



## Synthesis, Characterization with Studying Physical Properties by Free Radical Polymerization of Some New Resins Starting from 5-Styryl-1, 3, 4-Thiadiazol-2-amine

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### Abstract

Starting from 5-styryl-1,3,4-thiadiazol-2-amine[1], a variety of Schiff bases [2-6] prepared, Schiff base derivatives which containing heterocyclic rings have been synthesized [7-11] as monomers. Then addition reaction (free radical polymerization) for monomers by using AIBN as initiator in (50-70) °C obtaining [12-16] resins. All proposed structure were supported by FTIR, solubility, softening points, and some derivatives evaluated by <sup>1</sup>H-NMR, Elemental analysis, thermal analysis (TGA, DSC), X-Ray diffraction.

**Keywords:** Schiff bases, Derivatives with heterocyclic rings as monomers.

### Introduction

The development of simple Synthetic routes to widely used organic compound using readily available reagent is one of the main objectives of organic Synthesis. The use of Schiff bases covered wide area applications, in industry and biological field [1]. In industrial application Schiff base derivatives were used as a rubber accelerators [2], antioxidants [3] and corrosion inhibitors [2].

They have wide industrial applications as photo stabilizers for polyethylene. In analytical chemistry Schiff bases were used for uptake of metal ions [4], and the resins of some compounds are used in the accurate determination of trace elements in dilute solution, which is often hindered due to the sensitivity limits of the equipment used for the purpose [5], in this study number of new resins were synthesis by free radical polymerization using AIBN as initiator in (50-70) °C.

### Materials and Methods

#### General

Melting points were determined on Gallenkamp, melting point apparatus and were uncorrected. FTIR spectra of the compounds were recorded on a (SHIMADZU) FTIR. 8300 Spectrometer as KBR-disc, <sup>1</sup>H - NMR, spectra

were recorded at 200.13-50.32 MHz, respectively using tetra methyl Silane (TMS) as an internal standard, (DMSO) as a solvent. Elemental analyses were run using a perkin-Elmer RE 2400 (C.H.N) analyzer, thermal stability TGA & DSC. All analysis was performed in University of Baghdad/ College of Education for Pure Sciences Ibn-Al-Haitham Central Service Laboratory.

#### Materials

All the chemical used were supplied by (Merk, Fluka and BDH) chemicals, the solvents purified by distillation and dried with calcium chloride.

#### Measurement and Techniques

The purity of products were investigated by (T.L.C) technique by using a mixture of benzene- ethanol (5:5 v/v) as elute and iodine chamber for spot location.

#### Differential Scanning Calorimetry and Thermal Gravimetric Analysis

Differential Scanning Calorimetry (DSC) and Thermal gravimetric analysis (TGA) was carried out using LINSEIS (DSC), equipped with an internal cooler 2P-cooling accessory, and some of them were performed in Chemistry department, College of Education

for Pure Sciences \ Ibn AL-Haitham [The Central Service Laboratory].

### X-Ray Diffraction Analysis

Investigated crystalline resins were evaluated by using (X-Ray diffraction analysis) using X-Ray Diffract meter Siemens SRS D 500 equipped with Copper( $\lambda = 1.54 \text{ \AA}$ ) Ascan rat of  $4\theta/\text{min}$  over the rang of (1-60) ( $2\theta$ ) was used for detecting the characteristic diffraction peaks of the synthesis resins in the pure state.

### Softening Point Instrument

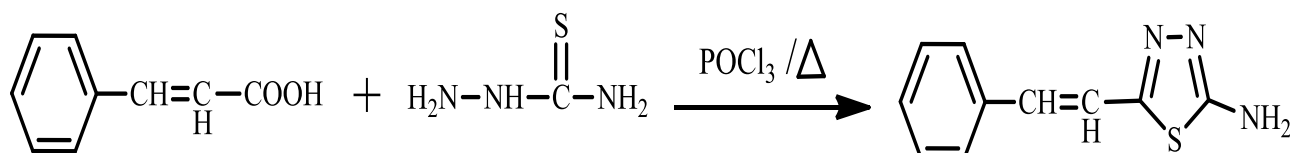
Softening point/ REICHERI THERMOVER/ OREICHERT-Jung was recorded in University of Bagdad, College of Science, and Department of Chemistry.

### Synthesis 5-styryl-1, 3, 4-thiadiazol-amine [1][7]

Mixture (0.01 mol) of  $\alpha$ -phenyl acrylic acid with (0.01mol) thiosemicarbazide in (10ml) of  $\text{POCl}_3$  was Refluxed 4hrs,the excess of  $\text{POCl}_3$  removed and the residue dissolved in distilled water (50ml) then heated for 1hrs.Then the resulting product cooled, filtered and neutralized with KOH. The precipitate was filtered, dried and re-crystallized in ethanol. (m.p 238 – 240 oC) solid, violet.

### Synthesis of Schiff bases [C<sub>2</sub>-C<sub>6</sub>] (6)

Schiff bases [C<sub>2</sub>-C<sub>6</sub>] were prepared by well estabale procedure in the literature[8], condensing (0.01mol) compound [1] with (0.01mol) corresponding substituted different aldehydes and ketons in acetic acid, The mixture was refluxed for (30min), the products were separated by filtration .the physical properties were listed Table



[C<sub>1</sub>]

Scheme-1: synthesis of[C<sub>1</sub>]

The FTIR spectrum [10] [1] showed the strong stretching ( $3302\text{cm}^{-1}$ ) due to ( $\text{NH}_2$ ) groups, ( $2931\text{-}2858\text{cm}^{-1}$ ) for ( $\text{CH}_2$ ), ( $1658\text{cm}^{-1}$ ) for (C=N) in thiadiazol ring, (  $1260\text{-}1045\text{cm}^{-1}$ ) for (c-o-c), ( $830\text{cm}^{-1}$ ) for (1,4-disubst), ( $3090\text{cm}^{-1}$ ) for (Ar-H), ( $1340\text{cm}^{-1}$ ); for (C-N);  $^1\text{H-NMR}^{(10)}$  (DMSO-d<sub>6</sub>)  $\delta$ : (6.6-7.8)ppm due to (Ar-H), (9.5)ppm due to (2H,NH<sub>2</sub>), (1.42-

(1)investigated by T.L.C (m.p 212 – 214 C<sup>o</sup>) solid, red, for [C<sub>3</sub>] m.p (204-206) C<sup>o</sup> yield (80), [C<sub>4</sub>] m.p (217-219), yield (75),[C<sub>5</sub>] m.p (221-223),yield (75),[C<sub>6</sub>] m .p (209-211) ,yield(70) ..

### Synthesis of Schiff base derivatives containing heterocyclic ring as monomer [C<sub>7</sub>-C<sub>11</sub>] [8]

A250ml necks mixture of (0.04mol) [C<sub>7</sub>-C<sub>11</sub>], thio acetic acid (0.04mol) in dry benzene(30 ml) was refluxe for(10 hrs , checked by T.L.C), the solvent was removed then was boiling with absolute ethanol(15ml), precipitate collected by filtration, then washed with ethanol to obtain brown precipitate, m .p ( 180-182 )C<sup>o</sup>.yield( 70 )% for [C<sub>7</sub>],m .p ( 174-176 )C<sup>o</sup>.yield(65 )% for[C<sub>8</sub>],m. p(171-173 )C<sup>o</sup>.yield( 60 )% for [C<sub>9</sub>],m .p (166-168 )C<sup>o</sup>.yield(65 )% for[C<sub>10</sub>], and m .p (163-165 ) [C<sub>11</sub>].yield(60 )% respectively.

### Synthesis of resins [C<sub>12</sub>-C<sub>16</sub>] [9]

The polymerization of these monomers was carried out in THF by using AIBN as initiator .A solution of the monomers (2.5 g m ) in THF(15ml) and (5mg) of initiator were mixed in round bottle . The mixture was heat in oil bath (50-70) C<sup>o</sup> .After (2hrs). The contents in flask were poured into large amount of (methanol- water) to precipitate the resins and evaporated under vacuumed, purity by T.L.C see Table (1).

### Results and Discussion

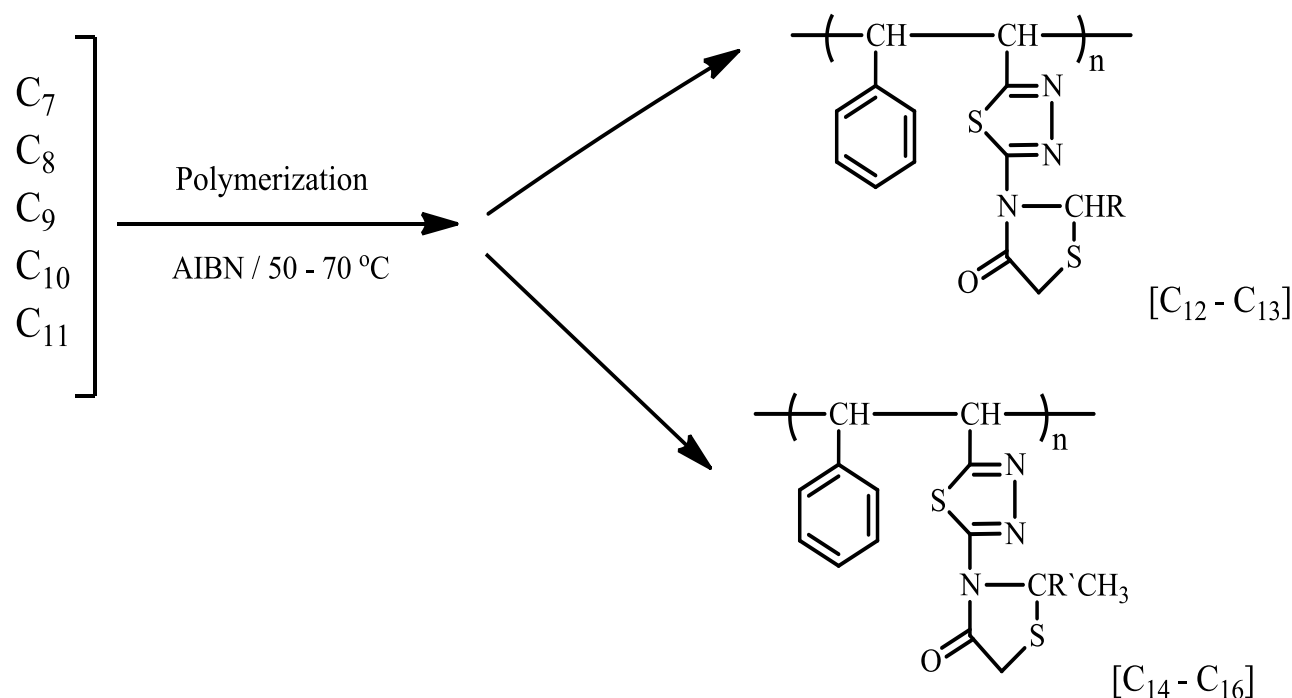
Considerable interest have been expressed in synthesis of schiff bases in recent year due to their industrial and biological importance, starting from (5-styryl-1, 3, 4-thiadiazol-2-amine) [1].

2.81)ppm for (2H,CH<sub>2</sub>); Elemental analysis (C.H.N) for compound [1] were fitted according to the (Table 3) . Therefore Schiff base [C<sub>2</sub>-C<sub>6</sub>] prepared by the condensation of the corresponding compound [1] with substituted aromatic aldehyde and ketone in refluxing ethanol.



Compound [9] indicated in FTIR spectrum of stretching vibration is more broad bands for (OH)vibration(3406-3369) $\text{cm}^{-1}$ , bands at (2958-2877) $\text{cm}^{-1}$  for (CH<sub>2</sub>) and strong vibration at (1226-1168)  $\text{cm}^{-1}$  for (C-O-), (3076)  $\text{cm}^{-1}$  for (=CH), (1689)  $\text{cm}^{-1}$  for (C=N) and (1585) $\text{cm}^{-1}$  for (C=C); <sup>1</sup>H-NMR( DMSO-

d6)  $\delta$ : (7.03)ppm due to (Ar-H), (2.4-3.5)ppm for(H,CH<sub>2</sub> ), Elemental analysis for compound[9] were fitted according to the ( Table 3). Similarly reacts compounds [C<sub>7</sub>-C<sub>11</sub>] with AIBN initiator afforded [C<sub>12</sub>-C<sub>16</sub>] derivatives respectively.



Scheme-4: Synthesis of [C<sub>12</sub>-C<sub>16</sub>]

The FTIR spectrum of compound [14] stretching vibration of (OH) at (33373-3306)  $\text{cm}^{-1}$ , (=CH) at (3009), (CH<sub>2</sub>) at (2926-2854)  $\text{cm}^{-1}$ , amide carbonyl group(C=O) at (1735)  $\text{cm}^{-1}$  and (C=C) at (1627-1514)  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>)  $\delta$ : (6.8-8.9)ppm due to (Ar-H), (9.09-9.7) due to (H,OH), (2.1-2.4)ppm for (2H,CH<sub>2</sub>). Elemental analyses for compounds [14] were fitted according to the (Table 3).

All these steps were summarized in schemes (1-4) physical properties of all mentioned and other details [FTIR, Elemental analysis, TGA & DSC analysis, <sup>1</sup>H-NMR , data are listed in Tables (1-7) respectively, curing thermal stability of some compounds were evaluated by using (TGA &DSC) Table (5) are clearly show the temperature rate belong to different type dissociated for derivatives, Fig(11-14) .

Table 1: Dapcited physical properties for [1-16] compounds

No	Molecular formula	M.P C <sup>0</sup>	Colour	Yield %	Purification solvent	Comp No	Molecular formula	M.P C <sup>0</sup>	Colour	Yield %	Purification solvent
1	C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> S	238-240	Pale violate	90	Ethanol	9	C <sub>20</sub> H <sub>19</sub> N <sub>3</sub> S <sub>2</sub> O <sub>3</sub>	171-173	Brown	60	THF
2	C <sub>16</sub> H <sub>8</sub> N <sub>3</sub> SBr	212-214	Deep Red	87	Ethanol	10	C <sub>18</sub> H <sub>14</sub> N <sub>3</sub> S <sub>3</sub> O <sub>3</sub> Br	166-168	Brown	65	THF
3	C <sub>19</sub> H <sub>10</sub> N <sub>3</sub> S	204-206	Brown	80	THF	11	C <sub>19</sub> H <sub>13</sub> N <sub>4</sub> S <sub>2</sub> O <sub>3</sub> Br	163-165	Brown	60	THF
4	C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> S	217-219	Brown	75	THF	12	C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> S <sub>2</sub> O <sub>2</sub>	oily	Brown	70	Methanol
5	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> S <sub>2</sub> Br	221-223	Brown	75	THF	13	C <sub>20</sub> H <sub>15</sub> S <sub>2</sub> N <sub>3</sub> O <sub>3</sub>	oily	Brown	72	Methanol
6	C <sub>17</sub> H <sub>13</sub> N <sub>4</sub> Br	209-211	Brown	70	THF	14	C <sub>20</sub> H <sub>17</sub> S <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	oily	Brown	65	Methanol
7	C <sub>17</sub> H <sub>12</sub> N <sub>3</sub> S <sub>2</sub> O <sub>2</sub>	180-182	Brown	70	THF	15	C <sub>19</sub> H <sub>14</sub> S <sub>3</sub> N <sub>3</sub> O <sub>3</sub> Br	oily	Brown	65	Methanol
8	C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> S <sub>2</sub> O <sub>3</sub>	174-176	Brown	65	THF	16	C <sub>19</sub> H <sub>15</sub> S <sub>2</sub> N <sub>4</sub> O <sub>3</sub> Br	oily	Brown	65	Methanol

**Table 2: FTIR spectral data of [1-16]**

No	VNH <sub>2</sub>	VCH <sub>2</sub>	VC-O-C	V=CH	Others	No	VOH	VCH <sub>2</sub>	VC-O-C	V=CH	Others
1	3302	2931 2858	1260 1045	3090	NH(3190),C-S(666),C=N(1658) in thiadizol ring ,C=C(1597) VC-N(1338)	9	3406-3369	2958-2877	1201 1205	3076	C=O(1761-1716), C=C(1610-1595), C-S(671)
2	-	2900 -2800	1200 1212	3091-3028	VC=N(1687-1670), VC=C(1583), C-Br(761)	10	-	2910 2875	1240 1210	3020	C=O(1745),C=C(1556),C-S(698)
3	-	2954 2896	1192 1100	3019	VC=N(1686)) VC=C(1587),	11	-	2935 2870	1235 1228	3009	C=O(1753),C=C(1601-1596),C-S(675)
4	-	2974	1226 1168	3055	VC=N(1689),OH(3471) VC=C(1585)	12	-	2900 2865	1268 1238	3068	C=O(1765),C=C(1596),C-S(689)
5	-	2985 2980	1218 1210	3044-3056	VC=N(1615) VC=C(1600-1591),C-Br(782)	13	-	2910 2845	1250 1255	3056	C=O(1711-1709),C=C(1601-1594),C-S(621)
6	-	2972 2968	1220 1214	3067-3078	VC=N(1612) VC=C(1578-1589)	14	3373-3306	2926-2854	1260 1265	3009	C=O(1735),C=C(1627-1514),C-S(686)
7	-	2945-2838	1265-1212	3026-3067	VC=N(1603-1623),VC=C(1565),	15	-	2956-2823	1254-1222	3045	C=O(1712-1734),C=C(1600-1587),C-S(621-619)
8	-	2966-2834	1240-1245	3058-3059	VC=N(1649-1641),VC=C(1600-1589)	16	-	2954-2892	1283-1289	3071	C=O(1725), C=C(1598), C-S(659)

**Table 3: Depacited Elemental analysis (C.H.N. S) for some compounds**

Comp. No	% C(found)	%H(found)	%N(found)	%S(found)
1	59.41 (61.11)	3.96 (4.15)	20.79 (21.43)	15.84 (16.14)
2	51.61 (52.21)	2.69 (2.97)	11.29 (12.45)	8.60 (9.44)
4	68.12(69.11)	3.47(4.46)	13.25(14.21)	10.09(11.09)
8	56.1(57.09)	3.74(4.44)	9.81(10.02)	14.9(15.85)
11	49.67(50.67)	3.92(4.91)	12.20(13.10)	13.94(14.85)
15	54.11(55.09)	3.50(4.50)	10.5(11.45)	8.00(9.00)

**Table 4: Depacited<sup>1</sup> H-NMR spectrum data for some compounds**

No. comp	<sup>1</sup> H-NMR/ppm	No. Comp	<sup>1</sup> H-NMR/ppm
1	δ:3.9-4.4 for(H,CH <sub>2</sub> ),6.6-7.8(Ar-H),9.5(H,NH)	9	δ:(2.4-3.5)for (H,CH <sub>2</sub> ), 7.03 (Ar-H)
4	δ:(2.4-3.4)for(H,CH <sub>2</sub> ), 7.4-7.9(Ar-H) , 10.3(H,OH)	15	δ:(2.1-2.4)for(H,CH <sub>2</sub> ), ( 6.8-8.9) (Ar-H), (9.09-9.7) for(H,OH)

**Table 5: Thermal behavior data for synthesized Resins [C<sub>13</sub>-C<sub>16</sub>]**

Comp. No	On set point C <sup>o</sup>	T <sub>g</sub>	Off set point C <sup>o</sup>	Char%
13	44.9	47.7	64.1	80%
14	414.6	415.5	426.7	87%
15	53.5, 131.5,323.2	54.6, 133.3, 328.3	72.3,142.7, 334.2	87%
16	100 ,112.5	101.7	108.5-124.1	88%

\*On set point temperature recorded by (TGA &DSC).

\*The midpoint temperature of base line shift on the subsequent (TGA&DSC) trace (as heating rate 10 C<sup>o</sup>/min) was defined as.

\*Residual weight percentage at (600) C<sup>o</sup> under Nitrogen flow.

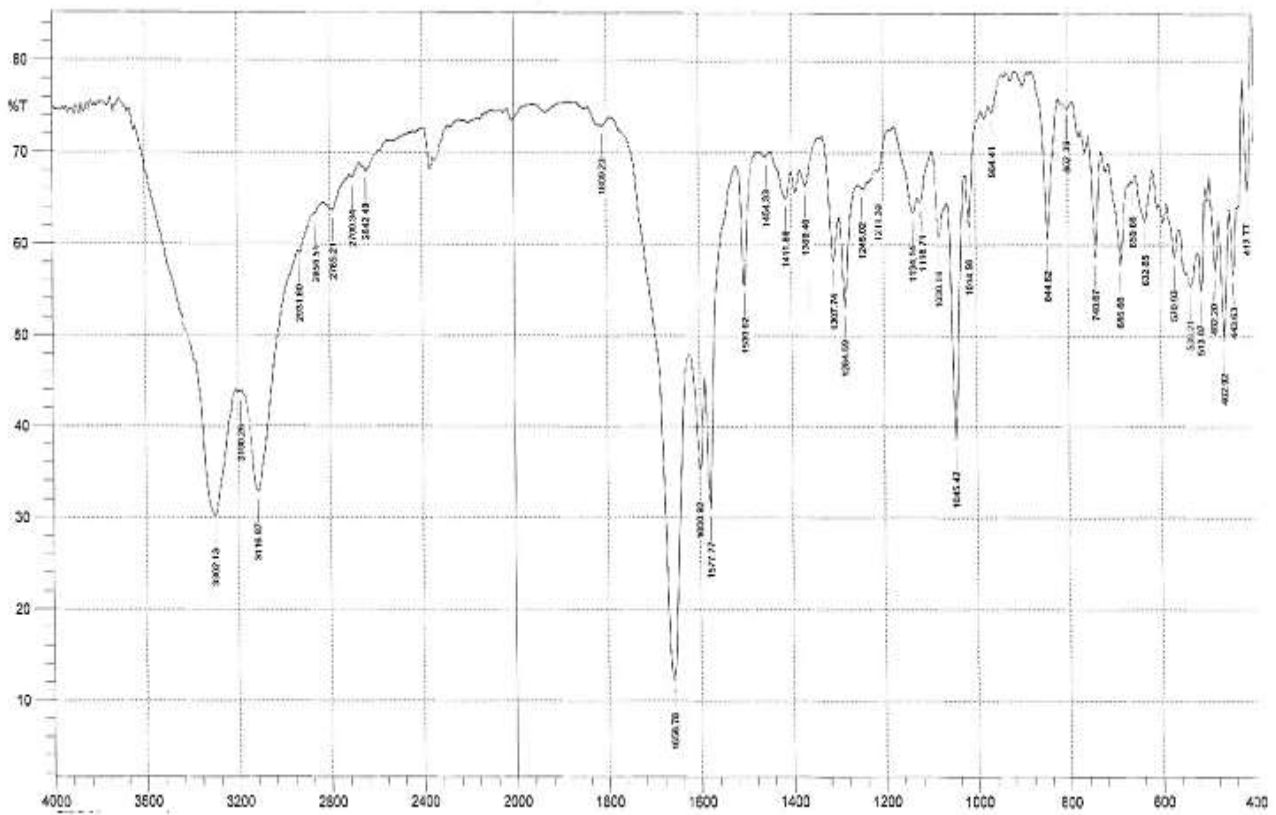
**Table 6 : Solubility of [ 12-16] Resins**

Comp.No	DMF	DMSO	Triethyl amine	CH <sub>3</sub> Cl	THF	Cyclo hexane	m-Cresol
12	++	++	++	-	-	+	-
13	++	++	++	-	-	+	-
14	++	++	+	-	-	+	-
15	++	++	+	-	-	+	-
16	++	++	+	-	-	+	-

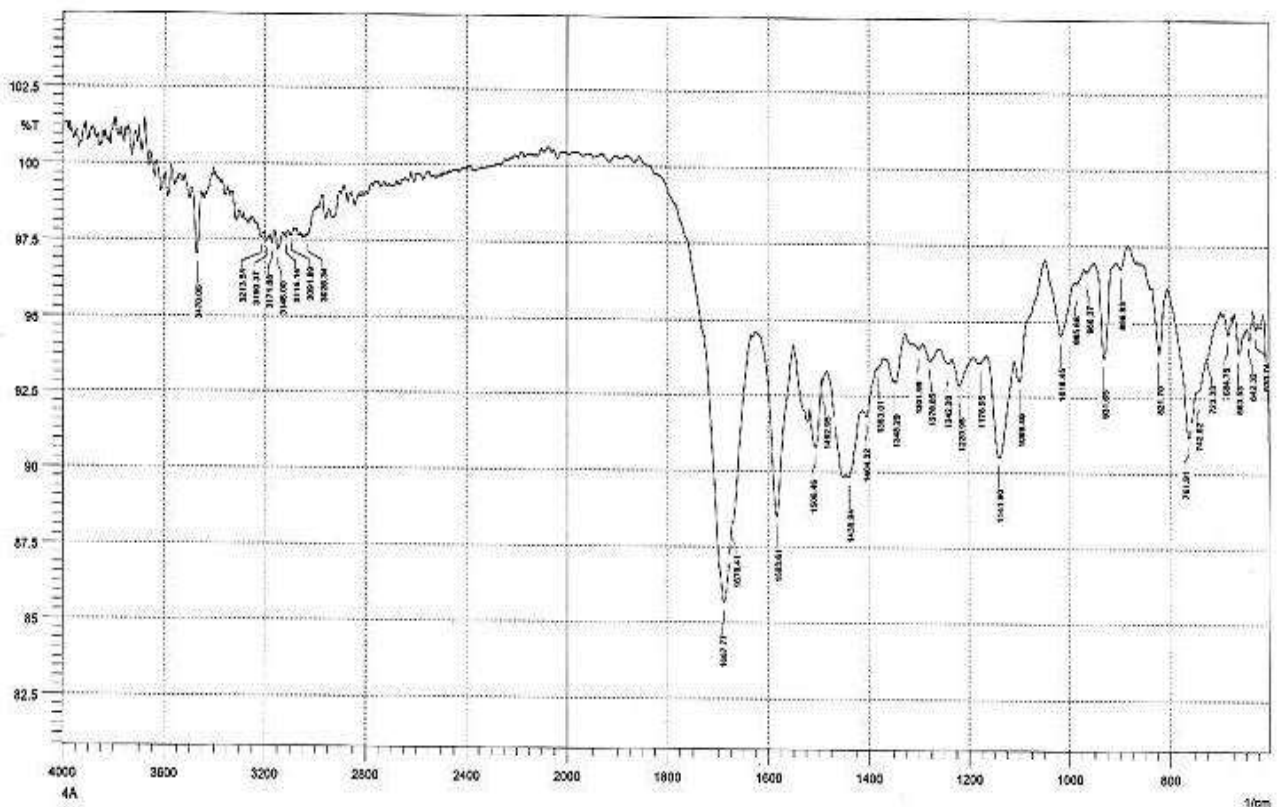
Where(++)= Soluble at room temperature , (+)= Soluble with heat , (-)= Insoluble even with heating.

**Table 7: Softening points of [12-16] Resins**

Comp.No	Softening point (C <sup>o</sup> )
12	250-261
13	203-210
14	>300
15	>300
16	>300



**Fig. 1: FT-IR of [C1]**



**Fig. 2: FT-IR of [C2]**

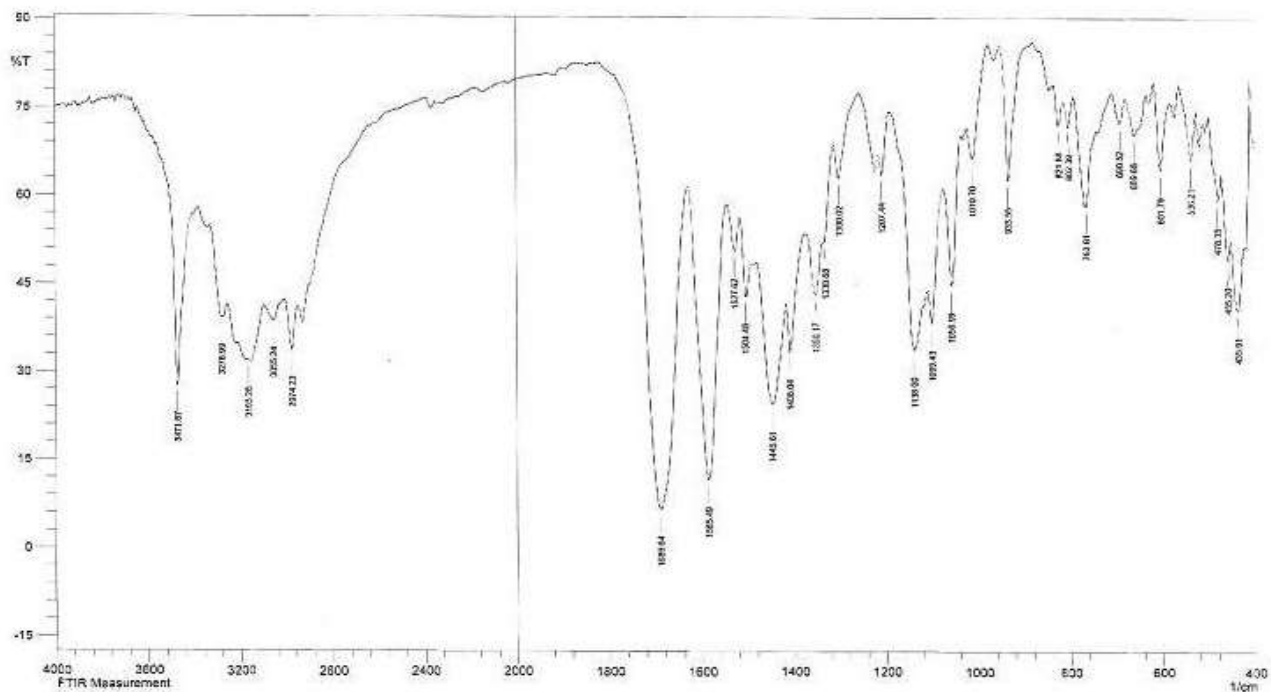


Fig. 3: FT-IR of [C4]

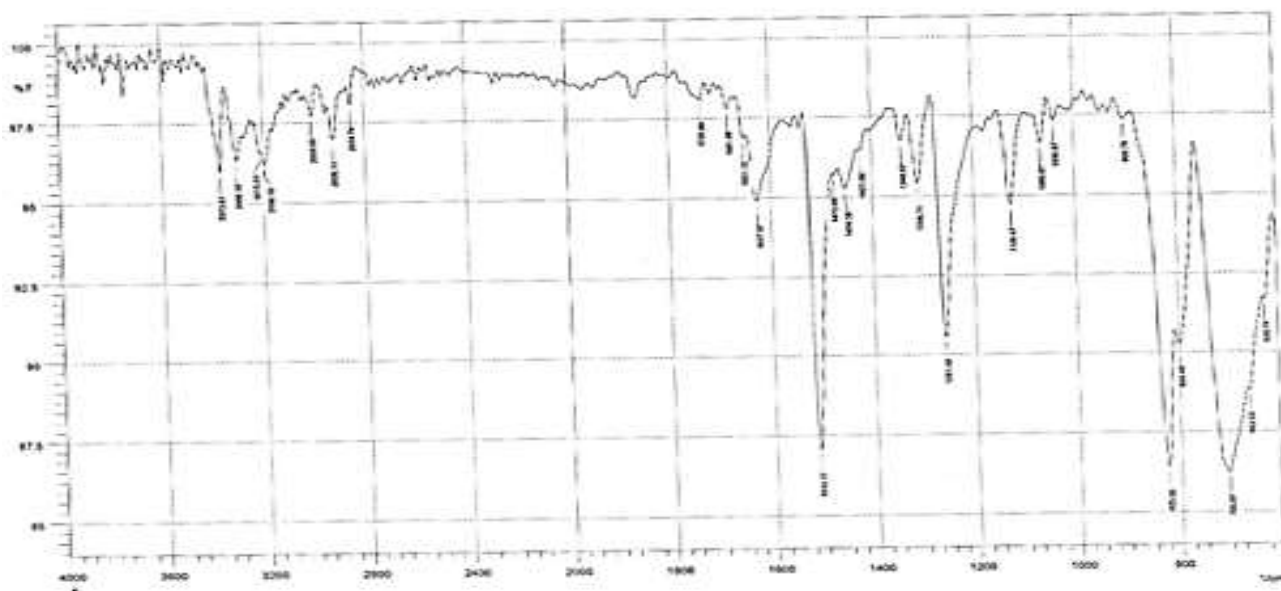


Fig. 4: FT-IR of [C12]

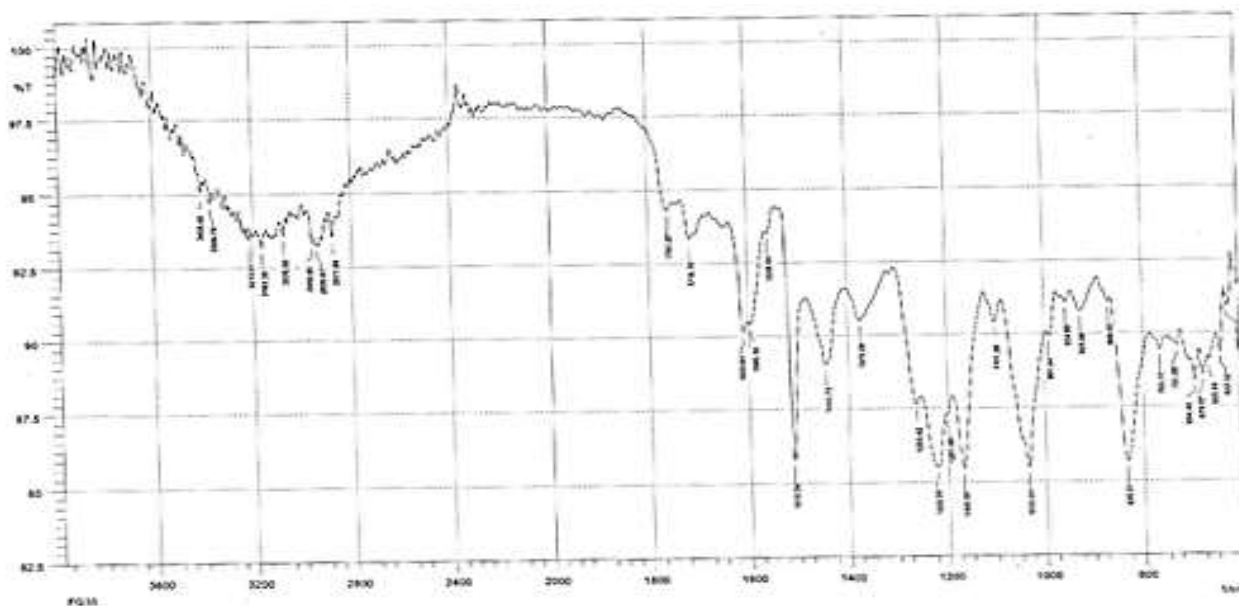


Fig. 5: FT-IR of [C9]

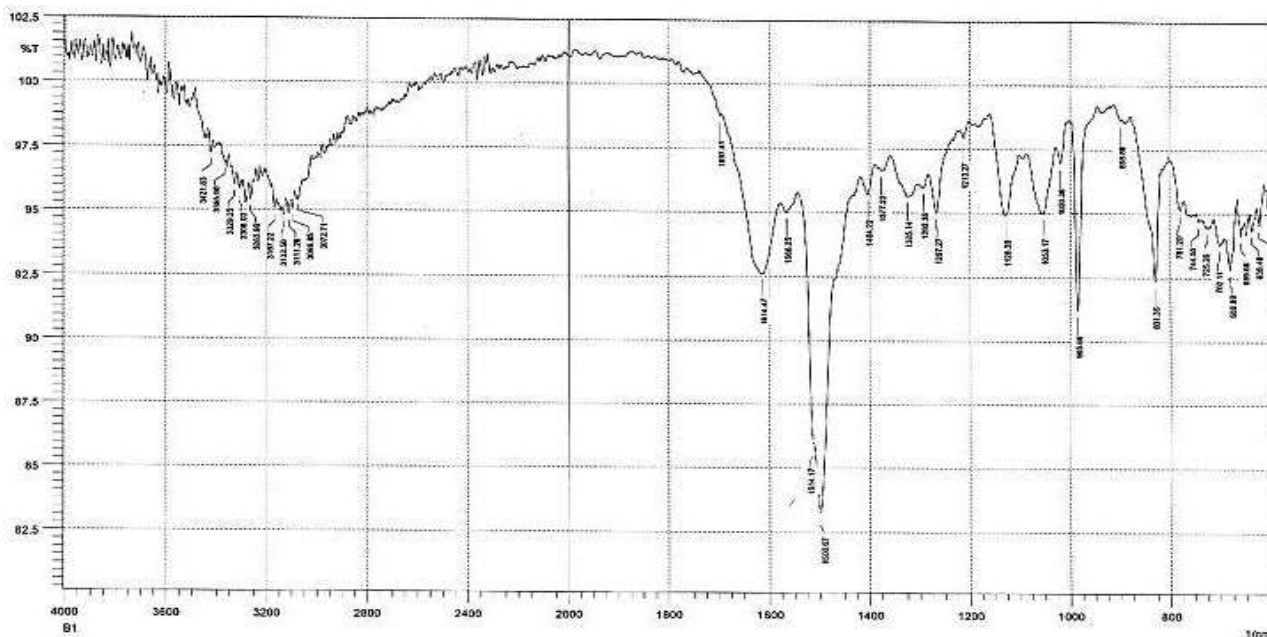


Fig. 6: FT-IR of [C14]

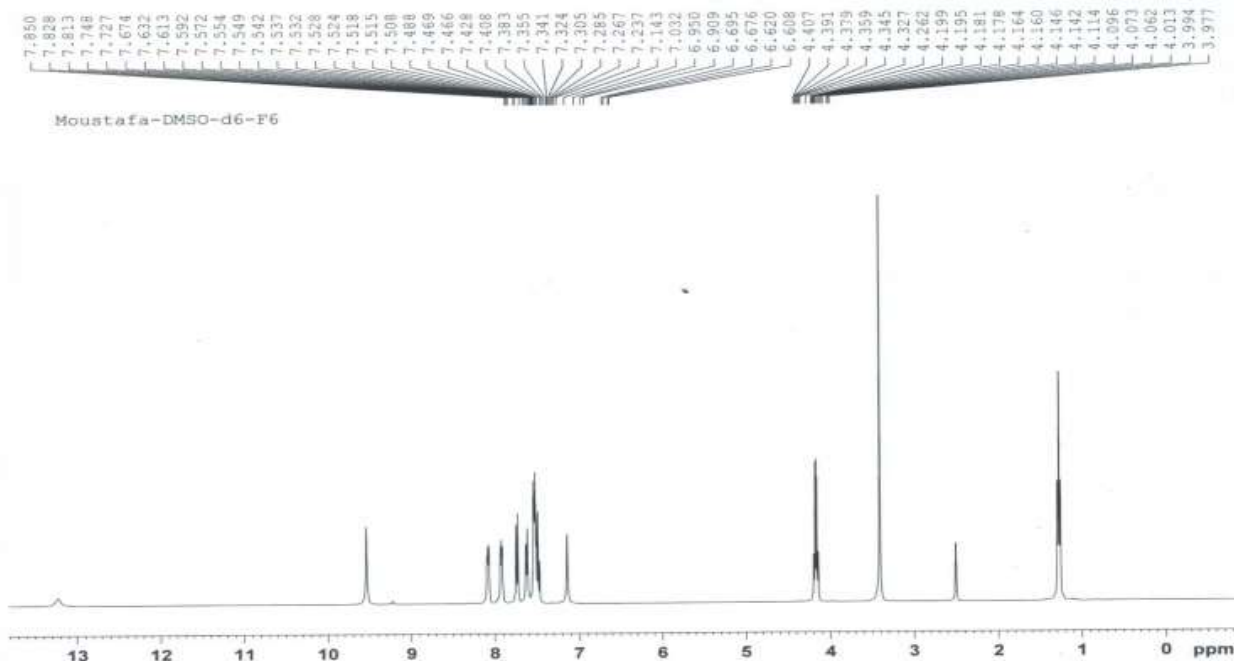


Fig. 7: H-NMR spectrum of [C1]

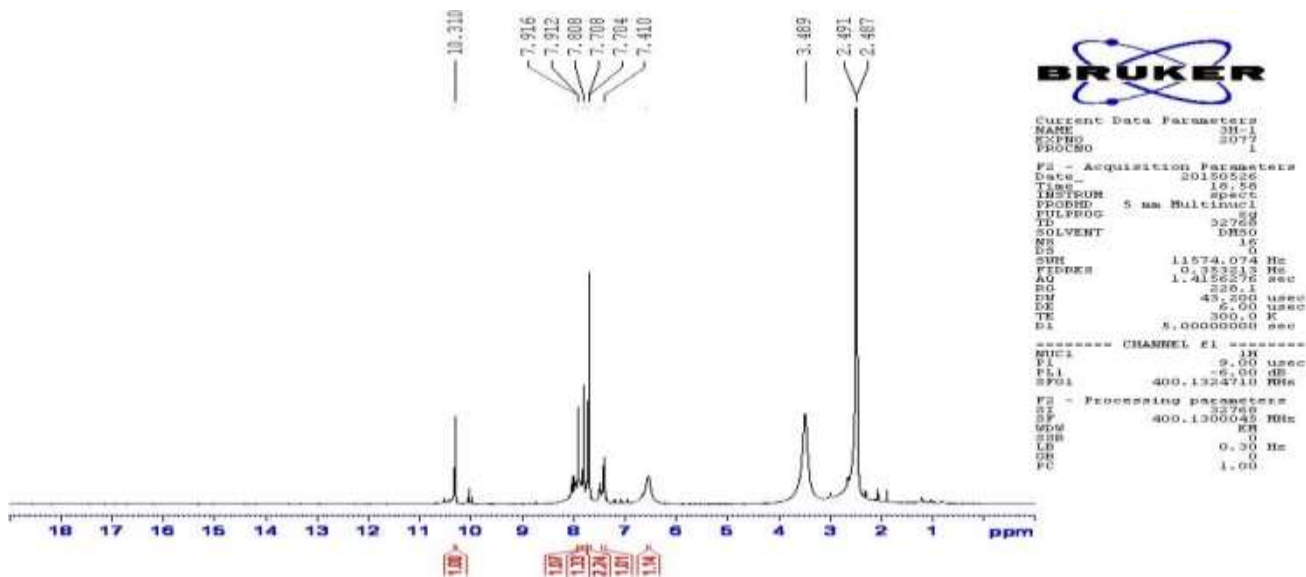


Fig. 8: H-NMR spectrum of [C4]



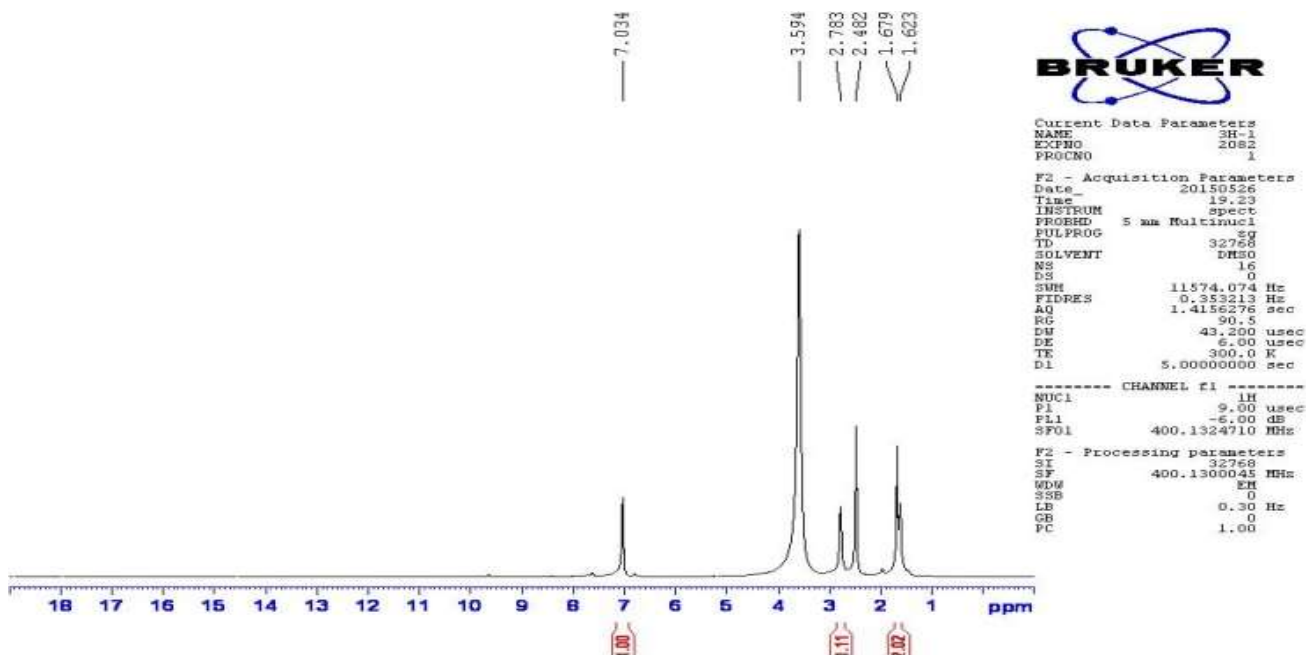


Fig. 9: H-NMR spectrum of [C9]

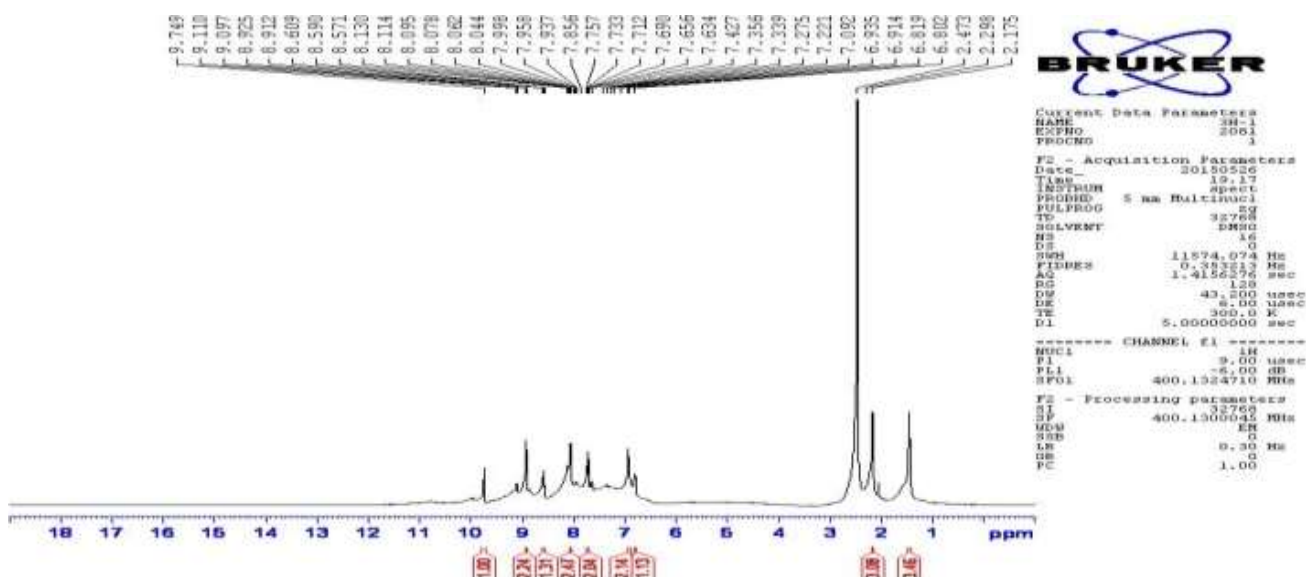


Fig. 10: H-NMR spectrum of [C15]

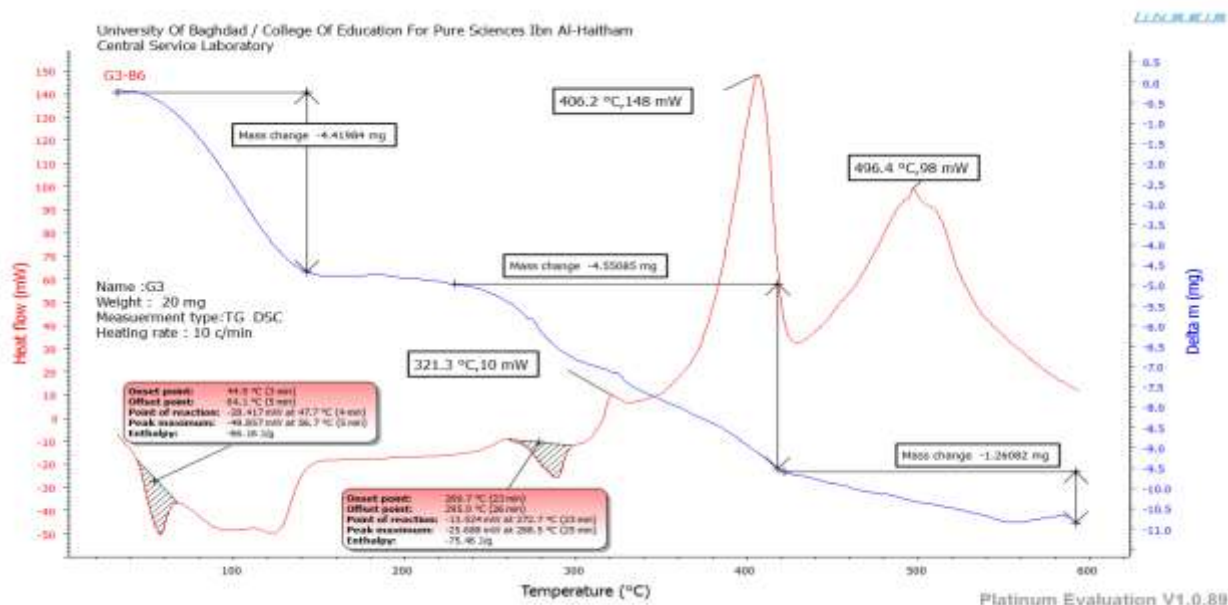


Fig. 11: TGA & DSC thermo gram of resin [C13]

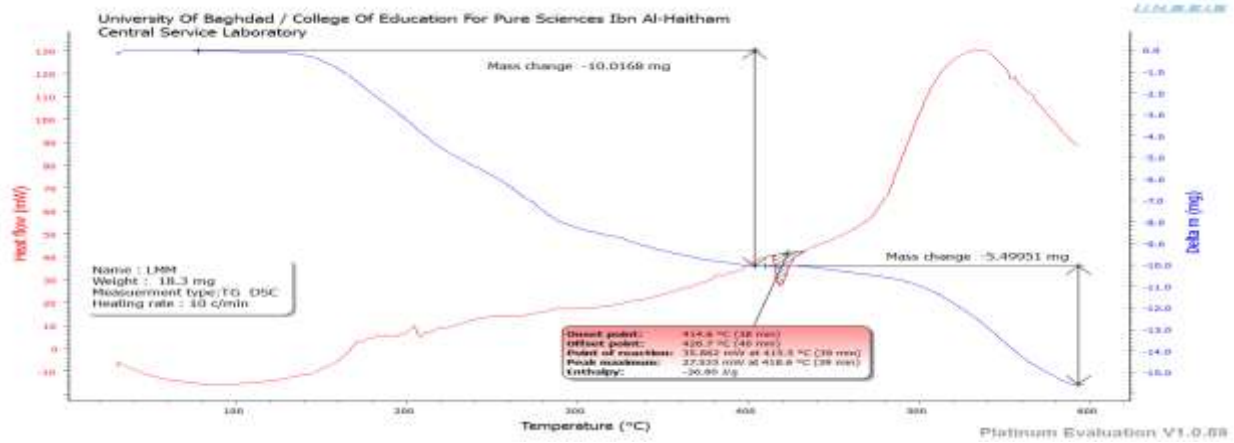


Fig. 12: TGA & DSC thermo gram of resin [C14]

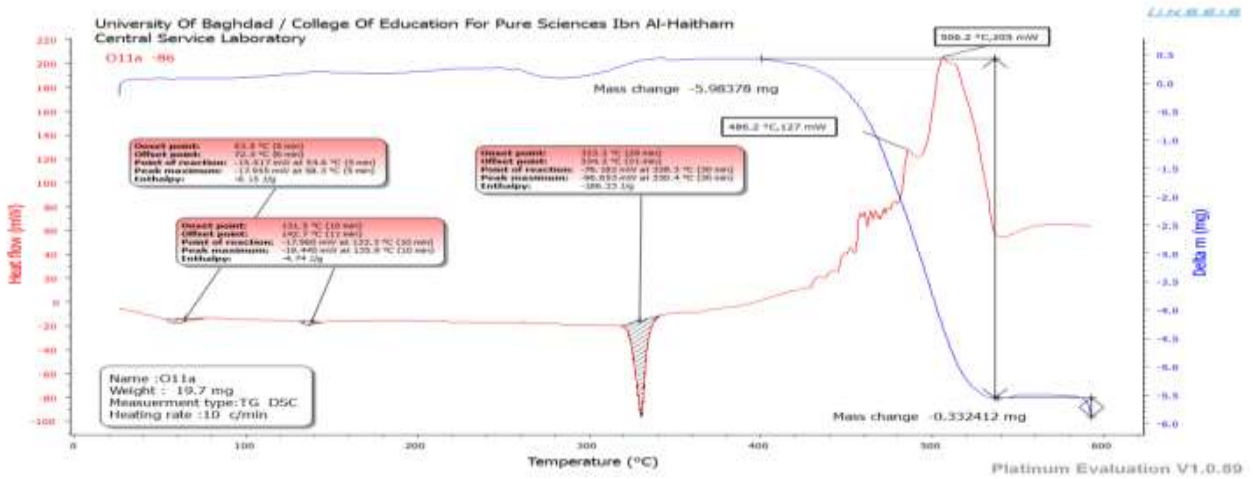


Fig. 13: TGA & DSC thermo gram of resin [C15]

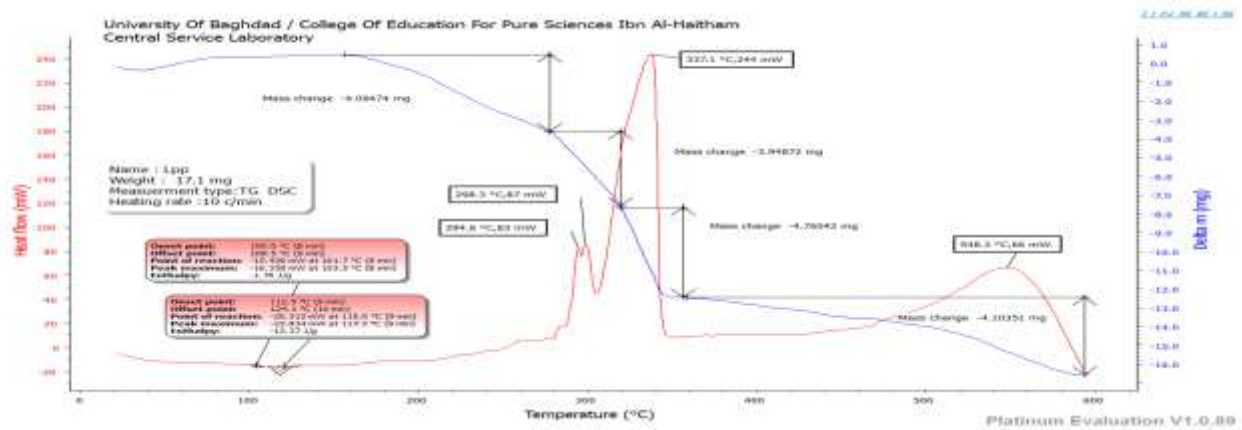


Fig. 14: TGA & DSC thermo gram of resin [C16]

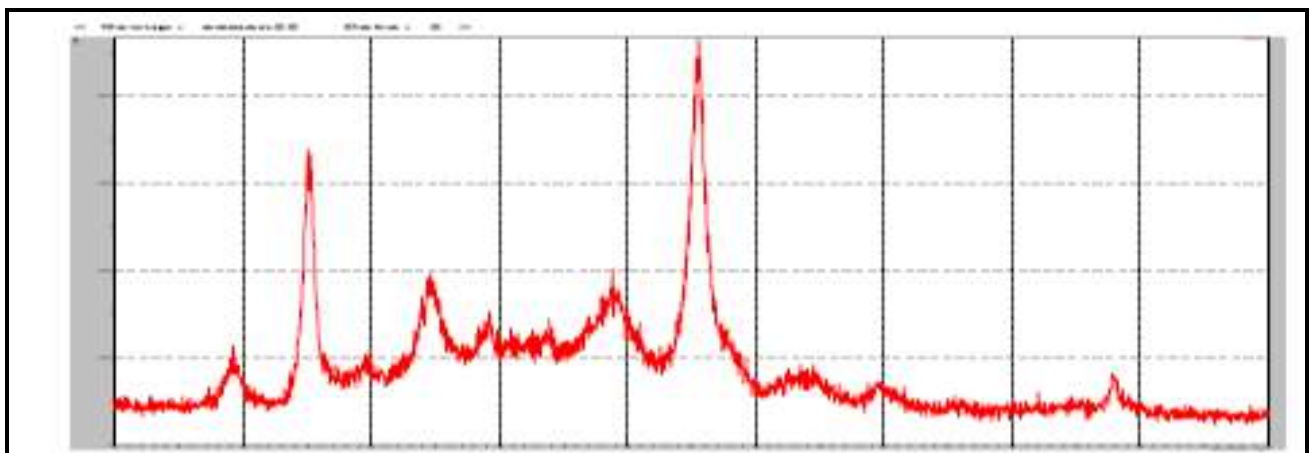


Fig. 15: X-Ray of resin [C12]

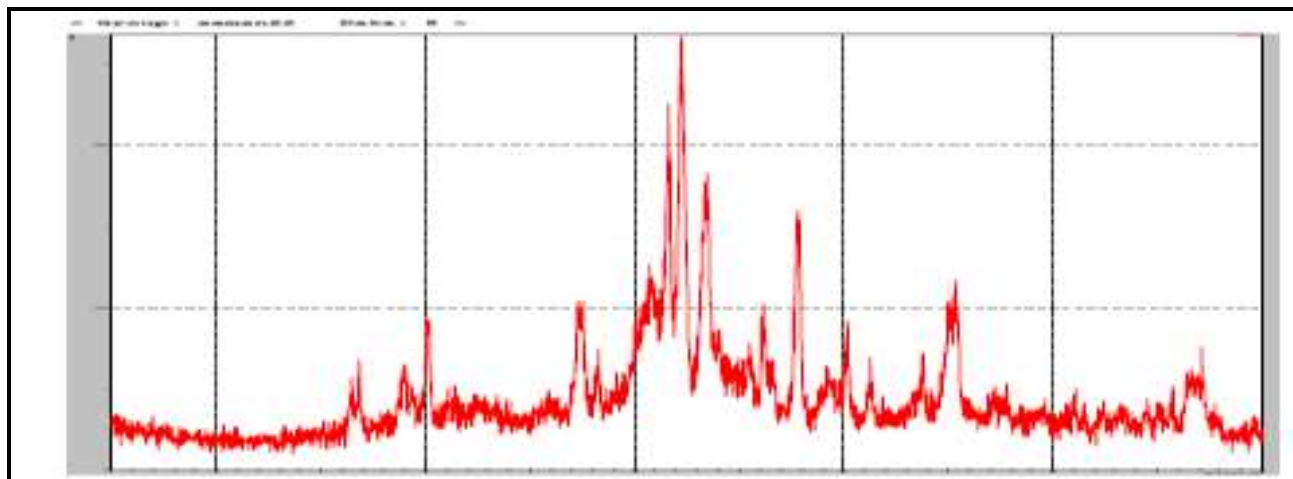


Fig. 16: X-Ray of resin [C13]

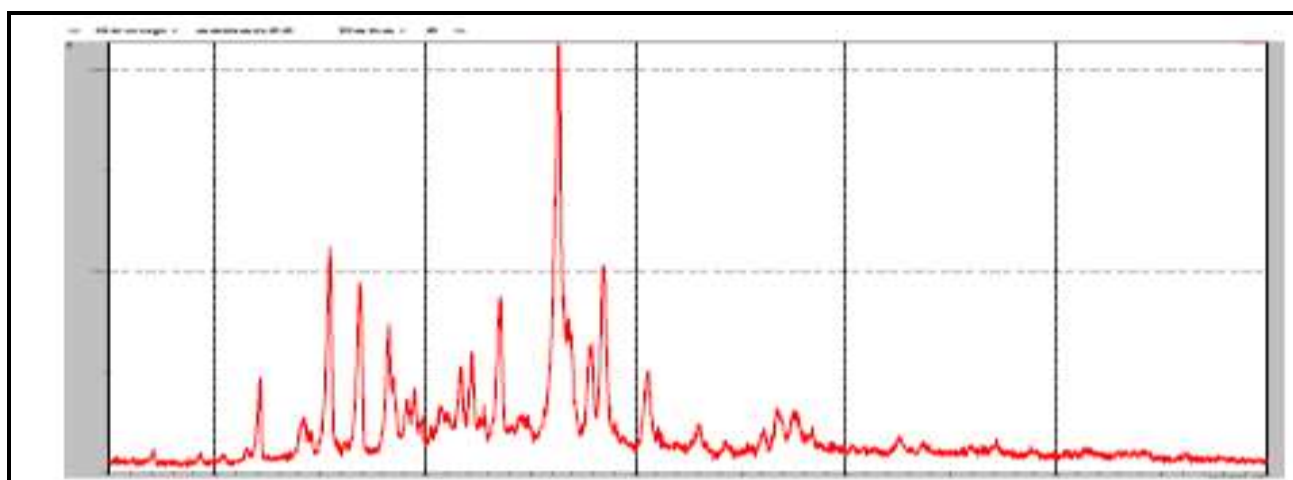


Fig. 17: X-Ray of resin [C14]

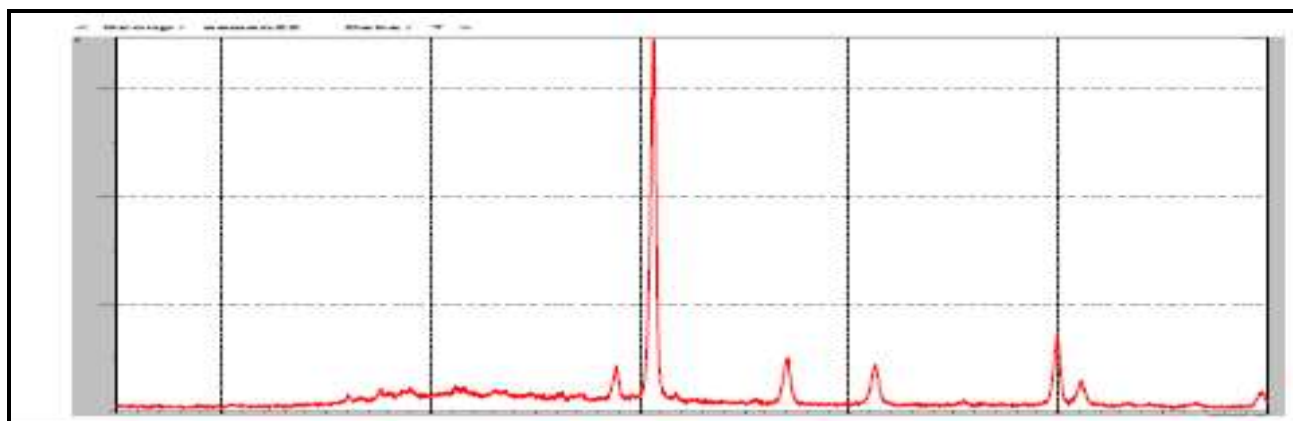


Fig. 18: X-Ray of resin [C16]

## Conclusion

Through this work we have succeeded synthesis monomers with heterocyclic ring which give highly thermal stability and good solubility and agreement with proposed structure. Most of the synthesized Schiff base derivatives were potential lead for industrial application and biological activity respectively, on the basis of observed results it may be concluded that the substitution favors the activity. The derivatives are

known to be influenced to a great extent by two aryl structure, i.e. Schiff base derivative resins molecular and their substitution. Especially the hydroxyl substituent's is one of the key group of enhance greatly the industrial application mainly due to its easy conversion of phenoxy radical through the hydrogen atom transfer mechanism, there are a number of structurally diverse Schiff bases have been synthesis and evaluated for industrial application and biological activity.

## References

1. Hakan B, Nesrin K, Deniz S, Ahmet D, Sengul Neslihan D (2010) *Molecules*,15: 2427-2438.
2. Verma C, Olasunkanmi LO, Ebenso EE, Quraishi M (2016) Adsorption behavior of glucosamine-based,pyriidine-fused heterocycles as green corrosion inhibitors for mild steel;experimental and theoretical studies, *J. Phys Chem.*, 120:11598-611.
3. Raied M, Sh Azhar A, Mahmood AA (2014) *Molecules*, 19:3436-3449.
4. Shohei M, Tatsuhiko A, Koki I, Makote F (2014) *Journal of the American Chemical Society*, 136(32):17899-17901.
5. Jamil DM, Al-Okbi AK, Al-Baghdadi SB, Kadhim A (2018) "Experimental and theoretical studies of Schiff bases as corrosion inhibitors , *J. Chem. Cent.*, 12:7.
6. H Schiff (1864) *Ann* 131: 118.
7. Mahmoud AS (2014).Ph.D. Thesis, University of Baghdad, Iraq,"Preparing of New Organic Compounds with Liquid Crystalline Properties".
8. Sarah S.A (2014) Ph.D. Thesis, University of Baghdad, Iraq."Synthesis and Characterization with Study of the Thermal Properties and Biological Activity for Some New Monomers and Polymers Containing Heterocyclic Rings".
9. Simon H, Xuan L, Jean NO, Oliver Jean, D Mathias D (2014) *Polymers*, 6:1437-1488.
10. RM Si inverstein (1981)"Specro metric Identification of Organic compound", 4th Ed, 2.
11. DH Williams Felming, Translated by Sarkss JY (1986) "Spectroscopic Methods in Organic Chemistry", Baghdad University, 1st Edition.