

Sizing and Thermal Stability of Prepared Tetraaminophthalocyaninatocopper(II) Derivatives-grafted Polymers

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Abstract

Different polymers were prepared by condensation polymerization of sebacic anhydride and adipic anhydride with ethylene glycol and poly(ethylene glycol). Their number average molecular weights were determined by end group analysis. Then, they were grafted on the prepared phthalocyaninatocopper(II) compounds with the general formula $(\text{NH}_2)_4\text{PcCu}(\text{II})$ having amino groups of 3,3',3'',3'''- or 4,4',4'',4'''- positions. All prepared polymers, compounds, and phthalocyaninatocopper(II)-grafted polymers were characterized by FTIR.

The sizing measurements were carried out in 3,3',3'',3'''- $(\text{NH}_2)_4\text{PcCu}(\text{II})$ and 4,4',4'',4'''- $(\text{NH}_2)_4\text{PcCu}(\text{II})$ compounds with and without grafting polymers. The results showed that the grafting process led to decreasing in particle size and increasing in surface area.

The grafting process was reflected positively on the thermal degradation of 3,3',3'',3'''- $(\text{NH}_2)_4\text{PcCu}(\text{II})$ and 4,4',4'',4'''- $(\text{NH}_2)_4\text{PcCu}(\text{II})$ grafted polymers. They had higher thermal stability accompanied with higher char residue and $T_{50\%}$ weight loss with 3,3',3'',3'''- $(\text{NH}_2)_4\text{PcCu}(\text{II})$ and their grafted polymers being the best.

Key words: sizing, thermal stability, tetraaminophthalocyaninatocopper(II), condensation polymerization, grafting, poly(ethylene glycol)

Introduction

Phthalocyanines are solid materials that also known as azaporphyrin derivatives. The phthalocyanines are planar aromatic macro cycles and consisting of four isoindole subunits presenting an 18-electron aromatic cloud delocalized over an arrangement of alternating carbon and nitrogen atoms [1].

Phthalocyanine-containing polymers can be considered as robust and processable materials in which the relative orientation of the constituent phthalocyanine units can be controlled by strong covalent bonding [2-4]. For this reason, the integration of phthalocyanines into macromolecules is a powerful tool to obtain new materials with outstanding properties [5,6].

There are mainly two routes to graft polymers into phthalocyanine, one of them involves the polymerization or (copolymerization) reaction of unsymmetrical substituted phthalocyanine, i.e. holding reactive sites on one isoindole subunits. This involves at least two steps, or even more, reaction steps which must be carried out in heterogeneous phase reaction. Also, it has been reported in the literature the synthesis and characterization of polymeric phthalocyanines obtained through the olefin metathesis polymerization of terminal olefin groups in the side chains of unsymmetrical phthalocyanine monomers [7]. The second one requires the preparation of a polymer (or copolymer) with active side functional groups that can react in a further step with an appropriately functioned phthalocyanine [1]. Both routes should be performed in suspension of solid phthalocyanine in a suitable solvent. In both cases the aim is to create chemical bonding between grafted polymer and 3,3',3'',3'''- or 4,4',4'',4'''-traaminophthalocyaninatocopper(II) compounds. The second route is chosen for this work because of its simplicity.

Phthalocyanines have a thermal stability with no degradation up to (400-500) °C, and most complexes do not decompose below 900°C under vacuum [8]. The thermal stability of phthalocyanines showed attractive properties such as chemical inertness, semiconductivity, catalytic activity and photoconductivity [9]. These desirable properties prompt many investigators to incorporate the phthalocyanine structure in the synthesis of thermally stable polymers [10], and this is the main target of the current work.

Materials and Methods

Apparatus

Infrared spectra were recorded on Shimadzu FTIR-8400S double beam spectrophotometer. The particle size

measurements were carried out in the range of 0.02 µm to 2000 µm using Laser Diffraction Particle Sizing technique built in Master sizing-2000. The thermal analysis of the compounds was carried out using a (TGA Q50-USA) with the range (20-700) °C at a constant heating rate of 10 °C min⁻¹ under continuous nitrogen flow.

Preparation of 3- and 4-nitro phthalic anhydride

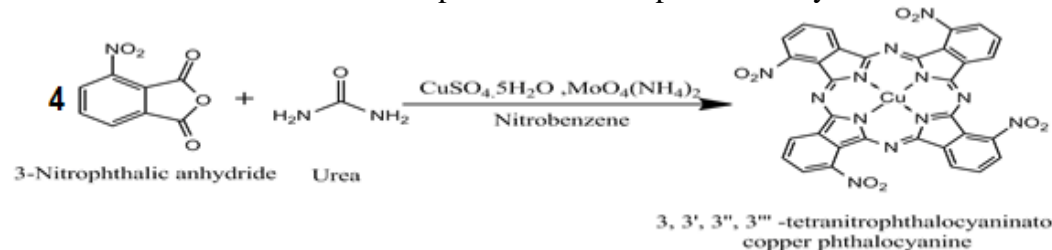
In a 100ml round-bottom flask fitted with a reflux condenser, 21g (0.1mol) of 3-nitrophthalic acid and 20g (18.5ml, 0.2mol) excess of acetic anhydride were placed. The mixture was heated to boiling until a clear solution was obtained, and heating was extended for another 10 minutes. The hot mixture was poured into a large porcelain dish and was allowed to cool. It was washed twice with 15ml absolute ethanol followed by filtration and dried in air for a short time [11]. The yield of 3-nitrophthalic anhydride, was 17g (88%), mp 163-165 °C (Lit. mp 163-164 °C). The same procedure was applied to the synthesis of 4-nitrophthalic anhydride using about 21g (0.1mole) of 4-nitro phthalic acid and acetic anhydride 20g (18.5ml, 0.2mol), and the yield 17g (88%), mp 116-120 °C.

Preparation of 3, 3', 3'', 3'''-tetranitrophthalocyaninatocopper(II) [12]

Hydrated cupric sulphate, CuSO₄.5H₂O, (2 g, 8mmol), 3-nitro phthalic anhydride (4.73g, 32mmol), ammonium molybdatetetrahydrate (0.2g 0.18mmol), ammonium chloride (0.5g, 9mmol) and excess of urea (30g, 0.5mol) were grounded and placed in 250 ml round bottom flask containing 100ml of nitrobenzene, Scheme 1. The temperature of the stirred reaction mixture was raised gradually to 185 °C and kept at this temperature for 5hrs. The hot mixture was filtered and the solid product was washed with ethanol repeatedly to remove the excess of nitrobenzene. The solid product was dried and added to 200ml of 1N HCl

and then refluxed for 1hr, cooled to room temperature to give solid product that was filtered. The solid product was poured into 200 ml of 1N NaOH and refluxed for 1hr, filtered and washed with distilled water. The blue powder

was obtained with 82% yield. The complex 4,4',4'',4'''-tetranitrophthalocyaninatocopper(II) was synthesized with 84% yield in the same procedure using the prepared 4-nitrophthalic anhydride.



Scheme 1: Preparation of 3,3',3'',3'''-tetranitrophthalocyaninatocopper(II) [12]

Preparation of 3,3',3'',3'''-tetraaminophthalocyaninatocopper(II), and 4,4',4'',4'''-Tetraaminophthalocyaninatocopper(II)

A mixture of 3,3',3'',3'''-tetranitrophthalocyanine or 4,4',4'',4'''-tetranitrophthalocyanine (4g, 0.0053mol) and 10g (0.041mol) of Na₂S.9H₂O (excess) in 50 ml of water was heated at 60 °C with stirring for 12hrs. The reaction mixture was cooled and filtered. The solid product was refluxed with 50ml of aqueous solutions 0.5N of NaOH for 1hr follow by of aqueous solutions 0.5N of HCl for 1hr. The mixture was filtered and washed with hot water and dried at 110 °C. The yields were about 69-70% .

Preparation of oly(ethylene adipate), (PEA) and poly(ethylene sebacate), PES

These two polymers were prepared by simple condensation polymerization. Ethylene glycol monomer (6.2g, 0.1mol) was dissolved in dry toluene (80ml), and the solvent was distilled off to a final volume of 30 ml to remove the residual water adsorbed to the polymer. Adipoyl chloride (20.13g, 0.11mol) or sebacoyl chloride and triethyl amine (20.2ml, 0.2mole) were added to the reaction mixture, and stirred at 25 °C for 18hrs.

The products were isolated by precipitation from diethyl ether, and then dissolved in methylene chloride and fractionally precipitated by slowly adding to diethyl ether. The products were white solid followed the filtration and drying processes with 90-91% yield [13,14]. They were characterized by infrared spectroscopy, and their molecular weights were determined by carboxyl-end group analysis and the results obtained are shown in Table 1.

Preparation of poly(ethylene glycol)–sebacic acid polyester

Poly(ethylene glycol)–sebacic acid polyester was prepared following the same procedure mentioned above using 0.2629g (0.0011mol) of sebacoyl chloride with 6g (0.001mol) of poly(ethylene glycol) having molecular weight 6000 or 10g (0.001mol) of poly(ethylene glycol) having 10000 molecular weight and 20g (0.001 mol) of poly(ethylene glycol) having 20000 molecular weight to give a white solid product with yield 75%,72% and 70% respectively. It was also characterized by infrared spectroscopy. Number average molecular weights of all the prepared polymers were determined by carboxyl-end group analysis method. The obtained results are also listed in Table 1.

Table (1): Results of polymers molecular weights determined by end-group analysis

No.	Polymer name and symbol	Structure	Determined molecular weight of the resulting polymer (g/mole)
1	poly(ethylene adipate), PEA		2100
2	poly(ethylene sebacate), PES		2230
3	Poly(ethylene glycol)-sebacic acid with PEG 6000, PEG ₁ S		12500
4	Poly(ethylene glycol)-sebacic acid with PEG 10000, PEG ₂ S		21680
5	Poly(ethylene glycol)-sebacic acid with PEG 20000, PEG ₃ S		22040

Grafting process of phthalocyanines with different prepared polymers

A phthalocyanine derivative 0.5g was added to a certain polymer solution prepared by dissolving 1g in 20 ml ethanol. The mixture was transferred to a one-neck round bottom flask, then it was refluxed for 3hrs and left to cool

down to ambient temperature. The solid was filtered and washed three times with ethanol. The solid product was dried at room temperature. It was characterized by infrared spectroscopy [15]. Table 2 exhibits the yield of the grafting process of phthalocyanine derivatives with different polymers.

Table (2): % Yields of phthalocyanine grafted different polymers

No.	Polymer name and symbol	Grafted Yield (%)	
		3,3',3'',3'''-(NH ₂) ₄ PcCu(II)	4,4',4'',4'''-(NH ₂) ₄ PcCu(II)
1	poly(ethylene adipate), PEA	88	89
2	poly(ethylene sebacate), PES	86	88
3	Poly(ethylene glycol)-sebacic acid with PEG 6000, PEG ₁ S	81	82
4	Poly(ethylene glycol)-sebacic acid with PEG 10000, PEG ₂ S	90	90
5	Poly(ethylene glycol)-sebacic acid with PEG 20000, PEG ₃ S	86	88

Results and discussion

Characterization of phthalocyanine compounds by FTIR

All prepared compounds, polymer and the grafted products were characterized by IR-spectroscopy in the form of KBr discs. The IR spectra of 3,3',3'',3'''-(NO₂)₄PcCu(II) and 4,4',4'',4'''-(NO₂)₄PcCu(II) are shown in Figure 1 and Figure 2 respectively. They

revealed that a presence of a band at 1537cm⁻¹ assigned for N-O bond asymmetric stretching, while the symmetric stretching appears at 1342 cm⁻¹, literature range (1340-1330) cm⁻¹ [16]. This is beside the presence of other bands assigned to the Pc's chemical structure, for example, C=N bond and C=C bond, and the stretching band for C-N bond appears at 1249 cm⁻¹ [17,18].

Reduction of the nitro groups to amino groups was proved by the disappearance of the bands assigned for nitro groups at 1537 cm^{-1} , and appearance of a new characteristic broad band assigned for N-H asymmetric stretching band at 3431 cm^{-1} , Figure 3, for 3,3',3'',3'''-(NH₂)₄PcCu(II) derivative and at a 3421 cm^{-1} for 4,4',4'',4'''-

(NH₂)₄PcCu(II) derivative, Figure 4. Literature range ($3400\text{-}3300\text{ cm}^{-1}$) and symmetric stretching at 3338 cm^{-1} , and at 3352 cm^{-1} , for 4,4',4'',4'''-(NH₂)₄PcCu(II) derivative, literature range ($3330\text{-}3250\text{ cm}^{-1}$) [19]. These bands accompanied with bands at 1622 cm^{-1} assigned for the N-H bending vibration, literature range ($1650\text{-}1580\text{ cm}^{-1}$) [18].

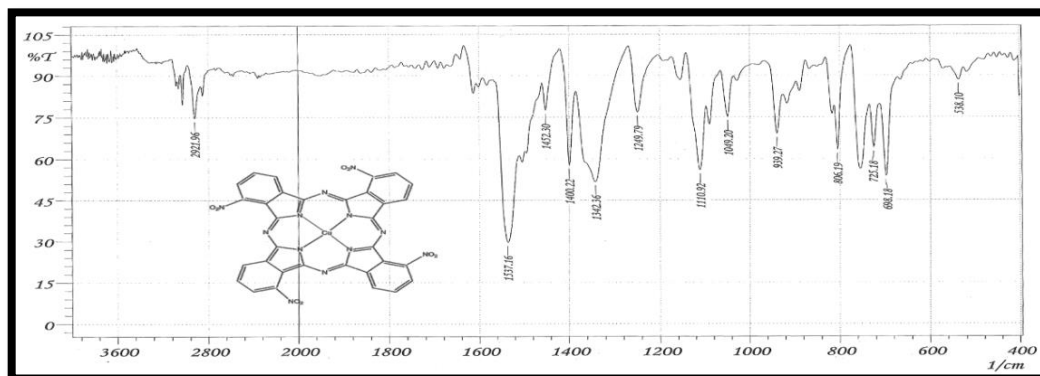


Fig. (1): FTIR spectrum of 3,3',3'',3'''-tetranitrophthalocyaninatocopper(II) derivative

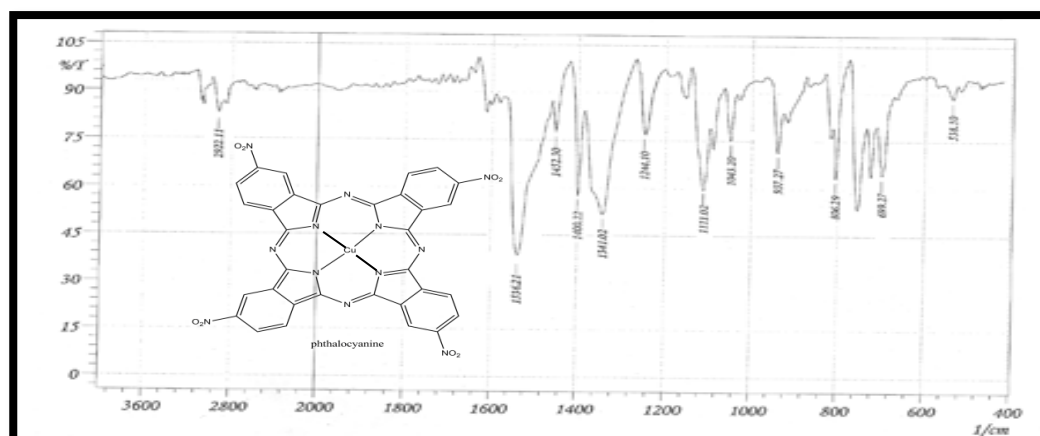


Fig. (2): FTIR spectrum of 4,4',4'',4'''-tetranitrophthalocyaninatocopper(II) derivative

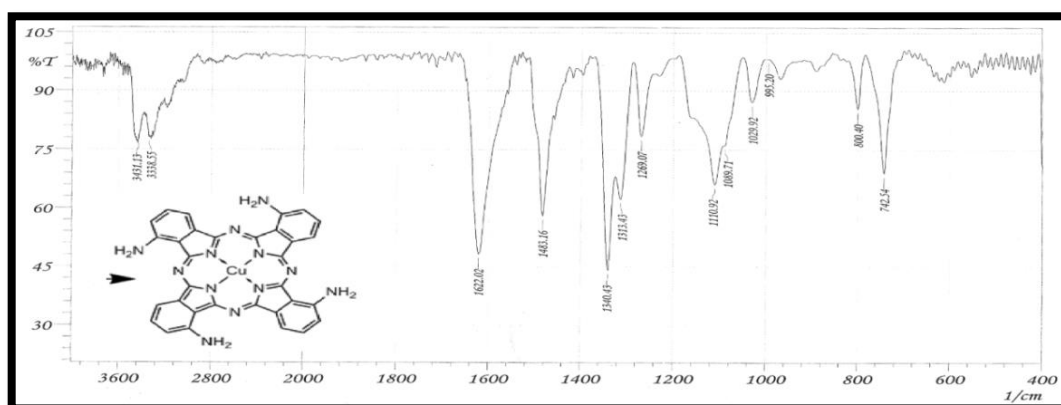


Fig.(3): FTIR spectrum of 3,3',3'',3'''-tetraaminophthalocyaninatocopper(II) derivative

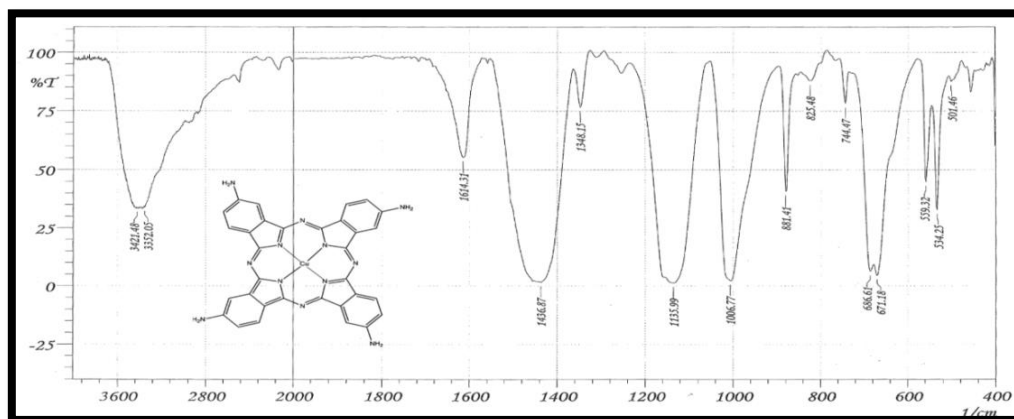


Fig. (4): FTIR spectrum of 4,4',4'',4'''-tetraminophthalocyaninatocopper(II) derivative

FTIR characterization of prepared polymers

The spectra of polymers were demonstrating broadening under the O-H stretching vibration between 3700 and 2400 cm^{-1} , characteristic of the hydrogen bonded -OH groups of the carboxyl end groups and associated with stretching vibration bands of carbonyl groups of polymers at (1700-1690) cm^{-1} [18], Figure 5 is a representative figure of the infrared spectra of the all prepared

polymers. In addition, the presence of ester group gave a strong peak at (1735-1730) cm^{-1} for stretching carbonyl-ester group as well as two peaks at (1250-1215) cm^{-1} and (1180-1170) cm^{-1} assigned for C-O bond of ester groups. Other peaks at 2933 cm^{-1} and 2856 cm^{-1} represent symmetric and asymmetric stretching of the aliphatic C-H bond of methylene groups respectively [19,20]. Table 3 shows the important bands and their functional group assignments.

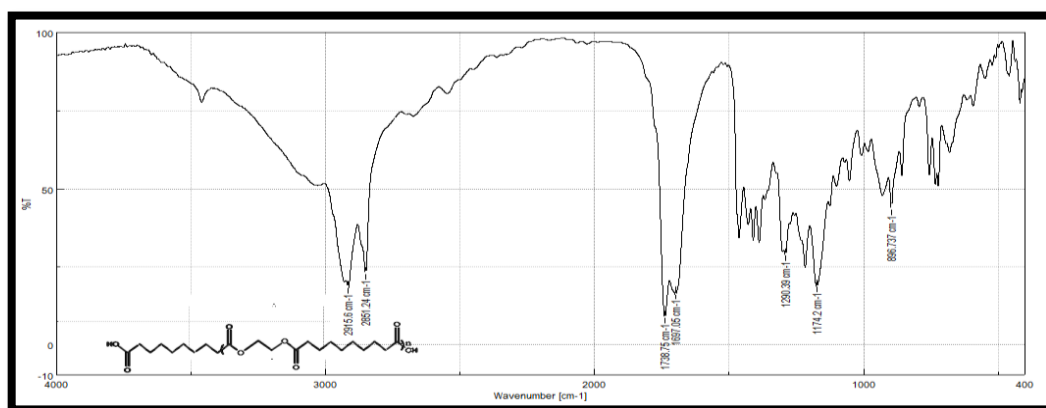


Fig.(5): Representative FTIR of prepared polymers [poly(ethylene sebacate)]

Table (3): The most important stretching bands of the polymers

Vibrations (cm^{-1})	Bond	Functional group
1735-1730	C=O	-CO-O-
(1250 -1215) + (1180-1170)	C-O	-CO-O-
1700-1690	C=O	-CO-OH
3700-2400	O-H	-CO-OH
1040-1100	C-O	-O-C-O-
(2933-2925) + (2858 - 2856)	C-H	-CH ₂ -

FTIR characterization of phthalocyaninatocopper(II) grafted polymers

It has been reported [21] that the strength of the solid-grafted polymer interaction can be enhanced by introducing a polymer having a functional group, such as carboxyl group, which is able to bind to solid

through a covalent bond, and this is the case here. All the polymers prepared have carboxyl end-groups are able to react with amino groups of 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) to form new amide functional groups. This may reflect positively on the properties of Pc derivatives that can be used for various applications.

Figure 6 shows the IR spectrum of 3,3',3'',3'''-tetraaminophthalocyaninato copper(II)-grafted PEA. As expected, it shows the disappearance of hydrogen bonded hydroxyl groups and appearance of a new characteristic N-H stretching band of the amide group at 3330 cm⁻¹, and for 4,4',4'',4'''-tetraaminophthalocyaninato copper(II)-grafted PEA at 3350 cm⁻¹, Figure 7, literature range (3330-3060) cm⁻¹, while the N-H bends vibration at 1580 cm⁻¹

and at 1570 cm⁻¹ respectively, the literature range (1570-1515) cm⁻¹ [19]. The carbonyl amide group appears as shoulder at 1690 cm⁻¹ with a sharp stretching band of the ester carbonyl group at 1740 cm⁻¹ due to the higher concentration of the latter group for 3,3',3'',3'''-tetraaminophthalocyaninato copper-grafted PEA and at 1728 cm⁻¹ for 4,4',4'',4'''-tetraaminophthalocyaninato copper-grafted PEA, literature range (1735-1730) cm⁻¹ [19]. Also, the grafting process is confirmed by the appearance of new stretching bands assigned for aliphatic methylene C-H at 2921 cm⁻¹ for 3,3',3'',3'''-tetraaminophthalocyaninatocopper(II)-grafted PEA and at 2927 cm⁻¹ for 4,4',4'',4'''-tetraaminophthalocyaninatocopper(II)-grafted PEA (literature range 3000-2850) cm⁻¹, Figures 3 and 4.

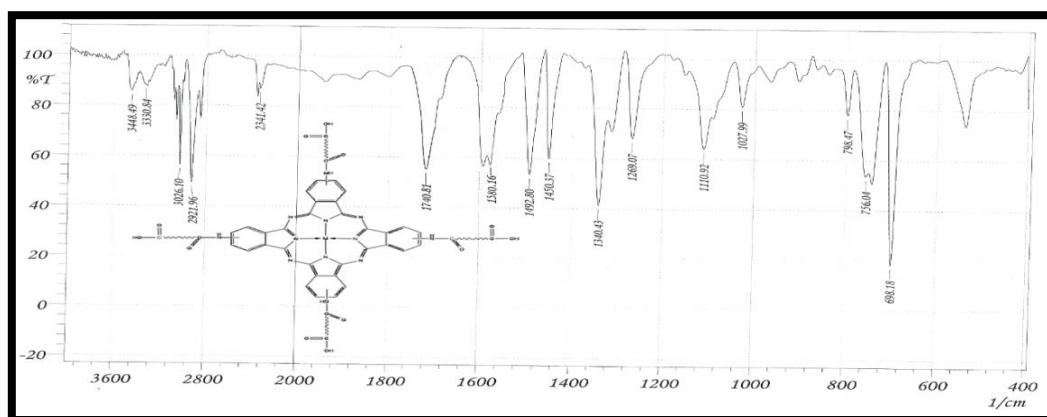


Fig. (6): FTIR spectrum of 3,3',3'',3'''-tetraaminophthalocyaninatocopper(II)-grafted PEA

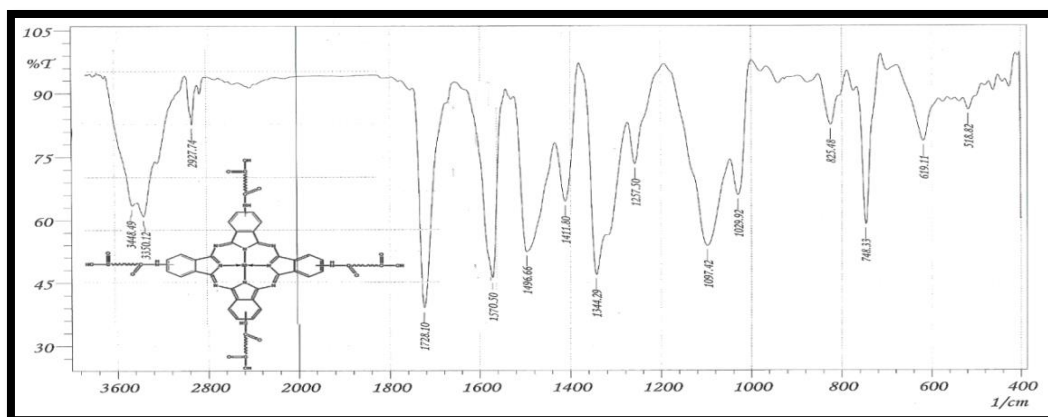


Fig. (7): FTIR spectrum of 4,4',4'',4'''-tetraaminophthalocyaninatocopper(II)-grafted PEA

IR spectra of grafted 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) with PES show no much difference between that of PEA grafted 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II), Figure 3 and Figure 4. Grafting 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) grafted with PEG₁-S, PEG₂-S and PEG₃-S which have different chain lengths and having ether linkages in poly(ethylene glycol) segment than the ester linkage and the amide linkage. This may reflect on their IR spectra causing a decrease in intensity of the stretching vibration of

the amide NH group and the carbonyl group, Figure 8 and Figure 9 are considered as representative Figures, and Table 4 lists the important bands and their functional group assignments for the above grafted polymers on 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II).

Table (4): The most important stretching bands of the polymer

Vibrations (cm ⁻¹)	Bond	Functional group
1735-1730	C=O	-CO-O-
1697-1680	C=O	NH-CO-
1089-1040	C-O-C	-CH ₂ -O-CH ₂ -
2925-2852	C-H	-CH ₂ -

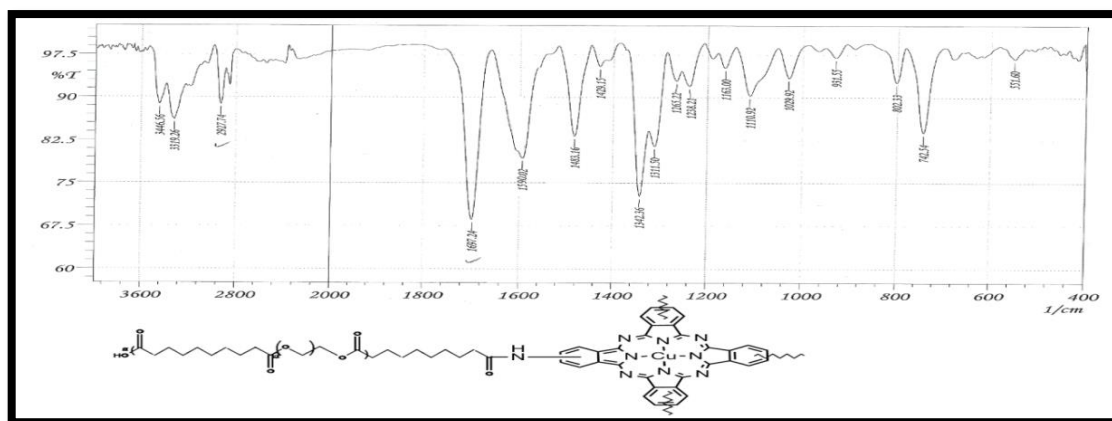


Fig. (8): FTIR spectrum of 3,3',3'',3'''-tetraaminophthalocyaninatocopper(II)-grafted PEG₁-S

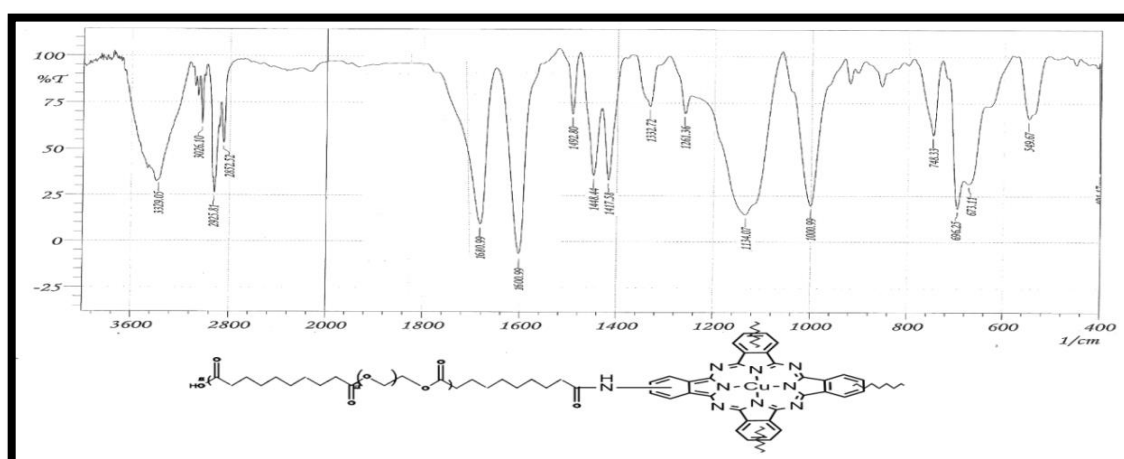


Fig.(9): FTIR spectrum of 4,4',4'',4'''-tetraaminophthalocyaninatocopper(II)-grafted PEG₁-S

Thermal stability of phthalocyanine compounds and their grafted polymers

Thermal gravimetric analysis (TGA) is one of the methods of thermal analysis techniques used to study the thermal stability of a wide variety of materials. The results obtained from thermal gravimetric of the Pc derivatives and their grafted polymers are listed in Table 5.

The data in the Table 5 illustrate that 3,3',3'',3'''-(NH₂)₄PcCu(II) degrade at 419 °C, while the 4,4',4'',4'''-(NH₂)₄PcCu(II) degrades at 318 °C. This implies that 3,3',3'',3'''-(NH₂)₄PcCu(II) is more thermally stable than 4,4',4'',4'''-(NH₂)₄PcCu(II). This may be attributed to the fact that 3-

substituted precursor can dictate predominant forms of the least structurally crowded and least soluble phthalocyanine [22]. The other reason may be due to steric hindrance raised from the formation of the hydrogen bonding between hydrogen atom of the amino groups of 3Pc and the nitrogen of Aza Bridge to form hexagonal rings [23]. In contrast, this suggested structure was never formed in 4,4',4'',4'''-(NH₂)₄PcCu(II), because their amino groups were far away compared to their positions in 3,3',3'',3'''-(NH₂)₄PcCu(II) and the hydrogen bonding was never formed. Therefore, one can conclude that the hydrogen bonding formed in 3,3',3'',3'''-(NH₂)₄PcCu(II) increases thermal stability.

Table (5): Decomposition temperatures, % char residue and T_{50%} weight loss for Pc's and their grafted polymers compounds

Sample	Decomposition Temperature (°C)			Char Residue at 500 °C (%)	T _{50%} Weight loss (°C)
	D.T ₁	D.T ₂	D.T ₃		
3Pc-NH ₂	419	---	---	64	573
3Pc-PEA	440	557	---	58.7	536
3Pc-PES	272	412	---	36	440
3Pc-PEG ₁ -S	330	490	---	64	500
3Pc-PEG ₂ -S	250	---	---	18	360
3Pc-PEG ₃ -S	445	---	---	56	524
4Pc-NH ₂	318	---	---	48	460
4Pc-PEA	294	561	---	39.2	443
4Pc-PES	290	384	484	52.1	516
4Pc-PEG ₁ -S	290	559	---	40	443
4Pc-PEG ₂ -S	280	450	---	22	360
4Pc-PEG ₃ -S	294	595	---	38.7	433

It is also clearly shown that phthalocyanine (in 3,3',3'',3'''- and 4,4',4'',4'''-substituted positions) before grafting have only one decomposition temperature for each one, while after the polymer grafting process, their thermograms exhibit more than one at most. The two decompositions confirm that grafting polymers on Pc molecules increase the degree of degradation and the range of thermal decomposition and enhance their thermal stability and in

turn may increase the area of their applications.

Sizing measurements

Particle size distribution is the statistical relation between amount and size of a given solid powder, also it exhibits the statistical relation between amount (normalized particle amount), and the size (particle diameter). All Figures demonstrate different attitude in particle size distribution shape in comparison to polymer grafted

phthalocyanine derivatives. Figures 10 and 11 show the particle size distribution of ungrafted 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) respectively and Figures 12 and 13 for grafted phthalocyanine derivatives. These changes in shape imply that real grafting were obtained, and can be considered as another proof for the grafting process beside the infrared spectra.

The calculated results obtained are listed in Table 6. Examining Table 6,

one can observe that the specific surface area increases for the polymer grafted phthalocyanine in both 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II). In comparison with ungrafted compounds, this indicates that the grafting process increases the surface area of solid particles, while other parameters (particle size, surface weight mean, volume weight mean and [d (0.1), d (0.5) and d (0.9)] decrease compared with 3Pc and 4Pc before grafting.

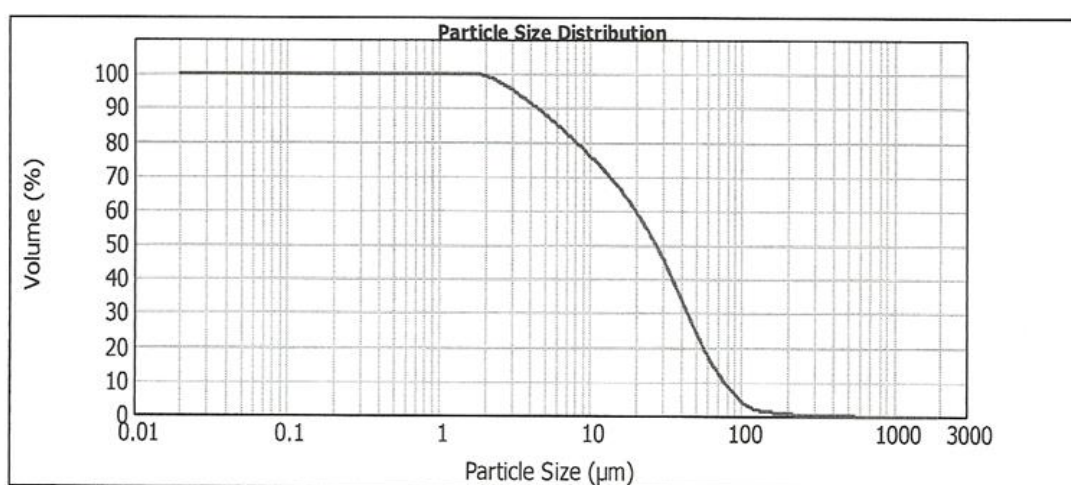


Fig.(10): Particle size distribution of 3,3',3'',3'''-(NH₂)₄PcCu(II) powder

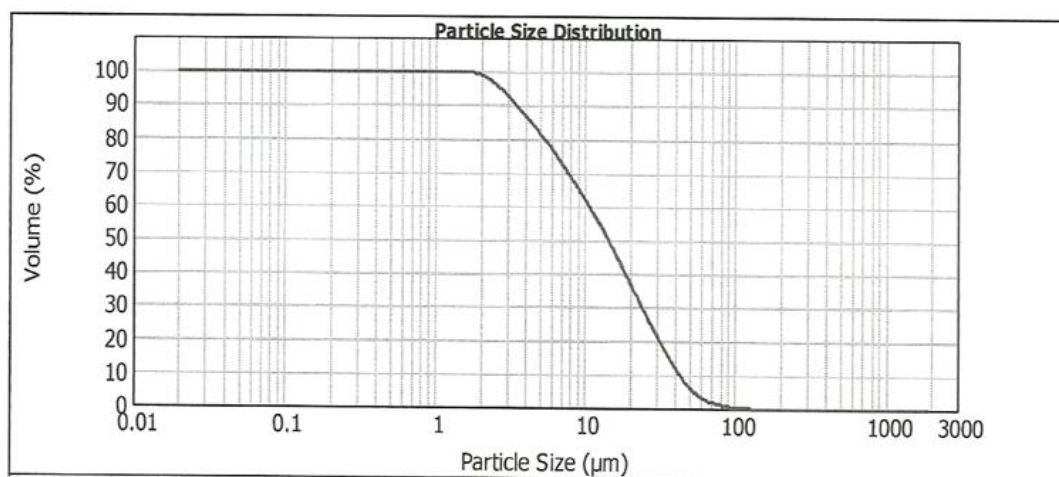


Fig. (11): Particle size distribution of 4,4',4'',4'''-(NH₂)₄Pc Cu(II) powder

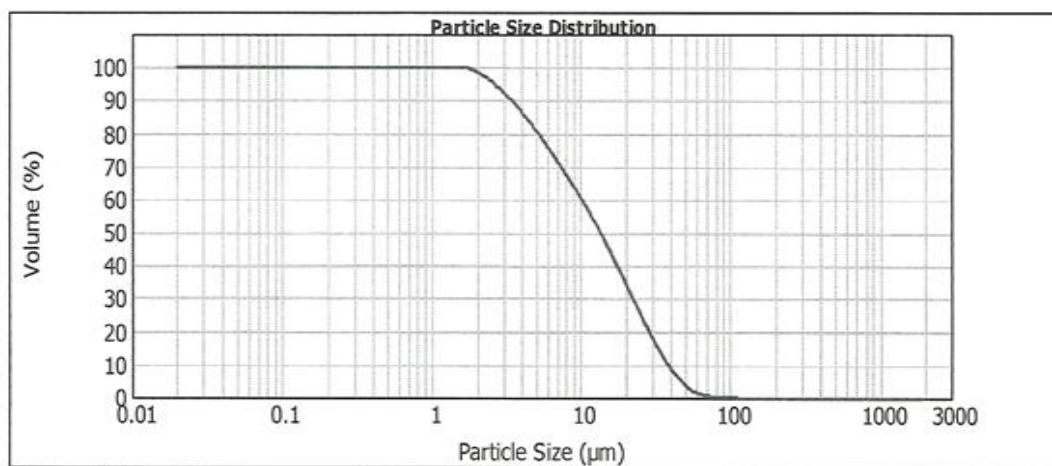


Fig. (12): Particle size distribution of 3,3',3'',3'''-(NH₂)₄PcCu(II)-grafted PES powder

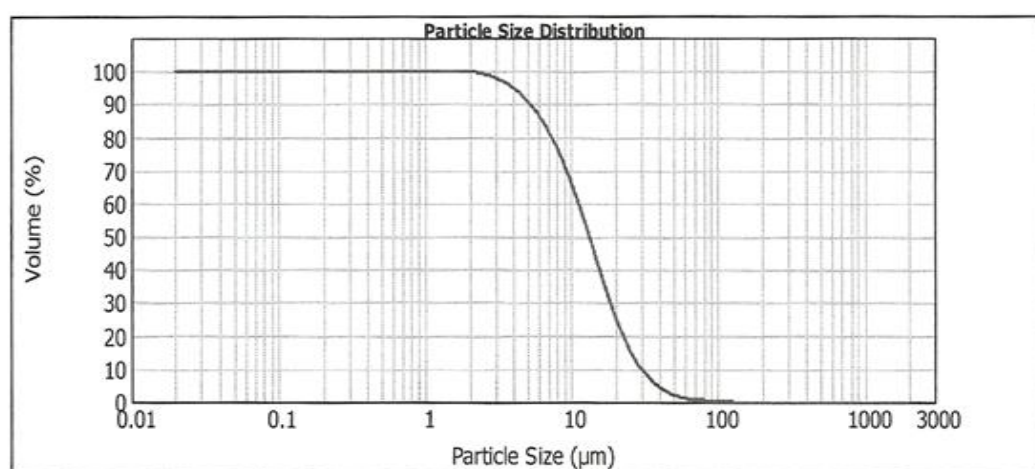


Fig. (13): Particle size distribution 4,4',4'',4'''-(NH₂)₄PcCu(II)-grafted PES powder

The aggregation tendency of phthalocyanines is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and kind of substituents, type of metal ions and temperature [24].

One of the obtained results about the complexes whose bulky group substituted at the peripheral positions was a decreasing of the aggregation [25]. Therefore, particle size and other parameters decreased after grafting which may be attributed to polymer chain that decrease the ability of phthalocyanine molecular for aggregation by the bulky effect of these chains and at the same time increases the specific surface area. Therefore, this

indicates the occurrence of grafting process. On the other hand, larger molecular weight of all the polymers which are grafted with phthalocyanine prevented particle growth through steric hindrances. The presence of functional groups on polymer chains that's grafted with Pc may ensure nanoparticle's surface stabilization through electrostatic repulsive forces leading to prevent particles to grow [26].

Sizing measurements revealed that the specific surface area of 3,3',3'',3'''-(NH₂)₄PcCu(II)-grafted different polymers have higher value compared with the analogous of the second group, i.e. 4,4',4'',4'''-(NH₂)₄PcCu(II)-grafted different polymers. Whereas, lower value for other parameters (Particle size, surface

weight mean, volume weight mean and [d (0.1), (0.5) and (0.9)] were obtained. This may be attributed to the differences in steric hindrance between the 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) group as discussed before leading to decrease in aggregation ability of 3,3',3'',3'''-(NH₂)₄PcCu(II) groups more than in 4,4',4'',4'''-(NH₂)₄PcCu(II) groups [27]. These results are in good agreement with thermal

Conclusions

1. The two phthalocyanine derivatives (3,3',3'',3'''- and 4,4',4'',4'''-

tetraaminophthalocyaninatocopper(II)) and the different polymers were prepared and characterized in success.

2. The results of surface area and particle size measurements of the polymers grafted 3,3',3'',3'''- and 4,4',4'',4'''- tetraaminophthalocyaninato copper(II), beside the IR spectra might confirm that real grafting was obtained.

3. The grafting process increases thermal stability in comparison to the 3,3',3'',3'''-(NH₂)₄PcCu(II) and 4,4',4'',4'''-(NH₂)₄PcCu(II) by two or more decompositions.

Table (6): Specific surface area, surface weight mean, volume weight mean and [d (0.1 d (0.5) and d (0.9)] parameters of ungrafted and polymer-grafted 3- and 4-tetraaminohthalocyanine

Item	Particle Size	Surface Weight Mean	Vol. Weight Mean	d(0.1)	d(0.5)	d(0.9)	Uniformity	Specific Surface Area
3Pc-NH ₂	40	12.235	35.602	4.423	27	76.32	0.873	0.2
3Pc +PEA	20	8.615	19.441	3.468	14.30	42.43	0.869	0.284
3Pc +PES	20	8.251	17.695	3.43	13.5	38.23	0.816	0.297
3Pc +PEG ₁ -S	15	7.636	16.717	3.521	11.51	33.33	0.932	0.321
3Pc +PEG ₂ -S	15	6.461	13.533	4.21	6.24	32.36	1.41	0.379
3Pc +PEG ₃ -S	36	9.341	29.846	3.37	23.16	67.72	0.872	0.262
4Pc	30	15.568	30.711	7.131	24.21	58.86	0.722	0.156
4Pc + PEA	24	12.42	25.87	5.453	19.79	52.62	0.77	0.197
4Pc +PES	16	10.155	16.143	5.231	13.19	29.74	0.608	0.241
4Pc +PEG ₁ -S	18	11.557	19.065	5.93	15.12	33.12	0.648	0.212
4Pc +PEG ₂ -S	23	13.437	21.839	6.592	18.87	40.07	0.568	0.182
4Pc +PEG ₃ -S	24	11.786	22.29	4.868	19.53	53.31	0.68	0.208

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References

- [1] Torre, G., Bottari, G., Hahn, U. and Torres T. 2010. Coordination Chemistry Reviews. Struct. Bond.135 (2):1-44.
- [2] Pavan, V.S., Neti, K., Wang, J., Dengb, S. and Echegoyen, L. 2015. High and Selective CO₂ Adsorption

by a Phthalocyanine Nanoporous Polymer. J. Mater. Chem. 3:10248-102488.

- [3] Wohrle, D. 2010. Phthalocyanines in Macromolecular Phases – Methods of Synthesis and Properties of the Materials. Macromol Rapid Commun., 22:68-97.
- [4] Wohrle, D. and Schnurpfeil, G. 2003. In Porphyrin Handbook, Vol 17, Kadish, K.M., Smith, K.M. and Guillard, R. (Eds), Academic Press, San Diego.
- [5] Huang, C. and Zhang, Q. 2005. Fully Functionalized High-Dielectric-

- Constant Nanophase Polymers with High Electromechanical Response. *Adv. Mater.* 17(3):1153-1158.
- [6] Choi S., Hong S.H., Cho S.H., Park S., Park S.M., Kim, O. and Ree, M. 2008. High performance programmable memory devices based on hyperbranched copper phthalocyanine polymer thin films. *Adv. Mater.* 20:1766-1771.
- [7] Yoshimoto, S. and Itaya, K. 2007. Advances in Supramolecularly Assembled Nanostructures of Fullerenes and Porphyrins at Surfaces. *J. Porphy. Phthaloc.* 11:313-333.
- [8] Kendal, D.N. 1953. Identification of Polymorphic Forms of Crystals by Infrared Spectroscopy. *Anal. Chem.* 25(3):382-389.
- [9] Boas, J.F., Fielding, P.E., Mackay, A.G. 1974. Thermal Stability and Radiation Pamage in the phthalocyanines. *Aust. J. Chem.* 27(1):7-19.
- [10] Achar, B.N., Fohlen, G.M., Parker, J.A. 198. Process for Preparing Phthalocyanine Polymer from Imide Containing Bisphthalonitrile. US Patent; 4,649,189.
- [11] Vogel A. I. 1978. Textbook of Practical Organic Chemistry, (4th edn), Longman, UK, Scientific and Technical.
- [12] Achar, B.N., Fohlen, G.M., Parker, J.A., Keshavaye, J. 1987. Synthesis and Structural Studies of Metal(II) 4,9,16,23-Phthalocyanine tetraamines. *Polyhedron.* 6:1463-1467.
- [13] Crompton, T.R. 2009. Introduction to Polymer Analysis, Smithers Rapra, UK.
- [14] Margerison, D. and East, G.C. 1967. An Introduction to Polymer Chemistry, Pergamon Press Ltd., Oxford.
- [15] Sultan, M.T., Al-Dujali, A.H. and Al-Lami, H.S. 2010. Synthesis and Free-Radical Alumina-Grafting Polymerization of Acrylic Acid Monomer and Their Schiff-Base Derivatives. *Iraqi J. Polym.* 128 (14(2)).
- [16] Al-Assadi M.J. 2006. Preparation of Some Peripherally Polymerized Metallophthalocyanine and Study of Their Spectroscopic and Electrical Properties, Ph.D Thesis, University of Basrah.
- [17] Boucher L.J. 1979. Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York.
- [18] Silverstein, R.M., Webster, F.X. and Kiemle, D.J. 2005. Spectrometric Identification of Organic Compounds (7th Edn), John Wiley & Sons Inc., New York.
- [19] Ebert, A.A. and Gottlieb, H.B. 1952. Infrared Spectra of Organic Compounds Exhibiting Polymorphism. *J. Amer. Chem. Soc.* 74:2806-2810.
- [20] Workman, J. 1999. Handbook of Organic Compounds: NIR, IR, Raman and UV-Vis Spectra, Marcel Dekker Inc., New York.
- [21] Al-Lami, H.S., Billingham, N.C. and Calvert, P.D. 1992. Controlled Structure Methacrylic Copolymers as Dispersants for Ceramic Processing, *Chem. Mater.*, 4:1200-1207.
- [22] Brewis M., Clarkson G. J., Humberstone P., Makhseed S., McKeown N. B. 1998. The Synthesis of some Phthalocyanines and Naphthalocyanines Derived from Sterically Hindered Phenols. *Chem. J.* 4(9):1633-1640.
- [23] Barker C. A. 2007. Synthesis and Properties of Novel Phthalocyanines a Related N-Containing Macrocycles, Ph.D thesis, University of Durham, U.K.
- [24] Leznoff, C.C., Lever, A.B. (eds). 1996. Phthalocyanines: Properties and Applications, vols (1-4). VCH Publisher, Cambridge.

