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## Synthesis of New polymers of Triazole Derivatives

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### Article Informations

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### ABSTRACT

Thiatriazole is an important monomer, whereby it has two types of functional groups: amine and thiol. Within the frame of this work, the triazole monomer has been prepared from its oxadiazole. Two types of polymers were prepared from this monomer via condensation with terephthaldehyde and succinyl chloride, whereby the binding units of the resulting polymers are differs, azomethine and amide respectively. Infrared spectroscopy and elemental analysis were used to identify the polymers. DTA, TGA and DSC analysis indicate the thermal history of the polymers. It was shown that polymer (1) was more flexible than polymer (2) due to the lower Tg value due to the presence of the azomethene group. The Tg are (138oC) and (190oC) respectively. Also the DTA, and TGA indicate that polymer (2) has higher thermal stability than polymer 1 due to the presence of the amide group.



## Introduction

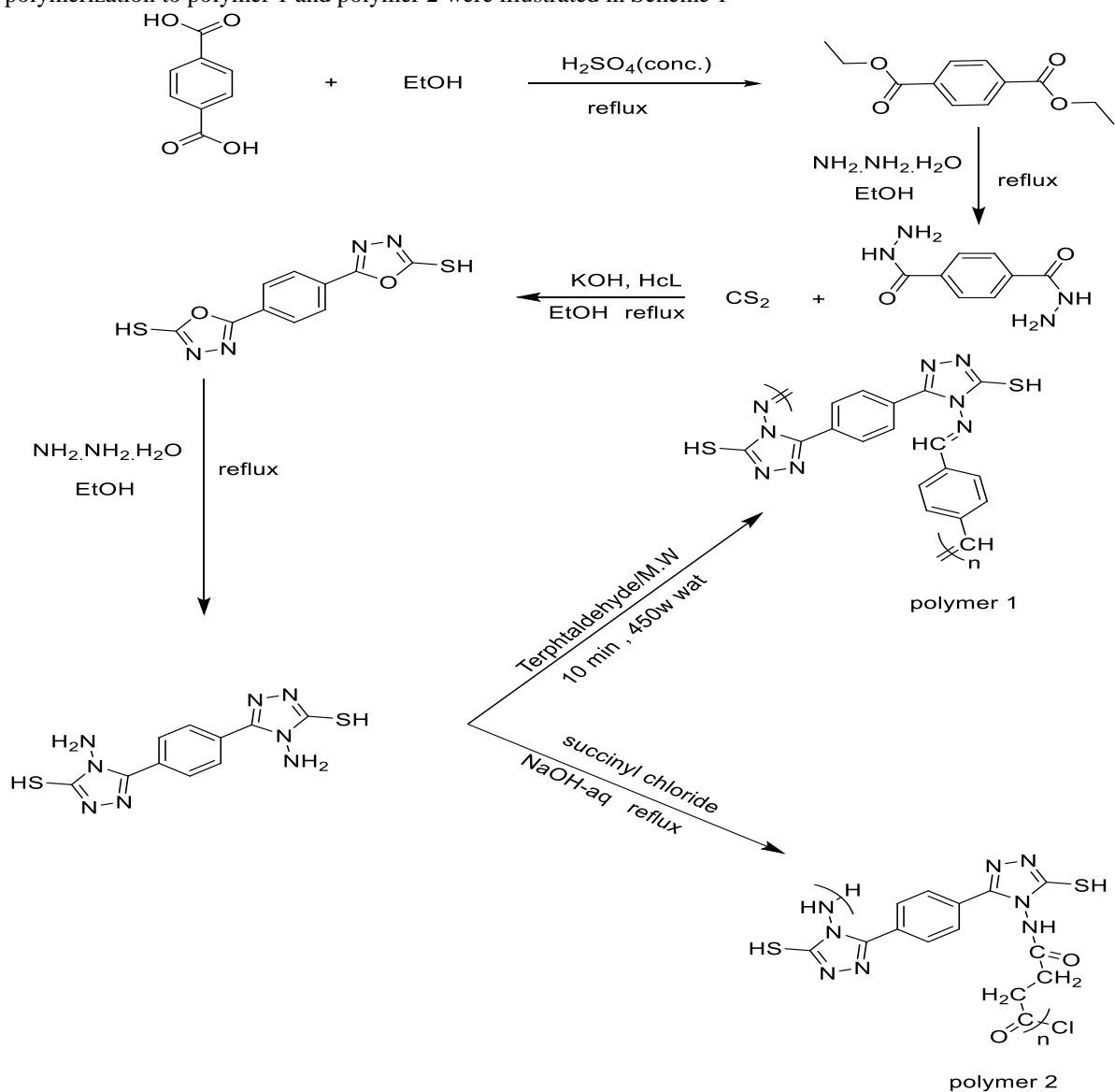
Triazoles are heterocyclic aromatic compounds with the general molecular formula  $C_2H_3N_3$  [1] and relatively high stability compared with other three adjacent nitrogen compounds, in spite that, some triazoles are relatively easily cleaved by ring chain tautomerism [2]. The ability of triazoles to form hydrogen bonding increases the solubility [3]. Triazole compounds and their heterocyclic derivatives are of great importance because they have medical effectiveness [4][5], as they represent the active group in many drugs such as triazolam, alprazolam, and etizolam, in addition to their commercial importance in the dye industry [6]. Bio-isostere derivative of triazole has received considerable attention in pharmaceutical and medicinal chemistry, which are used in the discovery and development of drugs of triazole [7]. Other specific applications of triazole and triazole derivatives, were facilitators of proton transport in polymer membrane fuel cells [8].

A selective synthesis of disubstituted triazoles by the building of primary amines, enolizable ketones, and 4-nitrophenyl azide as a source of dinitrogen group has been developed [9]. A catalyzed copper reaction was used to synthesize the derivative of 1,2,3-triazoles [benzimidazole-linked] by the reactions between aromatic azides and n-propynylated benzimidazole in the presence of copper as catalyst [10].

In this study, a new derivative of triazole has been prepared and used to synthesis the monomer of these derivatives followed by a polymerization step to form a spectroscopically identified compound.

## Experimental:

"A series of reaction steps for preparing the triazole derivative monomer, which undergoes two polymerization to polymer 1 and polymer 2 were illustrated in Scheme 1"



**Scheme 1:** The chemical steps for the synthesis of triazole derivative -monomer and polymers 1 and 2.

## The synthesis of triazole derivative -monomer

Triazole compounds possess two amino and mercapto groups, which are nucleophilic sites useful for organic synthesis [11]. A series of reaction steps was followed to prepare the triazole derivative monomer, which then undergoes polymerization according to the following steps

### 1-Preparation of ester:

This step includes the formation of ester by reflux of terephthalic acid in absolute ethanol and acidic medium according to the following procedure [12]: 0.1 mole (16.6g) of terephthalic acid was dissolved in 200 ml of absolute ethanol and 8 ml of conc. sulfuric acid was added. The reaction mixture was refluxed for ten hours. After refluxing, the excess ethanol was distilled off, crushed ice (50 ml) was added to the mixture with stirring, and the precipitate formed was filtered, dried, and recrystallized from ethanol. The measured melting point of the dried white product is (58-60) oC. The reaction has been summarized in Figure 1.

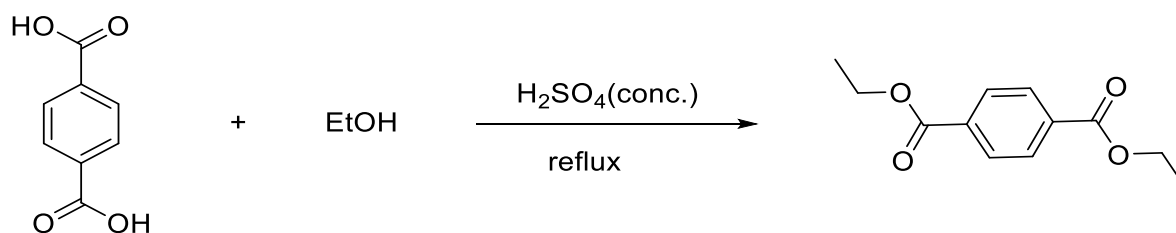


Figure 1. The chemical reaction of formation of the terephthalate ester

### 2- Preparation of acid hydrazide

The formed ester in the last step was reacted with the hydrazine hydrate according to the following procedure: 0.02mole, (4.44 g) of ester, and 30 ml of 0.08 mole of hydrazine hydrate were charged to the reaction vessel, and the mixture was refluxed for three hours using oil bath, then 100ml of absolute ethanol was added and refluxed with the reaction mixture for another three hours using water bath. The excess ethanol was distilled off, the precipitate was cooled, filtered, dried, and recrystallized form ethanol, the measured melting point of the dried white product was 310 to 312o C [12]. Figure 2 shows the chemical reaction of the preparation of acid hydrazide.

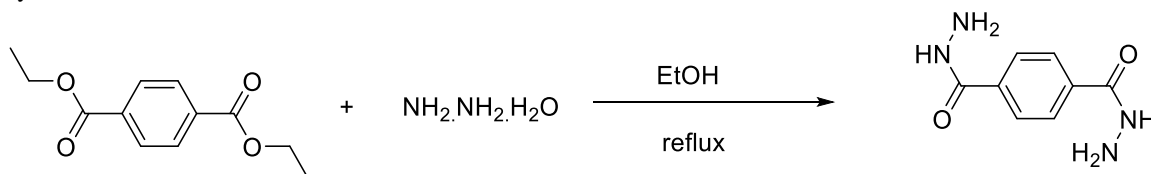


Figure 2. The chemical reaction of the formation of the acid hydrazide

### 3-Preparation of 1,3,4-oxadiazole

The 0.025 mole (4.85 g) of hydrazide derivatives was mixed with 3g of potassium hydroxide dissolved in a minimum amount of water and added to a reaction vessel containing 75 ml of absolute ethanol, followed by a gradual addition of 3 ml of carbon disulfide with stirring in a cold-water bath, the mixture was refluxed for ten hours. The excess ethanol was distilled and 100ml of crushed ice was added with stirring and acidifying using (1N) HCl to pH=2. The precipitate was filtered, dried, and recrystallized from ethanol-water[13,14]. The measured melting point of the formed dried precipitate is 288 to 291°, and its color is light yellow. Figure 3 shows the chemical equation of the preparation of oxadiazole.

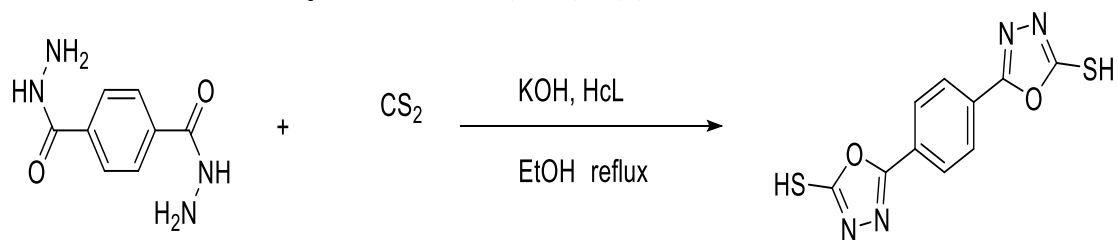


Figure 3. The chemical reaction of the formation of 1,3,4-oxadiazole

#### 4-Preparation of triazole derivative (monomer :

The final step in synthesis of the monomer consists of mixing 0.01 mole (2.78g) of oxadiazole with 10 ml of the hydrazine hydrate in 100 ml of absolute ethanol. The mixture was refluxed for 8 hours, the excess of ethanol was distilled off and 100 ml of crushed ice was added with stirring, the pH of the mixture was adjusted to 2 using 1N HCl. The precipitate was filtered, dried, and recrystallized from ethanol [13]. The measured melting point of the dried precipitate is 230-232 oC, its color is off-white. Figure 4 shows the chemical reaction of this step.

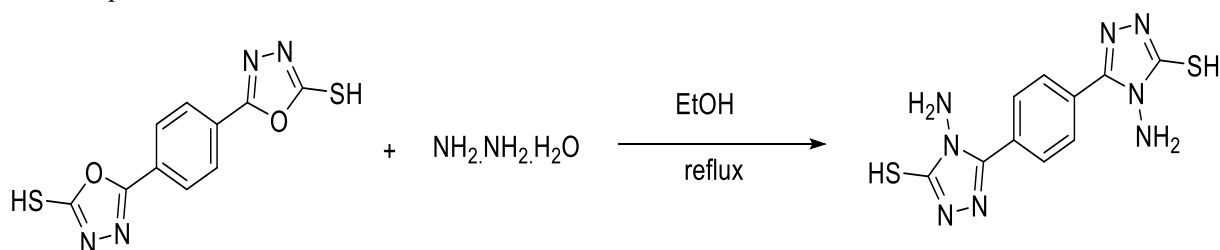


Figure 4. The chemical reaction of the formation of triazole derivative (monomer)

#### Preparation of Polymer (1):

Terephthalaldehyde the isomer of benzene di-carboxaldehyde, was used to prepare the polymer of triazole derivative by mixing 0.005 moles (1.53g) of triazole derivative, with 0.005 moles (0.67g) of terephthalaldehyde in a test tube, the mixture is then put in a microwave oven (450 watts) for 10 minutes. The appearance of dark yellow indicates the formation of the polymer as shown in the chemical equation in Figure 5. The melting point of the product is 305o C.

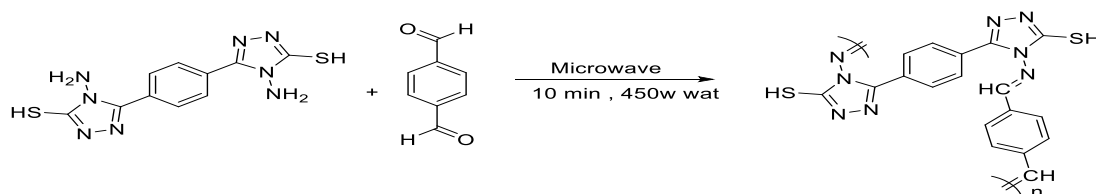
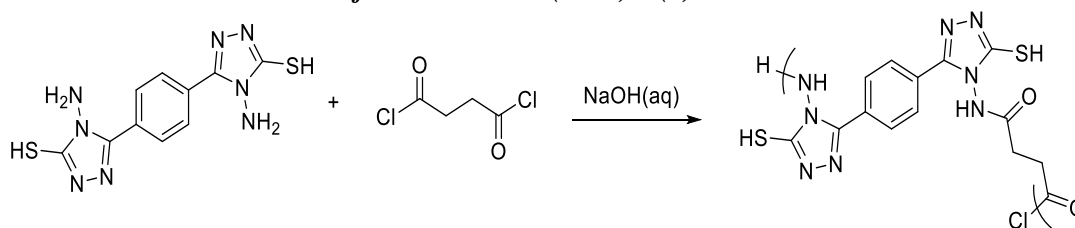


Figure 5. The chemical reaction of the formation of triazole derivative (polymer 1)

#### Preparation of Polymer (2):

Succinyl chloride, the acyl chloride derivative was used to form the triazole derivative polymer 2 by adding 0.05 moles of succinyl chloride in dry normal hexane to 0.005 moles (1.53 g) of triazole derivative dissolved in 10% solution of sodium hydroxide gradually with stirring for one hour, then the precipitate was separated by using a centrifuge, washed with distilled water and dried, the measured melting point of the dried polymer 312oC and its color is light yellow, the chemical reaction is shown in Figure 6.



**Figure 6.** The chemical reaction of the formation of triazole derivative (polymer 2)

## Results and Discussion

Proving the structural formula of the polymers formed

1.Elemental Analysis (CHNS)

2.Elemental analysis (**CHNS**) was used for proving the composition of prepared polymers. The elemental analysis data for polymer exhibit a reasonable agreement between the found and calculated data as shown in Table 1.

**Table (1):** The (CHNS) analysis data of prepared Polymers

sample	% Calculated				% Found			
	C	H	N	S	C	H	N	S
<b>Polymer(1)</b>	53.59	2.72	27.79	15.88	52.11	4.35	29.3	13.4
<b>Polymer (2)</b>	43.29	3.09	28.86	16.49	44.08	4.12	29.86	14.92

## FTIR analysis

Figure (7) shows the IR spectrum of prepared monomer triazol derivative.

Figure (8) shows the IR spectrum of prepared polymer (1), whereby the band appeared at (1772) cm<sup>-1</sup> belonged to (C=N) of the azomethane group, another evidence for the formation of this polymer is the disappearance of (NH<sub>2</sub>) group at (3253) cm<sup>-1</sup> which was appeared in the spectrum of the monomer figure (7)

Figure (9) represents the IR spectrum of the prepared polymer (2), in which new bands appeared at (1557 s 1601) cm<sup>-1</sup> for (C= O) of amide groups and at (3066) cm<sup>-1</sup> for methylene group are very good evidence for the formation of this polymer. The IR spectra data of monomer and polymers are shown in Table (2) and in Figures 7, 8, and 9 respectively.

**Table (2):** The IR characteristic bands and their locations for organic compounds (monomer, polymer 1, and polymer 2)

Groups	IR-V(cm <sup>-1</sup> )						
	C=N (triazole)	S-H	C-S (Aromatic)	N-N	C=O (amid)	N-H (amid)	other
<b>Sample</b>							
<b>monomer</b>	1479	2550	1291 1320	1414	----	-----	NH <sub>2</sub> 3253
<b>Polymer 1</b>	1480	2559	1240,1266 1280,1308	1416	----	-----	C=N (Azomethene) 1772
<b>Polymer 2</b>	1473	2588	1124,1168 1291,1317	1414	1557 1601	3464	CH <sub>2</sub> (methylene) 3066

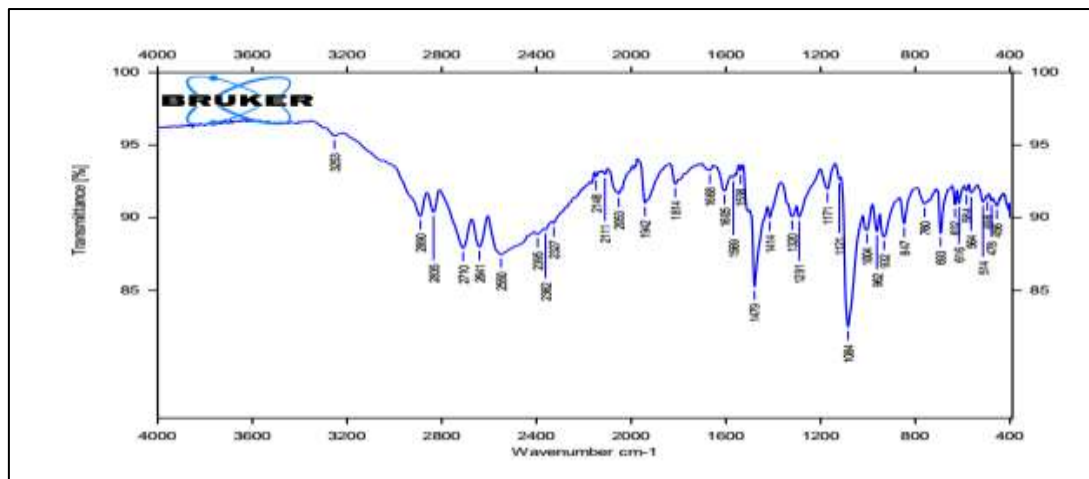


Figure 7. IR – spectrum of the triazole monomer

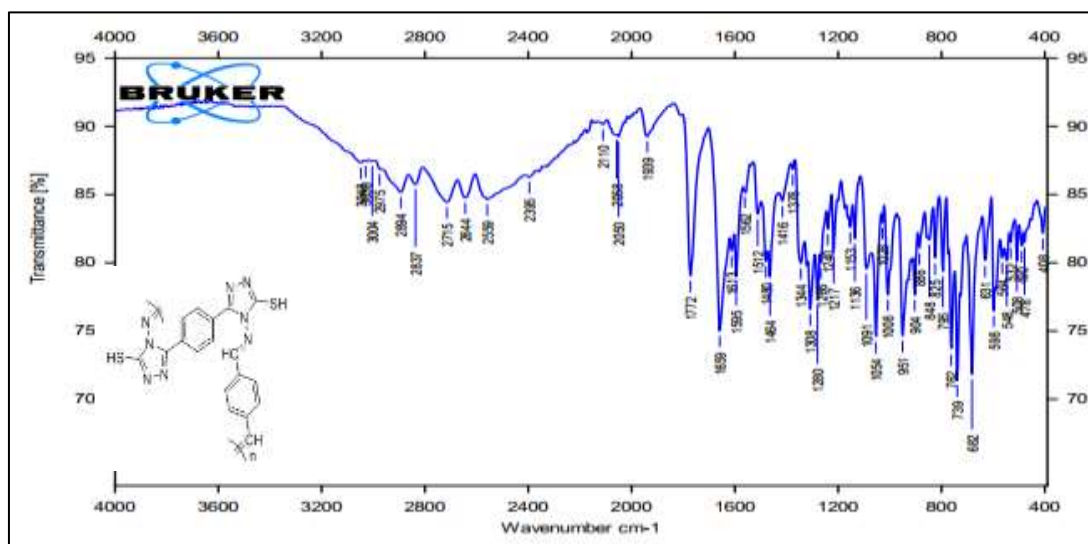


Figure 8. IR – spectrum of polymer(1)

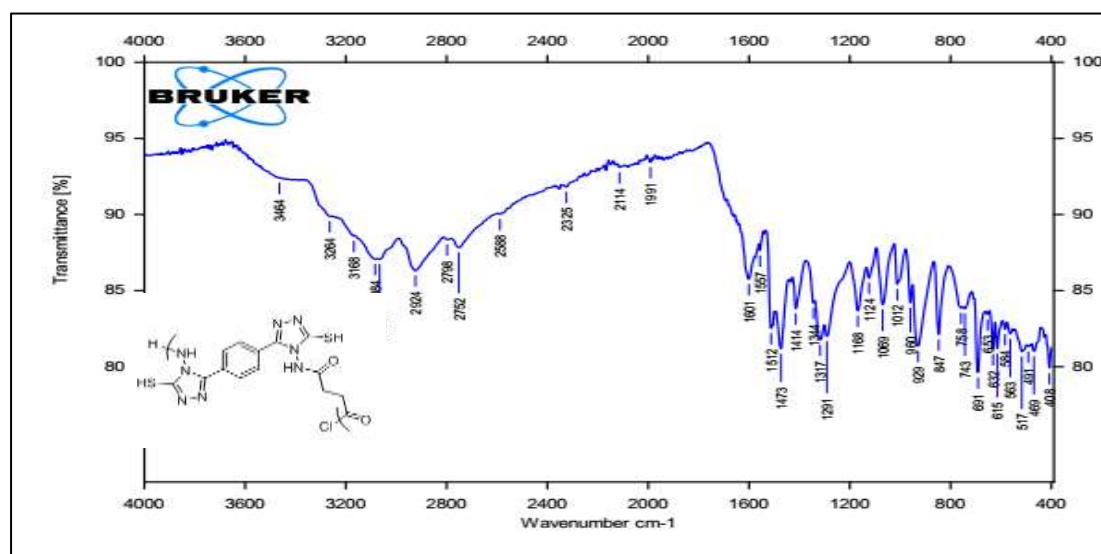


Figure 9. IR – spectrum of polymer (2)

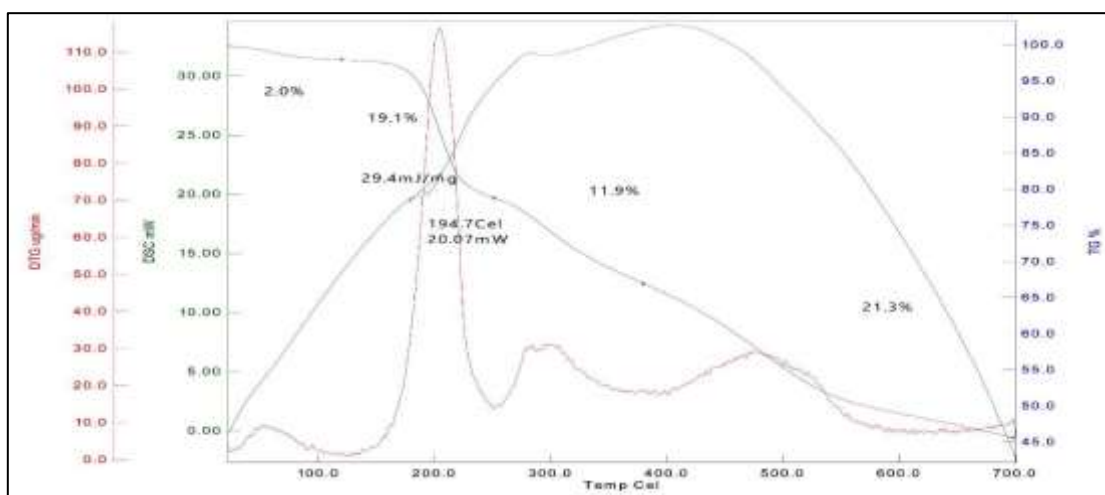
**Thermal analysis:**

The Differential Thermal Analysis (DTA) technique: determines endo- and exothermic event temperatures, and shows phase transitions. Thermogravimetric Analysis (TGA) technique: determines decomposition/mass loss over a temperature range and Differential Scanning Calorimetry (DSC) technique: used to investigate the response of polymers to heating. DSC can be used to study the melting of a crystalline polymer or the glass transition temp. of the prepared polymers were recorded at heating rate of (20o C/ min) under a nitrogen atmosphere. DSC thermogram of the polymer (1) shows Tg at (138oC), while the TGA and DTG differential thermogravimetry is a derivative of TGA that measures the rate of weight change as a function of temperature and reveal the thermal history. The Sample loses (15.5%) of its weight at (135oC), (52.8%) at (241oC) and completed decomposition at (500oC). (Figure 10)

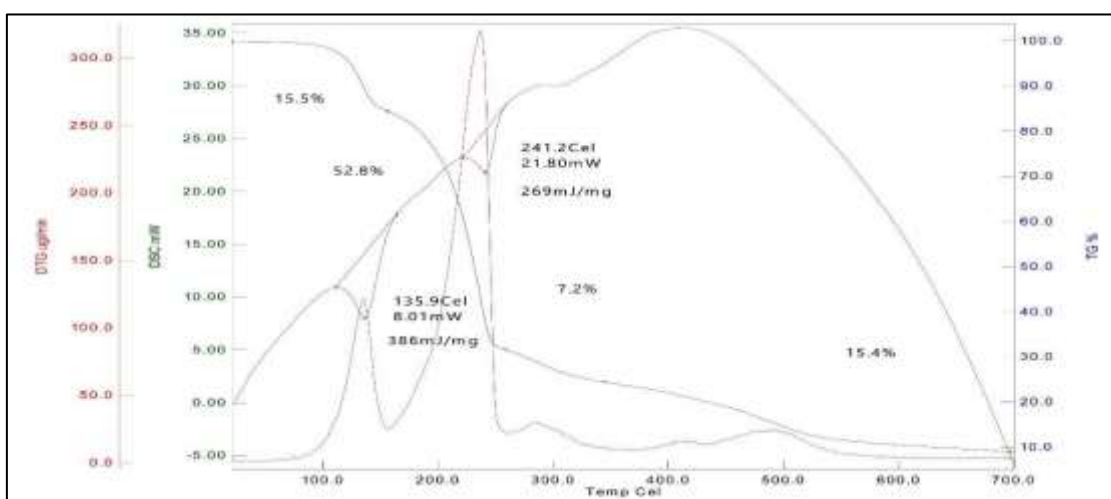
On the other hand, the DSC thermogram of the polymer (2) shows Tg at (190o C). TGA and DTA (figure 11) indicate that the sample loses about (19.1%) of its weight at (194.7oC) and (50%) at (550oC).

The results indicate that polymer (1) was more flexible than polymer (2) due to the lower Tg value due to the presence of the azomethene group.

As well as, the polymer (2) showed more thermal stability due to the presence of the amide group, which is difficult to decompose



**Figure 10.** Thermogram of polymer (1)



**Figure 11.** Thermogram of polymer (2)

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