SYNTHESIS, CHARACTERIZATION AND STUDY OF KINETICS OF THERMAL DEGRADATION
OF NOVEL HOMOPOLYESTERS BASED ON S-TRIAZINE

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ABSTRACT
The novel polyesters were synthesised by polycondensation reaction of 2-(N-morpholino)-4,6-bis(phenoxy-4'-carbonyl chloride)-s-triazine and various aromatic/aliphatic diols. Synthesized novel polyesters were characterized by various techniques like, solubility, density, viscosity, spectral study and thermal analysis. All the homopolyesters illustrates reasonable thermal stability, which signifies that the materials can be considered as high-performance materials. They had a reduced viscosity 0.9 - 0.5 g/dl, which points out that high molecular weight range need for excellent mechanical and thermal properties. Activation energy (Ea) is also verified from thermograms.

KEYWORDS: Polyesters, Polycondensation, High thermal stability, Thermal degradation, Activation energy and Stability.

INTRODUCTION
　　Polymers can be found in almost all around us, in our clothes and furniture, in the food we eat, in the hygiene products we use, and in the cars we drive. Not only that but polymers are also found in medicines, silicone implants artificial body parts, and so on. Thus polymer chemistry is one of the mainly significant and fast emergent exclusive branches of science as it plays an essential position in our everyday life.
　　In current years' synthetic polymer materials have expand greatly recognition and significance because of their wider range of scientific and technological applications. Attention has recently been paid to synthesizing high-performance polymers with high thermal stability and heat resistance with good mechanical properties, as they are required in modern technological applications[i].
　　The thermal stability of polymers can be improved either by increasing cross-linking or by establishing aromatic rings in the parent chain. However, many times such highly stable aromatic polymers suffer from some disadvantages. They may be easily broken or insoluble in general solvents. They may have such a melting point that they may decompose at

processing temperature. Due to these deficiencies such highly aromatic polymers are not processable and so of no more commercial value[ii-iv].

To defeat these general difficulties with aromatic polymers, stable ring systems such as borazine, phosphazine, triazine, etc. can be used and diverse techniques to attach these nuclei with thermal stable linkages can be studied[v].

The diverse approaches that have been employed to develop the processibility of these polymers comprise the introduction of flexible linkages, asymmetric units, bulky pendant groups and non-coplanar structures into the polymer chain[vi-xiv].

As an approach to improving the stability and processibility of polymers, numerous research reports have illustrated the synthesis and properties of polycyanurates[xv,xvi]. The selection of *s*-triazine ring is due to its high thermal stability derived from its molecular symmetry and aromaticity[xvii-xix]. *s*-Triazine ring could give toughness to the polymers. The rings also work as heat resistant[xx-xxii]. Aromatic polyesters containing *s*-triazine rings in the main chain possess high thermal stability, good solvent resistance and high stiffness [xxiii].

The present paper reports about the synthesis and characterisation of novel homopolyesters, which are synthesised from 2-(N-morpholino)-4,6-bis(4-(benzoylchloride) oxy)-s-triazine **(6)** and various aromatic and aliphatic diols such as Bisphenol A (BPA), Bisphenol C (BPC), Resorcinol (R), Catechol (C), Phenolphthalein (Ph), Ethylene glycol (EG), Diethylene glycol (DEG) and Triethylene glycol (TEG)using high-temperature polycondensation technique.

MATERIALS AND METHODS
Materials and methods
The solvents like chloroform, acetone, dimethylformamide, benzene, carbon tetrachloride, methanol, ethanol and other general chemicals used were laboratory grade reagents. Cyanuric chloride received from Atul Ltd., Atul, Valsad (m.p. 146°C) was dissolved in pure benzene and recrystalized to purify it. Bisphenol A (BPA),Bisphenol C (BPC), Resorcinol (R), Catechol (C), Phenolphthalein (Ph), Ethylene glycol (EG), Diethylene glycol (DEG) and Triethylene glycol (TEG) were obtained from Atul Ltd. (Valsad, Gujarat) and were used as received. Reactions for all compounds synthesized were monitored using thin layer chromatography (TLC) in 1:1 acetone and n-hexane solution.

The synthesised homopolyesters were characterised by their yields,colour,solubility, density, viscosity, H^1-NMR, IR and TGA. IR spectra of all the homopolyesters have been scanned in KBr pellets on'Thermo Scientific NICOLET–S10FT-IR spectrometer using the standard procedure.1H-NMR was performed on a Bruker Advance II 400 NMR spectrometer (Fallanden, Switzerland). The High resolution (400MHz) ^{1}H NMR spectra of solution of representative homopolyesters sample were measured in deuterated dimethyl sulfoxide (DMSO-d_6) using TMS as an internal reference. All the thermograms of polyesters have been obtained on the 'Perkin-Elmer Pyris-1 TGA'at a constant heating rate of 10°C/min. in thetemperature range from ambient temperature to about 600°C.

Experimental methods
(a) Synthesis of 2-(N-morpholino)-4,6-dichloro-s-triazine (3)
A slurry of cyanuric chloride **(1)** (18.44gm, 0.1mol) in 60ml acetone was mixed with stirring to a cold solution of NaHCO₃ (9.3gm) in 100ml of distilled water, in a 3-necked flask (250ml) equipped with a stirrer. A solution of morpholine **(2)** (8.68ml, 0.1 mol) in 10ml acetone was added to the cold slurry of cyanuric chloride. The mixture was stirred for 2 hours at 0-5°C and the pH was maintained neutral. The white colour product was filtered and recrystalized from ethanol and dried in a vacuum desiccator. Yield 77% and m.p. 138–139°C.
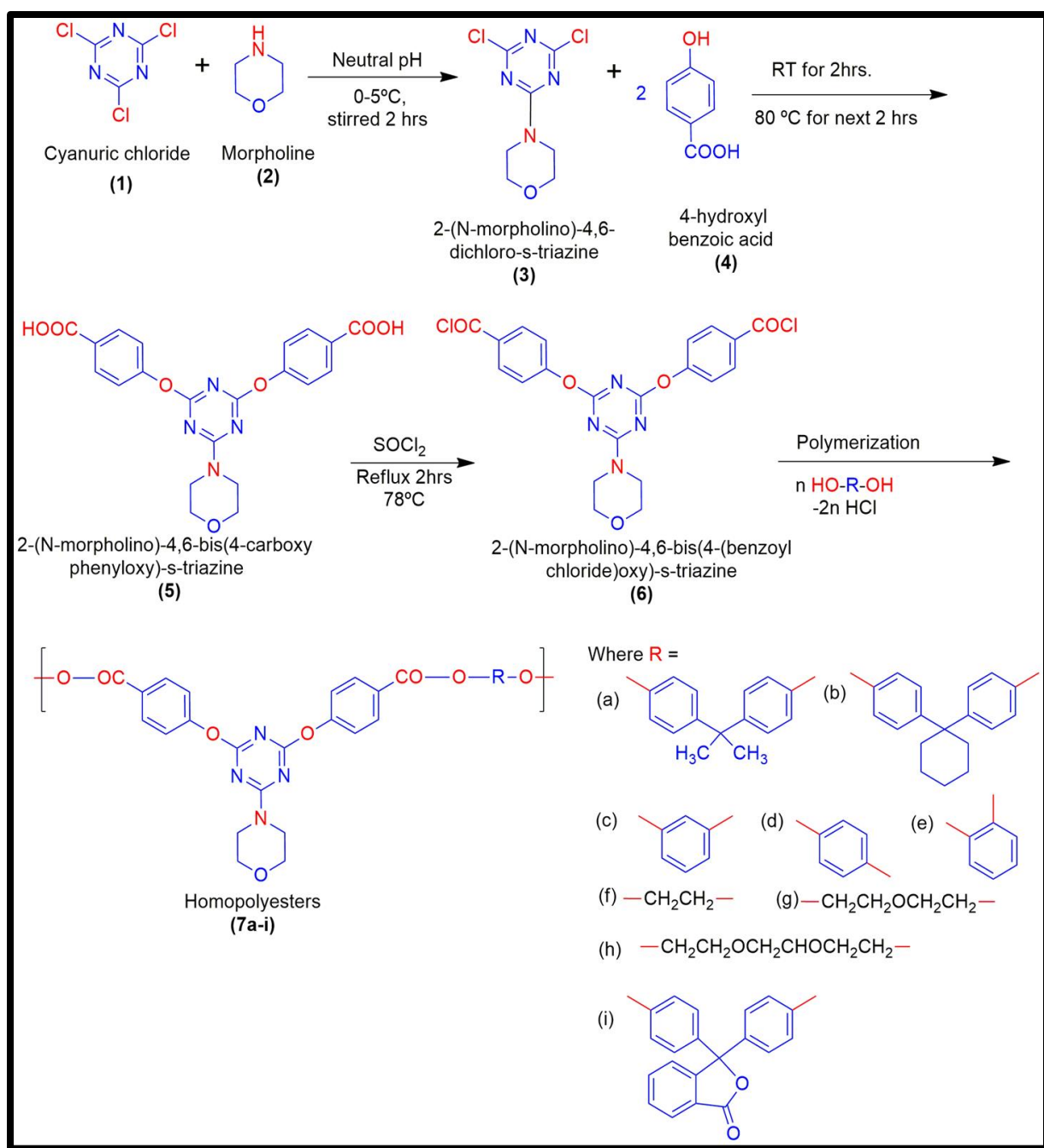
Figure 1. *Reaction Scheme*

(b) Synthesis of 2-(N-morpholino)-4,6-bis(4-carboxyphenyloxy)-s-triazine (5)

A solution of 2-(N-morpholino)-4,6-dichloro-s-triazine(**3**) (23.5gm, 0.1mol) in 40mL of acetone inRBF was taken. A mixture of NaOH (16.0gm, 0.4mol) and 4-hydroxyl-benzoic acid (**4**) (27.6gm, 0.2mol) in 40mL double distilled water was added slowly at room temperature in a solution of 2-(N-morpholino)-4,6-dichloro-s-triazine (**3**) with constant stirring. The reaction was continued for 4 hours, first 2 hours at room temperature and after that, 2 hours at 80°C temperatures. At the end of the reaction, the yellow solid separated from

the reaction mixture was filtered and washed several times with hot water and dried in vacuum at 100°C.Yield 73.0% and m.p. 242–243°C.

(c) Synthesis of 2-(N-morpholino)-4,6-bis(4-(benzoylchloride)oxy)-s-triazine (6)

2-(N-morpholino)-4,6-bis(4-carboxyphenyloxy)-s-triazine **(5)** (5.08gm, 0.01mol) was taken in a dry RBF fitted with the condenser then added $SOCl_2$ (7.26ml, 0.1mol) from the top of the condenser. Refluxed the reaction mixture at 78°C for 2 hours. At the end of the reaction, distilled off the excess $SOCl_2$ and recover the dry product from RBF. Yield 67% and m.p. 207–208°C.

(d) Synthesis of homopolyesters (7a-i)

A mixture of 2-(N-morpholino)-4,6-bis(4-(benzoyl chloride)oxy)-s-triazine **(6)** in a minimum quantity of DMF (approx. 10mL) was heated to about 150°C, add cetrimide (0.25gm) and various diols (0.02mol). The reaction temperature was raised to 165°C and heated for 8 hours. The reaction mixture was cooled and poured with constant stirring in 250mL of ice cold-water. The solid was filtered, washed with hot water and finally with methanol to remove unreacted material.

RESULTS AND DISCUSSION
Solubility characteristics

Solubility tests of synthesized homopolyesters were presented in Table-1, which shows that the methylated solvents are good solvents for all the homopolyesters. It is also noticed that solubility increase with temperature and those polyesters that have partial solubility at 25ºC get dissolved at higher temperature. All the homopolyesters are soluble in polar aprotic solvents like DMF and DMSO. DMF is found to be best solvent for all the homopolyesters.

Table 1. Solubility of homopolyesters in various solvents

Solvent	7a	7b	7c	7d	7e	7f	7g	7h	7i
Benzene	- -	- -	- -	- -	- -	- -	- -	- -	- -
Toluene	- -	- -	- -	- -	- -	- -	- -	- -	- -
Chloroform	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Acetone	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -	$\pm$ -
Carbon Tetrachloride	- -	- -	- -	- -	- -	- -	- -	- -	- -
Dimethyl Formamide	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Methanol	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
1,4-Dioxane	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +	$\pm$ +
1,2-Dichloro Ethane	- -	- -	- -	- -	- -	- -	- -	- -	- -

+ = soluble, $\pm$= partly soluble, - = insoluble, Where, the first and second symbol point out the solubility of polyester at R.T. and at 50°C correspondingly.

Density characteristics

The density of a polymer is usually determined pycnometrically in a liquid inert to the polymer. The suspension method is a very convent method of determining polymer density. The density of each polyester was determined at 25±3ºC by suspending each of the polyesters in a liquid mixture of carbon tetrachloride and acetone and subsequently measuring the density of the liquid mixture with a pycnometer, which is presented in Table-2. This liquid system is found to be inert to all polyesters since they remain in a state of suspension even for a prolonged time. Estimated accuracy of density is ±0.0001g/cm^3.

The highest density is 1.251g/cm^3 for 7d while the lowest density is 1.110g/cm^3 of 7f. The sequence of density of polyesters is as follow: 7i>7e>7c>7d >7a>7b>7h>7g>7f

Table 1. Colour, Yield and Density of homopolyesters

Polymer Code	Colour	Yield (%)	Density (g/cm^3)
7a	Black	60	1.201
7b	Black	65	1.198
7c	Brown	70	1.216
7d	Red	82	1.209
7e	Brown	71	1.221
7f	Grey	80	1.110
7g	Light Grey	81	1.114
7h	Black	85	1.115
7i	Red	78	1.251

Viscosity Measurements

Dilute solution viscosity measurements were carried out using an Ubbelohde suspended level viscometer. Intrinsic viscosity, reduced viscosity, and inherent viscosity for all the homopolyesters at various concentrations were determined at 25±1ºC. The relative viscosity (η_{rel}) and specific viscosity (η_{sp}) were also calculated. Reduced viscosity and inherent viscosity were then calculated from experimental data.At different concentrations, the solution viscosity of 7g is given in Table-3. Huggins and Kraemer plots for determination of intrinsic viscosity of 7g are shown in Figure-1. The respective intrinsic viscosity of synthesized homopolyesters is given in Table-4.

Table 2. Solution viscosity of homopolyester 7g
Solvent: DMF, t_0=42.2 sec

Conc (g/dl)	Flow time t sec	$\eta_{rel}=t/t_0$	$\eta_{sp}=\eta_{rel}-1$	$\eta_{red}=\eta_{sp}/C$	ln η_{rel}/C
0.2	46.6	1.104	0.104	0.521	0.495
0.4	51.05	1.209	0.209	0.524	0.475
0.6	55.55	1.316	0.316	0.527	0.458
0.8	60.2	1.426	0.426	0.533	0.444
1	64.95	1.539	0.539	0.539	0.431

Table 3. **Huggins and Kraemer constants for homopolyesters**

Polymer code	Reduced viscosity η_{sp}/C (dl/g)	Inherent viscosity $\ln \eta_{rel}/C$ (dl/g)	Intrinsic viscosity $[\eta]$ (dl/g)	Huggins slope	Kraemer slope	Huggins constant K_H	Kraemer constant β
7a	0.931	0.659	0.68185	0.2618	-0.0154	0.6695	06780
7b	0.923	0.520	0.71673	0.1963	-0.1975	0.7548	0.7382
7c	0.709	0.496	0.57762	0.1443	-00671	0.5679	0.5586
7d	0.762	0.372	0.50789	0.2354	-0.1316	0.5202	0.5001
7e	0.791	0.302	0.62270	0.1398	-0.3302	0.6310	0.6328
7f	0.603	0.282	0.48146	0.1403	-0.2028	0.4691	0.4633
7g	0.539	0.436	0.49813	0.04186	0.08109	0.1687	0.30989
7h	0.547	0.436	0.51154	0.04782	0.07387	0.19169	0.2846
7i	0.604	0.333	0.47256	0.1511	-0.1300	0.4723	0.4742

Spectral study

The IR spectra of all the synthesized homopolyesters of 7g is shown in figure 2. IR spectra of the homopolyesters a broad band at 3020-3680 cm^{-1} indicates the presence of -COOH group. The bands around 1510-1440 cm^{-1} supports the existence of *s*-triazine moiety. In spectra of the entire polyesters band observed, at 1105-1200 cm^{-1}, which is attributed to C-O-C stretching[xxiv]. The band at 1310-1360 cm^{-1} is of aromatic C-N stretching linkage (N-containing six-member ring). The band observed at around 1260-1300 cm^{-1} is attributed to symmetric stretching vibration of C-O-C (ether) linkage. Band obtained at 1360-1400 cm^{-1} is of C-H bending of –CH$_2$ group. The homopolyesters involving the aromatic diols in their backbone exhibit bands in the region of 610-670 cm^{-1}, which may be due to out of plane bending vibrations of C-H bands of aromatic rings. The band observed at 595 cm^{-1} in the spectrum of 7g is attributed to the vibration of aliphatic chain.
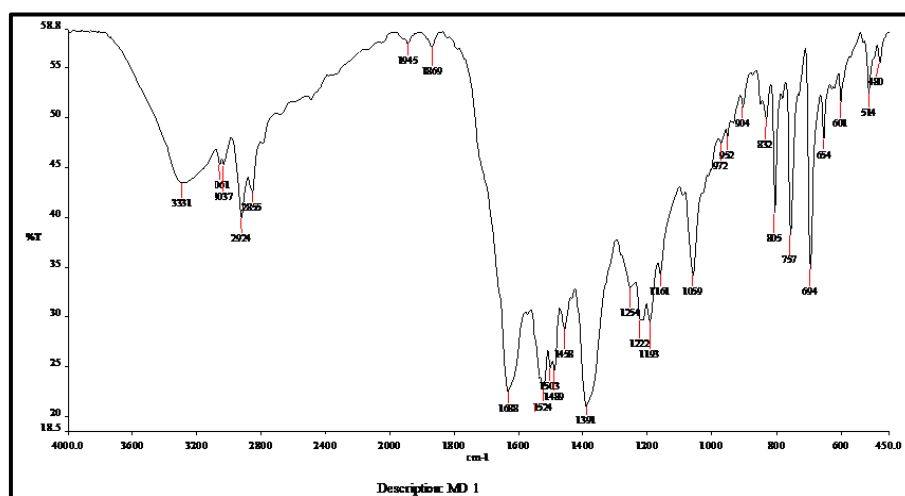

Figure 2. *IR spectrum of 7g*

1H NMR spectra for homopolyesters 7g is shown in figure-3. 1H NMR (δ ppm) shows peak at 2.8 (t, –CH$_2$- group of morpholine ring), 6.6-7.4 (m, C–H of aromatic ring), 3.2 (t, -CH$_2$CH$_2$- of DEG), 3.5, 3.8 (t, -OCH$_2$- of morpholine and DEG),4.1 (t, -CH$_2$OCO- of DEG).

Thermo Gravimetric Analysis (TGA)
All the thermograms of polyesters have been obtain on the 'Perkin- Elmer Pyris-1 TGA' at a constant heating rate of 10ºC/minute in the temperature range from ambient temperature to about 600ºC.All homopolyesters decomposes in one distinct weight loss step. The homopolyesters begins to decompose at about 180-90ºC. The first step decomposition encompasses a temperature range of 200-350ºC involving about 56-59% weight loss. After that the sample decomposes up to 620-30ºC leaving about 15-20% residue.
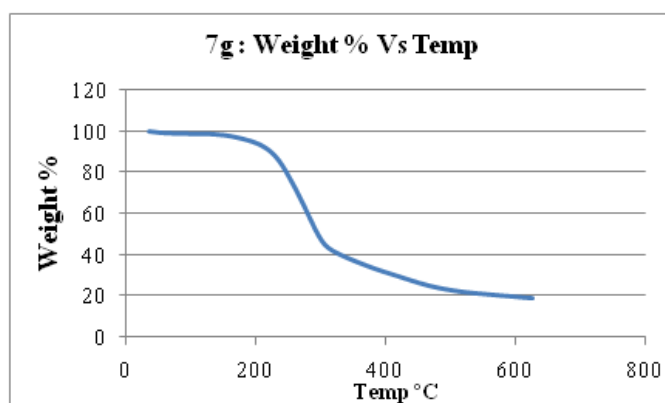

Figure 3. TGA graph of 7g

Evaluation of kinetic parameters
TGA thermograms obtained at a heating rate of 10ºC/ minute have been analyzed as per the graphical methods, proposed by Broido, Horowitz and Metzger. Broido, Horowitz and Metzger methods[xxv,xxvi] are exemplified for 7g is shown in figure 4.
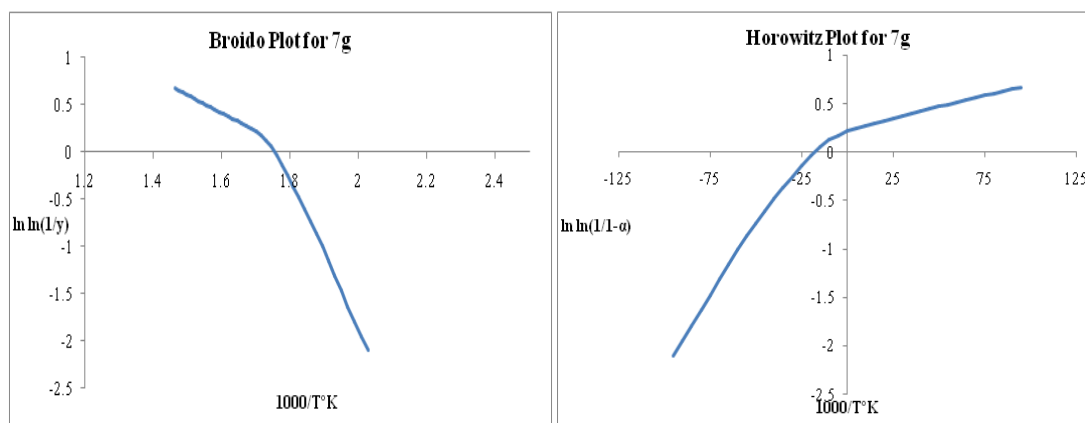

Figure 4. Plots of Broido and Horowitz-Metzer of 7g

Table-4 **Activation energy calculation for 7g**

Polymer code	Broido		Horowitz & Metzger		
	Slope	Ea (K.Cal/mol)	Slope	T$_S$ (ºK)	E$_a$ (Cal/mol)
7g	-4.6894	-9.31784	0.013432	588	9227.79

CONCLUSION

Our aim to synthesize polymers having high thermal stable polymers, in this direction the reported novel homopolyesters shows thermally stability at higher temperature. The novel homopolyesters were synthesised from 2-(N-morpholino)-4,6-bis(phenoxy-4'-carbonyl chloride)-s-triazine with various aromatic and aliphatic diols. The structures of synthesized novel homopolyesters were confirmed by spectroscopic analysis. The density of 7i was found the maximum, due to compact structure of polyester. The maximum Reduced viscosity shows by 7a and lowest for 7g, where 7a shows maximum Inherent viscosity and Intrinsic viscosity and 7f shows minimum Inherent viscosity and Intrinsic viscosity as evaluated using Huggins and Kraemer plots. Determination of the activation energy of a homopolyesters provides one the chance to observe the character of changes that take place in a material at every operational stage. The Broido method is free from temperature characteristics and thus expected to provide reliable estimates of Ea compared to Horowitz & Metzger method. In accordance with the Broido method, 7g have activation energy of -9.31784 kCal/mol. On considering Horowitz & Metzger method, 7g have activation energy of 9227.79 Cal/mol. In equation for calculation of activation energy having different parameters, so they give different values of activation energy.

Declaration of competing interest
The authors do not have any conflicts of interest.

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