

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Optical Properties and AFM Study of New Polymers Derived From Poly(Vinyl Chloride)-2-Acetoxy Benzoic Acid Complexes.

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ABSTRACT

In this work, Films of modified Poly(vinyl alcohol) with different transition metal complexes, Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) have been prepared in order to evaluate the role of some transition metal in the modification of optical properties of the polymer. The change in the values of energy gap has been interpreted in terms of the type of metal complexes. PVC-L-Cu(II) has the highest conductivity which is supported by the lowest optical band gap. Surface morphology of the sample were studied by atomic force microscope (AFM). Optical properties like direct band gaps were investigated by UV-vis analysis.

Keywords: poly(vinyl alcohol), optical properties, transition metal complexes, AFM.

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INTRODUCTION

The biggest advantage of conductive polymers is their processibility [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 polarisation properties [2].

The incorporation of the dopants into polar organic polymers can induce pronounced changes in various properties of polymers in order to modify and improve its properties[3]. Various composite materials have been recently synthesized by starting from different polymers and a wide variety of dopants like metals, oxides, inorganic salts, and other particles [4]. Synthesis of polymer- bound chelating ligands and the selective chelation of specific metal ions is a field of active research [5]. Recently, scientists were able to modify PVC by introduction aromatic and heterocyclic moieties through halogen displacement reaction [6]. 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 [7]. This article discloses the investigation of the effect of transition elements on the electrical properties of the Novel materials.

EXPERIMENTAL

Instrumentation

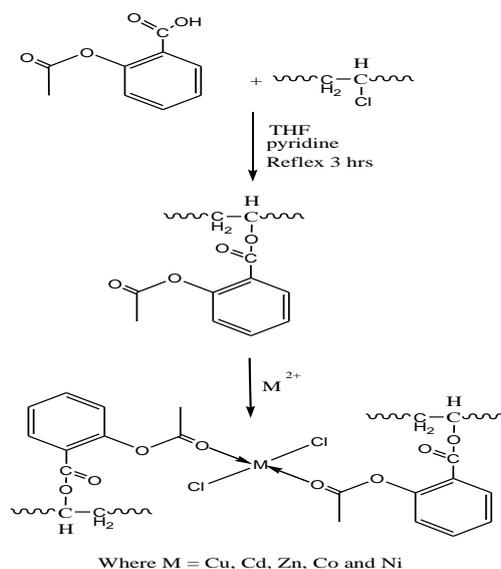
All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The Fourier transform infrared spectroscopy (FTIR) spectra were obtained in the range 4000-400 cm^{-1} using KBr disc on FTIR 8300 Shimadzu spectrophotometer. UV-vis. spectrums were measured using Shimadzu UV-Vis 160 A-Ultraviolet-visible spectrophotometer in range 200-1100 nm.

Synthesis of modified polymer (PVC-L)

A mixture of 1 gm of PVC dissolved in 20 ml and 1 gm from Aspirin, (2-Acetoxy benzoic acid) and 5 drops of pyridine was refluxed for three hrs in THF solvent. The precipitated modified polymer is separated the solvent evaporator process [8].

Synthesis of polymer metal chelates

The Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) polymeric metal chelates have been prepared using PVC-L and the procedure is as follows: 0.3 gm of synthesized modified polymer (PVC-L) and 0.05 gm of metal salt solution were dissolved in 5 mL of tetra hydro furan (THF) and reflux 3 hrs in order to form the complex [PVC-L-M(II)] [9], Scheme 1.



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

Purification of Poly(vinyl Chloride)

Commercial Poly(vinyl chloride) (PVC) supplied from (Pet Kim company, Turkey) 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 hrs.

Films preparation

A certain concentration of PVC and PVC-L-M(II) solution (5 gm/100 mL) in THF was used to prepare polymer films with a thickness of 40 μm (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 200-900 nm by using computerized Shimadzu UV-VIS 160A-Ultraviolet spectrophotometer full-scale. 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 was made for prepared samples before and after conjunction. The spectra were used to carry out the energy gap by plotting $(\alpha h\nu)^2$ vs $(h\nu)$ with $r = 1/2$ 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 [8].

RESULT AND DISCUSSION

The FTIR spectrum of the Aspirin (2-Acetoxy benzoic acid), shows a characteristic stretching absorption bands at 1691 cm^{-1} , 1739 cm^{-1} , 1139 cm^{-1} , $2800\text{-}3200\text{ cm}^{-1}$, 1602 cm^{-1} and 3012 cm^{-1} assigned to C=O (carboxylic acid), C=O (ester), C-O, O-H, C=C and the stretching of aromatic C-H respectively. The FTIR of PVC-L graft polymer spectrum shows the following features, a strong band at $\nu(615)\text{ cm}^{-1}$ was observed which could be attributed to $\nu(\text{C-Cl})$ band which is differ from PVC without modification $\nu(609)$. Also the disappearance of O-H band good indicator for formation the PVC-L compound.

The reaction between PVC-L with Ni(II), Cu(II), Zn(II), Cd(II) and Co(II) gave different types of complexes. In the free ligand, the bands at 1600 cm^{-1} and 1139 cm^{-1} were assigned to the stretching of C=O and C-O of the ester were shifted to a lower frequency region. This shift is probably due to the complexation of the metal to the ligand through oxygen of the carbonyl group. Stretching of metal-oxygen and metal-Cl bands of the complexes appeared in low frequency region ($452\text{-}462\text{ cm}^{-1}$ and $258\text{-}267$) respectively [10,7]. The IR data of the complexes are shown in Table 1. The Table lists the stretching frequency (ν) for some of the characteristics groups exhibited by the ligand and complexes.

Electronic absorption bands for ligand and PVC-complexes are show in Table 1. 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.

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

Compound	Absorption Bands(nm)	Assignment	FT-IR (cm^{-1})	Assignment
Ligand (L)	231	$\pi \rightarrow \pi^*$	1691	C=O (Acid)
			1739	C=O (Ester)
			1139	C-O
	307	$n \rightarrow \pi^*$	2800-3200	O-H
			1602	C=C
			3012	C-H
PVC-L	232	$\pi \rightarrow \pi^*$	1696	C=O (Acid)
			1739	C=O (Ester)
			1137	C-O
			1606	C=C
	306	$n \rightarrow \pi^*$		

			3010	C-H
PVC-L-Ni(II)	227	$\pi \rightarrow \pi^*$	1729	C=O (Ester)
			1696	C=O (Acid)
	287	$n \rightarrow \pi^*$	459	M-O
			424	d-d
PVC-L-Zn(II)	231	$\pi \rightarrow \pi^*$	1725	C=O (Ester)
			1695	C=O (Acid)
	297	$n \rightarrow \pi^*$	462	M-O
			261	M-Cl
PVC-L-Cd(II)	226	$\pi \rightarrow \pi^*$	1731	C=O (Ester)
			1697	C=O (Acid)
	276	$n \rightarrow \pi^*$	452	M-O
			258	M-Cl
PVC-L-Cu(II)	225	$\pi \rightarrow \pi^*$	1722	C=O (Ester)
			1696	C=O (Acid)
	267	$n \rightarrow \pi^*$	457	M-O
			597	d-d
PVC-L-Co(II)	225	$\pi \rightarrow \pi^*$	1730	C=O (Ester)
			1696	C=O (Acid)
	284	$n \rightarrow \pi^*$	460	M-O
			260	M-Cl

Atomic force microscope is an excellent tool to measure the roughness factor, pore size and also two and three dimensional topographic images of the sample. In the present study, AFM technique has been used to view the two and three dimensional images of the prepared sample over the scanned area $5.0 \mu\text{m} \times 5.0 \mu\text{m}$. The PVC-L-Cu(II) and PVC-L-Zn sample having maximum conductivity was subjected to atomic force microscopic studies and its topographic and three-dimensional images are shown in Figure 1 and 2.

The relation between $(\alpha h\nu)^2$ vs photon energy for modified and complex PVC are shown in Figures 3-8 for allowed transition. The difference in the values of energy gap Table 2 could be attributed to the type of metal complexes. The effect of the metal complexes addition on the values of activation energies is investigated and the result are shown in Table 2. In addition, the shift in the energy gap could be attributed to the formation of polarons and bipolarons [11].

The evidence of polar on 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 was investigated and the results shown in Table 2.

Table 2. Indicate the energy band gap according to the direct allowed transition

Sample	E_g eV
PVC	5.79
PVC-L	3.52
PVC-L-Zn(II)	3.3
PVC-L-Cd(II)	2.57
PVC-L-Co(II)	2.56
PVC-L-Ni(II)	2.26
PVC-L-Cu(II)	2.07

The results presented in Figures 3-8 indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from valance band to bonding bipolaron band [6]. 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. Conductivity measurement of PVC with additive can obtain by adopting the data of energy gap [12-14]. The conductivity measurement for PVC in the presence of additive increase in the following order:

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

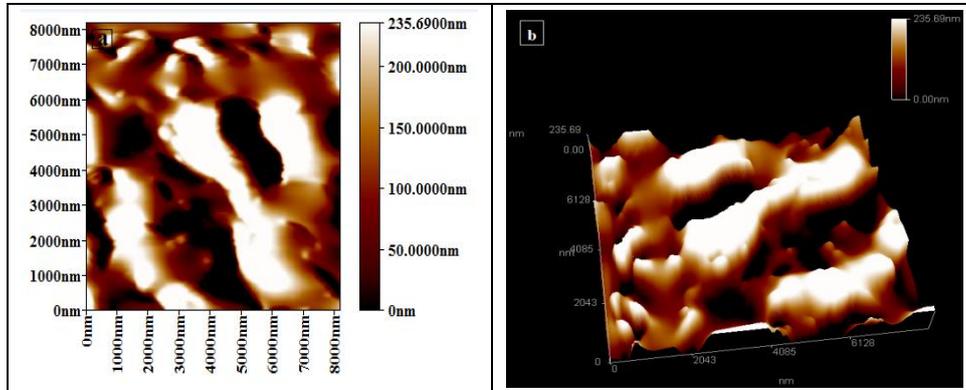


Figure 1. Topography image of the sample [PVC-L-Cu(II)] having maximum conductivity, (a) 2D image; (b) 3D image

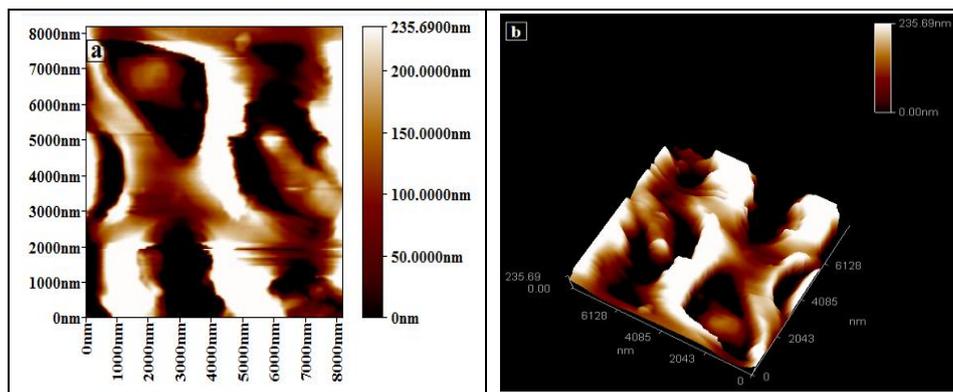


Figure 2. Topography image of the sample [PVC-L-Zn(II)], (a) 2D image; (b) 3D image

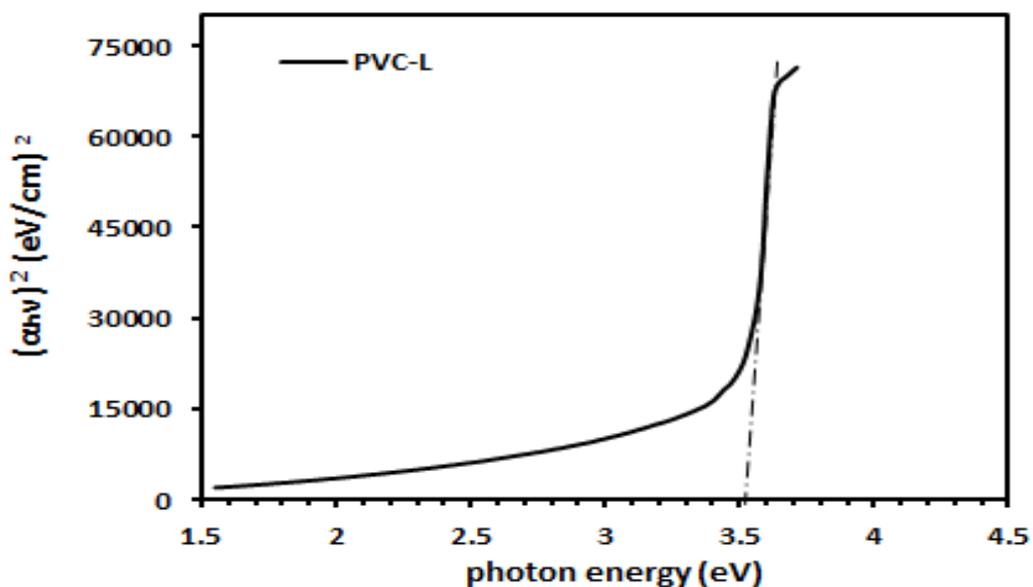


Figure 3. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L

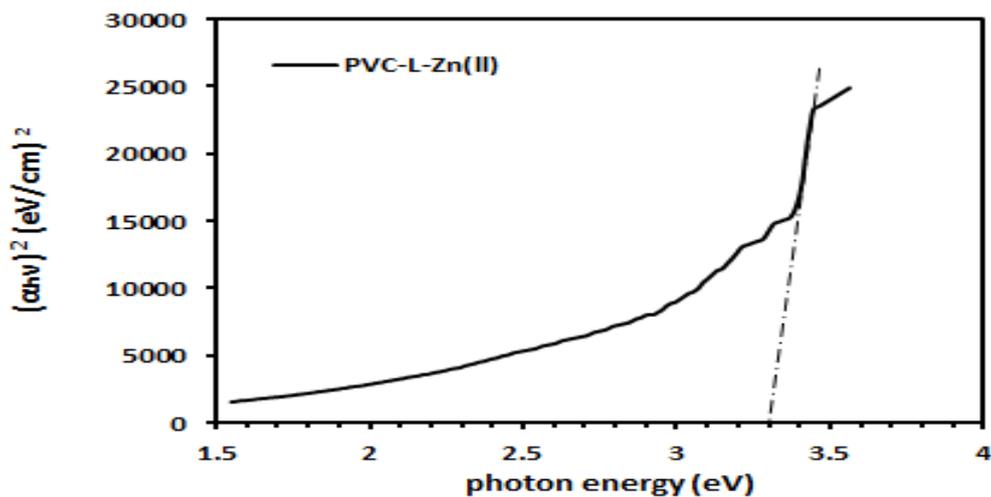


Figure 4. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Zn(II)

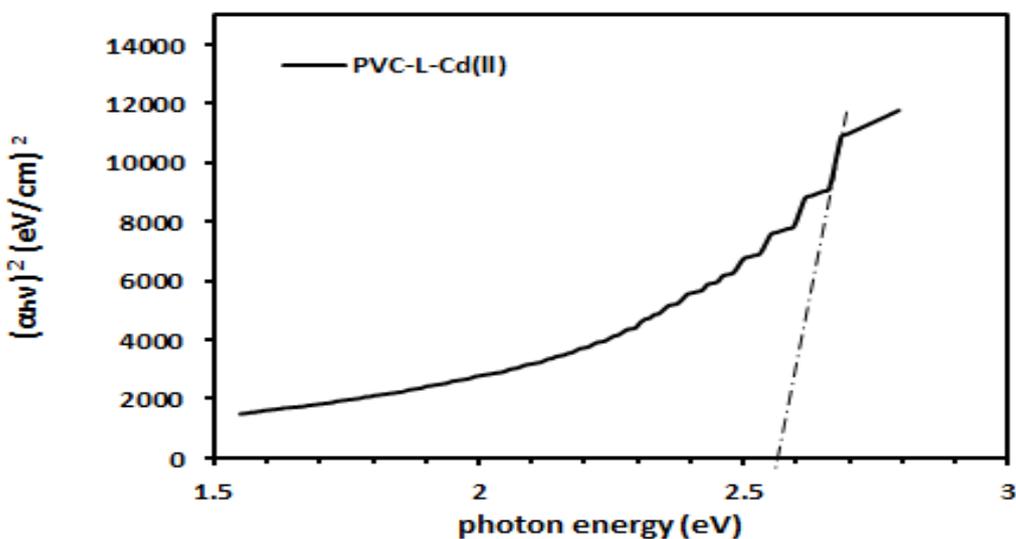


Figure 5. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cd(II)

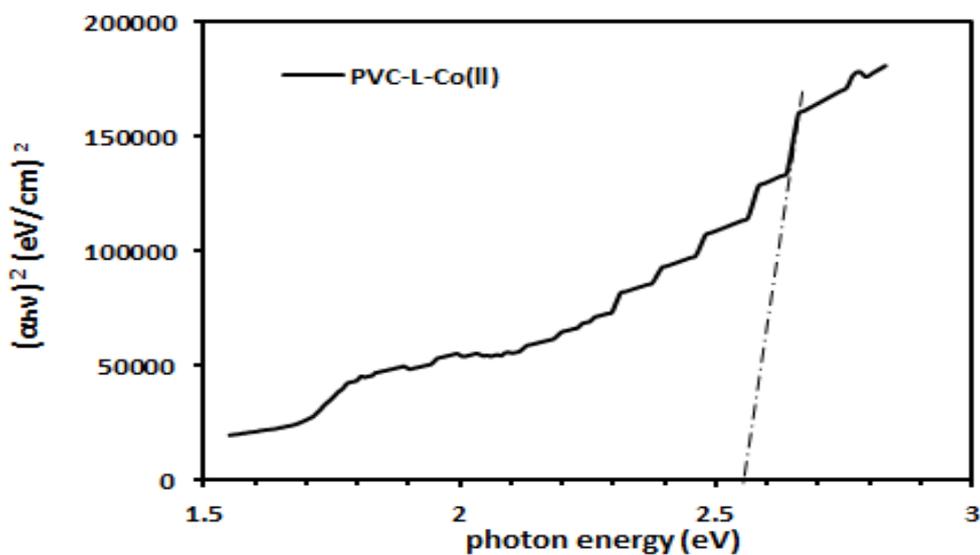


Figure 6. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Co(II)

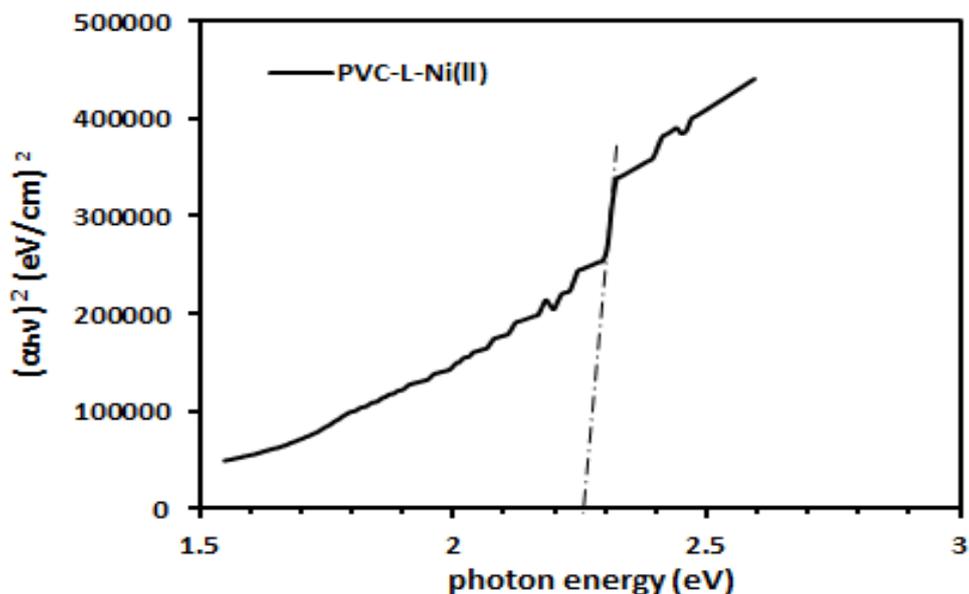


Figure 7. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Ni(II)

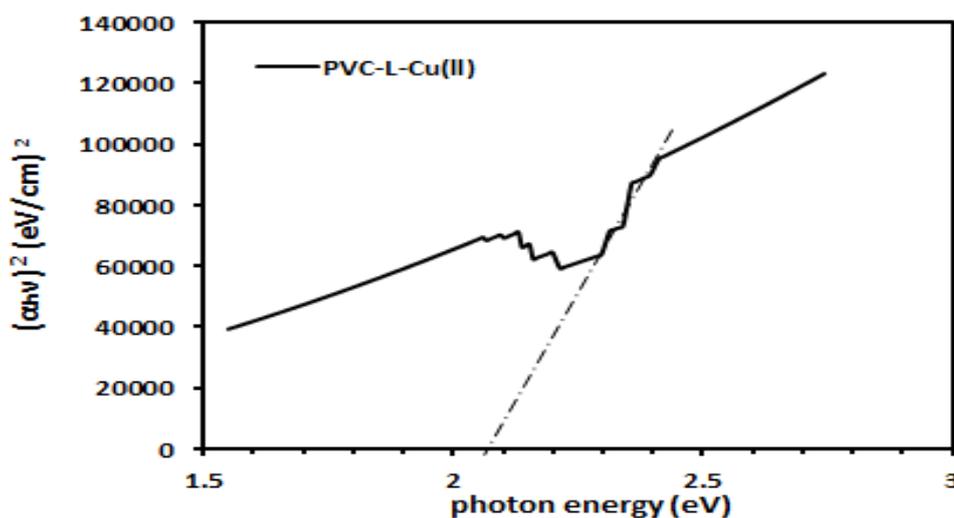


Figure 8. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cu(II)

CONCLUSION

PVC bound 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.

ACKNOWLEDGMENTS

The authors extend their appreciation to the Al-Nahrain University, University of Nizwa and University of Balochistan for continued support.

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