

Title	4 - アミノ桂皮酸二量体をモノマーとするバイオベースポリアミド/イミドの合成
Author(s)	Kumar, Amit
Citation	
Issue Date	2016-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/13524
Rights	
Description	Supervisor:金子 達雄, マテリアルサイエンス研究科, 博士

Doctoral Dissertation

**Syntheses of bio-based polyamide/imides
derived from 4-aminocinnamic acid dimer as
monomers**

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03/2016

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Abstract

Due to limitation of oil-field and hence petroleum-derived products, bio-based materials are indispensable in low-carbonation society establishment. Super engineering plastics from biomolecules are suitable for the materials in terms of available amount and cost. The development of these high performance bio-based polymers is crucial to establish sustainable low-carbon society. The syntheses of high performance bio-based polymer including polyamide and polyimides (PIs) with photofunction properties derived from bioavailable starting material was the uttermost focus of this research.

The bio-based monomers of polyamide and polyimide such as diamine and diacid were synthesized along with the synthesis of total bio-based polyamide. The detailed syntheses are discussed in Chapter 2. New route for the synthesis of monomer diamines 4,4'-diaminostilbene (DAS), 4,4'-(ethane-1,2-diyl)dianiline (EDDA) and diacid N,N'-diacetyl-4,4'-diamino- α -truxillic acid (DADTA) from bio-derived 4ACA was explored. The prepared monomers were characterized using ^1H NMR and ^{13}C NMR. A novel diamine i.e. 3,6-bis(4-aminobenzyl)piperazine-2,5-dione (BAPD) was prepared by a series of chemical modification starting with 4-aminophenylalanine (4APhe) by optimizing each step and the synthesis route was established. The prepared diamine DAS and diacid DADTA were employed to react in presence of TTP in DMAc to form total bio-based polyamide which was characterized by FT-IR, GPC and TGA. From TGA it was observed that the polyamide showed high T_{d10} at 367 °C.

In Chapter 3, fully bio-based and semi-bio-based PIs were synthesized and characterized w.r.t their thermal and mechanical properties. DAS and EDDA were synthesized from bioavailable molecule via Grubb's coupling reaction. PAAs were synthesized by condensation polymerization of DAS with dianhydrides (yields: 90-98%). PAA films were prepared by spin-coating which were then thermally imidized to prepare PIs film. Molecular weights ranged $2.2 \times 10^5 - 4.0 \times 10^5$ g/mol for M_w . Inherent viscosities ranged 0.41-6.62 dl/g (PAA-1f highest). PIs showed high degradation temperatures of T_{10} ranging 500-600 °C. The tensile strength of PI-1f^{##} was found to be 132 MPa higher than that of KaptonTM. Thus every biopolyimide prepared here showed high thermal and mechanical properties. The effect of various factors such as polymerization time and mixture of dianhydride were carried out. As per GPC the 32 h polymerization time was found to be good, however, 24 h polyimides gave good thermal and mechanical properties. The polyimide from mixture of dianhydride possesses the properties lying from the polyimide from pure dianhydride.

Chapter 4 deals with the photo-functional properties of PAAs and PIs. All the PAAs synthesized from amine DAS were found to be UV-vis active and the fluorescence studies revealed the effect of UV-vis irradiation on PAAs. UV-vis irradiation was found to control the fluorescence intensity due to the crosslinking of PAA chains which was proved by ^1H -NMR hence UV-vis irradiation can help in modifying the polymers fluorescence properties to the desired one. The crosslinking and inter conversion of *trans* to *cis* to cyclobutane was proposed and confirmed.

KEYWORDS: stilbenes, polyimides, high performances, photofunctions, aromatic diamines.

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PREFACE

The synthetic work embodied in this thesis has been carried out in the School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST) under the inspiring guidance of Prof. Tatsuo Kaneko. The extent of information derived from the existing literature has been indicated in the report at appropriate places giving the source(s) of information.

I owe my deep sense of gratitude to Prof. Tatsuo Kaneko, Prof. Kohki Ebitani, Prof. Kazuaki Matsumura, Prof. Ashok K. Prasad and Prof. Rajeev Singh for their invaluable guidance, constant encouragement, precious suggestions and utmost care throughout the course of the project work.

It is needless to say that I stand solely responsible for any lapses that might have occurred in carrying out and presentation of this work, despite all the precautions taken to the best of my ability.

AMIT KUMAR

ACKNOWLEDGMENT

This research study entitled “Syntheses of bio-based polyamide/imides derived from 4-aminocinnamic acid dimer as monomers” was performed at School of Materials Sciences, Japan Advanced Institute of Science and Technology (JAIST), Japan and was financially supported by Advanced Low Carbon Technology Research and Development Program (JST ALCA, 5100270), Tokyo, Japan and MEXT.

First and foremost I would like to express my sincere gratitude to my respected supervisor, Associate Professor Tatsuo Kaneko in JAIST for his active valuable guidance, suggestions and kind support during my staying in Japan at professional and personal level.

I also express my specially thank my second supervisor Professor Kohki Ebitani, my advisor for minor research Associate Professor Kazuaki Matsumura in JAIST, Professor Ashok K. Prasad in University of Delhi and Professor Rajeev Singh in ARSD college, University of Delhi for their valuable guidance.

I am very grateful to Dr. Maiko Okajima for her concern and efforts even at personal level that kept me going smoothly to complete my study without any difficulties in JAIST.

I also thank Assistants Professor Seiji Tateyama and Dr. Akio Miyasato for their guidance and to all appreciate comment and suggestions.

I also would like to thank Dr. Katsuaki Yasaki for his guidance and help for his co-research to carry out the photo-functional property of the polyimides.

I would like to thank all of my lab mates, Dr. Wang Siqian, Dr. Nguyen Thi Le Quyen, Dr. Kai Kan, Dr. Phruetchika Suvannasara, Dr. Shin Hojoon, Ms. Pham Thi Thanh Huyen, Mr. Jin Xin, Mr. Hieu Duc Nguyen, Ms. Kittima Amornwachirabodee, Mr. Masanori Miyasato, Ms. Nupur Tandon, Ms. Rupali Sharma, Mr. Kawamoto Hirotooshi, Mr. Kohei Goto, Mr. Takahiro Noda, Mr. Hiroshi Shimosegawa, Mr. Ryosuke Mishima and Mr. Motoki Misumi, for their help and sharing happy time during my stay in JAIST.

I extend my thanks to Dr. Mohammad Asif Ali for his immense help and support during all these year without which it wouldn't be possible.

I express my deep sense of gratitude to Vinod Khatri, Amit Kumar, Balram Rathi, Yogesh Kumar, Abdullah khan, Vijay Bahadur, Anil Kumar Singh, Akanksha Matta, Prashant Kumar, Shiv Kumar, Abhishek Kumar Singh, Badri Prasad, Atul Kumar, Jyoti Arora, Neha Yadav and Saumya Dabral and all the other lab members for their assistance and moral support during my minor research in University of Delhi.

Last but not least I thank Neeraj Kumar Mishra in ARSD College, University of Delhi for his kind help.

Finally, I would like to dedicate this research to my mother and extent my heartfelt appreciation to my family and friends for thoughtful attention and continuous encouragements.

February 2016

JAIST

Kumar

Amit

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

The modern era is referred as Petroleum age due to the dependence of mankind on petroleum derived materials. The various components of petroleum are being used for running factories, automobile, central heating and it has provided us with unprecedented standard of living since its discovery. People have used petroleum for thousands of years for variety of purposes. More than 4,000 years ago, natural seeps of tar-like asphalt called bitumen was used to fortify walls and towers in ancient Babylon and Jericho. Ancient Persians used petroleum for medicine and light.

It is an extremely versatile substance; refining it creates everything from asphalt and gasoline to lighter fluids and natural gas along with a variety of essential elements such as sulphur and nitrogen. Petroleum products are also vital ingredients (“feedstocks”) in the manufacture of medicines, chemicals and plastics.

1.2 Petroleum and its limitations

It is a yellow to black naturally occurring liquid found in geological formations beneath the earth’s surface. This liquid is further refined into various fuels and chemicals. Broadly it consists of hydrocarbon of varying molecular weight along with other organic compounds. The petroleum fields were created by the remains of small animal and plant life being compressed on the sea bed by billions of tons of silt and sand several million years ago. Thus petroleum is naturally occurring but still considered to be non-renewable resource as it takes millions of years to form.

The consumption of natural resources especially non-renewable has drastically increased in past decades due to human activities. The exponential increase in

population and their requirement of fuel as well as materials to be used in day to day life is building the pressure over petroleum industry to increase the production. It has been estimated that there will be an average of 2 % annual growth in global oil demand over the years ahead along with conservatively a three percent natural decline in production from existing reserves. Therefore dependence of mankind over petroleum and petroleum derived products is a matter of concern in modern world due to limited oil resources [1-5].

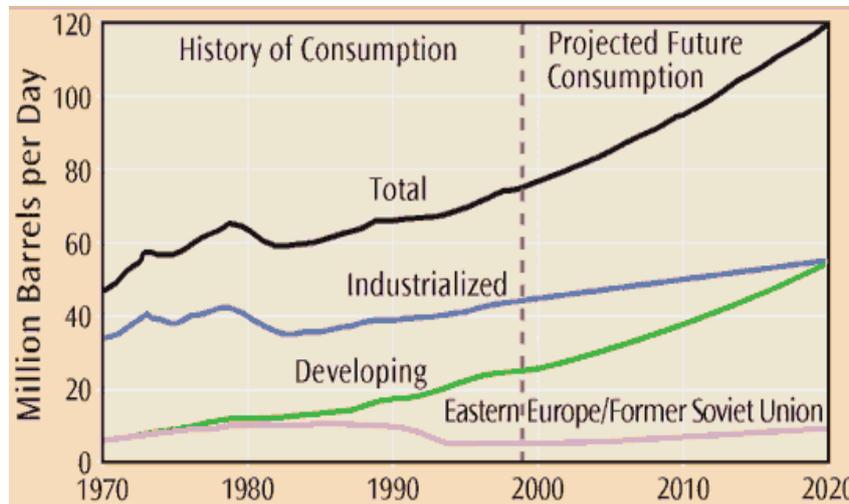


Figure 1.1 Graph showing the world oil consumption by region. (1970-2020)

(source: Association for the study of Peak oil, www.asponews.org)

Further the rate of consumption of petroleum is way higher than the discovery of oil peak due to over consumption [6]. In the last 20 years, only three fields (in Norway, Columbia and Brazil) have been found with more than one billion barrels each. None produces more than 200,000 barrels a day. From 1990 top 200 a total of 42 billion barrels of new reserves were discovered. In the same period the world consumed 250 billion barrels.

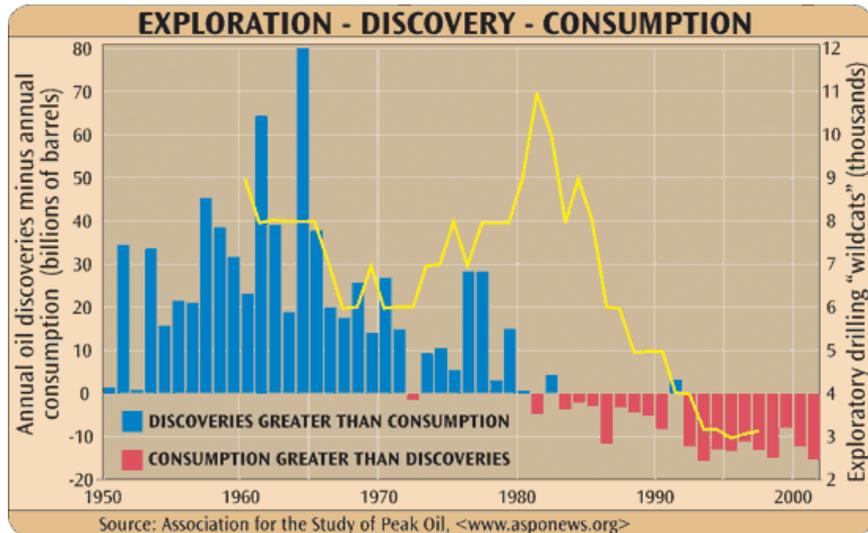


Figure 1.2 Plot showing the exploration, discovery and consumption of petroleum. (1950-2000) (source: Association for the study of Peak oil, www.asponews.org)

Only a small percentage of petroleum oil gets converted to gasoline and rest is being consumed as precursors for various chemicals and synthetic materials such as polymers. Bio-based chemicals and polymers are safe, green and environment friendly alternate which can reduce the load over petroleum industry and are indispensable to low-carbonation society establishments [7].

The decrease in oil peak and the limitation of petroleum production, new materials are been investigated to fuel the automobile. Biodiesel, synthetic petrol and diesel are such examples. Biodiesel refers to a vegetable oil - or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, soybean oil, animal fat (tallow)) with an alcohol producing fatty acid esters [8-14]. These alternate fuels have helped in reducing the pressure but due to their low popularity and high production cost they are not widely acceptable. Therefore in order to reduce the pressure further over petroleum industry it is better to look for new materials to be used as feed stock for the

synthesis of polymers. This will not only help in cutting down the consumption of petroleum but also provide the greener way for the polymer syntheses.

1.3 Plastic and its problem

Plastics comprise a wide range of synthetic or semi synthetic organic polymers derived most frequently from petroleum-related products. They are produced in massive quantities (millions of tonnes annually) and are used in the manufacture of most of the everyday products [15-20]. Since plastics are light, strong, durable and inexpensive, their usage is massive. Most plastics contain organic polymers which are based on carbon atoms chain alone or with carbon along with oxygen, sulfur, or nitrogen as well [21-29].

The limitation of petroleum, petroleum derived products and over use of these non-renewable resources, not only brings the issue of their extinction but also the need to develop the material which can focus on the replacement of non-renewable resource by renewable resource such as bio-derived or bio-based materials. Substances which are directly derived from biomass are called bio-derived while the substances derived from these bio-derived materials are called bio-based. Along with the extinction issue, the excess use of material prepared from them persists in the nature for longer period of time and add more waste in nature [30].

During the fabrication and processing different chemicals called additives are mixed in the pure polymer derived by both chemical and petroleum to enhance their properties such as antioxidants are being mixed to increase the prolong longevity and phthalates are being mixed to increase the plasticity. These additives have a very drastic impact on human health in long run such as hormonal and developmental disorder. Not

only these additives but the plastic itself is considered as global contaminant due to their non-degradability. Moreover chemicals from plastics leach out during washing, heating or burning into food chain and liquids we consume. The CDC found BPA in the urine of 93 % of surveyed Americans over the age of six in 2009 survey.

Often considered degradable or oxy-degradable conventional plastic bags are actually not bio-degradable but photo-degradable which means on exposure to sunlight they break down into smaller pieces, becoming microscopic pieces of plastic which are actually the smaller fragments. These smaller fragments or pieces slowly but eventually end up mixing first into watersheds and lastly into the ocean which account for ocean plastic pollution. This ocean plastic pollution is one of the main reason of contaminated sea food chain and sudden death of sea animals.

1.4 Bio-plastics and their applications

The organic material that stores sunlight in the form of chemical energy together with matter that makes up the Earth's living organisms is referred as Biomass. In recent years the global market of biomass derived products and packaging has increased. The biomass derived products provide an alternate to petroleum derived products and make human less dependent on fossil fuel and its corresponding rising cost. Huge amounts of biomass are mismanaged or destroyed every year such as cleared brush that is not collected and utilized, unharvested or unattended brush in forests, post-harvest chaff, sugar cane stalks (bagasse), wheat straw, bamboo and rice fibers, and much more. Utilization of these natural resources in creating feedstock for bio-based products eliminates the need to dispose off the agricultural waste by burning, burying or letting it rot in fields and wetlands. Thus it is not only socially beneficial but environmentally

beneficial as well. Moreover, utilization of biomass can reduce our need to import foreign oil and look for new sources domestically. There are a variety of options available to replace traditional plastic with bio-plastic, with more products being added all the time. Bio-plastic products are typically made from plant matter such as vegetable starch, cane sugar, cellulose (wood fibers) and lactic acid. Bio-plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch, pea starch or microbiota [31].

Bio-based polymers are derived from monomers derived from the biomass while bio-plastic are the polymer which are environmental friendly. However, bio-plastic is misleading because it suggests that any polymer derived from the biomass is environmentally friendly. Bio-based polymers are similar to a petro-based and one does not imply any superiority with respect to the environment unless the comparison of respective life cycle assessments is favourable [32].

1.5 Various available bio-plastics and their uses

1.5.1 Cellophane: Plastic made from wood

Cellophane is one of the first plastics ever made. It is composed from cellulose which is one of the components of a trees and plants. Cellulose and thus cellophane can be obtained through sustainable growing practices or as by-products of wood harvest. Cellulose based plastics by BioMass Packaging[®] made by Nature Works LLC is a 100 % cellulose bio-plastic with excellent oxygen, grease, oil and moisture barrier characteristics. NatureFlex[™] by Innovia Films (U.K.) is a major source of renewable cellophane film which is generally compost in several weeks in a home compost pile or a commercial compost facility. Sandwich wrap, food wrap, and transparent food bags

are common example of cellophane packaging. There are various modified cellophane films which have a layer of petro-based plastic such as PVC.

1.5.2 PLA (Polylactic Acid) is plastic made from vegetable starch

PLA is prepared by polymerizing lactic acid. It is an alternative for food packaging, which resembles petro-based plastics PET (polyethylene terphthalate) and PS (polystyrene). Corn dextrose is utilized by Nature Works LLC company to produced lactic acid by fermentation. The compound is converted to lactide and the molecules are linked into long chains or polymers becoming polylactic acid (PLA) and sold under the trademark Ingeo™ by U.S. Company Nature. PLA is used for making various daily household things such as clear cold drink cups, coated paper cups, deli, takeout containers and as well as fresh produce packaging.

1.5.3 PSM (Plastarch material)

It is a bio-degradable, thermoplastic resin made up of modified starch combined with several other bio-degradable materials. PSM can withstand high heat conditions with melting temperature 156 °C. It is stable in the atmosphere, but bio-degradable in microorganism exist places such as compost, wet soil, fresh water, seawater, and activated sludge. The application of PSM is wide ranging from food packaging to utensils, personal care items, plastic bags, temporary construction tubing, industrial foam packaging, industrial and agricultural film, window insulation, construction stakes.



Figure 1.3 Application of bio-plastics in different walks of life.

(source: Ford's Bio-Plastic Technology, www.trucktrend.com/features/1109dp-fords-bio-plastic-technology)

1.5.4 Mater-BiTM

Mater-BiTM is produced by Novamont which is an Italian research company. It is an innovative family of bio-plastics that uses substances obtained from plants, such as starch from wheat, potato and non-genetically modified corn starch. It is the first completely bio-degradable and compostable bio-polymer ever invented. The amylose and amylopectin are the constituents of the starch used as raw material. It is used to make BioBag[®] branded certified compostable bags. BioBag[®] is the world's largest brand of certified compostable bags and films made from Mater-BiTM. The materials such as bio-degradable diapers, toys, crockery, bio-plastic bags and packaging, shopping bags, waste bags and food service items such as plates and cutlery.

1.5.5 TPS (Thermoplastic starch)

It is made from amylose molecule derived from starch extracted from corn, wheat, rice, potato and maize. Special properties of amylose allow a wide range of applications. It has been used for packaging of food, cosmetic and pharmaceutical materials. EcoPlastic™ is produced from a range of compounded resins Plantic's resin. BioMass Packaging® uses TPS to manufacture custom products such as water-soluble candy trays.

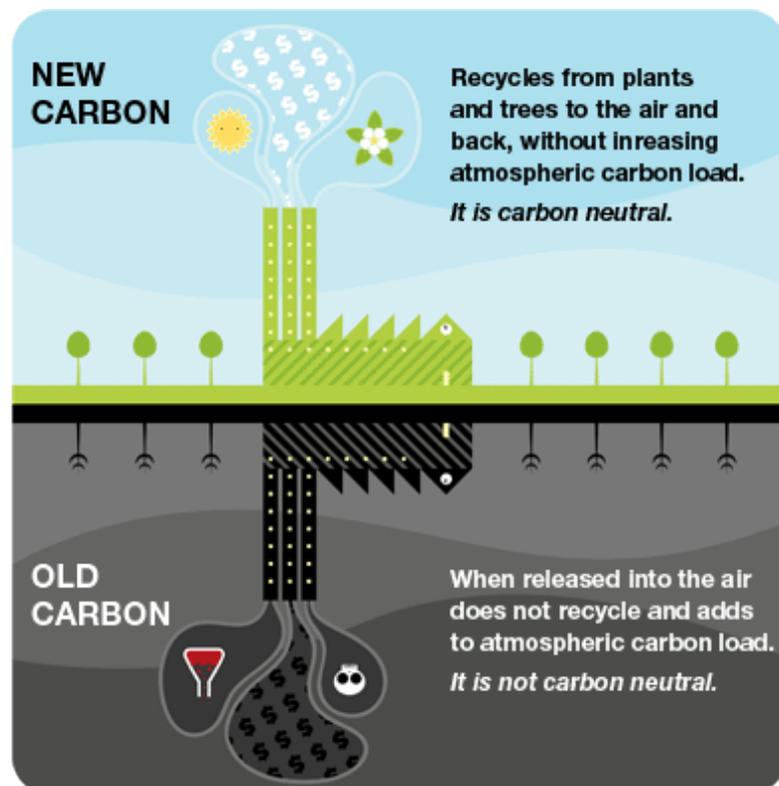


Figure 1.4 Role of bio-based plastic in carbon neutrality.

(source: BioMass Packaging® www.biomasspackaging.com/education/carbon-neutrality)

1.6 Bio-based plastics and carbon cycle

Along with the replacement of petro-based plastics, bio-based plastics open up a wide range of merit as long as environment issues are concerned. Products and packaging made from biomass are considered *carbon neutral*. As plants grow, they absorb carbon from the atmosphere and release the same amount of carbon when burned or composted which balance out the level of carbon in the environment. While when petrochemicals and products derived from them are burned or decomposed, they add up the extra carbon in the environment which is not carbon neutrality.

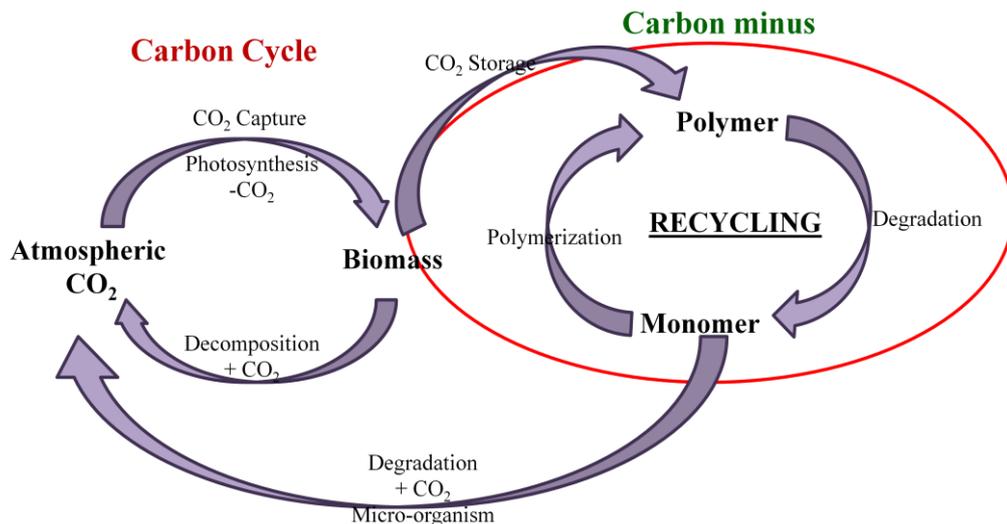


Figure 1.5 Flow chart showing role of bio-based plastic in carbon minus.

Recycled bio-based products can actually help reduce greenhouse gases in our environment in the long term. For example, as sugar cane plants grow, they absorb CO₂ already present in the atmosphere. Utilizing the salvaged waste fibers left over after harvest instead of burning them prevents the release of CO₂ and pollution into the air. Also by recycling the polymer again and again helps in fixing the carbon and thus carbon-minus from the environment which helps in decreasing the amount of

greenhouse gases and thus contribute to the global warming issue which is a concern topic of today's world. Today there are various properly managed municipal composting facility where engineered can be composted safely. In this environment, breakdown occurs in a combination of water, heat and microbial activity, resulting in a mixture of carbon dioxide and water vapor, which is completely mineralized by microorganisms and turned into humus or compost [33].

There are a number of problems associated with these bio-plastic and bio-based plastics [34-36]. Due to their low thermal and mechanical stability, field of application of these plastics are limited which fails to fulfil the demand of modern day requirement of industries. Also their poor stability restricts them to be used under harsh environment. The solution to these problems comes with the term high-performance polymers.

1.7 High-performance polymers

Polymers which can withstand the harsh thermal and/or mechanical conditions as well as overcome the problems associated with traditional polymers are called high-performance polymers but such polymers are usually defined with the organized system and depending on the area of application. As the name suggests, they show a high degree of performance mechanically and/or thermally, not only these but depending upon the type it may show promising performance such as thermal or electrical, conductivity or insulation properties or as flame retardants [37]. Molecular weight and molecular weight distribution, primary-, secondary-, tertiary structure, symmetry and bonding, inter/intra chain interaction or linkage, additives, stabilizers used and type of hybrid material are some factors which can alter the properties and contribute to a great

extent to the high performance of such polymers [38]. Due to their high performance their field of application is vast which includes medical application, automobile industry thus transportation, insulations that is electrical and communication field [39].

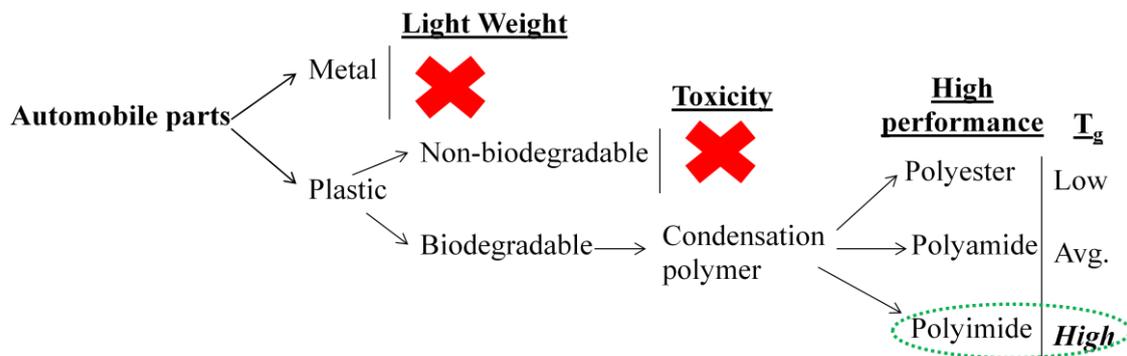


Figure 1.6 Flow chart showing the relation between the type of polymer and requirement of high-performance plastic.

As the above flow chart suggests the requirement of high-performance plastic can majorly be fulfilled by three polymer types (i) polyamides, (ii) polyimides and (iii) polyamide-imides.

1.7.1 Polyamides

A polyamide is a macromolecule with repeating units linked by amide bonds [40]. They can occur both naturally and artificially. Examples of naturally occurring polyamides are proteins, such as wool and silk. Artificially made polyamides can be made through step-growth polymerization or solid-phase synthesis, examples being nylons, aramids and sodium poly(aspartate). Synthetic polyamides are commonly used in textiles, automotives, carpet and sportswear due to their extreme durability and strength. Automobiles are the major consumer, accounting for 35% of polyamide (PA) consumption. The polyamides can be classified by various methods depending upon

type of main chain and monomer used (e.g. aliphatic, semi-aromatic and aromatic), number of monomers used (e.g. homopolymer and copolymer) and depending upon the crystallinity of the polyamide (e.g. amorphous, semi-crystalline and crystalline). The type of monomer used has a greater effect on the properties of the polyamide determining the chain flexibility and structural regularity which determines the formation of crystalline phase and mechanical properties due to the formation of hydrogen bonds which increases the chain interaction resulting in higher yield stress, fracture stress, impact strength, tear strength and abrasion resistance by using them as fiber, film or filler material to be used in excellent heat resistance environment [37, 41-43]. Some well known examples of polyamide are as follows along with the company producing them at commercial level. Aliphatic polyamides are NylonTM from Dupont, TechnylTM from Rhodia, RilsanTM and RilsamidTM from Arkema. Semi-aromatic polyamide includes TrogamidTM from Evonik Industries and AmodelTM from Solvay. KelvarTM and NomexTM from DuPont, TeijinconexTM, TwaronTM and TechnoraTM from Teijin and KermelTM from Kermel belong to aromatic polyamides (also known as aramid) [44].

The thermal property of polyamide depends upon the polyamide back bone, T_g ranging from 50 °C to 250 °C whereas the melting point usually high, ranging from 200 °C to 500 °C depending upon the crystallinity of polyamide. The polymer chain length and the molecular weight depend upon the type of polymerization method. There is restriction of high molecular-weight polymers by melt process due to instability of monomer diamines and diacids. Hence solution phase method is employed which requires special grade of solvents.

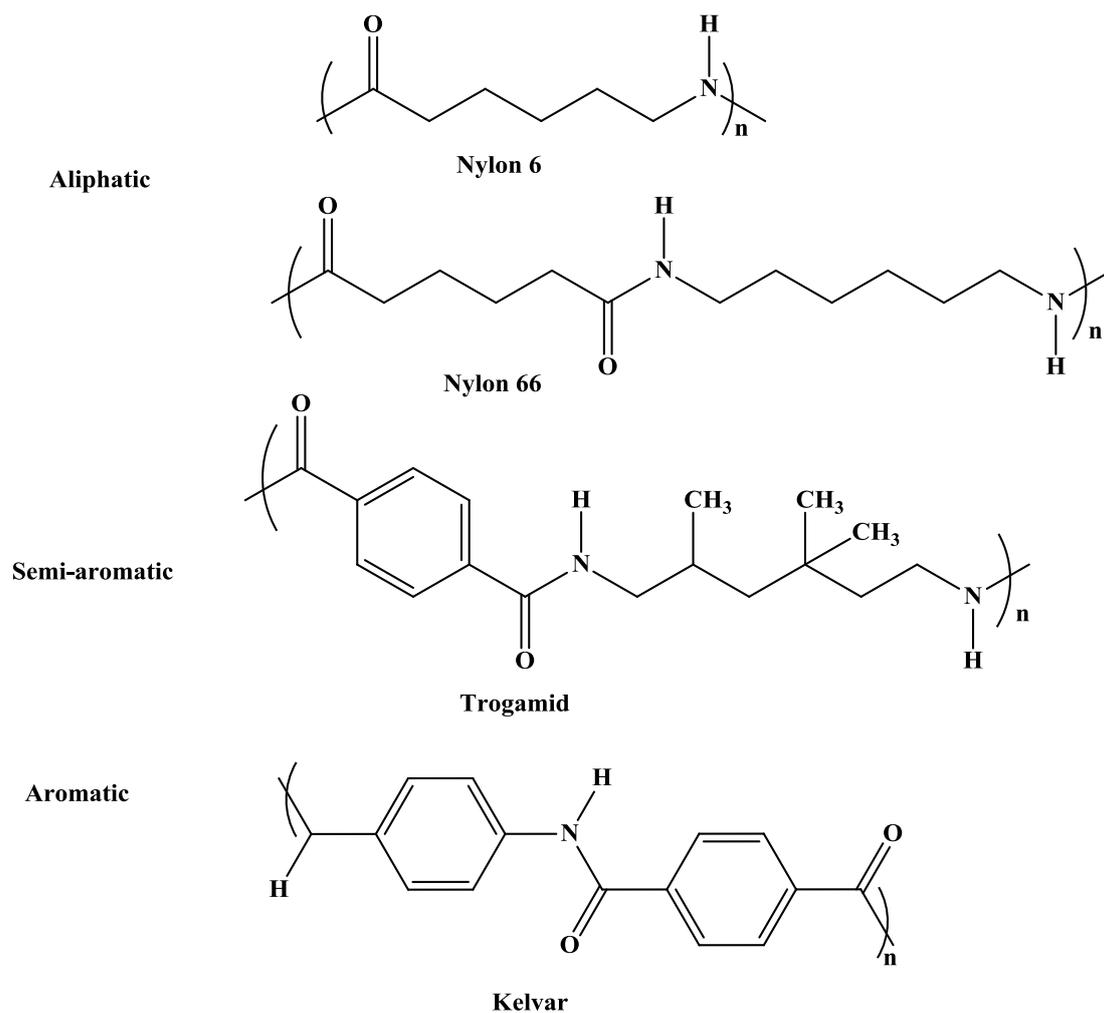


Figure 1.7 Examples of some well-known polyamides.

1.7.2 Polyimides

Polyimides are a class of thermally stable polymers that are often based on stiff aromatic backbones. The aromatic polyimides constitute the major category of such materials. The properties of polyimides can be dramatically altered by minor variations in the structure. The small changes in the structures of the dianhydride and diamine components have a large effect on the thermal as well as mechanical properties of the final polyimide.

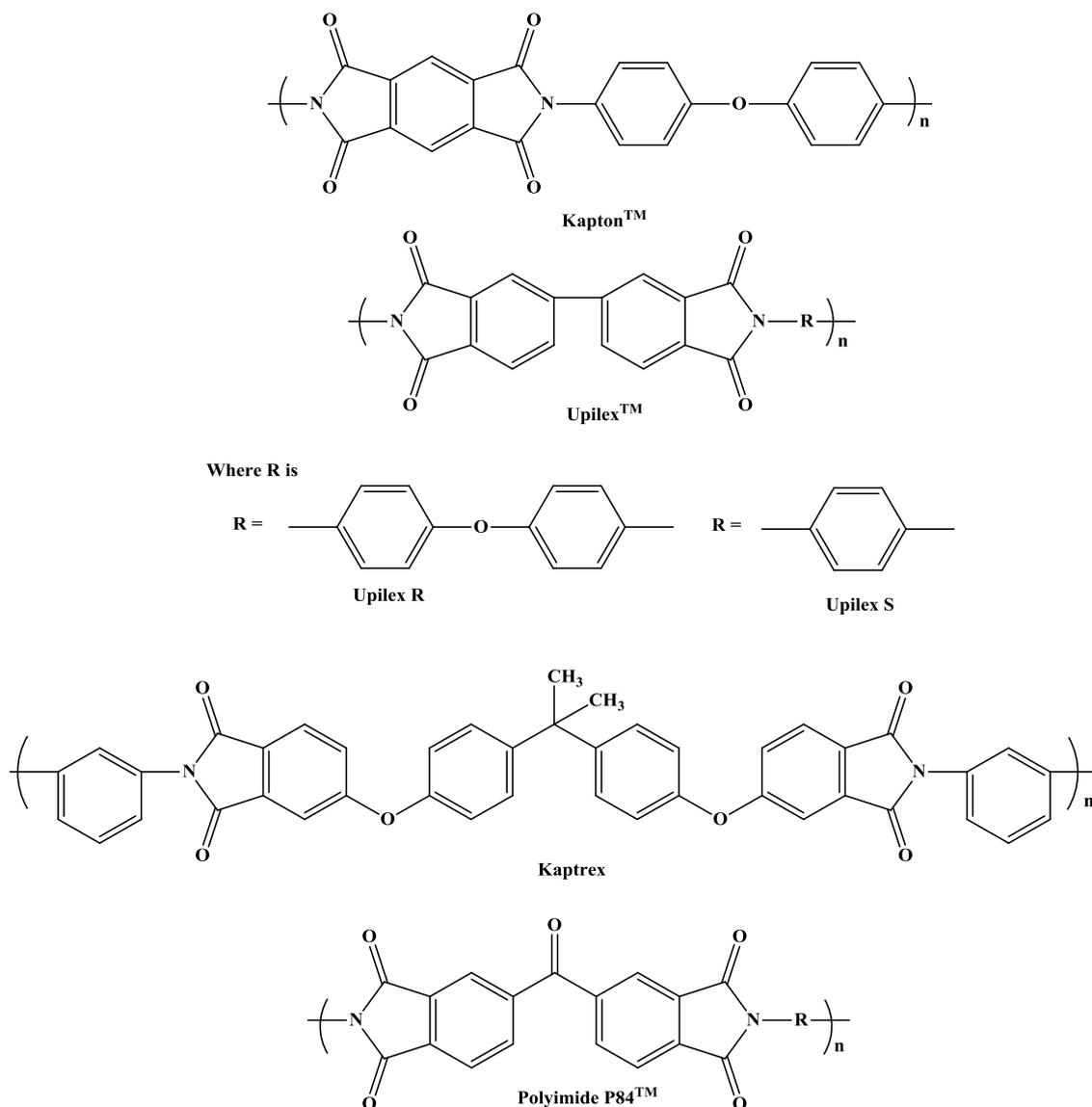


Figure 1.8 Examples of some well-known polyimides.

The conventional and most widely used method in polyimides synthesis is the two-step method [45]. As the name suggest it involves two steps, in the first step equimolar amount of a dianhydride and a diamine are allowed to react at ambient conditions in a dipolar aprotic solvent such as N,N-dimethylacetamide (DMAc) or Nmethylpyrrolidinone (NMP) to yield the corresponding poly(amic acid), which is then imidized into the final polyimide either by *in situ* imidization or stepwise imidization

[46]. In 1950's, this method of using soluble precursor for polyimides synthesis was first developed by workers at Dupont and it is the primary route by which most polyimides are made even today [47]. Due to planar aromatic and hetero-aromatic structures most polyimides are infusible and insoluble and thus usually need to be processed from the solvent route. The method introduced by the workers at Dupont provided the first solvent based route to process these polyimides. Also they introduced the first polyimide of significant commercial importance-‘Kapton™’ to world which was prepared from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). The reaction involved in poly(amic acid) and then polyimide synthesis look simple but in actual it is a complex scheme which interrelate many elementary reactions [48]. The reaction conditions and even the mode of monomer addition have a tremendously affect on course of these reactions [49, 50]. However, choice of monomers, solvents, reaction conditions and the various side reactions involved in the synthesis determines the success of the overall reaction to yield high molecular weight polymers.

1.7.3 Polyamide-imides

Polyamide-imides may be thermosetting or thermoplastic amorphous polymers that have exceptional mechanical, thermal and chemical resistant properties [51]. These properties put polyamide-imides at the top of the price and performance pyramid. Polyamide-imides are produced by Solvay Advanced Polymers under the trademark Torlon™. Wire coating is done using polyamide-imides and it the application where it has been used extensively. There are various methods available for the synthesis of polyamide-imides. The easy method involves the utilization of isocyanates and TMA (trimellitic acid-anhydride) in NMP. Second method makes use of a diamine

and TMA with propylene oxide in NMP. As the name suggests polyamide-imides, these polymers possess the properties from both polyamides and polyimides such as high mechanical strength, melt processing, exceptional high heat capability and broad chemical resistance [52]. This class of polymers can be processed into a wide variety of forms, from injection or compression moulded parts and ingots to coatings, films and fibers. The articles prepared from these materials are generally thermal cured after processing.

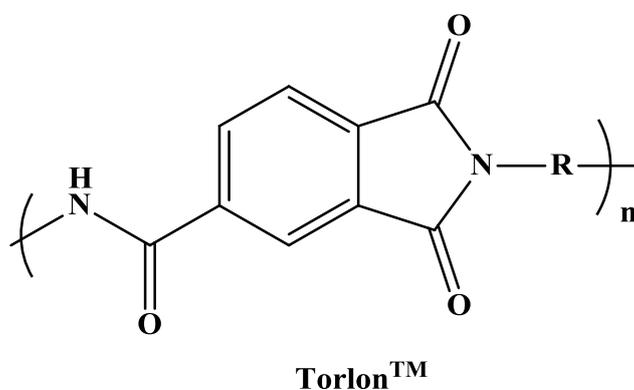


Figure 1.9 Structure of polyamide-imide Torlon™.

The high temperature and chemical resistance of polyamide-imides make them ideal candidates for membrane based gas separations. Thus polyamide-imides based membranes could find extensive application in the separation of contaminants such as CO₂, H₂S and other impurities from natural gas wells. The high pressure at natural gas wells requires material with high mechanical stability. The strong interaction between the contaminant molecules such as polarisable CO₂ and highly polar H₂S and polymer membrane causes swelling and plasticization [53]. The strong intermolecular interactions arising from the polyimide functions as well as the ability of the polymer

chains to form hydrogen bond with one another as a result of the amide bond polyamide-imides can resist plasticization.

However, the monomers of polyamides, polyimides, polyamide-imides and many other polymers are generally derived from petroleum. Further the diamines which are the basic monomer and required for the synthesis of polyamides and polyimides are toxic to biological system therefore can't be synthesized directly by biological system. Hence, the need of alternate methods to utilize bio-based materials for the syntheses of bio-derived aromatic diamines.

1.8 Bio-derived starting materials

Biomass is a biological material derived from living or recently living organisms. The bio-derived materials are directly obtained from biomasses which are required for the sustainable environment by the syntheses of bio-based polymers. There are various bio-derived materials which have been discussed earlier in this chapter. Now the focus is on the introduction of the bio-derived starting materials and monomers synthesized from these bio-derived materials for the syntheses of various polymer types.

1.8.1 4-Aminocinnamic acid (4ACA)

Cinnamic acid derivatives are widely present in living system. It is obtained from oil of cinnamon or from balsams such as storax [54]. It is also found in shea butter and is the best indication of its environmental history and post-extraction conditions. Cinnamic acid has a honey-like odour and its more volatile ethyl esters (ethyl cinnamate) are flavouring components in the essential oil of cinnamon in which related cinnamaldehyde is the major constituent. Cinnamic acid is also a part of the

biosynthetic shikimate and phenylpropanoid pathways. Biosynthetically it is obtained by action of the enzyme phenylalanine ammonia-lyase (PAL) on phenylalanine.

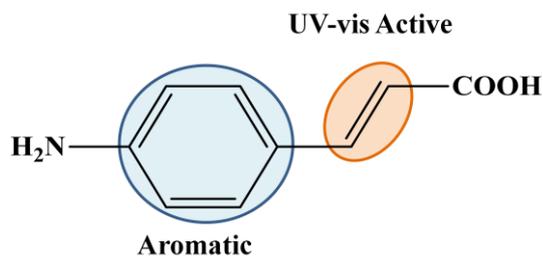


Figure 1.10 The chemical structure of 4ACA along with its property.

Chemically cinnamic acid can be modified to get 4ACA first by nitration followed by reduction of nitro group. However, biosynthetically the 4ACA involves the utilization of recombinant *E.coli.* via deamination by recombinant phenylalanine ammonia lyases (rPAL) of 4-aminophenylalanine which itself in bio-based material [55-57].

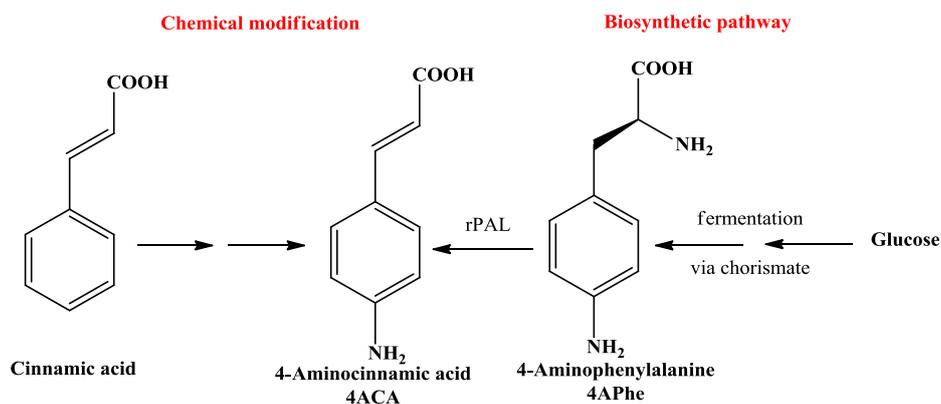


Figure 1.11 Chemical and biosynthetic pathways for the synthesis of 4ACA from cinnamic acid and 4-aminophenylalanine respectively.

1.8.2 4-Aminophenylalanine (4APhe)

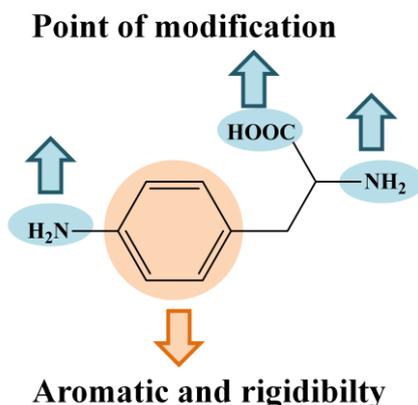


Figure 1.12 The chemical structure 4Ahe.

L-Phenylalanine (Phe) is biologically converted into L-tyrosine, another one of the DNA-encoded amino acids. L-tyrosine in turn is converted into L-DOPA, which is further converted into dopamine, norepinephrine (noradrenaline) and epinephrine (adrenaline). The latter three are known as the catecholamine. Phenylalanine is found naturally in the breast milk of mammals. It is used in the manufacture of food and drink products and sold as a nutritional supplement for its reputed analgesic and antidepressant effects. It is a direct precursor to the neuromodulator phenylethylamine, a commonly used dietary supplement.

4APhe is amino derivative of amino acid phenylalanine. 4APhe can be produced chemically from phenylalanine first by nitration using nitric acid/sulphuric acid followed by reduction using Pd/C. As per the reports 4APhe is bacterial product during as an intermediate of antibiotics and also glucose or biomass has been utilized to produce 4APhe which is a well-established method [57, 58].

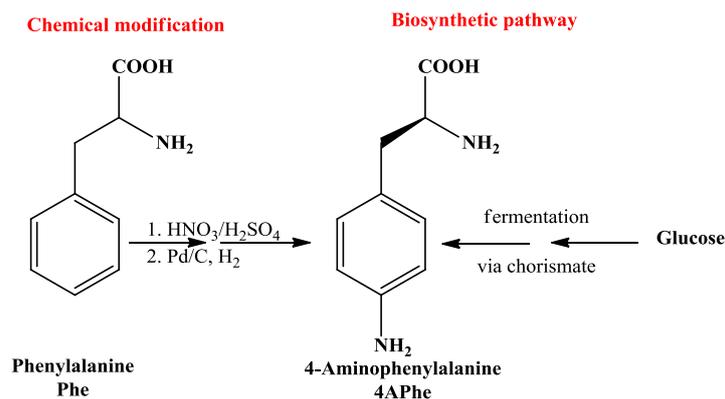


Figure 1.13 Chemical and biosynthetic pathways for the synthesis of 4-aminophenylalanine from phenylalanine and glucose respectively.

1.8.3 1,2,3,4-Cyclobutane tetracarboxylic acid dianhydride (CBDA)

CBDA is a dianhydride compound which can be prepared from maleic acid dimethyl ester by UV irradiation of maleic acid dimethyl ester and then ring closure by acetic anhydride to produce CBDA [59].

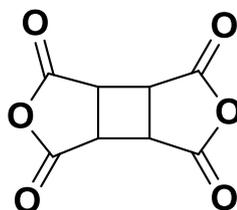


Figure 1.14 The chemical structure of CBDA.

The detailed synthesis of monomer and total bio-based polymer such as polyamide and polyimides is described in the next chapter utilizing the above mentioned monomer.

CHAPTER 2

**SYNTHESES OF BIO-BASED DIAMINES, DIACID
AND TOTAL BIO-BASED POLYAMIDE**

2.1 Introduction

Increasing demand of the polymers due to their application in different walk of life, in industry and almost in every field caused the rise in the production of various polymers. The global production of plastics have risen more than hundred million tons. However, most of the plastic has been produced by petroleum derived products which is itself dealing with a problem of cost and non-renewability. Up to 10% of the total U.S. oil consumption is used for the production of conventional plastics. As oil prices continue to rise, so does the cost of plastic materials, virtually all of which are petro-based. These costs are passed on to both the consumers and businesses. Looking at the near future, our widespread use of petro-based plastic products and our dependence on fossil fuels is economically unsustainable. Petro-based plastics are toxic to the environment and toxic to us. These products may remain for centuries in our surrounding environment and add up to the pollution. The solution of these problems exists in our earth only, which is “biomass”. Biomass is the matter made up of the Earth's living organisms. It also refers to organic material that stores sunlight in the form of chemical energy. In the effort to become less dependent on fossil fuel and its corresponding rising costs, there's a growing global market for products and packaging made from biomass. These products are referred to as bio-based.

Biomass materials such as proteins, fat, carbohydrates, nucleic acids and their metabolites including amino acids, mono-, di-saccharides, fatty acids, cinnamates, lactates, terpenes, alkaloids, etc can be utilized to produce various value added products. Monosacarrides, lactates, cinnamates etc are bio-available compounds which can be and have been used and converted to starting materials to synthesize bio-based monomers.

Some of these bio-based monomers have been utilised to prepare various types of polymers. These bio-derived polymers deal with the drawback in their application due to their poor thermal and mechanical properties which restricts them to be used as super-engineering plastics [60-65].

Polyamides such as KevlarTM and Polyimides such as KaptonTM are well known to be used as super-engineering plastics. However, the monomer diamine of both the polymers, *p*-phenylene diamine for KevlarTM and 4,4'-oxydiphenylamine for KaptonTM are petro-based instead of bio-based. The monomers used so far for the syntheses of bio-plastics are themselves not thermally stable so the materials prepared by them are also lacking these properties therefore, they have low thermal stability. To enhance the thermal and mechanical properties of bio-plastics, the introduction of stable functionality or moiety can play a key role in preparing high-performance plastics. The aromatic rings and piperazine moiety are rigid and stable therefore, introduction of these units in monomer can greatly enhance the thermal and mechanical properties. The aromatic diamine monomers of polyamides, polyamide-imides and polyimides are usually toxic to micro-organism so they have a restriction to be prepared directly by them. The alternate method to prepare such aromatic diamine monomers is by chemical modification of bio-available materials.

4-aminocinnamic acid (4ACA) can be prepared by the nitration of cinnamic acid (CA) followed by reduction of nitro group. It can also be produced using recombinant *Escherichia coli* from 4-aminophenylalanine (4APhe) [66-70]. 4ACA can be produced from biomass material such as cinnamic acid and glucose based material such as 4APhe [71, 72]. Bio-available cinnamic acid from oil of cinnamon or balsams of storax can be

converted to 4ACA by chemical modification. First nitration at para position of cinnamic acid followed by selective reduction of nitro group, cinnamic acid can be chemically converted to 4ACA. Also some bacteria produced 4-aminophenylalanine (4APhe) as an intermediate of antibiotics as well as there are established systems for fermenting glucose biomass to produce 4APhe [72, 73]. 4APhe has been used to prepare 4ACA by microbial deamination using recombinant *Escherichia coli* which were screened and developed to possess the phenylalanine ammonia lyase activity [74]. 4ACA and 4-APhe are the potential candidates to be used for the synthesis of diamines.

In this chapter we are focusing on the syntheses of diamines 4,4'-diaminostilbene (DAS), its reduced counterpart 4,4'-(ethane-1,2-diyl)dianiline (EDDA) from 4-aminocinnamic and novel diamine 3,6-bis(4-aminobenzyl)piperazine-2,5-dione (BAPD) from 4-aminophenylalanine which were used for the synthesis of a series of polymers including polyamides and polyimides.

2.2 Experimental

2.2.1 Materials

4-ACA was purchased from TCI (Tokyo, Japan). Trimethylsilyl chloride ((CH₃)₃SiCl), Grubb's catalyst 2nd generation and *N,N*-dimethylacetamide (DMAc, 99.8 % anhydrous) were purchased from Aldrich Chemical. Ammonia solution and Lithium aluminium hydride (LiAlH₄) were purchased from Kanto chemical Co. Inc. Benzyl chloroformate (CbzCl), Di-*t*-butyl dicarbonate (Boc), *N,N'*-Dicyclohexylcarbodiimide (DCC) and Hydroxybenzotriazole (HOBt) were purchased from Sigma Aldrich.

2.2.2 Characterization

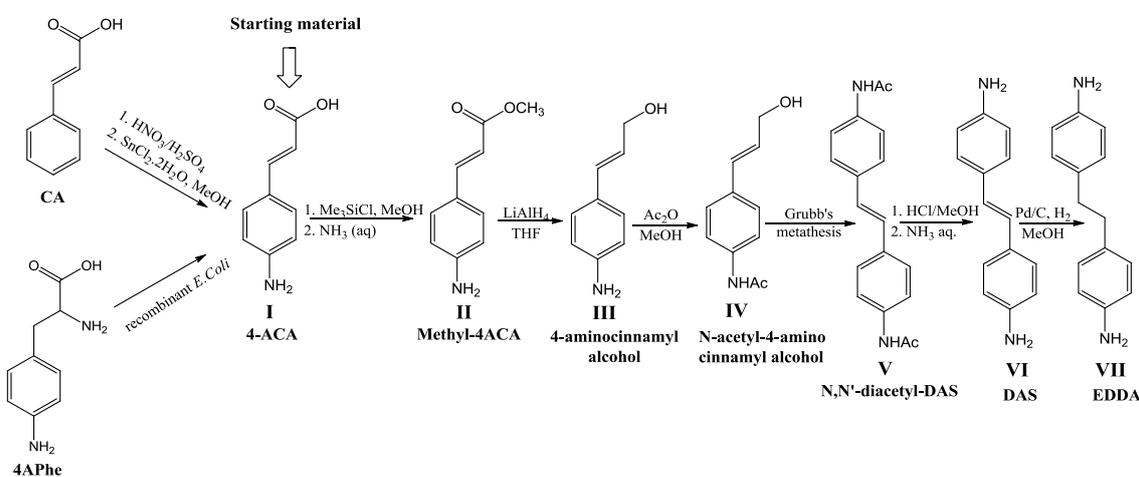
¹H-NMR and ¹³C-NMR were performed on a Bruker Biospin AG 400 MHz, 54 mm spectrometer using DMSO-*d*₆ as the solvent. The FT-IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer between 4000 and 400 cm⁻¹ using a diamond-attenuated total reflection (ATR) accessory. Thermogravimetric analysis (TGA) was performed on Seiko Instruments SII, SSC/5200 at a heating rate of 10 °C/min under a nitrogen atmosphere. The tensile measurements were carried out at an elongation speed of 0.5 mm/min on a tensometer, the Instron 3365 at room temperature. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the molecular weight distribution (PDI) were determined by gel permeation chromatography (GPC, concentration 5 g/L, DMF eluant) after calibration with pullulan standards (GPC; Shodex GPC-101 with a connection column system of 803 and 807, concentration 5 g/L, DMF eluant). The mass spectra were measured using a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS, Solarix) and

scanned from m/z 50 to m/z 1000. The solubility of the polymers was investigated using 1 mg of sample in 1 mL of solvent at room temperature and at 50 °C.

2.2.3 Monomer Syntheses

2.2.3.1 Synthesis of diamine DAS and EDDA

The systematic representation of synthesis of DAS and EDDA from 4ACA is shown in Scheme 2.1.



Scheme 2.1 Synthesis of DAS and EDDA monomers from 4ACA.

The systematic representation of synthesis of DAS and EDDA from 4ACA is shown in Scheme 1.

a) Preparation of methyl-4-aminocinnamic acid ester (methyl-4ACA) from 4ACA.

30 mmol of 4ACA (5.00 g, 30.64 mmol) was mixed methanol (50 ml) in a two neck flask round bottom flask under nitrogen atmosphere to obtain a mixture in suspended state. TMSCl (6.2 g 7.6 mL, 60 mmol) was added drop wise with constant stirring at room temperature. The mixture became clear after complete addition of TMSCl and after some time solid started separating out. This mixture was stirred for 12 h at room temperature. The solvent was evaporated and crude sample was dried under vacuum.

Thus prepared compound was treated with ammonia and the compound was extracted with ethyl acetate. The collecting ethyl acetate organic layer was dried over MgSO_4 and evaporated. Thus compound obtained was found to be methyl-4-ACA in > 99 % yield. The specifications were as follow: ^1H NMR (400 MHz, DMSO-d_6 , δ , ppm): 3.67 (s, 3H), 5.78(s, 2H), 6.23 (d, 1H, $J = 8$ Hz), 6.56 (d, 2H $J = 16$ Hz), 7.37 (d, 2H, $J = 8$ Hz), 7.47 (d, 1H $J = 16$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6 , δ , ppm): 51.5, 111.0, 114.0, 121.7, 130.7, 146.0, 152.0, 167.9. Mass: $m/z = 178.08617$ (experimental), 177.0790 (calculated). Melting point: 129 °C.

b) *Preparation of 4-amino-cinnamyl alcohol from 4-aminomethylcinnamate.* LiAlH_4 (4.5 g, 117.5 mmol) and anhydrous THF (40 ml) was mixed in a two neck round bottom flask under nitrogen atmosphere. A solution of methyl-4-ACA (4.18 g, 23.5 mmol) in anhydrous THF (20 ml) was slowly added into the $\text{LiAlH}_4/\text{THF}$ mixture. After complete addition the reaction mixture was stirred for 90 mins. The reaction was quenched by addition of ethanol and then water followed by the filtration. The compound was extracted by ethylacetate (40 ml) 3 times and the organic layer was dried over MgSO_4 and evaporated. The crude compound was purified by column chromatography using silica and 10 % ethylacetate/ petroleum ether as eluent. The yield of thus obtained compound was found to be 60 % (purity > 95 %) with some residual impurity which was eliminated during purification after next step i.e. acetylation of 4-aminocinnamyl alcohol. The specifications were as follow: ^1H NMR (400 MHz, DMSO-d_6 , δ , ppm): 4.04 (t, 2H), 4.69 (t, OH), 5.15 (s, 2H), 6.01 (dt doublet of triplet, 1H, $J = 16$ Hz), 6.33 (d, 1H, $J = 16$ Hz), 6.50 (d, 2H $J = 8$ Hz), 7.08 (d, 2H, $J = 8$ Hz). ^{13}C NMR (100 MHz, DMSO-d_6 , δ , ppm): 61.9, 113.9, 124.6, 124.8, 127.0, 129.6, 148.1. Mass: $m/z = 150.09133$ (experimental), 149.0841 (calculated). Melting point: 38 °C.

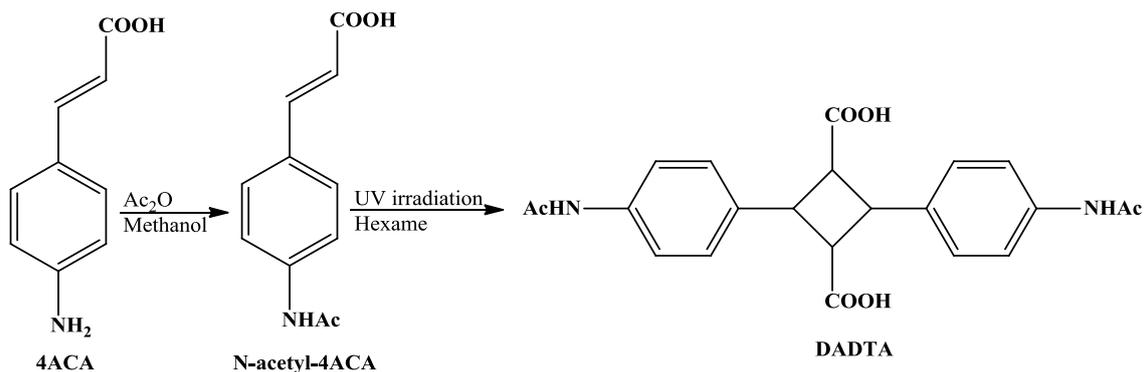
c) *Preparation of N-acetyl-4-aminomethylcinnamyl alcohol from 4-aminocinnamyl alcohol.* 4-aminocinnamyl alcohol (2.01 g, 13.4 mmol) was mixed with methanol (30 ml) in a two neck round bottom flask under nitrogen atmosphere. Acetic anhydride (5.5 g, 5 ml, 53.6 mmol) was added to the reaction mixture. The mixture was stirred overnight, evaporated and purified via column chromatography using silica gel and 10 % ethyl acetate/petroleum ether as eluent. The 100 % purified compound was obtained in 80 % yield. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.03 (s, 3H), 4.09 (t, 2H), 4.82 (t, 1H) 6.26 (td, 1H, *J* = 16 Hz), 6.47 (d, 1H, *J* = 16 Hz), 7.33 (d, 2H, *J* = 8 Hz), 7.53 (d, 2H, *J* = 8 Hz), 9.94 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 23.9, 61.6, 118.9, 126.4, 128.2, 129.1, 131.2, 138.4, 168.1. Mass: *m/z* = 192.10182 (experimental), 191.0946 (calculated). Melting point: 135 °C.

d) *Preparation of N,N'-diacetyl-4,4'-diaminostilbene from N-acetyl-4-aminocinnamyl alcohol using Grubb's catalyst.* N-acetyl-4-aminocinnamyl alcohol (1 g, 5.2 mmol,) and Grubb's second generation catalyst (5 mole percent, 0.27 mmol, 233 mg) was taken in a round bottom flask followed by addition of 30 ml THF under nitrogen atmosphere. The mixture was refluxed at 70 °C for 24 h. The solvent was evaporated and the compound was separate by column chromatography using silica gel and 10 % ethyl acetate/petroleum ether. The compound was obtained in 30 % yield, however, the conversion was 100 %. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.05 (s, 3H), 7.06 (s, 1H), 7.49 (d, 2H, *J* = 8 Hz), 7.57 (d, 2H, *J* = 8 Hz), 9.98 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 24.5, 119.5, 127.0, 127.1, 132.5, 139.1, 168.7. Mass: *m/z* = 295.14403 (experimental), 294.1368 (calculated). Melting point: 218 °C.

e) *Preparation of DAS from N,N'-diacetyl-DAS.* N,N'-diacetyl-DAS (0.25 g, 0.85 mmol) was mixed with methanol (5 ml) in a two neck round bottom flask under nitrogen. HCl conc (1.5 ml) was added and the mixture was stirred for 6 h. The solvent was evaporated under vacuum followed by the addition of ammonia solution and then extracted using ethyl acetate 3 times (10 ml). The collected ethyl acetate organic layer was dried over MgSO₄, and it was then evaporated. The compound was obtained in 82 % yield. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 5.15 (s, 4H), 6.56 (d, 2H, *J* = 8 Hz), 6.74 (s, 2H), 7.20 (d, 4H, *J* = 8 Hz). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 114.0, 123.8, 125.8, 126.8, 147.7. Mass: *m/z* = 211.12286 (experimental), 210.1157 (calculated). Melting point: 207 °C.

f) *Preparation of EDDA from DAS.* DAS (0.1 g, 0.48 mmol) and 10 % Pd/C (0.22 g) was mixed with methanol (5 ml) in a two neck round bottom flask and H₂ gas was bubbled into the mixture while stirring. After 5 h the color of reaction mixture turned pink from orange. The reaction mixture was filtered and solvent was evaporated to get shiny pink crude product which was recrystallized using ethanol to get pink colored crystalline 90 % yield. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.61 (s, 4H), 4.79 (s, 2H), 6.49 (d, 2H, *J* = 8 Hz), 6.85 (d, 2H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 37.1, 113.9, 128.7, 129.0, 146.3. Mass: *m/z* = 213.14217 (experimental), 212.1313 (calculated). Melting point: 137 °C.

2.2.3.2 *Synthesis of “N,N'-diacetyl-4,4'-diamino-α-truxillic acid”(DADTA):*



Scheme 2.2 Synthesis of DADTA from 4ACA.

4-aminocinnamic acid (5 g, 30 mmol) was mixed in 60 ml methanol in a round bottom flask. Acetic anhydride (10.7 g, 9.9 ml, 105 mmol) was added into the mixture dropwise with continuous stirring under nitrogen atmosphere. After the complete addition of acetic anhydride the mixture was stirred overnight (12 h). The precipitate thus formed was filtered, washed with methanol and dried under vacuum. The crude sample was collected in 97 % yield. The specifications were as follow: ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 2.07 (s, 3H), 6.41 (d, 1H), 7.52 (d, 1H), 7.63 (m, 4H), 10.12 (s, 1H), 12.26 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 24.06, 117.19, 118.84, 128.79, 128.96, 141.11, 143.58, 167.72, 168.53.

Thus prepared N-acetyl-4-aminocinnamic acid (2g) was mixed with hexane (50 ml) in a round bottom flask. The flask was placed under UV lamp (mercury lamp, power 2.5 mW/cm^2) and stirred. The reaction was monitored by using NMR at different time intervals to check the completion of reaction. After 24 h, the reaction mixture was filtered and dried under vacuum and 2,4-bis(4-acetamidophenyl)cyclobutane-1,3-dicarboxylic acid was collected as cream colour powder (99% yield). The specifications were as follow: ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 2.07 (s, 6H), 3.75 (dd, 2H, $J = 8, 12 \text{ Hz}$), 4.22 (dd, 2H, $J = 8 \text{ Hz}, 12 \text{ Hz}$), 7.28 (d, 4H, $J = 8.4 \text{ Hz}$), 7.52 (d, 4H, $J = 8.4$

Hz), 9.91 (s, 2H), 12.06 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): δ 23.92, 40.49, 46.32, 118.78, 127.89, 133.92, 137.88, 168.13, 172.91.

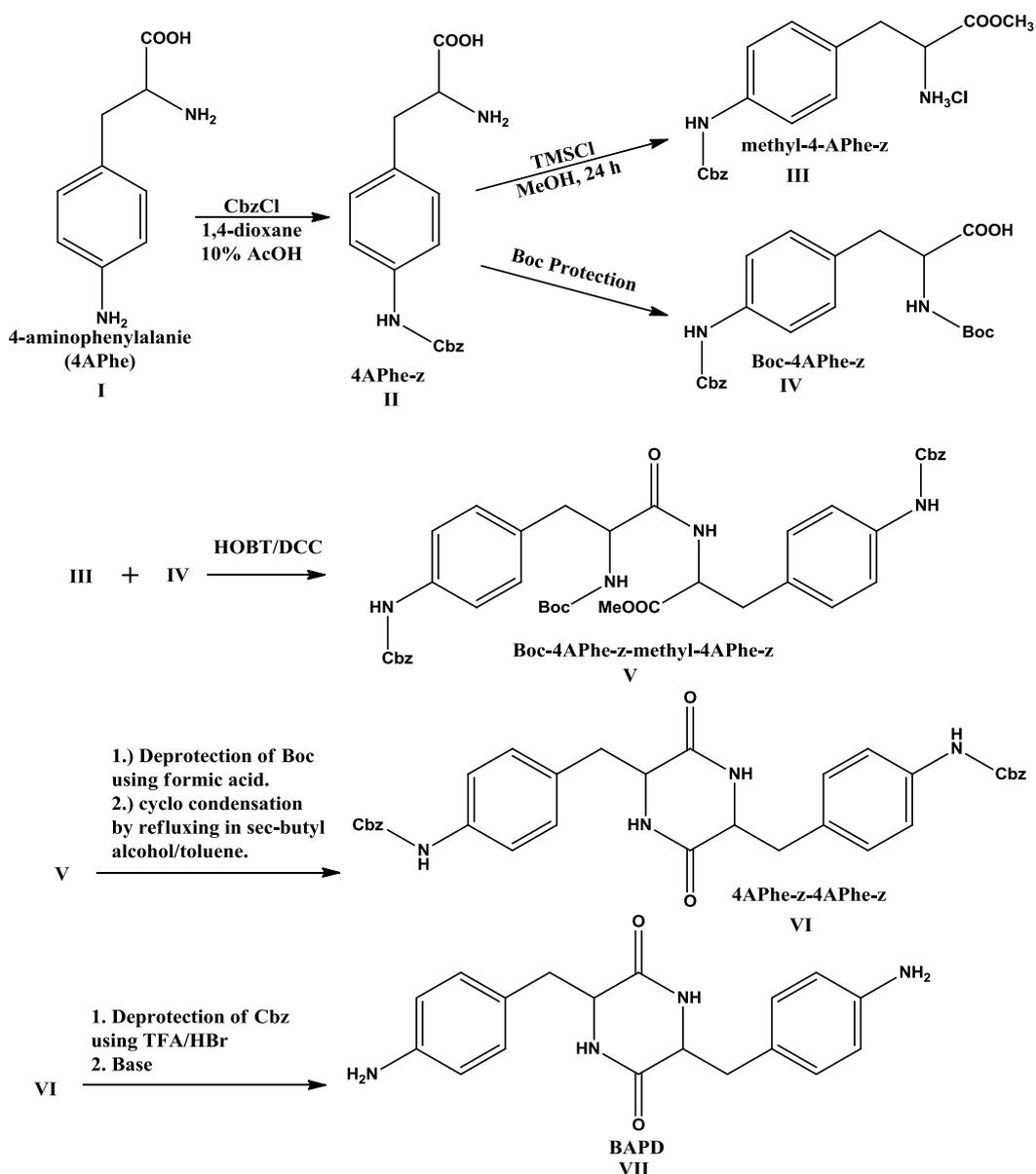
2.2.3.3 Synthesis of 3,6-bis(4-aminobenzyl) piperazine-2,5-dione (BAPD):

The systematic representation of synthesis of BAPD from 4APhe is shown in Scheme 2.3.

a) Synthesis of compound II (4APhe-z) from 4APhe (Protection of aromatic NH₂ of 4APhe): To a solution of 4APhe (2 g) in 10 % AcOH (68 ml), added 5 M NaOH solution drop by drop to raise the pH to 3. Now added a solution of CbzCl (1.2 ml) in 1,4-dioxane (68 ml), slowly and stirred overnight. The pH was adjusted to pH = 7 by adding 5 M NaOH solution and/or by adding distilled water. Filtered and washed with water and then dried. The product 4APhe-z was obtained as white shiny powder in 72 % yield. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.76 (dd, 1H, J = 8.8 Hz, 14 Hz), 3.08 (dd, 1H, J = 3.4 Hz, 14 Hz), 3.60 (t, 1H, J = 3.4), 5.15 (s, 2H), 7.18 (d, 2H, J = 8.4 Hz), 7.40 (m, 7H), 9.72 (s, 1H).). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 36.38, 55.68, 65.65, 118.24, 127.99, 128.07, 128.41, 129.63 131.65, 137.45, 153.39, 169.20, 190.79.

b) Synthesis of compound III (Methylation of 4-APhe-z using TMSCl): 5 g of 4-APhe-z was taken in a flask followed by the addition of 90 ml dry MeOH. TMSCl (8 ml) was added and stirred for 24 h at room temperature. The solvent was removed and the solid was recrystallized from dry MeOH and diethylether to get 4-APhe-z methyl ester hydrochloride salt in 90 % yield. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.06 (dd, 1H, J = 7.2 Hz, 14 Hz), 3.15 (dd, 1H, J = 5.2 Hz, 14 Hz), 3.65 (s, 3H), 4.17 (t, 1H J= 5.2 Hz), 5.14 (s, 2H), 7.14 (d, 2H, J = 8.8 Hz), 7.40 (m,

7H), 8.77 (s, 3H), 9.82 (s, 1H).). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 35.11, 52.49, 53.27, 65.65, 118.30, 128.00, 128.41, 129.76, 129.87.65, 136.61, 138.22, 153.33, 169.29, 170.20.



Scheme 2.3 Synthesis of 3,6-bis(4-aminobenzyl) piperazine-2,5-dione from 4APhe.

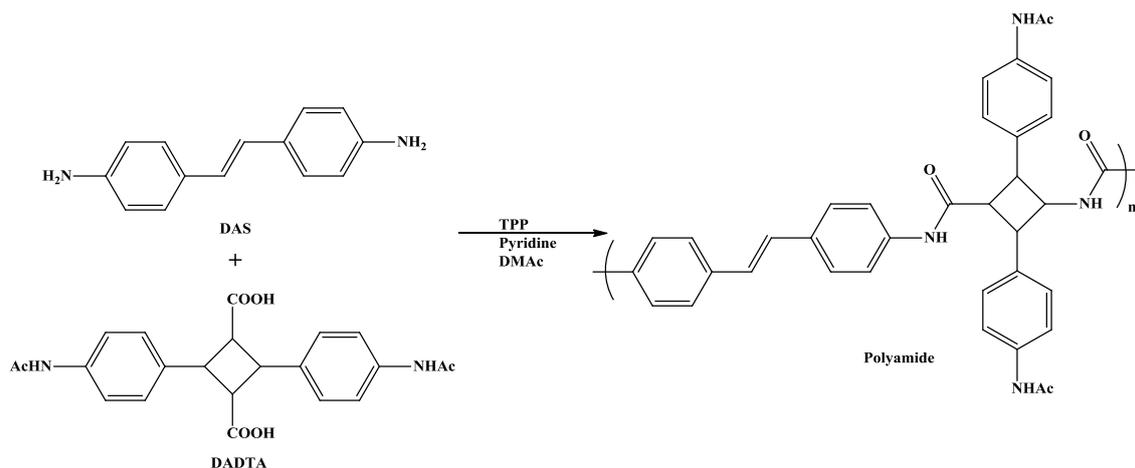
c) *Synthesis of compound VI via synthesis of compound V (Synthesis of cyclic dipeptide via synthesis of linear dipeptide):* To a cooled (0 °C) solution of boc-4APA-z (7.5 g, 18 mmol, 1 eq.) in dry DCM (105 ml), 1-hydroxybenzotriazole (2.67 g, 19.8 mmol, 1.1 eq.) was added followed by the addition of dicyclohexylcarbodiimide (4.45 g, 21.6 mmol, 1.2 eq.). The reaction mixture was stirred for an hour and allowed it to warm to room temperature then solution of compound IV 4-APhe-z methyl ester hydrochloride salt [(4-(benzyloxycarbonyl)amino)phenylalanine methyl ester hydrochloride salt] (7.22 g, 19.8 mmol, 1.1 eq.) in DMF (20 mL) was added followed by the addition of triethyl amine (3 mL, 21.6 mmol, 1.2 eq.). The reaction was stirred further for 24 h. The precipitated dicyclohexylurea was filtered off and washed with little DCM. The filtrate was evaporated under high vacuum. The crude compound was acidified under ice cold condition with 1N HCl to pH 2~3 and extracted with DCM. The organic layer was washed with saturated NaHCO₃ which was emulsified and compound was separated by evaporation under *vacuum* leaving behind the crude compound V (13.01 g, 98 %).

A 500 ml flask was charged with formic acid (720 ml, 98 %) and compound V (12 g) followed by stirring for 5 h at room temperature. After 3 h, excess formic acid was removed in *vacuum* (temperature less than 30 °C was maintained). To this added 480 mL 2-butanol and 240 mL toluene and refluxed at 110 °C for 5 h followed by filtration and drying. Yield = 71 % (7.08 g). The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.14 (dd, 2H, J = 6.4 Hz, 13.6 Hz), 3.54 (dd, 2H, J = 4.4 Hz, 13.6 Hz), 4.17 (t, 2H, J = 4.4), 5.12 (s, 4H), 6.94 (d, 4H, J = 8.4 Hz), 7.35 (m, 14H), 7.89 (s, 2H), 9.75 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 38.99, 55.49, 65.60, 117.99, 127.96, 128.03, 128.39, 130.08, 130.39, 136.60, 137.65, 153.31, 166.13.

d) *Synthesis of compound VII BAPD*: 6 g of compound VI was taken in 200 ml flask followed by the addition of 60 ml 33 % HBr/AcOH solution. The mixture was stirred at room temperature for 3 h 30 mins. Diethylether was added and decanted several times. The procedure was repeated many times to remove excess acetic acid and HBr. The crude sample was dried under vacuum over night. (Yield 4.9 g, >99 %). After drying the compound was dissolved in 200 ml water followed by addition of NH₃ (aq) drop by drop till the pH become 12 while stirring. The mixture was heated and kept for cooling. Yield (1.93 g) 60 %. The specifications were as follow: ¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 2.08 (dd, 2H, J = 6.8 Hz, 13.6 Hz), 3.48 (dd, 2H, J = 4 Hz, 13.6 Hz), 3.80 (t, 2H, J = 4), 4.89 (s, 4H), 6.47 (d, 4H, J = 8 Hz), 6.70 (d, 4H, J = 8H), 7.63 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 55.84, 113.77, 123.19, 130.24, 147.15, 166.35.

2.2.4 Polyamide Synthesis

General procedure for the synthesis of aromatic polyamide using DAS and DADTA is as follow. DAS (1 mmol, 0.21 g) was dissolved in 5ml of DMAc in a round bottom flask under nitrogen atmosphere followed by the addition of DADTA (1 mmol, 0.41 g) and dissolved. To this added 488μL of pyridine and 660 μL TPP, stirred for 1 h at 50 °C, 3 h at 70 °C and 24 h at 110 °C. The reaction mixture was diluted using 3ml DMAc and precipitated using hot methanol. Filtered and washed by hot ethanol and water. The obtained solid i.e. polyamide fibril was dried under reduced pressure and characterised.



Scheme 2.4 Synthesis of polyamide based upon DAS and DADTA.

2.3 Results and discussion

2.3.1 Monomer Syntheses

2.3.1.1 Synthesis of diamines DAS and EDDA

Olefin metathesis enables the redistribution of fragments of alkenes by scission and regeneration of carbon-carbon double bond [75]. It has become an efficient tool for synthetic organic chemistry due to simplicity and fewer undesired by-products. In contrast to other olefin metathesis catalysts, Grubbs' catalysts tolerate other functional groups in the alkene, are air-tolerant and are compatible with a wide range of solvents [76-80]. We then developed the novel synthesis route for the synthesis of aromatic diamine using Grubbs olefin metathesis reaction with 4ACA derivative.

Diamine monomers DAS and EDDA were prepared by a series of reaction starting from 4-aminocinnamic acid. Firstly 4ACA was converted to methyl-4-aminomethylcinnamate by TMSCl [81, 82]. As reports suggest, esters can be more readily converted to alcohol then their corresponding carboxylic acid using LiAlH_4 [83-

85]. The product was purified in order to eliminate all the impurities, however, upto 95 % pure 4-aminocinnamyl alcohol was prepared by repeated column chromatography due to inseparable impurity present in it which was eliminated by column chromatography after acetylation of amine group. The inseparable impurity could not be identified as it was present in very small percentage, however, the proton peaks arising from impurity could be seen in ^1H NMR.

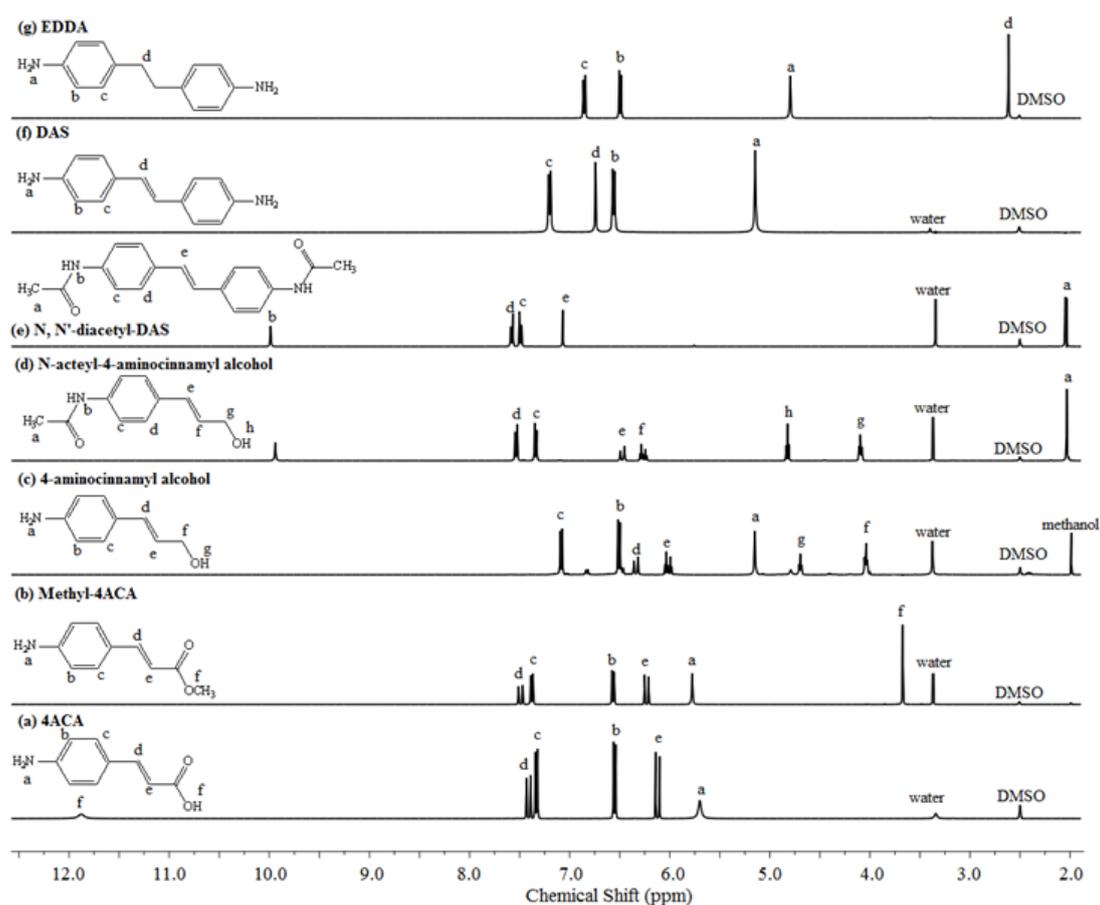


Figure 2.1 ^1H -NMR of various intermediates in the synthesis of DAS. (a) 4ACA, (b) methyl-4ATA, (c) 4-aminocinnamyl alcohol, (d) N-acetyl-4-aminocinnamyl, (e) N,N'-diacetyl-DAS, (f) DAS (g) EDDA.

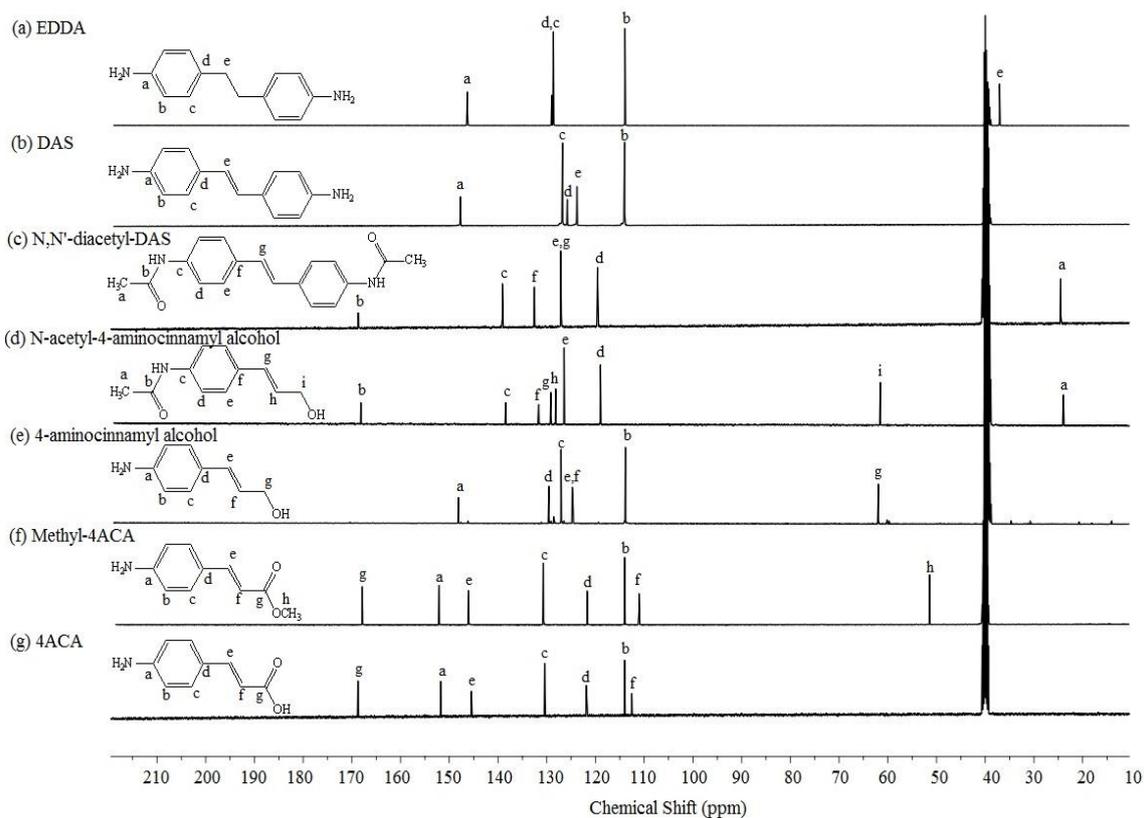


Figure 2.2 ^{13}C NMR spectra of various intermediates in the synthesis of DAS (a) 4ACA, (b) methyl-4ATA, (c) 4-aminocinnamyl alcohol, (d) N-acetyl-4-aminocinnamyl, (e) N,N'-diacetyl-DAS, (f) DAS (g) EDDA.

Also the free amine group of methyl-4-aminocinnamyl alcohol was acetylated using acetic anhydride to avoid the interference of free amine group in Grubbs olefin metathesis [86, 87]. The protection of amino group was done by simple method of acetylation. Thus prepared N-acetyl-4-aminocinnamyl alcohol was used a precursor for Grubbs olefin metathesis in order to synthesize DAS. The free diamine monomer DAS was prepared by deacetylation using HCl in methanol followed by neutralization by ammonia. The diamine EDDA was prepared from DAS by reducing the double bond using Pd/C and H_2 . The detailed synthesis has been discussed earlier in this chapter with respective yield at each step. The prepared intermediates in the synthesis of DAS were

purified after each step and characterized by ^1H -NMR (Figure 2.1) and ^{13}C -NMR (Figure 2.2).

In Figure 2.1, the change in proton shift can be seen due to the conversion of one intermediate to other starting from 4ACA to the final product 4,4'-diaminostilbene. The same result is observed in ^{13}C -NMR (Figure 2.2). The complex peaks and the number of peaks for N-acetyl-4-aminocinnamyl alcohol become simplified and less peak after it gets converted to DAS.

2.3.1.2 Synthesis of “N,N'-diacetyl-4,4'-diamino- α -truxillic acid” (DADTA):

N,N'-diacetyl-4,4'-diamino- α -truxillic acid (DADTA) was synthesized by a perfect [2+2] photocycloaddition of N-acetyl-4-aminocinnamic. The cyclobutane ring, the double bond moieties are reversible depending upon the wavelength of UV light used. The cyclobutane ring of α -truxillic acid, a dimer, was occurred with ultraviolet light source above 260 nm which was stable at elevated temperature [88]. However, photolabile under deep ultraviolet light, below 260 nm, cyclobutane was cleaved to the initial of double bond moiety.

DADTA was prepared in good yield > 99 % yield simply by first converting the 4ACA to N-acetyl-4-aminocinnamic acid and then irradiation it at >260 nm UV-vis under UV lamp after suspending it in hexane. The photodimerized structure was confirmed by ^1H NMR (Figure 2.3) and ^{13}C NMR (Figure 2.4).

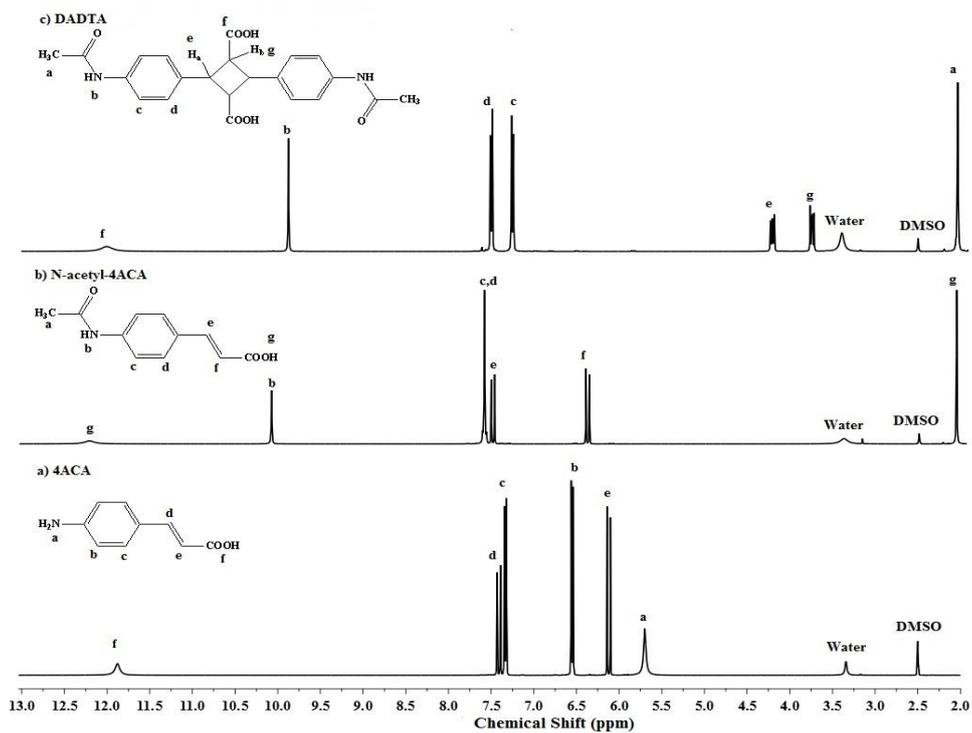


Figure 2.3 $^1\text{H-NMR}$ of a) 4ACA, b) N-acetyl-4ACA and c) DADTA.

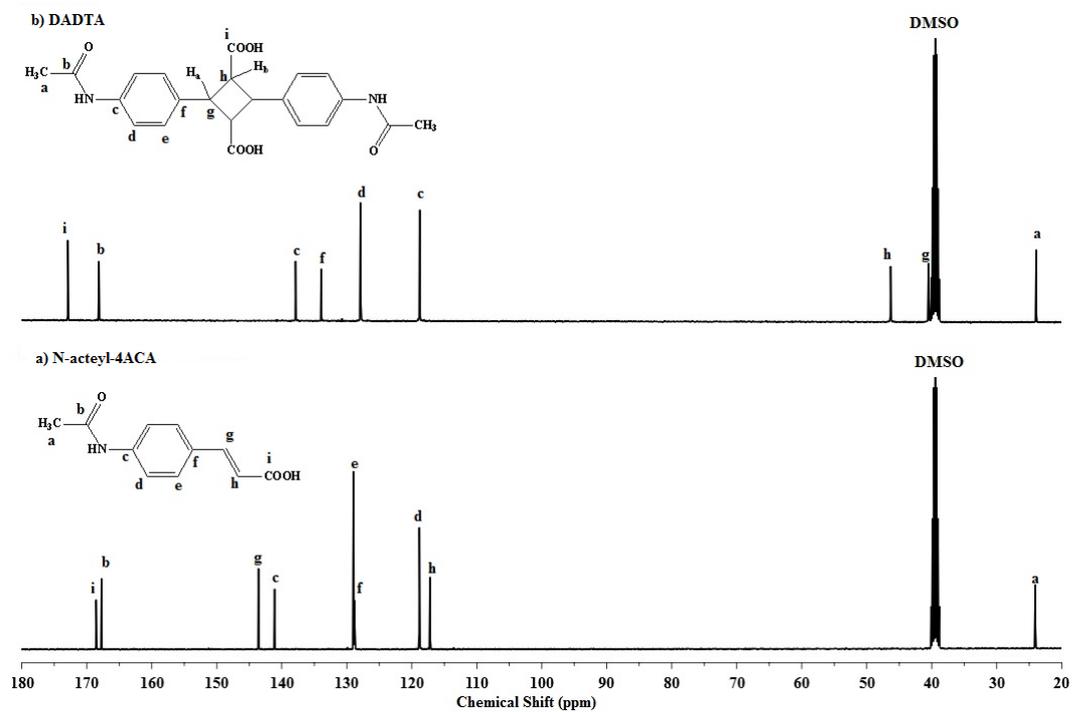


Figure 2.4 $^{13}\text{C-NMR}$ of a) N-acetyl-4ACA and b) DADTA.

2.3.1.3 Synthesis of 3,6-bis(4-aminobenzyl) piperazine-2,5-dione:

Piperazine moiety is well known because of its stability and activity. Various potent drugs contain this active moiety some of which act as NMDA glycine inhibitors, amoxicillin sodium, inhibitors of LFA-1 and etc [89, 90]. There are many reports regarding the synthesis of different piperazine derivative by various methods [91-96]. The detailed synthesis, properties and application has been reported earlier [97-101].

Due to the activity of piperazine moiety, the interest towards the piperazine derivative is increasing. We synthesized a diamine from 4-APhe which not only contains the diamine but also the phenyl ring in its chain along with piperazine moiety which makes them perfectly suitable to be used in the synthesis of polymers.

The diamine monomer BAPD was prepared starting with 4-APhe by protecting first the aromatic amine group by benzyl chloroformate (-Cbz or z) then the protection of aliphatic amine by di-tertbutyl dicarbonate (-boc) and lastly the protection of carboxylic acid by forming methyl ester using TMSCl separately and following the synthesis route first forming the linear dipeptide and then cyclocondensation described by K. B. Joshi, S. Verma [102-107].

BAPD was prepared in good yield and characterized by various available techniques such as ^1H NMR and ^{13}C NMR. The purity of all the intermediate was analyzed and confirmed by the NMR. All the intermediate were prepared in high yield and were pure enough to proceed for the next step. The ^1H NMR and ^{13}C NMR spectra of intermediate synthesized along with final diamine BAPD are shown in Figure 2.5 and 2.6 respectively.

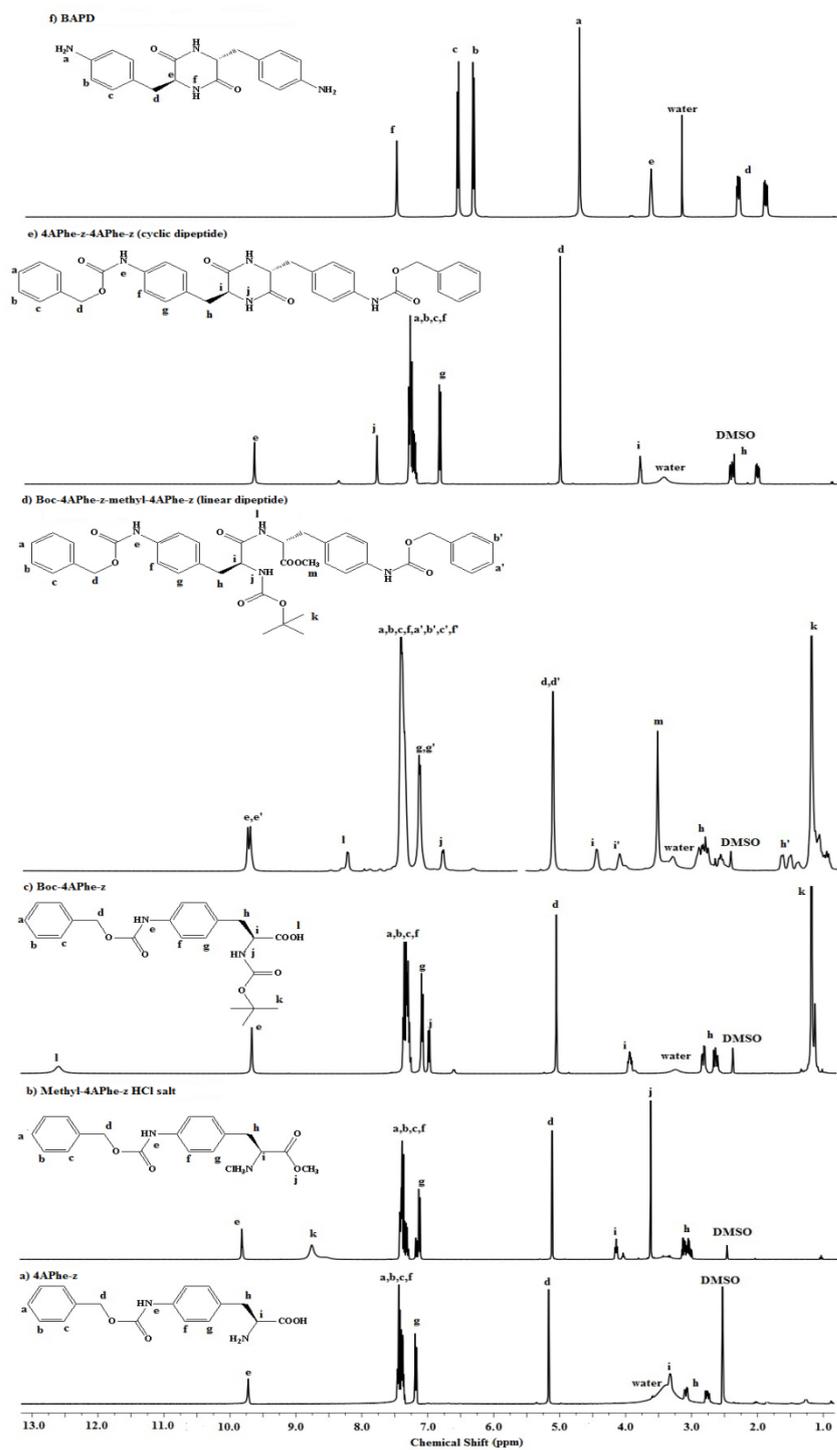


Figure 2.5 $^1\text{H-NMR}$ of all the intermediates in the synthesis of BAPD. a) 4APhe-z, b) Methyl-4APhe-z, c) Boc-4APhe-z, d) Boc-4APhe-z-methyl-4APhe-z (linear dipeptide), e) 4APhe-z-4APhe-z (cyclic dipeptide) and f) BAPD.

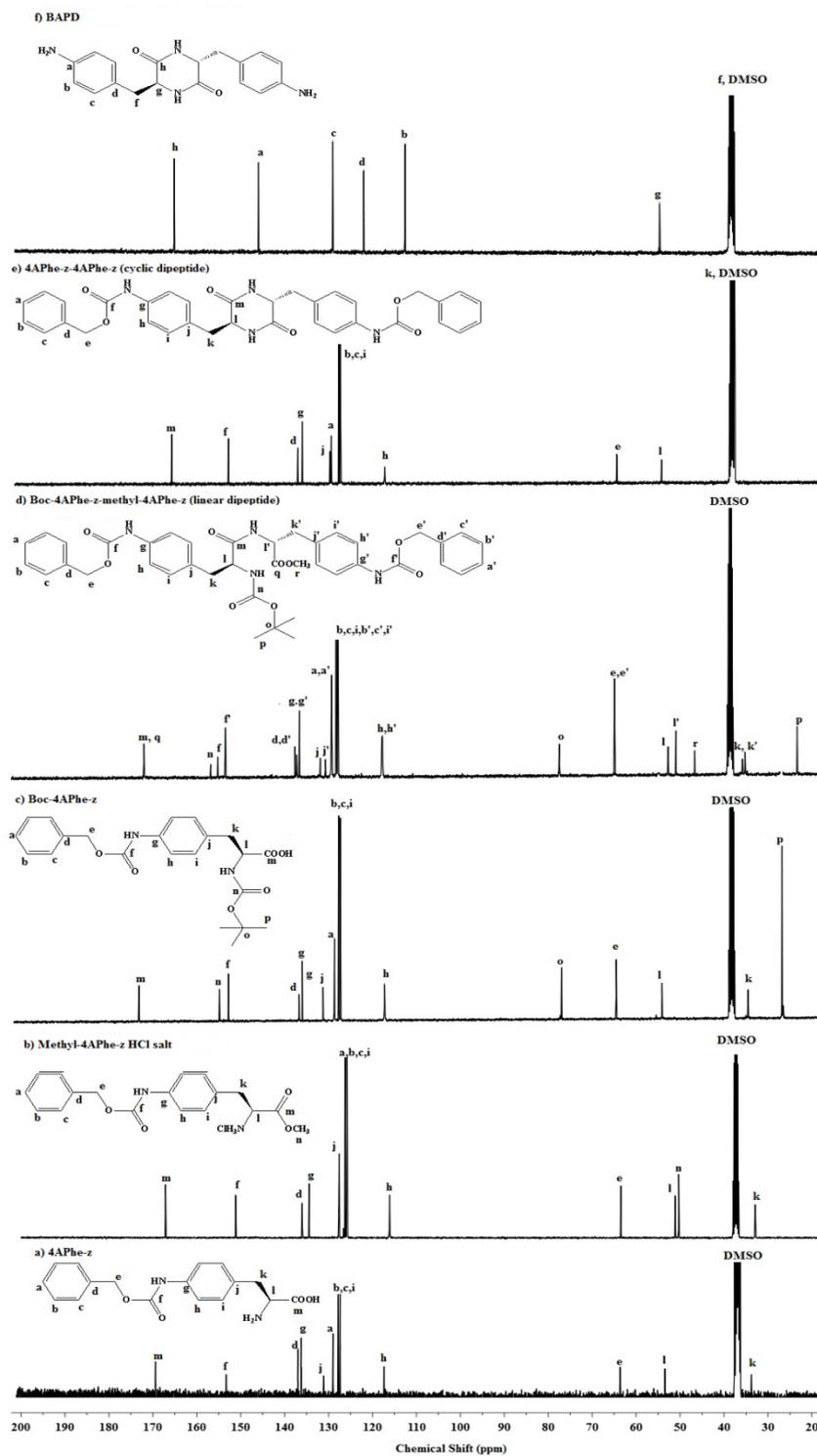


Figure 2.6 ^{13}C -NMR of all the intermediates in the synthesis of BAPD. a) 4APhe-z, b) Methyl-4APhe-z, c) Boc-4APhe-z, d) Boc-4APhe-z-methyl-4APhe-z (linear dipeptide), e) 4APhe-z-4APhe-z (cyclic dipeptide) and f) BAPD.

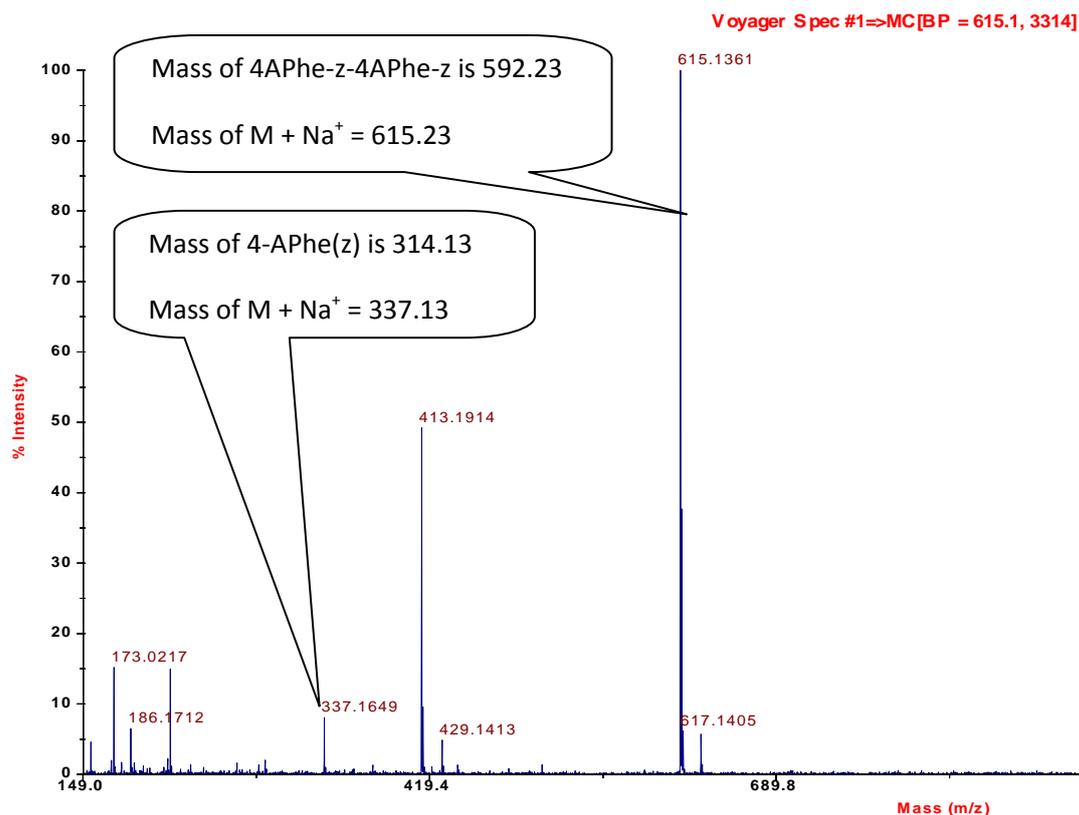


Figure 2.7 Mass spectra of 4APhe-z-4APhe-z (cyclic dipeptide).

The molecular weight of synthesized diamine BAPD (at 4APhe-z-4APhe-z stage) was confirmed by MALDI-TOF and the spectrum is shown in Figure 2.7. The mass peak at 615.23 corresponds to the M-Na⁺ which confirmed the formation of 4APhe-z-4APhe-z, however, due to presence of sodium it gets ionised as M-Na⁺. The mass peaks at lower value were due to fragmentation and the peak at 337.13 was due to the symmetrical cleavage which gave rise to the monomer 4APhe-z. The TGA showed that the synthesised BAPD was thermally stable showing 5 % and 10 % degradation temperature 362 and 372 °C respectively (Figure 2.8).

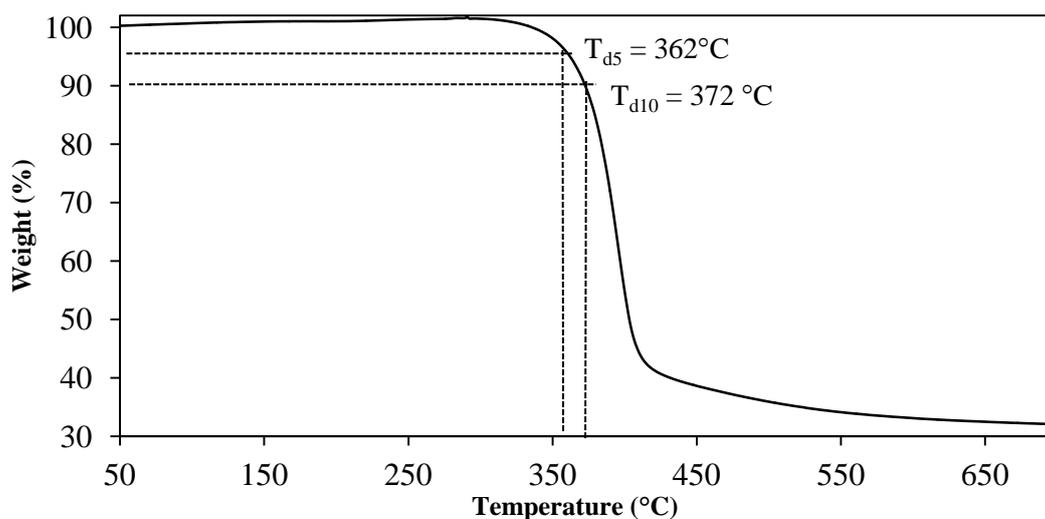


Figure 2.8 TGA of BAPD showing T_{d5} and T_{d10} .

2.3.2 Polyamide Synthesis and characterization

The synthesis route of polyamide DAS-DADTA has been discussed earlier in (Scheme 2.4). The DAS-DADTA polymer was interesting because polyamide was synthesized from the bio-derived monomers which were synthesized from bio-available compounds. Polyamide was prepared by polycondensation using $(\text{PhO})_3\text{P}$ (TPP) and pyridine as a coupling agent in DMAc at 110°C under nitrogen atmosphere for 24 hours. The resulting product showed a yellow solution which did not exhibit any obvious change in viscosity.

Polyamide fibrils were prepared by precipitation of polyamide solution in hot methanol, washing by water/ethanol and dried under vacuum overnight. They appeared as off white fibrils (Figure 2.9a) and then dissolved polymer fibrils with concentration of 0.2 g/mL in DMAc. Polymer solution was casted on glass plate and heated over hot plate at $60\text{-}70^{\circ}\text{C}$. The obtained polyamide showed yellow color transparency and flexible film (Figure 2.9b).

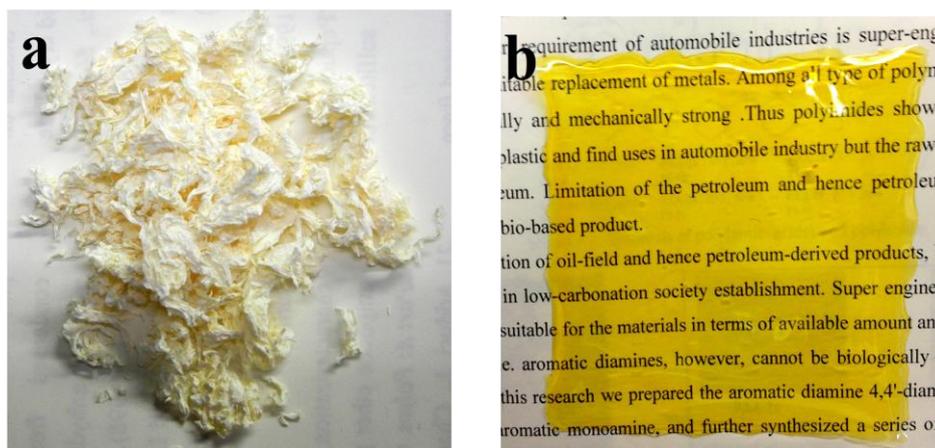


Figure 2.9 Polyamide from DAS-DADTA (a) as precipitated (fibrils) (b) film after solvent casting.

2.3.2.1 Molecular weight of DAS-DADTA polyamide

The number average molecular weight (M_n), weight average molecular weight (M_w) and PDI of synthesized polyamide were determined by the help of GPC (gel permeation chromatography). The number average molecular weight (M_n) was found to be 8.76×10^4 , weight average molecular weight (M_w) was found to be 12.43×10^4 and PDI = 1.42. The obtained polyamide showed low molecular weight.

2.3.2.2 FT-IR of DAS-DADTA polyamide

The FTIR spectra of polyamide (Figure 2.10) exhibited the characteristic absorption peak of polyamide at 1690 cm^{-1} ($\text{C}=\text{O}$ symmetric stretching of amide), 1665 cm^{-1} corresponds to N-H bending of amide. Moreover, it showed the amide region peak at 3352 cm^{-1} which corresponds to N-H stretching of amide, the alkyl absorption peak of the diacid at 2901 cm^{-1} for C-H stretching of acetyl, the benzene ring absorption of DAS moiety and DADTA moiety at 1510 cm^{-1} for C=C stretching of aromatic ring and 1438 cm^{-1} for C-H overtone aromatic ring.

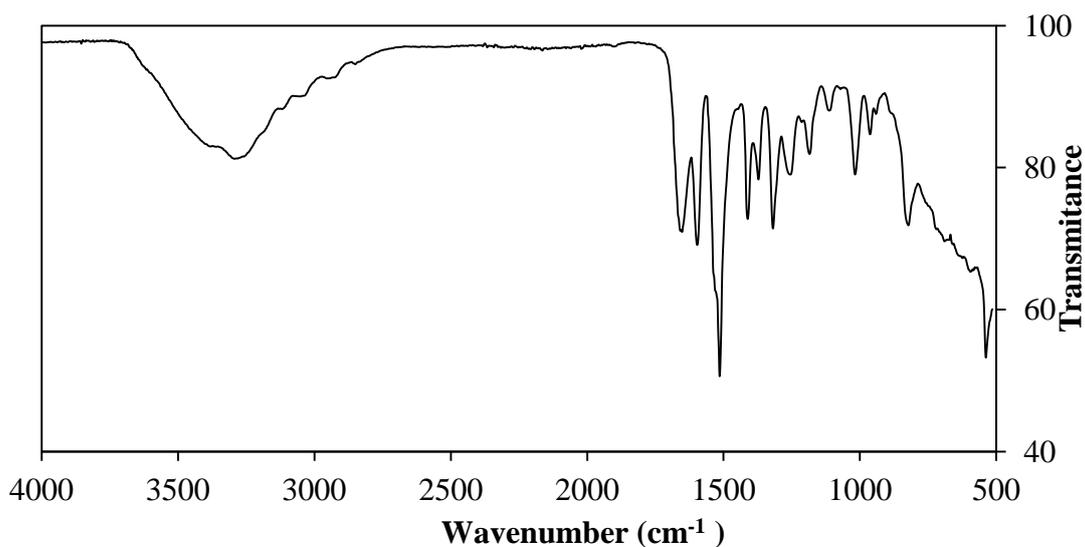


Figure 2.10 FT-IR spectrum of DAS-DADTA polyamide.

2.4.2.3 Thermal property (TGA) of DAS-DADTA polyamide

The TGA of the DAS-DADTA polyamide polymer was analyzed. The thermal property of polyamide has to be good to be used as high-performance polymer. Figure 2.12 shows a thermogravimetry curve, the 10 % weight loss temperature was observed at 367 °C i.e. $T_{d10} = 367\text{ °C}$.

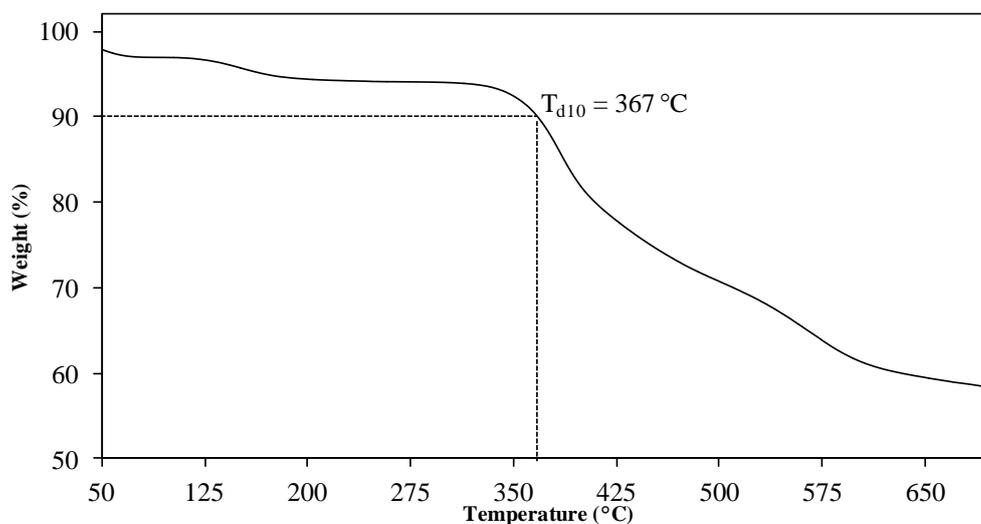


Figure 2.11 TGA spectrum of DAS-DADTA polyamide showing T_{d10} .

2.3.3.3 Mechanical properties of DAS-DADTA polyamide

The tensometer, Instron 3365-L5, Canon was used to determine the mechanical properties of the prepared polymer. Mechanical properties of polyamide were measured at room temperature. The tensile strength of the polyamide has been found to be 56 MPa with young modulus 2.2 GPa and % elongation 2.4.

2.3.3.4 DAS-DADTA polyamide's solubility in various solvents

The DAS-DADTA polyamide was found to be soluble in organic solvents such as DMF, DMAc, DMSO and NMP. Therefore these solvents can be used further to cast the polymer into film or desired shape.

Table 2.1: Solubility of DAS-DADTA polyamide.

Solvent	DAS-DADTA solubility	Solvent	DAS-DADTA solubility
Water	-	Acetone	-
Methanol	-	Dichloromethane	-
Ethanol	-	Dimethylformamide	++
Hexane	-	Dimethylacetamide	++
Chloroform	-	Dimethylsulfoxide	++
Ethylacetate	-	N-methylpyrrolidine	++
Diethylether	-	Conc. Sulphuric acid	+

+: Soluble at room temperature, ++: Highly soluble at room temperature,
-: Insoluble at their boiling point

2.4 Conclusion

The chapter detailed with the synthesis of bio-based monomers of polyamide and polyimide such as diamines and diacid. New route for the synthesis of monomer diamines (DAS and EDDA) and DADTA from bio-derived 4ACA was established and characterized using ^1H NMR and ^{13}C NMR. Also a novel diamine i.e. BAPD was

prepared and the synthesis route was established and each step was optimized. The characterization of this novel diamine was done by NMR, ^{13}C NMR and FT-ICR MS. The prepared diamine DAS and diacid DADTA were employed to react in presence of TTP in DMAc to form total bio-based polyamide which was characterized by FT-IR, GPC and TGA. From TGA, it was observed that the polyamide showed high T_{d10} at 367 °C. Although DAS-DADTA polyamide showed high thermal stability but found to be poor in mechanical strength. This problem of poor mechanical strength was overcome by synthesizing the polyimide utilizing diamines DAS and EDDA with commercially available dianhydrides and trimellitic anhydride chloride.

CHAPTER 3

SYNTHESES AND CHARACTERIZATION OF BIO-BASED POLYIMIDES USING DIAMINES DERIVED FROM BIO-BASED 4ACA.

3.1 Introduction

The ability of polyimides (PIs) to sustain the harsh chemical, thermal, mechanical conditions and their structural stability makes them the best candidates to be used as high-performance plastic. Due to their broad spectrum of application in the various fields such as automobiles industry, transportation, electronics, aerospace etc, their consumption is increasing tremendously [108-110]. Higher thermal and mechanical stability is attributed to their stable structure which is due to the presence of resonance stabilization, molecular symmetry, high molecular weight, high molecular distribution, rigid intra-chain structure and their hybrid (fillers, clays, miscellaneous nanoparticles) [111]. Further the rigidity in their structure provides them the low coefficient of thermal expansion which makes them appropriate for the application where there is the possibility of structure deformability at higher temperature [112-115].

As discussed in the earlier chapters, the monomer aromatic diamines which is one of the basic unit are generally petro-chemically derived which is dealing with the problem of non-renewability, high cost and limited amount. Moreover the diamine are toxic to plants therefore cannot be produced directly by them. Synthesis of bio-based diamines and using them for the synthesis of bio-based polyimides are the solution to these problems as it helps in reducing the consumption of petrochemicals as well as reducing the greenhouse gases from the environment by fixing the biomass in the form of polymers.

In this chapter, the utilization of aromatic diamines DAS and EDDA for the synthesis of bio-based high-performance polyimides will be discussed with their synthesis and characterization. The detailed synthesis of aromatic diamines has been

discussed earlier hence the synthesis's result can be used further in order to prepare the synthesized aromatic diamines. In order to prepare the series of polyimides from diamines DAS and EDDA, different available dianhydrides such as 1,2,3,4-cyclobutane tetracarboxylic dianhydride (CBDA), pyromellitic anhydride (PMDA), 3,4:3',4'-biphenyl tetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (OPDA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DPSDA) were polycondensed to prepare poly(amic acid)s (PAAs) and then thermally imidized to get respective polyimides. The different dianhydrides were used because there is a drastic impact of monomer's structure on polymer's properties and to understand the structure-property relationship [116, 117]. The current chapter will focus on the thermal and mechanical properties of polyimide.

3.2 Experimental

3.2.1 Materials

4ACA and pyromellitic dianhydride (PMDA) were purchased from TCI. 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (OPDA), 1,2,3,4-tetracarboxycyclobutane dianhydride (CBDA) and trimethylsilyl chloride (TMSCl) were purchased from Aldrich. N,N-dimethylacetamide (DMAc) (99.8% anhydrous) was purchased from Kanto chemical and was used as received. All the dianhydrides were purified before using by refluxing with acetic anhydride for 6 h, cooling to 0-5 °C. The crystals were carefully collected by filtration, washed in hot dioxane and dried in *vacuum*. All other

chemicals were used as such unless mentioned. All other reagents such as methanol, ethanol, acetone and hexane were obtained from various commercial sources and used as a solvent for reactions.

3.2.2 Polymer syntheses

3.2.2.1 Synthesis of PAA

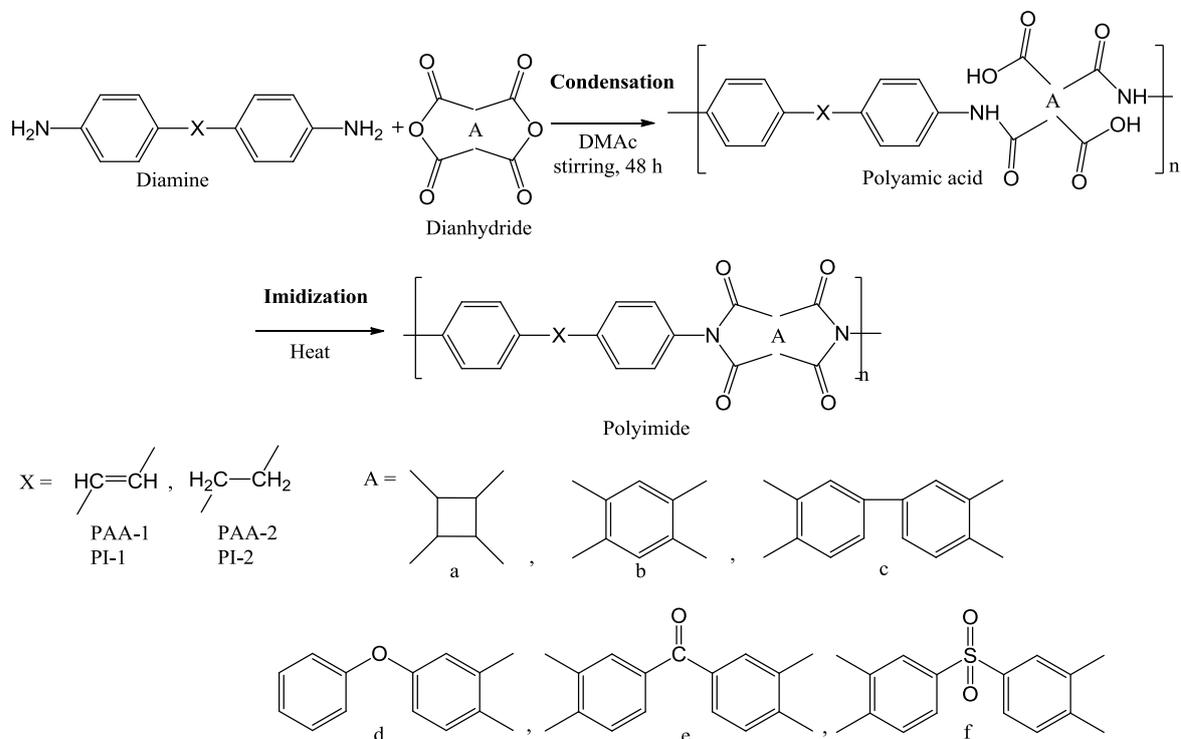
The synthesis of poly(amic acid) (PAA) is an example of addition polymerization where equimolar amounts of dianhydrides and diamine are used with some suitable solvent as shown in Scheme 3.1. The general procedure for the synthesis of PAA is as follows. DAS (0.252 g, 1.2 mmol) was dissolved in DMAc (2.4 ml, 0.5 M) in a 10 mL flask under nitrogen atmosphere.



Figure 3.1 Synthesis of PAA.

Dianhydrides such as CBDA (0.235 g, 1.2 mmol), PMDA (0.261 g, 1.2 mmol), BPDA (0.353 g, 1.2 mmol), BTDA (0.387 g, 1.2 mmol), OPDA (0.372 g, 1.2 mmol) and DSDA (0.430 g, 1.2 mmol) were then added into the diamine solution which produced an orange to yellow solution. The reaction mixture was vigorously stirred by an overhead stirrer at room temperature for 48 h to yield a viscous PAA solution. The PAA solution was diluted by suitable amount of DMAc and then added dropwise into water/methanol/acetone to precipitate as solid fibrils PAA which were collected by filtration, washed thoroughly with warm water and dried in a vacuum. PAA film of thickness 30-45 μm was obtained by dissolving polymer fibrils in DMAc/DMF forming a yellow solution, poured on a silicon wafer / aluminium plate by spin coating (spin rate

= 100 rpm for 2 min, 200 rpm for 2 min, 500 rpm for 1 min, MS-A100 Spincoater, Misaka Co., Ltd.) and dried by heating over hot plate. Similar procedure was repeated to get PAAs using EDDA diamine and different dianhydride.



Scheme 3.1 Synthesis of bio-based PAA and PI from 4ACA derived monomers DAS and EDDA.

3.2.2.2 Synthesis of PIs

PI films were obtained by thermal imidization of the PAA in an oven for 1 h each at 100, 150, 200 and 250 °C, respectively, under vacuum. Figure 3.1 shows the prepared poly(amic acid) and polyimide film. Similar procedure was repeated to get PIs using EDDA diamine and different dianhydride.

3.2.3 Characterization

The Characterization of poly(amic acid)s and polyimides were done using various mentioned techniques depending upon the required information. Some characterization such as $^1\text{H-NMR}$ was carried out using PAAs as PIs are insoluble in many of the solvents. FT-IR spectra were taken for PAAs and PIs to evaluate the change in structure and confirmation of imidization. Molecular mass determination was performed also by using PAAs fibrils by dissolving PAAs in DMF at concentration 2.5mg/mL. Thermal analyses (TGA & DSC) were done using 5mg of sample. Mechanical properties were determined by first making PAA films by spin coatings which were thermally imidized to get PI films. Detailed analyses techniques and methods of determination of each property were explained in the respective sections along with the details of instrument used.

3.2.3.1 Structural analyses ($^1\text{H-NMR}$ and FT-IR)

Physical appearance of PAAs fibril, PAA films and PI films were observed by eye such as colour of fibrils and films or by touching them. $^1\text{H-NMR}$ measurements were performed on a Bruker Biospin AG 400 MHz, 54 mm spectrometer using $\text{DMSO-}d_6$ as the solvent. The FT-IR spectra of PAAs and PIs were recorded with a Perkin-Elmer Spectrum One spectrometer between 4000 and 400 cm^{-1} using a diamond-attenuated total reflection (ATR) accessory.

3.2.3.2 Molecular weight and viscosity measurement

The number average molecular weight (M_n), the weight average molecular weight (M_w) and polydispersity index (PDI) of polymers were determined by gel

permeation chromatography (GPC, conc. 2.5 mg/mL, DMF as an eluent) after calibration with the pullulans as standard at 40 °C. Inherent viscosities of polymers were measured using Ubbelohde viscometer at 30 °C in DMAc at a polymer concentration of 0.5 dL/g.

3.2.3.3 Thermal analyses: Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The thermal properties of various PIs were analyzed by using Seiko Instruments Inc., SSC/5200 SII for TGA. The thermal degradation behaviour of PIs (T_{d5} and T_{d10}) was investigated by heating from 50 °C to 700 °C at a rate of 10 °C/min under a nitrogen atmosphere. Whenever DSC was performed, Seiko Instruments Inc., EXSTAR X-DSC7000 SII was used. DSC measurement was performed using both the heating and cooling rates at 10 °C/min under nitrogen atmosphere and the temperature ranged from 50 °C to 350 °C. Three cycles of heating and cooling per sample was done while DSC analyses.

3.2.3.4 Mechanical properties analyses: (Tensile strength, Young modulus and % elongation)

The mechanical properties (tensile strength, young modulus and % elongation) were determined using a tensometer, Instron 3365-L5, Canon at room temperature (maximum load was 5 kN, and the elongation speed was 0.5 mm.min⁻¹). The mechanical properties determination was carried out on PI films after making the specimens using a cast cutter.

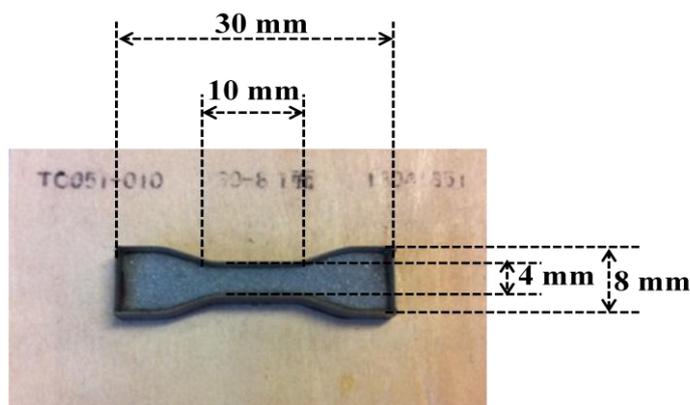


Figure 3.2 Specimen cast cutter and dimensions of film to be prepared.

Specimens for mechanical properties determination was prepared by keeping the film over a rubber and simply pressing the cast cutter and collecting the specimen thus obtained.

3.2.3.5 UV-vis spectroscopy

Ultraviolet-visible (UV-vis) spectra were taken using Perkin Elmer, Lambda 25 UV/Vis spectrophotometer at room temperature in 200-800 nm spectral regions by preparing PAAs solution in DMF (concentration was adjusted to bring the absorbance nearly to 1).

3.2.4 Effect of polymerization time on polymer properties

The effect of polymerization time on polymer properties were studied by monitoring the polymerization reaction for diamine DAS and dianhydride DSDA. The Polymerization reaction was monitored throughout the polymerization time and samples at different polymerization time were collected by taking out the sample and precipitation using water/methanol/ethanol. Further the PAAs film at different polymerization time were prepared using directly the reaction mixture, diluting the

reaction mixture using DMAc and solvent cast method with the help of spin coating over a silicon wafer or aluminium plate. The PAAs films were collected by heating the samples after spin coating at 60 °C. PIs films were obtained by thermal imidization of the PAAs in an oven for 1 h each at 100, 150, 200 and 250 °C, respectively, under vacuum.

The Characterization of poly(amic acid)s and polyimides prepared in this section were done by similar methods as mentioned in previous section.

3.2.5 Effect of dianhydride mixture on polymer properties

The effect of using mixture of dianhydride on polymer properties was studied by preparing polymer from diamine DAS and 1:1 mixture of DSDA and BTDA by the method discussed earlier. The Polymerization reaction was monitored throughout the polymerization time and samples at 24 h and 48 h polymerization time were collected by taking out the sample and precipitation using water/methanol/ethanol. Further the PAAs film at different polymerization time were prepared using directly the reaction mixture, diluting the reaction mixture using DMAc and solvent cast method with the help of spin coating over a silicon wafer or aluminium plate. The PAAs films were collected by heating the samples after spin coating at 60 °C. PIs films were obtained by thermal imidization of the PAAs in an oven for 1 h each at 100, 150, 200 and 250 °C, respectively, under vacuum. The Characterization of poly(amic acid)s and polyimides prepared in this section were done by similar methods as mentioned in previous section.

3.3 Results and discussion

3.3.1 Polymer Synthesis

3.3.1.1 Structural analyses ($^1\text{H-NMR}$ and FT-IR)

PAAs were prepared by the polycondensation of the prepared diamine of DAS and EDDA with stoichiometric amounts of the dianhydrides CBDA, PMDA, BPDA, OPDA, BPDA, and DSDA (Scheme 3.1). The resulting PAAs were abbreviated as PAA-1a, PAA-1b, PAA-1c, PAA-1d, PAA-1e and PAA-1f for DAS based PAAs and PAA-2a, PAA-2c and PAA-2f for EDDA based diamine as shown in Table 3.1. Almost all PAA's fibrils were found to be of cream colour (very light yellow) except PAA-4 which was orange in colour. However, the fibril's lengths of PAAs were different with each other. Some of the PAAs were easy to breakdown because of stiffness of fibrils and became powder like.

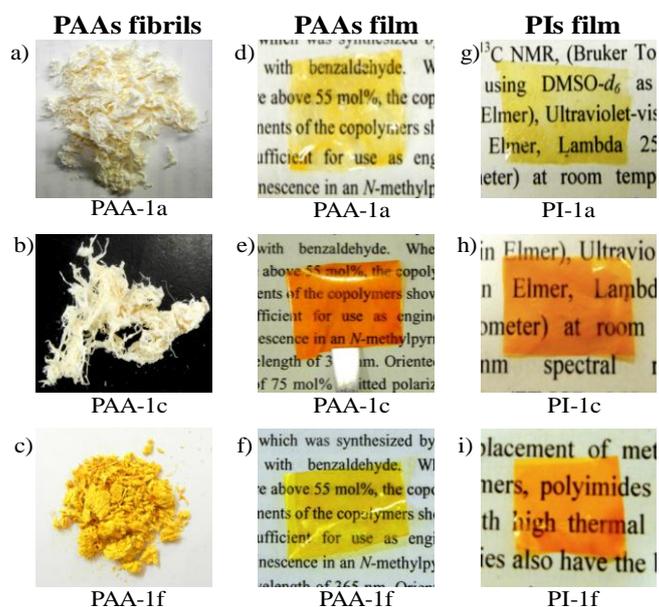


Figure 3.3 PAAs fibrils [(a) PAA-1a, (b) PAA-1c and (c) PAA-1f], PAAs film [(d) PAA-1a, (e) PAA-1c and (f) PAA-1f] and PIs [(g) PI-1a, (h) PI-1c and (i) PI-1f].

Table 3.1 Yield of PAAs and the observation during polymerization.

Polymer	Yield (%)	Reaction mixture ^a	Film property
PAA-1a	96	c,d,f	Flexible
PI-1a	ND	ND	Brittle
PAA-2a	94	c,d,f	Flexible
PI-2a	ND	ND	Flexible
PAA-1b	96	b,e	Flexible
PI-1b	ND	ND	Brittle
PAA-1c	98	c,e	Flexible
PI-1c	ND	ND	Flexible
PAA-2c	98	c,e	Flexible
PI-2c	ND	ND	Brittle
PAA-1d	90	c,d	Flexible
PI-1d	ND	ND	Flexible
PAA-1e	91	c,e	Flexible
PI-1e	ND	ND	Flexible
PAA-1f	92	c,e	Flexible
PI-1f	ND	ND	Flexible
PAA-1f [#]	91	c,e	Flexible
PI-1f [#]	ND	ND	Flexible
PAA-1f ^{##}	92	c,e	Flexible
PI-1f ^{##}	ND	ND	Flexible
PAA-2f	92	c,e	Flexible
PI-2f	ND	ND	Flexible

^aObservation during reaction, ^bTranslucent, ^cTransparent, ^dHomogeneous viscous solution, ^eHomogeneous highly viscous solution, ^fGel, ND refers to not determined, [#]Polymerization time is 8 h, ^{##}Polymerization time is 24 h.

The ¹H NMR spectra of PAAs are shown in Figure 3.4. In ¹H NMR spectra of PAAs derived with DAS, the main chain proton signals for amides, aromatics proton of dianhydride, aromatic proton of diamine DAS and $-\text{CH}=\text{CH}-$ appeared around 10.7–10.1, 8.6–7.3, 7.6–7.1 and 7.6–7.4 ppm respectively. In case of EDDA derived

PAAAs, $-\text{CH}=\text{CH}-$ protons peaks was replaced by proton peak of $-\text{CH}_2-\text{CH}_2-$ at 2.8–2.7 ppm, however, other peaks remained unaltered. PAAAs showed signals from CBDA protons around 3.8-3.1 ppm in addition to the above mentioned signals. Among all the dianhydride used CBDA is a special type of anhydride as it can be prepared from bio-available maleic anhydride. Reports suggest maleic anhydride after UV irradiation undergoes (2 + 2) cyclo addition resulting in the formation of CBDA [119]. Hence CBDA derived PAAAs (PAA-1f and PAA-2f) and PIs (PI-1f and PI-2f) are fully bio-based polymer, however, rest of the polymer were semi bio-based.

The DMAc solution of PAAAs was utilized for preparing PAAAs films, by spin coating and evaporating the solvent at 60-70 °C (Figure 3.3). DAS based PAAAs film were yellow to orange colored while EDDA based PAAAs film were colorless to light yellow. The PIs films were obtained by stepwise thermal imidization by keeping the PAAAs films at 100, 150, 200, and 250 °C for 1 h at each step in an oven. The film became darker in color ranging yellow to dark orange. The imidization caused ring-closing reactions, resulting in more efficient charge transfer from electron rich diamines to electron deficient dianhydrides leading to the color change [118]. The complete imidization was confirmed by FT-IR spectra. The PIs were represented as PI-1a, PI-2a, PI-1b, PI-1c, PI-2c, PI-1d, PI-1e, PI-1f and PI-2f, as shown in Table 3.1.

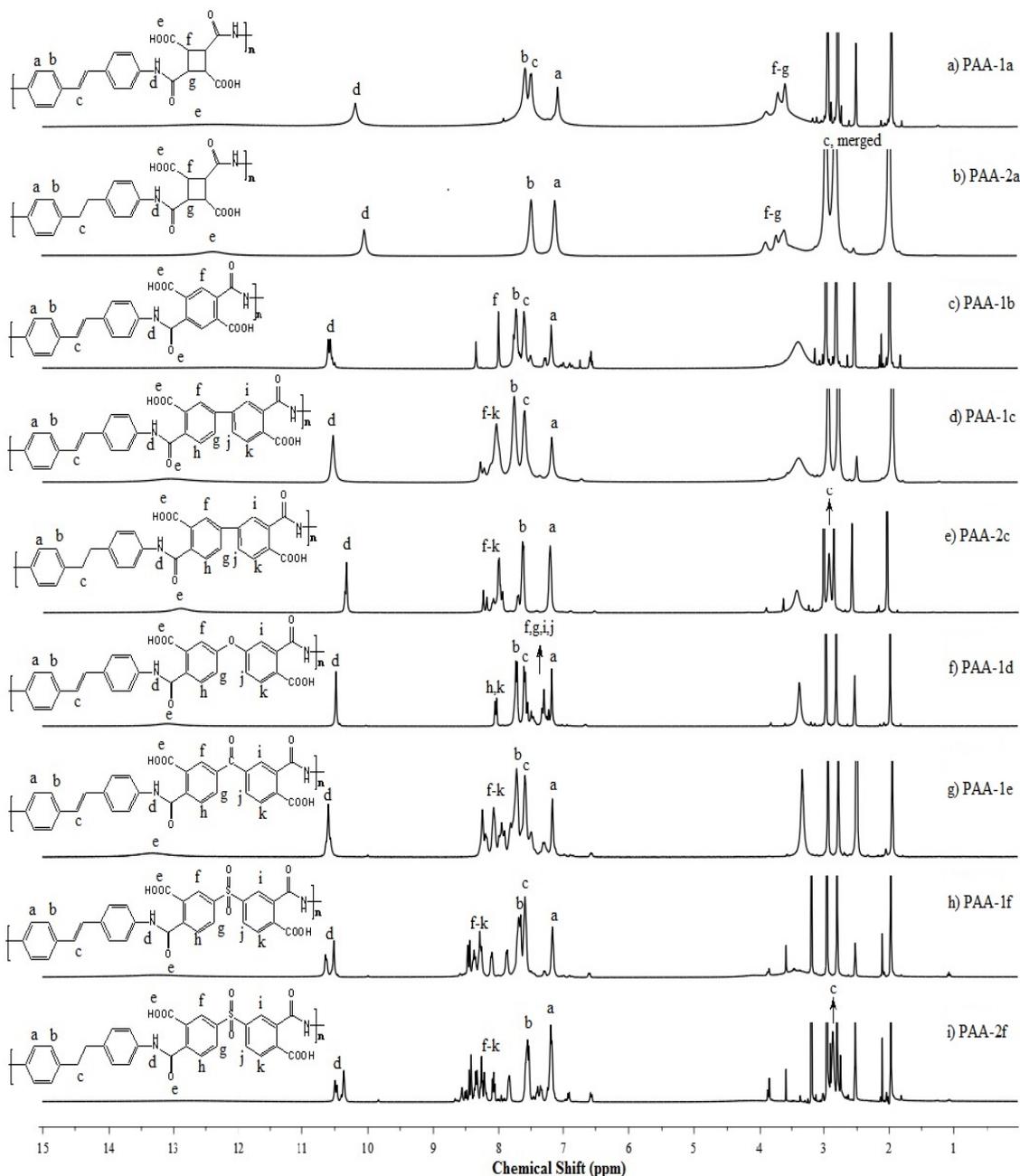


Figure 3.4 ^1H NMR spectra of (a) PAA-1a, (b) PAA-2a, (c) PAA-1b, (d) PAA-1c, (e) PAA-2c, (f) PAA-1d, (g) PAA-1e, (h) PAA-1f and (i) PAA-2f.

Figures 3.5 and 3.6 show the FT-IR spectra of the PAAs and PIs, respectively. In all the samples the following peaks were observed: broad band in the range 2500 to 3500 cm^{-1} (O–H stretching of carboxylic acid group’s hydroxyls), two different carbonyl peaks at 1720 cm^{-1} (C=O stretching, carboxylic) and 1670 cm^{-1} (C=O

stretching, amide), and 1520 and 1430 cm^{-1} (aromatic C–H overtone aromatic). After imidization 1720 cm^{-1} (C=O stretching, carboxylic) and 1670 cm^{-1} (C=O stretching, amide) were replaced by a small peak at 1780 cm^{-1} (C=O asymmetric stretching) and a big peak at 1712 cm^{-1} (C=O symmetric stretching) which were characteristic to PI structures. Furthermore, other peaks at 1518 cm^{-1} (C–C stretching of aromatic), 1441 cm^{-1} (C=C stretching of p-substituted benzene) 1376 cm^{-1} , (C–N stretching of imide), and 1175 cm^{-1} (imide ring deformation) appeared, which indicated a complete imidization [120]. These results clearly indicated the formation of the expected PIs, which were clear, flexible and strong. OPDA derived PI-1d showed IR peak at 1235 cm^{-1} corresponding to C–O stretching of ether group and DSPDA derived PI-1f and PI-2f showed asymmetric and symmetric S=O stretching at 1323 and 1148 cm^{-1} respectively [121].

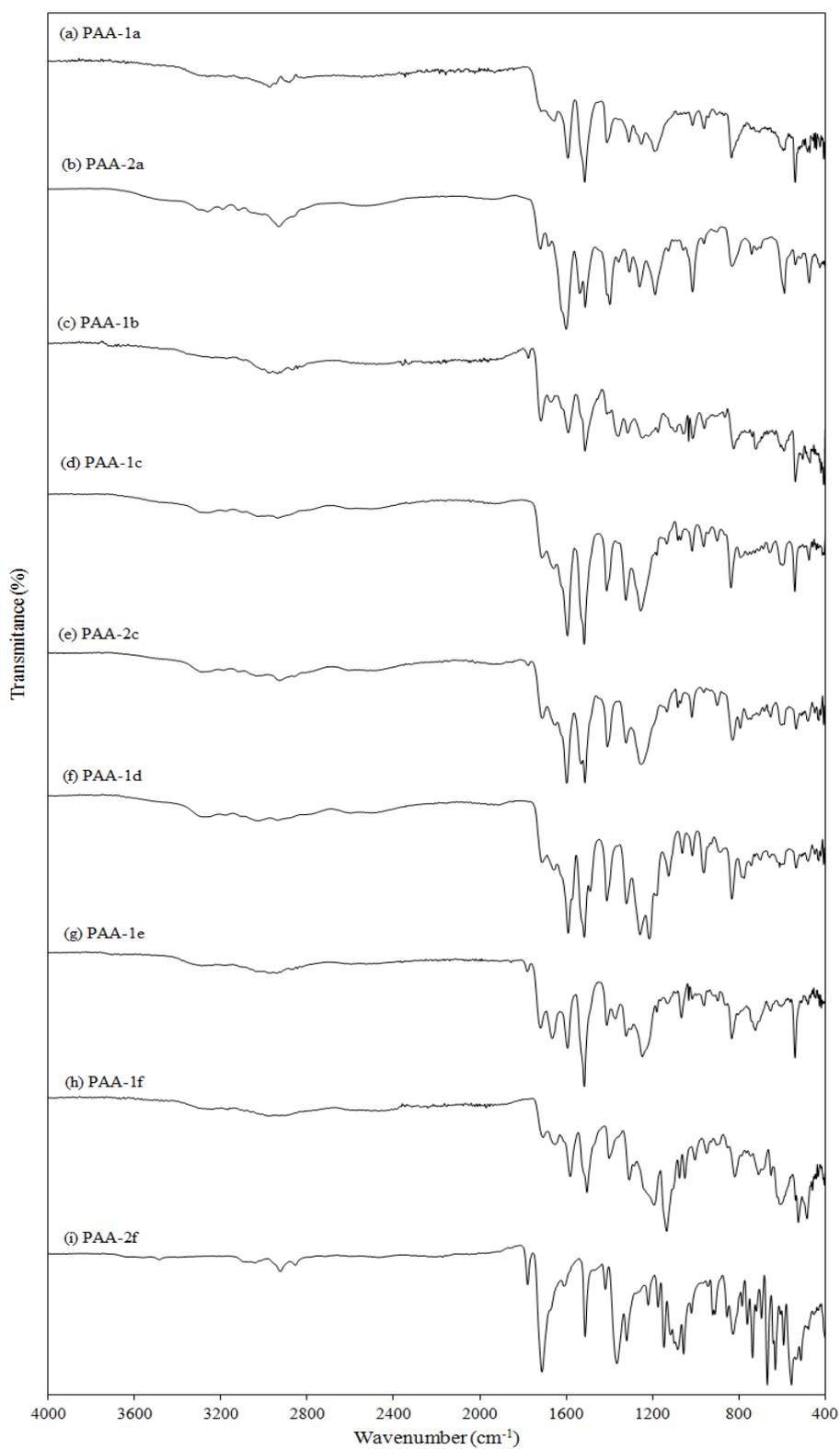


Figure 3.5 FT-IR spectra of (a) PAA-1a, (b) PAA-2a, (c) PAA-1b, (d) PAA-1c, (e) PAA-2c, (f) PAA-1d, (g) PAA-1e (h) PAA-1f and (i) PAA-2f.

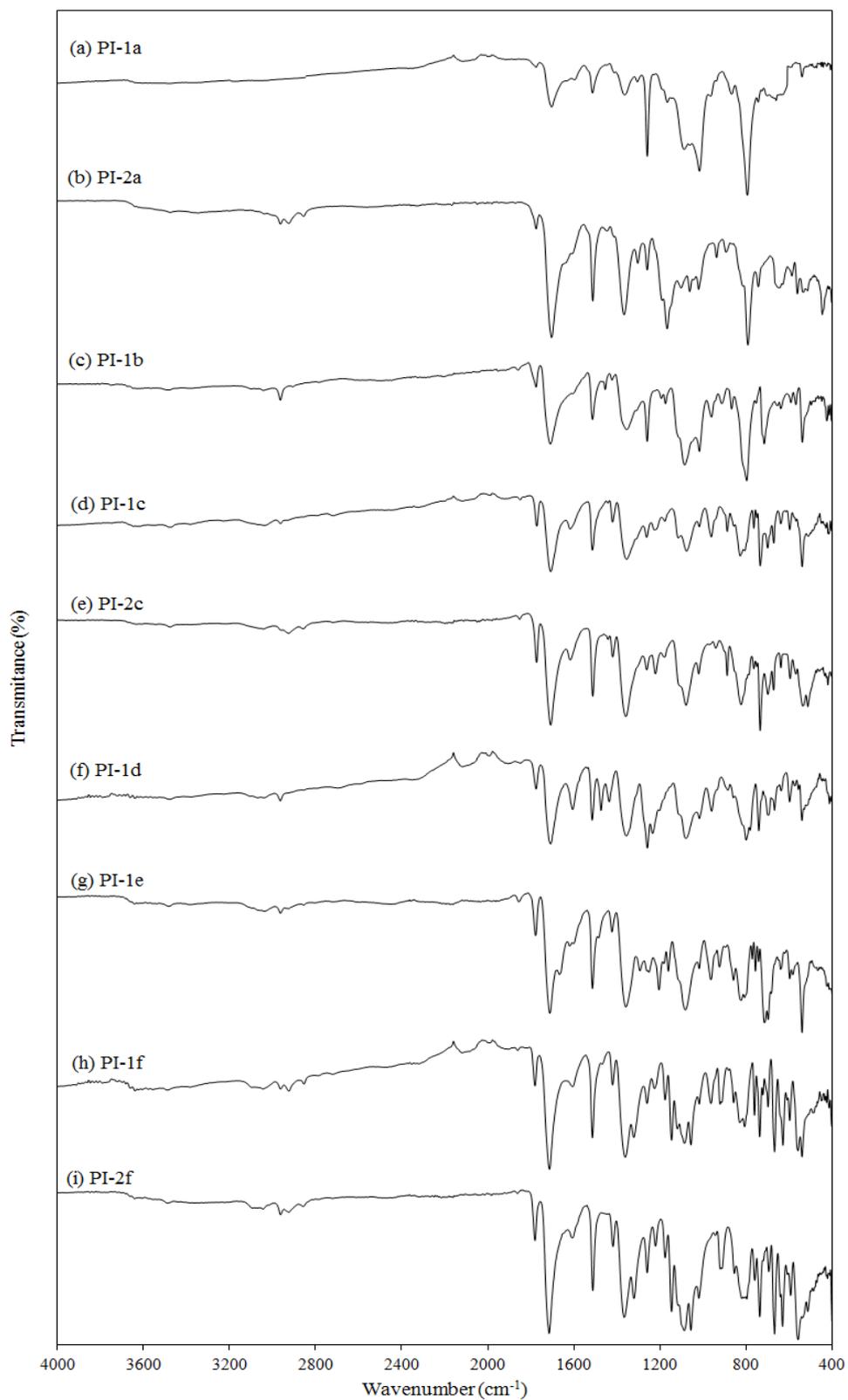


Figure 3.6 FT-IR spectra of (a) PI-1a, (b) PI-2a, (c) PI-1b, (d) PI-1c, (e) PI-2c, (f) PI-1d, (g) PI-1e (h) PI-1f and (i) PI-2f.

3.3.1.2 Molecular weight and viscosity measurement

The weight-average molecular weight of (M_w), number average molecular weight (M_n) and polydispersity index (PDI) were determined using GPC by dissolving PAAs in suitable amount of DMF and the results are summarized in Table 3.2.

Table 3.2 Inherent Viscosities, M_w , M_n , and PDI of prepared PAAs.

Polymer	η_{inh} (dl/g) ^a	M_n ^b	M_w ^b	PDI ^b
PAA-1a	6.62	2.50×10^5	4.04×10^5	1.62
PI-1a	ND	ND	ND	ND
PAA-2a	0.52	3.07×10^5	4.71×10^5	1.53
PI-2a	ND	ND	ND	ND
PAA-1b	0.54	1.72×10^5	2.21×10^5	1.29
PI-1b	ND	ND	ND	ND
PAA-1c	1.04	2.48×10^5	3.82×10^5	1.57
PI-1c	ND	ND	ND	ND
PAA-2c	0.48	2.35×10^5	3.84×10^5	1.63
PI-2c	ND	ND	ND	ND
PAA-1d	0.41	2.22×10^5	3.23×10^5	1.48
PI-1d	ND	ND	ND	ND
PAA-1e	0.51	1.83×10^5	2.95×10^5	1.61
PI-1e	ND	ND	ND	ND
PAA-1f	0.49	2.43×10^5	3.73×10^5	1.53
PI-1f	ND	ND	ND	ND
PAA-1f [#]	0.53	2.82×10^5	4.30×10^5	1.52
PI-1f [#]	ND	ND	ND	ND
PAA-1f ^{###}	0.55	2.86×10^5	4.42×10^5	1.54
PI-1f ^{###}	ND	ND	ND	ND
PAA-2f	0.41	2.15×10^5	3.27×10^5	1.51
PI-2f	ND	ND	ND	ND

^a η_{inh} : Inherent viscosities measured with PAA at a concentration 0.5 g/dL in DMAc at 30 °C, ^b M_w , M_n , PDI: The weight-average molecular weight, the number-average molecular weight and the distribution of polymer molecular weight of PAA using GPC, ND refers to not determined, [#]Polymerization time is 8 h, ^{###}Polymerization time is 24 h.

PAAs exhibited high molecular weight M_w and M_n value ranges of 2.2×10^5 – 4.4×10^5 g/mol for M_w and 1.7×10^5 – 2.8×10^5 g/mol for M_n respectively and the PDI

ranged from 1.29 to 1.61. The results of GPC (M_w , M_n and PDI) showed prepared PAAs have high molecular mass which confirm the formation of PAAs. The viscosity gives the idea and index of molecular weight. The PAA solutions found to have inherent viscosities of 0.49-6.62 dL/g at 30 °C, indicating high molecular weight of the polymers. The inherent viscosity of PAA-1a was relatively very high because of the presence of cyclobutane moiety. Of all the bio-based PAAs, PAA-1a formed a gel after polymerization and showed the highest viscosity possibly due to the aliphatic cyclobutane ring of CBDA. Carboxylic acid attached to the CBDA ring in PAA-1 has a higher reactivity than an aromatic acid, occasionally causing the addition of COOH to the central double bond of stilbene moiety in PAA-1a, resulting in cross-linking of the polymer chains. If the reaction occurred with only 1 % probability, the viscosity would be increased. As CBDA can be photochemically produced from bio-based therefore, PAA-1a is fully bio-based PI who found to exhibit the highest molecular weight ($M_w = 4.04 \times 10^5$ and $M_n = 2.05 \times 10^5$) and the highest viscosity ($\eta_{inh} = 6.62$ dL/g) at 30 °C of all the PAAs prepared. The total bio-based PAAs, PAA-1a and PAA-2a showed highest molecular weight and high viscosity which can be due to the presence of inter and intra molecular hydrogen bonding in the polymer chain due to the presence of short i.e. four membered cyclobutane ring.

3.3.1.3 Thermal analyses: Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric analysis (TGA) was utilized in order to investigate the thermal degradation of PIs. TGA was carried out under nitrogen atmosphere at a heating rate of 10 °C/min. T_{d5} and T_{d10} represents the 5% and 10% weight-loss temperatures

respectively and the results are summarised in Table 3.3 and shown in Figure 3.7(A). The T_{d5} ranged from 397-550 °C while T_{d10} ranged from 406-600 °C which indicates a high degree of resistance towards thermal degradation.

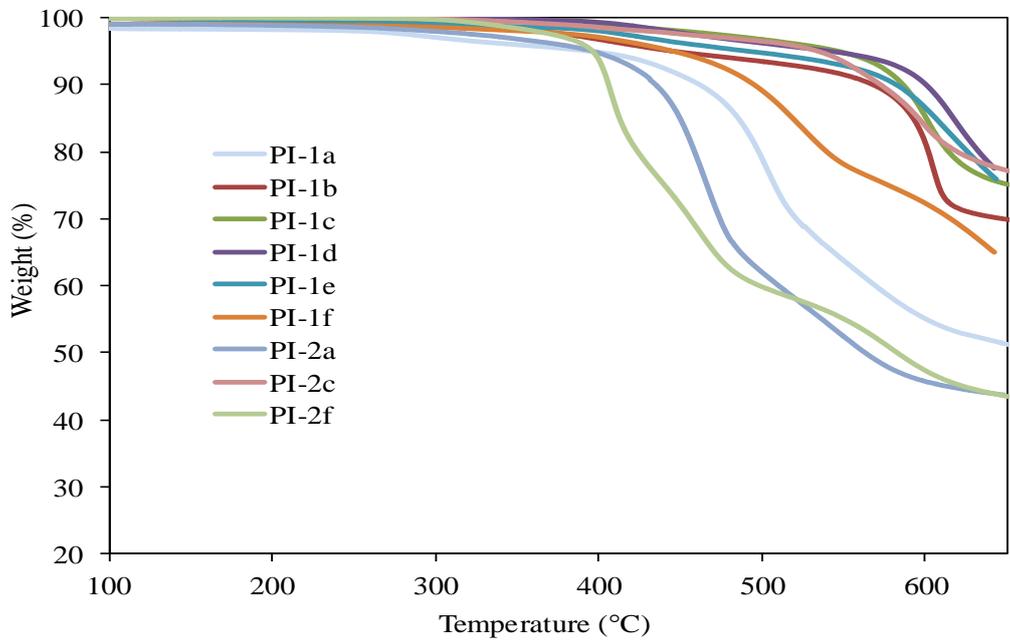
Table 3.3 Glass transition temperature (T_g) and TG analysis of the PIs prepared.

	T_g (°C) ^a	TGA (°C) ^b	
		T_{d5}	T_{d10}
PI-1a	ND	399	462
PI-2a	ND	398	435
PI-1b	330	443	567
PI-1c	ND	549	587
PI-2c	ND	535	573
PI-1d	ND	540	599
PI-1e	250	489	581
PI-1f	ND	447	498
PI-1f [#]	ND	438	498
PI-1f ^{##}	ND	439	494
PI-2f	ND	397	406
Kapton TM	ND	430	553

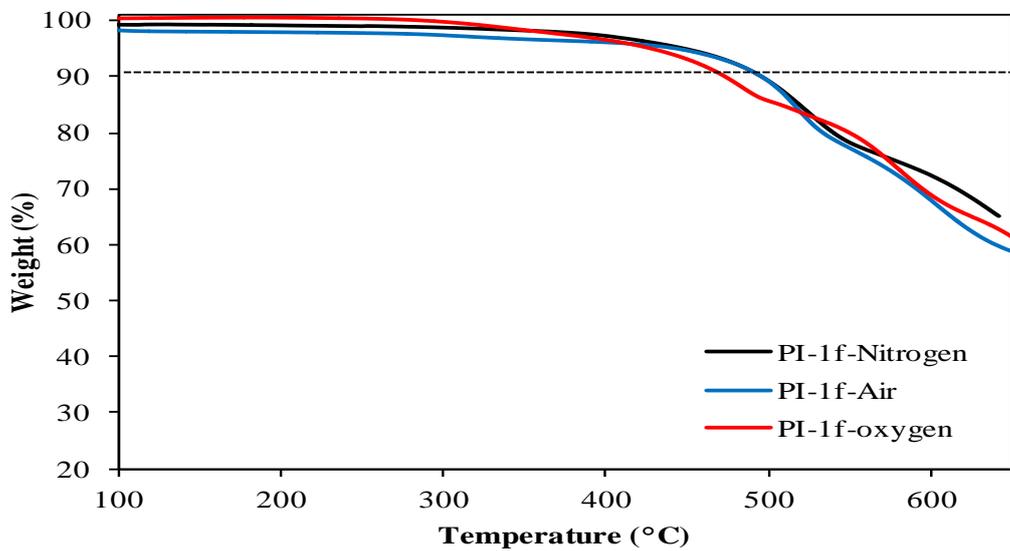
^a T_g : Glass transition temperature (measured using DSC at a heating rate of 10 °C/min in N₂ atmosphere), ^b T_{d5} , T_{d10} : Temperature at 5% and 10% weight loss which was measured using TGA at a heating rate of 10 °C/min under N₂ atmosphere, ND refers to not determined, [#]Polymerization time is 8 h, ^{##}Polymerization time is 24 h.

DAS based PIs, PI-1a, PI-1c and PI-1f showed higher T_{d5} and T_{d10} compared to their counter EDDA based PIs PI-2a, PI-2c and PI-2f which are due to the slightly more steric hindrance due to two extra hydrogen atoms in EDDA diamine. Also this could be due to the extended conjugation in DAS based PIs which is absent in EDDA based PIs. PI-1d showed highest T_{d10} 600 °C which could be due to presence of oxygen from OPDA in the backbone chain whose lone pair can participate in extending the conjugation. However, CBDA derived PIs PI-1a and PI-2a showed lower T_{d10} than 500 °C due to the lower amount of aromatic i.e. benzene rings than the others. PIs prepared

here showed high T_{d10} and high degree of thermal resistance than conventional bio-based aliphatic and aromatic bio-based polymers reported thus far.



(A)



(B)

Figure 3.7 TGA curves of PI films measured under a nitrogen atmosphere (A) and TGA curves of PI-1f in different atmosphere (B) at a heating rate of 10 °C/min.

Changing the atmosphere from pure nitrogen to air did not significantly affect the stability of the PIs since air contains much more nitrogen than oxygen. The PIs maintained their stability towards oxidative thermal degradation in nitrogen and air. However, T_{d10} was found to drop by 20-50 °C under a pure oxygen atmosphere due to high oxidative thermal degradation. Representative results of the TGA in different atmosphere of PI-1f are shown in Figure 3.7(B). Overall, PIs showed good thermal stability under nitrogen, air and oxygen atmospheres. TGA were carried out upto 650 °C as this temperature is high enough to evaluate the thermal stability. However, TGA upto 800 °C was also carried out for PI-1f to evaluate the residual weight which was found to be nearly 20 %.

The differential scanning calorimetry (DSC) analysis was carried to determine the T_g values of the PIs under a nitrogen atmosphere and summarized in Table 3.3. The backbone structure of dianhydride plays an important role in T_g values of PIs [120, 121]. PI-1b and PI-1e were found to be 330 °C and 250 °C respectively. Due to measuring limit of the DSC machine, rest of the PIs exhibited no T_g below 350 °C, which means that they could not determine T_g values due to their decomposition temperature was lower than T_g phenomena. The charge transfer from electron rich bio-derived diamine to electron deficient dianhydride and high stability of 5-membered imide ring due of extended $n-\pi$ conjugation between carbonyl group and lone pair of nitrogen could be the reasons of high T_g values. Materials with such high T_g properties may be suitable for applications in superengineering plastics.

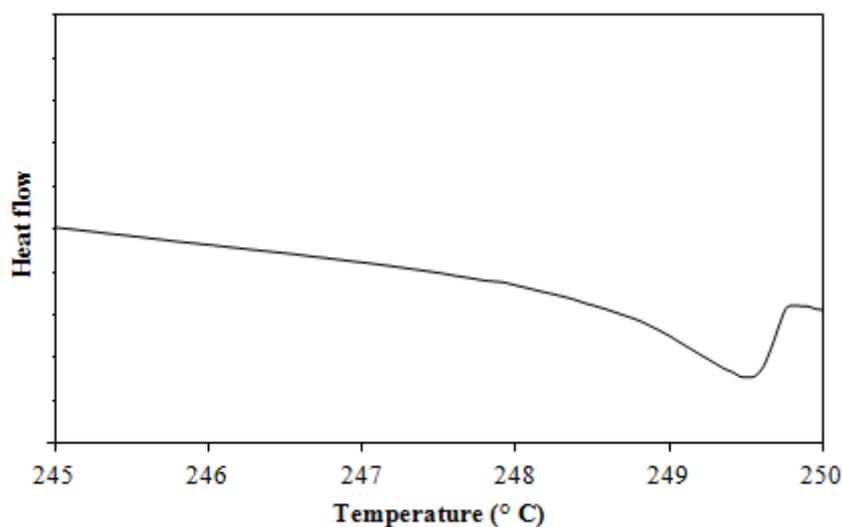


Figure 3.8 DSC curve of PI-1e showing the T_g .

3.3.1.4 Mechanical properties analysis: (Tensile strength, Young modulus and % elongation)

The mechanical properties such as tensile strength, young modulus and elongation were determined using tensometer at an elongation speed of 0.5 mm/min at room temperature. The results are summarized in Table 2. As elongation % is the significance of flexibility, the PI-1f was most flexible than the other PIs due to the presence of more flexible sulfone unit in the dianhydride DSDA. PI-1a and PI-1b prepared from DAS diamine and dianhydride PMDA and CBDA respectively were found to be highly brittle due to rigidity in their corresponding dianhydride used. The brittleness was so high that it was unable to prepare PI films to test their tensile strength. The PI films had tensile strength values in the range of 54-132 MPa, young modulus in the range of 2.3-4.3 GPa, and % elongation in the range of 1.5-7.8 %. The tensile strength, young modulus and % elongation of PI-1f were at 81 MPa, 4.3 GPa and 7.8 % respectively, which indicates that the PI-1f film was the strongest and toughest. Although for PI-1f^{##}, which was prepared from DAS and DPSDA at polymerization

time 24 h, found to be the mechanically more stable as per the tensile strength 132 MPa with young modulus 2.4 GPa and % elongation 5.6. The tensile strength of PI-1f^{##} was found to be more than the commercially available, most famous and extensively used polyimide KaptonTM. Total bio-based PI-1a was too brittle to be examined for tensile properties due to highly rigid dianhydride CBDA and diamine DAS. However, PI-2a was enough flexible but showed lower than expected mechanical properties.

Table 3.4 Mechanical properties (Tensile strength, Young modulus and % Elongation) of bio-based and semi bio-based PIs.

	Tensile strength (MPa) ^a	Young modulus (GPa) ^a	Elongation (%) ^a
PI-1a	ND	ND	ND
PI-2a	24	2.3	1.1
PI-1b	ND	ND	ND
PI-1c	60	2.3	2.6
PI-2c	70	2.8	2.5
PI-1d	54	2.4	2.2
PI-1e	65	4.3	1.5
PI-1f	81	3.0	7.8
PI-1f [#]	106	2.8	3.9
PI-1f ^{##}	132	2.4	5.6
PI-2f	ND	ND	ND
Kapton TM	120	0.3	15.8

^aTensile strength, Modulus and Elongation were measured using tensometer at room temperature, ND refers to not determined, [#]Polymerization time is 8 h, ^{##}Polymerization time is 24 h.

3.3.1.5 UV-vis Spectroscopy

The UV-vis spectroscopy was carried out by dissolving suitable amount of PAAs in DMF. λ_{\max} of PAAs derived from DAS were found to be in the visible range due to the extended conjugation by unsaturation as expected by compounds contained stilbene moiety. The λ_{\max} ranges from 348 to 358 nm depending upon the type of dianhydride

used, however, the absence of unsaturation and hence no extended conjugation in EDDA derived PAAs resulted in no absorbance in visible region (Figure 3). The λ_{\max} of PAA-1b and PAA 1c was found to be higher than other PAAs i.e. 358 nm and 357 nm respectively. The high value of λ_{\max} could be due to the rigidity in the dianhydride structure and thus in their respective PAAs. The λ_{\max} of PAA-1e is of least value 348 nm due to the presence of carbonyl linker between the two phenyl ring in BTDA. λ_{\max} of PAA-1d, and PAA-1f were 354 nm for each.

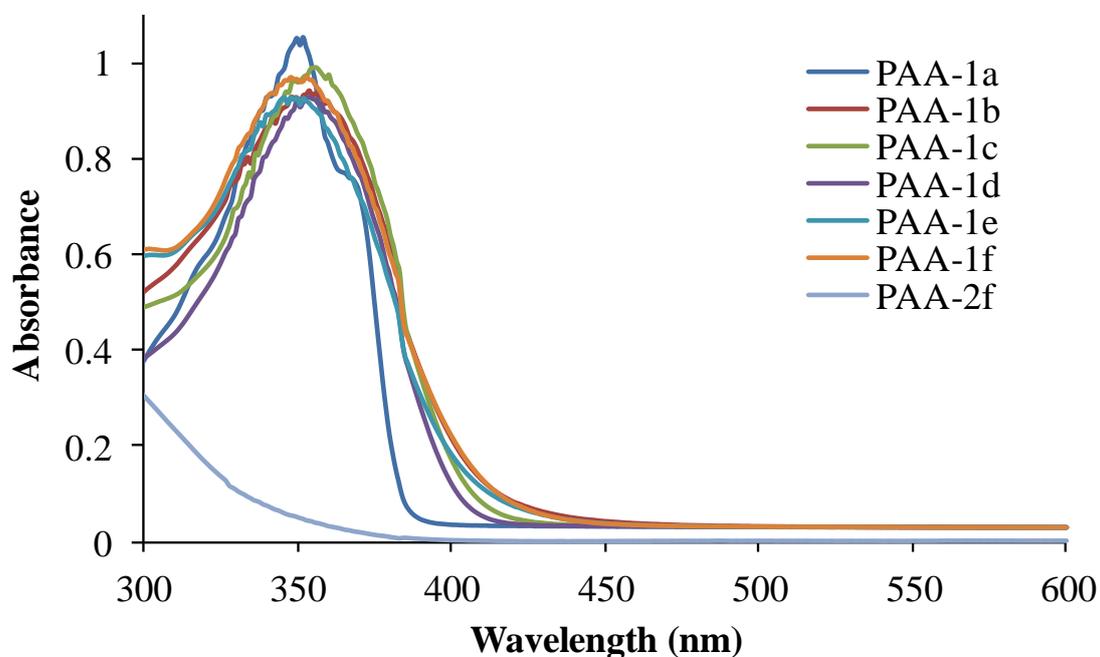


Figure 3.9 UV-vis spectra of PAAs.

Since the PIs were insoluble in any of the solvent PI films were used in order to determine the transmittance. Figure 3.10 shows the wavelength dependence of transmittance of the PI films, where the transmittance ranges from 38 to 72 %.

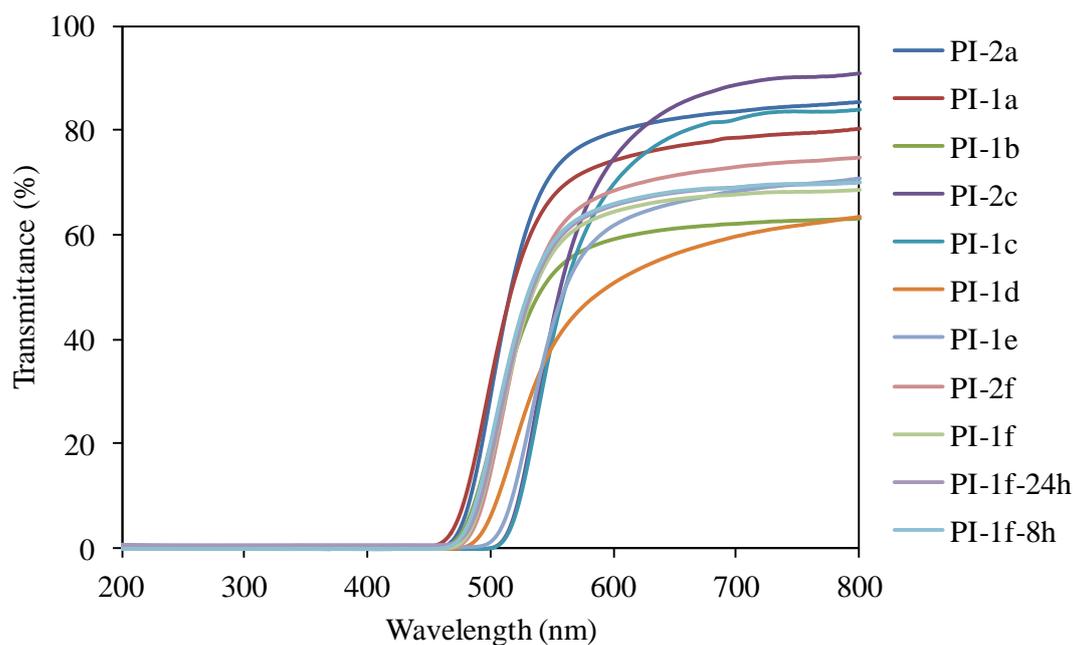


Figure 3.10. Transmittance spectra of total bio-based and semi bio-based PIs showing no transmittance upto 450 nm.

3.3.1.6 Solubility:

The solubility and chemical resistance of all the prepared polymers was investigated in various solvents shown in Table S1. The solubility of the polymers was tested by dissolving them in three groups of solvent: (A) nonpolar solvent such as hexane, benzene, toluene, dichloromethane (DCM), chloroform and diethyl ether, (B) polar protic solvent such as distilled water, methanol, ethanol, and conc. sulfuric acid, and (C) polar aprotic solvent such as acetone, acetonitrile, ethyl acetate, THF, DMF, DMAc, NMP and DMSO. The DAS based PAAs were only soluble in polar solvents such NMP, DMAc, DMF, and DMSO at room temperature and at 50 °C. In addition to this EDDA based PAAs and PIs were soluble in conc. H₂SO₄. However, DAS derived PAAs became darker in conc. H₂SO₄. On the other hand, all of the PIs were insoluble in any of the solvents, even after heating except PI-1f which was partially soluble in conc. H₂SO₄

which shows that PIs are highly chemical resistant. It was found that DAS-derived PIs were insoluble even at 50 °C in all of the solvents shown above, while EDDA-derived PIs were soluble in conc. H₂SO₄.

Table 3.5 Solubility of bio-based PAAs and PIs in various solvents.

Polymer → Solvent	PAA-1a	PI-1a	PAA-2a	PI-2a	PAA-1b	PI-1b	PAA-1c	PI-1c	PAA-2c	PI-2c	PAA-1d	PI-1d	PAA-1e	PI-1e	PAA-1f	PI-1f	PAA-2f	PI-2f
Hexane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Hexane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Toluene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DCM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chloroform	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Diethylether	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ethanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Conc. H ₂ SO ₄	±	-	+	+	-*	-	-*	-	+	+	±	-	-*	-	-*	±	+	+
Acetone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Acetonitrile	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ethylacetate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
THF	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NMP	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
DMSO	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
DMF	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
DMAc	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-

+:Soluble at room temperature, -: Insoluble , ±: partially soluble after 2 days and *: polymer film become darker

3.3.2 Effect of polymerization time on polymer properties

3.3.2.1 Structural Analysis

Almost all PAA's fibrils were found to be of cream colour (very light yellow) at each polymerization time. The PAAs films were yellow in colour and after thermal imidization the colour of the films became a bit darker as compared to their PAAs film.

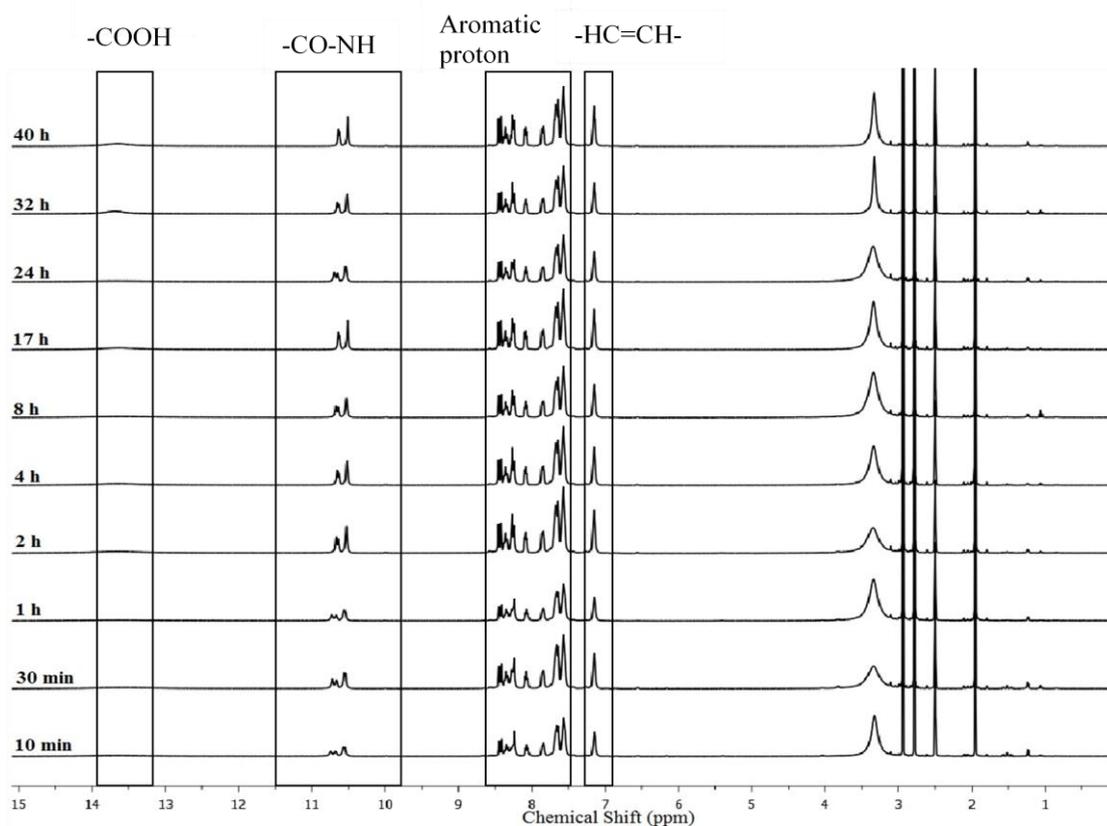


Figure 3.11 ¹H-NMR of PAA-1f at different interval of time during the monitoring of reaction with time.

The ¹H NMR spectra of PAAs are shown in Figure 3.11. The peak were assigned as: carboxylic acid protons in the range 13.5-13.8 ppm, amide protons in the range of 10.7-10.1 ppm, the aromatic dianhydride protons in the range of 8.5-7.3 ppm, aromatic diamine protons of benzene ring were observed in the range of 7.8-7.6 ppm, aliphatic unsaturated proton of diamine in the range of 7.4-7.2 ppm.

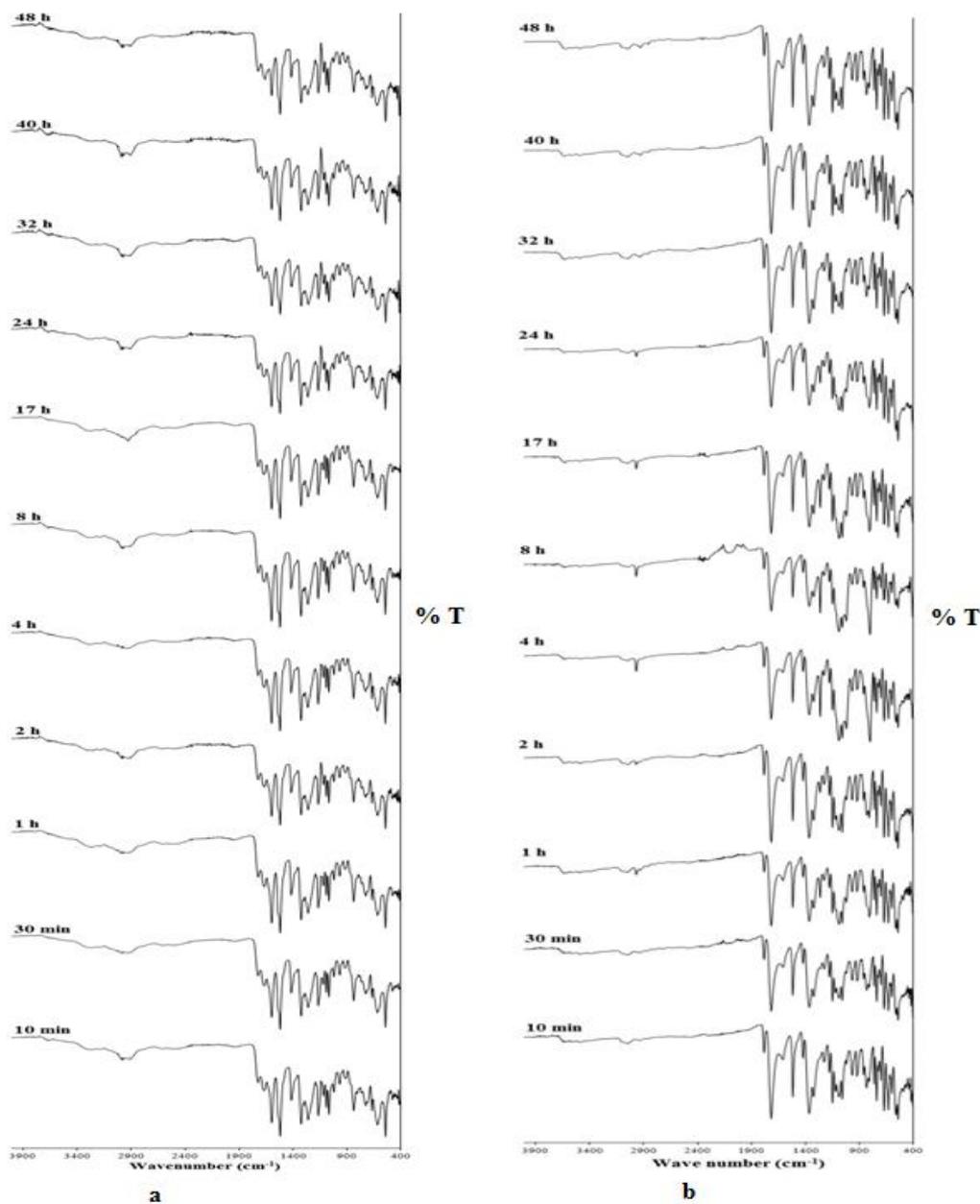


Figure 3.12 IR of PAA-1f at different polymerization time. **a)** IR of PAA films and **b)** IR of PI films.

The FT-IR spectra of PAAs (Figure 3.12a) showed broad absorption bands in the region of 2500 to 3500 cm^{-1} (O-H stretching), the carboxylic absorption peak of the ring-opening dianhydride at 1715-1740 cm^{-1} (C=O stretching, carboxylic), 1662-1678

cm^{-1} (C=O stretching, amide) and 1520 cm^{-1} , 1436 cm^{-1} (C-H overtone aromatic), in all PAA's samples.

After thermal imidization FT-IR of PIs (Figure 3.12b) showed absorptions; double carbonyl peaks small peak at 1778 cm^{-1} which corresponds C=O asymmetric stretching, large peak at 1713 cm^{-1} corresponds to C=O symmetric stretching), peak at 1518 cm^{-1} corresponds to C-C stretching of aromatic, peak at 1441 cm^{-1} corresponds to C=C stretching of *p*-substituted benzene, peak at 1363 cm^{-1} corresponds to C-N stretching of imide, peak at 1176 cm^{-1} corresponds to imide ring deformation, these peaks indicated complete imidization. All the PIs showed the peaks assigned to asymmetric and symmetric S=O stretching at 1325 cm^{-1} and 1148 cm^{-1} . These results clearly indicated the complete imidization and formation of the expected PIs.

3.3.2.2 Molecular weight

The weight-average molecular weight of (M_w), number-average molecular weight (M_n) and polydispersity index (PDI) were determined using GPC. The results are tabulated and shown in Table 3.6.

The weight-average molecular weight of (M_w) and the number-average molecular weight (M_n) followed the same trend. Both M_n and M_w were found to be increasing from 30 mins and become maximum at 32 h polymerization time, however, after 32 h both the molecular masses were found to decrease with polymerization time. The maximum M_n was 3.15×10^5 and M_w was 4.74×10^5 at 32 h. The decrease in both the molecular masses could be due to the scissoring of polymer chain due to extending polymerization time. The results of GPC (M_w , M_n and PDI) showed prepared PAAs have high molecular mass which confirm the formation of PAAs.

Table 3.6 M_n , M_w and PDI for PAA-1f at different polymerization time.

Time	PAA film	PI film	$M_n^a \times 10^5$	$M_w^a \times 10^5$	PDI ^a
30 min	Flexible	Flexible	2.44	3.00	1.23
1 h	Flexible	Flexible	2.57	3.85	1.51
4 h	Flexible	Flexible	2.65	4.23	1.59
8 h	Flexible	Flexible	2.82	4.30	1.52
24 h	Flexible	Flexible	2.86	4.42	1.54
32 h	Flexible	Flexible	3.15	4.74	1.51
40 h	Flexible	Flexible	2.66	3.65	1.39
48 h	Flexible	Flexible	2.43	3.73	1.53

^a M_w , M_n , PDI: The weight-average molecular weight, the number-average molecular weight and the distribution of polymer molecular weight of PAA using GPC.

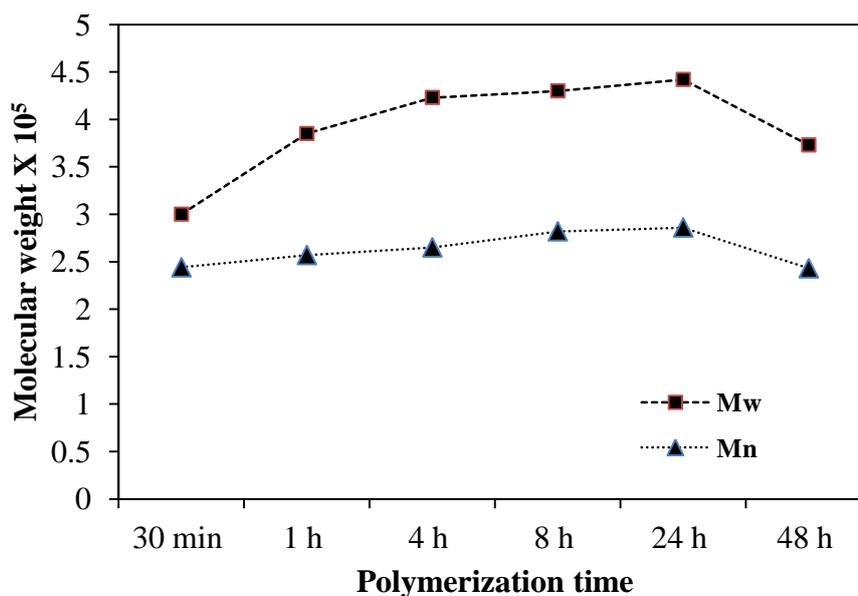


Figure 3.13 Change of M_n and M_w with polymerization time.

3.3.2.3 Thermal Analysis

Thermal gravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 10 °C/min was performed for all the prepared PIs and T_{d5} and T_{d10} i.e. 5% and 10%

weight loss temperature respectively were determined. The results are summarized in Table 3.7.

Table 3.7 Effect of polymerization time on Tensile strength, Young modulus, % Elongation and Degradation temperature (T_d).

Time	Tensile strength (MPa) ^a	Young's modulus (GPa) ^a	Elongation (%) ^a	T_{d5} (°C) ^b	T_{d10} (°C) ^b
30 min	57.5	1.6	3.5	404	465
1 h	43.0	1.9	2.3	432	482
4 h	58.0	2.4	2.4	451	497
8 h	106.4	2.8	3.9	438	498
24 h	132.1	2.4	5.6	439	494
48 h	81.0	3.0	7.8	447	498
Kapton TM	120.0	0.7	15.8	435	452

^aTensile strength, Modulus and Elongation were measured using tensometer at room temperature, ^b T_{d5} , T_{d10} : Temperature at 5% and 10% weight loss which was measured using TGA at a heating rate of 10 °C/min under N₂ atmosphere

3.3.2.4 Mechanical properties analysis: (Tensile strength, Young modulus and % elongation)

Effects of polymerization time on mechanical properties of PIs are summarized in Table 3.7. The mechanical properties (tensile strength, young modulus and elongation) were found to be increasing with polymerization time and become maximum at 32 h polymerization time, however, after 32 h both the tensile strength and young modulus were found to decrease with polymerization time. The decrease in both tensile strength and young modulus could be due to the scissoring of polymer chain arising from extending polymerization time. The % elongation kept on increase with polymerization time.

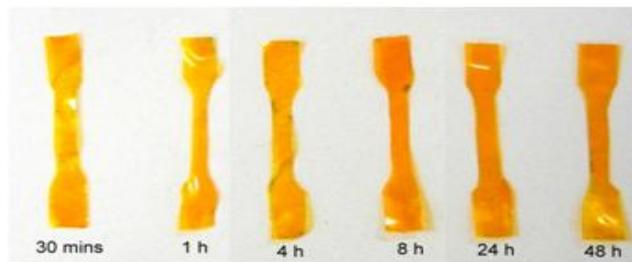


Figure 3.14 Polyimide films for the mechanical properties measurement at different polymerization time.

3.3.3 Effect of mixture of dianhydride on polymer properties

3.3.3.1 Structural Analysis

PAA's fibrils were found to be cream colour (very light yellow). The PAAs films were yellow in colour and after thermal imidization the colour of the films became a bit dark compared to their PAAs film (Figure 3.15).



Figure 3.15 PAA and PI films of polymers prepared from DAS and mixed dianhydrides (BTDA and DSDA).

The FT-IR spectra of PAAs (Figure 3.16) showed broad absorption band in the region of 2500 to 3500 cm^{-1} (O-H stretching), the carboxylic absorption peak of the ring-opening dianhydride at 1715-1740 cm^{-1} (C=O stretching, carboxylic), 1662-1678

cm^{-1} (C=O stretching, amide) and 1520 cm^{-1} , 1436 cm^{-1} (C-H overtone aromatic), in all PAA's samples. After thermal imidization FT-IR of PIs showed absorptions; double carbonyl peaks small peak at 1778 cm^{-1} (C=O asymmetric stretching), large peak at 1713 cm^{-1} (C=O symmetric stretching), 1518 cm^{-1} (C-C stretching of aromatic), 1441 cm^{-1} (C=C stretching of *p*-substituted benzene), 1363 cm^{-1} (C-N stretching of imide), 1176 cm^{-1} (imide ring deformation) appeared, which indicated complete imidization. All the PIs showed the peaks assigned to asymmetric and symmetric S=O stretching at 1325 cm^{-1} and 1148 cm^{-1} . These results clearly indicated complete imidization and formation of the expected PIs.

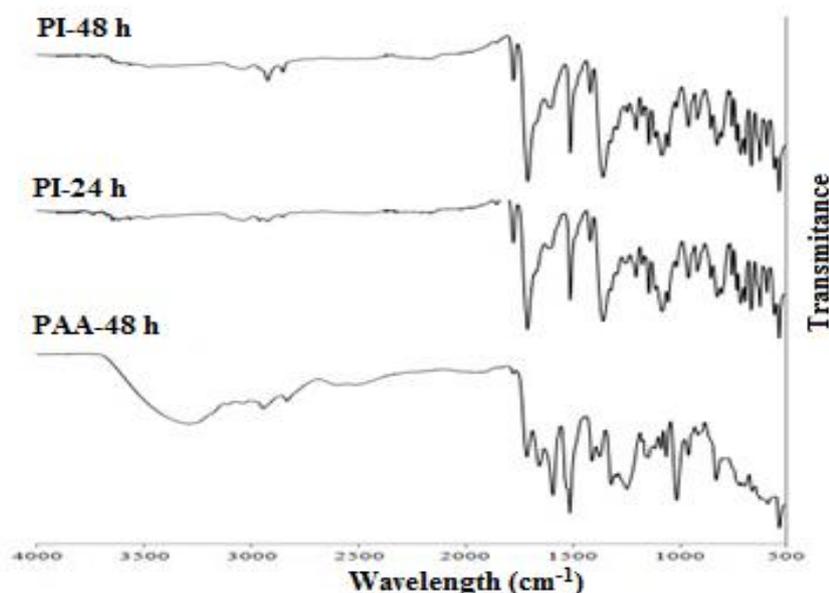


Figure 3.16 IR of PAA and PIs of mixture of dianhydride.

3.3.3.2 Molecular weight

The weight-average molecular weight of (M_w), the number-average molecular weight (M_n) and the polydispersity index (PDI) were determined using GPC. The results are tabulated and shown in Table 3.8. The weight-average molecular weight of (M_w)

and number-average molecular weight (M_n) were found to be least affected by mixture of dianhydride used. The M_n , M_w and PDI of PAA prepared from mixture of dianhydride after 48 h were almost similar to PAA prepared using DSDA dianhydride. The results of GPC (M_w , M_n and PDI) showed prepared PAAs have high molecular mass which confirm the formation of PAAs.

Table 3.8 M_n , M_w and PDI for PAAs of mixture of dianhydride at different polymerization time.

Dianhydride	Time	PAA film	PI film	$M_n^a \times 10^5$	$M_w^a \times 10^5$	PDI ^a
BTDA+DSDA (1:1)	24 h	Flexible	Flexible	2.14	3.23	1.51
	48 h	Flexible	Flexible	2.53	3.78	1.49
BTDA	48 h	Flexible	Flexible	1.83	2.95	1.61
DSDA	48 h	Flexible	Flexible	2.43	3.73	1.53

^a M_w , M_n , PDI: The weight-average molecular weight, the number-average molecular weight and the distribution of polymer molecular weight of PAA using GPC.

3.3.3.3 Mechanical properties analysis: (Tensile strength, Young modulus and % elongation)

Effects of mixed dianhydride on mechanical properties of PIs are summarised in Table 3.9. The mechanical properties (tensile strength, young modulus and elongation) were found to be depending upon type of dianhydrides used. The % elongation was found to increase from 3.8 % at 24 h polymerization time to 6.3 % at 48 h polymerization time. Tensile strength and % elongation in mixed dianhydride PI at 48 h polymerization time was found be close to the PI prepared from DSDA, however, the young modulus was nowhere close to any of the pure PIs. The young modulus of mixed dianhydride based PI at 48 h was lower than both the PIs prepared from neat

dianhydrides. Thus the properties of polyimides from mixture of dianhydrides were found to be in between the polyimides from pure dianhydrides.

Table 3.9 Tensile strength, young modulus and % elongation of PIs prepared from mixture of dianhydride.

Dianhydride	Time (h)	Tensile strength ^a (MPa)	Young modulus ^a (GPa)	Elongation ^a (%)
BTDA+DSDA (1:1)	24	77.0	1.99	3.8
	48	79.6	1.22	6.3
BTDA	48	65	4.3	1.5
DSDA	48	81	3.0	7.8

^aTensile strength, Modulus and Elongation were measured using tensometer at room temperature

3.4 Conclusion

4ACA was utilized to prepare bio-based aromatic diamine DAS. The synthetic route for synthesis of DAS from 4ACA is novel and utilizes bio-based starting material 4ACA. DAS was polycondensed with various available dianhydrides such as Pyromellitic anhydride (PMDA), Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), 3,3',4,4'-diphenylsulfone tetra carboxylic dianhydride (DSDA), 3,4:3',4'-biphenyl tetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (OPDA) and 1,2,3,4-cyclobutane tetracarboxylic dianhydride (CBDA) to syntheses PAAs first followed by PIs by thermal imidization. Among all the dianhydride used CBDA is the only dianhydride which can be prepared from biomaterial hence, the PAA-1a and PI-1a is totally bio-based. **PAA-1a** is fully bio-based PI which found to exhibit the **highest molecular weight ($M_w = 4.04 \times 10^5$ and $M_n = 2.05 \times 10^5$) and the highest viscosity ($\eta_{inh} = 6.62$ dL/g)** among all the prepared PAAs. Rests of the polyimide prepared are semi-bio-

based as only the diamine used was bio-based. The tensile strength, young modulus, and % elongation of PI-1f were at 81 MPa, 4.3 GPa, and 7.8 %, respectively, which indicate that the PI-1f film was the strongest and toughest. Although for PI-1f^{##} which was prepared from DAS and DSDA at polymerization time 24 h, found to be best as per the tensile strength 132 MPa with young modulus 2.4 GPa and % elongation 5.6. The tensile strength of PI-1f^{##} was found to be more than the commercially available, most famous and extensively used polyimide KaptonTM. The PAAs were additionally found to be UV active due to the presence of double bond in the polymer chain inherited from monomer diamine DAS.

The polymerization time was found to affect the properties of poly(amic acid) and polyimide. PAA-1f was chosen to study the effect of polymerization time. As per GPC the 32 h polymerization time was found to be good, however, 24 h polyimides gave good thermal and mechanical properties. The polyimide from mixture of dianhydride posses the properties lying from the polyimide from pure dianhydride.

CHAPTER 4

**PHOTOFUNCTION BEHAVIOUR OF HIGH-
PERFORMANCE, BIO-BASED POLYIMIDES FROM
4ACA**

4.1 Introduction

Application of polyimides is vast from automobile industry to medical application. Structure and properties of the polyimides determines their field of application. Recently polyimides have also been applied in medical field [122-124]. The ability of polyimide to sustain the harsh chemical, thermal, mechanical conditions and their stability makes them best candidates to be used as high-performance plastic. Higher thermal and mechanical stability is attributed to their stable structure as discussed earlier. The property of polyimide is majorly dependent on the monomers used if their specific character is inherited to the polyimide structure. Polyimide generally absorbs UV-Vis or UV/Vis due to charge transfer [125-127]. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the polyimide. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

In the past polyimides were found to be fluorescence active while the phenomenon in the case of PIs is not clearly understood [128-130]. However the polyimide can be designed to be fluorescence active. It has been clarified that fully aromatic PIs have strong charge transfer (CT) interactions and their lowest excited states are attributed to CT(π - π^*) states which emit weak fluorescence [131-134]. During the past decade, considerable interests have been devoted to aromatic polyimides in response to the increasing technological applications in a variety of fields such as the aerospace, automotive industries, interlayer dielectric insulators, alignment layers for liquid crystal displays and the microelectronics industry, because of their excellent thermal, chemical, mechanical stabilities and good film formability [135]. Fully

aromatic polyimides are also known to show fluorescence in the visible region [136, 137]. Since the fluorescence generally originates from the charge transfer (CT) excitation and emission mechanisms [138], the quantum yields of the fluorescence observed for conventional polyimides are relatively low due to their strong CT nature. Hence, a limited number of studies are reported for applications of fully aromatic polyimides to emitting layers in which dye-moieties are incorporated in the main chains or dye compounds are doped [139, 140].

As discussed in earlier chapters, the aromatic diamines monomers which is one of the basic unit are generally petro-chemically derived which is dealing with the problem of non-renewability, high cost and limited amount. Moreover the diamine are toxic to plants therefore can't be produced directly by them. Synthesis of bio-based diamines and using them for the synthesis of bio-based polyimides are the solution to these problems as it helps in reducing the consumption of petrochemicals as well as reducing the greenhouse gases from the environment by fixing the biomass in the form of polymers. Bio-based compound such as 4-aminocinnamic acid (4ACA) which can be produced enzymatically from glucose and 4APA which can be produced chemically/enzymatically from cinnamic acid and can be utilized for the synthesis of aromatic diamines. 4ACA is converted to starting materials in order to synthesize bio-based monomers DAS by a series of chemically reaction (discussed in chapter 2).

4,4'-Diaminostilbene (DAS), its mono- and di-protonated forms exhibit fluorescence. Their UV absorption and fluorescence emission spectra in different solvents and proton concentrations have been measured [141]. The effects of UV on DAS derivatives showed the [2+2] cycloaddition and isomerisation from *trans* to *cis*

form have been reported [142, 143]. Stilbene-triazine compounds have been applied as fluorescent whitening and UV absorbing agents [144].

In this chapter the photofunction properties such as UV-vis absorption, change in UV-vis absorbance, crosslinking w.r.t UV irradiation, fluorescence and change in fluorescence intensity w.r.t UV irradiation of the prepared bio-based PAAs and PIs were studied. The current chapter will focus on the photo-function properties of the prepared polyimides with special reference to UV-vis, fluorescence and crosslinking.

4.2 Experimental

4.2.1 Materials

The bio-based PAAs and PIs synthesized in Chapter 3 were used for further analysis.

4.2.2 Photofunction properties

The photofunction properties such as UV-vis absorbance, change in UV-vis absorbance, UV induced cross linking, fluorescence, change in fluorescence intensity and photo bending studies were carried out using PAAs as PIs were insoluble in any of the solvents. The presence of unsaturation in the polymer chain which was inherited from the monomer diamine DAS made the PAAs to be UV-vis active. The unsaturated aliphatic linker between the two phenyl rings of DAS moiety remained unaltered during thermal imidization process, similar results can be expected from the corresponding PIs. This property of prepared polymers was explored in order to examine the photofunction behaviour and change in various optical properties due to UV irradiation.

4.2.2.1 UV-vis

The UV-vis was performed utilizing PAAs in DMF as PIs were insoluble in any organic solvent. Ultraviolet-visible (UV-vis) spectra were taken using Perkin Elmer, Lambda 25 UV/Vis spectrophotometer at room temperature in 200-800 nm spectral regions by preparing PAAs solution in DMF (concentration was adjusted to bring the absorbance nearly to 1).

a) Effect of UV irradiation on UV-vis absorption

The effect of UV-vis irradiation on absorption value of PAAs has been studied by irradiating the solution of PAAs in DMF by UV under the UV lamp in UV-vis range which includes their λ_{\max} . Further the change in absorbance was monitored w.r.t UV irradiation time by taking the UV-vis spectra after each UV irradiation intervals and plotting the UV absorption value with time of irradiation. UV irradiation was carried out on a Xe lamp (300 W, Asahi Spectra Co. Ltd.; MAX-303) equipped with band-pass filter of different wavelength range.

b) Effect of UV irradiation on degree of cross linking

The effect of UV-vis irradiation on degree of cross linking of PAAs has been studied by irradiating the DMF solution of PAAs by UV under the UV lamp in range which includes their λ_{\max} . Further the change in absorbance was monitored w.r.t UV irradiation time by taking the UV-vis spectra after each UV irradiation intervals and plotting the UV absorption value with time of irradiation and by utilizing the

absorbance value, the degree of cross-linking in PAAs were plotted w.r.t time of irradiation.

4.2.2.2 Fluorescence

Fluorescence data were collected using either solution of PAAs in DMF or solid film. Fluorescence study was carried out using FP-6500, JASCO. PAA-1a (as solution) and PAA-1f (as solid) for fluorescence study. The excitation max (EX λ_{max}) and emission max (EM λ_{max}) for both in solution state and ion solid film were recorded and compared.

a) Effect of UV irradiation on fluorescence intensity

The effect of UV-vis irradiation on fluorescence intensity of PAAs has been studied by irradiating the DMF solution of PAAs by UV under the UV lamp in range which includes their λ_{max} . The change in the intensity of fluorescence was seen under the UV lamp. Further the fluorescence spectra were taken either by PAAs solution in DMF or by film.

b) Characterization by $^1\text{H-NMR}$

Characterization of samples of PAAs was done by $^1\text{H-NMR}$ technique. The ^1H NMR spectra were obtained by a Bruker Biospin AG 400 MHz using $\text{DMSO-}d_6$ as solvent. $^1\text{H-NMR}$ spectra were taken after each UV irradiation interval to observe the structural changes in the polymer chain.

4.3 Results and Discussion

4.3.1 UV-vis

The UV-vis spectroscopy was carried out by dissolving suitable amount of PAAs in DMF. λ_{max} of PAAs derived from DAS were found to be in the visible range due to the extended conjugation by unsaturation as expected by compounds containing stilbene moiety. The λ_{max} ranges from 348 to 358 nm depending upon the type of dianhydride used, however, the absence of unsaturation and hence no extended conjugation in EDDA derived PAAs resulted in no absorbance in visible region (Figure 3). The λ_{max} of PAA-1b and PAA 1c was found to be higher than other PAAs i.e. 358 nm and 357 nm respectively. The high value of λ_{max} could be due to the rigidity in the dianhydride structure and thus in their respective PAAs. The λ_{max} of PAA-1e is of least value, 348 nm due to the presence of carbonyl linker between the two phenyl ring in BTDA. λ_{max} of PAA-1d, and PAA-1f were 354 nm for each.

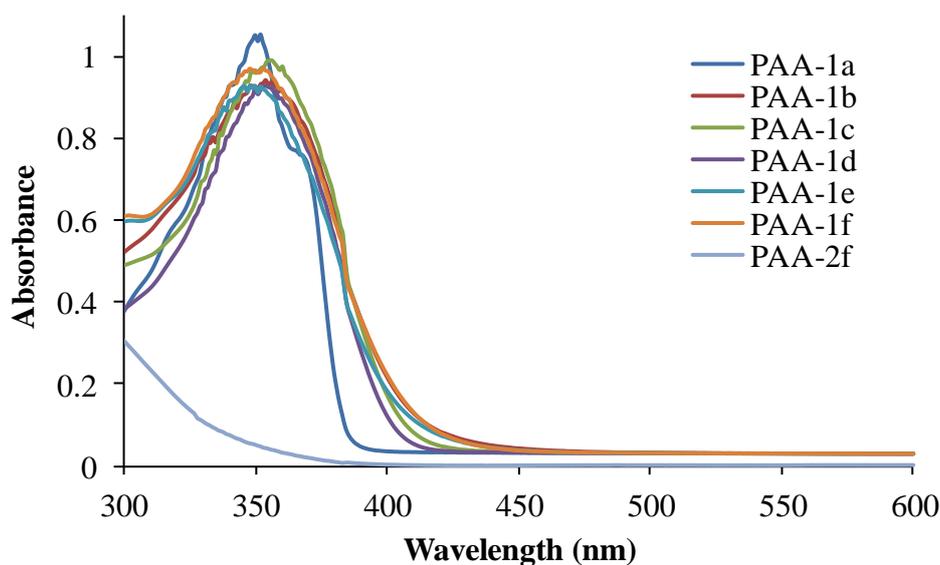


Figure 4.1 UV-vis spectra of PAAs.

Also as PAAs derived from EDDA were not UV-vis active due to absence of unsaturation and no extended conjugation, only DAS based PAAs were used for further studies. The unsaturated aliphatic linker between the two phenyl rings of DAS moiety remained unaltered during thermal imidization process and similar results can be expected from the corresponding PIs.

4.3.1.1 *Effect of UV irradiation on UV-vis absorption*

The effect of UV irradiation on absorbance was studied by prolonged irradiation of DMF solution of PAAs at $\lambda = 310\text{-}330$ nm by a focused UV beam from a Xenon lamp (MAX-303, Asahi Spector Co., Ltd.). The UV-vis spectra were recorded at different interval of irradiation time. As absorbance is due the presence of extended conjugation arising from unsaturated aliphatic linker (-C=C-) in DAS derived PAAs, we thought if we could alter the unsaturation and convert it into aliphatic part, there should be decrease in absorbance. As expected, we observed decrease in absorbance w.r.t irradiation time for all the DAS derived PAAs. The PAAs were undergoing (2+2) cycloaddition by utilizing -C=C- bond and forming cyclobutane ring resulting decrease in the PAA with photo absorbing -C=C- group and hence decrease in absorbance (Figure 4.2).

The dianhydride used played an important role in the rate of decrease in absorbance. The rate of decrease of absorbance at λ_{max} by UV irradiation studied. The absorbances at the λ_{max} of the respective PAAs were recorded w.r.t time of UV irradiation and graph was plotted between the absorbance and UV irradiation time (Figure 4.3).

CBDA and BPDA derived PAAs PAA-1a and PAA-1c respectively showed maximum decrease in the initial time which could be due to photo absorbing nature of

cyclobutane ring of CBDA and the continuous conjugation in biphenyl ring in BDPA which made efficient UV absorber which were absent on rest of the dianhydride derived PAAs. However, after 4 h no appreciable change in absorbance was noticed which could be the equilibrium state between the $-C=C-$ and cyclobutane ring.

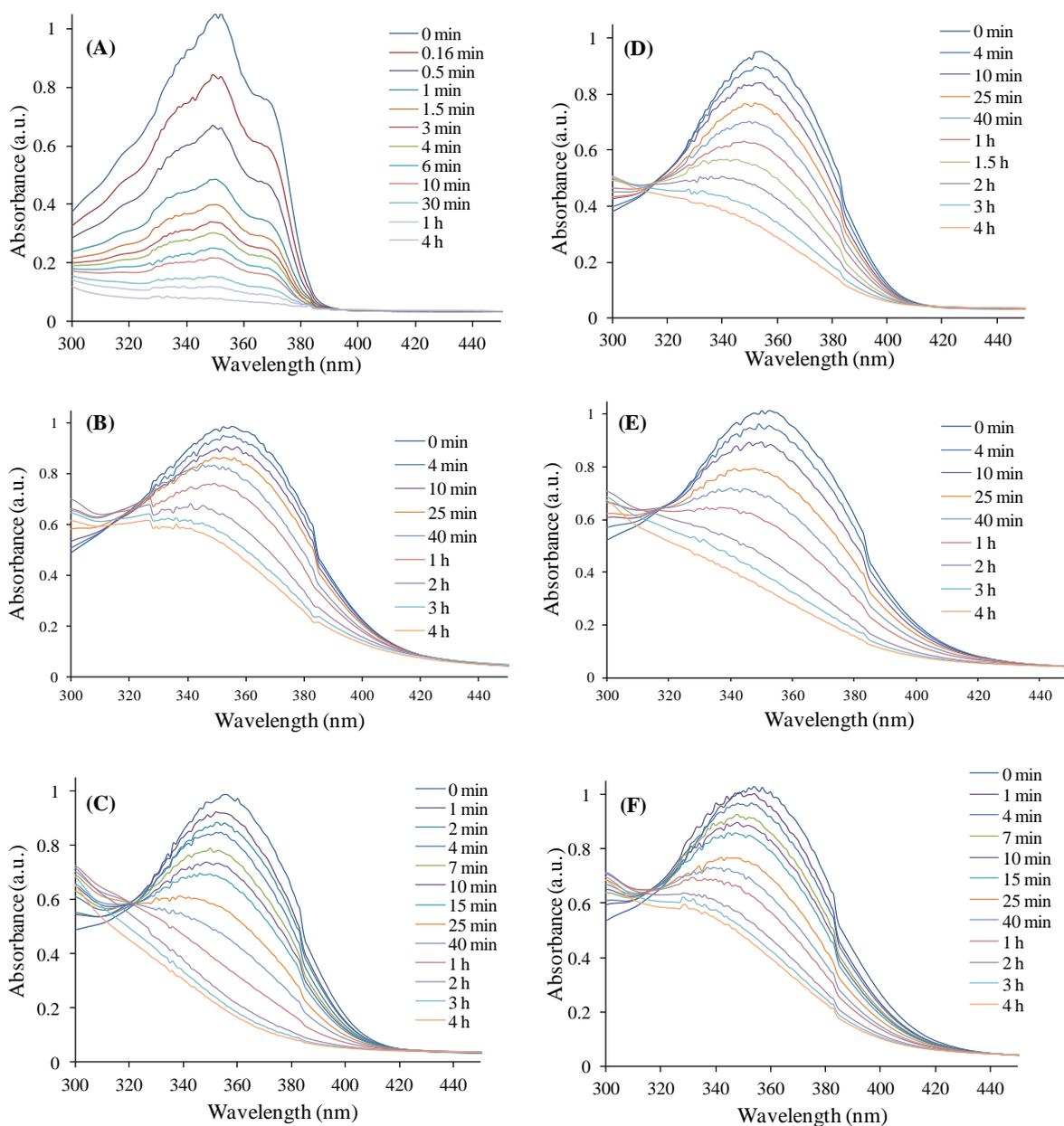


Figure 4.2 UV irradiation time dependence UV-vis spectra of DAS based PAAs, (A) PAA-1a, (B) PAA-1b, (C) PAA-1c, (D) PAA-1d, (E) PAA-1e and (F) PAA-1f.

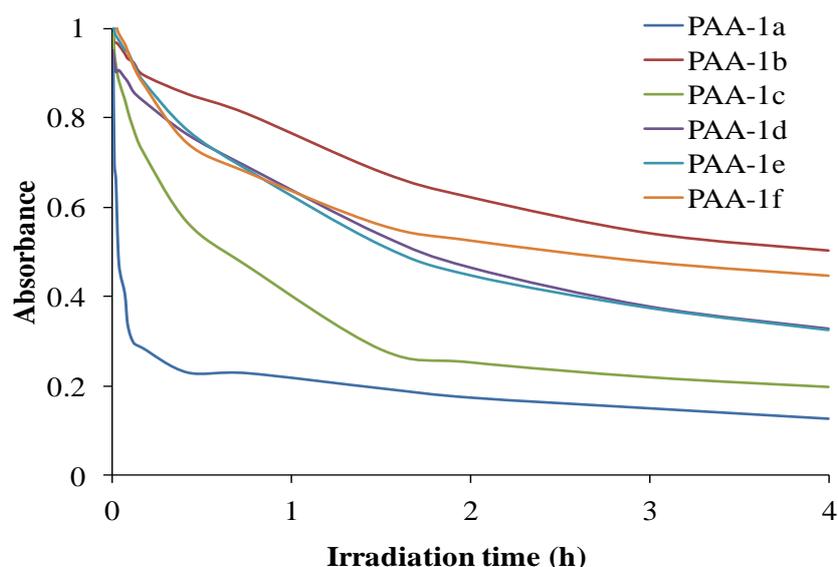


Figure 4.3 Decrease in absorbance w.r.t UV irradiation time at λ_{\max} (A) PAA-1a ($\lambda_{\max} = 350$ nm), (B) PAA-1b ($\lambda_{\max} = 358$ nm), (C) PAA-1c ($\lambda_{\max} = 357$ nm), (D) PAA-1d ($\lambda_{\max} = 354$ nm), (E) PAA-1e ($\lambda_{\max} = 348$ nm) and (F) PAA-1f ($\lambda_{\max} = 354$ nm).

4.3.1.2 Effect of UV irradiation on degree of crosslinking

The effect of UV irradiation on absorbance was studied by prolonged irradiation of DMF solution of PAAs at $\lambda = 310$ - 330 nm by a focused UV beam from a Xenon lamp (MAX-303, Asahi Spector Co., Ltd.). The UV-vis spectra were recorded at different interval of irradiation time.

The formation of cyclobutane ring after irradiation is nothing but the crosslinking of polymer chains. The cross linking degree of PAAs were determined by using the following equation:

$$\text{Cross linking degree (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

Where, A_0 is the absorbance at 0 min and A_t is the absorbance at time 't'.

The PAA-1a and PAA-1c showed the maximum cross linking degree (Figure 4.4) as evident from the decrease in absorbance which is due to the same higher photo absorbing ability of corresponding CBDA and BPDA dianhydride.

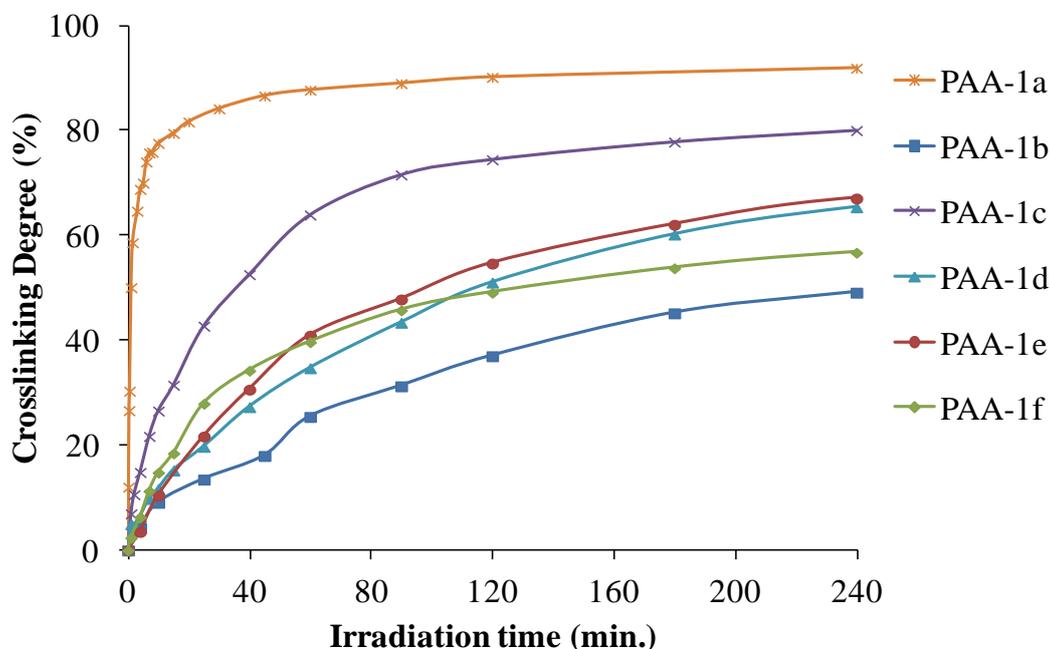


Figure 4.4 Effect of UV irradiation time on crosslinking degree of PAAs.

After exposure to UV-vis light, PAAs can readily absorb photon hence become activated and can utilize this absorbed energy either in isomerisation from *trans* to *cis* form or in [2+2] cycloaddition where latter is been used for the crosslinking between the polymer chains. The cross linking degree was found to be dependent upon the type of polymer as well as time of UV irradiation. As diamine used is same for all the prepared PAAs (PAA-1a to PAA-1f), therefore, whatever effect on the degree on crosslinking is there it is majorly because of the type of the dianhydride used, however, its only because of DAS's inherited double bond (unsaturation) which made them UV and fluorescence active.

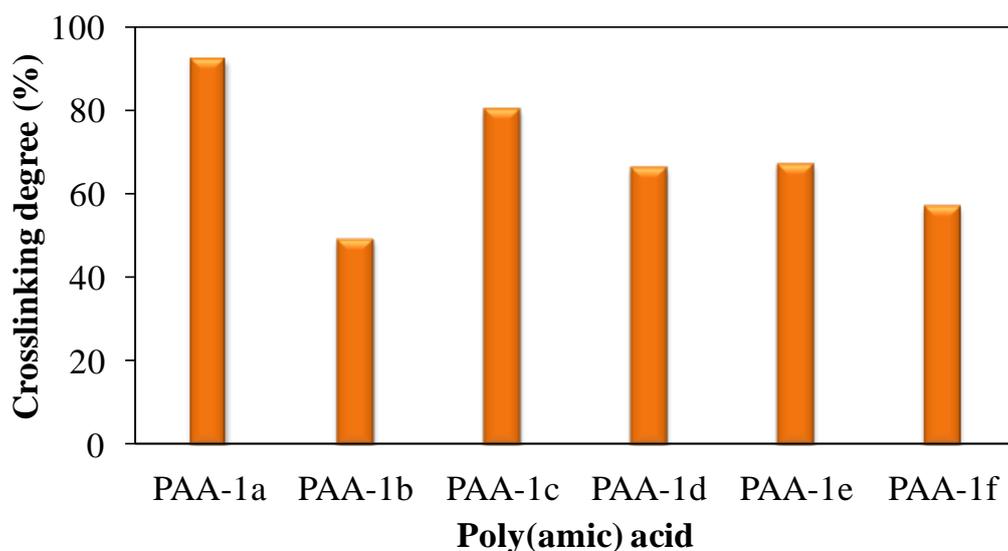


Figure 4.5 Comparative study of crosslinking degree of PAAs after 4 h of UV irradiation time.

Table 4.1 Crosslinking degrees of PAAs after 4 h UV irradiation time and time taken for maximum crosslinking degree observed.

Polymer	Crosslinking degree (in %)	
	After 4 h	Maximum (time)
PAA-1a	92	92 (4 h)
PAA-1b	49	63 (16 h)
PAA-1c	80	80 (4 h)
PAA-1d	66	81 (15 h)
PAA-1e	67	70 (6 h)
PAA-1f	57	66 (12 h)

The % of cross linking degree was obtained w.r.t irradiation time which showed the increase in crosslinking which is the crosslinking of polymer chain by forming a four member ring due to the opening of double bond present in polymer chain. The comparative study of crosslinking degree of PAAs is shown in Figure 4.4. Figure 4.5 shows that after irradiating PAAs solution for 4 h, the maximum drop in absorption or maximum crosslinking occurred in PAA-1a and the least in PAA-1b. **Trend of**

crosslinking degree in prepared PAAs was as follow: PAA-1a > PAA-1c > PAA-1e > PAA-1d > PAA-1f > PAA-1b. Hence, the order for inducing crosslinking of dianhydride used in PAAs is: CBDA > BPDA > BTDA > OPDA > DSDA > PMDA (Figure 4.5). Hence the PAA-1a was used for further studies such as fluorescence.

4.3.2 Fluorescence

PAA-1a (as solution) and PAA-1f (as solid) for fluorescence study. The excitation max (EX λ_{\max}) was observed at 348 nm while emission max (EM λ_{\max}) was observed at 389 nm for PAA-1a while for PAA-1f excitation max (EX λ_{\max}) was observed at 354 nm while emission max (EM λ_{\max}) was observed at 380 nm.

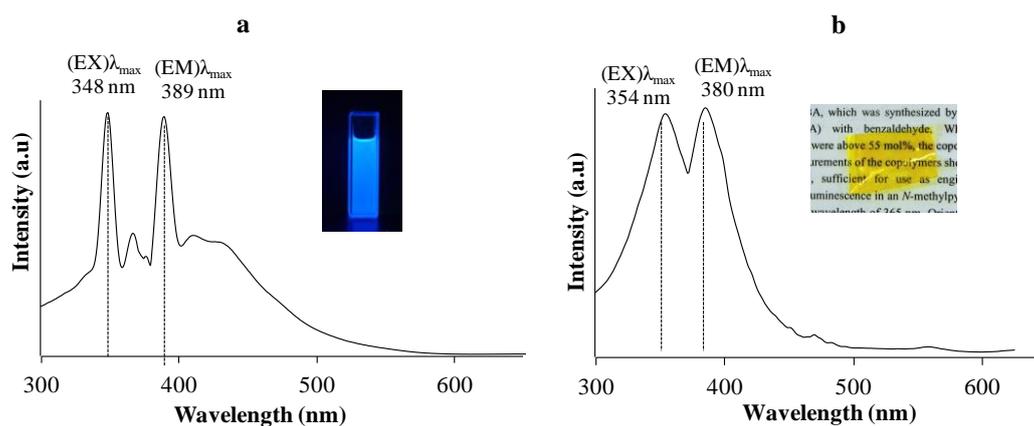


Figure 4.6 Fluorescence spectra of a) PAA-1a (in solution state (in DMF) and b) PAA-1f in solid state (as film).

4.3.2.1 Effect of UV irradiation on fluorescence intensity

As explained above, because of higher photoactivity and high crosslinking degree of PAA-1a, it was used further to study the effect of UV irradiation on fluorescence. Also the PAAs are UV-vis and fluorescence active because of presence of

double bond therefore the intensity of fluorescence should decrease with increasing UV irradiation time because of crosslinking of PAA chains through double bond.

The expected results are obtained from the fluorescence analyses. The intensity of fluorescence was found to decrease with irradiation time which is shown in Figure 4.7. The maximum fluorescence intensity was found without irradiation which kept on decreasing with time of irradiation and at 8 h irradiation almost no fluorescence was observed. Hence the fluorescence ability of PAA can be controlled by UV irradiation time and the fluorescence intensity can be tuned as per the requirement based upon application. Thus such polymer can play a key role in making materials which are required to possess control fluorescence at particular wavelength range.

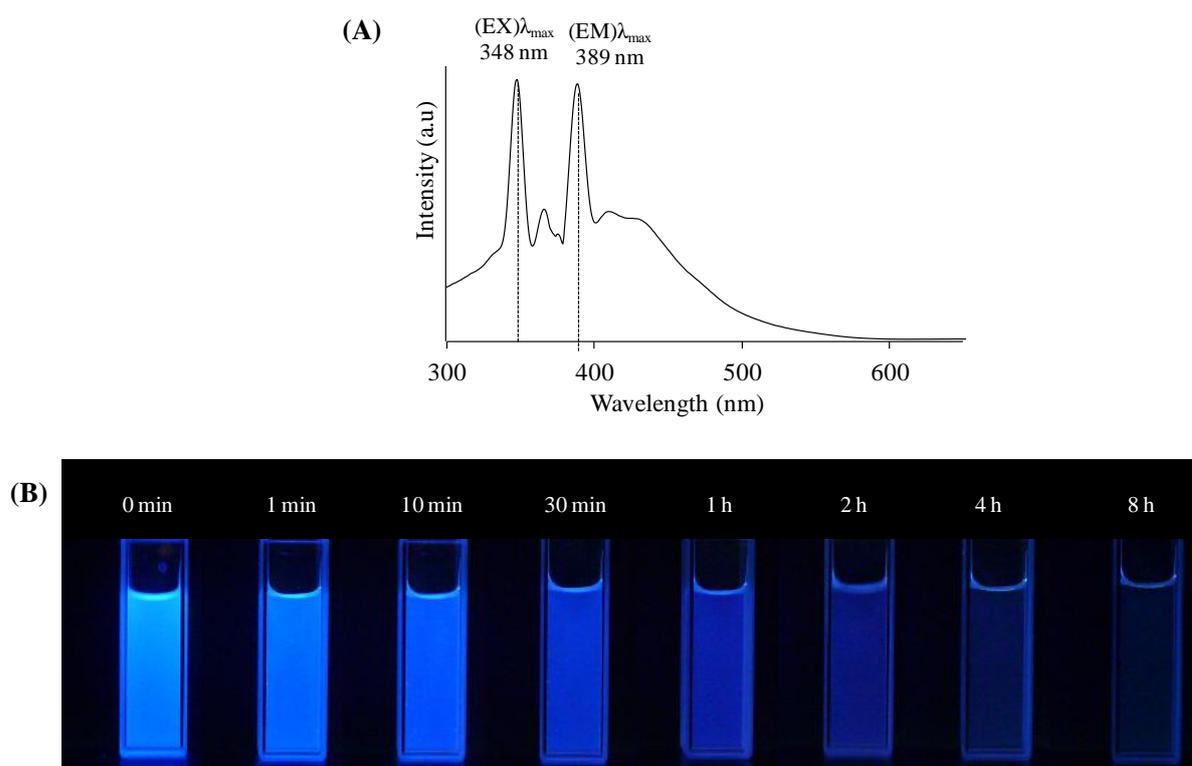
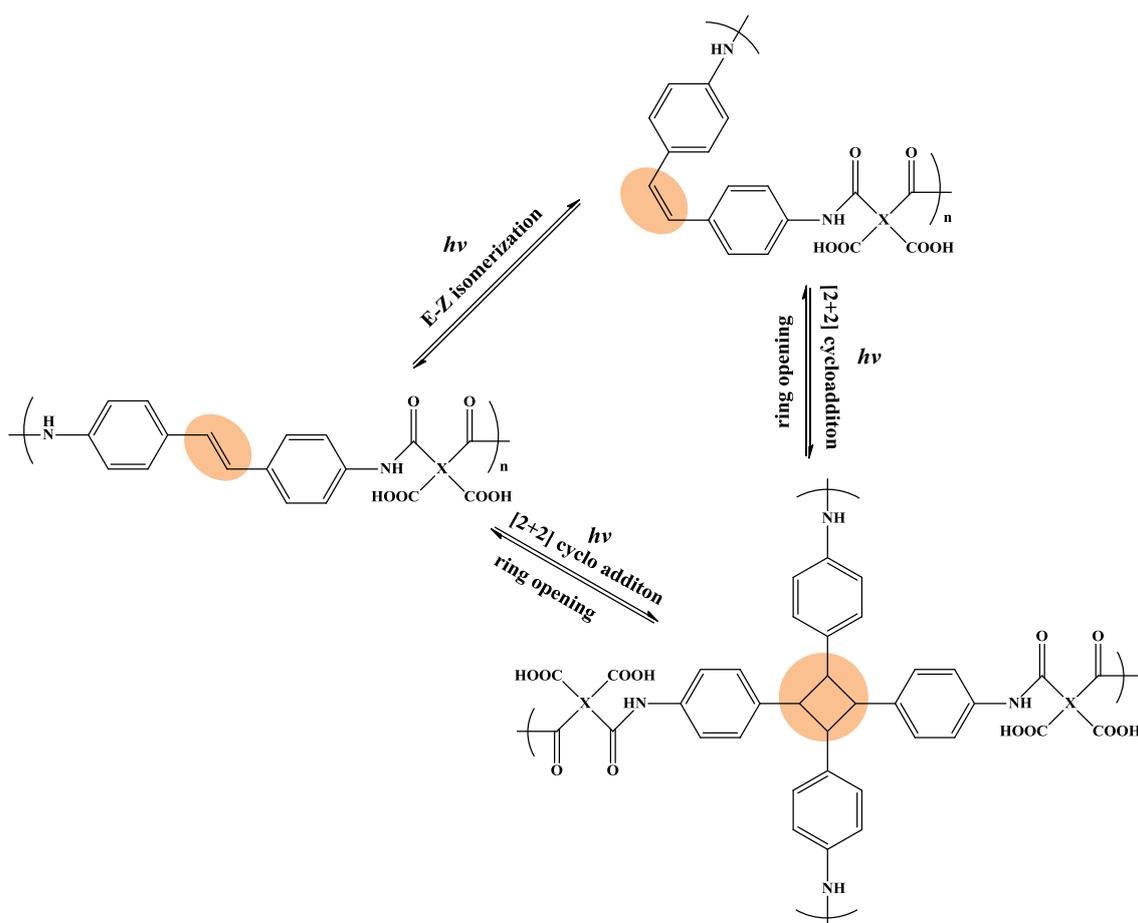


Figure 4.7 Fluorescence images showing the decrease in fluorescence intensity with UV irradiation time.

4.3.2.2 Characterization by $^1\text{H-NMR}$

The NMR spectra were taken after irradiation to analyse the change in structure and for the conformation of [2+2] cycloaddition and *trans* to *cis* isomerisation. $\text{H}^1\text{-NMR}$ of samples PAA-1a and PAA-1f were carried after each UV irradiation interval. The $\text{H}^1\text{-NMR}$ peak at 3.6 ppm, 6.5 ppm and 7.2 pm corresponds to cyclobutane proton and vinyl protons. Figure 4.8 and Figure 4.9 shows the $\text{H}^1\text{-NMR}$ spectra of PAA-6 and PAA-3 respectively. Occurrence of new peak confirms the formation of cyclobutane ring by the opening of double bond and undergoing cycloaddition. Scheme 1 shows the proposed mechanism of the cycloaddition.



Scheme 4.1 Proposed mechanism of cycloaddition in PAAs of DAS.

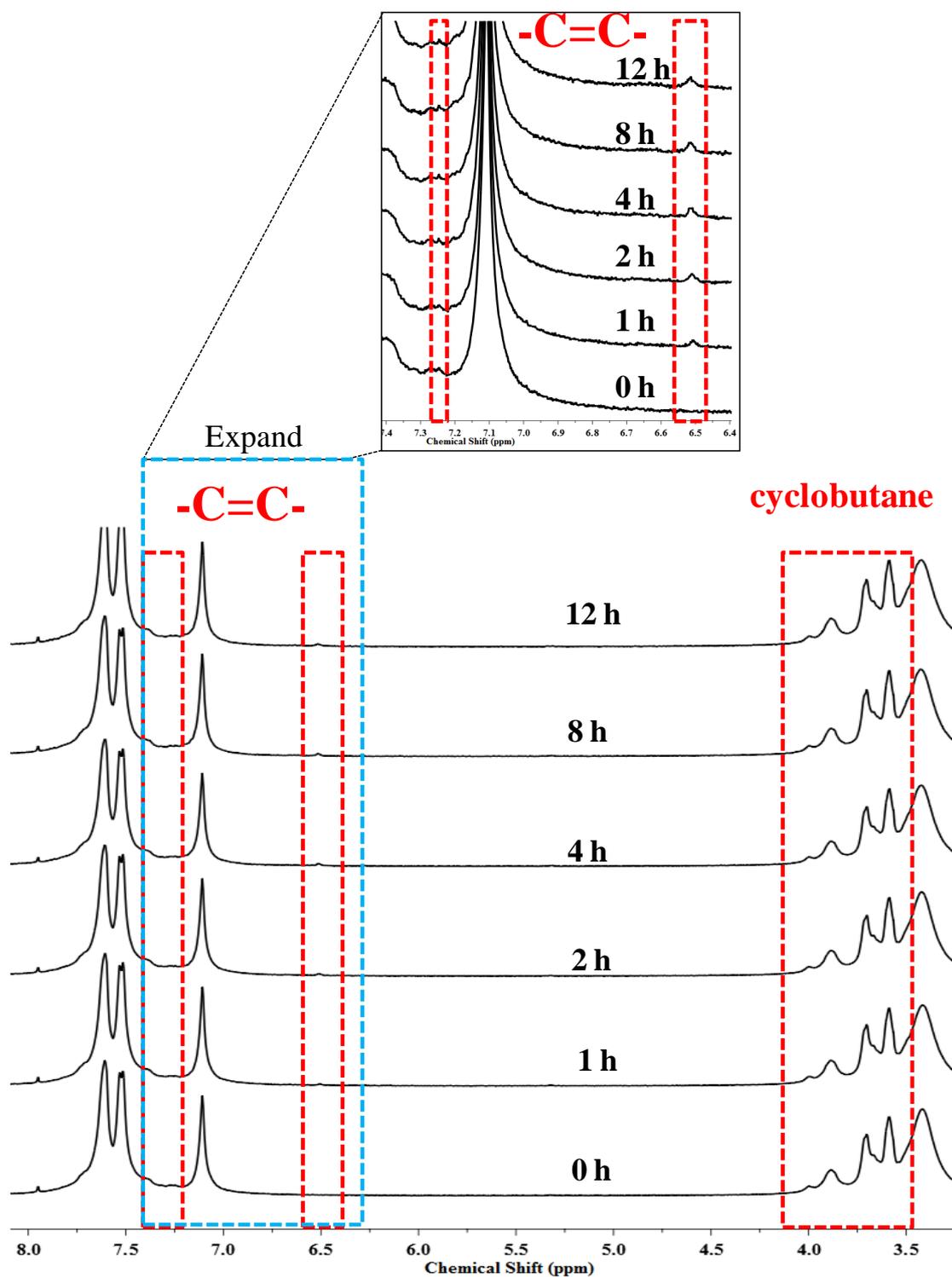


Figure 4.8 $^1\text{H-NMR}$ spectra of PAA-1a at different UV-vis irradiation time.

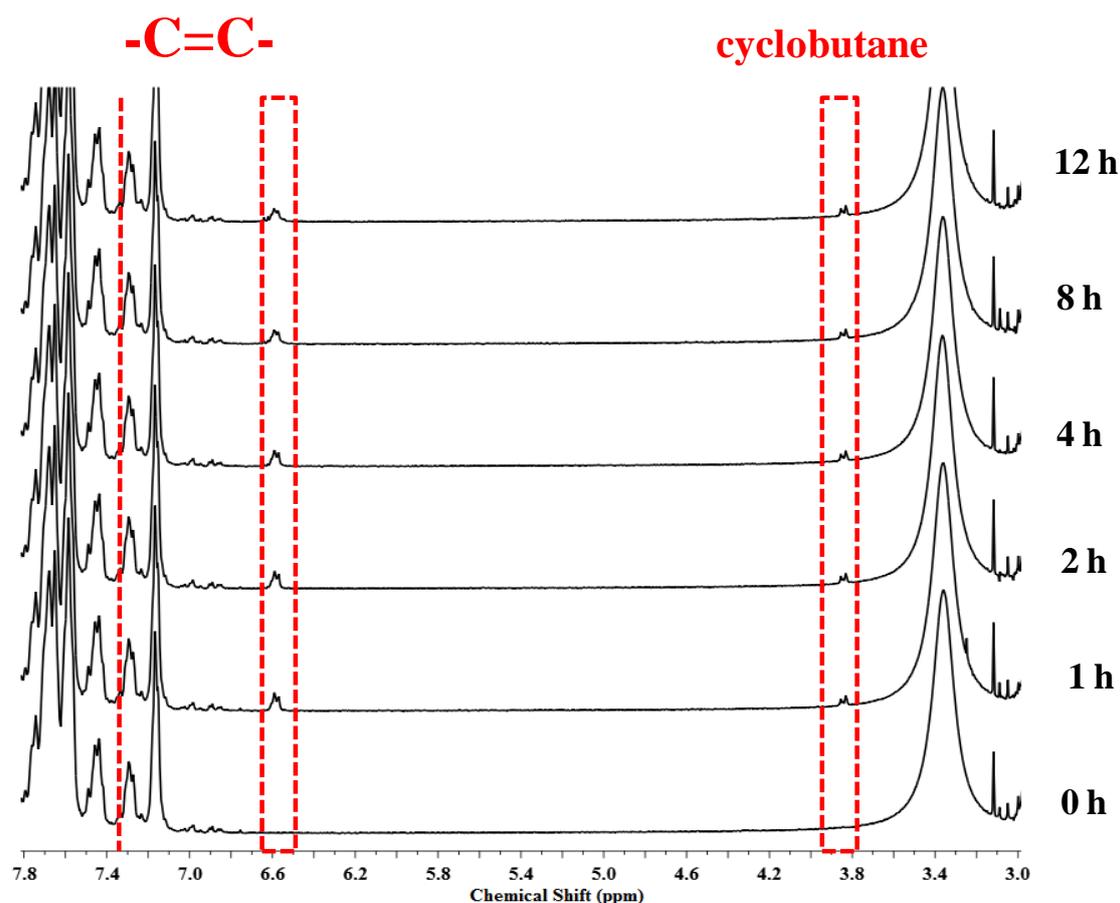


Figure 4.9 ¹H-NMR spectra of PAA-1f at different UV-vis irradiation time.

4.4 Conclusion

Photo-functional 4ACA was utilized to prepare bio-based photo-functional aromatic diamine 4,4'-diaminostilbene "DAS". A series of photo-active poly(amic acid)s and thus PI were prepared by the polycondensation of DAS with various available dianhydrides such as Pyromellitic anhydride (PMDA), Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), 3,3',4,4'-diphenylsulfone tetra carboxylic dianhydride (DSDA), 3,4:3',4'-biphenyl tetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (OPDA) and 1,2,3,4-cyclobutane tetracarboxylic dianhydride (CBDA). Photo-activity of prepared PAAs was explored by UV-vis and fluorescence.

Also the effects of UV irradiation time on PAA's properties were explored such as intensity of UV absorption and fluorescence.

All the polyimides were found to be UV-vis active and the fluorescence studies revealed the effect of UV-vis irradiation on PAAs. The fluorescence intensity can be altered by controlling the UV-vis irradiation time which can help in modifying the polymer properties to the desired one. UV activity of PAA-1a was found to be highest among all the prepared PAAs. Further the effect of UV-irradiation on fluorescence was studied on PAA-1a. The fluorescence intensity was found to depend on UV irradiation time which is due to the crosslinking of PAA chains which was confirmed by ¹H-NMR. The crosslinking and inter conversion of *trans* to *cis* to cyclobutane proposed and confirmed. The fluorescence intensity can be altered by controlling the UV-vis irradiation time which can help in modifying the polymer properties to the desired one.

CHAPTER 5

CONCLUSION REMARK

The development of these high performance bio-based polymers is crucial to establish sustainable low-carbon society. The syntheses of high performance bio-based polymer including polyamide and polyimides (PIs) derived from bio-available starting material was the uttermost focus of this research.

The **chapter 2** detailed with the synthesis of bio-based monomers of polyamide and polyimide such as diamine and diacid. New route for the synthesis of monomer diamines 4,4'-diaminostilbene (DAS), 4,4'-(ethane-1,2-diyl)dianiline (EDDA) and diacid N,N'-diacetyl-4,4'-diamino- α -truxillic acid (DADTA) from bio-derived 4ACA was established and characterized using ^1H NMR and ^{13}C NMR. Also a novel diamine i.e. 3,6-bis(4-aminobenzyl) piperazine-2,5-dione (BAPD) was prepared and the synthesis route was established and each step was optimized. The prepared diamine DAS and diacid DADTA were employed to react in presence of TTP in DMAc to form total bio-based polyamide which was characterized by FT-IR, GPC and TGA. From TGA it was observed that the polyamide showed high T_{d10} at 367 °C. Although DAS-DADTA polyamide showed high thermal stability but found to be poor in mechanical strength.

In **Chapter 3**, the synthesis and characterization of fully bio-based and semi-bio-based PIs were carried out. In order to prepare PIs, DAS was polycondensed with various available dianhydrides to syntheses PAAs first followed by PIs by thermal imidization. Among all the dianhydride used CBDA is the only dianhydride which can

be prepared from biomaterial hence, the PAA-1a and PI-1a is totally bio-based. Rests of the polyimide prepared are semi bio-based as only the diamine used was bio-based. PI-1f^{##} which was prepared from DAS and DPSDA at polymerization time 24 h, found to be best as per the tensile strength 132 MPa with young modulus 2.4 GPa and % elongation 5.6. The tensile strength of PI-1f^{##} was found to be more than the commercially available, most famous and extensively used polyimide KaptonTM.

The polymerization time found to affect the properties of poly(amic acid) and polyimide. PAA-1f from the chapter 3 was chosen to study the effect of polymerization time. As per GPC the 32 h polymerization time was found to be good, however, 24 h polyimides gave good thermal and mechanical properties. The polyimide from mixture of dianhydride possesses the properties lying from the polyimide from pure dianhydride.

The photo-functional properties of PAAs and PIs were examined in **Chapter 4**. All the PAAs were found to be UV-vis active and the fluorescence studies revealed the effect of UV-vis irradiation on PAAs. The fluorescence intensity can be altered by controlling the UV-vis irradiation time which can help in modifying the polymer properties to the desired one. UV activity of PAA-1a was found to be highest. Further the effect of UV-irradiation on fluorescence was studied on PAA-1a. The fluorescence intensity was found to depend on UV irradiation time which is due to the crosslinking of PAA chains which was proved by ¹H-NMR. The crosslinking and inter conversion of *trans* to *cis* to cyclobutane proposed and confirmed. The fluorescence intensity can be altered by controlling the UV-vis irradiation time which can help in modifying the polymer properties to the desired one.

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ACADEMIC ACHIEVEMENTS

Publications:

- 1) **Kumar A.**, Iwatani K., Nishimura S., Takagaki A., and Ebitani K. (2011). Promotion effect of coexistent hydromagnesite in a highly active solid base hydroxalcalite catalyst for transesterifications of glycols into cyclic carbonates. *Catal. Today*, 185, 241-264.
- 2) Okajima M., **Kumar A.**, Kaneko T. and *et. al.* (2013). Anionic complexes of MWCNT with supergiant cyanobacterial polyanions. *Biopolymers*. 99(1), 1-9.
- 3) Gandhi N., **Kumar A.**, Kumar C., Chaudhary P., Singh R. and Kaushik N. K. (2015) Synthesis, characterization, thermal and biological activity of some novel Cadmium (II) – pyridine and purine base complexes. *Main Group Chemistry*, 15, 35-46.
- 4) Mishra N., Kumar C., **Kumar A.**, Kumar M., Chaudhary P. and Singh R. (2015) Structural and optical properties of SnO₂-Al₂O₃ nanocomposite synthesized via the sol-gel route. *Materials Science-Poland*, <http://www.materialsscience.pwr.wroc.pl/>, DOI: 10.1515/msp-2015-0101.
- 5) **Kumar A.**, Chaudhary P., Singh R. and Kaushik N. K. (2015) Organotin(IV) complexes of thiohydrazones of phenethylamine: Synthesis, characterization, thermal and biological properties. *Main Group Chemistry*, DOI 10.3233/MGC-150196.
- 6) **Kumar A.**, Yasaki K., Ali, Md. A., Tateyama S., Takaya N., Singh R. and Kaneko T. (2016) High performance and photo-functional polyimides from 4-aminocinnamic acid via synthesis of 4,4'-diaminostilbene. *Polymer*, 83, 182-189.

- 7) **Kumar, A.**, Yadav, N., Bhatt, M., Mishra, N. K., Chaudhary, P. and Singh, R. (2015) Sol-gel derived nanomaterials and its application: A Review. *Research Journal of Chemical Sciences*, 5(12), 1-6.
- 8) Kumar C., Mishra N., **Kumar A.**, Bhatt, M., Chaudhary P. and Singh R. (2015) Structural investigation of nanomixed xSnO₂-Al₂O₃ synthesized by sol-gel route. *Appl. Nanosci.*, DOI 10.1007/s13204-015-0515-6.
- 9) **Kumar A.**, Yasaki K., Ali, Md. A., Tateyama S., Takaya N., Singh R. and Kaneko T. (2016) ¹H-NMR and FT-IR dataset based structural investigation of poly(amic acid)s and polyimides from 4,4'-diaminostilbene. *Data in Brief*, 7, 123–128.
- 10) **Kumar, A.**, Mishra, N. K., Kumar, C., Chaudhary, P. and Singh, R. (2016) Structural and optical investigation of alumina nanoparticles via the sol-gel technique. (*Accepted in International Journal of Nanoscience*).
- 11) **Kumar, A.**, Bahuguna, G., Mishra, N. K., Chaudhary, P. and Singh, R. (2016) Green synthesis of silver nanoparticles using aqueous flower extract of *Combretum Indicum*. (Submitted in Applied Nanoscience)

Conferences:

1. **National Conference on Nanoscience – Opportunities and Challenges, Maitreyi College, University of Delhi**, “Ultra-high performance and photo-functional total/semi-biobased polyimides from 4-aminocinnamic acid”. (Oral)
2. **National Conference on Nanoscience – Opportunities and Challenges, Maitreyi College, University of Delhi**, “Synthesis of silver nanoparticles using plant extract”. (Poster)

3. **National Conference on Nanoscience – Opportunities and Challenges, Maitreyi College, University of Delhi**, “Structural determination of $x\text{SnO}-\text{Al}_2\text{O}_3$ nanomixed metal oxide synthesized via sol-gel route”. (Poster)
4. **National Conference on Nanoscience – Opportunities and Challenges, Maitreyi College, University of Delhi**, “Synthesis of $\text{TiO}_2-\text{Al}_2\text{O}_3/\text{SnO}_2$ nanomixed metal oxides via sol-gel route and their structural investigation”. (Poster)
5. **3rd National Conference on Nanoscience and Instrumentation Technology, NCNIT-2015**, National Institute of Technology, Kurukshetra, Haryana, India, “Photo-functional semi bio-based polyimides with high performance from 4-aminocinnamic acid”. (Oral)
6. **3rd National Conference on Nanoscience and Instrumentation Technology, NCNIT-2015**, National Institute of Technology, Kurukshetra, Haryana, India, “Sol-gel synthesis of $\text{SnO}-\text{Al}_2\text{O}_3$ nanocomposite and its application in gas adsorption”. (Poster)
7. **3rd National Conference on Nanoscience and Instrumentation Technology, NCNIT-2015**, National Institute of Technology, Kurukshetra, Haryana, India, “Morphological and structural investigation of alumina nanoparticles synthesized via sol-gel technique”. (Poster)
8. **3rd National Conference on Nanoscience and Instrumentation Technology, NCNIT-2015**, National Institute of Technology, Kurukshetra, Haryana, India, “Synthesis of nanoporous alumina and mixed oxides alumina nanoparticles via sol-gel technology”. (Oral)
9. **ISCAS-2015, 9th National conference on Solis State Chemistry and Allied Areas**, Bhaskaracharya College of Applied Sciences, University of Delhi, India.

- “High performance and photo-functional polyimides from 4-aminocinnamic acid via synthesis of 4,4’-diaminostilbene”. (**Oral**)
10. **ISCAS-2015, 9th National conference on Solis State Chemistry and Allied Areas**, Bhaskaracharya College of Applied Sciences, University of Delhi, India. “Synthesis, characterization and morphological study of mixed Sn-Al oxide nanocomposite”. (**Poster**)
11. **ISCAS-2015, 9th National conference on Solis State Chemistry and Allied Areas**, Bhaskaracharya College of Applied Sciences, University of Delhi, India. “Synthesis and characterization of mixed alumina nanoparticles via sol-gel technique”. (**Poster**)
12. **2014, Emerging Trends of Nanotechnology in Drug Discovery**, Sri Venkateswara College, University of Delhi, India. (**Attended**)
13. **2014, National Conference on Recent Trend in Research in Chemical Sciences Manipal University, Jaipur, India**. “Synthesis and characterization of thioamides via bio-available amino acids and their metal complexes”. (**Oral**)
14. **2012, Rocky Mountain Regional Meeting, Denver, Colorado, United States**. “High performance bio-derived polyimides from 4-aminocinnamic acid”. (**Oral**)

Awards:

1. **Indian Association of Solid State Chemistry and Allied Scientists (ISCAS) Endowment Medal 2015.**
2. **Best Oral presentation award** in ISCAS-2015, Solis State Chemistry and Allied Areas conference.

3. **Guest Editor**, Special Issue, “Bioactivities of Organotransition Metal Complexes including Metallocene, **Bioinorganic Chemistry and Applications** journal (2014).
4. **Distinguished Alumni Award**, ARSD, University of Delhi (2014).
5. Recipient, **MEXT Scholarship, Japanese Government** (Ministry of Education, Culture, Sports, Science, and Technology) (April 2013-June2014).
6. **Qualified NET-2011 (June), JRF-UGC** in Chemical Sciences, Certificate number Sr. No.: 2061110075 and Ref. No.: 19-06/2011(i)EU-IV