



## Synthesis and Characterization and Thermal Properties of New Linked Azo-Phenol-Formaldehyde Resins

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### Abstract

Four azo-phenol-formaldehyde resins were synthesized via reaction of phenol with four different types of diazonium salts then resulted azo dyes reacted with formaldehyde. Structures of all new compounds were elucidated with Fourier transform infrared spectroscopy, Nuclear magnetic resonance and Differential scanning calorimetry to assess the thermal characteristics of the produced resins (DSC).

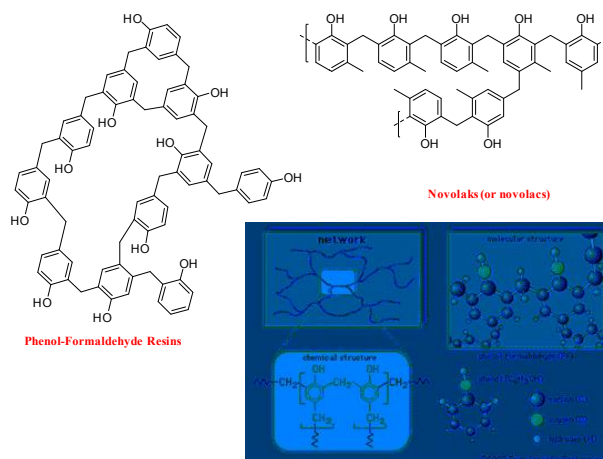
**Keywords:** diazonium salts, substituted phenols, pendent group, modified resins, thermal properties.

### Introduction

The discovery of new generation of acoustic insulation materials,[1] and flame retardant,[2, 3] thermal insulation[4, 5] have attracted worldwide industrial and commercial attentions[6]. Phenol-formaldehyde resin (phenolic resin) is any number of synthetic resins made by reacting aromatic phenol with formaldehyde.[7] Phenol-formaldehyde resins were the first completely synthetic polymers to be commercialized. In the first decades of the 20<sup>th</sup> century, Bakelite,[8] a trademarked phenolic plastic, revolutionized the market for molded and laminated parts for use in electrical equipment. Phenolics are still very important industrial polymers, though their most common use today is in adhesives for the bonding of plywood and other structural wood products. They are especially desirable for exterior plywood, owing to their good moisture resistance. Phenolic resins, invariably reinforced with fibres or flakes, are also molded into insulating and heat-resistant objects such as appliance handles, distributor caps, and brake linings [9].

In industrial practice, there are two basic methods for making the polymer into useful resins. In one method, an excess of formaldehyde is reacted with phenol in the presence of a base catalyst in water solution to yield a low-molecular-weight prepolymer called a resole. [10]

The other method involves reacting formaldehyde with an excess of phenol, using an acid catalyst. This process produces a solid prepolymer called a novolac (or novolak), which resembles the final polymer except that it is of much lower molecular weight and is still thermoplastic (that is, it can be softened by reheating without undergoing chemical decomposition).[11]



**Figure 1: Phenol-formaldehyde resin (phenolic resin)**

On the other hand, Dyes are type of organic compounds that can provide bright and lasting colour to other substance [12]. Azo dyes are widely used in

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industry and daily life, for example, as components in permanent hair dyes. Additionally, azo-compounds represent the largest class of dyes applied in the textile, food, and cosmetic industries[13].

Azo dyes used as components in permanent hair dyes can only be decolorized by drastic methods such as chemical bleaching using hydrogen peroxide. However, this treatment may cause hair damage and health problems.[14] Hence, the use of these methods requires extreme precautions in order to prevent these adverse effects. Therefore, it would be useful to develop a customer friendly and safe treatment method avoiding the use of hazardous chemicals. Enzymes that specifically oxidize or reduce azo-bonds and, thereby, decolorize dyed hair could be an elegant alternative since they can be used under mild conditions and they do not have negative effects both on hair and skin [15].

According to above survey, we aim to synthesize some new linked azo-phenol-formaldehyde resins to study their thermal properties with their characterization as new azo-phenol-formaldehyde resins starting from azo dye derivatives with formaldehyde.

### Results and Discussion

First step in synthesis of resin is synthesis of azo dye derivatives, we synthesize new azo dye derivatives

according to literature method[16]. At this method, substituted aniline reacted with sodium nitrite in acidic medium of HCl to afford diazonium salt (Scheme 1). Diazonium salt reacted with phenol at basic medium to give azo dye monomers  $M_1$ - $M_4$  (Scheme 1)[16].

### Scheme (1) show the preparation of azo compounds

The structure of new monomers is elucidated and proved according to analytical and spectroscopic analysis. IR spectra revealed strong absorption bands in region  $\nu = 3195$ - $3400$   $\text{cm}^{-1}$  of phenolic OH), Also, C-H aromatic protons appeared in the range of  $3093$ - $3100$   $\text{cm}^{-1}$ . The most characteristic absorption band of azo group (N=N-) appeared at  $\nu = 1583$ - $1599$   $\text{cm}^{-1}$  and absorption band of aromatic C=C appeared at  $\nu = 1471$ - $1503$   $\text{cm}^{-1}$  (Figures 1-4).

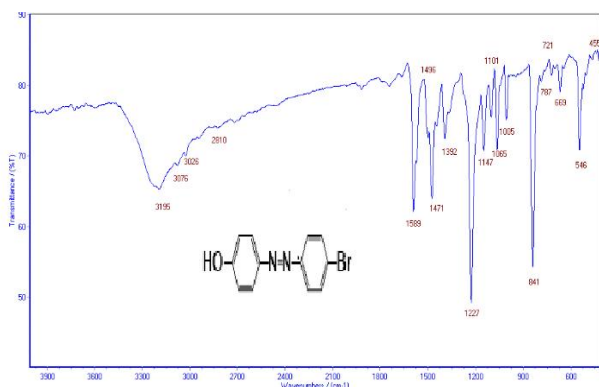


Fig. (1): FT-IR spectrum of  $M_1$

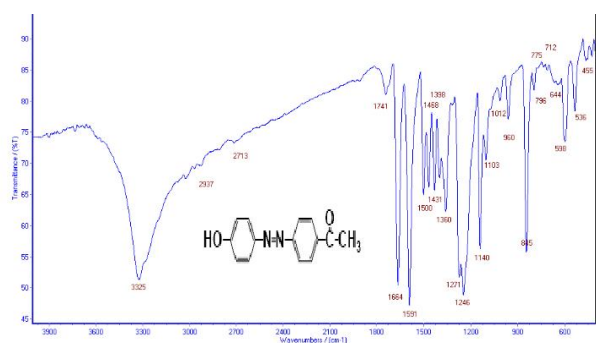


Fig. (3): FT-IR spectrum of  $M_3$

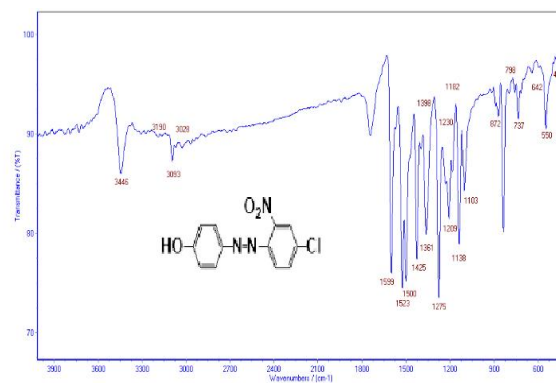


Fig. (2): FT-IR spectrum of  $M_2$

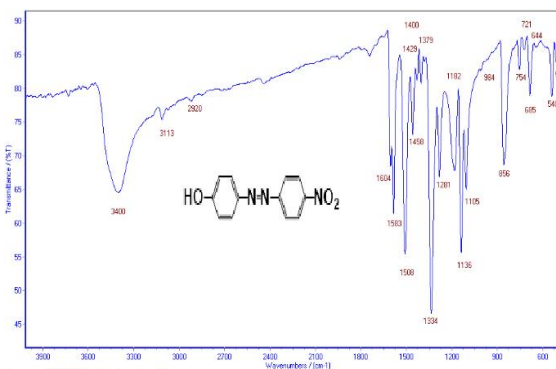
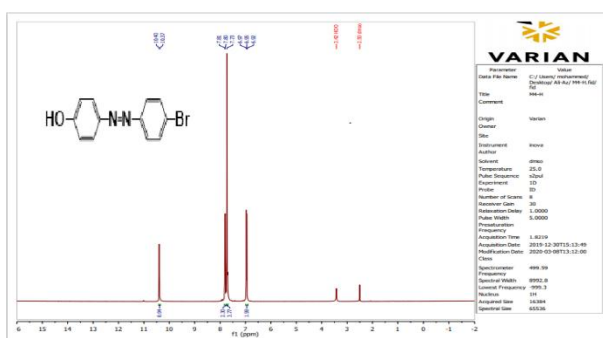
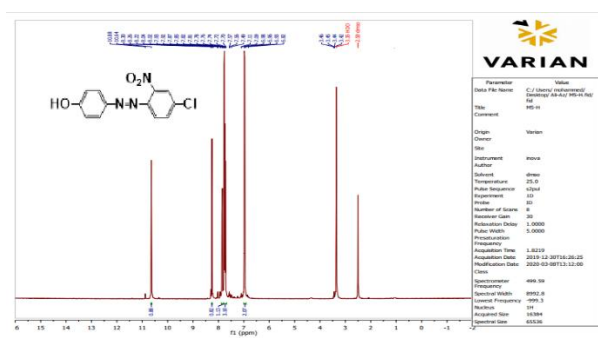
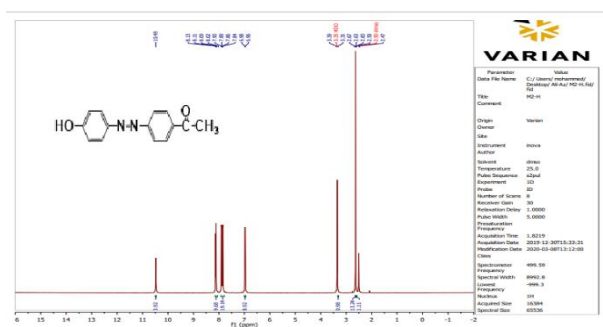
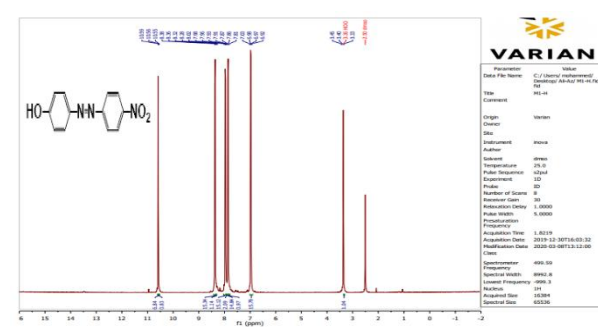
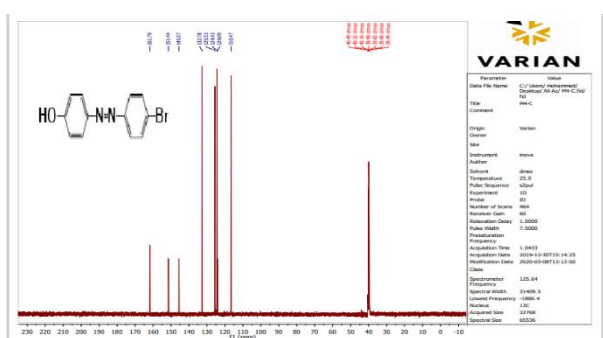
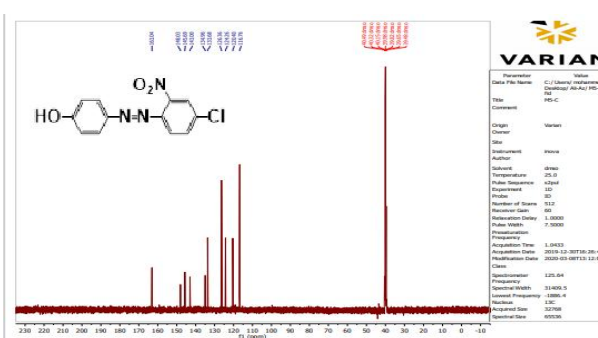
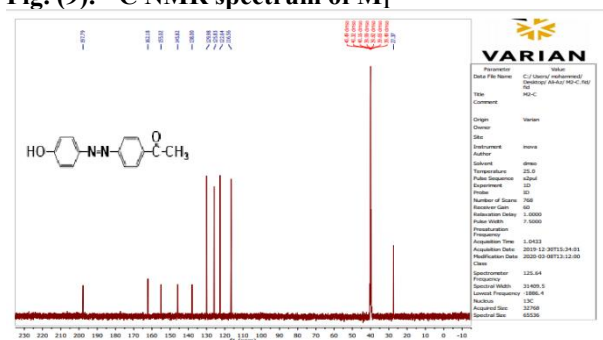
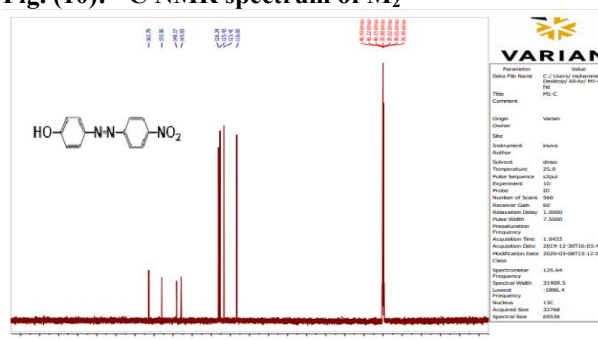


Fig. (4): FT-IR spectrum of  $M_4$

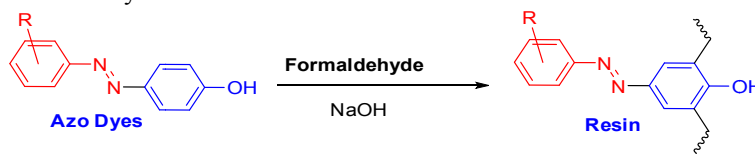
Fig. (5): <sup>1</sup>H NMR spectrum of M<sub>1</sub>Fig. (6): <sup>1</sup>H NMR spectrum of M<sub>2</sub>Fig. (7): <sup>1</sup>H NMR spectrum of M<sub>3</sub>Fig. (8): <sup>1</sup>H NMR spectrum of M<sub>4</sub>Fig. (9): <sup>13</sup>C NMR spectrum of M<sub>1</sub>Fig. (10): <sup>13</sup>C NMR spectrum of M<sub>2</sub>Fig. (11): <sup>13</sup>C NMR spectrum of M<sub>3</sub>Fig. (12): <sup>13</sup>C NMR spectrum of M<sub>4</sub>

Also, structures of new azo dye derivatives M<sub>1</sub>-M<sub>4</sub> were confirmed on the basis of NMR, <sup>1</sup>H NMR spectra revealed signals at  $\delta$  6.92-8.13 ppm that indicate aromatic ring protons and at  $\delta$  10.37-10.64 ppm that attributed to phenolic OH proton (Figures 5-

8). In the same manner, <sup>13</sup>C NMR spectra revealed signal at  $\delta$  27 ppm of methyl protons, while the signal at  $\delta$  116-125 ppm, which attributed to aromatic carbons of monomers and at  $\delta$  155, 197 that assigned to (carbonyl carbon (C=O) and carbon attached with substitutes (NO<sub>2</sub>), (N=N), (C=O). (Figures 9-12).

Azo dye monomers  $M_1$ - $M_4$  are assigned as building moiety to synthesize phenolic resins by employing it to condense with formaldehyde under novolac

preparation conditions [17, 18] to afford new linked azo-phenolic resins (Scheme 2).



Monomer  $M_1$ , Resin  $P_1$   
 Monomer  $M_2$ , Resin  $P_2$   
 Monomer  $M_3$ , Resin  $P_3$   
 Monomer  $M_4$ , Resin  $P_4$

Scheme (2) show the preparation of resin compounds

Table (1): Physical properties of all prepared compounds.

Comp. No.	Yield	Color	Milting Point ( $^{\circ}\text{C}$ )
$M_1$	81	Yellow	137-140
$M_2$	89	Orange	160-163
$M_3$	90	Yellow	190-192
$M_4$	91	Orange	196-198
$P_1$	78	Yellow	>360
$P_2$	80	Brown	>360
$P_3$	77	Orange	>360
$P_4$	79	Brown	>360

Structures of new resin compounds  $P_1$ - $P_4$  were confirmed on the bases of analytical and spectroscopic analyses such as TG, DSC, FTIR.

IR spectra showed broad absorption bands at  $\nu = 3550$ - $3388\text{ cm}^{-1}$  which revealed the presence of O-H,

at  $\nu = 3100$ - $3093\text{ cm}^{-1}$  that attributed to aromatic C-H. Also, at  $\nu = 2930$ - $2897\text{ cm}^{-1}$  that assign to methylene groups and at  $\nu = 1589$ - $1587\text{ cm}^{-1}$  of azo group (N=N-), while aromatic C=C) appear at  $\nu = 1499$ - $1456\text{ cm}^{-1}$  (Figures 13-16).

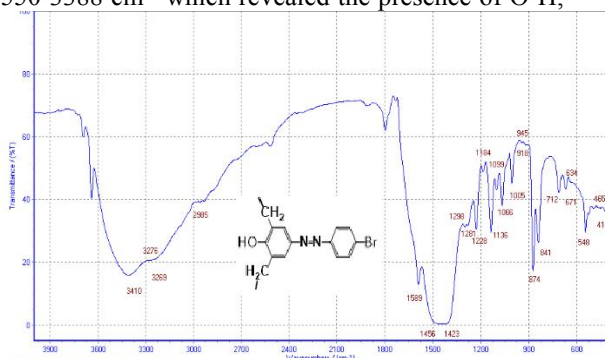


Fig. (13): FT-IR spectrum of  $P_1$

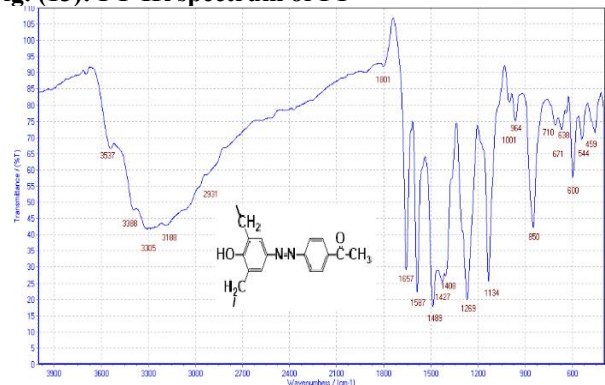


Fig. (15): FT-IR spectrum of  $P_3$

#### Thermal Analysis

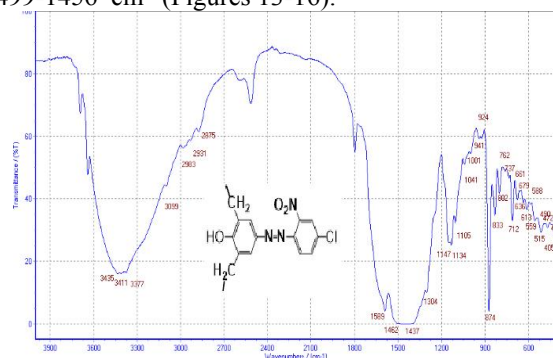


Fig. (14): FT-IR spectrum of  $P_2$

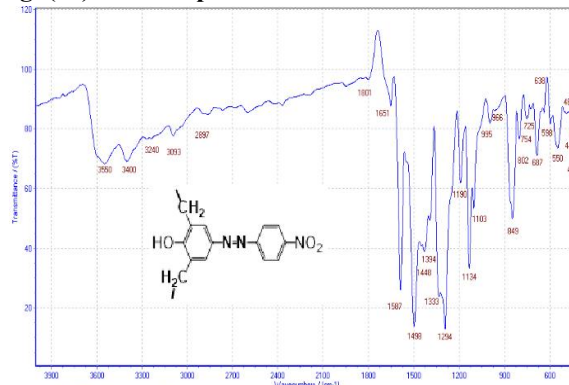


Fig. (16): FT-IR spectrum of  $P_4$

The thermal stability of the modified resins assessed use TGA and DSC measurements on patterns ramped from ambient temperature to 650 C in a nitrogen atmosphere (Figures 17-20). TG curves showed that new synthesized resins were thermally stable; it is widely known that modified phenol formaldehyde resins degrade in three stages: the first stage occurs around (200-300) C, most likely due to the loss of tiny terminal groups.

The primary weight loss stage occurs during the second phase (thermal reforming) at temperatures ranging from (350-500) C. This is most likely due to methylene bridge breakage into phenol and cresol homologs. The third stage (ring stripping) involves

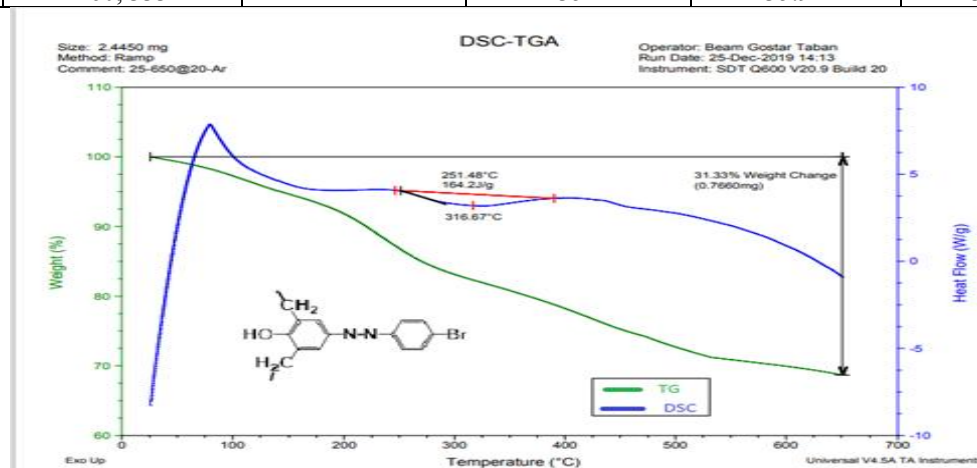
the breakdown of phenol groups at temperatures ranging from (500 – 600) C.

The resin samples created a single or two exothermic peaks in the (154–352) °C area, according to the DSC curves. The curing process was responsible for both exotherms seen in the resin systems. The lower exothermic peak in the (154–212) The lower exothermic peak in the (317–352) C range was attributed to chain-building condensation reactions involving hydroxymethyl collection joined to several phenolic species, whereas the upper exothermic peak in the (317–352) C range was attributed to the reaction of free formaldehyde to the phenolic ring (26). (27).

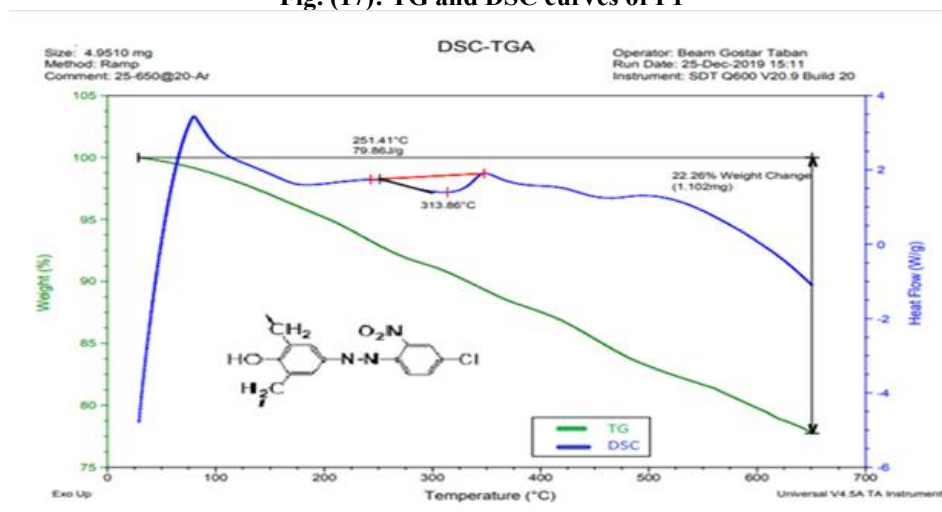
The table below displays the study's findings. (2).

**Table2.** The onset temperature, peak temperature and  $\Delta H$  of adhesives.

Resin ID	Onset Temperature (°C)	Peak 1 Temperature (°C)	Peak 2 Temperature (°C)	Weight Change %	$\Delta H$ (J/g)
P1	251	-	317	31.33	164
P2	251	-	314	22.26	80
P3	113, 243	154	314	32.71	265, 146
P4	160, 333	212	352	35.91	33, 709



**Fig. (17):** TG and DSC curves of P1



**Fig. (18):** TG and DSC curves of P2

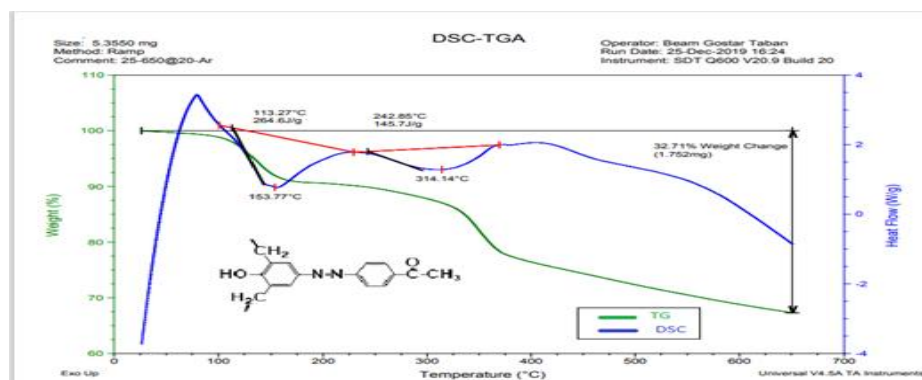


Fig. (19): TG and DSC curves of P3

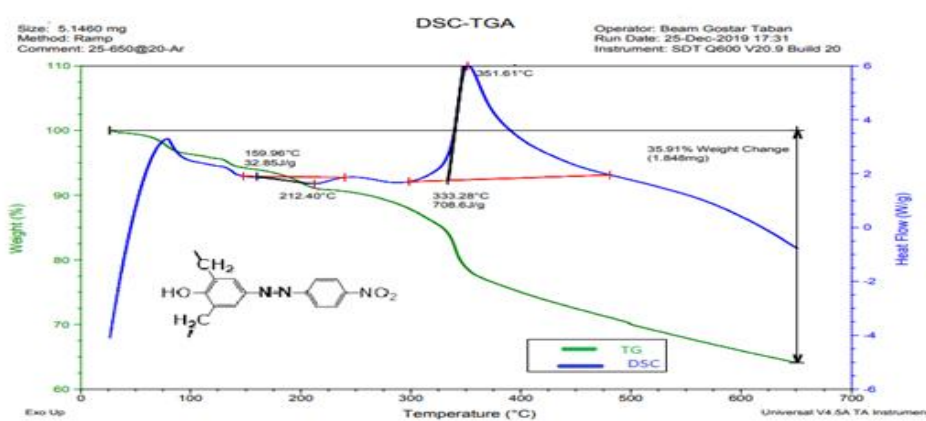


Fig. (20): TG and DSC curves of P4

### Conclusion

In this work, we concluded that a modified phenol formaldehyde resins were prepared via two steps. First step involves reaction of phenol with diazonium salts to afford substituted phenols, linked with para positioned azo group. Second step involves the interaction of azo substituted phenol with formaldehyde in the presence of sulfuric acid to get azo-phenol-formaldehyde resins. Formation of monomers were confirmed by FTIR and NMR spectra. The prepared resins confirmed by FTIR and DSC results indicated that, the resins exhibited thermal stability.

### Experimental

#### Preparation of Monomers (M<sub>1</sub>-M<sub>4</sub>)

Substituted aniline (0.025 mole) with concentrated HCl (10ml) and water (10ml) and chilling in an ice bath at (0-5) °C. To obtain the solution, NaNO<sub>2</sub> (0.025mole) was dissolved in water (5ml) and cooled at (0-5) °C (B). Then, at (0-5) °C, solution (B) was added drop by drop to solution of phenol while stirring. The mixed result was dropped into a solution of phenol (0.025mole) diluted in (10% ) NaOH (25ml) at (0-5) °C. For a period of time, the combination was left at room temperature (20 min).

The resulting precipitate washed with water, filtered, and recrystallized from 100% ethanol. Table 1 shows the physical characteristics (1). Scheme (1) depicts the synthesis of azo compounds.

#### Preparation of Phenol Formaldehyde Resins (P<sub>1</sub>-P<sub>4</sub>)

Substituted phenol (2g) and (5ml) of formaldehyde and three drops of concentrated H<sub>2</sub>SO<sub>4</sub> were refluxed for one hour at 80 °C in a water bath. The color plastic was formed. The resulting precipitate with water rinsed and filtered. Table (1) shows the physical characteristics. Scheme (2) depicts the synthesis of resin compounds.

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