

# Thermal Stability of Novel Maleimide Polymers Based on Dapsone

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## ABSTRACT

In the present study, new homo and Copolymers maleimide were synthesized based on the polymerization of maleimide compound which synthesized from sulfa drugs. The first step including Azo coupling reaction of Dapsone with *p*-nitroaniline to synthesized compound (A). The compound (A) was converted to Amic acid, compound (B) via reaction with maleic anhydride. The compound (B) when react with acetic anhydride in the presence of sodium acetate it will be give maleimide compound (C). The Homopolymaleimide polymer (D) can be obtained by heated maleimide compound (C) with AINB initiator. While maleimide compound (C) was converted to copolymer maleimide when react with acryl amide in the presence of AINB initiator using DMF as a solvent. All the synthesized compounds have been characterized by TLC, FT-IR, <sup>1</sup>H-NMR Spectroscopy and <sup>13</sup>C NMR spectroscopy and study the thermal properties.

**Keywords:** TGA, DSA, Dapsone, Maleimide.

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## INTRODUCTION

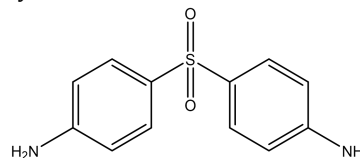
Thermogravimetric analysis (TGA) or thermogravimetry (TG) and Differential Scanning Calorimetric (DSC) is one of the Thermal analysis methods in which the thermal stability of polymer will be study via the determine the change of the weight of the polymer as a function of time or Temperature in controlled atmosphere <sup>(1)</sup>, in which the atmosphere used can be inert gases, or oxidizing, such as air or reducing, such as forming gas (normally consist of 10% hydrogen in nitrogen). In the case analysis of polymers, a reducing atmosphere is used <sup>(2)</sup>. Thermogravimetry method is most beneficial for dehydration, desorption, decomposition and oxidation processes <sup>(3)</sup>. Differential Scanning Calorimetric (DSC) is a technique of thermal analysis utilized to determine the physical properties of the polymer such as glass transition, melting crystalline polymer <sup>(4)</sup>, and changes in the enthalpy or entropy <sup>(5)</sup>. The construction of DSC instrument is consist of the measurement chamber and computer. There are two pans are heated in the measurement chamber one for the sample and another one for the reference, the computer will be utilized to monitor and regular the rate of the temperature change in the two pans, normally the rate of temperature change is about 10 °C per minute, the change of temperature between the substance and the reference is near to zero, and in which the change of temperature between two pans depended on the composition of the pan content and also the physical change like phase change, the result is plot of the different of heat (q) against the temperature (T)<sup>(6)</sup>.

Sulfa drugs are chemical compounds containing of sulfonamide moiety (SO<sub>2</sub>NH<sub>2</sub>) in their structure <sup>(7)</sup>. Last time sulfa drugs was synthesized to use as antimicrobial agent <sup>(8)</sup> and today are still widely used as preventive and therapeutic compounds against of different bacterial infection in various applications such as eye infection, influenza, meningitis, actinomices infections and urinary tract infections <sup>(9-10)</sup>. and also used as antibiotic to treatment the infectious diseases such as inhibitor agent against tumor cells <sup>(11)</sup>, anti-thyroid <sup>(12)</sup>, hypolycaemic<sup>(13)</sup>,

anticancer, anti-inflammatory<sup>(14)</sup> and several other applications in different fields<sup>(15-17)</sup>.

The chemistry of maleimide has a great interesting in both scientific and industrial field, maleimide are unsaturated imide compounds has a functional group – CO-NH-CO-. The N-H group of maleimide can be replaced by either alkyl or aryl groups <sup>(18-19)</sup>. This work focused on the synthesis *N*-substituted maleimide from Dapsone.

The synthesized maleimide can by polymerized via addition polymerization with free radical initiators <sup>(20)</sup>.



**Figure 1:** Structure of Dapsone

## MATERIAL AND METHODS

All the chemicals are commercially available and used without further purification these included Dapsone supplied by Fluka AG, *p*- amino acetophenone and sodium acetated by sigma – Aldrich, maleic anhydride and acetic anhydride supplied by Fluka AG, DMF, Methanol and Ethanol, sigma – Aldrich. Melting points of prepared compounds were determined using a stuart melting point SMP30 apparatus. The FTIR spectra for prepared compounds were recorded on Bruker FTIR -8400S spectrophotometer using KBr disc. The <sup>1</sup>H-NMR spectra were recorded on a Fourier transform Bruker spectrometer operating at 400 MHz in DMSO- d and <sup>13</sup>CNMR in DMSO.

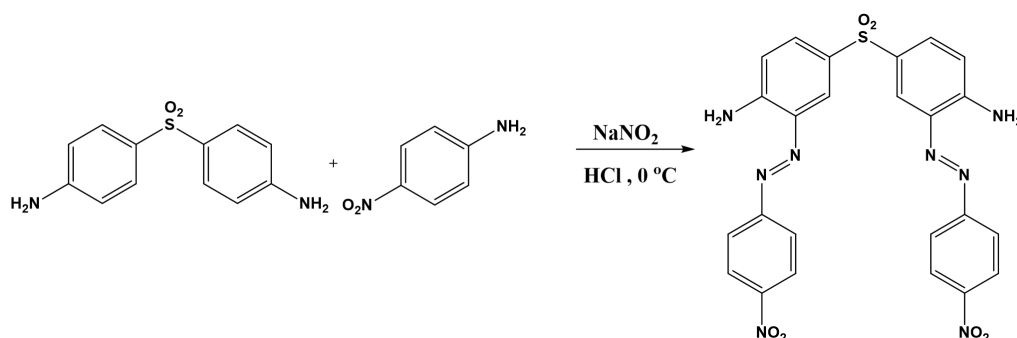
### Synthesis of Azo Compound (A):

(0.02 mole, 2.8g) from (*p*-nitroaniline) was dissolved in the beaker containing 3ml of concentrated hydrochloric acid and 12 ml of distilled water and then cooled the solution at (0-5 °C) in ice water bath. The sodium nitrate solution was prepared in another beaker by dissolved (0.02 mol.,1.38 g) in 5ml of distilled water and also cooled at (0-5 °C) and then added it slowly to solution one at the same temperature with constant stirring by the magnetic stirrer.

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The formed diazonium salt solution was kept at (0-5 °C) and added dropwise to (0.01 mol., 2.48 g) Dapsone solution prepared in 10% sodium hydroxide solution, the pH was maintained between (7-8) at temperature (0-5 °C)

and then the mixture was stirred for 30 min. The final product was precipitated, filter out and then wash it with distilled water several times and recrystallized with ethanol.

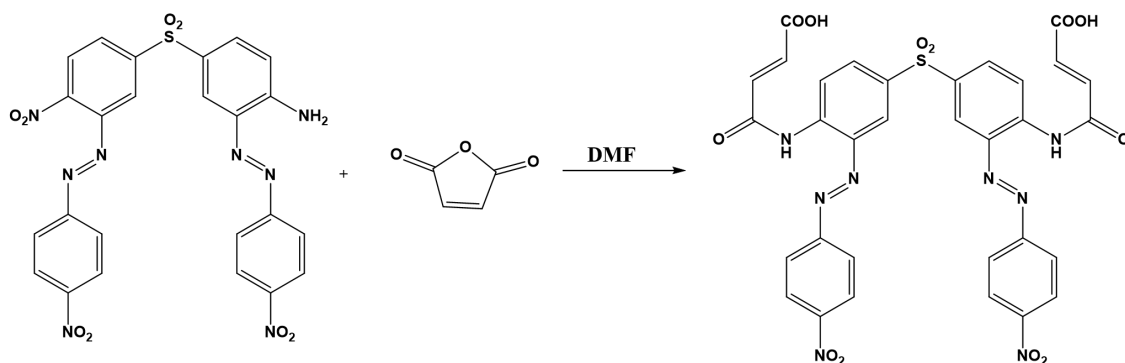


**Scheme I: synthesis of monomer (A)**

### Synthesis of Amic acid Compound (B):

(0.02 mol., 1.96 g) of maleic anhydride was dissolved in 10 ml of dimethylformamide (DMF) and then added directly for 10 min to (0.01 mol., 5.2 g) of (A) compounds it was dissolved in 10 ml of DMF respectively. The solution of mixture is stirred by using magnetic stirrer for

2 hr at room temperature. The reaction progress is monitored by using TLC and finally the reaction mixture was poured in to crushed ice to precipitate crude (B) filter out the end product and dried it by oven at 60 °C and recrystallized by using ethanol.

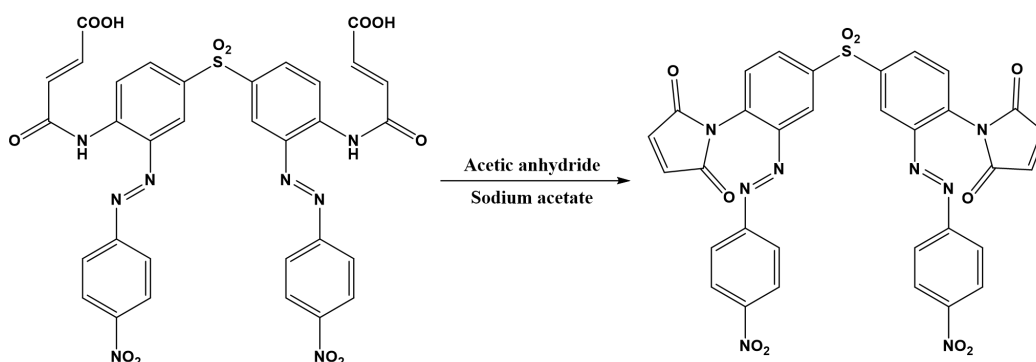


**Scheme (II): synthesis of amic acid (B)**

### Preparation of Maleimide Compound (C):

(0.001 mol., 0.72 g) of compound B, was dissolved in 25 ml of acetic anhydride, and added to this solution 0.6 g of anhydrous sodium acetate and then stirred the mixture for 6 hours at 60 °C. The progress of the reaction is

monitored by the TLC. After the reaction is complete it was left to cool and then pour in to crushed ice to obtaining compound (C), filtered and dried at 70 °C and recrystallized via ethanol.

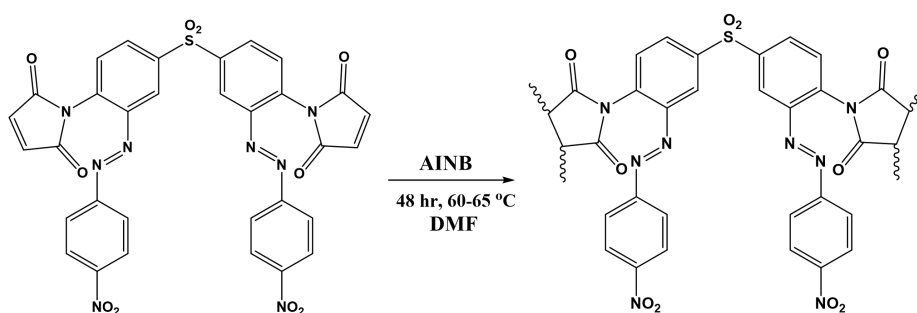


**Scheme (III): synthesis of Maleimide (C)**

### Synthesis of Homopolymer maleimide compound (D):

In three neck bottom flask dissolved a (0.001 mol., 0.7 g) from compound (C) in 25 ml of DMF and added small amount of AIBN approximately 0.1 g as a free radical initiator and heat the mixture on the hot plate stirrer at

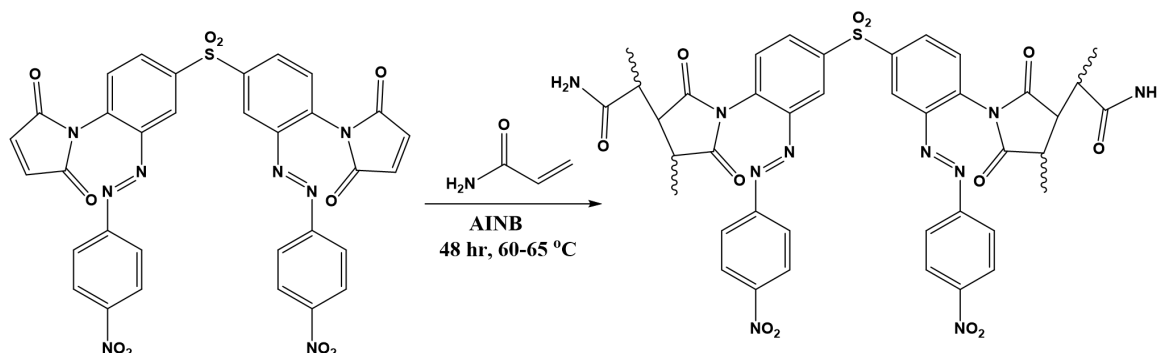
65 °C for 48 hours. The homopolymer was isolated by precipitation in the mixture of methanol and water and finally the isolated polymer was washed several times with methanol and dried via oven at 60 °C.



**Scheme (IV): synthesis of Homopolymer of maleimide**

In three neck bottom flask dissolved a (0.001 mol, 0.7g) from compound (C) in 25 ml of DMF and added (0.001 mol, 0.08 g) of acrylamide with small amount of AIBN approximately 0.1g as a free radical initiator and head the mixture on the hot plate stirrer at 65 C for 48 hours. The

copolymer was isolated by precipitation in the mixture of methanol and water and finally the isolated polymer was washed several times with methanol and dried via oven at 60 C.



**Scheme (V): synthesis of copolymer of maleimide**

## Results and discussion

The synthesis of homo and copolymer maleimide has been performed following the steps. In the First step, azo compound (A) was synthesized by reaction Dapsone with *p*-nitroaniline in the presence of DMF as a solvent at room temperature as shown in Scheme-1. Then the compound (B) has been synthesized by treatment the compound A with maleic anhydride also in the presence of DMF solvent and room temperature. And then, the compound (C) were synthesized by the reaction of compound (B) with acetic anhydride and sodium acetate in DMF at 55-

60 °C . The homopolymer of maleimide compound can be obtained by treating the compound (C) at 60 °C with AIBN initiator for 48h and same procedure it follows to synthesis copolymer maleimide by reaction compound (C) with acrylamide by using AIBN initiator. All the synthesized compounds recrystallization by ethanol and which determined by TLC and elemental analysis. Spectral data (IR, <sup>1</sup>H-NMR, <sup>13</sup>CNMR) of all the newly synthesized compounds were in full agreement with the proposed structures.

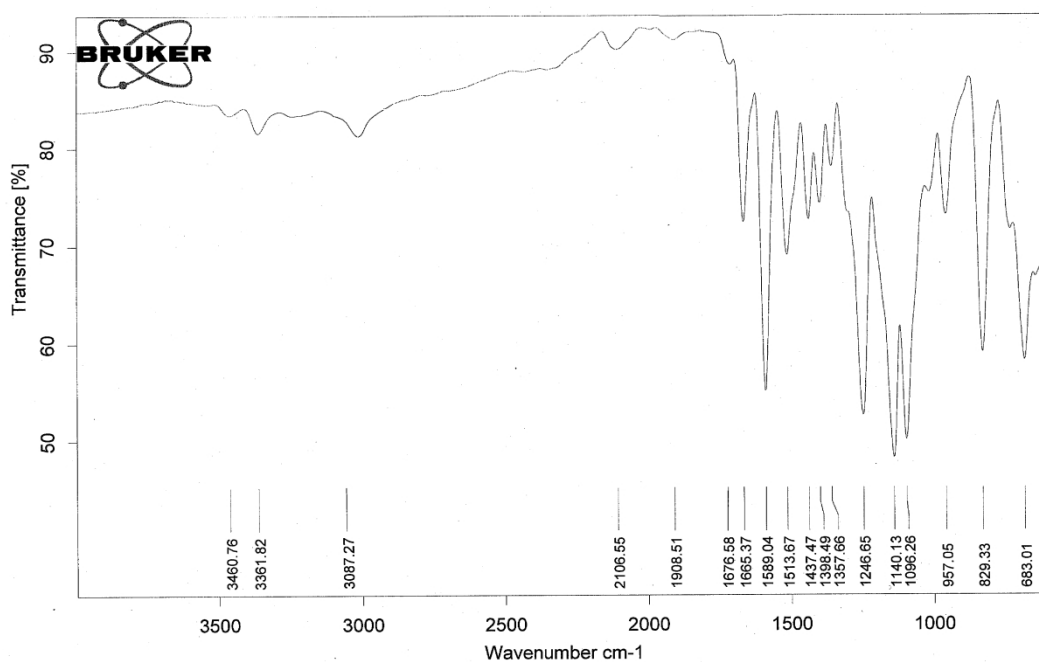


Fig 1: FTIR of Azo compound (A)

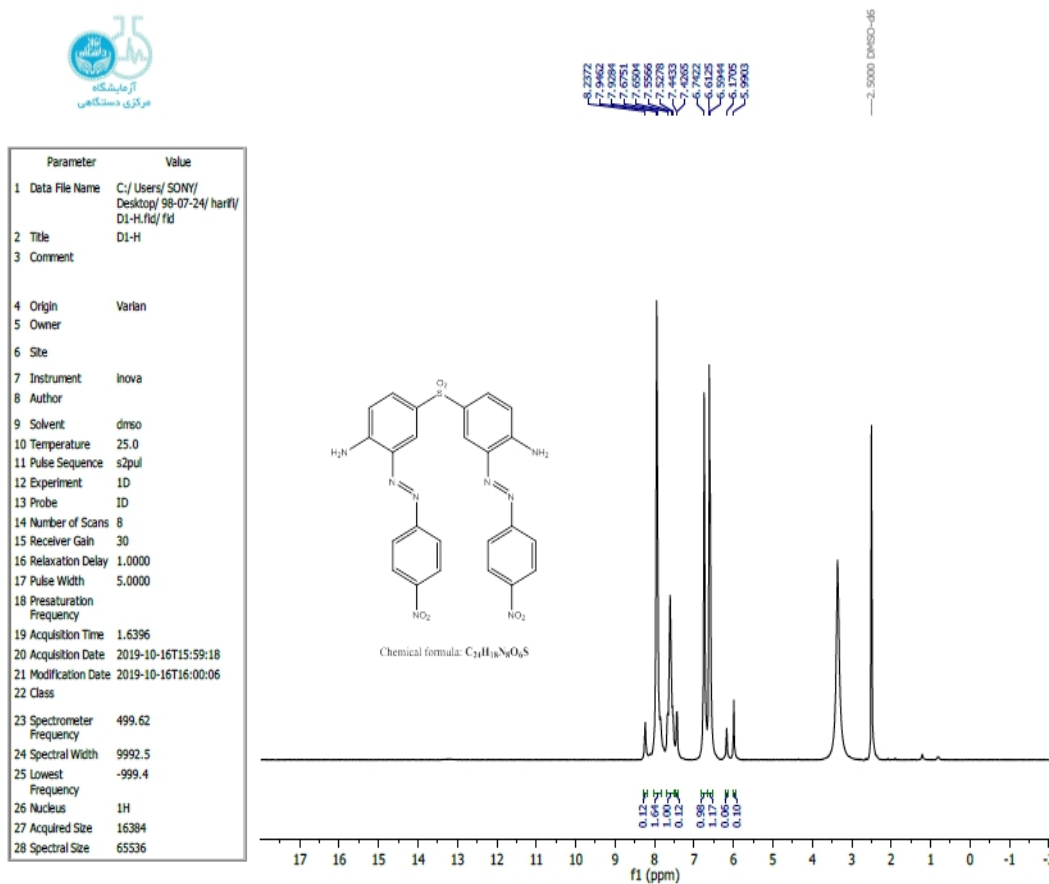


Fig 2: <sup>1</sup>H-NMR spectrum for Azo compound (A)

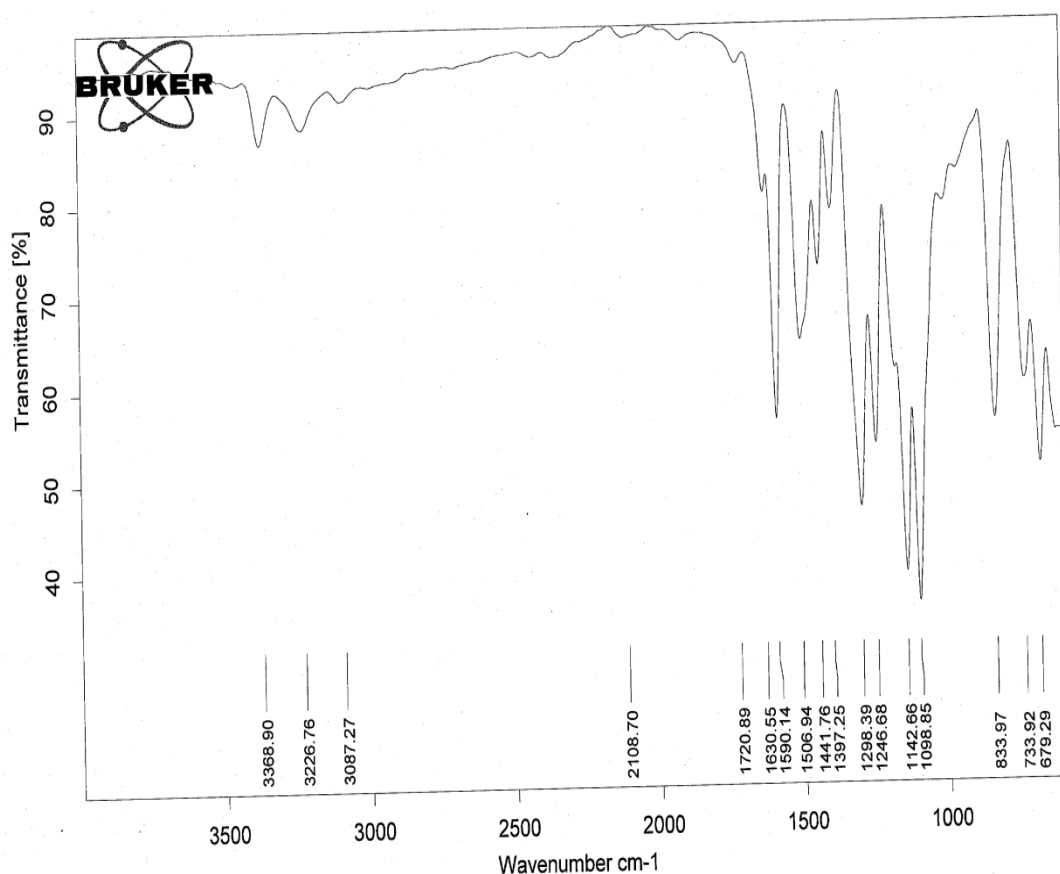


Fig 3: FTIR of Amic acid compound (B)

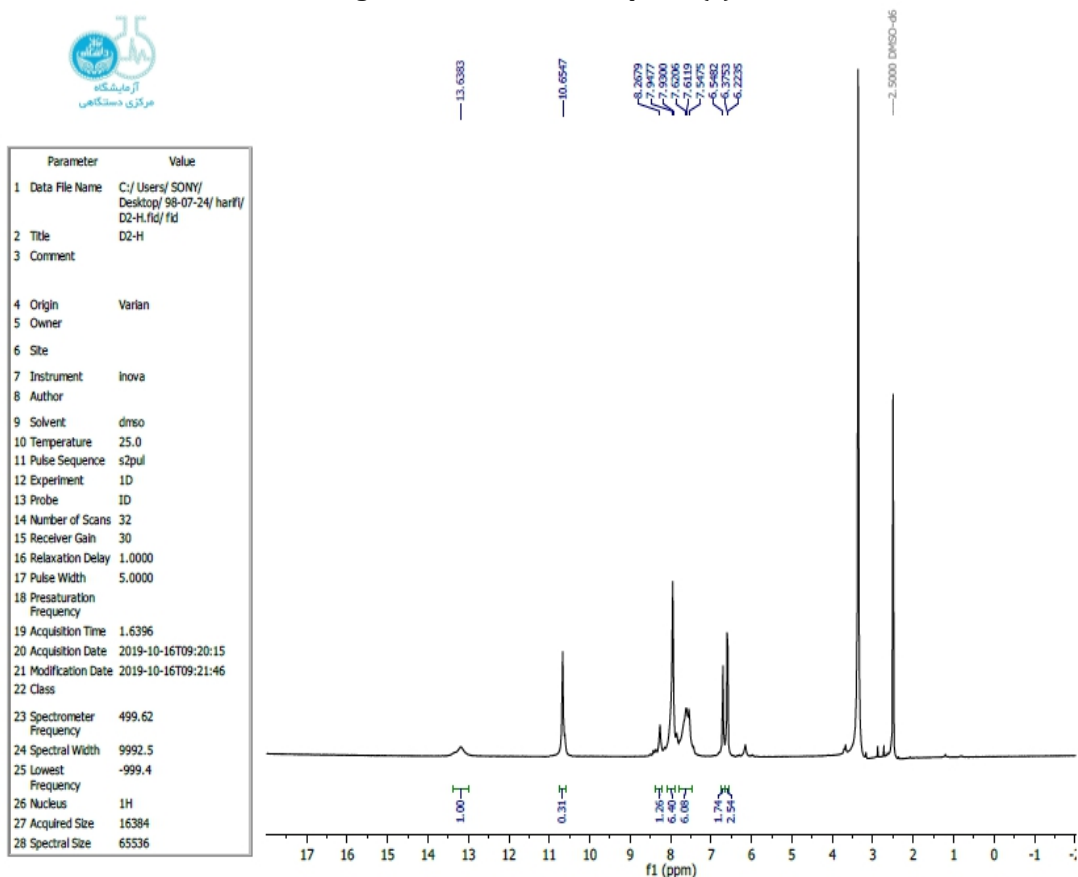


Fig 4: <sup>1</sup>H-NMR spectrum for Amic acid compound (B)

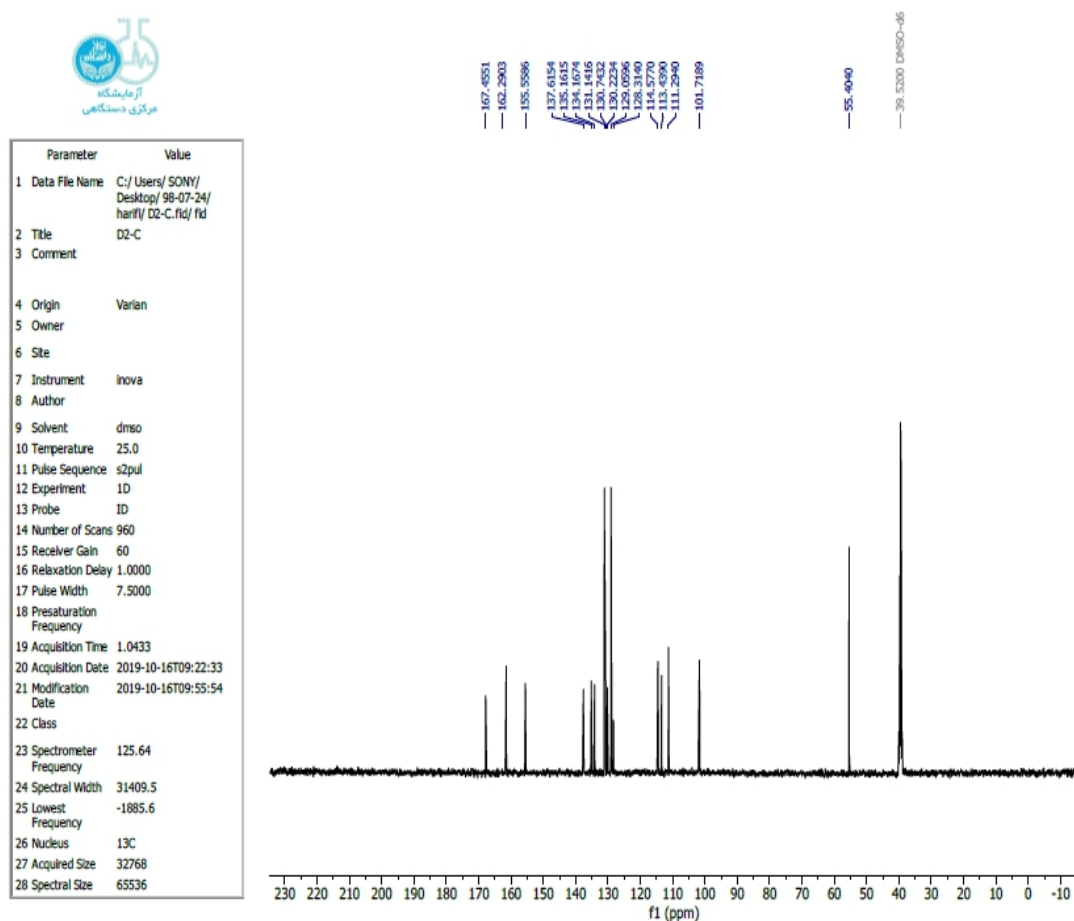


Fig 5 :<sup>13</sup>C-NMR spectrum for Amic acid compound (B)

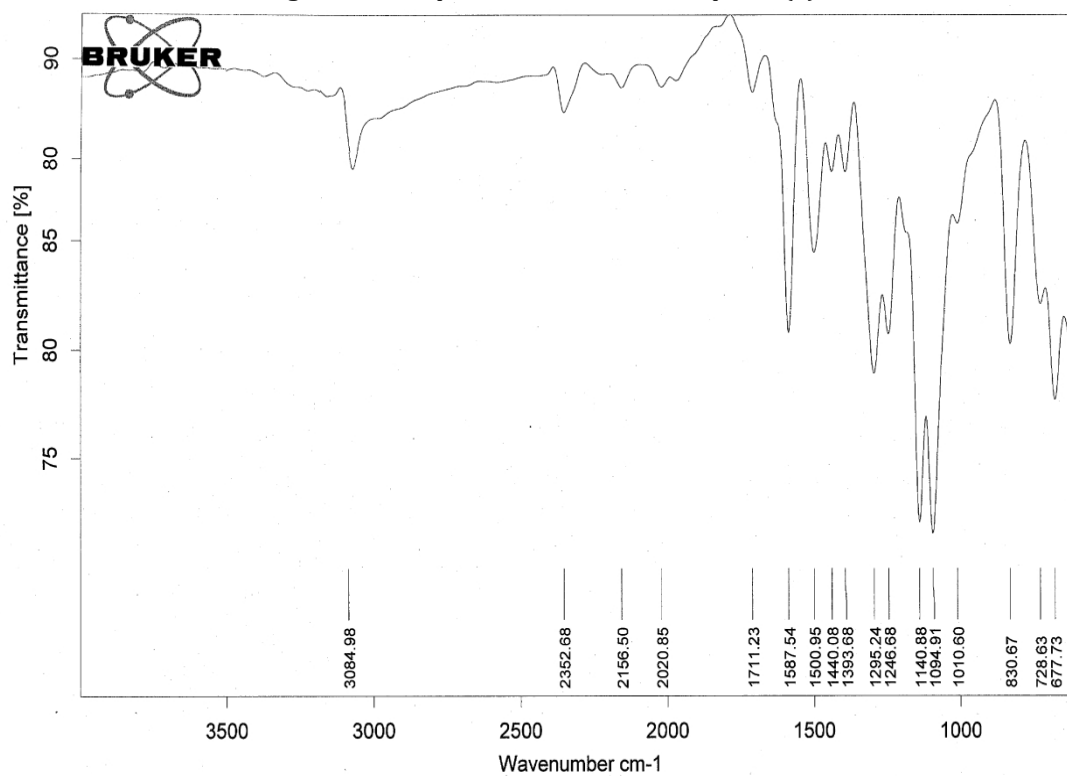


Fig 6: FT-IR of maleimide compound (C)

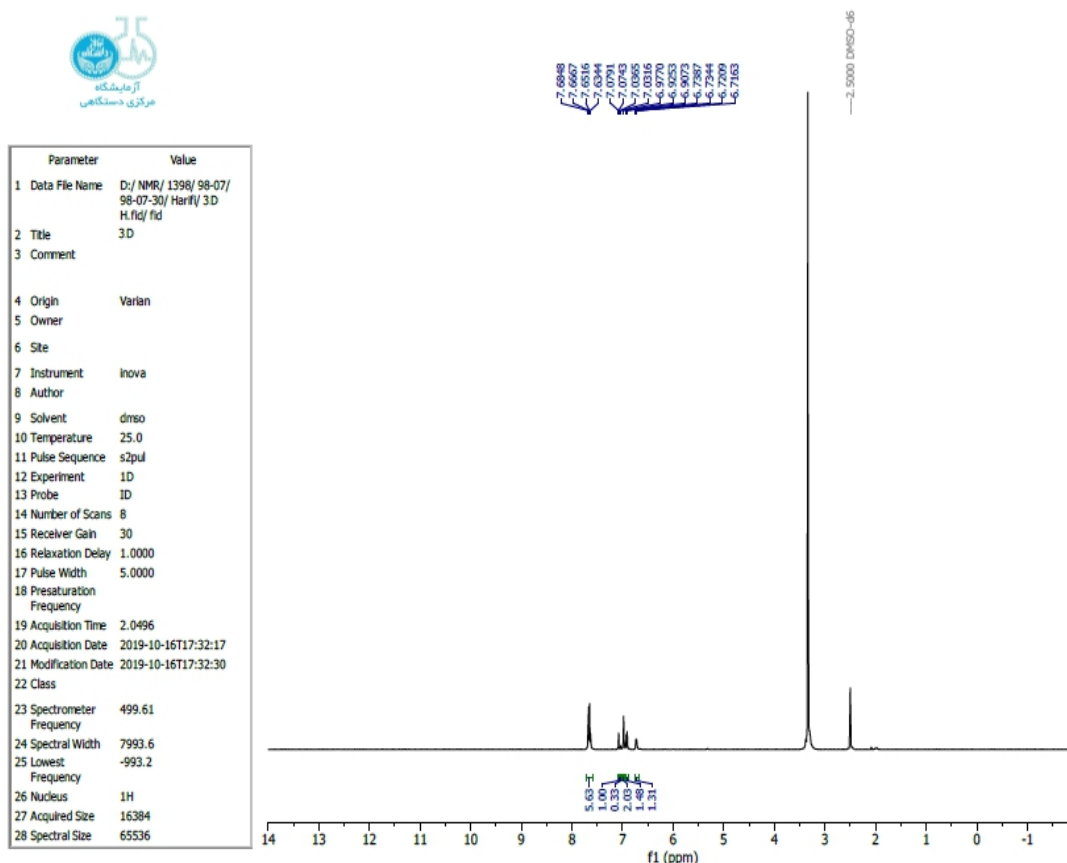


Fig 7: <sup>1</sup>H-NMR spectrum for Maleimide compound (C)

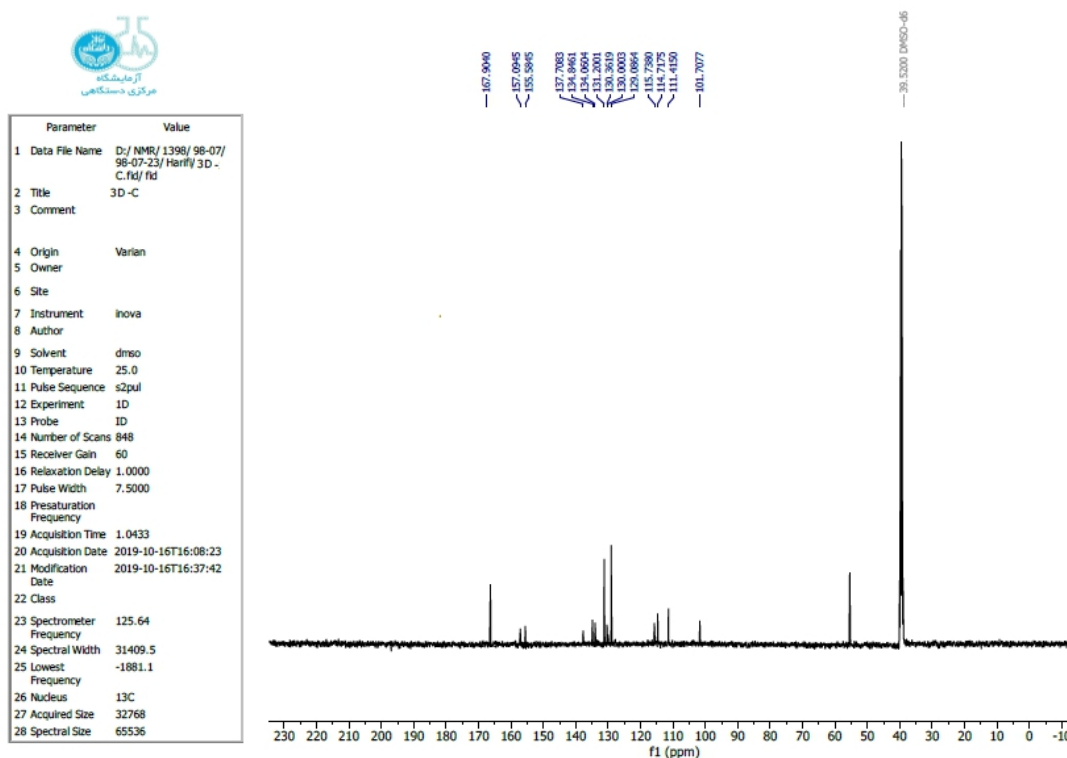


Fig 8: <sup>13</sup>C-NMR spectrum for Maleimide compound (C)



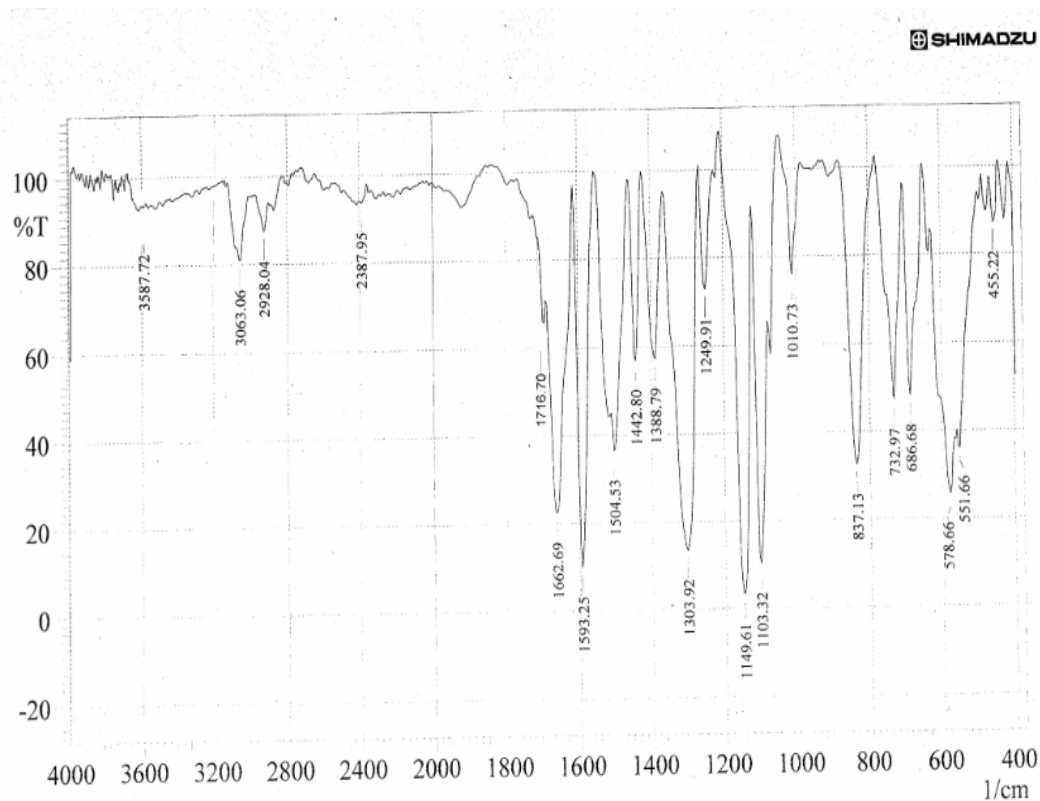


Fig 9: FT-IR spectrum for homopolymer maleimide (D)

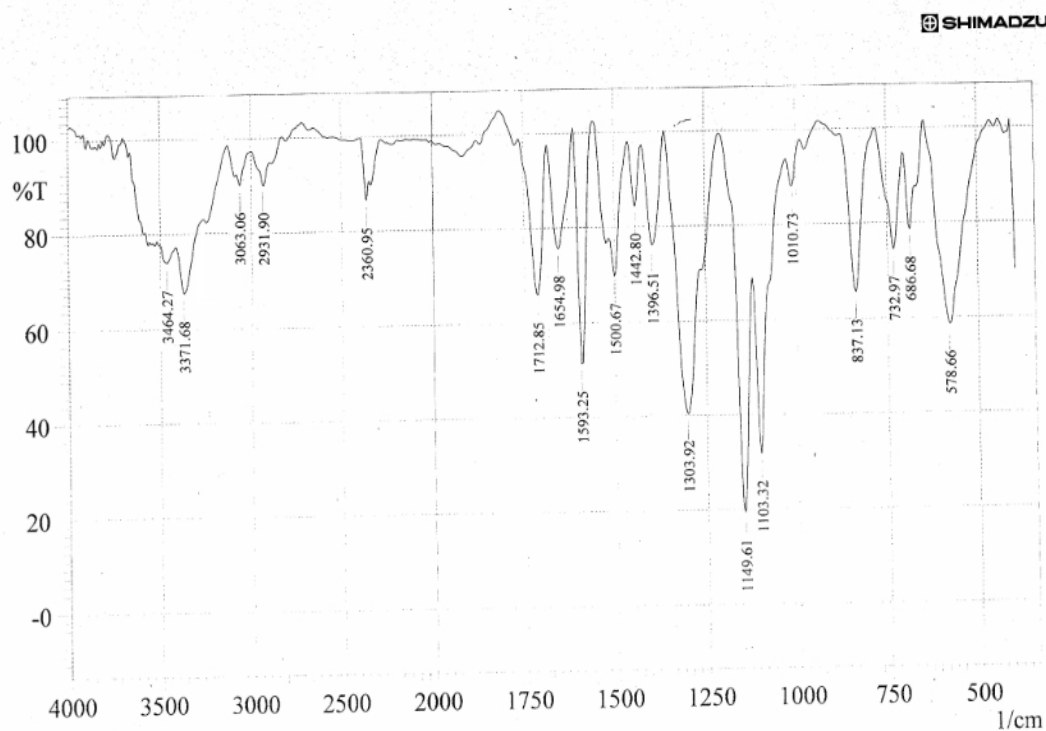


Fig 10: FT-IR spectrum for Copolymer maleimide (E)



Sample: D31  
Size: 3.9080 mg  
Method: Ramp  
Comment: 25-1000@20-Ar

DSC-TGA

File: Z:\199-06-25 99060619\D31\D31.001  
Operator: Beam Gostar Taban  
Run Date: 20-Sep-2020 09:36  
Instrument: SDT Q600 V20.9 Build 20

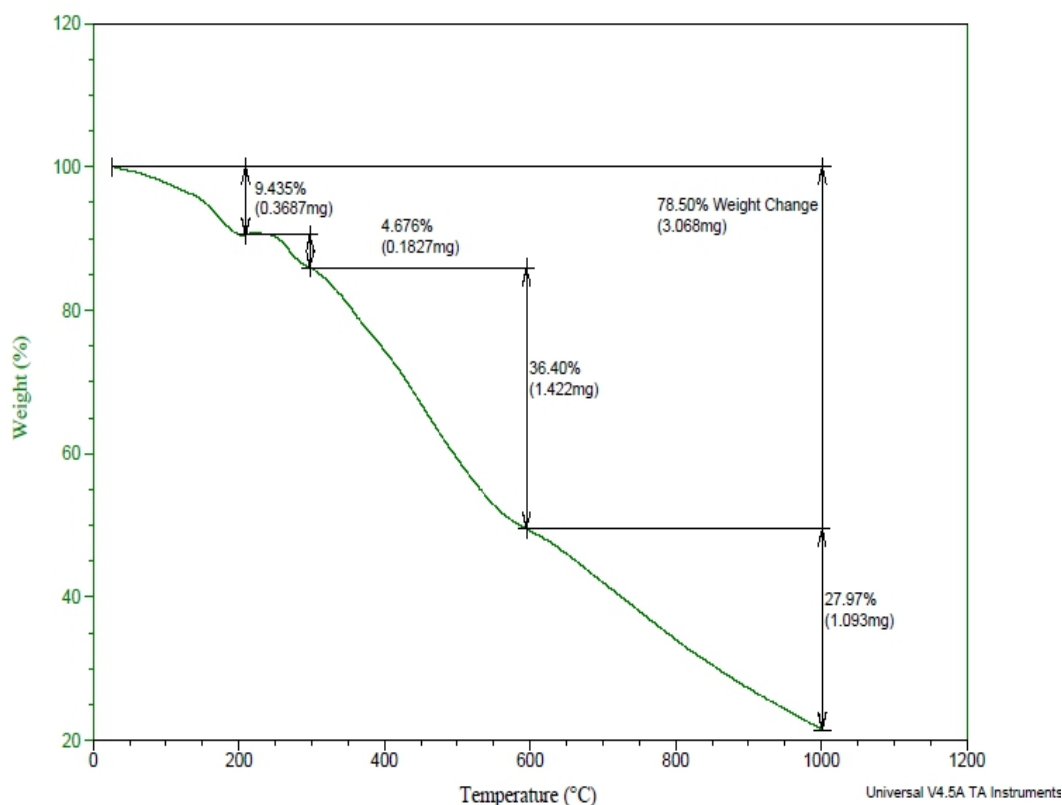


Fig 11: TGA diagram of Homopolymaleimide D

Sample: D31  
Size: 3.9080 mg  
Method: Ramp  
Comment: 25-1000@20-Ar

DSC-TGA

File: G:\199-06-25 99060619\D31\D31.001  
Operator: Beam Gostar Taban  
Run Date: 20-Sep-2020 09:36  
Instrument: SDT Q600 V20.9 Build 20

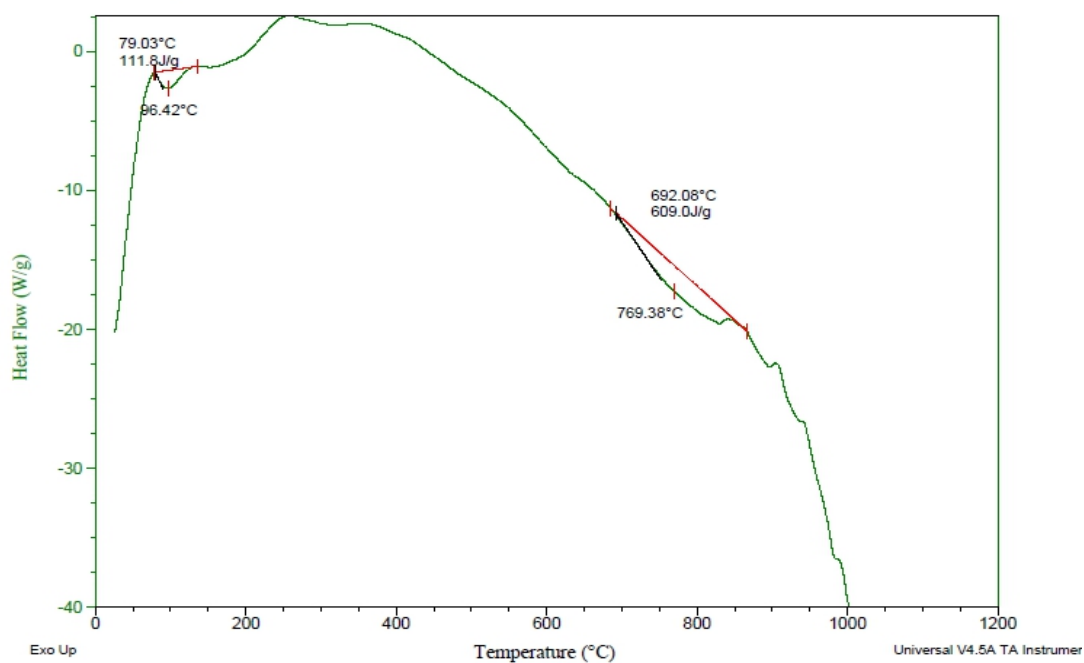


Fig 12: DSC diagram of Homopolymaleimide D

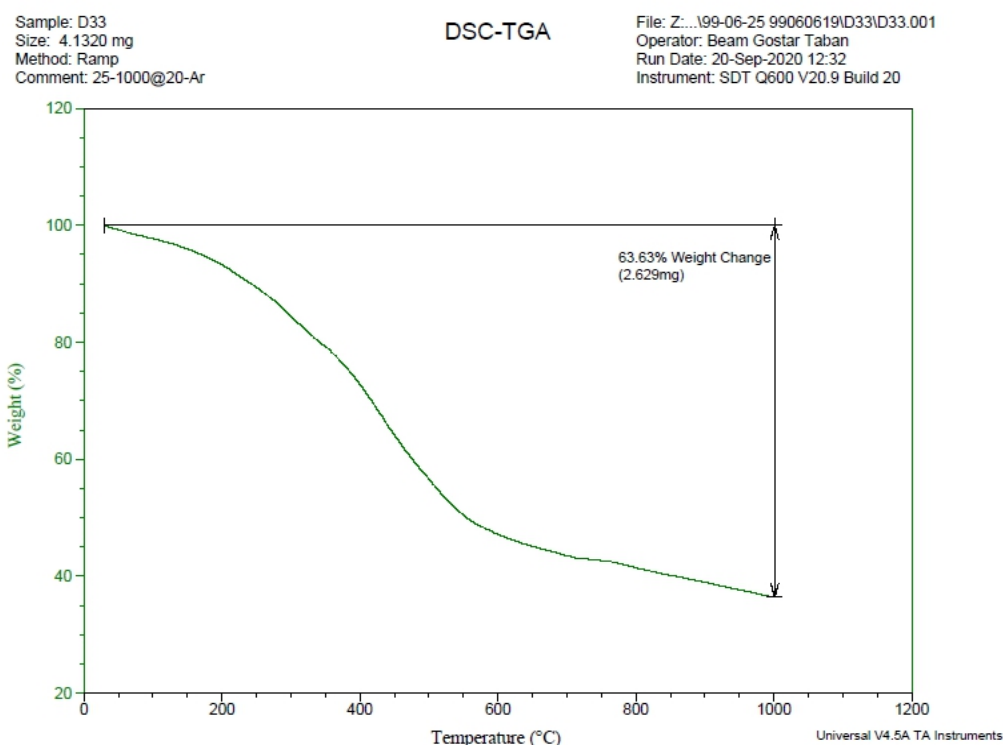


Fig 13: TGA diagram of Copolymaleimide E

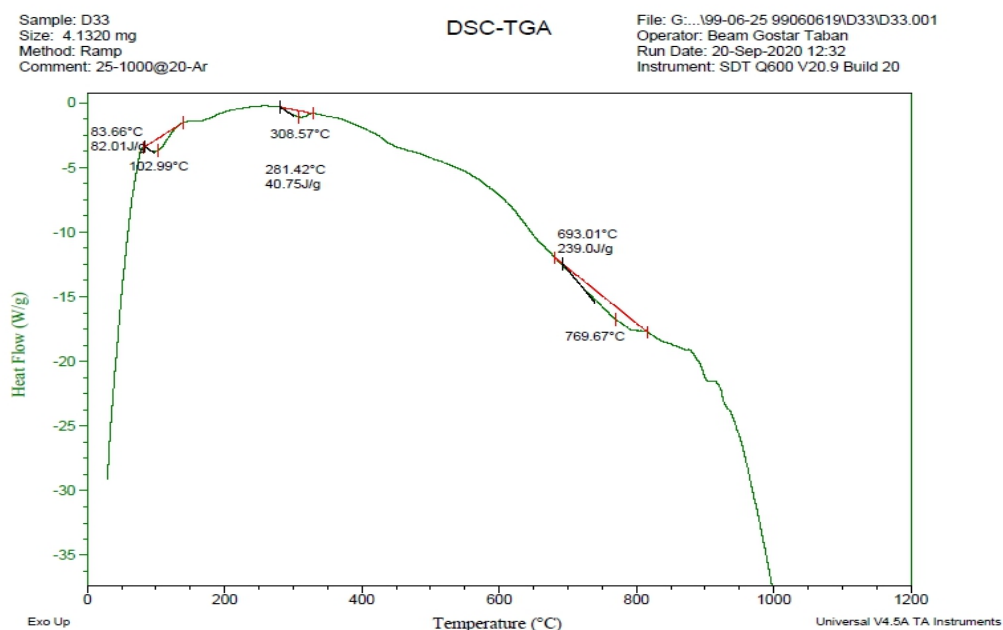


Fig 14: DSC diagram of Copolymaleimide E

**Compound (A) 4,4'-sulfonylbis(2-((E)-(4-nitrophenyl) diazenyl) aniline):**

Orang powder, MWt:527, yield 80%, mp. 140-142 °C, FT-IR (KBr): 3471 symmetric (NH<sub>2</sub>), 3361 asymmetric (NH<sub>2</sub>), 1589 (N=N), 1628 and 1443 (C=C), 1676, 3089 Aromatic (CH), 1357 and 1140 (SO<sub>2</sub>), 957 and 829 (C-S). <sup>1</sup>H-NMR(DMSO-*d*<sub>6</sub>): δ 5.9. (s, 1H, NH<sub>2</sub>), 7.42- 8.23 (dd, 12H, Aromatic).

**Compound (B) 4,4'-((sulfonylbis(2-((E)-(4-nitrophenyl) diazenyl)-4,1-phenylene)) bis(azanediyl)) bis (4-oxobut-2-enoic acid):**

Yellow powder, MWt:723, yield 71%, mp. 161-163 °C, FT-IR (KBr): 3368 (OH) carboxylic acid, 3226 (N-H), 3087 Aromatic (CH), 1720 (C=O) carbonyl group, 1630(C=O) amide, 1590 (N=N), 1398 and 1142 (SO<sub>2</sub>). <sup>1</sup>H-

NMR(DMSO-*d*<sub>6</sub>): δ, 13.10 (s, 1H, -OH carboxylic acid), 10.79 (s, 1H, -NH amide), 6.62-8.00 (dd, 12H Aromatic), 6.55-6.57 (CH=CH), 2.85. <sup>13</sup>C NMR spectrum of compound showed δ, 167.91 (C=O carboxylic acid), 162.29 (C=O amide), 155.55, 137.61, 135.16, 134.16, 131.14, 130.74, 128.31, 114.57, 113.43, 11.29, 101.71, (C=C aromatic), 130.22, 128.31 (HC=CH amic acid).

**Compound (C) 1,1'-(sulfonylbis(2-((E)-(4-nitrophenyl) diazenyl)-4,1-phenylene)) bis (1H-pyrrole-2,5-dione):**

Brown powder, MWt:687, yield 65%, mp. 165-168 °C, FT-IR (KBr): 3084 Aromatic (C-H), 1711 (C=O) carbonyl group, 1589 (N=N) and (C=C), 1393 (SO<sub>2</sub>), 1140 (C-N), 830 (C-S). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ, 6.71-7.68 (dd, dd, H, Aromatic), 7.03 (d, 2H, Alkene maleimide). <sup>13</sup>C NMR

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spectrum of compound showed:  $\delta$ , 167.90 (C=O) for two carbonyl group of maleimide ring, 157.09, 155.58, 137.70, 134.84, 134.06, 131.20, 130.36, 129.05, 115.73, 114.71, 111.41, 101.70 (C=C aromatic) and (HC=CH of maleimide).

### Compound (D):

Dark brown powder, yield 68%, mp. 250-253 °C, FT-IR (KBr): 3063 Aromatic (C-H), 2928 Aliphatic (CH), 1716

(C=O carbonyl group), 1662 (C=O carbonyl conjugated ketone), 1593 (N=N), 1388 (SO<sub>2</sub>), 1149 (C-N).

### Compound (E):

Black powder, yield 60%, mp. 255-258 °C, FT-IR (KBr): 3464 symmetric (NH<sub>2</sub>), 3371 asymmetric (NH<sub>2</sub>), 3063 Aromatic (C-H), Aliphatic (C-H), 2931 Aliphatic (CH), 1712 (C=O carbonyl group), 1654 (C=O amide) 1593 (N=N), 1396 (SO<sub>2</sub>), 1149 (C-N).

### Thermal analysis:

**Table 1:** TG analysis data of prepared Maleimide polymers:

Polymer Code	Temperature scale (°C)	Percentage loss%	weight	Decomposition Temperature T <sub>D</sub> (°C)
D	0-200	9.43		1000
	200-300	4.67		
	300-600	36.40		
	600-1000	27.97		
E	0-1000	100		>1000

**Table 2:** DSC analysis data of prepared Maleimide polymers

Polymers code	Glass Transition T <sub>g</sub> (°C)	Crystallization State T <sub>c</sub> (°C)	Melting State T <sub>m</sub> (°C)
D	96.42	769.38	1000
E	102.99	308.57	769.67

## CONCLUSION

In summary prepared new maleimide from reactant the sulfa drug (Dapsone) and then prepared two polymers Homo and copolymers compounds of maleimide, first time by reacting the new maleimide prepared is heating with AINB initiator and then with acrylic amide to synthesis copolymer maleimide.

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