



## Synthesis and optical properties characterization of poly(vinyl chloride) modified by various alcohol

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### ABSTRACT

The reaction of Poly (vinyl chloride) (PVC) with different alcohols (L) in Tetrahydrofuran (THF) forms the PVC-L compounds. The resulted compounds have been characterized by spectroscopic methods. The structures of these complexes were studied by FTIR and UV-VIS spectrophotometry. The optical properties in the region from (200-900 nm) were recorded using UV-VIS spectrophotometer. The optical data analyzed and interpreted in term of the theory of phonon assisted direct electronic transitions. The measured values of energy gap ( $E_g$ ) for pure and modified PVC get favor the following order:

PVC > PVC-LI > PVC-LII > PVC-LIII > PVC-LIV > PVC-LV > PVC-LVI > PVC-LVII

**Keywords:** Modified PVC, Optical properties, Energy Gap.

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### INTRODUCTION

One way of improving the properties of a polymer is by binding the polymer to a chelating ligand. Those affected properties include enhanced thermal stability, multiphase physical responses, compatibility, impact response, flexibility, and rigidity. The synthesis of such polymer has been an active field of research for a while [1-3]. The selection of ligand has covered a wide spectrum of chelating molecules such as polydentate amines, crownethers, phosphines and bipyridines which have been utilized to bound with mainly poly (styrene-divinylbenzene) copolymers [4,5].

These studies are mostly concerned with ion-binding and catalytic aspects. However, studies concerning whether, and to what extent, such organic compounds can influence the properties of the macromolecule are rare [6].

PVC is the most versatile plastic [7], and there have been reports of modification of this polymer through the introduction of aromatic and heterocyclic moieties through halogen displacement reaction [8]. This modification has resulted in an overall improvement in photochemical stability and optical properties [9-11]. The halogen displacement reaction introduced an easy way of attaching the ligand to the polymer and the subsequent synthesis of the immobilized complexes [12].

In this work, we will describe the modification of PVC through the anchoring of different alcohols acting as ligands and report the change in the optical properties of the polymer.

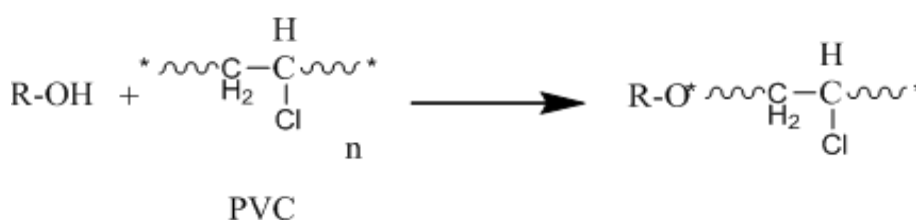
### EXPERIMENTAL SECTION

#### (1) Purification of Poly (vinyl chloride) [13]

Commercial Poly (vinyl chloride) was freed from additives by re-precipitation from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours.

#### (2) Synthesis of PVC Ligand compound

A mixture of 0.1 mole of PVC dissolved in THF and 0.05 mol alcohol and 5 drops of pyridine was refluxed for four hours in THF solvent. The precipitated product presumed to be modified polymer separated by evaporating the solvent. The scheme of synthesis of PVC-L is as shown in Fig. (1).



Fig, (1): Reaction scheme for synthesis of PVC-L

#### (3) Preparation of the Films:

A certain concentration of PVC and PVC-L solution (5g/100ml) in THF was used to prepare polymer films with a thickness of 30 $\mu$ m (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hours. To ensure the removal of any possible residual THF solvent, film samples were further dried at room temperature for three hours under reduced pressure. The structure of the modified polymers established on the bases of Fourier transform infrared spectroscopy (FTIR). The optical absorbance (A) of each sample was measured as a function of wavelength ( $\lambda$ ) ranged from 200 to 900 nm by using computerized Shimadzu UV-VIS 160A-Ultraviolet-spectrophotometer with full-scale absorbance up to (2.5). The light sources are halogen lamp and socket-deuterium lamp. The detector is Si-photodiode and all measurements were performed at room temperature. UV-VIS absorption spectroscopy was carried out for prepared samples before and after conjunction. The absorption spectra were used to calculate the direct optical energy gap. The absorption coefficient ( $\alpha$ ) was determined from the spectra using the formula ( $\alpha = 2.303 A/d$ ) [14] where d sample thickness. When a direct band gap exists, the absorption coefficient has the following relation dependence on the energy of incident photon ( $h\nu$ ) [15].

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \quad (1)$$

Where  $E_g$  is the direct band gap, and C is a constant. The optical energy band gap could be determined by extrapolating the straight line portion of the  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) on the energy axis.

### RESULTS AND DISCUSSION

The modification of PVC with alcohol that illustrate in Table (1) was performed by nucleophilic attack of (O) atom on the carbon carrying chlorine atom in the polymeric chain followed by departure of chlorine anion as a good leaving group.

Apparently, the nucleophilic attack of the oxygen atom (O) of alcohols on the chlorine-carrying carbon atom of the polymer has provided the modified PVC. Table (1) lists the information regarding the used alcohols:

Table (1): Alcohols used in PVC modification

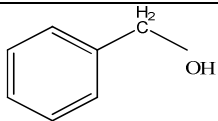
Sample of PVC-modification	Alcohol	Chemical Formula
LI	Benzyl alcohol	
LII	Methanol	CH <sub>3</sub> OH
LIII	Propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH
LIV	Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH
LV	Pentan-2-ol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>
LVI	Allyl alcohol	CH <sub>2</sub> =CHCH <sub>2</sub> OH
LVII	2-ethoxy ethanol	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH

Table (2): Absorption and IR Spectra of PVC-L

Complex	Electronic absorption peaks (nm)	Assignment	IR (cm <sup>-1</sup> )	Assignment
PVC		261	614	C-Cl stretching
			2910	C-H stretching
PVC-LI	260 266 305 510	л- л* л- л* Charge transfer (d-d)	2913	C-H (aliphatic)
			614	C-Cl
			1428	CH=CH <sub>2</sub>
			3591	OH
			3050	C-H (aromatic)
PVC-LII			2921	C-H (aliphatic)
			625	C-Cl
			1429	CH=CH <sub>2</sub>
			3630	OH
PVC-LIII	279 285	л- л* л- л*	2967	CH <sub>3</sub>
			626	C-Cl
			2912	C-H (aliphatic)
			1430	CH=CH <sub>2</sub>
			3633.23	OH
PVC-LIV	244 267	л- л* л- л*	2965	CH <sub>3</sub>
			2912	C-H (aliphatic)
			627	C-Cl
			1419	CH=CH <sub>2</sub>
PVC-LV			3621	OH
			2910	CH <sub>3</sub>
			2914	C-H (aliphatic)
			616	C-Cl
			1429	CH=CH <sub>2</sub>
PVC-LVI	277 285 320	л- л* л- л* Charge transfer	3632	OH
			2965	CH <sub>3</sub>
			2914	C-H (aliphatic)
			615	C-Cl
			1428	CH=CH <sub>2</sub>
PVC-LVII			3631	OH
			2999	CH <sub>3</sub>
			2799	CH <sub>2</sub>
			2909	C-H (aliphatic)
			628	C-Cl
			1422	CH=CH <sub>2</sub>
			3613	OH

The structure of the modified polymers were established on the bases of FTIR and UV-VIS spectroscopy. Each polymer showed band characteristics of its own. The modification of PVC with alcohol was confirmed by FTIR spectroscopy. The disappearance of the absorption band due to (-OH) stretching frequencies of hydroxyl clearly indicates the reaction between PVC and hydroxyl groups. However, this compound still shows the characteristic vibrations of the O-H in PVC-L (modified polymer). As shown in Table (2), the following features

could be seen in the IR spectra: A strong band at  $\nu$  (614-628)  $\text{cm}^{-1}$  was observed which could be attributed to  $\nu$  (C-Cl) band.

UV-VIS spectroscopy was also used to characterize the prepared polymers using THF as a solvent. These spectra show absorption bands which could be attributed to charge transfer and  $\pi$ - $\pi^*$  electronic transitions. These transitions are assigned in accordance with the structure of the ligand and the chelated polymer. As shown in Table (2) the increase of the absorbance in the UV- range for sample of the modified PVC compared with unmodified PVC can be explained by the formation of conjugation double bonds (band corresponding to the  $\pi$ - $\pi^*$  transitions) in the modified polymer resulting from the introduction of the aromatic ring into the polymer. The shifting in the absorbance to longer wavelengths (i.e. the bathochromic effect) is a good evidence for the above modification. Transitions of the d-d type appeared in the visible region. These transitions are assigned in relevance to the structures of complexes [13]. Fig. (1) represents absorption spectra (A) of all samples.

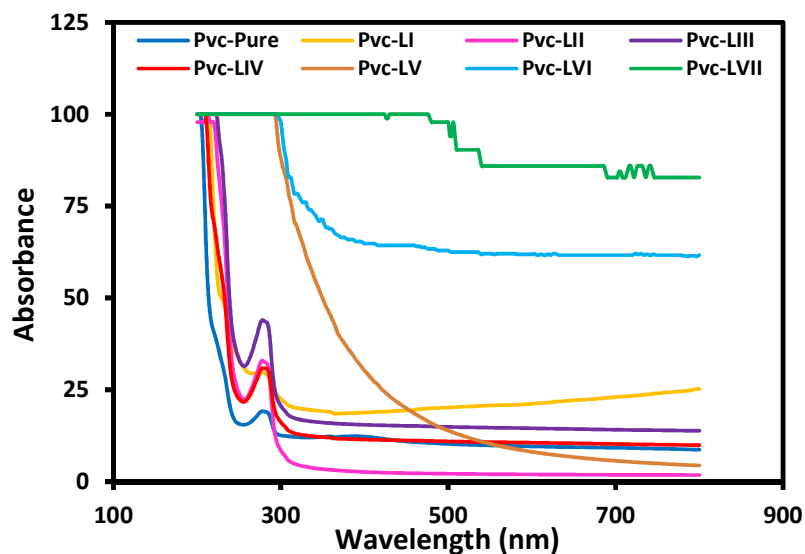


Fig. (1): Absorption spectra of modified PVC samples

Plots of the absorbance of  $(\alpha h\nu)^2$  versus photon energy for modified PVC are shown in Figs. (2-9) for modified polymer. For allowed transitions, there is a shift in the energy gap of the modified polymers due to formation of polarons which physically are moving electrons or holes with surrounding deformation. These quasi-particle entities produce discrete energy levels in the bandgap and reflect the absorption coefficient. The evidence of polaron formation was afforded by the reaction in band to band transition due to shifting the band density of state toward the energy gap[16]. The Energy gaps were measured as the behavior of a conductivity measurement of pure and modified PVC can be obtained by adopting the data of the energy gap, (Table-3 and Figs. 2 to 9). When the optical band gaps were compared with each other, their order follows:

PVC >PVC-LII> PVC-LI >PVC-LV >PVC-LIII> PVC-VII >PVC-LIV >PVC-LVI

Table (3): Optical band gap according to the direct allowed transition

Sample	$E_g$ (eV)
PVC- Pure	5.79
LI	5.5
LII	5.15
LIII	5.11
LIV	5.07
LV	3.75
LVI	3.71
LVII	2.03

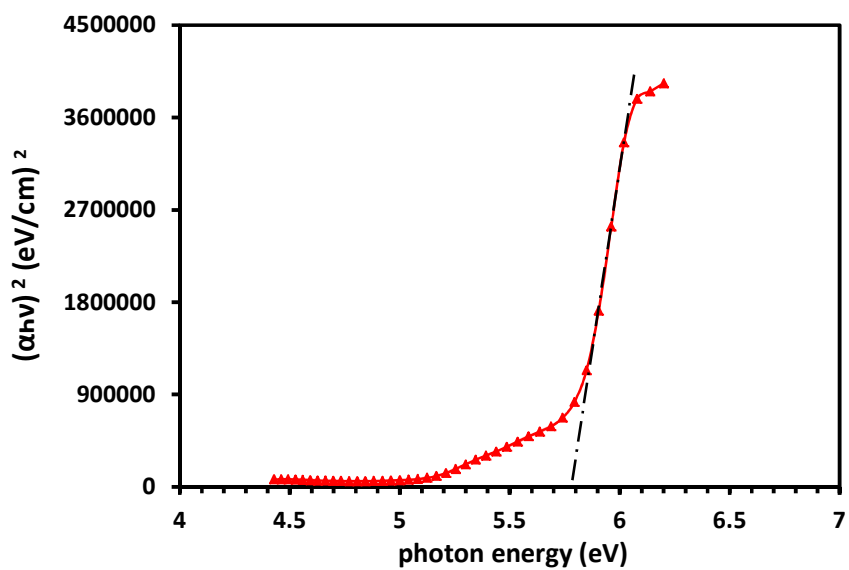


Fig. (2): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-Pure

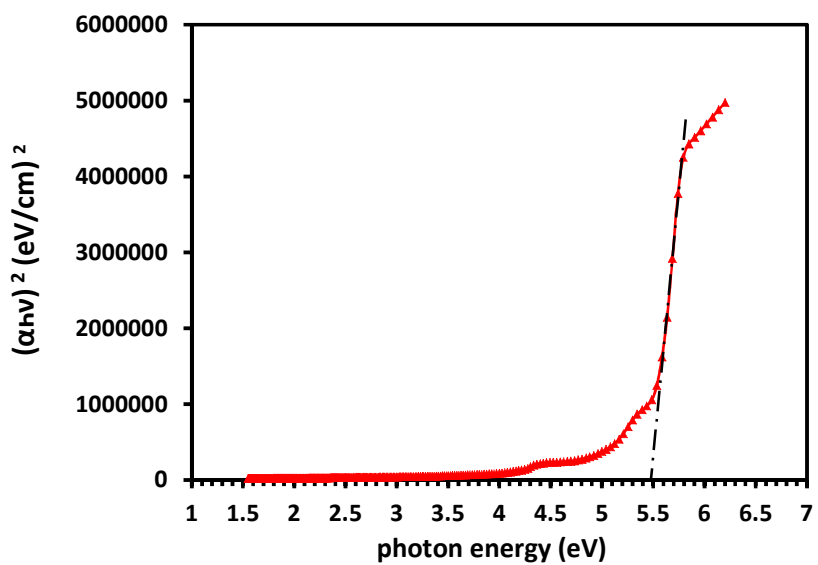
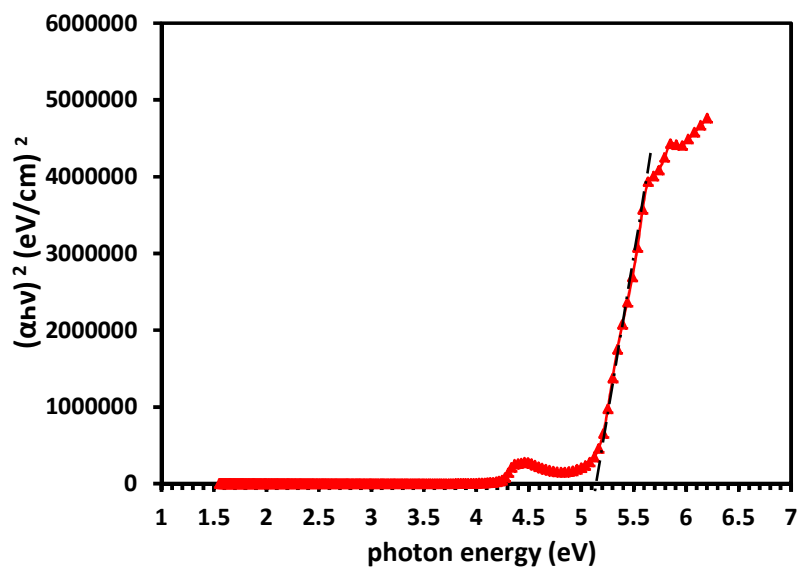
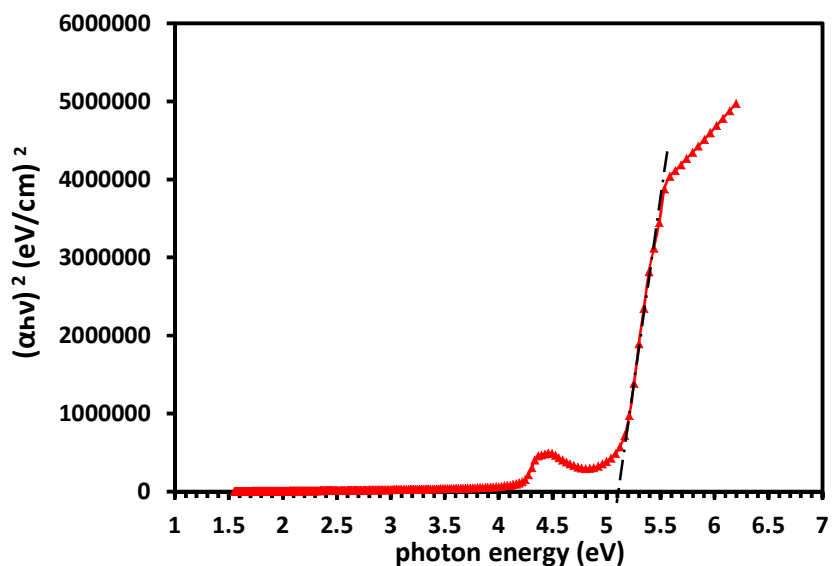


Fig. (3): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LI

Fig. (4): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LIIFig. (5): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LIII

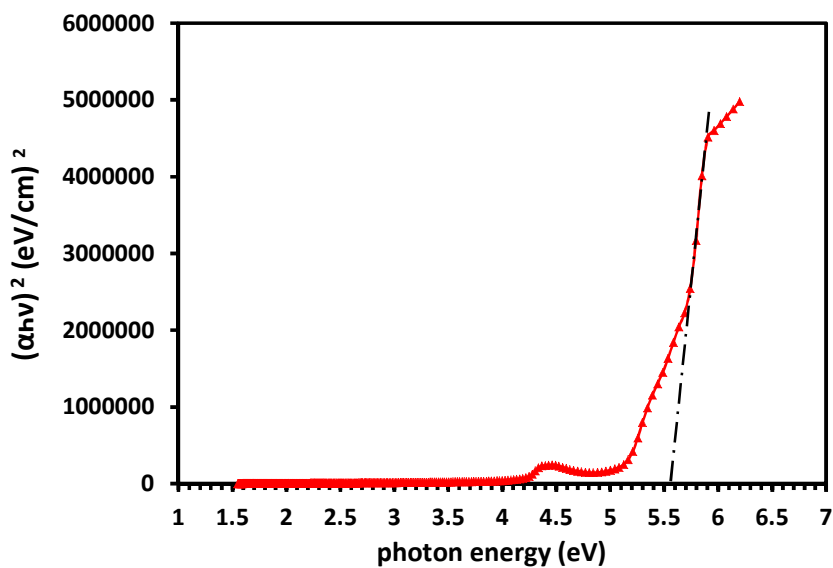


Fig. (6): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LIV

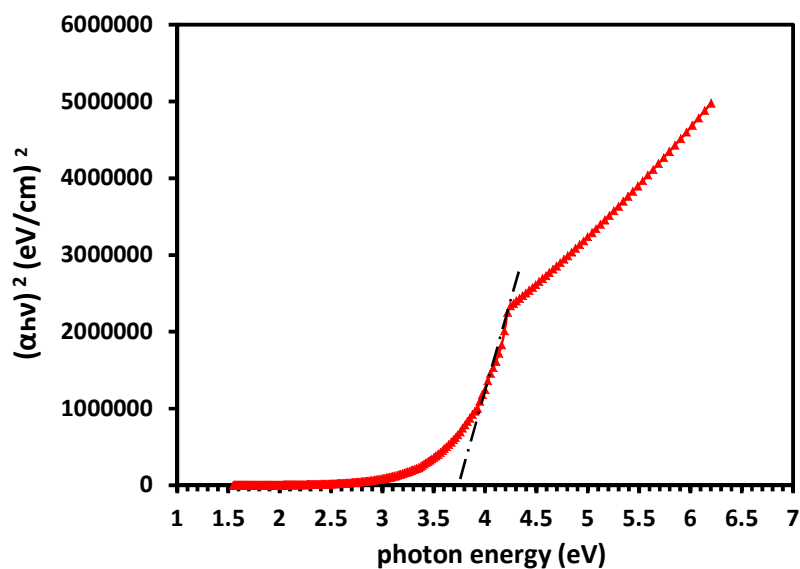
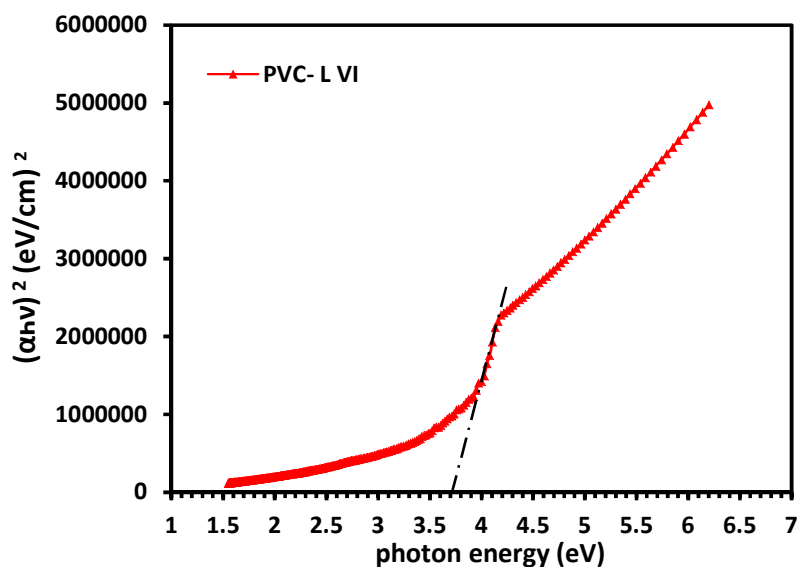
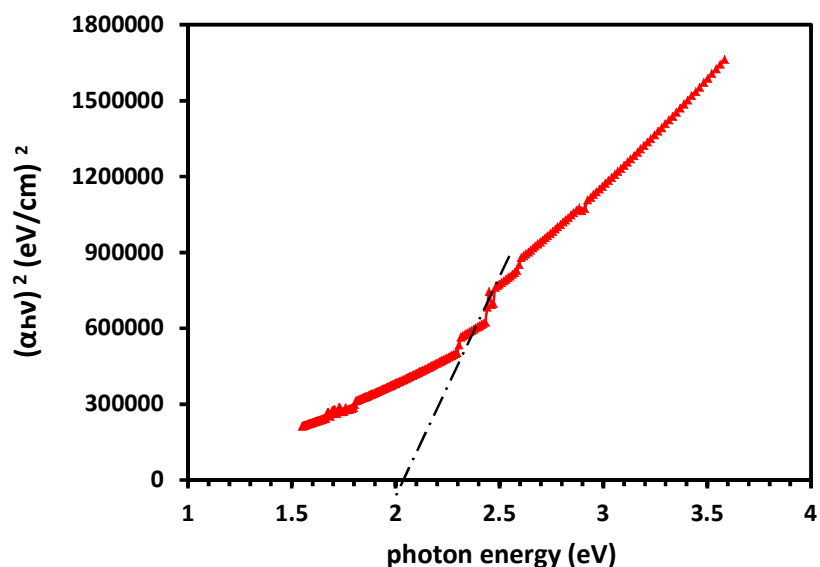


Fig.(7):Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LV

Fig. (8): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LVIFig. (9): Allowed direct transition  $(\alpha h\nu)^2$  vs photon energy for modified PVC-LVII

### CONCLUSION

PVC bound R-OH can be synthesized by Cl displacement reaction between PVC and (L) in alkaline conditions. The structure of the modified polymers were establish on the bases of its FTIR and UV-VIS spectroscopy. Each polymer showed band characteristic of its own structure. The energy gaps were measured as a function of conductivity and found to decrease when pure PVC is chelated to the ligand.

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