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THE PRODUCTION OF ELECTRICALLY-CONDUCTING NANOPOLYMERS AND THEIR APPLICATION IN TEXTILES

Annotation: *A broad spectrum of polymers is used in electrospinning to produce micro- or nanofibers suitable for a wide variety of applications. These polymers range from natural- or naturally occurring polymers- to synthetic polymers, or a combination thereof.*

This research aims at studying the electrical application of carrier polymers and employing that thereafter in textile technology to obtain a final textile product that has special uses. For this purpose, the focus was on preparing transport polymers and studying their electrochemical and chromatic properties. Thus, the research involved the following activities:

1- Conjugate groups have been synthesized that contain carbazole and phenothiazine.

2- The periodically unchanging electrochemical and optical properties have been studied.

3- The electrochemical composition of polymers, according to their basic structure (base), as well as the resulting polymers and electrical conductivity have been studied.

4- A programmed electrospinning device has been manufactured, which allows the resulting polymers to be applied directly to the fabric.

5- The resulting polymer, made by electrospinning, has been applied, and its morphological structure and electrical conductivity have been studied.

Key words: *electrospinning, composition of polymers, morphological, conductivity, carbazole and phenothiazine.*

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ПРОИЗВОДСТВО ЭЛЕКТРОПРОВОДЯЩИХ НАНОПОЛИМЕРОВ И ИХ ПРИМЕНЕНИЕ В ТЕКСТИЛЬНОЙ ПРОМЫШЛЕННОСТИ

Аннотация: *Широкий спектр полимеров используется в электроспиннинге для получения микро - или нановолокон, пригодных для широкого спектра применений. Эти полимеры варьируются от природных - или встречающихся в природе - до синтетических полимеров или их комбинации.*

Это исследование направлено на изучение электрического применения полимеров-носителей и их последующего использования в текстильной технологии для получения конечного текстильного продукта, имеющего специальное применение. С этой целью основное внимание уделялось получению транспортных полимеров и изучению их электрохимических и хроматических

свойств. Таким образом, исследование включало в себя следующие виды деятельности:

Синтезированы 1 - Конъюгатные группы, содержащие карбазол и фенотиазин.

2 - исследованы периодически изменяющиеся электрохимические и оптические свойства.

3 - изучен электрохимический состав полимеров в соответствии с их основной структурой (основой), а также полученные полимеры и электропроводность.

4 - изготовлено запрограммированное электроспиннинговое устройство, позволяющее наносить полученные полимеры непосредственно на ткань.

5 - полученный полимер, сделанные раньше было по-другому, был применен, и ее морфологической структуры и электрической проводимости были изучены.

Ключевые слова: *электроспиннинг, состав полимеров, морфология, электропроводность, карбазол и фенотиазин.*

1. Introduction:

Electrospinning has been used extensively in the electrostatic formation of fibers, where fibers with diameters ranging from 2 nm to a few microns have been produced from polymeric solutions of natural or synthetic polymers. Commercial interest in this technology has started to rise dramatically over the past decade due to the broadening application base of these fibers [1,c.504.2,c.2387].

The possibility of continuous production of nanofibers with this technology, as well as the wide spectrum of polymers with diameters that can be fine-tuned, resulted in focusing much research on how to develop this technology and work on transferring it from the laboratory qualitative field to the quantitative field with the development of investment prospects for these nanofibers.

The high specific surface area of nanofibre mats makes them very suitable in a wide variety of applications; They have been used as nanocatalysts and substrates in living tissue engineering, protective clothing, filtration, and biomedical, pharmaceutical, optical electronics, healthcare, and defense and security applications, as well as environmental engineering [3,c.2223,4,c.1197].

This research has relied upon the conjugate polymers that contain carbazole elements because of their great importance from the electro-molecular point of view. This is associated with molecules that can be easily employed thanks to their properties, including electrical conductivity, fluorescence, photoelectric radiation, and others.

Carbazole derivatives have an important place among the conjugate groups used in building electronic equipment due to their high temperature stability, blue (azure) light, and the possibility of obtaining P-type conductors. [5,c.1357,7,c.1273]

2. Materials & Methods

2.1. Electrospinning Device

An electrospinning device, with point aggregator and needle extrusion head that can be programmatically, simultaneously, and horizontally moved along the (X,Y) axes within the work area, has been manufactured. The vertical distance between these two parts can be adjusted along the (Z) axis during stoppage to produce non-woven networks of nanofibers arranged in a specific geometric structure on the cloth layer directly separating the two heads (Figure 1).

Figure 1 - Vertical Electrospinning Device

2.2. Potentiograph

The electrochemical study has been performed on a Titraiab 865 potentiograph made by the French company RADIOMETER according to the standard specification of the cell with three electrodes; a working electrode (MC305PT) made from platinium, an ITO electrode, and an auxiliary electrode made from silver chloride (MC6091) as controller electrode at room temperature.

The ITO electrode consists of glass sheets covered on one side with a layer of indium tin oxide with $R_s = 8 - 12\Omega$ from Aldrich.

Before conducting the measurements, the plates were washed with acetone, and as a background electrolyte,$(C_2H_5)_4NCLO_4$ was used, and the solvent was acetone nitrile.

The studied monomer solution (0.001 molecules / liter) and the background electrolyte Et_4NClO_4 in acetone nitrile were placed in an electrochemical cell and studied using the cyclic volt-ampere method. The voltage scanning speed (V_{scan}) *was unified in all the cases and equalled 50 mV/sec.*

To study the electrochemical behavior of the polymeric plates, and the polymers formed on the surface of the working electrode, they were washed with nitrile acetone and dried o separate the original monomer from the background electrolyte. After that, they were studied in the background electrolyte Et_4NClO_4 (0.1 molecule/liter) in acetone nitrile (without the monomer).

2.3. Spectrophotometer

The ultraviolet (UV) spectra were recorded on the analytikjena SPEKO 2000 Spectrophotometer. As a solution for imaging and taking spectra, acetone nitrile CH_2Cl_2, has been used (In the case of studying electrochemical spectra).

2.4. Fluorescence Device

The fluorescence spectra have been imaged and taken using the fluroscence device "RF-5301 PC" of the Japanese company «Simadzu». The solution used for taking the spectra was CH_2Cl_2.

2.5. Four-Probe Conductivity Meter:

To determine the electrical conductivity value, the four-probe conductivity meter made by SIGNATONE have been used along with the KEITHLEY220 electrical supply device and the KEITHLEY617 voltmeter.

2.6. Examining the samples using a scanning electron microscope SEM

The samples have been examined using a scanning electron microscope that captures enlarged images of the samples. The resulting images will be analyzed using the Image j software.

The electron microscope, figure (2), is one of the most significant microscopic imaging devices, which has many uses in modern engineering and medical sciences. It is characterized by its high magnification ability due to the use of an electronic radiation consisting of a bundle of high-energy electrons colliding vertically with the surface of the studied sample. The signals reflected and emitted by the sample are collected using different reagents.

Figure 2 shows the VEGA II XMU scanning electron microscope at the Atomic Energy Commission in Damascus

2.7. Polymers Used in Electrospinning

The polymer (shown in Fig. 3), prepared from carbazole and phenothiazine according to the following intermediate reactions [8,9,10], has been used:

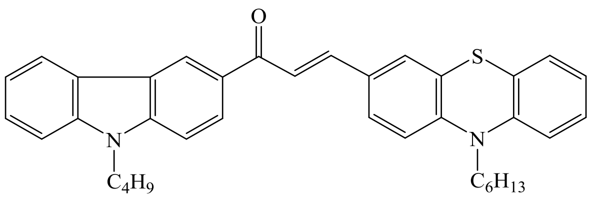
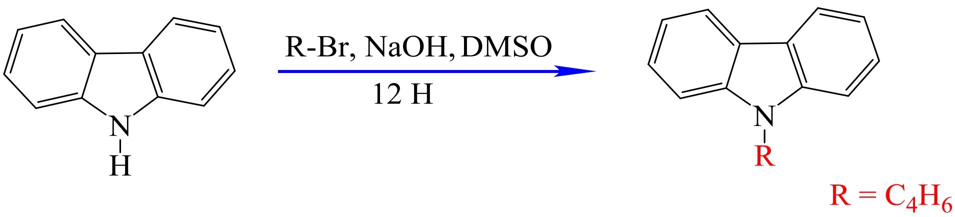
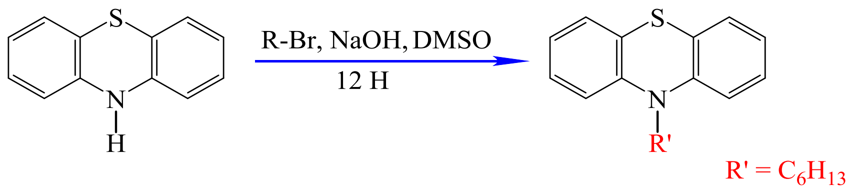


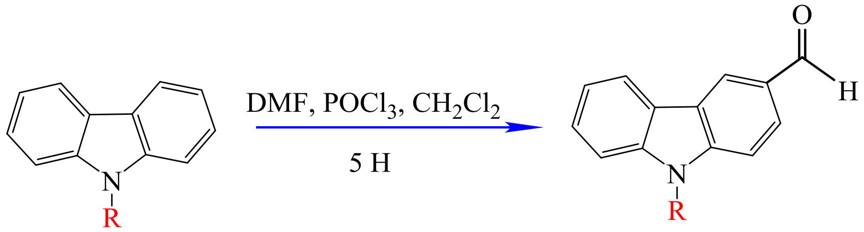
Figure 3: The polymer formula used in electrospinning



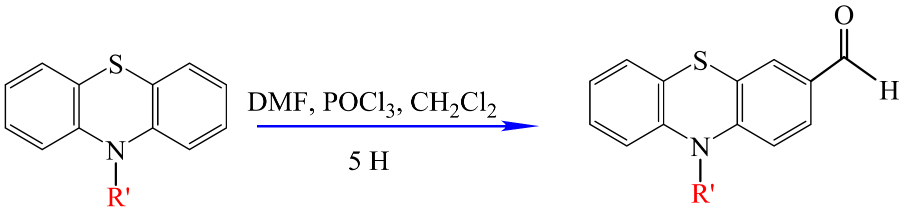
Carbazols alkylation reaction



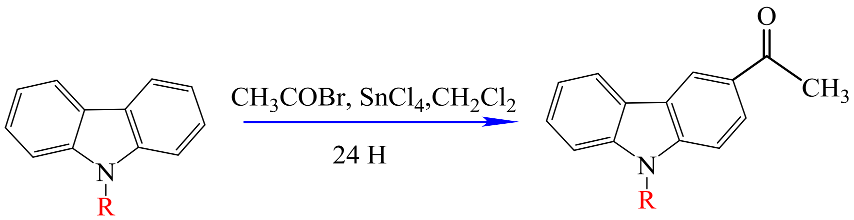
Phenothiazines alkylation reaction



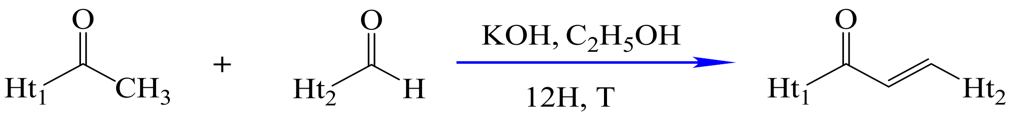
Carbazols formation reaction



Phenothiazines formation reaction



Carbazols acylation reaction



Chalcones formation reaction

3. Results & Discussion

The heterocyclic donor bond (π) has a high positioning of the random (amorphous) phase -HOMO- in the orbit, and thus is susceptible to oxidation, making it suitable for using the polarization method to assess its electronic properties.

The polar oxidation potential of $E^{ox}_{1/2}$ in contrary conditions to the electrical polarization process is associated with ionization potentials, and thus with the HOMO energy levels.

The ease of determining the semi-wave and reconfigured potential differences $E_{1/2}^{red}$ also makes the polar method convenient to quantitatively evaluate the properties of receptor and periodically heterogeneous clouds of electrons, because during the reconfiguration, the electron occupies the LUMO orbit.

The potential values of the oxidizing semi-waves $E_{1/2}^{ox}$ $E_{1/2}^{red}$ of carbazoles and phenothiazines are shown in the table(1) $[11, c. 573]$.

Table (1) - Redox polarization potentials of $E_{1/2}^{ox}$ of the reconfigured carbazoles and phenothiazines $E_{1/2}^{red}$.

Structure	$E_{1/2}^{ox}$ $\left(E_{1/2}^{red}\right)$, v^*
Carbazole	*1,20*
Phenothiazine	*0,63*

$*$ *For the* $AgCl$ *electrode solution:* CH_3CN.

From the data presented in the table(1), it has been shown that the introduction of donor electron substitutions reduces the oxidation potential of the carbazole compounds (and increases the HOMO level). The introduction of receptor electron substitutions increases the oxidation potential (reduces the HOMO level).

In the case of phenothiazines and the already non-substituted molecule, the oxidization potential is smaller. This is explained by the more sophisticated coupling system and the donor characteristics of the sulfur atom. However, the appearance of substituted methyl increases this potential due to the complex difficulties arising when absorbing a molecule on the surface of the electrode $[12]$. The potential values of the semi-waves obtained using the periodic volt ampere meter are 0.67 and 1.23 volts for phenothiazine and carbazole respectively.

The slight difference in the values obtained compared to the theoretical data is due to the use of different conditions for the experiments.

In order to study the behavior of the prepared chalcone and evaluate its electrochemical properties, electron donation potential, and electrochemical polymerization efficiency , this material has been examined using the periodic volt ampere meter as shown in Figure 4.

The measurements were performed in dry acetone nitrile. The voltage change speed (V_{scan})was constant and equalled 50mV / s. A working ITO pole, a controller AgCl pole, and a Et_4NClO_4 background solution (0.1 parts/liter) were used, whereas the monomer concentration was 1×10^{-3} molecules/liter.The results obtained using the periodic volt-ampere meter method are shown in Table (2).

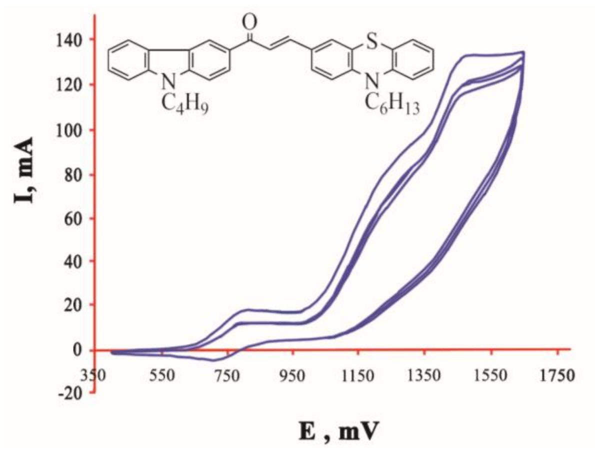
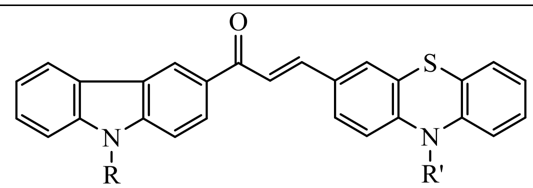


Figure 0 the periodic volt-ampere diagrams of the prepared chalcone (H_3CN solution ,ITO working pole, Et_4NClO_4 background electrical solution, volt scanning speed 50 millivolts / s)

Analyzing the results of periodic volt-ampere measurements shows that the values of reverse oxidation and reduction at the potentials are $(0.7 - 0.9)$V.

In Table (2), the values of the oxidation and reduction potentials of the half-waves $\left(E_{1/2}\right)$ of the prepared chalcone are given.

Table 2 $E^{ox}_{1/2}$ - Oxidation potentials of semiwaves $E^{red}_{1/2}$ and reduction potentials of the prepared chalcone (CH_3CN solution, ITO working potential, Et_4NClO_4 *background solution, voltage scanning speed 50 millivolts/s*)

$E^{red2}_{1/2}$,B	$E^{red1}_{1/2}$,B	$E^{ox1}_{1/2}$,B	$E^{ox1}_{1/2}$,B	structure
1.44	0.77	1.37	0.74	

∗ In order to easily relate the oxidization and reduction potentials of the semiwaves of specific parts of the molecules, the potential values corresponding to the respective colors are highlighted:

The potential of the separated portion of the first electron of the molecule in the phenothiazine element *green* and the second electron in the carbazole element brown.

The potential resonance states of the structures of extreme cations formed upon the oxidation of chalcones are shown in Diagram 5.

The electrochemical reactions of the prepared chalcone are described and are compatible with examples in scientific references $[11, c. 578 - 12, c. 309]$.

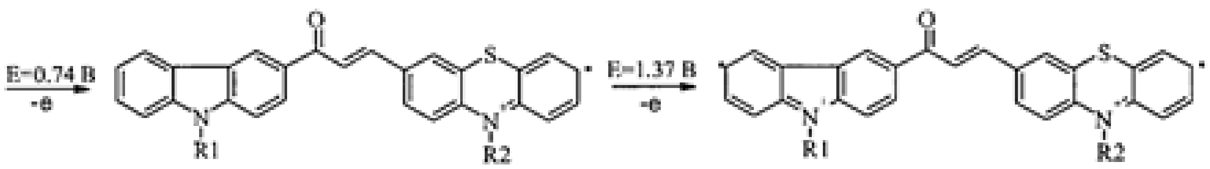


Diagram 5

<u>Optical properties of chalcones.</u>

The resulting chalcone appeared in the form of a brightly colored substance with fluorescent properties. Therefore, it was better to study their absorption and fluorescence spectra (the resulting radiations (Figure 6). The absorption and fluorescent spectra are taken in CH_2Cl_2.

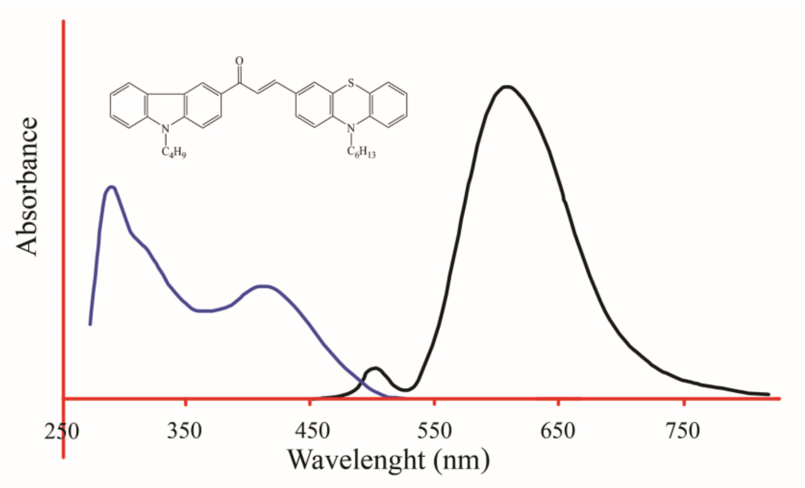
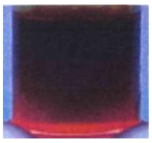
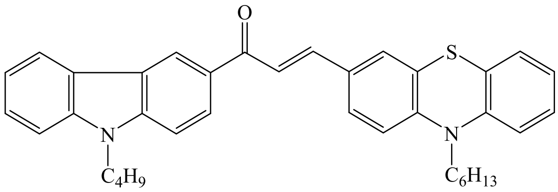


Figure 6 - Absorption (blue line) and fluorescence (black line) spectra of the prepared chalcone.

Data in maximum values of absorption and fluorescence of the difference HOMO- LUMO, energy levels, and the form of the solutions of the chalcones CH_2Cl_2 in daylight and in ultraviolet radiation UV are shown in Table 3. The difference between energy levels HOMO- LUMO for the monomers were calculated from the wavelengths of the red absorption region bounds are calculated by [12, c. 309]:

$$E_g = 1240/\lambda_{onset}$$

Table 3 The appearance of the solution of the chalcone prepared in daylight and in UV, the maximum values of of the fluorescence λ_{fI} of the absorption, and λ_{abc} the difference HOMO-LUMO of the energy levels E_g.

E.g , e.V	***λ_{abs} , Nm***	***λ_{fI} , Nm***	***The appearance in the UV*** light	***The apperance in daylight***	***Chalcones Formulae***
2.44	***290 414***	***505 610***			

- Preparation of the Polymeric Solution

After installing the manufactured device, the polymeric solution was prepared in preparation for the electrical spinning process to produce networks of nanofibers, and a mixture of the prepared chalcone and polylactic acid was used.(PLA) at different concentrations using a mixture of solvents.

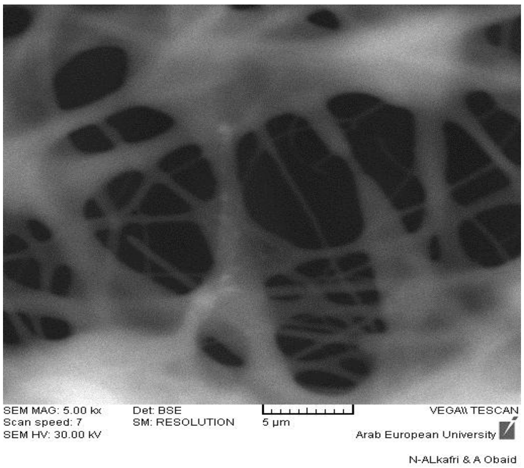
Preparation Method To prepare a 7% solution, 7 gr)) ofPLA, and (3.5 gr) of the prepared chalcone, and add (10 ml) of MDF, (30 ml) of acetone, and (60ml) of distilled water to them. The mixture is placed in a beaker, stirred with a magnetic stirrer, and heated to 80□ 30̊ for 30 minutes.

Setting the Parameters of the Electrical Spinning Process

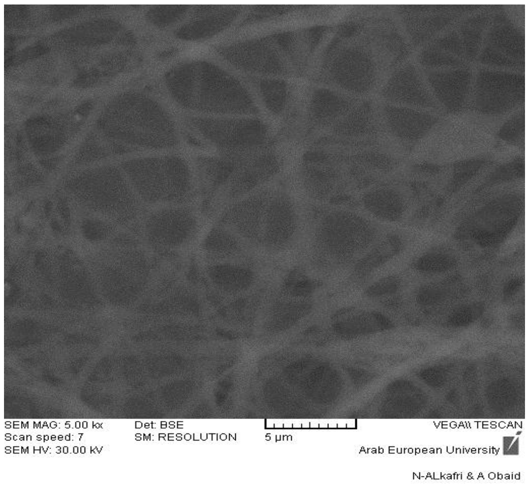
Table 4 : Shows the operating parameters of the five samples

The aggregator used	A point aggregator positioned on the bottom surface of the polyester plain fabric
PLA concentration	7%
Chalcone concentration /23/	3.5%
Electrical voltage	10-20 kv
The distance between the needle and the aggregator axis	3-7 cm
Solution flow rate	0.4 ml/h
Needle movement speed	30%
Operating time	15Sec
Humidity	40 %
Temperature	℃ 25

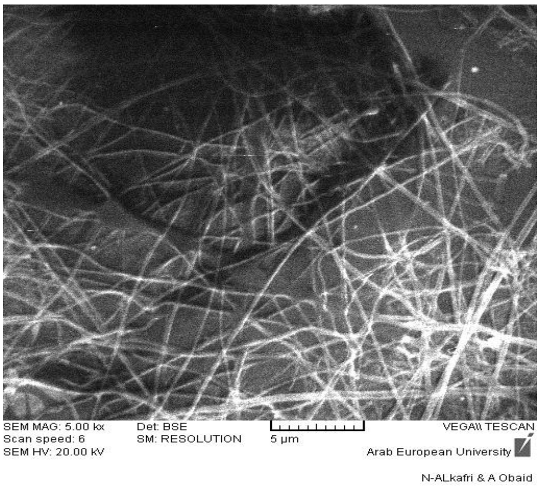
Examining the samples using a scanning electron microscope SEM:



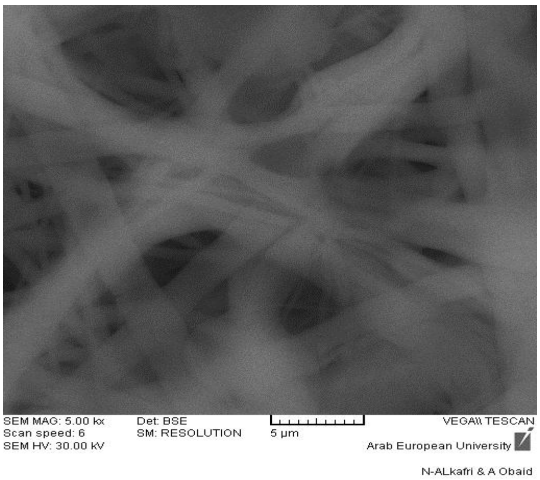
Sample 1



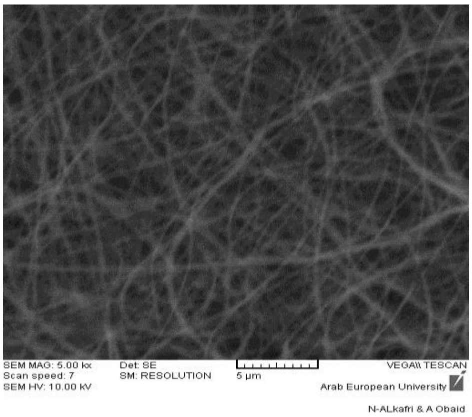
Sample 2

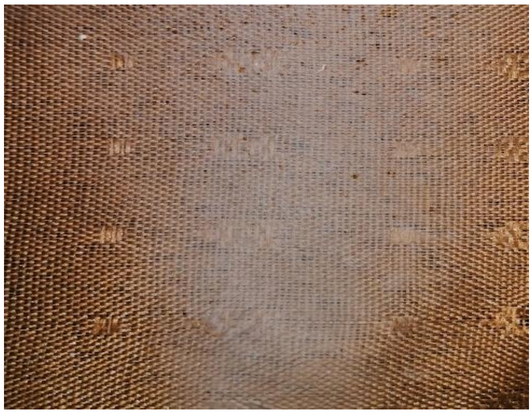


Sample 3



Sample 4





Sample 5

Figure 7 Electron microscope images of the tested samples

Table 5 shows the values of the resulting diameters

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Average	378.35	429.55	284.95	311.3	430.85
Deviation	134.2889	104.5157	36.50591	87.53231	90.77866

The electrical conductivity of the polymer was measured after being extruded onto the fabric (PLA/HA 2:1) using the the four-probe technology and was found to equal 0.0022 S/cm

Conclusions

1- Entrances and methodology have been designed for the synthesis of heterogeneous conjugate groups that are both electron donor and receptor, which has the potential of being used as materials for fabricating molecular electronics equipment: Organic photodiodes $(OLED_S)$, solar batteries, organic field transistors, $(OFET_S)$and others.

2- The condensation of carbonyl derivatives of carbazole, thiophene and phenothiazine and the synthesis of new groups of halcones with the electronic structure D-A-π – D (D-donor, A- receptor, π-conjugation group)

3- Electrochemical polymerization was performed of cyclic heterocyclic complex groups containing in their composition the elements carbazole, phenothiazine, and thiophene. New polymer films have also been obtained on the surface of working electrodes made from ITO and platinum.

4- On the basis (rules) of the given electrochemical and optical studies, the ionization potentials (HOMO energy energy levels), electron affinities (LUMO energy levels), and the width of the forbidden (no-go) regions of the cyclic heterocyclic conjugate polymers have been calculated. A relationship has also been established between the structure of the studied compounds and their indicated characteristics.

5- These polymers can be used due to their variable potential properties $(HOMO\ ,LUMO\ \ ,E_g)$ to prepare electronic and electro-optical equipment.

6- Due to their variable potential energy properties, these polymers can be used to prepare electronic and electro-optical equipment.

7- It is very cheap and environmentally friendly to find a relatively stable suspension of these polymers compared to other solvents.

8- A device has been manufactured with the following specifications:

- The movement of the extruder and collector is automated
- An aggregator has been designed, which works well with cloth or aluminum sheets, ensuring the direct extrusion on any type of fabric, and providing the fabric with electrical conductivity.

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