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Nitrogen containing polymers-based triazine: synthesis, characterization and its applications for scavenging of copper(II)

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ABSTRACT

The present work reported the synthesis of four polymers based on 4,6-dichloro-*N*-(4-methoxyphenyl)-1,3,5-triazin-2-amine (PMA) as a monomer with different diamines (ethylenediamine (EDPMA), 1,4-diaminobutane (BDPMA), piperazine (PZPMA) and *p*-phenylenediamine (PDPMA)). The prepared porous organic polymers (POPs) were characterized using Fourier transform infrared spectroscopy, elemental microanalysis (CHN), gel permeation chromatography (GPC) and the Brunauer–Emmett–Teller surface area. The thermal behavior was studied using thermogravimetric analysis and differential scanning calorimetry. The thermal properties showed a promising data to be used as flame retardant polymers, where the limited oxygen index value for EDPMA, BDMA, PDMA and PZPMA was 30.5, 28.4, 35.5 and 35.7, respectively. Transmission electron microscopy was employed to study the effect of type of the repeating unit on morphology and shape of polymers. The results revealed that polymers are porous with a maximum porosity of (0.016 $cm^3 g^{-1}$) and surface area of (41.60 $m^2 g^{-1}$). The chelation behavior of the prepared polymers towards Cu(II) was studied, and the loading percentage was measured using inductively coupled plasma mass spectrometry. The thermal properties of the prepared complexes were studied as well.

Keywords: s-Triazine; Copper(II); Metal–polymer complex; Thermal analysis

1. Introduction

Porous organic polymers (POPs) are an important class among all adsorbents, due to the ease of incorporation different functional groups, with higher surface area and well-defined porosity, resulting in many different structures for various applications [1,2]. He et al. [3] reported the synthesis of novel POP (TSPNS) via Friedel–Crafts reaction between triazine and thiophene. The resulting compound was tested against removal of Cu(II) from aqueous solution, with a maximum adsorption capacity of 98.33 mg g^{-1}. The author attributed the high efficiency to the presence of N and S heteroatoms, which could easily form the coordination complex with copper.

Recently, the use of 1,3,5-triazine moiety in construction of coordination complexes has been growing significantly [4–7]. The unique symmetrical structure of *s*-triazine allows for the design of remarkable architectures, either mono-, di- or tri-substituted-1,3,5-triazine ligands [6–8].

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One of the most important applications for *s*-triazine-based ligands is metal removal; there are various methods applied for the removal of metal ions from wastewater [9–11]. Adsorption was the most efficient and economical method for this purpose; that is why the design and development of a novel functional porous adsorbents gain much significance in the recent years [12–16].

s-Triazine-based complexes were also employed for non-linear optical (NLO) materials, which were applied for diverse optics-related applications such as communications, data storage, etc. [17]. In order to improve the NLO response of *s*-triazine, Shanmugakala et al. [17] developed a series of transition metals complexes (ML) and $(ML2)^{+2}$ types, where M = Cu(II), Ni(II) and Co(II). They found that ligands act as tri-dentate through nitrogen atoms in triazine and pyrazolyl rings, and the (ML) and $(ML2)^{+2}$ types exhibit square pyramidal geometry, and octahedral geometry, respectively. The antimicrobial activity of complexes and ligands was tested; the results showed that metal(II) complexes show better activities rather than ligands by themselves.

Herein, we report the synthesis and characterization of four POPs based on triazine moiety. The ability of these polymers for complexation with copper(II) in an aqueous media was described as well, because copper is a toxic metal which is released from various industries such as mining, smelting, plating, electroplating, brass manufacturing and petroleum refining.

2. Experimental section

2.1. Materials

Cyanuric chloride, piperazine, *p*-phenylenediamine and 1,4-diaminobutane obtained from Sigma-Aldrich (USA). *p*-Anisidine and triethylamine were obtained from Winlab (USA), and ethylenediamine and copper(II) sulfate pentahydrate were obtained from Panreac (Spain).

2.2. Characterization techniques

Nuclear magnetic resonance spectra for the prepared monomer (^{1}H NMR and ^{13}C NMR spectra) were recorded on a JOEL 400 (Japan). Fourier transform infrared spectroscopy (FTIR) was recorded on a Shimadzu model IRAffinity Spectrometer, as the samples were prepared as KBr discs. Elemental microanalysis (CHN) was measured using Perkin-Elmer 2400 CHNS/O Series II elemental analyzer. The surface areas of polymers were determined through the adsorption of nitrogen (N_2) gas (at 77 K) using Micromeritics (Gemini VII, 2390 Surface Area). The samples were degassed under nitrogen flow for 1 h at 150°C to eliminate moisture and gasses before analysis. Molecular weight (gel permeation chromatography [GPC]) was measured by Viscotek, HT-GPC Module 350A, using tetrahydrofuran (THF) as solvent. Thermal behavior of the prepared polymers and complexes was studied using both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In TGA measurements, the sample was studied under nitrogen with flow rate of 60 mL min^{-1}, in the temperature range 25°C–800°C with heating rate of 10°C min^{-1} using Mettler Toledo model TGA/DSC1. While in DSC, the study was carried on Shimadzu DSC-60A in which Specimens of (4–8 mg) were encapsulated in aluminum pans and were heated or cooled under dry nitrogen atmosphere with heating rate of 10°C min^{-1}. Size and shape of polymers were measured using transmission electron microscopy (TEM, JEOL JEM 2100 F Japan). After powder was dispersed and sonicated via probe-sonicator in ethanol, it was added to a carbon-coated copper grid. The measurements of copper (Cu) content were performed using inductively coupled plasma-optical emission spectrometer (ICP-OES; iCAP 6000 SERIES). All the samples were performed in triplicate, and the results reported are the mean values. The operating conditions were (RF power 1,150 W, nebulizer gas flow 0.70 L min^{-1}, argon gas flow 60 psi, flush pump rate 25 rpm, analysis pump rate 50 rpm, auxiliary gas flow 0.5 L min^{-1}, coolant gas flow 12 L min^{-1}, and normal purge gas flow).

2.3. Synthesis of 4,6-dichloro-N-(4-methoxyphenyl)-1,3,5-triazin-2-amine (PMA)

4,6-Dichloro-*N*-(4-methoxyphenyl)-1,3,5-triazin-2-amine was prepared by following the reported method in the literatures with slight modification [18,19]. A solution of *p*-methoxyaniline (24.60 g, 200 mmol) in acetone (100 mL) was added dropwise to a solution of cyanuric chloride (36.88 g, 200 mmol) in acetone (200 mL) at 0°C. After the addition had been completed, a solution of $NaHCO_3$ (21.20 g, 200 mmol) in 200 mL water was added to the mixture, and the reaction mixture was stirred for 2 h at 0°C. After completion of the reaction, excess of water was added and the crude precipitate product was filtered, washed with water and then dried under vacuum.

2.4. Synthesis of 4,6-dichloro-N-(4-methoxyphenyl)-1,3,5-triazin-2-amine-based polymers

A solution of 11 mmol ethylenediamine, 1,4-diaminobutane, piperazine or *p*-phenylenediamine in 10 mL benzene was added dropwise to a solution of 10 mmol PMA in 30 mL benzene at room temperature, and was stirred for 1 h at the same temperature. And then, triethylamine (2.12 g, 21 mmol) was added to the mixture and left under reflux overnight. After the completion of the reaction, it was left to cool, and then petroleum ether 60–80 was added to precipitate the product. The product was filtered, washed with water and then dried in vacuum oven at 60°C overnight to obtain the corresponding polymer (EDPMA, BDPMA, PDPMA and PZPMA).

2.5. Synthesis of polymers complexes of Cu^{2+}

For all preparations, 50% mixture of methanol and doubly distilled water was employed as a solvent. Copper(II) sulfate pentahydrate (1 mmol) dissolved in 10 mL water was added dropwise to 1 mmol of polymer suspended in 10 mL methanol. The mixture was heated at 60°C for 1 h and left to evaporate in the hood at room temperature overnight. The obtained precipitate was filtered off, washed with water and was dried in vacuum oven at 80°C.

3. Results and discussion

3.1. Synthesis of s-triazine-based monomers

4,6-Dichloro-*N*-(4-methoxyphenyl)-1,3,5-triazin-2-amine (PMA) was synthesized according to the previously reported method [18,19], the reaction was performed under 0°C to avoid further substitution of the remaining two chlorides. The structures of PMA monomer (Fig. 1) were prepared and characterized using FTIR, ^{1}H NMR and ^{13}C NMR.

The product was obtained as violet solid, yield 53%, m.p. 140°C–142°C, FTIR (cm^{-1}): 1,554 ($u_{C=N}$), 1,608, 1,460 and 1,428 ($u_{C=C}$). ^{1}H NMR (DMSO-d_6): δ 3.74 (s, 3H, CH_3), 7.49–6.87 (m, 4H, 4 Ar-H), 10.98 (s, H, NH) ppm. ^{13}C NMR (DMSO-d_6): δ 55.3, 114.0, 123.4, 129.6, 156.7, 163.6, 168.6, 169.6 ppm.

3.2. Synthesis of s-triazine-based polymers

The polymerization reactions between 4,6-dichloro-*N*-(4-methoxyphenyl)-1,3,5-triazin-2-amine (PMA) and different diamines, as shown in Fig. 1, were done by nucleophilic polymerization as reported previously [20], using triethylamine as HCl scavenger.

3.3. Fourier transform infrared spectroscopy

FTIR spectra of the prepared polymers showed characteristic peaks for NH in range of 3,334 to 3,398 cm^{-1}, C-H; sp^3 and sp^2-hydrogen in the range 2,912 to 2,997 cm^{-1} and at 1,608, 1,568, and 1,417 cm^{-1} for C=N and C=C (Fig. 2). In addition, the elemental analysis of the polymers confirmed their structures, which are in a good agreement with the calculated values, as indicated in Table 1.

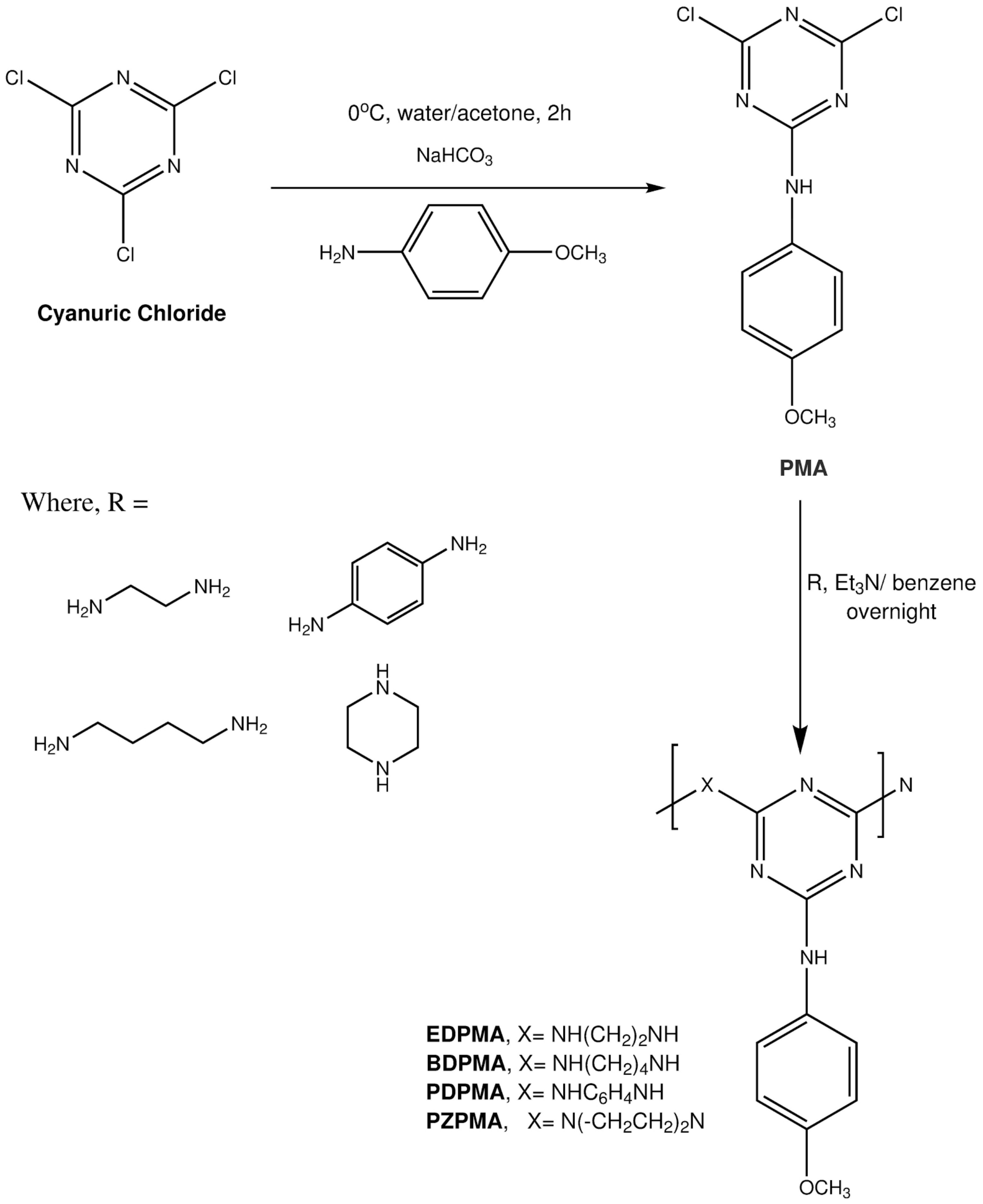

Fig. 1. Synthesis of *s*-triazine based polymers.

3.4. Gel permeation chromatography

Due to poor solubility of the prepared polymers, only EDPMA was soluble in THF, and the number-average molecular weight (M_n) was estimated as a representative for the series. The results showed that the M_n is 37,803 g mol^{-1} and polydispersity index (M_w/M_n) is 13.464.

3.5. Surface area (BET)

The Brunauer–Emmett–Teller (BET) surface area and the total pore volume of the prepared polymers were measured using the N_2 adsorption method. The results are given in Table 2, where the BDPMA polymer showed the lowest surface area (6.01 m^2 g^{-1}), which reveal that BDPMA has the most compact structure among the four polymers with minimum porosity (0.002 cm^3 g^{-1}). On the other hand, EDPMA revealed to have the highest surface area (41.60 m^2 g^{-1}), and the highest porosity (0.016 cm^3 g^{-1}).

3.6. Thermogravimetric analysis

The study of the thermal degradation behavior of the prepared polymers was done using TGA technique; the degradation curves are depicted in Fig. 3, and the thermal analytical data are listed in Table 3.

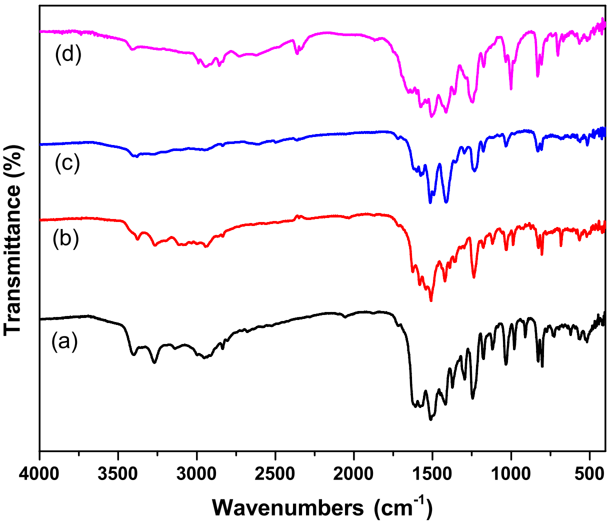

Fig. 2. FTIR of the prepared polymers, where (a) EDPMA, (b) BDPMA, (c) PDPMA and (d) PZPMA.

The thermal results revealed that the prepared polymers have a relative high thermal stability. Structural-thermal property correlation was investigated, based on incorporating different types of aromatic and aliphatic diamines (short chain, relatively long chain and cyclic) in the polymer main chain.

As observed from the thermograms, the thermal degradation of EDPMA and BDPMA was classified into two main steps, with initial decomposition temperature of 171°C based on 13% mass loss for EDPMA, due to the release of water and ammonia [19] and 66°C based on 6% mass loss for BDPMA due to the release of water. The decomposition of the polymer was slow in this stage, but above 300°C, the weight loss become faster in the main decomposition step, then it decreased rapidly when it reached 550°C, which may be due to the presence of the aromatic moiety and the triazine ring. From the results, it appears that EDPMA has a relative higher thermal stability than BDPMA. This could be attributed to the longer chain in BDPMA polymer, which leads to increases in the flexibility of the polymeric main chain.

On the other hand, the thermal degradation of PDPMA and PZPMA was classified into three main steps; the first initial decomposition temperature occurs at 75°C–85°C based on a mass loss of 7.9% and 11.4% for PDPMA and PZPMA, respectively, which is due to the release of water, followed by a second step which occurs after 200°C, and then the main decomposition step which occurs after 350°C with a faster weight loss. Generally, PZPMA is thermally more stable than PDPMA, and this is due to the chair form of piperazine within the polymer structure.

Both polymers PDPMA and PZPMA are relatively higher in thermal stability than EDPMA and BDPMA. This is due to the presence of benzene ring as well as a six-membered ring containing tertiary amino groups within the polymer main chain [19].

Table 2
BET surface areas, pores volumes and pores sizes of the prepared polymers

Code	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (Å)
EDPMA	41.60	0.016	21.0
BDPMA	6.01	0.002	12.39
PDPMA	10.34	0.004	20.02
PZPMA	8.85	0.003	19.14

Table 1
Elemental microanalysis of the prepared polymers

Polymer code	Calculated (%)				Found (%)			
	C	H	N	O	C	H	N	O
EDPMA	57.13	6.27	30.75	5.85	54.75	5.22	28.55	11.48
BDPMA	59.78	7.02	27.89	5.31	55.69	6.34	22.45	13.52
PDPMA	63.54	5.33	26.15	4.98	59.92	6.42	23.07	10.59
PZPMA	61.13	7.05	26.73	5.09	58.71	5.28	22.11	13.9

Limited oxygen index (LOI) is defined as the minimum amount required for oxygen to support a combustion, the theoretical values of LOI were calculated for all polymers, employing Van Krevelen correlation [21]:

$$\text{LOI} = 17.5 + 0.4\,(\text{CR}) \tag{1}$$

From the char residue results, it appears that all the polymers show an effective char-forming ability, which is higher in the second part of polymer, due to the presence of aromatic benzene ring and a six-membered ring in the main chain of polymers.

3.7. Differential scanning calorimetry

The study of thermal transitions of the prepared polymers was done using DSC technique. The DSC data were derived from the second run, as all samples were heated first at 100°C to ensure the elimination of any thermal history, cooled down with the same rate to room temperature and then undergo a second run at 350°C. DSC thermograms of the prepared polymers are shown in Fig. 4, and the thermal parameters are listed in Table 4.

The results revealed that the glass transition temperature T_g for EDPMA is 113°C compared with 109°C for BDPMA, and PDPMA has T_g of 116°C. Thus, the T_g variation of these polymers depends on the nature of the monomer involved in the main chain, which affects the chain mobility of the polymers, which is in a good agreement with the data from TGA. PZPMA did not exhibit a glass transition temperature; however, it shows a very broad melting peak (T_m) at 186°C.

From the results, it appears that all polymers might be partially crystalline polymers, as they exhibit a glass transition temperature as well as melting and crystallization peaks.

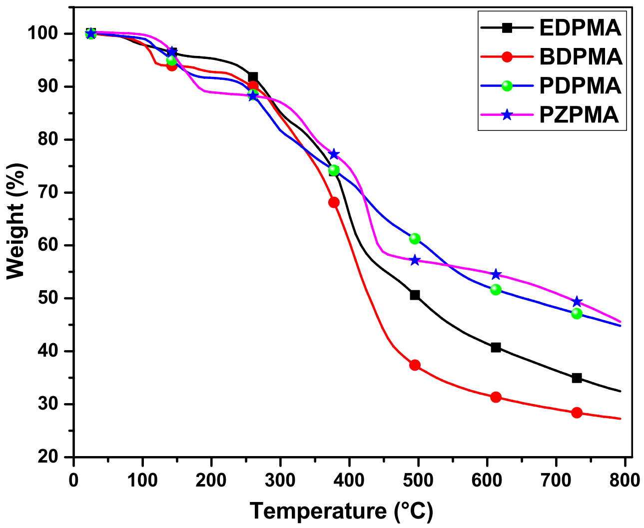

Fig. 3. TGA curves of the prepared polymers.

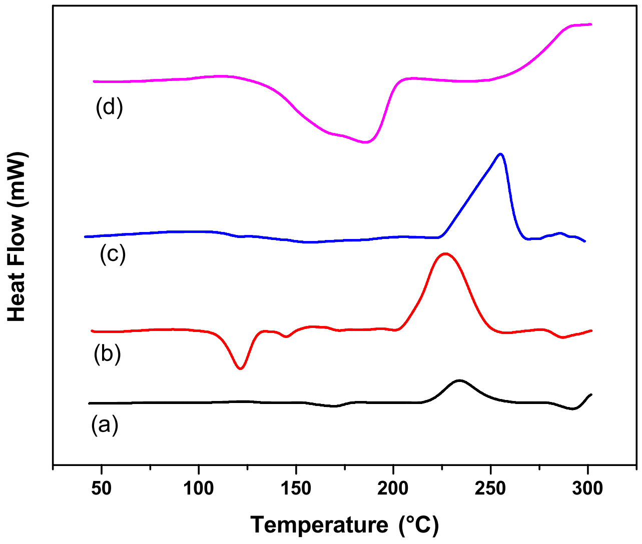

Fig. 4. DSC curves of the prepared polymers, where (a) EDPMA, (b) BDPMA, (c) PDPMA and (d) PZPMA.

Table 3
Thermal decomposition data of the prepared polymers

Code	Stage	T_{range} (°C)	Mass loss (%)	DTG (°C)	T_{onset} (°C)	T_{50} (°C)	LOI[a]	Residue[a] (%)
EDPMA	I	171–326	13.1	292	243	508	30.47	32.42
	II	327–463	27.9	400				
BDPMA	I	66–158	5.7	119	269	437	28.42	27.3
	II	342–542	43.5	417				
PDPMA	I	75–207	7.9	119	254	662	35.5	44.9
	II	208–375	16.5	274				
	III	377–621	23.3	434				
PZPMA	I	85–223	11.4	155	272	726	35.7	45.6
	II	266–386	11.1	346				
	III	385–485	19.7	439				

[a] Calculated at 800°C.

3.8. Transmission electron microscopy

The TEM images of the prepared polymers are represented in Fig. 5. The analysis showed that all polymers might be partially crystalline, which agrees with the DSC as polymers exhibited a glass transition as well as a melting and crystallization peaks.

3.9. Copper polymers complexes

Copper complex of the triazine-based ligand were prepared via the addition of copper ion to the suspended polymer with stirring for 1 h at 70°C. The copper complex was obtained after the evaporation of water/methanol mixture at room temperature. The elemental analysis of the copper polymer complex confirmed the incorporation of copper, as indicated in Table 5. The proposed formation of copper complex with the prepared polymers is shown in Fig. 6.

Table 4
DSC parameters of the prepared polymers

Code	T_g (°C)	Peak (°C)	Onset (°C)	Endset (°C)	Heat (J g^{-1})
EDPMA	113	169 endo	156	177	6.2
		234 exo	220	249	46.1
BDPMA	109	145 endo	140	152	2.6
		227 exo	208	247	80.3
PDPMA	116	255 exo	227	264	106.7
PZPMA	N/A	186 endo	137	201	161.7

As shown in FTIR spectra of the prepared polymer complexes (Fig. 7), after Cu(II) incorporation, the aromatic C–H stretching peaks in 2,700–300 cm^{-1} region nearly disappear; whereas, peaks in 3,000–3,600 cm^{-1} region which is attributed to N–H are weakened; in addition, the peaks at 1,033 and 1,118 cm^{-1} which are attributed to the alkoxy group also weakened. These results suggest that N and O atoms of the triazine-based polymers can form coordination complex with Cu(II) as illustrated in Fig. 6.

3.10. Thermal stability of copper polymers complexes

The thermograms of TGA and DSC showed that the thermal behavior of the polymers was affected by the

Table 5
Elemental microanalysis of polymers complexes

Polymer code	C (%)	H (%)	N (%)	Cu* (%)
EDPMA-Cu	52.75	4.56	24.31	3.39
BDPMA-Cu	48.46	4.70	20.41	3.58
PDPMA-Cu	55.44	4.37	23.48	5.11
PZPMA-Cu	33.27	3.53	15.42	28.84

*Cu was determined using ICP-MS.

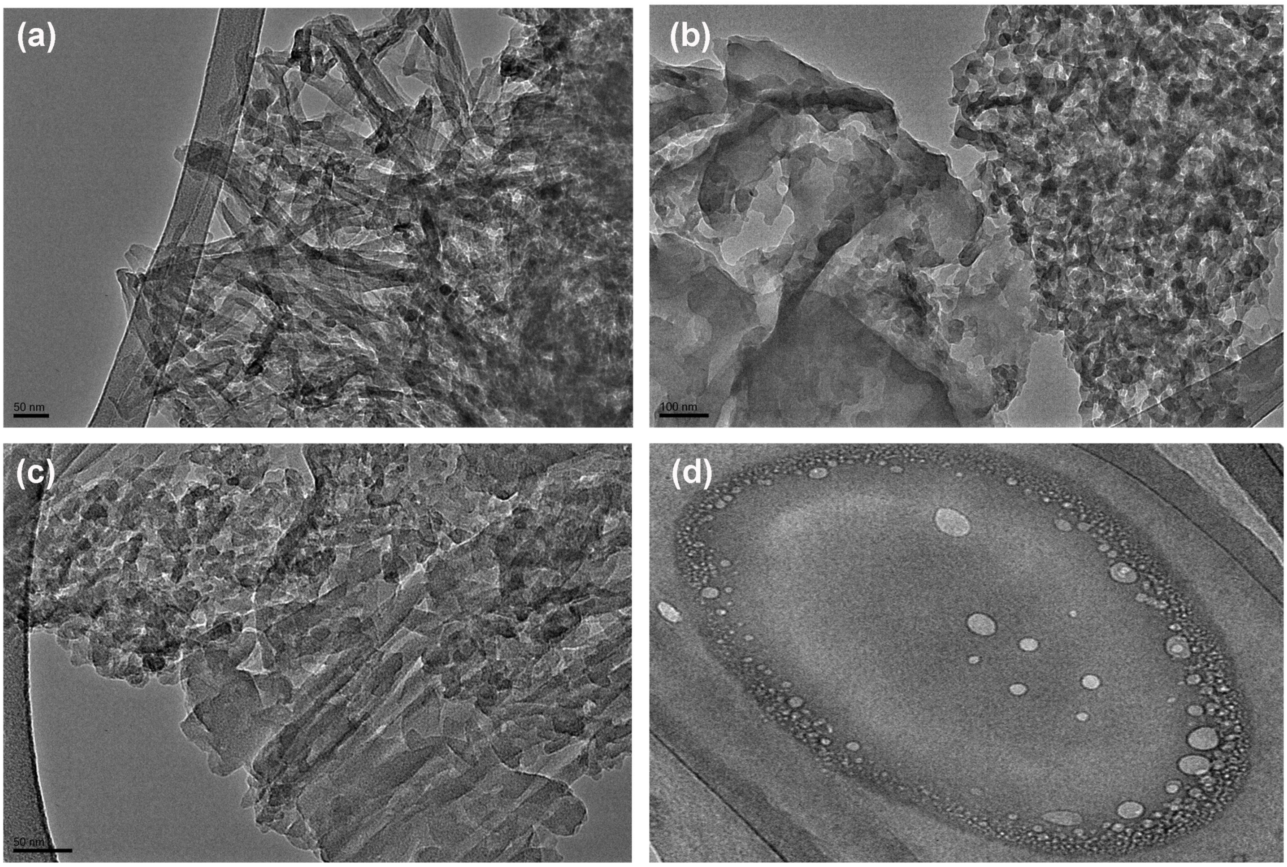

Fig. 5. TEM of the prepared polymers, where (a) EDPMA, (b) BDPMA, (c) PDPMA and (d) PZPMA.

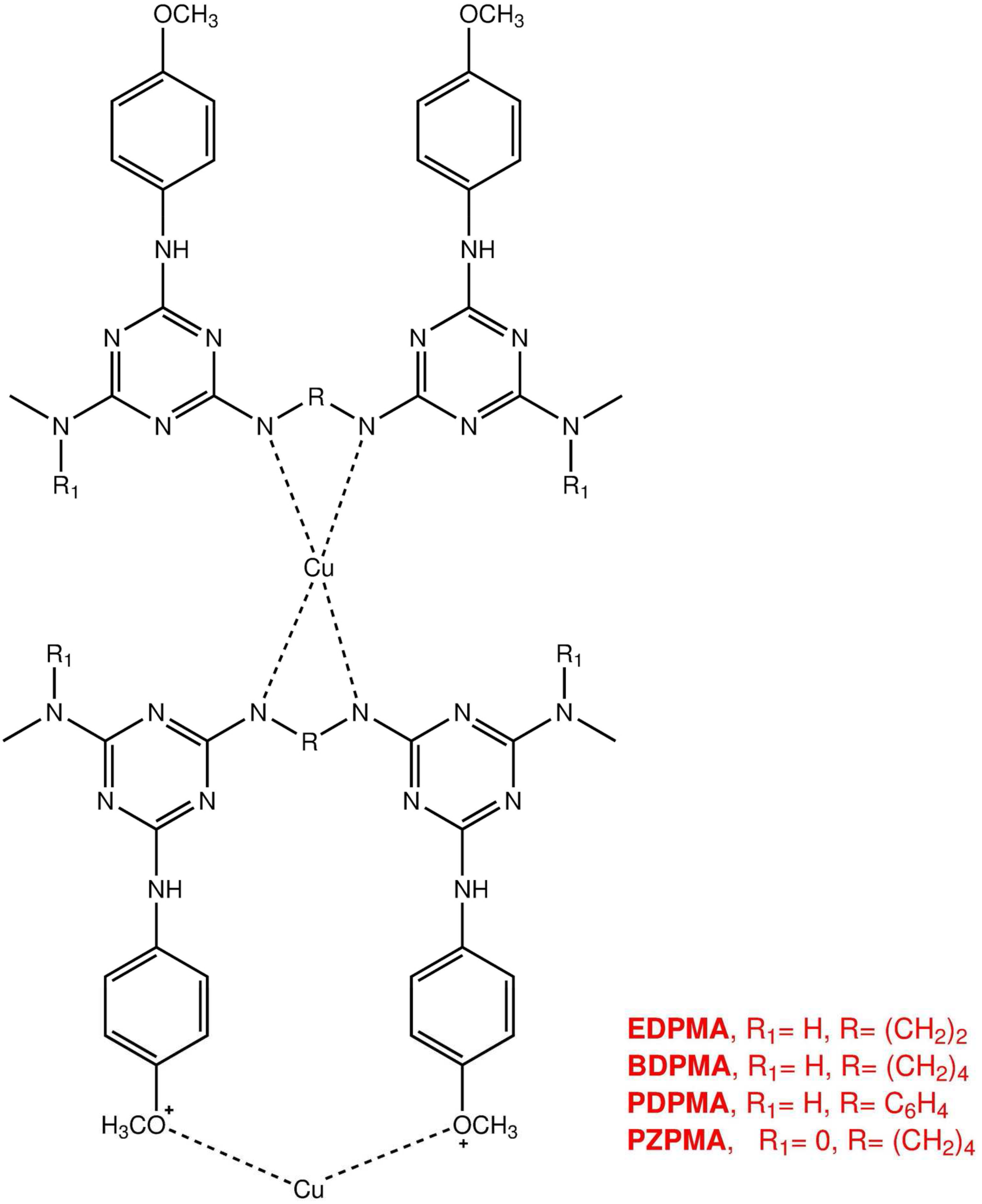

Fig. 6. Proposed structure for copper complexes of triazine-based polymers.

incorporation of the copper metal (Cu^{2+}) ions, by comparing the polymers (Figs. 3 and 4) to the same polymer after metal complexation (Figs. 8 and 9). This indicates that the presence of (Cu^{2+}) ions caused a significant increase in thermal stability of the polymers. As for EDPMA, it has two degradation steps with initial decomposition temperature of 171°C and 327°C with onset of 243°C; whereas in EDPMA-Cu, one degradation step was observed at 221°C with onset of 322°C, which is a proof for increasing the thermal resistance after the incorporation of copper metal ion. Same results were obtained for the other polymers. As for BDPMA, it has two degradation steps which start at 66°C and 342°C with onset of 269°C; whereas, there is only one degradation step in BDPMA-Cu at 215°C with onset of 318°C. The same applies for PDPMA and PZPMA that decompose in three degradation steps with onset of 254°C and 272°C, which has been shifted to 296°C and 278°C, respectively.

Generally, after the incorporation of copper metal ion, the first peak of degradation conducting the release of water and ammonia was not observed; this may be due to the change in the intermolecular structure of the polymers as it decomposes in only one step to copper oxide. In addition, the initial decomposition temperature and onset for all the polymers were shifted to higher values, which is a proof for the improvement of the thermal resistance of the polymers. TGA and DSC data are summarized in Table 6.

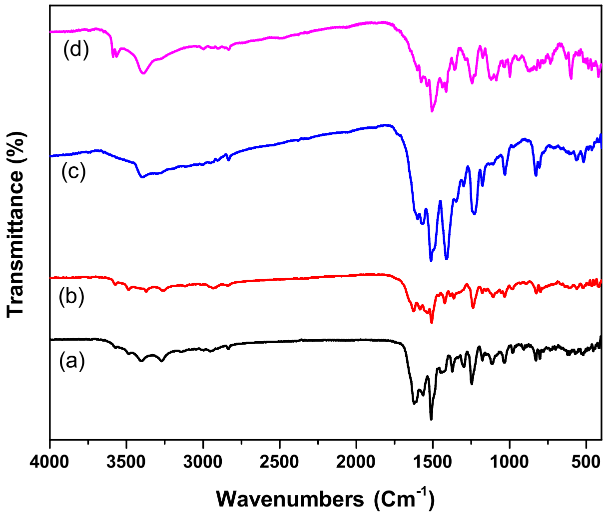

Fig. 7. FTIR spectra of the complexes, where (a) EDPMA-Cu, (b) BDPMA-Cu, (c) PDPMA-Cu and (d) PZPMA-Cu.

4. Conclusion

The synthesis of four different polymers based on triazine moiety was reported, the structural, thermal and morphological characterization of polymers were performed using different techniques, it was found that polymers are porous with a maximum porosity of (0.016 cm^3 g^{-1}) and surface area of (41.60 m^2 g^{-1}). The thermal properties of the prepared polymers showed a promising data to be used as flame retardant polymers, where the LOI value for all the polymers was greater than 26; best results were obtained with the phenylenediamine and piperazine derivatives (35.5 and 35.7, respectively). The triazine-based polymers also showed a promising scavenging behavior in aqueous media towards Cu(II) with a maximum adsorption capacity of 288.4 mg g^{-1} (28.84%) in case of PZPMA. The TGA and DSC showed that the thermal resistance of the polymers was improved and all peaks were shifted to higher values after the incorporation of copper metal into the polymers.

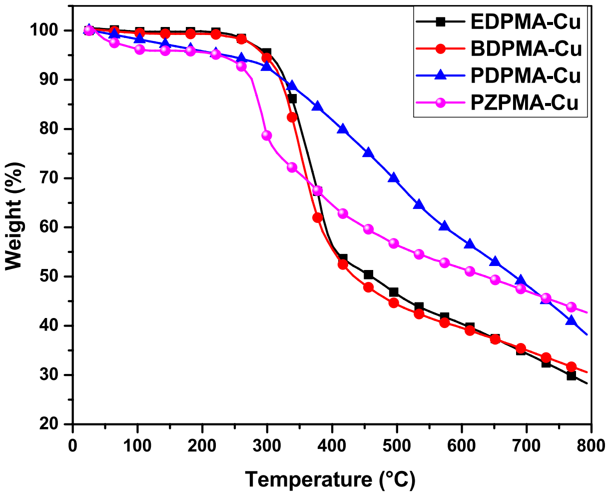

Fig. 8. TGA of the polymers copper complexes, where (a) EDPMA-Cu, (b) BDPMA-Cu, (c) PDPMA-Cu and (d) PZPMA-Cu.

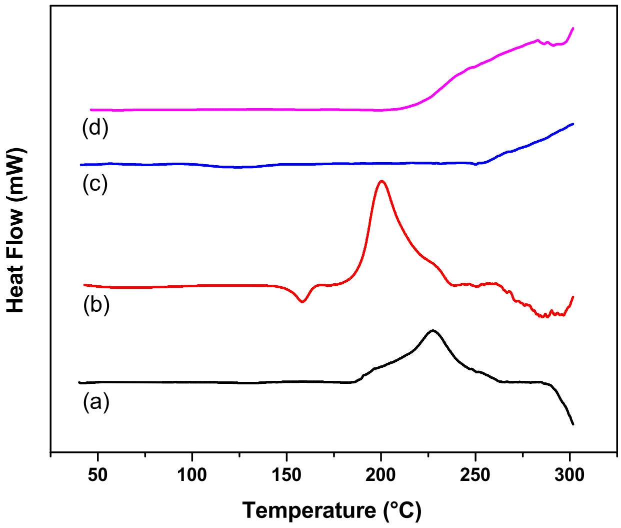

Fig. 9. DSC of the polymers copper complexes, where (a) EDPMA-Cu, (b) BDPMA-Cu, (c) PDPMA-Cu and (d) PZPMA-Cu.

Table 6
Thermal data of TGA and DSC for the copper complex

Code	T_{range} (°C)	Mass loss (%)	DTG (°C)	T_{onset} (°C)	T_{50} (°C)	LOI[a]	Residue[a] (%)	T_g (°C)	DSC peaks (°C)
EDPMA-Cu	221–442	47.63	388	322	468	28.83	28.33	122	227 exo
BDPMA-Cu	215–505	54.77	357	318	442	29.74	30.61	140	200 exo
PDPMA-Cu	254–628	38.82	515	296	690	32.81	38.28	116	N/A
PZPMA-Cu	217–438	33.68	298	278	644	34.60	42.74	N/A	N/A

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