



SYNTHESIS OF THERMALLY STABLE FLUORESCENT COPOLYESTER CONTAINING COUMARIN MOIETY

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Abstract

A series of ten water insoluble colored copolyesters were synthesized by polycondensation method. The synthesized aromatic copolyesters having different aliphatic-aromatic diols in the chain and s-triazine ring as main moiety. The copolymer was synthesized by usage of monomer named as 6-(N-Diphenylaminy)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [DCTC]. The polycondensation of (N-Diphenylaminy)-2, 4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1, 3, 5-triazine [DCTC] was carried out by using different aliphatic-aromatic diol to obtain the polyester chain. The physical properties i.e. solubility and color was studied. All the synthesized polyesters were dark brown, light brown, golden and maroon colored and soluble in most of polar solvent such as DMF, DMSO, acetone, THF, ethyl acetate, while insoluble in water. The inherent and reduced viscosities were performed by Ubbelohde solution viscometer and intrinsic viscosity was measured by using Huggins and Kramer's equations. The range of viscosity in this obtained series was 0.441-0.640 g/dl. The fluorescence property was used to prove the highest intensity of copolyester and emission band observed in the range of 110nm-600nm. From all the ten synthesized polyesters in series shows DHC-7 has highest intensity as from others. The polymers are macromolecules with enormous applications having fluorescent property. Due to their unique mechanical property and workability, the emerging applications involve the fields

such as optical materials, analytical chemistry, a biological assays explosive sensing, analytical chemistry, biological detect projects. Moreover, fluorescent polymeric assemblies and nanoparticles have become a focus of intensive investigation in diverse fields based on fluorescent assays for detection and labelling. The newly synthesised polymers were characterised by UV, IR, NMR, TGA, DSC and fluorescence spectra. The following paper represents the study of new polymeric compounds that could act as fluorescent polymeric material.

Key words s-triazine, coumarin, aromatic diols, fluorescence.

Introduction

Polymers possess a remarkable direct impact on the way of people nearly in every region of the world [1]. A great deal of additional human resources is required to be added year after year to polymer based industries and research institutions. The polymer materials possess wide range of variety and versatility based on their performance, applications and characteristics [2]. The polymeric materials have gained much more popularity due to their low density, chemical inertness, corrosion resistance, fire resistance, elasticity or rigidity, low cost and cheap finishing products [3]. They play a critical and ubiquitous role in everyday life.

For the fundamental of life basic role ranges from elastomers, well-known artificial plastics to natural biopolymers such as nucleic acids and proteins [4]. As the future unfolds, plastics and other synthetic polymers will have multipurpose roles in medicine, electronics, aerospace, and

advanced structural composites [5]. New materials are expected to be developed and moulded all over in complex processes [6].

Due to increasing demand of polymers in fields like microelectronic industries, aerospace and automobile shows high performance characteristics in polymeric material [7, 8]. The use of these aromatic polymers is growing steadily. However, these polymers are generally refractory and deficit so the properties were essential for successful fabrication into useful forms [9, 10]. Many researchers have tackled these inherent problems over the few decades by modifying the monomers structures [11]. Polymers are used in a broad variety of applications [12]. They find wide use in almost all consumer products including plastic parts, cloths, lightweight jackets, shoes, sports articles, electronic items [13], agricultural appliances, navy materials, sanitary, lenses and optical coatings, and photo resistors for semiconductor manufacture etc [14]. A digital printing technology uses a variety of polymers as critical components [15], polymers for ion-exchange resins and flame retardants as well as in biomedical applications [16, 17].

Polymers containing s-triazine ring have become a subject of major interest because the thermal stability of the triazine ring makes it an attractive monomer for use in high temperature polymers [18, 19]. Extensive literature exists on thermally stable polymers in which aromatic and heterocyclic rings are linked together in main chain [20, 21]. A variety of polymers containing s-triazine nuclei in the main chain have been reported [22, 23]. The choice of this heterocyclic ring is based on its molecular symmetry and aromaticity [24]. Many reports are available regarding the theoretical studies of s-triazine and its derivatives [25]. All these experimental facts lend support to the belief that cyanuric chloride behaves like an acid chloride moreover s-triazine based polymers had an enlarged awareness in material science.

Through this work we aim to synthesize and characterize polymeric material having high heat resistivity, fluorescent property and compatibility which will further enhance the stability effect of other polymeric materials. The future goal is to focus on the mechanism of polymeric materials and to work out various approaches to target applications such as consumer products, agricultural appliances, navy materials, digital printing technology.

Experimental

Materials

Freshly prepared double distilled water was used for the preparation of solutions. Chemicals such as sodium hydroxide pellets, sodium bicarbonate, thionyl chloride, cetramide were used as received. The solvents carbon tetrachloride, chloroform, methanol, ethanol, acetone, Benzene, n-butanol, ethyl acetate, amyl acetate, isoamyl acetate, dimethyl formamide(DMF), dimethyl sulfoxide(DMSO) were received from Merck. Cyanuric chloride was purified by repeated crystallization from pure benzene (m.p146°C). piperidine (BDH), Phenolphthalein (BDH LR), catechol, diethylene glycol, ethylene glycol, hydroquinone, resorcinol, 1,4-dihydroxy anthraquinone, 1,5-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone (Cibatul, Atul) were received and purified by recrystallization from rectified spirit.

Measurements

The chemical structure of the intermediates and target materials have been scanned in KBr pellets on "IR affinity1, (DRS 8000A) Shimadzu Pvt. Ltd. (Japan) FT-IR Spectrometer Spectrum" and nuclear magnetic resonance spectrophotometer (Joel EX-400 FTNMR) in CDCl₃ with TMS as an internal standard. Thin layer chromatography was performed with Merck pre-coated TLC sheets GF254, and the spots were detected by UV irradiation or by spraying 50% alcoholic H₂SO₄ and visualizing after heat treatment in the hot air oven. Thermal properties, phase transition temperatures and enthalpies were determined by differential scanning calorimeter (Perkin-Elmer DSC-7) at a heating rate of 5 K/min. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer model TGA Pyris 1 system at a heating rate of 20 K/min in N₂ atmosphere.

Synthesis of Monomer

Synthesis of 4-dichloro-6-(N-DiphenylAminyl)-1, 3, 5-triazine [DT] (1)

A solution of cyanuric chloride (18.44g, 0.1mol) in a 60ml acetone was added with stirring to a cooled solution (0-5°C) of sodium bicarbonate (10.6g) in 100ml of distilled water, in a three-necked flask (250ml) equipped with a mechanical stirrer. This resulted in the formation of slurry of cyanuric chloride. A solution of diphenyl amine (17g, 0.1mol) in 10ml of acetone

was added to the cold slurry of cyanuric chloride. The mixture was stirred for 2 hour at 0-5°C. The white coloured product was filtered, and recrystallized from ethanol and dried in vacuum desiccators. The yield was 80%. M. P. 132°C.

Synthesis of (N-Diphenylaminy)-2, 4-bis (7-Hydroxy-Coumarin-3-carboxylicacid) 1, 3, 5 triazine [DCT] (2)

A solution of 2,4-dichloro-6-(N-DiphenylAminyl)-1,3,5-triazine [DT] (31.7g, 0.1mol) in 40ml of acetone was mixed with solution of NaOH (16g, 0.4mol) and 7-Hydroxy-3-carboxycoumarin (HCC) (41.2g 0.2mol) in 80ml double distilled water. Reaction was stirred for 2 hr at room temperature and 2 hr at 80°C. Separated solid was collected and washed with hot water. Product was dried in vacuum at 100°C. The yield was 92%. The product was recrystallized from acetone. M. P. 158 °C.

Synthesis of 6-(N- Diphenylaminy)-2,4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1,3,5-triazine [DCTC] (3)

Thionyl chloride (11.9ml, 0.1mol) was added into 6-(N-Diphenyl Aminyl)-2,4-bis-(7-Hydroxy-Coumarin-3-carboxylicacid)-1,3,5-triazine [DCT] (6.56g 0.01mol) in a dry round bottom flask. The reaction mixture was refluxed at 78°C for 2 hour. At the end of the reaction, excess thionyl chloride was distilled and dry product was collected. The yield was about 72%. The product was recrystallized from dimethyl formamide. M. P. 273 °C.

Synthesis of Copolymer

(N-Diphenylaminy)-2,4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1,3,5-triazine [DCTC] (0.01mol) and DMF (approx. 10ml) was stirred in a round bottom flask, then initiator citramide (0.25g) was added and heated up to 150°C. Then [Bisphenol-A + Catechol] (0.01mol)-DHC-1 each was added. The reaction temperature was raised to 160-170°C and heated for 8 hours. The reaction mixture was cooled and poured with constant stirring in 250ml of ice-cooled water. Solid was filtered, washed with hot water and dried. The yield was about 68%. The rest of the copolyesters were synthesized from 6-(N-Diphenylaminy)-2, 4-bis-(7-Hydroxy-Coumarin-3-Carbonyl Chloride)-1, 3, 5-triazine [DCTC] and combinations of [Bisphenol-A +

Hydroquinone]-DHC-2, [Bisphenol-A + Resocinol]-DHC-3, [Bisphenol-A + Phenolphthalein]-DHC-4, [Phenolphthalein + Catechol]-DHC-5, [Phenolphthalein + Hydroquinone]-DHC-6 [Phenolphthalein + Resorcinol]-DHC-7, [Phenolphthalein + Etheylene glycol]-DHC-8, [Catechol + Hydroquinone]-DHC-9, [Catechol + Resorcinol]-DHC-10diols by the similar method.

Results and Discussion

Color

The Copolyesters obtained from coumarin and various diols had unique colours. Formed polyesters are mostly brown and coffee in colour. Copolyesters related to ethylene glycol, resorcinol, and phenolphthalein were dark brown in colour. Hydroquinone and Bisphenol-A are light brown in colour.

Solubility

The Copolyester was soluble in different solvents which reveals that their insolubility in aliphatic chlorinated solvents like Chloroform, carbon tetrachloride. It was also found that copolyesters are insoluble in halogenated and non halogenated aromatic compounds like chlorobenzene and benzene. Copolyesters were soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, ether and ethyl acetate. Copolyesters were partly soluble in methanol, ethanol, n-butanol, isopropyl alcohol and ether but at higher temperature some copolyesters were soluble.

Viscosity

Dilute solution viscosity measurements were carried out using Ubbelohde suspended level viscometer. The copolyester solutions were prepared in DMSO and were filtered through G-3 sintered glass funnel prior to flow time measurements. Measurement of solution viscosity is generally made by comparing time 't' required for specific volume of polymer solution to flow through a capillary tube with the corresponding efflux time 't₀' of the solvent. Flow time of solvent (t₀) is 124 sec.

Intrinsic, Reduced and Inherent viscosity for all the copolyesters at various concentrations were determined at 25 ± 0.1°C. The relative (η_{rel}) and specific (η_{sp}) viscosities were calculated. Typical Huggins and Kraemer plots were used to obtain intrinsic viscosity for copolyesters. Intrinsic, reduced and inherent viscosities along with

Huggin's and Kraemer's constants for 1% solution are shown in **Table 1**

The observations of intrinsic viscosities of copolyesters were based on monomer containing N-diphenyl amine and coumarin in its backbone. Copolyesters DHC 1-10 reveals that DHC-4 which contain Bisphenol-A and phenolphtheline as diol has the highest solution viscosity and which can be due to high molecular weight compound where as DHC-8 has the lowest intrinsic viscosity which contain aliphatic diol ethylene glycol. The range of viscosity in this series was 0.441-0.640 g/dl. The copolesters which conatin aromatic diols have high viscosity and aliphatic diols have low viscosity such as DHC-8 and DHC-9 which has diethylene glycol and ethylene glycol as diols. The viscosity of DHC-1 is less than DHE-4 but higher than the rest of the copolyesters. The intrinsic viscosity of the polyesters obtained from the coumarin and N-diphenyl amine follows the sequence given below

DHC-8<DHC-9<DHC-10<DHC-6<DHC-5<DHC-7<DHC-2<DHC-3<DHC-1<DHC-4

Table 1: Various viscosity values and Huggins's and Kraemer's constants

Polymer	Intrinsic viscosity [η]	Reduced viscosity η_{sp} / C	Inherent viscosity $\ln\eta_{rel} / C$	Huggin's constant K'	Kraemer's constant K''
DHC-1	0.60	0.68	0.52	0.218	0.212
DHC-2	0.53	0.62	0.48	0.321	0.168
DHC-3	0.57	0.67	0.52	0.304	0.152
DHC-4	0.64	0.69	0.53	0.141	0.254
DHC-5	0.52	0.58	0.46	0.230	0.205
DHC-6	0.49	0.55	0.44	0.232	0.208
DHC-7	0.53	0.58	0.45	0.189	0.264
DHC-8	0.44	0.48	0.39	0.226	0.231
DHC-9	0.47	0.53	0.43	0.279	0.199
DHC-10	0.48	0.54	0.43	0.267	0.215

IR Analysis

IR spectra of copolyester DHC-4 showed O-H stretching vibration of -OH group at 3291 cm^{-1} , N-H stretching vibration of secondary amine at 3424 cm^{-1} , C-H stretching vibration of -OCH₃ group at 2960 cm^{-1} , C-H stretching vibration of -CH₂- group at 2845 cm^{-1} , C=C stretching vibration of aromatic ring at 1608 cm^{-1} , C-N stretching vibration of tertiary amine group at 1533 cm^{-1} .

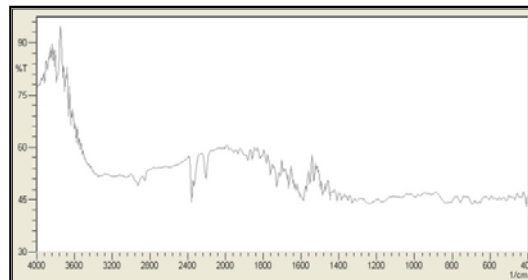


Figure 1: IR spectrum of DHC-4

IR spectra of copolyester DHC-7 showed O-H stretching vibration of -OH group at 3315 cm^{-1} , N-H stretching vibration of secondary amine at 3400 cm^{-1} , C-H stretching vibration of -CH₂- group at 2400 cm^{-1} , C=C stretching vibration of aromatic ring at 1850 cm^{-1} , C-N stretching vibration of tertiary amine group at 1585 cm^{-1} .

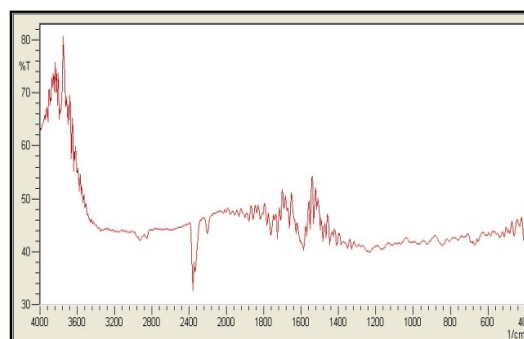
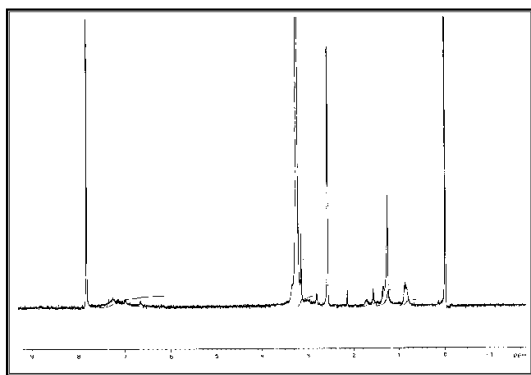


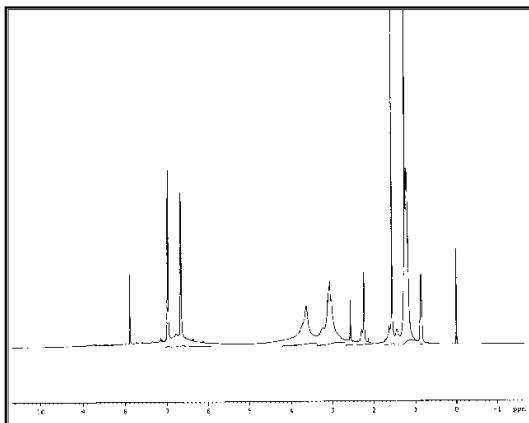
Figure 2: IR spectrum of DHC-7

¹H-NMR Spectra:

In ¹H-NMR spectrum of copolyesters DHC-2 and DHC-6 singlet appear at 3.94δ were of -NH- protons, at 3.67 and 3.69δ indicates the presence of -CH₂- group in the structure. The protons 4.90δ, and 6.78-7.80 were of -OH proton and aromatic protons. The shift at 0.87δ indicates the presence -CH₂- group of diethylene Glycol. Chemical shifts at 3.63-3.69δ prove the presence of -CH₂- group in N,N-diphenylamine. Singlets of 1.55δ gives the conformation of -CH₃ group of bisphenol-A.



‘Figure 3’: ¹H-NMR spectrum of DHC-2



‘Figure 4’: ¹H-NMR spectrum of DHC-6

Thermogravimetric Analysis

The TGA data were used to determine the initial degradation temperature, degradation rate, residual weight at the end of degradation. The weight loss of copolyesters during thermal degradation is a function of degradation rate and degradation time. At higher heating rate, although the degradation rate was higher, the time to reach a given temperature became shorter and the residual weight at a given temperature during thermal degradation may be higher. The remaining solid residue after complete pyrolysis was char and ash. TGA was used to determine the thermal degradation characteristics and kinetic parameters.

An attempt is made to assess the thermal stability of some of the copolyesters qualitatively based on visual obtained thermograms. T_0 and T_{10} are some of the main criteria of the thermal stability of the copolyesters. The higher the T_0 and T_{10} the higher will be the heat stability of copolyesters. TGA curve obtains at a scan rate of $10^\circ\text{C}/\text{min}$ for copolyesters. There were two obvious oxidation zones during oxidation of copolyester in air. The oxidation rate of the first zone was much higher than that of the second zone. The pyrolysis and oxidation rates increased with the heating rate in

DHC-3. TGA indicated that the starting temperatures of pyrolysis of DHC-3 in air increased with the increase of heating rate and initial moisture content. When the samples were heated, decomposition initially starts at 161°C and two stages of weight loss were observed. The first one was completed before 500°C in the samples. The second stage appears in the temperature range from 550°C to 620°C .

In DHC-4 the maximum rate of decomposition starts at 230°C and 525°C . At this temperature polymer shows weight loss about 40-45% and 60-70% respectively. 50% weight loss is shown at 500°C . After 500°C , the sample degrades slowly and shows total 92% weight loss at 700°C .

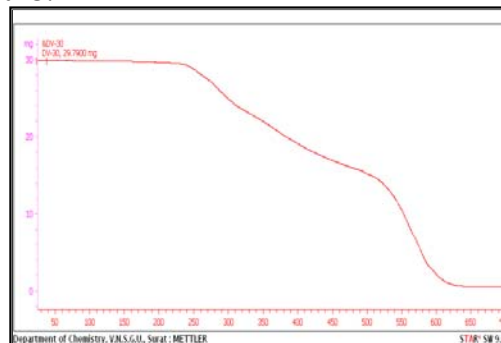


Figure 5’: TGA of DHC-3

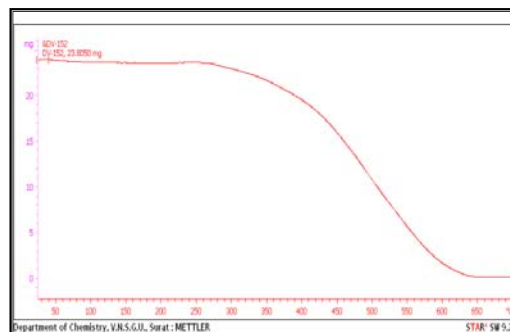


Figure 6’: TGA of DHC-4

Fluorescence Spectra

The fluorescence spectrum of DHC-6 and DHC-7 of coumarin based copolyesters with aromatic diols are shown in **Figure 7** and **figure-8**. Copolyester DHC-6 and DHC-7 were dissolved in $\text{DMSO}-D_6$ and then excited at 200 nm and 210 nm respectively. Emission spectra were recorded between 110 and 600 nm. Upon excited at 200 nm, the fluorescence spectrum of DHC-6 indicates broadened emission range is at 140-550 nm and emission peak is at 300 nm and upon excited at 210 nm, the fluorescence spectrum of DHC-7 indicates broadened emission range at 210-550 nm and the emission peak is at 300 nm.

The fluorescence intensity of polyester DHC-7 is much higher than polyester DHC-6. This is due to high fluorescence structure of compound.

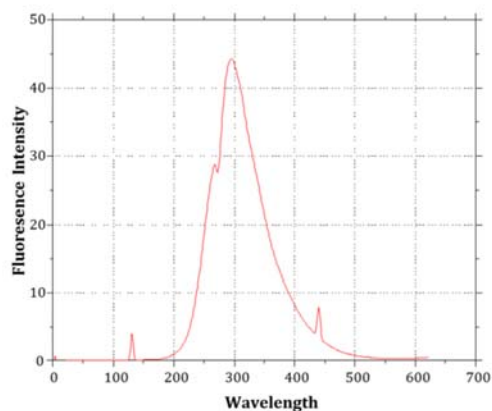


Figure 7: Fluorescence spectrum of DHC-6

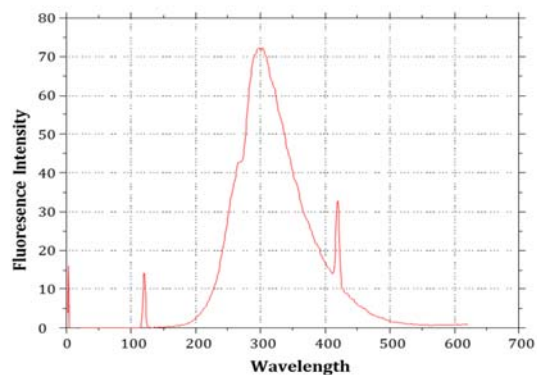


Figure 8: Fluorescence spectrum of DHC-7

Conclusion

The paper concludes synthesis, characterization and properties of copolyesters. The colour of most of the copolyesters is dark. The solubility in different solvents reveals that aromatic copolyesters are insoluble in aliphatic chlorinated solvents like Chloroform, carbon tetrachloride. They are insoluble in halogenated and non halogenated aromatic compounds like benzene and chlorobenzene. Copolyesters are soluble in dimethyl formamide, dimethylsulfoxide, tetrahydrofuran, ether and ethyl acetate. They are partly soluble at room temperature in methanol, ethanol, n-butanol and isopropyl alcohol but soluble at higher temperature. A fluorescent spectrum of the polyester has proved their fluorescence depending on the structure of the copolyester.

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Supporting Information Available NMR spectra, NMR titration experiment curves, and geometries of the optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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