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A Novel Synthesis, Characterization and Studying of Alkynes dimers

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Abstract:
In recent years, it has been increased interest in the synthesis and Characterization of different chemical. This study deals with the synthesis of four novel monomers of terminal acetylene, and their reactivity by the oxidative coupling to synthesize of diacetylene, which are:
P–ethanmide -3-phenoxy—propa-1-yne). (2P), P–(2-amino–propanoicacid)-3-phenoxy –propayne. (2T), Mercapto – (2-amino –propanoic acid) -3-propyne. (2S), m- carbaldehyde-3-phenoxy –propayne. (2M) and Six dimers are Synthesis, four of them are Homo Diacetylene, which are 1,6 –diphenoxy - p – Ethan amide -2,4-hexa-di- yne. (3P), 1,6 -diphenoxy – p - (2-Amino-propanoic acid)- 2,4-hexa- diy-ne(3T), 1,6 - diphenoxy –m - Carbaldehyde-2,4-hexa-di-yne. (3M) and 2,4 –hexadi-yne- di- (propion amino carboxylic acid) – dithiol. (3S), and the other two are Hetero Diacetylene: (1- (2-amino –propanoic acid-3- phenoxy) -6- (m- carbaldehyde-3-phenoxy) -2,4- hexa di-yne). (P-T), (1- (m-Carbaldehyde-3-phenoxy) -6-(Ethanamide -3- phenoxy) - 2,4-hexa di-yne). (P-M).
Polymer composites Has been prepared from diacetylene on the polystyrene (Psty + Dimers) and it is done by carrying the compounds (dimers) that doped with iodine. The study of electrical conductivity (EC) is done to prepared composites and the composites gave the characteristics of the semiconductors, It was also characterized by (HNMR, 13C), FTIR) spectrum and melting point. The results were obtained good agreement with the hypothetical case.

Keywords: Diacetylene, propargyl bromide, oxidative coupling, Alkynes dimmers.

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1. Introduction:

The chemistry of diacetylene has garnered a lot of interest recently. Today, there are numerous studies about the synthesis and characteristics of these dimers [1-3]. Diacetylene is distinguished by its multi-unit type (oligomers). Because they have a conjugation system of type, are densely electronic, and exhibit high-temperaturetemperature stability, such as -C-C-C-, they have good optical properties, particularly if they have aromatic groups and double bonds that allow electrons to be released, resulting in high conductivity. Superconductive is the name of it [4,5].
Alkynes dimers have been utilized to improve the ability to create charge-transfer complexes with Lewis acids (electronic acceptor). These complexes, which have been widely used in a variety of sectors as pathogenic agents, colorimetric biosensors, electrical devices, and to create polydiacetylenes (PDA), which have a wide range of potential applications, if nitrogen N and sulfured S atoms were present in their structure. Because of the delocalized (π) electrons in their conjugated chains, substantial attention has been drawn to the fields of electronics, photonics, and non-linear optics [6, 7].

There are two types of alkynic dimers depending on the replacement groups (R), homo diacetylenes and hetro diacetylenes, that can cross-link when exposed to UV light or heated without emitting volatile byproducts [8,9] The Glaser reaction, which was conducted in the presence of a cuprous salt, CuCl, and air as an oxidant, is typically used to create diacetylenes[10].

Includes the use of terminal alkynes in the presence of transition complex catalysts in reactions that have many characteristics with coordination polymerization reactions but have a different mechanism. Eglington and Galbraith suggested an alternate synthesis in 1956 [11] by reacting the terminal acetylene with cupric acetate in pyridine. Halo acetylene coupling was first described by Cadiot and Chodkiewicz in 1957. This process is often accomplished by reacting the terminal acetylene with sodium hypobromite, while there are other options using terminal acetylene in the presence of cuprous [12]. This process is the most effective way to create asymmetrically disubstituted diacetylene. Diacetyl Grignard acetylide production using other methods However, there are a number of well-known forms of the oxidative coupling reaction, including the Glaser method, the Hay method, the Songashira Hagihara method, the Ulman method, and the Cadiot-Chodikiewicz method [13].

Iodine has been selected in this study as a stimulant that increases the oxidative level and activates the transport of electrons through the bodies of dimers for use as a component of electronic circuits. The process of creating composites by combining them with plastic to create a semiconductor simultaneously is also referred as.2.

2. Experimental work

2.1 Chemicals and reagents:

All the reagents and solvents were purchased, Tyrosine Systeine, m-Hydroxy benzaldehyde, Ethanol (absolute), methanol, DMF, Chloroform, Sulfuric acid, Potassium hydroxide, Pyridine, and Ammonium chloride from BDH Co. (paracetamol powder) from China Co. Tetra hydro furan (THF), Iodine, Diethyl ether, Dichloromethane and Propargyl bromide from Flulka Co. The reaction was monitored by thin-layer chromatography (TLC) carried out on a silica plate. All solvents were purified prior to use according to standard literature methods.

2.2 Instrumentation:

In Al Baath University Syria, the products were identified using HNMR, and C13 spectra were obtained using a Bruker 400 MHZ spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. On the infrared FTIR Nicoletir 100 - spectrophotometer, FT-IR spectra were captured. A Fisher-Johns melting apparatus was used to determine the melting points and the EC was measured using a Digital Pico Ammeter (Rookie) in India.

A- Monomer Synthesis: The four Alkynes monomers were synthesized: (2P), (2T), (2M), and (2S). The thirst monomers were prepared from the phenolic and pharmaceutical compounds and the other sulfur compounds (2S). By reacting them with an unsaturated alkyl halide (RX) by substitution reaction with SN2 mechanism. Shown Table-1.

General Synthetic Procedure: Three-neck round-bottomed flask equipped with a reflux condenser a dropping funnel and thermometer. (2.5g, 0.44 mmol) was dissolved in an organic solvent (25ml alcohol) and made stirring for 15 minutes, (2 - 2.5g, 0.016 mmol) of a substrate such as Tyrosine was added to the mixture. A (2ml, 0.016 mmol) of Propargyl bromide was then added drop-wise to the well-stirred reaction, the reaction mixture was heated to 60-70C0 for 2-3 hour. The Reaction was stopped and the mixture was cooled to room temperature. Ice water was added on reaction mixture and the crude product was extracted twice by in ethylene dichloride as a solvent. The organic layer was evaporated and crystals product was obtained. Crystals were dried by an oven for 2 hours at (50 C0). A small amount was saved for analysis (FT.IR and mp).

B-Synthesis of Alkynes's Dimers: The Six dimers (Diacetylene) are prepared by Oxidative Coupling reaction with Glaser methods which were Homo Diacetylene:

(3P),(3T),(3M) and(3S). Hetero Diacetylene: (P –T) and (P-M). Shown inTable.2.

General Synthetic Procedure : (50 ml) Erlenmeyer flask while stirring, (1.5g) monomer (2P, 2T, 2M, 2S) or hetero monomer (P-T, P-M) dissolved in 6ml methanol each alone, and (0.5ml) pyridine was added with 0.2 cuprous chloride (CuCl) as catalyst to the mixture, small side tube contacted with balloon as the pure oxygen gas provider, Then, the balloon was filled by oxygen twice through of reaction. The resulting solution was stirred vigorously at room temperature for 2 hours approximately.

The reaction finished when the balloon size was stable for 1.5 hours. (6ml) hydrochloric acid was added to the reaction flask and cooled in an ice bath, a saturated solution of ammonium chloride was poured, and the product was extraction recrystallization twice with ether. Table.1.

Table1. synthesis of monomers by using (2ml) Propargyl bromide

M	Substrate	Wt. (gm. mmol)	Solvent (ethanol)	Base	Time (hr.)	Temp. (C^{o})	Yield %	M.P. (C^{o})
2P	P-Hydroxy phenyl ethamide	2.5g- 0.016 mmol	25ml	2.5g KOH	3	65-70	201-202	82
2T	Tyrosine (Amino Acid)	2g- 0.011 mmol	25ml	2.5g KO H	1.5	70	160-162	95
2M	m-Hydroxy benzaldehyde	2.4g- 0.01 mmol	50ml	1.12 NaOH	1.5	60	138-140	50
2S	Cysteine (Amino Acid)	2g -0.016 mmol	25ml	2.5g KOH	1.5	70	122-124	95

Table2. synthesis of Alkynes Dimers via monomer

Dimers Prepared	M	Wt. (gm)	Time of Reaction (hr.)	Yield%	M.P.(C^{0})
(3P)	(2P)	1	2	80	180-182
(3T)	(2T)	1	2	75	240-242
(3S)	(2S)	0.5	2	50	207-208
(3M)	(2M)	0.5	2	81	195-197
(P-T)	2P + 2T	0.3 + 0.3	5	62	190-192
(P-M)	2P + 2M	0.4 + 0.6	5	75	210-212

A- **Doping of Alkynes's Dimers:**

Six acetylene dimers prepared (3P,3T,3S,3M, P-T, P-M) doping by chemical doping method in order to increase the EC, using the pure iodine within the system designed for this purpose, which consists of two flask connected through pipe provider for closing and opening is linked to a pipe connected to a vacuum pump. Heat of iodine and allow vapor to pass through a link or connect to a second flask containing specimens of acetylene dimers.

B-Preparation of Alkynes dimers (3P,3T,3S, 3M, P-T, P-M) with polystyrene (Psty) :

Three composites were prepared at different concentrations for each of Alkynes's dimers in a total of 18 composites specimens.

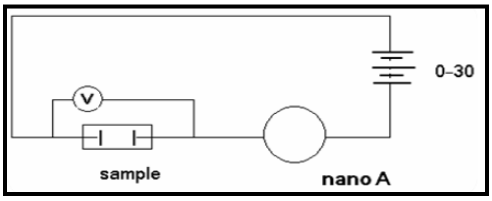
In a 100 ml round flask equipped with a condensation, 1g of pure (Psty) was dissolved in 10 ml chloroform as a solvent and 0.5g of (3P, 3T,3S,3M, P-T, and P-M) Alkynes dimers was dissolved in 10 ml chloroform as a solvent also, The mixture was added to the reaction vessel, They were prepared in the different percentages (0.08,0.011,0.022) wt /v %. lately, the heating of the composite to warm and stir for an hour and then the mixture poured into a glass mold with a dimension of (1 cm * 10cm) (thicken:0.09-0.11) preparation of a thin film for measurements of EC. Shown in Table- 3.

Table 3. Composites of (Psty + Alkynes dimers) in different concentration

Composites	Composites (Psty + 3P)	Composites (Psty + 3S)	Composites (Psty + 3T)	Composites (Psty + 3M)	Composites (Psty + P - M)	Composites (Psty + P - T)
Conc. Wt/V %	0.08	0.02	0.1	0.06	0.4	0.1
	0.011	0.002	0.014	0.0025	0.057	0.085
	0.022	0.005	0.028	0.017	0.11	0.028

A- **The Measurement of EC** :

EC was measured for composites specimens (Psty + 3P,3T,3S,3M, P-T, P-M) via an electrical laboratory cell had been designed for this purpose scheme1. The conductivity was calculated by Ohm's law, where: σ = IL / AV, where ... A = cross-sectional area cm^2, V = voltage, L = length specimens in cm, I = current amperes unit and the resistance is represent the invers of EC, where (σ) = I / V, ($\Omega^{-1}cm^{-1} = S\ cm^{-1}$).

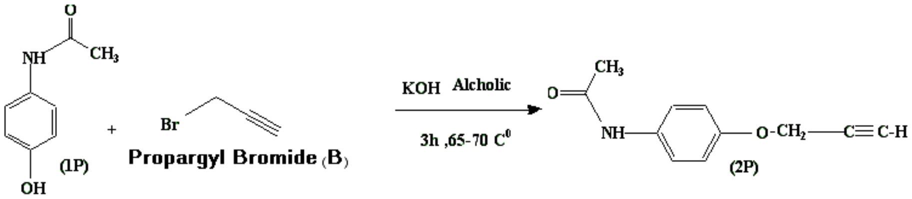


Scheme 1. An electrical circuit for measurement of the conductivity.

3. Results and Discussion

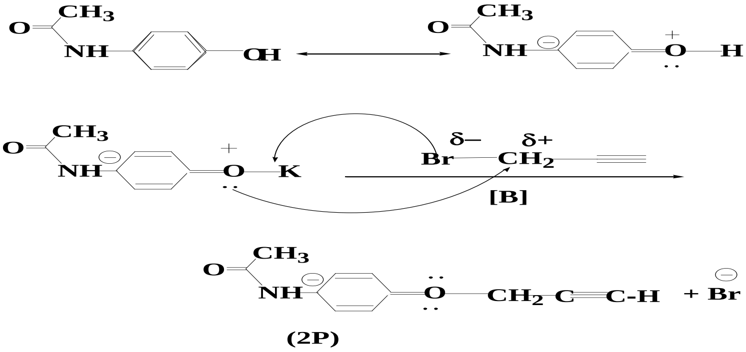
A- Synthesis and Characterization of the Terminated Alkynes monomers:

The monomer (2P) was synthesized in high yield from P - Hydroxy phenyl ethamide (1P) and propargyl bromide (B) in the presence of alcoholic potassium hydroxide. Shown in Scheme. 2.

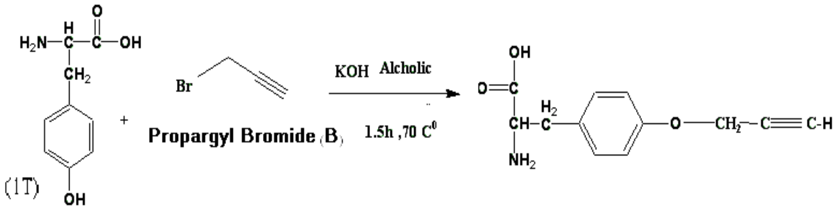


Scheme 2. Synthesis of monomer (2P).

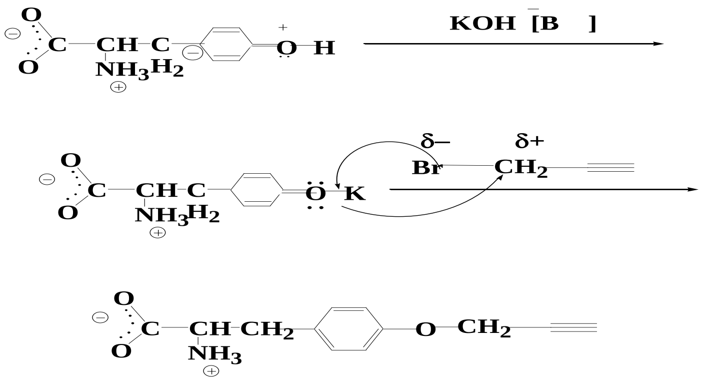
- The reaction was followed S_N2 mechanism. The phenoxide group was the one rich group rich by electrons, bromine was substituted and replaced with the base as following:



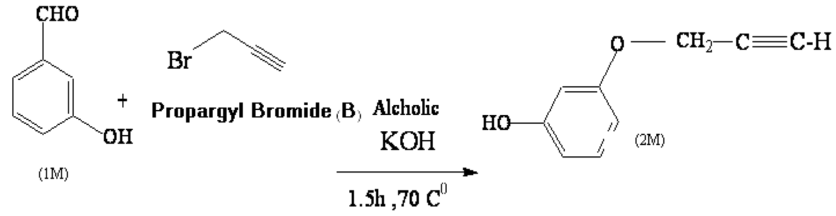
- The monomer (2T) was Synthesized by reaction of hydroxyl group in Tyrosine with Propargyl bromide in alcoholic potassium hydroxide to produce (2T) compound. The reaction also followed S_N2 mechanism. Scheme. 3



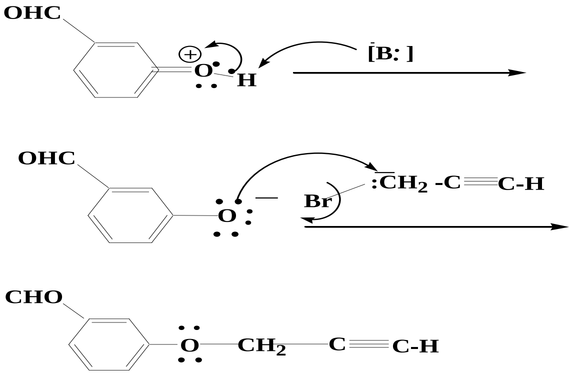
Scheme 3. Synthesis of monomer (2T).



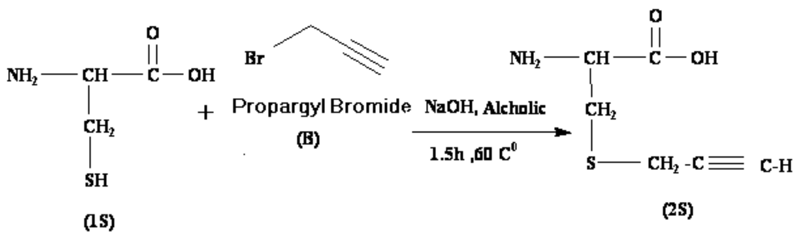
- Monomer (2M) was Synthesized via the same reaction and also followed S_N2 mechanism Scheme. 4.



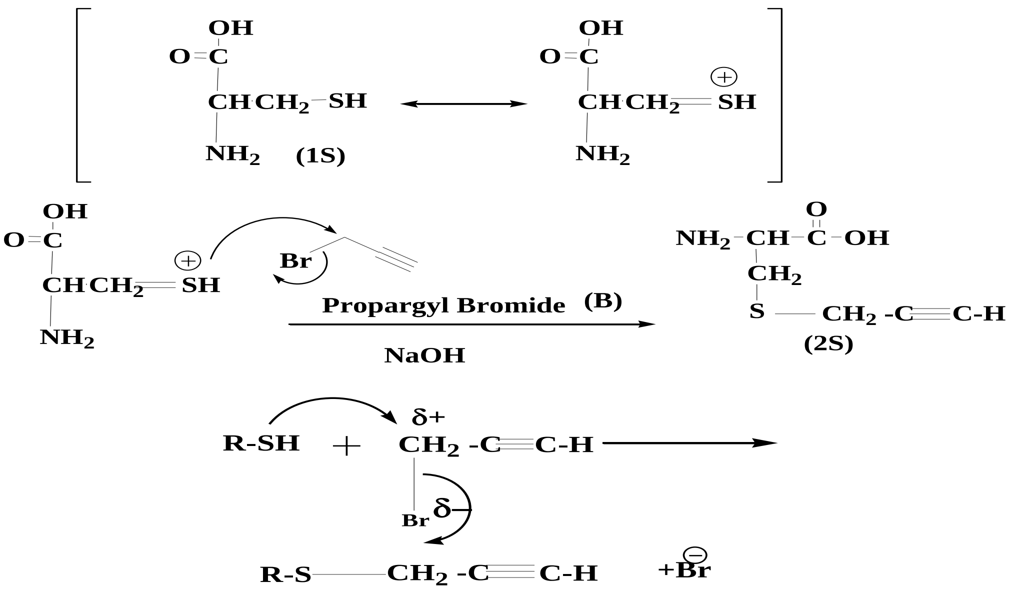
Scheme 4. Synthesis of monomer (2M).



- Monomer (2S) was Synthesized by reaction of SH group in Cysteine (amino acid) with Propargyl bromide in alcoholic sodium hydroxide via S_N2 mechanism: Scheme. 5.

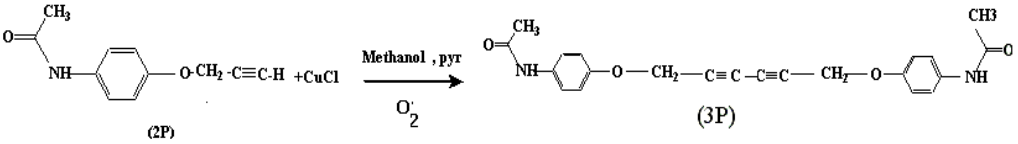


Scheme 5. Synthesis of monomer (2S).



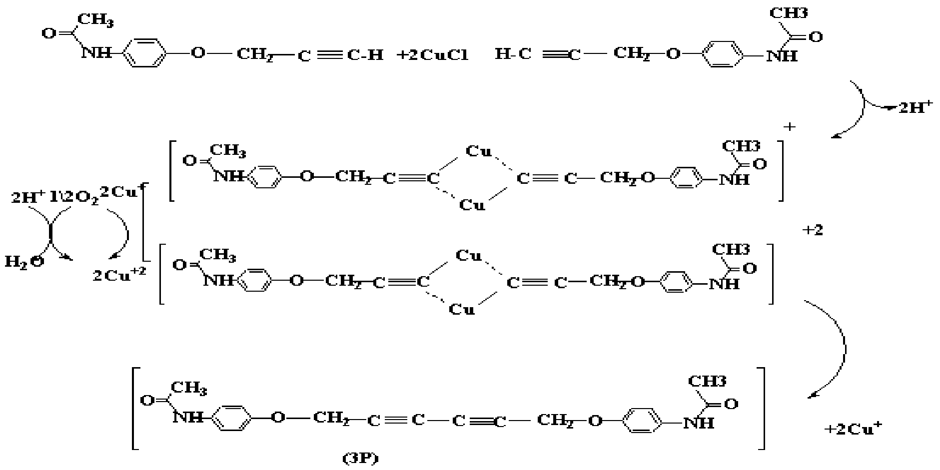
3.1. Synthesis of Homo Dimers:

Homodimer (3P) was synthesized by an oxidative coupling (Glaser) reaction, when (2P) monomer was dissolved in methanol and pyridine was added as a strong base while CuCl was the catalyst, the flask caped and balloon filled with oxygen. When the balloon reached a constant volume, that mean the reaction was completed. Scheme. 6.

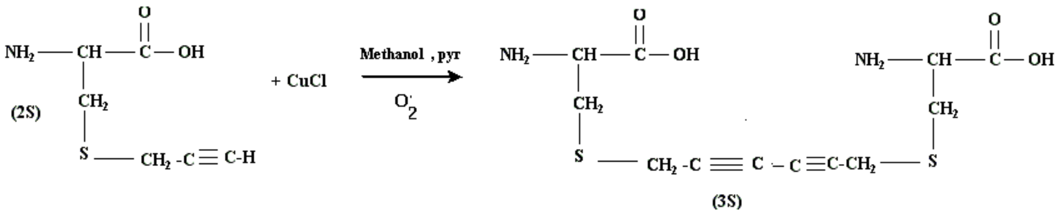


Scheme 6. Synthesis of Homo Dimers (3P)

The mechanisms of reaction of Homo dimerization (3P) took out by two steps. Firstly, by ionization of CuCl and the other step transfer via of electron to formation free radical dimerization as following:

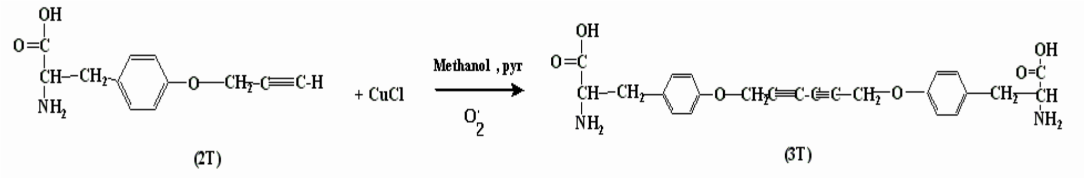


Homo dimer (3S) was synthesized from 2S according to Scheme 6.

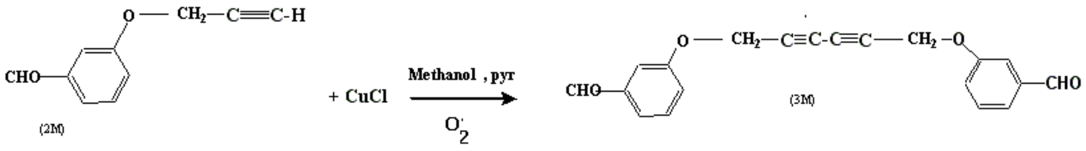


Scheme 7. Synthesis of Homo Dimers (3S).

The mechanism of reaction to (3S, 3T, 3M) as similar as to the previously Scheme. 8 & 9.



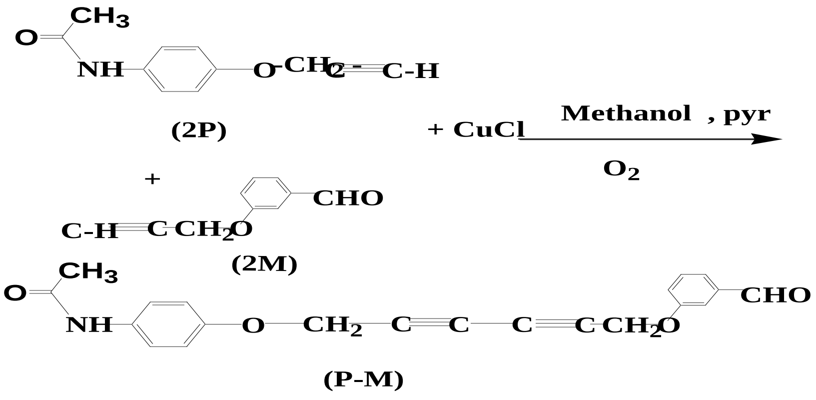
Scheme 8. Synthesis of Homo Dimers (3T).



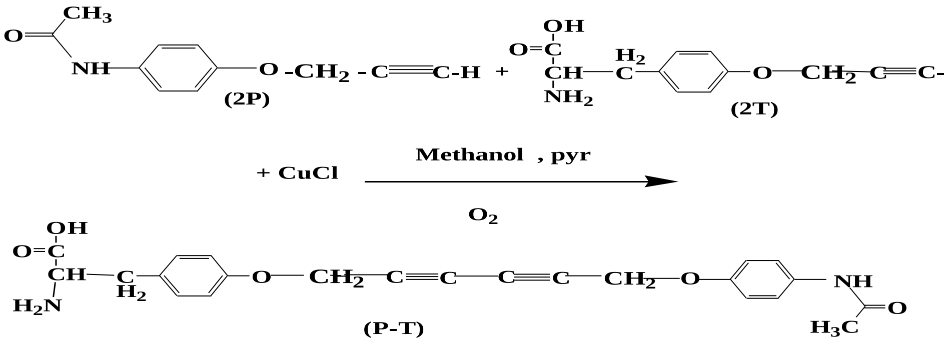
Scheme 9. Synthesis of Homo Dimers (3M).

3.2. Synthesis of Hetro Dimers :

Hetro Dimers (P-M) and (P-M) were synthesized by reacting monomers (2P), (2M) and (2T) according The Glaser coupling in the presence of CuCl as following:



Scheme 10. Synthesis of Homo Dimers (P-M).



Scheme 11. Synthetic route to Homo Dimers (P-T).

All of the chemical structure of the monomers and dimers were characterized using several spectroscopic methods such as H, ^{13}C, NMR and FT-IR spectral where shown in the Table. 4. and Fig. 3- 4. below [14].

Table 4. the FTIR spectra for all compounds.

Groups	2P	2M	2T	2S	3P	3M	3T	3S	P-M	P-T
C≡C	2374	2371	2375	2374	2336	2371	2373	2974	2371&2361	2371&2365
H-≡C	3200	3300	3211	3234	-	-	-	-	-	-
C-O-C	1121	1121	1274	-	1279	1068	1274	-	1069	1069
CH2-	-	1404	1404	1487	1404	1403	1403	1404	1482	1482
C=C Aromatic	1570	1578	1533	-	1589	1068	-	-	1539	1539
C-H Aromatic	3010	3069	3069	-	-	3025	-	3025	3079	3079
C-S-C	-	-	-	614	-	-	-	1620	-	-
COOH	-	-	2817	2589	-	-	2807	2854	2653	2653
C=O	1654	1702	1722	1620	1686	1689	1644	-	1685	1685

The H-NMR spectrum exhibits structural characteristics of Dimer due to chemical shift (δ). In general, all of the spectral data show in Table.5.

Table 5. the chemical shift in (δ) for all Dimers

Groups	3P	3M	3T	3S	P-M	P-T
-C≡C- Dimer	2.580(s)	2.499(s)	2.501(s)	2.580(s)	2.506(s)	2.503(s)
C=C-H aromatic	(7.3&7.6) (m)	(7.2&7.3) (m)	(7.2&7.5) (m)	-	(7.1&7.3) (m)	(7.5&7.3) (m)
HN-C=O Amide	2.01(s)	-	-	-	-	-
CH2-CH	-	-	-	-	7.35(m)	-
H-C=O Aldehyde	-	7.03(m)	-	-	7.54(m)	-

- EC of Composites (Psty + Dimers):

As table.6 EC of the composites increase as concentration increase for the synthesized dimers ,however, the compounds have a semiconductors properties because of materials have a high conductivity (1.1*10^{-12} SCm^{-1}) , but a semiconductors have (10^{3} – 10^{-12} SCm^{-1}) and an Insulators have low conductivity (10^{-12} – 10^{-22} SCm^{-1}) . Table. 6. Fig.5.

Table 6. Values of EC of Composites (Psty + Dimers) Relationships among current (I), voltage (V) and conductivity (S) with Conc.

Comp.	n.	Conc.%	I nA	V (volt)	Cond. (S)
3S	1	0.02	0.0000002	29.9	6.68896E-09
	2	0.002	0.0000001	29.9	3.34448E-09
	3	0.0057	0.00000003	29.9	1.00334E-09
3P	1	0.08	0.0000001	29.9	3.34448E-09
	2	0.011	0.0000001	29.9	3.34448E-09
	3	0.022	0.0000002	29.9	6.68896E-09
3T	1	0.1	0.00000003	29.9	1.00334E-09
	2	0.014	2.2E-08	29.9	7.35786E-10
	3	0.028	0.00000001	30	3.33333E-10
3M	1	0.06	0.0000015	7.9	1.89873E-07
	2	0.0025	0.0000018	29.2	6.16438E-08

	3	0.017	0.00000005	29.2	1.71233E-09
P-M	1	0.4	0.0000004	15.85	2.52366E-08
	2	0.057	3.5E-08	15.85	2.2082E-09
	3	0.11	0.00000004	15.85	2.52366E-09
P-T	1	0.1	0.0000005	29.2	1.71233E-08
	2	0.085	0.0000008	29.2	2.73973E-08
	3	0.028	0.0000004	29.2	1.36986E-08

4. **Conclusions:**

A series of novel diacetylene (Hom & Hetro) Alkynes dimers were hence by an oxidative coupling reaction (Glaser reaction), and novel of four synthesized monomers which was synthesized via reaction of propargyl bromide with different compounds. This study explains that the oxidative coupling was a successful method to synthesis diacetylene in less time and cost. And the doping of compounds is a good method to increase the EC and use for the preparation of composites materials such as semiconductor and their use in electronic circuits, all the practical data comes in according to literature (H,13C NMR, FTIR & physical properties).

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