

Synthesis of Some New Resins From Poly (Phenol-Furfural) And Cyclic Anhydride

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ABSTRACT

In this work , the synthesis of some new resins from conversion of poly (2 or 3 or 4- nitro phenol- furfural) to poly (2 or3 or 4-amino pheunol- furfural), by reaction with cyclic anhydride, where explored . The obtained new resins containing an amic acids residue were characterized with IR, UV, ¹HNMR, CHN analysis, Intrinsic viscosities and S.P where by polymers or resins. Will have an intermediate molecular weight might be proved.

Introduction

The phenolic resins may be considered to be the first polymeric products, produced commercially from simple compounds of low molecular weight, i.e. they were the first truly synthetic resins to be exploited. To day these materials are widely used as a molding powders laminating resins, or casting resins, as binders and impregnates, in surface coating, adhesives and a miscellany of other(1).

Although numerous reports about the modification of the phenol-formaldehyde resins (1-5), and single article of the poly (2 or 3 or 4-nitro or chloro or bromo-phenol-furfural resin(6) have been published, but it is not easy to locate any report dealing with the preparation of phenol-furfural containing pendant amic acid in their repeating units. In this article, poly (phenol-furfural) containing an amic acid groups in the repeating units in two different routs were synthesized.

EXPERIMENTAL PART

Materials and Instruments

Softening points were determined on Thermal microscope (Kofler method) .Proton –Nuclear magnetic resonance spectra were recorded using A varian A60MHZ spectrophotometer using (DMSO-d₆) as a solvent .Ultra violet spectra were recorded using Shimadzu U.V-VIS recording spectrophotometer using DMSO as solvents .Thermal analysis were performed using Santon Redcroft DTG , TG model 760 .Cannon Vensik was used to determined intrinsic viscosity using DMSO as solvents . Methyl ,Ethyl Ketone and other chemical were purchased from fluka, BDH, or Aldrich .

Preparation of poly(2, 3,4-nitrophenol-furfural) resins (6)

2 -, 3-, 4-, nitrophenols were allowed to react with two mole . of furfural while 3-nitrophenol was reacted with 3 moles of furfural , according to the literature(6)

Preparation of poly(4-nitrophenol-furfural) resins(6)

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In a 250 ml round bottom flask (1.39g) of 0.01 mole of 2 or 3 or 4-nitrophenol and 1ml of 40% NaOH was heated . To this solution (1.94g) of 0.02 mole of furfural was added with stirring . The mixture was refluxed with heating and stirring for 2.5h., during which a colorless resin was formed and separated with a pressure – equalized funnel. Conversion was calculated to be 75%, the softening points was more than 300°C and the IR spectrum in KBr disk showed the following major absorption; 3450cm⁻¹(vO-H phenolic) ; 3100cm⁻¹(vC-H aromatic) ; 2980cm⁻¹ (vC-H aliphatic) ; 1600cm⁻¹(vC=C aromatic) ; 1250cm⁻¹(δC-O-C asym.); 1040cm⁻¹(δC-O-C sym.); 630cm⁻¹(δO-H phenolic) ; 1530cm⁻¹(vNO₂asym.); 1300cm⁻¹(vNO₂asym.); 880cm⁻¹(vC-N).

Preparation of poly(4-aminophenol-furfural) Resin

Crystalline sodium sulfide mono hydrate (1.00g) 0.01 mole and (0.5 g) of powder sulfur and (1.0g) 0.025 mole of sodium hydroxide pellet were suspended in 100ml of toluene in a 250ml round bottom flask and fitted with a reflux condenser. The mixture was heated on a steam bath for (20 - 25)minutes with occasional stirring. The content were poured into another round bottom flask containing hot solution of (2.97g, 0.01mole) of poly (4-nitrophenol-furfural)in 100ml toluene and the mixture was refluxed for another 4 hrs resulting in a clear yellow gum, the separated polymer was dried at 80 0C. Conversion was 73%, the IR spectrum in KBr disk showed the following absorption; 3500cm⁻¹(vN-H doublet) ; 3450cm⁻¹(vO-H Phenolic) ; 3075cm⁻¹(vC-H aromatic) ; 2981cm⁻¹ (vC-H aliphatic); 1600, 1550cm⁻¹(vC=C aromatic) ; 1253cm⁻¹ (δC-O-C asym.); 1047cm⁻¹(δC-O-C sym.).

The polymer of 2-, or 3- aminophenol- furfural were prepared according the same above procedure .

For 2- aminophenol-furfural

Conversion was 70%, the IR spectrum in KBr disk showed the following absorption; 3475cm⁻¹(vN-H doublet) ; 3450cm⁻¹(vO-H Phenolic) ; 3050cm⁻¹(vC-H aromatic) ; 2989cm⁻¹ (vC-H aliphatic); 1600, 1558cm⁻¹(vC=C aromatic) ; 1250cm⁻¹(δC-O-C asym.); 1050cm⁻¹(δC-O-C sym.).

For 3- aminophenol-furfural

Conversion was 78%, the IR spectrum in KBr disk showed the following absorption; 3500cm⁻¹(vN-H doublet) ; 3455cm⁻¹(vO-H Phenolic) ; 3034cm⁻¹(vC-H aromatic) ; 2987cm⁻¹ (vC-H aliphatic); 1593, 1559cm⁻¹(vC=C aromatic) ; 1250cm⁻¹(δC-O-C asym.); 1055cm⁻¹ (δC-O-C sym.).

Preparation of poly N-(phenol-furfural) amic acid

Method A:

Preparation of poly N-(4-phenol-furfural)Phthalamic acid

The poly (4-aminophenol-furfural) (2.07g) of 0.01 mole (structural unit) was dissolved in 150ml of methylethylketone in a 250ml round bottom flask. A solution of (1.48g , 0.01 mole) of phthalic anhydride was added to the flask at temperature less than 250C. The mixture was stirred 5h at room temp. filtered and added 100ml of cold methanol, the white precipitate was formed, washed with ether and dried with drying pistol apparatus. Other N (2-,3-, phenol-furfural) substituted amic acid polymers were prepared as above according to literature(8).

Method B:

1- Preparation of N-(hydroxyl phenyl) phthalic acid and maleamic acid.

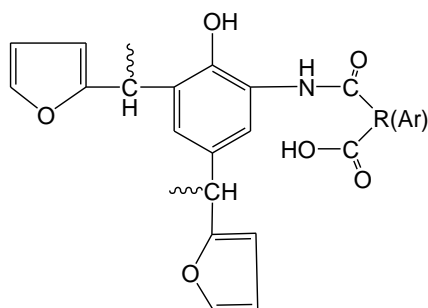
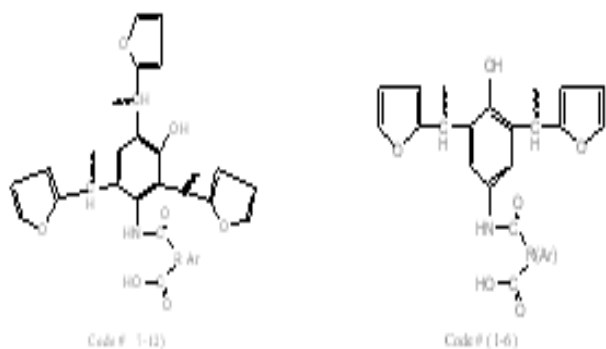
Ortho-, or meta-, or para- amino phenols, were

allowed to react with phthalic – or maleic anhydride according to the literature (5,7).

2(Poly condensation N-(hydroxyl phenyl) amic acids with furfural via an acid catalyst.

In a 250ml three – necked flask supplied with a reflux condenser, thermometer, and dropping funnel (6gm) 0.029mole of N-(hydroxyl phenyl) amic acid , (3.88g , 0.04mole) of furfural, (compound 1 to 6) or (5.76g, 0.06mole) compound (7 to 12) and 15 ml of methyl ethyl ketone were placed. The dropping funnel was charged with 0.2 ml of conc. H₂SO₄ and 0.6 ml of distilled water. The mixture was stirred and refluxed at 110 oC for 5h. The polymeric residue was dissolved in the least amount of light naphtha and the resulting precipitate filtered and dried in a drying pistol under reduce pressure.

Table I and II listed some of the physical properties of the products.



Code # (13-18)

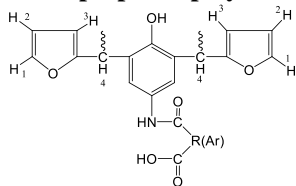
Table 1: % Conversion, Intrinsic viscosities and UV absorption of the prepared Poly(N- phenyl furfural) substituted amic acids.

Code #	Ar (R)	% Conversion		η	S. P.(°C)	UV absorption nm, DMF
		Method1	Method2			
1		65	69	0.891	286-293	259 310
2		73	79	0.793	274-281	263 313
3		79	84	0.771	280-288	253 307
4		68	77	0.778	266-272	271 343
5		66	69	0.753	263-267	263 311
6		69	75	0.699	269-277	269 317
7		63	68	0.693	253-260	263 327
8		65	71	0.666	228-235	261 321
9		59	64	0.684	233-239	259 313

14	3491	3340	3097		2884	1695	1695		1589, 1554	1490
15	3441	3349	3100		2930 2885	1690	1690		1600, 1553	
16	3451	3297	3134		2890	1700	1673		1593, 1560	1491
17	3448	3321	3111		2981 2894	1705	1675		1599, 1555	1490
18	3446	3340	3197		2930 2888	1700	1667		1595, 1571	1481

	5 O ₆ N=	5 (65. 12)	0 (3.9 4)	3 (3.6 1)	Carboxylic(10.00); δNH (8.88); δC ₆ H ₂ (7.41- 7.87); δC ₁ -H Furan (6.11- 6.34) fused with O-H Phenolic and CH=CH aliphatic ; δC ₂ -H Furan fused with δO-H phenolic.
3	C ₂₀ H ₁	63.3	4.6	3.8	δO-H Carboxylic(10.00); δN- H (8.79); δC ₆ H ₂ (7.31- 7.77); δC ₁ -H (6.13) Furan fused with O-H Phenolic (6.05 – 6.31).
	7 O ₆ N=	9 (65. 27)	3 (4.3 9)	1 (3.1 9)	

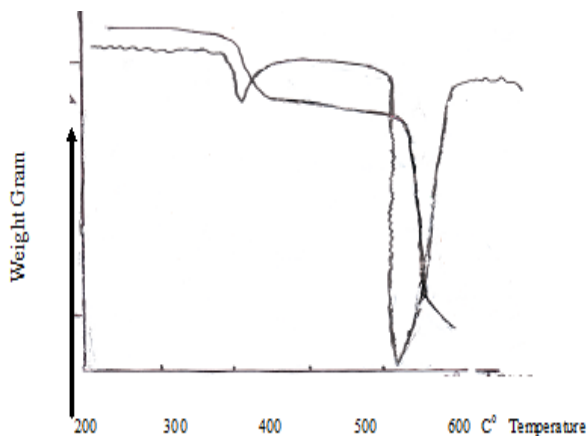
Table (III) Elemental analysis and H n.m.r (DMSO d6) of the prepared polymers



Code #	Molecular formula	Elemental analysis Cal/(Found)			δH-NMR (p.p.m) spectra
		%C	%H	%N	
1	C ₂₄ H ₁ 7 O ₆ N = 415	69.3 9 (69. 05	4.0 9 (4.0 1)	3.3 9 (3.1 0)	δO-H Carboxylic(10.00); δN- H (8.73); δC ₆ H ₂ (7.53- 7.99); δC ₁ -H (6.13) Furan fused with O-H Phenolic and CH—CH aromatic ; δC ₃ -H (5.96) Furan ; δC ₂ - H furan (5.19) fused with C ₄ -H.
2	C ₂₀ H ₁	65.7	4.1	3.8	δO-H

Table (IV) Data obtain from TG and DTG analysis of some the new polymer

Code #	Sample weight (mg)	Thermal range (°C)	Start temp. (°C)	Peak1 temp. (°C)	Peak2 temp. (°C)	Weight residue
1	4.15	Room-600	300	320 Wt. lose 0.18 mg	510 Wt. lose 1.34 mg	2.63
2	3.65	Room-600	300	318 Wt. lose 0.178 mg	500 Wt. lose 1.35 mg	212
3	3.67	Room-600	300	325 Wt. lose 0.200 mg	517 Wt. lose 1.38 mg	2.09



TG and DTG curve of Resin code # 1

Table (V) Solubilities of new polymers

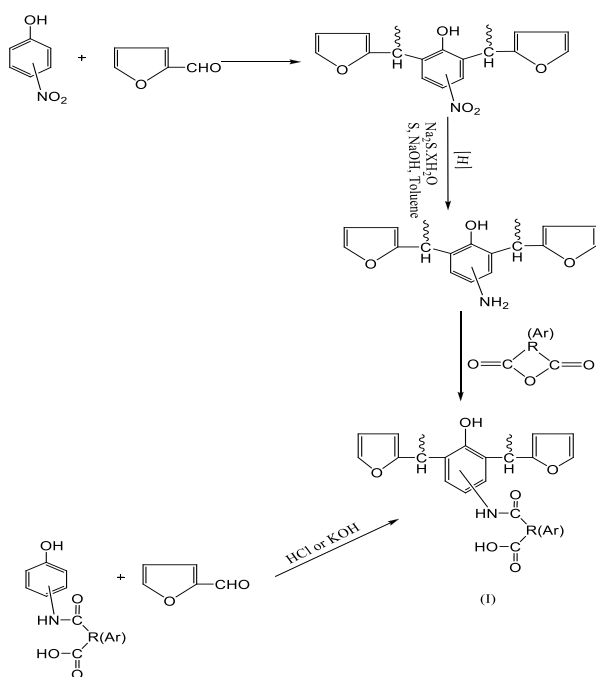
Code#	benzene	Water	methanol	ethanol	Dioxane or cyclo hexane	Benzene or toluene	Dichloro methane or ethane	Petrofeum ether	Chloroform or CCl ₄	THF	DMF	DMSO
1	In	In	In	In	In	In	In	In	In	In	S	S
2	In	In	In	In	In	In	In	In	In	In	swelling	S
3	In	In	In	In	In	In	In	In	In	PSH	S	S
4	In	In	In	In	In	In	In	In	In	PSH	S	S
5	In	In	In	In	In	In	In	In	In	PSH	S	S
6	In	In	In	In	In	In	In	In	In	PSH	S	S
7	In	In	In	In	In	In	In	In	In	In	In	PSH
8	In	In	In	In	In	In	In	In	In	In	In	PSH
9	In	In	In	In	In	In	In	In	In	In	In	PSH
10	In	In	In	In	In	In	In	In	In	In	In	PSH
11	In	In	In	In	In	In	In	In	In	In	In	PSH
12	In	In	In	In	In	In	In	In	In	In	In	PSH
13	In	In	In	In	In	In	In	In	In	In	In	PSH
14	In	In	In	In	In	In	In	In	In	In	In	PSH
15	In	In	In	In	In	In	In	In	In	In	In	PSH
16	In	In	In	In	In	In	In	In	In	In	In	PSH
17	In	In	In	In	In	In	In	In	In	In	In	PSH
18	In	In	In	In	In	In	In	In	In	In	In	PSH

Abrev. In = insoluble, s = soluble, PSH = partial soluble hot

Result and discussion

The reaction of furfural with p-nitro phenol in the basic or acidic medium gave the poly (nitro phenol furfural) resin. An attempts to reduce other metal such as zinc or tin metal. However, the use of sodium bisulfide in basic medium in presence of sulfur was successful. It seems that metal such as iron form coordination complexes that are difficult to be purified while the use of sodium sulfide would help to avoid such complexations.

The poly(N-substituted furfural) amic acids resin (I) were synthesized by two different routes. In the first method, the poly (amino phenol furfural) resin was prepared by starting from a reaction of p-nitro phenol, furfural and reduction. The product was allowed to react with different cyclic anhydrides to produce the corresponding (I) which is obtained in fair yields. The second route for the preparation of (I) were accomplished by direct displacement reaction between amic acids monomer and furfural in acidic or basic catalyst, the product (I) were increasing in yields percentage. Scheme 1 give clear demonstration to the reaction path :



Schem (1)

Table I and II lists some physical and chemical properties of the poly (N-substituted furfural) amic acids resins (I) elemental analysis showed good agreement of the calculated and found percentages and also I.R spectrum show appearance of OH phenolic at (3400-3509) cm⁻¹, NH at (3217-3349) cm⁻¹, carbonyl of carboxylic acid at (1660-1682) cm⁻¹ and carbonyl of the amide group at (1684-1703) cm⁻¹. Ultraviolet absorption of the new prepared resin containing pendant amic acids (I) showed two peak. First at λ_{max} (251-271)nm due to π→π* transitions and the second at (307 – 343) due to n→π*.

The NMR spectra of the new resins showed shifted for (S-C-H) furan vinylic group fused with O-H phenolic and CH₂=CH_{aromatic} at δ(6.05-6.34); δN-H(8.73- 8.79) ; δ O-H carboxylic at (10.00); δC6H2 (7.31- 7.99) indicating polymer formation . Their thermal stabilities are attributed mainly to high polarity and partly to the ring structure of their repeating units. This means that the main use of polymers is as thermosetting plastic. All the prepared polymers showed high softening points with wide ranges in general. This means that the compounds have high (T_g) temperature and are thermally stable in general. In all of the TG curve indicated, the initial drop in weight is due to dehydration water in substituted poly amic acid and convert to corresponding imides at 300C°, the other peak due to loses two molecule of furan(see table IV). All resins are insoluble in most organic solvents expect DMF and DMSO (see table V).

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تصنيع بعض الراتنجات من Poly (Phenol-Furfural) , Cyclic Anhydride

نبيل جمال عايد

الخلاصة:

تم في هذا البحث تحضير عدد من الراتنجات الجديدة وذلك من تحوير راتنج بولي(2 او 3 او 4-نايتروفينول -فورفورال) إلى راتنج بولي (2 او 3 او 4-امينو فينول - فورفورال) بوساطة تفاعله مع عدد من الانهيدريدات الحلقية ، فتم الحصول على عدد من الراتنجات الجديدة الحاوية على أحماض الاميك، وقد تم تشخيصها عن طريق طيف الأشعة تحت الحمراء ، وفوق البنفسجية، وطيف الرنين النووي المغناطيسي ، والتحليل الدقيق للعناصر CHN , قياس اللزوجة الجوهرية بالاضافة الى قياس درجة التلين (S.P) للبوليمرات او الراتنجات.