Synthesis & Characterization Of Poly [N - acryl - N - sulfonic acid - N\ yL - 2 - substituted - 4 - oxo - thiazolidine] Maleic and Succinic DiImide

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Abstract

In the present investigation, new polymers of Poly [N - acryl - N - sulfonic acid - N\ yL - 2 - substitute - 4 - oxo - thiazolidine] Maleic and Succinic 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_2SO_4, 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 hydraizide with different (aliphatic and aromatic) aldehyedes 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] . There chemical structures have been confirmed by melting points , FTIR,^{1}HNMR and ^{13}C-NMR (some of them). All the synthesized polymers were characterized by FT– IR spectra, softening points and TGA,DTG (some of them)

Keyword: maleic and succsinic anhydride, poly imide, Thiazolidine.

تحضير وتشخيص بولي [N– أكريل – N – حامض السلفونيك – N\ – يل – 2 – معوض – 4– اوكسو ثايازوليدين]سكسنك أو ماليك داي إيمايد

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الخلاصة:

فـــــي هذا البحث تم تحضير بولي [(N– أكريل– N– حامض السلفونيك)– N\ –يل (– 2– { الكيل أو أريل }– 4 اوكسو ثايازوليدين)]سكسنك أو ماليك داي إيمايد جديدة م ن خ.لال سبع خطوات ، الخطوة الاولى تتضمن استرة انهيدريدات مختلفة بأستخدام م ول واحد م.ن الميثانول المطلق بوجود قطرات م.ن حامض الكبريتيك المركز لنحصل على مجموعة استر واحدة [I] ، الذي بدوره يتفاعل مع الثايونيل كلورايد ليعطينا استر وكلوريد الحامض [II] . ثم يتفاعل مع حامض السلفانلك ليعطينا المركب [III] ، ومن ثم يتفاعل م.ع الهيدرازين هيدريت ليعطينا حامض الهيدرازايد [IV] ، مركبات قواعد شف الجديدة [IIIV–V] تم تحضيرها م ن تفاعل حامض الهيدرازايد م.ع الديهايدات وكيتونات م ختلفة (اليفاتية واروم اتية) بوجود حامض الخليك الثلجي . م.شتقات الثايازوليدين 4 اون [IIX–IX] نتجت من خلال اضافة 2 مركبتو استك أسد الى مركبات قواعد شف والخطوة الاخيرة تتضمن اضافة بولي اكريلويل كلورايد لانتاج الهوليمرات [IVX–IIIX] ، وتم اثبات ذلك وبوهنة التراكيب الكيميائية بأستخدام الطرق الطيفية ،الاشعة تحت الحمراء

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FT–IR ، اطياف الرنين المغناطيس ^{1}H–NMR واطياف ^{13}C–NMR ، أما البوليمرات المحضرة فقد تم أجراء قياسات أطياف FT–IR لها إضافة الى درجات التلين ،أما إستقرارية هذه البولمرات تم معرفته عن طريق التحاليل الوزنية الحرارية

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 (Figure **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.

Figure 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.

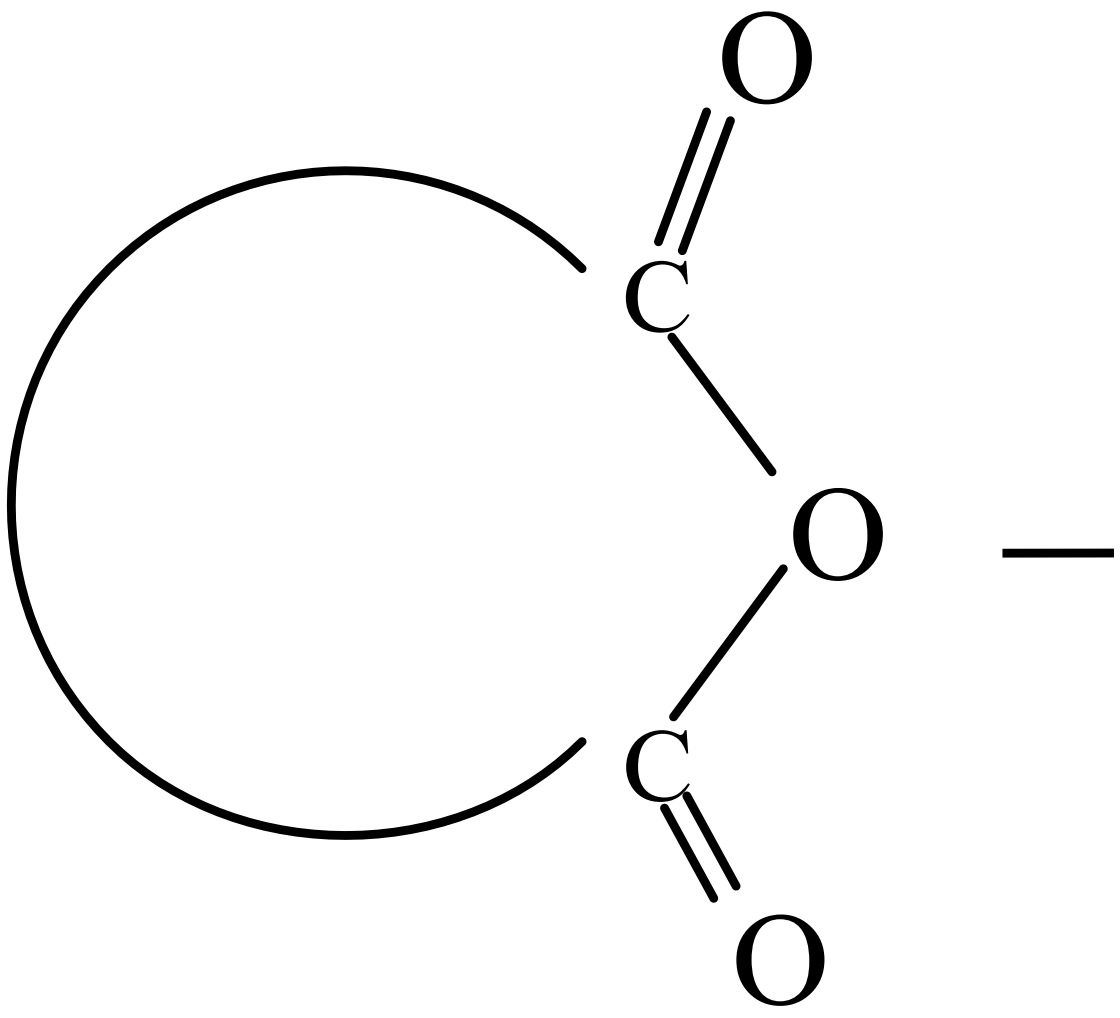
Acryloyl chloride can be polymerized easily to linear polymer at room temperature by exposure to ultra-violet light in quartz tubes[5]. This important polymer can be enter many reactions to get a large numbers and types of polymers which added good physical properties and high thermal stability.

1- Experimental Materials

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

2- Instruments

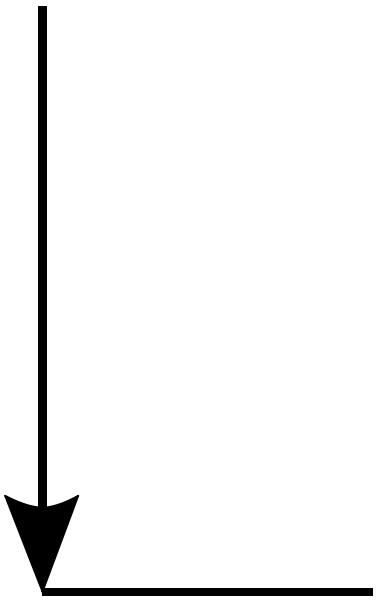
1. Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus, in Baghdad University, College of Science.
2. Softening points were determined using thermal microscope (Kofler-Method). Reichert thermovar. SP. 10/0.25, 160, in Baghdad University, College of Science.
3. 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_{50} Shimadzu, Japan. Such analyses were in the Ministry of Industry and Materials, Ibn Sina State Company.
5. ^{1}H-NMR and ^{13}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.



Maleic anhydride

or

(VIII)



3- General Preparation of Mono Methyl Ester(I)[6] **:**

Placed (0.02 mol) of cyclic anhydride (maleic or succinic) and (0.02 mol) of absolute methanol with a few drops of conc. H_2SO_4 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.

4- General Preparation of Methyl ester acid chloride(II)[7] **:**

In 50 ml a round flask was placed (0.011 mol) of mono methyl ester(I) 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.

5- General Preparation of N-p-benz sulfonic acid Mono Methyl ester(III)[8]**:**

A(0.011 mol) of Methyl ester for (maleic or succinic) acid chloride(II) 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.

6- General Preparation of N-p-benz sulfonic acid amide (male or succin)acid hydrazide(VI) [9]**:**

In 50 ml a round flask were placed (0.001mol) of N-p-benz sulfonic acid (male or succin) mono methyl ester (III)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.

7- General Preparation of N-p-benz sulfonic-/N-alkyl imine di amide(V-VIII)[10] **:**

A (0.001 mol) of N-p-benz sulfonic acid (male or succin) acid hydrazide(VI) 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.

8- General Preparation of N-p-benz sulfonic-/N-(2-di substitutedl-4-one)-3-yl- thiazolidine imine di amide(IX-XII)[11]:

In 50 ml a round flask were placed (0.0003 mol) of N-p-benz sulfonic-/N-alkyl imine di amide) (V-VIII)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)

9- General Preparation of Poly [N - acryl - N - sulfonic acid - N\ yL - 2 - substituted - 4 - oxo - thiazolidine] maleic or succinic diimide(XIII-XVI) [12-14] **:**

Equal molar of poly acryloyl chloride and N-p-benz sulfonic-/N-(2-di substituted-4-one)-3-yl-thiazolidine imine di amide (IX-XII)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 %	Recrystalization
1		White	30-35	70	THF
2		Brown	210-212	82	Ethanol
3		Pale-brown	145-147	76	DMF
4		Pale-yellow	129-131	73	Ethanol

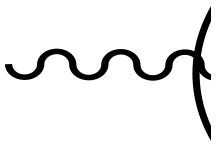
5		Yellowish-Green	259-261	88	Ethanol
6		White	275-277	71	Ethanol
7		Pale-brown	0ily	67	Ethanol
8		Yellow	264-266	70	Acetone
9		Pale-yellow	281-283	90	Acetone

Comp. No.	**Compound Structure**	**Color**	**Melting point°C**	**Yield %**	**Recrystalization**
10		Pale-brown	212-214	78	Acetone
11		Brown	oily	71	Acetone
12		White	56-58	78	THF
13		Deep brown	135-137	69	Ethanol
14		Pale-yellow	96-98	72	DMF

15		Pale-brown	181-183	73	Ethanol
16		Brown	258-260	75	Ethanol
17		Pale-yellow	268-270	65	Ethanol
18		Brown	oily	68	Ethanol

Comp No.	**Compound Structure**	**Color**	**Melting point°C**	**Yield %**	**Recrystalization**
19		Pale-yellow	213-215	66	Acetone
20		Yellow	221-223	77	Acetone
21		Pale-yellow	243-245	69	Acetone
22		Brown	oily	66	Acetone

Table 2 - Physical properties of the prepared poly diimides

Comp. No.	**Structure**	**Conversion %**	**Softening point °C**	**Colour**
23		78	150-160	White
24		85	177-183	Yellowish-Green
Comp. No.	**Structure**	**Conversion %**	**Softening point °C**	**Colour**
25		73	170-185	Yellow
26		70.7	160-175	Yellowish-Orange
27		72	155-165	Pale-Yellow
28		84.2	185-190	Pale-Yellow

29		71	145-160	yellow
30		73	130-145	Yellowish-Orange

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 from(1-30) 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 (1730) cm^{-1} (C=O) ester, (1710-1715) cm^{-1} (C=O) carboxylic ,(2854-2950)cm^{-1} ν(C-H) aliphatic and (3000-3050)cm^{-1} (OH) carboxylic. These bands and others are shown in Tables (3-A,3-B) .

FT-IR spectra of compounds (2,3,13,14) showed characteristic absorption bands at (1630-1635)cm^{-1} , (1535-1600) cm^{-1}, (1300-1311) cm^{-1}, (2825-2985) cm^{-1}, (3000-3065) cm^{-1}, (3172-3320) cm^{-1} and (3330-3420)cm^{-1} due to ν(C=O) amide, ν(C=C) aromatic ,ν(C-N) , ν(C-H) aliphatic , ν(C-H) aromatic, ν(N-H) amide and ν(NH_2). These bands and others are shown in Tables (3-A,3-B).

FT-IR spectra of compounds (4-7,15-18) showed characteristic absorption bands at (1590-1650)cm^{-1} due to ν(C=N), and (1460-1470)cm^{-1} ,(1345)cm^{-1} due to ν(NO_2) asym , ν(NO_2) sym. These bands and others are shown in Tables (3-A,3-B).

FT-IR spectra of compounds (8-11,19-22) showed characteristic absorption bands at (620-690)cm^{-1} and (1690-1730) cm^{-1} due to ν(C-S) and ν(C=O) lactam .These bands and others are shown in Tables (3-A,3-B) and Figures. (2-4).

Table 3-A- FT-IR spectra of the prepared compound (cm^{-1})

Comp. No.	**ν(C=O) amide**	**ν(C=C) aromatic**	**ν(C=C) olefinic**	**ν(C=N)**	**ν(C-N)**	**ν(C-H) aliphatic**	**ν(C-H) aromatic**	**ν(N-H)**	**ν(C-S) Thiazole ring**	**Other bands**
1	-	-	1645	-	-	2854 2955	-	-	-	**ν(C=O) ester** 1730 **ν(C=O) carboxylic** 1710 **ν(O-H) carboxylic** 3000
2	1631	1546 1580 1593	1680	-	1300	2885 2905	3000	3320	-	**ν(C=O) ester** 1720

3	1630	1535 1570	1600	-	1311	2918	3000	3280	-	**ν(NH_2)** 3330 3420
4	1680	1580 1550 1530	1600	1640	1313	2817 2900	3010	3320	-	-
5	1680	1520 1560 1580	1600	1640	1330	2916	3065	3285	-	**ν(NO_2) asym.** 1460 **ν(NO_2) sym.** 1345
Comp. No.	**ν(C=O) amide**	**ν(C=C) aromatic**	**ν(C=C) olefinic**	**ν(C=N)**	**ν(C-N)**	**ν(C-H) aliphatic**	**ν(C-H) aromatic**	**ν(N-H)**	**ν(C-S) Thiazole ring**	**Other bands**
6	1630	1500 1550	1580	1600	1320	2873 2914	3040	3180	-	-
7	1670	1510 1550 1570	1600	1650	1320	2883 2980	3040	3398	-	-
8	1631	1500 1545 1575	1600	-	1320	2880 2920	3060	3125	635	**ν(C=O) lactam** 1718
9	1633	1548 1577	1593	-	1315	2852 2927	3066	3176	685	**ν(NO_2) asym** 1496 **ν(NO_2) sym.** 1330 **ν(C=O) lactam** 1730
10	1670	1550 1580	1650	-	1380	2925 2958	3060	3300	685	**ν(C=O) lactam** 1730
11	1651	1523 1550 1555	1600	-	1392	2920 2978	3062	3240	663	**ν(C=O) lactam** 1716

Table 3-B- FT-IR spectra of the prepared compound (cm^{-1})

Comp. No.	**ν(C=O) amide**	**ν(C=C) aromatic**	**ν(C=N)**	**ν(C-N)**	**ν(C-H) aliphatic**	**ν(C-H) aromatic**	**ν(N-H)**	**ν(C-S) Thiazole ring**	**Other bands**
12	-	-	-	-	2870 2950	-	-	-	**ν(C=O) ester** 1730 **ν(C=O) carboxylic** 1715 **ν(O-H) carboxylic**

									3030
13	1635	1546 1580 1600	-	1310	2825 2920	3065	3172	-	**ν(C=O) ester** 1725
14	1630	1520 1600	-	1309	2985	3000	3226	-	**ν(NH_2)** 3335 3420
Comp. No.	**ν(C=O) amide**	**ν(C=C) aromatic**	**ν(C=N)**	**ν(C-N)**	**ν(C-H) aliphatic**	**ν(C-H) aromatic**	**ν(N-H)**	**ν(C-S) Thiazole ring**	**Other bands**
15	1630	1550 1570	1600	1360	2885 2920	3060	3178	-	-
16	1630	1521 1550	1600	1330	2955	3045	3240	-	**ν(NO_2) asym.** 1470 **ν(NO_2) sym.** 1345
17	1631	1548 1575	1600	1319	2800 2970	3085	3330	-	-
18	1631	1520 1560	1590	1381	2877 2985	3069	3160	-	-
19	1630	1548 1570 1602	-	1360	2877 2920	3060	3174	620	**ν(C=O) lactam** 1690
20	1680	1500 1590	-	1330	2990	3090	3190	680	**ν(NO_2) asym.** 1540 **ν(NO_2) sym.** 1398
21	1670	1570 1580 1590	-	1369	2852 2923	3060	3210	690	**ν(C=O) lactam** 1731
22	1647	1516 1525 1545	-	1342	2897 2981	3055	3240	636	**ν(C=O) lactam** 1720

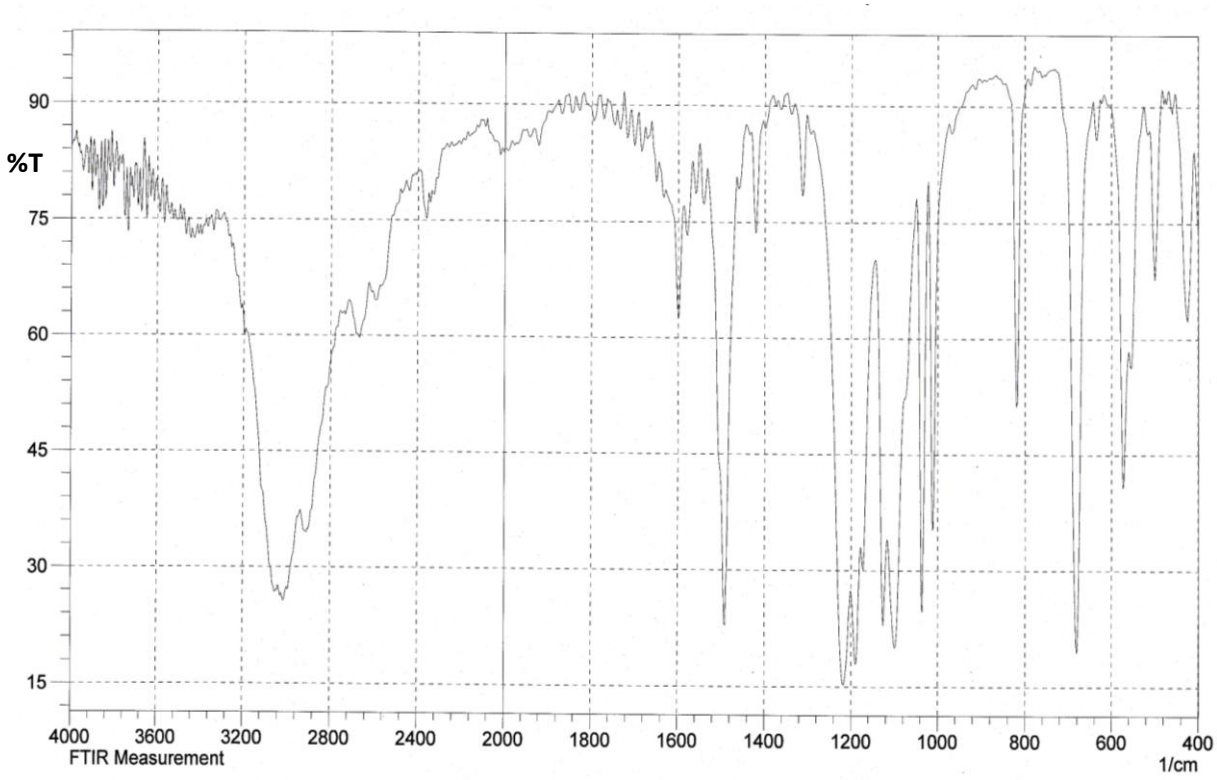


Figure 2-FT-IR Spectrum of Compound 4

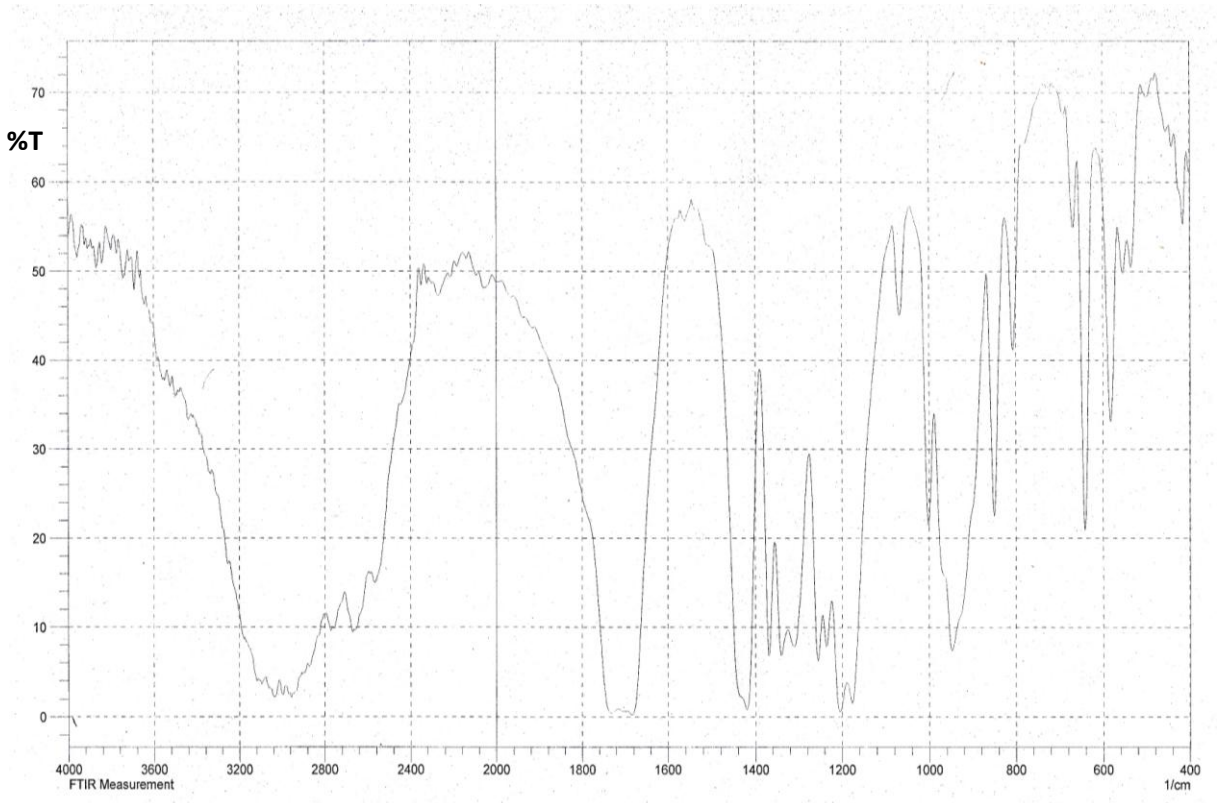


Figure 3-FT-IR Spectrum Of Compound 12

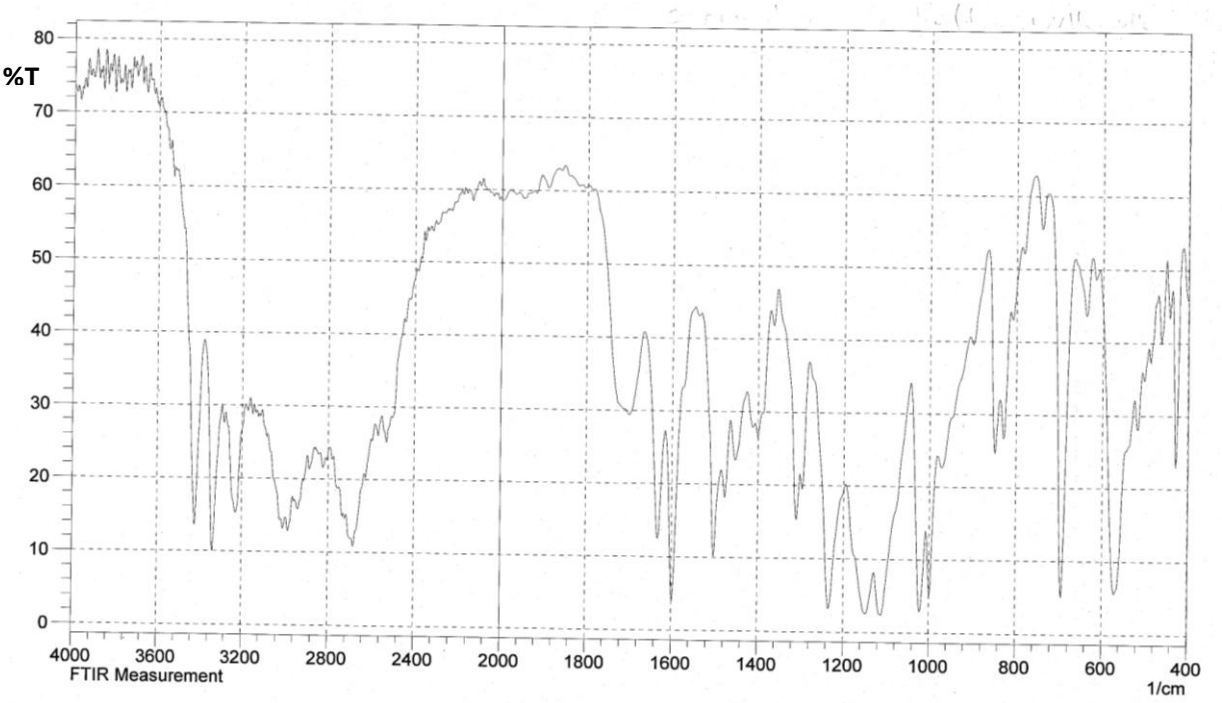


Figure 4-FT-IR Spectrum Of Compound 14

FT-IR spectra of polymers (23-30) showed characteristic absorption bands at (1700-1740) cm^{-1} , (1575-1640) cm^{-1}, (1345-1420) cm^{-1}, (2880-2975) cm^{-1},(3000-3065) $cm^{-1}$and (625-685) cm^{-1} due to ν(C=O) imide, ν(C=C) aromatic ,ν(C-N) ,ν(C-H) aliphatic ,ν(C-H) aromatic and ν(C-S) thiazole ring. FT-IR spectra of polymers(23-26). showed characteristic absorption bands at (1600-1650) cm^{-1} due to ν(C=C) olefinic. These bands and others are shown in Table (4) and Figures. (5-7) .

Table 4 - FT-IR spectra of the prepared polymer (cm^{-1})

Comp. No.	ν(C=O) imide	ν(C=C) aromatic	ν(C=C) olefinic	ν(C-N)	ν(C-H) aliphatic	ν(C-H) aromatic	ν(C-S)
23	1720	1498 1548 1606	1630	1420	2881 2954	3065	685
24	1710	1523 1560	1600	1345	2880 2900	3000	680
25	1735	1520 1580	1650	1360	2865 2920	3060	645
26	1700	1520 1550 1606	1650	1395	2895 2975	3040	685
27	1700	1500 1550 1600	-	1420	2840 2937	3062	685
28	1733	1530 1550	-	1400	2970	3050	650
29	1730	1550 1575	-	1379	2852 2956	3000	620
30	1737	1541 1600	-	1395	2855 2920	3000	667

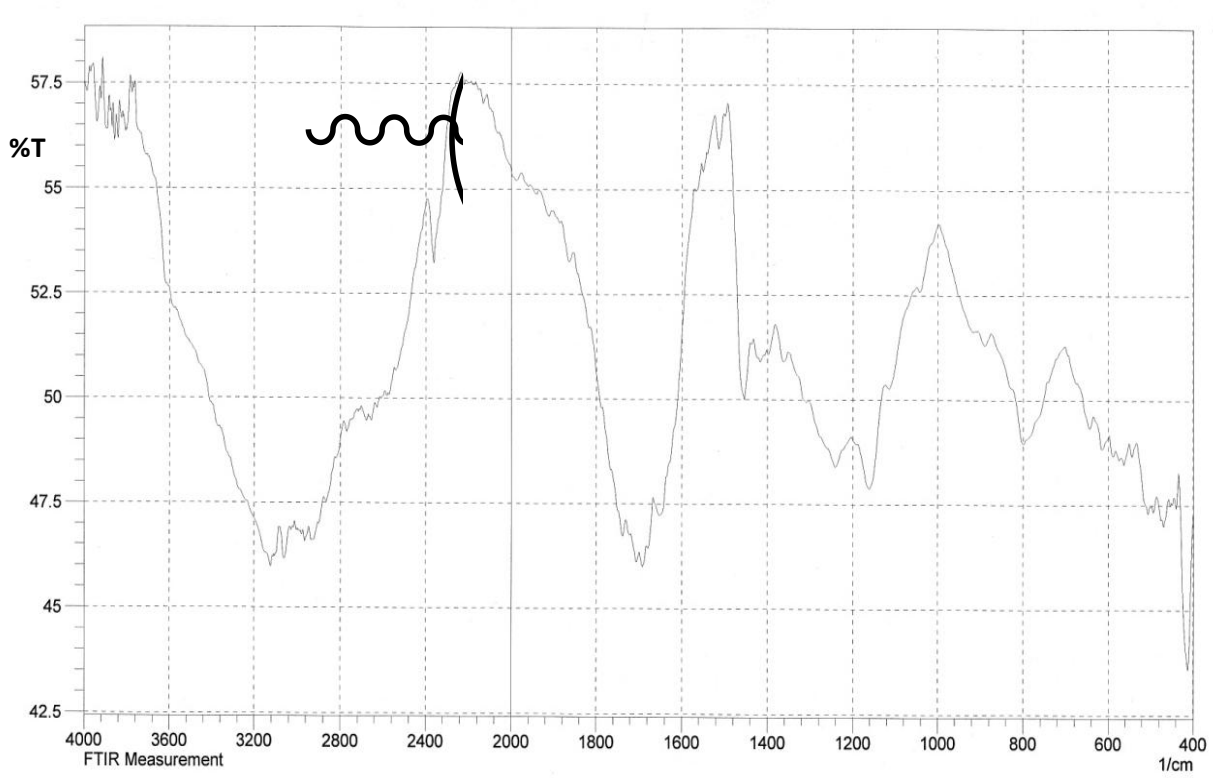


Figure 5 -FT-IR Spectrum Of Polymer 25

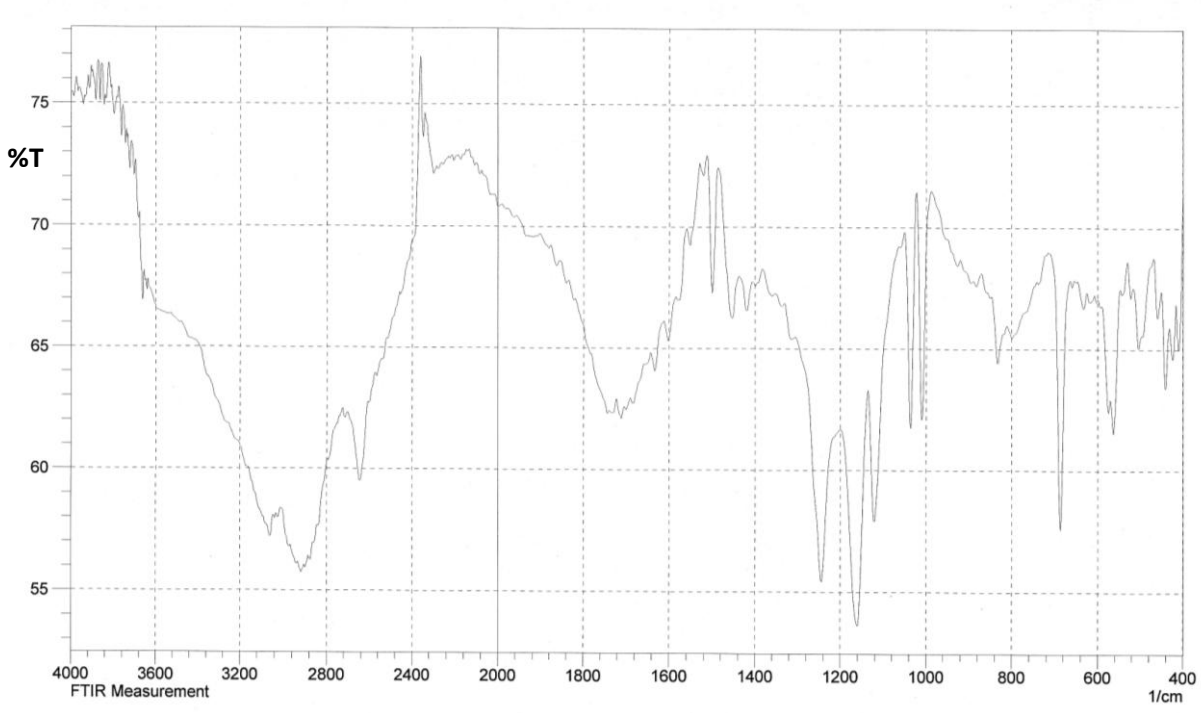


Figure 6-FT-IR Spectrum Of Polymer 27

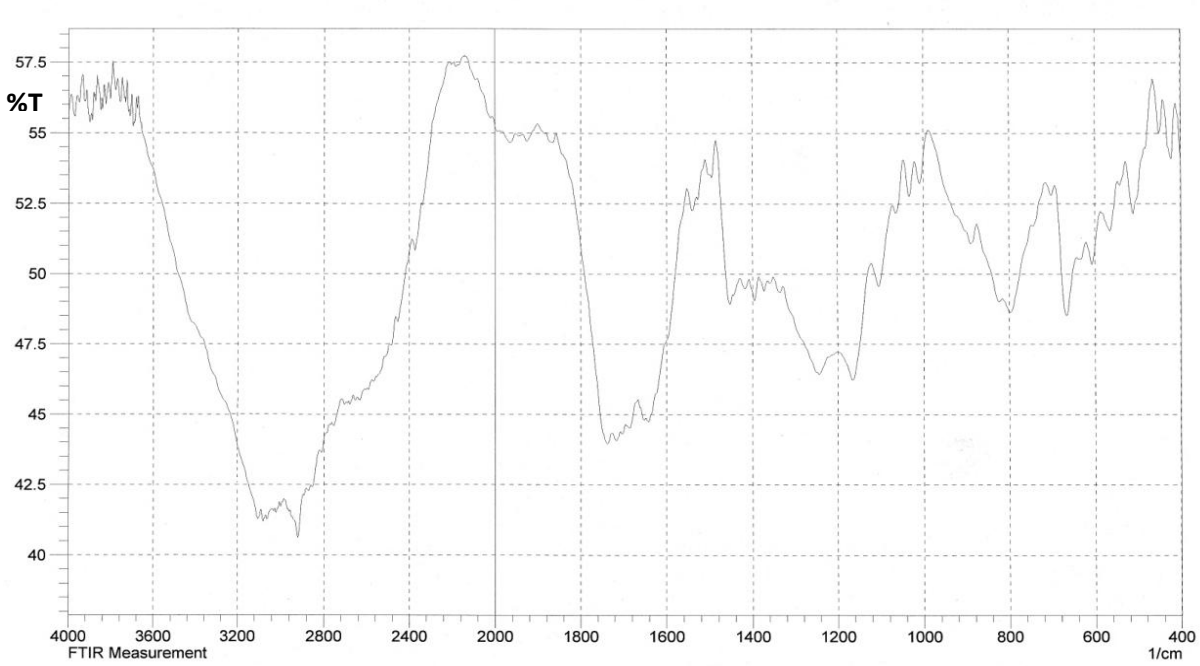


Figure 7-FT-IR Spectrum Of Polymer 30

The[1]H-NMR spectrum of compounds (2) showed the signals at δ (1.9) ppm for proton (OH) ,δ (2.4-2.5) ppm for proton (CH_3), δ (3.1-4) ppm for proton (CH), δ (6-7) ppm for proton (HAr), δ (8.5) ppm for proton (NH), while a signal for compounds (13) at δ (1.8) ppm for proton (OH) , δ (1.9) ppm for proton (CH_2) ,δ (2.4-2.5) ppm for proton (CH_3), δ (6-6.76) ppm for proton (HAr), δ (8.6) ppm for proton (NH) as show listed in Table (5).
The ^{13}C-NMR spectrum of compounds (2) showed the signal at δ (46) ppm for (CH_3), δ (119) ppm and δ (122) ppm to aromatic carbon while (C=C) olefinic appeared at δ (127) ppm and δ (133) ppm , δ (147)ppm and δ (166) ppm attributed to carbonyl group (C=O), while a signal for compounds (13) at δ (29) ppm and δ (38.9) ppm for (CH_2), δ (45.9) ppm for (CH_3) ,δ (121.7) ppm and δ (127) ppm for aromatic carbon, δ (146) ppm andδ (174)ppm attributed to carbonyl group (C=O) listed in Table (6) and Figures (8-11).

Table 5- The [1]H-NMR chemical shifts of the prepared compound (ppm)

Comp. No.	**Structure**	**Chemical shifts**
2		δ1.9 (s, $1H^1$); δ2.4-2.5 (s, $3H^2$) δ3.1-4 (m, $2H^3$, $2H^4$); δ6-7 (m, HAr); δ8.5 ($1H^7$).
13		δ1.8 (s, $1H^1$); δ1.9 (q, $4H^2$) δ2.4-2.5 (s, $3H^3$); δ6-6.76 (m, HAr); δ8.6 ($1H^6$).

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

Comp. No.	**Structure**	**Chemical shifts**
2		δ46 (C^1); δ119 (C^2,C^3);δ,122 (C^4,C^5); δ127 (C^6); δ133(C^7); δ,134 (C^8,C^9); δ147(C^{10}); δ166 (C^{11}) .
13		δ29 (C^1); δ38.9 (C^2);δ45.9(C^3); δ121.7 (C^4,C^5); δ127(C^6,C^7); δ,134 (C^8,C^9); δ146(C^{10}); δ174 (C^{11}).

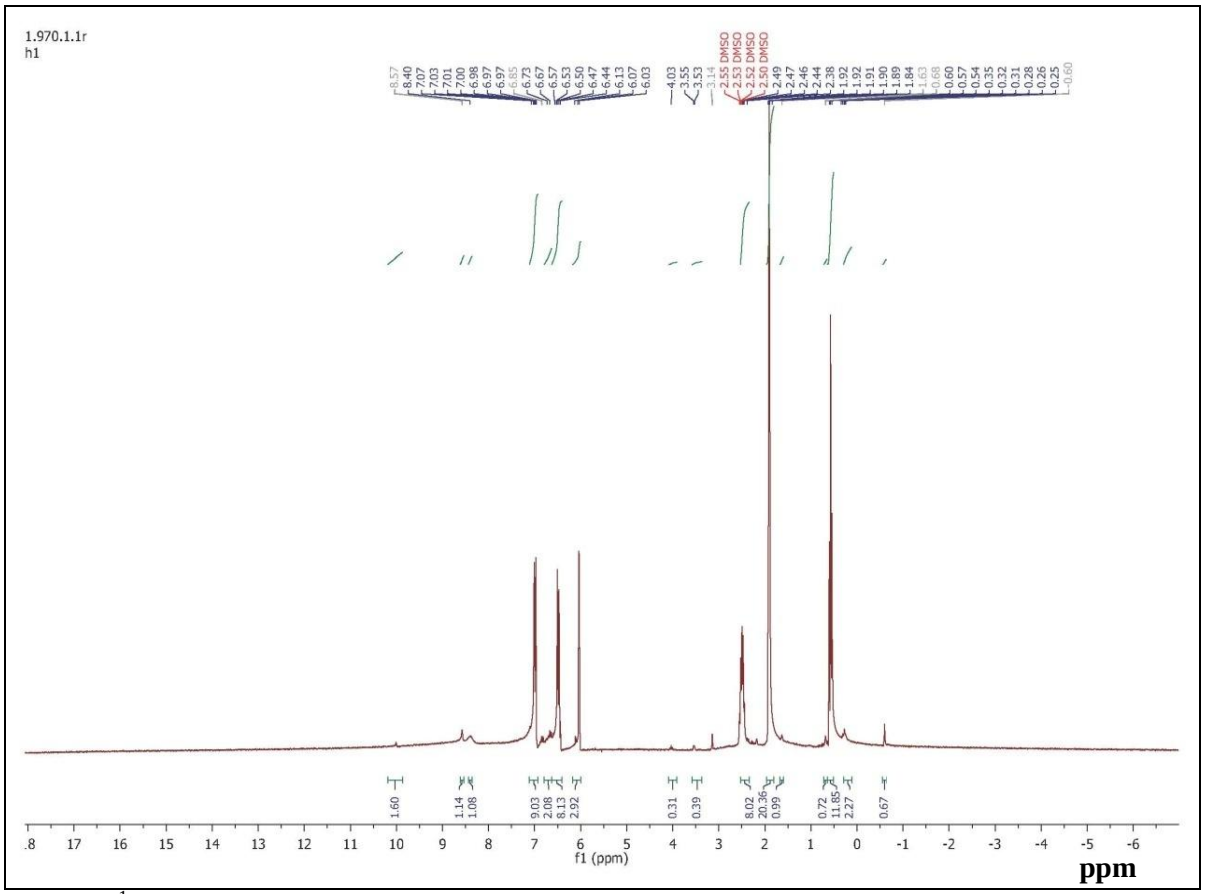


Figure 8-^{1}H-NMR Spectrum Of Compound 2

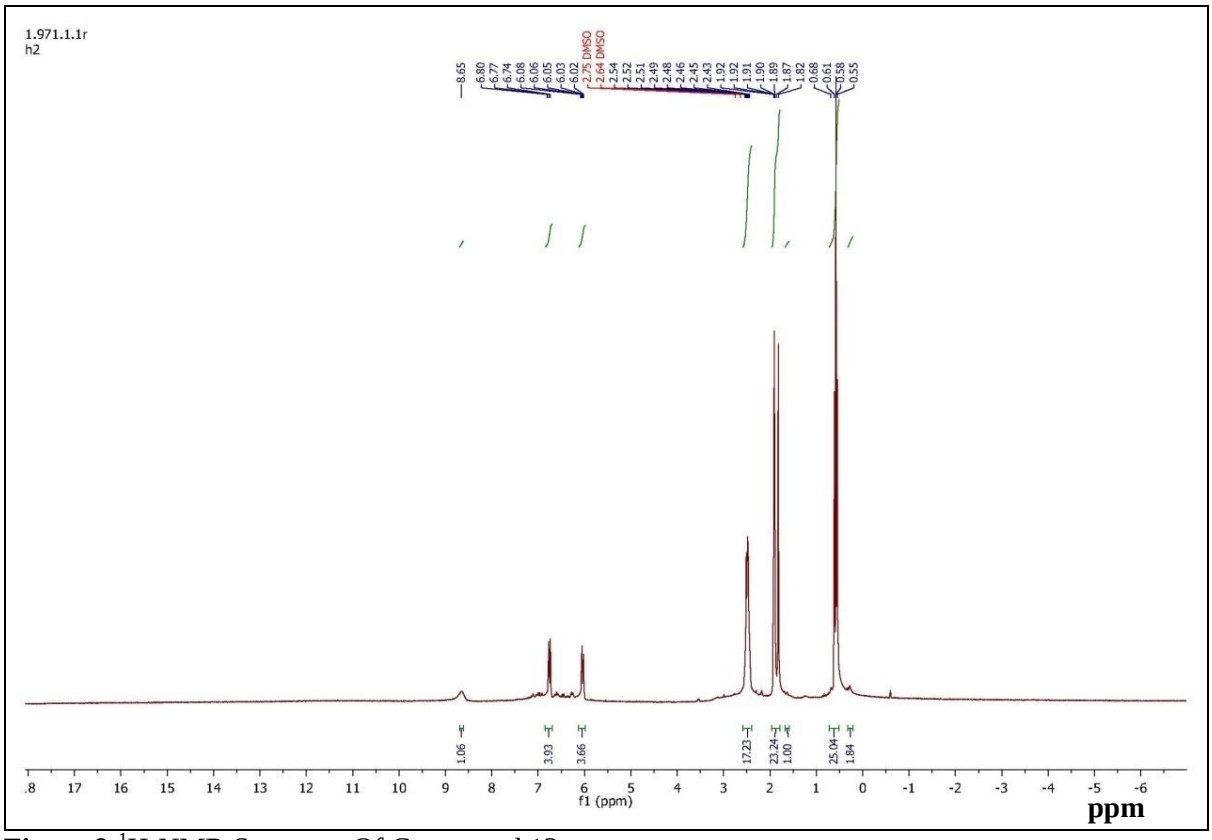


Figure 9-^{1}H-NMR Spectrum Of Compound 13

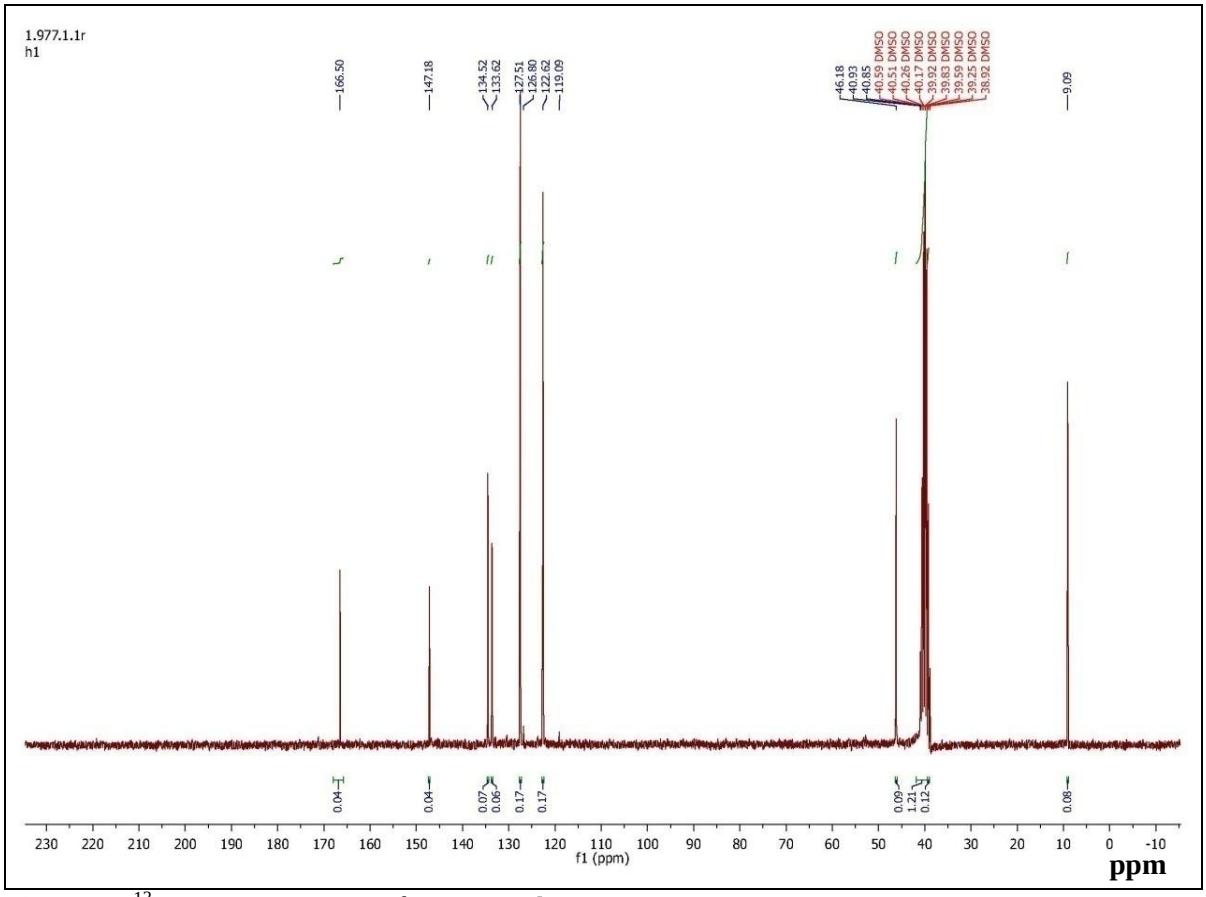


Figure 10-^{13}C-NMR Spectrum Of Compound 2

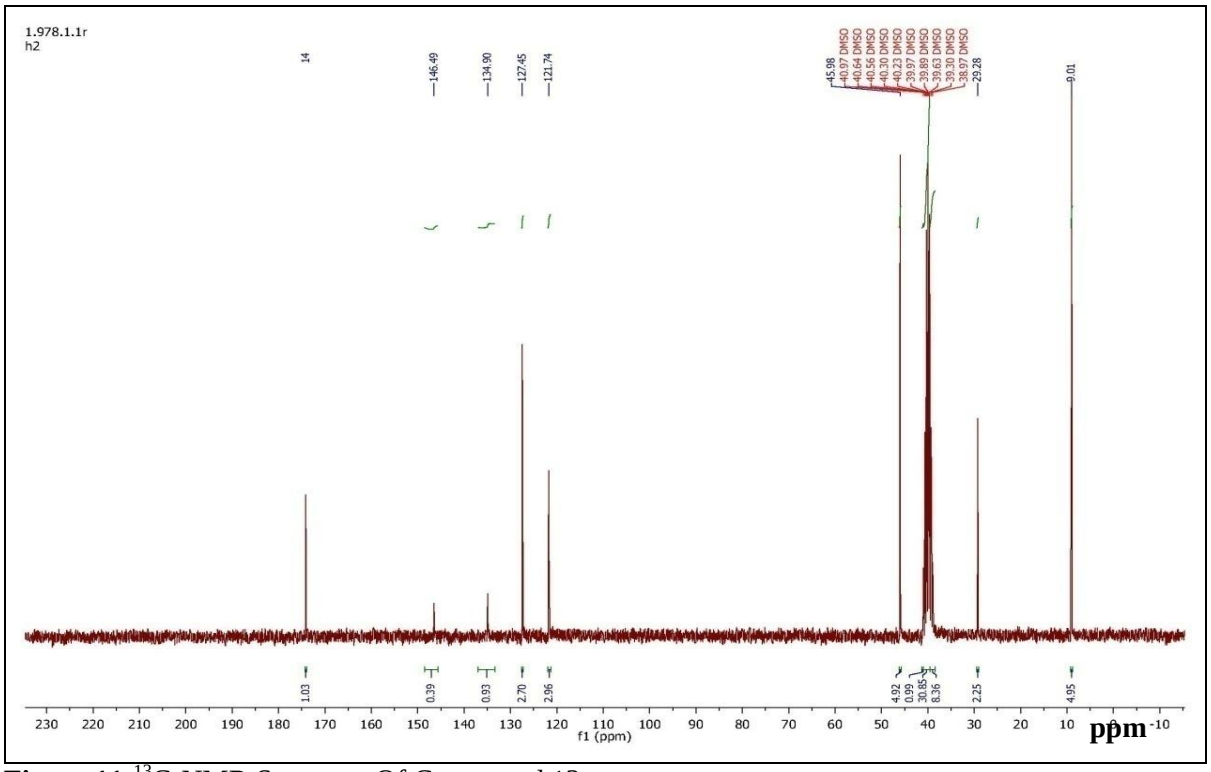


Figure 11-^{13}C-NMR Spectrum Of Compound 13

The thermal analysis was conducted at temperatures (20-40)ºC with heating rate 20.0 ºC/min. in 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 figures-12, 15.

Table 7 - TGA and DTG of some of the prepared poly diimides

Comp. No.	Compound structure	10% wt Loss temp ºC	50% wt Loss temp ºC	100% wt Loss temp ºC
23		190.69	420	825
26		186.76	397.67	830
28		218.39	392.27	840
30		209.3	414.1	845

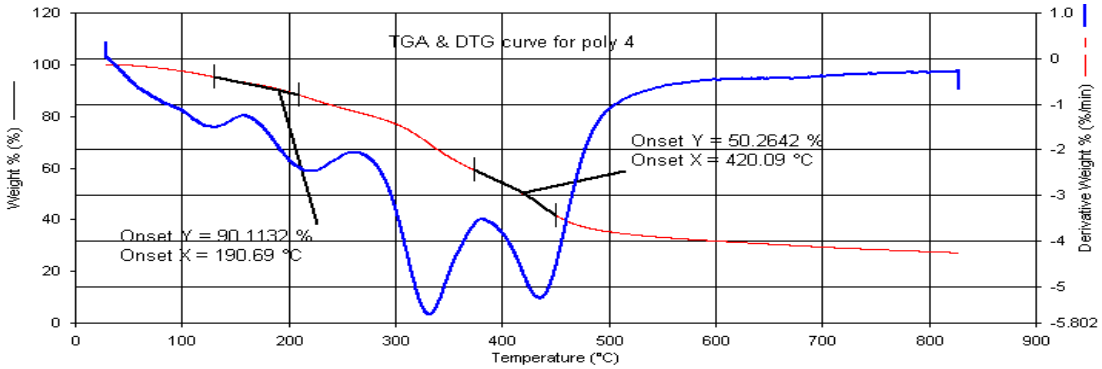


Figure 12-TGA And DTG Of Polymer 23

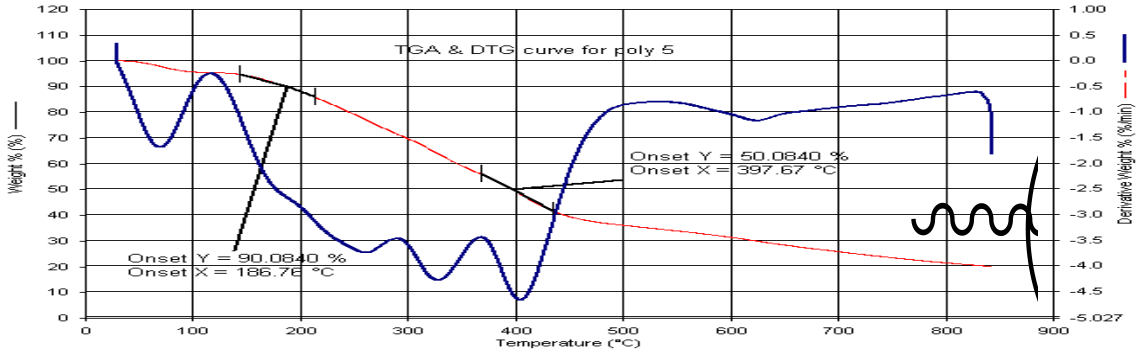


Figure 13-TGA And DTG Of Polymer 26

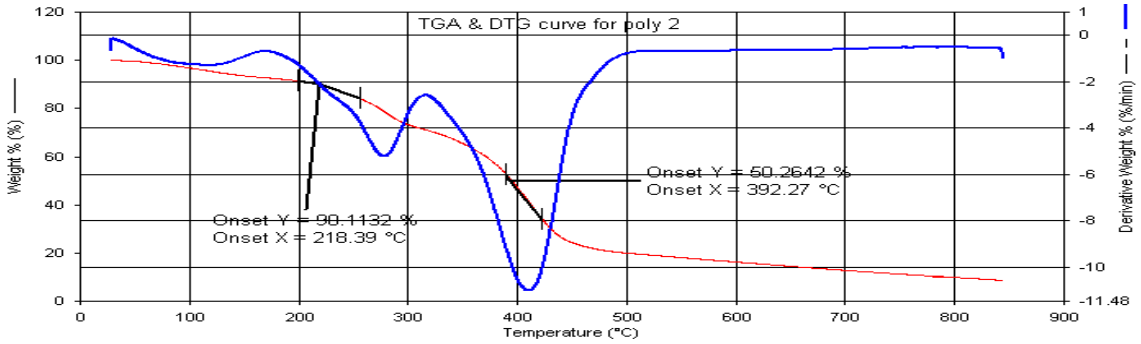


Figure 14-TGA And DTG Of Polymer 28

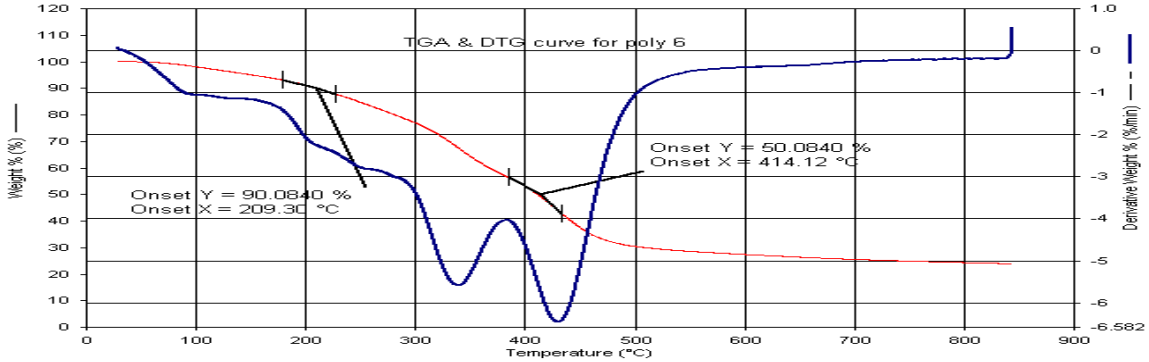


Figure 15-TGA And DTG Of Polymer 30

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