Synthesis and Study of Thermally Stable Fluorescent Polyesters

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Abstract

Variouscompounds containing heterocyclic ring have been synthesized by the polycondensation method. Numbers of derivatives containing s-triazine ring and coumarin have been reported as hetrocyclic compounds. Ten Polyesters were synthesised having different aliphatic-aromatic diols in the chain having s-triazine ring as main moiety. The polyesters were synthesized by polycondensation of (N-diphenylaminyl)-2,4-bis-(7-hydroxy-coumarin-3-carbonyl chloride)-1,3,5-triazine with aliphatic and aromatic diols. The colour and solubility of synthesized polyesters were in different solvents. The viscosity was studied for polyesters. This polyesters show inherent viscosity ranging from 0.402- 0.709 dlg^{-1}*in DMF at 25°c. The synthesized polyesters were characterized by 1H-NMR, FT-IR, fluorescence spectra. The measured data indicate that synthesized aromatic fluorescent polyesters are used in various fields.*

Keywords: Trizine, N-Diphenylamine, Coumarin, Viscosity, Fluorescence

Introduction

The macromolecular chemistry is a multidisciplinary science that deals with the chemical synthesis and chemical properties of polymers. It is emerging as a necessary part of human life and it impacted on the system in which world exists. There is an amazing variety in the properties of polymeric materials [1,2]. Polymers are used in a broad variety of applications [3].There is still a great opportunity to become aware of these materials and improve their properties as polymeric material. Now a day growing demands for extremely specialized materials for utilization with specific properties. There is huge demand for fluorescent polymers for past several decades. Organic fluorescent polymers have been extensively studied[2,4]. Research on fluorescent material has attracted great attentions due to wide range of applications such as clean energy technologies,[3],explosive sensing, [4,5]PH/temperature sensor ,biological imaging[6],life science, material science, ultrasensitive molecular diagnosis and novel light-emitting nano devices ,[7] and biological detection schemes, smart polymer machines, fluorescent chemo sensor, fluorescent molecular thermometers, fluorescent imaging, drug delivery carriers, and so on. Different methods have been used developed to synthesize fluorescent polymers by many research groups, with new architecture which contain various amounts of fluorophores and show bright fluorescence are synthesized for various applications.Research on fluorophore-enriched polymers has become an interesting field because of their multipurpose applications as luminescent probes in various areas[8-11]In general, there are two ways to synthesize such fluorophore-enriched polymers. Fluorescent polymers can be synthesized by polymerization of fluorescent functional monomers, using fluorescent compounds as initiator, fluorescent compounds as chain transfer agents, chemical bonding between fluorescent groups and polymers, and polymerization of nonfluorescent functional monomer[12,13],the second is the chemical variation of polymers by fluorescent molecules or fluorescent oligomers[10,14,15]. The aim of present work was to synthesize polyesters with high fluorescence intensity for the coming use in different field.

Experimental

Materials and methods

Freshly prepared double distilled water was used for the preparation of solutions.Chemicals such as Sodium hydroxide pallets, Sodium bicarbonate, Thionyl chloride, Cetramide were used as received. The solvents carbon tetrachloride, chloroform, methanol, ethanol, acetone, Benzene, n-butanol, ethylacetate, amyl acetate, isoamyl acetate, dimethyl formamide(DMF), dimethyl sulfoxide(DMSO) were received from Merck. Caynuric chloridewas purified by repeated crystallization from pure benzene(m.p146^{0}C). N,N-diphenylamine(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.

Synthesis of monomer DCTC

The monomer 6-(N- DiphenylAminyl)-2,4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1,3,5-triazine [DCTC] was prepared from 6-(N-DiphenylAminyl)-2,4-bis-(7-Hydroxy-Coumarin-3-carboxylic acid)-1,3,5 triazine [DCT] which was prepared from 2, 4-dichloro-6-(N-DiphenylAminyl)-1, 3, 5-triazine [DT] and substituted coumarin by reported method.

Synthesis of Polyesters

6-(N-Diphenylaminyl)-2,4-bis-(7-Hydroxy-Coumarin-3-carbonyl Chloride)-1,3,5-triazine [DCTC] was taken in the minimum quantity of DMF in a round bottom flask and then stirred thoroughly. Then initiator cetrimide was added and heated up to 150°C. Different diols were added into the reaction mixture and temperature was raised to 160-180^{o}C and heated for 8 hrs. The reaction mixture was cooled and poured into 250ml of ice-cooled water constant stirring. Solid was filtered, washed with hot water and dried. Ten polyesters from DHE-1 to DHE-10 were synthesised by taking diethylene glycol, ethylene glycol, catechol, resorcinol, hydroquinone, phenolphthalein, Bisphenol-A, 1,4dihydroxyanthraquinone, 1,5 dihydroxyanthraquinone, 1,8dihydroxyanthraquinone respectively.

Properties of Polyesters

Polyesters prepared from coumarin and a variety of diols have exclusive colours. Coumarin and Diphenyl amine based polyesters show different colours. Most of the polyesters are brown in colour. Polyesters related to Ethylene Glycol, Resorcinol, Phenolphthalien and 1, 4- Anthraquinone containing yellowish brown, dark brown, brown and light brown colour respectively. Anthraquinone containing polymers have different colour from each other.

Solubility

Relative solubility of various polyesters obtained from coumarin and N-diphenyl amine in different solvents were carried out at room temperature and 50^{0}C. The solubility of the polyesters in different solvents reveals that polyesters were insoluble in aliphatic chlorinated solvents like chloroform, carbon tetrachloride. It is also found that polyesters were insoluble in halogenated and non halogenated aromatic compounds like chlorobenzene and benzene. Polyesters were soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydro furan, ether and ethyl acetate but polyesters obtained from Phenophthelin and Bisphenol-A are insoluble in acetone. Polyesters are partly soluble at room temperature in methanol, ethanol, n-butanol, isopropyl alcohol and ether but some of polyesters are soluble at higher temperature.

Viscosity

Intrinsic, Reduced and Inherent viscosity for all the polyesters at various concentrations were determined at 25 ± 0.1°C. The relative (η_{rel}) and specific (η_{sp}) viscosities, Reduced and Inherent viscosities were calculated from experimental data. Typical Huggins and Kraemer plots were used to obtain intrinsic viscosity for some of polyesters. Intrinsic, reduced and inherent viscosities along with Huggin's and Kraemer's constants for 1% solution are shown in figure 1 and table 1.

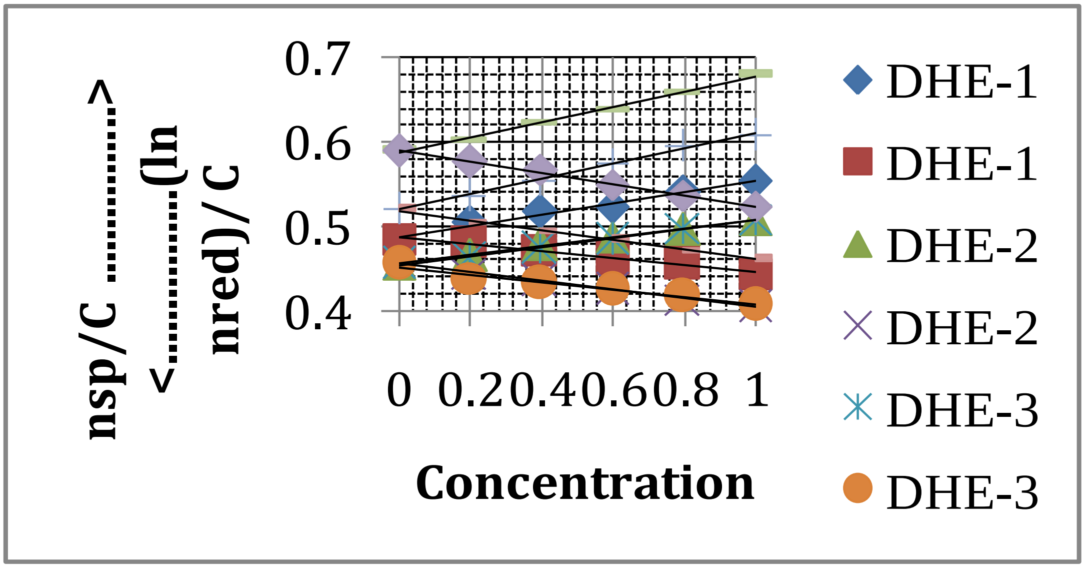

Figure 1: Typical Huggins and Kraemer plots for Intrinsic Viscosity **DHE-**1 to **DHE-5**.

The observations of intrinsic viscosities of Polyesters DHE 1-10 reveals that DHE-7 which contain Bisphenol –A as diol has the highest solution viscosity and which can be due to high molecular weight compound, whereas DHE-3 has the lowest intrinsic viscosity which contain aliphatic Ethylene Glycol. The range of viscosity in this series was 0.455 -0.615 g/dl. The polymers which conatin aromatic diols have high viscosity and the aliphatic diols have low viscosity such as DHE-3 and DHE-2 which has diethylene glycol and ethylene glycol as diols. The viscosity of DHE-5 is less than DHE-7 but higher than the rest of the polyesters. The intrinsic viscosity of the polyesters obtained follows the sequence given here.

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

Polymer	Intrinsic viscosity [η]	Reduced viscosity η_{sp} / C	Inherent viscosity $\ln\eta_{rel}$ / C	Huggin's constant K'	Kraemer's constant K"
DHE-1	0.492	0.552	0.434	0.242	0.239
DHE-2	0.475	0.508	0.407	0.144	0.302
DHE-3	0.455	0.507	0.402	0.251	0.256
DHE-4	0.510	0.559	0.444	0.206	0.275

DHE-5	0.590	0.679	0.522	0.255	0.195
DHE-6	0.505	0.561	0.449	0.229	0.219
DHE-7	0.615	0.709	0.536	0.248	0.208
DHE-8	0.494	0.583	0.445	0.376	0.194
DHE-9	0.515	0.601	0.474	0.324	0.154
DHE-10	0.535	0.591	0.464	0.250	0.250

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

Characterization

All the synthesised polyesters were characterised by visible absorption spectra, some representative IR spectra and NMR spectra. The visible absorption spectra of all synthesised polyesters have been recorded in DMF and observed in range of 550 to 380nm. The colour observed of each polyester was due to oscillation of electrons and presence of substituents.

IR Spectra

IR spectra of polyester DHE-1 showed O-H stretching vibration of –OH group at 3440 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}.IR spectra of polyester DHE-3 showed O-H stretching vibration of –OH group at 3445 cm^{-1}, N-H stretching vibration of secondary amine at 3424cm^{-1}, C-H stretching vibration of -OCH3 group at 2960 cm^{-1}, C-H stretching vibration of -CH2- group at 2842 cm^{-1}, C=C stretching vibration of aromatic ring at 1607 cm^{-1}, IR spectra of polyester DHE-8 showed O-H stretching vibration of –OH group at 3438 cm^{-1}, N-H stretching vibration of secondary amine at 3424cm^{-1}, C-H stretching vibration of -OCH3 group at 2940 cm^{-1}, C-H stretching vibration of -CH2- group at 2843 cm^{-1}, C=O stretching vibration of –COOR group at 1708 cm^{-1}.Examination of IR absorption frequencies reveals that the polyesters exhibit strong or moderately strong absorption at a frequency of 803cm^{-1} and 1464-1511cm^{-1} which may be attributed to out of plane and in-plane vibrations of s-triazine ring respectively, 1737cm^{1} and 1612cm^{-1} which may be attributed to vibrations involving lactone and ester groups respectively.

^{1}HNMR Spectra

In ^{1}H-NMR spectrum of polyesters DHE-2 and DHE-6 singlets appear at 3.94δ were of -NH- protons, at 3.67 and 3.69δ indicates the presence of $–CH_2-$ group in the structure. The protons 4.90δ, and 6.78-7.80 were of -OH proton and aromatic protons.The multiplate signal of aromatic protons appears at 7.05-7.63δ, 6.66-7.08δ, 6.63-7.28δ, 7.89-7.96δ, 6.58-7.58δ in DHE-2, DHE-6, DHE-7, DHE-8 and DHE-10 respectively. The shift at 0.87δ indicates the presence $–CH_2-$ group of Diethylene Glycol. Chemical shifts at 3.63-3.69δ prove the presence of $–CH_2-$ group in N,N-diphenylamine. Singlets of 1.55δ gives the conformation of $–CH_3$ group of Bisphenol-A.

Thermogravimetric analysis:

The TGA data were used to determine the initial degradation temperature, degradation rate, residual weight at the end of degradation, and degradation kinetic parameters. The weight loss of polyesters 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 polyesters qualitatively based on visual obtained thermograms. T_0 and T_{10} are some of the main criteria of the thermal stability of the polyesters. The higher the T_0 and T_{10}, the higher will be the heat stability of polyesters. TGA curve obtains at a scan rate of 10°C/min for polyestes.

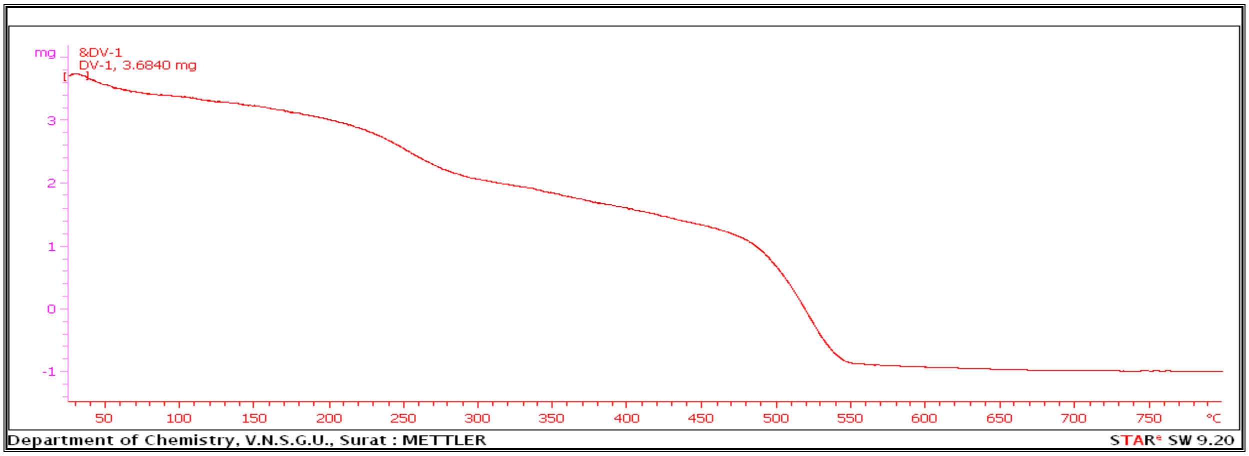

Figure 2: TGA of DHE-8

Fluorescence Spectra:

The fluorescence spectrum of the polymer DHE-1 is basaed on the coumarin, diphenyl amine monomer with the aromatic diol Catechol figure 3. Polyester DHE-1 were dissolved in DMSO-D_6 and then excited at 190nm. Emission spectra were recorded between 110 and 600 nm. Upon excitation at 110 nm, the fluorescence spectrum of DHE-1 indicates broadenedeimission range between 100-600nm and emission peak at 290nm. The decrease of fluorescence intensity does not follows the first-order kinetics model. One can suggest that at least two processes are responsible for the decrease of fluorescence: (1) concentration of fluorescent decreases due to photocyclization reaction, and (2) fluorescence photoquenching operates in this system via intermolecular mechanism of energy transfer in photostationary state. Emission band of DHE-1were located in the same spectral region.

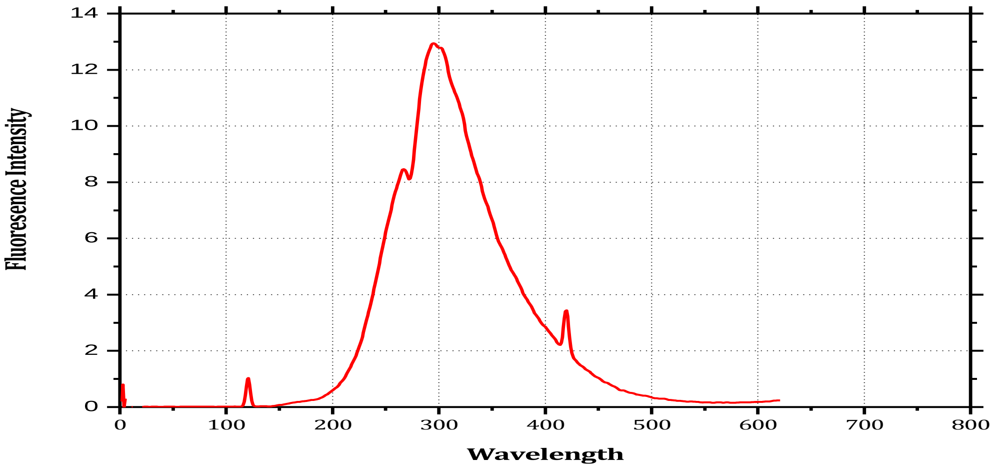

Figure 3: Fluorescence spectrum of DHE-1

Result and Discussion

The resulting novel polyesters were obtained in good yields (80-95%), with variety of colours. DHE-2 showed yellowish brown colour but DHE-4 showed dark brown and DHE- 7 and DHE-8 were reddish brown and light brown respectively. All the novel polyesters were insoluble in benzene and chloro benzene, completely soluble in Ethyl acetate, DMF and DMSO but partly soluble in methanol, tetrahydrofuran, n-butanol, isopropyl alcohol and ether. The inherent viscosities of novel polyesters showed ranging between 0.402- 0.709 dlg^{-1}.The intrinsic viscosity of polyesters were given this sequence DHE-3<DHE-2<DHE-1<DHE-8<DHE-6<DHE-4<DHE-9<DHE-10<DHE-5<DHE-7.The highest intrinsic viscocity was of DHE-7 due to molecule structure of polyester in which bisphenol-A was used as diol. The thermal properties of the DHE-8 were evaluated by TGA at heating rate of 10^0C/min under a nitrogen atmosphere. TGA thermogramsin fig.(2) polyesters exhibited good thermal stability. The 10% weight loss temperatures of the aromatic polyesters in nitrogen was recorded at 300^0C for DHE-8 . The amount of residue of these polyesters in a nitrogen atmosphere was more than 44% at 550^0C. The high char yields of these polyesters could be ascribed to their high aromatic content. The series of polyesters showed higher thermal stability compared to the corresponding counterpart without coumarin moiety. This might be explained by the fact that the presence of coumarin moiety.

Conclusions

It describe the synthesis of fluorescence and thermally stable polyesters by polycondentation of coumarin probe carboxylic acid and aliphatic-aromatic diols. The resulting polyesters show excellent colours, soluble in organic solvents and good thermal stability. All the synthesized polyesters show excellent fluorescence which can be used in diverse fields.

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