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Photostabilization of polyvinyl chloride by some new thiadiazole derivatives

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ABSTRACT

(5-Amino-1,3,4-thiadiazole-2-yl)phenol and it derivatives have been synthesized and characterized by spectral methods lik (FT-IR, UV-Vis, and ^{1}H NMR) and elemental analysis beside the measurements of their physical properties. All the prepared compounds were used as photo stabilizer with polyvinyl chloride. The rate of photo degradation and photo stabilization for PVC films were monitored with irradiation time by measuring the carbonyl (Ico) index values. In addition, the effect of concentrations additives on the rate of photo degradation and photo stabilization process was also studied. We found that the rates were increased with increasing of additives concentrations. Besides, the effect of film thickness is studied and the results showed that the increasing of film thickness will decrease the rate of photo degradation as the following sequences: [5] > [2] > [1] > [3] > [4] > PVC. Degree of deterioration (α), average number of cuts per single polymer chain (s), were calculated for PVC films as a control and that which contains the additives. According to the experimental results obtained several mechanisms were suggested depending on the structure of the additive. Among then UV absorption and radical scavenger for photo stabilizer additive mechanisms were suggested.

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1. Introduction

The five-member heterocyclic compounds particularly nitrogen and sulphur heterocyclic: thiadiazole, contain the five membered unsaturated aromatic ring structure composed of two nitrogen atoms and one sulfur atom [1-4]. 1,3,4-Thiadiazole moiety in which sulfur is present at position 1, and two nitrogen atom at position 3 and 4 [5]. Thiadiazoles are an important class of heterocyclic compounds that has diverse applications in organic synthesis, technological, oxidation inhibitors, dyes, metal complexing agents, and corrosion inhibitors and biological applications [6-17].

Polyvinyl chloride is one of the four major commercial polymers used widely for both domestic and industrial purposes. It is a low cost-high volume synthetic polymer used in home construction, electrical insulation, and for various other purposes. In 2000, over one billion pounds of PVC were produced. The primary drawback of the polymer is its instability at temperatures above 60 °C and when exposed to ultraviolet radiation. As a result of degradation, PVC releases toxic hydrogen chloride gas, which is primarily responsible for the death in household fires. Destabilization causes substantial damage to the material and loss of its many useful physical and chemical properties. The purpose of stabilization, therefore, is to maintain the original characteristics of the polymer and to ensure its desired service life [18]. Polyvinyl chloride has very limited solubility. The most effective solvents are those which appear to be capable of some form of interaction with polymer. It has been suggested that PVC is a week proton donor and effective solvents are proton accepter [19]. Thus the PVC polymer is soluble at room temperature in oxygen-containing solvents such as ethers e.g. dioxane, tetrahydrofuran, ketones [20].

Plastics can be protected against thermal and photo-degradation by using efficient stabilizers designed to prohibit or slow down the degradation process in order to prolong the use life of the plastic [21-24]. The low cost and the good performance of polyvinyl chloride products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structure and siding. However, ultimate user acceptance of the PVC products for outdoor building applications will depend on their ability to resist photodegradation over long periods of sunlight exposure [25]. The photostabilizing effect on thiadiazole compounds in films of PVC had been studied [26].

The aim of the present work is to synthesis and study the activity of thiadiazole compounds [1-5] that might act as new types of photosensitizers for the photodegradation of poly(vinyl chloride). These thiadiazole compounds are 2-(5-amino-1, 3, 4-thiadiazol-2-yl)phenol (**1**), 2-(((5-(2-hydroxy phenyl)-1, 3, 4-thiadiazol-2-yl)amino)methyl)isoindoline-1, 3-dione (**2**), 2-[5-({[(4-nitrophenyl)amino]methyl}amino)-1,3,4-thiadiazol-2-yl]phenol (**3**), 2-[5-({[(2-nitrophenyl)amino] methyl}amino)-1,3,4-thiadiazol-2-yl]phenol (**4**) and 2-[5-({[(4-

hydroxyphenyl)amino]methyl}amino)-1, 3, 4-thiadiazol-2-yl] phenol (**5**). The effects of concentration of these additives, polymer film thickness on the photo degradation process are also to be investigated. It is also aimed in this work to compare the mechanism of action of these additives and their effects on the rate of photo degradation of these polymers under condition employed in this research work.

2. Experimental

2.1. Chemicals

All chemicals used were of reagent grade supplied by either Merck or Fluka and used as supplied. The FT-IR spectra in the range 4000-400 cm^{-1} (KBr) were recorded on FT-IR-84005 Shimadzu spectrophotometer. The UV-visible spectra were measured in ethanol using (Hitachi U-2000) Ultra-violet spectrophotometer in the range 200-800 nm. GallenKamp M.F.B600.010F melting point apparatus was used to measure the melting points of all the prepared compounds. Elemental microanalysis was carried out using CHNOS elemental analyzer model 5500 Carlo-Erba instruments. The ^{1}H NMR spectra were recorded on Bruker spectrometer model ultra-shield at 300 MHz in the University of Al-Al-Bayt, Amman, Jordan. All compounds were dissolved in DMSO-*d*$_6$ solution with TMS as internal standard.

2.2. Materials

2-(5-Amino-1, 3, 4-thiadiazol-2-yl)phenol (**1**), 2-(((5-(2-hydroxyphenyl)-1, 3, 4-thiadiazol-2-yl)amino)methyl) isoindoline-1, 3-dione (**2**), 2-[5-({[(4-nitrophenyl)amino]methyl}amino)-1, 3, 4-thiadiazol-2-yl]phenol (**3**), 2-[5-({[(2-nitrophenyl)amino]methyl}amino)-1,3,4-thiadiazol-2-yl]phenol (**4**) and 2-[5-({[(4-hydroxyphenyl)amino]methyl}amino)-1,3,4-thiadiazol-2-yl]phenol (**5**) were prepared by the method previously described by Mahendrasinh *et al.* [27].

2.3. Films preparation

A poly(vinyl chloride)[supplied from Petkim Company (Turkey)] solution (5 g/100 mL) in tetrahydrofuran (THF) was used to prepare different thickness of polymer films (Measured by digital micrometer type 2610A, Germany) with 0.1-0.5% (*w*:*w*) of the prepared compounds. The films were prepared by evaporation technique at room temperature for 24 h to remove the possible residual solvent (THF). Film samples were further dried at room temperature for 3 h under reduced pressure. The films were fixed on stand specially used for irradiation which is aluminum plate (0.6 mm) in thickness supplied Q-panel Company.

2.4. Irradiation technique

Accelerated weatherometer Q.U.V. tester (Philips Germany), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate which has two holes in the front side and another one behind each side which contains lamps type (Fluorescent Ultraviolet Lights) 40 watt each, the lamps are of the type (UV-B313) giving spectrum range between 290-360 nm and the maximum wavelength is 313 nm. The polymer film samples vertically fixed and parallel to the lamps assure the vertical incidence of UV radiation on the samples, the places of the irradiated samples are changed places from time to time to make sure that the intensity of light incident on all sample is equal.

2.5. Photodegradation measurements

The photodegradation of polymer film samples were followed using Shimadzu spectrophotometer model FT-84005. The absorption spectra of the film samples were recorded in the range of 4000-400 cm^{-1}. The carbonyl groups absorption is allocated at 1720 cm^{-1} [28]. The photodegradation during different irradiation times were followed through the variation in carbonyl absorption band. Then carbonyl index (Ico) was subsequently calculated by comparing the FT-IR absorption peaks at 1720 cm^{-1} with reference peak at 1428 cm^{-1}. This method is called band index method [29], which includes:

$$Is_{co} = \frac{As}{Ar} \tag{1}$$

As: Absorbance of peak under study, Ar: Absorbance of reference peak., Is_{co}: Index of the group under study.

The absorbance (A) at the specified wavenumber for carbonyl for PVC was calculated using the following relation shown in Equation (2).

$$A = 2 - \log T\ \% \tag{2}$$

Actual absorbance, the difference between the absorbance base line and top of the absorption peak is calculated using the base line method [30].

2.6. Determination of viscosity average molecular weight ($\bar{M}_v$)

The viscosity property was used to determine the molecular weight of polymer using Mark-Houwink relation (3) [31]:

$$[\eta] = K(\bar{M}_v)^{\alpha} \tag{3}$$

where: [η] = Intrinsic viscosity, K and α are constants depending on polymer, solvent and temperature (In this work, K = 1.38×10^{-4}, α = 0.77.

The intrinsic viscosity of polymer solution was measured with an Ostwald U-tube viscometer. Solution was made by dissolving the polymer in a solvent (g/100 mL) and the flow time of polymer solution (t) and pure solvent (t_o) were measured respectively.

The single-point measurements were converted to intrinsic viscosities by the relation (4) [31]:

$$[\eta] = \left(\sqrt{2}/C\right)(\eta_{sp} - \ln \eta_{re})^{1/2} \tag{4}$$

where [η] = Intrinsic viscosity, η_{sp} = Specific viscosity, η_{re} = Relative viscosity and C = Concentration of polymer solution in THF solvent (g/100 mL).

3. Results and discussion

The structure of all the newly synthesized 1,3,4-thiadiazole derivative were confirmed on the basis of their chemical structure using FT-IR, UV-Visible, ^{1}H NMR and CHN analysis. The chemical structures and spectra data FT-IR, UV-Visible, ^{1}H NMR and CHN analysis are given in Table 1 and 2.

In order to study the photo chemical activity of these additives for the photostabilization of PVC films, the carbonyl index were monitored with irradiation time using FT-IR spectrophotometry. The irradiation of PVC films using light of wave length λ = 313 nm led to new changes in their FT-IR spectrum. Appearance of bands at 1770 and 1720 cm^{-1}, respectively, are attributed to the formation of carbonyl groups. The first is related to chloroketon while the second one is assigned to aliphatic ketone, together with formation of a band at 1633 cm^{-1} related to polyene group [32].

The absorption of the carbonyl group are used to follow the extend of polymer degradation during irradiation, this absorption was calculated as carbonyl index (Ico). Accordingly, one could expect that the growth of carbonyl index is a measure for the extent of degradation.

Table 1. Physical properties of compounds **1**-**5**.

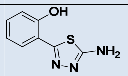
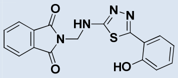
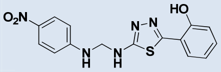
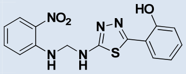
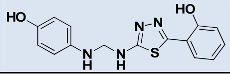
Compound	Structure	Molecular formula	Yield, %	M.p., °C (Lit)	Color	Recrystallization solvent	Elemental analysis		
							C%	H%	N%
							Calculated (Found)	Calculated (Found)	Calculated (Found)
1		$C_8H_7N_3OS$	68	136-137 (135)	Yellow	DMF	49.74 (48.83)	3.62 (3.64)	21.76 (19.87)
2		$C_{17}H_{12}N_4O_3S$	60	110-112 (112)	Pale yellow	DMF	56.95 (55.22)	3.40 (4.01)	15.90 (13.98)
3		$C_{15}H_{13}N_5O_3S$	65	117-118 (116)	Brown	DMF	52.47 (51.79)	3.79 (4.22)	20.40 (18.75)
4		$C_{15}H_{13}N_5O_3S$	59	122-190 (120)	Yellow	DMF	52.47 (51.79)	3.79 (4.22)	20.40 (18.75)
5		$C_{15}H_{14}N_4O_2S$	50	137-139 (137)	Yellow	DMF	57.32 (56.89)	4.45 (5.03)	17.83 (1.69)

Table 2. Characterization of FT-IR, ^{1}H NMR and UV absorption bands of compounds **1**-**5**.

Compound	IR, cm^{-1}							λ_{max}, nm	^{1}H NMR
	ν_{N-H}	ν_{Ar-CH}	γ_{O-H}	ν_{C-S}	$\nu_{C=N}$	$\nu_{C=C}$	ν_{others}		
1	3391, 3220	3090	3458	1070	1620	1600	-	267, 296, 350	-
2	3290	3070	3460	1078	1640	1599	$\nu_{C=0}$(1735), $\nu_{C-H\ aliph.}$ (2945, 2860)	266, 378, 389, 401	7.4-8.7 (m, 8H, Ar-CH), 5.1 (s, 1H, NH), 5.9 (s, 2H, CH_2)
3	3280	3060	3470	1080	1639	1610	ν_{NO2}(1533, 1360), $\gamma_{(=C-H)}$ (840), $\nu_{C-H\ aliph}$ (2958, 2869)	212, 255, 343	7.2-8.7 (m, 8H, Ar-CH), 5.8 (s, 1H, NH), 5.3 (s, 2H, CH_2), 10.3 (s, 1H, OH)
4	3293	3091	3421	1087	1640	1593	ν_{NO2}(1533, 1333), $\gamma_{(=C-H)}$ 753, $\nu_{C-H\ aliph.}$ (2929, 2891)	243, 287, 337	-
5	3310	3100	3489	1088	1935	1610	$\gamma_{(=C-H)}$ 840, $\nu_{C-H\ aliph.}$ (2935 , 2850)	255, 285, 362	6.2-8.5 (m, 8H, Ar-CH), 5.8 (s, 1H, NH), 4.8 (s, 2H, CH_2), 10.6 (s, 1H, OH)

As shown in Figure 1 the presence of compounds **1**-**5** show lower growth rate for carbonyl indices with irradiation time for PVC film without additives (Control).

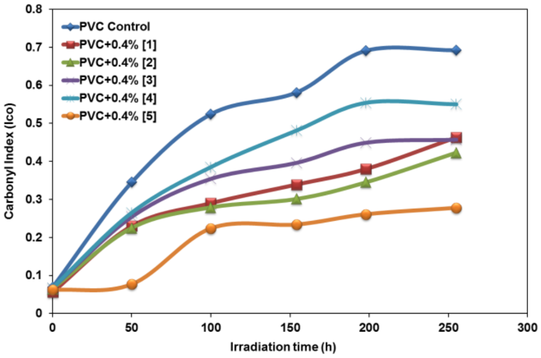


Figure 1. The variation in the carbonyl index (Ico) with irradiation time for PVC film (35 μm) in thickness containing (0.4% wt) of additives **1**-**5**.

As observed from the results obtained in Figure 1 that the growth rate of carbonyl indices with irradiation time is lower in the presence of additives **1**-**5** with respect to the poly(vinyl chloride) without additives (control). So, these additives in their FT-IR spectral behavior might all be considered as photostabilizers. The relative photostability of additives incorporated with PVC is increased in the order: [5] > [2] > [1] > [3] > [4] > PVC.

The calculated values of carbonyl indices for different concentration 0.1-0.5% (*w*:*w*) for different concentration of additive **5** are shown in Figure 2.

The calculated values of carbonyl indices for different concentration 0.1-0.5% (*w*:*w*) of additive **5** are shown in Figure 3.

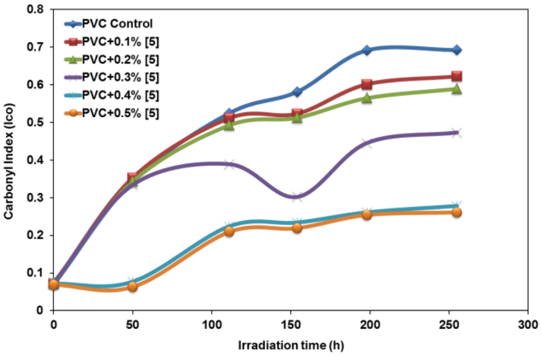


Figure 2. Change in carbonyl index with irradiation time for PVC film (35 μm in thickness containing different concentrations of compound **5**.

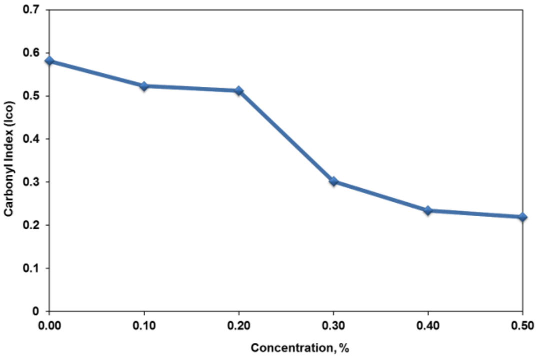


Figure 3. Changes in carbonyl index (Ico) with irradiation time (154 h) for PVC films (35 μm) thickness containing different concentrations of additive **5**.

Results of Figure 2 and 3 show that the carbonyl indices decrease with increasing concentration of additives in films. The photooxidation of 1000 µm and ~80 µm thickness of unstabilized PVC was reported in literature [33] as well as other studies [34,35] concerning influence of films thickness in the presence of additives.

Figure 4 reveals the relationship between the carbonyl index and film thickness, which indicates the decrease of photodegradation with increasing of thickness of the film.

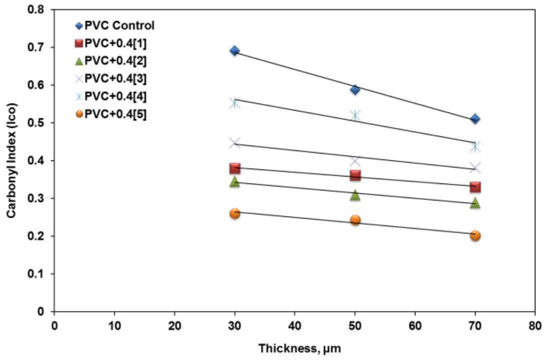


Figure 4. The relationship between the carbonyl indices with different thicknesses at 198 h irradiation time PVC films containing 0.4% of additives.

3.1. Molecular weight changes during photolysis

In the present work, the application of Equations (4) and (5) in degradation of PVC films was examined. The degradation was followed by the determination of the change in molecular weight by measuring the intrinsic viscosity, Table 1.

Viscosity measurement for PVC films (control) (50 µm thick.) and with 0.4% of additives **1**-**5** were carried out before and after irradiation time, in tetrahydrofuran solvent at 40 °C.

It is worth to mention that traces of the films with additives are not soluble in THF of irradiation indicating that cross-linking or branching in the PVC chain dose occur during photolysis course [36].

The plots in Figure 5 indicate a rapid decrease in ($\overline{M_v}$) initially, then shows down, suggesting that the initial rapid drop in ($\overline{M_v}$) is due to the main chain scission at various location that is distributed along the polymer chain and the photodegradlation becomes slower.

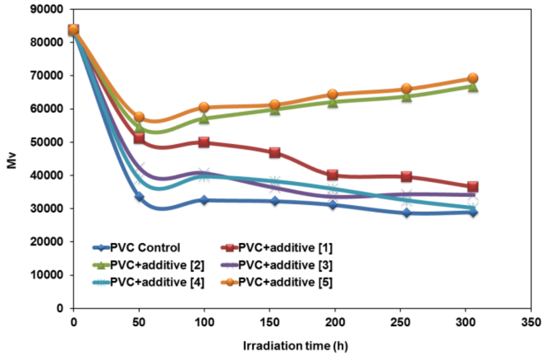


Figure 5. Changes in the viscosity-average molecular weight during irradiation of PVC films (50 µm) (control) and with 0.4 wt.% of additives.

For better support of this view, the number of average chain scissions (average number cut per single chain) (S) was calculated using relation (5):

$$S = \bar{M}v,0 / \bar{M}v,t \quad (5)$$

where $\bar{M}v,0$ and $\bar{M}v,t$ are viscosity average molecular weight at initial (0) and t radiation times, respectively. The plot of S *vs* time is shown in Figure 6.

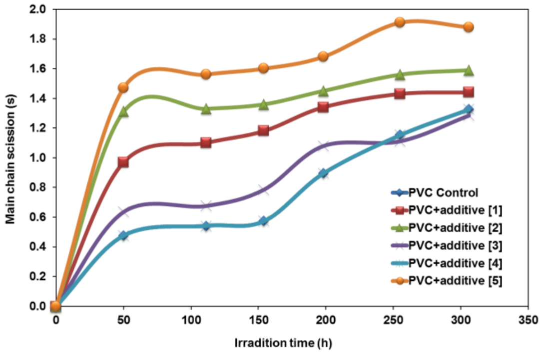


Figure 6. Changes the average number cut per single chain (s) during irradiation of PVC films (50 µm) (control) and with 0.4 wt.% of additives.

The curve indicates an increase in the degree of branching such as that might arise from crosslinking occurrence. It is observed that an insoluble material was formed during irradiation which provided additional evidence to the idea that cross-linking does occur.

For randomly distributed weak bond links, which break rapidly in the initial stages of photodegradation, the degree of deterioration α is given as:

$$\alpha = m/\overline{Mv} \quad (6)$$

where m is the initial molecular weight. The plot of a as a function of irradiation time is shown in Figure 7. The values of the irradiated samples are higher when additives are absent and lower in the presence of additives compared to the corresponding values of the additive free PVC. In the initial stages of photodegradation of PVC, the value of α increases rapidly with time, these indicators indicate a random breaking of bonds in the polymer chain.

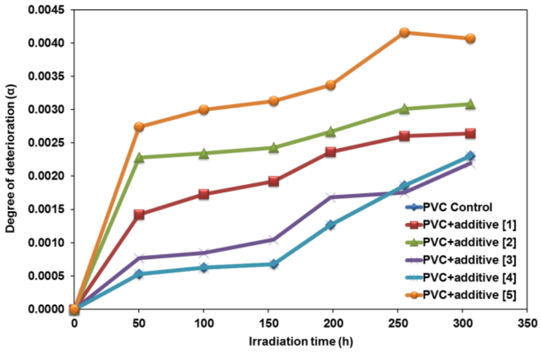
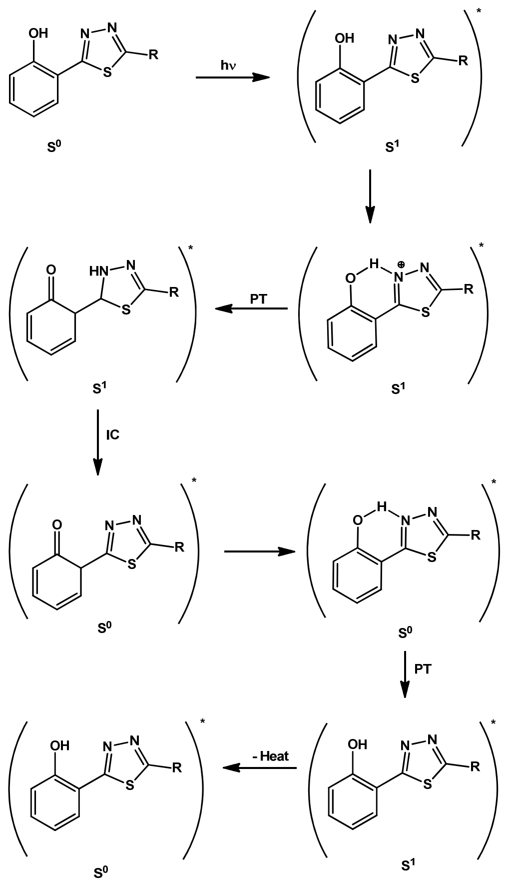


Figure 7. Changes in degree of deterioration (α) during irradiation of PVC films (50 µm) (control) and with 0.4 wt.% of additives.

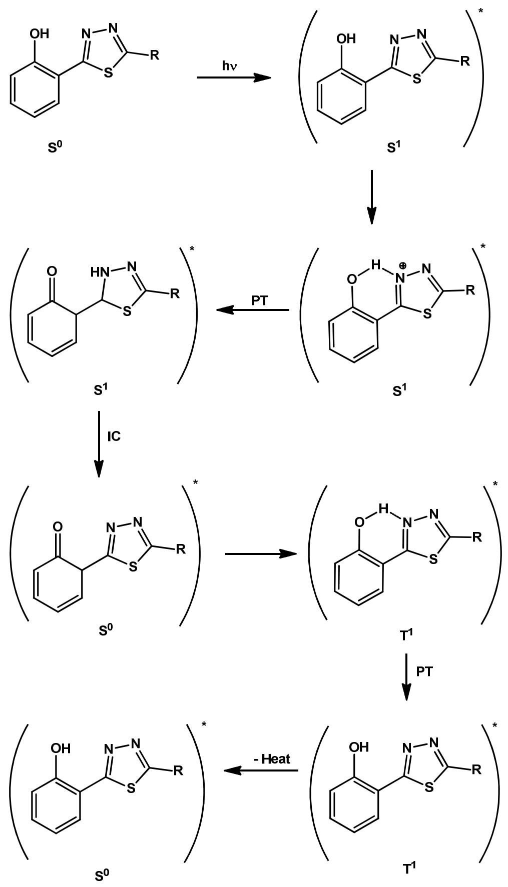
3.2. Suggested mechanisms of photostabilization of PVC by 2-(5-amino-1,3,4-thiadiazol-2-yl) phenol

Through the overall results obtained, the efficiency of thiadiazole derived as photostabilizers for PVC films can be arranged according to the change in the carbonyl concentration as a reference for the comparison as shown in Figure 1-5: [5] > [2] > [1] > [3] > [4] > PVC.

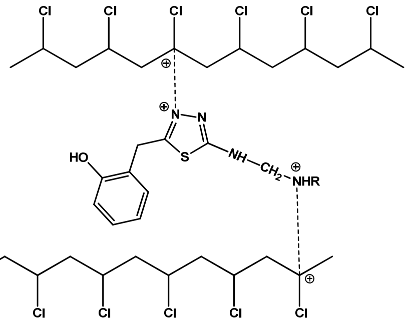
These additive stabilizes PVC by different mechanisms, such as UV absorber, screener or by radical scavenger. These stabilizers provide very good long-term stability and are usually referred to these mechanisms.



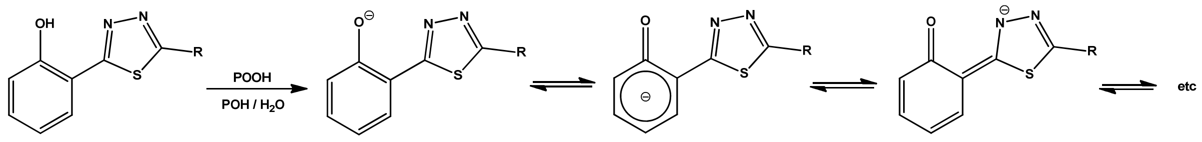
Scheme 1



Scheme 2



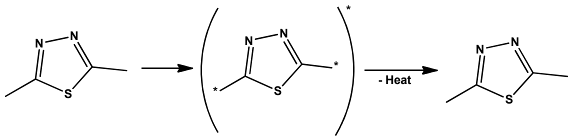
Scheme 3



Scheme 4

The most probable mechanism involved in a photo-stabilization is the energy change of absorbed photon to the intermolecular proton transfer. This reaction may occur by two proposed cycles Scheme 1 and 2, the first passes by inter system crossing (ICS) process to the excited triplet state, while the second is referred to internal conversion (IC) process to the ground state.

The rings of 1,3,4-thiadiazole or 1,2,4-triazole play a role in the mechanism of the stabilizer process by acting as UV absorber. The UV light absorption by this modified polymers containing 1,3,4-thiadiazole and triazole dissipates the UV energy to harmless heat energy Scheme 5.



Scheme 5

4. Conclusions

The present paper describes the photostabilization of PVC films using additives of 1,3,4-thiadiazole compounds. These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl index for PVC films.

[5] > [2] > [1] > [3] > [4] > PVC (6)

These additives stabilize the P VC films through UV absorption or screening, and radical scavenger mechanisms.

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