Semiconducting behaviour and Thermal study of Terpolymeric Resin Derived from p-Nitrophenol, Resorcinol and Formaldehyde

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ABSTRACT

The resin PNPRF-I were derived from acid catalyzed polycondensation using 1M HCl at 120-125^{0}C by varying monomer composition ratio. The resin obtained by condensing p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) was abbreviated as PNPRF-I. The tentative structure of this resin was determined by elemental analysis, ^{1}H NMR, FT-IR and UV-Vis spectra. The molecular weight determination was carried out by non-aqueous conductometric titration. The conductivity of PNPRF-I were found to be in range 0.0926 x 10^{-6} to 0.3294 x 10^{-6} mho cm^{-1} respectively for temperature range 343-573K. The activation energy of conduction for PNPRF-I were found to be 4.089 kJ mole^{-1}.On the basis of above studies, this polymer can be ranked as semiconductor. The thermokinetic parameters were determined using Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range (228-463^{0}C).The values of activation energies (Ea), entropy (ΔS) and free energies (ΔG) were in good agreement. The order of degradation reaction determined by FC method was confirmed by SW method.

Keywords: Polycondensation, Resin, Electrical conductivity, Semiconductor, Terpolymer, Thermal degradation

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INTRODUCTION

The semi conducting property of terpolymer resins have gained sufficient ground in recent years. Electrically conducting polymer resin is 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 type of material capable of replacing expensive metals but also new concept to explain their high conductivity. In fact, their conductivity and other properties such as thermo conduction, photoconduction, luminescence, etc. are in close connection with their physical and chemical structure. In this connection, studies were made to establish a correlation between the chemical structure and characteristics defining semiconducting properties. Work on organic conducting polymers has been carried out extensively due to wide applicability in area of electronics [1-2]. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives and aerospace industries because of their chemical resistance and electrical insulation properties [3].Various researchers were synthesized and characterized the formaldehyde based terpolymeric resins using various functional phenols as one of the monomer [4-8]. Gurnule W.B. *et al* [9-11] have reported semiconducting studies of 8-hydroxyquinoline-melamine/ biuret–formaldehyde terpolymer resins. Borole and co-workers [12] synthesized and characterized the poly (aniline-co-o-anisidine-co-o-toluidine) this films in inorganic and organic supporting electrolytes. The influence of inorganic and organic supporting electrolytes on electrochemical, optical properties of terpolymer thin films has been investigated.

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The films were characterized by conductivity measurements using four-probe technique. Borkar *et al* [13, 14] studied electrical and optical properties of conducting copolymer: poly (aniline-co-nethylaniline) and poly (aniline-co-m-methylaniline). The products have been characterized by solubility, spectroscopic method, and electrical conductivity measurement. The conductivity of copolymers decreases with increasing N-ethylaniline content. In our laboratory extensive research work has been carried out on synthesis, characterization and thermal degradation of p-hydroxybenzaldehyde, resorcinol and formaldehyde [15-16]. Dharkar *et al* studied the conductivities of melamine-aniline-formaldehyde terpolymer resins and its polychelates. The activation energy values were found to be in range of 0.847 to 1.156 eV [17].Rahangdale *et al* have reported synthesis and electrical conductance studies of *p*-Cresol-adipamide- formaldehyde copolymer [18]. Conducting property of resin was reported due to delocalized p electrons of aromatic systems in polymer matrix.

Thermal study of various polymeric resins reported [19-21].Khedkar *et al* [22] reported thermal study of m-cresol, hexamine and formaldehyde terpolymer resin, termokinetic parameters studied by Freeman-Caroll and Sharp-Wentworth method.

The present paper deals with the semiconducting behavior and thermal study of p-nitrophenol-resorcinol-formaldehyde (PNPRF-I) terpolymeric resin.

MATERIALS AND METHODS

Chemicals
All chemicals were AR grade and chemically pure grade. p-Nitrophenol, resorcinol and formaldehyde were procured from Sd fine, India. Triple distilled water was used for all the experiments.

Synthesis of p-nitrophenol-resorcinol-formaldehyde terpolymer resin
A mixture of p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-125^{0}C for six hours with intermittent shaking. The resinous redish-brown colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove p-nitrophenol-formaldehyde and resorcinol –formaldehyde copolymer which might be produced along with terpolymer. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipited by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The PNPRF-I resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PNPRF-I was found to be 73.34%.
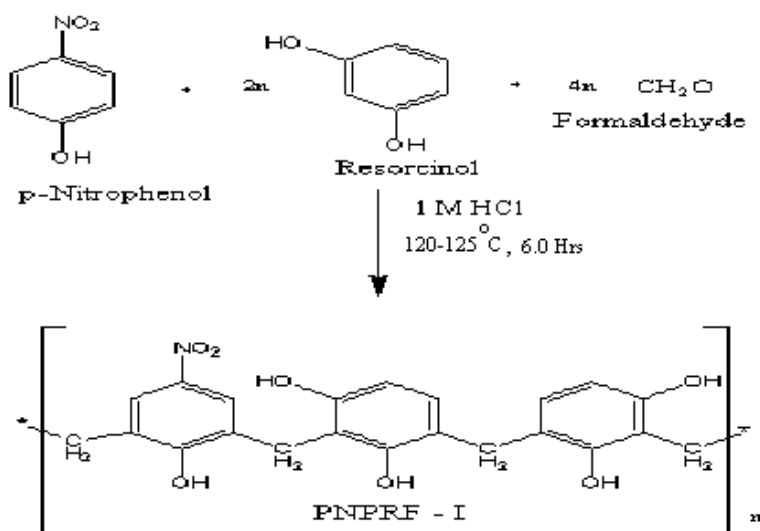
Scheme 1: Synthesis of PNPRF-I Resin.

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Table 1. Synthetic detail of PNPRF-I resin

Resin	p-nitrophenol	Resorcinol	Formaldehyde	Catalyst 1M HCl	React. Temp (^{0}C)	Time (hrs)	Yield %
PNPRF-I	0.1M	0.2M	0.4M	150ml	120-125	6	73.34

RESULTS AND DISCUSSION

Characterization of PNPRF-I resin
Elemental analysis and molecular weight determination of PNPRF-I resin
PNPRF-I resin were buff, redish–brown colored. The synthesized PNPRF –I resin were mostly soluble in DMF, DMSO and aq. NaOH. The resin was insoluble in acids and common organic solvents. Elemental analysis were carried out at CIMFR unit, Nagpur, by analytical Functional Testing Vario MICRO CHN elemental analyzer (Germany), Serial no-11083059.The number average molecular weights(Mn) were determined by non-aqueous conductometric titration in DMF using 0.1M KOH in absolute alcohol as titrant. From the graph of specific conductance against miliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (Mn) was calculated for each terpolymer resin using following equations [23-24].

DP = (Total miliequivalents of the base required for last break) / (miliequivalents of base required for first break.)

Table 2.Elemental analysis and molecular weight determination of PNPRF-I resin

Resin	%C		%H		%N		DP	Molecular weight (M_n)	Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found				
PNPRF-I	64.54	64.31	4.64	4.72	3.42	3.91	30	12270	$C_{22}H_{19}NO_7$	409

Mn = DP x Molecular weight of the repeating unit
The repeating Unit weight was obtained from elemental analysis.
The Elemental analysis and molecular weight determination data of PNPRF-I resin is given in following Table 2.

IR spectra of PNPRF-I resin
IR spectra of synthesized terpolymeric resin were recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu, model No-8101A.FT-IR spectra of PNPRF-I resin is shown in Figure1.

FT-IR spectral data is given in Table 3.

Table 3. **FT-IR data of PNPRF –I resin**

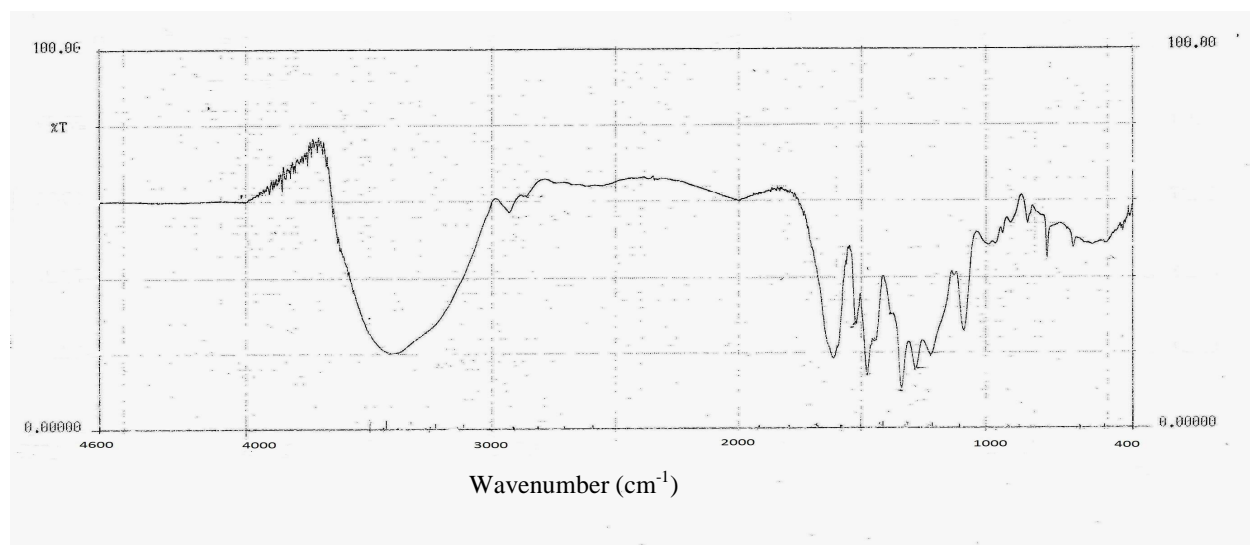| PNPRF-I Freq.cm^{-1}	Assignment
3350	H- Bonded Phenolic -OH
2928	CH- Str.
1560, 1338	Ar-NO$_2$
1282, 902.8	*Res-CH$_2$-Res, CH-def
933.7	Res-CH$_2$-Pnp, CH-def
833	1,2,3,4 tetra substituted aromatic ring
1221, 1089	1,2,3,5 tetra substituted aromatic ring

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Figure 1: **FT IR spectra of PNPRF – I resin**

*Res-Resorcinol,*Pnp–p-Nitrophenol

The broad band at 3350 cm^{-1} was assigned to stretching vibration of hydrogen bonded phenolic group [25]. The absorption at 2928 cm^{-1} was assigned to-CH$_2$- stretch shows the linkage of CH$_2$ in resin PNPRF-I resin [26].The peak at 1338 cm^{-1} and 1560 cm^{-1} was attributed to (N=O) for symmetrical and asymmetrical stretch respectively .The IR peaks at 1282 cm^{-1}, 902.8 cm^{-1} was attributed to CH-deformation in Res-CH$_2$-Res moiety .The weak bands at 933.7 cm^{-1} was shown in the spectra of PNPRF-I resin which were assigned to the CH-deformation in Res-CH$_2$-pnp moiety. Moreover the absorption at 833 cm^{-1} in the spectra of PNPRF-I resin was attributed to 1,2,3,4 tetra substituted aromatic ring and the peak at 1221 cm^{-1},1089 cm^{-1} for PNPRF-I cm^{-1} was attributed to 1,2,3,5 tetra substituted aromatic ring [27].

^{1}H NMR Spectra of PNPRF-I resin

^{1}H NMR spectra of terpolymeric resin using DMSO -d^6 solvent were scanned by BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh.

The ^{1}H NMR spectral data is tabulated in Table 4. The ^{1}H NMR spectra of PNPRF-I resin shown in Figure 2.The NMR characterization of resin was based on data available in literature [28].The PNPRF-I terpolymer resin shows signal at 5.3δ ppm may be attributed to phenolic –O**H** (pnp-moiety). Signals at 4.9δ ppm may be due to Phenolic (-O**H**) that is (res.moiety) in PNPRF-I resin. The signal at 7.1δ ppm may be due to aromatic proton in PNPRF-I terpolymeric resin. Signal at 3.7δ ppm may be due to Res-C**H$_2$**-Res in PNPRF-I resin. Signals at 2.5δ ppm may be due to pnp-C**H$_2$**-Res moiety in PNPRF-I resin.

Table 4. ^{1}H NMR data of PNPRF-I resin

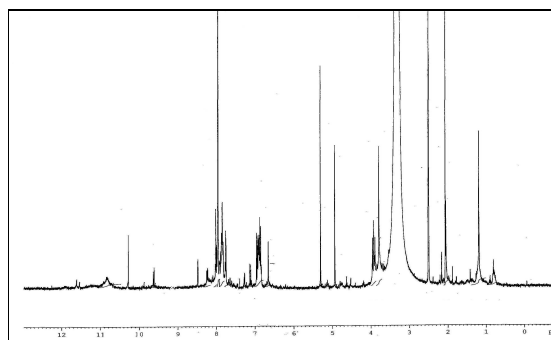| PNPRF-I δ ppm	Nature of proton assigned
3.7	Res-C**H$_2$**-Res
2.5	Pnp-C**H$_2$**-Res
7.1-8.2	Aromatic- **H**
5.3	Phenolic - O**H**(Pnp moiety)
4.9	Phenolic - O**H**(Res moiety)

Figure 2. ^{1}H NMR spectra of PNPRF – I resin

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UV-Vis spectra of PNPRF-I resin
UV-Vis spectra of terpolymer resin in DMSO Solvent recorded by UV-Vis Double Beam Spectrophotometer Schimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy, RTM Nagpur University, Nagpur. The UV-Vis spectral data given in Table 5. The UV-Vis spectra of PNPRF-I resin shown in Figure 3.

Table 5. UV-Vis data of PNPRF-I resin

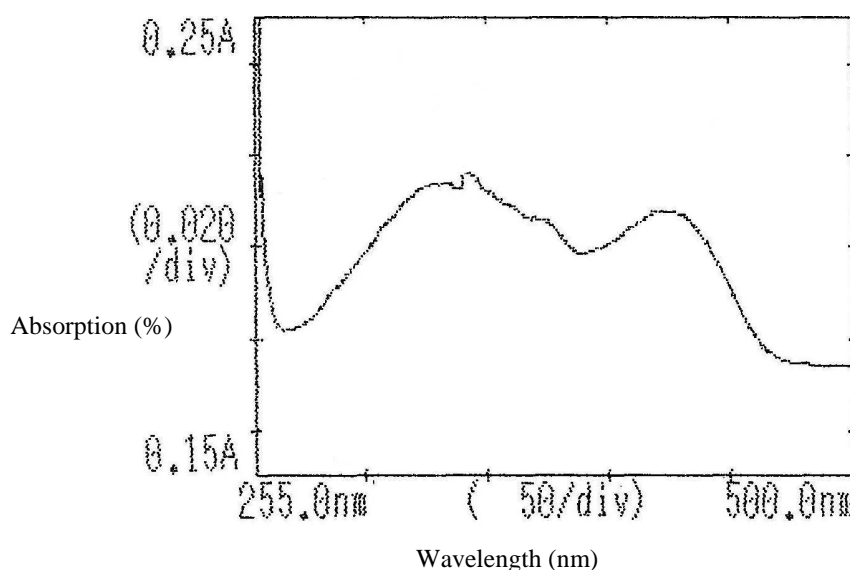| Resin	Wavelength,nm range for n-π^* transition	Wavelength,nm range for $\pi-\pi^*$ transition	Group (moiety)
PNPRF-I	425	341	Pnp moiety

Figure 3: UV-Vis spectra of PNPRF-I resin

The band at 341 nm was due to NO_2 –group in conjugation with an aromatic nucleus and was characteristic of $\pi-\pi^*$ transition while the band at 425 nm was assigned to n-π^* electronic transition in PNPRF-I resin [29-30]. $\pi-\pi^*$ transition shows hypsochromic shift while n-π^* transitions shows bathochromic shift in PNPRF-I (fig.3).

Electrical conductivity of PNPRF-I resin
The DC conductivities of PNPRF-I resin were studied for temperature range 343 to 573K. The specific conductance of these resins was calculated from the values of specific resistance. The electrical conductivity as a function of temperature of the polymer was studied. The electrical conductance of polymeric materials depends upon incalculable parameters such as porosity, pressure, method of preparation and atmosphere. Generally polymers containing aromatic nuclei in the polymeric matrix exhibit lower activation energy than those with aliphatic system [31-32].The powdered samples of PNPRF resins were palatalised by hydraulic press at pressure of 17 lb inch^{-2}.The surface of pallet were made conducting by applying graphite paste. The diameter and thickness was measured using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method [33]. The electrical conductivity was found in the range of 0.0926 x 10^{-6} to 0.3294 x 10^{-6} mho cm^{-1} for PNPRF-I resin. The plot of log σ versus1/T was found to be linear in the temperature range under study, which indicate that the Wilson's exponential law, **σ = σ^o exp $^{(-Ea/kT)}$** was obeyed.

Where,
 k=Boltzmann constant,
σ =Electrical conductivity at temperature T,
σ^o= Electrical conductivity at temperature T→∞,
Ea=Activation energy of conduction.

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The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots was found to be 4.089 kJmole[-1] for PNPRF-I resin respectively. Electrical conductivity plot of PNPRF-I resin given in Figure 4. Electrical conductivity data of PNPRF-I resin shown in Table 6.
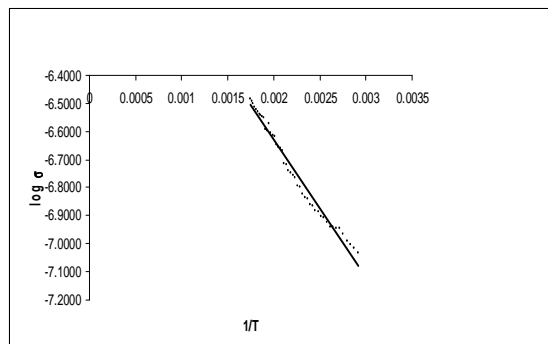

Figure 4: Electrical conductivity plot of PNPRF-I resin

Table 6 .Electrical conductivity data of PNPRF-I resin.

Resin	Temperature Range(K)	Activation energy (kJ mole[-1])	Activation energy (eV) x 10^{23}
PNPRF-I	343-573	4.089	15.37

Thermogaravemetric analysis of PNPRF-I Terpolymer resin
Thermo gravimetric analysis (TGA) of PNPRF-I terpolymer resin sample have been carried out by using Perkins Elmer Diamond TGA/DTA analyser at heating rate of 10^0C per minute in argon environment up to 1000^0C using Platinum foil crucible at Dept. of Material Science, VNIT, Nagpur, Maharashtra.

The Freeman–Carroll and Sharp-Wentworth [34-36] methods have been employed for the calculation of kinetic parameters of the newly synthesized PNPRF-I terpolymer resin with help of dynamic TG curve. In present work thermo kinetic parameters were determined by using following methods.

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

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \left[-\frac{Ea}{2.303\,R} \right] \times \frac{\Delta(1/T)}{\Delta \log W_r} + n.$$

Where,
dw/dt = rate of change of weight with time
Wr = Wc-W (difference between weight loss at completion of reaction, and at time t)
Wc = Weight loss at completion of reaction
W = Total weight loss up to time t
Ea = Energy of activation
n = Order of reaction

The plot of $\dfrac{\Delta \log\, dw/dt}{\Delta \log\, Wr}$ vs $\dfrac{\Delta 1/T}{\Delta \log\, Wr}$ gives a straight line, from slope, energy of activation (Ea) can be determined, with the help of intercept order of reaction (n) can be obtained.

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

$$\log \frac{(d\alpha/dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303\,RT}$$

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Where,

dα/dt = Fraction of weight loss with time

β = Linear heating rate

A = Frequency factor

α =Fraction of amount of reactant

By plotting the graph between log $\log \dfrac{d\alpha/dt}{(1-\alpha)^n}$ vs $\dfrac{1}{T}$ we obtained the straight line which give energy of activation (Ea) from its slope and frequency factor (A) can be evaluated from intercept. The change in entropy (ΔS), change in free energy (ΔG) can also be calculated by further calculations.

Thermogram of PNPRF-I terpolymer resin shown in following fig 5. The initial loss up to 150^0C was due to loss of water present in PNPRF-I terpolymer resin. The decomposition of resin between 228^0C to 463^0C was studied. The order of decomposition was found to be 0.781 as determined by Freeman-Caroll method, which was further confirmed by Sharp-Wentworth method. FC method and SW method plots of PNPRF-I terpolymer resin is shown in fig 6-7. Thermokinetic parameters of PNPRF-I terpolymer resin are tabulated in table 7.
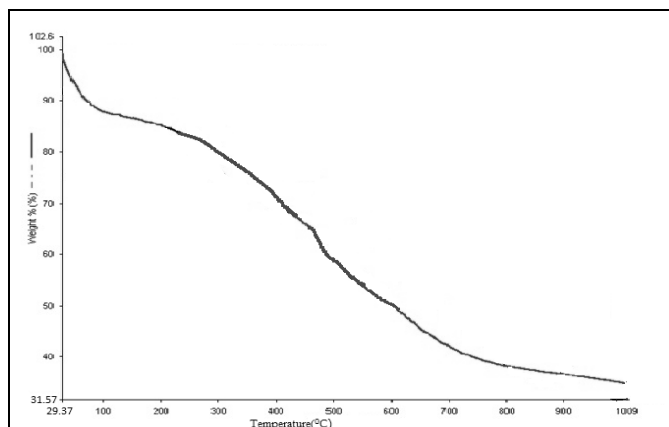

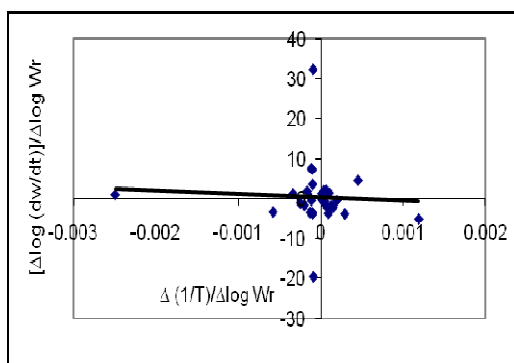**Figure 5: Thermogram of [PNPRF]ₙ**
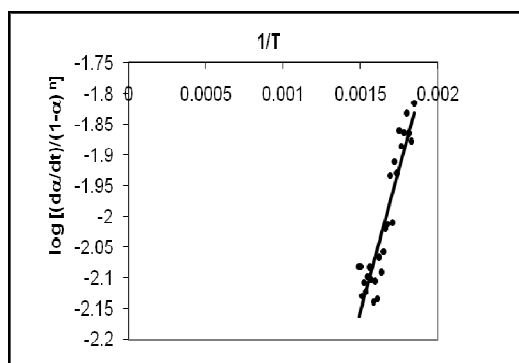

Figure 6: FC plot of [PNPRF]ₙ   **Figure 7: SW plot of [PNPRF]ₙ**

Table 7: Thermokinetic parameters of PNPRF-I terpolymer resin

PNPRF-I Terpolymer resin	Decomposition Temp (°C)	Ea (kJ)	A (min⁻¹)	ΔS*(J/K)	ΔG* (kJ)	Order (n)
FC method		17.81	164.89	-251.193	168.501	
SW method	228-463	17.09	147.13	-245.795	152.372	0.781

FC=Freemann-Carroll, SW= Sharp-Wentworth

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CONCLUSION

The data of Elemental analysis, UV–Vis spectra, FTIR spectra, ^{1}H NMR spectra, non aqueous conductometric titrations supports to the above tentative structure of PNPRF-I terpolymeric resin. Electrical conductivity of PNPRF-I terpolymeric resin increases by increasing temperature. Hence, this terpolymer shows semiconducting behaviour.From TGA data of PNPRF-I terpolymer resin, the activation energy obtained by FC method is slightly higher than that obtained by SW method. The values of activation energies, entropy, free energy and frequency factor of degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. The order of reaction is in a fraction due to solid state degradation. In pursuance of straight line graph obtained in SW plot when placed n=0.781 confirm the said order that was obtained in FC method.

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