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Structural and thermokinetic study of resin-I derived from p-hydroxyacetophenone, quinhydrone and melamine

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ABSTRACT

The terpolymer resin p-hydroxyacetophenone- quinhydrone –melamine(abbreviated as PAQM-I) was synthesized by the condensation of p-hydroxyacetophenone (0.1M), quinhydrone (0.1M) and melamine (0.1M) in the presence of polyphosphoric acid (PPA). The structure of resin was determined by its elemental analysis, UV-VIS, IR and NMR data. The molecular weight of terpolymer was determined by non-aqueous conductometric titration technique. Thermo kinetic parameter was determined by Freeman-Carroll (FC) and Sharp-Wentworth (SW) method. The order of degradation reaction determined by FC method was confirmed by SW method.

Keywords: Thermal degradation, Terpolymer, Thermo kinetic parameter, Freeman- Carroll method, Sharp-Wentworth method.

INTRODUCTION

Since last two decades it has been seen ever increase interest in synthesis of thermally stable terpolymeric resin owing to superiority in reference to industrial applicability at elevated temperature, low production cost and ease of manufacture. Thermally stable terpolymers recently become boon to polymer chemist due to superiority over copolymers. The polymers can be used as adhesive, retardants, surface coating and dyes, fungicides in plants and living tissues, ion exchangers, semiconductors, rectifiers, rechargeable electrical cells. Many co-workers were tried to improve the thermal stability at elevated temperature by changing the monomer composition in polymer synthesis [1-7]. Thermo gravimetric studies of polymer provide information about the degradation pattern during heating and thermal stability. Phenolic resins have a large number of practical applications in insulating materials, electronic controls, aerospace industry, and machine parts. Because of their high thermal stability, chemical and heat resistance [8].Hiwase *et al* have reported thermo kinetic parameters of resin derived from p-hydroxybenzaldehyde, resorcinol and formaldehyde [9].Gurnule *et al* have reported thermodynamic parameters and order of thermal stabilities of terpolymers by using TGA [10]. Masram *et al* reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [11].Recently Urade *et al* reported thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis (2-amino-1, 3, 4-thiazole) and glycerol [12].

In present work thermo kinetic parameters were determined by using following methods.

A) Freeman - Carroll Method (FC): In this method the kinetic parameters are determined by following expression, [13-16]

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

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 is used to evaluate the kinetic parameters, [17-19]

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

Where dα/dt is fraction of weight loss with time, n is the order of reaction, A is frequency factor, and β is linear heating rate and α is the fraction of amount of reactant.

MATERIALS AND METHODS

Experimental:-

Preparation of PAQM-I

A mixture p-hydroxy acetophenone (0.1M), quinhydrone (0.1M) and melamine (0.1M) in presence of polyphosphoric acid (PPA) was stirred for 1hrs in ice bath. Then the reaction mixture was refluxed using oil bath at 128^oC-130^oC for 8 hrs with intermittent shaking. The resinous product so obtained was repeatedly washed with distilled water, dried in air and powdered .The product was extracted with diethyl ether to remove co- polymeric impurities which might be formed along with terpolymer. Product was further dissolved in 10% sodium hydroxide solution and reprecipitated by gradual drop wise addition of 1:1 hydrochloric acid with constant stirring. PAQM-I so obtained was filtered and washed several times with hot water and the dried. The synthetic details are shown in the Table1.

Table1: Synthetic details of PAQM-I

Parameters/conditions	specifications
Terpolymeric resin	PAQM-I
p-Hydroxy acetophenone	0.1M
Quinhydrone	0.1M
Melamine	0.1M
Temperature	120^oC-130^oC
Time	8 hrs
yield	68%

RESULTS AND DISCUSSION

Elemental analysis and molecular weight determination: - The terpolymer resin was analyzed for carbon, hydrogen and nitrogen content. The elemental analysis was carried out at IIT, Powai, Mumbai. The elemental analysis data are tabulated in table2.

The number average molecular weight of PAQM-I terpolymer was determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.1M) in absolute ethanol. The average degree of polymerization was calculated by using formula, [20-22]

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

The number average molecular weight was calculated as**,**

Mn = DP x Molecular weight of the repeating unit

The repeating unit weight was obtained from elemental analysis as shown in Table2.

The average degree of polymerization and number average molecular weight of terpolymer resin was found to be 14 and 6132 respectively.

Table2. Elemental analysis and molecular weight determination of PAQM-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				
PAQM-I	63.01	63.08	4.1	4.18	25.57	25.64	14	6132	$C_{23}H_{18}N_8O_2$	438

UV-VIS spectra of PAQM-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 spectrum so obtained is shown in fig1. The weak peak at 254nm assigned to n-σ*transition indicate presence of ether (–O-) group. Absorption at 371 nm was assigned to π-π* due to unsaturation. The absorption at 402nm (hump) was assigned to n–π*.

IR spectra of PAQM-I resin

IR spectra of synthesized terpolymeric resin was recorded at Department of pharmacy, RTM Nagpur University, Nagpur using FT-IR spectrophotometer Shimadzu model No-8101A. FT-IR spectral data are given in following Table3 [23-31].The absorption at 3300-3350 cm^{-1} was assigned to C=N group (Imines).The sharp peak at 1686 cm^{-1} was assigned to C=O str.in α,β unsaturated cyclic ketone.The medium band at 1310 cm^{-1} was attributed to C-N str. in aromatic amine. Similarly peak at 1381cm^{-1}, 1468cm^{-1} was assigned to C-O-C str. in ether moiety. The medium band at 1655 cm^{-1} was assigned to NH def. But –NH str. peaks were not clearly observed in IR spectrum this may be due to overlapping of imines absoption for C=N str.

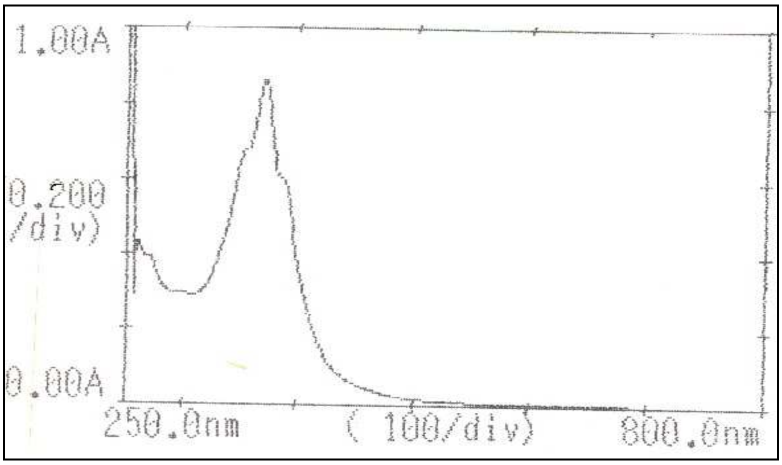


Fig. 1- UV-VIS spectra of PAQM-I resin

Table3. FT-IR spectral data [22-30]

IR (wave number in cm^{-1})	Nature of fragment assigned
3300-3350	C=N- str.
1686	C=O str.(α,β unsaturated ketone)
1655	N-H Def
1600	C=Cstr.
1381, 1468	C-H def.
1310	C-N str. Aromatic amine
1114, 1232	C-O str. in Ether moiety
837	p-Disubstituted aromatic ring

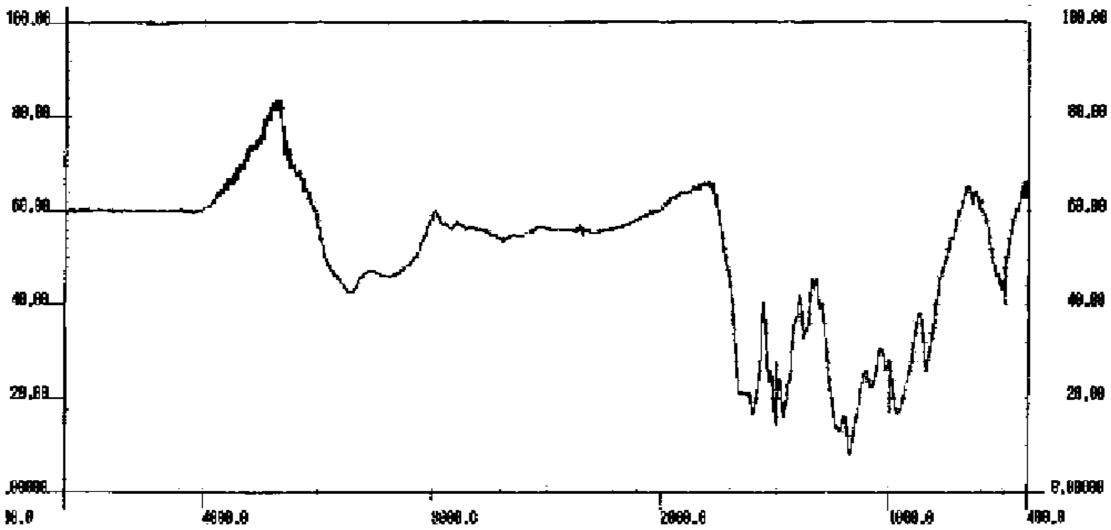


Fig. 2- IR spectra of PAQM-I resin

^{1}H NMR Spectra of PAQM-I resin:-

^{1}H NMR spectra of terpolymeric resin using DMSO -d^6 solvent was 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 PAQM-I resin is shown in Figure 3.The NMR characterization of resin is based on data available in literature. In NMR spectrum of the PAQM-I resin the unsymmetrical pattern at 6.9-7.7δ was due to the aromatic proton .The singlet at 2δ was assigned to CH_3 proton in CH_3-C=N moiety. The strong signal at 4.5δ was due to $-NH_2$ group. The singlet at 1.2δ was attributed to proton in Cyclohexa-2, 5-diene-1, 4-diimine moiety.

Table 4: NMR spectra of PAQM-I resin [16, 32-33]

δ in ppm	Nature of fragment assigned
6.9-7.9	Aromatic protons(unsymmetrical pattern)
4.5	N-$\mathbf{H}_2$
2.0	$\mathbf{CH}_3$-C=N
1.2	Proton in Cyclohexa-2,5-diene-1,4-diimine moiety

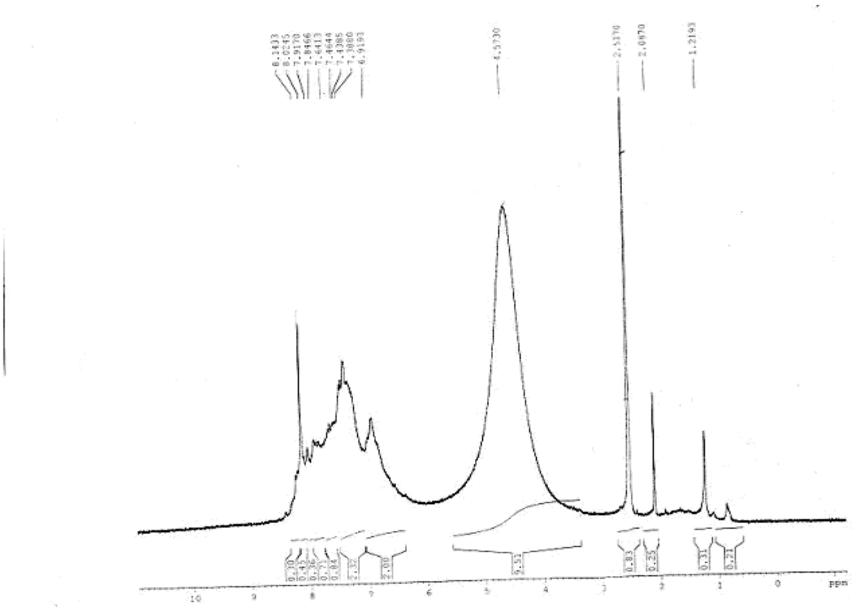


Fig. 3- ^{1}H NMR Spectra of PAQM-I resin

According to data obtained in physicochemical methods; the tentative structure of terpolymeric resin was assigned as shown in fig. 4

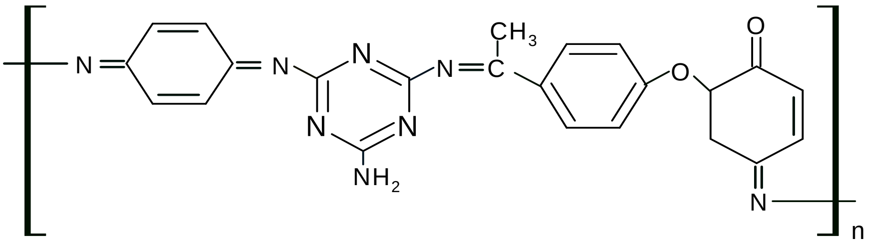


Fig. 4- Tentative structure of PAQM-I

Thermo gravimetric analysis: The thermo gram of PAQM-I terpolymer resin as shown in fig. 5, was recorded at Dept. of Material Science, VNIT Nagpur using Perkin Elmer Diamond TGA/DTA analyzer in argon environment. The polymeric sample was allowed to heat up to 1002^{0}C. The thermo gram reveals that initial weight loss up to 130^{0}C due to loss of water. The decomposition of resin between 675^0C to 825^0C was studied. FC and SW plots are shown in fig. 6a and fig. 6b respectively. The order of decomposition was found to be 1.5 as determined by FC method which was further confirmed by SW method. Thermo kinetic parameters are tabulated in Table 5.

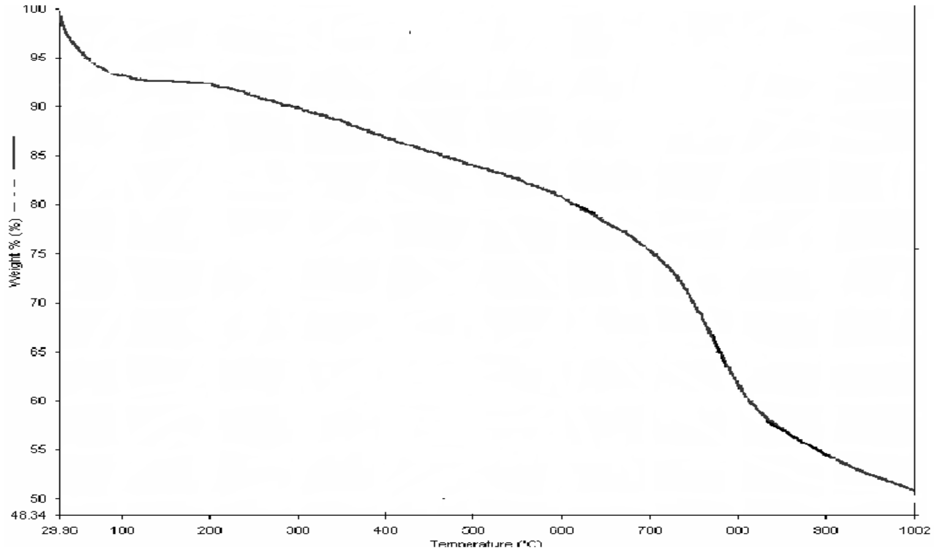
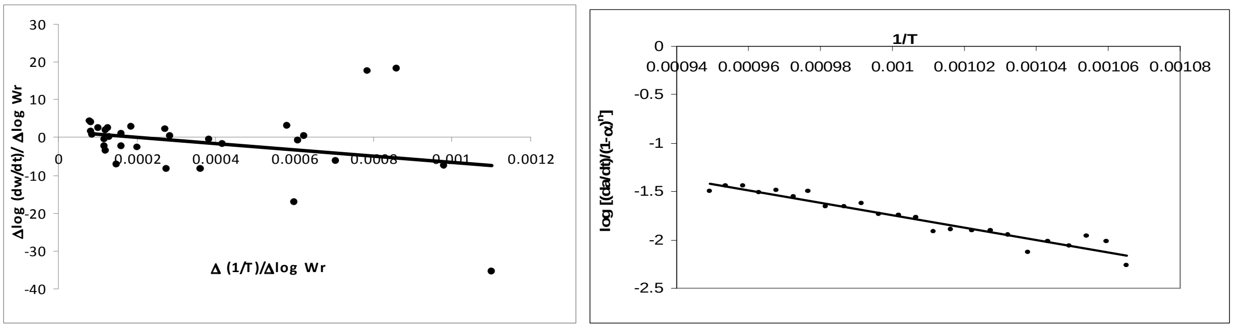


Fig. 5- Thermo gram of PAQM-I



(a) **(b)**

Fig. 6- (a) Freeman-Carroll plot of PAQM-I **(b) Sharp-Wentworth plot of PAQM-I**

Table 5: Thermo kinetic parameters of PAQM-I terpolymeric resin

PAQM-I terpolymeric resin	Ea (kJ)	Z (min^{-1})	ΔS* (J/K)	ΔG* (kJ)	Order (n)
FC method	117.41	8.9×10^4	-184.26	305.0	1.5
SW method	124.17	5.5×10^4	-180.3	307.4	

FC=Freeman-Carroll, SW= Sharp-Wentworth

CONCLUSION

The elemental analysis and spectral studies such as UV-VIS, IR, NMR data is in good agreement with assigned tentative structure of PAQM-I terpolymeric resin. The activation energies, entropy and free energy of degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. The value of frequency factor and low value of entropy indicate the slow degradation of well ordered resin. The high value of energy of activation relative to thermal energy suggest that the PAQM-I resin is thermally stable below 675^{0}C. The fractional order of degradation is attributed to solid state degradation.

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