Synthesis and photochemical study of some metal complexes of poly(vinyl chloride)-2-mercapto-5-phenyl 1,3,4-oxadiazole

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Abstract

Poly(vinyl chloride) (PVC) has been reacted with 2-mercapto-5-phenyl 1,3,4-oxadiazole (L) in THF to form the PVC-L compound, which has been characterized by spectroscopic methods. PVC-L has further been reacted with 1,2 dichloroethane solutions of Cu^{II}, Ni^{II}, Zn^{II} and Sn^{II} to form the intensely colored PVC-L-M^{II} complexes. The structures of these complexes have been characterized by IR and Uv-Vis. Spectrophotometry.

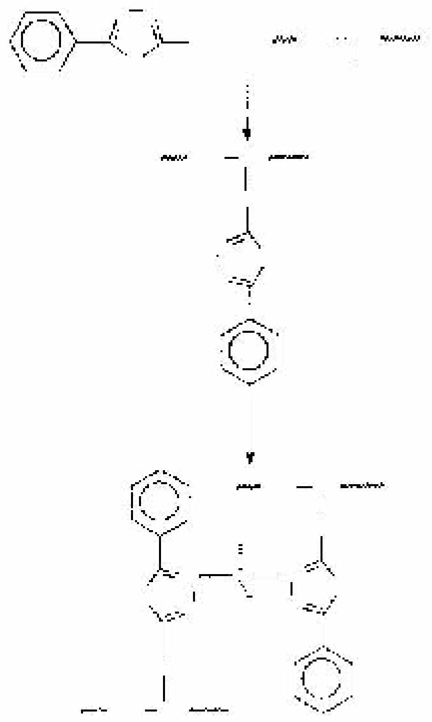
The photostabilization of PVC-L-M^{II} films complexes was investigated, the photostabilization activity of these compounds were determined by monitoring the carbonyl and polyene indices with irradiation time.
All results obtained show that the rate of photodegradation of PVC-L-M^{II} films, 30 micrometer in thickness following the trends:

PVC> PVC-L> PVC-L-Sn^{II}> PVC-L-Zn^{II}> PVC-L-Ni^{II}> PVC-L-Cu^{II}

According to the experimental results obtained several mechanisms were suggested depending on the structure of the PVC-L-M^{II} complexes.

Introduction

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research(1). A number of ligands including polydentate amines, crown ethers, phosphines, bipyridines, and naphthyridines have been bound with mainly polystyrene divinylbenzene copolymers(2-5). These studies are mostly concerned with ion-binding and catalytic(7) aspects. Very little information appears to exist as to whether, and to what extent, such metal ion complexation can influence the properties of the macromolecule. Recently, scientists does able to modified(8-9) PVC by introduction aromatic and heterocyclic moieties through halogen displacement reaction. PVC, thus modified, showed improved overall photochemical stability. 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. In view of paucity of any information on PVC in this line, we undertook the synthesis of PVC-2-mercapto 5 phenyl 1,3,4-oxadiazole compound and the corresponding Cu^{II}, Ni^{II}, Zn^{II} and Sn^{II} complexes. This article will describe the synthetic procedure adopted (Scheme 1) and the photostability of these complexes towards UV light.



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

Experimental

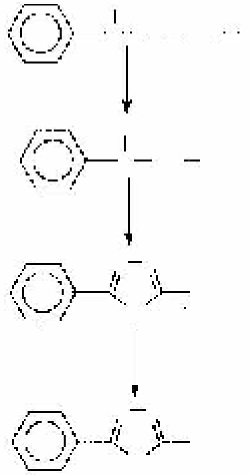
Materials

Purification of Poly(vinyl chloride)[10]

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 hours.

Synthesis of 2-mercapto-5-phenyl 1,3,4-oxadiazole [12]

A mixture of ethyl benzoate (0.1 mole) and hydrazine hydrate (0.1 mole) was refluxed for two hours, ethanol (50 ml) was added and refluxed for (5) hours. The precipitate benzoyl hydrazine which separated on cooling was filtered and washed with cold methanol. To a solution of benzoyl hydrazine (0.02 mole) in ethanol (100ml) at (0°C) were added carbon disulfide (0.04mol) and potassium hydroxide (0.02 mole), the mixture was refluxed for (7) hours. The solvent was evaporated and the residue is dissolved in water and acidified with dilute hydrochloric acid. The precipitate was filtered and crystallized from (ethanol water) to give 2-mercapto-5-phenyl 1,3,4-oxadiazole. The steps of the synthesis of 2-mercapto-5-phenyl 1,3,4-oxadiazole are shown in Scheme (2).



Scheme (2) Reagents and conditions. (I) NH_2NH_2, EtOH, reflux, 7 hr. (II) CS_2, pyridine, reflux 7 hrs. (III) HCl.

Synthesis of PVC Ligand compound [13]

A mixture of 0.1 mole of PVC dissolved in THF and 0.05 mole from a prepared ligand and 5 drops of pyridine was refluxed for five hours in THF solvent. The precipitated modified polymer is separated the solvent evaporator process.

Synthesis of PVC Ligand complex [12]

A general procedure can be adopted for the preparation of all the metal complexes as follows : PVC-L-M^{I} 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 1,2 dichloromethane, colored precipitates were obtained which were then filtered, washed with excess of absolute ethanol. Scheme (1) shows reactions for the synthesis of PVC-L-M^{I} polymer. The physical data of the prepared PVC-complexes are found in Table (1)

Table (1) Physical data of the prepared complexes

Symbol	Color	Decomposition Point °C
L	White	212-214 m. p.
PVC-L	Yellow	265
PVC-L-Cu	Green	> 300
PVC-L-Ni	Yellow	288
PVC-L-Sn	Yellow	> 300
PVC-L-Zn	Brown	277

Experimental Techniques

Films Preparation

A certain concentration of PVC and PVC-L-M^{I} solution (5g/100ml) in tetrahydrofuran (THF) was used to prepare different thickness of polymer films, (measured by a micrometer type 2610 A, Germany) with and without various concentrations of the complexes prepared. The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stand specially used for irradiation which is made of aluminum plate (0.6 mm) in thickness supplied from (Q-panel) company USA.

Irradiation experiments

Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and another one behind. Each side contains lamps type (Fluorescent Ultraviolet Lights) 40 watt each. These lamps are of the type (UV-B 313) giving spectrum range between (290 to 360 nm) and the maximum wavelength light intensity is at is (313nm).

The polymer film samples vertically fixed and parallel to the lamps to be sure that UV incident radiation is vertically incident on the samples. The irradiation samples are changed places from time to time to be sure that the intensity of light incident on all samples were equal.

Photodegradation measuring methods

Measuring the photodegradation rate of polymer films using infrared spectrophotometery

The photodegradation of polymer film samples were followed by monitoring of FTIR spectra in the range (4000-400) cm^{-1} . The spectra were recorded using FTIR 8300 Shimadzu Spectrophotometer.

The position of carbonyl absorption bands is specified at 1722 cm^{-1} and (1602 cm^{-1})[15] for the calculation carbonyl and polyene indicies respectively.

The photodegradation during different irradiation times were followed by observing changes in carbonyl and polyene peaks. Then carbonyl ($I_{c.o}$) and polyene (I_{po}) indices were calculated by comparison of the FTIR absorption peak at 1722 cm^{-1} and 1602 cm^{-1} with reference peak at 1328 cm^{-1}, respectively. This method is called band index method(11) which includes:

$$I_s = \frac{A_s}{A_r}$$

A_s = Absorbance of peak under study.
A_r = Absorbance of reference peak.
I_s = Index of the group under study.

Actual absorbance, the difference between the absorbance of base line and top peak (A Top Peak – A Base Line), is calculated using the Base Line method(9).

Results and Discussion

Spectrophotometry

The FTIR spectrum of 2-mercapto-5-phenyl 1,3,4-oxadiazole shows the following characteristic bands, a weak band at v(2767) cm^{-1} could be attributed to v(S-H) stretching. A strong peak at 1610 cm^{-1} was observed related to v(C=N) cm^{-1} also the bands at v(1184) and v (1020) cm^{-1} which be attributed to v(C-O-C) asym. and sym. respectively.

The FTIR of PVC-L graft polymer spectrum shows the following features, a strong band at v(615) cm^{-1} was observed which could be attributed to v(C-Cl) band which is differ from PVC with out modification v(609). Also the disappearance of S-H band good indicator for formation the PVC-L compound.

In the FTIR of the PVC-complexes, a shift in v(C=N) cm^{-1} for all complexes as shown in Table (1).And new bands appear in the range v(455-485) cm^{-1} which could be attributed to (M-N) bond and this gives further evidences for the structures of complexes.

Table (2) shows the electronic absorption bands for ligand and PVC-complexes. The bands are classified into three distinct groups: belong to ligand transitions appeared in the UV. region and charge transfer while d-d transitions appeared in the visible region. These transitions are assigned in relevance to 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			609	C-Cl stretching
			2910	C-H stretching
L	240	$\pi \rightarrow \pi^*$	2767	S-H stretching
	243	$\pi \rightarrow \pi^*$	1184	Asym. (C-O-C)
			1022	sym. (C-O-C)
			1610	C=N stretching
PVC-L	240	$\pi \rightarrow \pi^*$	2856	C-H (aliphatic)
	252	$\pi \rightarrow \pi^*$	615	C-Cl stretching
			1616	C=N stretching
			1042	sym. (C-O-C)
			1197	Asym. (C-O-C)
PVC-L-Sn	237	$\pi \rightarrow \pi^*$	1618	C=N stretching
	277	$\pi \rightarrow \pi^*$	620	C-Cl stretching
			1035	sym. (C-O-C)
			1122	Asym. (C-O-C)
			332	Sn-N
			260	Sn-Cl
PVC-L-Zn	232	$\pi \rightarrow \pi^*$	1625	C=N stretching
	270	$\pi \rightarrow \pi^*$		
	310	Charge transfere	622	C-Cl stretching
			1051	sym. (C-O-C)
			1126	Asym. (C-O-C)
			524	Zn-N
			236	Zn-Cl
PVC-L-Ni	230	$\pi \rightarrow \pi^*$	1629	C=N stretching
	264	$\pi \rightarrow \pi^*$	624	C-Cl stretching
	340	Charge transfer	1049	sym. (C-O-C)
	622	(d-d)	1168	Asym. (C-O-C)
			529	Ni-N
			243	Ni-Cl
PVC-L-Cu	235	$\pi \rightarrow \pi^*$	1618	C=N stretching
	272	$\pi \rightarrow \pi^*$	626	C-Cl stretching
	308	Charge transfer	1055	sym. (C-O-C)
	440	(d-d)	1170	Asym. (C-O-C)
			460	Cu-N
			234	Cu-Cl

Irradiation of polymers

poly(vinyl chloride) 2-mercapto-5-phenyl 1,3,4-oxadiazole Cu(II), Ni(II), Zn(II) and Sn(II) complexes were used as photostabilizer.

In order to study the photochemical activity of these PVC-complexes films , the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry.

The irradiation of PVC and PVC-L-M^{II} films with light of wavelength, λ = 313 nm led to a clear change in their FTIR spectrum, as shown in Figure (1). Appearance of bands in 1772 cm^{-1} and 1724 cm^{-1} respectively, were attributed to the formation of carbonyl groups related to chloroketone and the second one is due to aliphatic ketone, together with formation of a band at 1604 cm^{-1} related to polyene group[18].

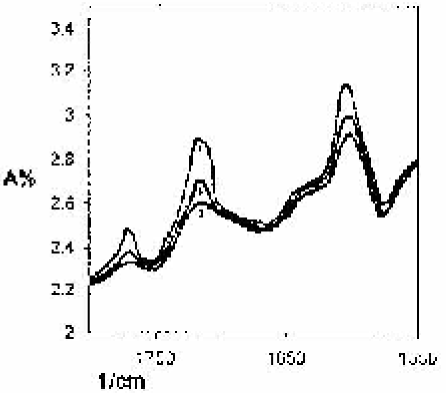


Figure (1): Change in IR spectrum of PVC-L-Ni^{II} film (30μm) complexes (1. at zero time 2. after 100 hrs 3. after 250 hrs irradiation).

The absorption of the polyene and carbonyl groups are used to follow the extend of polymer degradation during irradiation. These absorption was calculated as carbonyl index (I_{co}) and polyene index (I_{PO})

Therefore, one should expect that the growth of carbonyl index is a measure to the extent of degradation. As seen from Figure (2) that the presence of PVC-L, PVC-L-Sn^{II}, PVC-L-Zn^{II}, PVC-L-Ni^{II}, PVC-L-Cu^{I} and PVC-L-Cu^{II} show lower growth rate of carbonyl index with irradiation time with respect to PVC film without additives (control).

As shown in Figure (2), the growth of carbonyl index with irradiation time is lower than PVC (control). So, these PVC-complexes might be considered as photostabilizers polymer.

The efficient photostabilizer show a longer induction period. Therefore, from Figure (2), the PVC-L-Cu^{II} is the most active photostabilizer, followed by PVC-L-Ni^{II} then PVC-L-Zn^{II} then PVC-L-Sn^{II} and PVC-L which is least active.

As it was mentioned before polyene compounds are produced during photodegradation of PVC. Therefore, polyene index (I_{PO}) was monitored with irradiation time in the PVC and PVC-complexes. Results are shown in Figure (3).

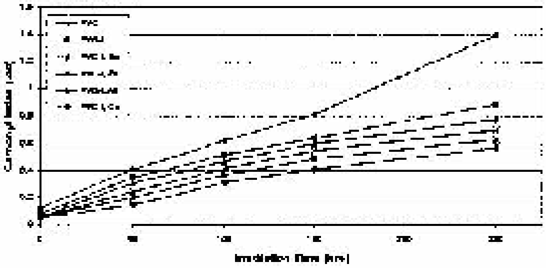


Figure (2): The relationship between the carbonyl index and irradiation time for PVC-L-M^{II} films (30 μm) thickness.

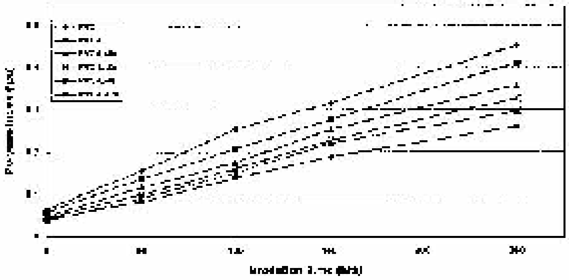
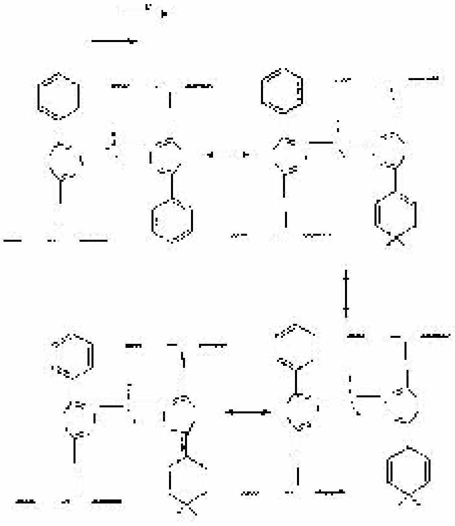


Figure (3): The relationship between the polyene index and irradiation time for PVC-L-M^{II} films (30 μm) thickness.

Suggested mechanisms of photostabilization process

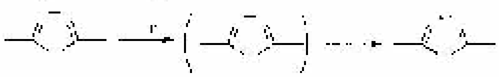
Metal complexes generally known as photostabilizers for poly olefins(17) through both peroxide decomposer and excited state quencher. Therefore, it is expected that these complexes act as radical scavengers through energy transfer and by forming unreactive charge transfer complexes between the metal chelate and excited state of the chromophore (POO˙) and stabilize through resonating structures as shown in Scheme (3)



Scheme (3): Suggested mechanism of photostabilization of complexes as radical scavengers.

The 1,3,4-oxadiazole ring in this compound plays a role in the mechanism of the stabilizer process by acting as UV absorber.

The UV light absorption by these additives containing -1,3,4oxadiazole dissipates the UV energy to harmless heat energy Scheme (4). Further more this ring play a role in resonating structures conjugation of radical in peroxide decomposer Scheme (3), which support the ideas that this compounds as photostabilizer.



Scheme (4): Suggested mechanism of photostabilization of-1,3,4 oxadiazole compounds as UV absorber.

Further that the complextions process lead to increase the cross linking between the PVC series, which increase the efficiency of photostabilizing towards UV light.

Conclusion

PVC bound 2-mercapto-5-phenyl 1,3,4-oxadiazole(L) 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} and Sn^{II} yield intensely colored PVC-L-M^{II} complexes which exhibit improved overall photostabilization process. The activity of these polymeric complexes in photostabilization which increase in the order:

PVC> PVC-L> PVC-L-Sn^{II}> PVC-L-Zn^{II}> PVC-L-Ni^{II}> PVC-L-Cu^{II}

$\longrightarrow$

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