Synthesis, Characterization and Study of Electrical Properties for Some Metallopolymerized Derivate From Benzillic Acid

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Abstract:

Anew two Metallopolymerized were prepared by using Benzillic acid. The prepared polymers were identified by FTIR, U.V-Visible and CHN analysis. The electrical properties were studied with iodine doping at different temperature in the range (20° C- 100° C). The conductivity of prepared polymers were increased with increasing the temperature and doping, the polymers displayed semiconducting properties (σ = 10^{-4} ohm⁻¹.cm⁻¹).

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المستخلص

تم تحضير نوعين من البوليمرات الفلزية المشتقة من حامض البنزاليك و '4,4-داي نايترو حامض البنزاليك. شخصت البوليمرات المحضرة بتقنيات متعددة منها مطيافة الاشعة تحت الحمراء IR والاشعة فوق البنفسجية U.V وتحليل العناصر الدقيق CHN. درست التوصيلية الكهربائية للبوليمرات المحضرة قبل التشويب وبعد تشويبها بأستخدام اليود وبدرجات حرارية مختلفة C⁰C-۱۰۰⁰C. كما تم التوصل الى كون البوليمرات المحضرة تزداد توصيليتها بزيادة التشويب ومع زيادة درجة الحرارة لذا فهي تمتلك صفات مواد اشباه موصلة اذ ان التوصيلية التي تم الحصول عليها ¹⁻⁴0m

Introduction:

Azo dyes have found widespread applications in the textile and food industries and elsewhere. To improve the soluble in water, azo dyes often contain one or more sulphonic acid groups⁽¹⁾.

Conjugated polymers have been widely studied because of their potential use as light weight and flexible substitutes for metals in a variety of applications ^(2, 3). Materials based on conjugated polymers function as conductors of electricity because of electron delocalization through their planar π -system. Interest in conjugated polymers that contain transition metal back bones has been sparked by the promise of a new glass of material that will combine the attractive electrical properties of metals with the strength flexibility and process ability of organic polymers ⁽⁴⁾. Previous attempts, however, to synthesize "organometallic" polymers have typical afforded poorly conducting and poorly soluble oilgomeric materials that are of dubious practical use ⁽⁵⁾.

The planner π -system that gives conjugated polymers their desired electrical conductivities also causes them to be intractable and infusible. These latter characteristic contribute to a decrease in mechanical strength and processability, which have slowed the incorporation of conjugated polymers in device applications. Sensitivity to ambient conductions (e.g. oxygen, heat and light) has also limited the widespread use of conjugated polymers. Over coming these limitations will be necessary before conjugated polymers will be of practical utility in all but highly specialized technologies ⁽⁶⁾.

In the present study anew metallopolymerized containing some of metals (Cu and Zn) were prepared and study the electrical properties with iodine doping and the relationship with crystal structures of polymers.

Key Word: Electrical Properties, Polymer Derivative from Benzillic Acid Experimental Chemicals:

Benzillic acid (99.90%), ethanol (99%), urea (99.97%), methanol (99.9%),
THF (99.7%), CuCl₂ (99.90%), ZnCl₂ (99.90%), 1, 4-diaminobenzene (99.99%), benzene (99.0%), hydrochloric acid (36.0%) and carbon tetrachloride (99.99%) were supplied from Aldrich and Fluka Companies.

Instruments

- 1. FTIR-Infrared Photometer (8400S) from made by (SHIMADZU) in the range (4000-400cm⁻¹) from Petrochemical Laboratories/ Basra.
- 2. U.V-Visible was recorded in the range (300-700nm) on a thermal tcelios V (4.60) was used.
- 3. Elemental Analysis (CHN) from College of Science/ Cairo University.
- 4. Electrical conductivity (Voltmeter, Power Supply, Resistance, Temperature Recorded and Measured Sample Cell) was used under vacuum in Chemistry Department/ Education College.

Synthesis of Benzillyl Alcohol

Benzillyl alcohol was prepared depending on Ref. [Organic Synthesis, Part III, P.374 (1941)].

Synthesis of Benzilladehyde

Benzilladehyde was prepared depending on Ref. [Organic Synthesis, Part III, P.541 (1941)].

Synthesis of dibenzilladehyde Schiff-base [1]

4.24g (0.02mole) benzilladehyde and 0.6g (0.01mole) were mixed with 100ml ethanol and the mixture was heated under the refluxed for (45min). The mixture was cooled, filtered and dried at 50° C under vacuum oven ⁽⁷⁾. The structure product was showed in the scheme (1).



Synthesis of Metal Complex Schiff-base [2]

8.96g (0.02mole) dibenzilladehyde Schiff-base and 1.30g (0.01mole) ZnCl₂ or 1.28g (0.01mole) CuCl₂ were mixed with 100ml benzene and heated under refluxed for 30min. The product was cooled, filtered and dried at 60[°]C under vacuum oven ⁽⁸⁾. The metal complex Schiff-base was showed in the structure [2].



Synthesis of Metallopolymerized Schiff-base [3]

8.64g 1,4-diamino benzene was dissolved in a hot mixture of 2.5ml HCl and 20ml water. Temperature was decreased from 5^{0} C to 0^{0} C and solution was tetrazotised by addition 1.0g NaNO₂ in 7ml water within 1min. The tetrazo solution was left in ice for 10min and then added to solution of 0.6g metal complex Schiff-base [2] and 3g crystallized sodium acetate in 50ml water. Then the resultant mixture was heated at 80^{0} C⁽⁹⁾. Purification was made by hot water. The metallopolymerized Schiff-base was showed in structure [3].



Result and Discussion:

The dibenzilladehyde Schiff-base, metal complex Schiff-base and metallopolymerized Schiff-base as KBr discs were identified by FTIR. The principle FTIR absorption bands were observed in the monomer, complex and polymer in the Table (1). In the spectrum of structure [1] an absorption (3500-3450cm⁻¹) clearly indicates the existence of (O-H) group, in addition to many of bands at 3063cm⁻¹, 1638cm⁻¹, 1580cm⁻¹, (1539-1431cm⁻¹) and 795 cm⁻¹ which may be attributed to aromatic (C-H) stretching, C=N, C=C, ring

stretching aromatic and C-H bending, while in structure [2] the O-H group was disappeared and the stretched of C=N group was appeared at 1597cm⁻¹, in addition to appeared peak at 802-795cm⁻¹ which may be attributed to metal bonded with compound. The spectrum of structure [3] (polymer) was appeared a band absorption of medium intensity at 1540-1530cm⁻¹ which may be attributed to N=N group, in addition to other peaks which was showed in above ^(8, 9).

Compound	Wave numbers(cm ⁻¹)							
	О-Н	C=N	N=N	С-Н	M-bonded	C=O	Ring Stretching	
1	3500-3450	1588	-	3060	802	1645	1539, 1508, 1431	
2	-	1597	_	3060	798	1650	1505, 1469, 1441	
3	-	1595	1530	3062	795	1630	1491, 1426	

Table (1) the absorption bands of compounds (1-3)

The electronic absorption spectra of the prepared compounds were measured in THF, the absorption maximum (λ_{max}) of the $\pi \rightarrow \pi^*$ transition to the structure [1] at 460nm and 487nm, respectively as shown in Figure (1) ⁽⁹⁾. Figure (2) shows the (λ_{max}) of the $\pi \rightarrow \pi^*$ transition to the structure-Cu, Zn [2] at 438nm, 565nm and 440nm, 570nm ⁽⁹⁾, while the (λ_{max}) of the prepared polymer (structure-Cu, Zn [3]) were appeared peaks at 390nm, 656nm and 394nm, 660nm, respectively due to the electron conjugated was increased along of the polymer structure and presence of the metal in the structure, as shown in Figure (3). The elemental analysis (CHN) shows the practical and theoretical values in Table (2).

Compound	P	ractical Valu	e %	Theoretical Value %			
Compound	С	Н	Ν	С	Н	Ν	
1	76.70	5.26	6.49	77.60	5.35	6.25	
2 (Complex-Cu)	68 44	5 16	6 31	69.04	4 36	5 56	
2 (Complex-Zn)	67.63	4.86	6.27	68.66	4.34	5.53	
3 (Polymer-Cu)	65.66	3.79	9.97	67.96	4.20	11.32	
3 (Polymer- Zn)	65.31	3.72	9.89	67.74	4.19	11.29	

Table (2) the values of CHN for Compounds (1-3)



Figure (2)



Electrical Properties:

The electrical conductivities were measured using the (voltmeter, resistance, power supply, sample cell, temperature recorder). The conductivities were calculated according to the Ahrrenious equation (1), which applied for prepared polymers. The prepared polymers were in form discs and covered by silver paint two form two electrodes. Doping of polymers with iodine were dissolved in carbon tetrachloride and stirred at 70° C for (72h), after that the polymerized doping were filtered and dried at 50° C under vacuum oven. The maximum conductivities of polymer doped are 10^{-1} ohm⁻¹.cm⁻¹.

$$\ln \sigma_{\pm} = \ln c - \frac{\Delta E}{KT} \qquad \dots \dots \dots (1)$$

:

σ: Conductivity (ohm⁻¹.cm⁻¹). $σ^0$: Pre-exponential conductivity ΔE : Activation energy (eV). K: Boltzmann constant (eV). T: Temperature (Kelvin).

Figures (4) and (5) show the electrical conductivity of prepared metal polymers (Cu, Zn), respectively at different temperature. Iodine was increased conductivity of conjugated system by forming electrons. The conductivity was increased with temperature which was like semiconductors. The values of conductivity for prepared polymers as shown in Table (3).

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Polymers	Conductivity (ohm ⁻¹ .cm ⁻¹) before doping	ΔE (eV) before doping	Conductivity (ohm ⁻¹ .cm ⁻¹) after doping	ΔE (eV) after doping
Cu-polymer	9.678*10 ⁻⁵	0.0361	7.85*10 ⁻⁴	0.026
Zn-polymer	8.36*10 ⁻⁵	0.0414	6.79*10 ⁻⁴	0.030

Table (3) the values of conductivity for prepared polymers



Figure (4) the electrical conductivity for Cu-polymer



Figure (5) the electrical conductivity for Zn-polymer

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