

Synthesis, Studying The Thermal Properties Of Some New Monomers And Polymers By Ring Opening

Tamador Ali Mahmood^a , Selvana Adwar Yousif^a , Farah Saadoon Jaafar^{*b} , Iftikhar Ahmad Hussein ^c and Iman Mahdi Mohammed Hasan^a

^aDepartment of Chemistry, College of Science for Women, University of Baghdad, Iraq.

^bIbn Sina University of Medical and Pharmaceutical Sciences, Iraq, Baghdad.

^cDepartment of Chemistry, College of Science, University of Baghdad, Iraq.

Email fsjakam@gmail.com

Abstract: A new series of monomers starting from (4,4'-biphenyl diamine) derivatives have been synthesized, then all monomers which have opened oxazirine ring are then polymerized by steps of polymerization. Derivatives formed were more comparable effective than the reference standard polymer induced writing test. All proposed structures were supported by FTIR, and some derivatives evaluated by ¹H-NMR, Elemental analysis, Solubility, Softening point, Thermal analysis (TGA, DSC), X-Ray diffraction.

Keywords: Polymerization, Methylol derivatives, Oxazirine ring opening, Heterocycles, Biphenyl diamine derivatives.

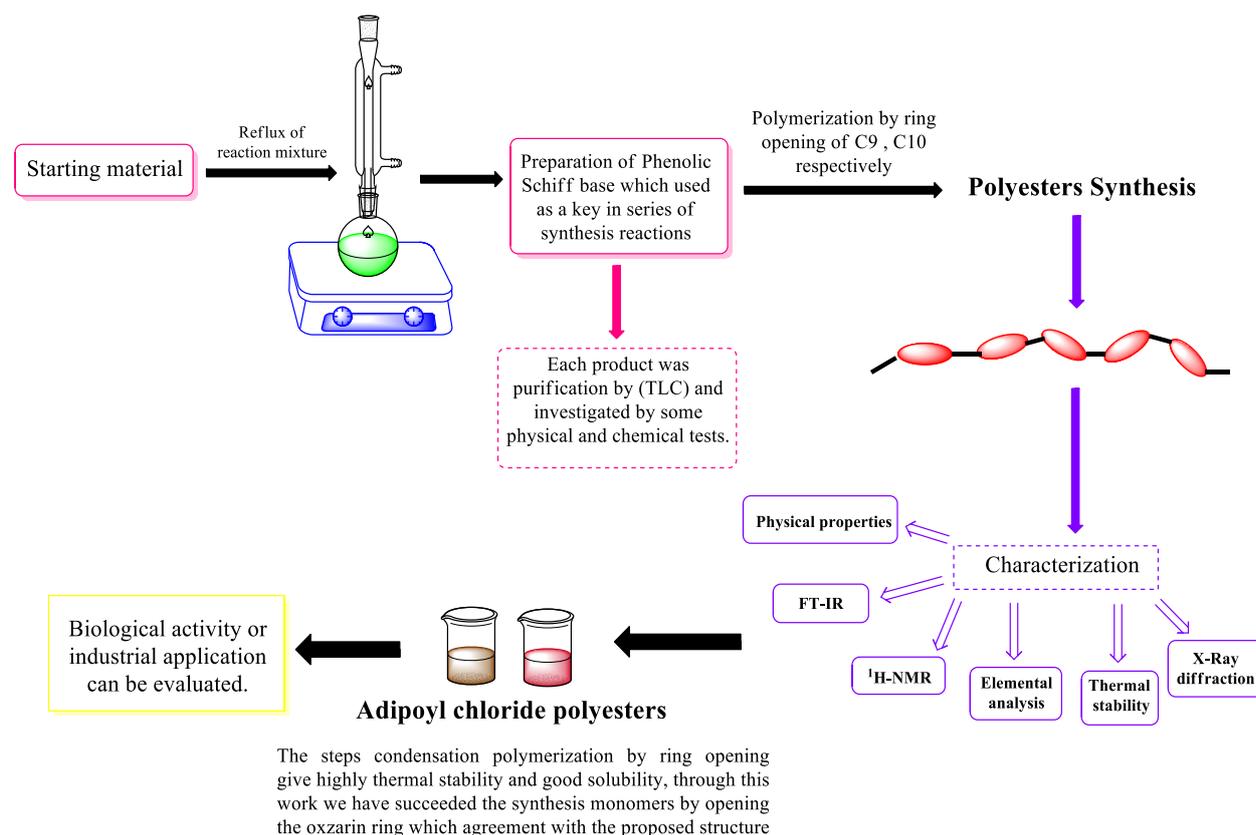


Fig. 1 : Graphical abstract show the summary of preparation steps for adipoyl chloride polyesters

1. INTRODUCTION

Schiff bases are well-known inter-mediates for synthesizing various heterocyclic compounds and have been reported to possess various applications. Schiff bases are the compounds which containing azomehine groups (HC=N). They were first reported by Hugo Schiff in 1864, then Schiff bases are some of the most widely used organic compounds which have also been shown to exhibit abroad of industrial applications including biological activity [1-5] and new series of phenolic Schiff bases (methylolic, etheric, epoxy) used as a rubber accelerators[6], antioxidant[7]. In analytical chemistry phenolic derivatives were used for uptake of metal ions [8], corrosion inhibitor[8,9].

They have wide industrial applications as photostabilizers for polyethylene. and the phenolic resins of in this study a number of methylolic, etheric and epoxy Schiff bases were prepared from the condensation reaction of aromatic aldehydes with [4,4'-biphenyl diamine], then rings opening as a monomers and reacts with adipoylchlorid by steps condensation of the polyester prepared[10-15].

2. MATERIALS AND METHOD

2.1. Materials:

The employed chemicals were to fit with (Fluka, BDH, and Merk). The solvents were purified by distillation and dried with CaCl_2 , and the products purity was investigated by (TLC) technique using an iodine chamber for spot location and with a mixture of ethanol with benzene (5:5 v/v) as elute.5.

2.2. Methods:

All spectra of FTIR were recorded by FTIR-Spectrometer model: (SHIMADZU-8300) using KBR-disc, while the $^1\text{H-NMR}$, spectra were scanning at 200.13-50.32 MHz, using the internal standard of Tetramethyl Silane (TMS) and the solvent of Dimethyl sulfoxide (DMSO).

Melting points were determined on Gallen Kamp apparatus. The device model (Perkin-Elmer RE 2400) was utilized as elements analyzer of (C/H/N/S), Thermal stability (TGA, DSC) and X-Ray diffraction analyses were performed in IRAN, Tehran (Ferdowsi University of Mashhad).

2.3. Techniques of thermal analysis (TGA & DSC):

(TGA) Thermal gravimetric analysis and (DSC) Differential Scanning Calorimetry were carried out using (DSC) LINSEIS with an internal cooler 2P-cooling accessory were performed in the department of engineering chemistry in Ferdowsi University of Mashhad, Tehran/Iran. The programmed heating rate of $20^\circ\text{C}/\text{min}$ from $(25-1000)^\circ\text{C}$ under inter-atmosphere (N_2 gas). Therefore that heat lost or absorbed were recorded (Table 6).

2.4. Softening point instruments:

Softening point recorded by/ REICHERI THERMOVER/ OREICHERT-Jung in the department of chemistry, college of science, University of Baghdad, Iraq.

2.5. Pattern X-Ray diffraction:

Patterns recorded by diffractometer SIEMENS (SRS D500) , ($\lambda=1.54 \text{ \AA}$) and scan rate equal to $(4.0/\text{min})$, over the range of $(1-60) (2\theta)$ by equipped with copper using for detection the distinctive diffraction peaks of the pure polymers which synthesized. The analysis of X-ray was carried out in Engineering Chemistry department, (Ferdowsi University of Mashhad), Tehran, Iran.

3. EXPERIMENTAL:

3.1. Phenolic Schiff base (1) synthesis:

Compound (1) synthesized by producer in literature [10] (4.9 gm, 0.02 mol) [4,4'-biphenyl diamine] with (4.9 gm,0.04 mol) (4-hydroxy benzaldehyde) using (TLC) to investigated the red solid product with (m.p $212-214$) $^\circ\text{C}$.

3.2. Methylolic phenolic Schiff base resin (2) synthesis: [17]

In 250 ml (0.02 mol) of compound (1) and (1.5 ml) solution (41-37)% formaldehyde in (50 ml) (THF), then mixed gently with (10%) ethanolic (NaOH) , added gently and a portion of keep (pH) of mixture reaction in oil bath, heated mixture in oil bath (50-60)°C for (3 hrs), mixture cooled (5-10) °C, neutralized using solution from alcohol (10%) phosphoric acid, then extract the organic layer and dissolved it using tetrahydrofuran to purified then filtered to elimination the salt and the solution of product was dried by molecular sieves and solvent evaporated by rotary evaporator , the final product was dehydrated by vacuum oven at (40°C/24 hrs).

3.3. Etheric phenolic Schiff base (3-5) synthesis: [18,19]

(0.08 mol) of appropriate alcohol (CH₃OH, C₂H₇OH, C₄H₉OH), respectively, with (1ml) concentration H₂SO₄ in groats ice (0-2)°C, (0.4 mol) compound (2) which added gently (1hrs), Refluxing with increased the temperature gradually until reach to boiling of alcohol, preserved the mixture in boiling alcohol for 24 hrs., then we neutralized the pH of the mixture with base (cooled NaOH).The oily product formed and was extracted by chloroform (CHCl₃), evaporated under vacuum, purified with TLC technique.

3.4. Epoxy etheric schiff bases (6-8) synthesis: [20,21]

(0.01mol) of compounds (3-5), respectively, with (0.12 mol) eipychlorohydrine in ice water (0-5)°C for (15 min) with added gently (0.14 mol) alcoholic (NaOH) in two fractions at stable temperature of about (60-65)°C with continuous stirring for (2 hrs.) , in the case of addition of first fraction the aqueous layer was separated from organic layer, and after this added second fraction, of alcoholic (NaOH) and stirred with mixture for (1hr.).Left mixture at the same temperature for (50 min.) again the aqueous layer was separated, organic layer dried, excess of eipychlorohydrin with solvent evaporated under reduced pressure, and the products purification by (TLC).

3.5. Schiff bases with opening ring (9-11) synthesis: [22]

A mixture from (30 ml) cold methanol in (1-2)°C with (0.01 mol) of compounds (6-8) and (0.015mol) morpholin in oil bath (80-100)°C for refluxing (72 hrs.), cooling mixture and solvent evaporated and purification by (TLC).

3.6. Polyesters Synthesis (12,13): [23]

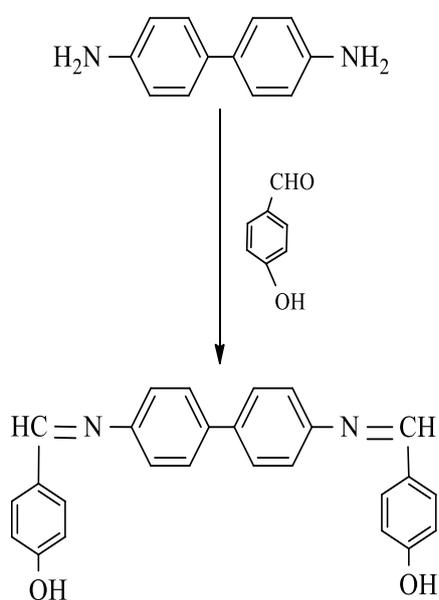
Firstly prepared acid chloride [22] adding slowly (10ml) of thionyl chloride to (0.03 mol,5gm) adipic acid to (3-5) drops of [DMF], the mixture refluxed at (79)°C for (1.5 hrs.) to formed adipoyl chloride polyester (12 and 13) were prepared by polymerization steps of a mixture of (0.08 mol) of monemers (9-10) which dissolved in dry pyridine, in ice water bath with (1-3) drops of [DMF] and (0.08mol) of adipoyl chloride, mixture stirring for (6 hrs.) [Checked by TLC], Refluxed (1hr) in (79-

80)°C, the product was poured into ice distilled water which acidified with (HCl), filtered, dried precipitate. All steps were explained in scheme (1-6), physical properties, FT-IR, ¹H-NMR, (C.H.N.S) analysis, and thermal stability (TGA,DSC), X-Ray diffraction. All those listed in tables (1-6).

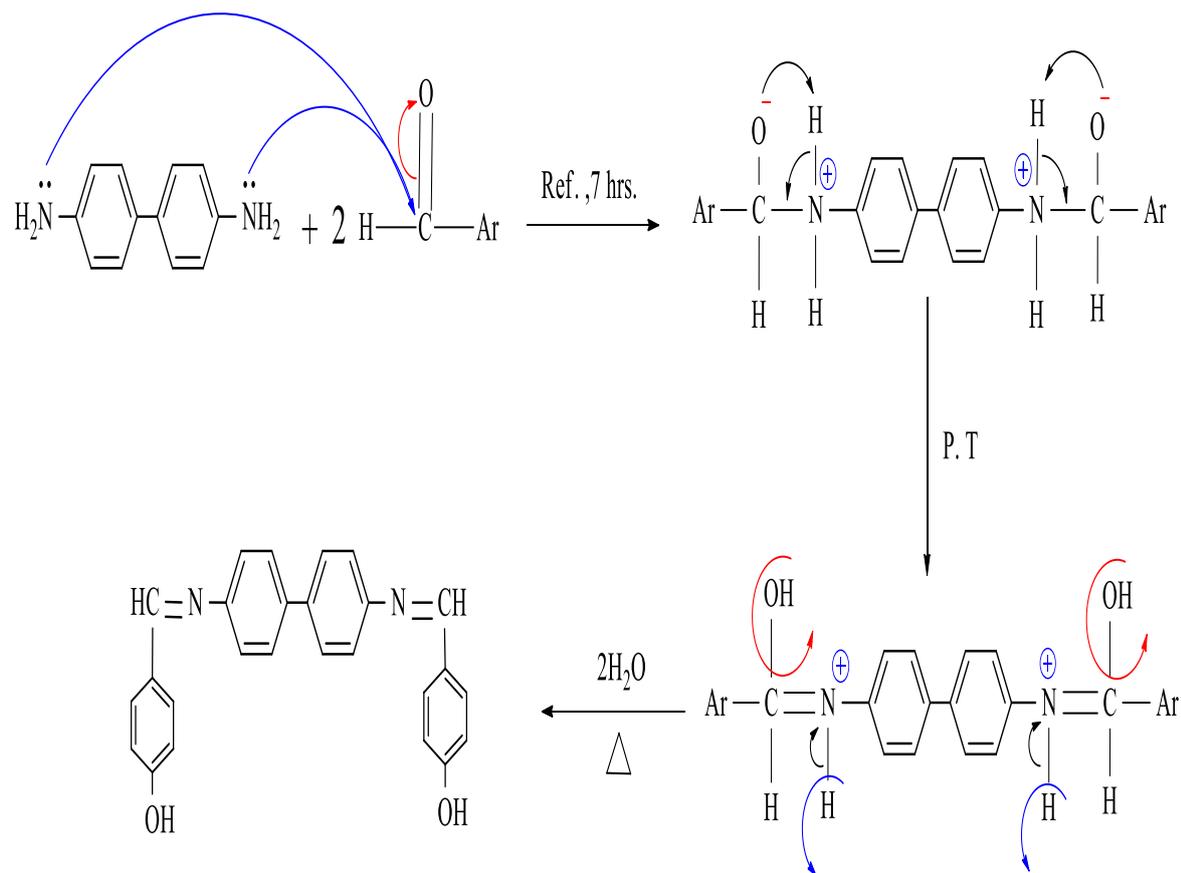
4. RESULTS AND DISCUSSION

4.1. Synthesis

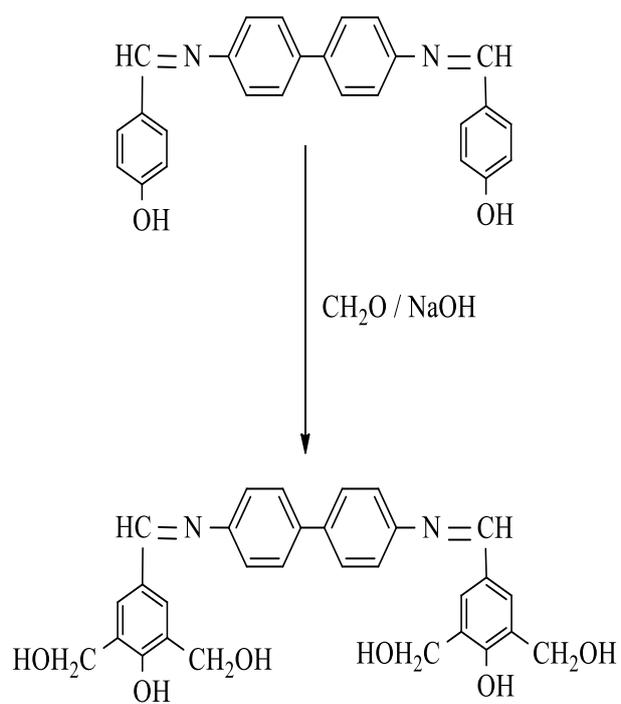
To prepare Schiff base (1), the condensation process was performed between (4-hydroxybenzaldehyde) and (4,4'-biphenyl diamine) refluxing in ethanol, as in scheme 1, then compound (1) refluxing with formaldehyde afforded methylolic compound (2) which included hydroxyl methylene group (-CH₂OH) and its very reactive functional groups, which shown in scheme 2.



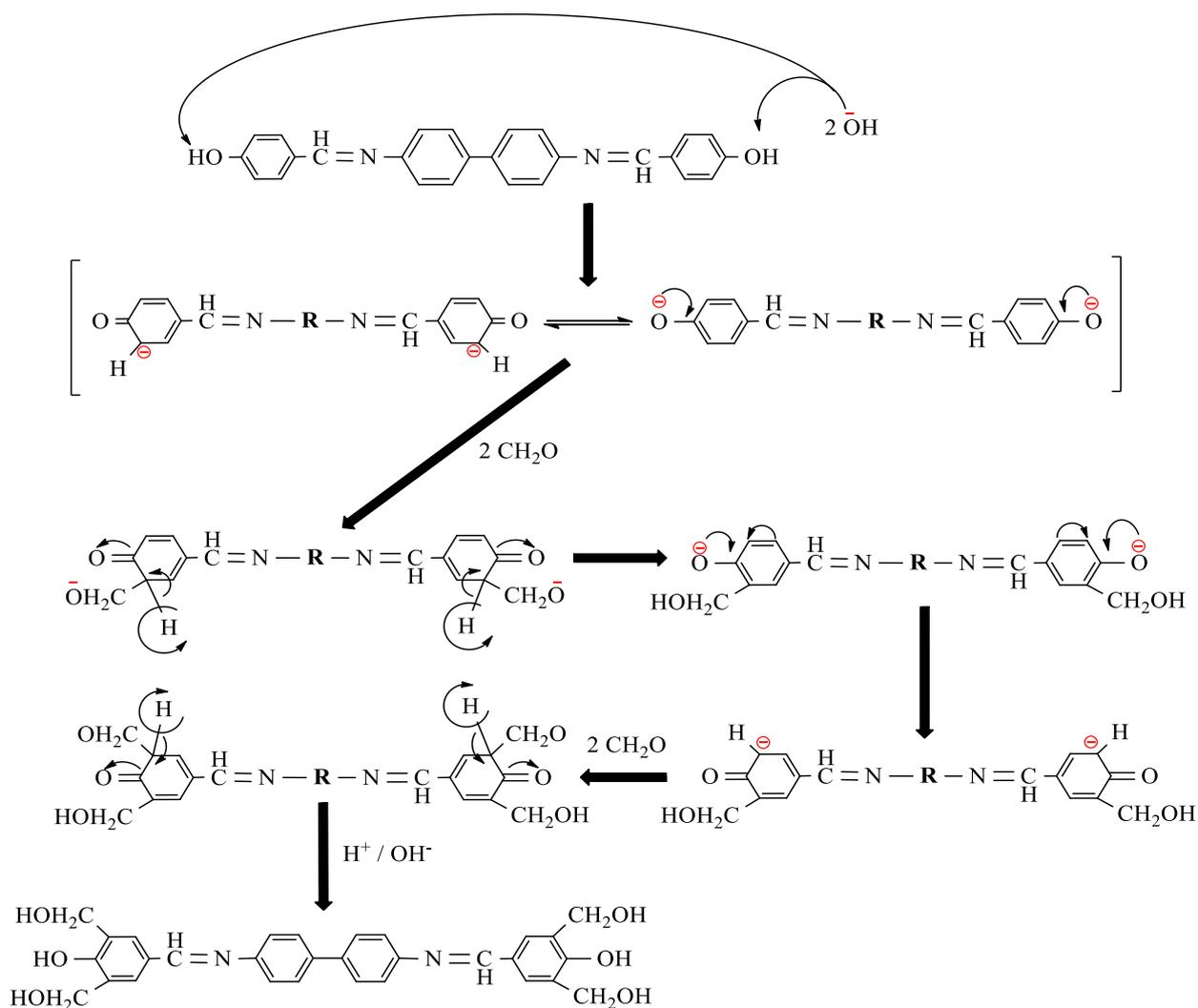
Scheme 1a. Reaction of preparation of compound (1)



Scheme 1b. Pathway of preparation of compound (1).



Scheme 2a. Reaction of preparation of compound (2)



Scheme 2b. Pathway of preparation of compound (2).

Compound (2) (FTIR) spectrum of methylolic groups bands at $(3444.87-3342.64) \text{ cm}^{-1}$ with stretching bands for (C=N) at $(1644.42) \text{ cm}^{-1}$, band for (C-O-C) at $(1232.51-1282.66) \text{ cm}^{-1}$, (Ar-H) $(3001.24) \text{ cm}^{-1}$, at $(2954-2896) \text{ cm}^{-1}$ for aliphatic (CH_2), $^1\text{H-NMR}$ for compound (2) show (DMSO- d_6) δ : $(1.06-2.90) \text{ ppm}$ for (t,2H,- CH_2), δ : $(7-8) \text{ ppm}$ return to (Ar-H) group and δ : $(10-11) \text{ ppm}$ for (H,OH), Then compound (2) react with alcohols (methanol, ethanol, Butanol) afforded compounds (3-5) shown in scheme 3.

FTIR spectrum of compound (3) which appears a strong vibration at the region $(1226-1168) \text{ cm}^{-1}$ that return to (C-O-C), also $(3026.31-3082.25) \text{ cm}^{-1}$ according to the group (Ar-H), and sharp bands due to stretching vibration of (CH_2) groups in the region $(2980-2975) \text{ cm}^{-1}$ for etheric band (C-O) at $(1296.16) \text{ cm}^{-1}$, From $^1\text{H-NMR}$ of compound (3) we noted (DMSO- d_6) δ : $(11.5) \text{ ppm}$ for (H,OH), δ : $(2-$

2.2) ppm for (3H, CH₃), δ :(13.5) ppm for (C-O-C), δ : (6.7-8.5) ppm due to (Ar-H), all were fitted according to the (Tables 3 and 4) , then the compounds (3-5) with eipychlorohydrine afforded (6-8) derivatives respectively, as shown as in scheme 4.

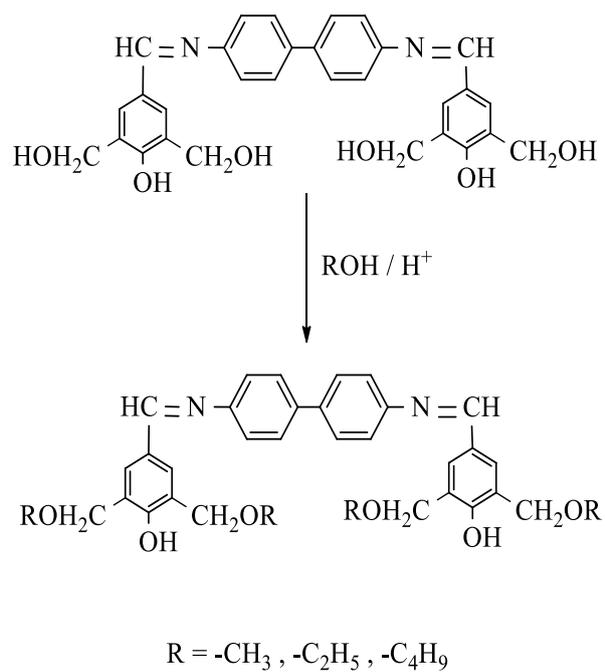
In compound (6) FTIR spectrum recorded a sharp band for oxarine ring which absorbed at (910-893.04) cm⁻¹, strong bands (2931-2873) cm⁻¹ due to methylene group (CH₂); also we observed the (C-O) bond in the range (1130-1090) cm⁻¹, ¹H-NMR (DMSO-d₆) δ : (1.9-2.1) ppm due to (3H, CH₃), δ : (6.9-7.5) ppm for (Ar-H); at δ : (9.5) ppm for (C-O-C), compounds (6) were fitted according to the (Table 3,4). Compounds (6-8) react with morpholine products (9-11) derivatives, respectively, scheme 5.

FT-IR of compound (10) was obtained the absorption for (OH) at (3462.29-3394.5) cm⁻¹, while the etheric group (C-O-C) appeared in the region (1268-1238) cm⁻¹, ¹H-NMR spectrum showed (DMSO-d₆) δ :(1.39-1.41) ppm for (2H,CH₂), δ (Ar-H) was (7-8) ppm while δ : (9.8,9.9,10.5,14) ppm due to (H,OH), the both spectra for compound (10) were fitted according to the (Tables 3 and 4), thionyl chloride was reacted with adipic acid to produce adipoylchlorid which react with compounds (9,10) as a monomers by steps polymerization to prepared poly esters (12,13) in scheme 6.

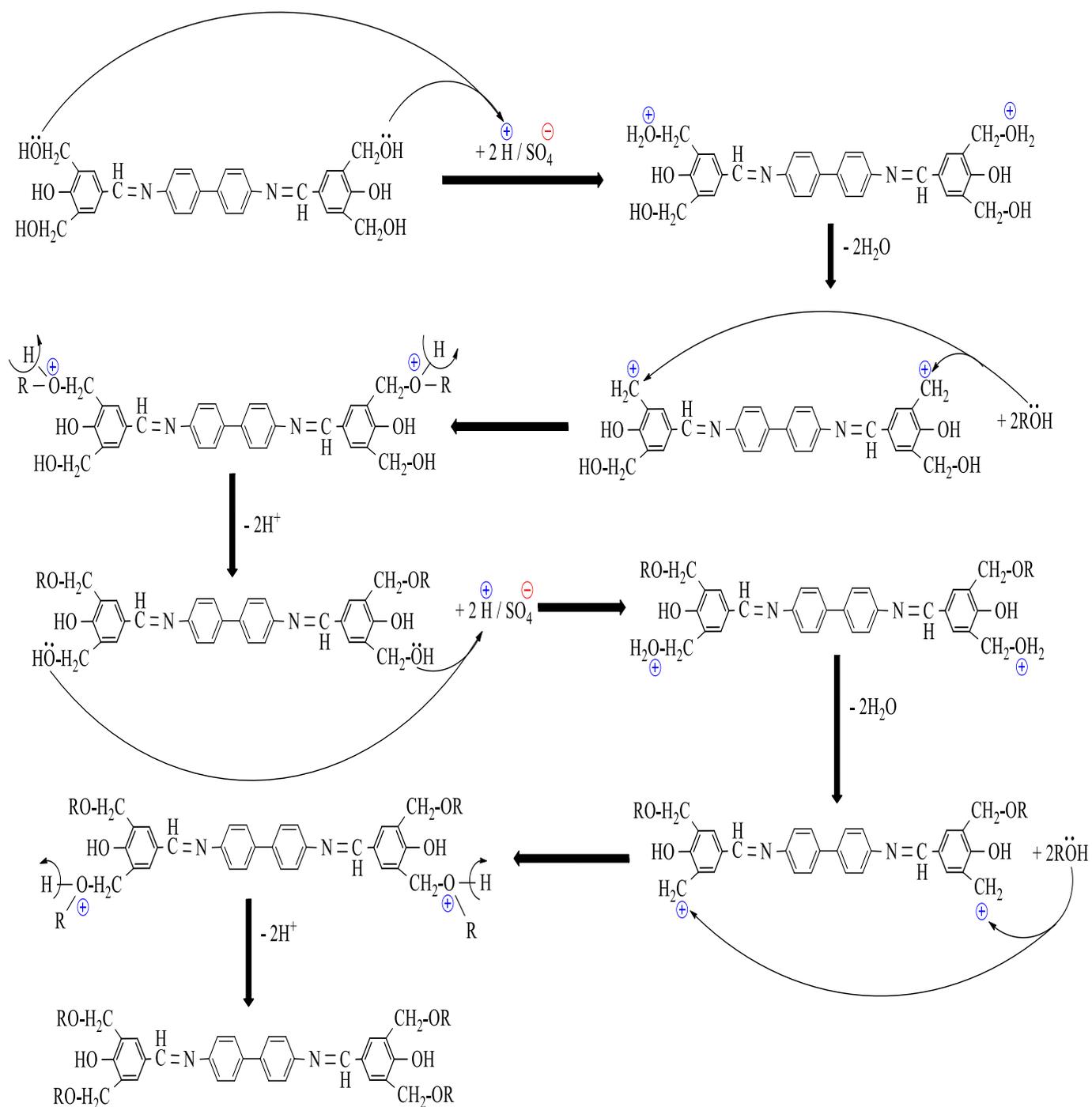
The FTIR spectrum of compound (12) obtained absorption (C=O) at (1720.50) cm⁻¹ and (C=N) at (1642.36)cm⁻¹,¹H-NMR (DMSO-d₆) δ : (7.2) ppm return to (Ar-H); (9.3) ppm refer to (C=O);(1.39-1.41) ppm for (2H,CH₂); the spectra for compounds (12) were fitted according to the (Tables 3 and 4).

FTIR spectra of compound (13) shows the stretching vibration of (C=O) at (1776.37) cm⁻¹ and (C=N) at (1635.64) cm⁻¹, ¹H-NMR appeared (DMSO-d₆) δ :(7-8) ppm indicate to (Ar-H); while δ : (9.8,10.3,12.5) ppm due to (C=O) and δ : (1.39-1.41) ppm for (2H,CH₂).Spectra of compounds (13) were fitted according to the (Tables 3 and 4).

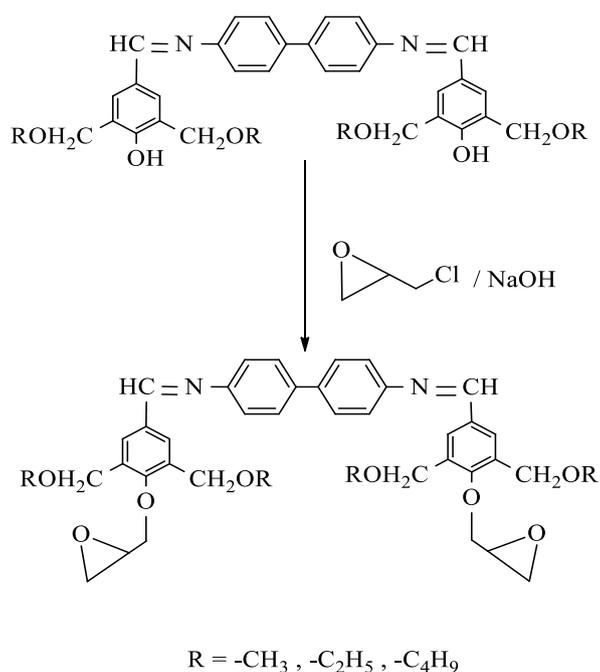
Curing thermal stability of some compounds were evaluated by using (TGA,DSC) in Table (6) which are clearly show the temperature rates belong to different types dissociated for derivatives,(C.H.N.S) analysis for compounds (12,13) as polyesters ¹H-NMR, physical properties, softening point and solubility data were consecutively included in (Tables 1-5).



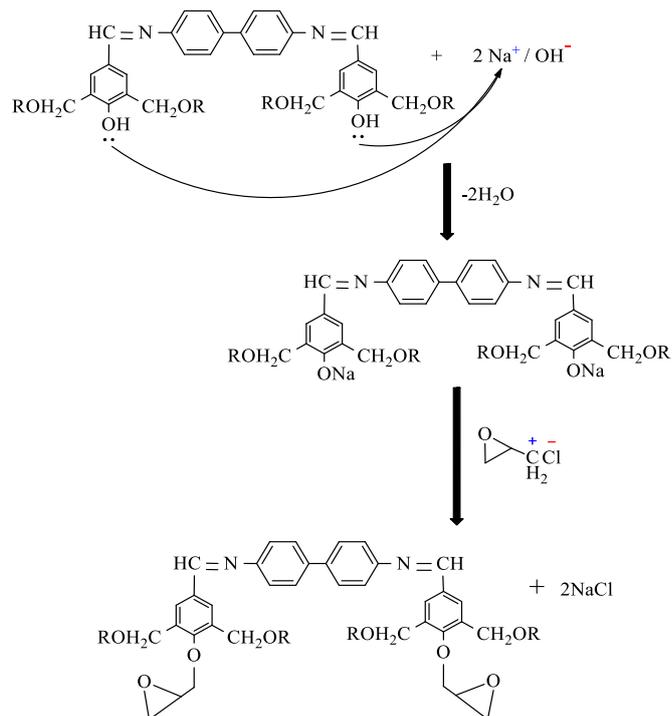
Scheme 3a. Reaction of preparation of compounds (3-5).



Scheme 3b. Pathways of preparation of compounds (3-5).

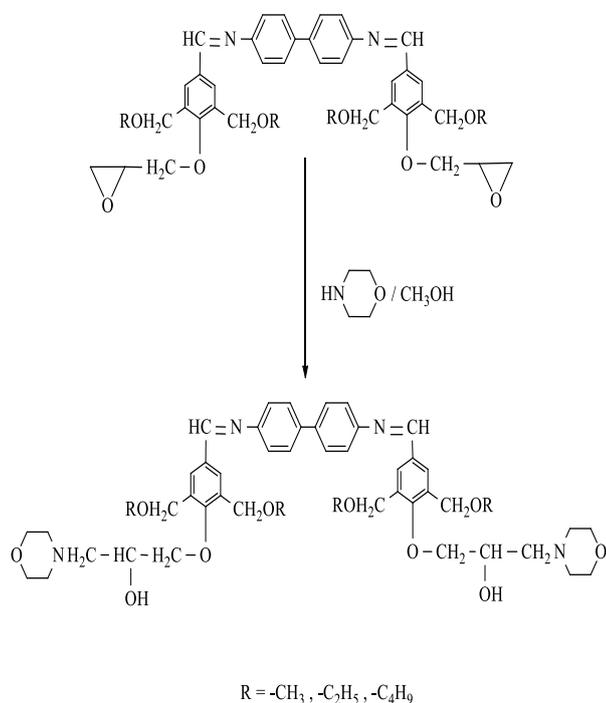


4. a

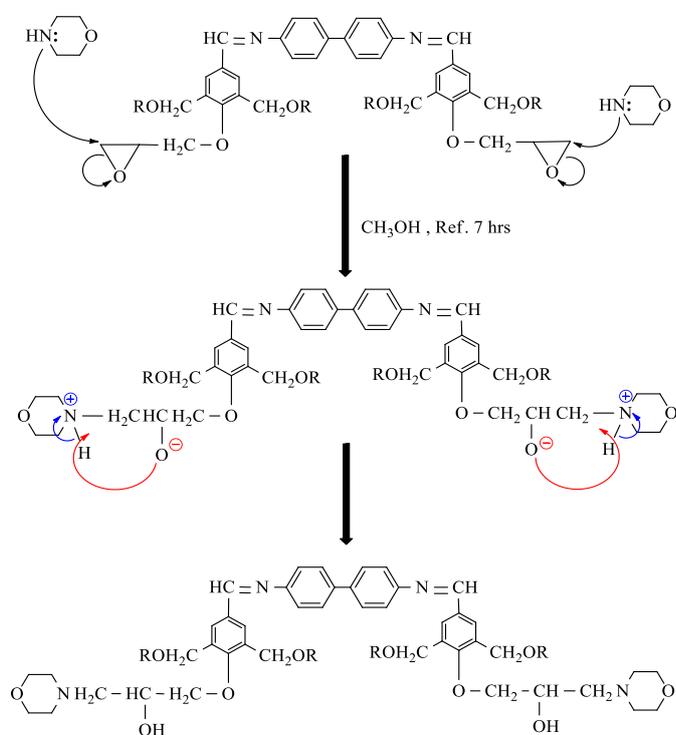


4. b

Scheme 4. a. Reaction of preparation of compounds (6-8), **b.** Pathways of preparation of compounds (6-8).

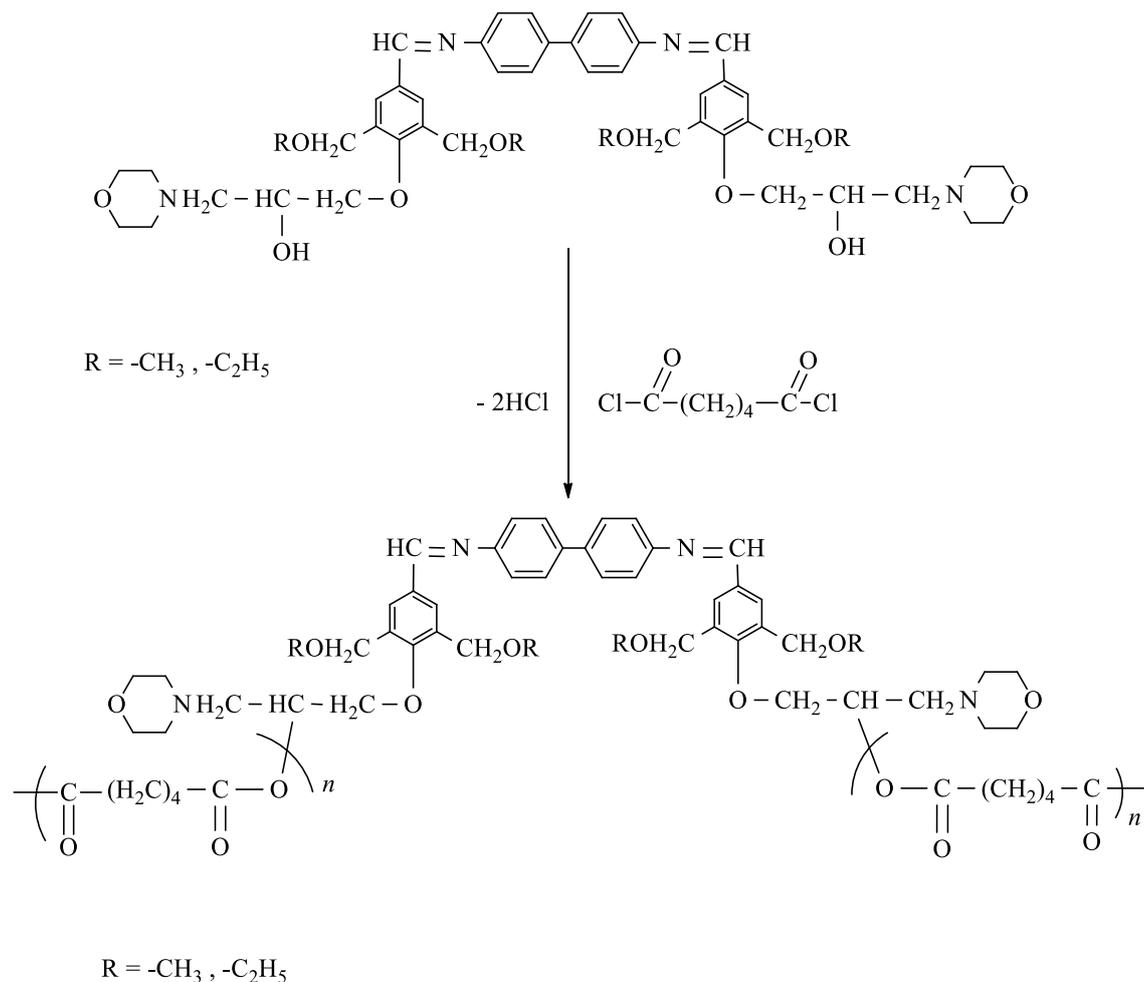


5. a



5. b

Scheme 5. a. Reaction of preparation of compounds (9-11), **b.** Pathways of preparation of compounds (9-11).



Scheme 6. Pathways of preparation of compounds (12 and 13).

Table 1 . Shows the physical properties of the synthesized compounds (1-13).

Comp. No	M.P. °C	Color	Yield%	Purification solvent	Comp. No	M.P. °C	Color	Yield%	Purification solvent
1	212-214	Red	90	Ethanol	7	Oily	Brown	60	THF
2	Oily	Deep Red	87	Ethanol	8	Oily	Brown	65	THF
3	Oily	Brown	80	THF	9	Oily	Brown	60	THF
4	Oily	Brown	75	THF	10	Oily	Brown	70	Methanol
5	Oily	Brown	75	THF	11	Oily	Brown	72	Methanol

6	Oily	Brown	65	THF	12,13	Oily, Oily	deep red, Brown	65,67	Methanol
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Table 2. (C/H/N) analysis for synthesized polymers

Comp. No	% Elemental analysis calculated (found)			Comp. No	% Elemental analysis calculated (found)		
	C	H	N		C	H	N
12	76.73 (72.73)	7.42 (9.10)	3.58 (4.69)	13	77.33 (78.39)	7.88 (8.90)	3.34 (4.69)

Table 3. FTIR spectral data of (1-13) in cm-1

Comp. No	vOH	vCH ₂	vC-O-C	vC-O	Others	Comp. No	vOH	vCH ₂	vC-O-C	vC-O	Others
1	3402 .45 3378 .94	2976.2 2	1205	1128.2 1	(Ar-H) = 1008.45 1034.54 (C=N) = 1600.54	7	3290 3155	2910 2875	1240 1210	1202 1120	 = 917-892
2	3444 .87 3342 .64	2910	1200	1123 1177	(Ar-H) = 3101.54 (C=N) = 1602 (C=C) = 1597	8	3100 3280	2935 2870	1235 1228	1213 1108	 = 914-944
3	3225 3265	2954 2896	1245 1227	1192 1199	(C=N)= 1612.49 (Ar-H) = 3026.31, 3082.25 (=CH) = 3080	9	3479 3437	2900 2865	1268 1238	1220 1225	(VC-N) = 1220
4	3200	2980	1226	1197	(C=N) = 1608	10	3437	2910	1250	1175	(VC-N) = 1238

	3245	2975	1268	1160	(=CH) = 3100		3479	2845	1255	1195	
5	3285	2985	1218	1176	(C=N) = 1615	11	3245.	2762	1298.1	1134	(C=N) = 1666.12
	3260	2980	1210	1779	(=CH) = 3009		78	.55	3	.11	
6	3257	2931	1201	1110	 = 910-893.04	12	3241.	2885			(C=N)=1642.36 (C=O)=1720.50 (C=N) = 1635.64 (C=O) = 1776.37
	3225	2873	1205	1045			61	.12	1233	1185	
							3202.	2910	1282	1153	
							01	.05	1254.4	1189	
							3245	2897	4	.78	
							3266.	.56	1223..	1200	
				67	2934	65					
					.56						

 Table 4. ¹H-NMR spectral data for some compounds in ppm

Comp. No	¹ H-NMR/ data	Comp. No	¹ H-NMR/ data	Comp. No	¹ H-NMR/ data
2	δ (Ar-H) = 7- 8 . δ (3H,CH ₂) = 8.5-6.2. δ (2H, CH ₂) = 1.42-2.81. δ (H,OH) = 10-11	3	δ (Ar-H) = 6.7-8.5 δ (3H,CH ₃) = 2-2.1 δ (H,OH) = 11.5 δ (H,C-O-C) =13.5	12	δ (Ar-H) = 7.2 δ (H,C-O-C) = 9.3 δ (2H,CH ₂) = 1.44-12.55
6	δ (Ar-H) = 6.9-7.8 δ (H,C-O-C) = 9.5 δ (t,2H,CH ₂)= 1.06-2.90	10	δ (Ar-H) = 7-8 δ (H,OH) = 9.8-9.9, 10.5 δ (2H,CH ₂) = 1.39-1.41 δ (NH) =14	13	δ (Ar-H) = 7-8 δ (H,C-O-C) = 9.8-10.3 δ (2H,CH ₂) = 1.9- 2

Table 5. Solubility and Softening points of monomers and polymers (9-13)

Comp. No	DMF	DMSO	Triethyl amine	CHCl ₃	THF	Cyclo hexane	m-Cresol	Softening points °C
9	++	++	+	-	-	-	-	203-213
10	++	++	+	-	-	-	-	232-245

11	++	++	+	-	-	-	-	251-263
12	++	++	+	-	-	-	-	>300
13	++	++	+	-	-	-	-	>300

* Where (++) = soluble at room temperature; (+) = soluble with heat; (-) = insoluble even with heating.

4.2. Thermal properties

(TGA) and (DSC) were used to investigate the thermal properties of all synthesized polymers. Thermal stability of the polymers was studied in the range (0-625)°C char yield and the results revealed that polyester derivatives from diacid chloride demonstrated higher thermal stability. All the information of thermal behavior of the prepared polymers are summarized in (Table 6) which they showed high glass transition temperature **T_g** of poly ester with aromatic rings have higher **T_g** values of these polymers leading to more cross-linking in the chain of the polymers relative to poly which increase the thermal stability.

Generally, **T_g** value decreased with decreasing stiffness of the diamine component which exhibited the highest **T_g** value (517)°C in the series of polymers because of the presence of two rigid in 1,4 location component leading to increased ester group linkage rigidity than polymers containing linkage unit. The polymers (12,13) revealed residual yields of nitrogen of more than (56.5)% at 600°C. The relation between the structures of the synthesized polymers and their thermal stability from the above results, the thermal stability order of the synthesized is : stability increase by increasing the molecular weight of poly ester for polymer 13> more stability of polymer 12 .

Table 6. Thermal behavior data for synthesized compounds

Comp. No	On set point °C	Off set point °C	T _g °C	%Char
6	273.7	288.7	281.1	4.4
7	298.2	310.2	304.1	1.2
10	100.0,112.5	108.5,124.5	101.7,115.0	2.9
11	44.9,269.7	64.1 ,295.0	47.7 ,272.7	52.75
12	51.9 ,106.7 ,321.1	78.9 ,123.9 ,328.9	58.4 ,112.8 ,325.5	56.50
13	53.5 ,131.5 ,323.2	72.3 ,142.7 ,334.2	54.6 ,133.3 ,318.3	70.56

- To set temperature recorded by (TGA) and (DSC).
- The midpoint temperature of baseline shift on the subsequent TGA and DSC trace (as heating rate 10°C / min) was defined as T_g.

- Residual weight percentage at 600°C under Nitrogen flow.

4.3. X-Ray diffraction analysis

Diffraction analysis investigated the structure including atomic arrangement, crystalline size and imperfections also from x-rays.

1. To be the point internal stress of small crystalline regions, shape, and size.
2. To be specified the orientation of a single crystal to grain.
3. Calculate the average spacing between a row of atoms and layers.
4. To search the crystal structure of unknown material.
5. Using to identify the nature of the polymer weathered amorphous or crystalline.

CONCLUSION

The steps condensation polymerization by ring opening give highly thermal stability and good solubility, through this work we have succeeded the synthesis monomers by opening the oxzarin ring which agreement with the proposed structure.

The hydroxyl substituent (as in phenolic Schiff base derivatives) are one of the key group to enhancing greatly the industrial application mainly and its easy conversion of phenoxy radical hydrogen atom to move mechanism, for that there are a number of divers phenolic Schiff bases have been prepared and evaluated for biological activity or industrial application.

CONSENT FOR PUBLICATION

Not applicable.

FUNDING

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CONFLICT OF INTEREST

No conflict of interest, financial or otherwise.

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Declared none.

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