Synthesis, polymeric and studied new derivative 2-aminobenzothiazole imide

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Abstract— Prepared new substituted and unsubstituted poly imides compounds from using reaction of acrylol chloride with different amides (aliphatic, aromatic) in the presence of a suitable solvent and amount triethyl amine (Et3N) with heating. The Structure confirmation of all polymers were provide using FT-IR,1H-NMR,13C-NMR and UV spectroscopy. Thermal analysis (TG) for some polymers confirmed their thermal stabilities. Other physical properties including softening points, melting point and solubility of the polymers were also measured.

Index Terms— *Synthesis, polymeric, aminobenzothiazole*

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1 INTRODUCTION

Benzothiazole is a privileged bicyclic ring system. Due to its potent and significant biological activities it has great pharmaceutical importance, hence, synthesis of this compound is of considerable interest[1]. Also it has been found that 2-substituted benzothiazole have good potential to exhibit anti-cancer activity[2,3,4]. Acryloyl chloride are polymerized easily to linear polymer if they are carefully protected from oxygen and water before and during polymerization of acryloyl chloride is readily accomplished in bulk at room temperature by exposure to ultra-violet light in quartz tubes[5]. Poly imides have become one of the most important and versatile classes of high performance polymer[6] due to excellent mechanical and thermal properties. Aromatic heterocyclic imides of important in preparing of most commercial polyimides. In 2001[7] advanced research was published in the field of aerospace application. The research was carried by Connell. J. W and Watson KA. Through the preparation a space environmentally stable polyimides with a unique combination of properties including pale color in thin films, atomic oxygen resistance. UV- radiation resistance, solubility in organic solvents in the imide from high glass transition Tg temperature and high thermal stability by reacting novel aromatic diamine, bis(3-aminophenyl)-3,5-di(triflouromethyl) phenyl phosphine oxide with various aromatic di anhydrides in a polar aprotic solvent. Potentially use full in a variety of applications of space craft such as thin film membranes an antennae second surface mirrors, thermal, optical cotings and multi-layer thermal insulation materials blanket.

1.1 EXPERIMENTAL:

Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus. FT-IR spectra were recorded using solid KBr discs by testing Shimadzu FT-IR 8000 series Fourier transform, infrared spectrophotometer. Thermal analyses were performed using thermal analysis system consisting from TG50 Shimadzu, Japan. Ibn Sina in Iraq. 1H-NMR and 13C-NMR spectra. Company Bruker, model ultra shield 300MHz, were made at the chemistry department, Al-Albyt university, Jordan.

A) *Preparation of 2-aminobenzothiazole Derivatives[8,9]*
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 and starting material of the synthesized compounds are given in Table (1).

B) *General Procedure Preparation of 2-[N-(sub benzoyl)amidyl sub benzo thiazole]*
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 (Et3N) in (25 ml) of suitable solvent (Benzene) and refluxed (1-3) hrs. After the solvent was removed and recrystallized from ethanol.

C) *General Procedure Preparation of Poly 2-(N-acryl-N-sub 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 (Et3N) 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 is shown in Table (1). All physical properties are listed in Table (1).

2 RESULTS AND DISCUSSION

2.1 PREPARATION OF [2-(N-BENZOYL) AMIDYL SUB BENZOTHIAZOLE]

All compounds characteristics (m.p, FT-IR, UV and C.H.N). Preparation of poly [2-(N-acryl-N-benzoyl) imidyl substituted benzothiazole. Table (1) polymer was prepared by the reaction of poly (acryloyl chloride) with different amides [A] in presence of triethyl amine (Et3N) as a catalyst [10].

The mechanism of reaction involves a nucleophilic attack on the carbonyl as in shown below [11].

Structures confirmation of all prepared polymer proved using FT-IR, UV, 1H-NMR, 13C-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 ----C) and (3010-3100)cm-1 ν(C-H) aromatic as shown Table (2).1H-NMR spectrum of polymers [7,9,11] showed the signals at δ(1.021) (t, 2H), δ(3-3.9) (m, 1H,) while a signal at δ(7-8) (d or m, 1H, Ph-H) for compounds[4,6,8] and at δ1.02 (s, 3H, Ph-CH3), as show listed in Table (3). The 13C-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 λmax at 300nm and 380nm which attributed to (π→π*) and (n→π*) 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 (20-40)°C with heating rate 20.0 °C/min. in N2 atmosphere. Thermal stability of the product was estimated from TG and DTG thermo grams. See Table (5), it was found that the prepared polymers high stability, resists to isomerization by heat, light or using acidic or basic solution[12,13].

Table (1): Physical properties of the poly imide

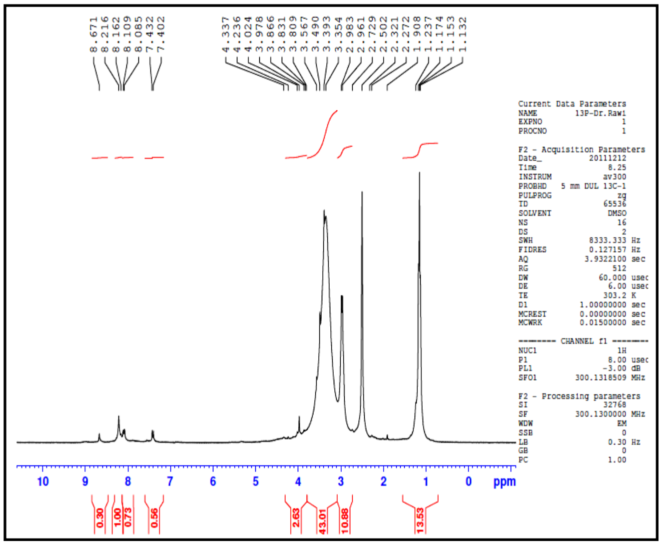
Comp. No.	Compound structure	Conversion %	Softing point °C	Colour	Solvent used in reaction
1		85.7	182-192	Brownish yellow	THF or DMF
2		84.9	170-185	Brownish yellow	THF or DMF
3		87.3	140-165	Light yellow	THF or DMF
4		80	135-148	Light Brown	THF or DMF
5		79.4	150-163	Light Brown	THF or DMF
6		84	190-202	Light yellow	THF or DMF
7		82	130-142	Light yellow	THF or DMF
8		84	210-220	Brown	THF or DMF
9		80	140-153	Brown	THF or DMF
10		81		Light yellow	THF or DMF
11		80	190-200	Light green	THF or DMF
12		85	130-140	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	1442	1600	2947 2978	3055	1546	640	-
2		1678	1442	1600	2947 2978	3035	1519	613	C-NO_2 1346
3		1693	1400	1600	2943 2978	3132	-	-	-
4		1678	1441	3174 1604	2943 2978	3174	-	613	-
5		1678	1446	1604	2943 2978	3186	-	609	C-NO_2 1346
6		1698	1400	1589	2920 2940	3070	-	610	C-NO_2 1350
7		1680	1400	1600	1920	3005	-	610	C-NO_2 1360
8		1690	1410	1602	2990	3030	-	620	C-NO_2 1340
9		1691	1392	1585 1600	2837 2900	3097	1591	584	C-Cl, C-NO_2 1037, 1444
10		1701	1300	1554 1581	2897 2823	3070	1554	651	C-Cl 1072
11		1681	1442	1585	2900 2950	3100	1539	610	C-Cl 1034
12		1690	1390	1600	2990 2980	3010	1530	610	C-Cl 1010 C-NO_2 1360

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

Comp. No.	Compound structure	Chemical shifts
4		δ1.03(s,3H⁴); δ3-3.5 (t, 2H², $\left(\underline{H}_2C-CH\right)_n$; δ4.2(m, 1H¹), $\left(\underline{H}_2C-CH\right)_n$; δ7-8 (m, HAr)
6		δ1.08(t, 2H⁶, $\left(\underline{H}_2C-CH\right)_n$); δ2.6(3H¹); δ3.4(m, 1H⁵, $\left(\underline{H}_2C-CH\right)_n$); δ7.4(d, 1H², HAr); δ7.9(d, 1H³, HAr); δ 7.9(s, 1H⁴, HAr)
7		δ1.18(t, 2H², $\left(\underline{H}_2C-CH\right)_n$; δ2.7(m,1H¹, $\left(H_2C-\underline{CH}\right)_n$); δ7.5(m,1H⁸, HAr); δ7.8(d, 1H⁷, 1H⁶, HAr); δ8(d, 1H¹⁰, 1H⁹, HAr); δ8.1(d,,1H⁵,HAr); δ8.26(d, 1H⁴, HAr); δ8.5(s, 1H³, HAr)
8		δ1.03(t, 2H⁶, $\left(\underline{H}_2C-CH\right)_n$); δ3.0(s,2H¹) δ3.5(m,1H⁵, $\left(H_2C-C\underline{H}\right)_n$); δ7.4(d, 1H³,HAr) δ8.1(d,H², HAr); δ8.3(s,1H⁴, HAr)
9		δ1.2(t,2H², $\left(\underline{H}_2C-CH\right)_n$); δ3.3(m,1H¹, $\left(H_2C-CH\right)_n$); δ(7.3-7.8)(d, H⁹, H⁶, HAr); δ7.8 (t, 1H⁷, 1H⁸, HAr); δ8.2(d, H⁵, HAr); δ8.3(d, H⁴, HAr); δ8.5(s, H³, HAr)



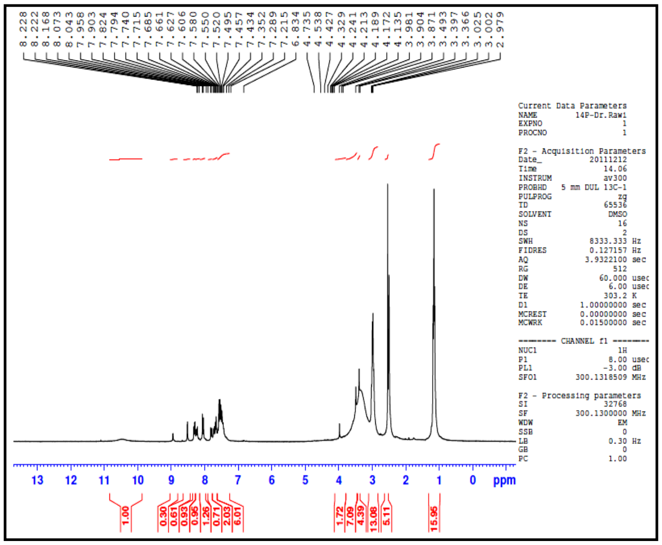


Fig.(1): 1H-NMR for compound [8]

Fig.(2): 1H-NMR for compound [9]

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

Comp. No.	**Compound structure**	**Peak**	
		λ_{max} (nm)	**ABC**
1		300.5	1.158
2		356.5	1.573
3		376.2	1.123
4		318.0	2.353
5		317.5	1.709
6		365.5	1.387
7		319.0	1.589
8		370.0	1.412
9		422.0	1.392
10		346.0	1.639
11		336.0	1.984
12		332.5	1.24

Comp. No.	Compound structure	10% wt Loss temp ºC	50% wt Loss temp ºC	Peak 1 Temp ºC	Peak 2 Temp ºC
1		217.2	341.75	250	389
2		207.77	298.66	245.2	393.15
3		178	260	256.9	287.2
11		206.77	224.3	235	314.6
12		212.67	377.1	271.7	237.15

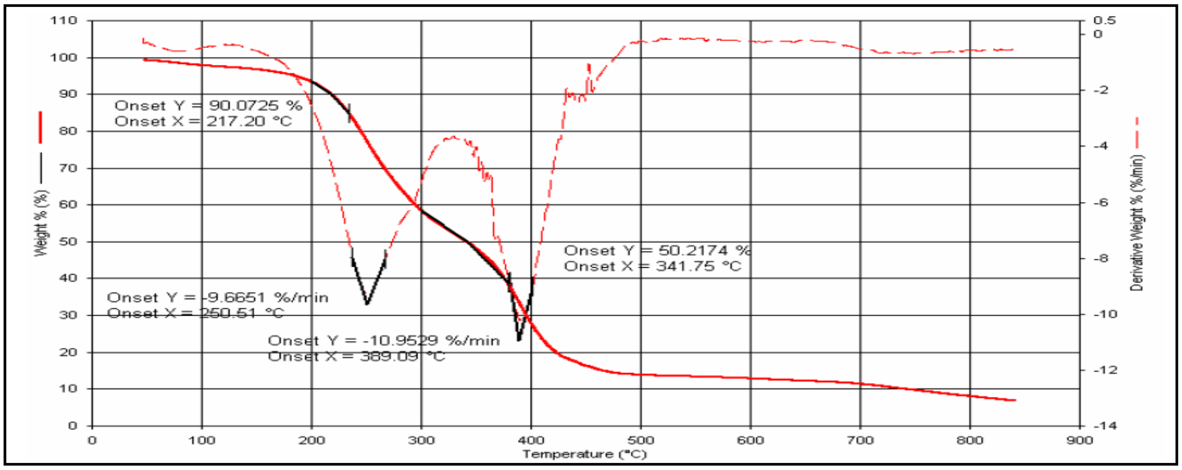


Fig.(3): TG for compound [1]

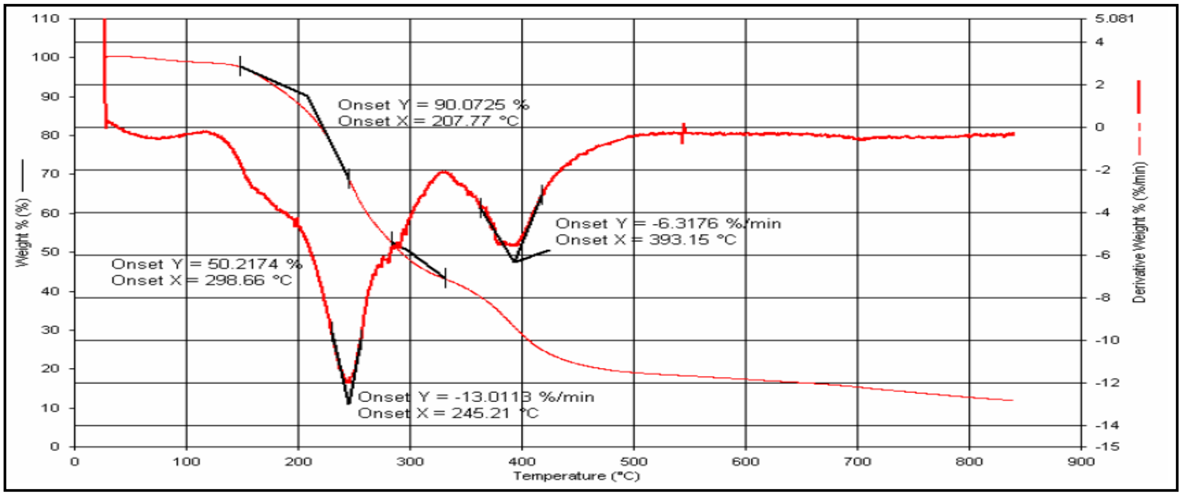


Fig.(4): TG for compound [2]

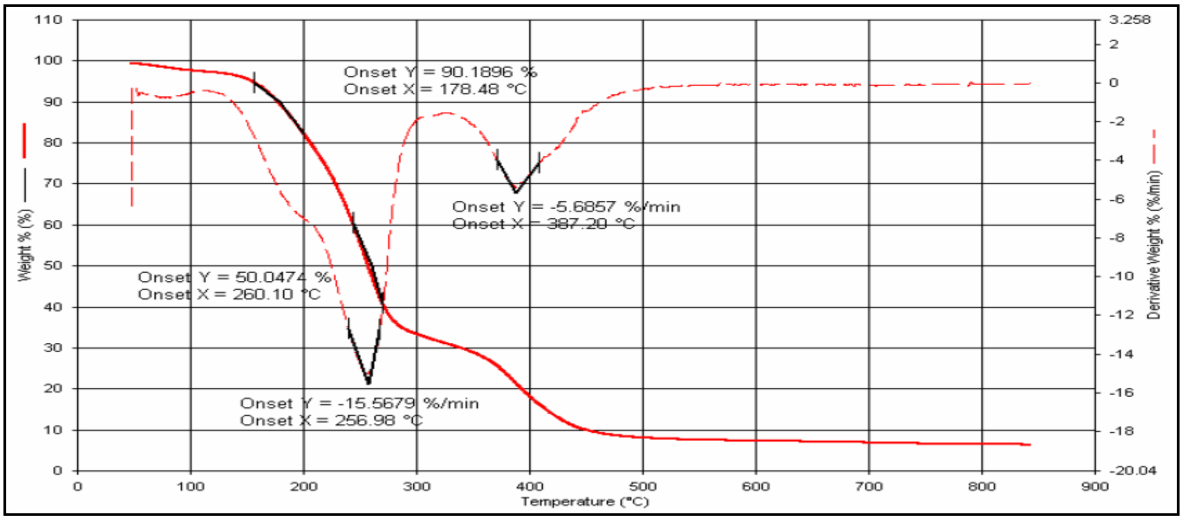


Fig.(5): TG for compound [3]

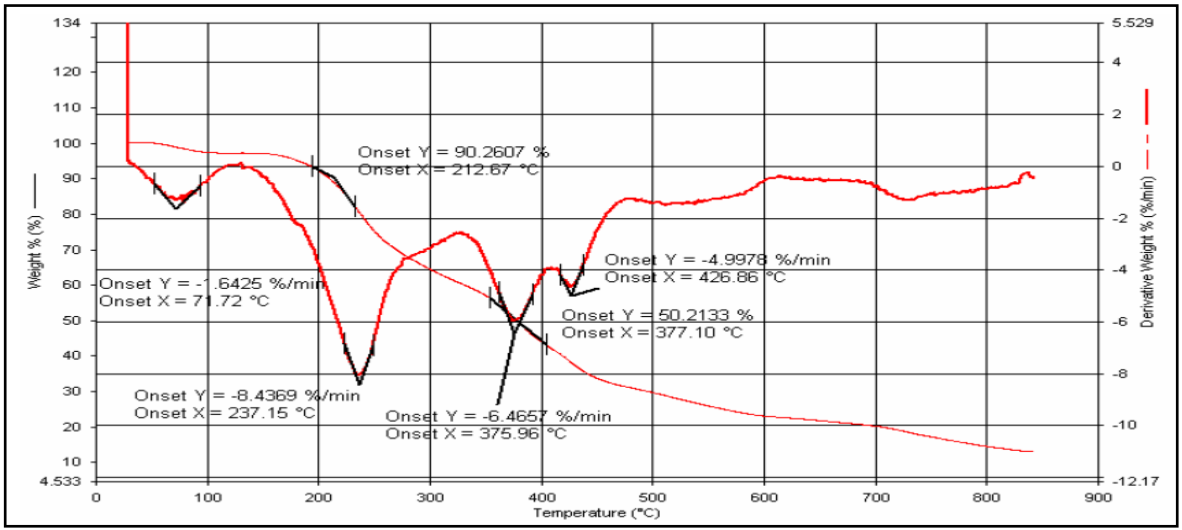


Fig.(6): TG for compound [11]

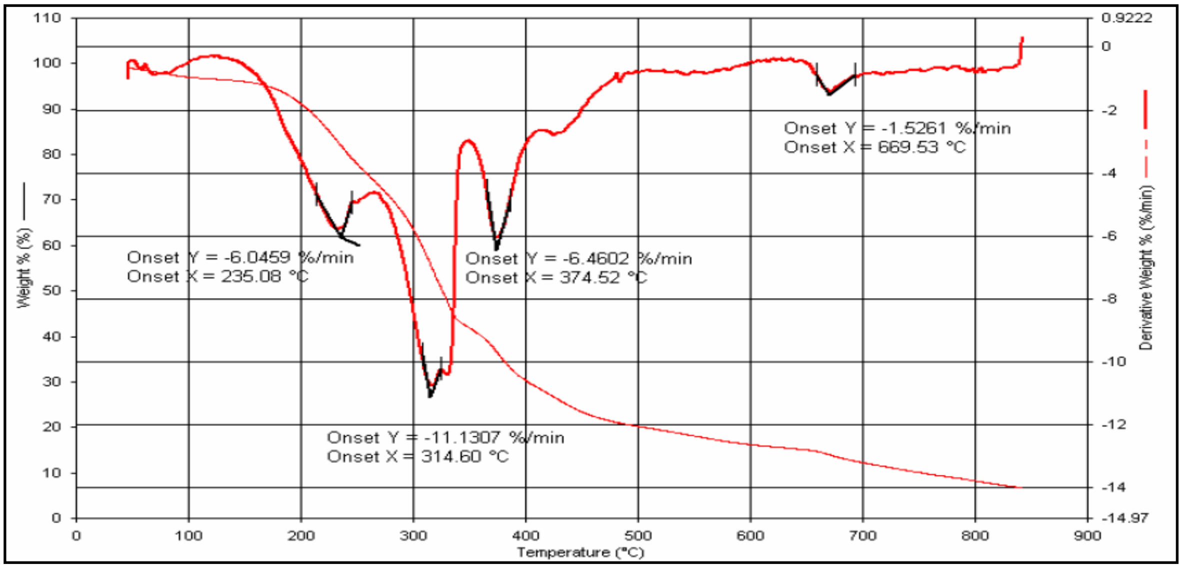


Fig.(7): TG for compound [12]

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