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Design and Study of Fluorescent Property of Polymeric Materials Containing Heterocyclic Compounds in Their Backbone

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Abstract

The fluorescent polymeric assemblies and nanoparticles have become a focus of intensive investigation in diverse fields based on fluorescent assays for detection and labelling. The aromatic polymers with their fluorescent property are used in wide range of applications ranging from optical materials, analytical chemistry, a biological assays explosive sensing, analytical chemistry, public health issues, biological detectprojects and in various fields. A water insoluble aromatic polymer structures with their hydrophobic nature containing several heterocycles of various types were synthesised. It was synthesized by the reaction of cyanuric chloride, substituted coumarin and 2,4-Thiazolidinedione. Taking cyanuric chloride as their back bone series of polymers were synthesised by using different aliphatic and aromatic diols. The solubility,colour and viscosity of new polymers were studied. The new synthesised polymers were also characterised by UV, IR and fluorescence spectra.

Keywords:substituted coumarin, 2,4-Thiazolidinedione, cyanuric chloride, fluorescence spectra

Introduction

The polymer chemistry is one of the unique branches of chemistry, as it possesses a remarkable direct impact on the way of people nearly in every region of the world. 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. 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. As of the surprising variety of properties of polymeric materials [1]. They play a critical and ubiquitous role in everyday life [2]. This role ranges from well-known artificial plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are fundamental for life. Natural polymeric resources such as amber, shellac and natural rubber have been used for centuries. A range of some other natural polymers be present, such as cellulose, made of up from the core part of wood and paper. The list of synthetic polymers includes synthetic nylon, rubber, neoprene, Bakelite, PVC, polyethylene, polystyrene, polypropylene, PVB, polyacrylonitrile, silicone, and countless more [3]

Due to increased demand of polymers with high performance characteristics in various fields including theaerospace, automobile, and microelectronic industries,the use of these aromatic polymers is growing steadily. However, these polymers are generally intractable and lack of the properties essential for successful fabrication into useful forms. Many researchers have tackled these inherent problems over the few decades by modifying the monomers structures [4,5].

Polymers are used in a broad variety of applications. They find wide use in almost all consumer products including plastic parts, cloths, lightweight jackets, shoes, sports articles, electronic items [6], appliances, cookware, countertops, flooring, telephones, toys, siding, sheathing, sporting goods, packaging, auto parts, circuit boards, bottles, containers, fishing lines, gaskets, ropes, stamp making, oil filed scale inhibitors [7], agricultural appliances, navy materials, sanitary, lenses and optical coatings, and photo resistors for semiconductor manufacture etc. A digital printing technology uses a variety of polymers as critical components [8]. They also find wide use in packaging materials

[9], films and film supports, textiles, industrial yarns, automobile bumpers, moulded items, lubricants, coating agents, adhesives, fibres , and other not reusable articles[10], as well as in biomedical applications.

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. Extensive literature exists on thermally stable polymers in which aromatic and heterocyclic rings are linked together in main chain [11,12,]. A variety of polymers containing s-triazine nuclei in the main chain have been reported [13,14]. The choice of this heterocyclic ring is based on its molecular symmetry and aromaticity.

Many reports are available regarding the theoretical studies of s-triazine and its derivatives. Reading through of literature on synthesis of various alkoxy, aryloxy and amine or substituted amino derivatives of 2,4,6-trichloro-s-triazine suggests that cyanuric chloride should be the classed as an acylhalide [15]. An amino group on the s-triazine ring has a character like that of an amino group in an amide because of the electron attracting effect of the s-triazine ring. Thus it does not react with carboxylic acid chloride at low temperature. Analogously, a chloride group on the s-triazine ring doesn't react with an acid but it reacts with an alcohol or phenol [16]. All these experimental facts lend support to the belief that cyanuric chloride behaves like an acid chloride.Over the past few decades, s-triazine-based polymers have had enlarged awareness in material science.

Synthesis of Polymer

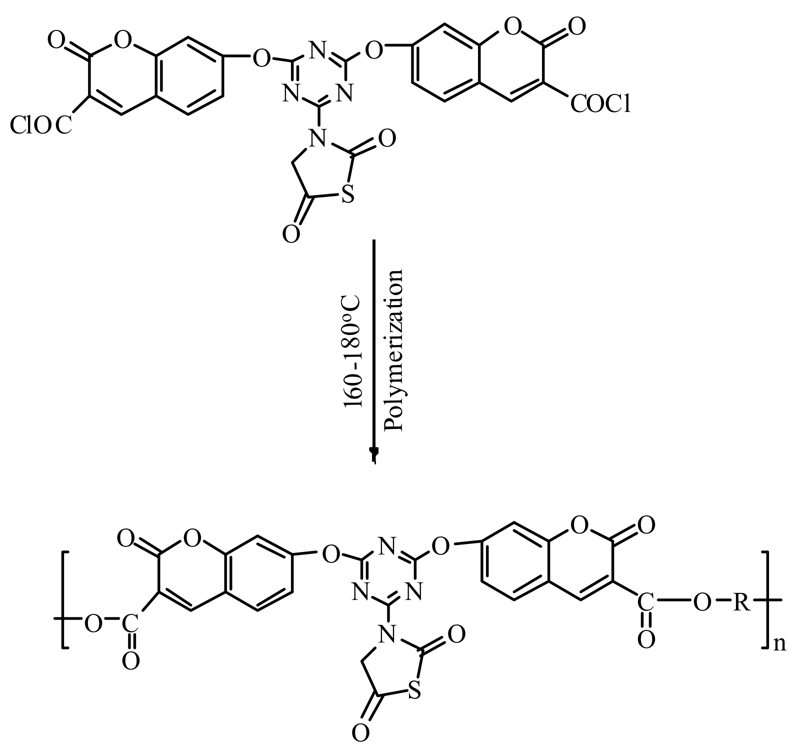
Synthesis of Monomer

6-(2,4 thiozilidine dione)-2,4-bis-(7-Hydroxy- Coumarin-3-Carbonyl Chloride)-1,3,5-triazine [TCTC]

Thionyl chloride (11.9ml, 0.1mol) was added into6-(2,4 thiozilidine dione)-2,4-bis-(7-Hydroxy-Coumarin-3-Carbonyl Chloride)-1,3,5-triazine [TCTC](6.56g 0.01mol) in a dry round bottom flask.The reaction mixture was refluxed at 78^{o}C for 2hours. At the end of the reaction,excess thionyl chloride was distilled and dry product was collected. The yield was about 70%. The product was recrystallized from dimethyl formamide.M.P. 273^{0}C.

Synthesis of Polyesters

6-(2,4 thiozilidine dione)-2,4-bis-(7-Hydroxy- Coumarin-3-Carbonyl Chloride)-1,3,5-triazine(0.01 mol [TCTC] was taken in the minimum quantity of DMF(approx.10ml) in a round bottom flask and then stirred thoroughly. Then initiator cetrimide (0.25g) was added and heated up to 150^{0}C. Bisphenol-A (0.02 mol) was added in to the reaction mixture and temperature was raised to 160-180^{0}C and heated for 8 hours.The reaction mixture was cooled and poured into 250ml of ice-cooled ware constant stirring. Solid was filters,washed with hot water with hot water and dried. The yield was about 65%. Likewise different diols were added and polyesters were synthesised(scheme-1).



Scheme:1 polymerization (1-6)

[PEBPA] : Yield 84%, 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).

[PEHq] : 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).

[PEPh] : 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).

[PEC] : Yield 80%, 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).

[PEEG] : 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).

[PER] : Yield 83%, 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).

Result and Discussion

Colour

Substituted coumarin and thiozilidine 2,4 dione based polyesters show different colours. Formed polyesters are mostly brown and coffee in colour. Polyesters related to Ethylene Glycol, Resorcinol, Phenolphthaleinare dark brown in colour. Hydroquinone and Bisphenol-A are light brown in colour.

No.	**Polyesters from TCTC**			
	Codes	**Diol**	**Color**	**Density(gm/cm^3)**
1	PEBPA	Bisphenol-A	Light brown	1.129
2	PEPh	Phenolphthalein	Coffee Brown	1.176
3	PER	Resorcinol	Brown	1.152
4	PEHq	Hydroquinone	Brown	1.159
5	PEC	Catechol	Light Brown	1.148
6	PEEG	Ethylene Glycol	Brownish	1.119

Solubility

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

Solvent	1	2	3	4	5	6
Acetone	++	++	++	++	++	++
Chloroform	--	--	--	--	--	--
CCl_4	--	--	--	--	--	--
DMF	++	++	++	++	++	++
Chlorobenzene	--	--	--	--	--	--
DMSO	++	++	++	++	++	++
Methanol	±±	±±	±+	±±	±±	±+
Ethanol	±+	±+	±+	±+	±+	±+
Cyclohexane	-±	-±	-±	-±	-±	±±

Fluorescence Spectra

The graph of florescence intensity vs wave length is mentation in figure 1. The fluorescent spectrum of the polymer PEC is based on Coumarin and thiozilidine 2,4 dione with the aromatic diol Catechol as shown in the figure. It showed that the absorption takes place by polymer from 200-290nm and emission takes place from 290-550nm. The highest intensity of polymer is at 290nm due to coumarin as an pendent molecule. The polymers shows significant intensity due to the aromatic diol.

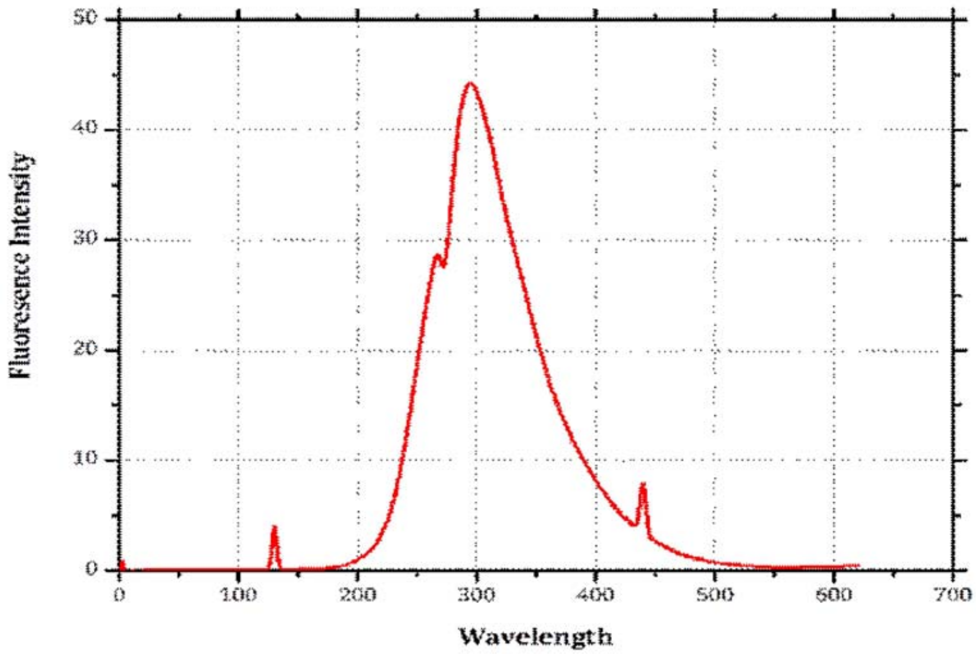


Figure 1: Florescence spectra of PEC polymer

Conclusion

The conclusion reveals that it gives explanation of the synthesis, characterization,and properties of polyesters. The colour of most of the polyesters were dark. The solubility of the polyesters in different solvents reveals that polyesters are insoluble in aliphatic chlorinated solvents like Chloroform,carbon tetrachloride. They are insoluble in halogenated and non-halogenated aromatic compounds like benzene and chlorobenzene. Polyesters are soluble in dimethyl formamide,dimethyl sulfoxide,tetrahydro furan,ether and ethyl acetate.Theyarepartly 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 polyester.

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