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Synthesis of azo polymers by etheric derivatives polymerization of allyl bromide and studying their bandgap and determine some of their properties

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Abstract: In this research, two ether derivatives of phenolic azo dyes were synthesized via Williamson's reaction according to the S_N2 mechanism. The prepared compounds were radically polymerized using (AIBN) as an initiator and their structures were identified by FT-IR and ^{1}H-NMR. Furthermore, thermal properties of these polymers was made by (DSC). Bandgap energy have been calculated to indicate the ability of these polymers as optical semiconductors, it was 2.8ev, 2.4ev for $P(AO_2)$ and $P(AON_1)$ respectively. Beside the determination of refractive index, kinematic viscosity, density, and degree of Turbidity.

Keywords: Azo polymer, Williamson reaction, radically polymerized, AIBN, etheric derivatives, bandgap, DSC.

اصطناع بوليميرات آزو ببلمرة مشتاقات إيتيرية لبروميد الآليل ودراسة فجوتها الطاقية وتعيين بعض خصائصها الفيزيائية

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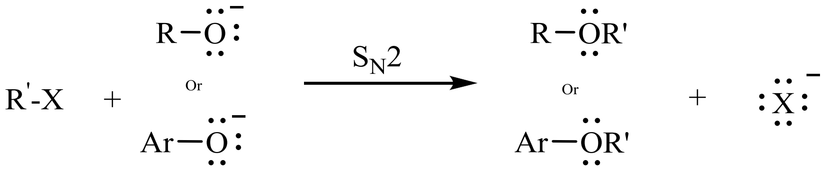
المستخلص: في هذا البحث، أُصطنع مشتقان ايتريين لاصبغة ازو فينولية عن طريق تفاعل ويليمسون وفقاً لآلية. الاستبدال النيكلوفيلي S_N2. تمت بلمرة المركبات المحضرة بلمرةً جذرية باستخدام (AIBN) كبادئ وأُثبتت بنى المركبات المصطنعة بواسطة مطيافيات FT-IR و ^{1}H-NMR. بالإضافة إلى دراسة الخصائص الحرارية للبوليميرات المُحضرة بواسطة (DSC). دُرست عرض الفجوة الطاقية وذلك لمعرفة امكانية استعمال البوليميرات كأنصاف نواقل ضوئية وكانت قيمتها 2.4ev, 2.8ev لكل من $P(AO_2)$ و $P(AON_1)$ على التوالي. كماعُينت كل من قرينة الانكسار واللزوجة الكيناميكية والكثافة ودرجة العكارة.

الكلمات المفتاحية: بوليميرات الآزو، مشتقات إيتيرية، تفاعل وليمسون، بلمرة جذرية، AIBN، فجوة الطاقة، لزوجة كيناميكية، DSC.

Introduction.

Optical properties of Polymers have gained large attention especially in the field of optical storage media and semi-photoconductive[1], due to the quick evolution of manufacturing technology and evolution in polymers structural stability, processability and modifiability. many functional polymers have been synthesized for a variety of purposes, one of the most distinguished is the azo polymers, the presence of the azo functional groups -N=N- in the polymeric structure gives interesting chemical, physical and biological properties[2]. Since the 1960s azo polymers have appeared as materials with substantial applications[3]. Many methods were developed to integrate the azo functional groups into polymeric structures, either within the main chain or on the side chain of the polymer. In general, azo polymers have been synthesized, in many applications, by three main methods chain polymerization, step polymerization, and post-polymerization modification. Thus, Research on azo polymers have a tremendous potential as Smart light-responsive materials. Moreover, precise light modeling research, in the past decades, broadens our understanding on polymer usage and soon become substantial in many scientific explorations[4].

An important route to unsymmetrical ethers is a nucleophilic substitution reaction S_N2 known as The Williamson reaction process is still considered one of the best ways to synthesize an ether, from an alkyl halide with alkoxide or phenoxide ions.[5]



This reaction was developed by Alexander Williamson in 1980 by the reaction between the alkoxide ion or phenoxide with primary alkyl halides and one of the most important properties of this reaction is that there's not water as a by-product of the reaction.[6.7]

The purpose of this research is to combine the vinyl group with azo-phenol dyes, which leads to convert the dyes into colored polymers. And study the possibility of using them as optical semiconductors by determining the bandgap, along with identifying some physical properties of the polymers.

Measurements: All materials are commercial reagent grade and were obtained from Merck Co. and Sigma-Aldrich Co. FT-IR spectra were recorded on Jasco FT-IR 4100 and Shimadzu obtained by the potassium bromide disk method. ^1H-NMR spectra were recorded on a (Bruker AVANCE) 400 MHz spectrometer and $CDCl_3$-D_1 was used as NMR solvent, with TMS as an internal standard. Differential scanning calorimetry (DSC) data was obtained on a DSC-SETARAM (DSC131) instrument at a heating rate of 10° C/min from 25 to 440° C made in France which equipped with liquid nitrogen without a cooling system. The bandgap was measured using spectroscopic ellipsometry combined with transmittance measurements (T), the Refractive index meter brand a Kruss optronic gmbh Germany. turbidity meter type

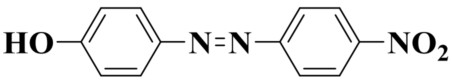
Martini instruments Mi 415, Ostwald viscometer type Fungilab Size150, density meter brand Iso lab D 97877 Wertheim – Germany.

Synthesis of 4-(4-nitrophenyl) diazenyl) phenol (APh1) and (4-phenyldiazenyl) phenol (APh2):

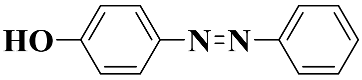
Hydrochloric acid (37%) (0.04 mol, 3.36 mL) was added to the mixture of Aromatic Amine (10 mmol), and 30 mL water, after that, the mixture is cooled to 0° C, then an aqueous solution of $NaNO_2$ (6.9 g, 10 mmol) was slowly added at 0–5° C, the mixture was stirred for 15 min at 0-5° C. A pale yellow and transparent diazonium salt solution was obtained. Then the coupling was carried out by slowly adding the diazotization solution to a solution of phenol (0.941 g 10 mmol), 0.4 g NaOH and 6.26 g Na_2CO_3 in 36 ml water at 0-5° C, after the obtained mixture was stirred at 0–5° C for 3 h, dark red, the colored precipitate of 1 was filtered off and washed several times with acidic water then with water. The resulting precipitate was collected and dried under vacuum. the crude precipitate was recrystallized from ethanol.

Table (1) Azo-phenolic dyes Synthetic in the first stag.

Aromatic Amine	Dye	Melting point	Yield
p-Nitro Aniline 1.380g	APh_1	218 C°	88%
0.91ml Aniline	APh_2	153 C°	83%



APh_1



APh_2

(KBr, Cm^{-1}): **APh_1** 3425 (-OH stretching); 3150 (C_{SP}^{2}-H); 1445 (-N=N-), 1505 1400 (NO_2), 1590 (C=C). (λ max, nm);386.

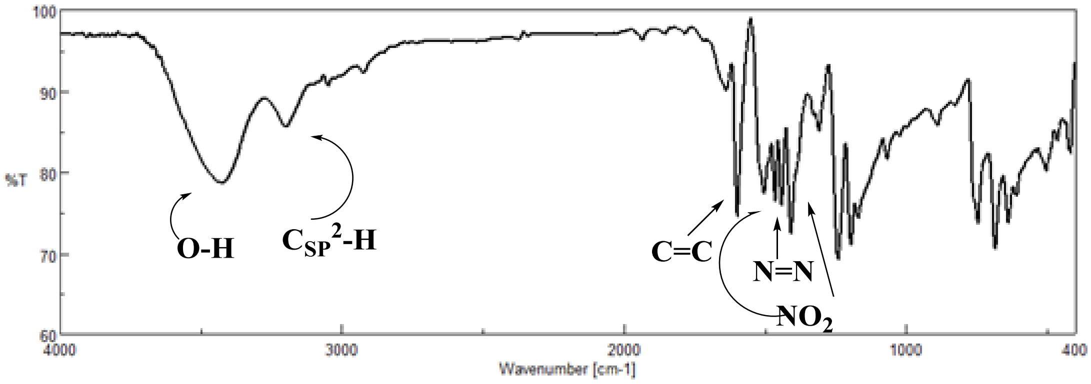


Figure (1) FT-IR spectrum of APh_1

APh_2 3445 (-OH stretching); 3190 (C_{SP}^{2}-H); 1506 (-N=N-), 1605 (C=C). (λ max, nm);354.

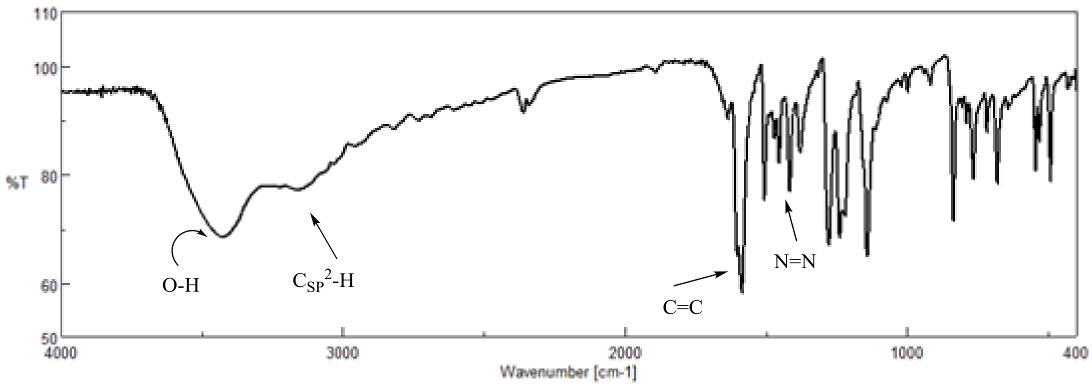


Figure (2) FT-IR spectrum of APh_2

Synthesis of Monomers, 1-(4-(allyloxy) phenyl)-2-(4-nitrophenyl) diazene (AON_1), 1-(4-(allyloxy) phenyl)-2-phenyldiazene (AO_2):

In an inert atmosphere of N_2, the first solution containing (10 mmol) of APh_1, **APh_2** 10 mmol of potassium carbonate anhydrous and a trace of potassium iodide, were mixed and stirred for 1 h at room temperature.

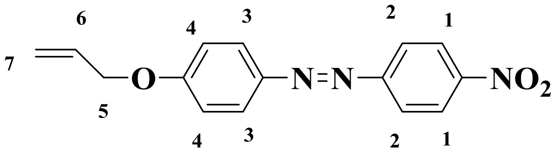
The second solution containing (10 mmol) of allyl bromide and 30 mL of DMF, this solution was added dropwise to the first one and stirred for 48 h at room temperature.

After cooling down, the resulting insoluble inorganic salt was removed by filtration, the residue was poured into a large quantity of water, and extracted by chloroform three times. The chloroform solution was dried over sodium sulfate anhydrous and the inorganic salt was removed by filtration, then dried under vacuum.

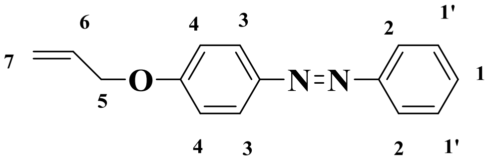
After that, the crude product was purified by silica gel column chromatography eluting with (Ethyl acetate/ n-Hexane) (v/v) to afford a dark orange precipitate product. The pure compound was dried in a vacuum desiccator by P_2O_5. Yield: 67%,60%. M.P 144C°, 137 C°. for **AON_1** and **AO_2**, respectively.

Table (2) etheric derivatives Synthetic in the second stage by Williamson reaction.

etheric derivatives	Dye	Ethyl acetate/ n-Hexane	Melting point	Yield
AON_1	APh_1	30/70	144 C°	%67
AO_2	APh_2	08/20	137 C°	%60



AON_1



AO_2

AON_1: IR (KBr, Cm^{-1}): 3100 (C_{SP}^2-H); 2950 (C_{SP}^3-H); 1498 (-N=N-); 1103 1247 (C-O-C) alkyl aryl ether, 1247 1602 (NO_2), (C=C) 1581.

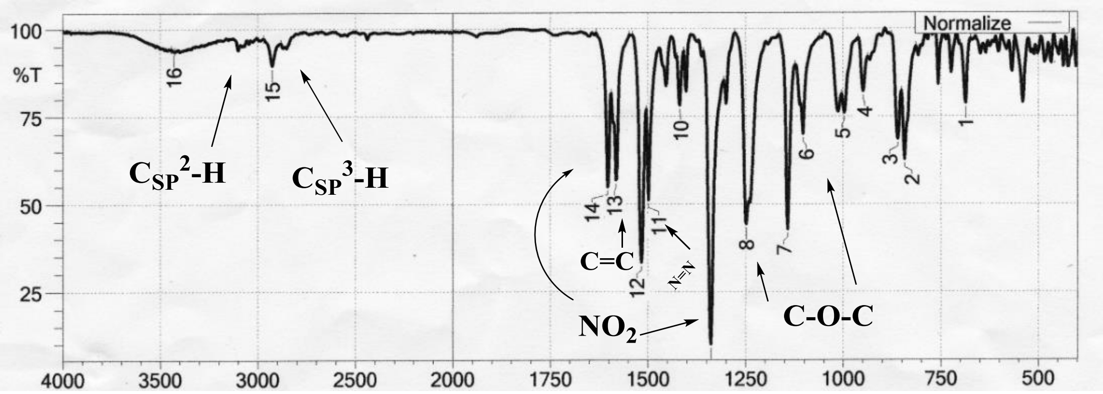


Figure (3) FT-IR spectrum of AON_1

^{1}H-NMR (400 MHz), ($CDCl_3$-d), δ (ppm), J(Hz): (1,1') (C-H Ar) 8.35 (dt, J_4=2.56 Hz, J_3 =4.48 Hz, J_2 =8.88Hz, 2H), (2,2',3,3') 7.96(m, 4H), (4,4') 7.04(dt, J_4=3Hz, J_3 =5.04Hz, J_2=9Hz, 2H), (5,5') (CH_2-O-) 4.52(dt, J_4=1.4 Hz, J_3 =2.92 Hz, J_2=5.28 Hz,2H), (6) (=CH-) 6.07(m,1H), (7,7') (CH_2=) 5.3 (m,1H) 5.4(m,1H).

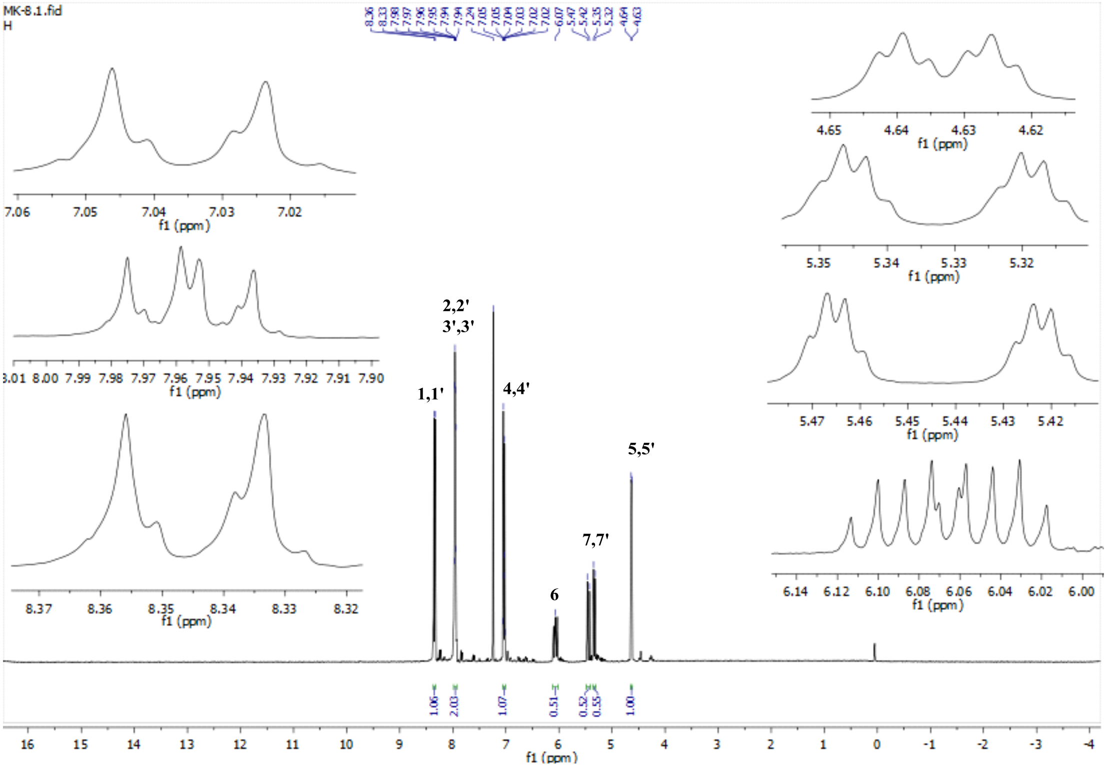


Figure (4) ^{1}H-NMR spectrum of AON_1

AO_2: IR (KBr, Cm^{-1}): 3125 ($C_{SP}{}^2$-H); 2975 ($C_{SP}{}^3$-H); 1502 (-N=N-); 1095 1303 (C-O-C) alkyl aryl ether, (C=C) 1589

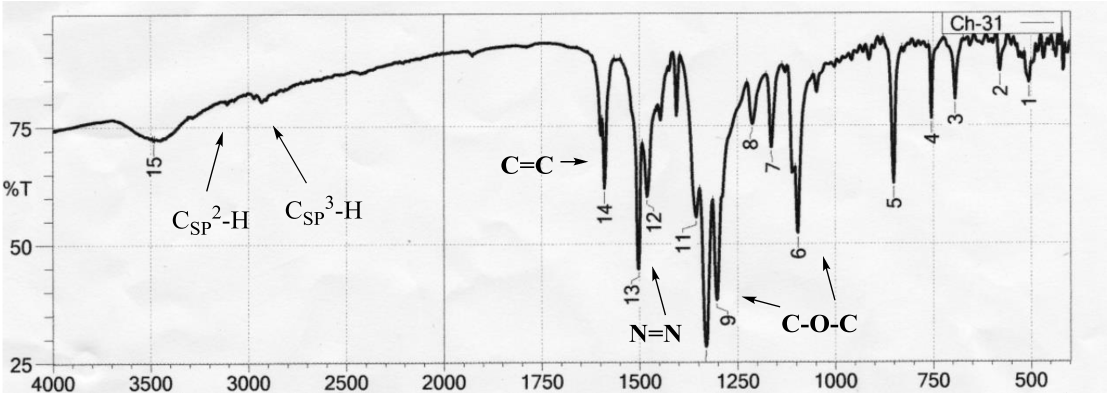


Figure (5) FT-IR spectrum of AO_2

^{1}H-NMR (400 MHz), ($CDCl_3$-d), δ (ppm), J(Hz):, (C-H Ar) (1) δ= 7.42(m,1H), (1',1'') δ=7.48(m,2H), (2,2') δ=7.89(dt, J4=3.08,Hz,J3= 5Hz, Hz,J2=6.92 Hz,2H), (3,3') δ=7.85 (dd,J3=1.36 Hz,J2=8.48 Hz,2H), (4,4') δ=7 (dt J4=3.12Hz,J3 5.2 Hz,J2=9.08 Hz,2H), (5,5') (CH_2-O-) δ= 4.6 (dt,J4=1.48Hz,J3= 2.96 Hz,J2=5.32Hz,2H), (6) (=CH-) δ= 6.04(m,1H), (7,7') (CH_2=) δ= 5.3 (m,1H) 5.4 (m.1H).

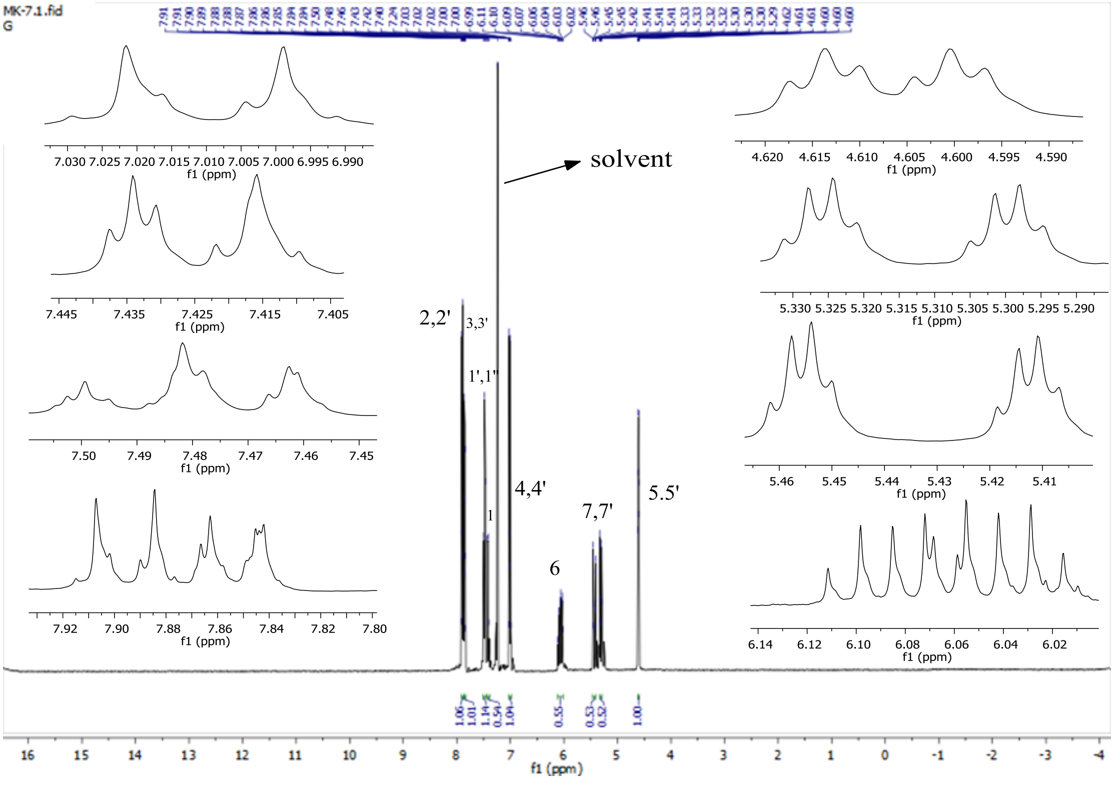


Figure (6) ^{1}H-NMR spectrum of AO_2

Synthesis of polymers:

(10 mmol,2.38 g) of AON1, AO2 was dissolved in 20 ml of THF, and (1mmol, 0.1642 g) 1% mol (based on the monomer) of AIBN was added. The monomer solution was degassed by passing nitrogen

for 30 min and polymerized at 65°C for 48 h. At the end of the reaction, the polymers obtained were precipitated in methanol, the pure compound was dried in a vacuum desiccator with P_2O_5.

Thin-film preparation:

The solutions of the polymers P(**AON_1**), **P(AO_2)** in chloroform were spun coated on the substrates at 1000 rpm for 60 s. Promptly after the deposition, the films were cured in an oven at 65°C for 120 min in order to eliminate the solvent.

Results and discussion.

The dyes had been synthesized by the classical Azo dyes synthesis method.[8.9]

At the next stage, the ether derivatives of the prepared dyes had been synthesized by Williamson Reaction, depending on the nucleophilic-substitution S_N2 mechanism.[10.11]

The IR spectrum of these dyes has shown the disappearance of the OH stretch absorption band and the Appearance of two new bands that belong to the ether group (C-O-C).

In the third stage, the polymerization process was carried out according to the radical polymerization method using the 2,2'azobisisobutyronitrile (AIBN) initiative.[12.13.14.15]

Depending on the (C=C) group that existed in the monomer structure, and in comparison, with similar compounds previously studied.[16.17]

The ^{1}H-NMR spectrum of the formed polymers shows the appearance of new peaks belonging to CH_3-, -CH_2- and CH groups resulting from the radical polymerization process. It also appears that the termination step took place through disproportionation process, due to the appearance of two peaks between 5,3 ppm and 6.1 ppm, back to the protons of the allyl group for AON1 and AO2 respectively.

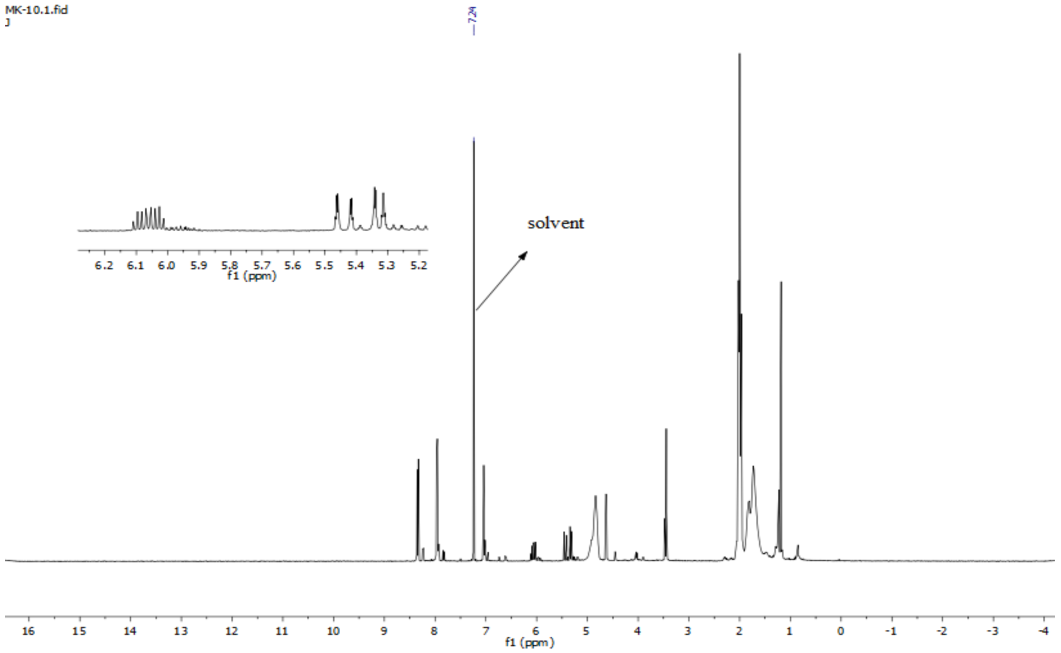


Figure (7) ^{1}H-NMR spectrum of $p(AON_1)$

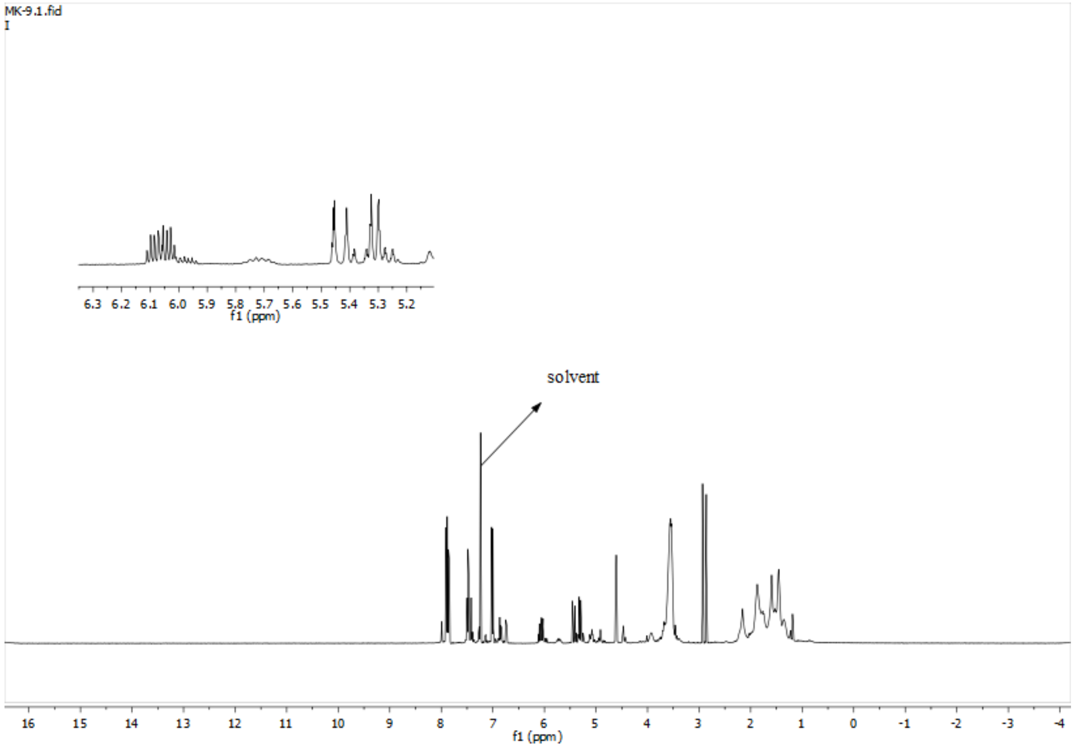


Figure (8) ^{1}H-NMR spectrum of p(AO2)

Thermal properties:

The thermal properties of the prepared polymers were determined by differential scanning calorimetry (DSC). Figures (9) and (10)

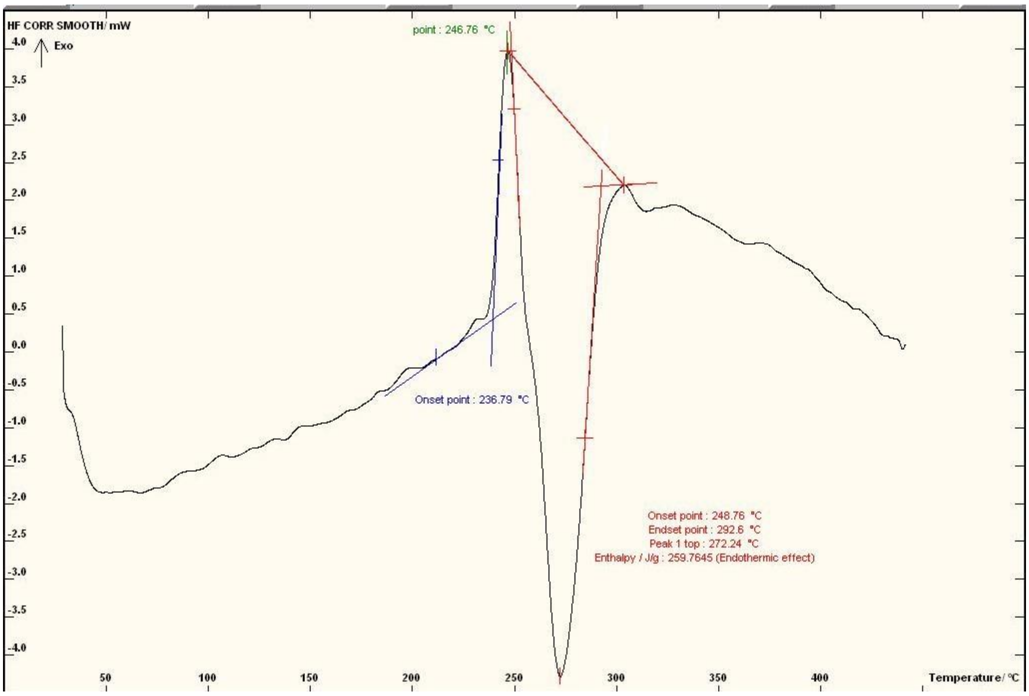


Figure (9) DSC Curve of the P(ANO1)

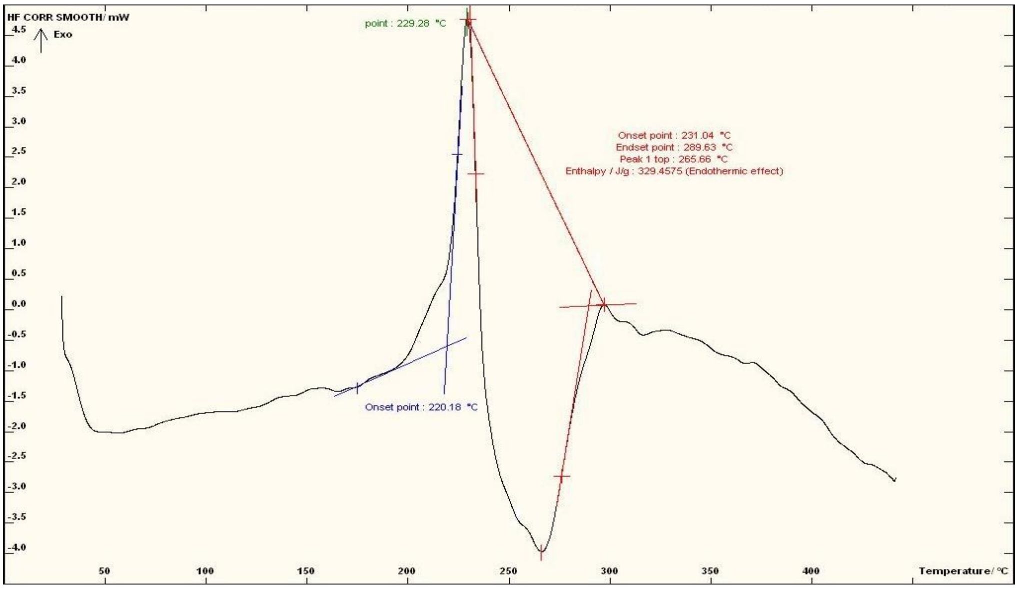


Figure (10) DSC Curve of the P(AO2)

The Curves illustrate glass-transition temperatures (Tg) of polymers to be 190° C and 160° C for AON1 and AO2, respectively.

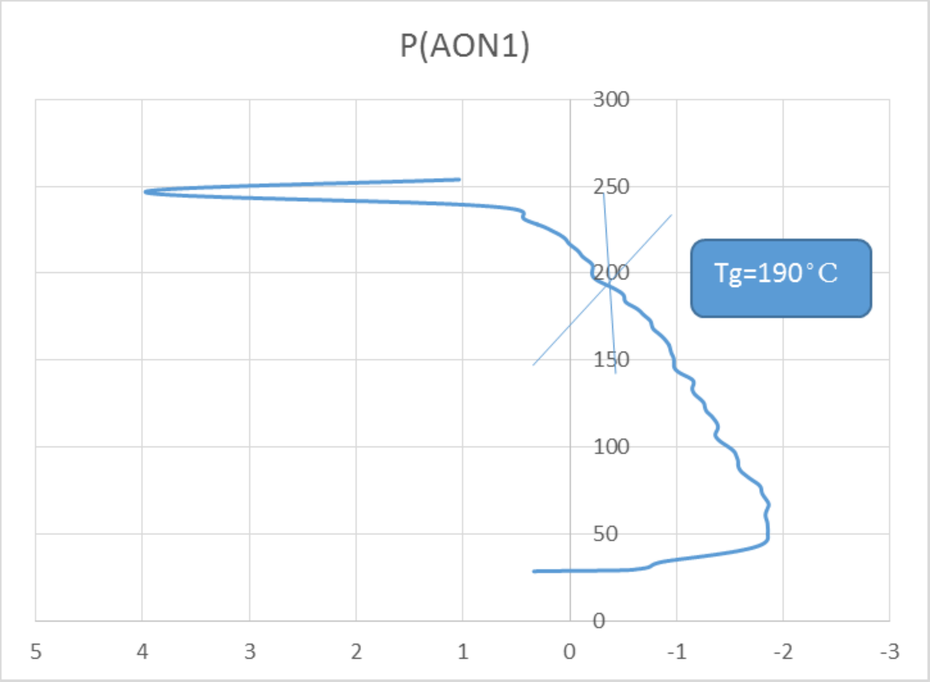


Figure (11) Curve (Tg) of the P(AON1)

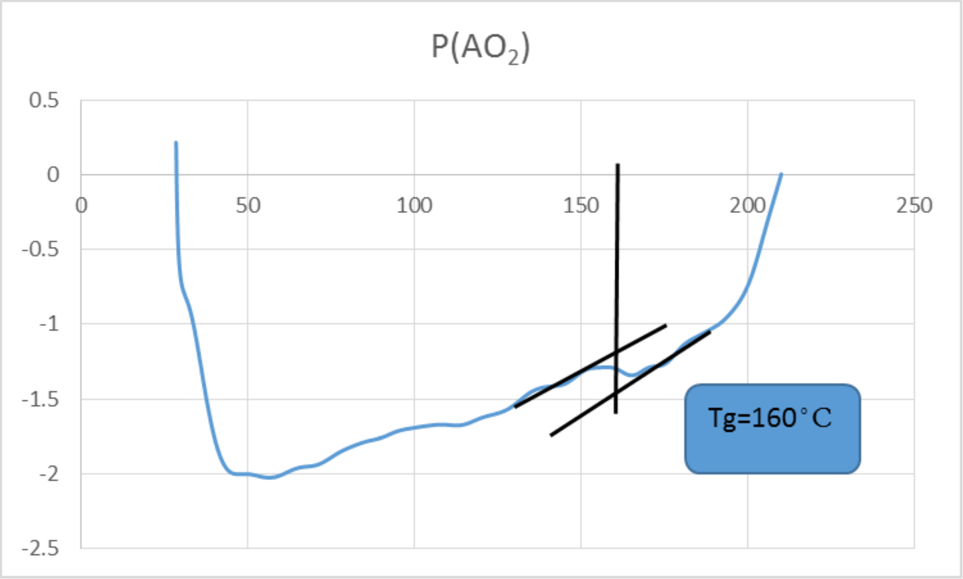


Figure (12) Curve (Tg) of the P(AO2)

In addition to two peaks, the first is exothermic and the second is endothermic. Concerning the exothermic peak to be around 249° ,231° C for AON1, and AO2, respectively. Attributed to the cis form switched back to the trans form thermally[18], Regarding the endothermic peak to be around 272°,265°C for AON1, and AO2, respectively. Attributed to the degree of dissociation.

The comparison curve between the two polymers shows the shift of temperatures for both the glass-transition temperatures, the exothermic peak, and the endothermic peak, towards the higher values, because of the pulled nitro functional group.

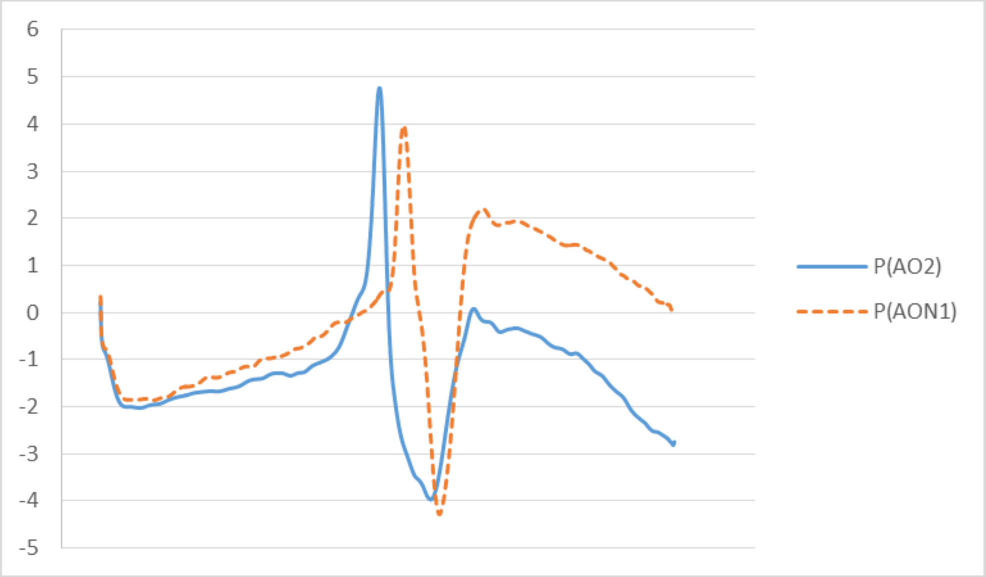


Figure (13) The comparison curve between P(AON1) and P(AO2)

The Optical and physical properties:

One of the most important factors controlling optical properties is the optical energy bandgap (Eg). Which was determined using Tauc's method. it's used to determine the bandgap in semiconductors[19.20] and to describe the optical properties of amorphous materials.[21]

That by plotting the function $(\alpha h\nu)^{1/n}$ versus $h\nu$ and using the equation:

$$(\alpha h\nu) = B (h\nu - Eg)^{n}$$

B: Constant depends on the properties of the valence and the conduction bundles. α (Cm^{-1}): the absorption coefficient, $h\nu$(eV): the photon energy. Eg: band gab. n=0.5 for a direct allowed transition, n=1.5 a direct forbidden transition. n=2, n=3 for an allowed and forbidden indirect transition respectively.[22.23 .24]

Figures (14) and (15) shows The bandgap curves of P(AON1) and P(AO2), respectively

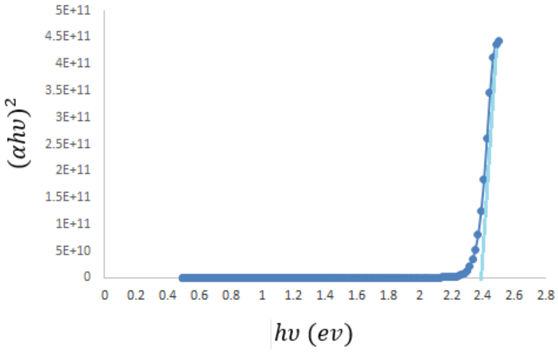


Figure (14) The bandgap curve of the P(AON_1)

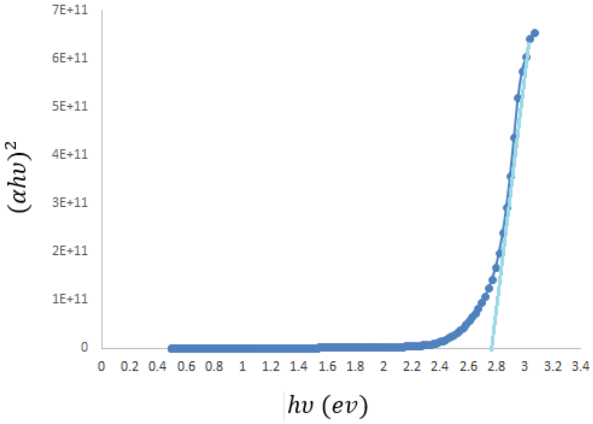


Figure (15) The bandgap curve of the P(AO_2)

Table (3) The bandgap value for P(AON1) and P(AO2)

	P(AON_1)	P(AO_2)
Bandgap	2.4	2.8

One can notice that the value of the optical energy band gap of prepared and studied azo polymers changes in the following way: P(AO_2)> P(AON_1).

In this regard, the value of the optical energy band gap can be reduced by adding a pulling functional group (NO_2). [15]

Some physical properties of the prepared polymers were determined in order to know any possibile application later on. Refractive index, density, and viscosity given in Table 2 were measured in a chloroform solution (10 g/L). Moreover, the degree of Turbidity for the prepared polymers aqua solutions were measured at a concentration of 10 g/L.

Table (4) physical properties values for P(AON1) and P(AO2)

	P(AON_1)	P(AO_2)
Refractive index	1.4405	1.4397
(Kinematic Viscosity)	0.6149	0.57695
Density	1.4931 g\ml	1.4850 g\ml
Degree of Turbidity	61 NFU	400 NFU

Conclusion.

the polymers were prepared by radical polymerization using AIBN as an initiator from synthesized monomers containing the functional –C=C- group. The DSC curves of the two polymers showed an endothermic peak due to degree of dissociation and an exothermic peak due to attributed to the cis form switched back to the trans form. Measuring the bandgap for the polymers demonstrated using them as optical semiconductor. The value of the bandgap can be reduced by adding pulling functional groups. Refractive index, density, viscosity and degree of Turbidity were determined in order to know any possible application later on.

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