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Synthesis of new Polyimides Derived from 4- minoantipyrine

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Abstract:

In the present study, new five polymers of acryloyl chloride have been synthesized by reaction 4-aminoantipyrine with many substituted acid chloride (A-E). Then condensation of polyacryloyl chloride with the product in one step (A-E), in a suitable solvent in the presence amount of (Et_3N) to obtain new polyimides(A1-E5). The prepared compounds were characterized by UV. FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and measuring of other physical properties such as softening point, melting point and solublities.

Key words: 4-aminoantipyrine, polyimides derivatives, polyacryloylchloride

Introduction:

Recently there has been an increasing interest in synthesis of heterocyclic compounds that have biological and commercial importance. Pyrazoles belong to the five membered heterocyclic system [1]. Some of the synthetic compounds containing pyrazole moiety have been focused in the field of medicinal chemistry [2].Antipyrine compounds play an important role in modern organic synthesis, not only because they constitute a particularly useful class of hetero cyclic compounds[3],but also because they are of great biological interest. They have been found to have biological, clinical and pharmacological applications [4,5], one of the most important derivatives of antipyrine is 4-aminoantipyrinep that has played an important role in organic chemistry, 4-aminoantipyrin(AAP) is an important derivative of the 5-pyrazolone class which is used for the detection and determination of number of compounds[6-8] ,and also as an inhibitor of mild steel corrosion in HCl or sulphuric acid solution [9,10]. Derivatives of 4-aminoantipyrine are also used as hair colour additives [11]. Polyimides (PIS) are classified as a group of super-engineering plastics owing to their excellent thermal stability [12]. They are a class of representative high-performance which involv aromatic and hetero cyclic rings in the main chains and also are well known as heat-resistant organic materials

polymers that have been widely used in flexible displays [13]. Polymer electronic memories, per evaporation, bio fuels separation and many other fields of microelectronics [14], optics, aerospace industries and biomedical [15] engineering. However, poly imide materials are usually difficult to be processed because of their infusibility at high temperature and insolubility in most solvents [16]. In order to improve the solubility and melting ability of polyimides, many studies have focused on introducing the fluorocontaining group, or flexible groups into polymer backbone [17]. This study aims at the synthesis of new polyimides contain antipyrine ring which were known as a high biological effectiveness.

Material and Methods:

All chemicals used in this work were obtained from Fluka, Mark, BDH and were used without further purification.

1-Melting points were determined in Gallen Kamp melting point apparatus and were uncorrected.

2-UV-Visible spectra were recorded on shimadzu T60 spectrophotometer using ethanol as a solvent.

3-FT-IR spectra were recorded on shimadzu-8400 Fourier transform infrared spectrophotometer as KBr disc.

4-Softing points were determined by using Reichert Thermovar with Reichert Jung Temperature Controller.

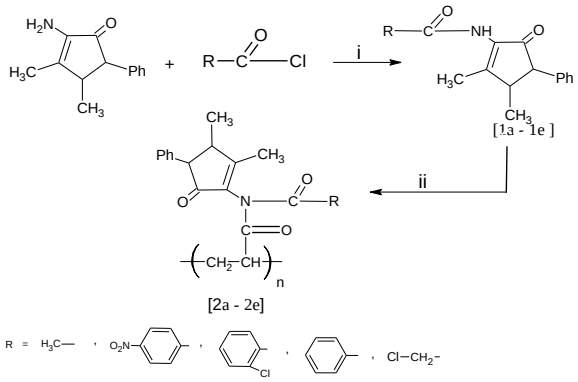
5-^{1}H-NMR and ^{13}C-NMR spectra were recorded on Brukerspecrospin Ultra shield that were magnets 300 MHz in strument using tetra methyl silane (TMS) as an internal standard and DMS.d6 as solvent in Al-Albate University in Jordan.

General Procedure Preparation of [(subs. Aryl or acetyl) subs. 4-aminoantipyrine] Amide [18].

A mixture of 4-aminoantipyrine(0.01 mol), substituted. benzoyl chlorid(0.01 mol) and tri ethyl amine Et_3N (drops) with ethanol as a solvent in (100 ml) round bottom flask were refluxed for (4 hrs.) after that the solvent was removed and the product was recrystallized from ethanol. All physical properties are recorded in Table (1).

General procedure preparation of poly (N-acryl-N-substituted or unsubstituted acetyl of benzoyl) Imidyl substituted 4-aminoantipyrine [19].

In around bottom flask dissolved (0.01 mol) of N-subamidyl sub. 4-aminoantipyrine in (25 ml) THF and mixed with poly a cryloyl chloride (0.01 mol), (drops) of trimethyl amine Et_3N were added in a 100 ml round bottom flask. The mixture was refluxed for (6-8 hrs.) after cooling the solvent was removed. The separated was filtered and purified by dissolving in DMF and repreciptating from water or acetone. All physical properties are recorded in Table (1)



Reagent and Conditions
(i) Ethanol, Et_3N, Reflux
(ii) Polyacryloyl chloride, THF, Et_3N, Reflux

Scheme (1): Synthesis of polyimides derived

Table (1) physical properties for [(sub.Aryl or Actyl)] sub.4-Aminoantipyrine and all product polymers.

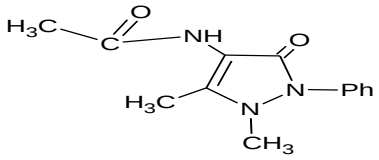
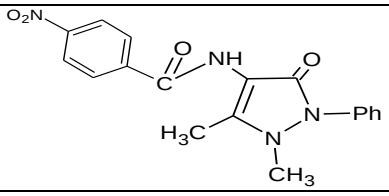
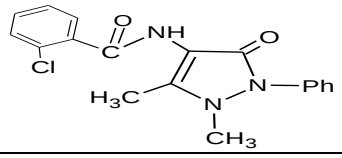
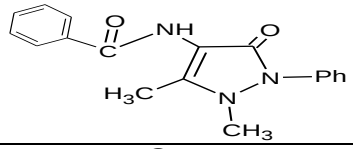
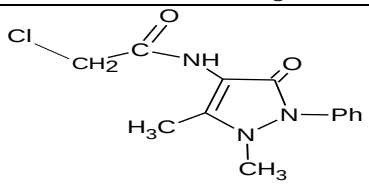
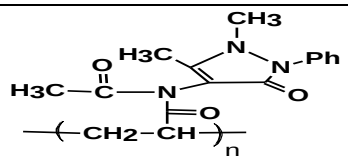
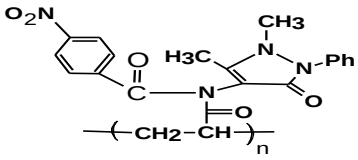
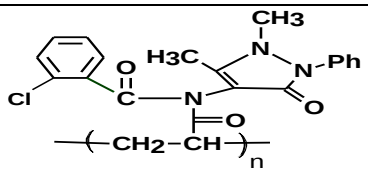
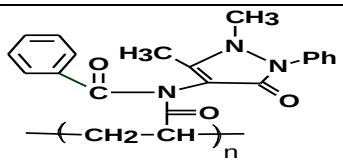
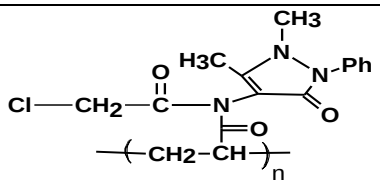
Comp. No.	Compound structure	Color	Melting Point	% Yield	Solvent used in reaction
1a		Brown	198-200	91	Ethanol
1b		Reddish brown	150-152	95	Ethanol
1c		Yellow	220-222	89	Ethanol
1d		Brown light	Oil	-	Ethanol
1e		Red	115-117	73	Ethanol
2a		Dark brown	Softing point C° 160-170	83	THF
2b		Brown	110-120	75	THF
2c		Light brown	188-196	90	THF
2d		brown	115-124	81	THF
2e		Orange	225-232	90	THF

Table (2) FTIR spectral data (wave number υ^{-}) cm^{-1} for all compounds

Comp. No.	C-H Aliphatic cm^{-1}	C-H Aromatic cm^{-1}	υ (C=O) cm^{-1}	υ (C-N) cm^{-1}	υ (C=C) cm^{-1}	N-H) (υ cm^{-1}	Others cm^{-1}
1a	2932	3051	1610 1664	1489	1566	3469	-
1b	2850- 2992	3051-3109	1656 1714	1489	1635	3427	υ (C-NO2) 1338 ,1569
1c	2910	3130	1640 1677	1490	1615	3390	υ (C-Cl) 841,1144
1d	2812-2987	3062	1630 1700	1490	1589	3455	-
1e	2912	3132	1620 1647	1489	1575	3390	υ (C-Cl) 842,1157
2a	2920	3047-3151	1608 1635 1712	1492	1577	-	-
2b	2735-2939	3055-3109	1604 1662 1712	1489	1573	-	υ (C-NO2) 1350 ,1523
2c	2816-2985	3153	1647 1678 1698	1494	1612	-	υ (C-Cl) 862,1180
2d	2738-2976	3150	1650 1667 1716	1473	1580	-	-
2e	2866-2958	3120	1647 1701 1735	1492	1608	-	υ (C-Cl) 871,1176

Results and Discussion:

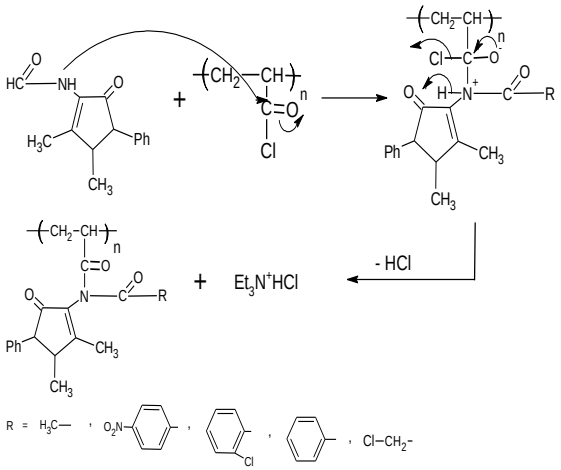
4-aminoantipyrine and its derivatives are an important type of nitrogen containing heterocyclic compound which has attracted considerable attention on medicinal chemists due to their antimicrobial. For this purpose, new 4-aminoantipyrine derivatives were synthesized .The starting material for the synthetic polyimide is 4-aminoantipyrine which condensed with different substituted acid chlorides through nucleophilic substitution of chloride with amino group lead to amide derivatives (1a-1e).

The FT-IR spectrum[20] of compounds (1a-2a) showed the absence of (-NH_2) stretching together of starting material, Figure (1), with appearance of band at (3469-3330) cm^{-1} and(1714-1647) cm^{-1} attributed to (N-H) and(C=O),the FT-IR spectrum of compound(1d) showed clear absorption bund at(3455)cm^{-1} for(NH), (1630) and (1700) cm^{-1}for(C=O), (3062)cm^{-1}for(C-H aromatic) and (2987,2812)cm^{-1}for(C-H aliphatic) as shown in Table(2), and Figure(2).

UV. Spectrum of compounds [1a] and [1b] showed an absorption λ max at (252) nm and (260) nm which was due to ($\pi - \pi^*$). The absorptions are listed in Figure [4] and [5].

The H^1-NMR spectrums of compounds [1c] showed signals at (2.253)ppm attributed to (CH_3) proton and multiple signals at (7.117-7.55) ppm due to aromatic protons and signlet signal at (6.64) ppm due to (N-H) proton for amide[21] as shown in Figure [8], and compound [1d] showed signals at (3.049) ppm attributed to (CH_3) proton and multiple signals at (7.303-7.974) ppm due to aromatic protons and signlet signal at (5.476) ppm due to (N-H) proton for amide as shown in Figure [9]. In the ^{13}C-NMR spectrum of compound [1c] showed a signal at (166) ppm for carbonyl group, while the aromatic carbon appeared at (124- 137) ppm as shown in Figure (10) while compound [1d] showed a signal at (160.38) ppm for carbonyl group, whereas the aromatic carbon appeared at (107-135.36) ppm as shown in Figure [11].

In order to obtain polyimides (2a-2e), the amides (1a-1e) were subjected to another nucleophilic substitution by treating with poly acryloyl chloride using triethylamine (Et_3N) as a catalyst. The mechanism of the reaction involves anucleophilic attach on the carbonyl as shown below [22].



Scheme (3): Mechanism of product polymers.

The FT-IR spectrum of compound (2d) (see Figure3) showed the disappearance of amide bands (N-H) at (3455)cm^{-1} and appearance of band at (1650), (1667) and(1716)cm^{-1}attributed to(C=O amide), also the appearance bands at (3055)cm^{-1}, (2735,2939) $cm^{-1}$and (1489)cm^{-1} for (C-H aromatic), (C-H aliphatic) and (C-N) respectively, all these bands are listed in Table(2). Compounds (2a) and (2b) showed an absorption λ max at (264) nm, (270) nm which are attributed to (π –π*) as shown in Figures [6] and [7].

H^1-NMR spectra of compounds (2c, 2d) are shown in Figures (12, 13). There Figures depicted different signals, two multiple at 1.64 ppm and 2.86 ppm as signal for ethylene (acryl).The C^{13}-NMR spectrum of compounds (2c) and (2d), the ethylene carbon appeared at (36.4) ppm and (40.9) ppm and aromatic carbon at (123.8-137.0) and [125-135] while the imide carbonyl appeared at (165.1) and (157) ppm as shown in Figures [14] and [15].

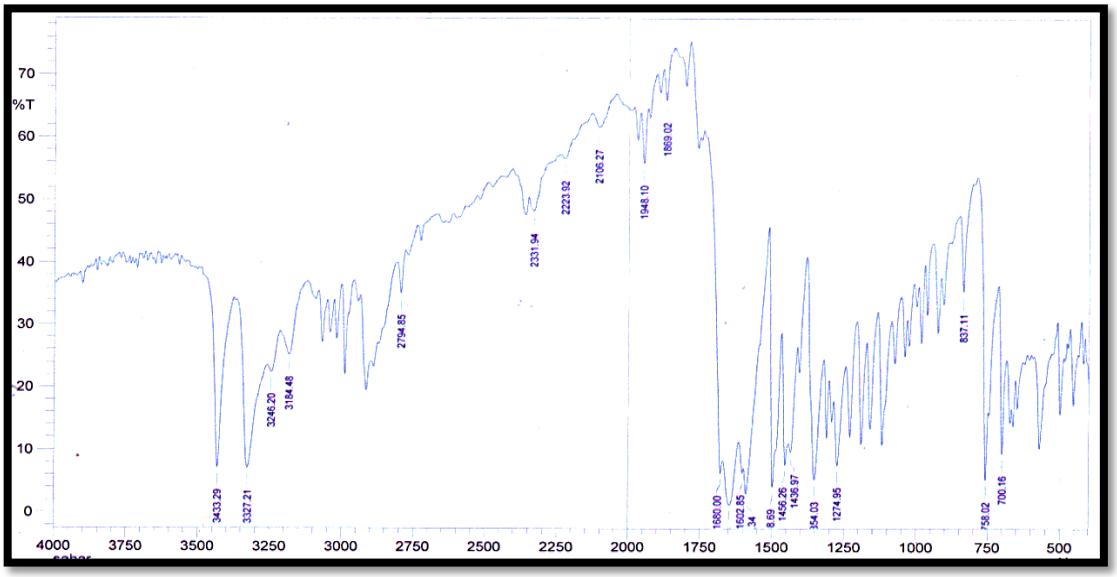


Fig. (1) FTIR for Starting material

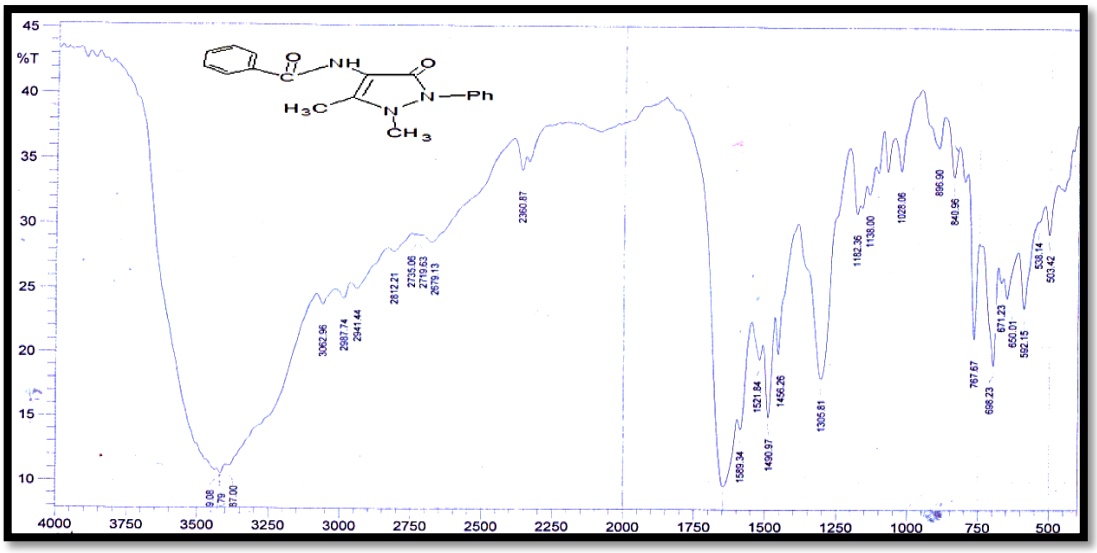


Fig. (2) FT-IR spectrum for compound (1d)

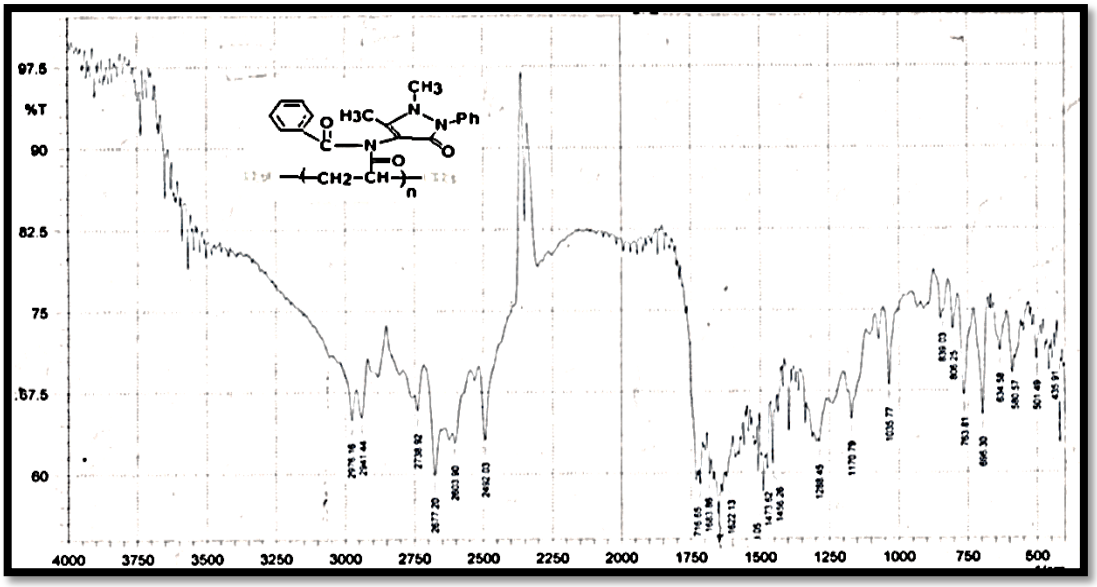


Fig.(3) FT-IR spectrum for compound (2d)

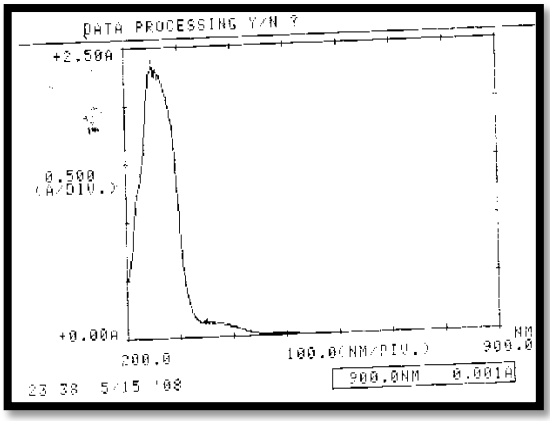


Fig. (4): UV. Spectrum of compound (1a)

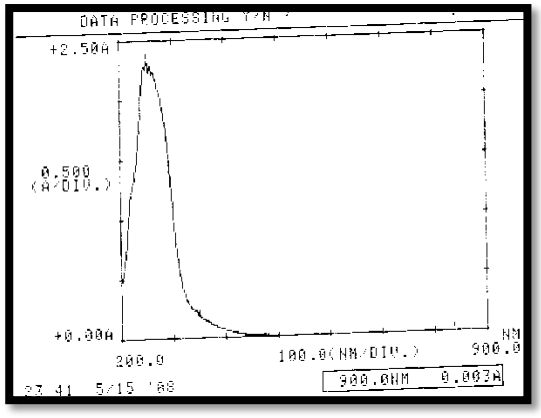


Fig.(5): UV. Spectrum of compound (1b)

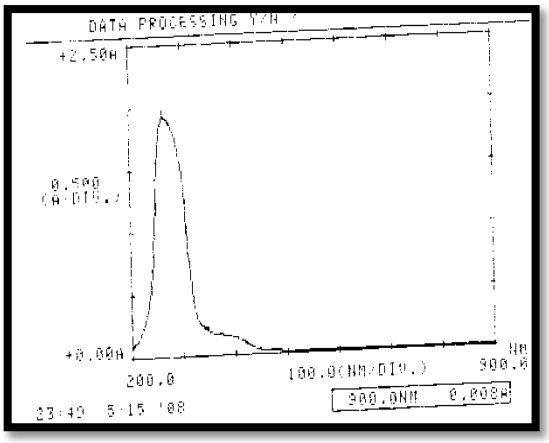


Fig. (6): UV. Spectrum of compound (2a)

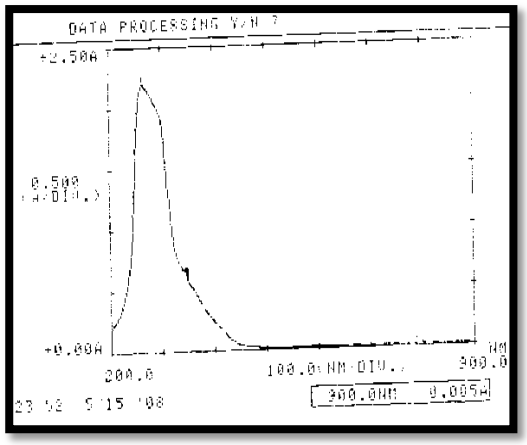


Fig. (7): UV. Spectrum of compound (2b)

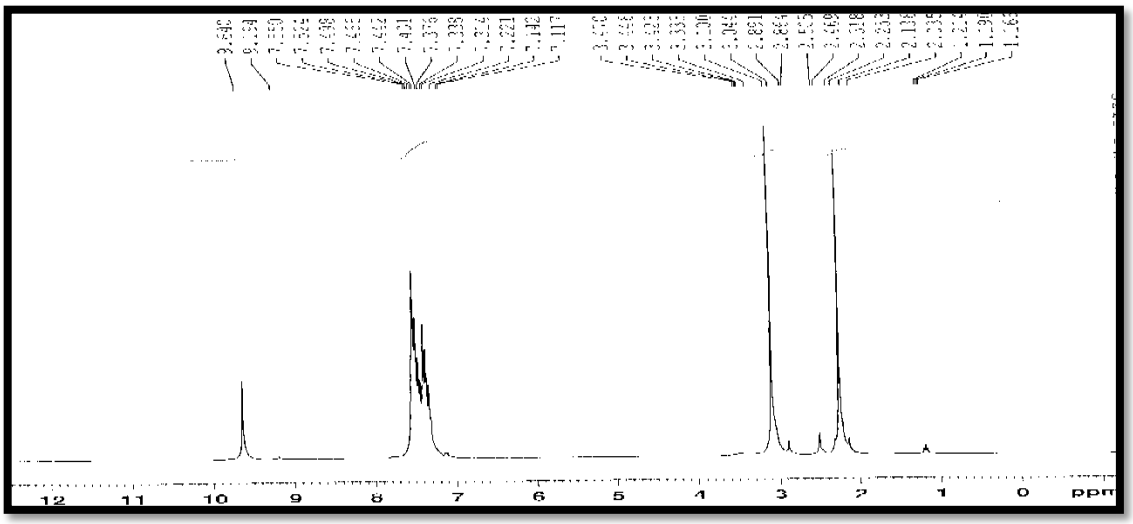


Fig. (8)[1] H-NMR spectrum for compound (1c)

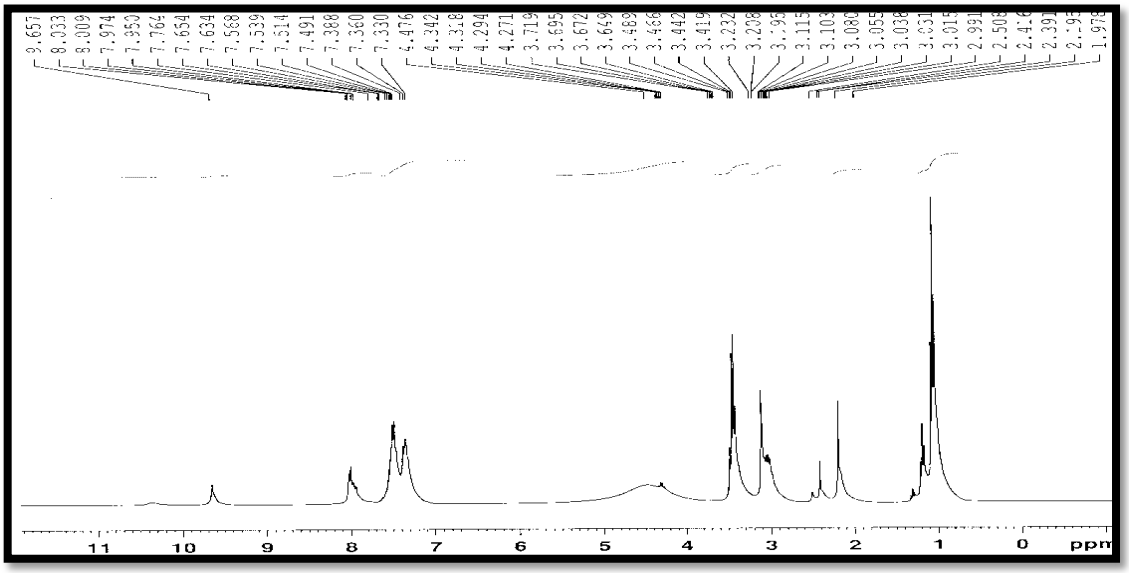


Fig. (9)[1] H-NMR spectrum for compound (1d)

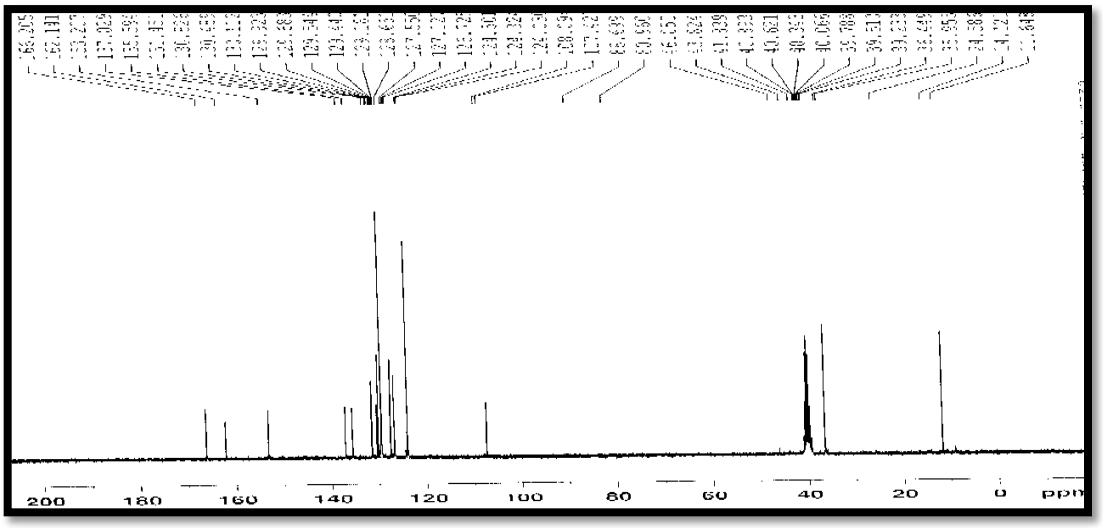


Fig. (10)[13] C-NMR spectrum for compound (1c)

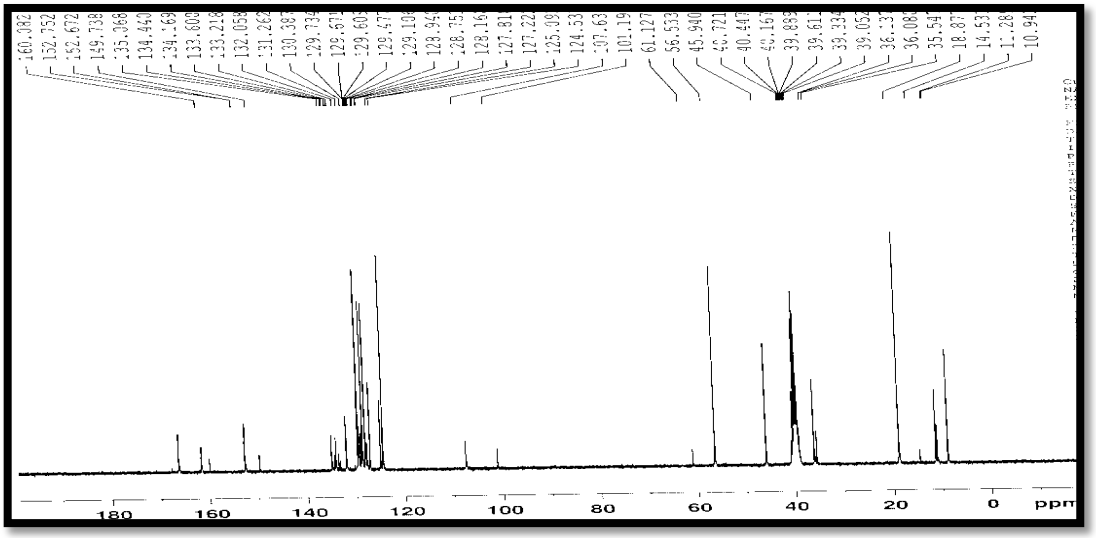


Fig.(11)[13] C-NMR spectrum for compound (1d)

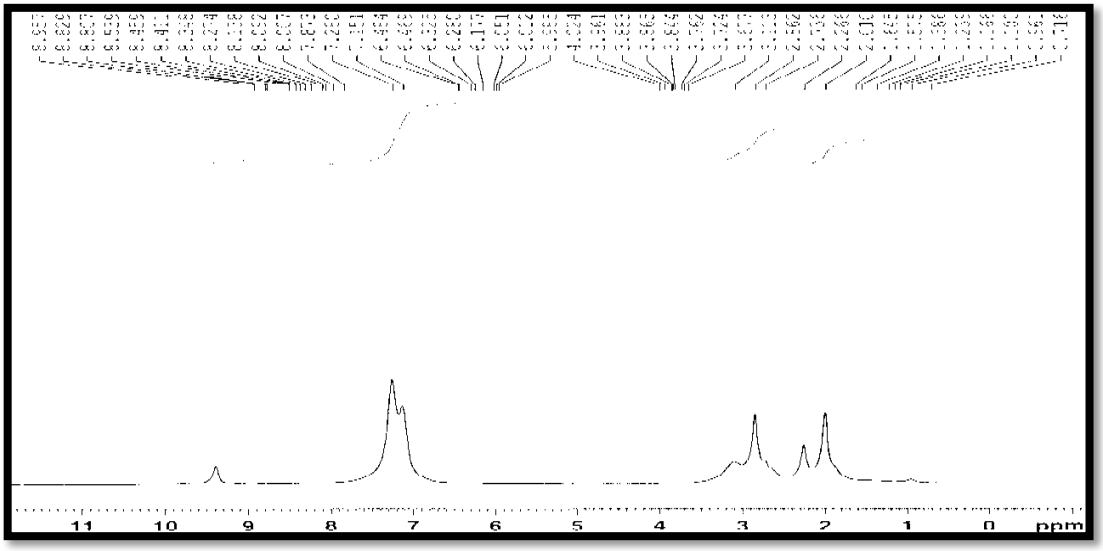


Fig. (12)[1] H-NMR spectrum for compound (2c)

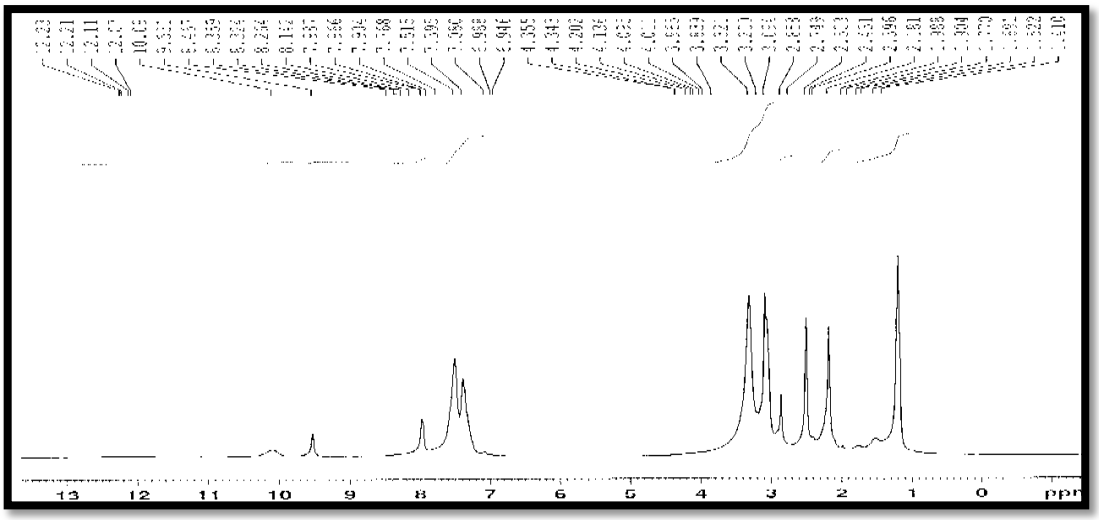


Fig. (13)[1] H-NMR spectrum for compound (2d)

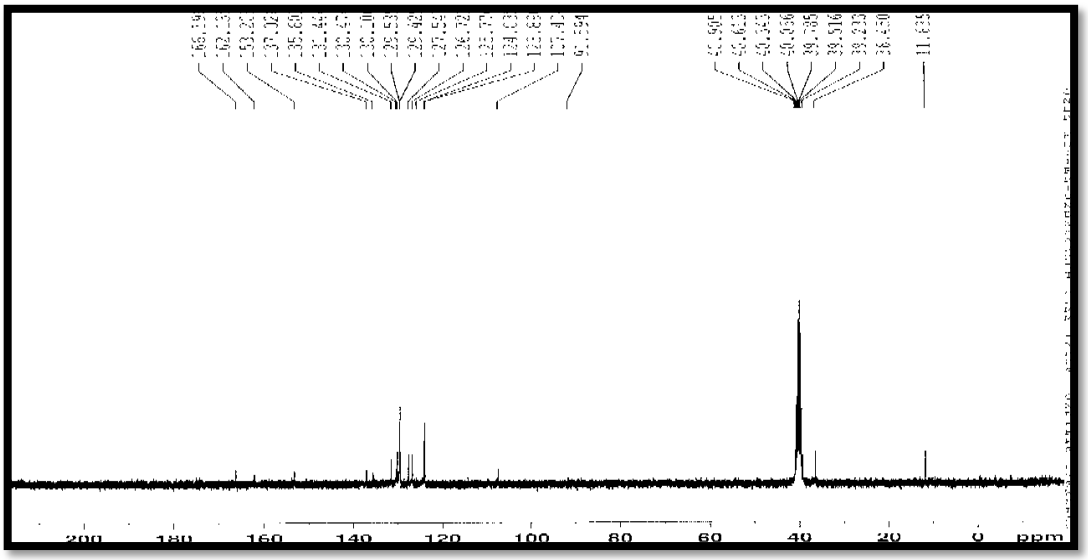


Fig. (14)[13] C-NMR spectrum for compound (2c)

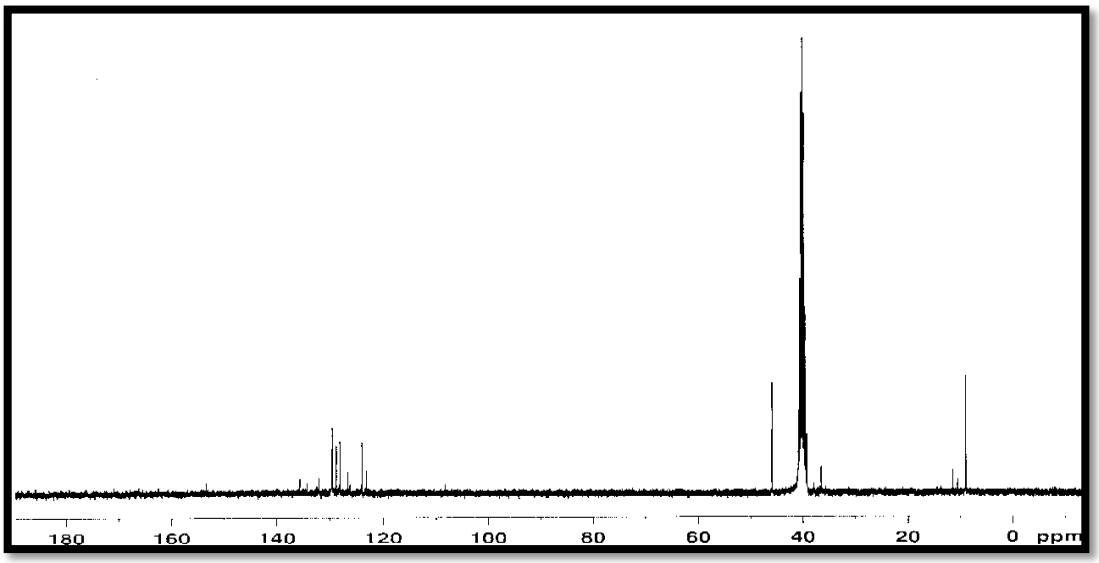


Fig. (15)[13] C-NMR spectrum for compound (2d)

Conclusions:

Polyimides derivatives (2a-2e) containing different groups and obtained via 4-aminoantypyrine with many substituted acid chloride to get(1a-1e) compound, then they were subjected to reaction with poly acryloyl chloride in THF as a solvent with drops of Et_3N to give new five polyimides (2a-2e). Their structures were confirmed by UV., infrared and ^{1}H-^{13}C-NMR spectrometric analysis.

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تحضير بولي ايمايدات جديدة مشتقة من 4-امينوانتي بايرين

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الخلاصة:

في هذا البحث تم تحضير خمسة بوليمرات جديدة من تحوير بولي اكريلويل كلورايد،حيث حضرت هذه البوليمرات بخطوتين، الخطوة الاولى تضمنت تحضير:

N-(sub.or unsub. benzoyle and sub. or unsub. acetyl amid sub. 4-amino antipyrin (A-E)

وذلك بتكاثف 4-امينو انتي بايرين مع بعض كلوريدات الحوامض المعوضة وغير المعوضة (الاليفاتية و الاروماتية)، اما الخطوة الثانية تضمنت تفاعل بولي اكريلويل كلورايد مع الامايدات المختلفة المحضرة في الخطوة الاولى (A-E) في مذيب مناسب وكمية مناسبة من ثلاثي اثيل امين (Et_3N) مع التسخين ليعطي بولي ايمايدات جديدة (A_1-E_5)، وتم تشخيص المركبات المحضرة باستخدام اطياف الاشعة فوق البنفسجية FT.IR, UVواطياف الرنين النووي المغناطيسي H^1-NMR, C^{13}-NMR بالاضافة الى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والذوبانية.

الكلمات المفتاحية: 4-امينوانتي بايرين، مشتقات بولي ايمايدات، بولي اكريلويل كلورايد