

Materials

N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea (L1)	(IBT)
[N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea] tin(II)	Sn(IBT)
[N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea] Cobalt(II)	Co(IBT)
[N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea] Nickel(II)	Ni(IBT)
[N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea] copper(II)	Cu(IBT)
N-diPropyl-N'-2,4-dichlorobenzoyl thiourea (L2)	(PBT)
[N-diPropyl-N'-2,4-dichlorobenzoyl thiourea] tin(II)	Sn(PBT)
[N-diPropyl-N'-2,4-dichlorobenzoyl thiourea] Cobalt(II)	Co(PBT)
[N-diPropyl-N'-2,4-dichlorobenzoyl thiourea] nickel(II)	Ni(PBT)
[N-diPropyl-N'-2,4-dichlorobenzoyl thiourea] copper(II)	Cu(PBT)

Experimental

Synthesis of ligands

All chemicals used for the preparation of the title compounds were of reagent grade quality. Some of the solvent was distilled before use. The ligands were prepared with a procedure similar to that reported in the literature⁽¹⁴⁾. A solution of 2,4-dichlorobenzoyl chloride) (0.01 mol) in acetone (50 cm³) was added drop wise to a suspension of potassium thiocyanate (0.01 mol) in acetone (30 cm³). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of amine (0.01 mol) in acetone (10 cm³) was added and the resulting mixture was stirred for 2h. Hydrochloric acid (0.1 N, 300 cm³) was added to the solution, which was then filtered. The solid product was washed with water and purified by recrystallization from an ethanol/dichloromethane mixture(1:1)⁽¹⁵⁾.

N-diisobutyl-N-2,4-dichlorobenzoyl thiourea(IBT): Yellow, Yield: 71%, m.p.:110-112°C, anal. Calcd. for C₁₆H₂₂N₂O₂SCl₂: IR(KBr,cm⁻¹): ν(C=O) 1700(s), ν(C=S) 1620(s), ν(N-H) 3240(br.).

N-dipropyl-N-2,4-dichlorobenzoyl thiourea (PBT) :White Yellow,

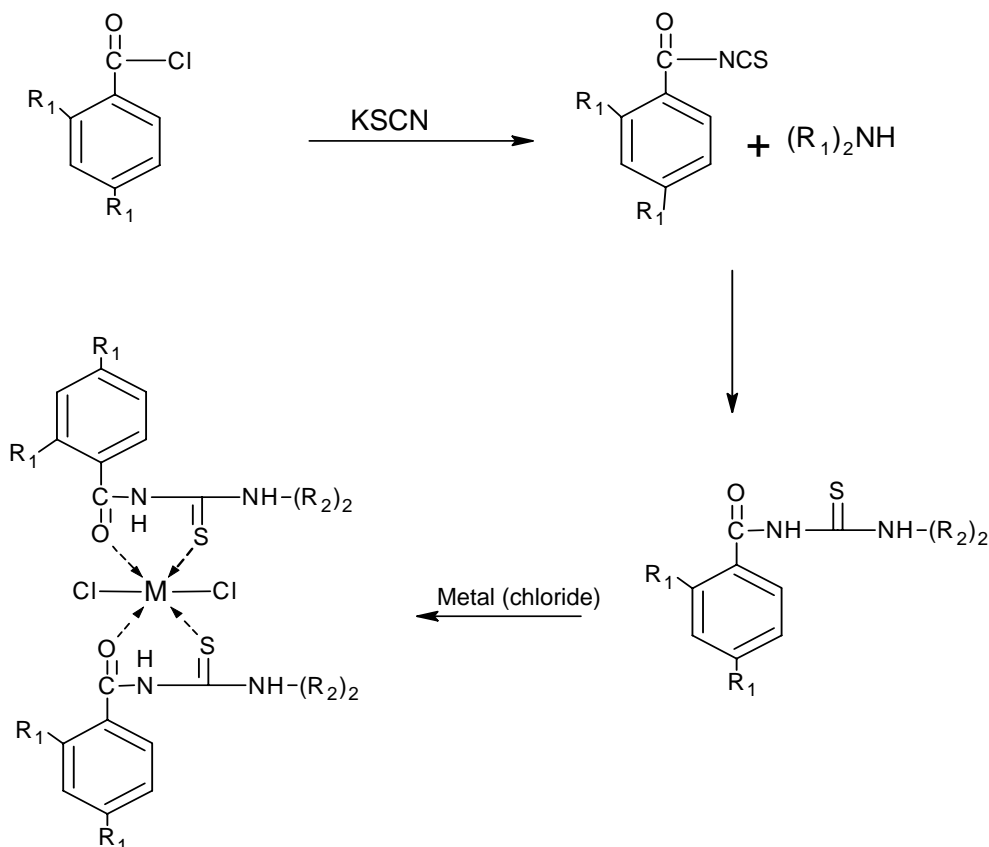
Yield:82%, m.p.: 121-123°C, anal. Calcd. for C₁₄H₁₈N₂O₂SCl₂: IR (KBr,cm⁻¹): ν(C=O) 1685(s), ν(C=S) 1610(s), ν(N-H) 3225(br.).

Preparation of Complexes

A general procedure can be adopted for the preparation of all the metal complexes as described below: L-M complexes were obtained by dissolving 1.5 mol of the appropriable metal salt (SnCl₂, CoCl₂, NiCl₂.6H₂O and CuCl₂.2H₂O) in ethanol and dissolving 0.5 mol of L in ethanol, and then the PH was raised to 8 by adding 5% w/v of NaHCO₃ solution. different intensely colored precipitates were obtained which were then filtered, washed with excess of absolute ethanol. Scheme (1) show reaction for synthesis of L-M and the physical data of the prepared complexes are found in Table (1)

Table (1) Physical data and elemental analysis of the prepared compounds

Symbol	Color	m. p. °C	C% cal. (found)	H% cal. (found)	N% cal. (found)	Cl% cal. (found)
IBT (L1)	Yellow	110-112	53.3(53.6)	6.11(6.13)	7.7(7.5)	
[Sn(IBT)Cl ₂]	Reddish Yellow	165-169	42.2(41.5)	4.84(5.18)	6.1(6.3)	15.4(15.31)
[Co(IBT)Cl ₂]	Blue	140-143	45.2(45.9)	5.18(5.12)	6.59(6.3)	
[Ni(IBT)Cl ₂]	Green	182-184	45.2(44.5)	5.18(5.2)	6.59(6.6)	16.5(16.11)
[Cu(IBT)Cl ₂]	Pal green	177-179	44.9(44.7)	5.15(5.1)	6.56(6.41)	
PBT (L2)	White Yellow	121-123	50.6(50.8)	5.42(5.4)	8.43(8.42)	
[Sn(PBT)Cl ₂]	Red	195-197	39.4(40.1)	4.22(4.31)	6.56(6.51)	
[Co(PBT)Cl ₂]	Pal Blue	128— 130	42.37(42.61)	4.54(4.52)	7.06(7.1)	17.66(17.91)
[Ni(PBT)Cl ₂]	Blue	160-162	42.36(42.11)	4.54(4.55)	7.07(6.8)	
[Cu(PBT)Cl ₂]	Pal green	165-167	42.13(42.16)	4.51(4.34)	7.02(7.06)	17.55(18.2)



Where M = Sn(II), Co(II), Ni(II) and Cu(II)
R₁ = Cl, R₂ = propyl or Isobutyl

Scheme (1)

Purification of Poly (vinyl chloride) ⁽¹⁶⁾

Commercial Poly(vinyl chloride) (PVC) supplied from Petkim company (Turkey) was freed from additives by re-precipitation of PVC from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours

Experimental Techniques

Films Preparation

Different concentration of Poly(vinyl chloride) solution (g/ml) in tetrahydrofuran (THF) was used to prepare 50 μm thickness of polymer films, (measured by a micrometer type 2610 A, Germany) with and without 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 five hours under reduced pressure. The films were fixed on stand specially used for irradiation which is aluminum plate (0.6 mm) in thickness supplied from (Q-panel) company.

Irradiation experiments

Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Q. panel, company, U S A), 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. There lamps are of the type (UV-B 313) giving spectrum range between (290-360 nm) and the maximum wavelength 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 sample is equal.

Photodegradation measuring methods

A. Measuring the photodegradation rate of polymer films using infrared spectrophotometry

The photodegradation of polymer film samples were followed by mentoring of IR spectra in the range (600-4000) cm^{-1} the spectra were recorded using IR SP3-100 Shimadzu Spectrophotometer.

The position of carbonyl absorption is specified at 1722cm^{-1} , and polyene group at $(1602\text{ cm}^{-1})^{(17)}$.

The photo degradation during different irradiation times were followed by observing changes in carbonyl and polyene peaks. Then carbonyl (Ico) and polyene (Ipo) indices were calculated by comparison of the IR absorption peak at 1722cm^{-1} and 1602cm^{-1} with reference peak at 1328cm^{-1} , respectively. This method is called band index method⁽¹⁷⁾ which includes:

$$I_s = \frac{A_s}{A_r} \dots\dots\dots(1)$$

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 ($A_{\text{Top Peak}} - A_{\text{Base Line}}$), is calculated using the Base Line method⁽¹⁸⁾.

B. Determination of viscosity average molecular weight

(\bar{M}_v) using viscometry method:

The viscosity property was used to determine the molecular weight of polymer, using the Mark- Houwink relation⁽¹⁹⁾.

$$[\eta] = K \bar{M}_v^\alpha \dots \dots \dots (2)$$

$[\eta]$ = is the intrinsic viscosity.

K , α = are constants dependent upon the polymer-solvent system at a particular temperature.

1. The single-point measurements were converted to intrinsic viscosities by the relation (3)(20).

$$[\eta] = \left(\sqrt{2/c}\right) (\eta_{sp} - \ln \eta_{re})^{1/2} \dots \dots \dots (3)$$

C = Concentration of polymer solution (gm/100ml). By applying equation (3), the molecular weight of degraded and undegraded polymer can be calculated.

Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution. The following equations were used⁽¹⁹⁾,

$$[\eta] = 1.38 \times 10^{-4} \bar{M}_w^{0.77} \dots \dots \dots (4)$$

Equation (4) was used to calculate (\bar{M}_v) for PVC films with and without additives.

conductance measurements

Electrolytic conductivity measuring set model Jenway 4070. Was used to record the specific conductance at room temperature.

Results and Discussion

Identification of the chelating complexes.

Spectroscopy

Several metal complexes of N-diisobutyl-N'-2,4-dichlorobenzoyl thiourea (IBT) and N-diPropyl-N'-2,4-dichlorobenzoyl thiourea (PBT) as a ligands with Sn(II), Co(II), Ni(II) and Cu(II) were prepared and used as additive for the photostabilization of PVC films. The IR of these molecules

shows the following characteristic bands. a strong band at $\nu(1700)\text{cm}^{-1}$ and $\nu(1685)\text{cm}^{-1}$ in both ligands (L1 and L2) relatively could be attributed to $\nu(\text{C}=\text{O})$ stretching and a strong peak at 1620cm^{-1} and 1610cm^{-1} were observed related to $\nu(\text{C}=\text{S})\text{cm}^{-1}$ also the bands at $\nu(1170)\text{cm}^{-1}$ and $\nu(1165)\text{cm}^{-1}$ which be attributed to $\nu(\text{N}-\text{C}=\text{S})\text{asym}$. And the bands at $\nu(1525)\text{cm}^{-1}$ and $\nu(1520)\text{cm}^{-1}$ which be attributed to $\nu(\text{N}-\text{C}=\text{O})\text{ asym}$ in the two ligands respectively as shown in table 2 and 3 and these agreements with the literature data⁽²¹⁻²³⁾.

The IR of the complexes a shift in $\nu(\text{C}=\text{O})\text{ cm}^{-1}$ and $\nu(\text{C}=\text{S})\text{ cm}^{-1}$ for all complexes for lower vibration frequency as shown in Table (2, 3), which give further evidences for the structures of complexes which is tetrahedral and this information is good agreement with the literature data⁽²¹⁻²⁵⁾. Table (2,3) shows also the electronic absorption bands for ligands and complexes. The bands are classified into three groups: Those that 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. The electronic spectra of all complexes for both ligands (L1, L2) except the Sn(II) complexes show the charge transfer transitions between 308-325nm. The electronic spectra of the Co(II) complexes show a band at 500,520nm which can be assigned to $4\text{T}2\text{g} \rightarrow 4\text{T}1\text{g}$ transition, in agreement with a tetrahedral environment for the metallic cation. Both Ni(II) complexes (for L1 and L2) are give a two bands, the first at 390,400nm which assigned to $3\text{T}2\text{g} \rightarrow 3\text{T}1\text{g}$ transition and 620nm which assigned to $3\text{T}2\text{g} \rightarrow 3\text{A}2\text{g}$ transition and these confirm the

tetrahedral formula of the complexes. The Cu(II) complexes shows a band at 380,400nm for (L1, L2) complexes relatively which can be tentatively

assigned to $E_{2g} \rightarrow T_{2g}$ transition of the tetrahedral structures of the complexes and all these data in agreement with literatures^(26,27).

Table (2) Absorption and IR Spectra of L1 and L1-M^{II}

Complex	Electronic absorption peaks (nm)	Assignment	IR (cm ⁻¹)	Assignment
L1	243	$n \rightarrow \pi^*$	1620	C=S (s)
	262	$n \rightarrow \pi^*$	1170	(N-C=S) (s)
			1525	(N-C=O) (s)
			1700	C=O (s)
L1-Sn	240	$n \rightarrow \pi^*$	1605	C=S (s)
	252	$n \rightarrow \pi^*$	1160	(N-C=S) (s)
	310	Charge transfer	1510	(N-C=O) (s)
			1675	C=O (s)
L1-Co	232	$n \rightarrow \pi^*$	1590	C=S (s)
	270	$n \rightarrow \pi^*$	1155	(N-C=S) (m)
	315	Charge transfer	1505	(N-C=O) (m)
	520	d-d	1660	C=O (s)
L1-Ni	275	$n \rightarrow \pi^*$	1600	C=S (s)
	340	Charge transfer	1150	(N-C=S) (m)
	390	(d-d)	1515	(N-C=O) (s)
	620	(d-d)	1670	C=O (s)
L1-Cu	235	$n \rightarrow \pi^*$	1605	C=S (m)
	270	$n \rightarrow \pi^*$	1165	(N-C=S) (s)
	308	Charge transfer	1520	(N-C=O) (s)
	380	(d-d)	1685	C=O (m)

Table (3) Absorption and IR Spectra of L2 and L2-M^{II}

Complex	Electronic absorption peaks (nm)	Assignment	IR (cm ⁻¹)	Assignment
L2	240	$n \rightarrow \pi^*$	1610	C=S (s)
	265	$n \rightarrow \pi^*$	1165	(N-C=S) (s)
			1520	(N-C=O) (s)
			1685	C=O (s)
L2-Sn	230	$n \rightarrow \pi^*$	1620	C=S (m)
	252	$n \rightarrow \pi^*$	1170	(N-C=S) (s)
			1525	(N-C=O) (s)
			1695	C=O (s)
L2-Co	240	$n \rightarrow \pi^*$	1585	C=S (s)
	260	$n \rightarrow \pi^*$	1155	(N-C=S) (m)
	323	Charge transfere	1510	(N-C=O) (s)
	500	(d-d)	1660	C=O (s)
L2-Ni	225	$n \rightarrow \pi^*$	1585	C=S (s)
	260	$n \rightarrow \pi^*$	1145	(N-C=S) (m)
	325	Charge transfer	1520	(N-C=O) (m)
	400	(d-d)	1660	C=O (s)
L2-Cu	230	$n \rightarrow \pi^*$	1580	C=S (s)
	265	$n \rightarrow \pi^*$	1155	(N-C=S) (m)
	310	Charge transfer	1505	(N-C=O) (s)
	400	(d-d)	1660	C=O (m)

(S)= strong, (m)= medium

Conductance measurements

The conductance is another technique used to confirm the structures of the prepared complexes proposed in

table(1). The molar conductance of the chelate complexes and for the free ligands using chloroform solvent are recorded and tabulated in table (4).

Table (4) Molar conductance of the metal chelate complexes and their free ligands in chloroform at 25°C (ohm⁻¹. mole⁻¹. m²).

Complex number	Molar conductance (ohm ⁻¹ . mole ⁻¹ . m ²)
L1	5.2
L1-Sn	38
L1-Co	32
L1-Ni	36
L1-Cu	39
L2	6.7
L2-Sn	39
L2-Co	39
L2-Ni	40
L2-Cu	29

The result in table (4) show that complexes have higher values of molar conductance than the free ligands as a comparison, this electrolytic behavior of complexes indicates the non ionic forms of these complexes

Photo – activity of the synthesis complexes as additives in PVC films

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

The irradiation of PVC films with light of wavelength $\lambda=313\text{nm}$ led to a clear change in their IR spectrum. Appearance of bands in 1775cm^{-1} and 1726cm^{-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 1605cm^{-1} related to polyene group(21). The hydroxyl band was very weak to allow accurate

quantitative determination of hydroperoxide and alcohol functions (22).

The absorption of the polyene and carbonyl groups are used to follow the extend of polymer degradation during irradiation. This 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 Figures (1,2) that the presence of L1, L1-Sn, L1-Co, L1-Ni, L1-Cu, L2, L2-Sn, L2-Co, L2-Ni, L2-Cu show lower growth rate of carbonyl index with irradiation time with respect to PVC film without additives (control).

As shown in Figures (1,2), the growth of carbonyl index with irradiation time is lower than PVC control. So, these additives might be considered as photostabilizers of PVC polymer.

The efficient photostabilizer show a longer induction period. Therefore, from Figure (1), the L1,2-Sn is the most active photostabilizer, followed by L1,2-Ni, L1,2-Cu, and L1,2-Co which is less active.

As it was mentioned before polyene compounds are produced during photodegradation of PVC. Therefore, polyene index (I_{PO}) was monitored with irradiation time and the presence and absence of these additives. Results are shown in Figure (3,4).

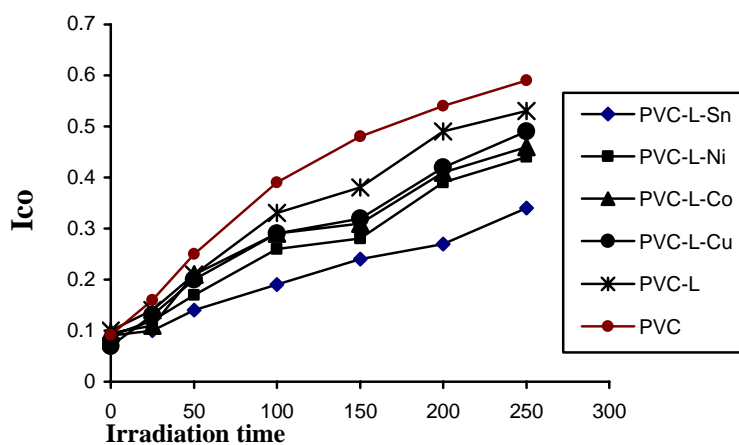


Figure (1) The relationship between the carbonyl index and irradiation time for PVC films ($50 \mu\text{m}$) thickness containing different additives of L1 and its complexes, concentration of additives are fixed at 0.5% by weight.

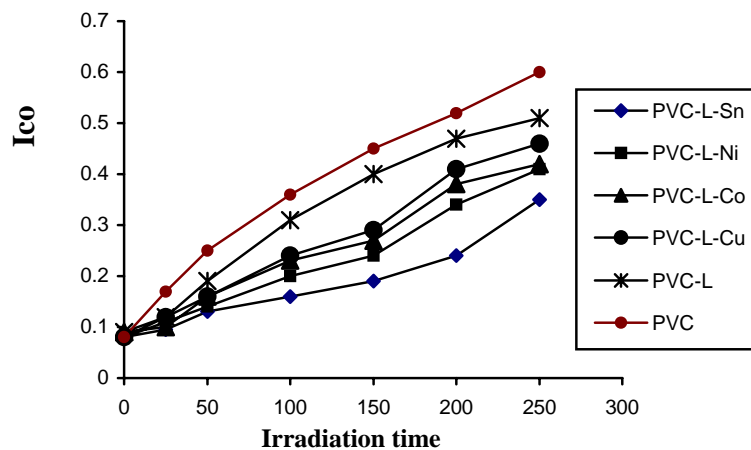


Figure (2) The relationship between the carbonyl index and irradiation time for PVC films ($50 \mu\text{m}$) thickness containing different additives of L2 and its complexes, concentration of additives are fixed at 0.5% by weight.

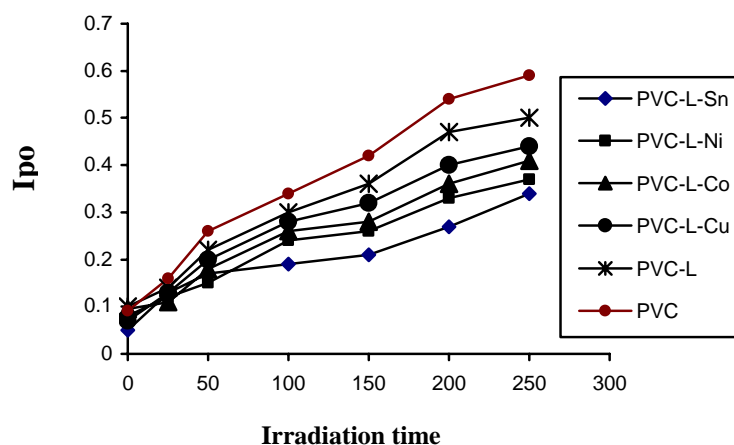


Figure (3) The relationship between the polyene index and irradiation time for PVC-L1-M^{II} films (50 μm) thickness.

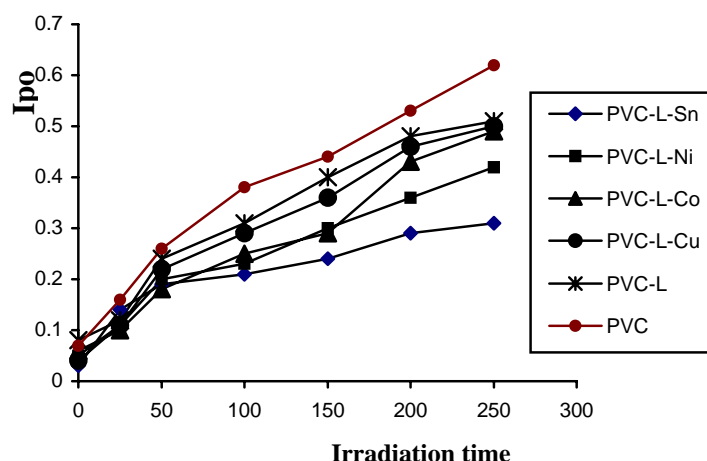


Figure (4) The relationship between the polyene index and irradiation time for PVC-L2-M^{II} films (50 μm) thickness.

Variation of PVC molecular weight during photolysis in presence of complexes

An analysis of the relative change in viscosity average molecular weight (\bar{M}_v), described by Scott(23) has been shown to provide a versatile test for random chain scission. Figure (3) shows

the plot of (\bar{M}_v) versus irradiation time for PVC film with and without 0.5% (wt/wt) of the five additives, with absorbed light intensity of 1.052×10^{-8} ein. $\text{dm}^{-3} \cdot \text{s}^{-1}$. (\bar{M}_v) is measured using equation (4) and THF as a solvent at 25 °C.

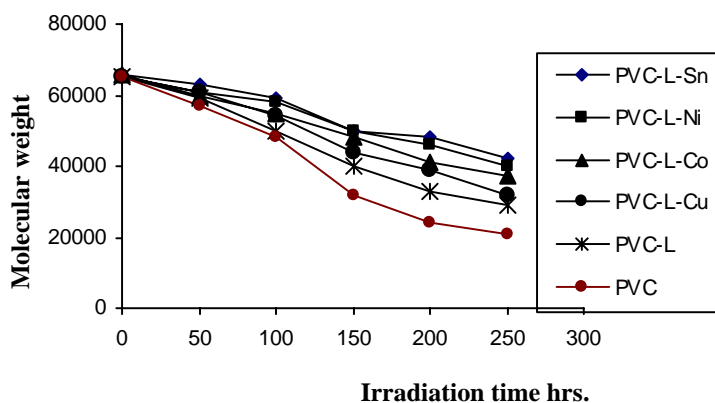


Figure (5) Changes in the viscosity average molecular weight (\bar{M}_v) during irradiation of PVC films (50 μm) (control) and with 0.5 wt% of additives of L1 and its complexes.

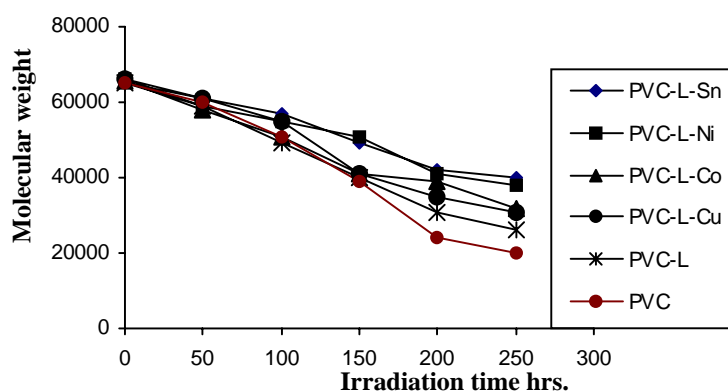
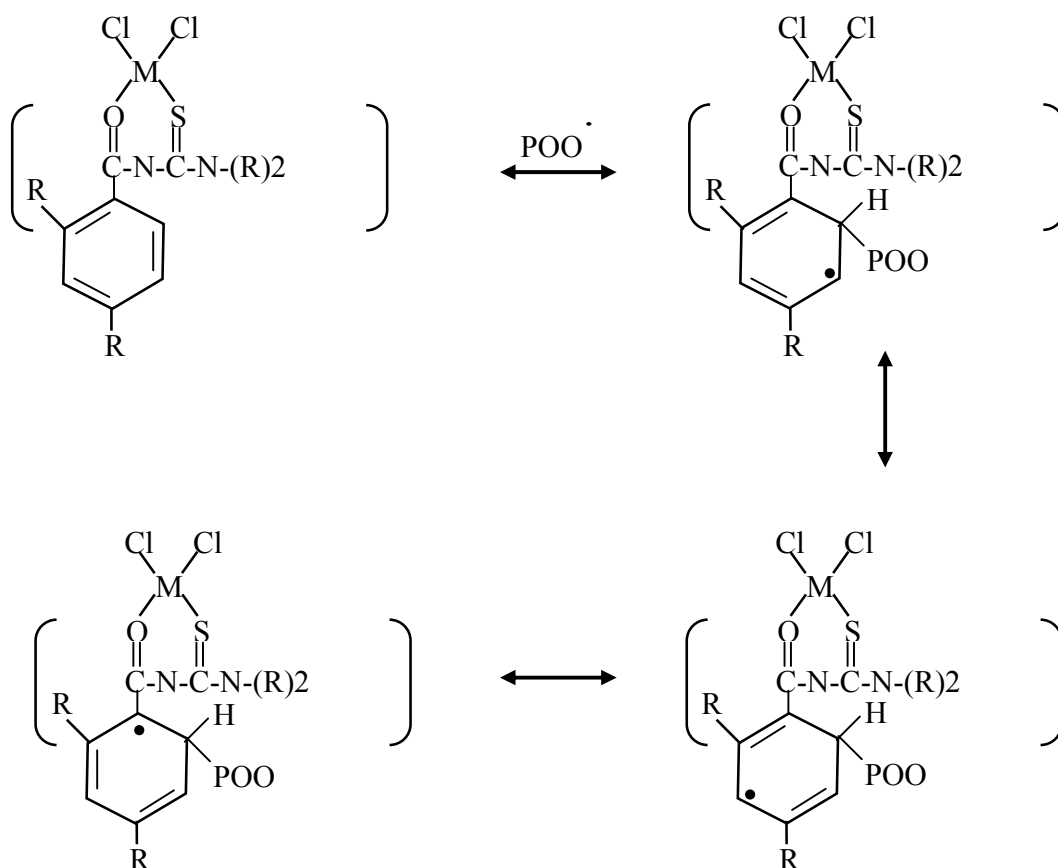


Figure (6) Changes in the viscosity average molecular weight (\bar{M}_v) during irradiation of PVC films (50 μm) (control) and with 0.5 wt% of additives of L1 and its complexes.

Suggested mechanisms of photostabilization process

Metal complexes generally known as photostabilizers for polyolefins⁽²⁴⁾ 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 `



Scheme (2) Suggested mechanism of photostabilization of complexes as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.

The ring of both ligands in these compounds plays a role in the mechanism of the stabilizer process by acting as UV absorber.

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