

Synthesis of Polyimides derived from 2,6-diamino-4-methyl-1,3,5-triazine

Rana Rafeh Hamza

Department of Chemistry, College of Science for Women, University of Baghdad, Iraq .

Email: ranar_2010@yahoo.com

Received 30/9/2015

Accepted 20/12/2015



This work is licensed under a [Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License](http://creativecommons.org/licenses/by-nc-nd/4.0/)

Abstract:

This work included synthesis of several new polymers of polyacryloyl chloride in two steps . The first step the included the reaction of N-(sub. or un sub. benzoyl and sub. or un sub. acetyl) amidyl sub. 2,6- diamino -4-methyl-1,3,5-triazine (1-5) by condensation of many substituted acid chlorides with 2,6- diamino -4-methyl-1,3,5-triazine . While the second step included the reaction of polyacryloyl chloride with the produced compounds (1-5) in step (1) in the presence amount triethyl amine (Et₃N) to obtain new polyimides (6-10). The prepared compounds were characterized by UV. , FT-IR, and some of them by ¹H-NMR and ¹³C- NMR spectroscopy.

Key words: 2,6- diamino -4-methyl-1,3,5-triazine, polyacryloyl chloride , polyimides derivatives .

Introduction:

Triazine derivatives are used in pharmaceutical industry as coupling agents for the synthesis of peptides and as side chain of antibiotics , as well as in formulating bactericides and fungicides[1-2]. 1,3,5-triazine are amongst the oldest known organic molecules ; originally they were called the symmetric triazines usually abbreviated as s. or syn- triazines[3]. Som of the substituted 1,3,5-triazine have reported to possess interested biological activities[4]. wide range of 1,3,5-triazines exhibit selective their bicidal properties , such as anti – cancer,

antiviral[5], bactericidal , fungicidal[6], antimalariol agents and antituberculosis[7]. One of the most important derivatives of 1,3,5-triazine is 2,4-diamino-6- methyl-1,3,5-triazine that has played an important role in organic chemistry[8]. It is used as an intermediate for pharmaceuticals and as a modifier and flexibizer of for maldehyde resins[9], which reacted with sub. or unsub. benzoyl and sub. or unsub. acetyl to give N-(sub. or unsub. benzoyl and sub. or unsub.acetyl amidyl sub. 2,4-diamino-6- methyl-1,3,5-triazine , which reacted with poly

acryloyl chloride to give new poly imides derivatives for 2,4-diamino-6-methyl-1,3,5-triazine. Polyimides (PIS) are classified as a group of super-engineering plastics owing to their excellent thermal stability[10], and they are a class of high – performance representative and involving aromatic and hetero cyclic rings in the main chains that are well known as heat-resistant organic materials. Polymers have been widely used in flexible displays[11]. Like Polymer electronic memories, prevaporation, biofuels separation and many other fields of microelectronics[12], optics , a erospace industries and biomedical engineering [13]. However polyimide materials are usually difficult to be processed because of their infusibility at high temperature and insolubility in most organic solvent[14]. in order to improve the solubility and melting ability of polyimides, many studies have been focused on introducing the fluorocontaining groups, or flexible group into the polymer backbone[15].

Materials and Methods:

All chemicals used in this work from BDH , Merk and Fluka were used without further determination .

Melting points were determined in Gallen kampf melting point apparatus and were uncorrected. UV-visible spectra were recorded on shimadzu T_{60u} spectrophotometer using ethanol as a solvent, FT-IR – 8400 Fourier transform infrared spectrophotometer as KBr disc. Softing points were determined by using Reichert Thermovar with Reichert Jung

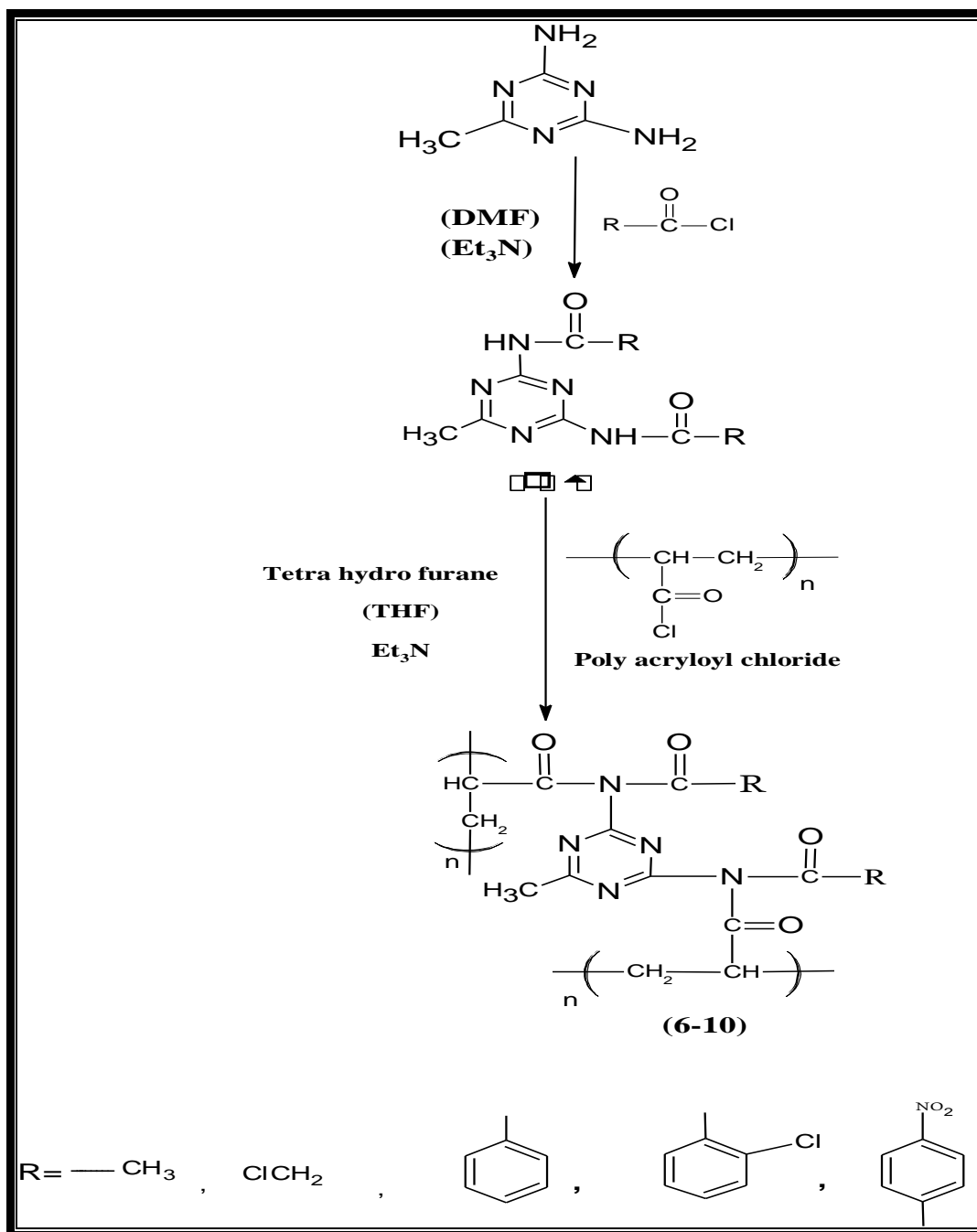
Temperature Controller , 1H-NMR and ¹³C- NMR spectra were recorded on Bruker specrospin Ultra shield magnets 300MHz in strument using tetra methyl silane (TMS) as an internal standard and DMSO.d₆ as a solvent in Al-Albata University in Jordan.

General procedure preparation of [(subs. Aryl or acetyl) subs. 2,6 – diamino-6- methyl- 1,3,5-Triazine[14] (1-5):

mixture of 2,6 – diamino-6-methyl- 1,3,5-Triazine (0.02 mol) , sub. benzoyl chloride (0.04 mol) and triethyl amine Et₃N (4-5 drops) with DMF as a solvent in (100 ml) round bottom flask were refluxed for (4 hrs.). After that, the solvent was removed and recrystallized from ethanol . All physical properties for products compounds are listed in Table (1).

General procedure preparation of poly (N-acryl-N-sub. or unsub. acetyl of benzoyl) Imidyl substituted 2,6 – diamino-6- methyl- 1,3,5-Triazine[14] (6-10):

Dissolved (0.02) of N-subamidyl – sub. 2,6 – diamino-6- methyl- 1,3,5-Triazine in (25 ml) THF and mixing with poly acryloyl chloride (0.02 mol) and add (1 ml) triethyl amine(Et₃N) in (100 ml) round bottom flask . The mixture was refluxed for (6-8 hr.). After cooling, the solvent was removed. The separated sold was filtered and purified by dissolving in DMF and reprecipitating from water or acetone. This procedure was applied on compounds as shown in Table (2). All physical properties are listed in Table (2).



Scheme (1): The general pathway of the reaction.

Table (1): The physical properties for [(sub. Aryl or actyl) sub.(trimethoprim)] Amide

| Comp No. | Compound structure | Name | Colour | Melting Point | %conversion | Solvent use in react. |
|----------|--------------------|--|--------|---------------|-------------|-----------------------|
| 1. | | <i>N,N</i> -(6-methyl-1,3,5-triazine-2,4-diyl)diacetamide | Yellow | Oily | 86 | DMF |
| 2. | | <i>N,N</i> -(6-methyl-1,3,5-triazine-2,4-diyl)bis(2-chloroacetamide) | Blake | Oily | 78 | DMF |
| 3. | | <i>N,N</i> -(6-methyl-1,3,5-triazine-2,4-diyl)dibenzamide | White | 160-163 | 90 | DMF |
| 4. | | <i>N,N</i> -(6-methyl-1,3,5-triazine-2,4-diyl)bis(2-chlorobenzamide) | Brown | Oily | 80 | DMF |
| 5. | | <i>N,N</i> -(6-methyl-1,3,5-triazine-2,4-diyl)bis(4-nitrobenzamide) | White | 181-182 | 73 | DMF |

Table (2): The physical properties of polymers (6-10):

| Comp. No. | Compound structure | colour | Softing point | % conversion | Solvent used in reactio |
|-----------|--------------------|-----------------|---------------|--------------|-------------------------|
| 6. | | Brown | 102-108 | 90 | THF |
| 7. | | Yellowish brown | 132-136 | 86.66 | THF |

| | | | | | |
|-----|--|---------------|---------|-------|-----|
| 8. | | Yellow | 100-104 | 80 | THF |
| 9. | | Reddish Brown | 142-147 | 92.85 | THF |
| 10. | | Yellow | 99-110 | 70 | THF |

Table (3): FT-IR spectral data for all product compounds

| Comp. No. | $\nu(\text{C-H}) \text{ cm}^{-1}$ aromatic | $\nu(\text{C-H}) \text{ cm}^{-1}$ aliphatic | $\nu(\text{C=O}) \text{ cm}^{-1}$ | $\nu(\text{N-H}) \text{ cm}^{-1}$ | $\nu(\text{C-H}) \text{ cm}^{-1}$ and $\nu(\text{C=N}) \text{ cm}^{-1}$ | Others |
|-----------|---|--|-----------------------------------|-----------------------------------|---|--------------------------------------|
| 1. | 3039 | 2777-2993 | 1651 | 3363 | 1465 1539 | - |
| 2. | 3062 | 2777-2939 | 1701 | 3390 | 1469 1597 | (C-Cl) 752 |
| 3. | 3155 | 2738-2978 | 1685 | 3313 | 1473 1543 | - |
| 4. | 3008 | 2777-2989 | 1651 | 3417 | 1465 1543 | (C-Cl) 1018 |
| 5. | 3059-3113 | 2738-2978 | 1693 | 3448 | 1477 1543 | (C-NO ₂) 1350 1519 |
| 6. | 3190 | 2938-2976 | 1701 | - | 1477 1539 | - |
| 7. | 3050 | 2738-2939 | 1635 | - | 1435 1473 | (C-Cl) 848 |
| 8. | 3065 | 2730-2970 | 1697 | - | 1475 1541 | - |
| 9. | 3055 | 2939 | 1716 | - | 1471 1627 | (C-Cl) 1035 |
| 10. | 3111 | 2941-2978 | 1689 | - | 1465 1653 | (C-NO ₂) 1346 1521 |

Results and Discussion:

The present work involved two steps, The first step includes the preparation of new five amides (1-5) that were prepared by the reaction of 2,4-diamino-6-methyl-1,3,5-triazine with different substituted acid chlorides. The synthesis of these compounds was carried out lined in scheme (1).

The starting material for the synthetic polyimides is 2,4-diamino-6-methyl-1,3,5-triazine which condensed with different substituted acid chlorides through nucleophilic substitution of

chloride with amino group lead to amides (1-5) (Scheme 2).

The FT-IR spectrum of compounds (4) and (5) showed the absence of ($-\text{NH}_2$) stretching together with appearance of band at 3355 cm^{-1} and 1693 cm^{-1} attributed to (N-H) stretching of amide, amide respectively, which indicated the substitution and formation of amides as shown in Table (3), Figure (4) and (5). Attributed UV. Spectrum of compounds (1) and (4) showed an absorption λ_{max} at (273) nm

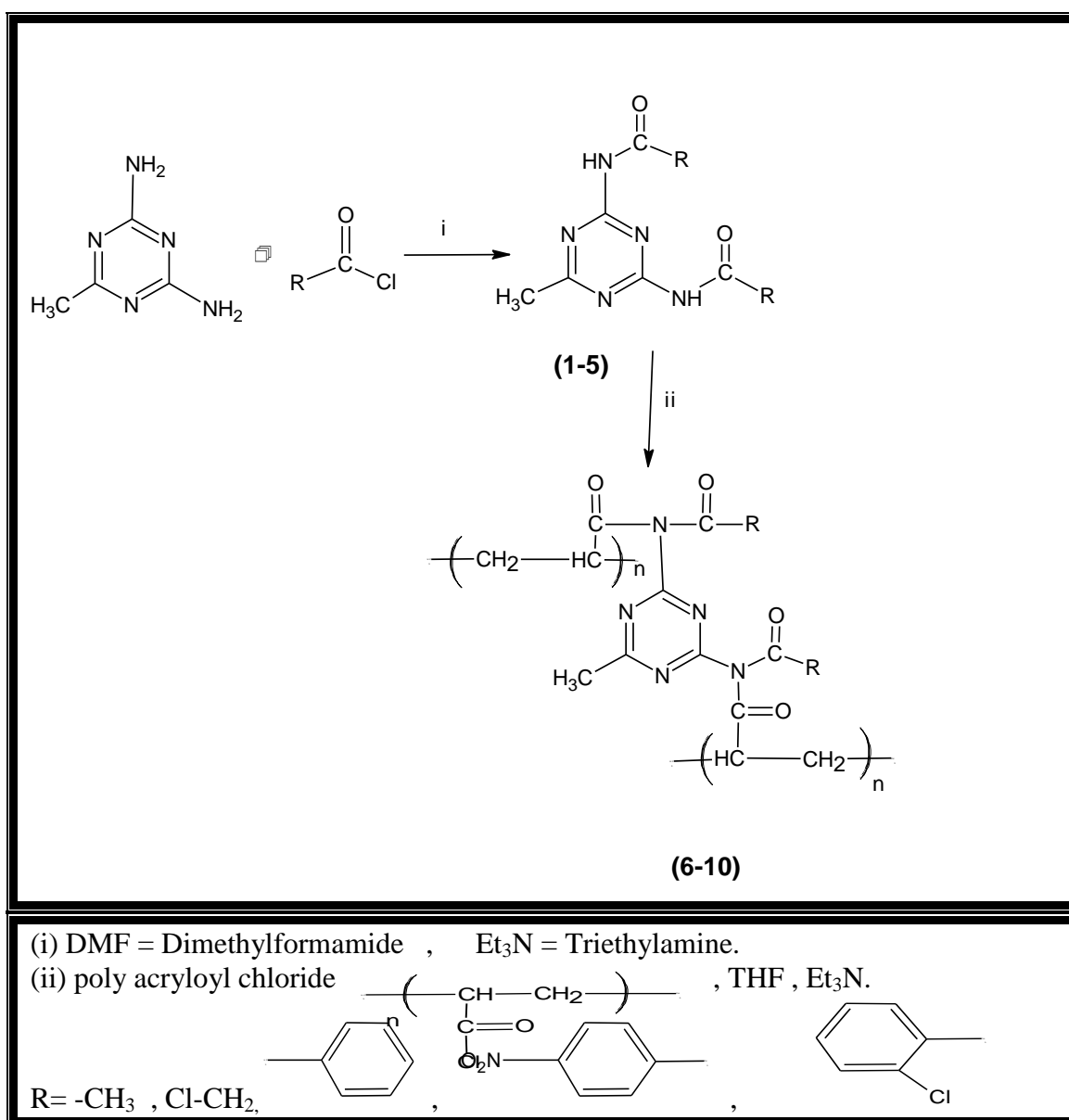
and (294) nm which to (π - π^*). The absorption is listed in Figure (1) and (3).

The ¹H-NMR of compounds (2) and (4) showed the signals at (2.116 - 3.600) ppm and was attributed to (CH₃) proton and multiple signals at (7.187 - 7.939) ppm due to aromatic protons and singlet at (9.218) ppm due to (N-H) protons for amide [17-18] as shown in Figure (9) and (11).

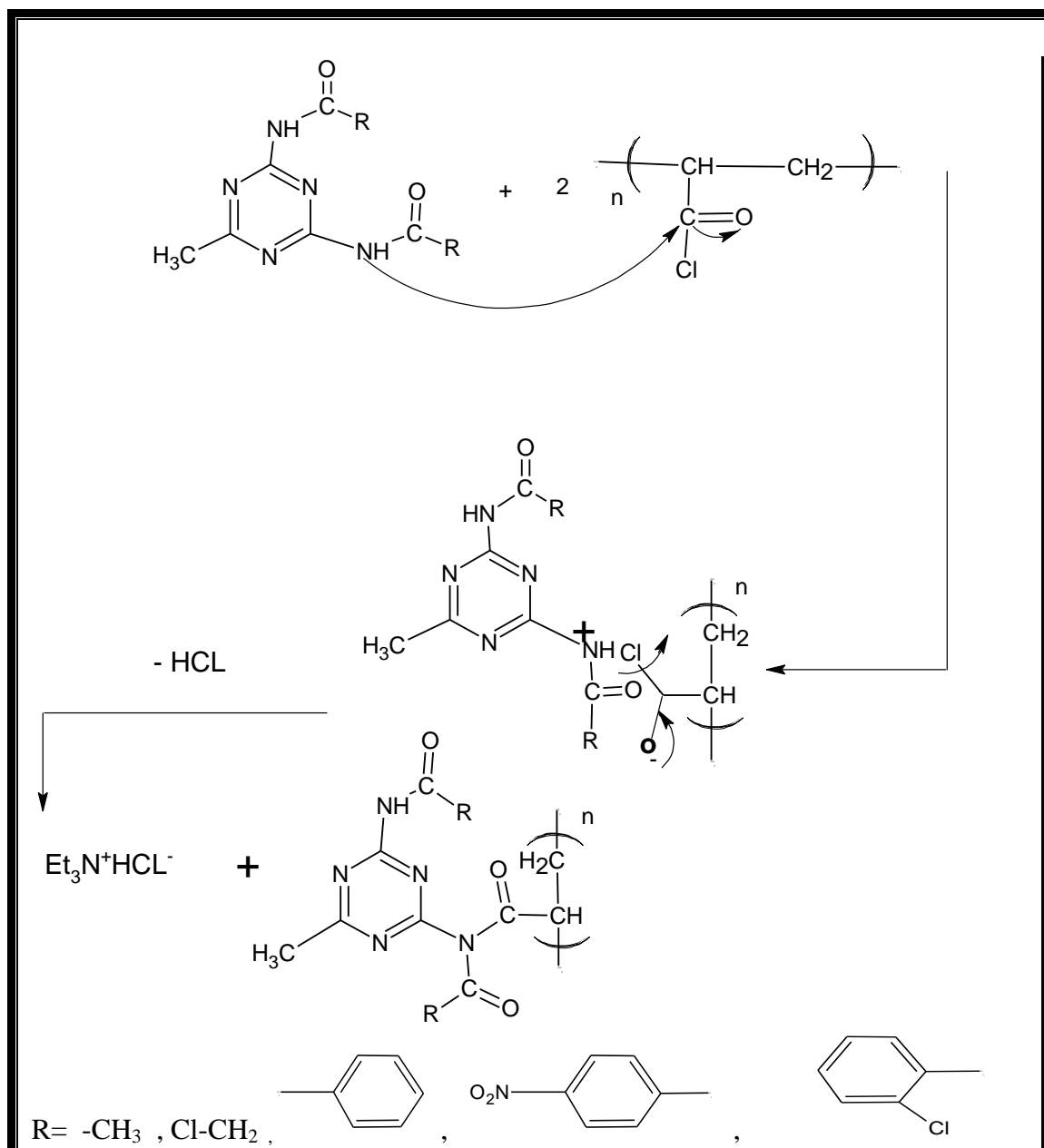
The ¹³C-NMR spectrum of compounds [2] and [4] showed the signal at (168-174) ppm for carbonyl group while the aromatic carbon

appeared at (104-114) ppm as shown in Figure (10) and (12).

The second step: included the of preparation new five polyimides (6-10) that were prepared by the reaction of amides (1-5) in the first step with polyacryloyl chloride subjected to another nucleophilic substitution by treating with poly acryloyl chloride using triethyl amine (Et₃N) as catalyst. The mechanism of reaction involves a nucleophilic attack on the carbonyl as shown in Schemes (3) [14].



Scheme (2): The products of the general reaction.



Scheme (3): The mechanism of reaction.

The FT-IR spectrum showed the disappearance of amide bands $\nu(\text{N-H})$, $\nu(\text{C=O})$, with appearance bands at $(1716) \text{ cm}^{-1}$ attributed to (C=O) amide as shown in Table (3) Figure (6) Another evidence for compounds (7) and (9) its $^1\text{H-NMR}$ spectrum that showed different signals , two multiplet at $(1.799-1.976) \text{ ppm}$ and $(2.753-2.792)$

ppm as signals for ethylene (acryl) protons as shown in Figure (13) and (15).

The $^{13}\text{C-NMR}$ spectrum of compounds (7) and (9) the ethylene carbon appeared at $(39.707-42.697) \text{ ppm}$, and aromatic carbon at $(127.4 - 131.9) \text{ ppm}$ while the imide carbonyl appeared at $(167.5) \text{ ppm}$ as shown in Figure (14) and (16).

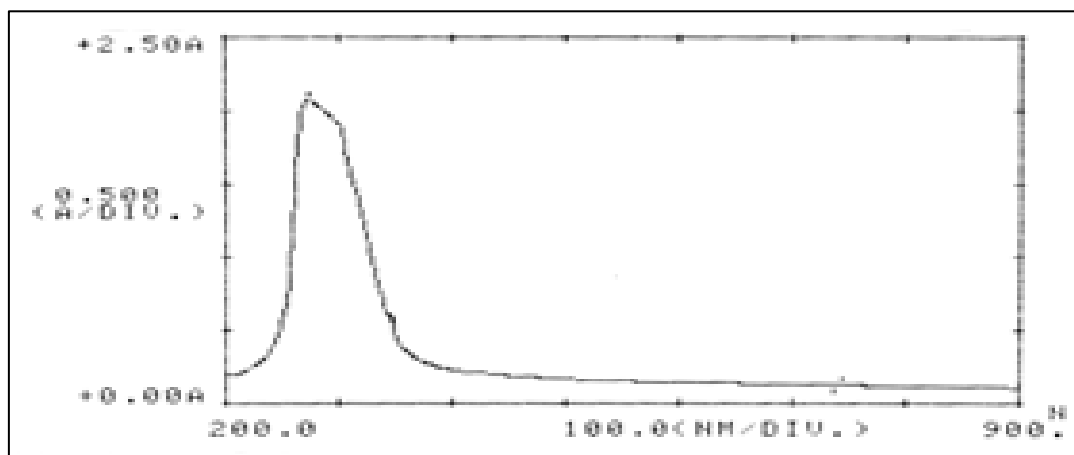


Fig. (1): UV. Spectrum of compounds (1)

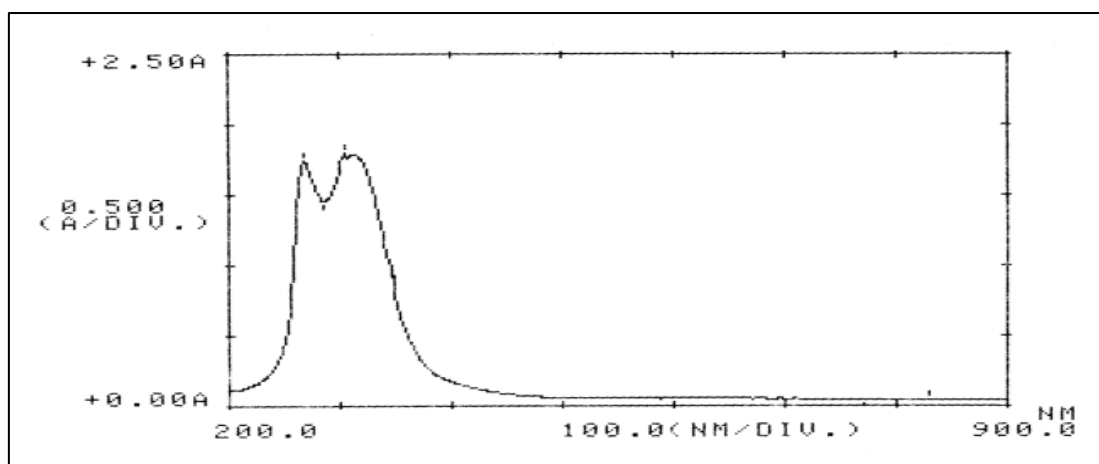


Fig. (2): UV. Spectrum of compounds (6)

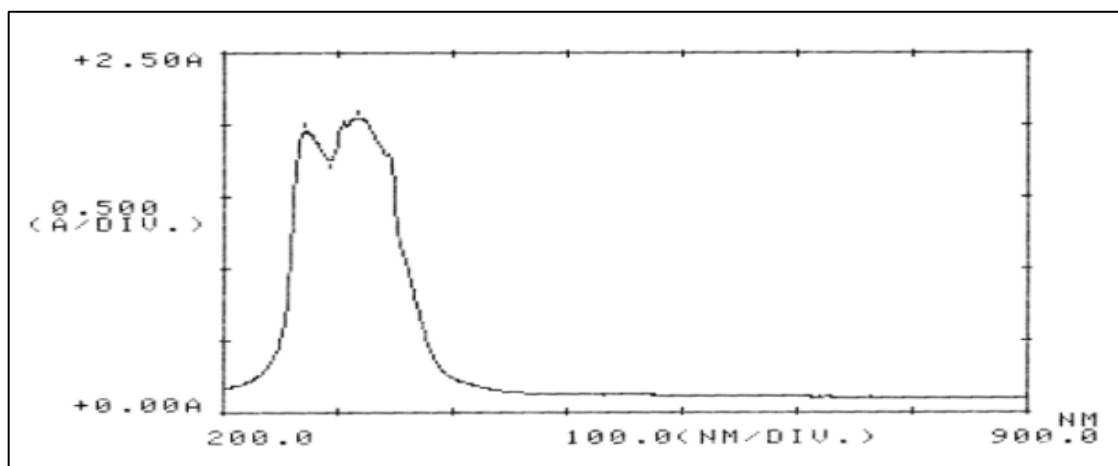


Fig.(3): UV. Spectrum of compounds (4)

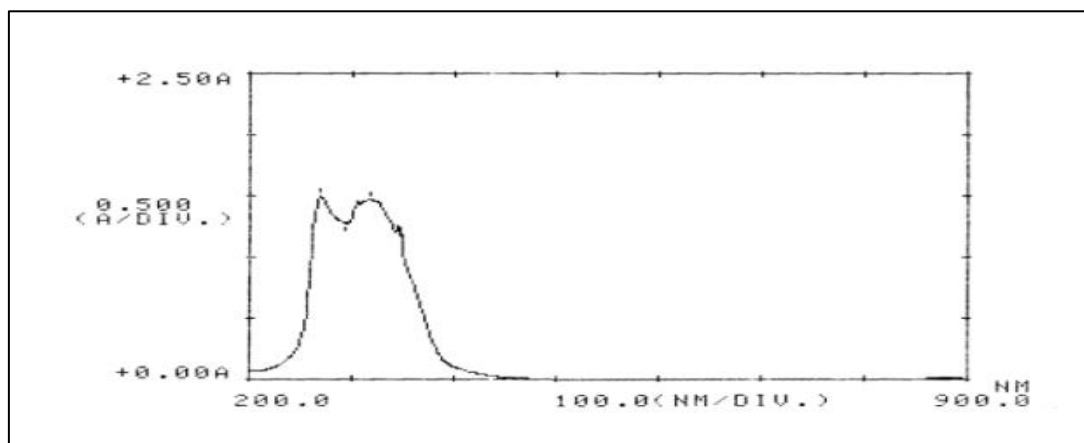


Fig. (4): UV. Spectrum of compounds (9)

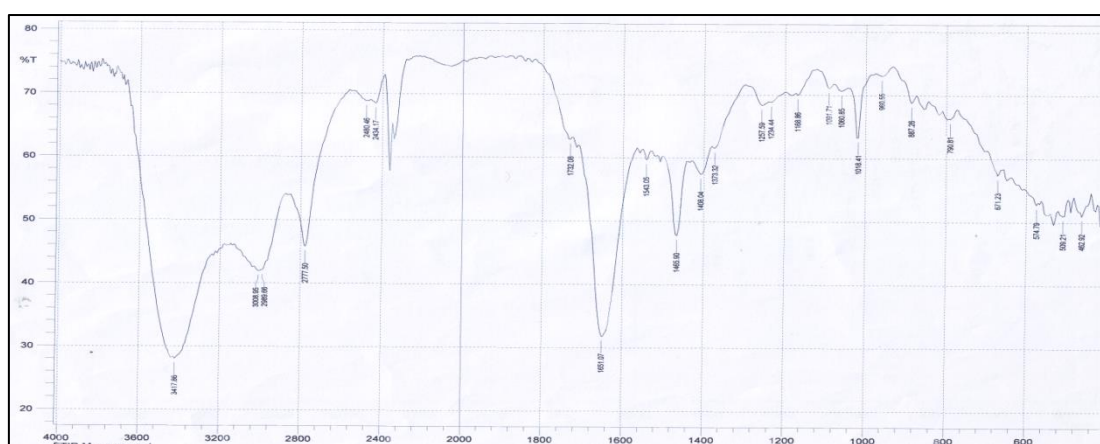


Fig. (5): FT-IR spectrum of compounds (4).

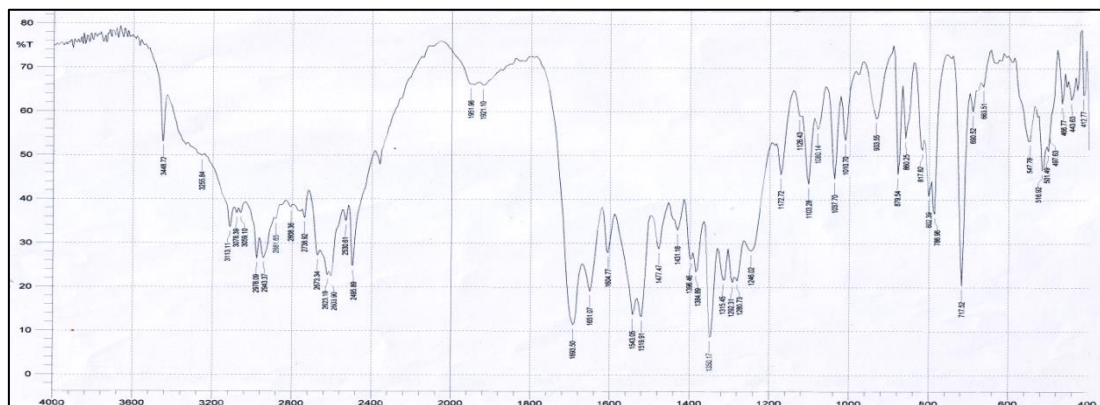


Fig. (6): FT-IR spectrum of compounds (5).

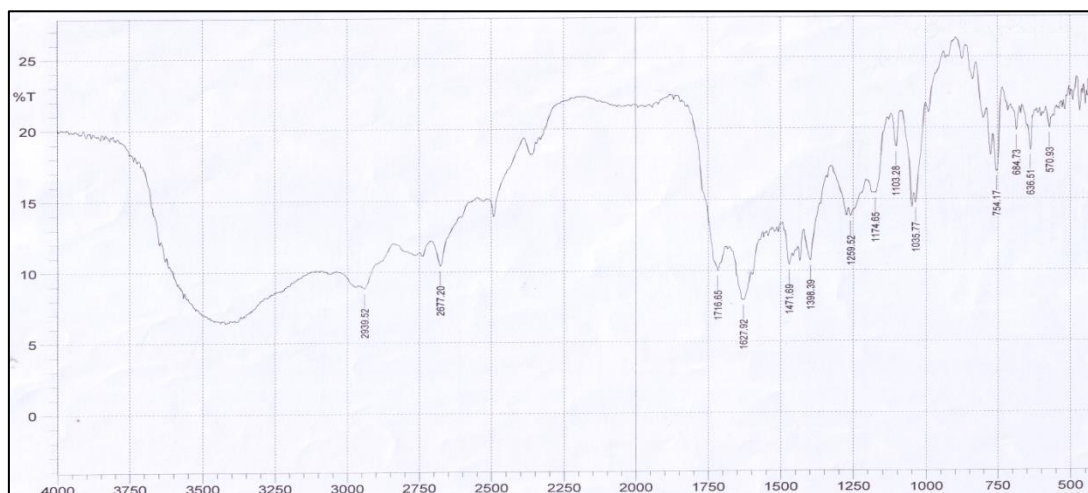


Fig. (7): FT-IR spectrum of compounds (9).

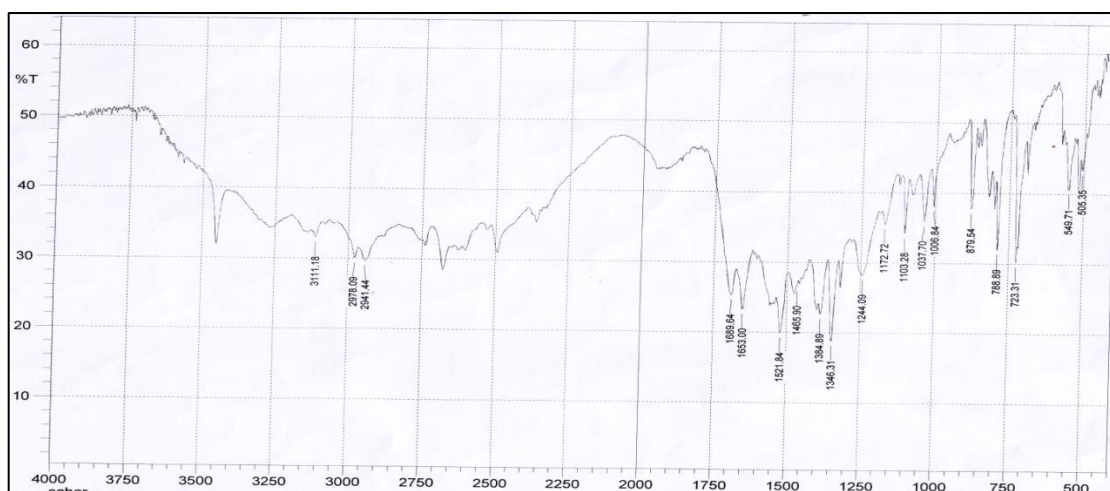


Fig. (8): FT-IR spectrum of compounds (10).

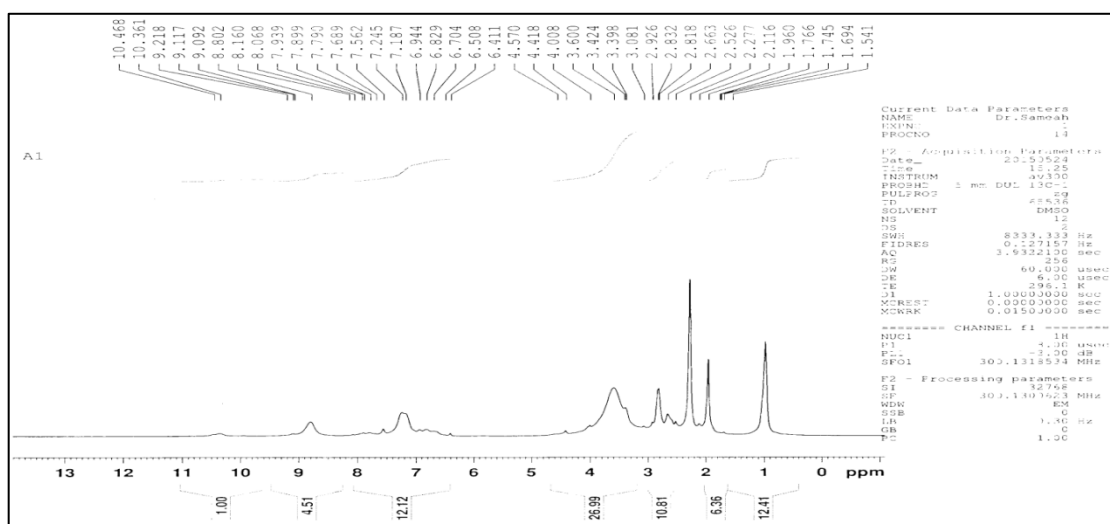


Fig.(9): ¹H-NMR of compound (2).

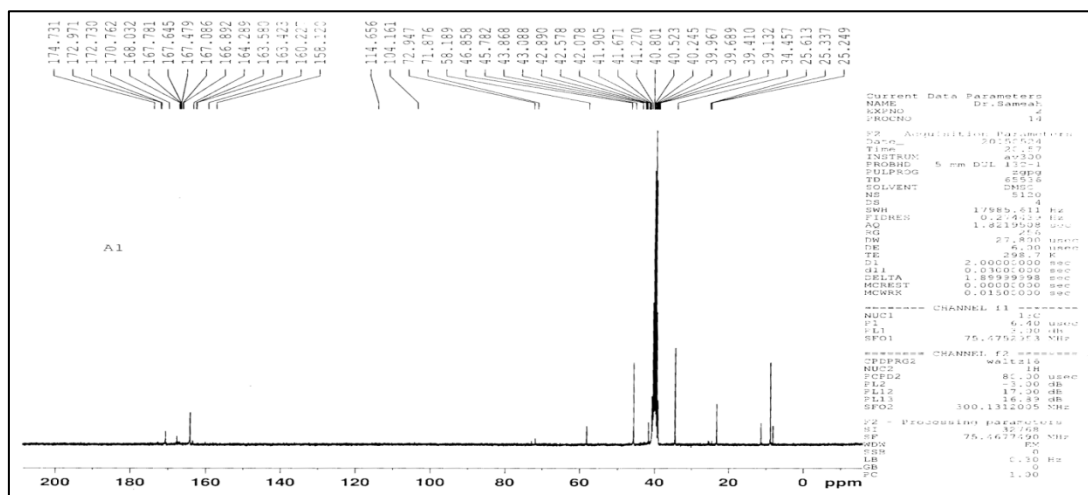


Fig. (10): ¹³C-NMR spectrum of compounds (2).

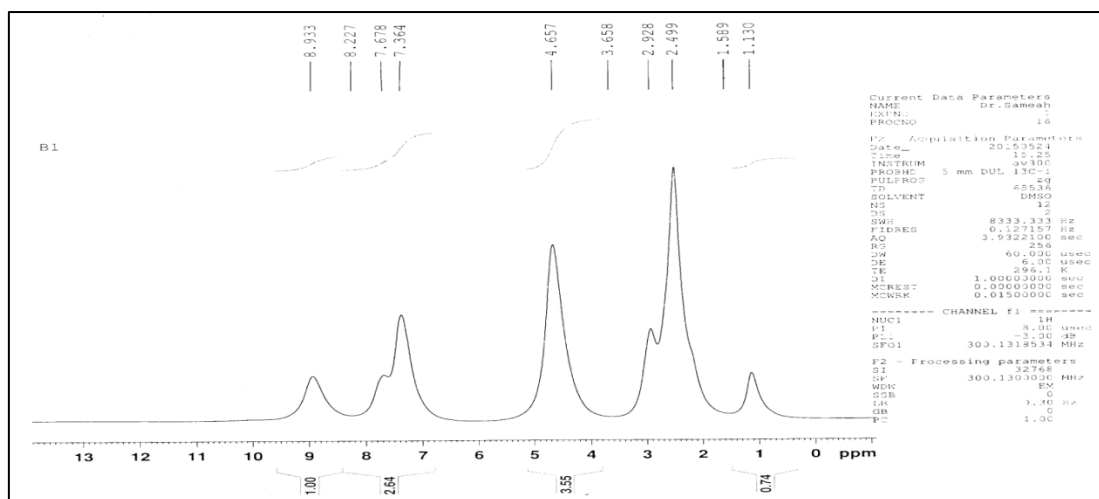


Fig.(11): ¹H-NMR of compound (4).

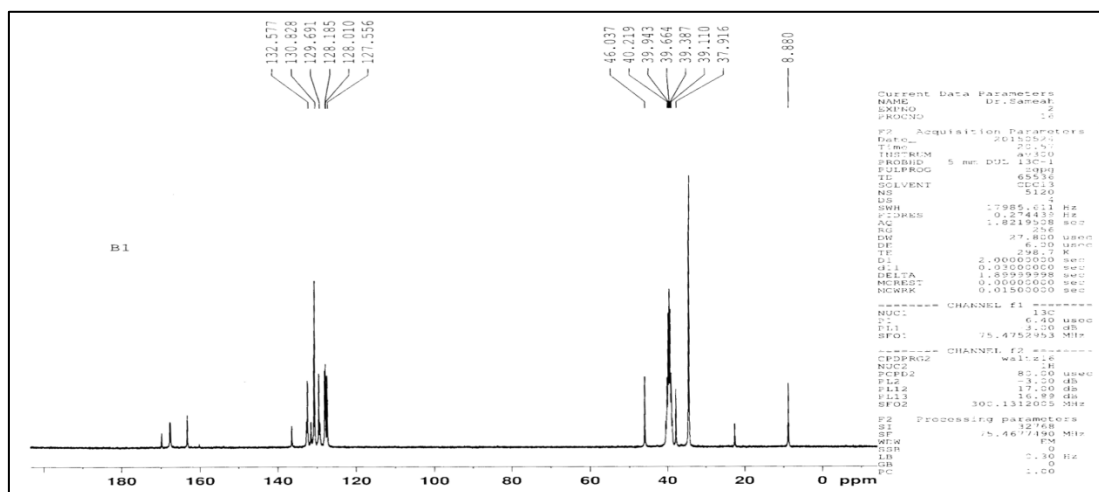


Fig. (12): ¹³C-NMR spectrum of compounds (4).

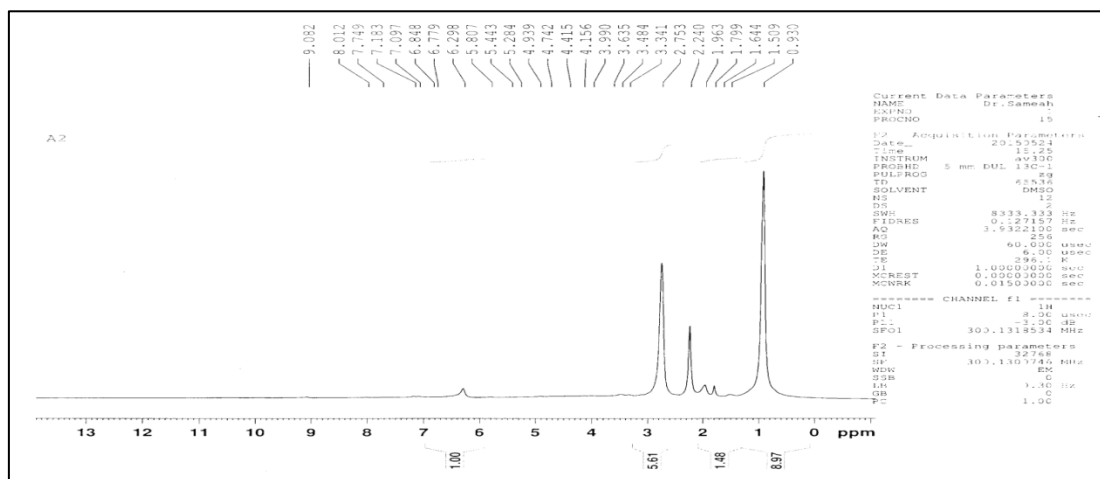


Fig. (13): ¹H-NMR of compound (7).

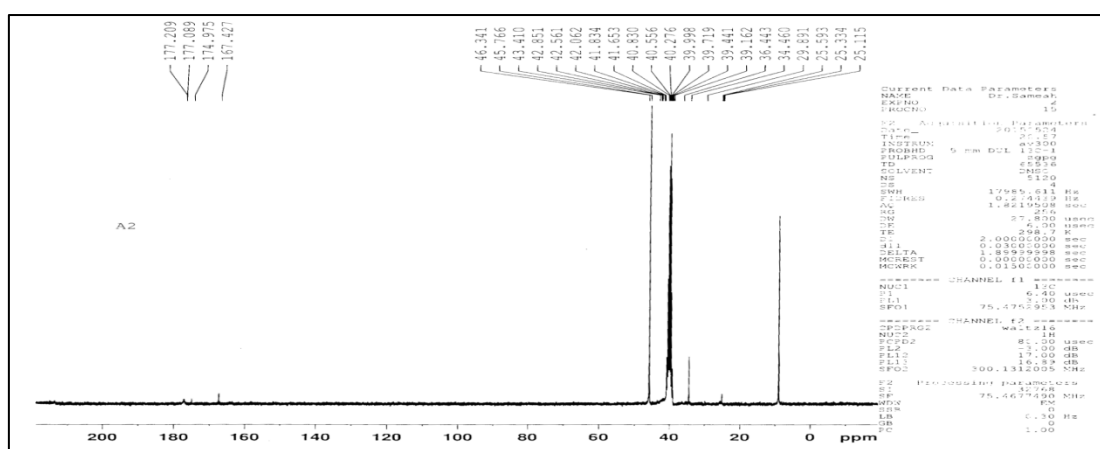


Fig.(14): ¹³C-NMR spectrum of compounds (7).

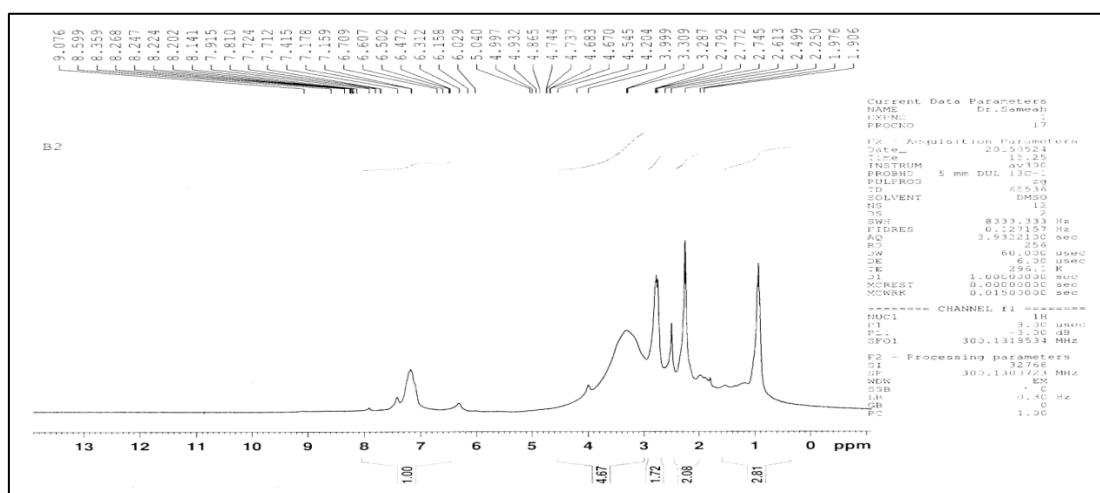


Fig. (15) ¹H-NMR of compound (9).

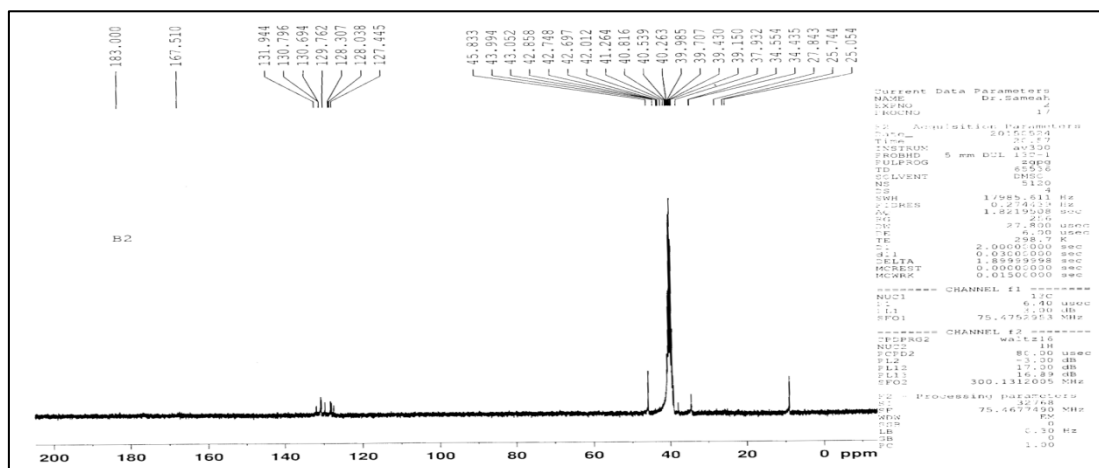


Fig.(16): ^{13}C -NMR spectrum of compounds (9).

References:

- [1] Bansal, R. K. 2010. Hetero cyclic chemistry. 4th Edn, New Age International publisher, New Delhi., 454.
- [2] Basesia, D. K.; Shrivastava, B.; Dubey, B. K. and Sharma, P. 2013. Synthesis, Characterization and antimicrobial activity of novel substituted aryl-1,3,4- oxadiazole – [3,2-a]- 1,2,5 - triazine derivatives. International Journal of Drug Delivery, 5(2): 379 - 388.
- [3] Sheena, Y. M.; Shyma, Y. M.; Hema, V. T.; Mauojkumar, T. K. and Alsenoy, C. V. 2011. Vibrational Spectroscopic studies and Computational study of 2,4- diamino-6- methyl-1,3,5- triazin-1- ium 4- cyanobenzoate. International Journal of Industrial Chemistry, 2 (4): 209-222.
- [4] Gogin, L. L.; Zhizhina, E. G.; PAI, Z. P. and Parmon, V. N. 2009. Methods for Obtaining and Prospects of Developing an Up-to-Date Low-Waste Production of Guanidines in Russia. Chemistry for Sustainable Development, 17(3): 331-339.
- [5] Eissa, H. H, 2012. Synthesis and Characterization of New Azo - Schiff Bases and Study Biological activity. Journal of current Research in Science, 1 (2): 96-103.
- [6] Qiang, Y.; Dirk, S.; Alexander, E. and Per, C. 2008. Synthesis of Novel Homo - N- Nucleoside Analogs Composed of a Homo - 1,4- Dioxane Sugar Analog and substituted 1,3,5- triazine Base Equivalents. Molecules., 13(2): 3092-3106.
- [7] Trentacoste, S. V. 2001. Atrazine effects on testosterone level androgen-dependent reproductive organs in peripubertal melle rats. J. Androl., 22 (1): 142-148.
- [8] Villanueva, C. M. 2004. Atrazine in municipal drinking water and risk of low birth weight, preterm delivery, and small - for- gestational- agestatus. Occup' Environ Med., 62(6): 400-405.
- [9] Tabatabaei, Z. and Mehdiporn, S. 2015. Poly (ether - imide) and related sepiolite nano composites: investigation of physical thermal, and mechanical properties, polym.h Adv. Technol., 26(4): 308-314.
- [10] JIN, Q. and Yamashita, T. 1993. Poly imides with Ali cyclic Diamines - 1- syntheses and Thermal properties. J. Of polymer science part A: polymer chemistry, 31(2): 2345- 2351.
- [11] Ahamed, L. S. 2011. Synthesis of new polyester Amides from polyvinyl Alcohol and convert some of them to polyester- imide. J. Of Al-Nahrain University, 14(2): 29-42 (2011).

- [12] Tian, X.; Jiang, X. and Lu, H. 2012. Synthesis and characterization of soluble and transparent Co-polyimides with controlled glass transition temperature", Indian Journal of chemical Technology, 19(4): 271-277.
- [13] Khammas, S. J.; Sadiq, A. S. and Mahmood, T. A. 2014. Synthesis of polymeric chain", J. Baghdad for Sci., 11 (4): 1567-1576.
- [14] Al-Tamimi, E. O. and Al-Mouamin, T. M. 2013. Synthesis and characterization of new polyimide contain Heterocyclic. J. Baghdad for Sci., 10(4): 1203-1210.
- [15] Dhahir, S. A.; Hamad, A. H.; Salman, M. K. and Ahmed, R. K. 2010. Safety method, Spectrophotometric Determination of Sulfamethaxazole drug in bulk and Pharmaceutical Preparations. Baghdad Science J., 7(1): 607-613.
- [16] Hussain, S. M. 2003. Modification of poly [acryloyl chloride] and poly [styrene-co-butadiene] rubber to polymers containing pendant amic acids, imides, and isoimides. Isomerization of the polymers containing isoimides to be corresponding imides. Ph.D. Thesis, College of Science, University of Baghdad.
- [17] Silverstein, R. M.; Bassler, G. C. and Morrill, T. C. 1981. Spectrometric Identification of Organic Compounds, 4th Ed, John Wiley and Sons, New York, 124-125.
- [18] Mohrig, J. R.; Hammond, C. N. and Schatz, P. E. 2010. Techniques in Organic Chemistry, 3rd Ed, W. H. Freeman and Company, New York, 228-229 (2010).
- [19] Crews, P.; Rodriguez, J. and Jaspars, M. 1998. Organic Structure Analysis. Oxford University press. 95-96.

تحضير بولي ايميدات جديدة مشتقة من 2، 6 – داي امينو -4- مثيل 1، 3، 5- ترايازين

رنا رافع حمزة

قسم الكيمياء / كلية العلوم للبنات / جامعة بغداد / العراق

الخلاصة:

يتضمن هذا البحث على تحضير عدة بوليمرات جديدة ومختلفة لـ بولي اكريلول كلورايد، و بخطوتين حيث تضمنت الخطوة الاولى تحضير (N-(sub. Or unsub. Benzoyl and sub. Or unsub. Acetyl) amidyl sub. 2,6-diaamino -4- methyl -1, 3, 5 – triazine (1-5) الحوامض المعوضة وغير المعوضة (اليفاتية، اروماتية) مع 2، 6 – داي امينو -4- مثيل 1، 3، 5- ترايازين. اما الخطوة الثانية تتضمن تفاعل بولي اكريلول كلورايد مع الامايدات المختلفة المحضرة في الخطوة الاولى (1-5) في مذيب مناسب وكمية مناسبة في ثلاثي اثيل امين (Et_3N) مع التسخين ليعطي بولي ايميدات جديدة (6-10)، وتم تشخيص المركبات المحضرة باستخدام اطياف الاشعة فوق البنفسجية U. V. ، FT-IR ، اطياف الرنين المغناطيسي 1H -NMR و ^{13}C -NMR بالاضافة الى القياسات الفيزيائية المختلفة من درجات التلين ودرجات الانصهار والذوبانية.

الكلمات المفتاحية: 2، 6 – داي امينو -4- مثيل 1، 3، 5- ترايازين ، بولي اكريلول كلورايد، مشتقات البولي ايميد