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Synthesis, semiconducting behavior and thermal study of terpolymeric resin derived from p-hydroxyacetophenone, resorcinol and glycerol

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ABSTRACT

The resin PARG-I was derived from p-Hydroxyacetophenone, Resorcinol and Glycerol. PARG-I was synthesized by condensation of p-Hydroxyacetophenone (0.1M), Resorcinol (0.1M) and Glycerol (0.3M) in the presence of polyphosphoric acid (PPA). The tentative structure of resin was determined by elemental analysis, FT-IR and UV-VIS spectra. The molecular weight determination was carried out by non-aqueous conductometric titration. The conductivity of PARG-I was found to be in range 2.5912×10^{-6} to 6.4955×10^{-6} mho cm^{-1} respectively for temperature range 343-438K. The DC conductivity of sample was determined by two probe method. The activation energy of conduction for PARG-I was found to be $11.56 \text{ kJ mole}^{-1}$. The thermo-kinetic parameters were determined using Freeman-Carroll (FC) and Sharp -Wentworth (SW) method in temperature range 143 -343°C. The values of activation energies (E_a), apparent entropy (ΔS^*) and Free energies (ΔG^*) were in agreement. The order of degradation determined by FC method was confirmed by SW method.

Keywords: Polycondensation, Resin, Electrical conductivity, Semiconductor, Terpolymer, Thermal degradation, Wilson's exponential law.

INTRODUCTION

In recent years the resins have attracted much interest due to their application in waste water treatment, metal recovery and for the identification of specific metal ions. The semi conducting property of terpolymer resins have been gained sufficient ground in recent years. Terpolymer containing multifunctional aromatic rings has a large number of practical applications in electronic controls, insulating materials, protective adhesives and aerospace industries owing to their high thermal stability, heat and electrical resistance. Thermal properties of polymers are generally improved by the addition of inorganic additives. Various researchers were synthesized and characterized the formaldehyde based terpolymeric resins using various functional phenols as one of the monomer [1-4]. Masram *et al* studied synthesis of the resin salicylic acid-butyleneamine-formaldehyde (SBDF) in presence of a hydrochloric acid catalyst with molar proportion 1:1:2 and the electrical conductivity [5]. The plot of $\log \sigma$ versus $1/T$ was found to be linear in the temperature ranges which indicate that Wilson's exponential law $\sigma = \sigma^0 \exp (\Delta E/kT)$ was obeyed. The energy of activation (E_a) of electrical conduction calculated from the slopes was found to be in range of $1.67 \times 10^{-22} \text{ JK}^{-1}$. Rahangdale *et al* reported synthesis and electrical conductance studies of p-cresol-adipamide-formaldehyde polymer [6]. Conducting property of resin was reported due to delocalized π -electrons of aromatic systems in polymer matrix.

Thermal analysis of the newly synthesized resin of p-hydroxybenzoic acid, thiosemicarbazide with formaldehyde, by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (E_a) and order of reaction (n) were determined by applying Freeman-Carroll method [7]. M. Karunakaran *et al* [8] prepared terpolymeric resin by the condensation of resorcinol, thiourea and formaldehyde in the presence of 2M HCl as catalysts at $140 \pm 2^\circ\text{C}$. The Doyle, Horowitz and Metzger, Broido, Dharwadkar and Kharkhanavala methods were used to calculate the thermodynamic parameters, which include enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), free energy of activation (ΔG^*) and kinetic parameters like energy of activation (E_a) and pre-exponential factor (A) for various steps of thermal decomposition of RTF-I [8]. Thermogravimetric analysis of 8-HQ5-SAOF-II resin studied by Singru [9]. Kapse *et al* studied thermokinetic study of PAQM-I resin. Thermo kinetic parameter was determined by Freeman-Carroll (FC) and Sharp-Wentworth (SW) method [10]. The present paper deals with the synthesis, semiconducting behavior and thermal study of terpolymeric resin derived from p-hydroxyacetophenone, resorcinol and glycerol.

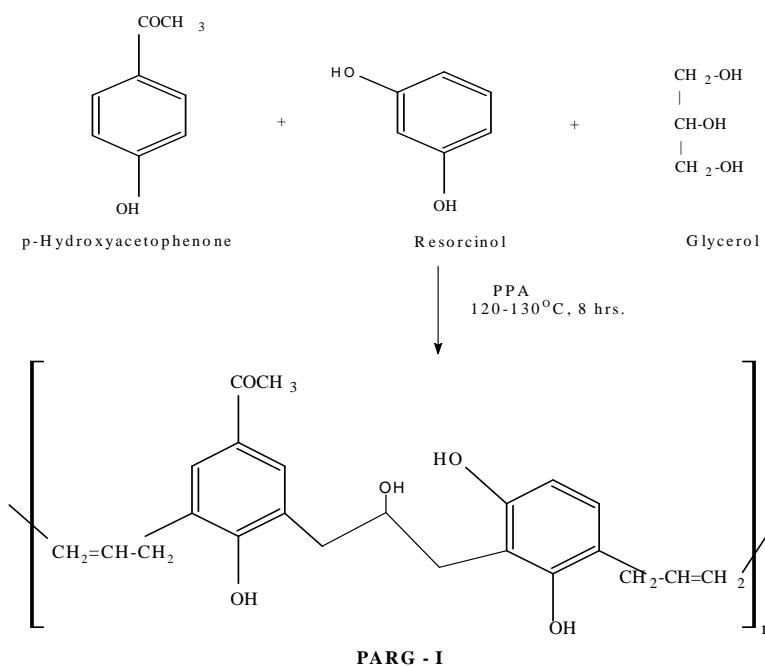
MATERIALS AND METHODS

Chemicals

All chemicals were of AR grade and chemically pure grade. P-hydroxyacetophenone, resorcinol and glycerol, PPA were procured from SD fine, India. Double distilled water was used for all experiments.

Table 1: Synthesis details of PARG-I Resin.

Resin	p-Hydroxyacetophenone	Resorcinol	Glycerol	Dehydrating agent	Reaction temperature ($^\circ\text{C}$)	Time (Hrs)	Yield
PARG-I	0.1M	0.1M	0.3M	PPA	120-130	8.0	74%



Scheme 1: Synthesis of PARG-I

Fig 1. Tentative str. Of PARG-I

Synthesis of p-Hydroxyacetophenone-Resorcinol-Glycerol terpolymer resin

The mixture of p-Hydroxyacetophenone (0.1M), Resorcinol (0.1M) and Glycerol (0.3M) was refluxed in presence of PPA (20) in oil bath at 120 - 130°C for 8.0 hrs with intermittent shaking. The brownish product 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 copolymer which might be produced along with terpolymer. It was further purified by dissolving in 2% NaOH solution, filtered and reprecipitated by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The PARG-I resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PARG-I was found to be 74%.

RESULTS AND DISCUSSION

Elemental analysis and molecular weight determination of PARG-I resin

PARG-I resin was brown colored. The synthesized PARG-I resin was mostly soluble in DMF, DMSO and aq.NaOH. The resin was insoluble in acids and common organic solvents. Elemental analysis was carried out at IIT, Powai, Mumbai, by CHNS elemental analyzer. The number average molecular weight (M_n) were determined by non-aqueous conductometric titration in DMSO using 0.1M KOH in absolute alcohol as titrant. From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (D_p) and the number average molecular weight (M_n) were calculated for each terpolymer resin using following equations [11-13].

$$\overline{D_p} = \frac{\text{Milliequivalent of base required for last break}}{\text{Milliequivalent of base required for first break}} \quad (1)$$

$$\overline{M_n} = \overline{D_p} \times \text{Repeat unit weight} \quad (2)$$

Table2: Elemental analysis and molecular weight determination of PARG-I resin

Resin	% C		% H		D_p	Molecular Weight (M_n)	Molecular formula of Repeating Unit	Molecular Weight of Repeating Unit
	Cal.	Found	Cal.	Found				
PARG-I	69	68	6.0	5.5	19	7524	$C_{23}H_{24}O_5$	396

The repeating unit weight was obtained from elemental analysis [14].

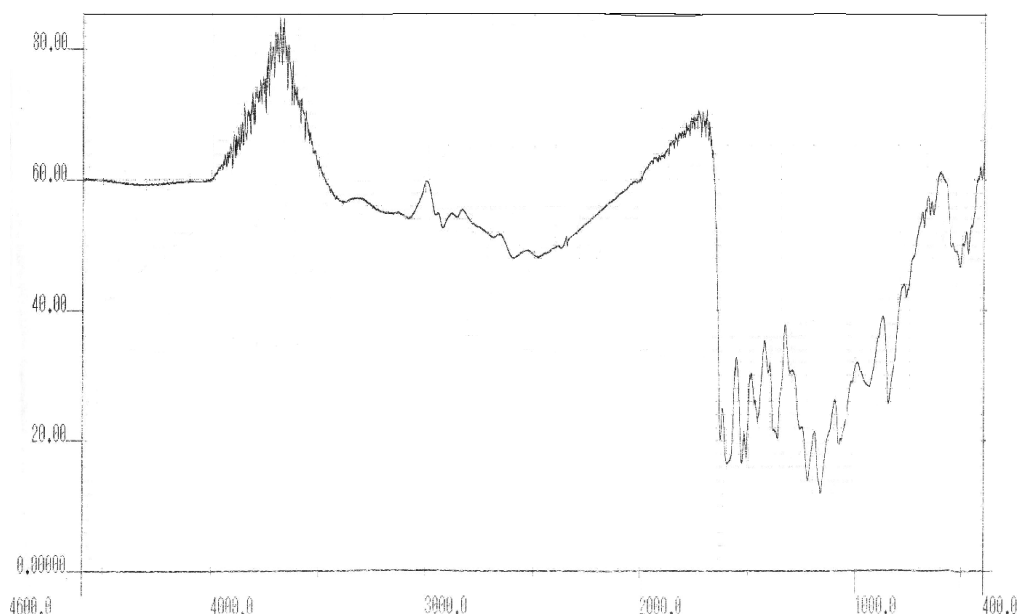


Figure 2: FT-IR spectrum of PARG-I Resin

Spectral analysis

FTIR spectra of synthesized terpolymeric resin were recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu, Model No-8101A. UV-Vis spectra of terpolymer resins in DMSO solvent recorded by UV-Vis Double Beam Spectrophotometer Shimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy; RTM Nagpur University, Nagpur.

FT-IR spectrum data of PARG-I Resin

FT-IR spectrum is shown in figure 2 and related data is tabulated in table 3.

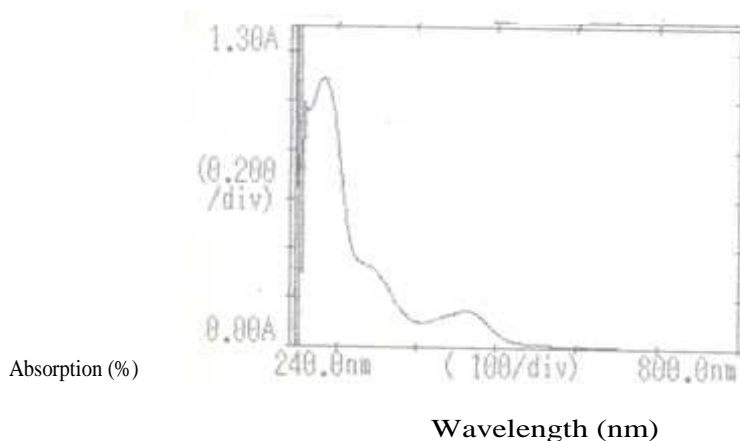
Table 3: FT-IR data of PARG-I Resin

Frequency in cm^{-1}	Nature of Fragment Assigned	Frequency in cm^{-1}	Nature of Fragment Assigned
3350	-OH stretch	1367	OH bend (in plane) phenolic
3100	CH Aromatic stretch	1221, 1226, 1076	1,2,3,5-tetrasubstituted Aromatic ring
3075, 2955, 2922.5	CH Aliphatic str.	937	Out of length C-H bending in alkene
1630	C=O stretch in ketone	843	1,2,3,4-tetra substituted aromatic ring
1508, 1533	Aromatic ring C=C stretch.	681	C=C bend
1473	Aliphatic C-H deformation	653	-OH bending out of plane
1387, 1261, 1226	Phenolic (C-O) stretching	1615	C=C str.(aliphatic)

The broad band at 3350cm^{-1} was assigned to stretching vibration of hydrogen bonded phenolic group. The absorption at 3100cm^{-1} was assigned to -CH Aromatic str. The peak at 3075cm^{-1} was attributed to -CH aliphatic stretch. The broad band at 1630cm^{-1} may be due to the stretching vibrations of $>\text{C}=\text{O}$. The presence of band at 1221, 1226, 1076cm^{-1} suggests that the aromatic ring is 1, 2, 3, 5- substituted. Peak 937cm^{-1} suggests out length C-H bending alkene. The band at 843cm^{-1} , 653cm^{-1} was assigned 1, 2, 3, 4-tetra substituted aromatic ring and O-H bending out of plane and 1615cm^{-1} was assigned to C=C str. [15-18].

UV-VIS spectra of PARG-I resin

The UV-VIS spectral data [19] is tabulated in the following Table 5. The UV-VIS spectra of PARG-I resin shown in figure 3.

**Figure 3: UV-VIS spectra of PARG-I resin****Table 4: UV-VIS spectral data of PARG-I resin**

Resin	Transition	Wavelength (nm)	Moiety assigned
PARG-I	283	$\pi - \pi^*$	C = O
	464	$\pi - \pi^*$	C = C
	630	$n - \pi^*$	C = O

UV-VIS spectra of PARG-I resin was scanned from 190 - 700nm. 283 nm was assigned to $\pi - \pi^*$ transition due to C=O group. A peak at 464 nm was assigned to $\pi - \pi^*$ due to conjugation. The n - π^* transition at 630 nm was due to C=O.

Electrical conductivity of PARG-I resin

The DC conductivities of PARG-I resin was studied for wide temperature range. The electrical conductivity as a function of temperature of polymer was studied. The powered samples of PARG-I resin was palletized by hydraulic pressure of 17lb inch⁻². The surface of pallet was 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. The plot of log (σ) verses 1/T was found to be linear in the temperature range under study, which indicates that the Wilson's exponential law [20],

$$\sigma = \sigma^0 \exp^{(-\Delta E/kT)} \quad (3)$$

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.

The energy of activation (E_a) of electrical conduction of PARG-I resin calculated from the slope of the plot. Electrical conductivity plot of PARG-I resin is given in figure 4. Electrical conductivity data of PARG-I resin is shown in table 5.

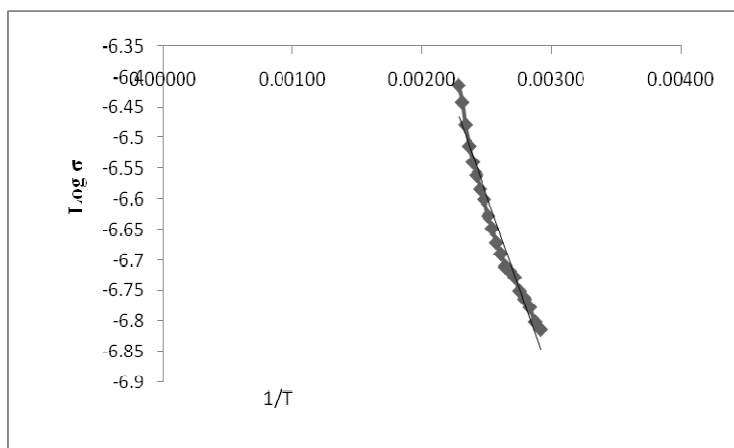


Figure 4: Electrical conductivity of PARG-I resin.

Table 5: Electrical conductivity data of PARG-I resin.

Resin	Temperature Range (K)	Activation Energy kJmol ⁻¹
PARG-I	343 - 438	11.56

Thermogravimetric analysis (TGA) of PARG-I resin

Thermogravimetric analysis (TGA) of PARG-I terpolymer resin sample have been carried out by using Perkin Elmer Diamond TGA/DTA analyzer in argon environment at Dept. of Material Science, VNIT Nagpur. The polymeric sample was allowed to heat up to 1000°C. The Freeman-Carroll and Sharp-Wentworth methods have been employed for the calculation of kinetics parameters of the newly synthesized PARG-I terpolymer resin with help of dynamic TGA curve [21-22]. In present work thermo kinetic parameters were determined by using following methods.

A) Freeman - Carroll Method (FC): In this the kinetic parameters determined by following expression,

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \left[-\frac{Ea}{2.303 R} \right] \times \frac{\Delta(1/T)}{\Delta \log W_r} + n. \quad (4)$$

Where

dw/dt = Rate of change of weight with time,

W_r = Difference between weight loss at completion of reaction and at time t ,

Ea = Activation energy,

n = Order of reaction

B) Sharp-Wentworth method (SW): Following expression have been used to evaluate the kinetic parameters,

$$\log \frac{(d\alpha/dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303 RT} \quad (5)$$

Where $d\alpha/dt$ is fraction of weight loss with time,

n is the order of reaction,

A is frequency factor,

β is linear heating rate and

α is the fraction of amount of reactant.

Thermogram of PARG-I terpolymer resin is shown in following figure 5. The initial loss up to 140°C was due to loss of water present in PARG-I terpolymer resin. The decomposition of resin between 143-343°C was studied. The order of decomposition was found to be 2.2 as determined by Freeman-Carroll method, which was further confirmed by Sharp-Wentworth method. FC and SW method plots of PARG-I terpolymer resin is shown in figure 6-7. Thermokinetic parameters of PARG-I terpolymer resin is tabulated in the table 6.

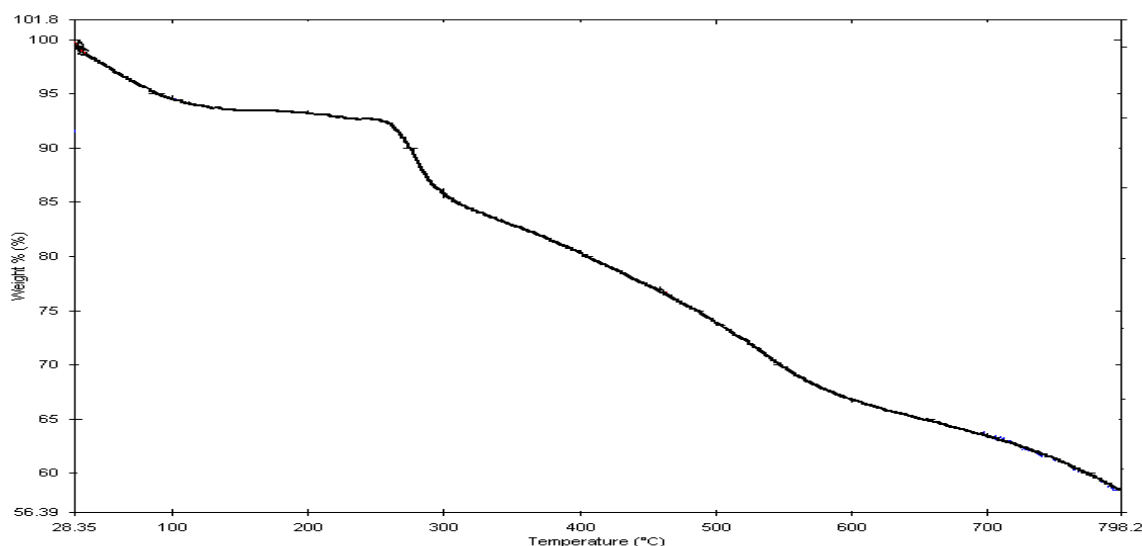


Fig.5 Thermogram of PARG-I

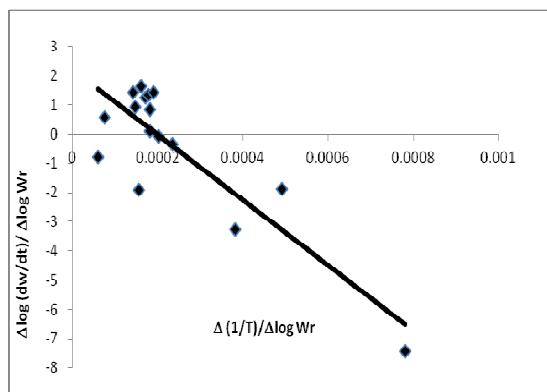


Fig.6 FC plot of PARG-I

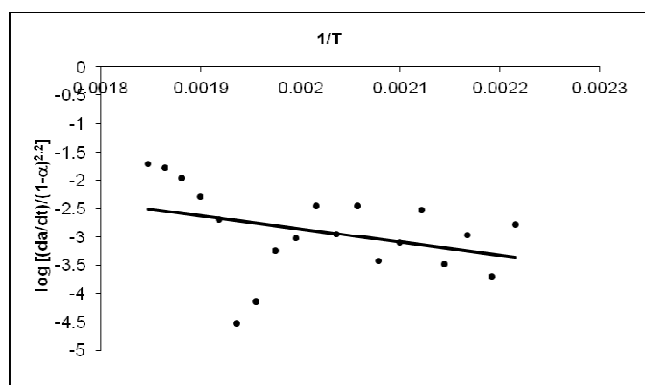


Fig7 .SW of PARG-I

Table 6: Thermokinetic parameters of PARG-I terpolymer resin

PARG-I Terpolymer Resin	Decomposition Temperature (°C)	Ea (kJ)	A (min ⁻¹)	ΔS* (J/K)	ΔG (kJ)	Order (n)
FC method	143-343	42.981	4.452x10 ²	-221.88	165.19	2.2
SW method		44.612	6.486x10 ²	-247.58	181.20	

CONCLUSION

The data of Elemental analysis, UV-VIS spectra, FTIR spectra, non aqueous conductometric titrations supports to the above tentative structure of PARG-I terpolymer resin. Electrical conductivity of PARG-I terpolymeric resin increases by increasing temperature. Hence, this terpolymer shows semiconducting behavior. The values of activation energies, apparent entropy, free energy and frequency factor of degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreements. The order of reaction is in a fraction due to solid state degradation. The straight line graph was obtained in SW plot when placed $n = 2.2$ confirmed the said order which was obtained in FC method.

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