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Influence of Annealing on the Optical Properties of Polyacrylonitrile Thin Films

Mohammad Malik Abood[1]*, Ikram Kamal Jasim[2] , F. Bahrani[2] , Kahtan A. Mohammed[3] And Ali Q. Abdullah[2]

[1]Ministry of Education, General Directorate for Education in Najaf, Iraq, Najaf

[2]Physics department, College of Science, Basrah University

[3]Faculty of pharmacy, Jabir Ibn Hayyan Medical University, Najaf, Iraq

*Corresponding author: Email address: *mohammadmalikmfjm@gmail.com*

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Abstract

In this paper, a polyacrylonitrile polymer was prepared and study its optical properties with different temperatures a films clear change from light brown to very dark brown at a temperature range (25- 280ºC), although the polymer is characterized by high transparency and analyzing the absorbance spectrum of the prepared films, the direct energy gap was calculated, which was in the range of 4.01eV for without annealing films to decrease to 1.63eV for films annealing at a temperature of 280ºC with these changes in properties, these films can be used in optical applications such as solar cells and photodetectors.

Introduction

Polyacrylonitrile (PAN) both semi-crystalline and non-crystalline polymers come in different forms. Polymer crystalline structures play an important role in the physical, chemical, electrical, mechanical, and thermal properties. The crystalline PAN structures and unit cells have been under contention since the PAN heat history exhibited many polymorphs [1]. Despite being thermoplastic, it does not disintegrate in typical circumstances. It disintegrates first, then melts. If heating rates reach 50°C per minute or higher, melting occurs above 300°C [2]. It is a polymer with many uses. Reverse osmosis hollow fibers, textile fibers, PAN peroxide fibers, ultra-filtration membranes, and other goods are all used in the production process. [3]. It has properties including low density, thermal stability, high strength and modulus of elasticity. Polyacrylonitrile (PAN) has very good chemical and physical

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properties that make it very easy to form nanofibers such as good commercial availability, mechanical properties and environmental stability [4][5]. Because of these special qualities, PAN is a crucial polymer in high technology. Super capacitors, solar cells, photodetectors [6], catalysis, sensors, and energy conversion and storage are just a few of its numerous uses. Awnings for the outdoors, fiber-reinforced concrete, and hot gas filtration systems have all used homo polymers of poly acrylonitrile as fibers [7]. Knitted clothing, including socks and sweaters, are frequently made using copolymers that contain polyacrylonitrile as fibers [8], in addition to outdoor goods like tents and related stuff. Clothing that says "acrylic" on the label is made of a polymer called polyacrylonitrile. In 1942, it was transformed into spun fibers and sold under the brand name Orlon [9]. Due to the presence of a high polarity group (CN) along the polymer chain, polyacrylonitrile is a versatile polymer [7]. In this study, the optical characteristics of the produced Polyacrylonitrile polymer were examined at various temperatures.

Excremental part

Preparation of acrylonitrile polymer (PAN)

Polyacrylonitrile (PAN) C_3H_3CN with a molecular weight of 15000 g / mol was used in this research, and the prepared solvent dimethylformamide (DMF) C_3H_7NO was obtained from the BDH company. PAN thin films were synthesized by melting 2g of PAN in 15 ml of dimethylformamide (DMF) solvent. The solution is placed on the mechanical stirrer at a temperature of 70ºC for two hours with continuous stirring. The thin films were prepared using the simple method of spin casting. Wide-area films and different thicknesses can be obtained by pouring the polymer solution on sheets of glass of dimensions (2×2) cm^2, which are cleaned well by washing them with a group of polar solvents such as ethanol and exposure to the plates into a stream of distilled water using an ultrasonic device (NT-628+) manufactured by (GUANGZHOU HENWEI ELECTRONICS TECHNOLOGY) then the glass plates are dried and kept in a dry place [8].

Annealing of polymeric films

The prepared films are placed in the electric oven with a range of up to 1000ºC obtained from the Qallenhamr company. The glass slides were exposed to different temperatures, ranging from (150, 180, 200, 250, 280) ºC, respectively, where the films were left for two hours at a constant temperature [9]. Figure 1. shows the annealing samples.

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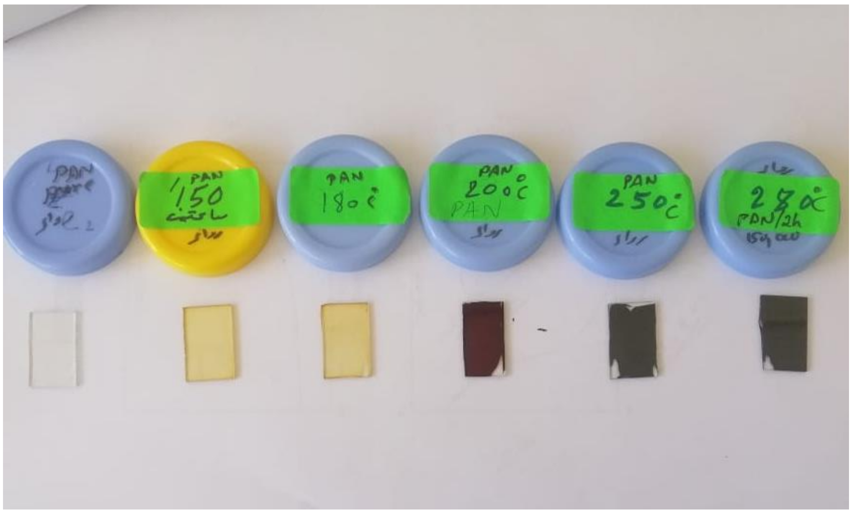

Figure 1: Polyacrylonitrile thin films after annealing

Results and discussion

Figure (3) shows the absorbance spectrum of films treated with different temperatures, as shown previously (untreated, 150, 180, 200, 250, 280ºC), respectively. It is noted in figure (3) that with an increase in the annealing temperature there is a displacement towards the red wavelengths (large wavelengths). The reason is that the increase in temperature works to break the triple bonds that link carbon with nitrogen (the cyanide group) and double bonds are formed forming what is known as cyclic structures, and this is a very clear process during the color change of the membranes from light brown to dark brown[10]. Figure (2) show scheme of PAN structure during cyclization.

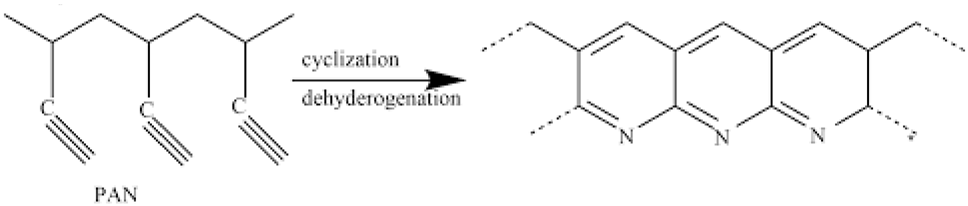

Figure (2): Structures of PAN during the Cyclic Reaction [9]

To determine the optical band gap of the materials in transmitting radiation, optical characteristics are studied. The relationship between the absorption coefficient (α) was also drawn like a function of the energy of the incident photon as illustrated in Figure (3) using the following equations [11]:

$$\alpha = 2.303\left(\frac{A}{d}\right) \qquad (1)$$

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It is clear that the shift that happened towards lower energy values can be observed, and this is due to the high in the ring structures as a result of the effect of temperature, and, accordingly, the films change colors from light brown to very dark brown, as shown previously.

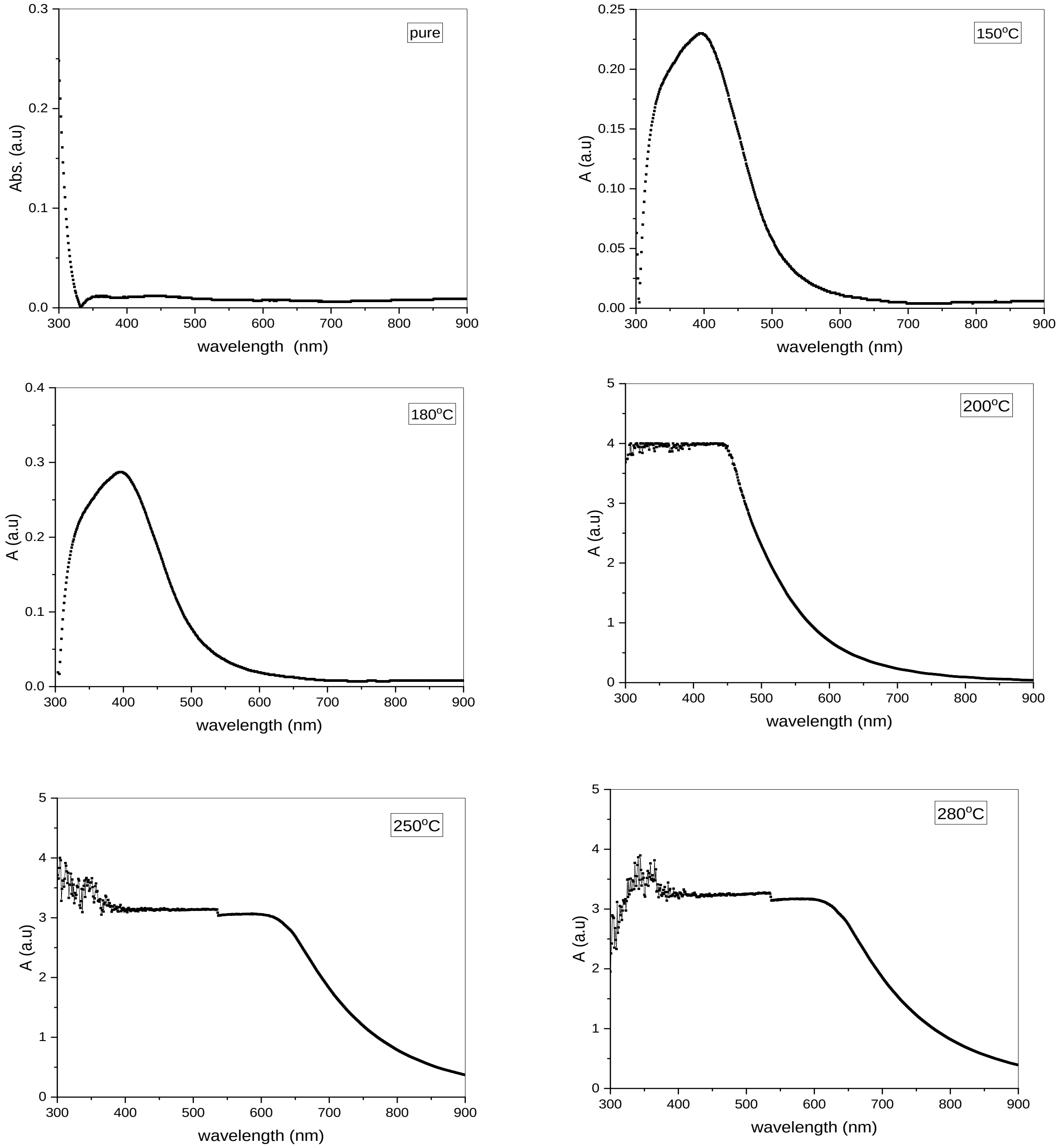

Figure (3):the absorbance spectrum as a function of wavelength at different heat treatments (pure, 150,180,200,250,280) ºC.

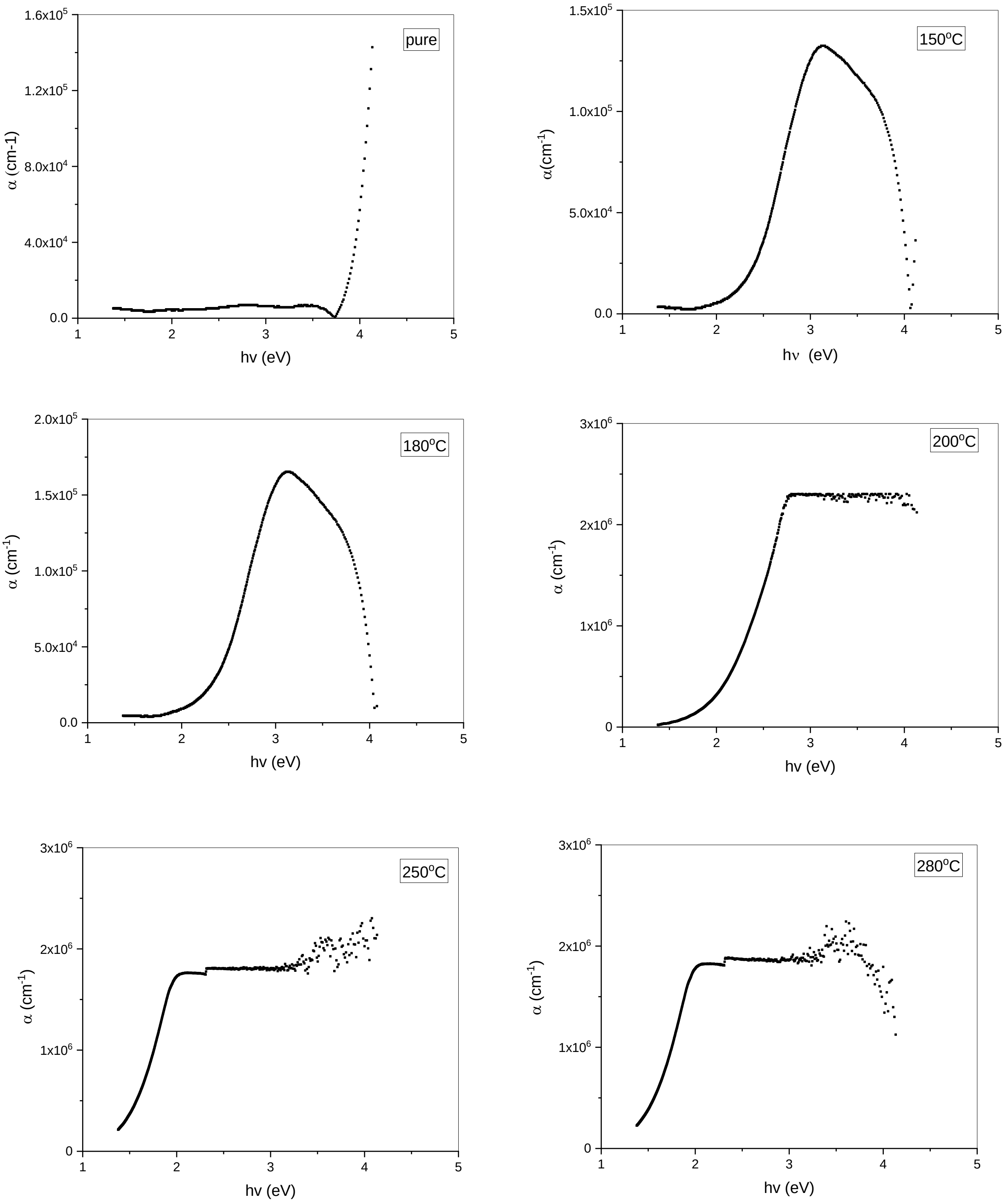

Figure (4): The spectrum of the absorption coefficient as a function of the incident photon energy at different heat treatment (pure, 150,180,200,250,280) ºC.

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In general, the semiconductor and insulator are spliced into two forms: (I) direct band gap and (II) indirect band gap. If the top of the valance band and bottom of the conduction band are the same, then the direct band gap exists, if it is not the same, then the indirect band gap transition are obtained [12].

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

Where, Eg is optical energy band gap, A is proportionality constant, and is absorption coefficient. where n for direct and indirect transitions, respectively, equals ½ and 2 for direct and indirect transitions respectively.

The direct energy gap of the films prepared under study and annealing at different temperatures calculated by drawing the relationship between $(\alpha h\nu)^2$ as a function of the energy of the incident photon as shown in Figure (5) and from the linear region it is possible to draw a straight line cutting the x-axis, where the cut-off value represents the direct energy gap of the prepared films.

Table (1) shows the values of the direct energy gap with different annealing temperatures. It is noted from the table that an increase in the annealing temperature leads to a decrease in the energy gap.

Table (1): Energy gap values for direct transitions of films prepared from annealing Polyacrylonitrile at different temperatures.

Annealing Temperature(°C)	E_g(eV)
Pure	4.01
150	2.58
180	2.57
200	2.44
250	1.66
280	1.63

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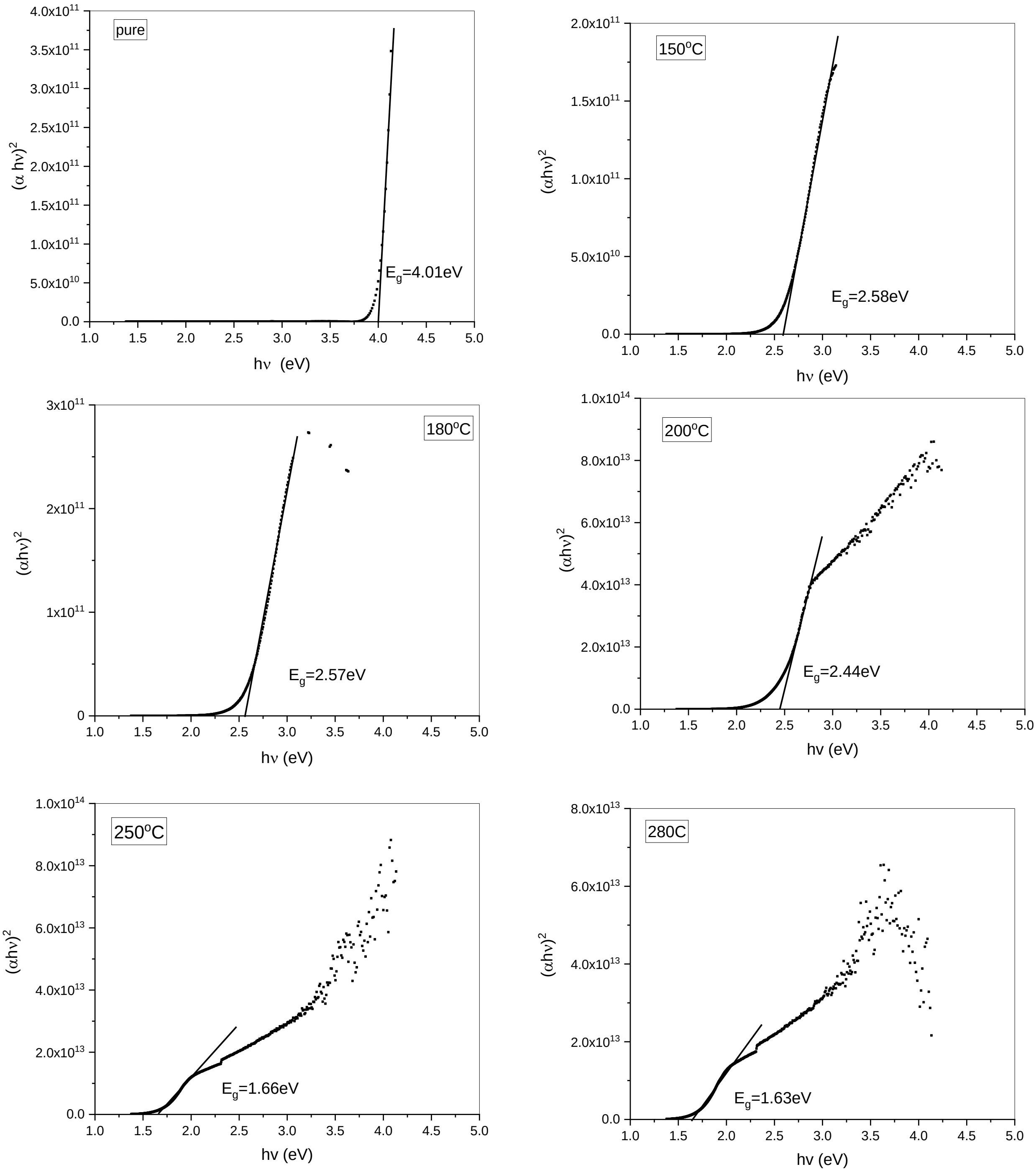

Figure (5): The spectrum of the absorption coefficient as a function of the incident photon energy at different heat treatment (pure, 150,180,200,250,280ºC).

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Conclusion

A different temperatures for the purpose of being able to include the films in one of the electronic applications, where a clear change in the color of the films was observed from light brown to very dark brown at a temperature of 280ºC, although the polymer is characterized by high transparency and analyzing the absorbance spectrum of the prepared films, the direct energy gap was calculated, which was in the range of 4.01eV for without annealing films to decrease to 1.63eV for films annealing at a temperature of 280ºC. The possibility of including the polymer in one of the electronic applications such as solar cells, because it has a small energy gap after heat treatment.

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