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The Preparation, Characterization and the Study of Thermal Properties to Some Co-Phthalocyanine Polymers Derivative from Epichlorohydrine and Dichlorodimethyl Silane

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Abstract

A novel class of polymer containing the metallophthalocyanine ring [MPc, M= Co(II)] in the chain was synthesized by polycondensation of 4,4',4''-tetraminophthalocyanato cobalt (II) with epichlorohydrine and dichlorodimethyl silane by [1:2] mole ratio (MPc: Epichlorohydrine or dichlorodimethyl silane). The structures of the polymers were characterized by FTIR, U.V-Visible spectrophotometry, and X-ray diffraction. The thermal stabilities of the polymers were evaluated by dynamic thermo gravimetric analysis (TG) and diffraction scanning calorimetric (DSC).

Keywords: cobalt phthalocyanine polymer; thermal stability phthalocyanine polymer.

1. Introduction

Phthalocyanines are one of the most studied classes of organic functional materials with high potential in electrooptics. Due to their 18-p electron macrocyclic aromatic system, closely related to that of the naturally occurring porphyrin ring, and relative facile tailoring of molecular structure by chemical modification, they found numerous commercial applications, among others: photoconductors in xerography [1], optical

data storage [2], solar energy conversion [3], electrochromic and electroluminescent displays [4].

Phthalocyanine (Pc) polymers have various functions, for example, stacked polyphthalocyanines for electroconductors [5], copolymerized phthalocyanine polymers for organic photoconductors [6], thermally stable polymers containing metallophthalocyanines [7] and so on, have already been prepared.

Metallophthalocyanine (MPc) has also attracted considerable interest because of its structural similarity to the active centre of naturally occurring haemoenzymes.

Among the various photosensitizers being investigated, phthalocyanines have been found to be highly promising. Owing to their strong Q-band absorptions at the red visible region (700 nm), these pigments can be excited at longer wavelengths than porphyrin-based photosensitizers such as photofrin, which is the first clinically approved photosensitizer [8].

2. Experimental

2.1 Chemicals

4-nitro phthalic acid (99%) (Merk), Ammonium molybdate (98%) (RDH), Cobalt sulphate hydrate (99.5%) (Fluka), Dichloro dimethyl silane (99%) (Aldrich), Epichlorohydrine (99%) (Aldrich), Sodium hydroxide (97.5%) (Thomas

The macrocycles are also relatively nontoxic in the dark and have relatively high singlet oxygen quantum yields. These unique features, together with their ease of functionalization and formulation, have aroused intense interest in the use of these functional dyes as second generation photosensitizers in photodynamic therapy (PDT) [9].

In this paper, we report on the effect of different substitution epichlorohydrine and dichlorodimethyl silane with 4,4',4'',4'''-tetraaminophthalocyanato cobalt (II) to prepare Co-phthalocyanine polymers and study the thermal stability properties.

Baker), Urea (99%) (Fluka), Hydrochloric acid (37%) (BDH), Acetone (99.5%) (GCC), Ethanol (99.9%) (Scharlau), Benzene (99%) (BDH), DMF (99%) (GCC) and DMSO (99.5%) (GCC).

2.2 Instruments

1. FTIR-Infrared spectrophotometer (8400S) made by (SHIMADZU) the range (4000-400 cm^{-1}).
2. UV-Visible spectrophotometer made (Thermo Spectronic- $\text{He}\lambda_{10}\text{S}_\alpha$) the range (900-200 nm).
3. X-ray Diffraction measurement made (Philips Analytical) the range position (10-70 $^\circ$).
4. Thermo Gravimetric Analysis (TG) made by (England) - PL- TG) the range (25-900 $^\circ\text{C}$).
5. Diffraction Scanning Calorimetric (DSC) made by (England) - PL- DSC) the range (25-500 $^\circ$

3 Preparation Methods

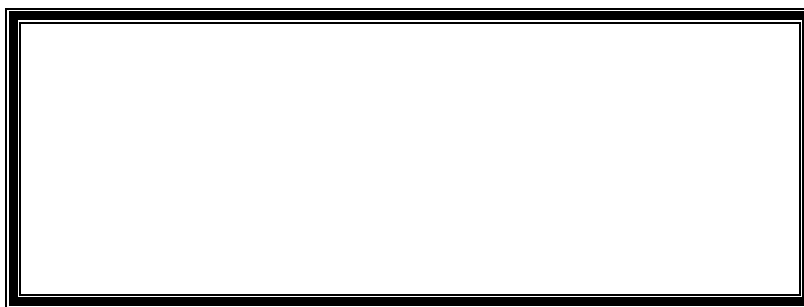
The 4,4',4'',4'''-tetra **nitro** and **amino** phthalocyanato cobalt (II) were prepared by depending on the reference [10].

3.1 Preparation of polymers [1:2] mole ratio:

3.1.1. Preparation of poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II))

In three necks round bottom (0.258 g, 2mmol) dichloro dimethyl silane was dissolved in (25ml) DMF solvent with stirring and

cooling the mixture at 5 $^\circ\text{C}$. (0.631g, 1mmol) 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) was dissolved in (25ml) DMF solvent and adding drop by drop to the first solution with keeping the temperature less than 10 $^\circ\text{C}$. After the end of adding the mixture was heated at (80-85 $^\circ\text{C}$) for (2h), the product was cooled, filtered and dried to obtain dark green crystals with yield (0.64g, 85%), as shown as in Scheme (1) [11].

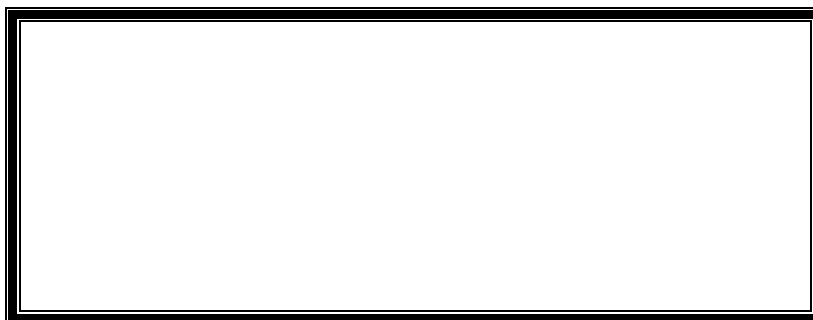


Scheme (1) preparation of poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio

3.1.2. Preparation of poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)):

In three necks round bottom (0.185 g, 2mmol) epichlorohydrine and (0.631g, 1mmol) 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) was dissolved in

(50ml) DMF solvent by catalyst (22%) NaOH solution. The mixture was refluxed with stirring at (110⁰C) for (20h), the product was cooled, filtered and dried to obtain dark green crystals with yield (0.66g, 76%), as shown as in Scheme (2) [12].



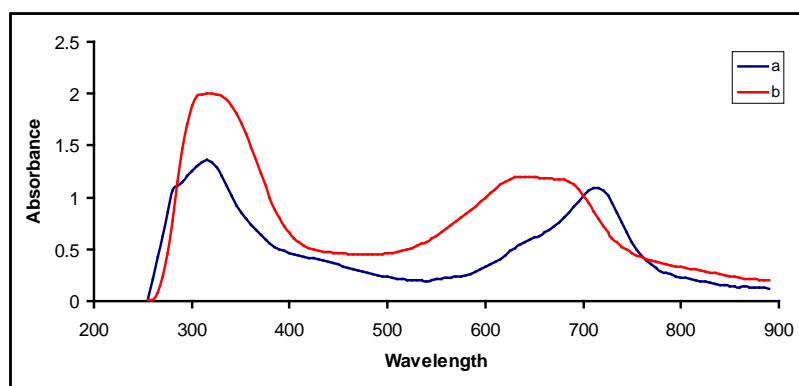
Scheme (2) preparation of poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio

4- Results and Discussion

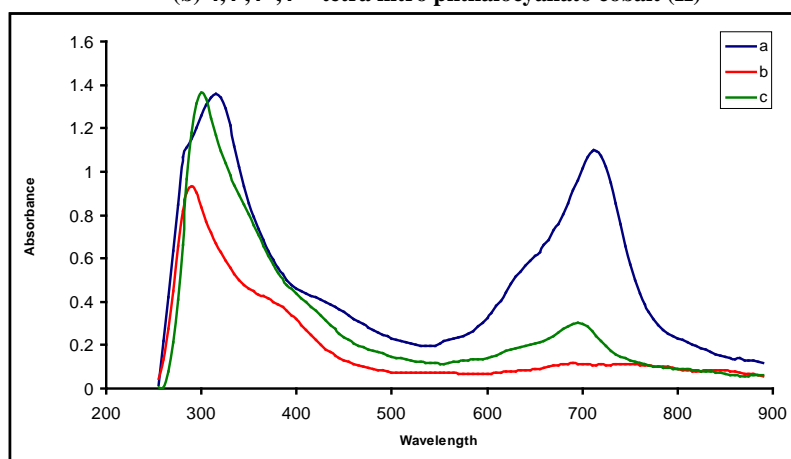
Figure (1) and Table (1) show the absorption spectra for 4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II) and 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) compounds, it shows Q-band and B-band at (640nm, 300nm) and (710nm, 315nm) respectively. The Q-band and B-band for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) are red shifted +70nm and +15nm it compared with the 4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II) may be attributed to the presence of the four amine groups which are not reacted and this leads to increase the delocalization on the phthalocyanine rings [13].

Figure (2) and Table (1) show the absorption spectra for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II), poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio and poly(tetra (2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio, it shows Q-band and B-band at (710nm, 315nm), (690nm, 298nm) and (700nm, 300nm) respectively. The Q-band and B-band for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) and poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) compared with 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) are blue shifted -20nm , -17nm

and -10nm , -15nm may be attributed to the reaction of the amine groups which leads to reduce the delocalization on the phthalocyanine rings [14].



**Figure (1) : UV-Visible absorption spectra for
(a) 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)
(b) 4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II)**



**Figure (2) : UV-Visible absorption spectra for
(a) 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)
(b) poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio
(c) poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio**

Table (1): The UV-Visible absorption data for prepared compounds

Compounds	Q- Band λ_{\max} (nm)	B- band λ_{\max} (nm)
4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II)	640	300
4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)	710	315
poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II))	690	298
poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II))[1:2] mole ratio	700	300

Figures (3)-(6) and Table (2) show the FTIR-spectra to the prepared compounds. Figure (3) the FTIR-spectrum for 4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II) shows the characteristic bands (N-O) asymmetric stretching at 1521 cm^{-1} and symmetric stretching at 1334 cm^{-1} [15].

Figure (4) the FTIR-spectrum for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) shows the characteristic bands at 3410 cm^{-1} and 3370 cm^{-1} which may be attributed to the (N-H) asymmetric and symmetric stretching respectively, in addition to display band at 1510 cm^{-1} which may be attributed to the (N-H) bending vibration [16].

Figure (5) the FTIR-spectrum for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio shows the appearance of new bands 1260 cm^{-1} and 800 cm^{-1} for $\text{Si}(\text{CH}_3)_2$ and the disappearance the bands for (NH_2) , in addition to the appearance of new band at

3425 cm^{-1} for (N-H) which is resulted from connection with dichloro dimethyl silane and other bands at 2964 cm^{-1} , 2855 cm^{-1} and 1326 cm^{-1} which may be attributed to (C-H) aliphatic asymmetric, symmetric stretching and bending vibration respectively [17].

Figure (6) the FTIR-spectrum for poly(tetra (2-hydroxy propyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio shows the disappearance the bands for (NH_2) and appearance of new band 3420 cm^{-1} for (N-H) which is resulted from connection with epichlorohydrine and the appearance of new band 3458 cm^{-1} for (O-H). The bands at 2950 cm^{-1} , 2846 cm^{-1} and 1335 cm^{-1} which may be attributed to (C-H) aliphatic asymmetric stretching and bending vibration respectively [17], other bands $500\text{-}600\text{ cm}^{-1}$, $720\text{-}756\text{ cm}^{-1}$, $810\text{-}930\text{ cm}^{-1}$ and $1000\text{-}1141\text{ cm}^{-1}$ are vibration frequencies which are attributed to phthalocyanine compounds.

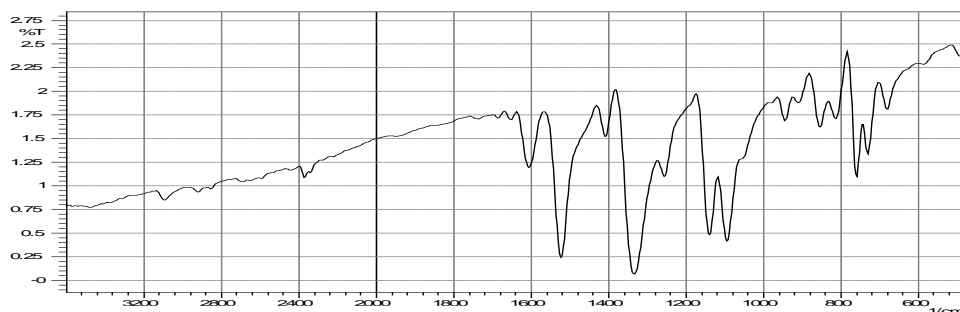


Figure (3): FTIR-spectrum for 4,4',4'',4'''-tetra nitro phthalocyanato cobalt (II)

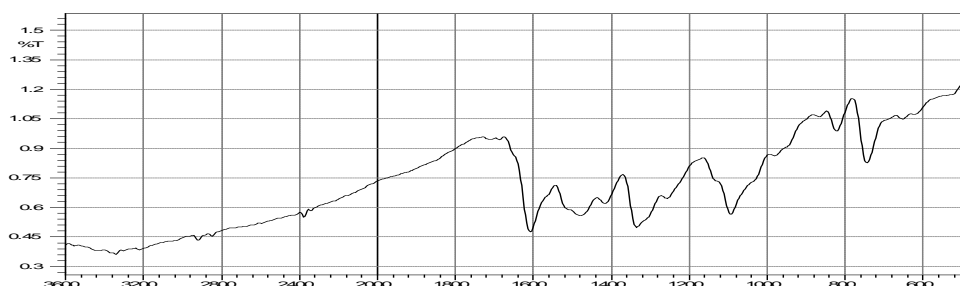


Figure (4): FTIR-spectrum for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)

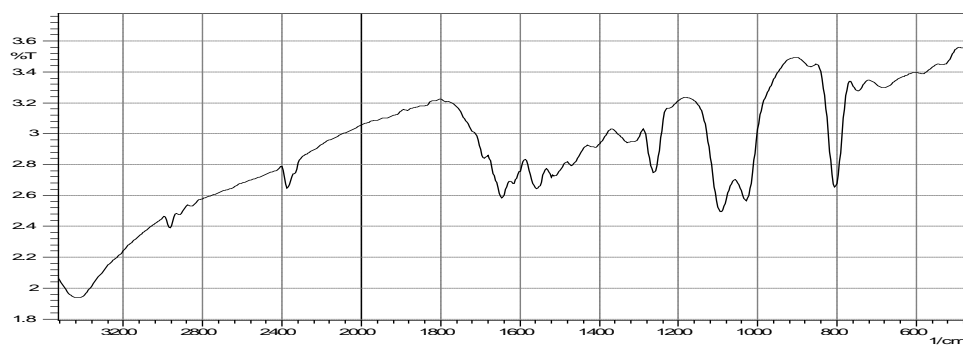


Figure (5): FTIR-spectrum for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio

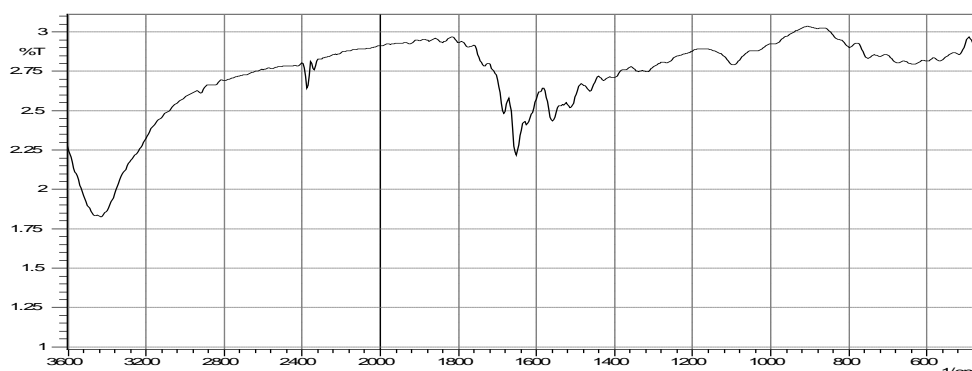


Figure (6): FTIR-spectrum for poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio

Table (2): The FTIR absorption data for prepared compounds

Compounds	ν (cm ⁻¹) O-H	ν (cm ⁻¹) N-H	ν (cm ⁻¹) C-H	ν (cm ⁻¹) C=C	ν (cm ⁻¹) C=N	ν (cm ⁻¹) N=O	ν (cm ⁻¹) Si(CH ₃) ₂
4,4',4",4'''-tetra nitro phthalocyanato cobalt (II)	-	-	3028 asy 3010 sy 1220 b	1407	1606	1521asy 1334 sy	-
4,4',4",4'''-tetra amino phthalocyanato cobalt (II)	-	3410 asy 3370 sy	3034 asy 3010 sy	1415	1606	-	-
poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio	-	3425 asy 1512 b	2964 asy 2855 sy	1469	1645	-	1260 800
poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II))[1:2] mole ratio	3458	3420 asy 1512 b	2950 asy 2846 sy	1462	1650	-	-

Figures (7)-(9) show the X-ray diffraction spectra for the prepared compounds. From the spectra of polymers we result it is less width of band and more crystalline

regularity comparing with 4,4',4",4'''-tetra amino phthalocyanato cobalt (II) as shown in the Table (3) [18].

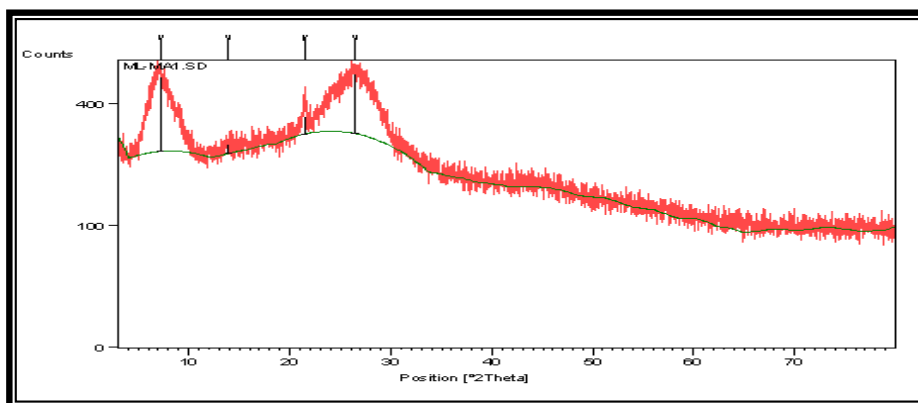


Figure (7): X-ray diffraction spectrum for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)

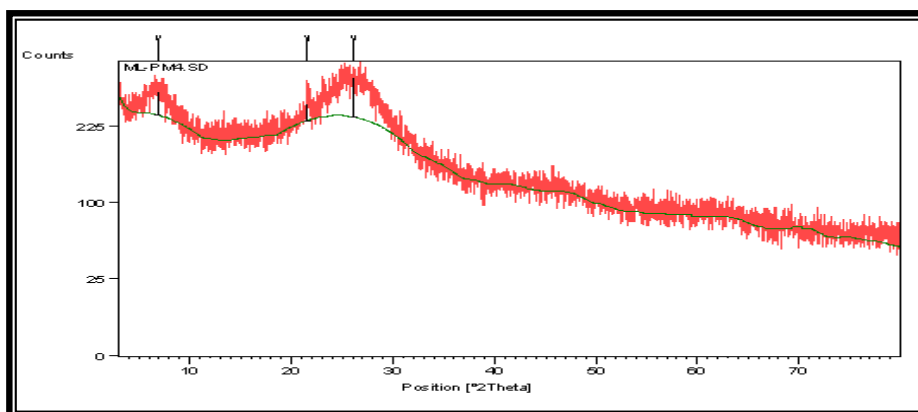


Figure (8): X-ray diffraction spectrum for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio

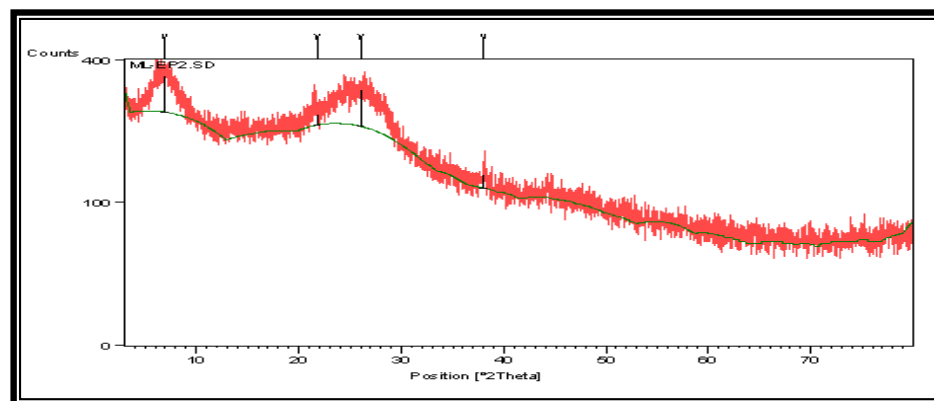


Figure (9): X-ray diffraction spectrum for poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio

Table (3): X-ray diffraction data for prepared compounds

Compounds	Area[cps*20Th.]	d-spacing[Å]	2θ
4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)	663.78, 53.66, 58.34, 968.86	12.254, 6.349, 4.1335, 3.036	7.207, 13.936, 21.480, 26.435
poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio	164.28, 21.26, 437.28	12.85, 4.114, 3.406	6.869, 21.582, 26.136
poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II))[1:2] mole	293.54, 66.16, 428.91, 21.45	12.759, 4.081, 3.421, 2.362	6.922, 21.754, 26.025, 38.050

In the present paper the thermal stability for prepared compounds are studied by two techniques: thermo gravimetric analysis (TG) and diffraction scanning calorimetric (DSC). Figures (10)-(12) show the TG-curves for prepared polymers are more thermal stability from 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II), so that the poly

(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio is more thermal stability from poly(tetra (2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio due to the silicon atom has d-orbital, as shown in the Table (4) [19].

Table (4): The TG data for prepared polymers

Compounds	decomposition degree (°C)				activation energy (Kj/mol)	char cont. at (850°C)
	1	2	3	4		
4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)	59	465	770	-	33.75	60.4%
poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio	63	340	470	760	54.72	52.2%
poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II))[1:2] mole ratio	70	460	750	-	47.82	56%

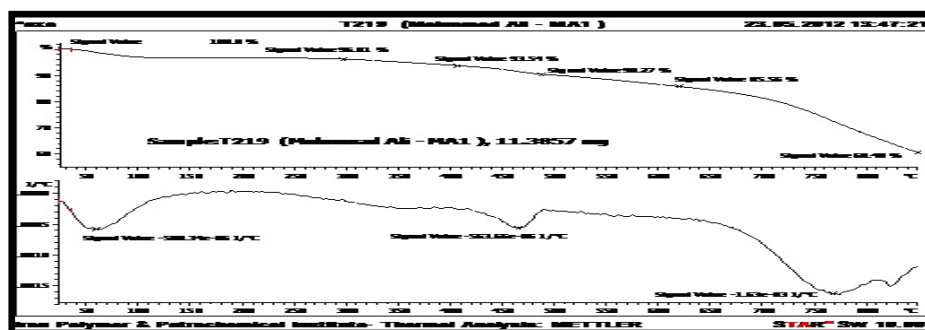


Figure (10): TG-curve for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)

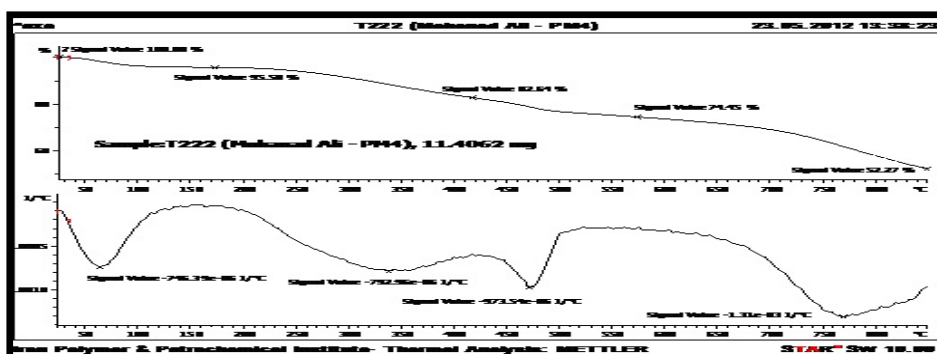


Figure (11): TG-curve for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio

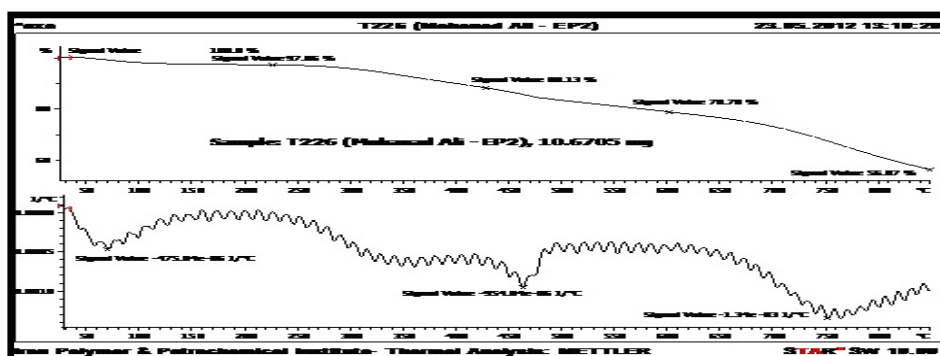


Figure (12): TG-curve for poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio

Figures (13)-(15) show the DSC-curves for the prepared polymers, the all curves are appeared bands at 65-100⁰C which may be attributed to vapor solvent. In DSC-curve for poly (tetra(dimethyl silane imino) phthalocyanato cobalt (II)) [1:2] mole ratio begins to decompose at 190⁰C, it is more decomposition than 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) which is decomposed at 213⁰C due to the presence

of aliphatic groups in the polymer structure. While the DSC-curve for poly(tetra (2-hydroxypropyl imino) phthalocyanato cobalt (II)) [1:2] mole ratio begins decompose at 227⁰C, it is less decomposition than 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II) due to the presence to the hydrogen bonds in the polymer structure [19].

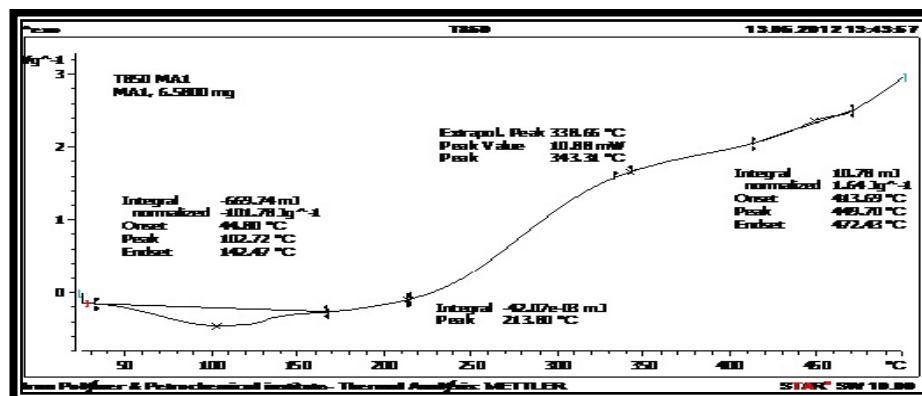


Figure (13): DSC-curve for 4,4',4'',4'''-tetra amino phthalocyanato cobalt (II)

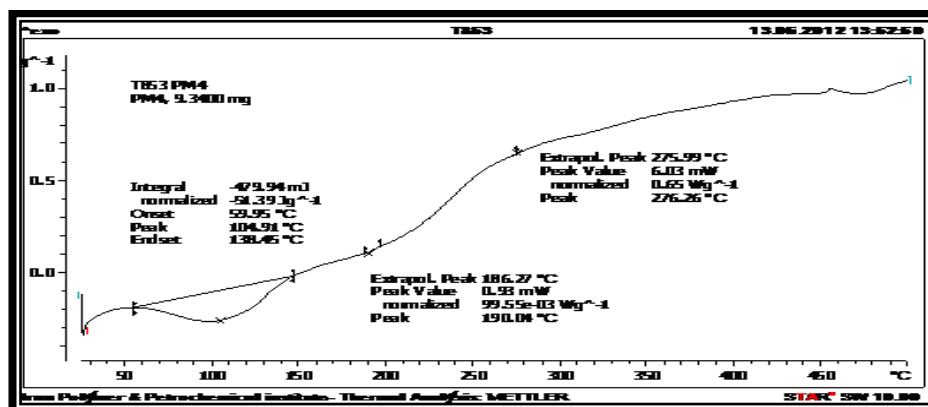


Figure (14): DSC-curve for poly(tetra(dimethyl silane imino) phthalocyanato cobalt (II) [1:2] mole ratio

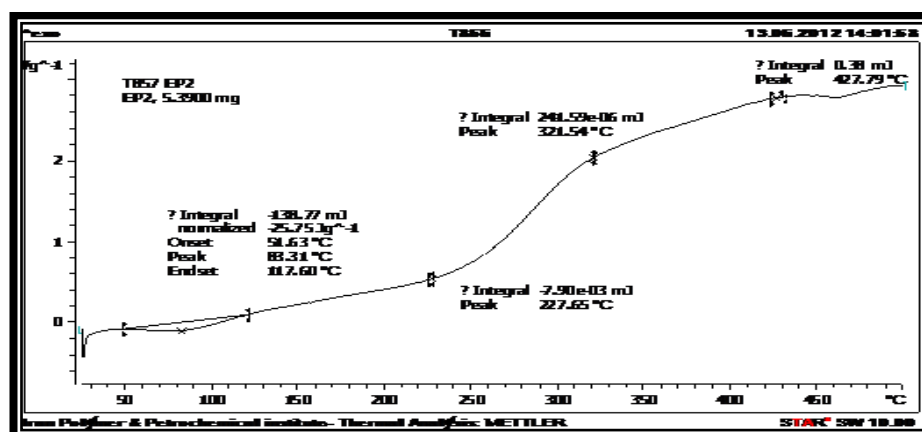


Figure (15): DSC-curve for poly(tetra(2-hydroxypropyl imino) phthalocyanato cobalt (II) [1:2] mole ratio

References

- [1] Ganicz T., Makowski T. and Tracz A., *eXPRESS Polymer Letters.*, 6, 5, 373–382 (2012).
- [2] Gao Z., Liang J. and X. Tao, *Macromolecular Research*, 20, 5 (2012)
- [3] Li L., Tang Q., Li H., Hu W. and Zhu D., *Pure and Applied Chemistry*, 80, 2231–2240 (2008).
- [4] Hirofusa S., Shun-Ichi k. and Kenji H., *Journal of Porphyrins and Phthalocyanines*, 2, 31–38 (1998).
- [5] Jie F., Xi-you L., Dennis K. and Chi W., *Langmuir*, 18, 3843-3847 (2002).
- [6] Allen C., Sharman W. and Lier, J., *J. Porphyrins Phthalocyanines*, 5, 161(2001).
- [7] Anokhin D., Rosenthal M., Makowski T., and Ivanov D., *Solid Films*, 517, 982–985 (2008).
- [8] Sergeyev S., Pouzet E. and Geerts Y. H., *Journal of Materials Chemistry*, 17, 1777–1784 (2007).
- [9] Geerts Y., Debever O. and Sergeyev S., *Journal of Organic Chemistry*, 5, 1–9 (2009).
- [10] Mohanad. J., *Ph.D.Thesis*, University of Basrah, Iraq (2006).
- [11] Wedad. S., *Ph.D.Thesis*, University of Basrah, Iraq (1999).
- [12] Yue S., Yi-Ben X., and Cheng , Z., *Chin. Phys. Lett.*, 21, 9 (2004).

