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Brief Summary of Minor Research Project

OBJECTIVES OF THE PROJECT:

The main objectives of the proposed research work were

- 1) To synthesize and characterize bifunctional diamines having heterocyclic moiety.
- 2) To synthesize processable polymers by using newly synthesized monomer and their characterization.
- 3) To study structure property relationship.

ACHIEVEMENTS FROM THE PROJECT

1 Introduction

Thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for ceramics and metals in the automotive, aerospace, and microelectronics industries. Aromatic polyamides are one of the most important classes of high performance polymers, because they possess excellent mechanical properties, thermal stability, chemical resistance and low flammability [1,2]. However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition or melting temperatures. It is a result of chain stiffness and intermolecular hydrogen bonding between amide groups [3]. To balance the thermal stability and the processability, numerous methods to obtain polyamides with chemically modified chain structures have been introduced. These methods include incorporation of movable atoms or kink units or flexible spacer units into the diamine fragment [4–12]. The introduction of bulky pendant (cardo) groups into the backbone of polymers is another approach to improve solubility and thereby processability. Commercial wholly aromatic polyamides have been well known for their thermal stability, excellent mechanical strength and good chemical resistance, which qualify them as high performance polymeric materials [13], the incorporation of the flexible linkages (e.g. $-\text{O}-$, $-\text{SO}_2-$, etc.) [14], lowers the segmental rotational barrier and increase the conformational freedom, cardo groups (such as cyclododecylidene, pyrene, and naphthalene, etc.) [15] or molecular

asymmetry (*ortho*, *meta* linkages) [16] into the backbone or addition of bulky side group (such as *tert*-butyl, norbornane units) [17–21]. For example, the bis (ether- amine)s and its aromatic polymer with cyclohexane group was synthesized and showed solubility in organic and polar solvents [22, 23]. Many efforts have been recently devoted to design, investigate and synthesize biocompatible, biodegradable polymers for applications in medicine for either the fabrication of biodegradable devices or as drug delivery systems [24-27].

The importance of polyamides is due to

1. The known attractive properties of polyamides at high temperature.
2. Cheap and easily available monomers and intermediates towards polyamides synthesis by suitable methods, for low temperature reaction.
3. Structure and property relation also identified.

2 Methods for the synthesis of aromatic polyamides

There are several methods for the preparation of polyamides as follows.

- 1) Low temperature polycondensation of acid chlorides and diamines.
- 2) Direct polycondensation of dicarboxylic acids and diamines.
- 3) Polyamides from N-silylated diamines and diacid chlorides.
- 4) Polyamides from diisocyanates and dicarboxylic acids.
- 5) Transition metal-catalysed polycondensation of aromatic diamines, dihalides and carbon monoxide.
- 6) Thermal polycondensation.

1) Low temperature polycondensation of diacid chlorides and diamines:-

At higher temperature the wholly aromatic polyamides undergoes decomposition and aromatic diacids gets oxidized or sublimed [28]. To overcome these difficulties the aromatic polyamides are synthesized by low temperature polycondensation (acyl halide method)

In this method polyamidation can be carried out at low or moderate temperatures without the use of excessive heating. Carboxyl group of monomer was converted to reactive derivatives such as acid chlorides. This method is based on well known Schotten-Baumann reaction [29-30].

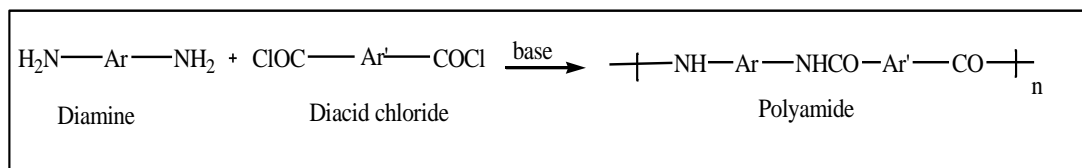
These are classified into two methods

- a) Interfacial polycondensation method and
- b) Solution polycondensation as reviewed by Morgan [31]

a) Interfacial polycondensation method

This method is carried out using a diamine and a diacid chloride in a pair of mutually immiscible solvents, one of which is preferably water and other usually a hydrocarbon such as carbon tetrachloride, dichloromethane, xylene, toluene, hexane. The water phase contains diamine and an excess amount of alkali, added as an acceptor of hydrochloric acid. The organic phase consists of the organic solvent and diacid chloride. The polycondensation may be carried out either in a static system or in a stirred mixture [32-40].

In the interfacial polycondensation the monomer diffusing to interface, reacts only with growing polymer chain ends resulting in high molecular weight polymer.

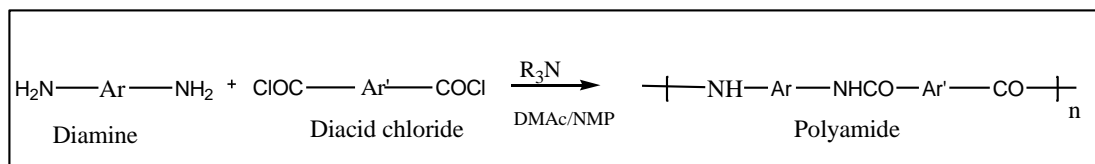


The interfacial polymerization is mostly conducted at the temperature that are close to room temperature, because rise in temperature increases the side reactions, decreasing polymer yield and molecular weight. However at the optimum temperature, the process can differ from room temperature. The presence of inorganic base during the interfacial polymerization is essential to neutralize the by product. The salt thus formed lowers the rate of polymerization. If the concentration of the inorganic base is high the acid chloride may undergo hydrolysis to form unreactive acid which retards the rate of polymerization. The choice of organic solvent is very important, since the polymerization occurs on the organic side to interface, which controls the molecular weight of the polymer. The interfacial polymerization is influenced by nature of solvent, the reactant concentration and the temperature [41-48]. There are some disadvantages such as cost and hydrolytical instability of the acid chlorides, and the solvent required during the polymerization is in large quantity.

b) Solution polycondensation method

Use of acid halide in polyamide was first reported in 1953 by Frankel et.al. [49].

It is carried out in a mixture consisting of an organic solvent and an acid acceptor, usually a tertiary amine [50]. The solvent for polymerization must be inert to reactants and the polymer formed should have solubility in the same solvent. The solvents preferred are polar aprotic amide solvents, such as DMAc, NMP. The solvents such as DMF, DMSO cannot be used because they react with acid chloride.



In solution polymerization the diamine is dissolved in amide solvent and diacid chloride is added in small portions or at once at lower temperature. As the molecular weight increases, the precipitation of polymer may occur, if solvation power of organic solvent is poor. The suitable solvent to get high molecular weight polymer is hexmethyl phosphoramide and N-methyl pyrrolidine (2:1) by volume. The addition of salts like lithium chloride, calcium chloride can increase the solvation power of solvent, so as to achieve high molecular weight polymers.

The results of solution polycondensation depend on many factors, such as monomer and solvent purity, monomer addition, stirring rate, temperature, added acid acceptor [51,52] etc.

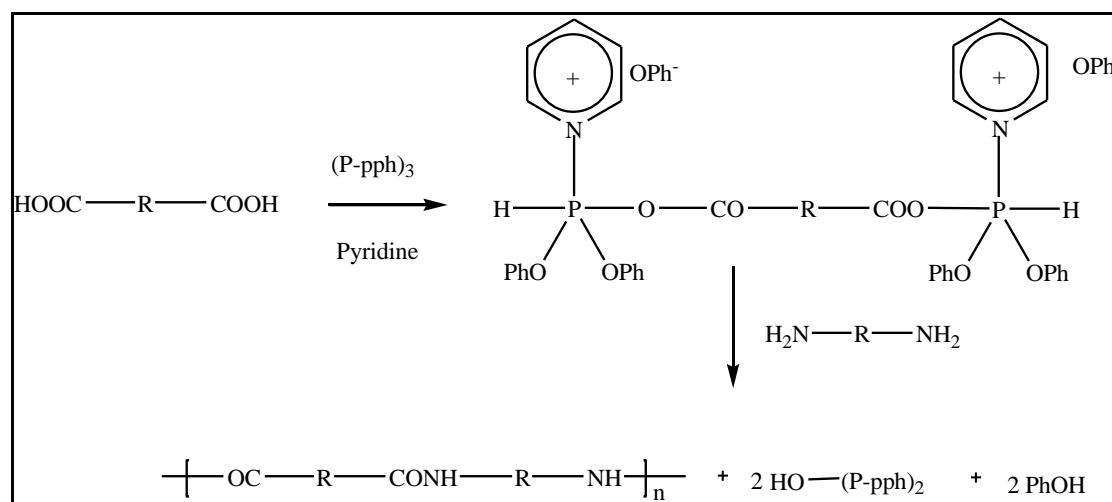
2) Direct polycondensation of dicarboxylic acids and diamines by condensing agents

Polyamides are also made by the polycondensation of diamine and diacid with non activated groups under mild conditions, with the help of an activating or condensing agent. This method avoids long and difficult syntheses and the handling of easily hydrolysable products such as diacid chlorides. The use of phosphorus compounds as activating agents such as, triarylphosphite, diphenyl phosphites, phosphorus trichloride and a few special phosphates has been reported. Thionyl chloride and 4-tosyl chloride have also been used. Among the variety of agents triphenyl phosphite has been found to be the most efficient. Pyridine is used as an acid acceptor.

To attain high molecular weight it is necessary to obtain, first solubilization of the reactants and the polymer formed. Besides the choice of the solvent, often of amide type N-

methyl pyrrolidone, N,N-dimethyl formamide, N,N-dimethyl acetamide, this requires the use of adequate additives. The additives are usually metal salts such as, lithium chloride, calcium chloride or polymer matrices⁷. The reaction can be conducted at room temperature or temperature can be raised to 115°C under optimal reaction conditions. Direct polycondensation is rapid; generally, conversion is complete within 2 h.

Different mechanisms have been postulated by Ogata and Tanaka [53], Yamazaki et. al. [54] and Aharoni et.al. [55] these reactions have been proposed to proceed via the N-phosphonium salts of pyridine followed by aminolysis.



Direct polycondensation gives low results in both molecular weight polymer and yield when applied to wholly aliphatic monomers, mainly due to the absence of suitable solvent for highly crystalline aliphatic polyamides and high basicity of aliphatic amino group. Other salts like magnesium chloride, zinc chloride, potassium bromide also facilitate the condensation reaction. Lithium chloride gives more favorable results than lithium bromide, lithium fluoride. The high molecular weight polymers were obtained when a concentration of about 4 wt% lithium chloride or 8% calcium chloride was used in mixture. The choice of solvent, temperature and amount of pyridine are important in polycondensation reaction. N-Methyl pyrrolidone (NMP) is effective solvent for these type of reactions. The viscosity of polymer also depends on the amount of pyridine used in the NMP-pyridine mixed solvent systems. The highest viscosity

value relatively high pyridine content (40% W/V) was observed; suggesting that the solvent mixed composition has strong solvating power compared to the NMP alone.

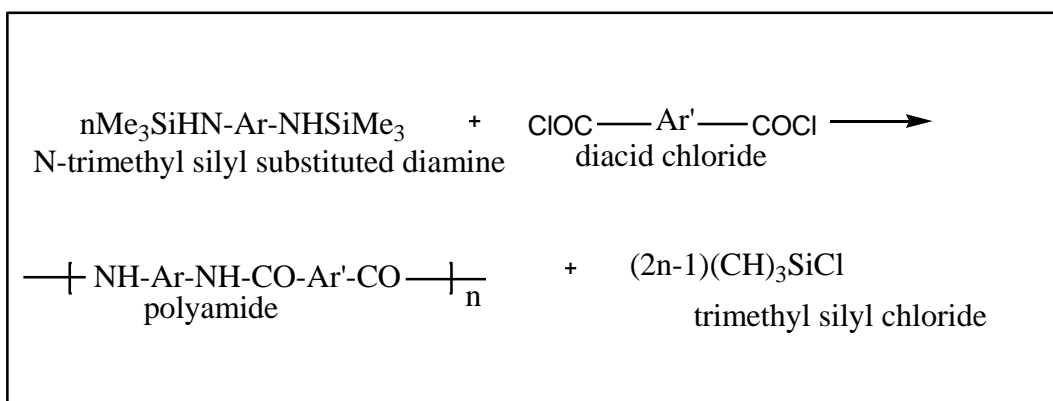
High molecular weight polyamides were obtained by replacing pyridine by functional polymers such as poly(4-vinyl pyridine) [56], (polyethylene-oxide) [57], poly(vinyl pyrrolidone) [58] etc.

The polymerization is carried out at moderate temperatures without removing the side products and avoids the tedious acid chloride step.

3) Polyamides from N-silylated diamines and diacid chlorides

The use of silylated monomers in the synthesis of polymers was demonstrated by Klebe's [59] in 1960, Kricheldroff [60, 61] synthesized polymers from o- silylated bisphenols in the beginning of 1980 and once again this field of silylated monomers become active.

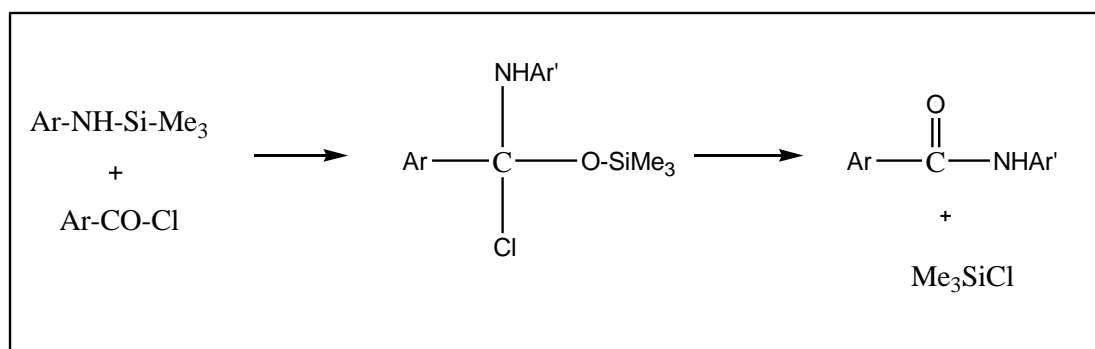
Imai et.al. [62, 63] synthesized high molecular weight polyamides by solution polycondensation of N-silylated aromatic diamines with aromatic diacid chlorides in NMP at 100°C with the elimination of trimethyl silyl chloride.



The high reactivity of N- silylated amines towards acid chloride is explained by the fact that silicon has affinity towards oxygen, chloride and fluoride. The nucleophilic addition and elimination reaction for N (trimethyl silyl) substituted amine and diacid chloride takes place as explained below.

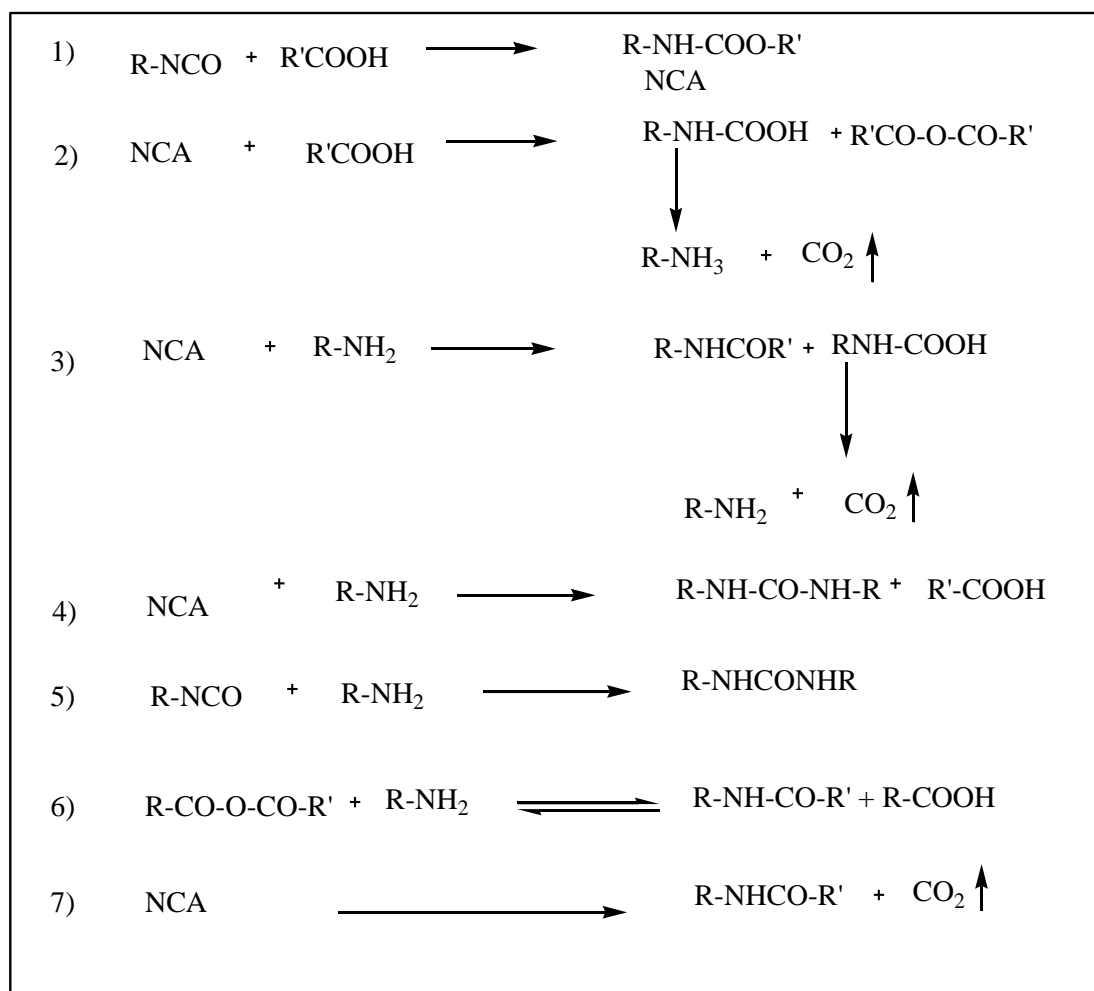
In the first step, the reaction of the carbonyl oxygen of an acid chloride to the silicon of N-silylated amine facilitates the nucleophilic attack of nitrogen of N-silylated amine at the carbonyl carbon of acid chloride, thereby quickly giving tetrahedral intermediate. In the second step, the elimination of chloride in form of intermediate is enhanced by the presence of the β-

silicon through the, sigma effect forming rapidly the amide along with the elimination of trimethyl silyl chloride. These diamines can be purified by simple distillation. The polycondensation with aromatic diacid chloride proceeds under mild conditions. The inherent viscosities of these polyamides are much higher than those obtained from corresponding unsubstituted diamines [64, 65].

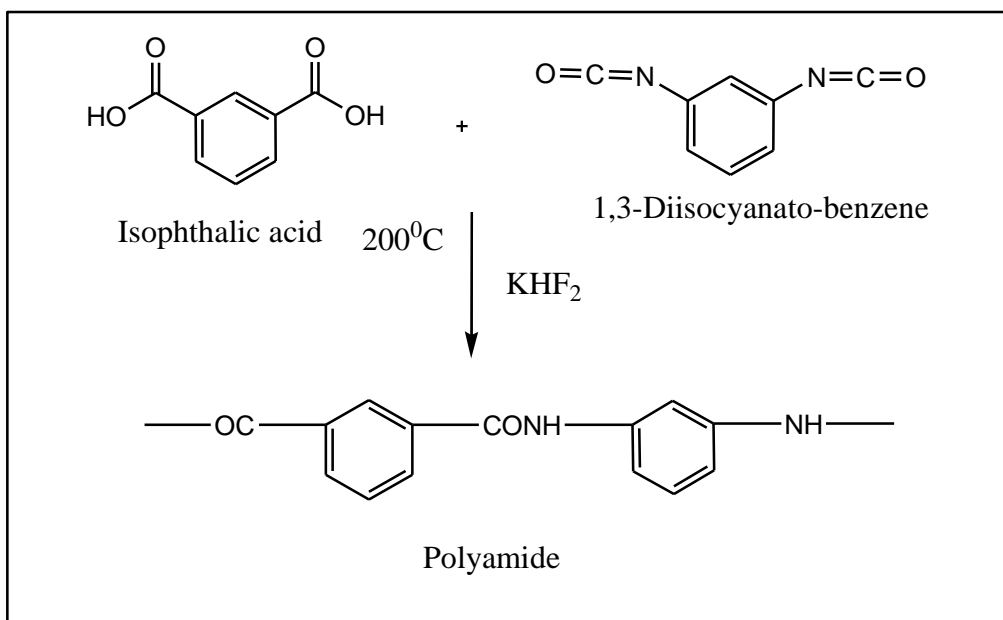


4) Polyamides from diisocyanates and dicarboxylic acids

The reaction of isocyanate and a carboxylic acid has known to form amide [65]. The carboxylic acid reacts with isocyanate to form N-carboxyl anhydride (NCA). D'olieslager [66] and later Bausiaux proved that the carboxylic acid in solution reacts with NCA by the nucleophilic attack to yield carboxylic anhydride and an unstable carbamic acid, which rapidly decomposes to an amine and carbon dioxide.



The liberated amine then can react with variety of species in solutions (NCA, carboxylic anhydride, isocyanate) to form product such as amide or urea. The byproduct urea is thermally unstable at elevated temperatures and can dissociate to amine isocyanate. In addition, intermolecular displacement of NCA to amide has been proposed involving a cyclic four membered transition state.

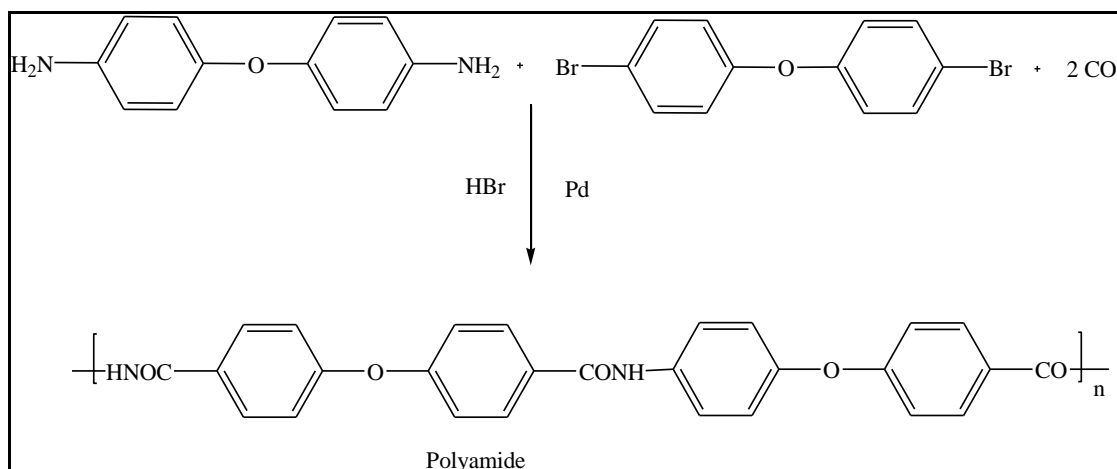


Polyamides are prepared by condensation of aromatic diisocyanates and dicarboxylic acids with elimination of carbon dioxide without use of any condensing agent

Polymerization process requires high temperature usually more than 100°C to achieve high molecular weight polymer. Some polymers also formed in presence of AlCl₃ catalyst or hydrogen chlorides at relatively low temperature [67-69].

5) Transition metal catalysed polycondensation of aromatic diamines, dihalides and carbon monoxide

Transition metal were used not only for polymerization of vinylic monomers but also used as a catalyst for the synthesis of condensation polymers such as polyamides, polyesters, polyethers [70-74]. Heck [75-80] demonstrated novel palladium catalysed carbon-carbon coupling reaction for the synthesis of arylalkyl compounds from aromatic halides and vinylic compounds. Based on these reactions aromatic polyamides from aromatic dibromides, aromatic diamines and carbon monoxide were synthesized using palladium as a catalyst [81-84].



High molecular weight aromatic –aliphatic polyamides (85), polyesters (86) and polyhydrazides (87) have been prepared successfully using palladium catalysed carbonylation polycondensation method.

6) Thermal polycondensation method

Polyamides are generally considered polycondensates, regardless of the process used for the synthesis. i.e polyamidation. Thermal polycondensation is characterized by the use of external heating. The synthetic aspects of thermal polycondensations, monomer synthesis and polycondensation reactions have been reviewed [88-94].

3 Structure-property relationships in polyamides

Aromatic polyamides are thermally stable polymers with attractive combination of excellent chemical and mechanical properties, they are used in advanced technologies and have been transformed into high-strength and flame resistant fibers and coatings, with applications in the aerospace and armament industry, bullet-proof body armor, protective clothing, sport fabrics, electrical insulation, asbestos substitutes, and industrial filters, among others [95,96]. Owing to their chemical structure, they exhibit extremely high transition temperatures that lie above their decomposition temperatures. However, their applications are usually hampered by their poor solubility which makes their processing very hard and difficult. Aliphatic – aromatic polyamides from aromatic diamines and aromatic dicarboxylic acids have been synthesized. However, it is less important towards aromatic-aliphatic polyamides because of low nucleophilicity of aromatic diamines.

Tremendous synthetic efforts, in the area of high-performance polymers have been focused on improving their processability and solubility through design and synthesis of new

monomers. The processability and solubility increases without affecting the thermochemical properties. Several attempts have been made to reduce glass transition temperature or enhance the solubility of polyamides. Introduction of flexibilising groups like ethers, carbonyl, sulphone, sulphone-ether, siloxane, aliphatic linkage and kinked structures have a profound effect on lowering the glass transition temperature while increasing solubility without much affecting the thermal properties.

A variety of structural modifications to the polyamide backbone have been employed in order to increase the solubility and consequently improving the processing process. Such trials included insertion of flexible side groups on the main chain [97-99], insertion of flexible linkage on the main chain [100-106] and utilization of noncoplanar or asymmetric monomers. They exhibit some interesting and potentially useful characteristics that have enormous technical and economic importance. They have favorable rheological behavior which allowed for successful preparation of fibers and films; they possess high thermal and thermo-oxidative properties

The introduction of ether linkage in the polymer backbone improves the solubility, processability and hydrolytic stability [107]. synthesized polyamide containing oxyphenylene groups in the main chain and showed that the polymers was enhanced with increasing the number of oxygroups in the main chain. The polyamides containing sulphone group in polymer chain have been reported good thermal, mechanical properties, better solubility and low glass transition temperature similarly ether group introduction showed same properties Stille et. al.[108] Polyamides with ether sulphone linkages synthesized by solution and interfacial polycondensation method. Polymers with enhanced solubility and thermo chemical properties were obtained.

The introduction of siloxane moiety in the polymer backbone increases heat resistance, surface properties, gas permeability, chain flexibility and plasma resistance. Introduction of aliphatic units in the polymer backbone enhances the solubility of polymer Mahajan et.al. [109], Srinivasan et.al. [110], these polyamides were amorphous and better solubility.

The presence of pendant group in polymer backbone enhances the solubility in organic solvents relative to unsubstituted polymers. Prestor et.al. [111-112] synthesized polyamides containining pendant carboxylic acid linkages by solution or interfacial polycondensation. These polymers show good thermal, solubility properties.

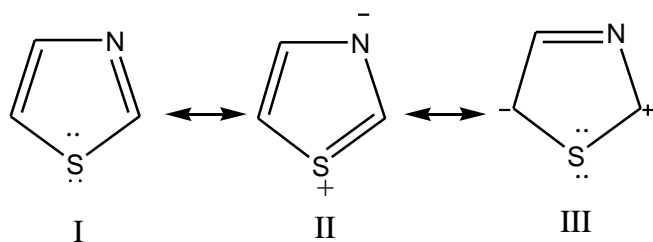
Glass transition temperature (T_g) increases by the introduction of rigid rod like structure along the polymer backbone. On the other hand kinked structures such as m-phenylene linkages make the polymer more soluble in organic solvents. However the glass transition temperature decreases. Korshak [113] and Imai et.al. [114]. Synthesised polyamides having high solubility and glass transition temperature by introducing bulky and stiff structure into the polymer backbone. Fluorine containing aromatic polyamide showed good solubility in organic solvents as compared to other halogen. Polyamides containing di, trifluoroalkyl groups showed good solubility and thermal properties.

A) POLY (AMIDE)

1 Introduction

Aromatic polyamides are one of the most important classes of high performance polymers, because they possess excellent mechanical properties, thermal stability, chemical resistance and low flammability. However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition or melting temperatures. It is a result of chain stiffness and intermolecular hydrogen bonding between amide groups. However, these wholly aromatic polyamides usually shows poor solubility in common organic solvents and their extremely high melting temperatures, which lie above their decomposition temperatures, give rise to processing difficulties and so limit their application. In order to overcome these drawbacks, considerable efforts have been made to modify their chemical structure to improve processability and solubility, so that to facility their use in a specific field. There are various approaches for improvement of the solubility and processability of polyamides without sacrificing their high thermal stability and mechanical properties, these methods include incorporation of kinked units or flexible spacer units into the diamine fragment. The introduction of bulky pendant (cardo) groups into the backbone of polymers is another approach to improve solubility and thereby process ability such as, the incorporation of the flexible linkages (e.g. $-O-$, $-SO_2-$, etc.) lowers the segmental rotational barrier and increase the conformational freedom, cardo groups (such as cyclododecylidene, pyrene, and naphthalene, etc.), molecular asymmetry (*ortho*, *meta* linkages)] into the backbone or addition of bulky side group (such as *tert*-butyl, norbornane units).

One of the best approaches to introduce heterocyclic moiety which disturbs the regularity and increases processability of the polymers heterocyclic compounds occur widely in nature. A large number of heterocyclic compounds are essential to life. Thiazole featuring both a nitrogen and sulfur as part of the five-membered heterocyclic ring form the basis of many synthetic drugs, dyes and industrial products [115]. The history of thiazole can be traced back to 1879 when Hoffman [116] published his work on benzothiazoles. The systematic study of thiazole and its derivatives was initiated from Hantzsch's [117] group in 1887. A myriad of papers have been reported in the field of thiazole chemistry since these determining works cover diverse aspects like physical properties, methods of synthesis, structure and reactivity correlation, reaction mechanism, biological and industrial utility [118]. Thiazole rings are planar and aromatic. The marked aromatic character of thiazole is explained on the basis of delocalization of lone pair of electrons from the sulfur atom completing the needed 6 π electrons to satisfy Huckel's rule [119]. In 1947, Roberts [120] suggested the reactivity of thiazole and its derivatives towards the electrophilic and nucleophilic reagents, which may be effectively explained by considering the following resonance structures (II) and (III) of the conventional structure (I) without recourse to the resonance involving the sulfur atom.



Present investigation

Aromatic polyamides possess many desirable characteristics such as excellent thermal stability and mechanical properties. The relationship between their primary structure and properties gives a widened scope of application.

To improve the methods such way that increases stability without affecting thermal stability. In present investigation new diamine viz. N, N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPITPA) (II) was synthesised. It was characterised by IR, ^1H and ^{13}C NMR, mass spectroscopically.

The introduction of heterocyclic moiety in the polymer backbone on the properties of aromatic polymers has been studied in detail in section IIA and IIB.

2 Experimental

Materials

Dimethyl formamide (DMF), thionyl chloride, , m-aminoacetophenone, isophthalic acid, terephthalic acid, 4,4'-diphenoxy diphenyl ether (S. d.fine), triphenyl phosphite (TPP) were used after purification. N, N'- Dimethyl acetamide (DMAc) was refluxed over barium oxide over 4 h distilled under vacuum and stored over Linde type 4A molecular sieves. Pyridine, lithium chloride, N-methyl-2-pyrrolidone (NMP), methanol, m-cresol and ethanol were purified prior to use.

3 Synthesis of monomers

3.1 Synthesis of N,N'- bis (3- acetyl phenyl) isophthalimide (APITPA) (I)

In 100 mL three neck round bottom flask equipped with magnetic stirrer, a nitrogen gas inlet, thermowell and CaCl₂ guard tube were charged with m-aminoacetophenone 0.274 g (0.002 mol) and dry DMAc (6 mL) . The mixture was stirred under nitrogen atmosphere till the complete dissolution takes place and it was cooled to -15° C to a cooled reaction mixture added isophthaloyl chloride 0.166 g (0.001 mol) in lots and few crystals of LiCl. The mixture was stirred at 0°C for 1.5 h and then for 1.5 h at 25°C.(Scheme 2A-1)

The solution was stirred at room temperature for 24 h. The viscous solution was poured in methanol with stirring to get white solid. Then filtered and washed with methanol to obtain white colored product.

Yield 0.38 g (95%)

Melting point 210°C

3.2 Synthesis of N, N'-bis[3-(2-amino-thiazol-4-yl)-phenyl]isophthalamide (ATPITPA) (II)

In a 100 mL three neck round bottom flask added compound (I) 0.4 g (0.001mol) and iodine 0.252 g (0.002 mol) and thiourea 1.2 g (0.004 mol) and stirred the mixture in DMAc at 120°C for 24 h. Then poured the reaction mixture with stirring in water, the yellow solid was obtained. The precipitate was washed successively with water and then by ethanol.

Yield 0.460 (90%).

Melting point >300°C

4 Synthesis of polyamide

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.512 g (0.001mol) and 0.166 g (0.001mol) isophthalic acid, 0.200 g lithium chloride (8 wt% based on solvent N-methyl pyrrolidine and pyridine mixture) and 0.744 g (0.63 mL, 2.4 mmol) triphenyl phosphite (TTP), 0.5 mL pyridine, 2 mL NMP. The mixture was stirred well at room temperature and then temperature was slowly raised to 100°C and heated at 100°C for 3 h under nitrogen. After cooling the resulting viscous mixture was poured into rapidly stirred methanol. The precipitated polymer was filtered, washed with methanol and air dried. Polymer was purified by dissolving in N,N-dimethyl acetamide (DMAc) and reprecipitated by methanol. The precipitate was filtered, washed with methanol and dried under vacuum at 80°C for 8 h. The yield was 85% and the reduced viscosity of polymer in DMAc at 30°C was 0.45 dL/g.

All other polyamides i.e. PA-2 to PA-9 were prepared by similar procedure.

5 Results and discussion

Aromatic polyamides have commercial utility, because of fibers and films of these polymers not only possess excellent physical properties at room temperature but retain their strength and excellent response to work loading at elevated temperature for prolonged period of time. Most of polyamides were derived from aromatic diamines and diacid chlorides by low temperature solution polycondensation technique.

In the present investigation polyamides were synthesized by Yamazaki's polycondensation method using condensing agent as triphenyl phosphite. The direct method of polycondensation avoids as it tedious work up in preparation in acid chloride and other difficulties in obtaining diacid chloride.

Aromatic polyamides exhibit a series of outstanding characters [121]. However, the commercial applications of these materials are often limited because of their poor solubility and high softening or melting temperatures. To overcome these problems, many efforts have been devoted to enhance the solubility of polyamides including incorporation of flexible linkages [122-123], introduction of non-coplanar groups or unsymmetrical structures into the polymer backbone. In addition, introducing heteroaromatic rings, such as the thiazole unit, into the main chain of a synthetic polymer is expected to impart certain properties such as chemical stability, thermal and thermo-oxidative stability to the polymer. Heteroaromatic ring of thiazole was

expected to provide molecular irregularity and decrease interchain interaction and the ability for polymer chains to pack while providing a barrier to segmental mobility, thus resulting in an enhanced solubility and increased Tg of the polymers.

6 Characterization of monomer

Newly synthesised compounds N, N'- bis(3- acetyl phenyl) isophthalimide (APITPA) (I) and N, N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (ATPITPA) (II) were characterized by IR, ¹HNMR, ¹³CNMR, and mass spectroscopic method.

Compound (I) (ATPIPA) was confirmed by, IR (cm⁻¹), 1667cm⁻¹ (–C=O stretching of (CONH)), 2908 cm⁻¹ (aliphatic CH stretching) and 1602 cm⁻¹ (NH bending) (Figure2A.1)

¹HNMR (200 MHz, DMSO: ppm): 10.36 ppm (s,2H) amide proton. The singlet peak at 2.86 ppm (s, 6H) was due to aliphatic methyl proton. 7.45-8.35 ppm (multiplet) aromatic proton's were observed in range.(Figure2A.2)

¹³CNMR (50 MHz DMSO; PPM) spectra showed 16 peaks for 16 different carbon atoms. Peak at 26.96 ppm was assigned to methyl carbon, peak at 165 ppm assigned to carbonyl carbon of amide group and at 197 ppm due to carbonyl carbon of acetyl group.(Figure 2A.3)

Compound (II) was assigned by (IR) 1672 cm⁻¹ (–C=O stretching of (CONH)) 3365 cm⁻¹ (NH stretching of primary amine).The absorption peak at 2903.2983 cm⁻¹ corresponds to NH-stretch.(Figure 2A.4)

¹HNMR (200 MHz ,DMSO; ppm) 10.38 ppm (s, 2H) was assigned for amide proton , 6.97 ppm (s, 2H) was assigned to proton of NH₂ group. The aromatic protons were exhibited peaks in range 7.33-8.60 ppm. (multiplet).(Figure 2A.5)

¹³CNMR (50 MHz, DMSO; PPM) showed 15 peaks for 15 different carbon atoms. The peak at 165 ppm was assigned to carbonyl carbon of amide group. (Figure 2A.6)

Mass spectroscopically confirmed the structure of diamine. The molecular ion peak at 512 m/e⁺ was assigned as a base peak. (Figure 2A.7)

7 Characterization of polyamide

Polyamides were synthesized by using isophthalic acid and compound (II) were confirmed by spectral analysis such as IR, ¹HNMR, ¹³CNMR.

IR spectra showed the characteristic absorption band at 1659 cm⁻¹ and 3063cm⁻¹ due to –C=O stretching of (CONH) group. (Figure 2A.8)

¹H NMR

The peak at 10.27 ppm was assigned to amide proton. The disappearance of peak at 6.97 ppm indicates the polyamide formation. (Figure 2A.9)

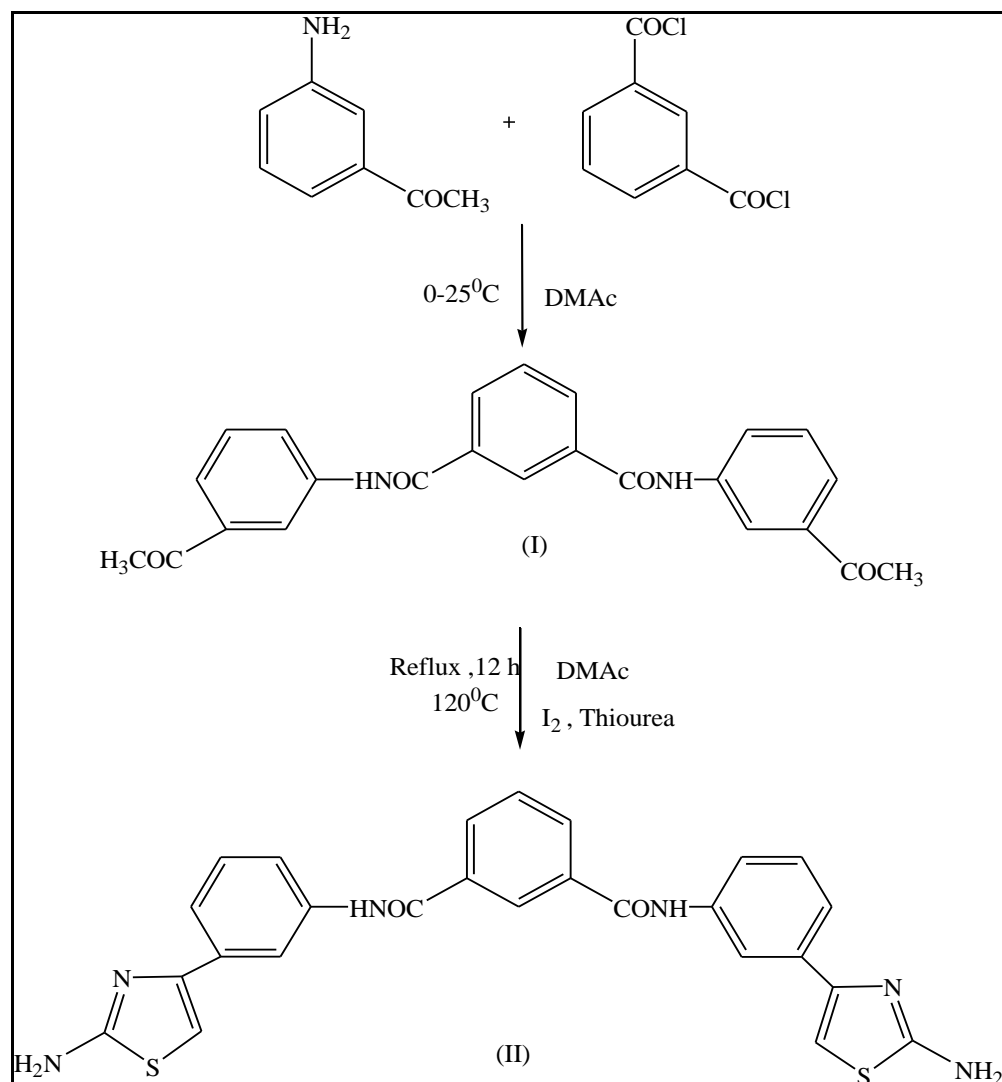
¹³C NMR

The peak at 165 ppm was assigned to carbonyl carbon of amide group. (Figure 2A.10)

Polyamides synthesized by using various aromatic dicarboxylic acids and thiazole diamine, were soluble in polar aprotic solvent such as DMAc, DMF, DMSO, Pyridine and NMP. While the PA-5 shows less solubility which was synthesized from ODA and TPA due to chain stiffness.

The yield of synthesized polymer was quantitative 95% showed the built of moderate molecular weight polymer. The inherent viscosity range between 0.2-0.6 dL/g. XRD data showed that all polymers were semicrystalline in nature. (Figure 2A.11)

From thermogravimetric analysis synthesized polymers were showed about 35% char yield at 900°C, which indicates that polymers were thermally stable. The glass transition temperature was in the range 167 to 225°C (Figure 2A.12,13).



Scheme 1: Synthesis of N,N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl]-isophthalamide (ATPITPA) (II)

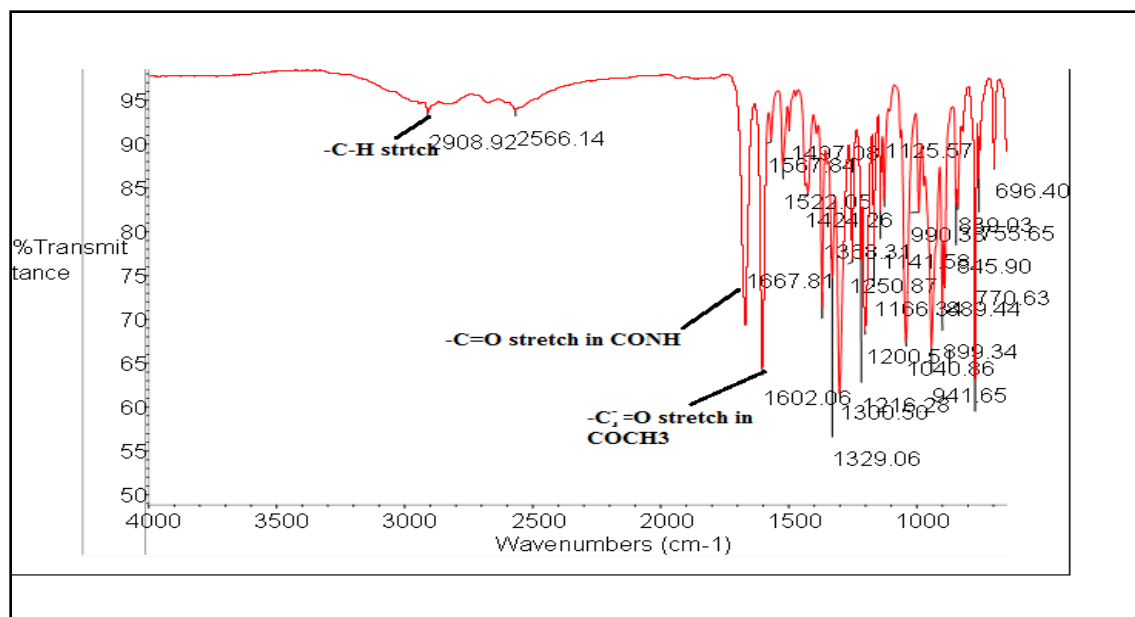


Figure 1: IR spectra of compound (I) (APITPA)

¹H NMR SPECTRA:-

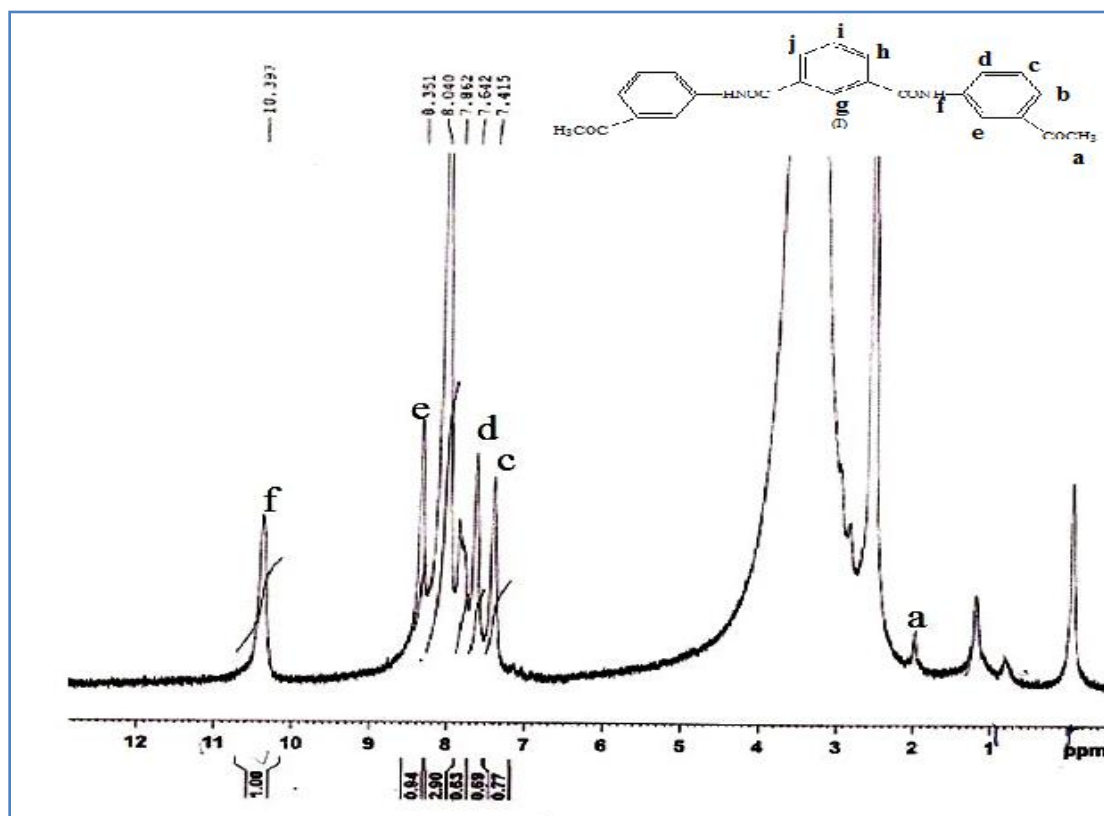


Figure 2: ¹H NMR of compound (I) (APITPA)

¹³CNMR SPECTRA:-

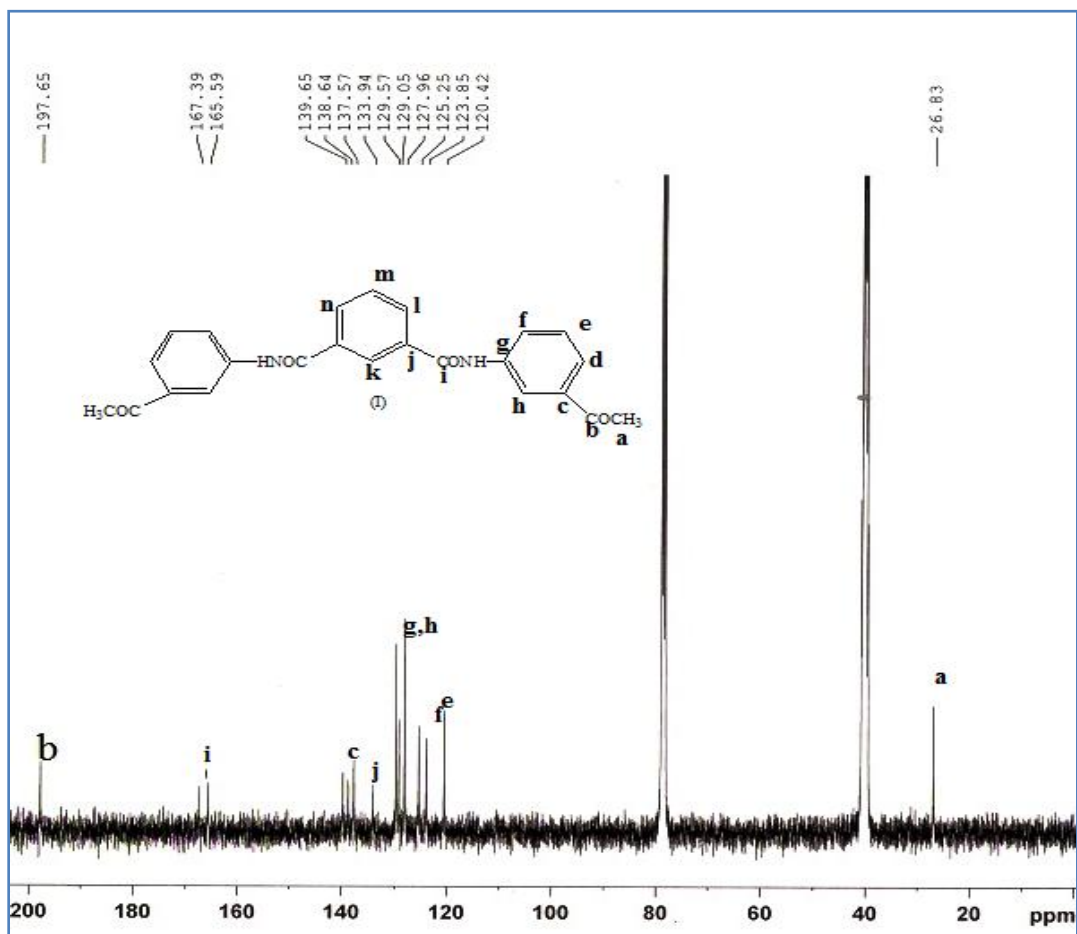


Figure 3: ¹³CNMR of compound (I) (APITPA)

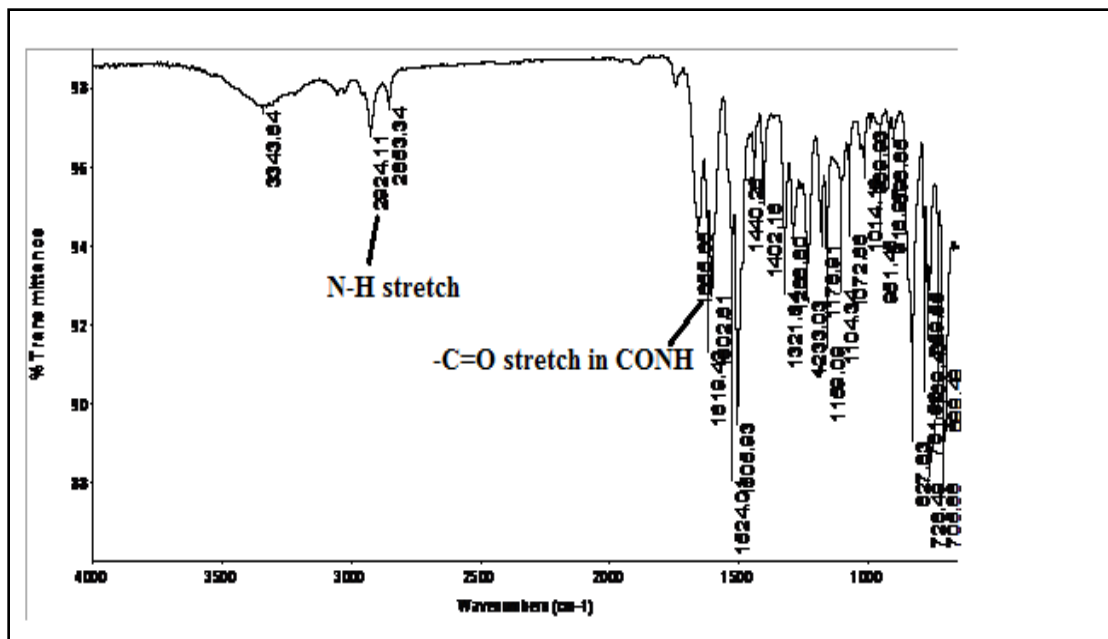


Figure 4: IR spectra of compound (II) (ATPITPA)

¹H NMR SPECTRA:

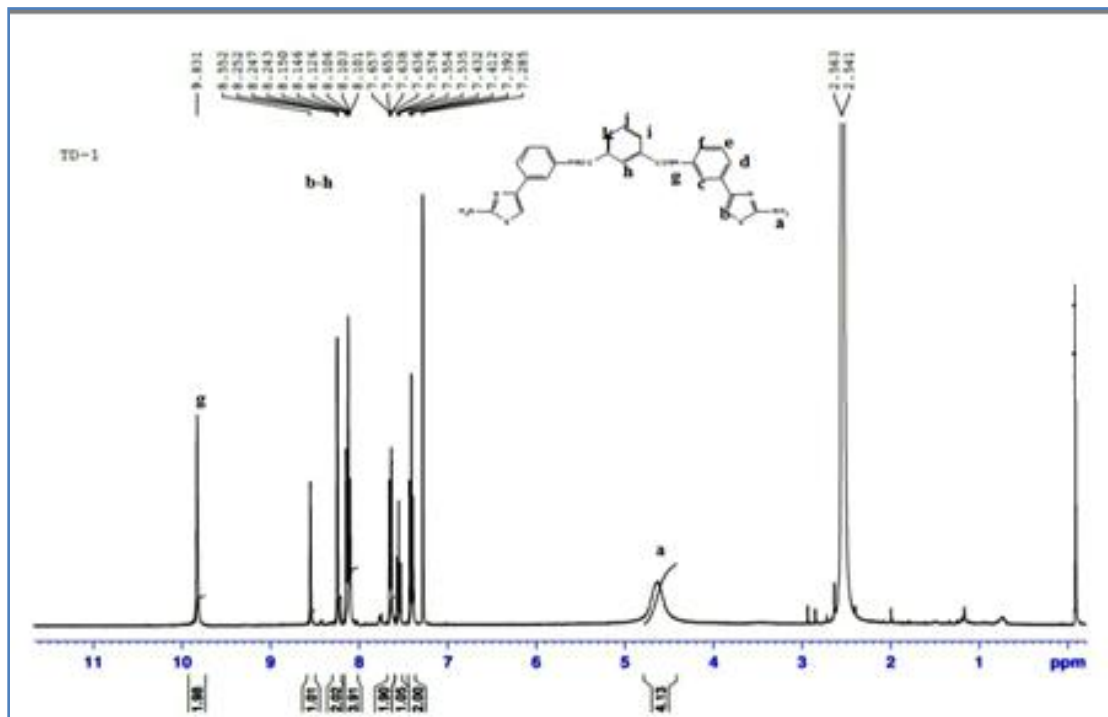


Figure 5: ¹H NMR of compound (II) (ATPITPA)

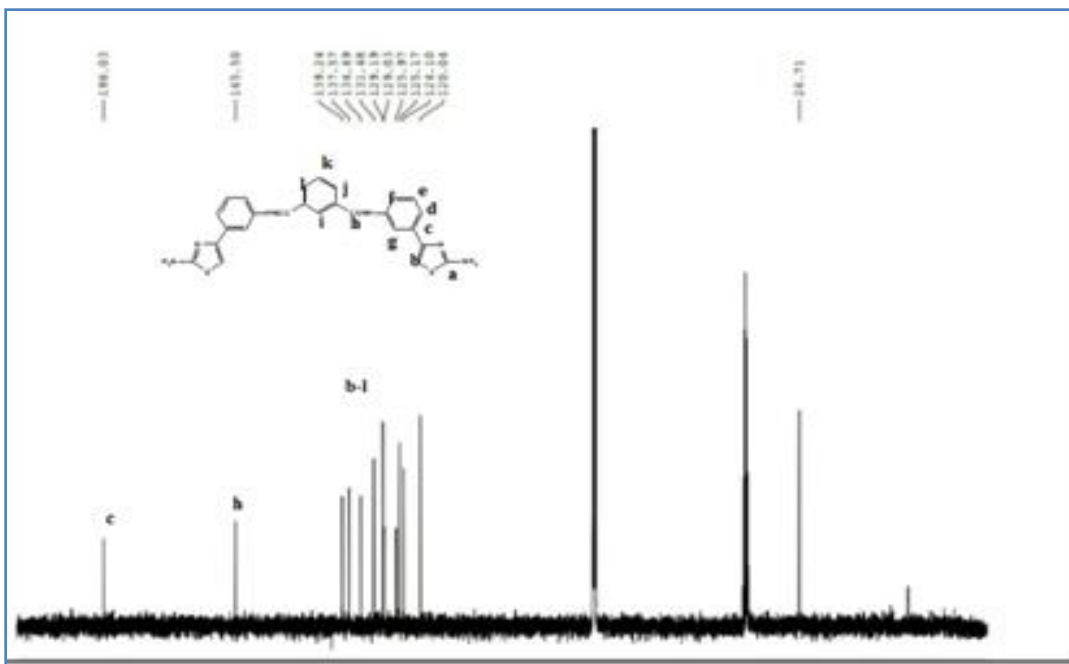


Figure 6: ¹³CNMR compound (II) (ATPITPA)

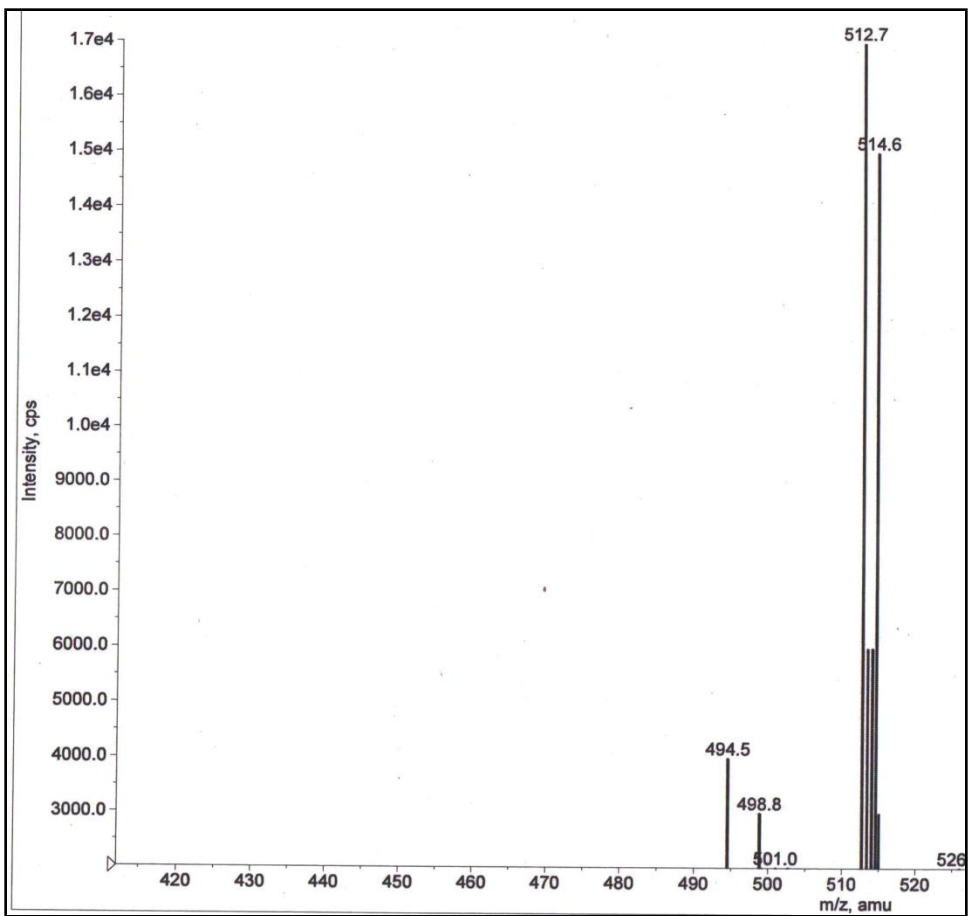
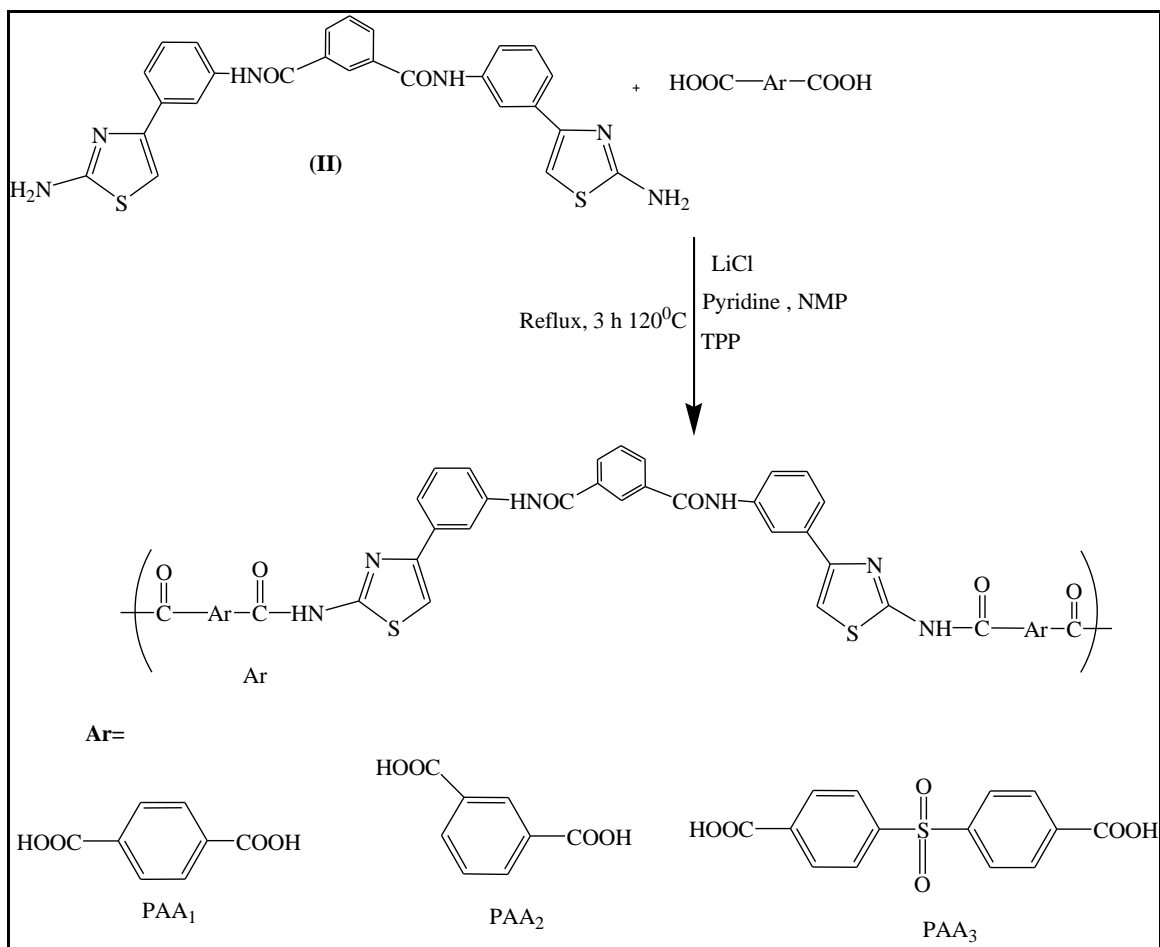
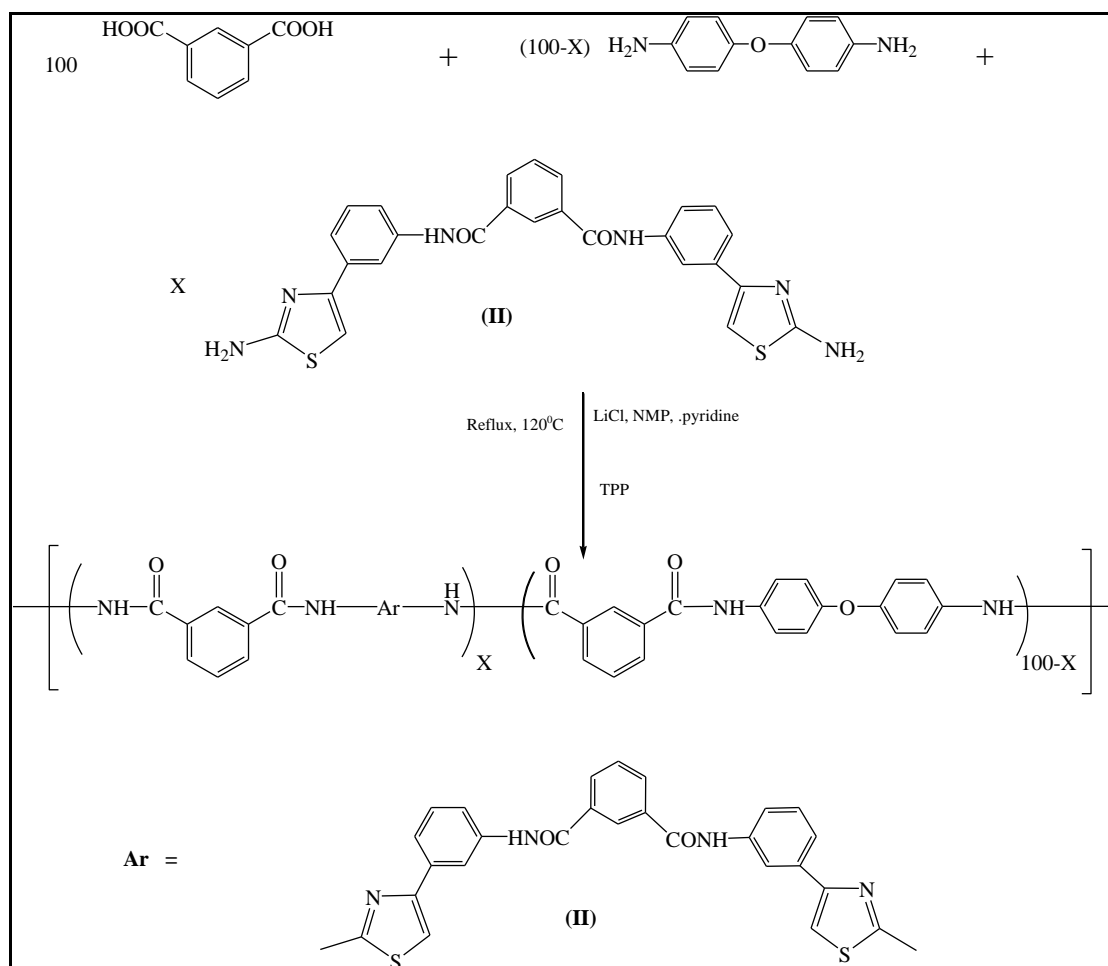


Figure 7:-Mass spectra of compound (II) (ATPITPA)



Scheme 2: Synthesis of polyamide from (ATPITPA) (II) and dicarboxylic acid



Scheme 3: Synthesis of copolyamides (PA) from (ATPITPA) (II) and aromatic diacids

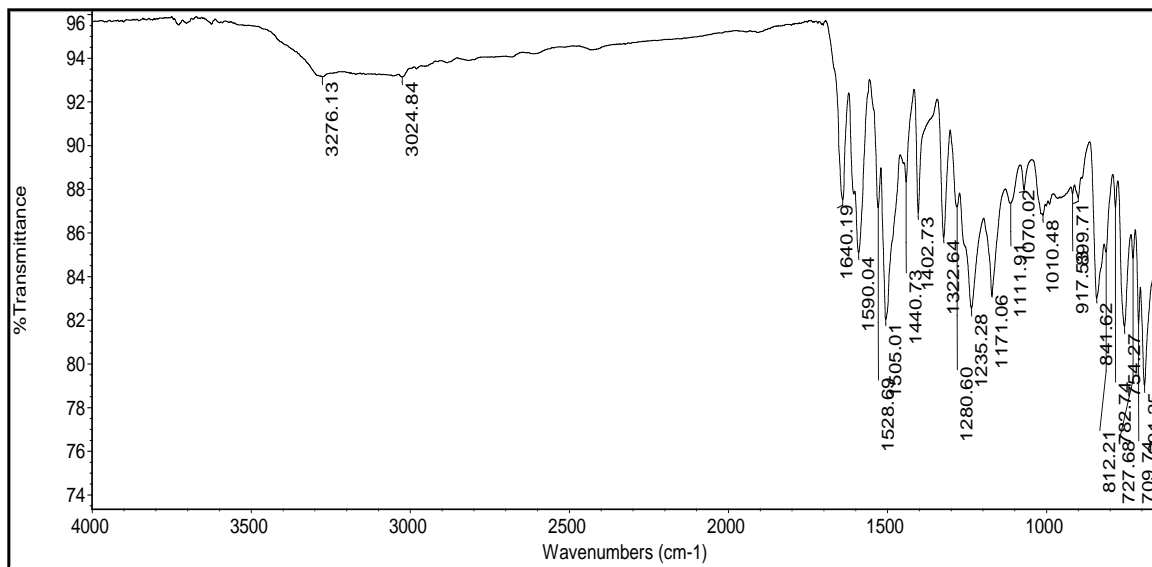


Figure 8: IR spectra of (PA-2) from (ATPITPA) (II) and IPA

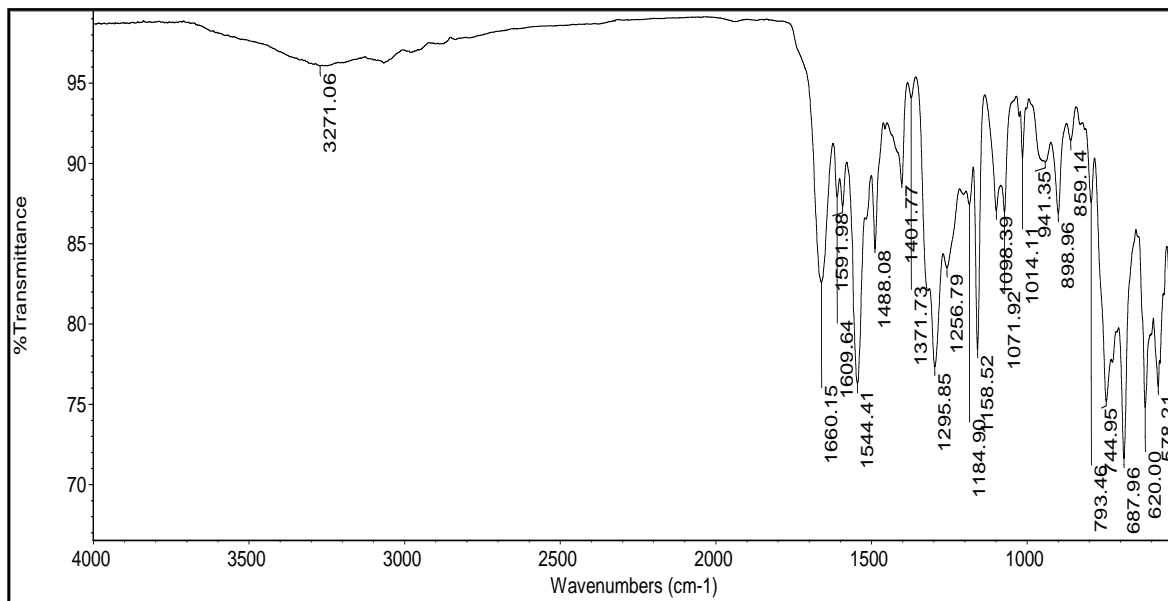


Figure 9: IR spectra of (PA-3)

from (ATPITPA) (II) and DCDPS

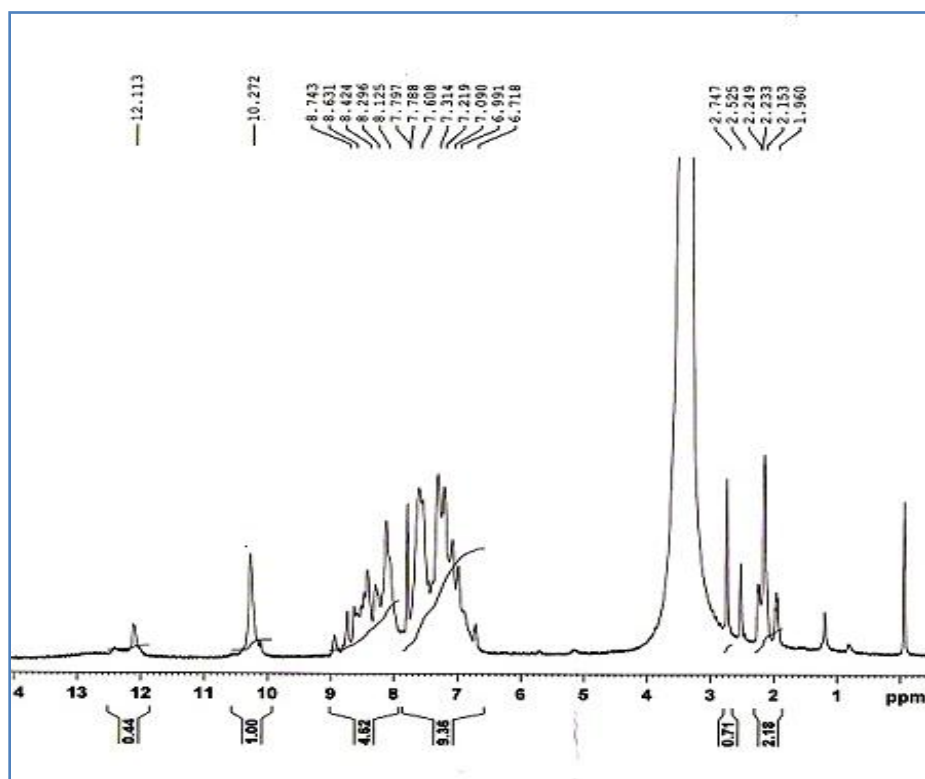


Figure 10 : ^1H NMR of polyamide from (ATPITPA) (II) and IPA

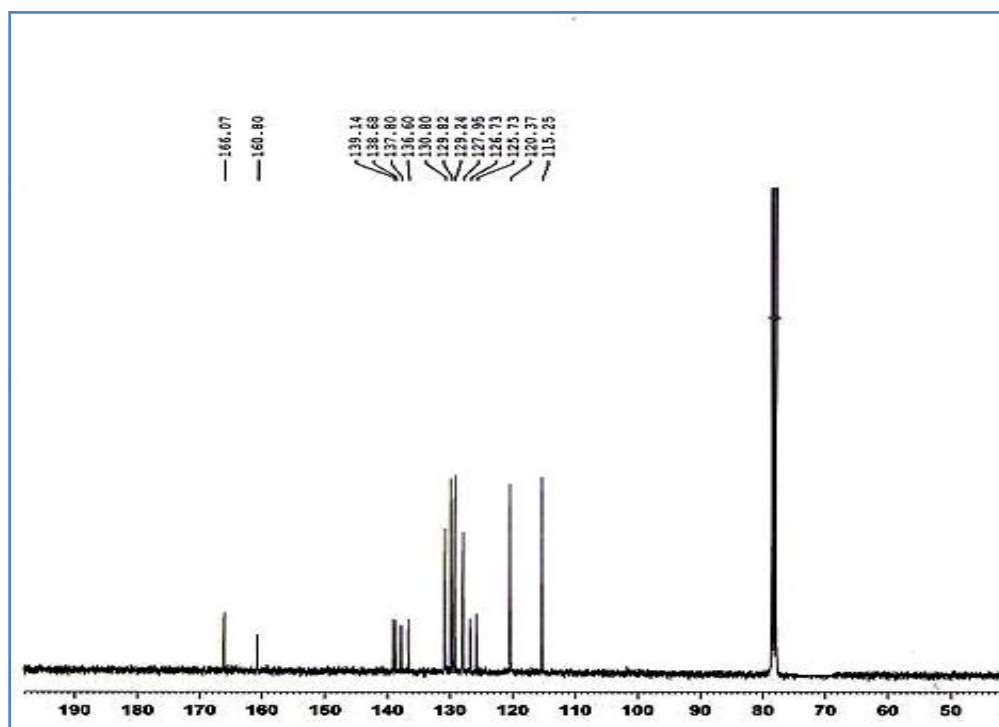


Figure 11: ^{13}C NMR of polyamide from (ATPITPA) (II) and IPA

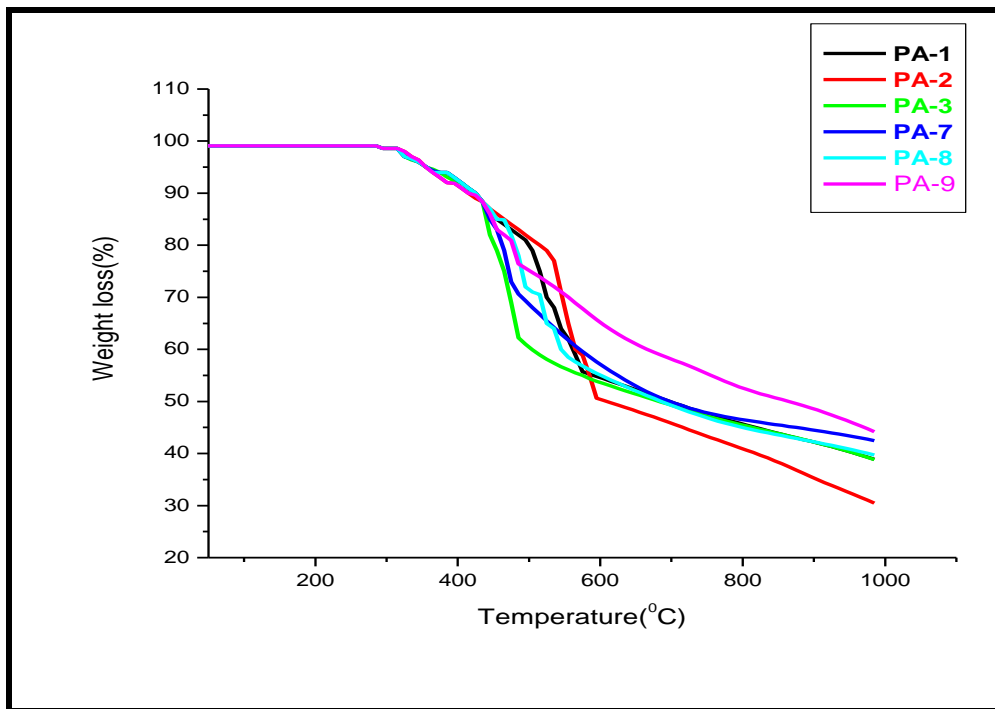


Figure 12: TGA of polyamide

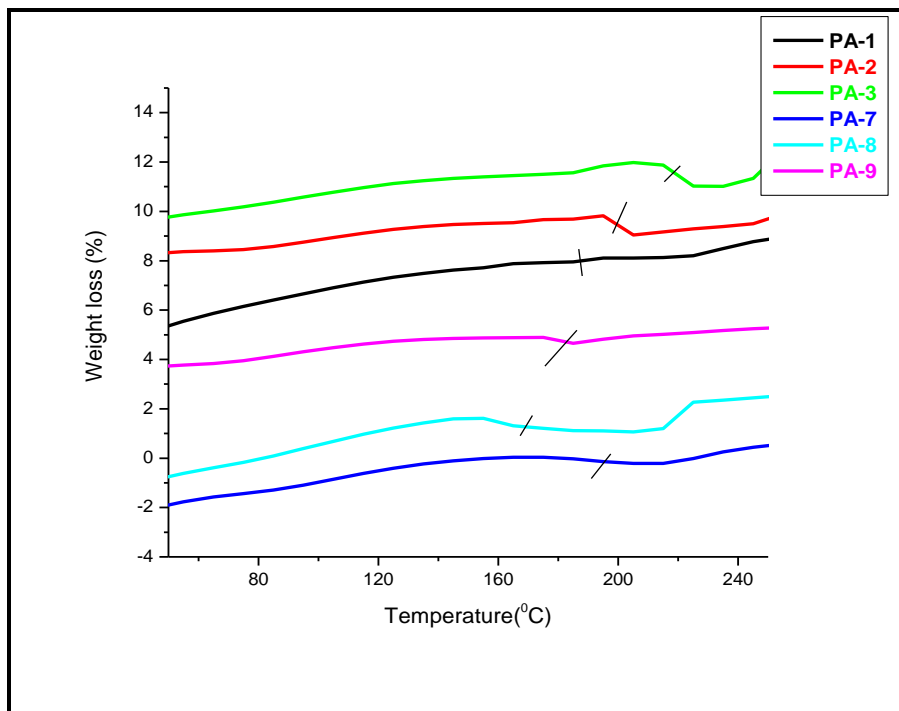


Figure 13: DSC of polyamide

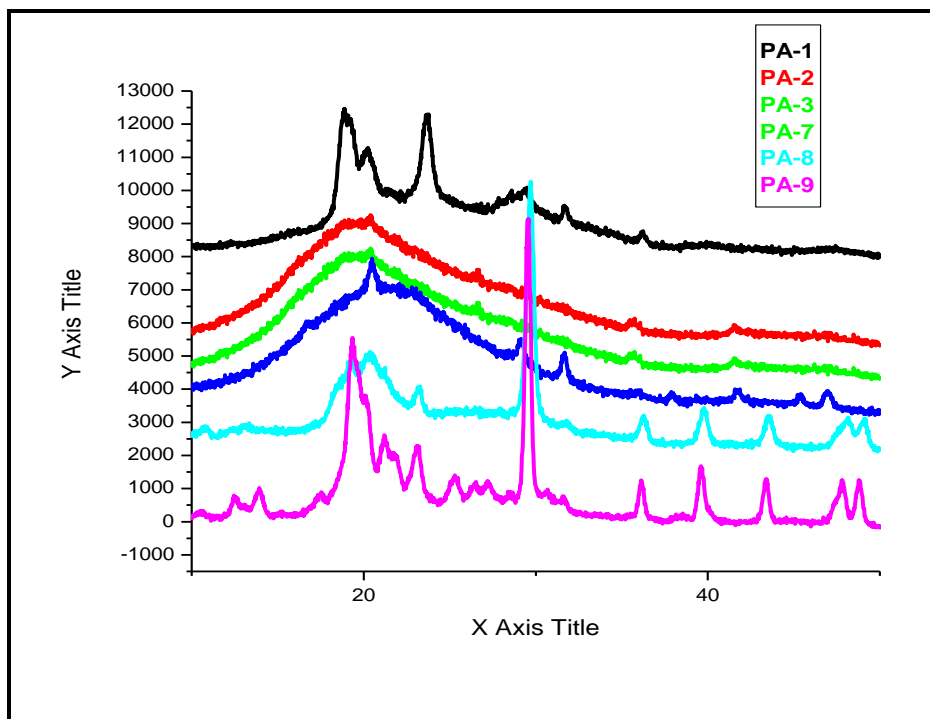


Figure 14: XRD of polyamide

Table-1: Synthesis of polyamides using aromatic diamines and dicarboxylic acid

Sr.No.	Polymer code	Yield (%)	η_{inh} Viscosity dL/g
1	PA-1	95	0.33
2	PA-2	95	0.43
3	PA-3	90	0.56

4	PA-4	95	0.36
5	PA-5	90	0.41
6	PA-6	95	0.28
7	PA-7	90	0.31
8	PA-8	90	0.28
9	PA-9	95	0.34

Table 2: Solubility of polyamides

^a ++ soluble at room temperature +- soluble on heating; -- insoluble

Polymer Code	SOLVENT										
	DMAc	DMSO	DMF	NMP	PYRIDINE	cresol	Nitrobenzene	DCM	CHCl ₃	ethanol	Conc H ₂ SO ₄
PA-1	++	++	++	++	+-	+-	+-	--	--	--	++
PA-2	++	++	++	++	+-	+-	+-	--	--	--	++
PA-3	++	++	++	++	+-	+-	+-	--	--	--	++
PA-4	++	++	++	++	+-	+-	+-	--	--	--	++
PA-5	++	++	++	++	+-	+-	+-	--	--	--	++
PA-6	++	++	++	++	+-	+-	+-	--	--	--	++
PA-7	++	++	++	++	+-	+-	+-	--	--	--	++
PA-8	++	++	++	++	+-	+-	+-	--	--	--	++
PA-9	++	++	++	++	+-	+-	+-	--	--	--	++

PA-1 = ATPITPA + IPA

PA-2 = ATPITPA + TPA

PA-3= ATPITPA + DCDPS

PA-4 = ODA+ IPA

PA-5= ODA+ TPA

PA-6 = ODA + DCDPS

PA-7= ATPITPA + ODA (75:25)

PA-8 = ATPITPA + ODA (50:50)

PA-9= ATPITPA + ODA (25:75)

Table-3: Synthesis and properties of polyamides from (II) (ATPIPTA) and aromatic diacid

Polymer code	Diamine	Diacid	T _i (⁰ C) ^b	T ₁₀ (⁰ C) ^c	Residue at 900 ⁰ C(%) ^e	T _g (⁰ C) ^f
PA-1	ATPIPTA	IPA	312	415	38	188
PA-2	ATPIPTA	TPA	320	425	30	215
PA-3	ATPIPTA	DCDPS	305	455	38	218
PA-4	ODA+IPA	N.E	N.E	N.E	N.E	N.E
PA-5	ODA+TPA	N.E	N.E	N.E	N.E	N.E
PA-6	ODA+DCDPS	N.E	N.E	N.E	N.E	N.E
PA-7	ATPIPTA+ODA (25+75)	IPA	298	439	37	225
PA-8	ATPIPTA+ODA (50+50)	IPA	305	470	35	179
PA-9	ATPIPTA+ODA (75+25)	IPA	345	487	42	167

N.E. Not evaluated

^a n_{inh} was measured with 0.5%(w/v) solution of polyamide at 30±0.1⁰c in DMAc.

^b Initial decomposition temperature.

^c Temperature at which 10% weight loss is observed.

^d Temperature at which 30% weight loss is observed

^e % of char yield

^f Glass transition temperature measured on DSC at a heating rate of 10⁰C /min under N₂

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SUMMERY OF THE FINDINGS

Synthesis of polyamide from newly synthesized diamine (II) and aromatic diacids showed good thermal stability and solubility in polar aprotic solvent such as DMAc, DMF, DMSO, NMP. Inherent viscosities were in the range from 0.2-0.56 dL/g indicates moderate to high molecular weight polymer. All polymers were amorphous in nature. The introduction of heterocyclic moiety i.e thiazole unit is in polymer backbone.

CONTRIBUTION TO THE SOCIETY

Polyamides having thiazole moiety overcomes the difficulties of conventional polyamides. These polyamides are processable as well as thermally stable. The key property of most of the polymers which was thought to distinguish from metals was the inability to carry electricity. During the past 15 to 20 years a new organic polymers has been developed with the surprising ability to conduct electricity. One important area is that Organic Photovoltaic cell (OPV). It is rise to possible applications rechargeable batteries, electrolytic capacitors, LED's etc they contains heteroatoms having lone pair of electrons to conduct electricity.

Polymers having heretocyclic moiety and meta linkage which disturbs regularity and increases solubility. Polymer based solar cell improve power conservation efficiency as well as stability. These ployamdes shows corrosion inhibitors, high optical transparency, high refractive index, low birefringence and high potential bioactivity.

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Principal Investigator.