Optical properties of Polystyrene doped with KPF_6 thin films

Ali S. Ali

Al-Muthanna University, College of science, Department of physics

Basrah-Iraq

Abstract:

Thin films of Polystyrene (PS) doped with Potassium hexafluoro phosphate (KPF_6) for different weight ratio (0, 5, 7.5, 10%) were prepared by the cast method. The Absorption spectra of thin films were studies at the wavelength range (300-700nm). There are represented by The Absorption (A) and Transmittance (T) spectra. The Absorption coefficient (α), Reflection coefficient (R) and Urbach (Localized State) energy (Eu) were computed.

We found that the polymeric films having the $\pi \rightarrow \pi^*$ electronic transitions and indirect energy gap which is decrease with increased the weight ratio of KPF_6 from (2.45)eV for PS pure to (2.1)eV for the ratio 10% of added. But there is increase in the phonon energy with increase KPF_6; also, we found that the Urbach energy was unstable with increase the KPF_6.

Keyword: Polystyrene , Optical constant, Urbach energy, doped , Potassium hexafluoro phosphate (KPF_6)

1- Introduction:

Commercial polymer based materials are usually complex. They consist of a large number of components, which can be other polymers, low molecular weight organic additives, or non-organic fillers. The large number of components is dictated by the desired bulk properties, such as mechanical toughness, thermal expansion, but also by their surface properties, such adhesion, abrasion, and optical appearance.(Monika Spienger,2003)

Among the optical properties reaction absorption and scattering of light are the most

important. Since all polymers possess specific absorption bands in the infrared part of the spectrum, the infrared spectrum is one of the most valuable in the analysis of polymers (K.S.majdi, 1997), Polystyrene is one of the polymers that is known can be see in Figure(1)

Polystyrene is a thermoplastic substance, which is in solid (glassy) state at room temperature, but flows if heated above its glass transition temperature of about 100°C (for molding or extrusion), and becomes solid again when cooled. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. It can be cast into molds with fine detail. Polystyrene can be transparent or can be made to take on various colors.(G. Natta, 1960)

Polystyrene foams are good thermal insulators and are therefore often used as building insulation materials, such as in structural insulated panel building systems. They are also used for non-weight-bearing architectural structures (such as ornamental pillars). PS foams exhibit also good damping properties, therefore it is used widely in packaging. Because polystyrene is an unfuctionalized aromatic hydrocarbon polymer (Green, B., 1969). He was soluble in most organic solvents such as ethylacetate, dichloromethane, Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF), toluene and chloroform, and it was insoluble in water, low molecular weight alcohols, diethyl ether and hexanes (Shemyakin, 1965).

The aim of this work is prepare thin films polystyrene doped with KPF_6 using cast methods and study their optical properties for it represented by the Absorption and Transmittance spectra, Reflection coefficient (R) and Urbach (Localized State) energy (E_u) to know the effect of KPF_6 on polystyrene.

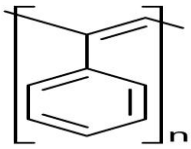


Fig.(1): Chemical Structure of polystyrene

2- Experimental method:

Glass substrates were cleaning before deposition process by distilled water and dried. Thin films of PS were prepared by cast method. The polymer (PS) was easy soluble at the temperature of (50^{o}C) in a chloroform ($CHCl_3$) solvent using magnetic stirrer for 60 min. This solution mixed with different weight ratio (0%, 5%, 7.5%, 10%) of Potassium hexafluoro phosphate (KPF_6) as table (1). Each ratio of solution was casting on glass substrate (2.5x7) cm^2.

Table(1):shows the weight ratio to Prepared thin films.

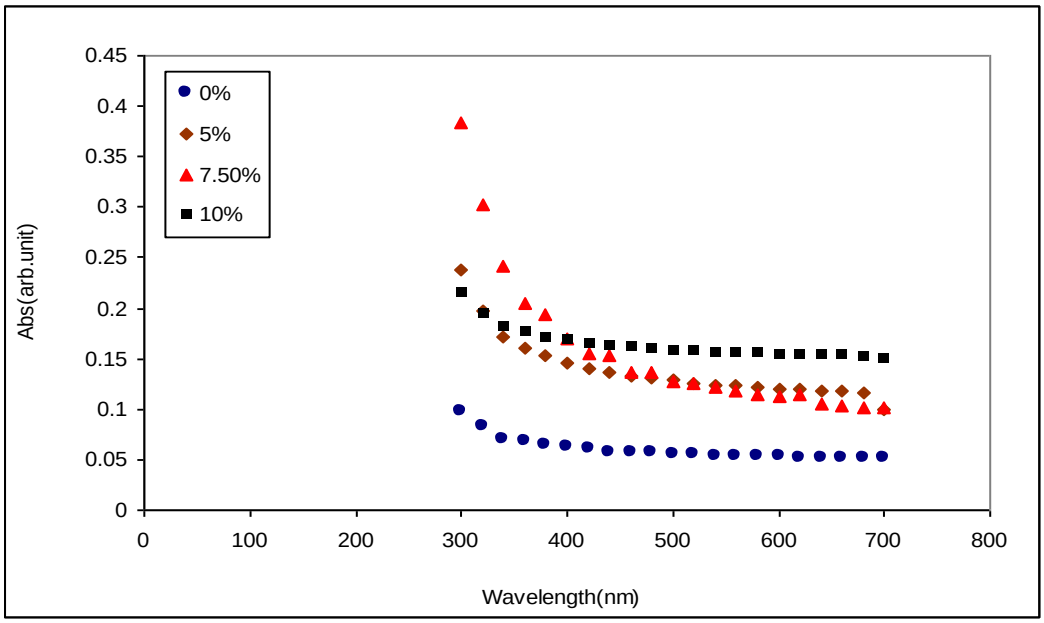
No. of Sample	PS(gm)	KPF_6(gm)	$CHCl_3$(ml)	Wt.%
1	1	0	20	0
2	0.95	0.05	20	5
3	0.925	0.75	20	7.5
4	0.9	0.1	20	10

The preparing films put at room temperature (25^oC) for (24 hr.) to get polymerized homogeneous solid films of doped PS. The thicknesses of the films were measured by using (digital thickness gauge meter with stainless steel substrate).The optical measurements were recorded at room temperature using (PU-1100-UV-VIS. Spectro-photometer) in wavelength range (300-700) nm.

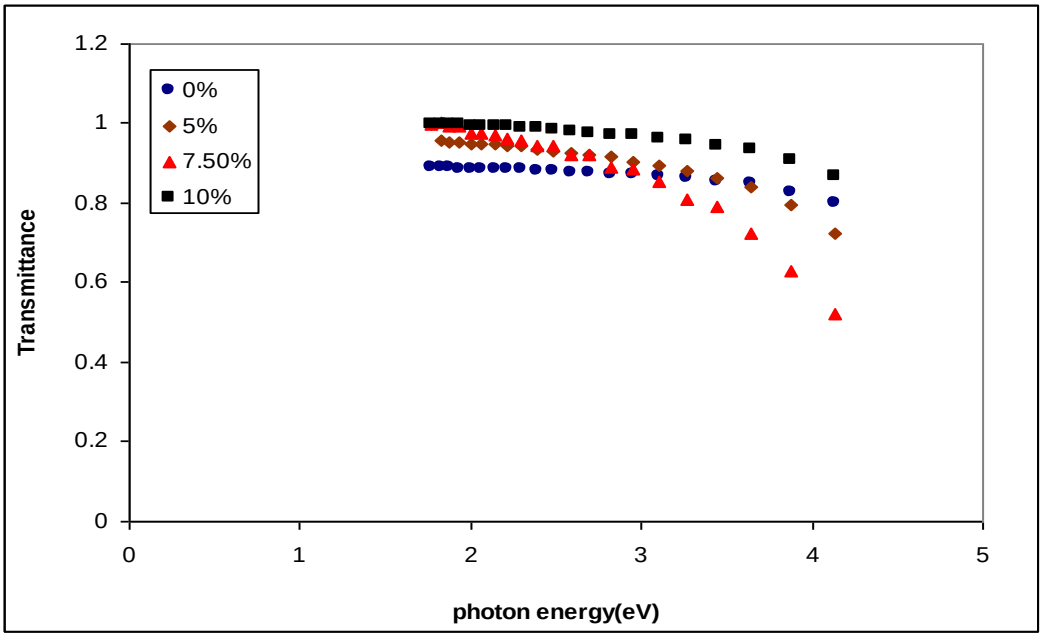
3- Results and Discussion:

3.1. Optical studies

The Absorption (A) and Transmittance (T) spectra for polymer thin films(PS/KPF_6) were recorded using UV-VIS Spectrophotometer in the wavelength range (300-700)nm as Figs.(2&3) respectively. From figures we found that the Absorption was increases with increasing the weight ratio of KPF_6 at the wavelength above 400nm, and it was stable with increase the wavelength, also we see that the transmittance spectrum was increases with increasing the weight ratio of KPF_6. That is because of polystyrene was a transparent and decreases his transparency with increase the weight ratio of KPF_6. The absorption bands in the investigated range of wavelength are associated to the $\pi \rightarrow \pi^*$ electronic transitions (Basma A. El-Badry, 2009 and Tanu Sharma, 2007). This type of transitions occurs in the unsaturated centers of the molecules, i.e. in compounds containing double and also in aromatics. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelengths.



Fig(2): Absorption Versus wave number



Fig(3): Transmittance Versus photon energy

The Absorption coefficient (α) of thin films can be estimated after the correction of the reflectivity by (Ali S. Ali, 2010):

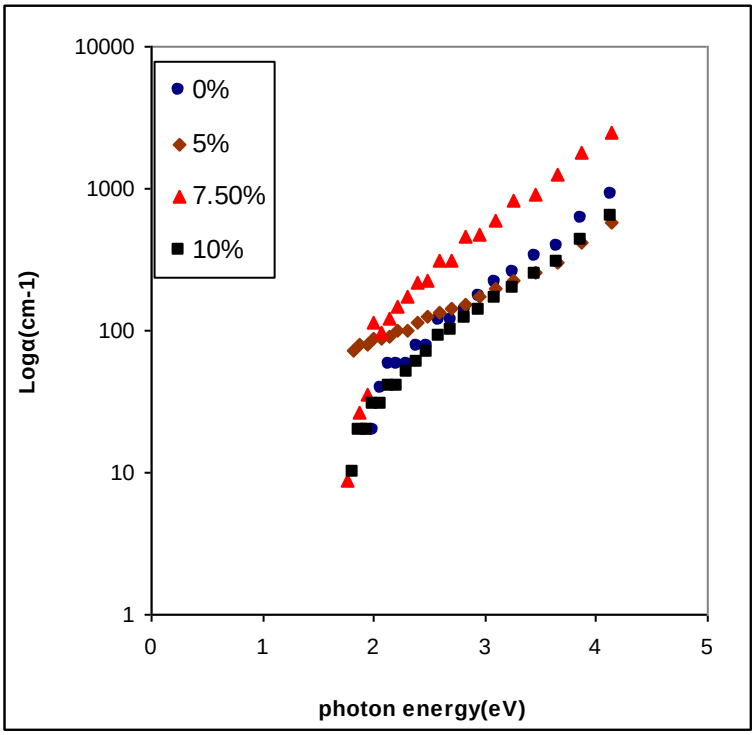
$$\alpha = \frac{2.303}{d} A \qquad \text{.....(1)}$$

Were,d, is the thickness of the film and ,A, is the Absorbance.

The study of α was very important to defined type of transition for the electron such as [allowed direct, forbidden direct, allowed indirect and forbidden indirect]. This case dependent on α values; if $\alpha > 10^4$ that is lead to the transition was allowed or forbidden direct and when $\alpha < 10^4$ these values lead to allowed or forbidden indirect. The absorption coefficient data for all ratio of Fig(4) were analyzed to obtain information on the non-vertical allowed transitions in frame of the theory of bardeen et.al. (Ali S. Ali, 2010 and 2007):

$$\alpha = \frac{A(h\upsilon - Eg \pm Ep)^2}{h\upsilon} \qquad \text{.....(2)}$$

Where ,Eg, is the indirect band gap and ,Ep, is the energy of the absorbed (+) or emitted (-) phonons.

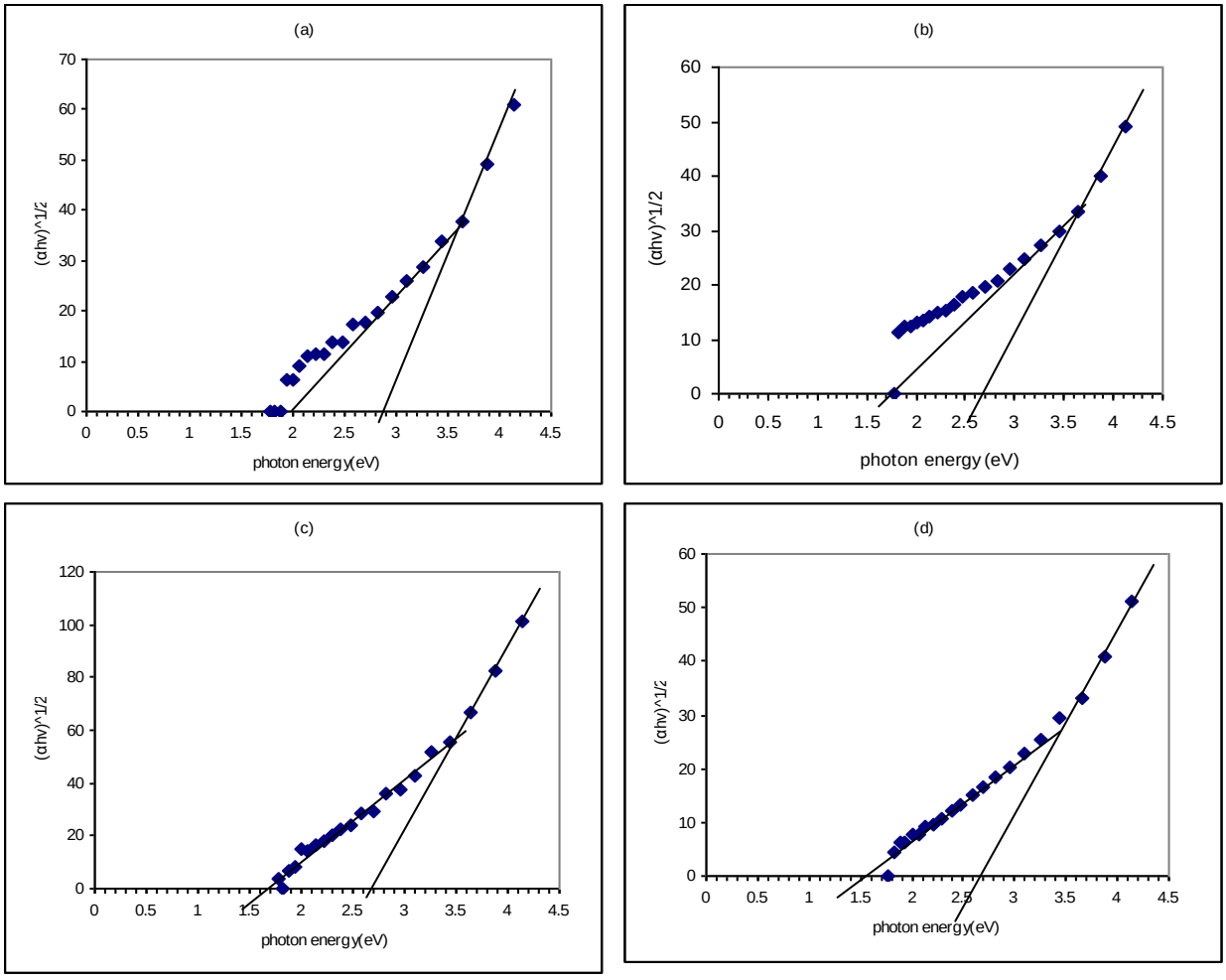


Fig(4): log α versus photon energy for all weight ratio of KPF6

The plot of $(\alpha h\upsilon)^{1/2}$ versus photon energy are shown in Fig (5) with two straight lines are obtained for each case, one at lower energy corresponds to phonon absorption transition and the photon energy intercepts at Eg-Ep. The other lines correspond to phonon energy emission processes and photon energy intercept at Eg+Ep. From intercepts its found Eg and Ep. From figure (5) show the indirect energy gap is equal to (2.45)eV for PS(pure) and the phonon energy that was conjugateed for it is equal to (0.45)eV, this results are presented in table (2).

Table(2):shows the photon and Phonon energy for thin films

No. of Sample	Wt.%	Eg(eV)	Ep(eV)
1	0	2.45	0.45
2	5	2.2	0.5
3	7.5	2.15	0.55
4	10	2.1	0.6



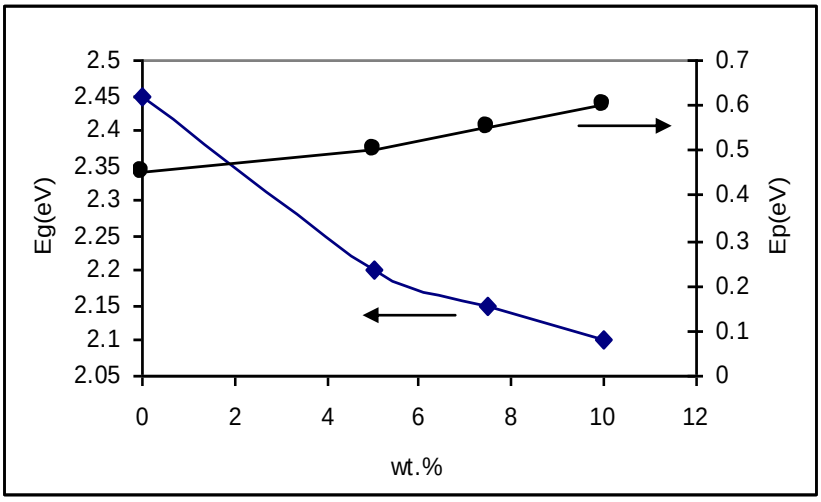
Fig(5): $(\alpha hu)^{1/2}$ versus photon energy for a) PS(Pure) , b) PS/KPF_6 (5%), c) PS/KPF_6 (7.5%) and d) PS/KPF_6 (10%)

Fig(6) shows the relationship between E_g and E_p with the weight ratio of KPF_6 , from figure we found that the E_g was decreases with increasing the KPF_6 But E_p was increases with increasing the KPF_6. This result confirms that the doping produces defects in the polymer polystyrene structure (band fraction, free radical, etc.)(Mathai CJ, 2002)

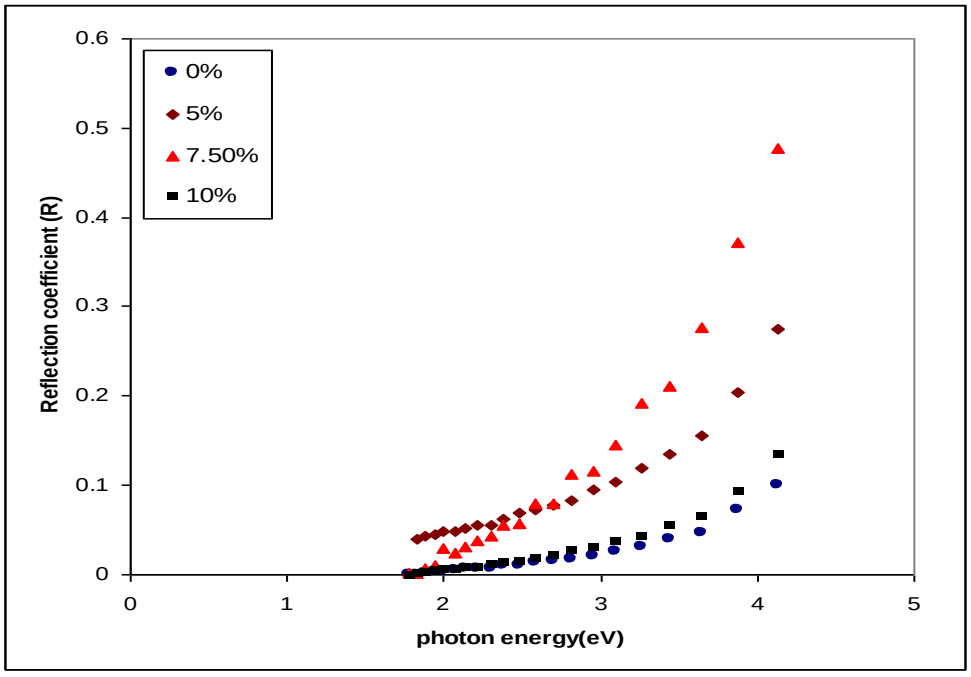
The reflection coefficient (R) can be determined using the following relation (Hashim M. Jabbar, 2010):

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Fig(7) shows the reflection coefficient (R) versus photon energy which indicates that R increased with increase the photon energy for all ratio especially at the ratio (7.5%)



Fig(6): Energy gap and photon energy versus weight ratio of KPF_6.



Fig(7): reflection coefficient versus photon energy for all weight ratio of KPF_6.

3.2. Urbach′s energy

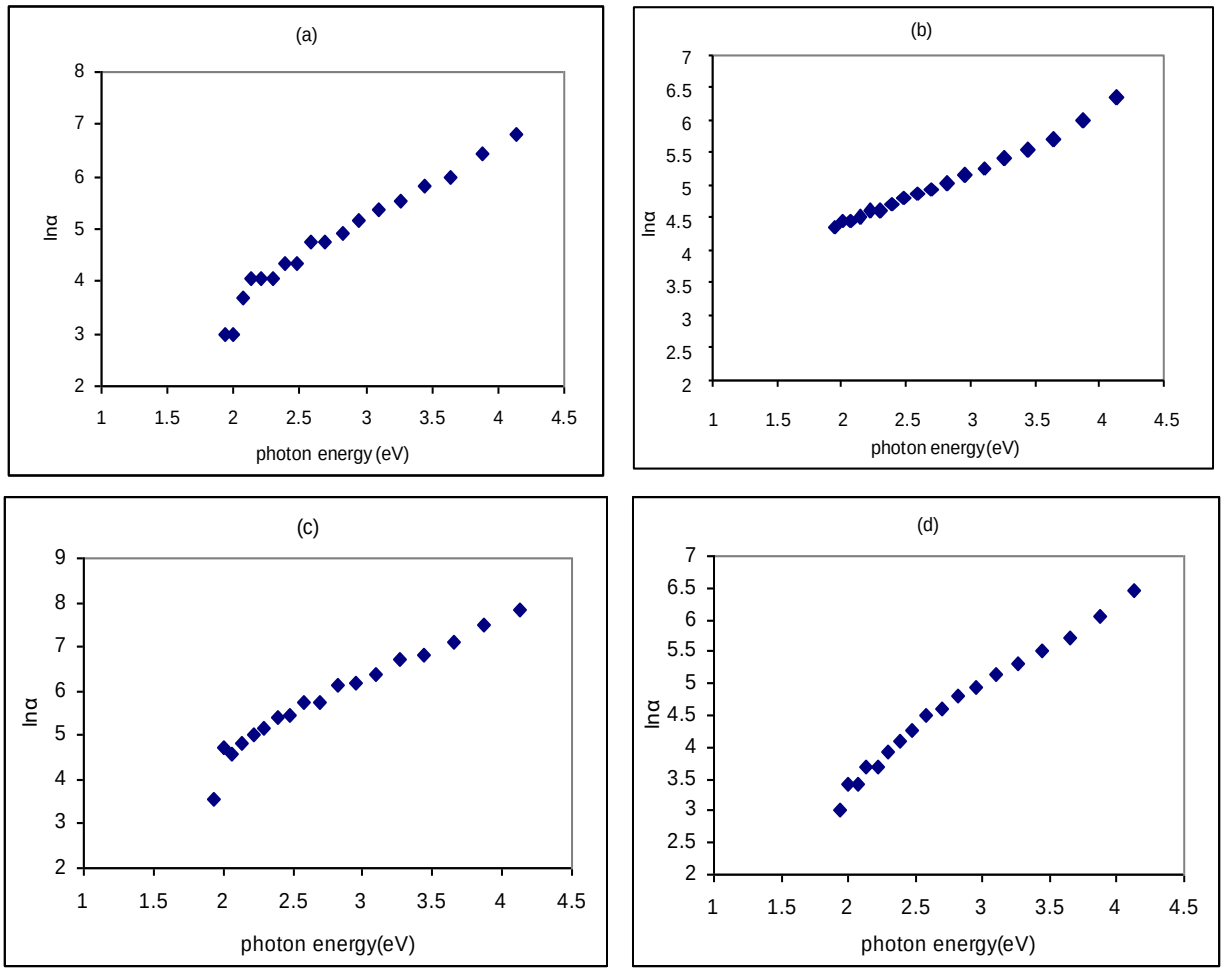
The absorption coefficient $\alpha(h\upsilon)$ near the band edge for noncrystalline materials shows an exponential dependence on the photon energy $(h\upsilon)$ which follows the Urbach's formula (Basma A. El-Badry, 2009):

$$\alpha(h\upsilon) = \alpha_o \exp(h\upsilon / E_u) \quad \text{.....(4)}$$

Where α_o is constant, E_u is an energy that represents the width of the tail of localized states in the forbidden band gap, υ is the frequency and h is planck's constant. The origin of E_u is considered as thermal vibrations in the lattice (M MADANI, 2010). Figure (8) shows the logarithm of the absorption coefficient as a function of the photon energy for polystyrene with KPF_6 at different weight ratios. The values of the Urbach′s energy were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy regions of these curves and listed in Table (3). (Zaki MF, 2008).

Table (3): The Urbach′s energy of polymer thin films

Wt.%	Eu(eV)
0	0.655
5	0.384
7.5	0.654
10	0.850



Fig(8): ln α versus photon energy of a) PS(Pure) , b) PS/KPF_6 (5%), c) PS/KPF_6 (7.5%) and d) PS/KPF_6 (10%)

4- Conclusions:

1- The transition obtained for polymer PS-KPF6 thin films were be indirect transition with the type $\pi \rightarrow \pi^*$ transition.
2- The energy gap (Eg) of polymeric thin films was decreases with increased KPF_6.
3- The phonon energy (Ep) of polymeric thin films were increases with increased KPF_6 with the large value.
4- The Absorption (A) and Transmittance (T) were increases with increasing the weight ratio of KPF_6.
5- The Urbach′s tail energy were unstable with increasing the KPF_6 ratio.

5- References:

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الخلاصة:

تم تحضير اغشية رقيقة من بوليمر بولي ستايرين (PS) المشوب بـالبوتاسيوم هيكسا فلوروفوسفات (KPF_6) بطريقة الصب البرمي وبنسب وزنية مختلفة % (0, 5, 7.5, 10)، ودرست طيف الامتصاص لها ضمن الول الموجي (300-700)nm . تم دراسة طيفي الامتصاصية (A) والنفاذية (T) كدالة للطول الموجي. حسبت كل من معامل الامتصاص (α)، معامل الانكسار (R) وكذلك طاقة اورباخ.

وقد وجد ان الانتقال للالكترونات في الاغشية البوليمرية المحضرة هو من النوع $\pi \leftarrow \pi^*$ وانها تمتلك طاقة فجوة غير مباشرة تقل مع زيادة النسب الوزنية من اضافة KPF_6 من (2.45eV) للبولي ستايرين الغير مشوب الى (2.1)eV للنسبة 10% من الاضافة. في حين تكون هناك زيادة بطاقة الفونون مع زيادة KPF_6. وكذلك نجد ان طاقة اورباخ تكون غيرمستقرة مع زيادة KPF_6.