European Journal of Chemistry 5 (4) (2014) 652-656

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Study of the optical properties of poly(vinyl chloride)-4-[(5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl]phenol complexes

Noora Asaad Witwit

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, 10072, Iraq

**Corresponding author at: Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, 10072, Iraq.*
Tel.: +964.771.1088603. Fax: +964.771.1088603. E-mail address: nona_witwit@yahoo.com (N.A. Witwit).

ARTICLE INFORMATION

DOI: 10.5155/eurjchem.5.4.652-656.1100

Received: 07 June 2014
Received in revised form: 15 July 2014
Accepted: 03 August 2014
Online: 31 December 2014

KEYWORDS

PVC
FT-IR
UV-Vis
Thiadizol
Energy gap
Optical properties

ABSTRACT

The most widely practiced reaction of diazonium salts is azo coupling. In this process, the diazonium compound is attacked by an electron-rich substrate. When the coupling partners are arenes (phenols), the process is an example of electrophilic aromatic substitution. Poly (vinyl chloride) (PVC) react with 4-[(5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl]phenol (L) in THF to form the PVC-L compound, which have been characterized by spectroscopic methods. PVC-L has further been reacted with different metals ions to form PVC-L-M^{II} complexes. The structure of these complexes has been characterized by FT-IR and UV-Vis spectrophotometry. The optical properties in the region from 200-900 nm were also 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.

1. 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, crown ethers, phosphines and bipyridines have been bound with mainly poly(styrene-divinyl benzene)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 [8-10]. 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 [11]. This article will describe the modification of PVC with anchoring ligand and study its optical properties.

2. Experimental

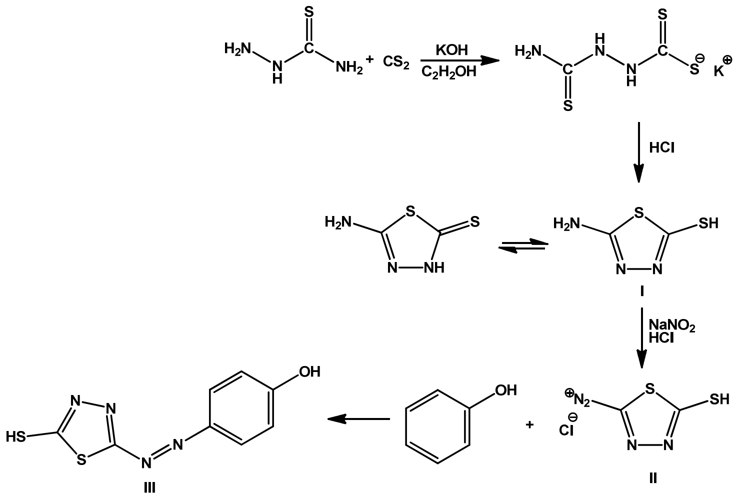
2.1. Instrumentation

All the melting points were recorded on a hot stage Gallen Kamp melting point apparatus, and are presented without corrections. The Fourier transform infrared spectroscopy (FT-IR) spectra were obtained in the range 4000-400 cm^{-1} using KBr disc on FTIR 8300 Shimadzu spectrophotometer. Ultraviolet-visible spectrums were measured using Shimadzu UV-Vis 160 A-Ultraviolet-visible spectrophotometer in range 200-1000 nm. The softening points were determined using thermal microscope (Kofler method), Reichert thermovar. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker model AC-200P spectrometer (200 MHz). Solvents and starting compounds were Merck or Aldrich and purity confirmed by FT-IR.

2.2. Synthesis of 5-amino-3H-1,3,4-thiadiazole-2-thione (I)

A mixture of potassium hydroxide (0.31 g, 5.34 mmole) and carbon disulfide (5 mL, 5.52 mmole) was dissolved in anhydrous ethanol (15 mL), later followed by addition of thiosemicarbazide (0.5 g, 5.49 mmole) dissolved in anhydrous ethanol. The reaction mixture was stirred and heated to reflux for 8 h.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) © 2014 Eurjchem Publishing - Printed in the USA
http://dx.doi.org/10.5155/eurjchem.5.4.652-656.1100



Scheme 1

The ethanol was removed by evaporation in vacuum, and the residue was dissolved in water (50 mL). This was slowly acidified with 5 mL of concentrated HCl. The precipitate was filtered to produce compound **I**. The crude product was washed with cold water, and this yellow solid was recrystallized out of ethanol to give a white solid [12-14] (Scheme 1). Color: White. Yield: 74%. M.p.: 229-231 °C (Lit.: 232 °C [15]). ^{1}H NMR (200 MHz, DMSO-*d*$_6$, δ, ppm): 7.0 (s, 2H, NH_2), 13.2 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-*d*$_6$, δ, ppm): 181.2, 161.2. FT-IR (KBr, ν, cm^{-1}): 3340, 3251, 3132, 2925, 1609, 1475, 1362, 1328, 1059. MS (EI, *m/z* (%)): 132.98 (M$^+$, 100). Anal. calcd. for $C_2H_3N_3S_2$: C, 18.03; H, 2.27 ;N, 31.55. Found: C, 18.00; H, 2.20; N, 31.57%.

2.3. Synthesis of 4-[(5-Mercapto-1,3,4-thiadiazol-2-yl) diazenyl]phenol (III)

To a solution of compound **I** (0.5 g, 3.75 mmole) in 10 mL of water, was added 5 mL of concentrated HCl, which was subsequently diazotized by treatment with sodium nitrate (0.31 g, 4.49 mmole) at 0 °C with stirring for 20 minutes. The resulting solution of diazonium salt **II** was slowly added with vigorous stirring at 0-5 °C, over a solution of phenol (0.42 g, 4.5 mmole) dissolved in sodium hydroxide (1 M, 20 mL). More sodium hydroxide (20 mL, 1 M) was added to the reaction mixture and allowed to react for 3 hours. Finally, acidification of the mixture with 1 M HCl produced an orange colored precipitate, which was filtered off and recrystallized from dimethylformamide:water (2:1, *v*:*v*) to give a dark orange solid as in Scheme 1 [16]. Color: Dark orange. Yield: 45%. M.p.: 187-189 °C. ^{1}H NMR (200 Mhz, $CDCl_3$, δ, ppm): 6.97 (d, 2H, Ar-H), 7.83 (d, 2H, Ar-H). FT-IR (KBr, ν, cm^{-1}): 3100-3500 (OH), 1600 (C=N), 1535 (N=N). MS (EI, *m/z* (%)): 238.00 (M, 100.0%). Anal. calcd. for $C_8H_6N_4OS_2$: C, 40.33; H, 2.52 ;N, 23.52. Found: C, 40.3; H, 2.5; N, 23.5%.

2.4. Purification of poly(vinyl chloride) [17]

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.

2.5. Synthesis of PVC ligand compound [17]

A mixture of 0.1 mole of PVC dissolved in THF and 0.05 mole from 4-[(5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl] phenol (**III**) and 5 drops of pyridine was refluxed for four hours in THF solvent. The precipitated modified polymer separated by evaporated the solvent. Color: Brown. Yield: 69%. Softing p.: 249-253 °C. FT-IR (KBr, ν, cm-1): 617 (C-Cl), 2912 (C-H), 1535 (N=N), 1360 (S-C). Anal. calcd. for $C_{12}H_{14}N_4S_2$: C, 51.79; H, 5.03; N, 20.14. Found: C, 51.8; H, 5.03; N, 20.14%.

2.6. Synthesis of PVC ligand complex [17]

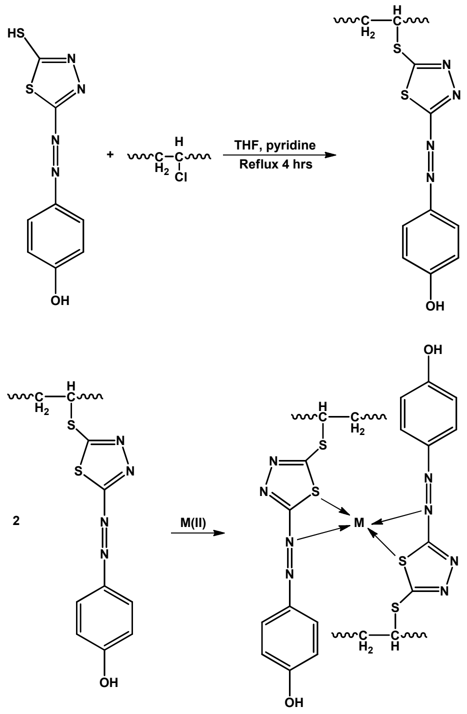
A general procedure can be adopted for the preparation of all the metal complexes as follows: PVC-L-M^{II} complexes were obtained by dissolving 0.5 mol of the appropriate transition metal salt in ethanol and dissolving 1.5 mol of PVC-L dissolved in THF, colored precipitates were obtained then the precipitate was filtered, washed with excess of absolute ethanol. (Scheme 2) shows reactions for the synthesis of PVC-L-M^{II} polymer [18]. The physical data of the prepared PVC-complexes are found in Table 1.

Table 1. Physical data of the prepared complexes.

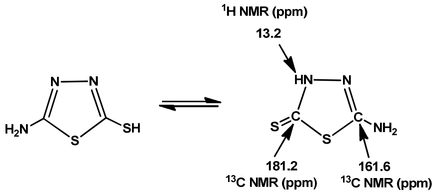
Sample	Color	Softing point (°C)
PVC-L	Brown	249
PVC-L-Sn	Yellow	288
PVC-L-Zn	Reddish brown	267
PVC-L-Cu	Dark green	273

2.7. Films preparation

A certain concentration of PVC and PVC-L-M^{II} solution (5 g/100 mL) in THF was used to prepare polymer films with a thickness of 30 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 to 900 nm by using computerized Shimadzu UV-VIS 160A-Ultraviolet spectro-photometer 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 $(\alpha h\upsilon)^2$ *vs* $(h\upsilon)$ 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 [19].



Scheme 2



Scheme 3

3. Result and discussion

The compound 2-amino-5-thiol-1,3,4-thiodiazol (**I**) was obtained following a procedure described in the experimental part (Scheme 1). The formation of compound **I** was confirmed on the basis of a ^{1}H and ^{13}C NMR and FT-IR spectroscopic analysis, showing a stable tautomeric structure for this compound.

The chemical shift of the C-2 (^{13}C NMR) in compound **I** represents the chemical shift characteristic of the carbon atom of a thione group and also in the ^{1}H NMR spectrum a NH can be observed, representative of a thioamide (13.2-14.0 ppm) instead of a thiol (SH) group (2.0-4.0 ppm). It can therefore be concluded that compound **I** exists in its thione form in dimethyl sulfoxide solution (Scheme 3).

The most widely practiced reaction of diazonium salts is azo coupling. In this process, the diazonium compound is attacked by coupled to electron-rich substrates. When the coupling partners such phenols, the process is electrophilic aromatic substitution, the aryldiazonium cation is the electrophile and the activated arene is a nucleophile [20].

The modification of PVC with 4-[(5-mercapto-1,3,4-thia diazol-2-yl)diazenyl]phenol (**III**) was performed by nucleophilic attach of S 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 was established on the bases of its FT-IR and UV-VIS spectroscopy. Each of the polymers showed band characteristic of its own structure. The modification of PVC with sulphur can be demonstrated by FT-IR spectroscopy, the disappear of the absorption band due to (-SH) stretching frequencies of sulphur clearly indicate the reaction between PVC and sulphur.

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 $\pi \rightarrow \pi^*$ 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. The *d-d* transitions appeared in the visible region. These transitions are assigned in relevance to the structures of complexes [21,22].

The relation between $(\alpha h\upsilon)^2$ *vs* photon energy for modified and complex PVC are shown in Figures 1-4 for allowed transition. The shift in the energy gap could be attributed to the formation of polarons and bipolarons.

Table 2. Absorption and IR spectra of PVC-L and PVC-L-M^{II}.

Complex	**Electronic absorption peaks (nm)**	**Assignment**
PVC	261	π-π*
PVC-L	277	π-π*
	289	π-π*
PVC-L-Cu	260	π-π*
	266	π-π*
	305	π-π*
	510	d-d
PVC-L-Sn	244	π-π*
	267	π-π*
PVC-L-Zn	277	π-π*
	285	π-π*
	320	π-π*
Complex	**IR (cm^{-1})**	**Assignment**
PVC	614	C-Cl stretching
	2910	C-H stretching
PVC-L	617	C-Cl
	2912	C-H
	1535	N=N
	1360	S-C
PVC-L-Cu	2910	C-H (alphatic)
	623	C-Cl
	1520	N=N
	1330	S-C
	420	Cu-S
	524	Cu-N
PVC-L-Sn	2912	C-H (alphatic)
	615	C-Cl
	1512	N=N
	1328	C-S
	442	Sn-S
	559	Sn-N
PVC-L-Zn	2914	C-H (alphatic)
	615	C-Cl
	1525	N=N
	522	Zn-N
	1300	C-S
	436	Zn-S
	522	Zn-N

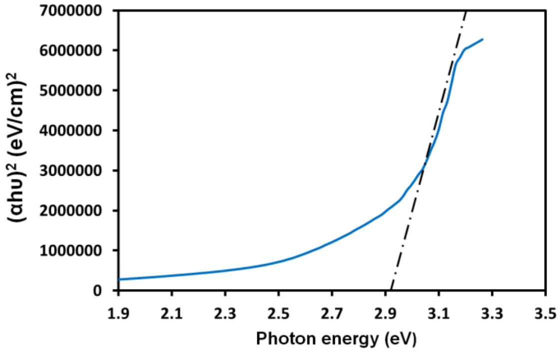


Figure 1. Allowed direct transition (αhυ)^2 *vs* energy for PVC-L.

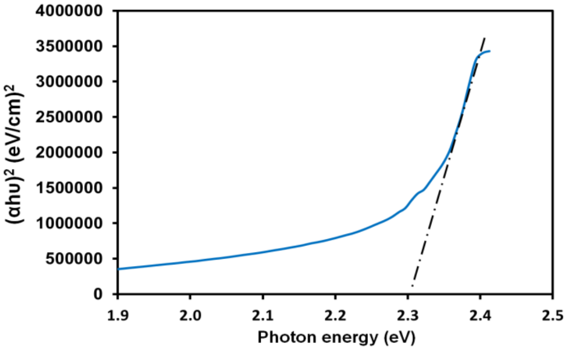


Figure 3. Allowed direct transition (αhυ)^2 *vs* energy for PVC-L-Zn^{II}.

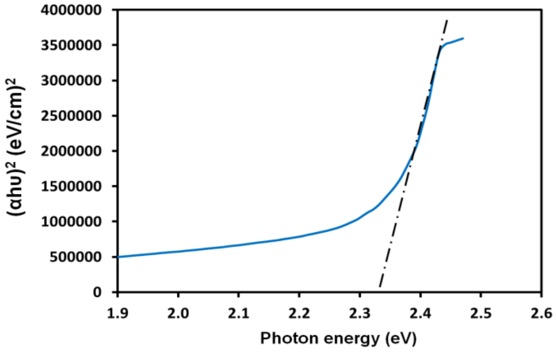


Figure 2. Allowed direct transition (αhυ)^2 *vs* energy for PVC-L-Sn^{II}.

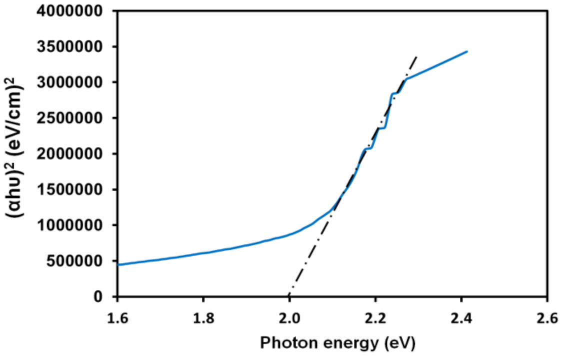


Figure 4. Allowed direct transition (αhυ)^2 *vs* energy for PVC-L-Cu^{II}.

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 1 was investigated and the results shown in Table 3. The results presented in Figures 1-4 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 [23]. Conductivity measurement of PVC with additive can obtain by adopting the data of energy gap [24,25], (see Table 3 and Figures 1-4). The conductivity measurement for PVC in the presence of additive increase in the following order: PVC-L-Cu > PVC-L-Zn > PVC-L-Sn > PVC-L > PVC [17].

Table 3. Indicate the energy band gap according to the direct allowed transition.

Sample	E_g (ev)
PVC	5.79
PVC-L	2.91
PVC-L-Sn	2.33
PVC-L-Zn	2.30
PVC-L-Cu	2.00

4. Conclusion

Azo compounds were synthesized, which were derived from heterocyclics and basic phenolic-type structures. Possibilities for synthesis with more complex structures were certainly possible, and their applications are yet to be developed and were synthesized from reaction of diazonium salts is azo coupling with phenol. PVC bound 4-[(5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl]phenol can be synthesized by Chlorine displacement reaction between PVC and L in alkaline condition. Subsequent complexation of PVC-L with Cu^{II}, Zn^{II}, and Sn^{II} yield intensely colored PVC-L-M^{II} complexes those 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.

Acknowledgement

Gratefully acknowledged the funding support from The Chemistry Department in College of Science, Al-Nahrain University, Iraq.

References

[1]. Amit, B.; Rawlins, J. W.; Ray, P. Polymer Crafting and Crosslinking. John Wiley & Sons Inc., 2009.
[2]. Chen, Y.; Song, Y.; Zhang, Y.; Lang. *Inorg. Chem. Commun.* **2008**, *11*, 572-575.
[3]. Gustafsson, B.; Hakansson, M.; Jagner, S. *Inorg. Chim. Acta* **2003**, *350*, 209-214.
[4]. Genhua, Z.; Pan, C. *Polymer* **2005**, *46*, 2802-2810.
[5]. Jumat, S.; Salah, N.; Ahmed, A.; Yousif, E. *Chem. Tech. Res.* **2011**, *3(2)*, 981-987.
[6]. Moulay, S. *Progr. Polymer Sci.* **2010**, *35*, 303-331.
[7]. Claudiu, L.; Edina, R.; Bogdan, M.; Teodora, Z.; Gheorghe, H. U. P. B. *Sci. Bull. Series B* **2010**, *72*, 127-140.
[8]. Yousif, E.; Hameed, A.; Bakir, E. *J. Al-Nahrain Univ. (Science)* **2007**, *10*, 7-12.
[9]. Mohammed, A.; Yousif, E.; Alwash, A.; Yang, F. *Iraqi J. Polymers* **2009**, *13(2)*, 27-36.
[10]. Yousif, E.; Hameed, A.; Kamil, A.; Farina, Y.; Asaad, N.; Graisa, A. *Aust. J. Basic Appl. Sci.* **2009**, *3(3)*, 1786-1794.
[11]. Aliwi, M.; Yousif, E; Otaiwi, A. *Iraqi J. Polymers* **2005**, *10(1)*, 53-64.
[12]. Guha, P. C. *J. Am. Chem. Soc.* **1922**, *44*, 1510-1517.
[13]. Kumar, S.; Kaushik, D.; Bawa, S.; Khan, S. *Chem. Biol. Drug Design* **2012**, *79(1)*, 104-111.
[14]. Gaber, M.; El-Sayed, Y. S.; El-Baradie, K. Y.; Fahmy; R. M. *Spectrochim. Acta A* **2013**, *107*, 395-370.
[15]. Abdel-Rahman T. M. Phosphorus Sulfur **2006**, *181(8)*, 1737-1754
[16]. Pedro, O. L.; Leonel, V.; Claudio, A.; Miguel, G.; Pedro, O. L. *J. Chil. Chem. Soc.* **2007**, *52(1)*, 1120-1122.
[17]. Abdallh, M. *J. Al-Nahrain Univ. (Science)* **2013**, *16(2)*, 24-29.
[18]. Ahmed, A.; Najim, T.; Salimon, J.; Salih, N.; Graisa, A.; Farina, Y.; Yousif, E. *ARPN-J. Eng. Appl. Sci.* **2010**, *5*, 43-45.
[19]. Yousif, E.; Adel, H.; Moued, F. *J. Appl. Sci. Res.* **2010**, *6(7)*, 879-882.
[20]. Smith, Michael B.; Jerry, M. Advanced Organic Chemistry, 6th edition, New York: Wiley, 2007.
[21]. Al-Ramadan, Y. *Optical Mater.* **2000**, *14*, 287-290.
[22]. Yousif, E. *J. King Saud Univ.* **2012**, *24*, 167-170.
[23]. Al-Daeif, Y.; Yousif, E.; Abdul Nabi, M. *J. Al-Nahrain Univ. (Science)* **2012**, *15(2)*, 79-83.
[24]. Salimon, J.; Salih, N.; Ahmed, A.; Yousif, E. *Int. J. ChemTech Res.* **2011**, *3(2)*, 981-987.
[25]. Yousif, E.; Abdallh, M.; Hashim, H.; Salih, N.; Salimon, J.; Abdallh, B. M.; Win, Y. *Int. J. Ind. Chem.* **2013**, *4(4)*, 1-8.