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Synthesis and Characterization of New Polyesters Derived From 4, 4'-Azodibenzoic Acid, Malic Acid and Adipic Acid With Aromatic Diols

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Abstract

A series of new aromatic polyesters have been synthesized by polycondensation of different aromatic diols (M_1, M_2 ,M_3) with different dicarboxlic acids (4,4'azo di benzoic acid, malic acid and adipic acid) using dibutyltine dilaurate as catalyst . The preparation of thermally stable polyesters was successfully applied with good yields (60-85%). All polyesters (PE1-PE4) containing aliphatic methylene linkage, and azo group in the main chain. The resulted polymers are readily soluble in aprotic polar solvents , such as (pyridine , $CHCl_3$, CH_2Cl_2 , 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 were characterized by FT-IR and ^{1}HNMR spectroscopies.

Keywords: Aromatic polyester, 4, 4'-Azodibenzoic acid, Aromatic diols, Di carboxylic acids

تحضير وتشخيص بولي استرات جديدة مشتقة من 4،4' ازو ثنائي حامض البنزويك وحامض الماليك وحامض الأديبيك مع مركبات أروماتية ثنائية الهيدروكسيل

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الخلاصة

تم تحضير سلسلة من البولي استرات الجديدة باستخدام مركبات أروماتية ثنائية الهيدروكسيل (M1، M2، M3) مع حوامض مختلفة (4,4' ازو ثنائي حامض البنزويك ،حامض الماليك وحامض الأديبيك) باستخدام (ثنائي بيوتيلتين ، ثنائي لوريت) كعامل مساعد . حضرت البولي استرات المستقرة حراريا بنجاح مع نسبة تحويل (60–85 ٪) . جميع البولي استرات (PE1 – PE4)المحضرة تحتوي على (رابطة المثيلين أو مجموعة الازو) في السلسلة الرئيسية . البوليمرات المحضرة قابلة للذوبان بسهولة في المذيبات القطبية مثل (البيريدين ، $CHCl_3$ ، CH_2Cl_2 ، هيدروكسيد الصوديوم ، H_2SO_4 ، HNO_3 ، الأسيتون ، البنزين ، DMF، DMSO، THF) دون الحاجة للتسخين . التحليل الحراري للبولي استرات (TGA) يؤكد الاستقرار الحراري. تم تشخيص المونوميرات والبولي استرات المحضرة باستخدام تقنية FT –IR و ^{1}HNMR.

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Introduction

High temperature or thermally stable materials are one of the specialty areas within polymer science which have been recognized for about 60 years and their applications are growing steadily. The most significant categories of these polymers are polyimide, polyamide, polyarylate, and their copolymers. Polyarylates belong to the class of high-performance engineering plastics and they have good thermal and mechanical properties[1, 2]. However, because of their limited solubility in organic solvents and their high melting or high glass transition temperatures, polyarylates are generally difficult to process by virtue of their rigid structures. Introduction of bulky and pendent units and also disruption of symmetry are important methods to overcome this drawback [3-6]. Recently many attempts been made by researchers on high-performance polymers, with outstanding thermal stability and solubility, and provided great impetus to the discovery of a variety of thermostable and processable polymers.

Aromatic polyesters are materials exhibiting an excellent pattern of physical properties. They are significant category of high performance and engineering materials which exhibit good thermal stability, solvent resistance and good mechanical properties and therefore, they are applied widely in the aviation, automobile, and electronic industries[7, 8]. Aromatic polyesters are also well known as rigid-rod liquid-crystalline polymers[9, 10]. Aromatic polyesters are certainly one of the most successful classes of high-temperature polymers [11]. 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. These studies include: **1-** Introducing of soft segments on the main chain such as methylene group. **2-** Breaking its symmetry and regularity, making crystallization impossible [12]. In this work, four aromatic polyesters (PE1- PE4) have been synthesized in high yields by polycondensation between different aromatic diols and different dicarboxlic acids using dibutyltine dilaurate as catalyst. Qualitative structure analysis of the polymers and monomers have been carried out by the using of FT-IR, and ^{1}HNMR spectroscopy. Thermal stability also was systematically investigated.

Expermintal

Materials

Dichloromethane, hexane, were purchased from(BIOSOLVE); hydrochloric acid ,salicylaldehyde, benzaldehyde, all from (Himedia); diethyl ether from (IGCC / England); phenol, p-aminophenol, 4-chlorobenzaldehyde, glacial acetic acid, Piperidine, Pyridine, terphthaldehyde, dimethyl sulphoxide (DMSO), p-hydroxyacetophenone, terohthaldehyde, tetrahydrofurane (THF), all were obtained from (MERCK); absolute ethanol from (Scharlab S.L); N,N-dimethylformamide (DMF)from (ALDRICH)**.**

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 spectra were recorded on a type of Bruker, Ultra, shield 300MHZ,Switzearland and using (DMSO-d_6) as solvent in the University of Educational teacher -Tehran Iran),(Thermogravimetry analyses (**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.

Synthesis of monomers

1- Synthesis of 1,4- di [bis (4-hydroxy phenyl methyl] benzene(M1)

In a suitable round-bottomed flask equipped with a reflux condenser. (0.1M) solution of H_2SO_4 in methanol (60% :40%), phenol (4.5 gm ,48 mmol) and terephthalaldehyde (1.5gm,12mmol) were added and the mixture was refluxed at 120°C for 10 hrs. with constant stirring . Upon completion of the reaction , the solvent was removed under vacuum[13] . The yield was (71%) of brown crystals, m.p= (120 °C). Figure-1 Shows structure of monomer (M1).

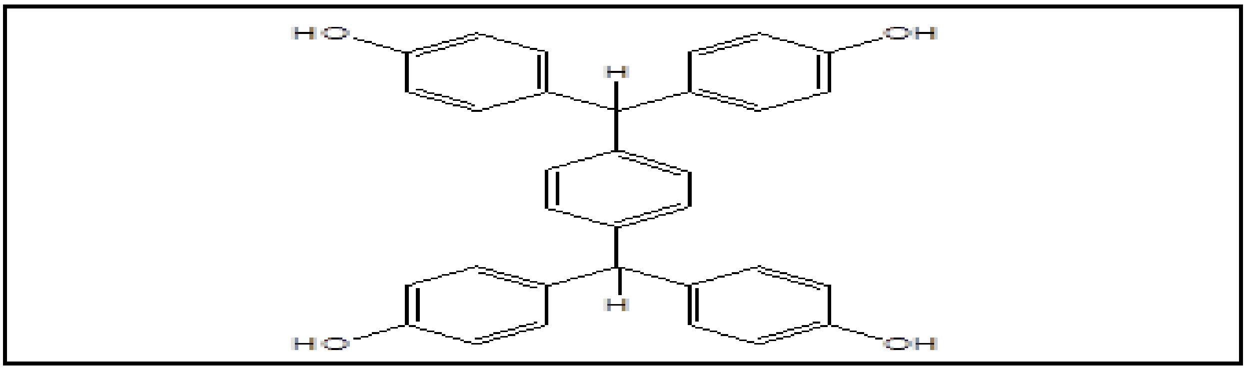


Figure1- structure of M1.

2- Synthesis of bis(4-hydroxy phenyl) -2,4 di chloro phenyl)methane (M2)

This monomer was synthesized by same procedure used in preparation of (M1) by using 2,4 dichlorobenzaldehyde(1.34gm ,7mmol) and phenol(1.31 gm),(14 mmol). The yield was (60%), m.p= (101^{o}C). and the color is yellow.

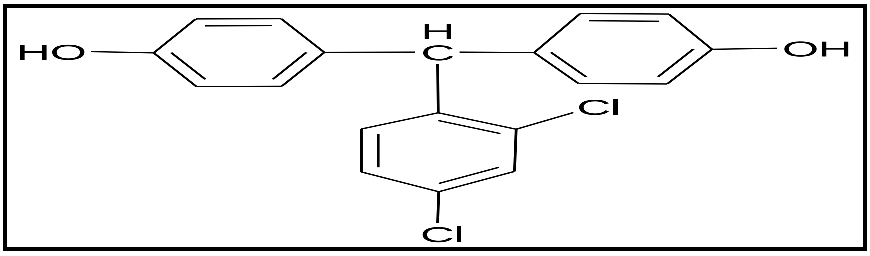


Figure 2- structure of M2

3- Synthesis of bis (2-bromo 4-hydroxy phenyl) - di phenyl methane (M3)

A mixture of benzophenone (2.91gm),(16mmol) , 3-bromo phenol (4gm),(32 mmol), HCl catalyst (9.3gm) and thioglycolic acid (0.5gm) as promoter was placed in a three neck round bottomed flask in thermostat bath at 60^{o}C for 6hrs. .After a definite period of time, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was washed, dried [14]. The yield was (85%) of yellow crystals, m.p= (187-190^{O}C). Figure -3 shows the structure of monomer (M3).

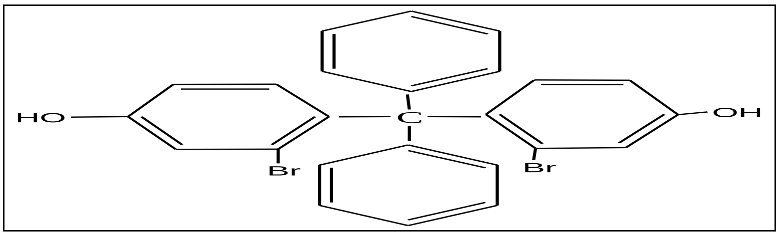
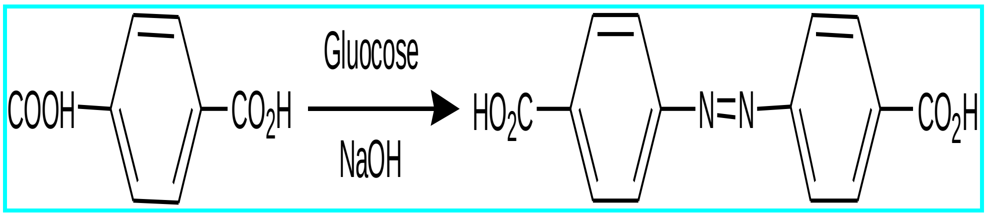


Figure 3- structure of M3

4- Synthesis of $4,4^{\backslash}$-Azodibenzoic acid [6]

$4, 4^{\backslash}$ Azodibenzoic acid was prepared according to atypical procedure, shown in scheme(1). (Thirteen gm of 4-nitrobenzoic acid (79mmol) was heated in a solution of(50 gm) of sodium hydroxide in 250mL of water at 50 °C. 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 8hrs. with vigorous stirring until orange- colored crystals were formed [6] .



Scheme1- Preparation of 4, 4′ Azodibenzoic acid

5- Synthesis of polyesters[PE1-PE4]

Dihydroxy monomers and di acid monomers , as shown in Table- 1 were mixed at 120^{o}C under constant stirring. After the solubility of the acid in dihydroxy monomer, the dibutyltine dilaurate catalyst (0.15 wt.(%)) was added and the temperature was increased up to 160^{o}C and was kept for 1hr The materials were dried under vacuum at 50^{o}C giving rise to the P.E series . The materials were obtained as powders [15].

T**able 1-** synthesis of polyesters [PE1-PE4].

polyester	Monomers		diacid gm/mmol	Dihydroxy gm / mmol	Color
	Di carboxylic acid	Dihydroxy monomer			
PE1	Malic acid	M1	1.2gm	1gm	white
PE2	4,4′ Azodibenzoic acid	M2	2.4gm	1.3gm	Orang
PE3	Malic acid	M2	2.4 gm	1.1gm	Orang
PE4	Adipic acid	M3	1.2gm	1gm	White

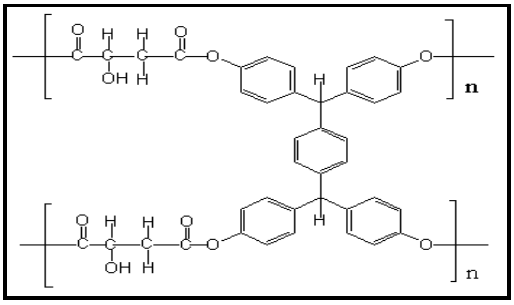


Figure 4- structure of PE1.

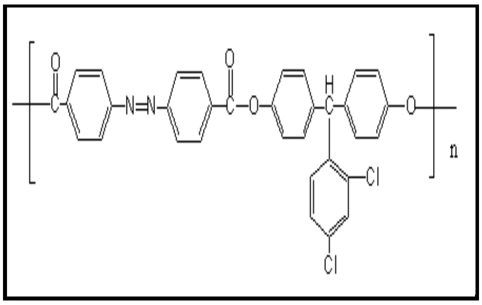


Figure 5- structure of PE2.

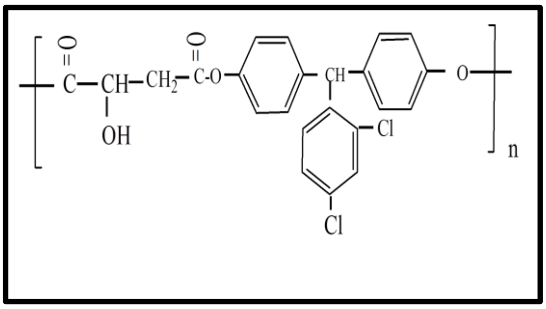


Figure 6- structure of PE3.

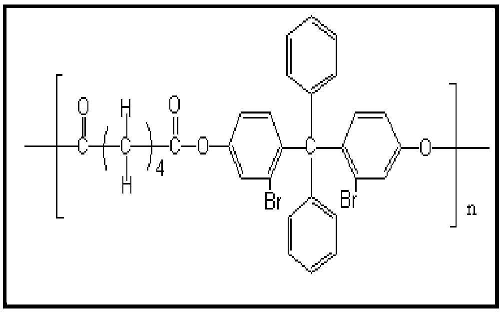


Figure 7- structure of PE4.

Results and Discussion

Synthesis of monomers:

Synthesis and characterization of 4, 4′-Azodibenzoic acid

The FTIR spectrum of (*4,4*\ *Azodibenzoic acid*) as shown in Figure- 8 indicates absorption bands of υ (C=C) aromatic at (1589cm^{-1}), υ (C-H) aromatic at (3109 cm^{-1}) , υ (O-H) at (3425 cm^{-1}), υ (C=O) at (1651cm^{-1}), υ (C-O) at (1103 cm^{-1}) υ (C-N) at (1311 cm^{-1}), and υ (N=N) at (1500 cm^{-1}) .

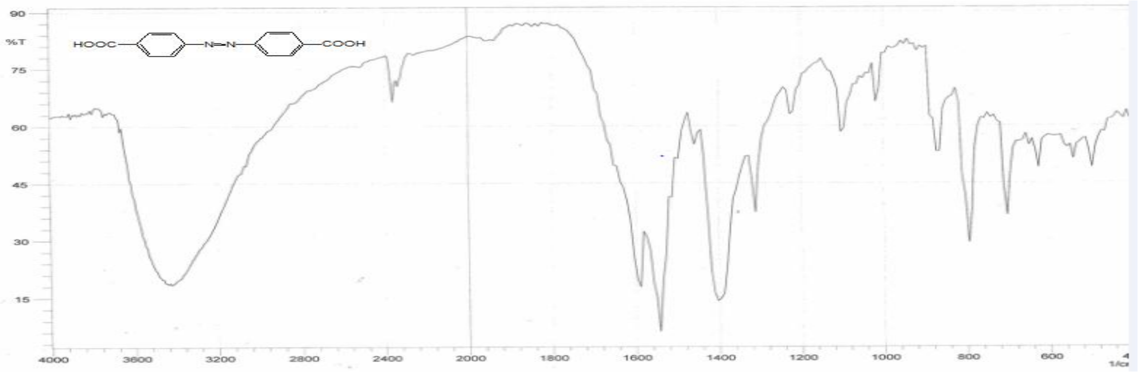
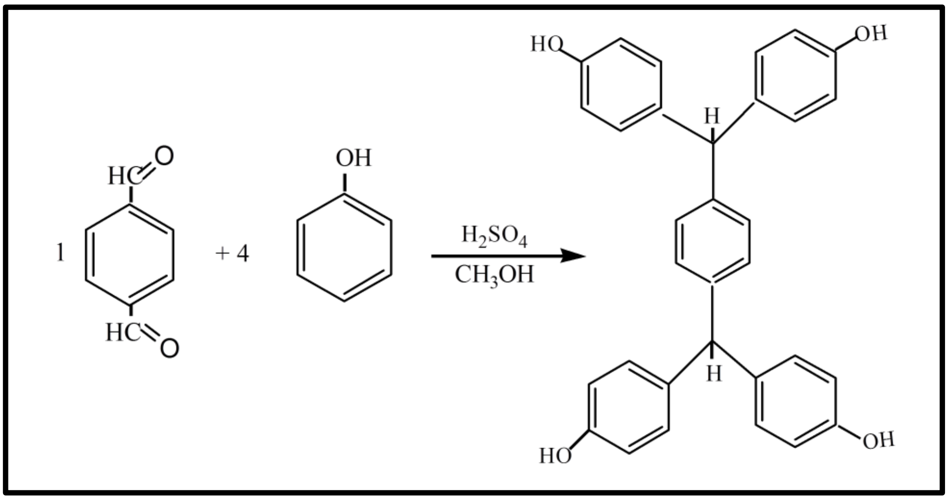


Figure 8- FTIR spectrum of (4, $4^{\backslash}$ Azodibenzoic acid).

Synthesis and Characterization of (M1)

This monomer was synthesized by the condensation of one mole of terphthaladehyde with four moles 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 2- Synthesis of (M1).

The FTIR spectrum of (M1) as shown in Figure-9 indicates absorption bands of υ (C=C) aromatic at (1596 cm^{-1}),υ (C-H) aromatic at (3062 cm^{-1}), υ (O-H) at (3425 cm^{-1}), (C-H) aliphatic at (2962 cm^{-1}), and υ (C-O) at (1110 cm^{-1}) .

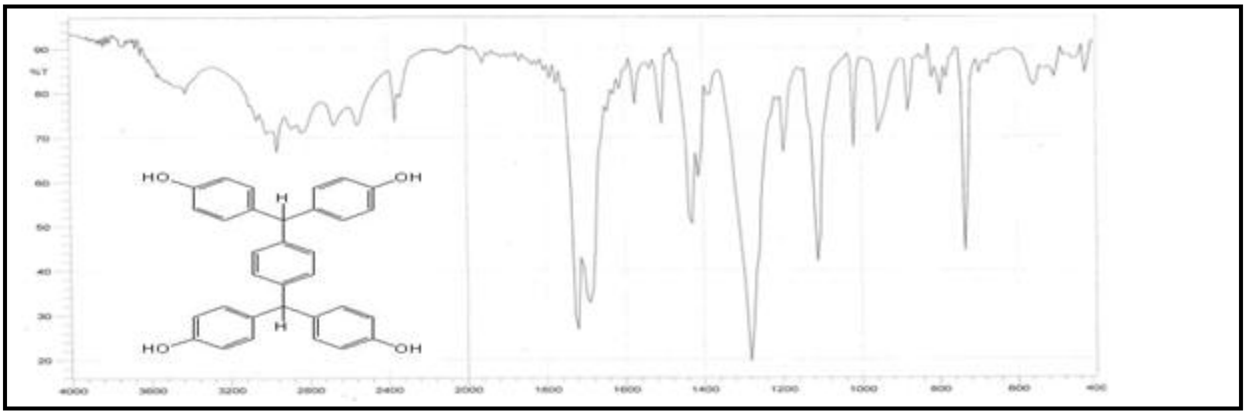
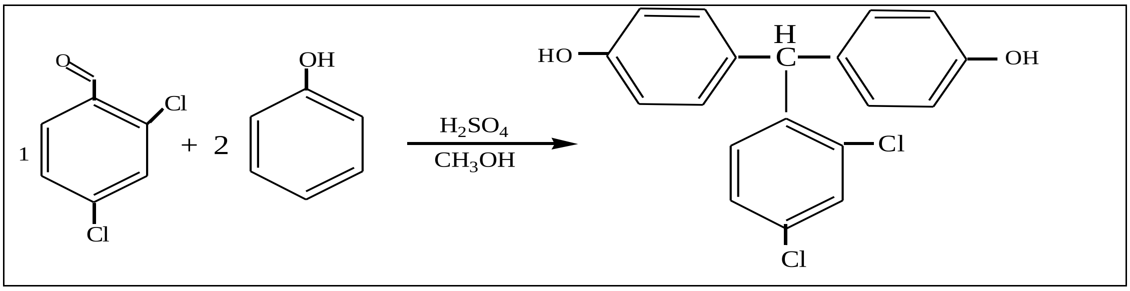


Figure 9- FTIR spectrum of (M1).

Synthesis and characterization of (M2)

This monomer was synthesized by the condensation of one mole of 2,4dichloro benzaldehyde with two moles of phenol in the presence of H_2SO_4 and methanol as catalysts at 120 ^{O}C for 10 hrs. . This monomer was characterized by FTIR and ^{1}HNMR.



Scheme 3- Synthesis of (M2).

The FTIR spectrum of (M2) as shown in Figure-10 indicates absorption bands of υ (C=C) aromatic at (1627cm^{-1}), υ (C-H) aromatic at (3039 cm^{-1}), υ (O-H) at(3300 cm^{-1}), υ (C-H) aliphatic at (2962 cm^{-1}),υ (C-O) at (1110 cm^{-1}) and (918 cm^{-1}) to υ (C-Cl).

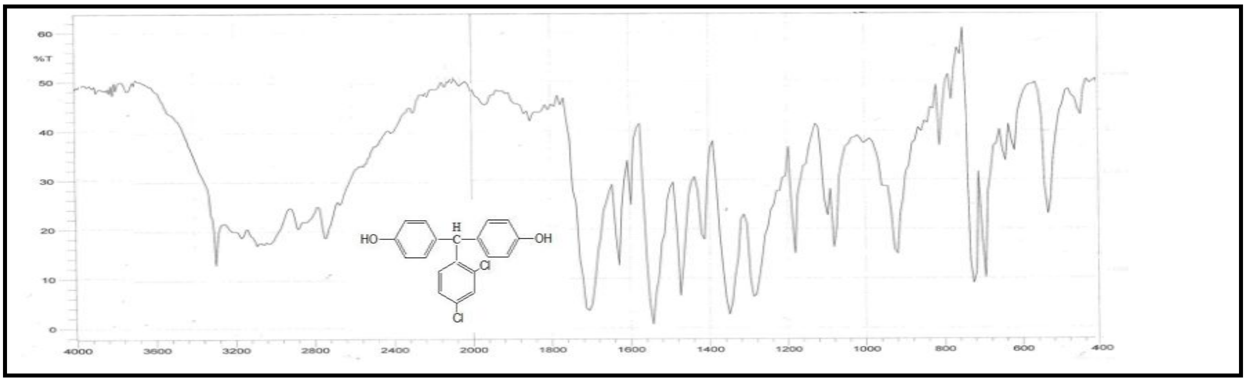


Figure 10- FTIR spectrum of (M2).

^{1}H-NMR spectrum of (M2), is shown in Figure-11 assigns the following chemical shifts; δ (2.476) ppm for DMSO, δ (5.047) ppm (s,1H) for C-H group, (6.878-7.916) ppm (11H) for Ar-H group, δ (7.9) (s,3H ,3OH) group.

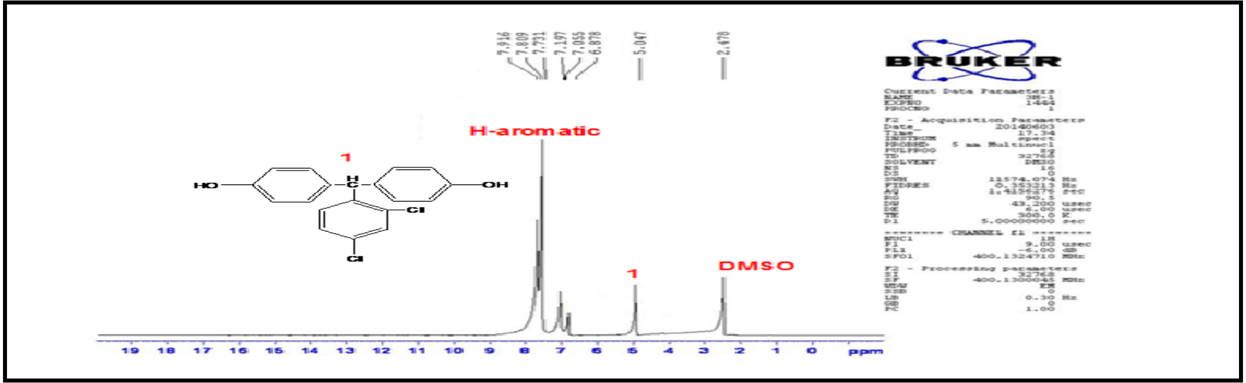
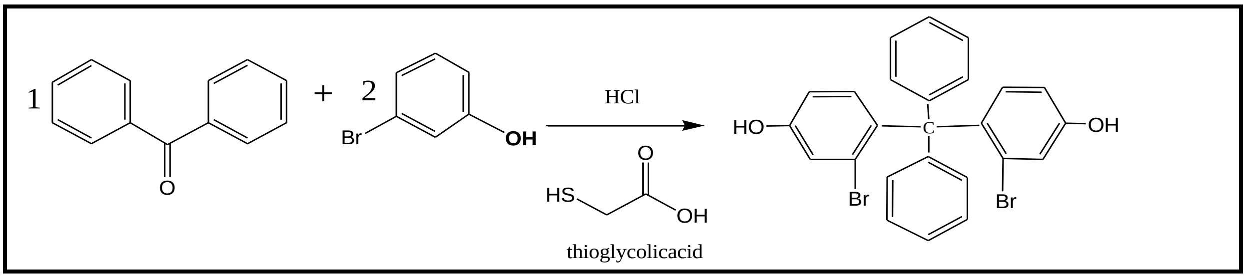


Figure 11- ^{1}HNMR spectrum of (M2).

Synthesis and characterization of (M3)

This monomer was synthesized by the condensation of one mole of benzophenone with two moles of 3-bromo phenol in the presence of acid catalyst , and suitable promoter at 60 ^{O}C for 6 hrs.This monomer was characterized by FTIR.



Scheme 4- Synthesis of (M3).

The FTIR spectrum of (M3) as shown in Figure-12 indicates absorption bands of υ (C=C) aromatic at ($1650 cm^{-1}$), υ (C-H) aromatic at ($3101\ cm^{-1}$), υ (O-H) at ($3332\ cm^{-1}$),υ (C-O) at ($1110\ cm^{-1}$) and ($702 cm^{-1}$) due to υ (C-Br) .

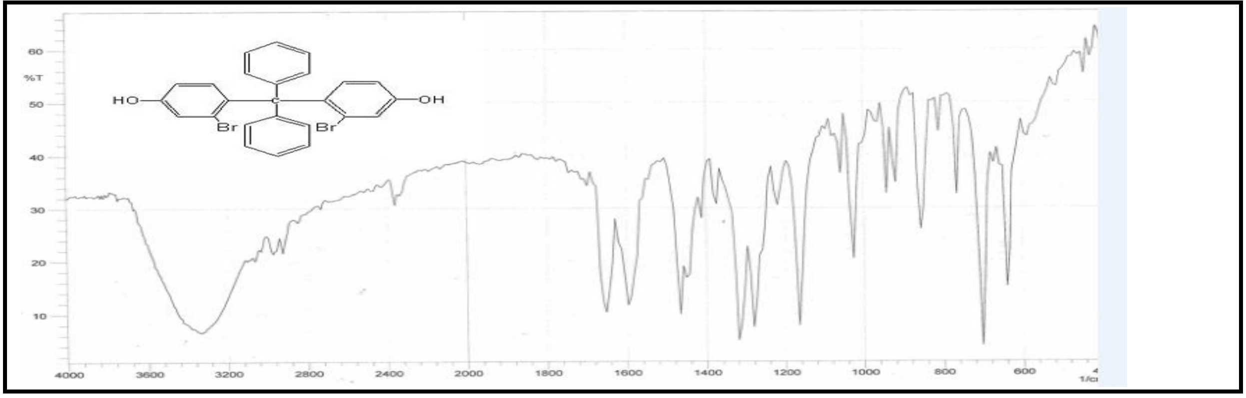
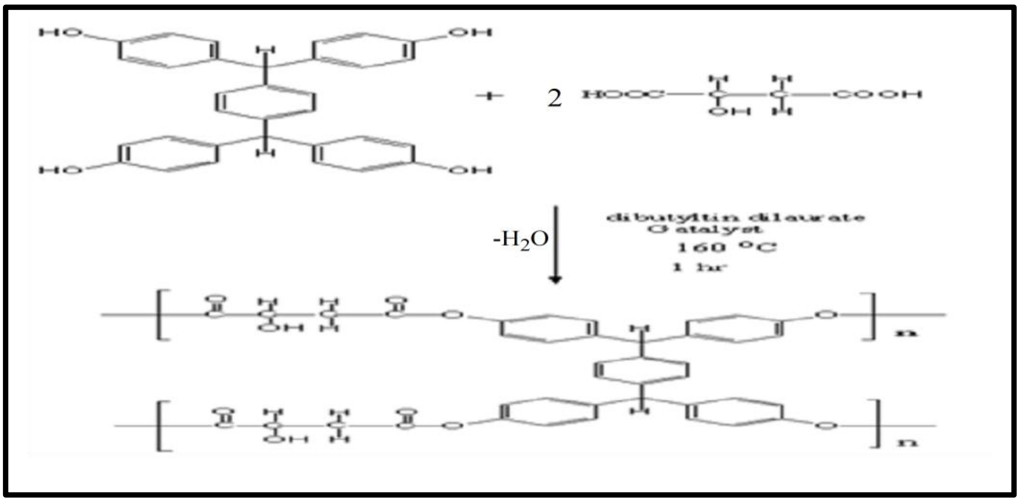


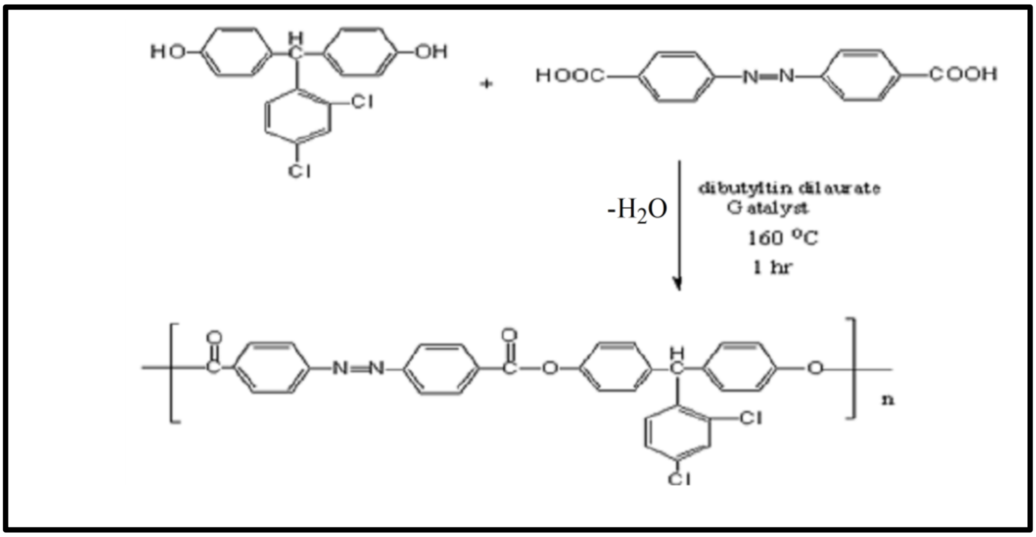
Figure 12- FTIR spectrum of (M3).

Synthesis of polyester (PE1- PE4)

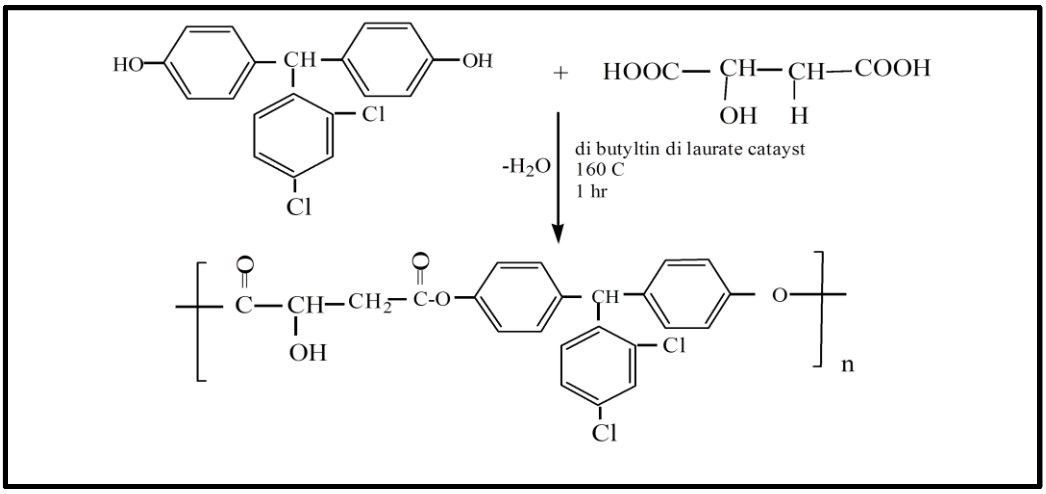
In this section polycondensation method was used for synthesis of a series of new polyesters from the direct polycondensation reaction of malic acid with new different aromatic di hydroxy monomers[M1, M2], respectively, and reaction of $4,4^{\backslash}$ azo di benzoic acid with aromatic di hydroxy monomer [M2] , and reaction of adipic acid with new aromatic di hydroxy monomer [M3] by using the di butyltin dilaurate as catalyst (0.15 wt.(%)). These polymers have a soft segment such as methylene unit in main chain for improving solubility in organic solvents. These polyesters were characterized by FT-IR and^{1}H-NMR spectra.



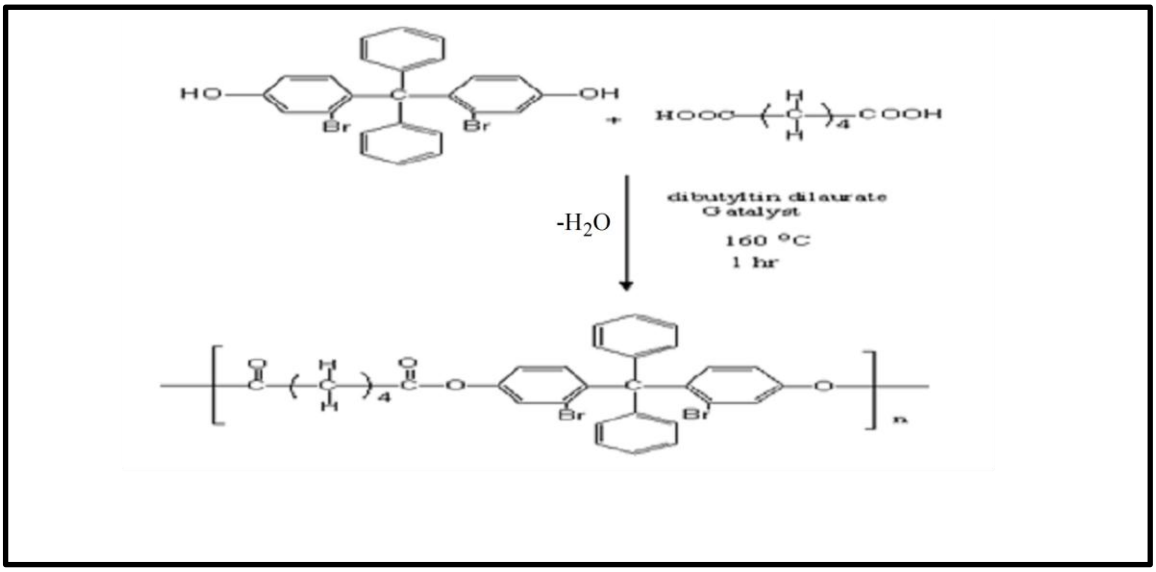
Scheme 5- synthesis of PE1.



Scheme 6- synthesis of PE2.



Scheme 7- synthesis of PE3.



Scheme 8- synthesis of PE4.

Synthesis and Characterization of polyesters (PE1-PE4)

FT-IR spectrum of PE1

The FT-IR spectrum of (PE1) as shown in Figure-13 showed absorption bands at (3425cm^{-1}) due to υ (O-H) , (2962 cm^{-1}) to (aliphatic- CH str.), (3062 cm^{-1}) due to (aromatic CH str.), (1720 cm^{-1}) due to (C=O str. ester) ,and (1596cm^{-1}) due to υ(C=C) aromatic .

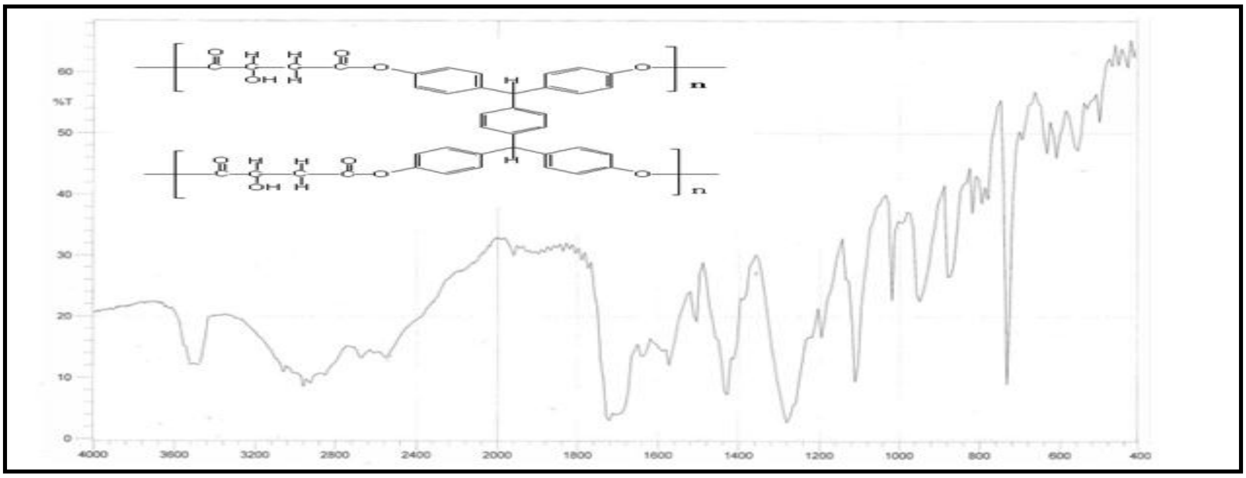


Figure 13- FTIR spectrum of PE1.

^{1}H-NMR spectrum of (PE1), is shown in Figure-14 assigns the following chemical shifts; δ (2.461) ppm for DMSO, δ (2.169) ppm (2H) for CH$_2$, δ (6.227-7.346) ppm (20H) for Ar-H group, δ (3.853)ppm (1H) for group (3) , δ (4.474) ppm for (CH).

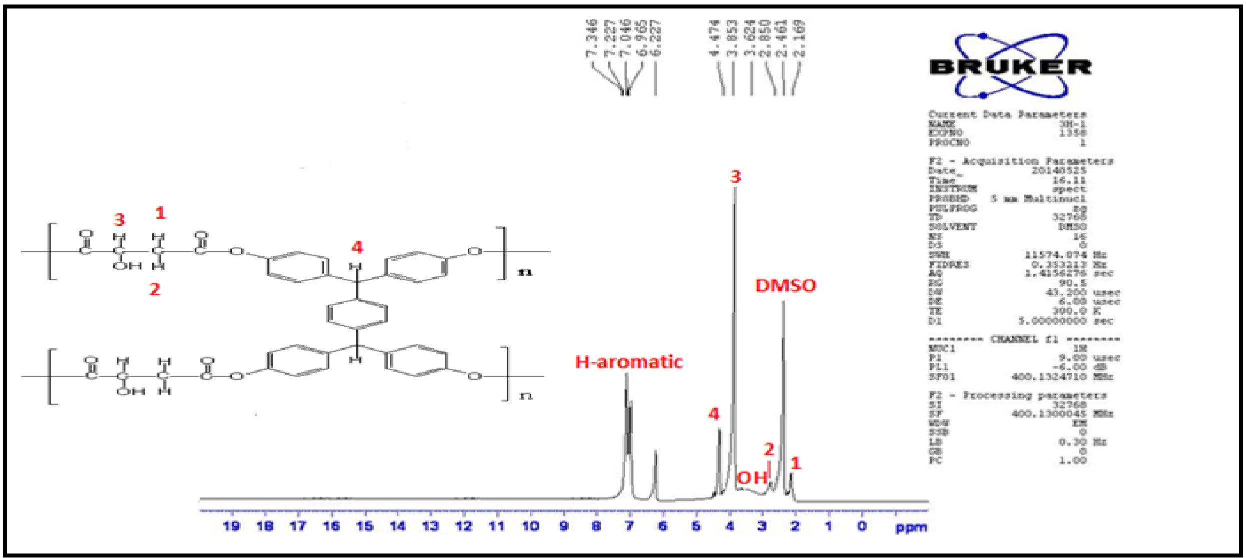


Figure 14- ^{1}HNMR spectrum of PE1.

FT-IR spectrum of PE2

The FT-IR spectrum of (PE2) as shown in Figure-15 indicates absorption bands at (2962 cm^{-1}) due to (aliphatic- CH str.), (3109cm^{-1}) due to (aromatic CH str.) ,(1728 cm^{-1})due to (C=O str.) , (1627cm^{-1}) due to υ(C=C) aromatic,(918 cm^{-1}) due to υ(C-Cl) ,(1311 cm^{-1}) due to υ (C-N) and at (1500cm^{-1}) due to υ(N=N).

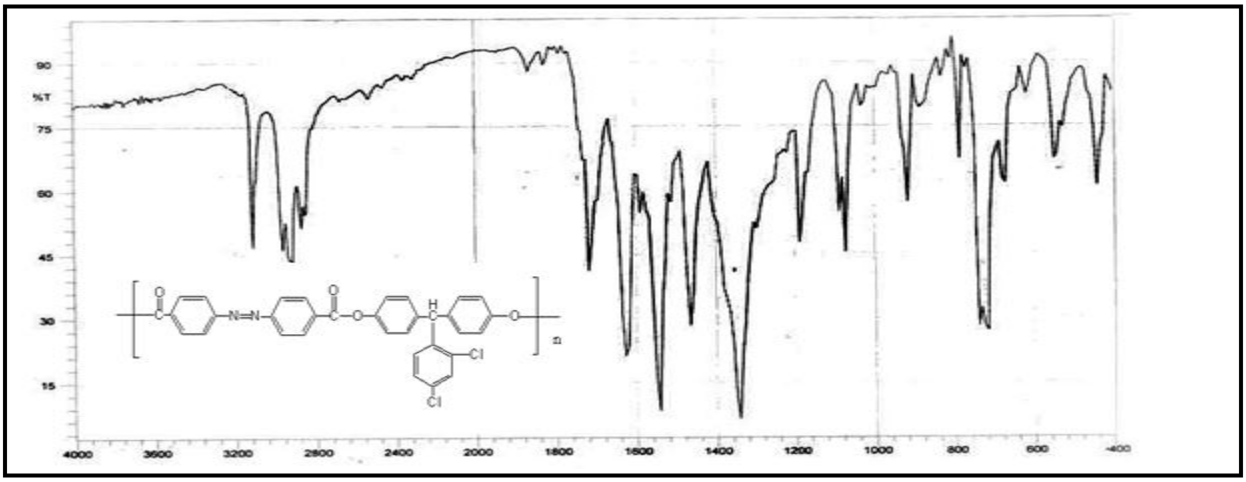


Figure 15- FTIR spectrum of PE2.

^{1}H-NMR spectrum of (PE2), is shown in Figure16- assigns the following chemical shifts; δ (2.461) ppm for DMSO, δ (0.9-1.4) ppm (1H) for CH, δ (7.2-8.2) ppm (19H) for Ar-H group.

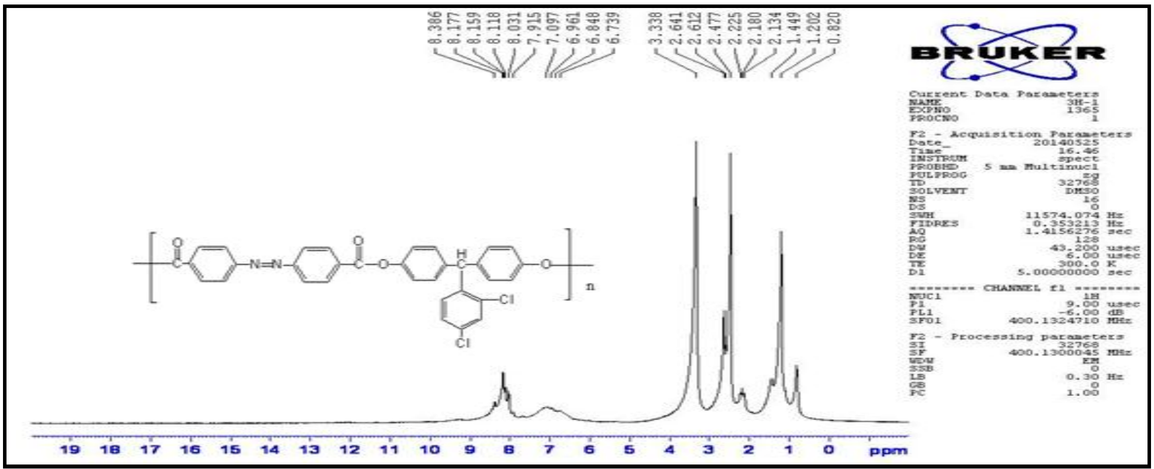


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Figure 16- ^{1}HNMR spectrum of PE2

FT-IR spectrum of PE3

The FT-IR spectrum of (PE3) as shown in Figure-17 indicates absorption bands at (3494cm^{-1})due to υ (OH) , (2923 cm^{-1})due to (aliphatic- CH str.), (3101 cm^{-1})due to (aromatic CH str.) , (1712 cm^{-1})due to (C=O str., ester), (1596cm^{-1}) due to υ (C=C) aromatic , and (918 cm^{-1})due to υ (C-Cl).

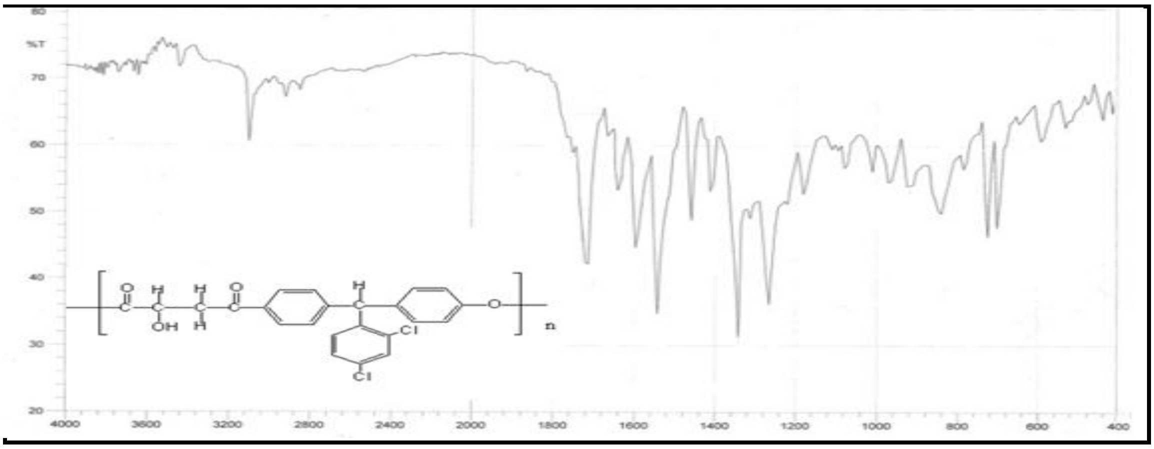

Figure 17- FTIR spectrum of PE3.

^{1}H-NMR spectrum of (PE3), is shown in Figure-18 assigns the following chemical shifts; δ (2.613) ppm for DMSO, δ (2.35 1 -2.481) ppm due to (CH_2), δ (3)ppm to group(3) δ (8.023-8.874) ppm (11H) for Ar-H group, δ (3.853)ppm (1H) for group (3) , δ (4.624) ppm (1H) for (CH) , δ (9)ppm (1H) for (OH) proton.

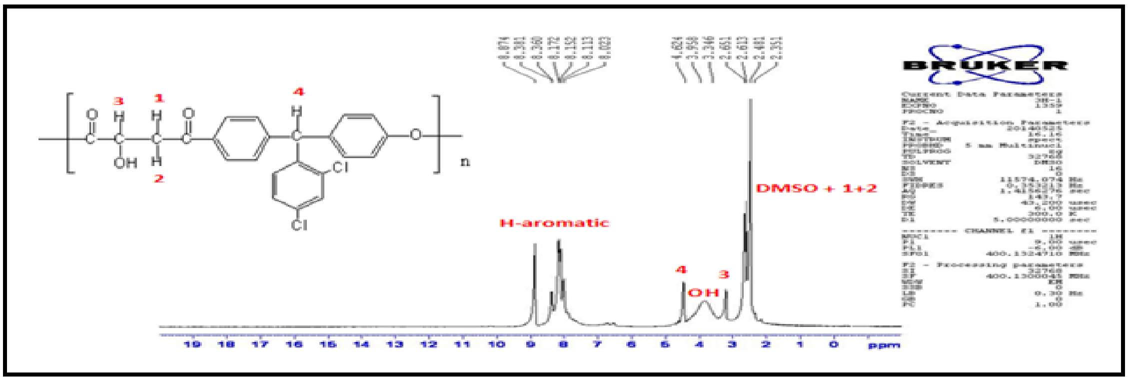

Figure 18- ^{1}HNMR spectrum of PE3.

FT-IR spectrum of PE4

The FT-IR spectrum of (PE4) as shown in Figure-19 indicates absorption bands at (3193cm^{-1}) due to (CH-Ar str.) , (2923 cm^{-1}) due to (aliphatic- CH str.),(1743cm^{-1}) due to (C=O str. ester) , (1596 cm^{-1})due to υ(C=C) aromatic, and (702cm^{-1})due to υ(C-Br).

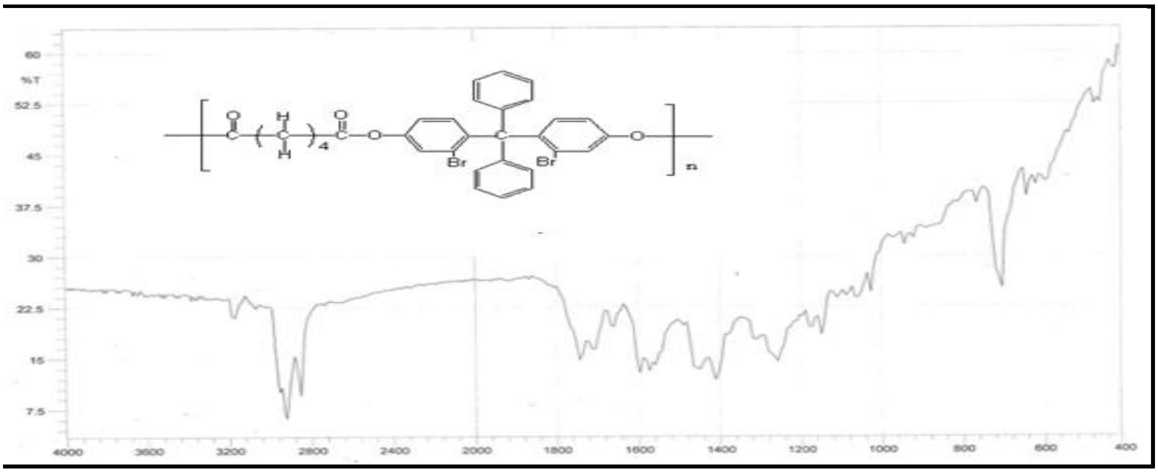

Figure 19- FTIR spectrum of PE4.

^{1}H-NMR spectrum of (PE4), is shown in Figure-20 assigns the following chemical shifts; δ (2.479) ppm for DMSO, δ (3.319) ppm belong to 4(CH_2) protons, δ (6.624-7.729)ppm for aromatic protons .

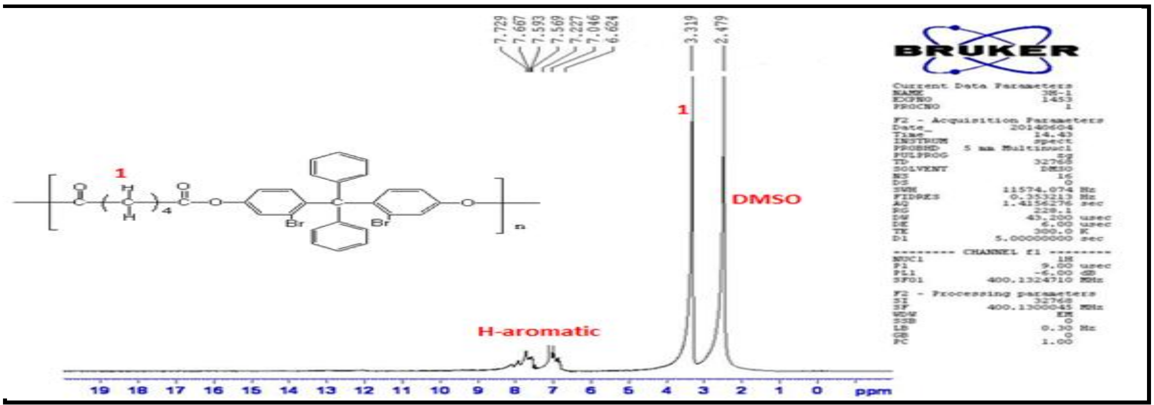

Figure 20- ^{1}HNMR spectrum of PE4.

Solubility of polyesters

Solubility of polyesters PE1-PE4 was qualitatively tested in organic solvents and the results are summarized in Table-2. The method that attempt to enhance their process abilities and solubility 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 [16] .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 a solvent .All of the newly synthesized polyesters have good solubility in common polar and dipolar aprotic solvents without need for heating.

Table 2- solubility of polyesters.

Solvents	**Polyesters**			
	PE1	**PE2**	**PE3**	**PE4**
pyridine	+ -	+ +	+ -	+ +
$CHCl_3$	+ -	+ +	+ +	+ +
CH_2Cl_2	+ +	+ +	+ -	+ -
NaOH	+ -	+ -	+ +	+ +
H_2SO_4	+ -	+ + +	+ + +	+ -
HNO_3	+ +	+ -	+ +	+ +
Acetone	+ -	+ -	+ + +	+ +
Benzene	+ +	+ +	+ +	+ +
DMF	+ +	+-	++	++
DMSO	+ + +	+ +	+ -	+ +
THF	+ +	+ -	+ -	+ + +

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

Thermal analysis of polyesters

Thermo gravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight changes that occurs as a specimen is heated. The measurement is normally carried out in atmosphere, such as Helium or Argon, and the weight is recorded as function of increasing temperature. Sometimes, the measurement is performed in an oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan [17] . 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 and the results such as T_i , T_{op} , T_f , $T_{50\%}$, % residue at 800 ^oC , and char yields at 500°C are summarized in Table- 3 .The temperatures of 50% weight loss of (P.E1-P.E4) as a standard indication for thermal stability of polymers were all from 761 to 800°C, The char yields of **(PE1-PE4)** at 500°C are 73% until 81% in Argon atmosphere , which indicate they could meet high temperature resistant requirements as some special materials in modern aerospace . Weight residue of **(PE1-PE4)** at 800°C is the highest than aromatic polyester of this series (50% - 55%).

Table 3- Thermal behavior data of aromatic polyester.

Aromatic polyester	**DT/°C**				**$T_{50\%}$**	**Residue at °C800**	**Char % *at* *500°C***
	T_i	**T_{op1}**	**T_{op2}**	**T_f**			
PE1	311	429	620	800 >	761	50%	81%
PE2	200	380	450	800 >	800	52%	70%%
PE3	318	400	550	800 >	799	55%	73%
PE4	400	600		800 >	766	55%	74%

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.*

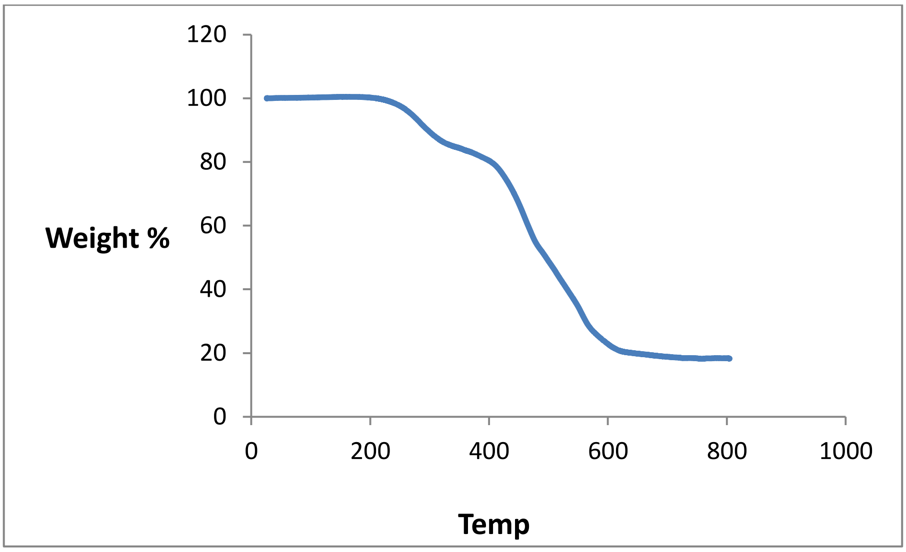

Figure 21- TGA curve of PE1.

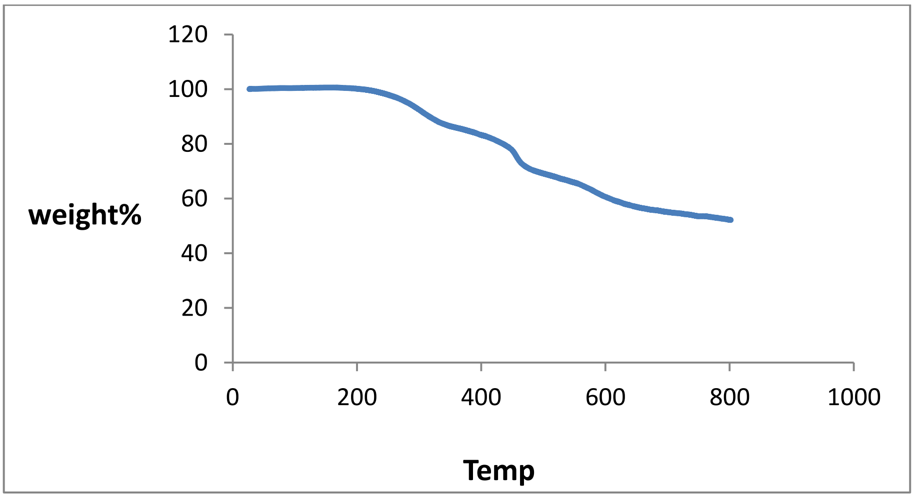

Figure 22- TGA curve of PE2.

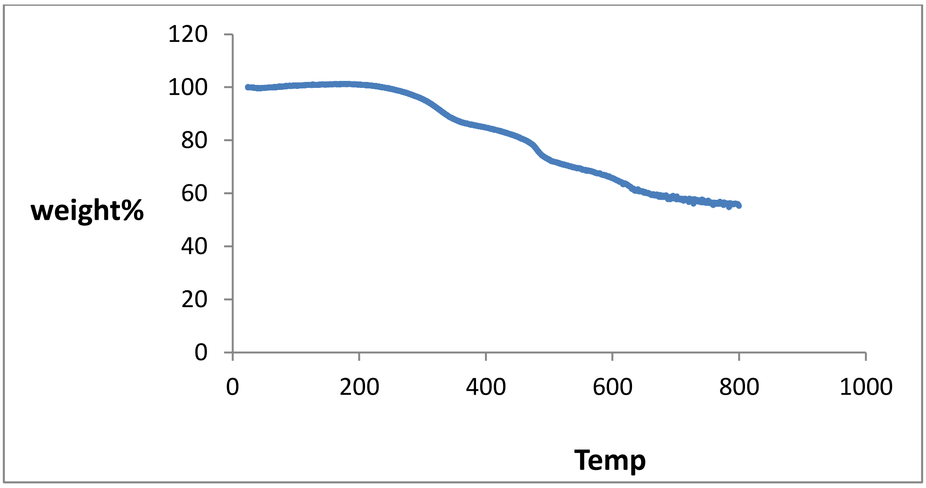

Figure 23- TGA curve of PE3.

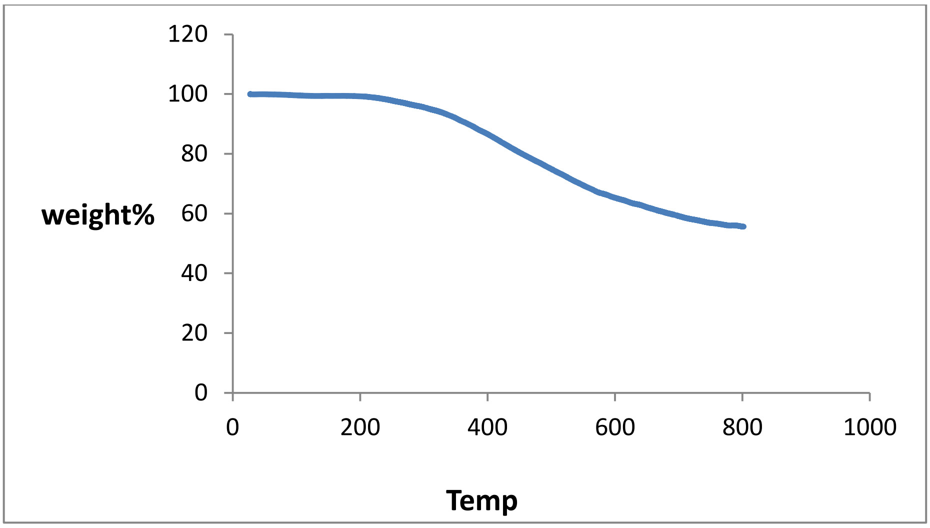

Figure 24- TGA curve of PE4.

Conclusions

In this research, direct polycondensation was carried out by the reaction of dicarboxylic acid monomers with several aromatic diols to prepare new aromatic polyesters in the presence of the dibutyltin dilaurate as catalyst. Introducing of aliphatic methylene linkage, and azo group to aromatic polyesters, polymers with substantially increased solubility and good thermal stability were obtained. The resulting polyesters can be used for film forming and coating materials.

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