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Synthesis, Modification and Characterization of New Phenolic Resins linked to Tetrabromophthalimide

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Abstract

The present work aimed to synthesize new phenol resins *via* incorporation of structural modification through introducing new phenolic compounds containing cyclic imide moiety in reaction with formaldehyde. The synthesis of these new resins involved three steps. First, one of the three *N*-(hydroxyphenyl)tetrabromophtalamic acids **1**-**3** were processed *via* a reaction between tetrabromophthalic anhydride and aminophenols. Amic acids **1**-**3** were dehydrated in the second step by smelting, producing the identical *N*-(hydroxyphenyl)tetrabromophthalimides **4**-**6**. The new imides represent the new phenolic component that was presented in condensation reaction with formaldehyde in the third step, creating the target phenolic resins **7**-**9**. The work also involved curing the new resins through esterification of phenolic OH groups by treatment with benzoyl chloride. The chemical structures of prepared compounds were confirmed according to FT-IR, ^{1}H NMR, and ^{13}C NMR spectral data. As a conclusion, the present work supply of new phenolic resins and the presence of the cyclic imide (tetrabromophthalimide) moiety in their structures exhibit high softening points and resistance to solubility, which fit with some applications, while subsequent curing through esterification exhibits better solubility and lower softening points, which fit with other applications.

Keywords: Modified resins, Phenolic resins, Tetrabromophthalamic acid, Tetrabromophthalimides.

تحضير وتحوير وتشخيص راتنجات فينولية جديدة مرتبطة برباعي بروموفثال ايمايد

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الخلاصة

يهدف البحث الحالي الى تحضير راتنجات فينولية جديدة من خلال ادخال تحوير تركيبي وذلك باستخدام مركبات فينولية جديدة تحتوي على مكونة الايمايد الحلقي (رباعي بروموفثال ايمايد) وادخالها في تفاعل مع الفورمالديهايد. يتضمن تحضير الراتنجات الجديدة ثلاث خطوات يتم في الاولى تحضير حوامض -N(هيدروكسي فينيل) رباعي بروموفثال اميك (1-3) من تفاعل رباعي برومو انهيدريد الفثاليك مع مركبات أمينوفينول. أما في الخطوة الثانية فيتم سحب جزيئة الماء من حوامض الاميك (1-3) باتباع طرق الصهر للحصول على الايمايدات المقابلة N-(هيدروكسي فينيل) رباعي برومو فثال ايمايد (4-6). الايمايدات

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المحضرة (4−6) تمثل المكونة الفينولية الجديدة والتي تم أدخالها في تفاعل التكاثف مع الفورمالديهايد في الخطوة الثالثة للحصول على الراتنجات الفينولية المطلوبة (7−9). كذلك تضمن البحث معالجة الراتنجات المحضرة (7−9) من خلال استرة مجاميع الهيدروكسيل الفينولية وذلك بمعاملتها مع كلوريد البنزويل. تم تشخيص المركبات المحضرة اعتمادا على مطيافية FT−IR ,[1]H NMR ,[13]C NMR كاستنتاج لهذا العمل تم الحصول على راتنجات فينولية جديدة تضم في تركيبها مكونة الايمايد الحلقي والتي اكسبت الراتنجات الجديدة مواصفات مرغوبة مثل مقاومة الانصهار ومقاومة الذوبانية مما يناسب تطبيقات معينة بينما ادت المعالجة بالاسترة لاحقا الى منح الراتنجات مواصفات جديدة مثل زيادة قابلية الذوبان وانخفاض درجات التلين مما يجعلها مناسبة لتطبيقات اخرى

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1. Introduction

Phenolic resins are the most significant thermosetting resins produced *via* acid- or base-catalyzed polycondensation of formaldehyde and phenolic compounds [1-3]. Because of their excellent heat properties, strong mechanical strength, water resistance, heat resistance, and chemical stability [4,5], these resins have been extensively applied in many applications like automotive, aerospace, varnishes for wood, adhesives, phenolic foam, and surface coatings [6-9]. Because of all these important properties and the wide spectrum of various applications, it is not surprising that a great number of studies and research have been conducted to incorporate structural modifications [10] using other aldehydes or different phenols [11] or adding different additives [12] to acquire new resins having new properties. Three new phenolic resins bearing a tetrabromophthalimidyl moiety were synthesized in this work by polycondensation of *N*-(hydroxyphenyl)tetrabromophthalimide with formaldehyde under conditions similar to those used in resol preparation. The synthesized phenolic resins were adjusted by esterification with benzoyl chloride in the presence of pyridine. Both the newly synthesized and modified resins exhibit good properties that may serve different applications, like plasticization and the application of non-flammable materials or as flame-retardants.

2. Experimental

All the used synthetic compounds were purchased from Aldrich, Merck, and BDH companies. The FT-IR spectral data of the combined mixtures and resins were recorded using KBr discs on a Shimadzu FTIR-8400 Fourier Infrared Transform spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectral data were registered on a Bruker 400 MHz apparatus utilizing tetramethylsilane as the internal standard and DMSO-d_6 as a solvent. The melting points of the prepared compounds were not entirely settled by Gallenkamp capillary softening point equipment, while the melting points of synthesized and modified resins were determined by a thermal microscope Riecher thermover.

*2.1. Synthesis of N-(hydroxyphenyl)tetrabromophthalamic acids **1-3***

A solution of tetrabromophthalic anhydride (2.32 g, 5 mmol) in dry acetone (20 mL) was added dropwise to *ortho*-, *meta*-, and *para*-aminophenol (0.54 g, 5 mmol), respectively, in dry acetone (10 mL) with stirring and cooling [11,13]. After completion of the addition, the mixture was stirred at room temperature for two hours. The solid crude material was then filtrated, washed with dry ether, and recrystallized in a suitable solvent.

*2.2. Synthesis of N-(hydroxyphenyl)tetrabromophthalimides **4-6***

The titled compounds **4-6** were synthesized by dehydrating the phthalamic acids **1**-**3**. The dehydration was performed through the fusion of amic acids **1**-**3** until complete melting [11], followed by heating at ten degrees above the amic acid melting point for one hour. The framed solid was cleansed by recrystallization from dioxane or chloroform.

*2.3. Synthesis of N-(tetrabromophthalimidyl)phenol formaldehyde resins **7-9***

A mixture of the prepared imides **4-6** (1.11 g, 2 mmol), formaldehyde (3 mL, 81.4 mmol), and ammonia solution (1.5 mL, 25%) was refluxed for 6 hours with blending [11]. The mingled materials contained two layers; the upper one was discarded while the lower layer was treated with glacial acetic acid until neutralization, and then dried in an oven at 80 °C. The output resin was purged by liquefying in DMF and then precipitating with water.

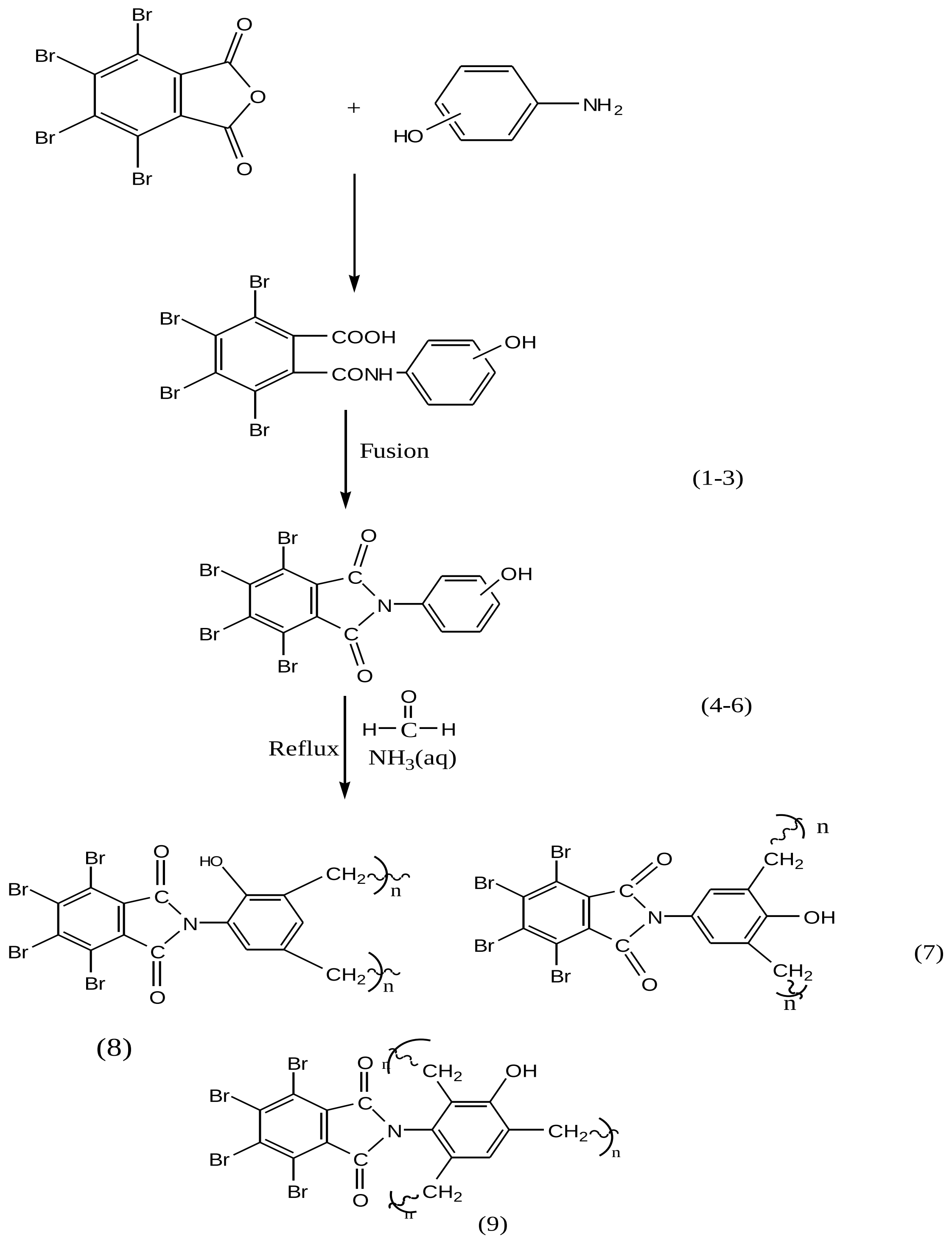
*2.4. Curing of resins **7-9** to the corresponding poly N-(benzoyloxyphenyl) tetrabromophthalimidyl formaldehyde **10-12***

Benzoyl chloride (4 mL, 30 mmol) was added slowly to the mixture of synthesized phenolic resins (10 mmol), DMF (25 mL), and pyridine (10 mL) with stirring at 5 °C [11]. The resultant mixture was stirred for 6 hours at room temperature before filtration. The filtrate was evaporated, and the solid crude material was refined by dissolving in DMF and precipitating with water.

3. Results and discussion

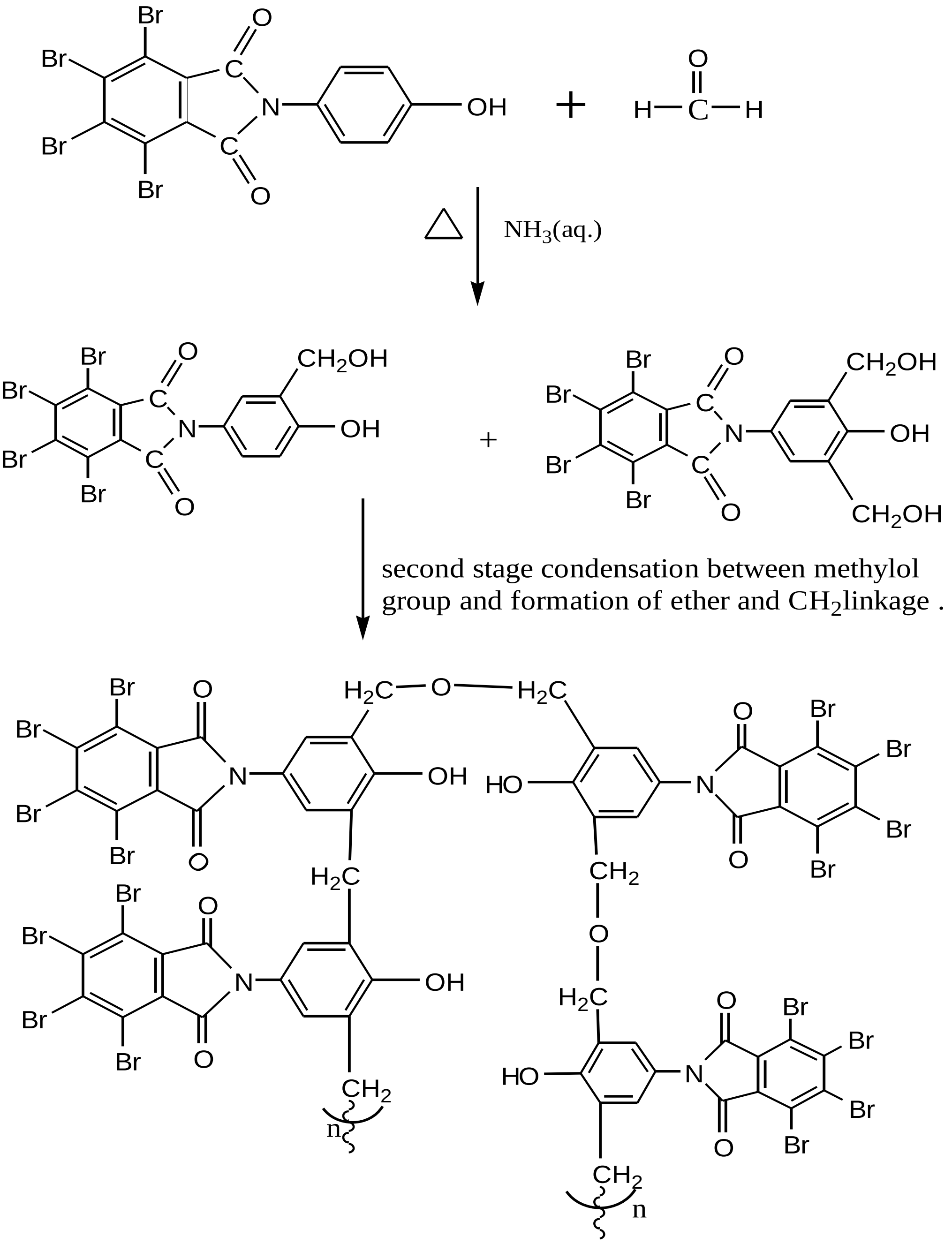
The synthesis and modification of phenolic resins is still an important topic that researchers are interested in, and many studies have been published on it. Thus, the objective of the current work is the synthesis and change of modern phenolic resins considering the presentation of a new phenolic moiety. In the polymer condensation with formaldehyde, the compound *N*-(hydroxylphenyl)tetrabromophthalimide is formed. The incorporation of a tetrabromophthalimide component in the new phenolic resins improves their chemical and thermal stability since polyimides are thermally and chemically stable polymers [14-17] with high mechanical strength. Furthermore, it has been reported that the incorporation of cyclic imides into many polymeric chains improves their thermal and substance stabilities [18]. As a result, we chose the tetrabromophthalimide moiety for incorporate in the new resins with the aim of producing phenolic resins with improved properties. The synthesis of the target phenolic resins was performed in three steps, as shown in Scheme 1. In the initial step, three *N*-(hydroxyphenyl) tetrabromophthalamic acids **1**-**3** were prepared *via* the reaction of *para*-, *meta*-, and *ortho*-amino phenols with tetrabromophthalic anhydride. In the second stage, amic acids **1**-**3** were dried out by combination, yielding *N*-(hydroxyphenyl)tetrabromophthalimides

4-**6**, which were then polycondensed with excess formaldehyde under heat and basic conditions, yielding the target phenolic resins **7**-**9**.



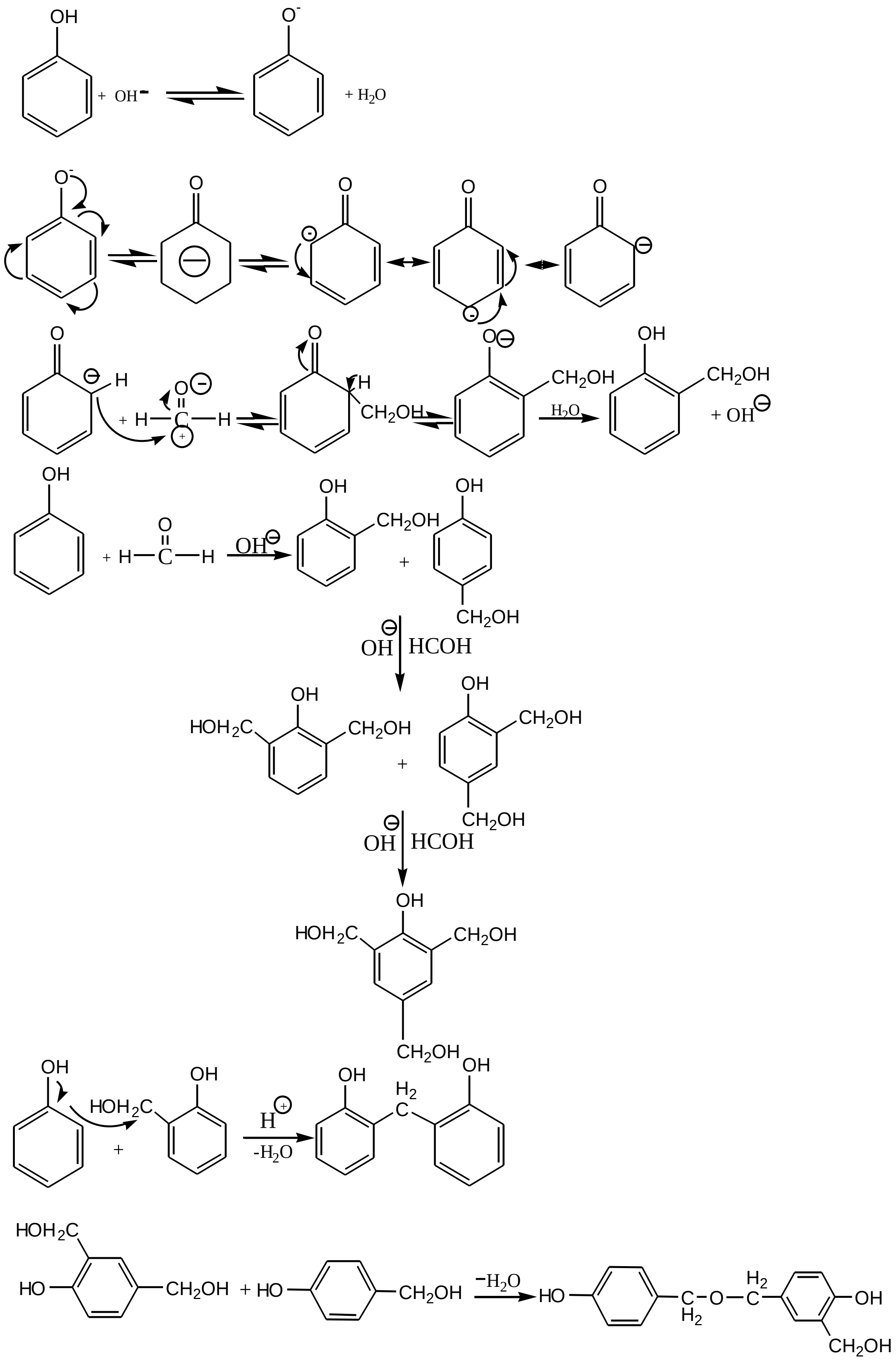
Scheme 1: Synthetic of phenolic resins

The first stage in the base-catalyzed condensation reaction producing a mixture of monomethylol, dimethylol, and trimethylol phenols. The second stage involved a condensation reaction between methylol groups leading to link formation between phenolic rings through methylene or ether bridge producing resol phenolic resins as shown in Scheme 2.



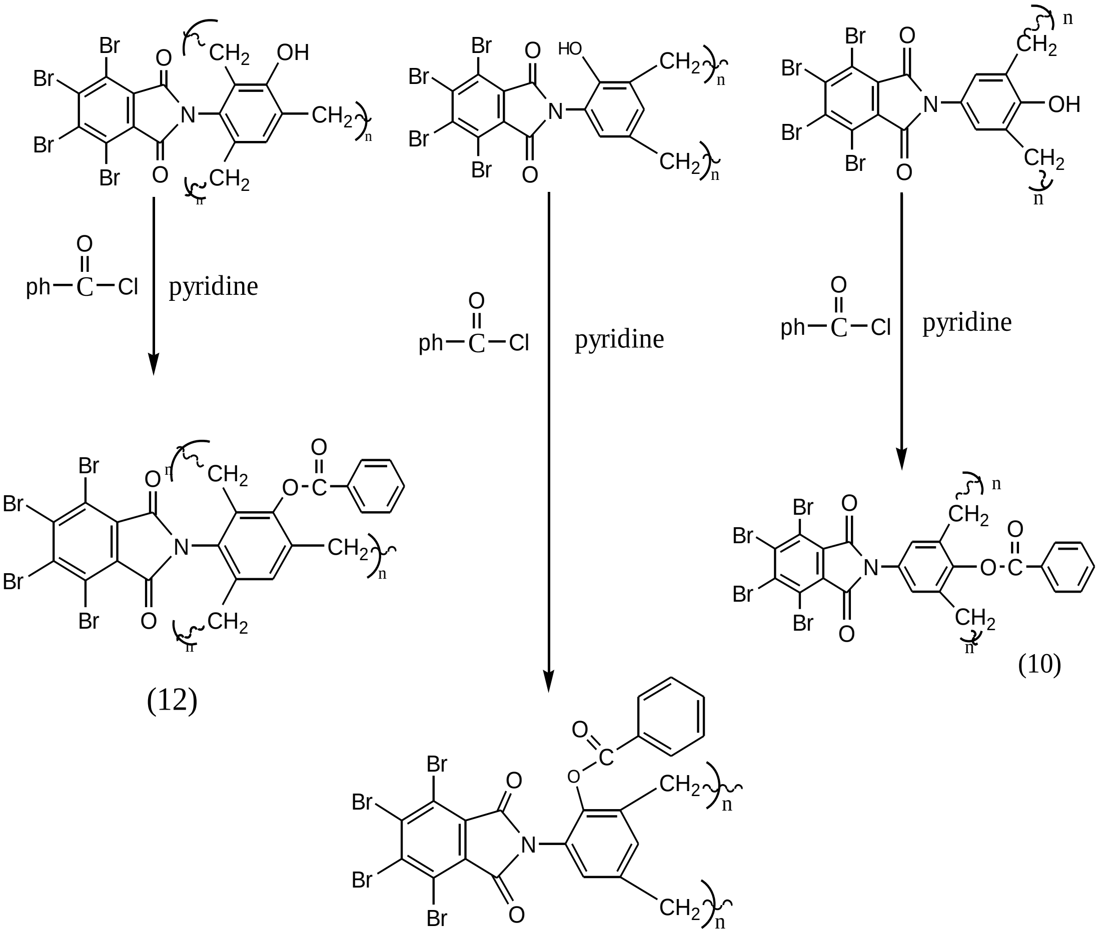
Scheme 2: synthetic mechanism of resol phenolic resins

As shown in Scheme 3, the general mechanism steps of this condensation reaction involved producing a mixture of monomethylol, dimethylol, and trimethylol phenols, then involving the condensation reaction between methylol groups, leading to link formation between phenolic rings *via* a methylene or ether bridge.



Scheme 3: The mechanism of the condensation reaction

The physical properties of the prepared amic acids **1-3**, imides **4-6**, and resins **7-9** are listed in Tables 1, 2, and 3, respectively. The physical properties of the prepared resins **7-9** clearly indicated that the presence of tetrabromophthalimide components in their structures gave them great warm strength, as demonstrated by their high softening points (more than 360 °C). Their opposition against dissolvability in numerous solvents consequently the tars were insoluble in many solvents, including chloroform, acetone, tetrahydrofuran, diethyl ether, dioxane, and benzene, while they showed acceptable solubility in DMF, DMSO, and hot ethanol. The prepared compounds were characterized using FT-IR, ^{1}H NMR, and ^{13}CNMR spectroscopy. The FT-IR spectral data of the prepared amic acids **1-3** show distinct retention groups at 3421-3433 cm $^{-1}$, 3193-3375 cm^{-1}, which correspond to *v*(O-H) carboxyl and *v*(N-H) amide, respectively [19]. The absorption bands for *v*(C=O) carboxyl and *v*(C=O) amide appeared at 1710-1718 cm^{-1} and 1649-1670 cm^{-1}, respectively. The FT-IR spectral data of *N*-(hydroxylphenyl)tetrabromophthalimides **4-6** revealed two absorption bands at 1770-1776 cm^{-1}, 1720-1724 cm^{-1} which were attributed to the asymmetric *v*(C=O) imide and the symmetric *v*(C=O) imide, respectively. The spectra also reveal distinct new absorption bands at 1377-1390 cm^{-1} due to *v*(C-N) imide. The FT-IR spectral data of the target phenolic resins **7-9** showed two new strong absorption peaks at 1236-1238 cm $^{-1}$ and 1006 cm^{-1}, which belong to the *v*(C-O-C) ether. Other distinct peaks for asymmetric and symmetric v(C-H) aliphatic were found at 2921-2985 cm^{-1}, 2871-2875 cm^{-1} [19]. The appearance of these absorption bands is an excellent proof of the formation of methylene and ether bridges, and this proves the success of phenolic resin formation. The FT-IR spectral data of amic acids **1-3**, imides **4-6**, and phenolic resins **7-9** are listed in Tables 4, 5, and 6, respectively. The ^{1}H NMR and ^{13}C NMR spectral data were also used to prove the chemical structures of the prepared compounds. The ^{1}H NMR spectrum of amic acid **1** revealed mutilate signals at 6.84-8.12 ppm due to aromatic protons, signals between 11.42 and 11.44 ppm back to NH proton and signals from 12.02 to 12.44 ppm belong to OH protons [19]. The ^{13}C NMR spectrum of compound **1** exhibited signals at 129.1-144.2, 172.9, and 172.9 ppm, which are attributed to the aromatic carbons, C=O amide and C=O carboxyl carbons, respectively. The ^{1}H NMR spectra of the prepared imides **4** and **5** showed signals at 6.87-7.94, and 9.86-9.87 ppm, which belong to aromatic and OH phenolic protons, respectively. The ^{13}C NMR spectra of imides **4** and **5** showed signals at 111.8-154.4 and 158.1-166.4 ppm for aromatic carbons and C=O imide carbons, respectively. On the other hand, the ^{1}H NMR spectra of the prepared phenolic resins (**7**, **8**, and **9**) showed signals at 4.09-4.81 and 5.04-5.17 ppm that belong to OCH_2 and CH_2 protons, respectively. More signals appeared at 6.87-8.65 and 8.25-10.0 ppm, which belong to aromatic protons and OH protons, respectively. The ^{13}C NMR spectra of phenolic resins (**7**, **8**, and **9**) showed signals at 70.2-79.8 ppm due to OCH_2 and CH_2 carbons, signals at 100.3-159.6 ppm attributed to the aromatic carbons, and signals at 156.7-169.1 ppm belonging to C=O imide carbons [19]. All the details of the ^{1}H NMR and ^{13}C NMR spectra of the preparation are shown in Tables **7** and **8**. This work also included the modification of the pre-arranged resins 7-9 *via* the presentation of a phenolic hydroxyl group in an esterification reaction with benzoyl chloride in the presence of pyridine. During the esterification response, phenolic hydroxyl bunches are completely changed over to benzoyl bunches, as displayed in Scheme 4.



Scheme 4: Modification of phenolic resins by esterification

The physical properties of modified resins **10-12** are explained in the following Table 9. The FT-IR spectra of the cured resins showed a decrease in intensity of the *v*(O-H) phenolic absorption band and showed new absorption bands at 1722-1730 cm^{-1}, 1201-1272 cm^{-1} and 1124 cm^{-1}, which are expected to be *v*(C=O) ester, asymmetric *v*(C-O) ester, and asymmetric *v*(C-O) ester, respectively **[11]**. The appearance of these absorption bands, along with the positive results in the hydroxamic acid test for the ester group, are excellent proofs of the success of the esterification reaction. The FT-IR spectra of compounds **10-12** showed other absorption bands at 1650-1668 cm^{-1}, 1766-1774 cm^{-1}, 1527-1602 cm^{-1}, 1375-1382 cm^{-1}, and 1018-1022 cm^{-1}, which are expected to be asymmetric *v*(C=O) imide, asymmetric *v*(C=O) imide, *v*(C=C), *v*(C-N) imide and *v*(C-O) ether, respectively. The FT-IR spectral data of compounds 10-12 are listed in Table 10. The ^{1}H NMR spectral data of compounds **10-12** show signals at 1.91 and 2.09 ppm that belong to the protons of the methylene group (CH_2), a singlet signal at 3.02 ppm that belongs to the OCH_2 ether group protons, and multiple signals at 7.30-7.48 ppm due to aromatic protons. The ^{13}C NMR spectra of modified phenolic resins **10-12** showed a signal at 21.3 ppm due to the carbon of the methylene group (CH_2), 53.9 ppm for the carbon of the OCH_2 ether group, 121.3-150.8 ppm due to the aromatic carbons, 163.4 ppm of the C=O group, and 169.7 ppm attributed to the C=O ester carbon. It is recognizable that the actual properties of the altered tars demonstrate that the esterification strategy was appropriate for working on the actual properties of pitches **7-9**. Since the existence of C-O-C, ester securities in the integrated ester moiety have displayed adjusted saps delicate quality and adaptability, prompting the decline of their conditioning focuses and protection from dissolvability. In this way, the relieved gums showed low mellowing focuses adjacent to great solvency in numerous solvents, including chloroform, acetone, THF, DMF, and DMSO. These new properties make the relieved gums suitable for applications such as glues and coatings [20,21]

Table 1: Physical properties of compounds **1-3**

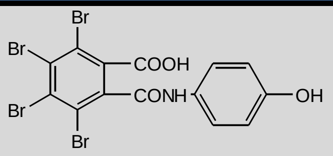
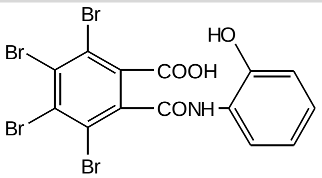
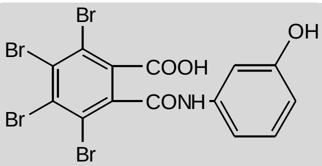
Compound number	Compound structure	Color	Yield (%)	Melting point (°C)	Recrystallization solvent
1		Faint pink	94	308-310	Acetone
2		Dark pink	95	305-307	Acetone
3		Faint yellow	92	280-282	Dioxane

Table 2: Physical properties of compounds **4-6**

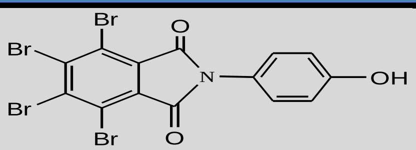
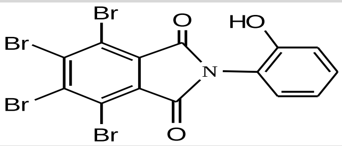
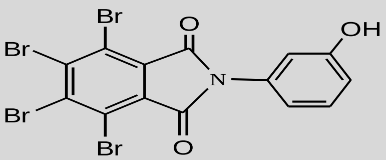
Compound number	Compound structure	Color	Yield (%)	Melting point (°C)	Recrystallization solvent
4		Black	88	222-224	Dioxane
5		Black	85	160-162	Chloroform
6		Black	90	241-242	Dioxane

Table 3: Physical properties of polymers **7-9**

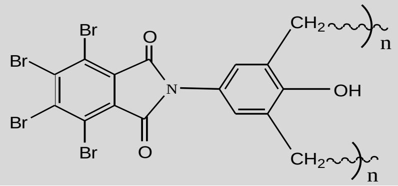
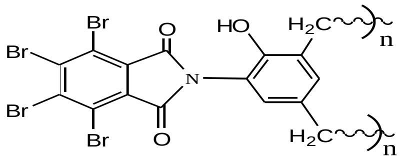
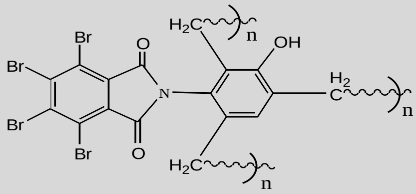
Polymer number	Polymer structure	Color	Conversion ratio (%)	Softening pointn (°C)	Purification
7		Gray	86	> 360	Dissolving in DMF then precipitation by water
8		Dark gray	82	> 360	
9		Black	81	> 360	

Table 4: FT-IR spectral data (*v*, cm^{-1}) of compounds **1-3**

Compound number	O-H N-H	C-H Aromatic	C=O carboxyl	C=O Amide	C=C Aromatic	C-Br
1	3421 3280	3010	1710	1649	1608 1560	555 644
2	3433 3375 3193	3030	1718	1649	1614 1596	530 642
3	3433 3290	3006	1718	1670	1612 1556	524 640

Table 5: FT-IR spectral data (*v*, cm^{-1}) of compounds **4-6**

Compound number	O-H phenolic	C-H Aromatic	C=O Imide	C=C Aromatic	C-N Imide	C-Br
4	3440	3020	1770 1720	1575	1390	665
5	3440	3050	1776 1724	1575	1388	665
6	3446 3427	3002	1776 1722	1575	1377	649

Table 6: FT-IR spectral data (*v*, cm^{-1}) of polymers **7-9**

Polymer number	O-H phenolic	C-H Aromatic	C-H Aliphatic	C=O Imide	C=C Aromatic	C-N Imide	C-O Ether	C-Br
7	3461 3427	3000	2952 2921 2871	1772 1714 1685	1558	1371	1236 1006	513 673
8	3446 3284	3072 3004	2954 2873	1772 1681	1558	1373	1236 1006	644 671
9	3431 3411	3035	2985 2875	1772 1668 1639	1560	1371	1238 1006	641

Table 7:[1]H NMR spectral data of compounds **1**, **4**, **5**, **7**, **8**, and **9**

Compound number	[1]H NMR spectral data (ppm)
1	6.84-8.12 (4H, Ar-H), 11.42-11.44 (1H, NH), 12.02-12.44 (1H, OH)
4	6.87-7.94 (4H, Ar-H), 9.86 (1H, OH)
5	6.89-8.35 (4H, Ar-H), 9.87 (1H, OH)
7	4.30-4.81 (2H,CH_2O), 5.05(2H, CH2), 6.87-8.15 (2H, Ar-H), 8.25-8.75 (1H, OH)
8	4.42-4.56 (2H, CH_2O),5.06 (2H, CH_2), 7.23-8.65 (2H, Ar-H), 9.63 (1H, OH)
9	4.09-4.70 (2H, CH_2O), 5.04-5.17 (2H, CH_2), 7.83-8.26 (1H, Ar-H), 10.0 (1H, OH)

Table 8: [13]C NMR spectral data of compounds **1**, **4**, **5**, **7**, **8**, and **9**

Compound number	[13]C NMR spectral data (ppm)
1	129.1-144.2 (12C, Ar-C),172.9 (1C, CONH), 172.9 (1C, COOH)
4	116.0-136.9(12C, Ar-C), 158.1-163.8 (1C, CON-)
5	111.8-154.4 (12C, Ar-C), 163.4-166.4 (1C, CON-)
7	70.2-79.8 (OCH_2 and CH_2), 111.3-151.5 (12C, Ar-C), 156.7-162.5 (1C, CON-)
8	70.2-79.7 (OCH_2 and CH_2) , 119.3-159.6 (12C, Ar-C), 165.8-169.1 (1C,CON-)
9	70.2-79.7 (OCH_2 and CH_2), 100.3-151.8 (12C, Ar-C), 157.4 (1C, CON-)

Table 9: Physical properties of modified resins **10-12**

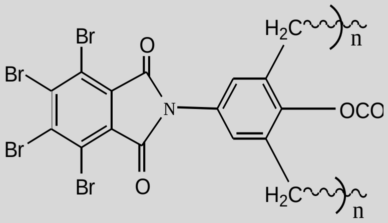
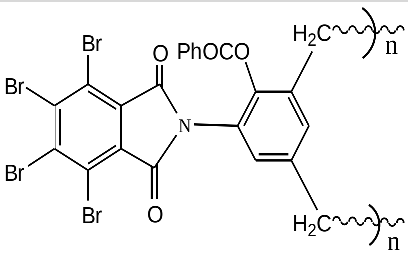
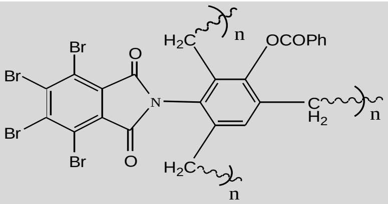
Compound number	Compound Structure	Color	Conversion ratio (%)	Softening point (°C)	Purification
10		Brown	80	115-122	
11		Brown	77	81-92	Dissolving in DMF then precipitation by water
12		Dark Brown	75	90-98	

Table 10: FT-IR spectral data (v, cm^{-1}) of modified resins **10-12**

Polymer number	C-H Aromatic	C-H Aliphatic	C=O Imide	C=O Ester	C=C	C-N Imide	C-O Ether	C-O Ester	C-Br
10	3050	2927 2856	1774 1650	1722	1602 1527	1382	1249 1022	1272 1124	665
11	3076	2975 2889	1772 1668	1730	1656	1377	1232 1618	1124	522 642
12	3070	2931 2877	1766 1662	1726	1554	1375	1020	1201 1124	642 663

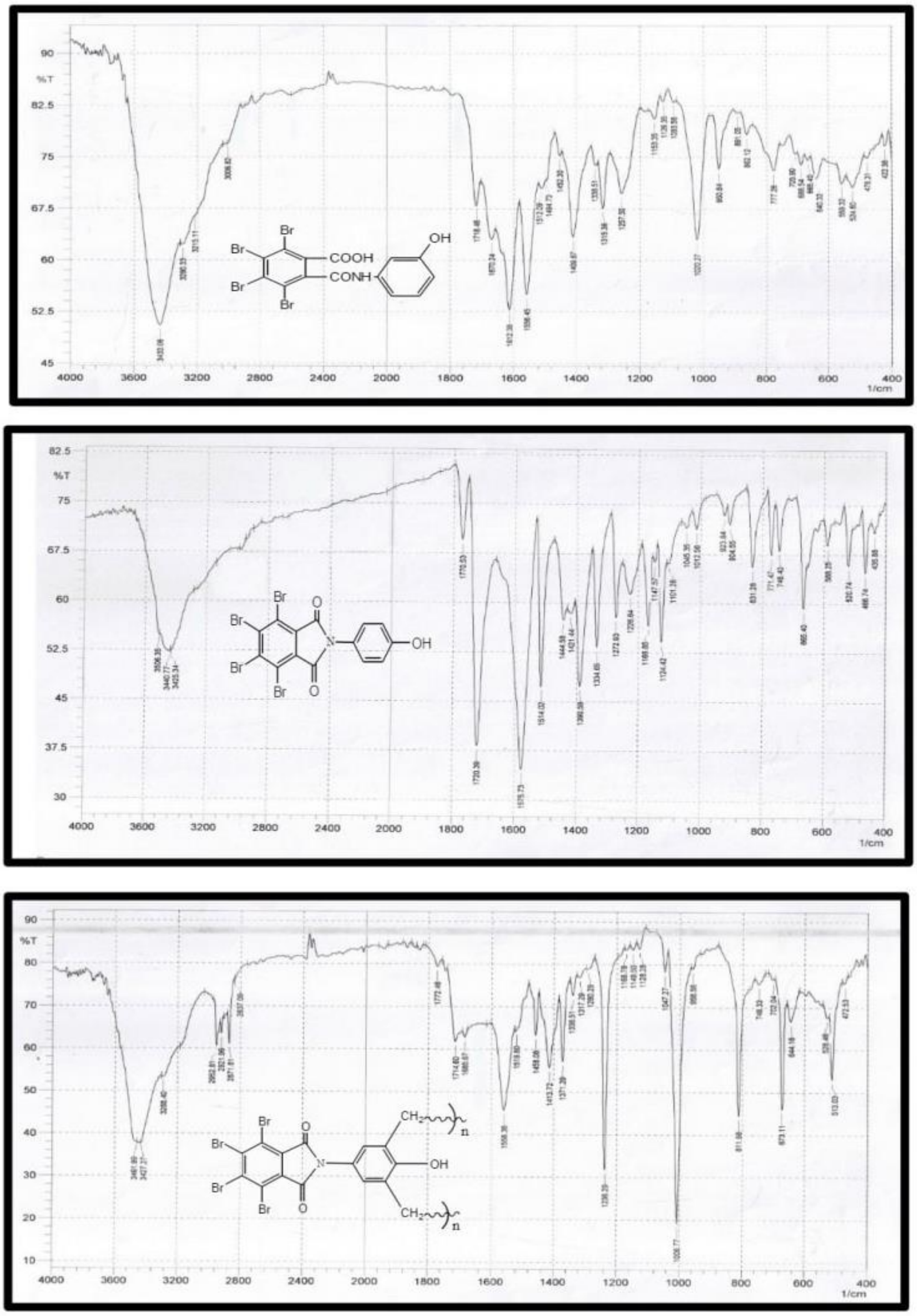


Figure 1: FT-IR spectra of compounds **3**, **4**, and **7**

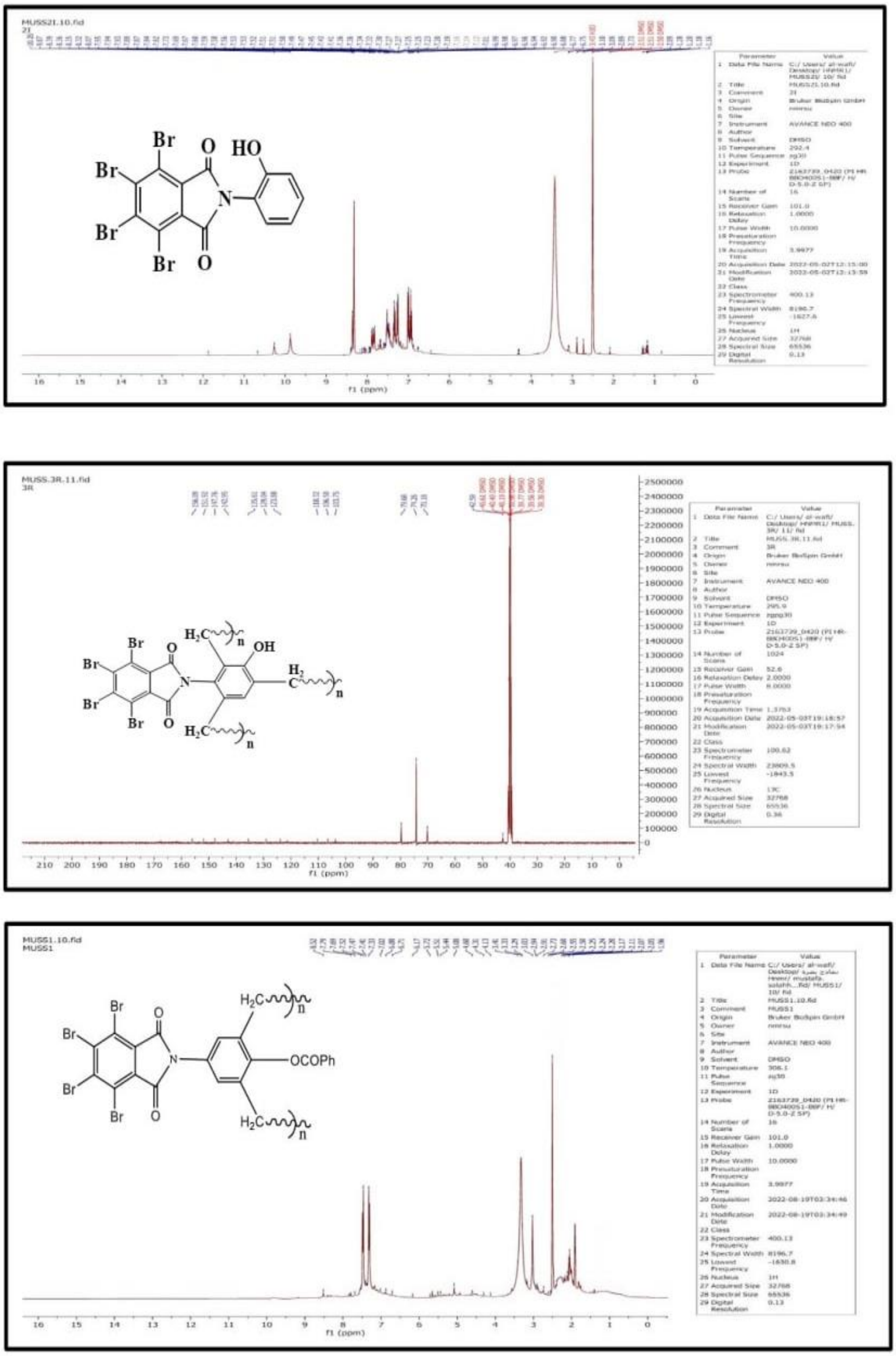


Figure 2: ^{1}H NMR and ^{13}C NMR spectra of compounds **5**, **9**, and **10**

4. Conclusion

The present work supplies us with new phenolic resins containing the important tetrabromophthalimide component. The presence of this component in the new resins exhibits good thermal stability along with resistance to solubility in many organic solvents, and these properties give these resins the possibility of being introduced in certain applications. Besides, it is noticeable that the modification of the new resins *via* esterification of phenolic (OH) groups. This is because treatment with benzoyl chloride has a clear effect on the resin's physical properties; thus, the presence of ester groups in the modified resins decreases their melting points and enhances their solubility in other organic solvents, and this fits with other applications, as plasticization. Furthermore, several studies have shown that the presence of multiple halogen substituents in the same molecule increases its flame resistance. Therefore, we expected the new resins to possess good flame resistance due to the presence of four bromo groups in their molecules, and this will give these resins the opportunity to be used in applications of non-flammable materials or as flame-retardants.

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