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Thermal Degradation Studies of Terpolymer Derived from 2-Aminothiophenol and Butanediamine.

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ABSTRACT

2-ATPBDAF terpolymer has been synthesized by using three monomers namely 2-aminothiophenol, butanediamine and formaldehyde by the condensation polymerization reaction in the presence of 2M HCl as a catalyst using 1:1:2 molar ratios of reacting monomers. The composition of the terpolymer has been determined by Elemental analysis and viscosity has been determined by Ubbelohde Viscometer. UV-Visible, FT-IR and $^1\text{H-NMR}$ spectral studies have been carried out to elucidate and confirmed the most probable structure of synthesized terpolymer. The number average molecular weight was determined by non-aqueous conductometric titration. Thermal studies of the terpolymer have been carried out to determine their mode of decomposition, activation energy, order of reaction, frequency factor, entropy change, free energy change and apparent entropy change. Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters, while the data from Freeman-Carroll method have been used to determine various thermodynamic parameters.

Keywords: Polycondensation, spectral studies, kinetic parameters, thermodynamic parameters

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INTRODUCTION

Terpolymer having good thermal stability has enhanced the development of polymeric material. The study of the thermal degradation of terpolymers has recently become a subject of interest. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries, etc. because of their high thermal stability and heat and chemical resistance, again terpolymer has very useful applications as high temperature flame resistant fibers, coating materials, semiconductors, catalyst and ion-exchanger resins.

Thermal degradation study of terpolymer resins derived from 2,4-dihydroxypropiophenon, biuret and formaldehyde by using acid catalyst have been studied by Tarase et al [1, 2]. Thermal study and characterization of terpolymer 2,2-biphenol- tetraethylenepentamine-formaldehyde has been carried out by Belsare et al [3]. Thermogravimetric analysis of urea-formaldehyde polycondensate has been reported by Zeman and Tokarova [4]. Shah et al synthesized the terpolymer from salicylic acid, formaldehyde and resorcinol [5]. Gupta and other researchers [6] studied the thermal degradation and kinetic study of terpolymer resin derived from p-hydroxybenzaldehyde, succinic acid and ethylene glycol. Comparative thermokinetic study between PARG-I and PARG-II terpolymeric resins has been carried out by Kapse et al [7] which is derived from p-hydroxyacetophenone, resorcinol and glycerol. Chauhan [8] synthesized terpolymer using p-acetylpyridineoxime, p-methylacetophenone and formaldehyde by condensation polymerization in the presence of an acid catalyst. Ingle et al carried out thermokinetic study of p-toluenesulfonic acid-m-cresol-formaldehyde terpolymer resin [9]. Melamine-aniline-formaldehyde terpolymeric ligand has been synthesized by Dharkar and other researchers [10] and studied by thermal degradation analysis. Dhore et al [11, 12] studied the thermal degradation and ion-exchange studies of terpolymers derived from 4-aminosalicylic acid, oxamide and formaldehyde. Kalbende et al [13] carried out non-isothermal thermogravimetric analysis of cross-linked phenol based copolymer resins and characterized by elemental analysis and spectroscopic methods. Masram [14] carried out thermal degradation study of salicylic acid-diaminonaphthalene-formaldehyde terpolymer in acidic medium.

A wide variety of thermally stable polymers have been synthesized and the sequence of their thermal stabilities has been predicted from their TG data. The present synthesized terpolymer deals with the synthetic and thermal degradation properties of a newly terpolymer derived from 2-aminothiophenol, butanediamine and formaldehyde. The Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters. Energy of activation (E_a), thermodynamic parameters viz. z , ΔS , ΔF , S^* and order of reaction (n) were determined by applying Freeman-Carroll method.

EXPERIMENTAL

2-aminothiophenol and butanediamine are of analytical grade purity which is purchased from Acros Organics Chemicals, Belgium; and formaldehyde (37%) was purchased from S. D. Fine Chemicals, India. All the solvents used like N, N-dimethylformamide, dimethylsulphoxide, tetrahydrofuran, acetone and diethyl ether were procured from Merck, India.

Synthesis

2-ATPBDAF terpolymer was synthesized by condensation of 2-aminothiophenol (1.08 gm, 0.1 mol) and butanediamine (1.01 gm, 0.1 mol) using the linkage of formaldehyde (7.5 ml, 0.2 mol) with the molar ratios of 1:1:2 in presence of 2M hydrochloric acid (200 ml) as a catalyst. The mixture was heated at 150 °C in an oil bath for six hours with frequent shaking [15-17]. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The pale white colored product obtained was immediately removed from the flask as soon as the reaction period was over. The yield of this terpolymer was found to be 80.99 %. The proposed reaction for the synthesis of 2-ATPBDAF terpolymer is shown in Figure 1 and synthetic details are reported in Table 1.

Characterization of terpolymer

Terpolymer was subjected to elemental analysis for carbon, hydrogen, nitrogen and sulphur on Elementar Vario EL-III Elemental Analyzer and UV-VIS spectra of terpolymer in DMSO solvent recorded by

Varian carry 5000 UV-VIS spectrophotometer at STIC, Cochin University of Science and Technology, Cochin. FT-IR spectra was recorded on Perkin Elmer Spectrum RX-1 spectrometer in the range of 4000 to 400 cm^{-1} and $^1\text{H-NMR}$ study has been carried out using Bruker Avance-II, 400 NMR spectrometer with DMSO-d_6 as a solvent were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh.

The number average molecular weight (\overline{Mn}) of this terpolymer has been determined by conductometric titration method in nonaqueous medium using standard potassium hydroxide (0.05 M) in absolute ethanol as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g of each terpolymer. There are several breaks before the complete neutralization of all phenolic thiol and amine groups. The first break in the plot was the smallest break and it is assumed that this corresponds to a stage in titration when an average of one phenolic thiol and amine group of each chain was neutralized. From the plot, the first and final breaks were degree of polymerization (\overline{Dp}) and hence the number average molecular weight (\overline{Mn}) of terpolymer has been determined using the following formula:

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

$$\overline{Mn} = \overline{Dp} \times \text{weight of repeat unit (monomer)}$$

The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots using Ubbelohde viscometer [18-20] fabricated in our research laboratory at different concentrations ranging from 0.3 to 0.05 % of terpolymer in DMSO at 27 $^{\circ}\text{C}$. Intrinsic viscosity $[\eta]$ was calculated from relevant plots of Huggin's equation and Kraemer's equation. Huggin's [21] and Kraemer's [22] constants were determined by (1) and (2).

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

$$\ln \eta_{rel}/C = [\eta] + K_2 [\eta]^2 \cdot C \quad (2)$$

where,

η_r is the relative viscosity,

$[\eta] = \lim_{C \rightarrow 0} (\eta_{sp}/C)$,

K_1 is Huggin's constant and K_2 is Kraemer's constant.

Thermal studies

Non-isothermal thermogravimetric analysis of newly prepared terpolymer has been carried out on Perkin Elmer Pyris 1, DTA-7 thermogravimetric analyzer at heating rate of 10 $^{\circ}\text{C}$ per minute in air atmosphere in the temperature range 50-600 $^{\circ}\text{C}$ at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Anand, Gujarat. The thermogram is recorded for sample. With the help of thermogravimetric data, the thermal activation energies (E_a) and order of reaction (n) calculated. Also, other thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (z) are determined and reported in the Table 7.

Theoretical considerations

Thermogram expresses the dependence of change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters. Kinetics parameters have been determined using Sharp-Wentworth [23] and Freeman-Carroll [24] techniques as follows:

Sharp-Wentworth technique:

$$\log \frac{dc/dt}{1-c} = \log \left(\frac{A}{\beta} \right) - \frac{E_a}{2.303R} \cdot \frac{1}{T} \quad (3)$$

Where,

dc/dt = Rate of change of fraction of weight with change in temperature;
 β is linear heating rate, dT/dt ;
 c is the fraction of polymer decomposed at time t .

Thus, a linear plot of $\log \frac{dc/dt}{1-c}$ versus $\frac{1}{T}$ is obtained whose slope gives the value of E_a and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order is correct.

Freeman-Carroll technique:

$$\frac{\Delta \log(dw/dt)}{\Delta \log Wr} = \left(-\frac{E_a}{2.303 R} \right) \cdot \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log Wr} + n \quad (4)$$

Where,

dw/dt = Rate of change of weight with time.
 $Wr = Wc - W$; Wc = Weight loss at the completion of reaction;
 W = Total weight loss upto time.
 E_a = Energy of activation;
 n = Order of reaction.

The $\Delta \log(dw/dt)$ and $\Delta \log Wr$ values are taken at regular intervals of $1/T$. In this case $\frac{\Delta \log(dw/dt)}{\Delta \log Wr}$ vs $\frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log Wr}$ gives a straight line. The slope and intercept are equal to $-(E_a/R)$ and n respectively.

RESULTS AND DISCUSSION

The percentage of C, H, N and S content during elemental analysis are shown in Table 2 used to assign empirical formula and empirical weight for 2-ATPBDAF terpolymer. Composition of terpolymer was assigned on the basis of elemental analysis and was found to be in good agreement with that of calculated values.

The results of conductometric titration method in nonaqueous medium have been presented in Table 3 and shown in figure 2. From the plot, the first and last break was noted. The average degree of polymerization (\overline{Dp}) and hence the number average molecular mass (\overline{Mn}) of terpolymer has been determined using the above formula [25].

Viscosity measurements were carried out using Ubbelohde viscometer. According to the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 , respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give $[\eta]$ value in both plots. The calculated values of the constants K_1 and K_2 in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably. It was observed that terpolymer having higher (\overline{Mn}) shows higher value of $[\eta]$ [26]. Viscometric data are tabulated in Table 3 and shown in figure 3.

UV-Visible spectra

The UV-Visible spectrum of 2-ATPBDAF terpolymer is represented in Figure 4 and recorded in pure dimethylsulphoxide in the wavelength region 200-800 nm. The spectra displayed two characteristic broad bands at wavelengths 300 and 285 nm respectively. The more intense band observed at 285 nm may be accounted for $\pi \rightarrow \pi^*$, allowed transition of phenyl ring which is due to substitution of auxochromic -SH and -NH₂ groups on chromophore (phenyl ring). While the later and less intense band may be due to $n \rightarrow \pi^*$ electronic transition indicates the presence of auxochromic -SH and -NH₂ groups [27].

The appearance of former and more intense bands can be accounted for $\pi \rightarrow \pi^*$ transition, the auxochromic substituents (-SH and -NH₂ groups) which shows the interaction with n electron of the benzene ring. This interaction stabilizes n^* state and thus lowers the energy as a result bathochromic shift is caused. The presence of aromatic thiol and amino groups (auxochromes) are responsible for hyperehromic shift in

λ_{max} and losses the fine structure of band. As -SH and -NH₂ groups are electron releasing groups and, increases both the wavelength and the intensity of secondary absorption band.

FT-IR spectra

IR-spectrum of terpolymer has been presented in Figure 5 and desired values with their assignments are reported in Table 4. Broad and medium band which appeared at 3434 cm⁻¹ may be assigned due to >NH stretching vibration of secondary amine [28]. Aromatic C-H group represent weak band for stretching vibration at 3057 cm⁻¹. Weak band appeared at 2555 cm⁻¹ may be attributed due to Ar-SH (aromatic thiol) group. The presence of >NH bending of secondary amine may be ascribed as sharp band at 1676 cm⁻¹. A medium band appeared at 1487 cm⁻¹ may be attributed to >C=C< stretching in substituted aromatic ring. Medium band at 1342 cm⁻¹ is due to C-N stretching of aromatic amine (Ar-NH₂). The presence of methylene bridge (-CH₂-) in the polymeric chain can be accounted by the presence of medium and weak bands at 1445 cm⁻¹, 1291 cm⁻¹ and 731 cm⁻¹ for bending, wagging and rocking vibrations respectively. The presence of tetrasubstitution of aromatic ring is recognized from the medium and weak band appearing at 1059 and 837 cm⁻¹ respectively.

¹H- NMR spectra

¹H-NMR spectrum of the terpolymer has been shown in Figure 6 and described in the Table 5 which was scanned by using the solvent DMSO-d₆. Sharp singlet observed at δ 8.1 ppm is due to meta proton of aromatic ring [29]. Sharp singlet peak observed at δ 7.2 ppm is due to proton of Ar-SH group of thiophenol. Sharp singlet peak appeared at δ 7 ppm may be assigned due to presence of proton of -CH₂-NH-CH₂- linkage of -NH- bridge. Medium singlet peak appeared at δ 6.65 ppm for Ar-NH₂ group (Aromatic amine). Methylenic protons of -NH-CH₂-CH₂- moiety may be recognized as triplet signal appearing at δ 4.2 ppm. A singlet observed at δ 2.6 ppm may be recognized for methylene proton of Ar-CH₂-NH- moiety. Methylene proton of -CH₂-CH₂-CH₂- linkage appeared as quintet at δ 1.5 ppm.

Thermogravimetric analysis

Thermogram of terpolymer has displayed three stages of decomposition with loss of one water molecule in the first step. Observed weight loss of 6.81 % when temperature was raised to 110 °C, which is corresponding to entrapped moisture and correlated with theoretical value 7.05 %. The second step of decomposition starts from temperature 110 to 270 °C which represents the degradation of one -SH and one -NH₂ groups attached to the benzene ring corresponds to weight loss 26.02 % found against 26.27 % calculated theoretically. At last benzene ring with two methylenic groups degrade nearly in the temperature range 270 to 580 °C corresponding to 66.07 % weight loss against calculated 66.27 % with remaining behind moiety. The synthesized terpolymer was half decomposed at 310 °C temperature.

A plot of percentage weight loss vs temperature is shown in Figure 7 for a representative 2-ATPBDAF terpolymer. From the TG curve, results of thermogravimetric analysis are reported in Table 6. This kinetic analysis should be a starting point to obtain the useful information on the behavior of samples. The results obtained from different kinetic models demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data and level of degradation [30]. Thermal analysis of 2-ATPBDAF terpolymer has been carried out and representative graphs for Freeman-Carroll (Figures 8 and 9) and Sharp-Wentworth (Figure 10) methods have been plotted.

The kinetic parameters computed by the above mentioned kinetic equations and thermodynamic parameters calculated on the basis of thermal activation energy calculated by Freeman-Carroll method are shown in Table 7 using the following equations.

Entropy change

$$\text{Intercept} = \frac{\log_7(kR)}{h\phi E} + \frac{\Delta S}{2.303R} \quad (5)$$

where, K = 1.3806 x 10⁻¹⁶ erg./deg./mol.
 R = 1.987 cal./deg./mol.
 h = 6.62 x 10⁻²⁷ erg. sec.

- ϕ = 0.166
- ΔS = Entropy change
- E = Activation energy from graph.

Free energy change

$$\Delta F = \Delta H - T \cdot \Delta S \tag{6}$$

- where, ΔH = Enthalpy Change = Activation Energy
- T = Temperature (K)
- ΔS = Entropy change from (i) used.

Frequency factor

$$B_{2/3} = \frac{\log z E_a}{\phi R} \tag{7}$$

$$B_{2/3} = \log 3 + \log(1 - 3\sqrt{1 - \alpha}) - \log P(x) \tag{8}$$

- where, z = frequency factor
- B = calculated from equation (3.29)
- α = degree of transformation [$\alpha = w/Wc$]
- w = wt. loss at time 't'
- Wc = max.loss in wt. on the TG curve
- $\log P(x)$ = calculated from Doyle's table corresponding to activation energy.

Apparent entropy change

$$S^* = 2.303 \log \frac{Zh}{kT^*} \tag{9}$$

- where, z = from relation (7)
- T^* = temperature at which half of the compound is decomposed from its total loss.

From the above discussion, it is therefore concluded that for each technique, the values of kinetic parameters depend on calculation technique used. Total calculations obtained from different kinetic models demonstrated that the numerical value of kinetic parameters depends on the mathematical model used to analyze the experimental data and level of degradation.

However, in Freeman-Carroll and Sharp-Wentworth methods, some abnormal points were ignored to get a clear picture of most of the points so quite good straight line plots are obtained using two methods. From abnormally low values of frequency factor, it may be concluded that decomposition reaction of 2-ATPBDAF terpolymer can be classed as a "slow" reaction and no other possible reason can be given [31-33].

Sharp-Wentworth method is applied to calculate the activation energy which is found to be in well agreement with Freeman-Carroll method and similarity of values indicates a common reaction mode [34, 35]. Fairly similar results in the kinetic parameters i.e. E_a , n and z are obtained by Sharp-Wentworth and Freeman-Carroll methods. The higher thermal stability of terpolymer, may be due to the stronger intermolecular hydrogen bonding present in the polymer structure because of water of crystallization which would be more difficult to break and more resistant to higher temperature [36]. It is difficult to draw any unique conclusion from the magnitude of thermal activation energy as decomposition mechanism is expected to be complicated. This is expected as the decomposition of terpolymer is not obeying first order kinetics perfectly [37, 38] and these observations are in harmony with the findings of Coat and Redfern [39, 40] Jacobs and Tompkin [41] and other earlier researchers [42, 43].

Table 1: Synthetic details of 2-ATPBDAF terpolymer

Terpolymers	Reactants			Molar ratios	Catalyst 2M HCl (ml)	Reflux Temp. °C	Yield (%)	Time (hr)
	Aminothiophenol (2-ATP) (mol)	Butanediamine (BDA) (mol)	Formaldehyde (F) (mol)					
2-ATPBDAF	0.1	0.1	0.2	1:1:2	200	150	80.99	6

Table 2: Elemental analysis data of 2-ATPBDAF terpolymer

Terpolymers	C (%)		H (%)		N (%)		S (%)		Empirical formula of the repeating unit	Empirical formula weight
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.		
2-ATPBDAF	60.41	60.76	7.88	8.02	17.51	17.72	13.08	13.50	C ₁₂ H ₁₉ N ₃ S ₁	237

Table 3: Molecular weight determination and viscometric data of 2-ATPBDAF terpolymer

Terpolymer	Empirical formula of repeat unit	Empirical Weight of repeat unit	Average degree of polymerization (\overline{DP})	Average molecular weight (\overline{Mn})	Intrinsic viscosity $[\eta]$ dl g ⁻¹	Huggin's Constant (K ₁)	Kraemer's Constant (K ₂)	K ₁ +K ₂
2-ATPBDAF	C ₁₂ H ₁₉ N ₃ S ₁	237	16.5	3910.5	0.72	0.294	0.275	0.569

Table 4: IR spectral data of 2-ATPBDAF terpolymer

Observed Wavenumber (cm ⁻¹)	Assignment
3434 b, m	>NH stretching (Sec. amine)
3057 w	C-H stretching (aromatic)
2555 w	Ar-SH (Aromatic thiol)
1676 sh	>NH bending (Sec. amine)
1487 m	>C=C stretch in aromatics
1342 m	C-N stretch in aliphatic amine
1059 m } 837 w }	Tetrasubstituted benzene ring
1445 m } 1291 w } 731 w }	Methylene bridge (-CH ₂) modes Bending Wagging Rocking

b: broad; st: strong; m: medium; sh: sharp; w: weak.

Table 5: ¹H-NMR spectral data of 2-ATPBDAF terpolymer in DMSO-d₆

Chemical shift (δ) ppm of terpolymer	Nature of proton assigned
8.1 s	Meta proton of Ar-H
7.2 s	Proton of Ar-SH (thiophenol)
7 s	Amino proton of -CH ₂ -NH-CH ₂ - linkage (NH bridge)
6.65 s	Proton of Ar-NH ₂ (aromatic amine)
4.2 t	Methylene proton of -NH-CH ₂ -CH ₂ - linkage
2.6 s	Methylene proton of Ar-CH ₂ -NH- linkage
1.5 q	Methylene proton of -CH ₂ -CH ₂ -CH ₂ -linkage

Table 6: Thermal degradation behavior of 2-ATPBDAF terpolymer

Terpolymer	Temp. Range (°C)	Stages of decomposition	Species Degraded	Wt. Loss (%)	
				Expt.	Calc.
2- ATPBDAF	50-110	First	Loss of one H ₂ O molecule	6.81	7.05
	110-270	Second	Loss of one -SH and one -NH ₂ groups	26.02	26.27
	270-580	Third	Loss of phenyl ring with two (-CH ₂) groups	66.07	66.27

Table 7: Result of thermogravimetric analysis of 2-ATPBDAF terpolymer

Terpolymer	Half decomposition temp. T* (°C)	Activation Energy (KJ/mol)		Entropy Change ΔS (J)	Free energy change ΔF (KJ)	Frequency factor z (sec ⁻¹)	Apparent entropy Change S* (J)	Order of reaction n
		F-C	S-W					
2-ATPBDAF	310	12.994	12.132	-8.051	15.489	282.95	-24.04	1.05

FC= Freeman-Carroll; SW= Sharp-Wentworth

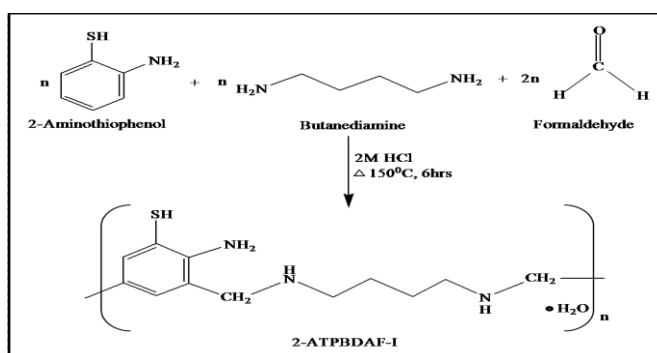
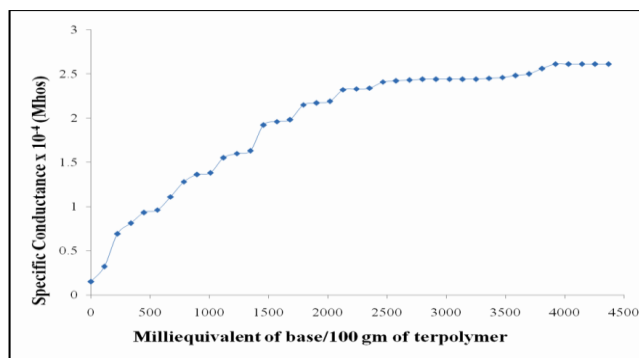
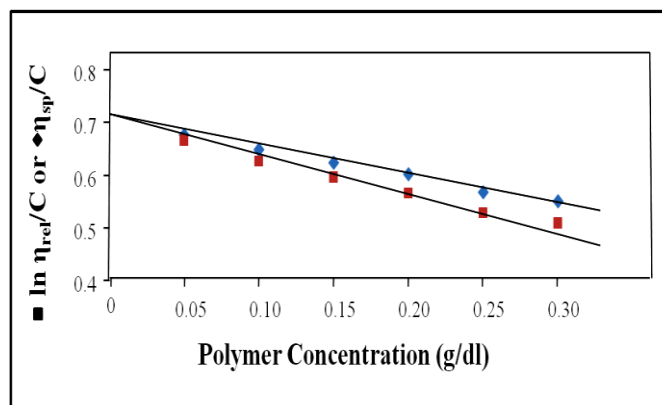

Figure 1: Proposed reaction for 2-ATPBDAF terpolymer

Figure 2: Conductometric titration curve of 2-ATPBDAF terpolymer


Figure 3: Viscometric plot of 2-ATPBDAF terpolymer

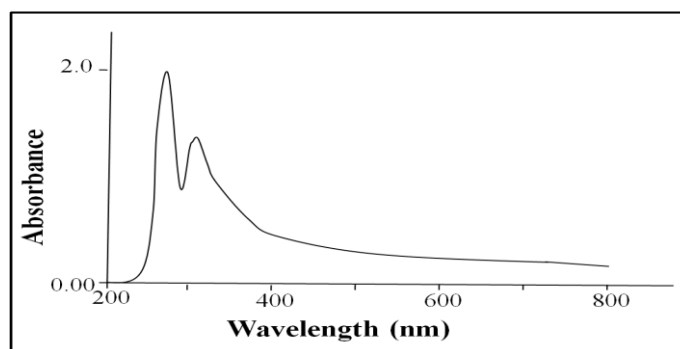


Figure 4: UV-Visible spectrum of 2-ATPBDAF terpolymer

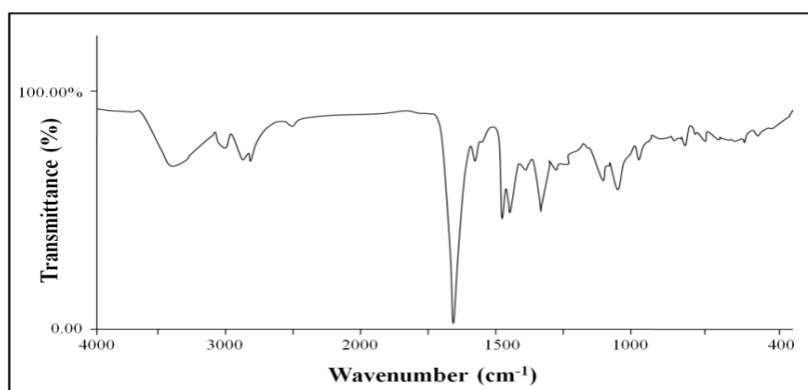


Figure 5: FT-IR spectrum of 2-ATPBDAF terpolymer

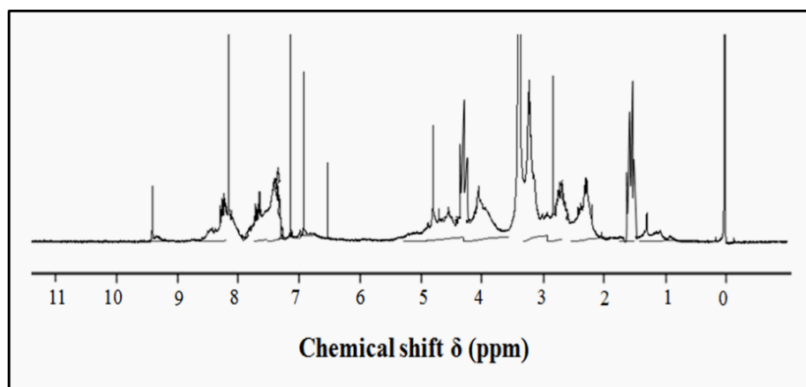


Figure 6: ¹H-NMR spectrum of 2-ATPBDAF terpolymer

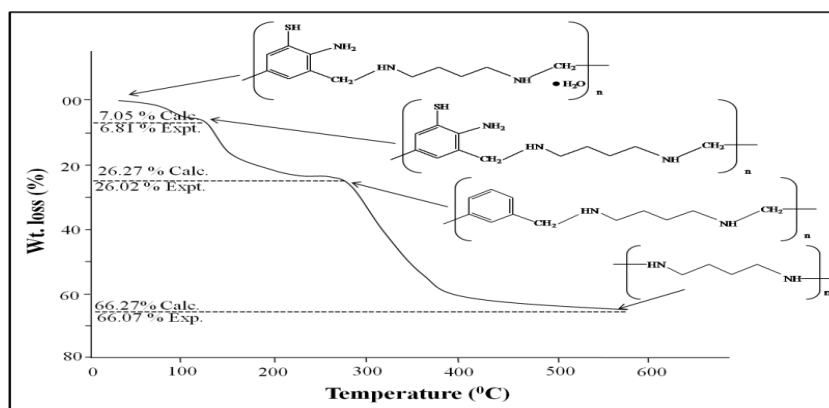


Figure 7: TGA curve of 2-ATPBDAF terpolymer

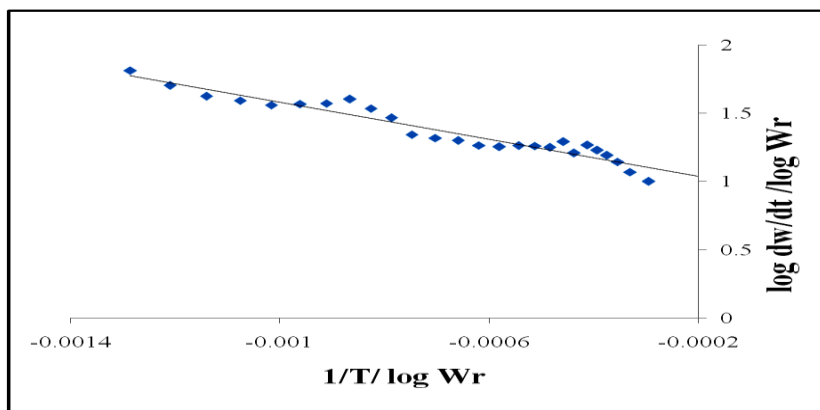


Figure 8: Thermal activation energy plot by Freeman-Carroll method of 2-ATPBDAF terpolymer

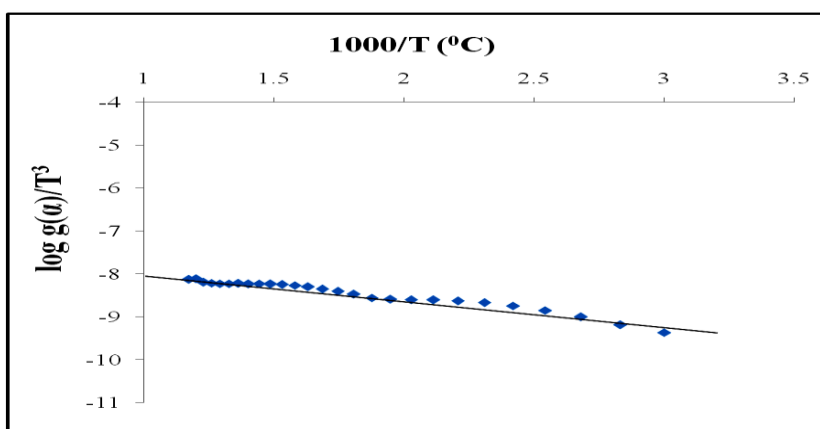


Figure 9: Freeman-Carroll plot of 2-ATPBDAF terpolymer

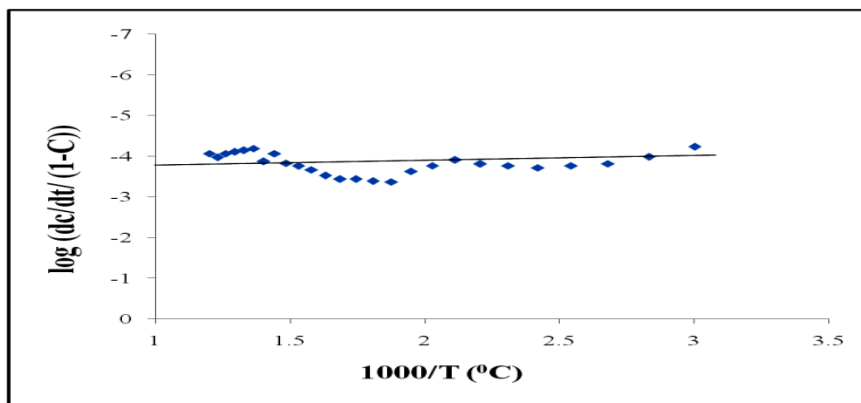


Figure 10: Sharp-Wentworth plot of 2-ATPBDAF terpolymer

CONCLUSIONS

- From the elemental analysis, UV-Visible, FT-IR and ¹H-NMR spectral studies the proposed structure of targeted terpolymer 2-ATPBDAF has been confirmed.
- The presence of -CH₂- bridge in the FT-IR spectra shows the formation of terpolymer.
- Sharp-Wentworth method is applied to calculate the activation energy which is found to be in well agreement with Freeman-Carroll method and similarity of values indicates a common reaction mode.
- Thermally stable terpolymer prepared which is resistant to higher temperature

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REFERENCES

- [1] Tarase MV, Zade AB, Gurnule WB. *J Ultra Sci* 2007; 3(1): 41.
- [2] Tarase MV, Zade AB, Gurnule WB. *J Appl Polym Sci* 2008; 108(2): 738-746.
- [3] Belsare PU, Zade AB. *Der Pharma Chemica* 2013; 5(4): 325-334.
- [4] Zeman S, Tokarova LA. *Thermochemica Acta* 1992; 197: 181-189.
- [5] Shah AV, Desai PR, Patel NB. *Iran Polym J* 2007; 16(10): 699.
- [6] Gupta AN, Hiwase VV, Kalambe AB. *Der Pharmacia Lettre* 2013; 5(2): 105-112.
- [7] Kapse SK, Hiwase VV, Kalambe AB, Kene JD. *Res J Chem Sci* 2014; 4(2): 81-86.
- [8] Singh Chauhan NP. *J Therm Anal Calor* 2012; 110(3): 1377-1388.
- [9] Ingle SS, Hiwase VV, Kalambe AB. *Arch App Sci Res* 2012; 4(5): 1932-1937.
- [10] Dharkar KP, Khamborkar AK, Kalambe AB. *Res J Chem Sci* 2012; 2(12): 11-16.
- [11] Dhore MS, Zade AB. *J Eng Technol* 2013; 2(4): 33-41.
- [12] Dhore MS, Butoliya SS, Zade AB. *Int Chem Sci Res J, ChemXpress* 2014; 3(2): 61-73.
- [13] Kalbende PP, Tarase MV, Zade AB. *Res J Pharm Biol Chem Sci* 2012; 3(4): 1276.
- [14] Masram DT. *E-J Chem* 2009; 6(3): 830-834.
- [15] Ameta R, Patel V, Joshi J. *Iran Polym J* 2007; 16(9): 615-625.
- [16] Lingala PS, Paliwal LJ, Juneja HD. *Proc Nat Acad Sci* 2001; 71: 205.
- [17] Patel SA, Shah SS, Patel RM, Patel PM. *Iran Polym J* 2004; 13(6): 445-453.
- [18] Young RJ, Lovell PA. *Introduction to Polymers*, Second edition, Nelson Thornes, 1991.
- [19] Chauhan NPS. *J Therm Anal Calor* 2012; 110(3): 1377-1388.
- [20] Chauhan NPS. *Designed Monom Poly* 2013; 16(6): 543-555.
- [21] Huggin ML. *J Am Chem Soc* 1942; 64: 2716.
- [22] Kraemer EO. *Industr Eng Chem Res* 1938; 30(10): 1200-1203.
- [23] Sharp JB, Wentworth SA. *Anal Chem* 1969; 41: 2060.
- [24] Freeman ES, Carroll BJ. *Phys Chem* 1958; 62: 394.
- [25] Rahangdale PK, Gurnule WB, Paliwal LJ, Kharat RB. In, *Proceeding of national conference on recent trends in nanoscience*; 2006; 222.
- [26] Gurnule WB, Juneja HD, Paliwal LJ. *J Indian Chem Sci* 1999; 16: 6-8.
- [27] Patle DB. Ph.D. Thesis, R.T.M. Nagpur University, Nagpur, 2012.
- [28] Kalbende PP. Ph.D. Thesis R.T.M. Nagpur University, Nagpur, 2013.
- [29] William H. Fleming Ian. *Spectroscopic Methods in Organic Chemistry*, UK, McGraw Hill Book Co, 1975.
- [30] Paik P, Kar KK. *Polymer Degradation and Stability* 2008; 93: 24.
- [31] Jadhao MM, Paliwal LJ, Bhave NS. *Ind J Chem* 2005; 44-A: 1110.
- [32] Kalbende PP, Zade AB, Tarase MV. *J Indian Chem Soc* 2013; 90: 1-10.
- [33] Butoliya SS, Zade AB, Gurnule WB. *E-J Chem* 2010; 7(4): 0000.
- [34] Aswar AS, Mahale RG, Kakde PR, Bhadange SG. *J Indian Chem Soc* 1998; 75: 395.
- [35] Leipoldt JG, Meyer H. *Polyhedron* 1987; 6: 1361.
- [36] Donia AM, El-Boraey HA. *J Anal Appl Pyrol* 2002; 63: 69.
- [37] Christensen PE. *J Food Sci* 2006; 19(1): 163-172.
- [38] Rahangdale PK, Gurnule WB, Paliwal LJ, Kharat RB. *Progress in crystal growth and character of matter* 2002; 45: 155-160.
- [39] Coats AW, Redfern JP. *Nature* 1964; 201(4914): 68-69.
- [40] Coats AW, Redfern JP. *J Polym Sci Part B* 1965; 3: 917.
- [41] Jacobs PWM, Tompkins FC. *"Chemistry of Solid States"*. WI Garner Pub. London, 1955, pp. 188.
- [42] Zsago JJ. *Phys Chem* 1968; 72: 2406.
- [43] Singru RN, Zade AB, Gurnule WB. *J Appl Polym Sci* 2008; 109: 859.