Synthesis, Characterization, and Thermal Study of Terpolymeric Resin Derived from m-cresol, Hexamine and Formaldehyde

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Abstract: Terpolymeric resin was prepared from m-cresol (0.1M), hexamine (0.05M) and formaldehyde (0.2M) by acid catalyzed polycondensation method using 1M HCl in temperature range of 122-130 °C. The resin was abbreviated as m-CHF-I. The molecular weight of terpolymer was determined by non-aqueous conductometric titration technique. The structure of resin was determined by its elemental analysis, UV-VIS, IR, and NMR data. The thermokinetic parameters were determined using Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range (410-485 °C). The values of activation energies (E_a), 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, TGA, polycondensation, resin, thermal analysis.

Introduction

In recent years, considerable interest has been shown in the synthesis and study of chelating resins containing resin with Nitrogen, Sulphur and Oxygen donor atoms on polymeric interface. These polymeric resins, nowadays, have been received much attention and importance, only due to their wide range industrial application. The terpolymers can be used as adhesive, retardants, surface coating, dyes, fungicides in plants and living tissues, ion exchangers, semiconductors, rectifiers, rechargeable electrical cells etc. Thermally stable polymer recently become boon to polymer chemist due to applicability at elevated temperature beside challenges that have to face owing to thermal instability and low processability. In this connection many co-worker tried to improve the thermal stability by changing the monomer composition in polymer synthesis¹⁻⁹.

Thermogravimetric study of polymer provides information about the degradation pattern during heating and thermal stability. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, aerospace industry, machine parts etc. because of their high thermal stability, chemical and heat resistance¹⁰.

Hiwase *et al*¹¹ have reported thermokinetic parameters of resin derived from p- hydroxy benzaldehyde, resorcinol and formaldehyde.

Gurnule *et al*¹² have reported thermodynamic parameters and order of thermal stabilities of tercopolymers by using TGA. Aswar *et al*¹³ 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. Masram *et al*¹⁴ reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde.

In present work thermokinetic parameters were determined by using following methods.

A) Freeman-Carroll Method (FC):

In this the kinetic parameters determined by following expression,¹⁵⁻¹⁶

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

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

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

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.

Preparation of m-CHF-I

A mixture of m-cresol (0.1 M), hexamine (0.05 M) and formaldehyde (0.2 M) with 1M HCl was refluxed over oil bath at 122-130°C for 6 hrs with stirring. The solid product so obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with hot water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove copolymer which might be present along with the terpolymer. It was dissolved in 1M NaOH and reprecipitated using 1:1 HCl solution. The product finally collected by filtration, washed with hot water dried, powdered and kept in vacuum. The yield was found to be 74%. The synthetic details are shown in Table 1.

Table 1: Synthetic details of m-CHF-I.

parameters/conditions	specifications
Terpolymeric resin	m-CHF-I
m-Cresol	0.1 M
Hexamine	0.05 M
Formaldehyde	0.2 M
Catalyst, 1 M HCl	100 mL
Temperature	122-130 °C
Time	6.0 hrs
Yield	74 %

Result and Discussion

Elemental Analysis:

The terpolymeric resin was analyzed for carbon, hydrogen, nitrogen and oxygen content. The elemental analysis was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh. The details of elemental analysis are incorporated in Table 2.

The number average molecular weight of m-CHF-I terpolymer has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.1M) in absolute ethanol as a titrant. The conductance versus milliequivalent (Meq.) of KOH per 100g of resin was plotted. The large numbers of breaks were observed in the plot. The average degree of polymerisation and hence the number average molecular weight of terpolymer have been determined using the following relations²⁰⁻²⁵.

$$\overline{DP} = \frac{\text{Milliequivalent of base required for complete neutralisation}}{\text{Milliequivalent of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP} \times \text{molecular weight of repeat unit}$$

The molecular weight of repeat unit was calculated using elemental analysis data as shown in Table 2. The average degree of polymerisation and number average molecular weight of terpolymer resin were found to be 15.0 and 5160 respectively.

Table 2: Elemental Analysis of m-CHF-I.

%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%O Found (Calc.)	empirical formula of repeat unit	Molecular weight of repeating unit
69.81 (69.76)	7.23 (7.55)	4.17 (4.06)	18.79 (18.63)	C ₂₀ H ₁₆ NO ₄	344

UV-VIS Spectrum:

The UV-VIS spectrum of m-CHF-I resin was recorded by instrument Shimadzu UV-VIS-NIR spectrophotometer Model No.1601. The spectrum so obtained is shown in fig. 1. The

peak at 284.16 nm assigned to $n-\pi^*$ transition due to phenolic group. Absorption at 252.6 nm was assigned to $\pi-\pi^*$ due to aromatic ring. The absorption at 236.86 nm was assigned to $n-\sigma^*$ which was support to ether linkages in structure of resin in fig. 4.

Figure 1: UV-VIS spectra of m-CHF-I.

FTIR and NMR Data of m-CHF-I:

The IR spectra (fig. 2) of m-CHF-I terpolymeric resin was carried out at Pharmacy Department, Mahatma Jyotiba Phule Campus, R. T. M. Nagpur University and NMR spectra (fig. 3) of m-CHF-I resin was carried out at Sophisticated Analytical Instrumental Facility(SAIF) Punjab University, Chandigarh which is presented in Table3.

Table 3: IR and NMR spectra of m-CHF-I resin²⁶⁻³².

IR (wave number in cm^{-1})	Nature of fragment assigned	δ in ppm	Nature of fragment assigned
3300-3350	-NH-	2.23-2.27	$\text{CH}_2\text{-NH-CH}_2$ Moiety
3602	-OH (Phenolic)	3.7-4.0	-NH- Bridges
1595	Aromatic C=C str.	4.7	Ar-OH Moiety
1358	-C-N-str.	2.3	Ar-CH ₃ Moiety
1100-1200	C-O-C (Ether linkage)	6.7-7.9	Ar-H (unsymm. pattern)
1124(m), 915(w)	N-C-N def.	2.7	Ar-CH ₂ -
1022(w), 850(w)	C-N-C def.		

According to data obtain in physicochemical methods, the tentative structure terpolymeric resin was assigned as shown in fig. 4.

Figure 2: IR spectra of m-CHF-I resin.

Figure 3: NMR spectra of m-CHF-I resin.

Figure 4: Tentative structure of m-CHF-I.

Thermogravimetric Analysis:

The thermogram of m-CHF-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 upto 950°C. The thermogram reveals that initial weight loss up to 150°C due to loss of water. The decomposition of resin between 410 to 485°C was studied. FC and SW plots are shown in fig. 6a and fig. 6b respectively. The order of decomposition was found to be zero order as determined by FC method which was further confirmed by SW method. Thermokinetic parameters are tabulated in Table 4.

Figure 5: Thermogram of m-CHF-I resin.

Figure 6: (a) FC plot.

b) SW plot.

Table 4: Thermokinetic parameters of m-CHF-I terpolymeric resin.

m-CHF-I terpolymeric resin	Ea (kJ)	A (min ⁻¹)	ΔS* (J/K)	ΔG* (kJ)	Order (n)
FC method	58.56	3954	-179.61	190.1	0.07~ 0.0
SW method	58.56	5901	-176.28	187.66	
FC=Freemann-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 m-CHF-I terpolymeric resin. The activation energies, entropy and free energy of zero order degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are in good agreement. Low value of frequency factor and entropy indicate the slow degradation of resin. The high value of energy of activation relative to thermal energy suggests that the m-CHF-I resin is thermally stable below 400°C.

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