SYNTHESIS AND THERMAL STUDY OF TERPOLYMERIC RESIN DERIVED FROM P-HYDROXYACETOPHENONE, RESORCINOL AND GLYCEROL

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Abstract:

The resin PARG-II was derived from p-Hydroxyacetophenone, Resorcinol and Glycerol. PARG-II was synthesized by condensation of p-Hydroxyacetophenone (0.2M), Resorcinol (0.1M) and Glycerol (0.4M) 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 thermo-kinetic parameters were determined using Freeman-Carroll (FC) and Sharp -Wentworth (SW) method in temperature range 203-377°C.The values of activation energies (Ea), 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, Terpolymer, Thermal degradation, Freeman-Carroll, Sharp –Wentworth.

Introduction

The terpolymers offer novelty and versatility; hence they occupy the pivotal position in the field of material science. Some of the important applications have been reported in the field of activators, ion-exchangers, catalyst and semiconductors. The thermal stability of polymer was evaluated by thermogravimetry. The study of the thermal degradation of terpolymer resins have recently become subject to interest. Thermally stable terpolymers resin have been important polymeric materials due to

versatile applicability at elevated temperatures owing to durability and light in weight [1-4].

Review of literature

Thermogravimetric study of polymer provides information about the degradation pattern during heating and thermal stability. Kapse *et al* reported synthesis of p-hydroxyacetophenon, melamine and quinhydrone using molar ratio 1:1:1. The tentative structure of resin was assigned by UV-Visible, IR, ^{1}H-NMR study and thermo kinetic parameters were determined by Freeman-Carroll and Sharp-Wentworth method [5]. Michael *et al* studied the thermal decomposition behavior of 8-hydroxyquinoline-guanidine-formaldehyde terpolymers [6].

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 (Ea) and order of reaction (n) were determined by applying Freeman-Carroll method [7]. M. Karunakaran *et al* prepared terpolymeric resin by the condensation of resorcinol, thiourea and formaldyde in the presence of 2M HCl as catalysts. 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 (Ea) and pre-exponential factor (A) for various steps of thermal decomposition of RTF-I [8]. Themogravimetric analysis of 8-HQ5-SAOF-II resin studied by Singru [9]. The present paper deals with the synthesis and thermal study of terpolymeric resin derived from p-hydroxyacetophenone, resorcinol and glycerol.

Material 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.

Synthesis of p-Hydroxyacetophenone-Resorcinol-Glycerol terpolymer resin

The mixture of p-Hydroxyacetophenone (0.2M), Resorcinol (0.1M) and Glycerol (0.4M) was refluxed in presence of PPA in oil bath at 120 - 130ºC for 8.0 hrs with intermittent shaking. The brownish product was repeatedly washed with cold distilled water, dried in air and powered. 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 reprecipited by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The PARG-II resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PARG-II was found to be 79%.

Table 1: Synthesis details of PARG-II Resin.

Resin	p-Hydroxy acetophenone	Resorcinol	Glycerol	Dehydrating agent	Reaction temperature (ºC)	Time (Hrs)	Yield
PARG-II	0.2M	0.1M	0.4M	PPA	120-130	8.0	79%
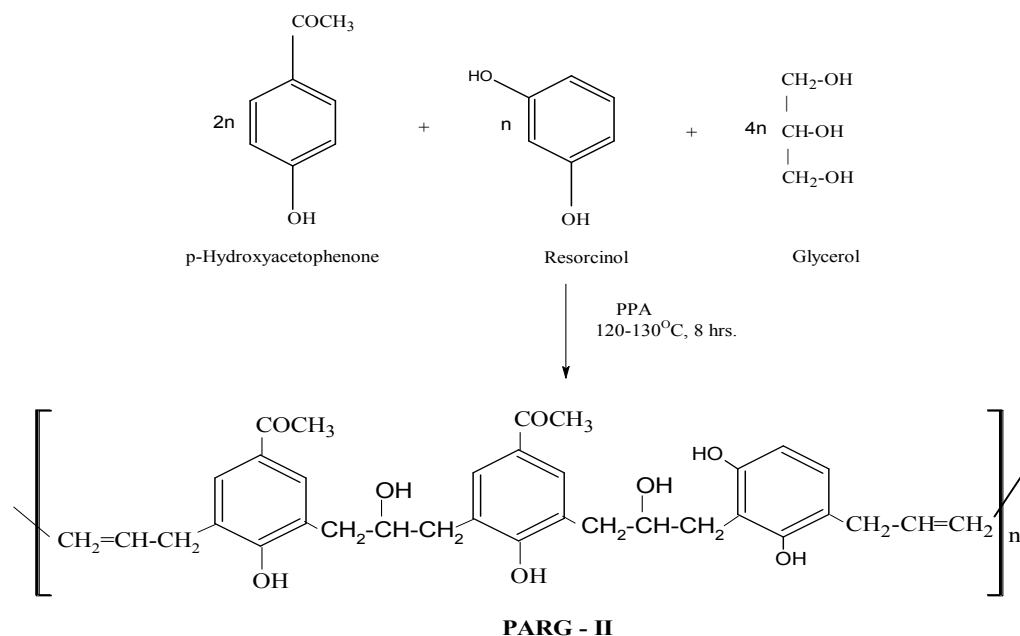
Scheme 1: Synthesis of PARG-II Resin.

FIG1. Tentative structure of PARG-I

Result and Discussion

Elemental analysis and molecular weight determination of PARG-II resin

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 (Mn) 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 [10-12].

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

$$\overline{M_n} = \quad \times \quad \text{nit weight} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \ (2)$$

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

Resin	% C		% H		Dp	Molecular Weight (Mn)	Molecularformula of Repeating Unit	Molecular Weight of Repeating Unit
PARG-II	Cal.	Found	Cal.	Found	18	12240	$C_{34}H_{40}O_{10}$	680
	71	70	5.88	5.5				

The repeating unit weight was obtained from elemental analysis [13].

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 Schimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy; RTM Nagpur University, Nagpur.

FT-IR spectrum data of PARG-II Resin

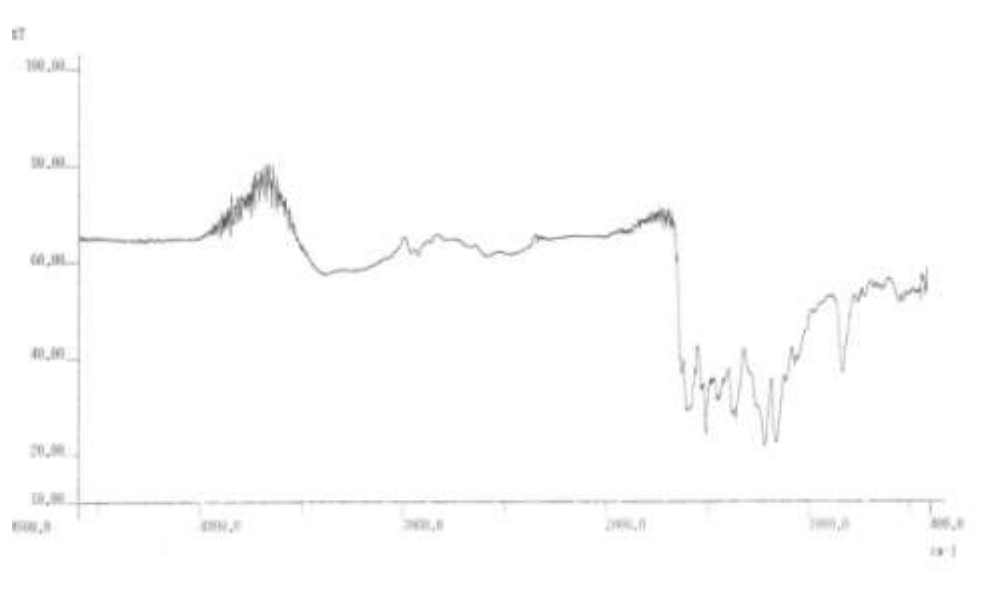FT-IR spectrum is shown in figure 2 and related data is tabulated in

table 3.

Fig2.FTIR spectra of PARG-II

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

Frequency in cm^{-1}	Nature of Fragment Assigned	Frequency in cm^{-1}	Nature of Fragment Assigned
3340	-OH stretch(alcoholic)	1578,1560,1533,1491	Aromatic ring C=C Stretch.
3230	-OH (phenolic) stretch.	1039, 1076	1,2,3,5-tetrasubstituted Aromatic ring
2961	CH Aliphatic str.	1381	-OH bending phenolic
2926	Ar-CH substituted str.	1303	-CH$_2$ twisting wagging vibration
2890	C-H stretch.	835	1,2,3,4-tetra substituted aromatic ring
1636	C=O stretching in Ketone	636	-OH bending out of plane
1605,1510	Aromatic Nucleus	1615	C=C str.(aliphatic)
1224	Phenolic (C-O) Stretching	1167,1116	Secondary alcohol(C-O)stretching

The broad band at 3340cm^{-1} was assigned to stretching vibration of hydrogen bonded alcoholic

Group. The absorption at 3200cm^{-1} was assigned to Phenol –OH stretch. The peak at 3075 cm^{-1} was attributed to –CH aliphatic stretch. The broad band at 1630 cm^{-1} was assigned to the stretching vibrations of >C=O. The presence of band at 1039, 1076 cm^{-1} suggests that the aromatic ring is 1, 2, 3, 5- substituted and the band at 835 cm^{-1} was assigned 1, 2, 3, 4-tetra substituted aromatic ring ·Peak at 636 represented O-H bending out of plane. Band at 1167 and 1116 cm^{-1}was assigned to (C-O) stretching in sec. alcohol. 1303 cm-1 was attributed to CH_2 twisting wagging vibration [14-15].

UV-Vis spectra of PARG-II resin

The UV-VIS spectral data is tabulated in the following Table 4. The UV-VIS spectra of PARG-II resin shown in figure 3
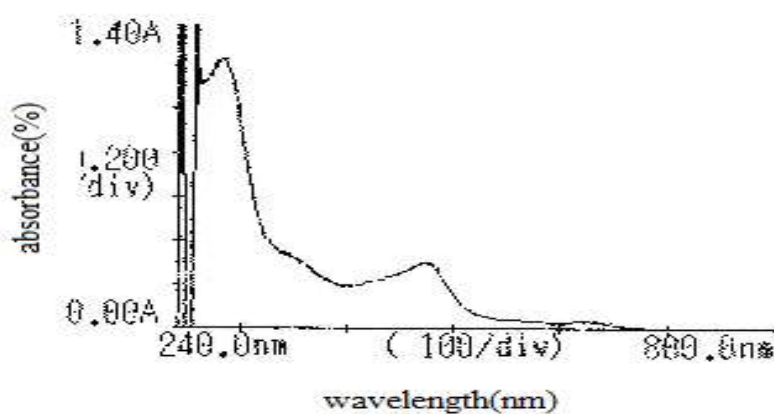

Fig.3 UV-Vis spectra of PARG-II

Table 4: UV-VIS spectral data of PARG-II resin.

Resin	Transition	Wavelength (nm)	Moiety assigned
PARG-II	282	π – π*	Aromatic
	474	π - π*	C = O
	630	n - π*	C = O

UV-VIS spectra of PARG-I resin was scanned from 190 - 700nm. 282 nm was assigned to $\pi - \pi^*$ transition due to aromatic ring. A peak at 474 nm was assigned to $\pi - \pi^*$ due to conjugation. The $n - \pi^*$ transition at 630 nm was due to C=O [18].

Thermogravimetric analysis (TGA) of PARG-II resin

Thermogravimetric analysis (TGA) of PARG-II terpolymer resin sample has 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 800^0C. The Freeman-Carroll and Sharp-Wentworth methods have been employed for the calculation of kinetics parameters of the newly synthesized PARG-II terpolymers resin with help of dynamic TGA curve [19-24]. 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 [25],

$$\frac{\Delta \lg(dw/dt)}{\Delta \lg W_r} = \left[- \frac{Ea}{2.303\,R} \right] \times \frac{\Delta(/T)}{\Delta \lg W_r} + \imath. \qquad \text{............................ (4)}$$

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 [26],

$$\log \frac{(d\alpha\, dt)}{(1-\alpha^{\,n}} = \log \frac{A}{\beta} - \frac{Ea}{2.303\,RT} \qquad \text{............................. (5)}$$

Where dα/dt is fraction of weight loss with time,
n = the order of reaction,

A = frequency factor,

β =linear heating rate and

α = the fraction of amount of reactant.

Thermo gram of PARG-II terpolymers resin is shown in following figure 4. The initial loss up to 150ºC was due to loss of water present in PARG-II terpolymers resin. The decomposition of resin between 203-377ºC was studied. The order of decomposition was found to be 0.6 as determined by Freeman-Carroll method, which was further confirmed by Sharp-Wentworth method. FC and SW method plots of PARG-II terpolymers resin is shown in figure 5-6. Thermo kinetic parameters of PARG-II terpolymers resin is tabulated in the table 6
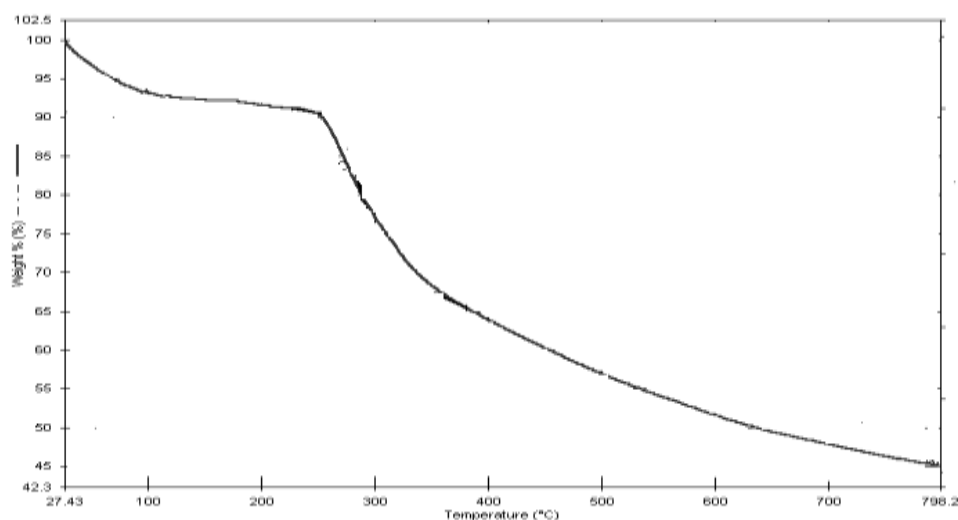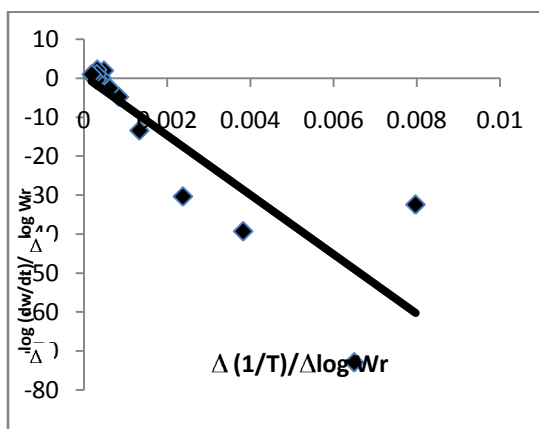

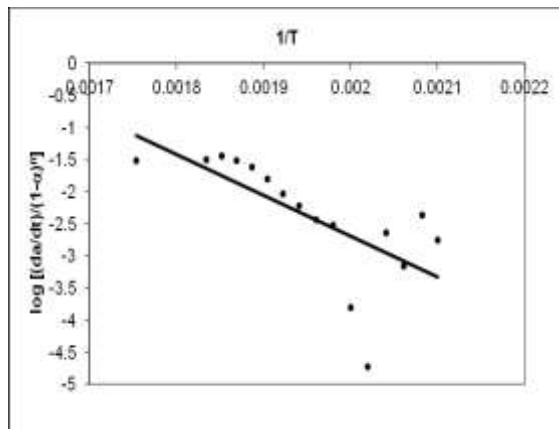Fig.4 Thermogram of PARG-II

Fig.5 FC plot of PARG-II   Fig6 .SW of PARG-II

Table 6: Thermokinetic parameters of PARG-II terpolymer resin

PARG-II Terpolymer Resin	Decomposition Temperature (^{o}C)	Ea (kJ)	A (min^{-1})	ΔS^* (J/K)	ΔG^* (kJ)	Order (n)
FC method		120.01	6.49x10^{10}	-71.601	160.34	
SW method	203-377	118.79	8.33x10^{10}	-73.0	160.25	0.6

Conclusion

The data of Elemental analysis, UV-VIS spectra, FTIR spectra, non aqueous conductometric titrations supports to the above tentative structure of PARG-II terpolymers resin. 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 = 0.6 confirmed the said order which was obtained in FC method.

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