

Synthesis and Optical Properties Study of Some Metal Complexes of Poly (Vinyl Chloride)-Pyridine-4-Carbohydrazide

Mustafa S. Abdalh

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

Abstract

Poly (vinyl chloride) (PVC) react with pyridine-4-carbohydrazide (L) in THF to form the PVC-L compound, which have been characterize by spectroscopic methods. PVC-L has further been reacted with different metals ions to form PVC-L-M^{II} complexes. The structures of these complexes have been characterized by FTIR and UV-VIS. Spectrophotometry. The optical properties in the region from (200-900 nm) were studied using UV-VIS spectrophotometer. The optical data analyzed and interpreted in term of the theory of phonon assisted direct electronic transitions. According to energy gap data the conductivity of PVC and the complexes.

Keywords: PVC, phonon.

Introduction

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions to bring specific properties to the modified material, such as enhanced thermal stability, multiphase physical responses, compatibility, impact response, flexibility, and rigidity is a field of active research (1,2). A number of ligands including polydentate amines, crownethers, phosphines and bipyridines have been bound with mainly poly(styrene-divinylbenzene) copolymers (3,4). These studies are mostly concerned with ion-binding and catalytic aspects. Very little information appears to exist as to whether, and to what extent, such organic compounds can influence the properties of the macromolecule (5). Recently, scientists were able to modify PVC, one of the most versatile plastics (6), by introduction aromatic and heterocyclic moieties through halogen displacement reaction (7). PVC, thus modified, showed improved overall photochemical stability and optical properties (8, 9). The facial chlorine displacement from PVC indicated the possibility on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes (10). This article will describe the

modification of PVC with anchoring ligand and study its optical properties.

Experimental

Purification of Poly (vinyl chloride)

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.

Synthesis of PVC Ligand compound

A mixture of 0.1 mole of PVC dissolved in THF and 0.05 mole from pyridine-4-carbohydrazide and 5 drops of pyridine was refluxed for four hours in THF solvent. The precipitated modified polymer separated by evaporated the solvent.

Synthesis of PVC Ligand complex

A general procedure can be adopted for the preparation of all the metal complexes as follows : PVC-L-M^{II} complexes were obtained by dissolving 0.5 mol of the appropriate transition metal salt in ethanol and dissolving 1.5 mol of PVC-L dissolved in THF, colored precipitates were obtained then the precipitate was filtered, washed with excess of absolute ethanol. Scheme (1) shows reactions for the synthesis of PVC-L-M^{II} polymer (13). The

physical data of the prepared PVC-complexes are found in Table (1).

Table (1)

Physical data of the prepared complexes.

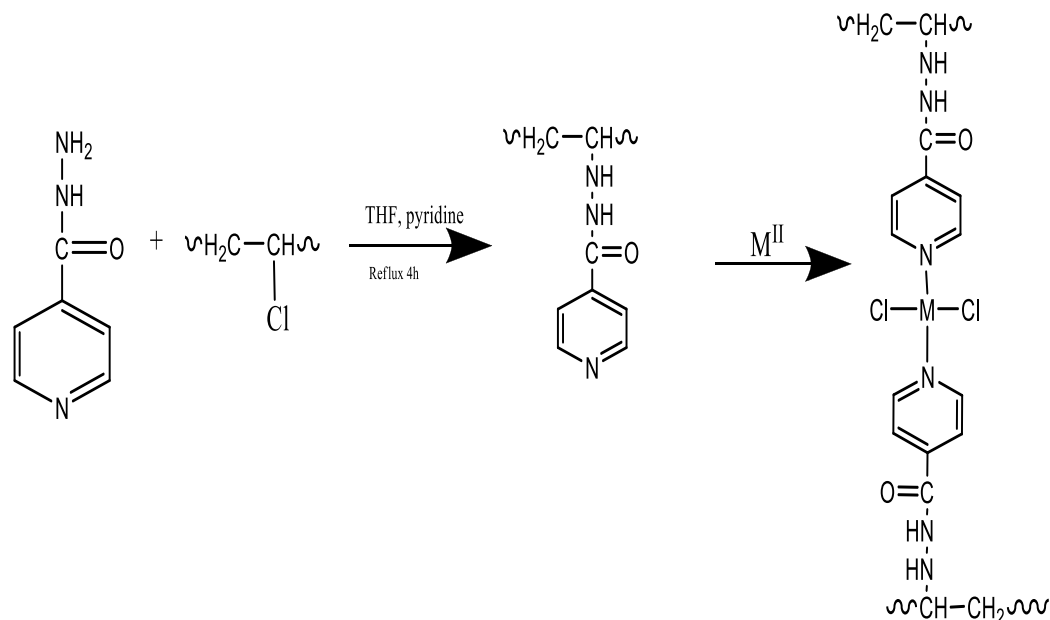
Sample	Color	Decomposition Point °C
PVC-L	Yellow	257
PVC-L-Cu	Green	280
PVC-L-Ni	Yellow	273
PVC-L-Sn	Brown	291
PVC-L-Zn	Brown	278
PVC-L-Cd	Pal yellow	> 300

Films Preparation

A certain concentration of PVC and PVC-L- M^{II} solution (5g/100ml) in THF was used to prepare polymer films with a thickness of 30 μ m (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature

for 24 hours. To remove the possible residual THF solvent, film samples were further dried at room temperature for three hours under reduced pressure.

The optical absorbance (A) of the sample was measured as a function of wavelength (λ) ranged from 200 to 900 nm by using computerized Shimadzu UV-VIS 160 A-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 spectroscopy's were made for prepared samples before and after conjunction. The spectra were 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 [11].



Scheme (1) Reaction scheme for synthesis of PVC-L- M^{II} .

Result and Discussion

The modification of PVC with pyridine-4-carbohydrazide was performed by nucleophilic attack of (N) atom on the carbon carrying chlorine atom in the polymeric chain followed by departure of chlorine anion as a good

leaving group. The structure of the modified polymers were establish on the bases of its FTIR and UV-VIS spectroscopy. Each of the polymers showed band characteristic of its own structure.

The modification of PVC with amine can be demonstrated by FTIR spectroscopy, the disappear of the absorption band due to (-NH₂) stretching frequencies of amine clearly indicate the reaction between PVC and amine, this compound clearly show characteristic vibrations of the C=N and N-H also in PVC-L (modified polymer) spectrum shows the following features, a strong band at

$\nu(622) \text{ cm}^{-1}$ was observed which could be attributed to $\nu(\text{C-Cl})$ band which is differ from PVC without modification $\nu(614) \text{ cm}^{-1}$.

In the FTIR of the PVC-complexes, a shift in $\nu(\text{C=N}) \text{ cm}^{-1}$ for all complexes as shown in Table (2) and new bands appears in the range $\nu(460-547) \text{ cm}^{-1}$ which could be attributed to (M-N) bond and this gives further evidences for the structures of complexes.

Table (2)
Absorption and IR Spectra of PVC-L and PVC-L-M^{II}.

Complex	Electronic absorption peaks (nm)	Assignment	IR (cm ⁻¹)	Assignment
PVC		261	614	C-Cl stretching
			2910	C-H stretching
PVC-L	279 285	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	622	C-Cl
			2918	C-H
			1638	C=N
			1675	C=O
			3277	N-H
PVC-L-Cu	266 271 314 503	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ Charge transfer (d-d)	2912	C-H (aliphatic)
			613	C-Cl
			1616	C=N
			3262	N-H
			496	Cu-N
			241	Cu-Cl
PVC-L-Sn	241 263	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	2918	C-H (aliphatic)
			617	C-Cl
			1622	C=N
			3283	N-H
			512	Sn-N
			231	Sn-Cl
PVC-L-Cd	271 289 311	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ Charge transfer	2924	C-H (aliphatic)
			633	C-Cl
			1645	C=N
			3283	N-H
			547	Cd-N
			236	Cd-Cl
PVC-L-Zn	270 283 327	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ Charge transfer	2924	C-H (aliphatic)
			609	C-Cl
			1631	C=N
			3283	N-H
			529	Fe-N
			248	Fe-Cl
PVC-L-Ni	273 281 328 563 604	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ Charge transfer (d-d) (d-d)	2930	C-H (aliphatic)
			617	C-Cl
			1627	C=N
			3300	N-H
			460	Ni-N
			234	Ni-Cl

UV-VIS technique is used to characterize the prepared polymers in THF as a solvent, the UV-VIS spectra show absorption bands could be attributed to charge transfer and $\pi \rightarrow \pi^*$ electronic transitions, these transitions are assigned in the relevance to the structure of the ligand and the modified 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 $\pi \rightarrow \pi^*$ transitions) in the modified polymer resulting from introducing aromatic ring thus, the shifting in the absorbance to longer wavelengths (i.e. the bathochromic effect) is a good evidence that modification. d-d transitions appeared in the visible region. These transitions are assigned in relevance to the structures of complexes (14, 15).

The relation between $(\alpha h\nu)^2$ versus photon energy for PVC (pure and modified) are shown in Figs. (1-7) for allowed transition. Fig.(1) show single absorption peaks and this is confirm that pure PVC (Control) has no any electronic transition in the visible region. For modified and complex polymers (Figs. 2-7) the shift in the energy gap could be attributed to the formation of polarons and bipolarons. The evidence of polaron formation is made that the reaction in band to band transitions due to the shifting the band density of state toward the energy gap. This observation is not like doping of conventional semiconductor when the band to band absorption strength dose not affected by the formation of dopant state in the energy gap. The effect of modification and complex formation on the values of activation energies 1 and 2 was investigated and the results shown in Table (3). The results presented in Figs. (2-7) indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from valance band to bonding bipolaron band. The second band represents the transition from valance band to anti-bonding bipolaron band which is in a good agreement with results are obtained by other workers (12). Conductivity measurement of PVC with and without additive can obtain by adopting the data of energy gap, (see Table (3) and Figs. from (1 to 7)). The conductivity

measurement for PVC in the presence of additive increase in the following order:

PVC-L-Zn > PVC-L-Cu > PVC-L-Cd > PVC-L-Ni > PVC-L-Sn > PVC-L > PVC

Table (3)

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

sample	Eg1 (ev)	Eg2 (ev)
PVC	-	5.79
PVC-L	3.62	3.73
PVC-L-Sn	3.31	3.38
PVC-L-Zn	2.89	3.02
PVC-L-Cu	2.95	3.19
PVC-L-Ni	3.24	3.32
PVC-L-Cd	2.97	3.21

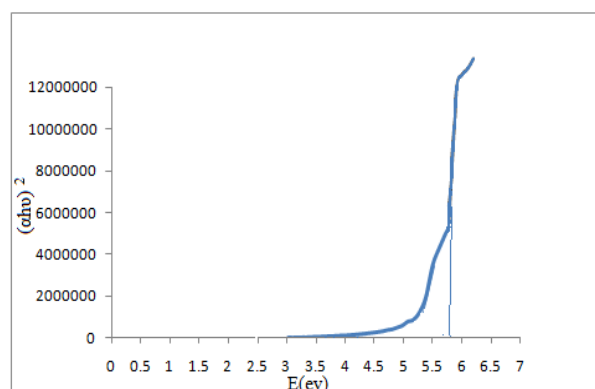


Fig.(1) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for pure PVC.

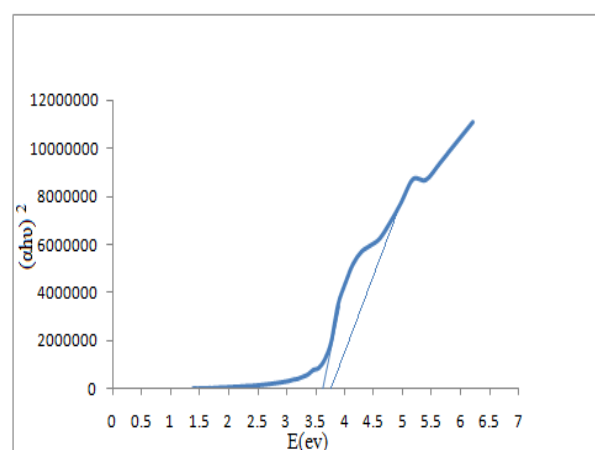


Fig.(2) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L.

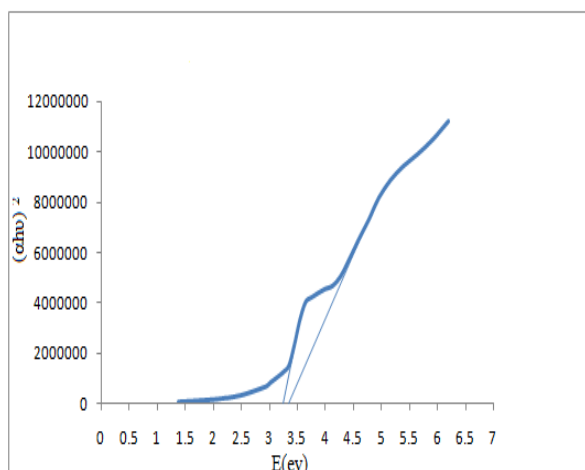


Fig.(3) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L-Sn^{II}.

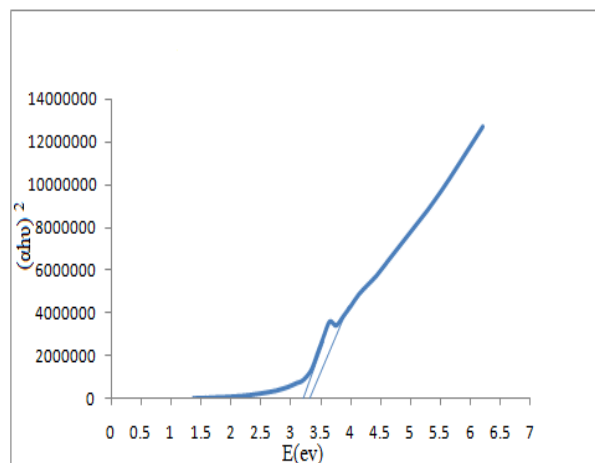


Fig.(6) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L-Ni^{II}.

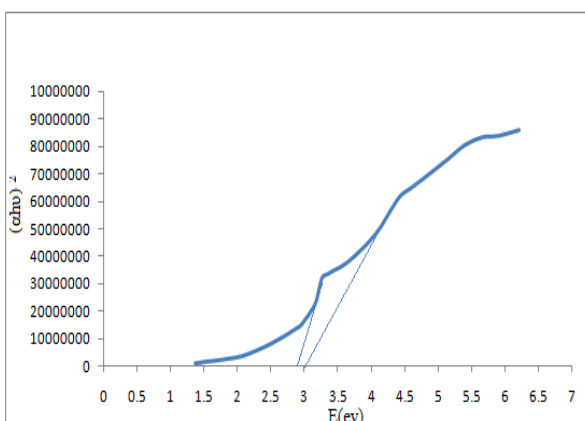


Fig.(4) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L-Zn^{II}.

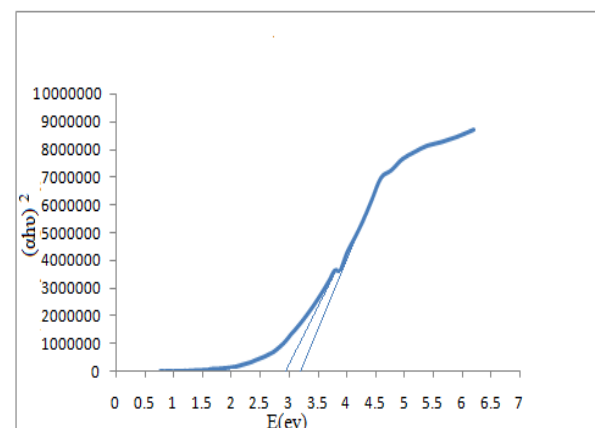


Fig.(7) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L-Cd^{II}.

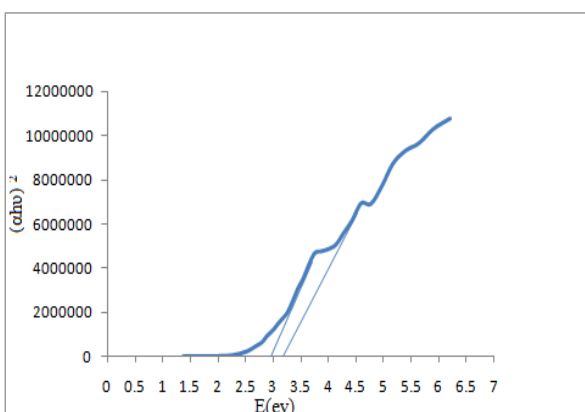


Fig.(5) Allowed direct transition $(\alpha h\nu)^2$ Vs Energy for PVC-L-Cu^{II}.

Conclusion

PVC bound pyridine-4-carbohydrazide can be synthesized by Cl displacement reaction between PVC and (L) in alkaline condition. Subsequent complexation of PVC-L with Cu^{II}, Ni^{II}, Zn^{II}, Co^{II} and Sn^{II} yield intensely colored PVC-L-M^{II} complexes which exhibit improved overall optical properties. The energy gaps were measured as behavior of conductivity and it is conceded that the energy for PVC is affected by modification and complexation.

References

- [1] Amit, B., Rawlins, J.W., Ray, P., Polymer Crafting and Crosslinking. JOHN WILEY & SONS, INC, 2009.
- [2] Chen, Y., Y. Song, Y. Zhang and Lang. A tricobalt(II) coordination polymer incorporating in situ generated 5-methyltetrazolate ligands. Inorganic Chemistry Communications, 11: PP. 572-575, 2008.
- [3] Gustafsson, B., Hakansson, M., Jagner, S. "Complexes between copper(I) chloride and polydentate aromatic amines". Inorganica Chimica Acta, 350: PP. 209-214, 2003.
- [4] Genhua, Z., Pan, C. Preparation of star polymers based on polystyrene or poly(styrene-*b*-Nisopropyl acrylamide) and divinylbenzene via reversible addition-fragmentation chain transfer polymerization Polymer, 46: PP.2802-2810, 2005.
- [5] Jumat S., Nadia S., Ahmed A., Emad Y. optical properties of some metal complexes of poly(vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole. Int.J. ChemTech Res. 3(2):PP.981-987, 2011.
- [6] Moulay, S. Chemical modification of poly(vinyl chloride)-Still on the run. Progress in Polymer Science, 35, PP. 303-331, 2010.
- [7] Claudiu, L., Edina R., Bogdan M., Teodora Z, Gheorghe H. Chemical modification of PVC for polymer matrices with special properties. U.P.B. Sci. Bull., Series B, 72, PP. 127-140, 2010.
- [8] Yousif, E., Hameed, A., Bakir, E. Synthesis and photochemical study of poly(vinyl chloride)- 1,3,4-oxadiazole and 1,3,4-thiadiazole. Journal of Al-Nahrain University (Science), 10: PP. 7-12, 2007.
- [9] Mohammed A., Emad Y., Atheel A., Yang F. Optical properties Modification of poly(vinyl chloride) using complexes of 2-amino-5-(2-acetyloxyphenyl)-1,3,4-thiaziazol. Iraqi J. Polymers, 13, No.2, PP. 27-36, 2009.
- [10] Aliwi, M., Yousif, E., Otaiwi A. Synthesis and photochemical study of some metal complexes of poly(vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole. Iraqi Journal of polymers, 10(1): PP. 53-64, 2005.
- [11] Yousif E., Hassan O., Otaiwi A. and Farina Y. Studying the conductivity of Poly (vinyl chloride) using 2-thioacetic acid benzothiazole complexes as additives by measuring forbidden energy gap. Iraqi Journal of polymers. 12(1): PP. 5-78, 2008.
- [12] Al-Ramadan Y. optical properties of poly(vinyl chloride)/poly(ethylene oxide) blend. Optical materials, (14): PP.287-290, 2000.
- [13] Ahmed Ahmed, Tariq Najim, Jumat Salimon, Nadia Salih, Abdualbasit Graisa, Yang Farina, Emad Yousif. Optical properties modification of poly(vinylchloride) using complexes of 2-aminoacetate benzothiazole. ARPN Journal of Engineering and Applied Sciences, 5: PP. 43-45, 2010.
- [14] Emad Y. Synthesis, spectroscopic studies and fungicidal activity of some dioganotin(IV) with 2[(pheylicarbonyl) amino] propanoato. Journal of King Saud University, 24: PP.167-170, 2012.
- [15] Emad, Y., Hadeel A., Farah M. Synthesis and characterization of some metal ions with 2-amino acetate benzothiazol. Journal of applied sciences research, 6(7): PP. 879-882, 2010.

الخلاصة

تم مفاعلة البولي فنيل كلورايد مع البيريدين-٤-كاربوهيدرازيد لتكوين PVC-L والذي تم مفاعله مع عدد من العناصر الانتقالية لغرض تكوين المعقد PVC-L-M^{II}. تم تشخيص المعقدات باستخدام تقنية الـ FTIR و UV-VIS الخصائص البصرية تم دراستها في المنطقة (200-900 nm). تم حساب التوصيلية الكهربائية من خلال حساب فجوة الطاقة.