

MODIFICATION OF PHTHALIMIDYLPHENOL-FORMALDEHYDE RESINS VIA ESTERIFICATION

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Abstract

N-(hydroxyphenyl) phthalimides were allowed to condense with formaldehyde in the presence of an acid catalyst to produce three phenol-formaldehyde resins having pendant phthalimides. The prepared phenolic resins were modified by esterification of phenolic hydroxyl groups.

Esterification was achieved via treatment of phenolic resins with different acid chlorides in the presence of triethylamine to obtain new resins having new properties in hope to serve new applications.

Introduction

Phenolic resins are the most important thermosetting resins which are used in a wide variety of applications include varnishes, adhesives, laminates, casting, binders and surface coatings⁽¹⁻³⁾.

Since the discovery of phenol-formaldehyde resin in 1907 many attempts have been carried by several workers to incorporate structural modifications⁽⁴⁻⁷⁾.

Modifications were performed through using of aldehydes other than formaldehyde or by using different phenols to obtain new resins having new properties.

In the present work three phenol-formaldehyde resins having pendant phthalimide groups in the repeating units were prepared via poly condensation of N-(hydroxyphenyl) phthalimides with formaldehyde under conditions similar to those of Novolac preparation.

The prepared phenolic resins were modified by esterification which was performed via treatment of resins with different acid chlorides in the presence of triethylamine.

The nine cured resins have new properties in hope to use in new applications.

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- U.V. spectra were recorded on Shimadzu UV-VIS recorder.
- 4- C.H.N. analyses were determined by Perkin-Elmer 240 element analyzer.
- 5- Softening points were determined on Thermal Microscope Reichert Thermover, SP1, 160.
- 6- Intrinsic viscosities were determined with Automatic viscometer Tafesa Ubbelohde viscometer at 25°C using DMF and acetone as solvents.

1- Preparation of N-(hydroxyphenyl) phthalamic Acids [1-3]

Ortho, meta and p-aminophenols were allowed to react with phthalic anhydride according to literatures⁽⁸⁻⁹⁾.

The prepared amic acids were purified by recrystallization from ethanol. Table (I) lists melting points, percent yields and spectral data of the prepared amic acids.

2- Preparation of N-(hydroxyphenyl) phthalimides [4-6]

The titled imides were prepared by dehydration of the corresponding amic acids according to literature procedure⁽¹⁰⁾ using fusion technique. The resulted imides were purified by recrystallization from cyclohexane.

Table (II) lists melting points, percent yields and spectral data of the prepared imides.

3- Preparation of N-phthalimidyl phenol-formaldehyde resins Via Polycondensation [7-9]

The titled compounds were prepared according to literatures^(11,12) with few modifications:

In three-necked flask fitted with a reflux condenser, thermometer and dropping funnel 2.3g (0.01 mole) of N-(hydroxyphenyl) phthalimides, (2 ml) of formalin 37% and (10 ml) DMF were placed. The dropping funnel was charged with (0.2 ml) of conc. H₂SO₄ and (0.5 ml) of distilled water. The acid catalyst was added dropwise with stirring and the mixture was refluxed at 110°C for 3 hrs.

The evolved water and solvent were distilled off under reduced pressure and the polymeric residue was dissolved in DMF then filtered and the filtrate was added to excess water to precipitate the polymer. The precipitated polymer was filtered, washed with water then with petroleum ether and dried in an oven at (60-70)°C for 24 hrs. Table III lists some physical properties, U.V data and major IR absorptions of the prepared resins.

Modification of the Prepared Phenol-Formaldehyde Resins Via Esterification

Modification of the prepared resins by esterification includes the following preparations:

4-Esterification of The Prepared Phenolic Resins to The Corresponding Benzoates [10-12]

Esterification of phenolic resins was performed according to literature procedures⁽¹³⁾ with some modifications:

In a suitable round bottomed flask (0.01 mole) of the prepared phthalimidyl phenolic resin was dissolved in (30 ml) of DMF then (1.2 ml) of triethylamine was added. To this solution (2 ml) of benzoyl chloride was added dropwise through a pressure-equalized funnel with stirring and cooling then stirring was continued for another six hrs. at room temperature.

The mixture was filtered then the filtrate was evaporated under reduced pressure and the residue was extracted with water and chloroform. The organic layer was

dried and the solvent was evaporated to yield a thick oil which was purified by passing its chloroform solution through a florisil column or by recrystallization from cyclohexane.

Table (IV) lists physical properties, U.V absorptions and major IR absorptions of the prepared phthalimidyl benzoyloxyphenyl-formaldehyde resins.

5- Esterification of The Prepared Phenolic Resins to The Corresponding Methacrylates [13-15]

The titled compounds were prepared by following the same procedure used in the preparation of benzoates [10-12] except the using of methacryloyl chloride instead of benzoyl chloride.

Table (V) lists physical properties, U.V absorptions and major IR absorptions of the prepared phthalimidyl methacryloyloxy phenyl-formaldehyde resins.

6- Esterification of The Prepared Phenolic Resins to The Corresponding Cinnamates [16-18]

The titled compounds were prepared by following the same procedure used in the preparation of benzoates [10-12] except the using of cinnamoyl chloride instead of benzoyl chloride.

Physical properties, U.V absorptions and major IR absorptions of the prepared phthalimidylcinnamoyloxyphenyl-formaldehyde resins are listed in Table (VI).

Discussion and Results

The aim of the present work is to incorporate structural modification on the prepared phthalimidyl phenol-formaldehyde resins to obtain new properties which in turn fitted with new applications. Performing this aim includes many steps the first one involved preparation of three N-(hydroxy phenyl)phthalamic acids through reaction of phthalic anhydride with o, m and p-aminophenols.

Dehydration of the prepared phthalamic acids to the corresponding N-(hydroxy phenyl)phthalimides was performed in the second step by using fusion technique while the third step involved polycondensation of the prepared imides with formaldehyde in the presence of acidic catalyst to produce

phenol-formaldehyde resins having pendant phthalimides.

Modification of the prepared phenolic resins was performed in the fourth step of this work via esterification of phenolic hydroxyl groups.

Esterification was achieved by treatment of the prepared (phthalimidyl phenol-formaldehyde) resins with different acid chlorides including benzoyl, methacryloyl and cinnamoyl chlorides in the presence of triethylamine to produce the corresponding benzoate, methacrylate and cinnamate esters.

Physical properties, spectral data and C.H.N. analyses of the prepared compounds are listed in Tables (I-VII) while Figures (1-6) show IR and U.V spectra for some of them.

Success of esterification reaction was confirmed by disappearance of phenolic hydroxyl absorption band and appearance of two characteristic clear absorption bands in IR spectra of the cured resins in the regions (1724-1767) cm^{-1} and (1125-1203) cm^{-1} which were attributed to (ester C=O) and (ester C-O) respectively⁽¹⁴⁾.

The cured resins also give positive results in characteristic test for ester.

On the other hand U.V spectra of the cured resins showed absorptions at λ_{max} (331-344) nm due to $\pi \rightarrow \pi^*$ transitions in the conjugated system of carbonyl groups with phenyl ring in phthalimidyl moiety and phenyl ring with attached benzoate, methacrylate and cinnamate groups⁽¹⁵⁾.

It is important to mention here that incorporation of benzoate, methacrylate and cinnamate groups in the prepared phenolic resins supply us with new resins having new properties. It is noticeable that some of the cured resins are oils while others are solids having low softening points and all of them are soluble in many organic solvents and have low intrinsic viscosities in the range (0.16-0.55) dL/gm.

In general all these physical properties make the cured resins suitable for certain applications such as adhesives, brake-lining and varnishes since flexible and oily phenolic resins are suitable for these applications^(2,3).

As a final result it is clear that the present work supply us through modification with new resins having new properties in hope to serve new applications.

Table (I):
Physical properties and spectral data of Amic acids.

| Comp. No. | Compound structure | Yield % | Melting point °C | U.V. λ_{max} (nm) | Major IR absorptions, cm^{-1} | | | |
|-----------|--------------------|---------|------------------|-------------------------------------|--|-----------------|----------------------------|-----------------------|
| | | | | | $\nu\text{O-H}$ | $\nu\text{N-H}$ | $\nu\text{C=O}$ carboxylic | $\nu\text{C=O}$ amide |
| 1 | | 94 | 220-222 | 268 | 3150 | 3000 | 1690 | 1660 |
| 2 | | 90 | 212-214 | 280 | 3350 | 3200 | 1700 | 1625 |
| 3 | | 93 | 294-295 | 277 | 3250 | 3100 | 1700 | 1650 |

Table (II):
Physical properties and spectral data of phthalimides.

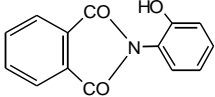
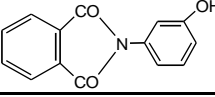
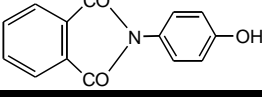
| Comp. No. | Compound structure | Yield% | Melting point °C | U.V. λ_{\max} (nm) | Major IR absorptions, cm^{-1} | | |
|-----------|---|--------|------------------|----------------------------|--|-----------------------|-----------------|
| | | | | | $\nu\text{O-H}$ phenolic | $\nu\text{C=O}$ Imide | $\nu\text{C-N}$ |
| 4 |  | 84 | 206-208 | 285 | 3379 | 1699 | 1388 |
| 5 |  | 91 | 202-203 | 285 | 3321 | 1707 | 1395 |
| 6 |  | 87 | 280-282 | 285 | 3412 | 1714 | 1394 |

Table (III):
Physical properties and spectral data of phenolic resins.

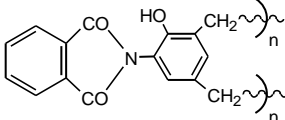
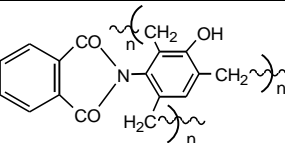
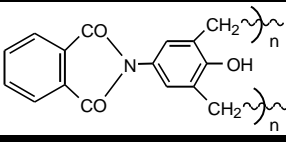
| Comp. No. | Polymer structure | Conv. % | Softening point °C | $[\eta]$ dL/g | U.V. λ_{\max} (nm) | Major IR absorptions, cm^{-1} | | |
|-----------|---|---------|--------------------|---------------|----------------------------|--|-----------------------|-----------------|
| | | | | | | $\nu\text{O-H}$ phenolic | $\nu\text{C=O}$ Imide | $\nu\text{C-N}$ |
| 7 |  | 78 | 275-290 | 1.01 | 331 579 | 3402 | 1712 | 1402 |
| 8 |  | 81 | > 320 | 1.2 | 338 491 | 3421 | 1713 | 1375 |
| 9 |  | 74 | 300-310 | 0.98 | 333 540 | 3410 | 1712 | 1390 |

Table (IV):
Physical properties and spectral data of (phthalimidyl benzyloxy phenyl-formaldehyde) Resins.

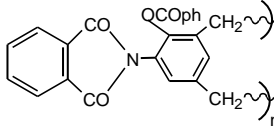
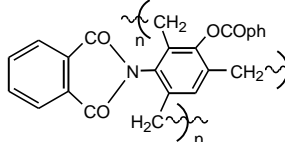
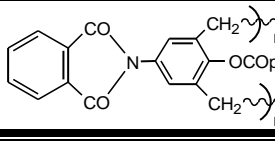
| Comp. No. | Compound structure | Yield % | Softening point °C | $[\eta]$ dL/g | U.V. λ_{\max} (nm) | Major IR absorptions, cm^{-1} | | |
|-----------|---|---------|--------------------|---------------|----------------------------|--|-----------------------|-----------------------|
| | | | | | | $\nu\text{C=O}$ Ester | $\nu\text{C=O}$ Imide | $\nu\text{C-O}$ Ester |
| 10 |  | 80 | 45-55 | 0.24 | 331 | 1766 | 1700 | 1170 |
| 11 |  | 83 | 66-68 | 0.51 | 344 | 1762 | 1715 | 1125 |
| 12 |  | 85 | 60-71 | 0.44 | 336 | 1789 | 1689 | 1175 |

Table (V):

Physical properties and spectral data of (phthalimidyl methacryloyloxy phenyl-formaldehyde) Resins.

| Comp. No. | Polymer structure | Yield% | Softening point °C | [η] dL/g | U.V. λ_{\max} (nm) | Major IR absorptions, cm^{-1} | | |
|-----------|-------------------|--------|--------------------|-----------------|----------------------------|--|--------------------------|--------------------------|
| | | | | | | $\nu_{\text{C=O}}$ Ester | $\nu_{\text{C=O}}$ Imide | $\nu_{\text{C-O}}$ Ester |
| 13 | | 72 | Oil | 0.16 | 334 | 1733 | 1701 | 1184 |
| 14 | | 75 | 62-70 | 0.4 | 331 | 1730 | 1700 | 1157 |
| 15 | | 88 | Oil | 0.18 | 338 | 1724 | 1627 | 1145 |

Table (VI):

Physical properties and spectral data of (phthalimidyl cinnamoyloxy phenyl-formaldehyde) Resins.

| Comp. No. | Polymer structure | Yield % | Softening point °C | [η] dL/g | U.V. λ_{\max} (nm) | Major IR absorptions, cm^{-1} | | |
|-----------|-------------------|---------|--------------------|-----------------|----------------------------|--|--------------------------|--------------------------|
| | | | | | | $\nu_{\text{C=O}}$ Ester | $\nu_{\text{C=O}}$ Imide | $\nu_{\text{C-O}}$ Ester |
| 16 | | 81 | 65-75 | 0.48 | 335 | 1760 | 1704 | 1185 |
| 17 | | 90 | 72-84 | 0.55 | 333 | 1767 | 1701 | 1200 |
| 18 | | 84 | 50-55 | 0.3 | 331 | 1766 | 1697 | 1203 |

Table (VII)

C.H.N. Analysis of some of the prepared and cured resins.

| Comp. No. | Calculated | | | Found | | |
|-----------|------------|------|------|-------|------|------|
| | %C | %H | %N | %C | %H | %N |
| 7 | 72.45 | 4.15 | 5.28 | 72.67 | 4.42 | 5.59 |
| 8 | 73.38 | 4.31 | 5.03 | 73.71 | 4.52 | 5.32 |
| 11 | 75.39 | 4.19 | 3.66 | 75.14 | 4.39 | 3.84 |
| 12 | 74.79 | 4.06 | 3.79 | 74.49 | 4.29 | 3.64 |
| 14 | 72.83 | 4.62 | 4.04 | 72.48 | 4.43 | 4.21 |
| 16 | 75.94 | 4.30 | 3.54 | 75.7 | 4.16 | 3.43 |
| 18 | 75.94 | 4.30 | 3.54 | 76.21 | 4.20 | 3.69 |

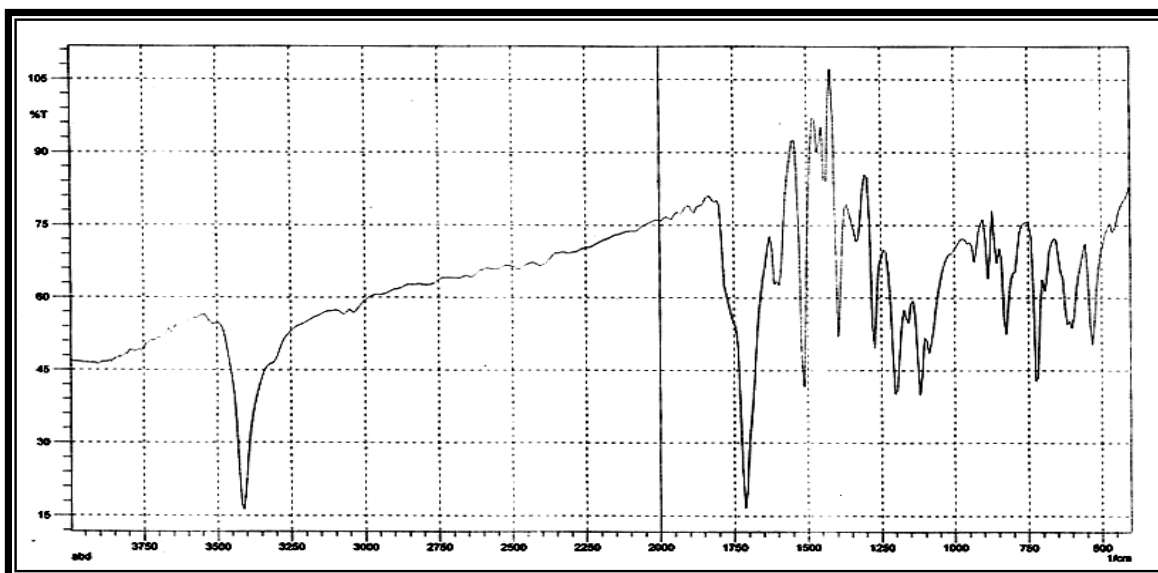


Fig.(1) FTIR spectrum of compound (9)

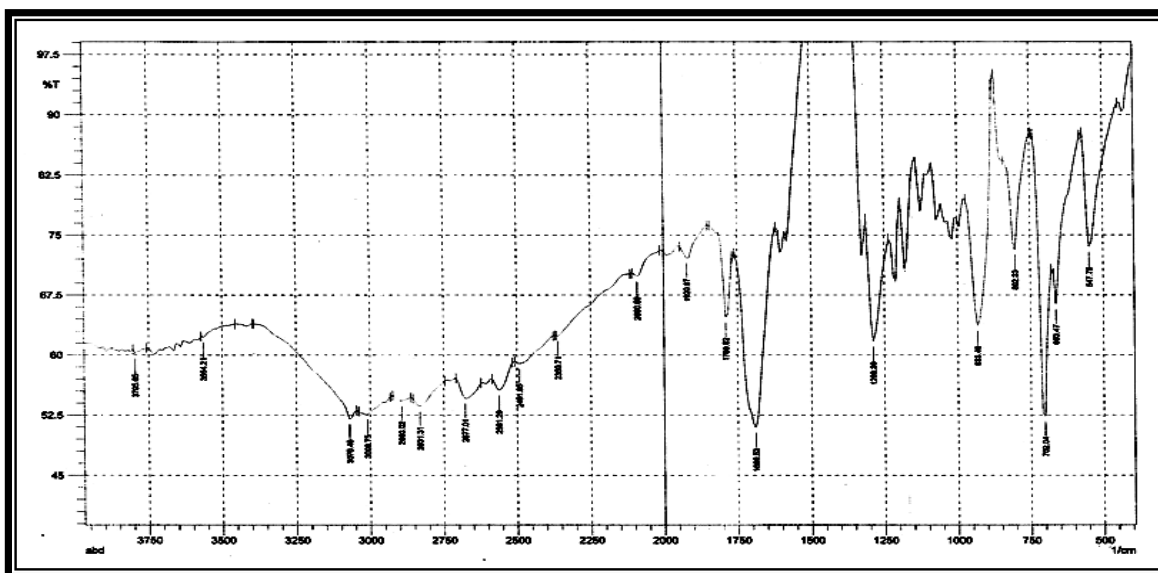


Fig.(2) FTIR spectrum of compound (12)

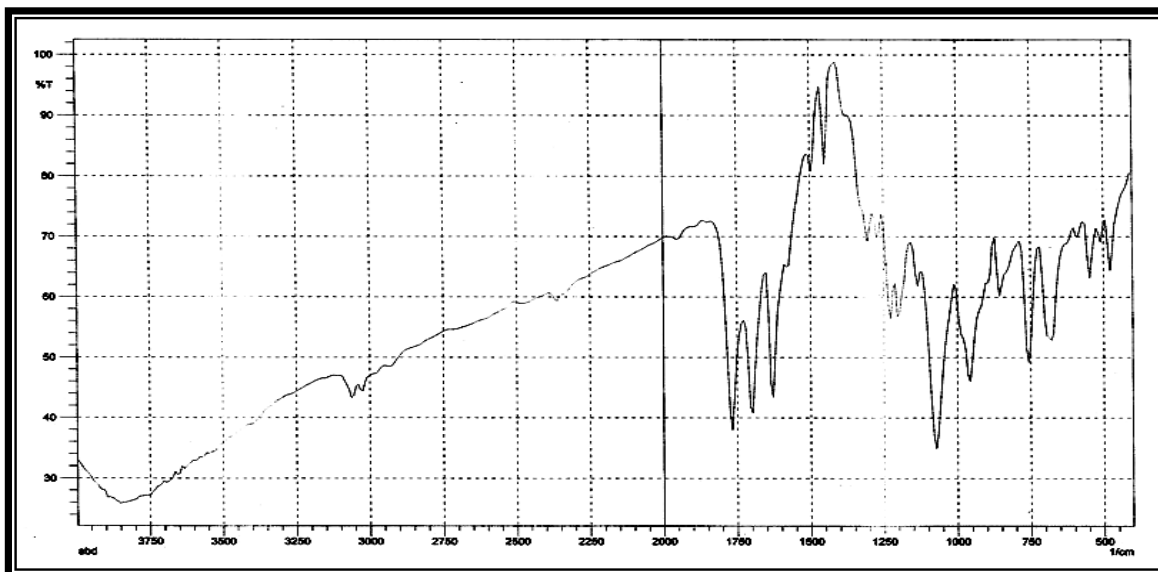


Fig.(3) FTIR spectrum of compound (18)

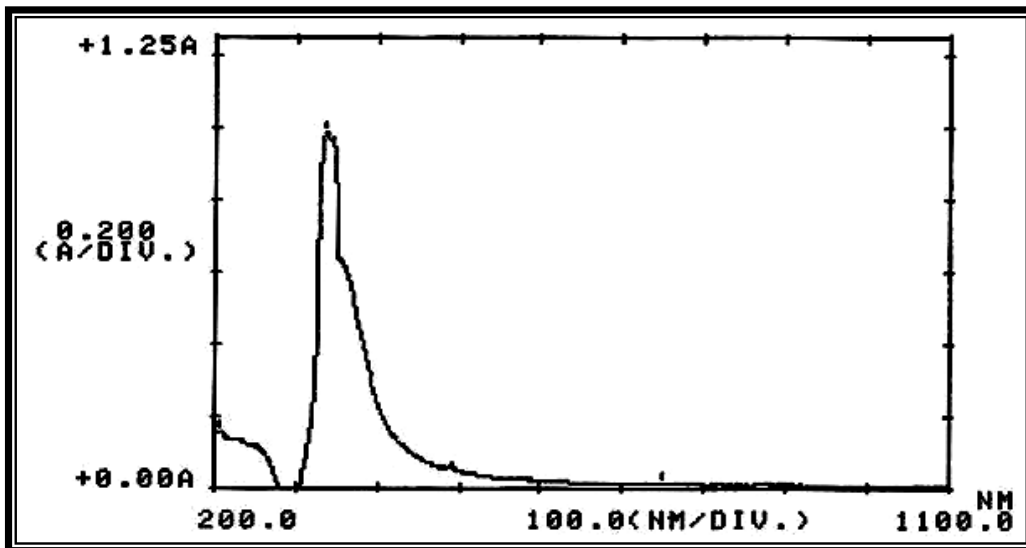


Fig.(4) U.V. spectrum of compound (12)

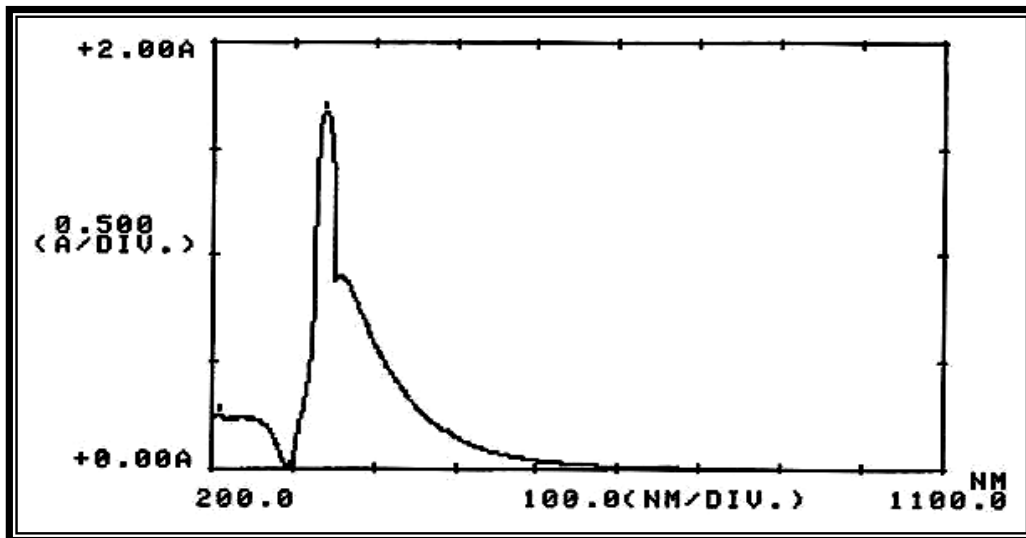


Fig.(5) U.V. spectrum of compound (15)

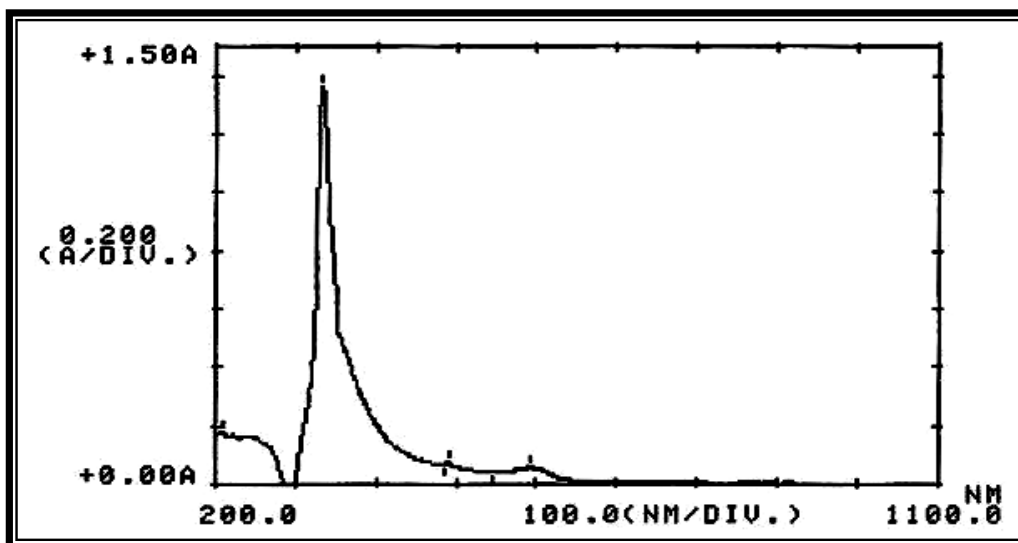


Fig.(6) U.V. spectrum of compound (17)

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الخلاصة

تضمن البحث ادخال مركبات N-(هيدروكسي فينيل) فثال ايميدات في بلمرة تكثيفية مع الفورمالديهايد بوجود عامل مساعد حامضي للحصول على راتنجات فينول-فورمالديهايد معوضة بمجاميع متدلبيه من الفثال ايميدات.

بعد ذلك تمت معالجة الراتنجات المحضرة من خلال اجراء استرة لمجاميع الهيدروكسيل الفينولية المعوضة في هذه الراتنجات، حيث انجزت الاسترة من خلال معاملة الراتنجات الفينولية مع كلوريدات حوامض مختلفة بوجود ثلاثي اثيل امين وبذلك تم الحصول على راتنجات جديدة ذات مواصفات جديدة مما يفسح المجال امام استخدام هذه الراتنجات في تطبيقات جديدة.