

# Preparation and Characterization of New Aromatic Polyimides from 1,2,4,5-Benzene tetracarboxylic Acid Dianhydride and New Aromatic Diamines

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## Abstract

A series of new aromatic polyimides (Pi1 - Pi6) containing methylene unit, flexible ether linkages (containing naphthalene rings), and Schiff-base linkages were prepared by solution polycondensation reaction of 1,2,4,5-benzene tetracarboxylic dianhydride (BTDA) with new various aromatic diamines using a standard two-stage process with thermal imidization of poly(amic acid) films. The monomers were characterized by FT.IR, and some them by <sup>1</sup>H. NMR. The resulting polymers were characterized by means of FT.IR, <sup>1</sup>H.NMR spectroscopy, and solubility tests. All polyimides were readily soluble in polar aprotic solvents. The thermal stability, melting temperature and glass transition temperature of these polyimides were measured using differential scanning calorimetry (DSC). These polymers formed tough flexible films by solution casting.

**Key Words:** Polyimide, Aromatic Polyimides, 1,2,4,5-Benzene tetracarboxylic Acid Dianhydride, Aromatic Diamines

## الخلاصة

سلسلة من البولي أيميدات الأروماتية الجديدة Pi1 - Pi6 المحتوية على وحدة المثلين ، روابط ايثرية مرنة (محتوية على حلقات نفثالين) لقواعد شف-بيس حضرت من تفاعل بلمرة التكثيف بين حامض 1,2,4,5-بنزين رباعي كاربوكسيليك ثنائي الانهيدرايد مع مونيمرات أروماتية متنوعة وجديدة باستخدام عملية قياسية من مرحلتين مع عملية تكوين الأصرة الاميدية الحرارية لأفلام بولي (حامض أميك). المونيمرات شخصت بوساطة تقنيتي الأشعة تحت الحمراء والبعض منها شخص بطيف الرنين النووي المغناطيسي. البوليمرات الناتجة ايضا شخصت بوساطة أطياف الأشعة تحت الحمراء و البعض منها شخص بالرنين النووي المغناطيسي، واختبارات الذوبانية. هذه البولي أيميدات كانت سهلة الذوبان في المذيبات اللابروتية القطبية. الاستقرارية الحرارية ودرجة الانتقال الزجاجي لهذه البولي أيميدات تم قياسها بوساطة تقنية المسح الحراري التفاضلي. هذه البوليمرات شكلت أفلام مرنة خشنة بوساطة حالة المحلول.

مفتاح الكلمات : بولي أيميدات، بولي أيميدات أروماتية ، حامض 1,2,4,5-بنزين رباعي كاربوكسيليك ثنائي الانهيدرايد ، مونيمرات أروماتية ثنائية الأمين

## Introduction

Since 1960, essentially the beginning of the search for high temperature polymers, more attention was focused on polyimides than any other high performance/high temperature polymers. This is primarily due to the availability of polyimide monomers (particularly aromatic dianhydrides and diamines), the ease of polymer synthesis, and their unique combination of physical and mechanical properties<sup>[1-3]</sup>. One of the ways to meet the more and more stringent requirements for thermally and chemically stable materials used in various branches of modern technology is their development on the basis of aromatic polyimides, a class of polymers known for their high thermal stability, excellent electrical and mechanical properties<sup>[4,5]</sup>, and good chemical resistance. But because they soften or melt at high temperatures and have poor solubility in common organic solvents, they have low processability and limited use<sup>[6,7]</sup>. To overcome these drawbacks, many investigations have focused on modification of their chemical structure; for example, through the introduction of flexible linkages, asymmetric units, or bulky substituents into their polymer backbones<sup>[8-13]</sup>.

Furthermore, pyridine would display excellent stabilities derived from its molecular symmetry and aromaticity, as well as polarizability resulting from nitrogen atom in its ring<sup>[14]</sup>, so new kind of monomer holding pyridine unit have been synthesized and employed in preparation of the polymer at elevated temperature<sup>[15]</sup>.

Therefore, this study is concerned with the synthesis and properties of new polyimides containing both methylene unit, flexible ether linkages (containing naphthalene rings), and Schiff-base linkages in the main chain with the aim to obtain thermally and chemically stable polymers.

## Experimental

### Instruments

Fourier transform infrared (FTIR) spectra were recorded on a SHIMADZU-FTIR-8400S spectrometer (Japan) with KBr pellets in the optical range of 400–4000 $\text{cm}^{-1}$  at Al-Qadisiya university. <sup>1</sup>H. NMR spectra were registered using a Bruker, 250Mhz, spectrometer, at polymer laboratories Co Iran using DMSO as a solvent. Differential scanning calorimetry (DSC) were measurements by DSC 131 Evo, SETARAM, (France) using a heating rate of 10°C/min in N<sub>2</sub> atmosphere within the temperature range of 30–600°C at AlQadisiya university . The sample weight used approximately (10mg) mg. The peaks are used to determine the thermal properties of the samples. The Solubility of the polymers was determined with (0.01gm) of polyimide in (2ml) of a solvent.

### Materials

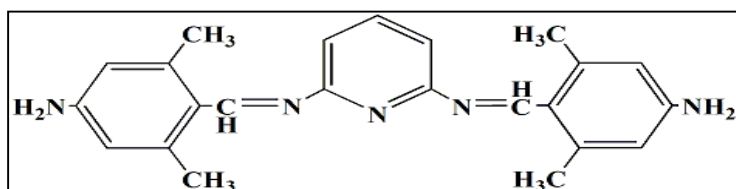
Absolute Methanol, Acetic acid, Palladium on Charcoal10% , all from (*BDH/England*); Dichloromethane from (*BIOSOLVE*); Hydrochloric acid, Salicylaldehyde, all from (*HiMedia*); Diethyl ether from (*IGCC /England*); Aniline, 3-Chloroaniline, 2-Bromoaniline, 4-Chlorobenzaldehyde, 2,6-Diamino pyridine, Dimethyl Sulphoxide (DMSO), m-Cresol, N,N-Dimethylacetamide, 4-(dimethyl amino)benzaldehyde, Tetrahydrofurane (THF) , all from (*MERCK*); Absolute Ethanol from (*Scharlab S.L*); 1,2,4,5-benzene tetracarboxylic acid dianhydride, Acetone, Isoquinoline, P-Chloronitrobenzene, all from (*ALDRICH*); N,N-Dimethylformamide (DMF) from (*Sinopharm Chemical Reagent*); B-naphthalene, and Hydrazine monohydrate from (*THOMAS-BAKER*).

### Synthesis of Monomers :

2.3.1 Synthesis of 2,6-Bis [(4-amino-2,6-dimethyl phenyl)methylene ]diaminopyridine [M1]:-

This monomer was prepared by the condensation of 4-amino(2,6Dimethyl)benzaldehyde (3gm, 20mmol) and 2,6-diaminopyridine (1.1gm, 10mmol) in 15ml of methanol, by boiling the mixture under reflux at 120°C for 3h. The precipitated was filtered and recrystallized

from methanol and dried in a *vacuum* desiccators<sup>[16]</sup> to yielding 2.93gm (79%wt) of light green crystals. m.p 79-83°C.

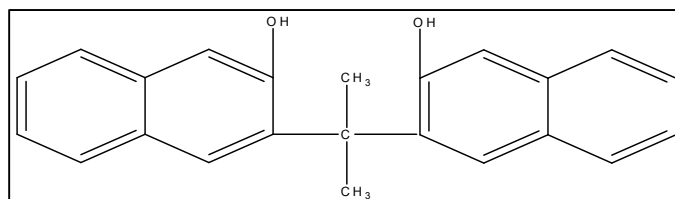


Scheme 1 : Structure of M1 (Schiff-Base).

Synthesis of 3-(2-(2-hydroxynaphthalen-3-yl)propan-2-yl) naphthalen-2-ol (HNPN):-

A mixture of 2-Naphthol(6.6gm/ 20mmol), acetone (0.74gm / 10mmol) , HCl catalyst (37.5g) as catalyst and thioglycolic acid (0.5 gm) as promoter were placed in a three necked-round bottom flask equipped with a condenser, mechanical stirrer and

thermometer and it was kept in a thermostat bath at 60°C for 6hr. After a definite period of time, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was washed, dried and weighed<sup>[17]</sup> to yielding 2.6gm (79%wt) of light pink crystals. m.p 68-70°C.

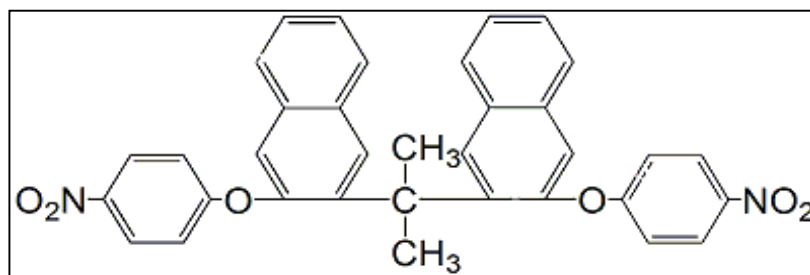


Scheme 2 : Structure of [HNPN]

**Synthesis of 1- (4-nitrophenoxy) -4-(2-(3-(4-nitrophenoxy) naphthalene-2-yl) propane -2- yl) naphthalene (NPNPNP)** :-

A mixture of 3-(2-(2-hydroxy naphthalene-3-yl)propan-2-yl)naphthalene-2-ol (3.3gm, 10mmol), p-chloro nitro benzene (3.16gm , 20mmol), potassium carbonate (7gm , 50mmol), and (20ml) of DMF was

refluxed at 140-142°C for 8hs under nitrogen. After completion of the reaction, the reaction mixture was added to water to precipitate product. The resulting solid was filtered and recrystallized from 2-methoxyethanol<sup>[18]</sup> to produce 4.6gm (80%wt) of light brown crystals. m.p 93-95°C.

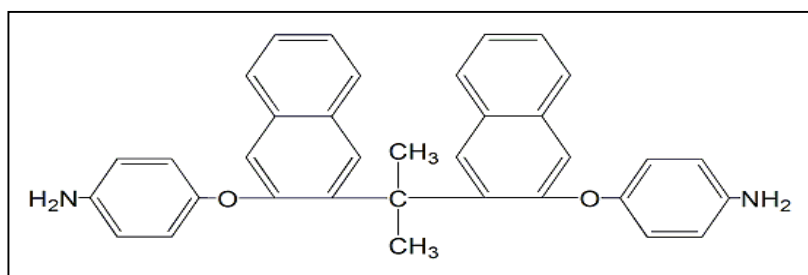


Scheme 3 : Structure of (NPNPNPN).

**Synthesis of 4-((3-(2-(4-(4-aminophenoxy)naphthalen-1-yl)propan-2-yl)naphthalene -2-yl)oxy)aniline [M2] :**

(4gm , 6mmol) of the (NPNPNPN) 0.2gm of 10% Pd/C and 100ml of ethanol were introduced into a three-necked flask to which 20ml of hydrazine monohydrate was added dropwise over a period of 1h at 85°C. After completing the addition, the reaction was continued at reflux temperature for another

4hs. To the suspension, 40ml of THF was added to re-dissolve the precipitated product, and refluxing was continued for 1h. The mixture was filtered to remove the Pd-C, and the filtrate was poured into water. The product was filtered off, washed with hot water and dried in *vacuum*<sup>[19,20]</sup> to yielding 2.6gm (86%wt) of deep yellow crystals. m.p (110-115°C).



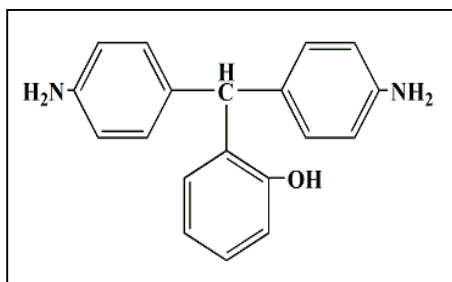
Scheme 4 : Structure of M2.

**Synthesis of 2-(bis(4-aminophenyl)methyl)phenol [M3] :-**

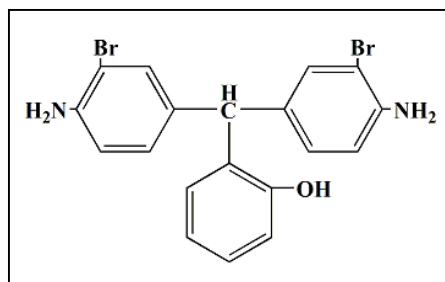
To a 0.1M solution of H<sub>2</sub>SO<sub>4</sub> in methanol ( 60% : 40% ), Aniline (2gm , 21mmol) and Salicylaldehyde (1.2gm , 10mmol) were added and the mixture was refluxed at 120°C for 10hs with constant

stirring. Upon completion of the reaction, the solvent was removed under *vacuum* and to the residue water (2×25 ml) and then CH<sub>2</sub>Cl<sub>2</sub> (50ml) were added. The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub><sup>[21]</sup> to yielding 2.3gm (79%wt) of deep yellow crystals. m.p 75-95°C.

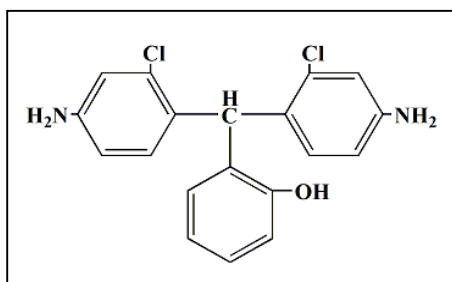




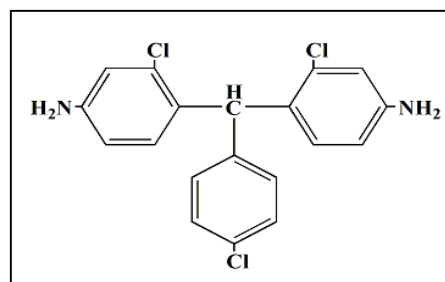
Scheme 5 : Structure of M3.



Scheme 6 : Structure of M4.



Scheme 7 : Structure of M5.



Scheme 8 : Structure of M6.

The other diamino compounds were prepared by the same procedure as above using 2-Bromo aniline with Salicylaldehyde (M4), 3-Chloro aniline with Salicylaldehyde (M5), 3-

Chloro aniline with 4-Chlorobenzaldehyde (M6), respectively, and are shown in (Table1)

Table 1 : Synthesis of Monomers ( M6 , M7 , M8 ).

Monomers	Substance		Weight gm	Yield (%wt)	Color	m.p/°C
	Aniline or Derived	Benzaldehyde Derived				
(M4)2-(bis(4-aminobromophenyl)methyl) phenol	3.6gm (21mmol)	1.22gm (10mmol)	3.36	75	deep brown	130 <i>Decomposition</i>
(M5)2-(bis(4-aminochlorophenyl)methyl) phenol	2.69gm (21mmol)	1.22gm (10mmol)	2.6	72	deep green	240 <i>decomposition</i>
(M6) 4-4'-((4-chlorophenyl)methylene) bis (2-chloroaniline)	2.69gm (21mmol)	1.41gm (10mmol)	2.7	71	light green	125-130

### Synthesis of Polyimides (Pi1 - Pi6):-

The polyimides (Pi1 - Pi6) indicated in (Table 2) were prepared by adding the diamine (1mmol) to m-cresol containing a catalytic amount of Isoquinoline and stirring

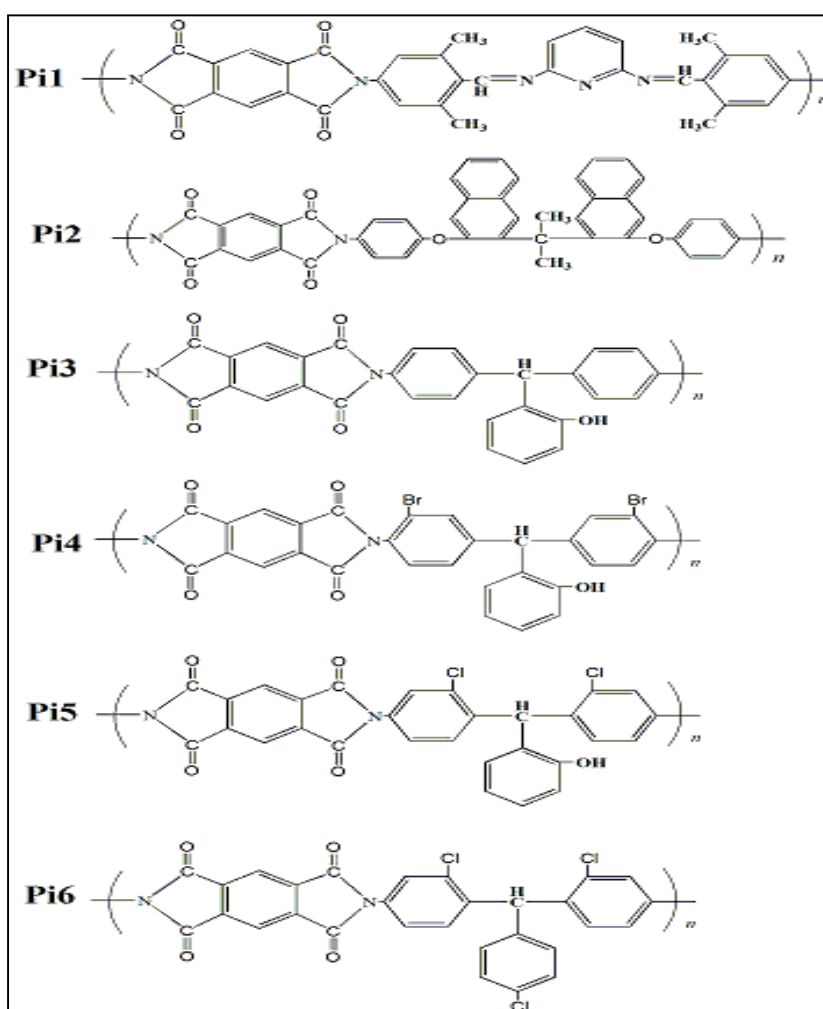
under a nitrogen atmosphere for 0.5h at room temperature. A stoichiometric quantity of 1,2,4,5-benzene tetracarboxylic acid dianhydride (0.22 / 1mmol) was added, the solids content was adjusted to 20% (w/w), the

reaction was heated to 200°C and stirred at 200°C under a nitrogen atmosphere for 4–6hs to form a viscous solution. The cooled polyimide solution was diluted with m-cresol

and poured into methanol in a blender to precipitate a fibrous solid that was isolated, subsequently washed in boiling methanol twice and dried in air at 150°C for 4hs<sup>[22]</sup>.

**Table 2 : Synthesis of Polyimides (Pi1 - Pi6).**

Polyimides	Monomers	diamine	Yield (%wt)	Color
	diamine	Gm		
Pi <sup>1</sup>	M1	0.371	79	pale white
Pi <sup>2</sup>	M2	0.512	77	very-light green
Pi <sup>3</sup>	M3	0.290	78	yellow
Pi <sup>4</sup>	M4	0.448	79	deep brown
Pi <sup>5</sup>	M5	0.360	78	brown
Pi <sup>6</sup>	M6	0.379	77	brown

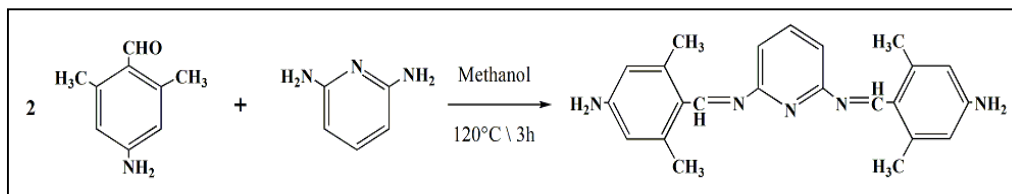


### 3. Results and Discussion

#### 3.1 Synthesis of Monomers :-

3.1.1 Synthesis of 2,6-Bis [(4-amino-2,6-dimethyl phenyl)methylene ]diaminopyridine [M1]:-

M1 is prepared by the condensation of two molecules of 4-amino(2,6-Dimethyl)-benzaldehyde with one molecule of 2,6-diaminopyridine in the presence of Methanol at 120°C for 3h. This monomer was characterized by FTIR spectrum.



Scheme 10 : Synthesis of M1

#### Characterization of M1 Monomer :-

The FTIR spectrum is shown in (Figure 1) which indicated absorption bands at (3625cm<sup>-1</sup>) to (-NH<sub>2</sub> group), (3050cm<sup>-1</sup>) to (aromatic -CH stretching), (2916cm<sup>-1</sup>) to

(aliphatic -CH stretching), absorption bands around (1604–1589cm<sup>-1</sup>) show the presence of the aromatic ring, and (1680cm<sup>-1</sup>) to heteroaromatic ring (C=N).

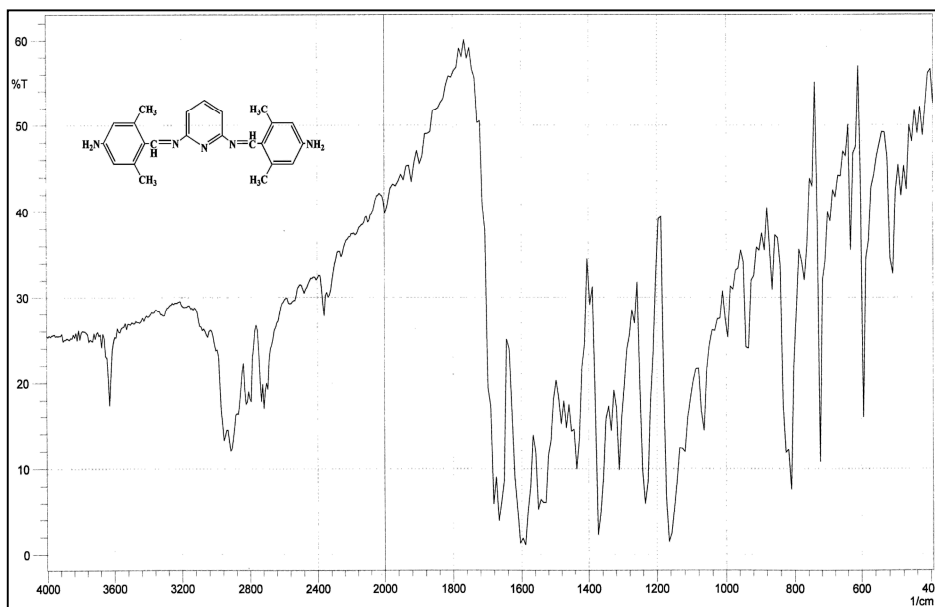
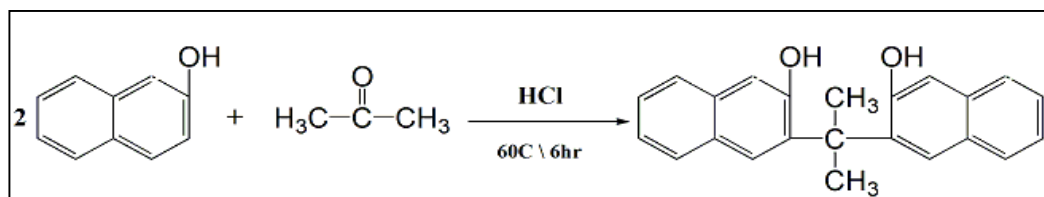


Figure 1 : FTIR spectrum of M1.

#### Synthesis of 3-(2-(2-hydroxynaphthalen-3-yl)propan-2-yl) naphthalen-2-ol (HNPN) :-

(HNPN) is prepared by the condensation of two molecules of 2-Naphthol with one

molecule of Acetone in the presence of HCl as a catalyst and thioglycolic acid as promoter at 60°C for 6h.



Scheme 11 : Synthesis of (HNPN) .

**Characterization of (HNPN)****Monomer :-**

The FT.IR spectrum of (HNPN) shows the absorption band of (C=C Aromatic) at

1550 $\text{cm}^{-1}$ , (C-H Aromatic) at 3150  $\text{cm}^{-1}$ , (OH phenolic) at 3250  $\text{cm}^{-1}$ , and (C-H Alkane) at 2900  $\text{cm}^{-1}$ .

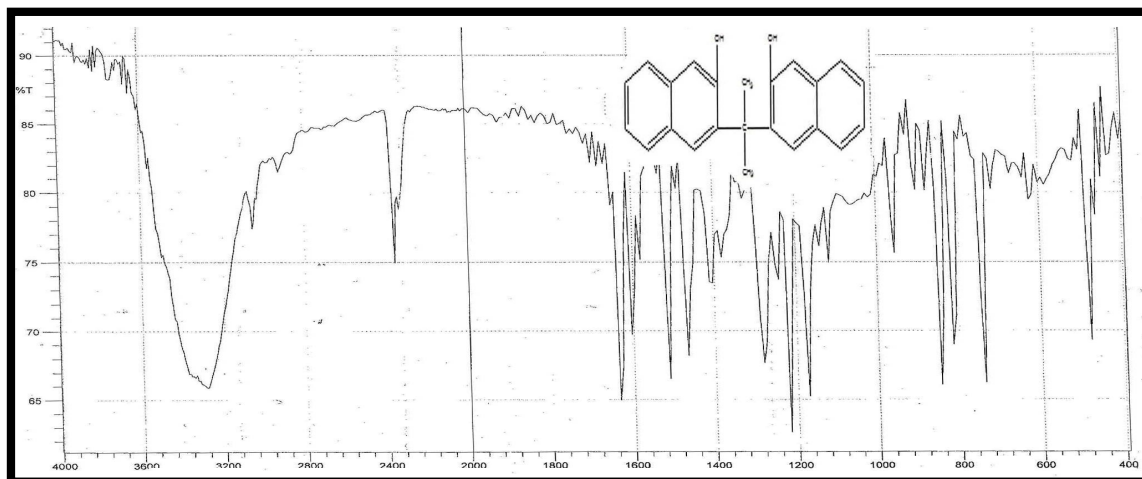
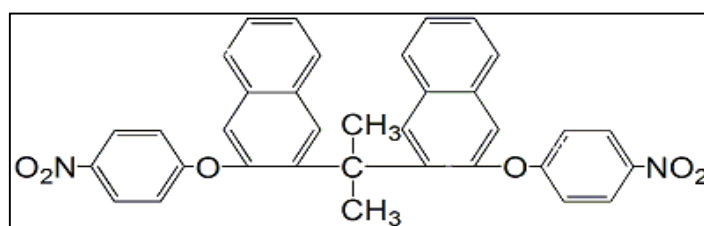


Figure 2 : FTIR spectrum of [HNPN]

**Synthesis of (NPNPNPN). :-**

(NPNPNPN). is prepared by the condensation of one molecule of (HNPN) with two molecules of 4-Chloronitrobenzene in the presence of potassium carbonate and DMF as a solvent at 140-142°C for 8hs. This monomer was characterized by *FTIR spectrum*.



Scheme 12 : Synthesis of (NPNPNPN).

### Characterization of (NPNPN).

In the FT.IR spectrum of, the characteristic absorptions of the (-OH group) disappeared, and two strong absorptions

appeared at (1510), (1350) $\text{cm}^{-1}$  to (-NO<sub>2</sub>) asymmetric and symmetric stretching, respectively, and absorption band at (1210 $\text{cm}^{-1}$ ) due to (-C-O-C- ether linkage).

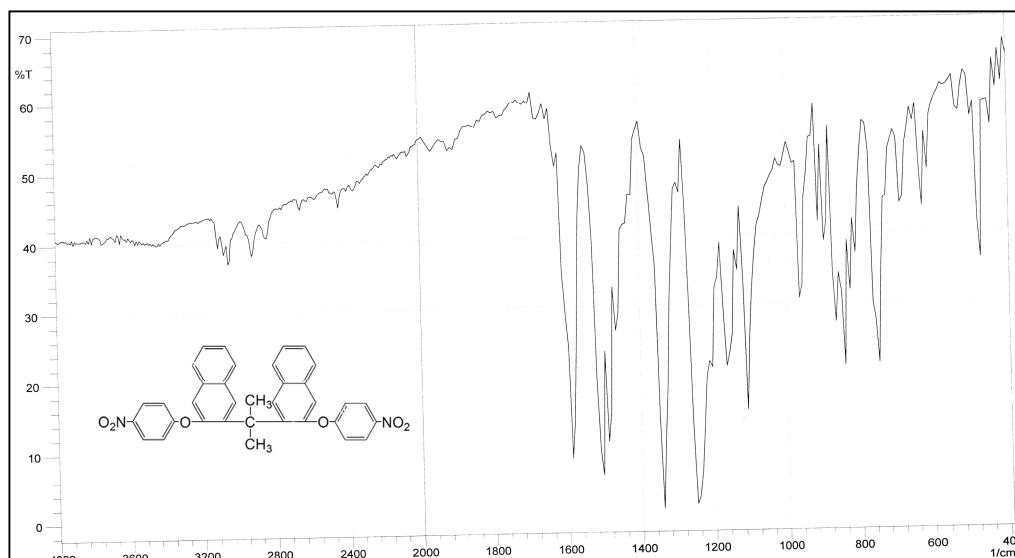
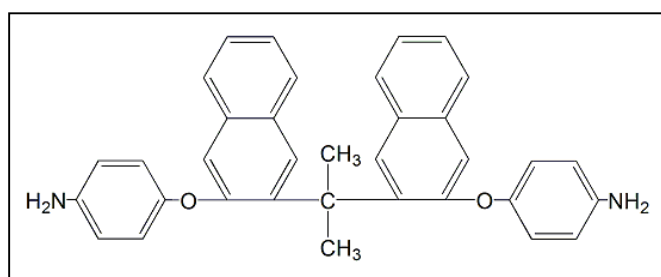


Figure 3 : FTIR spectrum of(NPNPN). .

### Synthesis of [M2] :-

The catalytic hydrogenation of nitro group in the (NPNPN) to amino compound in M2 was accomplished by using hydrazine

monohydrate and catalytic amount of Pd/C as reducing agent at 85°C for 5hs. This monomer was characterized by *FTIR spectrum*.



Scheme 13 : Synthesis of M2.

### Characterization of M2 Monomer :-

According to the FT.IR spectrum of M2 monomer, conversion of nitro group to amine group was confirmed by disappearance of absorption bands at (1510), (1284) $\text{cm}^{-1}$  to

(-NO<sub>2</sub>) asymmetric and symmetric stretching, respectively, and presence of bands at (3312 – 3280)  $\text{cm}^{-1}$  to (-NH stretching) and (1610  $\text{cm}^{-1}$ ) (-NH deformation), respectively.

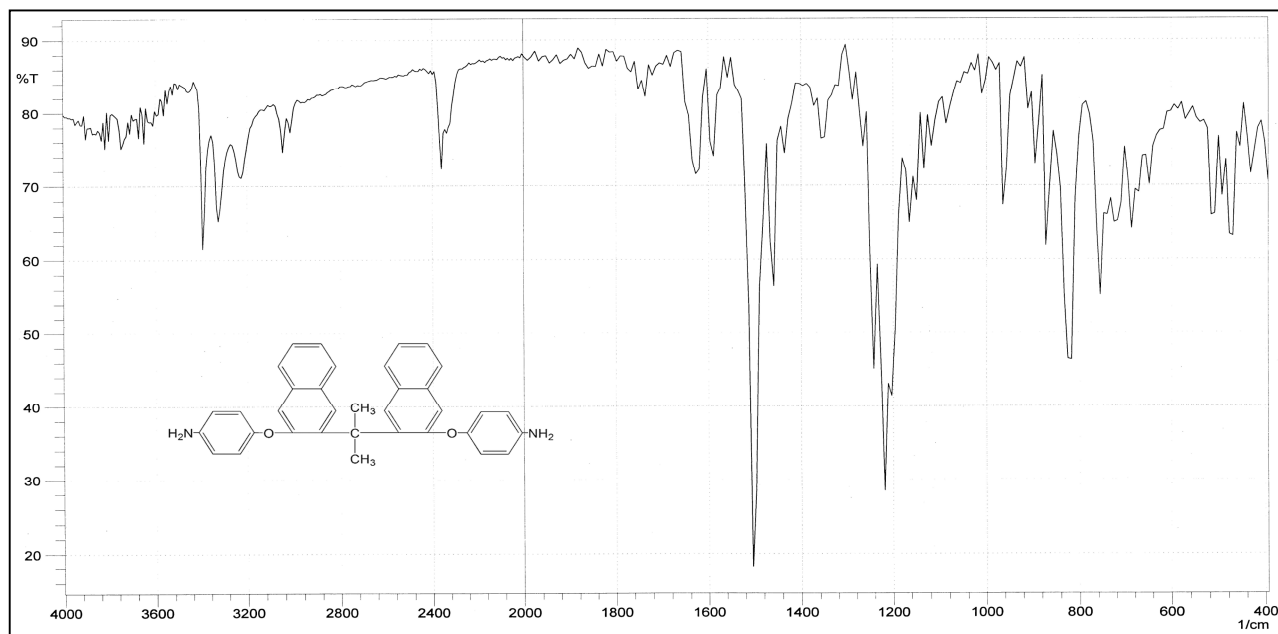
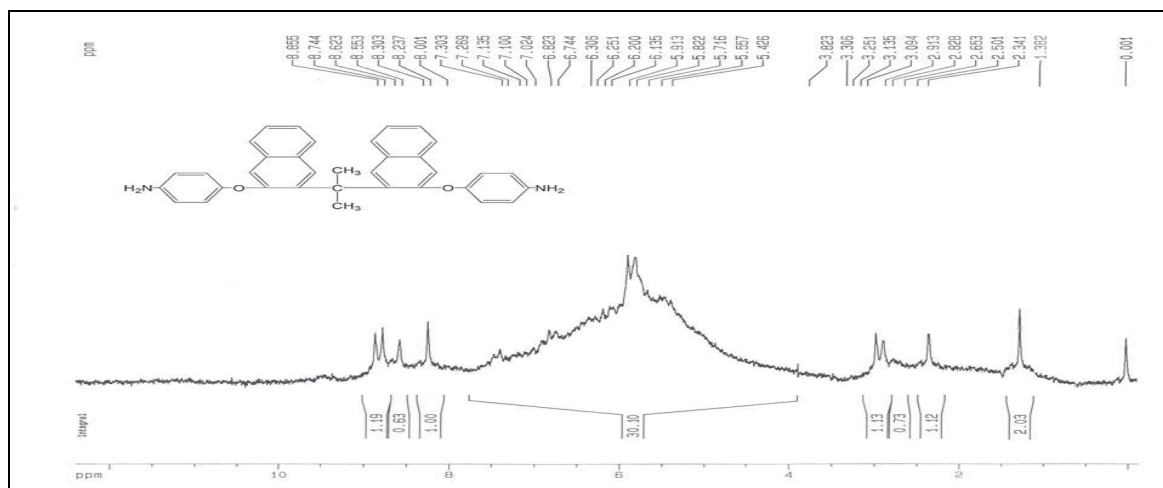


Figure 4 : FTIR spectrum of M2.

$^1\text{H.NMR}$  spectrum of (M2), is shown in (Figure 5) assigns the following chemical shifts;  $\delta$  (2.5) ppm for DMSO,  $\delta$  (1.3) ppm

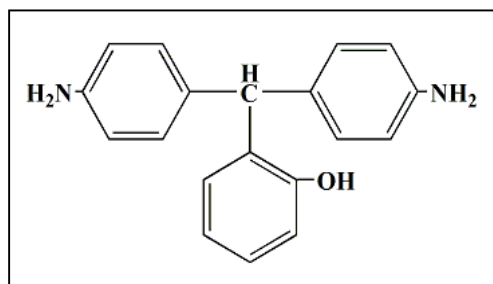
(s,6H) for  $\text{CH}_3$ ,  $\delta$  (5.7) (s,4H) for  $\text{NH}_2$  group,  $\delta$  (6.1 -8.8) ppm (s, 20H) for ArH group.

Figure 5 :  $^1\text{H.NMR}$  spectrum of M2

### Synthesis of [M3] :-

M3 is prepared by the condensation of one molecule of Salicylaldehyde with two molecules of aniline in the presence of

(60% : 40%) solution of ( $\text{H}_2\text{SO}_4$  in methanol) at  $120^\circ\text{C}$  for 10hs. This monomer was characterized by *FT.IR spectrum*.



Scheme 14 : Synthesis of M3

**Characterization of M3 Monomer :-**

FT.IR spectrum of (M3) is shown in (Figure 6) which indicated absorption band at ( $3376\text{cm}^{-1}$ ) to ( $-\text{OH}$  group), ( $3414\text{cm}^{-1}$ ) to ( $-\text{NH}_2$  group), ( $3112\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$

stretching), ( $2910\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$  stretching), and absorption bands around ( $1608\text{--}1540\text{cm}^{-1}$ ) show the presence of the aromatic ring. The characteristic absorption of ( $\text{C}=\text{O}$  aldehyde) disappeared.

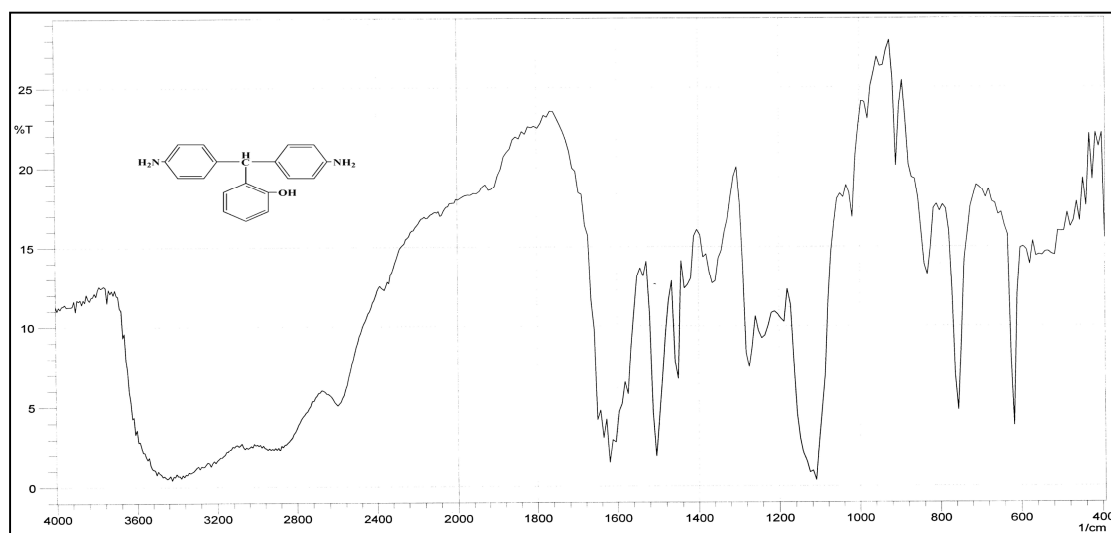
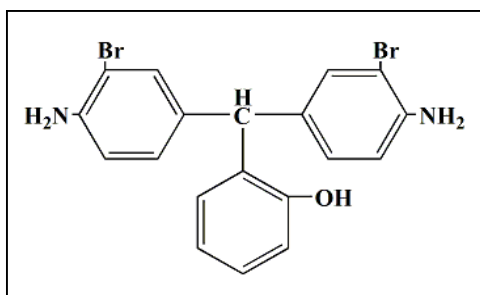


Figure 6 : FTIR spectrum of M3.

**Synthesis of [M4] :-**

M4 is prepared by the condensation of one molecule of Salicylaldehyde with two molecules of 2-BromoAniline in the

presence of (60% : 40%) solution of ( $\text{H}_2\text{SO}_4$  in Methanol) at  $120^\circ\text{C}$  for 10hs. This monomer was characterized by *FT.IR spectrum*.



Scheme 15 : Synthesis of M4.

**Characterization of M4 Monomer :-**

FT.IR spectrum of (M4) is shown in (Figure 7) which indicated absorption band at ( $3396\text{cm}^{-1}$ ) to ( $-\text{OH}$  group), ( $3418\text{cm}^{-1}$ ) to ( $-\text{NH}_2$  group), ( $3210\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2919\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$

stretching), ( $529\text{ cm}^{-1}$ ) to ( $\text{C}-\text{Br}$ ), and absorption bands around ( $1618-1550\text{cm}^{-1}$ ) show the presence of the aromatic ring. The characteristic absorption of ( $\text{C}=\text{O}$  aldehyde) disappeared.

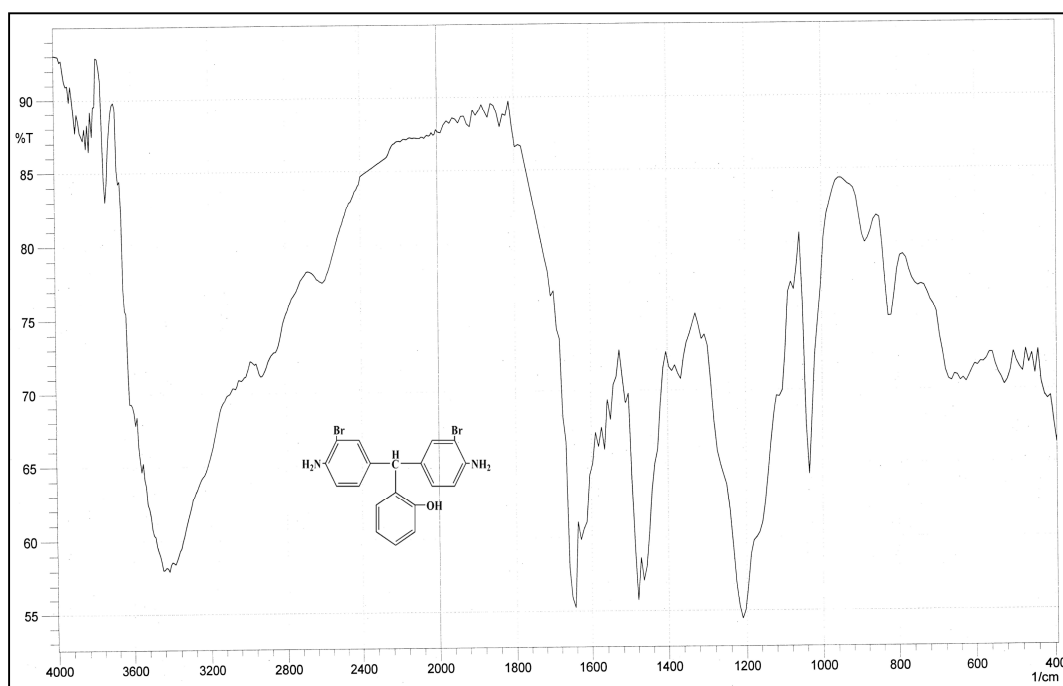


Figure 7 : FTIR spectrum of M4.

$^1\text{H}$ .NMR spectrum of (M4), is shown in Figure 8 assigns the following chemical shifts;  $\delta$  (2.5) ppm for DMSO,  $\delta$  (6.2) ppm

(s,1H) for C-H,  $\delta$  (6.0) (s,4H) for  $\text{NH}_2$  group,  $\delta$  (6.2 -8.9) ppm (s, 10H) for ArH group  $\delta$  (6..6) ppm (s,1H,OH) . .



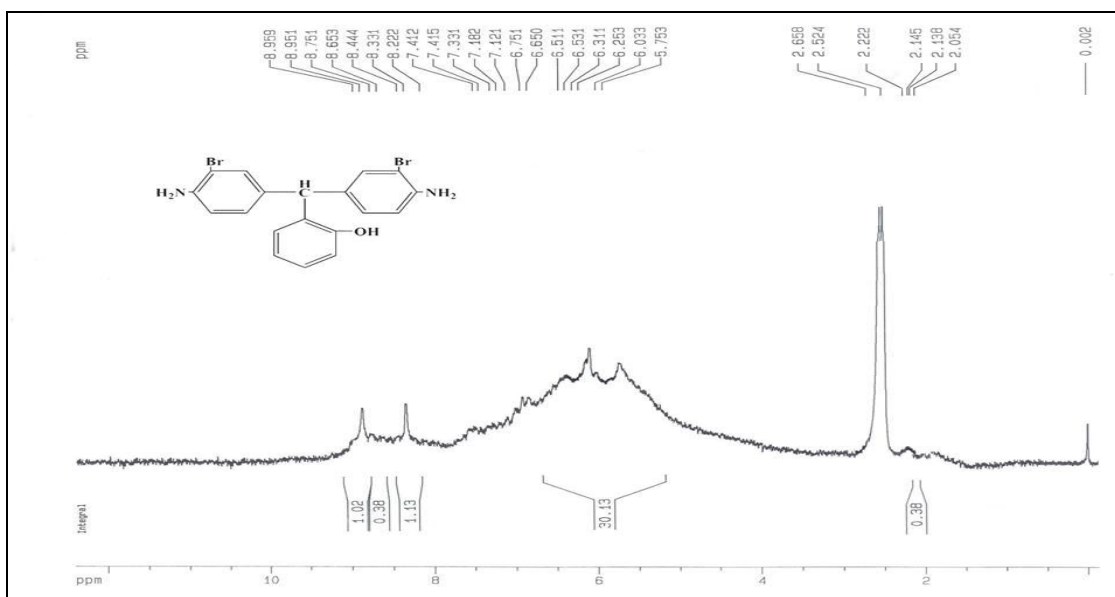
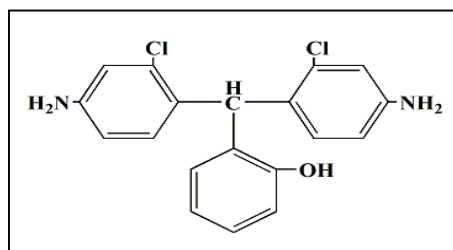


Figure 8: <sup>1</sup>H-NMR spectrum of (M4)

### Synthesis of [M5] :-

M5 is prepared by the condensation of one molecule of Salicylaldehyde with two molecules of 3-ChloroAniline in the

presence of (60% : 40%) solution of (H<sub>2</sub>SO<sub>4</sub> in Methanol) at 120°C for 10hs. This monomer was characterized by FTIR spectrum.



Scheme 16 : Synthesis of M5

### Characterization of M5 Monomer :-

FT-IR spectrum of (M5) is shown in (Figure 9) which indicated absorption band at (3387cm<sup>-1</sup>) to (-OH group), (3413cm<sup>-1</sup>) to (-NH<sub>2</sub> group), (3217cm<sup>-1</sup>) to (aromatic -CH stretching), (2913cm<sup>-1</sup>) to (aliphatic -CH stretching), (821cm<sup>-1</sup>) to (C-Cl), and absorption bands around (1614-1544cm<sup>-1</sup>) show the presence of the aromatic ring. The characteristic absorption of (C=O aldehyde) disappeared.

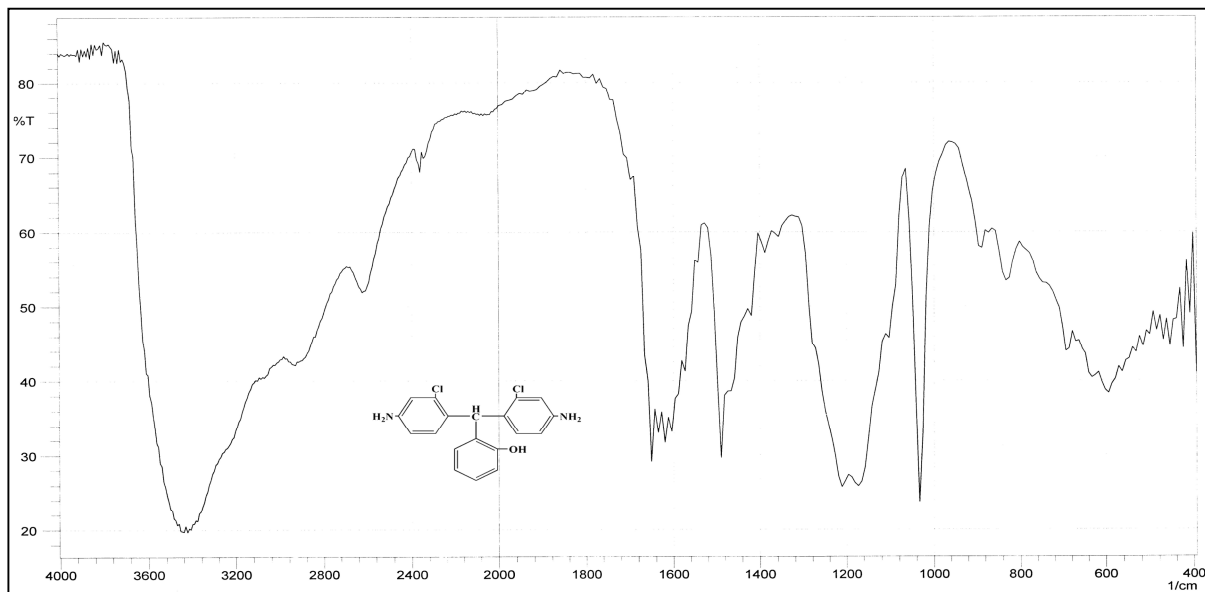


Figure 9 : FT-IR spectrum of M5.

$^1\text{H}$ .NMR spectrum of (M7), is shown in Figure 10 assigns the following chemical shifts;  $\delta$  (2.5) ppm for DMSO,  $\delta$  (5.8) ppm

(s,1H) for C-H,  $\delta$  (6.2) (s, 4H) for  $\text{NH}_2$  group,  $\delta$  (6.3 -8.6) ppm (s, 10H ) for ArH group,  $\delta$  (6.01) ppm (s,1H,OH).

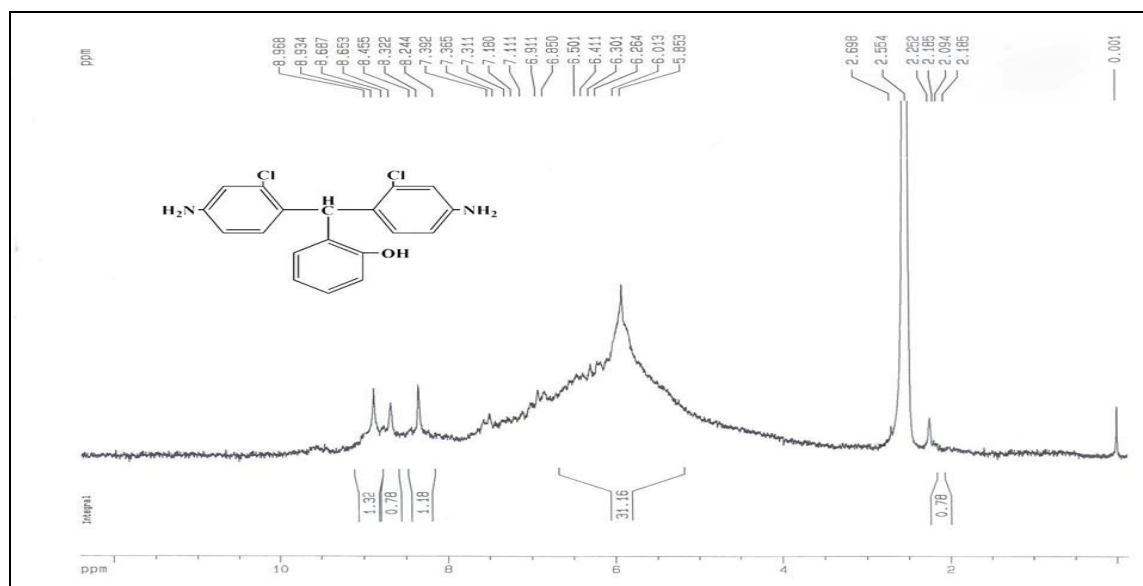
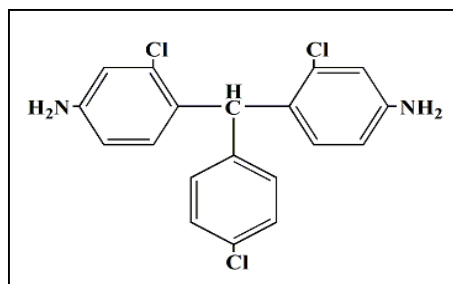


Figure 10 :  $^1\text{H}$ .NMR spectrum of (M5)

**Synthesis of [M6] :-**

M6 is prepared by the condensation of one molecule of 4-Chlorobenzaldehyde with two molecules of 3-ChloroAniline in the

presence of (60% : 40%) solution of (H<sub>2</sub>SO<sub>4</sub> in Methanol) at 120°C for 10hs. This monomer was characterized by *FT.IR spectrum*.

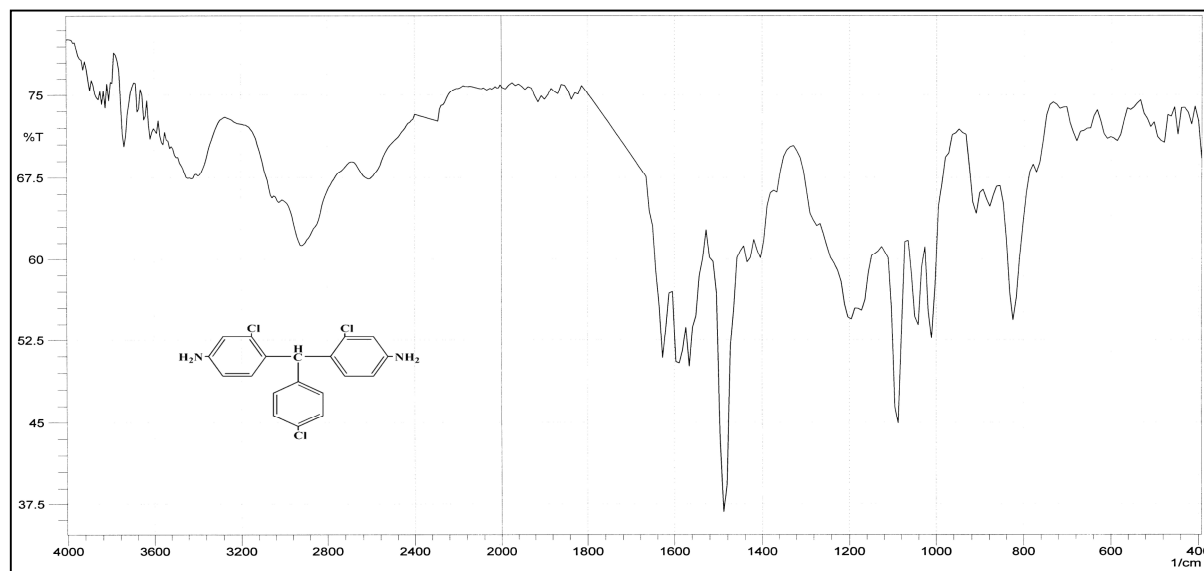


**Scheme 16 : Synthesis of M6**

**Characterization of M6 Monomer :-**

FT.IR spectrum of (M6) is shown in (Figure 11) which indicated absorption band at (3419cm<sup>-1</sup>) to (-NH<sub>2</sub> group), (3050cm<sup>-1</sup>) to (aromatic -CH stretching), (2919cm<sup>-1</sup>) to

(aliphatic -CH stretching), (822cm<sup>-1</sup>) to (C-Cl), and absorption bands around (1622-1555cm<sup>-1</sup>) show the presence of the aromatic ring. The characteristic absorption of (C=O aldehyde) disappeared.



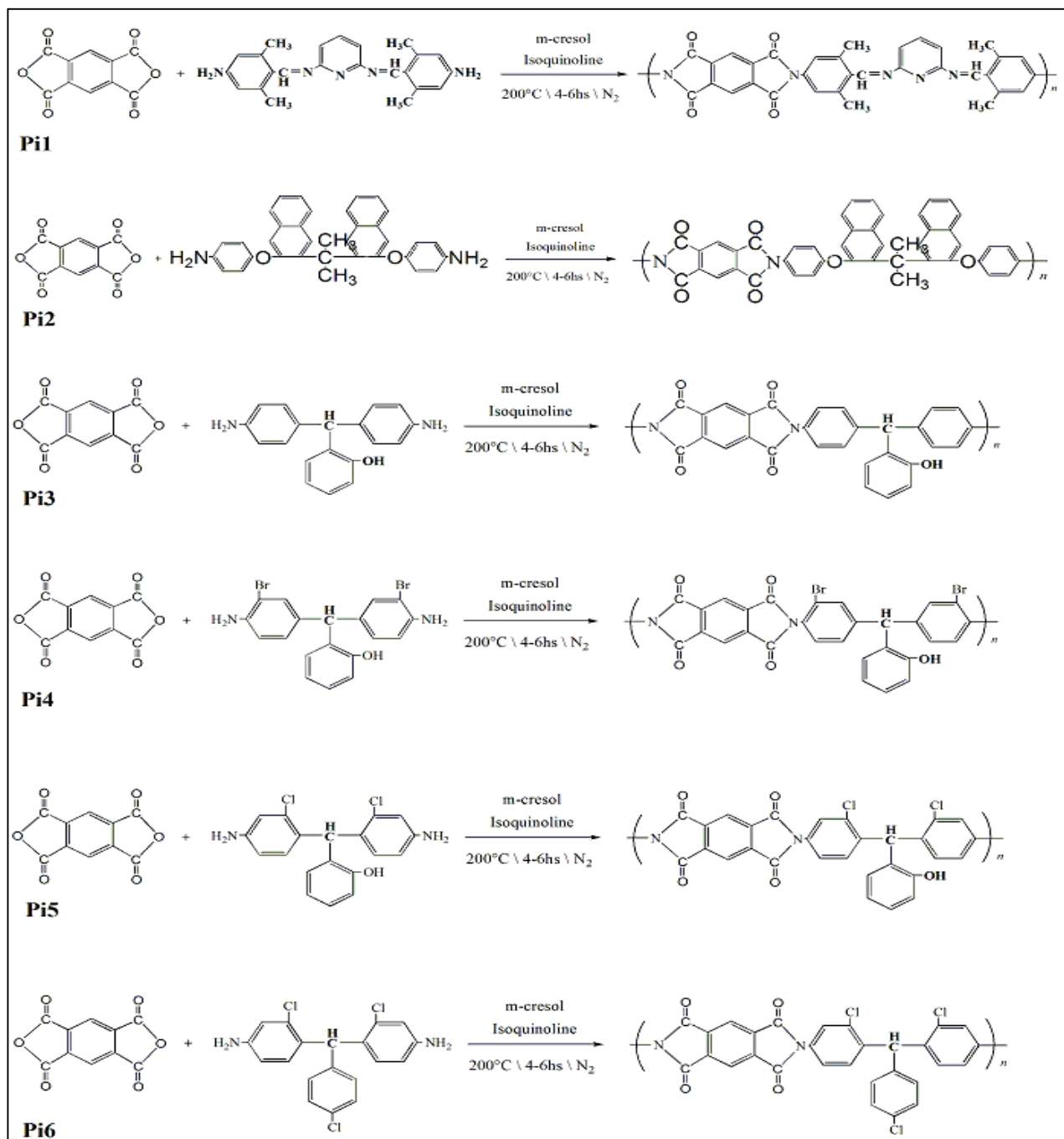
**Figure 11 : FT.IR spectrum of M6.**

**Synthesis of Polyimides (Pi1 - Pi6):-**

In this section, we used polycondensation method for synthesis of a series of six new

polyimides from the direct polycondensation reaction of 1,2,4,5-benzene tetracarboxylic acid dianhydride with six new different aromatic diamines [M1 , M2 , M3 , M4 , M5 and M6], respectively, by using m-cresol as solvent containing a catalytic amount of Isoquinoline. These polymers have a soft

segment such as methylene unit, ether linkages, and Schiff-Base groups in main chain for improving solubility in organic solvents in compared to aromatic Polyimides. These new Polyimides were characterized by *FT.IR* and *<sup>1</sup>H.NMR spectra*.



Scheme 17 : Synthesis of Pi1 - Pi6.

## Characterization of Polyimides [Pi1 - Pi6] :-

### FT.IR spectrum of Pi1:-

FT.IR spectrum of (Pi1) is shown in (Figure 12) which indicated absorption bands at ( $3344\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3077\text{cm}^{-1}$ )

to (aromatic  $-\text{CH}$  stretching), ( $2922\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$  stretching), the sharp band at ( $1655\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), ( $1566\text{--}1552\text{cm}^{-1}$ ) to ( $\text{C}=\text{C}$ ) ring, and ( $1505\text{--}1483\text{cm}^{-1}$ ) to ( $\text{C}=\text{N}$ ). Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.

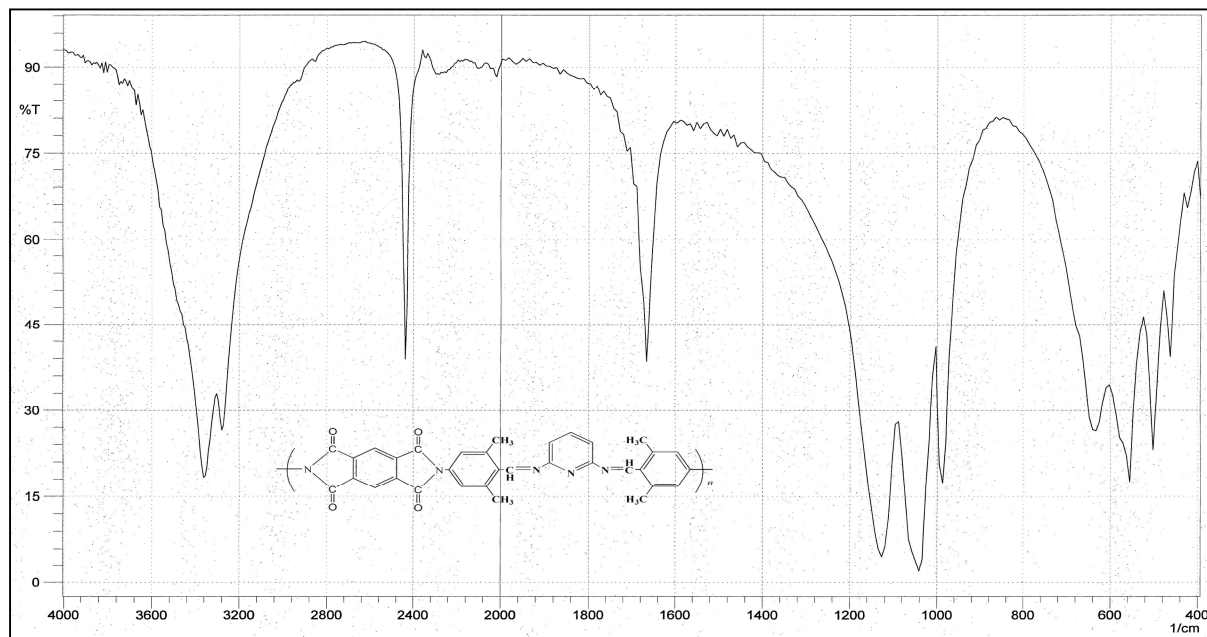


Figure 12 : FTIR spectrum of Pi1.

### FTIR spectrum of Pi2:-

FT.IR spectrum of (Pi2) is shown in (Figure 13) which indicated absorption bands at ( $3340\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3071\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2929\text{cm}^{-1}$ ) to

(aliphatic  $-\text{CH}$  stretching), the sharp band at ( $1650\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), ( $1555\text{--}1544\text{cm}^{-1}$ ) to ( $\text{C}=\text{C}$ ) ring, and ( $1212\text{cm}^{-1}$ ) due to ( $-\text{C}-\text{O}-\text{C}$ -ether linkage). Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.

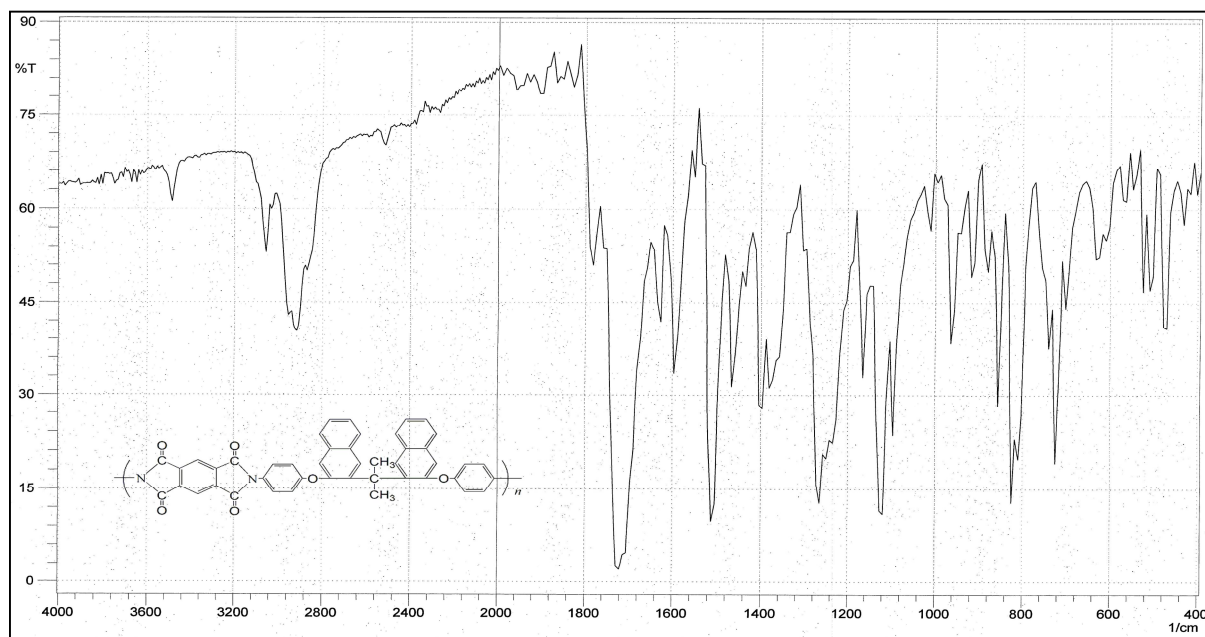


Figure 13 : FTIR spectrum of Pi2.

<sup>1</sup>H-NMR spectrum of (Pi2), is shown in Figure 14 assigns the following chemical shifts; δ (2.5) ppm for DMSO ,δ (1.9) ppm

(s,6H) for CH3, δ (7.2-8.3) ppm ,for Ar-H group .

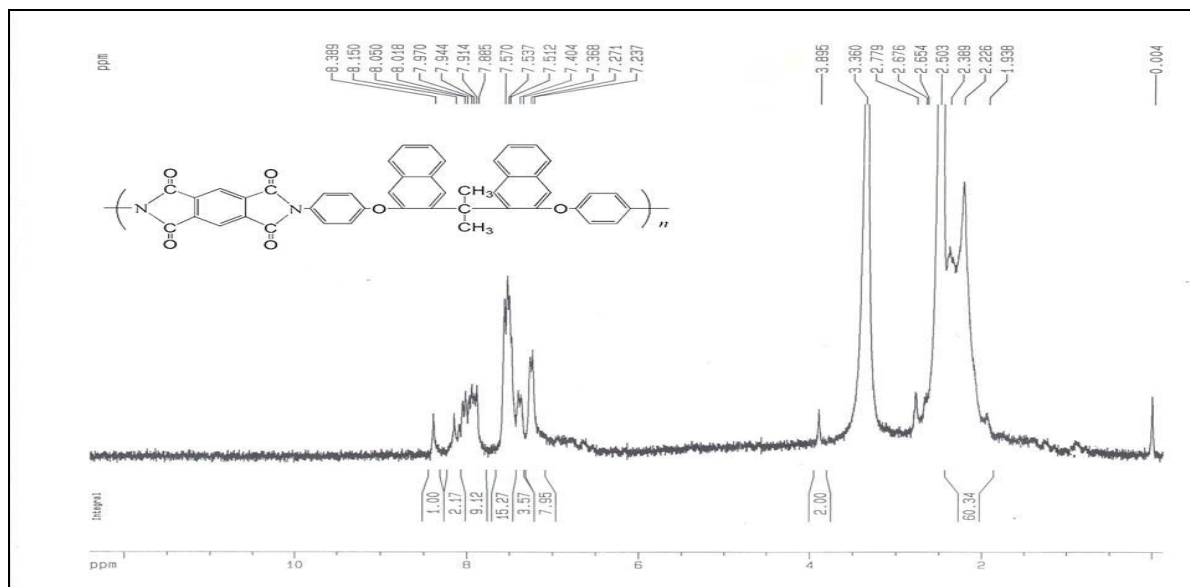


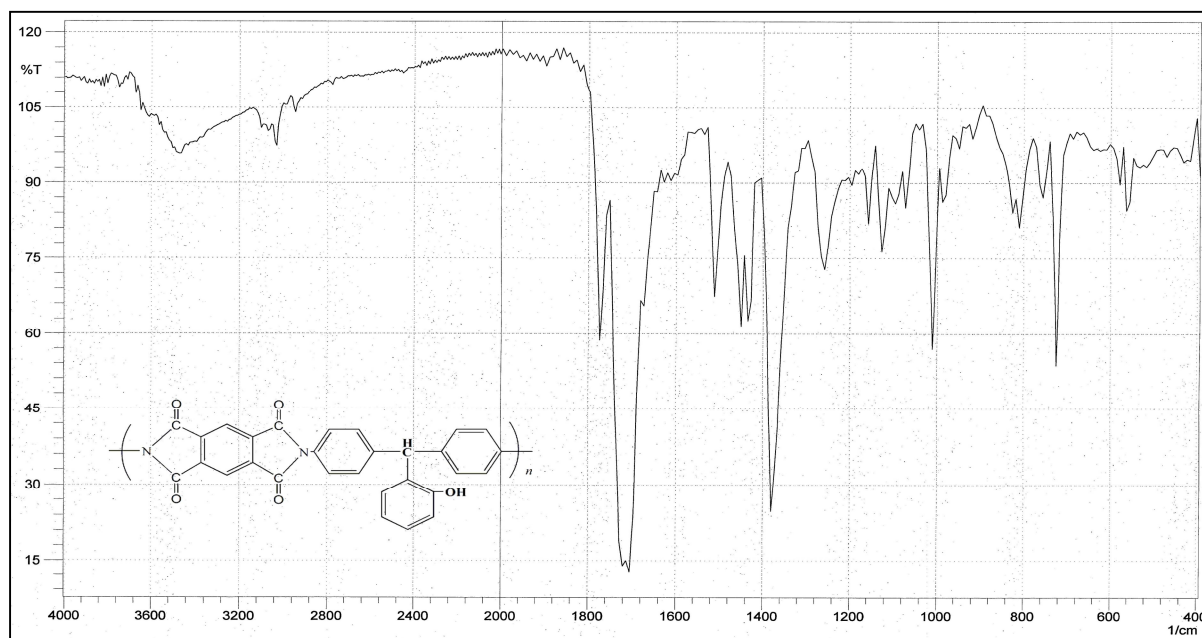
Figure 14: <sup>1</sup>H.NMR spectrum of (Pi2)



**FT.IR spectrum of Pi3:-**

FTIR spectrum of (Pi3) is shown in (Figure 15) which indicated absorption band at ( $3356\text{cm}^{-1}$ ) to ( $-\text{OH}$  group), ( $3333\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3072\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2922\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$

stretching), the sharp band at ( $1655\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), and absorption bands around ( $1629\text{--}1551\text{cm}^{-1}$ ) show the presence of the aromatic ring. Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.

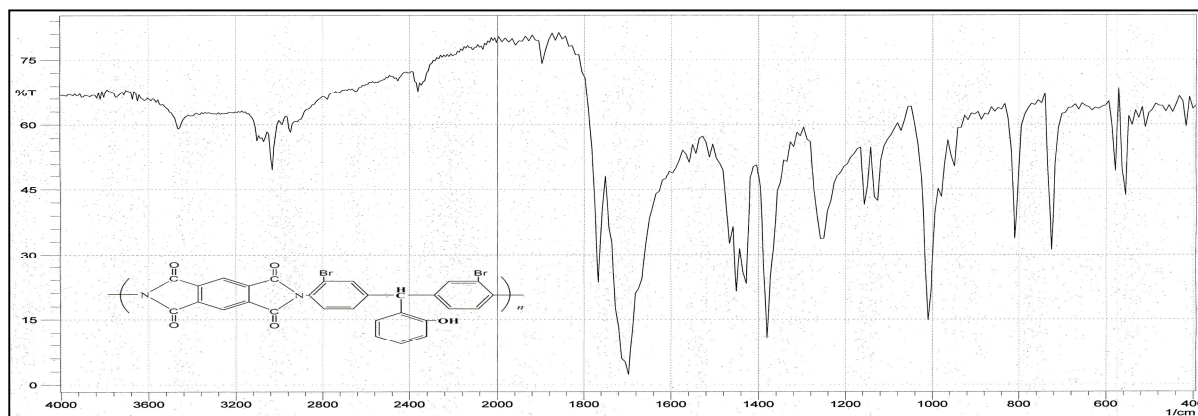


**Figure 15 : FT.IR spectrum of Pi3.**

**FT.IR spectrum of Pi4:-**

FTIR spectrum of (Pi4) is shown in (Figure 16) which indicated absorption band at ( $3346\text{cm}^{-1}$ ) to ( $-\text{OH}$  group), ( $3322\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3077\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2933\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$

stretching), the sharp band at ( $1644\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), ( $644\text{cm}^{-1}$ ) to ( $\text{C}-\text{Br}$ ), and absorption bands around ( $1621\text{--}1542\text{cm}^{-1}$ ) show the presence of the aromatic ring. Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.

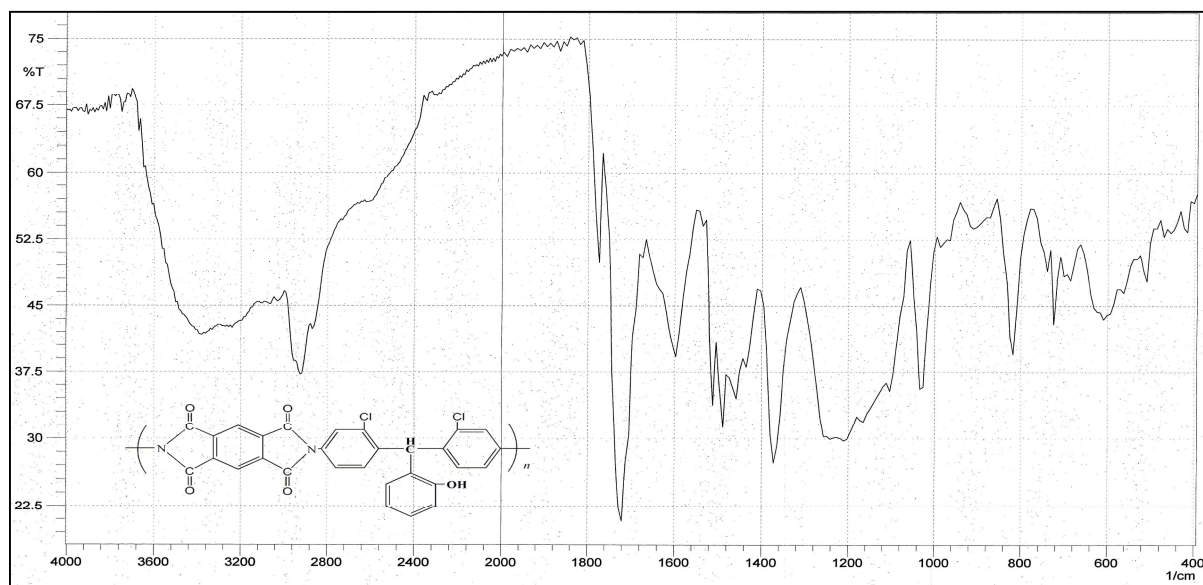


**Figure 16 : FT.IR spectrum of Pi4.**

**FT.IR spectrum of Pi5:-**

FTIR spectrum of (Pi5) is shown in (Figure 17) which indicated absorption band at ( $3341\text{cm}^{-1}$ ) to ( $-\text{OH}$  group), ( $3318\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3066\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2925\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$

stretching), the sharp band at ( $1638\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), ( $844\text{cm}^{-1}$ ) to ( $\text{C}-\text{Cl}$ ), and absorption bands around ( $1619-1539\text{cm}^{-1}$ ) show the presence of the aromatic ring. Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.

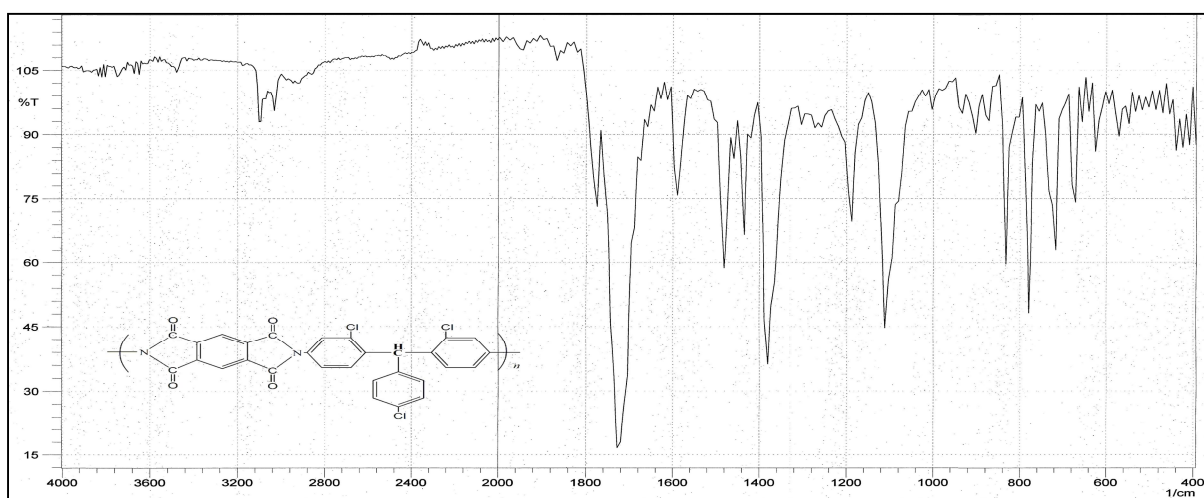


**Figure 17 : FT.IR spectrum of Pi5.**

**FT.IR spectrum of Pi6:-**

FTIR spectrum of (Pi6) is shown in (Figure 18) which indicated absorption band at ( $3313\text{cm}^{-1}$ ) to ( $-\text{NH}$  stretching), ( $3060\text{cm}^{-1}$ ) to (aromatic  $-\text{CH}$  stretching), ( $2927\text{cm}^{-1}$ ) to (aliphatic  $-\text{CH}$  stretching), the sharp band at

( $1634\text{cm}^{-1}$ ) to ( $\text{C}=\text{O}$  amide), ( $853\text{cm}^{-1}$ ) to ( $\text{C}-\text{Cl}$ ), and absorption bands around ( $1614-1533\text{cm}^{-1}$ ) show the presence of the aromatic ring. Characteristic absorption of ( $\text{C}=\text{O}$  anhydride) disappeared.



**Figure 18 : FTIR spectrum of Pi6.**



$^1\text{H-NMR}$  spectrum of (Pi6), is shown in Figure 19 assigns the following chemical shifts;  $\delta$  (2.5) ppm for DMSO,  $\delta$  (5.2) ppm

(s,6H) for  $\text{CH}_3$ ,  $\delta$  (5.7),  $\delta$  (6.4 -8.4) ppm for Ar-H group .

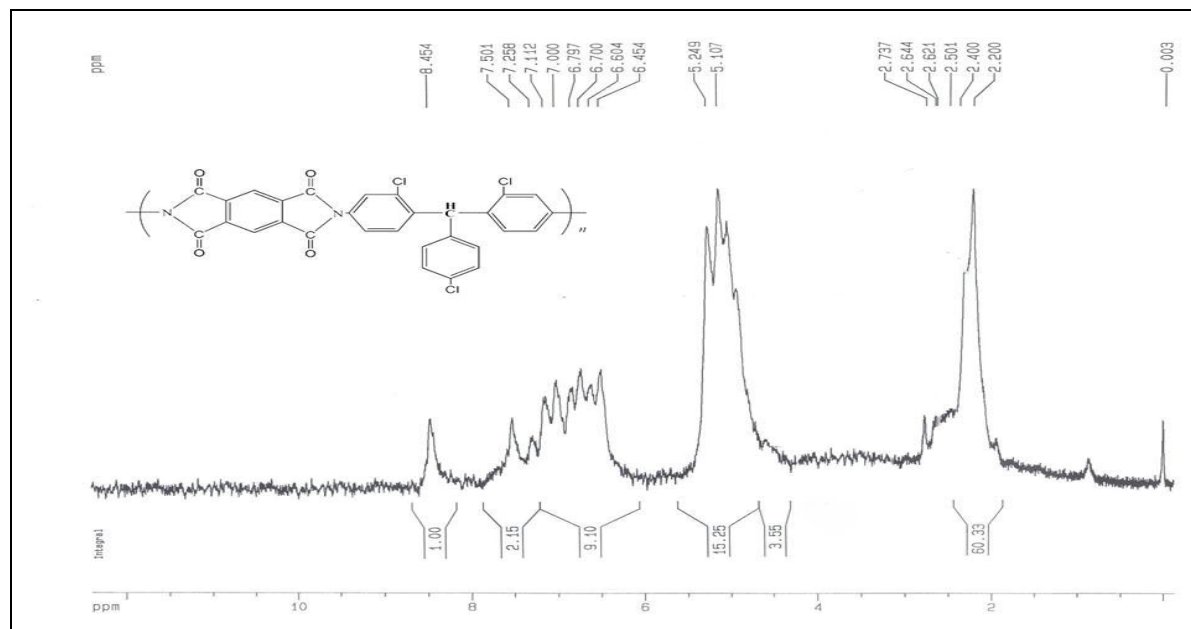


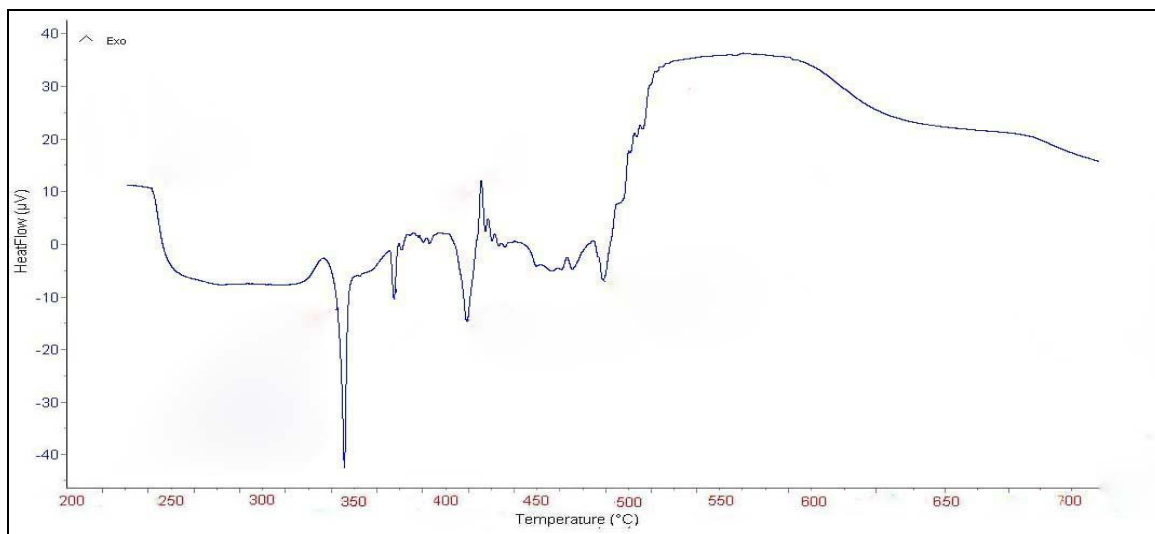
Figure 19:  $^1\text{H-NMR}$  spectrum of (Pi6)

## Differential scanning calorimetry Study

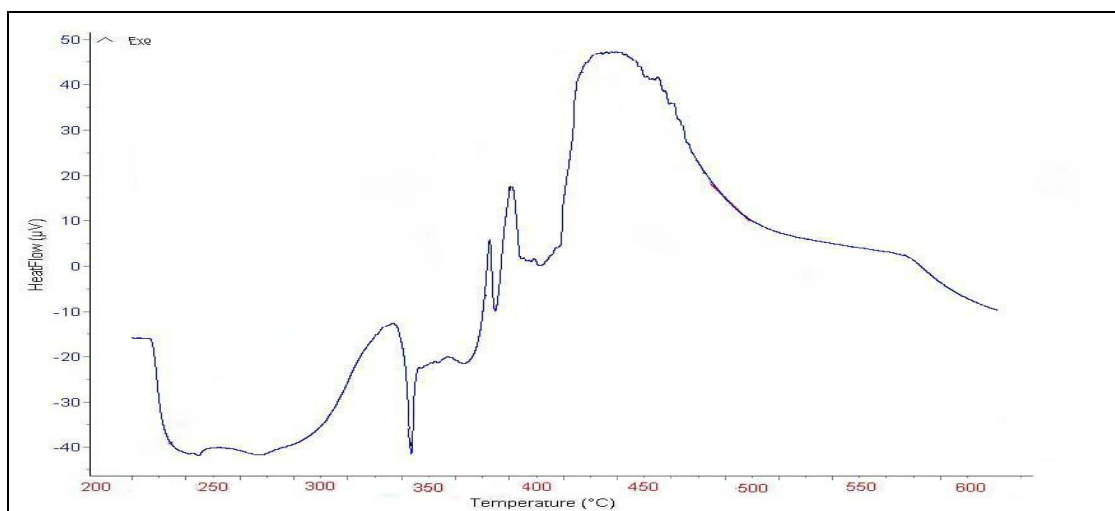
The analyses of thermal properties of the polyimides have been made by the help of their DSC thermograms. Presence of more than one endotherms in the thermograms revealed that polyimides undergo more than one phase transition processes when subjected to thermal treatment<sup>[23]</sup>.

The DSC curves are shown in figures (20-25). Glass transition temperature ( $T_g$ ) of all polyimides were in the range (  $231\text{ }^\circ\text{C}$  -  $254\text{ }^\circ\text{C}$  ), in case of polyimide ( Pi2) it is

interesting to note that the presence of ether linkages brings much more flexibility to the macromolecular chain and decreases the glass transition temperature. In the same time, the presence of pyridine group into the diamine segment increased the glass transition of the corresponding polyimides  $T_g$  values . It was observed that substitution on aromatic rings in Pi1 produce a pronounced effect on  $T_g$  values. DSC data indicated that the Pi1 containing symmetric tetramethyl substitution resulted chain stiffening effect in higher  $T_g$  .



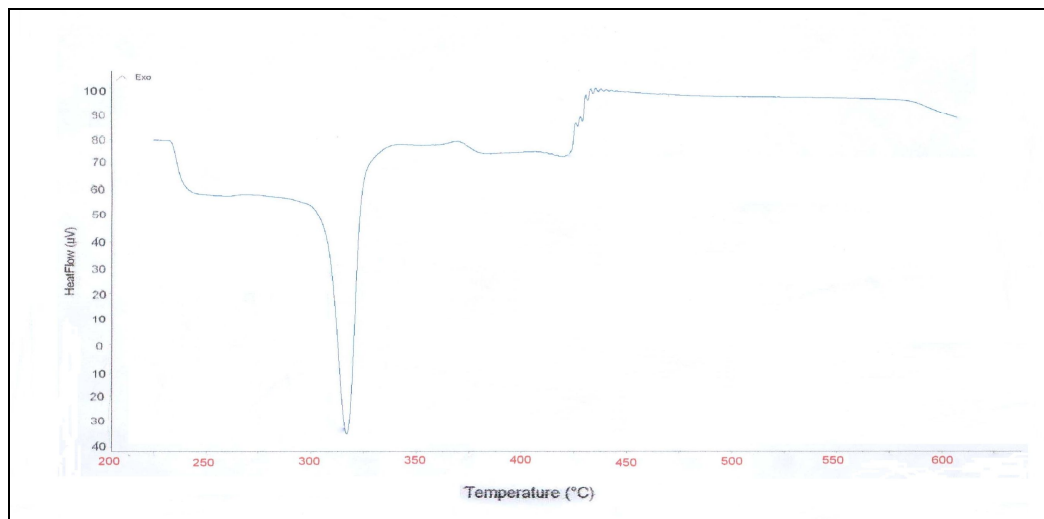
**Figure 20 :DSC curve of polymer (Pi 1)**



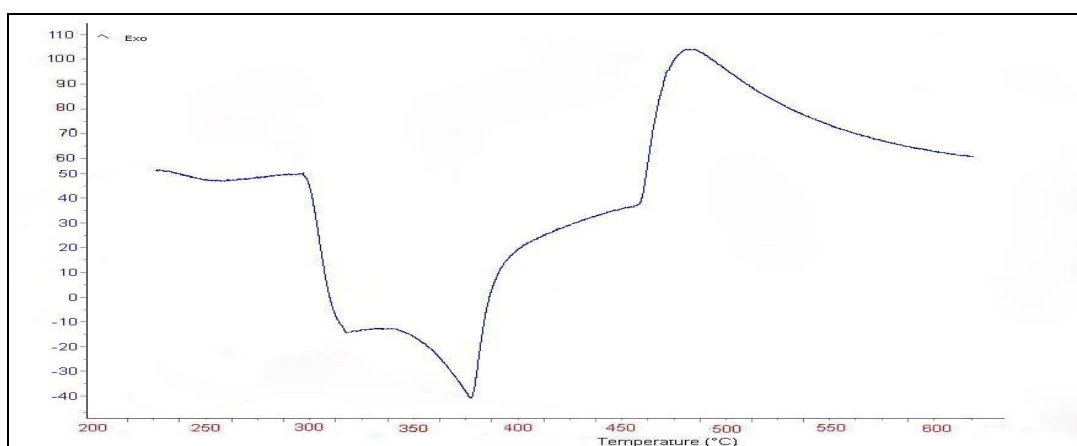
**Figure 21 :DSC curve of polymer (Pi 2)**

Thus it will be interesting to introduce different chain ends using substitution reaction since end group modification in (Pi4, Pi5, and Pi6 ) had a strong effect on Tg as observed in previous studies [24-26]. Usually , amore polar functional group causes Tg to be higher as the polymer chains more rigid parts and / or a polymer contains less free volume

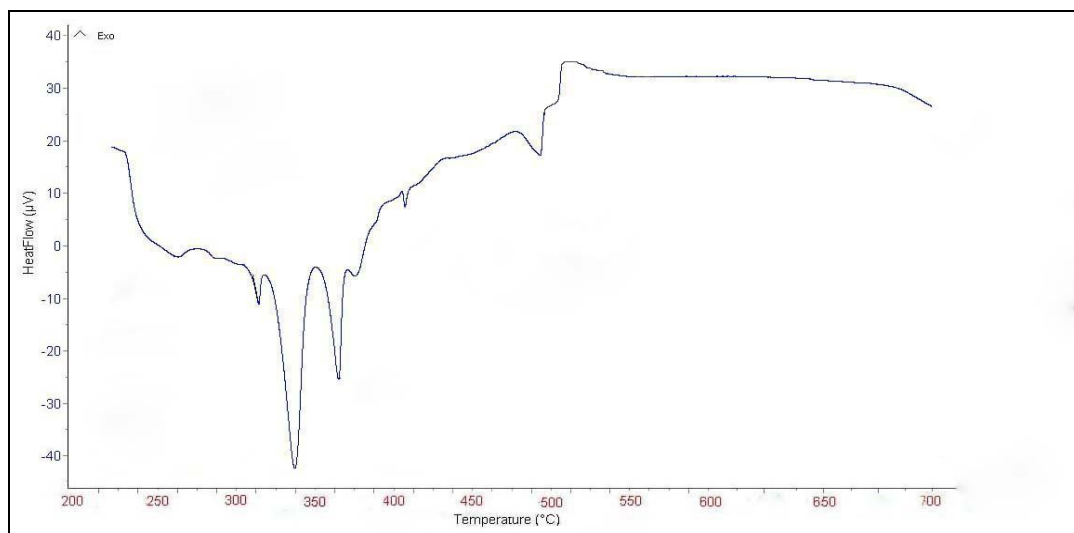
.Tg of polyimides may be strongly dependent on the inter-association of functional groups with the neighboring molecule as well as the volume fraction occupied by terminal groups [26]. It seems that several factors such as the rigidity, polarity, length and steric hindrance of terminal functional groups can influence Tg of resultant polymers.



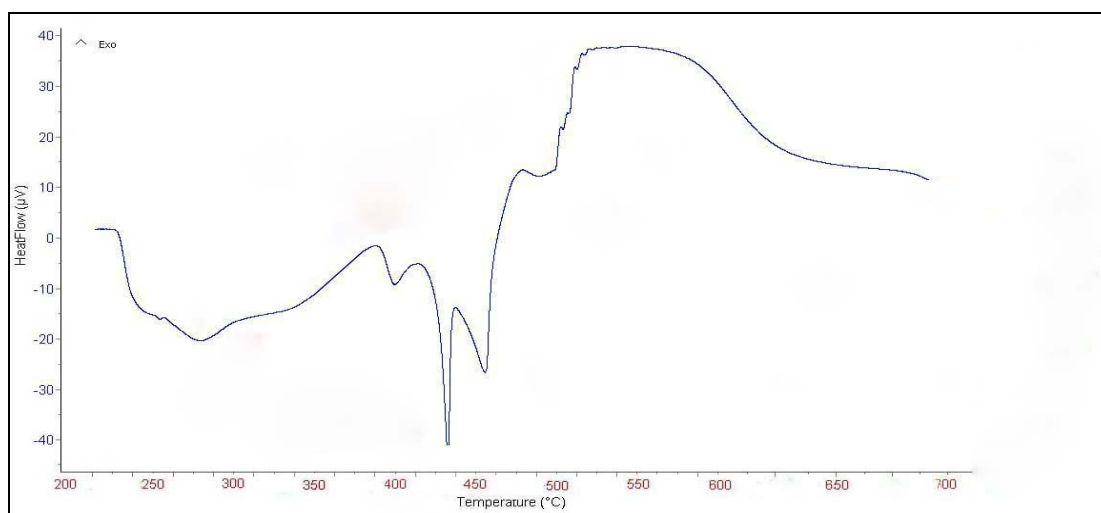
**Figure 22 :DSC curve of polymer (Pi 3)**



**Figure 23 :DSC curve of polymer (Pi 4)**



**Figure 24 :DSC curve of polymer (Pi 5)**



**Figure 25 :DSC curve of polymer (Pi 6)**

The endothermic peaks of polyimides are related to melting temperature. This increased in  $T_m$  is assigned to the containing rigid pyridine and phenylene moieties incorporated into the polymer back bone during synthesis of polyimides. Hence ,  $T_m$  is higher fore Pi1 , Pi4 , Pi5 and Pi6 as the polymer chain more rigid parts and / or a polymer contains less free volume . Samples usually showed multiple endotherms which are explained as due to the fusion of different population of crystallites with different sizes . as expected ,  $T_m$  values are lower for Pi2 and Pi3 due to the

higher chain flexibility of the formers afforded with increasing the amount of methylene of polymeric back bone and steric hindrance of terminal functional groups can influence  $T_m$  of resultant polymers. In addition, the polymer Pi2 , has the lowest thermal stability than the other polymers. This behavior can be explained by the presence of methylene units which are more vulnerable to thermo-oxidative processes <sup>[27-29]</sup>. The  $T_g$ ,  $T_m$  and  $T_c$  obtained from DSC are reported in Table (3).

**Table (3). The glass transition, melting temperature and crystallization temperature obtained from DSC.**

Samples	Tm ( <sup>o</sup> c)	Tg( <sup>o</sup> c)	Tc( <sup>o</sup> c)
Pi1	512	254	348
Pi2	410	231	244
Pi3	425	231	325
Pi4	458	254	318
Pi5	493	246	265
Pi6	502	245	279

### Solubility of Polyimides :-

Solubility of Polyimides Pi1 - Pi6 was qualitatively tested in organic solvents and the results are summarized in (Table 4). The method that attempt to enhance their processabilities and solubilities were either by introducing bulky groups, flexible linkages, or molecular asymmetry into the polymer backbones. In this work, the attachment of bulky pendant groups in polymer backbone not only could provide an enhanced solubility

because of decreased packing density and crystallinity, but also could impart an increase in Tg by restricting the segmental mobility<sup>[30]</sup>.

One of the major objectives of this work was producing Polyimides with improved solubility. The Solubility was investigated as (0.03gm) of polymeric sample in (3ml) of a solvent. All of the newly synthesized Polyimides have good soluble in common polar and dipolar aprotic solvents without need for heating.

**Table 4 : Solubility of Polyimides : Pi1 - Pi6**

Solvent	Polyimides					
	Pi1	Pi2	Pi3	Pi4	Pi5	Pi6
DMAc	+ -	++	++	+ -	+ -	+ -
DMF	++	+ -	++	+ -	++	+ -
NMP	+ -	+ -	+ -	++	+ -	++
Pyridine	+ -	++	++	++	++	+ -
<i>m</i> -Cresol	+++	++	+++	++	+ -	++
THF	++	++	+ -	+ -	+ -	+ -
CHCl <sub>3</sub>	+ -	+ -	++	+ -	++	+ -
CH <sub>2</sub> Cl <sub>2</sub>	++	+++	++	+ -	+ -	++
DMSO	+++	+++	++	++	++	++
<i>Conc.</i> H <sub>2</sub> SO <sub>4</sub>	++	++	+ -	++	+ -	++

Full Soluble.    +++    Soluble at room.T.    ++    Partially Soluble.    + -

## Conclusions

Several systematically varied aromatic polyimides were prepared by the classic two-step procedure from dianhydrides 1,2,4,5-Benzene tetracarboxylic Acid with various structurally different diamines, and almost all the polymers afforded flexible and tough polymers by successive heating the poly (amic acid) to elevated temperature. The introduction of pyridine and phenylene groups into the diamine segment, in addition to amore polar functional group causes (Tg) to be higher as the polymer chains more rigid parts and / or a polymer contains less free volume. However, the attachment of ether linkage groups brings much more flexibility

to the macromolecular chain and decreases the glass transition of the polyimides. The polyimides containing chain more rigid parts and / or a polymer contains less free volume have higher melting temperature(Tm) for Pi1 , Pi4 , Pi5 and Pi6. The polymers were characterized by proton nuclear magnetic resonance spectroscopy and infrared spectroscopy confirmed the molecular composition of six strictly alternating, highly ordered polyimides having methylene chains as flexible spacers and phenylene or pyridine hetryclic groups as the rigid segments. All polyimides were readily soluble in polar aprotic solvents

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