Preparation ,Characterization and Thermal Properties of New Aromatic Polyester Based on Di ,Tri and Tetra Hydroxyl Monomers with 4,4Azo Di Benzoic Acid and Adipic Acid

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Abstract

A series of new aromatic Polyesters were synthesized by polycondensation of various aromatic monomers di ,tri and tetra diols (BCAHPMNM , BHPMB, BHPPB , BPBHP) with Acids(4,4Azo Di benzoic acid and Adipic acid) using dibutyltine dilaurate as Catalyst .all polyesters(P.E1-P.E4)containing pyridine heterocyclic group, aliphatic methylene linkage, and Azo group. The yield of Polyesters varies from 60-85%. All of these new aromatic polyester show very good solubility in common organic solvents , such as (pyridine , CHCl3 , CH2Cl2 , NaOH , H_2SO_4 , HNO_3 , Acetone , Benzene , DMF , DMSO , THF) without need for heating. Thermal analysis of polyesters by thermo gravimetric analysis (TGA) reveals that these Aromatic polyesters possess thermal stability. Monomers and polyesters characterized by FT-IRand^{1}HNMRspectrosticcopy.

Keywords: Aromatic polyester , 4,4Azo Di benzoic acid , Adipic acid, dibutyltine dilaurate.

1-INTRODUCTION

Polyesters are a class of polymers that can be formulated to be hard or soft, brittle or flexible depending on the structure and can therefore be used in various applications. These applications include fibers (e. g. polyethylene terephthalate (PET)) (1-3), coatings (4-5), plasticizers (6), adhesives, polyurethane based resins, films, laminates, industrial construction, insulation, molding compounds, etc.(5-6). Polyesters are used for these applications because of their low cost (2-3, 5, 7), ease of process (7), and ease of combination with reinforcements (2-3, 7). In addition, these polymers cure rapidly without any volatile products (2-3, 7-8), have excellent dimensional stability, have high impact resistance, transparency and good weathering resistance (5). The development of process able high-performance polymers with increased thermal stability, heat resistance and good mechanical properties has become an important problem (9). Aromatic polyesters have excellent physical and mechanical properties and are among the most important commercially available polymers with widespread application, especially in the food and beverage packaging. However, due to their strong resistance to bacterial or fungal attack they usually remain unaltered under the environment conditions, and result in a considerable waste stream (10-13). Aromatic polyesters are certainly one of the most successful classes of high-temperature polymers. However these polymers encounter processing difficulty due to their infusibility and poor solubility in organic solvents Therefore, more researches have been focused on maintaining considerable thermally stable and improving their solubility(13-15). In the present work, four aromatic polyesters (P.E1- P.E4) have been synthesized in high yields from the polycondensation between (di ,Tri and Tetra) hydroxyl monomers containing methylene unit,Azo group and pyridine hero cyclic ring with 4,4 Azo di benzoic acid and Adipic acid using dibutyltine dilaurate as Catalyst, and qualitative structure analysis of the polymers and monomers have been carried out by the using of FT-IR, and ^{1}HNMR spectroscopy, thermal stability were systematically investigated .

2- EXPERIMENTAL

2.1 Materials

Dichloromethane,Hexane, all from (BIOSOLVE); Hydrochloric acid ,Salicylaldehyde, Benzaldehyde, all from (HI media); Diethyl ether from (IGCC / England); phenol, P-aminophenol,4-Chlorobenzaldehyde,Glacial acetic acid, Piperidine, PyridineTerphthaldehyde, Dimethyl Sulphoxide (DMSO), P-hydroxyacetophenone, Terohthaldehyde, Tetrahydrofurane (THF), all frome(MERCK); Absolute Ethanol fromd (Scharlab S.L); N,N-Dimethylformamide (DMF)from (ALDRICH).

2.2 Instruments

FTIR 8400S, Fourier Transform infrared spectrophotometer, SHIMADZU, Japan),(Oven ,Trip International Corp. Italy),(Measuring the degree of fusion (Melting Points)Stuart smp30 melting point apparatus) ,(Hot plate stir , BibbyStrlintd. UK),(Measurement of ^{1}HNMR: recorded NMR spectra using a type of Bruker, Ultra, Shiel 300MHZ,Switzear, Land and using (DMSO-d^6) as solvent at the University's Educational teacher -Tehran Iran),(Thermogravimetry analysis (TGA) were performed on a Polymer laboratories co England, Model PL-TG at Iran polymer & petrochemical institute, using a heating rate of 10°C/min in Argon atmosphere within the temperature range of 25–800°C).

2.3 monomer Synthesis

2.3.1 Bis(3-chloro aniline 4-hydroxy phenyl)methyl 4-nitro phenyl) Methan (M1) :

Amixture of P- Nitro acetophenone (2.72gm(16mmol) , 2-Chloro phenol (4gm(42mmol), HCl catalyst (37.5gm) and thioglycolic acid(0.5gm) protomer were placed in athree neeked –round bottom flask equipped with the acondenser, mechanical stirrer and thermometer and it was kept in athermostate bath at $60^{o}C$ for6hs .After adefinite period of time, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was washed, dried (16).the yield was (85%) of yellow crystals, m.p= $(187-190^{O}C)$,Figure **(1)** Structure of monomer (M1).

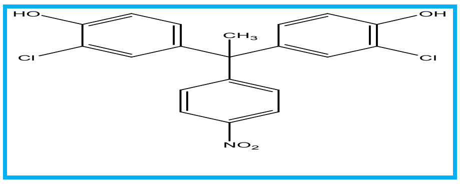


Figure (1) Structure of M1

2.3.2 Synthesis1,4-(bis(4- hydroxyphenyl)methyl)Benzene(M2) :

To a 0.1M solution of H_2SO_4 in methanol (60% : 40%), phenol(2gm,21mmol) and salicylaldehyde(1.5gm,12mmol) were added and the mixture was refluxed at $120^{o}C$ for 10 hs with the constant stirring . Upon completion of the reaction , the solvent was removed under vacuum(17) . the yield was (71%) of brown crystals, m.p= $(80^{O}C)$ crystals . Figure(2) Structure of monomer (M2).

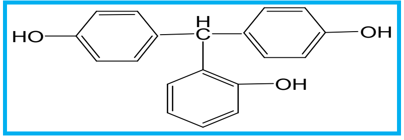


Figure (2) Structure of M2

2.3.3 Synthesis of 4(4-(2,4 bis(4-hydroxy phenyl pyridine(2,4-bis(4-hydroxy phenyl pyridine (M3)

In a(150ml) round-bottomed flask equipped with a reflux condenser **,** a mixture of Terephthalaldehyde (1.34 gm, 10mmol), P-hydroxy acetophenone(6.62gm,48mmol), ammonium acetate(7.5gm), and glacial acetic acid(20ml)was refluxed at $140-142^{o}C$for 2hs. Upon cooling,crystals separated ,which were filtered and washed first with acetic acid (50%) and then with cold ethanol. These product crystals were recrystallized from absolute Ethanol, and then dried at $60^{o}C$ under vacuum(18,19) the yield was (77%) of white crystals, m.p= $(140^{O}C)$, Figure(3) Structure of monomer (M3).

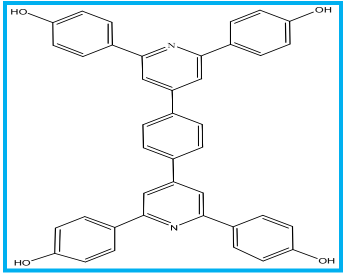


Figure (3) Structure of M3

2.3.4 Synthesis of 6-(4-Bromo phenyl) 2,4 bis (4-hydroxy phenyl) pyridine (M4):

This monomer synthesis by same way that (M3) is formed . but by using metrials (4-bromo benzaldehyde) (1.41gm,7mmol) and (4-hydroxy acetophenone) (1.31 gm,24mmol) where yield (80%), m.p= $(101^{o}C)$. and color is yellow. Figure (4) structure of monomer (M4).

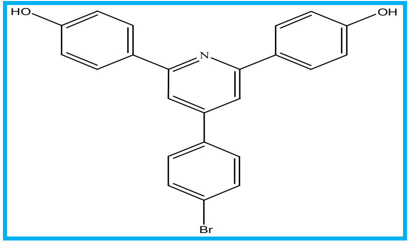
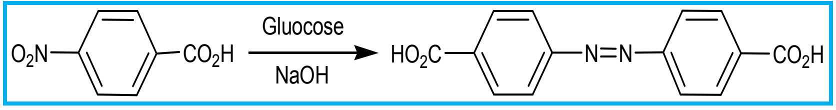


Figure (4) Structure of M4

2.3.4 Preparation of 4,4Azodibenzoic acid

4,4Azodibenzoic acid was prepared according to atypical procedure, shown in scheme(1) (Thirteen grams of 4-nitrobenzoic acid (79mmol) was heated in asolution of 50 gm of sodium hydroxide in 250mL of water at 50C.A

Solution of 100gm of glucose in 150 mL water was added slowly at this temperature with occasional shaking .The reaction mixture was then cooled to ambient temperature and aerated for 8h with vigorous stirring until orange- colored Crystals were formed(20) .



Scheme(1)Preparation of 4,4Azodibenzoic acid

The FTIR spectra of (***4,4Azodibenzoic acid***) as shown in(Figur5) which indicates absorption band of C=C Aromatic at1589cm-1, C-H Aromatic at3109 cm-1, OH at3425 cm-1, C-H aliphatic at2839 cm-1, C=O at 1951cm-1, and C-O at 1103 cm-1, , and C-N at1311 cm-1.

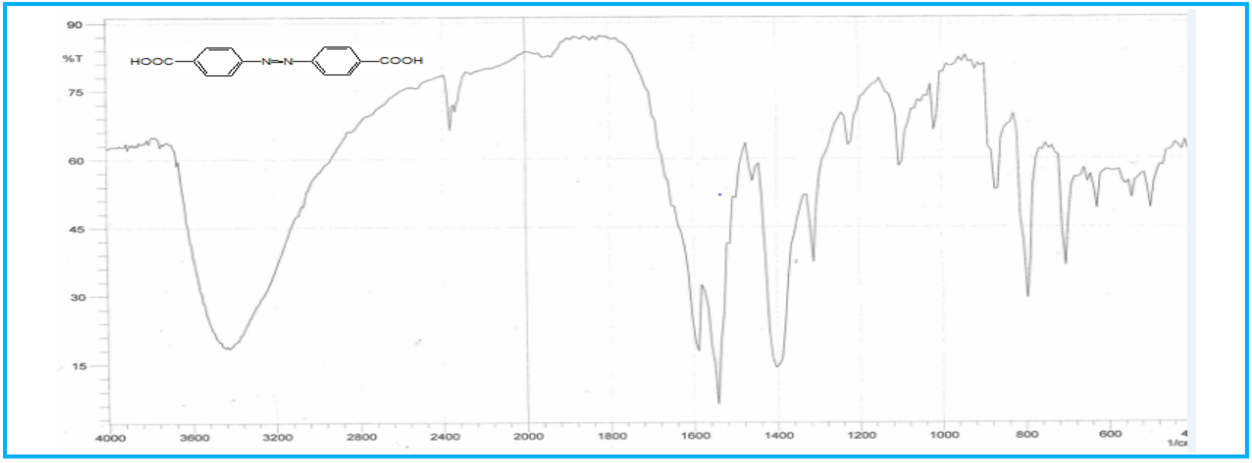


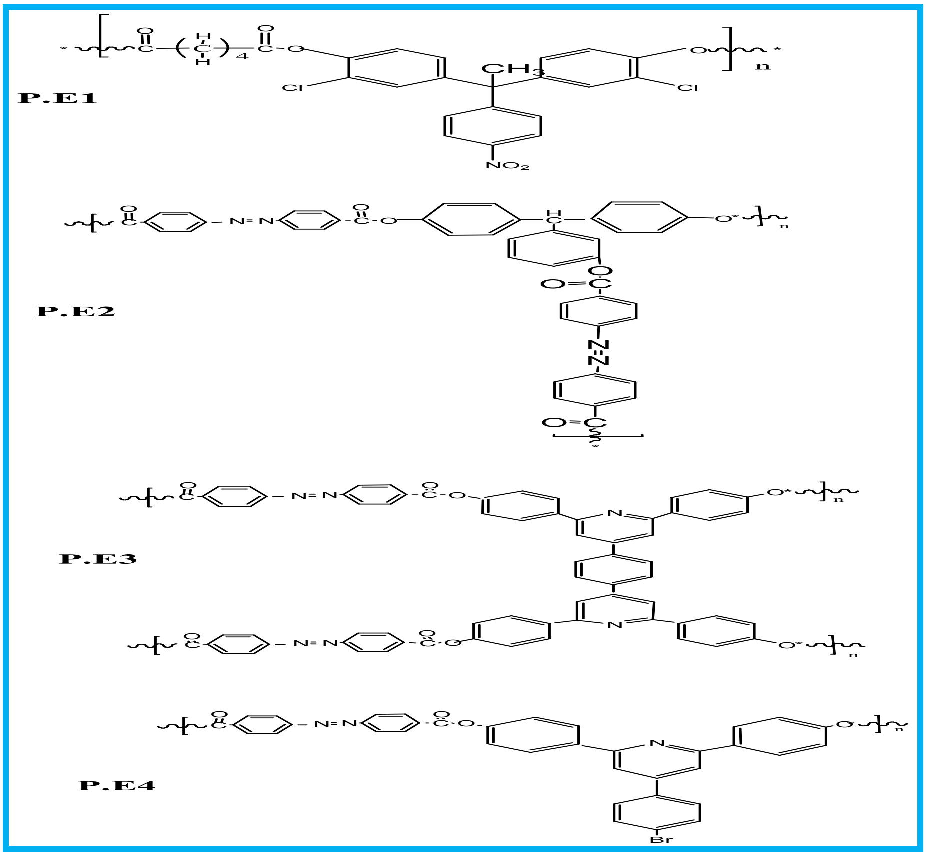
Figure 5 : FTIR spectra of (4,4Azodibenzoic acid)

2.3.4 Synthesis of polyesters[P.E1-P.E4].

Dihydroxy monomer and Di acid , as shown in (Table 1) were mixed at 120°C under constant stirring . After the dissolution of the acid in Dihydroxy monomer,the dibutyltine dilurate catalyst (0.15 wt.(%)) was added and the temperathure was increased up to 160°C and was kept at this temperature for 1hour . The materials were dried under vacuum at 50°C giving rise to the P.E series . The materials were obtained as powders(21) .

1) Synthesis of polyesters [P.E1-P.E4]. (Table

polyester	Monomers		diacid gm/mmol	Dihydroxy gm / mmol	Yield (%wt)	Color
	diacid	Dihydroxy				
P.E1	Adipic acid	M1	1.2gm	1gm	77%	white
P.E2	4,4Azodibenzoic acid	M2	2.4gm	1.3gm	85%	Orang
P.E3	4,4Azodibenzoic acid	M3	2.4 gm	1.1gm	78%	Orang
P.E4	4,4Azodibenzoic a aci	M4	1.2gm	1gm	75%	Yellow



Figur (6) Structure of P.E1-P.E4

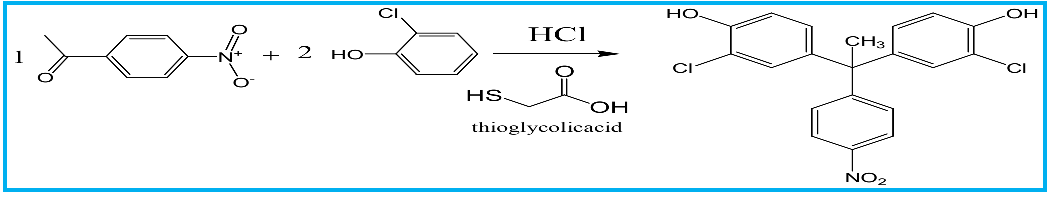
Results and Discussion 3-

Synthesis of monomers:- 3.1.

3.1.3 Synthesis and caractization

Bis(3-chloro aniline 4-hydroxy phenyl)methyl 4-nitro phenyl) methan (M1):

This monomer was synthesized by the condensation of one molecule of P-nitro acetophenone with two molecules of 2-Chloro phenol in the presence of acid catalyst , and suitable promoter at 60 ^{O}C for 6 h. This monomer was characterized by FTIR .



Scheme(2) Synthesis of (M1)

Characterization of [M1]

FT-IR spectrum :-

The FTIR spectra of (M4) as shown in(Figur6) which indicates absorption band of C=C Aromatic at1697cm-1, C-H Aromatic at3109 cm-1, OH at3425 cm-1, C-H aliphatic at2923 cm-1, and NO2 at1527cm-1,and C=O at 1951cm-1, and C-O at 1164 cm-1,C-Cl at 748cm-1, and C=N at1257 cm-1.

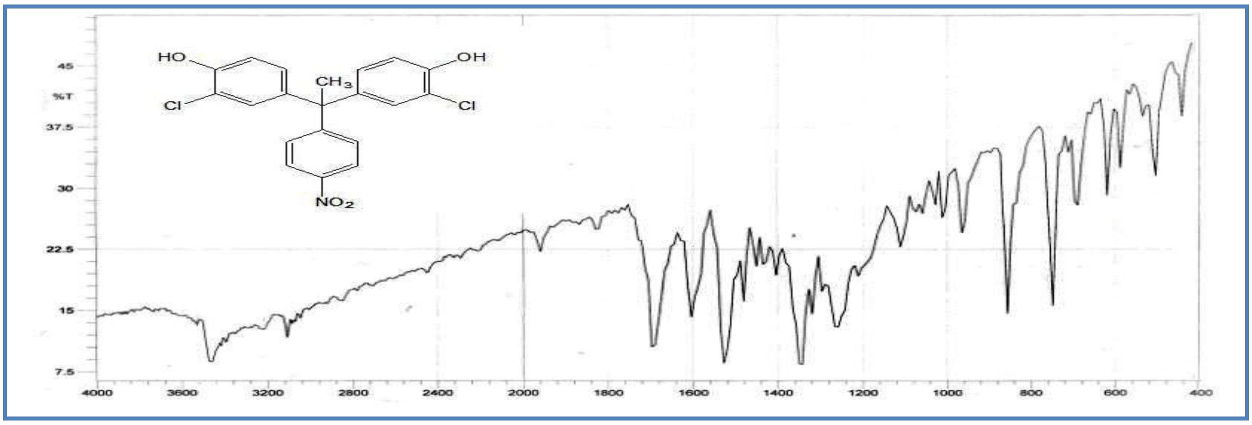
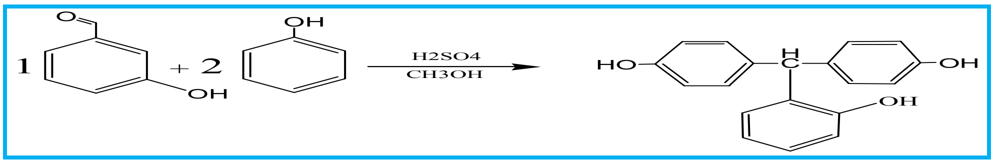


Figure 7 : FTIR spectra of (M1)

3.1.2 Synthesis and Characterization of1,4-(bis(4- hydroxyphenyl)methyl)Benzene(M2):

This monomer was synthesized by the condensation of one molecule of salicylaldehyde with two molecules of phenol in the presence H_2SO_4 and methanol as catalysts at 120 ^{O}C for 10 hrs **.** This monomer was characterized by FTIR .



Scheme(3) Synthesis of (M2)

Characterization of [M2]

FT-IR spectrum :-

The FTIR spectra of (M2) as shown in(Figur7) which indicates absorption band of C=C Aromatic at1666 cm-1, C-H Aromatic at3062 cm-1, OH at3379 cm-1, C-H aliphatic at2862 cm-1, and C-N at1230 cm-1,and C=N at 1550 cm-1, and C-O at 1095 cm-1.

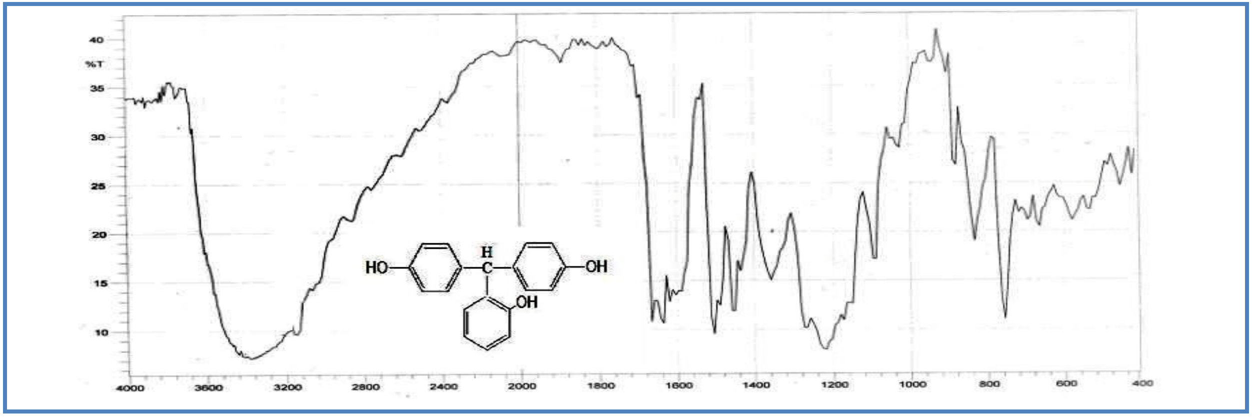
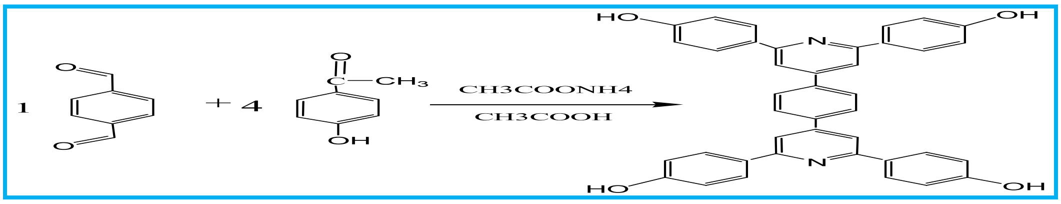


Figure 8 : FTIR spectra of (M2)

3.1.3 Synthesis and Characterization of 4(4-(2,4Bis (4-hydroxy phenyl pyridin)2,4-Bis hydroxyl phenyl pyridin (M3):

This monomer was synthesized by the condensation of one molecule of Terphthaldehyde with four molecules of 4- hydroxyl aceto phenone in the presence of ammonium acetate and glacial acetic acid at 140 142 ^{O}C for 2 hrs **.** This monomer was characterized by FTIR characterized by FTIR .



Scheme 4 synthesis of M3

Characterization of [M3]

FT-IR spectrum **:-**

The FTIR spectra of (M1) as shown in(Figur8) which indicates absorption band of C=C Aromatic at1697 cm-1, C-H Aromatic at3062 cm-1, OH at3250 cm-1, C-H aliphatic at 2985 cm-1, and C-N at1280 cm-1,and C=N at 1573 cm-1, and C-O at 1134 cm-1.

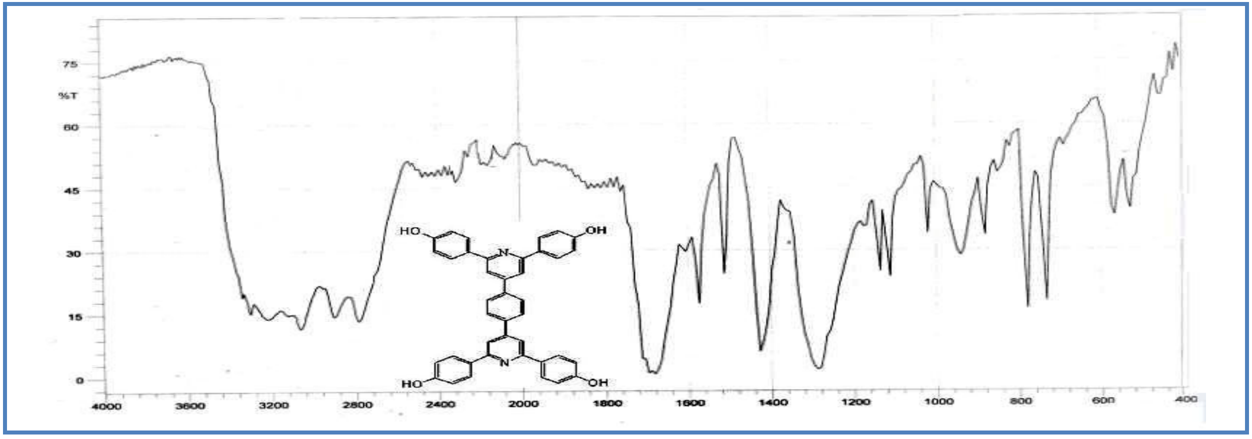
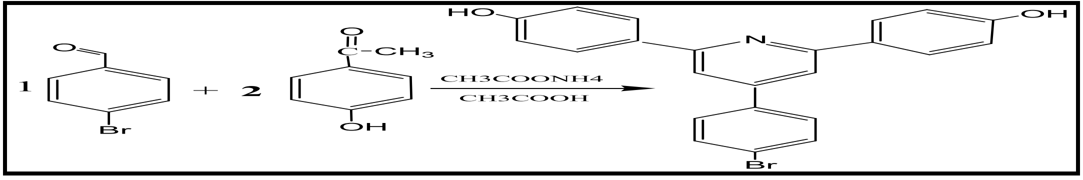


Figure 9 : FTIR spectra of (M3)

3.1.4 Synthesis and Characterization of 6-(4-bromo phenyl)2,4 bis(4-hydroxy phenyl) pyridine (M4)

This monomer was synthesized by the condensation of one molecule of 4- Bromo benzaldehyde with two molecules of 4- hydroxyl aceto phenone in the presence of ammonium acetate and glacial acetic acid at 140 142 ^{O}C for 2 hrs **.** This monomer was characterized by FTIR**.**



Scheme 5 synthesis of M4

Characterization of [M3]

FT-IR spectrum :-

The FTIR spectra of (M4) as shown in(Figur9) which indicates absorption band of C=C Aromatic at1650 cm-1, C-H Aromatic at 3170 cm-1, OH at3300 cm-1, C-H aliphatic at 2893 cm-1, and C-N at1265 cm-1,and C=N at 1512 cm-1, and C-O at 1172cm-1,C-Br at 810 cm-1.

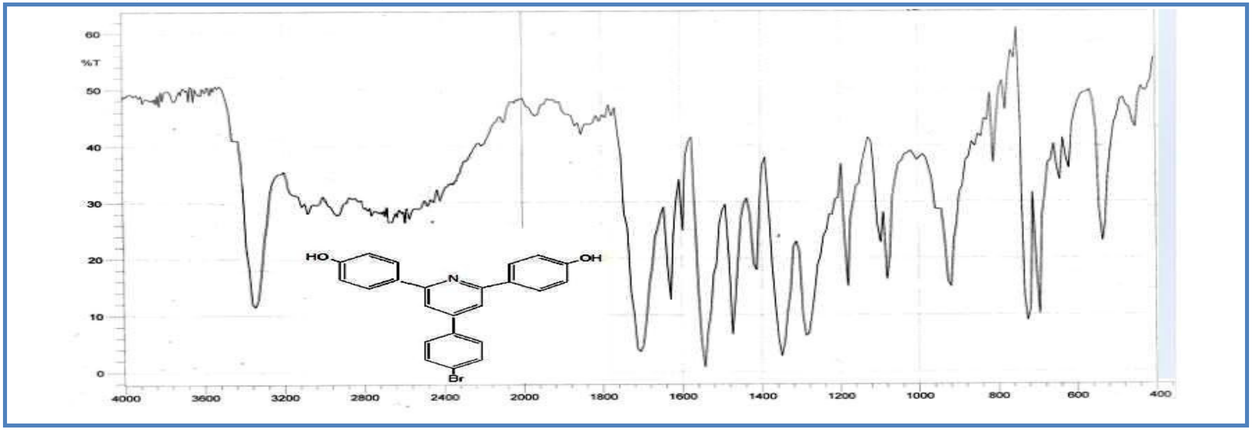


Figure10: FTIR spectra of (M4)

^{1}H-NMR spectrum of (M4), is shown in Figure() assigns the following chemical shifts; δ (2.477) ppm for DMSO, δ (4.877) ppm (s,1H) for OH group, δ(3.392) ppm (s,1H) for H2O, δ (6.678-8.055) ppm (14H) for Ar-H group(23) .

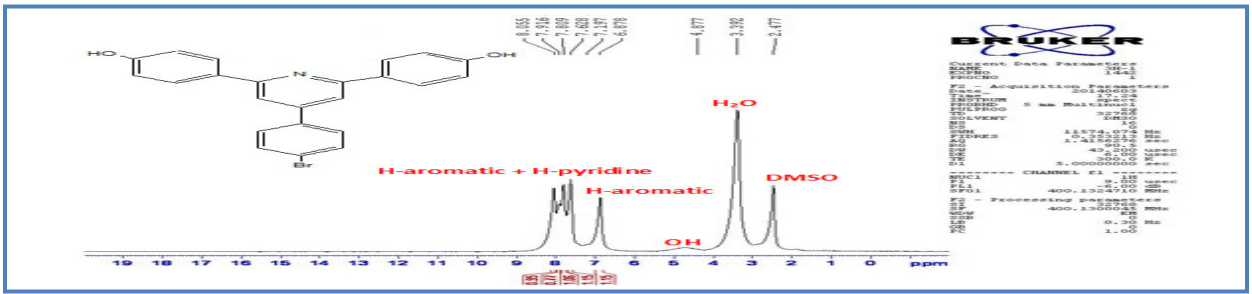
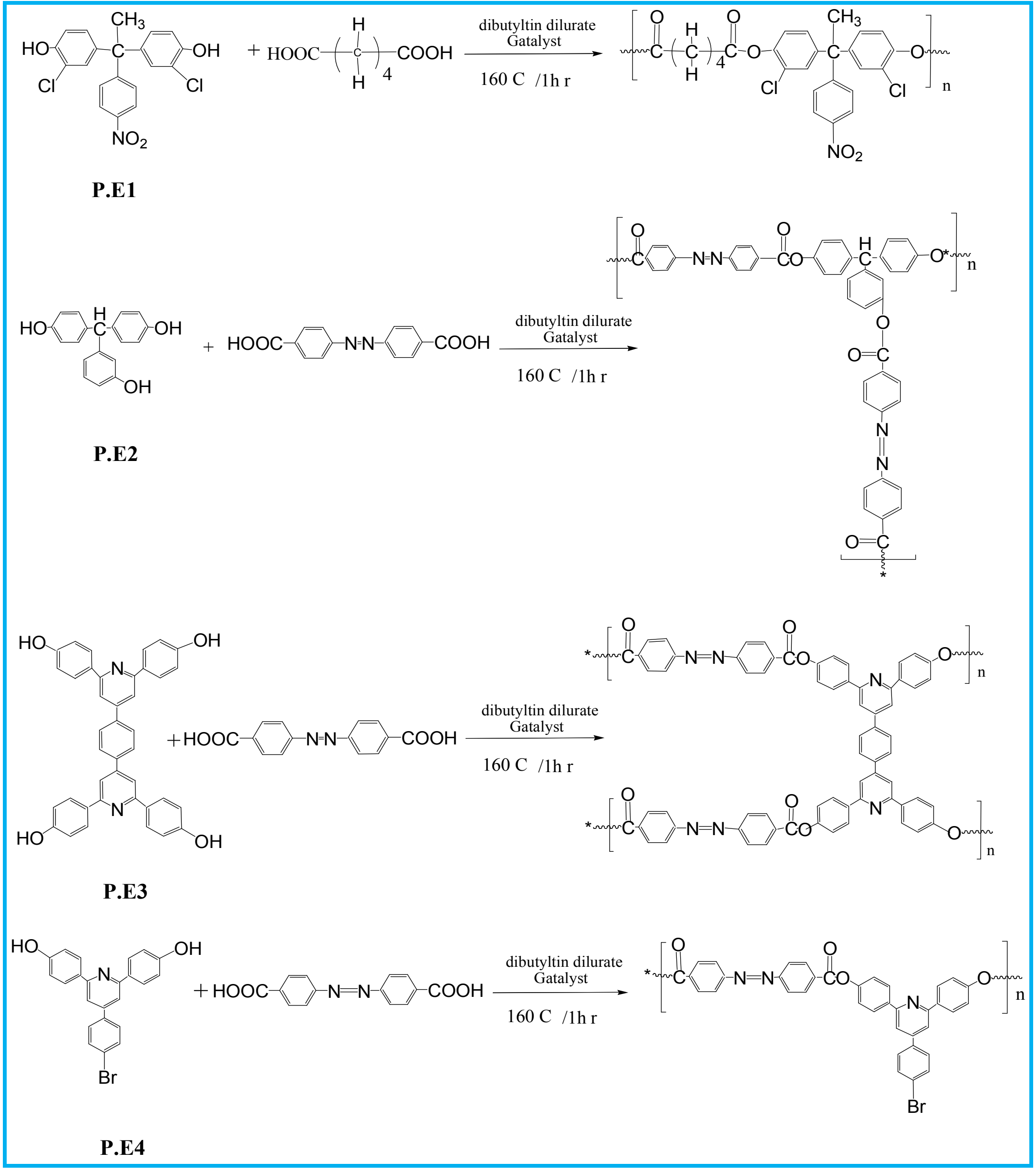


Figure 11 ^{1}HNMR spectra of M4

Synthesis of polyester [P.E1- P.E4] 3.2.

In this section, used polycondensation method for synthesis of a series of new polyester from the direct polycondensation reaction Adipic acid with new aromatic di hydroxyl monomer [M1] and new polyester from the direct polycondensation reaction of 4,4Azo di benzoic acid with new aromatic di, Tri and Tetra hydroxyl monomers[M2,M3,M4] respectively, by using the dibutyltin dilaurate Gatalyst(0.15 wt.(%)). These polymers have asoft segment such as methylene unit, pyridine hetrocyclic ring and Azo group in main chain for improving solubility in organic solvents. These polyesters were characterized by FT-IR and ^{1}H-NMR spectra .



Scheme 6 synthesis of P.E1-P.E4

Characterization of polyesters [P.E1-P.E4]

FT-IR spectrum of P.E1

The FT-IR spectrum of (P.E1) as shown in (Figur11) which indicates absorption band at (3109cm^{-1}) to (aromatic-CH2str) , (2923 cm^{-1}) to (aliphatic- CH str),(1944 cm^{-1}) to (C=O str, , (1782 cm^{-1})to (C=O str, ester) ,(1596 cm^{-1}) to(C=C) ,(1450 cm^{-1})to (N=N) (1225 cm^{-1}) to (C=N) ,(1180 cm^{-1}) to (C-O str),(1226 cm^{-1}) to (C-N) (856 cm^{-1}) to(C-Cl)**(22).**

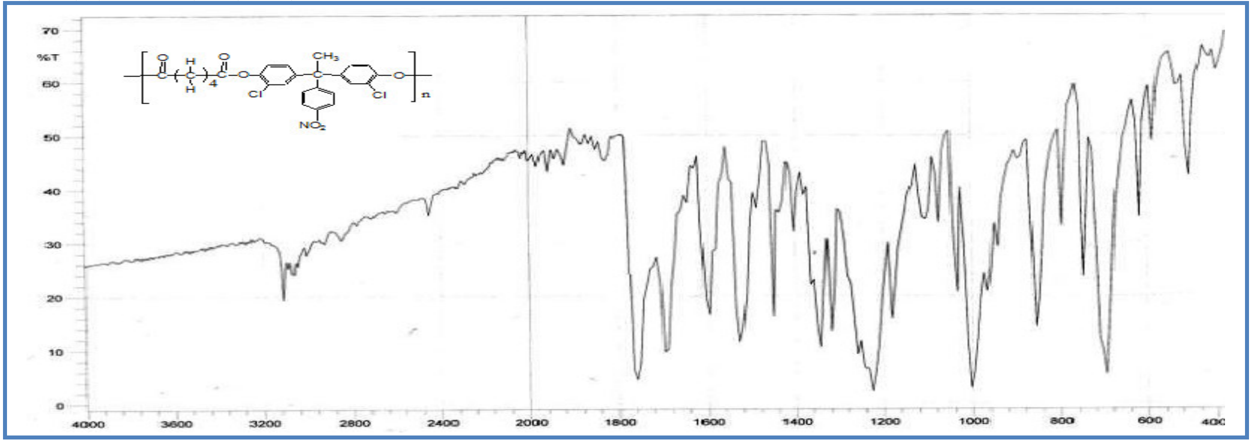


Figure 12 : FTIR spectra of (P.E1)

^{1}H-NMR spectrum of (M4), is shown in Figure(12) assigns the following chemical shifts; δ (2.484) ppm for DMSO, δ (5.190) ppm (1H) for CH, δ(3.394) ppm (1H) forCH2, δ (7.426-8.833) ppm (10H) for Ar-H group(23) .

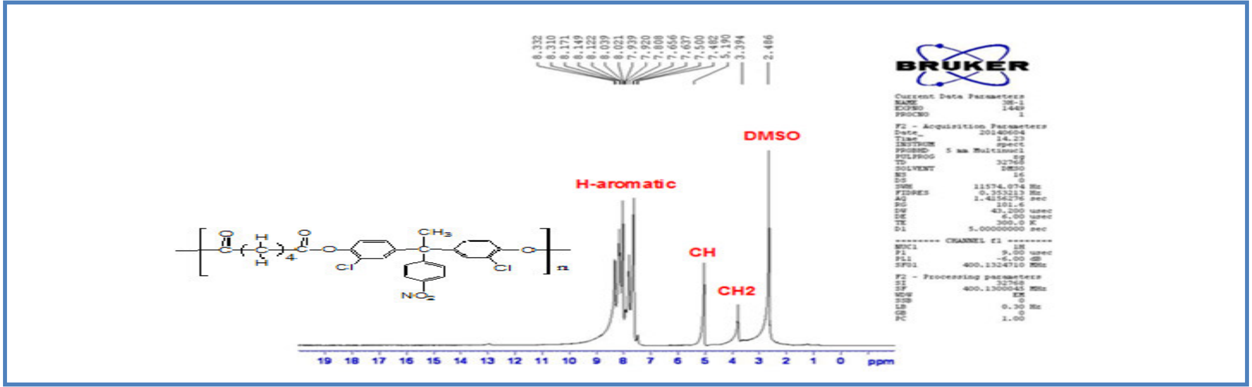


Figure 13 ^{1}HNMR spectra of P.E1

FT-IR spectrum of P.E2

The FT-IR spectrum of (P.E2) as shown in (Figur13) which indicates absorption band at (3070cm^{-1}) to (aromatic-CH2str) , (2962 cm^{-1}) to (aliphatic- CH str),(1944 cm^{-1}) to (C=O str,ester) , (1789 cm^{-1})to (C=O str) ,(1697 cm^{-1}) to(C=C) ,(1465 cm^{-1})to (N=N) (1225 cm^{-1}) to (C=N) ,(1010 cm^{-1}) to (C-O str),(1296 cm^{-1}) to (C-N)(22).

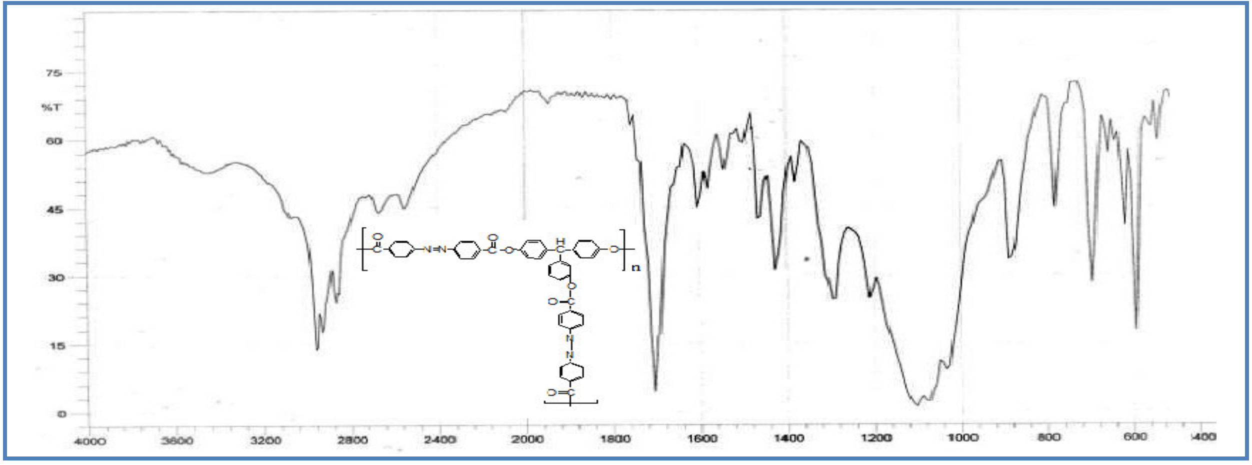


Figure 14 : FTIR spectra of (P.E2)

^{1}H-NMR spectrum of (M4), is shown in Figure(14) assigns the following chemical shifts; δ (2.474) ppm for

DMSO, δ (4.152) ppm (1H) for CH, δ (7.486-8.137) ppm (27H) for Ar-H group(23) .

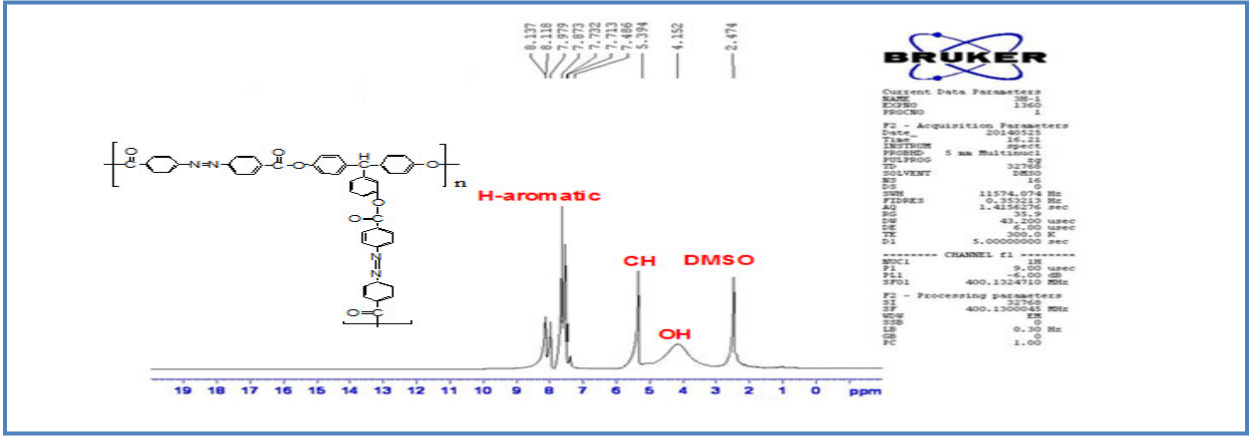


Figure 15 ^{1}HNMR spectra of P.E2

FT-IR spectrum of P.E3

The FT-IR spectrum of (P.E3) as shown in (Figur 15) which indicates absorption band at 3070cm^{-1}) to (aromatic-CH2str) , (2923 cm^{-1}) to (aliphatic- CH str),(1944 cm^{-1}) to (C=O str,ester) , (1712 cm^{-1})to (C=O str) ,(1573 cm^{-1}) to(C=C) ,(1427 cm^{-1})to (N=N) 1288 cm^{-1}) to (C=N) ,(1221 cm^{-1}) to (C-O str)(22) **.**

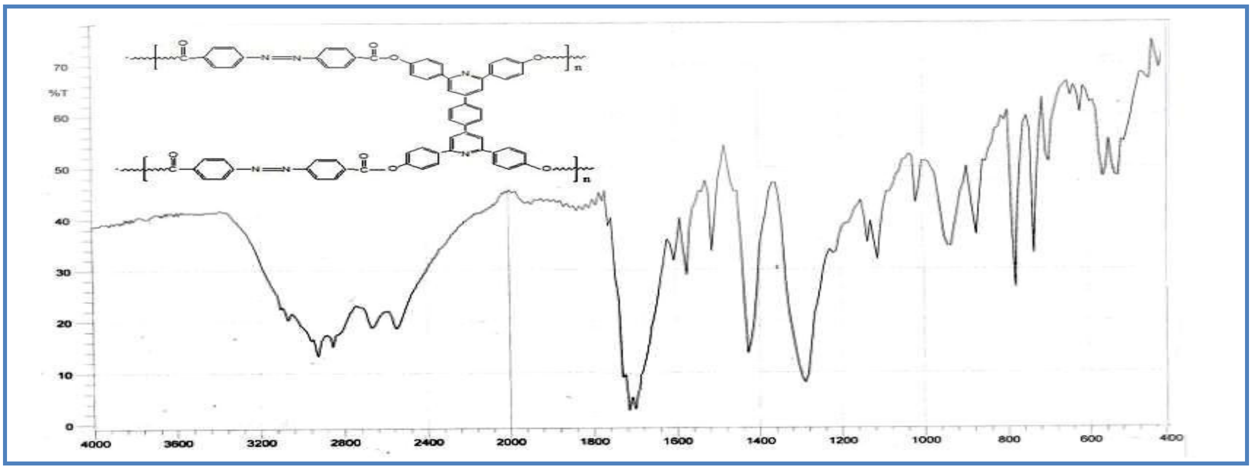


Figure16: FTIR spectra of (P.E3)

^{1}H-NMR spectrum of (P.E3), is shown in Figure(16) assigns the following chemical shifts; δ (2.483) ppm for DMSO, δ (6-660-8.144) ppm (40H) for Ar-H group (23).

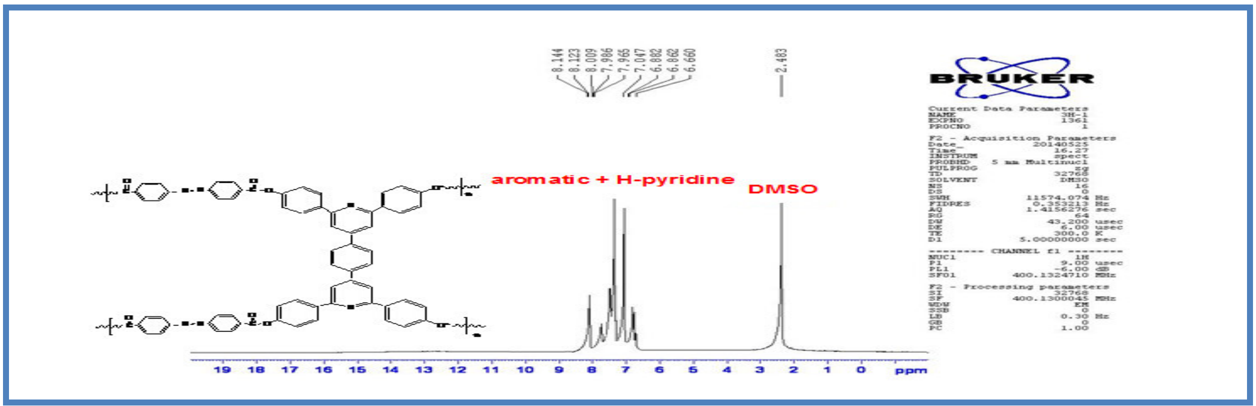


Figure 17^1 HNMR spectra of P.E3

FT-IR spectrum of P.E4

The FT-IR spectrum of (P.E4) as shown in (Figur17) which indicates absorption band at (3150cm^{-1}) to (aromatic-CH2str) , (2954 cm^{-1}) to (aliphatic- CH str),(1951 cm^{-1}) to (C=O str,ester) , (1704 cm^{-1})to (C=O str) ,(1589 cm^{-1}) to(C=C) ,(1458cm^{-1})to (N=N) ,(1226 cm^{-1}) to (C-O str)(22) .

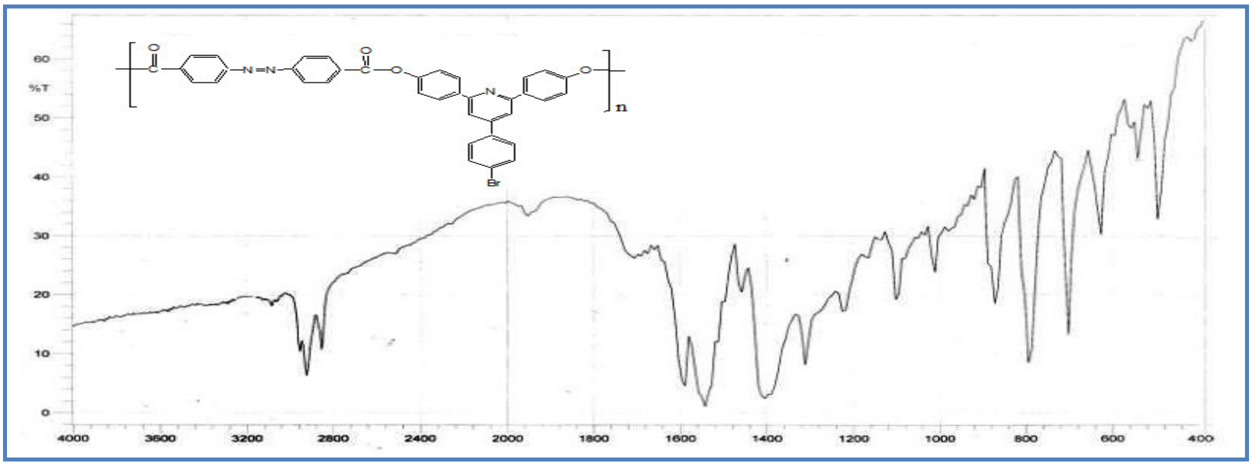


Figure 18 : FTIR spectra of (P.E4)

^{1}H-NMR spectrum of (P.E4), is shown in Figure(18) assigns the following chemical shifts; δ (2.470) ppm for DMSO, , δ(3.352) ppm (s,1H) for H2O, δ (6.859 -8.099) ppm (22H) for Ar-H group(23) .

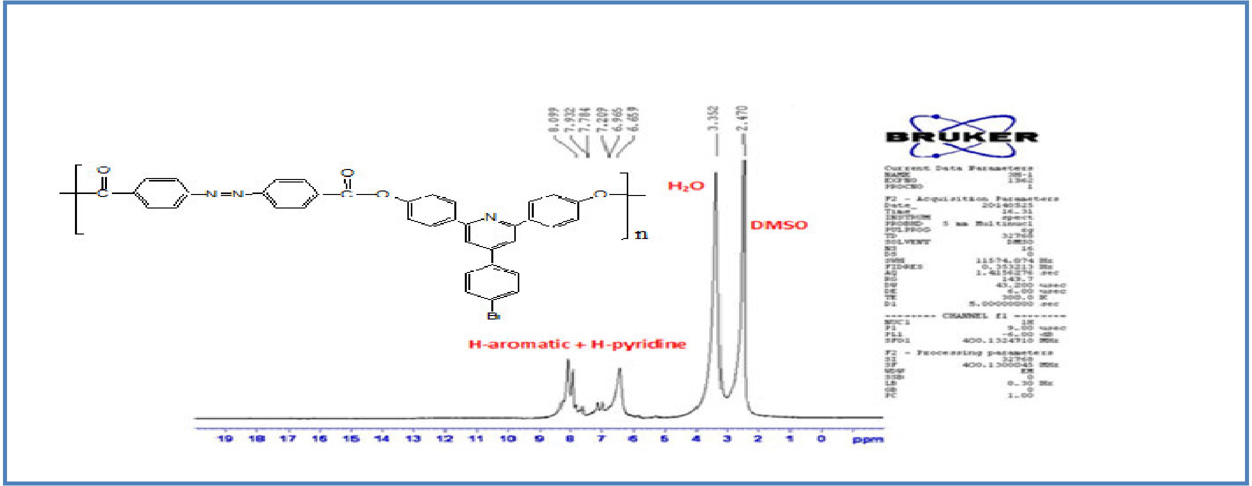


Figure 19^1 HNMR spectra of P.E4

Solubility of polyesters:- 3.3

Solubility of polyesters P.E1-P.E4 was qualitatively tested in organic solvents and the results are summarized in (Table 1). The method that attempt to enhance their process abilities 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 and crystallinity , but also could impart an increase in Tg by restricting the segmental mobility .One of the major objectives of this work was producing polyesters with improved solubility . The Solubility was investigated as (0.01gm) of polymeric sample in (2ml) of asolvent .All of the newly synthesized polyesters have good soluble in common polar and dipolar aprotic solvents without need for heating.

Table(1) Solubility of polyesters :-

Solvent	**Polyester**			
	P.E1	**P.E2**	**P.E3**	**P.E4**
pyridin	+ -	+ +	+ -	+ +
CHCl3	+ -	+ +	+ +	+ +
CH2Cl2	+ +	+ +	+ -	+ -
NaOH	+ -	+ -	+ +	+ +
H2SO4	+ -	+ + +	+ + +	+ -
HNO3	+ +	+ -	+ +	+ +
Acetone	+ -	+ -	+ + +	+ +
Benzen	+ +	+ +	+ +	+ +
DMF	+ +	+-	++	++
DMSO	+ + +	+ +	+ -	+ +
THF	+ +	+ -	+ -	+ + +

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

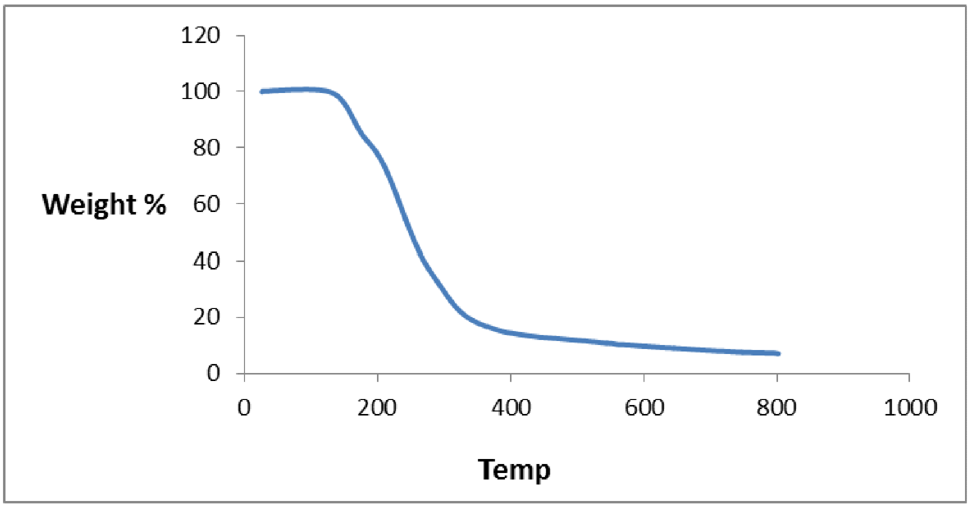
3.4 Thermal analysis of polyester

Thermo gravimetric Analysis (TGA) involves determining changes in mass as a function of temperature. It is commonly used to research degradation temperatures, absorbed content of materials, levels of inorganic and organic parts contained in a material and analyses solvent residues . It employs a sensitive electronic balance from which the sample is suspended in a furnace controlled by a temperature programmer (22) . The thermal properties of four samples of these polyester were investigated by means of thermo gravimetric analysis (TGA) in Argon atmosphere at heating rate of 10°C/min . The results such as T_i , T_{op} , T_f , $T_{50\%}$, % Residue at 800 ^{o}C , and char yields at 500°C are summarized in (*Table*).The temperatures of 50% weight loss of (P.E1-P.E4) as a standard indication for thermal stability of polymers were all from 248 to 761°C, The char yields of (P1-P4) at 500°C are 11% until 83% in Argon atmosphere , which indicate they could meet high temperature resistant requirements as some special materials in modern aerospace . weight residue of (**P.E1-P.E4)** at 800°C are the highest than Aromatic polyester of this series, (7% until 50%).

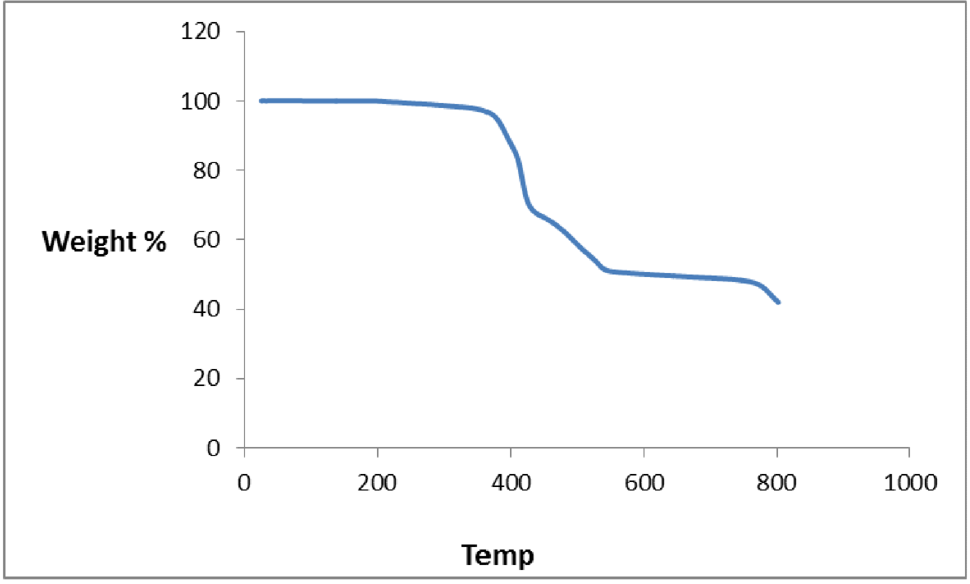
Table(2) : Thermal behavior data of Aromatic polyester:-

Aromatic polyester	***DT/°C***				**$T_{50\%}$**	**Residue at ^{o}C800**	**Char % *at 500°C***
	T_i	**T_{op1}**	**T_{op2}**	**T_f**			
P.E1	152	380	-----	800 >	248	7%	11%
P.E2	382	444	575	800 >	546	42%	58%
P.E3	311	429	620	800 >	761	50%	83%
P.E4	222	302	429	800 >	492	18%	48%

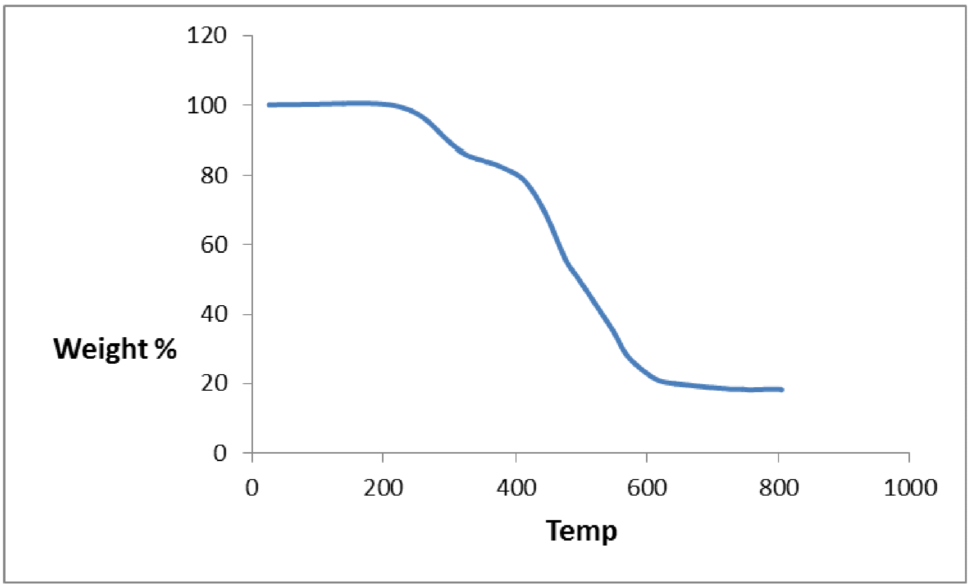
DT : *Decomposition temperature.*
T_i : *Initial decomposition temperature.*
T_{op} : *Optimum decomposition temperature.*
T_f : *Final decomposition temperature.*
$T_{50\%}$: *Temperature of 50% weight loss, obtained from TGA.*
Char% *at 500°C* : *Residual weight percentage at 500°C in* Argon *by TGA*



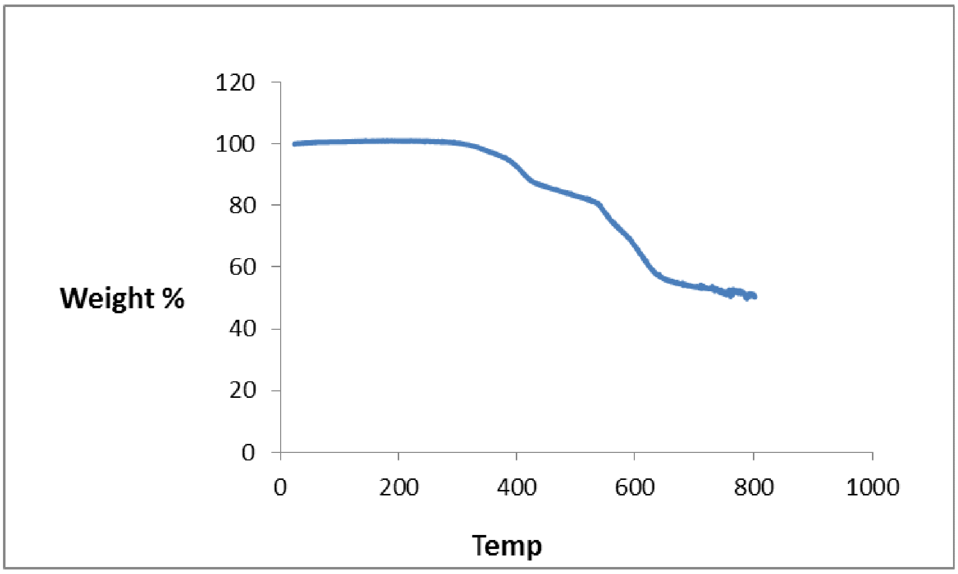
Figur 20 TGA curve of P.E1



Figur 21 TGA curve of P.E2



Figur 22 TGA curve of P.E3



Figur 23 TGA curve of P.E4

Conclusions

In this work several new polyesters (PE1-PE4) have been synthesized by the solution polycondensation reaction of the monomer with four different of aromatic diols in hexane presence of dibutyltine dilaurate as catalyst. These new polyester are soluble in various organic solvents and have good thermal stability . These properties can make these polyesters attractive for practical applications such as process able high- performance engineering plastics.

REFERENCES

1-P.M.Patel, K.C.Patel and S.K.Patel (2010)," Studies on synthesis, Viscosity, Infrared Spectra and Thermo gravimetric",Malaysian Polymer Journal. 5(1),P: 55-67.

2- S.G. Sanadhya , S. L. Oswal and K.C .Parmer (2014)," Synthesis and characterization of aliphatic-aromatic polyesters using interfacial polycondensation technique",Journal of Chemical and Pharmaceutical Research. 6(4), P: 705-714.

3-S.Katoch, V.Sharma and P.P.Kundu(2010). "Water sorption and diffusion through saturated polyester and their nanocomposites synthesized from glycolyzed PET waste with varied composition", Chemical Engineering Science .65 ,P:4378-4387.

4-H.Hall, S.Ahad, R.Bates, M.Bertucci, C.contreras,A.Dospinoiu, G.Lin, N.Singletary andA.Somogyi (2011)," Structural Analysis of Aromatic Liquid Crystalline Polyesters ", Polymers.,(3) , P: 367-387.

5- L.S.Prabha , R.Nanthini, G.Krishnaveni (2012)," Synthesis and characterization of novel biodegradable aliphatic copolyesters - poly(ethylene sebacate-co-propylene succinate) and poly(ethylene sebacate-co-propylene adipate)" , Journal of Chemical and Pharmaceutical Research . 4(5), P:2442-2457.

6- U. Edlund and A.-C. Albertsson (2003)," P olyesters based on diacid monomers", Advanced Drug Delivery Reviews. 55, P: 585–609.

7- P.Zhao,w.Liu,Q.Wu and J. Ren(2010)," Prepar at ion, Mechanical, and Thermal Properties of Bio degradable Polyesters/Poly(Lactic Acid) Blends", Journal of Nanomaterial's .4(6) P:8.

9-S.L. Oswal and A.K. Pandya (2004)," Synthesis and Characterization of Linear Aromatic Polyester-amides from Diacid Chlorides and Aminophenols",Iranian Polymer Journal . 13(3), P: 205-212.

10- C. S. Wu (2012),"polyester/polyaniline composite and its improved counterpart ", Express Polymer Letters.6(6), (2012) P:465–475.

11-P.N. Honkhambe , N.S. Bhairamadgi and M.V. Biyani (2010)," Synthesis and characterization of new aromatic polyesters containing cardo decahydronaphthalene groups", European Polymer Journal. 46 ,P: 709–718.

12-W. Cui, Q. Jiao, Y. Zhao, H. Li, H. Liu and M. Zhou (2012)," Preparation of poly(ethylene terephthalate)/layered double hydroxide Nano composites by in-situ polymerization and their thermal property", express Polymer Letters .6(6), P: 485–493.

13-S. S. Sahay and K.Krishnan (2005)," Analysis of the nonisothermal crystallization kinetics in three linear aromatic polyester systems", Thermochimica Acta .430 ,P:23–29.

14- Y.S.Park and J.W.Lee and J. Jin (2002), " Synthesis and Liquid Crystalline Properties of Hyperbranched Aromatic Polyesters Consisting of Azoxybenzene Mesogens and Polymethylene Spacers", Bull. Korean Chem. Soc. 23(9),P:1201-1207.

15-E.B. Belal (2013)," Biodegradation of Aliphatic-aromatic Coplyester under Thermophilic Conditions", Research Journal of Environmental and Earth Sciences. 5(11) , P: 677-690.
16- A. Rahimi and S. Farhangzadeh (2001) , "*Kinetics Study of Bisphenol A Synthesis by ondensation Reaction*" , Malaysian Polymer Journal. (10) ,p: 1 .
17- R.Sarma , and J. Baruah (2004). "Synthesis and Characterization of Bis-(3,5-dimethyl-4- hydroxyphenyl) (aryl) Methane as Precursor forThree State Indicator", *Dyes and Pigments*. 61 : 39–47.
18- B .Tamami and H. Yeganeh,. (2001). "Synthesis and Characterization of Novel Aromatic Polyamides Derived from 4-aryl-2,6-bis(4-aminophenyl) Pyridines", *Polymer*. 42 : 415–420.
19- B .Tamami and H .Yeganeh (2002). "Synthesis and Properties of Novel Aromatic Polyamides Based on 4-aryl-2,6-bis(4-chlorocarbonyl phenyl) Pyridines", *European Polymer Journal*. 38 : 933–940.
20-K.Faghihi and M.Hagibeygi (2007)," New Aromatic Polyamide with Azo and Phosphine Oxide Groups in the main chain",Turk J Chem . 31,P:65-73.
21- H.Guimaraesa ,M. Brioudea, P.Fiuzaa,A. Pradob, S.Boaventuraa,and M.Josea(2007),"Synthesis and Characterization of aliphatic polyesters from Glycerol , by –product of Biodiesel production , and adipic acid ", Materials Research. 10(4),P: 335-339.
22- I .Hamilton (2009). "The Development of Microwave Thermal Analysis (MWTA) and its Application to the Study of Carbons and Other Materials", Thesis. Ph.D., *University of Huddersfield*. : 29.