Synthesis, Characterization and Kinetics of Thermal Decomposition Study of Resin-II Derived from p-Nitrophenol, Resorcinol and Formaldehyde

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Abstract

The resin(abbreviated as PNPRF-II) was derived from acid catalyzed polycondensation of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) using 1M HCl at 120-125^{0}C. The tentative structure of this resin was determined by elemental analysis, 1H NMR, FT-IR and UV-Vis spectra. The molecular weight was determined by non-aqueous conductometric titration. The thermokinetic parameters were determined using Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range (217-502^{0}C).The values of activation energies (Ea), entropy (ΔS) and free energies (ΔG) obtained by both method. The order of degradation reaction determined by FC method was confirmed by SW method.

Keywords: Polycondensation, Resin, Terpolymer, Activation energy, Thermal degradation.

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1. Introduction

Recently, there has been growing interest in finding new applications for available polymers in all spheres of life [1–6]. The work on polymers has long been an interesting topic of scientific research and industrial applications due to its potential to promote improvement in some physical properties of the resultant polymer composites such as stiffness, modulus, mechanical strength, electrical and thermal conductivity, temperature performance and dimensional stability [7–9]. Various researchers were synthesized and characterized the formaldehyde based terpolymeric resins using various functional phenols as one of the monomer [10-14]. Synthesis, charectarisation and thermal study of terpolymeric resin derived from m-cresol, melamine and formaldehyde studied [15]. Structural and thermokinetic study of resin-I derived from p-hydroxyacetophenone, quinhydrone and melamine reported [16]. Thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino-1, 3, 4-thiadiazole) and glycerol studied Urade et al [17].

An ecofriendly synthesis of terpolymeric resin anthrinilic acid-thiourea and formaldehyde were studied, the kinetic parameters has been evaluated on the basis of the thermogravimetric data [18]. Masram et al reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [19]. Thermogaravemetric study of polymer provides information about the degradation pattern during heating and thermal stability reported [20]. The kinetics of degradation can generate parameters, which can be subsequently used to deduce the lifetime of polymers at different temperature [21]. It is almost impossible to obtain the exact kinetics parameters for each reaction involved in the polymer decomposition and apparent kinetics parameters are often used to represent the behavior of polymer decomposition in general [22]. Actually these parameters rather represent

the overall weight loss behavior during the thermal decomposition as a function of temperature. Hence in literature several methods have been reported for the determination of kinetic parameters from thermal analysis [23]. Many coworkers determined various kinetic parameters such as ΔS, A and ΔG by using Freemen Carroll and Sharp-Wentworth method [24-25]. Present paper deals with the synthesis, characterization and kinetics of thermal decomposition study of PNPRF-II resin by using following methods [26-27].

1.1 Freeman-Carroll method

In this method activation energy and order of degradation is related with following expression,

$$\frac{\log(dw/dt)}{\log W_r} \quad \frac{Ea}{2.303\,R} \quad \frac{(1/T)}{\log W_r} \quad n.$$

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 $\frac{\log\, dw/dt}{\log\, Wr}$ vs $\frac{1/T}{\log\, Wr}$

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.

1.2 Sharp-Wentworth method

Following expression has been used to evaluate the kinetic parameters.

$$\log \frac{(d\quad/dt)}{(1\quad)^n} \quad \log \frac{A}{} \quad \frac{Ea}{2.303\,RT}$$

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 $\log \frac{d\quad/dt}{(1\quad)^n}$ vs $\frac{1}{T}$ 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.

2. Experimental

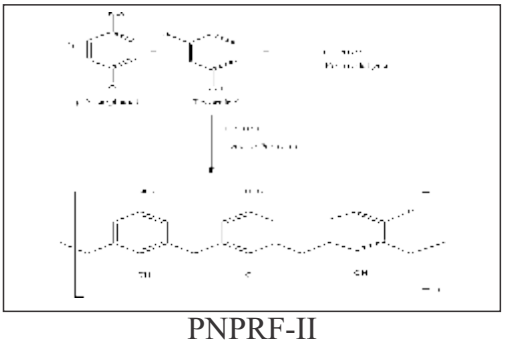
2.1 Materials

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

2.1.1 Synthesis of p-nitrophenol-resorcinol-formaldehyde terpolymer resin (PNPRF-II)

A mixture of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-1250C for six hours with intermittent shaking. The resinous reddish-brown colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The powder product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with diethyl ether to remove p-nitrophenol-formaldehyde co-polymer and resorcinol-formaldehyde copolymer. 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 to avoid the lump formation. The PNPRF-II resin so obtained was filtered, washed several times with hot distilled water. The yield of PNPRF-II terpolymer resin was found to be 73.05%. Following reaction scheme was used to synthesize of PNPRF-II resin.



PNPRF-II

Figure 1: Scheme-synthesis of PNPRF-II resin resin

Table 1: Synthetic details PNPRF-II resin

Resin	p-nitrophenol	Resorcinol	Formaldehyde	Catalyst IM HCl	React. Temp (^{0}C)	Time (hrs)	Yield
PNPRF-II	0.2 M	0.1M	0.4M	150ml	120-125	6	73.05

3. Results and Discussion

3.1 Characterization of PNPRF-II resin

PNPRF-II resin was buff, reddish –brown colored. The synthesized PNPRF-II resin was mostly soluble in DMF, DMSO and aq. NaOH. The resin was insoluble in acids and common organic solvents.

3.2 Elemental analysis and molecular weight determination

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 weight (Mn)was determined by non-aqueous conductometric titration in DMF using 0.1M KOH in absolute alcohol as titrant.From the graphs of specific conductance against miliequivalents of base, first and last break were noted .The degree of polymerization (DP) and the number average molecular weight (Mn) have been calculated for terpolymer resin PNPRF-II using following equations,

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

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-II resin are given in following table 2.

Table 2: Elemental analysis and molecular weight determination of PNPRF-II Resin

Resin	%C		%H		%N		*DP (n)	Molecular weight (M_n)	Molecular Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found				
PNPRF-II	60.27	60.01	4.10	4.07	6.39	6.53	21	9198	$C_{22}H_{18}N_2O_8$	438

3.3 Spectral Analysis

3.3.1 IR spectrum of PNPRF-II 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 spectrum of PNPRF-II resin is shown in Figure 2. FT-IR spectral data is given in following table 3.

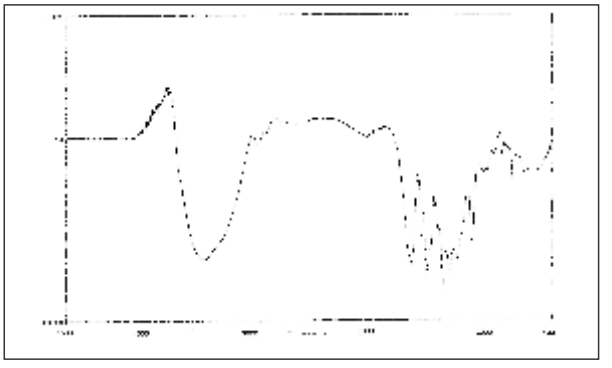


Figure 2: FT-IR spectrum of PNPRF- II resin

Table 3: FT-IR data of PNPRF-II resin

PNPRF-II Freq. cm-1	Assignment
3353	H- Bonded Phenolic -OH
2939	CH- Str.
1560, 1338	Ar-NO2
992.8	*Pnp-CH2-Pnp, CH- def.
933.7	Res-CH2-Pnp, CH-def
831	1,2,3,4 tetra substituted aromatic ring
1223, 1088	1,2,3,5 tetra substituted aromatic ring

*Res-Resorcinol,*Pnp–p-Nitrophenol moiety*

The broad band at 3353 cm-1 was assigned to stretching vibration of hydrogen bonded phenolic group. [28] The absorption at 2939 cm-1 was assigned to-CH2- stretch shows the bridges of CH2 in PNPRF-II resin.[29] The peaks at 1338 cm-1 and 1560 cm 1 was attributed to (N=O) for symmetrical and asymmetrical stretch respectively . The weak band at 992.8 cm-1 represents the C-H deformation in pnp-CH2-pnp moiety.

The weak band at 933.7 cm-1 was assigned to the C-H deformation in res-CH2-pnp moiety. Moreover the absorption at 831 cm^{-1} was attributed to 1, 2, 3, 4 tetra substituted aromatic ring and the bands at 1223 cm^{-1}, 1088 cm^{-1} were attributed to 1, 2, 3, 5 tetra substituted aromatic ring respectively [30].

3.3.2 ^{1}H NMR Spectrum of PNPRF-II resin

^{1}H NMR spectra of terpolymeric resin using DMSO-d6 solvent were scanned on BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh. The 1H NMR spectral data is tabulated in table 4. The 1H NMR spectrum of PNPRF-II resin is shown in figure 3. The NMR characterization of resin is based on data available in literature. [31] The signal at 5.1 ppm was attributed to Phenolic -OH (pnp-moiety). The signal at 7.6 ppm was due to aromatic proton in PNPRF-II terpolymeric resin. Signal at 2.5 ppm was assigned to proton in pnp-CH2-Res moiety. Signal at 2.07 ppm was due to C-H protons in pnp-CH2-pnp moiety in PNPRF-II resin.

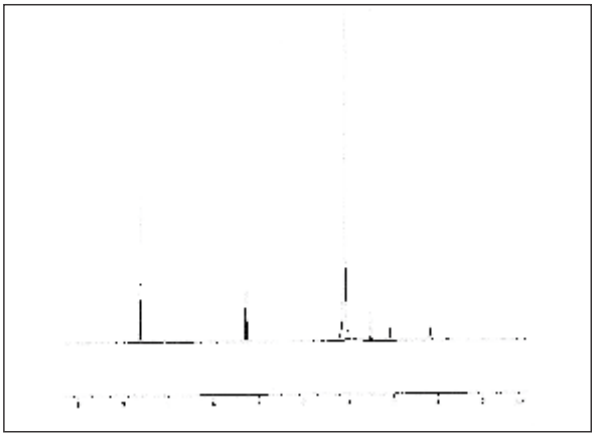


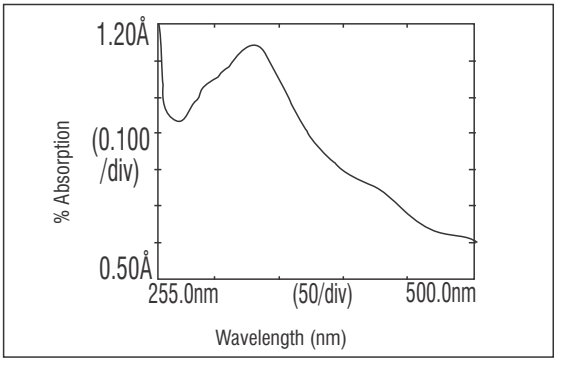
Figure 3: ^{1}HNMR spectrum of PNPRF– II resin

Table 4: ^{1}H-NMR data of PNPRF-II resin

PNPRF-II ppm	Nature of proton assigned
2.5	Pnp-CH2-Res
2.07	Pnp-CH2-Pnp
7.6	Aromatic- H
5.1	Phenolic - OH(Pnp moiety)

3.3.3 UV-Vis spectrum of PNPRF-II 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 spectrum of PNPRF-II resin is shown in figure 4. The UV-Vis spectral data is given in table 5.



Figue 4: UV-Vis spectrum of PNPRF-II resin

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

Resin	Wavelength,nm range for n- * transition	Wavelength,nm range for * transition	Wavelength,nm range for n- * transition
PNPRF-II	433	328Pnp	Pnp

Spectra depicted two characteristic bands in the resin of 328 nm and 433 nm in PNPRF-II resin [32-33]. The band at 328 nm indicates the presence of -NO2 group containing N=O bond in conjugation with an aromatic nucleus and was assigned to of * transition while the hump in the region of 433 nm was due to n- * electronic transition.

3.3.4 Thermogaravemetric analysis of PNPRF-II Terpolymer resin

Thermo gravimetric analysis (TGA) of PNPRF-II terpolymer resin sample have been carried out by using Perkins Elmer Diamond TGA/DTA analyzer 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.

Thermogram of PNPRF-II terpolymer resin shown in following figure 5. The initial loss up to 1500C was due to loss of water present in PNPRF-II terpolymer resin. The decomposition of resin between 2170C to 5020C was studied. The order of decomposition was found to be 0.722 as determined by Freeman-Caroll (FC) method which was further confirmed by Sharp-Wentworth (SW) method. FC and SW plots of PNPRF-II terpolymer resin is shown in figure 6-7. Thermokinetic parameters of PNPRF-II terpolymer resin are tabulated in table 6.

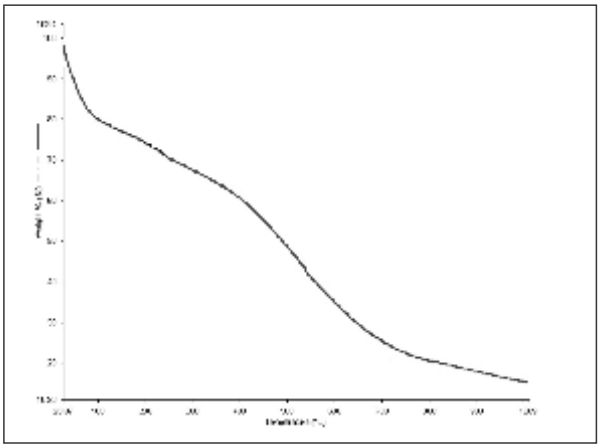


Figure 5: Freemann-Carroll Plot of $[PNPRF-II]_n$

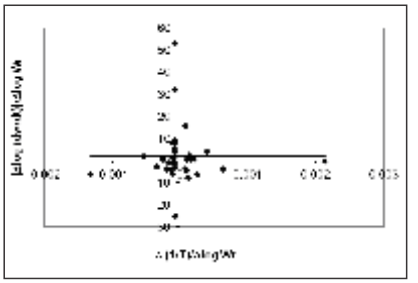


Figure 6: Freemen-Carroll Plot of [PNPRF-II] n

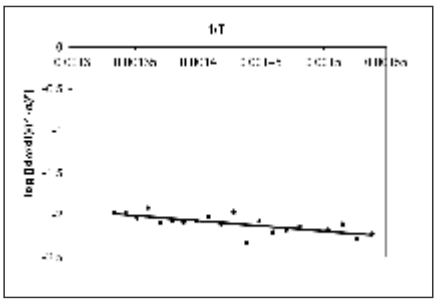


Figure 7: Sharp-Wentworth Plot of [PNPRF-II] $_n$

Table 6: Thermokinetic parameters of PNPRF-II terpolymer resin

PNPRF-II Terpolymer resin	Decomp-osition Temp	Ea (kJ)	△S*(J/K)	A(min^{-1})	△G*(kJ)	Order (n)
FC method	217-502	15.24	189.62	-253.090	154.358	0.722
SW method		15.12	177.93	-250.120	152.850	

FC=Freemann-Carroll, SW= Sharp-Wentworth

4. Conclusions

The data of Elemental analysis, UV–Vis spectra, FT-IR spectra, 1H NMR spectra, non aqueous conductometric titration supports to the above tentative structure of PNPRF-II terpolymeric resin. From TGA data of PNPRF-II 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.[34] In pursuance of straight line graph obtained in SW plot when placed n=0.722 confirm the said order that was obtained in FC method.

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