**International Academy of Science,
Engineering and Technology**
Connecting Researchers; Nurturing Innovations
IASET

SYNTHESIS, CHARACTERIZATION AND STUDY OF NOVEL ALKYNE POLYMERS

TARIQ ABED-JALEEL

Department of Chemistry, College of Science, University of Anbaar, Iraq

ABSTRACT

A Novel acetylenic polymers were prepared through a polymerization of a new monomers using an ionic radical process of the transition complex.

Oxidative Coupling process has been used forpolydiacetylene (PDA) synthesis, while a free radical polymerization methods under atmospheric N_2 gas, has been used, for polyacetylene syntheses (PA). The synthesized polymers were characterized by FT-IR, H^1NMR spectra, viscosity and Mwtaverage. The new acetylene polymers were used as composites on polystyrene to improve the Electrical Conductivity of the semi- conductor materials. During this work, $PdCl_2$, CuClwere used as catalyst, THF and DMF as solvent.

KEYWORDS: Alkynic Polymers, Poly Diacetylene, Composites, Conductivity

INTRODUCTION

Alkynic polymer, has been of great interest due to its conjugated functionality group, however, this polymer and its derivatives have not been well studied because of synthetic difficulties. Conjugated polymers are attracting chemists attention for more than two because these polymers exhibit some unique properties such as conductivity, non-linear optical properties and fluorescence.[1-3]

The conductive polyacetyleneoccupied and demonstrated the importance of industrial .and efficiency proved in the industry solar cells, polymers batteries and devices as parts in electronic. Different methods were used for Preparation of these polymers including thermal polymerization, photo and radiation[4-5]. Alkynicpolymers used as part of the conductive such diodes at the electric form.[6]

The common way to produce this type of polymers is the Hay method which uses transitional catalysis such as (cuprous chloride), Glaser Coupling method and Eglitonmethod are used palladium, molybdenum, and copper as complexes catalysts, of initiations polymerization. [7- 8]

Recent research able us to produce polyacetylene similitude or like to the semiconductor or the connected metal, where conjugated polyacetylene is relatively have small energy gap **(1 - 4ev)**. Doping methods was increased the movement of charge carriers which gives ability of the high electrical conductive in the doping case and the common materials, used with doping are iodine, bromine, and arsenicare made in several methods, including of electrical, chemical complexes and the charge transfer the double method has been used in this study. chemical doping and composite are a method to increase the electrical conductivity properties**.**[9-11] Polydiacetylenes(PDAs) are conjugated polymeric materials with unique optical properties. Poly Diacetylenes was discovered by Carl Glaser in 1869. It involves cuprous chloride (CuCl) promoted oxidative homo-coupling reaction of terminal alkynes in the presence of oxygenin organic solvents, ammonia and ammonium chloride.[12]

The purpose of this paper is synthesis a novel poly-acetylene **(PA)** and

Poly-Diacetylene **(PDA)**from polymerization reaction of terminal acetylenic monomers which were prepared in the laboratory. product was doping with iodine element **(I_2)** to improve electrical conductivity by increasing the oxidative degree and electrons transfer ability in the polymers chains, Then the composites was prepared from **(PA)** and **(PDA)** on the polystyrene, to development of the electrical conductivity properties of the insulating materials to semiconductor.

EXPERIMENTAL SECTION

Materials and Procedure

Chemicals: m-Hydroxybenzaldhyde, Ethanol (absolute), methanol, DMF, Chloroform, Sulfuric acid, Potassium hydroxide, Pyridine and Ammonium chloride from BDH Co. P- hydrxy phenyl ethanmide- (paracetamol powder) from China Co. Tetrahydrofuran (THF), Iodin, Diethylether, Dichloromethane and Propargyl bromide from Fluka Co. The reaction monitored by thin layer chromatograph (TLC) carried out on silica plate. All solvents were purified prior to use according to standard literature methods.

Instrumentation: The products were characterized by H^1NMR spectra recorded an a Bruker **400** MHZ spectrometer in $CDCl_3$ as the solvent and TMS as internal stander in al Baath –Univ- Syria. FT-IR spectra were recorded on Nicoletir 100FTIR – spectrometer from 400 to 4000 $cm^{-1}$and samples in KBrdisc form. Electrical Conductivity were measured in Digital pico ammeter Rookee India and Melting points were obtained from a Fisher-Johns melting apparatus.

Monomer Synthesis: Alkynicmonomers were synthesized by the reaction of propargyl bromide with unsaturated alkyneic halide RX, through **SN2** mechanism:a-**p-ethanmide-3-phenoxy—propa-1-yne (A), b- m-carbaldehyde –3-phenoxy –propayne (B).**

General Synthetic Procedure

In a three-neck, round bottomed flask equipped with a reflux condenser, a dropping funnel, thermo-meter and provided with a magnetic stirrer. The flask was charged with alkaline base (2.5g, 0.44 mmol, KOH) dissolved in an organic solvent (25ml alcohol) period stirring of 15 minutes, (2 - 2.5g, 0.016 mmol) of substrate such as (m-Hydroxybenzaldehyde), was added to the mixture. A (2ml, 0.016 mmol) of freshly distilled Propargyl bromide was then added drop-wise to the well stirred reaction mixture, the reaction mixture was heated to 60-70C^0. After 2-3h reaction stopped and mixture cooled to room temperature. Ice water was added on reaction mixture and the crude product extracted twice with (2^x12ml) in dichloroethylen. The organic layer evaporated and crystallized product obtained. Crystals was dried in an oven for 2h at 50 C^0. melting point and FT-IR Spectral was recorded.

Polymers Synthesis

Synthesis of Poly-Diacetylene (PDA): Polymerization carried out under atmosphere oxygen(pure and dry).In **50ml** flask (equipped with small side tube contacted with ballonet as the oxygen stores) **0.51g** of monomer **(A)** and0.4mg Palladium chloride $PdCl_2$ (catalyst) dissolved in 7ml pyridine, then mixed with a solution of 0.1g cuprous chloride CuCl (co - catalyst) in 3ml THF. The reaction mixture was stirred at **40C^0** under Oxygen for **5 hrs**, the polymerization stopped by the added a few drops of methanol, when the balloon size was stability. After the polymerization time the resulting polymer solution was precipitated into an excess amount of methanol. The precipitated polymer was filtered and dried at 40 C^0 for 4hrs. The dried yellow crystal polymer gives a yield **77%,** melting point, FT-IR and HNR Spectral was

recorded.

Synthesis of Poly-Acetylene (PA): Polymerization was carried out under pure and dry Nitrogen gas N_2. In 50 ml flask 0.43g of monomer **(B)** was dissolved in 3 ml DMF, **o.2mg** Palladium chloride (catalyst) dissolved in 0.5ml pyridine, and then stirred at room temperature under Nitrogen (N_2) atmosphere for 4hrs. The polymerization stopped by adding few drops of methanol. The product was filtered under vacuum pressure and recrystallized from methanol. A white crystal of polymer (PAs) was obtained at yield **60%**. Melting point**,** FT-IR spectral was recorded.

Doping of Polymers: prepared Polymers have been doped by chemical doping method due to increase the electrical conductivity, using the pure iodine within the system designed for this purpose, which consists of two flask connected through pipe provider for closure and opening is linked to a pipe connected to a vacuum pump. Heat of iodine and allowed vapor to pass through a link of connect to a second flask containing specimens of polyacetylene.

Preparation of composites polymers: In a 100 ml round flask equipped with a condensation, 1g of pure polystyrene (Psty) was dissolved in 10 ml benzeneas a solvent, and 0.3g of **(PDA) or (PA)**alkynic polymers was dissolved in 10 ml benzene else, were together added to the reaction flask. After that heating of the mixture to warm and stirred for 1 hr, the mixture was poured into a glass mold capacity 1 cm x 10cm for preparation of the thin film, and leave to dry at room temperature for 10hrs.film were cut and compression in IR device specimens of 1 ton pressure, to make discs at 1.5 cm for diameter and thickness ranges (0.09 - 0.11) mm due to measuring electrical conductivity. The composites were prepared in the different percentages of polymers on the polystyrene **Table 1.**

Table 1: Composites of (Psty + Alkynicpolymers) in Different Concentration

No	Composites	Concentration Wt/V %
1	Composites (Psty + PA)	0.10
	= =	0.08
	= =	0.02
2	Composites (Psty + PDA)	0.208
	= =	0.003
	= =	0.005

Measurement of Viscosity and Average Molecular Weight

Average molecular weight were measured by viscosity method**.** ($\overline{M_v}$)Several mathematically equation are used to calculated the true viscosity of novel polymers. Relative Viscosity was calculated by use eq.1:

$$\mu rel = \frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{1}$$

Specific Viscosity by eq.2:

$$\eta spe = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta rel - 1 \tag{2}$$

Reduced Viscosity with eq3

$$\eta red = \frac{\eta sP}{C} = \frac{\eta red - 1}{C} \tag{3}$$

Inherent Viscosity eq.4

$$\eta inh = \frac{\ln \eta red}{C} \; . \tag{4}$$

Intrinsic Viscosity at eq.5

$$[\eta] = \left(\frac{\eta sP}{C} \right)_{c \to 0} = (\eta inh)C \to o \cdots \tag{5}$$
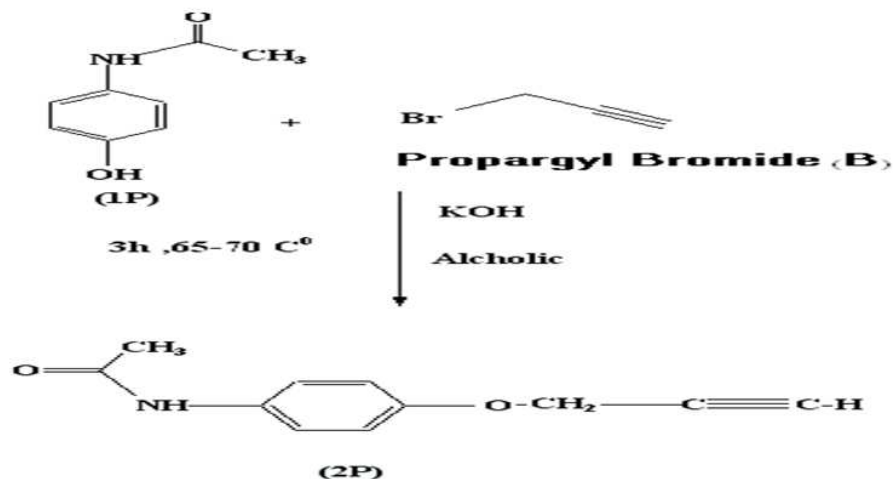
Then drawn of the linear relationship between the values of the reduced viscosity on the y-axis against the concentration of the solution **(C)** on the X-axis. And the intersection of this straight line with the reduced viscosity axis represents the intrinsic viscosity .**(η)**

Measurement of Electrical Conductivity: Electrical conductivity has been measured of the composites specimens of **(PDA)** and **(PA)** using electrical cell was laboratory designed for this purpose. Volumetric connectivity was measured of to shed suitable voltage between the electrodes and then measure the current output by using the following equation: $\sigma = IL / AV$, where ... A = cross-sectional area cm^2, V = voltage, L = length specimens in cm, I = currentamps unit and also the resistance is represent the invers of electrical conductivity cond. $(\sigma) = I / V$, $(\Omega^{-1}cm^{-1} = S\ cm^{-1})$.

RESULTS AND DISCUSSIONS

### Preparation and Characterization of the Terminal Acetylenemonomers

Monomer **A** was prepared from conversion of hydroxyl group in the (p – hydroxyl phenyl ethamide) paracetamol, to phenoxide ion which is a good nucleophile reagent using of alcoholic potassium hydroxide, it is rapidly attack the propargylbromid, by SN2 mechanism reaction. Scheme 1


Scheme 1: Syntheic Route to Monomer A

The Reaction Followed of SN2 Mechanism, to Rapidly form (A) as Terminal Alkynes Monomer as Following :
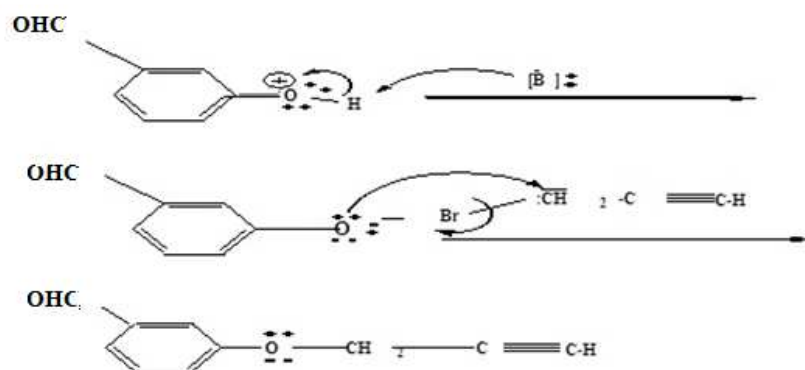
(2 P)
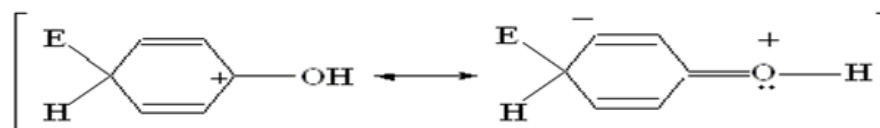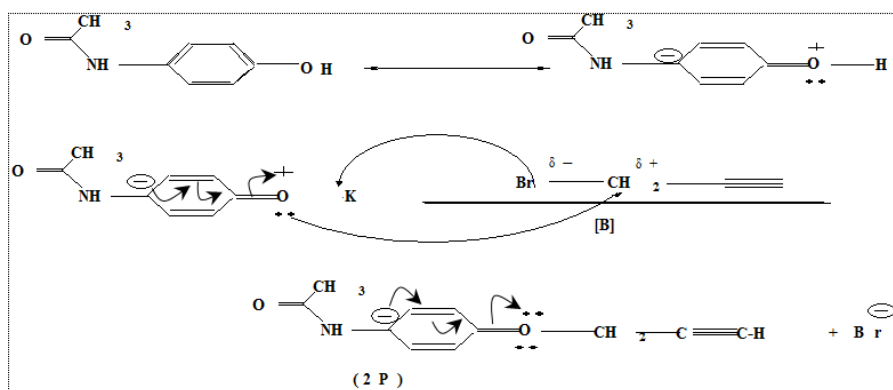
Monomer B was prepared with reaction of hydroxyl group in m- Hydroxybenzaldehyde and Propargy l bromide with alcoholic potassium hydroxide to formation of B compound in Barbeer reaction method, [13]shown in **Scheme 2.**
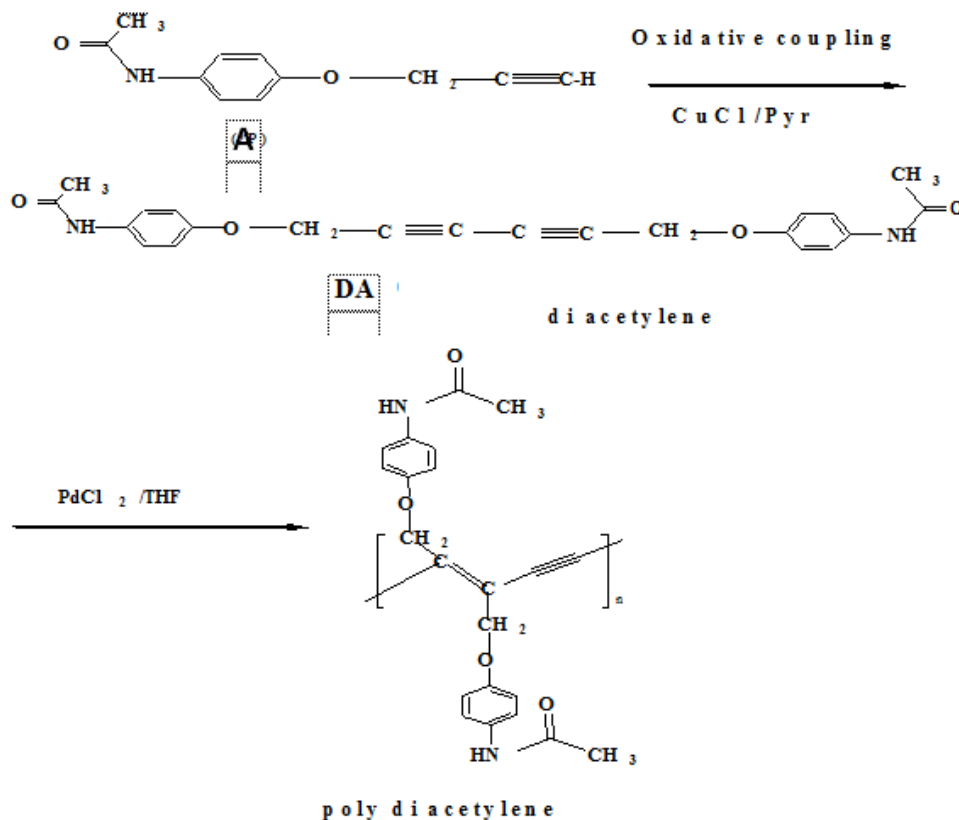

Scheme 2: Synthetic Route to Monomer B
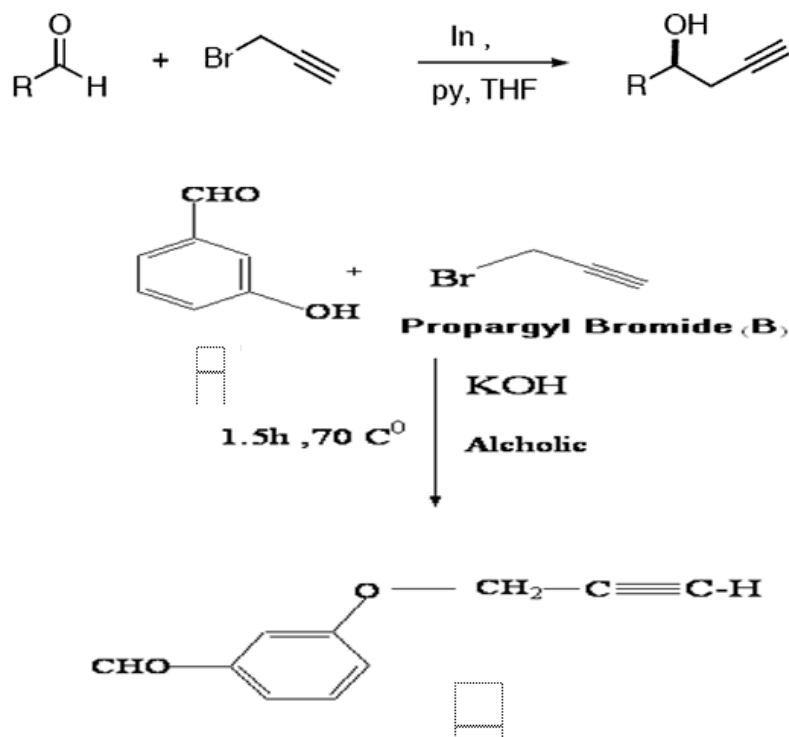
Mechanism is shown in below and also followed **SN2**

Spectroscopy methods were used for characterized monomers such as. **FT-IR**show the characteristic of ≡C-H stretching for terminal acetylene in monomers **(A,B)** where are clearly observed at (3200 – 3300 cm^{-1}), absorption bands for C-O-C at (1121- 1121cm^{-1}) indicate of stretching in ether, -CH$_2$ -at (1404 cm^{-1}) stretching in aliphatic, C=Cat (1570 - 1578cm^{-1}) for aromatic ring, absorption b and s for C-H in aromatic ring (3010–3069 cm^{-1}) and peak for C=Oat(1654 – 1702 cm^{-1})stretching in aldehyde and amide.[14] are shown in **Figure 1,**

Preparation and Characterization of the Poly- Diacetylene (PDA)

Polymerization reaction of **(PDA)** includes a two steps, firstly prepared of acetylene dimer AD by Glaser coupling process of monomer A, and other polymerization by oxidative coupling under oxygen atmospheric, by using cuprous chloride CuCl as catalysts factors, and THF as asolvent, where are doing to remove hydrogen atoms from the terminal acetylene, On the other hand the using palladium dichloride PdCl$_2$ as catalyst were dissolved in pyridinium (basic) which works to removing the hydrogen atom from acetylene dimer, by reduction one of the two group of triple bond to formation double bond as free radical ion. The palladium be acta stripe factors to hydrogen atom and happening of trans (R) group in the double bond. The methanol were used to precipitate the polymer at yield 82%, Schemes **(3)**, The **(PDA)** are synthesized by the topochemical polymerization of diacetylenes, and believed the **(PDA)** exist in two mesomeric forms.
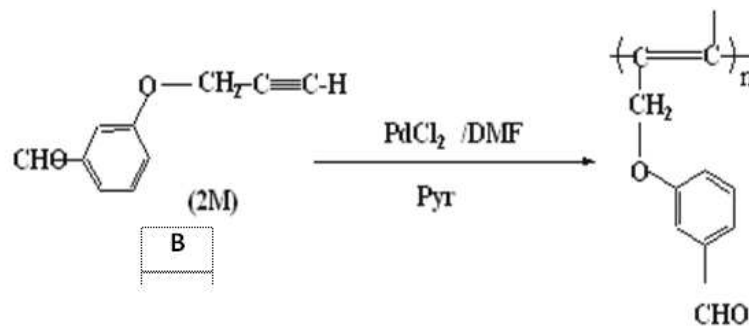

Scheme 2: Synthetic Route to (PDA)

Suggested mechanism of Poly Diacetylene (PDA) Synthesis are followed
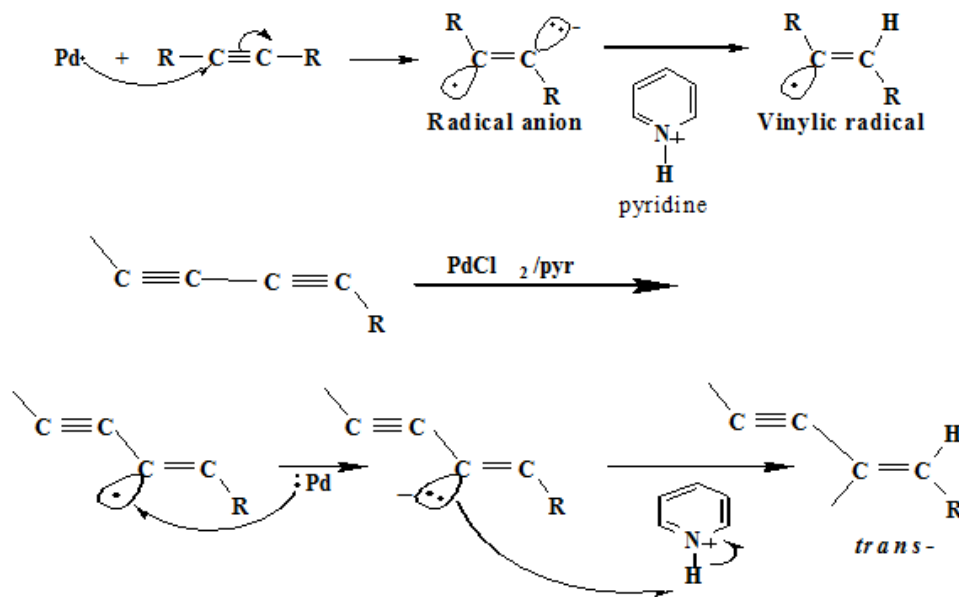
PDA were Characterized by FT- -IR Spectra, showed stretching-**C≡C-** for Dimer at (2363cm^{-1}**),** C=C Alkenat (1637cm^{-1}**),** C- H alken (3028 cm^{-1}**), Figure 1**. HNMR spectral showed the chemical shift to -C≡C- CH$_2$ at (2.50)δ(s), phenyl group at(8.0)δ(m)- (7.43)δ(m), R$_2$C=C-H)in (3.8)δ(s), C = O at ((9.03)δ(s), and -C≡C –C= C at (2.7)δ (s)**,),** **Figure 2.**

Preparation and Characterization of the Poly- Acetylene (PA)

PA were prepared by a free radicals Polymerization of monomer **m-**carbaldehyde-3-phenoxy –propayne **(B),** under nitrogen atmospheric (N$_2$), the reaction includes withdrawing terminal hydrogen atoms from the monomer, then to reduce the secondary alkene group by PdCl$_2$ (strong catalysts)which dissolved in DMF and pyridine as a base to assist for removal of hydrogen atoms and breaking the one of the (π) bonds to conversion **SP^3** hybridization to **SP^2,** Frohner and Wucke studied the kinetics of the reaction and found that the initial polymerization rate is high and that the polyacetylene yield is proportional to the concentration of the cobalt (catalysis) species. scheme (2). **FT-IR** was used to characterize the polymer. Spectra showed disappeared the triple bond of terminal alkyne ≡ C - H in 3300 cm^{-1}, absorption band for – C ≡ C - H at 2371 cm^{-1}, strong stretching band were appeared at 1615 cm^{-1} for. – C= C -,peak at 2980 cm^{-1}appears that corresponds to H – C stretching[15] absorption band for C= O at1630 cm^{-1}in aldehyde group and stretching band at 1426 cm^{-1}indicate to C- H aliphatic**), Figure 1**.

Scheme 2: Synthetic Route to (PA)

Spectra of **HNMR** showed- CH2- for alkanes (1.2) δ(s), Ar – CH aromatic hydrogen at (1.2) δ (s), RO – CH ethers in (3.3)δ(s), -C= C– to (5.3) δ(m), phnyl group C=C- H aromatic ring (7.5) δ(m), also hydrogen of aromatic ring at (8.2) δ(m) and H-C=O hydrogen for aldehyde at (9.4) δ(s), **Figure 2.**
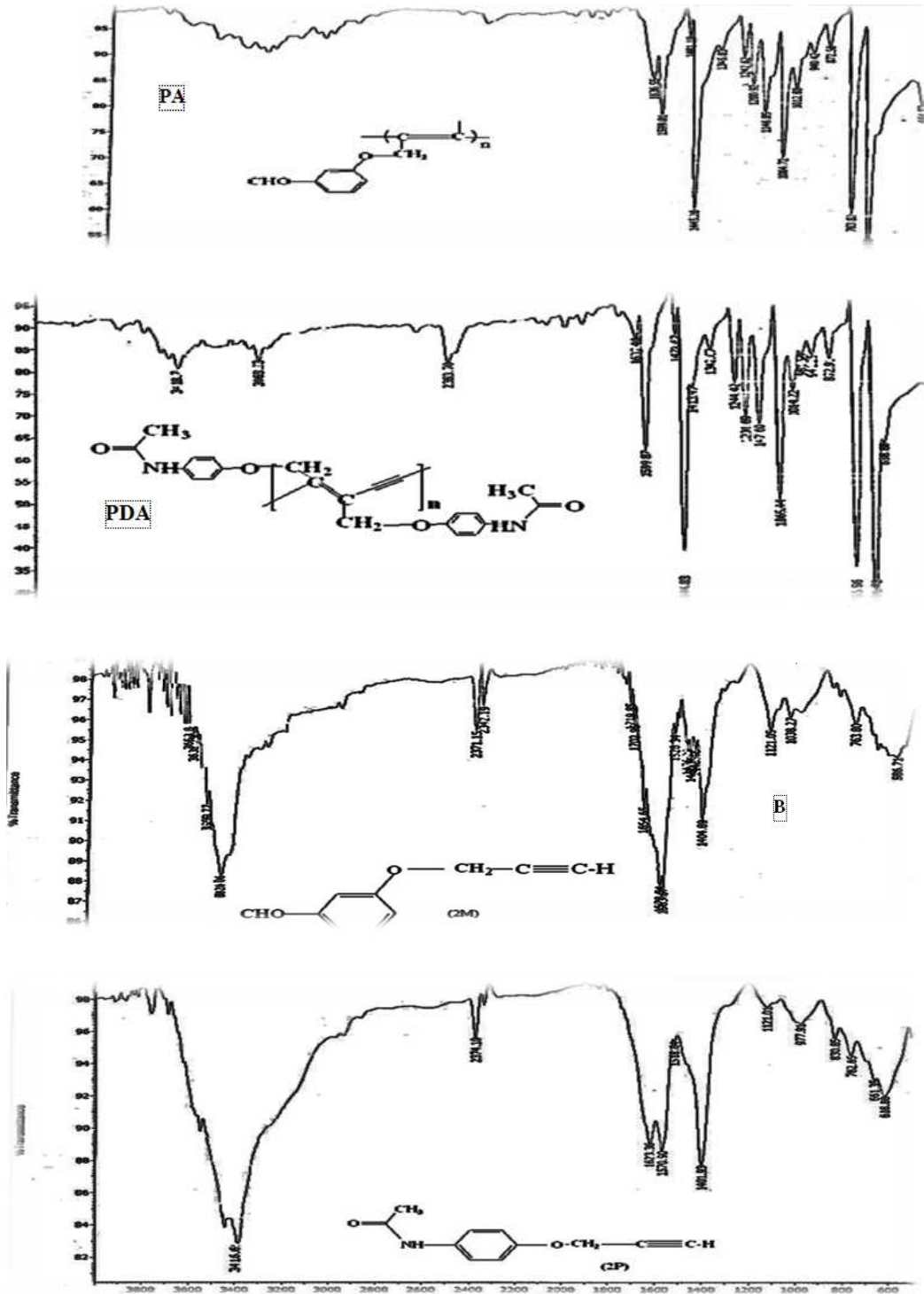

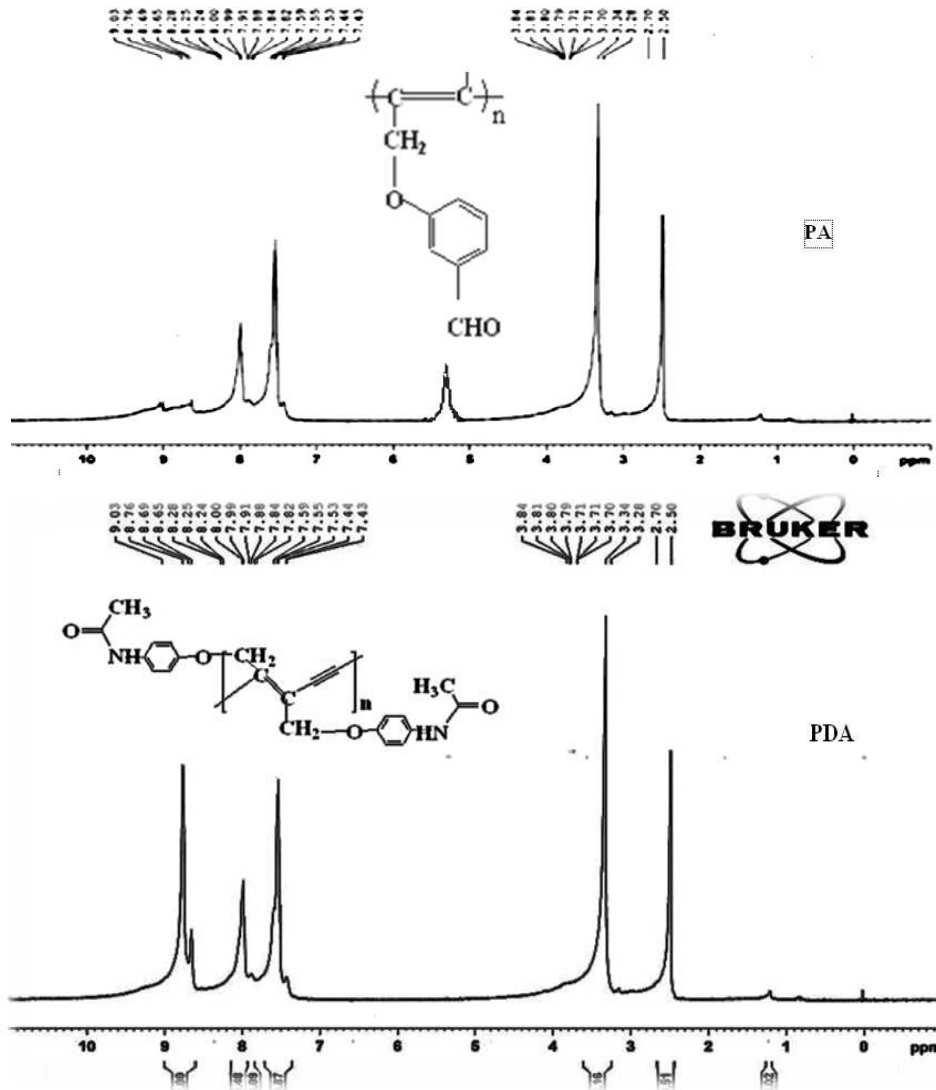**Figure 1: FT-IR Spectrum of Monomers & Polymers**

Figure 2: H^{1}NMR Spectrum of Polymers

Measurement of Average Molecular Weight

Average molecular weight of (**PDA**) and (**PA**) was calculated with Mark –Houwnik equation:

$$\left[\eta \right] = K \times \overline{M}_v^{\,a}$$

(6)

From the values of viscosity which are calculated by use of several mathematically relationship. shown in the table. (**2 – 4**) and **Figure (3, 4)**

Table 2: Values of Specific Viscosity and Reduced Viscosity of (PDA)

No	t	Conc.	ηrel=t/t0	ηSP=η rel-1	ηsp=η rel-1/c
1	10.24	0.00006	1.024	0.024	400
2	10.23	0.000052	1.023	0.023	442.3076923
3	10.17	0.000047	1.017	0.017	361.7021277
4	10.14	0.000042	1.014	0.014	333.3333333
	t$_0$=10				

Table 3: Values of Specific Viscosity and Reduced Viscosity of (PA)

No	t	Conc.	ηrel=t/t0	ηSP=η rel-1	ηsp=η rel-1/c
1	10.7	0.0006	1.07	0.07	116.6666667
2	10.58	0.00052	1.058	0.058	111.5384615
3	10.5	0.00047	1.05	0.05	106.3829787
4	10.04	0.00042	1.004	0.004	9.523809524
	t_0=10				

Values of intrinsic viscosity(**η**)to(**PDA**) was calculated from **Figure 3:** and to(**PA**) from **Figure 4**
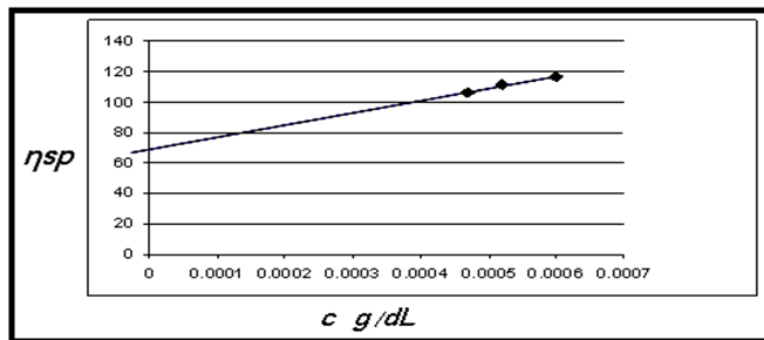

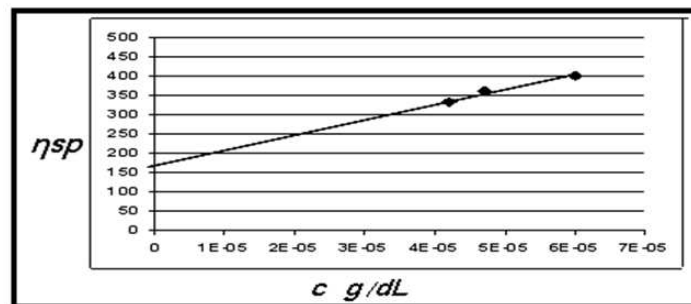**Figure 3: Relationship between Specific ViscosityηSp and Concentration of (PDA)**

Figure 4: Relationship between Specific Viscosity ηsp and Concentration of (PA)

Values of **a** and **k** were obtained from another polyacetylene has a known values of **a**, **k** and viscosity are**η = 0.34, Mw =9700.** And by using electronic program with an computing methods.

Table 4: Values of k, a, $\bar{M}v$ and Intrinsic Viscosity of PDA and PA

Polymer	k	a	Intrinsic Viscosity(dl/g)	$\bar{M}v$	temperature
PDA	0.05	0.729	175	66171	30
PA	0.05	0.729	97	27722	30

Electrical Conductivity of Polymers

Electrical conductivity were calculated for composites polymers in different concentrations and that from division of output current on the input voltage. Calculated of the polystyrene conductivity give the value is $1.1*10^{-12}$ SCm^{-1}) (insulators plastic). Insulator material has low conductivity (10^{-12} – 10^{-22} SCm^{-1}), but a semiconductor has (10^3 – 10^{-12} SCm^{-1}). The conductivity of the polyacetylene composites are increases with increasing concentration of

polymer (proportional relationship).[16]Table 5. Figure 5.

Table 5: Values of Electrical Conductivity of Composites PDA & PA

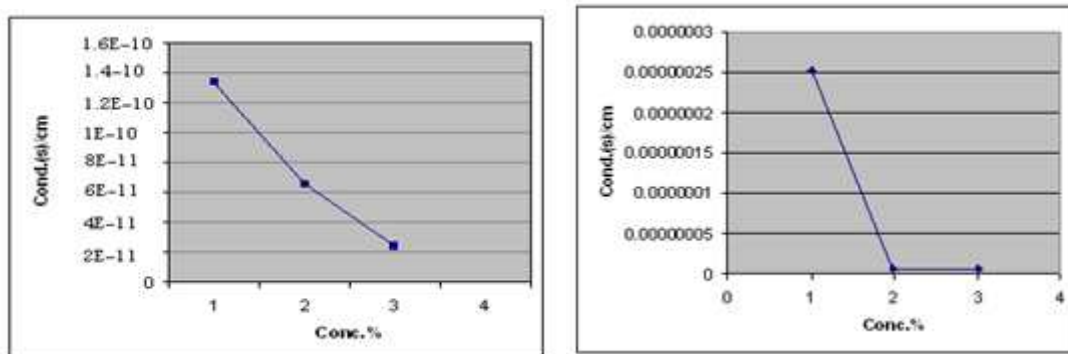| Comp.	n.	Conc.%	I nA	V (volt)	Cond. (S)
PA	1	0.2	0.0000008	29.2	2.73973E-08
	2	0.03	2.3E-09	29.2	7.87671E-11
	3	0.025	5E-09	29.2	1.71233E-10
PDA	1	0.02	4E-09	29.2	1.36986E-10
	2	0.003	2E-09	29.2	6.84932E-11
	3	0.005	1E-09	29.2	3.42466E-11

PDA PA

Figure 5: Relationship between Conductivity and Concentration of Polymer Composites

CONCLUSIONS

Successfully anovel **(PDA&PA)** has been synthesized by oxidative coupling reaction and free radical, which their prepared from novel monomers and in less time and cost method. Spectroscopic methods FTIR, HNMR of polymers showed that the characteristic of C= C stretching frequencies in (1615 - 1637cm⁻), (3.88 - 5.30δ), and in monomer materials showing -≡C-H of terminal acetylene at (3200 – 3300 cm⁻¹). All results of this study are found to lie in good agreement with the hypothetical case emphasizing the accuracy of the reactions.

REFERENCES

1. BarisKiskan,YusufYagci. Elsevier Ltd 2008, 49, 2455- 2460.

2. Yoshihito Honsho. Alkinori Saeki and Shu Seki., International Journal of Spectroscopy; 2012, 12, 7, 1155-1164.

3. Alan J. Heeger Alan G. MacDiarmid Hideki Shirakawa, the RoyalSwedish Academy of Sciences. Nobleprice in chemistry 2000 to discovery conductive polymer

4. BoChen, JianpingDeng and Wantai Yang, ColloidPolym. Sci, 2011,289,133–139

5. Abbas Ali Esmaili, Mohammad Ali Nasseri, HamidVesalipoor, ARKIVOC

6. Beom Jin Kim, Dong Kung Oh, and Ji Young Chang, Macromolecular Research, 2008, 16, 2, 103-107.

7. EunYoungPark, JunWooKim, DongJuneAhn, Jong-ManKim, Macromol. RapidCommun. 2007, 28,171–175

8. Kevin K. Dunham, Lacie H and Bakthan S., 1156 High St, Santa Cruz, 2006CA 95064.

9. Brenhart S., Hartwig Sch.; Malgorsats B.; Gearge N.; Ardreev C; Juergen S. in spectrochimicaActa; Part A, 2005,61, 1395-1401.

10. Conte, G.; Ely, F.; Gallardo, H.; Bortoluzzi, A. J.; Liq. Cryst 2006, 32, 36, 1213-1223

11. Wei Zhang, HaiboXu, Yun Chen, Si Cheng. ACS Appl. Mater. Interfaces, 2013, 5, 11, 4603–4606

12. Li. S.L and Stuup S.L, Macromolecules, 1997, 3o, 5313-5320.

13. Dolhem, F.; Al Tahli, F.; Lievre, C.; Demailly, G. Eur. J. Org. Chem., 2005, 23, 5019-5023

14. YorikoSonoda. Molecules. 2011, 16, 119-148; doi: 10.3390.

15. Keda Hu, Haishen Yang, Wei Zhang and Yang Qin .Chemst. scien.2013**,** 4, 3649-3653.

16. Bora Yoon, JustynJaworski and Jong-Man Kim., Supramolecular Chemistry 2013, 25, 1,54–59. 2008, 14, 343-349.