

## Synthesis, Characterization of New di Schiff base Derivatives from Dapsone, Their Polymerization and Thermal Study

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### Abstract

Schiff bases were containing (-C=N-) functional group and found to be a versatile compound. In this study new three Schiff bases compounds were prepared in the presence of catalyst through condensation products of 4,4'-sulfonyldianiline with carbonyl compounds using microwave. These compounds characterized by using FTIR, H-NMR and Mass spectroscopy. Also, they were polymerized to produce poly ester and phenolic resin through condensation polymerization, their thermal stability was evaluate using (TGA and DSC) techniques, the result show that the polymers have decomposition temperature more than 150 C<sup>0</sup> and also the results show that the weight residue more than 70%, and the phenolic resin was more stable than polyester.

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## 1. Introduction

Schiff bases compounds prepared from the reaction of carbonyl compounds with primary amine (especially aromatic amine), and they were first synthesized Schiff P Pin 1864.<sup>[1]</sup> Schiff base is named imine<sup>[2]</sup>, this ligand is contains a carbon-nitrogen double bond, aryl or alkyl group linked on the nitrogen atom. The general structure of imine is  $R-CH=N-R'$  where R and R' is aryl or alkyl group<sup>[3]</sup>. The most method synthesized imine by using condensation reaction between raw materials and using reflux in the presence of drops of acid such as (p-toluene sulphonic acid), which gives proton to the carbonyl in order to form ion then amine added to the carbonium ion by quick step and the next step including removal of the proton (Deprotonation) from the compound and lose quickly water to form Schiff base<sup>[4]</sup>. The other methods using a microwave technique to synthesized imine, and this method as anew tools in green chemistry. Also, this method has many applications in the synthesis of many organic compounds. In this field of technique using solvent free or less solvent conditions are attractive contributory, low cost, less pollution and high yields together with clarity in processing and handling. Simple reaction, shorter time of reactions and high yield are the Main advantages of this techniques.<sup>[5,6]</sup> The reaction of Schiff base was widely used in organic synthesis; with many advantages such as simple reaction conditions, also they are using for protecting some reactive groups in the synthesis of a series of organic ligands. In polymer chemistry which containing azomethine group wide range of application such as corrosion inhibitors<sup>[7]</sup>. Also, Schiff - base reactions used in synthesis of many kinds of polymers containing the azomethane group. On the other hand, covered some of important development on the functions and applications of these polymers. In this study new Schiff base and their polymers were prepared from 4,4'-sulfonyldianiline using microwave as a tool in the synthesis

## 2. Experimental

### 2.1. General

Melting points were uncorrected. NMR spectra were acquired with a Bruker Ultra Shield (300 MHz). The chemical shifts were referenced to tetra methyl silane (TMS) as an internal standard. GC mass spectra were acquired with Shimadzu Qp5050A. Thermal study of the prepared polymers was done using thermal analysis (TGA, DSC) under inert atmospheric condition and a heating rate of 20 °C/ min.



## 2.2. Synthesis of di Schiff base and their polymers

### 2.2.1. Synthesis of di Schiff base compounds

In a 100 ml beaker, dissolved (0.02 mole) of aldehyde or ketone derivatives in 10 ml of absolute ethanol then add (0.001 g) of p-toluene sulphonic acid and leave for 10 min. Then added (0.02 mole) of 4,4'-sulfonyldianiline (Dapsone) dissolved in 10 ml ethanol (abs.) to previous mixture. Then place the mixture in Microwave for (3-5) min. according to the type of aldehyde or ketone derivatives, followed the reaction by T.L.C. Paper. cooling the product in ice path for 15 min. Different colored crystal was obtained then filtered the product and recrystallization by using absolute ethanol.

#### **4,4'-(1,1'-(4,4'-sulfonylbis(4,1-phenylene) bis(azan-1-yl-1-ylidene)) bis(ethan-1-yl-1-ylidene)) dibenzene-1,3-diol (1):**

From 2,4-dihydroxy acetophenone (3) yield 93%, m.p. (110-112) °C. ;Mass spectrum M.wt. (  $M^+ = 516$  ), the FTIR spectrum of this compound ,  $\nu(\text{cm}^{-1})$  3452 (OH stretching), 3074 (due to C–H stretching of aromatic ring), 2924 (attributed to C–H stretching of aliphatic), 1631 (due to C=N stretching), 1604 ( due to C=C stretching of aromatic ring), 1214 (C–N stretching), H-NMR spectrum,  $\delta_{\text{H}}(\text{DMSO})$  (12.63) ppm (2H,s,5,5'), (10.64) ppm ( 2H,s,3,3), (7.76-7.80) ppm (4H,d,1,1'), (7.44-7.48) ppm ( 4H,d, 2,2') (6.61-6.63) ppm (4H,d, 7,7') ,(6.27-6.42) ppm (4H,d, 6,6'); (6.00) ppm (2H,s,4,4') , (2.20) ppm ( 6H, s, 8,8').

#### **3,3'-(4,4'-sulfonylbis(4,1-phenylene) bis(azan-1-yl-1-ylidene) bis(methan-1-yl-1-ylidene)) diphenol (2):**

From 3-hydroxy benzaldehyde (4) yield 73%, m.p. (58-60) °C. ;Mass spectrum M.wt. ( $M^+ = 456$ ), the FTIR spectrum ,  $\nu(\text{cm}^{-1})$  3452 ( due to OH stretching), 3097 (was attributed to C–H stretching of aromatic ring), 1627 (related to C=N stretching), 1593 (due to C=C stretching of aromatic ring), 1212 (C–N stretching), H-NMR spectrum,  $\delta_{\text{H}}(\text{DMSO})$  (9.94) ppm (2H,s,4,4'), (8.51) ppm (2H,s,8,8'), (8.03-8.07) ppm (4H,d,1,1'), (7.85-7.89) ppm ( 4H,d, 2,2') (6.60-6.70) ppm (8H,m, 3,3', 5,5',6,6',7,7').



**4,4'-(4,4'-sulfonylbis(4,1-phenylene) bis(azan-1-yl-1-ylidene) bis(methan-1-yl-1-ylidene) diphenol (3):**

From 4-hydroxy benzaldehyde (6) yield 88%, m.p. (116-118) °C. ;Mass spectrum M.wt. ( $M^+ = 456$ ) , the FTIR spectrum was,  $\nu(\text{cm}^{-1})$  3460 (due to OH stretching), 3024 (due to C–H stretching of aromatic ring), 1635 (attributed to C=N stretching), 1585 (C=C stretching of aromatic ring), 1215 (due to C–N stretching), H-NMR spectrum,  $\delta_{\text{H}}(\text{DMSO})$  (12.5) ppm (2H,s,5,5'), (8.95) ppm (2H,s,8,8'), (8.07-8.10) ppm (4H,d,1,1'), (7.91-7.88) ppm ( 4H,d, 2,2'), (7.68-7.70) ppm (4H,d, 3,3',7,7') , (7.46-7.48) ppm (4H,d, 4,4',6,6').

**2.2.2. Synthesis of polymers (E, R1-R3)****Synthesis of polyester (E)**

Polyester derived from di Schiff base (1) and Sebacoyl chloride was synthesis using 0.70g (0.0013 mole) of Schiff base dissolved in 20 mL 1,2- dichloroethane in three neck flask containing condenser, thermometer and dropping funnel then 1.5 ml. of triethylamine added to the reaction mixture, and dropwise addition of 0.5 ml (0.0013 mole) of Sebacoyl chloride dissolved in 5mL dichloroethane to the reaction mixture with continuous stirring. After the complete of the addition, the temperature rise to 50°C in order to complete the reaction for one hour, then triethyl ammonium chloride salt was removed by filtration. The filtrate was evaporated, off white solid precipitate was obtained and washed twice with diethyl ether and dried under vacuum.

**Synthesis of phenolic resin (R1-R3)**

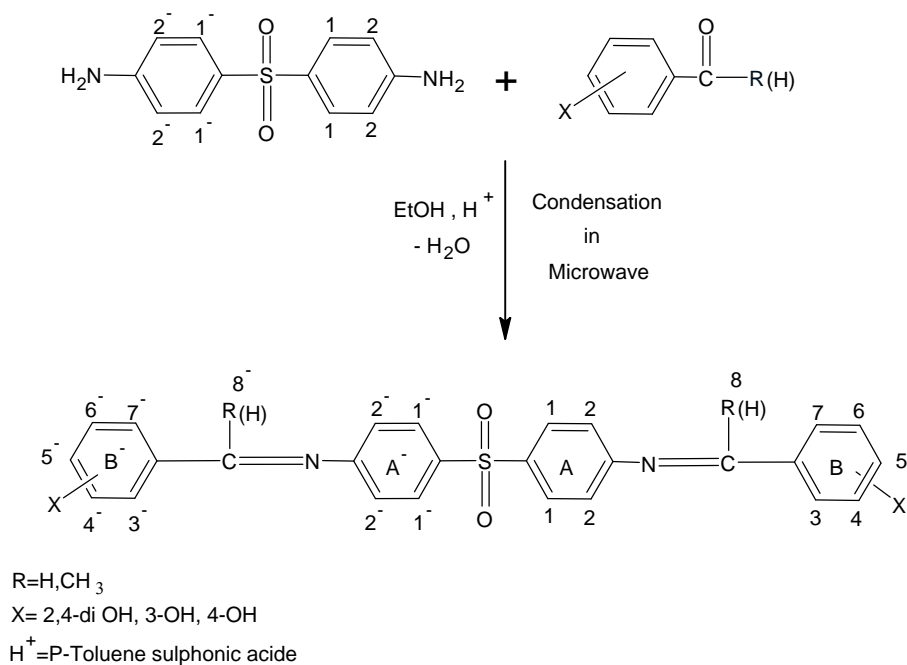
Phenolic Resin derived from di Schiff base (1,2,3) and formaline solution were prepared in general procedure: A mixture of di Schiff base 1g (0.002 mole), dissolved in 5ml ethanol and formaline solution 35% with ratio of (phenolic: formalin 1.2) and it was placed in three neck flask containing condenser, thermometer and dropping funnel. The dropping funnel was charge with sodium hydroxide solution (10%) to make the the reaction mixture (PH= 9-10). The reaction mixture was heated at 65-70 °C for two hours with good stirring then cool the product and neutralized with 10% phosphoric acid solution to obtain viscous oily layer, which was wash with warm water in order to remove excess formaline and unreacted product to get the final viscous products.



### 3. Results and Discussion

#### 3.1 Reaction Scheme

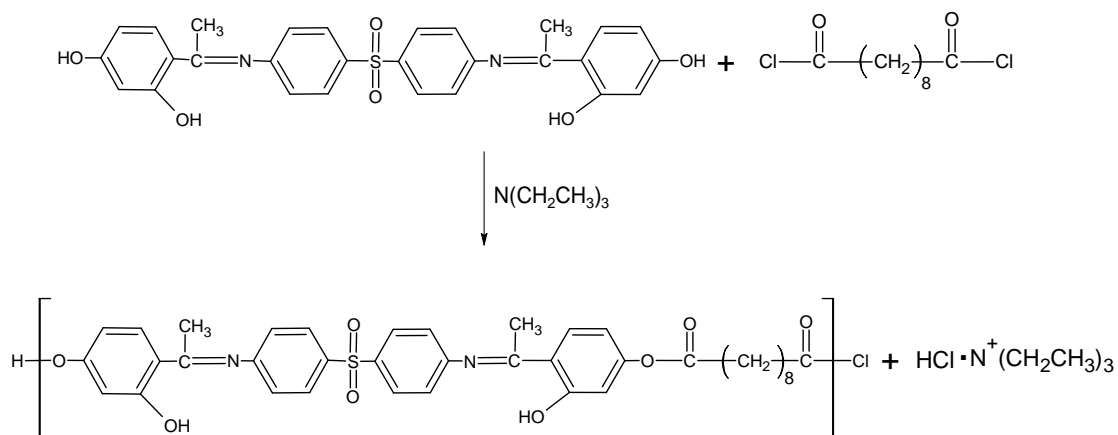
Treatment of the 4,4'-sulfonyldianiline with aldehydes or ketone in ethanol and used of p-toluene sulphonic acid as catalyst, were done under irradiated microwave (332w) after purification from recrystallization, the pure di Schiff base derivatives (1-3) in 73-93% yield, (Scheme 1). The proposed chemical structures of the prepared compound were provided from their Mass spectroscopy, FT-IR, and  $^1\text{H}$  NMR measurements.



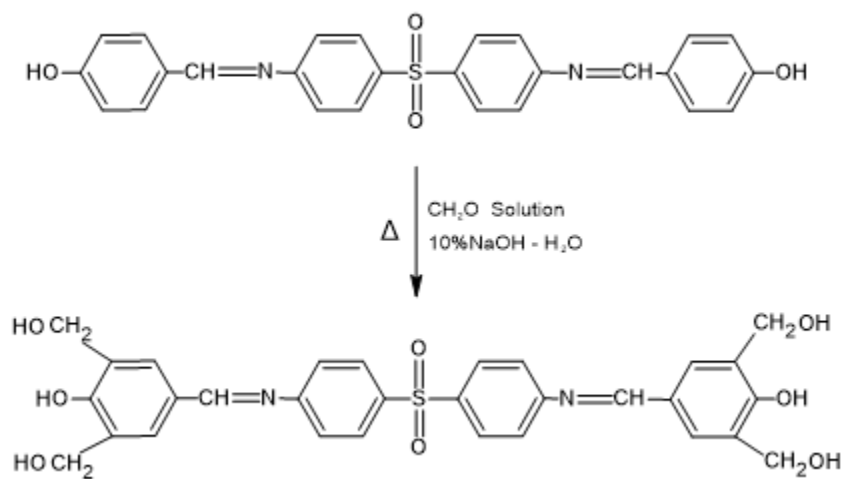
Scheme(1):Rute of the prepared di schiff base

Scheme 2,3 show the route for the prepared polymers from Schiff-base compounds.

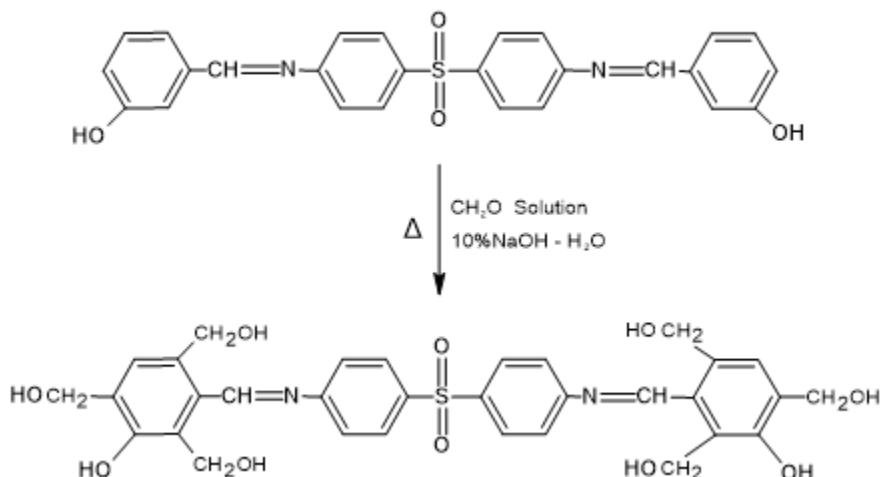




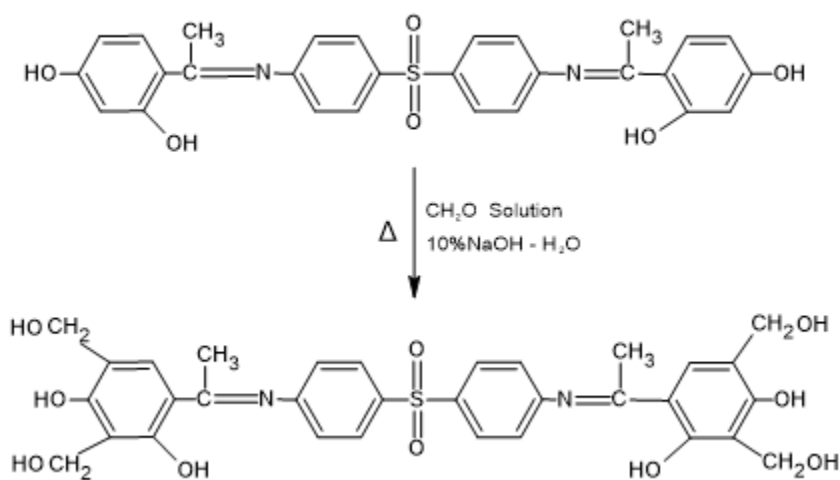
Scheme(2):Polyester preparation



Scheme (3): phenolic resin, R1



Scheme (4): phenolic resin, R2



Scheme (5): phenolic resin, R3

### 3.2 Characterization of the prepared di Schiff base and their polymers

The FT-IR spectra of di Schiff base compounds were shown in Figures (1-3) and was identification, the results shown that the bands of carbonyl groups ( $1680-1750$   $\text{cm}^{-1}$ ) was disappearance, these facts confirmed the correct expected chemical structure of these compounds.

All the FTIR spectra of di Schiff base showed absorption bands at ( $1627-1635$   $\text{cm}^{-1}$ ) which related



to the stretching vibration of (C=N) group, also absorption bands at (1210-1219)  $\text{cm}^{-1}$  which appeared due to (C-N) stretching, while the absorption bands at (1585-1604)  $\text{cm}^{-1}$  was attributed to the stretching of aromatic carbon bonds. The C-H stretching aromatic rings showed absorption bands within the range (3024-3097)  $\text{cm}^{-1}$ , while the C-H stretching vibration aliphatic absorption bands was appeared at (2924)  $\text{cm}^{-1}$ . The O-H stretching in compound (1,2 and 3) showed absorption bands within the range (3452-3460)  $\text{cm}^{-1}$ . In the case of  $^1\text{H}$  NMR measurements, the spectra of the prepared di Schiff base compounds which are shown in Figures (4-6). The spectra indicate <sup>[8-10]</sup> the presence of azomethine group (CH=N) singlet signal at (8.51-8.95) ppm in compounds (6,7). The  $\text{CH}_3$  protons (8) of compound (5) showed singlet signal at (2.20) ppm. The aromatic protons of ring (A) in the positions (1,1') showed doublet signals within the range (7.76-8.10) ppm because interaction with one protons in (2,2') position, while the other two protons in (2,2') position showed doublet signals within the range (7.44-7.91) ppm because interaction with protons in (1,1') position. The proton of aromatic ring (B) in the position (3,3' and 7,7') in compound (7) showed doublet signals at (7.68-7.70) ppm because interaction with protons in (4,4' and 6,6'), while the other two protons in positions (4,4' and 6,6') showed doublet signals within the range (7.46-7.48) ppm because interaction with protons in (3,3' and 7,7'). The aromatic protons in compound (6) showed multiple signal within the range (6.60-6.70) ppm which appeared to protons in positions (3,3',5,5',6,6',7,7') in compound (6).

In compound 5 the proton in position (7,7') showed doublet signals within the range (6.61-6.63) ppm because interaction with proton in position (6,6'), while the proton in position (6,6') showed doublet signals in the range (6.27-6.42) ppm. While the other proton in positions (4,4') showed singlet signal in 6.00 ppm. For mass spectroscopy, study Scheme (4) show the fragmentation products of 2,3 di Schiff bases. While the FTIR Spectra of the prepared polymers were shown in Figures (7-10) From Fig. (7) for polyester, new band appear at (1763)  $\text{cm}^{-1}$  was attributed to the polyester linkage  $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$  which does not find in the spectrum of di Schiff base (Figure 1). Also, another band at (1033)  $\text{cm}^{-1}$  was related to the ether (C-O-C) bond. On the other hand, the band at (1643)  $\text{cm}^{-1}$  was attributed to the C=N- Schiff base and it is still present, and band at (3375)  $\text{cm}^{-1}$  was related to the remaining of unreacted hydroxyl group. In the case of Figures (8-10) show the spectrum of phenolic resin prepared from di Schiff base (1,2,3) which contained band at (3417)  $\text{cm}^{-1}$  was attributed to the OH to groups present on the polymer chain, and new band at (2916)  $\text{cm}^{-1}$  was related to the stretching vibration of methylene groups ( $-\text{CH}_2-$ ).





while the band at  $(1589) \text{ cm}^{-1}$  due to Azomethine  $-\text{CH}=\text{N}-$  remain unchanged through the polymerization of Schiff base.

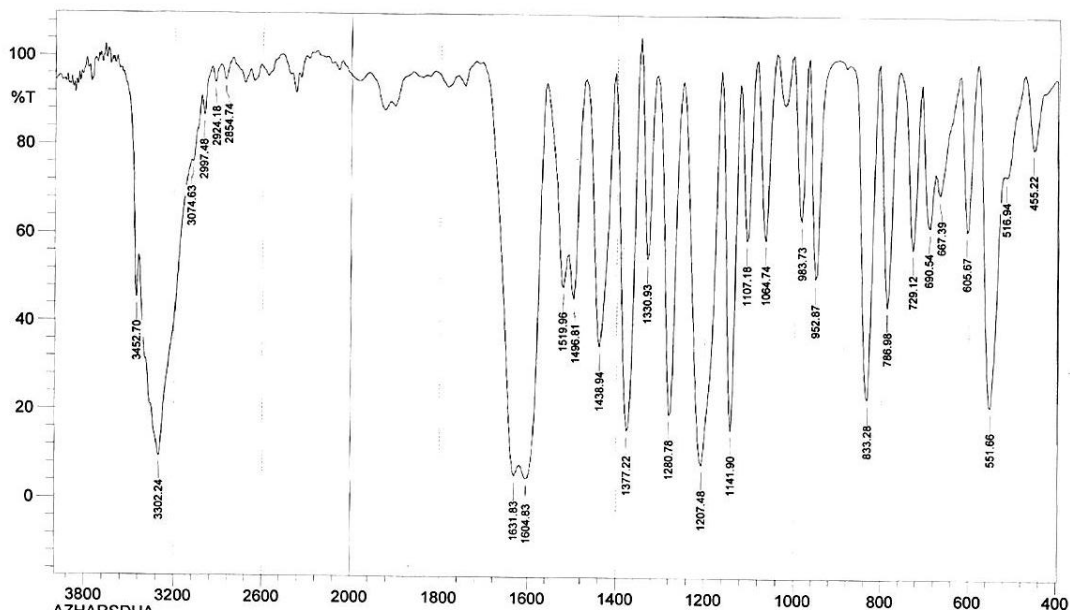


Figure 1: FTIR spectrum of di Schiff-base 1.

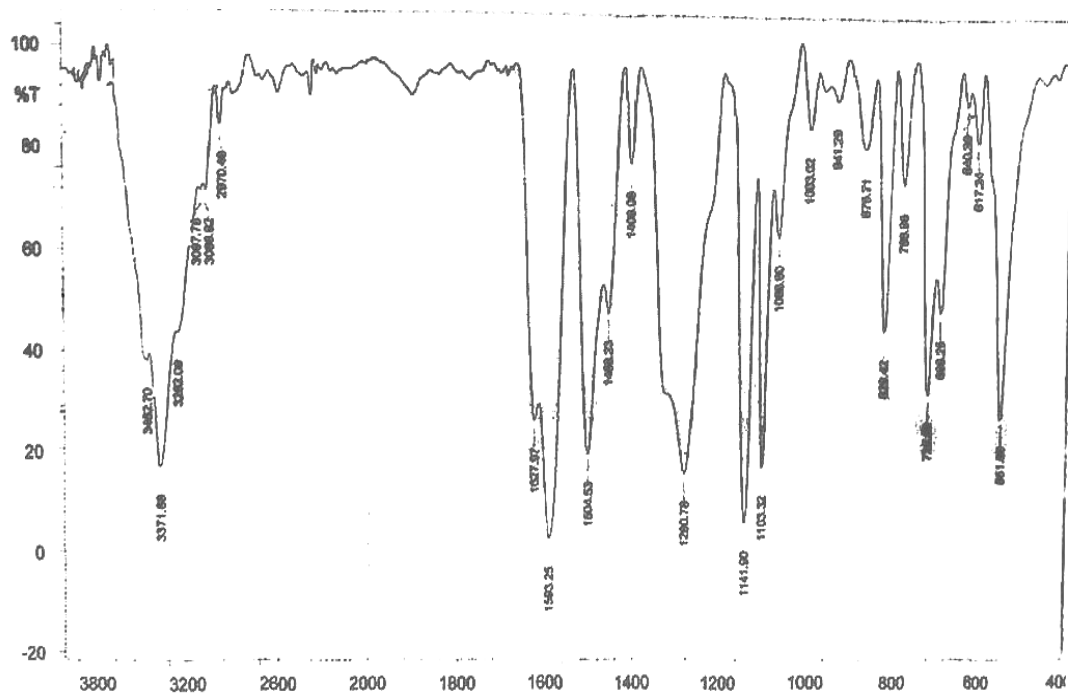


Figure 2: FTIR spectrum of di Schiff base 2



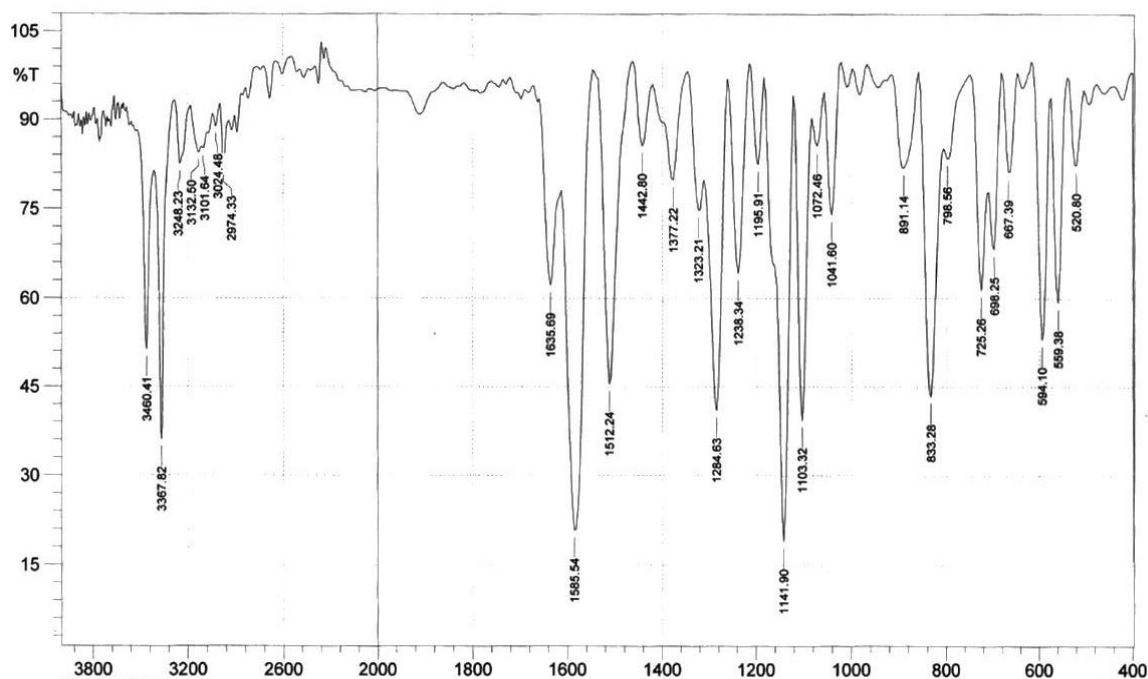


Figure 3: FTIR spectrum of di-Schiff base 3

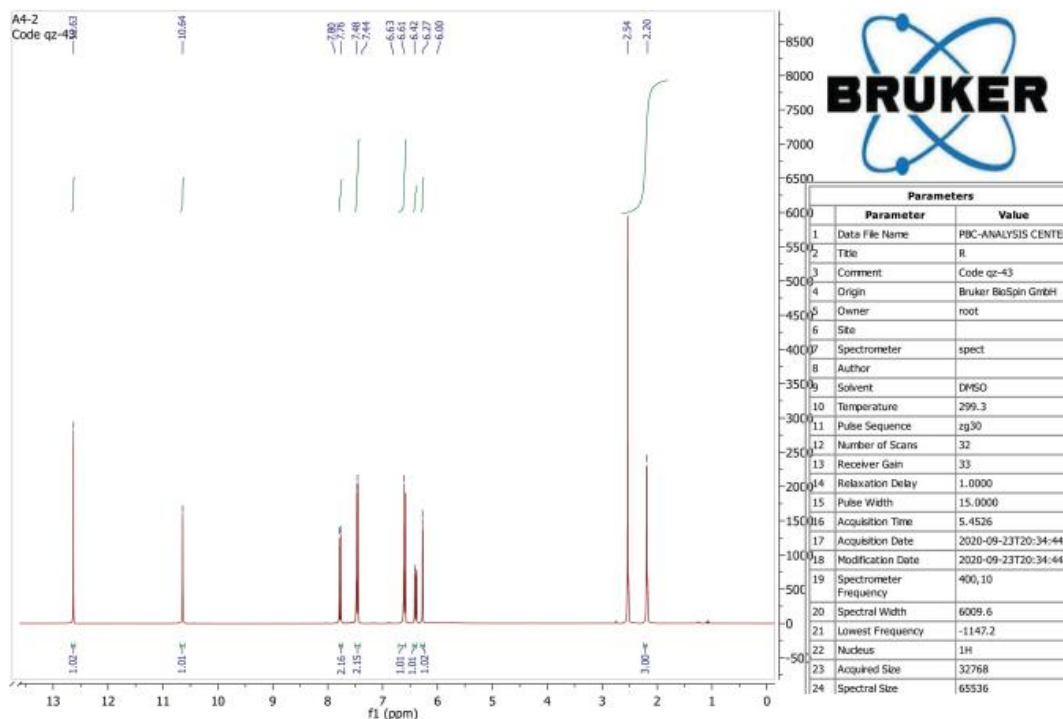


Figure 4: <sup>1</sup>H NMR spectrum for di-Schiff base 1.





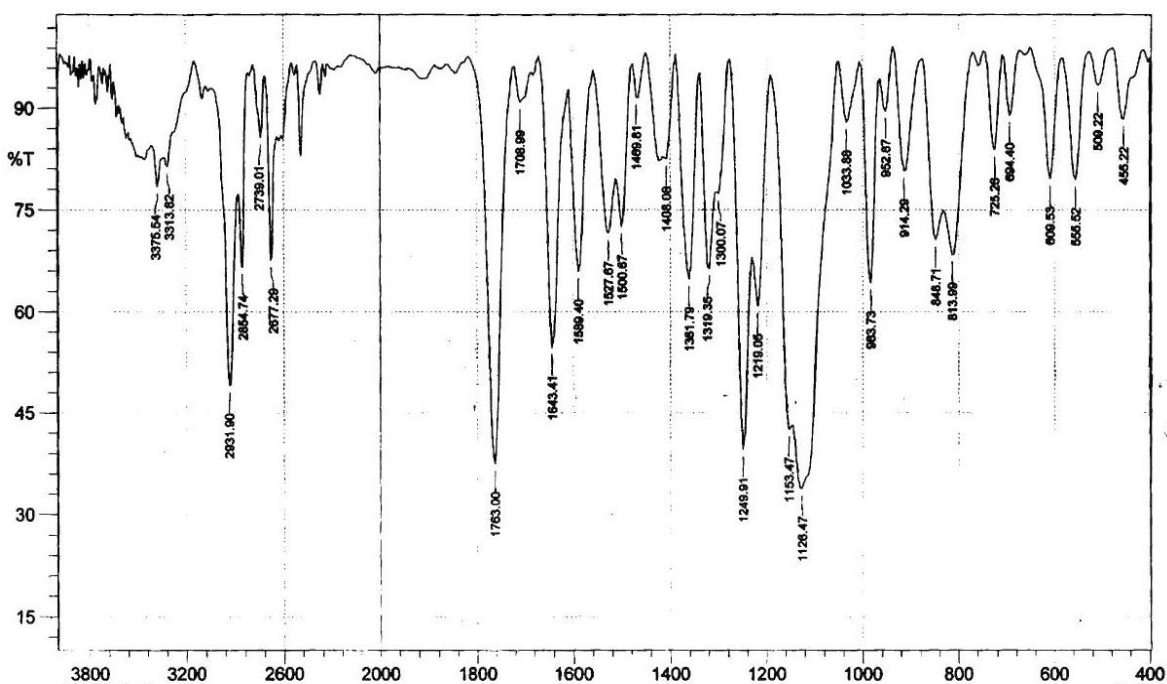


Figure 7: FTIR spectrum of polyester (E)

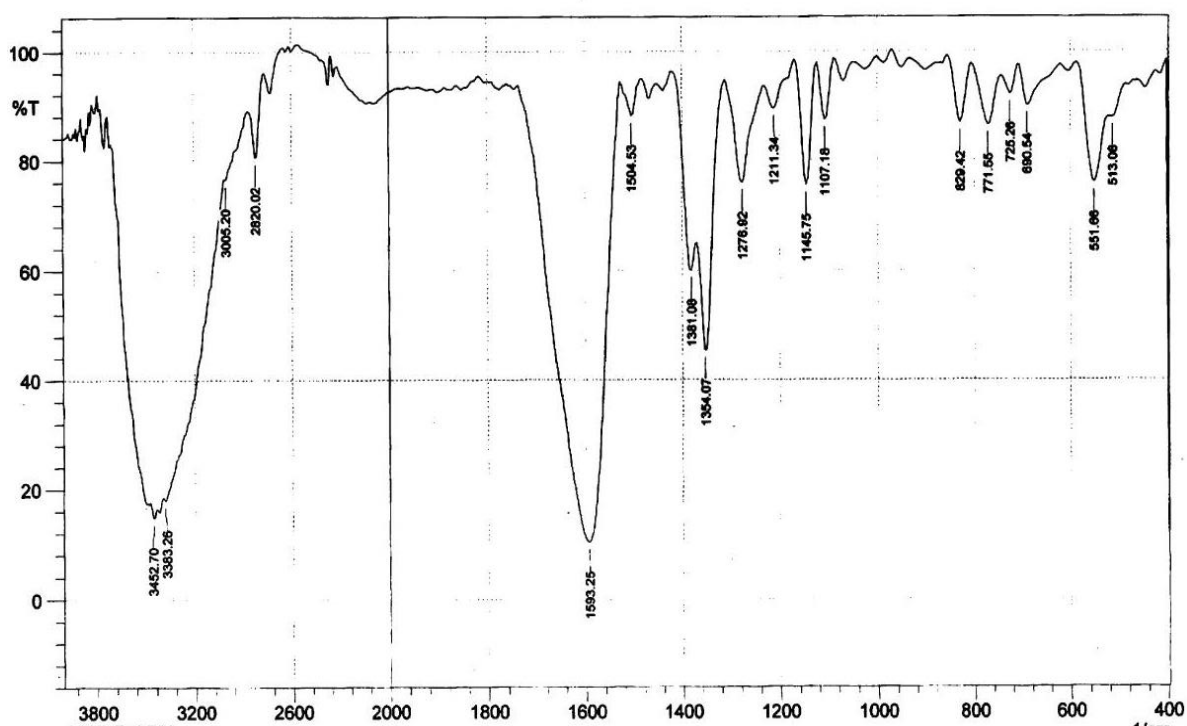


Figure 8: FTIR spectrum of phenolic resin (R<sub>1</sub>)



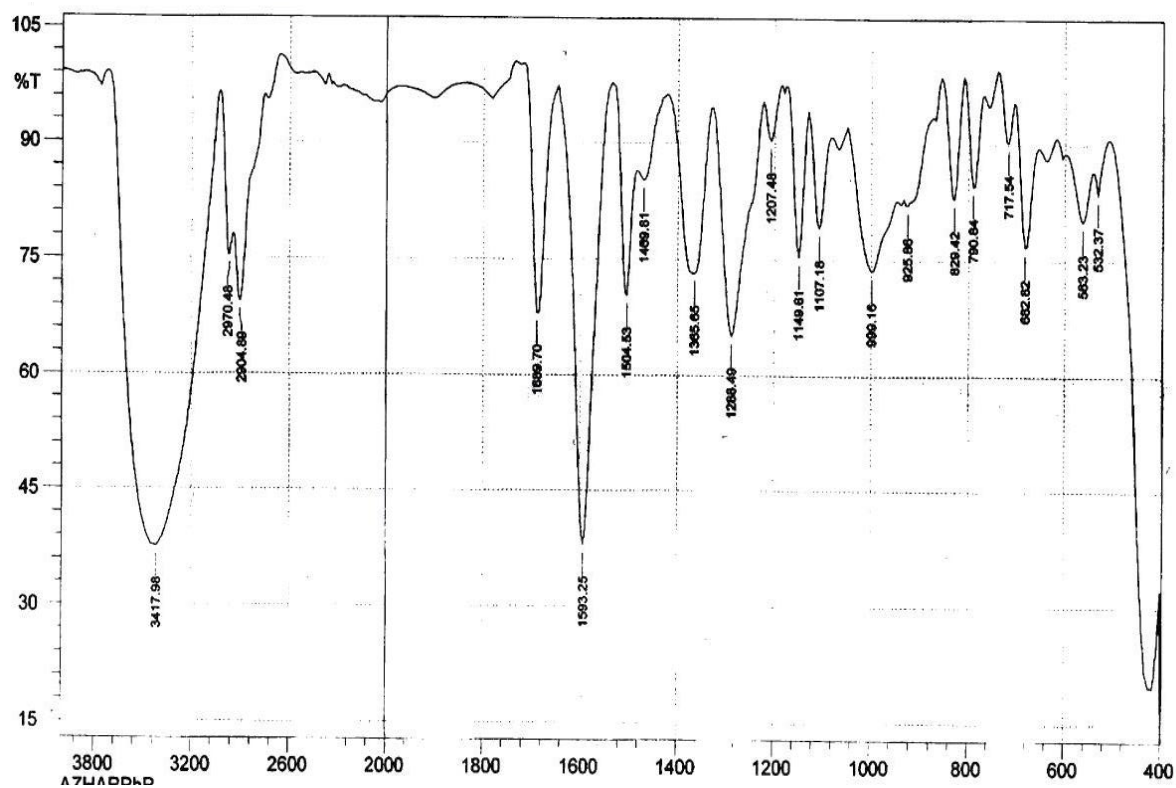


Figure 9: FTIR spectrum of phenolic resin (R<sub>2</sub>)

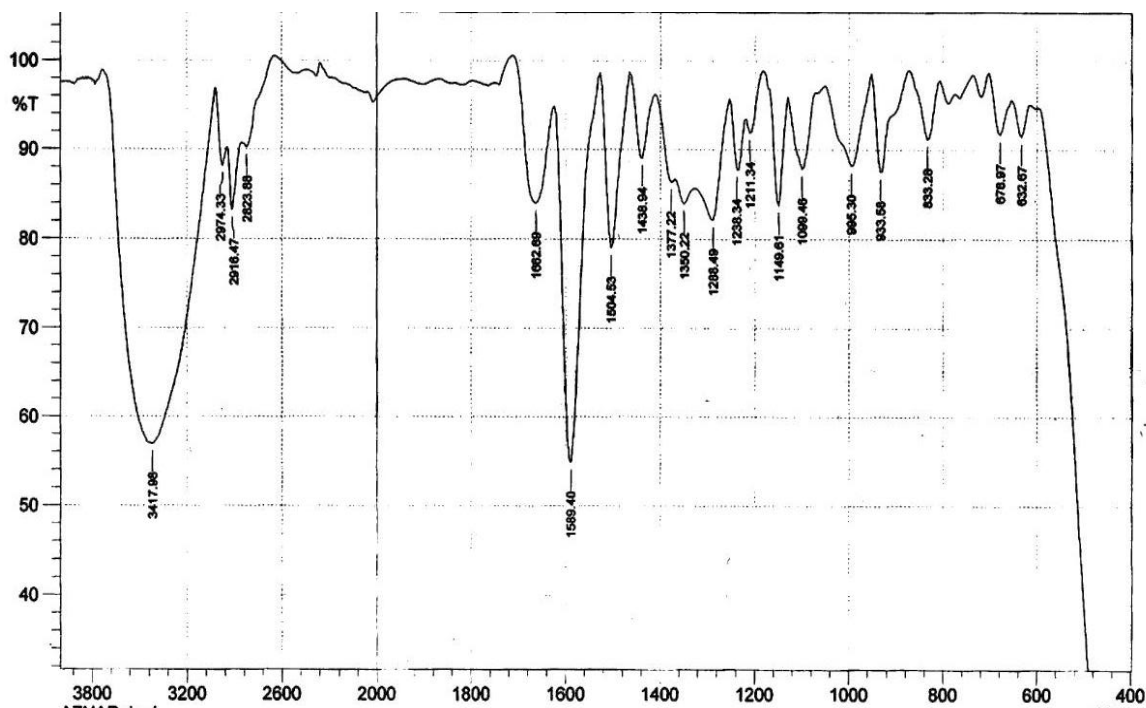
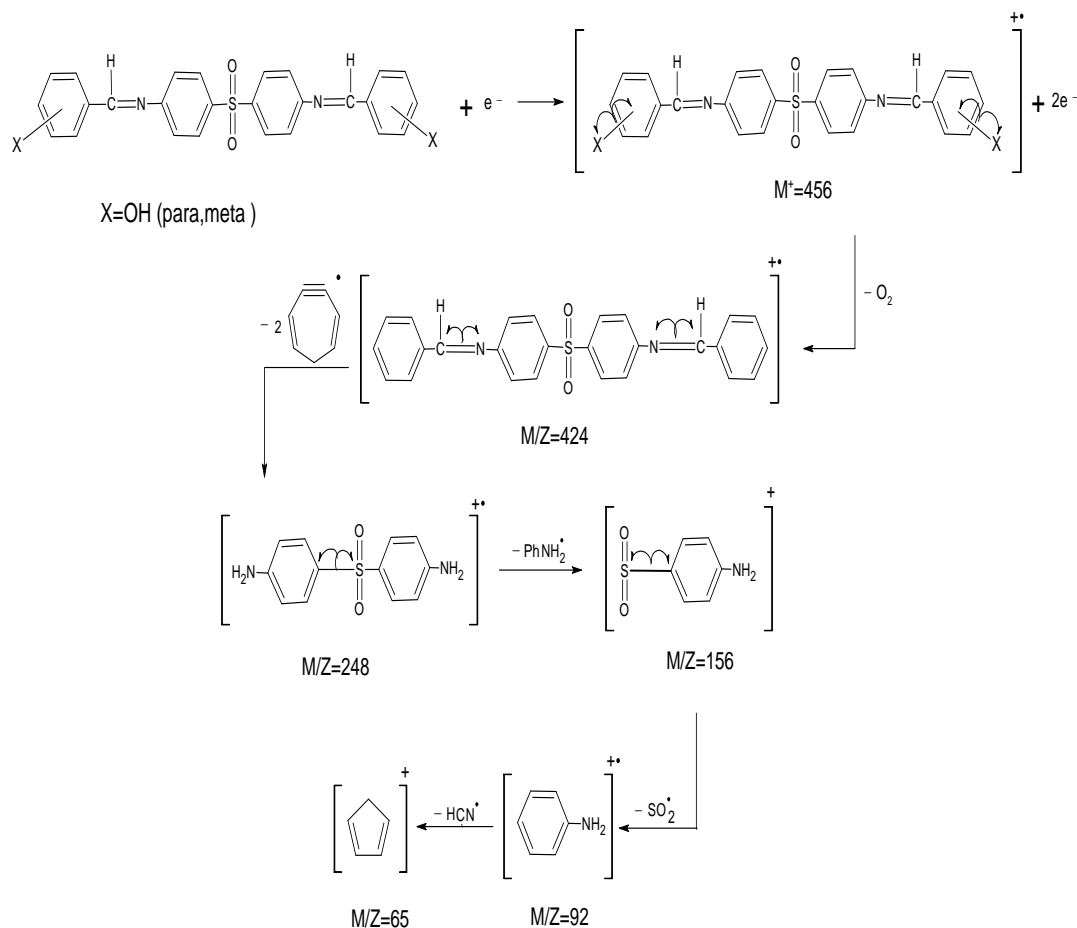


Figure 10: FTIR spectrum of phenolic resin (R<sub>3</sub>)





Scheme (6) Mechanism of fragmentation of 2 and 3 di Schiff base compounds

### 3.3 Thermal properties of synthesized polymers

Thermal analysis of polymers typically involves a combination of various techniques, including thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and evolved gas analysis (EGA).<sup>[11]</sup>

In TGA it determines the quantity and the frequency of weight variations of the samples against temperature and time in a controlled atmosphere. TGA can be used primarily to investigate the thermal stability, oxidative stability as well as the compositional properties (e.g. fillers, polymer resin, solvents) of the samples.<sup>[12,13]</sup>

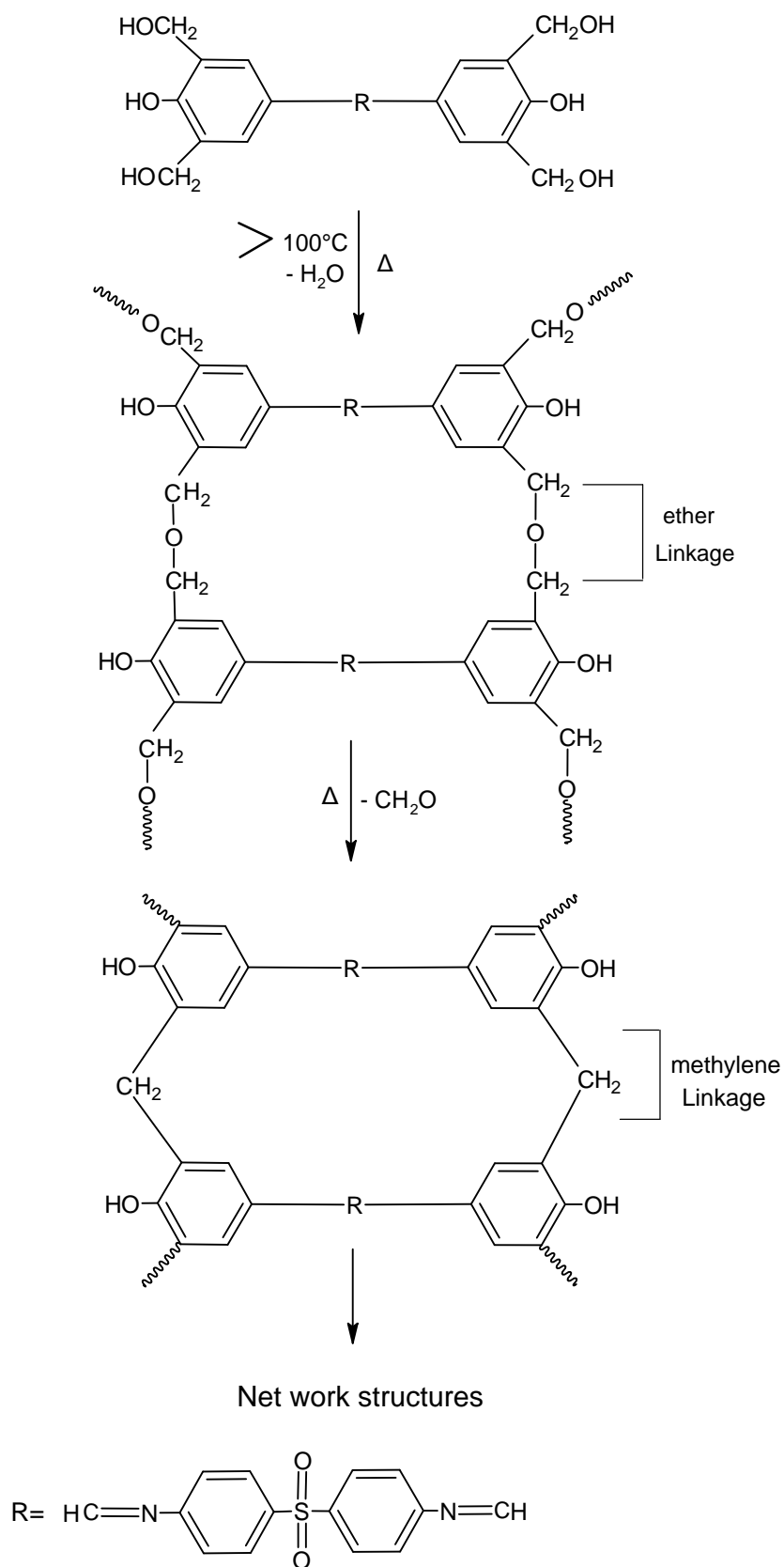
While the Differential Scanning Calorimetry (DSC) is a classic thermal analysis method of the thermal effects under controllable program temperature.<sup>[14]</sup> It is used in the research and development, it has been widely used in various occasion. Using the DSC method, we can study





the curing reaction of polymers, phase transition, melting of polymers, glass transition, temperature and the crystallization process. <sup>[15]</sup> For TGA study Figures (11-14) show the thermogram of the prepared polymers. Figure (11) show the spectrum of polyester, which have three stages of decomposition, first from 250 to 375°C, the second from 375 to 500°C. While the other from 500 to 800 C<sup>0</sup>. On the other hand, the temperature of 50% weight loss was 430 °C and weight residue was 18% at 800 °C. For the phenolic polymers Figures (12-14), show the TGA/DSC thermogram for polymers (R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>) respectively, the obtained result show that the curing temperature from DSC thermogram was 132 °C, 132 °C and 134 °C respectively this indicate the curing of the methylol resin presence in these polymers to formation of ether linkage then more cross linking occur when the temperature was rise, as shown in the scheme (5). while the TGA thermogram of these polymers show one decomposition temperature at 190 C<sup>0</sup>, 178 °C and 167 C<sup>0</sup> respectively. Also, the weight residue at 350 C<sup>0</sup> was 72.5%, 71.5% and 72.5% their high weight residue due to the more crosslinking in their polymer chain compared with polyester resin, so the prepared phenolic resin was more stable than polyester resin. Table (1) show some thermal parameter obtained from these thermograms.





Scheme(7) General curing of phenolic resin





Table 1: Some thermal parameter obtained from these thermograms

Curing temperature (DSC)	Rate of decomposition %/ min TGA	Residual at 350°C % TGA	Temperature at 50 % weight loss °C TGA	Decomposition temperature °C TGA			Sample No
				DT <sub>3</sub>	DT <sub>2</sub>	DT <sub>1</sub>	
---	3.56	55	430	649	434	259	E
132	2.01	72.5	> 350	-	-	190	R <sub>1</sub>
132	2.54	71.5	>350	-	-	178	R <sub>2</sub>
134	2.23	72.5	>350	-	-	176	R <sub>3</sub>

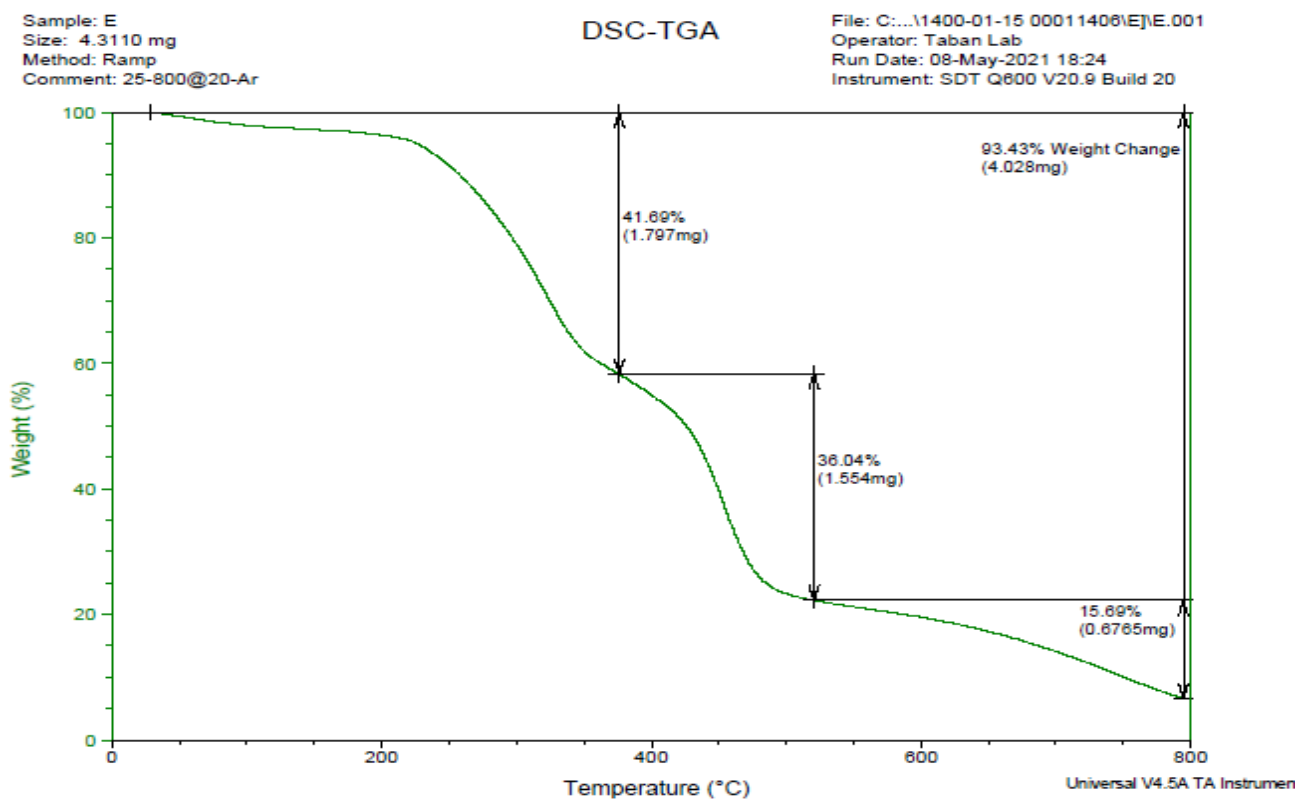


Figure 11: TGA thermogram of polyester prepared from Schiff-base 1.



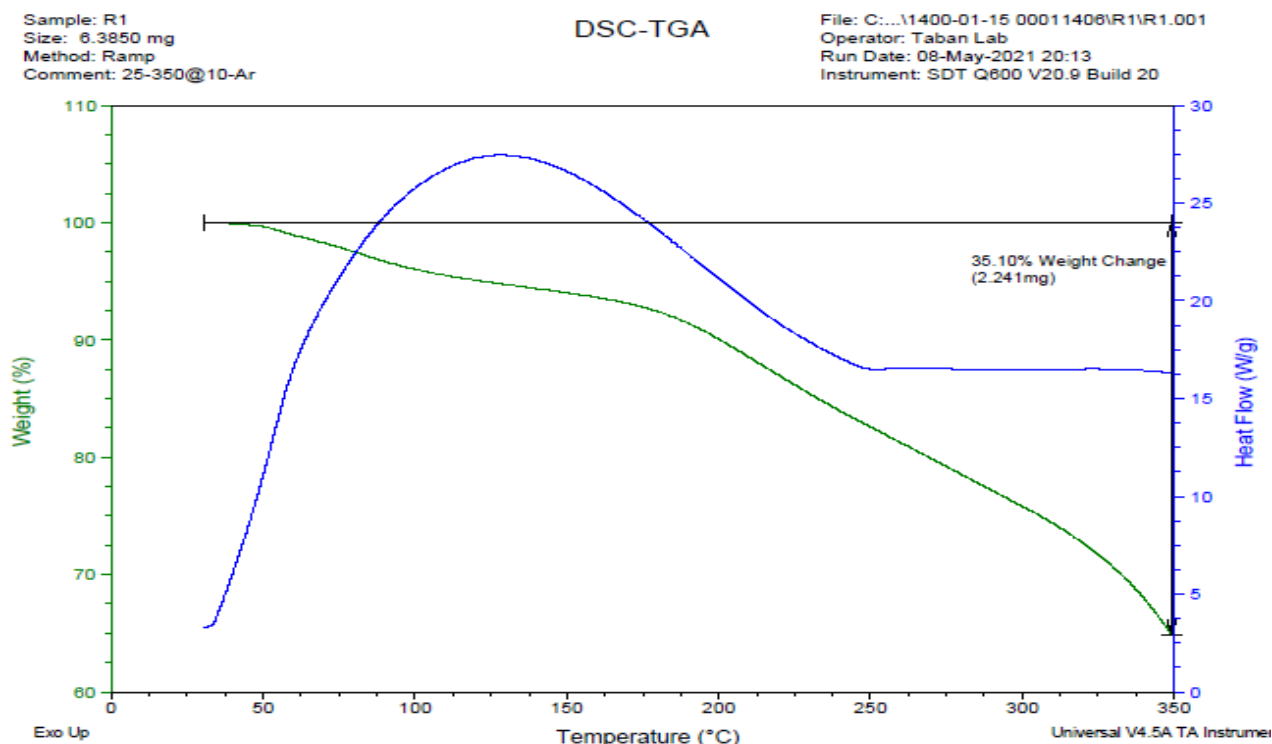


Figure 12: TGA-DSC thermogram of phenolic resin prepared from Schiff-base 1

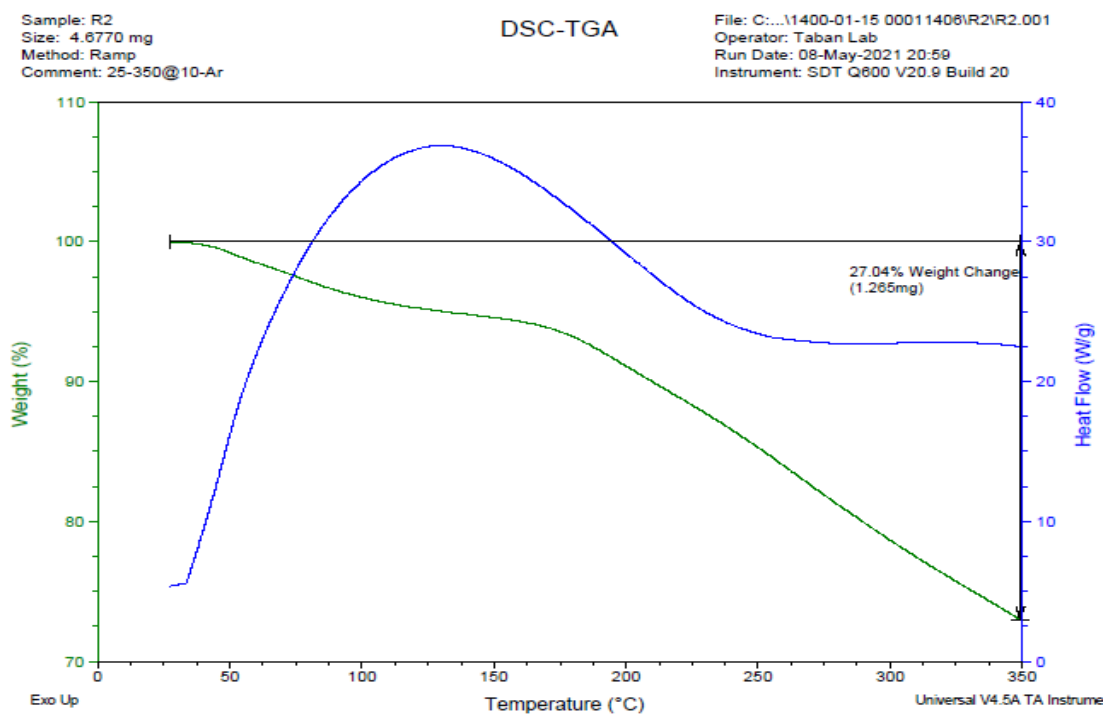


Figure 13: TGA-DSC thermogram of phenolic resin prepared from Schiff-base 2



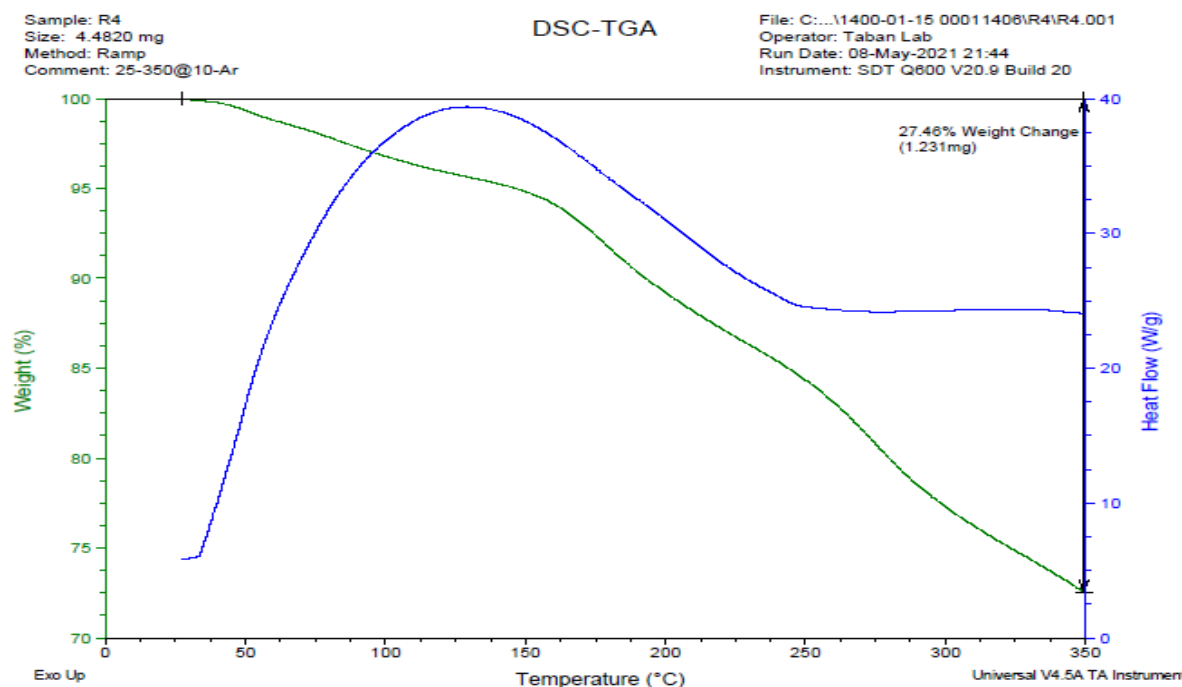


Figure 14:TGA-DSC thermogram of phenolic resin prepared from Schiff-base 3

#### 4. Conclusion

Schiff-base compounds are used in the field of chemistry with many advantages because they are used for synthesized a series of organic compounds and also in polymer chemistry. In this article new Schiff-based based on dapsone were prepared and characterized using FTIR, H-NMR and Mass spectroscopy, the results show good evidence with the chemical structure of the prepared compounds. On the other hand, new polymeric (polyester and phenolic resin) were prepared from these Schiff-base during condensation polymerization, thermal study and evaluation of these polymers were done using (TGA, DSC) techniques, and the result shown that these polymers have higher chare residue (more than 55% at 350 C<sup>0</sup>), also these polymers are differed in their rate of decomposition.



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### تحضير وتشخيص بعض قواعد شف مشتقة من الدابسون، بلمرتها ودراسة خصائصها الحرارية

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#### المستخلص

في هذه الدراسة حضرت ثلاث مركبات من قواعد شف من خلال تفاعل مركب الدابسون مع مركبات الكربونيل بوجود حامض الكبريتيك كعامل مساعد وباستخدام تقنية المايكرووفيف . شخضت المركبات المحضرة بالطرق الطيفية , حيث استخدمت تقنيات ( FTIR,HNMR ,Mass Spectroscopy ) لتحديد التركيب الكيميائي لنواتج التفاعل . ثم تم تحضير مجموعة من البوليمرات من البلمرة التكتيفية لتلك المركبات المحضرة وتم عزل نواتج البلمرة ثم درست الخواص الحرارية لها باستخدام تقنيتي ال ( التحليل الحراري الوزني والمسح التفاضلي المسعري ) وتبين بان تلك البوليمرات لها درجات تفكك اعلى من 150 درجة مئوية وان المتبقي من عملية القياس كانت بحدود 70 % مما يؤهلها باستخدامها كعوازل حرارية

