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Synthesis, Characterization and Thermal Degradation Studies of Terpolymer resin derived from 2,6-dihydroxyacetophenone, ethylenediamine and formaldehyde

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ABSTRACT

The terpolymer resin has been synthesized by the condensation of 2, 6-dihydroxyacetophenone, ethylenediamine and formaldehyde in the presence of 2M HCl as catalyst with 1:1:2 molar ratio of reacting monomers. Composition of terpolymer resin was determined on the basis of elemental analysis. The number average molecular weight of the terpolymer was determined by conductometric titration in non aqueous medium. Viscosity measurements were carried out to ascertain the characteristics functions and constants of terpolymer resin. The terpolymer resin was further characterized by UV-Visible absorption spectra, IR and NMR spectra. Thermal degradation curve has been discussed in order to determine its mode of decomposition, order of reaction, activation energy, frequency factor, entropy change, free energy change and apparent entropy change. Kinetic parameters were calculated by using Freeman-Carroll and Sharp-Wentworth methods. The data obtained from Freeman-Carroll method was used to determine various thermodynamic parameters. Synthesized terpolymer shows antibacterial activity.

Keywords: Synthesis, Characterization, Thermal degradation, Antibacterial activity

INTRODUCTION

The use of polymers in all spheres of life has been abundantly increased in recent years. Various workers have pressing demand to synthesize eco-friendly polymers having some biological activities like antimicrobial. The study of the thermal degradation of terpolymer resins have recently became a subject of interest. Polymer additives improve manufacture process and product quality. It can form continuous phase of coating with no deleterious effects on coating, and having better thermal stability (Chauhan *et al*. 2010).

Terpolymer resins, having good thermal stability, have enhanced study of the development of polymeric materials. Terpolymers of substituted acetophenone with formaldehyde/ furfuraldehyde have shown excellent thermal and antimicrobial activity (Chauhan *et al*. 2011). The synthesis of functional terpolymer has gained a lot of attention in recent years due to their applications in adhesives, coating materials, semiconductor, catalyst, flame resistant fibers, ion exchange, and thermally stable and biologically active resins. However, the insolubility and instability of terpolymers have limited their practical applications, but attachment of appro-priate pendant groups or constituents to the polymer backbone cannot only help to improve the processability and stability but also equip it with new functionalities (Vega *et al*. 2006 and Panday and Srivastava, 2002). The research of activated oxime-based monomer and its polymer is focused mainly on maleimide. Soykan and Erol (2003) have reported a synthesis of maleimide monomer N-(4-acetylphenyl) maleimide (NAPMI), and their oxime, carbazone, and thiosemicarbazone derivatives of NAPMI having excellent thermal stability and antimicrobial activity. Such multifunctional poly-mers have been receiving an increasing attention in material science and life science. Hemvichian and Ishida (2002) studied the degradation process of polybenzox-azine in common type (PBA-a) by using TGA and GCeMS. Jadhao *et al*. studied the thermal degradation of terpolymer resins derived from 2,2-dihydroxybiphenyl, Urea, and Formaldehyde (Jadhao *et al*. 2006) Terpoly-mers are useful material in fabrication due to flexibility, chemical inertness as well as being light in weight. Polymers with highly conjugated chain have attracted much attention in the last few years because they are materials of electronics (Singru and Gurnule, 2010, Diaz *et al*., 1999, Suh and Shim, 2000).

MATERIALS AND METHODS

Materials

Solvents like dimethyl formamide and di-methyl-sulph-oxide were used after distillation. 2,6- Di-hydroxy-aceto-phenone ethylene diamine, and Formaldehyde 37% were purchased of market and are from Merck (Maharashtra, India). All other chemicals used were of chemically pure grade.

Synthesis of Terpolymer Resin:

A mixture of 2,6-Dihydroxyacetophenone (0.1 mol), ethylenediamine (0.1 mol) and formaldehyde (0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 mL) HCl as a catalyst has been prepared in round bottom flask. The resultant mixture was refluxed over an oil bath at 110ºC ± 2ºC for 5 hrs with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled electrically with the help of dimmerstat. The resinous black solid mass obtained was immediately removed from the flask as soon as the reaction period was over. The separated terpolymer resin was washed with hot water and ethanol to remove unreacted starting materials and monomers. The properly washed resin was dried, powdered and then extracted with chloroform to remove 2,6-Dihydroxyacetophenone - formaldehyde copolymer which might be present along with 2,6-DHAEDF-I terpolymer and then it is purified. Excellent yield of terpolymer resin was obtained by this reaction [Fig.1].

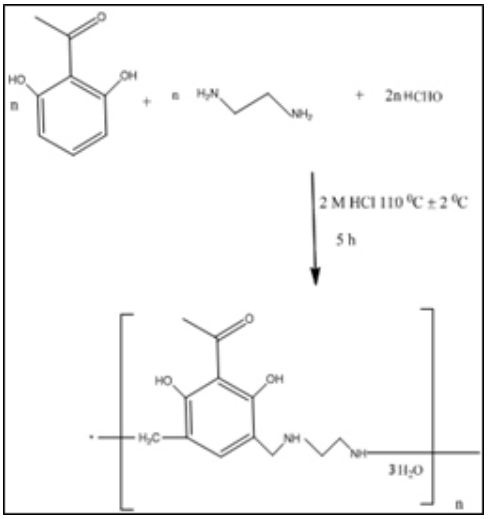

Fig. 1: Reaction and suggested structure of 2,6-DHAEDF-I terpolymer resin

Antibacterial Activities:

Agar diffusion method was used for antibacterial studies. Nutrient agar medium was used for culture of the bacteria. The composition was peptone (10.0 g), sodium chloride (10.0 g), yeast extract (5.0 g) and agar (20.0g) in 1000 ml of distilled water. 20 mg sample was dissolved in 1 ml of dimethylsulphoxide solvent and Ciprofloxacin standard antibiotic of known concentration was used for analysis. Initially, the stock cultures of bacteria were revived by inoculating in broth media and grown at 37 ^{0}C for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs. Old cultures (100 µl, 10-4 cfu) and spread evenly on the plate. After 20 min, the wells were filled with of compound at different concentrations. The control wells with Ciprofloxacin

were also prepared. All the plates were incubated at 37^0C for 24 hrs and the diameter of inhibition zone were noted. Concentration of samples for antibacterial activity was taken from 100-1000µg/ml. The antibacterial activities of the terpolymer were screened on various bacteria at these concentrations. The synthesized polymer has shown moderate / poor antibacterial activities as compared to standard Ciprofloxacin.

Spectral and elemental analysis:

Electronic absorption spectra of the terpolymer was recorded at room temperature in the range 200-800 nm using UV-Visible-NIR Spectrometer Hitachi 330, Perkin Elmer Spectrometer was used for recording FTIR spectrum of the terpolymer resin to identify the linkage and functional groups. The proton NMR spectrum of the 2,6-DHAEDF-I terpolymer resin was recorded in DMSO-d6 solvent using BRUKER AVANCE II 400 NMR Spectrometer. Intrinsic viscosity (η) was measured in DMSO at 32 ^{o}C using Tuan Fuoss Viscometer. Molecular weight determined by non-aqueous conductometric titration using DMSO. Surface morphology of the terpolymers was studied by Scanning Electron Microscopy (SEM) Jeol 6390LV at Sophisticated Analytical Instrument Facility, STIC Cochin. The elements such as C, N and H present in the 2,6-DHAEDF-I were determined by Perkin Elmer elemental analyser.

Thermogravimetric analysis:

The modes of thermal degradation of the terpolymer 2,6-DHAEDF-I was analysed using thermogravimetric analyser (Diamond TG/DTA thermal analyser) at heating rate of 10^oC/ min in static air atmosphere. Based on the results obtained, the degradation pattern, activation energy (Ea), order of reaction (n), entropy change (ΔS). Free energy change (ΔF), apparent entropy (S*) and frequency factor (Z) were calculated by Freeman-Carroll (Freeman and Caroll, 1958) and Sharp-Wentworth methods (Sharp and Wentworth 1969).

RESULTS AND DISCUSSION

Spectral Analysis

Solubility:

The 2,6-dihydroxyacetophenone ethylenediamine with formaldehyde terpolymer resin was soluble in solvents like N, N-dimethyl formamide (DMF), dimethylsulphoxide (DMSO) and concentrated aqueous NaOH and KOH, whereas resin was insoluble in toluene, xylene and benzene. The elements such as carbon (%C), hydrogen (% H), and nitrogen (% N) contents were analysed for the 2,6-DHAEDF-I terpolymer resin. Based on the analytical data, the empirical formula of the repeating unit for the 2,6-DHAEDF-I resin was found to be $C_{12}N_2O_3H_{16}.3H_2O$.

FTIR Spectra:

The recorded FTIR spectrum of the terpolymer resin is shown in Fig.2. The spectrum shows a broad band at 3282.55 cm^{-1} due to (-OH) stretching of Ar-OH involved in the intramolecular hydrogen bonding. The band at 3150.00 cm^{-1} is due to NH-stretching of amino group, this band seems to be merged with –OH group present in the resin. The pentasubstitution in the benzene ring is established by the presence of medium bands at 813.77 cm^{-1}. The band at 1711.00 cm^{-1} may be assigned to (>C=O) stretching of ketonic group.

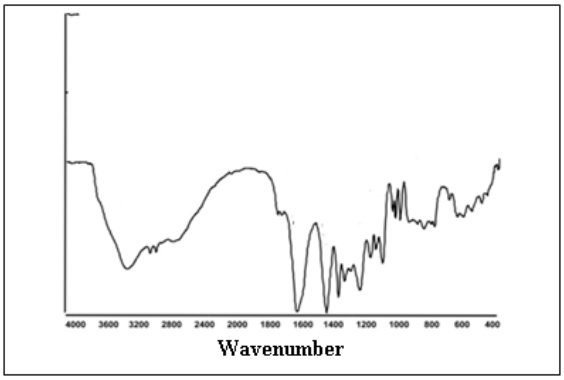

Fig. 2: IR Spectra for 2,6 DHAEDF-I terpolymer resin

^{1}H-NMR:

^{1}H-NMR spectrum of 2,6-DHAEDF-I terpolymer resin shown in Fig.3. The NMR spectrum revels that the signal around 3.57 δ (ppm) are due to the methylenic protons of the Ar-CH_2-NH- linkage. The multiplate signals observed in the range at 6.70 δ (ppm) indicates the presence of aromatic protons. The signal displayed at 11.25δ (ppm) may be due to the phenolic protons (Ar-OH).

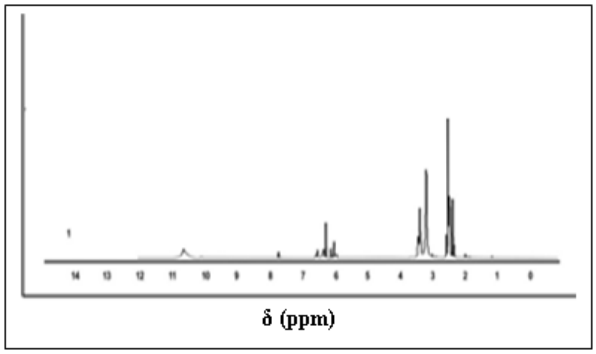

Fig 3: ^{1}H-NMR spectra of 2,6 DHAEDF-I Terpolymer Resin

A weak signal appeared in the region 6.36δ (ppm) is assigned to the protons of –NH- bridge. The methyl proton of the Ar-CO-CH_3 moiety may be identified by the intense peak at 2.51-2.61 δ ppm.

UV-Visible spectra:

UV-Visible spectra of 2,6 DHAEDF-I in DMSO were recorded in the range of 200-800 nm. UV-Visible spectrum of the terpolymer resin is shown in Fig. 4. The spectrum exhibits two characteristic bands at 355 nm and 263 nm. These observed positions for the absorption bands have different intensities. The band at 263 nm intense band which may be accounted for a π→π* transition While the less intense band at 355 nm, is due to n→π* transition.

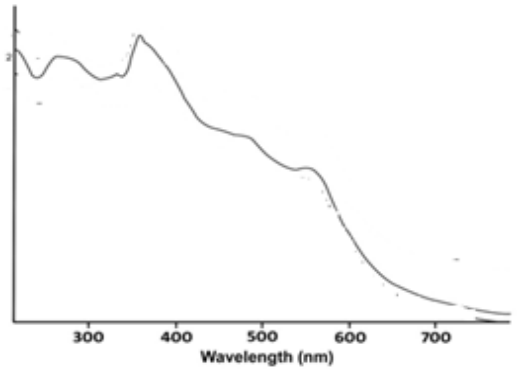

Fig. 4: UV-Visible spectrum for 2,6-DHAEDF-I Terpolymer

Formula for calculating thermodynamic parameters using Freeman-Carroll method.

Entropy Change (ΔS)

Intercept= $\frac{\log kR}{h\Phi Ea} + \frac{\Delta S}{2.303R}$ [1]

Where, k=1.3806x10^{16}erg/deg/mole
R=1.987cal/deg/mole
(8.314J/K/mol)
h = 6.625 x 10^{-27} erg sec
ϕ = 0.166
ΔS= change in entropy

Free energy change (ΔF)

ΔF = ΔH - TΔS [2]

Where, ΔH = Enthalpy change = Activation energy
T = Temperature in K
ΔS = Entropy change {from [1] used}

Frequency Factor (Z)

$$B_{2/3} = \frac{\log Z E_a}{R\Phi} \quad \textbf{[3]}$$

$$B_{2/3} = \log 3 + \log[1 - 3\sqrt{1-\alpha}] - \log\ p(x) \quad \textbf{[4]}$$

Where, Z = Frequency factor
B = Calculated from equation [4]
log p(x) = Calculated from Doyle's graph
α =degree of transformation [α= w/W_c]

Apparent entropy (S*)

$$S^* = 2.303 \log \frac{Zh}{kT^*} \quad [5]$$

Where,
Z = from relation [3]
T* = Temperature at which half of the compound is decomposed from it total loss.

Table 1 shows thermal degradation behavior of the terpolymer and Fig.5 shows TGA-DTA curve. Thermal activation energy plot and Freeman Carroll plots for 2,6-DHAEDF-I terpolymer resin are shown in Fig 6. and Fig. 7 respectively. Kinetics parameter such as entropy change (ΔS), free energy change (ΔF), apparent entropy (S*) and frequency factor (Z) were calculated based on the thermal activation energy the expression shown in equation [1], [2], [3] and [4]. Using the Freeman-Carroll and Sharp-Wentworth methods, the kinetic parameters were calculated and present in table.2. The activation energy values calculated from FC and SW are in good agreement with each other. The low frequency factor value predicts that the degradation reaction is slow and no other possible reason can be given (Jacobs and Eompkins, 1955 and Ozawa, 1985). This is further supported by negative value of the entropy change which suggests more ordered structure for activated terpolymer than reactants. However, a few points do not fall on straight line in Fig 6. which show that the reaction does not obeys the first order kinetics perfectly.

Antibacterial Activity

In order to explore antibacterial activity of 2,6-DHAEDF-I resin have been tested for antibacterial activity against *Bacillus substilus*, *Escherchia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* and terpolymer shows moderate antibacterial activity against *P. aeruginosa, Bacillus substilus*, *Escherchia coli*, *Staphylococcus aureus* shows poor antibacterial activity (Table 3).

Table 1: Thermal degradation behaviour of 2,6 DHAEDF-I Terpolymer Resin

Terpolymer	Temperature Range (^{0}C)	Stage of Decomposition (DTA Peak)	Species degraded	% mass loss	
				Found	Calc.
2,6 DHAEDF-I	R.T –317 ^{0}C	First	Loss of $3H_2O$ molecule	11.65	12.05
2,6-DHAEDF-I	317 – 557 ^{0}C	Second (Exo, b)	Loss of side chain (-CH_2-NH-CH_2-CH_2-NH-,$COCH_3$,2OH,-CH_2) and partial degradation of aromatic nucleus	91.66	91.72

Table 2: Results of thermogravimetric analysis of 2,6 DHAEDF-I

Terpolymer	Decomposition Temp. (^{0}C)	Half Decomposition Temp. (^{0}C)	Activation Energy kJ/mole		Kinetic Parameters by FC				
			FC	SW	ΔS (J)	ΔF(kJ)	Z (S^{-1})	S* (J)	n
2,6 DHAEDF-I	317^{0}C	437	31.94	33.30	-165.73	44.11	39.11	-30.26	0.90

Table 3: Relative antibacterial activity of 2,6-DHAEDF-I terpolymer

Sr. no.	Terpolymers	Concentration screened (µg/mL)	Diameter of inhibition zones in mm			
			E. coli	*P. aeruginosa*	*S .aureus*	*B. subtilis*
1	2,6 DHAEDF-I	100	NF	NF	NF	NF
		250	NF	NF	NF	NF
		500	NF	NF	NF	NF
		1000	4.0	4.0	4.0	4.0
2	Ciprofloxacin (Standard)	100	23	01	21	15
		250	26	03	25	19
		500	28	08	27	22
		1000	31	14	34	25

***NF-** Not found.

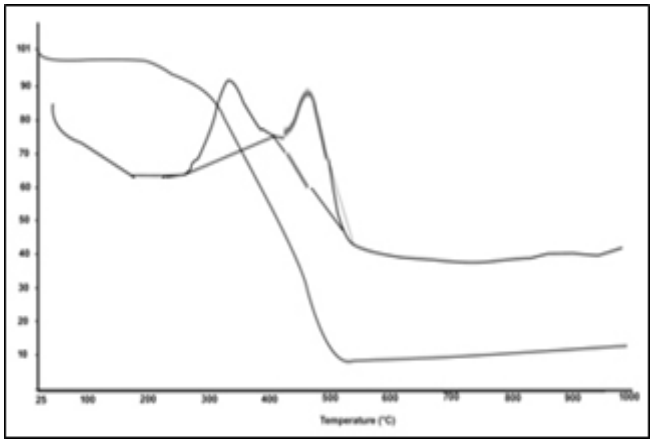

Fig. 5: 2,6 DHAEDF-I TGA-DTA curve

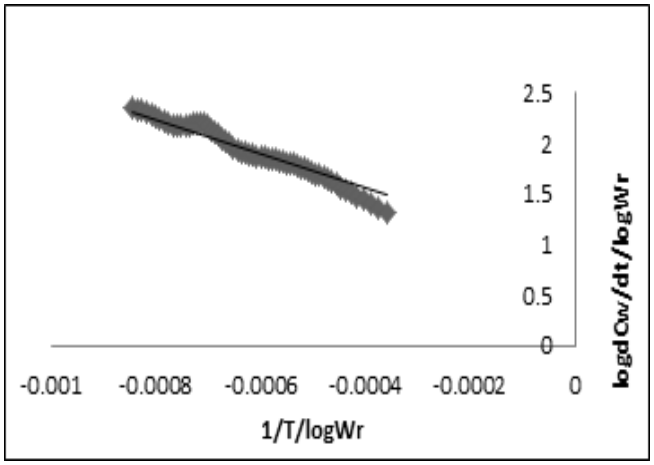

Fig. 6: Thermal Activation Energy Plot of 2,6 DHAEDF-I Terpolymer Resin.

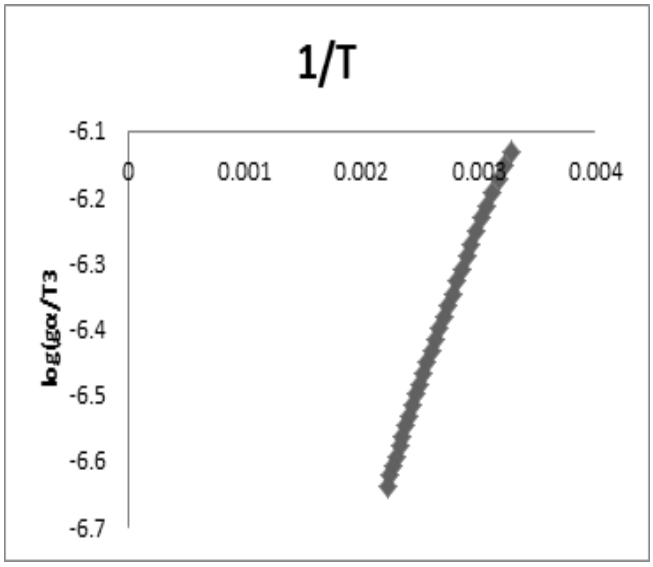

Fig. 7: Freeman-Carroll plot of 2,6-DHAEDF-I-I Terpolymer Resin

CONCLUSION

Terpolymer involving 2,6-dihydroxyacetophenone, ethylenediamine and formaldehyde was synthesized in the presence of hydrochloric acid as a catalyst by condensation reaction at 110± 2 ^{0}C for 5 hours. The spectral characterizations of the terpolymer confirm the linear structure. TGA curve shows that the terpolymer resin had good thermal stability. The activation energy calculated for the resin by Freeman-Carroll and Sharp-Wentworth methods was found to be in good agreement with each other. The low frequency factor and the negative entropy values calculated from Freeman–Carroll method suggested that the thermal decomposition would be a slow reaction. The thermal degradation kinetics indicate that 2,6 DHAEDF-I terpolymer shows one step degradation after loss of water molecule. The 2,6 DHAEDF-I terpolymer resin shows moderate/poor antibacterial activity against all bacteria screened and no antifungal activity againt *C. albicans* and *A. niger*.

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Conflicts of interest: The authors stated that no conflicts of interest.

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