



Research Article

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## Synthesis and characterization of poly [N-acryl-N-sulfonic acid-N<sup>1</sup>yl-2-substituted-4-oxo-thiazolidine] glutaric and phthalic diimide

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### ABSTRACT

In the present investigation, new polymers of Poly [ N - acryl - N - sulfonic acid - N<sup>1</sup>yl - 2 - substitute - 4 - oxo - thiazolidine ] Glutaric and Phthalic diimide were synthesized by seven steps; first step includes esterification of different cyclic anhydride, using one mole of absolute methanol in the presence few drops of conc. H<sub>2</sub>SO<sub>4</sub>, yielded mono group ester [I], which was reaction with thionyl chloride to give ester acid chloride [II]. Then reacted with sulfanilic acid to product compound [III], which was condensation with hydrazine hydrate to give acid hydrazide [IV]. The new different Schiff bases [V-VIII] were synthesized by reaction of acid hydrazide with different (aliphatic and aromatic) aldehydes and ketones in the presence of glacial acetic acid. Thiazolidine-4-one derivatives [IX-XII] have been obtained from the addition of 2-mercapto acetic acid to Schiff bases and the final step was added poly acryloyl chloride to product polymers [XIII-XVI]. Their chemical structures have been confirmed by melting points, FTIR, <sup>1</sup>HNMR and <sup>13</sup>C-NMR (some of them). All the synthesized polymers were characterized by FT-IR spectra, softening points and TGA,DTG (some of them).

**Keyword:** glutaric & phthalic anhydride, poly imide, amide, Thiazolidine.

### INTRODUCTION

There are numerous biologically active molecules with five membered rings, containing two hetero atoms. Thiazolidinone is an important scaffold known to be associated with several biological activities. A comprehensive review has been written on 4-thiazolidinones in 1981[1]. 1,3-Thiazolidine-4-ones are heterocycles that have an atom of sulfur at position 1, an atom of nitrogen at position 3 and a carbonyl group at position 4 (Fig. 1). Substituent's in the 2-,3-, and 5-position may be varied, but in this review we focused only modifications in the positions 2 and 3. Numerous methods for the synthesis of thiazolidinones and also their diverse reactions offer enormous scope in the field of medicinal chemistry.

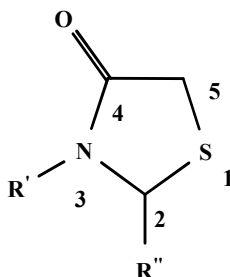


Fig. (1). General structure of 1,3-thiazolidin-4-one.

Aromatic polyimide's (PIs) have excellent thermal stability and high mechanical properties, along with good chemical resistance and electrical properties [2]. Because of these outstanding properties, their application in fiber, films, coating and composites has been extensively investigated for many years[3,4]. To meet the requirements for

the advanced application in the severe environment, the mechanical properties of PIs need to be highly improved while maintaining the good thermal properties and chemical resistance, which is also a task of research at all times.

Acryloyl chloride can be polymerized easily to linear polymer at room temperature by exposure to ultra-violet light in quartz tubes[5]. This important polymer can be enter many reactions to get a large numbers and types of polymers which added good physical properties and high thermal stability.

## EXPERIMENTAL SECTION

### 2-1- Materials

Most of chemicals used were supplied from Fluka , Merck and BDH Chemicals Co. and used as received.

### 2-2- Instruments

1. Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus, in Baghdad University, College of Science.
2. Softening points were determined using thermal microscope (Kofler-Method). Reichert thermovar. SP. 10/0.25, 160, in Baghdad University, College of Science.
3. FT-IR spectra were recorded using solid KBr discs by testing Shimadzu FT-IR 8000 series Fourier transform infrared spectrophotometer, in Baghdad University, College of Science and Ibn Sina State Company .
4. Thermal analysis were performed using thermal analysis system consisting of TG<sub>50</sub> Shimadzu, Japan. Such analyses were in the Ministry of Industry and Materials, Ibn Sina State Company.
5. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Fourier transform varian spectrometry, company Bruker, model, Ultra shield 300MHz, origin: Switzerland, with tetramethyl silane as internal standard in DMSO measurements were made at the Chemistry Department, Tarbiat Modares University, Iran.

The reaction sequence leading to the formation of new compounds and polymers are outlined in Scheme 1.

### 2-3- General Preparation of mono methyl ester [6] :

Placed (0.02 mol) of cyclic anhydride (glutaric or phthalic) and (0.02 mol) of absolute methanol with a few drops of conc. H<sub>2</sub>SO<sub>4</sub> in (50)ml a round-bottomed flask with a magnetic bar stirrer. The mixture was refluxed in water bath for 5 hours. A solution put in watch class and left to cool at room temperature then evaporated and collected. The formed white solid was recrystallized from THF.

### 2-4- General Preparation of methyl ester acid chloride [7] :

In 50 ml a round flask was placed (0.011 mol) of mono methyl ester and (0.022 mol) of thionyl chloride were reflux in a water bath at 30–40 °C for 3 hours , The yield was colorless liquid.

### 2-5- General Preparation of N-P-benz sulfonic acid mono methyl ester [8] :

A(0.011 mol) of Methyl ester (glutaric or phthalic) for acid chloride was dispersed in(30ml) dry toluene .To this suspension was added (0.011 mol) of sulfanilic acid and (1.2ml) of triethylamine acting. The mixture was refluxed for 48h at110°C to produce a brown solid .The product was filtered and washed with toluene then dichloromethane and purified with acidified ethanol.

### 2-6- General Preparation of N-P-benz sulfonic acid amide(gluta or phthal)acid hydrazide [9] :

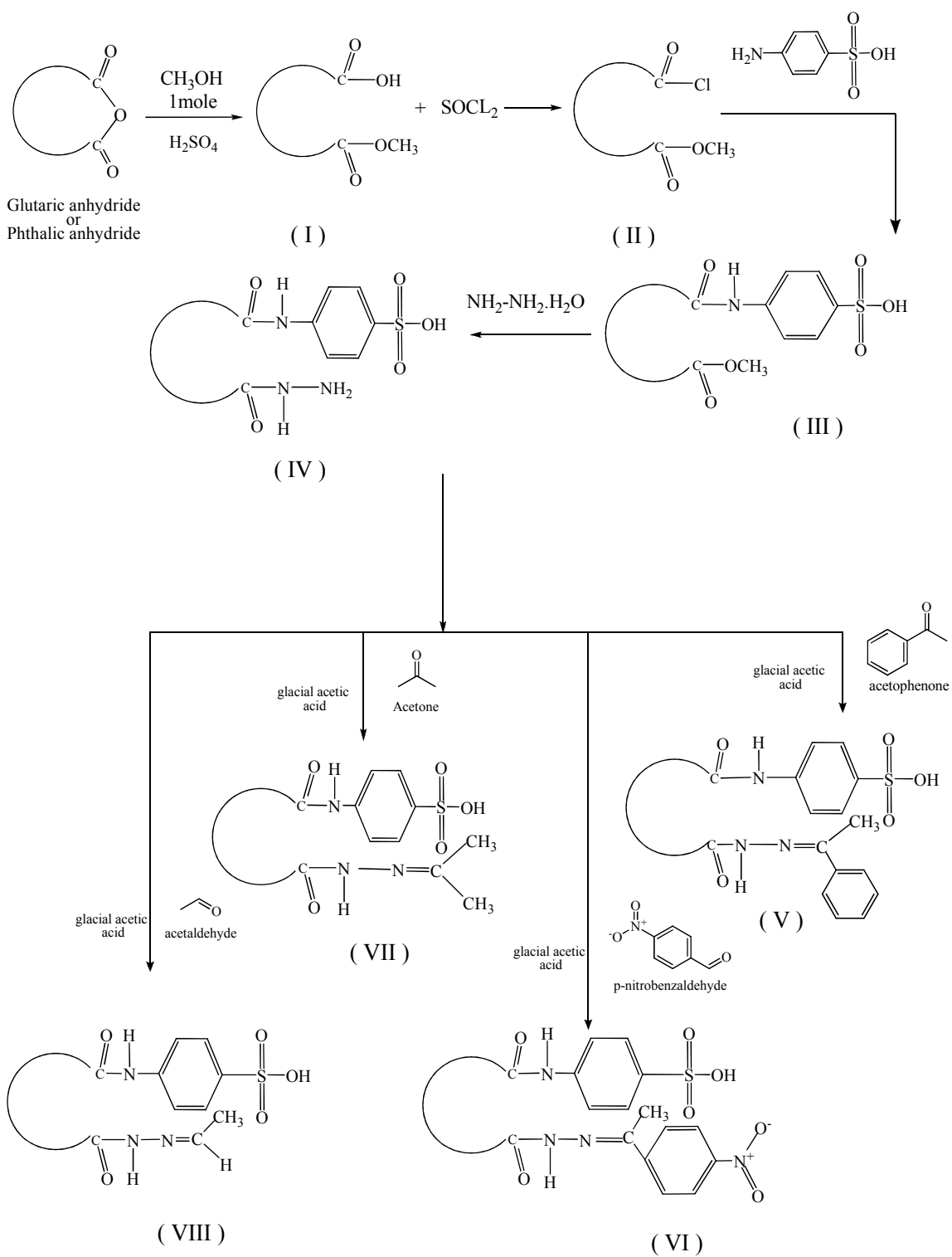
In 50 ml a round flask were placed (0.001mol) of N-P-benz sulfonic acid (glutaric or phthalic) mono methyl ester and hydrazine hydrate (0.001mol), in ethanol (10ml).The mixture was refluxed for 4 hours, then left to cool at room temperature. The formed precipitate was filtered and recrystallized from DMF.

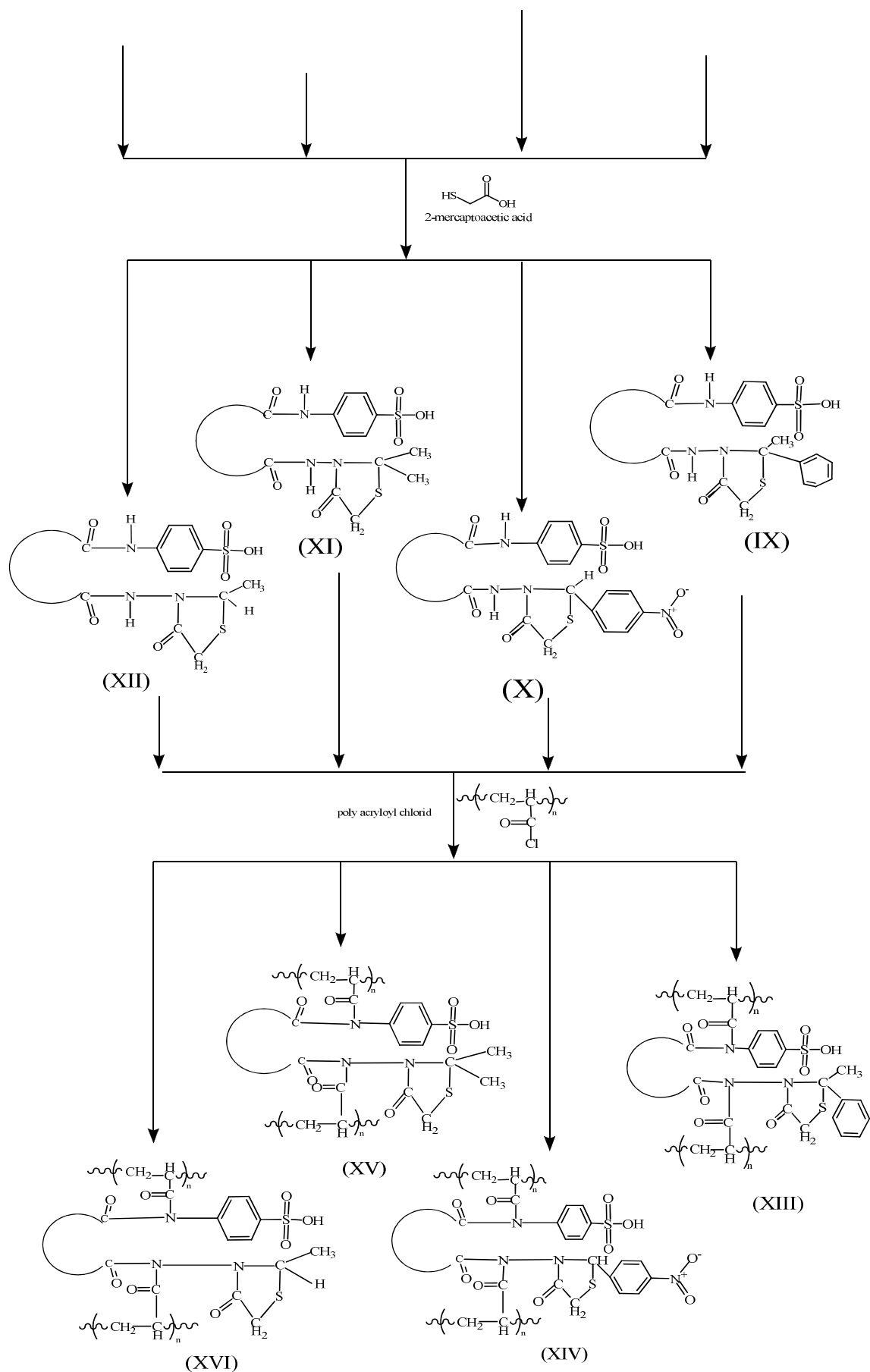
### 2-7- General Preparation of N-P-benz sulfonic-/N-alkyl imine cyclic di amide [10] :

A (0.001 mol) of N-P-benz sulfonic acid amide(glutaric or phthalic) acid hydrazide was dissolved in (15 ml) of ethanol, and a few drops of a glacial acetic acid were added, various aldehydes or Ketones (0.001 mol) were dissolved in suitable amount of ethanol. The mixture was heated at (70-75) °C for 5 hours. After cooling the yellow or orange precipitate was separated, filtered and recrystallized from ethanol.

### 2-8- General Preparation of N-P-benz sulfonic-/N-(2-di alkyl-4-one)-3-yl- thiazolidine imine cyclic di amide [11] :

In 50 ml a round flask were placed (0.0003 mol) of N-P-benz sulfonic-/N-alkyl imine cyclic di amide) and 2-mercapto acetic acid (0.0003 mol). The mixture was refluxed in (20ml) dry benzene for 6 hours. The mixture then evaporated and neutralized with cold dilute sodium bicarbonate solution , the formed product was filtered and recrystallized from acetone, Physical properties are listed in Table (1) .





Scheme 1

**2-9- General Preparation of Poly [ N - acryl - N - sulfonic acid - N<sup>1</sup>yl - 2 - substituted - 4 - oxo - thiazolidine ] glutaric or phthalic diimide [12-14] :**

Equal molar of poly acryloyl chloride and N-P-benz sulfonic-/N-(2-di alkyl-4-one)-3-yl- thiazolidine imine cyclic di amideone were dissolved in (25 ml) DMF, refluxed the mixture for (8 hr). After cooling and removed the solvent, the solid separated was filtered and purified by dissolving in THF and reprecipitated from water. Physical properties are listed in Table (2) .

**Table ( 1 ) : The physical properties of prepared compounds**

Comp. No.	Compound Structure	Color	Melting point °C	Yield %	Recrystallization
1		White	53-55	63	THF
2		Dark Green	159-161	67	Ethanol
3		Pale-Yellow	130-132	75	DMF
4		Yellow	144-146	60	Ethanol
5		Yellow	255-257	60	Ethanol
6		Pale-Yellow	151-153	73	Ethanol
7		Pale-Brown	oily	58	acetone
8		Yellow	170-172	66	acetone
9		Yellowish- Green	207-209	75	acetone
10		Pale-Brown	113-115	64	acetone

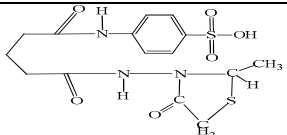
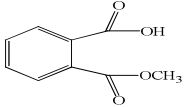
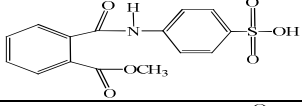
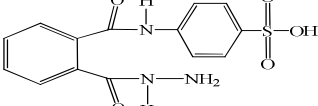
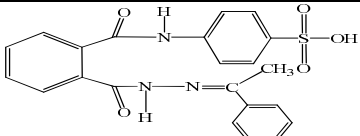
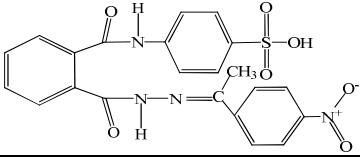
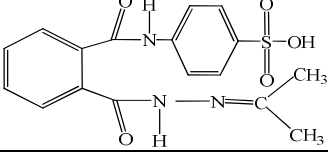
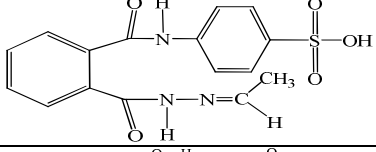
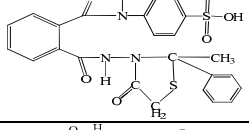
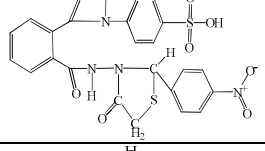
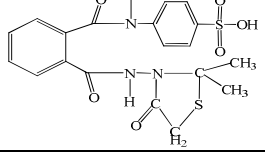
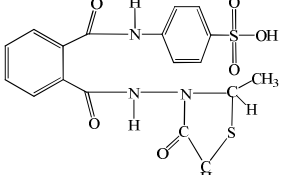
11		Brown	122-124	59	acetone
12		white	82-84	80	THF
13		Deep-Brown	222-224	75	Ethanol
14		Pale pink	161-163	69	DMF
15		Yellow	189-191	55	Ethanol
16		Pale Yellow	177-179	78	Ethanol
17		Pale-Brown	212-214	66	Ethanol
18		Pale white	oily	50	Ethanol
19		Yellowish- Green	230-232	67	acetone
20		Yellow	212-214	63	acetone
21		Yellow	155-157	70	acetone
22		Brown	239-241	55	acetone

Table (2): Physical properties of the prepared poly diimides

Comp. No.	Structure	Conversion %	Softening point °C	Colour
1		73.8	175-185	Pale- Brown
2		86.9	190-205	Yellow
3		74	140-155	Pale-Yellow
4		74	160-165	Orange
5		81	170-180	Pale-Yellow
6		88	200-205	Yellow
7		71	155-160	Yellow
8		72	145-150	Pale-Yellow

## RESULTS AND DISCUSSION

Although there are several procedures for the preparation of N – substituted of them was found suitable for the preparation of poly diimide from reaction of poly acryloyl chloride prepared ,all compounds characteristics by (m.p and FT-IR),while prepared polymer by ( s.p , FT-IR and TGA).

FT-IR spectra of compounds (1,12) showed the same bands appearance[15]. Stretching band at (1726-1735)  $\text{cm}^{-1}$  (C=O) ester, (1710-1712)  $\text{cm}^{-1}$  (C=O) carboxylic, (2850-2960) $\text{cm}^{-1}$   $\nu$ (C-H) aliphatic and (3004-3062) $\text{cm}^{-1}$  (OH) carboxylic. These bands and others are shown in Table (3).

FT-IR spectra of compounds (2,3,13,14) showed characteristic absorption bands at (1630-1660) $\text{cm}^{-1}$ , (1500-1600)  $\text{cm}^{-1}$ , (1319-1350)  $\text{cm}^{-1}$ , (2823-2995)  $\text{cm}^{-1}$ , (3080-3100)  $\text{cm}^{-1}$ , (3190-3225)  $\text{cm}^{-1}$  and (3332-3395) $\text{cm}^{-1}$  due to  $\nu$ (C=O) amide,  $\nu$ (C=C) aromatic,  $\nu$ (C-N),  $\nu$ (C-H) aliphatic,  $\nu$ (C-H) aromatic,  $\nu$ (N-H) amide and  $\nu$ (NH<sub>2</sub>). These bands and others are shown in Table (3).

FT-IR spectra of compounds (4-7,15-18) showed characteristic absorption bands at (1600-1620) $\text{cm}^{-1}$  due to  $\nu$ (C=N), and (1500-1555) $\text{cm}^{-1}$ , (1301-1345) $\text{cm}^{-1}$  due to  $\nu$ (NO<sub>2</sub>) asym,  $\nu$ (NO<sub>2</sub>) sym. These bands and others are shown in Table (3).

FT-IR spectra of compounds (8-11,19-22) showed characteristic absorption bands at (659-698) $\text{cm}^{-1}$  and (1716-1733)  $\text{cm}^{-1}$  due to  $\nu$ (C-S) and  $\nu$ (C=O) lactam. These bands and others are shown in Table (3) and Figs. (2-4).

Table (3): FT-IR spectra of the prepared compound( $\text{cm}^{-1}$ )

Comp. No.	$\nu$ (C=O) amide	$\nu$ (C=C) aromatic	$\nu$ (C=N)	$\nu$ (C-N)	$\nu$ (C-H) aliphatic	$\nu$ (C-H) aromatic	$\nu$ (N-H)	$\nu$ (C-S) Thiazole ring	Other bands
1	-	-	-	-	2900 2960	-	-	-	$\nu$ (C=O) ester 1726 $\nu$ (C=O) carboxylic 1712 $\nu$ (O-H) carboxylic 3062
2	1630	1544 1570 1600	-	1320	2883 2975	3080	3190	-	$\nu$ (C=O) ester 1724
3	1660	1500 1515 1600	-	1340	2925 2995	3100	3225	-	$\nu$ (NH <sub>2</sub> ) 3340 3395
4	1650	1550 1555 1570	1600	1361	2900 2990	3060	3205	-	-
5	1630	1495 1520	1600	1330	2875 2993	3060	3110	-	$\nu$ (NO <sub>2</sub> ) asym. 1555 $\nu$ (NO <sub>2</sub> ) sym. 1345
6	1631	1550 1575	1600	1320	2837 2993	3064	3184	-	-
7	1650	1500 1560	1600	1340	2887 2950	3050	3230	-	-
8	1603	1530 1568	-	1361	2854 2958	3062	3153	688	$\nu$ (C=O) lactam 1755
9	1627	1550 1595	-	1330	2852 2927	3090	3200	684	$\nu$ (NO <sub>2</sub> ) asym 1500 $\nu$ (NO <sub>2</sub> ) sym. 1346 $\nu$ (C=O) lactam 1730
10	1633	1575 1600	-	1300	2852 2920	3064	3190	685	$\nu$ (C=O) lactam 1720
11	1662	1500 1555	-	1388	2862 2927	3070	3197	659	$\nu$ (C=O) lactam 1716
12	-	1530 1581	-	-	2850 2954	3070	-	-	$\nu$ (C=O) ester 1735 $\nu$ (C=O) carboxylic 1710 $\nu$ (O-H)

									carboxylic 3004
13	1633	1545 1570 1595	-	1350	2823 2930	3085	3193	-	$\nu(\text{C=O})$ ester 1710
14	1631	1548 1575 1600	-	1319	2833 2983	3085	3193	-	$\nu(\text{NH}_2)$ 3332 3392
15	1631	1548 1575	1600	1319	2833 2983	3085	3193	-	-
16	1635	1540 1566	1602	1320	2854	3060	3203	-	$\nu(\text{NO}_2)$ asym. 1500 $\nu(\text{NO}_2)$ sym. 1301
17	1645	1544 1573	1620	1350	2831 2935	3050	3238	-	-
18	1631	1546 1577	1600	1319	2804 2966	3062	3328	-	-
19	1674	1548 1570	-	1360	2839 2945	3085	3188	688	$\nu(\text{C=O})$ lactam 1730
20	1618	1570 1595	-	1352	2960	3055	3210	642	$\nu(\text{NO}_2)$ asym. 1540 $\nu(\text{NO}_2)$ sym. 1310
21	1641	1580 1590	-	1369	2854 2958	3060	3210	698	$\nu(\text{C=O})$ lactam 1731
22	1631	1575 1600	-	1313	2850 2923	3040	3176	686	$\nu(\text{C=O})$ lactam 1733

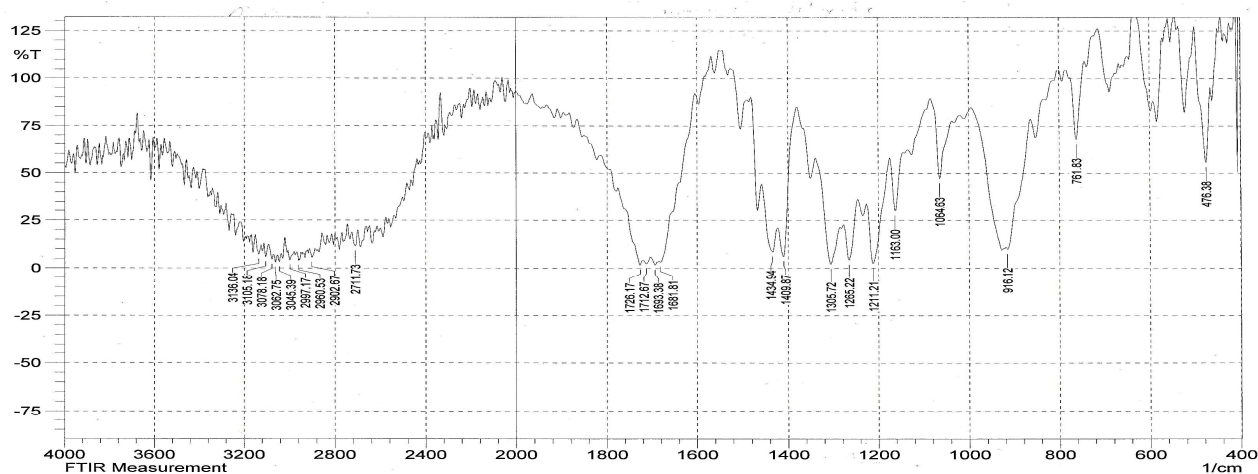


Fig. No. ( 2 ) : FT-IR OF COMPOUND [ 1 ]

FT-IR spectra of polymers (1-8) showed characteristic absorption bands at  $(1740-1760) \text{ cm}^{-1}$ ,  $(1510-1596) \text{ cm}^{-1}$ ,  $(1330-1363) \text{ cm}^{-1}$ ,  $(2800-2993) \text{ cm}^{-1}$ ,  $(3047-3110) \text{ cm}^{-1}$  and  $(649-686) \text{ cm}^{-1}$  due to  $\nu(\text{C=O})$  imide,  $\nu(\text{C=C})$  aromatic,  $\nu(\text{C-N})$ ,  $\nu(\text{C-H})$  aliphatic,  $\nu(\text{C-H})$  aromatic and  $\nu(\text{C-S})$  thiazole ring. These bands are shown in Table (4) and Figs. (5,6).

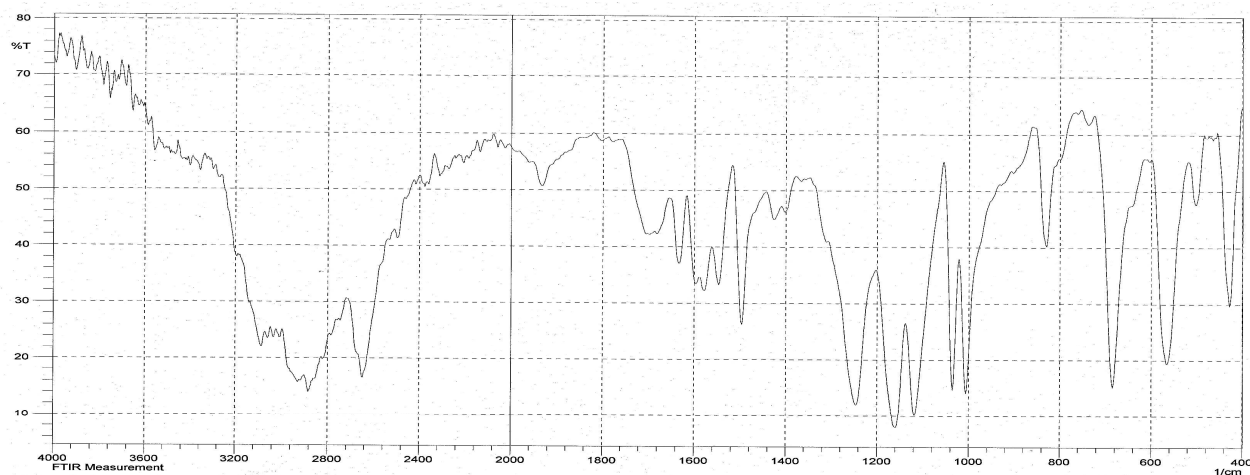


Fig. No. ( 3 ) : FT-IR OF COMPOUND [ 13 ]

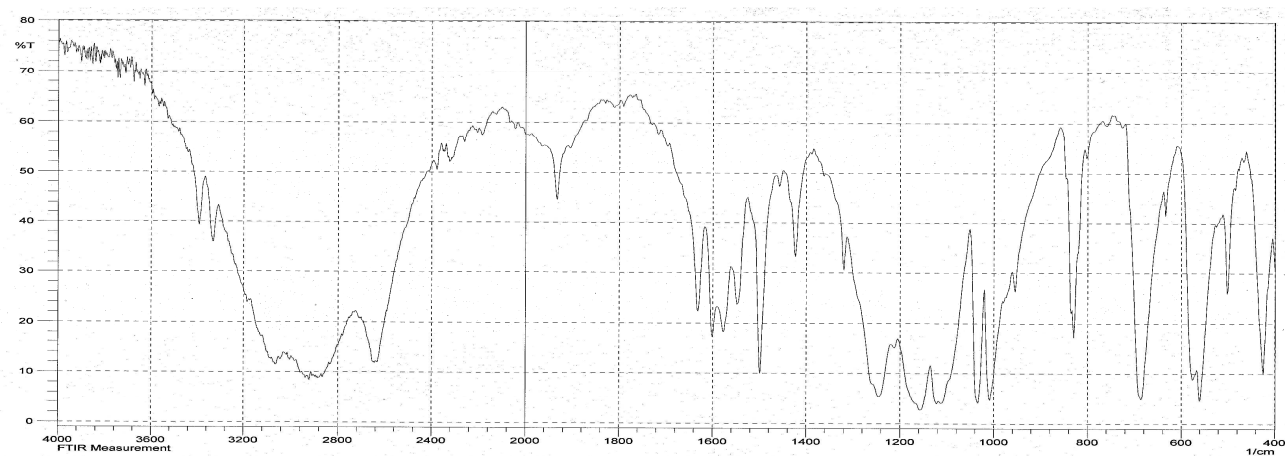


Fig. No. ( 4 ) : FT-IR OF COMPOUND [ 14 ]

Table (4): FT-IR spectra of the prepared polymer(cm<sup>-1</sup>)

Comp. No.	$\nu(\text{C=O})$ imide	$\nu(\text{C=C})$ aromatic	$\nu(\text{C-N})$	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-S})$
1	1745	1560 1570	1363	2800 2960	3050	686
2	1760	1523 1560 1596	1350	2810 2980	3047	684
3	1755	1540 1565 1580	1340	2848 2974	3090	686
Comp. No.	$\nu(\text{C=O})$ imide	$\nu(\text{C=C})$ aromatic	$\nu(\text{C-N})$	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-S})$
4	1740	1530 1540 1580	1330	2840 2933	3110	661
5	1745	1510 1540	1363	2830 2925	3070	660
6	1760	1510 1550	1344	2833 2920	3056	680
7	1760	1530 1570	1340	2852 2993	3060	649
8	1740	1540 1560	1350	2870 2950	3100	677

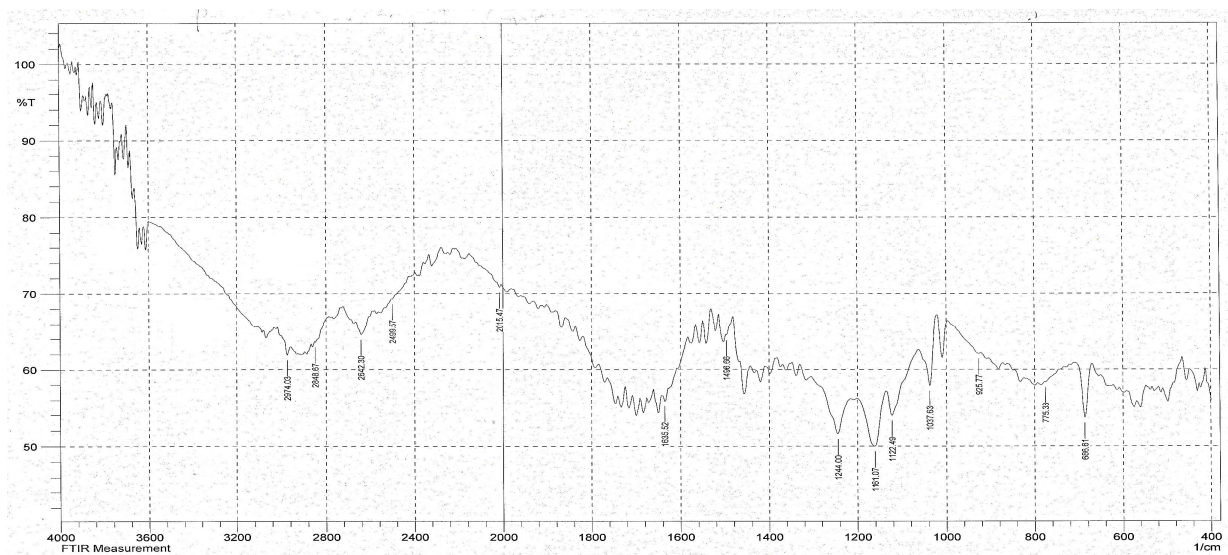


Fig. No. ( 5 ) : FT-IR OF POLYMER [ 3 ]

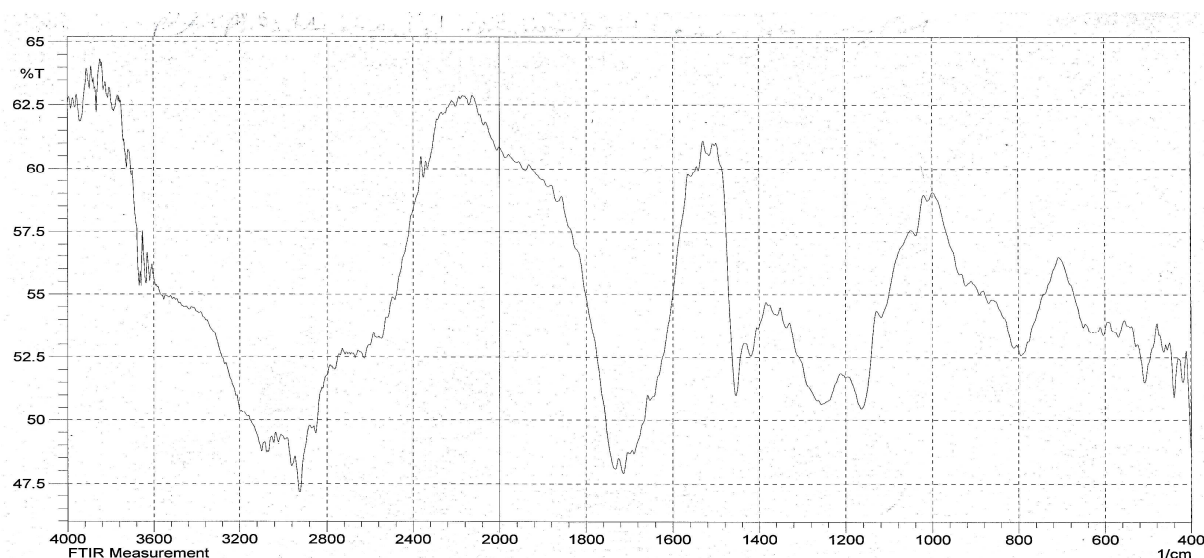


Fig. No. ( 6 ) : FT-IR OF POLYMER [ 7 ]

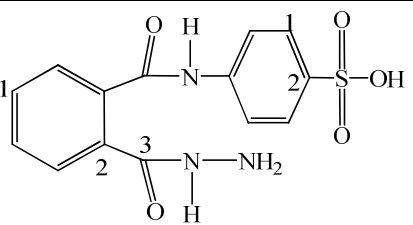
The  $^1\text{H}$ -NMR spectrum of compounds(14) showed the signals at  $\delta$  (2)ppm for proton(OH) , $\delta$  (6.5- 7.5 )ppm for proton(HAr),  $\delta$ (8)ppm for proton (NH) as show listed in Table (5).

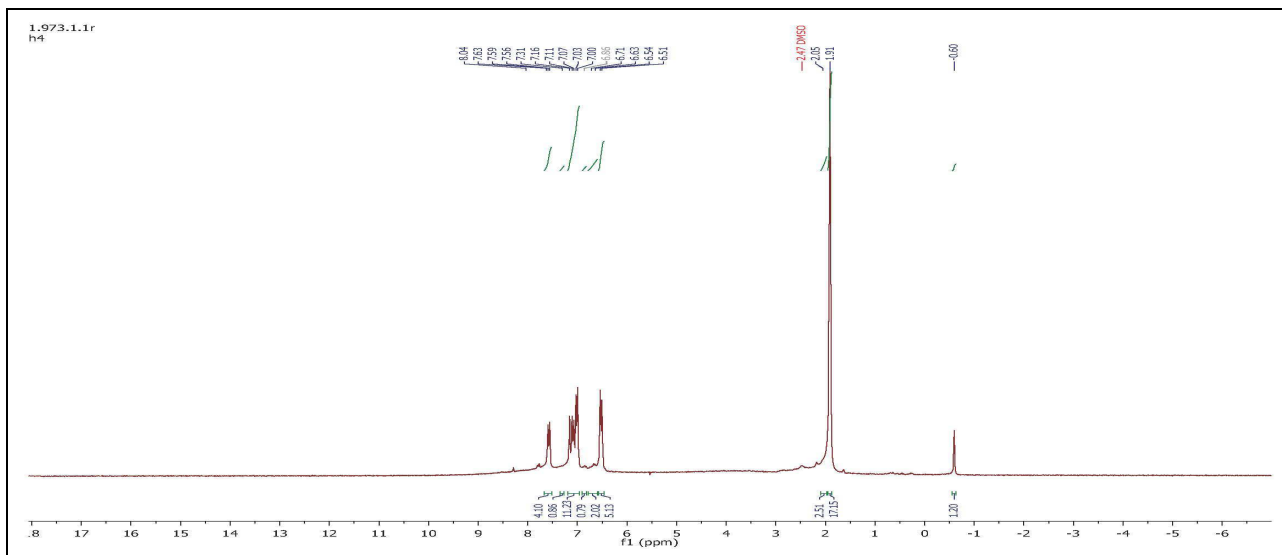
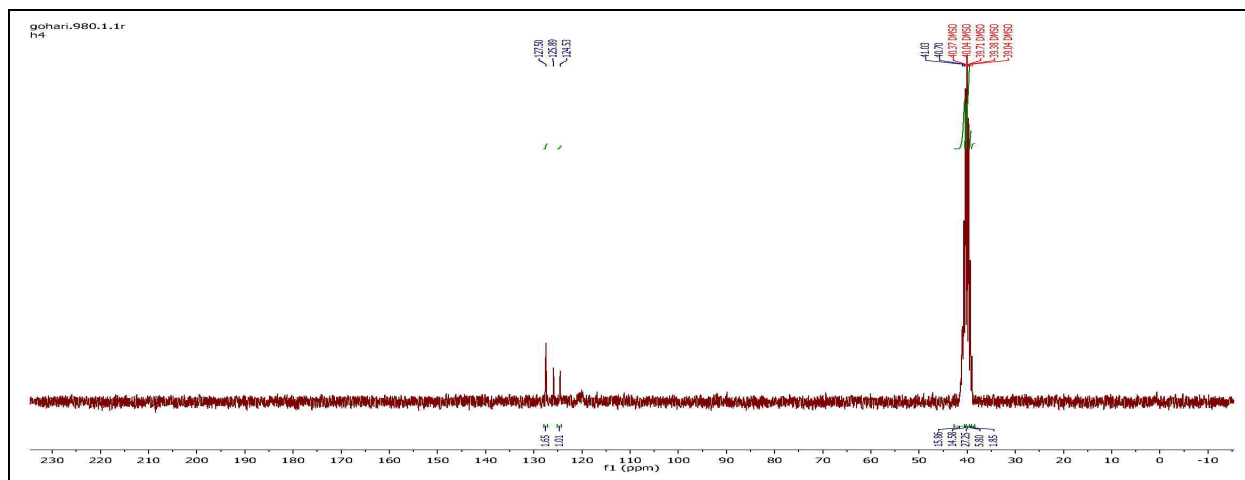
Table (5): The  $^1\text{H}$ -NMR chemical shifts of the prepared compound(ppm)

Comp. No.	Structure	Chemical shifts
14		$\delta$ 2 (s, 1H <sup>1</sup> ); $\delta$ 6.5-7.5 (t, 3H <sup>2</sup> ) $\delta$ 8 (s, 1H <sup>3</sup> ).

The  $^{13}\text{C}$ -NMR spectrum of compounds(14) showed the signal at  $\delta$ (124),(125) ppm for aromatic carbon while the carbonyl group (C=O) show signal at  $\delta$  (127) ppm) listed in Table (6) and Figs. (7,8).

Table (6): The  $^{13}\text{C}$ -NMR chemical shifts of the prepared compound(ppm)

Comp. No.	Structure	Chemical shifts
14		$\delta 124.5 (\text{C}^1)$ ; $\delta 125.8 (\text{C}^2)$ ; $\delta 127.5 (\text{C}^3)$ .

Fig. No. ( 7 ) :  $^1\text{H}$ -NMR OF COMPOUND [ 13 ]Fig. No. ( 8 ) :  $^{13}\text{C}$ -NMR OF COMPOUND [ 13 ]

The thermal analysis was carried out at temperatures (20-40) $^{\circ}\text{C}$  with heating rate 20.0  $^{\circ}\text{C}/\text{min}$ . in  $\text{N}_2$  atmosphere. TG analysis provides a change in the mass of the polymer during heating Thermal stability of the product was estimated from TG and DTG thermo grams, it was found that the prepared polymers high stability, as show in Table (7) and Figs. (9-11).

Table(7): TGA and DTG of some of the prepared poly diimides

Comp. No.	Compound structure	10% wt Loss temp °C	50% wt Loss temp °C
1		232.12	394.73
2		219.78	402
3		266.4	409.4

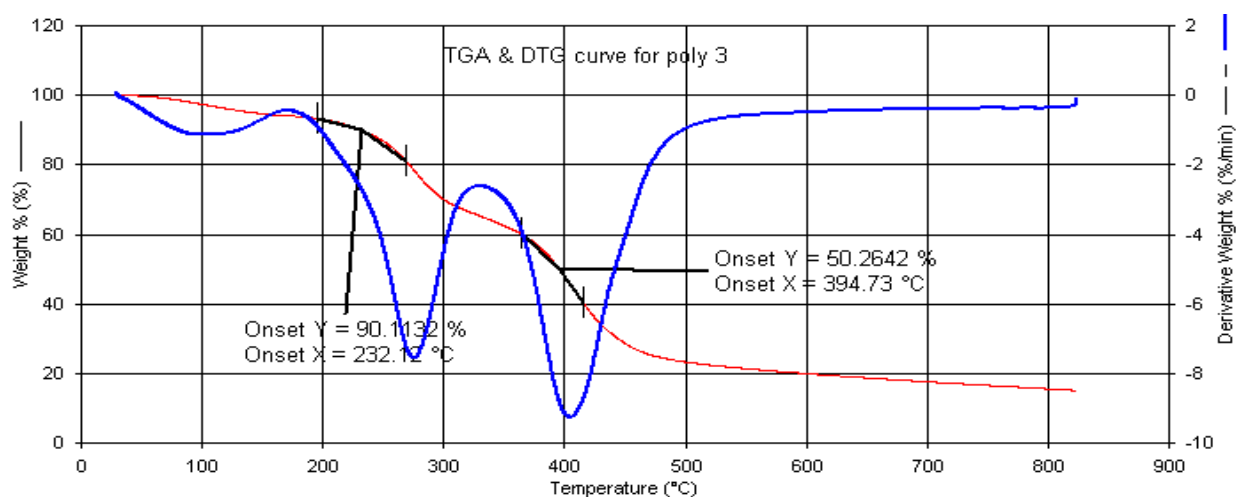


Fig. No. ( 9 ) : TGA and DTG for poly [ 1 ]

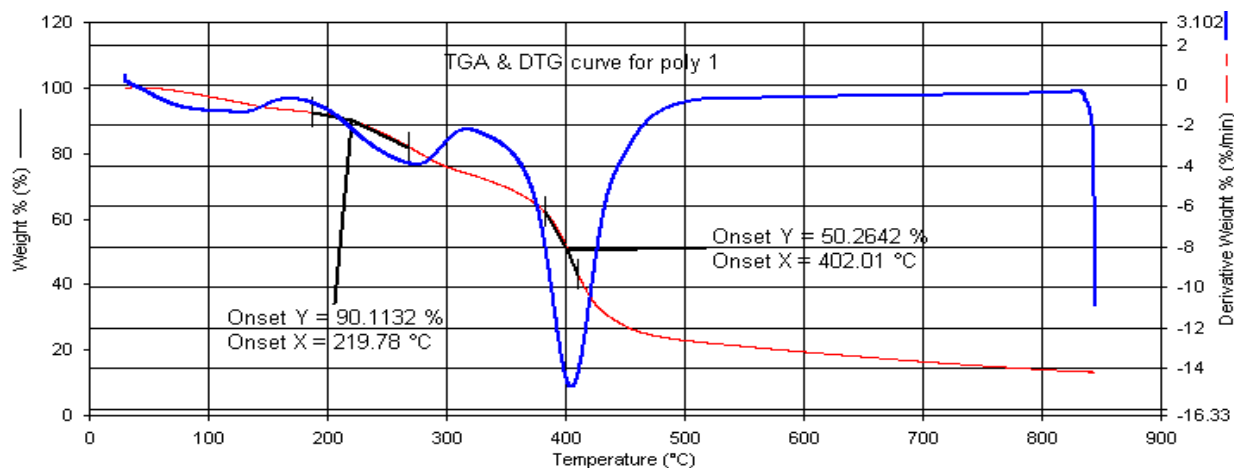


Fig. No. ( 10 ) : TGA and DTG for poly [ 2 ]

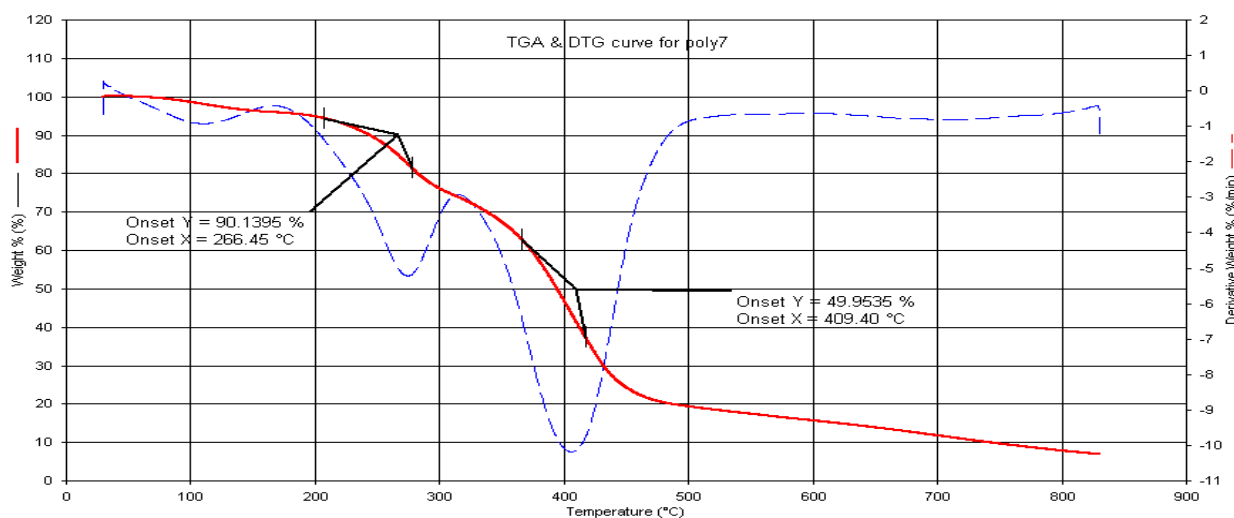


Fig. No. ( 11 ) : TGA and DTG for poly [ 3 ]

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