



SYNTHETIC PROTOCOLS AND SIGNIFICANCE OF HETEROCYCLIC FLUORESCENT - REINFORCING POLYMERS: A COMPREHENSIVE REVIEW

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ABSTRACT

Fluorescent High-Performance polymers are well known as high performance engineering thermoplastics because of their good thermal stability, chemical resistance and excellent mechanical properties. Polymers having S-triazine ring become a subject of interest because of enhanced toughness and low moisture absorption and commercially available high performance engineering plastic materials. However, the thermal stability of triazine ring makes it an attractive monomer for use in high temperature polymers. Synthesis of polymers containing chromophoric groups which are responsible for fluorescent property have significant applications in fields such as biosensors, clean energy technologies, explosive sensing, pH/temperature sensor, biological imaging, life science, material science, ultrasensitive molecular diagnosis and novel light - emitting nano devices. The aromatic azo group is being more interest because of the existence of cis-trans isomerism and its effect on the photochromic properties of the polymers. Therefore, polymers having azo group have potential use in a variety of applications. Fluorescent polymers can be developed with different methods; generally, there are two methods for preparation of fluorescent polymers. One of them is polymerization of a monomer having a fluorescent chromophore such as fluorescent compounds as initiator, fluorescent compounds as chain transfer agents, chemical bonding between fluorescent groups and polymers. The second way, chemical alteration of commercially available polymers having reactive groups by using fluorescent dyes or organic molecules.

Keywords: Fluorescent, High performance, S-triazine, Thermoplastics.

1. INTRODUCTION

With the development of science and technology, the people of modern civilized world seeking for the advanced materials, in this regard chemists from the all over the world have contributed a lot for the modernization of our society. One of such major gift that chemist has ever donate to the human society is the "polymer" or "polymeric materials" without which the world would have been in a totally different position [1-7]. Polymer science is a comparatively new field. Polymeric materials for experimental use, which are made from natural substances, has been reported for centuries; however, only the pioneering work of the late Hermann Staudinger (1926), a Nobel laureate, in the 1920s gave the basis for a systematic understanding of this class of materials.

Polymers are utilized in wide range of applications as coating, as adhesive, as engineering plastic, for packaging and for clothing. Polymers are widely used in

the automotive industry, aerospace industry, computer industry, building trades and many other applications. For example, automobile bumpers are now made with a polymer blend that has sufficient toughness to meet state and federal standards.

Naturally occurring polymers which were isolated from plants and animals have been used for many centuries. Numerous polymers have been ready for using new scientific tools. The utilization of polymers is raised due to low cost and ease of shaping. The energetic growth of polymer science and the wide usage of polymeric materials in all fields of technology have developed the interest towards various problems of physics and chemistry of polymers.

Synthetic polymers are widely used as substitutes for metal, wood, stone, glass, paper and a variety of macromolecular substances. Therefore, polymer require specific properties such as toughness, flexibility, insulation, etc., which are related to the molecular

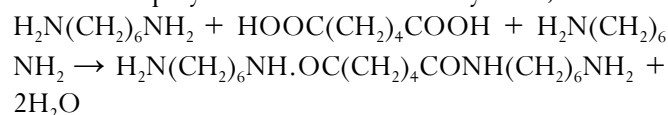
weight, structure, molecular-weight distribution and copolymer composition of the product polymer. These ultimate properties of the polymer are largely captured in the reactor. The reactor must destroy the heat of polymerization; provide necessary residence time and provide uniform mixing for good temperature control and reactor homogeneity; control the degree of back mixing in continuous polymerizations. In addition, the reactor system must be agreeable to control and be stable under normal operation. Polymerization systems engineering is a branch of systems engineering that deals with polymerization reactor systems. In this field of systems engineering includes analysis, modeling, dynamic and stability studies, synthesis and control of polymerization reactor systems.

Polymers are all around us in everyday use, in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from greek words, poly means 'many' and mers means 'parts or units of high molecular mass each molecule' of which consist of a very big number of single structural units joined together in a regular manner. In other words, polymers are huge molecules with high molecular weight which are also called macromolecules and build up by linking together of a large number of small molecules which are called monomers. The reaction by which the monomers combine to form polymer is known as polymerization [8]. The polymerization is a chemical reaction in which two or more substances incorporate together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight and the product is called polymer and the starting material is called monomer. A polymer may be defined as a large molecule comprised of repeating structural units joined by covalent bonds. In this affirmation, a large molecule is commonly arbitrarily regarded either as one having a molecular weight of at least 1000 or as one containing 100 structural units or more. By a structural unit is meant a relatively simple group of atoms joined by covalent bonds in a specific arrangement. Since covalent bonds also connect the structural units to one another and polymers are distinguished from those solids and liquids wherein repeating units are held together by ionic bonds, metallic bonds, hydrogen bonds, dipole interactions or *Van der Waals* forces.

In polymerization, when a single type monomers take part, resulting polymer is known as 'homopolymer', whereas the polymeric compound made up of two

different types of monomers in the same polymer chain is known as 'copolymer'. Polymers can be classified in number of ways as: on the basis of polymerization; polymers can be distinguished as homopolymer and copolymer. On source of availability; polymers are classified as natural and synthetic polymers, on the mode of synthesis; polymers classified as addition and condensation polymers. Polymers are also classified as thermoplastic, thermosetting, elastomers and fibres. Teflon, PVC and Polyethylene are known as thermoplastics polymers which are soften on heating and on reversing harden. Polyester and Polysiloxanes are thermosetting polymers which undergo irreversible or permanent change on heating. Elastomers polymers possess elastic character e.g. Natural rubber and fibers in which polymers chains are held together by H-bonds, dipole-dipole interaction. Polymers are also classified as linear; cross linked and branched polymers on the basis of their structure. Organic polymer, inorganic polymer and element organic polymer are the types of polymer based upon the chemistry of polymers. Amorphous and crystalline polymers are depending upon the morphological behavior. Polymers are also classified as charged polymers containing some free functional groups and uncharged polymers.

The major alternative type of polymer is prepared by condensation polymerization in which a simple molecule is eliminated and two other molecules condense. Mostly simple molecule is water, but alternatives include ammonia, an alcohol and a variety of simple substances are eliminated. The formation of a condensation polymer can best be illustrated by the condensation of hexamethylenediamine with adipic acid to form the polyamide best known as Nylon-6, 6.



This formula has been written in order to show the elimination of water.

The product of condensation can continue to react through its end groups of hexamethylenediamine and adipic acid and thus a high molecular weight polymer is obtained. The important part for determining the properties of polymers are the molecular structure and the arrangements of polymer chains. Polymers are obtained at several distinct levels such as primary structure is the monomer chemical structure specified with given functional groups and correlated with electronic structure. Secondary structure is the chain

specified by the geographical arrangements of some many repetitive units in the polymer chains.

Tertiary structure is the global form of macromolecule as determined by weak *Van der Waals* forces, hydrogen bonds and the sum of conformational restraint. The molecular chains in general are dressed in zigzag or helical shapes. Normally the chains are not linearly stretched but wrapped up. The shape of molecules can be thread-like, cross-linked either as single distinguished units or intertwined with each other through covalent bonds, this cause to amorphous or crystalline arrangements as the quaternary structures.

During the last years, several new families of high performance polymers and engineering plastics have been reported. They have been utilized in large area such as aerospace, electronics, automotives etc. as compared to the commodity or conventional polymers, excellent thermal and thermo-oxidative resistance, low water absorption, good chemical resistance, high mechanical strength, excellent stiffness and high compression strength [9], even at elevated temperatures. High-performance thermosetting polymers are constructed to provide special properties in highly demanding environments. They usually revealed high dimensional stability at elevated temperatures; these combinations of properties are useful for advanced composites and for fabricating electronic components. With the arrival of high-performance engineering thermoplastics substantial increase in toughness was achieved in the resin and the resultant fibre-reinforced composites [10].

In the last four decades there are major advances in the characterization of polymers. Sophistication in methods of measuring molecular weight such as the cryoscopic and vapour pressure methods, almost the whole range of the spectrum has been called into service to illuminate polymer structure. Ultraviolet and visible spectroscopy, infrared spectroscopy, Raman and emission spectroscopy, photon correlation spectroscopy, nuclear magnetic resonance and electron spin resonance all play a part in our understanding of the structure of polymers; X-ray diffraction and small-angle X-ray scattering have been utilized with solid polymers. Thermal behavior in its various characteristic, including differential thermal analysis and high-temperature pyrolysis followed by gas-liquid chromatography, has also been of notable value. Other separation methods include size exclusion and hydrodynamic chromatography. Electron microscopy is of certain interest with

particles formed in emulsion polymerization. Thermal and gravimetric analysis gives useful information in many cases. There are a number of standard works that can be consulted [11-14].

In last few decades, there is a high demand for fluorescent materials and research on fluorescent polymers has received a great attention because of their substantial properties and important application in the fields of materials and life science. The latest research progress in fluorescent polymers is focused on the formation and photoluminescence of fluorescent polymers with new construction. There are different methods to classify fluorescent polymers such as based on their solubility, fluorescent polymers can be divided into three types which are hydrophobic, hydrophilic and amphiphilic, individually. Different type of methods to design and synthesis of fluorescent polymers have also been developed. Various ways used for synthesis of fluorescent polymers such as 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 non-fluorescent functional monomer. Fluorescent polymers are functional macromolecules with huge important applications. Their emerging applications include the fields of fluorescent probe, smart polymer machines, fluorescent chemosensor, fluorescent molecular thermometers, fluorescent imaging, drug delivery carriers, and so on. Polymers are suitable due to the fact that they are easily processable to small particles and thin films that can be deposited onto optical fibers and waveguides for sensor fabrication. Advanced strategies like electrostatic layer-by-layer assembly and self-assembly of amphiphilic block copolymers which were containing chromophores have also been used for the formation of fluorescent systems.

Organic fluorescent polymers have been broadly studied in the research laboratory for several years [15]. They have been used for the detection of a number of analytes, including explosives [16, 17] and biological analytes [18]. Conjugated polymers have been used in the fabrication of organic light-emitting diodes (OLEDs) [19] and in the field of organic photovoltaics (OPVs) [20] and they have been used broadly in the development of clean energy technologies [21]. Moreover, the doping of conjugated polymers with both metals and nonmetal dopants has led to the development of highly conductive organic polymer-

based devices [22].

In recent years, there is a main focus on the development and study of high performance reinforcing materials like polyamide, polyester, aramid, glass, and carbon fibres in appropriate polymeric matrices. [23].

2. POLYESTERS

A repeating unit of the ester (-COOR-) group in the polymer chain known as polyesters. Polyesters are generally synthesized by condensation of polyfunctional carboxylic acids with polyfunctional alcohol or polycondensation of hydroxycarboxylic acids and polymerization of cyclic esters [24]. In other words, the production of polyesters is direct esterification of dicarboxylic acids with diols [25]. Polyesterification is an example of condensation polymerization. In polyesterification, monomeric units are added to the growing chains and individual chains also react with one other because they may have both carboxyl and hydroxyl terminal groups. The esterification conditions also permit constant trans- esterification within the chain itself. Polyesters [26-28] are one of the most adaptable synthetic polymers. Polyesters are manufactured in high volume per year worldwide [26].

The history of thermoplastic polyesters goes back to 1929 with the pioneering work of 'Carothers'. In 1932, He has described the first thermoplastically processible polyesters prepared from adipic acid and ethylene glycol. Polyesters only became of industrial interest in 1941, with the synthesis of high melting point products based on terephthalic acid [27-33]. Carothers systemically investigated reactions of diols with diacids [34]. He was not successful in synthesis of a polyester fiber and switched the focus of his research [35]. In 1942, John Whinfield and W. Dickson have made the first high molecular weight PET. Other polyesters were investigated after produced these fibers and have since become very important compounds (Sandler, 1974). Among these polyesters, the most economically important types of polyesters include poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT). Poly(trimethylene terephthalate) (PTT) was commercialized very recently. PET is used worldwide for the production of synthetic fibers, films, beverage bottles, and molded plastic parts, because of its good physical properties [36].

Various kinds of polyesters were synthesized over the past decades from various types of diacid chlorides and diols. Thermally stable polyesters synthesized from

isophthalic and terephthalic acids with bisphenol-A was commercialized. Although, polyesters were generally difficult to process because of their limited solubility in organic solvents and their melting temperature or high glass-transition temperature by virtue of their rigid structures.

Liquid crystal polyesters, which are known as liquid crystal polymers, are aromatic copolyesters. Polymer gives the chain rigidity owing to the presence of phenyl rings in the backbone, making a rod-like chain structure. Generally, the phenyl rings are arranged in para linkages to give good rod-like structures [37]. The resulting materials are toughened with high mechanical properties, but as a result of the oriented liquid crystal behavior, the properties will be anisotropic. The designer must be aware of this to properly design the part and gate the molds [38]. The phenyl ring also helps to rise the heat distortion temperature [37].

Polyesters are widely used commercially as fibres, plastics, composites and for coatings applications too [39-41]. Aromatic polyesters show good thermal stability, solvent resistance and good mechanical properties. Therefore, polyesters are widely utilized in the aviation, automobile, and electronic industries [42-45]. However, most polyarylates show difficulties in processing because of their high glass transition or melting temperatures coupled with insolubility in common organic solvents.

Aromatic polyesters are well known as high performance engineering thermoplastics because of their good thermal stability, chemical resistance and excellent mechanical properties [46-47]. A numerous method are available to synthesize desire polyesters with promising properties. High-viscosity polyesters can be synthesized from simple aromatic dicarboxylic acids and aromatic diols using SOCl₂/pyridine condensing agent [48-50].

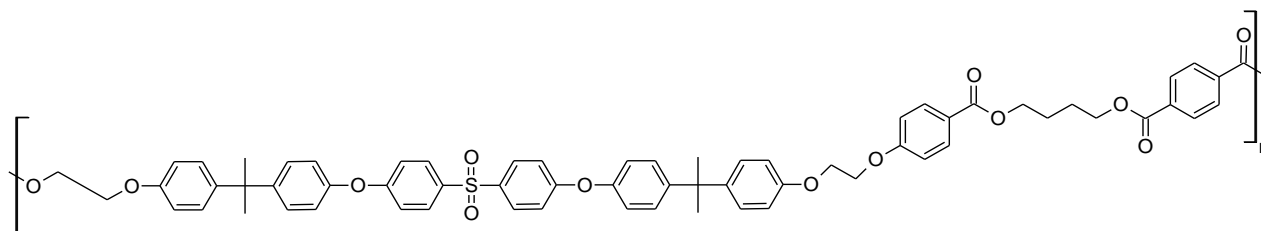
In recent years, synthesis of polyesters containing chromophoric groups have become important. For example, the aromatic azo groups which can form a part of the main chain. The aromatic azo group is being more interest because of the existence of cis-trans isomerism and its effect on the photochromic properties of the polymers. Therefore, polymers having azo group have potential use in a variety of applications.

V. Sreenivasulu Reddy et.al have reported fluorine containing polyesters of 4-(2 hydroxyhexafluoro-2-propyl)benzoyl chloride and the copolyesters of 1,3- and 1,4- bis(2-hydroxyhexafluoro-2-propyl)benzene with

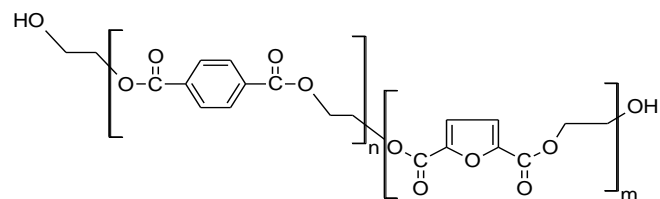
three aromatic diacids. The polyesters showed inherent viscosities of these polyesters ranged from 0.12 to 0.85 dL g⁻¹ while the thermal stabilities of synthesized polyesters have been (10% weight loss under nitrogen) ranged from 317°C to 376°C. The spectra of polyester shown a band about 1770cm⁻¹ from the ester C=O. These highly crystalline polyesters show limited solubility in common organic solvents but are all soluble in dimethylacetamide-LiCl [51].

A series of polyesters from 1,6- or 4,9-diamantanedicarboxylic acyl chlorides with aryl ether diols have been reported by Chern et al. The polyester had been made under high temperature solution method. The temperatures of polyesters at 5% weight loss ranged from 338 to 395°C in air and from 385 to 403°C in N₂ atmosphere. The glass transition temperatures of polyesters were found to be in range of 90-108°C and 102-132°C by means of differential scanning calorimetry and dynamic mechanical analysis respectively. The synthesized polyesters had tensile strengths of 34.9-45.5 MPa, elongation to breakage values of 3.5-4.6%, and initial moduli of 1.4-1.6 GPa [52].

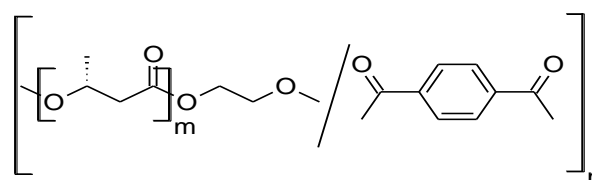
Copolyesters from terephthalic acid and 2,5-furandicarboxylic acids have been synthesized by Sousa et al. which are characterized by FT-IR and ¹H NMR spectroscopy. In FT-IR, revealed a sharp band near 1713 cm⁻¹, arising from C=O stretching vibration, typical of ester group. The thermal stability of synthesized polyesters was up to 260°C [53].



Degradation of polyesters reported as above 350°C and displayed a two-step, weight loss profile under a nitrogen atmosphere. The high molecular weight segmented block copolymers with alternating PSU and poly(butylene terephthalate) (PBT) sequences significantly affected the crystallization and thermomechanical properties of PBT and as a result these copolymers offer impact as chemically resistant, high-temperature thermoplastics due to their crystallinity, thermal stability and high-temperature operating window [55].



Novel block copolyester containing biocompatible and biodegradable biopolyester blocks was prepared by polycondensation of telechelic hydroxylated poly[(R)-3-hydroxyoctanoate] and telechelic hydroxylated poly[(R)-3-hydroxybutyrate] with terephthaloyl chloride (TeCl). The polyesters found to exhibit promising thermoplastic properties [54].



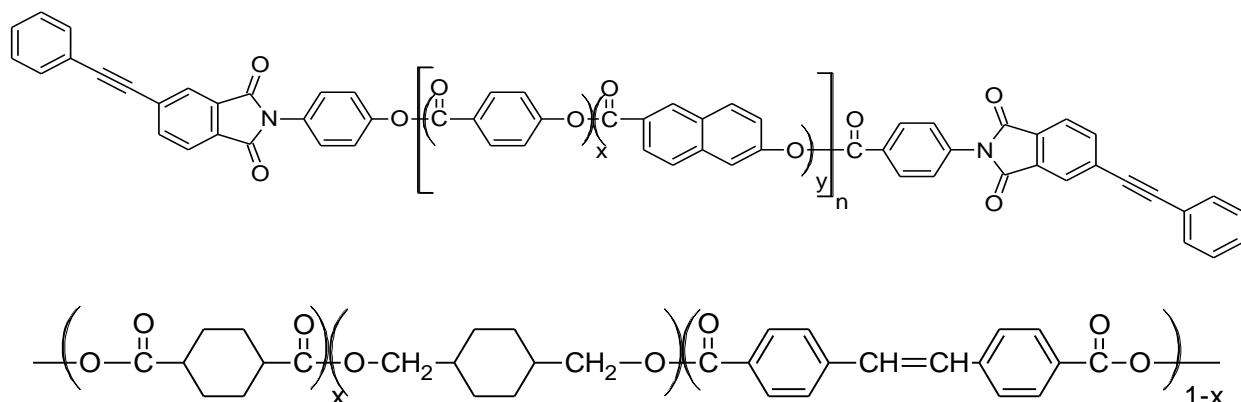
Dennis et al. have synthesized and characterized polysulfone-containing poly(butylene terephthalate) segmented block copolymers which were reported as high-temperature thermoplastics with tunable thermomechanical properties. The block copolymers reported as phenol-terminated polysulfone (PSU) showed that crystallinity-dependent plateau regime above the copolymers glass transition temperature (T_g) from DMA, while SAXS and WAXD confirmed a semicrystalline morphology below 80 wt % PSU.

Synthesis of Thiol-Functionalized Poly(ethylene glycol)-b-polyesters have been developed [56] as degradable gelation property which bearing high molecular weight as well as number-average molecular weights (M_n) in the range of 3300-5800 and 3600-4600, respectively. The gel polyesters were synthesized by aqueous solutions of the disulfide block copolymers which at high concentration and underwent a gel-sol transition upon an increase in temperature.

Aryl ethynyl terminated liquid crystalline oligomers and their cured polymers have been designed by

Knijnenberg et al [57]. Synthesized polyesters were highly thermally stable. Thermal stability was exhibited up to 490 °C in air and nitrogen. Rheology experiments showed that these reactive nematic oligomers are melt-stable for at least 30 min at 300°C and exhibit complex melt viscosities $|\eta^*|$ as low as 1 Pa.s at 100 rad.s⁻¹.

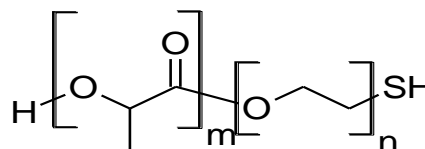
Montgomery et al. have synthesized the thermally stable and UV crosslinkable copolyesters having structural units of Poly(1,4-cyclohexylenedimethylene-1,4-cyclohexane dicarboxylate) (PCCD) and copolymers containing trans-4,4'-stilbene dicarboxylate. They have developed a photoreactive group has been incorporated



Liquid-Crystalline Polyester with 4-cyano-4-alkoxyazobenzene side groups have been reported by Zebger et al. The polyester has been synthesized by means of transesterification of 2-[8-(4-((4-cyanophenylazo) phenoxy)octyl)]-1,3-propanediol and diphenyl tridecanedioate in the melt under vacuum at elevated temperature. UV-vis spectroscopy was used to characterize the steady state of the photoisomerization process and the orientation order of the photochromic moiety. FTIR spectroscopy was carried out in order to investigate the different mobility and the changes in orientational order of the chromophore, the ester linkage, the methylene units of the main chain, and the alkylene spacer by monitoring the dichroic ratios of characteristic absorption bands [59].

Choi et al [60] have designed the self-assembly of hydrogen-bonded polymeric rods based on the lattice of cyanuric acid and melamine. These synthesized polyesters have been characterized by ¹H-NMR spectroscopy, IR spectroscopy, gel permeation chromatography (GPC) and transmission electron microscopy (TEM). The length of the polyester bundles ranged from 100 to 1500 nm, and their diameter was found to be in the range from 15 to 500 nm.

into the backbone of an engineering thermoplastic polyester resulting in a polymer stable at 250°C that is highly UV crosslinkable at room temperature. The structural units were synthesized, and their thermal stability was confirmed by parallel plate rheometry and the absence of crosslinks upon melt processing at 250-300°C [58].



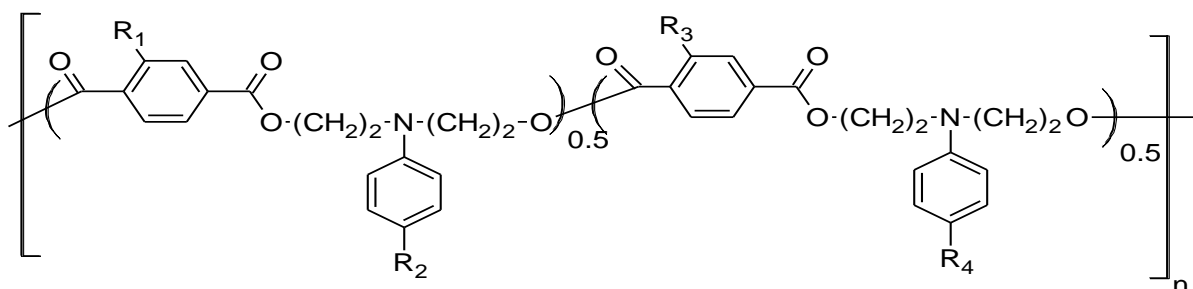
Latha et al. synthesized polyester from 1,1-bis(4-hydroxyphenyl)cyclohexane with various aliphatic and aromatic diacid chlorides by interfacial polycondensation technique. Thermal properties were studied using thermogravimetric analysis and differential scanning calorimetry. The thermogravimetric data revealed that the polymers were stable up to 190°C and start to degrade thereafter. The thermal stability initially increased with increased in spacer length and then decreased owing to negative effects of the spacer. It was concluded that the activation energy of polyester increases with the increase in alkyl chain length [61].

Thermally stable series of high molecular weight condensation polymers have been developed and characterized by random arrangements of ester and ether linkages within the polymer chain. The thermal properties of polyesters were excellent with high molecular weight [62].

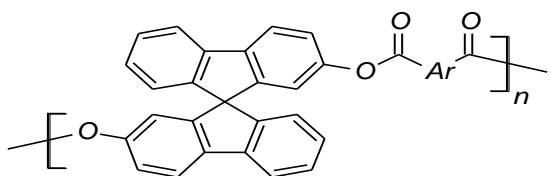
Aliphatic-aromatic polyesters have been prepared using interfacial polycondensation technique of various diacid chlorides such as adipoyl chloride (ADCL) and sebacoyl chloride (SECL) with various diols. The resulting polyesters were characterized for solubility test, elemental analysis, intrinsic viscosity measurements,

FT-IR, and $^1\text{H-NMR}$ spectral analysis and thermogravimetric analysis. The polyesters showed good thermal stability. The thermal stability of polyesters was due to on the type of diacid and/or diol moieties and their chemical structure. It was found that by replacing aromatic rings in place of aliphatic chain in the polyester, the thermal stability increased. The Intrinsic viscosity of polyesters was reported in the range of 0.160-0.229 dl g $^{-1}$ [63].

Polyesters with nonlinear optical properties have been reported by Ambrosanio et al. Homo- and copolymers

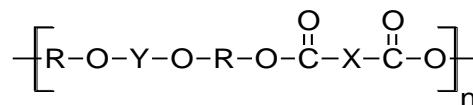


Seto et al. have synthesized a synthesis of symmetrical (C_2) aromatic polyesters bearing 9,9'-spirobifluorene entity via polycondensation of 2,2'-dihydroxy-9,9'-spirobifluorene with bis(acyl chloride)s at 230°C in diphenylether. The spiro polyesters possess sufficiently high molecular weight (Mw 13,400-41,600). The polyesters were found to have good solubility in typical organic solvents such as CHCl_3 and THF easily to afford the tough, transparent and flexible cast films. The glass transition temperatures (T_g) calculated by different scanning calorimeter analysis exhibited in a range 177-352°C while the 5% decomposition temperatures (T_{d5}) measured by thermogravimetric analysis were over 416°C both under nitrogen atmosphere and in air. In addition, polyesters exhibited higher refractive index rather than that of commercially available 9,9-diarylfuorene-containing polyesters, in addition to very low degree of birefringence presumably due to the C_2 -symmetric structure [65].



Aromatic polyesters containing 9,10-diphenylanthracene fluorophores along the main chain or both in

have been synthesized by polycondensation of terephthalic acid and propoxyterephthalic acid with two different second order NLO-active chromophores derived from 4-[N,N-bis(2-hydroxyethyl)amino]-benzaldehyde. Polymers exhibited good optical clarity, satisfactory thermal stability above the glass transition temperature [64].



the pendent and main chain were found to exhibit photoluminescence in solution as well as in thin films. The diphenylanthracene fluorophores exist either both in the main chain and the side chain or only in the side chain, the polyesters reveal photoluminescence over a broad range of wavelength from 400 to about 700 nm with the maximum emitting intensity at about 450 nm. The diphenylanthracene pendent groups were attached to the terephthaloyl unit of the aromatic polyester main chains through the oxyhexamethyleneoxy spacer. It was established that the polymer that contains the fluorophore in the main chain shows a rather sharp luminescence and emitting intensity [66].

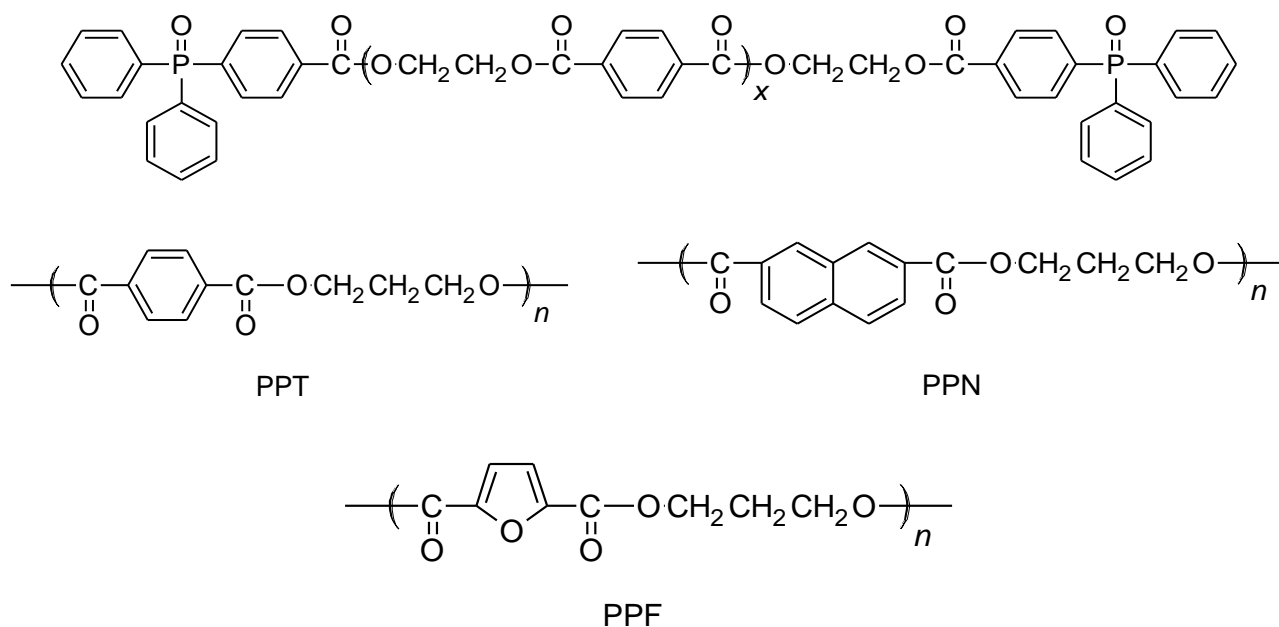
Aromatic polyesters with isophthaloyl, pyridine-2,6-dicarbonyl and pyridine,2,5-dicarbonyl units in the main chain were synthesized and characterized by inverse gas chromatography (i.g.c.). The polyesters containing complex 'triad' monomers and aromatic diols were collected by high temperature solution poly condensation. Inherent viscosity of polyesters has been measured with ubbelohde viscometer at 25°C in chloroform. Inherent viscosities were in the range from 0.27-0.96 dL/g. It has been reported that thermal stability of polyesters decreased with addition of pyridine unit [67].

Telechelic phosphine oxide polyesters have been synthesized by Lin et al. [68] and characterized using NMR spectroscopy, mass spectroscopy, and elemental

analysis. NMR spectroscopy, FT-IR, and UV-vis indicated that the cobalt(II) ion correlated with the phosphineoxide end groups. The complexes shown higher melt viscosity than analogues without cobalt salts, and the phosphine oxide end groups aided the dispersion of cobalt(II)chloride in a PET matrix.

Poly(propylene-2,5-furan dicarboxylate) (PPF) which was synthesized from monomers derived from renewable resources were being reported to use PPF as

a replacement for its terephthalate (PPT) and naphthalate (PPN) homologues. From the conventional and temperature-modulated differential scanning calorimetry it was found that the different structural rings and the ultimate chain rigidity of the samples play a big role on their thermal properties. On this basis, the more rigid PPN showed higher glass transition temperature and thermal stability than PPF and PPT [69].



David H. Wang et al. [70] have developed a series of aromatic polyesters containing multiple alkyl side chains which were prepared from the 2,2'-disubstituted-4,4'-dihydroxybiphenyl monomers and 2,2'-bis-(trifluoromethyl)-4,4'-biphenyldicarboxylic acid using diisopropylcarbodiimide as a dehydrating agent and 4-(dimethylamino)pyridinium 4-toluenesulfonate as a catalyst at room temperature. Their thermal and solution properties has been evaluated and compared with the polyester without multiple alkyl side chains. The polyesters revealed better solubility in common solvents such as chlorinated solvents and THF but lower thermal stability than the polyester without multiple alkyl side chains. The intrinsic viscosities also carried out of the polyesters which were ranged from 0.68 to 2.53 dL/g and their number-average molecular weights ranged from 19,300 to 61,400.

Co-polyesters of poly(butylenes-co-1,4-cyclohexanedimethylene 2,5 furandicarboxylic acid) have been reported by L.D. et al. which were synthesized from 2,5-furandicarboxylic acid (FDCA),

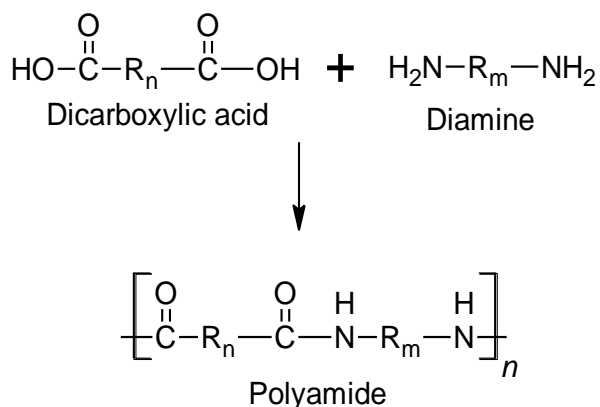
1,4-butanediol (BDO) and 1,4-cyclohexanedimethanol (CHDM) via a two-step esterification-polycondensation method. They have reported that co-polyesters had random sequence structure, and their composition could be regulated by changing the feed molar ratio of CHDM/BDO. The incorporation of 1,4-cyclohexanedimethanol could modify the thermal performance of 2,5-furandicarboxylic acid based polyester, and the T_g, T_m and T_{dmax} raised with 1,4-cyclohexanedimethanol content rising, which gave a green substitute for PET to manufacture heat resistant drink bottles or food packaging materials from furanic co-polyesters. Most importantly, the higher T_g and T_m of poly(butylenes-co-1,4-cyclohexanedimethylene 2,5 furandicarboxylic acid) make them to become a new type of thermoplastic engineering plastics [71].

3. POLYAMIDES

Polyamide, in other way also known as 'Nylon' which was investigated by the American chemist *Wallace Hume Carothers* in 1935 [14]. At that time, *Carothers* was

working for *Du Pont* (an American chemical industry) as a group leader.

The main characteristic of polyamide is that they contain a persisting amide group (-CONH-) in the chain [72]. Polyamide can be divided in two categories, namely aromatic and aliphatic. Nylons are formally identified by the number of carbon atoms present in the monomer. Two monomers are often needed, a diamine and a diacid monomers. Therefore, polyamides are differentiated by two numbers: the first one corresponds to the number of carbon in the diamine and the second one to that in the diacid. Polyamides can be synthesized in several ways such as bulk polyamidation (polycondensation), anionic polymerization, polyamidation in solution [73]. Such as polyamides are synthesized by the condensation polymerization between a diamine $\text{NH}_2\text{-(CH}_2)_6\text{-NH}_2$ and a dibasic acid, $\text{HOOC-(CH}_2)_4\text{-COOH}$ [74-78].



Polyamides are broadly used as engineering polymers, with a multitude of applications such as fibers for clothing, ropes, structural and mechanical components, reinforcements in tires and adhesives. Because of their excellent properties, polyamides cover a substantial part of the world engineering polymers market [79]. The main user is the transportation manufacturing industry, covering 35% of the polyamide (PA) consumption [80]. Aromatic polyamides are of commercial importance and academic interest [81]. They exhibit high thermal stability and excellent mechanical properties. However, they are generally difficult to process into fibres and films because of their insoluble nature or limited solubility in organic solvents and their high softening or melting temperatures. The processing of these polymers by thermoplastic methods has been difficult because they tend to degrade before or at the softening or melting temperature [82].

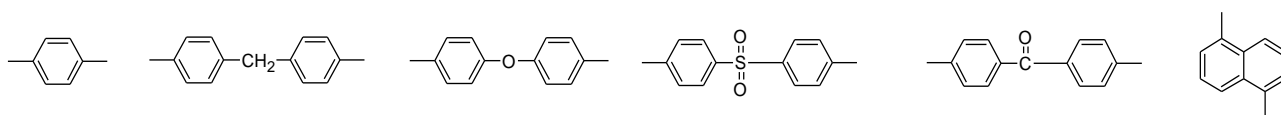
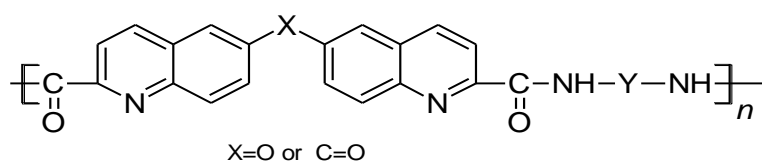
In the last few decades, thermally stable polymers have received great interest due to increasing demand for high temperature polymers as replacements for metals or ceramic in the automotive, aerospace and microelectronics industries. Aromatic polyamides are certainly one of the most successful classes of high temperature polymers: they possess thermal stability, chemical resistance, low flammability and have excellent mechanical properties when used as fibers [83-85]. Sometime, polyamides are difficult to process due to limited solubility in organic solvents and high glass transition (T_g) or melting temperatures (T_m), caused by the chain stiffness and intermolecular hydrogen bonding between amide groups [86].

Aromatic polyamides and polyimides are well accepted as high-performance polymers due to their good thermal and chemical stability, excellent mechanical properties, high glass transition temperatures and are widely used in various fields including aerospace and electronics industries [87-90].

Y. Bai et al. have reported copolyamide based on Nylon 66, was synthesized by solution melt polycondensation of hexanedioic acid and sodium 5-sulfoisophthalate with 1,6 diaminohexane. Synthesized polyamides have been confirmed by various spectroscopic techniques (FT-IR, Raman, and ^1H NMR). The thermal properties of the polyamides were carried out by TGA and DSC. They have found that the average strength of the intermolecular hydrogen bond of the water-soluble copolyamides becomes weak with increasing the temperature, according to the temperature dependence of FTIR spectra [91].

Aromatic polyamides derived from heterocyclic diamine have been synthesized by direct and indirect polycondensation of these diamines with various aromatic dicarboxylic acids. These aramids revealed inherent viscosities in the range 0.43-0.84 dl/g having good thermal stability [92].

Heterocyclic aromatic polyamides from 6,6'-methylenediquinoline unit with various aromatic diamines have been prepared by Bottino et al [93] via phosphorylation route. The polymers have been characterized by elemental analysis, infrared, thermogravimetric analysis and differential scanning calorimetry. The inherent viscosities are found to be in the range of 0.20-0.85 dL g⁻¹. Thermal property of polyamides at 10% weight loss in nitrogen and air were above 420°C and glass transition temperatures in the range 184-294°C.

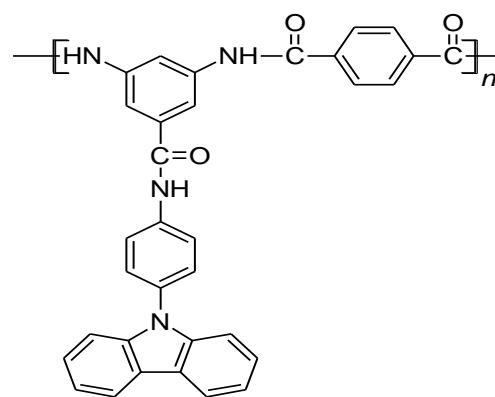


Xiaowen Cui and Deyue [94] Yan have prepared odd-even polyamides via step-heating melting-polycondensation of 1,11-diaminoundecane with dodecanedioic acid and decanedioic acid, respectively. The odd-even polyamides were characterized by various spectroscopic techniques (FTIR, Raman, NMR) to establish the structure pattern. The thermal properties of the polyamides were evaluated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The crystalline transitions of the synthesized polyamides have been studied by wide angle X-ray diffraction (WAXD) and fourier transform infrared spectroscopy (FTIR). From the real time FTIR spectra, it was noticed that the intensity of hydrogen bond became weak, and the twisting of the C-CO and C-N bonds became enhanced during vibration mode. The vibration of the methylene units strengthens and the trans-zigzag conformation decreased. The ordered stacking of the methylene segments became gradually disordered by insertion of the gauche conformation during the crystalline transition process.

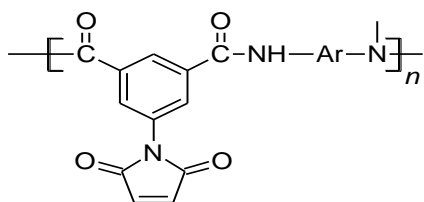
Microwave assisted synthesis of azo (-N=N-) based hydantoin polyamides were discovered by Faghihi and Hagibeygi [95] in the presence of a small amount of a polar organic medium such as o-cresol. Polyamides revealed inherent viscosity between 0.35 and 0.60 dL g⁻¹. Polyamides were characterized by elemental analysis, thermal gravimetric analysis (TGA and DTG), solubility test and FT-IR spectroscopy. Solubility for polymers revealed that polymers were soluble at room temperature in polar solvents like N, Ndimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide, tetrahydrofuran and N-methyl-2-pyrrolidone. The polyamides found to have good thermal stability.

Heterocyclic polyamides based on carbazole- pendent was prepared by Ghaemy and Alizadeh via direct polycondensation of N-(4-(carbazol-9-yl)phenyl)-3,5-diaminobenzamidamide with diamines. All polyamides were found to be amorphous and inherent viscosities

were reported from 0.51 to 0.65 dL/g. The glass transition temperatures (T_g) of these polymers were affected considerably by their chemical structure and ranged from 195 to 300°C. TGA studies showed that the useful levels of thermal stability associated with relatively high temperatures of 10% weight loss in the range of 385-480°C in nitrogen atmosphere. These polymers showed strong UV-vis absorption maxima in solution and in solid state and their photo- and chemiluminescence properties were found to be affected by their chemical structure. The aliphatic polyamides emitted blue light (λ_{e.max} = 435-450 nm), whereas the aromatic polyamides emitted green light (λ_{e.max} = 485-492 nm) both in solution and solid state [96].



Polyamides bearing N-phenylmaleimide moieties have been reported by Liu et al. Both of the maleimide and carboxylic acid groups in 5-maleimidoisophthalic acid (MIPA) are reactive favouring an amine group. The selective reaction between carboxylic acid and amine groups was successfully developed and applied in preparation of polyamides and copolyamides possessing maleimide pendants. The chemical structures of the polymers have been confirmed with FTIR, ¹H NMR, and elemental analysis. Phosphorylation on polymers determined this kind of polyamide could be used as reactive polymers for further modification and functionalization [97].

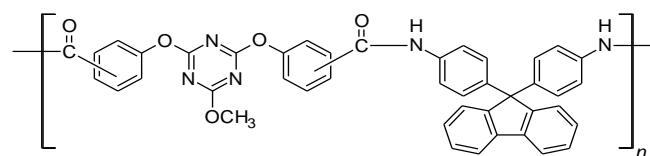


Polyamides, polyesters and semiflexible polyethers having substituted 9,10-di(4-biphenyl) atrhacene segments in the main chain were synthesized through pyrylium salts. They were demonstrated by viscosimetry, FT-IR, NMR, X-ray, differential scanning calorimetry, thermomechanical analysis, UV-vis and luminescence spectroscopy. Polyamides had higher Tgs (165-220°C) than polyesters (100-106°C) and polyethers (98-105°C). The polymers with biphenyl pendent groups showed lower Tgs and higher thermal stability than their counterparts with phenyl pendent groups. All polymers showed violet to blue photoluminescence in solution and in solid state with maxima at 366-422 and 435-463 nm, respectively. The polymers carrying biphenyl pendent groups exhibited in solution more broad emission spectra and higher quantum yields than the corresponding polymers with phenyl pendent groups [98].

More et al. have developed aromatic diacid monomer viz., 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was synthesized starting from cardanol and was characterized by FTIR, ¹H- and ¹³C NMR spectroscopy. Aromatic polyamides having ether linkages and pendant pentadecyl chains was prepared by phosphorylation polycondensation of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid with five commercially available aromatic diamines such as 1,4-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline, 1,3-phenylenediamine, and 4,4'-(hexafluoroisopropylidene) dianiline. They have studied viscosity measurement; inherent viscosities of the polyamides were in the range 0.45-0.66 dL/g in N, N-dimethylacetamide at 30 ± 0.1°C. The glass transition temperature observed for the polyamides was in range 139-189°C. The temperature at 10% weight loss (T₁₀) has been studied by TGA in nitrogen atmosphere; thermal stability of the polyamides was in the range 425-453°C manifesting their good thermal stability [99].

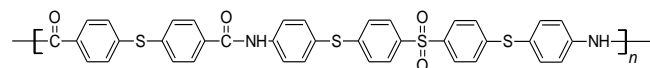
Sagar et al. [100] have synthesized thermally stable polyamides having s- triazine rings and fluorine "Cardo" groups by low temperature interfacial polycondensation of two s-triazine ring containing diacyl chlorides such

as 2,4 bis-(4chlorocarbonyl phenoxy)-6 methoxy- s-triazine with cardodiamine such as 9-9-bis (4 amino-phenyl) fluorine. Synthesized polymers were characterized by elemental analysis, viscosity measurement, X-ray diffraction studies, thermogravimetry and IR, ¹H and ¹³C-NMR spectroscopy. Inherent viscosity of synthesized polyamides was found in the range of 0.52 and 0.60 dl/g in Dimethylacetamide at 30°C. Most of the polyamides were soluble in polar solvent at room temperature such as DMSO, DMAc, N-N Dimethyl-fomamide, N-Methyl-2-pyrrolodine and m-cresol. Thermogravimetric analysis revealed that polyamides were thermally stable at 360°C.



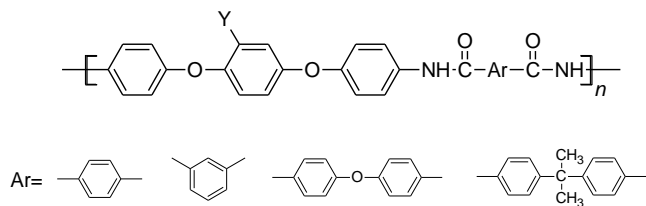
Aromatic polyamides which contains heterocyclic moiety are shown to high thermal stability. Tamami et al. reported that polyamides derived from 4- aryl-2, 6-bis (4- aminophenyl) pyridines has promising thermal stability and high solubility in polar aprotic solvents owing to incorporation of pyridine probe. Thermogravimetric analysis of the polyamides designated no weight loss below 360°C under nitrogen atmosphere. The inherent viscosity was reported in the range of 0.5-1.2 dl/g. polyamides started to lose weight around 400°C [101].

G. Zhang et al. have developed two kinds of monomers containing the thioether units 4,4'-thiodibenzoyl chloride and 4,4'-bis(4-chloroformylphenylthio) benzene were synthesized in two steps. Synthesized monomers were reacted with diamine containing thioether (-S-) and sulfone units to prepare a polyamide containing high contents of thioether groups. The intrinsic viscosities of the polyamides were 0.81-0.93 dl/g. These polymers exhibited good optical properties, including an optical transmittance of the aromatic polyamide film at 450 nm. The polyamides also had excellent thermal properties, with glass transition temperatures (Tg) of 230-246°C and initial degradation temperatures (Td) of 477-473°C [102].



C.H. Lin et al. have reported polyamides which were synthesized by direct polycondensation of the diamine

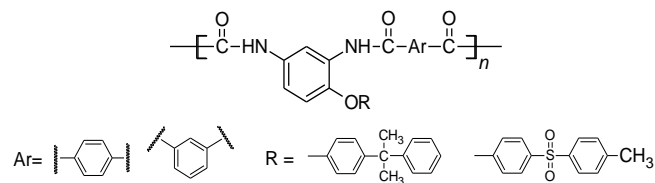
with various aromatic diacids using triphenyl phosphite and pyridine as condensing agents. The number-average molecular weights of the polyamides range from 4.2×10^4 to 10.5×10^4 g/mol, and the weight-average molecular weights are in the range of $7.5-28.2 \times 10^4$ g/mol. The Tgs of these polyamides range from 210 to 255°C by which studied by dynamic mechanical analysis. The degradation temperatures (Td 5%) and char yields at 800°C in nitrogen range from 460 to 486 °C and 59-68 wt%, respectively [103].



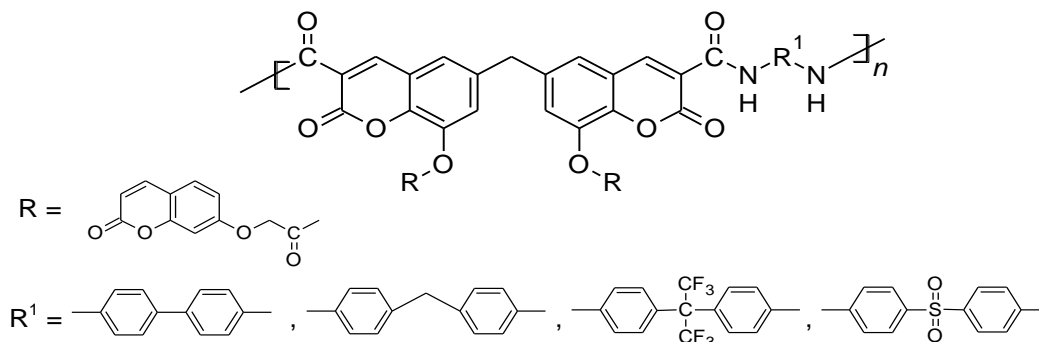
Thermally stable hyperbranched polyamide-ethers having pyrimidine moieties were prepared using monomer 6-hydroxy-2,4-bis(4-nitrobenzamide) pyrimidine (NAL), which was prepared through amidation and characterized by FTIR, ¹H, ¹³C NMR spectrometry and elemental analysis. Inherent viscosity of synthesized polymers was found to be 0.41 and 0.23 dL/g. Polyamides were soluble in different organic solvents including NMP, DMAc and DMSO but partially soluble in DMF. Glass transition temperature (Tg) of thermally stable polyamides was affected by nature of end groups as well as introduction of pyrimidine rings [104].

Pal et al. have reported four new aromatic polyamides containing pendant groups which were synthesized by low temperature interfacial polycondensation of two asymmetrically substituted diamine monomers with two aromatic diacid chlorides. Polyamides derived from asymmetrically substituted meta-phenylene diamine monomers showed constitutional isomerism and the constitutional order in terms of the s parameter

determined by ¹H NMR spectroscopy was in the range 0.35-0.37. Polyamides containing pendant groups were soluble in polar solvents such as NMP, DMAc and DMF. The TGA analysis showed that initial decomposition temperature in nitrogen atmosphere, of polyamides was in the range 371-410°C indicating their good thermal stability [105].



Marioara Nechifor have developed monomer diacid, 6,6'-methylenebis{2-oxo-8-[2-[(2-oxo-2H-chromen-7-yl)oxy]acetoxy]-2H-chromene-3-carboxylic acid}, having two substituents (2-oxo-2H-chromen-7-yl) oxyacetate in the aromatic moiety which is used in synthesis of polyamides with photosensitive coumarin pendant groups by direct polycondensation reaction with different type of aromatic diamines using triphenyl phosphite and pyridine as condensing agents. Properties of polyamides examined by DSC, TGA, GPC, and wide-angle X-ray scattering, viscosity and solubility measurements. Inherent viscosity values (0.40-0.87 dL/g) were owing to bulky side chains in the structure of aromatic polyamides. Solubility of these polymers in aprotic polar solvents such as NMP (N-methylpyrrolidone), DMAc, DMSO and DMF, and in less polar solvents like Py and THF. These aromatic copolyamides showed good thermal properties correlated with glass transition temperatures (Tg) in the range of 221-257 °C and the onset of decomposition in air above 390°C. UV illumination ($\lambda > 300$ nm) of the polymer films induced crosslinking between polyamide molecules through a $[2\pi + 2\pi]$ photocycloaddition at the C=C bond of coumarin moieties [106].



4. HETEROCYCLES IN POLYMER BACKBONE

4.1. S-triazine based polymers

1,3,5-triazine was accidentally initially synthesized by Nefin 1895 by treating hydrogen cyanide with ethanol in an ether solvent saturated with hydrogen chloride. The resultant salt was then treated with base and distilled to give 1,3,5-triazine in low yields, 10%. Polymers based on s-triazine and their derivatives have been highly studied and utilized since the 1950s.

Number of derivatives containing S-triazine ring have been reported as heterocyclic compounds [107-109]. They are utilized mostly as reactive dyes, polymers and pharmaceutical drugs [110]. Polymers having S-triazine ring become a subject of interest because of good thermal stability, enhanced toughness and low moisture absorption and commercially available high performance engineering plastic materials [111]. Triazine based material reveals outstanding high temperature performance which could be assigned to the N-heterocyclic structures [112]. Polymers containing the triazine ring as part of the polymer chain are usually insoluble and infusible. However, the thermal stability of triazine ring makes it an attractive monomer for use in high temperature polymers.

A symmetrical triazine is a six-membered heterocyclic compound composed of three nitrogen atoms and three carbon atoms alternatively placed in the ring. Symmetrical triazine (1, 3, 5- or γ -triazine) is a bridged as S-triazine. S-triazine is in nature quite stable, aromatic in character and susceptible to nucleophilic attack. It rapidly decomposes in water [113].

For the synthesis of different derivatives, S-triazine is not normally utilized as the starting material owing to its high reactivity. A 2,4,6-trichloro-s-triazine (cyanuric chloride) is one of the main forms in which other derivatives are synthesized. It occurs as white crystals and has a pungent odor [114]. Cyanuric chloride, an economical, easily available reagent, of low toxicity and less corrosive than other similar reactants, has been widely used in organic reactions. There are many nucleophiles that have the possibility to replace chlorine of cyanuric chloride. The replacement process of chlorine atom of cyanuric chloride is a stepwise process at different temperatures by different nucleophiles, such as $-\text{NH}_2$, $-\text{NH}-\text{NH}_2$, $-\text{NHOH}$, $-\text{CN}$, $-\text{SN}$, $-\text{N}_3$ etc. The reactivity of the three chlorine atoms in cyanuric chloride against nucleophilic reagents decreases as substitution reaction proceeds. The first substitution takes place between -15°C to 5°C . The 2nd substitution

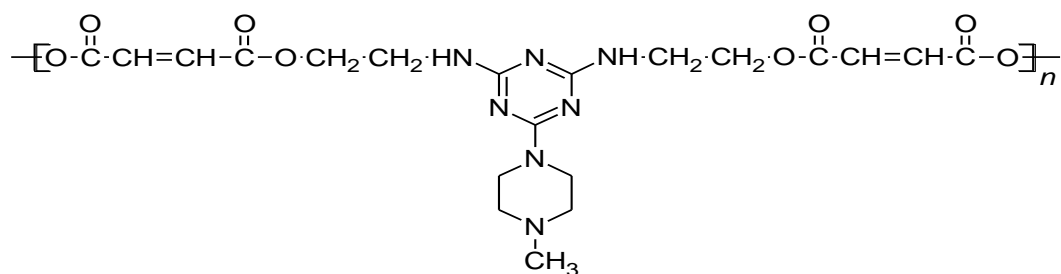
occurs at 30°C to 50°C , and the 3rd substitution occurs 90°C to 100°C [115,116]. The stepwise substitution with increasing temperature is due to decreasing electrophilicity of the centers by inductive electron releasing through the bonds [117].

Various derivatives of cyanuric chloride are used to synthesize dyes, herbicides, insecticides, fungicides, pesticides, pharmaceuticals, polymers, biological molecules. Cyanuric chloride can also be used as an intermediate for manufacturing optical brighteners, tanning agents and softening agents [118-121].

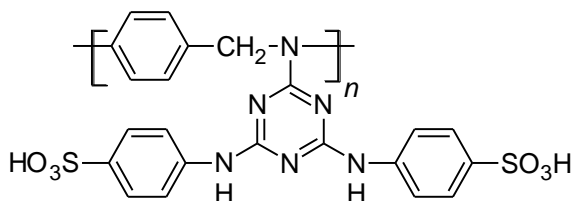
s-Triazine based thermally stable and fluorescent type polyesters have been reported by Vasava et al [122], which were prepared by polycondensation of cyanuric chloride with different aliphatic-aromatic diols in the chain. The viscosity was studied for all the polyesters. This polyester exhibited inherent viscosity ranging from 0.402- 0.709 dl g⁻¹ in DMF at 25°C . The thermal properties of the polyesters were estimated by the TGA at a heating rate of $100^\circ\text{C}/\text{min}$ under N_2 atmosphere. The 10% weight loss temperature of the aromatic polyesters in nitrogen was recorded at 300°C . The high char yields of these polyesters could be attributed due to their high aromatic content. The series of polyesters revealed higher thermal stability compared to the corresponding counterpart without coumarin moiety.

High-temperature phthalonitrile polymers based on 1,3,5-triazine have been prepared by Sheng et al. These polymers showed excellent thermal stability, the T_g values were higher than 350°C . TGA studies of the polymers have been done under nitrogen and in air atmospheres. T_d , 5% were 507 and 503°C for polymers under nitrogen atmosphere, respectively, with their char yield at 900°C being 73% and 74%, which revealed that high thermal stabilities are achieved. In air atmosphere, both of them showed outstanding thermo-oxidative properties with higher T_d , 5% of 503 and 505°C , respectively. Probably, aromatic ring structures combined with N-heterocyclic rings in the polymer backbones may be attributed to the high thermal stabilities for polymers [123].

S-triazine containing unsaturated polyesters and epoxy resin residues has been reported by Patel and Chaudhari. This unsaturated epoxy polyester was evaluated for their thermal properties. Polyesters were found to start degrade at about 200°C and their initial weight loss was about 5%. A weight loss about 13% was established at 300°C and the products were completely beyond $800-850^\circ\text{C}$. Polyesters have been confirmed with IR and NMR spectroscopy [124].



Ion-exchange resin has been prepared by Singh et al. and characterized with IR. In the IR spectrum secondary amine NH (3400 cm^{-1}), methylated group ($2930, 2850, 1430\text{ cm}^{-1}$), s-triazine and aromatic ($3030, 1500, 1600\text{ cm}^{-1}$). Thermal properties also have been done. The degradation starts from 280°C , loss rapidly between 300°C to 500°C and almost lost 85% at 650°C [125].

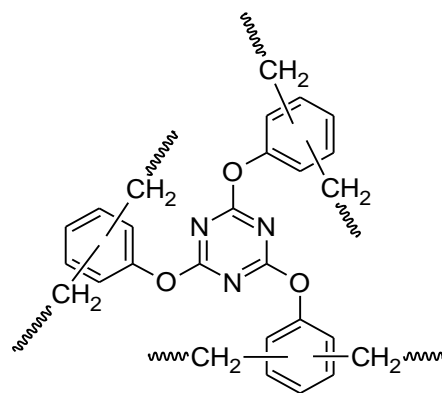


Polymeric properties and biocidal polypropylene was synthesized by mean of reactive extrusion process. Biocidal halamine structure of polypropylene was prepared using an N-halamine precursor, 2, 4-diamino-6-diallylamino-1, 3, 5-triazine followed by chlorination. The Fourier transformed spectroscopy (FTIR) results and nitrogen analysis confirmed the graft polymerization on polypropylene backbone during the reactive extrusion. Polymers revealed additional peaks in the region of $1500\text{-}1700\text{ cm}^{-1}$. The peak at around 1615 and 1550 cm^{-1} were attributed amino-azine and planner triazine ring, respectively. Another band at 815 cm^{-1} was out of plane ring deformation, a characteristic band of triazine ring containing two or three amine groups [126].

4,4'-bipyridine-cyanuric chloride polymers have been synthesized by Bourlinos et al. Cyanuric chloride, in which the reactivity of the chlorine atoms permits the preparation of a series of triazine derivatives. Thermal properties results showed that the perceived weight loss up to 120°C was due to the evaporation of absorbed solvent molecules. A sudden weight loss revealed between 200°C and 350°C that is showed to the thermal decomposition of the central triazine molecules (200°C) and ($>300^\circ\text{C}$) due to the bridging bipyridinium units [127].

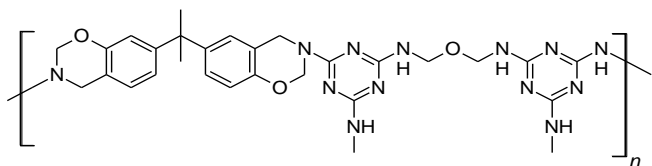
Photoactive poly(amide-imide) have been synthesized by Khoei and Zamani. The resulting polymer has been characterized by IR, ^1H NMR and TGA techniques. Thermogravimetric analysis designated that polymer was thermally stable in nitrogen atmosphere. In addition, the initial decomposition temperature, 5% and 10% weight loss (T_5, T_{10}) were $284, 356$ and 408°C . The residual weight percent at 700°C was 51.5%, which revealed that it is thermally stable [128].

Reghunadhan Nair et al. have synthesized higher crosslink phenolic triazine resin which was reported as a high temperature resistant polymer. GPC analysis revealed that the cyanate derivatives influenced closely higher molecular weights. It was established that the presence of triazine crosslinks were found to disfavour the char forming reaction of the otherwise high-char yielding maleimide-novolac resins. [129].

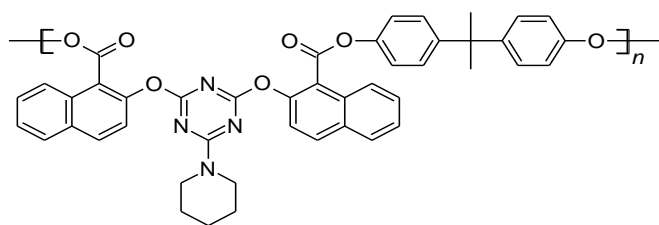


Heterocyclic polymers based on benzoxazine and s-triazine have been synthesized from melamine and formaldehyde with phenol or bisphenol A by Shi et al. Synthesized polymers revealed low viscosity at room temperature, good film forming characteristics and high chemical and thermal stability mainly owing to the addition of melamine into the network of the polymers. Synthesized benzoxazines has been characterized by proton nuclear magnetic resonance spectroscopy and fourier transform infrared spectroscopy. Thermal properties of polybenzoxazine have been evaluated by

differential scanning calorimetry, dynamic mechanical analysis and thermogravimetric analysis [130].



Polyimide having S-Triazine ring have been reported H.S. Patel and V.C. Patel. The polyimides are inconvenient to process due to high thermal stability and insolubility. The bands around at 1250 and 850 cm^{-1} due to the presence of s-triazine ring, $3300\text{-}3400\text{ cm}^{-1}$ assigned the stretching vibration of -NH- , $1590\text{-}1690\text{ cm}^{-1}$ indicating the stretching vibration of -C=N- of S-triazine ring. The TGA of polyimides revealed initial weight loss about 3% at 300°C presumably due to residual solvent a decompose in one step. The rate of weight loss is high around 500°C and completed around 750°C [131].



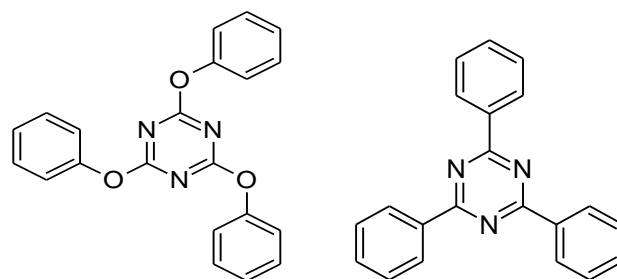
Polyesters based on s-triazine have reported by Patel et al. The polymer having s-triazine moiety in their backbone are distinctive in the sense that they show a different combination of properties such as high softening temperature and thermal stability together with solubility. The reduced viscosity of polyesters evaluated with a 1 g/dl solution in DMF at 25°C was found in the range of $0.34\text{-}0.62\text{ dl/g}$. The density of the polyester was in the range of $1.118\text{-}1.208\text{ g cm}^{-3}$. Thermal properties of these polymers was established, initial weight loss in the range of $200\text{-}270^\circ\text{C}$, 10% weight loss in the range of $240\text{-}310^\circ\text{C}$ and maximum weight loss in the range of $280\text{-}310^\circ\text{C}$ [132].

Maleimide-incorporated vinyl polymers based on butyl acrylate (BuA), methyl methacrylate (MMA) and styrene (STY) with pendant phenol functions have been synthesized by free radical copolymerization with N-(4-hydroxy phenyl) maleimide. Thermal curing of these polymers through the cyclotrimerization of the pendant cyanate groups cause to crosslinked imido-phenolic-triazines. The thermal stabilities of the phenol

precursors depended on the backbone structure. Presence of maleimide upgraded the thermal stability. Inspite of the presence of imide and triazine groups in the crosslinked network was conducive for decreasing the rate of thermal degradation at higher temperatures; they triggered an early onset of decomposition because of steric factors [133].

I.B. Recalde et al. have reported dicyanate ester resin. The family of the ester cyanate resin having the highly reactive cyanate group ($\text{-O-C}\equiv\text{N}$). They have low dielectric losses, good adhesive properties, low moisture absorption, high resistance to the flame, values of glass transition temperature, T_g in the range of $250\text{-}300^\circ\text{C}$ and temperature of thermal degradation around 400°C [134].

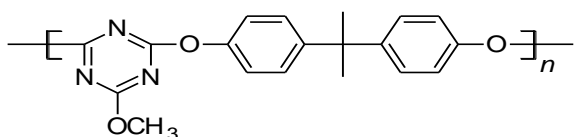
R.H. Lin et al. have reported that the polymers, which were containing a single s-triazine ring with different substitution groups, were tested. This demonstrates that the s-triazine ring itself is not the origin of the fluorescence. The interaction of the s-triazine ring with the substitution groups evidently was responsible for the fluorescence emission. Even if the oxygen atoms interrupt the conjugation of the formed s-triazine ring with the neighboring phenylene rings, fluorescence emission was detected [135].



Polycyanurates have been synthesized by polycyclotrimerization of cyanate ester with bisphenol - E and this polymer revealed good thermal stability, 5% weight loss in the range of $252\text{-}411^\circ\text{C}$, 50% weight loss in the range of $381\text{-}698^\circ\text{C}$ [136].

Polycyanurates derived from 2-diethylamino-4,6 dichloro- s-triazine and aromatic diols, have been synthesized by interfacial polycondensation which was reported by Desai et al. Thermal properties of synthesized polymers showed that the polycyanurates have good thermal stability due to the aromatic diol component of the molecular chain with s-Triazine moiety. Viscosity measurement also have been done in the ranged $0.179\text{-}0.373\text{ dl/g}$. IR spectra of these

polycyanurate attributed, absorption frequencies band at 805-810 and 1580-1435 due to the s-triazine ring [137]. Poly[2-methoxy-4,6-di(p,p'-isopropylidene diphenyloxy)-s-triazine] has been designed by interfacial polycondensation of 2-methoxy-4,6-dichloro-s-triazine with bisphenol-A. These polymers have been proved with IR and NMR spectroscopy. P.P. Shah has carried out intrinsic viscosity in different solvent. Intrinsic viscosity, in chloroform, in the range of 0.80- 3.10 dl/g, in 1,2 - Dichloroethane (0.93-2.54dl/g), in 1,2 Dichloroethane-n-butanol (0.88-2.33 dl/g). The IR spectrum revealed absorption bands at 1390-1350 cm^{-1} and 1120-1180 cm^{-1} characteristic of stretching vibration of the C-O-C linkage of an aryl-ether system. The bands in the 1670-1430 cm^{-1} region are attributed to aromatic double bonds and that at 820 cm^{-1} to out-of-plane vibration of the triazine ring. Bands at 1090-1075 cm^{-1} are due to C---O stretching vibrations [138].

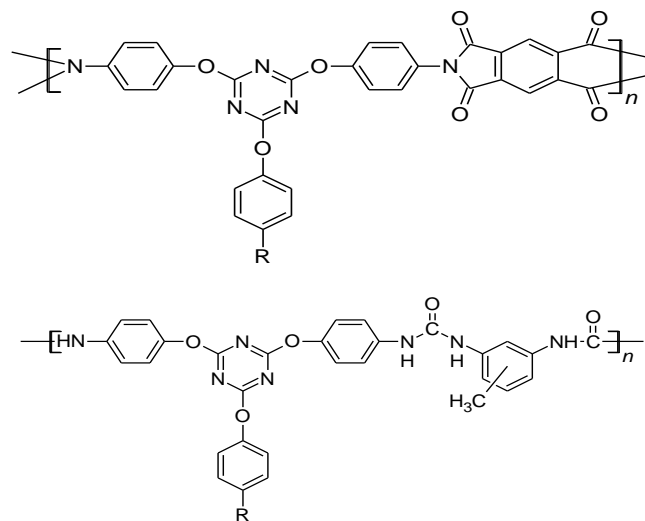


Aromatic polyazomethines containing S-Triazine ring have been synthesized by Sarwade et al. and reported that polymers have low inherent viscosity. The low values of η_{inh} of the polyazomethines in m-cresol may be owing to the hydrolysis of the polymers by a small amount of water present in the system. Thermal properties of these polymers also have been carried out, all the polymers attributed similar pattern of decomposition. 10% weight loss of these polymers in the range of 350-490 $^{\circ}\text{C}$ [139].

Naik et al have reported polycyanurates which were synthesized by interfacial polycondensation of 2-diphenylamino-4,6- dichloro s-triazine and aromatic diols. Reduced viscosities of synthesized polymers were in the range of 0.1- 0.19 dl/g and were soluble in chlorinated solvents such as chloroform, dichloroethane and methylene chloride. The density and thermal stability of the polymers also evaluated. Polycyanurates which were derived from bis phenol-A and bis phenol-c to establish outstanding thermal stability than others [140].

Crosslinkable polyimides, polyamides and polyureas derived from 2,4,6 Tris (4-Aminophenoxy)-s-Triazine have been reported by Melissaris et al[141]. Inherent viscosities of synthesized polymers were found in the range of 0.17- 0.34 dl/g. It was concluded that

crosslinked polymers have limited solubility. Thermal analyses of polymers reveal that polymer were stable up to 412-291 $^{\circ}\text{C}$ and 410-290 $^{\circ}\text{C}$ in N_2 and air, respectively. Thermal stabilities of crosslinked polymers with respect to the chemical structure of the polymer backbone were in the order: polyimide > polyamide > polyuria.



E. Bacu et al. have prepared new functionalized derivatives of phenothiazinyl-S-Triazine with potential pharmacological properties were acquired by nucleophilic substitution of halogen atom with hydrazine or amino alcohol. The polymers have been proved with IR, NMR spectroscopy. Stretching band at 1729 cm^{-1} due to (CO amide), NH amide II stretching band around 1576 cm^{-1} , 1780 (CO carboxylic), 3404 (NH_2), 2900-3350 (NH and OH associated) [142].

A. A. F. Iskander et al [143] have reported the chemistry and properties of two new series of polymers which were containing N- and O-naphthyl-s-triazines and the polymers were characterized by different techniques such as infrared, ultraviolet, fluorescent emission, elemental, thermal analyses and scanning electron microscopy (SEM). The polymers were readily soluble in polar aprotic solvents while insoluble in water and halogenated solvents. The polymers showed high thermal stability up to 900 $^{\circ}\text{C}$. Interestingly, the naphthyl/phenyl interchange led to improve the thermal properties. The kinetic data obtained from the nonisothermal decomposition of the prepared polyamides series were also studied. The polymers attributed emissions ranging from blue to orange wavelength depending on the nature of the signaling unit. The naphthyl/phenyl interchange led to either appreciable red-shifted absorptions in some cases or

blue-shifted absorptions in other cases and this behavior may be attributed to the contorted, twisted structural nature of the naphthalene ring. They have reported these polymers high-temperature materials and also as heat-resistant polymeric materials.

S. Oprea and V.O. Potolinca have developed three series of poly(urethane urea) with heterocyclic triazinemoieties in the main chain. The molecular motions were investigated by the use of dielectric spectroscopy in relation with temperature and frequency. They have reported, the addition of triazine derivatives into poly(urethane urea) backbone chain strengthen the physically crosslinked network, having thus significant influence on properties such as thermal and dielectric properties. Thermal property of polymers also studied by DSC, The glass transition temperatures and dielectric transition temperatures slightly decreased with the increase in the triazine derivative molar ratio [144].

A blue-fluorescence 2,4,6-tris(4-fluorophenyl)-1,3,5-triazine monomer was synthesized under mild reaction conditions. 2,4,6-tris(4-fluorophenyl)-1,3,5-triazine which had three active fluorine groups, was easily incorporated into stable cross-linked fluorescent polymeric nanoparticles via precipitation polymerization with 6-(4-hydroxyphenyl)pyridazin-3(2H)-one. The fluorescent polymeric nanoparticles were highly dispersible in water and showed uniform size, intense blue fluorescence, and excellent biocompatibility, making them promising for live cell imaging label applications [145].

Four types of new poly(arylene ether *s*-triazine)s having alkyl-, aryl- and chloro-substituted phthalazinone moieties in the main chain were synthesized by direct solution polycondensation of 2,4-bis(4-fluorophenyl)-6-phenyl-*s*-triazine with each of methyl-, phenyl- and chloro-substituted phthalazinones. The incorporation of phthalazinone and side groups into the poly(arylene ether *s*-triazine) backbone led to good solubility and maintaining other attractive properties. Inherent viscosities of the polymers were ranging from 0.38 to 0.55 dL g⁻¹. The polymers were soluble in *N*-methyl-2-pyrrolidone, pyridine, *N,N*-dimethylacetamide, hot *N,N*-dimethylformamide and sulfolane. The resulting polymers revealed glass transition temperatures in the range of 255 to 265 °C and thermal decomposition temperatures for 10% mass loss ranging from 476 to 599 °C which were studied by differential scanning calorimetry and thermogravimetric analysis, respectively. These polymers having *s*-triazine moiety

showed good thermal stability and high mechanical strength with the incorporation of alkyl-, aryl- and chloro-substituted phthalazinone moieties into their backbones, which makes them an attractive series of high-performance structural materials [146].

4.2. Coumarin based polymers

Coumarin was first reported and isolated in the 1820's and identified as the hay-like sweet aroma of the tonka bean [147,148]. After then, more than 1000 derivatives have been interrogated with naturally occurring coumarin derivatives isolated from species of plant life.

Coumarins and their analogues have outstanding property of photochemical and photophysical [149–151]. In particular, some coumarin derivatives cause a photoinduced cyclodimerization [152, 153] to a cyclobutane-based dimer. The reverse process (photocleavage) can be induced upon irradiation with higher energy photons (wavelength = 254 nm) [154–158].

Cheng- Mei Liu et al have reported that photodimerization of coumarin was first investigated by Ciamician and Silber [159]. The dimerized product showed a melting point of 262 °C [160], much higher than the original coumarin's melting temperature of 68–70 °C. In 1904, Storr reported a dimer with a melting point above 320 °C [160,161]. Researchers have studied the photophysics of coumarin compounds since the 1940s due in part to the tenability of their absorbance and fluorescence [162–178].

Coumarin and its derivative utilized in different fields such as photoreactive polymers, drug, dyes. Coumarin-based fluorescent dyes have been used not only for basic science such as physics, chemistry, medical science, and clinical science but also for industry and engineering [179,180]. Photo reactive polymers have received significant interest due to their technological application. Polymers with coumarin moieties have been useful in many fields such as fluorescence materials and laser dyes, nonlinear optical materials, photorefractive materials, electroluminescent material, etc. The fluorescence of coumarins is widely used as a research tool in polymer science [181,182].

Nechifor have synthesized monomer diacid, 6,6'-methylenebis{2-oxo-8-{2-[(2-oxo-2H-chromen-7-yl)oxy]acetoxy}-2H-chromene-3-carboxylic acid}, having two substituents (2-oxo-2H-chromen-7-yl)oxyacetate in the aromatic moiety and used in a direct polycondensation reaction with various aromatic diamines using triphenyl phosphite and pyridine as

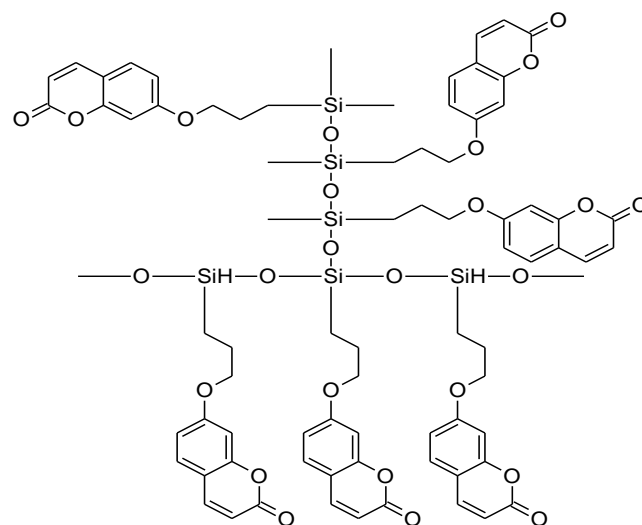
condensing agents to give a series of new aromatic polyamides with photosensitive coumarin pendent groups. The properties of polyamide have been evaluated by DSC, TGA, GPC (gel permeation chromatographic analysis), and wide-angle X-ray scattering, viscosity and solubility measurements. The aromatic polyamides had inherent viscosity values (0.40-0.87 dL/g) due to bulky side chains in the structure. Solubility of these polymers in aprotic polar solvents such as NMP (N-methylpyrrolidone), dimethyl sulfoxide and dimethylformamide, in less polar solvents like Pyridine and tetrahydrofuran. Gel permeation chromatography demonstrated high molecular weights (49,400-63,900 g mol⁻¹) which allowed transparent, flexible and tough films to be cast from polymer solutions. These aromatic copolyamides revealed good thermal properties correlated with glass transition temperatures (T_g) in the range of 221-257°C and decomposition in air above 390 °C. UV brightness (k > 300 nm) of the polymer films induced crosslinking between polyamide molecules through a [2π + 2 π] photocycloaddition at the C=C bond of coumarin moieties [183].

Onciu have synthesized coumarin-containing monomer, 7-[2'-(1,3-diamino-5-benzoyloxy)ethyl] oxy-chromen-2-one and synthesized monomer used in a direct polycondensation reaction with different aromatic diacids to give polyamides containing chromenyl side groups. Inherent viscosities of these polyamides reported above 0.78 and up to 1.21 dL/g. The number-average molecular weights were noted in the range of 27,000-46,000 g/mol. All the resulting polymers were amorphous and soluble in polar solvents like N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dioxane. Differential scanning calorimetry (DSC) of the polyamides showed distinct glass transitions on the curves ranging from 191°C to 223°C. Coumarin chromophores underwent [2+2] cycloaddition reaction under λ=313 nm light irradiation to yield crosslinked network structures [184].

Monomers having coumarin groups [2-(7-Cumarinyloxy)ethoxy] dimethyl terephthalate and [6-(3-carboxy)coumarinyl] diacetylhydroquinone have been prepared. Hyperbranched and comb-like coumarin-containing polymers were synthesized using above mentioned monomer polymerized by high temperature polycondensation. All polymers were completely soluble in chlorinated aliphatic

hydrocarbons. M_n in the range of 2000-50000. All polymers were amorphous with T_g in the range of 100-230°C and thermostability of 370-415°C. All polymers were established to be blue emitters emitting light in the range 450-492 nm [185].

Photosensitive polysiloxanes having coumarin in the side chains were synthesized by polycondensation. The photochemical behavior was studied by UV/Vis and refractive index measurements. The high thermal stability and the variable glass transition temperatures together with the good optical properties make these excellent for the use in a large variety of applications where photo tunable polymers are required [186].

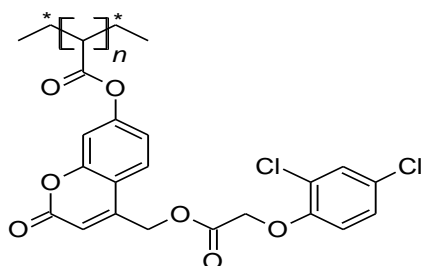


Qi Fu et al. have developed hyperbranched polymer endcapped with 4-methylcoumarin group by thiol-ene addition reaction of thiol-modified hyperbranched polyester with a vinyl monomer (7-(4-vinylbenzyloxy)-4-methylcoumarin). The polymer has been characterized with ¹H NMR and FT-IR spectroscopies. Its reversible photo-crosslinking/photo-cleavage behavior was assessed based on the UV-vis spectroscopic analysis. The absorbance at 319 nm in the UV-vis spectrum gradually declined under UVA irradiation (λ_{max} 365 nm), and then rapidly recovered under UVC irradiation (λ_{max} 254 nm) [187].

Photo-reversible nanocomposites of polyurethanes were developed by C. Salgado, which were based on coumarin and poly(ε-caprolactone) with different molecular weights. The polymer showed good thermal stability. The presence of coumarin improved the thermal stability of PUs [188].

Reversibly photo-cross-linkable pH-responsive block copolymer poly(ethylene oxide)-b-poly((2-

(diethylamino)ethyl methacrylate-co-4-methyl-7-(methacryloyloxyethoxy)coumarin)) (PEO-b-P(DEA-co-CMA)) was synthesized by atom transfer radical polymerization (ATRP) and characterized using dynamic light scattering, transmission electron microscopy, UV-vis spectra and ¹H NMR spectroscopy measurements. The photo-crosslinking was proved to be reversibly controlled under alternative irradiation of UV light at 365 nm and 254 nm UV-vis absorbance at 320 nm started to recover, the reverse photo-cleavage reaction bringing back coumarin side groups [189].

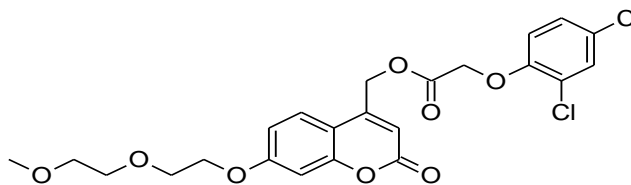


Chamsaz et al have reported the synthesis and photochemical behavior of photoresponsive polyesters based on alkoxyphenacyl and coumarin chromophores. The alkoxyphenacyl polyesters have UV absorption from 250 to 320 nm with λ_{max} at 278 nm. The coumarin based polymers have UV absorption from 250 to 370 nm with λ_{max} at 322 nm. Such photoresponsive and biodegradable polymers are potentially useful for drug delivery or tissue engineering applications [191].

Benoit et al. have reported a new class of dual-responsive coumarin-based copolymers, which were sensitive to temperature and light (UV and near infrared). The reported polymers, triethylene glycol methyl ether methacrylate (TEGMA) and 6-bromo-4-hydroxymethyl-7-coumarinyl methacrylate (CMA) were prepared by reversible addition-fragmentation chain transfer (RAFT) process. The thermosensitivity of copolymers P(TEGMA-co-CMA) were studied by turbidimetry measurements. Reported polymers showed dual thermal and light-responsive properties [192].

Mohamed et al have synthesized bifunctional benzoxazine monomer (coumarin-Py BZ) having both coumarin and pyrene groups through the reaction of 4-methyl-7-hydroxycoumarin (coumarin-OH), para-formaldehyde, and amino-pyrene (Py-NH₂) in 1,4-dioxane. FTIR and ¹H and ¹³C nuclear magnetic resonance spectroscopy affirmed the structure of this coumarin-Py BZ monomer. The curing behavior of

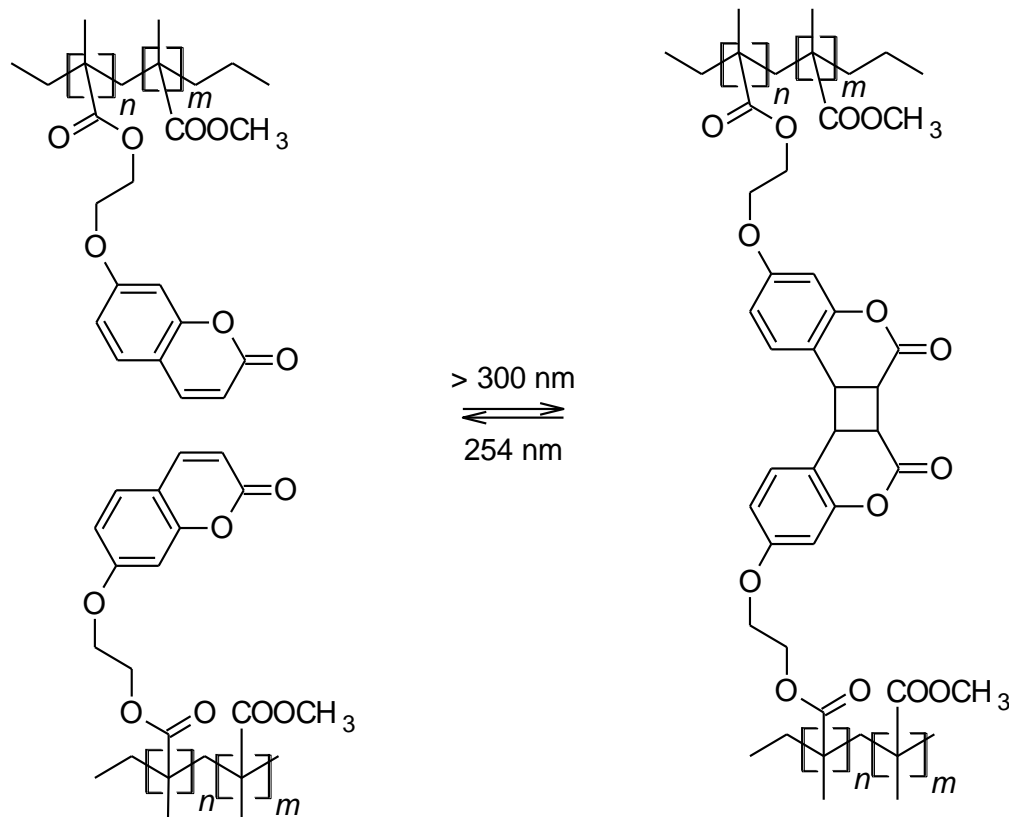
Atta et al. have developed polymeric controlled-release formulations for pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) on acrylate and polyethylene glycol (PEG) based coumarin-2,4-D polymers. Photophysical study revealed that coumarin-2,4-D polymers are fluorescent in nature. Both acrylate and polyethylene glycol (PEG) based coumarin-2,4-D polymers were shown to release 2,4-D in aqueous ethanolic solvent with UV light (\geq 310 and 350 nm). The coumarin-2,4-D polymers revealed very good thermal stability [190].



coumarin-Py BZ to be monitored by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and FTIR spectroscopy, both before and after photodimerization of the coumarin moiety. DSC studies showed that the glass transition temperature of poly(di-coumarin-Py BZ) was higher than that of its corresponding polymer (poly(coumarin-Py BZ)) [193]. Senocak et al. have prepared and characterized new hybrid materials based on reduced graphene oxide (rGO) or single-walled carbon nanotubes (SWCNTs) covalently functionalized by 4,4-difluoro-8-(4-propyloxy)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BODIPY) or 7-(prop-2-yn-1-yloxy)-3-(3,4,5-trimethoxyphenyl)-coumarin as light harvesting groups were described. The formation of novel nanomaterials was confirmed by the FT-IR, UV-Vis and Raman spectroscopies and thermogravimetric analysis [194].

Multivalent photo-crosslinkable coumarin-containing polybenzoxazine polymers have been reported by R-C Lin. The typical absorption peaks of coumarin and its derivatives visible between 250 and 300 nm, corresponding to $\pi - \pi^*$ transition, with another $\pi - \pi^*$ absorption signal, due to the pyrone unit, appearing between 310 and 340 nm. UV radiation for 30 min led to a decline in the intensity of the absorption signal at 318 nm, confirming that dimerization through $[2\pi + 2\pi]$ cycloaddition of the olefinic bond demolished the delocalized π system [195].

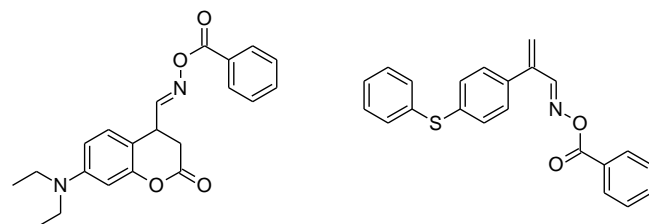
lliopoulos et al. have prepared coumarin-based copolymers, the optical absorption spectra of Pm in thin film allowed one major absorption range (280-350 nm)



Visible light initiated thiol Michael addition polymerizations with coumarin based photobase generators have been reported by Zhang et al. In UV-vis analysis, 400-500 nm light irradiation, the absorption spectra of coumarin - tetramethyl guanidine in methanol changed owing to the phototriggered transformation of the coumarin structure [197].

Li et al. have developed coumarin based oxime ester photoinitiators, containing diethyl amino coumarin moieties as chromophores and oxime-ester groups as initiation functionalities and studied their structure-property relationship. The substitution positions of the oxime-ester on the coumarin ring, notable effect the absorption behavior and the fluorescence emission spectra. Due to the efficient initiation mechanism combined with a broad absorption band, ranging from 400 nm up to 480 nm, the investigated oxime-ester could effectively induce acrylate and thiol-based click photopolymerization under visible LED irradiation. Furthermore, It was established that the sufficient thermal stability of the photoinitiators, in the dark, by TGA and DSC [198].

attributed to the absorption of the coumarin chromophore. The absorption spectra change during irradiation of the film at $\lambda > 300$ nm [196].



Kedia et al. have synthesized copolymer having several pendent dyes (coumarin derivatives) along the side chain and its fluorescence parameters have been observed in pure solvents and also as a function of composition of binary solvent mixtures. Fluorescence parameters of the free fluorophore show powerful dependence on the nature of the immediate environment around it [199].

Concellon et al have prepared nanoporous polymers from columnar hexagonal hydrogen-bonded complexes, whose order is fixed by coumarin photoinduced [2 + 2] cycloaddition (photodimerization). Two different hydrogen-bonded complexes have been used and consisted of a melamine (M) or tris(triazolyl)triazine (T) derivative acting as central templates and three peripheral carboxylic acids having coumarin units.

These polymers with columnar hexagonal nanopores utilized in a wide range of molecular recognition, filtration, separation or catalysis [200].

Polymethacrylates with coumarin side chains have been reported by Obi, Irradiation with 313 nm light resulted in the decrease in absorbances at λ_{\max} for all of the polymers, whereas a slight increase in absorbances at wavelengths shorter than 250 nm was noticed, being in line with the [2+2] cycloaddition at the C=C bond of coumarin moieties to give a benzenoid absorption band. Absorbances of the peak centered at around 1400 cm^{-1} due to the C=C bond decreased upon photoirradiation for each polymer, indicating the photodimerization of coumarins. The peak around 1500 cm^{-1} for each film increased by photoirradiation and the peaks around 1150 and 1250 cm^{-1} became broader. This behavior is considered to also be caused by the formation of cyclobutane [201].

4.3. Fluorescence Properties in Polymers

Photosensitive organic polymers have received increasing interest in the last ten years due to their potential application in optoelectronic devices [202]. Fluorescence is a phenomenon in which a molecule is electronically excited by absorption of ultraviolet, visible or near infrared radiation. The excited molecule then decays back to the ground state, or to a lower-lying excited state, by emission light. The emitted light is detected. Photoluminescence processes are subdivided into fluorescence and phosphorescence.

Fluorescence was first observed as long ago as 1565 and gets its name from the fact that the mineral fluor spar was found to glow under UV radiation. In all forms of luminescence, it is compulsory for a molecule to be raised into an excited electronic state before it can emit radiation. Fluorescence is determined from other types of photoluminescence by the fact that the excited molecule returns to the ground state immediately after excitation, the time spent in the excited state being typically of the order of 10^{-8} s. The spectral range for most molecular fluorescence measurement is 200 to 1000 nm ($10,000$ to $50,000\text{ cm}^{-1}$). Fluorescence analysis may be carried out on liquid, gaseous and solid samples. Solvents do not interfere unless they absorb at the wavelength used to excite the analyte or act to decrease the efficiency with which the excited analyte molecule fluoresces.

Fluorometry is more discriminating than UV/VIS absorption spectrometry for two reasons. First, many

molecules absorb strongly in the UV or visible range but do not show detectable fluorescence. Second, two wavelengths (excitation or emission) are available in fluorometry, but only one wavelength is available in absorptiometry. If two samples constituents with similar absorption spectra fluoresce at different wavelengths, they may be determined from one another by favorable choice of emission wavelength. Similarly, two compounds that have similar fluorescence spectra but absorb strongly at different wavelength may be determined by proper choice of excitation wavelength. Fluorescent compounds may have a clutter of overlapping bands of a mixture of the absorption and fluorescence spectra. Such samples must be subjected to preliminary clean up and separation or specialized sample preparation and measurement techniques may be used, these may be instrumentally complex or time-consuming. Because fluorescence measurements are quick and use relatively inexpensive and rugged instrumentation, fluorescence can be used to screen samples, to generate preliminary data that allow an analyst to decide whether a sample requires detailed characterization, maybe by a more expensive and complex technique such as gas chromatography/ mass spectrometry. This is especially favourable for environmental samples, which usually are very complex. Small, portable fluorometric instruments are suitable for performance of such screening operations in the field.

The initial step in a fluorescence measurement is electronic excitation of an analyte molecule via absorption of photon. Once formed, an excited molecule has available a variety of decay processes by which it can rid itself of the energy conveyed to it by absorption. In addition to fluorescence, there are nonradiative decay processes, leading to release of energy in the form of heat rather than light. Other sample constituents may interact with an excited analyte molecule in such a way to prevent it from fluorescing; such process is called quenching. Also an electronically excited molecule may undergo chemical reaction.

The phosphorescence is of much longer duration than fluorescence. Thus, when the exciting radiation is switched off the fluorescence intensity falls to zero very rapidly (within about 10^{-8} s). phosphorescence emission however, continues long after the excitation radiation is removed, sometimes for a matter of seconds or even minutes. This enabled us to observe phosphorescence without interference from fluorescence by a process known as time resolution.

Fluorescence and phosphorescence are forms of luminescence in which light or UV radiation is emitted by a compound following excitation with radiation of shorter wavelength in accordance with Stokes' Law. Phosphorescence has a longer wavelength than fluorescence and also has a longer lifetime. Both processes involve the excitation of molecules into electronic excited states and the emission of luminescence competes with other processes by which the molecule can lose its excess energy. The energy can be transferred directly to other molecules by a process known as quenching or dissipated through the vibrational motion of molecule. Quenching depends on collision between molecules and the vibrational process is facilitated by internal transfer of energy by internal conversion and inter system crossing as a result of which the molecule passes over into a lower-lying electronic state. In the case of phosphorescence, it is necessary to prevent quenching by observing the sample in the solid state or protected from collision in some other way.

There are two different types of fluorescence spectra, the excitation spectrum and the emission spectrum. These bear a mirror – image relationship to each other which is particularly apparent when the bands reveal vibrational fine structure. The separation between the band maxima is known as the Stokes' shift. The phosphorescence spectrum has a similar vibrational fine structure to the fluorescence spectrum though in practice this is often obscured because the sample is in a different physical state. The transition involved in these spectra can be conveniently shown on a Jablonki diagram which also identifies the specific vibrational levels involved by the use of the vibrational quantum number as a label. The 0,0 transition is common to both spectra but usually appears at longer wavelength in the emission spectrum because of solvent interaction.

The excited state associated with phosphorescence is a triplet state which has a very long lifetime (typically 10-3 s) compared with the singlet state (10^{-8} s) because the transition to the (singlet) ground state is spin-forbidden. This accounts for the long lifetime of phosphorescence emission. The triplet state is also involved in another type of long-lived luminescence called delayed fluorescence.

In many fluorescence spectrometers, one can simultaneously vary the wavelength of the excitation and emission radiation. Such measurements commonly called synchronous scanning and are useful in the analysis of mixtures [203].

Fluorometry is a multidimensional technique from which several types of information (in addition to spectra and signal intensities) can be obtained. The fluorescence of a molecule may be partially or fully polarized. Measurements of fluorescence polarization can provide important information, particularly for macromolecules; the use of polarized fluorescence measurement is widespread in biological and science.

Fluorescence of organic molecules have finite lifetimes, usually nanosecond due to singlet excited state of molecule. The fluorescence or phosphorescence rate of a molecule can be measured and changes in fluorescence spectra as a function of time can be obtained. Measurement of time-resolved spectra or decay times can aid in analytical application of fluorometry and can also provide unique fundamental information in the study of very fast chemical and physical phenomena.

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa found out that a thin film of polyacetylene which was oxidized with iodine vapors, turning the material into a conductor for this investigation they got the Nobel Prize in Chemistry. Since 1980s, fluorescent polymers utilized in commercial development further attracted tremendous scientific and industrial interest due to their potential in achieving the goal of light emitting device technology that is economically viable for solid-state lighting and displays, which offer important gains in power efficiency, color quality, and life time at lower cost and less environmental impact than traditional incandescent and fluorescent lighting [204-214]. Fluorescent polymers are organic macromolecules which consist of at least one chain of alternating double- and single-bonds. They derive their semiconducting properties from having the extensive delocalization of π -electron bonding along the polymer chain and this delocalized π electron system makes them capable of absorbing sunlight, creating photo generated charge carriers and transporting these charge carriers. Moreover, these significant properties can be altered by the inclusion of functional side groups as well as substitution of the intractable conducting polymers backbone with alkyl and alkoxy substituents [215-221]. Rustemeyer et al have reported photochromic cooligomers from pyridazine spirodihydroindolizine and styrene synthesized by free radical polymerization. The addition of spirocyclopropene caused to cooligomers in which the pendant pyridazine subunits are transformed into photochromic spirodihydroindolizines. Polymers have been characterized by NMR and SEC. All

cooligomers reveal a shoulder at $\lambda = 390$ nm and a maximum at $\lambda = 317$ nm. After irradiation with the UV-lamp for 3 min another absorption appears at $\lambda = 534$ nm for the open form. It should be noted that this spectrum is a superposition of the closed and open form in the photochemical equilibrium attributed between an ultrafast photochemical opening and a fast thermal cyclization [222].

Photochromic poly (methyl methacrylate-co-diarylethene)s have been synthesized by L. Shen et al. Poly(methyl methacrylate)s substituted with photochromic diarylethenes as the main backbone or pendant functional groups were prepared by atom transfer radical polymerization (ATRP), using methyl methacrylate and 5,5'-dihydroxymethyl substituted dithienylethene as the monomers. The resulting photochromic copolymers showed good photochromic properties, good fluorescence, easy film-forming performance, and outstanding thermal properties [223]. Photochromic polymers have been prepared by a conventional radical polymerization of styrene derivatives having diarylethene chromophores as the pendant. The polymers revealed reversible photochromism in the film as well as in solution. In the film, sometime, the photocyclization quantum yield of diarylethene moieties in the polymer decreased in comparison with that in solution owing to the structural restriction in the polymer matrix. The terpolymer has thermal stability, fatigue-resistance, high content of the chromophores, and the brilliant color in the solid state [224].

Watkins and Fujiwara have reported Bis-spiro-naphthooxazine based photochromic polymer materials. For the spirooxazine molecule, the absorbance in the spectrum comprises of localized π - π^* transition in the UV region corresponding to the acoplanarity of the indoline and oxazine moieties of the molecule. Upon photo-irradiation with UV light (340 nm), the formation of colored isomer is observed with λ_{max} in the range of 550 to 630 nm [225].

Photochromic polymer and hybrid material having azo methylisoxazole dye have been reported by Ortyl et al. The maximum absorption band of the film was noticed at 412-414 nm and 422 nm for polymer and hybrid materials, respectively. Illumination of the films with light caused isomerization of the diazo group demonstrated by decrease of the absorbance. The magnitude of modulation of real part of the refractive index was in the range between 0.017 and 0.026 [226].

Photochromic polymers carrying [2.2] paracyclophane bridged Imidazole dimer has been reported by Kimoto et al. They have observed that the photochromic behavior is not affected by the environment around the photochromes and copolymerization with other monomers both in solution and film, which cannot be realized in any other normal photochromic systems. The comparable photochromic behavior of the homopolymers and copolymers in solution and film indicates that the photochromic unit is independent from the local environment, which allows effective molecular design of the photochromic monomer unit to achieve desired photochromic properties of the polymer [227]. Spiropyran-Based photochromic polymer nanoparticles with optically switchable luminescence have been synthesized by Zhu et al. As photochromic materials, colorless spiropyrans undergo photoinduced ring-opening reactions under ultraviolet irradiation to yield their isomers merocyanine forms, which have strong solvatochromic visible absorption bands in the range of 500-600 nm. Fluorescence switching with UV and visible light is reversible; the wavelength at which fluorescence is most rapidly switched on is 350 nm, the absorption maximum of the spiropyran [228].

Sznitko have prepared photochromic polymer having azobenzene side groups, Excitation and emission spectra revealing a broad band photoluminescence in the visible light region were evaluated for sample. The emission band obtained between wavelengths 550 - 700 nm with maximum situated at $\lambda_{max} = 614$ nm. The excitation band obtained between 350- 590 nm with maximum situated at $\lambda_{max} = 586$ nm [229].

Rhodamine-based functional molecule Rh-OH have been synthesized. It attributed the force-induced MCL properties in solid state but an inert response to UV light irradiation. Rh-OHs were covalently embedded in the polyurethane-based elastomeric PU-Rh-1 film, which showed novel mechanical force and UV light dual sensitivities. The film could be repeatedly printed with the patterns on demand by UV-irradiation and erased easily by heating without reduction of intensity, which was quite different from the behaviour of Rh-OH molecule in the solid state. The force and UV light induced color change of the film originated from the isomerization of Rh-OH from a twisted spiro-lactam in the ring closed form to a planarized zwitterion in the ring-open state [230].

Rodriguez et al. have reported that the use of photochromic polymer films poly (methyl methacrylate)

sensitized with DisperseRed-I, to control the guided wave of an integrated polymer device. This property photochromic thin films showed possibilities, optoelectronic devices requiring the reconfiguration of optical interconnection such as optical switches, modulators, data routers or variable frequency filters [231].

Light -controlled selective Mg deposition on diarylethene-doped polymer surfaces have been exhibited. A small amount of photochromic diarylethene molecules doped to the polymers switched the physical property of the polymer surfaces, resulting in selective deposition. Fine metal patterns on the diarylethene-5%-doped Polystyrene surfaces were accomplished with laser scanning and maskless vacuum deposition. It was reported that the selective metal deposition on diarylethene-doped polymer films will contribute to fine metal electrode patterning, and therefore large scale integration for polymer electronics [232].

Corredor et al. have reported photochromic polymer composites having a mixture of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (diarylethene 1) and fluorene derivatives 2,2 ϵ -(9,9-didecyl-9H-fluorene-2,7-diyl)bis(ethene-2,1-diyl)bis-(4,1-phenylene) dibenzo[d]thiazole (2) or poly(9,9-didecyl-2,7-dipheylaminofluorene). Two-photon excitation of the closed form of diarylethene 1 at 800 nm [233].

Naphthopyran polymer conjugates have been prepared by Ercole et al. and evaluated photochromic properties. Upon termination of uv light the samples decolorize spontaneously in the dark owing to the thermal back reaction which occurs as the naphthopyran open form undergoes ring closure. The sample is continuously irradiated for 1000 s and then the decoloration kinetics of the sample are investigated in the dark at 20°C upon cessation of UV irradiation [234].

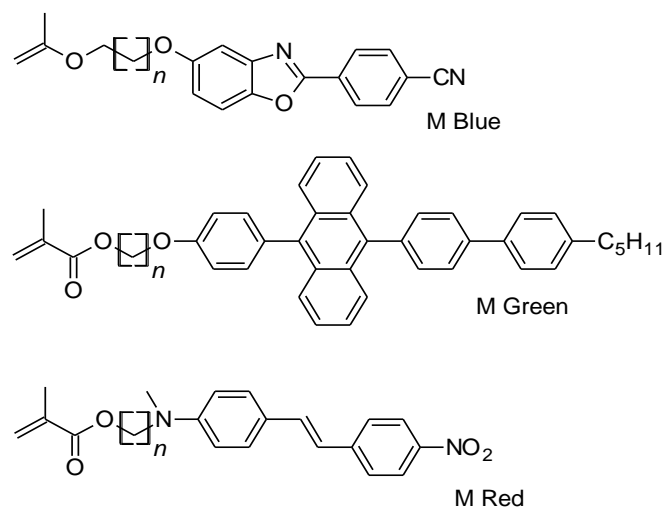
Dunaev et al. have reported photochromic polymers, photochromic polymers in a polymer binder as a two-photon recording medium for an optical 3D memory and photo switches of optical signals are revealed. The materials showed thermally irreversible photochromic transformations [235].

Polymers which were containing chiral (-)- menthyl groups have been developed by Liu et al. The thermal stabilities of the polymers were evaluated by TGA. The weight loss of the polymers around 400 and 460°C owing to the occurrence of the thermal degradation of the ester/ acetate side chain and then the main chain.

UV irradiation caused the E/Z isomerization leading to the variation of UV-vis spectrum around 360 and 450 nm [236].

Photosensitive copolymer of N-isopropylacrylamide and methacryloyl derivative of spirobenzopyran have been synthesized by Ivanov et al. UV spectra of the copolymer aqueous solution (1 mg/ml) before and after UV irradiation. The non-irradiated sample attributed a sharp UV-absorption band with maximum at 300 nm of methacryloyl derivative of spirobenzopyran, which allows estimation of MSBP (methacryloyl derivative of spirobenzopyran) content in the copolymer. The molecular weight of the copolymer was 21,000 g/mol as determined by dynamic light scattering, Mn/Mw= 1.23 [237].

Hu and Xu [238] reported 3- alkoxy substituted polythiophene which was prepared at low temperature. The UV- vis spectra of polymer were revealed a maximum absorption band at 520 nm in the film. This indicates that the packing of polymer chains in the condensed phase is anticipated to favour a coplanar arrangement of the adjacent thiophene rings. The polymers attributed two thermal weight loss steps due to the side chain and degradation of backbone and also, the glass transition temperature of the polymer depends on the length and flexibility of the pendant groups.



Liquid crystalline terpolymers having azobenzene and dye moieties have been prepared by Gimenez et al. The UV/ vis spectra were complex due to overlap of the absorption bands. Although, the absorption band at longer wavelengths in the case of TPgreen and TP red (474 and 445 nm, respectively) was only due to the absorption of the respective dye unit. The photochromic properties of the azobenzene are unchanged but the

integration of the different dyes results in a change in the absorption. However, the fluorescence of the dyes is strongly extinguished in the presence of the azobenzene moiety [239].

Feng et al. have prepared optically active poly (N-methacryloyl L. luciene methyl ester), they have done thermogravimetric analysis. The weight loss of the polymer in two steps for the samples with one starting at 240°C the other at 317°C [240].

Dutta et al. have reported two random copolymers of sodium N-acryloyl-L-valinate and N-dodecylacrylamide in buffered (pH 8.0) aqueous solution containing 0.1 M NaCl. NPN revealed a very weak fluorescence with emission maximum (λ_{max}) at 460 nm [241].

Chen et al [242] have synthesized amphiphilic hyperbranched polymer by a convenient attachment of photoresponsive spiropyran molecules to functional ends of a biodegradable hyperbranched polyphosphate. First, 365 nm UV light irradiated, the micelles transformed from colourless to red. At the same time, a gradually enhanced peak at 575 nm which is the characteristic absorption peak of MC can be found in the UV spectrum of the micelles with increasing the UV irradiation time. These results indicate that colorless SP with a closed form changed to colored MC with an open form. Then, at 620 nm visible light for 2 h, the solution converted from red to colorless and the absorption peak of MC at 575 nm decreased and at last disappeared with the increase of the visible light irradiation time. These results are signs of the reversible conversion of red MC to colorless SP. In order to test the cyclic reversible response ability of the micelles, the sample was irradiated with 365 nm UV light and 620 nm visible light alternatively.

Fluorescent polymeric particles have been synthesized by Bretler and Margel. These particles were colourless in visible light since the SpiroPyran molecules entrapped within the particles were in the spiro form. Upon UV irradiation the particles become photochromic and fluorescent due to the transition of the SP entrapped molecules from the spiro form to the MC form. A fluorescence measurement has been noted excitation at 600 nm wavelength and emission at 640 nm [243].

Angiolini et al have synthesized and characterized methacrylic polymers bearing side- chain permanent dipole azobenzene chromophores spaced from the main chain by chiral moieties. The thermal stability of these polymers was evaluated by TGA. Initial decomposition in air ranging around 300°C, The UV spectra in DMA

solution of polymers and models display two absorption bands centered in the 450±510 and 280±330 nm spectral regions, the former, more intense, related to the combined contributions of the n- π^* , first $\pi-\pi^*$ and internal charge transfer electronic transitions of the azobenzene chromophore, and the latter to the $\pi-\pi^*$ electronic transition of the aromatic ring [244].

Polymethacrylates based on L- lactic acid and azobenzene chromophores have been reported by Angiolini et al. UV spectra in THF and CHCl₃ solution of polymers, as well as of the showed in the 250-550 nm region two bands centered around 335 and 450 nm, related to the $\pi-\pi^*$ and n- π^* electronic transition of the azobenzene chromophore in trans configuration. The 4'-unsubstituted derivatives of these polymers λ_{max} values close to 320 and 440 nm for the same transitions due to the presence of the electron withdrawing groups which induce conjugation in the azoaromatic system to a larger extent [245].

Altomare and Solaro [246] have reported optically active (meth)acrylic homopolymers, Irradiation at 366 nm of the polymer samples in chloroform solution promotes the trans - cis isomerization of the side chain azobenzene chromophores. This process gives rise to a shift towards higher frequencies and a decrease in intensity of the $\pi-\pi^*$ absorption band. All trans poly(meth)acrylic and trans- methacrylic in chloroform solution showed very weak negative bands centred at 430-440 nm.

Copolymers of (-) menthyl acrylate with 4-hydroxystilbene acrylate have been reported by A. Altomare, The UV- visible spectra of synthesized polymers in all- trans configuration in the 350-240 nm spectral region show a broad structured band with two relative maxima at about 300 and 312.5 nm and two shoulders at about 288 and 325 nm. In the same region trans-stilbene shows a band with relative maxima at 298.3 and 310.4 nm and two shoulders at 291.7 and 322.1 nm attributed to the first $\pi-\pi^*$ electronic transition. The fluorescence spectra of trans -SP consist of a rather well structured band with relative maxima at 342 and 359 nm and a shoulder at about 380 nm [247].

Adriaencens et al. have synthesized conjugated polymers, Initially the absorption band at 301 nm, started from the precursor polymer, diminished upon increasing the temperature, while a new absorption band at 374 nm arises due to the formation of rather short conjugated sequences. A red shift upon increasing the elimination temperature, indicating that the

effective conjugation length of the conjugated pi system increases and reaches a maximum absorbance around 475 nm (λ_{max}) at 110°C above 110°C, however, a blue shift can be noticed owing to a thermochromic effect [248].

5. CONCLUSION

The literature survey reveals that aromatic polymers with heterocyclic framework showed good thermal stability, chemical resistance and excellent mechanical properties. We have also discussed the synthetic approach of fluorescent polymers which are applicable in biosensors, clean energy technologies, explosive sensing, pH/ temperature sensor, biological imaging, life science, material science, ultrasensitive molecular diagnosis and novel light-emitting nano devices. Henceforth this review reveals the extensive information of fluorescent heterocyclic polymers. The methodology in the review will motivate future researcher to synthesize fluorescent polymers with heterocyclic framework.

Conflict of interest

None declared

6. REFERENCES

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