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Synthesis And Characterization Of (P-Hydroxybenzoic Acid Urea Formaldehyde) Copolymer Chelates With Pb(II),Zn(II) And Cd(II) Ions

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Abstract

Copolymer { p-hydroxybenzoic acid urea formaldehyde}(PUF) was prepared from the reaction of {p- hydroxybenzoic acid}(P) + {urea}(U) + {formaldehyde}(F) using HCl as a catalyst.

Formation of Pb(II),Zn(II) and Cd(II) polymers were obtained from the reaction of the copolymer (PUF) with some ions. The polymeric structures were elucidated by Fourier transform infrared spectroscopy (FTIR) and Atomic Absorption spectroscopy (AA), thermogravimetric analysis (TGA) and derivative of the thermogravimetric analysis (DTG) has been carried out to ascertain relative thermal stability of copolymer and its polymeric complexes and the pat of H_2O in the structure. Form the obtained data an octahedral geometry around Pb(II),Zn(II) and Cd(II))ions have been suggested.

Key words: Urea , *Co Polymer* and derivative of therthermogravimetric (DTG).

المستخلص

يحضر الكو بولمر اليوريا – فورمالدهايد بارا هايدروكسي حامض البنزوك من تفاعل بارا هايدروكسي حامض البنزويك مع اليوريا والفورمالدهايد يوجود حامض الهليدروكلوريك كعامل مساعد .

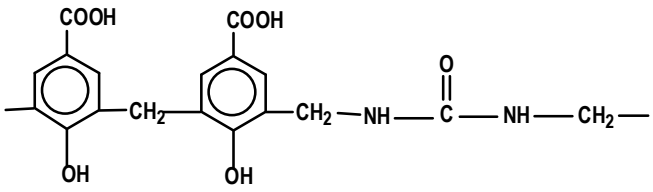
والبولمرات المتناسقة مع ايونات الرصاص الثنائي والزنك الثنائي والكادميوم الثنائي نحصل عليها من تفاعل الكو بولمر اليوريا – فورمالدهابد بارا هايدروكسي حامض مع ايونات الرصاص الثنائي والزنك الثنائي والكادميوم الثنائي وان الصيغة البنائية للبولمرات المتناسقه ظهرت بواساطة تحليل طيف الاشعة تحت الحمراء وتحليل الامتصاص الذري،التحليل الحراري، والتحليل الحراري التفاضلي وبالنتيجة يكون الكوبوليمرات المتناسقة ذات ثبات حراي والشكل المتوقع ثماني السطوح وتحتوي على جزيئي ماء متناسقة.

الكلمات المفتاحيه :– يوريا، كوبوليمر ،التحليل الحراري التفاضلي

Introduction

One approach in the field of supramolecular chemistry has been used to investigate the use of polymeric ligands in develop complexes with metal centres that have unusual coordination and new properties[1- El. Sonbati AZ. (2003), 2-Mohamed Jaber Al-Jbori (2009)] Various hydroxylbenzoic acid polymers with (formaldehyde) copolymers have documented to be used as ion exchangers application [Donaruma 4 R- C. DeGeiso, L. G. Donaruma (1962).

The suggested structure of copolymer is shown in Figure (1) [Joshi and Pate,1983].



Figre (1)

Structure of p-hydroxybenzoic acid-urea-fomraldehyde copolymer

The chelating polymers contain various ligands and have reported that they are more practical than gel-type resins for the removal and recovery of heavy metal ions from industrial waste[7 - Maeda (1984)] and recovery of Uranium from sea water ect.[8-Egawa, (1967). 9- Egawa (1984)].

The present paper deals with preparation and characterization of new copolymer derived from {p hydroxybenzoicacid}, {urea} and {formaldehyde}, and its polymeric complexes.[Chatterjeee, 1970].

Experimental

All reagents were obtained commercially (Aldrich) and used without purification FTIR spectra were recorded as KBr discs using a Shimadzu 8400 FTIR Spectrophotometer in range (4000−400)cm^{-}.

Thermogravimetricanalysis(TGA) and derivative of therthermogravimetric (DTG) behavior of polymeric compounds were evaluated using Stanton Redcroft TG-760 series on samples weighting about 65 mg at 20 °C / min heating rate in the oxygen atmosphere, up to 1000 °C.

2 – Preparation

a - PREPARATION OF COPOLYMER

The p-hydroxybenzoicacidureaformaldehyde(PUF) copolymer was preparted by mixing with stirring of (P) (0.4 mol), (U) (0.2 mol), 37 %aq (F) (0.6 mol), and HCl (2M, 200 mL) was heated at 100 °C on an oil bath for 5 hours . The obtained solid product was removed from the flask and then washed with cold water, and allowed dry to give a powder [Joshi and Patel,1983].

The product was repeatedly washed with water at poiling-point to remove unreacted monomers. The air dried co polymer was Soxhlet extracted with ether to remove the excess of p-hydroxybenzoic acid and p-hydroxybenzoic acid-formaldehyde co polymer which might be present along with (PUF) copolymer. For further purification it was dissolved in 8% NaOH and filtered. The copolymer was optained by slow addition of 1:1 (v/v) concentrated HCl /water with constant stirring. It was filtered, washed with water at boiling point, dried in air, and then dried in vacuum over drying reagent .Yield (47.2%)

b -PREPARATION OF CHELATES

A solution of (10 m mol) (PUF) copolymer in (100 ml of DMF) was added through a a sentred glass filteration crucible funnel nitrate cdmium nitrate(0.005 mol) ,lead nitrate(0.005 mol) and Zinc nitrate (0.005 mol) the mixtures were dissolved in (100 ml) DMF with a slight amount of water. Upon addition of saturated aqueous solution of Na(OAC),the pH of solution become 5.5 and a solid product precipted . The products were put on heated water bath They were collected, and washed with DMF, hot water, and acetone. The obtained solids were powdered and dried in a vacuum desiccator over drying reagent. Yield (52.68%) for p-hydroxybenzoic acid-urea-formaldehyde chelate

with Pb(II), (18.67%) p-hydroxybenzoic acid-urea-formaldehyde chelate Zn(II) and (29.32%) p-hydroxybenzoic acid-urea-formaldehyde chelate with Cd(II) to 0.005 mol corresponding nitrated (with Pb(II), Zn(I I) and Cd(II)

3. Results and Discussion

3 .1 FTIR spectra

The FTIR spectra of polymer and its complexes with Pb(II), Zn (II) and Cd(II) showed no significant differences from each other, but they differ from that of the ligand in some prominent frequencies.

Band detected around 3383 cm^{-1} - 3416 cm^{-1} , 3467 cm^{-1} , 3416 cm^{-1} (see Table 1) and Figures (4- 7) in the spectra of polymeric compounds are less broad than that for ligand , signaling hydrogen bonding is disappeared in the polymeric complexes and the involvement of –OH group (phenolic) in the chelation. Bending frequency of the –OH at 1213 cm^{-1} in the polymeric ligand is shifted to a higher frequency in all polymeric compounds supporting the –OH involvement in the formation of compound (Table1). Bands exhibited in the free copolymer at 1687 cm^{-1} and 1438 cm^{-1} are due to ν_{as} ,V_s (COO^-) respectively This band is shifted to lower frequencies for ν_{as}, ν_s (COO^-) appeared around 1610 cm^- and 1400 Cm^- respectively indicating the involvement of the (COO^-) in coordination [11- Yu Pang Dan Tian (2011)].The stretching vibration of asymmetric ν_{as} and symmetric ν_s (COO^-) modes, should be helping in elucidating the structure of the complexes. The $\Delta(\nu_{as} - \nu_s)$ value of (210, 216 and 220) for Pb(II),Zn(II) and Cd(II) respectively is consistent with carboxylate monodentate coordination fashion the metal ion (Fig 2) [12- Martini (2002). 13- 4Lewandowski (2005). 14- Czakis-Sulikowska (2003)]. New band in all polymeric compounds detected at 949, 930,and 950 cm^- assigned for Pb(II),Zn(II) and Cd(II), respectively referring to the coordination H_2O (aqua) coordination. δ **N-H** is found unaltered in the chelates, suggesting they does not involve in coordination the urea unit. A band at 475 cm^- could attrbute to ν (Pb– O) and 480 cm^- may be due to ν (Zn– O) and 480 cm^- may be due to ν (Cd– O) [15- Nakamoto (1963). 16- Real (2013), 17- Mishra. ,Mishara (2012)

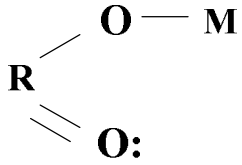


Figure (2) Carboxylate monodentate coordination with M= Pb(II) ,Zn(II) and Cd(II)

3 .2 Dynamic methods associated with weight change:

(a) Thermogravmetry (TG) is a technique which records the weight of a material in an medium heated or loss of weight at a planned average as a position of temperature or time.

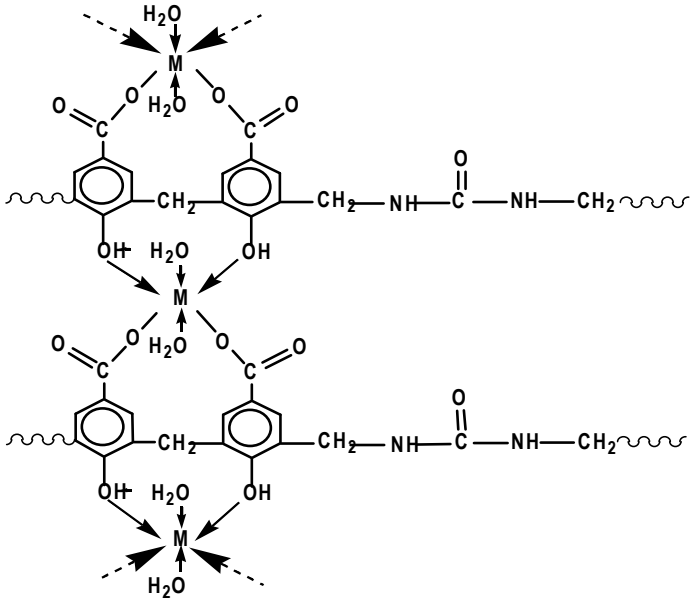
(b) (DTG) is a mechanism which yields the first derivative of (DTG) curve with consideration to either temperature or time .

The TG and DTG curves for the polymeric compounds and ligand are given in the Figures [8 - 11]. TGA (Table 2) indicate which the polymeric coordinates decompose in the tow steps. The rate of decomposition in the first step is slow compared with second

step. In the second step the value of decomposition was completed around(600 °C) for coordinates . The potential of coordinate with molecules of water as proposed is definite by the TGA from FTIR spectra. Weight loss in Pb(II), Zn (II) and Cd(II) chelates in the range 150-250 °C may be due to the two water molecules[18- Joshi R. M. (1983) 19-Strat (2006)].

Losing of water molecule at higher temperature, indicated the bind water is aquo molecule [20-Suzana Pereira Nunes (2016)]. The required weight loss is a little higher than observed in this area and this on account of some other series degradation reactions implicated in pyrolysis of the coordinate's.

Figure (3), represents the proposed chemical structure of complexes



Figre (3) p-hydroxybenzoic acid-urea-formaldehyde copolymer chelate with (M)
M= in Pb(II), Zn (II) and Cd(II)

Conclousion

Copolymer {phydroxybenzoic acid urea formaldehyde}(PUF) was prepared from the reaction of {phydroxybenzoic acid} (P) {urea} (U) {formaldehyde}(F).Then the Copolymer chelates with Pb(II), Zn(II) and Cd(II) ions. And measured by FTIR and A.A spectroscopy the thermogravimetric analysis (TGA) and derivative of therthermogravimetric (DTG). data have been suggested an octahedral geometry around Pb(II), Zn(II) and Cd(II) ions. and copolymer chelates are more high stability than Copolymer ligand.

References

El. Sonbati AZ. EI-Bindary AA. Diab MA, 2003,Spectrochimical Acta Part A 59:443. Doi:10:1016/SI386-1425(02)00222-6 .

Mohamed Jaber Al-Jbori Amar H. Al- Dujaili Aiyaa E. Al-Janabi, 2009, Tansiton Mt Chem34;109-113 Dol 10.1007/s11243-008.9165-9

Donaruma, L. G., 1962, (to E. I. du pont de Nemours and Co.), U. S. Patent 3,052,515 Chem. Abstr., 57, 13467a.

DeGeiso, R. C., Donaruma, L. G. and Tomic, E. A., Org. J., 1962, 1424 , Chem., 27.
DeGeiso, R. C., Donaruma, L. G. and Tomic, E. A., 1962, Anal. Chem.,34, 845.
Joshi, R. M., and Patel, M. M., Proc J. Macromol.,1983, Sci– chem. A19(5), pp.705- 722.
Maeda, H. and Egawa H J., 1984, Appl Polym. Sci., 29, p2281 .
Egawa., H, Maeda, H. and Nonaka. T . ,1980, Nippon Kagaku Kaishi, p1767.
Egawa., H, Nonaka, T ., and Ikari , M. J.,1984, Appl Polym. Sci., 29,p 2045,
Chatterjeee, S. K. J. ,1970, Polym. Sci., Part A-1, 8, p1299.
Yu Pang Dan Tian, Yuhui Luo, Xiao Fei Zhu and Hoeg Zhang. J. , 2011, Coord. Chem. , No. 11,pp2002 – 2009.
Martini, D., Pellei, M., Pettinari, C., Skelton, B. W., White, A. H. , 2002, Inorg. Chem. Acta.,72, p333.
Lewandowski, W., Kalinowska, M., Lewandowska, H. ,2005, Inorg. Chem. Acta.,71, p358.
Czakis-Sulikowska, D. J. , 2003, Therm. Anal. Cal. &1, 395.
Nakamoto , K. ,1963, ((Infrared Spectra of Inorganic and Coordination Compounds)), Wily. New York.,2Ed, p 206.
Real, A. J. and Abbs Fen, T. F. , Reji, J ., 2013, Chem. Pherm. Res., 5(1), pp115 – 122 .
Mishra., A. P., Mishara, R., Jain, R. and Gupta, S.; J.,2012,Mycobiology,40(1),pp20– 26.
Joshi, R. M. and Pate, M.M., 1983, Macromol. J. Sci – Chem., A19 (6), pp 919- 927.
Strat , M., Vasiliu , S., Strat , G., Luca C. , Grecu , I., Gurlui , S. Stratulat, S. I. J Optoelectronics and Advanced Materials 8, (1) February p. 181-184 (2006)
Suzana Pereira Nunes, 2016,Block Copolymer Membranes for Aqueous Solution pplications,J.*Macromolecules*, *49* (8), pp 2905–2916 .

Table (1)/FTIR spectral data of ligand and chelates polymers (Cm^{-})

Groups	Ligand	Chelate with Pb(II)	Chelate with Zn(II)	Chelate with Cd(II)
O-H polymericν	3383	3416	3416	3367
$_{as}$ C-O in CO_2^- ν	1687	1606	1610	1610
δ N-H	1573	1554	1550	1558
$_{s}$ C-O in CO_2^- ν	1438	1390	1400	1390
δ -CH(in plan) aromatic	1120	1130	1122	1130
Aqua		949	910	950
M–O		475	480	447

Table (2)/ Thermal data of ligand and chelates polymers

Polymer	T1°C	%Wt at T1		T2°C	%Wt at T2		T3°C	%Wt at T3	
		lose	remain		lose	remain		remain	lose
1	**120**	**16.28**	**83.72**	**269**	**40.58**	**59.42**	**562**	**18.03**	**81.97**
2	**250**	**16.97**	**83.13**	**499**	**59.14**	**40.86**	**879**	**28.00**	**72.00**
3	**116**	**0.17**	**98.83**	**167**	**4.77**	**95.33**			
4	**143**	**5.45**	**94.55**	**286**	**32.02**	**67,98**	**508**	**32.20**	**67.80**

1 = Ligand p-hydroxybenzoic acid-urea-formaldehyde copolymer
2 = p-hydroxybenzoic acid-urea-formaldehyde chelate with Pb^{II}
3 = p-hydroxybenzoic acid-urea-formaldehyde chelate with Zn^{II}
4 = p-hydroxybenzoic acid-urea-formaldehyde chelat with Cd^{II}

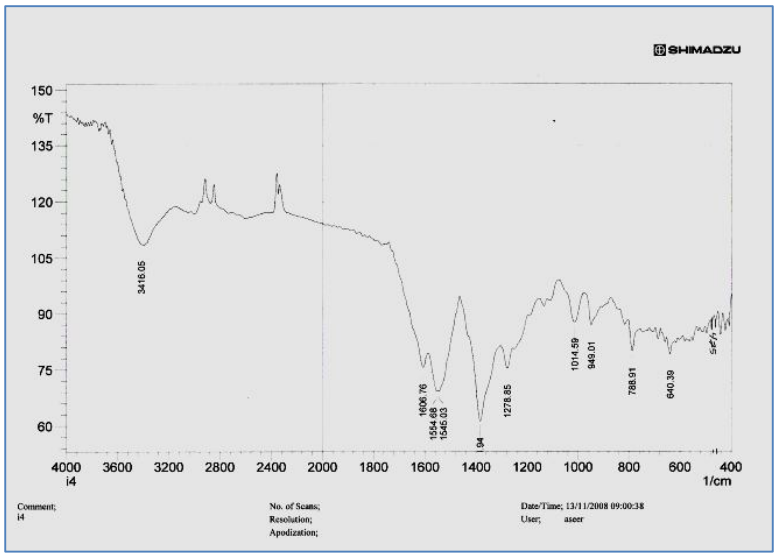


Figure **(4) FTIR Spectrum of the polymer :**
Chelate p- hydroxybenzoic acid ureaformaldehyde with Pb(II)

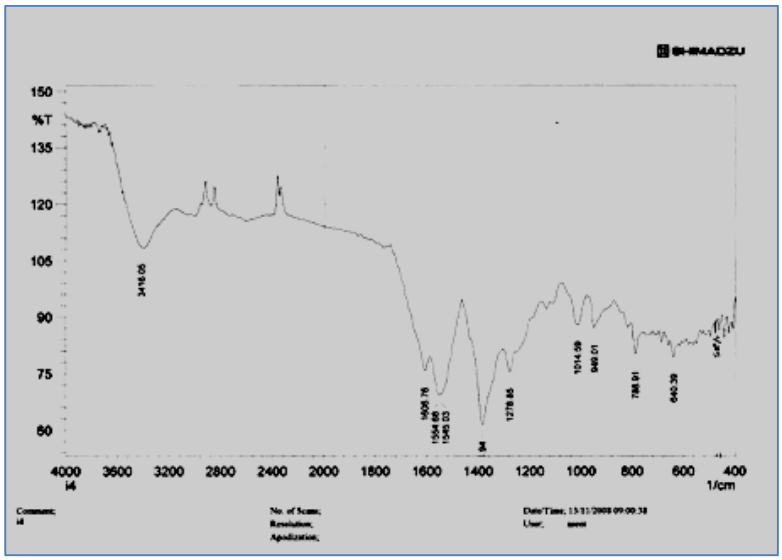


Figure **(5) FTIR Spectrum of the polymer :**
Chelate p- hydroxybenzoic acid ureaformaldehyde with Zn(II)

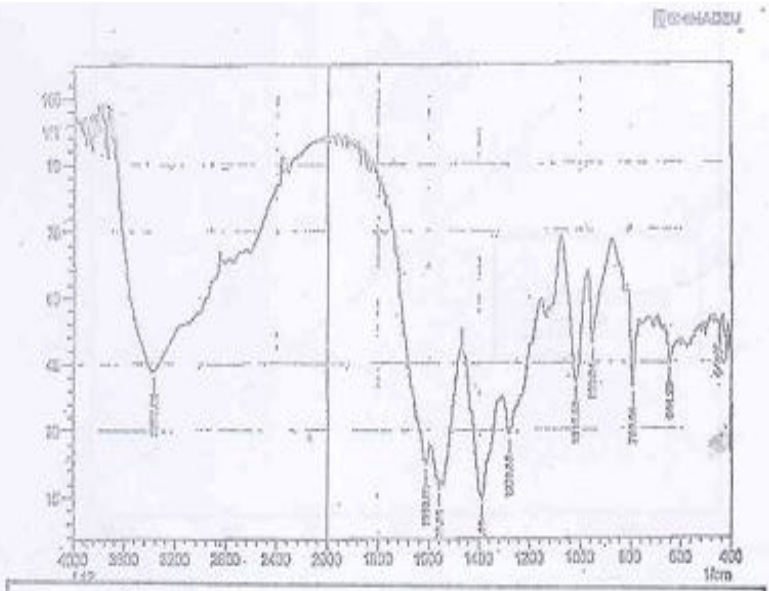


Figure (6) Chelate p- FTIR Spectrum of the polymer : hydroxybenzoic acid urea formaldehyde with Cd(II)

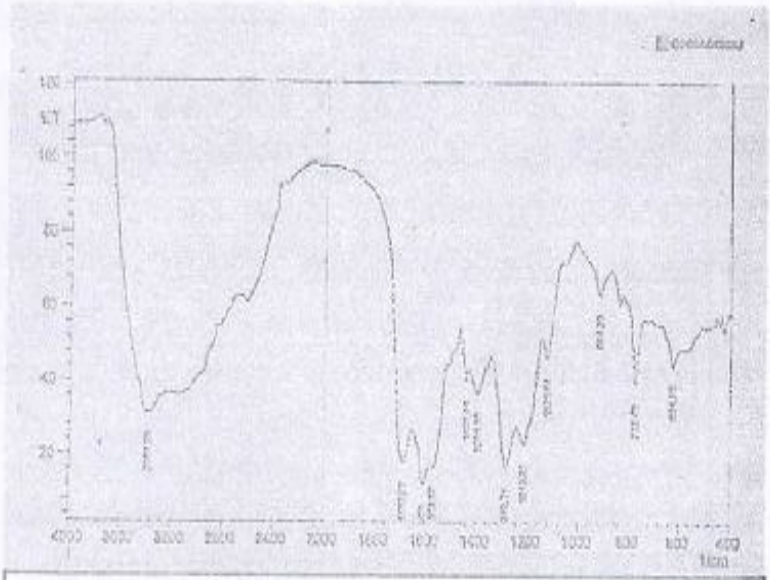


Figure (7) FTIR Spectrum of the polymer : copolymer p- hydroxybenzoic acid ureaformaldehyde

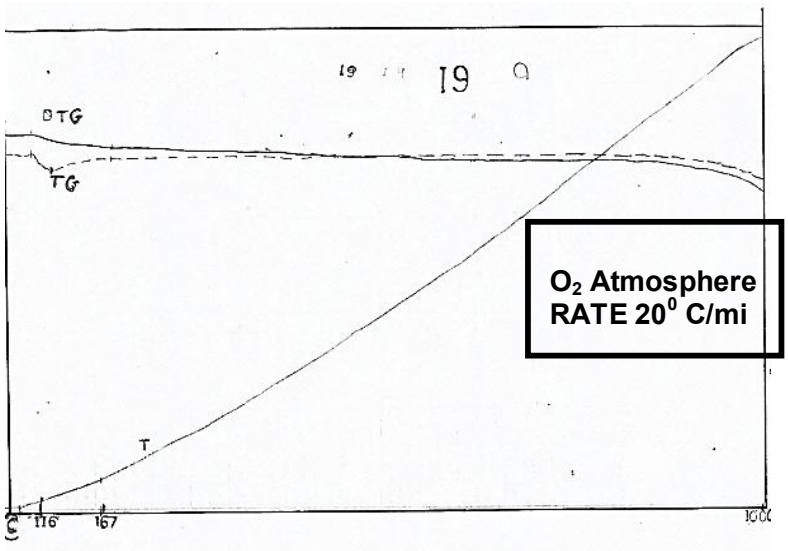


Figure **(8) Thermogravimetric analysis of the polymer : Chelate p- hydroxybenzoic acid ureaformaldehyde with Pb(II)**

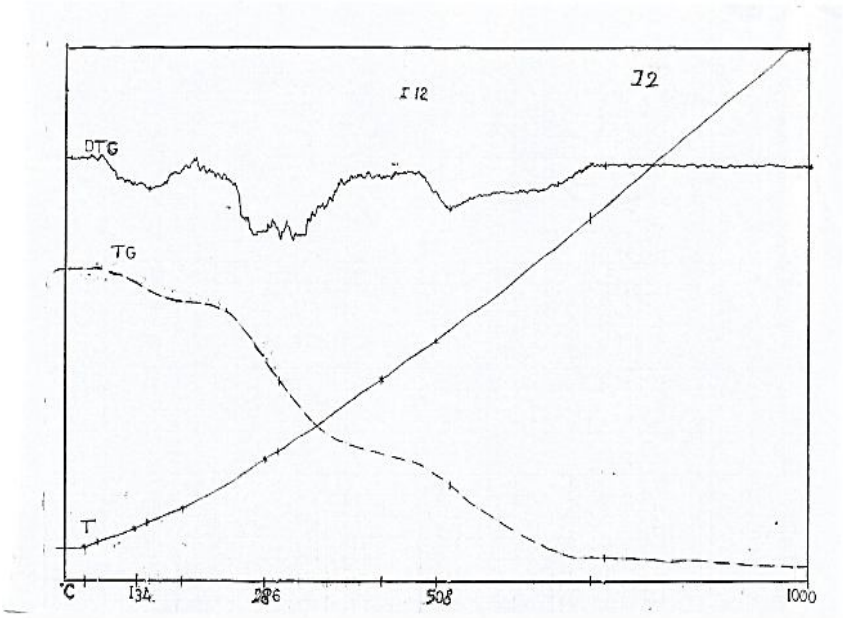


Figure **(9) Thermogravimetric analysis of the polymer : Chelate p- hydroxybenzoic acid ureaformaldehyde with Zn(II)**

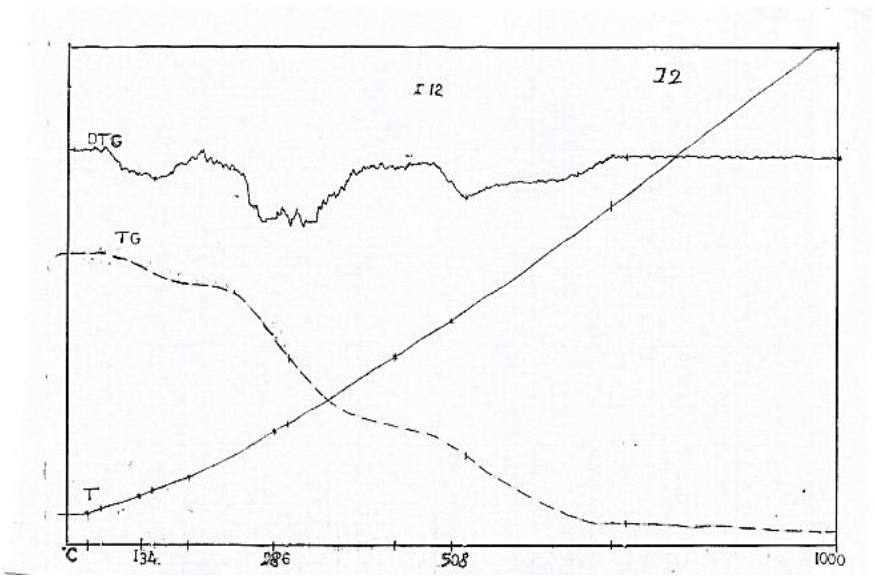


Figure **(10) Thermogravimetric analysis of the polymer : Chelate p- hydroxybenzoic acid ureaformaldehyde with Cd(II)**

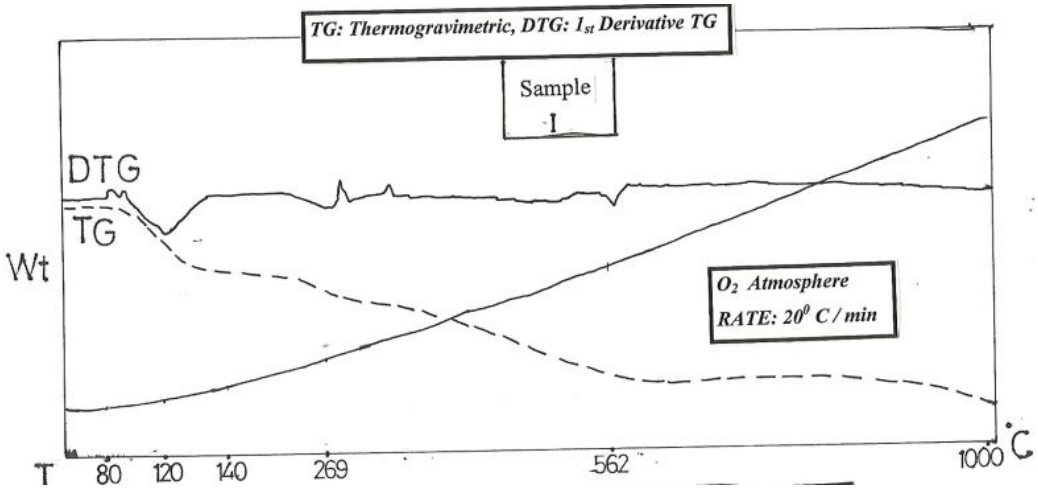


Figure **(11) Thermogravimetric analysis of the polymer : copolymer p- hydroxybenzoic acid ureaformaldehyde**