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Original Article

Thermal Degradation of Terpolymer Derived from 2, 4-dihydroxyacetophenone, propylenediamine and Formaldehyde

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ABSTRACT

The terpolymer (2,4-DHAPrDF) was synthesized by condensation of 2,4-dihydroxyacetophenone and paraphenylene diamine with formaldehyde in the presence of 2 M HCl as a catalyst at 130 ± 2 ^{O}C for 5 h. The terpolymer 2,4-DHAPrDF was characterized by elemental analysis FTIR, ^{1}HNMR and UV-Visible spectroscopy. The thermal decomposition behavior 2,4-DHAPrDF was studied using thermogravimetric analysis (TGA/DTA) in a static oxygen atmosphere at a heating rate 10 ^{O}C /min. Freeman-Carroll, Sharp-Wentworth methods were used to calculate thermal activation energy (Ea), the order of reaction (n), entropy change (ΔS) Synthesized terpolymer resin shown moderate antibacterial activity and porous morphology.

Key words – synthesis, characterization, conductometric titration, intrinsic viscosity, Freeman Carroll and Sharp-Wentworth methods and Antibacterial activities.

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INTRODUCTION

Due to the global applications of polymeric materials, polymer science and technology have been developing rapidly and attracted much attention towards the polymer scientists. Polymers have been found to be very useful applications as adhesive, high-temperature, flame-resistant fiber, coating materials, semiconductors, catalyst and ion exchange resins [1].The use of polymers in all spheres of life has been abundantly increased in recent years. Although 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 [2].

Terpolymer resins, having good thermal stability, have study of enhanced the development of polymeric materials. Terpolymers of substituted acetophenone with formaldehyde /furfuraldehyde, these terpolymers have shown excellent thermal and antimicrobial activity [3]. Michael et al. prepared terpolymer of 8-hydroxyquinoline, guanidine and formaldehyde and also studied thermal degradation to ascertain its thermal stability [4]. Katkamwar et.al. synthesized terpolymer resin (8-HQDF) by condensation of 8-hydroxyquinoline,dithioxamide and formaldehyde in acedic medium[5]. Kushwaha et al. synthesized resin from p-nitrophenol-resorcinol- formaldehyde which shows antibacterial activity [6]. Singru et al studied the thermoanalytical and kinetic study of resins derived from 8-hyderoxyquinoline-5-sulphonic acid -oxamide-formaldehyde[7].

Jadhao et al. studied the thermal degradation of terpolymer resins derived from 2,2-dihydroxybiphenyl, Urea, and Formaldehyde [8].Terpolymers are useful material in fabrication, flexibility, chemical inertness as well as being light in weight. Polymers with highly conjugated chain have attracted much attention in the last few year because they are materials of electronics[9-11].

Many papers were devoted in the last decades to synthesize environmental friendly antimicrobial polymers from renewable sources, due to the important role of these resins in the development of fiber reinforced composites for biomedical application[12]. This article describes the compositions of newly synthesize resin 2,4-dihydroxyacetolphenone (2,4-DHA) and Propylenediamine (Pr) with formaldehyde their characterization by elemental analysis, The molecular weight and intrinsic viscosity were determined by non-aqueous conductometric titration and viscosity in DMSO, FTIR Spectra UV-visible absorption spectra, NMR spectra and Thermal analysis giving their relative thermal stabilities by applying the Freeman-Carroll and Sharp- Wentworth methods. Energy of activation Ea, themodynamic parameters viz. Z, ΔS, ΔF, S* and order of reaction n were determined by applying Freeman-Carroll method.

EXPERIMENTAL

Method: All the Chemicals were AR grade or chemically pure grade. 2, 4 dihydroxy acetophenone purchased from Aldrich Chemical, formaldehyde from Merck while DMF and DMSO (HPLC grade) were used.

Synthesis of Terpolymer Resin: A mixture of 2,4-Dihydroxyacetophenone (0.1 mol), propylenediamine (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 for heating at 130ºC ± 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 pink solid mass was obtained 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 acid monomers. The properly washed resin was dried, powdered and then extracted with chloroform to remove 2,4-Dihydroxyacetophenone-formaldehyde copolymer which might be present along with 2,4-DHAPrDF terpolymer and then it is purified. Excellent yield of terpolymer resin was obtained by this reaction [Fig.1].

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 Gentamycin 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

Gentamycin 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 were taken as 800 µg/ml. The antibacterial activities of the terpolymer were screened on various bacteria at these concentrations. The synthesized polymer has shown moderate antibacterial activities as compared to standard Gentamycin [13,14].

Spectral and elemental analysis: Electronic absorption spectra of the terpolymer was recorded at room temperature in the range 185-2600 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 2,4-DHAPrDF terpolymer resin was recorded in DMSO- d6 solvent using BRUKER AVANCE II 400 NMR Spectrometer. Intrinsic viscosity (η) was measured in DMSO at 32 ºC using Tuan Fuoss Viscometer. Molecular weight determined by non-aqueous conductometric titration using DMSO. Surface morphology of the terpolymers were 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 2,4-DHAPrDF were determined by Perkin Elmer elemental analyser.

Thermogravimetric analysis: The modes of thermal degradation of the terpolymer 2,4-DHAPrDF was analysed using thermogravimetric analyser (Diamond TG/DTA thermal analyser) at heating rate of 10ºC/ min in static air atmosphere. Based on the results obtained, the degradation pattern, activation energy (Ea), (n) order of reaction, entropy change (ΔS). Free energy change (ΔF), apperent entropy (S*) and frequency factor (Z) were calculated by Freeman-Carroll[15] and Sharp-Wentworth[16] methods.

RESULTS AND DISCUSSION

Solubility: The 2,4-dihydroxyacetophenone propylenediamine 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 2,4-DHAPrDF terpolymer resin and presented in the Table-1. Based on the analytical data, the empirical formula of the repeating unit for the 2,4-DHAPrDF resin was found to be $C_{13}N_2O_3H_{18}.2H_2O$

Spectral Analysis

FTIR Spectra: The recorded FTIR spectrum of the terpolymer resin is shown in Fig.2. The spectrum shows a broad band at 3399.19 cm^{-1} due to (-OH) stretching of Ar-OH involved in the intramolecular hydrogen bonding. The band at 2928.68 cm^{-1} is due to NH-stretching of amino group, this band seems to be merged with a group of –OH group present in the resin. The pentasubstituted in the benzene ring is established by the presence of medium bands at 916.52 cm^{-1} . The band at 1628.13 cm^{-1} may be assigned to (>C=O) stretching of ketonic group.

^{1}HNMR: ^{1}HNMR spectrum of 2,4-DHAPrDF terpolymer resin shown in Fig.3. The NMR spectrum revels that the signal around 3.3-4.76 δ (ppm) are due to the methylenic protons of the Ar-CH_2-NH- linkage. The multiplate signals observed in the range at 7.1-7.6 δ (ppm) indicates the presence of aromatic protons. The signal displayed at 8.4 δ (ppm) may be due to the phenolic protons (Ar-OH). A weak signal appeared in the region 6.30-6.58 δ (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 2.0 - 2.8 δ ppm.

UV-Visible: UV-Visible spectra of 2,4- DHAPrDF in DMSO were recorded in the range of 200-800 nm. UV-Visible spectra of the terpolymer resin is shown in Fig. 4. The spectra exhibits two characteristic bands at 300-320 nm and 240-280 nm. These observed positions for the absorption bands have different intensities. The band at 240-280 nm intense band which may be accounted for a $\pi\rightarrow\pi^*$ transition While the less intense band at 300-320 nm, is due to $n\rightarrow\pi^*$ transition.

Molecular Weight Determination: The number average molecular weight of newly synthesized 2,4- DHAPrDF terpolymer resin was determined by conductometric titration in non-aqueous medium using potassium hydroxide as a titrant. The conductometric titration curve is depicted in Fig. 5. The plot indicate that there are numerous breaks before complete neutralization of all the phenolic hydroxyl groups. The Mn of these polymer was found to be (3146).

Viscosity Determination: Viscosities of terpolymer sample was measured by using Tuon-Fuoss viscometer. The intrinsic viscosity [η] was determined by

Huggins equation

$$\eta_{sp}/C=[\eta] + K_1[\eta]^2C \qquad (1)$$

Another useful equation known as Kraemer equation is as follows:

$\ln \eta r/C = [\eta] - K_2[\eta]^2C$ (2)

In accordance with the above relation, the plot of η_{sp}/C and ln ηr/C against C were found to be linear , giving slopes K_1 and K_2 respectively. The intercept on the axis of viscosity function gave the [η] value in both plots. conditions where t_0 is the flow time of a given volume of the solvent ant t is the flow time of a same volume of solution, respectively.

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = (\eta_0 - 1)$$

The viscometric parameter called intrinsic viscosity (η) for a polymer solvent system at a given temperature is given by intercept of the linear plot of ηsp/C vs. C i.e., by extrapolating the plot to a condition of zero concentration.

$$[\eta] = \left[\frac{\eta_{sp}}{C}\right]_{c \to 0}$$

The calculated values of constants K_1 and K_2 [Table-1] of the terpolymer in most cases satisfy the relation

$K_1 + K_2 = 0.5$ favorably.

Formula for calculating thermodynamic parameters using Freeman-Carroll method.

Entropy Change (ΔS)

$$\text{Intercept} = \frac{\log kR}{h\Phi Ea} + \frac{\Delta S}{2.303R} \quad [5]$$

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

ф = 0.166

ΔS= change in entropy

Free energy change (ΔF)

ΔF = ΔH - TΔS [6]

Where, ΔH = Enthalpy change = Activation energy

T = Temperature in K

ΔS = Entropy change {from [5] used}

Frequency Factor (Z)

$$B_{2/3} = \frac{\log Z E_a}{R\Phi} \quad \textbf{[7]}$$

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

[8]

Where, Z = Frequency factor

B = Calculated from equation [8]

log p(x) = Calculated from Doyle's graph

α =degree of transformation [$\alpha = w/W_c$]

Apparent entropy (S*)

$$S^* = 2.303 \log \frac{Zh}{kT^*}$$ [9] Where,

Z = from relation [7]

T* = Temperature at which half of the compound is decomposed from it total loss.

Sharp-Wentworth and Freeman Carroll method for 2,4-DHAPrDF terpolymer resin is shown in Fig 8. And Fig. 10 respectively. Kinetics parameter such as entropy change (ΔS), free energy change (ΔF), apperent entropy (S*) and frequency factor (Z) were calculated based on the thermal activation energy the expression shown in eq [5], [6], [7] and [8]. Using the Freeman-Carroll and Sharp-Wentworth methods, the kinetic parameters were calculated and present in table.3. The activation energy values calculated from FC and SW are in good agreement with each other. The low frequency factor value predict that the degradation reaction is slow. This further supported by negative value of the entropy change. However a few points do not fall on straight line in graph Fig 8. And 10. Which show that the reaction does not obeys the exact first order kinetics.

Antibacterial Activity: In order to explore antibacterial activity of 2,4-DHAPrDF 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 and negligible activity against other bacteria.

SEM Analysis: The scanning electron microscopic images clearly show the porous morphology of the terpolymer (Fig. 11) and found to contain microporous structures as well. These microporous structure clearly indicate that polymers may be useful in catalytic applications and adsorption phenomena.

CONCLUSION

Terpolymer involving 2,4-dihydroxyacetophenone, paraphenylenediamine and formaldehyde was synthesized in the presence of hydrochloric acid as a catalyst at 130± 2 _C for 5 h. 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 2,4DHAPrDFterpolymer shows one step degradation. The 2,4-DHAPrDF terpolymer resin shows moderate antibacterial activity against the P.aruginosa. The 2,4-DHAPrDF terpolymer resin shows microporous morphology.

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Table 1: Empirical Formula, Molecular Weight And Intrinsic Viscosity data Of 2,4-DHAPrDF Terpolymer Resin

Terpolymer	% C	% H	% N	Empirical formula of repeating unit	Empirical formula weight	Dp	Mn	Intrinsic viscosity [η]dl g^{-1}	(K_1) Huggins constant	(K_2) Krammers constant	K_1+K_2
2,4-DHAPrDF	54.09	7.05	9.13	$C_{13}N_2O_3H_{18}$ .2H_2O	286	11	3146	0.121	1.4345	-0.9550	0.47

Table 2: Results of Thermogravimetric Analysis of 2,4DHAPrDF Terpolymer Resin

Terpolymer	Temperature Range (^{0}C)	Stage of Decomposition (DTA Peak)	Species degraded	% mass loss	
				Found	Calc.
2,4-DHAPrDF	150 – 260 ^{0}C	First	Loss of 2H_2O molecule	12.58	12.58
2,4-DHAPrDF	265 – 567 ^{0}C	Second (Exo, b)	2-OH, Side chain –CH_2-NH-CH_2-CH_2-CH_2-NH- attached to aromatic nucleus, $COCH_3$,-CH_2, Partial degradation of aromatic nucleus.	90.25	91.24

Table-3 : **Thermogravimetric Data and Decomposition Temperature range of 2,4 DHAPrDF Terpolymer**

Terpolymer	**Decompo Temp T (^{0}C)**	**Half Decomp Temp (^{0}C)**	**Activation Energy**		**Kinetic Parameters by FC**				
			FC	**SW**	**ΔS (J)**	**ΔF (kJ)**	**Z (S^{-1})**	**S* (J)**	**n**
2,4-DHAPrDF	265	407	25.98	23.32	-153.63	114.01	114.81	-25.81	0.99

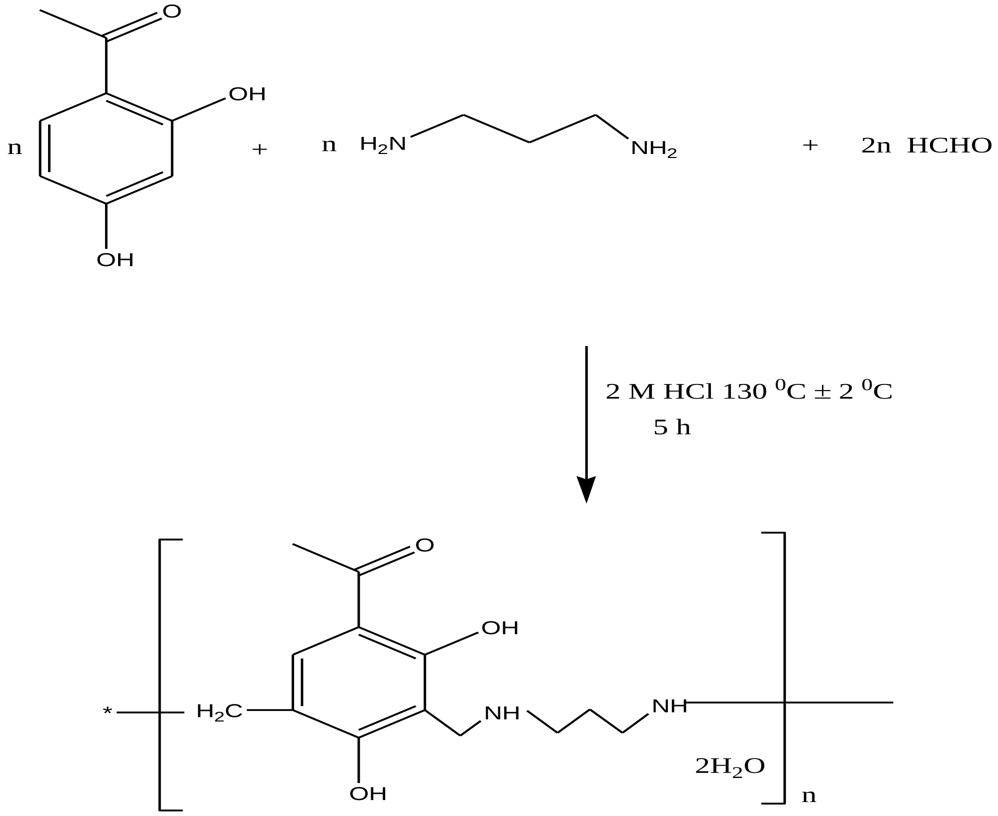

Fig. 1 Reaction and suggested structure of 2,4-DHAPrDF terpolymer resin

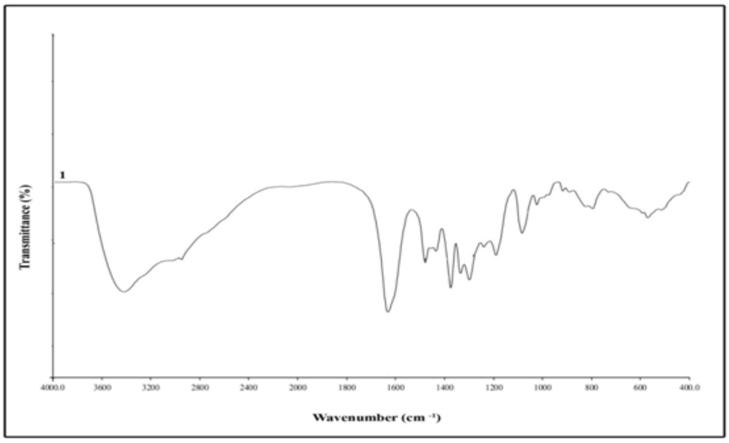

Fig. 2 IR-spectra for 2,4-DHAPrDF Terpolymer

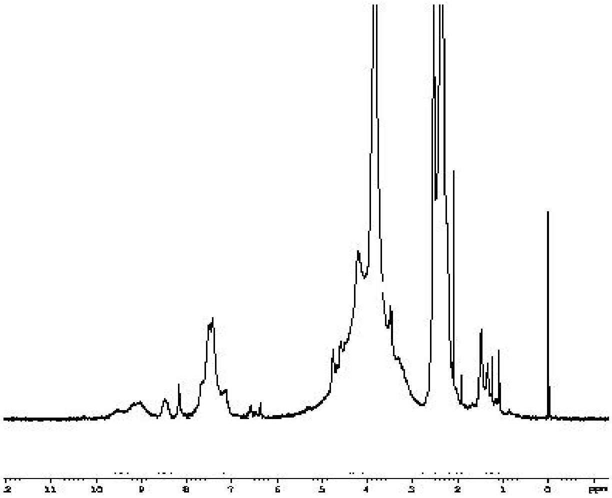

Fig. 3 ^{1}HNMR-spectra for 2,4-DHAPrDF Terpolymer

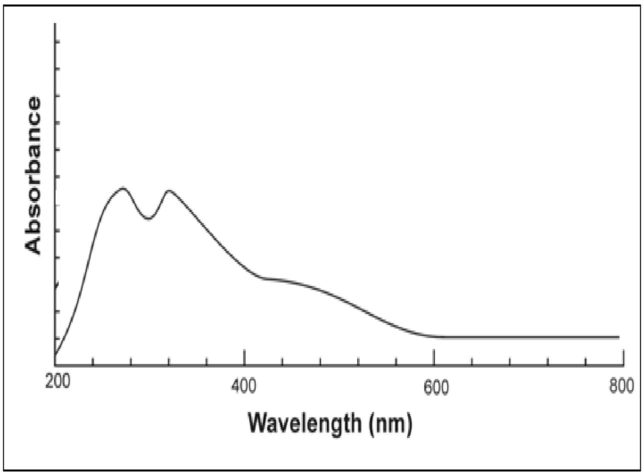

Fig.4 UV-spectra for 2,4-DHAPrDF Terpolymer

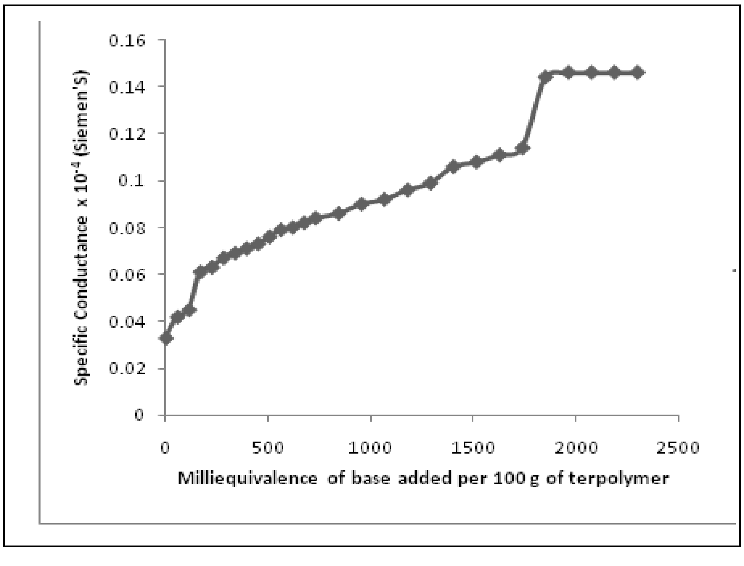

Fig. 5: Conductometric Titration Curves of 2,4-DHAPrDF Terpolymer Resin

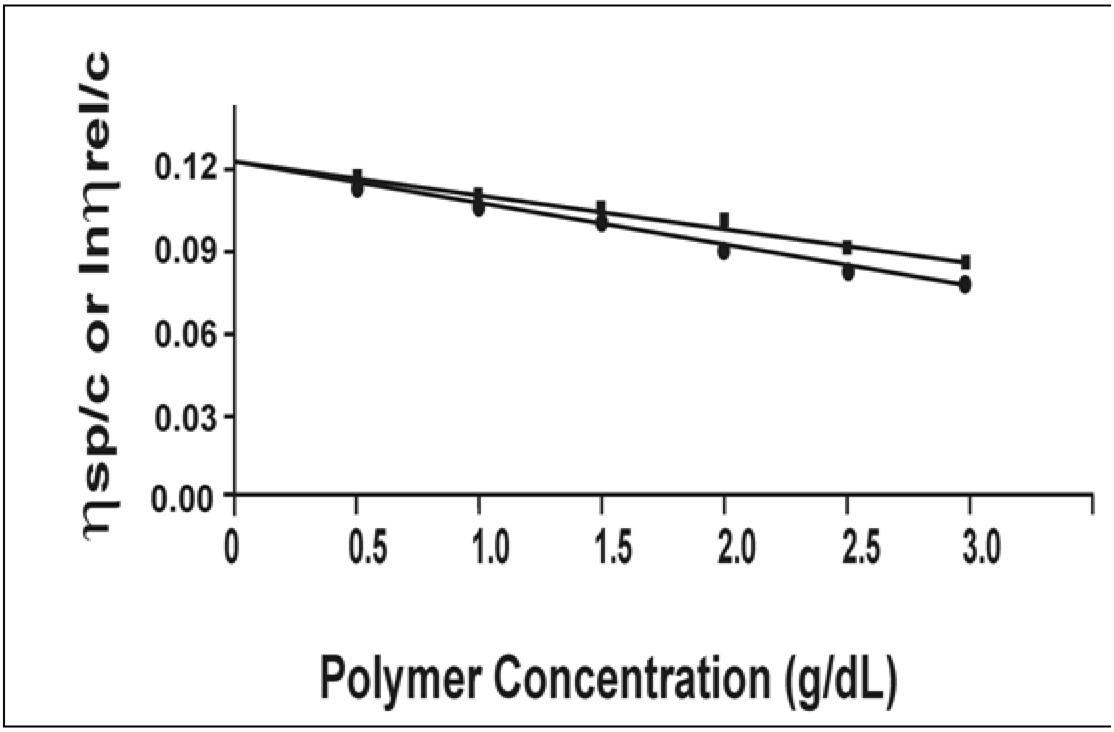

Fig.6. Huggins and Krammer plots for terpolymer 2,4-DHAPrDF

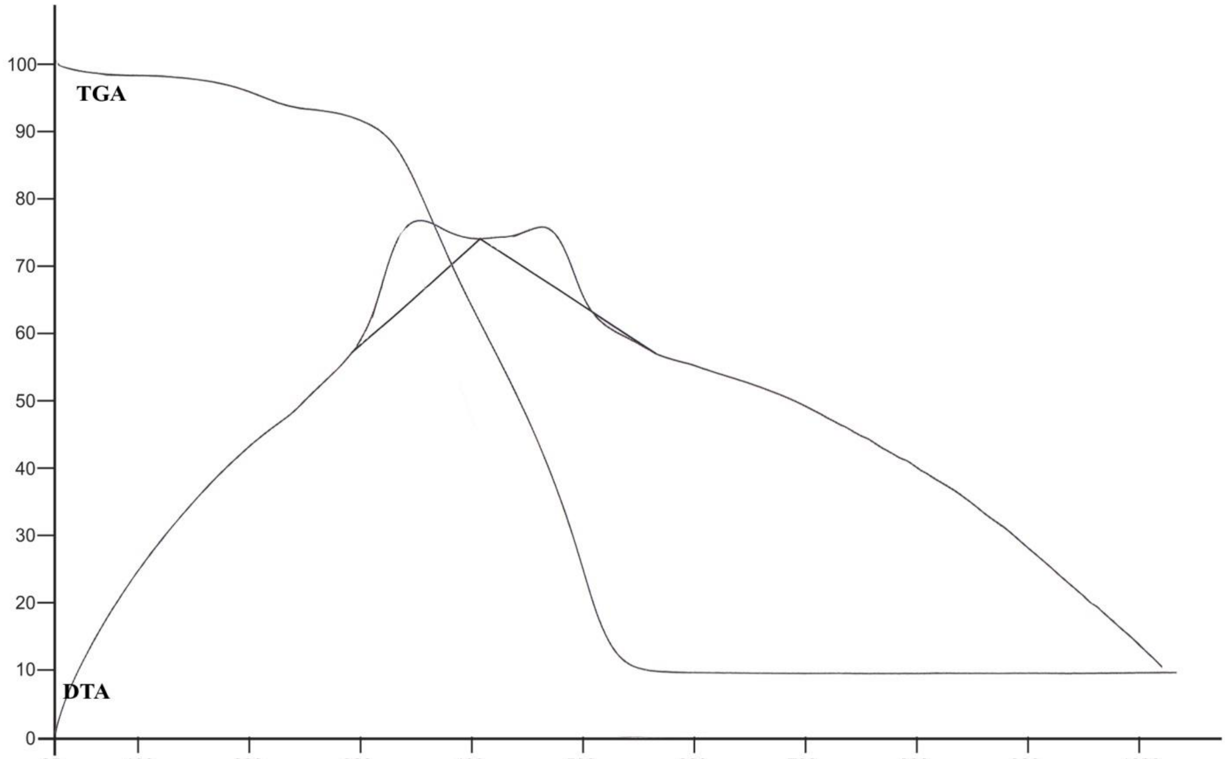

Fig. 7: 2,4-DHAPrDF-I(TGA THERMOGRAM)

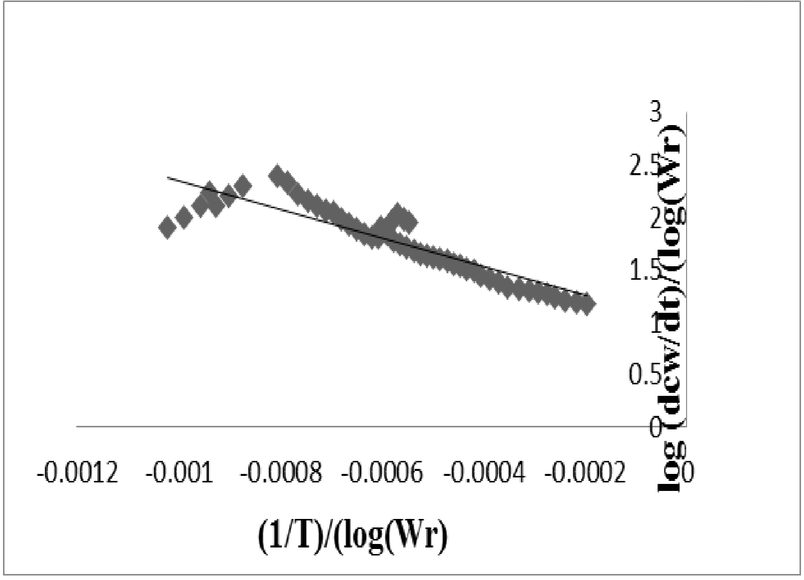

Fig. 8: Thermal Activation Energy Plot of 2,4-DHAPrDF Terpolymer Resin

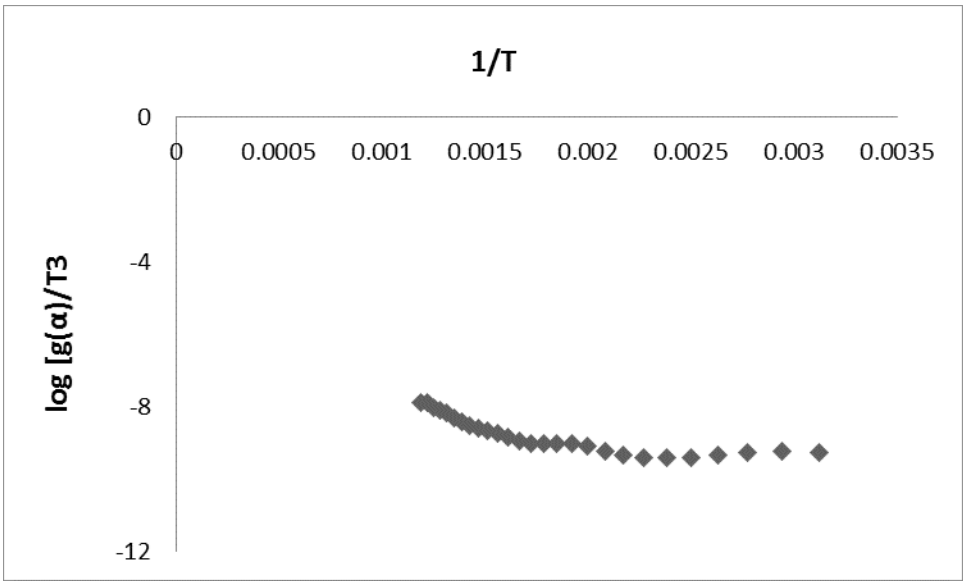

Fig. 9: Freeman-Carroll plot of 2,4-DHAPrDF-I Terpolymer Resin

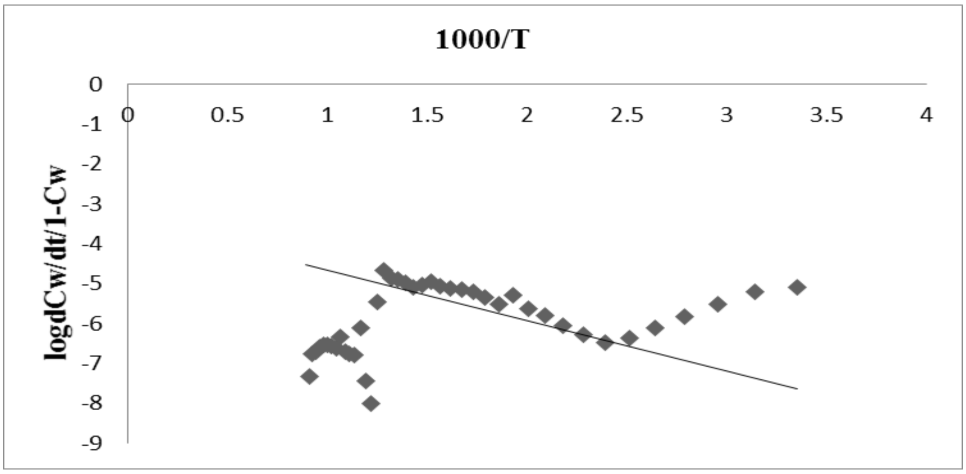

Fig.10:Sharp-Wentworth plot of 2,4-DHAPrDFTerpolymer Resin

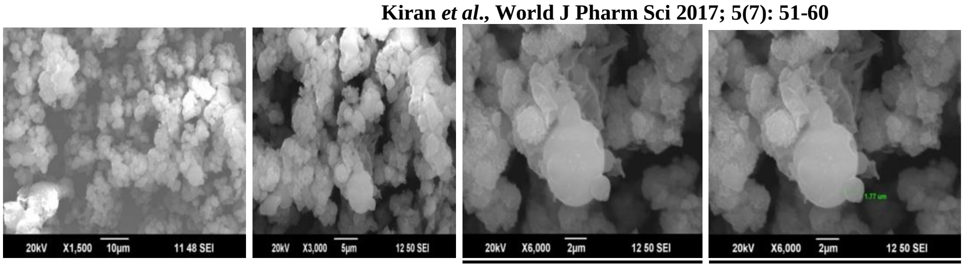

Fig. 11 SEM Images of 2,4-DHAPrDF Terpolymer Resin

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