

# Studies on Thermal and Photoisomerization Properties of Polyesters Possessing Azomethine Moieties in the Back Bone

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**Abstract.** Various aliphatic and aromatic diacid chlorides were solution polycondensed with azomethine diol, [(4-(4-hydroxy-3-ethoxy phenyl) iminomethyl)] phenol (HEPIMP), in the presence of triethylamine catalyst at room temperature to produce a series of aliphatic and aromatic azomethine polyesters. Fourier Transform IR and NMR spectroscopy techniques were utilised to analyse the diol monomer HEPIMP. UV-Visible spectroscopy was used to investigate their photoisomerization behaviour in solution. The structure and thermal behaviour of prepared aliphatic and aromatic azomethine polyesters were studied. Limiting oxygen index values were calculated from the Van Krevelen equation to investigate the self-extinguishing character of the synthesised azomethine polyesters, and it was noticed that aromatic polyesters have greater Limiting Oxygen Index value than aliphatic polyesters. The pre exponential factor (A) and activation energy (E<sub>a</sub>) were determined using the Arrhenius, Horowitz-Metzger and Broido models for studying decomposition kinetics.

**Keywords:** Aromatic polyesters, Azomethine bisphenols, thermal properties, photoisomerization.

## 1 Introduction

Polyesters are a special type of high-performance and engineering polymers [1] with a wide range of uses in daily life, including textiles, automobiles, pharmaceuticals, biomedical, coating industries, structural engineering, and electronics. Polyazomethines possess a strong heat resistance, semi-crystalline behaviour and high optical transmittance [2]. Due to their high T<sub>g</sub> and T<sub>m</sub>, as well as their poor solubility in common solvents, many aromatic polymers are hard to process [3]. These limitations frequently limit their use in a variety of applications. Along with its intriguing qualities including syn-anti isomerism [4], excellent heat stability [5], optical activity [6], liquid crystallinity [7], and dielectric properties [8] the existence of azomethine linkage in the polymer is of specific interest.

The preparation of cardo polyesters, azomethine polyesters, and their thermal degradation kinetics were previously reported [9,10]. The present study uses the solution polycondensation technique to synthesize polyesters by reacting HEPIMP with aliphatic and aromatic acid

chlorides, and then performing spectral and thermal characterizations on the synthesized polymers. To calculate the  $E_a$  (activation energy) and choose the suitable mechanism to explain the degradation pattern, a complete thermogravimetric analysis was performed utilising non-isothermal/dynamic techniques. The regression coefficient and  $E_a$  for the degradation of polyesters were determined from the Arrhenius, Horowitz- Metzger, and Broido approaches, and the findings were compared. Using a UV reactor and spectrophotometer, the photoisomerization property of the diol monomer HEPIMP was analyzed.

## 2. Experimental

### 2.1. Materials

S.D fine chemicals (Mumbai, India) provided adipic acid and terephthalic acid. Merck (Mumbai, India) provided p-amino phenol and THF(Tetrahydro furan) and Ranbaxy (New Delhi, India) provided the thionyl chloride . The process described in the literature [11] was utilised to purify all of the other solvents used in the analysis. Sigma Aldrich (Munich, Germany) provided 3-ethoxy-4-hydroxybenzaldehyde (EHB), triethylamine, and succinyl chloride, which were used without additional purification.

### 2.2. Characterization

Using 0.2-0.5mg of substances in 5ml of solvent, the solubility of diol monomer HEPIMP and polymers S3P1, S3P2, and S3P3 was examined. The Oswald viscometer was used to determine the inherent viscosity of a 0.4 g/dL polymer in DMSO solvent at 25<sup>o</sup>C. Utilising potassium bromide (KBr) pellets, the IR spectra were taken using a Shimadzu FTIR spectrophotometer. The Cary 60 Ultra Violet spectrophotometer (Agilent Technologies, Germany) was used to record UV spectra in DMSO polymer solution. Deuterated DMSO was used to record <sup>1</sup>H & <sup>13</sup>C NMR spectra on a NMR (400 MHz) spectrometer (Bruker, USA). An internal standard of tetra methyl silane (TMS) was used to measure the chemical shifts. Vario EL III (Germany) C,H,N,S analyzer was used for the elemental analysis. The DSC study was performed on Perkin DSC with 10<sup>o</sup> C min<sup>-1</sup> rate of heating under a N<sub>2</sub> atmosphere. Under nitrogen atmosphere, thermo gravimetric analyser (Seiko Instruments, Japan) was used to perform a thermogravimetric analysis with 10<sup>o</sup> C min<sup>-1</sup> heating rate. UV spectrophotometer was utilized to study the photoisomerization of the produced monomer HEPIMP in solution. The DMSO solution of monomer taken in a quartz cuvette was exposed to a mercury lamp in a photoreactor and subsequently spectral analysis was performed on a Agilent UV spectrophotometer.

### 2.3. Investigation of thermal degradation

With a single heating rate measurement and no pre-assumptions, the Arrhenius, Horowitz-Metzger, and Broido methods were utilised to determine n- reaction order,  $E_a$ -activation energy, and A-frequency factor in this study. Using the Arrhenius relation [12], the activation energy and specific rates were obtained. Using the linear regression technique, the following kinetic equations were utilised to get the parameters of the thermogravimetric weight loss.

$$d\alpha'/dt = k_b (1-\alpha')^b \quad (1)$$

$$\ln (d\alpha'/dt) = \ln k_b + \ln (1-\alpha')^b \quad (2)$$

$$K_b = A \exp\left(\frac{-EA}{RT}\right) \quad (3)$$

$$\ln K_b = \ln A - \frac{EA}{RT} \quad (4)$$

T represents the absolute temperature, and R represents the gas constant. Combination of these equations gives:

$$\ln\left[\frac{d\alpha'/dt}{(1-\alpha')^b}\right] = \ln A - \frac{EA}{RT} \quad (5)$$

A straight line was obtained when  $\ln\left[\frac{d\alpha'/dt}{(1-\alpha')^b}\right]$  is plotted against  $1/T$ . The activation energy is estimated based on the slope, while the intercept 'A' is determined based on the intercept.

### 2.3.1. Broido Model

The well-known Broido method [13] was used to calculate the  $E_A$  associated with every stage of decomposition.  $E_A$  is determined using the following equation.

$$\ln [-\ln(1-\alpha')] = \frac{-EA}{RT} + K \quad (6)$$

The plot of  $\ln [-\ln(1-\alpha')]$  against  $1/T$  was used to calculate  $E_A$ .

### 2.3.2. Horowitz - Metzger approach

Horowitz & Metzger [14] developed a method to determine activation energy ( $E_A$ ) of polymer degradation. The following is the equation that was used to calculate  $E_A$ .

$$\ln [\ln (W_0/W_t)] = E_A \theta / RT_s^2 \quad (7)$$

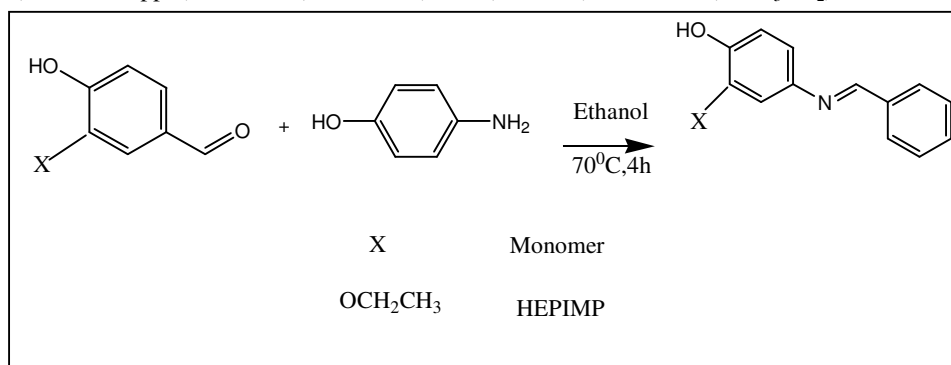
( $W_0$  - starting sample weight,  $W_t$  - sample weight at time 't',  $\theta = T - T_s$ ,  $T_s$  - peak maximum temperature, T - temperature at a specific weight loss)

The slope of a graph of  $\ln [\ln (W_0/W_t)]$  against  $\theta$  produces a straight line from which  $E_A$  can be calculated.

## 2.4. Synthesis

### 2.4.1. Preparation of HEPIMP

Ethanol solution of EHB (0.1 mol) was mixed with p-aminophenol (0.1 mol) and heated at 70°C for 4 hours and then cooled. The precipitated solid was filtered, washed using ethanol, and dried in vacuum [10,15,16]. Melting point: 181°C, Yield: 81%, Fig 1 depicts the preparation scheme. Calculated elemental analysis for  $C_{15}H_{15}O_3N$ : C, 70.03; H, 5.83; N, 5.44 %. Discovered: C, 67.56; H, 5.53; N, 6.05 %. FTIR ( $cm^{-1}$ ): 3313 ( $\gamma_{O-H}$ ), 1510 ( $\gamma_{C=C,Ar}$ ), 3083 ( $\gamma_{C-H}$ ), 1221 ( $\gamma_{C-O}$ , phenol), 1602 ( $\gamma_{CH=N}$ ).  $^1H$ -NMR (ppm, standard-TMS): 6.76-7.47 (m, Aromatic Protons), 4.05- 4.10 (q), 1.34- 1.38 (t) ( $-OCH_2CH_3$ ), 8.41 (s,  $CH=N$ ).  $^{13}C$  -NMR (DMSO- $d_6$ , ppm): 111-155 (Ar Carbons), 159 ( $-CH=N-$ ), 14.7, 63.8 ( $-OCH_2CH_3$ ).



**Fig 1.** Synthesis of HEPIMP

#### 2.4.2. Preparation of aliphatic and aromatic acid chlorides

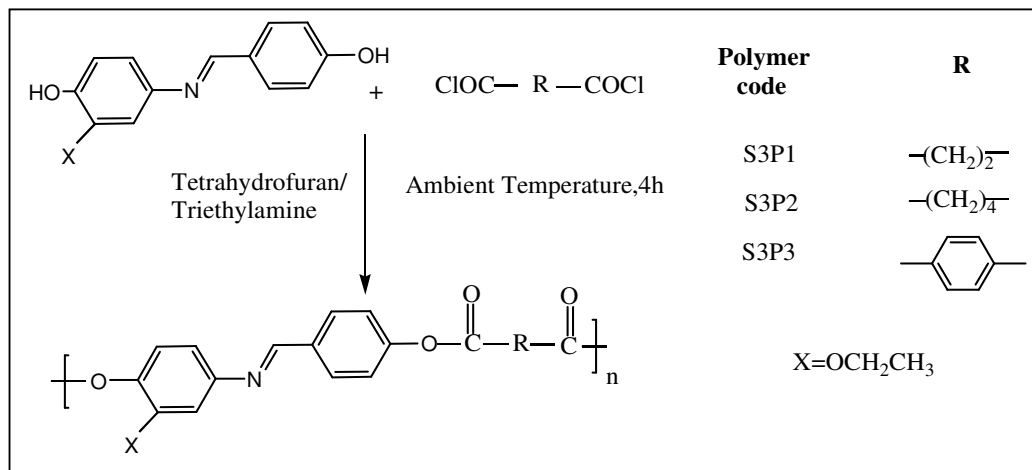
Adipic acid (0.1 mol) and thionylchloride (0.24 mol) were refluxed in a round bottomed reaction flask using an oil bath for 4 hours and unreacted thionyl chloride was removed at lower pressure after refluxing. Refluxing terephthalic acid and thionylchloride for 12 hours with two drops of pyridine catalyst yielded terephthaloyl chloride. Using n-hexane, the solid product was recrystallized [17].

#### 2.4.3. Synthesis of poly [4-[(4-hydroxy -3-ethoxyphenyl) iminomethyl] adipate (S3P2).

HEPIMP (0.005 mole) was dissolved in THF (20 ml) with 0.010 mole triethylamine and 10 minutes of agitation. Adipoyl chloride (0.005 mol) dissolved in 20 mL THF was added to this mixture and rapidly agitated for about 4.5 hours at room temperature. The solution viscosity gradually increased over this time and the product started to precipitate. The yellowish polymer that formed was separated and dried after washing with dimethyl ketone. The polyester was produced with a 79% yield [10]. Fig 2 depicts the preparation scheme. FTIR ( $\text{cm}^{-1}$ ): 1507 ( $\gamma_{\text{C}=\text{C}(\text{Ar})}$ ), 1624( $\gamma_{\text{CH}=\text{N}}$ ), 1744 ( $\gamma_{>\text{C}=\text{O}}$  of ester), 1168–1030 ( $\gamma_{\text{C}-\text{O}(\text{Ar})}$ ).  $^1\text{H-NMR}$  (ppm): 6.67 – 7.41 (m, Ar), 8.51 (s,  $-\text{CH}=\text{N}-$ ), 1.18 – 2.29 (m,  $-\text{CH}_2-$ ), 4.07- 4.20 (q,  $-\text{OCH}_2\text{CH}_2$ ).  $^{13}\text{C-NMR}$  (DMSO- $d_6$ , ppm): 170.6 ( $-\text{COO}-$  carbon), 166.9 (azomethine carbon), 112 -156.9 (Ar carbons), 14.5, 64.7 ( $-\text{OCH}_2\text{CH}_2$ ), 23.9–36.2( $-\text{CH}_2-$  of acid spacer carbons). All the other polyesters S3P1 and S3P3 were synthesized by the analogous procedure. Name of the other synthesized polymers are given below:

poly [4-[(4-hydroxy -3-ethoxy phenyl) iminomethyl] succinate (S3P1)

poly [4-[(4-hydroxy -3-ethoxy phenyl) iminomethyl] terphthalate (S3P3)



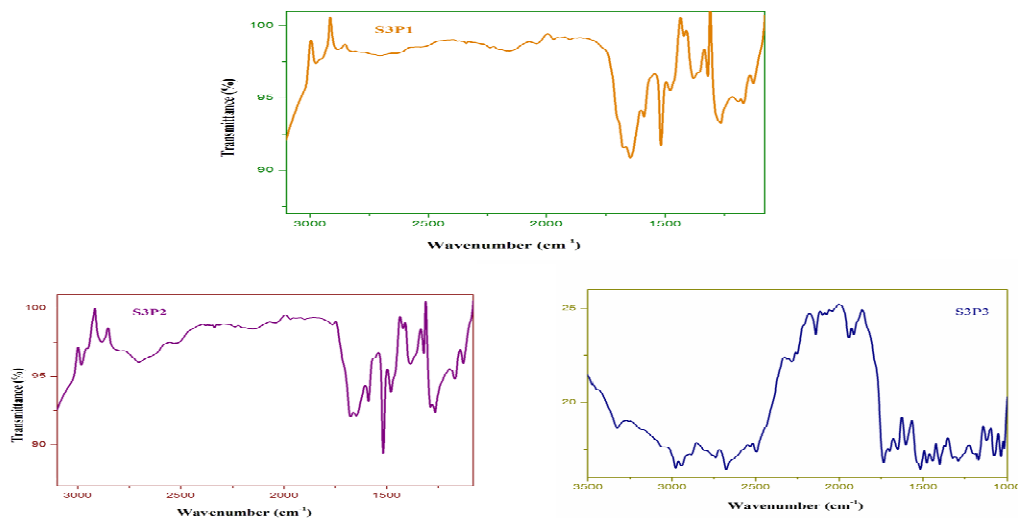
produced in good yield (77-80 %). One of the most significant prerequisites for the application of polymers is their solubility. As a result, the synthetic polyesters' solubility in various organic solvents was examined. Table 1 shows the solubility, yield percentage, and

solution viscosity of the polyesters. All aliphatic polymers were soluble in DMSO, whereas polyesters derived from aromatic acid chlorides were insoluble in all the solvents tested. The viscosity of synthesized polymers in DMSO was 0.36 to 0.47 dL/g. FTIR, UV, and NMR spectroscopy methods confirmed the structure of the produced polymers. The presence of ester links was confirmed by the elimination of the diol monomer's  $\text{-OH}$  stretching frequency at  $3313\text{ cm}^{-1}$  and the formation of the typical carbonyl peak at around  $1746\text{ cm}^{-1}$  in all polymers (Fig 3). The  $\text{-CH=N-}$  and  $\text{-CH-}$  stretching frequencies were appeared around  $1624$  and  $2933\text{ cm}^{-1}$  respectively. Fig 4 shows the  $^1\text{H NMR}$  spectrum of polymer S3P2. In the range of 6.67-7.41 ppm, the protons of aromatic groups emerged as a broad multiplet. At 8.51 ppm, the imine  $\text{-CH=N-}$  protons resonated. The ethoxy protons resonated at 4.07–4.20 ppm, while the  $\text{-CH}_2\text{-}$  protons of acid moiety appeared at 1.18–2.29 ppm [18].

**Table 1.** Solubility, Yield and Viscosity of Polymers

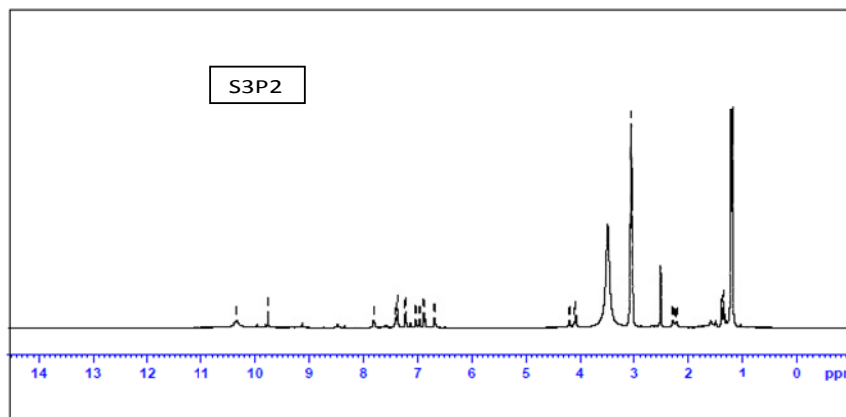
Polymer code	Yield %	Solubility								Inherent viscosity dL/g
		$\text{CH}_2\text{Cl}_2$	THF	$\text{CHCl}_3$	1,4 dioxane	Acetone	DMF	DMSO	MeOH	
S3P1	77	--	--	--	--	--	++	++	--	0.36
S3P2	79	--	--	--	--	--	++	++	--	0.47
S3P3	80	--	--	--	--	--	--	--	--	--

++: Soluble --: Insoluble



**Fig 3.** FTIR spectra of polyesters ( S3P1, S3P2 & S3P3)

Fig 4.  $^1\text{H}$  NMR spectrum of polyester S3P2



3.2  
Photoisomerization studies

UV spectroscopy was used to analyse photoisomerization in the presence of UV light (365nm) illumination at various time intervals. After UV irradiation, the absorption spectra were recorded immediately. The significant absorption at approximately 312-348 nm in the UV spectrum corresponds to the E isomer's  $\pi-\pi^*$  transition (trans isomer). At the time of UV irradiation, the absorbance at 312-348 nm reduced and a moderate increase in absorbance at around 359 - 399 nm was noticed, which corresponds to the Z isomer's  $n-\pi^*$  transition (cis isomer). It's important to note that the intensity of the majority of the polymers has increased. Disorganization generated by randomly oriented azomethine chromophores has been attributed to this phenomenon. Because of the non-linear shape of the cis-isomer, this type of isomerization has been widely observed in compounds having low molecular weight. The concentration of E-isomer reduced as irradiation time increased, but the amount of Z-isomer increased [19]. The E - Z absorbance of monomer HEPIMP as a function of time is shown in Fig 5.

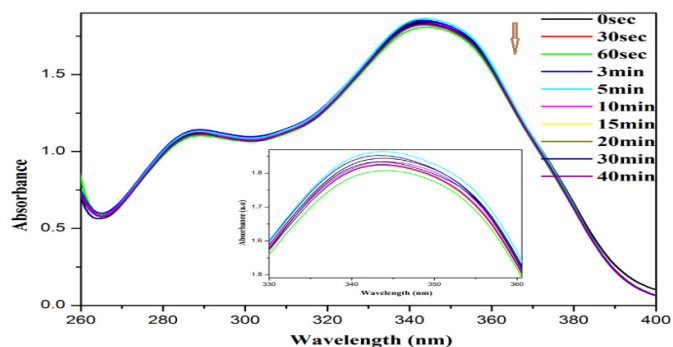
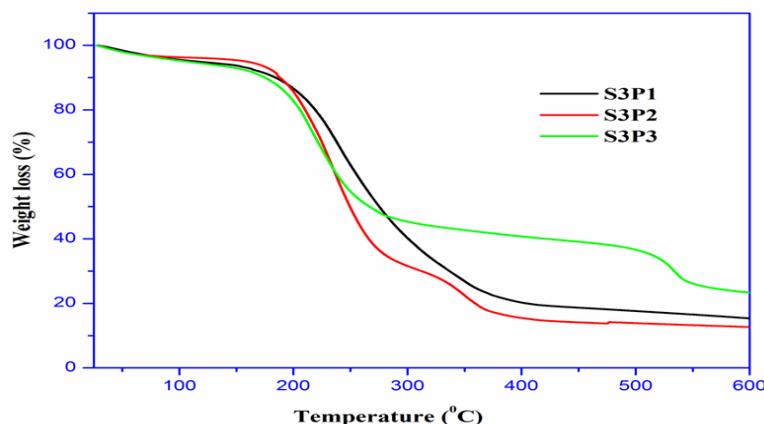


Fig 5. The absorption spectra of HEPIMP at various time intervals of irradiation

### 3.3. Thermal properties

Thermogravimetric method was used to analyze the thermal stability of synthesised polyesters (S3P1-S3P3). Fig 6 shows the TGA traces of these polymers. The temperature relevant to 10, 20, 30, 40, and 50% weight loss, as well as Tmax, were calculated from the thermogram and are summarised in Table 2. The 10 % weight loss for the polyesters S3P1, S3P2, and S3P3 occurred at around 184°C, 190°C, and 180°C [20]. At 600°C, the aromatic polyester S3P3 exceeded the aliphatic polyesters in terms of stability and char yield. This could be attributed to greater crystallinity in the polyester produced from terephthalic acid's hard domain [21].



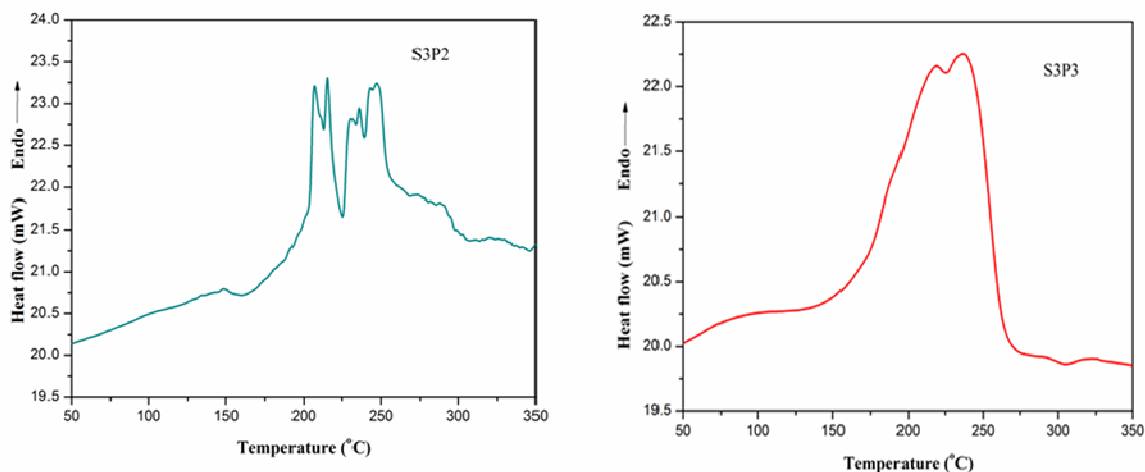
**Fig 6.** TGA thermogram of polyesters derived from HEPIMP

**Table 2.** TGA data of polyesters derived from HEPIMP

Polymer Code	Temperature (°C) corresponds to					Char Yield (%) at 600 °C	LOI
	10%Wt loss	20%Wt Loss	30%Wt loss	40%Wt Loss	50%Wt loss		
S3P1	184	219	238	256	276	15.3	23.7
S3P2	190	211	225	237	249	12.7	22.6
S3P3	180	206	221	258	266	23.4	26.9

The LOI value of polyesters (S3P1-S3P3) was shown to be between 23.7 and 26.9. According to the LOI data, polyesters S3P1 and S3P2 do not have self-extinguishing properties. The aromatic polyester S3P3 showed LOI value higher than 26 and indicated the self-extinguishing character. The occurrence of endothermic peak at approximately 226-267°C in the DSC trace (Fig 7) suggested the melting of microcrystalline regions [22]. The presence of an alkoxy group attracts an electron

from the following aromatic unit, forcing the chain to align in a linear fashion and



boosting the polymer chain's close packing, resulting in increased crystallinity.

**Fig 7.** DSC traces of polyesters (S3P2 & S3P3)

### 3.4. Kinetic parameters

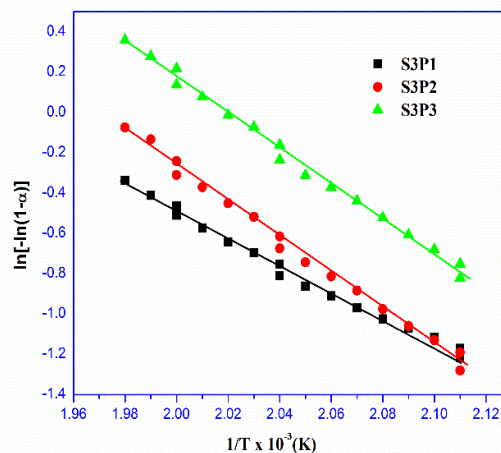
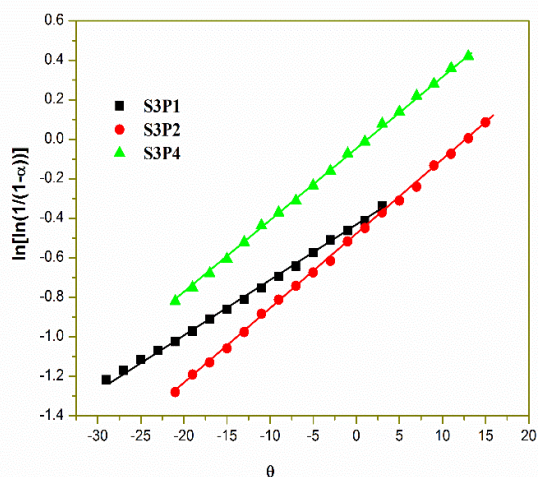
Kinetic factors can be used to predict degradation behaviour under various conditions by associating them with the polymeric material's thermal stability. In this study, the  $E_A$  of polyester thermal degradation was computed using the Arrhenius, Horowitz–Metzger, and Broido approaches. To get parameters such as frequency factor ( $A$ ),  $E_A$ , and reaction order ( $n$ ), the Arrhenius method was utilised. A graph of  $\ln\left[\frac{d\alpha/dt}{(1-\alpha)^b}\right]$  vs  $1/T$  in the Arrhenius method yielded a straight line.  $E_A$  was calculated from the slope, while  $A$  was determined from the intercept. The plot of  $\ln[-\ln(1-\alpha)']$  against  $1/T$ , in Broido's approach produced a straight line. In the Horowitz–Metzger approach, a plot of  $\ln[\ln(1/(1-\alpha)')] against  $\theta$  revealed an excellent approximation to a straight line. The slope of a straight line was used to calculate  $E_A$ . Fig (8) shows representative plots for Broido's and Horowitz–Metzger techniques. Table 3 summarises the  $R^2$  and calculated  $E_A$  values. It was suggested that a rise in  $E_A$  is typically accompanied by a rise in 'A.' All polyesters showed second-order breakdown kinetics [10,15]. This could be because the polyesters contain weak ester bonds, which breakdown selectively to create free radicals. In all three models, the  $E_A$  of aliphatic polyester is lower than that of aromatic polyester. According to the present study, aromatic polyesters are more stable than aliphatic polyesters.$

**Table** Error! No text of specified style in document.. Kinetic parameters of the thermal decomposition of polyesters.

Polymer	Arrhenius method	Broido method	Horowitz-Metzger
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code							method	
	$E_A$ (kJ/mol)	A (Sec <sup>-1</sup> )	N	R <sup>2</sup>	$E_a$ (kJ/mol)	R <sup>2</sup>	$E_a$ (kJ/mol)	R <sup>2</sup>
S3P1	12.47	2.68	2	0.990	12.98	0.996	12.45	0.998
S3P2	12.11	2.89	2	0.998	13.30	0.999	11.71	0.999
S3P3	28.27	3.94	2	0.991	29.46	0.999	27.67	0.999



**Fig 8.** Broido and Horowitz-Metzer models for degradation of polyesters (S3P1-S3P3)

#### 4. Conclusions

Polyesters with azomethine linkages were synthesized utilizing triethylamine as a catalyst in a solution polycondensation reaction of the diol monomer HEPIMP with different aliphatic and aromatic diacidchlorides. At ambient temperature, these polyesters were insoluble in aprotic solvents including CH<sub>2</sub>Cl<sub>2</sub>, THF, and CHCl<sub>3</sub>, but soluble in solvents like DMF and DMSO. FTIR and <sup>1</sup>H-NMR spectral techniques were used to determine the polymers structure and formation. The inherent viscosity of all synthesized polyesters that are soluble in DMSO was determined to be between 0.36 and 0.47 dL/g. Polyesters have been found to be thermodynamically stable up to 184°C. Increasing the spacer length initially boosted the

thermal stability of aliphatic polyesters, but it later decreased the thermal stability. Since the Limiting Oxygen Index of the polymer S3P3 is higher than 26, it is expected to exhibit self-extinguishing character. The  $-OCH_2CH_3$  substituent attached to the polymer chain's aromatic ring adds to the polyesters' lower heat stability. Various approaches were used to investigate the kinetics of degradation of the polyesters, and all the polyesters generated followed second order degradation kinetics. The  $E_a$  of aliphatic polyester is lower than that of aromatic polyester in all the three models used in the present study. Aromatic polyesters have a higher level of stability than aliphatic polyesters.

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