Ultra-violet spectra studies of photostabilization rate in PVC films by using some transition metal complexes

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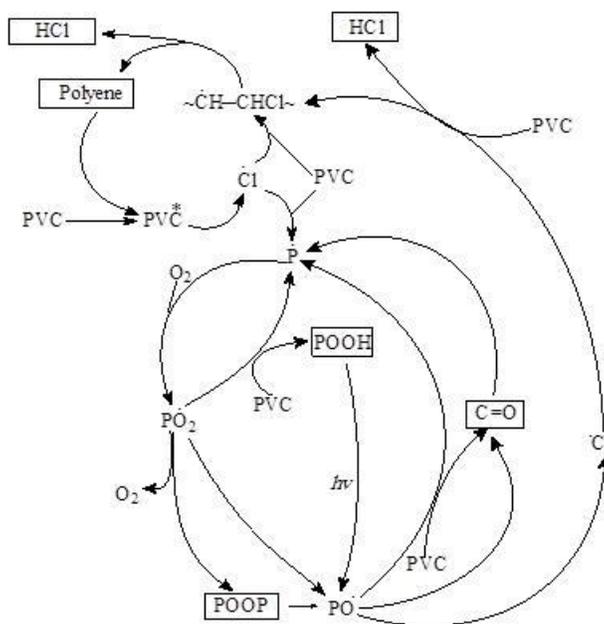Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
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Novelty and Highlights:

- The photostabilization of poly(vinyl chloride) films by metal complexes of the ligand 4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol was investigated.
- The photodegradation rate constant (k_d) was discussed to determine the photostabilizers efficiency against UV-light.

- ### Graphical Abstract:

Ultra-violet spectra studies of photo stabilization rate in PVC films by using some transition metal complexes

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Abstract:

The photostabilization of poly(vinyl chloride) films by New metal complexes of the ligand 4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol with the metal ions Cu(II), Cd(II), Sn(II), Zn(II) and Ni(II) was investigated. The PVC films containing concentration of complexes 0.5% by weight were produced by the casting method from tetrahydrofuran (THF) solvent. The photodegradation of the obtained films was investigated using UV-visible spectra. The photostabilization activity of these compounds was determined by calculating the photodecomposition rate constant (k_d) for the modified PVC.

Introduction

All commercial organic polymers will degrade in air when exposed to sunlight, although there is a very wide range of photo-oxidative susceptibilities. It is usually the absorption of near ultraviolet (UV) wavelengths which leads to bond-breaking reactions and the concomitant loss of useful physical properties and/or discoloration [1]. Exposure to sunlight can have adverse effects on the useful great interest of plastic products. Ultraviolet (UV) radiation can break down the chemical bonds in a polymer. Photo-degradation causes cracking, chalking, colour changes and the loss of physical properties [2,3] The advantage of PVC over other polymers is based in its low cost of production, processing, excellent mechanical properties, high compatibility with additives and their possibility to be recycled [4]. 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 [5]. There is a great interest at present in the photo-oxidative degradation of polymeric materials because macromolecules have increasingly widespread commercial applications [6]. Almost all synthetic polymers require stabilization against the adverse effect. With the development of synthetic resins, it became necessary to look for ways and means to prevent or at least reduce the damage caused by the environmental parameters, light, air and heat. This can be achieved through addition of special chemicals, light stabilizers or UV stabilizers, that have to be adjusted to the nature of the resin and the specific application considered [7, 8]. The photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of stabilizer: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) free radical scavengers, of these it is generally believed that types (c-e) are the most effective [9]. The purpose of this work was to investigate by k_d value the activity of the prepared complexes as photostabilizers against UV light in the PVC polymer films.

Experimental

Materials

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification.

Synthesis of 4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1, 2, 4] triazole-3-thiol (ligand) [10]

The Schiff base was prepared by the condensation of respective aldehyde & amino compound. The hot ethanol

solution of 4-Amino-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol (1 g) mixed with a solution of the Bnezaldehyde (0.52 ml) in absolute ethanol with some drops of glacial acetic acid .The mixture was refluxed for 3 hour to obtained the yellow precipitate. The precipitated obtained was filtered and crystallized from ethanol to give the yellow precipitate. Yield (67 %), m.p. (215-217 °C), the structure of the prepared ligand is shown in Figure 1.
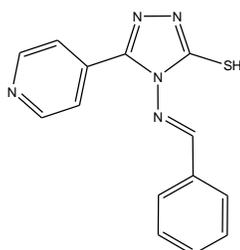
4-(Benzylidene-amino)-5-pyridin-4-yl-4*H*-[1,2,4]triazole-3-thiol

Figure 1. Structure of the Ligand

Synthesis of metal complexes [11]

The metal complexes of the Schiff base were prepared by the addition of a hot ethanolic solution of the suitable metal salt [Copper (II) acetate, Cadmium (II) acetate dihydrate, Tin (II) chloride, Zinc (II) acetate dehydrate or Nickel (II) nitrate hexahydrate] to hot ethanolic solution of the ligand in 2:1 (ligand : metal) molar ratios. The resulting mixtures were stirred under reflux for 1h whereupon the crystalline coloured complexes precipitated. The resulted complexes were collected by filtration and dried at room temperature. Then the precipitate was washed by hot methanol to yield a purified precipitate, see Figure 2.

Films preparation [12]

The best solvent for PVC is tetrahydrofuran. The films were prepared by evaporation technique at room temperature for 24 h. Fixed concentrations of PVC solution (5%) in THF were used to prepare polymer films with 40 μm thickness. The prepared complexes (0.5% concentrations by weight) were added to the films starting at 0 concentrations (blank). It was necessary to control the hygrometry and the rate of evaporation of solvent during casting to maintain good optical quality and very limited turbidity. After complete dissolution, The resulting solution was spread on glass frame and left overnight. The films that formed upon complete evaporation of the solvent at room temperature, these films were paste onto cartoon papers, these papers contain hole in dimension (2x2) cm.
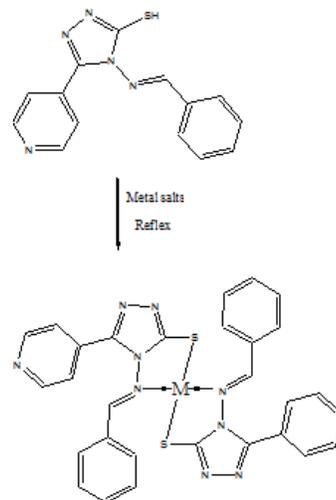
Where M= Cu (II), Cd(II), Sn(II), Zn(II) or Ni(II)

Figure 2. The chemical step for synthesis of Complexes

Accelerated testing technique

UV lamp giving spectrum range between 290-360 nm with a maximum wavelength 313 nm was used for irradiation of polymer films. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on the samples. Each sample was held at a constant distance of 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.

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

The Shimadzu UV-VIS. 160 A-Ultra-violet spectrophotometer was used to measure the changes in the UV-Visible spectrum during different irradiation times for each polymer films at maximum absorption band (λ_{max} = 200-400 nm). The photodegradation rate constant for the Photostabilizer (k_d) was calculated using the first order kinetic equation,

$$\ln(a-x) = \ln a - k_d \, t \qquad (1)$$

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, A_∞ represents the absorption

intensity at infinite irradiation time and A_t represents the absorption intensity after t time of irradiation, then:

$$a = A_o - A_\infty \qquad (2)$$

$$x = A_o - A_t \qquad (3)$$

$$a - x = A_o - A_\infty - A_o + A_t = A_t - A_\infty \qquad (4)$$

Substitution of a and (a - x) in equation (1) to give:

$$\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - k_d t \qquad (5)$$

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 [13].

Results and discussion

The irradiation of PVC films with UV light of wavelength, λ= 313 nm led to a clear change in the FTIR spectrum [14].The complexes of the ligand 4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1,2,4]triazole-3-thiol with the metal ions Cu(II), Cd(II), Sn(II), Zn(II) and Ni(II) were used as additives for the photostabilization of PVC films. It has been noticed that these additives used in the present work are photo-decomposed during the photolysis. Thus the photodecomposition rate constant (k_d) was calculated. The (k_d) values were computed using the UV spectra changes of PVC films thickness (40 μm) containing 0.5 % of additives. The plot of irradiation time versus ln $(A_t - A_\infty)$ gives straight line which indicates primarily the first order reaction. The slope equal to the decomposition rate constant (k_d). Figures 3 to 8 show the variation of ln $(A_t - A_\infty)$ with irradiation time for all additives in Poly(vinyl chloride) films at the wavelength 313 nm. 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.
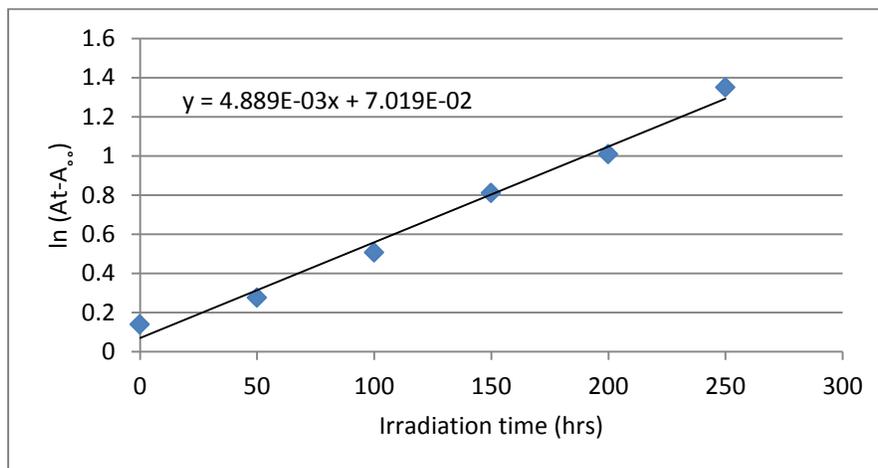

Figure 3. Variation of natural logarithm of $(A_t–A_\infty)$ with irradiation time of PVC (control) film (40 μm)

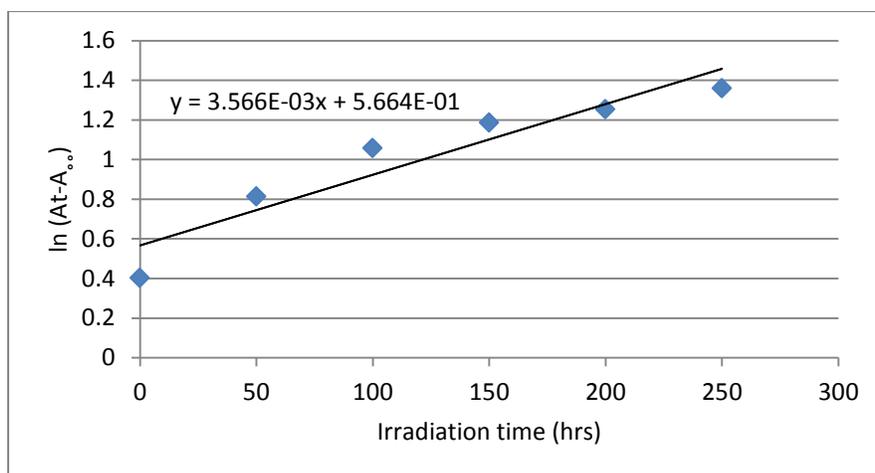Figure 4. Variation of natural logarithm of (A_t-A_∞) with irradiation time of CuL_2 in PVC film (40μm)
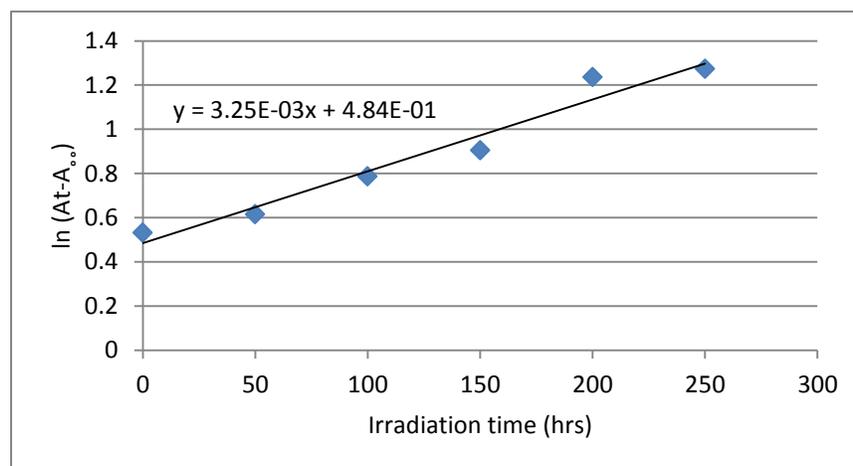

Figure 5. Variation of natural logarithm of (A_t-A_∞) with irradiation time of CdL_2 in PVC (40 μm).
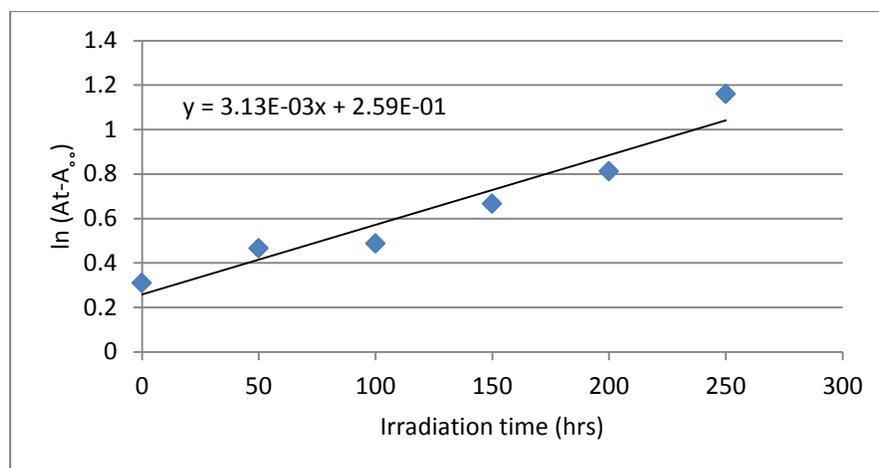
Figure 6. Variation of natural logarithm of (A_t–A_∞) with irradiation time of ZnL_2 in PVC film (40 μm)

Table 1. Photodecomposition rate constant (k_d) of PVC films thickness (40μm) containing 0.5 % of additives

compounds	$k_d\,(S^{-1})$
PVC (control)	4.88 x 10^{-3}
PVC + CuL_2	3.56 x 10^{-3}
PVC + CdL_2	3.25 x 10^{-3}
PVC + ZnL_2	3.13 x 10^{-3}
PVC + SnL_2	3.00 x 10^{-3}
PVC + NiL_2	1.43 x 10^{-3}

The photostabilizers always possess low (k_d) values, which mean that these modified polymers are stable towards UV light. One could notice that (k_d) values are sensitive to the type of additives in Poly(vinyl chloride) films, which decrease in the following order,

PVC (blank) > PVC+ CuL_2> PVC+ CdL_2> PVC+ ZnL_2> PVC+ SnL_2> PVC+ NiL_2
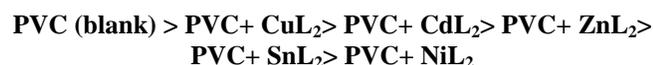
And this might point out to increase the photo-stability of the additives in this term.

Conclusions

The photostabilization of poly(vinyl chloride) films by using Bis(4-(Benzylidene-amino)-5-pyridin-4-yl-4H-[1, 2,and 4]triazole-3-thiol) complexes (0.5%wt) concentration in PVC films have been studied. These additives behave successfully as Photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in observed rate constant.

CuL_2 > CdL_2 > ZnL_2 > SnL_2 > NiL_2

Increase the activity

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