Photochemical Study of Different Thicknesses of Polystyrene Films Containing Ni(II) Complex against photodegradation

Raghad Haddad
Private Uruk University, College of Pharmacy, Baghdad - Iraq
Corresponding author: raghadhaddad89@yahoo.com

Abstract

Ni (II) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiolcomplex was synthesized and used as a photostabilizer for polystyrene (PS) films. Polystyrene has been dissolved with Ni (II) complex in chloroform solvent to form PS films in different thickness (40, 50, 60, 70, and 80 µm), which containing 0.5 w\v% concentration, and casting method was used to remove chloroform. The photostabilization activity of these compounds was determined by monitoring the carbonyl index, weight loss method with irradiation time and morphology study. There are several mechanisms were predict according to the results acquired, depending on the structure of the complex: a) UV. absorber or screening, b) peroxide decomposer, and c) radical scavengers.

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Keywords: Polymers, Photodegradation, Ni(II) complex, PS, Photochemistry.

1.Introduction:

Polystyrene is the one of the most important polymers that is used in different applications. PS is widely used in our live such as packaging, laboratory ware, and electronics. Polystyrene polymer has several types relying upon the positions of phenyl groups along the polymeric chain [1]. Cover signal lamps of some cars was made from PS this is one of the most uses of PS [2]. In recent years, polymers become essential in our life but when they are exposed to natural weathering [3-5] such as light, heat, energy they undergoes rapid photodegradation. Breaking of the polymer chains by UV radiation causes photooxidative degradation which produces free radicals and reduces the molecular weight, that is leads to loss of mechanical properties and useless it. The deterioration sighs of physical properties for polymers is yellowing (changing the color to yellow), loss of gloss (Matting) and mechanical properties (Cracking), and others caused by UV light [6]. Photodegradation processes such as: photolytic, photooxidative, and thermooxidative reactions occurs on surface of natural and manufactured polymers when they absorb UV. radiation [7]. Photodegradation and photooxidation degradation of polystyrene [8-10] have been discussed many papers and reviews. Photodegradation is caused by the absorption of photons thatis found in sunlight, such as infrared radiation (760 - 2500nm.), visible light (400 - 760 nm), and ultraviolet light UV-A (315-400 nm), UV-B (280-315 nm). Photooxidation of polymers is a reason for irreversible deterioration for a number of substances and cause loss of physical and mechanical properties of plastics [11-15]. It is realized that all plastics degrade under the effect of sunlight. Therefore stabilization became necessary to prevent, or decrease, the deterioration caused by the environmental factors such as light, heat and air. The photostabilization of polymers means retardation or elimination of photochemical process that happen in polymers during irradiation. There are many types of stabilizer depending on the activity of stabilizer: (a) UV absorbers, (b) light screeners,(c) peroxide decomposers,(d) excited state quenchers and (e) radical scavengers[16-18].In this paper we prepared compounds as a photostabilizer used to inhibit the photodegradation of PS, and studied in different thickness from the polymer(40, 50, 60, 70, and 80 µm).

2. Experimental

All reagents, starting materials and solvents were prepared commercially and used without any purification. Infrared (FTIR) spectra for compounds were recorded by FTIR.8300 Shimadzu spectrophotometer in the frequency range from 4000-200 cm^{-1}.An accelerated weather-meter QUV tester (Q-Panel Company, Homestead, FL, USA) was used to irradiate PS films at room temperature with a UV light (λmax = 365 nm). Morphological study for the surface of the films was recorded by MEIJI TECHNO microscope, (Japan).

2.1 Synthesis of $Ni(L)_2$ complexes

Ni(II) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiolcomplex, was synthesis by the method described by Haddad et al. (2013)[19]: Fig.(1).

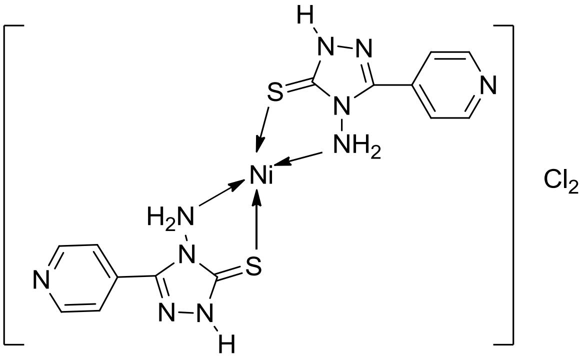


Fig.(1): Suggested structure of Ni(II) complexes.

2.2 Film preparation

Polystyrene (PS) has been dissolved with Ni (II) complex by utilizing chloroform as solvent to form PS films with Ni (II) complex in different thickness. A solution of (5%, 6%, 7%, 8% and 9% w/v) polymer in chloroform was used to prepare films. Micrometer type 2610A, Germany was used to measure their thickness and their thicknesses were (40, 50, 60, 70, 80 μm). Evaporation technique for 24 hours at $25C^0$was used to prepare films, to remove the residual chloroform solvent [20-21].

2.3 Irradiation experiment

6.2×10^{-9} Ein Dm^{-3} $S^{-1}$is intensity of UV. Light that was used for irradiation of PS films, its wavelength (365 nm). The polymer film samples were placed parallel to one other and the lamp of the UV. radiation is vertically incident on the samples.10 cm is the distance between the films and the source of light. The polymeric film samples were vertically fixed parallel to the lamps to ensure that the radiation is perpendicular to the films. The intensity of light incident on all samples should be equivalent by rotating the films from time to time [22].

2.4. Photodegradation measuring methods:

2.4.1. Photodegradation rate Study by FTIR spectrophotometer:

The photodegradation degree for the films was measured by checking FTIR spectra in the range (4000-400) cm^{-1} before and after irradiation. The absorption of carbonyl is appeared at 1720 cm^{-1}. The carbonyl peak intensity method was used to measure photodegradation rate at different irradiation times, this is called index method [22], as relation bellow:

$$Is = \frac{As}{Ar} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Is: index of group under study[22]
As: absorbance of peak under study
Ar: absorbance of reference peak.

2.4.2. Photodegradation Study by Weight loss Method:

The stabilizing efficiency of Ni(II) complex was determined by measuring the PS % weight loss in presence and in absence of additives , before and after irradiation time. Where W_1 is the weight before irradiation, and W_2 is the weight after irradiation, by using the following equation [23].

$$\text{Weight loss \%} = [(W_1 - W_2) / W_1]\ 100 \ \ldots\ldots (2)$$

2.4.3. Photodegradation Study by Morphology Method:

Microscope was used to check the morphology for the films surface [24] (Before and After irradiation) and shows the top surface for these films. The surface morphology of PS films of irradiated and none irradiated and in the presence and absence of the additive were studied.

Results and discussion

Ni(II) with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiolas complex was used as additives for the photostabilization of PS films in different thickness against photodegradation. The carbonyl index with irradiation time was monitored by using IR spectrophotometry to study the photochemical activity of these additives as photostabilizerfor PS films. Appearance of a band at 1720 cm^{-1} was ascribed to formation carbonyl groups. Carbonyl index (I_{CO}) method was used to study the photodecomposition for PS films. The irradiation of PS films in various thicknesses by UV light with wavelength λ=365 nm is led to a change in FTIR chart [25]. Li and his co-workers are demonstrated that the photooxidation rate decrease with increasing film thickness [26] because the oxygen diffusion rate for a given polymer is proportional to the surface area and decrease with increasing thickness, as shown in Fig.(2 and 3).

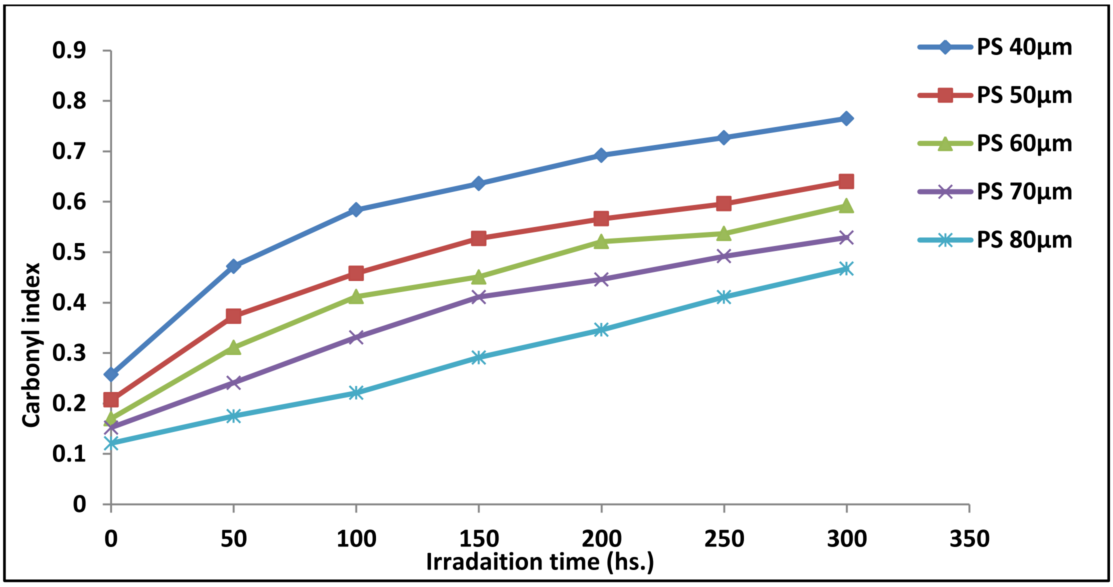


Fig.(2): Relationship between (I_{CO}) and irradiation time for PS blank films in different thicknesses.

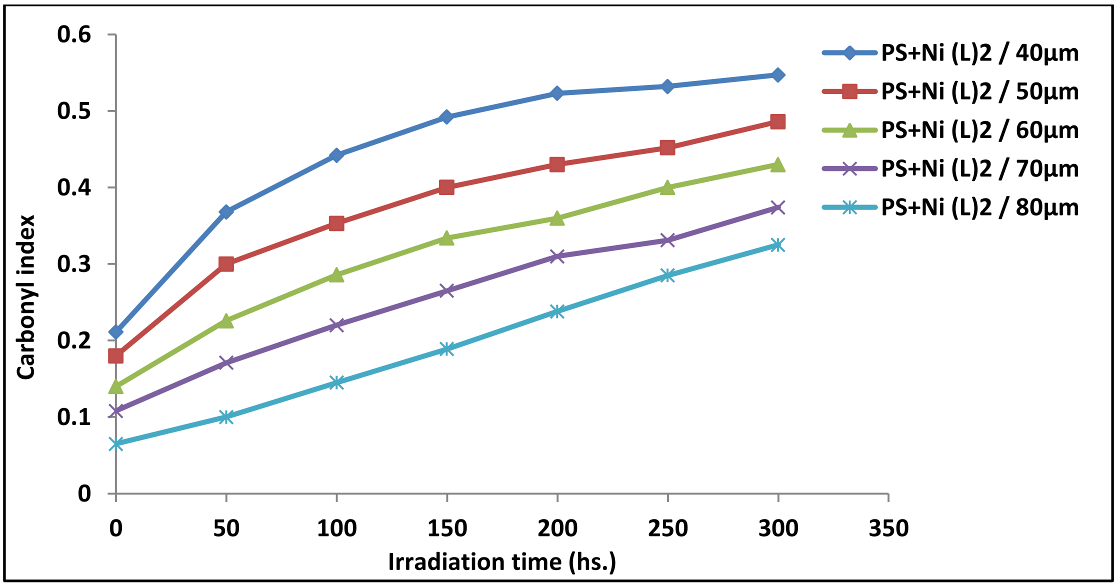


Fig.(3): Relation between (I_{CO}) and irradiation time for PS+Ni(L)$_2$ in different thicknesses.

However, Figures 4 to 8 show the relation of I_{CO} for PS films with and without additives. Films with additives showed lower growth rate with irradiation time with respect to blank films [3]. So these additives could be considered as photostabilizers of PS against degradation.

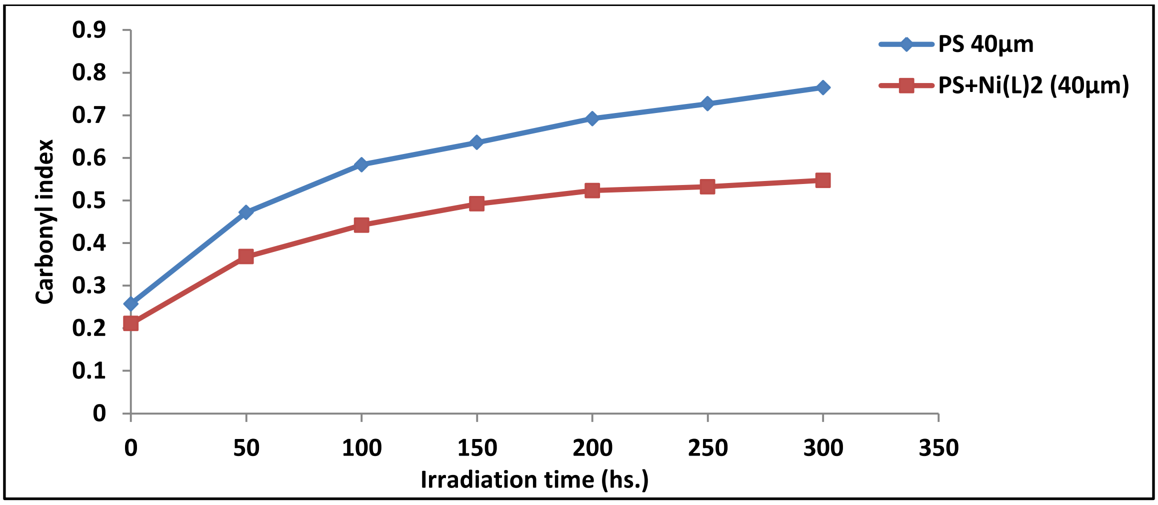


Fig.(4): The relation between (I_{CO}) and irradiation time for PS (blank) and PS+Ni(L)$_2$ in 40µm thickness.

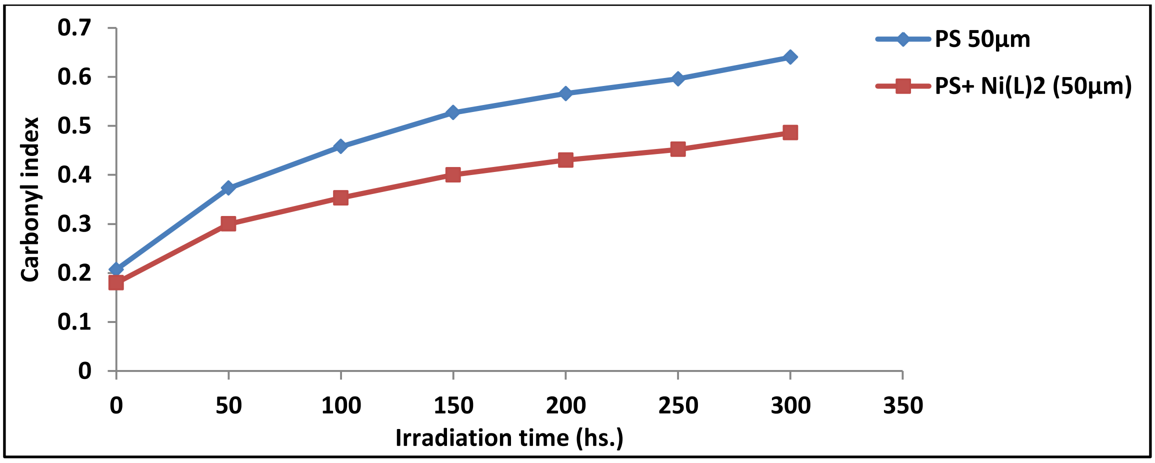


Fig.(5): The relation between (I_{CO}) and irradiation time for PS (blank) and PS+Ni(L)$_2$ in 50µm thickness.

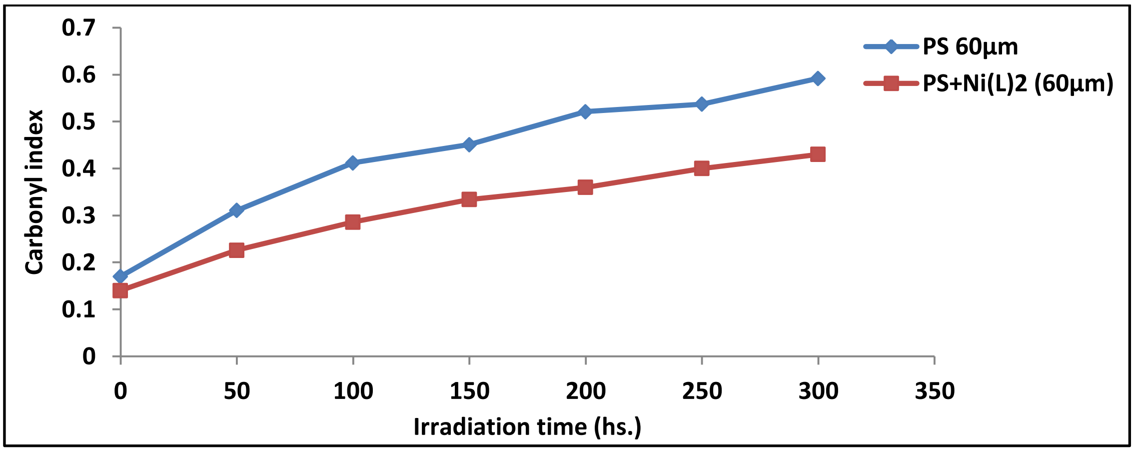


Fig.(6): The relation between (I_{CO}) and irradiation time for PS (blank) and PS+Ni(L)$_2$ in 60µm thickness.

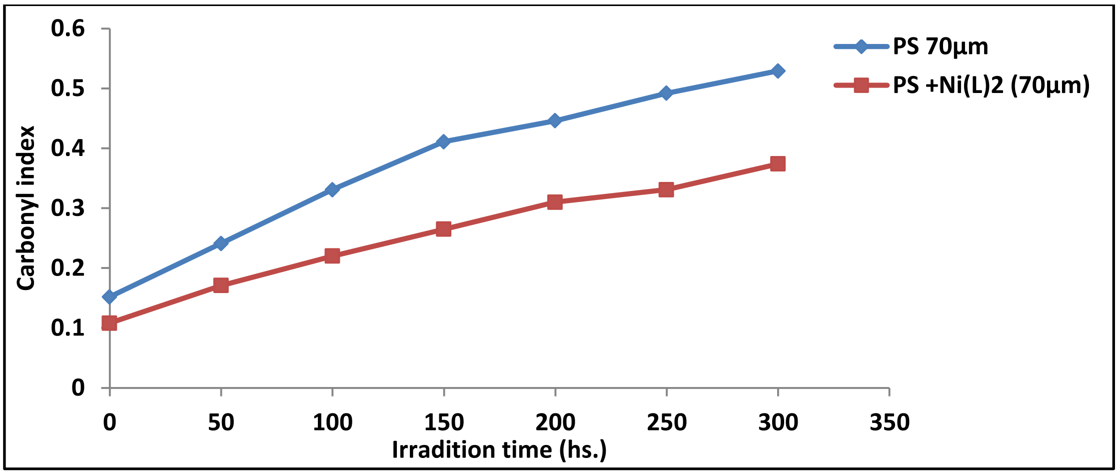


Fig. (7): The relationship between (I_{CO}) and irradiation time for PS (blank) and PS+Ni$(L)_2$ in 70μm thickness.

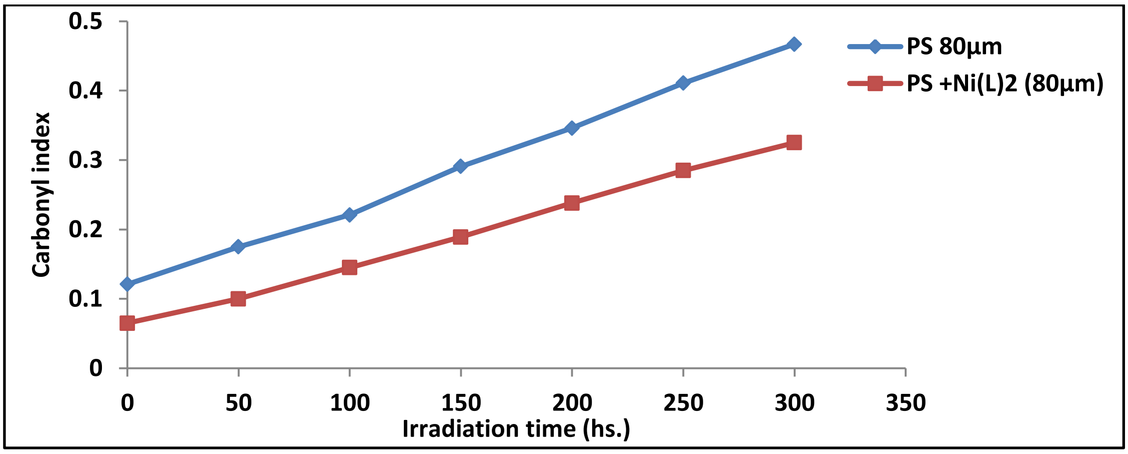


Fig. (8): The relationship between (I_{CO}) and irradiation time for PS (blank) and PS+Ni$(L)_2$ in 80μm thickness.

In this study, different thicknesses of PS (40, 50, 60, 70, 80 μm) with and without additive (0.5%) concentration was used to study the photodegradation of PS films. From the results we indicate that the rate of photooxidation carbonyl at irradiation time is diminished with increasing film thickness for all additives utilized, compared with PS control. Film thickness is one of the parameters that affecting on the mechanism of photooxidation and the rate of degradation. Therefore, the Ni complexes considered as the photostabilizer for PS [27]. for the effect of thickness on the rate of photodegradation and photostabilization of vinyl polymers using the Fe(III), Mn(III), Ni(II) and Cu(II) acetylacetonate complexes as additives in polystyrene films. Fig.(9) explain the photodegradation process of PS.

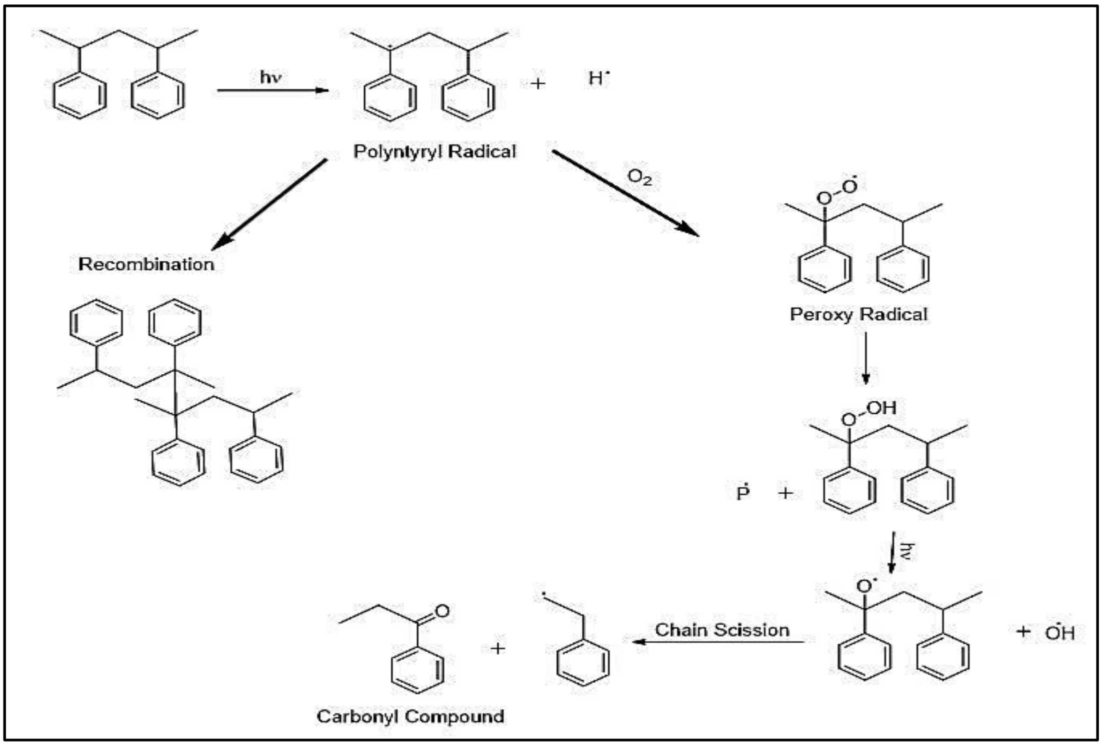


Fig.(9): The general process for photodegradation of polystyrene [17].

3.2. Weight loss method to determination the Stabilizing efficiency:

The % weight loss method for degraded PS films in absence and in presence of (Ni (II)) compound as additive was used to investigate the stabilizing efficiency for them by applying equation 2, From our study in this work we conclude that the rate of weight loss for the films gradually increased with increasing degradation time [28, 29]. Figures (10 to 16) show the results of weight loss % as a function of irradiation time. These showed lower function in the presence of additives. From the results we notice that % polymer weight loss decrease in the presence of additive so this additive have stabilizing effect against photodegradation.

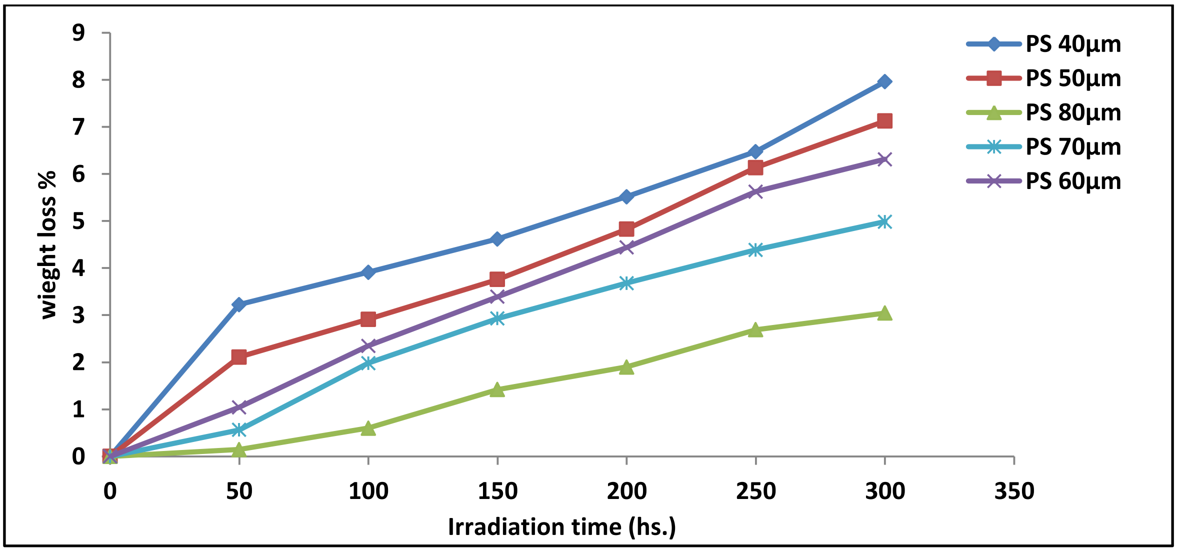


Fig.(10): Loss in weight (%) vs. irradiation time for PS blank films in different thickness.

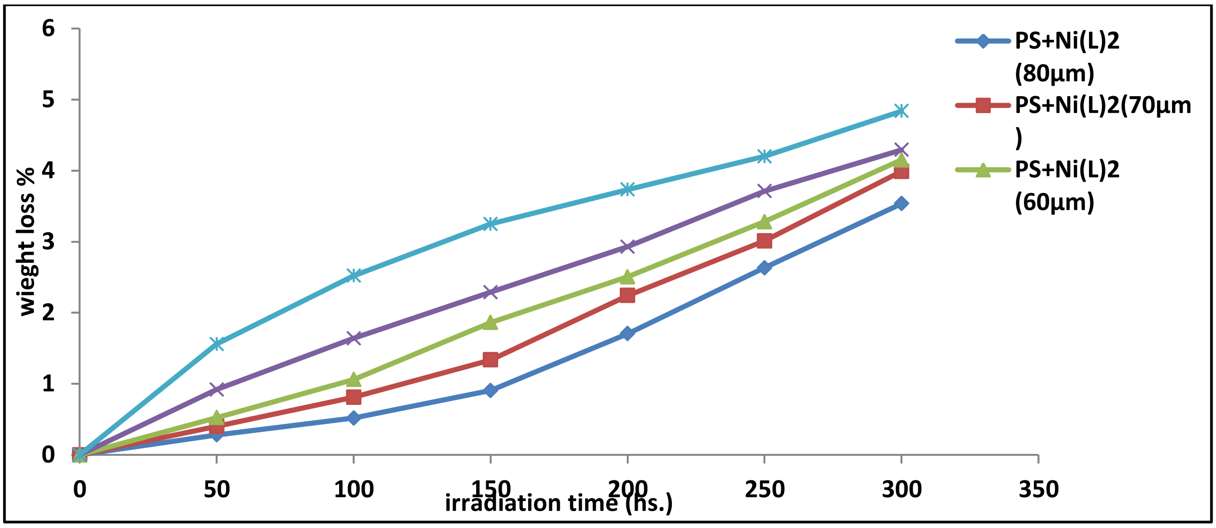


Fig.(11): Loss in weight(%) vs. irradiation time for PS+Ni(L)$_2$ films in different thickness.

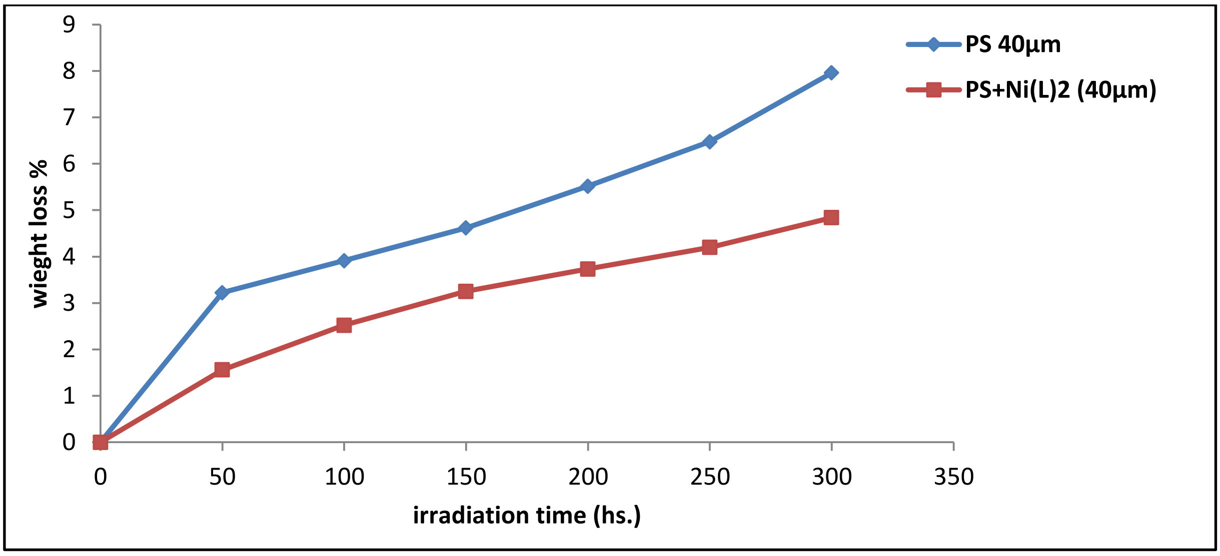


Fig.(12): Loss in weight(%) vs. irradiation time for PS blank and PS+Ni(L)$_2$ films in 40µmthickness.

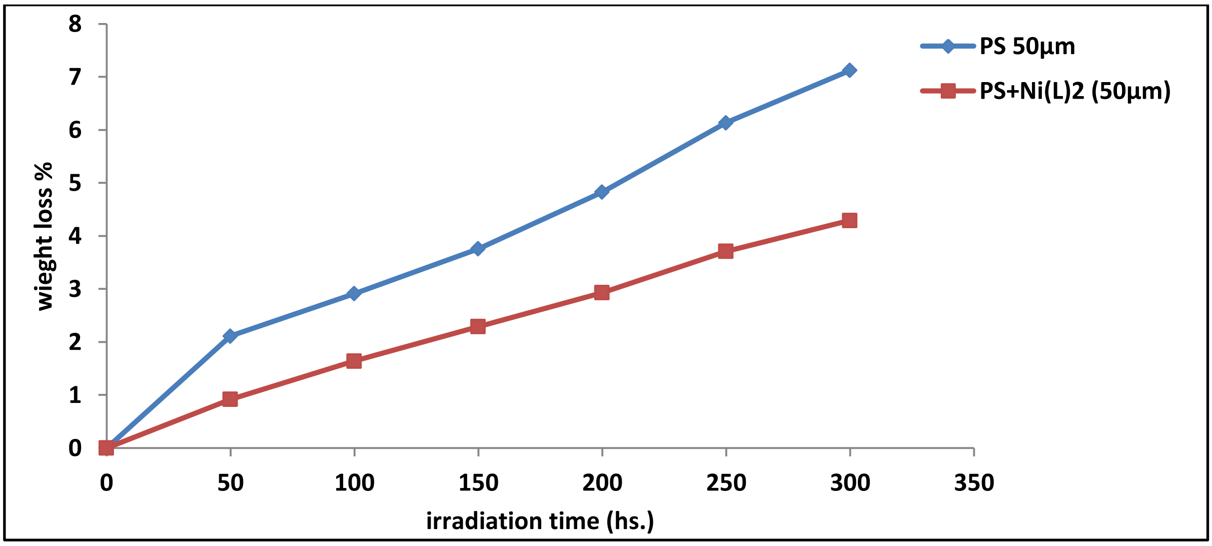


Fig.(13): Loss in weight(%) vs. irradiation time for PS blank and PS+Ni(L)$_2$ films in 50µm thickness.

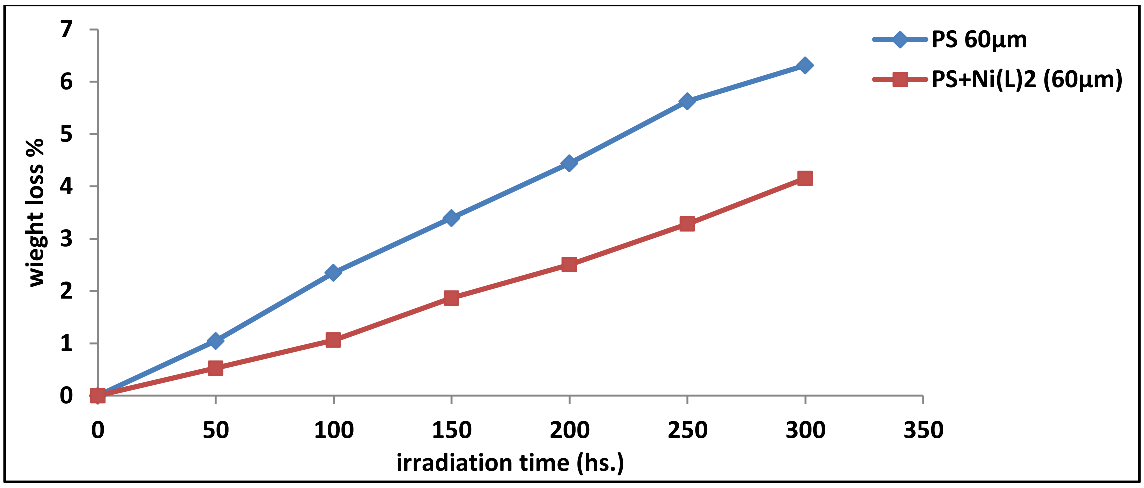


Fig.(14): Loss in weight(%) vs. irradiation time for PS blank and PS+Ni(L)$_2$ films in 60µm thickness.

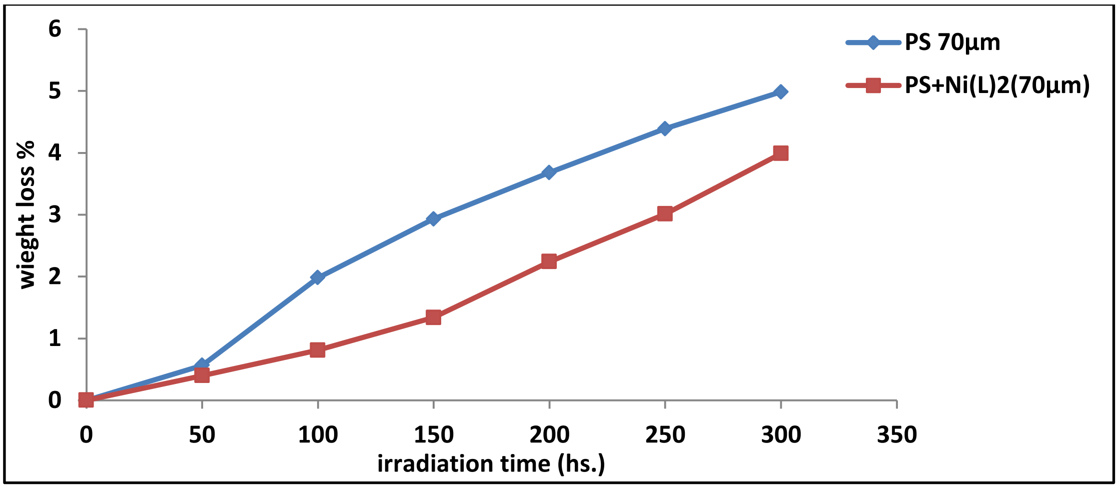


Fig.(15): Loss in weight(%) vs. irradiation time for PS blank and PS+Ni(L)$_2$ films in 70µmthickness.

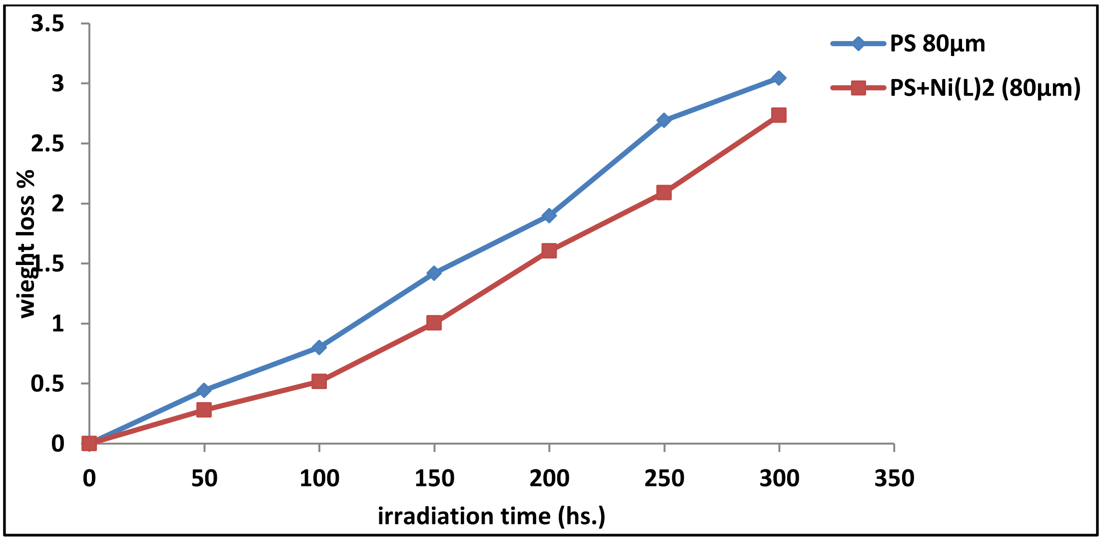
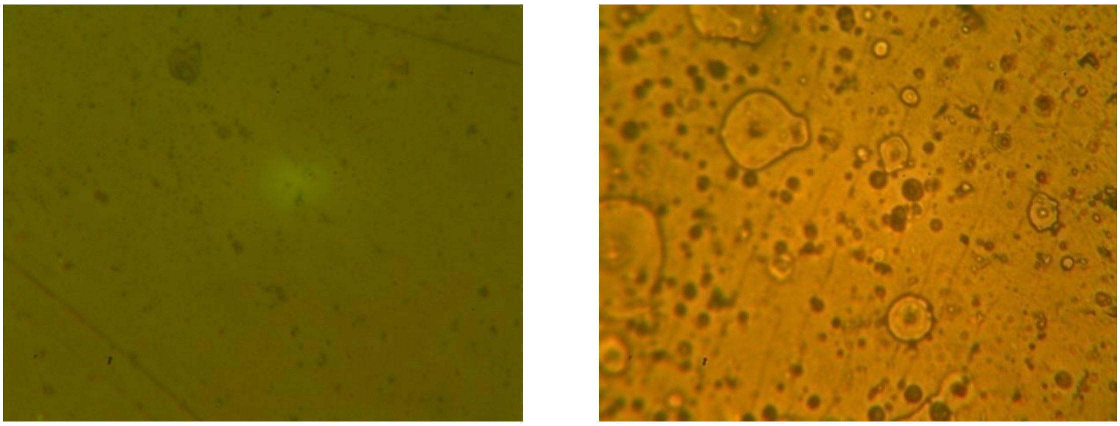


Fig.(16): Loss in weight(%) vs. irradiation time for PS blank and PS+Ni(L)$_2$ films in 80µmthickness.

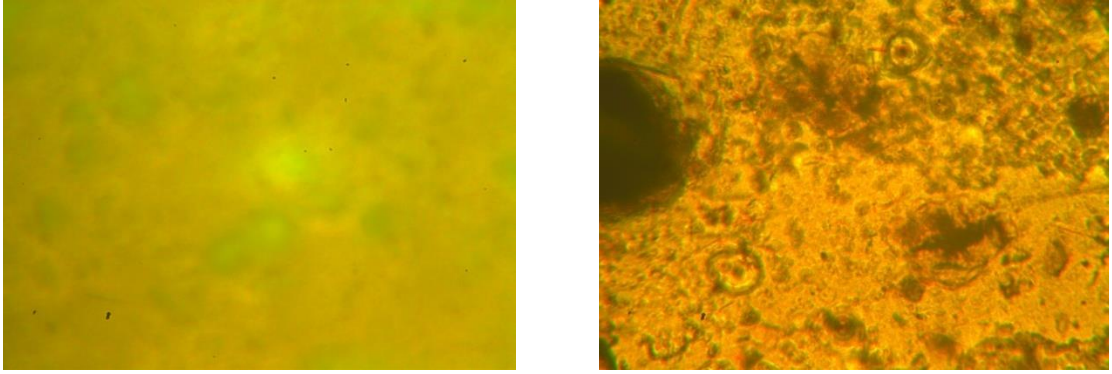
3.3. Surface Morphology for the Films

The surface morphology examination for the polymer gives reasonable picture about some of the physical properties for it such as: the crystalline case, surface irregularity, smoothness of the surface. Also shows the defects that accrue on surface of polymer due to photodegradation [30].

Before irradiation the microscopic image for the surface of PS (blank) film was smooth and empty of any white spots, while after 300h irradiation the PS film surface full of white spots. These spots are the holes or grooves that occur due to degradation. However, the white spots on the surface of polymer become fewer in the case of modified polymers compared with polymer blanks films; this indicated the good efficiency for the prepared additive and how it protect the surface from deterioration [31, 32], as shown in Fig.(17).



PS (blank) before irradiation **PS (blank) after 300 hs. irradiation**



PS+Ni(l)$_2$ before irradiation **PS+ Ni(l)$_2$ after 300 hs. irradiation**

Fig.(17): Microscopic images of PS(blank) and PS+Ni(L)$_2$.

time.

3.4. Photostabilization Suggested Mechanisms for PS films by Ni (II) Triazole Complex:

Photostabilization of PS with Ni (II) triazole complex proceeds through the UV absorber, radical scavenger and peroxide decomposer mechanisms.

Generally, Nickel complexes known as photostabilizers for poly olefins through excited state quencher and peroxide decomposer, so these Metal chelate complexes in this work is consider as photostabilizers for PS by both excited-state quencher and peroxide decomposer [33, 34] as mechanism shown below See Fig. (18):

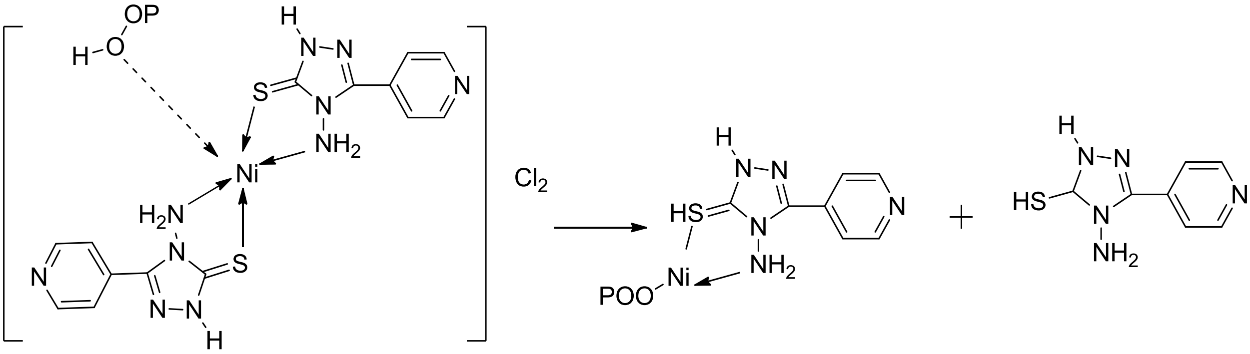


Fig.(18): Suggested peroxide decomposer mechanism.

Another mechanism for the ring of triazole in this compound is as UV absorber [35] and it plays an important role in the mechanism of stabilizing process, it dissipates the UV energy to harmless energy such as heat. The Nickel chelate complex also shows radical scavengers mechanism by energy transfer through formation unreactive charge transfer complexes between the metal chelate and excited state of the chromophore (POO$^{\cdot}$) so the stabilization activity is caused by resonating structures [35] as in Fig.(19) below:

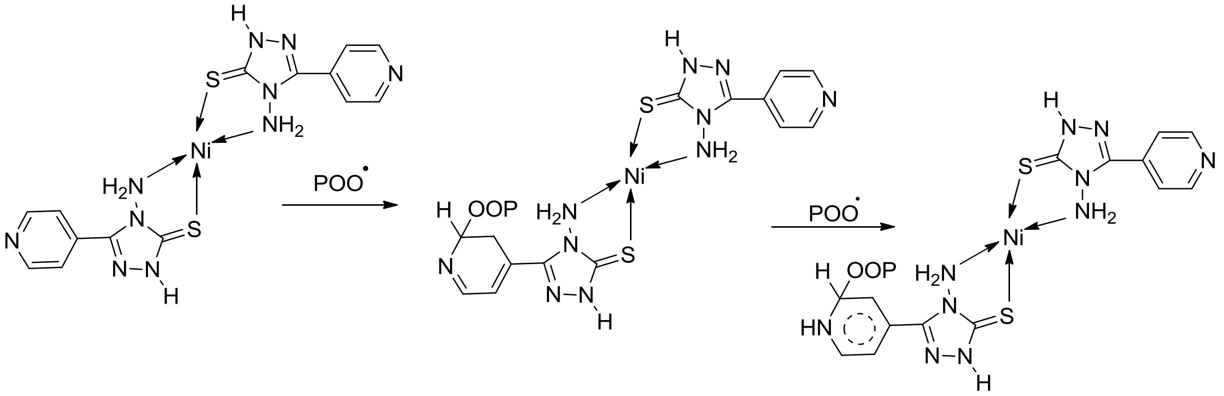


Fig.(19): Suggested radicals scavengers mechanism.

4. Conclusion

In the work, the photostabilization of polystyrene polymer in different thickness by using Bis(4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol) with Ni(II) complex have been studied. This complex act as photostabilizer for PS films against photodegradation by UV. light. From the results we conclude that the photooxidation rate decrease with increasing film thickness. In this paper UV absorber, radical scavenger and peroxide decomposer mechanisms were suggested to stabilize the PS films.

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