Heterocyclic Letters
Vol. 15| No.3|531-539|May-July|2025
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

SYNTHESIS, CHARACTERIZATION AND THERMAL ANALYSIS OF S-TRIAZINE BASED NOVEL HOMOPOLYESTERS

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ABSTRACT

The novel polyesters were synthesised by polycondensation reaction of 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoyl chloride 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 - 0.1 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[xxiv] in continuous of our previous work about the synthesis and characterisation of novel homopolyesters, here we reported about characterization of homopolyesters 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 the temperature range from ambient temperature to about 600°C.

Experimental methods

(a) Synthesis of 4,6-dichloro-N,N-diphenyl-s-triazin-2-amine (3)

A slurry of cyanuric chloride **(1)** (18.44gm, 0.1mol) in 60ml acetone was mixed with stirring to a cold solution of $NaHCO_3$ (9.3gm) in 100ml of distilled water, in a 3-necked flask (250ml) equipped with a stirrer. A solution of Diphenyl amine **(2)** (16.9ml, 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 76% and m.p. 145–46°C.

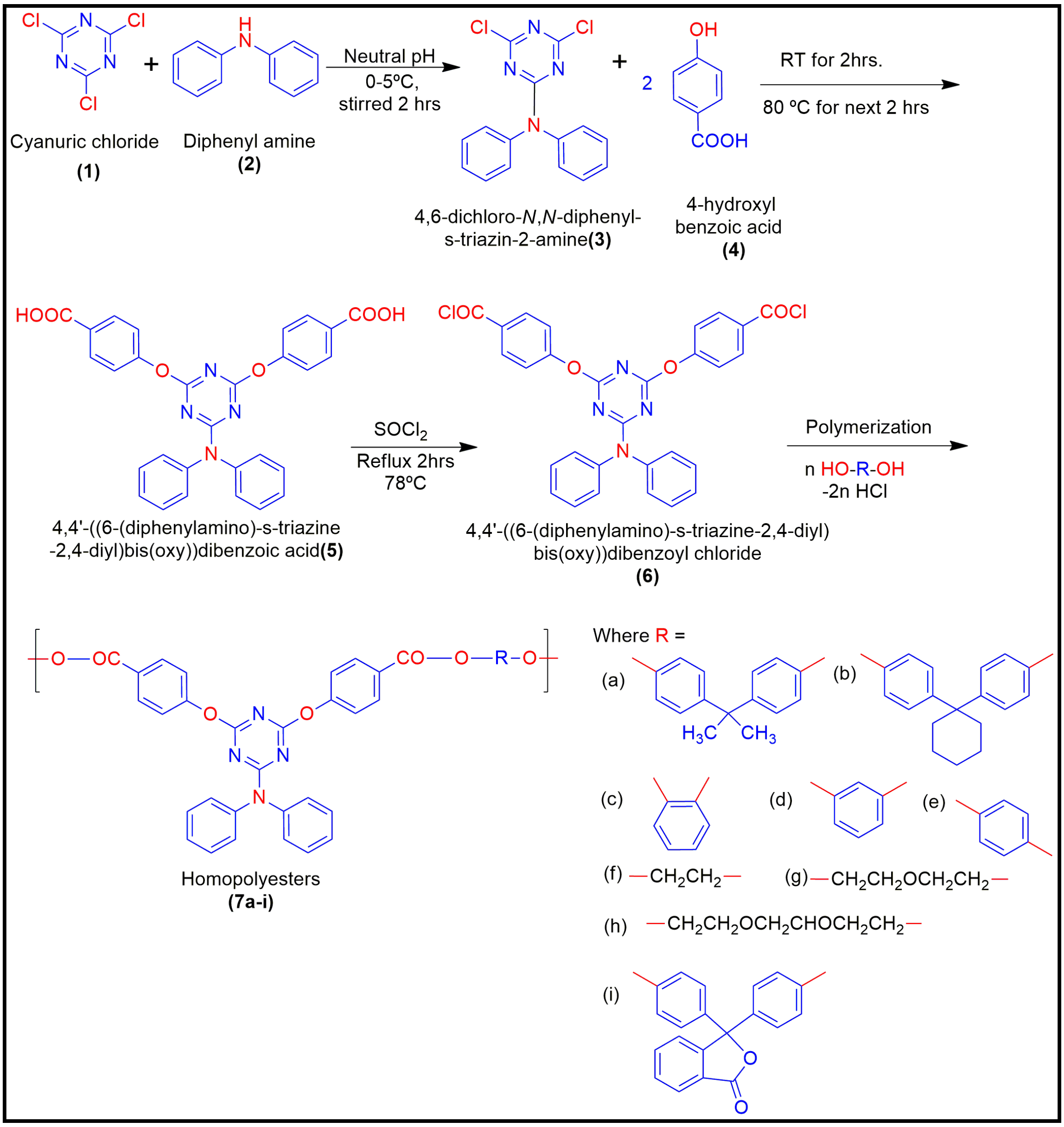

Figure 1. ***Reaction Scheme***

(b) Synthesis of 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoic acid(5)

Take a solution of 4,6-dichloro-N,N-diphenyl-s-triazin-2-amine **(3)** (31.7gm, 0.1mol) in 40mL of acetone. 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 4,6-dichloro-N,N-diphenyl-s-triazin-2-amine **(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 68% and m.p. 259–60°C.

(c) Synthesis of 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoyl chloride (6)

Take 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoic acid**(5)** (5.20gm, 0.01mol) in a dry RBF and then add $SOCl_2$ (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 dry product collected from RBF. Yield 65% and m.p. 214–15°C.

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

A mixture of 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoyl chloride **(6)** (5.57gm, 0.01mol) in a minimum uantity of DMF (approx. 10mL) was heated to about 150°C, then added 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	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Carbon Tetrachloride	- -	- -	- -	- -	- -	- -	- -	- -	- -
Dimethyl Formamide	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Methanol	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
1,4-Dioxane	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
1,2-Dichloro Ethane	- -	- -	- -	- -	- -	- -	- -	- -	- -

+ = soluble, ± = 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>7a>7b >7h>7g>7f>7d>7c

Table 1. **Colour, Yield and Density of homopolyesters**

Polymer Code	**Colour**	**Yield (%)**	**Density (g/cm^3)**
7a	Black	64	1.158
7b	Cream	60	1.147
7c	Brown	72	1.119
7d	Brown	72	1.12
7e	Brick Red	85	1.190
7f	Grey	80	1.122
7g	Grey	81	1.125
7h	Dark Brown	80	1.130
7i	Red	75	1.210

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	43.39	1.028	0.028	0.140	0.139
0.4	44.6	1.056	0.056	0.142	0.138
0.6	45.85	1.086	0.086	0.144	0.138
0.8	47.05	1.114	0.114	0.143	0.135
1	48.25	1.143	0.143	0.143	0.133

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 [η] (dl/g)**	**Huggins slope**	**Kraemer slope**	**Huggins constant K_H**	**Kraemer constant β**
7a	0.933	0.661	0.68187	0.2619	-0.0153	0.6694	06781
7b	0.924	0.522	0.71674	0.1965	-0.1972	0.7549	0.7383
7c	0.711	0.499	0.57764	0.1445	-00669	0.5681	0.5588
7d	0.765	0.376	0.50792	0.2357	-0.1312	0.5205	0.5004
7e	0.145	0.136	0.14047	0.00380	0.02179	0.191653	-1.06911
7f	0.549	0.438	0.40343	0.1591	0.03918	1.024007	0.240729
7g	0.143	0.133	0.14044	0.00378	0.02177	0.191651	-1.06908
7h	0.548	0.438	0.51156	0.04780	0.07388	0.19168	0.2847
7i	0.605	0.335	0.47258	0.1513	-0.1301	0.4724	0.4743

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 3393 cm^{-1} indicates the presence of -COOH group. The bands around 1491,848 cm^{-1} supports the existence of *s*-triazine moiety. In spectra of the entire polyesters band observed, at 1725,1393 cm^{-1}, which is attributed to C-O-C stretching^{xx}. The band observed at around 1255-1059 cm^{-1} is attributed to symmetric stretching vibration of C-O-C (ether) linkage. Band obtained at 1461 cm^{-1} is of C-H bending of $-CH_2$ group. The band observed at 595 cm^{-1} in the spectrum of 7g is attributed to the vibration of aliphatic chain.

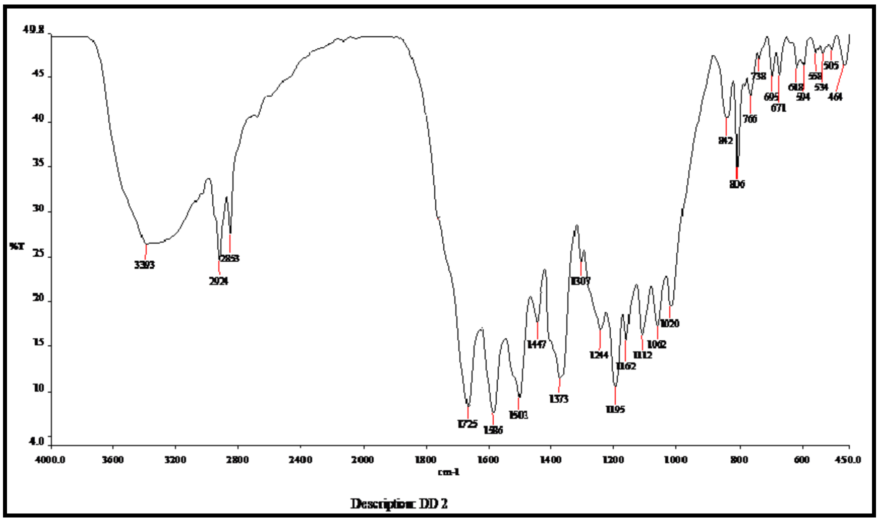

Figure 2. ***IR spectrum of 7g***

1H NMR spectra for homopolyesters 7g is shown in figure-3. 1H NMR (*δ* ppm) shows peak at 2.9 (t, $-OCH_2-$), 3.4 (t,$-CH_2CH_2-$), 4.4 (t, $-CH_2OCO-$) and 6.6-7.8 (m, C–H of aromatic ring).

Thermo Gravimetric Analysis (TGA)

All the thermograms of polyesters have been carried out 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 polymer begins to decompose at about 180ºC. The first step decomposition encompassing a temperature range 220-315ºC involving about 57.24% weight loss. After that the sample decomposes up to 625ºC leaving about 19.095% residue.

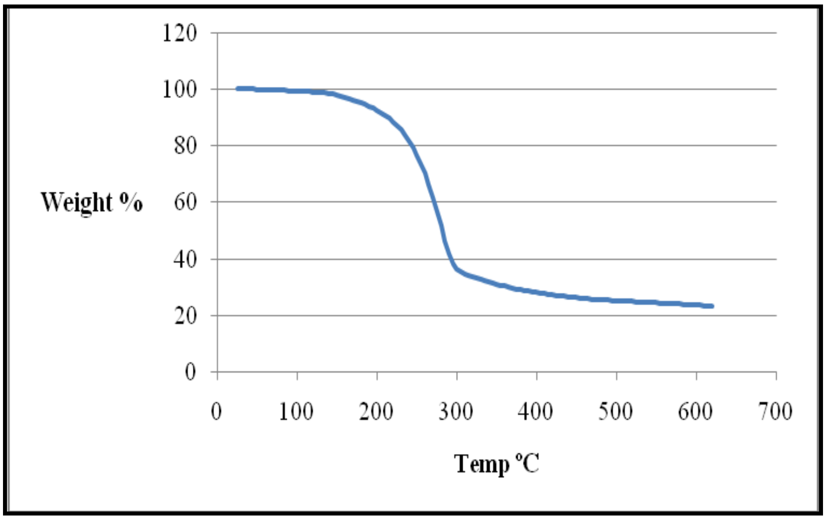

Figure 3. TGA graph of 7g

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^{xxvi,xxvii} are exemplified for 7g is shown in figure 4.

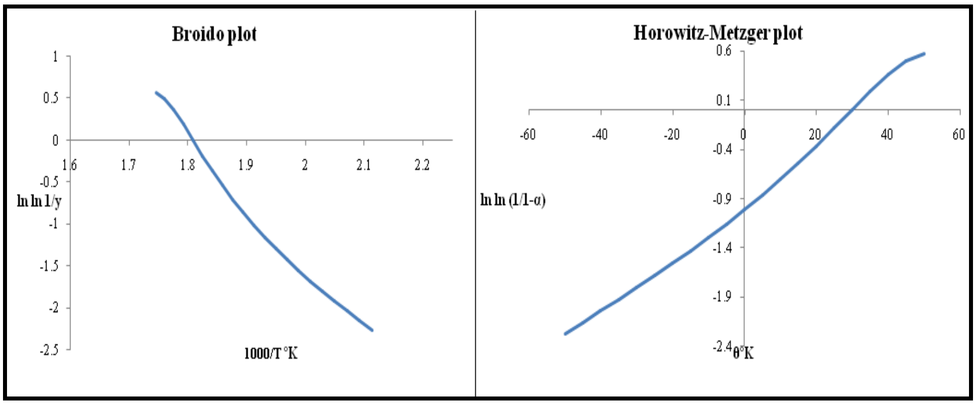

Figure 4. Plots of Broido and Horowitz-Metzer of 7g

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	-7.70469	-15.3092	0.029466	523	16015

CONCLUSION

In connection of our previous work in the direction to synthesis thermally stable polymers, the novel homopolyesters were synthesised from 4,4'-((6-(diphenylamino)-s-triazine-2,4-diyl)bis(oxy))dibenzoyl chloride 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 7g 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 -15.3092 kCal/mol. On considering Horowitz & Metzger method, 7g have activation energy of 16015 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.

Acknowledgment

The authors express their sincere thankfulness to Principal of Shri Maneklal. M. Patel Institute of Sciences and research, KSV, Gandhinagar and Department of Chemistry, K. K. Shah Jarodwala Maninagar Science College, Ahmedabad, for their research supports.

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Received on March 17, 2025.