Study The Rate Constant of Photodecomposition of Polystyrene Films in Presence of Some 4- amino-5-(2-(6-methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion Complexes

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Abstract

The photostabilization of polystyrene (PS) films by (4-amino-5-(2-(6-methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion(L) compounds was investigated. PS films containing concentration of complexes 0.5% by weight were produced by the casting method from chloroform as a solvent. The photostabilization activities of these compounds were determined by monitoring the carbonyl and hydroxyl indices with irradiation time. The photostabilization of PS films by prepared complexes was investigated. The PS films containing concentration of complexes 0.5% by weight were produced by the casting method from ($CHCl_3$) solvent. The photodegradation of the obtained films was investigated using UV-vis. spectra. The photostabilization activity of these compounds was determined by calculating the photodecomposition rate constant (*k*d) for the modified PS.

Keyword: Photochemistry, polystyrene, Photostabilizer, UV Absorber.

Introduction

Triazoles are five memberd heterocyclic compounds containing three nitrogen and two carbon atoms. The substituted triazole with sulphur atom and amine group are considered to be good coordinating ligands because they involved both hard nitrogen and soft sulfur atom as thio amide group, this ligand have doner group that coordinate with wide range of metal ions [1,2]. In this paper some complexes of substituted 1,2,4 triazol with thio and amino group has been used as photostabilizer for polystyrene. The low cost and the good performance of PS products have increased the utilization of this polymer in building and other application, it is a multipurpose polymer that is used in varied applications include rigid item. General purpose polystyrene is clear and hard which is used in packaging, laboratory ware, and electronics [3]. One of the important uses of PS is in the manufacture of cover signal lamps of some automobiles [4,5]. The photooxidative degradation processes of PS have been discussed in a number of reviews [6,7]. It is generally accepted that carbonyl formed during UV irradiation of polymers, is most probable and are responsible for the yellow coloration of the polymer [8].

The carbonyl groups generated during the photooxidation 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 [9]. The physical properties of additives and polymers play a very important role in determining the additives efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of additive (photostabilizer, antioxidant, thermal stabilizer…. etc.) must be evenly distributed which requires that it be compatible with the polymer matrix [10]. In this paper we report the prepared chelates were used to enhance the photostabilization Polymer (PS). 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 $CHCl_3$ solvent. The photostabilization of polymer films were studied at room temperature under irradiation of light λ=365 nm wave length with intensity $6.02*10^{-9}$ Ein Dm^{-3} S^{-1}. In the present study, we report kd values to investigate the activity of the prepared complexes as photostabilizers against UV light in the PS polymer films.

Experimental

Materials and Methods

All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The ultraviolet-visible (UV-VIS) spectra were recorded by using Shimadzu UV-VIS. 160 A-Ultra-violet spectrophotometer in the range of 200-1100 nm. [4-amino-5-(2-(6-methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion and matel complexes was prepared by the method previously described [11] as in Fig.(1).

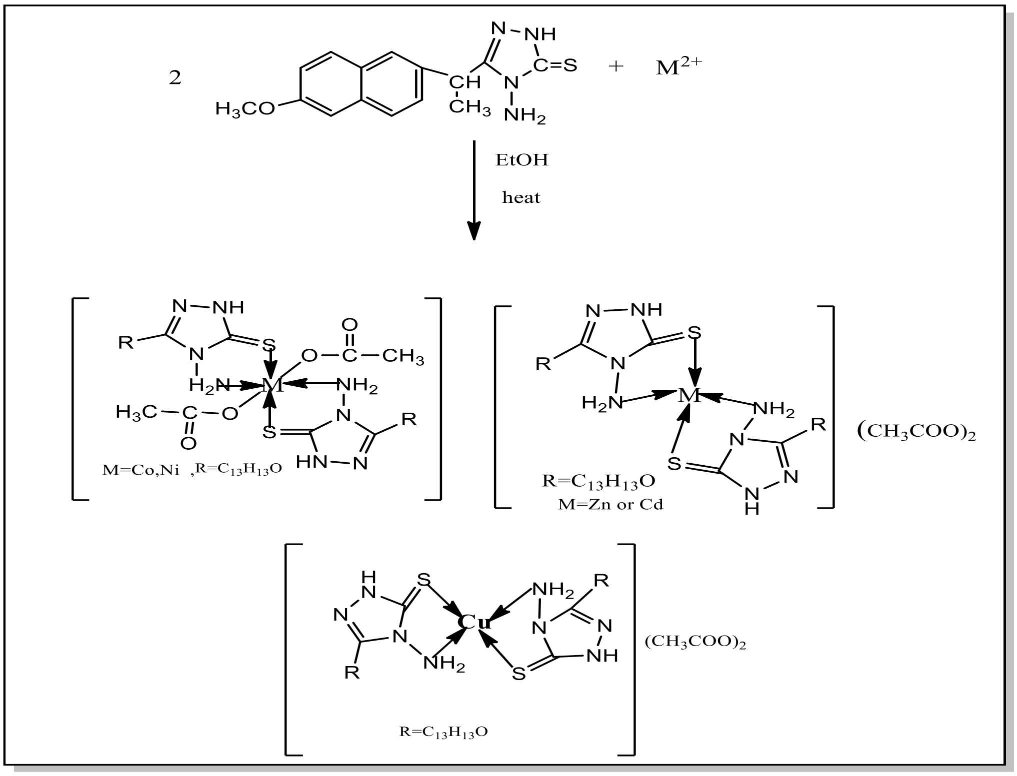

Fig.(1): The Synthetic route of the metal complexes derived from ligand.

Experimental Techniques

Film preparation

PS dissolved with metal complexes in $CHCl_3$ solvent to form PS 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 [12].

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 X 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 [13].

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:

$$\ln(a-x) = \ln a - K_d\, t \qquad (2)$$

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:

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

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

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

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.

Results and Discussion

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

The photooxidative degradation processes of PS have been discussed in a number of reviews [6,14]. It is generally accepted that carbonyl formed during UV irradiation of polymers, is most probable and are responsible for the yellow coloration of the polymer [7]. The carbonyl groups generated during the photooxidation process of polymer, extend the polymer film absorption to longer wavelengths [9,15]. 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 [9].

The physical properties of additives and polymers play a very important role in determining the additives efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of additive (photostabilizer, antioxidant, thermal stabilizer…. etc.) must be evenly distributed which requires that it be compatible with the polymer matrix [10,16]. The additives used in this study were chosen to be completely soluble in polymer solvent (Cloroform).

It has been notice that the additives used in the present work are 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 PS films thickness 40μm containing 0.5% 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. Fig.(2) to (7) shows the variation of ln (A_t - A_∞) with irradiation time for all additives in PS films at λ=365nm.

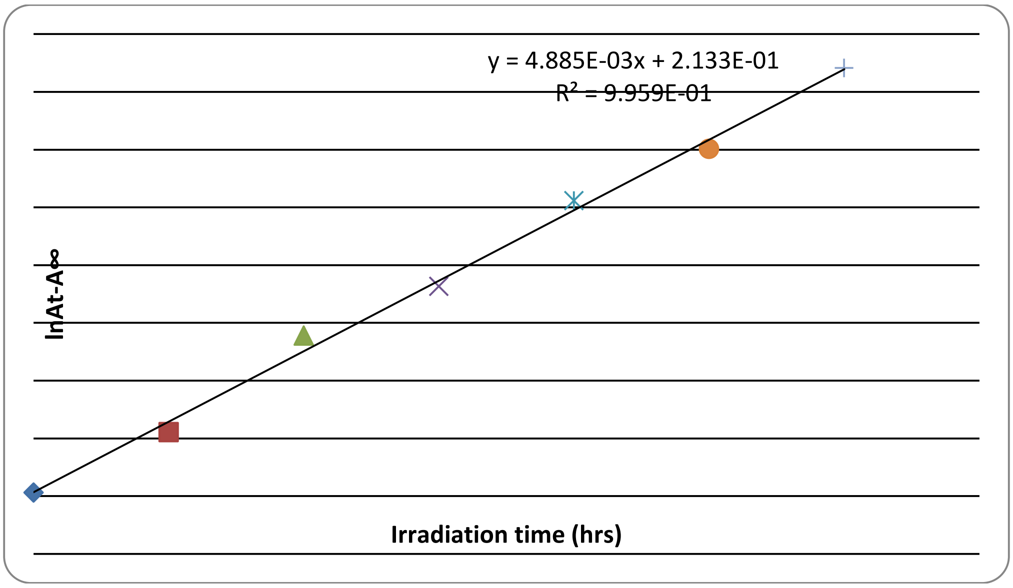

Fig.(2): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of PS (blank) film.

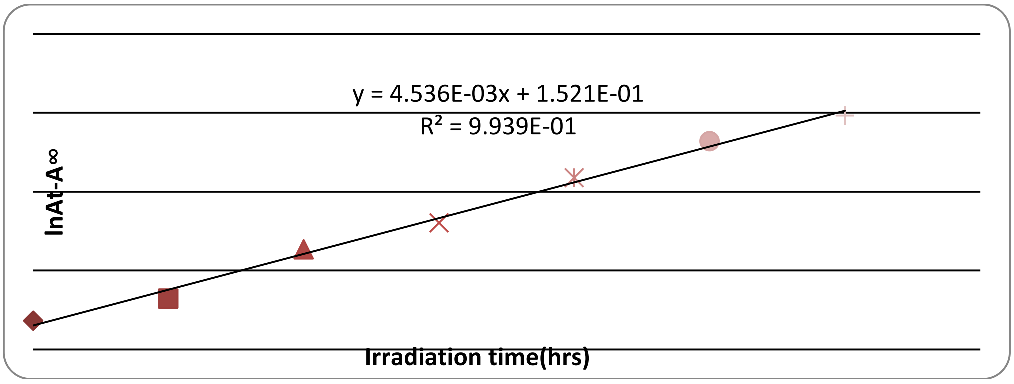

Fig.(3): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of (L) in PS film.

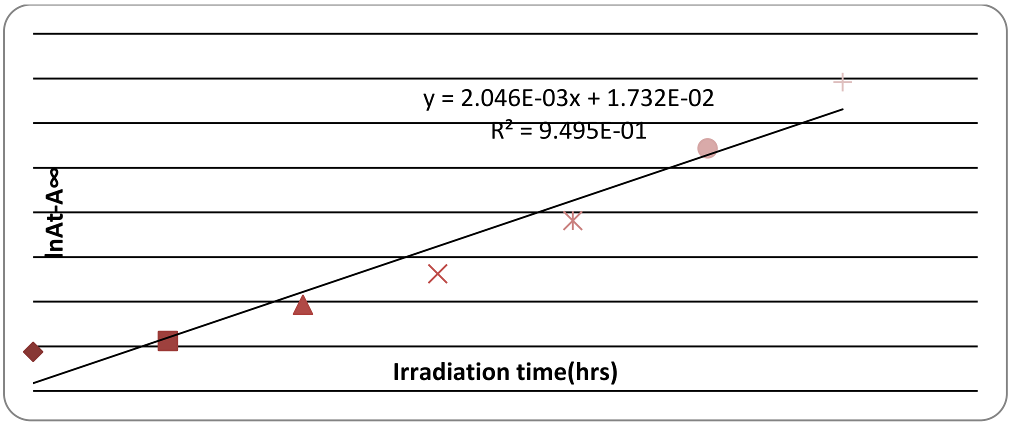

Fig.(4): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of (A_1) in PS film.

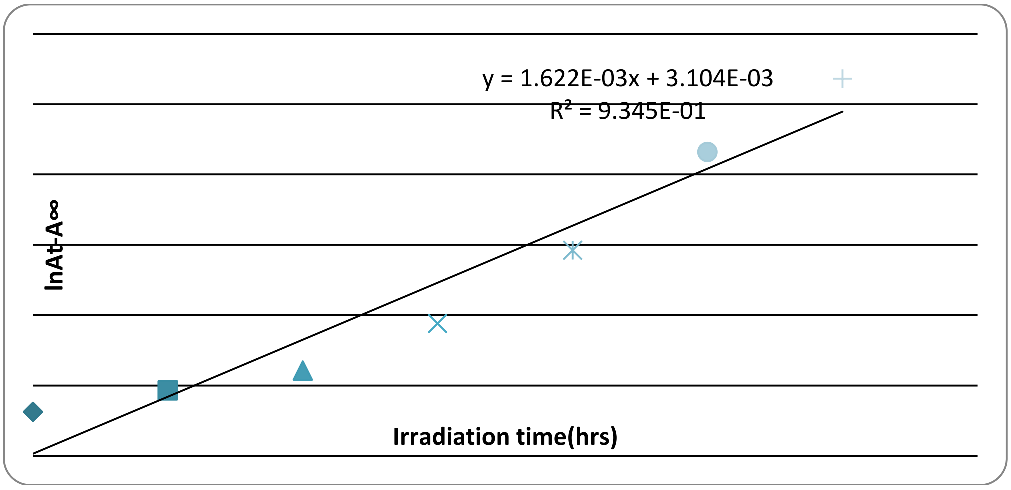

Fig.(5): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of(A_2) in PS film.

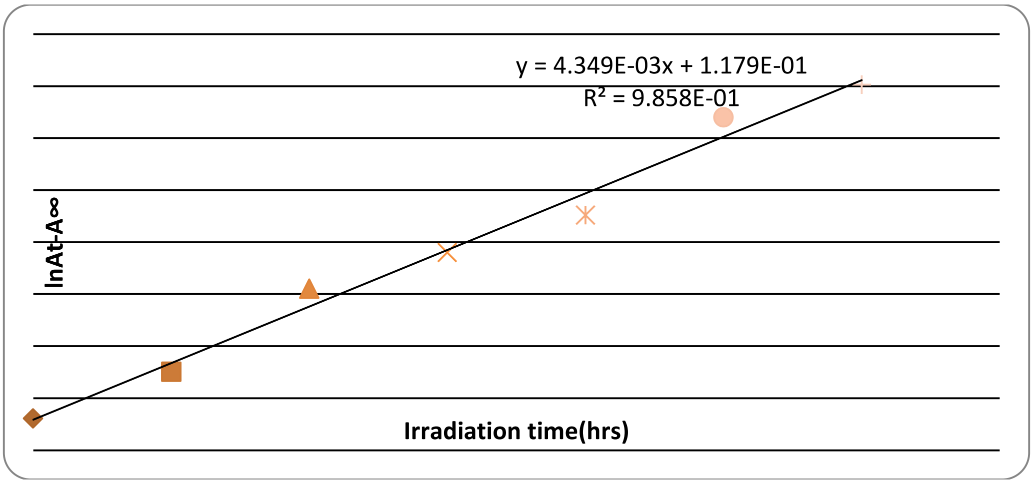

Fig. (6): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of (A_3) in PS film.

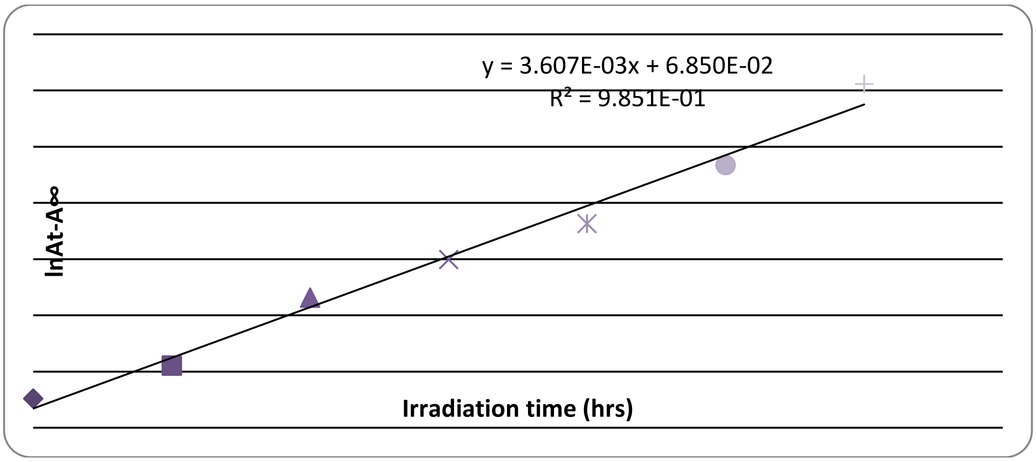

Fig.(7): Variation of natural logarithm of ln ($A_t - A_\infty$) with irradiation time of (A_4) in PS film.

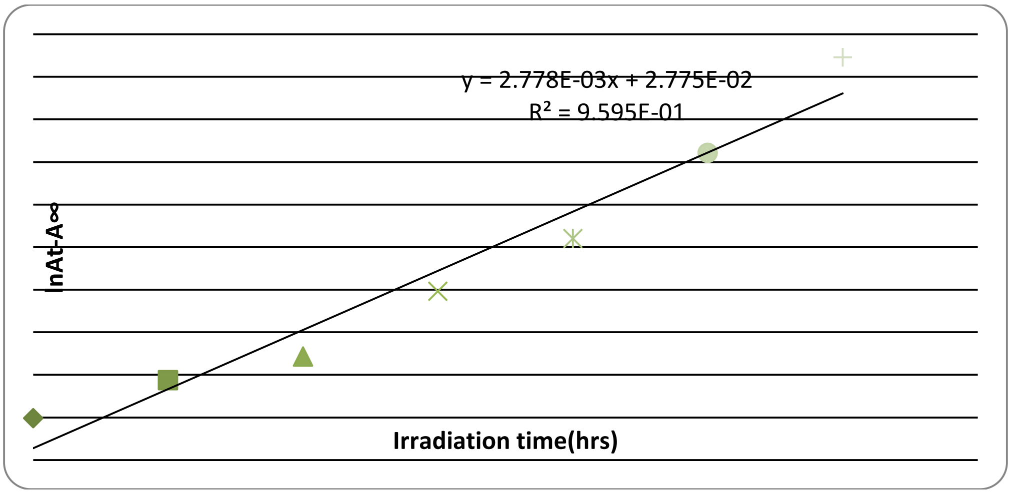

Fig.(8): Variation of natural logarithm of ln ($A_t – A_\infty$) with irradiation time of (A_5) in PS film.

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).

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

Compounds	*K_d (S^{-1})*
PS (blank)	$4.885*10^{-3}$
PS+L	$4.536*10^{-3}$
PS+(A_3)	$4.349*10^{-3}$
PS+(A_4)	$3.607*10^{-3}$
PS+(A_5)	$2.778*10^{-3}$
PS+(A_1)	$2.046*10^{-3}$
PS+(A_2)	$1.622*10^{-3}$

The photostabilizers always posses 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 PS films, which decrease in the following order:

PS >L(II) (A_3) > (A_4) > (A_5) > (A_1) > (A_2)

and this might point out to increase the photostability of this additives in this term.

Conclusion

Addition of the complexes (4- amino-5-(2-(6-methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion (L) to PS films have successfully worked as photoinducer for degradation process for PS films. The photostabilization of PS films were investigated. The additives take the following order in photostabilization activity according to their decrease in rate constant.

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الخلاصة

تم دارسة التثبيت الضوئي لرقائق متعدد الستارين بإستخدام ليكند جديد مع معقدتاتها من المركب [4-امينو-5-(2(6-ميثوكسي نفثالين)-2-يل) بابريدون)4,2,1-ترايزول-3-ثايون] تم انتاج الرقائق البلاستيكية التي تحتوي على 0.5% وزنآ من لليكند بطريقة الصب من مذيب كلوروفورم. وتم تحديد فعالية هذه المركبات في التثبيت الضوئي عن طريق حساب ثابت سرعة التحلل الضوئي للمثبت الضوئي (kd). وتعزى كفاءة هذه المركبات في التثبيت الضوئي لرقائق PS اكثر استقرارا من المثبت الضوئي.