

Synthesis and Study of Thermally Stable S-Triazine Based Polyamides

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Abstract: *The series of water insoluble aromatic polyamides were synthesized by polycondensation method. The synthesized aromatic polyamides 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. The fluorescent polymeric assemblies and nanoparticles have become a focus of intensive investigation in diverse fields based on fluorescent assays for detection and labelling. It was synthesized by the reaction of s-triazine, substituted coumarin and 2,4-dionethiozolodine. Taking s-triazineas their back bone,ten polyamide were synthesised by using different aliphatic and aromatic diols. The solubility,colour and viscosity of new polyamides were studied. The new synthesised polymers were also characterised by UV, IR, NMR and fluorescence spectra.*

Keywords: *Polyamides, Polycondensation, s-triazine, 2,4,dione thiozolodine, Coumarin.*

I. INTRODUCTION

Polymers possess 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. They play a critical and ubiquitous role in everyday life. 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.

II. PREVIOUS WORK

Due to increased demand of polyamides with high performance characteristics in various fields including the

aerospace, automobile, and microelectronic industries, the use of these aromatic polymers is growing steadily [1,2]. However, these polyamides are generally intractable and lack of the properties essential for successful fabrication into useful forms[3]. Many researchers have tackled these inherent problems over the few decades by modifying the monomers structures [4,5]. polyamides 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, molded items, lubricants, coating agents, adhesives, fibers , and other not reusable articles, polymers for ion-exchange resins and flame retardants [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. Read-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.

III. PROPOSED METHODOLOGY

1. Synthesis of monomer

Thionyl chloride (11.9ml, 0.1mol) was added into 6-(2,4thiozilidinedione)-2,4-bis-(7-Hydroxy-Coumarin-3-Carbonyl Chloride)-1,3,5-triazine [TCTC](6.56g 0.01) in a dry round bottom flask. The reaction mixture was refluxed at 78 degree 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. 273⁰C.

2. Synthesis of Polyamide

6-(2,4 thiozilidinedione)-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 citrimide (0.25g) was added and heated up to 150⁰C. o-Phenylene diamine (0.02 mol) was added in to the reaction mixture and temperature was raised to 160-180⁰C 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 diamines were added and polyamides were synthesised.

3. Properties of Polyamide:

3.1 Colour

Substituted coumarin and thiozilidine 2,4dione based polyesters show different colours. Formed polyamide are mostly brown and coffee in colour. Polyamide related to o,m-phenylene diamine are dark brown in colour.

3.2 Solubility

The Polyamides is soluble in different solvents which reveals that their insolubility in aliphatic chlorinated solvents like Chloroform, carbon tetrachloride. It is also found that Polyamides 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 Polyamides are soluble.

IV. EXPERIMENTAL RESULTS

4.1 IR Analysis

IR spectra of polyamide PHA-4 showed 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.

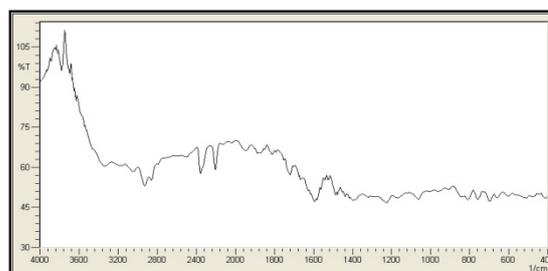


Fig. 4.1 IR spectra of PHA-4

4.2 ¹H-NMR Spectra:

In ¹H-NMR spectrum of polyesters PHA-2 and PHA-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 multiple signals of aromatic protons appear at 7.05-7.63δ, 6.66-7.08δ, 6.63-7.28δ, 7.89-7.96δ, 6.58-7.58δ in PHA-1, PHA-2, PHA-3, PHA-4 and PHA-5 respectively. 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.

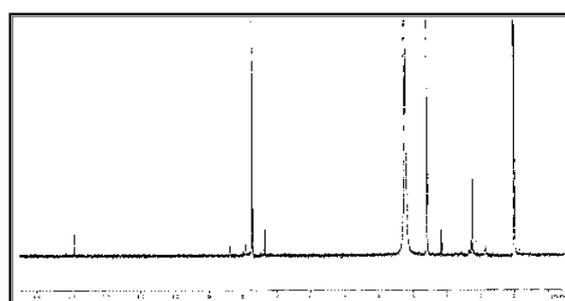


Fig. 4.2 NMR spectra of PHA-3

4.3 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 polyamide during thermal degradation is a function of degradation rate and degradation time. 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 polyamide 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 $10^\circ\text{C}/\text{min}$ for polyamide. The TGA of PHA-2 indicates the high stability of synthesized polyamides.

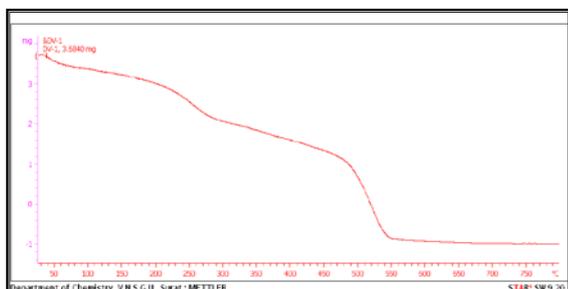


Fig. 4.3 TGA spectra of PHA-2

4.2 Fluorescence Spectra

The fluorescent spectrum of the polymer THE is based on Coumarin and thiozilidine 2,4-dione with the aromatic diamine o & p- phenylene diamine Polyamides as shown in the figure-4.4.

The absorption of polyamide PHA-4 was at 290nm and it gave high intensity.

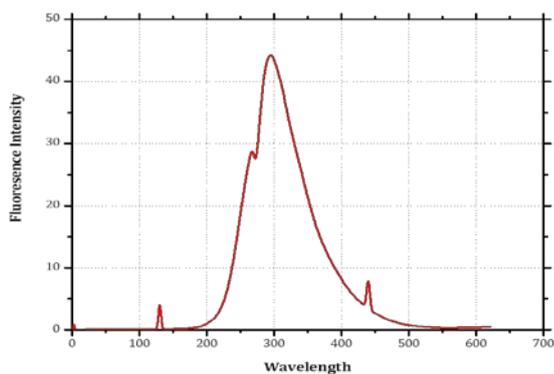


Fig. 4.4 Fluorescence spectra of PHA-4

V. CONCLUSION

The importance of this paper is that it gives explanation of the synthesis, characterization and properties of polyamides. The colour of most of the polyamides is dark. The solubility of the polyamides in different solvents reveals that polyamides are insoluble in aliphatic chlorinated solvents like Chloroform, carbon tetrachloride. They are insoluble in halogenated and non halogenated aromatic compounds like benzene and chlorobenzene. polyamides 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 polyamides has proved their fluorescence depending on the structure of the polyamides.

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VI. FUTURE SCOPE

The synthesized polyamides will useful aerospace, automobile, and microelectronic industries, lightweight jackets, shoes, sports articles, electronic items, 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, agricultural appliances, navy materials, sanitary, lenses and optical coatings, and photo resistors for semiconductor manufacture.

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