

SYNTHESIS AND CHEMICAL MODIFICATION OF NOVOLAC VIA INCORPORATION OF SILICON, PHOSPHOROUS, BORON, SULFUR AND SOME ORGANIC COMPOUNDS

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Abstract

Two types of novolac were prepared, namely / random (o,p-) and (o,o-) novolac. The prepared resins were modified by three methods, the first one includes esterification of phenolic hydroxyl groups in the prepared resins via their treatment with adipoyl chloride and urethane derivative by the reaction of toluene diisocyanate with resins . While the second modification includes incorporation of phosphorous, silicon, and boron into the novolac structure via reaction of P_2O_5 , $SiCl_2(CH_3)_2$, $SiCl_2(C_6H_5)_2$ and $Ba(OH)_2$ with novolac, Sulfure was incorporated into the novolac structure by preparation of 3,3,5,5 tetra methylol-4,4-dihydroxy diphenyl sulfone which then reacted with o,o- novolac and the third modification includes reaction of benzyl chloride with sodium salt of novolac and structure contains benzylic ether were obtained.

All prepared products were characterized by IR. HNMR, thermal analysis and some physical properties.

Introduction

Phenol-formaldehyde resins are the oldest commercial synthesis polymers first introduced around (100) years ago.

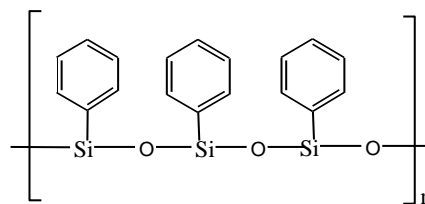
In recent decades extensive research efforts have been directed towards modification of phenolic resins via using of new aldehydes or new phenolic moiety in the synthesis of these resins in hope to enhance their properties⁽¹⁻⁵⁾.

Heat and flame resistance resins are obtained by the reaction of phenols and phenolic resin with metal halides such as (molybdenum trichloride, titanium trichloride, zirconium trichloride, tungsten trichloride) or metal organic compounds like (acetylacetones)⁶. If such metal containing resins are subjected to high temperature the decomposition is considerably slower than conventional resins.

The esterification⁷ of phenol novolac resins with inorganic polybasic acids such as phosphoric and boric acid or the reaction with phosphorus oxyhalides are a particular important in increasing the heat or flame resistance of phenolic resins, because of the high OH-functionality of novolacs.

The addition of silicon compound⁸ in order to improve the thermal resistance of phenol formaldehyde resin was recommended early. The reaction between phenol novolacs and

methoxy phenyl poly siloxanes as in structure (1)



The incorporation of silicon atoms in the polymer chain instead of the methylene linkage is obtained by reaction with p-silyl phenols, which are available by hydrolysis of phenoxy silicones with formaldehyde⁸.

The addition of silanes as adhesion promoters is widespread, for instance in the manufacturing of mineral wool mat, foundry sands, silicamicrosphere composites⁹.

In the present work two types of novolac were prepared, namely random (o,p-) and (o,o) novolac. The prepared resins were modified by three methods. The first one includes esterification of phenolic hydroxyl groups via their treatment with suitable acid chloride or urethane derivative, while the second esterification includes incorporation of phosphorous silicon, boron and sulfur into novolac structure via reaction of P_2O_5 , $SiCl_2(CH_3)_2$, $SiCl_2(C_6H_5)_2$, $SiCl_2$, $B(OH)_3$ and 3,3,5,5 tetra methylol -4,4 dihydroxy diphenyl sulfone. The third modification includes

etherification of sodium salt of novolac with benzyl chloride .

Experimental

1-Melting points were recorded by using Gallen Kamp MFB-600 capillary melting point apparatus.

2-Infrared spectra were recorded on IR model JASCOIR-810.

3-H-NMR spectra were recorded in yarmook university Jorden.

4-Thermal analysis was measured by TGA and DTG technique using Seko instrument Inc.

1-Preparation of O,P-Novolac (Random) (1)

o,p- novolac was prepared according to literatures ⁽¹⁰⁻¹¹⁾ with few modifications. In a 500 ml round bottom flask provided with a magnetic bar, thermometer and a reflux condenser ,was placed (94g.) (1mole) of phenol, (69g.) (0.85mole) of formaldehyde 37% and (1.45g.) (0.1mole)of oxalic acid which dissolved in 10ml distilled water. The mixture was refluxed for (1 hour) with stirring, then 30ml of water was added to the mixture , two layers were formed .The upper layer was decanted and the lower was distilled under vacuum at (50-100) mm Hg and 120C⁰ for 1 hour. The resulted polymer was decanted in plastic container until cooling, then was purified by dissolving it in ethanol and precipitated by distilled water. The above technique was repeated until pure product was obtained. All physical properties of the o,p-novolac are listed in Table (1).

2-Perparation of O,O Novolac Resin (2)⁽¹²⁻¹³⁾

In a 500 ml three necked bottom flask provided with magnetic bar, dropping funnel and a reflux condenser (94g.) (1mol) of phenol was placed together with (0.2g) (0.0027mole) of calcium hydroxide which dissolved in (5ml) distilled water .The mixture was heated to 165C⁰ with continuous stirring. A(69g) (0.85mole) of formaldehyde 37% was added drop by drop during dropping funnel for 2hrs. at (140-160) C⁰ with distillation of water during the reaction time .The unreacted substances (phenol, formaldehyde, water) were raised by distillation under vacuum (50-100) mm Hg to half hour at 180C⁰. The polymer was cooled and solidified at room

temperature then purified by dissolving in ethanol and reprecipitation by distilled water and dried at (80-90) C⁰ for 24 hours. All physical properties of the o, o-novolac are listed in Table (1).

3-Reaction of O,O-Novolac with Adipoyl chloride(3)

In a 100 ml three necked round bottom flask provided with a magnetic bar dropping funnel and a reflux condenser was placed (10g) of 0,0-novolac dissolved in 40 ml acetone. A (2g) (0.01mole) of adipoyl chloride was added through dropping funnel with continuous stirring at room temperature for 30 min. The mixture was refluxed for 4hours at (50-60)C⁰.The polymer was precipitated by addition of 300ml distilled water , purified by dissolving in ethanol and reprecipitate by distilled water dried at(80-90) C⁰ for 24hrs. All physical properties of the resin are listed in Table (1).

4-Reaction of O,O-Novolac withToluene-2,4diisocyanate(4)

In a 100 ml round bottom flask a (10g) novolac resin is dissolved in 40 ml acetone. One drop of triethyl amine was added with continuous stirring then (2g) (0.011)mole of toluene -2,4- diisocyanate (TDI) was added at room temperature. The polymer was precipitated by adding 500 ml distilled water, and filtered. Purification was made with the same method discussed previously. All physical properties of the resin are listed in Table (1).

5-Preparation of Phosphate Ester of O,O-Novolac (5)

Literature procedures were followed with few modifications ⁽¹⁴⁾ in a100ml two necked round bottom flask provided with a reflux condenser and thermometer (4.1g) 0,0-novolac resin was dissolved in 30ml chlorobenzene. The mixture was heated to 90C⁰. Then (0.9g) (0.06mole) phosphorous oxide is added for one hour with continuous stirring .The mixture was refluxed at 130C⁰ for 6hrs. Then was added to 50 ml hexane. The polymer is precipitated and purified by dissolving in THF and reprecipitated from distilled water. All physical properties of the resin are listed in Table (1).

6-Reaction of O,O-Novolac Resin modified with sulfur ,silicon and boron

The titled compounds were prepared according to literature procedures^(15, 16, 17).

7-Reaction of O,O-Novolac with benzyl chloride

A (5g) sodium salt of o, o-novolac dissolved in 50ml DMF which was placed in a round bottom flask provided with dropping funnel .A (5g) (0.039mole) benzyl chloride was added through dropping funnel with continuous stirring for (15min). The mixture was refluxed for 2hrs. The produced polymer is precipitated by adding to (500) ml of distilled water and dried at (80-90)C⁰. All physical properties of the resin are listed in Table (1).

Results and Discussion

The core of this work is to introduce modifications on the prepared o, o-novolac resin to produce new resins with new properties.

The phenolic resins are the oldest and lowest thermosetting polymer material .They are derived from the condensation of phenol and aldehydes such as formaldehyde.Improving the properties of phenolic resins are extensively studied by many authors⁽¹⁸⁾.

The first step includes preparation of o,o-novolac and esterification of phenolic hydroxyl groups with adipoyl chloride. IR. Spectrum of the resin revealed a clear bands in the region (1700)cm⁻¹ due to the stretching vibration of ester carbonyl group and in the region (2960)cm⁻¹ due to methylene group – (CH₂)_n-. Thus success of esterification reaction was confirmed by the disappearance of phenolic hydroxy absorption band. Fig. (12) showed H-NMR spectrum. The structure is as in Scheme (1).

Another esterification of OH phenolic groups by reaction with toluene 2,4- diisocyanate. The IR spectrum of the resin is revealed a band in the region (1725) cm⁻¹ due to carbonyl groups of urethane band (-O-CO-NH-)and appearance of new band in (1540) cm⁻¹ due to(N-H)amide and another band was appeared in (3000-2960)cm⁻¹ witch due to (C-H)aliphatic .H-NMR spectrum

revealed many signals as shown in Fig.(13). The structure as in Scheme (2).

The second step includes esterification of phenolic (o,o-novolac) resin with inorganic polybasic such as phosphorous penta oxide , silicon and boric acid which are of particular importance in increasing the heat or flame resistance of phenolic resins because of high OH-functionality of novolac the intermolecular cross linking)reaction takes place predominately with o,o-novolac,the intermolecular⁽¹⁹⁾ esterification seems to be the preferred reaction yielding 8-membered ring as in Scheme (3).








The increasing of thermal resistance of phenolic resins .which modified with boron⁽²⁰⁾ is attributed to a structure as in Scheme(4).

IR spectra of the prepared resin revealed a clear bands in (990-1040)cm⁻¹ ,(1200-1230) cm⁻¹ due to P=O and in region (490) cm⁻¹ due to O-P-O. In silicon resin many bands are appeared, in (810, 1265) cm⁻¹ due to Si-C aliphatic in (1120-1420) cm⁻¹ due to (Si-C) aromatic and in (1060) cm⁻¹ due to Si-O-C bond.

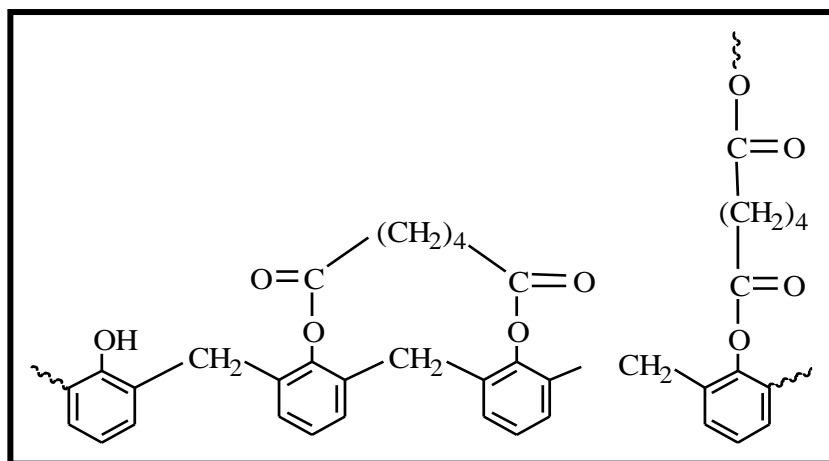
H-NMR spectra of phosphorous and boron resin are shown many signals in Figs. (14, 15).

Another modification was made with sulfur by the reaction of formaldehyde with 4,4-dihydroxy diphenyl sulfon, the hemiformal was produced. The hemiformal react with NaOH and converted to methylol group .The structure as in scheme (5) IR spectra showed two bands in the region (1310, 1160) cm⁻¹ due to str.Vib. of (S=O) and another band appeared in 860 cm⁻¹ due to aromatic (C-H) for tetra substitution (1,2,3,5). The third step includes etherification of o,o-novolac with benzyl chloride⁽²⁰⁻²⁴⁾. This modification was performed by reaction of o,o-novolac with benzyl chloride in DMF according to the procedure of Williamson synthesis. IR spectrum of the prepared resin showed band in region (1250) cm⁻¹ due to ether band. Thus success of etherification reaction was confirmed by disappearance of phenolic hydroxy absorption band in IR spectrum and appearance of a new clear absorption band in the region (710) cm⁻¹ due to unsubstituted at the aromatic ring in benzyl⁽²⁵⁻²⁶⁾.

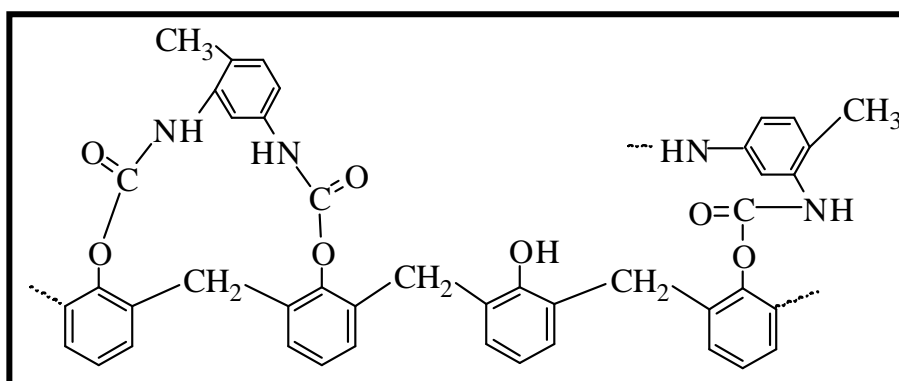
H-NMP spectra of resins (2, 3, 4, 5 and 9) showed signals at 3.7-3.9 (S, 2H,

-CH₂-), 6.7 (S, 3H, ) , 6.9 (S, H, OH) and 1.1-1.3 (m, 4H, -CH₂-CH₂-), 2.2 (t, 4H, -C(=O)-CH₂), 3.8 (S, 2H, -Ar-CH₂-Ar), 6.7 (S, 3H, ) , 6.9 (S, 1H,) and 2.25 (S, 3H, -CH₃), 3.7-3.6 (d, 2H, -CH₂-), 6.75-(S, 3H, ) , 6.9 (S, 1H, ) and 3.87 (S, 2H, -CH₂-), 6.6 (S, 3H, ) , 6.87 (S, 1H, ) and 4.6-4.8 (d, 2H, -CH₂-O-CH₂-), 7.2 (S, 3H, ) , respectively.

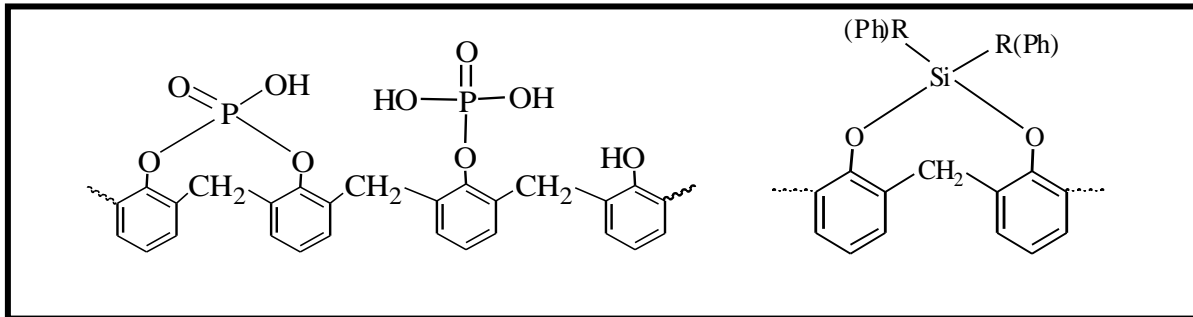
Physical, properties of the prepared resins are listed in Table (1), and their IR spectra are shown in Figs. (1-10). HNMR spectra for some of these prepared resin are shown in Figs.(11-15). The thermal properties of all prepared resins are shown in Table (2). Table (2) indicate loss of resin weight with increase of temperature.



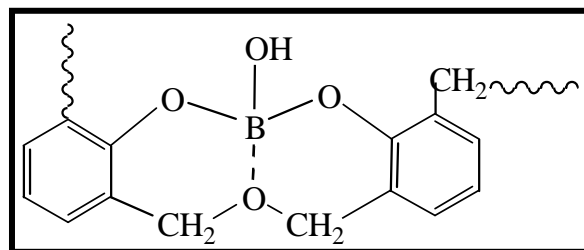
Scheme (1).



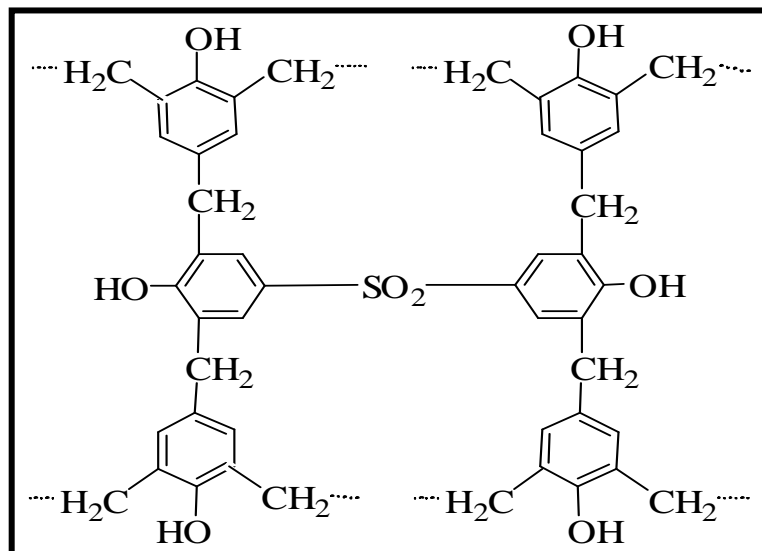
Scheme(2).



Scheme (3).

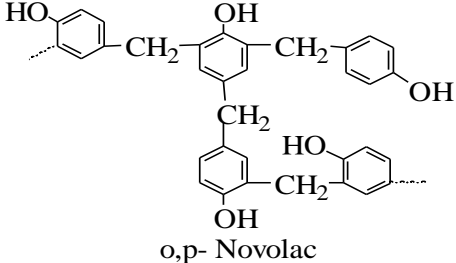
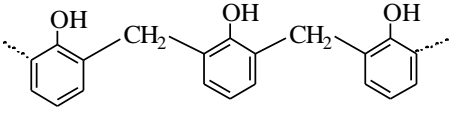
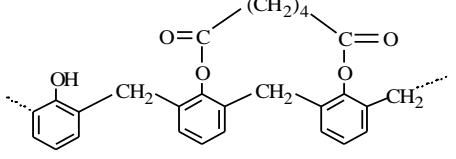
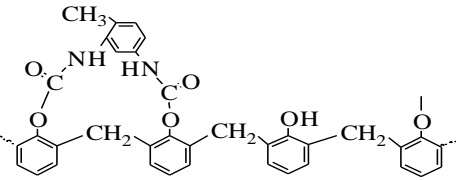
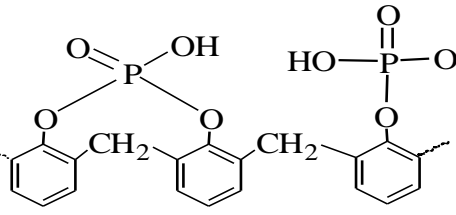
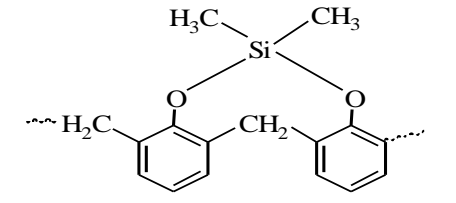


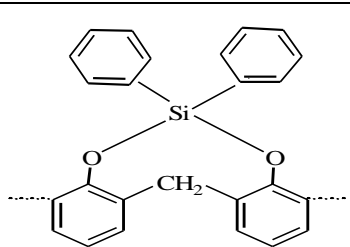
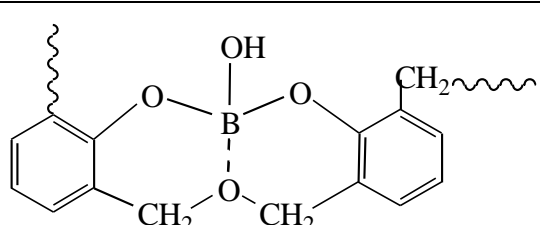
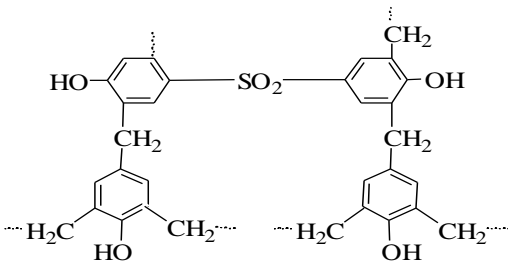
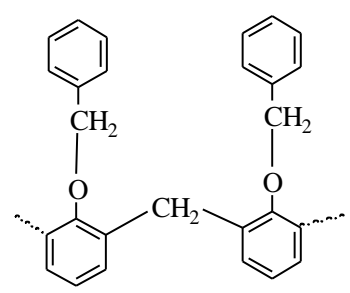
Scheme (4).



Scheme (5).

Table (1)
Physical properties of all prepared resins.

Comp. No.	Compound Structure	Conv. %	Softening Point C	Color	dl/gm
1	 <p>o,p- Novolac</p>	85	82-85	Yellow	0.6
2	 <p>o,o'-Novolac</p>	82	70-72	Brown	0.425
3	 <p>o,o'-novolac with adipoyl chloride</p>	90.8	55-57	Brown	0.486
4	 <p>o,o'-novolac with 2,4-di isocyanate toluene</p>	96.6	-	Yellow	0.744
5	 <p>0,0'-novolac with phosphorous pentoxide</p>	79	100-105	Brown	1.296
6	 <p>with dimethyl di chloro silane</p>	79	92-90	Brown	1.13

Comp. No.	Compound Structure	Conv. %	Softening Point C	Color	dl/gm
7	 <p>with diphenyl dichloro silan</p>	64	102-105	Brown	0.911
8		54	110-115	yellow	0.447
9		82	134-136	Brown	1.561
10		65	100-105	Orange	0.987

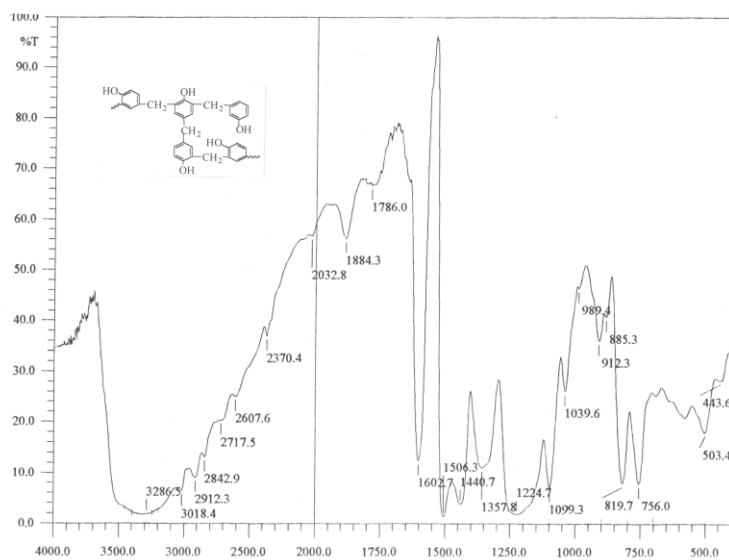


Fig.(1):FTIR spectrum for resin(1).

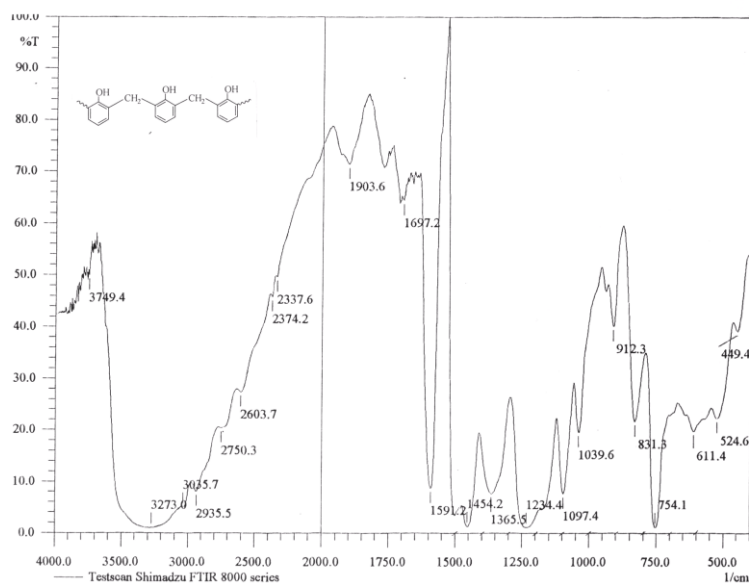


Fig.(2):FTIR spectrum for resin(2).

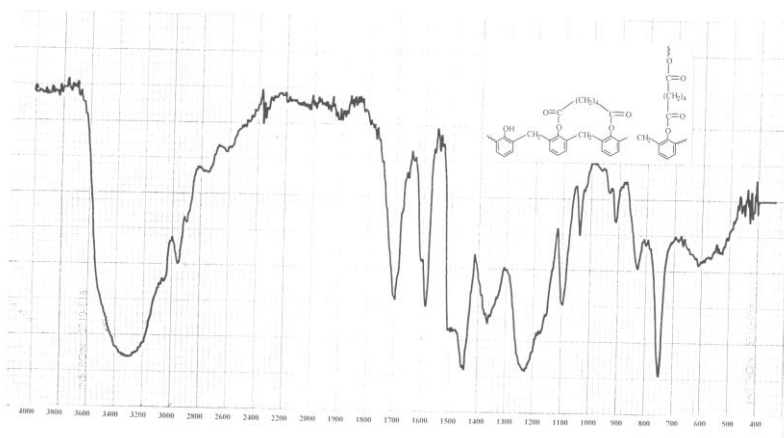


Fig.(3) : IR spectrum for resin(3).

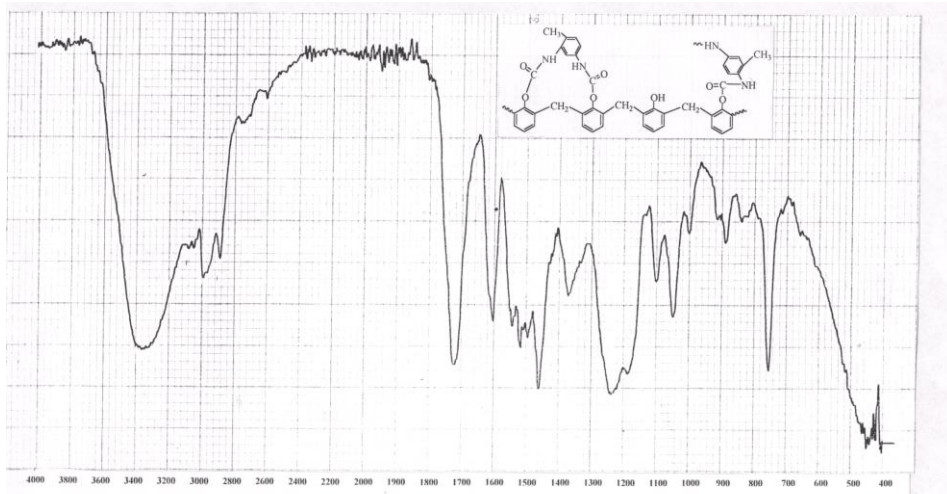


Fig.(4):IR spectrum for resin(4).

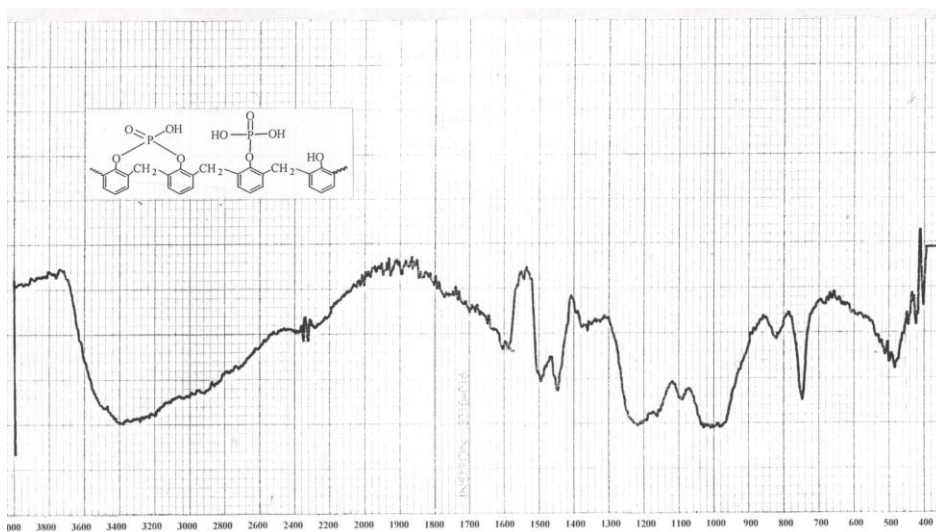


Fig.(5):IR spectrum for resin(5).

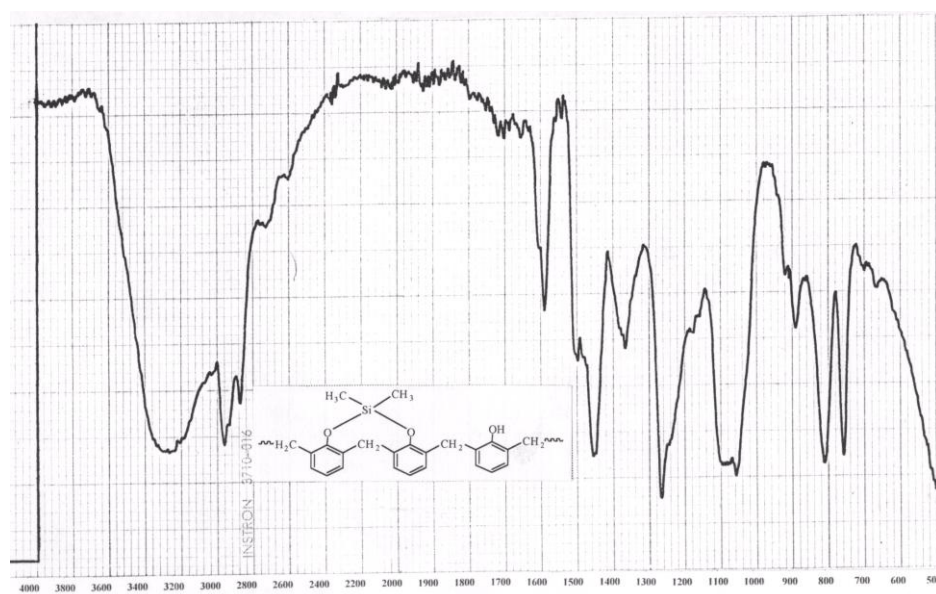


Fig.(6):IR spectrum for resin(6).

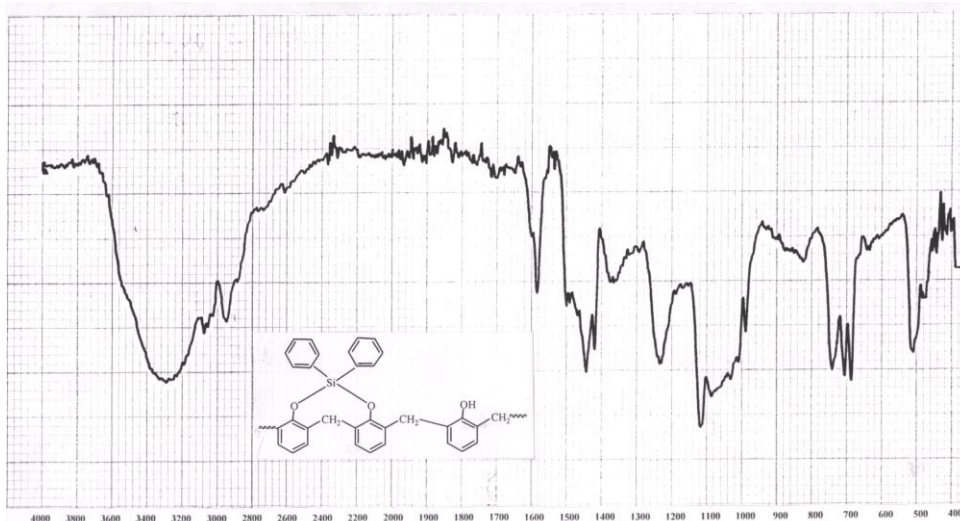
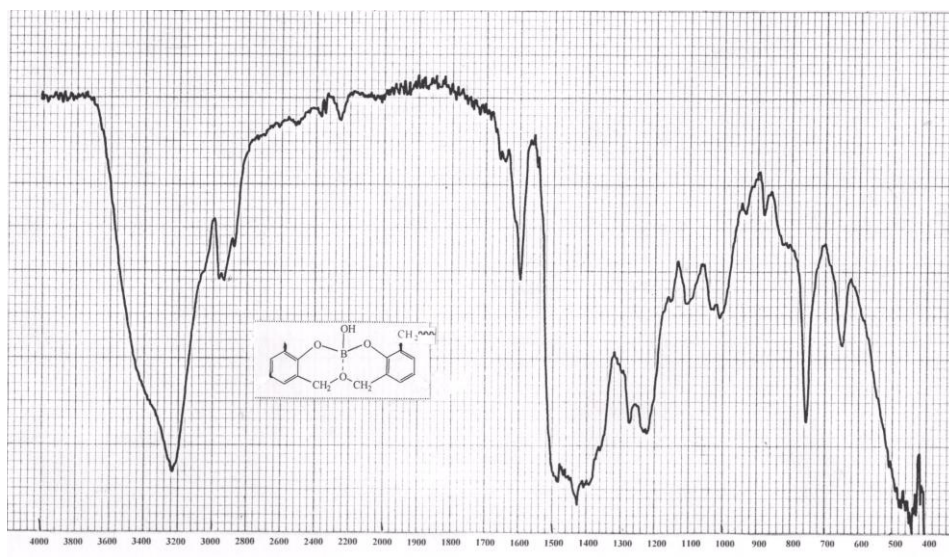


Fig.(7): IR spectrum for resin (7).



ig.(8): IR spectrum for resin (8).

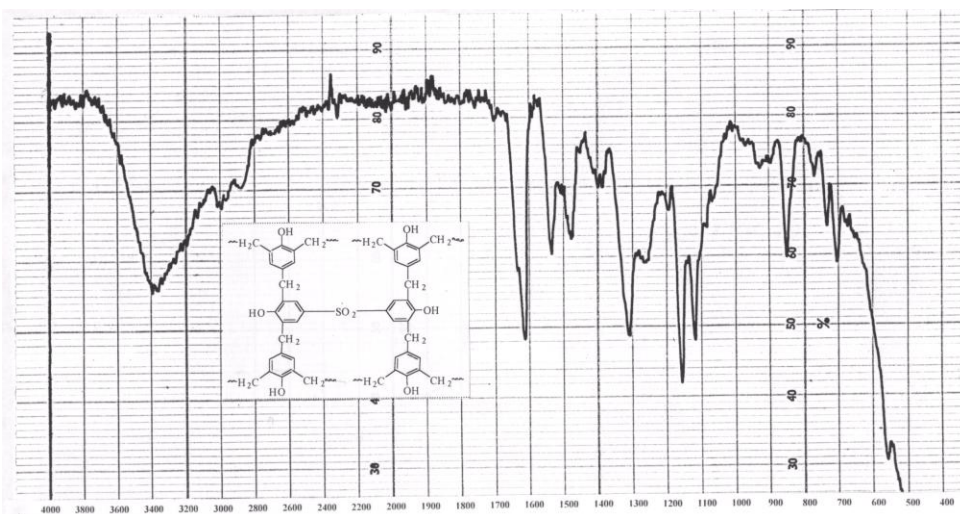


Fig.(9): IR spectrum for resin (9).

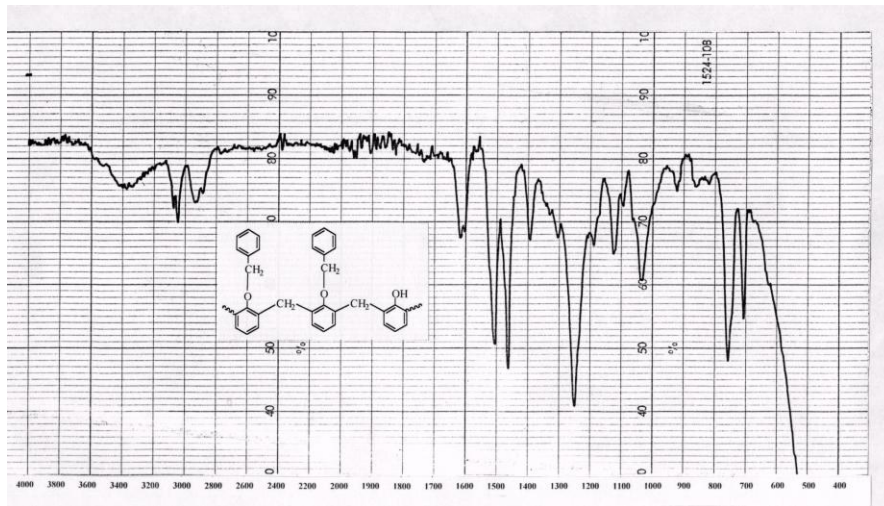


Fig.(10): IR spectrum for resin (10).

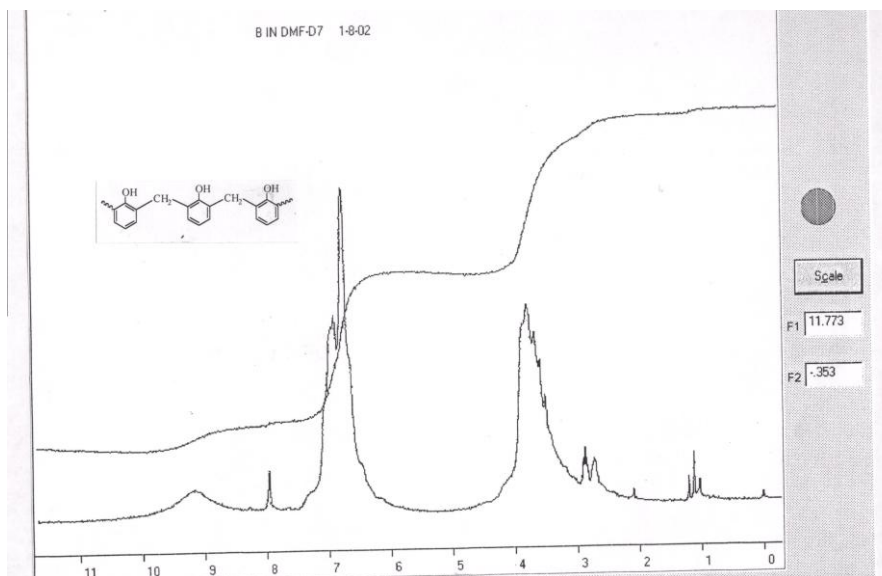


Fig. (11): H NMR Spectrum for resin(2).

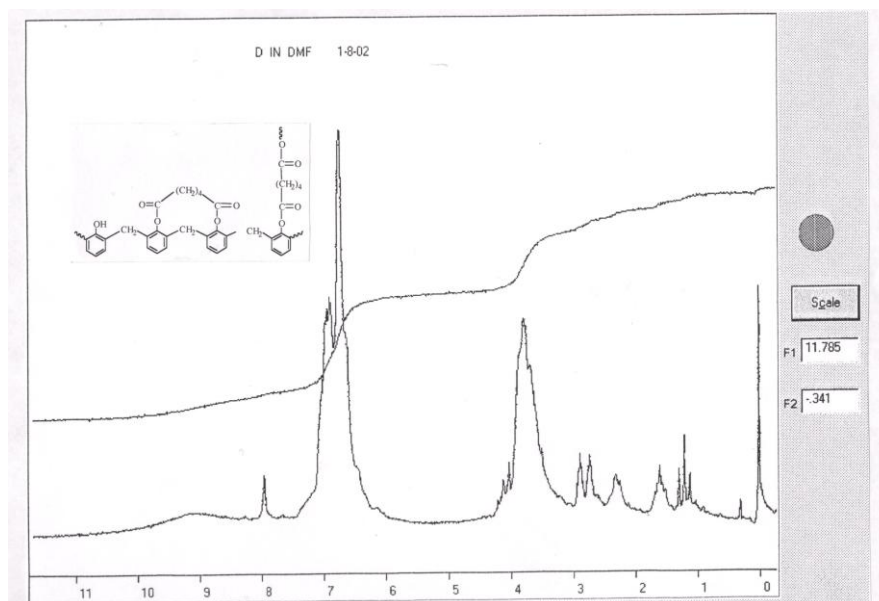


Fig. (12): H-NMR Spectrum for resin (3).

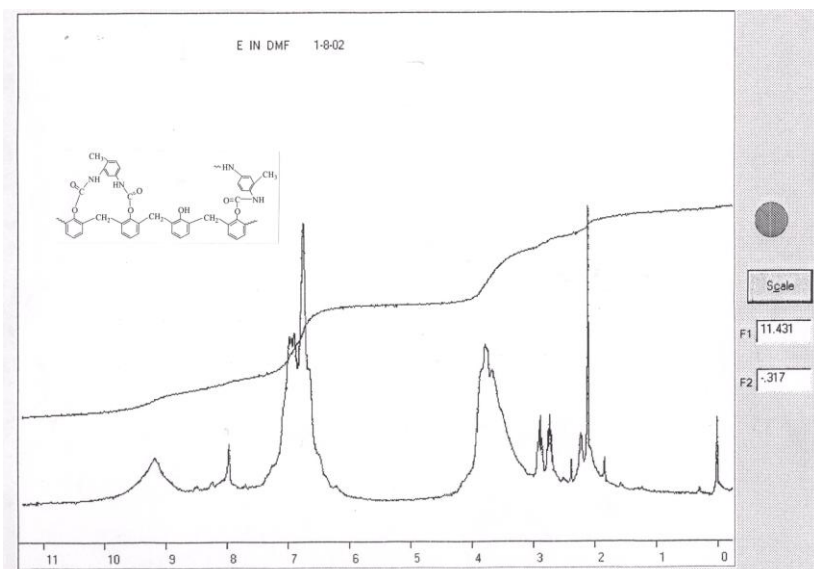


Fig. (13): H-NMR Spectrum for resin (4).

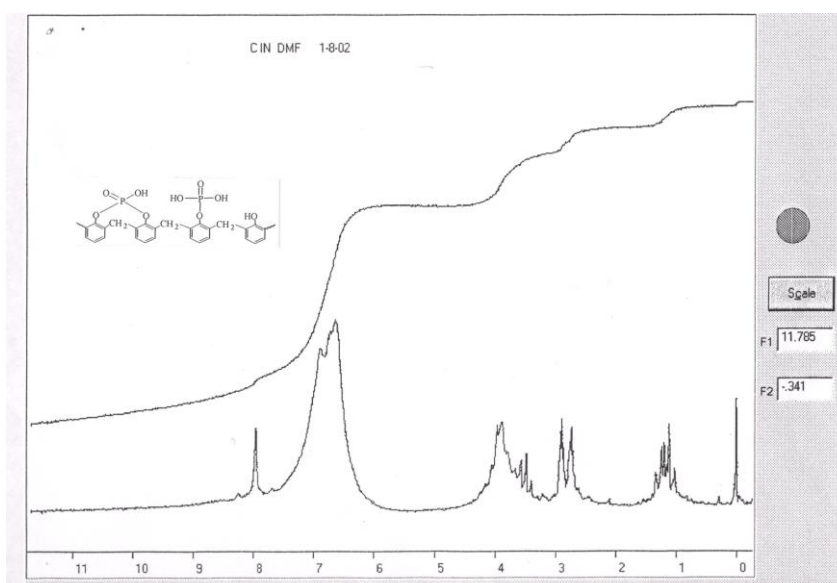


Fig. (14): H-NMR Spectrum for resin (5).

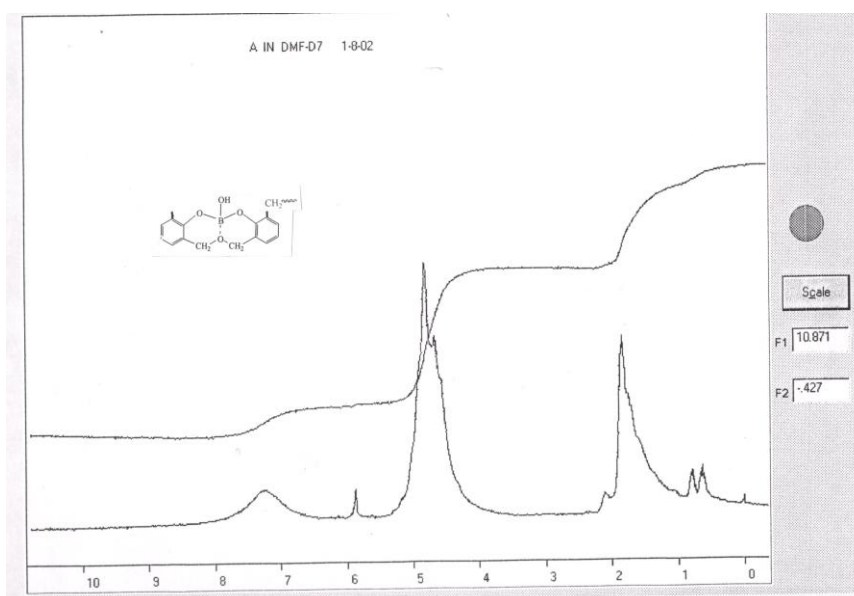


Fig. (15): H-NMR Spectrum for resin (9).

Table (2)
Thermal properties of the prepared resins.

Cod	Losses of resin of weigh of 300C ^o %	Losses of resin of weigh of 500C ^o %	Temp. of losses 50% from weigh	Temp. of losses 100% from weight	Temps. of decomposition		
					T ₁	T ₂	T ₃
1	10	37	564	668	129.5	418.1	630
2	27.7	52.3	491	612	252.9	491.8	600
3	20	52.3	476	648	128	407.7	587
4	14.7	38.5	564	688	136	413.4	634.6
5	7	29.3	596	700 <	367.5	625.1	-
6	20.8	41.2	554	700 <	227.4	326.2	594
7	20.8	39.3	536	700 <	220	-	575.3
8	3.9	18.5	738	795	541.1	-	786
9	11.6	38.5	533	800 <	220	395.1	523.8
10	15.4	53	466	800 <	131	417	599.3

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الخلاصة

تضمن البحث تحضير نوعين من الراتنج هما راتنج النوفولاك العشوائي (اورثو،بارا) -نوفولاك (o,P-novolac) والنوع الثاني (اورثو،اورثو) -نوفولاك (o,o-novolac) وتم تشخيصها بتقنية H-NMR،IR واجراء التحاليل الحرارية وايجاد اللزوجة الجوهرية. المرحلة الثانية من البحث تضمنت اجراء ثلاثة انواع من المعالجات على النوفولاك المحضر، تضمنت المعالجة الاولى اجراء تفاعل استرة مجاميع الهيدروكسيل المعوضة في النوفولاك بمعاملته مع كلوريد الاديوبيل وتكوين اواصر استرية ومع 2, 4 ثنائي ايزوسيانات التولوين وتكوين اصرة يورثانية. اما المعالجة بالطريقة الثانية فقد تضمنت الارتباط بين عناصر الفسفور، السليكون والبورون مع النوفولاك المحضر من خلال التفاعل مع المركبات خامس اوكسيد الفسفور، ثنائي مثيل ثنائي كلور وسايلان وثنائي فنييل ثنائي كلور وسايلان وحامض البوريك على التوالي، اما الكيريت فقد تم ادخاله الى تركيب الراتنج ال (o,o-نوفولاك) من خلال تحضير المركب 3,3,5- رباعي مثيلول -4,4- ثنائي هيدروكسي ثنائي فنييل سلفون ومن ثم مفاعله مع الراتنج ال (o,o-نوفولاك) . اما المعالجة بالطريقة الثالثة فقد تضمنت تفاعل ملح الصوديوم لل (o,o-نوفولاك) مع كلوريد البنزويل حيث تكونت اصرة اثيرية بين الراتنج والكاربون البنزويلية . تم تشخيص جميع المركبات بالطرق الكيمائية والطيفية مثل IR,H-NMR، كذلك درست خواصها الحرارية بتقنية TGA ، DTG وكذلك استخدام مطيافية الامتصاص الذري لتحديد نسب عناصر السليكون، والفسفور، والبورون في الراتجات المحضرة وكذلك قيست اللزوجة الجوهرية للبوليمرات الذائبة.

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