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# FACILE SYNTHESIS OF NEW THERMALLY STABLE AND ORGANOSOLUBLE POLY (AMIDE-IMIDE)S BASED ON NON-COPLANER HETEROCYCLIC MOIETY CONTAINING AMINES

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## ABSTRACT

A series of novel aromatic poly and copoly (amide-imide)s (PAIs) are prepared from two dicarboxylic acid anhydride (PMDA, BTDA) a and synthesized diamines. Synthesis of a new diamine containing thiazolidine unit N, N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (ATPIPA) was synthesized by reaction of isophthaloyl chloride with m/p-aminoacetophenone followed by reaction with iodine, thiourea and characterized by different spectroscopic methods. Diamines and all polymers are characterized by FT-IR, NMR spectroscopic techniques. The polymers obtained have good thermal stability and glass transition temperature (Tg*)* in the range of 170-185ºC. The resulting polymer exhibit inherent viscosity in the range of 0.2 to 0.37 dL/g. These polymers are found to be soluble in aprotic polar solvents such as NMP, DMSO, DMF and DMAc. Wide angle X-ray diffraction revealed that these polymers are predominantly semicrysatlline to amorphous in nature.

## KEYWORDS

Poly (amide-imide), Thiazole diamine, Aromatic anhydride, Thermal stability and Glass transition temperature.

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## INTRODUCTON

Polyimides are an essential class of engineering thermoplastic that possess advantageous physical properties such as high thermo oxidative property, solvent resistance, toughness, high modulus, chemical resistance and relatively low dielectric constant[1-6]. These polymers are used in a variety of applications such as coatings, composites, adhesives, aerospace, optoelectronics and microelectronics[7-13]. However, commercial use of these polymers is often limited due to their poor solubility in most organic solvents and their high softening or melting temperature. In order to overcome these limitations, various approaches to processable aromatic polyimides have focused on chemical modifications, mainly by preparing new monomers that provide less molecular order, better torsional mobility and low intermolecular interactions and improvement in solubility of polymers in organic solvents without sacrificing the above excellent properties. Some general approaches that have been commonly implemented, are incorporation of flexible linkages, attachment of bulky pendant substituents, use of asymmetric monomers, non-coplanar biphenyl moiety and heteroaromatic rings into polyimide chains[14-22]. Among various strategies adopted so far to improve processability of polyimides, Insertion of an amide group in imide backbone has proven satisfactory. PAIs contain amide and cyclic imide units along the chain and hence inherit desirable characteristic balanced between those of polyimides and this class of polymers offer a good compromise between solubility, high thermal properties and processability[23-25].

## EXPERIMENTAL

## MATERIAL AND METHODS

Dimethyl formamide (DMF), thionyl chloride, methanol, m-aminoacetophenone, isophthalic acid, terephthalic acid, m-cresol, ethanol (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. Pyridines, lithium chioride, N-methyl-2-pyrrolidone (NMP) were purified prior to use. Pyromellitic dianhydride (PMDA) (Aldrich) and 3, 3, 4, 4-benzophenone tetracarboxylic dianhydride (BTDA) was obtained from Merck in the form of yellow powder. It was first recrystallised from dry acetic anhydride and purified by sublimation under reduced pressure.

### Characterization

IR spectra were recorded at a resolution of 4 cm$^{-1}$ with co-addition of 32 scans using a Thermo-scientific Nicolet iS10 smart IR. $^1$HNMR spectra were recorded with a Bruker 400 MHz and 100 MHz for $^{13}$C measurements using $CDCl_3$ or DMSO solvent. Thermo gravimetric analysis (TGA) was performed with Perkin-Elmer TGA-7 system at a heating rate of 10ºC/min in a nitrogen atmosphere from 60 to 1000ºC. Wide angle X-Ray diffraction patterns of polymers were obtained on a Rigaku Ultima-IV X-ray diffractometer. Dried polymer powder samples were exposed to the X-ray measurement.

## MONOMER SYNTHESIS

### Synthesis of N, N'- bis (3- acetyl phenyl) isophthalimide (I) (APIPTA)

In 100mL three neck round bottom flask equipped with magnetic stirrer, a nitrogen gas inlet, thermo well and $CaCl_2$ guard tube were charged with m-aminoacetophenone 0.274 g (0.002mol) and dry DMAc (6mL). The mixture was stirred under nitrogen atmosphere till the complete dissolution takes place and it was cooled to -15ºC. In a cooled reaction mixture add lot wise isophthalyol chloride 0.166 g (0.001mol) and few crystals of LiCl. The mixture was stirred at 0ºC for 1.5 h and then for 1.5 h at 25ºC

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: - 210ºC

**IR (cm$^{-1}$)**: 1667 cm$^{-1}$ (–C=O stretch), 2908 cm$^{-1}$ (aliphatic CH stretching) and 1602 cm$^{-1}$ (NH bending)

**$^1$HNMR (DMSO, ppm)** (s, 2H) 2.86 (s, 6H), 7.45-8.35 (multiplate) aromatic protons

**$^{13}$CNMR (DMSO, ppm)** 196, 168, 159, 80, 40.

### Synthesis of N, N'-Bis-[3-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (II) (ATPIPTA)

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

Yield:-0.460 (90%).

**IR**: 1672 $cm^{-1}$ (C=O stretching of (CONH)) 3365 $cm^{-1}$ (NH stretching of primary amine). (Figure No.1)

**$^1$HNMR:** (200 MHz, DMSO; ppm) 10.38ppm (s 2H) was assigned to amide proton, 4.14ppm (s, 2H) was assigned to proton of $NH_2$ group. 6.97ppm group. The aromatic protons were exhibited peaks in range (7.33-8.60 ppm (multiplate). (Figure No.2).

**$^{13}$C NMR:** (50 MHz, DMSO; PPM) showed the 15 peaks for 15 different carbon atoms. The peak at 165 ppm was assigned to carbonyl carbon of amide group (Figure No.3).

**Mass:** The molecular ion peak at 512 m/e+ was assigned as a base peak. This confirmed the compound (II) structure (Figure No.4).

### Polymer synthesis

Aromatic poly (amide-imide)s were synthesized by two step polycondensation of aromatic diamine and aromatic anhydride at low temperature to form linear open chain poly (amic acid). In the second step the conversion of polyamic acid to polyimides was performed by chemical process initially and subsequent thermal, viz. acetic anhydride, pyridine, benzene and successive heating upto 300ºC, for cyclodehydration to form polyimides. During imidisation the color of poly (amic acid) changed from yellow to brown as imidisation proceeded. The poly (amic-acid) and polyimide were characterized by IR, $^1$HNMR, TGA-DSC and XRD analysis.

### Poly (amide-imide) formation

In a three neck round bottom flask equipped with magnetic stirrer, a nitrogen gas inlet, thermo well and $CaCl_2$ guard tube, 0.512 g (0.001mole) and 4mL dry DMAc were placed. The mixture was stirred under nitrogen atmosphere till the complete dissolution and was cooled to -15ºC, solid aromatic anhydride (0.001mole) was added. Add few crystals of LiCl at 0ºC for 1.5 h and then at 25ºC for 1.5 h. The solution was stirred at room temperature for 24 h. The viscous solution added in methanol the white solid was obtained, continued stirring for 30 min, filtered and washed with methanol and dried.

### Chemical cyclisation

To a reaction mixture 2mL of pyridine, 4mL acetic anhydride was added in order to cyclic-dehydrate the polyamic acid. The reaction mixture was maintained a room temperature for two hour, then heated upto 120ºC for another 2 hours. The reaction mixture was poured into excess methanol with vigours stirring. The white precipitate was collected and washed thoroughly with hot water and methanol. Subsequently, it was dried in oven for 100ºC.

## RESULTS AND DISCUSSION

Aromatic polyimides as commercialized heterocyclic polymers, have exhibited remarkable composite characters, such as excellent thermal stability, balanced mechanical and electrical properties, as well as good chemical and irradiation resistance.

Incorporation in the main chain of other rigid group whose rigidity is not far lower or higher than that of the imides group is another important method for preparing polyimide with improved processability and balanced thermal resistance. The processability of these polyimide is improved by distortion of the main chain regularity and thermal stability is maintained by retained rigidity of the main chain. Since amide bond is a bit less rigid than imide bond, therefore poly (amide-imide)s are certainly the most important type of modified polyimides. The introduction of heterocyclic ring i.e. thiazole unit containing amide linkage into the backbone of polymers is another approach to improve solubility and thereby processability. They exhibit a valuable set of properties the combination of increased thermal stability and increased solubility in organic solvents contributed by the cardo groups.

### Characterization of polyimides

### IR Spectra

The IR spectrum of poly(amic acid) exhibited absorptions at 3274 $cm^{-1}$ due and 1655 $cm^{-1}$ due to –C=O stretching of amide linkage. (Figure No.5).

The IR spectrum of polyimides showed adsorptions at 1780, 1720 $cm^{-1}$ (-C=N) and 3600 $cm^{-1}$ (C-N) which confirms the formation of polyimides. The absorption band at 3274, 1655 $cm^{-1}$ were absent suggesting total cyclisation of poly (amic-acid) to polyimide. (Figure No.6)

### $^1$HNMR Spectra

$^1$HNMR spectra confirms the structure of poly (amide-imide)s by assigning the peak at 10.48 ppm confirmed the amide linkage. In between 7-9 ppm assigned for aromatic proton. (Figure No.7)

### $^{13}$CNMR Spectra

It exhibits 20 different peaks corresponding to the different 20 carbons in spectra. The peak at 161 ppm and 166 ppm confirms the polyimide formation. (Figure No.8).

### XRD Spectra

From XRD data a P I-2, PI-3 were crystalline in nature while PI-4, PI-5 copolymers were amorphous in nature (Figure No.9). Significance solubilities of polyimides were tested at 3% (w/v) concentration in various organic solvents and data is summarized in Table No.1. Polyimides were soluble in polar solvent such as NMP, DMAc, DMSO etc. at room temperature. Polyimides were insoluble in $CHCl_3$, m-cresol etc.

The improved solubility of polyimides especially that of polyimides derived from rigid dianhydrides could be attributed to the cooperative effect of weakning of the intermolecular interaction and due to heterocyclic unit changes in the rigid structure and regular planarity disturb and solubility and processability increases.

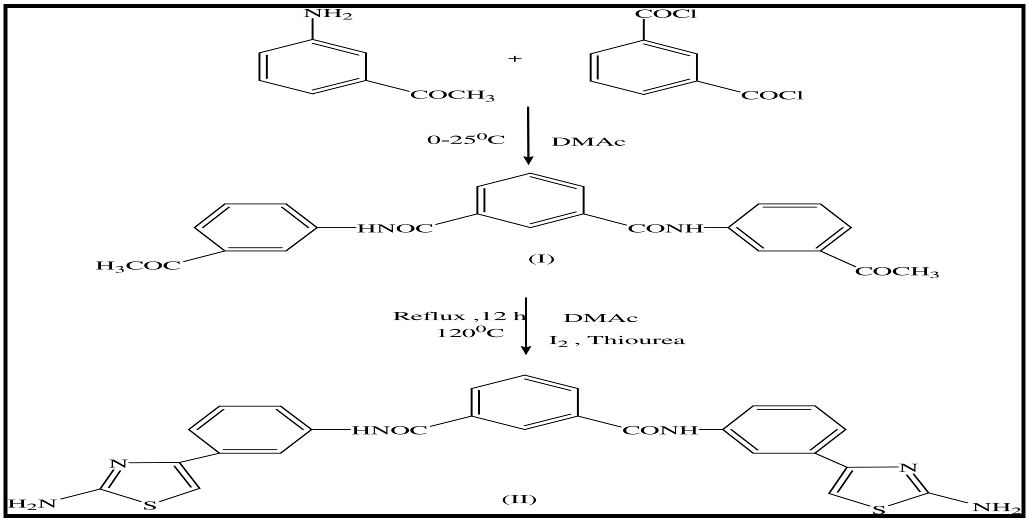
From thermo gravimetric analysis thermal stability of polyimides with heterocyclic unit was investigated by thermogravimetric analysis (TGA) at a heating rate of 10ºC/ minute under nitrogen. The Initial decomposition temperature (IDT) and temperature at which 10% weight loss observed are given in the Table No.2. Thermal degradation of polyimides began in the temperature range 250ºC and showed stepwise degradation with increase in temperature (Figure No.10). Tg values of polyimides and copolyimides containing heterocyclic unit were lower than those of the other polyimides. The depression of Tg values with increase in side chain length indicates that side chains act on main chains as a bound solvent or as an internal plasticizer (Figure No.11).

**Table No.1: Yield and viscosity data of poly (amide-imide)**

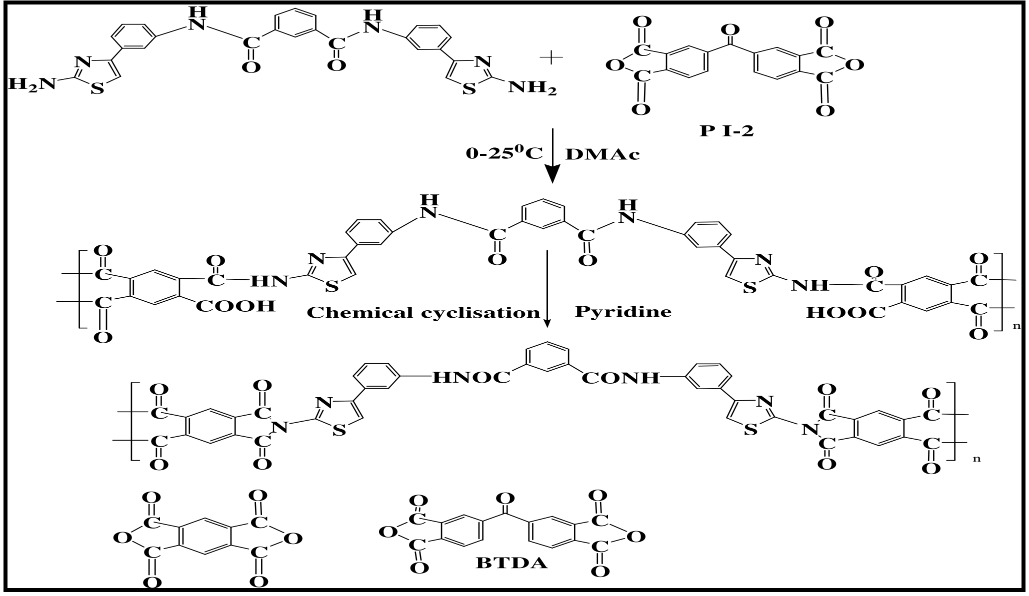
| S.No | Polymer Code | Diamine | Dianhydride | Yield (%) | $n_{inh}$ (dL/g)$^a$ |
|---|---|---|---|---|---|
| 1 | PI-1 | ATPIPTA | PMDA | 90 | 0.19 |
| 2 | PI-2 | ATPIPTA | BTDA | 95 | 0.33 |
| 3 | PI-3 | ATPIPTA +ODA (75:25) | BTDA | 97 | 0.22 |
| 4 | PI-4 | ATPIPTA +ODA (50:50) | BTDA | 96 | 0.26 |
| 5 | PI-5 | ATPIPTA +ODA (25:75) | BTDA | 98 | 0.37 |

**Table No.2: Thermpgravimetry data of poly (amide-imide)s from Thiazole diamine and aromatic dianhydrides**

| S.No | Polymer Code | Diamine | Dianhydride | $T_i$(°C)$^b$ | $T_{10}$(°C)$^c$ | Residue at 900ºC | $T_g$(ºC)$^e$ |
|---|---|---|---|---|---|---|---|
| 1 | PI-1 | ATPIPTA | PMDA | --- | -- | -- | -N.E. |
| 2 | PI-2 | ATPIPTA | BTDA | 298 | 352 | 9 | 170 |
| 3 | PI-3 | ATPIPTA +ODA (75:25) | BTDA | 302 | 387 | 8 | 185 |
| 4 | PI-4 | ATPIPTA +ODA (50:50) | BTDA | 295 | 335 | 11 | 171 |
| 5 | PI-5 | ATPIPTA +ODA (25:75) | BTDA | 301 | 415 | 33 | 179 |



**Scheme No.1: Synthesis of N, N'-bis-[3-(2-amino-thiazol-4-yl)-phenyl] isophthalamide (ATPITPA) (II)**



**Scheme No.2: Synthesis of poly (amide-imide)s from (ATPITPA) (II) and aromatic dianhydride**

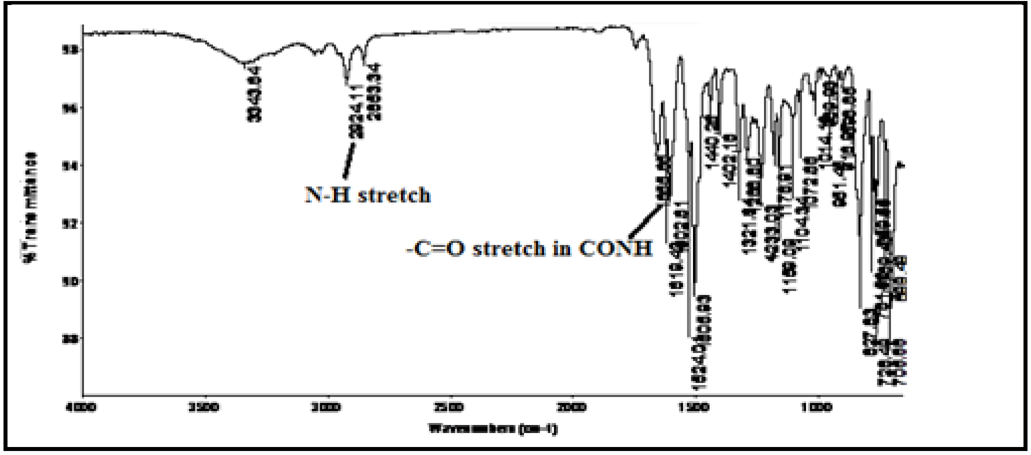


**Figure No.1: IR spectra of compound (II) (ATPITPA)**

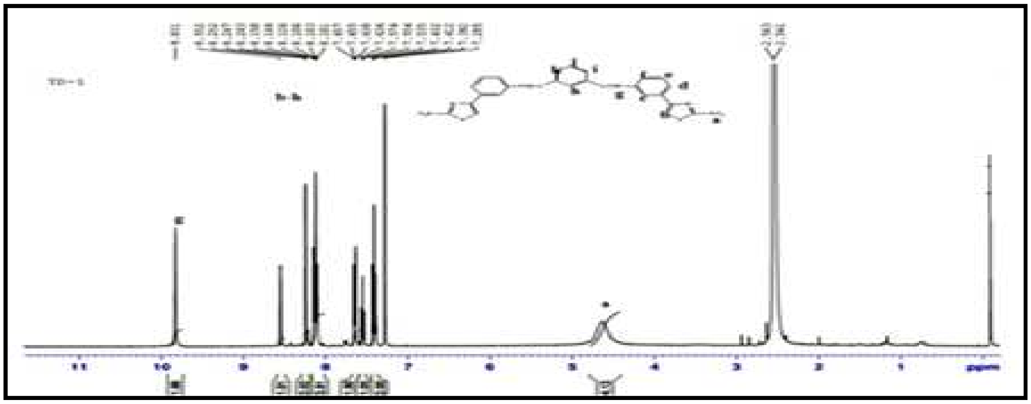


Figure No.2: $^1$HNMR of compound (II) (ATPITPA)

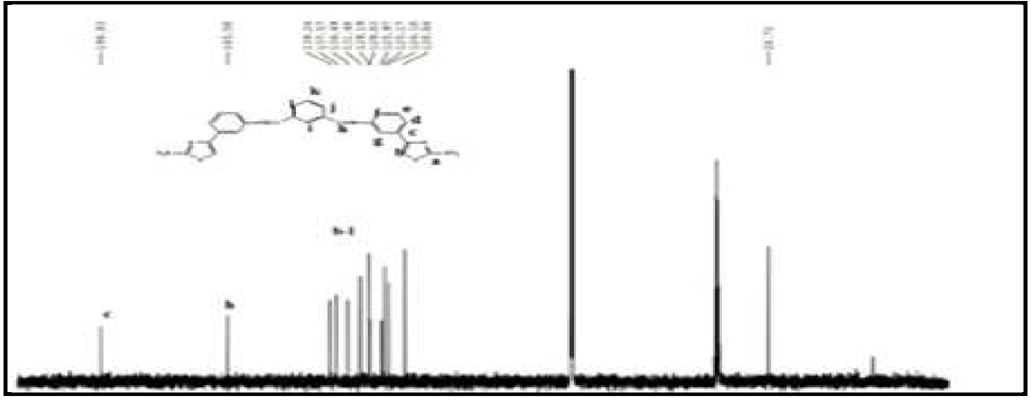


Figure No.3: $^{13}$CNMR compound (II) (ATPITPA)

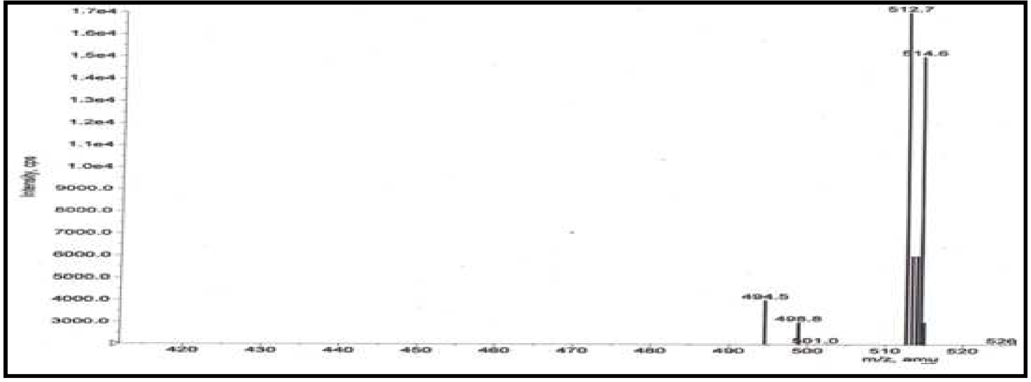


Figure No.4: Mass spectra of compound (II) (ATPITPA)

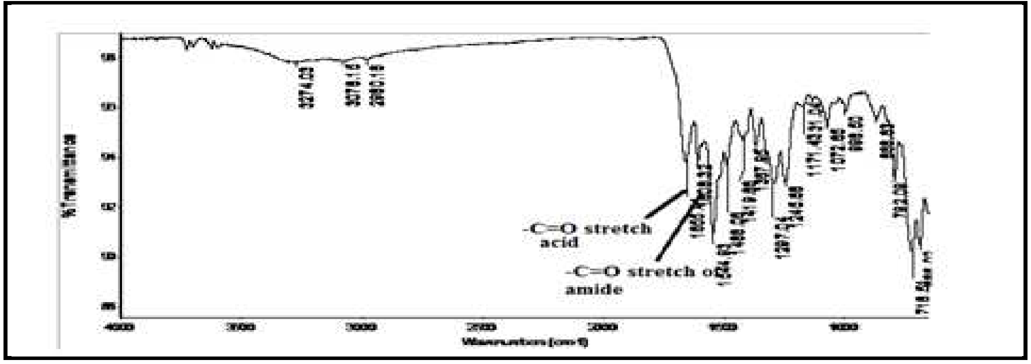


Figure No.5: IR Spectra of poly (amic-acid)

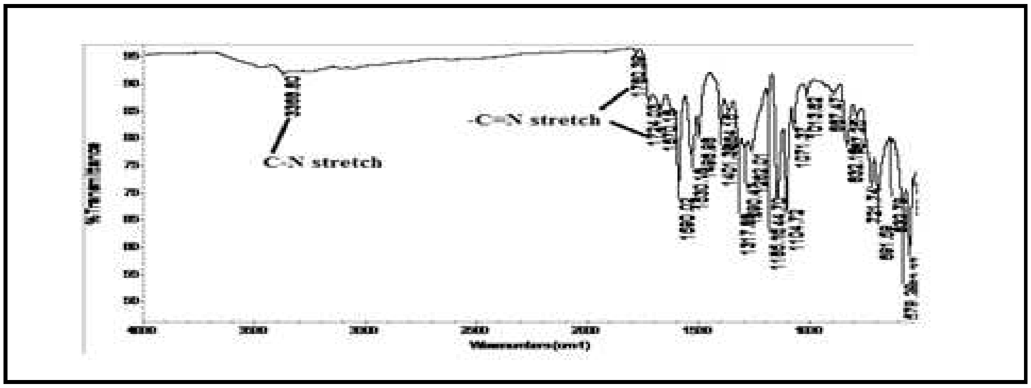


**Figure No.6: IR Spectra of poly (amid-imide) from (ATPITPA) (II) and BTDA**

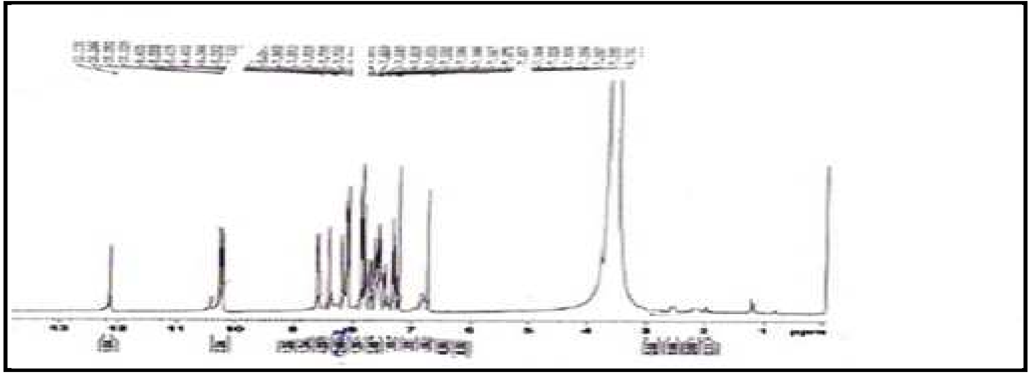


**Figure No.7: $^1$HNMR of poly (amide-imide) from monomer (II) and BTDA**

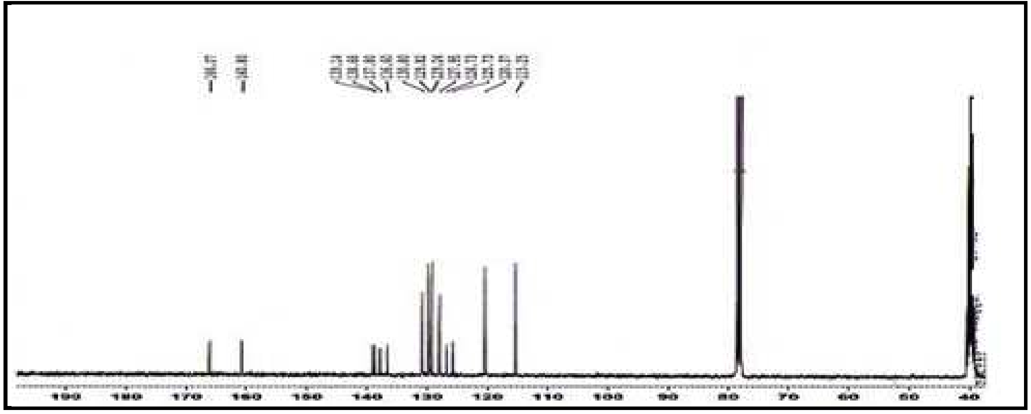


**Figure No.8: $^{13}$CNMR of (ATPITPA) ( II) and BTDA**

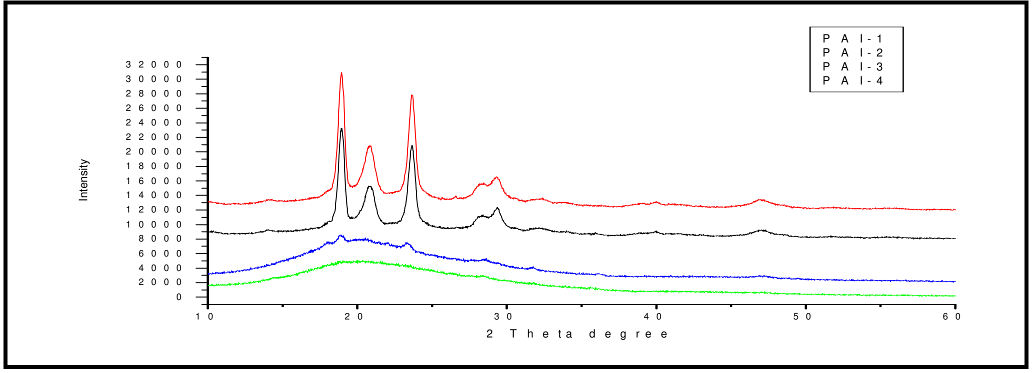


**Figure No.9: XRD of poly (amide-imide)s**

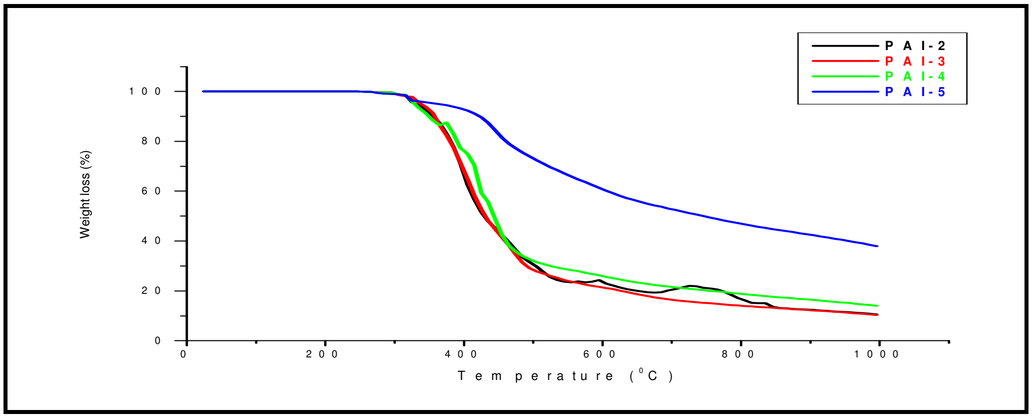


**Figure No.10: TGA of poly (amide-imide)s**

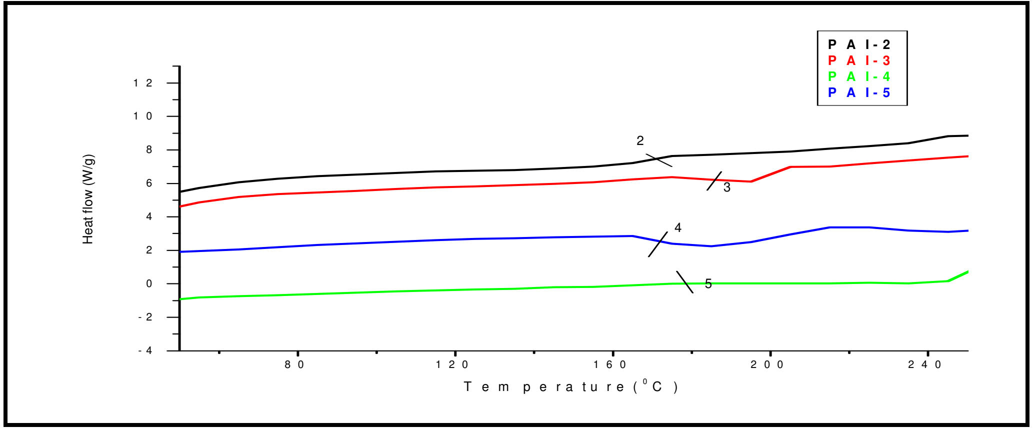


**Figure No.11: DSC poly (amide-imide)s**

## CONCLUSION

The series of synthesized poly (amide-imide)s from a new monomer II (ATPIPA) with PMDA and BTDA were obtained in quantitative yield. Polymers were characterised by infrared, $^{1}$HNMR, $^{13}$CNMR spectroscopy, viscosity, solubility, XRD and thermal analysis. They had viscosities in the range of 0.19 to 0.37 dL/g in DMAc at 30ºC. PI-5 showed high percentage of char yield at 900ºC.

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## CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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