



Study of heterocyclic fluorescent probe containing polyesters: Synthesis, characterization and thermal degradation

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ABSTRACT

A series of heterocyclic fluorescent probe containing polyesters was synthesized by high temperature condensation polymerization technique using citrimide as initiator at 170°C in DMF. All the polyesters were characterized by IR and ¹H NMR spectroscopy. The inherent and reduced viscosities were checked by Ubbelohde solution viscometer, intrinsic viscosity was measured using Huggins and Kraemer's equations. Solubility properties of all the polyesters were checked in polar and nonpolar solvents. Density of all the polyesters was measured by pycnometer. Thermogravimetric analysis of all the polyesters was carried out in air. Unique property of fluorescence of these polyesters makes them valuable high performance material for the commercial use.

Keywords: 7-hydroxy coumarin 4-acetic acid, 7-hydroxy 4-methyl coumarin, Fluorescence, s-triazine, TGA, Viscosity, Polycondensation, Aromatic polyesters.

INTRODUCTION

A fluorescent material composed of polymer as a substrate was first reported by Wolf and Pressley in 1963. Since then, polymers functionalized by chromophores have attracted more and more attention and recently various new materials have been prepared [1]. A number of articles have been recently published on the preparation and properties of luminescent materials [1-7]. Among these materials, coumarin component containing materials have been useful in many fields due to their high emission yield, excellent photo-stability and extended spectral range, such as fluorescent images [8], non-linear optical materials [9], liquid crystals [10] and fluorescent labels for fluorescence energy transfer experiments [11].

Coumarins (2H-chromen-2-ones) have been freshly paid much attention for their fluorescent properties and physiological activities. They are widely used as laser dyes due to their high photostability and quantum yield of photoluminescence, the chemical modification of coumarins allows us to vary emission wavelength continuously throughout the visible spectrum. Coumarins were also found to be electroluminescent [3].

Polymers are generally difficult to process because of their limited solubility in organic solvents and their high melting temperature or high glass-transition temperature by virtue of their rigid structure [12, 13]. Therefore development of polyesters which can be made processable at normal temperature is an important goal. As an approach to improve the processibility of heterocyclic polymers without extreme loss of thermal stability, a number of published reports have described the synthesis and study of s-triazine [14-17] and coumarin [1, 3-7] containing polymers. The presence of s-triazine ring in the main chain alters the properties of polymers to great extent. Polymeric materials containing coumarin emitter units have advantage over low molecular weight analogies, especially in making Electroluminescence devices. Bearing in mind those coumarin and s-triazine containing polyesters presented the best combination of emission properties and processibility. Materials such as coumarin based polymers have been the potential to be used as multifunctional fluorescent material [1].

The aim of the present work involves the preparation and characterization of new kind of fluorescent polyesters bearing excellent combination of high performance properties evolving due to attachment of s-triazine ring with coumarin ring.

Present investigation involves the synthesis and characterization of linear hetero-aromatic polyesters from 2-(7-hydroxy 4-methyl coumarino)-4, 6-bis(7-hydroxy-coumarin-4-acetyl chloride)-s-triazine [HHCT] and various diols including Bisphenol-S, Hydroquinone, Catechol, Resorcinol, Phenolphthalein, Ethylene glycol, Diethylene glycol, 1, 4-dihydroxy anthraquinone and 1, 5-dihydroxy anthraquinone.

EXPERIMENTAL SECTION

2.1 Materials:

Cyanuric chloride (Fluka, Switzerland) was purified by crystallization from pure benzene (m.p.146°C). Phenolphthalein (BDH) was purified by crystallization from ethanol (m.p.262°C). Resin grade Bisphenol-A (cibatul, Atul) was repeatedly crystallized from 50% aqueous acetic acid and finally purified by recrystallization from benzene (m.p.150°C). Bisphenol-S (Atul Ltd.) was recrystallized from benzene (m.p.187°C). Resorcinol, Catechol and Hydroquinone (Sisco) were purified by recrystallization from rectified spirit. 1, 4-dihydroxy anthraquinone & 1, 5-dihydroxy anthraquinone (Sisco) were purified by recrystallization from alcohol. Ethylene glycol (Merck) was used as received.

2.2 Measurements:

The thermograms were obtained on a thermobalance "TGA METTLER TOLEDO STAR SW 9.20" at a heating rate 10°C/min. in nitrogen atmosphere. FTIR spectra of all the polyesters were recorded on "Thermo Nicolet iS10 (Thermofisher)" using KBr pellet technique. The NMR spectra were recorded in deuterated dimethylsulphoxide using TMS as an internal reference on a "Bruker Avance II ¹H NMR spectrometer" (400 MHz). Viscosities of polyesters were measured for 1 g/dl solution in DMF using an Ubbelohde viscometer. Densities of polyesters were measured by using pycnometer. Fluorescence spectra are recorded on "Edinburgh Instrument – FLS920" using 450-W-Xenone CW-lant source.

2.3 Material Synthesis:

2.3.1 Preparation of 7-hydroxy coumarin-4-acetic acid (3): [18]

This compound has been synthesized in a previous work.

2.3.2 Synthesis of 2-(7-hydroxy 4-methyl coumarino)-4, 6-dichloro-s-triazine [HT] (5): [19]

A solution of compound **1** (18.44 g, 0.1 mol) in a 60 ml acetone was added with stirring to a cooled solution (0-5 °C) of sodium bicarbonate (10.6 g) 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 7-hydroxy 4-methyl coumarin (17.60 g, 0.1 mol) in 10 ml of acetone was added to the cold slurry of cyanuric chloride. The mixture was stirred for 2 hr at 0-5 °C. The resulting product was filtered, dry and recrystallized from ethanol. Yield 80%, M. P. 114 °C.

2.3.3 Synthesis of 2-(7-hydroxy-4-methyl coumarino)-4,6-bis-(7-Hydroxy-Coumarin-4-Acetic acid)-s-triazine [HHT] (6): [19]

A mixture of NaOH (16 g, 0.4 mol) and compound (44 g, 0.2 mol) in 80 ml double distilled water was added slowly to the solution of compound **2** (32.40 g, 0.1 mol) in 40 ml of acetone at room temperature with constant stirring for 2 hr, then further reflux at 80 °C for 2 hr. At the end of the reaction mixture was filtered and washed with 3×100ml of hot water and dried in vacuum at 100 °C. The product was recrystallized from acetone. Yield 88%, M. P. 145 °C.

2.3.4 2-(7-hydroxy 4-methyl coumarino)-4, 6-bis-(7-Hydroxy-Coumarin-4-Acetyl Chloride)-s-triazine [HHCT] (7):

A mixture of compound **3** (6.91 g, 0.01 mol) and thionyl chloride (11.9 ml, 0.1 mol) was reflux at 78 °C for 2 hr. After the completion of the reaction, product was obtained by the distillation of excess thionyl chloride. Yield 74%, M. P. 288 °C.

2.3.5 General Procedure for the Synthesis of Polyesters (5a-j):

A mixture of Compound **7** (7.28 g, 0.01 mol) in DMF (approx. 10ml) and initiator citrimide (0.25 g) was refluxed at 150°C for 0.5 hr. After adding diol (0.02 mol) reaction temperature was raised to 160-170°C for 8 hr. The resultant mixture was cooled and poured in 250 ml of ice-cooled water with constant stirring. Solid was filtered, washed with hot water and finally with methanol to remove unreacted monomer and dried.

RESULTS AND DISCUSSION

3.1 Density Measurement:

Densities of polyesters were calculated by pycnometer at $25 \pm 3^\circ\text{C}$ by suspension method, which is especially suitable for powdered sample. The densities of the polyesters synthesized were found to be in the range 1.109-1.171 gm/cm^3 shown in Table 1.

Table 1: Physical Data of Polyesters (Polyesters from OHCT are as under)

No.	Polyesters from OHCT				
	Codes	Diols	Colour	Density (gm/cm^3)	Yield (%)
5a	PEBPA	Bisphenol-A	Black	1.219	62
5b	PEBPS	Bisphenol-S	Black	1.205	68
5c	PEPh	Phenolphthalein	Brown	1.230	71
5d	PEDHA-1, 4	1, 4-Dihydroxy Anthraquinone	Dark Brown	1.225	57
5e	PEDHA-1, 5	1, 5-Dihydroxy Anthraquinone	Light Brown	1.220	65
5f	PER	Resorcinol	Brick Red	1.192	65
5g	PEHq	Hydroquinone	Brown	1.186	62
5h	PEC	Catechol	Grey	1.173	57
5i	PEEG	Ethylene Glycol	Black	1.241	55
5j	PEDEG	Diethylene Glycol	Black	1.252	58

Decreasing order of polyesters is shown below:

PEDEG > PEEG > PEPh > PEDHA-1, 4 > PEDHA-1, 5 > PEBPA > PEBPS > PER > PEHq > PEC

3.2 Solubility Measurement:

Polyesters are readily soluble in acetone, Dimethyl formamide and Dimethyl sulfoxide. It is also found that the polyesters were insoluble in halogenated aliphatic and aromatic solvents like chloroform, carbon tetrachloride, chlorobenzene and bromobenzene are shown in Table 2. The polyesters are also insoluble in common organic solvents like benzene, nitro benzene and partly soluble in cyclohexane, methanol, ethanol and dioxane. The polyesters, which are partly soluble at room temperature, get soluble at higher temperature.

Table 2 : Solubility Data of Polyesters

Solvent	5a	5b	5c	5d	5e	5f	5g	5h	5i	5j
Acetone	++	++	++	++	++	++	++	++	++	++
Chloroform	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--
CCl_4	--	--	--	--	--	--	--	--	--	--
DMF	++	++	++	++	++	++	++	++	++	++
Chlorobenzene	--	--	--	--	--	--	--	--	--	--
Bromobenzene	--	--	--	--	--	--	--	--	--	--
Nitrobenzene	--	--	--	--	--	--	--	--	--	--
DMSO	++	++	++	++	++	++	++	++	++	++
Petroleum ether	--	--	--	--	--	--	--	--	--	--
Methanol	±±	±±	±±	±±	±±	±±	±±	±±	±±	±±
Ethanol	±±	±±	±±	±±	±±	±±	±±	±±	±±	±±
Cyclohexane	-±	-±	-±	-±	-±	±±	±±	±±	-±	-±
Dioxane	++	++	++	++	++	±±	±±	±±	++	++

The first and second symbol indicates the solubility of polyesters at 25°C and at 50°C respectively. + = Soluble, - = Insoluble, ± = partly soluble

3.3 Viscosity Measurement:

Intrinsic, reduced and inherent viscosities along with Huggins and Kraemer's constants for 1% solution for polyesters are shown in Table 3.

Table 3: Viscosity Data of Polyesters

No.	Intrinsic viscosity $[\eta]$	Reduced viscosity of 1% solution η_{sp}/C	Inherent viscosity $\ln \eta_{rel}/C$	Huggin's constant K'	Kraemer's constant K''
5a	0.599	0.693	0.527	0.253	0.214
5b	0.554	0.646	0.498	0.296	0.181
5c	0.569	0.654	0.503	0.269	0.221
5d	0.515	0.567	0.449	0.226	0.251
5e	0.528	0.583	0.459	0.215	0.269
5f	0.488	0.543	0.434	0.233	0.221
5g	0.504	0.559	0.444	0.219	0.246
5h	0.468	0.535	0.429	0.298	0.176
5i	0.430	0.465	0.382	0.180	0.270
5j	0.445	0.488	0.397	0.252	0.227

The intrinsic viscosity of the polyesters follows the sequence given below:

PEBPA > PEPH > PEBPS > PEDHA-1, 5 > PEDHA-1, 4 > PEHq > PER > PEC > PEDEG > PEEG

Polyesters were dissolved in DMF to measure their viscosity in ubbelohde solution viscometer. Intrinsic viscosity was obtained from the combined plots of reduced viscosity versus concentration and inherent viscosity versus concentration. The intrinsic viscosity $[\eta]$ was determined in each case from the best pair of the curves having the same intercept and the value of Huggins (K') and Kraemer's (K'') constants such that $K' + K'' \pm 0.5$.

Huggin's equation: $\eta_{sp}/C = [\eta] + k' [\eta]^2 C$

Kraemer's equation: $(\ln \eta_{rel})/C = [\eta] - k'' [\eta]^2 C$

3.4 Thermo Gravimetric Analysis:

All the polyesters showed a more or less similar pattern of decomposition. Results are summarized in Table 4. Polyesters follow two-steps thermal degradation. Methods used for the assessment of thermal stability of polymers from TG traces have been briefly reviewed by Reich and Levi [20]. These methods can broadly be classified as qualitative and semiquantitative. Several thermal regions were selected on Thermogram for comparison of the relative thermal stabilities of the polyesters. The characteristic temperatures for the assessment of relative thermal stability of polyesters such as initial decomposition temperature T_0 , temperature T_{10} for 10% weight loss, temperature T_{max} for maximum rate of decomposition, temperature T_s for half volatilization, are shown in Table 4. The higher value of T_{10} the greater the thermal stability of a polymer [21].

Table 4: Thermal Characteristics of Polyesters

No.	T_0 (°C)	T_{10} (°C)	T_{max} (°C)		T_s (°C)
			Step-I	Step-II	
5a	110	150	165	310	374
5b	125	168	192	338	394
5c	165	258	240	330	411
5d	152	244	228	218	398
5e	212	266	256	356
5f	225	272	270	370
5g	182	268	316	344	356
5h	170	255	300	324
5i	216	256	284	316	338
5j	200	247	275	314

A comparison of T_{10} for polyesters indicates the following order of stability:

PEBPA < PEBPS < PEDHA-1, 4 < PEPH < PEC < PEHq < PEDEG < PEDHA-1, 5 < PEEG < PER

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

PEBPA < PEBPS < PEDHA-1, 4 < PEPH < PEDHA-1, 5 < PER < PEDEG < PEEG < PEC < PEHq

On the basis of T_s the order of stability is

:
PEDEG < PEC < PEEG < PEDHA-1, 5 = PEHq < PER < PEBPA < PEBPS < PEDHA-1, 4 < PEPH

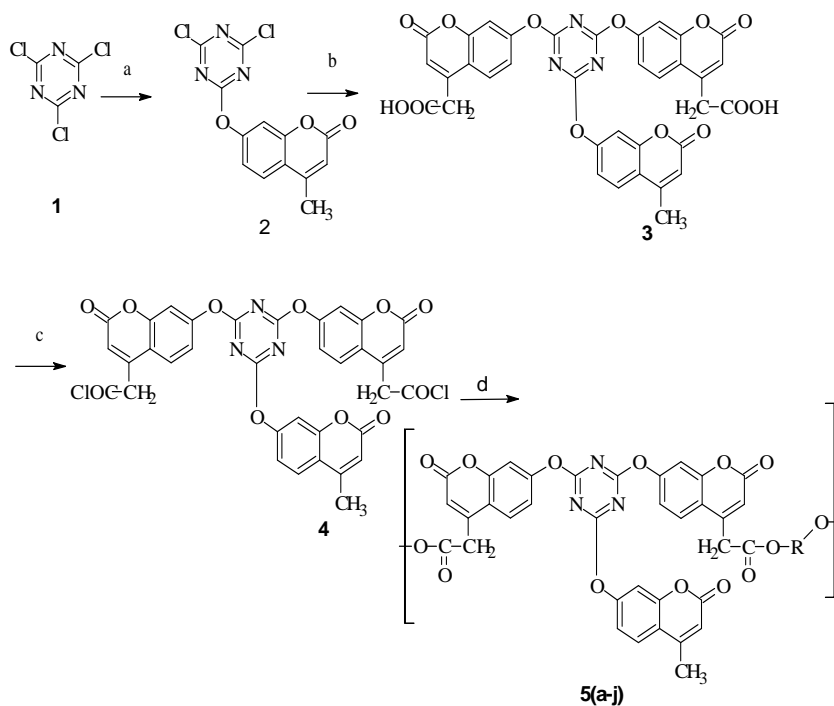
Table 5: Application of the Broido method to the thermogram of 5a

T (°C)	Wt	$Y=(Wt-Wa)/(Wo-Wa)$	1/Y	$\ln[\ln(1/Y)]$	T (K)	$1/T * 10^{-3} (K^{-1})$
250	12.97	0.4500	2.2222	-0.2250	523	1.9120
260	12.71	0.4066	2.4590	-0.1056	533	1.8761
270	12.42	0.3583	2.7906	0.0259	543	1.8416
280	12.05	0.2966	3.3707	0.1948	553	1.8083
290	11.68	0.2350	4.2553	0.3703	563	1.7761

Table 6: Application of the Horowitz-Metzger's method to the thermogram of 5a

T (°C)	Wt	1-a	1/(1-a)	$\ln[\ln(1/(1-a))]$	θ (°C)
250	12.97	0.4500	2.2222	-0.2250	-20
260	12.71	0.4066	2.4590	-0.1056	-10
270	12.42	0.3583	2.7906	0.0259	0
280	12.05	0.2966	3.3707	0.1948	10
290	11.68	0.2350	4.2553	0.3703	20

Scheme 1:



Reagents: a) 7-hydroxy 4-methyl coumarin in acetone, 0-5 °C, 2 hr; b) 5 in acetone, 3 in NaOH, 2 hr at rt then 2 hr at 80 °C; c) 6 in $SOCl_2$ 2 hr at 78 °C; d) 7, HO-R-OH(a-j) in DMF, citrimide, 8 hr at 160-170 °C.

Polyesters generally form 10% weight loss in the range of 180-250°C. They form weight loss in the temperature range of 200-280°C which is their first step degradation. Then above 565°C they form maximum weight loss almost more than 50%. Data shows that in starting heating range, polyesters which contain phenolphthalein, Bisphenol-S, Diethylene glycol, Ethylene glycol, Hydroquinone, Catechol and Resorcinol are more stable than others.

A single heating rate method has been employed for the treatment of TGA data, to evaluate activation energy (E_a) for each step of thermal decomposition of polyesters. Application of Horowitz and Metzger's method involves the knowledge of T_s , while Broido's method [22] does not involve any other temperature characteristics. Thus, between two methods, Broido's method is expected to provide reliable estimates of E_a . Values of activation energy (E_a) were calculated according to the method of Broido, which range between 3.74 and 8.99 Kcal/mol for the first step, 2.05 to 3.46 for second step and 2.18 to 2.81 for third step thermal decomposition of polyesters. These studies reveal that, the thermal stability of polyesters is significantly related to the aromatic as well as aliphatic diol component in the molecular chain.

The thermal property of the polyesters was assessed by Thermo gravimetric analysis. Thermal data of the polyesters were applied to the Broido and Horowitz & Metzger's methods. By using Broido method, activation energy of each steps for all the polyesters were calculated.

Chart 1: Fluorescence spectra of compounds-5c, 5g and 5j

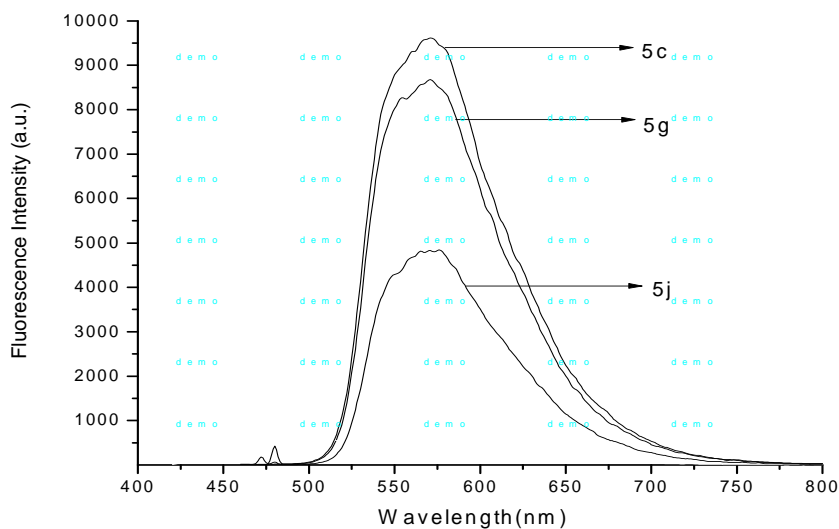


Chart 2: Thermal Gravimetric Analysis of compounds-5a, 5c, 5f, 5i and 5j

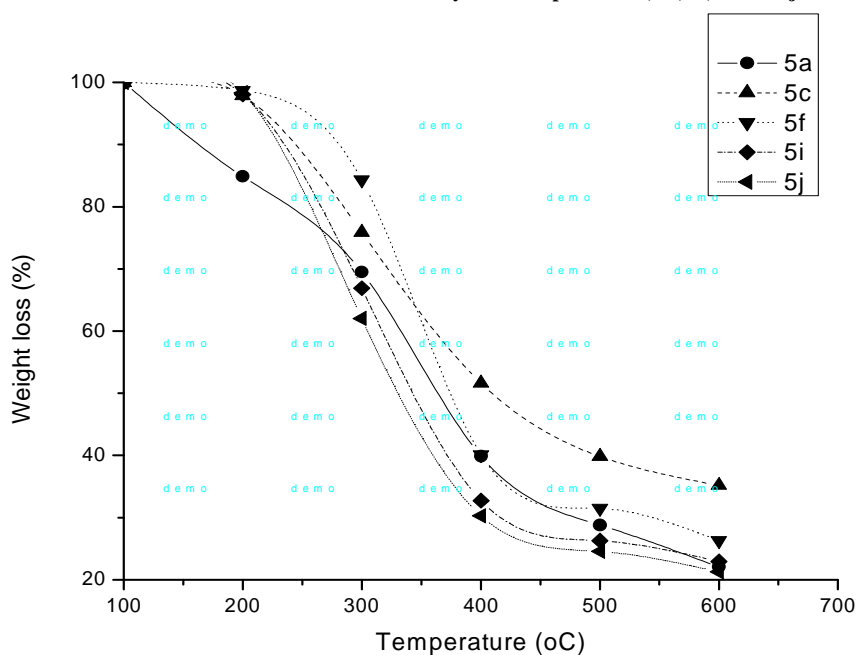


Fig. 1 Broido plot for 5a

3.5 Fluorescence: (Chart 1)

Fluorescence property of polyester was measured and compared with fluorescence spectra of the coumarin. 0.04% solution of polyester and coumarin in dimethyl formamide were irradiated in air with xenone lamp. Solutions were excited at their corresponding excited wavelength and emission spectra were recorded.

Chart 1 shows the emission spectra of the coumarin and PEDHA-1, 5. Coumarin was dissolved in DMF and then excited at 360nm. Upon excitation at 360nm, the fluorescent spectrum of coumarin shows characteristic emission of coumarin ring. Major fluorescence was observed at 409 and 440nm. The strongest emission was located around 440nm. Similarly, PEDHA-1, 5 was dissolved in DMF and then excited at 357nm. PEDHA-1, 5 has shown major fluorescence at 389 and 445nm. From these two maxima 445nm has strongest emission.

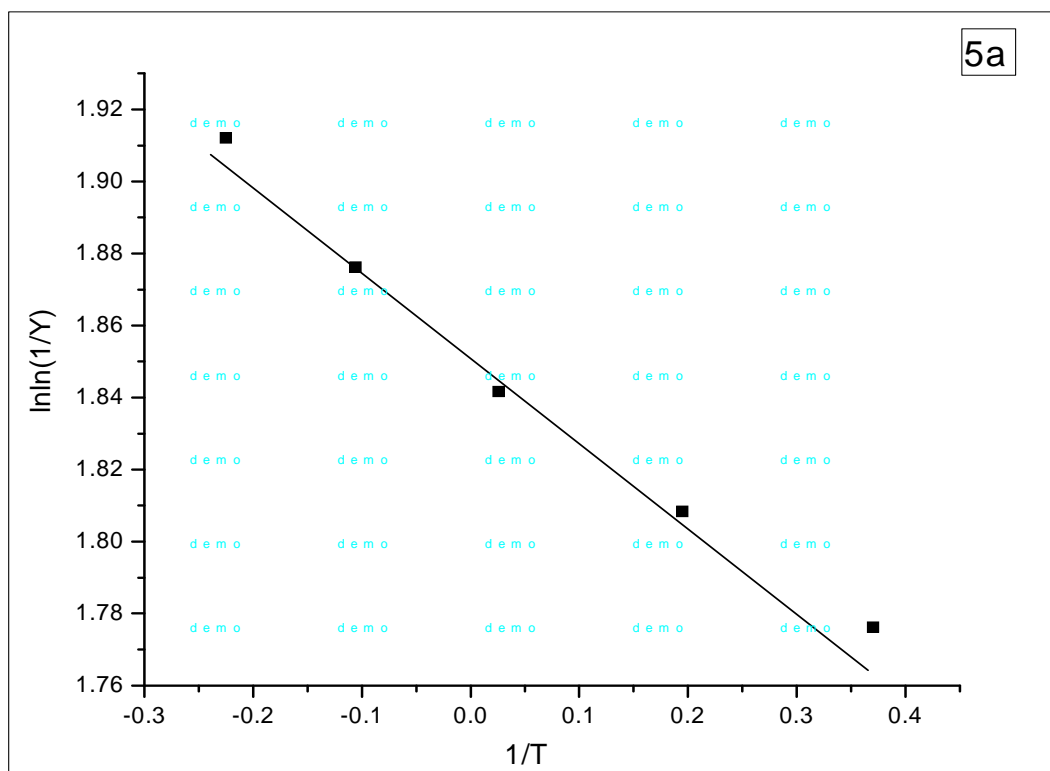
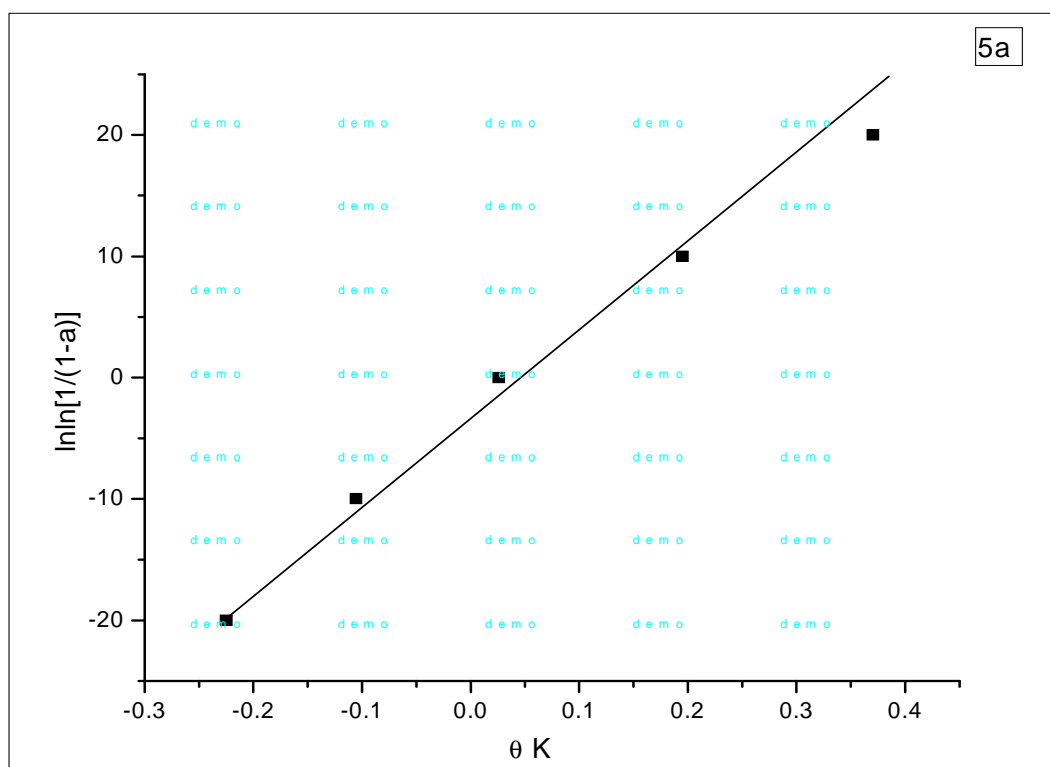


Fig. 2 Horowitz-Metzger plot for 5a



[PEBPA] 5a: Yield 62%, IR (KBr) cm^{-1} : 1528.8 ($-\text{C}=\text{N}-$), 1147.6 (Ar-O-Ar) (Asym), 1039.1 (Ar-O-Ar) (Sym), 1662.5 ($>\text{C}=\text{O}$), 1784.3 ($>\text{C}=\text{O}$ (lactone)), 3222.6 ($-\text{OH}$). ^1H NMR (DMSO, d_6): δ 2.48 (s, 2H, $>\text{CH}_2$), 6.55 (s, 2H, 2 Coumarin ring), 7.65 (s, 2H, 2 Coumarin ring), 7.58 – 7.68 (d, 4H, 2 Coumarin ring), 6.54 – 7.59 (m, 22H, Ar-H), 7.64 – 8.45 (t, 3H, Ar-H), 2.65 (s, 6H, 2 $-\text{CH}_3$) 7.69 – 8.48 (t, 3H, Ar-H), 8.45 (s, 2H, 2-OH).

[PEBPS] 5b: Yield 68%, IR (KBr) cm^{-1} : 1521.7 (-C=N-), 1121.2 (Ar-O-Ar) (Asym), 1042.9 (Ar-O-Ar) (Sym), 1698.2 (>C=O), 1792.7 (>C=O (lactone)), 3206.3 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.48 (s, 2H, 2 >CH₂), 6.55 (s, 2H, 2 Coumarin ring), 7.65 (s, 2H, 2 Coumarin ring), 7.58 – 7.68 (d, 4H, Coumarin ring), 6.68 – 7.62 (m, 22H, Ar-H), 7.61 – 8.42 (t, 3H, Ar-H), 8.49 (s, 2H, 2 -OH).

[PEPh] 5c: Yield 71%, IR (KBr) cm^{-1} : 1552.4 (-C=N-), 1171.5 (Ar-O-Ar) (Asym), 1028.4 (Ar-O-Ar) (Sym), 1658.8 (>C=O), 1758.4 (>C=O (lactone)), 3105.7 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.57 (s, 2H, >CH₂), 6.73 (s, 2H, Coumarin ring), 7.88 (s, 2H, Coumarin ring), 7.55 – 7.72 (d, 4H, Coumarin ring), 8.14 (d, 1H, Benzofuran ring), 8.36 – 8.63 (t, 2H, Benzofuran ring), 6.73 – 7.56 (d, 14H, Ar-H), 7.59 – 8.38 (t, 3H, Ar-H), 8.44 (s, 2H, 2-OH).

[PEDHN-1,4] 5d: Yield 57%, IR (KBr) cm^{-1} : 1543.1 (-C=N-), 1184.9 (Ar-O-Ar) (Asym), 1065.1 (Ar-O-Ar) (Sym), 1672.6 (>C=O), 1742.7 (>C=O (lactone)), 3115.4 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.64 (s, 2H, >CH₂), 6.63 (s, 2H, 2 Coumarin ring), 7.68 (s, 2H, 2 Coumarin ring), 7.51 – 7.69 (d, 4H, 2 Coumarin ring), 7.05 – 7.45 (d, 4H, Anthraquinone ring), 7.38 (t, 2H, Anthraquinone ring), 6.65 – 7.45 (m, 6H, Ar-H), 7.62 – 8.45 (t, 3H, Ar-H), 8.39 (s, 2H, 2 -OH).

[PEDHN-1,5] 5e: Yield 65%, IR (KBr) cm^{-1} : 1538.2 (-C=N-), 1118.7 (Ar-O-Ar) (Asym), 1049.3 (Ar-O-Ar) (Sym), 1686.7 (>C=O), 1783.4 (>C=O (lactone)), 3211.9 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.52 (s, 4H, 2 >CH₂), 6.48 (s, 2H, 2 Coumarin ring), 7.59 (s, 2H, 2 Coumarin ring), 7.41 – 7.72 (d, 4H, 2 Coumarin ring), 7.24 – 7.39 (d, 4H, 2 Anthraquinone ring), 7.42 (t, 2H, 2 Anthraquinone ring), 6.53 – 7.55 (m, 6H, Ar-H), 7.67 – 8.49 (t, 3H, Ar-H), 8.45 (s, 2H, 2 -OH).

[PER] 5f: Yield 65%, IR (KBr) cm^{-1} : 1535.0 (-C=N-), 1128.3 (Ar-O-Ar) (Asym), 1038.1 (Ar-O-Ar) (Sym), 1689.5 (>C=O), 1752.5 (>C=O (lactone)), 3316.3 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.48 (s, 2H, >CH₂), 6.51 (s, 2H, Coumarin ring), 7.69 (s, 2H, Coumarin ring), 7.52 – 7.63 (d, 4H, Coumarin ring), 6.68 – 7.62 (m, 9H, Ar-H), 7.61 – 8.42 (t, 4H, Ar-H), 8.41 (s, 1H, -OH).

[PEHq] 5g: Yield 62%, IR (KBr) cm^{-1} : 1556.3 (-C=N-), 1133.7 (Ar-O-Ar) (Asym), 1047.8 (Ar-O-Ar) (Sym), 1672.1 (>C=O), 1767.3 (>C=O (lactone)), 3339.1 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.38 (s, 2H, 2 >CH₂), 6.56 (s, 2H, 2 Coumarin ring), 7.56 (s, 2H, 2 Coumarin ring), 7.45 – 7.75 (d, 4H, 2 Coumarin ring), 6.56 – 7.48 (m, 14H, Ar-H), 7.72 – 8.51 (t, 3H, Ar-H), 8.38 (s, 2H, 2 -OH).

[PEC] 5h: Yield 57%, IR (KBr) cm^{-1} : 1536.1 (-C=N-), 1152.3 (Ar-O-Ar) (Asym), 1059.2 (Ar-O-Ar) (Sym), 1645.4 (>C=O), 1783.2 (>C=O (lactone)), 3351.6 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.51, 2.54 (s, 2H, >CH₂), 6.68 (s, 2H, 2 Coumarin ring), 7.39 (s, 2H, 2 Coumarin ring), 7.49 – 7.63 (d, 4H, 2 Coumarin ring), 6.49 – 7.34 (m, 10H, Ar-H), 7.56 – 8.41 (t, 7H, Ar-H), 8.47 (s, 2H, 2 -OH).

[PEEG] 5i: Yield 55%, IR (KBr) cm^{-1} : 1542.8 (-C=N-), 1159.8 (Ar-O-Ar) (Asym), 1061.1 (Ar-O-Ar) (Sym), 1632.4 (>C=O), 1783.2 (>C=O (lactone)), 3341.1 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.39 (t, 8H, 4 >CH₂), 6.58 (s, 2H, 2 Coumarin ring), 7.52 (s, 2H, 2 Coumarin ring), 7.62 – 7.78 (d, 4H, Coumarin ring), 6.55 – 7.51 (m, 6H, Ar-H), 7.62 – 8.49 (t, 3H, Ar-H), 8.41 (s, 2H, 2 -OH).

[PEDEG] 5j: Yield 58%, IR (KBr) cm^{-1} : 1537.1 (-C=N-), 1172.5 (Ar-O-Ar) (Asym), 1039.0 (Ar-O-Ar) (Sym), 1667.8 (>C=O), 1765.8 (>C=O (lactone)), 3378.2 (-OH). $^1\text{H NMR}$ (DMSO, d_6): δ 2.47 (t, 16H, 8 >CH₂), 6.45 (s, 2H, 2 Coumarin ring), 7.62 (s, 2H, 2 Coumarin ring), 7.41 – 7.64 (d, 4H, 2 Coumarin ring), 6.30 – 7.76 (m, 6H, Ar-H), 7.56 – 8.41 (t, 3H, Ar-H), 8.47 (s, 2H, 2 -OH).

CONCLUSION

A series of novel linear polyesters containing s-triazine ring with 7-hydroxy coumarin 4-acetic acid linkage [HHCT], in the main chain was successfully synthesized by high temperature polycondensation. All the polyesters were characterized by spectral data. All the polyesters have poor solubility in halogenated and non polar solvents but good solubility in DMF, DMSO and acetone. These polyesters have good intrinsic viscosity in the range of 0.430-0.599. These polyesters show good thermal stability. All the polyesters start decomposing in the range of 180-250 °C and their maximum weight loss was shown at about 300°C. Fluorescence spectra show that coumarin containing polyesters have maintained the fluorescence property of coumarin even after polymerization and because of this property polyesters may find application as valuable high performance material for the commercial use.

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