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Studies on the Photostability of Polystyrene Films with New Metals Complex of 1, 2, 4-triazole-3-thione Derivate

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ABSTRACT

The new complexes including Cu(II), Co(II), Ni(II), Pt(IV), and Pd(II) metals with 4,4'-(((1E,1'E)-1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione) have been synthesized of utilizing us polystyrene (PS) photostability. The supplement (0,5 w / v%) was for the production of polystyrene (PS) in the form of tetrahydrofuran (THF). Polystyrene films were exposing irradiation (250 – 380 nm) absorption light intensity of 6.02 x 10^{-9} ein dm^{-3} s^{-1} at room temperature, through the changes that occur to each of viscosity average molecular weight (Mv), main chain scission (S), degree of polymerization (DP_n), weight loss %, hydroxyl index (I_{OH}), carbonyl index (I_{Co}) determined the photo stabilization activities of the films.

Keyword: Terephthaldehyde, polystyrene films, 1, 2, 4-triazole-3-thione, photostability, photodegradation

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INTRODUCTION

One of the organic compounds is a polymer genesis of duplication units (low molecular weight) called monomers design of the significant polymers is Polystyrene utilized widely several commercial industrial fields. Material molecules of considerable length it's called plastic one of the most used materials in daily life and has some properties such as zero electrical conductance, low cost, substantial mechanical strength, extensively using environment. Applications of polymers have disadvantages such as biodegradation at the increased temperature on the other hand[1], many advantages (e.g. building construction, hardness, available and low price. when exposed polymeric materials such as Polystyrene (PS) by UV light lead to photodegradation that causes undesirable due to the absorption of a photon[2]. The requirements for studying the change that occurs to the polymer are prerequisites to the presence of chromophore groups. Further investigators must investigate routes to stabilize artificial polymers against heat, air, and light. Cobalt(II), nickel(II), copper(II), palladium(II) and platinum(IV) tetradentate ligand complexes[3] were succeeded applied to photo stabilize Polystyrene[4]. Cu(II), Co(II), Ni(II), Pt(IV), and Pd(II) into 4,4'-(((1E,1'E)-1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thioine)

EXPERIMENTAL

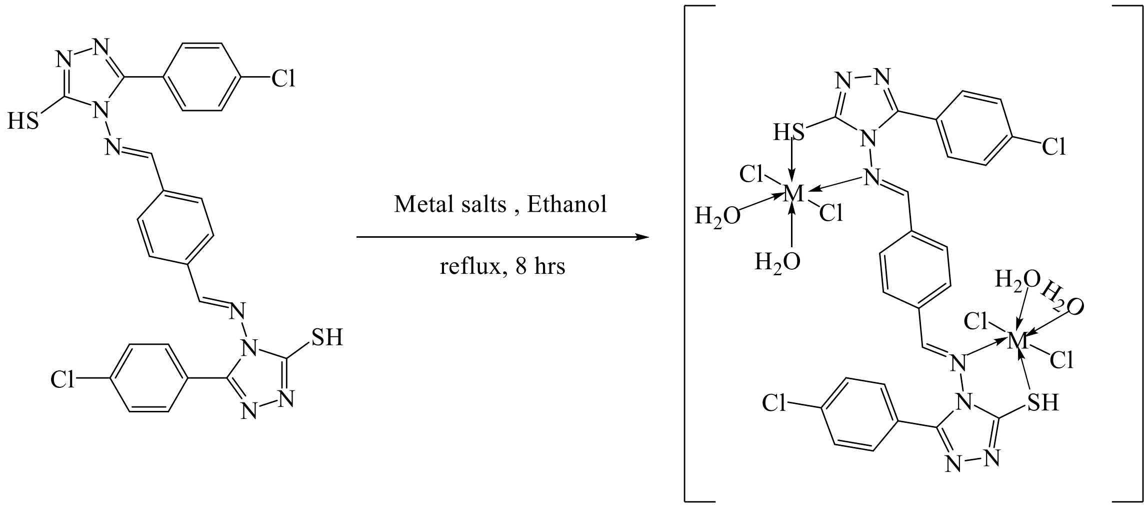
A. Metal complexes synthesis

New ligand and complexes (Table 1) were all prepered[5] (Scheme 1) by the method described by were characterized[6] using the Fourier transform infrared (FT-IR), Ultraviolet-visible (UV-visible), Proton nuclear magnetic resonance (^{1}HNMR) and carbon^{13} nuclear magnetic resonance (^{13}CNMR) [5].

Table 1: Structure of new ligand (L) and metal (M_2L) complexes applied in this study

Symbol	Name
L	4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)
Co_2L	[4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)] cobalt(II)
Ni_2L	[4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)] nickel(II)
Cu_2L	[4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)] copper(II)
Pd_2L	[4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)] palladium(II)
Pt_2L	[4,4'-((1,4-phenylenebis(methaneylylidene))bis(azaneylylidene))bis(5-(4-chlorophenyl)-4*H*-1,2,4-triazole-3-thione)] platinum(IV)

The FT-IR spectrum of the new(L) ligand appears the band stretching at 3246,3053, 2935, 2754, 1693, 1599, 1425, and 1028 cm^{-1} that was assigned to NH, aliphatic C-H, S-H, aromatic C-H, CH=N imine, C=C, C=S, and C-S bands respectively[7]. Terminus tautomerism (deprotonation) the new ligand linkage to "S" atom of metal ion from a five-membered chelate ring distinguished more stable[8]. The observed of (CH=N) imine of complexes[9] was shifted to depress confront to ligand, attribute to coordinate with the ligand. Also, these bands (C-S) shifted lower frequencies because of complexation, whereas the (S-H) band in ligand wholly evanescence upon complexation finally aromatic C-H (3053 cm^{-1}) and C=C (1599 cm^{-1}) bands don't display shift due to didn't engage in complexation. New bands showed because (M-S) and (M-N) frequencies attribute to complexation[10]. The UV-visible spectrum for new ligand observed (3) bands absorption at 266, 336, and 346 nm attribute (π-π^*), (π-π^*) and (n-π^*) electronics transition, at the same order. The displayed shifted compared to ligand the electronic transition[11] [12]of metal d-orbital (d-d) were showed in Ni(II), Cu(II), Pd(II) Pt(IV) and Co(II).In contrast, the Pd(II) was diamagnetic for d^{10} ion. NMR spectrum information for new ligand[13]: ^{1}HNMR (500 MHz, ppm, DMSO-d_6) 13.97 ppm (s, S-H), 9.98 ppm (s, CH=N imine), 8.04 ppm (s, 6H benzene ring). ^{13}CNMR (125 MHz, DMSO-d_6; ppm) 167 ppm (C of triazole), 148 ppm (C of CH=N imine), 129 (C of benzene ring)[14, 15].



M= Co(II), Ni(II), Cu(II), Pd(II) and Pt(IV)

Scheme 1: Synthesis of the M_2L complexes

B. Film Preparation

Polystyrene films, new ligand, metal complexes dissolved in tetrahydrofuran (THF) fixed concentration of polystyrene solution[16] (5g/100ml) in (THF) was utilized to prepare polystyrene films with 40 μm thickness (measured via a micrometer kind 2610A, Germany) the film evaporation technique at 25 °C for 20 hrs. to remove the residual tetrahydrofuran[17].

IRRADIATION EXPERIMENTS

A. Accelerated Testing Technique

Expose polystyrene films to UV light at a wavelength of (250 – 380 nm) and maximum light intensity 6.02×10^{-9} ein dm^{-3} s^{-1}. Distance between the source (UV light) and the polystyrene films (8 cm) was fixed parallel to each other[18, 19].

B. Measurement of the photodegradation rate of polymer films used infrared spectrophotometry.

The degree of photodegradation of polystyrene films via measurement Fourier transforms infrared (FT-IR) spectrum at region (4000 – 400 cm^{-1}) using 8300 Shimadzu FT-IR spectrophotometer. The position of a hydroxyl group (I_{OH}) and carbonyl group (I_{co}) observed at 3412, 1726 cm^{-1} respectively different irradiation time of photodegradation[20] change hydroxyl peak intensity by (Eq. 1) [18]

$$Is = As / Ar \qquad (1)$$

C. Limitation of the viscosity rate Mwut. used a viscometer process[21]

Viscosity techniques mention the average molecular of the polymer was utilized to calculate the average Mwut [22] from "Mark – Houwink equation" (Eq. 2) where α and K = constants, rely on the polymer-solvents related to temperature. $[\eta]$= intrinsic viscosity.

$$[\eta] = K\, Mv\, \alpha \qquad (2)$$

Measurement of the intrinsic viscosity by using "Ostwald U-tube viscometer the polymer is dissolved by solvent benzene (g/100ml) at 25 °C specific viscosity $[\eta_{sp}]$[23] was used to calculated by (Eq. 3) $[\eta_{sp}]$ = specific viscosity

$[\eta_{re}]$ = relative viscosity

t = the flow times of the solution

$[\eta_{sp}] = \eta_{re} - 1$ (3)

$\eta_{re} = t / t_o$ (4)

Measurement was transformed into intrinsic viscosity used (Eq. 5)

C= the concentricity of solution polymers (g/100ml).

$[\eta] = (\sqrt{2}/C)\,(\eta_{sp} - \ln \eta_{re})^{½}$ (5)

The intrinsic viscosity[24] in the tetrahydrofuran (THF) solution was measured for the molecular weight of polystyrene (Eq. 6)

$[\eta] = 11.8 \times 10^{-4}\, Mv^{0.73}$ (6)

D. Measurement photodegradation by weight loss

The stabilization effective was monitoring from by the weight loss in the absence and presence of additional used (Eq. 7) [25]

Weight loss % = $[(w_1-w_2) / w_1] \times 100$ (7)

RESULTS AND DISCUSSION

The Five metal complexes of Cu(II), Co(II), Ni(II), Pt(IV), and Pd(II) with 4,4'-(((1E,1'E)-1,4-phenylenebis(methaneylyldene))bis(azaneylyldene))bis(5-(4-chlorophenyl)-4*H*-1,2,4triazole-3-thione) have been used polystyrene as a films. FT-IR spectrum gives The strength band in (3412 and 1725 cm^{-1}) attribute of hydroxy and carbonyl group[26], in specific., as the result of oxidation growth, is degraded by radiation; the formation hydroxyl group is due to broadband occurrences of the 3600–3200 cm^{-1} band (see figure 1).

Figures (2, 3) showing an exposure ray rate of (I_{CO}) and (I_{OH}) indexes increased by the Sensitivity raying duration relative to Polystyrene without addition, showing Cu[II], Co(II), Ni(II), Pt(IV) and Pd(II) metals. The most efficient photo stabilizes were observed with Pt (IV).

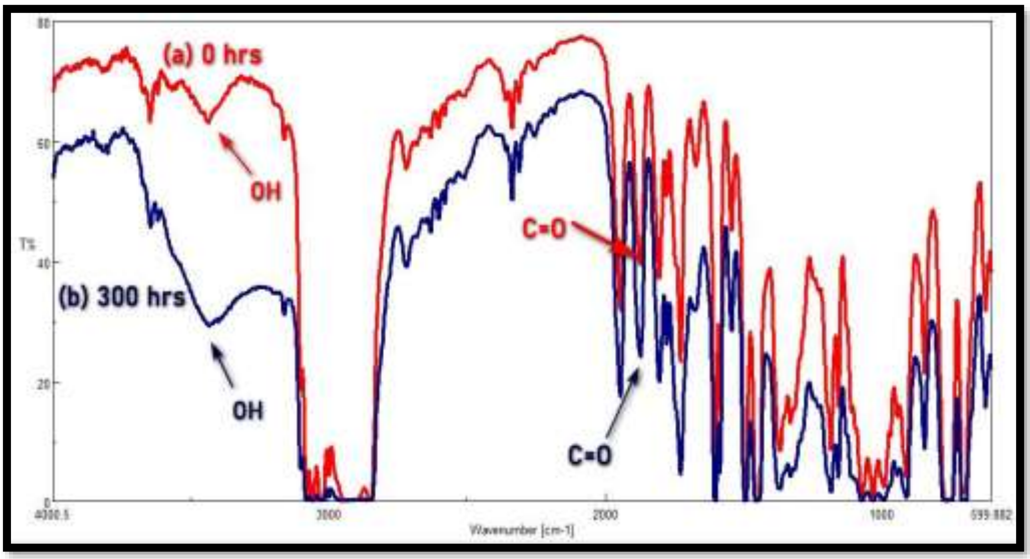


Figure 1: FT-IR polystyrene film spectrum (a) before and (b) after 300 hours of irradiation

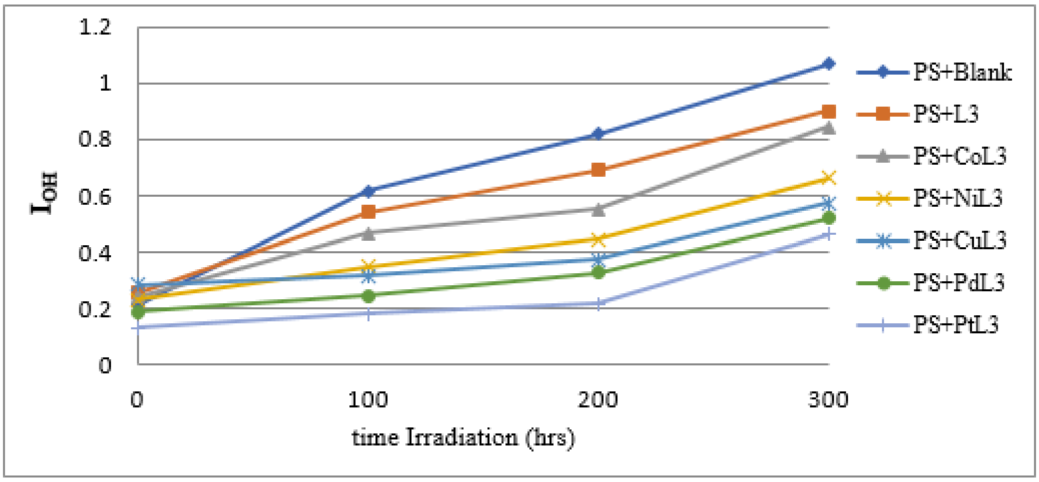


Figure 2: I_{OH} hydroxy index versus polystyrene film time irradiation (40 μm) (0.5 W / v) additional

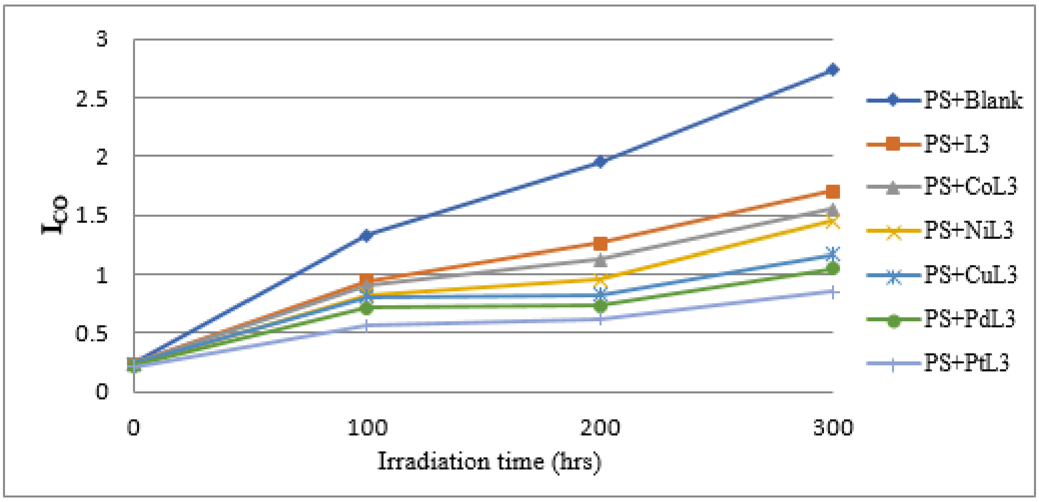


Figure 3: ICO carbonyl index versus polystyrene film (40 μm) time irradiation extra (0.5 w / v) additional

A. Limit the adequacy of the weight loss stabilization process.

Polystyrene film degradation, molecular weight reduction and volatilization (M.wt) from loss of weight Daten Figure (3)[27] display Pt(IV) with the highest efficiency of stability due to decreased weight losses in order:

PS > L_3 > CoL_3 > NiL_3 > CuL_3 > PdL_3 > PtL_3

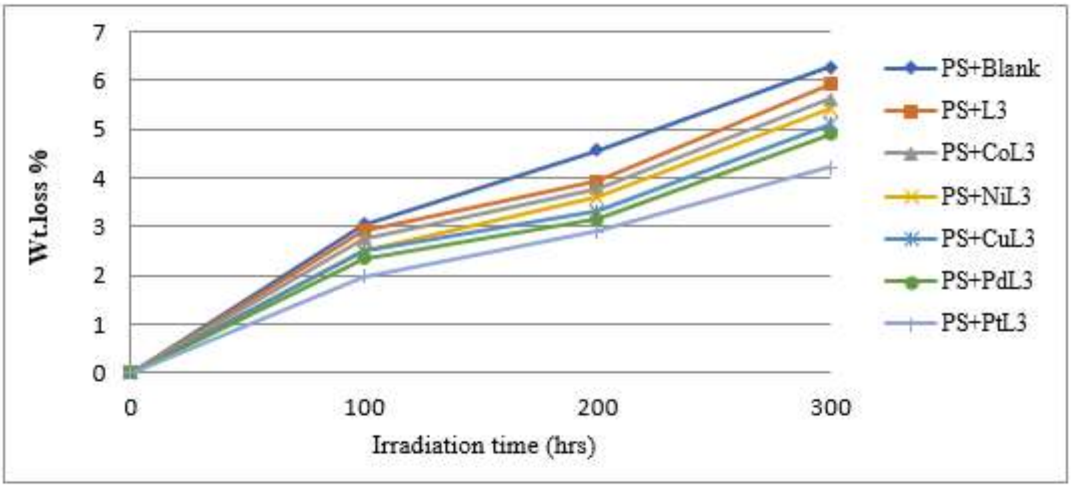


Figure 4: Additional thickness (0.5 w / v) loss of irradiation weight for PS films (40μm)

B. Molecular weight during photolysis variations of polystyrene films

Figure (4) indicates that polystyrene degradation contributed to a lower level of polystyrene and indicates a rapid initial decline in Mv due to a large chain break at a separate location in the polystyrene chain. Mv plot against exposure demonstrates additional time of film (0,5% w / v) irradiation [28][29]. The total number of chain scissors using S (Eq. 8) where

Mv,o = Average Mwut viscosity at experiment start.
Mv,t = Mwut average irradiation time viscosity.
$S = Mv,o / Mv,t - 1$ (8)

Table 2: Difference of (Mv) extra thickness (0,5 w / v) with time PS (40 µm) film irradiation

Compound	**Irradiation time (hrs.)**			
	0	**100**	**200**	**300**
PS+Blank	278439	233169	169218	93192
PS+L3	293861	244517	181139	102866
PS+CoL3	305422	263120	201389	133821
PS+NiL3	310791	278430	217160	137778
PS+CuL3	314933	281501	238710	144930
PS+PdL3	322575	290144	247114	168900
PS+PtL3	328116	299173	253319	178663

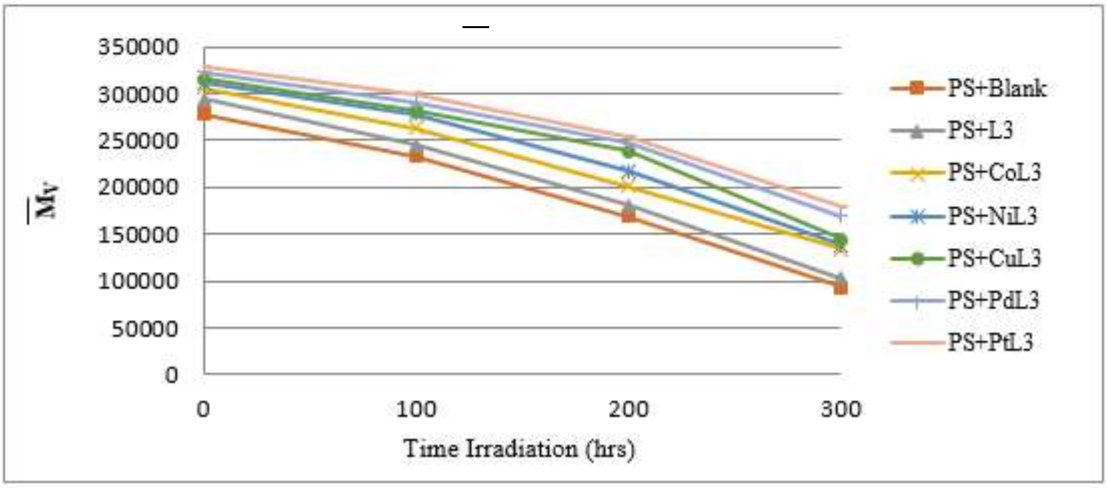


Figure 5: Average difference in viscosity Mwut Mv ~~with~~ an additional irradiated time of films PS (40µm) with the additional thickness (0.5w / v)

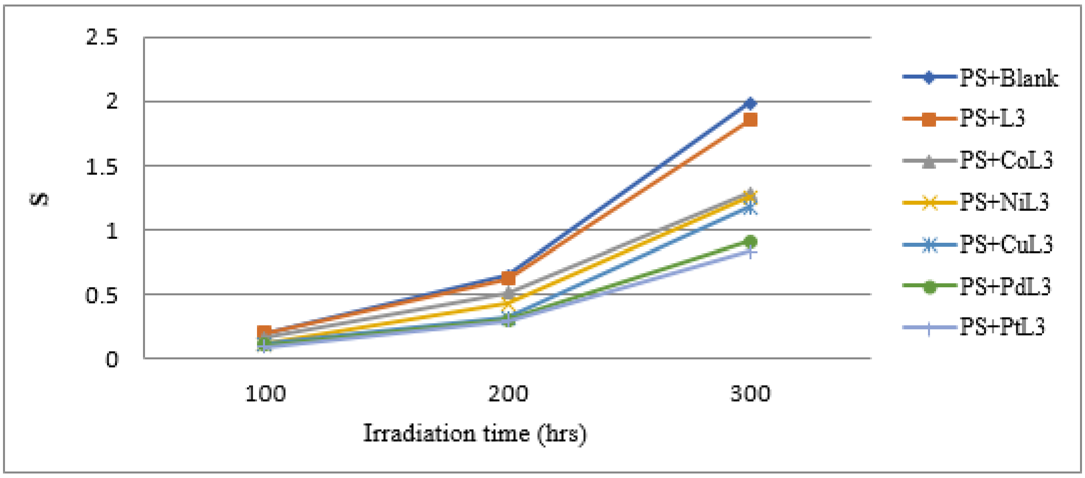


Figure 6: Difference between main split chain (S) and additional thickness (0.5 W / v) times PS film irradiation (40µm)

The level of branching indicates an increase from data since cross-link can calculate the level of retrogradation (α) via (Eq. 9) where

m = Primitive molecular weight

$\alpha = m \times S / Mv$ (9)

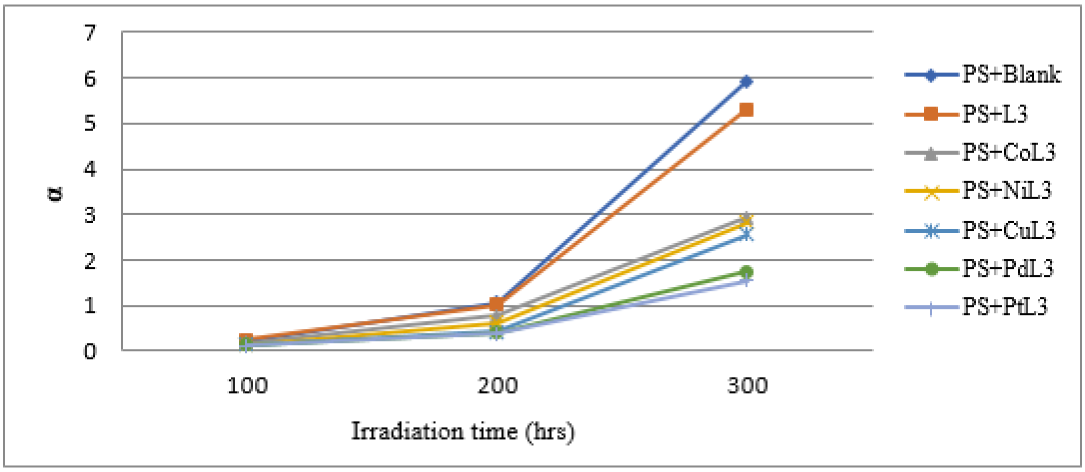


Figure 7: Value (α) disparity for the time radiation of P.S (40μm) film (0.5 w / v) additional thickness

The degree of retrogradation rate (α) versus the radiation time as shown in Figure (5) the primary phases in polystyrene image, α grade assembly period (DP) (30), the number of the polystyrene monomeric unity (Eq. 10), where the irradiation grade is shown; M_o = Monomer's molecular weight.

M_n = the molecular weight average number

$DP_n = X_n = M_n / M_o$ (10)

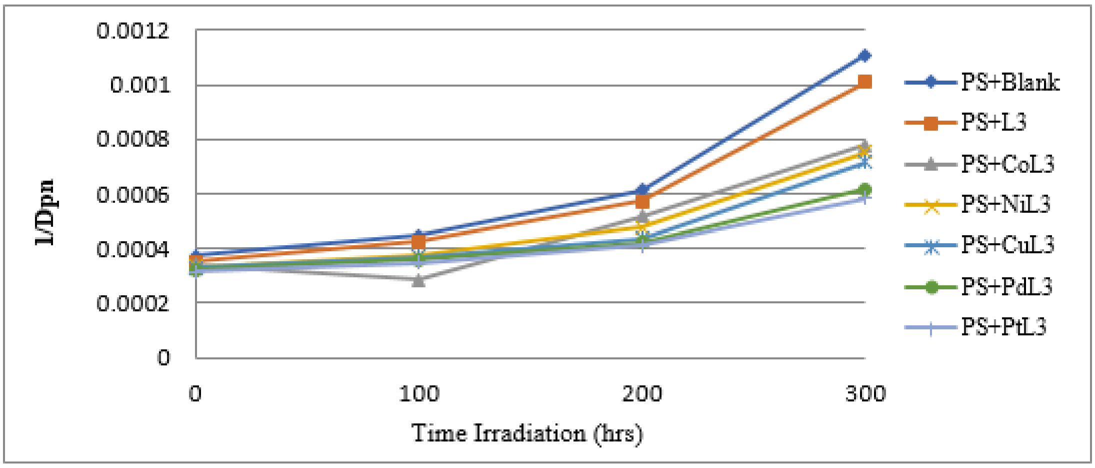
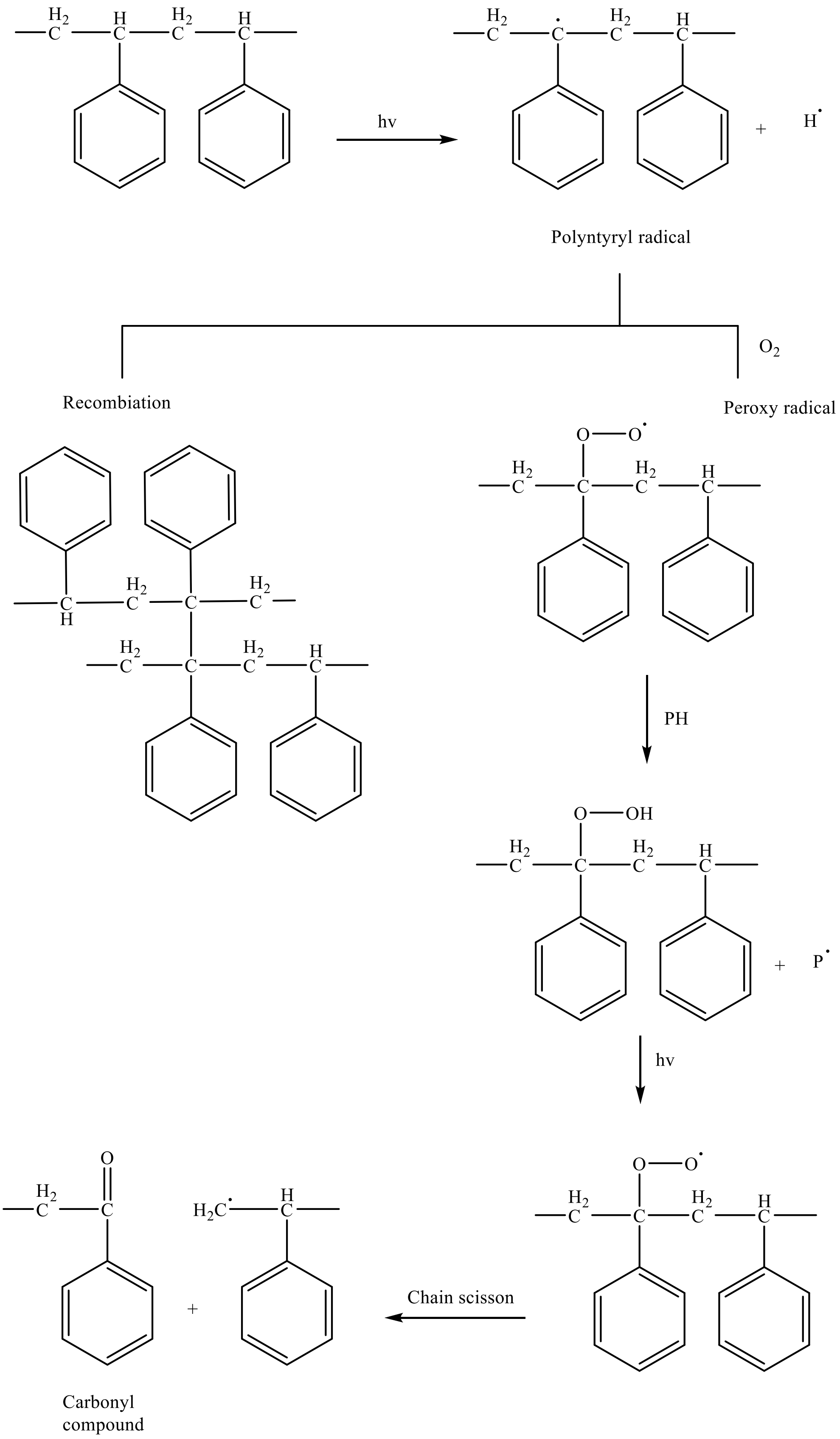


Figure 8: Distinction of 1 / DPn to the additional thickness of PS film irradiation time (40μm) (0.5 w / v)

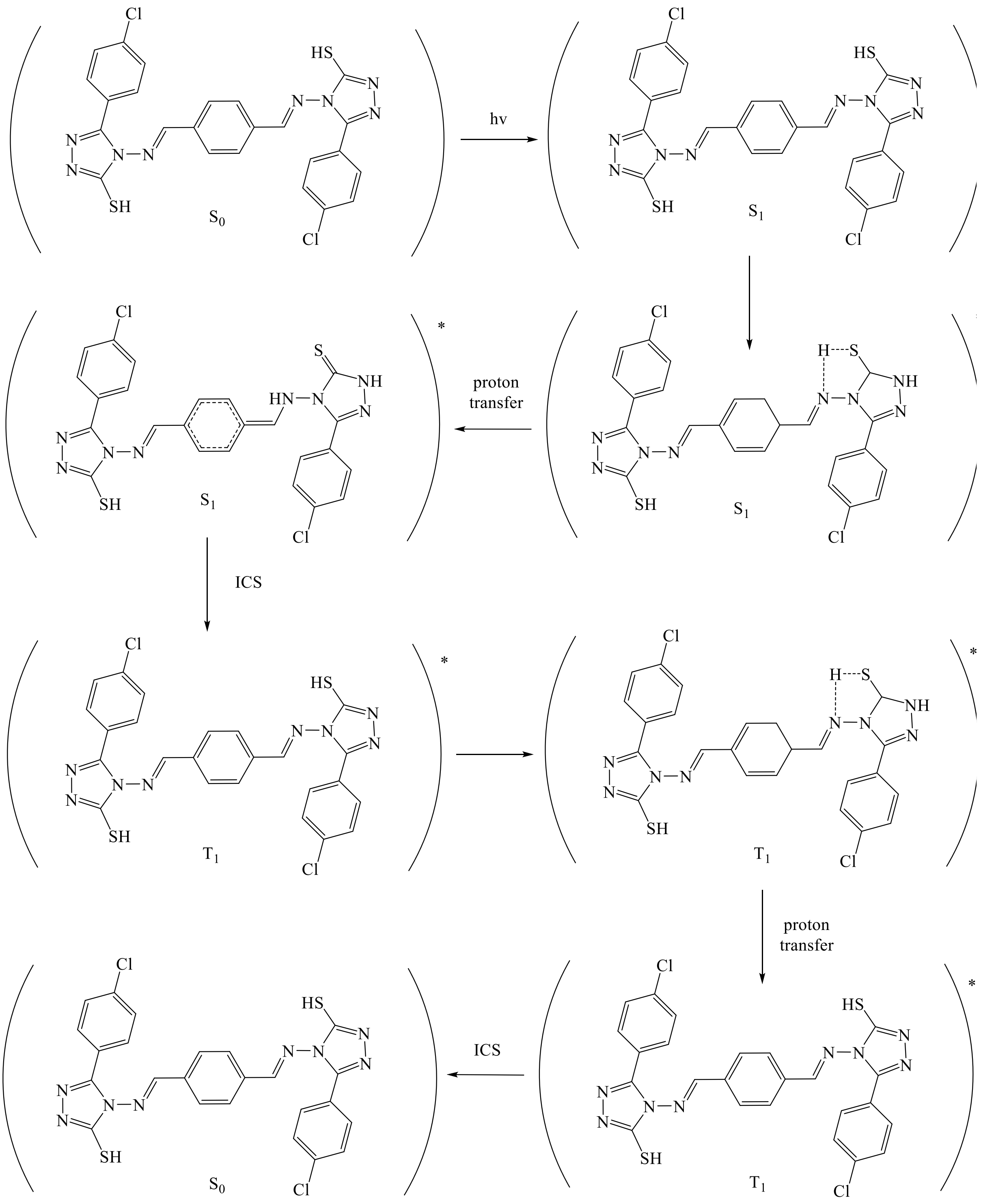
A reverse plot of polymerization (1 / DPn) against the irradiation time Figure (6) shows an increase in radiation time (1 / DPn)[31], compared with an added sample in front of blank.

C. Mechanisms suggested by which the Polystyrene PS additives are stabilized

The ultra-violet-light derivative complexes in 1,2,4-triazole-3-thion induce radical scavenging and peroxide degeneration in polystyrene photography stability, and the 1,2,4-triazole-3-thion ring is critical in photo-stabilization if ultraviolet light absorption exposures lead to an ultraviolet energy decrease in the aromatic ring. The conservation of transmission energy between chelates and chromophore excitations (POO•) (Schema 2, 3), may result in radical cavities in the complex of microphones. All this movement towards film stabilization by resonance[32]. All commercial polymers are necessary to break down the polymer (C-C) bond result from degradation, when exposed to ultraviolet light permanently. Energy transfer highly impotent in polymers is directly linked to effects of stabilization of the photograph and photodegradation which can occur through the following process I inter-molecular transfer energy among photo stabilizer (acceptor) molecules and an exciting polymer (donor) molecule. (ii) Intramolecular energy transfer this process occurs between the molecules of polymer (acceptor) and another thrilling chain (dono) chromophore.[33].



Scheme 2: Polystyrene photooxidation scheme.



Scheme 3: the mechanism of althrough absorption of the UV light and the dissipation of energy as heat for the photo station of Polystyrene.

CONCLUSIONS

The photo stabilization efficiency of these complexes and ligand following the order of:

$PtL_3 > PdL_3 > CuL_3 > NiL_3 > CoL_3 > L_3 > PS$

Resulting of decreasing in the rate molecular weight, weight loss, the hydroxyl and carbonyl groups indexes, obviously the addition substantiation very good long time constancy, and the complex containing platinum was more the devilishly efficacious photo stabilizer.

THE PURPOSE OF STUDYING THE APPLICATIONS

From this work were exposed polystyrene PS films additive of the ligand and their complexes to ultraviolet light for a different period's time to prove of the polymers increased lifetime or vice versa from through monitoring photodegradation of hydroxyl group (I_{OH}) and a carbonyl group (I_{CO}) in FT-IR spectrum, average molecular weight (Mv), weight loss (wt loss %), Polymerization degree (1 / DPn) and main chain scission.

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