High Performance Materials Based on Polyamides:

Synthesis, Characterization and Potential Applications

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By
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بسم الله الرحمن الرحيم

I dedicate this humble effort to my beloved parents.

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Hufsa Basheer

Forwards

The work described in this dissertation concerns the synthesis of terpolyamides using aromatic and aliphatic diamines. Different concentrations of diamines were condensed with different diacid chlorides to synthesize six varying series of polyamides. The aim of this work was to study the effect of addition of aliphatic content on the polymer chain.

The entire work is summarized into three chapters. A brief introduction of polyamides and ferrocene-based polyamides including their different synthetic schemes and potential applications is presented in *Chapter 1.* As well as it also contains plan of work along with details of instrumentation. All the experimental details are summed up in *Chapter 2.* Finally, *Chapter 3* comprises of results and discussions of structure elucidation by analytical techniques and spectral results. The supplementary data present in appendix includes FTIR, ^{1}H NMR,^{13}C NMR, viscosity, TGA and DSC thermograms.

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List of Abbreviations

B.p	Boiling point
Cp	Cyclopentadienyl
DCM	Dichloromethane
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
FT-IR	Fourier Transform Infrared
HMDA	Hexamethylenediamine
M.p	Melting point
NMR	Nuclear Magnetic Resonance
TEA	Triethylamine
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
WAXRD	Wide-Angel X-Ray Diffraction

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List of Sample Codes

List of Sample Codes based on Diamine

D = 2,2′-bis[4,4′-(aminophenoxy)phenyl]propane

Name of Polymers	Composition Ratio of Diamine (Aliphatic : Aromatic)	Sample Codes
Terephthalyol-based terpolyamide	0:100	$\mathbf{PD_{(100)}A_{(0)}T}$
	50:50	$\mathbf{PD_{(50)}A_{(50)}T}$
	70:30	$\mathbf{PD_{(30)}A_{(70)}T}$
	90:10	$\mathbf{PD_{(10)}A_{(90)}T}$
	100:0	$\mathbf{PD_{(0)}A_{(100)}T}$
Isophthalyol-based terpolyamide	0:100	$\mathbf{PD_{(100)}A_{(0)}I}$
	50:50	$\mathbf{PD_{(50)}A_{(50)}I}$
	70:30	$\mathbf{PD_{(30)}A_{(70)}I}$
	90:10	$\mathbf{PD_{(10)}A_{(90)}I}$
	100:0	$\mathbf{PD_{(0)}A_{(100)}I}$
Ferrocene-based terpolyamide	0:100	$\mathbf{PD_{(100)}A_{(0)}F}$
	50:50	$\mathbf{PD_{(50)}A_{(50)}F}$
	70:30	$\mathbf{PD_{(30)}A_{(70)}F}$
	90:10	$\mathbf{PD_{(10)}A_{(90)}F}$
	100:0	$\mathbf{PD_{(0)}A_{(100)}F}$

List of Sample Codes

List of Sample Codes based on Diamine

D’ = 2,2’-bis[4,4’-(aminophenoxy)phenyl]hexaflouropropane

Name of Polymers	Composition Ratio of Diamine (Aliphatic : Aromatic)	Sample Codes
Terephthalyol-based terpolyamide	0:100	$\mathbf{PD'_{(100)}A_{(0)}T}$
	50:50	$\mathbf{PD'_{(50)}A_{(50)}T}$
	70:30	$\mathbf{PD'_{(30)}A_{(70)}T}$
	90:10	$\mathbf{PD'_{(10)}A_{(90)}T}$
	100:0	$\mathbf{PD'_{(0)}A_{(100)}T}$
Isophthalyol-based terpolyamide	0:100	$\mathbf{PD'_{(100)}A_{(0)}I}$
	50:50	$\mathbf{PD'_{(50)}A_{(50)}I}$
	70:30	$\mathbf{PD'_{(30)}A_{(70)}I}$
	90:10	$\mathbf{PD'_{(10)}A_{(90)}I}$
	100:0	$\mathbf{PD'_{(0)}A_{(100)}I}$
Ferrocene-based terpolyamide	0:100	$\mathbf{PD'_{(100)}A_{(0)}F}$
	50:50	$\mathbf{PD'_{(50)}A_{(50)}F}$
	70:30	$\mathbf{PD'_{(30)}A_{(70)}F}$
	90:10	$\mathbf{PD'_{(10)}A_{(90)}F}$
	100:0	$\mathbf{PD'_{(0)}A_{(100)}F}$

ABSTRACT

Six series of terpolyamides having iso- propylidene and hexafluoroisopropylidene linkages in the molecular structure of polymer chain were synthesized successfully by combining aromatic and aliphatic diamine with three acid dichlorides. The aromatic diamines used were 2,2'-bis[4,4'-(aminophenoxy)phenyl]propane and 2,2'-bis[4,4'-(aminophenoxy)phenyl] hexaflouropropane whereas the acid dichlorides used were terephthalyol dichloride, isophthalyol dichloride and 1,1'-ferrocene dicarboxylic acid chloride. Thirty different grades of polymers were obtained via polycondensation method by varying the concentration of aliphatic diamine i.e. 1,6-hexanediamine. The effect of its subsequent increase in concentration was studied on the properties of resulting polyamides. All the synthesized materials were characterized by spectroscopic techniques including FT-IR and NMR , X-ray diffraction analysis, inherent viscosity, solubility, DSC and TGA. As well as CO_2 Adsorption activity was performed on the synthesized polymers. It was observed that fluoro polymers showed more CO_2 adsorption activity than non-flouro polymers and among fluoro polymers the ferrocene-based flouro polymers had more CO_2 capture activity than other organic analogues.

Chapter 1

Introduction

The search of unscrambling the mysteries of nature has enthused man towards searching and utilizing the earth’s natural assets. For existence, nature picks up the best of its occupants and clears out the rest. On the basis of this thinking, man had striven hard to persist the disciplinary rule books of the nature by adapting and also inventing the prevailing conditions of the environment. The essential requirements of an earliest man were the materials, without which evolution would not been possible. The increased requirement of a man on certain materials has directed the historians towards the terms for the original eras as the Stone Age, Iron Age and the Bronze Age. Ancient man didn’t need much thinking about use of the natural resources that’s why he used these resources as their fundamental form like stone, metal and wood. By the passage of time, the response in the worth and variety of materials was increased. To resolve such challenges, man hired systematic information in order to get maximum from natural earth’s assets[1]. The advancement to new as well as superior approaches was achieved by man to produce better and improved materials. These new approaches directed man towards the usage of the metals or the natural polymers such as wood, cotton in order to fulfill his desires till 19th century. Yet early 20th century was considered as the revolutionary era for material science because at that time steel and aluminium developed as new tools for the material engineers. Meanwhile this field is progressing continuously, providing superior materials like (high performance polymers) thus subsidizing the socio-economic advances of human society. Latest research is concentrated to prepare novel polymeric materials having enhanced characteristics such as better thermo-mechanical stability, improved conductance or insulation and flame retarding properties[2]. Polymer is an important class of materials that has either supplemented or substituted the conventional substances like wood, metals, glass in recent technical applications. Today it is difficult to visualize our life without polymers as they have become a main part of our consumer goods ranging from simple shopping to machineries for automobiles and aircrafts.

Properties of these polymers are crucial for their performance and differ intensely with temperature, strain rate as well as microstructure of polymer. The polymerization depends on all the attached constituents that occur in the chemical i.e. termed as monomer, that have same empirical formula but different structural formula which contribute to their totally exceptional physical and chemical properties[3]. The precise combination of monomers and the order in which they are arranged along the chain ultimately controls the mechanical properties of the material which they form. The recent IUPAC description of a macromolecule mentions an individual polymer molecule or an individual macromolecule however the term polymer mentions to a chemical material which consist of many macromolecules. Scientists have invested great effort into understanding and mimicking the natural processing and properties of these materials. As Jacob Berzelius created the terminology of polymer in 1833 but its practice and idea was taken after 90 years by Hermann Staudinger who was awarded by Nobel prize (1953) in salutation of his role in the field of Chemistry and for creating a historic milestone in the Polymer Science[3a, 4].

1.1 Polymers

Molecule comprised of multiple repeating units, which have characteristic high molecular mass and unique properties, is called as polymer. These multiple repeating units are termed as monomers, which develops the structural skeleton of a polymer [5]. The polymers can exist in different forms linear, branched or interconnected to form three-dimensional network.

1.2 Properties and Performance

Stucturally, the polymer is designed by monomers bonded in a covalent fashion to generate unique properties [6]. The polymer size is considered as important property during its processing and is indicated by molecular weight or the degree of polymerization DP, defined as repeating units present in a polymeric chain. When the relative molar mass of a molecule is 1000 or the DP value is 100, then the molecule is consdered as polymer [5b]. Physical properties including mechanical strength, hardness, visco-elasticity and solubility depends on the chain length or relative molar mass of polymer. Polymers are considered as polydispersed materials because the accurate prediction of its molecular weight is difficut due to the presence of many polymer chains with various lengths.

Hence, the average molecular weight is determined by summing up the average of molecular weights of all the polymeric chains in the sample[7].

1.3 Classification of polymers:

The huge variety and adaptability of the polymers require it to be categorized in an efficient way. The main principle of classification of polymers is based on source. Polymers are divided into two classes natural and synthetic polymers. The polymers obtained through resources present in nature are termed as natural polymers whereas synthetic polymers comprise all those which are man-made. On the broader aspect, polymers are classified as Organic and Inorganic polymers [7a, 10].

Organic polymers consist of carbon containing monomers that have organic moieties in the polymer chain linked together through covalent bonds. Polymers which are inorganic in nature consist of non-carbon monomers present in the back bone of polymer [7a, 11].

Most of the materials which are inorganic in nature contains the main group elements of the periodic table. The elements accquiring more attention in the research and development field includes silicon, phosphorus and iron[7].

Another class of polymers containing both organic and inorganic content, provides unique properties, are termed as Hybrid polymers. The material is synthesized by introducing a metal into a polymeric chain this gives the unique and enhanced properties such as thermal stability, heat resistant and electrical properties etc [7b, 12]. Polymers are classified on different basis. Some of them are explained as:

1.3.1 Based on the repetition or variety of monomers:

Polymers are classified as:

Homopolymer: When the polymer is formed by the same monomer all over its chain, it is named as homopolymer.

Copolymer: It is termed when the polymer is designed by at least two different monomers along the whole chain.

1.3.2 Based on reaction towards thermal treatment:

All polymers are divided in two main sets depending upon thermal behavior. Polymers which are easily softened on heating and molded in a desired shape are termed as *thermoplastics*. This type of material can be recycled by heat and pressure. The examples of commercial thermoplastics are polystyrene, polyolefin and poly (vinyl chloride). Whereas, *thermosets* are the polymers resist high temperature softening, solvent effects and cannot be processed thermally. For composites and coatings, thermosets are considered as appropriate materials. Some examples of thermosets include epoxy, the unsaturated polyesters and phenol–formaldehyde resins[9].

1.3.3 Based on the mechanism of polymerization

Upon the mechanism of polymerization, the polymers are categorized as *addition* or *condensation*—a scheme recognized by Wallace Carothers. Polystyrene polymerized through addition of the styrene monomers is an example of an addition polymer as shown in Figure 1.1. Vinyl-based monomers and olefins are also used for addition polymerization. Some other polymers that are polymerized not through addition but via ring-opening polymerization of a sterically hindered monomer with cyclic structure as shown in Figure 1.2. The formation of polyoxymethylene through ring-opening polymerization of trioxane is given in this figure .Table 1.1 shows the details about chemical structure of monomers and nomenclature commonly used of the most important addition-type polymers.

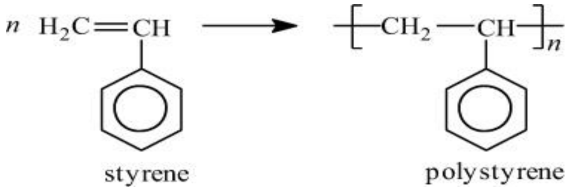


Figure 1.1-Polymerization of styrene.

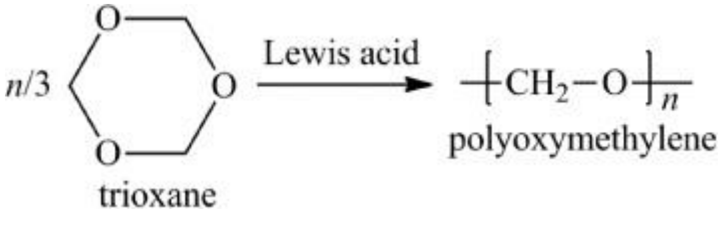
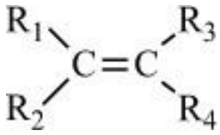
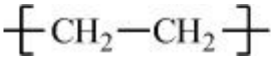
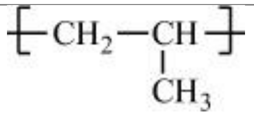
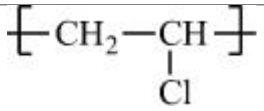


Figure 1.2-Ring-opening polymerization of trioxane.

Table 1.1- Examples of some important addition polymers derived from ethylene



Polymer	R_1	R_2	R_3	R_4	Repeating Unit
Polyethylene	H	H	H	H	 $\left[CH_2-CH_2 \right]$
Polypropylene	H	H	H	CH_3	 $\left[CH_2-\underset{CH_3}{\underset{\vert}{CH}} \right]$
Poly(vinyl chloride)	H	H	H	Cl	 $\left[CH_2-\underset{Cl}{\underset{\vert}{CH}} \right]$

1.3.4 Condensation polymers:

Polymers synthesized by random reaction of two molecules either a monomer, or oligomer,each one having with functional end units, like carboxylic acid or hydroxyl groups, are classified as polycondensation. Usually small molecules in the form of a gas, water or salt are eliminated in this reaction. High molecular weight polymers are synthesized by condensation reactions with high yield. By the polycondensation of adipic acid and hexamethylenediamine, nylon-6,6 is synthesized. In this reaction two molecules of water for each repeating unit are eliminated. Another example of polycondensation is formation of polycarbonate through bisphenol-A and phosgene. In this case two molecules of hydrogen chloride are produced as side product for every single repeating unit. The by-product changes when *sodium salt* of the bisphenol-A are polymerized, sodium chloride is eliminated instead of hydrogen chloride. In this case salt will precipitate out from the organic solvent during polymerization consiquently it can be easily removed as shown in Figure 1.3.

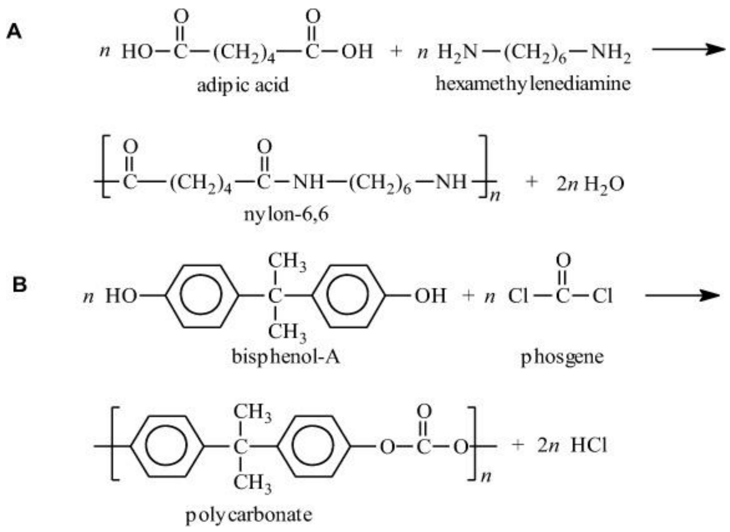
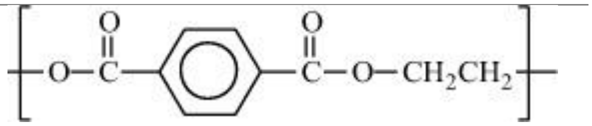
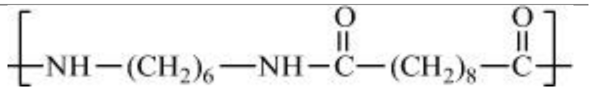


Figure 1.3- Two examples of a condensation polymerization.
A. Polyamidation of nylon-6,6.
B. Polymerization of bisphenol-A polycarbonate

While here are some other examples of the condensation polymers shown in Table 1.2.

Table 1.2- Examples of some condensation thermoplastics

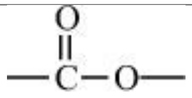
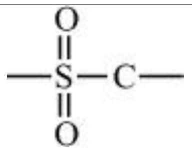
Polymer	Repeating Unit
Poly(ethylene terephthalate)	
Poly(hexamethylene sebacamide) **(nylon-6,10)**	

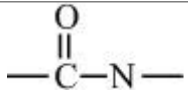
1.3.5 Based on the Polymer Structure

In addition to classification based on processing and the polymer characteristics, it can also be categorized based on their chemical structure. For example, Homochain polymers which have all the carbon atoms along their backbone. These materials might be further divided on the presence of single or double bonds in the main chain. Polyalkylenes (or polyalkylidenes) are carbon-chain polymers with only single bonds throughout the chain. Examples include polystyrene, polyolefins , and poly (vinyl chloride). On the other hand carbon-chain polymers having double bonds like diene elastomers .i.e. polyisoprene and polybutadiene are termed as polyalkenylenes.

Heterochain polymers comprised of more than one type of monomer in their main chain. These polymers are assembled into groups according to the kind of the chemical groups (e.g., carbonyl, amide, or ester) located in their backbone. The most important classes of the organic heterochain polymers are given in Table 1.3. Polysiloxanes is another important class of the polymers with heterochains with –Si–O– backbone linked to methyl or other substituent groups.

Table 1.3- Backbone structures of some important organic heterochain polymers

Polymer Classification	Backbone Group
Carbon–Oxygen Polymers	
• **Polyethers**	—C—O—
• **Polyesters of carboxylic acids**	 $-\overset{O}{\overset{\|}{C}}-O-$
Carbon–Sulfur Polymers	
• **Polysulfones**	 $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-C-$
Carbon–Nitrogen Polymers	

• **Polyimines**	$—C{=}N—$
• **Polyamides**	 $—\overset{\overset{O}{\|}}{C}—N—$

8, 13

1.3.6 Based on performance :

On the basis of properties and nature of the polymers,their performance differs with temperature ranges that they can bear easily deprived of damage of the basic polymer structure[5a]. In material engineering, the polymeric materials are categorized into three different classes. Polymers with an effective temperature range upto 200° F are named as commodity polymers or the general purpose polymers. [5]. These materials display good resistance to stimulus such as chemicals and solvents but exhibit inferior mechanical properties. These materials possess high co-efficient of thermal expansion. These polymers are used in the general packaging plastic to light duty structural applications[5b, 14].

The other class of polymers exhibit superior properties than the other one and is named as engineering polymers .The operating temperature of this class is high up to 300 °F. This material produced combination of mechanical and thermal properties which allows them to be employed in engineering applications[5a, 15].

High performance polymers makes the last class characterized by their extraordinary high temperature tolerance. Such polymers are also called as speciality polymers with excellent set of properties such as resistance to chemicals, solvents and radiations etc. These can withstand temperatures greater than 300 °F and some have their service temperatures skiped up to 800 °F [5a, 14].They show better dimensional stability and amazing flame retarding property. Due to all desireable characteristics this class is considered as most expensive materials among all the polymers[16].

1.4 Polyamides

Polyamides, also known as nylons, are essentially man-made polypeptides. Aliphatic polyamide, commonly known as nylon, was invented by Wallace Carothers in 1935 whilst working at the Du Pont Company and was the world’s first synthetic fiber. Nylons have found their largest application range in tires, carpets, stockings, upholstery, and adhesives and have become indispensable in today's society. All polyamides have a recurring amide group (–CONH–) present in the molecular structure and can be splitted into two major categories, namely aliphatic polyamides and aromatic polyamides. The aromatic polyamides form the focus of this thesis.

1.4.1 Structure

Polyamides are synthetic polymers with periodic amide groups(-CO–NH) in them as an integral part of the main chain as shown in Figure 1.4[11], synthesized by polycondensation reaction where diacid or acid dichloride react to form diamine, results in a bifunctional chain that continuously grow by the condensation of monomers with the elimination of a water molecule or a HCl in each consecutive step**.**

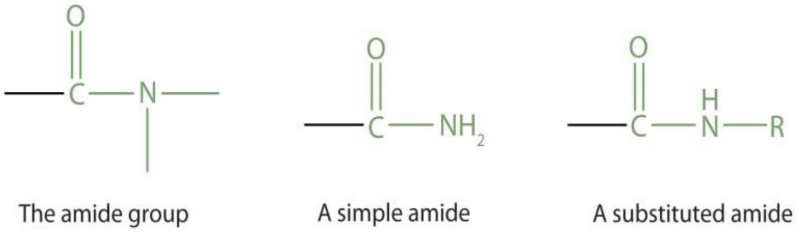


Figure 1.4- Amide linkages

Polyamide was first discovered as nylon by an American chemist named Wallace Hume Carothers (1953) at Du Pont [4]. This discovery was based on an amide linkage developed between hexamethylene diamine and adipic acid in the polymer chain.And as a result the polyamide nylon 6,6 was formed. The name was derived from monomers because the two monomers used in this synthesis comprised of six carbon atoms in their structure.The general reaction in this synthesis is shown in Figure 1.5.

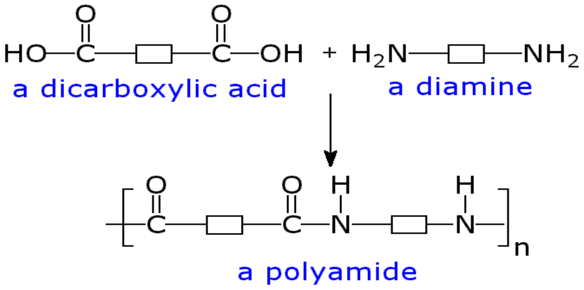


Figure 1.5- Synthesis of polyamide

Thermoplastic polymers are commonly used in all the fields of life from common use to high performance applications[17]. Long aliphatic chain to the aromatic system is the wide range of monomers. The nature of monomers decides the properties of the resulting polymer and in turn this extremely affects the characteristics from silky materials (Nylon) to bullet proof materials(Kelvar)[16].

1.4.2 Aramids & Nylon:

Polymers containing amide linkage are broadly divided into two classes, Nylon and Aramids. This classification depends on type of the monomers used and also on the resultant differences in the polyamide structure. Nylon refers to the polymers synthesized by aliphatic monomers and resultant polymer is aliphatic. The first high molecular weight aliphatic polyamide was Nylon 6,6 prepared by Carothers[18]. After that many different types of nylons are being synthesized commercially such as nylon 6,6; nylon-6,9; nylon-12; nylon-4,6 etc. As Nylon 6,6 is synthesized from two monomers of six carbon atoms each whereas polycaprolactum(Nylon 6) is designed by the polymerization of a single monomer with six carbon atoms. These materials are characterized by their plane, shiny surface and exist as a auxiliary for silk. These polymers are very stable but with low mechanical strength and still used in variety of applications ranging from silky clothing to the lubricants and mechanical parts[16].

Aramids form another class of polyamides with aromatic constituents.Aramids are commonly exist in nature and can also be synthesized by man. These materials exhibit superior properties like high thermal stability along with chemical resistance and electrical and mechanical properties. Due to stiff and rigid phenyl rings in the structure exceptional thermal and mechanical stability is induced. Infact, a polyamide is called as an aramid if it possess 85% or more of amide funtionality linked to the phenyl rings[16, 17b]. Kelvar is a common aramid formed by the reaction between . It has a high compact structure which results in high compact resistance so it is extensively used in making bullet-proof vests. Structure of Kelvar is shown in Figure 1.6.

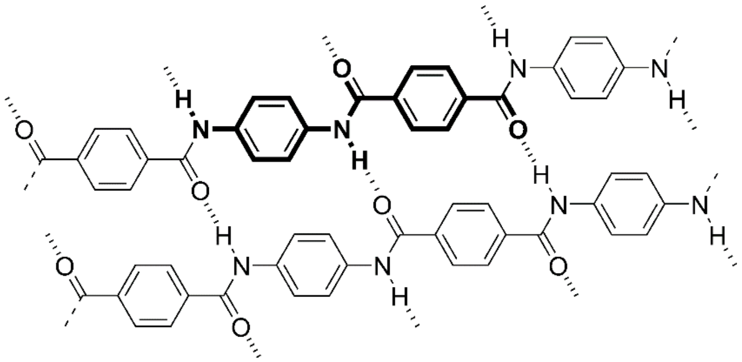


Figure 1.6 -Structure of Kelvar

1.4.3 Crystal structure and hydrogen bonding in polyamides

Important concepts in the field of polyamides are crystal structure and hydrogen bonding. An ideal polymer crystal is made up of an ordered, infinite repetition of identical structural units in space, referred to as the crystalline state.When there is irregularity in the structure , the polymer is in the so-called amorphous state. Generally polymers donot show an ideal crystal structure because of the long chain and irregularity of the polymer molecules. Most of the polymers possess the amorphous nature. Some polymers like polyamides show semicrystalline nature, indicating that both crystalline and semicrystalline regions are in polymeric chain.[19].

Crystals of polymers are usually thin and possess lamellar nature. The polymer's molecular chains are folded back and forth between the two principal faces of each lamella[20].

Many polymers, such as polyamides, exhibit a form of cross-linking in the polymer crystal through hydrogen bonding. Hydrogen bonding is a special case of the dispersional forces which are present between molecules in the absence of strong permanent dipoles[21]. Under regular circumstances, a neutral hydrogen should form a covalent bond with only one other atom. It is known, however, that under the right conditions a hydrogen atom is attracted by rather strong forces to two atoms, thus forming a hydrogen bond between these two atoms. In the extreme event, the hydrogen atom loses its electron to another atom and the bare proton forms the hydrogen bond. Generally hydrogen bond is present among the proton donor amide group and a proton-acceptor carbonyl group[22].

1.4.4 Effect of water on polyamides

Next to the interactions between polyamide chains leading to hydrogen bonding and crystallization as discussed above, there are also external interactions between the polyamide chain and its surroundings. One such interaction is between water molecules and the amide group. The water present is dependent on relative humidity of the air with which the polyamide is in equilibrium. The amount of water adsorbed at a given temperature and relative humidity is proportional to the amorphous fraction.The sorption of water by polyamides has a major effect on the polyamide's mechanical properties,similar to the effect water has on the mechanical properties of silk. The modulus and yield stress decreases, and the elongation and energy to break increases with an increase in water content. Water present in the amorphous phase exerts a plasticizing effect on all aliphatic polyamides that is quantitatively the same. Therefore the reported properties of polyamides are usually those of a mixture of polyamide and water[23].

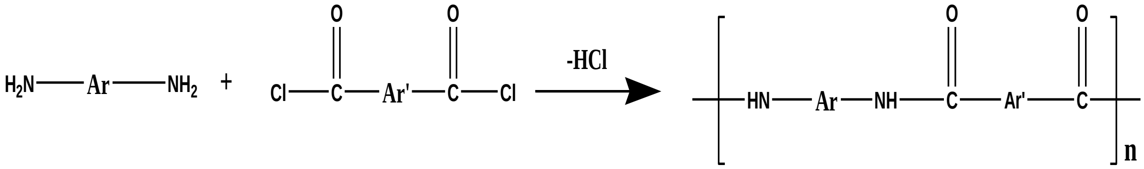
Polyamides are also sensitive to hydrolysis by water molecules due to the amide group present in the polymer main chain. During hydrolysis, water present in the amorphous phase at elevated temperatures can cause a reversal of the leading to a decrease in the degree of polymerization. At high temperatures the decomposition of polyamides proceeds very rapidly in water because under these conditions water possesses acid-like properties which favor hydrolysis. For example, 30 minutes at 380℃ and 280bar completely decomposes PA-6,6 to monomer units. At lower temperatures, particularly below 374℃, the decomposition rate is relatively low[24].

1.5 Synthetic Routes

Polyamides are produced by reacting diamine with diacid or diacid chloride.The reaction proceeds through polycondensation along with the removal of a small molecules like water or HCl. The series of methodology used to design aliphatic, semi-aromatic and aromatic polyamides are outlined in this section. Novel techniques employed for improving the yield of synthetic reactions are also highlighted below.

1.5.1 Low temperature solution polycondensation:

This method compromises a simple but fast way to produce polyamides. The synthetic protocol not only follows low temperature pathway but is very desirable as it diminishes the risk of side-products formation. In the scheme 1.1. given below, diamine is allowed to react with diacid chloride to produce the polyamide[17b].

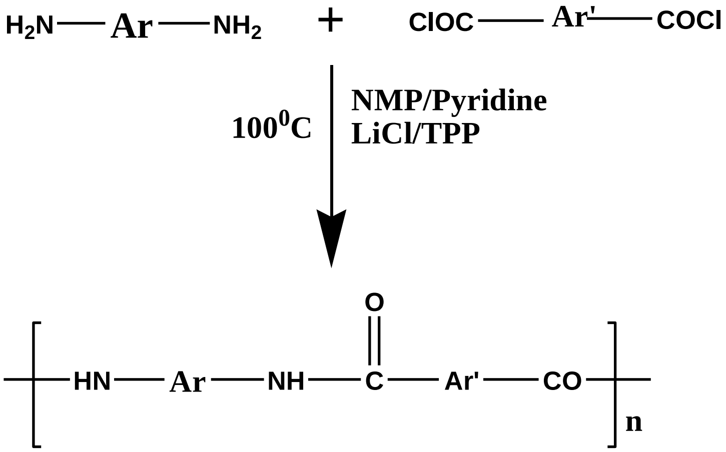


Scheme 1.1-General reaction of low temperature polycondensation

In order to achieve polymer chains with high molecular weights, various factors play crucial role like purity, stiochiometry and monomeric concentration alongwith the rate of stirring and temperature. The suitable solvent should be used because polar aprotic solvents e.g DMSO and DMF will eventually react with monomer i-e., diacid chloride[27].

1.5.2 Solution polycondensation method:

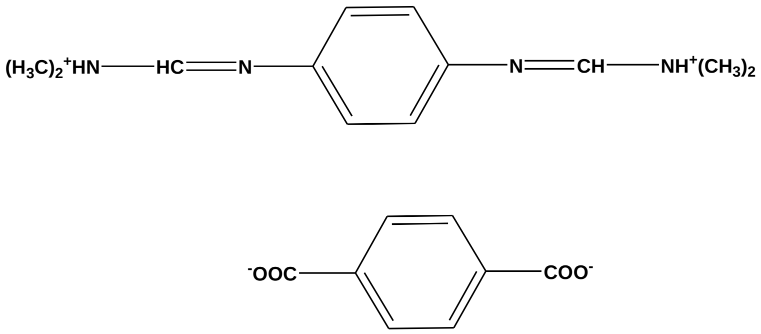
This method involves reaction through polycondensation in an amide solvent e.g N-methyl pyrrolidone (NMP), , dimethyl acetamide (DMAc) hexamethylphosphoramide (HMPA) or Tetra methyl urea (TMU), the polar solvent act as acid scavanger for the hydrogen chloride formed in the reaction as shown in Scheme 1.2. In order to obtain high molecular weight polymers stoichiometry, purity and the concentration of the monomers, reaction conditions like temperature and reaction rate, nature of solvents, solubility of the polymer and stirring rate etc are important factors[28].



Scheme 1.2- Solution polycondensation method

1.5.3 By heating of formamidinium salt:

Formamidinium salt shown in Figure 1.7 is heated by bulk or suspension polymerization technique, using the polymer precursors at a high temperture range of appproximately 200-225°C.As a result, the required polyamide is obtained by the elimination of dimethylformamide[26].

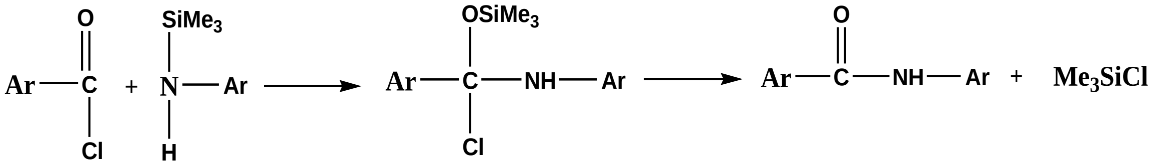


Formamidinium salt

Figure 1.7- Structure of formamidinium salt

1.5.4 By polycondensation of N-silylated diamine and a diacid chloride:

Trimethylsilyl chloride is used for obtaining high MW polymer i.e. polyamide because silyl salt activate diamine at low temperature 21°C. nucleophilic addition elimination reaction mechanism in two-steps has been planned for the acyl exchange of an acid chloride by an N-silylated amine[29] , shown in Scheme 1.3.



Scheme 1.3-polycondensation of N-silylated diamine and a diacid chloride

1.6 Properties & Performance of polyamides:

Polyamides specially aramids offers favourable set of properties. Here is a brief detail of the certain properties of the polyamides given below:

1.6.1 Melting point:

Generally polyamides have relatively high melting points in comparison with the other polymers due to the presence of special type of bond i-e., hydrogen bonds existing between the periodically occuring amide groups. Polyamide's physical properties are greatly influenced by changing the density of hydrogen bonds[25].

1.6.2 Solubility:

Polyamides have strong hydrogen bonding which is effective along the whole polymer chain and is responsible of its additional stability and resistance towards the chemicals and solvents [16, 17b].All the polyamides are likely to be soluble in basic solvents for instance NMP, DMSO and sulphuric acid. Whereas few ionic salts like LiCl or $CaCl_2$ also increase the solubility of polymers in suitable solvents[30]. Difficulties in processibility alongwith characterization of polymer are attributed to insolubility factor. Hence, reseachers are attentive towards the integration of flexible spacer for improving solubility of polymer chains[31].

1.6.3 Electrical properties:

It is expected that aromatic polyamides display electrical properties at unusual high temperatures[32].This property allows polymers to be engaged as insulators in circuit boards and in electronic appliances.

1.6.4 Structural effects in polyamides:

Properties of polyamides depend upon attached monomers, intermolecular forces (hydrogen bonding) and the degree of crystallinity. Another important aspect is length of the added aliphatic spacer [16, 33]. The occurrence of the amide linkage and wide-ranging hydrogen bonding in the polymeric chains results in very effective and strong intermolecular stacking of the polymer chain. Owing to this , these polyamides are frequently employed in industries and in manufacturing common household supplies[33-34].The structural features of these materials also show difficulty in their processing and charcterization. For instance, polyamides in the organic solvents exhibits limites solubility and at very high temperature it can melt or soften and may cause degradation[35]. Upon introduction of some suitable soluble linkages alongwith inorganic moieties can create ease of processibility without any compromise on required features like stability, strength etc[36].

1.6.5 Thermal and mechanical properties:

Polyamides has always being a major subject of interest for material scientists and engineers because of their mechanical and thermal properties in all thermoplastics[16]. Due to their structural property relationship, these materials or thermoplastics are being used as high performance materials[32]. They display thermal stability at extremely high temperatures and also their degradation offers the formation thick char which is itself a thermal insulator.

1.6.6 Liquid crystalline behaviour:

Generally polyamides are amorphous to crystalline in nature but aramids display crystal behaviour in their structure due to flexible orientation of aromatic groups and strong hydogen bonding. Liquid crystalline behaviour is determined in the case of solution of aramids linked at para position and is similar to the polypeptides[33-34].Meta-analogous donot exhibit such behaviours rather they show association with the ionic salts in solution[37].

1.7 Applications of polyamides:

The polyamides, aliphatic and aromatic, possess beneficial properties allowing them to be used in several industries. Their versatality in the form and functioning results in wide range of use from the textile to the mechanical tools and also automotive parts of machine[1, 16]. PAs are extensively employed in fire proofing clothing and due to their high impact strength, they are widely used in bullet-proof jackets. These materials have rare toughness, stability and strength and being used in cargo-covers, cords, tires, sport goods etc[32, 38].

Polyamides have unique experience of electrial properties and high temperature tolerance which accelerates their practical applications in electrical equipments , motors and transformers[35a].The resistance of aramids to ultraviolet (U.V.) and ionizing radiations is superior to that of nylons. The ‘Nomex’ fiber retains 76% of its original strength after exposure to 1550C in a vendee Graft generator, where as nylon 6, 6 are destroyed by the same exposure. Hence the aramides are used as tire cord in tire carcasses and as the belt in bias-belted and radial-belted tires, V-belts, cables, parachutes, body amour and in rigid reinforced plastics in general and more specifically in high performance boats and air crafts, in circuit boards, in filament wound vessels, in fan blades and in sporting goods.

The exceptional stability of polyamides towards hydrolysis makes them best for designing of water-proofing agents e.g. filter bags, the cloths for presses used in the industries and for thread used in automated machines[16, 33]. PAs show resistance towards chemicals such as alkalis and some solvents.

Hence aramids are employed as an protective clothing in industries, clothing of welders, protective shields, coats for fire department, jump suits used by forest fighters, fight suits weared by pilots of armed services, mail bags, carpets, cargo and boat covers etc. Due to the high dimensional stability, the aramides fibers of moderately high modulus are used in reinforcement of tire nose and v-belts.

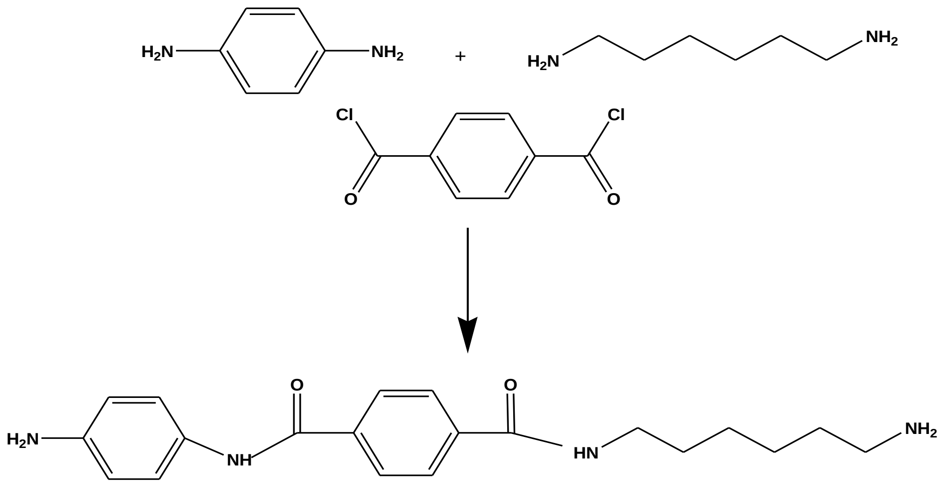
Their good selectivity characteristics make their use in reverse osmosis membranes.Their durability and light weight behaviour allow them to offer medical applications. Polyamides are used in the preparation of gas separation modules.These materials are also extensively employed in the isolation and removal of various salts from sea or brackish water[39].

Moreover, the excellent opto-electronics and liquid crystalline properties mark them as ideal candidates for electronic devices and appliances[35a].

1.8 Terpolymer:

1.8.1 Structure

The word ter used for combination of three units repeating alternatively in the polymer chain. Terpolymers are synthesized by the polycondensation mechanism by reacting three monomers together alongwith the removal of a small molecule. Ethylene–Methyl Acrylate–Acrylic Acid is a commercially available thermoplastic terpolymer.The example of synthesis of a terpolymer is shown in Scheme 1.4.



Scheme 1.4- Synthesis of a terpolymer.

1.8.2 Performance & properties:

The term polymer denotes to a mixture of three monomers altogether. These monomers are joined to each other via functional groups. The additional and improved properties are exhibited by polymer due to combination of individual qualities of three monomers[40]. Practically terpolymer can not be just considered as a mixture of monomers rather it is a combination of particular characteristics that are combined together in our desireable extents by reacting monomers. Mostly the improvement detected in the terpolymer is its stability compared to other polymers. Along with stability, the tolerance range of high temperature also improved upto many folds[41]. This behaviour depicts in their glass transition temperature which exhibits that these materials are more stable thermally.

Terpolymers generally have reactive functional groups with active coordination centers like O, N and S in the polymeric structure. Hence, they can form co-ordinate covalent bonds easily with some metal ions like Fe^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}. These materials are also employed as ion-exchange resins because of their selectively chelating property with metal ions and removing them from the desired media.

Terpolymers also display resistance towards chemicals however due to the reactive centers in polymer microstructure, these polymeric materials show better processibility due to enhanced solubility [42].

1.8.3 Applications:

Terpolymers are generally employed as sealants because of their exceptional adhesion property, exceptionally high durability and high thermal stability[43]. The terpolymer chemistry has improved the sealant industry due to extraordinarily high adhesion with all type of materials like bricks, plastics, concrete etc at temperatures where almost all of the sealants fail[43]. Mostly,these materials are regarded as high performance universal sealants[44]. They show various applications because of selective chelating ability and hence used in ion-exchange resins, purification methods and in treatment plants for waste water. The capability of terpolymers to remove the metal ions is unique and the efficiency is good over a wide range of pH and for extended time[41]. Novel polyvinyledene fluoride based terpolymers show much better and improved properties as compared to most of the ferroelectric polymers[41b].

Terpolyamides having fiber forming ability is being used in hot melt adhesives. The terpolyamide fibers have outstanding resistance against boiling water ,moisture and weathering [40]. These are also designed as reinforcement for the rubber tires in automobiles and in making different shapes of objects by film casting, extrusion etc[44-45].

1.9 Ferrocene:

Metals of the first transition series of the Periodic Table have been synthesized as Bis-(cyclopentadienyl complexes) and isolated. They are known as metallocenes. The complex which have iron as metal center is called ferrocene which has sublime properties and it serves in numerous applications[46]. The structure of ferrocene is shown in Figure 1.8

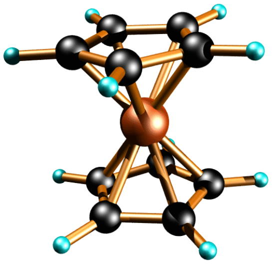


Figure -1.8 Structure of Ferrocene

1.9.1 Discovery of ferrocene

The discovery and synthesis of ferrocene is the revival of the organometallic chemistry[47]. Ferrocene discovery was an accidental and aided to be a major advancement in the field of chemistry and organometallic chemistry. Reacting cyclopentadienyl magnesium bromide and ferric chloride, Pauson and Kealy of Duquesne University (in 1951) synthesized ferrocene. They decided to oxidatively couple the diene but fortunately they found an orange dusty powder which displayed remarkable stability upto 400℃[48].

1.9.2 Physical properties of ferrocene

Ferrocene is thermally very stable withstanding heat upto 470℃. It is an orange color crystalline compound having melting point about 173-174℃ and boils at 249℃. It is fairly soluble in most of the organic solvents such as benzene, dichloromethane etc but shows insolublility in water. It is moderately resistant towards air and moisture[43].

1.9.3 Chemical properties

Ferrocene, although a stable compound but still it shows reactivity in many chemical reactions. These reactions are unable to disturb the aromatic system. Extensive derivatization of ferrocene is carried out by the reactions on cyclopentadienyl rings. Reactions common to ferrocene include protonation, redox reactions, electrophilic substitution and metallation[46].

1.9.4 Ferrocene-based polymers

Metal atom attached to the organic moieties develop a new class of compound, organometallics. Until the discovery of ferrocene, the progress was very slow and unsatisfactory, but after the tremendous discovery an amazing revolution in field comes out. Polymers exhibit enhanced resistance against light, temperature, air and chemicals due to the addition of ferrocene. Such polymeric materials have sublime properties which includes thermal stablility and high performance. These remarkable properties because of ferrocene have encouraged researchers to design more ferrocene-based polymers such as ferrocene in the main chain of polymer, side chain ferrocene based polymers and ferrocene based dendritic polymers etc[49].

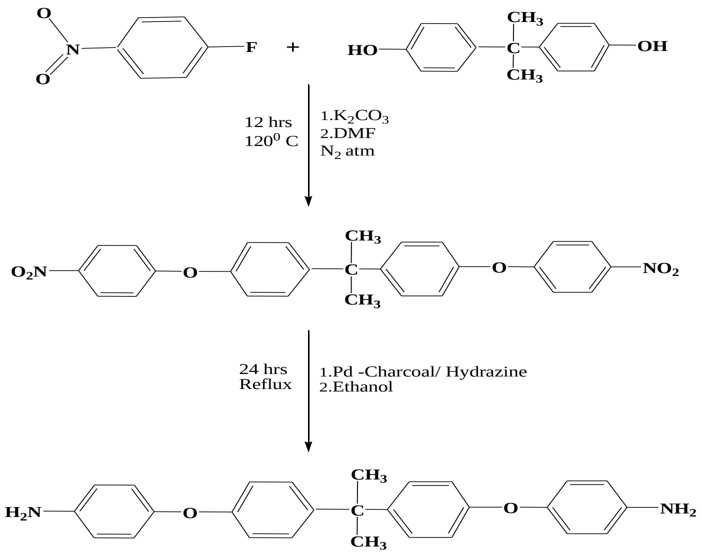
1.9.5 Properties and applications of ferrocene-based polymers

Ferrocene provides the polymers with unique properties with several applications in daily lives, in technology and industry. Materials with ferrocene moiety have thermo-mechanical, opto-electronic and magnetic properties. Few applications are explained here in detail.

Amperometric enzyme electrode are fabricated as a derivative of ferrocene based polymer[50]. For the detection of glucose, siloxane polymers with ferrocene functionality are frequently employed in designing amperometric bio-sensors and as mediators in glucose oxidase modified carbon paste electrodes[51,52]. Ferrocene-based materials are widely employed in electrosynthesis and electrolysis[53]. Polyferrocenylsilanes show ferromagnetic properties with super paramagnetic nanostructures[54]. Ferrocenebased polymers are also employed for making electrical components due to their better redox properties. Due to high thermal stability,the ferrocene based block copolymers show potential application in fire-retarding materials and production of fire-proof clothing[55]. They also act as potential candidates in the treatment of cancer [56].

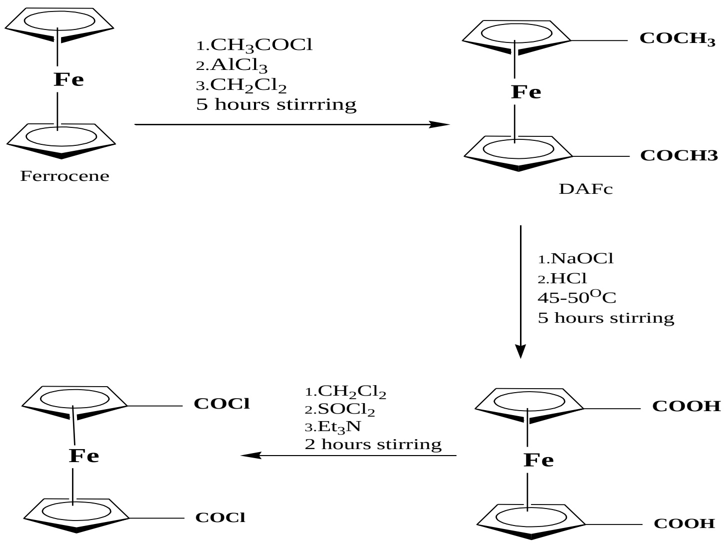
1.10 Plan of work:

The objective of this work was to synthesize six series of terpolyamides via polycondensayion method. The synthesized polymers were then characterized by using different analytical techniques like FT-IR and NMR spectroscopy , thermogravimetry, differential scanning calorimetry, XRD and viscometry.

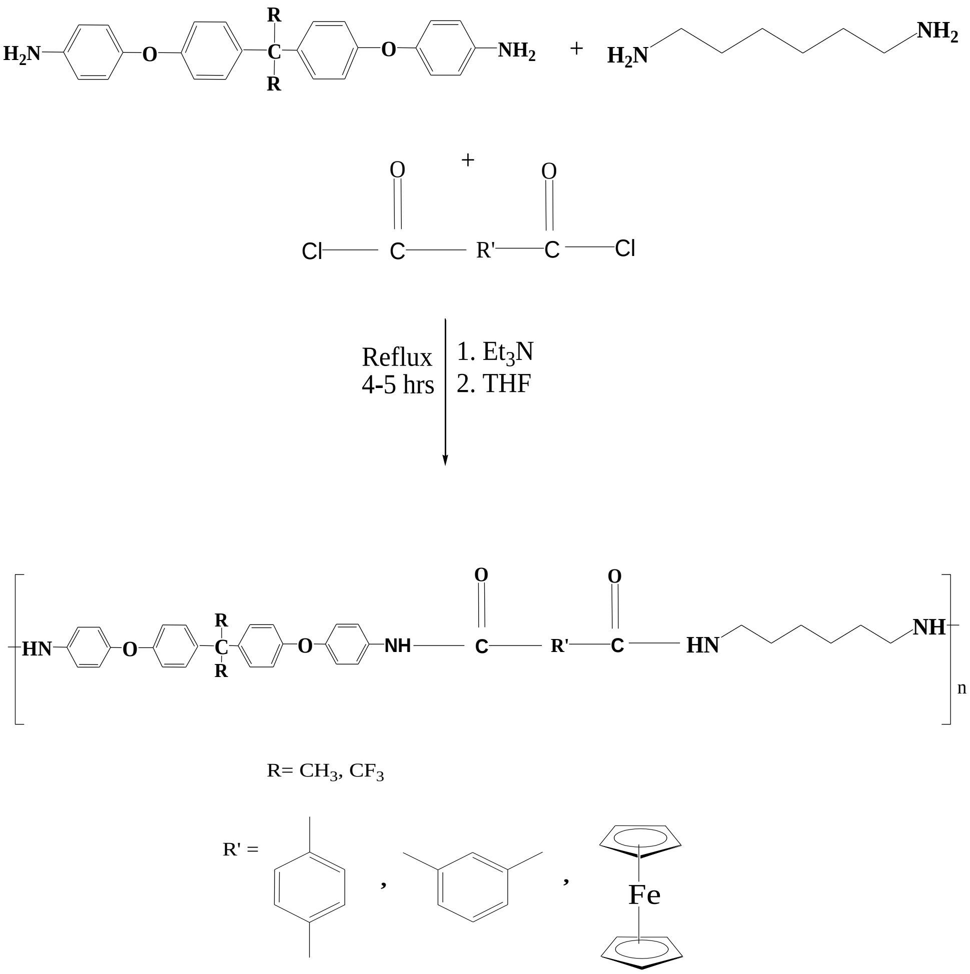


2,2'-Bis[4-4(aminophenoxy) phenyl] propane

Scheme 1.5- Synthesis of diamine



Scheme 1.6- Synthesis of 1,1’-ferrocenedicarboxylic acid chloride (FcDc)



Scheme 1.8- Synthesis of organic and ferrocene based polyamides

1.11 Characterization techniques:

A brief discussion of the characterizations techniques employed on the synthesized terpolymers is outlined in this section.

1.11.1 Solubility

The solubility of chemical compound and polymers is an important feature for deciding its utility. Solubility data provides information regarding its structure and indicates the stability, crystallinity alongwith extent of cross linking in the polymeric chains[57].

1.11.2 Infrared spectroscopy

One of the frequently used analytical technique for the functional groups detection is infrared spectroscopy. The peak in specific region confirms the corresponding functional groups present in the product. For polymers, this method is mostly used because the sample can be analyzed in solid state and the problem of solubility is avoided.

Upon irradiation of sample, the excitation to a higher energy level of molecule takes place. The wavelength of absorbed light is directly related to the difference of energy between the ground and excited states. This specific wavelength is characteristic for structure of the molecule. The FT-IR spectrum comes as a result is a plot between % transmittance and wave number (cm^{-1}). Some of the typical applications related to FT-IR spectroscopic analysis includes identification of the materials, constituents in the multi-layered and materials like residues, fibers and particulates etc[58].

1.11.3 Nuclear magnetic resonance spectroscopy

The technique which gives complete information about the structure, dynamics, reaction state, and chemical environment of the molecule, is nuclear magnetic resonance spectroscopy. 2–50 mg of a purified sample, dissolved in a suitable solvent, is used for analysis. The position of different NMR signals is reported relative to the reference signal, usually TMS (tetramethylsilane). The signal is presented as chemical shift (parts per million), by dividing Hz by MHz and multiplied by a million[59,60].

Proton NMR spectra of most of the organic compounds are explained by the chemical shifts in the range of +14 to 0 ppm and by the spin-spin coupling between the protons. The abundance of the individual proton is reflected by the integration curve [61].

Carbon-13 nuclear magnetic resonance is another form of nuclear magnetic resonance (NMR) spectroscopy. It is like the proton NMR and used in the identification of carbon atoms in organic moieties, just as proton NMR recognizes hydrogen atoms in a sample. For the chemical structure elucidation ^{13}C NMR is considered as an important tool. It detects only the isotope ^{13}C, with only 1.1% natural abundance and ^{12}C is not detectable because it is NMR inactive due to zero net spin[62].

1.11.4 Differential scanning calorimetry (DSC)

This technique is employed to determine heat flow from a substance by means of function of temperature relative to a reference. DSC provides information about physicochemical properties and the heat capacity of a certain substance. The sample and reference both are exposed to same environmental conditions and amount of the heat flow is also same. Rapid absorption of heat by the substance produce a signal to the heat sensor and change is recorded and presented in the form of a peak. Enthalpy change is shown by the area under that peak. DSC is mostly used for analyzing the polymers. The positive peaks present in the spectrum indicates the exothermic process takes place in the curing of polymer after glass transition temperature[63].

1.11.5 Thermogravimetric analysis (TGA)

The technique calculates the variation in the weight of sample as a function of temperature or usually time. This technique is basically employed for determining thermal behaviors of material. Substances are analyzed according to their degradation behavior owing to several phenomena like decomposition or oxidation. The plot of the weight loss vs. change in temperature is the final result of analysis and known as thermogram. This technique is versatile in its purpose as it can be used for the polymeric material in almost all forms such as films, fibers, thermosets or thermoplastics[64].

1.11.6 X-Ray powder diffraction studies

XRD is a simple, effective and non-destructive method that provides an information about the phase change and the measurements of unit cell by crystalline material. The sample can be in any form either powdered or finely divided material. When the X-rays are allowed to fall on the sample, the constructive interference occurs and satisfies the Bragg's equation ($n\lambda=2d\sin\Theta$). In the X-ray diffractometer, sample rotates through an angle of Θ in the path of beam however the detector is being rotated with an angle of 2Θ[65].

1.11.7 Viscosity measurement

The resistance to flow of fluid is viscosity. Viscometric analysis is an efficient method for determining the molecular weight of polymers. Viscosity data is direct indication of the concentration and molecular weight of polymers. Different viscosities are employed to measure the required parameters[66].

Melt viscosity:

This method is suitable for the polymers with higher viscosities and insoluble in any of solvent. It is a reliable method for the molecular weight determination of polymers.

Solution viscosity:

The method is based on dissolving the polymer in a solvent and then determining viscosity with viscometer. Different expressions are commonly used here such as specific viscosity, relative viscosity, inherent viscosity and intrinsic viscosity[67].

Chapter 2

Experimental details

2.1 Experimental details

The synthesis of ferrocene containing monomers and the polymerization reactions require inert environment, pure reagents as well as dried solvents to attain improved yield and the high molecular weight of polymers. Here in chapter 2 different techniques for chemical purification and for drying solvents are briefly described. Moreover, it includes synthesis of monomers, polymers and techniques employed for characterization in detailed procedures.

2.2 Chemical and reagents

In all the synthetic methods, good quality chemicals and solvents were used to ensure the highest purity of the targeted materials. Ferrocene, bisphenol, 4-flouro nitrobenzoic acid, triethyl amine, acetyl chloride, aluminium chloride, terephthaloyl chloride and isophthaloyl chloride were obtained by Sigma Aldrich(Germany) and used without applying any pre-treatment conditions. Sodium hypochlorite solution used was commercially available.

1,6-Hexandiamine (60% aqueous solution) was purchased from Across Organics(Newjersey,USA) and 2,2′-bis[4,4′-(aminophenoxy)phenyl]hexafluoropropane was from TCI.

All solvents used for the synthetic procedures, i.e. ethanol, DMF, THF, dichloromethane and diethyl ether obtained from Lab Scan were carefully dried using different standard methods available. TLC (Thin layer chromatography) were performed to observe the reaction's progress and to verify the product's purity.

2.3 Drying and purification of solvents

2.3.1 Dimethyl formamide

DMF (b.p. 153℃/760 mmHg) was distilled and collected at its boiling point using the available distillation technique.

2.3.2 Ethanol

Ethanol (b.p. 78℃/760 mmHg) was first pre-dried by treating over calcium chloride for 12 hours then was distilled using magnesium turnings and some crystals of iodine which act as an indicator.

2.3.3 Tetrahydrofuran

THF (b.p. 66℃/760 mmHg) was dried using sodium wires in the presence of benzophenone which act as an indicator. The change in colour of the sodium benzophenone ketyl complex from green to blue indicates the reaction’s completion.

2.3.4 n-Hexane

n-Hexane (b.p. 68℃/760 mmHg) was firstly pre-dried with calcium hydride for atleast 12 hours then it was distilled using sodium wires in the presence of benzophenone which act as an indicator.

2.3.5 Dichloromethane

DCM (b.p. 40℃/760 mmHg) was first pre-dried using calcium chloride for atleast 24 hours then it was filtered. After that it was refluxed over phosphorus pentaoxide for about one hour. At the end, it was collected after distillation.

2.3.6 Chloroform

Chloroform (b.p. 60℃/760 mmHg) was first treated over calcium chloride for 24 hours then was distilled and refluxed using phosphorous pentaoxide.

2.4 Synthesis of monomers

2.4.1 Synthesis of 2,2’-bis[4,4’-(aminophenoxy)phenyl]propane

The preparation of the above mentioned diamine was carried out in a 250 mL of two-necked flask equipped with a condensor, a magnetic stirrer and a nitorgen tube. This synthesis was carried out in inert conditions. For this reason, all the gases and moisture contents were removed by creating vacuum in the assembly first and then by flushing the nitrogen gas to ensure inert and moisture free environment.

In this method, 5g (0.0219 moles) of bisphenol was reacted with 6.9g(0.0438 moles) of 4-flouronitrobenzene in the presence of 6.5g (0.0438 moles) anhydrous potassium carbonate and 70 mL of dimethylformamide (DMF) as a solvent. The reaction mixture was refluxed at 120℃ for 12 hours under inert atmosphere. The change in colour showed the progress of reaction. As the reaction proceeded, yellow colour appeared confirming the formation of dinitro compound that is an intermediate product in this process. After cooling at room temperature, the whole reaction mixture was allowed to pour in 500 mL of water of to get yellow precipitates which were thoroughly washed with water and were collected by filtration. The crude product obtained was recrystallized from ethanol. The obtained dinitro compound is shown in Figure 2.1.

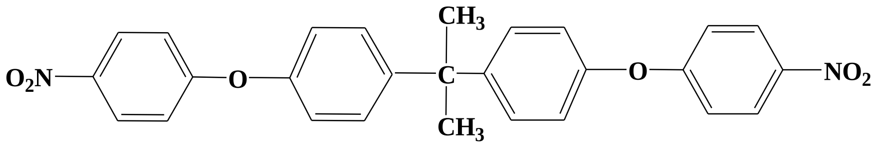
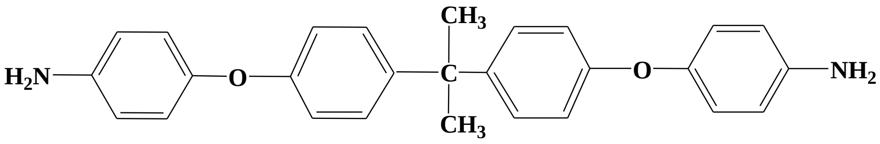


Figure 2.1- Structure of dinitro compound

In a pre-baked 250 mL of two-necked flask attached with a condensor, a magnetic stirrer and a nitorgen tube, the prepared dinitro compound about 2g (0.004 moles) synthesized was further reduced by treating it with 0.1g of 5% palladium charcoal and 10 mL hydrazine monohydrate in ethanol (80 mL). The whole reaction miture was stirred for 24 hours and then refluxed under nitrogen atmosphere for 5-6 hours. TLC was used to monitor the progress of the reaction. The diamine (synthesized) shown in Figure 2.2 appeared in the form of white crystals which was collected by filtration and the filtrate obtained was concentrated on rotary evaporator to get further product. The solid white colored precipitates were then recrystallized from ethanol.



2,2'-Bis[4-4(aminophenoxy) phenyl] propane

Figure 2.2- Structure of 2,2′-Bis[4,4′-(aminophenoxy)phenyl]propane

2.4.2 Synthesis of 1,1′-ferrocenedicarboxylic acid chloride(FcDc)

Synthesis of 1,1’-ferrocenedicarboxylic acid chloride(FcDc) was carried out in a three step route which is given below:

2.4.2 (a)Synthesis of 1,1′-diacetylferrocene (DAFc)

In a pre-baked 250 mL of two-necked flask equipped with a condensor, a magnetic stirrer and a nitorgen tube a suspension of 17.33g(129.83mmol)aluminium chloride in freshly dried dichloromethane was added and allowed to stir for 20 minutes. Then 8.79 mL (123.65 mmol) acetyl chloride was added at 0℃ the temperature was maintained using ice bath. The whole reaction mixture was allowed to stir for 30-40 mintues resulting in the formation of a clear solution. In this reaction mixture, a solution of 10g (53.76 mmol) ferrocene in dry dichloromethane was added dropwise at room temperature. which was further stirred for 7-8 hours at room temperature. Then ,the reaction mixture was poured in a separating funnel containing ice. Two phase system was developed the upper layer aqueous layer has a small amount of product whereas the lower layer organic layer has greator amount of the product. The system was allowed to stand for sometime so that the maximum separation could take place. The organic layer was separated out and the aqueous layer was extracted with small portions of chloroform. All batches of organic layer was combined and then treated with anhydrous sodium sulphate,a drying agent. After this, the solution was filtered and half of the solvent removed by rotary evaporation. To this slurry, n-hexane was added and again evaporated to half and allowed to cool slowly. Reddish maroon crystals of 1,1′-diacetylferrocene were obtained by filtration and washed with n-hexane and dried. To check the purity of product TLC was taken using solvent system consisting of mixture of n-hexane and ethyl acetate.Yield 65%, m.p. 125-127℃ (literature: 127-127.5℃). The obtained 1,1’-diacetylferrocene is shown in Figure 2.3.

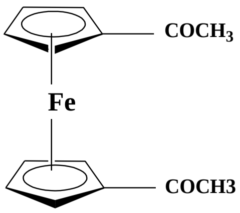


Figure 2.3- Structure of 1,1′-diacetylferrocene

2.4.2 (b) Synthesis of 1,1′-ferrocenedicarboxylic acid (FcDA)

For the synthesis of 1,1′-ferrocenedicarboxylic acid (FcDA) shown in Figure 2.4, 5g(18.52 mmol) of 1,1′-diacetylferrocene (DAFc) was added in a two-necked pre baked 250 mL flask attached with a condensor, a magnetic stirrer and a nitrogen gas tube. 150 mL of available commercial bleach (Robin bleach i.e. 12-15% solution of sodium hypochlorite) was added dropwise via dropping funnel in one hour under inert atmosphere. The reaction mixture was allowed to stir at 45-50℃ using water bath. After half an hour, remaining 50 mL portion of bleach was added and the reaction mixture was stirred for 12 hours at same temperature. After completion of reaction, the mixture was hot filtered and then acidified with 10% dil.HCl solution. Precipitates of the crude acid obtained upon acidification were dissolved in potassium carbonate solution and then filtered again which were then acidified with 10% dil.HCl. At the end, orange precipitates of pure acid were obtained upon filtration. Yield 65% ,m.p = 310℃ (literature value > 250℃).

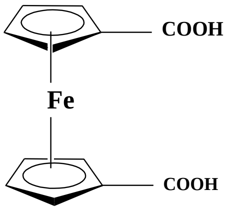


Figure 2.4- Structure of 1,1′-ferrocenedicarboxylic acid (FcDA)

2.4.2 (c) Synthesis of 1,1′-ferrocenedicarboxylic acid chloride

A two necked 250 mL flask attached with a condensor, a nitrogen gas tube and a magnetic stirrer was subjected with 3g (10.95 mmol) of 1,1′-ferrocenedicarboxylic acid (FcDA) and 20 mL freshly dried dichloromethane .The reaction mixture was stirred until a clear solution was formed. Now 2.5 mL (23 mmol) of thionyl chloride was added in the flask at once followed by the addition of 10 mL of triethylamine,dissolved in 10 mL of dichloromethane at 0℃. The reaction mixture was stirred for 2 hours at room temperature. After completion of the reaction, all the solvent and thionyl chloride was evaporated. Black mass is formed which is dissolved in diethyl ether in inert atmosphere filtered using canula. The filtrate was evaporated on vacuum leaving behind the red crystals of 1,1’-ferrocenedicarboxylic acid chloride. Yield 88%. The sturcture of 1,1’-ferrocenedicarboxylic acid chloride is shown in Figure 2.5.

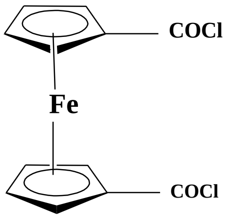


Figure 2.5- Structure of 1,1’-ferrocenedicarboxylic acid chloride

2.5 General procedure for the synthesis of polymers:

Six different series of terpolymers were synthesized by using different monomers; each series comprises of varying amount of diamine monomers. Synthesis of all these polymers was carried out by using same reaction conditions in order to analyze the effect caused by changing the concentration of monomers i.e. diamines. A vacuum line assembly was used for the polymerization reactions to attain inert conditions. First, the vacuum was created in order to remove air or any moisture contents and then flushing of dry N_2 was allowed to create an inert envoirnment. The reaction was carried out in a two necked (pre-baked) 250 mL flask attached with a condensor and a magnetic stirrer,corresponding mixture of the diamines with various compositions was added along with THF (20 mL) and then the reaction mixture was allowed to stir for 15 minutes to form a clear solution (homogenous). Then 10 mL of TEA (triethylamine) was added in the reaction mixture. The whole reaction mixture was alllowed to stir for atleast 20 minutes and during this time the temperature was maintained at 0℃ by using the ice bath. Diacid chloride which was dissolved in the dried THF then added drop wise by vigorous stirring for 5-6 hours. Then the whole reaction mixture was allowed to reflux for 1 hour. The product precipitated was collected by filtration and washed with the THF and methanol in order to remove any unreacted reactant or side products. Hence the resulting product was then air dried. All the synthesized polymers showed a good yield (>70%) collected in the end of reaction.

<u>Synthesis of PDAT series</u>:

For the synthesis of PDAT series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D = 2,2′-bis[4,4′-(aminophenoxy)phenyl]propane

A = 1,6-Hexanediamine

T = Terephthalyol dichloride

1-Synthesis of $PD_{(100)}A_{(0)}T$

$PD_{(100)}A_{(0)}T$ was synthesized by the above mentioned general procedure using 1.92 mmol diamine “D” and the acid chloride “T”. Color : White. Yield : 80%.

2-Synthesis of $PD_{(50)}A_{(50)}T$

$PD_{(50)}A_{(50)}T$ was synthesized using following mentioned procedure in the presence of mixture 0.96 mmol of two diamines i.e. “D” and “A” in 50:50 ratio respectively and 1.92 mmol of the acid chloride “T”. Color : White. Yield : 76%.

3-Synthesis of $PD_{(30)}A_{(70)}T$

$PD_{(30)}A_{(70)}T$ was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. “D” and “A” in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride “T”. Color : White. Yield : 77%.

4-Synthesis of $PD_{(10)}A_{(90)}T$

$PD_{(10)}A_{(90)}T$ was synthesized using procedure as described above in the presence of mixture of two diamines i.e. “D” and “A” in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride “T”. Color : White. Yield : 79%.

5-Synthesis of $PD_{(0)}A_{(100)}T$

$PD_{(0)}A_{(100)}T$ was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer “A” and the acid chloride “T”. Color : White. Yield : 77%.

Synthesis of PDAI series:

For the synthesis of PDAI series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D = 2,2′-bis[4,4′-(aminophenoxy)phenyl]propane

A = 1,6-Hexanediamine

I = Isophthalyol dichloride

1-Synthesis of $PD_{(100)}A_{(0)}I$

$PD_{(100)}A_{(0)}I$ was synthesized by the above mentioned general procedure using 1.92 mmol diamine “D” and the acid chloride “I”. Color : White. Yield : 79%.

2-Synthesis of $PD_{(50)}A_{(50)}I$

$PD_{(50)}A_{(50)}I$ was synthesized using following mentioned procedure in the presence of mixture 0.96 mmol of two diamines i.e. “D” and “A” in 50:50 ratio respectively and 1.92 mmol of the acid chloride “I”. Color : White. Yield : 76%.

3-Synthesis of $PD_{(30)}A_{(70)}I$

$PD_{(30)}A_{(70)}I$ was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. “D” and “A” in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride “I”. Color : White. Yield : 77%.

4-Synthesis of $PD_{(10)}A_{(90)}I$

$PD_{(10)}A_{(90)}I$ was synthesized using procedure as described above in the presence of mixture of two diamines i.e. “D” and “A” in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride “I”.Color : White. Yield : 78%.

5-Synthesis of $PD_{(0)}A_{(100)}I$

$PD_{(0)}A_{(100)}I$ was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer “A” and the acid chloride “I”. Color : White. Yield : 79%.

Synthesis of PDAF series:

For the synthesis of PDAF series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D = 2,2′-bis[4,4′-(aminophenoxy)phenyl]propane
A = 1,6-Hexanediamine
F = 1,1′-Ferrocenedicarboxylic acid chloride

1-Synthesis of $PD_{(100)}A_{(0)}F$

$PD_{(100)}A_{(0)}F$ was synthesized by the above mentioned general procedure using 1.92 mmol diamine “D” and the acid chloride “F”. Color : White. Yield : 77%.

2-Synthesis of $PD_{(50)}A_{(50)}F$

$PD_{(50)}A_{(50)}F$ was synthesized using above mentioned general procedure in the presence of mixture of two diamines i.e. “D” and “A” in 50:50 ratio (0.92+0.92) mmol respectively and the acid chloride "F" of about 1.92 mmol. Color : Dark Brown. Yield : 76%.

3-Synthesis of $PD_{(30)}A_{(70)}F$

$PD_{(30)}A_{(70)}F$ was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. "D" and "A" in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride "F". Color : Dark Brown. Yield : 75%.

4-Synthesis of $PD_{(10)}A_{(90)}F$

$PD_{(10)}A_{(90)}F$ was synthesized using procedure as described above in the presence of mixture of two diamines i.e. "D" and "A" in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride "F".Color : Dark Brown. Yield : 72%.

5-Synthesis of $PD_{(0)}A_{(100)}F$

$PD_{(0)}A_{(100)}F$ was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer "A" and the acid chloride "F".Color : Dark Brown. Yield : 74%.

<u>Synthesis of PD′AT series</u>:

For the synthesis of PD'AT series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D′ = 2,2′-bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane
A = 1,6-Hexanediamine
T = Terephthalyol dichloride

1-Synthesis of $PD'_{(100)}A_{(0)}T$

$PD'_{(100)}A_{(0)}T$ was synthesized by the above mentioned general procedure using 1.92 mmol diamine D′ and the acid chloride "T". Color : White. Yield : 82%.

2-Synthesis of $PD'_{(50)}A_{(50)}T$

$PD'_{(50)}A_{(50)}T$ was synthesized using following mentioned procedure in the presence of mixture 0.96 mmol of two diamines i.e. D′ and "A" in 50:50 ratio respectively and 1.92 mmol of the acid chloride "T". Color : White. Yield : 78%.

3-Synthesis of $PD'_{(30)}A_{(70)}T$

PD′$_{(30)}$A$_{(70)}$T was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. D′ and “A” in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride “T”. Color : White. Yield : 77%.

4-Synthesis of PD′$_{(10)}$A$_{(90)}$T

PD′$_{(10)}$A$_{(90)}$T was synthesized using procedure as described above in the presence of mixture of two diamines i.e. D′ and “A” in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride “T”. Color : White. Yield : 75%.

5-Synthesis of PD′$_{(0)}$A$_{(100)}$T

PD′$_{(0)}$A$_{(100)}$T was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer “A” and the acid chloride “T”.Color : White.Yield : 77%.

Synthesis of PD’AI series:

For the synthesis of PD’AI series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D′ = 2,2′-bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane
A = 1,6-Hexanediamine
I = Isophthalyol dichloride

1-Synthesis of PD′$_{(100)}$A$_{(0)}$I

PD′$_{(100)}$A$_{(0)}$I was synthesized by the above mentioned general procedure using 1.92 mmol diamine D′ and the acid chloride “I”. Color : White. Yield : 83%.

2-Synthesis of PD′$_{(50)}$A$_{(50)}$I

PD′$_{(50)}$A$_{(50)}$I was synthesized using following mentioned procedure in the presence of mixture 0.96 mmol of two diamines i.e. D′ and “A” in 50:50 ratio respectively and 1.92 mmol of the acid chloride “I”. Color : White. Yield : 79%.

3-Synthesis of PD′$_{(30)}$A$_{(70)}$I

PD′$_{(30)}$A$_{(70)}$ was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. D′ and “A” in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride “I”. Color : White. Yield : 77%.

4-Synthesis of PD′$_{(10)}$A$_{(90)}$I

PD′$_{(10)}$A$_{(90)}$I was synthesized usnig procedure as described above in the presence of mixture of two diamines i.e. D′ and “A” in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride “I”.. Coor : White. Yield : 76%.

5-Synthesis of PD′$_{(0)}$A$_{(100)}$I

PD′$_{(0)}$A$_{(100)}$I was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer “A” and the acid chloride “I”.Color : White. Yield : 78%.

Synthesis of PD′AF series:

For the synthesis of PD’AF series different concentrations of monomers are used to synthesize different terpolymers. In this series, the monomers used are as follows:

D′ = 2,2′-bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane
A = 1,6-Hexanediamine
F = 1,1′-Ferrocenedicarboxylic acid chloride

1-Synthesis of PD′$_{(100)}$A$_{(0)}$F

PD′$_{(100)}$A$_{(0)}$F was synthesized by the above mentioned general procedure using 1.92 mmol diamine D′ and the acid chloride “F”. Color : White. Yield : 77%.

2-Synthesis of PD′$_{(50)}$A$_{(50)}$F

PD′$_{(50)}$A$_{(50)}$F was synthesized using following mentioned procedure in the presence of mixture 0.96 mmol of two diamines i.e. D′ and “A” in 50:50 ratio respectively and 1.92 mmol of the acid chloride “F”. Color : Dark Brown. Yield : 75%.

3-Synthesis of PD′$_{(30)}$A$_{(70)}$F

PD′$_{(30)}$A$_{(70)}$F was synthesized by the aforementioned procedure in the presence of mixture of two diamines i.e. D′ and “A” in 30:70 ratio (0.576+1.344) mmol respectively and 1.92 mmol of the acid chloride “F”. Color : Dark Brown. Yield : 76%.

4-Synthesis of PD′$_{(10)}$A$_{(90)}$F

PD′$_{(10)}$A$_{(90)}$ was synthesized using procedure as described above in the presence of mixture of two diamines i.e. D′ and “A” in 10:90 ratio (0.192+1.728) mmol respectively and 1.92 mmol of the acid chloride “F”. Color : Dark Brown. Yield : 72%.

5-Synthesis of PD’$_{(0)}$A$_{(100)}$F

PD’$_{(0)}$A$_{(100)}$F was synthesized via general procedure given above using 1.92 mmol aliphatic diamine monomer “A” and the acid chloride “F”.Color : Dark Brown. Yield : 71%.

CHAPTER 3

RESULTS AND DISCUSSION

Six series of the terpolyamides were produced using standard procedures .Three different diacid chlorides were used i.e. Terephthaloyl chloride, Isophthaloyl chloride and 1,1′-ferrocenendicarboxylic acid chloride. With these diacid chlorides, three different diamines i.e. 2,2′-bis[4,4′-(aminophenoxy)phenyl]propane, 2,2′-bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane and 1,6-Hexanediamine were reacted in different ratios to formulate six different series. The comprising 5 different grades of polymers depend upon the composition is shown in Table 3.1.

This work was done to determine the effect caused by the continous increase of flexible diamine on physicochemical properties of resulting polyamides.The NMR and FT-IR results of terpolyamides confirm their successful synthesis. All terpolyamides were checked for crystallinity, thermal stability, viscosity and solubility.

Table 3.1- Composition ratio of diamines in polymer grades

Codes	% composition of aromatic diamine D	% composition of aliphatic diamine A
$\mathbf{D_{(100)}A_{(0)}}$	100	0
$\mathbf{D_{(50)}A_{(50)}}$	50	50
$\mathbf{D_{(30)}A_{(70)}}$	30	70
$\mathbf{D_{(10)}A_{(90)}}$	10	90
$\mathbf{D_{(0)}A_{(100)}}$	0	100

3.1 Monomers: synthesis and characterization

Two monomers were synthesized i.e. the aromatic diamine (D) and is ferrocene-based diacid chloride (FDc). The synthetic scheme of these monomers was a multistep process and carried out using following standard methods. The synthesis of ferrocenedicarbonyl chloride was performed according to a slightly improved method reported in the literature[66, 68]. The synthesized monomers were chracterized by common spectroscoptic techniques which confirmed their successful formation[69]. Physical properties of the synthesized monomers is shown in Table 3.2.

Table 3.2-Physical properties of monomers

Monomer	Colour	Melting point (℃)	Physical state	Yield %	Solubility
D	White	80	Crystalline	78	Ethanol,THF, DMF,Chloroform
FDc	Red	310	Amorphous	60	Chloroform, Ethanol,DMSO

3.2 FT-IR spectroscopic analysis of monomers

FT-IR data of the synthesized diamine is given in Table 3.3 while tha data of 1,1′-ferrocenedicarboxylic acid chloride is shown in Table 3.4.

Table 3.3-FT-IR spectral data of the diamine synthesized

Sample code	NH_2-strech cm^{-1}	sp^2 C-H stretch cm^{-1}	sp^3 C-H stretch cm^{-1}	(Aro)CN-stretch cm^{-1}	C-O-C cm^{-1}	NH_2-bend cm^{-1}
D	3401,3422	3039	2964	1364.16	1217.78	1611.15

Table 3.4-FT-IR spectral data of 1,1′-ferrocenedicarboxylic acid

Sample code	O-H cm^{-1}	Ar-H cm^{-1}	C=O cm^{-1}	Fe-Cp cm^{-1}
FDc	3356	3125	1686	508

3.3 Synthesis of polymer and its characterization

Synthesis of organic and ferrocene-based polyamides

The synthesis of terpolyamides involved the polymerization of mixture of diamines with three different acid chloride which lead to five different grades of polymers in each series with various compositions. For polymerization, the method adopted was low temperature solution polycondensation because it has numerous advantages over other methods such as the possibility of the side reactions was reasonably reduced as well as this method is quite simple and efficient. The whole reaction was performed in an inert environment. At the start, the temperature was allowed to maintain at 0℃ because the reaction shows exothermic behaviour. Formation of side products may cause chain growth's inhibition and disturb the stoichemistry of molecules [70]. When half of the initial hour passed, temperature was raised slowly to room temperature and thewhole reaction mixturewas stirred for atleast 5-6 hours followed by reflux for 2-3 hours. The increase in temperature was done in order to ensure the completion of reaction[71]. This is because at low temperature the amino groups attached to it are less reactive so by increase in temperature will cause their maximum interaction. For polymerization the solvent used was THF instead of any other polar aprotic solvents (like NMP). This is because THF is a better choice of solvent when there is a nedd to synthesize moderate molecular weight polymers [71-72]. TEA(Triethylamine) was used to speed up the reaction as it easily accepts the acid formed during the reaction resulting in the formation of triethylammonium chloride formed as a byproduct which was removed by washing the product with methanol.

3.4 Characterization of organic and ferrocene-based terpolyamides

The synthesis of ferrocene containing terpolyamides and their organic analogues was ensured by different characterization techniques that includes solubility, infra-red spectroscopy (IR), nuclear magnetic spectroscopy (NMR), X-ray diffraction analysis (XRD), thermogravimetric studies (TGA), differential scanning calorimetry studies (DSC), and viscosity measurements. The color (physical) of all ferrocene containing polymers was Dark Brown while the tere and iso polymers were white in color. All the polymers were synthesized in good yield.

3.4.1 Solubility

The terpolymers were tested for the solubility in different organic solvents. The limited solubility of the polyamides is primarly because of the presence of extensive hydrogen bonding operative in the polymer chains and the solubility data is given in Table 3.5.

It was observed that by increasing the concentration of aliphatic diamine in the polymer, the solubility factor also increases in the polar aprotic solvents for example DMSO[73]. Whereas, all the polymers were appeared as insoluble in less or moderately polar protic/aprotic solvents because of the presence of strong hydrogen bonding[72, 74].

The solubility of ferrocene containing polymers was improved in DMSO due to the presence of bulky ferrocenyl moiety which disturbs the chain to chain interactions[75]. Isophthaloyl based terpolymers exposed better solubility because of decrease in chain to chain interaction and the subsequent penetration of the solvent molecules was increased due to meta-linked monomers. All the terpolyamides were completely soluble in the sulphuric acid due to the high polarity of acid.

Table 3.5-Qualitative solubility data of synthesized terpolyamides

Samples	Acetone	EtOH	$CHCl_3$	MeOH	THF	DMF	DMSO	NMP	H_2SO_4
$PD_{(100)}A_{(0)}T$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(50)}A_{(50)}T$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(30)}A_{(70)}T$	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
$PD_{(10)}A_{(90)}T$	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
$PD_{(0)}A_{(100)}T$	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +
$PD_{(100)}A_{(0)}I$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(50)}A_{(50)}I$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(30)}A_{(70)}I$	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
$PD_{(10)}A_{(90)}I$	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
$PD_{(0)}A_{(100)}I$	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +
$PD_{(100)}A_{(0)}F$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(50)}A_{(50)}F$	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
$PD_{(30)}A_{(70)}F$	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +

PD$_{(10)}$A$_{(90)}$F	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD$_{(0)}$A$_{(100)}$F	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +
PD’$_{(100)}$A$_{(0)}$T	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(50)}$A$_{(50)}$T	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(30)}$A$_{(70)}$T	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(10)}$A$_{(90)}$T	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(0)}$A$_{(100)}$T	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +
PD’$_{(100)}$A$_{(0)}$I	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(50)}$A$_{(50)}$I	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(30)}$A$_{(70)}$I	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(10)}$A$_{(90)}$I	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(0)}$A$_{(100)}$I	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +
PD’$_{(100)}$A$_{(0)}$F	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(50)}$A$_{(50)}$F	- -	- -	- -	- -	- -	- -	+ + +	+ + +	+ +
PD’$_{(30)}$A$_{(70)}$F	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(10)}$A$_{(90)}$F	- -	- -	- -	- -	- -	+ -	+ + +	+ + +	+ +
PD’$_{(0)}$A$_{(100)}$F	- -	- -	- -	- -	- -	+ +	+ + +	+ + +	+ +

(- - = insoluble , + - = partially soluble upon heating

+ + = soluble at room temperature , +++= Completely soluble upon heating)

3.4.2 FT-IR spectral analysis

The synthesized polymers were analyzed by FT-IR spectroscopy to check the presence of expected functional groups. In FT-IR analysis, the fundamental stretching modes of the hydrogen bonding interactions operative throughout the polymer structure can be easily studied[71].

The spectra obtained of all the synthesized polymers indicates a prominent (clear) band in the region of 3500-3300 cm^{-1} that is the characteristic of the N-H strectching frequency[74, 76]. Another most prominent peak observed was due to stretching frequency of the carbonyl of the amide group. This functional band was appeared around 1675-1622 cm^{-1} . The lowering of stretching frequency occurred due to conjugation factor which causes an increase in single bond character of carbonyl group[69a]. Another characteristic band was due to the bending vibration of N-H bond. This band was observed around 1562-1507 cm^{-1} [77]. The ether linkage present in the aromatic diamine appeared in the region of 1155-1015cm^{-1} whereas this band was completely absent in aliphatic polyamides. The aromatic and aliphatic moieties were also confirmed by their respective functional peaks in expected regions of IR spectrum. Appearance of somewhat higher absorption frequencies of carbonyl functional group in the case of isophthaloyl containing polyamides than to the respective terephthaloyl terpolymides was owing to the hydrogen bonding present in the polyamides. Hydrogen bonding is more operative in the case of terphthaloyl based terpolymides due to highly ordered polymer microstructure[77].

The IR of ferrocene containing polymers were identified by the sharp peaks appeared in the fingerprint region. These peaks were due to ring stretching vibrations of the Fe-Cp and were appeared in the range of 475-511 cm^{-1} [78]. The FT-IR data of all the synthesized terpolyamides is given in the Tables 3.6 and 3.7.

Table 3.6-FT-IR spectral data of terpolyamides based on D

Code	**N-H cm^{-1}**	**Ar-H cm^{-1}**	**C-H cm^{-1}**	**C=O cm^{-1}**	**N-H bend cm^{-1}**	**C-N cm^{-1}**	**C-O-C cm^{-1}**	**Fe-Cp cm^{-1}**
PD$_{(100)}$A$_{(0)}$T	3391	3157	----	1644	1529	1219	1102	----
PD$_{(50)}$A$_{(50)}$T	3309	3100	2938-2859	1630	1540	1287	1149	----
PD$_{(30)}$A$_{(70)}$T	3307	3115-3048	2936-2860	1622	1538	1284	1091	----
PD$_{(10)}$A$_{(90)}$T	3301	3052-3048	2935-2859	1625	1537	1249	1101	----
PD$_{(0)}$A$_{(100)}$T	3305	3114	2969	1640	1562	1217	----	----
PD$_{(100)}$A$_{(0)}$I	3351	3152	----	1652	1537	1288	1074	----
PD$_{(50)}$A$_{(50)}$I	3412	3130-3052	2938	1646	1525	1313	1102	----
PD$_{(30)}$A$_{(70)}$I	3369	3160	2968-2838	1646	1540	1324	1106	----
PD$_{(10)}$A$_{(90)}$I	3310	3045	2936-2854	1625	1530	1289	1155	----
PD$_{(0)}$A$_{(100)}$I	3389	3080	2943	1639	1539	1286	----	----
PD$_{(100)}$A$_{(0)}$F	3477	3150	----	1675	1507	1283	1076	474

PD$_{(50)}$A$_{(50)}$F	3448	3110	2944-2862	1634	1519	1273	1065	492
PD$_{(30)}$A$_{(70)}$F	3373	3117	2938-2845	1634	1540	1318	1055	495
PD$_{(10)}$A$_{(90)}$F	3464	3110	2949-2850	1645	1520	1233	1014	486
PD$_{(0)}$A$_{(100)}$F	3410	3135	2920	1652	1535	1216	----	511

Table 3.7- FT-IR spectral data of terpolyamides based on D′

Code	**N-H cm^{-1}**	**Ar-H cm^{-1}**	**C-H cm^{-1}**	**C=O cm^{-1}**	**N-H bend cm^{-1}**	**C-N cm^{-1}**	**C-O-C cm^{-1}**	**Fe-Cp cm^{-1}**
PD′$_{(100)}$A$_{(0)}$T	3300	3100	----	1648	1535	1236	1035	----
PD′$_{(50)}$A$_{(50)}$T	3300	3115-3048	2936-2859	1625	1537	1259	1099	----
PD′$_{(30)}$A$_{(70)}$T	3310	3100	2935-2861	1624	1538	1284	1050	----
PD′$_{(10)}$A$_{(90)}$T	3499	3082	2935-2862	1625	1537	1249	1101	----
PD′$_{(0)}$A$_{(100)}$T	3305	3115	2968	1623	1562	1217	----	----
PD′$_{(100)}$A$_{(0)}$I	3350	3050	----	1664	1535	1235	1098	----
PD′$_{(50)}$A$_{(50)}$I	3441	3160-3052	2932-2859	1646	1525	1313	1106	----
PD′$_{(30)}$A$_{(70)}$I	3320	3145	2938-2854	1625	1530	1292	1020	----
PD′$_{(10)}$A$_{(90)}$I	3389	3080	2938	1648	1540	1286	1093	----
PD′$_{(0)}$A$_{(100)}$I	3469	3160	2957	1639	1538	1324	----	----
PD′$_{(100)}$A$_{(0)}$F	3317	3100	----	1680	1508	1207	1076	480

PD’$_{(50)}$A$_{(50)}$F	3370	3030-3050	2970	1628	1530	1210	1057	492
PD’$_{(30)}$A$_{(70)}$F	3432	3130	2977	1628	1540	1264	1034	468
PD’$_{(10)}$A$_{(90)}$F	3402	3052	2970	1633	1540	1212	1034	475
PD’$_{(0)}$A$_{(100)}$F	3330	3134	2931-2853	1625	1536	1262	----	502

3.4.3 NMR spectroscopic studies

The synthesized polymers were characterized by NMR spectroscopy and the data obtained confirms the formation of these compounds. The NMR analysis of the synthesized polyamides were recorded in deuterated dimethyl sulfoxide(DMSO).This technique can give detailed informations about the structure, reaction state, and chemical environment of the molecules. The location of different NMR signals depends on the external magnetic field strength and the reference frequency, these signals are usually reported relative to a reference signal, usually TMS (tetramethylsilane) is used as a reference.This operation thus gives a locator number called the "chemical shift" having units of parts per million which gives information about the structure of the molecule[59].

The spectral data showed the appearance of different signals in ^{1}H NMR spectra which was due to different types of protons present in the polymer structure. A sharp signal appeared at 10 ppm was due to the presence of amide protons which confirmed the successful formation of polyamides. Phenyl group is present in all compounds which is verified by the appearance of multiplets in the range of 6-8 ppm, according to the substituents attached. There also appeared a singlet at 1.1-1.5 ppm in the spectra of polymers which is due to the protons of methyl groups present in the polymer chain[69b]. ^{1}H NMR spectral dataof the polymers is shown in Table 3.8.

Table 3.8-^{1}H NMR data of the selected polymers

Code	chemical shift δ(ppm) Amide protons (CONH)	Aromatic protons	Aliphatic protons ($-CH_3$)
$PD_{(100)}A_{(0)}T$	10.4	6.5-8.1	1.16
$PD_{(100)}A_{(0)}I$	10.5	6.5-8.6	1.19
$PD'_{(100)}A_{(0)}T$	10.5	6.6-8.1	1.19
$PD'_{(100)}A_{(0)}I$	10.4	6.6-8.6	1.14

The ^{13}C spectral data showed the appearance of different signals in NMR which was due to different types of carbons present in the polymer structure. A sharp signal appeared in the range of 160-165 ppm was assigned to the carbon of the carbonylic amide. Phenyl group present in all compounds is evident by the appearance of different signals of carbons in the range of 115-140 ppm, according to the substituents attached. A singlet at 31 ppm in the spectra of polymers is significant of the aliphatic carbon of methyl groups present in the polymer chain[69b].The ^{13}C NMR data of the synthesized polymers is given in the Table 3.9.

Table 3.9-^{13}C NMR data of the selected polymers

Code	chemical shift δ(ppm) Amide (CONH)	Aromatic	Aliphatic carbon ($-CH_3$)
$PD_{(100)}A_{(0)}T$	165	115.3-155.4	31
$PD_{(100)}A_{(0)}I$	165	115.3-156.4	30
$PD'_{(100)}A_{(0)}T$	165	117.5-158.8	30
$PD'_{(100)}A_{(0)}I$	165	117.5-159.6	31

3.4.4 Thermal analysis

Thermal analysis of the synthesized terpolyamides includes degradation studies by the thermogravimetric analysis (TGA) and identification of glass transition temperature using differential scanning calorimetry (DSC). The thermal stability of the polymer towards degradation reflects its uses in various potential applications. In case of polyamides due to the high thermal stability they are considered ideal for a wide range of applications and by varying the concentration of the monomers, the thermal properties can be tailored as per requirement. Thermal analysis (i.e.TGA & DSC) was performed at a heating rate of 10℃/min in the N_2 atmosphere. Different parameters were employed to determine the stability of synthesized terpolymers were: T_g represents the glass transition temperature, T_i the initial decomposition temperature and T_{10} the temperature at which 10% weight loss occurs. The glass transition temperature of a polymer provides an insight into the structural details of polymers and their properties such as ductility ,toughness etc [79].

All the synthesized terpolyamides were based on both aliphatic and aromatic diamines. The stability of aliphatic repeating unit was expected to be less than that of aromatic unit. The reason for this is that the aromatic linkages are resonance stabilized which require additional energy for degradation than that of the aliphatic C-H bond, that has lower dissociation energy[80]. The thermal analysis data showed that ferrocene-based terpolyamides have highest thermal stability than all the other six series owing to the presence of metal atom in the polymer structure[81].

The terephthaloyl containing polyamides also appeared with improved thermal stability because of highly packed and ordered arrangment in the polymer chains due to para-catenation of terephthalic acid. Hence this structural feature made them resistent towards degradation while rest of the analogues found less stable. Thermal analysis data of all the synthesized terpolyamides is given in the Table 3.10 which resembles the reported literature[82]. It was concluded that terpolyamides which have higher aromatic effect had higher glass transition temperatures while those having higher aliphatic effect showed lower temperatures as well as lower thermal stability.

Table 3.10-Thermal analysis data of synthesized terpolyamides

Code	**T_g (℃)**	**T_i (℃)**	**T_{10} (℃)**
$PD_{(100)}A_{(0)}T$	260	480	485
$PD_{(50)}A_{(50)}T$	235	420	460

PD$_{(30)}$A$_{(70)}$T	220	410	430
PD$_{(100)}$A$_{(0)}$I	230	390	405
PD$_{(50)}$A$_{(50)}$I	225	350	365
PD$_{(30)}$A$_{(70)}$I	200	325	345
PD$_{(100)}$A$_{(0)}$F	325	510	525
PD$_{(50)}$A$_{(50)}$F	285	480	495
PD$_{(30)}$A$_{(70)}$F	225	455	465
PD’$_{(100)}$A$_{(0)}$T	275	495	505
PD’$_{(50)}$A$_{(50)}$T	260	435	440
PD’$_{(30)}$A$_{(70)}$T	245	410	430
PD’$_{(100)}$A$_{(0)}$I	250	400	410
PD’$_{(50)}$A$_{(50)}$I	235	345	350
PD’$_{(30)}$A$_{(70)}$I	215	330	345
PD’$_{(100)}$A$_{(0)}$F	350	520	535
PD’$_{(50)}$A$_{(50)}$F	300	490	500
PD’$_{(30)}$A$_{(70)}$F	235	460	470

Thermal stability trend observed in the synthesized terpolyamides is as follows.

PDAF > PDAT > PDAI

3.4.4.1 Thermal stability comparison of fluoro and non-fluoro polyamides

Mainly two different types of terpolyamides have been synthesized based on two types of diamines i.e. fluoro polyamides and non-fluoro polyamides. It was observed that fluoro polymers had relatively higher thermal stability than the non-fluoro polymers. This is because the C - F bond (bond energy - 107 kcal/ mol) of the CF$_3$ group is energetically more stronger than C - H bond (bond energy - 87.3 kcal/mol) of CH$_3$. Therefore the energy required to break the C-F bond will be higher thatof than C-H bond leading to the high thermal stability these polyamides. These polyamides had also higher

T_g values which may be due to sterical hindrance offered by the bulky hexafluoroisopropylidene group which retards segmental mobility and hence markedly increase its glass transition temperature than that of the homologous counterpart.[83].

A clear comparsion of thermal analysis data is shown in the Table 3.11.

Table 3.11- Thermal stability comparison of fluoro and non-fluoro polyamides

Code	T_g (℃)
$PD_{(100)}A_{(0)}T$	260
$PD_{(100)}A_{(0)}I$	230
$PD_{(100)}A_{(0)}F$	275
$PD'_{(100)}A_{(0)}T$	275
$PD'_{(100)}A_{(0)}I$	250
$PD'_{(100)}A_{(0)}F$	295

∴ D = 2,2′-Bis[4,4′-(aminophenoxy)phenyl]propane

∴ D′= 2,2′-Bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane

3.4.5 WAXRD Analysis

Polymer crystallinity is an essential phenomena in determining not only the nature of the polymer microstructure but also the rigidity of polymer. This is an important factor in suggesting many structural features which includes rigidity, brittleness, toughness and mechanical strength of the polymers[19,21].

The nature of synthesized terpolyamides was determined by their X-Ray diffractograms. X-Ray diffraction patterns which are recorded at room temperature. Typical pattern of the peaks in the region of 2Θ = 15-30° was evident in these diffractograms which is a characteristic of polymers. From the obtained diffractograms shown in Figure 3.1-3.3, it is obvious that among the organic terpolyamides,terephthaloyl based terpolyamides show more crystalline structure whereas the ferrocene containing terpolyamides were amorphous in nature. As the terephthaloyl based terpolyamides had para catenation of the monomers leading to closed and ordered packing of the polymer chains so this resulted in crystalline structure[36b], while in ferrocene-based terpolyamides the bulky ferrocene moiety cause disturbance in polymer chains thus preventing the ordered arrangment of the polymer. Hence, all the ferrocene-based terpolyamides were amorphous in nature[43].

It was observed that by increasing the aliphatic content, polymers showed progression from semicrystalline to amorphous behaviours. This was occurred because the chain packing was becoming disorganized due to increase in flexible chain and decrease in the stiffness of the aromatic linkage in polymer chains [65,73]. All the synthesized terpolymers show crystalline structure except ferrocene containing terpolymers.Both the amorphous and crystalline polymers show their own distinct characteristics, worth and uses. For instance, the crystalline polymers have good tensile strength and higher tensile modulus due to better packing of the polymer chains but they have low impact resistance. On the other hand, the amorphous polymers show low tensile strength and the tensile modulus but have excellent impact resistance[65].

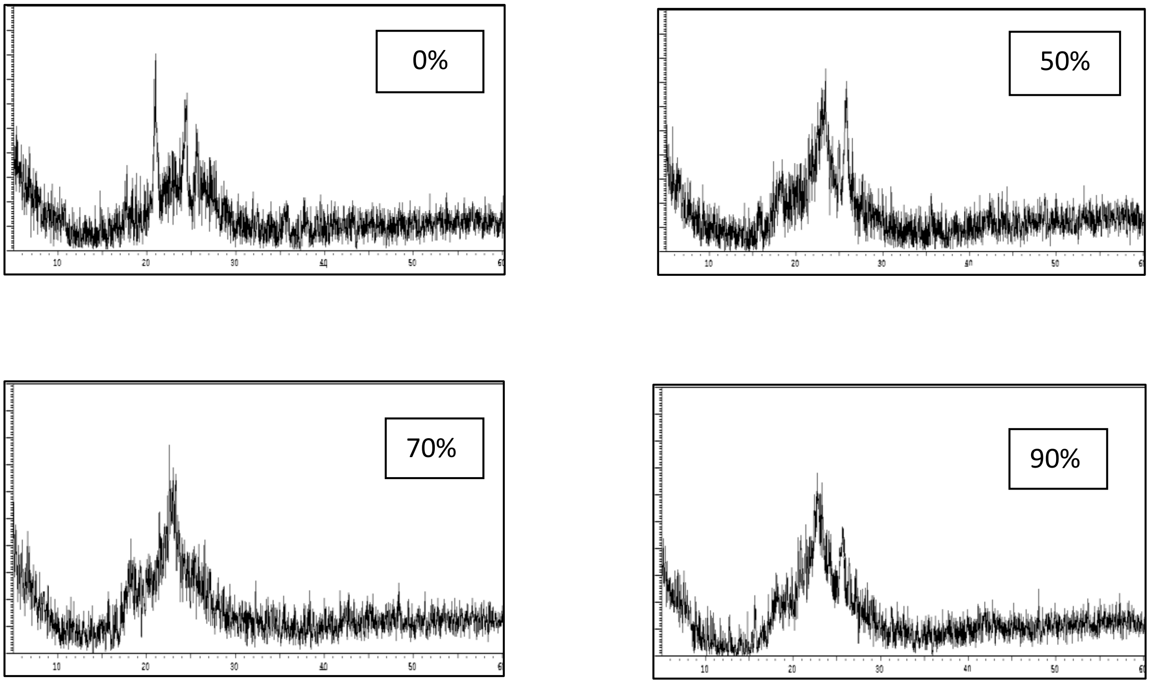


Figure 3.1: WAXRD spectra of terephthaloyl based organic terpolyamides

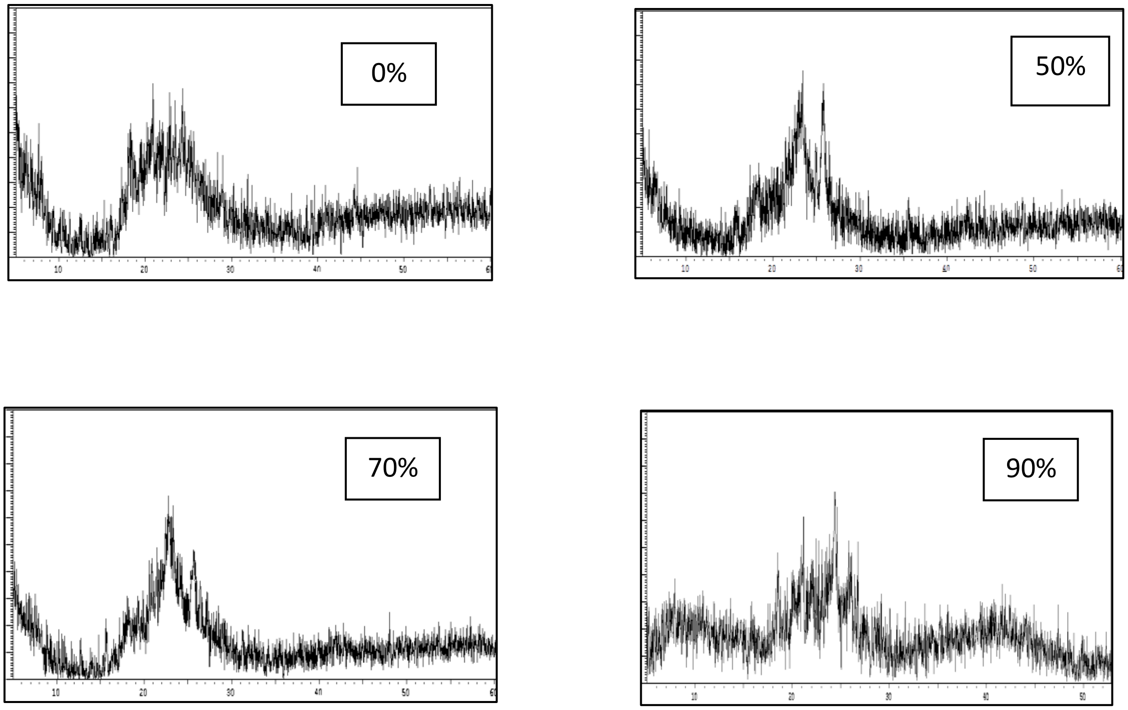


Figure 3.2: WAXRD spectra of isophthaloyl based organic terpolyamides

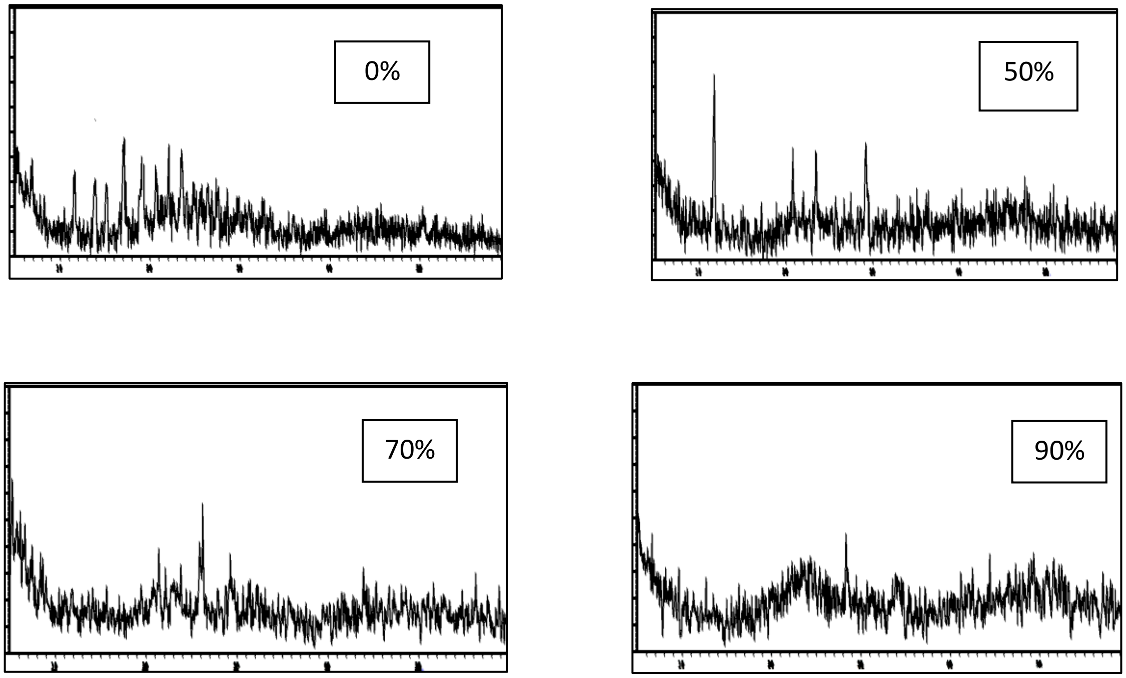


Figure 3.3:WAXRD spectra of ferrocene based terpolyamides

3.4.6 Viscometric analysis

The viscosity data of all the synthesized terpolyamides was obtained in NMP solvent at room temperature using Ubbelohd’s viscometer. It was observed that all the polymers showed inherent viscosity in the range of 0.06-1.14 dl/g which means that polymer solutions were moderately viscous and had reasonable molecular weights[75b, 84]. The strong hydrogen bonding in the polyamide structure caused the unusual high viscous flow of this class of polymers as compared to other polymers. This behaviour can cause problem in the fabrication technique of the polymers such as in solvent-cast technology or film casting. This problem can be overcome by homogenous dissolution of polymer in the solvent with minimum reasonable viscosity or the addition of such specific unit which decreases its viscosity[85].

The viscosity data of the synthesized terpolyamides is shown in Table 3.12. It was observed that ferrocene-based polymers have highest viscosity ranges and by increasing the percentage of aliphatic spacer, viscosity of the synthesized polymers goes on decreasing in a random fashion. By the viscosity data, it was observed that by decreasing the aromatic diamine in the polymer chain the viscosity of the polymer also decreases continously. This was because of the free volume created in the polymer chain by the addition of methylene linkage[84].

The viscometric data showed that ferrocene containing polymers have higher viscosity than rest the of polymers. This was due to the bulky ferrocene moeity in the polymer chain which increase resistance in the flow of the solution.

From these results, we concluded that introduction of flexible linkages in the polymer structure will ease its processibility along with controlled behaviour of thermal properties of polymers[84].

Table 3.12-Viscometric data of the synthesized terpolyamides

POLYMER	η_{rel}	η_{sp}	η_{red}**(dL/g)**	η_{inh}**(dL/g)**
$PD_{(100)}A_{(0)}T$	1.171	0.171	0.856	0.790
$PD_{(50)}A_{(50)}T$	1.160	0.160	0.800	0.742
$PD_{(30)}A_{(70)}T$	1.121	0.121	0.606	0.571
$PD_{(10)}A_{(90)}T$	1.022	0.022	0.110	0.110
$PD_{(0)}A_{(100)}T$	1.008	0.008	0.091	0.040

PD$_{(100)}$A$_{(0)}$I	1.166	0.166	0.830	0.767
PD$_{(50)}$A$_{(50)}$I	1.152	0.152	0.761	0.708
PD$_{(30)}$A$_{(70)}$I	1.061	0.061	0.306	0.297
PD$_{(10)}$A$_{(90)}$I	1.022	0.022	0.110	0.109
PD$_{(0)}$A$_{(100)}$I	1.012	0.012	0.061	0.060
PD$_{(100)}$A$_{(0)}$F	1.166	0.216	1.081	0.970
PD$_{(50)}$A$_{(50)}$F	1.216	0.162	0.810	0.750
PD$_{(30)}$A$_{(70)}$F	1.162	0.134	0.672	0.630
PD$_{(10)}$A$_{(90)}$F	1.134	0.070	0.351	0.339
PD$_{(0)}$A$_{(100)}$F	1.070	0.056	0.281	0.273
PD’$_{(100)}$A$_{(0)}$T	1.056	0.216	1.081	0.970
PD’$_{(50)}$A$_{(50)}$T	1.212	0.162	0.810	0.790
PD’$_{(30)}$A$_{(70)}$T	1.172	0.134	0.672	0.630
PD’$_{(10)}$A$_{(90)}$T	1.134	0.070	0.351	0.339
PD’$_{(0)}$A$_{(100)}$T	1.070	0.056	0.281	0.273
PD’$_{(100)}$A$_{(0)}$I	1.056	0.166	0.830	0.767
PD’$_{(50)}$A$_{(50)}$I	1.166	0.152	0.761	0.708
PD’$_{(30)}$A$_{(70)}$I	1.152	0.061	0.306	0.297
PD’$_{(10)}$A$_{(90)}$I	1.061	0.022	0.110	0.109
PD’$_{(0)}$A$_{(100)}$I	1.022	0.012	0.061	0.060
PD’$_{(100)}$A$_{(0)}$F	1.012	0.216	1.081	1.140
PD’$_{(50)}$A$_{(50)}$F	1.256	0.162	0.810	1.010
PD’$_{(30)}$A$_{(70)}$F	1.224	0.134	0.672	0.804
PD’$_{(10)}$A$_{(90)}$F	1.174	0.070	0.351	0.567
PD’$_{(0)}$A$_{(100)}$F	1.120	0.056	0.281	0.450

Viscometric measurments were taken at the concentration of 0.1g/dl in NMP as a solvent. Here

η_{rel} relative viscosity = time of flow for solution/time of flow for solvent

η_{sp} specific viscosity = $\eta_{inh} - 1$

η_{red} reduced viscosity = η_{sp}/c

η_{inh} inherent viscosity= ln η_{rel}/c

Measured from 0.1g/dl at 25℃.

3.4.6.1 Viscosity comparison of fluoro and non-fluoro polyamides

Mainly two different types of terpolyamides have been synthesized based on two types of diamines i.e. fluoro polyamides and non-fluoro polyamides .It was observed that fluoro polyamides have greater viscosity measurements than non-fluoro polyamides. This was because of high molecular weight of these polymers due to the presence of fluoro group which ultimately increase its inherent viscosity. The molecular weights of these polymers would be reasonably high enough to develop the flexible, transparent, strong, and tough films from the resulting polymer solution[83]. The comparison of the viscosity measurements of the synthesized polymers is shown in the Table 3.13.

Table 3.13- Viscosity comparison of fluoro and non-fluoro polyamides

Polymer Code	η_{inh} (dL/g)
$\mathbf{PD_{(100)}A_{(0)}T}$	0.75
$\mathbf{PD_{(100)}A_{(0)}I}$	0.70
$\mathbf{PD_{(100)}A_{(0)}F}$	0.95
$\mathbf{PD'_{(100)}A_{(0)}T}$	1.19
$\mathbf{PD'_{(100)}A_{(0)}I}$	1.16
$\mathbf{PD'_{(100)}A_{(0)}F}$	1.22

∴ D = 2,2′-Bis[4,4′-(aminophenoxy)phenyl]propane

∴ D′= 2,2′-Bis[4,4′-(aminophenoxy)phenyl]hexaflouropropane

3.5 APPLICATION

3.5.1 Carbon-di-oxide capture activity

Today, CO_2 emissions is a severe problem for establishing a sustainable society. Therefore, there are motivations in the implementation of green chemistry concepts. These emissions are playing a primary role in the global climate change. For the human society of this era, the development of efficient as well as cost-effective methods for CO_2 adsorption is an important objective. In order to replace the currently used industrial method for chemical sorption of CO_2 , that has comparatively high energy demands, scientists have developed processes through which CO_2 can be adsorbed over alumina, zeolite and metal-organic frameworks (MOFs). It was considered that captured CO_2 can be deposited in the underground reservoirs. But, as it is the most naturally abundant C-1 building block available, the chemical conversion of captured CO_2 to the high-value products is attractive. Now-a-days, one of such product is the cyclic carbonate formed during coupling of CO_2 and epoxides which has many applications in the pharmacological and chemical industries[86].

The CMPs (conjugated microporous polymers) are important due to their porous structures having different organic functionalities which permit important synthetic diversification. A number of CMPs have been developed for its applications in various fields e.g. gas sorption, electronics and catalysis. Recently, several reports on the use of the metal-functionalized CMPs as gas sorption and catalytic properties, have been made. These materials combine the physical characteristics of the porous structures of the conjugated framework backbones of the CMPs with the chemical characteristics of attached metal-organic moieties which may lead to both CO_2 capture and its instantaneous conversion[86].

In this work, we studied the CO_2 capture activity of some organic and CMPs having metal functionality at the room temperature and atmospheric pressure.

3.5.2 CO_2 adsorption measurements

CO_2 adsorption measurements were performed using gravimetric method. Before adsorption measurements, the specimen was first treated in dynamic vacuum conditions at 373 K for 6 hours. Approximately, 5mg of specimen was heated at 373 K under flow of the argon and held there for 30min to remove moisture. Then specimen was allowed to cool at 313 K under the argon flow, and then the temperature was maintained constant. After half an hour, pure CO_2 gas was introduced into the furnace at 313 K, and the change in the weight was noted as a function of pressure. Flow rate of the CO_2 was retained at $30 ml min^{-1}$ [87].

3.5.3 Results & Discussion

CO_2 capture performance of the synthesized polyamides was taken as a function of pressure. The obtained data showed that these synthesized polymeric materials had reasonable potential to uptake CO_2 upto $6.5 cm^3/g$ at ambient pressures. The CO_2 uptake by these materials is mainly due to the presence of electron-rich groups containing fluorine, nitrogen and oxygen atoms resulting in the strong interaction with CO_2 molecules. Here the polar sites including NH, C=O and R-O-R in these polymers also have strong affinities towards CO_2 molecules[87].

The fluoro polymers have highest CO_2 uptake because of electron rich fluorine atom which have strong interaction with CO_2 molecule and further among the fluoro polymers the ferrocene-based polymers have highest CO_2 adsorption due to bulky ferrocene structure which result in small pore size generation which shows steep CO_2 uptake at low partial pressure. It is observed that CO_2 uptake continuously increases with pressure upto a certain point and then saturation is achieved. The data of CO_2 capture is given in Table 3.14 and graphical representation is given in Figure 3.4.

Table 3.14- CO_2 adsorption of the synthesized polyamides

POLYMERS	CO_2 UPTAKE
$PD_{(100)}A_{(0)}T$ (P-1)	2.5 cm^3/g
$PD_{(100)}A_{(0)}I$ (P-2)	2.8cm^3/g
$PD'_{(100)}A_{(0)}T$ (P-3)	4.0cm^3/g
$PD'_{(100)}A_{(0)}I$ (P- 4)	3.4cm^3/g
$PD_{(100)}A_{(0)}F$ (P-5)	3.7cm^3/g
$PD'_{(100)}A_{(0)}F$ (P-6)	6.5cm^3/g

3.5.4 GRAPHICAL REPRESENTATION OF CO_2 ADSORPTION

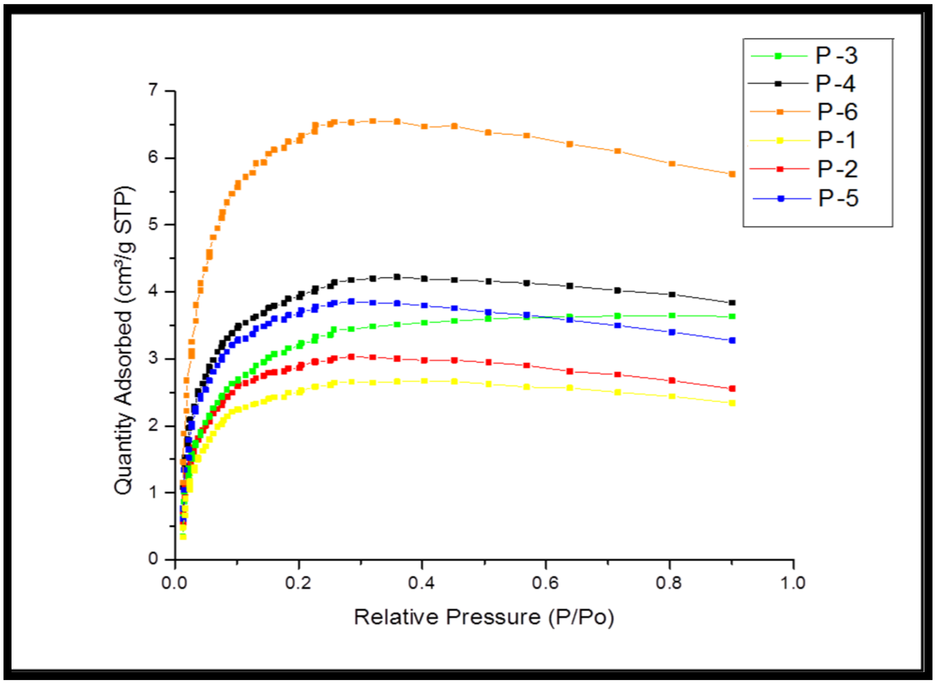


Figure 3.4

CONCLUSION

Six series of terpolyamides have been synthesized by reacting three different diamines with three different acid dichlorides. Thirty different grades of polymers have been prepared by changing the concentration of diamines. By using aliphatic and aromatic diamines, organic and ferrocene-based aromatic polyamides were synthesized successfully through low temperature solution polycondensation method. The synthesized polymer grades were then analyzed by different characterization techniques such as FT-IR spectroscopy, NMR spectroscopy, thermogravimetry (TGA), differential scanning calorimetry (DSC), XRD spectroscopy and solubility. The purpose of this work was to study the effect of increasing concentration of aliphatic diamine (HMDA) and to investigate changes in various physico-chemical properties of polyamides. The objective was achieved as the synthesized polymers showed remarkable improvement in their properties related to solubility, thermal stability, crystallinity and viscosity.

FT-IR and NMR analyse were performed to confirm successful syntheses of all the polymers. The glass transition temperature of fluoro polymers was higher as compared to non-fluoro polymers which proved their high thermal stability. Same trend was observed in the viscometric analysis. Ferrocene-based terpolyamides were found to exhibit less crystallinity than their organic analogues and by increasing the flexible spacer,crystallinity decreases.

Therefore, the approach of introducing flexible linkage in the polymer backbone can be used to improve the processibility of the polyamides by tailoring their properties as per requirement.

CO_2 Adsorption activity was also performed on the synthesized polymers. It was observed that fluoro polymers have more CO_2 uptake capacaity than non-flouro polymers and among fluoro polymers the ferrocene-based flouro polymers showed more CO_2 capture activity than other organic analogues.

Future plans

Future plan includes synthesis of novel polyamides by incorporating different lengths of methylene spacer to organic and organometallic polymers. This is expected to improve the physicochemical properties of the polyamides by the addition of the flexible methylene spacer. The presence of ferrocene unit and aromatic structure of polyamides would offer many advantages such as thermal stability and flame resistance etc. As well as we can determine the effect of addition of aliphatic unit over CO_2 adsorption activity of the polymers.

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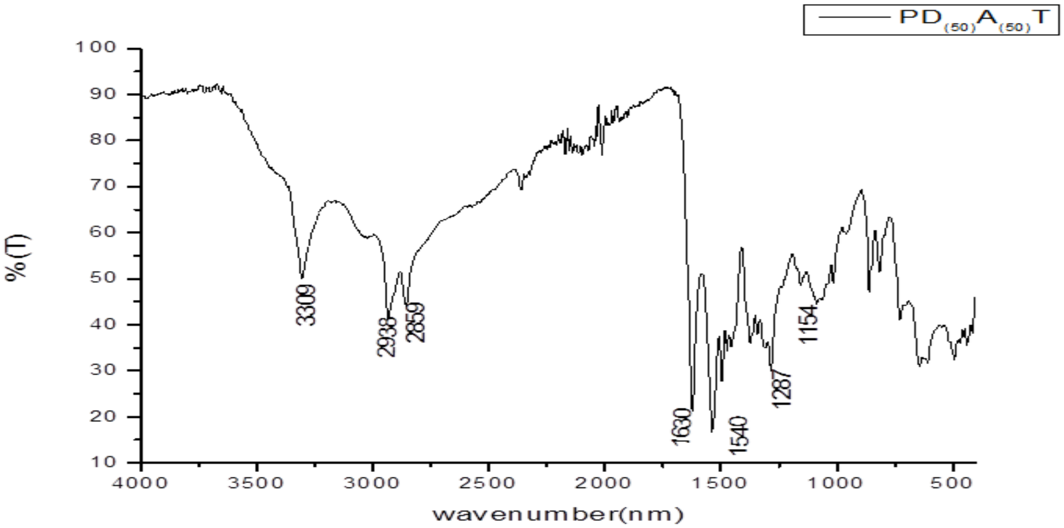
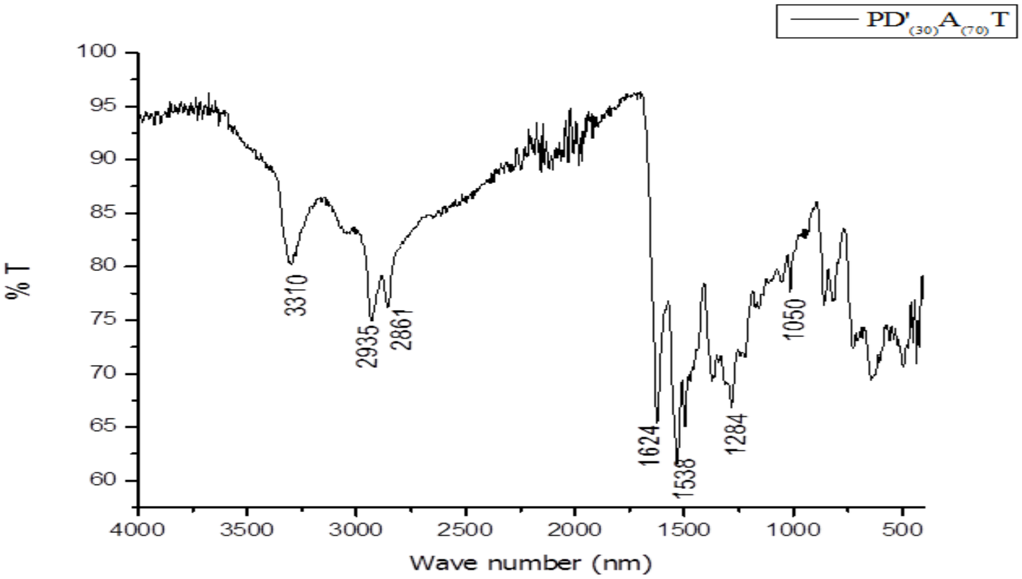
Appendix A

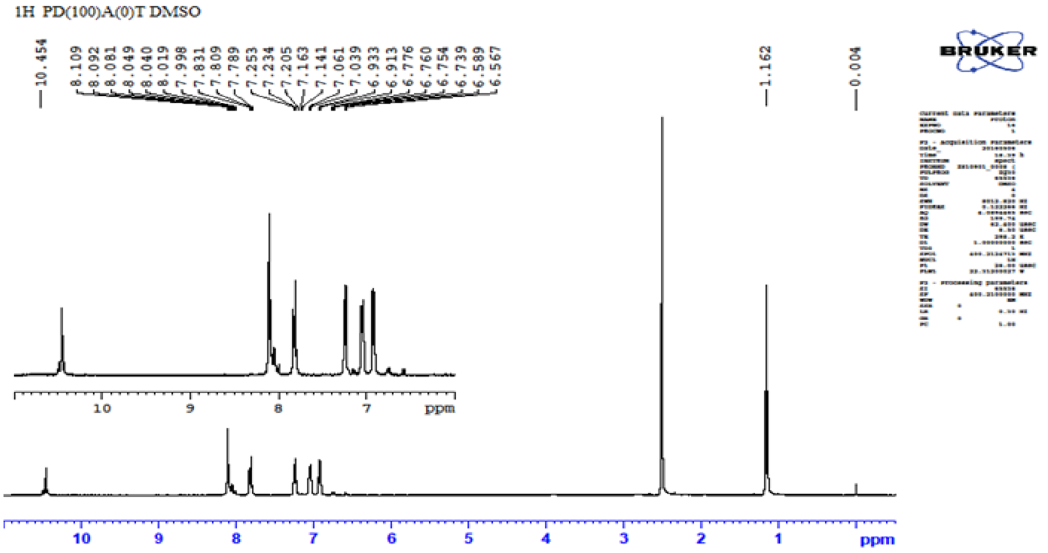


Representative FT-IR spectrum of terpolyamide based on D

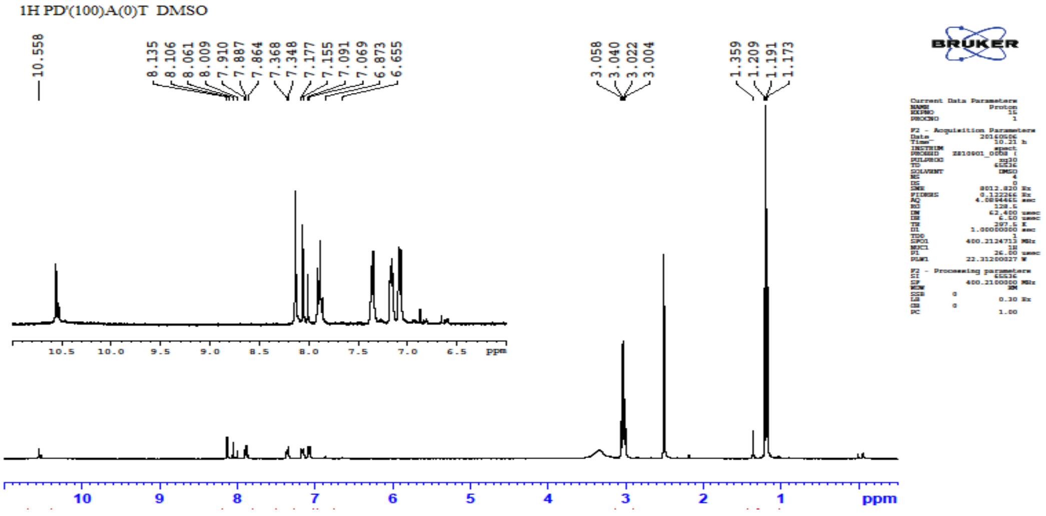


Representative FT-IR spectrum of terpolyamide based on D’

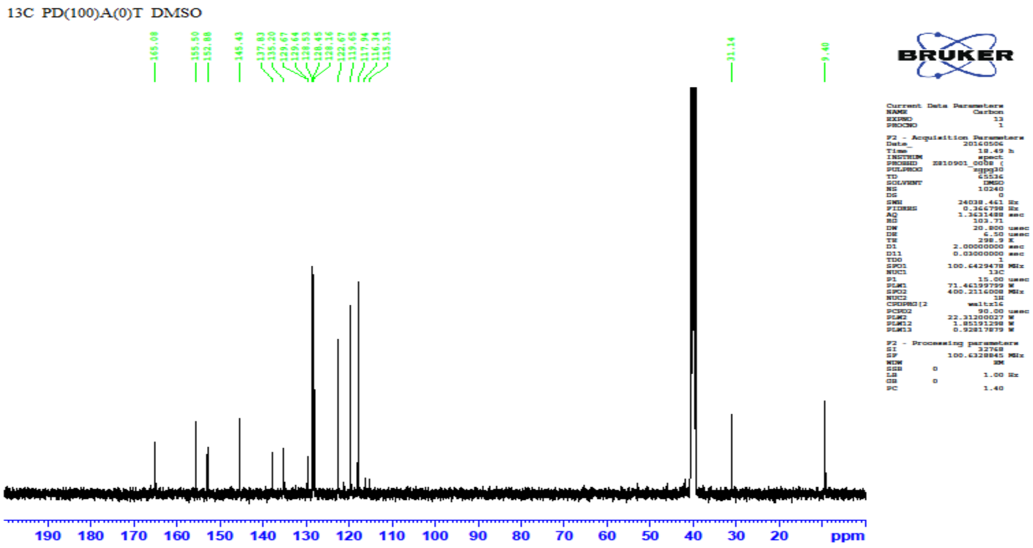
Appendix B



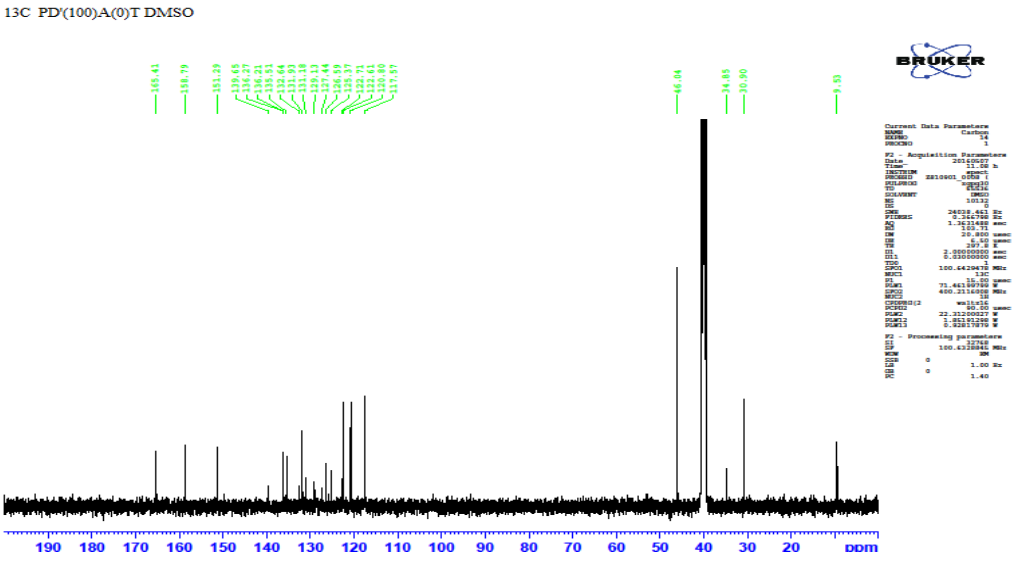
Representative ^{1}H-NMR spectrum of terpolyamide based on D



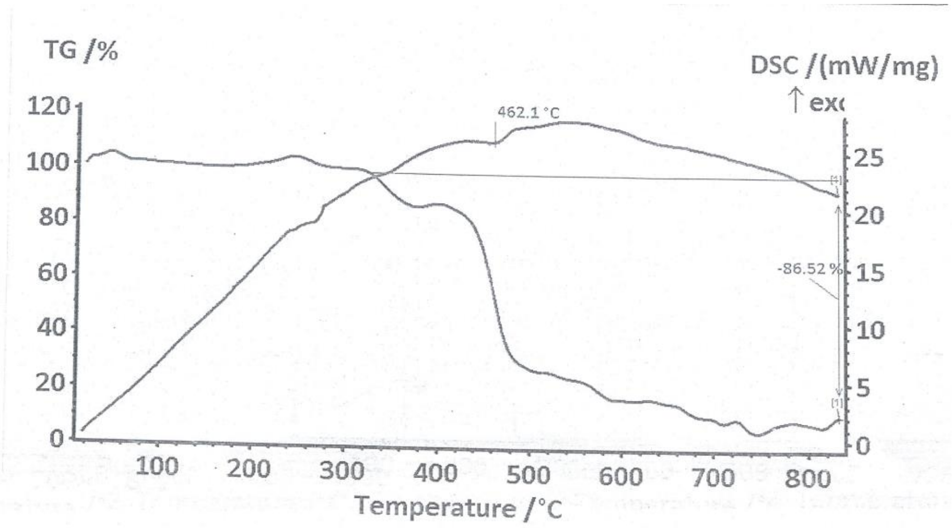
Representative ^{1}H-NMR spectrum of terpolyamide based on D’



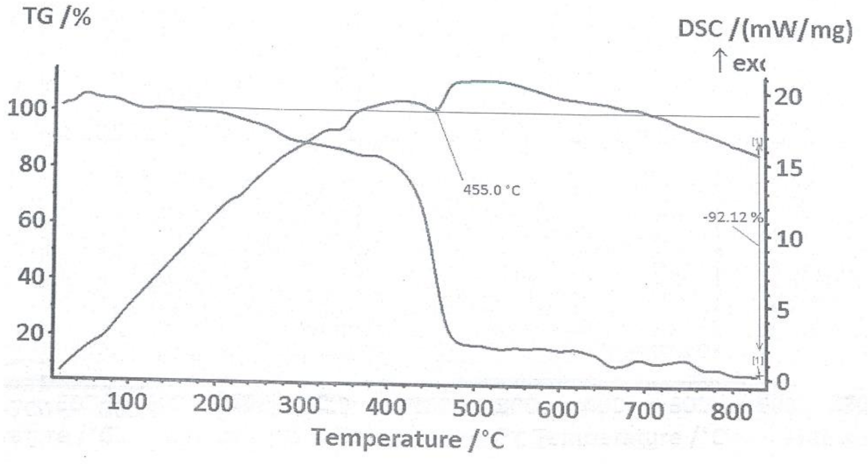
Representative ^{13}C-NMR spectrum of terpolyamide based on D



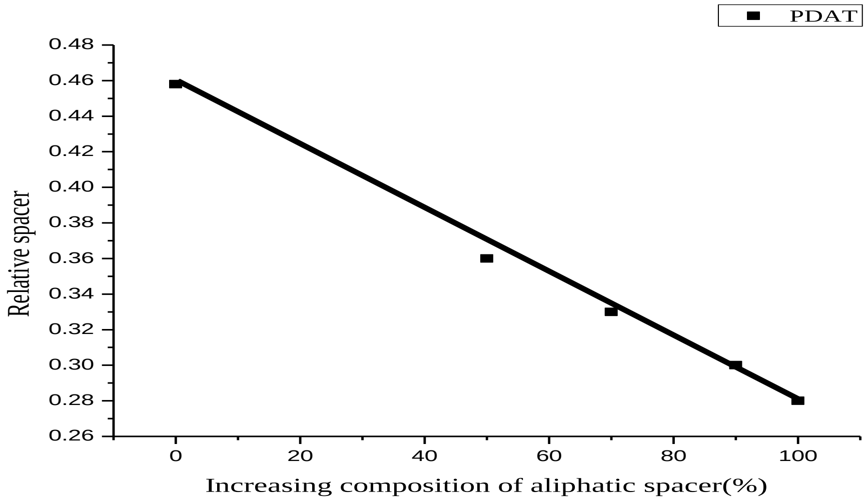
Representative ^{13}C-NMR spectrum of terpolyamide based on D’



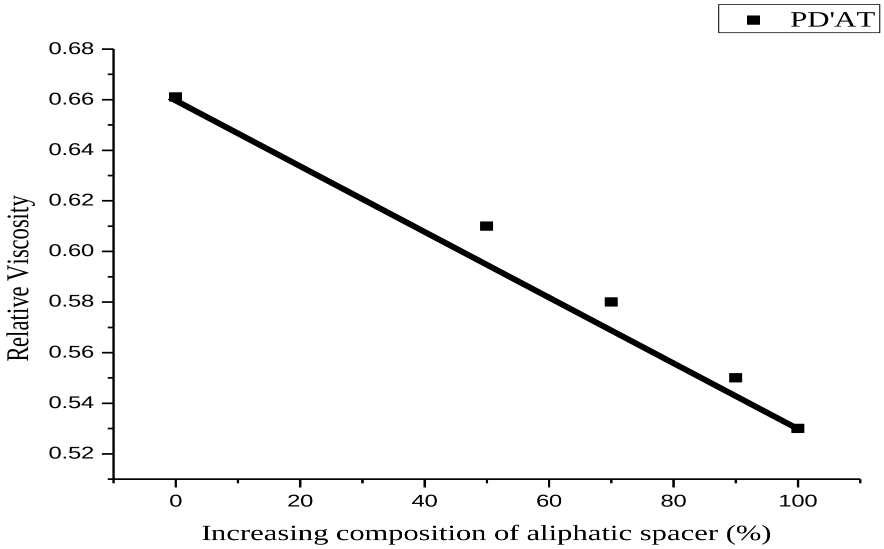
Representative TGA-DSC spectrum of terpolyamide based on D



Representative TGA-DSC spectrum of terpolyamide based on D’



Viscosity composition plot of terpolyamide based on D



Viscosity composition plot of terpolyamide based on D'