# Synthesis and Characterization of Several New Homopolymers, Copolymers and Phenolic Resins of N-Substituted Citraconisoimides

**Ahlam Marouf Al-Azzawi[1*], Mustafa Adnan Yaseen[2]**
[1]Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq
[2]Department of Applied Chemistry Division, University of Technology, Baghdad, Iraq

**Abstract**

Four N-substituted citraconisoimides were prepared via dehydration of the corresponding prepared citraconamic acids using N,N$^{\backslash}$-dicyclohexylcarbodiimide as dehydrating agent. The prepared citraconisoimides were introduced in free radical homopolymerization producing four new poly citraconisoimides. Also the prepared citraconisoimides were introduced in free radical copolymerization with three vinylic monomers including acrylonitrile, methylmethacrylate and methylacrylate producing new copolymers having different physical properties. Moreover two new phenolic resins containing pendent citraconisoimide moiety were prepared via condensation polymerization of N-(hydroxyphenol)citraconisoimide with formaldehyde. The new homopolymers and copolymers are of great importance since they contain isoimide ring in their repeating units which exhibit better processing properties and can rearrange gradually with time and use to the more stable structure of the corresponding imides having thermosetting properties.

**Keywords**: citracoisoimides, homopolymerization, copolymerization, phenolic resins

# تحضير وتشخيص عدد من البوليمرات الذاتية والمشتركة والراتنجات الفينولية الجديدة لمركبات N– معوض ستراكون ايسوايمايد

**احلام معروف العزاوي[1]* ، مصطفى عدنان ياسين[2]**
[1]قسم الكيمياء، كلية العلوم، جامعة بغداد، [2]قسم العلوم التطبيقية،الجامعة التكنولوجية، بغداد ، العراق

**الخلاصة**

تضمن البحث تحضير عدد من مركبات N–معوض–ستراكون ايسوايمايدات عن طريق سحب الماء من حوامض الستراكون آميك المقابلة باستخدام N,N$^{/}$–ثنائي سايكلوهكسيل كاربوثنائي ايمايد كعامل ساحب للماء بعد ذلك تم ادخال الستراكون ايسوايمايدات المحضرة في بلمرة ذاتية انتج ت اربعة من البوليمرات الذاتية (بولي ستراكون ايسوايمايد). كذلك فقد تم ادخال مركبات الستراكون ايسوايمايدات المحضرة في بلمرة مشتركة مع ثلاث مونوميرات فاينيلية هي اكريلونايترايل، مثيل ميث اكريلات ومثيل اكريلات للحصول على بوليمرات مشتركة جديدة ذات صفات فيزيائية مختلفة مما يسمح بتطبيقها في مجالات مختلفة. اضافة الى ذلك فقد تضمن البحث تحضير راتنجات فينول– فورمالديهايد جديدة حاوية على مجاميع متدلية من الستراكون ايسوايمايدات وذلك من خلال البلمرة التكثيفية لمركبات N–هيدروكسي فنيل ستراكون ايسوايمايد مع الفورمالديهايد. تعتبو البوليمرات الذاتية والمشتركة المحضرة ضمن هذا البحث غاية في الاهمية نظراً لاحتواءها على حلقة الايسوايمايد في وحداتها البنائية والتي تمنح البوليمرات خصائص تصنيعية افضل كما انها تترتب مع مرور الوقت والاستخدام الى تركيب الايمايد المقابل ذو الثبات الحراري الافضل.

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*Email: dr.ahlamm.77@yahoo.com

## Introduction

Polyimides have been noted for their outstanding thermal stability and electrical properties [1,2]. Some of these materials have been widely used in industry as structural materials and integrated circuit insulators [3-7]. However they are usually difficult to directly process in their imidized forms because of their high glass transition ($T_g$) and melting temperatures and their limited solubility, which limits their usefulness for many applications.

Efforts have been directed toward the synthesis of polyisoimides in order to develop novel soluble precursors of polyimides since polyisoimides possess general advantages in their processing properties including higher solubility, lower glass transition temperatures and can be converted to polimides without the formation of water or other volatile by products [8-10].

The present work reports free radical homopolymerization of several N-substituted citraconisoimides. The work involves also introducing of the mentioned citraconisoimides in free radical copolymerization with selected vinylic monomers. Moreover condensation polymerization of citraconisoimides with formaldehyde is performed producing new phenolic resins have pendent citraconisoimide moiety in their repeating units. A series of the analogus N-substituted citraconimides and their homopolymers were synthesized also and used for comparison.

## Experimental

All chemicals employed were purchased from BDH, Merk, Fluka and were used without further purification. Melting points were determined on Thomas Hoover apparatus and were uncorrected. FTIR spectra were recorded on SHIMADZU FTIR-8400 Fourier Transform Infrared Spectrophotometer as KBr disc. U.V spectra were recorded on SHIMADZU U.V-Visble recording spectrophotometer U.V 160. $^1$H-NMR spectra were recorded on Bruker 300MHz instrument using DMSO-$d_6$, $CDCl_3$ as solvents and TMS as internal reference. Elemental analyses were performed on Perkin Elmer 240 element analyzer. Intrinsic viscosities were determined with Automatic viscometer Tafesa ubbelohde viscometer at 25°C using DMSO and $CHCl_3$ as solvents. Softening points were determined on thermal microscope Riecher thermover.

### 1- Preparation of N-Substituted Citraconamic Acids (1-4)

N-substituted citraconamic acids were prepared via reaction of equimolar amounts of citraconic anhydride and substituted primary aromatic amine according to literature procedures [11]. Purification was performed by recystallization from ethanol, dioxane or acetone. Physical properties and FTIR spectral data of compounds (1-4) are listed in table-1.

### 2- Preparation of N-Substituted Citraconisoimides (5-8)

The titled compounds were prepared by dehydration of citraconamic acids (1-4) using N,N$^\backslash$-dicyclohexyl carbodeiimide (DCC) as dehydrating agent as follows [12]:

A solution of (0.01 mole) of (DCC) in (20 mL) of dichloromethane was added dropwise to a slurry of (0.01 mole) of N-substituted citraconamic acid in (20 mL) of dichloromethane with stirring and cooling to zero°C. when addition was completed the mixture was stirred for (24 hrs.) at room temperature followed by removal of the precipitate by filtration. The filtrate was concentrated then left until precipitation of isoimide which filtered and purified by recrystallization from a suitable solvent. Table-2 lists physical properties and spectral data of the prepared isoimides.

### 3- Preparation of N-Substituted Citraconimides (9-12)

N-substituted citraconimides were prepared by dehydration of citraconamic acids (1-4) using fusion technique according to literatures [13]. The resulted citraconimides were purified by recystallization from a suitable solvent and their physical properties are listed in table-3.

### 4- Preparation of Poly(N-Substituted Citraconisoimides) (13, 14)

The titled polymers were prepared via free radical chain growth polymerization as follows [14].

In dry polymerization bottle (0.001 mole) of N-substituted citraconisoimide was dissolved in (10 mL) of dioxane then (0.0002 g) of (AIBN) (Azo bisisobutyronitrile) was added (as initiator) and the bottle was flushed with nitrogen and firmly stoppered. The solution was maintained at (70-75°C) for 3 hrs. Then the resulted solution was poured into (20 mL) of methanol. The precipitated polymer was filtered, washed with methanol several times and dried. Physical properties of polymers (13-14) are listed in table-4 and their U.V and FTIR spectral data are listed in table-5.

**Table 1-** Physical properties and FTIR spectral data of citraconamic acids

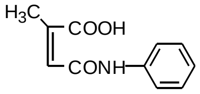
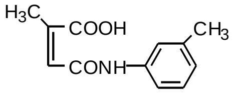
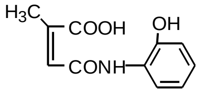
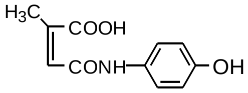
| **Comp. No.** | **Compound structure** | **Color** | **Yield %** | **Melting points °C** | **FTIR absorptions cm$^{-1}$** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **ν(O-H) carboxylic** | **ν(C=O) amide** | **ν(N-H) amide** | **ν(C=O) carboxylic** | **ν(C=C) aliphatic** | **Other** |
| 1 |  | White | 90 | 166-168 | 3217 | 1635 | 3286 | 1704 | 1535 | - |
| 2 |  | Faint pink | 85 | 150-152 | 3232 | 1636 | 3294 | 1697 | 1535 | - |
| 3 |  | Faint yellow | 95 | 154-155 | 3220 | 1626 | 3220 | 1701 | 1606 | νO-H phenolic 3355 |
| 4 |  | Deep yellow | 94 | 157-159 | 3230 | 1625 | 3230 | 1710 | 1590 | νO-H phenolic 3340 |

**Table 2-** Physical properties and FTIR spectral data of N-substituted citraconisoimides

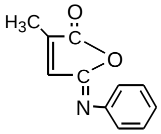
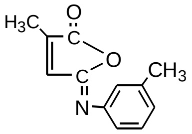
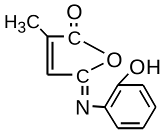
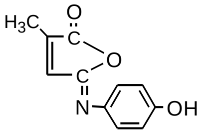
| **Comp. No.** | **Compound structure** | **Color** | **Yield %** | **Melting points °C** | **FTIR absorptions cm$^{-1}$** | | | | | **U.V. $\lambda_{max}$ (nm)** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **ν(C=O) lactone** | **ν(C=N)** | **ν(C=C) aliphatic** | **ν(C-H) aromatic** | **Other** | |
| 5 |  | Light tan | 90 | 90-92 | 1782 | 1677 | 1636 | 3078 | - | 260<br>291 |
| 6 |  | Light tan | 91 | 93-95 | 1782 | 1674 | 1612 | 3060 | - | 248<br>345 |
| 7 |  | Light tan | 85 | 78-80 | 1788 | 1674 | 1625 | 3055 | νO-H phenolic 3325 | 242<br>300 |
| 8 |  | Deep yellow | 80 | 104-105 | 1780 | 1675 | 1623 | 3050 | νO-H phenolic 3320 | 257<br>302 |

**Table 3-** Physical properties and FTIR spectral data of N-substituted citraconimides

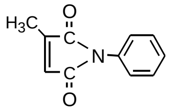
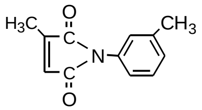
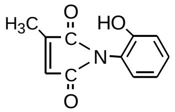
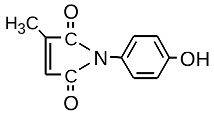
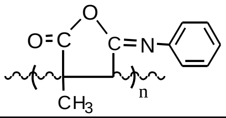
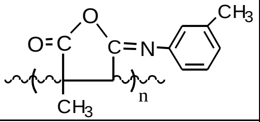
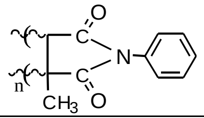
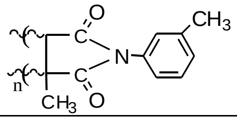
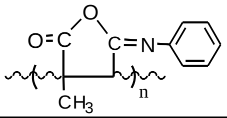
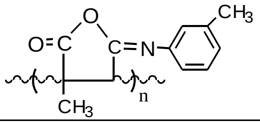
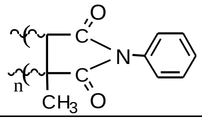
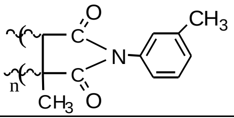
| **Comp. No.** | **Compound structure** | **Color** | **Yield %** | **Melting points °C** | **FTIR absorptions cm$^{-1}$** | | | | | **U.V. $\lambda_{max}$ (nm)** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **ν(C=O) imide** | **ν(C-N)** | **ν(C=C) aliphatic** | **ν(C=C) aromatic** | **Other** | |
| 9 |  | Yellow | 85 | 176-178 | 1712 | 1373 | 1658 | 1537 | - | 260<br>295 |
| 10 |  | White | 85 | 143-145 | 1712 | 1381 | 1628 | 1537 | - | 255<br>291 |
| 11 |  | Red | 80 | 137-139 | 1700 | 1370 | 1610 | 1520 | νO-H phenolic 3375 | 244<br>275 |
| 12 |  | Yellow | 82 | 166-167 | 1690 | 1377 | 1612 | 1525 | νO-H phenolic 3360 | 245<br>275 |

**Table 4-** Physical properties of poly citraconisoimides and poly citraconimides

| Comp. No. | Compound structure | Color | Yield % | Softening point °C | [η] dL/g | Solubility | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | THF | DMF | DMSO | Benzene | Dioxane | $CH_2Cl_2$ | acetone | EtOH |
| 13 |  | Deep brown | 75 | 200-208 | 0.79 | Sol. | Sol. | Sol. | Ps. | Psh. | Ps. | Ins. | Ins. |
| 14 |  | Faint yellow | 77 | 215-220 | 0.87 | Sol. | Sol. | Sol. | Psh. | Psh. | Ps. | Ins. | Ins. |
| 15 |  | Brown | 75 | 240-245 | 0.9 | Psh. | Sol. | Sol. | Ps. | Psh. | Psh. | Psh. | Ps. |
| 16 |  | Deep brown | 78 | 255-265 | 0.95 | Psh. | Sol. | Sol. | Ps. | Psh. | Psh. | Psh. | Ps. |

Sol. = soluble, Ps. = partial soluble, Ins. = Insoluble, Psh. = partial soluble in hot solvent

**Table 5-** Spectral data of poly citraconisoimides and poly citraconimides

| Comp. No. | Compound structure | FTIR absorptions $cm^{-1}$ | | | | U.V. $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| | | ν(C=O) lactone | ν(C=N) | ν(C=C) aromatic | ν(C-H) aliphatic | |
| 13 |  | 1744 | 1650 | 1535 | 2932 | 240<br>295 |
| 14 |  | 1745 | 1675 | 1570 | 2937 | 245<br>291 |
| | | ν(C=O) imide | ν(C-N) | ν(C=C) aromatic | ν(C-H) aliphatic | |
| 15 |  | 1712 | 1373 | 1542 | 2970 | 250 |
| 16 |  | 1713 | 1396 | 1566 | 2936 | 255 |

## 5- Preparation of Poly (N-Substituted Citraconimides) (15, 16)

The titled polymers were prepared by introducing N-substituted citraconimide in free radical chain growth polymerization following the same procedure used in preparation of polymers (13, 14). Physical properties of polymers (15, 16) are listed in table-4 and their U.V and FTIR spectral data are listed in table-5.

## 6- Preparation of (Citraconisoimide-acrylonitrile) Copolymers (17-20)

In a screw-capped polymerization bottle equimolar amounts (0.001 mole) of N-substituted citraconisoimide and acrylonitrile were dissolved in (10 mL) of dioxane then (0.0002 g) of AIBN was added (as initiator). The bottle was flushed with nitrogen for few minutes then firmly stoppered and maintained at (70-75)°C for 4hrs. The resulted solution was poured into (30 mL) of methanol and the precipitated polymer was filtered, washed with methanol and dried. Physical properties of copolymers (17-20) are listed in table-6 and their U.V and FTIR spectral data are listed in table-7.

## 7- Preparation of (Citraconisoimide-methylmethacrylate) Copolymers (21, 22)

The titled copolymers were prepared by following the same procedure used in synthesis of copolymers (17-20) except using of methylmethacrylate instead of acrylonitrile. Physical properties of copolymers (21, 22) are listed in table-6 and their U.V and FTIR spectral data are listed in table-7.

**8- Preparation of (Citraconisoimide-methylacrylate) Copolymers (23, 24)**

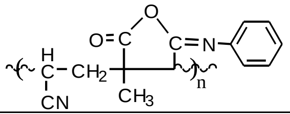
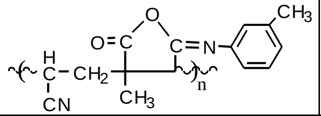
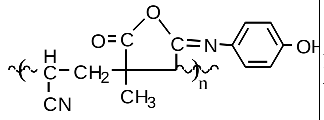
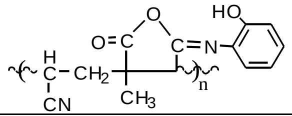
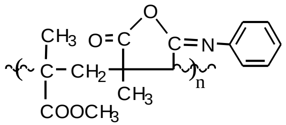
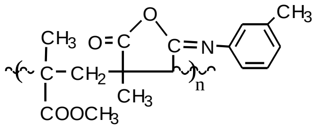
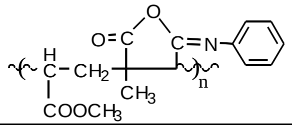
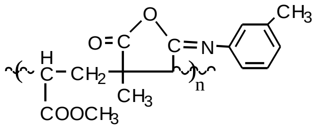
The lilted copolymers were prepared by following the same procedure used in synthesis of copolymers (17-20) except using of methylacrylate instead of acrylonitrile. Physical properties of copolymers (23, 24) are listed in table-6.

**9- Preparation of Phenol-Formaldehyde Resins Containing Pendant Citraconisoimide (25, 26)**

A mixture of (0.01 mole) of N-hydroxyphenyl) citraconisoimide, (0.01 mole) of (37%) formaldehyde and (10 mL) of DMF was placed in a three neck round bottomed flask equipped with reflux condenser, thermometer and dropping funnel. To this mixture a solution of (0.1 mL) Conc. $H_2SO_4$ dissolved in (0.5 mL) of distilled water was added drop wise with continuous stirring followed by reflux at (70°C) for 3hrs. [15].

The resulted mixture was poured into cold water with stirring and the obtained precipitate was filtered, washed with petroleum ether and dried. Physical properties of polymers (25, 26) are listed in table-8.

**Table 6-** Physical properties of N-substituted citraconisoimides copolymers (17-24)

| No | Compound structure | Color | Softening point °C | Conv. % | [η] dL/g | Solubility | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | THF | DMF | DMSO | Benzene | Dioxane | $CH_2Cl_2$ | Acetone | EtOH |
| 17 |  | Faint yellow | > 300 | 75 | 0.75 | Ps. | Sol. | Sol. | Ins. | Psh. | Ins. | Ins. | Ins. |
| 18 |  | Light tan | 250-260 | 75 | 0.71 | Ps. | Sol. | Sol. | Ins. | Psh. | Ins. | Ins. | Ins. |
| 19 |  | Light tan | 270-277 | 77 | 0.77 | Ps. | Sol. | Sol. | Ins. | Ps. | Ins. | Ins. | Ins. |
| 20 |  | Faint yellow | > 300 | 73 | 0.75 | Ps. | Sol. | Sol. | Ins. | Ps. | Ins. | Ins. | Ins. |
| 21 |  | Deep yellow | 280-295 | 75 | 0.79 | Psh. | Sol. | Sol. | Psh. | Sol. | Ins. | Sol. | Ins. |
| 22 |  | Yellow | 245-260 | 75 | 0.83 | Psh. | Sol. | Sol. | Psh. | Sol. | Ins. | Sol. | Ins. |
| 23 |  | Orange | Gummy | 76 | 0.7 | Sol. | Sol. | Sol. | Psh. | Psh. | Ps. | Psh. | Ins. |
| 24 |  | Yellow | Gummy | 67 | 0.76 | Sol. | Sol. | Sol. | Psh. | Ps. | Ps. | Psh. | Ins. |

Sol. = soluble, Ps. = partial soluble, Ins. = Insoluble, Psh. = partial soluble in hot solvent

**Table 7-** FTIR and U.V. spectral data of N-substituted citraconisoimides copolymers (17-24)

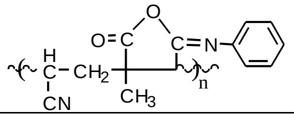
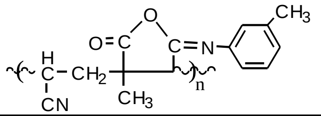
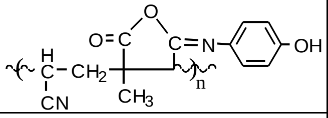
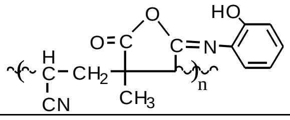
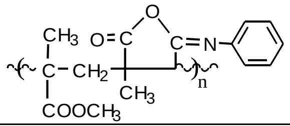
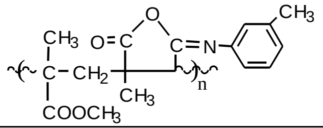
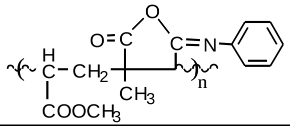
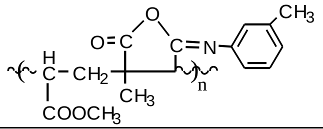
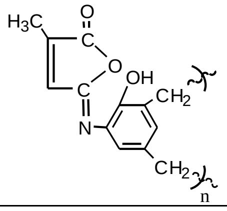
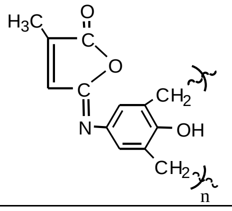
| **Comp. No.** | **Compound structure** | **FTIR absorptions cm$^{-1}$** | | | | | | **U.V. $\lambda_{max}$ (nm)** |
|---|---|---|---|---|---|---|---|---|
| | | **ν(C=O) lactone** | **ν(C=N)** | **ν(C-H) aliphatic** | **ν(C=C) aromatic** | **ν(C≡N)** | **Others** | |
| 17 |  | 1745 | 1690 | 2946 | 1545 | 2249 | - | 343<br>400 |
| 18 |  | 1740 | 1690 | 2937 | 1560 | 2245 | - | 315<br>340 |
| 19 |  | 1745 | 1660 | 2937 | 1545 | 2249 | ν(O-H) phenolic 3350 | 315<br>345 |
| 20 |  | 1745 | 1675 | 2947 | 1550 | 2248 | ν(O-H) phenolic 3330 | 325<br>367 |
| | | **ν(C=O) lactone** | **ν(C=N)** | **ν(C-H) aliphatic** | **ν(C=C) aromatic** | **ν(C-O) ester** | **Others** | |
| 21 |  | 1727 | 1649 | 2950 | 1565 | 1150 | - | 336<br>360 |
| 22 |  | 1726 | 1650 | 2923 | 1550 | 1211 | - | 322<br>373 |
| 23 |  | 1735 | 1625 | 2935 | 1545 | 1150 | - | 339<br>385 |
| 24 |  | 1744 | 1627 | 2950 | 1550 | 1155 | - | 329<br>366 |

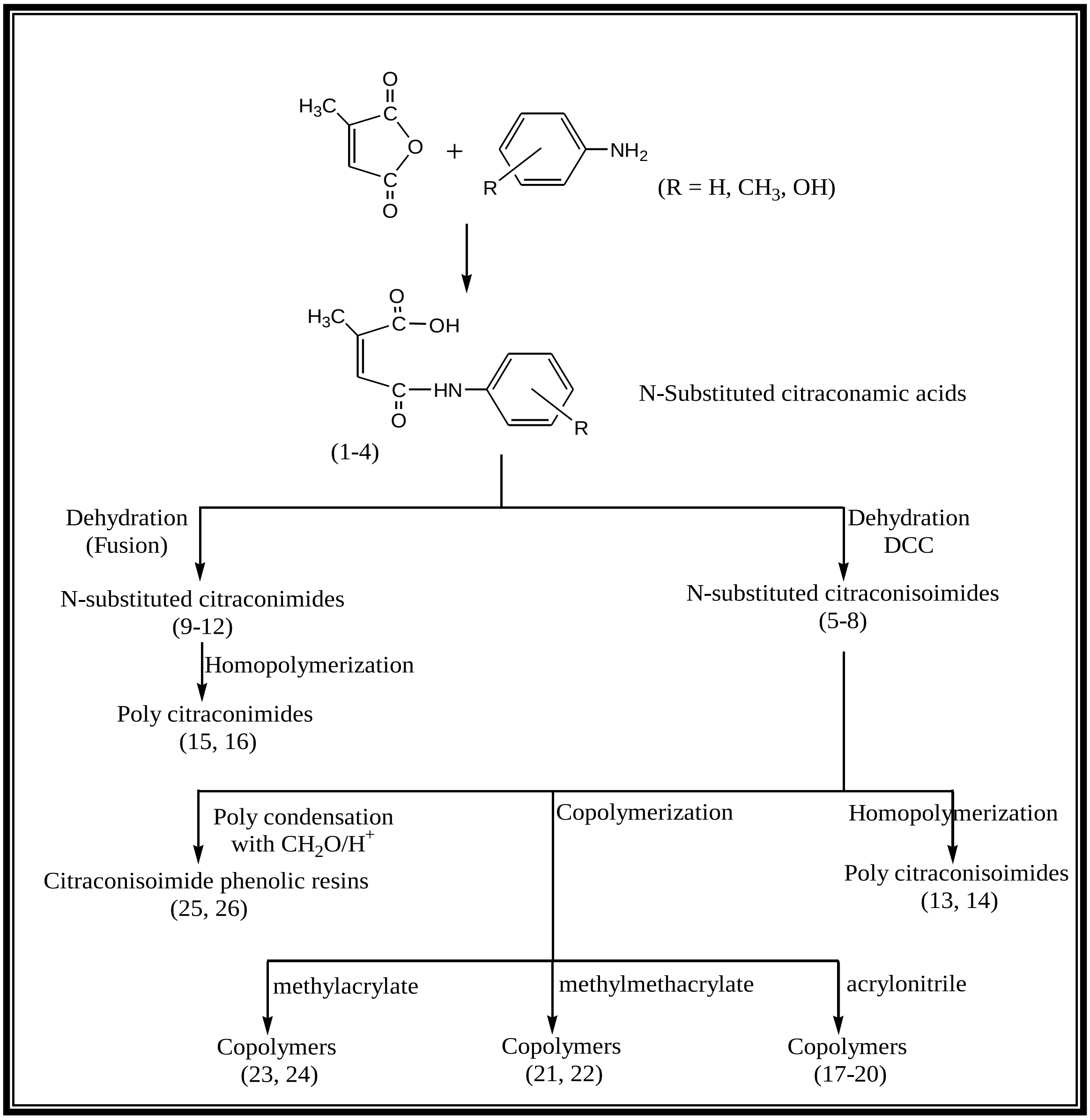
**Table 8-** Physical properties of N-substituted citraconisoimides phenolic resins

| **Comp. No.** | **Compound structure** | **Color** | **Softening point °C** | **Conv. %** | **[η] dL/g** | **Solubility** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **THF** | **DMF** | **DMSO** | **Benzene** | **Dioxane** | **$CH_2Cl_2$** | **Acetone** | **EtOH** |
| 25 |  | Faint brown | 250-255 | 79 | 0.69 | Psh. | Sol. | Sol. | Ins. | Psh. | Ins. | Ps. | Psh. |
| 26 |  | Yellow | 254-259 | 75 | 0.65 | Psh. | Sol. | Sol. | Ins. | Psh. | Ins. | Ps. | Psh. |

## Results and Discussion

Although numerous reports about homopolymerization and copolymerization of cyclic imides are found in literatures [16-21] we could not locate many syntheses of their polyisoimide isomers. This may be attributed to the lack of stability, low yields and difficulties in their purification in comparison with the corresponding imides.

So since polymerization of cyclic isoimides are rare in literatures and polymers containing isoimide moiety possess better processing properties the aim of the present work is directed toward synthesis of citraconisoimide homopolymers, copolymers and phenolic resins. Synthesis of the desirable mentioned polymers was performed through many steps described in Scheme (1).



**Scheme (1)**

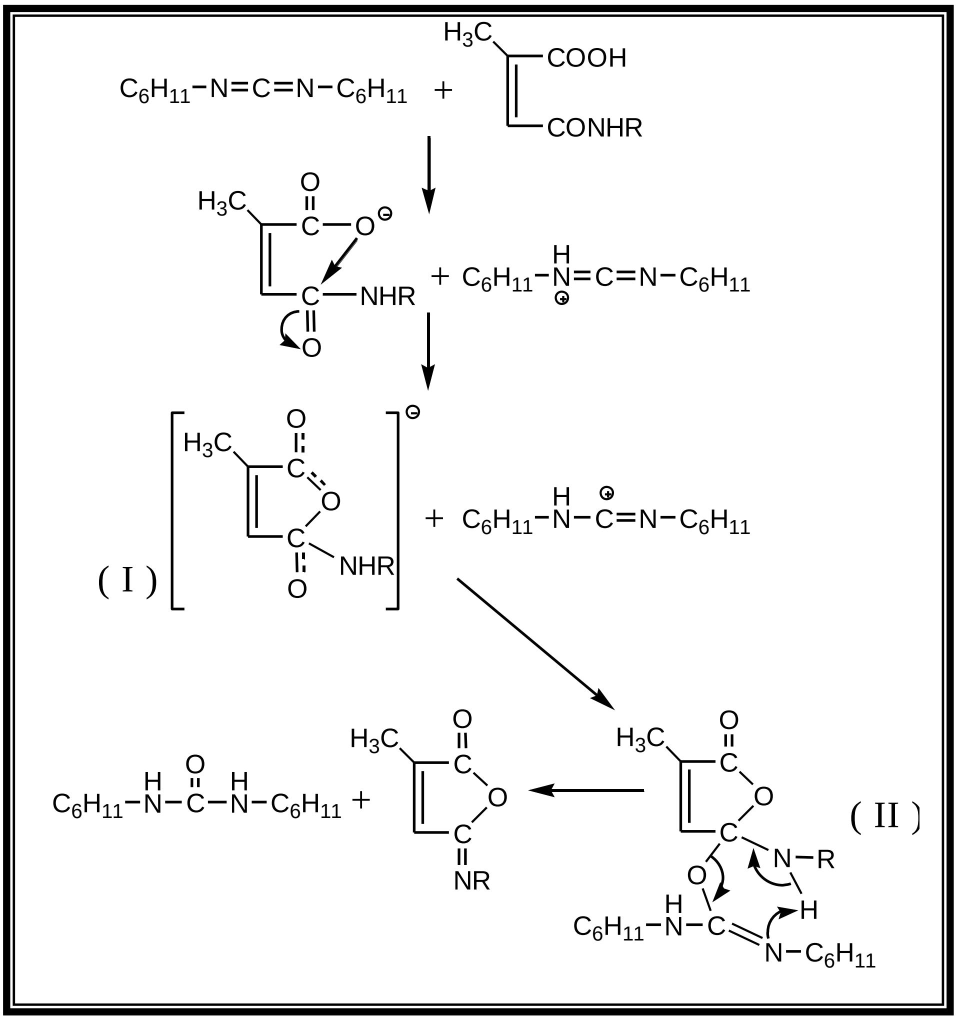
Synthetic route of the new compounds

The first step in the present work involved synthesis of four N-substituted citraconamic acids via reaction of citraconic anhydride with different aromatic primary amines. Physical properties and FTIR spectral data of amic acids are listed in table-1.

In general dehydration of amic acids produced two isomers imides and isoimides respectively depending on reaction conditions thus correct choice of reaction conditions especially temperature and suitable dehydrating agent could direct the reaction to the desirable product.

Thus the second step involved preparation of four citraconisoimides via dehydration of the prepared citraconamic acids using powerful dehydrating agent (DCC) at zero °C since these conditions were favorable in producing isoimides.

Mechanism for dehydration reaction proceeds by donation a proton from citraconamic acid to (DCC) leading to a ring-closed structure (I) which intern react with (DCC) cation producing six-membered ring transition state (II) which finally decomposed producing citraconisoimide as described in Scheme (2).



**Scheme (2)**

Mechanism steps for preparation of isoimides

The prepared citraconisoimides were characterized by FTIR and U.V. spectroscopy. FTIR spectra of citraconisoimides (5-8) showed disappearance of ν(O-H) carboxylic and ν(N-H) amide absorption bands which are important characteristic absorptions of amic acids, so their disappearance is a good proof for success of dehydration reaction.

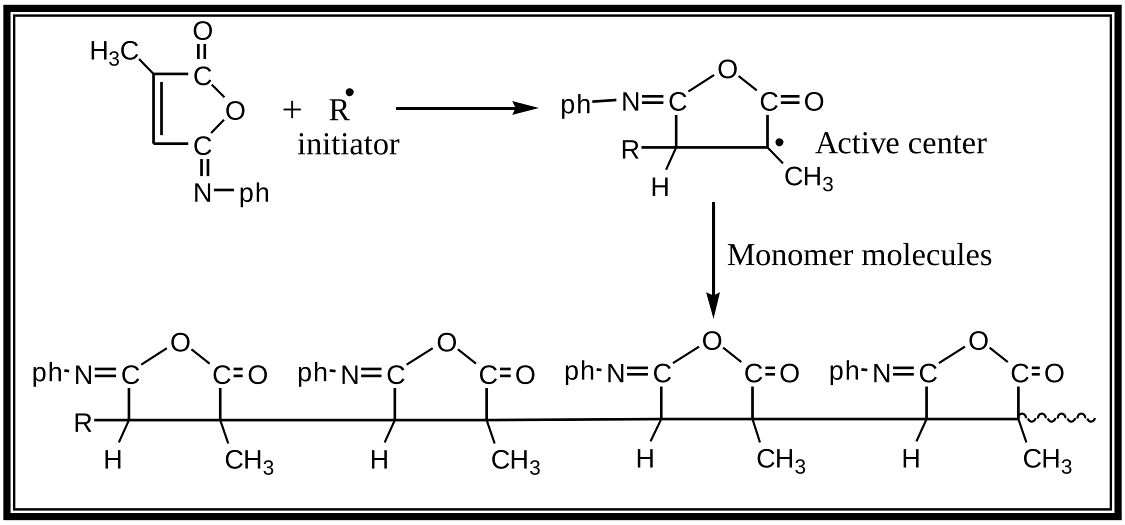
Also FTIR spectra of citraconisoimides showed clear characteristic band at (1780-1788) $cm^{-1}$ which belong to ν(C=O) lactone ring. Other bands were appeared at (1674-1677) $cm^{-1}$ and (1612-1636) $cm^{-1}$ due to ν(C=N) and ν(C=C) aliphatic respectively [22].

On the other hand U.V. spectra of citraconisoimides showed two clear bands at $\lambda_{max}$ (242-260) nm and (291-345) nm due to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transition in conjugated system of isoimide ring with substituted aromatic ring. HNMR spectrum of compound (5) showed signals at $\delta$ = (2.2), (6.9) and (7.2-7.4) ppm which were assigned for $CH_3$ protons, vinylic proton and aromatic protons respectively.

At the same time a series of four corresponding citraconimides were prepared via dehydration of the prepared citraconamic acids by fusion and their physical properties and spectral data were recorded. Comparison between physical properties and spectral data of citraconisoimides and corresponding citraconimides showed clear differences between them and gave us other proofs for success of citraconisoimide synthesis as shown in table-2 and 3.

In the third step of this work two of the prepared citraconisoimides were introduced in free radical chain growth homopolymerization using dioxane as solvent and (AIBN) as initiator. It is very necessary to mention here that success of free radical homopolymerization of citraconisoimides is very important result due to many reasons first synthesis of polyisoimides is very rare in literatures second free radical homopolymerization of the corresponding maleisoimides is failed completely to afford polymaleisoimide as reported in literatures [12] and instead affording polymaleimide due to the rearrangement to more stable maleimide units.

The reason for success of citraconisoimide hompolymerization may be attributed to the attachment of methyl group to isoimide ring so the monomer here represents stable more substituted vinylic system, moreover methyl group caused formation of stable tertiary free radical active center in initiation stage which introduced successfully in propagation process and exhibit the whole growing polymeric chain enough stability which avoid rearrangement to the corresponding polyimides as described in Scheme (3).



**Scheme (3)**

Mechanism of free radical homopolymerization

Free radical homopolymerization of two corresponding citraconimides were performed also and their physical properties and spectral data were recorded and used for comparison. The listed data in table-4 showed that poly citraconisoimides are colored solids having less softening points and less intrinsic viscosities than the corresponding poly citraconimides.

FTIR spectra of poly citraconisoimides showed characteristic absorption band at (1744-1745) $cm^{-1}$ due to ν(C=O) lactone and other bands at (1650-1675) $cm^{-1}$ and (1535-1570) $cm^{-1}$ belong to ν(C=N) and ν(C=C) aromatic, while FTIR spectra of poly citraconimides showed bands at (1712-1713) $cm^{-1}$ and (1373-1396) $cm^{-1}$ due to ν(C=O) imide and ν(C-N). U.V. spectra of poly citraconisoimides showed two clear bands at $\lambda_{max}$ (240-245) nm and (291-295) nm due to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) electronic transitions in isoimide ring conjugated to benzene ring system while U.V. spectra of poly citraconimides showed only one band at $\lambda_{max}$ (250-255) nm. FTIR spectral data of compounds (13-16) are listed in table-5.

H-NMR spectrum of polymer (14) showed signals at $\delta$ = (1.3, 2, 2.25) ppm which belong to aliphatic proton, protons of $CH_3$ group linked to benzene ring and protons of $CH_3$ group linked to isoimide ring respectively. Signals at $\delta$ = (7.3-7.55) ppm are belong to aromatic protons.

The other part in this work involved introducing of the prepared citraconisoimides in copolymerization reaction with three vinylic monomers including arcylonitrile, methylmethacrylate and methylacrylate respectively.

This part is very important since it involved many important points first it involved synthesis of new copolymers containing isoimide moiety and this is rare in literatures second we proved in this part that citraconisoimides have good ability for introducing free radical copolymerization successfully producing good yields of the desirable copolymers.

Moreover the prepared copolymers showed different physical properties which lead to wide using in different applications and finally thermal stability of these copolymers increased with time and use due to rearrangement of isoimide ring to the corresponding stable citraconimide ring.

Softening points, intrinsic viscosities and solubility of the prepared copolymers are listed in table-6 while FTIR and U.V. spectral data for them are listed in table-7.

FTIR spectra of acrylonitrile copolymers (17-20) showed a clear absorption band at (2245-2249) $cm^{-1}$ due to $\nu(C\equiv N)$ and this proved the presence of acrylonitrile units in the prepared copolymers. Other absorption bands are shown in (1740-1745) $cm^{-1}$ and (1660-1690) $cm^{-1}$ due to $\nu(C=O)$ lactone and $\nu(C=N)$ respectively.

$^1$H-NMR spectra of copolymers (17) and (18) showed many signals at $\delta$ = (1.05-2), 2.35, 3.15 and (6.8-7.35) ppm which belong to aliphatic protons, protons of $CH_3$ group linked to isoimide ring, (-CH-CN) and aromatic protons. Compound (18) showed signal at $\delta$ = (2.1) ppm belong to protons of $CH_3$ group substituted on benzene ring. On the other hand FTIR spectra of copolymers (21-24) revealed clear absorptions at (1726-1744) $cm^{-1}$, (1625-1650) $cm^{-1}$ and (1150-1211) $cm^{-1}$ due to $\nu(C=O)$ lactone, $\nu(C=N)$ and $\nu(C\text{-}O\text{-}C)$ ester respectively.

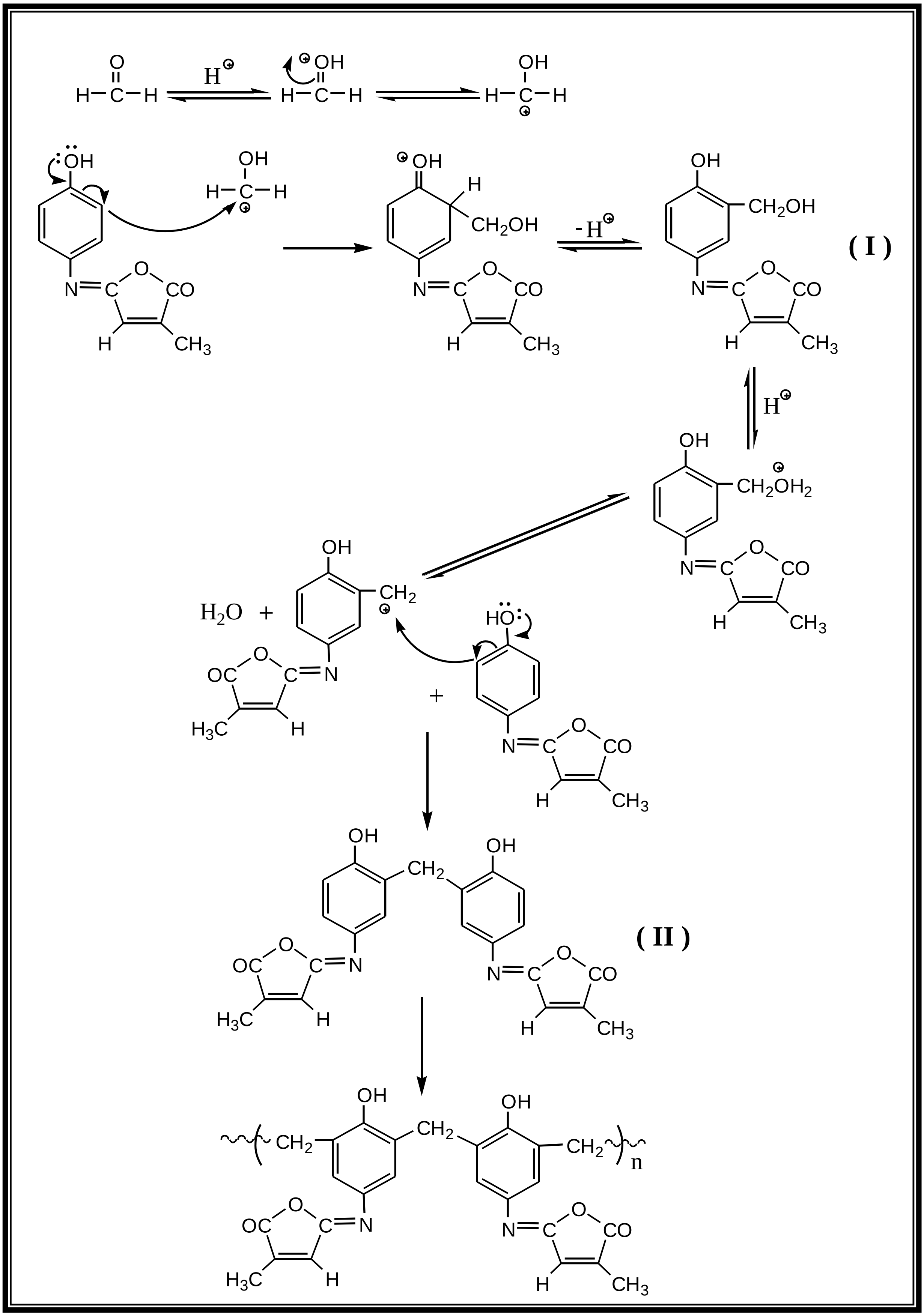
$^1$H-NMR spectra of copolymers (21-23) showed many signals at $\delta$ = (0.7-1.8), (2.25-2.5), (3.3-3.55) and (6.9-7.85) ppm which belong to aliphatic protons, protons of $CH_3$ group linked to isoimide ring, (-$COO\underline{CH_3}$) protons and aromatic protons. Compounds (21) and (22) showed another signal at $\delta$ = (2.5) ppm belong to protons of methyl group in methacrylate moiety, while compound (22) showed signal at $\delta$ = (2.05) ppm belong to protons of $CH_3$ substituted on aromatic ring (24).

U.V. spectra of the prepared copolymers (17-24) showed bands at $\lambda_{max}$ (315-343) and (345-400) nm. These absorptions were due to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions in ester group or cyano groups attached to substituted isoimide moiety.

Copolymers (21-24) gave positive results in characteristic test of esters proving success of copolymerization reaction.

In general copolymerization is very important technique which collects between different monomers together producing new polymers having new physico-chemical properties [25]. Thus prepared copolymers in this work showed different physical properties depending on the nature of vinylic monomers used in building their repeating units. The presence of polar cyano group in the repeating units of acrylonitrile copolymers (17-20) increased intermolecular interactions over all polymeric chains leading to increase crystallinity and this exhibit the polymers high softening points and resistance to solubility in many organic solvents. On the other hand introducing of methylmethacrylate and methylacrylate monomers in copolymerization with citraconisoimides exhibit the resulted copolymers softness, flexibility and good solubility in many organic solvents. These physical properties are fitted with the expected ones since incorporation of flexible moieties like esters decrease crystallinity and intermolecular interactions and this increase flexibility and solubility.

Since phenol-formaldehyde resins are very important polymers with wide spectrum of different applications [26-27] the present work involved also synthesis of new phenolic resins containing pendant citraconisoimide moiety in their repeating units. Synthesis of these resins was performed by condensation polymerization of the prepared N-(hydroxy phenyl)citraconisoimides with formaldehyde under conditions similar to those used in Novolac preparation including reflux at (70°C) for 3 hrs. in the presence of acid catalyst. N-(hydroxy phenyl) citraconisoimides were introduced successfully in this reaction since it represent a modified phenolic moiety which condensed with formaldehyde instead of known phenol producing the new phenolic resins as described in Scheme (4).



**Scheme (4)**

Mechanism steps for synthesis of the new phenolic resins

The first step in mechanism of this reaction involved reaction of proton with formaldehyde producing carbocation which introduced electrophilic substitution reaction on phenolic ring producing (methylol phenol) (I) which inturn introduced electrophilic substitution reaction with another phenolic ring under the influence of acidic medium producing di(hydroxy phenyl citraconisoimidyl)methane (II) which introduce subsequent electrophilic substitution reactions producing the desirable phenolic resins.

The prepared phenolic resins are colored solids having high softening points and their intrinsic viscosities are in the range (0.65-0.69) dL/g.

FTIR spectra of phenolic resins showed many clear absorption bands at (1730-1735) $cm^{-1}$, (1660-1680) $cm^{-1}$ and (3330-3525) $cm^{-1}$ which belong to ν(C=O) lactone, ν(C=N) and ν(O-H) phenolic respectively while U.V. spectra of these resins revealed two bands at $\lambda_{max}$ (265-266) and (281-290) nm which are due to $(\pi\rightarrow\pi^*)$ and $(n\rightarrow\pi^*)$ transitions in phenolic ring attached to isoimide moiety.

$^1H$-NMR spectrum of phenolic resin (25) showed signals at $\delta$ = (2, 3.3, 5.85, 6.3 and 7.1) ppm which belong to $CH_3$ protons, methylol protons, vinylic proton, phenolic OH proton and aromatic protons. Physical properties of the prepared phenolic resins are listed in table-8 and their FTIR and U.V. spectral data are listed in table-9.

$^1H$-NMR spectral data and C.H.N analysis for some of the prepared compounds in this work are listed in tables-10 and 11, respectively.

## Conclusions

The present investigation supplies us with very valuable information about the ability of citraconisoimides for chain growth homopolymerization, copolymerization and condensation polymerization. This information include the following:

1- The prepared N-subsituted citraconisoimides introduced successfully in free a radical chain growth homopolymerization producing new stable homopolymers.

2- The prepared N-substituted citraconisoimides introduced successfully in free radical chain growth copolymerization with different vinylic monomers producing new copolymers having different physical properties which may serve different applications.

3- N-(hydroxy phenyl)citraconisoimides introduced successfully in condensation polymerization with formaldehyde under conditions similar to those used in Novolac producing new phenolic resins containing pendant citraconisoimide moiety in their repeating units.

**Table 9-** FTIR and U.V. spectral data of N-substituted citraconisoimides phenolic resins

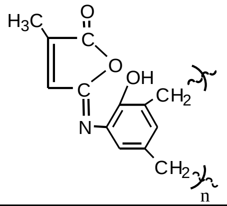
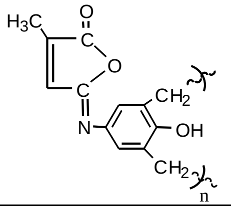
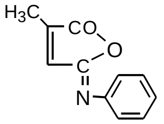
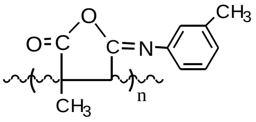
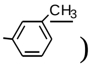
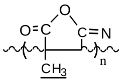
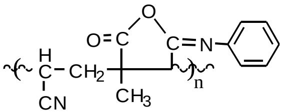
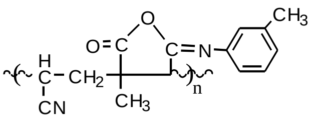
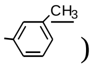
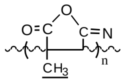
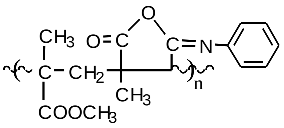
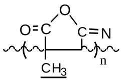
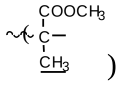
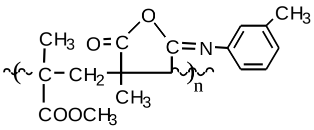
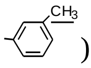
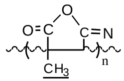
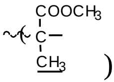
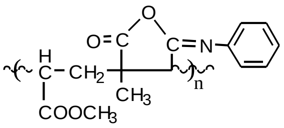
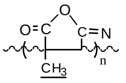
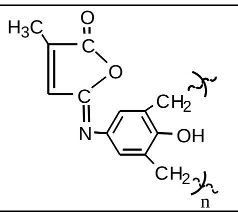
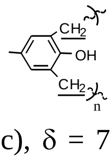
| Comp. No. | Compound structure | FTIR absorptions $cm^{-1}$ | | | | | | | U.V. $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|---|---|---|
| | | ν(C=O) lactone | ν(C=N) | ν(C-H) aromatic | ν(C=C) aromatic | ν(C-H) aliphatic | ν(C=C) aliphatic | ν(O-H) phenolic | |
| 25 |  | 1730 | 1660 | 3125 | 1550 | 2955 | 1610 | 3525 | 266<br>281 |
| 26 |  | 1735 | 1680 | 3090 | 1560 | 2945 | 1630 | 3330 | 265<br>290 |

**Table 10-** $^1$HNMR spectral data for some of the prepared compounds

| Comp. No. | Compound Structure | $^1$HNMR spectral data (δ ppm) |
|---|---|---|
| 5 |  | δ = 2.2(s, 3H, $CH_3$ protons), δ = 6.9(s, 1H, vinylic), δ = (7.2-7.4) m, 5H, aromatic protons |
| 14 |  | δ = 1.3(s, aliphatic proton), δ = 2(s, 3H, $CH_3$ protons  ), δ = 2.25(s, 3H, $CH_3$ protons  ), δ = (7.3-7.55) (m, 4H, aromatic protons) |
| 17 |  | δ = (1.4-2) d, aliphatic protons, δ = 2.35(s, 3H, $CH_3$ protons, δ = 3.15(t, -C<u>H</u>CN proton), δ = (7.05-7.3)(m, 5H, aromatic protons) |
| **Comp. No.** | **Compound Structure** | **$^1$HNMR spectral data (δ ppm)** |
| 18 |  | δ = (1.05-1.75) d, aliphatic protons, δ = 2.1(s, 3H, $CH_3$ protons  ), δ = 2.35(s, 3H, $CH_3$ protons  ), δ = 3.15(t, -C<u>H</u>CN proton),<br>δ = (6.8-7.35) (m, 4H, aromatic protons) |
| 21 |  | δ = (1-1.65) d, aliphatic protons, δ = 2.3(s, 3H, $CH_3$ protons  ), δ = 2.5(s, 3H, $CH_3$ protons  ), δ = 3.3(s, 3H, $OCH_3$ protons),<br>δ = (7.1-7.65) (m, 5H, aromatic protons |
| 22 |  | δ = (0.8-1.7) m, aliphatic protons, δ = 2.05(s, 3H, $CH_3$ protons  ), δ = 2.25(s, 3H, $CH_3$ protons  ), δ = 2.5(s, 3H, $CH_3$ protons )  ), δ = 3.35(s, 3H, $OCH_3$ protons), δ = (6.9-7.5) (m, 4H, aromatic protons) |
| 23 |  | δ = (0.7-1.8) m, aliphatic protons, δ = 2.5(s, 3H, $CH_3$ protons  ),<br>δ = 3.55(s, 3H, $OCH_3$ protons), δ = (7.2-7.85) (m, 5H, aromatic protons |
| 25 |  | δ = 2(s, 3H, $CH_3$ protons), δ = 3.3(m, 4H,  ), δ = 5.85(s, 1H, vinylic), δ = 6.3(s, OH phenolic), δ = 7.1(2H, aromatic protons). |

s: singlet d: doublet m: mltiplet

**Table 11-** C.H.N. Analyses for some of the prepared compounds

| **Comp. No.** | **Calculated** | | | **Found** | | |
|---|---|---|---|---|---|---|
| | **%C** | **%H** | **%N** | **%C** | **%H** | **%N** |
| 6 | 71.64 | 5.47 | 6.96 | 71.78 | 5.26 | 7.14 |
| 8 | 65.02 | 4.43 | 6.89 | 64.90 | 4.66 | 7.04 |
| 14 | 71.64 | 5.47 | 6.96 | 71.93 | 5.74 | 6.74 |
| 20 | 65.62 | 4.68 | 10.93 | 65.79 | 4.54 | 11.20 |
| 21 | 66.89 | 5.92 | 4.87 | 66.65 | 6.22 | 5.00 |
| 24 | 66.89 | 5.92 | 4.87 | 67.18 | 6.17 | 4.71 |
| 25 | 68.12 | 4.80 | 6.11 | 68.38 | 5.07 | 6.23 |

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