Synthesis Characterization and Studies of Photodegradation of PVC Films of(4-amino-5-(2-(2,3- dimethylphenyl)aminophnyl)-1,2,4-triazole-3-thion)with Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) Matel ions

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Abstract

A complexes of Co(II) , Ni(II), Cu(II), Zn(II) and Cd(II) with 4-amino-5-(2-(2,3- dimethylphenyl) aminophnyl)-1,2,4-triazole-3-thion)(L)was prepared and evaluated as a photodegradation for rigid Poly(vinyl chloride) (PVC). Polyvinyl chloride dissolved with metal complexes in THF solvent to form PVC films of 5% (40μm) thickness containing concentrations of the complexes by weight. These different samples were produced by the casting method from the solvent. The photodegradation of films was investigated using UV-visible spectra. The photostabilization activity of these compounds was determined by calculating the photodecomposition rate constant (Kd) for modified PVC films against a blank.

Keywords: photodegradation, 1,2,4-triazole, matel complexes,

1. Introduction

1, 2, 4- Triazole constitute an interesting group of heterocyclic compounds containing three 'N' atoms in a 5 -membered ring, and its derivatives represent some of the most biologically active classes of compounds possessing a wide spectrum of biological and pharmacological properties [1-6].Poly vinyl chloride (PVC) is one of the most extensive thermoplastic materials in the world due to its valuable properties, wide applications, high chemical resistance, barrier properties and low cost [7].During processing, storage and utilization, PVC degrades as it is exposed to high temperatures, high mechanical stresses or ultraviolet light, all in the presence of oxygen. Degradation of the polymer occurs by successive elimination of hydrogen chloride (HCl), which is called dehydrochlorination, yielding long polyenes, which are consequently causing discoloration, deterioration of the mechanical properties and a lowering of the chemical resistance [8,9]. As In recent years, the use of polymeric materials has rapidly increased but it is well established that rapid photodegradation of these materials is probable when they are exposed to natural weathering [10-12].The low cost and the good performance of poly (vinyl chloride) products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structure, and siding [7]. A wide variety of synthetic and naturally occurring high polymers absorb solar ultraviolet radiation and undergo photolytic, photooxidative, and thermooxidative reactions that result in the degradation of the material [13,14].To ensure the weather ability of these materials, the PVC needs to be compounded and processed properly using suitable additives, leading to complex material whose behavior and properties are quite different from the PVC by itself [15,16]. In this paper we report the prepared ligand thene characterized by using FT-IR, $^{-1}$H-NMR,UV-Vis spectroscopy ,C.H.N.S .of (4-amino-5-(2-(2,3-dimethylphenyl)aminophnyl) -1,2,4-triazole-3-thion) ,Chelates of (L) with Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) ions were prepared and characterized by FT-IR,UV-Vis spectroscopy and C.H.N.S,. As well as the chelates were used to enhance the photostabilization Polymer(PVC). Polymer has been mixed with these complexes in solvent which containing concentration of complex 0.5 % by weight, which produced by the casting method from THF solvent. The photostabilization of polymer films were studied at room temperature under irradiation of light $\lambda=313$ nm wave length with intensity $6.02*10^{-9}$ Ein Dm^{-3} S^{-1}

2. Experimental

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The Infrared (FTIR) spectra were recorded by using FTIR.8300 Shimadzu spectrophotometer in the frequency range of 4000-400 cm^{-1}. The ultraviolet-visible (UV-VIS) spectra were recorded using Shimadzu UV-VIS. 160 A-Ultra-violet spectrophotometer in the range of 200-1100 nm. Morphological study was recorded by using MEIJI TECHNO microscope, (Japan).

As self-reliant units, holons have a degree of independence and handle circumstances and problems on their particular levels of existence without reaching higher level holons for assistance. The self-reliant characteristic ensures that holons are stable, able to survive disturbances.

2-1- Synthesis of ligand (L)

The (L) was prepared starting from Mefenamic acid (MFA) according to the general steps[17-20],scheme(1).

2-1-1 Preparation of (2-(2,3-dimethyl phenyl)amino ethyl benzoate(G_1)

Sulphuric acid (8 ml) was added dropwise with continuous stirring to a solution of carboxylic acid (Mefenamic acid) (0.1 mol) in 200ml ethanol. The mixture was heated under reflux for 10 hours. On cooling, the mixture was poured on to crushed ice , the precipitated crystalline solid was filtered, washed with water, followed by 10% sodium hydrogen carbonate solution and finally with water then the crude product was recrystallized from ethanol, to give (84%) yield of compound [G_1],off white crystal with melting point (108-110)°C.

2-1-2 Preparation of (2-(2,3-dimethyl phenyl)amino ethyl benzohydrazide (G_2)

Ester of (G_1) (0.1 mol) was dissolved in absolute ethanol (50ml). To the above solution was added hydrazine hydrate 80% (0.1mol). The resulting reaction mixture was refluxed on a steam bath for10-12 hours. On cooling, cold water (150 ml) was added to the mixture and the separated white crystalline solid was filtered, washed with cold water, dried and crystallized from ethanol, to give (82%) yield of compound (G_2),white colors with melting point (156-158)°C.

2-1-3 Preparation of (2-(2,3-dimethyl phenyl)amino ethyl benzoyl)hydrazine carbodithioate (G_3)

Compounds (G_2) (0.05 mol) was treated with a solution of potassium hydroxide(0.0643 mol) in ethanol (70 ml) at 0°C with stirring, then (7 ml) of carbon disulfide was added dropwise and the reaction mixture was stirred overnight at room temperature. The solid product (G_3) was filtered, washed with cold methanol and dried.

2-1-4 Preparation of Ligand (4-amino-5-(2-(2,3- dimethylphenyl)aminophnyl)- 1,2,4-triazole-3-thion)(L)

A mixture of compound (G_3) (0.05 mol) and 80% hydrazine hydrate (10 ml) was heated under reflux till the evolution of hydrogen sulphide completely down (about 6 hour). On cooling, water (200 ml) was added and the mixture was neutralized with 10% hydrochloric acid and allowed to stand for three hours. The separated crude product was filtered, washed with water, dried and crystallized from ethanol, to give (80%) yield of compound [L], white powder with melting point (215-217)°C.

a).Preparation of metal complexes of (L) [$A_1 – A_5$]

The salts of [$Co(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.\ H_2O$, Zn $(CH_3COO)_2.2H_2O$ and $Cd(CH_3COO)_2.2H_2O$] were dissolved in ethanol and added to an ethanolic solution of (L) in (1:2) (metal : ligand) mole ratio respectively with stirring. The mixture was heated under reflux for (4) hours. During this period the precipitation was completed form. The product was then collected by filtration, washed with ethanol and dried under vacuum for (2) hours.

Experimental Techniques

Film preparation

Polyvinyl chloride dissolved with metal complexes in THF solvent to form PVC films of 5% (40µm) thickness containing concentrations of the complex by weight. Their thickness was 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 solvent [21].

Irradiation experiment

Accelerated testing technique

UV- Light lamp was used for irradiation of Polymer films, giving wavelength range between (250 to380 nm) and the maximum wavelength light intensity is at 6.2×10^{-9} Ein Dm^{-3} S^{-1}. The polymer film samples were fixed parallel to each other and the lamp of the UV. incident radiation is vertically incident on the samples. The distance between the polymer films and the source was (10 cm). The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same [22, 23].

Photodegradation measuring methods

Measuring the Photodegradation Rate of Polymer Films Using Ultraviolet-Visible Spectrophotometer

The ultraviolet-visible spectrophotometer type Shimadzu UV-VIS. 160 was used to measure the changes in the UV-visible spectrum during irradiation time for each compound at maximum absorption band (λ_{max}). The absorption spectrum was measured in the range of (200-400nm), and the (λ_{max}) at each absorption was also recorded for different irradiation times.

The infinite irradiation time was considered and the infinite absorption (A_∞) was assumed to be after the infinite irradiation time. To determine the photodegradation rate constant for photostabilizer (K_d), the first order equation was used:

$$\ln(a-x) = \ln a - K_d\, t \qquad \text{……………..(2)}$$

Where "a" represents the stabilizer concentration before irradiation and "x" represents the change in stabilizer concentration after irradiation time (t). If A_o represents the absorption intensity of the polymer film containing stabilizer before irradiation and A_t represents the absorption intensity after t time of irradiation, then:

$a = A_o - A_\infty$
$x = A_o - A_t$

$a - x = A_o - A_\infty - A_o + A_t = A_t - A_\infty$ ....(3)

Substitution of a and (a - x) from equation (3) in (2) gives:

$\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - K_d t$ .... (4)

Thus a plot of ln $(A_t - A_\infty)$ versus irradiation time (t) gives straight line with a slope equal (K_d) which indicates that photodecomposition of the additives is first order.

(5)

Results and discussion:

a-Elemental analyses

The physical and analytical data of the (L) ligand and [A_1-A_5] metal complexes are given in Table (1). The results obtained from elemental analysis are in satisfactory agreement with the calculated value. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The new (L) ligand was soluble in common organic solvents such as (ethanol, acetone and methanol), whereas [A_1 – A_5] of new complexes colored crystalline solid complexes were soluble in ($CHCl_3$, DMF and DMSO).

b).Proton nuclear magnetic resonance spectra of (L)

The nuclear magnetic resonance spectra of the newly synthesized ligand gave a satisfactory spectro data and the molecular structure was assigned on the basis of ^{1}H.N.M.R chemical shifts.The spectra was determined in d_6,DMSO solution as an internal reference. According to the results obtained from the chemical shifts spectra, the molecular structure of the ligand can be illustrated, $\delta H_{(1,2)}$=2.095-2.281ppm(6H,s,CH_3),$\delta H_{(3)}$=5.3ppm(2H,s,NH_2),$\delta H_{(4)}$=9.47ppm(1H,s,NH),$\delta H_{(5)}$=12.41ppm(^{1}H,s,NH),δPh=6.706-7.89ppm(7H) Fig.(1).

-Infrared Spectroscopic Study

The characteristic stretching vibration modes concerning (L) and its metal complexes are described in Table (2).(L) exhibited band at(3439),(3209,3269),(1643),(1041),(1591),(1380),(976,956) and (804)cm^{-1}, these can be assigned to ν(NH) ,($\nu_s NH_2$ and $\nu_{as} NH_2$), νC=N, νC=S,(δNH, νC=N,Thioamid(I)), (νC=N+νC=S, Thioamid (II)),(ν N…C…S, Thioamid(III)) and ν(C-S),Thioamid (IV)) respectively[24] .In all complexes [A_1---A_5], the ligand (L) behave as a bidentate coordinating with metal through sulfur of thiocarbonyl and nitrogen of amino group, therefor the bands due to ν(C=S), (ν_s and ν_{as} of NH_2) and four (I-IV) thioamide bands were shifted to a lower frequency as in Table (2). As well as a new bands for complexes (A_1-A_2) in the region (1521,1537)cm^{-1}wich may be assigned to the asymmetric vibration of coordinated carboxylate groups ($\nu_{as}coo^-$) and the bands in the region (1302-1305)cm^{-1} may be attributed to the symmetric vibration of carboxylate group ($\nu_s coo^-$)[25,26]. The large differences between the frequencies of [$\nu_{as}(coo^-)$] and [$\nu_s(coo^-)$],[Δν>200cm^{-1}] in [A_1 and A_2] complexes are indicative of the involvement of the coordination of the carboxylate groups to the metal ion in a monodentate fashion[26,27]. On Comperision with [G_1] and [G_2] complexes ,the newly synthesized copper, zinc and cadmium complexes[G_3,G_4 and G_5] show appearance of new bands in the region (1655-1665cm^{-1}) which may be assigned to the vibration of un coordinated carboxylate groups. Other low intensity bands observed in the region (445-460) ,(518-520) and (523-544)cm^{-1} are attributed to ν(M-S) and ν(M-N) respectively in the all complexes except ($A_1$and A_2) and ν(M-O) in the case of ($A_1$and A_2) complexes modes respectively[27].

C- Electronic Spectra, Magnetic susceptibility and conductivity measurements [28- 30]

The electronic spectra of the free ligands (L) and their complexes (A_1-A_5) were recorded in chloroform solution. The spectrum of (L) shows a strong band at 42194cm^{-1}, which is attributed to π→π* and another at 31545, 29411 cm^{-1} due to n→π*.

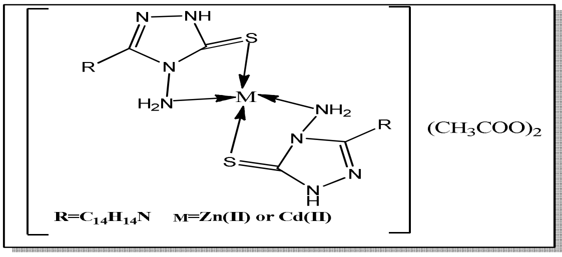
A_1: The measured magnetic moment was (4.2 B.M) this show the cobalt ion it,s brown complex typical of d^7 system with three unpaired electrons indicating a quartet state and suggest high spin octahedral geometry. The electronic spectrum of the brown (**A_1**) complex in chloroform exhibited two bands at 1538.4 and 18691 $cm^{-1}cm^{-1}$,assignable to$^4T_1g \rightarrow {}^4A_2g_{(F)}$ and $^4T_1g \rightarrow {}^4T_1g_{(P)}$ transitions respectively for an octahedral geometry of Co(II). The value of various ligand filed parameters (ν_1 , B^- ,β and Dq) have been calculated using (Tanabe-Sugano diagram) for d^7 system and found to be (7039.9, 623,0.642 and 934.5) respectively .The molar conductivity measurement in DMF showed that the complex was non electrolyte, Table (2).

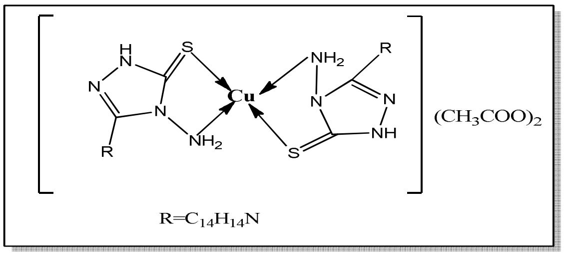
A_2: The light green (**A_2**) complex in chloroform exhibited bands at 15267 and 25974 cm^{-1} assigned to $^3A_2g \rightarrow {}^3T_1g_{(F)}$ (ν_2) and $^3A_2g \rightarrow {}^3T_1g_{(P)}$ (ν_3) transitions respectively, Table (2), which indicate octahedral geometry of Ni(II). The absence of any band below10.000 cm^{-1} eliminates the possibility of tetrahedral environment in this complex. The different ligand field parameters (B^- ,β and Dq) have been calculated using the same diagram and found to be (611, 0.54 and 1099.224) respectively (M-L) (Ni-L) bond is covalent. Magnetic moment (3.09 B.M) of solid complex, Table (2), showed a higher orbital contribution. Conductivity measurement in DMF showed that the complex was nonionic, Table (2).

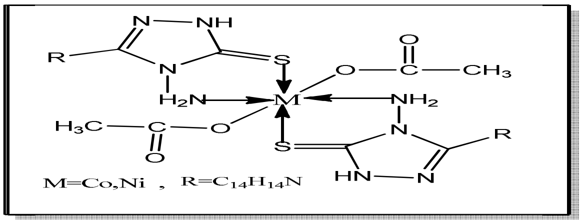
A_3:The measured magnetic moment was (1.92 B.M) this show the Cu(II) ion(**A_3**) it,s dark green complex typical of d^9 system. Electronic spectrum in chloroform, shows one broad band at 14084cm^{-1} which corresponds to $^2B_1g \rightarrow {}^2A_1g$ transition, and a shoulder band at 25773cm^{-1} which assigned to$^2B_1g \rightarrow {}^2B_2g + {}^2Eg$ transition. The position of these bands is in a good agreement with that reported for highly distorted octahedral geometry. Conductivity measurement in DMF showed that the complex was highly ionic,Table (2)

The two complexes [**A4**] and [**A5**] were colorless in chloroform solution, so that no (d-d) transition can be expected in the visible region, as well as were diamagnetic as expected for d^{10} ions. The conductivity measurements indicate ionic behavior of the complexes, Table (2).

General Proposed Stereo Chemistry Structure of Complexes (A_1-A_5): According to the results obtained from the elemental analysis, spectral studies, magnetic and conductivity measurements, the general structure of the above mentioned complexes (A_1-A_5)can be illustrated as follows:







Ultra-violet spectral studies of photodegradation rate of in PVC films

The metal complexes with(4-amino-5-(2-(2,3- dimethyl phenyl)aminophnyl)- 1,2,4-triazole-3-thion)(L)was used as an additive for the photodegradation of PVC films of thickness 40μm with concentrations of the complexes. The carbonyl groups generated during the photooxidation [31,32] process of polymer, extend the polymer film absorption to longer wavelengths. These groups absorb light when they irradiated with light of wavelength between (200-700 nm) and activated to the singlet and triplet excited states which enhances various successive photooxidation reactions [33]. Ultraviolet radiations are known to have deleterious effects on most industrial polymers inducing chemical modification and scission of polymer chain, which ultimately lead to an undesirable loss of the mechanical and surface properties of the irradiated material. Photodegradation of PVC causes discoloration (yellowing), cross-linking, and chain scission due to oxidation and effect of UV light and heat [34,35]. UV light induces the production of radicals by oxidation. The prepared complexes were used as photoinduced for PVC films comparing with PVC blank. The additives used in this study were chosen to be completely soluble in polymer solvent, (THF). The additive concentration plays an important role in photodegradation and photostabilization of polymers. So many investigators [36] have studied the effect of additives concentration in photodegradation and photostabilization of polymers. In this work, it has been noticed that the additives used photodecomposed during the photolysis. Thus the photo decomposition rate constant (K_d) was calculated. The K_d values were computed using the UV spectra changes of PVC films thickness 40μm containing 0.5% w/w from additives. The plot of irradiation time versus ln (A_t-A_∞), gives straight line which indicate primarily the first order reaction. The slope equal to the decomposition rate constant K_d. Figures (3 to 9) show the variation of ln (A_t - A_∞) with irradiation time for all additives in PVC films at λ=313nm. The values of the first order rate constant of all the modified polymers films (k_d) calculated by the same way and shown in Table (1). The photodegration always posses high K_d values, which mean that these modified polymers degradated towards UV light.

5. Conclusion

Addition of the complexes (4-amino-5-(2-(2,3- dimethyl phenyl)aminophnyl)- 1,2,4-triazole-3-thion)(L) to polyvinyl chloride (PVC) films have successfully worked as photoinducer for degradation process for PVC films. The photooxidation rate increased with increasing additive concentration.

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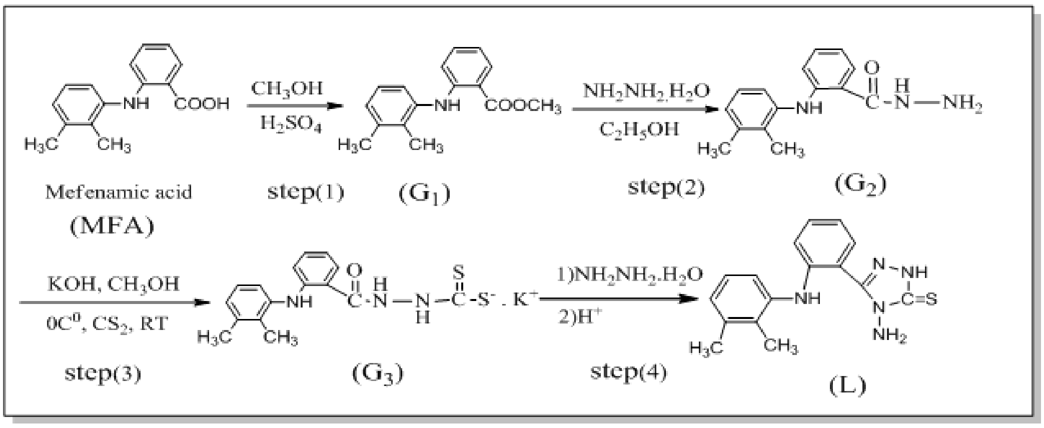

Scheme. 1 Synthesis of Ligand (L)

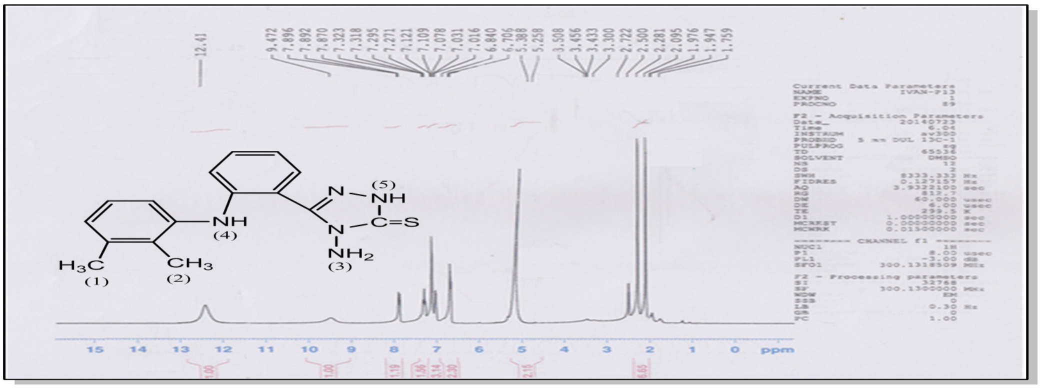

Fig.(1)^{1}H-NMR spctral of (L)

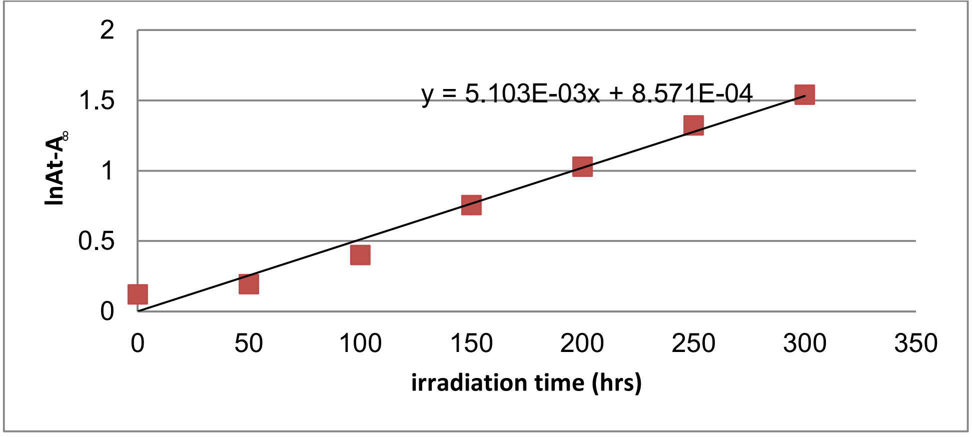

Fig. 2 Variation of natural logarithm of (A_t–A_∞) with irradiation time of PVC (control) film (40μm)

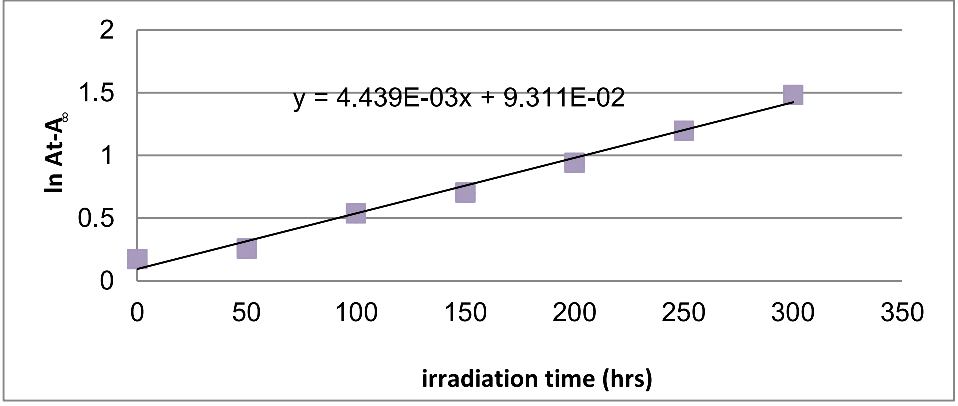

Fig. 3 Variation of natural logarithm of (A_t–A_∞) with irradiation time of (L) in PVC film (40μm)

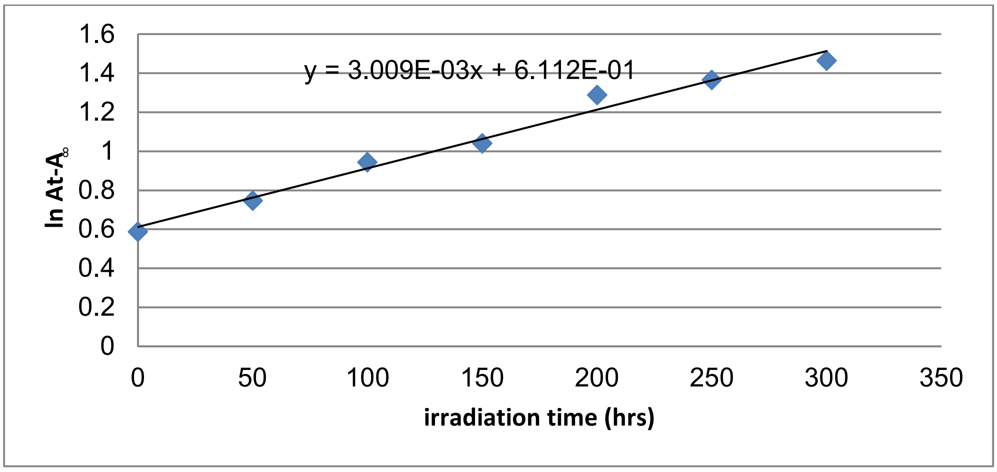

Fig. 4 Variation of natural logarithm of $(A_t–A_\infty)$ with irradiation time of (A_1) in PVC film (40μm)

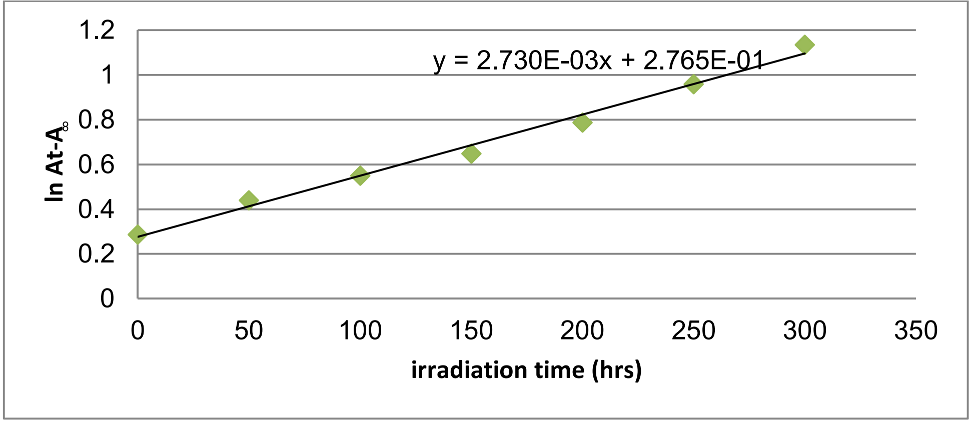

Fig. 5 Variation of natural logarithm of $(A_t–A_\infty)$ with irradiation time of (A_2) in PVC film (40μm)

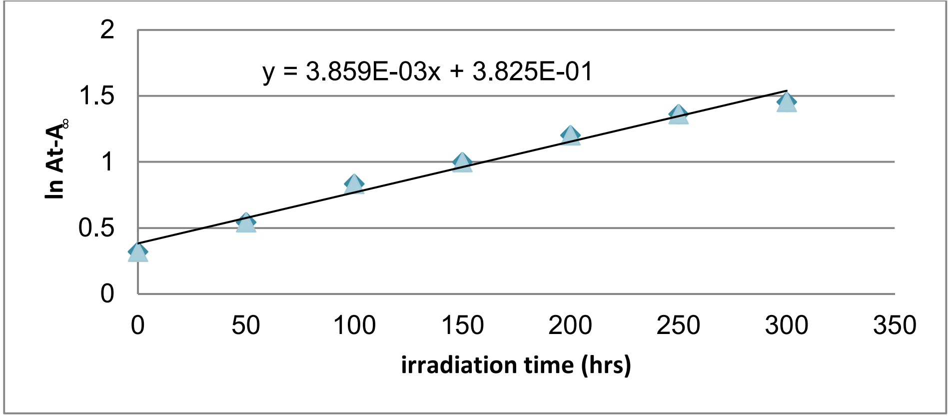

Fig. 6 Variation of natural logarithm of $(A_t–A_\infty)$ with irradiation time of (A_3) in PVC film(40μm)

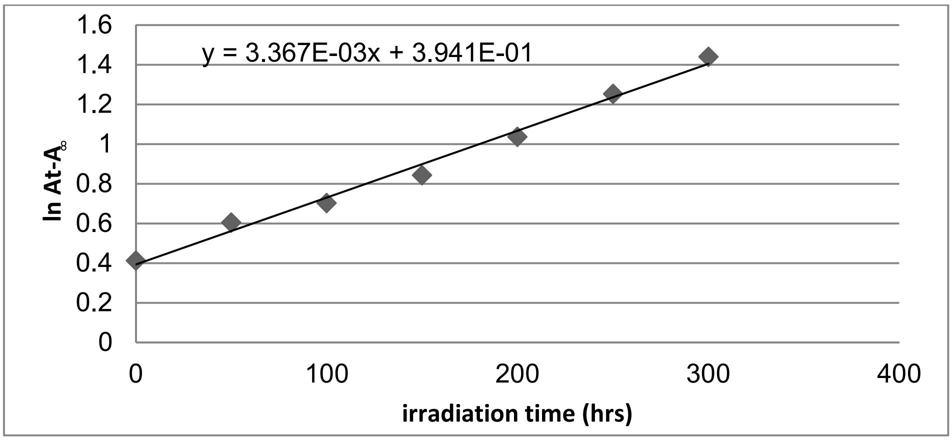

Fig.7 Variation of natural logarithm of (A_t–A_∞) with irradiation time of (A_4) in PVC film (40µm)

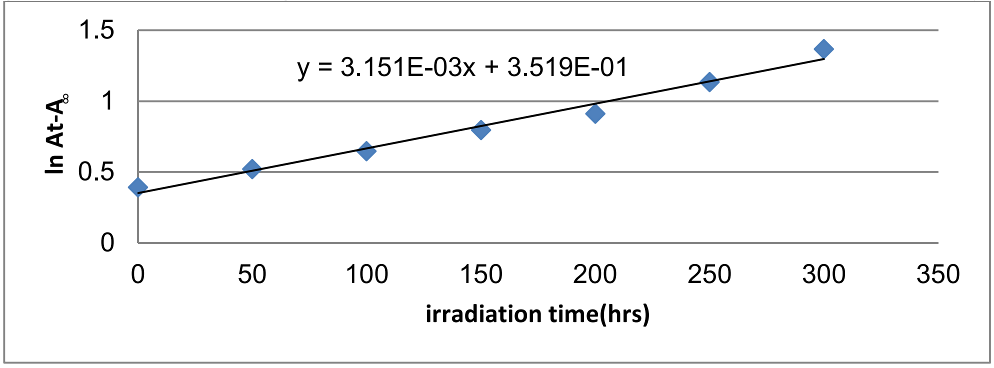

Fig. 8 Variation of natural logarithm of (A_t–A_∞) with irradiation time of (A_5) in PVC film (40µm)

The photostabilizers always possess low k_d values, which mean that these modified polymers are stable toward UV light. It can be noticed that k_d values are sensitive to the type of additives in PVC films, which decrease in the following order:

PVC >L> A_3 > A_4 > A_5 > A_1 > A_2

Table (1) Physical data for Ligand (L) and it͵s metal complexes(A_1-A_5)

Comp NO.	***Color***	***Melting point***	***Yield %***	***Metal analysis found Calc.***					***Suggested formula***
				C%	H%	N%	S%	M%	
L_I	White	215-217	80	61.73 62.02	5.47 5.61	22.51 22.95	10.29 11.06	-	($C_{16}H_{17}N_5S$)
[A_1]	Brown	234d	90	54.07 54.92	5.01 5.22	17.52 18.09	8.01 8.43	7.37 7.12	[$Co(C_{32}H_{34}N_{10}S_2)(CH_3COO)_2$]
[A_2]	Yellowish green	260d	78	54.09 54.75	5.01 5.16	17.53 17.85	8.01 8.22	7.35 7.50	[$Ni(C_{32}H_{34}N_{10}S_2)(CH_3COO)_2$]
[A_3]	Dark green	250d	88	53. 76 54.91	4.98 5.03	17.42 16.99	7.97 8.33	7.90 7.32	[$Cu(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$
[A_4]	Off white	200d	90	53.64 54.11	4.97 5.36	17.38 17.64	7.95 8.44	8.12 8.32	[$Zn(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$
[A_5]	Off white	270d	85	50.62 51.23	4.69 5.08	16.40 16.89	7.49 8.25	13.17 12.97	[$Cd(C_{32}H_{34}N_{10}S_2)](CH_3COO)_2$

d=decomp.

Table (2) stretching vibrational frequencies (cm^{-1}) located in the FT-IR spectra of (L.) and metal complexes

Comp. No.	$\nu_{C=S}$	$\nu_{C=N}$	νNH_2 (as,s)	ν_{NH}	ν_{COO^-} (as,s)(Coord.)	ν_{COO^-} un coord.	M-N	M-S	M-O
L	1041	1643	(3269,3209)	3439	-	-	-	-	-
[A_1]	1020	1640	(3252,3212)	3441	(1537,1305)	-	530	459	523
[A_2]	1030	1643	(3263,3211)	3440	(1512,1302)	-	532	457	540
[A_3]	1030	1640	(3252,3200)	3439	-	1665	529	460	-
[A_4]	1022	1640	(3252,3194)	3440	-	1655	530	455	-
[A_5]	1030	1645	(3240,3155)	3442	-	1660	533	454	-

Table(3) Electronic spectra ($CHCl_3$), Magnetic moment (B.M) and Conductance in (DMF) for ligand and it's metal complexes

Symb.	**Maximum absorption $\upsilon_{max}(cm^{-1})$**	**Band assignment**	**10Dq**	**Molar Cond. $S.cm^2.mol^{-1}$**	**μeff. B.M**	**Suggested geometry**
[A_1]	7039.9 (Cal.)	$^{4}T_{1}g\rightarrow{}^{4}T_{2}g_{(F)}$	9337.6	15.65	4.2	O.h
	1538.4	$^{4}T_{1}g\rightarrow{}^{4}A_{2}g_{(F)}$				
	1869.1	$^{4}T_{1}g\rightarrow{}^{4}T_{1}g_{(P)}$				
[A_2]	10992.24, (Cal.)	$^{3}A_{2}g\rightarrow{}^{3}T_{2}g_{(F)}$	10976	18.09	3.09	O.h
	15267	$^{3}A_{2}g\rightarrow{}^{3}T_{1}g_{(F)}$				
	25974	$^{3}A_{2}g\rightarrow{}^{3}T_{1}g_{(P)}$				
	33112	C.T				
[A_3]	14084	$^{2}B_{1}g\rightarrow{}^{2}A_{1}g$	-	168.22	1.92	S.p
	25773	$^{2}B_{1}g\rightarrow{}^{2}B_{2}g+{}^{2}Eg$				
[A_4]	32258	ILCT	-	166.86	0.0	T.h
	38167					
	47619					
[A_5]	31055	ILCT	-	170.9	0.0	T.h
	34482					
	47169					

Table (4) Photodecomposition rate constants (k_d) of PVC films thickness (40μm) containing 0.5 % of additives

compounds	**$k_d(S^{-1})$**
PVC (control)	$5.103*10^{-3}$
PVC+L	$4.439*10^{-3}$
PVC + (A_3)	$3.859*10^{-3}$
PVC + (A_4)	$3.367*10^{-3}$
PVC + (A_5)	$3.151*10^{-3}$
PVC + (A_1)	$3.009*10^{-3}$
PVC + (A_2)	$2.730*10^{-3}$