Synthesis of N-benzothiazole derivative imide on polymeric chain, have possible biological activity

Entesar O.AL-Tamimi[*] , *Mohmoud A-AL-Issa*[**]
*Hind F-AL-Gburi***

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Abstract:

In this reserch Some new substituted and unsubstituted poly imides compounds. were synthesized by reaction of acrylol chloride with different amides (aliphatic and aromatic) in a suitable solvent in the presence amount triethyl amine (Et_3N) with heating. The Structure confirmation of all polymers were confirmed using FT-IR,^{1}H-NMR,^{13}C-NMR and UV spectroscopy. Thermal analysis (TG) for some polymers showed their thermal stabilities. Other physical properties including softening points, melting point and solubility of the polymers were also measured

Key word: 2-aminobenzothaizol,acrylol chloride.

Introduction:

A heterocyclic compound is one which possesses a cyclic structure with at least two different kinds of hetero atoms in the ring. Nitrogen, oxygen and sulphur are the most common hetero atoms. Benzothiazole is a heterocyclic compound, weak base, having varied biological activities and still of great Scientific interest nowa days. They are widely found in bioorganic and medicinal chemistry with application in drug discovery[1]. Benzothiazole moieties are part of compounds showing numbering biological activities such as antimicrobial [2-6], anticancer [7-11], antilmintic and anti-diabetic activities. Polyimides have been widely used as high temperature insulators and dielectrics, coatings, adhesives and materials in a variety of advanced technologies related to microelectronics, where miniaturization and large-scal integration are important technical issues [13-14]. Then high thermal stability and balanced mechanical and electrical properties [15-17]. Polyimides are mainly used in the aerospace and electronics industries in the form of film and mouldings, but high melting point and insolubility in organic solvent limited their [18-20], application. furthermore,few successful attempts have been made to convert or modify some specific N-substituted imide to serve as ion exchange resins, such as cross linked poly[N-phenyl maleimide] which was prepared by free radical polymerization of the corresponding imide in benzene. The precipitated polyimides were hydrolyzed to obtain some pendant carboxylic groups on the polymeric chains. The last compounds were found to be useful cationic [21] exchange resins of good capacities.

Materals and Methods:

General

1. Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus.
2. FT-IR spectra were recorded using solid KBr discs by testing

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[*] Department of Chemistry, College of Science, University of Baghdad, Iraq
[**] Department of Chemistry, College of Science for Woman, University of Baghdad, Iraq

Shimadzu FT-IR 8000 series Fourier transform, infrared spectrophotometer.

3. Thermal analyses were performed using thermal analysis system consisting from TG_{50} Shimadzu, Japan. Ibn Sina in Iraq.
4. ^{1}H-NMR and ^{13}C-NMR spectra. Company Bruker, model ultra shield 300MHz, were made at the Chemistry Department, Al-Albyt University, Jordan.

1. Preparation of 2-aminobenzothiazole Derivatives[22, 23]

In a 250 ml round bottomed flask equipped with a magnetic bar stirrer and dropping funnel, a solution of bromine (1.2 ml) in glacial acetic acid (75 ml) was allowed to run through the dropping funnel drop wise during 30 min. To a mixture of Para substituted aromatic amine (0.03 mol) and ammonium thiocyanate (0.1 mol) in 150 ml glacial acetic acid with stirring. The mixture was stirred for 1 hr., then diluted with water and neutralized with solid sodium hydroxide. The precipitated substance was filtered, triturated and recrystallized from a suitable solvent to obtain 2-amino benzothiazole derivatives. The physical properties of the synthesized compounds are given in Table (1).

2. General Procedure Preparation of 2-[N-(sub or unsub benzoyl and sub or unsub acetyl)amidyl sub benzothiazole]

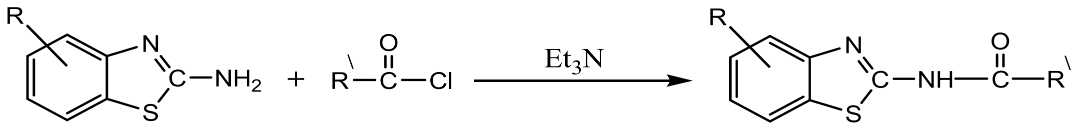
In a round bottom flask equipped with a magnetic bar stirrer and reflux condenser was placed a mixture of sub-benzoyl chloride (0.06 mol) and (0.06 mol) 6-sub-2-aminobenzothiazole with (3) drops of triethyl amine (Et_3N) in (25 ml) of suitable solvent (Benzene) and refluxed (1-3) hrs after the solvent was removed and recrystallized from ethanol.

3. General Procedure Preparation of Poly 2-(N-acryl-N-sub or unsub benzoyl) imidyl Substituted Benzothiazole

In a round bottom flask equipped with a magnetic bar stirrer was placed a mixture of poly (acryloyl chloride) (0.06 mol) and (0.06 mol) of 2-N-sub amidyl-sub benzothiazole with (1 ml) of triethyl amine (Et_3N) in (25 ml) of suitable solvent (THF or DMF) and refluxed for (5-7) hrs. after cooling and removed the solvent. The solid separated was filtered and purified by dissolving at DMF or DMSO and re precipitating from water or acetone. This procedure was applied on compounds as shown in Table (1). All physical properties are listed in Table (1).

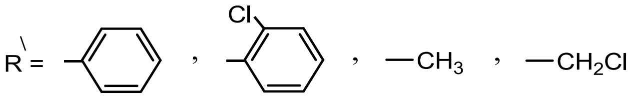
Results and Discussion:

Preparation of [2-(N-benzoyl) amidyl sub benzothiazole]

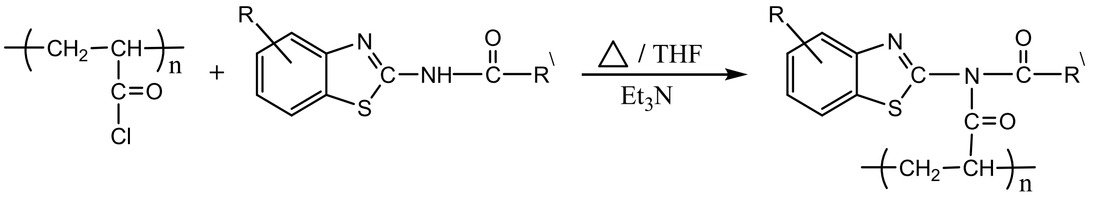


[A]

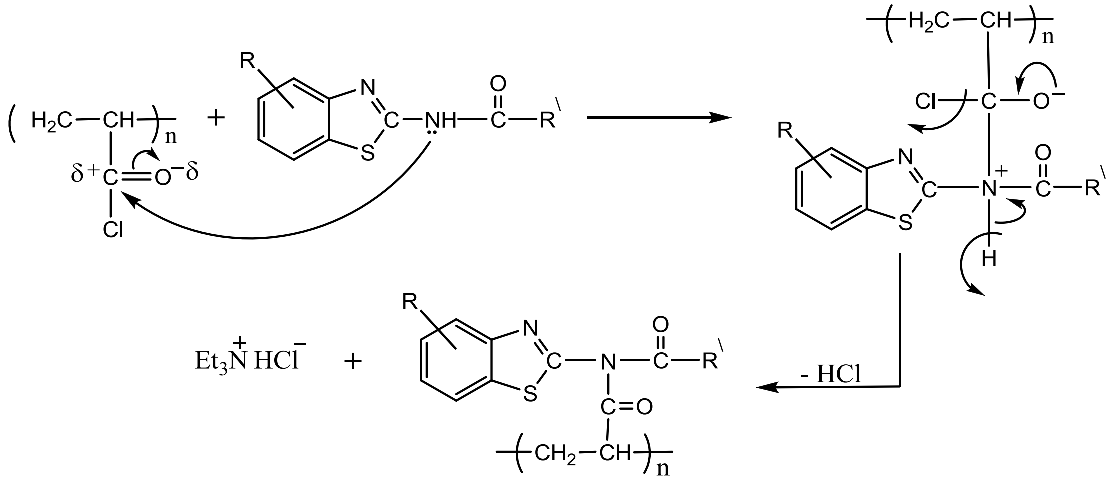
R = CH_3 , NO_2 , Cl



All poly [2-(N-acryl-N-benzoyl) imidyl substituted benzothiazole. were prepared by the reaction of poly (acryloyl chloride) with different amides . in presence of triethyl amine (Et_3N) as a catalyst [24].All these compounds characterised by (FT.IR,UV,and softing point),Table(1).

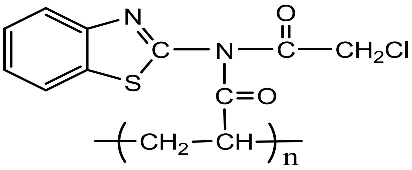
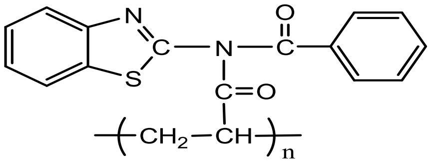
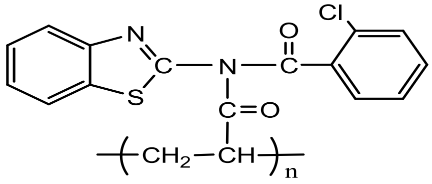
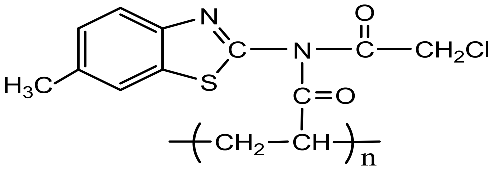
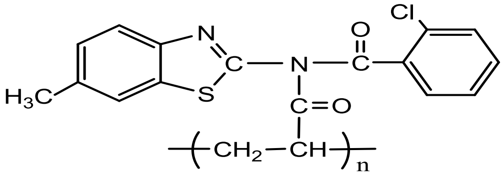
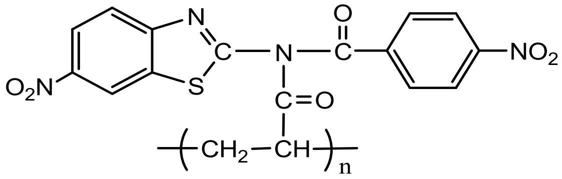
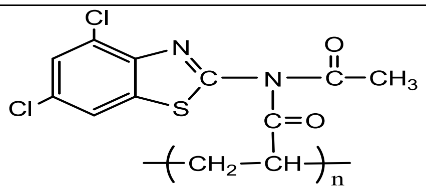


The mechanism of reaction involves a nucleophilic attack on the carbonyl as shown below [25].



Structures confirmation of all prepared polymer proved using FT-IR, UV, ^{1}H-NMR, ^{13}C-NMR, TG and physical properties including softening point, solubility, Tg and percent conversion of the polymers. FT-IR spectrum of compounds showed the same bands appearance. Stretching band at 1670cm^{-1} ν(C=O), (2800-2920)cm^{-1} ν(C-H) aliphatic, (1590-1630)cm^{-1} ν(C $\overset{---}{=}$ C) and (3010-3100)cm^{-1} ν(C-H) aromatic as shown Table (2).^{1}H-NMR spectrum of polymers [3,4,5] showed the signals at δ(1.2) (t, 2H,), δ(3.1) (m, 1H,) while a signal at δ(7-8) (d or m, 1H, Ph-$\underline{H}$) and δ1.02 (s, 3H, Ph-C$\underline{H_3}$), as shown listed in Table (3). The ^{13}C-NMR spectrum of compound showed the signal at (170-180)ppm for carbonyl group (C=O) and appeared at (120-140)ppm and appeared at (20-50.48)ppm. UV spectrum of compounds absorption λ_{max} at 300nm and 380nm which attributed to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions. See Table (4). TG analysis provides a change in the mass of the polymer during heating. The thermal analysis was carried out at temperatures (200-400)ºC with heating rate 20.0 ºC/min. in N_2 atmosphere. Thermal stability of the product was estimated from TG and DTG thermograms. See Table (5), it was found that the prepared polymers high stability, resists to isomerization by heat, light or using acidic or basic solution[26,27].

Table (1): Physical properties of the poly imide

Comp. No.	Compound structure	Conversion %	Softing point °C	Color	Solvent used in reaction
1	 Poly [2-(N-acryl-N-chloroacetyl) imidyl benzothiazole	75	120-135	Brownish yellow	THF or DMF
2	 Poly [2-(N-acryl-N-benzoyl) imidyl benzothiazole	80	120-135	Brownish yellow	THF or DMF
3	 Poly [2-(N-acryl-N-2-chlorobenzoyl) imidyl benzothiazole	82	125-140	Brownish yellow	THF or DMF
4	 Poly [2-(N-acryl-N-chloroacetyl) imidyl-6-methyl benzothiazole	78	112-125	Light yellow	THF or DMF
5	 Poly [2-(N-acryl-N-2-chlorobenzoyl) imidyl-6-methyl benzothiazole	85	120-132	Light yellow	THF or DMF
6	 Poly [2-(N-acryl-N-4-nitrobenzoyl) imidyl-6-nitro benzothiazole	80	200-205	Light yellow	THF or DMF
7	 Poly [2-(N-acryl-N-acetyl) imidyl-4,6-di-chloro benzothiazole	78	85-100	Light yellow	THF or DMF

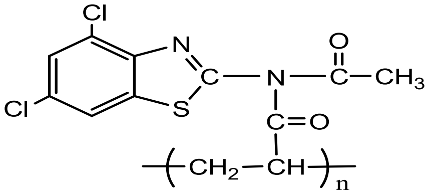
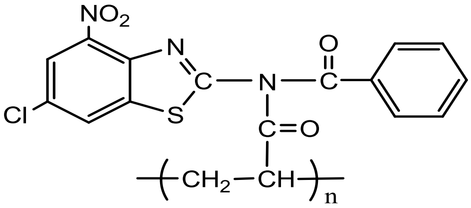
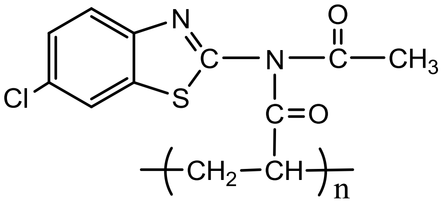
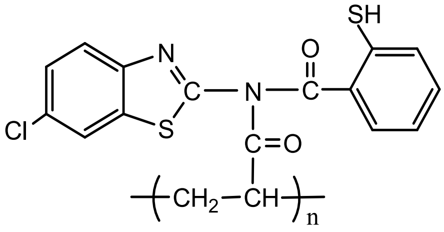
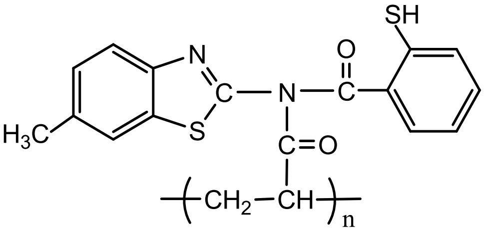
Comp. No.	**Compound structure**	**Conversion %**	**Softing point °C**	**Color**	**Solvent used in reaction**
8	 Poly [2-(N-acryl-N-acetyl) imidyl-2,4-di-chloro benzothiazole	70	170-180	Light yellow	THF or DMF
9	 Poly [2-(N-acryl-N-benzoyl)imidyl -4-nitro-6-chloro benzothiazole	85	95-105	Brown	THF or DMF
10	 Poly [2-(N-acryl-N-acetyl) imidyl-6-chloro benzothiazole	87	125-142	Brown	THF or DMF
11	 Poly [2-(N-acryl-N-2-mercaptobenzoyl) imidyl-6-chloro benzothiazole	85	170-180	Brown	THF or DMF
12	 Poly [2-(N-acryl-N-2-mercaptobenzoyl) imidyl-6-methyl benzothiazole	82	130-140	Light yellow	THF or DMF

Table (2): FT-IR spectra of the prepared heterocyclic polyimide

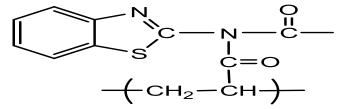
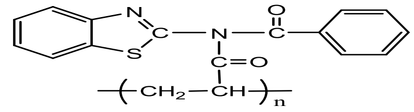
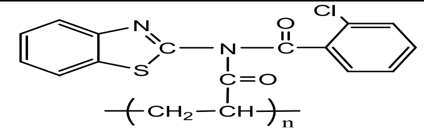
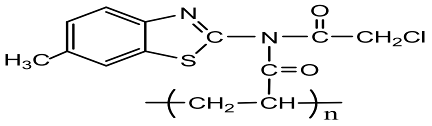
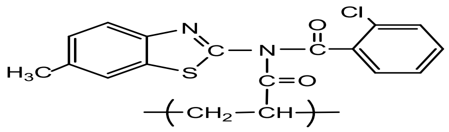
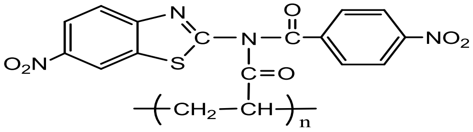
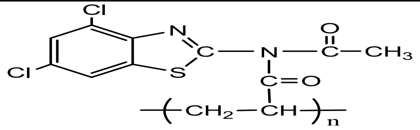
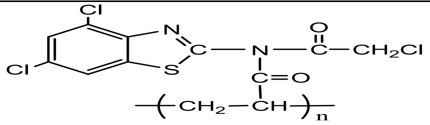
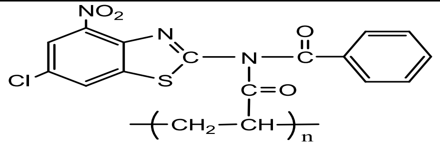
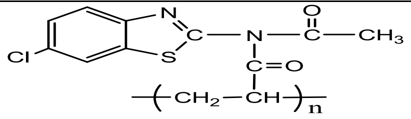
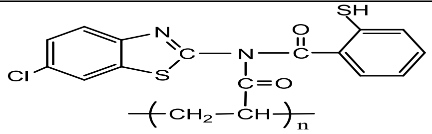
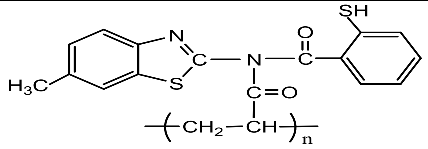
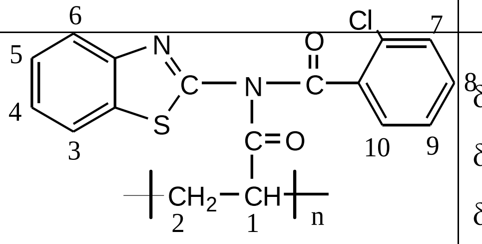
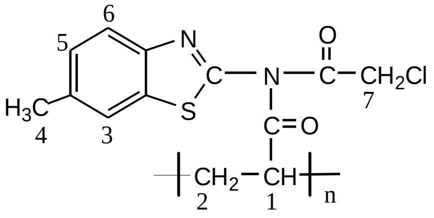
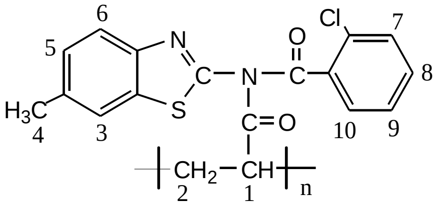
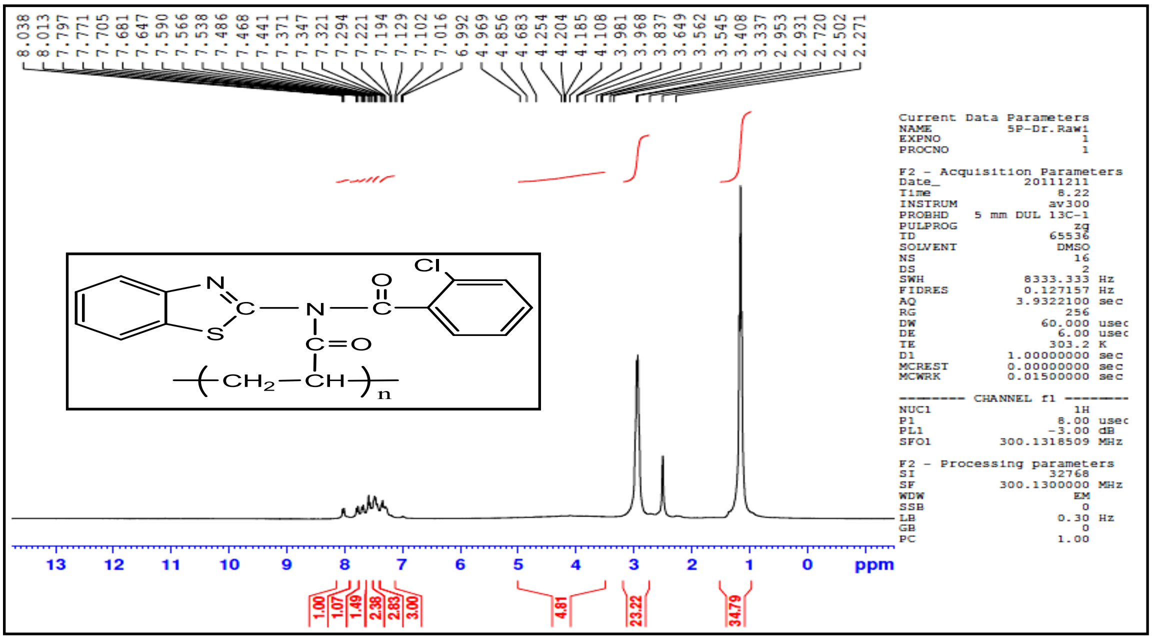
Comp. No.	**Compound structure**	**FTIR spectral data cm^{-1}**							
		ν(C=O) imide	**ν(C-N) imide**	**ν(C=C) aromatic**	**ν(C-H) aliphatic**	**ν(C-H) aromatic**	**ν(C=N) imine**	**ν(C-S)**	**Others**
1		1697	1410	1590	2900 2970	3010	1500	680	C-Cl 1010
2		1690	1420	1610	2905 2975	3000	1520	700	-
3		1685	1460	1600	2900	3000	1510	650	C-Cl 1000
4		1690	1400	1640	2890 2920	3100	1550	700	C-Cl 1005
5		1682	1480	1610	2945	3100	1500	650	C-Cl 1010
6		1685	1440	1640	2900	3010	1520	600	C-Cl 1100
7		1699	1400	1640	2945 2980	3020	1550	779	C-Cl 1157
8		1716	1431	1635	2947 2975	3074	1535	779	C-Cl 1157
9		1708	1400	1543	2943 2978	3100	1543	750	C-Cl 1037 $C-NO_2$ 1346
10		1695	1410	1600	2945 2985	3105	1540	650	C-Cl 1020
11		1697	1446	1636	2943 2978	3062	1535	763	C-Cl 1037
12		1700	1430	1620	2949 2980	3010	1510	610	-

Table (3): The ^{1}H-NMR chemical shifts of some of the prepared poly heterocyclic imides

Comp. No.	Compound structure	Chemical shifts
3		δ1.2 (t,2H^2, $-\!(\underline{H_2}C-CH)_n-$); δ3.01 (m, 1H^1, $-\!(H_2C-C\underline{H})_n-$); δ7-8 (m, HAr)
4		δ1.1 (s, 3H^4); δ1.1 (t, 2H^2, $-\!(\underline{H_2}C-CH)_n-$); $-\!(H_2C-C\underline{H})_n-$ δ3.1 (m,1H^1,); δ4.5 (s, 2H^7); δ7-8 (m, HAr)
5		δ1.2 (s, 3H^4); δ1.2 (t, 2H^2,$-\!(\underline{H_2}C-CH)_n-$); δ3 (m,1H^1, $-\!(H_2C-C\underline{H})_n-$); δ7-8 (m, HAr)



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PROCNO                     1

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PULPROG                   zg
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                 8333.333 Hz
FIDRES              0.127157 Hz
AQ                 3.9322100 sec
RG                       256
DW                    60.000 usec
DE                      6.00 usec
TE                     303.2 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.00 usec
PL1                    -3.00 dB
SFO1             300.1318509 MHz

F2 - Processing parameters
SI                     32768
SF               300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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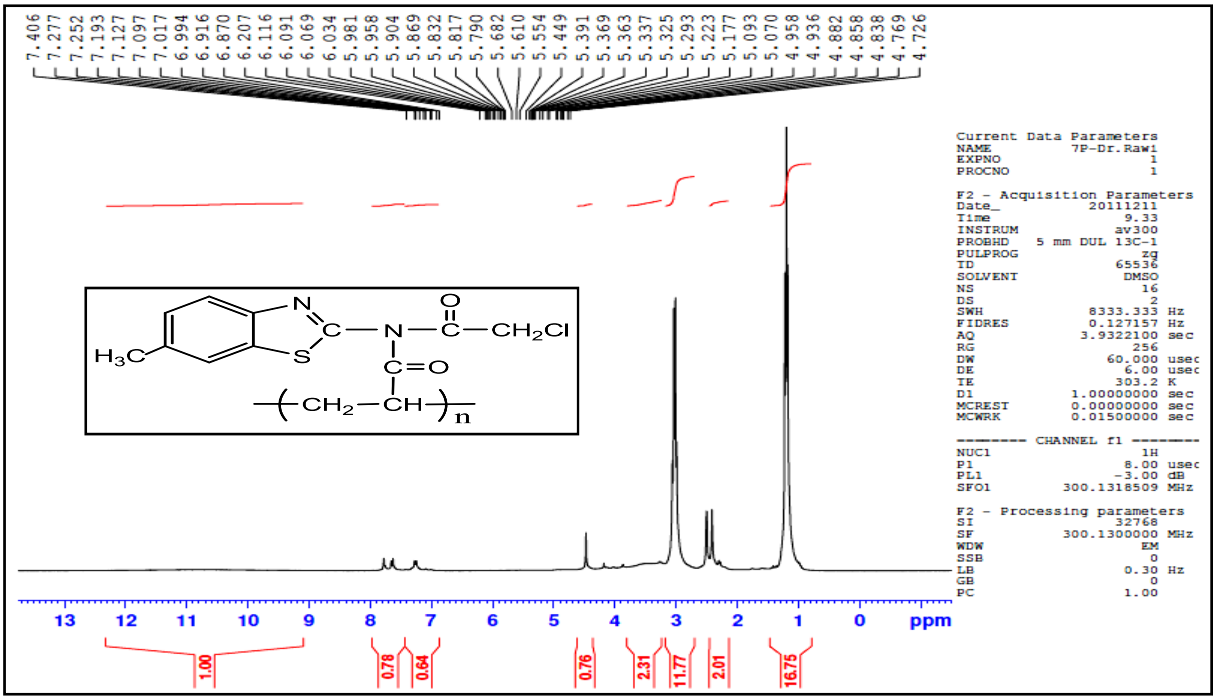
Fig.(1): ^{1}H-NMR for compound[3]



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PROCNO                 1

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TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
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FIDRES          0.127157 Hz
AQ             3.9322100 sec
RG                   256
DW                60.000 usec
DE                  6.00 usec
TE                 303.2 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                -3.00 dB
SFO1         300.1318509 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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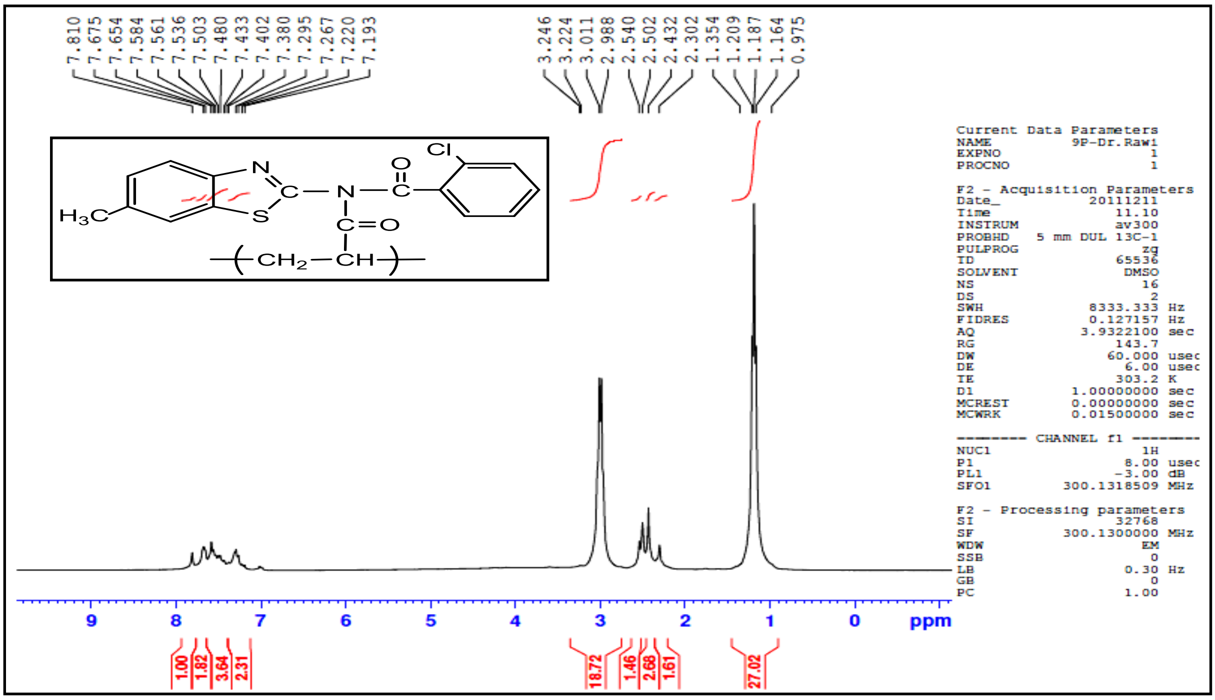
Fig.(2): ^{1}H-NMR for compound[4]



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EXPNO                  1
PROCNO                 1

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PULPROG               zg
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8333.333 Hz
FIDRES          0.127157 Hz
AQ             3.9322100 sec
RG                 143.7
DW                60.000 usec
DE                  6.00 usec
TE                 303.2 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                -3.00 dB
SFO1         300.1318509 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Fig.(3): ^{1}H-NMR for compound[5]

Table (4): UV spectra of the prepared heterocyclic polyimide

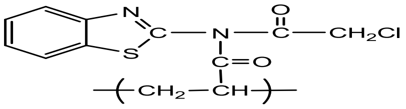
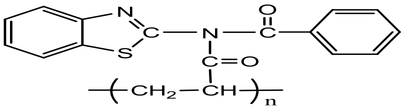
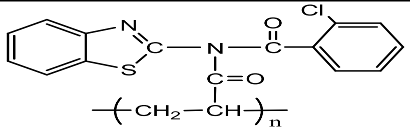
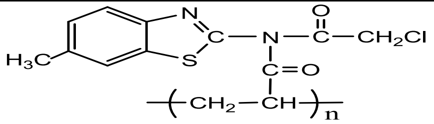
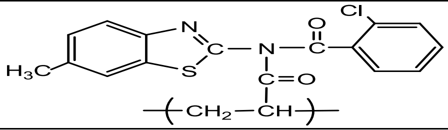
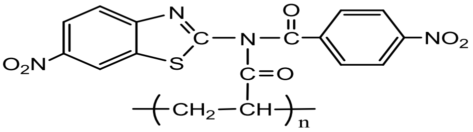
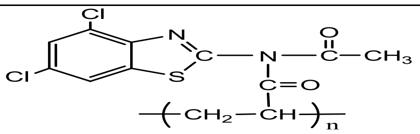
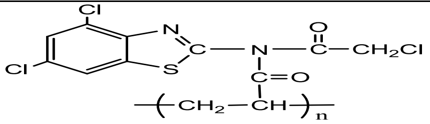
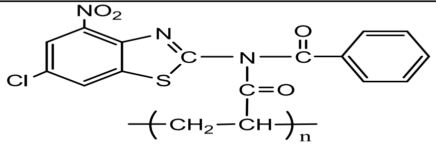
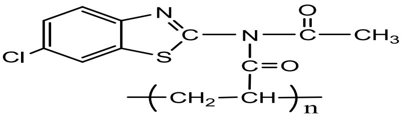
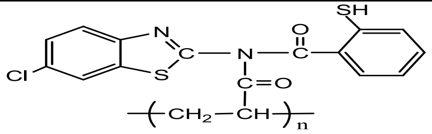
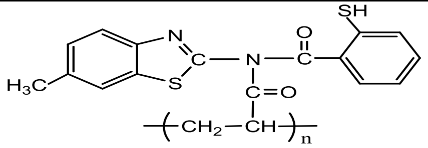
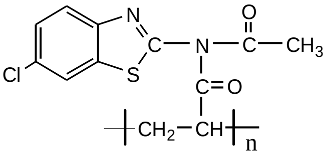
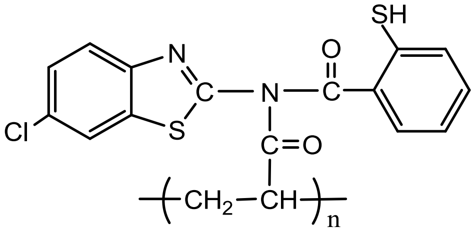
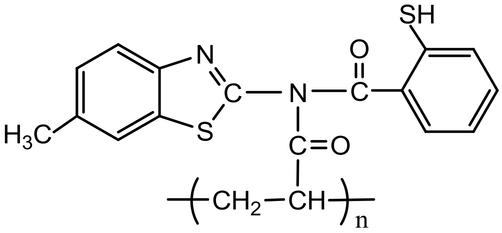
Comp. No.	Compound structure	Peak	
		λ_{max} nm	ABC
1		301	1.336
2		317 459.5	1.362 0.035
3		370	1.22
4		303.5	1.724
5		317	1.272
6		435.5 361.0	0.716 1.099
7		315	2.298
8		303.5 248	0.752 0.053
9		409.5 303	0.76 0.913
10		305	1.747
11		315.5 454	1.195 0.068
12		316 449.5	1.225 0.01

Table (5) : TG of some of the prepared poly heterocyclic imides

Comp. No.	Compound structure	10% wt Loss temp °C	50% wt Loss temp °C	Peak 1 Temp °C	Peak 2 Temp °C
10		177.39	266.63	180.9	253 392
11		175.21	341.7	279.95	339 384.8
12		189.65	269	236	286.8 377.9

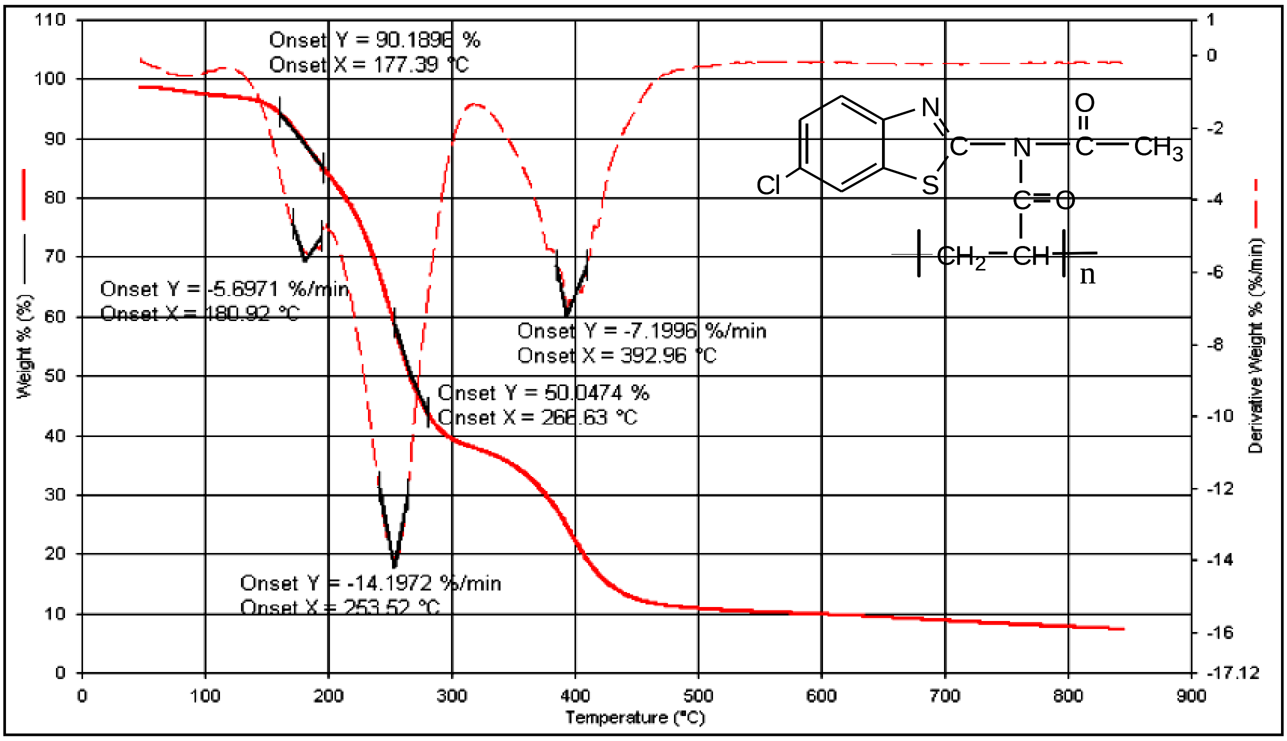


Fig.(4): TG for compound[10]

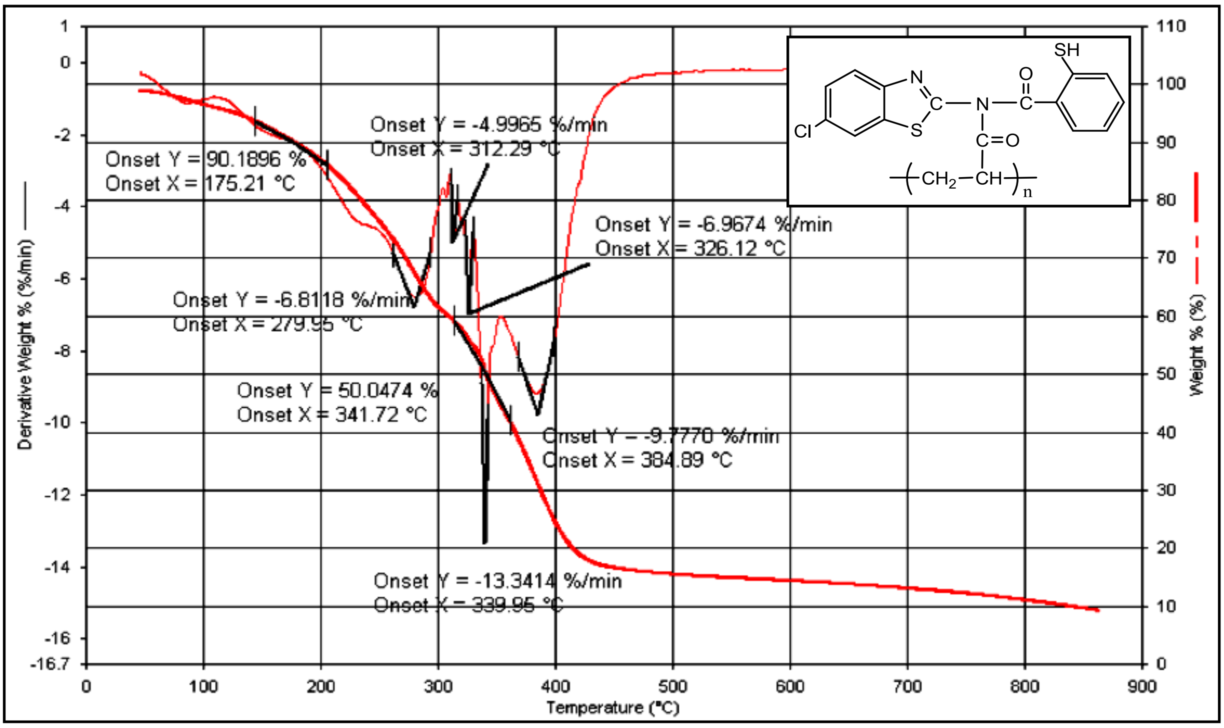


Fig.(5): TG for compound[11]

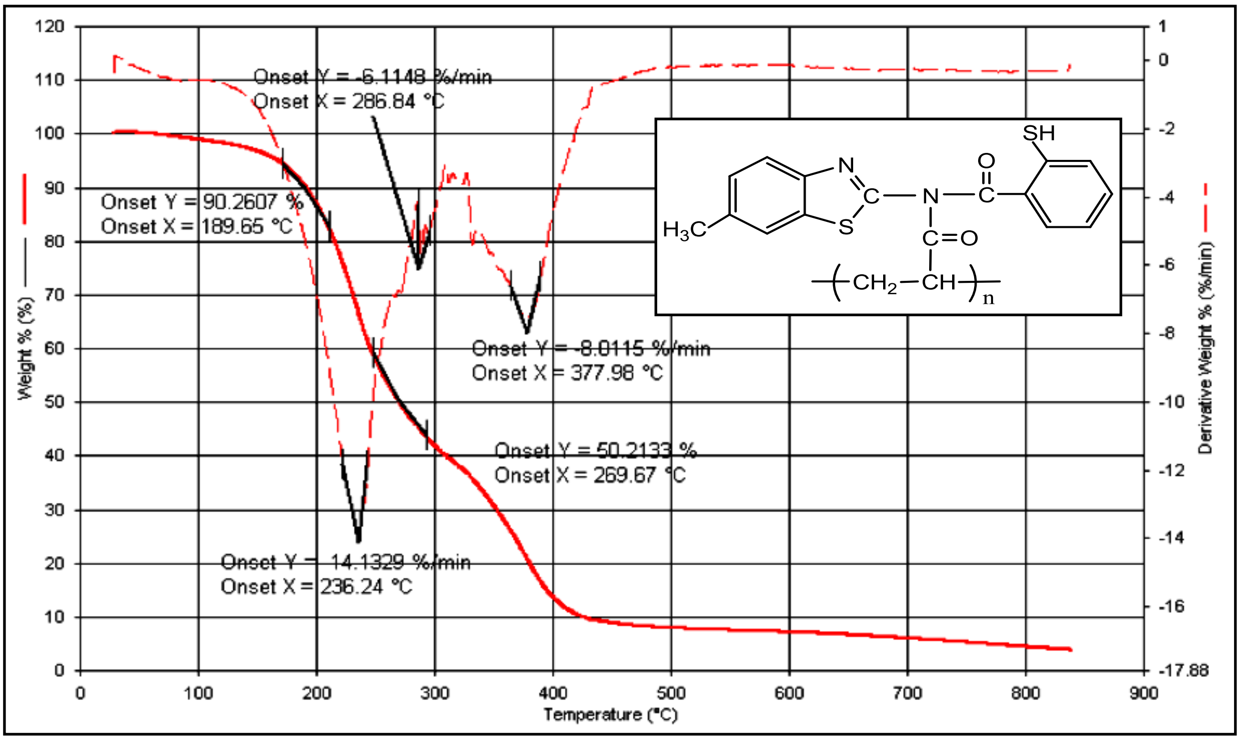


Fig.(6): TG for compound[12]

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(تحضير مشتقات ن _بنزوثايازول ايمايدعلى السلسله البوليمريه ،ذات فعاليه بايولوجية متوقعه)

انتصار عبيد التميمي [*]   ***محمود العيسى*** [**]   ***هند فاضل الجبوري*** [**]

*كلية العلوم –قسم الكيمياء ،
**كلية العلوم للبنات-قسم الكيمياء

الخلاصة:

في هذا البحث حضر بولي ايمايدات جديدة معوضة وغير معوضة من تفاعل بولي كلوريد الاكريلويل مع امايدات مختلفة (اليفاتية ، اروماتية) بوجود مذيب مناسب وكمية مناسبة من ثلاثي مثيل امين (Et_3N) مع التسخين. وتم اثبات التراكيب الكيميائية للبوليمرات المحضرة باستخدام الطرق الطيفية، اطياف الاشعة تحت الحمراء FT-IR، اطياف الرنين النووي المغناطيسي ^{1}H-NMR، اطياف ^{13}C-NMR واطياف الاشعة فوق البنفسجية UV كما تم التعرف على استقرارية بعض البوليمرات المحضرة حرارياً عن طريق التحاليل الحرارية بالاضافة الى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والذوبانية