Semiconducting behaviour and Thermokinetic study of Newly Synthesized p-Nitrophenol-Melamine-Formaldehyde Terpolymer Resin

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ABSTRACT

The resin (abbreviated as PNPMF) was derived from base catalyzed polycondensation of p-nitrophenol (0.1M), melamine (0.2M) and formaldehyde (0.4M) using 1M NaOH at 120-125^{0}C. The terpolymer resin was characterised by using elemental analysis and spectral analysis. In the present paper, electrical conducting behaviour of terpolymer resin and thermal decomposition were studied over a wide range of temperature. On the basis of electrical conductivity measurement, semiconducting behaviour of terpolymeric resin were studied. Detailed thermal degradation study of the terpolymer was carried out to ascertain its thermal stability. The thermokinetic parameters were determined using Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range (286-486^{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: Terpolymer, Polycondensation, Thermokinetic parameters, Electrical conductivity, Thermal degradation.
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INTRODUCTION

Phenolic resins have large number of practical application in electronic controls, insulating materials, protective adhesives, aerospace industries etc.because of their high thermal stability, heat and chemical resistance and electrical insulation properties [1-2]. Electrical conductivity properties of synthesised p-Cresol,Oxamide and formaldehyde terpolymer available in literature [3].Electrical conductivity studies on complexes reported [4-5].The semiconducting behaviour of polymeric ligand and its coordination polymer have been studied by electrical conductivity measurement at different temperatures [6].Patel have measured the electrical resistivity of 2,4-dihydroxyacetophenone-urea-formaldehyde polymeric ligand and its polychelates over a wide temperature range [7].Coordination polymers of Cu(II),Ni(II) with ethylene diaminetetrahalato and tetrathioazalatotetrathio flavane were prepared and their electrical conductivity has been studied [8-10].

Gurnule *et al* have reported thermodynamic parameters and order of thermal stabilities of tercopolymers by using TGA [11]. Aswar *et al* have reported the sequences of thermal stability of polymeric chelates predicted on the basis of decomposition temperatures and activation energy was found to be Ni> Mn> Cu>Co>Zn. Whereas kinetic and thermodynamic parameters were calculated from dynamic TGA by the use of Sharp-Wentworth and Freeman-Carroll methods [12]. The studies of the thermal degradation of terpolymer resins with chelates have recently become a subject of interest. Zhao Hong *et al*. studied the thermal decomposition behaviour of phosphorous containing copolystar [13].Various researchers have been studied the various applications of terpolymer resins [14-18]. Thermal study of various terpolymeric resins reported [19-22]. In our laboratory extensive research work has been carried out on synthesis, charectarisation and thermal degradation of p-hydroxybenzaldehyde, resorcinol and

formaldehyde [23].Ion-exchange properties of p-hydroxyacetophenone, hexamine and formaldehyde were studied [24].

Thermal analysis of metal complexes of α-oximinoacetoacet-o/p-toluidine thiosemicarbazones (OAOTTS and OAPTTS) with Ni (II), Co (II), Zn (II), Mn (II), Cd (II), Hg (II), and UO_2 (II) studied [25]. Thermal degradation kinetics and solid state, temperature dependant, electrical conductivity of charge transfer complex of phenothiazine with chloranil and picric acid were recorded [26]. The thermal behaviour of pristine and γ-irradiated CR-39 polymer (upto a maximum dose of 1800 kGy) has been studied using TGA [27]

The present communication deals with electrical conducting behaviour and thermal degradation study of newly synthesised terpolymer resin derived from p-nitrophenol, melamine and formaldehyde. The Freeman-Caroll and Sharp-Wentworth methods have been applied for calculation of kinetic parameters [28-30].Method for the estimation of kinetic parameters from thermogaravemetric studies are generally based on the assumption that the Arrhenius equations valid with thermal and diffusion barriers are negligible.

MATERIALS AND METHODS

Experimental
All chemicals were AR grade or chemically pure grade-nitrophenol, resorcinol and formaldehyde were procured from Sd fine, India. Triple distilled water was used for all the experiments.
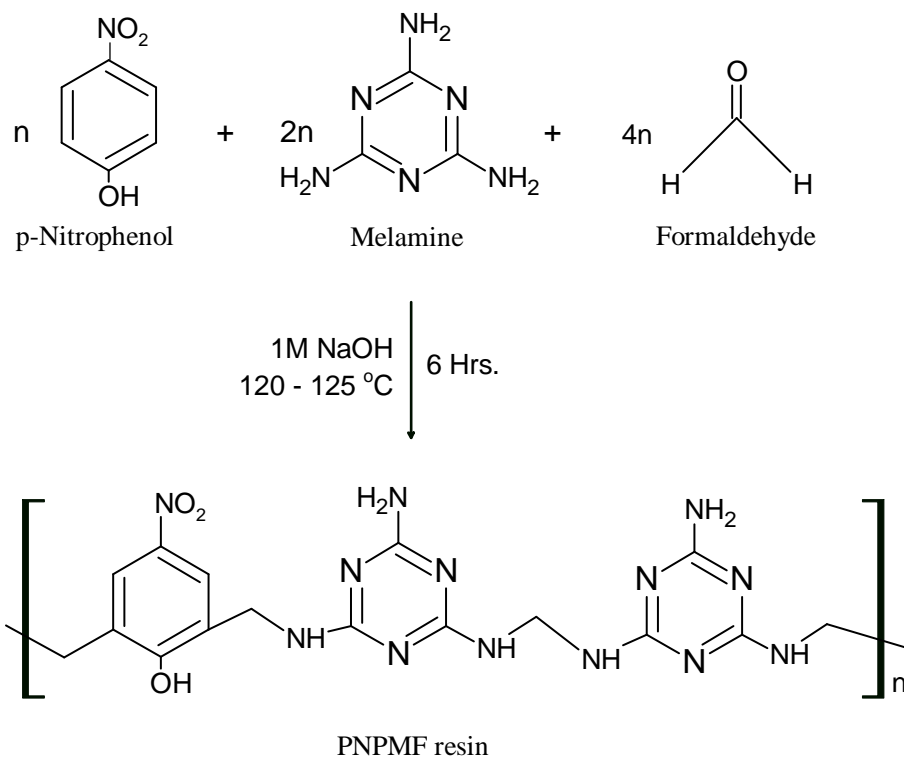
Scheme-Synthesis of PNPMF resin

Synthesis of p-nitrophenol-melamine-formaldehyde terpolymer resin
A mixture of p-nitrophenol (0.1M), melamine (0.2M) and formaldehyde (0.4M) was refluxed in presence of 1M NaOH (150ml) in oil bath at 120-125^{0}C for six hours with intermittent shaking. The resinous yellow coloured 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 melamine-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 PNPMF resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PNPMF was found to be 78.54%. Following reaction scheme was used to synthesize of PNPMF resin.

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RESULTS AND DISCUSSION

Electrical conductivity of PNPMF terpolymer resin
The DC conductivities of PNPMF terpolymer resin were studied for temperature range 328-573K. 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 [31-32].The powdered samples of PNPMF terpolymer resin were palatalised by hydraulic press at pressure of 17lb 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 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.

The energy of activation (Ea) of electrical conduction of PNPMF terpolymer resin calculated from the slope of the plot. Electrical conductivity plot of PNPMF terpolymer resin given in Fig 1.Electrical conductivity data of PNPMF terpolymer resin shown in Table 1.
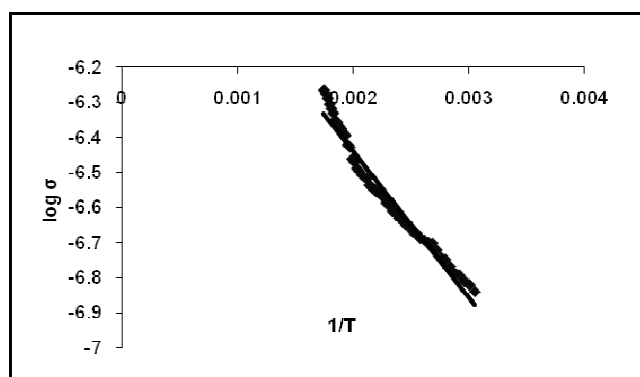

Fig. 1 Electrical conductivity plot of [PNPMF] $_n$

Table 1 .Electrical conductivity data of PNPMF Terpolymer resin

Terpolymer Resin	Temperature Range(K)	Activation energy (kJ mole^{-1})	Activation energy (eV) x 10^{23}	Electrical Conductivity σ x10^{-6} (Ω cm)$^{-1}$
[PNPMF]$_n$	328-573	3.484	13.10	0.1445-0.5407

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

Thermal analysis method is associated with a change in weight with respect to temperature. Heating performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studies. In dynamic TGA the sample is subjected to conditions increase in temperature at linear rate [34-35].
The Freeman–Carroll and Sharp-Wentworth methods have been employed for the calculation of kinetic parameters of the newly synthesised PNPMF terpolymer resin with help of dynamic TG curve [36-37]. In present work thermo kinetic parameters were determined by using following methods.

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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
W_r = 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.

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

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 PNPMF terpolymer resin shown in following fig 2. The initial loss up to 150^0C was due to loss of water present in PNPMF terpolymer resin. The decomposition of resin between 286^oC to 486^oC was studied. The order of decomposition was found to be 3.13 as determined by Freeman-Caroll method, which was further confirmed by Sharp-Wentworth method. FC method and SW method plots of PNPMF terpolymer resin are shown in fig 3-4. Thermokinetic parameters of PNPMF terpolymer resin are tabulated in Table 2.
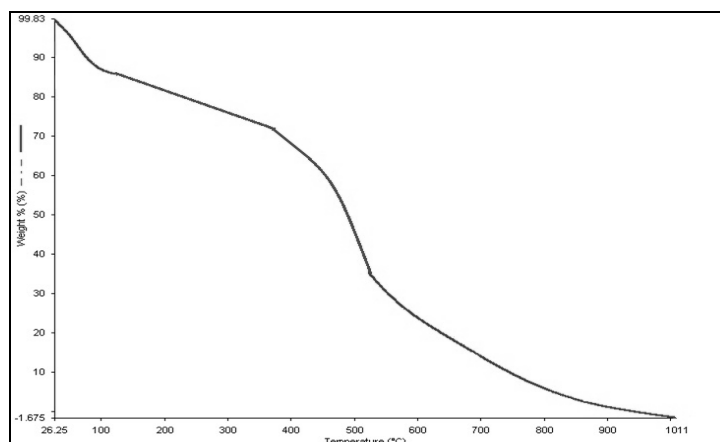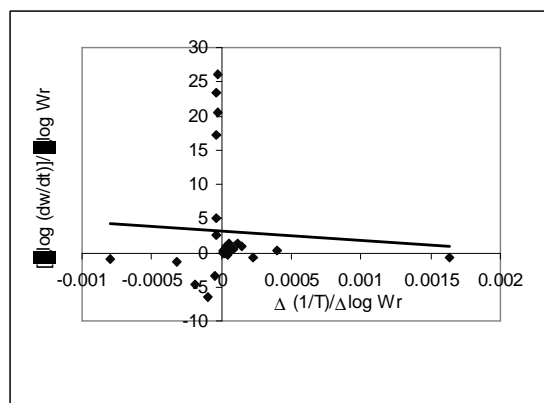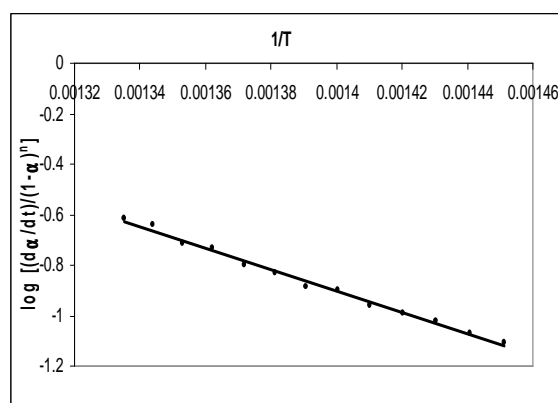

Fig-2. Thermogram of [PNPMF] ₙ

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Fig-3. FC plot of [PNPMF]$_n$

Fig-4. SW plot of [PNPMF]$_n$

Table.2 Thermokinetic parameters of PNPMF terpolymer resin

Terpolymeric ligand	Decomposition Temp.(^{0}C)	Activation energy, Ea(kJ)		Entropy Change, ΔS(J/K)		Free energy change, ΔG(kJ)		Frequency factor, A(min^{-1})		Order (n)
		FC Method	SW Method	FC Method	SW Method	FC Method	SW Method	FC Method	SW Method	
[PNPMF]$_n$	286-486	81.28	79.21	-232.172	-230.164	230.827	227.472	127.82	110.05	3.13

FC=Freemann-Carroll, SW= Sharp-Wentworth

CONCLUSION

From the results of temperature dependence of electrical conductivity of PNPMF terpolymer resin conclusions can be drawn.

1) At 328 K, PNPMF terpolymer has an electrical conductivity 0.1445x 10^{-6} (Ω cm)$^{-1}$.

2) At 328K, activation energy value of PNPMF terpolymer resin was found to be 13.10 x 10^{23} eV (Table-1).

3) The plot of log σ versus 1/T was found to be linear (fig.1) over a 328-573K range of temperature, indicating semiconducting behaviour of terpolymer resin.

4) From TGA data of PNPMF 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. In pursuance of straight line graph obtained in SW plot when placed n=3.13 confirm the said order that was obtained in FC method. The fractional order is attributed to solid state degradation.

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