ISSN NO. 2320-5407

Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/5021
DOI URL: http://dx.doi.org/10.21474/IJAR01/5021

RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND PHYSICO-CHEMICAL PROPERTIES OF COPOLYESTERS ONTAINING *s*-TRIAZINE RING IN THE MAIN CHAIN.

Rahul B. Tailor, Premlata H. Patel, Mohsin A. Belim, Savan V. Patel, Sejal M. Patel, Hushen U. Hajiyani, Paresh S. Patel and *Keshav C. Patel.
Department of Chemistry, Veer Narmad South Gujarat University, Udhna-Magdalla Road, Surat-395 007, Gujarat, India.

……

Manuscript Info

Manuscript History

Received: 28 May 2017
Final Accepted: 30 June 2017
Published: July 2017

Key words:-
Copolyesters, Density, Physico-chemical, Thermal stability, Viscosity

Abstract

A series of copolyesters has been synthesized by polycondesation of 2-(*N*-piperidino)-4,6-bis (2-napthoxy, 6-carbonyl chloride)-*s*-triazine [PNCCT] with various mixture of diols, such as [Hq + BPA], [C + BPA], [R + BPA], [C + BPC], [R + BPC], [BPC + BPS], [Hq + Ph], [Hq + C], [Hq + BPS] and [Hq + Eg]. All the synthesized copolyesters were characterized by solubility, density, viscosity, IR, ^{1}H NMR and TGA spectra. Modification and introduction of bulky pendent group in monomer structure is increases the thermal stability and solubility of the polymers. The density of all the copolyesters varies from 1.204 to 1.165 g/cm^3. The intrinsic viscosity, reduced viscosity and inherent viscosity were determined by using Huggins & Kraemer method. The activation energy was calculated by Broido and Horowitz & Metzger method for PE 8 (II) and PE 9 (II) were found 21.30 and 18.69 kcal/mol respectively. The synthesized polymers are found to stable more than 300 °C temperature so it can be used for high temperature applications.

……

Introduction:-

Today's requirement of novel polymers with improved property has been expanding with time and it can be said to be endless. Polymeric materials have potential use as rubbers, resins, plastics, composites, adhesives, laminates and coatings. The polymers science beginning and headway in the second and third decade of the twentieth century. Though introduced very late, polymers occupy a major place and pivotal position in our materials map today. In application prospects, performance and versatility in property that can hardly be occupied by any other kind of materials [1-4]. A literature survey reveals that the polymers based on *s*-triazine moiety and their derivatives have been extensively used since last few years. Recently most researchers working for the synthesis of high-performance polymers with high thermal stability and heat resistance with good mechanical properties, as they are required to use as engineering plastic materials. Now a day the copolyesters are largely used in various fields to achieve high thermal stability and good mechanicals property [5-8]. Polymers containing *s*-triazine ring in the main chain have excellent heat resistance and several are commercially available as high-performance engineering plastic materials. Hence, it was thought interesting to synthesize and characterize some copolyesters based on *s*-triazine [9-11]. In present investigation, we have synthesized and characterized copolyesters from diacid chloride of 2-(*N*-piperidino)-4,6-bis(2-napthoxy,6-carboxy)triazine and various equimolar mixtures of aromatic diols.

Corresponding Author:- Keshav C. Patel.
Address:- Department of Chemistry, Veer Narmad South Gujarat University, Udhna-Magdalla Road, Surat-395 007, Gujarat, India.

Materials:-

Fresh double-distilled water was used for the preparation of solutions. Solvents, like benzene, acetone, N,N-dimethyl formamide, carbon tetrachloride, methanol, ethanol, dimethyl sulphoxide, nitrobenzene, pyridine and hexane were all laboratory reagents, obtained from Merck and used as received. Cyanuric chloride (Fulka) was purified by repeated crystallization from pure benzene (m.p. 146 ˚C).

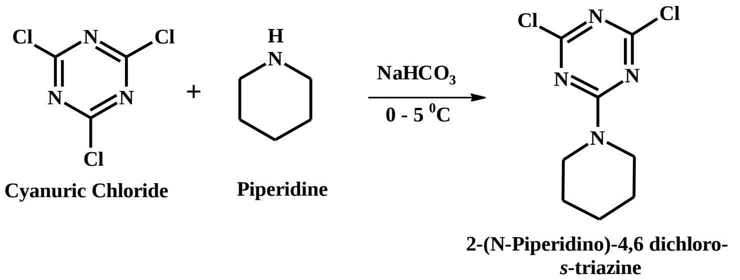
The resin grade bisphenol-A received form Atul Ltd. was repeatedly crystallized from 50% aqueous acetic acid. The crystals of bisphenol-A were filtered, thoroughly washed with water and dried. It was purified by recrystallization from benzene (m.p. 156 ˚C). Bisphenol-C was synthesized following a published procedure [12] and was crystallized from benzene (m.p. 187 ˚C). Phenolphthalein (BDH, m.p. 262 ˚C) was purified by crystallization from ethanol. Resorcinol, catechol and hydroquinone (Sisco lab) were purified by recrystallization from rectified spirit and 1,5-dihydroxy naphthalene (Sisco lab) was purified by recrystallization from aqueous alcohol. Ethylene glycol of better purity (Merck) was used as received.

Experimental:-

Step I: Synthesis of 2-(*N*-piperidino)-4, 6-dichloro-*s*-triazine [PDCT]:-

A solution of cyanuric chloride (18.44 g, 0.1 mole) in 60 ml acetone was added with stirring in a cold solution (0- 5 °C) of sodium bicarbonate (10.6 g) in 100 ml distilled water, in three necked 250 ml flask equipped with a mechanical stirrer. This results in the formation slurry of cyanuric chloride. A solution of piperidine (8.51 g, 0.1 mole) in 10 ml acetone was added to the cold slurry of cyanuric chloride with continuous stirring. After addition was completed, the reaction mixture was stirred for 2 hr at 0-5 °C. The light yellow colored product was filtered and recrystallized from ethanol and dried in a vacuum desiccator (yield 81 %, m.p. 90 °C) [13-14].

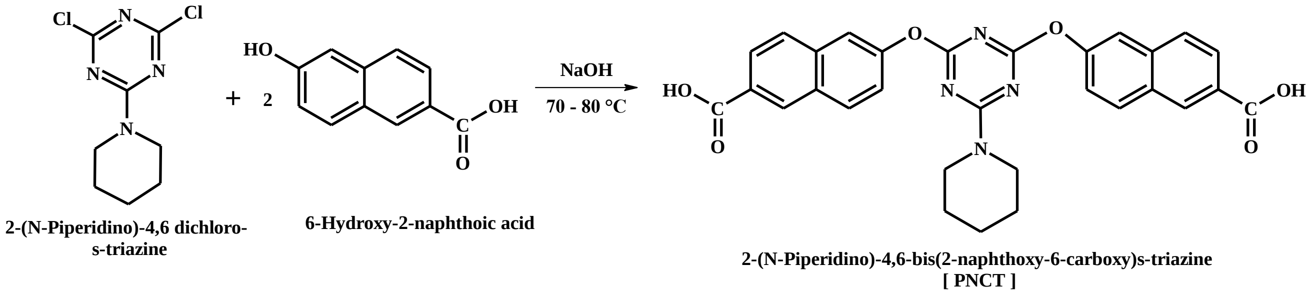
Scheme 1:-



Step II: Synthesis of 2-(*N*-piperidino)-4, 6-bis (2-napthoxy, 6-carboxy) triazine [PNCT]:-

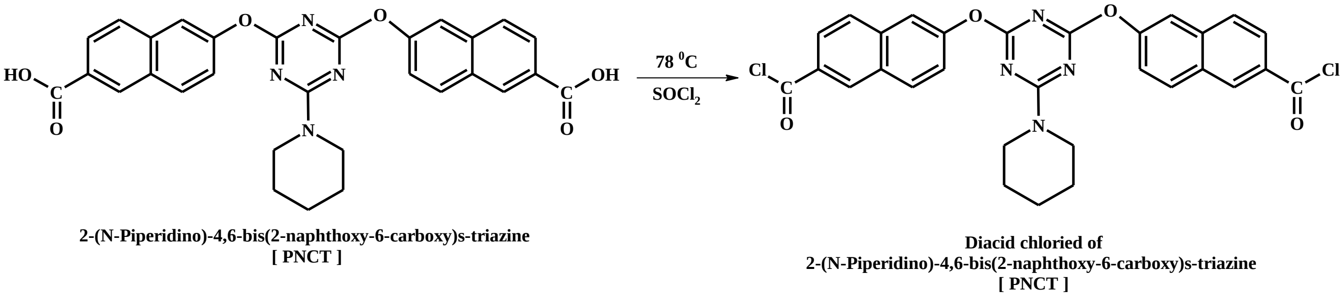
A solution of 6-hydroxy-2-naphthoic acid (37.6g, 0.2 mole) in NaOH (16.0 g, 0.4 mole) and 80 ml double distilled water was added slowly to 2-(*N*-piperidino)-4,6-dichloro-*s*-triazine [PDCT] (23.4 g, 0.1 mole) in 40 ml of acetone at room temperature with constant stirring. Reaction was continued for 4 hr first 2 hr at room temperature and then another 2 hr at 80 °C. At the end of the reaction, the white solid separated from the reaction mixture was filtered and washed several times with hot water and dried in vacuum at 100 °C. The product was recrystallized from acetone (yield was 80 %, m.p. 234 °C) [15-16].

Scheme 2:



Step III: Synthesis of 2-(*N*-piperidino)-4, 6-bis (2-napthoxy, 6-carbonyl chloride)-*s*-triazine [PNCCT]:-
Place 2-(*N*-piperidino)-4,6-bis(2-napthoxy,6-carboxy)-*s*-triazine [PNCT] (5.36 g, 0.01 mole) in a dry round bottom flask. Thionyl chloride (11.9 g, 0.1mole) was added at the top of the condenser and the reaction mixture was refluxed at 78 °C for 2 hr. At the end of the reaction, the excess of thionyl chloride was distilled off and dry product was recovered. The yield recrystallized from dimethyl formamide (yield about 78 % and m.p. 205 °C) [17-18].

Scheme 3:

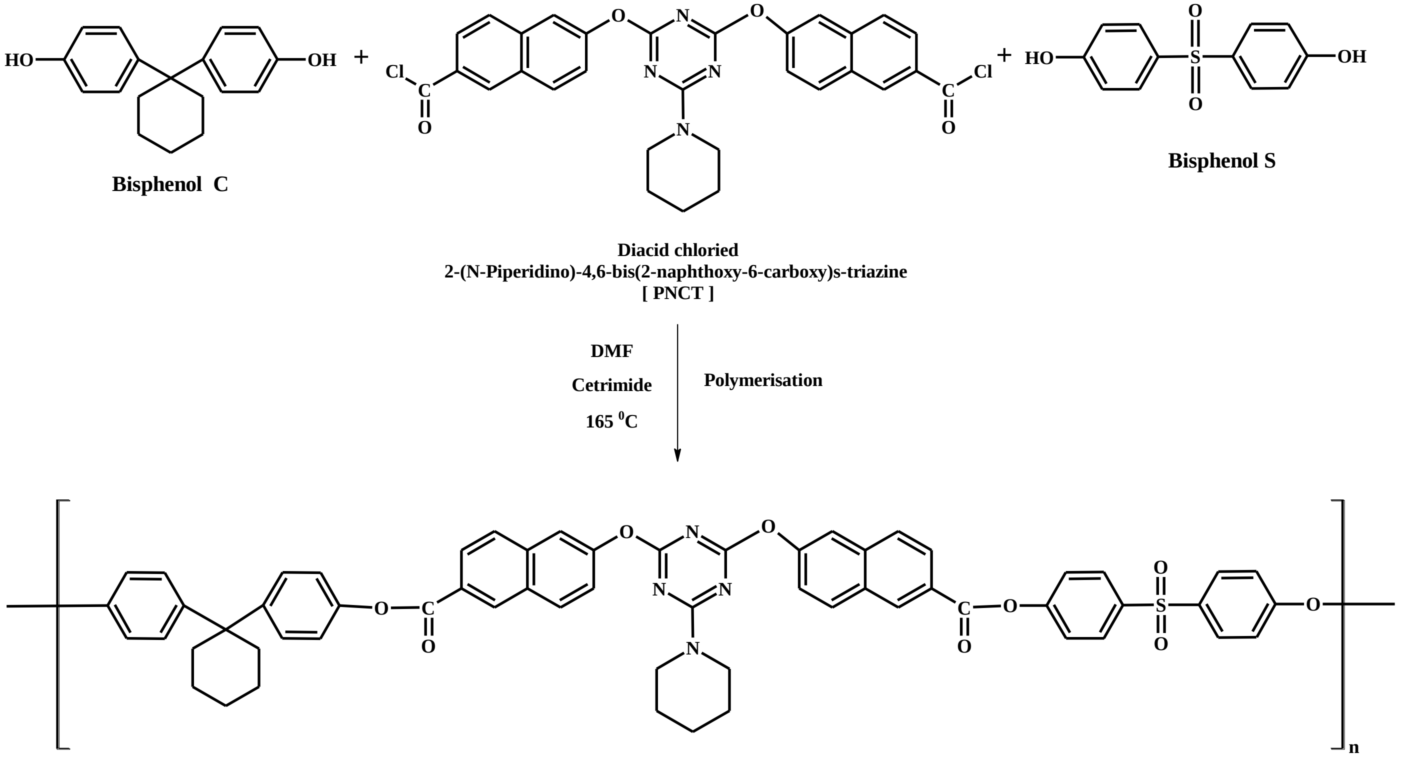


2-(N-Piperidino)-4,6-bis(2-naphthoxy-6-carboxy)s-triazine
[PNCT]

Diacid chloried of
2-(N-Piperidino)-4,6-bis(2-naphthoxy-6-carboxy)s-triazine
[PNCT]

Step IV: Synthesis of copolyesters from PNCCT and various mixture of diols:-
The copolyesters were synthesized by polycondensation of 2-(*N*-piperidino)-4,6-bis(2-napthoxy,6-carbonylchloride)-s-triazine [PNCCT] and various mixture of diols, such as [Hq + BPA], [C + BPA], [R + BPA], [C + BPC], [R + BPC], [BPC + BPS], [Hq + Ph], [Hq + C], [Hq + BPS] and [Hq + Eg] [19].

Scheme 4:



Bisphenol C

Bisphenol S

Diacid chloried
2-(N-Piperidino)-4,6-bis(2-naphthoxy-6-carboxy)s-triazine
[PNCT]

PE 6 (II) PE (BPC + BPS)

Measurements:-

FTIR spectra of all the polyesters were recorded on Perkin Elmer FTIR Paragon 1000 using KBr pellet technique. The NMR spectra were recorded on a Perkin-Elmer Model-32 ^{1}H NMR spectrometer (400 MHz). Density of the polymers has been determined pyknometrically at 25 ˚C using the suspension method. Solution viscosity measurements have been carried out for the homopolyesters. Reduced viscosities of polyesters were determined for 1 gm/dl solution in DMF using an Ubbelohde suspended level viscometer. Intrinsic viscosity was obtained from the plot of reduced viscosity vs. concentration and inherent viscosity vs. concentration according to Huggins [20] and Kraemer [21] equations. Thermogravimetric analysis of some selected homopolyesters has been carried out on the thermobalance Metter TA-4000 system with constant heating rate of 10 ˚C/min in the temperature range from ambient to 900 ˚C. All TGA have been analyzed as per the graphical methods proposed by Broido [22] and Horowitz & Metzger [23].

Result and Discussion:-

Various copolyesters were synthesized from PDCT and Mixture of different diols. The synthesized copolyesters have been evaluated for various physicochemical properties such as yield, color, solubility, density, viscosity, temperature characteristics, activation energy of thermal decomposition, IR and ^{1}H NMR spectroscopy.

Infrared Spectra:-

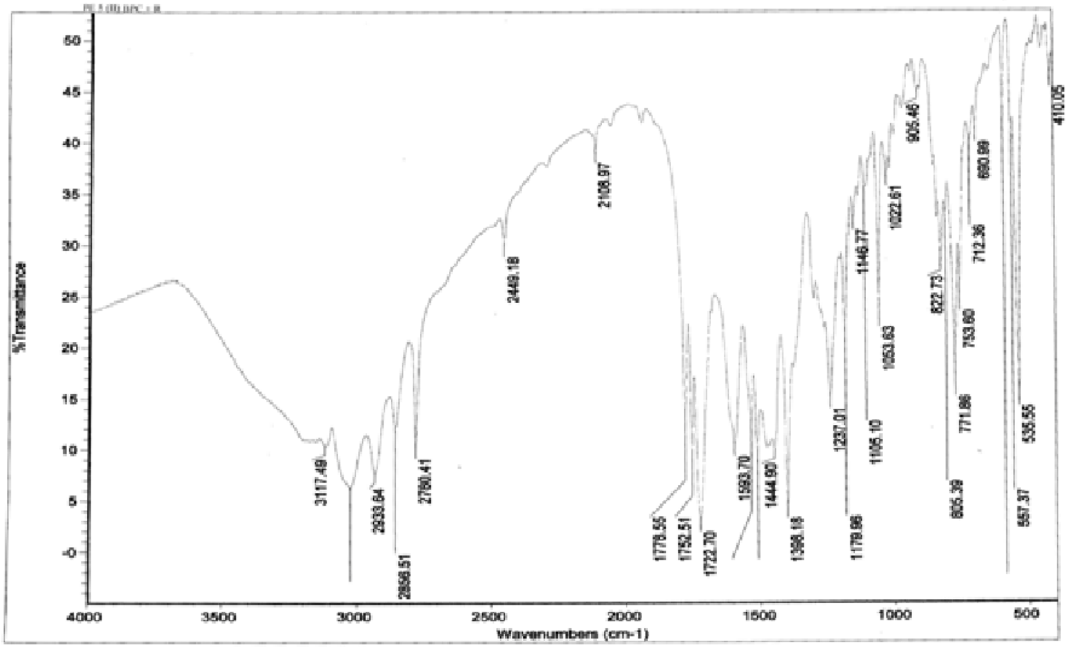


Figure_1 IR spectrum of PE 5 (II)

The IR spectral of PE 5 (II) showed deformation vibrational band of cyclohexane link at 557 cm^{-1}, m-substitution on phenyl ring at 712 cm^{-1}, C-H bending vibration of aromatic ring at 753-557 cm^{-1}, out of plane vibration of *s*-triazine ring at 805 cm^{-1}, C-H bending vibration of aromatic ring at 905 cm^{-1}, Vibration of aryl ether linkage symmetric at 1053 cm^{-1}, C-C (=O)-O ester stretching symmetric at 1179 cm^{-1}, aromatic C-N stretching at 1337 cm^{-1}, C-H bending vibration of methyl group at 1389 cm^{-1}, in plane vibration of *s*-triazine ring at 1444-1494 cm^{-1}, C-C (=O)-O ester stretching vibration at 1752 cm^{-1}, C-H stretching vibration of methyl group at 2780 cm^{-1}, C-H stretching vibration of methylene group at 3020 cm^{-1}.

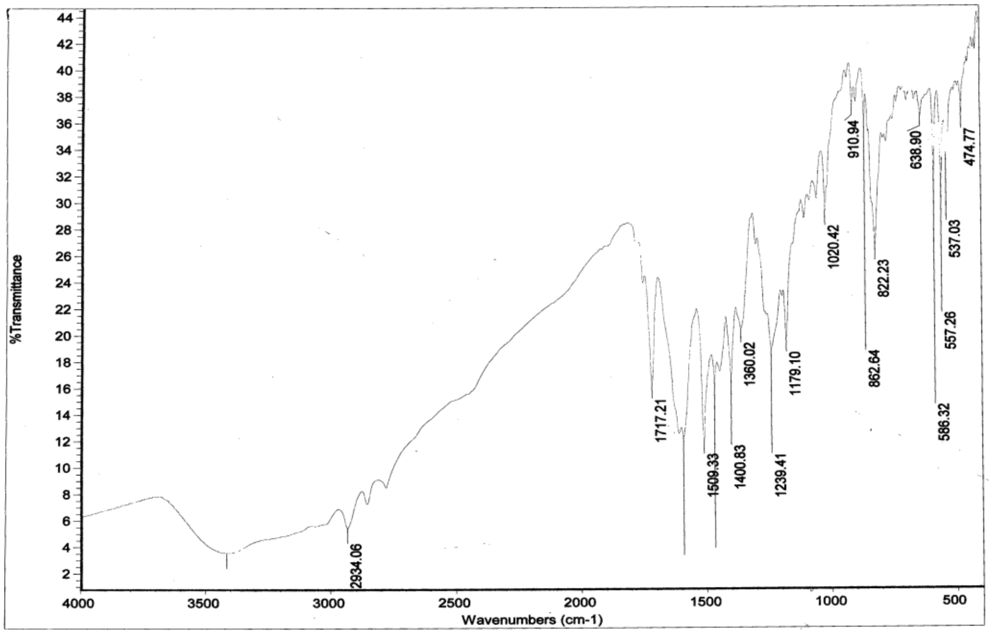


Figure_2 IR spectrum of PE 6 (II)

IR spectral data of PE 6 (II) showed out of plane vibration of *s*-trizaine ring at 822 cm^{-1}, SO_2 stretching vibration of sulphone group at 1179 cm^{-1}, C-H bending vibration of aromatic ring at 910 cm^{-1}, vibration of aryl ether linkage symmetric at 1020 cm^{-1}, C-C (=O)-O ester stretching symmetric at 1179 cm^{-1}, aromatic C-N stretching vibration 1360 cm^{-1}, C-H bending vibration of methyl group at 1400 cm^{-1}, in plane vibration of *s*-triazine ring at 1509 cm^{-1}, C-C (=O)-O stretching vibration of 1717 cm^{-1}, C-H stretching vibration of methylene group at 2934 cm^{-1}.

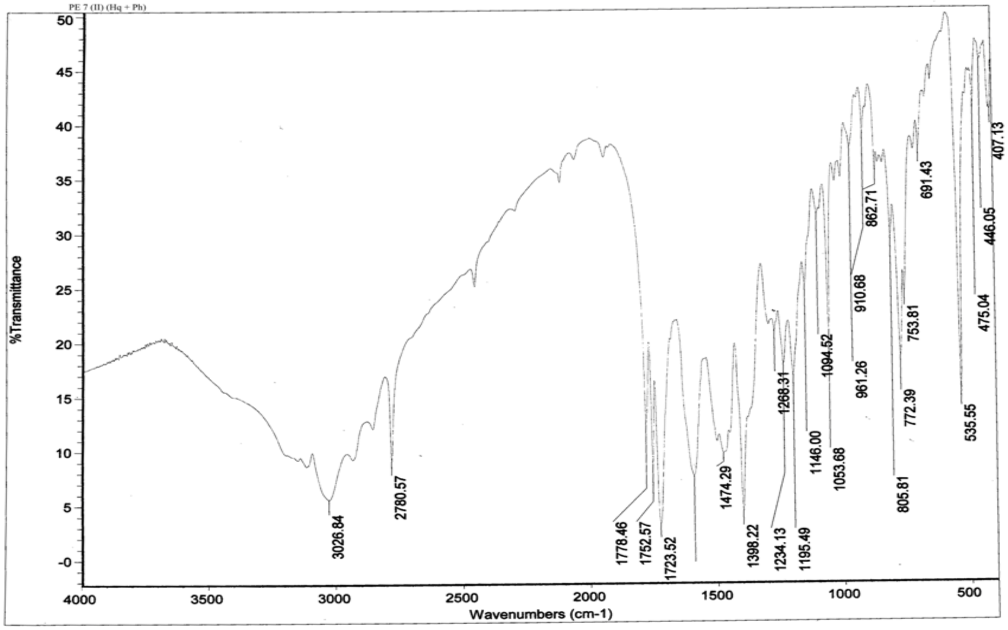


Figure_3 IR spectrum of PE 7 (II)

IR spectral data of PE 7 (II) in out of plane bending vibration of C-H bond of aromatic ring at 753-772 cm^{-1}, out of plane vibration of *s*-triazine ring at 805 cm^{-1}, C-H bending vibration of aromatic ring at 862 cm^{-1}, vibration of aryl ether linkage symmetric at 1053 cm^{-1}, C-C (=O)-O ester stretching symmetric at 1146 cm^{-1}, Vibration of aryl ether linkage Asymmetric at 1268 cm^{-1}, C-H bending vibration of methyl group at 1396 cm^{-1}, In plane vibration of *s*-

triazine ring at 1474 cm^{-1}, C-C (=O)-O ester stretching vibration at 1752 cm^{-1}, C-H stretching vibration of methyl group at 2780 cm^{-1}, C-H stretching vibration of methylene group 3026 cm^{-1}.

^{1}H NMR SPECTROSCOPY:

The ^{1}H-NMR spectra of PE 5 (II) at δ ppm: 8.74 (2H, s, Ar -CH-), 8.25 (2H, d, Ar –CH-), 8.00 (2H, d, Ar –CH-), 7. 91 (2H, d, Ar –CH-), 7.55 (2H, s, Ar –CH-), 7.22-7.38 (11H, m, Ar –CH-), 7.00 (1H, d, Ar –CH-), 6.85 (2H, d, Ar -CH-), 3.69 (4H, t, Methylene -CH_2-), 2.14-1.93 (4H, m, Methylene -CH_2-), 1.49-1.65 (12H, m, methylene -CH_2-).
The ^{1}H-NMR spectra of PE 8 (II) at δ ppm: 8.75 (2H, s, Ar –CH_2-), 8.26 (2H, d, Ar -CH_2-), 8.00 (2H, d, Ar -CH_2-), 7.93 (2H, d, Ar -CH_2-), 7.54 (2H, s, Ar -CH_2-), 7.38 (1H, d, Ar -CH_2-), 7.10-7.35 (9H, m, Ar -CH_2-), 3.70 (4H, t, Methylene -CH_2-), 1.52-1.65 (6H, m, Methylene-CH_2-).

Solubility:-
Polymer samples that swelled without dissolving at 25 °C were heated to 50 °C in order to effect the process of dissolution. Several solvents reported in Table 1 were tested for this purpose.

Table 1:- Solubility of polyesters in different solvents

Solvent	PE 1 (II)	PE 2 (II)	PE 3 (II)	PE 4 (II)	PE 5 (II)	PE 6 (II)	PE 7 (II)	PE 8 (II)	PE 9 (II)	PE 10 (II)
Chloro Benzene	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Benzene	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Toluene	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Chloroform	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Acetone	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +
Carbon Tetrachloride	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Di Methyl Formamide	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +
Ethyl Acetate	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +
Methanol	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Ethanol	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
DMSO	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +
1,4-Dioxane	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +
1,2 Dichloro Ethane	± +	± +	± +	± +	± +	± +	± +	± +	± +	± +
2 Chloro Propanol	± +	± +	± +	± +	± +	± +	± +	± +	± +	± +
Pyridine	+ +	+ +	+ +	+ +	++	+ +	+ +	+ +	+ +	+ +

+ = Soluble, - = Insoluble, + = Partlysoluble, 1st symbole indicates 25 + 1 °C 2nd at 50 + 1 °C.

Density characteristics:-
The density of each copolyster were determine at 25 ± 3 °C by suspending each of the polyesters in a liquid mixture of carbon tetrachloride and acetone and subsequently measuring the density of the liquid mixture by a pycnometer, are presented in Table 2. Density of all the copolyesters varies from 1.204 to 1.165 g/cm^3. The density of copolyesters varies with the different diols used, and decreased in the following order:

PE 2 (II) > PE 7 (II) > PE 6 (II) > PE 8 (II) > PE 9 (II) > PE 1 (II) >
PE 3 (II) > PE 5 (II) > PE 10 (II) > PE 4 (II).

Table 2:- Density of Copolyesters

Polymer Code	Yield (%)	Colour	Density (g /cm^3)
PE 1 (II)	71	Brown	1.187
PE 2 (II)	75	Brown	1.204
PE 3 (II)	83	Brown	1.175
PE 4 (II)	68	Brown	1.165
PE 5 (II)	84	Brown	1.175
PE 6 (II)	79	Black-Brown	1.195

PE 7 (II)	80	Brown	1.199
PE 8 (II)	71	Brown	1.193
PE 9 (II)	67	Brown	1.192
PE 10 (II)	73	Brown	1.169

Viscosity Measurements:-

Intrinsic viscosity, reduced viscosity and inherent viscosity for all the polyesters at various concentration were determined at 25 ± 1 °C. Typical Huggins & Kraemer plots were used to obtain intrinsic viscosity for each of polyesters. Solution viscosity of PE 1 (II) at different concentration is shown in Table 3. The Intrinsic viscosity of the polyesters synthesized from PNCCT and various mixture of diols, decreasing in the following sequence given below:

PE 6 (II) > PE 8(II) > PE 3 (II) > PE 1 (II) > PE 4 (II) > PE 7 (II) > PE 2 (II) > PE 10 (II) > PE 9 (II) > PE 5 (II)

Table 3:- Solution viscosity of copolyester PE 1 (II) Solvent: DMF t_0 = 172 seconds

Sr. No.	**Con. C (g/dl)**	**Flow time (t sec)**	$\eta_{rel} = t/t_0$	$\eta_{sp.} = \eta_{rel} - 1$	$\eta_{red} = \eta_{sp}/C$	$\ln\eta_{rel}/C$
1.	0.2	187.2	1.0883	0.0883	0.4415	0.423
2.	0.4	202.7	1.1784	0.1784	0.446	0.410
3.	0.6	218.8	1.2721	0.2721	0.453	0.401
4.	0.8	235.3	1.3680	0.3680	0.460	0.392
5.	1.0	252.2	1.4662	0.4662	0.466	0.382

Huggins & Kraemer constant for all polyesters were derived from the graph (Figures 1 to 5) is shown in the Table 4.

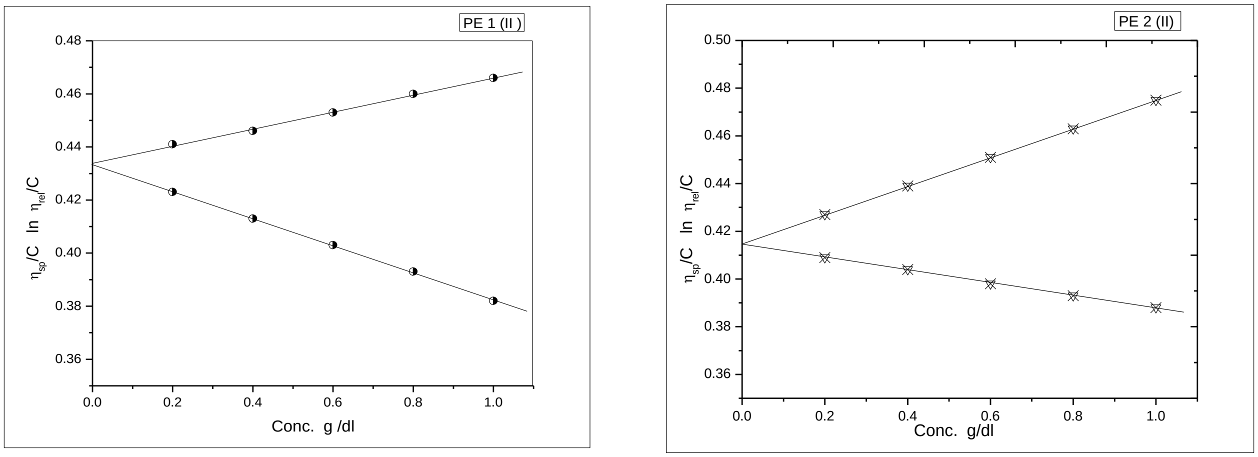


Figure_4 Huggins & Kraemer plot for intrinsic viscosity of PE 1 (II) & PE 2(II)

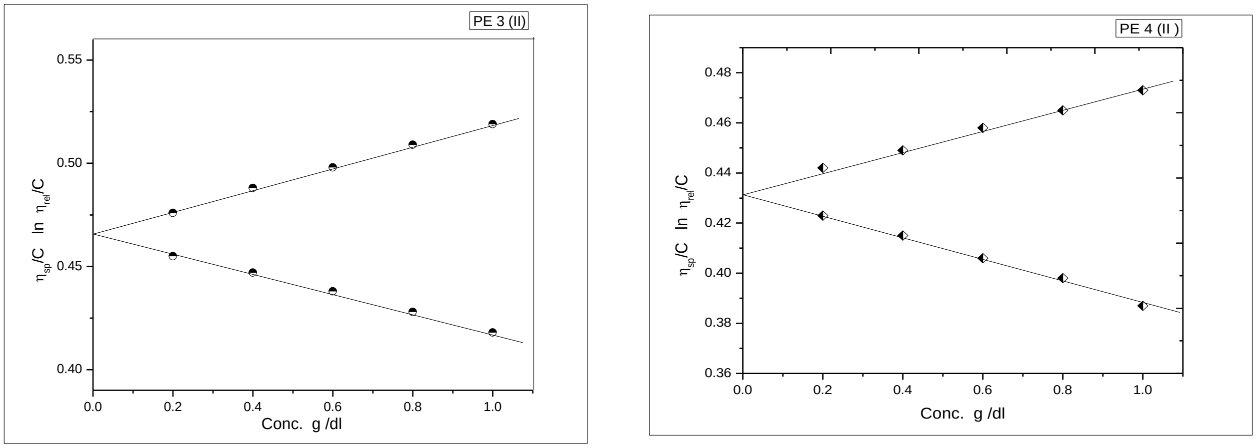


Figure_5 Huggins & Kraemer plot for intrinsic viscosity of PE 3 (II) & PE 4 (II)

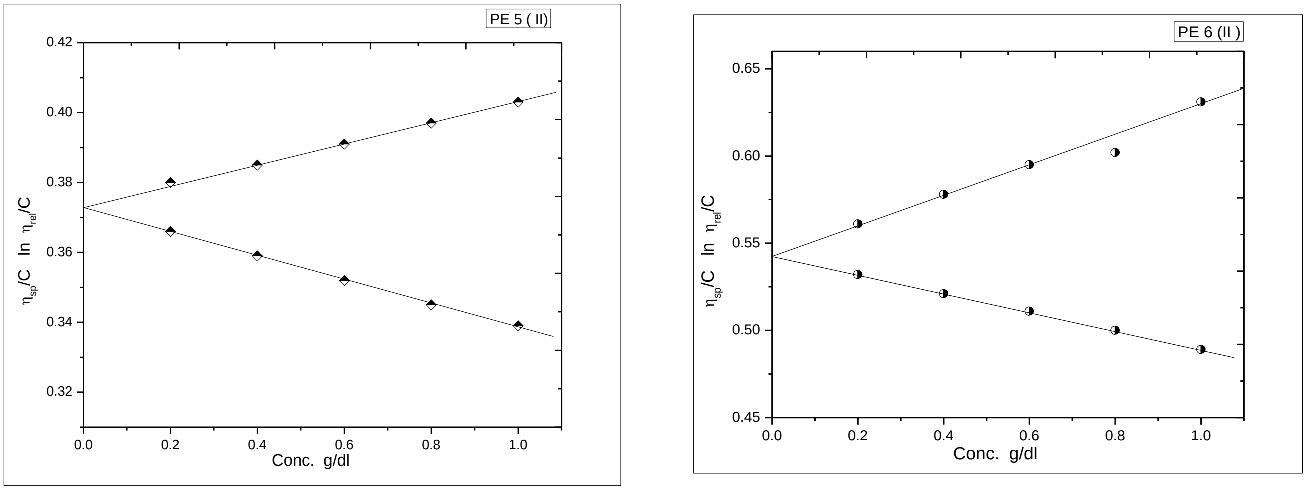


Figure_6 Huggins & Kraemer plot for intrinsic viscosity of PE 5 (II) & PE 6 (II)

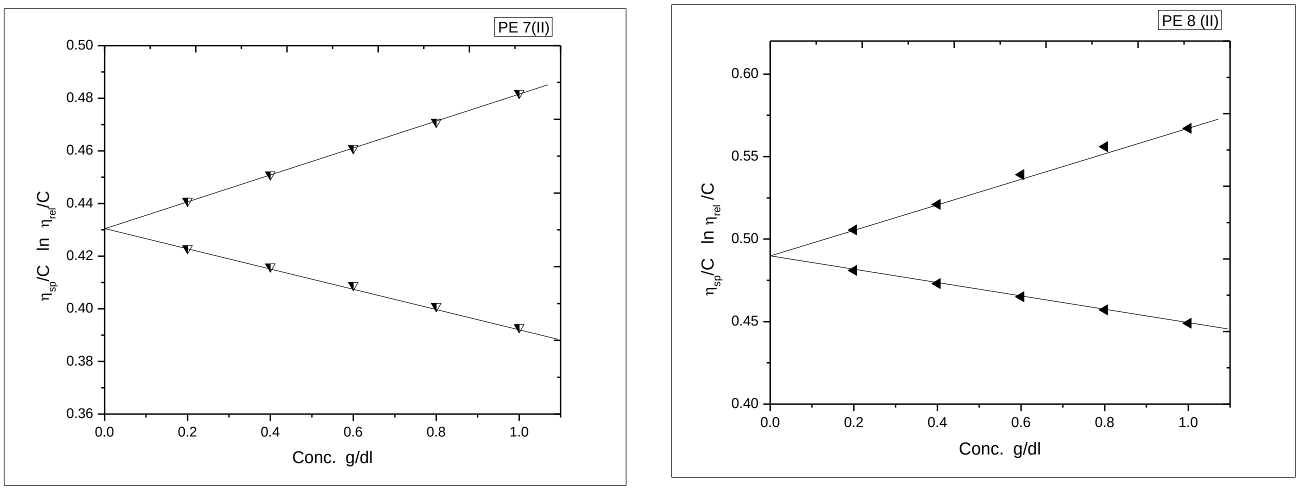


Figure_7 Huggins & Kraemer plot for intrinsic viscosity of PE 7 (II) & PE 8 (II)

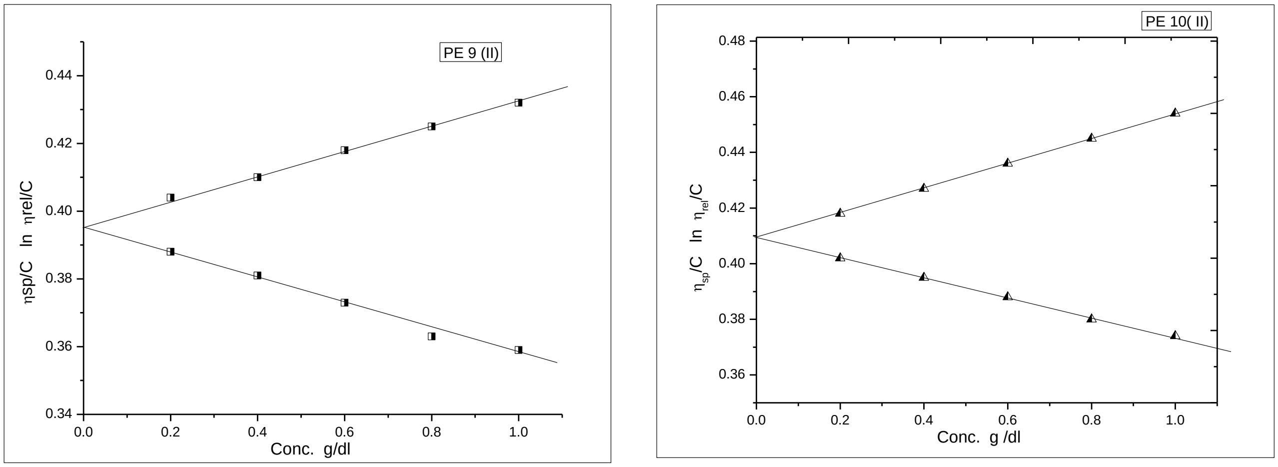


Figure_8 Huggins & Kraemer plot for intrinsic viscosity of PE 9 (II) & PE 10 (II)

Table 4:- Viscosity values and Huggins & Kraemer constant for copolyesters:

Polymer Code	Intrinsic	Reduced	Inherent	Huggins	Kraemer	Huggins	Kraemer

	Viscosity [η]	Viscosity η_{sp}/C	Viscosity $\ln\eta_{rel}$/C	slope	slope	Constant K	Constant β
PE 1 (II)	0.434	0.466	0.382	0.0325	0.052	0.171	0.278
PE 2 (II)	0.415	0.475	0.388	0.060	0.027	0.348	0.156
PE 3 (II)	0.466	0.519	0.418	0.057	0.042	0.244	0.221
PE 4 (II)	0.431	0.473	0.387	0.050	0.043	0.227	0.237
PE 5 (II)	0.373	0.403	0.338	0.027	0.033	0.215	0.251
PE 6 (II)	0.543	0.630	0.489	0.085	0.055	0.295	0.183
PE 7 (II)	0.431	0.481	0.393	0.055	0.045	0.270	0.205
PE 8 (II)	0.490	0.567	0.449	0.080	0.050	0.320	0.170
PE 9 (II)	0.395	0.431	0.359	0.040	0.033	0.230	0.230
PE 10 (II)	0.409	0.454	0.374	0.050	0.036	0.269	0.209

Thermo Gravimetric Analysis:-

TGA of PE 8 (II) and PE 9 (II) obtained at a heating rate of 10 °C/min. in nitrogen atmosphere showed in Figures 9 & 10. The characteristic data are presented in Table 5 gave the following information.

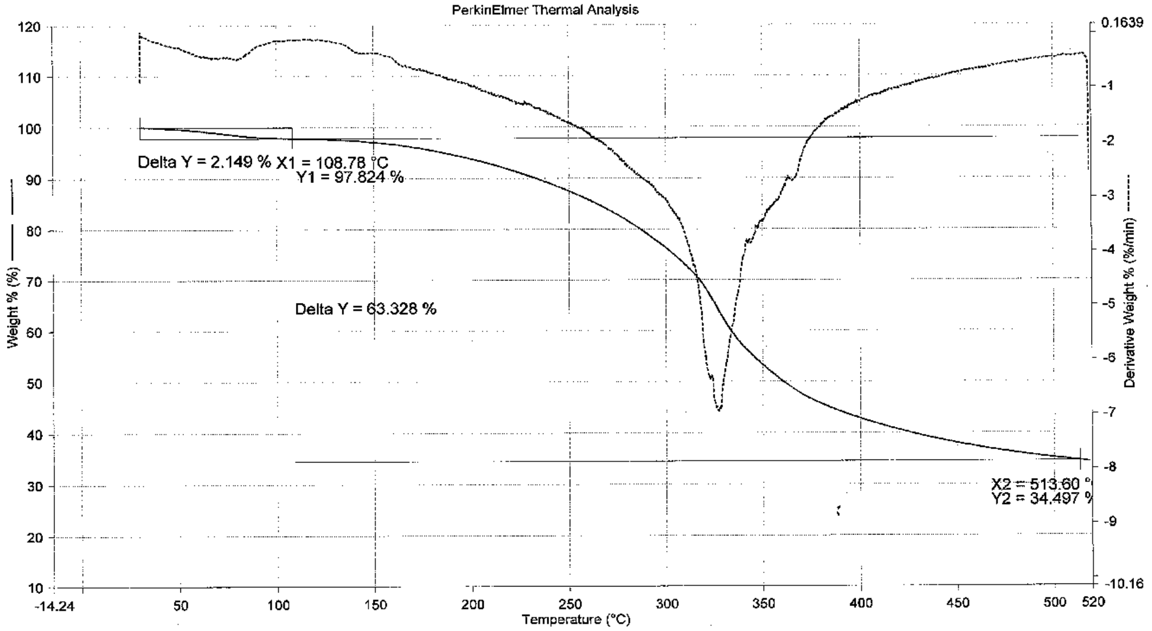


Figure_9 TGA of PE 8 (II)

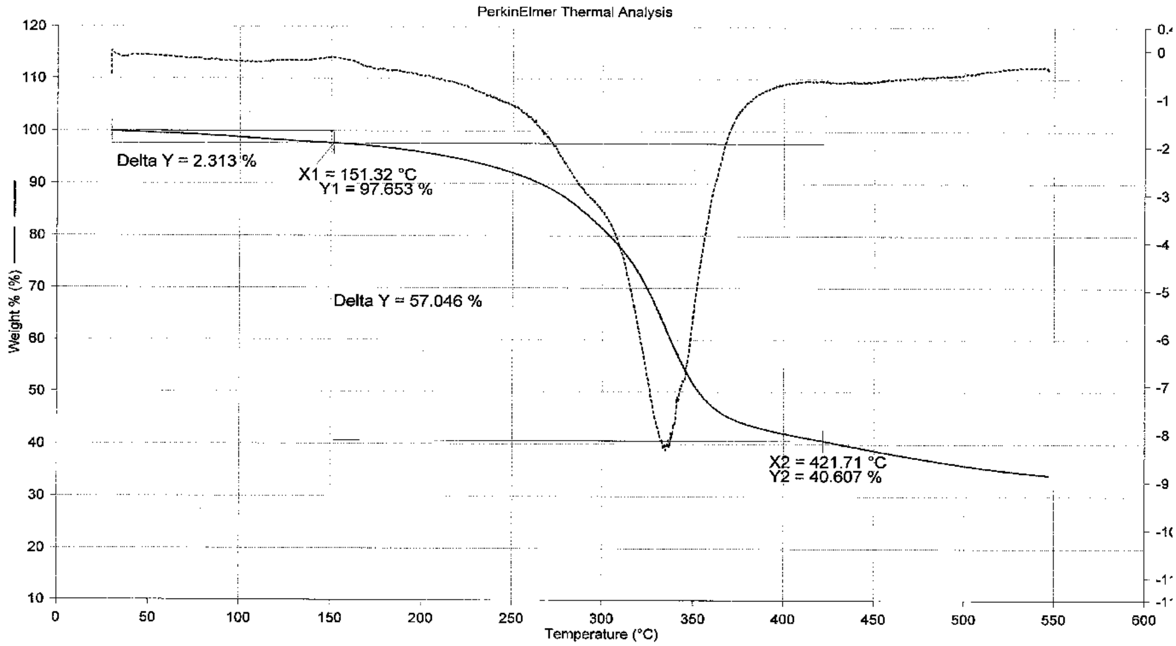


Figure_10 TGA of PE 9 (II)

Table 5:- Thermal data of PE 8 (II) & PE 9 (II)

Polymer	**T_0**	**T_{10}**	**T_{max}**		**T_S**
			Step I	**Step II**	
PE 8 (II)	140	240	320	-	335
PE 9 (II)	170	260	330	-	350

T_0 = Initial decomposition temperature.
T_{10} = Temperature for 10% weight loss.
T_{max} = Temperature for maximum rate of decomposition.
T_S = Half volatisation temperature.

PE 8 (II) decomposes single distinct weight loss step. The polymer begins to decompose at about 150 °C. The decomposition is marked with a rapid weight loss in the temperature range 200 - 450 °C during which the polymer samples losses 54 % of its weight. The maximum rate of weight loss occurs at 320 °C. After 450 °C the samples decomposes up to 520 °C leaving about 34 % residue.

PE 9 (II) decomposes single distinct weight loss step. The polymer begins to decompose at about 170 °C. The decomposition is marked with a rapid weight loss in the temperature range 190 - 400 °C during which the polymer samples losses 54 % of its weight. The maximum rate of weight loss occurs at 330 °C. After 450 °C the samples decomposes up to 550 °C leaving about 34 % residue.

The thermal stability of copolyester on the basis of initial decomposition temperature T_0 is found as follow:
PE 9 (II) > PE 8 (II).
Thermograms have been analyzed as per the graphical methods, proposed by Broido and Horowitz & Metzger.
Broido and Horowitz & Metzger methods are exemplified for PE 8 (II) in Table 6 & 7 respectively while for PE 9 (II) is shown in Tables 8 & 9 and the corresponding plots are shown in Figures 6 & 7 and 8 & 9.

Table 6:- Application of Broido method to thermogram of PE 8 (II):

T °C	**% Wt.**	$Y = \dfrac{W_t - W_\infty}{W_0 - W_\infty}$	**1/ Y**	**ln ln (1/Y)**	**T K**	**1000/ T (K^{-1})**
290	79.42	0.6858	1.4581	-0.9751	563	1.7761
300	76.80	0.6458	1.5484	-0.8273	573	1.745

310	75.20	0.6212	1.6097	-0.7422	583	1.715
320	70.15	0.5443	1.8372	-0.1971	593	1.686
330	62.74	0.4312	2.3191	-0.1729	603	1.658
340	56.92	0.3424	2.9205	0.0692	613	1.631
350	53.46	0.2895	3.4542	0.447	623	1.605

Table 7:- Application of Horowitz- Metzger method to thermogram of PE 8 (II):

T °C	**% Wt.**	**1 - α**	**1/ 1 - α**	**ln ln (1/1- α)**	**T K**	**ϴ**
380	380	79.42	0.6858	1.4581	-0.9751	-30
390	390	76.80	0.6458	1.5484	-0.8273	-20
400	400	75.20	0.6212	1.6097	-0.7422	-10
410	410	70.15	0.5443	1.8372	-0.1971	00
420	420	62.74	0.4312	2.3191	-0.1729	10
430	430	56.92	0.3424	2.9205	0.0692	20
440	440	53.46	0.2895	3.4542	0.447	30

Table 8:- Application of Broido method to thermogram of PE 9 (II):

T °C	**% Wt.**	$Y = \frac{W_t - W_\infty}{W_0 - W_\infty}$	**1/ Y**	**ln ln (1/Y)**	**T K**	**1000/ T (K^{-1})**
300	81.48	0.6282	1.5918	-0.7659	573	1.745
310	77.87	0.5558	1.7992	-0.5321	583	1.715
320	73.08	0.4596	2.1758	-0.2518	593	1.686
330	66.36	0.4336	2.3062	-0.1795	603	1.658
340	58.30	0.2979	3.3568	0.1914	613	1.631
350	51.60	0.1851	5.4024	0.5228	623	1.605
360	47.42	0.1148	8.7108	0.7722	633	1.579

Table 9:- Application of Horowitz- Metzger method to thermogram of PE 9 (II):

T °C	**% Wt.**	**1 - α**	**1/ 1 - α**	**ln ln (1/1- α)**	**T K**	**ϴ**
300	81.48	0.6282	1.5918	-0.7659	573	-30
310	77.87	0.5558	1.7992	-0.5321	583	-20
320	73.08	0.4596	2.1758	-0.2518	593	-10
330	66.36	0.4336	2.3062	-0.1795	603	00
340	58.30	0.2979	3.3568	0.1914	613	10
350	51.60	0.1851	5.4024	0.5228	623	20
360	47.42	0.1148	8.7108	0.7722	633	30

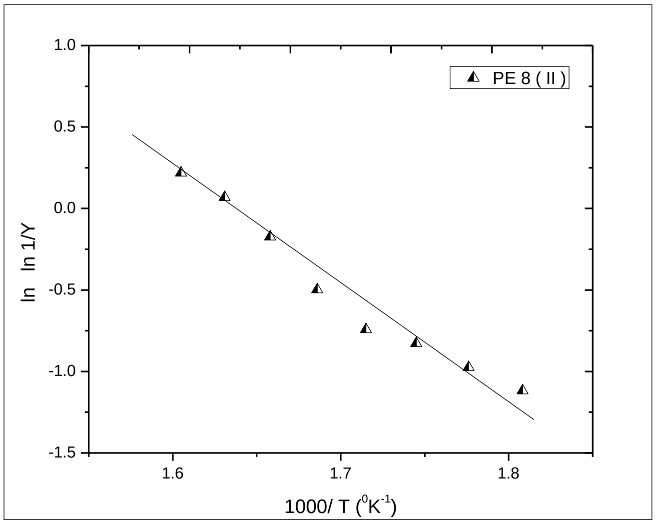


Figure_11 Broido plot for PE 8 (II)

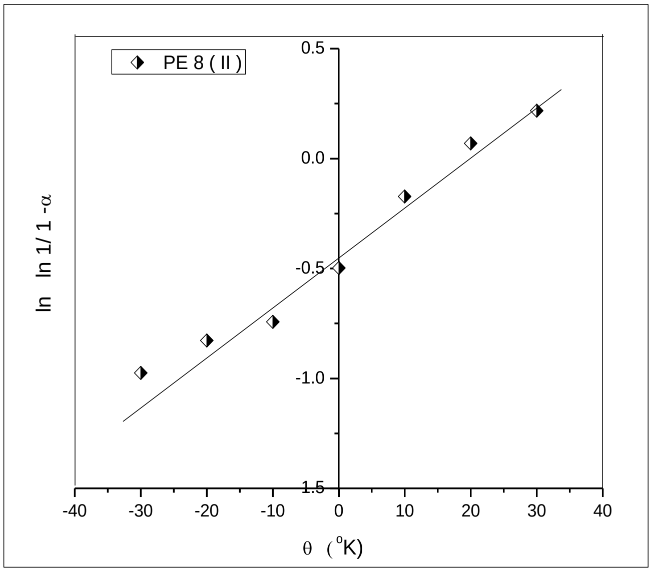


Figure _12 Horowitz- Metzger plot for PE 8 (II)

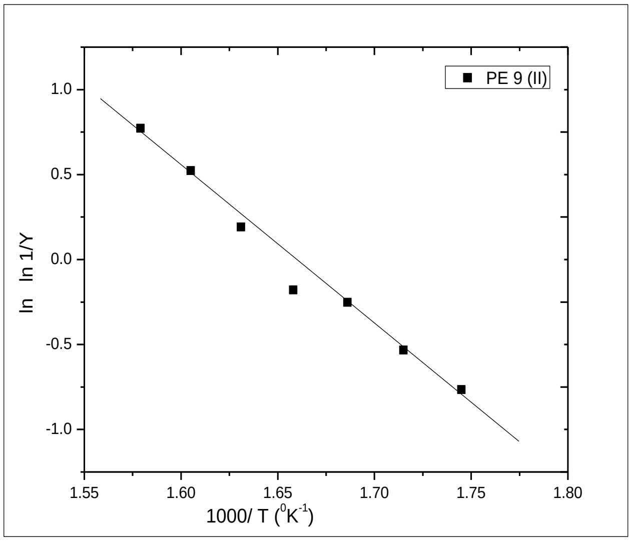


Figure_13 Broido plot for PE 9 (II)

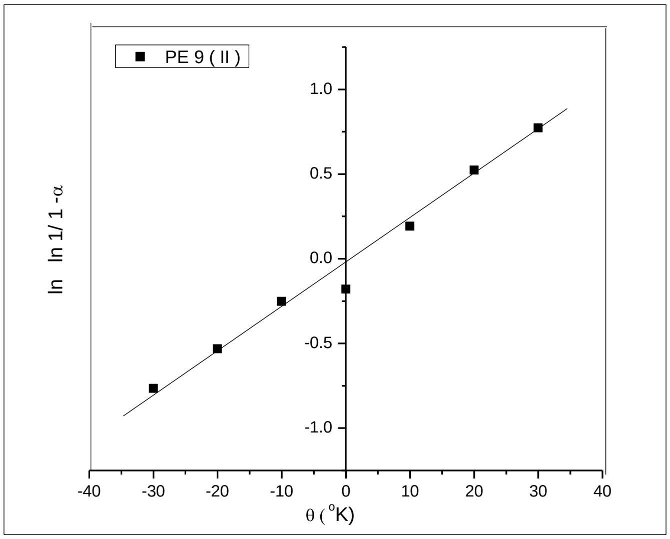


Figure _14 Horowitz Metzger plot for PE 9 (II)

Activation energy calculated by Broido and Horowitz & Metzger method which given in the Table 10.

Table 10:- Activation energy calculated by Broido and Horowitz & Metzger method:

Polymer code	**Broido**		**Horowitz & Metzger**		
	Slope	**Ea (K.Cal/mol)**	**Slope**	**Ts**	**Ea (K.Cal/mol)**
PE 8 (II)	-10.0	19.87	0.029	608	21.30
PE 9 (II)	-9.50	18.91	0.018	623	18.69

Conclusion:-

A series of copolyesters were synthesized from diacid chloride of 2-(*N*-piperidino)-4, 6-dichloro-*s*-triazine [PDCT] and various mixtures of diols. The synthesized polyesters have been found to be soluble in some common solvents like acetone, DMF and DMSO. Density of all the copolyesters varies from 1.204 to 1.165 g/cm^3. The intrinsic viscosity, reduced viscosity and inherent viscosity were determined by using Huggins & Kraemer method. The activation energy was calculated by Broido and Horowitz & Metzger method for PE 8 (II) and PE 9 (II) were found

21.30 and 18.69 kcal/mol respectively. The synthesized polyesters were found to be stable more than 300 °C temperature, thus the polymers can be used for the high temperature application.

Acknowledgements:-

Author like to thank the department of chemistry for providing facilities for research. One of the author also like to thank UGC-BSR for financial support.

Symbols and abbreviations:-

Hq: Hydroquinone,
C: Catachole,
BPC: Bisphenol-C,
BPS: Bisphenol-S
PE 1 (II): PE (Hq + BPA)
PE 2 (II): PE (C + BPA)
PE 3 (II): PE (R + BPA)
PE 4 (II): PE (C + BPC)
PE 5 (II): PE (R + BPC)
BPA: Bisphenol-A,
R: Resorcinol,
Ph: Phenolphthalenine,
PE: Polyester,
PE 6 (II): PE (BPC + BPS)
PE 7 (II): PE (Hq + Ph)
PE 8 (II): PE (Hq + C)
PE 9 (II): PE (Hq + BPS)
PE 10 (II): PE (Hq + EG)

Reference:-

1. J. P. Critchley, G. J. Knight and W. W. Wright Heat-resistant polymers, Plenum Press, New York, (1983).
2. R. B. Seymour and G. S. Krishenbaum, “High Performance Polymers: Their Origin and Development,” Elsevier, New York, (1986).
3. S. W. Kim, S. C. Shim, B. J. Jung and H. K. Shim, Synthesis and properties of new Polymer, J. Polym., Elseviers, 43, 4297 (2002).
4. D. M. Lewis and B. Voncina, Durable press finishing of cotton with polycarboxylic acids and preparation of thiosuccinyl-*s*-triazine, J. Appl. Polym. Sci., 81, 124 (2001).
5. W. T. Wang and S.C. Wu The liquid crystalline state of polyimide precursors. J. Polym. Sci., Polym. Chem. Ed., 26, 2749 (1988).
6. KUS Canan, Synthesis of new substituted 6-(morpholin4-yl)-1H-benzimidazole derivatives, Turk. J. Chem., 26, 559, (2002).
7. P. N. Sojitra, K. C. Patel and H. S. Patel, High Performance Polyamides based on s-Triazine Ring: Synthesis and Characterization, High Performance polymers, 22, 974–988 (2010).
8. P. N. Sojitra and K. C. Patel, Synthesis of polyamides by energy-efficient ultrasonic-assisted direct polycondensation, High Performance polymers, 23(8), 565–574 (2011).
9. H. S. Patel, V.C. Patel, Polyimides containing s-triazine ring, Eur. Polym. J., 37, 2263–2271, 2001.
10. H. S. Patel and K. C. Patel, Synthesis and Properties of Novel Polycyanurates Derived from 2-(*N*-piperidino)-4,6-bis (naphthoxy-2-carbonyl chloride)-*s*-triazine, , Int. J. Polym. Mater., 55, 1043 (2006).
11. H. S. Patel, R. R. Shah and K. C. Patel, Synthesis and Characterization of Polyamides Based on s-Triazine Moiety, Int. J. Polym. Mater., 56, 499 (2007).
12. H. S. Patel, N. B. Patel and K. C. Patel, Studies on Synthesis and Characterization of some Novel Aromatic Copolyesters based on *s*-Triazine, Iran. Polym. J., 14 (12), 1090-1098, 2005.
13. S. T. Asundaria, H. S. Patel and K. C. Patel, Synthesis and studies of homopolyamides based on 2,4-bis(6-chlorocarbonyl-2-naphthyloxy)-6-(4-methyl-1-piperazinyl)-*s*-triazine, Monatsh Chem, 141:917–927, (2010).
14. P. M. Patel, K. C. Patel and S. K. Patel, Studies on synthesis, viscosity, infrared spectra and thermogravimetric analysis of polyesters containing s-triazine ring in the main chain Malaysian Polymer Journal, Vol. 5, No. 1, p 55-67, (2010).
15. B. V. Patel, H. S. Patel, Copolyesters based on s-triazine moiety: Synthesis and characterization, Indian Journal of Chemistry, 47(B), 885-891, (2008).
16. S. T. Asundaria and K. C. Patel, Synthesis and characterization of novel copolyamides based on *s*-triazine derivatives, Int. J. Polym. Mater., 59, 370–386 (2010).
17. S. T. Asundaria, V. B. Patel and K. C. Patel, Synthesis and study of polycyanurates based on 2-carbazol-4, 6-dichloro-s-triazine, Polymer journal, 44 (5), 401-409, (2012).
18. Chun Soo Lee and Kazuyuki Maekawa, *Agricultural and Biological Chemistry*, 40, 4, 785-790 (2016).
19. S. T. Asundaria, V. B. Patel and K. C. Patel, Synthesis and studies of homopolycyanurates based on 2-carbazol-4, 6-dichloro-s-triazine, Russian journal of general chemistry 81 (10), 2183-2192, 2011.

20. M. L. Huggins, Theory of Solutions of High Polymers, J. Am. Chem. Soc., 64, 2716 (1942).
21. E. O. Kraemer, Molecular Weights of Celluloses and Cellulose Derivates, Ind. Eng. Chem. Anal., 30, 1200 (1938).
23. A. J. Broido, Thermal Analysis, Polym. Sci., A-27, 1761 (1969).
24. H. H. Horowitz and G. Metzger, A New Analysis of Thermogravimetric Traces, Anal. Chem., 35, 1464 (1963).