Synthesis and Characterization of New heterocyclic Polyacrylamides from Derivatives 2-Aminobenzothiazole

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Abstract:

The present work involved preparation of new hetro cyclic polyacrylamides (1-9) using reaction of polyacryloyl chloride with 2-aminobenzothiazole which prepeard by thiocyanogen method in the presence of a suitable solvent and amount tri ethyl amine (Et_3N) with heating. The structure confirmation of polymers were proved using FT-IR,^{1}H-NMR,C^{13}NMR and UV spectroscopy.Other physical properties including softening and melting points, and solubility of the polymers were also measured.

Key words: polyacrylamides, poly acryloyl chloride, 2-Aminobenzothiazole

Introduction:

Polyacrylamide is apolymer (-$CH_2CHCONH_2$-) formed from acrylamide subunits. It can be synthesid as asimple linear –chain structure or cross-linked, typically using N,N'-methyllenebisacrylamide. Polyacrylamide is not toxic .however, unpolymerized acrylamide, which is aneurotoxin, can be present in very small amounts in the polymerized acrylamide,[1-2] therefore it is recommended to handle it with caution. In the cross-linked form, the possibility of the monomer being present is reduced even further. It is highly water- absorbent, forming asoft gel when hydrated, used in such applications as poly acrylamide gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as athickener and suspending agent one of the largest uses for polyacrylamide is to flocculate solids in aliquid.this process applies to water treatment, and processes like paper making. Polyacrylamide can be supplied in apowder or liquid form, with the liquid form being subcate gorized as solution and emulsion polymer. Another common use of poly acrylamide and it's derivatives are in subsurface applications such as enhanced oil recovery.[3-4] The polymer is also used to make Gro-Beasttoys, which expand when placed in water, such as the Test Tube Aliens. Similariy, the absorbent properties of one of it's copolymers can be utilized as an additive in body- powder.[5-7] Polymacrylamide is often used in molecular biology application as amedium for electrophoresis of proteins and nucleic acids in atechnique known as PAGE .In this paper prepared polyacrylamide by Condensation poly acryloylechloride (PAC)with 2-amino benzothiazole derivatives.2-Aminobenzothiazole compounds are considered one of an important type of fused thiazoles anumber of 2-aminobenzothiazoles and derivatives were prepared by two methods. The first is Hugersch's method which concerns the reaction of thiourea derivatives with bromine in acetic acid. The second, thiocyanogen method which concerns the direct reaction of amine derivatives with

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potassium thiocyanate and bromine in glacial acetic acid,They have been studied extensively and found to have diverse chemical reactivity and broad spectrum of biological activity such as antitumor agents,antimicro-bial,analgesics,anti-inflammatory.[8-11]

Material and methods:

General

Chemicals employed were of analytical grade and used without further purification ,melting points were determined in Gallen kamp melting point apparatus and were uncorrected.UV-Visible spectra were recorded on ShimadzuT60u spectrophotometer using ethanol as a solvent, FT-IR spectra were recorded on Shimadzu FT-IR-8400 Fourier Transform infrared spectrophotometer as KBr disc**.** ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker specrospin Ultra shield magnets 300 MHz using tetramethyl silane (TMS)as an internal standared and DMSO**.**d_6 as asolvent in Al-Albate University in Jordan**.**

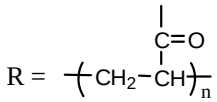
Preparation of 2-aminobenzothiazole Derivatives[12-13]

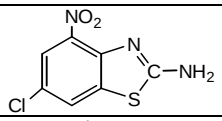
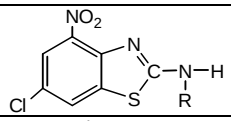
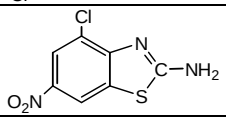
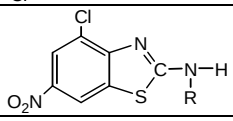
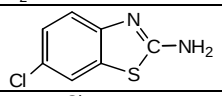
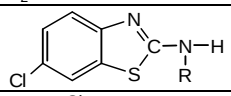
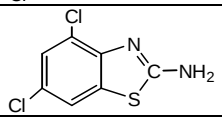
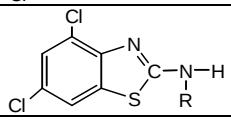
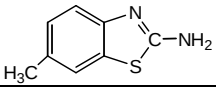
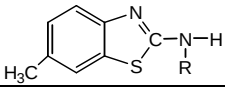
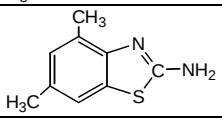
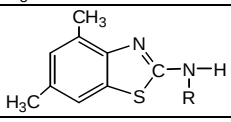
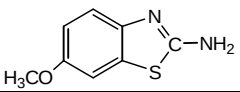
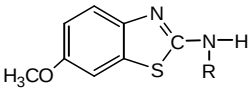
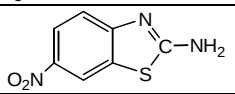
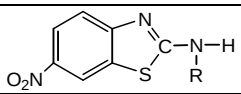
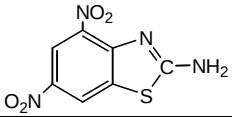
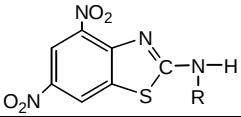
In a 250 ml round bottomed flask equipped with a magnetic bar stirrer and dropping funnel, a solution of bromine (1.2 ml) in glacial acetic acid (75 ml) was allowed to run through the dropping funnel dropwise during 30 min. to a mixture of para substituted aromatic amine (0.03 mole) and ammonium thiocyanate (0.1 mole) 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 collected, triturated and recrystallized from a suitable solvent.

General Procedure for Preparation of Poly Heterocyclic acrylamides

In around bottom flask equipped with a magnetic bar stirrer was placed a mixture of poly acryloyl chloride (0.06 mole) and (0.06 mole) of 2-aminobenzothiazole derivatives with (2 ml) of Et_3N (triethylamine) in (25 ml) of suitable solvent (THF, DMF) and refluxed for (7-10) hrs. After cooling, the excess of solvent was removed under vacum and the solid separated was filtered and purified by dissolving in DMF or DMSO and reprecipitating from water or acetone or ethanol. This procedure was applied on preparation compounds [1-9] as is shown in Table (1).All physical properties are listed in Table (3).

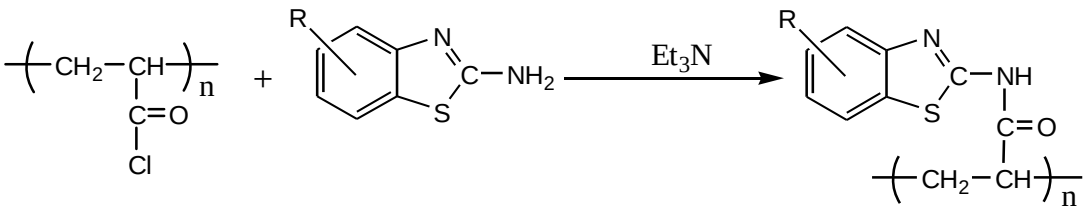
Table (1): Starting material and conditions of prepared poly heterocyclic acrylamides [1-9]

R = 

Structure one of starting material	Weight (gm)	Time reaction hr.	Structure of polymer	No. of product
	2.29	7		1
	2.29	8		2
	1.85	7		3
	2.19	9		4
	1.64	7		5
	1.78	7		6
	1.80	10		7
	1.95	8		8
	2.40	9		9

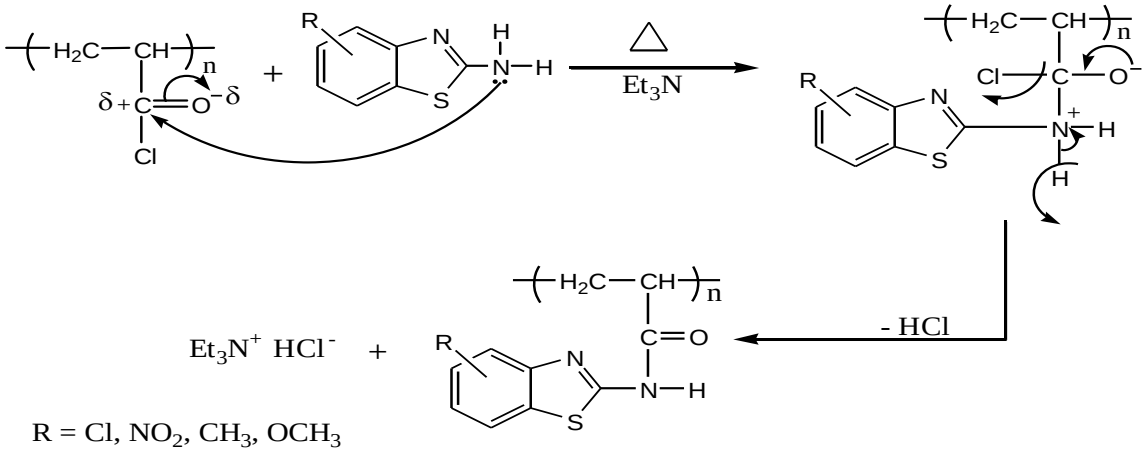
Results and Discussion:

preparation of [2-(N-acryl)amido substituted benzothiazole] [1-9]. New compounds [1-9] were prepared by the reaction of derivatives 2-aminobenzothiazole with poly (acryloyl chloride) in the presence of triethylamine (Et_3N). As shown below:



R = Cl, NO_2, CH_3, OCH_3

mechanism of the reaction involves a nucleophilic attack on the carbonyl as is shown below[11]:-



Scheme (1): Mechanism of preparation of poly [2-(N-acryl)amido substituted benzothiazole]

Structures confirmation of all prepared polymers were proved using FT-IR, UV, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Physical properties including melting point, softening point, solubility and percent conversion of the polymers were also measured. These and other physical properties are summarized in Table (2) and(3).

Poly [2-(N-acryl)amido-4-nitro-6-chlorobenzothiazole] [1] was prepared by refluxing poly acryloyl chloride with 4-nitro-6-chloro-2-amino benzothiazole in the presence of triethyl amine (Et_3N) in DMF for 7 hrs. Polymer [1] in, was a yellowish brown solid with softening point range of (185-215)°C, and its percent conversion was (76%). Compounds (2-9) were synthesized by the same way and purified by dissolving in a suitable solvent such as (THF, DMF, DMSO) with gentle heating and then filtered. The clear filtrate was added to suitable solvents such as (water, acetone, ethanol) and the precipitate was filtered and dried.

FT-IR spectrum of compound [1], in KBr disk showed characteristic absorption bands at 1620 cm^{-1}, 3260 cm^{-1}, 1350 cm^{-1} and 1140 cm^{-1} due to ν(C=C) aromatic, ν(C-H) aromatic, ν(C-NO_2) and ν(C-Cl) respectively.

Absorption bands due to ν(C=N) and ν(C-S) for thiazole ring appeared at 1512 cm^{-1} and 635 cm^{-1} respectively as shown in the Table(4) Fig.(1).

UV spectrum showed an absorption λ_{max} at 274 nm and 421 nm which was attributed to (n→π*) and (π→π*).as shown in Fig.(5).

FT -IR spectrum of compound [2] showed the same bands in compound [1] as shown in Table (4).

UV spectrum showed an absorption λ_{max} at 279 nm and 344 nm which was attributed to (n→π*) and (π→π*).

In the ^{1}H-NMR spectrum of polymer [2] showed a signal at δ8.102 ppm (1H, singlet) was attributed to (-NH) proton, and the signal at δ2.892 ppm was attributed to (-CH) for polymer group , whil the signal at δ1.125 ppm (2H) was attributed to the (H_2C-) protons, and the signal between δ(6.827-6.918) ppm for two aromatic protons ($1H^4$, $1H^5$) as shown in Fig.(8)

The ^{13}C-NMR spectrum of [2] showed a signal at 162.77 ppm for carbonyl group (C=O), a signals at 114.02-126.13 ppm due to aromatic carbons, signals at 151.84 ppm belong to carbon

atom in thiazole ring, showed signals at 19.02-56.48 ppm as shown in Fig.(9).

FT-IR spectrum of compound [3] $-(H_2C-CH)-_n$ showed characteristic absorption bands at 1596 cm^{-1}, 3070 cm^{-1}, 1049 cm^{-1}, 1542 cm^{-1} and 617 cm^{-1} due to ν(C=C) aromatic, ν(C-H) aromatic, ν(C-Cl), ν(C=N) thiazole ring and ν(C-S) thiazole ring respectively.

UV spectrum showed an absorption λ_{max} at 299 nm which was attributed to ($\pi\rightarrow\pi^*$).

^{1}H-NMR spectrum of polymer [3] showed a signal at δ7.867 ppm (1H, singlet) was attributed to (-NH) proton, and the signal between δ(7.223-7.767) ppm for three aromatic protons ($1H^4$, $1H^5$, $1H^6$), while the signal at δ2.793 ppm (1H, multiplet) was attributed to (-CH) for polymer group , and the signal at δ1.501 ppm (2H) was attributed to the (H_2C-) protons for polymer group $-(H_2C-CH)-_n$. The ^{13}C-NMR spectrum of [3] showed signal at 168.24 ppm for carbonyl group (C=O), and the signals at 119.03-135.00 ppm due to aromatic carbons, while the signal at 151.41 ppm was attributed to carbon atom in thiazole ring, and $-(H_2C-CH)-_n$ showed signals at (39.13-40.79) ppm .

UV spectrum showed an absorption λ_{max} at 300 nm which was attributed to ($\pi\rightarrow\pi^*$).

FT-IR spectrum of compound [5], showed characteristic absorption bands at 1620 cm^{-1}, 3139 cm^{-1}, 1550 cm^{-1} and 617 cm^{-1} due to ν(C=C) aromatic, ν(C-H) aromatic, ν(C=N) ,thiazole ring, ν(C=O) and ν(C-S) thiazole ring respectively as shown in Table (4).Fig(2).

UV spectrum showed an absorption λ_{max} at 300 nm which was attributed to ($\pi\rightarrow\pi^*$). ^{1}H-NMR spectrum of [5] showed a signal at δ8.243 ppm was attributed to (-NH) proton, while signal at δ3.188 ppm for (3H, singlet) was attributed to (CH_3) proton, and the signal at δ2.551 ppm (1H) was attributed to (-CH) for polymer group $-(H_2C-CH)-_n$,while the signal at δ1.159 ppm (2H) was attributed to the (CH_2) protons for polymer group ,and a signal between δ(7.955-8.204) ppm for aromatic hydrogen ($3H(H^4 + H^5 + H^6)$) The ^{13}C-NMR spectrum of [5] showed the signal at 171.56 ppm for carbonyl group N(C=O), and the signal at 132.65 ppm belong to carbon atom in the thiazole ring, while the signal at 35.22 ppm for carbon of methyl group (CH_3), and the signal at (103.30-120.41) ppm attributed to aromatic carbon, and $-(H_2C-CH)-_n$ appeared at (40.12-55.36) ppm

FT-IR spectrum of compound [6] showed the same bands in compound [5], show in Table(4).

UV spectrum showed an absorption λ_{max} at 300 nm which was attributed to ($\pi\rightarrow\pi^*$). As shown in Fig.(7).

FT-IR spectrum of compound [7] showed stretching bands at 1620 cm^{-1} aromatic ν(C=C), 3078 cm^{-1} aromatic ν(C-H), 1542 cm^{-1} thiazole ν(C=N), ,1635cm^{-1}thiazole ν(C=O), 663 cm^{-1} thiazole ν(C-S) and 1265 cm^{-1} methoxy group ν(C-O-C), shown in Table (4).

UV spectrum showed an absorption λ_{max} at 300 nm which was attributed to ($\pi\rightarrow\pi^*$).

FT-IR spectrum of compound [8] showed characteristic absorption bands at 1643 cm^{-1}, 3178 cm^{-1}, 1334 cm^{-1}, 1519 cm^{-1} and 663 cm^{-1} due to ν(C=C) aromatic, ν(C-H) aromatic, ν(C-NO_2), ν(C=N) thiazole and ν(C-S) thiazole respectively as shown in Table (4) .

UV spectrum showed an absorption λ_{max} at 272 nm and 385 nm which were attributed to ($n\rightarrow\pi^*$) ($\pi\rightarrow\pi^*$). As shwon in Fig.(6).

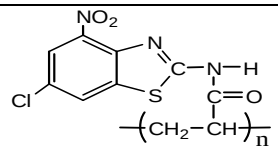
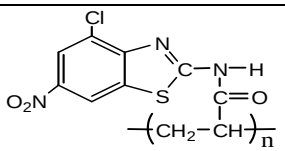
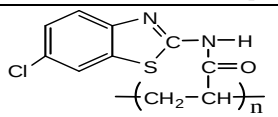
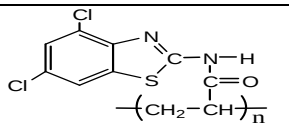
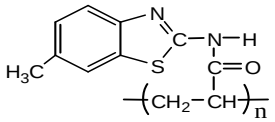
The ^{1}H-NMR spectrum of [8] showed a signal between δ(7.402-8.109) ppm for the three aromatic hydrogen (1H^{4}, 1H^{5}, 1H^{6}) while a signal at 8.262 ppm (1H, signlet) was attributeed to (-NH) proton, and the signal at δ2.502 ppm was attributed to (-CH) for polymer group, $-(H_2C-CH)_n-$,while the signal at δ1.056 ppm (2H) was attributed to(H_2C-) protons for polymer group

^{13}C-NMR spectrum of [8] showed the signal at 172.25 ppm for carbonyl group (C=O), and the signal at 159.07 for carbon atom in thiazole ring, while the signal at 117.31-132.04 ppm for aromatic carbons, $-(H_2C-CH)_n-$ appeared signals at (119.62-56.48) ppm .FT-IR spectrum of compound [9] showed the same bands in compound [8] as shown in Table (4), Fig.(3).

UV spectrum showed an absorption λ_{max} at 268 nm and 359 nm which was attributed to ($n\rightarrow\pi^*$) and ($\pi\rightarrow\pi^*$).The ^{1}H-NMR spectrum of [9], showed a signal at δ8.805 ppm (1H, singlet) was attributed to (-NH) proton, and the signal at δ3.102 ppm was attributed to (-CH) for polymer group $-(H_2C-CH)_n-$ while the signal at δ1.513 ppm (2H) was attributed to (CH_2) protons for polymer group $-(H_2C-CH)_n-$, and the signal between δ(7.100-8.156) ppm for two aromatic protons (1H^{4}, 1H^{5}) .

^{13}C-NMR spectrum of [9] showed signal at 176.17 ppm for carbonyl group (C=O), and the signal at 150.28 ppm attributed to carbon atom in thiazole ring,while the signal at (120.24-135.58) ppm for aromatic carbons, and $-(H_2C-CH)_n-$ appeared a signal at (39.14-40.80) ppm,

Table(2):physical properties of the prepared heterocyclic polyacrylamide

Code #	Structure	%Conversion	Softening point °C	m.p. °C	Colour	Solvent used in reaction
1	 poly [2-(N-acryl) amino-4-nitro-6-chlorobenzothiazole]	76	185-215	>360	Yellowish brown	THF DMF
2	 poly [2-(N-acryl) amino-4-chloro-6-nitrobenzothiazole]	87.5	200-225	>360	Yellowish brown	THF DMF
3	 poly [2-(N-acryl) amino-6-chloro benzothiazole]	63.5	220-250	287-295	Brownish yellow	THF DMF
4	 poly [2-(N-acryl) amino-4,6-dichloro benzothiazole]	60	220-255	>360	Gray	THF DMF
5	 poly [2-(N-acryl) amino-6-methyl benzothiazole]	70	180-210	>360	White	THF DMF

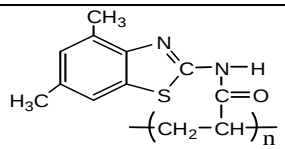
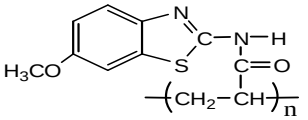
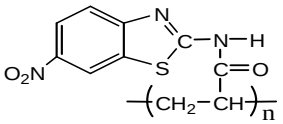
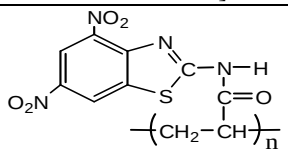
6	 poly [2-(N-acryl) amino-4,6-dimethyl benzothiazole]	62	190-230	256-262	Reddish yellow	THF DMF
7	 poly [2-(N-acryl) amino-6-methoxy benzothiazole]	70	230-255	>360	Black	THF DMF
8	 poly [2-(N-acryl) amino-6-nitro benzothiazole]	61	180-205	>360	Very dark gray	THF DMF
9	 poly [2-(N-acryl) amino-4,6-dinitro benzothiazole]	66.6	172-190	>360	Green	THF DMF

Table (3): Solubilities of the prepared heterocyclic poly acrylamides Abbreviation:- S = soluble, In = Insoluble, PS = Partial soluble, PSH = Partial soluble hot, PES = Petroleum ether spirit

Code #	Water	Ethanol	Dioxane	Benzene or toluene	$CHCl_3$ or CCl_4	Diethyl ether	Cyclo hexane	Acetone	THF	DMF	DMSO	PES
1	In	PS	In	In	In	In	In	PS	PS	PS	S	In
2	In	PS	In	In	In	In	In	PS	PS	S	S	In
3	In	In	In	In	In	In	In	In	PS	PS	S	In
4	In	In	PS	In	In	In	In	PS	PS	PS	S	In
5	In	In	In	In	In	In	In	In	In	PS	S	In
6	In	In	In	In	In	In	In	In	In	PS	S	In
7	In	In	In	In	In	In	In	In	PS	PS	S	In
8	In	In	PS	In	In	In	In	PS	PS	PS	S	In
9	In	In	PS	In	PS	In	In	PS	PS	PS	S	In

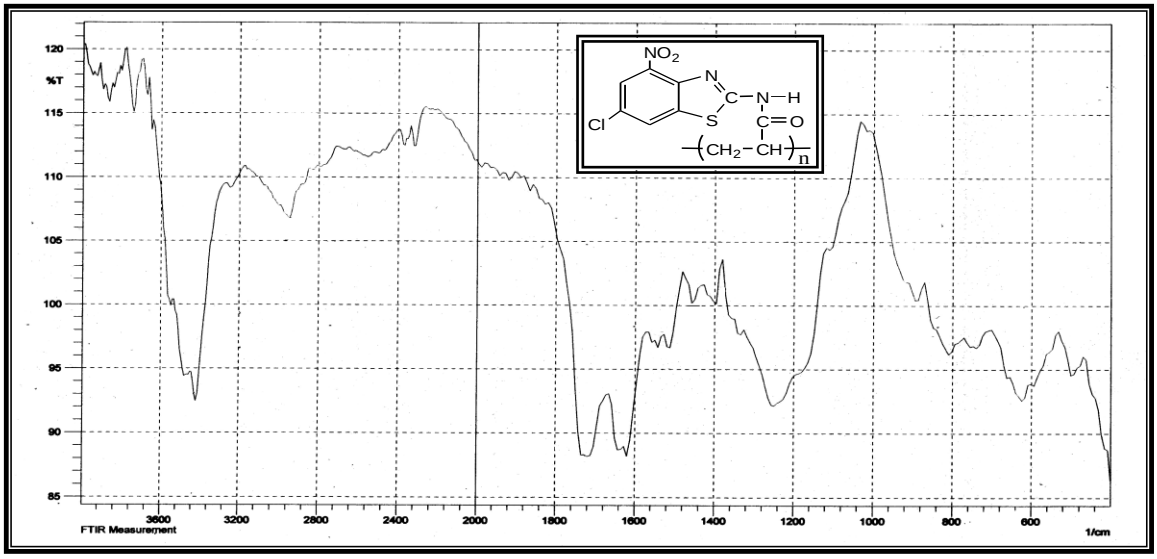


Fig. (1) : FT-IR spectrum of polymer [1]

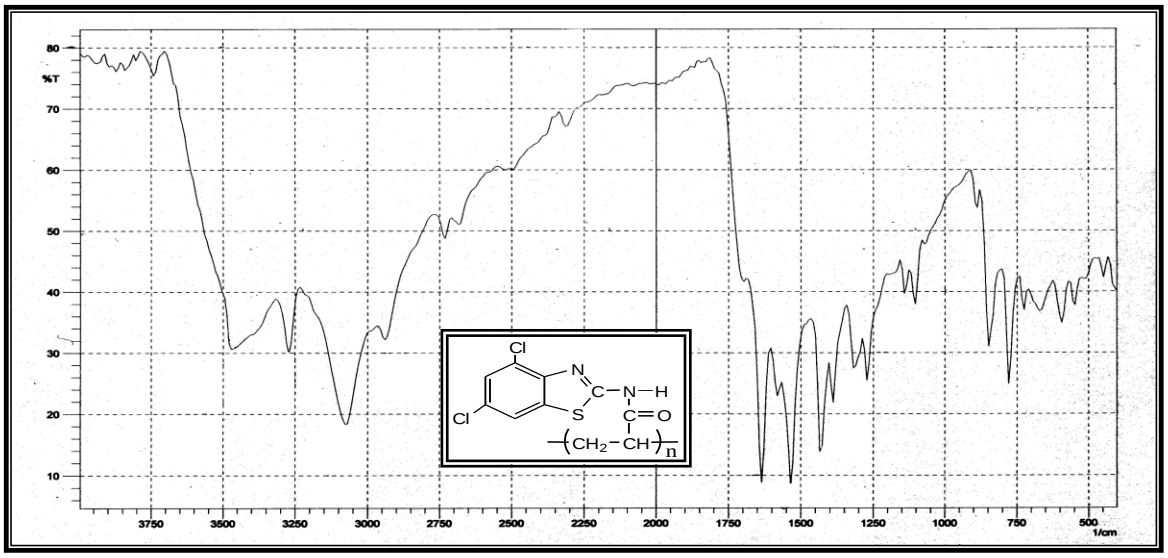


Fig. (2) : FT-IR spectrum of polymer [4]

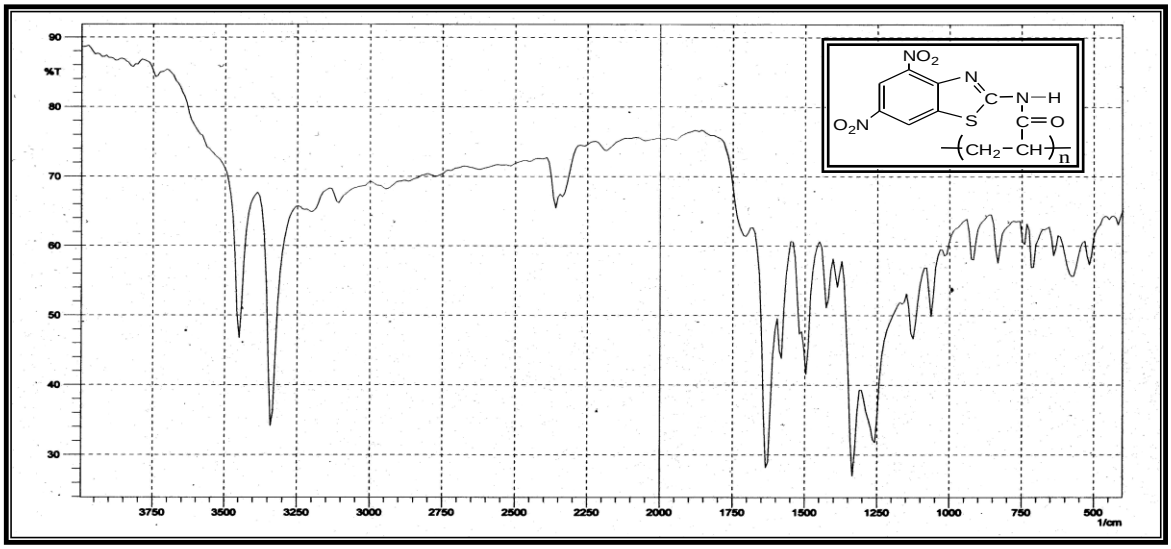


Fig.(3) : FT-IR spectrum of polymer [9]

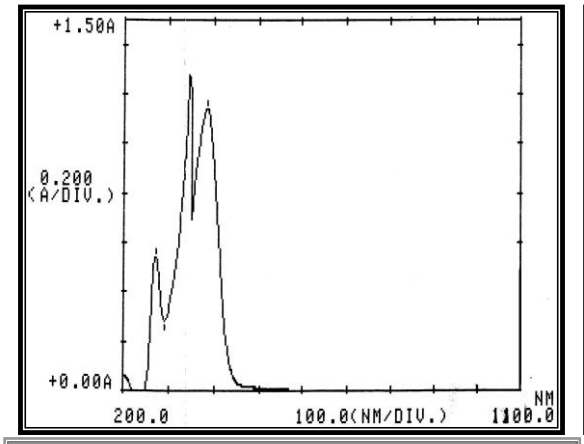


Fig. (4) : UV spectrum of polymer [2]

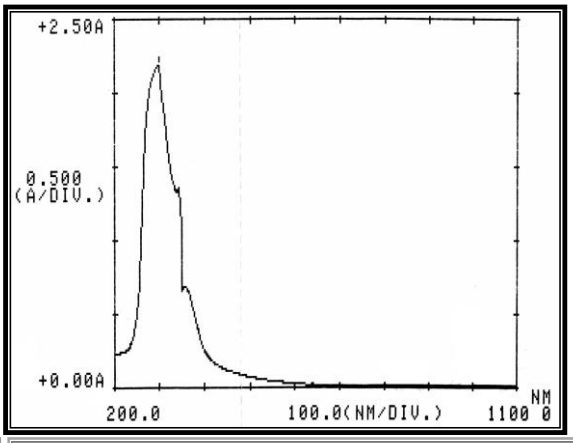


Fig. (5) : UV spectrum of polymer [1]

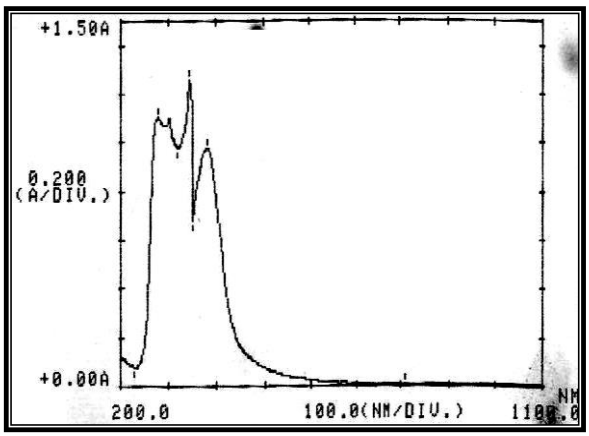


Fig. (6) : UV spectrum of polymer [8]

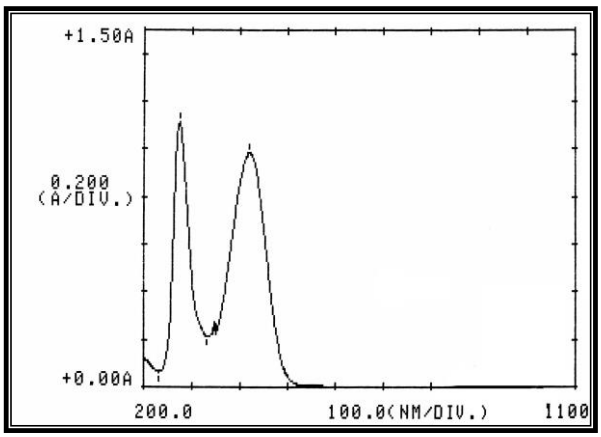


Fig. (7) : UV spectrum of polymer [6]

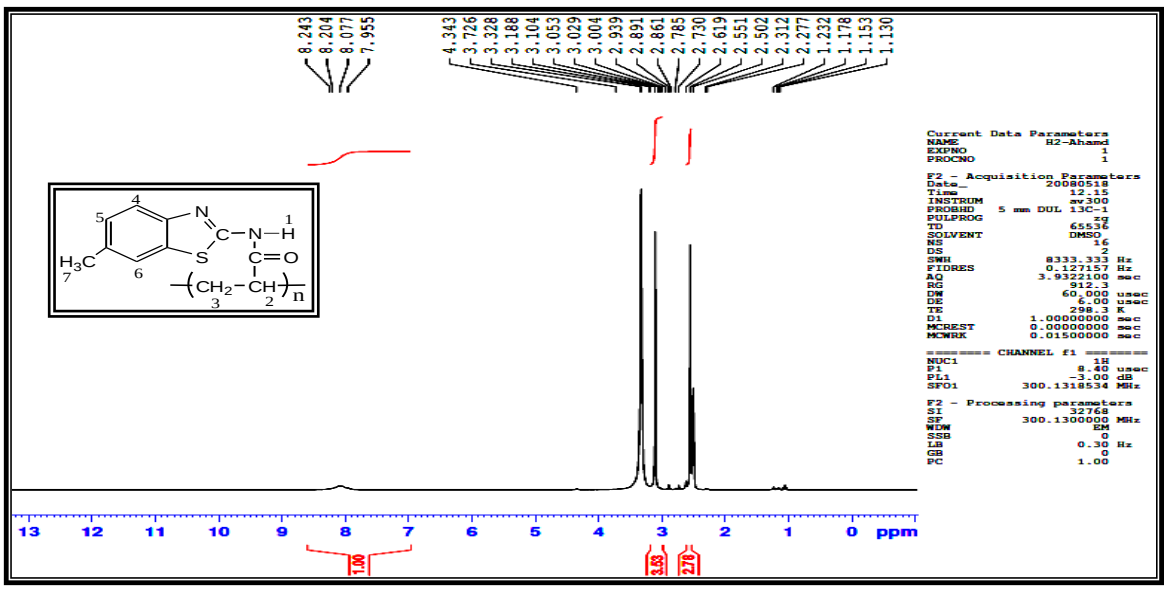


Fig. (10) : ^{1}H-NMR spectrum of polymer [5]

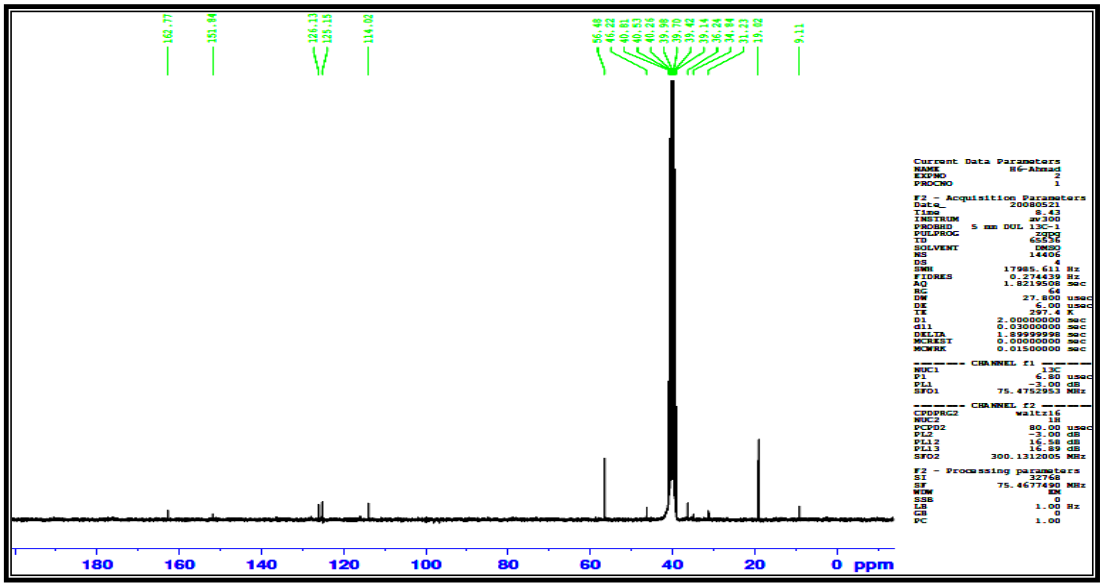


Fig.(9) : ^{13}C-NMR spectrum of polymer [2]

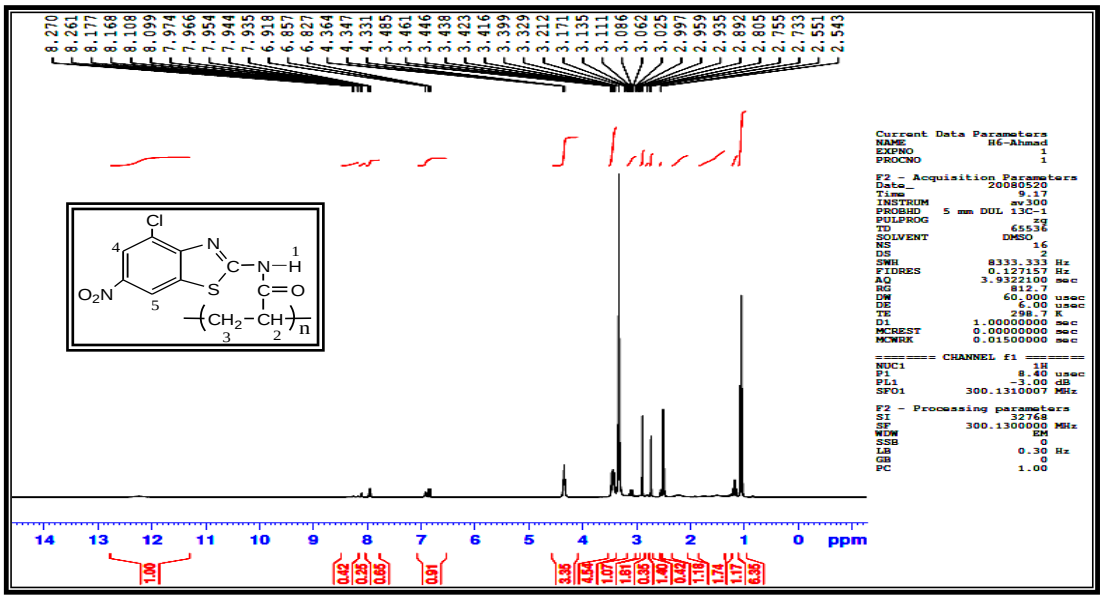
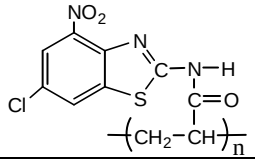
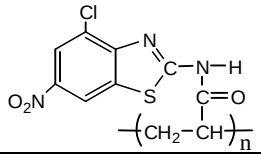
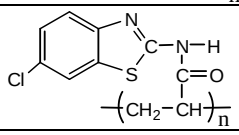
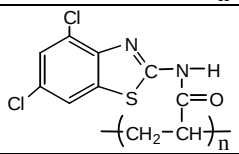
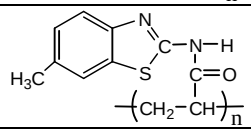
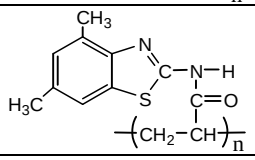
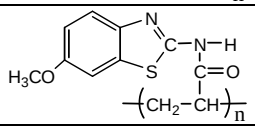
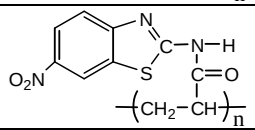
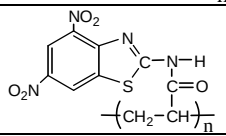


Fig. (8) : ^{1}H-NMR spectrum of polymer [2]

Table(4): FT-IR spectra of prepared Pheterocyclic polyacrylmides

Comp. No.	structure	ν(N-H)	ν(C=O) imide	ν(C-N)	ν(C=C) aromatic	ν(C-H) aliphatic	ν(C-H) aromatic	ν(C=N)	ν(C-S)	ν(C-O)	Other band
1		3440	1720	1400	1620	2950	3260	1512	635	1249	(C-NO_2) 1350 C-Cl 1140
2		3394	1712	1410	1635	2939	3125	1504	640	1249	(C-Cl) 1041 (C-NO_2) 1326
3		3435	1697	1415	1596	2950	3070	1542	617	1265	(C-Cl) 1049
4		3456	1635	1388	1557	2731-2939	3078	1535	671	1272	(C-Cl) 1103
5		3425	1704	1396	1620	(2761-2947)	3139	1550	617	1265	-
6		3409	1704	1396	1643	(2731-2947)	3116	1542	671	1257	-
7		3409	1635	1396	1620	(2715-2939)	3078	1542	663	1218	(C-O-C) 1265
8		3417	1704	1400	1643	2947	3178	1519	663	1296	(C-NO_2) 1334
9		3448	1704	1410	1635	(2715-2947)	3109	1581	650	1257	(C-NO_2) 1334

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تحضير وتشخيص بولي أكريل أميدات جديدة غير متجانسة من مشتقات2- أمينو بنزوثايازول

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الخلاصة :

حضر في هذا البحث بولي أكريل أميدات جديدة (1-9) من تفاعل بولي كلوريد الاكريلويل مع مشتقات 2-أمينو بنزوثايازول المحضرة بطريقة الثايو سيانوجين بوجود مذيب مناسب وكمية مناسبة من ثلاثي اثيل امين Et_3N مع التسخين وتم اثبات وبرهنة التراكيب الكيميائية للبوليمرات المحضرة باستخدام الطرق الطيفية ،اطياف الاشعة تحت الحمراء FT-IR ، اطياف الرنين النووي المغناطيسي ^{1}H-NMR واطياف ^{13}C-NMR واطياف الاشعة فوق البنفسجية UV بالاضافة إلى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والذوبانية.