

PAPER • OPEN ACCESS

## Synthesis and identification of a novel hyper branched polymers containing melamine derivative

To cite this article: Mustafa M. Hasan AL-Abayechi *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **571** 012092

View the [article online](#) for updates and enhancements.



**IOP | ebooks™**

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

## Synthesis and identification of a novel hyper branched polymers containing melamine derivative

Mustafa M. Hasan AL-Abayechi\*, Ali Jassim AL-Zuhairi\*\* and Mohammed N. AL-Baiati\*

\* Department of Chemistry/College of Education for Pure Sciences/ University of Kerbala/Kerbala/ Iraq

\*\*College of Engineering Al-Musayab/ University of Babylon/ Al-Musayab/ Babylon/ Iraq

[mohammad.nadhun@uokerbala.edu.iq](mailto:mohammad.nadhun@uokerbala.edu.iq)

**Key words:** Hyperbranched polymers, melamine derivative, heterocyclic compounds

### Abstract

The Poly-condensation of three-function cyanuric chloride monomer with dual-function different diamine monomer gave three different types of hyper branched polymers. The entire prepared polymers have been identified using IR and <sup>1</sup>HNMR spectrum.

### Introduction

Hyper branched polymers have received considerable attention from researchers in the fields of chemistry, and since the last few years this field has been growing rapidly and extensively, as it has been described in a number of publications [1]. Hyper branched polymers, as well as their derivatives are involved in various fields of chemistry such as; (i) Materials and nanotechnology as in nanofiltration membranes that used in water treatment [2-4] and also in the modification of surfaces for carbon nanotubes [5-7]. (ii) Light-emitting electronic materials such as poly fluorines that characterized by high luminous intensity, which is used in the manufacture of diode that emits blue light (LED) [8-10]. (iii) Coating as a corrosion-resistant coating [11] and antifouling coating through the coating prevention a good property for biofouling [12-14], and also a modifier of dyes by inserting dye particles into capsules made of hyper branched polymers [15-17]. (iv) Additives as reinforcements for epoxy resin for example hyper branched polymers for poly amidoamine [18-19] and polyimide [20-21]. (v) Chemo sensors explosive which is use the detection of explosives containing nitro-aromatic compounds [22-24]. (vi) Applications and biomaterials such as bioimaging and drug delivery, antifouling-antimicrobial-antibacterial material [25-27], and there are other uses in optical materials, absorption of UV , conductive polymers and many other uses may not yet be known [28]. Hyper branched polymers and their derivatives have many unique characteristics that are not available in the corresponding linear polymers such as low viscosity, better solubility, high polarity, the ability on chain entanglement, and



thermal stability (glass transition temperature) [29]. The structure of hyper branched polymers are characterized by its ability to develop, improve its properties and use it in high performance applications because it contains a huge number of functional end groups. Thiobarbituric acid and 1,3-cyclohexanedione have been condensed with aromatic aldehyde. The resultant compounds have been polymerized with different dihaloalkanes to give hyper branched polymers. The optical properties of the prepared polymers have been examined [30]. Melamine derivatives are polymers that have important industrial applications, such as electrical applications, agriculture and spinning, mechanical industry and some light manufacturing, these derivatives are used in the manufacture of insulators, fertilizers, high temperature resistant material, UV absorption, anti-corrosion [31-32]. Various products containing plastic, forming materials, water-soluble coatings and many other applications [33]. The industrial history of these derivatives is about 100 years old. It began in 1935 when melamine-formaldehyde resins were prepared by Henkel [34] in Germany. These resins formed from urea or phenol, and these resins gained wide popularity because of their good properties [34]. Heterocyclic moieties can be found in large number of compounds which display industrial applications. The activity of the compounds is mainly dependent on their molecular structures [35-37].

In this research, was accreditation of poly-condensation for a three-function cyanuric chloride (TCT) monomer with dual-function different diamine monomer, and three different types of hyper branched polymers were formed (A, B and C). These polymers are known as melamine derivatives (scheme.6, 7, 8).

## **Experimental part**

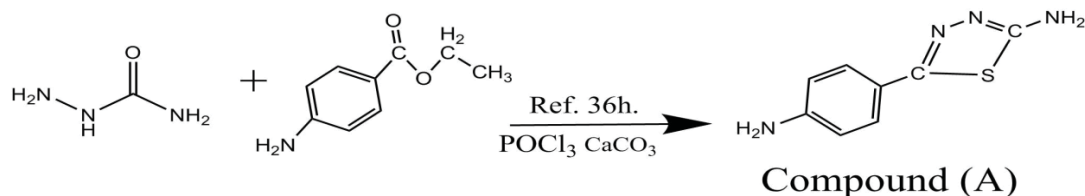
1) Chemicals were purchased from Aldrich and Lancaster chemicals and mostly used without further purification.

### **2) Typical procedure for the preparation of compound (A): [38]**

Preparation of (A) [5-(4-aminophenyl)-1, 3, 4-thiadiazol-2-amine]

(0.01mol) of ethyl 4-aminobenzoate with (0.01mol) of thiosemicarbazide were dissolved in  $\text{POCl}_3$  solvent and the mixture was refluxed for 36 hours. The mixture was slowly poured with continuous stirring on crushed ice and the acid mixture was neutralized by potassium carbonate  $\text{CaCO}_3$ , then the solution was left for 12 hours to settle down, then the mixture was filtered and the precipitate was obtained. The precipitate was washed with

distilled water, and recrystallized from ethanol. (scheme.1). Yield 82.1%, Mp (151-158)°C; IR (V/Cm): 3364 (NH<sub>2</sub>), 3232 (N-H), 1526-1602 (C=N), 698 (C-S), 1129 (N-N)



**Scheme (1): Synthesis of compound (A)**

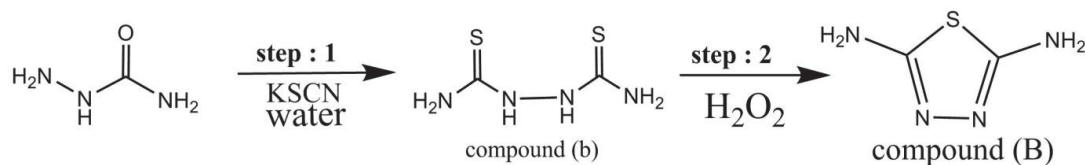
## 2) Typical procedure for the preparation of compound (B): [39]

### Step -1: Preparation of (b) [Bithiourea]:

About (1.65 gm, 0.022 mole) of semicarbazide and (2.137 gm, 0.022 mol) of potassium thiocyanate were dissolved in 6 ml distilled water and the mixture was placed in a round bottom flask. The mixture was stirred with refluxed for 5 hrs. The precipitate was recrystallized from boiling water (scheme.2). Yield 37 %, Mp (222-228)°C; IR (V/Cm): 3202 (N-H), 1620 (C=S), 1061 (C-N)

### Step- 2: Preparation of (B) [2, 5-diamino 1,3,4-Thiadiazol]:

About (5.0 gm, 0.033 mole) of Bithiourea was dissolved in (6.67 ml) of 3% H<sub>2</sub>O<sub>2</sub>. The mixture was refluxed with stirring for one hour at 50-60°C. After that, the mixture was cooled and was filtered under vacuum and then dried at 100°C. The precipitate was recrystallized from boiling water (scheme.2). Yield 77%, mp (215-218)°C; IR (V/Cm): 3291 (N-H), 2062 (C=N-N=C), 1592 (C=N), 1173 (N-N)

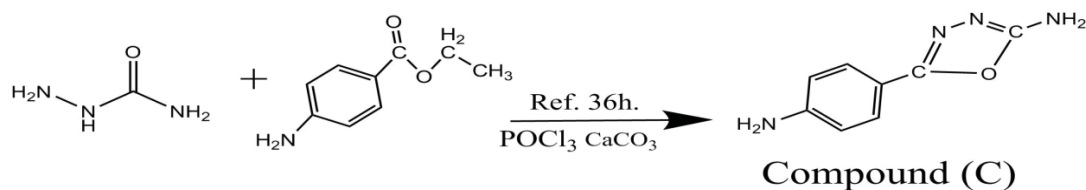


**Scheme (2): Synthesis of compound (B)**

### 3) Typical procedure for the preparation of compound (C): [38]

Preparation of (C) [5-(4-aminophenyl)-1,3,4-oxadiazol-2-amine]

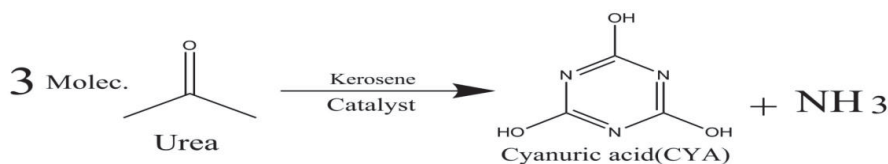
About (0.01mol) of ethyl-4-aminobenzoate with (0.01mol) of semicarbazide were dissolved in  $\text{POCl}_3$  solvent and the mixture was refluxed for 36 hours. The mixture was slowly poured with continuous stirring on crushed ice and the acid mixture was neutralized by potassium carbonate  $\text{CaCO}_3$ , then the solution was left for 12 hours to settle down, then the mixture was filtered and the precipitate was obtained. The precipitate was washed with distilled water, and recrystallized from ethanol. (scheme.3). Yield 50%, mp(89-91) $^{\circ}\text{C}$ ; IR (V/Cm):2361-2341 (NH-NH), 1599 (C=N),1021 (C-O ether),



**Scheme (3): Synthesis of compound (C)**

### 4) Typical procedure for the preparation of cyanuric acid:[40]

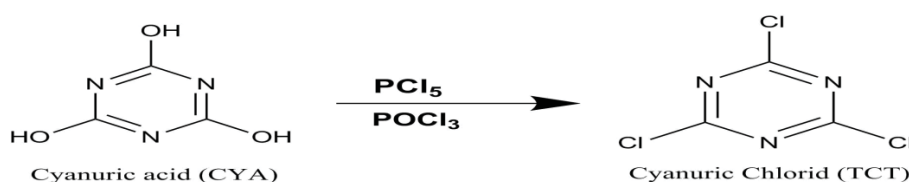
In a round bottom flask with three necks, 10 gm of urea was added to 20 mL kerosene (white oil), the mixture was stirred with heating (reflux) into 150 $^{\circ}\text{C}$  and placed under vacuum to 10 mm Hg, then was heated to 160-220 $^{\circ}\text{C}$ . At 220 $^{\circ}\text{C}$  the reaction was followed by litmus paper to ensure no more ammonia emission (pH = 4). After that, the mixture was cooled to 80 $^{\circ}\text{C}$  and was poured 15 ml of distilled water. The mixture was stirred for an hour. After that the mixture was filtered to obtain crystallized solids. Finally, the precipitate was dried at 150 $^{\circ}\text{C}$  for two hours. The precipitate was purified by recrystallization using boiling water (scheme.4). Yield 60%, mp(more than 360) $^{\circ}\text{C}$ ; IR (V/Cm): 3417(OH), 1664 (C=N), 1226 (C-O)



**Scheme (4): Synthesis of Cyanuric acid (CYA)**

### 5) Typical procedure for the preparation of cyanuric chloride:[41]

In a Round bottom flask with three necks, (0.9 gm, 0.007 mole) of cyanuric acid with (4.37gm, 0.021mole) of  $\text{PCl}_5$  and 4 ml of  $\text{POCl}_3$ ; The mixture was stirred with heating (reflux) into  $115^\circ\text{C}$  for 24 hrs until no more  $\text{HCl}$  was released. The mixture was distilled at a temperature of  $120^\circ\text{C}$  under vacuum to remove of the excess  $\text{POCl}_3$ . After that, the mixture was washed with chloroform. Finally, The solvent (Chloroform) was removed by rotary evaporator under vacuum and a precipitate was obtained (scheme.5). Yield 27%, mp( $132-138^\circ\text{C}$ ): IR (V/Cm):857-987 (C-Cl)



**Scheme (5): Synthesis of cyanuric chloride (TCT)**

#### 6) Typical procedure for the preparation of Polymers (M1, M2 and M3):

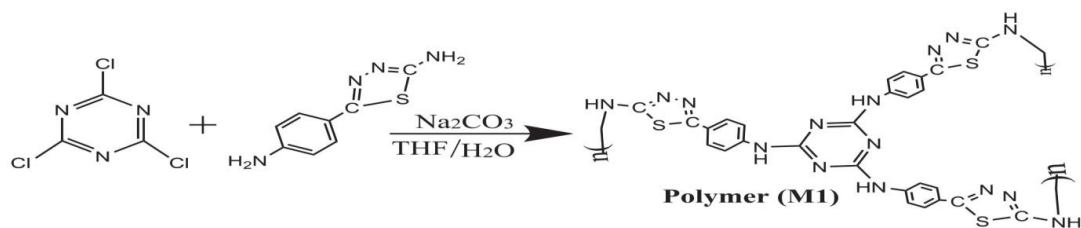
Compound (A for M1, B for M2 and C for M3)

About 5.0 gm of  $\text{Na}_2\text{CO}_3$  and 0.03 mol of the appropriate diamine, were dissolved in 100 ml THF and 100 ml deionized water, all of which are placed in 500 ml a round bottom flask and immersed in ice bath. 0.03 mol of cyanuric chloride was dissolved in 40 ml deionized water and added into the mixture through a separating funnel. The mixture was stirred at (0-5) °C for 10 hrs. After that, the precipitate was separated by a centrifuge. The Precipitate was washed three times using THF and deionized water respectively. Finally, the Precipitate is dried at 65°C for 24 hrs under vacuum.

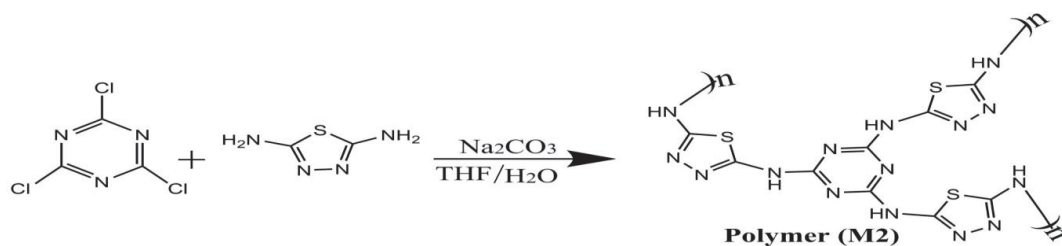
**Polymer M1:** Yield 13%, mp(more than 360)°C; IR (V/Cm):IR (v, cm<sup>-1</sup>): 1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).

**Polymer M2:** Yield 15%, mp(more than 360)°C; IR (V/Cm):1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).

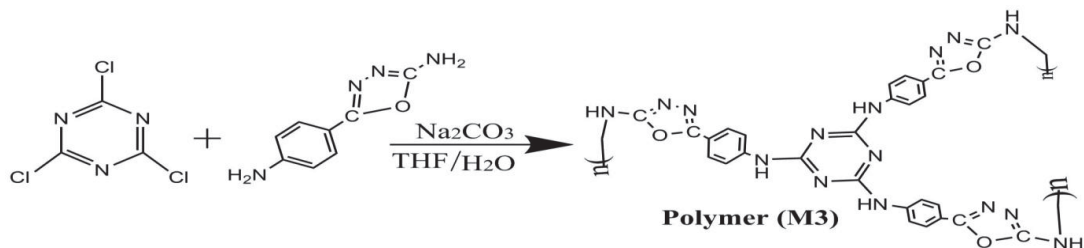
**Polymer M3:** Yield 15%, mp(233)°C; IR (V/Cm):1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).



Scheme (6): Synthesis of Polymer (M1)



Scheme (7): Synthesis of Polymer (M2)



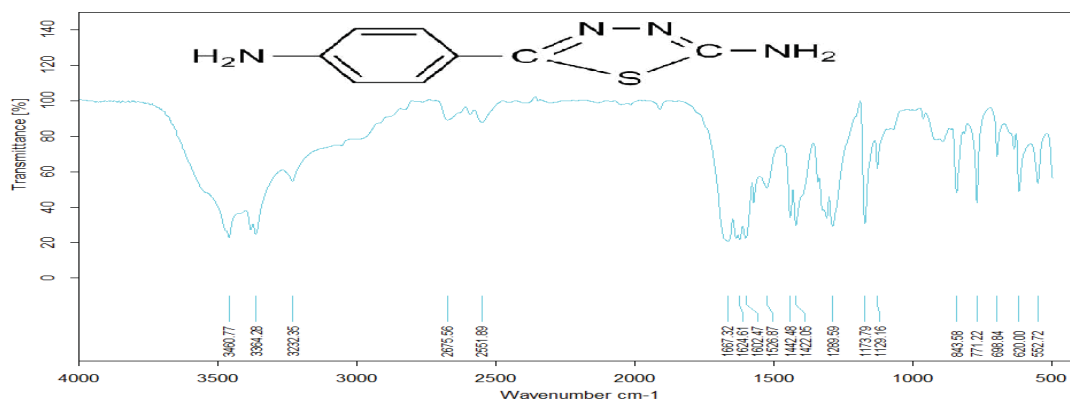
Scheme (8): Synthesis of Polymer (M3)

## Results and discussion

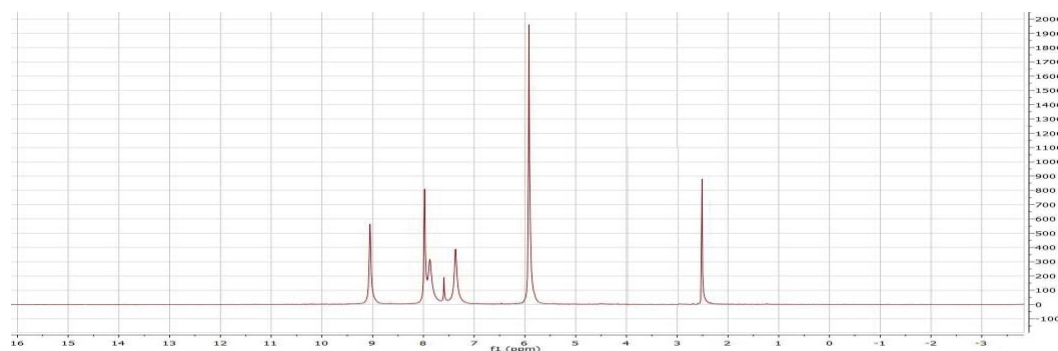
With the various diamines and the aromatic ring of cyanuric chloride (TCT) and with the presence of  $\text{PCl}_5$  and  $\text{POCl}_3$ , different heterogeneous ring compounds known as melamine derivatives were obtained. Compound (A) was generated in (scheme. 1):

As for the final step of compound formation (A), (scheme. 1), is the closing of the ring and the formation of the new thiadiazole ring substituted on the aromatic ring. The spectrum of FT-IR showed different peaks of the thiadiazole ring, as follows: ( $\text{NH}_2$ ) at  $3232\text{ cm}^{-1}$ , ( $\text{C}=\text{N}$ ) from  $(1526\text{ to }1602)\text{ cm}^{-1}$ , ( $\text{N}-\text{N}$ ) at  $1129\text{ cm}^{-1}$  and ( $\text{C}-\text{S}$ ) at  $698\text{ cm}^{-1}$ . The peaks of the thiadiazole ring appear a frequency less than the normal frequency, because it is a ring

substituted on aromatic ring, and the resonance, causing a decrease in frequencies of thiadiazole (Figure 1).

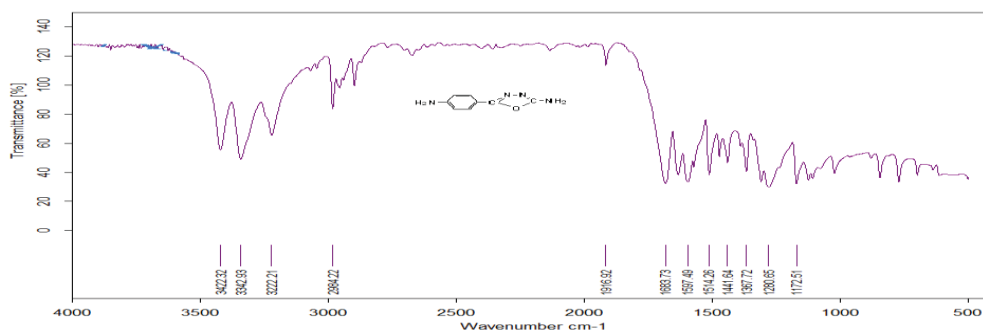


**Figure (1): The FT-IR spectrum of compound (A)**



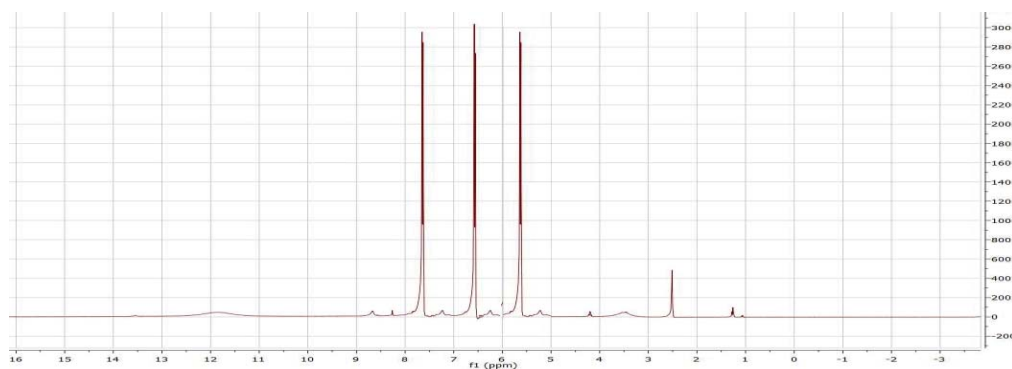
**Figure (2): The <sup>1</sup>H NMR spectrum of compound (A)**

The compound (C) (scheme. 3) was prepared in a similar way to the preparation of compound (A) with using of semicarbazide instead of thiosemicarbazid. The FT-IR spectrum of the final product (A) showed a peak of (C-O-C ether) at 1021 cm<sup>-1</sup> (Figure 3).



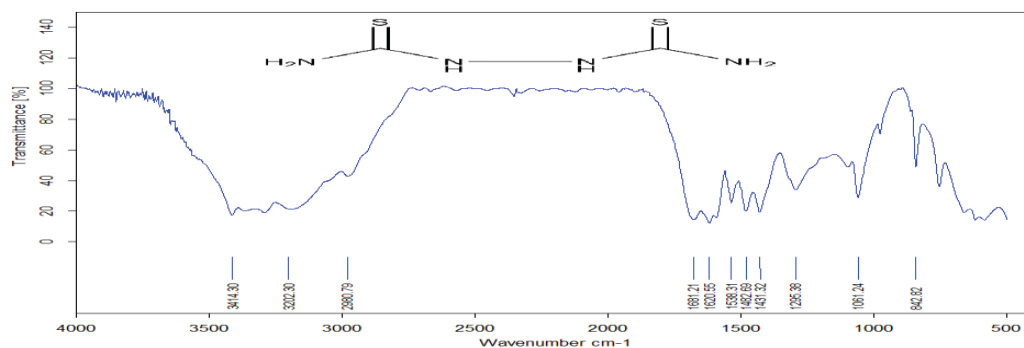
**Figure (3): The FT-IR spectrum of compound (C)**



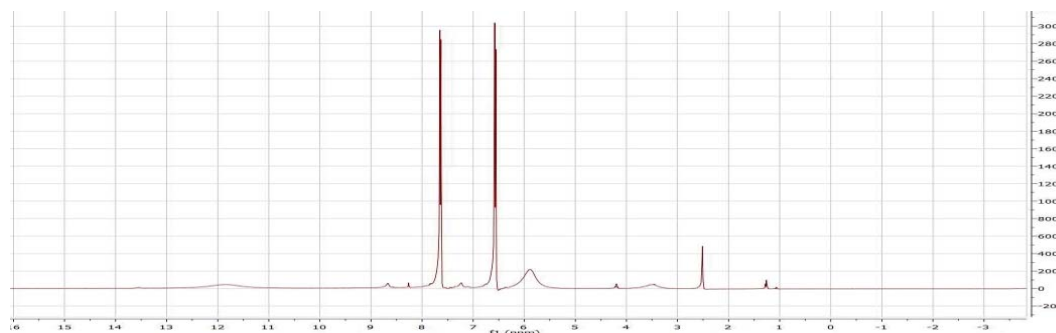


**Figure (4): The  $^1\text{H}$ NMR spectrum of compound (C)**

The compound (B) was prepared in two steps (scheme. 2). The step (1) was to prepare compound (b) of the semicarbazide reaction with KSCN and the presence of distilled water as a solvent. The compound (b) was prepared that containing two groups of carbonyl thioamide (scheme. 2, Step 1) (Figure 5). The FT-IR spectrum showed the peaks of: (N-H) at  $3202\text{ cm}^{-1}$  and the carbonyl thioamide group (C=O) at  $1620\text{ cm}^{-1}$  and (C-N) at  $1061\text{ cm}^{-1}$  Figure 6 has shown the  $^1\text{H}$ NMR spectrum of compound b

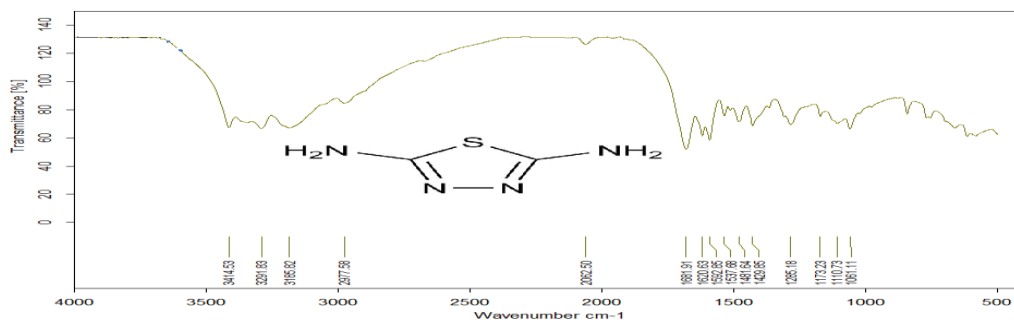


**Figure (5): The FT-IR spectrum of compound (b)**

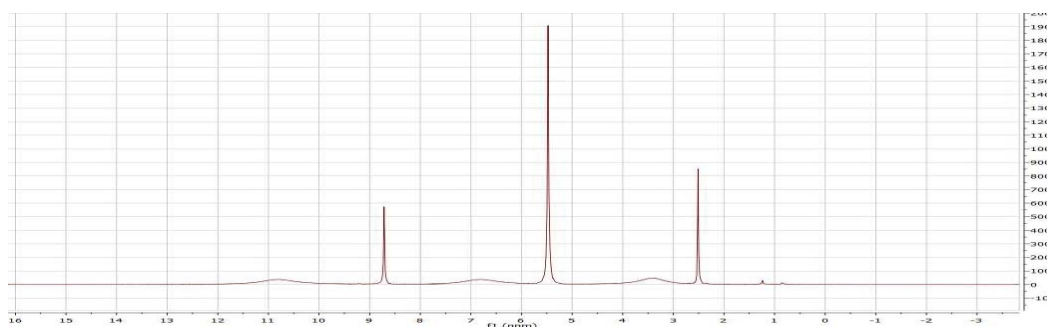


**Figure (6): The  $^1\text{H}$ NMR spectrum of compound (b)**

The final step for generating the compound (B) (scheme.2, step 2); Which is the closure of the ring by  $\text{H}_2\text{O}_2$  3%. The peaks of the thiadiazole ring appeared as follows: ( $\text{NH}_2$ ) at  $3291\text{ cm}^{-1}$  and the new peak of ( $\text{C}=\text{N}-\text{N}=\text{C}$ ) at  $2062\text{ cm}^{-1}$ , ( $\text{C}=\text{N}$ ) at  $1592\text{ cm}^{-1}$  and ( $\text{N}-\text{N}$ ) at  $1137\text{ cm}^{-1}$  (Figure 7). The following compounds (A, B and C) are white crystalline precipitation.

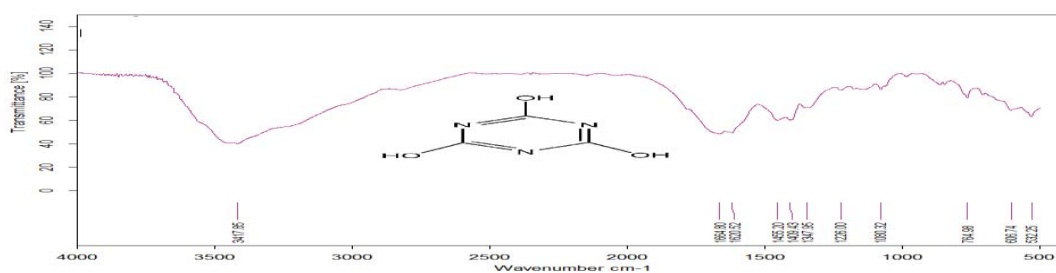


**Figure (7): The FT-IR spectrum of compound (B)**



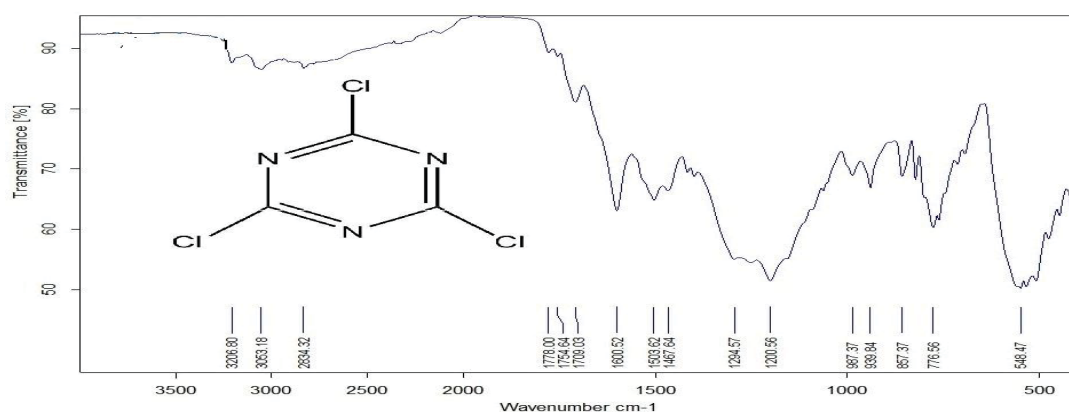
**Figure (8): The  $^1\text{H}$ NMR spectrum of compound (B)**

Cyanuric acid (CYA) (Figure 9) was prepared in a simple and less costly way, by the reaction of urea with kerosene under vacuum. It is a crystalline white precipitate and solid. The FT-IR spectrum showed a broad peak for acid ( $\text{O}-\text{H}$ ) at  $3417\text{ cm}^{-1}$  which indicates the acid was formed.



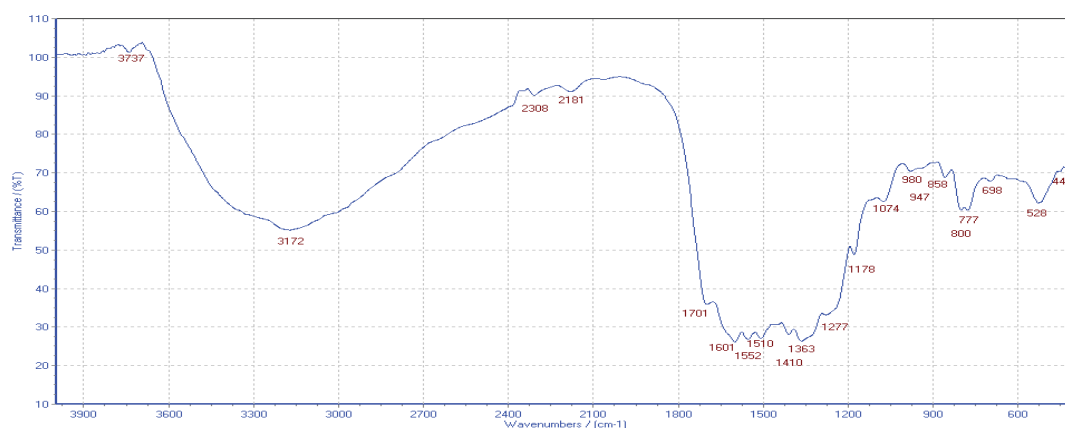
**Figure (9): The FT-IR spectrum of cyanuric acid**

Cyanuric chloride (TCT) (Figure 10) was prepared from (CYA) reaction with  $\text{PCl}_5$  and using  $\text{POCl}_3$  as a solvent and was refluxed for 24 hrs. It is a white precipitate, highly hydrolysable, which is the basic unit for the formation of hyper branched polymers by replacing the Chlorine atoms with a variety of diamins. The FT-IR spectrum showed the disappearance of the abroad peak of Cyanuric acid (CYA) from  $(3400 \text{ to } 3500) \text{ cm}^{-1}$ , and Appearance of a new peak for Chlorine at  $857 \text{ cm}^{-1}$  and extending to  $987 \text{ cm}^{-1}$ .

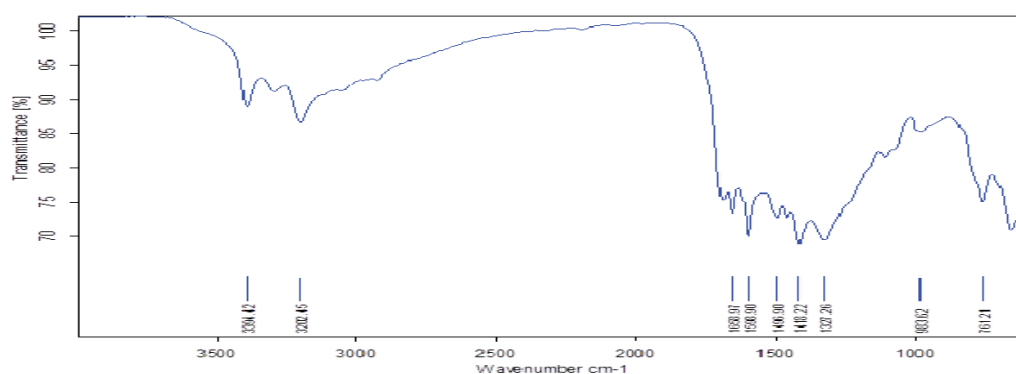


**Figure (10): The FT-IR spectrum of cyanuric chloride**

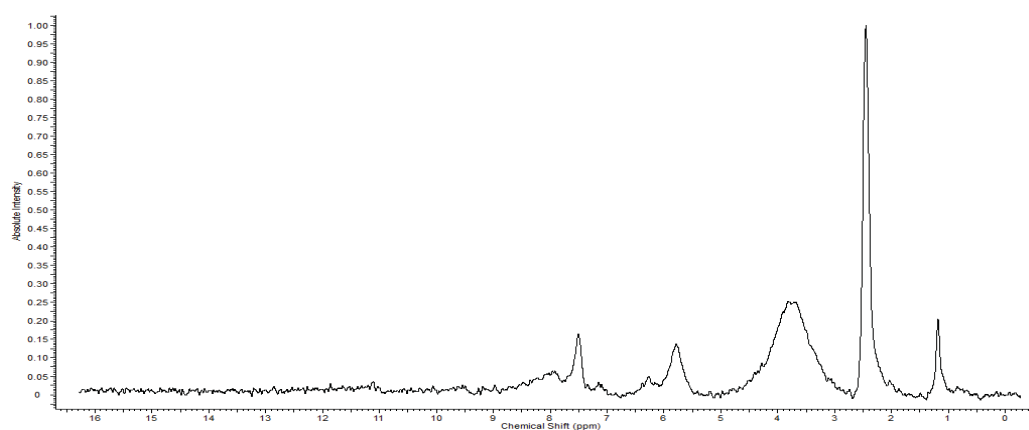
The Polymers (M1, M2 and M3) were synthesized from the reaction of compounds (A, B and C) respectively with TCT and were dissolved with distilled water and tetra hydro furan (THF) with continuous stirring for (15-24) hours. The FT-IR showed the disappearance of the double peak of the primary amine at the region  $(3200 \text{ to } 3450) \text{ cm}^{-1}$  Figures 12 and 14 shows the HNMR spectrum of M2 and M3 polymers respectively.



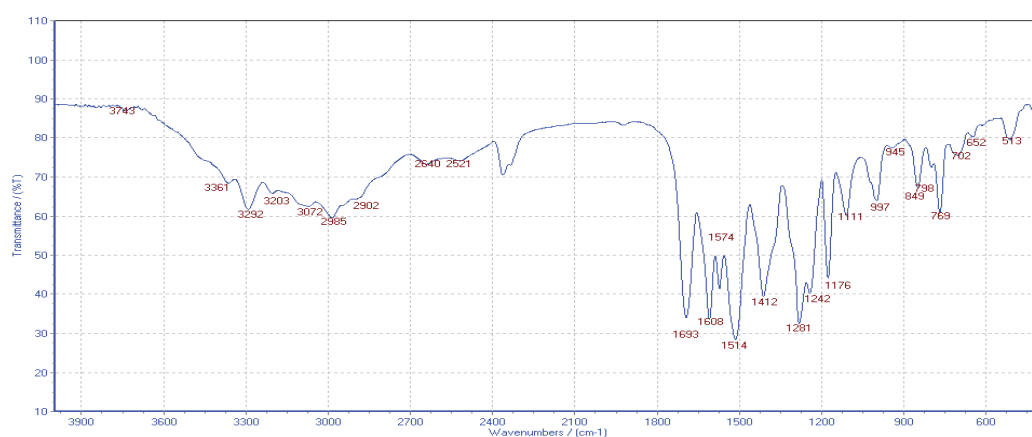
**Figure (11): The FT-IR spectrum of Polymer (M1)**



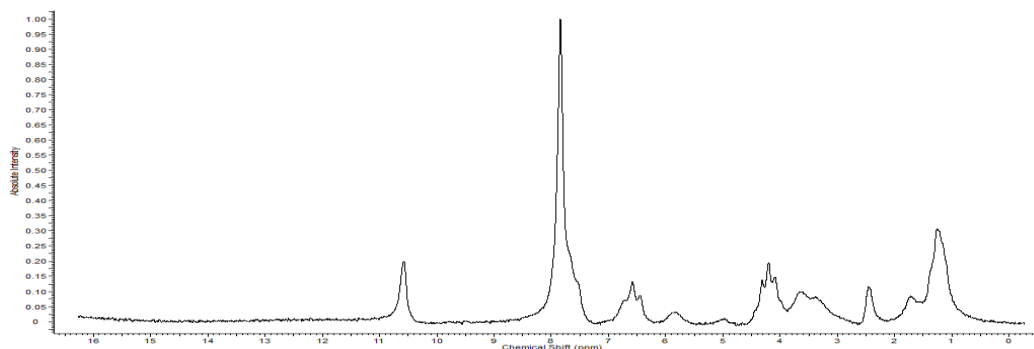
**Figure (12): The FT-IR spectrum of Polymer (M2)**



**Figure (13): The <sup>1</sup>H NMR spectrum of Polymer (M2)**



**Figure (14): The FT-IR spectrum of Polymer (M3)**



**Figure (15): The  $^1\text{H}$ NMR spectrum of of Polymer (M3)**

**Table 1: The physical properties of the synthesized compounds**

| No. | Compound   | M.wt<br>$\text{g.mol}^{-1}$ | m.p<br>$^{\circ}\text{C}$ | Yield<br>% | Color           |
|-----|------------|-----------------------------|---------------------------|------------|-----------------|
| 1   | a          | 210.26                      | 82-86                     | 87.5       | White           |
| 2   | A          | 192.24                      | 151-158                   | 82         | White           |
| 3   | b          | 150.22                      | 222-228                   | 37         | White           |
| 4   | B          | 116.14                      | 215-218                   | 77         | White           |
| 5   | c          | 194.19                      | 87-90                     | 78         | White           |
| 6   | C          | 176.18                      | 89-91                     | 50         | White           |
| 7   | CYA        | 129.08                      | >360                      | 50         | White           |
| 8   | TCT        | 184.40                      | 134-138                   | 27         | White           |
| 9   | Polymer M1 | 735.91                      | >360                      | 13         | Yellowish white |
| 10  | Polymer M2 | 479.56                      | >360                      | 15         | Yellowish white |
| 11  | Polymer M3 | 687.73                      | 233                       | 15         | Yellowish white |

## References

- [1] Tomalia, D.A. and Frechet J.M., 2001, Wiley, New York, USA ISEN: 9780471638506. Page: 647
- [2] X. Z. Wei, L. P. Zhu, H. Y. Deng, Y. Y. Xu, B. K. Zhu and Z. M. Huang, 2008 *J. Membr., Sci.*, 323, 278.
- [3] X. Z. Wei, X. Kong, J. Yang, G. L. Zhang, J. Y. Chen and J. D. Wang, *J. Membr.* 2013, *Sci.*, 440, 67.
- [4] J. X. Qin, S. S. Lin, S. Q. Song, L. Zhang and H. L. Chen, 2013 *ACS Appl. Mater. Interfaces*, 5, 6649.

- [5] Y. Y. Xu, C. Gao, H. Kong, D. Y. Yan, Y. Z. Jin and P. C. P. Watts, 2004, *Macromolecules*, , 37, 8846.
- [6] C. Gao, Y. Z. Jin, H. Kong, R. L. D. Whitby, S. F. A. Acqah, G. Y. Chen, H. Qian, A. Hartschuh, S. R. P. Silva, S. Henley, P. Fearon, H. W. Kroto and D. R. M. Walton, 2005, *J. Phys. Chem. B*, , 109, 11925.
- [7] C. Gao, S. Muthukrishnan, W. Li, J. Yuan, Y. Xu and A. H. E. Mu`ller, 2007 *Macromolecules*, , 40, 1803.
- [8] J. Li and Z. S. Bo, 2004, *Macromolecules*, 37, 20-23.
- [9] Y. Xin, G. A. Wen, W. J. Zeng, L. Zhao, X. R. Zhu, Q. L. Fan, J. C. Feng, L. H. Wang, W. Wei, B. Peng, Y. Cao and W. Huang, 2005, *Macromolecules*, 38, 6755.
- [10] L. Tsai and Y. Chen, 2007, *Macromolecules*, 40, 2984.
- [11] R. S. Mishra and A. S. Khanna, 2011, *Prog. Org. Coat.*, 72, 769.
- [12] M. D. Dimitriou, Z. L. Zhou, H. S. Yoo, K. L. Killops, J. A. Finlay, G. Cone, H. S. Sundaram, N. A. Lynd, K. P. Barteau, L. M. Campos, D. A. Fischer, M. E. Callow, J. A. Callow, C. K. Ober, C. J. Hawker and E. J. Kramer, 2011, *Langmuir*, 27, 13762.
- [13] C. S. Gudipati, J. A. Finlay, J. A. Callow, M. E. Callow and K. L. Wooley, *Langmuir*, 2005, 21, 3044.
- [14] Y. P. Wang, D. E. Betts, J. A. Finlay, L. Brewer, M. E. Callow, J. A. Callow, D. E. Wendt and J. M. DeSimone, 2011, *Macromolecules*, 44, 878.
- [15] Q. Zhu, F. Qiu, B. S. Zhu and X. Y. Zhu, *RSC Adv.*, 2013, 3, 2071. Review Article Chem Soc Rev Published on 23 April 2015. Downloaded by University of Michigan, Flint on 25/04/2015 23:56:16. View Article Online This journal is©The Royal Society of Chemistry 2015 Chem. Soc. Rev.
- [16] A. Sunder, M. Kramer, R. Hanselmann, R. Mulhaupt and H. Frey, *Angew. Chem., Int. Ed.*, 1999, 38, 3552.
- [17] D. Wilms, S. Stiriba and H. Frey, 2010, *Acc. Chem. Res.*, 43, 129.
- [18] H. A. Essawy, H. A. Mohamed and N. H. Elsayed, *J. Appl. Polym. Sci*, 2013, 127, 4505.
- [19] M. Morell, X. Ferná´ndez-Francos, X. Ramis and A. Serra, *Macromol. Chem. Phys.*, 2010, 211, 1879.
- [20] X. Ferná´ndez-Francos, D. Santiago, F. Ferrando, X. Ramis, J. M. Salla, A` . Serra and M. Sangermano, *J. Polym. Sci., Part B*, 2012: *Polym. Phys.*, , 50, 1489.
- [21] C. Acebo, X. Ferná´ndez-Francos, F. Ferrando, A` . Serra, J. M. Salla and X. Ramis, *React. Funct. Polym.*, 2013, 73, 431.

- [22] C. Y. K. Chan, J. W. Y. Lam, C. K. W. Jim, H. H. Y. Sung, I. D. Williams and B. Z. Tang, 2013, *Macromolecules*, , 46, 9494.
- [23] J. Liu, Y. Zhong, J. W. Y. Lam, P. Lu, Y. Hong, Y. Yu, Y. Yue, M. Faisal, H. H. Y. Sung, I. D. Williams, K. Sing Wong and B. Z. Tang, 2010, *Macromolecules*, 43, 4921.
- [24] W. Shu, C. Guan, W. Guo, C. Wang and Y. Shen, *J. Mater. Chem.*, 2012, 22, 3075.
- [25] Y. Nakayama, 2012, *Acc. Chem. Res.*, 45, 994.
- [26] R. B. Wang, L. Z. Zhou, Y. F. Zhou, G. L. Li, X. Y. Zhu, H. C. Gu, X. L. Jiang, H. Q. Li, J. L. Wu, L. He, X. Q. Guo, B. S. Zhu and D. Y. Yan, 2010, *Biomacromolecules*, , 11, 489.
- [27] M. Ahmed and R. Narain, 2012 *Biomaterials*, , 33, 3990.
- [28] Yan D. Y., Gao C. and Frey H., 2011, A John Wiley and Sons Inc., Hoboken, New Jersy, 217.
- [29] Gao ,C. and Yan D., 2004, *Prog. Polym. Sci.*, 29, 183-275, 263.
- [30] A.J Al-zuhairi, Allw, A.S, Obaid, K.A., Rasool, S. R. and Mousa, A. O., 2017, *J. engineering and Appli. Sci.*, 12, 6, 7800-7804.
- [31] Zeng Y.F., 1987, *Fine Chem. Ind.*, 2, 42–47.
- [32] Qiu, Y.; Gao L., 2005, *Mater. Res. Bull.*, 40, 794–799.
- [33] Wittcoff H.A., Reuben B.G. and Plotkin J.S., 2004, 2nd<sup>ed</sup>. Wiley, Hoboken, 63.
- [34] Hentrich, W. and Köhler, R., 1935, German Patent (647,303, February 26).
- [35] Aljamali N. M., Alzuhairi A. J., Abdul A. And Khattar M. T., 2016, *Academy of Biomedical and Clinical Science Journal*, 1: 22-26.
- [36] Al-Zuhairi A. J., Jawad A. A., Azzam A. A., Mousa A. O., and Nawfal S. H., 2017, *Res. J. Pharma. Biolo. and Chemi.Sci.*,**8**, 183-190
- [37] Al-Zuhairi A J, Jawad A R, Abbas A S., Al-Haideri M R, and Rasool S R, 2017, *J. Global Pharma Technology*, 12(09):389-396
- [38] A. H. Sharba, R. I. Al-Bayati, M. Aouad and N. Rezki, 2005 *Molecules*, 10, 1153-1160.
- [39] Adediji, J.F., S.A. Amolegbe, S. Adewuyi, C.A. Akinremi, Y.C. Oyeniran, and B.O. Afolayan. 2013.. *ISRN Inorganic Chemistry*. 2013, Article ID 329508, 7
- [40] She D., Yu H., Huang Q., Li F., Li C. 2010 , *Molecules* 15:1898–1902.
- [41] Yan Song, Yangzhen Guo, Xia Zhang, Yue Yang, Shuo Chen, Gaimei She and Dongmei She 2016 *Molecules*, 21, 89 1-8