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HETERO-AROMATIC-FLUORESCENT POLYESTERS: SYNTHESIS, CHARACTERIZATION AND PHYSICAL STUDY

Sachin K. Nizama¹, Nikita Mishra², Dilip Vasava^{*2}, Saurabh K. Patel¹

¹Department of Chemistry, Veer Narmad South Gujarat University, Udhna-Magdalla Road, Surat, Gujarat, India ²Department of Chemistry, School of Science, Gujarat University, Ahmedabad, Gujarat, India *Corresponding author: dilipvasava20@gmail.com

ABSTRACT

A new class of high performance hetero-aromatic-fluorescent polyesters containing coumarin and s-triazine rings was prepared by high temperature condensation polymerization technique using cetrimide as initiator at 170-180°C. All the polyesters were characterized by IR and ¹H NMR spectroscopy. The inherent and reduced viscosities were checked by Ubbelohde solution viscometer and intrinsic viscosity was measured using Huggins and Kraemer's equations. Solubility of all the polyesters was checked in polar and nonpolar solvents. Density of all the polyesters was counted by pycnometer. Thermo gravimetric analysis of all the polyesters has been carried out in air. The obtained polyesters have shown fluorescent property due to coumarin ring.

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

1. INTRODUCTION

Hetero-Aromatic polyesters are well-known as high performance polymeric materials. The heterocycles based condensation polymers have also been studied extensively because of their high thermal stability [1]. The choice of heterocyclic rings in the main chain of the synthetic polymer is to impart certain properties like high resistance to heat and chemical attack, good mechanical and dielectric properties and ease of processibility to the polymer. Polymers containing the triazine ring as part of the polymer chain are generally insoluble and infusible. However, the thermal stability of the triazine ring makes it an attractive monomer for use in high temperature polymers.

Fluorescence detection has been widely used as a versatile tool in analytical chemistry, biochemistry, cell biology, etc. A number of articles have been recently published on the preparation and properties of luminescent materials [2]. 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 [3], non-linear optical materials [4], liquid crystals [5], and fluorescent labels for fluorescence energy transfer experiments [6].

Although many papers and reviews have been published on the synthesis of coumarin [7, 8] very little attention has been paid to the incorporation of fluorescent brightening materials into polymer.

Polymers containing pendent α , β -unsaturated carbonyl groups undergo crosslinking upon irradiation with UV light and are regarded as negative-type photoresists. These polymers having good solubility, high photosensitivity, resistance towards solvents after cross linking, thermal stability and resistance towards plasmas and etching agents are very important for practical use as commercial negative photoresist materials [11].

By adding fluorochrome molecules like acridine, stilbene, rhodamine, terbium complex etc. in polymer chain, and many researchers have tried to produce fluorescence in polymer materials [12-14].

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 [15, 16]. 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 [17-20] and coumarin [7-10] 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-containing polyesters presented the best combination of processability and emission properties. Materials such as coumarin based polymers have been the potential to be used as multifunctional fluorescent material [21].

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 striazine ring with coumarin ring.

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

2. EXPERIMENTAL

2.1. Materials

Cyanuric chloride (Fluka, Switzerland) was purified by crystallization from pure acetone (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 acetone (M.P. 150°C). Bisphenol-C (Atul Ltd.) was recrystallized from acetone (M.P. 187°C). Resorcinol, Catechol and Hydroquinone (Sisco) °ere purified by recrystallization from rectified spirit. 1, 5dihydroxy Naphthalene & 1, 7-dihydroxy Naphthalene (Sisco) were purified by recrystallization from aqueous alcohol. Ethylene glycol (Merck) was used as received.

2.2. Measurements

The thermograms were obtained on a thermobalance "TGA Q500 V6.3 Build 189" at a heating rate of 10°C/min. in nitrogen atmosphere. FTIR spectra of all the polyesters were recorded on "Perkin Elmer FT-IR Spectrometer Paragon -500" using KBr pellet technique. The NMR spectra were recorded in deuterated dimethylsulphoxide using TMS as an internal reference on a "Perkin-Elmer Model-32 ¹H NMR spectrometer" (300 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 "RS-5301PC Spectro Fluoro Photometer" using 450-W-Xenone CW-lant source.

2.3. Material Synthesis (Scheme 1)

2.3.1. Preparation of 7-Hydroxy Coumarin-4-Acetic Acid (3) [22]

Compound 1 (21 g, 0.1 mol) and Conc. H_2SO_4 (32 ml) stirred at 60-65 °C. Compound 2 (11 g, 0.1 mol) was added with vigorous stirring at 0-5 °C over a period of 1-1.5 hr. Kept the solution for overnight at room temperature. Then solution was poured into ice water. The crude product precipitated was filtered and dissolved in saturated NaHCO₃ solution followed by clearing up with activated charcoal and filtration. Filtrate was acidified with conc. HCl to collect compound 3.

2.3.2. Synthesis of 2-(N-Diphenyl Anilino)-4, 6dichloro-s-triazine [DT] (5) [23]

A solution of compound 4 (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 Diphenyl Amine (17 g, 0.1mol) 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. 127°C.

2.3.3. Synthesis of 2-(N-Diphenyl Anilino)-4,6-bis-(7-Hydroxy-Coumarin-4-Acetic acid)-s-triazine [DHT] (6) [23]

A mixture of NaOH (16 g, 0.4 mol) and compound 3 (44 g, 0.2 mol) in 80 ml double distilled water was added slowly to the solution of compound 5 (32.0g, 0.1 mol) in 40 ml of acetone at room temperature with constant stirring for 2 hr, then further refluxed 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. 153°C).

2.3.4. 2-(N-Diphenyl Anilino)-4,6-bis-(7-Hydroxy-Coumarin-4-Acetyl Chloride)-s-triazine [DHCT] (7)

A mixture of compound 6 (6.81 g, 0.01 mol) and thionyl chloride (11.9 ml, 0.1 mol) was refluxed at 78° C for 2 hr. At the end of the reaction, product was obtained by the distillation of excess thionyl chloride (Yield 78%. M. P. 258°C).

2.3.5. General Procedure for the Synthesis of Polyesters (8a-j)

A mixture of Compound 7 (7.5 g, 0.01mol) in DMF (approx. 10ml) and initiator cetrimide (0.25 g) was refluxed at 150°C for 0.5 hr. Then various diols

(0.02mol) were added. Finally, the 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.

[PEBPA] 8a: Yield 87%, IR (KBr) cm⁻¹: 826.3 (-C=N), 1072.6, 1208.5 (Ar-O-Ar), 1596.5 (>C=O), 1754.7 (>C=O (lactone)), 3350.0 (-OH). ¹H NMR (DMSO, d₆): δ 4.02 (s, 2H, >CH₂), 6.54 (s, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 6.73 (d, 1H, Ar-H), 7.71 (d, 1H, Ar-H), 6.78-7.59 (m, 18H, Ar-H), 1.57 (s, 6H, -CH₃), 8.16 (s, 2H, -OH).



Scheme 1: Reagents: a) Conc. H_2SO_4 ; b) Diphenyl amine in acetone, 0-5°C, 2 hr; c) 5 in acetone, 3 in NaOH, 2 hrs. at RT then 2 hrs. at 80°C; d) 6 in $SOCl_2$ 2 hrs. at 78°C; e) 7, HO-R-OH(a-j) in DMF, cetrimide, 8 hrs. at 160-170°C.

[PEBPC] 8b: Yield 81%, IR (KBr) cm⁻¹: 814.5 (-C=N), 1069.8, 1226.6 (Ar-O-Ar), 1642.2 (>C=O), 1769.5 (>C=O (lactone)), 3359.4 (-OH). ¹H NMR (DMSO, d₆): δ 4.14 (s, 2H, >CH₂), 6.59 (s, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 6.68 (d, 1H, Ar-H), 7.79 (d, 1H, Ar-H), 7.00-7.60 (m, 10H, Ar-H), 1.41-2.46 (m, 10H, >CH₂), 8.20 (s, 2H, -OH).

[PEPh] 8c: Yield 85%, IR (KBr) cm⁻¹: 792.7 (-C=N-), 1084.0, 1206.7 (Ar-O-Ar), 1620.6 (>C=O), 1765.6 (>C=O (lactone)), 3374.6 (-OH). ¹H NMR (DMSO, d₆): δ 3.97 (s, 2H, >CH₂), 6.66 (s, 1H, Ar-H), 6.46 (s, 1H, Ar-H), 6.90 (d, 1H, Ar-H), 7.86 (d, 1H, Ar-H), 6.98-7.97 (m, 22H, Ar-H), 9.06 (s, 2H, -OH).

[PEDHN-1,5] 8d: Yield 83%, IR (KBr) cm⁻¹: 794.0 (-C=N-), 1087.4, 1266.3 (Ar-O-Ar), 1637.7 (>C=O), 1735.5 (>C=O (lactone)), 3314.0 (-OH). ¹H NMR (DMSO, d₆): δ 3.99 (s, 2H, >CH₂), 6.44 (s, 1H, Ar-H), 6.11 (s, 1H, Ar-H), 6.70 (d, 1H, Ar-H), 7.56 (d, 1H, Ar-H), 6.79-8.02 (m, 16H, Ar-H), 10.2 (s, 2H, -OH).

[PEDHN-1,7] 8e: Yield 72%, IR (KBr) cm⁻¹: 804.5 (-C=N-), 1058.7, 1218.6 (Ar-O-Ar), 1615.2 (>C=O), 1700 (>C=O (lactone)), 3380.0 (-OH). ¹H NMR (DMSO, d₆): δ 4.18 (s, 2H, >CH₂), 6.48 (s, 1H, Ar-H), 6.06 (s, 1H, Ar-H), 6.53 (d, 1H, Ar-H), 7.82 (d, 1H, Ar-H), 6.84-7.91 (m, 16H, Ar-H), 9.77 (s, 2H, -OH).

[PER] 8f: Yield 89%, IR (KBr) cm⁻¹: 809.0 (-C=N-), 1073.0, 1261.8 (Ar-O-Ar), 1617.8 (>C=O), 1734.1 (>C=O (lactone)), 3447.9 (-OH). ¹H NMR (DMSO, d₆): δ 4.08 (s, 2H, >CH₂), 6.34 (s, 1H, Ar-H), 6.29 (s, 1H, Ar-H), 6.61 (d, 1H, Ar-H), 7.66 (d, 1H, Ar-H), 6.87-7.56 (m, 14H, Ar-H), 9.37 (s, 2H, -OH).

[PEHq] 8g: Yield 70%, IR (KBr) cm⁻¹: 804.0 (-C=N), 1058.6, 1225.0 (Ar-O-Ar), 1622.8 (>C=O), 1732.7 (>C=O (lactone)), 3420.0 (-OH). ¹H NMR (DMSO, d₆): δ 4.11 (s, 2H, >CH₂), 6.49 (s, 1H, Ar-H), 6.21 (s, 1H, Ar-H), 6.70 (d, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.02-7.59 (m, 14H, Ar-H), 9.30 (s, 2H, -OH).

[PEC] 8h: Yield 68%, IR (KBr) cm⁻¹: 806.2 (-C=N-), 1064.3, 1243.6 (Ar-O-Ar), 1620.3 (>C=O), 1730.8 (>C=O (lactone)), 3389.0 (-OH). ¹H NMR (DMSO, d₆): δ 4.22 (s, 2H, >CH₂), 6.69 (s, 1H, Ar-H), 6.36 (s, 1H, Ar-H), 6.91 (d, 1H, Ar-H), 7.85 (d, 1H, Ar-H), 6.98-7.90 (m, 14H, Ar-H), 9.29 (s, 2H, -OH).

[PEEG] 8i: Yield 93%, IR (KBr) cm⁻¹: 799.6 (-C=N-), 1038.7, 1230.7 (Ar-O-Ar), 1628.9 (>C=O), 1698.3 (>C=O (lactone)), 3356.0 (-OH). ¹H NMR (DMSO, d₆): δ 3.84 (s, 2H, >CH₂), 6.52 (s, 1H, Ar-H), 6.31 (s, 1H, Ar-H), 6.80 (d, 1H, Ar-H), 7.61 (d, 1H, Ar-H), 7.05-7.60 (m, 10H, Ar-H), 4.08 (t, 2H, >CH₂), 4.12 (t, 2H, >CH₂), 8.44 (s, 2H, -OH).

[PEDEG] 8j: Yield 84%, IR (KBr) cm⁻¹: 844.3(-C=N), 1057.2, 1250.3 (Ar-O-Ar), 1136.4 (CH₂-O-CH₂), 1644.2 (>C=O), 1718.8 (>C=O (lactone)), 3409.6 (-OH). ¹H NMR (DMSO, d₆): δ 3.81 (s, 2H, >CH₂), 6.69 (s, 1H, Ar-H), 6.46 (s, 1H, Ar-H), 6.79 (d, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.48-7.98 (m, 10H, Ar-H), 4.01 (t, 4H, >CH₂), 3.71 (t, 4H, >CH₂), 8.67 (s, 2H, -OH).

2.4. Methods

Densities of polyesters were calculated by pycnometer at $25\pm3^{\circ}$ C by suspension method, which is especially suitable for powdered sample. Solubility of polyesters were checked in many polar and non polar solvents like Acetone, Chloroform, Benzene, Carbon tetrachloride, dimethyl formamide, chlorobenzene, bromobenzene, nitrobenzene, dimethyl sulfoxide, ether, methanol, ethanol, cyclohexane and dioxane. 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 [**ŋ**] 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 $K' + K'' \pm 0.5$.

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

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

The thermal property of the polyesters was assessed by Thermo gravimetric Analysis. Thermal data of the polyesters were applied to the Broido and Horrowitz & Metzger methods. By using Broido method, activation energy of each steps for all the polyesters were calculated. 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 xenon lamp. Solutions were excited at their corresponding excited wavelength and emission spectra were recorded.

3. RESULTS AND DISCUSSION

3.1. Density Measurement

The synthesized polyesters were almost dark or black in color. The densities of the polyesters were found to be in the range $1.119-1.176 \text{ gm/cm}^3$. Decreasing order of polyesters is shown below. Data are listed in table 1.

PEPh>PEDHN-1, 7>PEDHN-1, 5>PEHq>PER>PEC >PEBPC>PEBPA>PEDEG> PEEG.

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

Table 1: Physical Data of Polyesters

and aromatic solvents like chloroform, carbon tetrachloride, chlorobenzene and bromobenzene. 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 (50°C).

No	Polyesters from DHCI					
110.	Codes	Diol	Color	Density(gm/cm ³)		
8a	PEBPA	Bisphenol-A	Black	1.129		
8b	PEBPC	Bisphenol-C	Black	1.134		
8c	PEPh	Phenolphthalein	Coffee Brown	1.176		
8d	PEDHN-1,5	1,5-Dihydroxy Naphthalene	Brown	1.168		
8e	PEDHN-1,7	1,7-Dihydroxy Naphthalene	Dark Brown	1.170		
8f	PER	Resorcinol	Brick Red	1.152		
8g	PEHq	Hydroquinone	Brown	1.159		
<u>8ĥ</u>	PEC	Catechol	Light Brown	1.148		
8i	PEEG	Ethylene Glycol	Black	1.119		
8j	PEDEG	Diethylene Glycol	Black	1.121		

Table 2: Solubility Data of Polyesters

Solvent	8a	8b	8c	8d	8e	8f	8g	8h	8i	8j
Acetone	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Chloroform										
Benzene										
CCl_4										
DMF	+ +	+ +	+ $+$	+ +	+ $+$	+ +	+ $+$	+ $+$	+ +	+ +
Chlorobenzene										
Bromobenzene										
Nitrobenzene										
DMSO	+ +	+ +	+ $+$	+ +	+ $+$	+ +	+ $+$	+ $+$	+ +	+ +
Petroleum ether										
Methanol	<u>+</u> <u>+</u>	<u>+</u> <u>+</u>	<u>+</u> +	<u>+</u> <u>+</u>	<u>+</u> +	<u>+</u> +	<u>+</u> +	<u>+</u> +	<u>+</u> <u>+</u>	<u>+</u> <u>+</u>
Ethanol	<u>+</u> +	<u>+</u> +	<u>+</u> +	<u>+</u> +	<u>+</u> +	± +	<u>+</u> +	<u>+</u> +	<u>+</u> +	<u>+</u> +
Cyclohexane	- <u>+</u>	- ±	- ±	- ±	- ±	<u>+</u> +	<u>+</u> <u>+</u>	<u>+</u> +	- ±	- ±
Dioxane	+ +	+ +	+ +	+ +	+ +	<u>+</u> +	<u>+</u> +	<u>±</u> +	+ +	+ +

The first and second symbol indicates the solubility of polyesters at 25 °c and at 50 °c respectively. + = soluble, - = insoluble, $\pm =$ partially soluble

3.3. Viscosity Measurement

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

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

PEBPA>PEPh>PEBPC>PEDHN-1, 7>PEDHN-1, 5> PEHq>PER>PEC>PEDEG>PEEG

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 [24]. These methods can broadly be classified as qualitative and semi-quantitative. 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 volatization, are shown in Table 4. The higher value of T_{10} the greater the thermal stability of a polymer [25]. A comparison of T_{10} for polyesters indicates the following order of stability: PEDHN-1, 5 < PEDHN-1, 7 < PEHq < PEC < PER < PEBPA < PEDEG < PEBPC < PEEG < PEPh A comparison of thermal stability based on T_{max} for polyesters indicates the following order: PER < PEDHN-1, 5 < PEHq < PEDHN-1, 7 < PEC < PEDEG < PEEG < PEBPA < PEBPC < PEPh On the basis of T_s the order of stability is: PEEG < PEDHN-1, 7 < PEBPC < PEPh < PEC < PEBPA < PEDHN-1, 5 < PEDEG < PER < PEHq POlyesters generally form 10% weight loss in the range f 210, 270% The form 10% weight loss in the range

of 210-270°C. They form weight loss in the temperature range of 265-340°C which is thefirst step degradation. Then above 520°C, they form maximum weight loss almost more than 50%. From all these data, we can observe that in starting heating range, polyesters

which contain phenolphthalein, Bisphenol C, Bisphenol A, Ethylene glycol and Diethylene glycol are more stable than others.

A single heating rate method has been employed for the treatment of TGA data, to evaluate activation energy (Ea) 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 [26] does not involve any other temperature characteristics. Thus, between two methods, Broido's method is expected to provide reliable estimates of Ea. Values of activation energy (Ea) were calculated according to the method of Broido, which range between 4.02 and 5.19 Kcal/mol for the first step and 2.61 to 3.30 for second step thermal decomposition of polyesters. These studies reveal that, the thermal stability of polyesters is significantly related to the aromatic diol component in the molecular chain.

Table	3: Viscosity Data	of Polyesters			
No	Intrinsic	Reduced viscosity	Inherent viscosity	Huggin's	Kraemer's
110.	Viscosity [ŋ]	of 1% solution η_{sp} / C	$\ln \eta_{\rm rel}$ / C	constant K'	constant K"
8a	0.605	0.717	0.541	0.258	0.217
8b	0.560	0.654	0.503	0.303	0.179
8c	0.580	0.669	0.512	0.275	0.194
8d	0.505	0.591	0.464	0.247	0.247
8e	0.535	0.591	0.464	0.250	0.250
8f	0.495	0.551	0.439	0.211	0.251
8g	0.510	0.559	0.444	0.206	0.275
8ĥ	0.475	0.528	0.424	0.222	0.277
8i	0.445	0.488	0.397	0.220	0.252
8j	0.465	0.488	0.397	0.154	0.347

Table 4:	Thermal	Characteristics	of Polyesters

No	T (°C)	T (°C)	T _{max}	т (⁰ С)	
110.	$\Gamma_0(C)$	$I_{10}(C)$	Step-I	Step-II	$I_{s}(C)$
8a	190	235	300	540	510
8b	195	245	310	530	495
8c	210	270	340	550	505
8d	160	210	270	530	515
8e	170	215	280	535	490
8f	180	225	270	530	558
8g	165	230	265	540	541
8h	175	225	285	535	510
8i	190	250	295	520	490
8j	185	240	290	545	520

3.5. Fluorescence

Fig. 1 shows the emission spectra of the coumarin and PEHq. Coumarin was dissolved in DMF and then excited at 360 nm. Upon excitation at 360 nm, the fluorescent spectrum of coumarin shows characteristic emission of coumarin ring. Major fluorescence was

observed at 409 nm and 440 nm. The strongest emission was located around 440 nm. Similarly PEHq was dissolved in DMF and then excited at 354 nm. Same as coumarin, PEHq has major fluorescence at 386 nm and 435 nm. From these two maxima 386 nm has strongest emission.



Fig. 2: Fluorescence spectra of coumarin and PEHq

4. CONCLUSION

A series of novel linear polyesters containing s-triazine ring with 7-hydroxy coumarin 4-acetic acid linkage [DHCT], in the main chain was successfully synthesized high temperature polycondensation. All the by 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 0.445-0.605. These polyesters show good thermal stability. All the polyesters starts decomposed above 210°C and their maximum weight loss is shown after 300°C. From the fluorescence spectra we can conclude that coumarin containing polyesters have maintained the fluorescence property of coumarin after polymerization and because of this property polyesters become valuable high performance materials for the commercial use and application.

5. SYMBOLS AND ABBREVIATION

DT 2-(N-Diphenyl Anilino)-4, 6-dichloro-s- triazine
DHT 2-(N-Diphenyl Anilino)-4, 6-bis-(7-Hydroxy-
Coumarin-4-Acetic acid)-s-triazine
DHCT 2-(N-Diphenyl Anilino)-4, 6-bis-(7-Hydroxy-
Coumarin-4-Acetyl Chloride)-s-triazine
PEBPA Polyester from DHCT + Bisphenol A
PEBPC Polyester from DHCT + Bisphenol C
PEPh Polyester from DHCT + Phenolphthalein
PEDHN-1, 5 Polyester from DHCT + 1, 5-Dihydroxy
Naphthalene
PEDHN-1, 7 Polyester from DHCT + 1, 7-Dihydroxy
Naphthalene
PER Polyester from DHCT + Resorcinol
PEHq Polyester from DHCT + Hydroquinone
PEC Polyester from DHCT + Catechol
PEEG Polyester from DHCT + Ethylene Glycol
PEDEG Polyester from DHCT + Diethylene Glycol

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Conflict of interests

The authors declare the absence of conflict of interests.

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