Open Access
Baghdad Science Journal **Vol. 13(2s(Supplement))2016**
The 2nd National Conference of Chemistry

DOI: http://dx.doi.org/10.21123/bsj.2016.13.2.2NCC.0172

Synthesis and Characterization of Some New Monemer and Polymers Containing Hetero Cyclic Rings With Study of Their Physical Properties.

Ibtisam K. Jassim* ***Iman M. M. Hassan*****

*Department of Chemistry, College of Education Ibn-Al-Haitham, University of Baghdad, Iraq.
**Department of Chemistry, College of Science for Women, University of Baghdad, Iraq.

Received 17/9/2015
Accepted 20/12/2015

Abstract:

Number of new polyester and polyamide are prepared as derivatives from 5,5`-(1,4-phenylene)-bis-(1,3,4-thiadiazole-2-amine) [C_1], three series of heterocyclic compounds were synthesized.The first series includes the Schiff base [C_2] prepared from the reaction between compound [C_1] with p-hydroxy benzaldehyde in presence of acetic acid and absolute ethanol , then these derivatives have reaction with maleic anhydride , phthalic anhydride and sodium azide, respectively to obtain the compounds [C_{3-5}] contaning (oxazepine and tetrazole) rings.The third series of compounds [C_{1-5}] has transformed to their polymers [C_{6-15}] by reaction with adipoyl chloride and glutroyl chloride , respectively. The reaction was followed by T.L.C and identified by FT-IR , ^{1}H-NMR ,C.H.N analysis , softening point , viscosity, TGA , DSC and X-ray.

Key words: Heterocyclic rings , 1,3,4-Thiadiazole derivatives , Thermal properties.

Introduction:

Numerous papers in literature describing the reactions of various compounds with polymers in order to change the properties of the polymers [1,2], often these reactions have resulted in significant change in such properties as flammability , solubility , thermal degradation and strength[2]. 5,5`-(1,4-phenylene)-bis-(1,3,4-thia- diazole-2-amine) consititute an important class of compounds having awide number of variously subsitituted 1,3,4-thiadiazole derivatives[3,4], the industerial application in view of these observations synthesis of series of derivatives of 1,3,4-thiadiazole with its polymers has been synthesized[5].

Materials and Methods:

All the chemicals used were supplied by (Merk, Fluka and BDH), the solvent was purified by distillation and dried with calcium chloride. Melting point was determined on Gallenkamp (melting point) apparatus and was uncorrected, softening point,FTIR spectra were

designated by (SHIMADZU) / FTIR 8300 spectrometer as KBr. disc, result were given in (cm^{-1}) , ^{1}H-NMR spectra were recorded at 200.13 and 50.32 MH_Z respectively in (DMSO-d_6) which were reported in part per million (ppm) down field from internal tetramethylsilane (TMS) (chemical shift in δ values)In Tahran university. Elemental analysis was run by using a perkin – Elmer RE2400 (C.H.N) analyzer, ^{1}H-NMR, TGA, DSC, X-Ray , viscosity and microbial study All analyses were performed in center service laboratory\college of Education for pure service–Ibn-Al-Haitham University of Baghdad.

Prepration of 5,5`-(1,4-phenyl -ene)-bis(1,3,4-thiadiazole-2-amine) [C_1]

A mixture of terephthaldehyde (0.01 mol), thiosemicarbazide (0.02 mol) and phosphorus oxy chloride (25 mL) was refluxed for (4 hrs),then cooled and added distulled water with continuing refluxing (1 hr) , sodium hydroxide added until mixture pH =8 , diluted with distlled water. The precipitate filtered , recrystallized from ethanol. Physical properties are listed inTable (1) and spectra data listed in Table (3).

Prepration of 4,4'-(((5,5'-(1,4-phenylene)-bis-(1,3,4-thiadiazole-5,2-diyl))-bis-(azanylylidene))-bis-(methanylylidene))diphenol [C_2]

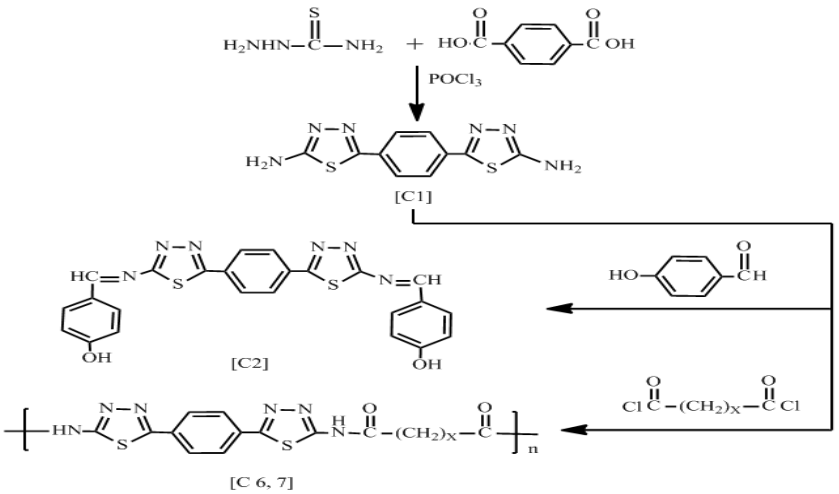
A mixture of compound [C_1] (0.033 mol), p-hydroxybenzaldehyde (0.066 mol), in absolute ethanol (25 mL) and (3-5) drops of glacial acetic acid , the mixture was refluxed for (1 hr). After the end of reaction (checked by TLC), cooling the precipitate then filtered it, collected then washed with cold ethanol and recrystallized from ethanol. Physical properties are listed in Table (1) and spectra data listed in Table**(3).**

Prepration of [3,3'-(5,5'-(1,4-phenylene)-bis-(1,3 ,4-thiadiazole-5,2diyl))bis-(2-(4-hydroxy phenyl)2,3-dihydro-1,3-oxazepine-4,7 -dione)] [C_3]; 4,4'-(5,5'-(1,4-phenylene)-bis-(1,3,4-thiadiazole-5,2-diyl))bis(3hydroxyphenyl)-3,4-dihydro benzo[e][1,3]oxazepine-1,5-dione) [C_4] and 4,4'-(1,1'-(5,5'-(1,4-phenylene)-bis-(1,3,4-thiadiazole-5,2-diyl))-bis-(4,5-dihydro-1H-tetrazole-5,1-diyl))diphenol [C_5]

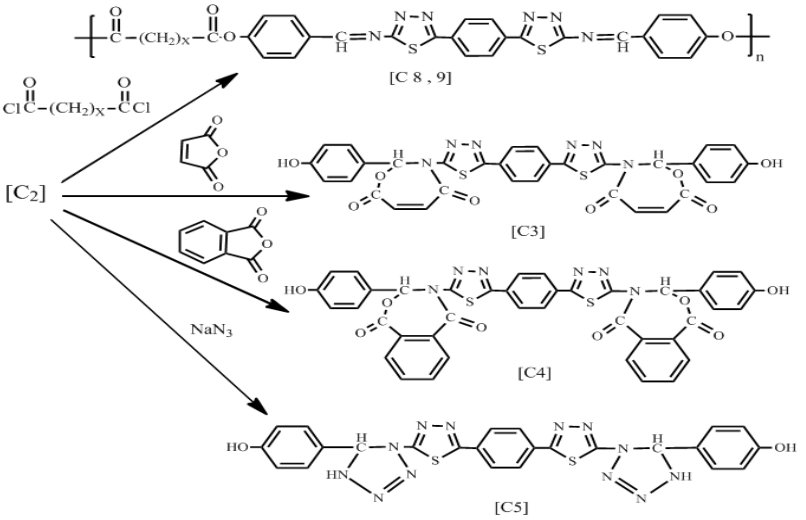
A mixture of [C_2] (0.01 mol) dissolved in dry benzene (20 mL) with malic anhydride (0.02 mol), phathalic anhydride (0.02 mol), sodium azide (0.02 mol) and dry THF (20 mL) were refluxed for (5 hrs) (checked by TLC). Excess solvent was distlled,filtered of and recrystallized from ethanol to obtain the compounds[C_{3-5}]. Physical properties are listed in Table (1) and spectra data listed in Table(3).

The polymerization of [C_1-C_5] compounds.

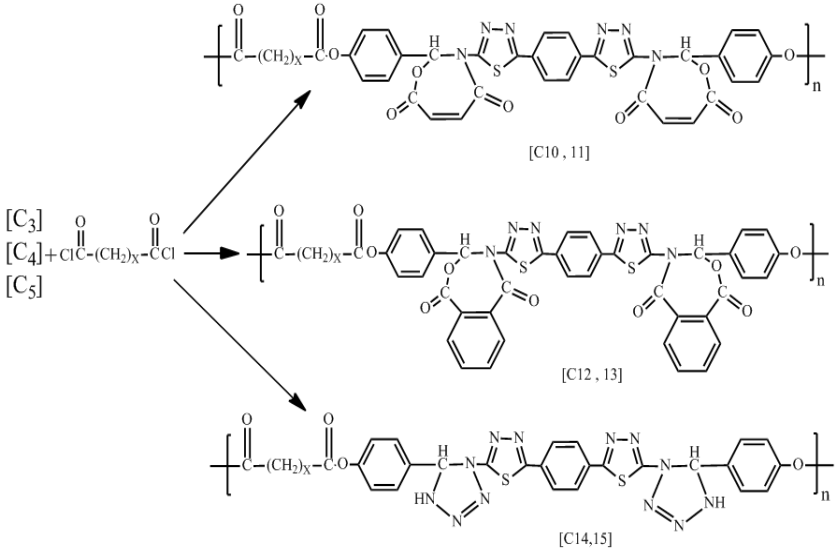
The polymerization of compounds [C_{1-5}] was carried out in dry pyridine by using adipoyl chloride, glutroyl chloriede respectively.The mixture was refluxed in water bath. After (6 hrs) (checked by TLC) , the contents of the flask were poured into ice distilled water to precipitate the polymers [C_{6-15}]. Physical properties are listed in Table (2) and spectra data listed in Table (3).



Step 1



Step 2



Step 3

Scheme (1) : Synthetic steps in this work (where X = 3,4).

Results and Discussion:

Some physical properties together with analytical and spectral data of the prepared compounds are summarized in Table (1,2 and 3). All prepared polymers were soluble in all common solvents such as Dimethylformamide, Dimethyl sulfoxide, Methyl chloride, Cyclohexane. The viscosity measurment of synthesized polymers was determined by using viscometer (type Ubbelohod viscometer) which was placed in water bath at 40ºC, Table 2 .

Table (1) : Physical properties of the prepared compound [C1-5].

Comp.	Molecular formula	m.p (ºC)	Yield %	Solvent for recrystallization
C_1	$C_{10}H_8N_6S_2$	251-252	82	Ethanol
C_2	$C_{24}H_{16}N_6S_2O_2$	257-259	82	Ethanol
C_3	$C_{32}H_{20}N_6S_2O_8$	263-265	70	Ethanol
C_4	$C_{40}H_{24}N_6S_2O_8$	249-251	70	Ethanol
C_5	$C_{24}H_{17}N_{12}S_2O_2$	243-245	75	Ethanol

Table (2): Physical properties of the prepared polymers [C6-15].

Comp.	S.P (ºC)	ηinh gm/IL	Comp.	S.P (ºC)	ηinh gm/IL
C_6	225-235	2.20	C_{11}	> 300	0.21
C_7	223-233	2.14	C_{12}	> 300	1.35
C_8	250-260	0.25	C_{13}	> 300	1.25
C_9	249-259	0.23	C_{14}	> 300	1.50
C_{10}	> 300	0.25	C_{15}	279-289	1.48

Table (3) : IR,^{1}HNMR Spectra and C.H.N.S analysis of compounds [C1-5].

Comp. No.	Major absorption cm^{-1}				^{1}HNMR Spectrum	% Elemental analysis Calc. (Found)			
	ν NH_2	ν OH	ν C=O	ν C=N		C	*H*	*N*	*S*
C_1	3471	-----	-----	1598	---------	43.48 (44.20)	2.90 (3.18)	30.44 (31.60)	23.19 (24.25)
C_2	-----	3489	1728	1681	Single δ= (10.3-10.5) ppm for (H-OH) and δ= (7.8-8) ppm for aromatic ring	59.50 (60.20)	3.31 (4.10)	17.36 (18.20)	13.22 (14.10)
C_3	-----	3474	1728	-----	---------	56.47 (57.10)	2.94 (3.10)	12.35 (13.00)	9.41 (10.20)
C_4	-----	3420	1735	-----	---------	61.54 (62.10)	3.08 (4.00)	10.77 (11.12)	8.21 (9.00)
C_5	-----	3390	1712	-----	Single δ= (10-10.8) ppm for (H-OH) , δ= (12.9) ppm for (N=N) , δ= (7.2-7.8) ppm for aromatic ring , δ= (8.2-8.5) ppm for tetrazole and δ= (10.04) ppm for (1H , NH)	50.62 (51.00)	2.99 (3.30)	29.53 (30.80)	11.25 (12.07)

FT-IR Spectra:

The FT-IR spectrum of compound [C_1] exhibited significant two bands in the region (3471 cm^{-1})[6] which attributed to the stretching vibration bands of NH_2 group beside this a band at about (1598 cm^{-1}) due to streching vibration band of cyclic imine group C=N [7,8]. The FT-IR spectrum of compound [C_2] by disappearance of νNH_2 absorption band combined with appearing of νOH absorption band at (3470 cm^{-1}) [6], also absorption band appeared at (1681 cm^{-1})[8] due to νC=N of schiff base. FT-IR spectra show a clear strong absorption band indicating ester formation at (1750-1765) cm^{-1} and (1180-1199) cm^{-1} for νC=O and C-O group respectively due to polyester [9]. Also clear absorbition band for νN-H of amide at aboute (3196-3220) cm^{-1} νC=O of amide at (1712-1735) cm^{-1} [7], as shown in Figures (1-5).

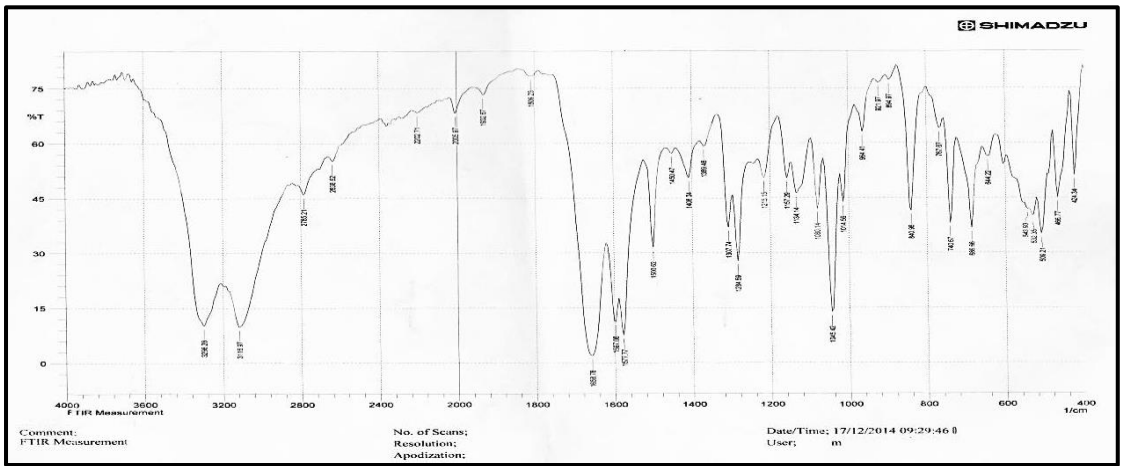


Fig.(1) : FT-IR of [C_1].

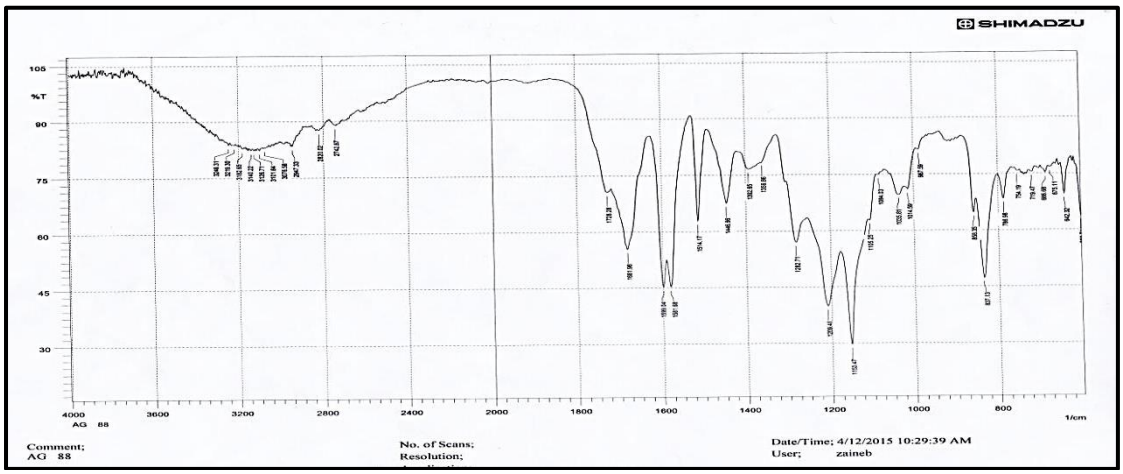


Fig.(2) : FT-IR of [C_2].

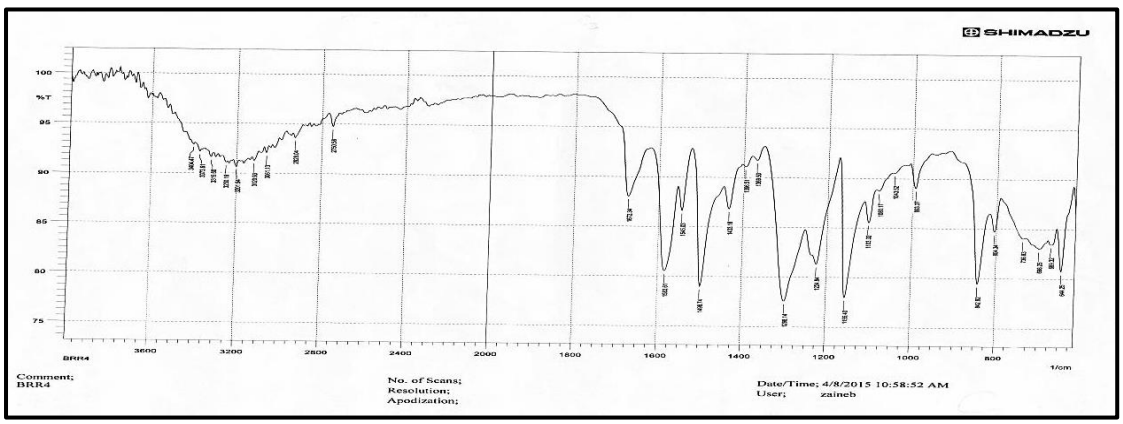


Fig.(3) : FT-IR of [C_3].

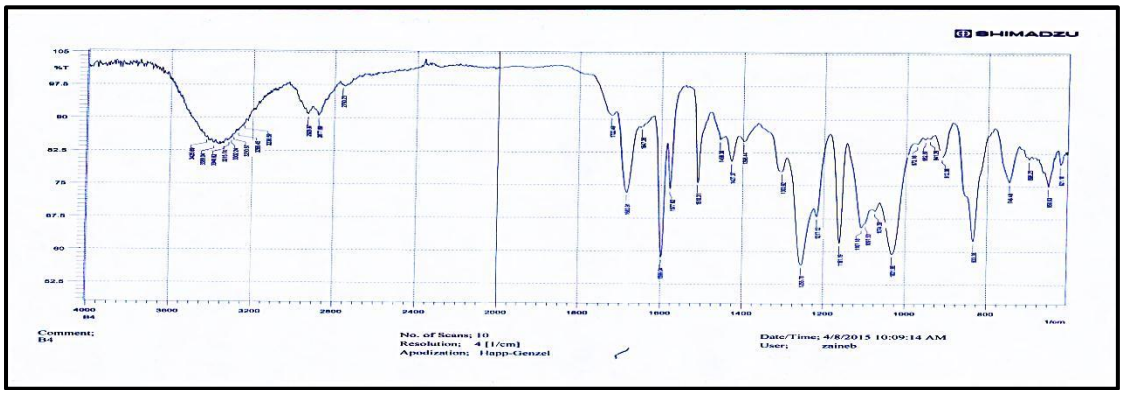


Fig.(4) : FT-IR of [C_4].

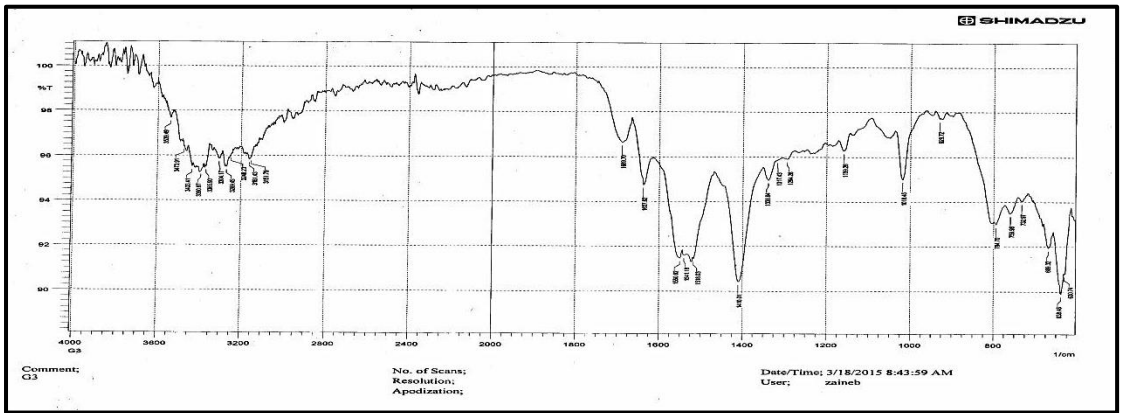


Fig.(5) : FT-IR of [C_5].

^{1}HNMR Spectra:

^{1}HNMR spectrum for [C_2] , Figure (6), shows a singlet at δ= (10.3-10.5) ppm for (H-OH) and δ= (7.8-8) ppm for aromatic ring, while ^{1}HNMR spectrum for [C_5] Figure (7), shows a singlet at δ= (10-10.8) ppm for (H-OH) , δ= (12.9) ppm for (N=N) , δ= (7.2-7.8) ppm for aromatic ring , δ= (8.2-8.5) ppm for tetrazole and δ= (10.04) ppm for (1H , NH).

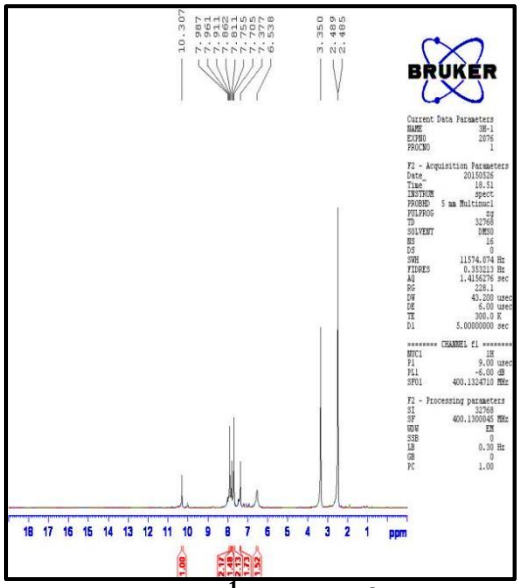


Fig.(6) : ^{1}HNMR of [C_2].

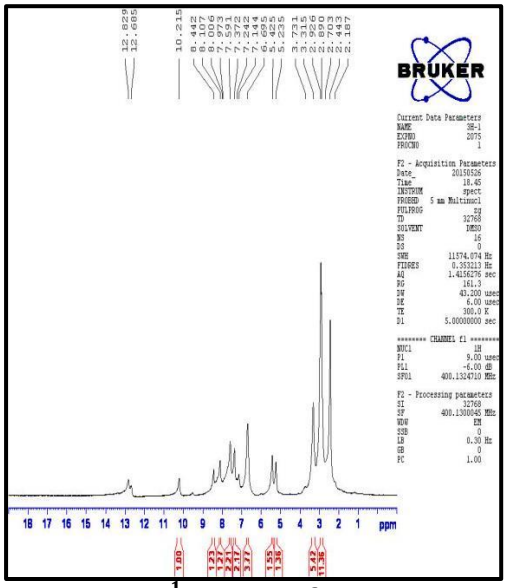


Fig.(7) : ^{1}HNMR of [C_5].

Thermal stability:

Thermal stability of the prepared polyester , polyamide was investigated by thermogravimetric analysis (TGA and DSC).The data showed that the weight of polymer [C_6] fell slightly at temperature (127-423)ºC , while weight of polymer [$C_{8,12}$] fell slightly at range of temperature (157-513)ºC and (171-374)ºC respectively. Also thermal analysis data showed that the prepared polymers have good thermal stability thus temperature of (10%) weight loss of polymers [C6,8,12], while the major weight loss of these polymer occurred at (577)ºC ,(638)ºC and (550)ºC respectively, as in Figures (8-10).

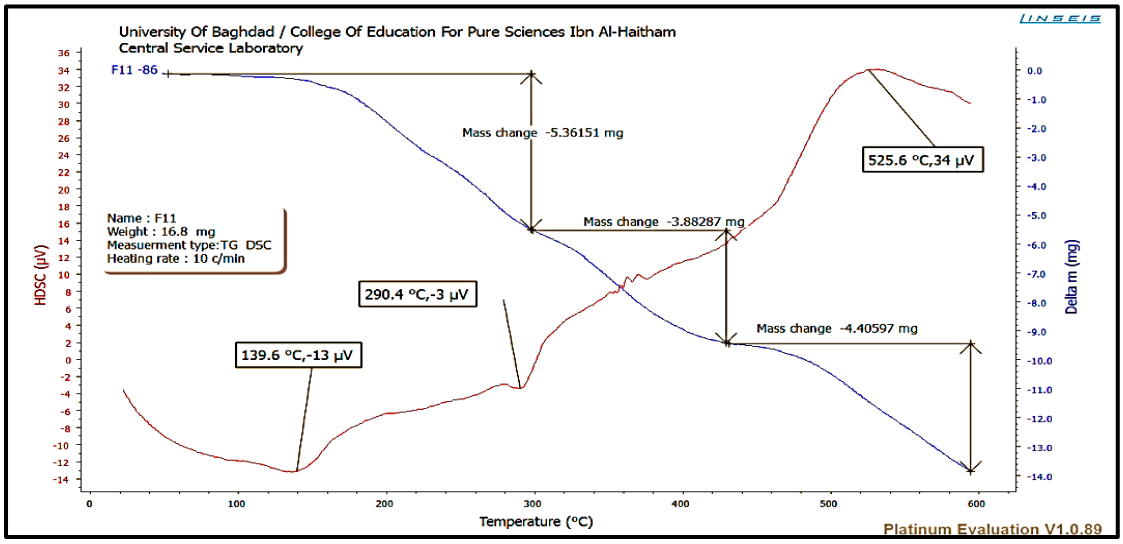


Fig.(8) : TGA and DSC of [C_6].

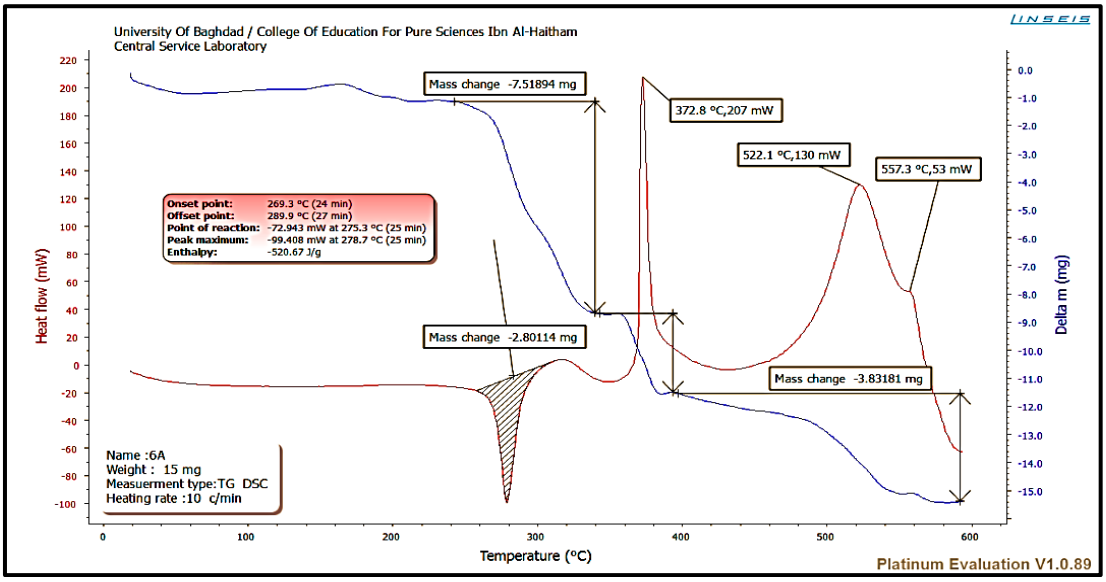


Fig.(9) : TGA and DSC of [C_8].

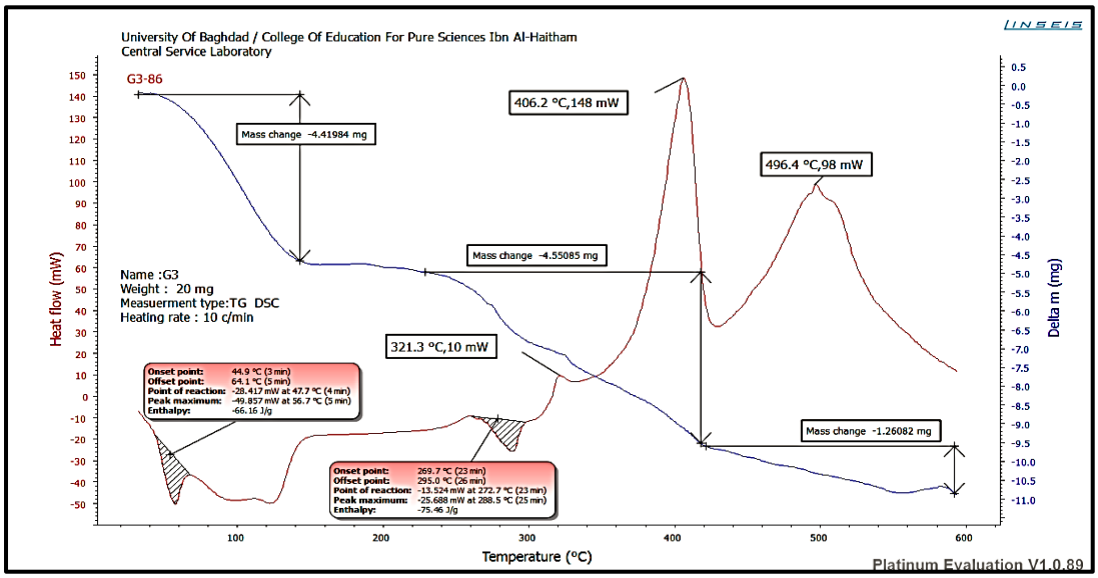


Fig.(10) : TGA and DSC of [C_{12}].

X-Ray diffraction:

X-ray diffraction is used to identify the nature of the polymer weather crystalline or amorphous. All the prepeared polymers [C_{6-15}] are crystalline, as in Figer(11).

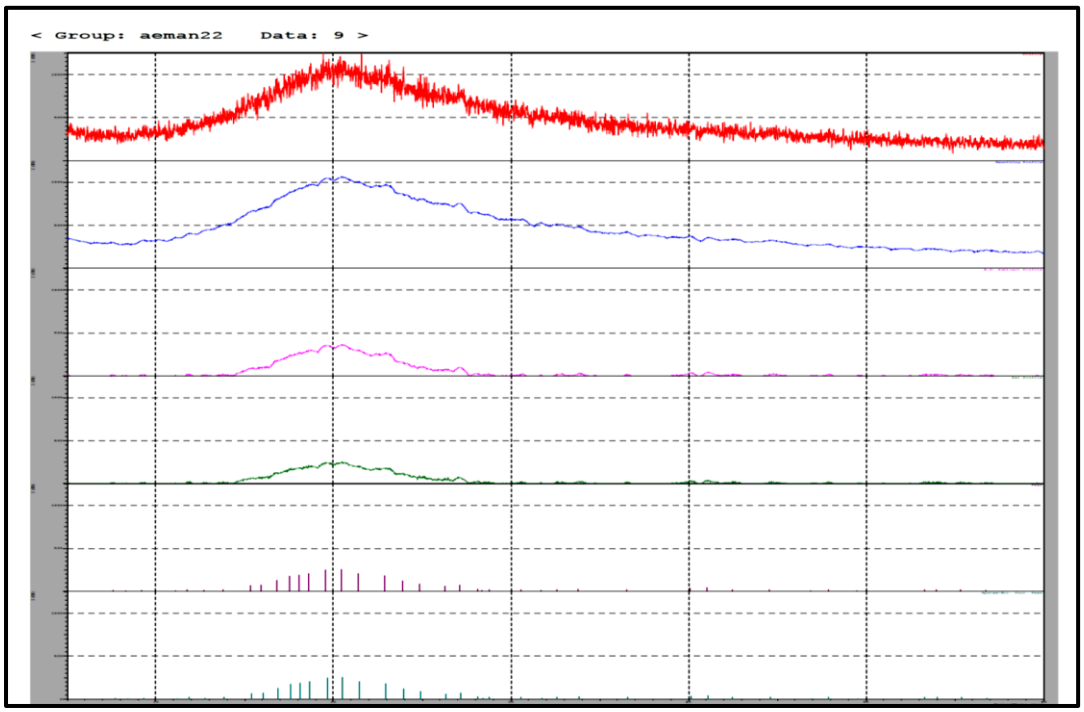


Fig.(11) : X-ray diffraction of polymers [C_{6-15}]

References:

[1] Benjamin, D. F. , Pathiraja ,A. G.and, Laurence, M. 2015. Biomedical applications of polymers derived by reversible addition – fragmentation chain-transfer (RAFT). Adv. Drug Deliv. Rev. :1-12. http://dx.doi.org/10.1016/j.addr.2015.05.016.

[2] Charles , G. G. and Keith , E. B. 2009. Biologically Active Modification of Poly vinyl Alcohol : The Reaction of Phenyl Isocyanate with

Polyvinyl Alcohol.121, Chapter 7 : 83–102. ACS Publication.

[3] Al-Kaddimy H. A. 2006 ,Synthesis and characterization of benzylidene-[1,3,4] thaidiazol- 2-yl-amine. AJPS, 3(1):32-39.

[4] Mustafa,M,M.,Alaa,H., Jawad,J, J. and Shneine,M, K. 2012 .Synthesis, characterization and evaluation of biological activity of new heterocyclic compounds containing 1,2,4- triazole and 1,3,4-thiadiazole rings. IJASTNET. 2(10):155-164.

[5] Bayram, G;Nevin ,T. and Esin, K; 2014.Synthesis, characterization, surface morphology properties and effects of annealing temperature on optical properties of poly(2-(((5-phenyl -1,3,4-thiadiazole-2-yl)imino) methyl) phenyl methacrylate) (PTMPMA). Polym. Bull. 71:2945–2961.

[6] Sayyah, M. and Mohamed, S. M. 2015.Preparation kinetics and characterization of poly o-hydroxy aniline in aqueous hydrochloric acid solution using $K_2Cr_2O_7$ as oxidizing agent. OSR-JAC. 8(2) : 28-43.

[7Mohamed, M, J; Jassem, I, K, and Muhanned ,A ,2013, Synthesis and Characterization of Five, Sevene Heterocyclic Membered Rings . J. Baghdad for Sci. 10(3) : 803-817.

[8] Nagham, M., Rasmey, J and Ali, F. 2014. Chemical Properties and Bioactive Study of (Benzanil and Oxazepam) Derivatives. Acta. Pharmica. ,1(1):8-15.

[9] Radhakrishnan,S, Akbary, I., Ahmady, A and Joseph, S. 2011. Synthesis and antimicrobial activity of a new series of 1,4 -dihydropyridine derivatives. J. Serb. Chem. Soc. 76(1):1–11.

تحضير و تشخيص بعض المونيمرات و البوليمرات الجديده الحاوية على حلقات غير متجانسة مع دراسة الخصائص الفيزيائية

أبتسام خليفة جاسم * **أيمان مهدي محمد حسن ****

* قسم الكيمياء، كلية التربية ابن الهيثم، جامعة بغداد، العراق .

**قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، العراق.

الخلاصة :

تم تحضير عدد من مركبات البولي استر و البولي امايد جديده ابتداءأ من المركب 5,5´ (4,1- ثنائي فنيلين) –(4،3،1- ثيادايازول-2-امين) [1] و بمفاعلته مع بارا-هايدروكسي بينزالديهايد لتكوين قاعدة شيف [2] و مفاعلتها مع انهدريد المالئيك و الفثاليك و ازيد الصوديوم لتكوين المركبات [3-5]في الخطوه الثالثه ومن ثم بلمرة المركبات المحضرة [1-5]مع كلوريد الاديبويك و كلوريد الكلوترويك على التوالي باستخدام البريدين الجاف لتكوين البوليمرات [6-15] و قد شخصت هذه المركبات المحضرة باستخدام طيف الاشعة تحت الحمراء وطيف الرنين المغناطيسي ^{1}HNMR و التحليل الدقيق للعناصر C.H.N. مع قياس الخصائص الحرارية TGA و DSC و قياس درجة التبلور بواسطة X-Ray و درجة الليونه و اللزوجة .

الكلمات المفتاحية:حلقات غير متجانسة-1,3,4,مشتقات الثاياديازول,الخصائص الفيزيائية.