Synthesis and Curing of Novel phenol-formaldehyde resins substituted with Citraconamic acids

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Abstract

Four new phenolic resins containing pendent citraconamic acids in their repeating units were prepared via condensation of formaldehyde with N-(hydroxy phenyl) citraconamic acids in the presence of acid or base catalyst.

The obtained resins were modified by two methods, the first one involved esterification and cyclization by using acetic anhydride and anhydrous sodium acetate, while the second involved free radical polymerization of vinylic bonds in the prepared resins producing cross linked thermally stable polymers.

The prepared and cured resins have new properties in hope to serve new applications.

Introduction

The most important thermosetting resins both from a historical stand point and in current commercial applications are phenol formaldehyde resins (1-3), thus a number of synthetic strategies have been carried out to incorporate structural modification to obtain new phenolic resins with new properties. Some strategies based on using of aldehydes other than formaldehyde or using other compounds similar to phenols while the others based on using new conditions in performing polycondensation reaction (4-6).

In the present work four novel phenolic resins having pendent citraconamic acid in their repeating units were synthesized via condensation of formaldehyde with N-(hydroxyl phenyl) citraconamic acids under conditions similar to novolac and resole preparations. The new resins were cured by two methods the first one includes esterification and cyclization to the corresponding poly [N - (acetoxy phenyl - formaldehyde) citraconimides] while the second involved polymerization of citracon vinyls.

Experimental

1. Melting points were determined on Gallen Kamp capillary melting point apparatus and were uncorrected.
2. FTIR spectra were recoded on Shimadzu FT-IR 8400 Fourier Transform Infrared spectrophotometer.
3. Softening points were determined on Reichert Thermovar with Reichert-Jung temperature controller.
4. Intrinsic viscosities were determined with Automatic viscometer Tafesa ubbelohde viscometer at 25C^0 using DMF as solvent.

1. Preparation of N-(hydroxy phenyl) citraconamic acids[1-4]

via The titled acids were prepared according to literature procedures(7) reaction of equimolar amounts of citraconic anhydride with o,m and p-amino phenols. The prepared acids were purified by recrystallization from dioxane.

Physical properties and spectral data of the prepared acids are listed in Table(I).

2.preparation of phenolic resins:poly [N-(phenol-formaldehyde) citraconamic acids] [5-8]

The titled phenolic resins were prepared by following two literature procedures [A] and [B] respectively with minor modifications (7).

Method [A]: poly condensation of citraconamic acids with formaldehyde using acid catalyst

In a suitable three neck round bottomed flask fitted with a reflux condenser, thermometer and dropping funnel (0.01mol) of N-(hydroxy phenyl) citraconamic acid, (0.8ml) of formaldehyde (37%) and (10ml)of DMF were placed.

The dropping funnel was charged with (0.1ml)of conc. H_2SO_4 and (0.5ml) of distilled water.

The acid was added dropwise with stirring then the mixture was refluxed at (110C^0) for 3hrs.

The resulted mixture was distilled under reduced pressure to remove the evolved water and solvent then the residue was dissolved in (5ml) of DMF and filtered.

The filtrate was added to excess cold water with stirring then the precipitated polymer was filtered, washed with petroleum ether and dried.

Method [B]: poly condensation of citraconamic acids with formaldehyde using base catalyst

(0.01mol) of N-(hydroxy phenyl) citraconamic acid, (3 ml) of formaldehyde (37%) and (1.5ml)of (25%) ammonia solution were placed in a round bottomed flask fitted with a reflux condenser. The mixture was refluxed for (1hr) then cooled to room temperature. The upper layer of the resulted mixture was discard while the residual viscous layer was treated with glacial acetic acid until neutralization, then was heated in an oven at (70-80) C^0 for 48 hrs.

Physical properties and spectral data of phenolic resins prepared by the two methods [A] and [B] are listed in Table (II).

Curing of the prepared phenol-formaldehyde Resins

Curing of the titled resins involved the followings:

3.Curing via esterifiation of poly [N- (phenol-formaldehyde) citraconamic acids] [5-8] to the corresponding poly [N-(acetoxy-phenyl-formaldehyde) citraconimides] [9-12]

In a suitable round bottomed flask fitted with a reflux condenser (2.2g,0.01mol)of the prepared phenolic resins [5-8] was dissolved in (15ml) of DMF then (5ml) of acetic anhydride and (0.5g) of anhydrous sodium acetate were added(8,9) .

The mixture was refluxed on a water bath for (1hr)with stirring then was cooled and poured in excess cold water with vigorous stirring. The resulted precipitate was filtered, washed with petroleum ether and dried.

Purification of the polymer was performed by dissolving it in (10ml)of DMF followed by reprecipitation by cold water then filtered and dried in an oven at (70-80)C^{0}for 24hrs.

Table(III) lists physical properties and spectral data of the cured resins [9-12].

4. Curing via free radical polymerization of vinylic bonds in the prepared poly [N-phenol-formaldehyde) citraconamic acids [13-16]

In a polymerization bottle (0.001mol)of the prepared polymers [5-8] was dissolved in (8ml) of DMF then (0.0002g) of benzoyl peroxide was added as initiator(10). After passing of N_2 gas the bottle was closed tightly then heated at (110-115)C^0 for 3hrs. The resulted mixture was poured into (50ml)of ice water then the precipitated polymer was filtered, washed with petroleum ether and dried.

Table(IV) lists physical properties and spectral data of the cured resins [13-16].

5. Curing via free radical polymerization of vinylic bonds in the prepared poly [N-(acetoxy phenyl- formaldehyde) citraconimides[17-20]

Vinylic bonds in the prepared poly[N-(acetoxy phenyl-formaldehyde) citraconimides][9-12] were polymerized free radically by following the same procedure used in the preparation of polymers [13-16].

Physical properties and spectral data of the resulted polymers[17-20] are listed in Table(V).

Results and Discussion

Since phenolic resins are very important polymers with a wide variety of applications include adhesives, casting, varnishes, binders and surface coatings, we try in this work to synthesize new phenolic resins by following a new strategy in building them. The new strategy involved using of new phenolic moiety substituted with citraconamic acid to condense with formaldehyde under conditions similar to those used in novolac preparation to produce finally phenolic resins with pendent citraconamic acid groups which exhibit new properties in hope to serve new applications.

Polycondensation was performed also under basic conditions similar to those used in resole preparation and the results showed that the prepared resins by the two methods (A) and (B) are very close in their physical properties as shown in Table(II).

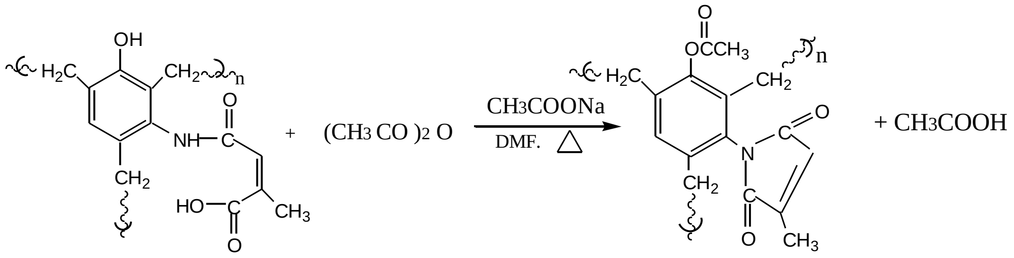
The prepared resins [5-8] are brown solids, insoluble in all organic solvents at room temperature with acceptable solubility in hot DMF, hot DMSO and not soften even at (300C^0).

It is important to mention here that incorporation of citraconamic acid groups in the repeating units of the prepared resins plays a vital role in raising thermal stability of the prepared polymers through high polarity of carboxylic groups and hydrogen bonding by amide groups which both increased interaction between the repeating units and this inturn increased attraction forces over all the polymeric chains leading to high thermal stability, which make the resins suitable for certain applications.

Also the presence of carboxylic groups in the new resins gives the possibility for using them as cation exchangers(7).

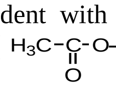
IR spectra of the new resins showed clear absorption bands in the region (3169-3450) cm^{-1}due to stretching vibrations of (O–H) carboxylic, (N–H) amide and (O– H) phenolic while the other bands appear at (1690-1710)cm^{-1}, (1620-1665) $cm^{-1}$and (1560- 1610) cm^{-1}due to υ(C=O) carboxylic, υ(C=O)amide and υ(C=C) vinylic respectively.

The second target of this work involved curing of the prepared resins. Curing was preformed by two methods the first one include esterification of phenolic hydroxyl groups and cyclization of the prepared resins [5-8] to the corresponding poly [N-(acetoxy phenyl- formaldehyde) citraconimides] [9-12] by treatment of the resins with acetic anhydride and anhydrous sodium acetate(8).



During this reaction three steps were achieved dehydration, cyclization and esterification of phenolic hydroxyl groups thus the resulted resins containing acetoxy phenyl citraconimide groups in their repeating units.

The cured resins are yellow to brown solids with softening points (191->300)C^0, their intrinsic viscosities are in the range (0.53-0.81) dL/g and insoluble in all organic solvents except DMSO and DMF.

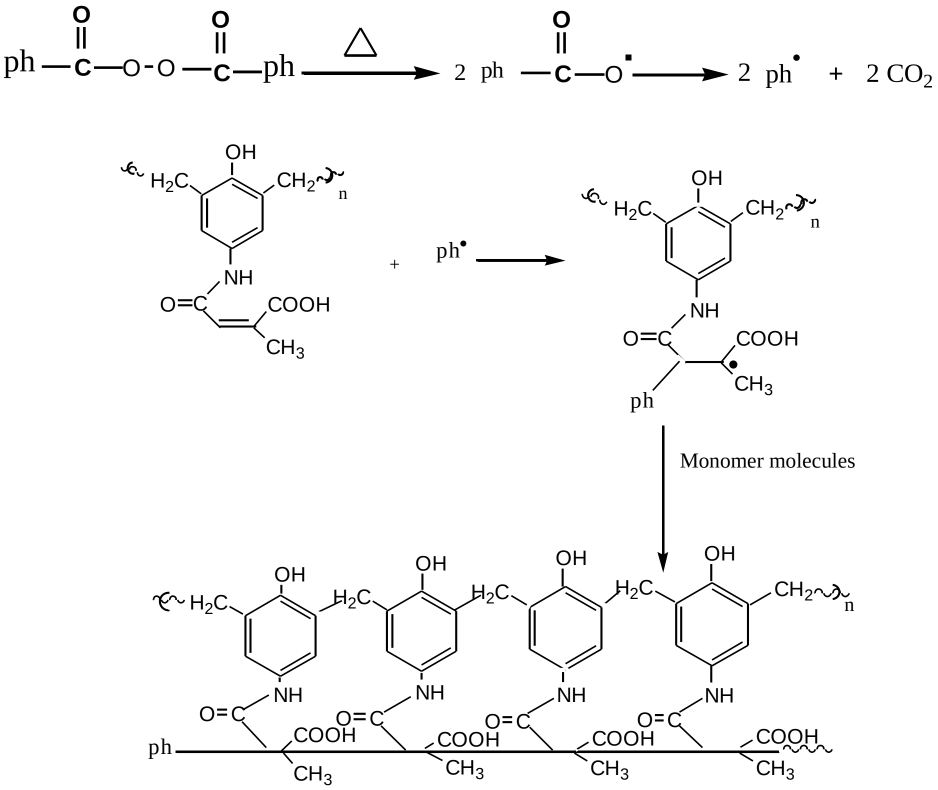
These physical properties of the cured resins are coincident with the expected ones due to the presence of ester ( $H_3C-\underset{\underset{O}{\|}}{C}-O-$)and ester (C–O–C) bonds which donate softness and flexibility(9).

Structures of the cured resins [9-12] were confirmed by IR spectra which showed disappearance of absorption bands of υ(O–H)carboxylic due to dehydration and υ(O–H) phenolic due to esterification and appearance of two clear characteristic absorption bands at (1760)$cm^{-1}$and(1190-1200)cm^{-1} due to stretching vibrations of (C=O)ester and (C-O-C)ester respectively. The cured resins [9-12] also give positive result in specific tests of esters.

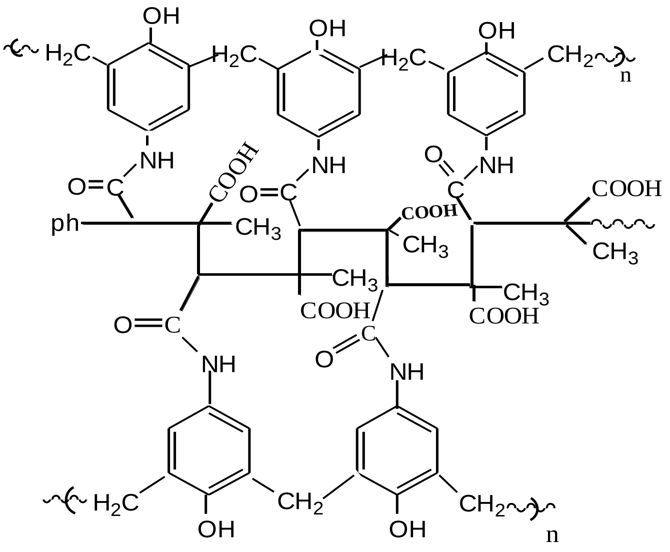
Physical properties and spectral data of the cured resins [9-12]are listed in Table(III).

The second method used in the curing of the prepared resins involved free radical polymerization(10) of citracon vinyls in both the pendent citraconamic groups in the resins [5-8]and pendent citraconimide groups in the resins [9-12] using benzoyl peroxide as initiator and DMF as solvent.

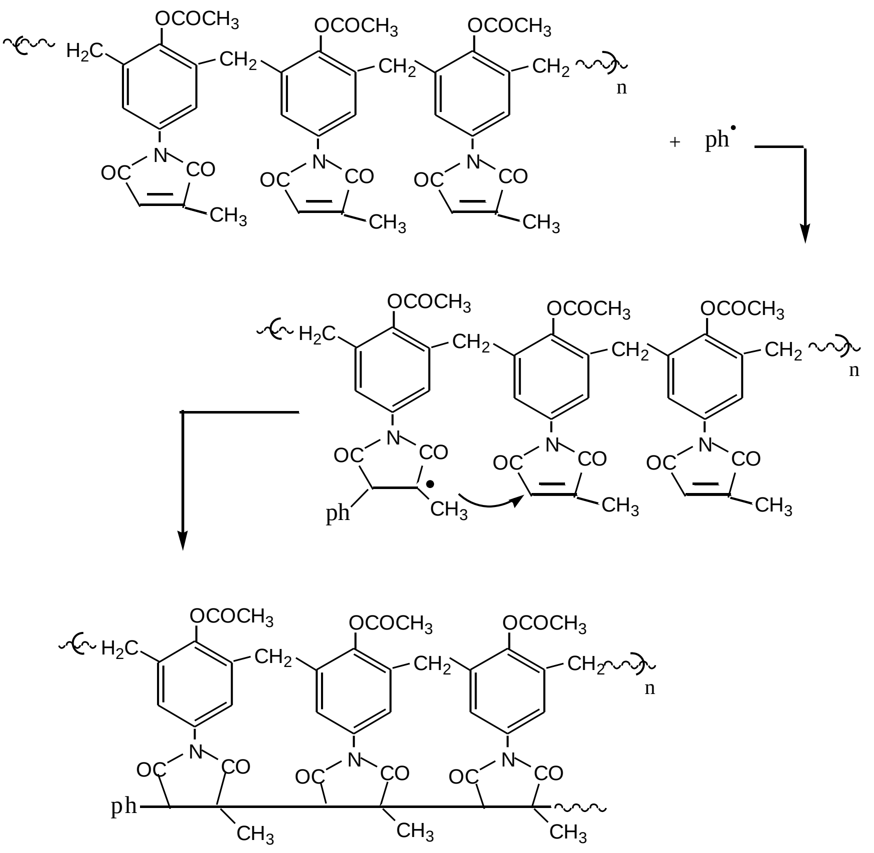
Chain growth polymerization of citracon vinyls in citraconamic groups can be expressed by the following suggested mechanism:



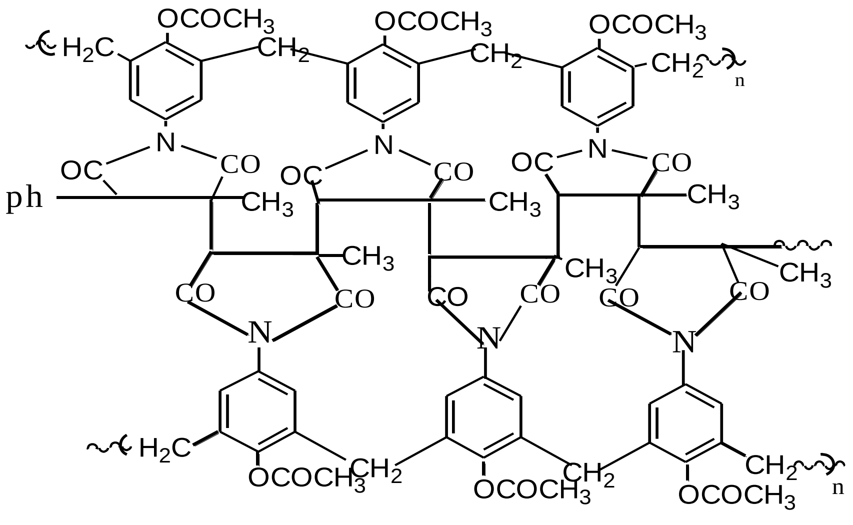
Polymerization may also involved linking between polymeric chains as shown in the suggested structures below:



0n the other hand the suggested mechanism of polymerization of citracon vinyls in pendent citraconimide groups can be expressed as follows:



Polymerization also occure between vinylic bonds in close polymeric chains producing cross linked polymers as shown in the suggested structures below:



It is noticable that in the case of curing the resins[5-8]the products are cross linked polymers which did not soften under heat and insoluble in all organic solvents while in the case of curing the resins [9-12] the products are cross linked polymers, soluble only in DMSO with higher softening points and higher intrinsic viscosities (0.96-1.14)dL/g than the starting resins before curing.

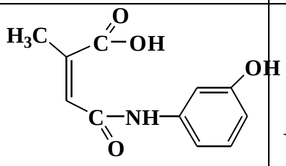
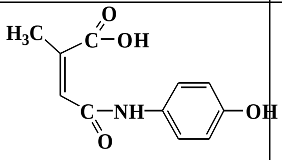
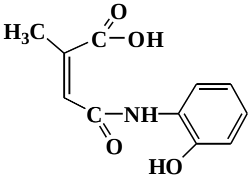
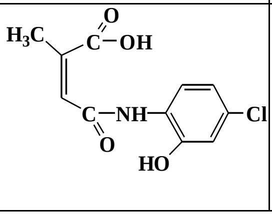
On the other hand all the obtained resins from free radical polymerization gave negative results with both $KMnO_4$ solution and Bromine in CCl_4 tests and this confirmed the absence of citracon vinyls due to saturation during polymerization.

IR spectra of the resulted cross linked polymers showed disappearance of vinylic ( ) absorption band and this similarly proved the success of curing via polymerization .

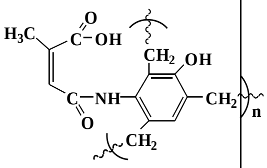
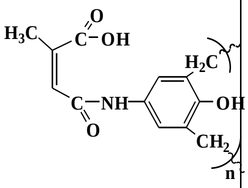
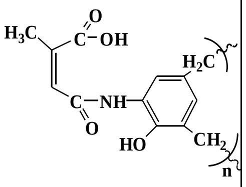
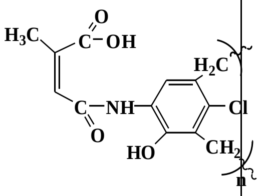
Physical properties and spectral data of the cured resins [13-16] and [17-20] are listed in Tables (IV) and (V) respectively.

As a final conclusion the present work supply us with new strategies in building new phenolic resins first by using new phenolic moiety substituted with citrconamic acid groups to condense with formaldehyde and second by curing the prepared resins via esterification and free radical polymerization producing cross linked thermally stable polymers in hope to serve new applications.

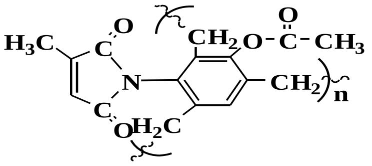
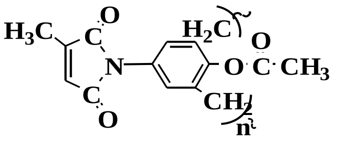
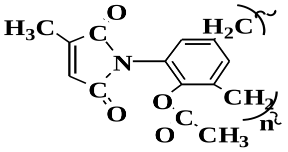
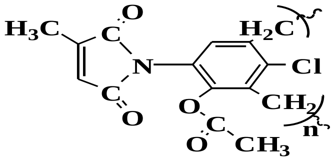
Table (I) physical properties and IR data of citraconamic acids

Comp. No.	Compound structure	Color	Melting Point C^0	Yield %	Major IR absorptions cm^{-1}					
					υ O−H phenolic	υ O−H carboxylic	N−H υ Amide	C=Oυ carboxylic	C=O υ Amide	C=C υ vinylic
١		Yellow	154-155	92	3362	3227	3317	١٧٠١	١٦٣٠	١٥٩٠
٢		Deep Yellow	157-158	89	3540	3230	3325	١٧١٠	١٦٢٥	١٥٩٠
٣		Yellow	150-152	93	3390	3091	3356	١٧٠١	١٦٢٦	١٦٠٨
٤		Pale Yellow	159-161	86	3300	3080	٣١٧٥	١٧١٠	١٦٢٥	١٥٩٠

Table(II)physical properties and IR data of of poly[N-(phenol-formaldehyde)citraconamic acids]

Comp. No.	Compound structure	Method	Color	S.P C^0	Conv. %	Major IR Absorptions cm^{-1}					
						O−H υ phenolic	N−H υ Amide	O−Hυ carboxylic	C=Oυ carboxylic	C=Oυ Amide	C=C υ vinylic
٥		A B	Pale Brown Brown	>300	92 81	٣٣٧٣	٣٣١٣	٣٢١٥	١٧١٠	١٦٦٠	١٦١٠
٦		A B	Brown Deep Brown	>300	٧٩ ٧٠	٣٣٧٠	٣٢٥٠	٣١٦٩	١٧٠٠	١٦٦٥	١٦١٠
٧		A B	Pale Brown Brown	>300	٨٠ ٨٠	٣٤٤٠	٣٣٧٠	٣٢٥٠	١٧٠٠	١٦٥٠	١٦٠٠
٨		A B	Red Brown	>300	٨١ ٧٤	٣٤٥٠	٣٣٩٠	٣٢٥٠	١٦٩٠	١٦٢٠	١٥٦٠

Table(III) physical properties and IR data of poly[N-(acetoxy phenyl-formaldehyde)citraconimides]

Comp. No.	Compound structure	Color	S.P C^O	Conv. %	[η] dL/g	Major IR Absorptions cm^{-1}			
						$C=O\ \upsilon$ Ester	$C=O\ \upsilon$ Imide	$C=C\ \upsilon$ vinylic	$C-O\ \upsilon$ Ester
9		Yellow	>300	٩٢	—	١٧٦٠	١٦٥٠	١٦٠٠	١٢٠٠
10		Pale Brown	191	٨٠	0.81	١٧٦٠	١٧٠٠	١٦٥٠	١٢٠٠
١١		Brown	٢٢٠	٨١	0.68	١٧٦٠	١٧٠٠	١٦٥٠	١١٩٠
١٢		Brown	١٩٨	٨٥	0.53	١٧٦٠	١٦٨٠	١٦٢٠	١٢٠٠

Table(IV)physical properties and IR data of the cured resins by polymerization

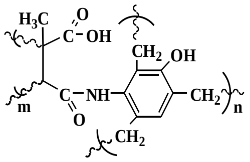
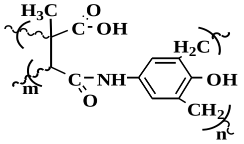
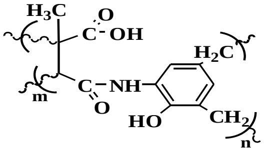
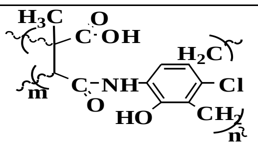
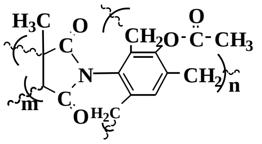
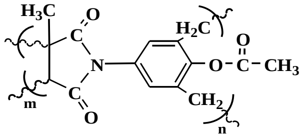
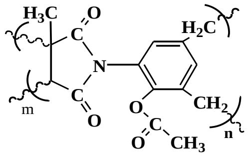
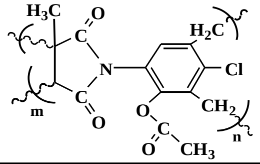
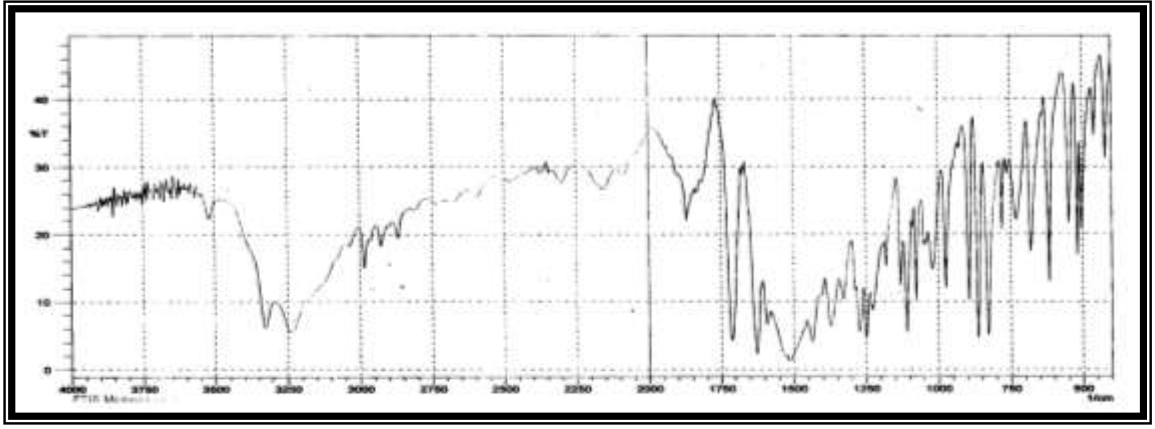
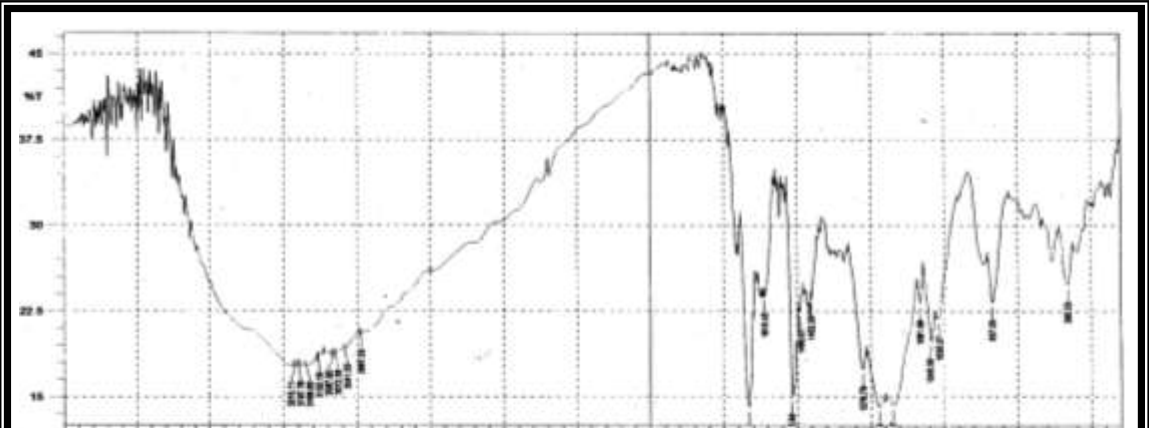
Comp. No.	Compound structure	Color	S.P C^0	Conv. %	Major IR Absorptions cm^{-1}				
					$O-H\ \upsilon$ Phenolic	$N-H\ \upsilon$ Amide	$O-H\ \upsilon$ carboxylic	$C=O\ \upsilon$ carboxylic	$C=O\ \upsilon$ Amide
13		Deep Brown	>300	80	٣٤٠٠	٣٢٥٠	٣١٨٠	١٧٠٥	١٦٤٧
١٤		Black	>300	٦٧	٣٤٥٠	٣٣٩٠	٣٢٣٠	١٧٠٩	١٦٤٧
15		Brown	>300	٦٤	٣٤٠٠	٣٢٥٠	٣١٥٠	١٧٠٠	١٦٥٠
١٦		Brown	>300	٧٢	٣٤٠٠	٣٢٥٠	٣١٨٠	١٧٠٥	١٦٥٠

Table (V) physical properties and IR data of the cured resins by polymerization

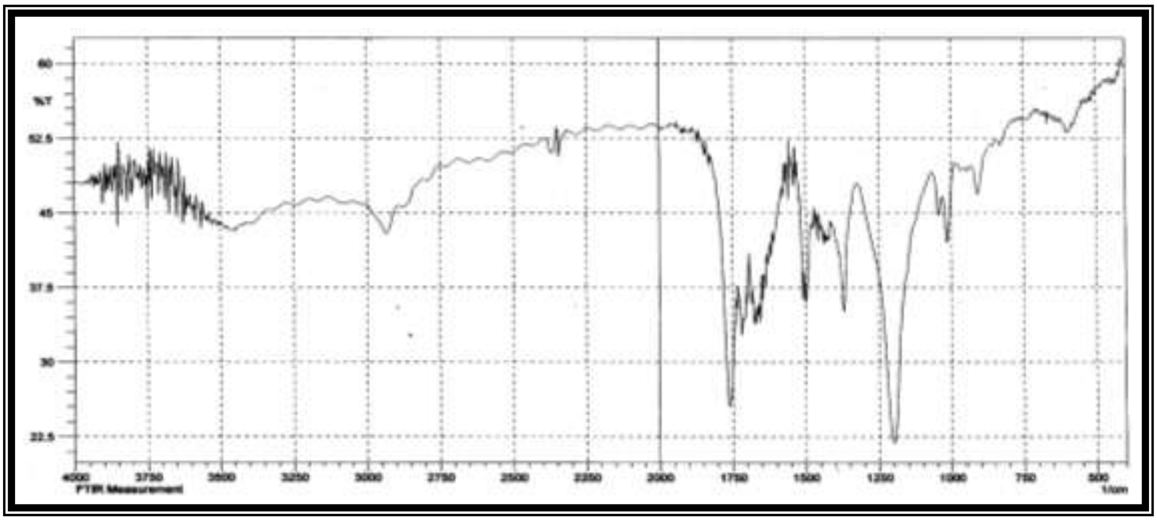
Comp. No.	Compound structure	Color	S.P C^0	Conv. %	[η] dL/g	Major IR Absorptions cm^{-1}		
						C=Oυ Ester	C=Oυ Imide	C-Oυ Ester
17		Brown	>300	٨٥	-----	1760	١٦٦٠	١٢٠٠
١٨		Brown	٢٠٥	٦٩	0.96	١٧٦٠	١٦٧٠	١٢٤٠
١٩		Yellow	٢٣٧	٧١	1.14	١٧٤٥	١٧٠٠	١١٨٠
٢٠		Yellow	٢١٣	٧٧	1.1	١٧٥٨	١٦٧٠	١٢٠٠



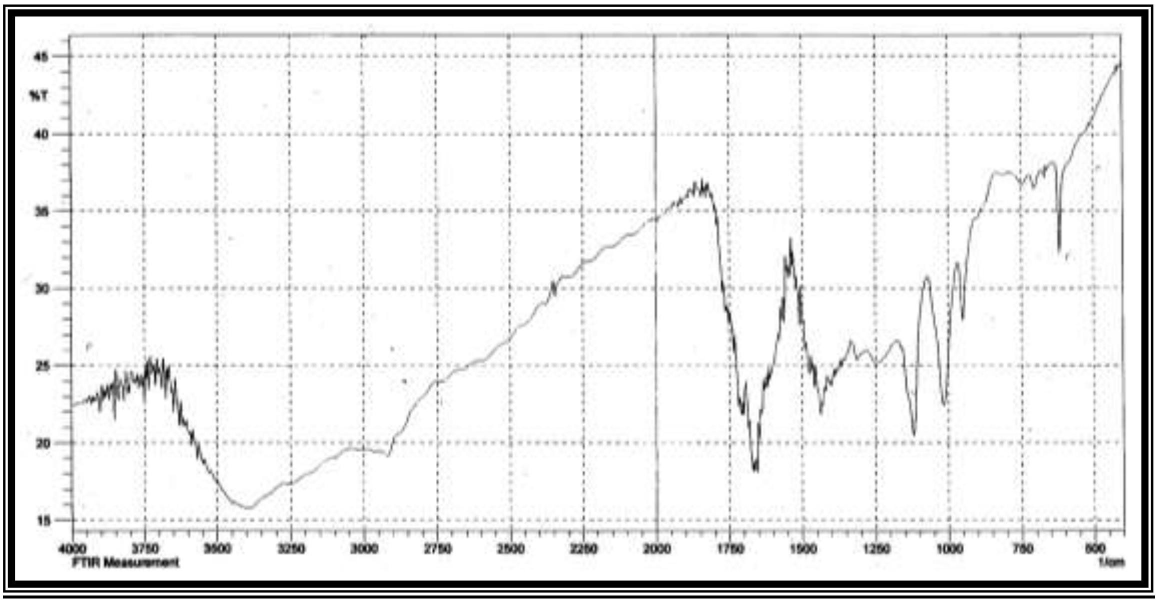
Fig(1)FTIR spectrum of compound [2]



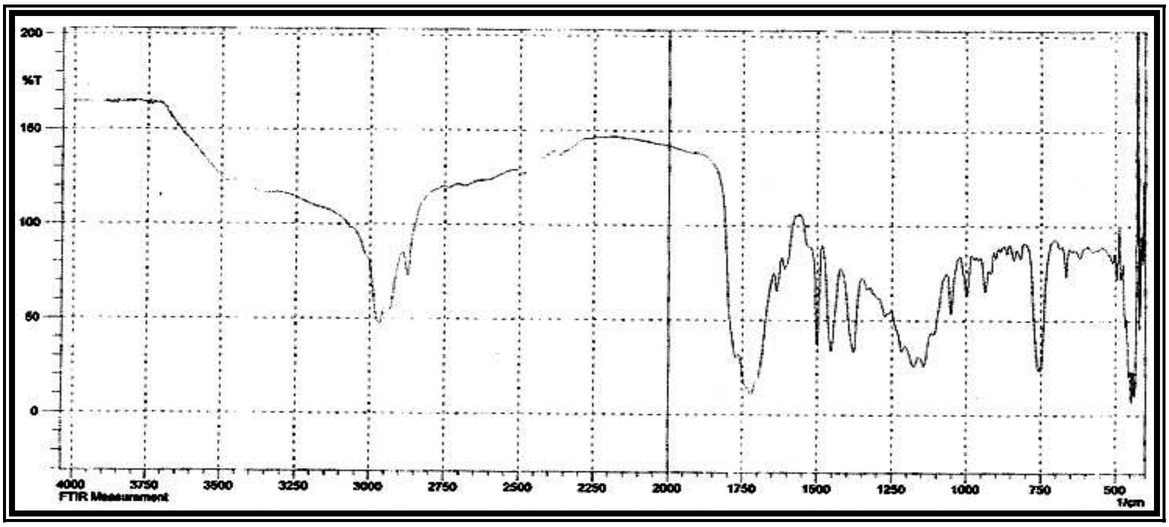
Fig(2)FTIR spectrum of compound [6]



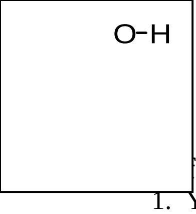
Fig(٣)FTIR spectrum of compound [١٠]



Fig(٤)FTIR spectrum of compound [١٤]



Fig(5) FTIR spectrum of compound [١٩]



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تحضير ومعالجة راتنجات فينول- فورمالديهايد جديدة معوضة بحوامض الستراكون آميك

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الملخص

تضمن البحث تحضير أربعة راتنجات فينولية جديدة حاوية على مجاميع متدلية من حوامض الستراكون أميك في وحداتها المتكررة وذلك من تكاثف الفورمالديهايد مع حوامض N-(هيدروكسي فنيل) ستراكون أميك بوجود عامل مساعد حامضي أو قاعدي.

بعد ذلك تم إجراء معالجة للراتنجات المحضرة بإتباع طريقتين تضمنت الأولى إدخال الراتنجات المحضرة في تفاعل أسترة وغلق حلقي باستخدام انهيدريد الخليك وخلات الصوديوم اللامائية بينما تضمنت الثانية إجراء بلمرة متسلسلة وفق الجذور الحرة للأواصر الفاينيلية الموجودة في هذه الراتنجات مما أسفر عن تكوين بوليمرات متشابكة مستقرة حراريا.

امتازت الراتنجات المحضرة والراتنجات بعد المعالجة بمواصفات جديدة مما يتيح استخدامها في تطبيقات جديدة.