol) with 37 % formaldehyde (11.1 ml, 0.3 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at $130^{\circ}\text{C}\pm 2^{\circ}\text{C}$ for 5h in an oil bath with occasional shaking to ensure thorough mixing. The separated cream color terpolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove p-cresol-formaldehyde copolymer which might be present along with p-COF-II terpolymer. The terpolymer resin was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The terpolymer sample p-COF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the terpolymer resin was found to be 80%. The reaction and suggested structure has been given in Fig. 1.

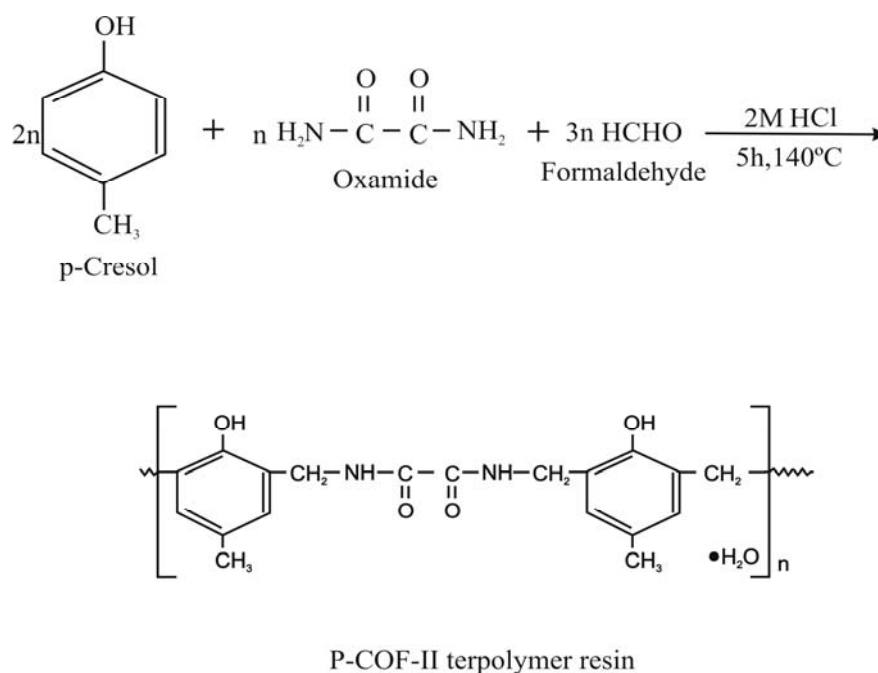


Fig. 1. Reaction and suggested structure of p-COF-II terpolymer resin

3. CHARACTERIZATION

The viscosities of the p-COF-II terpolymer were determined using Taun-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.031% of terpolymer in DMSO at 30°C. The intrinsic viscosity η was calculated by relevant plots of the Huggins' equation (1) and Kramer's equation (2).

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

$$\ln \eta_r / C = [\eta] + K_2 [\eta]^2 \cdot C \text{-----(2)}$$

Where C= concentration in gm/100 ml.

η_r = the ratio between viscosity of solution $[\eta]$ and viscosity of the solvent $[\eta_0]$ is known as relative viscosity $\eta_r = \eta/\eta_0$

η_{sp} = this function has been derived from relative viscosity and given by

$$\eta_{sp} = (\eta - \eta_0) / \eta_0 = \eta/\eta_0 - 1 = \eta_r - 1$$

$[\eta]$ = it is intrinsic viscosity obtained by extrapolating a plot of η_{sp}/C or $\ln \eta_r/C$ against concentration. $[\eta] = \lim_{C \rightarrow 0} (\eta_{sp}/C)$.

The intrinsic viscosity is characteristics parameter of a polymer.

The number average molecular weight (\bar{M}_n) was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (\bar{DP}) and the number average molecular weight (\bar{M}_n) has been calculated for terpolymer resin under investigation.

An infra-red spectrum of p-COF-II terpolymer resin was recorded on Perkin-Elmer-R-X-R spectrophotometer in KBr pallets in the wave number region of 4000-400 cm^{-1} at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University; Chandigarh. A Nuclear Magnetic Resonance (NMR) spectrum of newly synthesized terpolymer resin has been scanned on FT-NMR-cryo-magnet 400 MHz (Bruker) spectrometer using DMSO- d_6 at Sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. A ^{13}C nuclear magnetic resonance spectrum of the terpolymer resin was scanned on Bruker Advanced 400 spectrometer at National Chemical Laboratory (NCL), Pune. The x-ray spectra of terpolymer sample was taken on Philips PW-1700, Automatic x-ray diffractometer at Sophisticated Analytical Instrumentation Facility RTM, Nagpur University, Nagpur. The ion exchange property of the p-COF-II terpolymer resin was determined by the batch equilibrium method. TGA of terpolymer resin has been carried out by using Perkin-Elmer Pyrix-1TGA, DTA-7 Thermogravimetric Analyzer at heating rate of 10 °C per minute up to 800°C. SEM has been scanned by FEI-Philips XL-30 electron microscope.

4. RESULTS AND DISCUSSION

4.1. Infrared spectra

Infrared spectrum of the p-COF-II terpolymer resin has been shown in Fig. 2. Very broad band appeared in the region 3229 cm^{-1} may be assigned to the stretching vibration of phenolic -OH groups exhibiting intermolecular hydrogen bonding between -OH and $>\text{C}=\text{O}$ and NH group of amide. The band obtained at 1371 cm^{-1} suggests the presence of methylene (-CH₂-) bridges. A sharp and strong peak at 1607 cm^{-1} may be ascribed to aromatic skeletal ring. The 1,2,3,5 tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium absorption bands appeared at 912, 1098, 1149 cm^{-1} respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3011 cm^{-1} which seems to be merged with very broad band of phenolic hydroxyl group [15]. A sharp and strong peak at 1379 cm^{-1} may be ascribed to -CH₂- symmetrical deformation. A sharp peak at 2917 cm^{-1} may be ascribed to $>\text{CH}_2$, -NH, -CH₃ stretching. A sharp and strong peak at 1743 cm^{-1} may be due to $>\text{C}=\text{O}$ stretching (oxamide moiety). A broad and sharp peak at 1481 cm^{-1} may be ascribed to -NH bending of secondary amide. A sharp peak at 1286 cm^{-1} may be ascribed to -CH₂ bending (wagging & twisting). The band obtained at 1231 cm^{-1} suggests the presence of -CH₂- plane bending. The band obtained at 784 cm^{-1} suggests the presence of -CH₂ bending (rocking) and -NH deformation out of plane of secondary amide respectively.

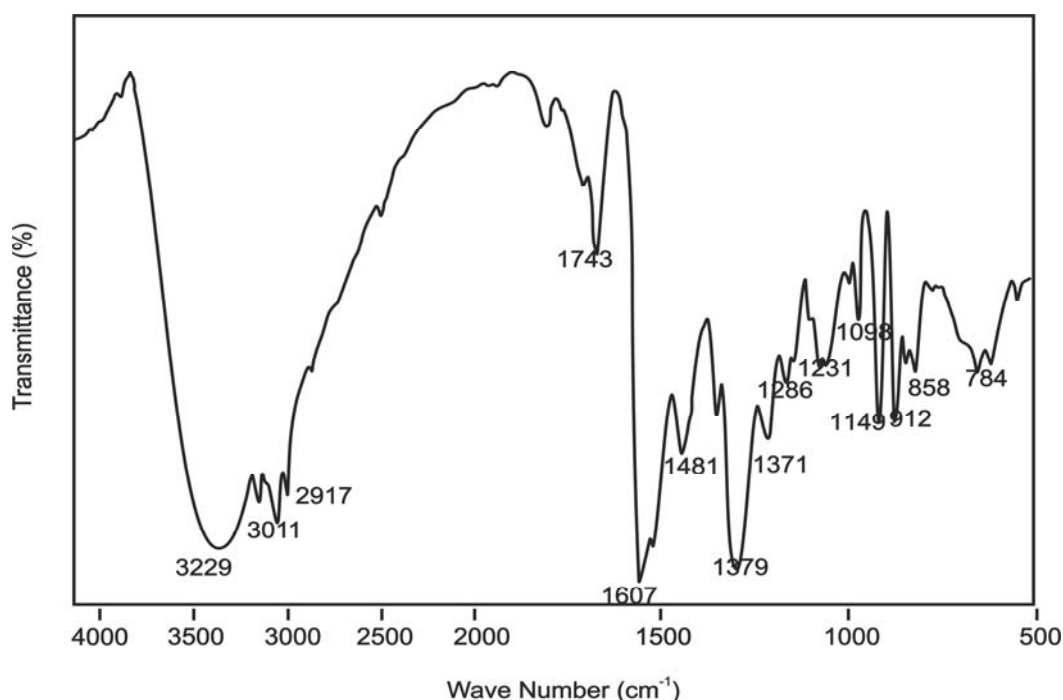


Fig. 2. Infrared Spectra of p-COF-II terpolymer resin

4.2. Nuclear magnetic resonance spectra

The NMR spectrum of p-COF-II terpolymer was scanned in DMSO-d₆ and has been shown in Fig.3. The chemical shift (δ) in ppm has been assigned on the basis of data available in literature [16]. The p-COF-II terpolymer resin shows an intense weakly multiplet signals at $\delta = 2.56$ ppm which may be attributed to methyl proton of Ar-CH₃ group. The singlet obtained in the region of $\delta = 3.46$ ppm may be due to the methylene proton of Ar-CH₂-N moiety. The signal in the region of $\delta = 4.60$ ppm is attributed to protons of >CHO group. The signal in the region of $\delta = 5.73$ ppm is attributed to protons of bridge -NH. The weak multiplet signal (unsymmetrical pattern) in the region of $\delta = 6.62$ ppm may be due to terminal methylene group. The signals in the range at $\delta = 8.65$ ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding of -OH group. The signal at $\delta = 1.20$ ppm may due to -CH₃-C \equiv moiety. The signal at $\delta = 2.80$ ppm and at $\delta = 3.37$ ppm may due to CH₂-N< moiety. The signal at $\delta = 7.52$ ppm may due to aromatic proton (Ar-H).

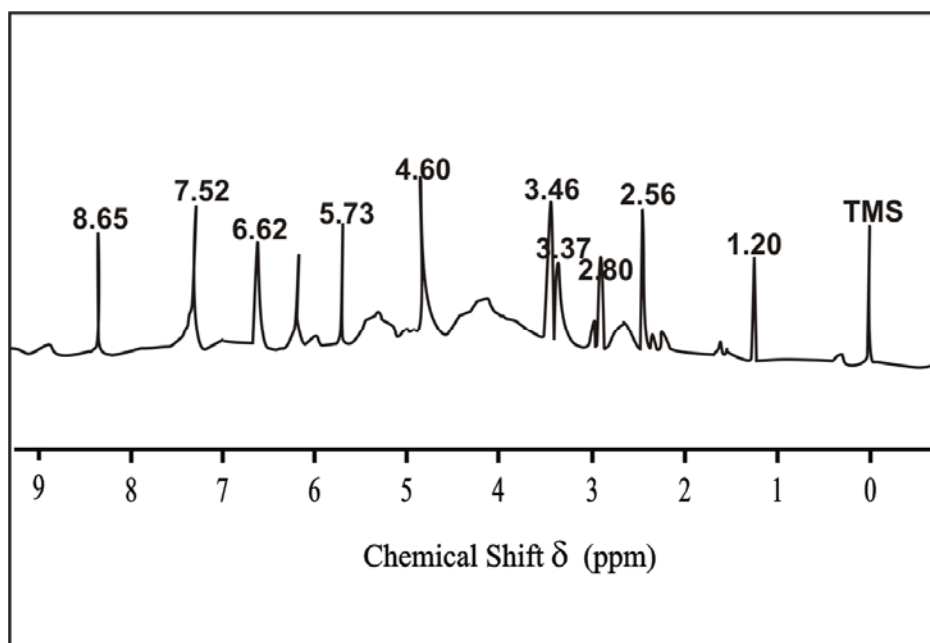


Fig. 3. Nuclear Magnetic Resonance Spectra of p-COF-II terpolymer resin

4.3. ¹³C Nuclear magnetic resonance spectra

¹³C NMR spectrum of p-COF-II terpolymer resin has been recorded as shown in Fig. 4. The ¹³C NMR spectrum of p-COF-II terpolymer resin shows the signals at 148.3, 188.5, 131.6, 140.3, 131.6 and 118.5 ppm. These signals may be due to C₁ to C₆ carbon atoms of aromatic benzene nucleus. The signals at 180.2 ppm may be due to C₁ to C₂ carbon of

carbonyl groups of oxamide moiety. The signal at 120.5 ppm may be assigned from -C-NH group and at 65.72 ppm may be assigned to C-OH group. Nearly at 40.5 ppm the signal is appeared, which may be corresponded to carbon atom of methyl group attached to aromatic benzene nucleus. The shifting of signals is due to the substitution in benzene. The ^{13}C NMR spectrum after analysis minutely confirmed that the monomers are arranged in a straight manner, giving the linear structure for terpolymer, which we have proposed is obviously correct given in Fig. 1.

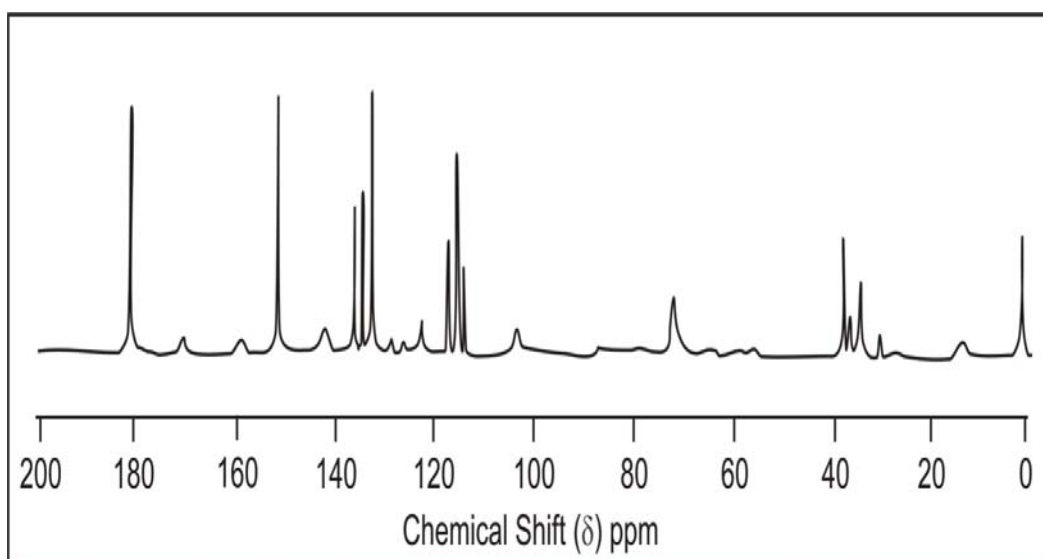


Fig. 4. ^{13}C Nuclear Magnetic Resonance Spectra of p-COF-II terpolymer resin

4.4. Scanning electron microscopy (SEM)

Scanning electron micrographs of the p-COF-II terpolymer resin has been recorded as shown in Fig. 5 at 1500X and 3000X magnification. The SEM micrographs of p-COF-II terpolymer resin sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions [17]. Thus SEM study shows that the p-COF-II terpolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.

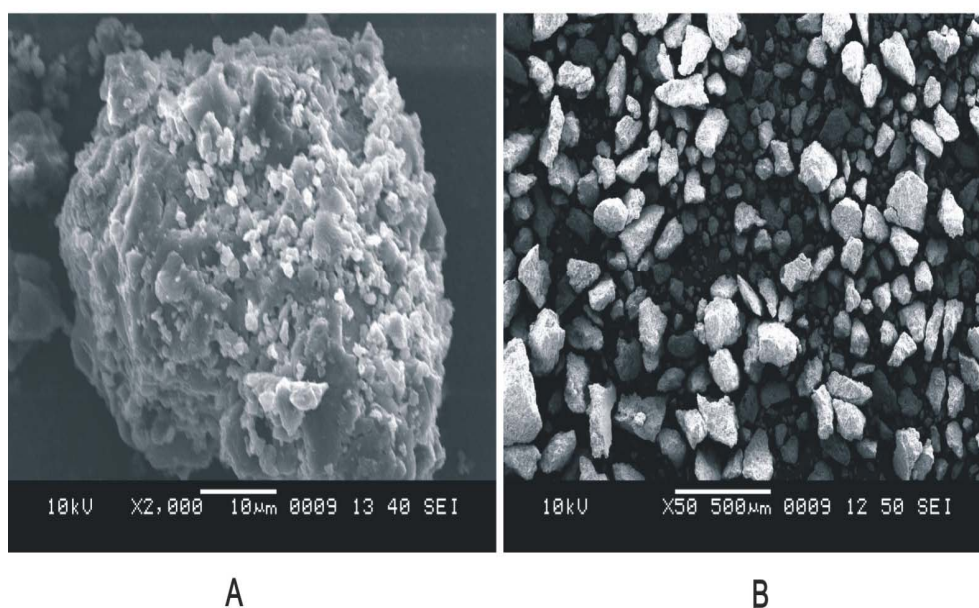


Fig. 5. Scanning Electron micrographs (SEM) of p-COF-II terpolymer resin

4.5. X-ray diffraction

X-ray diffraction pattern of p-COF-II terpolymer has been shown in Fig. 6. The x-ray diffraction diagram of the polymer displayed the main characteristic peak and a broad shoulder in the range of 22-23 2θ . In view of the relative half value width, it may be concluded that the polymer is partially crystalline. The broad characteristic peak indicates the amorphous nature of the polymer which can also be explained by SEM study. The XRD spectrum was used to calculate crystallite size of p-COF-II terpolymer resin using Scherres formula of Cullity.

$$d = \frac{0.9\lambda}{B \cdot \cos\theta_B}$$

Where λ is x-ray wavelength (1.54056\AA), θ_B is Bragg's diffraction angle and B is reflection broadening as full width at half maximum intensity. The particle size of p-COF-II terpolymer resin has been calculated which is found to be at around 145 nm.

The polymer under study is a terpolymer hence it is very difficult to assign its exact structure. However on the basis of the nature and relative position of the monomers, elemental analysis, IR, NMR, ^{13}C NMR and XRD spectral studies and taking into consideration the linear structure of other phenol-formaldehyde resin and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for p-COF-II terpolymer resin(Fig. 1).

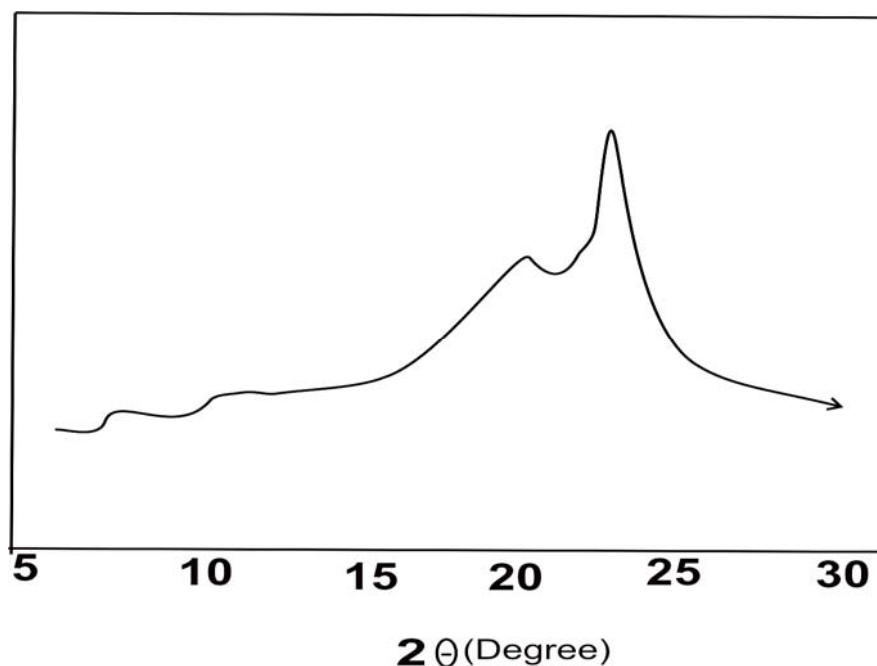


Fig. 6. X-ray diffraction pattern of p-COF-II terpolymer resin

4.6. Electrical conductivity

The thermal activation energy is found to be 0.85×10^{-4} eV and the values of electrical conductivity at different temperatures is found to be in the range of 1.29×10^{-9} to 2.91×10^{-9} $\text{ohm}^{-1}\text{m}^{-1}$.

The resistance values of the pellet of the polymer ranging from 303 K to 403 K were converted into conductivity values (σ) by taking into account the thickness of the pellet and its diameter and evaluating thickness area parameters of the pellet of a terpolymer. The temperature dependence of the electrical conductivity of the polymer has been shown in Fig.7. The electrical conduction of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation, atmosphere etc; activation energy (E_a) is not affected by these parameters and, therefore, it is fairly reproducible. The magnitude of activation energy depends on the number of electrons present in semiconductor materials. The more the number of π – electrons lowers the magnitude of activation energy and vice versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those with aliphatic system. Thus, the low magnitude of activation energy in p-COF-II resin may be due to the presence of large number of π electrons in the polymer chain. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation. The p-COF-II polymer shows the electrical conductivity in the range of 1.29×10^{-9} to 2.91×10^{-9} $\text{ohm}^{-1}\text{m}^{-1}$ and the plots of $\log \sigma$ versus $1/T$ is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law is obeyed.

$$\sigma = \sigma_0 \exp^{(-\Delta E / k T)}$$

Where, k = Boltzmann constant, σ = electrical conductivity at temperature T

σ_0 = electrical conductivity at temperature $T \rightarrow \infty$

ΔE = electrical conductivity energy of electrical conduction.

This relation has been modified in to the equation of straight line.

$$\log \sigma = \log \sigma_0 + \frac{-\Delta E}{2.303kT}$$

The energy of activation (E_a) of electrical conduction calculated from the slope of the plot between $\log \sigma$ versus $1/T$ is found to be 0.85×10^{-4} eV. It has been found under investigation that the order of thermal activation energy is just the reverse of electrical conductivity. The temperature dependence of electrical conductivity shows that conductivity increases with temperature. As the conductivity is found very low in the range of 10^{-10} ohm⁻¹ cm⁻¹ even at higher temperature, it indicates that p-COF-II polymer resin has low charge carrier intramolecular transfer. This indicates the semiconducting nature of the p-COF-II polymer resin.

4.7. Ion-exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al was used to study ion exchange properties of p-COF-II terpolymer resin. The results of the batch equilibrium study have been presented in Table 2, 3 and 4. Seven metal ions Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables: a) Electrolyte and its ionic strength, b) uptake time and c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake of the polymer similar to the earlier co-workers [18,19].

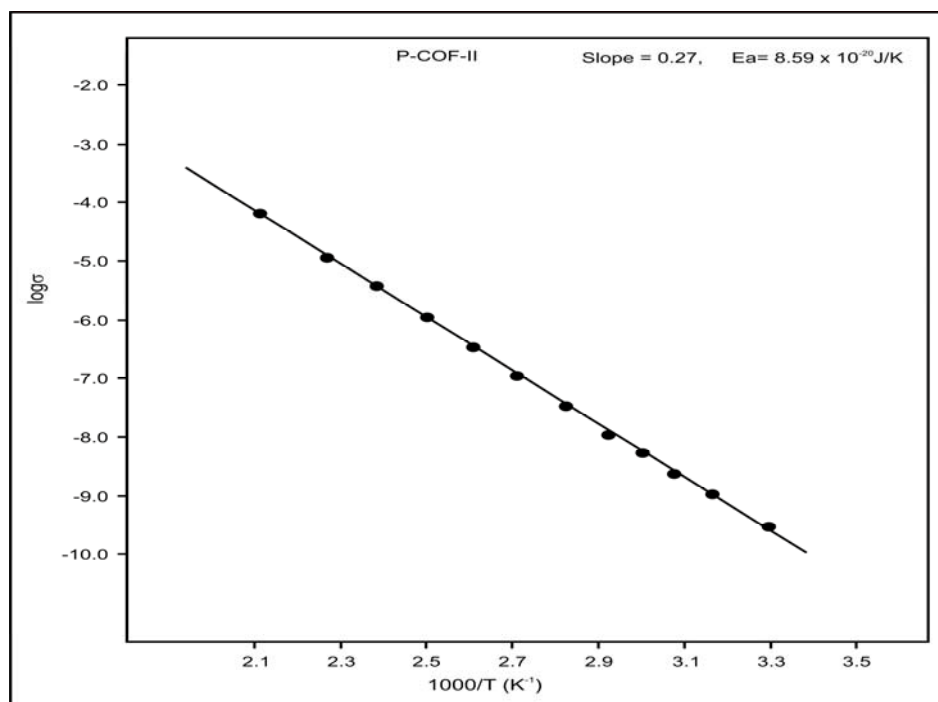


Fig. 7. Electrical conductivity plot of p-COF-II terpolymer resin

Table 1. Elemental analysis, molecular weight determination and intrinsic viscosity data of the p-COF-II terpolymer resin

Terpolymer	Empirical formula of repeat unit	Empirical weight of repeat unit (gm)	Average degree of polymerization (\overline{DP})	Average molecular weight (\overline{M}_n)	Intrinsic viscosity $[\eta]$ (dl/g)	Elemental Analysis		
						% of C	% of H	% of N
						Found (Cal.)	Found (Cal.)	Found (Cal.)
p-COF-II	C ₁₉ H ₁₄ N ₂ O	59	24.11	8655	1.49	62.45 (63.50)	5.15 (5.80)	7.28 (7.79)

4.7.1. Effect of electrolyte and its ionic strength on metal uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} at various concentrations on the equilibrium of metal-resin interaction. Table 2 shows that the amount of metal ions taken up by a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the

electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer decreases with increasing concentration of the electrolyte. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate and sulphate ions [19]. This may be explained on the basis of the stability constants of the complexes with those metal ions. SO_4^{2-} might form rather strong complexes with Fe^{3+} , Ni^{2+} , Cu^{2+} ions while NO_3^- , Cl^- and ClO_4^- might form weak complexes and therefore might not be expected to influence the position of the Fe^{3+} , Ni^{2+} and Cu^{2+} chelates equilibrium as much as SO_4^{2-} , NO_3^- , Cl^- and ClO_4^- might form rather strong chelates with CO^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field [19,20].

4.7.2. Estimation of the rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried while operating as close to equilibrium conditions as possible. Table 3 shows the results of rate of uptake of metal ion on p-CoF-II terpolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions require about 3hrs for the establishment of the equilibrium, whereas Cu (II), Ni (II), Co (II) and Zn (II) ions required about 5 and 6 hrs. Thus the rate of metal ions uptake follows the order $\text{Cu (II)} > \text{Ni (II)} > \text{Co (II)} \approx \text{Zn (II)} > \text{Cd (II)} > \text{Pb (II)}$ for all of the terpolymer [21].

4.7.3. Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table 4. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the p-COF-II terpolymer increases with increasing pH of the medium. The magnitude of increase, however, is different for different metal cations. The p-COF-II terpolymer resin takes up Fe (III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be $\text{Fe (III)} > \text{Cu (II)} > \text{Ni (II)} > \text{Co (II)} > \text{Zn (II)} > \text{Cd (II)} > \text{Pb (II)}$. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [22]. For example, the result suggest the optimum pH 6.0, for the separation of Co(II) and Ni (II) with distribution ratio 'D' at 445.4 and 914.1 respectively using the p-COF-II terpolymer resin as ion-exchanger.

Table 2. Evaluation of the effect of different electrolytes on the uptake of several metal ionsa by p-COF-II terpolymer resin

Metal ion	Electrolyte (mol/l)	pH	Weight of the metal uptake (mmol.g ⁻¹) in the presence of			
			NaNO ₃	NaCl	NaClO ₄	Na ₂ SO ₄
Fe(III)	0.01	2.5	1.06	0.56	1.18	3.17
	0.05		1.24	0.84	1.70	2.52
	0.10		1.45	1.06	1.92	1.99
	0.50		1.75	1.45	2.42	1.16
	1.00		2.23	2.06	3.01	0.73
Cu(II)	0.01	4.5	1.99	1.21	1.73	3.45
	0.05		2.17	1.86	2.36	2.81
	0.10		2.41	2.43	3.01	2.18
	0.50		2.73	3.01	3.69	1.35
	1.00		2.88	3.71	4.27	0.65
Ni(II)	0.01	4.5	0.87	0.74	1.33	2.92
	0.05		1.46	1.22	1.92	2.33
	0.10		2.02	1.69	2.51	1.74
	0.50		2.50	2.21	3.09	1.16
	1.00		3.22	2.98	3.68	0.57
Co(II)	0.01	5.00	1.40	1.33	1.16	1.87
	0.05		1.16	1.14	1.04	1.23
	0.10		0.92	0.97	0.86	0.92
	0.50		0.69	0.79	0.69	0.75
	1.00		0.45	0.57	0.41	0.51
Zn(II)	0.01	5.00	2.41	1.74	1.79	2.08
	0.05		2.02	1.47	1.66	1.42
	0.10		1.56	1.10	1.40	1.28
	0.50		1.17	0.84	1.16	0.89
	1.00		0.64	0.51	0.71	0.57
Cd(II)	0.01	5.00	2.43	2.30	1.95	1.66
	0.05		1.98	1.82	1.55	1.28
	0.10		1.49	1.42	1.11	1.02
	0.50		0.98	0.97	0.92	0.79
	1.00		0.77	0.66	0.68	0.57
Pb(II)	0.01	6.00	2.41	2.24	1.87	3.47
	0.05		1.77	1.67	1.52	2.84
	0.10		1.12	1.40	1.21	2.18
	0.50		0.45	1.21	0.93	1.56
	1.00		0.17	0.92	0.59	0.91

a [M(NO₃)₂] = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml Weight of resin = 25 mg; time: 24 h; Room temperature

Similarly, for the separation of Cu (II) and Fe (III) the optimum pH is 3, at which the distribution ratio 'D' for Cu (II) is 68.6 and that for Fe (III) are 368.2. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved [22].

Table 3. Comparison of the rates of metal (M) ions uptake by p-COF-II terpolymer resin

Metal ion	pH	Percentage of metal ion uptake ^b at different times (h)						
		1	2	3	4	5	6	7
Fe(III)	2.5	53.3	78.6	96.4	-	-	-	-
Cu(II)	4.5	49.5	61.3	68.6	79.9	93.7	-	-
Ni(II)	4.5	50.7	60.6	70.1	86.1	94.6	-	-
Co(II)	5	45.2	59.7	69.1	84.2	94.1	-	-
Zn(II)	5	49.1	59.6	69.5	84.5	96.1	-	-
Cd(II)	5	30.1	50.6	60.2	70.1	85.2	94.1	-
Pb(II)	6	28.5	49.3	57.2	69.2	84.1	95.7	-

^a [M(NO₃)₂] = 0.1 mol / l; volume : 2ml; NaNO₃ = 1.0 mol / L; volume: 25 ml, Room temperature.

^b Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium

Table 4. Distribution ratio D_a of various metal ions as function of the pH by p-COF-II terpolymer resin

Metal ion	Distribution ratio of the metal ion at different pH							
	1.5	2	2.5	3	3.5	4	5	6
Fe(III)	20.2	125.6	237.1	368.2	-	-	-	-
Cu(II)	-	-	-	68.3	93.4	212.1	681.4	1209.4
Ni(II)	-	-	-	52.1	74.8	230.4	462.1	914.1
Co(II)	-	-	-	41.5	65.4	155.8	248.2	445.4
Zn(II)	-	-	-	43.7	73.1	99.3	133.0	225.8
Cd(II)	-	-	-	31.2	65.7	107.1	174.2	234.3
Pb(II)	-	-	-	39.6	63.5	126.2	197.2	273.6

^a D = weight (in mg) of metal ions taken up by 1g of terpolymer/weight (in mg) of metal ions present in 1ml of solution.

^b [M(NO₃)₂] = 0.1 mol/l; volume : 2ml; NaNO₃ = 1.0 mol/l; volume: 25 ml, time 24 h (equilibrium state) at Room temperature.

4.8. Thermogravimetry of p-COF-II terpolymer resin

Thermogravimetry is found to be a very useful method to assess the thermal stability of a polymeric resin. Thermogram has been recorded in the temperature range of 40 °C to 800 °C which is shown in Fig. 8. The p-COF-II terpolymer resin exhibit three stage decomposition after loss of one water molecule in the temperature range of 40–140 °C (4.91% found and 5.01% calculated). The first step of decomposition starts from 140°C to 380°C corresponding the mass loss of 26.89% found and 27.01% calculated, which may be due to loss of the hydroxyl groups and two methyl groups attached to aromatic benzene ring. This degradation may be due to increasing strain by thermal vibrations. The second step starts from 380°C to 550 °C, correspond to the mass loss of 69.63% found and 69.91% calculated which may be due to degradation of two aromatic benzene nuclei. This degradation may be due to unzipping strain and unstability in the molecule. The third step of degradation starts from 580 °C to 800 °C, corresponding to the mass loss equal to 77.52% found and 77.71% calculated, which may be due to the degradation of side chain (-CH₂-NH) of oxamide moiety and consequently the residue left over is oxamide moiety having mass equal to 23.44% found and 22.29% calculated [23].

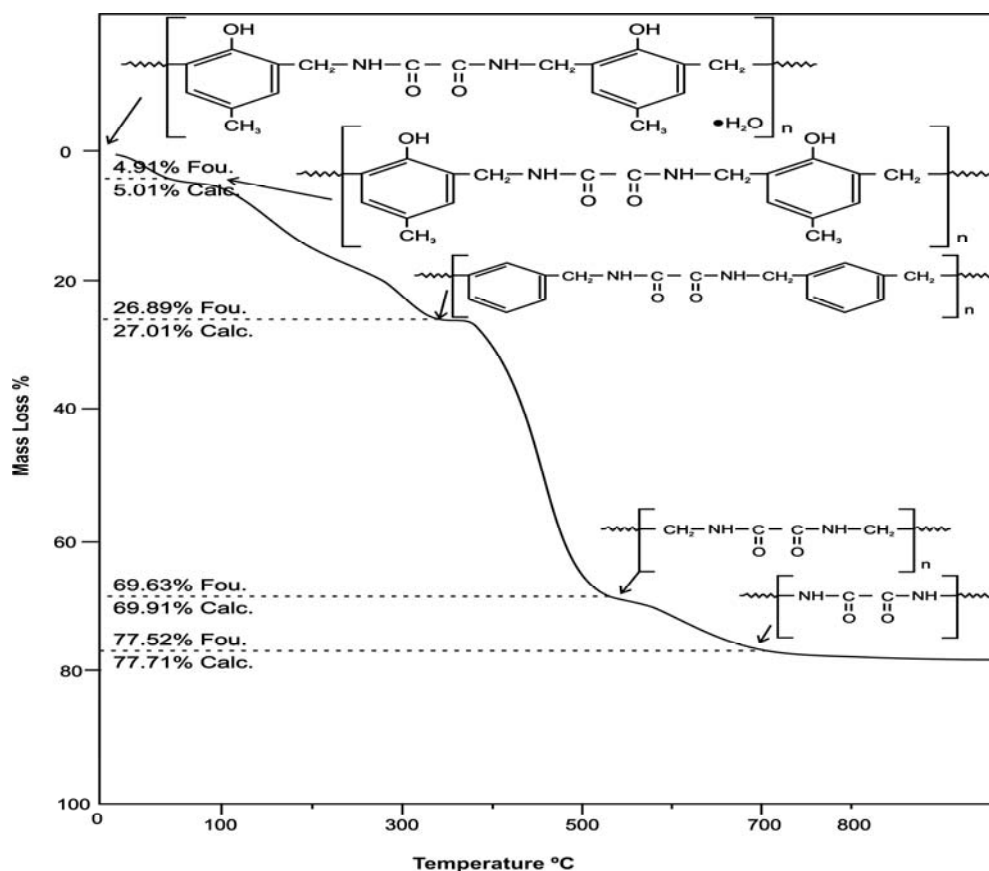


Fig. 8. Decomposition pattern of p-COF-II terpolymer resin

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the kinetic parameters of p-COF-II terpolymer resin.

Sharp-Wentworth method: In this method following expression is used.

$$\log \left[\frac{dc/dt}{\Delta(1-c)} \right] = \log(A/\beta) - E_a/2.303R \cdot 1/T$$

Where, A - constant of frequency factor

β is the linear heating rate. The graph of $\log \left[\frac{dc/dt}{\Delta(1-c)} \right]$ versus $1/T$ has been plotted. The graph is a straight line with E_a as slope and A as intercept. The linear relationship confirms that the assumed order (n) = 1 is correct.

Freeman-Carroll method: In this method following expression is used.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = (-E_a/2.303R) \cdot \frac{\Delta(1/T)}{\Delta \log W_r} + n$$

where dw/dt = rate of change of weight of terpolymer sample with respect to time, $W_r = W_c - W$, where W_c is the weight loss at the completion of the terpolymer reaction or at definite time and 'W' is the total weight loss up to time t. 'T' is the temperature, 'R' is the gas constant and 'n' is the order of reaction. Hence the graph of

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} \text{ versus } \frac{\Delta(1/T)}{\Delta \log W_r}$$

Should give on Y axis (x=0) an intercept for the value of n (the order of reaction) and the slope $m = -E_a/2.303 R$.

Using thermal decomposition data and then applying the Sharp-Wentworth method (Fig. 9) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [23] (Fig. 10 and 11). Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z) and Apparent entropy (S^*) calculated on the basis of thermal activation energy are given in Table 5. From abnormally the low values of frequency factor, it may be concluded that the decomposition reaction of p-COF-II terpolymer can be classed as a 'slow' reaction. There is no other obvious reason [24].

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is known not to obey first order kinetics perfectly [25,26].

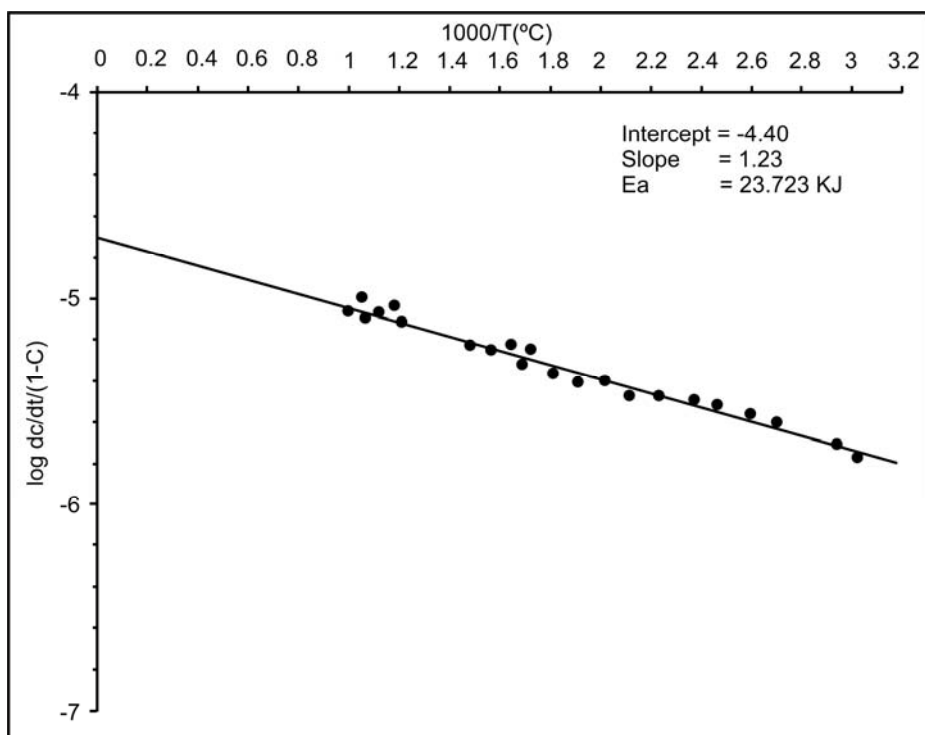


Fig. 9. Sharp – Wentworth plot of p-COF-II terpolymer resin

Table 5. Results of thermogravimetric analysis of p-COF-II terpolymer reins

Terpolymer resin	Half decomposition Temp. (°C)	Activation energy Ea (KJ)		Entropy change ΔS(J)	Free energy ΔF(KJ)	Frequency factor (Z)(Sec. ⁻¹)	Apparent entropy (S*)(KJ)	Order of reaction (n)
		FC	SW					
p-COF-II	673	25.848	25.446	164.521	100.375	705	-19.11	0.96

SW – Sharp-Wentworth Method

FC – Freeman–Carroll Method

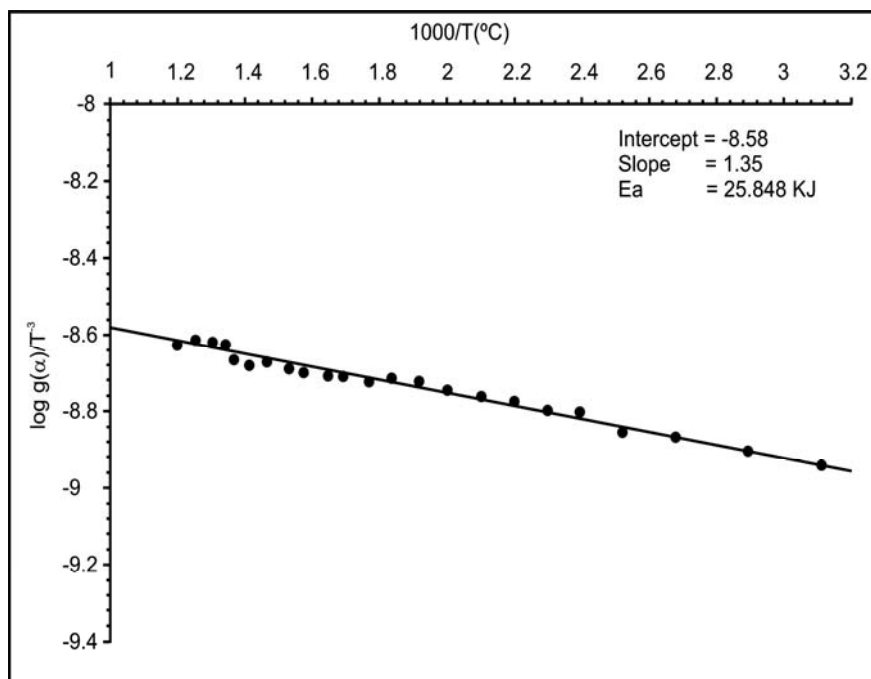


Fig. 10. Freeman – Carroll plot of p-COF-II terpolymer resin

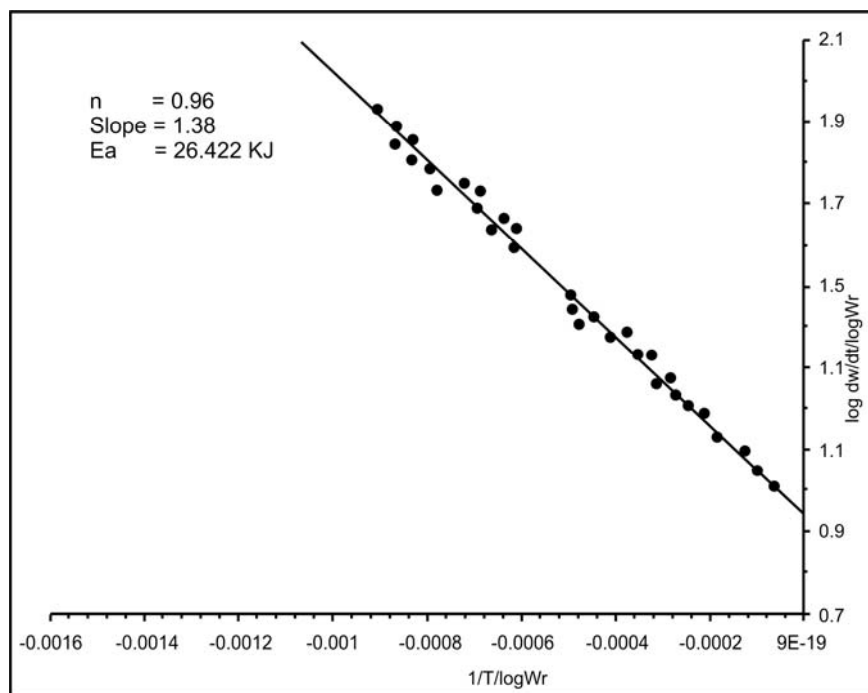


Fig. 11. Thermal energy plot of p-COF-II terpolymer resin

5. CONCLUSION

Electrical conductivity of p-COF-II terpolymer resin increases by increasing temperature. Hence this terpolymer may be ranked as semiconductor. The uptake capacities of metal ions by the terpolymer resin were pH dependent. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture. The p-COF-II terpolymer resin undergoes degradation at elevated temperature which indicates that the resin is thermally stable

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