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Synthesis and Curing of New Phenolic Resins Containing Pendant TetrachloroPhthalimides

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Abstract

Four new phenol-formaldehyde resins containing tetrachlorophthalimides in their repeating units were synthesized via condensation of formaldehyde with N-(hydroxy phenyl)tetrachlorophthalimides under conditions similar to those used in novolac preparation. In this work structural modifications were performed first via design and synthesis of new phenolic component represented by phenolic ring linked to thermally stable tetrachlorophthalimide moiety which condense with formaldehyde and second via introducing of phenolic hydroxyl groups present in the new synthesized resins by esterification reaction with acetyl chloride producing the corresponding acetoxy substituted resins. Both the prepared and the cured resins have new properties which may serve different applications.

Keywords: Phenol-formaldehyde resins, Tetrachlorophthalimide, Novolac, Structural modifications

تحضير ومعالجة راتنجات فينولية جديدة تحتوي على رباعي كلوروفثال ايمايدات متدلية

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الخلاصة

تم في هذا البحث تحضير اربعة راتنجات فينولية جديدة معوضة بمجاميع متدلية من رباعي كلوروفثال ايمايد في وحداتها المتكررة وذلك من خلال تكاثف الفورمالديهايد مع مركبات N-(هيدروكسي فنيل)رباعي كلوروفثال ايمايدات تحت ظروف مماثلة لظروف تحضير النوفولاك. تم انجاز التحوير التركيبي في هذه التحاضير من خلال تحضير مكونة فينولية جديدة متمثلة بحلقة فينول مرتبطة بمكونة رباعي كلوروفثال ايمايد المستقرة حرارياً ثم ادخالها في تفاعل تكاثف مع الفورمالديهايد.

اما التحوير التركيبي الثاني فقد تم انجازه من خلال معالجة الراتنجات الفينولية المحضرة وذلك بادخال مجاميع الهيدروكسي المعوضة اساساً في حلقاتها في تفاعل استرة مع كلوريد الاستيل مما اسفر عن تكوين راتنجات فينولية معوضة بمجاميع الاسيتوكسي. امتازت كل من الراتنجات المحضرة والراتنجات بعد المعالجة بمواصفات جديدة مما قد يسمح باستخدامها في تطبيقات مختلفة.

Introduction

Phenol-formaldehyde resins are the oldest commercial synthetic polymers which have excellent electrical, mechanical and chemical resistance and retention of properties after long term exposure to high temperatures [1, 2]. These properties made phenolic resins suitable for a variety of applications including laminates, molding, thermal insulating materials, coatings and adhesives [3-5]. Besides

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many efforts have been directed towards development of these resins via incorporating structural modifications[6-12]. In the present work four new phenol-formaldehyde resins having pendant tetrachlorophthalimides in their repeating units were prepared via poly condensation of N-(hydroxyphenyl) tetrachlorophthalimides with formaldehyde under conditions similar to those of novolac preparation. Tetrachlorophthalimide was choosed to incorporate in the newly synthesized phenolic resins since aromatic polyimides possess outstanding thermal, mechanical and electrical properties as well as excellent chemical resistance [13-16] and this in turn will enhance thermal and mechanical properties of the new resins leading to serve new applications.

Experimental

1. Materials

All chemicals employed were of analytical reagent grade and were used without further purification.

2. Instruments

FTIR spectra were recorded on a SHIMADZU FTIR 8400 Fourier transform Infrared spectrophotometer. ^{1}HNMR spectra were recorded on near magnetic resonance Bruker, ultrashield 300 MHz using DMSO-d_6 as solvent. Melting points were determined by using Gallen Kamp capillary melting point apparatus and were uncorrected. Softening points were determined on thermal microscope Riechertthermover.

1- Synthesis of N-(hydroxy phenyl) tetrachlorophthalamic acids (1-4)

Amino phenol (0.01 mol) dissolved in (30 mL) of dry acetone was added dropwise to (0.01 mol, 2.86 g) of tetrachlrorophthalic anhydride dissolved in (20 mL) of dry acetone with stirring and cooling [17, 18].

The resulted mixture was stirred for 2 h. at room temperature then the formed precipitate was filtered, washed with ether, dried and recrystallized from a suitable solvent.

2- Synthesis of N-(hydroxy phenyl) tetrachlorophthalimides (5-8)

Tetrachlorophthalamic acid (1 gm) was placed in a wide pyrex tube supplied with a thermometer and immersed in an oil bath [18]. The oil bath was heated gradually until the complete fusion of amic acid then oil bath temperature was kept at ten degrees above melting point of the used amic acid for 2h. The fused product was cooled to room temperature and the obtained solid was recrystallized from a suitable solvent.

3- Synthesis of N-(tetrachlorophthalimidyl)phenol-formaldehyde resins (9-12)

A mixture of (0.012 mol, 4.52g) N-(hydroxyphenyl)tetrachlorophthalimide, (0.01 mol) of formaldehyde 37% and (15 mL) of DMF was placed in a three neck round bottomed flask fitted with a reflux condenser, thermometer and dropping funnel [8,9]. The dropping funnel was charged with (0.2 mL) of conc. sulphuric acid and (1 mL) of distilled water then this solution was added drop wise with stirring and the resulted mixture was refluxed at 110°C for 3h.

The solvent was distilled off and the polymeric residue was dissolved in DMF then filtered and the filtrate was added to excess water to precipitate the polymer. The resulted polymer was filtered, washed with ether and dried in an oven at (65-70°C) for 24 h.

4-Curing via esterification of the synthesized phenolic resins to the corresponding poly [N-(acetoxy phenyl-formaldehyde)tetrachlorophthalimides] (13-16)

A mixture of (0.01 mol) of the prepared tetrachlorophthalimidyl phenolic resin, (20 mL) of DMF and (0.01 mol) of Et_3N was placed in a suitable round bottomed flask filtted with dropping funnel which was charged with (0.01 mol.) of acetyl chloride [8, 9].

Acetyl chloride was added dropwise to the mixture with stirring and cooling to (5°C) then stirring was continued for another six h. at room temperature. The resulted mixture was filtered then the filtrate was evaporated and the residue was dissolved in water then extracted with chloroform for three times. The organic layer was dried and the solvent was evaporated to yield a solid product which was purified by dissolving in DMF followed by precipitation by water, then filtration.

Physical properties of the prepared amic acids are listed in Table-1, of imides in Table-2, of phenolic resins in Table-3 and of the cured resins in Table-4 respectively.

Table 1- Physical properties of amic acids (1-4)

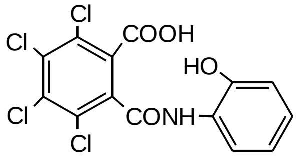
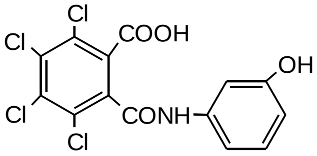
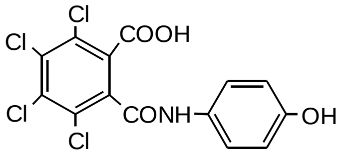
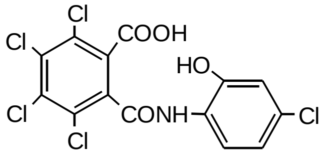
Comp. No.	Compound structure	Color	Yield %	Melting points °C	Recrystallization solvent
1		Gray	78	166-168	Ethanol
2		Bluish green	81	186-187	Ethanol
3		Faint green	76	170-172	Ethanol
4		Yellowish green	88	184-186	Ethanol

Table 2- Physical properties of cyclic imides (5-8)

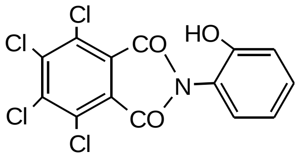
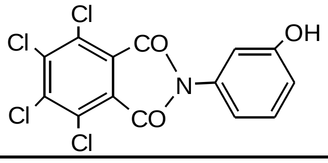
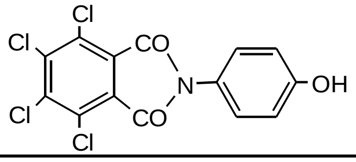
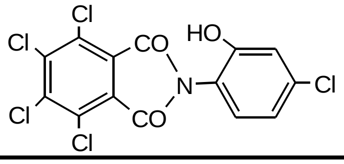
Comp. No.	Compound structure	Color	Yield %	Melting points °C	Recrystallization solvent
5		Deep gray	80	231-233	Acetone
6		Deep yellow	95	195 Dec.	Cyclohexane
7		Deep green	88	210-212	Cyclohexane
8		yellow	93	205 Dec.	Cyclohexane

Table 3- Physical properties of phenolic resins (9-12)

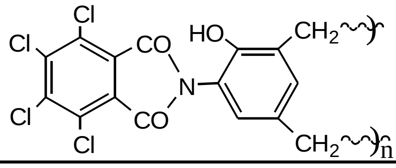
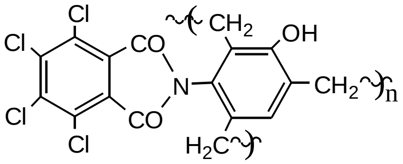
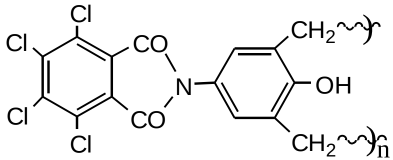
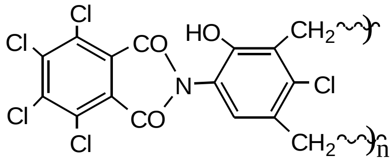
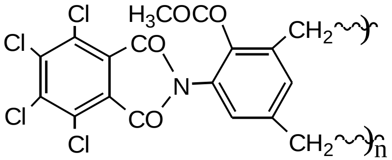
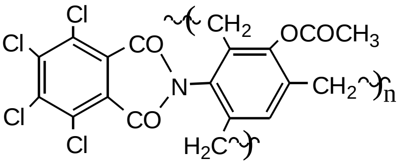
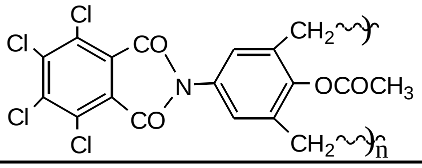
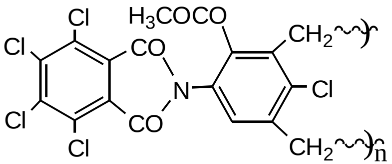
Comp. No.	Compound structure	Color	Yield %	Softening points °C	Purification
9		Black	75	277 Dec.	Dissolving in DMF then precipitation by water
10		Deep green	80	300 Dec.	Dissolving in DMF then precipitation by water
11		Deep green	65	295-300	Dissolving in DMF then precipitation by water
12		Green	83	280-290	Dissolving in DMF then precipitation by water

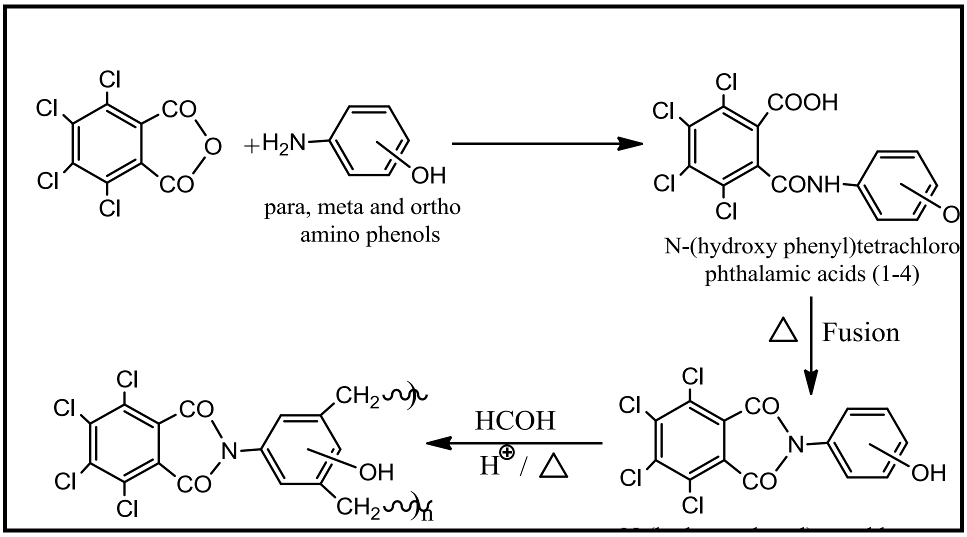
Table 4- Physical properties of cured resins (13-16)

Comp. No.	Compound structure	Color	Yield %	Softening points °C	Purification
13		Brown	67	192-198	Dissolving in DMF then precipitation by water
14		Faint brown	75	190-195	Dissolving in DMF then precipitation by water
15		Brown	77	188-192	Dissolving in DMF then precipitation by water
16		Deep brown	73	200-205	Dissolving in DMF then precipitation by water

Results and Discussion

Developments in the area of addition curable phenolic resins and the different strategies involved in their molecular design still the most important subject which play a vital role in synthesis, modification and applications of new phenol formaldehyde resins.

Thus the core of the present investigation is based on synthesis of new phenolic resins by structural modification through incorporation of thermally stable addition curable groups on the novolac repeating units. Performing the target of this work involved many synthetic steps which are summarized in Scheme-1.



Scheme 1- Synthetic sequence of phenolic resins

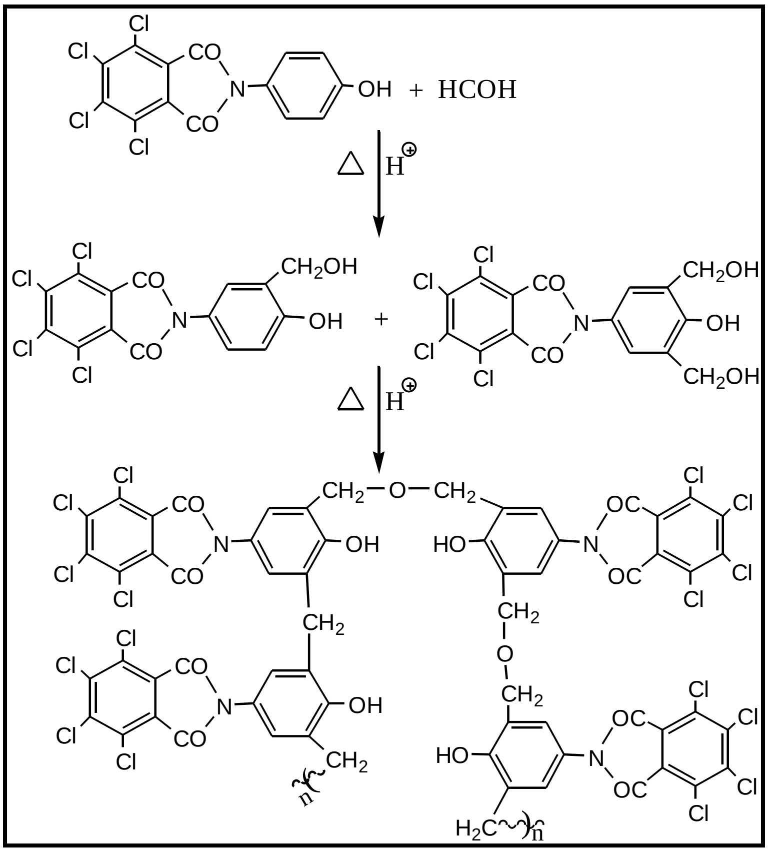
In the first step four N-(hydroxy phenyl) tetrachlorophthalamic acids (1-4) were prepared via reaction of ortho, meta and para-amino phenols with tetrachlorophthalaicanhydride [16, 17].

Dehydration of the prepared amic acids was performed in the second step by using fusion technique to produce the corresponding N-(hydroxy phenyl)tetrachlorophthalimides which in turn were introduced in condensation reaction with formaldehyde in the third step [9,18] producing the target phenolic resins (9-12).

Our new strategy used in building the target resins based on introducing of new phenolic moiety represented by phenolic ring linked to tetrachlorophthalimide in condensation reaction with formaldehyde. Tetrachlorophthalimide moiety was choosed as addition curable groups to incorporate in the new resins and this played an important role in affecting physical properties of the resulted resins since insertion of cyclic imide units in some polymer chains was greatly improved thermal and chemical stability of these polymers [8, 9].

The presence of tetrachlorophthalimide moiety in the chains of the newly synthesized phenolic resins exhibited them high thermal stability which was indicated through their high softening points, besides they showed resistance against solubility in many solvents including water, ethanol, acetone, benzene and dioxane, while they showed acceptable solubility in both DMF and DMSO.

The first stage in condensation reaction of phenolic imides with formaldehyde under heat and acidic conditions involved formation of mono methylol, dimethylol and trimethylol phenols while the later stage involved condensation reactions between methylol groups present in different phenolic rings leading to the formation of linkes between phenolic rings through ether ($-CH_2-O-CH_2-$) or methylene ($-CH_2-$) bridges producing the target phenolic resin as shown in Scheme-2.



Scheme 2- Stages of phenolic resins formation

Chemical structures of the prepared amic acids, imides and phenolic resins were confirmed in the basis of FTIR and ^{1}HNMR spectral data. FTIR spectra of the prepared amic acids (1-4) showed clear absorption bands at (3184-3477) cm^{-1} which were attributed to ν(O-H) carboxylic, ν(O-H) phenolic and ν(N-H) amide. Absorption bands due to ν(C=O) carboxyl and ν(C=O) amide appeared at (1712-1716) cm^{-1} and (1650-1660) cm^{-1} respectively while absorption bands due to ν(C-H) aromatic, ν(C=C) aromatic and ν(C-Cl) appeared at (3020-3089) cm^{-1}, (1596-1620) cm^{-1} and (1030-1103) cm^{-1} respectively [19].

^{1}HNMR spectrum of compound (2) N-(3-hydroxy phenyl) tetrachlorophthalamic acid showed signals at δ=(6-7.35) ppm belong to aromatic protons and singlet signal at (δ= 8.95) ppm belong to NH amide proton. Signals belong to OH phenolic proton and OH carboxyl proton appeared at (δ = 9.5-9.9) ppm and (δ = 10.6) ppm respectively.

^{1}HNMR spectrum of compound (3) N-(4-hydroxy phenyl) tetrachlorophthalamic acid showed two doublet signals at (δ= 6.73-6.76) ppm and (δ= 7.37-7.4) ppm belong to four aromatic protons. Other signals appeared at (δ= 9.34, 10.4 and 14) ppm belong to NH amide proton, OH phenolic proton and OH carboxyl proton respectively [19].

FTIR spectra of the prepared imides (5-8) showed two clear strong absorption bands at (1776-1787) cm^{-1} and (1704-1731) cm^{-1} due to asymmetric and symmetric ν(C=O) imide.

Absorption bands due to ν(C=C) aromatic and ν(C-N) imide were appeared at (1598-1612) cm^{-1} and (1365-1367) cm^{-1}, while absorption bands due to ν(O-H) phenolic, ν(C-H) aromatic and ν(C-Cl) appeared at (3417-3480) cm^{-1}, (3030-3078) cm^{-1} and (1090-1099) cm^{-1} respectively [20].

^{1}HNMR spectrum of compound (7) N-(4-hydroxy phenyl) tetrachlorophthalimide showed disappearance of ν(O-H) carboxyl and ν(N-H) amide signals. Signals of aromatic protons appeared as two doublets at (δ= 6.88 and 7.22) ppm while signal for phenolic (OH) proton appeared at (δ= 9.89) ppm.

FTIR spectral data of amic acids (1-4) and imides (5-8) are listed in Table-5 and Table-6 respectively while Figures 1-4 showed FTIR spectra and ^{1}HNMR spectra for compounds (2, 3, 6 and 7).

Table 5- FTIR spectral data (cm^{-1}) of amic acids (1-4)

Comp. No.	ν(O-H) and ν(N-H)	ν(C-H) aromatic	ν(C=O) carboxyl	ν(C=O) amide	ν(C=C) aromatic	ν(C-Cl)	Others
1	3267	3040	1712	1650	1620 1610	1030	-
2	3477 3394 3267	3089	1714	1654	1606	1043	-
3	3417 3274 3261	3020	1712	1650	1618	1103	p-sub. 825
4	3379 3184	3037	1716	1660	1596	1089	p-sub. 815

Table 6- FTIR spectral data (cm^{-1}) of cyclic imides (5-8)

Comp. No.	ν(O-H) phenolic	ν(C-H) aromatic	ν(C=O) imide	ν(C=C) aromatic	ν(C-N) imide	ν(C-Cl)	Others
5	3421	3078	1787 asy. 1731 sy.	1598	1365	1097	-
6	3417	3060	1778 asy. 1710 sy.	1612 1600	1367	1099	-
7	3419	3030	1776 asy. 1704 sy.	1612 1600	1367	1099	p-sub. 833
8	3480	3060	1780 asy. 1720 sy.	1605	1365	1090	p-sub. 822

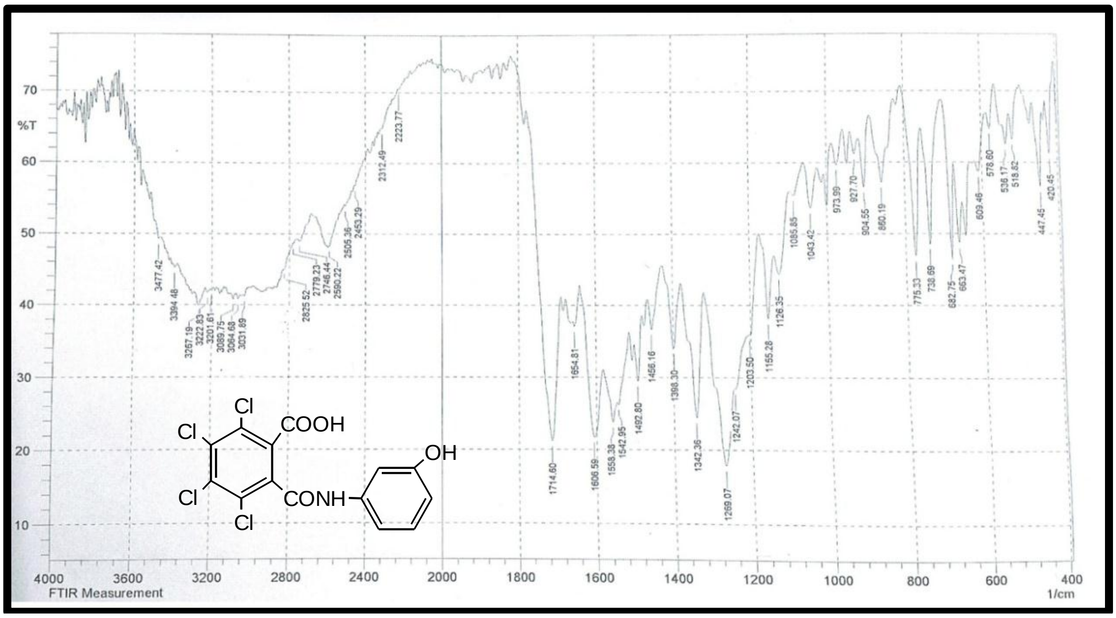


Figure 1- FTIR spectrum of compound (2)

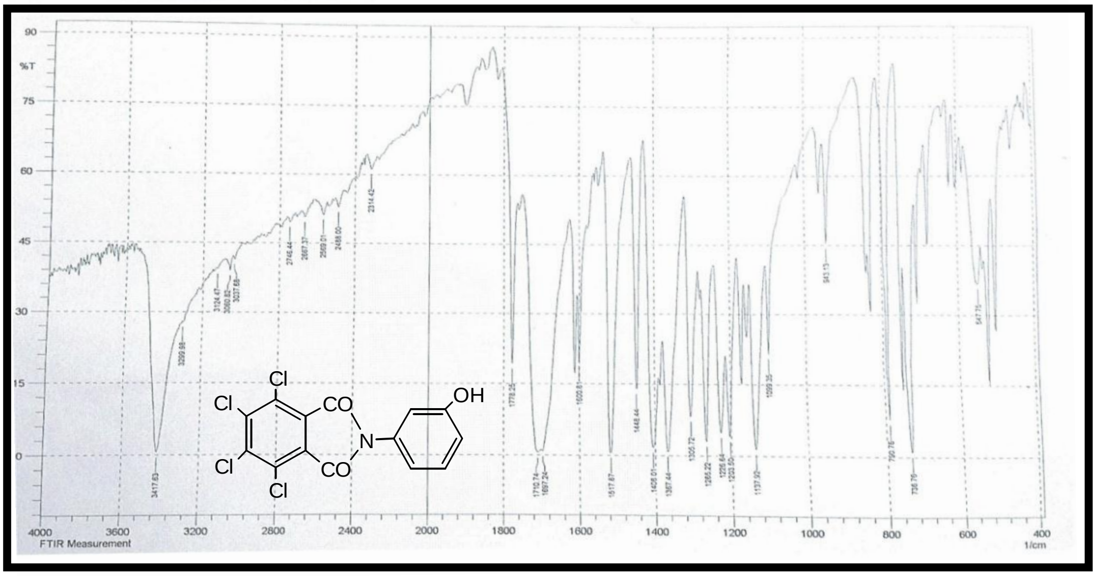


Figure 2- FTIR spectrum of compound (6)

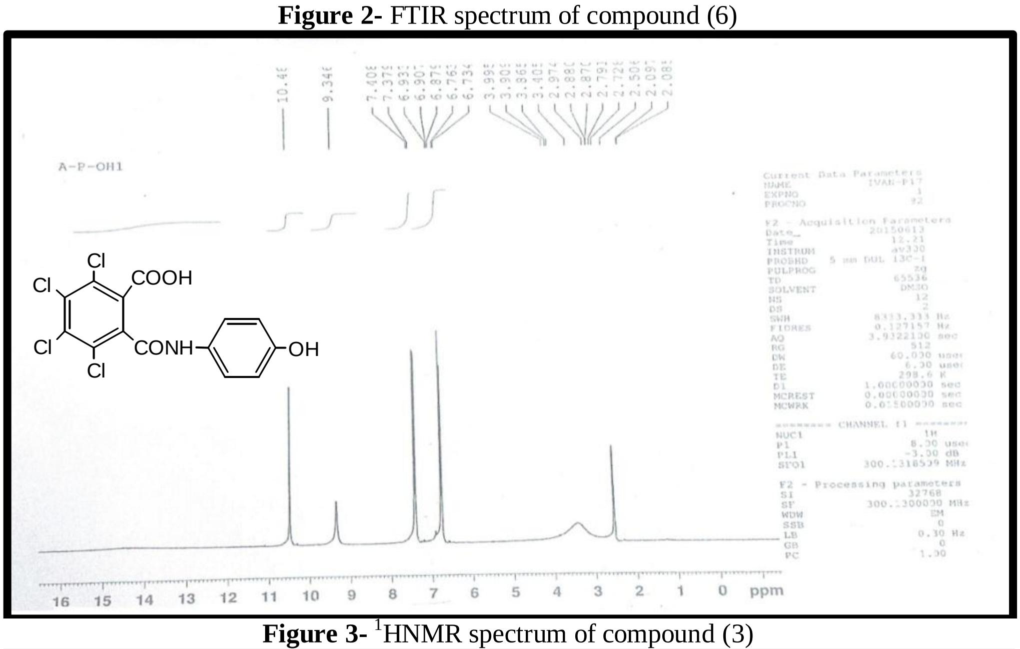


Figure 3- ^{1}HNMR spectrum of compound (3)

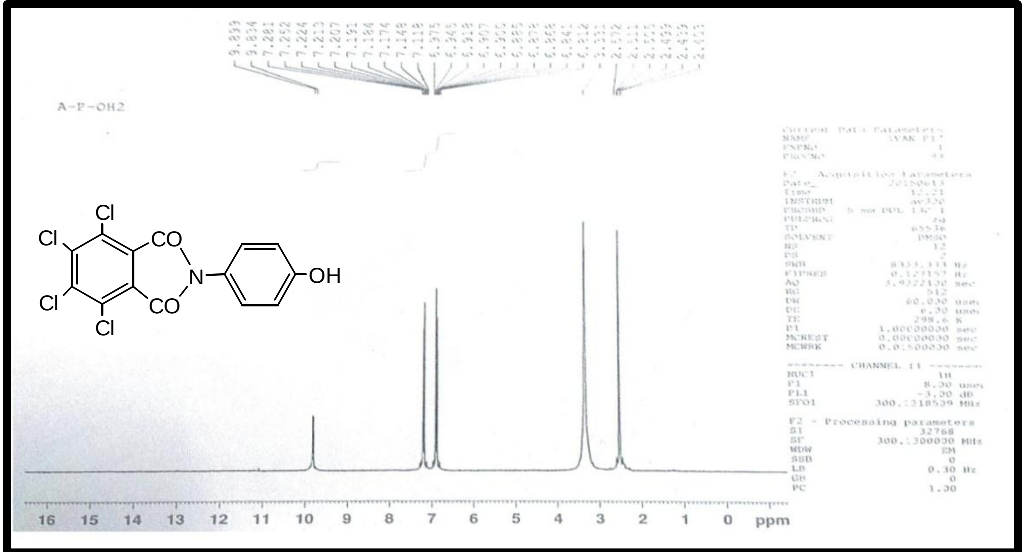


Figure 4- ^{1}HNMR spectrum of compound (7)

FTIR spectra of the prepared phenolic resins (9-12) showed clear absorption bands at (3294-3481) cm^{-1}, (1778-1785) cm^{-1} and (1712-1726) cm^{-1} due to ν(O-H) phenolic, asym. and sym. ν(C=O) imide. Besides the spectra showed new absorption bands at (2858-2962) cm^{-1} which were due to ν(C-H) aliphatic belong to (CH_2) in methylol groups and another new bands at (1000-1037) cm^{-1} which belong to ν(C-O-C) ether which linked between methylol groups in phenolic rings. The presence of these two new absorption bands is a clear evidence for the success of phenolic resins formation.

Moreover the spectra showed absorption bands at (3078-3090) cm^{-1}, (1596-1612) cm^{-1}, (1365-1369) cm^{-1} and (1078-1108) cm^{-1} which were attributed to ν(C-H) aromatic, ν(C=C) aromatic, ν((C-N) imide and ν(C-Cl) respectively [19].

^{1}HNMR spectra are used also in confirming chemical structures of the newly synthesized resins. ^{1}HNMR spectrum of phenolic resin (9) showed signals at (δ= 2.75 and 2.9) ppm belong to (CH_2) methylol protons and signals at (δ= 6.9-7.25) ppm and (δ= 9.83) ppm belong to aromatic protons and (OH) phenolic proton respectively.

^{1}HNMR spectrum of phenolic resin (10) showed signals at (δ= 2.7-2.9) ppm belong to (CH_2) methylol protons and signals at (δ= 6.82-7.35) ppm and (δ= 7.95) ppm belong to aromatic protons and (OH) phenolic proton respectively.

^{1}HNMR spectrum of phenolic resin (11) showed multiplet signals at (δ= 2.6-3) ppm belong to (CH_2) methylol protons and signals at (δ= 6.85-7.8) ppm and (δ= 9.8) ppm belong to aromatic protons and (OH) phenolic proton respectively. It is noticeable that the most important point in all ^{1}HNMR spectra of the new resins is the appearance of new signals at (δ= 2.6-3) ppm belong to (CH_2) methylol protons which represent a very clear proof for the success of the new phenolic resins formatiom. FTIR spectral data of the prepared phenolic resins are listed in Table-7, while FTIR and ^{1}HNMR spectra for some of them are shown in Figures 5-7.

Table 7- FTIR spectral data (cm^{-1}) of phenolic resins (9-12)

Comp. No.	ν(O-H) phenolic	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=O) imide	ν(C=C) aromatic	ν(C-N) imide	ν(C-Cl)	ν(C-O-C) ether
9	3434	3078	2906	1785 1726	1600	1367	1097	-
10	3429 3396	3078	2962	1784 1712	1608 1596	1365	1078	1012 1000
11	3398 3294	3078	2935 2858	1778 1712	1612	1369	1103	1010
12	3481	3090	2920	1784 1720	1602	1365	1108	1037

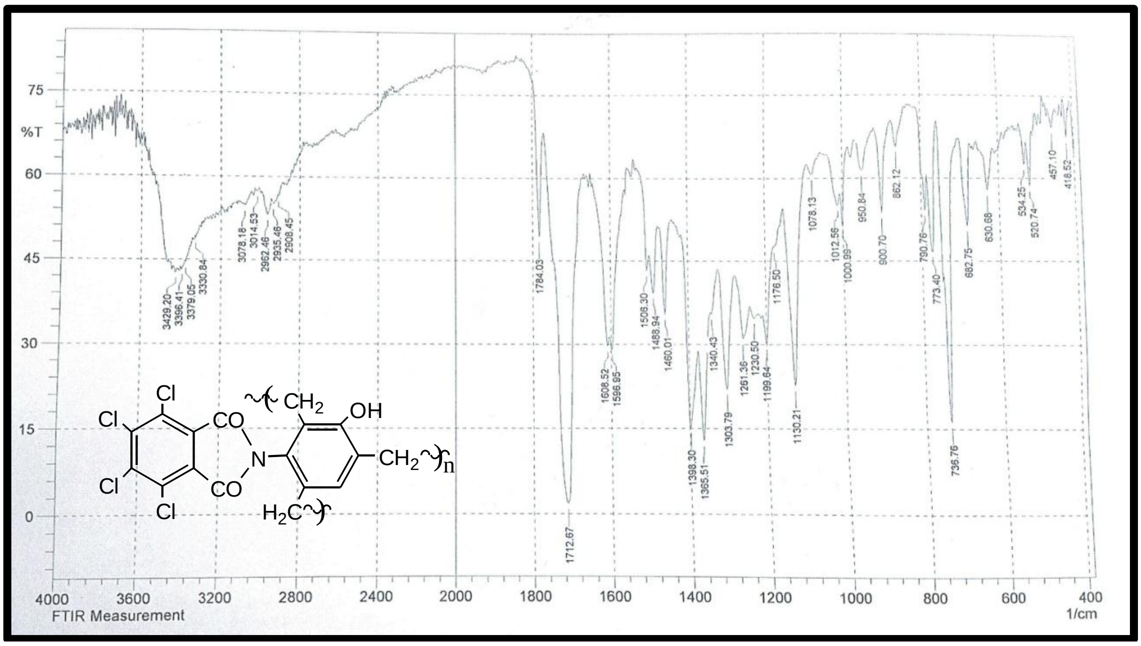


Figure 5- FTIR spectrum of compound (10)

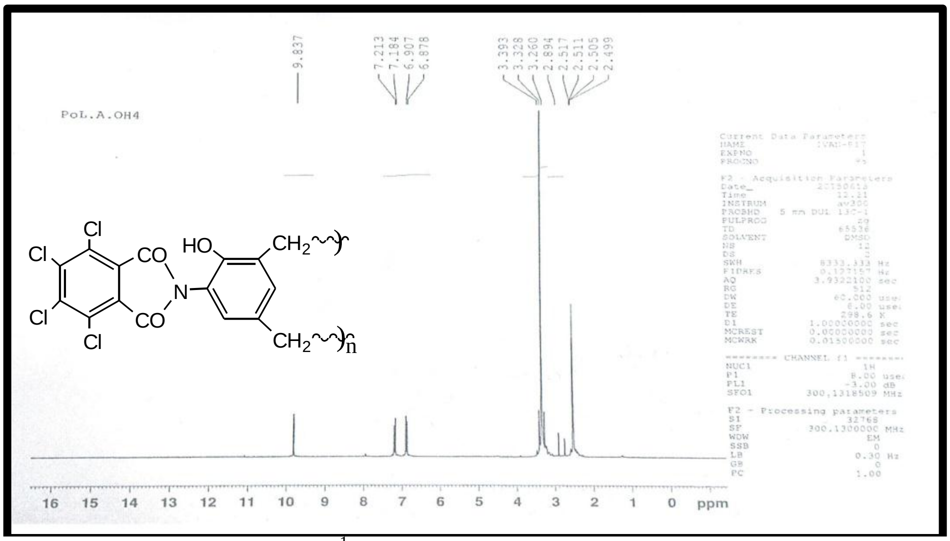


Figure 6- ^{1}HNMR spectrum of compound (9)

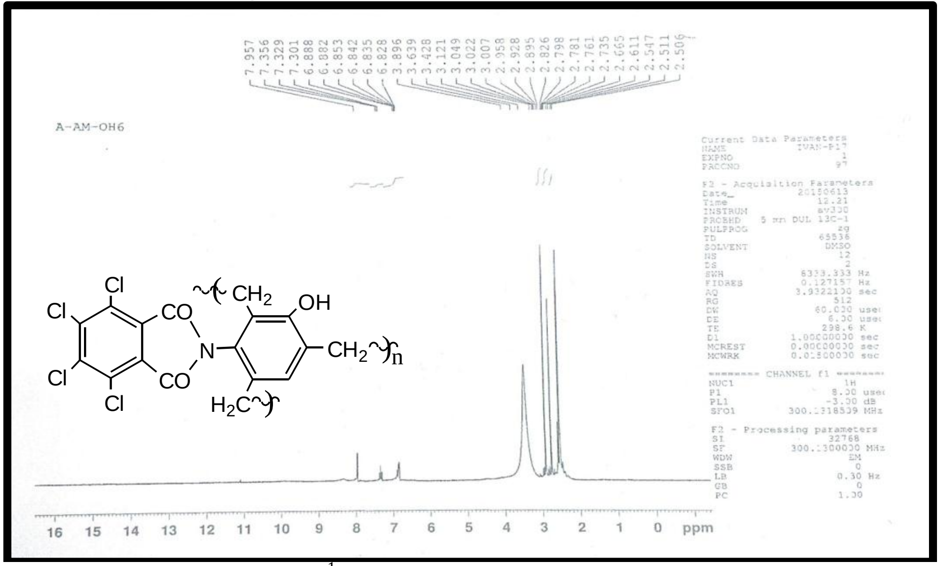
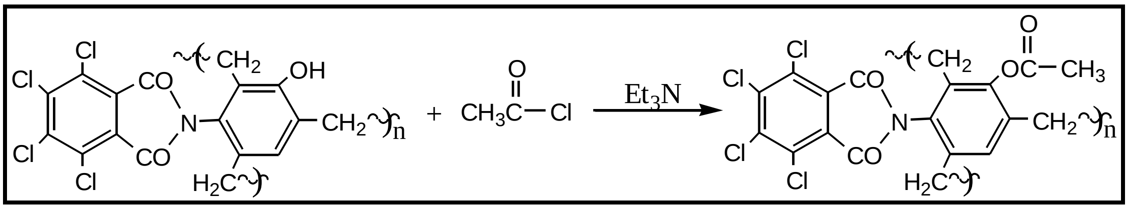


Figure 7- ^{1}HNMR spectrum of compound (10)

The second strategy used for curing phenolic resins involved modification of the newly synthesized phenolic resins via introducing of the present phenolic hydroxyl groups in esterification reaction with acetyl chloride in the presence of triethylamine [8].

Through esterification reaction hydroxyl groups are converted to acetoxy groups as indicated in the following equation.



It was found that esterification method was quiet convenient to incorporate structural modification in the prepared resins (9-12) since the modified resins (13-16) have different physical properties than those of the starting resins. The resulted modified resins have lower softening points and showed good solubility in all organic solvents.

These physical properties were in good agreement with the expected ones due to the presence of (C-O-C) ester bonds in the incorporated ester moiety which exhibit the modified polymers softness and flexibility and this lead to decrease their softening points and resistance to solubility which in turn made these resins suitable for certain applications like additives for lubricating oils and adhesives [2, 21].

FTIR spectra of the cured resins (13-16) showed atrophy in ν(O-H) phenolic absorption band indicating success of esterification process and the weak bands appeared at (3200-3477) cm^{-1} were due to ν(O-H) in methylol groups.

The spectra showed also clear absorption bands at (1730-1747) cm^{-1} and (1210-1278) cm^{-1} belong to ν(C=O) ester and ν(C-O-C) ester respectively [8]. Other absorption bands appeared at (1770-1785) cm^{-1}, (1710-1726) cm^{-1}, (1598-1612) cm^{-1}, (1365-1370) cm^{-1}, (1030-1097) cm^{-1} and (1000-1016) cm^{-1} which were due to asym. ν(C=O) imide, sym. ν(C=O) imide, ν(C=C) aromatic, ν(C-N) imide, ν(C-Cl) and ν(C-O) ether respectively.

Other details of FTIR spectral data for resins (13-16) are listed in Table-8, while FTIR spectrum of the cured resin (15) is shown in Figure-8.

Table 8- FTIR spectral data (cm^{-1}) of cured resins (13-16)

Comp. No.	ν(O-H) phenolic	ν(C-H) aromatic	ν(C-H) aliphatic	ν(C=O) imide	ν(C=C) aromatic	ν(C-N) imide	ν(C-Cl)	Other
13	3434(w)	3076	2918	1785 1726	1600	1365	1095	**ν(C-O) ether** 1014
14	3400	3076	2837	1782 1710	1598	1365	1080	**ν(C=O) ester** 1747 **ν(C-O) ester** 1215 **ν(C-O) ether** 1000
15	3477(w)	3062	2921 2893	1778 1710	1612	1369	1097	**ν(C-O) ester** 1278 1242 **ν(C-O) ether** 1016
16	3260 3200(w)	3050	2955 2880	1770 1710	1600	1370	1030	**ν(C=O) ester** 1730 **ν(C-O) ester** 1210

w = weak

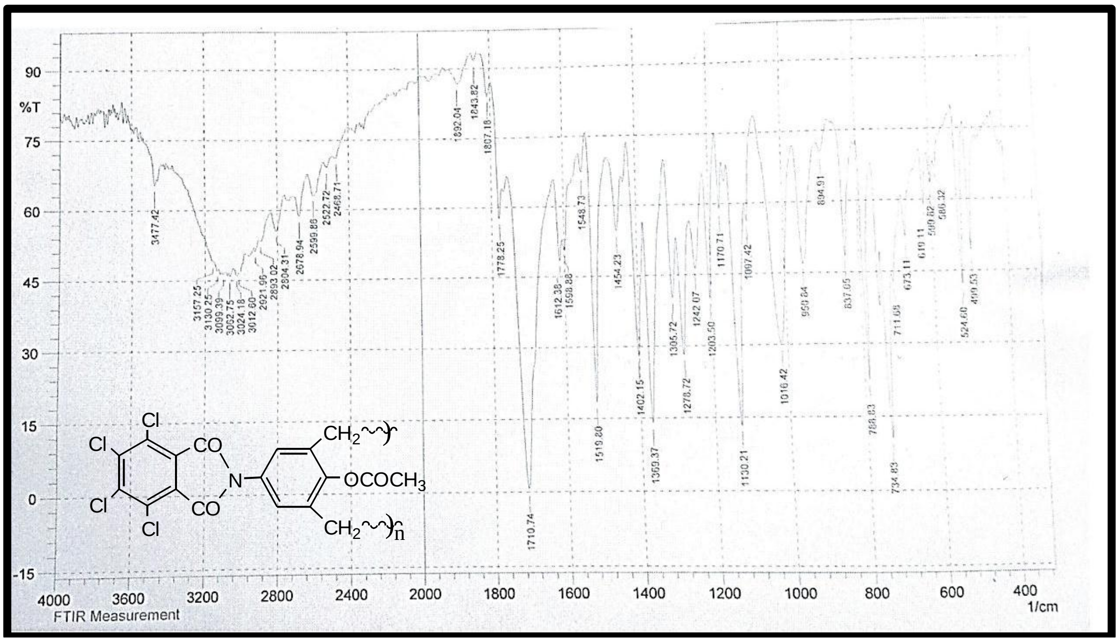


Figure 8- FTIR spectrum of compound (15)

Conclusion

The present investigation provides a suitable strategies for building new phenolic resins via design and synthesis of new phenolic moiety to condense with formaldehyde then using of esterification reaction to incorporate structural modification in the prepared resins. Both the newly synthesized and the cured resins have new properties which fitted with different applications.

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