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

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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 ¹HNMR 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-cyclohexanedion 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]

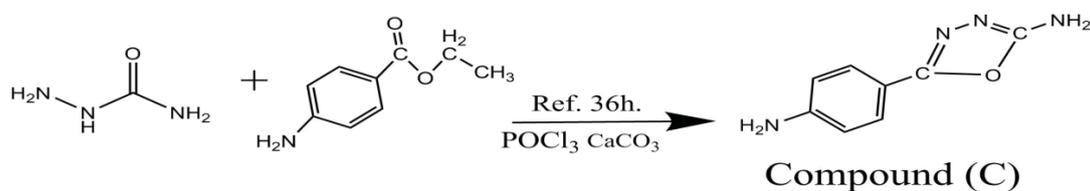
Preparation of (A) [5-(4-aminophenyl)-1, 3, 4-thiadiazol-2-amine]

(0.01mol) of ethyl 4-aminobenzoate with (0.01mol) of thiosemicarbazide were dissolved in POCl₃ 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 CaCO₃, 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

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

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

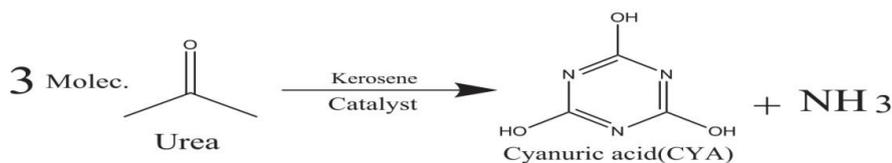
About (0.01mol) of ethyl-4-aminobenzoate with (0.01mol) of semicarbazide were dissolved in POCl_3 solvent and the mixture was refluxed for 36 hours. The mixture was slowly poured with continuous stirring on crushed ice and the acid mixture was neutralized by potassium carbonate CaCO_3 , then the solution 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]

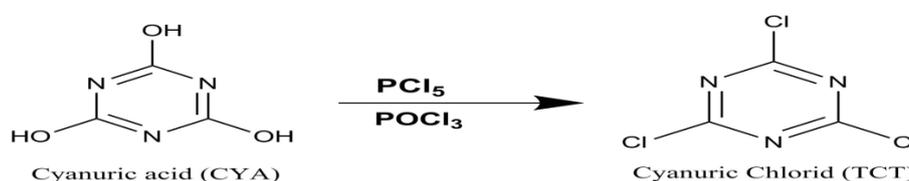
In a round bottom flask with three necks, 10 gm of urea was added to 20 mL kerosene (white oil), the mixture was stirred with heating (reflux) into 150 $^\circ\text{C}$ and placed under vacuum to 10 mm Hg, then was heated to 160-220 $^\circ\text{C}$. At 220 $^\circ\text{C}$ the reaction was followed 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 PCl_5 and 4 ml of POCl_3 ; The mixture was stirred with heating (reflux) into 115°C for 24 hrs until no more HCl was released. The mixture was distilled at a temperature of 120°C under vacuum to remove of the excess 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):

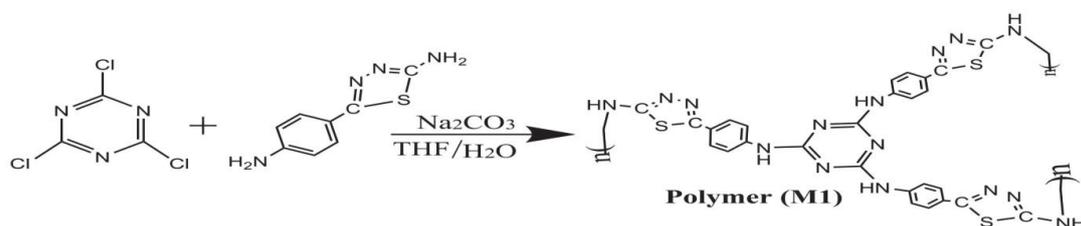
Compound (A for M1, B for M2 and C for M3)

About 5.0 gm of Na_2CO_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) $^\circ\text{C}$ 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.

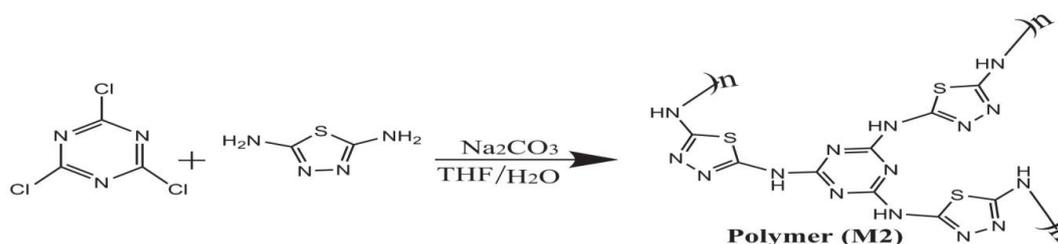
Polymer M1: Yield 13%, mp(more than 360) $^\circ\text{C}$; IR (V/Cm):IR (v, cm^{-1}): 1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).

Polymer M2: Yield 15%, mp(more than 360) $^\circ\text{C}$; IR (V/Cm):1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).

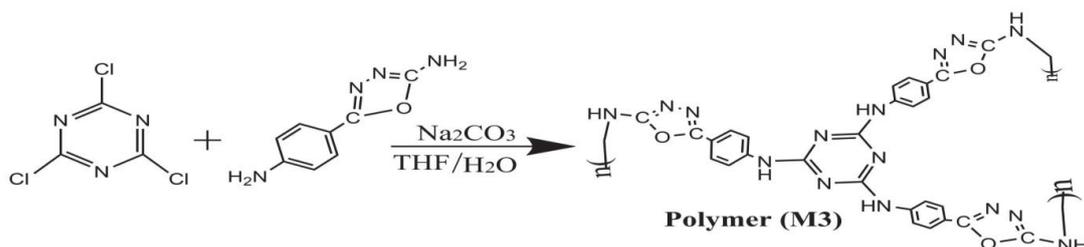
Polymer M3: Yield15%, mp(233) $^\circ\text{C}$; IR (V/Cm):1664 (C=N),(3118 and 2891) (Aromatic CH),3,200 (NH).



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 PCl_5 and 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: (NH_2) at 3232 cm^{-1} , ($\text{C}=\text{N}$) from (1526 to 1602) cm^{-1} , ($\text{N}-\text{N}$) at 1129 cm^{-1} and ($\text{C}-\text{S}$) at 698 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).

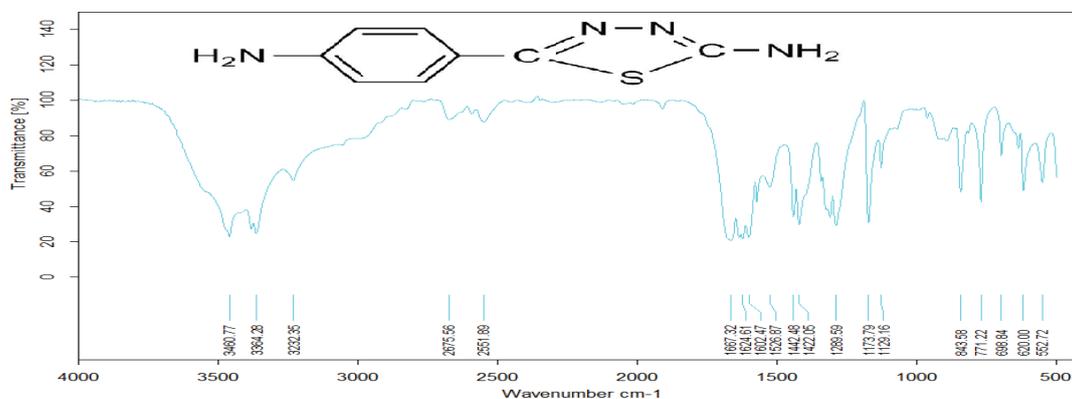


Figure (1): The FT-IR spectrum of compound (A)

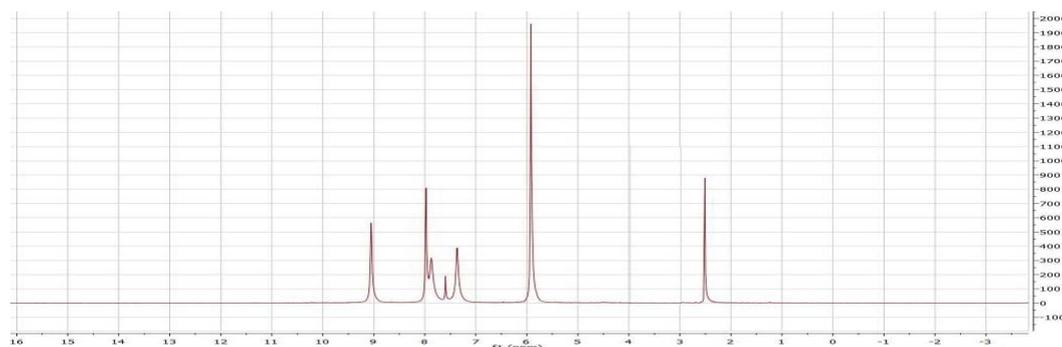


Figure (2): The ¹H NMR spectrum of compound (A)

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⁻¹ (Figure 3).

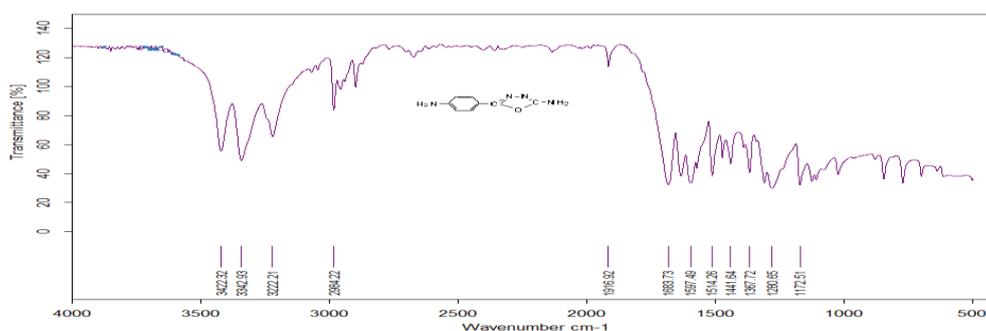


Figure (3): The FT-IR spectrum of compound (C)

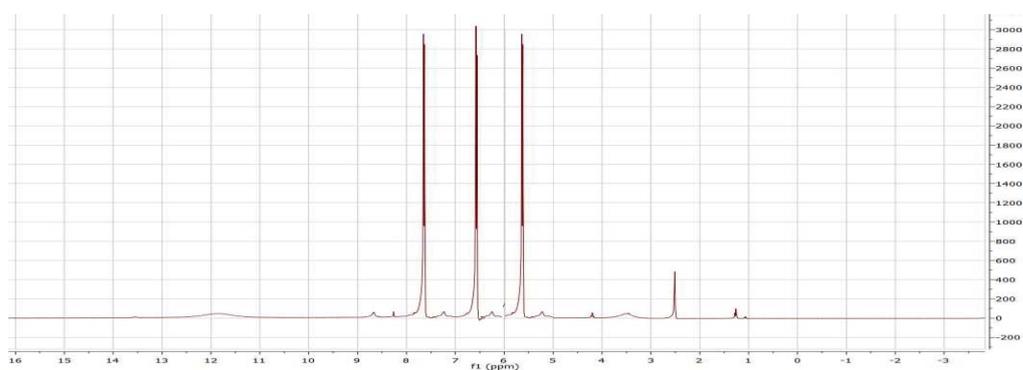


Figure (4): The ¹H NMR spectrum of compound (C)

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 cm⁻¹ and the carbonyl thioamide group (C=O) at 1620 cm⁻¹ and (C-N) at 1061 cm⁻¹ Figure 6 has shown the ¹H NMR spectrum of compound b

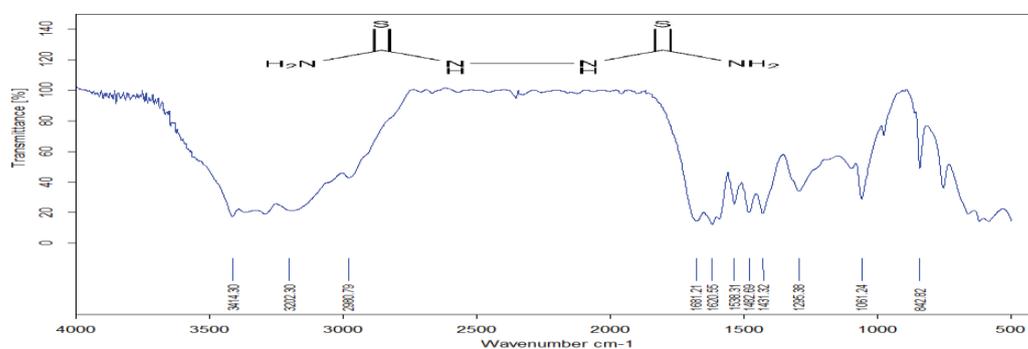


Figure (5): The FT-IR spectrum of compound (b)

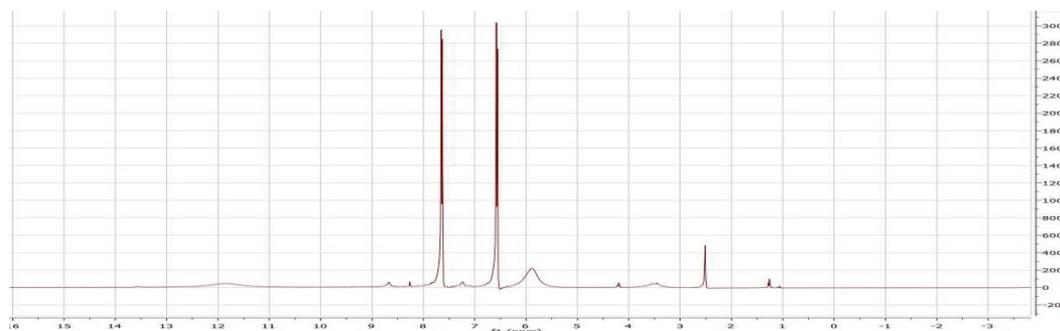


Figure (6): The ¹H NMR spectrum of compound (b)

The final step for generating the compound (B) (scheme.2, step 2); Which is the closure of the ring by H_2O_2 3%. The peaks of the thiadiazole ring appeared as follows: (NH_2) at 3291 cm^{-1} and the new peak of ($\text{C}=\text{N}-\text{N}=\text{C}$) at 2062 cm^{-1} , ($\text{C}=\text{N}$) at 1592 cm^{-1} and ($\text{N}-\text{N}$) at 1137 cm^{-1} (Figure 7). The following compounds (A, B and C) are white crystalline precipitation.

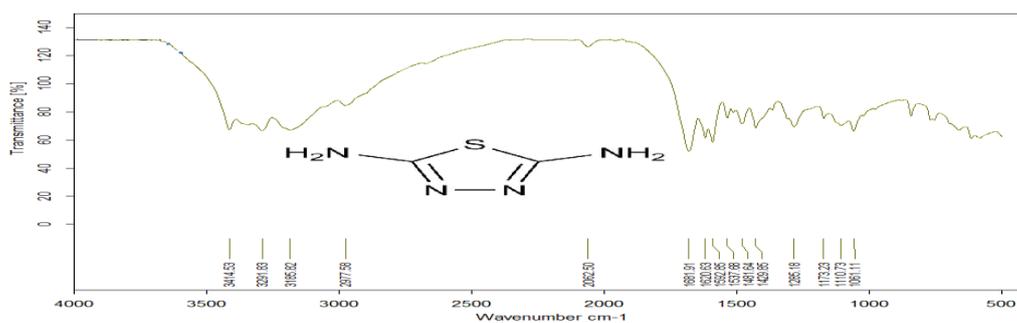


Figure (7): The FT-IR spectrum of compound (B)

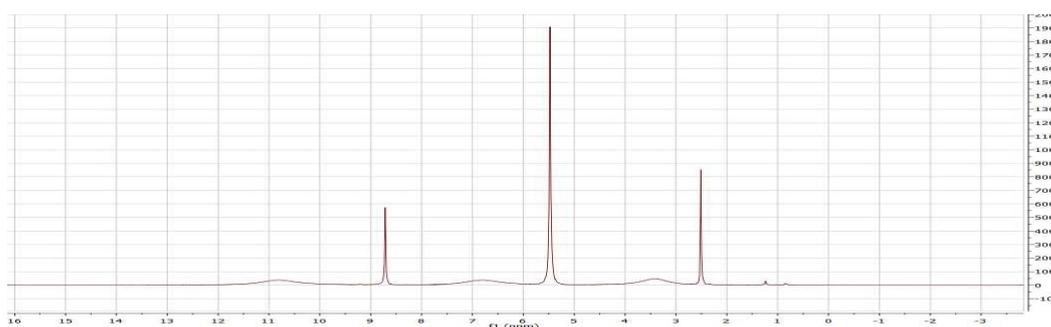


Figure (8): The ^1H NMR spectrum of compound (B)

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 cm^{-1} which indicates the acid was formed.

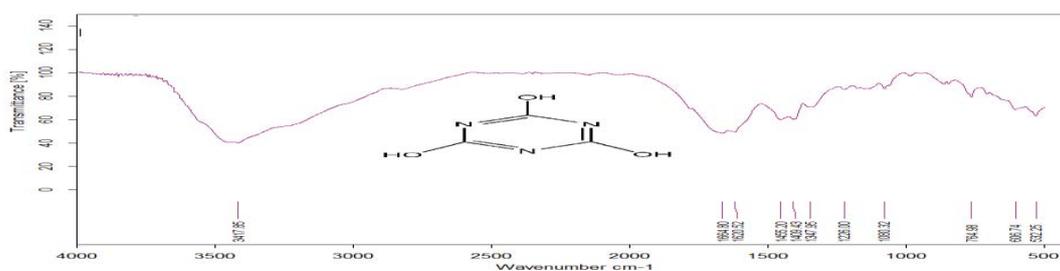


Figure (9): The FT-IR spectrum of cyanuric acid

Cyanuric chloride (TCT) (Figure 10) was prepared from (CYA) reaction with PCl_5 and using 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 cm^{-1} and extending to 987 cm^{-1} .

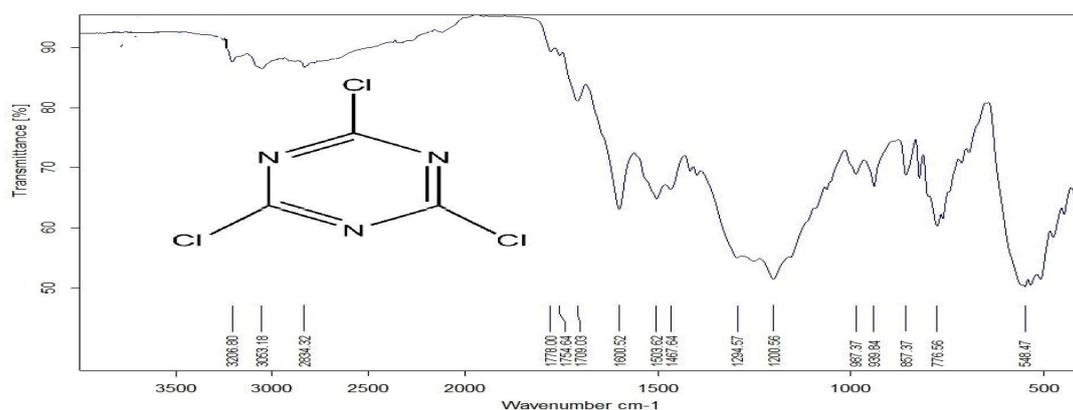


Figure (10): The FT-IR spectrum of cyanuric chloride

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.

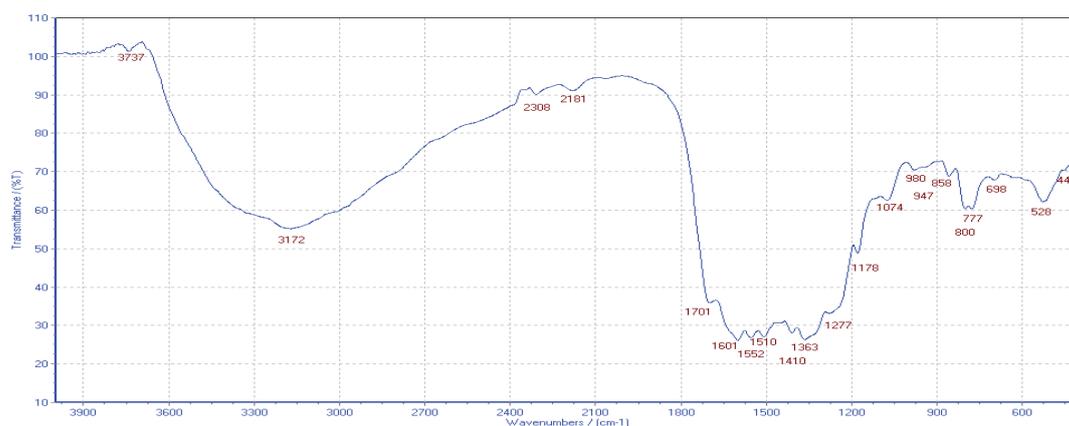


Figure (11): The FT-IR spectrum of Polymer (M1)

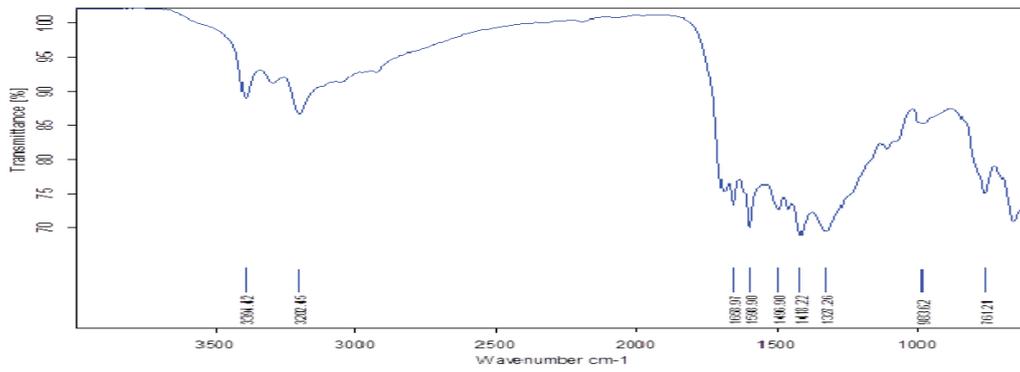


Figure (12): The FT-IR spectrum of Polymer (M2)

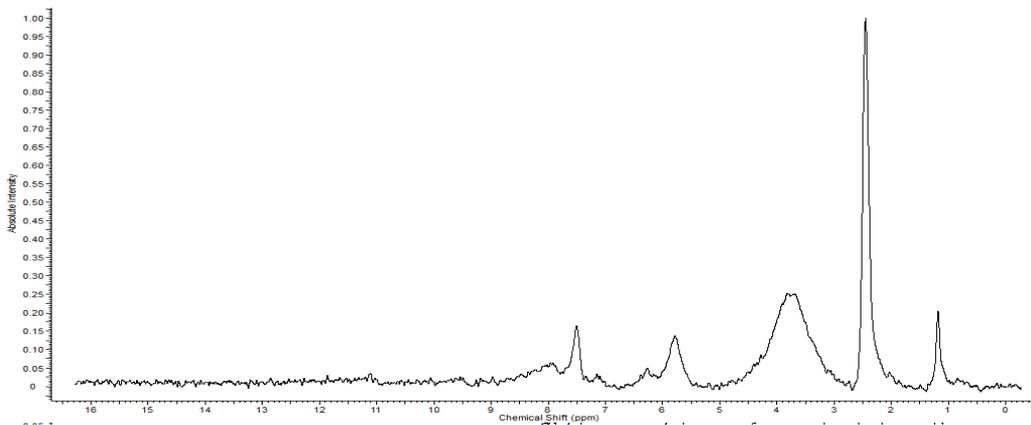


Figure (13): The ¹H NMR spectrum of Polymer (M2)

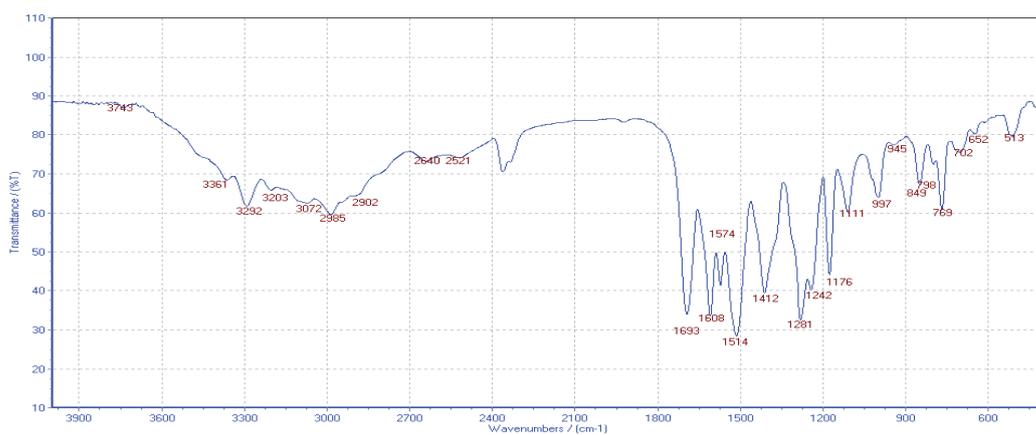


Figure (14): The FT-IR spectrum of Polymer (M3)

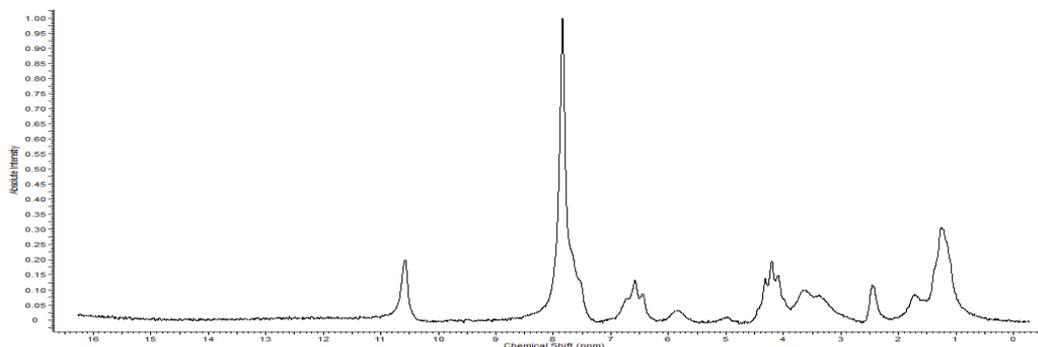


Figure (15): The ^1H NMR spectrum of of Polymer (M3)

Table 1: The physical properties of the synthesized compounds

No.	Compound	M.wt g.mol^{-1}	m.p $^{\circ}\text{C}$	Yield %	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

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