Preparation of Polyacetylene Composite with some Plastic and Semiconductor for Electrical Uses.

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A B S T R A C T
Three novel polyacetylenes:
Polyacetylene PAs, 1-ether- benzoic acid-2- ene - propylene (A).
Polydiacetylene (PDAs), hexa -1,6 diphthalmide - 2- ene – 4 –yne (B), and
Polyacetylene PAs , 1- phenyl - 3- butyne -1 -ol (C).

were prepared through polymerization of three Acetylinic monomers. They were prepared by by reaction of propargyl bromide, unsaturated alkyl halide RX and With, other various reagents). Polymerization was carried out by using selective catalyst such as CuCl, PdCl2 complexed of transition metals with dry and pure oxygen, polymers were extracted, purified and identified by FT-IR, HNMR Spectroscopy and melting points. Electrical conductivity of polymers was studied after doping with iodine (I2) to increase their conductivities. Composite plastic was prepared from polymethyl methacrylate PMMA as the matrix with Polyacetylene as the filler by cast molding the solution of plastic and polyacetylene was prepared by mixing with THF as solvent. The conductivities of the composite seem to be close to semiconductors and the results are in agreement with the literature and theoretical proposals.

Introduction
The conductive Polyacetylene occupied and demonstrated industrial importance and its efficiently was proved in the industry of Solar cells, Polymers batteries and devices as parts in electronics. These polymers were prepared in different methods, including thermal polymerization, photo polymerization and radiation, (1, 2) Using catalysis of polymerization (Initiation) is similar to Zekler-Natta catalyst such as copper salts, palladium, Molybdenum, and used the Propargyl halides and their derivatives in the preparation of the types of conductive Polyacetylene as well as the preparation of Homo diacetylene & Hetro diacetylene. In order to enter the terminal acetylene group easily during the reaction acetylinic monomers (3), also acetylene Polymers are used successive with manufacture of conductivity of polymers because of the Conjugation Bond type (π) which affected dominant factor on electrical conductivity. Acetylinic Polymers are also used as part of the conductive such as diodes at the electric circuit, and chemical composition occupies of the polymers Conjugation critical uses in Applied and to its impact on Stability, and increase the thermal stability and resistance to operating conditions in electronic devices, (4, 5, 6, 7) At the present time acetylene Polymers for medical uses, such as drugs for diseases treatment that affect cancer cells is developed and used as anti-cancer besides working for the inhibition of alsaitocrom( 8, 9,10) The common way to produce this type of polymers is the Hay method which uses transitional catalysis such as copperus chloride, Glaser Coupling method and Egliton method (11) use palladium, Molybdenum, and copper as complexes catalysts, of initiations polymerization, they are also used for the preparation of acetylene Copolymers, and the development of conductivity polymers with good electrical properties, though polymers have insulater characters of materials, the
recent research was able to produce polycetylene which is similar to the semiconductor or the connected metal, where conjugated polycetylene has relatively small Energy gap (1 - 4eV) . The electrons facilitates transfer to the conductivity band and gives the semiconductor its characteristics. Also they can increase conductivity of these polymers through Doping process in order to increase the oxidation state .where the particles of doping are made by of increasing the movement of charge carriers which give ability of the high conductive of electricis in the Doping case (12) The common materials, used with Doping are iodine , bromine, and arsenic . are made in several methods, including electrical , chemical , complexes and the charge transfer. The double method has been used in this study , chemical doping method and of the compsite to increase the electrical conductivity properties. The advantage of conductive polycetylene materials with high stability towards the operating conditions such temperature , humidity and environmental factors .is that it is used successfully in medicine and industry (13, 14) The present study aims to preparing the conjugated polycetylene and composito on the poly methyl metha acrylate PMMA (Plastic) for the development of the electrical conductivity properties of the insulating materials to semiconductor in order to be used in the Electrical circuits.

**Experimental**

**Materials and Methodology**

In this research the materials were used with of high purity, Propargyl bromide was distilled under vacuum pressure, and Cuprous chloride CuCl ,Palladium dichloride PdCl₂, were used as catalysts in the polymerization processes which they were bought (Fluka) and methyl metha Acrylate monomer (MMA) , Iodine I₂ (Fluka), methanol , pyridine, acetone, ether bought from (BDH) Recorded of spectra HNMR, using a BRUKER - 400.13MHZ Spectrophotometer. in CDCl₃ solvent, FTIR spectra mode 18300 shimadzu spectrophotometer Japan. With (400 - 4000) cm⁻¹ and use a disc models for Potassium bromide to preparation Specimens of FTIR, these measurements were conducted in the Al-Baath University in Homs – Syria.

**Synthesis of Monomers**

**Preparation 4 – benzoic acid propargyl ether. (a)**

The reaction comprised of, **two steps first** preparation of the compound 4 - hydroxyl benzoate. of reaction 4 g of p - hydroxyl benzoic acid, 10ml of methanol was added to in flask 250 ml a circular flat bottom equipped with a condensation and separating funnel, was prepared . The mixture refluxed and stirred by a magnetic stirrer for five minutes then we add 5 ml of acetyl chloride and slowly drop wise. By continued stirring for one hour at room temperature and then stopping the reaction product was nominated and dried under vacuum pressure in the desiccator for 24 hours .

**second step**, dissolving 4 g of p - hydroxyl benzoat (prepared in the previous step) in 10 ml of the dimethyl sulfoxide ( DMSO) with 6 g of potassium hydroxide KOH in a round flat bottom flask 250 ml, equipped with a condensation and separating funnel, for the addition. The mixture stirred by magnetic stirrer. Then was added and slowly continued was for reaction for an 1.5 hour, at room temperature then 30 ml of methanol was poured in to the reaction solution with the addition of the 4 g of sodium hydroxide (NaOH) and the product was extracted with methyl dichloride CHCl₂, the product was yellowish crystals form in yield 72%, and then dried in desiccator for 20 hours, melting point was 163 °C. Monomer was characterized with spectral FT-IR.
Preparation N – propargyl phthalimide (b).

The monomer b was prepared from reaction of Propargyl bromide with potassium phthalimide ((it was prepared by dissolving 9 g of phthalimide in 150 ml of absolute ethanol to circular flask 500 ml with flat bottom equipped with a condensation, the mixture heated in a water bath for 1 hr and then poured in to a hot solution of potassium hydroxide containing 3g* 3ml Dist. Water, cold solution and was precipitate potassium phthalimide for treatment with acetone to removal non-reaction material, then filtrated, Colorless precipitate of potassium phthalimid)) to 5 g of potassium phthalimide dissolved in 15 ml of dimethyl formamide (DMF) and heat the mixture to a 70 °C with stirring, then add 4 ml of Propargyl bromide drop wise then continue heating for 10 hours after it stopped the reaction and added 50 ml of distilled water after that mixture was cold recrystallize resulting in a mixture of methanol acetone and precipitate white crystals of the monomer N– propargyl phthalimide, M.p = 151 °C, yield 69%. monomer characterized with spectral FT-IR.

Preparation 4 – phenyl – 1 – butyne- 4 – ol. (c)

2.8 ml of Propargyl bromide was dissolved in 25 ml of tetrahydrofuran (THF) and 2 gs of zinc powder was added which was also dissolved in was THF in a round bottom flask of 100 ml equipped with a condensation and separating funnel for the addition, the mixture of Continuation with stirrers For 1.5 hr and then added 2 ml of benzaldehyde was dissolved in 10 ml of THF drop wise to reaction, and after that the reaction continued for 4 hrs at temperature 30 °C. Stopped stirring and add 100 ml of a saturated solution of ammonium chloride, then we left the mixture with stirring for 0.5 hr. Filtrate the mixture to remove zinc. And then 10% of hydrochloric acid was added then then extracted product by ether, then separated and dried organic layer with magnesium sulfate, and evaporated the solvent. The product was of yellow liquid which was characterized by FT-IR. Spectroscopy.

Preparation of Polymers
Preparation of Polyacetylene(PAs),1-ether-benzoic acid-2-ene - propylene (A).

2.5 gs of monomer a, added to 5 ml DMF in Erlenmeyer flask, 50 ml and 0.2 g of palladium chloride PdCl₂ was dissolved in 0.5 ml of pyridine (distilled and dried over sodium metal). The polymerization reaction was under atmosphere of nitrogen on magnetic stirrers at room temperature for 2.5 hrs. termination of the reaction by adding a few drops of methanol to precipitate the polymer we filtrated the solution under vacuum pressure to produce white crystalline, yield 65% which is characterized with FT-IR and HNMR spectrum.

Preparation of Polydiacetylene (PDAs), hexa -1,6 diphthalmide- 2-ene – 4- yne. (B) 0.8 g of monomer b, 0.4 mg of palladium dichloride PdCl₂ in 7 ml of pure pyridine, and 0.1 mg of Cuprous chloride CuCl in 3 ml were prepared in erlenmeyer flask of 100 ml. The flask was provided with a small side tube connecting to the balloon of oxygen store. The polymerization reaction was under atmospheric of oxygen, it was then Vigorously stirred with high speed to ensure complete reaction. Oxygen gas had been pumped (method of Glaser) twice in a flask reaction. The polymerization Continued for 5 hours. Few drops of methanol were added until termination of the reaction, The mixture to produce PDAs, then recrystallization with chloroform, white crystals of
polymer at yield 76%, which are characterized with FT-IR, HNMR.

Preparation of Polyacetylene (PAs)- 1- phenyl - 3-butyne -1 -ol(C)

prepared Polymer C as in the same method of preparation polymer A, the yield of product 70%, and characterized by FT-IR, HNMR.

Preparation of poly methyl metha acrylate (PMMA)

Monomer MMA was polymerized after washing twice with a solution of 10% sodium hydroxide and then it was distilled under vacuum pressure, dried over molecular sieves, to 8g from MMA in a volumetric flask 50 mL and initiator benzoyl peroxide.0.1% The Polymerization was under atmosphere of nitrogen, in temperature of 70°C for 30 minutes after that deposition of the polymer in ethanol and then dried, average molecular weight calculated (42146) unit by using the equation of Mark-Hovwink after measuring the intrinsic viscosity. \( [\eta] = K M^a \).

Doping of Acetylene Polymers

Three polacetylenes were prepared, A, B, C was doping using the pure iodine within the system designed for this Purpose, which consists of two flasks connected through pipe provided for closure and opening which is linked to a pipe connected to a vacuum pump. The researched heated the iodine and allowed vapor to pass through a link of connect to a second flask containing specimens of polymer

Preparation of composite polyacetylene (A, B, C) with poly methyl metha acrylate.

Three composites of Doping poly acetylene were prepared with poly methyl metha acrylate those; (PMMA + A ), (P MMA + B ), (P MMA + C )

To round flask 100 ml equipped with a condensation, to 5g of PMMA was dissolved in 10 ml benzene and then added to a solution 0.2g of polyacetylene A dissolve in 10 ml benzene else, after that heat to warm and stirring for 0.5 hr and then poured the mixture into a mold template is made of glass capacity 1 Cm x 10 cm for the preparation of overlay film, and left to dry at room temperature in summer 32 C° for three hours and then cut and compression the film in a IR device specimens compressor at a pressure of 1 ton to manufacture discs 1.5 cm in diameter and thickness ranges (0.09 - 0.11) mm for the purpose of measuring Electrical conductivity. that the composites prepared in the percentages by weight 4 -100 wt% of doping polyacetylene and in the same method was Prepared of the other composite (B,C).

Electrical measurements

Were measured electrical conductivity of the studied composite specimens of (PAs + PMMA) using of the electrical Laboratory cell designed for this purpose scheme (8) . Was measured of volumetric connectivity to shed suitable voltage between the electrodes and then measure the current output and using the following equation: \( \sigma = \frac{IL}{AV} \), where ... \( A = \) cross-sectional area cm², \( V = \) voltage, \( L = \) length specimens in cm, \( I = \) current amps unit and electrical conductivity.

Results and discussion:

The monomer a prepared by the reacting of 4 - hydroxy - benzoic acid, with presence of acetic chloride and methanol, the ester product in the first step of the reaction, This process included withdrawing of water molecule, then the Propargyl bromide was enters in SN2 reaction after withdrawal
of hydrogen atom in presence of strong base and DMSO as solvent, the ether product when the substitution reaction occurs on the oxygen atom, the ester precipitated in presence of alkaline methanol, therefore lose the acetyl group and turns back into a carboxylic again as shown in the scheme (1).

Scheme (1): the preparation of monomer (a).

Fig. (1) FT-IR spectrum of monomer show the stretching vibrations of terminal acetylene ≡ CH at 3415 cm$^{-1}$, and stretching vibrations C = O at 1620 cm$^{-1}$ and the Bending ≡ C-H in 750 cm$^{-1}$ and the band is weak to C ≡ C at 2375 cm$^{-1}$ and bending vibrations of aromatics C = C at cm$^{-1}$ 1570. cm$^{-1}$ fig (1).

The monomer b prepared from the reacting of potassium phthalamide and Propargyl bromide with alcoholic potassium hydroxide there where it works to show negative charge on the phthalamide nitrogen, the nitrogen atom becomes is a strong nucleophile reagent, that can attack the carbon atom was Contains the halogen Bromide in Propargyl bromide and displacement the halogen atom to give the resulting N-Propargyl phthalamide b. as well as the reaction in SN2 mechanism$^{16}$ scheme (2) Spectra of FT-IR show stretching vibrations to ≡ CH at 3295 cm$^{-1}$, stretching vibrations to C = O, at 1720 cm$^{-1}$, 1766 cm$^{-1}$, And the bending ≡ C-H in 736 cm$^{-1}$ and bending vibrations to Ar -C-H at 1326 cm$^{-1}$ and bending vibrations of

![Scheme (2): the preparation of monomer (b).](image)

C = C aromatics in cm$^{-1}$ 1530 cm$^{-1}$ fig (2). prepared the monomer c, scheme (3) from reaction of benzaldehyde with the Propargyl bromide in existence of zinc powder as a catalyst and solvent THF and an aqueous solution of saturated ammonium chloride, obtained the reaction with Barber mechanism to Produces a complex with zinc Propargyl to gives him the ability to push the electrons pair to attack on the electrophyl carbonyl group in the benzaldehyd, so made a new link on the carbon atom of the aldehyd group ,Then Withdraw of the aromatic hydrogen from the reaction medium to and formation OH group associated with the monomer product c fig. (3) spectrum of FT – IR show peak stretch to group ≡ CH at 3295 cm$^{-1}$, and the peak stretch to the group C ≡ C at 2252 cm$^{-1}$, peak stretch to the group OH in 3471 cm$^{-1}$ and stretch C = C in 1620 cm$^{-1}$.
Scheme (3): the preparation of monomer c
prepared two types of polymers the first is polyacetylene PAs of the polymer (C, A) under atmosphere of pure nitrogen and palladium dichloride salts PdCl$_2$ as catalysis has dissolved in DMF with presence of dry pyridine as a base. the polymerization were carried out at a temperature of 30 $^\circ$C and a time did not exceed 4hrs with strong stirring that the termination of polymerization determined by adding few drops from methanol as precipitator. and includes of the Polymerization reaction to removal terminal hydrogen atoms from monomer by help dichlor palladium catalyst and breaking of one bonds from $\pi$ triple bond to become hybridization than SP$^3$ to SP$^2$. Schemes (6, 8). (17)

The second type of polymer is poly diacetylene PDAs of the polymer B was prepared by oxidative coupling method in presence of an atmosphere of dry oxygen and the reaction by transition element technolgy like the method of Zeklar - Natta but differ in composition and mechanism .

And used of palladium dichloride PdCl$_2$ , Cuprous chloride CuCl ,where hydrogen atoms are removed from the terminal acetylene by the presence of cuprous chloride as a catalyst and THF solvent with Glaesr Coupling method ,the second step, the palladium dichloride support the formation of polydiacetylen and the removal of the hydrogen atom from acetylene , where reduced the two triple bond to one of acetylene group to double bond as a free ion, so the role of palladium as an striped of the hydrogen atom, and gets the anti in the double bond to substitutes R group.

Scheme (4) Mechanism preparation of poly diacetylene

Preparation of Polyacetylene (PAs), 1-ether benzoic acid- 2-ene- propylene (A)
The polymer was prepared with the same method above and the polymerization time was 2.5hr in 30$^\circ$C. after the reaction termination, the polymer was extraction from the solvent and dry under vacuum pressure for 12hrs in the room temperature scheme (5). FT-IR spectra, fig. (4) show a stretch vibrations C = C in 1870 cm$^{-1}$ of the conjugated double bonds, stretch to O- H at 3110 cm$^{-1}$ the carbonyl stretch C = O at the 1720 cm$^{-1}$, bendenig to C = C at 1550 cm$^{-1}$ and the bending of Ar - H aromatic in 740 cm$^{-1}$ and stretch bendenig to C-H aliphatic at 16101 cm$^{-1}$. 

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The HNMR spectra fig (5) show that the displacement of the Ar- -CH ring in, 7.25 δ , signal – COOH at 8.26 δ signal of a group - CH2 - in 1.38 δ , signal of the two double bond to the group C = C - C = C- in 5.35 δ. and strong signal in 5.42 δ belonging to the group R - O - C-H.

**Preparation Poly-diacetylene 1,6 di phthalmide - 2 - 3- dieen- 4yne. PDAs. (B)**

The Polymer B was Prepared by Oxidative coupling polymerization as was Previous, scheme (6) that the reaction time was 5 hrs. and the polymer was characterized by spectrum of Infrared FT-IR. that show disappearance a peak to ≡ CH at 3295 cm⁻¹, which represents the terminal acetylene frequencies and the appearance of successive stretch to the ethylene group (C = C) exist a weak peak at 2167 cm⁻¹. The vibrations of C = O at 1750 cm⁻¹ , and stretch to amid in 1720 cm⁻¹ , and the C ≡ C stretch with a weak peak at 2240 cm⁻¹ . Fig.(6).

And the HNMR spectrum fig. (7) show the following signals: the multi signals to the protons armatic ring (7.98) , (7.28) δ , signal to group C = C-CH₂ in (4.48) δ and a signal to the conjugation of C = C - C = C- at (5.81) δ.

**Preparation of Polyacetylene- 1- phenyl - 3- butyne -1 -ol, ( C)**

Prepared polymer C in the same way as the preparation of polymer A in scheme (7) . Time of the reaction was 2hrs. Polymer extracted and dried as in the Previous routes of polymerization. and Characterized by FT-IR spectroscopy the fig.(8) show the following peak, disappearance of peak ≡ C-H at frequency in 3210 cm⁻¹, stretch to a C- C = C- C = C in 1900 cm⁻¹, peak in the 3180 cm⁻¹ to OH and peak to group C - H in 3020 cm⁻¹,stretch of bending for a C-C in 1250 cm⁻¹ , the HNMR spectrum fig. (9) show signal to ethylene C = C - C = C-H at 5.2 δ , signal at 4.3 δ belonging to the OH, multiple signal to aromatic hydrogen atoms of Ar – H ring in 7.43 δ and the signal at 2.51 δ to methyl group - CH₃ - .
Electrical Conductivity Measurement of Polymers

Electrical conductivity of composite polymers (MC, MB, MA) was calculated. It was prepared from conjugated PAs with PMMA in the percentage weight (4 - 100) Wt%, see table (1). The calculated values of electrical conductivity of PMMA $1.2 \times 10^{-17}$ scm$^{-1}$ in the lowest values were given in the laboratory circuit (8). This means the activation energy is high to allow electron transference between parity band and conductivity band due to the large value to energy gap. The energy required for electronic transition in plastic (insulators) is much high, and the high values in the electrical conductivity of the composites are MB compared with the composite MA and MC because the conjugation between the triple bond and the double bond in polydiacetylene (MB) increases in connectivity and it is affected on accelerating the movement of electrons through $\pi$ bonds. The electrical conductivity increases when the percentage values increase in the polyacetylene as in a valuable 80% in composite MB.

Conclusions:

1 - Three terminal acetylene monomers were prepared by organic reactions from kind SN2.
2 – New polyacetylene PAs and polydiacetylene PDAs were prepared that have possible ability of semiconductor through electronic conjugation to give the highest values of electrical conductivity.
3 – The present study was able to develop the electrical properties from insulators to semiconductors.
4 – The methods of oxidative coupling succeeded in preparing polyacetylene in a short and cheap method.

References

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Fig. (5) HNMR Spectrum of Polymer (A)

Fig. (6) FT–IR Spectrum of Polymer (B)
Polydiacetylene PDAs

Fig. (7) HNMR Spectrum of Polymer (B)
Polydiacetylene PDAs

Fig. (8) FT–IR Spectrum of Polymer (C)

Fig. (9) HNMR Spectrum of Polymer (C)

Table (1) electrical values of conductivity of the composites (MC, MB, MA)

<table>
<thead>
<tr>
<th>% Wt PAs and PDAs in Composite</th>
<th>Conductivity values σ scm⁻¹</th>
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<tbody>
<tr>
<td></td>
<td>MA</td>
</tr>
<tr>
<td>100</td>
<td>1.12×10⁻⁴</td>
</tr>
<tr>
<td>80</td>
<td>2.67×10⁻⁵</td>
</tr>
<tr>
<td>60</td>
<td>1.15×10⁻⁵</td>
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<td>8</td>
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</tr>
<tr>
<td>6</td>
<td>2.51×10⁻¹²</td>
</tr>
<tr>
<td>4</td>
<td>3.54×10⁻¹⁴</td>
</tr>
</tbody>
</table>

A = Acetylene Polymer A, B = Acetylene Polymer B
C = Acetylene Polymer C, MA = PMMA+
Composite polyacetylen
تحضير بوليمرات أستمينية متراكبة مع بعض أنواع البلاستك وشبه موصلة للاستخدامات الكهربائية

طارق عبدالجميل منديل

الخلاصة:

تم في هذا البحث تحضير ثلاث بوليمرات أستمينية جديدة هي:

- Polyacetylene PAs, 1-ether- benzoic acid-2- ene - propylene (A).
- Polydiacetylene (PDAs), hexa-1,6 diphthalamide- 2- ene – 4–yne. ( B).
- Polyacetylene PAs, 1- phenyl - 3- butyne -1 -ol, ( C).

من مركب من ثلاث مونومرات أستمينية تم تحضيرها من تفاعل بروميド البرومبارجيل مع جزيئات مختلفة. أجريت عمليات البمرنة باستخدام عوامل المساعدة انتقائية هي أملاح العناصر الانتقالية مثل PdCl2، CuCl، ودرجة الأنصهار. وأجريت دراسة التوصيل الكهربائي للبوليمرات بعد تشويبها بالبليود (I2) لزيادة قابلية التوصيل الكهربائي. وحضرت متراكبات من البوليمرات الأستمينية المحمية على البولي ميثايل ميثا أكريليت PMMA، وكانت قيم التوصيلية المحسوبة ملائمة لأشباه الموصلات، والنتائج مطابقة مع الأدبيات والأفكار النظرية.