Synthesis, Photoisomerization properties and Thermal Degradation Kinetics of Polyesters Containing Azomethine moiety in the main chain

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ABSTRACT

A series of polyesters containing azomethine group in the main chain was synthesized by solution polycondensation of 4-[(4-hydroxy-3-methoxy phenyl)iminomethyl]phenol with various diacid chlorides. The synthesized polyesters were characterized systematically by Fourier transform infrared, UV and ^1H and ^{13}C NMR spectroscopy. UV analysis revealed that the synthesized polyesters have quite lower band gap than the corresponding monomer. The optical band gap values of monomer and polymer were found to be 2.80 and 2.64 respectively. Thermal properties were studied using thermo gravimetric analysis and differential scanning calorimetry. Thermogravimetric analysis indicated that the aromatic polymers had higher char yield. The self extinguishing property of the synthesized polymers was studied by the limiting oxygen index values. The aromatic polyesters had higher LOI than aliphatic polyesters. Thermal degradation kinetics have been studied using Arrhenius, Broido and Horowitz-Metzger models and calculated the activation energy (E_a) and pre-exponentional factor (A). The photoisomerization property was examined with UV spectroscopy and all these polymers showed in trans to cis isomerization 10–15 s, whereas reverse process took around 90 min in solution.

KEYWORDS *: Azomethine polyesters, Photo physical properties, Thermal properties, Activation energy, Non-isothermal method, Photoisomerization.*

1. INTRODUCTION

Aromatic polyesters are a distinct class of materials that are attracting technical interest on account of their impressive thermal and mechanical properties. They are well known for their fiber and film forming nature and some of them are biodegradable. Hence, their uses in medical and non-medical areas are widely

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accepted [1-3]. However, most of the aromatic polyesters are difficult to process due to their high glass transition or melting temperature coupled with their insolubility in common organic solvents [4-10]. These factors often restrict their use in many applications. Consequently, it was of interest to investigate the thermal stability and other properties of aromatic polyesters with various linkages in their backbone. When an azomethine linkage is present in a polymer backbone, it is of special interest due to its interesting properties such as syn-anti isomerism [11], good thermal stability [12], non-linear optical activity [13], ability to form metal chelates [14], fibre-forming [15,16], liquid crystalline property[17-19], semi conductivity [20,21] and dielectric property [22]. In recent years, poly azomethines also have been explored for applications in organic electronics, such as light-emitting materials [23], pHsensors [24] and metal collecting polymers [25]. A major drawback associated with aromatic poly azomethines is their limited solubility in most of the common organic solvents [26-30]. Their insolubility in common organic solvents limits their processability and applications [31]. A photoisomerization is the conversion of one isomer into another isomer by light. The molecules having azobenzene units exhibit reversible isomerization behaviour upon irradiations with UV and visible light. The more stable trans configuration converts into their cis configuration upon absorption of UV light [32]. In the present polyester system the trans to cis isomerization occurred at faster rate.

In our previous paper, we reported the synthesis of cardo polyesters and their thermal degradation kinetics [33]. In continuation of our research in this area the present study deals with the synthesis of polyesters by reacting 4-[(4-hydroxy-3-methoxy phenyl)iminomethyl] phenol with various aliphatic and aromatic acid chlorides by solution poly condensation technique. The spectral and thermal studies were performed on the synthesized polyesters. A detailed thermo gravimetric study of this system was carried out using dynamic / non-isothermal methods in order to determine the activation energy (E_a) and to select the most appropriate mechanism to describe the degradation behavior. The value of E_a for the decomposition of polyesters in various steps and the regression co-efficient have been calculated by employing the Arrhenius, Broido and Horowitz- Metzger methods and the results have been compared. The photoisomerization properties of polymers were investigated using UV reactor and UV spectrophotometer.

2 MATERIALS AND METHODS

2.1. Materials

Vanillin, adipic acid, terephthalic acid, isophthalic acid were obtained from S.D fine chemicals (Mumbai, Maharashtra, India). 4-Amino phenol and tetrahydrofuran were obtained from Merck chemicals (Mumbai, Maharashtra, India). Thionyl chloride was obtained from Ranbaxy (New Delhi, India). All the other solvents used in the study were purified by the procedure reported in the literature[34, 35]. Suberic acid, azelaic acid, succinyl chloride and triethylamine were procured from Sigma Aldrich (Munich, Germany) and used without further purification.

2.2. Characterization

The solubility of the monomer and polymers was tested with 0.2- 0.5mg of substance in 5ml of solvents at room temperature. Viscosity measurement was carried out with 0.4 g/dL of polymer solution in DMSO at 25°C using oswald viscometer. The infrared spectra were recorded on a Fourier transform spectrophotometer (Shimadzu, Japan) using potassium bromide (KBr) pellets. UV–

Visible spectra were recorded in DMSO solution with Cary 60 UV–visible spectrophotometer (Agilent Technologies, Germany). ^{1}H and ^{13}C nuclear magnetic assonance (NMR) spectra were recorded on a 400 MHz NMR spectrometer (AV-III 400, Bruker, Billerica, Massachusetts, USA) using deuterated DMSO. The chemical shifts were measured using tetra methyl silane (TMS) as an internal standard. The elemental analysis was carried out using vario EL III carbon, hydrogen, nitrogen and sulpher analyzer (Elementar Analysensysteme, Hanau, Germany). The differential scanning calorimetry (DSC) analysis was carried out using pyris 6 DSC (Perkin Elmer, Waltham Massachusetts, USA) with an empty aluminium pan as a reference at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Thermo gravimetric analysis (TGA) was performed on a thermal analyser (Seiko Instruments, SII Nanotechnology, Japan) under nitrogen atmosphere at a heating rate of 10°C min^{-1}. The photoisomerization study of the synthesized polyesters was performed in the solution state with a UV spectrophotometer. The polymer was dissolved in DMSO in a quartz cuvette and irradiated in a UV curing reactor with a medium-pressure Hg lamp (Heber Scientific Photoreactor, India 300–420 nm) exposed at a distance of 10 cm from the sample. Subsequently, the irradiated solution was subjected to UV spectral analysis on a Cary 60 UV–visible spectrophotometer (Agilent Technologies, Germany).

2.3. Thermal degradation study

Thermal analysis methods are often used for the determination of degradation processes that take place during progressive heating of a polymeric material as well as for evaluation of the kinetic parameters of each degradation step. In this article Arrhenius, Broido and Horowitz-Metzger methods were employed to evaluate activation energy (Ea), reaction order (n), and the frequency factor (A) using single heating rate measurement without making any assumptions. The kinetic parameters of the thermo gravimetric weight loss were calculated according to linear regression method using the following kinetic equation.

$$d\alpha/dt = k_n (1-\alpha)^n \quad (1)$$

$$\ln (d\alpha/dt) = \ln k_n + \ln (1-\alpha)^n \quad (2)$$

where α is the fraction of the sample weight at time't', k_n is the specific rate with kinetic reaction of order 'n' and $(1-\alpha)$ is the fraction of numbers of initial molecules not yet decomposed.

$$\alpha = W_0 - W_t / W_0 - W_f \quad (3)$$

where W_0 is the initial sample weight, W_t is the sample weight at time t and W_f is the final sample weight. The reaction rates $\frac{d\alpha}{d_t}$ were calculated using a differential technique with the heating rate of 20°C min^{-1} incorporated directly into the temperature versus sample weight fraction data, according to the procedure development by Wen and Lin [36]. The activation energy and specific rates were calculated from Arrhenius relation [37].

$$K_n = A \exp\left(\frac{-Ea}{RT}\right) \quad (4)$$

$$\ln K_n = \ln A - \frac{Ea}{RT} \quad (5)$$

where E_a is the activation energy, A is the pre-exponential factor, T is the absolute temperature and R is the gas constant. Equations (1) and (4) were combined and used in logarithmic form

$$\beta = \ln - \left[\frac{d\alpha/dt}{(1-\alpha)^n}\right] = \ln A - \frac{Ea}{RT} \quad (6)$$

A plot of $\ln\left[\frac{d\alpha/dt}{(1-\alpha)^n}\right]$ versus 1/T gives a straight line. From the slope, the activation energy is calculated and from the intercept 'A' is calculated.

2.3.1. Broido Model

The activation energy (E_a) associated with each stage of decomposition was also evaluated by the well-known Broido method [38]. The equation used for the calculation of E_a is

$$\ln [-\ln (1-\alpha)] = \frac{-Ea}{RT} + K \quad (7)$$

E_a was calculated from the plot of $\ln [-\ln(1-\alpha)]$ versus $^1/_T$.

2.3.2. Horowitz and Metzger model

Horowitz and Metzger [39] have demonstrated a method to calculate the activation energy (E_a) of polymeric substances. The equation used for calculation of E_a is given below

$$\ln [\ln (W_0/W_t)] = E_a\theta/RT_s^2 \qquad (8)$$

where θ = T-Ts; W_0 is the initial weight, W_t is the weight at any time 't,' T_s is the differential thermogravimetric peak temperature and T is the temperature at particular weight loss. A plot of ln [ln (W_0/W_t)] versus θ gives an excellent approximation to a straight line. From the slope, Ea is calculated.

2.4. Synthesis

2.4.1. Synthesis of 4-[(4-hydroxy-3- methoxy phenyl)imino methyl] phenol (HMPIMP)

To a stirred solution of 4-aminophenol (0.1 mol) in hot ethanol, ethanolic solution of 4 -hydroxy-3-methoxy benzaldehyde (0.1 mol) was added drop wise. The mixture was stirred for 4 h at 70°C and cooled. The solid precipitate formed was filtered, washed with ethanol and dried under vaccum . [Melting point: 205°C, Yield: 78%] . The scheme of preparation is shown in Figure 1. Analysis calculated for $C_{14}H_{13}O_3N$: C, 69.15; H, 5.349; N, 5.76 %. Found: C, 68.01; H, 5.44; N, 6.07 %. FTIR (KBr, cm^{-1}): 3288 (γ_{O-H}), 1548 ($\gamma_{C=C,}$ Ar), 3088 (γ_{C-H}), 1226 (γ_{C-O}, phenol), 1610 ($\gamma_{-CH=N}$). ^1H NMR (DMSO-d6, TMS, ppm): 6.8-8.4 (m, Ar Protons), 4.0 (s, 3H,-OCH_3), 8.97 (s, 2H, OH), 8.56 (s,-CH=N-). ^{13}C NMR (DMSO-d6, TMS, ppm): 109.36-155.7 (Ar Carbons), 160.3 (–CH=N-), 55.7 (-$0CH_3$).

2.4.2. Preparation of acid chlorides

Recrystallized adipic acid (100 mmol) and distilled thionylchoride (240 mmol) were placed in a 250 ml round bottomed flask and refluxed in an oil bath for 4 h. After refluxing, excess thionyl chloride was removed under reduced pressure. Suberyl chloride and azeloyl chloride were also prepared by adopting the same procedure[40]. Terephthaloyl chloride and isophthaloyl chloride were prepared by refluxing the respective diacids and thionylchloride for 12h with the addition of two drops of pyridine as a catalyst. The solid product obtained was recrystallized from n-hexane [41].

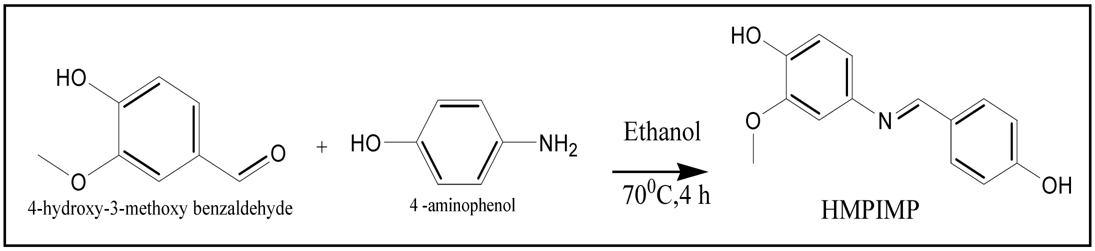

Fig. 1. Synthesis of HMPIMP

2.4.3. Synthesis of polymers

All the polymers were synthesized by solution poly condensation technique using triethyl amine as a catalyst.

2.4.4. Synthesis of poly [4-[(4-hydroxy -3-methoxy phenyl) iminomethyl] succinate (P1).

The monomer HMPIMP (0.005 mol) was dissolved in dry tetrahydrofuran (20 ml) and stirred for 5 min with the addition of triethylamine (0.010 mol). To this mixture succinyl chloride (0.005 mol) in 20 ml tetrahydrofuran was added dropwise using addition flask and the mixture was stirred vigorously for 4 h at ambient temperature. During this period the viscosity of the solution increased rapidly and the polymer began to precipitate. The brownish yellow polymer precipitated was filtered, washed with acetone and then dried under vaccum for 24 hours. The polyester was obtained with the yield of 72%. The scheme of preparation is shown in Figure 2.

FTIR (KBr,cm^{-1}): 1562 ($\gamma_{C=C}$ Ar), 1638 ($\gamma_{-CH=N-}$) , 1732 ($\gamma_{>C=O}$ of ester), 1171–1026 (γ_{C-O} Ar) . ^1H NMR (DMSO-

d_6, TMS, ppm): 6.75 – 7.43 (m, Ar), 8.56 (s,-CH=N-), 1.17 – 2.5 (m,-CH_2-), 3.83 (s,-OCH_3). ^{13}C NMR (DMSO-d_6, ppm): 191.4 (ester carbonyl carbon), 170.1 (CH=N carbon), 111.2-155.8 (Ar carbons), 56.05 (-0CH_3), 240.40 (-CH_2- carbons).

All the other polymers, P2, P3, P4, P5 and P6, were synthesized by the analogous procedure. Name of the other synthesized polymers are given below.

Poly [(4- (4- hydroxy-3-methoxy phenyl)iminomethyl)] adipate (P2)

Poly [(4-(4-hydroxy-3-methoxy phenyl)iminomethyl)] suberate (P3)

Poly [(4-(4-hydroxy-3-methoxy phenyl)iminomethyl)] azelate) (P4)

Poly [(4-(4-hydroxy-3-methoxy phenyl)iminomethyl)] terephthalate)(P5)

Poly [(4-(4-hydroxy-3-methoxyphenyl) iminomethyl)] isophthalate) (P6)

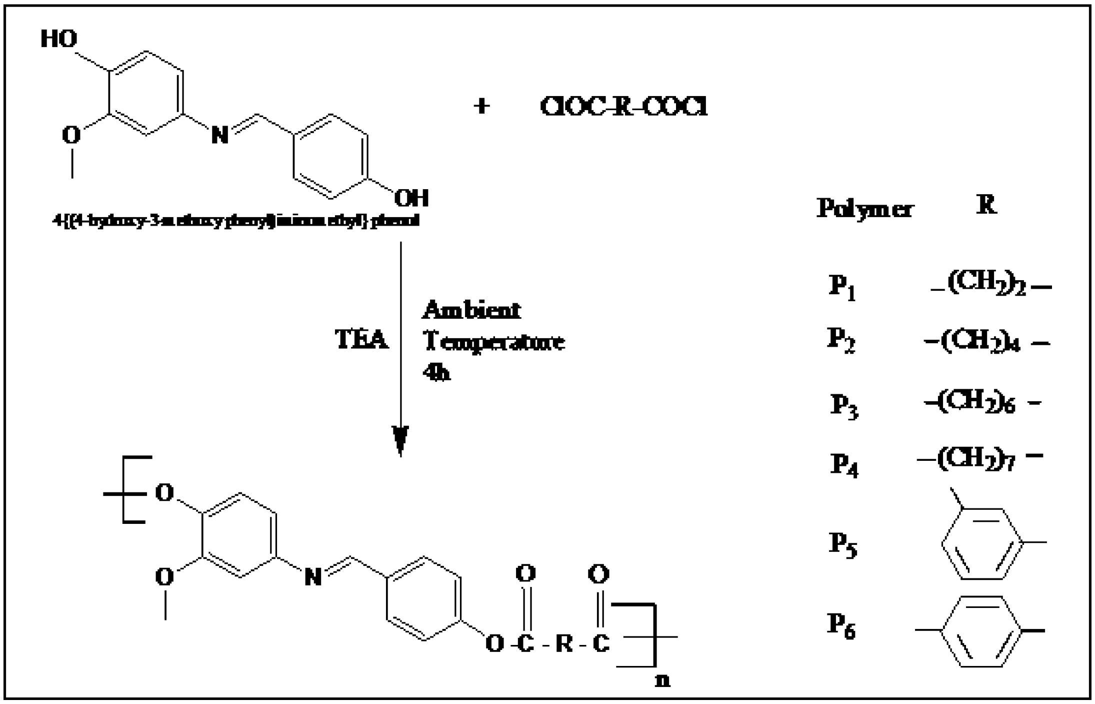

Fig. 2. Synthesis of Polyesters.

3. RESULT AND DISCUSSION

3.1. Synthesis and spectral characterization

All the polymers were prepared in good yield (72-80%) using solution poly condensation technique by reacting diol monomer, HMPIMP, with various acid chlorides. The scheme of synthesis of monomer and polymers are depicted in Figures 1 and 2. The solubility of the synthesized polyesters in various organic solvents was tested. The yield, solubility and viscosity data of the polyesters are given in Table 1. All the aliphatic polymers were soluble

TABLE 1. Yield, Solubility and Viscosity Data of the Polyesters

Polymer	Yield %	Solubility								Inherent viscosity (dL/g)
		CH_2Cl_2	THF	$CHCl_3$	1,4 dioxane	Acetone	Methanol	Ethanol	DMSO	
P1	75	—	—	—	—	—	—	—	++	0.31
P2	76	—	—	—	—	—	—	—	++	0.40
P3	72	—	—	—	—	—	—	—	++	0.53
P4	76	—	—	—	—	—	—	—	++	0.62
P5	80	—	—	—	—	—	—	—	—	-
P6	75	—	—	—	—	—	—	—	—	-

(++ soluble at room temperature, +- partially soluble at room temperature, — insoluble even on heating)

in dimethyl sulphoxide at room temperature whereas aromatic polyesters were insoluble in all the tested solvents. The inherent viscosity of aliphatic polymers was determined in DMSO and found to be 0.31 to 0.62 dL/g. The structure of the synthesized polyesters was confirmed by FTIR, UV-Vis and NMR spectroscopic techniques. The disappearance of –OH stretching frequency of the monomer at 3288 cm^{-1} and the appearance of characteristic carbonyl stretching frequency at 1735 cm^{-1} in all the polymers confirmed the presence of ester linkages. The stretching frequencies of –CH=N- and -CH groups of the polymers appeared at around 1628 and 2850 cm^{-1} respectively. The ^{1}H NMR spectrum of polyester P1 is shown in Figure 3. The aromatic protons appeared as a broad mulitiplet in the region of 6.75-7.43 ppm. The resonance peaks of imine -CH=N- protons appeared at 8.56 ppm. The methoxy protons resonated at 3.83 ppm and the -OCH_2 protons of acid moiety appeared in

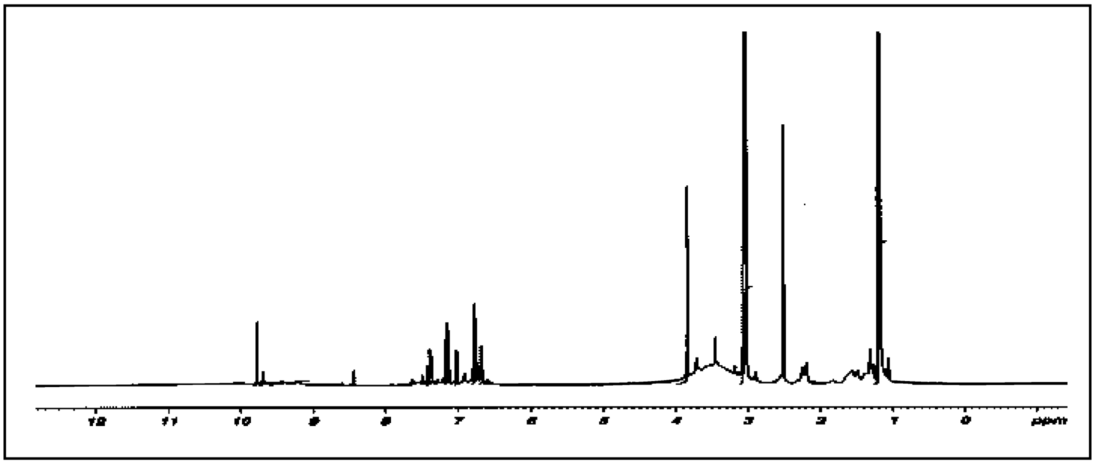

Fig. 3. ^{1}H-NMR spectrum of Polyester, P1.

the region of 1.17-2.50 ppm [42]. All the polymers were characterized with ^{13}C NMR spectroscopy. The ester carbonyl carbons appeared at around 191.4 ppm. The methylene carbons of acid spacer resonated in the region of 24.0- 40.2 ppm. The aromatic carbons of phenyl ring appeared between 111.2 and 153.8 ppm. The peak observed at 170.1 ppm is ascribed to -CH=N- carbon. The signal corresponds to methoxy carbon emerged at 56.05 ppm. All these spectral characterizations confirmed the formation of polyesters.

3.2. Photo physical properties

Photo physical properties of monomer and polymers were investigated using UV-Visible spectroscopy. The UV–Vis spectra of monomer and polymer (P4) were recorded in DMSO solution and shown in Figure 4. The absorption band of the monomer observed at 290 nm corresponds $\pi \rightarrow \pi^*$ transition of the benzene ring and the band appeared at 338 nm is assigned to $\pi \rightarrow \pi^*$ transition of the azomethine moiety [43]. In polymer, the $\pi \rightarrow \pi^*$ of transition of the benzene ring and azomethine appeared at 281 nm and 312 nm respectively. Figure 4 shows that the synthesized polymer has red shift absorption compared to the corresponding monomer due to their poly unsaturated structure. This poly unsaturation increases HOMO and decreases LUMO energy levels, resulting in lower band gaps. The optical band gap (Eg) of the monomer and polymer were determined using the equation $E_g = 1242 / \lambda_{onset}$, where λ_{onset} is the onset wavelength which can be determined from the intersection of two tangents in the absorption edges [44]. The optical band gap values of monomer and polymer were found to be 2.80 and 2.64 respectively. These results showed that the synthesized polymer has a lower optical band gap compared to the monomer.

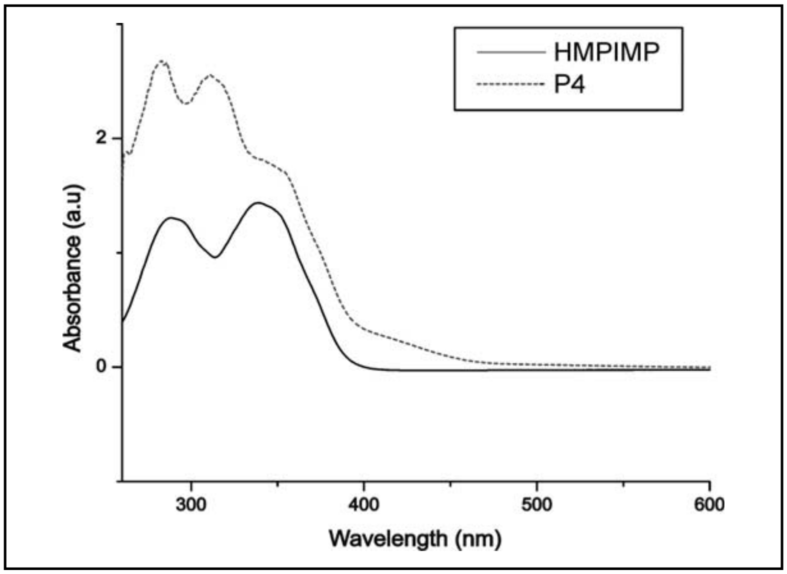

Fig. 4. UV-Vis spectrum of HMPIMP and Polyester P4.

3.3. Thermal properties

Thermal properties of the synthesized polyesters were studied using thermogravimetric analysis and differential scanning calorimetry under nitrogen atmosphere. The TGA traces of all the polyesters are shown in Figure 5. The temperatures corresponding to 10, 20, 30, 40 and 50% weight loss were determined from thermograms and are summarized in Table 2. The 10% weight loss occurred at 123 -176°C owing to loss of moisture and adsorbed solvent [45, 46]. The 50% weight loss occurred at 236 - 289⁰C. The data in Table 2 indicates that the thermal stability of the synthesized polymers is in the order: P5 > P6 > P3 > P4 > P1 > P2. Among the synthesized polyesters P3, P5 and P6 showed higher char yield at 600°C. The relatively lower thermal stability of all these polymers may be due to the presence of thermally weak methoxy substituent present in the aromatic ring of the polymer chain [47]. It was found that the synthesized aromatic polyesters are more stable than aliphatic polyesters. Among the aromatic polyesters, the polymer containing terephthaloyl units showed higher stability and char yield compared to the polyester containing isophthaloyl units. This may be due to higher crystallinity inside the hard domain of the polyester derived from terephthalic acid compared to that of the polyester derived from isophthalic acid [48].

The limiting oxygen index (LOI) value of the polymers was determined using the Van Krevelen equation [49] and was found to be in the range of 19.7-27.3. According to Van Krevelen, polymers having LOI above the threshold value of 26 possess self-extinguishing property [50]. The obtained LOI values indicated that the polyesters P5 and P6 have self-extinguishing properties. In aliphatic polyesters, the LOI value increases with increase in the number of methylene units in acid chlorides. Similarly among aromatic polyesters, the isophthaloyl polymer (P6) showed lower LOI value than terephthaloyl polymer (P5). This may be due to the lack of symmetry in P6 compared to terephthaloyl polyester.

TABLE 2. DSC and TGA Data of the Polyesters

Polymer Code	Tg^a in (°C)	Tm^a in (°C)	Temperature^b (°C)					Char yield (%) at 600 °C	LOI^c
			10%Wt. loss	20%Wt. loss	30%Wt. loss	40%Wt. loss	50%Wt. loss		
P1	202	-	123	184	206	221	236	5.56	19.7
P2	-	241	162	188	201	210	216	1.37	18.0
P3	-	221	159	192	207	217	226	9.97	21.4
P4	-	-	159	187	202	213	224	7.99	20.6
P5	-	-	154	185	200	258	376	26.0	27.9
P6	-	-	176	213	235	261	289	23.2	26.8

a. Measured by DSC.
b. Determined by TGA.
c. Determined with Van Krevelen's equation.

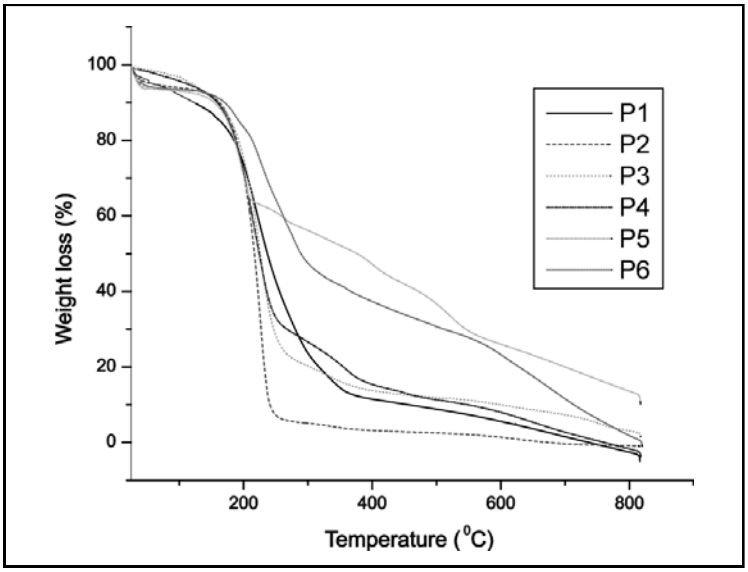

Fig. 5. TGA traces of the polyesters (P1-P6)

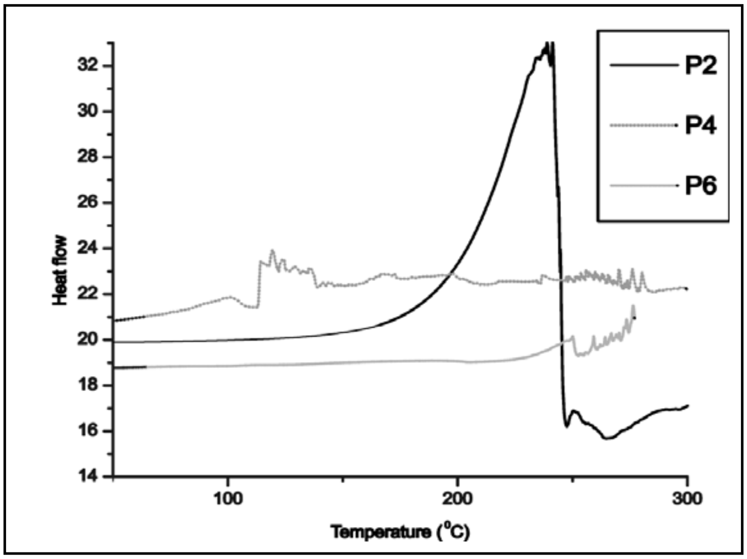

Fig. 6. DSC traces of the polyesters.

The DSC results of the synthesized polyesters are given in Table 2. Presence of melting peaks in the DSC traces (Figure 6) indicated that the synthesized polymers P2 and P3 are crystalline in nature. Aliphatic polymers which have lower number of methylene spacer showed Tg and Tm. This may be due to the increased number of methylene units in the

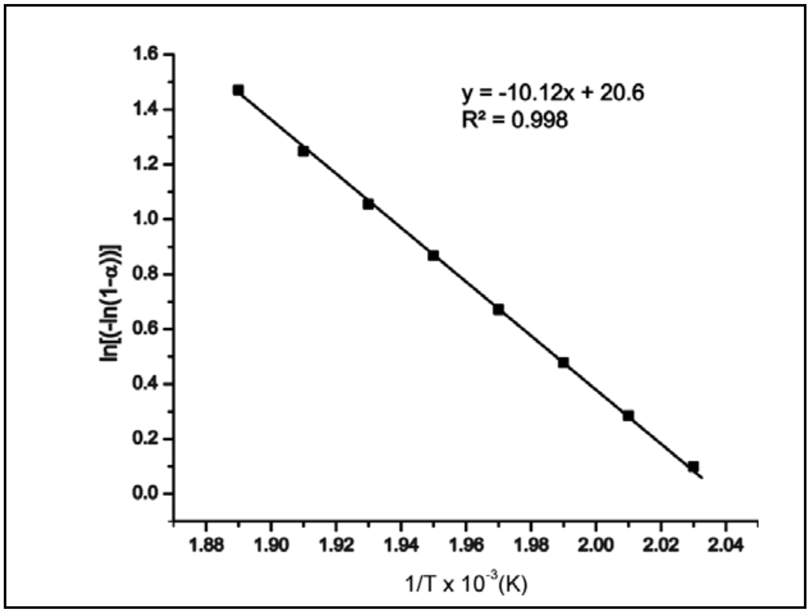

Fig. 7. Broido model of Polyester P4

polymer chain which increases the flexibility of polymer chain [51]. It was observed that aromatic polyesters, P5 and P6, neither showed Tg nor Tm. The increased rigidity inside the hard domain may be the reason for this observation.

3.4. Kinetic parameters

Kinetic parameters can be correlated with the thermal stability of the polymeric material, and it can be used for the prediction of degradation

TABLE 3. Kinetics parameters of the thermal decomposition of polyesters.

S. No.	Polymer code	Arrhenius method				Broido method		Horowitz-Metzger method	
		Ea KJ/mol	A Sec^{-1}	n	R^2	Ea KJ/mol	R^2	Ea KJ/mol	R^2
1	P1	21.70	3.22	2	0.964	11.36	0.998	9.670	0.994
2	P2	29.19	3.50	2	0.931	23.20	0.986	20.99	0.994
3	P3	30.68	3.52	2	0.939	19.87	0.999	17.16	0.997
4	P4	22.10	3.20	2	0.946	20.09	0.998	15.26	0.999
5	P5	49.80	4.15	2	0.956	38.90	0.967	51.68	0.983
6	P6	36.50	3.68	2	0.931	21.40	0.989	23.60	0.992

$E_{a:}$ activation energy; A: pre- exponentional factor; n: order of reaction; R^2: rate constant.

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behavior in various conditions. In the present investigation, Ea for the degradation of polyesters was determined using Arrhenius, Broido and Horowitz–Metzger methods. Kinetic parameters such as Ea, frequency factor (A) and order of the reaction (n) were determined by Arrhenius method. In Arrhenius method, a plot of ln $\left[\frac{d\alpha/dt}{(1-\alpha)^n}\right]$ versus $^1/_T$ gave a straight line. From the slope, Ea was calculated and from the intercept 'A' was calculated. Broido's method also gave a straight line for the plot of ln [-ln (1-α)] versus 1/T (Figure 7). In Horowitz–Metzger method, a plot of ln [ln (1/ (1-α))] versus θ showed an excellent approximation to a straight line. From the slope of the straight line, Ea was calculated. The regression analysis gives the slopes, constants and concurrency value (R^2) for degradation process. The linear plot with R^2 closer to one was chosen for all methods. The R^2 values and calculated Ea values are summarized in Table 3. It indicated that the increase in Ea is generally accompanied by an increase in 'A'. All the polyesters followed second order degradation kinetics. The ester linkages are weak points in the polyesters and they degrade selectively to form free radicals [52]. The Ea and R values were also determined by using Broido and Horowitz Metzger models using the equations (7) and (8) respectively and are summerized in Table 3. All the three models revealed that the Ea of aliphatic polyester is lower than those of aromatic polyester. It indicates that the aromatic polyesters have higher stability than aliphatic polyesters. Among aliphatic polyesters Ea and A values initially increases with increase

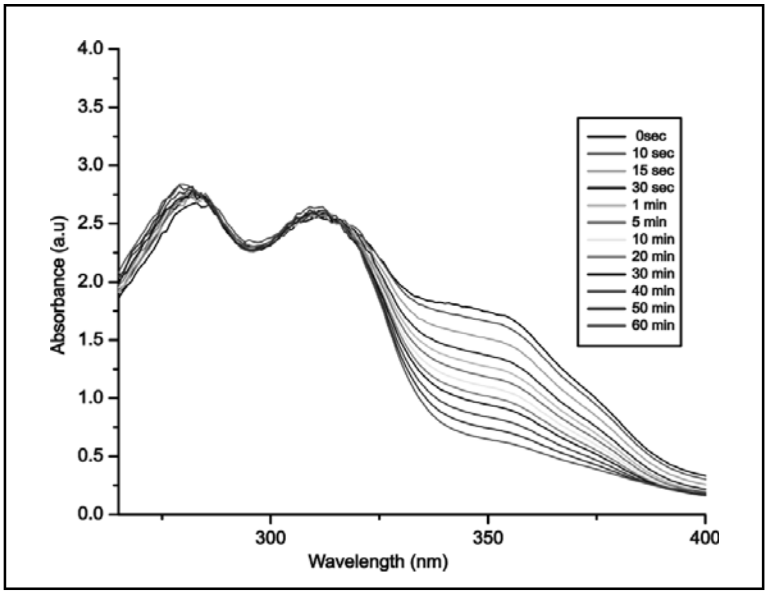

Fig. 8. Changes in UV spectral characteristics during photolysis of P4 in DMSO solution at various intervals of time

in spacer length upto seven methylene spacer, but further increase in the spacer length lead to decrease in E_a and A values due to opposing effects of the decoupling function of the spacer. Hence, it was observed that the polymer P4 has lower Ea and A than other aliphatic polyesters. Among the aromatic polyesters, the polyester P5 containing terephthaloyl units showed higher Ea and A values than the polyester P6 containing isophthaloyl units due to higher crystallinity and stability.

3.5. Photoisomerization studies

The scope of this investigation was to study the photoreactivity of the polymers in DMSO by irradiating with UV light and monitoring the changes using UV spectrophotometer. Figure 8 shows the changes in the UV spectral patterns during the photolysis of polymer P4 at various intervals of time. The strong absorbance in the UV region, 312 nm corresponds to the $\pi\rightarrow\pi^*$ transition of the E isomer (trans isomer). It decreased during UV irradiation, and a very weak absorbance at around 359 nm increased which represents the n- π^* transition of Z isomer (cis isomer). The photoisomerization study was performed using UV spectroscopy in the absence and presence of UV light illumination. Polymers (P1-P4) were illuminated with 365 nm UV light at different time intervals and immediately the absorption spectra were recorded. It is significant to note that there is an increase in intensity for most of the polymers.This increase has been assigned to disorganization caused by randomly oriented azomethine chromophores. As the exposure time was increased, concentration of E-isomer decreased, conversely concentration of Z-isomer increased [53]. It may therefore be concluded that the decrease in intensity of $\pi\rightarrow\pi^*$ transition of azomethine chromophores reveal ordered aggregation, while increase in intensity reflects the random orientation of chromophores. The thermal back relaxation process of the polymers (P1-P4) whose solution was kept in the dark and then at subsequent time intervals the spectral data were recorded. The results indicates that thermal back relaxation occurs within 90 min. The percentage relative reactivity value was calculated using the following expression and plotted against the irradiation time:

$$\% \text{ Relative reactivity} = (A_0 - A_t / A_0)\, 100$$

where A_0 is the absorbance before irradiation and A_t is the absorbance after irradiation time 't'. All the polymers showed a very low relative rate of conversation. This may be due to the methoxy substituent attached to the aromatic ring which hindered the polymer chains to orient in the appropriate fashion.

4. CONCLUSIONS

The polyesters containing azomethine linkage were synthesized from azomethine bisphenols by solution poly condensation technique using triethylamine as catalyst. The inherent viscosities of aliphatic polyesters were determined in DMSO and were in the range of 0.31 to 0.62 dL/g indicating the formation of medium to reasonably moderate molecular weight polymers. The formation of polyesters was confirmed using FTIR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopic techniques. The synthesized polymer has lower band gap than the monomer due to existence of polyunsaturated structure. The optical band gap values of monomer and polymer were found to be 2.80 and 2.64 ev respectively. The polymers P5 and P6 have LOI higher than the threshold value of 26 and thereby they are expected to have self-extinguishing properties. The relatively lower thermal stability of the polyesters is due to the weakly bonded $-OCH_3$ substituent present in the aromatic ring of the polymer chain. The DSC results indicated that the aromatic polyesters have neither T_g nor T_m. This may be due to increased rigidity inside the hard domain. Aliphatic polymers which have lower number of methylene spacer showed T_g and T_m. The kinetic parameters for thermal degradation of the polyester have been analyzed by Arrhenius, Broido and Horowitz-Metzger methods. All the polyesters followed second order degradation kinetics. The E_a of polyester increases with the increase in alkyl chain length of acid spacer but further increase in the spacer length reduced the E_a. All the models revealed that the E_a of aliphatic polyester is lower than those of aromatic polyester. This indicates that the aromatic polyesters have higher stability than aliphatic polyesters. The photoisomerization properties of these polymers revealed that trans to cis isomerization occur within 10–15 s, whereas the reverse process took around 90 min in solution.

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REFERENCES

1. W. Marrs, R. R. H. Pecers, R. H. Still, *J. Appl. Polym. Sci.* (1979) 1095.
2. M.A. Shenoy, E. A. Pereira, P. F. Parikh, *J. Appl Polym. Sci.* (2005) 606.
3. L. Zhang, C. Xiong , X. Deng, *J. Appl. Polym. Sci.* (1995) 103.
4. S. Mallakpour, Z. Rafiee. *Polym. J.* (2007) 1185.
5. G.S.Liou, H.M.Hsiao, H.M.Huang, C.W.Chang, H.J.Yen. *J. Polym. Res.* (2007) 191.
6. S.H.Hsiao, H.W.Chiang. *J. Polym. Res.* (2005) 211.
7. G.S. Liou, S.H. Hsiao, H.M. Huang and C.W. Chang, *Polym. J.* (2007) 448.
8. G.S. Liou, Y.T. Chern. *J. Polym. Sci. A: Polym. Chem.* (1999) 645.
9. J .Q. Su, *New chem mater.* (1994) 20.
10. S.A. Nye, S.A. Swint. *J. Polym Sci A: Polym. Chem.* (1994) 721.
11. R.S.Becker, W.F. Richney. *J Am Chem Soc* (1967) 1298.
12. C.H. Li, T.C. Chang. *J of Appl. Polym. Sci. Part A.* (1991)361.
13. Ilias Ali, S. M. AlZahrania, and S. K. Dolui. *Polymer Science Ser. B.* (2012) 342.
14. W.E. Rudzinski, S.R.Guthrie, P.E. Cassidy. *J Polym Sci Part A: Polym Chem.* (1988) l677.
15. H.H. Yang, Aromatic high-strength fibers. New York: Wiley-Interscience. (1989) p. 641
16. P.W.Morgan, S.L.Kwolek, T.C. Pleteher. *Macromolecules.* (l987) 729.
17. J.Barbera, L.Oriol, J.L. Serrano. *Liq Cryst.* (1992) 37.

18. S.Utkarsh, K.V.Rao, A.K. Rakshit. *J Appl Polym Sci.* (2003) 153.
19. D. Sek, *Euro Polym J.* (1984) 923.
20. Y.Saegusa, K.Sekiba, S. Nakamura. *J Polym Sci Part A : Polym Chem.* (1990) 3647.
21. A.Farcas, M.Grigoras, *Polym Inte.* (2003) 1315.
22. S. Dineshkumar, A. Muthusamy, J. Chandrasekaran. *J. Mole. Stru.* (2017) 730.
23. D.Sek, A. Iwan, B.Jarzabek, B.Kaczmarczyk, J.Kasperczyk, Z. Mazurak, M.Domanski, K. Karon,M. Lapkowski. *Macromolecules.* (2008) 6653.
24. M.K.Choi, H.L.Kim, D.H Suh. *J. Appl. Polym. Sci.* (2006) 1228.
25. M. Cazacu, M. Marcu, A.Vlad, A.Toth, C. Racles. *J. Polym. Sci. Part A: Polym. Chem.* (2003) 3169.
26. M.Grigoras, C.Catanescu. *J Macromol Sci C. Polym Rev.* (2004) C44, 1.
27. A. Iwan, D.Sek, P.Rannou, Kasperczyk, H.]aneczek, Z.Mazurak. *Synth Met.* (2004) 331.
28. M.Grigoras, C.O.Catanescu, C.I. Simionescu. *Rev Roum Chim.* (2001) 927.
29. G.F. D'Alelio, J.V.Crivello, R.K.Schoenig, T.F. Huemmer. *J Macromol Sci A.* (1967) 1161.
30. C.J. Yang, S.A.Jenekhe. Conjugated aromatic polyimines. *Macromolecules.* (1995) 1180.
31. H R. Kircheldorf, G. Schwarz. Handbook of Polymer synthesis part B in Kricheldorf HR (Ed). Dekker New York. (1992) pp.1673.
32. S.K. Prasad, G. Nair, G. Hegde. *J. Phys. Chem. B* 111 (2007) 345.
33. G. Latha1, M. Natarajan, K. Balaji , S. C. Murugavel. *High Perform Polym.* (2014) 125.
34. D.D.Perrin, W.L.F. Armarego. Purification of laboratory Chemicals. New York. NY:Pergamon. (1988).

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35. B.S. Furniss, A. J Hennaford, P.W.G. Smith, A.R. Tatchell. Vogel's Textbook of Practical Organic Chemistry. Singapore: Pearson Education. (2004).
36. W.V. Wen, J.W. Lin. *J. Appl Polym. Sci.* (1978) 2285.
37. L.H.Tagle and F.R .Diaz. *Int J Polym Mater.* (1998) 17.
38. Broido. A *J Polym Sci A-2.* (1969) 1761–1773.
39. H. H. Horowitz and G.A. Metzger. *Anal Chem.* (1963) 1464.
40. J.K.Stille and T.W Cambell, Condensation monomers. Newyork NY: Wiley. (1988) .
41. A. Muthusamy, S.C. Murugavel. *Polym.* (2006) 18, 227.
42. R.M .Silverstein, F.X. Webster. Spectroscopic identification of organic compounds. New York, NY: Wiley. (2002) 6 th ed. 43. I. Kaya, A.R. Vilayetoglu, H. Topak. *J. Appl. Polym. Sci.* (2002) 2004.
44. K.Colladet, M.Nicolas, L.Goris, L Lutsen, D.Vanderzande. *Thin Solid Films.* (2004) 451.
45. S.K.Dolui, D.Pal, S.Maiti . Synthesis of Novel Polyesterimide. (1985) 3867.
46. I. Kaya, M. Kamasi. Photophysical, *J of Macromol. Sci. Part A. pure & appl.chem.* (2014) 805.
47. S. Dineshkumar, A.Muthusamy, P.Chitra, S.Anand. *J. Adhe. Sci. & Tech.* (2015) 2605.
48. K. Balaji, S.C. Murugavel. *J Appl Polym Sci.* (2011) 3141.
49. D.W. Van Krevelen. *Polymer,* (1975) 615.
50. D.W. Van Krevelen. Properties of Polymers. New York, NY: Elsevier. (1990).
51. W. Huang, H. Xu, J.Yin. *Eur Polym J.* (2006) 946.
52. L.H.Tagle, F.R. Diaz. *Int J Polym Mater,* (1993) 37.
53. R.Balamurugan, P.Kannan. *J. Appl. Polym. Sci.* (2010) 1902.