Synthesis and Curing of Novel phenol-formaldehyde resins substituted with Citraconamic acids
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Abstract
Four new phenolic resins containing pendant citraconamic acids in their repeating units were prepared via condensation of formaldehyde with N-(hydroxy phenyl) citraconamic acids in the presence of acid or base catalyst.
The obtained resins were modified by two methods, the first one involved esterification and cyclization by using acetic anhydride and anhydrous sodium acetate, while the second involved free radical polymerization of vinlyc bonds in the prepared resins producing cross linked thermally stable polymers.
The prepared and cured resins have new properties in hope to serve new applications.

Introduction
The most important thermosetting resins both from a historical stand point and in current commercial applications are phenol formaldehyde resins (1-3), thus a number of synthetic strategies have been carried out to incorporate structural modification to obtain new phenolic resins with new properties. Some strategies based on using of aldehydes other than formaldehyde or using other compounds similar to phenols while the others based on using new conditions in performing polycondensation reaction (4-6).

In the present work, four novel phenolic resins having pendant citraconamic acid in their repeating units were synthesized via condensation of formaldehyde with N-(hydroxy phenyl) citraconamic acids under conditions similar to novolac and resole preparations. The new resins were cured by two methods the first one includes esterification and cyclization to the corresponding poly[N-(acetoxy phenyl - formaldehyde) citraconimides] while the second involved polymerization of citraconyl vinyls.

Experimental
1. Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected.
2. FTIR spectra were recorded on Shimadzu FT-IR 8400 Fourier Transform Infrared spectrophotometer.
3. Softening points were determined on Reichert Thermovar with Reichert-Jung temperature controller.
4. Intrinsic viscosities were determined with Automatic viscometer Tafesa ubbelohde viscometer at 25°C using DMF as solvent.

1. Preparation of N-(hydroxy phenyl) citraconamic acids[1-4]
via the titled acids were prepared according to literature procedures (7) reaction of equimolar amounts of citraconic anhydride with o,m and p-amino phenols. The prepared acids were purified by recrystallization from dioxane.

Physical properties and spectral data of the prepared acids are listed in Table(I).

2. Preparation of phenolic resins:poly [N-(phenolformaldehyde) citraconamic acids][5-8]
The titled phenolic resins were prepared by following two literature procedures [A] and [B] respectively with minor modifications (7).

Method [A]: poly condensation of citraconamic acids with formaldehyde using acid catalyst
In a suitable three neck round bottomed flask fitted with a reflux condenser, thermometer and dropping funnel (0.01mol) of N-(hydroxy phenyl) citraconamic acid, (0.8ml) of formaldehyde (37%) and (10ml) of DMF were placed.
The dropping funnel was charged with (0.1ml) of conc. H2SO4 and (0.5ml) of distilled water.
The acid was added dropwise with stirring then the mixture was refluxed at (110°C) for 3hrs.
The resulted mixture was distilled under reduced pressure to remove the evolved water and solvent then the residue was dissolved in (5ml) of DMF and filtered.
The filtrate was added to excess cold water with stirring then the precipitated polymer was filtered, washed with petroleum ether and dried.

Method [B]: poly condensation of citraconamic acids with formaldehyde using base catalyst
(0.01mol) of N-(hydroxy phenyl) citraconamic acid, (3ml) of formaldehyde (37%) and (1.5ml) of (25%) ammonia solution were placed in a round bottomed flask fitted with a reflux condenser. The mixture was refluxed for (1hr) then cooled to room temperature. The upper layer of the resulted mixture was discard while the residual viscous layer was treated with glacial acetic acid until neutralization, then was heated in an oven at (70-80°C) for 48 hrs.

Physical properties and spectral data of phenolic resins prepared by the two methods [A] and [B] are listed in Table (II).

Curing of the prepared phenol-formaldehyde Resins
Curing of the titled resins involved the followings:
3.Curing via esterification of poly [N-(phenolformaldehyde) citraconamic acids][5-8] to the corresponding poly [N-(acetoxy-phenyl-formaldehyde) citraconimides][9-12]
In a suitable round bottomed flask fitted with a reflux condenser (2.2g,0.01mol) of the prepared phenolic resins [5-8] was dissolved in (15ml) of DMF then (5ml) of acetic anhydride and (0.5g) of anhydrous sodium acetate were added (8,9).
The mixture was refluxed on a water bath for (1hr) with stirring then was cooled and poured in excess cold water with vigorous stirring. The resulted precipitate was filtered, washed with petroleum ether and dried.
Purification of the polymer was performed by dissolving it in (10ml) of DMF followed by reprecipitation by cold water then filtered and dried in an oven at (70-80°C) for 24hrs.
Table(III) lists physical properties and spectral data of the cured resins [9-12].


In a polymerization bottle (0.001mol) of the prepared polymers [5-8] was dissolved in (8ml) of DMF then (0.0002g) of benzoyl peroxide was added as initiator[10]. After passing of N2 gas the bottle was closed tightly then heated at (110-115)°C for 3hrs. The resulted mixture was poured into (50ml) of ice water then the precipitated polymer was filtered, washed with petroleum ether and dried.

Table(IV) lists physical properties and spectral data of the cured resins [13-16].

5. Curing via free radical polymerization of vinylic bonds in the prepared poly [N-(acetoxy phenyl-formaldehyde) citraconimides][17-20]

Vinylic bonds in the prepared poly[N-(acetoxy phenyl-formaldehyde) citraconimides][9-12] were polymerized free radically by following the same procedure used in the preparation of polymers [13-16].

Physical properties and spectral data of the resulted polymers[17-20] are listed in Table(V).

Results and Discussion

Since phenolic resins are very important polymers with a wide variety of applications include adhesives, casting, varnishes, binders and surface coatings, we try in this work to synthesize new phenolic resins by following a new strategy in building them. The new strategy involved using of new phenolic moiety substituted with citraconamic acid to condense with formaldehyde under conditions similar to those used in novolac preparation to produce finally phenolic resins with pendent citraconamic acid groups which exhibit new properties in hope to serve new applications.

Polycondensation was performed also under basic conditions similar to those used in resole preparation and the results showed that the prepared resins by the two methods (A) and (B) are very close in their physical properties as shown in Table(II).

The prepared resins [5-8] are brown solids, insoluble in all organic solvents at room temperature with acceptable solubility in hot DMF, hot DMSO and not soften even at (300°C).

It is important to mention here that incorporation of citraconamic acid groups in the repeating units of the prepared resins plays a vital role in raising thermal stability of the prepared polymers through high polarity of carboxylic groups and hydrogen bonding by amide groups which both increased interaction between the repeating units and this in turn increased attraction forces over all the polymeric chains leading to high thermal stability, which make the resins suitable for certain applications.

Also the presence of carboxylic groups in the new resins gives the possibility for using them as cation exchangers[9].

IR spectra of the new resins showed clear absorption bands in the region (3169-3450) cm⁻¹ due to stretching vibrations of (O–H) carboxylic, (N–H) amide and (O–H) phenolic while the other bands appear at (1690-1710)cm⁻¹, (1620-1665) cm⁻¹ and (1560-1610) cm⁻¹ due to υ(C=O) carboxylic, υ(C=O)amide and υ(C=C) vinylly respectively.

The second target of this work involved curing of the prepared resins. Curing was preformed by two methods the first one include esterification of phenolic hydroxyl groups and cyclization of the prepared resins [5-8] to the corresponding poly [N-(acetoxy phenyl-formaldehyde) citraconimides] [9-12] by treatment of the resins with acetic anhydride and anhydrous sodium acetate[9].

During this reaction three steps were achieved dehydration, cyclization and esterification of phenolic hydroxyl groups thus the resulted resins containing acetoxy phenyl citraconimide groups in their repeating units.

The cured resins are yellow to brown solids with softening points (191-300)°C, their intrinsic viscosities are in the range (0.53-0.81) dL/g and insoluble in all organic solvents except DMSO and DMF.

These physical properties of the cured resins are coincident with the expected ones due to the presence of ester (H₂C=O-C-O-) and ester (C-O-C-) bonds which donate softness and flexibility[9].

Structures of the cured resins [9-12] were confirmed by IR spectra which showed disappearance of absorption bands of υ(O–H )carboxylic due to dehydration and υ(O–H) phenolic due to esterification and appearance of two clear characteristic absorption bands at (1760)cm⁻¹ and(1190-1200)cm⁻¹ due to stretching vibrations of (C=O)ester and (C-O-C)ester respectively. The cured resins [9-12] also give positive result in specific tests of esters.

Physical properties and spectral data of the cured resins [9-12] are listed in Table(III).

The second method used in the curing of the prepared resins involved free radical polymerization[10] of citracon vinyls in both the pendent citraconimide groups in the resins [5-8] and pendent citraconimide groups in the
Chain growth polymerization of citracon vinyls in citraconamic groups can be expressed by the following suggested mechanism:

\[
\text{ph-C-O-O-C-ph} \xrightarrow{\Delta} 2 \text{ph-C-O}^* \xrightarrow{\cdot} 2 \text{ph}^* + 2 \text{CO}_2
\]

Polymerization may also involve linking between polymeric chains as shown in the suggested structures below:

On the other hand the suggested mechanism of polymerization of citracon vinyls in pendent citraconimide groups can be expressed as follows:
Polymerization also occur between vinylic bonds in close polymeric chains producing cross linked polymers as shown in the suggested structures below:

It is noticeable that in the case of curing the resins[5-8] the products are cross linked polymers which did not soften under heat and insoluble in all organic solvents while in the case of curing the resins [9-12] the products are cross linked polymers, soluble only in DMSO with higher softening points and higher intrinsic viscosities (0.96-1.14)dL/g than the starting resins before curing.

On the other hand all the obtained resins from free radical polymerization gave negative results with both KMnO₄ solution and Bromine in CCl₄ tests and this confirmed the absence of citracon vinyls due to saturation during polymerization.

IR spectra of the resulted cross linked polymers showed disappearance of vinylic ( ) absorption band and this similarly proved the success of curing via polymerization.

Physical properties and spectral data of the cured resins [13-16] and [17-20] are listed in Tables (IV) and (V) respectively.
As a final conclusion the present work supply us with new strategies in building new phenolic resins first by using new phenolic moiety substituted with citronamic acid groups to condense with formaldehyde and second by curing the prepared resins via esterification and free radical polymerization producing cross linked thermally stable polymers in hope to serve new applications.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Compound structure</th>
<th>Color</th>
<th>Melting Point °C</th>
<th>Yield %</th>
<th>Major IR absorptions cm⁻¹</th>
<th>O-H phenolic</th>
<th>O-H carboxyllic</th>
<th>N-H Amide</th>
<th>C=O Amide</th>
<th>C=O v</th>
<th>C=C v</th>
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<td>1</td>
<td>H₃C=C-CO-OH</td>
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<td>3227</td>
<td>3317</td>
<td>1701</td>
<td>1670</td>
<td>1690</td>
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<td>2</td>
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<td>89</td>
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<td>3230</td>
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<td>1670</td>
<td>1690</td>
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<td>93</td>
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<td>4</td>
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<td>3080</td>
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Table (I) physical properties and IR data of citronamic acids
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<thead>
<tr>
<th>Compound No.</th>
<th>Compound Structure</th>
<th>Method</th>
<th>Color</th>
<th>S.P.</th>
<th>Conv. °C</th>
<th>Conv. %</th>
<th>Major IR Absorptions cm⁻¹</th>
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<td></td>
<td></td>
<td><strong>O-H</strong>&lt;sub&gt;υ&lt;/sub&gt; phenolic</td>
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<td><img src="image" alt="Structure" /></td>
<td>A</td>
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<td>&gt;30</td>
<td>81</td>
<td>3373 3313 3215 1710 1660 1610</td>
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<td></td>
<td></td>
<td>B</td>
<td>Brown</td>
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<td>1</td>
<td><img src="image" alt="Structure" /></td>
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<td>Brown</td>
<td>92</td>
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<td>81</td>
<td>3373 3250 3169 1700 1660 1610</td>
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<td>81</td>
<td>3440 3373 3250 1700 1660 1610</td>
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<td>81</td>
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## Table (III) Physical properties and IR data of poly[N-(acetoxy phenyl-formaldehyde)citraconimides]

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Color</th>
<th>S.P C°</th>
<th>Conv. %</th>
<th>[η] dL/g</th>
<th>Major IR Absorptions cm⁻¹</th>
<th>Ester</th>
<th>C=O⁻U</th>
<th>C=O⁻U</th>
<th>vinylic</th>
<th>C=O⁻U</th>
<th>Ester</th>
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<tbody>
<tr>
<td>9</td>
<td><img src="image" alt="Structure" /></td>
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<td></td>
<td>&gt;300</td>
<td>44</td>
<td>1760, 1730, 1700, 1660</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td><img src="image" alt="Structure" /></td>
<td>Pale Brown</td>
<td>191</td>
<td>80</td>
<td>0.81</td>
<td>1760, 1730, 1700, 1660</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>11</td>
<td><img src="image" alt="Structure" /></td>
<td>Brown</td>
<td>22</td>
<td>81</td>
<td>0.68</td>
<td>1760, 1730, 1700, 1660</td>
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<tr>
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<td>198</td>
<td>80</td>
<td>0.53</td>
<td>1760, 1730, 1700, 1660</td>
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## Table (IV) Physical properties and IR data of the cured resins by polymerization

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<th>Compound structure</th>
<th>Color</th>
<th>S.P C°</th>
<th>Conv. %</th>
<th>Major IR Absorptions cm⁻¹</th>
<th>O-H⁻U Phenolic</th>
<th>N-H⁻U Amide</th>
<th>O-H⁻U carboxylic</th>
<th>C=O⁻U carboxylic</th>
<th>C=O⁻U Amide</th>
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<tr>
<td>13</td>
<td><img src="image" alt="Structure" /></td>
<td>Deep Brown</td>
<td></td>
<td>&gt;300</td>
<td>1400, 3600, 3400, 2180</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td><img src="image" alt="Structure" /></td>
<td>Black</td>
<td></td>
<td>&gt;300</td>
<td>1400, 3600, 3400, 2180</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>15</td>
<td><img src="image" alt="Structure" /></td>
<td>Brown</td>
<td></td>
<td>&gt;300</td>
<td>1400, 3600, 3400, 2180</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>16</td>
<td><img src="image" alt="Structure" /></td>
<td>Brown</td>
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<td>1400, 3600, 3400, 2180</td>
<td></td>
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Table (V) physical properties and IR data of the cured resins by polymerization

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Compound structure</th>
<th>Color</th>
<th>$S_P$ (dl/g)</th>
<th>Conv. (%)</th>
<th>$[\eta]$</th>
<th>Major IR Absorptions cm$^{-1}$</th>
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<tbody>
<tr>
<td>17</td>
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<td>80</td>
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<td>1760, 1165, 1140</td>
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<tr>
<td>18</td>
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<td>1160, 1170, 1140</td>
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<tr>
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<td>71</td>
<td>1.14</td>
<td>1145, 1180, 1140</td>
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<tr>
<td>20</td>
<td><img src="image4" alt="Structure 20" /></td>
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<td>113</td>
<td>77</td>
<td>1.1</td>
<td>1170, 1170, 1140</td>
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Fig(1) FTIR spectrum of compound [2]

Fig(2) FTIR spectrum of compound [6]
Fig(3) FTIR spectrum of compound [\textsuperscript{1}: ]

Fig(4) FTIR spectrum of compound [\textsuperscript{4}: ]

Fig(5) FTIR spectrum of compound [\textsuperscript{5}: ]