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Synthesis and thermal studies of polyesters derived from 6-(N-(3-Chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetylchloride)-1,3,5-triazine

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ABSTRACT

Polyesters containing substituted s-triazine ring in the backbone were synthesised by high temperature polycondensation of 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetylchloride)-1,3, 5-triazine with different diols such as Bisphenol-A, diethylene glycol, resorcinol, catechol, phenolphthalein, 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,8-dihydroxyanthraquinone, hydro quinone and ethylene glycol. All polyesters were obtained in good yield and were characterized by solubility, Viscosity measurement, FTIR and NMR spectral analysis. Thermal stability was studied by TGA technique. The synthesized polyester showed good thermal stability along with good solubility in common organic solvent.

Highlights:

- Polyesters containing substituted s-triazine ring in the backbone
- High Temperature polycondensation reaction
- Characterized by solubility, Viscosity measurement, FTIR and NMR spectral analysis
- The synthesized polyester showed good thermal stability
- Good solubility in common organic solvents

Keywords: Broido method, Horowitz and Metzger method, High temperature polycondensation, Polyesters, Triazine, Thermal Analysis.

INTRODUCTION

During the past few decades, the constant and increasing requirements of the automotive, aerospace, microelectronics and military industries have provided the driving force for the development of new high-performance polymers [1]. Aromatic polyesters containing the s-triazine ring in the main chain are known for their excellent high temperature properties, and several were commercialized as high-performance engineering plastic materials [2-3]. The attraction of the triazine building block derives from opportunities for molecular recognition and synthetic tailorability [4]. The s-triazine rings have been incorporated into the backbone of thermally stable polymers such as polyesters [5-6], polyamides-imides [7], polyimides [8], polyazomethines [9], polyureas [10], polysulfides [11], poly(arylene ethylene)s [12], and polyamides [13-

16]. It is known that polymers containing s-triazine as a heterocyclic unit in the main chain exhibit excellent thermal stability with improved solubility [17].

In the present investigation, the authors describe the synthesis of 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetylchloride)-1,3,5-triazine followed by its high temperature poly condensation with different types of diols such as Bisphenol-A, diethylene glycol, resorcinol, catechol, phenolphthalein, 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,8-dihydroxyanthraquinone, hydroquinone and ethylene glycol. To characterize the synthesized polymer sample, the study of solubility, viscosity measurement, IR spectra, NMR spectra and thermal behaviour have been carried out.

MATERIALS AND METHODS

Materials: The monomer 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetyl chloride)-1,3,5-triazine was synthesized as per the reaction shown in Figure 1. To prepare the solutions, double distilled water was used. N-(3-Chlorophenyl)piperazine was received from Ami Organics Pvt Ltd. Cyanuric chloride (Fluka) was purified by repeated crystallization from pure benzene. Citric acid (Fisher Scientific), resorcinol (Merck), catechol (Merck), hydroquinone (Merck) and phenolphthalein (Fisher Scientific) were used as received. 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone, 1,8-dihydroxyanthraquinone, Ethylene glycol and diethylene glycol were received from Atul Ltd, Atul. Chemicals such as thionyl chloride, sodium bicarbonate, sodium hydroxide were used as received from Fisher Scientific. Dimethylformamide dimethylsulfoxide, chloroform and other solvents were all laboratory reagents and were used as received from Fisher Scientific.

Synthesis of 7-hydroxy coumarin-4-acetic acid [HCA]: 7-hydroxy coumarin-4-acetic acid was synthesized as per reported method [18]. Citric acid (21g, 0.1mol) was heated with Conc. H_2SO_4 (32mL) at 60-65°C with constant stirring avoiding excess foaming. Then resorcinol (11g, 0.1mol) was added with vigorous stirring at 0-5°C over a period of 1-1.5 h. Stirring was continued at 5°C for 2 h. The reaction mixture was allowed to stand for 24 h at 30°C. Then the solution was poured into ice and water. The Solid was filtered and dissolved in saturated $NaHCO_3$ solution followed by clarification with activated charcoal and filtration. The filtrate was acidified with conc. HCl to collect 7-hydroxy coumarin-4-acetic acid.

Synthesis of 2,4-dichloro-6-(N-(3-chlorophenyl)piperazinyl)-1, 3, 5-triazine [CT]: A solution of Cyanuric Chloride (18.44g, 0.1mol) in acetone (60mL) was added with stirring to a cooled solution (0-5°C) of sodium bicarbonate (10.6g) in distilled water (100mL), in a three-necked flask (250mL) equipped with a mechanical stirrer. This resulted in the formation of slurry of cyanuric chloride. A solution of N-(3-chlorophenyl) piperazine (16.6mL, 0.1mol) in acetone (50mL) was added to the cold slurry of cyanuric chloride. The mixture was stirred for 3 h at 0-5°C. The white colored product was filtered, and recrystallized from ethanol and dried in vacuum desiccators. The yield was 92%.

Synthesis of 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-aceticacid)-1, 3, 5-triazine [CHT]: A solution of 2,4-dichloro-6-(N-(3-chlorophenyl)piperazinyl)-1,3,5-triazine [CT] (34.5g, 0.1mol) in acetone (60mL) was mixed with a solution of NaOH (16g, 0.4mol) and 7-hydroxycoumarin-4-acetic acid (HCA) (41.0g, 0.2mol) in double distilled water (80mL). Reaction was stirred for 2 h at room temperature and 2 h at 80°C. The separated solid was collected and washed with hot water. The product was dried in vacuum at 100°C. The yield was 87%. The product was recrystallized from acetone.

Synthesis of 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetylchloride)-1,3,5-triazine [CHAT]: Thionyl chloride (11.9ml, 0.1mol) was added into 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetic acid)-1,3,5-triazine [CHT] (7.2g 0.01mol) in a dry round bottom flask. The reaction mixture was refluxed at 78°C for 2 h. At the end of the reaction, excess thionyl chloride was distilled and dry product was collected. The yield was about 83%. The product was recrystallized from dimethyl formamide.

Synthesis of polyester of Bisphenol-A: 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetylchloride)-1,3,5-triazine [CHAT] (7.49g, 0.01mol) was taken into the minimum quantity of dimethylformamide (10mL) in a round bottom flask and then stirred thoroughly. Then initiator citrimide (0.25g) was added and heated up to 150°C. Bisphenol-A (4.56g, 0.02mol) was added into the reaction mixture and the temperature was raised to 160-180°C and heated for 8 h. The reaction mixture was cooled and poured into 250mL of ice-cooled water with constant stirring. The solid was filtered, washed with hot water and finally with methanol to remove unreacted monomer and dried. The yield was about 70%.

The other polyesters from 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetyl chloride)-1,3,5-triazine [CHAT] and various diols were synthesized by the similar method as mentioned above (See Figure 2).

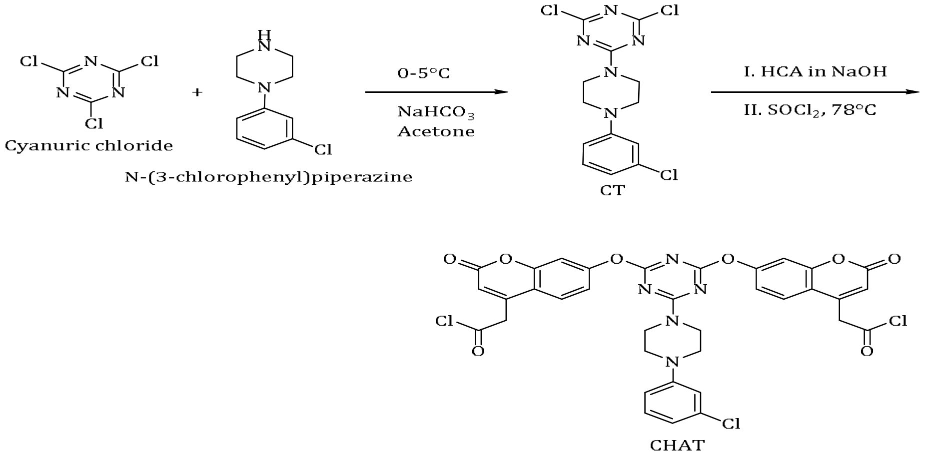

Figure 1: Reaction scheme for the synthesis of 6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetyl chloride)-1,3,5-triazine [CHAT]

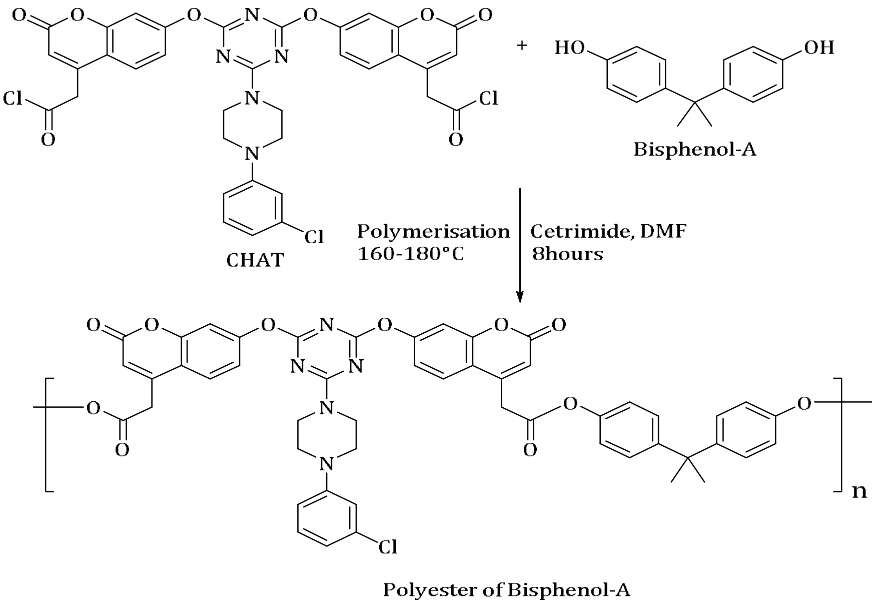

Figure 2: Reaction scheme for the synthesis of polyester from CHAT and Bisphenol-A

Measurements: Solubility tests were conducted with several solvents. Infrared spectra of the synthesized polymers were measured using KBr pellets on a PerkinElmer FTIR Spectrometer Spectrum RX I (RX-1). Nuclear magnetic resonance (NMR) spectroscopy of the polymers was carried out using deuterated dimethylsulphoxide as a solvent. NMR spectra were recorded on a 400Mhz sophisticated multinuclear FT NMR Spectrometer model Avance-II (Bruker) for the structure elucidation. The Viscosities of polyesters were conveniently measured using an Ubbelohde capillary Viscometer. The thermograms of polyesters were obtained on a Perkin Elmer Pyris-6 TGA system at a constant heating rate of 10°C/min in the temperature range from ambient temperature to 800°C.

RESULTS AND DISCUSSION

High temperature polycondensation of CHAT with various diols have been investigated in detail to examine various physicochemical properties such as yield, colour, solubility, viscosity, FTIR spectro scopy, NMR spectroscopy and thermal behaviour.

Yield and colour: Polyesters obtained from CHAT and various diols have unique colours. Table 1 shows the colour and the yield of synthesized polyesters. Bisphenol-A, diethylene glycol, catechol and hydroquinone containing polyester are brown in colour. Resorcinol and phenolphthalein containing polyesters are Light coffee in colour. 1,4-dihydroxyanthraquinone and 1,8-dihydroxyanthraquinone containing polyesters are respectively maroon and greenish brown in colour. 1,5-dihydroxyanthraquinone and ethylene glycol containing polyesters are respectively light brown and dark brown in colour.The yield of these polyesters varies from 76% to 59%. Highest yield of 76% is obtained from 1,4-dihydroxyanthraquinone and lowest yield of 59% is obtained from bisphenol-A.

Table 1: Yield and Colour of polyesters

No.	Code	Colour	Yield
1.	CP-21	Brown	59%
2.	CP-22	Brown	62%
3.	CP-23	Light Coffee	65%
4.	CP-24	Brown	64%
5.	CP-25	Light Coffee	73%
6.	CP-26	Maroon	76%
7.	CP-27	Light Brown	73%
8.	CP-28	Greenish Brown	75%
9.	CP-29	Brown	66%
10.	CP-30	Dark Brown	60%

Solubility: Relative solubility of various polyesters obtained from CHAT in different solvents is presented in table 2. Examination of the information presented reveals that polyesters obtained from CHAT are insoluble in aliphatic chlorinated solvents like chloroform and carbon tetrachloride. It is also found that polyesters are insoluble in halogenated and non-halogenated aromatic solvents like chlorobenzene and benzene. Polyesters are insoluble in tetrahydrofuran and ether. Polyesters are partly soluble in acetone, methanol, ethanol, n-butanol, isopropyl alcohol and ethyl acetate. Polyesters are completely soluble in dimethylformamide and dimethyl sulfoxide. It is noticed that solubility increased with temperature and those polyesters, which are partly soluble at 25°C get dissolve at higher temperature.

Viscosity: The polyesters solution were prepared in dimethylformamide and filtered through G-3 sintered glass funnel prior to flow time measurements. Intrinsic, Reduced and Inherent viscosity for all the polyesters at various concentrations were determined at 25 ± 0.1°C. Typical Huggins and Kraemer plots were used to obtain intrinsic viscosity for each of polyesters. Intrinsic, reduced and inherent viscosities along with Huggin's and Kraemer's constants for 1% solution are shown in Table 3. Examination of intrinsic viscosities of polyesters from CP-21 to CP-30 reveals that CP-21 has the highest solution viscosity, whereas CP-30 has the lowest. The intrinsic viscosity of the polyesters obtained from CHAT follows the sequence given below:

CP-21>CP-25>CP-26>CP-28>CP-27>CP-23>CP-29>CP-24>CP-22>CP-30

Table 2: Relative Solubility of Polyesters

Solvent	*CP-21*	*CP-22*	*CP-23*	*CP-24*	*CP-25*	*CP-26*	*CP-27*	*CP-28*	*CP-29*	*CP-30*
DMF	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Chloroform	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
CCl_4	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Acetone	± +	+ +	+ +	+ +	± +	± +	± +	± +	+ +	+ +
Benzene	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Cl-Benzene	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Methanol	± ±	± +	± +	± +	± ±	± ±	± ±	± ±	± +	± +
Ethanol	± ±	± +	± +	± +	± ±	± ±	± ±	± ±	± +	± +
THF	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
n-Butanol	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
IPA	± ±	± +	± +	± +	± ±	± ±	± ±	± ±	± +	± +
Ether	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Ethyl Acetate	± +	± +	± +	± +	± +	± +	± +	± +	± +	± +

\+ = Soluble, **-** = Insoluble, ±= Partly soluble. The first and second symbol indicates the solubility of polyesters at Room Temperature and at 50°C respectively.

Table 3: Various viscosity values and Huggins's and Kraemer's constants

Polymer	*Intrinsic Viscosity [η]*	*Reduced Viscosity $\eta_{sp/C}$*	*Inherent Viscosity ln $\eta_{rel/C}$*	*Huggin's constant K'*	*Kraemer's constant K''*
CP-21	0.667	0.723	0.544	0.119	0.265
CP-22	0.394	0.676	0.516	0.363	0.144
CP-23	0.491	0.626	0.486	0.247	0.211
CP-24	0.420	0.614	0.479	0.235	0.224
CP-25	0.595	0.565	0.448	0.222	0.218
CP-26	0.560	0.550	0.438	0.210	0.226
CP-27	0.515	0.533	0.427	0.180	0.250
CP-28	0.536	0.462	0.380	0.275	0.190
CP-29	0.457	0.450	0.372	0.375	0.136
CP-30	0.368	0.407	0.342	0.277	0.202

IR Spectroscopy: Several common characteristic absorption frequencies were observed in the IR spectra of synthesized polyesters. The typical characteristic FTIR bands observed around 1600-1621 cm^{-1} which may confirm the >C=O stretching frequency of the ester group. The polyesters exhibit bands at around 1703-1738 cm^{-1} that may be due to the >C=O stretching frequency of the lactone ring. The polyesters exhibit bands at around 3295-3357 cm^{-1} which attribute due to the stretching vibrations of –OH group. The FTIR bands around 1453-1466 cm^{-1} and 803-811 cm^{-1} may be due to the in plane and out plane vibrations of s-triazine respectively. The bands observed around 1130-1146 cm^{-1} and 720-728 cm^{-1} may attribute to the in plane and out plane –C-H bending vibrations of an aromatic ring. Furthermore, the band at 840-846 cm^{-1} support the presence of aromatic –C-H. The presence of ether linkage is supported by the appearance of a band at1230-1238 cm^{-1} and 1015-1030cm^{-1}. In addition to this, the spectra exhibited few other IR absorption frequencies, based on which these polyesters can be distinguished from each other. All these IR spectral features seem to confirm the assumed chemical structure of the polyesters.

NMR Spectra: High resolution NMR spectra of solution of polyesters were measured in deuterated dimethylsulphoxide using TMS as an internal reference. As a representative, the assignments of the chemical shifts for^{1}H-NMR spectrum of polyester CP-23 is given.
In ^{1}H-NMR spectrum of CP-23 the singlet at 2.82δ confirms the presence of two protons of -CH_2- group of coumarin. The multiplet signal of aromatic protons appears at 6.10-8.19δ. Chemical Sifts at 3.33δ and 3.70δ prove the presence of -CH_2- group of N-(3-Chlorophenyl)piperazine ring in the structure.

Thermogravimetric Analysis: For the qualitative assessment of relative thermal stability of polymers, several temperature characteristics are used which includes initial decomposition temperature (T_0), temperature for 10% weight loss (T_{10}), temperature for maximum rate of decomposition (T_{max}) and half volatisation temperature (T_s). The temperature characteristic of polyesters is shown in table 4.

Table 4: Temperature characteristic of polyester

Polymer	**T_0(°C)**	**T_{10}(°C)**	**T_{max}(°C)**	**T_S(°C)**
CP-25	190	280	300	560
CP-26	170	273	290	640
CP-27	203	240	282	410
CP-28	170	255	290	450
CP-30	230	266	330	377

The thermogram of CP-25 reveals that the decomposition occurs in a single step. Decomposition initially starts at 190°C which is supported by the TGA. Its maximum rate of decomposition found at 300°C and at that moment 13% weight loss is shown by polyester. 31% weight loss is shown between the temperature range of 217-377°C, after this moment sample degrades slowly and shows total 59% weight loss at 780°C. From the thermogram of CP-26, it is observed that the decomposition occurs in a single step. Decomposition initially starts at 170°C which is supported by the TGA. Its maximum rate of decomposition found at 290°C and at that moment 16% weight loss is shown by polyester. 27% weight loss is shown between the temperature range of 232-368°C, after this moment sample degrades slowly and shows total 56% weight loss at 780°C. The thermogram of CP-27 reveals single step degradation. Decomposition initially starts at 203°C. Its maximum rate of decomposition found at 282°C and at that moment 17% weight loss is shown by polyester. 38% weight loss is shown between the temperature range of 204-340°C. After 400°C, sample degrades slowly and shows total 66% weight loss at 780°C. The thermogram of CP-28 also shows single step degradation. The polyester begins to decompose at 170°C. 10% weight loss is observed at 255°C. The maximum rate of weight loss occurs at 290°C and that moment around 20% weight loss is shown by polyester. 40% weight loss is shown between the temperature ranges of 201-394°C. After 394°C polyester degrade slowly upto790°C and leaves about 27% residue. The thermogram of CP-30 shows one step degradation. From TGA it is observed that decomposition starts at

230°C. 10% weight loss is observed at 266°C. The maximum rate of weight loss occurs at 330°C and that moment around 28% weight loss is shown by polyester. 56% weight loss is shown between the temperature ranges of 238-398°C, the sample degrades slowly up to the end temperature and leaves about 12% residue.

Comparison of T_{10} for polyesters indicates the following decreasing order of thermal stability:
CP-30>CP-27>CP-25>CP-26, CP-28

A comparison of thermal stability based on T_{max} reveals that the thermal stability of the polyesters decreases in the following order:
CP-30>CP-25>CP-26, CP-28>CP-27

Evaluation of Kinetic Parameters: TGA thermograms obtained at a heating rate 10°C/min have been examined as per proposed by Broido [19] and Horowitz-Metzger [20]. A typical application of Broido's method [21-22] is shown in table 5. The Horowitz-Metzger method is shown in Table 6.

Table 5: Broido calculations for the TGA of CP-27

T(°C)	W_t residue	$Y=W_t-W_\infty/W_0-W_\infty$	1/Y	ln ln(1/Y)	T K	$1/T\times10^3K^{-1}$
290.26	7.808	0.6286	1.5907	-0.7674	563.26	1.78
300.26	7.395	0.5691	1.7573	-0.5731	573.26	1.74
310.26	6.959	0.5061	1.9760	-0.3841	583.26	1.71
320.26	6.553	0.4473	2.2356	-0.2175	593.26	1.69
330.26	6.181	0.3935	2.5412	-0.0697	603.26	1.66

Table 6: Horowitz & Metzger's calculations for the TGA of CP-27

T(°C)	W_t residue	$1-\alpha$	$1/1-\alpha$	$\ln\ln(1/1-\alpha)$	θ K
290.26	7.808	0.6286	1.5907	-0.7674	-20
300.26	7.395	0.5691	1.7573	-0.5731	-10
310.26	6.959	0.5061	1.9760	-0.3841	0
320.26	6.553	0.4473	2.2356	-0.2175	10
330.26	6.181	0.3935	2.5412	-0.0697	20

The straight lines in Broido and Horowitz & Metzger's plots are due to linear regression analysis of the experimental data. The values of apparent activation energy corresponding to degradation steps involved are evaluated from the data and are presented in table 7. An examination of an energy of activation E in Table 7 reveals that both the methods yield comparable value for E. The experimental points corresponding to the initial stage of thermal degradation tended to deviate from linearity. This deviation may be due to the fact that the decomposition of solid does not obey the first order of kinetics in initial stages.

Table 7: Energy of Activation (K.calmole^{-1}) calculated according to the method of Broido and Horowitz & Metzger's for the thermal decomposition of polyester

Polymer	**Energy of activation E (K.calmole^{-1})**	
	Broido method	Horowitz and Metzger's method
CP-25	13.39	25.56
CP-26	9.18	21
CP-27	11.83	16.23
CP-28	10.82	16.05
CP-30	14.23	14.50

Broido method is expected to provide comparatively reliable estimates of E than Horowitz-Metzger method as no other temperature characteristics are involved. The value of activation energy calculated according to the Horowitz and Metzger's method are in good agreement with these values.

APPLICATIONS

Several polyesters containing s-triazine ring have been synthesised by high temperature poly condensation reaction. The synthesised polymers exhibited excellent thermal stability and good solubility. Thus, these polymers can be considered as promising, processable, high-temperature-resistant, high-performance polymeric materials and these polyesters may be useful for applications in automobile and marine engineering.

CONCLUSIONS

A series of polyesters containing s-triazine ring in the backbone was synthesized by the high temperature polycondensation reaction. The properties of polyesters depend upon the structure and mode of their preparation. The introduction of s-triazine rings and flexibilizing linkages in the backbone of aromatic polyesters afforded soluble polymers with good thermal stability. Thus, these polymers can be considered as promising, processable, high temperature-resistant polymeric materials.

Abbreviations:

CP-21	Polyester of Bisphenol-A
CP-22	Polyester of Diethylene glycol
CP-23	Polyester of Resorcinol
CP-24	Polyester of Catechol
CP-25	Polyester of Phenolphthalein
CP-26	Polyester of 1,4-Dihydroxyanthraquinone
CP-27	Polyester of 1,5-Dihydroxyanthraquinone
CP-28	Polyester of 1,8-Dihydroxyanthraquinone
CP-29	Polyester of Hydroquinone
CP-30	Polyester of Ethylene glycol
CHAT	6-(N-(3-chlorophenyl)piperazinyl)-2,4-bis-(7-hydroxycoumarin-4-acetyl chloride)-1,3,5-triazine
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.

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