

Optical Properties and Morphological Study of New Films Derived From Poly(Vinyl Chloride)-Phenyl Phrine HCl Acid Complexes

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Abstract

The present study focused on modification of the optical properties of PVC films Phenyle Phrine HCl Acid complexes. Poly(vinyl chloride) (PVC) react with Phenyle Phrine HCl Acid (L) in THF to form the PVC-L compound. PVC-L has further been reacted with different metal's ions to form PVC-L-MII complexes. The structure of these complexes has been characterized by FT-IR and UV-Vis spectrophotometry. The optical data analyzed and interpreted in terms of the theory of phonon assisted direct electronic transitions. According to energy gap data, the conductivity of PVC and the complexes were obtained. From the microscopic image analysis, the relations between morphology and optical properties were explained.

Keywords: *Energy Gap, Optical properties.*

Introduction

There has been growing interest in the characterization of modified polymers. The optical characteristics are extremely important not only for scientific knowledge but also for modern technology applications [1]. In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarization properties [2,3]. Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions are a field of active research [4]. Poly(vinyl chloride) is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide [5]. Recently, scientists could modify PVC [6], by introduction aromatic and heterocyclic moieties through halogen displacement reaction [5]. The facial chlorine displacement from PVC indicated the possibility of easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes [7]. In the present paper, we report solid polymers films of PVC systems and study its optical properties.

Experimental Work

Instrumentation

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The

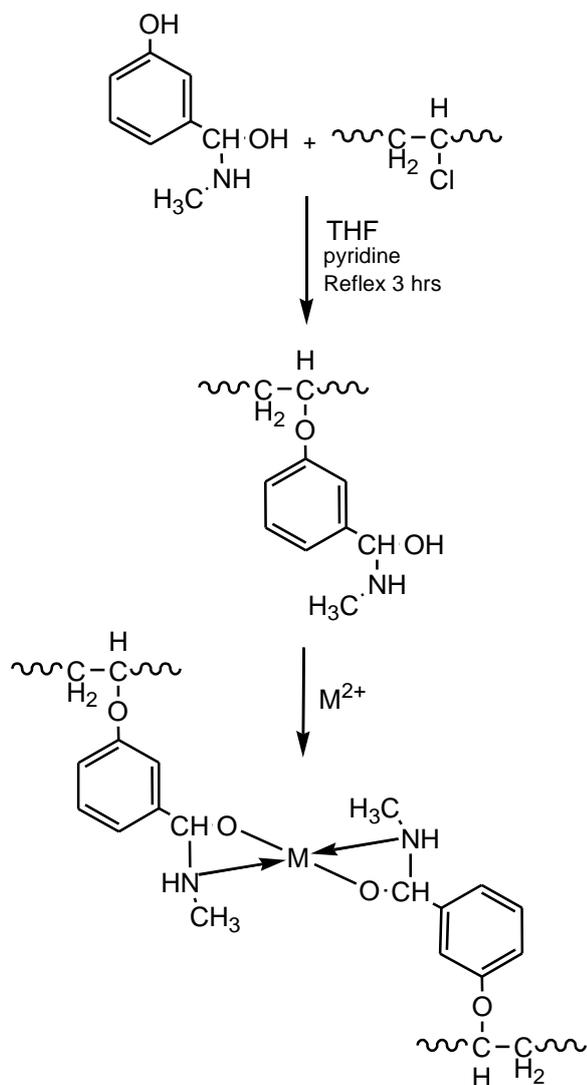
Fourier transformed infrared spectroscopy (FTIR) spectra were obtained in the range 4000-400 cm^{-1} using the KBr disc on FTIR 8300 Shimadzu spectrophotometer. UV-vis. Spectrums were measured using Shimadzu UV-Vis 160 A-Ultraviolet-visible spectrophotometer in range 200-1100 nm.

Synthesis of modified polymer (PVC-L)

phenyl phrine HCl (1mole) was added to (0.125g) poly(vinyl chloride) and three drops of pyridine in (25 mL) tetrahydrofuran (THF) was also added. A white precipitate was formed after refluxing the mixture for five hours. The modified polymer (PVC-L) was dried under vacuum [8].

Synthesis of PVC ligand complex

Metal complexes of poly (vinyl chloride)-phenyl prime HCl was prepared by the method described by Aliwi *et al.* [7]. Scheme 1, shows reactions for the synthesis of PVC-L-M^{II} polymer.



Scheme (1). Reaction for synthesis of PVC-L-M(II).

Purification of Poly(vinyl Chloride):

Commercial Poly(vinyl chloride) (Petkim company, Turkey) was purified by re-precipitation from tetrahydrofuran (THF) solution in ethanol, then dried under reduced pressure at room temperature for 24 hours.

Films preparation:

0.5% concentrations of PVC and PVC-L- M^{II} solution in THF were used to prepare 40 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hrs. film samples were further dried at room temperature for three hours under reduced pressure to remove the possible residual THF solvent. The optical absorbance

(A) of the sample was measured as a function of wavelength (λ) it ranged from 200 - 900 nm by using computerized Shimadzu Uv-Vis 160A-Ultraviolet-spectrophotometer 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 spectroscopies were made for prepared samples before and after modification. The spectra was used to carry out the energy gap by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ with (r) value (1/2) which indicates a transition of direct type. The linear portion was best fitted with ($r = 1/2$) Energy gap shift for all samples plotted as a function to conjunction type [9].

Result and Discussion

The FT-IR spectrum of phenyl phrine HCl exhibited (C=C), (C-H Ar.), (O-H) bands in 1595, 3010 and 3419 cm^{-1} . The (N-H) appeared in the region (3300-3400) cm^{-1} which undergo a shift to lower frequencies in complexes. The FTIR of a PVC-L graft polymer spectrum shows the following features, a strong band at $\nu(615)$ cm^{-1} was observed, which could be attributed to $\nu(\text{C-Cl})$ band, which is differed from PVC without modification $\nu(609)$. Also the disappearance of O-H band good indicator for formation the PVC-L compound.

In the FTIR of the PVC-complexes, a shift in $\nu(\text{N-H})$ cm^{-1} for all complexes. The presence of new medium intensity bands appeared in the 425-463 cm^{-1} region assignable to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ in the spectra of all the complexes [10] also support complexes structure. All important bands that appeared in the spectra of ligand, modified polymer and the complexes are given in Table (1).

Table (1)
FT-IR, Electronic spectra for the ligand and its prepared metal complexes.

<i>Compound</i>	<i>Colour</i>	<i>Absorption Bands(nm)</i>	<i>Assignment</i>	<i>FT-IR (cm⁻¹)</i>	<i>Assignment</i>
<i>Ligand (L)</i>	<i>White</i>	<i>225</i>	$\pi \rightarrow \pi^*$	<i>1595</i>	<i>C=C</i>
				<i>3010</i>	<i>C-H Ar.</i>
				<i>3419</i>	<i>O-H</i>
				<i>3302</i>	<i>N-H</i>
<i>PVC-L</i>	<i>Yellow</i>	<i>234</i>	$\pi \rightarrow \pi^*$	<i>1597</i>	<i>C=C</i>
				<i>3010</i>	<i>C-H Ar.</i>
				<i>3302</i>	<i>N-H</i>
<i>PVC-L-Co(II)</i>	<i>Blue</i>	<i>235</i>	$\pi \rightarrow \pi^*$	<i>452</i>	<i>M-O</i>
				<i>425</i>	<i>M-N</i>
<i>PVC-L-Cd(II)</i>	<i>pale-yellow</i>	<i>227</i>	$\pi \rightarrow \pi^*$	<i>453</i>	<i>M-O</i>
				<i>431</i>	<i>M-N</i>
<i>PVC-L-Cu(II)</i>	<i>Green</i>	<i>235</i>	$\pi \rightarrow \pi^*$	<i>3282</i>	<i>N-H</i>
				<i>455</i>	<i>M-O</i>
		<i>440</i>	<i>d-d</i>	<i>429</i>	<i>M-N</i>
<i>PVC-L-Zn(II)</i>	<i>Brown</i>	<i>232</i>	$\pi \rightarrow \pi^*$	<i>3298</i>	<i>N-H</i>
				<i>463</i>	<i>M-O</i>
				<i>435</i>	<i>M-N</i>

Table (1) shows the electronic absorption bands for ligand and PVC-complexes. The bands are classified into two distinct groups: belong to ligand transitions appeared in the UV. region and d-d transitions appeared in the visible region. These transitions are assigned in relevance to the structures of complexes. Surface topographies of polymer films were examined by using lab. microscope and optical microscope images of all polymers at 400× magnifications are given in Fig.(1).

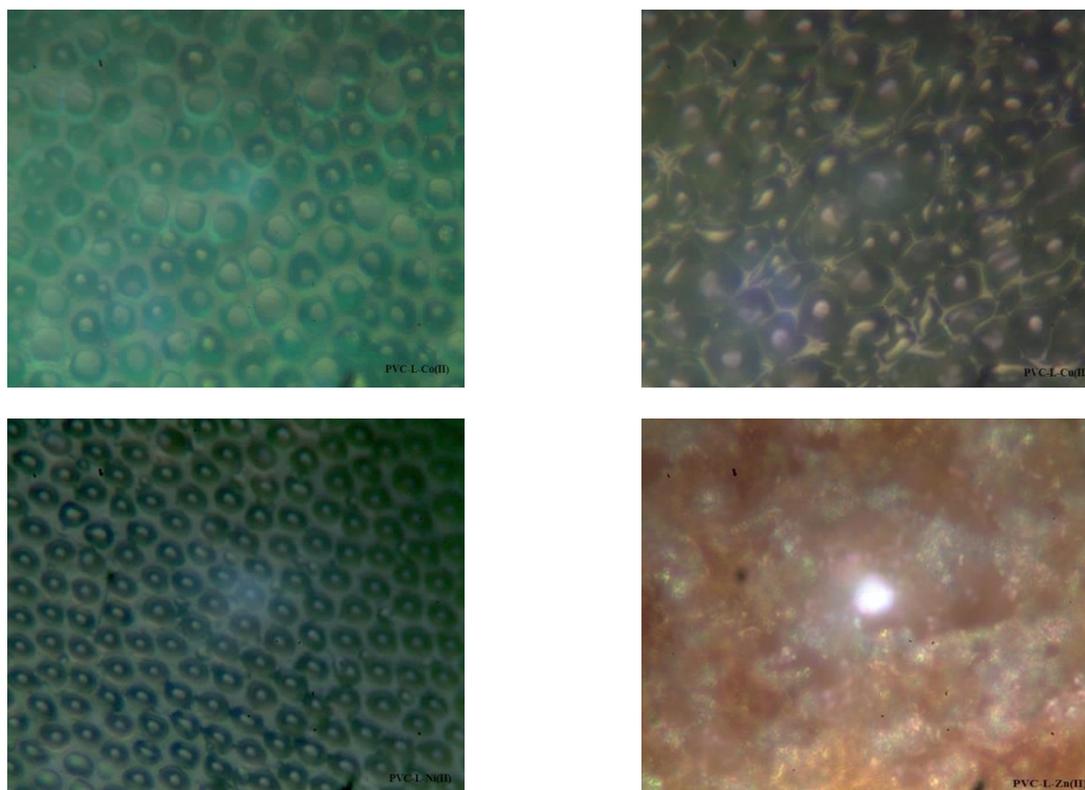


Fig.(1): Optical microscope images of all polymer films at 400× magnification.

The relation between $(\alpha h\nu)^2$ vs photon energy for modified and complex PVC are shown in Figs. (2) to (5) for allowed transition. The difference in the values of energy gaps could be attributed to the type of metal complexes [11]. The effect of the metal complexes addition to the values of activation energies is investigated, and the results are shown in Table (2). In addition, the shift in the energy gap could be attributed to the formation of polarons and bipolarons. The evidence of polar on formation is made that the reaction in a band to band transitions due to the shifting the band density of state in the energy gap. This observation is not like doping of conventional semiconductor when the band to band absorption strength does not affect by the formation of dopant state in the energy gap. The effect of modification and complex formation of the values of activation energies was investigated and the results shown in Table (2). The results presented in Figs. (2) to (5) indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from a valance band to a bonding bipolaron band. The second band represents the transition from a valance band to be anti? Bonding bipolaron band which is in

a good agreement with results are obtained by other workers [12]. Conductivity measurement of PVC with additive can obtain by adopting the data of an energy gap [13-15], see Table (2) and Figures (2-5). The conductivity measurement for PVC in the presence of an additive increase in the following order:

$$\text{PVC-L-Cd(II)} > \text{PVC-L-Zn(II)} > \text{PVC-L-Cu(II)} > \text{PVC-L-Co(II)} > \text{PVC}$$

Table (2)

Indicate the energy band gap according to the direct allowed transition.

Sample	E_g (eV)
PVC	5.79
PVC-L-Co	4.18
PVC-L-Cu	2.67
PVC-L-Zn	1.98
PVC-L-Cd	1.96

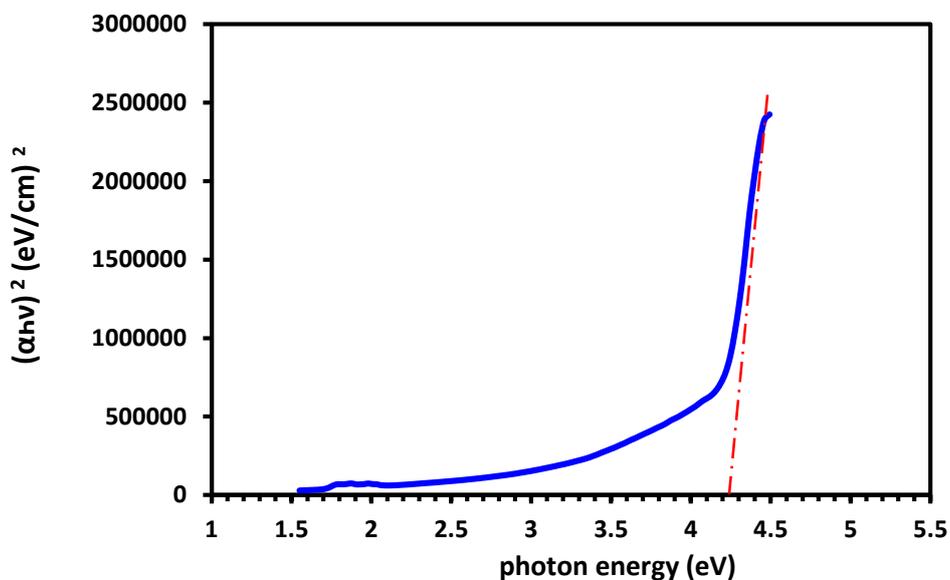


Fig.(2): Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Co(II).

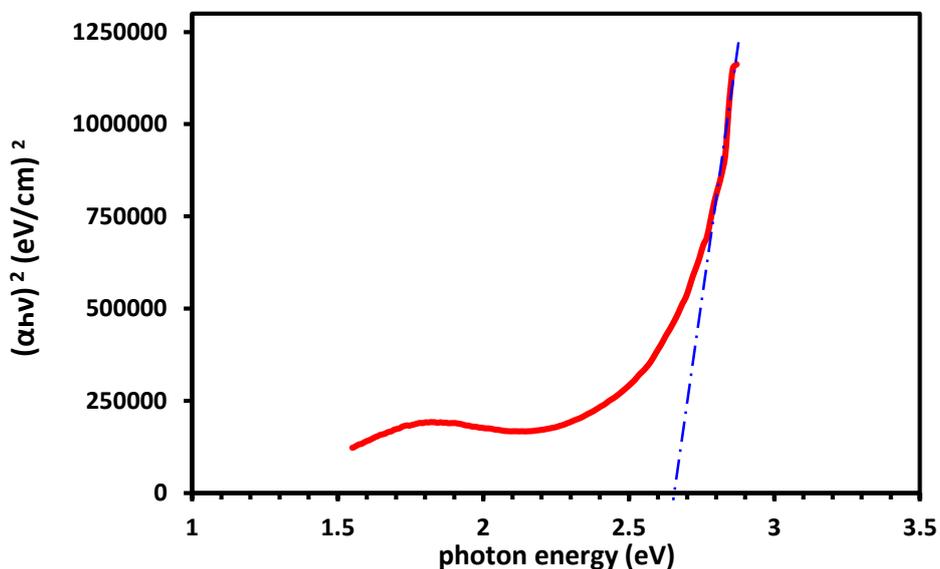


Fig.(3): Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cu(II).

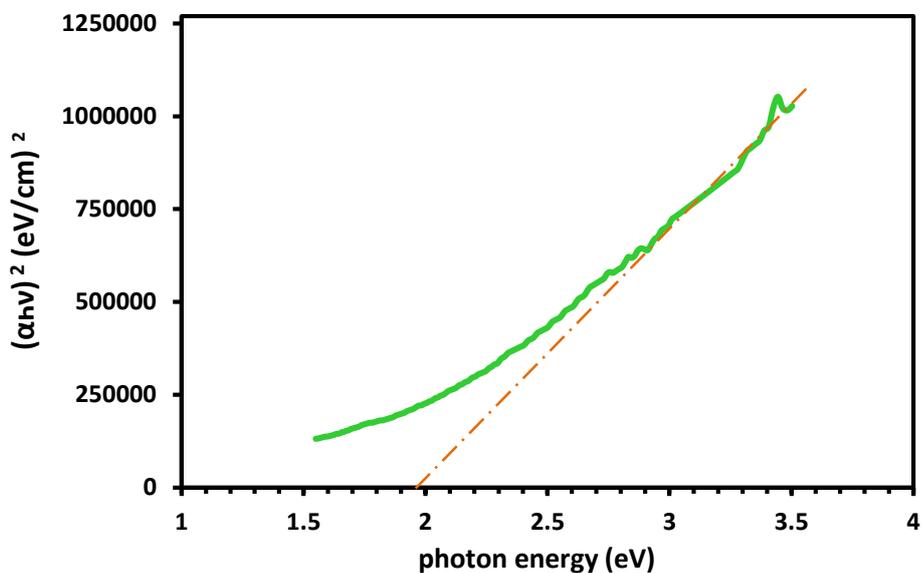


Fig.(4): Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Zn(II).

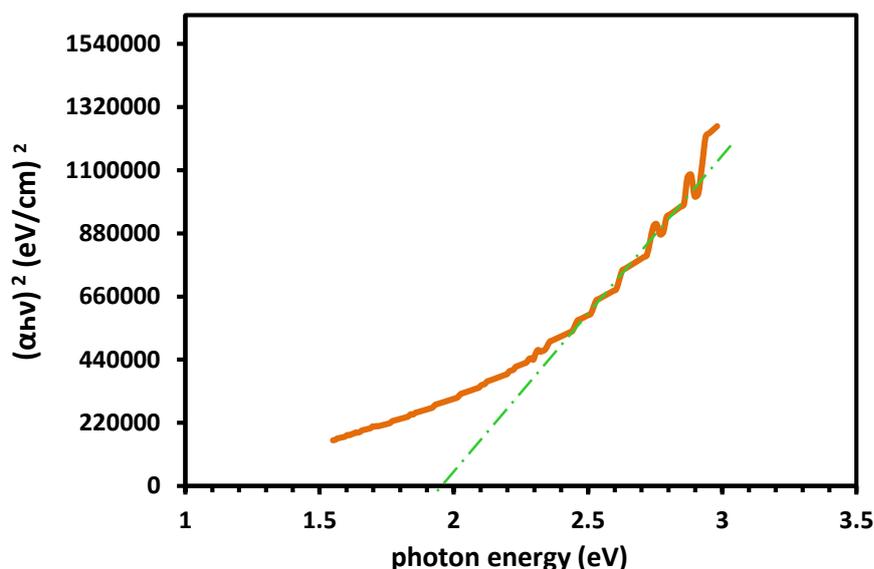


Fig.(5): Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cd(II).

Conclusion

The study on the effect of PVC modification with Phenyle Phrine HCl Acid complexes the repeating units on its optical properties has shown that the energy gap of modified polymers decreases in comparison with that of pure.

Acknowledgment

The authors acknowledge the Department of Chemistry, College of Science, Al-Nahrain University.

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الخلاصة

تم تحضير وتشخيص معقدات جديدة من تفاعل متعدد كلوريد الفانيل- فنيل فرين كلوريد الهايدروجين مع فلزات مختلفة. تم فحص التغيير في فجوة الطاقة لشرائح مركب PVC النقي والمشوب للمنطقة بين 200-900 نانوميتر في درجة حرارة الغرفة من خلال القياسات المستحصلة بطريقة الانتقالات الغير مباشرة للفونون. تم اعتماد النتائج المستحصلة ووجد ان هذه الخواص تتغير اعتمادا على طبيعة العنصر.