

Synthesis and Characterization of Novel Polyacetylene and Poly Diacetylene Substituted with Thiosaccharin

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ABSTRACT

Novel polyacetylene & Polydiacetylene Substituted with thio Saccharin were Synthesized by two routes, first polymerization of terminal propargyl Saccharin (laboratory prepared) to produce polyacetylene PAS, under nitrogen gas, in presence of PdCl₂ in DMF. The Polymerization reaction was carried on for 4hrs. at 30°C (Yield 78%). Second procedure was used to product PAS using Microwave Radations under the same conditions at 400 W, for 10 minutes, (Yield 70%). Another route was polymerization diacetylene (laboratory prepared) to produce Polydiacetylene PDAS, The Synthesis approach to PDAS is based on Oxidative Coupling polymerization under oxygen gas and THF, In basic medium (pyridine) and present CuCl, PdCl₂ as Catalytic, The polymer Yield 82% at reaction temperature 40 °C in 5 hrs. Instrumental analyses such HNMR, FR-IR, Spectroscopies. These Indicated that the new materials have Conjugated polymers within designed Substituents Saccharin.

Introduction

The poly acetylene has been traditionally used as a component in electronic circuits as application in the cell dual emission light (LED) light emitting diodes and occupies pharmaceutical importance [1]. There are many kinds of Poly acetylene and Poly diacetylene such as by extraction from some natural plant, and isolated from marine sponge, and in 1977, Shirakawa et al. discovered that the conductivity of Poly acetylene (PAs) increases significantly upon doping with various electron acceptors or electron donor. They Obtained a Nobel prize 2000 for chemistry. [2]

A Classical, effective and useful method for preparing Diacetylenes DAs was discovered by Carl Glaser in 1869. It involves cuprous chloride (CuCl) promoted oxidative homo-coupling reaction of terminal alkynes in the presence of oxygen, ammonia

and ammonium chloride. These reactions are generally carried out in organic solvents such as methanol, acetone, pyridine, benzene and toluene [3]. Before more than thirty years, Wegner reported that substituted diacetylene monomers polymerize topochemically in the solid state.[4] Poly diacetylene (PDA_s) are unique conjugated polymeric materials that are obtained by topochemical polymerization in the monomers diacetylene (DAs) crystal mostly under thermal and photochemical activation unlike other μ -conjugated polymers and PDA_s soluble in polar solvent are quite rare and must be blue to red .[5, 6,7] since the first report of the colorimetric detection of the Influenza virus by using a Poly diacetylene (PDA_s) film. [8] In the recent years, a great deal of interest has been focused on the synthesis of novel conjugated polydiacetylene. [9] . In contrast to Poly acetylene, a good solubility in a solvent brings about high process ability . So that they have designed and synthesized as special material with electrical conductivity .[10] . The

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Poly acetylene substitutes are an important class in Polymer science which increase efficiency when their uses are multiple [11]. Substituted polyacetylenes exhibit unique properties such as semi-conductivity, nonlinear optical properties, and high gas permeability due to the conjugated main chain and rigid molecular structure. Attachment of aromatic pendants to the polyacetylene backbone is one way to overcome problems associated with intractability and thermal degradation [12,13,14] The substituted poly acetylenes within thiosaccharin are not found in the scientific published literature .We expected that the addition of saccharin to acetylene molecule greatly increase the effectiveness of the polymer [15] because the molecular saccharin has activated the functional group, and the ring system has been viewed with considerable interest which is unsurprising in the pharmaceutical and flavor. Saccharin has been widely used in medicine and in a variety of food, [16].

The present study aims to synthesize and characterize the new substituted polyacetylene with saccharin, from polymerization of monomer (terminal propargyl saccharin) and polymerization of acetylene dimmers by oxidative coupling to synthesize a new poly diacetylene by two routes, firstly initial uses of microwave radiations and the other synthesis is under room temperature. And characterized by HNMR, FT-IR.

Experimental

Materials : The reagents and solvents, saccharin high purity, phosphorus penta sulfide, ammonium chloride, anhydrous magnesium sulfide, were obtained from Sigma-Aldrich Co. and were used as received unless otherwise specified propargyl bromide (purifications by distillation B.P 88 C⁰), ether, benzene $\geq 98\%$, Cuprous chloride $\geq 98.5\%$ BDH Chemicals Lt). Reagent grade solvents were dried and purified as

follows. Triethyl-Amine (TEA) was dried and distilled from calcium hydride. Methanol was dried over molecular sieves 4A⁰ and distilled from sodium. The Tetrahydrofuran (THF), and pyridine were dried and distilled from sodium . All glass ware was assembled and was then flame-dried while being swept with nitrogen.

Instrumentation: The H-NMR (400 MHz) spectra were recorded by using a BRUKER spectrometer and CDCl₃ as solvent, in Al-Baath – Univ – Hams/Syria. FT-IR spectra were obtained with the use of a PERKIN ELMER Spectrum 2000 FT-IR spectrometer in woman's education collage Anbar-Univ.

Monomer synthesis:

Preparation of Thiosaccharin (2):

In 100 mL flask Saccharin (0.05 gm, 10m mol) and phosphate penta sulphide (0.06gm, 14 mol) were heated at 78C⁰ for 15 minutes then the temperature was increased to 178C⁰ in 1hr, The reactant mixture was turned red in colour, the mixture was cooled, and the product was extraction with benzene. The solvent was evaporated and yellow crystals was collected and recrystallized with benzene to give thiosaccharin (2) (m.p=177-179C⁰, yield 80%). Preparation of monomer (S-Propargyl Thiosaccharin) 3.

In a 100 mL flask 3.5 gm Thiosaccharin and 35ml THF with 3ml Triethyl amine, was added. Mixture of 15ml THF and 1.5ml Propargyl bromide. The mixture was refluxed for 30 minutes in water bath at 50C⁰ then saturated ammonium chloride was added and the product extraction within diethyl ether and dried by anhydride magnesium sulfite. The product was precipitated and recrystallization with mixture 1:1 ethanol : chloroform, The product (M.P 159- 160 C⁰, yield 78%).

Diacetylene (Dimer) Synthesis (2,4- di yene- hexa- 1, 6- di thio saccharin) 4.

In 50ml Erlenmeyer flask, 1.5g monomer (S- Propargyl Thiosaccharin) dissolved in 6ml methanol, and 0.5ml pyridine then mixed with 0.2 cuprous chloride (CuCl) as catalyst, kept in Erlenmeyer flask equipped with small side tube contacted with ballonnet as the oxygen stores, then we closed the flask and paid a stream of dry oxygen, two times through the reaction . The resulting solution was stirred vigorously at room temperature for 2hrs . the reaction finished when the balloon size was stable for 1.5 hr. and 6ml Hydrochloric acid was added to the reaction flask, and cooled in ice bath, then saturated ammonium chloride was added, the product extraction was with ether organic layer.

Polymers synthesis

PolyDiacetylene (PDAs) Synthesis (1,6 disaccharin, hexa-2-yne-4ene) 5.

Polymerization was carried out under oxygen atmosphere. A typical polymerization procedure is as follows.

In 50ml flask (equipped with small side tube contacted with ballonnet as the oxygen stores) 1.2g Diacetylene substituted within Saccharin (monomer) and 0.4g Palladium chloride (catalyst) dissolved in 7ml pyridine, then mixed with a Solution of 0.1g cuprous chloride (catalyst) in 3ml THF, The action mixture was stirred at 40C⁰ temperature under Oxygen for 5hrs, the polymerization stopped by 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 C⁰ for 48hrs. The polymer yield was 82%.

Poly acetylene (PAs) Synthesis : poly (1-saccharin – propene, 2ene) 6.

Method. 1 (Room Temperature).

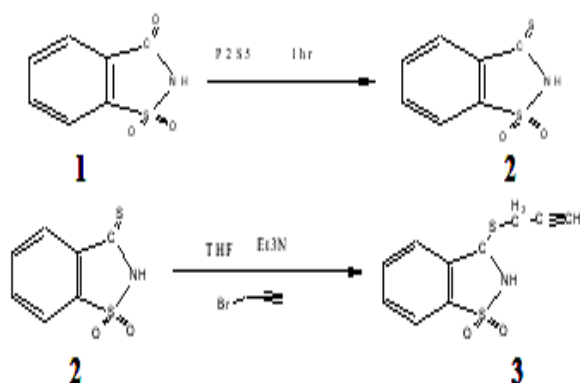
In 50 ml flask 0.5g S- Propargyl Saccharin (monomer) dissolved in 5 ml DMF, 0.4g Palladium chloride (catalyst) dissolved in 0.5ml pyridine, this mixture was stirred at room temperature under Nitrogen (N₂) atmosphere for 4hrs. The polymerization stopped by adding few drops of methanol. The product was filtered and recrystallized from methanol. The polyacetylene (PAs) yield was 78% .

Method II (microwave). The same procedures above were followed using microwave Radiations. The microwave oven was at power 400 W for 10 minute, Then it was lifted to cool at room temperature. The solid so formed was filtered and recrystallized from methanol. The yield of product was 70%.

Results and Discussion

Synthesis and Characterization of the Terminal Alkynes(monomer).

The Synthesis of terminal acetylene monomer (3) was performed in two steps. Firstly, initial conversion of saccharin 1 C₇H₅NO₃S to thiosaccharin 2C₇H₅NO₂S₂ was prepared by the direct reaction with phosphorous pentasulfide, that becomes more nucleophile when sulfur atom was substituted in Saccharin molecule. The subsequent step was the reaction with propargyl bromide was carried out in dry triethyl amine as acid receptor, the reaction followed SN₂ mechanism quickly because more nucleophile sulfur group attacked the bromine atom in propargyl (RX) and replaced to form propargyl thiosaccharin 3 as terminal alkynes, Scheme - 1.



Scheme (1) preparation of propargyl thiosaccharin

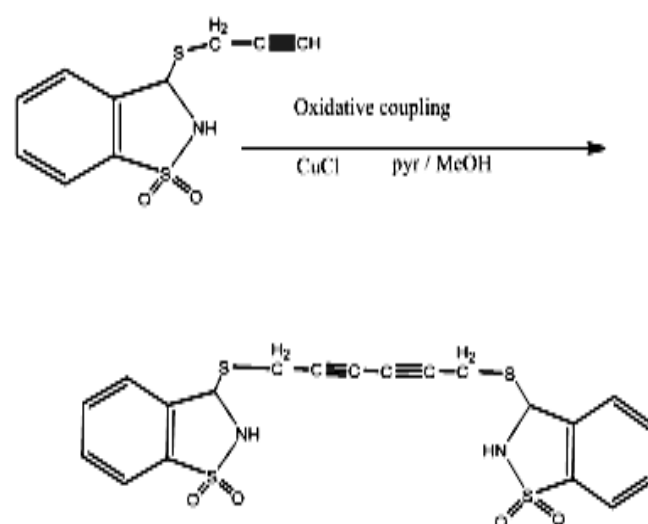
The monomer spectral was characterized and the chemical structure of propargyl thiosaccharin was confirmed by both FT-IR and H-NMR, the data analysis of FT-IR spectral show the stretching band of (N-H) at 3434 cm^{-1} (strong) stretching $\text{H}\equiv\text{C}$ - at 3268 cm^{-1} (Sharpe and strong) It confirms the success of the substituted on propargyl bromide, 3080 cm^{-1} str C-H stretching aromatic ring. (weak), 2933 cm^{-1} to C- H_2 str .aliphatic (weak), str. $\text{C}\equiv\text{C}$ - H at 2376 cm^{-1} , 2200 cm^{-1} to $\text{C}=\text{C}$ - H str. aromatic (weak), 1650 & 1722 cm^{-1} $\text{C}=\text{O}$, 1155 cm^{-1} SO_2 (Sharpe), 785 cm^{-1} bend $\text{C}=\text{O}$ (Sharpe).fig (1) . and strong str. - $\text{C}=\text{S}-\text{C}-\text{H}$ in 755 cm^{-1}

HNMR spectral show chemical shift terminal $\text{H}\equiv\text{C}$ The signal of terminal acetylene proton emerges as triplet at 2.39 ppm, and the two C3 protons of the propargyl part were noted at 4.16 ppm, the protons of aromatic ring part in saccharin where at 7.65. ppm 2prot., 7.75 4. ppm prot. 7, 95 . ppm 2 prot, signal 1.44. ppm to saturated alkane .signal $\text{R}-\text{S}-\text{C}-\text{H}$.

Diacetylene (PDAs) Synthesis and Characterization.

We have used and developed a simple strategy for the Poly Diacetylene (PDAs) Synthesis which includes prepared diacetylene (2,4- di yen- hexa- 1, 6 – di saccharin) 4, and represents the monomer of this reaction. The dimerization reaction depending on the

Glaser Oxidative Coupling conditions, [17] it was prepared by homodimerization and using CuCl as catalysis in present pyridinium as the basis and methanol as solvent, reaction assistant in the form a complexes were similar to coordination polymerizations in term of Zekler –Natta catalysis and they were different in mechanism. The mechanism of reaction show that happened two steps preliminary ionization or activation by cuprous ion composition followed electron transmission containing cupric ion and copper followed free radical dimmers.(Scheme 2).

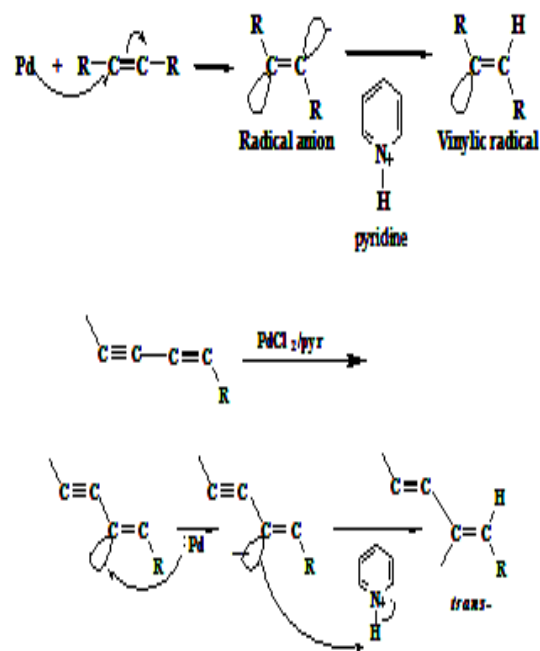


Scheme (2) Synthesis of Diacetylene (DAs)

The FT – IR, HNMR of dimer Spectra data analysis show disappeared the terminal alkyne band $\text{C}\equiv\text{H}$ at 3228 cm^{-1} and revealed stretching $\text{C}\equiv\text{C}$ at 2025 cm^{-1} , weak band at 2025 cm^{-1} to str. Alkyne $\text{C}\equiv\text{C}$, str.- CH_2 1400 cm^{-1} . HNMR and C^{13} HNR show signal at 78 pmm to $\text{C}-\text{C}\equiv\text{C}-\text{C}$ (dimer) 20 pmm to saturated aliphatic, signal at 74 ppm to $-\text{C}-\text{S}-\text{C}$, two signal in 124 ppm and 130 ppm 2 proton, 3 proton to aromatic rig, signal 134 ppm.

Poly Diacetylene (PDAs) 5. Polymerization reaction includes Oxidative Coupling mechanism under oxygen atmospheric, that catalytic factors technical by using. cuprous chloride CuCl where are

doing to remove hydrogen atoms from the terminal acetylene by presence cuprous chloride as catalysis factors, and THF solvent, such Glaser Coupling mechanism. The added palladium dichloride PdCl₂ (catalyst) dissolved in pyridinium (basic) in the composition reaction of polydiacetylene 4 where he works on removing the hydrogen atom of acetylene, where reduction one the two group of triple bond acetylene to double bond as free radical ion. The palladium be act hydrogen atom stripe factors and happening of trans (R) group in the double bond We use the methanol to precipitate the polymer within yield 82% Schemes (3), (4). The scientific reference defines Polydiacetylenes are synthesized by the topochemical polymerization of diacetylenes, most work has focused on the polymerization of crystalline diacetylenes. The polydiacetylene is believed to exist in two mesomeric forms.

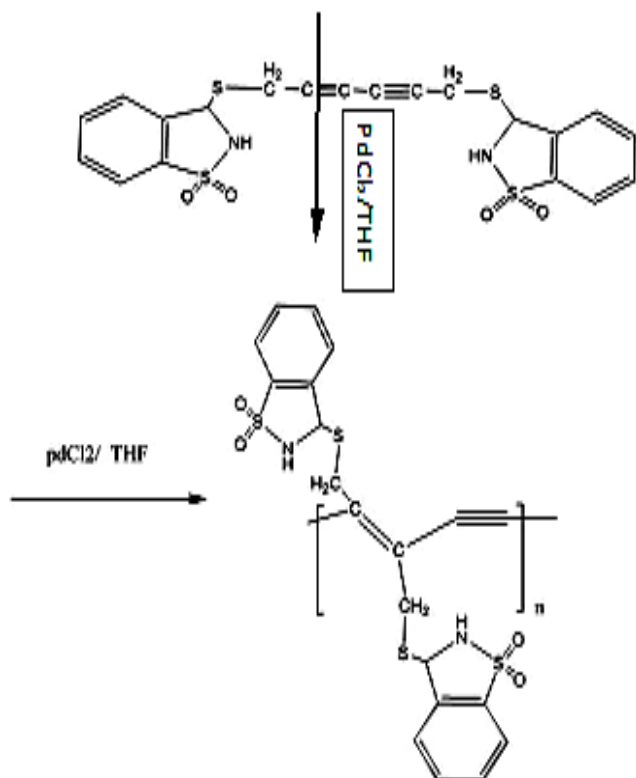


Scheme (4) : Suggested mechanism of Poly Diacetylene (PDAs) Synthesis.

Spectral Characterized by FT-IR, HNMR shows stretching C≡C in 2369 cm⁻¹ (weak), str. C=C in 1610 cm⁻¹ str. In 1450 cm⁻¹ C≡C-H and disappeared C≡C in 2025 cm⁻¹ of dimmers . and some band to Saccharin . str. N-H in 3400 cm⁻¹ str.Ar- H vw in 3110 cm⁻¹ str. SO₂ 1223 cm⁻¹ str. C-H in 1160 cm⁻¹ . HNMR show the chemical shift of signal in 1.6 ppm to acetylene conjugation C - C≡C-, signal in 7.28 ppm to C=C-H, signal in 7.45 ppm C₆H₅ - S - C, 8.2 ppm signal to secondary amine C - N - C.

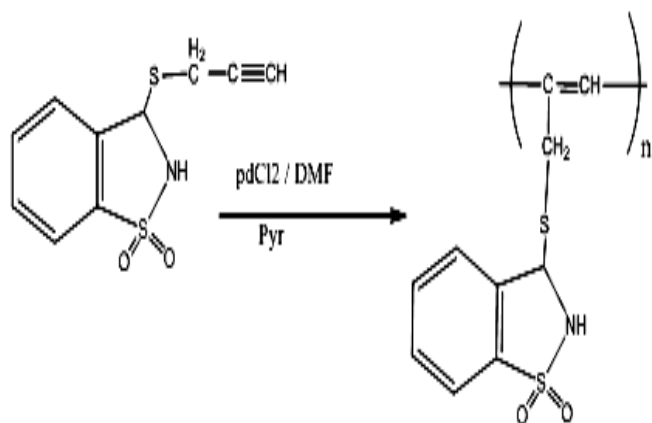
Polyacetylene (PAs)⁶ Synthesis and Characterization.

Polyacetylene was first prepared as a linear, high molecular weight, polyconjugated polymer of high crystallinity and regular structure . For a long time polyacetylene was considered of little interest regardless the method of preparation obtained as an air sensitive. [18, 19] .It was prepared by the direct Polymerization reaction S- Propargyl Thiosaccharin 3 (monomer) under nitrogen atmospheric the reaction



Scheme (3) Synthesis of Poly Diacetylene (PDAs)

ensure withdraw the terminal hydrogen atoms from the monomer then to reduce secondary Alkene group by strong catalysts such Palladium dichloride there is dissolve in DMF and pyridine existence as a base to assist in the removal of hydrogen atoms and breaking the one of π bonds to conversion SP^3 hybridization to SP^2 overall the reaction is free radical mechanism by linear chain, 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. [20]. Scheme (5). Spectral Characterized FT-IR and HNMR show disappeared the terminal alkyne band $\equiv C-H$ in 3228 cm^{-1} and str. $-C \equiv C-H$ 2376 cm^{-1} , and appeared strong band in 1605 cm^{-1} to str. $-C=C-$, and str. pack in 2930 cm^{-1} $H-C=C-$. and pack to Saccharin such str. 3400 cm^{-1} $N-H$, str $C-H$ 1446 cm^{-1} , str SO_2 in 1202 cm^{-1} , and other. HNMR Spectra .



Scheme (5) Synthesis of Poly acetylene (PAs)

The microwave method was used to prepare Polyacetylene .It gave crystals from polymer, time of 10 minutes by using micro- oven in radiations 400W. The Polymer Spectral Characterized at FT-IR, HNMR .show str, disappeared the terminal alkyne band $\equiv C-H$ in 3228 cm^{-1} , and the band form to Poly double. $-C=C-$ str 1632 cm^{-1} , and weak band to $H-C=C-H$

1729 cm^{-1} , band to $C-H$ aliphatic str, 1405 cm^{-1} many band to saccharin such $Ar-C=C-H$ weak str. 3145 cm^{-1} . and, strong str. $N-H$ 3407 cm^{-1} .weak band str. SO_2 in 1246 cm^{-1} .and str . $C=S-C-H$ in 716 cm^{-1} , HNMR. disappeared chemical shift of terminal $\equiv C-H$ at 2.39 ppm it was averment polymerization doing, and show signal in 1.3 PPM to $R-C=C-$, 0.86 ppm saturated aliphatic, 2.7 ppm to amine $C-N-H$, 7.3, 7.65 ppm aromatic ring .

Conclusions

Conversion Saccharin to thiosaccharin it was destination to increase the nucleophile of sulfide group in order to make the reaction fast with SN_2 mechanism. The synthetic strategy is used to prepare propargyl thiophene as monomer based on heterogeneous group substituted. For the purpose of initiating to synthesis of other molecules, we explained that the oxidative coupling was a successful method to synthesis of a novel substituted poly acetylene and polydiacetylene which was substituted within thiosaccharin in less time and cost. The use of microwave radiation is the good alternative energy which is better than thermal and it is good to reactions .

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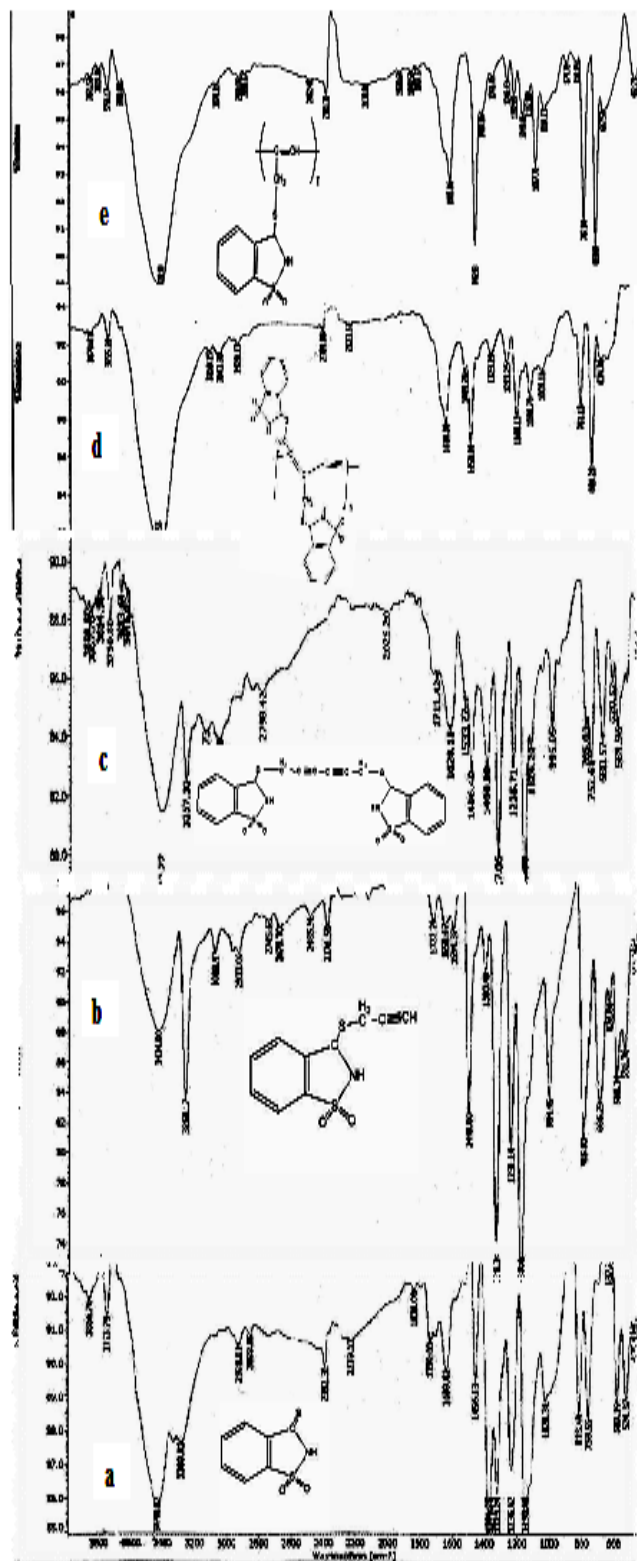


Fig. (1) FT – IR Spectral ; a- thiosaccharin,b- propargyl thiosaccharin, c- homo dimer propargyl thiosaccharin, d – poly diacetylene PDAs, e – poly acetylene PAs.

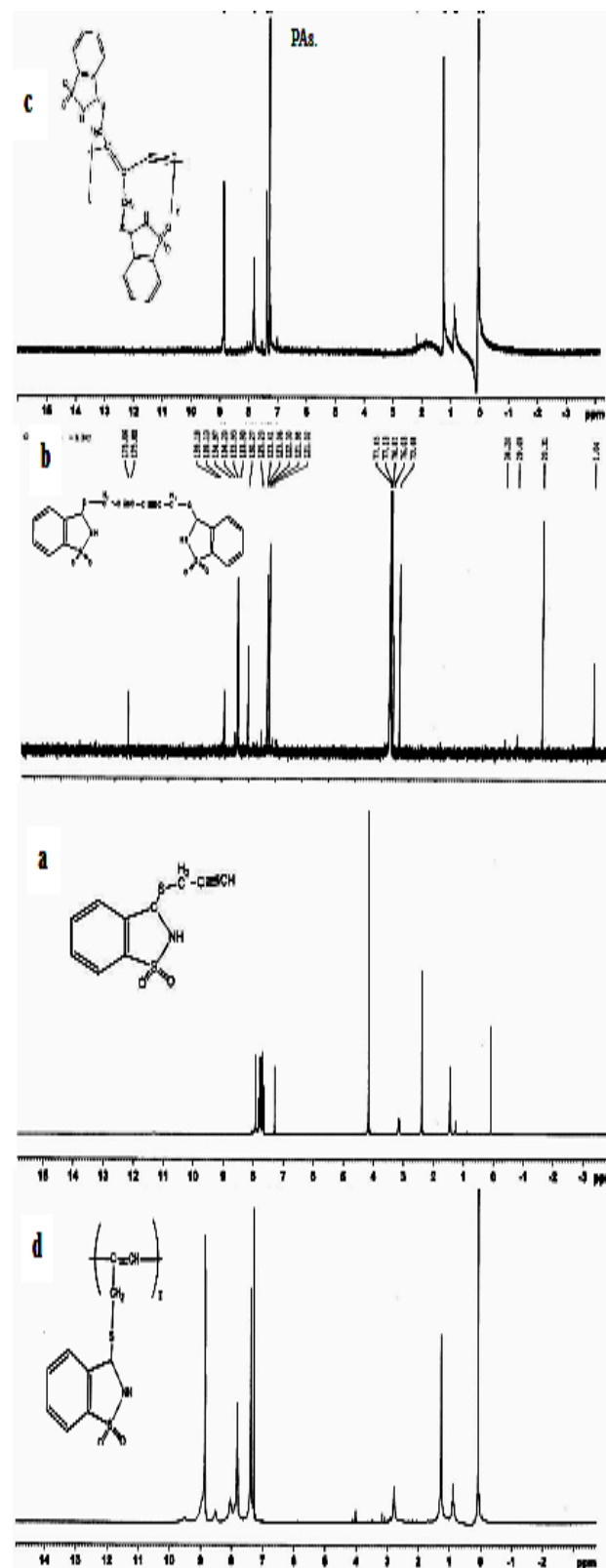


Fig. (2) HNMR, C13 NMR Spectra ; a - Propargyl thiosaccharin (monomer) b- Diacetylene DAs, C- Polydiacetylene PDAs, d- Polyacetylene PAs.

تحضير وتشخيص بولي أستلين وبولي داي أستلين جديدة معوضة بثايو سكارين

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الخلاصة

تم تحضير وتشخيص بولي أستلين وبولي داي أستلين جديدة بمسارين، الأول بلمرة بروبارجيل السكارين (مونومر محضر مختبرياً) لإنتاج البولي أستلين PAs في جو من النايتروجين النقي وبأستعمال ثنائي كلوريد البلاديوم PdCl₂ كعامل مساعد وDMF كمذيب وكانت الحصيلة 78%، بدرجة حرارة 30 م وزمن مقداره 4 ساعات. وإستخدمت طاقة المايكرويف بنفس ظروف التفاعل لتحضير البولي أستلين PAs فكانت الحصيلة 70% بطاقة 400 W في زمن 10 دقائق. المسار الآخر إشتمل على تحضير البولي داي أستلين من بلمرة الداى أستلين (دايمر محضر مختبرياً) بأستخدام PdCl₂, CuCl, كعوامل مساعدة، وTHF كمذيب، وفي جو من الأوكسجين النقي وكانت الحصيلة 82% في درجة حرارة 40 م وبزمن مقداره 5 ساعات. شخصت البوليمرات بمطيافية FT – IR, C13NMR, HNMR فأظهرت صحة التفاعلات المتوقعة .