

Studies on Synthesis and Physico-chemical Properties of some Novel Linear Homopolyesters Based on *s*-Triazine

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ABSTRACT

Eleven homopolyesters were synthesized by high temperature polycondensation of 2-(*N*-ethylanilino)-4,6-bis (phenoxy -2-carbonyl- chloride)-*s*-triazine [EAPCCT] with each of the following eleven diols: bisphenol-A (BPA), bisphenol-C (BPC), phenolphthalein (Ph), 1, 8-dihydroxyl anthraquinone (DHA-1,8), 1,4-dihydroxy anthraquinone (DHA-1,4), resorcinol (R), hydroquinone (Hq), catechol (C), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG). All the polyesters were characterized by solubility, density, and viscosity measurements, IR spectroscopy and thermogravimetric analysis methods. All the polyesters were soluble at high temperature in acetone, dimethylformamide, dimethylsulphoxide, dimethylacetamide, etc. and have reduced viscosities in the range 0.486-0.699 dL/g in the dimethylformamide at 30°C. Homopolyesters derived from 1,4-dihydroxy anthraquinone showed greater thermal stability than the other polyesters.

Key Words:

Polyesters;
2-(*N*-ethylanilino)-4,6-bis(phenoxy-2-carbonyl chloride)-*s*-triazine;
high temperature polycondensation;
IR spectroscopy;
thermogravimetric analysis.

INTRODUCTION

A survey of literature reveals that the polymers based on *s*-triazine and its derivatives have been extensively studied and utilized since 1950's. Extensive literature exists on thermally stable polymers in which aromatic and heterocyclic rings are

linked together in the main chain [1,2]. Aromatic polyesters containing *s*-triazine ring in the main chain are known for their excellent high temperature properties and several commercially available as high performance engineering plastic materials.

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The polymer containing *s*-triazine ring moiety in their backbone are unique in the sense of exhibiting unusual combination of properties such as high softening temperature and thermal stability together with solubility [3-5]. There are many reports about synthesis leading to linear polyesters from polycondensation of diacid chloride with diols [6-8]. The linear polyesters of high molecular weight afford synthetic fibres of excellent properties [9]. The presence of *s*-triazine ring in the polyester chain may alter the properties of polymers to great extent. Hence it was thought interesting to synthesize and characterize polyesters based on *s*-triazine.

EXPERIMENTAL

Materials

Dimethylformamide, methanol, acetone and other common chemicals used were laboratory grade reagents. Cyanuric chloride (Fluka mp 146°C) was purified by recrystallization from pure benzene. BPA (Resin grade, Cibatul, mp 156°C) was repeatedly crystallized from 50% aqueous acetic acid and finally recrystallized from benzene. Phenolphthalein (BDH, mp 262°C) was purified by crystallization from ethanol; resorcinol, catechol, and hydroquinone (Sisco lab) were purified by recrystallization from rectified spirit. 1,8- and 1,4-dihydroxy anthraquinone (Sisco Lab) were purified by recrystallization from aqueous alcohol. Ethylene glycol, diethylene glycol and triethylene glycol (Merck) were used as received.

Material Synthesis

Bisphenol-C (BPC) [10] (mp 187°C) was synthesized by published procedure and was crystallized from benzene.

Synthesis of Monomer EAPCCT

2-(*N*-Ethylanilino)-4,6-bis(phenoxy-2-carbonyl chloride)-*s*-triazine is prepared by the following reaction Scheme I. The procedure adopted for the synthesis of monomer is described as follows:

2-(*N*-Ethylanilino)-4, 6-dichloro-*s*-triazine (EADCT)

A solution of cyanuric chloride (18.44 g, 0.1 mol) in a 60 mL acetone was added along with stirring to a cold solution (0.5°C) of sodium bicarbonate (9.4 g, 0.1 mol) in 100 mL of distilled water, in a three-necked flask (250 mL), equipped with a mechanical stirrer. This

resulted in the formation of slurry of cyanuric chloride. A solution of *N*-ethylaniline (12.7 mL, 0.1 mol) in 10 mL acetone was added to the cold slurry of cyanuric chloride. After some time the reaction mixture was neutralized by saturated solution of sodium bicarbonate. The mixture was stirred for 2 h at 0-5°C. The white coloured product was filtered and recrystallized from ethanol and dried in a vacuum desiccator, with yield 90% and mp 127°C.

If the reaction had been carried out in water the reaction would be incomplete and with low yield. But the yield improved considerably if the cyanuric chloride was freshly precipitated by pouring an acetone or dioxane solution into ice cold water. The use of aqueous system allows the product to be isolated easily in higher yield [11].

2-(*N*-Ethylanilino)-4,6-bis(2-carbo phenoxy)-*s*-triazine (EACPT)

A solution of 2-(*N*-ethylanilino)-4, 6-bis-dichloro-*s*-triazine (I) (26.9 g, 0.1 mol) in 40 mL of acetone, a mixture of NaOH (16.0 g, 0.4 mol) and salicylic acid (2.76 g, 0.2 mol) in 80 mL double distilled water, was added slowly at room temperature in a solution of EADCT with constant stirring. The reaction was continued for 4 h; first 2 h at room temperature and then another 2 h at 80°C.

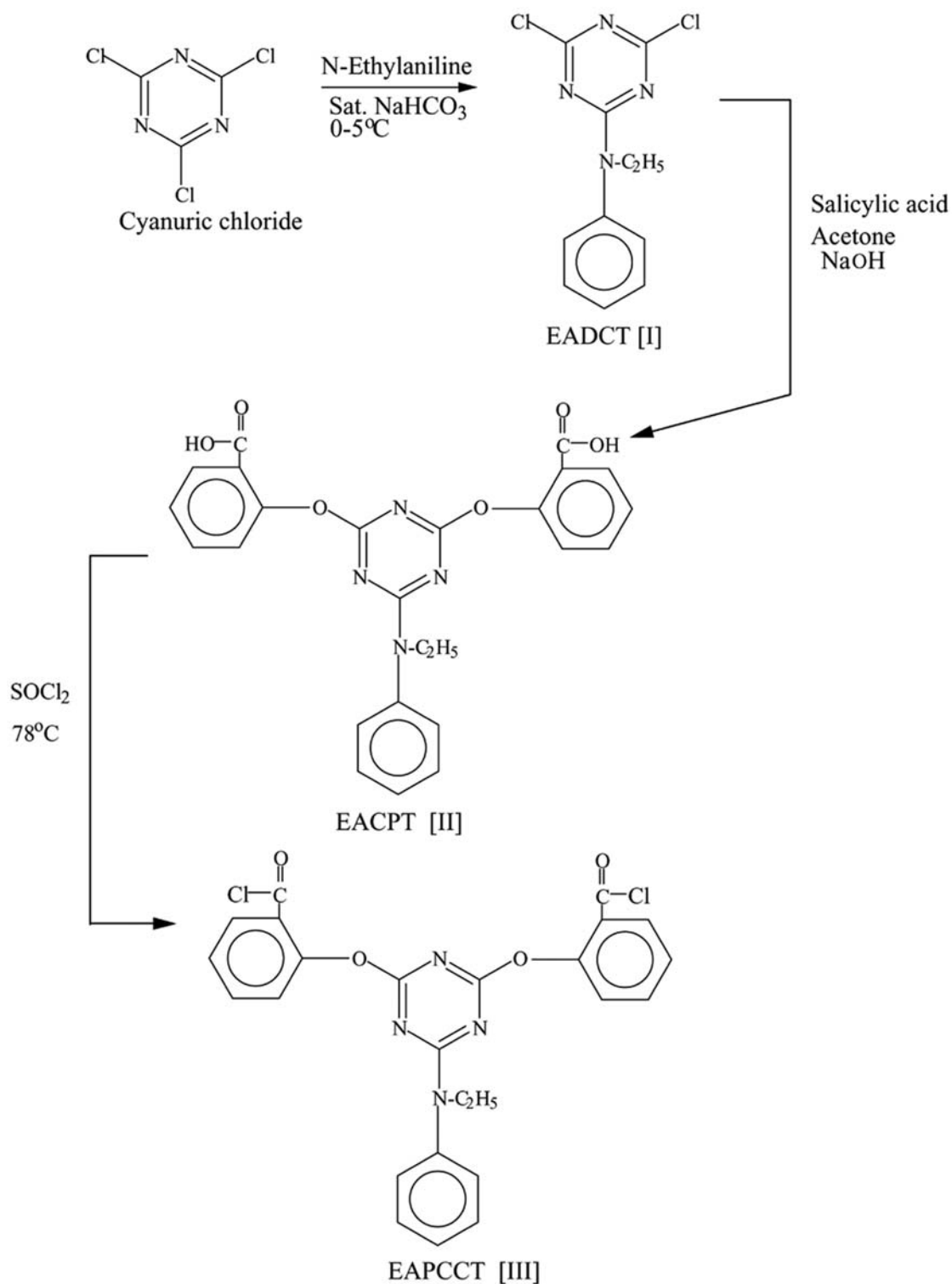
At the end of the reaction the white solid separated from the reaction mixture, was filtered and washed several times with hot water and dried in vacuum at 100°C. The product was recrystallized from acetone and the yield was 80% with mp 167°C.

2-(*N*-Ethylanilino)-4, 6-bis(phenoxy 2-carbonyl chloride)-*s*-triazine (EAPCCT)

2-(*N*-Ethylaniline) 4,6-bis(2-carbophenoxy)-*s*-triazine (II) (4.72 g, 0.01 mol) was placed in a dry round bottom flask. Thionyl chloride (11.9 mL, 0.1 mol) was added at the top of the condenser and the reaction mixture was refluxed at 78°C for 2 h. At the end of the reaction the excess of thionyl chloride was distilled off and dry product was recovered. The yield was about 80% and recrystallized from dimethylformamide and mp 198°C (Scheme I).

Synthesis of Homopolyesters

A mixture of 2-(*N*-ethylanilino)-4,6-bis(phenoxy 2-carbonylchloride)-*s*-triazine (III) (5.09 g, 0.01 mol) in



Scheme I

minimum quantity of DMF was heated to about 150°C. Cetrinide (0.25 g) and then bisphenol-A (4.56 g, 0.02 mol) was added. The reaction temperature was raised to 165°C and heated for 8 h. The reaction mix-

ture was cooled and poured along with constant stirring in to 250 mL of ice cold water. The solid was filtered and washed with hot water and finally with methanol to remove unreacted monomer and then dried. The yield

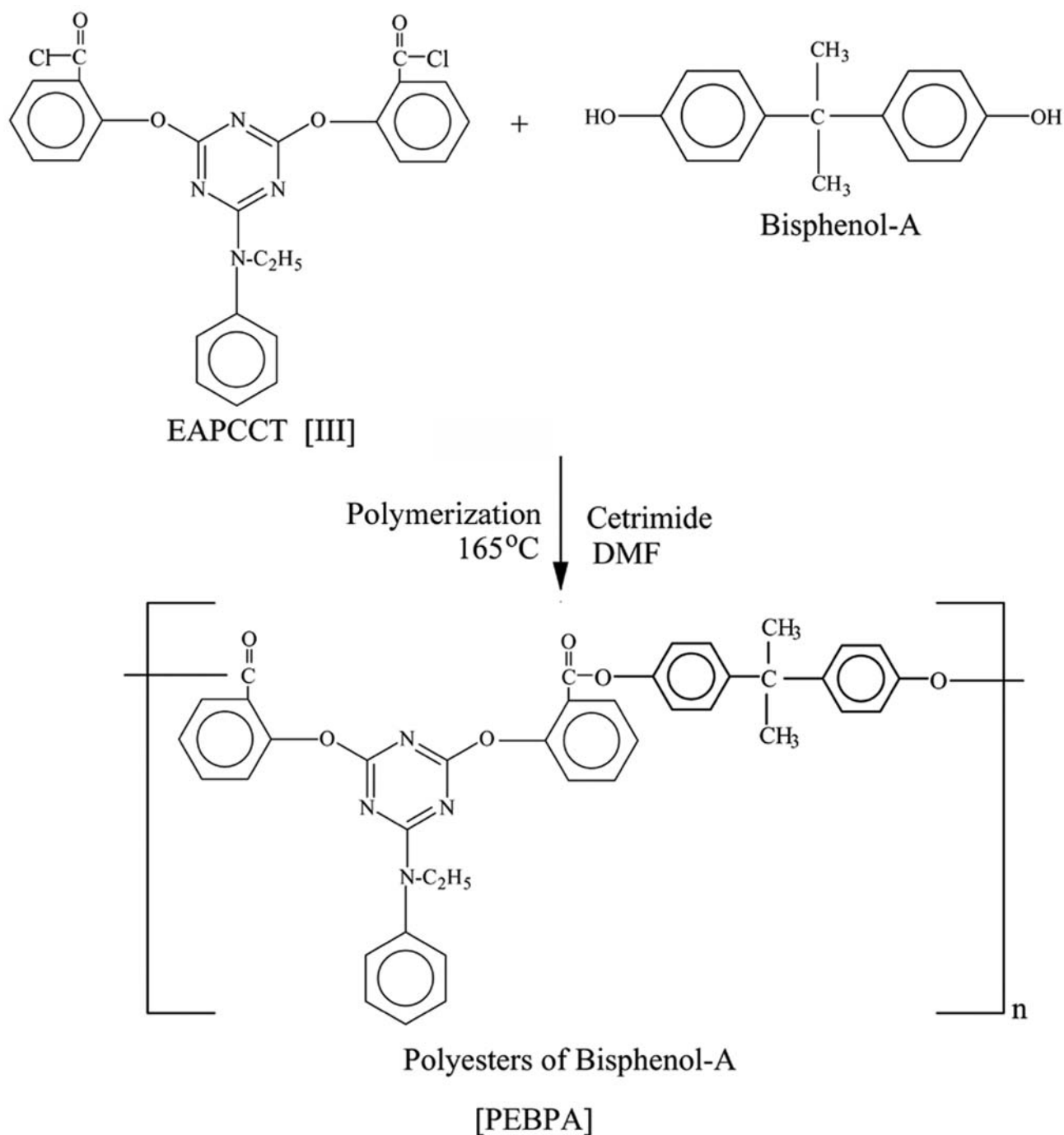
was about 78%.

The other polyesters from 2-(*N*-ethylanilino)-4,6-bis (phenoxy 2-carbonylchloride)-*s*-triazine and various diols such as bisphenol-C (BPC), phenolphthalein (Ph), resorcinol (R), hydroquinone (Hq), catechol (C), 1,8-dihydroxy anthraquinone (DHA-1,8), 1,4-dihydroxy anthraquinone (DHA-1,4), ethylene glycol

(TEG) were synthesized by the similar method as shown above (Scheme II).

RESULTS AND DISCUSSION

The high temperature polycondensation of EAPCCT



Scheme II

with BPA has been investigated in detail to examine the effect of variables such as the nature of organic solvent, reaction time, and temperature. The remaining variables, such as concentration of reactants, their ratio, rate of stirring, and initiator used were maintained nearly constant at all the tests. The quantity and quality of the polyesters obtained are presented in Table 1. Based on this data, suitable reaction conditions have been selected for the synthesis of polyesters with other aromatic diols. The reduced viscosity of the polymer solution (1 dL/g) in dimethylformamide is used as a criterion for the quality of the polymer formed in a given set of reaction conditions.

Solubility

Solubility of the homopolyester was determined for powdery samples in excess solvents. Most of the polyesters were soluble in a variety of solvents that included dimethylformamide, dimethylacetamide, dimethylsulphoxide, methanol, and tetrahydrofuran. Aliphatic and aromatic chlorinated solvents are non-solvents for polyesters. The solubility of polyesters markedly decreased with the decrease in the content of phenyl moiety in the polymer.

IR Spectral Characteristics

IR Spectra of all the polyesters were scanned in KBr on a Perkin Elmer FT-IR Paragon 1000 SPIR S.No. 42825. The IR spectra of the polyesters, Figures 1 and 2 exhibited several common characteristic absorption frequencies. The bands at 810-850 cm^{-1} and 1450-1510 cm^{-1} are attributed to out-of-plane and in-plane vibrations of

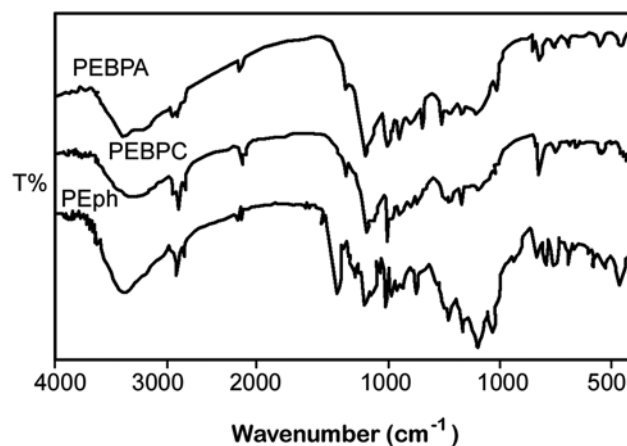


Figure 1. IR Spectrum of polyesters.

the *s*-triazine ring, respectively and the band at 1210-1230 cm^{-1} are attributed to the vibration involving the aryl-ether linkage. The band at 1740-1670 cm^{-1} is attributed to C-O stretching ester (aryl).

In addition, spectra exhibited several adsorption frequencies which distinguish the polyesters from each other. The frequencies (cm^{-1}) are 553 (C-C deformation vibration of propyl link, and 1165 (C-C skeletal vibration of propyl link) of PEBPA, 533 and 970 (all C-C deformation vibration of cyclohexane ring) for PEBPC, 750 co-disubstituted phenyl ring for PEph, 1630 (C=O (1,4-quinones)) stretching vibration for PEDHA-1,8 and PEDHA-1,4 [11-12].

¹H NMR Spectral Characteristics

¹H NMR Spectra of PEBPA in Figure 3 show chemical shifts, δ , at 6.60 -7.45 ppm due to the presence of aro-

Table 1. Systematic study of the high temperature polycondensation technique of EAPCCT (0.1mol) with BPA (0.2 mol) for optimization of reaction conditions.

System	Reaction temperature	Yield (%)	Product appearance	η_{sp}/c^* (dL/g)
DMF	100	50	Powdery	0.600
DMF	125	65	Powdery	0.635
DMF	150	70	Powdery	0.705
DMF	165	80	Powdery	0.721
DMF	200	75	Powdery	0.652

DMF = dimethylformamide

(*) 1 % polymer solution in dimethylformamide, emulsifier 0.125 g, time 8 h.

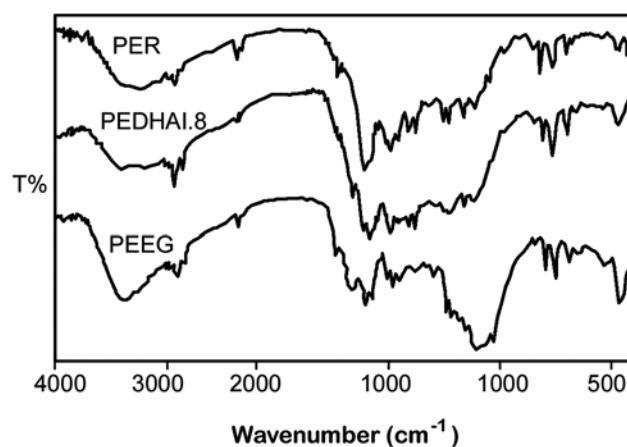


Figure 2. IR Spectrum of polyesters.

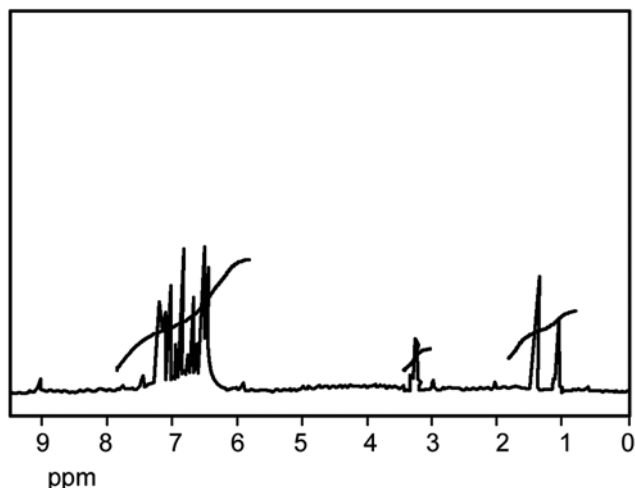


Figure 3. ^1H NMR Spectrum of PEBPA.

matic protons; 6H due to the methyl protons of isopropyl group produces singlet at 1.51 ppm; and 3H due to methyl group and 2H due to methylene group of ethyl group appear around 1.13 and 3.34, respectively.

^1H NMR Spectra of PETEG in Figure 4 shows chemical shifts, δ , at 6.84 -7.48 ppm maybe due to the presence of aromatic protons; 4H due to methylene group shows triplet at 2.93 ppm; 3H due to methyl group and 2H due to methylene group of ethyl group appear around 1.11 and 3.47, respectively.

Viscosity Measurements

Reduced viscosities of polyesters were determined with

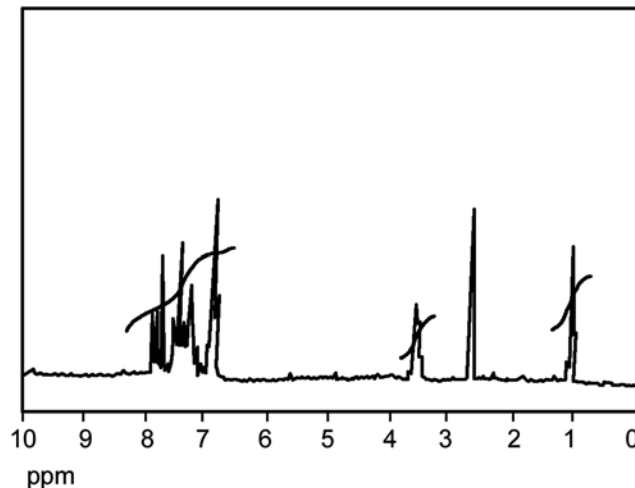


Figure 4. ^1H NMR Spectrum of PETEG.

1 dL/g solutions in dimethylformamide at 30°C using an Ubbelohde suspended level viscometer.

Examination of reduced viscosity values in Table 2 reveals that among dimethylformamide soluble polyesters PEBPA have the highest, whereas PETEG has the lowest solution viscosity. The trend of these values reflects the order of relative reactivity of diols,. BPA Is the least acidic and hence most reactive towards nucleophilic displacement reaction which leads to the formation of polyesters of a comparatively high molecular weight. The overall relative reactivity order of diols are as follows:



Table 2. Physical characteristics of polyesters.

Polymer code	Diol used	Product appearance	Yield (%)	Density (g/mL)	η_{sp}/c (dL/g)
PEBPA	BPA	Grey powder	78	1.154	0.600
PEBPC	BPC	Black powder	76	1.141	0.533
PEPh	Ph	Grey powder	77	1.210	0.565
PEDHA-1,8	DHA-1,8	Brown powder	77	1.174	0.535
PEDHA-1,4	DHA-1,4	Black powder	76	1.170	0.540
PER	R	Light brown	68	1.192	0.510
PEHq	Hq	Brown black	64	1.182	0.515
PEC	C	Dark grey	67	1.200	0.500
PEEG	EG	Black	72	1.116	0.480
PEDEG	DEG	Black	74	1.122	0.465
PETEG	TEG	Black	76	1.125	0.440

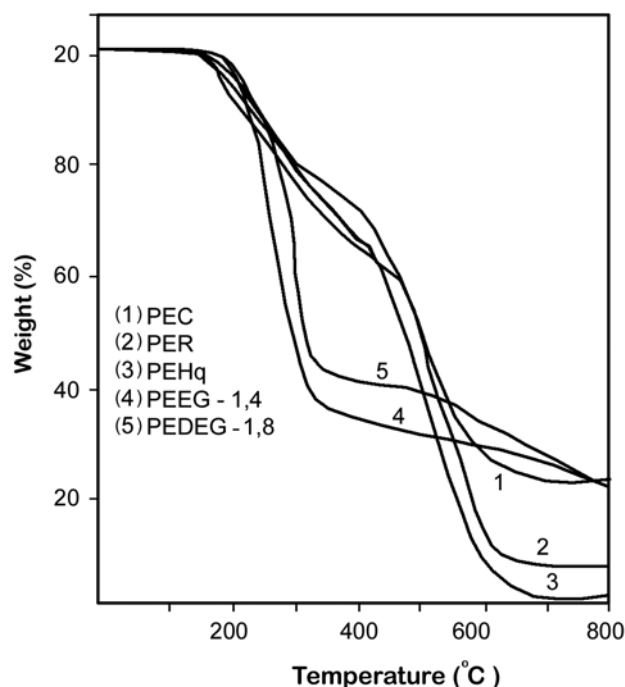


Figure 5. Thermogram of polyesters.

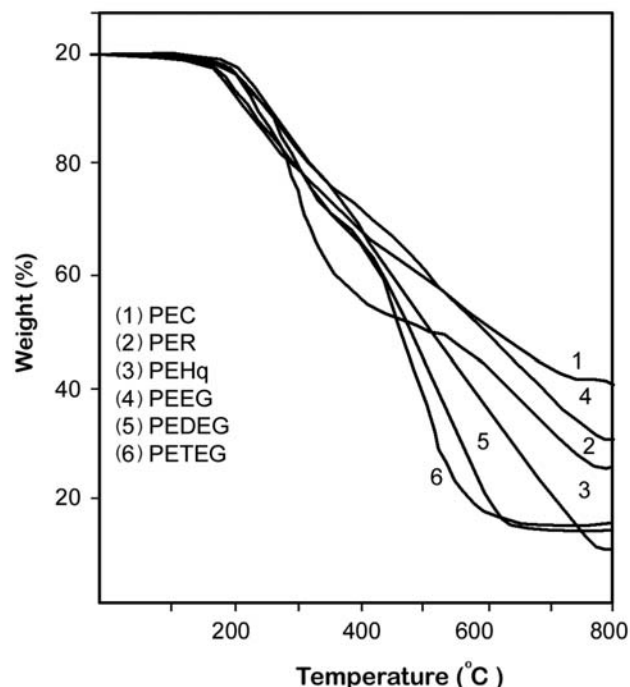


Figure 6. Thermogram of polyesters.

PEHq>PER>PEC>PEEG>PEDEG>PETEG

Density Measurements

Densities of the polyesters were determined at $25\pm3^\circ\text{C}$ using the suspended method [13] by a pycnometer and

are presented in Table 2. The densities of the polyesters synthesized were found to be in the range of 1.210-1.116 g/mL. The density of polyesters decreases as follows:

PEph>PEC>PER>PEHq>PEDHA-1,8>PEDHA-1,4>PEBPA>PEBPC>PETEG>PEDEG>PEEG

Table 3. Temperature characteristic of various homopolyesters.

Polymer	T_0	T_{10}	T_{\max}		T_s	Activation energy EA (kcal/mol)	
			Step I	Step II		Step I	Step II
PEBPA	175	220	280	530	480	5.72	17.26
PEBPC	160	230	270	510	495	5.50	13.97
PEPh	180	220	280	550	510	4.97	13.20
PEDHA-1,8	180	250	300	630	320	14.14	9.72
PEDHA-1,4	190	270	280	-	330	14.14	-
PER	150	235	300	650	520	10.66	7.31
PEHA	175	260	490	-	525	6.27	-
PEC	150	225	425	-	620	3.03	-
PEEA	170	260	280	-	580	9.07	-
PEDEG	175	245	300	515	470	7.07	10.56
PETEG	175	240	285	495	465	7.39	12.27

T_0 = Initial decomposition temperature; T_{10} = Temperature for 10% weight loss; T_{\max} = Maximum rate of decomposition temperature; and T_s = Temperature for 50% weight loss.

Thermal Decomposition Characteristics

All the thermograms of polyesters have been obtained on the thermobalance Mettler TA-4000 system at a heating rate of 10°C per minute in the temperature range from ambient temperature to 800°C. Thermograms obtained at a scan rate of 10°C per minute for all the polyesters are shown in Figures 5 and 6. The characteristics temperatures for assessment of relative thermal stability of polymers such as initial decomposition temperature T_0 , temperature T_{10} of 10% weight loss, temperature T_{max} of maximum rate of decomposition, temperature T_f of half volatilization are presented in Table 3. The higher the value of T_{10} [14] the greater is the thermal stability of a polymer. Comparison of T_{10} for polyesters indicates the decreasing order of stability as follows.

PEDHA-1,4>PEHq=PEEG>PEDHA-1,8> PEDEG >PETEG>PER=PEC>PEBPC>PEBPA=PEPH

A comparison of thermal stability based on T_{max} for polyesters indicates the following order:

PEHq>PEC>PEDHA-1,8=PER=PEDEG>PETEG >PEBPA=PEPh=PEDHA-1,4=PEEG>PEBPC

On the basis of T_g the order for stability is:

PEC>PEEG>PEHq>PER>PEPh>PEBPC>PEBPA >PEDEG>PETEG>PEDHA-1,4>PEDHA-1,8

TGA studies have provided insight into thermal degradation of polyesters during long term isothermal reactions. From the temperature dependence of weight loss, calculated by Broido's method [15], for degradation reaction the apparent activation energy was found in the range of 3.03 to 17.26 kcal/mol.

CONCLUSION

The present work deals with coloured polyesters. These polymers are amorphous coloured powders naturally. The linear polyester of high molecular weight affords synthetic fibres of excellent properties. As the polymer containing *s*-triazine ring, they exhibit different properties such as high softening temperature, solubility, thermal stability etc., also the presence of *s*-triazine ring in the polyester chain alter the properties of polymers to great extent.

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SYMBOLS AND ABBREVIATIONS:

η_{sp}/c	Reduced viscosity
D	Density
EA	Activation energy
T_0	Initial decomposition temperature
T_{10}	Temperature for 10% weight loss
T_{max}	Maximum rate of decomposition temperature
T_s	Temperature for 50% weight loss
BPA	Bisphenol A
BPC	Bisphenol C
Ph	Phenolphthalein
DHA-1,8	1,8-Dihydroxy anthraquinone
DHA-1,4	1,4-Dihydroxy anthraquinone
R	Resorcinol
Hq	Hydroquinone
C	Catechol
EG	Ethylene glycol
DEG	Diethylene glycol
TEG	Triethylene glycol
IR	Infrared
NMR	Nuclear magnetic resonance
TGA	Thermogravimetric analysis
EAPCCT	2-(<i>N</i> -Ethylanilino)-4,6-bis(phenoxy-2-carbonyl chloride)- <i>s</i> -triazine
EADCT	2-(<i>N</i> -Ethylanilino)-4,6-dichloro- <i>s</i> -triazine
EACPT	2-(<i>N</i> -Ethylanilino)-4,6-bis(carbo-2-phenoxy)- <i>s</i> -triazine
DMF	Dimethylformamide
PEBPA	Polyester of Bisphenol A
PEBPC	Polyester of Bisphenol C
PEPH	Polyester of phenolphthalein
PEDHA-1, 8	Polyester of 1, 8-dihydroxy anthraquinone
PEDHA-2, 4	Polyester of 1, 4-dihydroxy anthraquinone
PER	Polyester of resorcinol
PEHq	Polyester of hydroquinone

PEC	Polyester of catechol
PEEG	Polyester of ethylene glycol
PEDEG	Polyester of diethylene glycol
PETEG	Polyester of triethylene glycol

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