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## ORIGINAL ARTICLE

# New stabilizers for polystyrene based on 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds

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**Abstract** The photostabilization of polystyrene (PS) films by 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds was investigated. The PS films containing concentration of complexes 0.5% by weight were produced by the casting method from chloroform solvent. The photostabilization activities of these compounds were determined by monitoring the carbonyl and hydroxyl indices with irradiation time. The changes in viscosity average molecular weight of PS with irradiation time were also tracked (using benzene as a solvent). The quantum yield of the chain scission ( $\Phi_{cs}$ ) of these complexes in PS films was evaluated and found to range between  $3.31 \times 10^{-6}$  and  $7.89 \times 10^{-6}$ . Results obtained showed that the rate of photostabilization of PS in the presence of the additive follows the trend:

SN > SC > SB > SI > SP

According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among UV absorption, peroxide decomposer and radical scavenger for photostabilizer additives mechanisms were suggested.

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## 1. Introduction

Polystyrene is one of the important commercial polymers, widely used in various industrial fields. One of the important uses of PS is in the manufacture of cover signals lamp of some automobiles. PS is subjected to the irradiation of sunlight on outdoor exposure (Safy and El-Laithy, 1994). Many polymers undergo thermal oxidative degradation during processing. Over longer periods at ambient temperature polymers also deteriorate in the solid state through autooxidation and photooxidation. In outdoor applications where the materials are exposed to UV solar radiation, the energy of this radiation is

sufficient to initiate photochemical reaction leading to degradation. Plastics are commonly protected against such deterioration by the addition of antioxidants, light and heat stabilizers (Yousif et al., 2010).

There is a great interest at present in the photo-oxidative degradation of polymeric materials because macromolecules have increasingly widespread commercial applications. Polymeric synthetic, semisynthetic and natural are when exposed to the environment (Grassie and Scott, 1985). All commercial organic polymers degrade in air when exposed to sunlight as the energy of sunlight is sufficient to cause the breakdown of polymeric C–C bonds as a consequence of degradation. The resulting smaller fragments do not contribute effectively to the mechanical properties and the polymeric article because brittle. Thus the life of thermoplastics for outdoor applications becomes limited due to weathering (Andrady et al., 1998).

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 the 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. 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, d and e are the most effective.

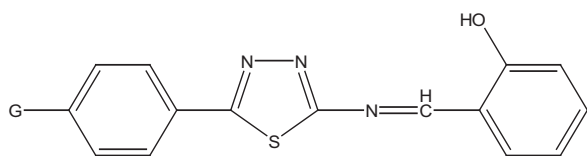
To our knowledge there is no attempt to investigate the photostabilization of PS films by Schiff bases compounds containing 1,3,4-thiadiazole rings, therefore, in this paper we report the designing of some Schiff bases and studied their use as a photostabilizing reagent.

## 2. Materials and methods

### 2.1. Materials

The following 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were all prepared by the method previously described by Salimon et al. (2010):

|  |    |
|--|----|
| 2N-Salicylidene-5-( <i>P</i> -nitro-phenyl)-1,3,4-thiadiazole  | SN |
| 2N-Salicylidene-5-( <i>P</i> -chloro-phenyl)-1,3,4-thiadiazole | SC |
| 2N-Salicylidene-5-( <i>P</i> -bromo phenyl)-1,3,4-thiadiazole  | SB |
| 2N-Salicylidene-5-( <i>P</i> -iodo-phenyl)-1,3,4-thiadiazole   | SI |
| 2N-Salicylidene-5-(phenyl)-1,3,4-thiadiazole                   | SP |



where G = –NO<sub>2</sub>, –Cl, –Br, –I or –H.

### 2.2. Experimental techniques

#### 2.2.1. Films preparation

Commercial polystyrene supplied by Petkim Company (Turkey) was re-precipitated from chloroform solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of polystyrene solution (5 g/100 ml) in chloroform were used to prepare polymer films with 40 μm thickness (measured by a micrometer type 2610 A, Germany). The films were prepared by the evaporation technique at room temperature for 24 h (Sastre et al., 1990). To remove the possible residual chloroform solvent, film samples were further dried at room temperature for 3 h under reduced pressure. The films were fixed on stands specially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

#### 2.2.2. Irradiation experiments

**2.2.2.1. Accelerated testing technique.** Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of PS films. The accelerated weathering tester contains a stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 W each. These lamps are of the type UV-B 313 giving spectrum range between 290 and 360 nm with a maximum wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular to the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same.

#### 2.2.3. Photodegradation measuring methods

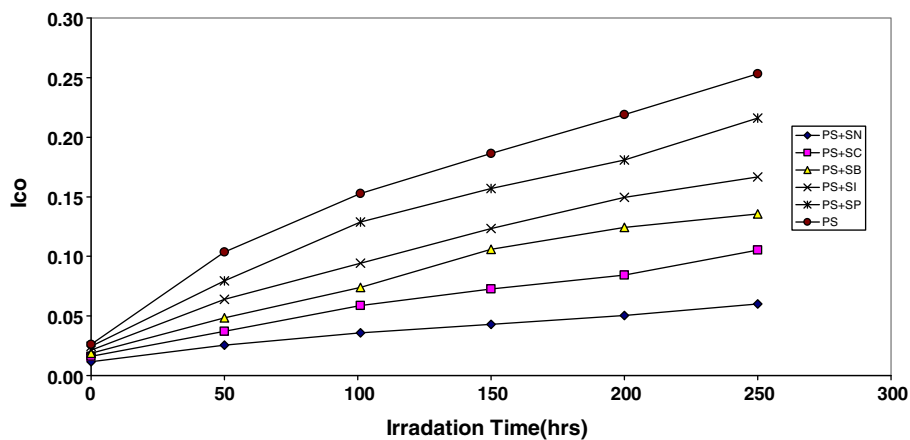
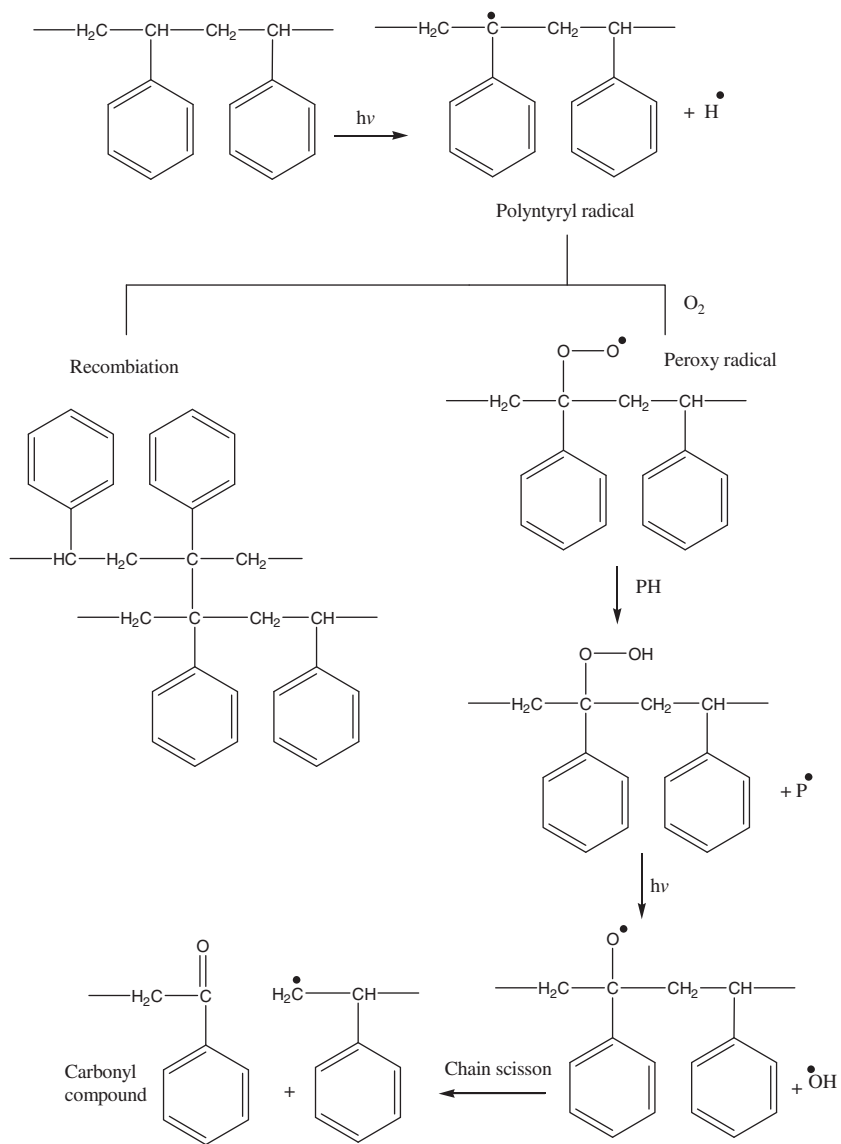
**2.2.3.1. Measuring the photodegradation rate of polymer films using infrared spectrophotometry.** The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000–400 cm<sup>-1</sup> using a FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified at 1720 cm<sup>-1</sup> and the hydroxyl group at 3450 cm<sup>-1</sup> (Rabek and Ranby, 1975). The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl and hydroxyl peaks. Then carbonyl and hydroxyl indices were calculated by comparison of the FTIR absorption peak at 1720 and 3450 cm<sup>-1</sup> with the reference peak at 1450 cm<sup>-1</sup>, respectively. This method is called the band index method which includes (Rabek and Ranby, 1975):

$$I_s = \frac{A_s}{A_r} \quad (1)$$

where  $A_s$  is the absorbance of peak under study,  $A_r$  the absorbance of reference peak and  $I_s$  is the index of group under study.

Actual absorbance, the difference between the absorbance of top peak and base line ( $A_{\text{Top Peak}} - A_{\text{Base Line}}$ ) is calculated using the Base Line method (Rabek and Ranby, 1975).

**2.2.3.2. Determination of average molecular weight ( $\bar{M}_v$ ) using viscometry method.** The viscosity property was used to deter-



**Figure 1** The relationship between the carbonyl index and irradiation time for PS films (40  $\mu\text{m}$  thickness) containing different additives. Concentration of additives is fixed at 0.5% by weight.

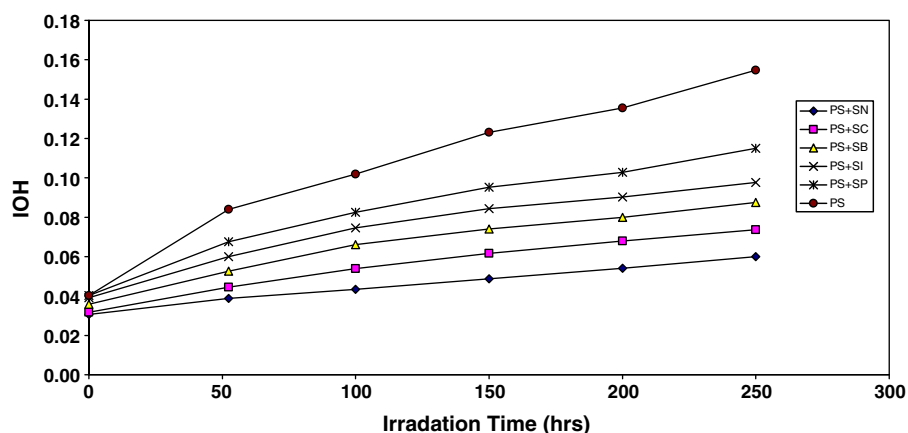
mine the average molecular weight of polymer, using the Mark–Houwink relation (Mark, 2007);  $[\eta]$  is the intrinsic viscosity,  $K$  and  $\alpha$  are constants that depend upon the polymer–solvent system at a particular temperature:

$$[\eta] = K\bar{M}_v^\alpha \quad (2)$$

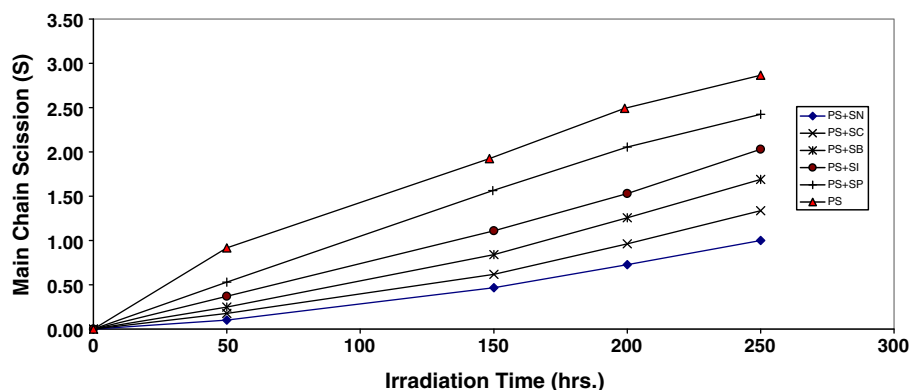
The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (g/100 ml) and the flow times of polymer solution and pure solvent are  $t$  and  $t_0$ , respectively. Specific viscosity ( $\eta_{sp}$ ) was calculated as follows:

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

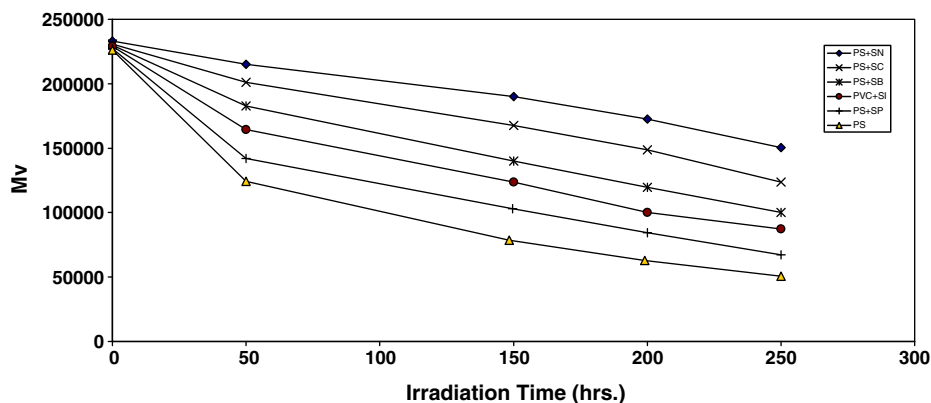
where  $\eta_{re}$  is the relative viscosity.



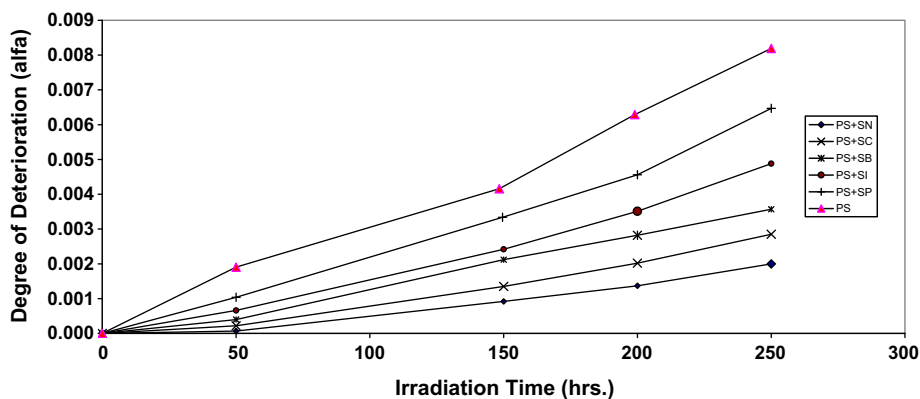
**Figure 2** The relationship between the hydroxyl index and irradiation time for PS films (40  $\mu\text{m}$  thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.



**Figure 3** Changes in the viscosity-average molecular weight ( $\bar{M}_v$ ) during irradiation of PS films (40  $\mu\text{m}$ ) (blank) and with 0.5 wt% of additives.



**Figure 4** Changes in the main chain scission ( $S$ ) during irradiation of PS films (40  $\mu\text{m}$ ) (blank) and with 0.5 wt% of additives.



**Figure 5** Changes in the degree of deterioration ( $\alpha$ ) during irradiation of PS films (40  $\mu\text{m}$ ) (blank) and with 0.5 wt% of additives.

**Table 1** Quantum yield ( $\Phi_{cs}$ ) for the chain scission for PS films (40  $\mu\text{m}$ ) thickness with and without 0.5 (wt/wt) additive after 250 h irradiation time.

| Additive 0.5% (wt/wt) | Quantum yield of main chain scission ( $\Phi_{cs}$ ) |
|-----------------------|--|
| PS + SP               | 3.31E-06   |
| PS + SI               | 4.20E-06   |
| PS + SB               | 5.78E-06   |
| PS + SC               | 6.25E-06   |
| PS + SN               | 7.89E-06   |
| PS (blank)            | 9.67E-05   |

The single-point measurements were converted to intrinsic viscosities by the relation (2):

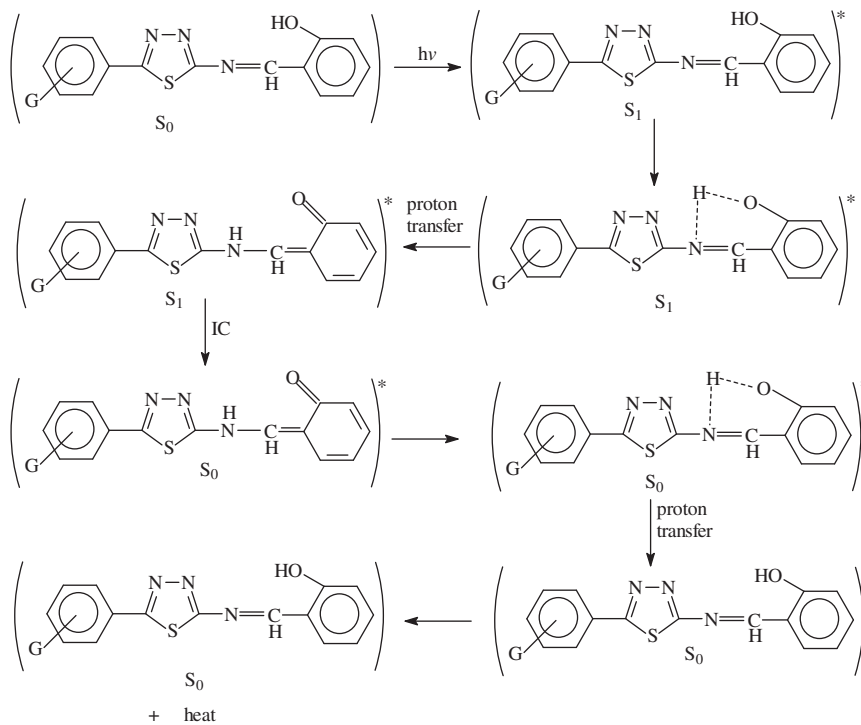
$$[\eta] = \left( \sqrt{2}/C \right) (\eta_{sp} - \ln \eta_{re})^{1/2} \quad (4)$$

where  $C$  is the concentration of polymer solution (g/100 ml).

By applying Eq. (4), the molecular weight of degraded and undergraded polymer can be calculated. Molecular weights of PS with and without additives were calculated from intrinsic viscosities measured in benzene solution using the following equation:

$$[\eta] = 4.17 \times 10^{-4} Mv^{0.6} \quad (5)$$

The quantum yield of main chain scission ( $\Phi_{cs}$ ) (Nakajima et al., 1990) was calculated from the viscosity measurement using the following relation:



**Scheme 2** The suggested mechanism of photostabilization of PS by SE, SN, SE and SP compounds through absorption of UV light and dissipation light energy as heat.

$$\Phi_{cs} = (CA/\overline{M}_{v,0}) \left[ ([\eta_0]/[\eta])^{1/\alpha} - 1 \right] / I_0 t \quad (6)$$

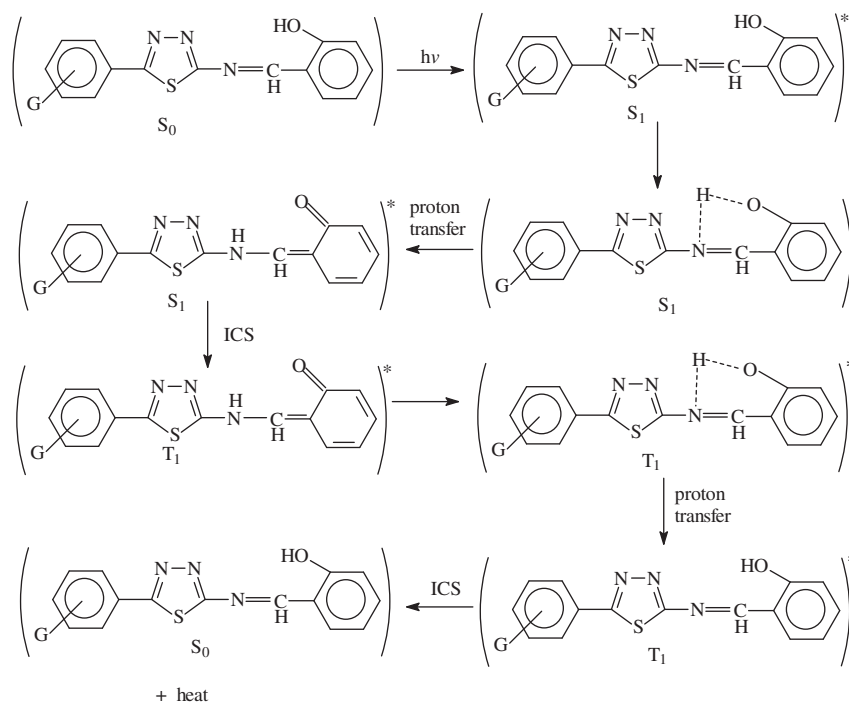
where  $C$  is the concentration,  $A$  the Avogadro's number,  $(\overline{M}_{v,0})$  the initial viscosity-average molecular weight,  $[\eta_0]$  the intrinsic viscosity of PS before irradiation,  $I_0$  the incident intensity and  $t$  is the irradiation time in second.

### 3. Results and discussion

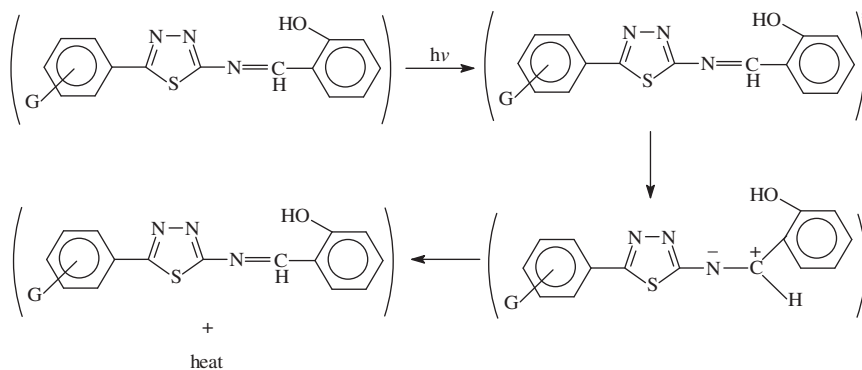
The 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were used as additives for the photostabilization of PS films. In order to study the photochemical activity of these additives for the photostabilization of PS films, the carbonyl and hydroxyl indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PS films with

UV light of wavelength,  $\lambda = 313 \text{ nm}$  led to a clear change in the FTIR spectrum. Appearance of a band at  $1720 \text{ cm}^{-1}$  was attributed to the formation of carbonyl groups. The hydroxyl band appeared at  $3450 \text{ cm}^{-1}$  was annotated to the hydroxyl group (Andrady and Searle, 1989). The absorption of the carbonyl and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index ( $I_{co}$ ) and hydroxyl index ( $I_{OH}$ ). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. A probable mechanism illustrating the experimental finding can be represented as follows (Safy and El-Laithy, 1994) (Scheme 1).

However, in Fig. 1, the  $I_{co}$  of SP, SI, SB, SC and SN showed lower growth rate with irradiation time with respect to the PS control film without additives. Since the growth of



**Scheme 3** The suggested mechanism of photostabilization of PS by SE, SN, SE and SP compounds through absorption of UV light and dissipation light energy as heat.



**Scheme 4** The suggested mechanism of photostabilization of PS by SE, SN, SE and SP compounds through absorption of UV light and dissipation light energy as heat.

carbonyl index with irradiation time is lower than PS control, as seen in Fig. 1, it is suitable to conclude that these additives might be considered as photostabilizers of PS polymer. Efficient photostabilizer shows a longer induction period. Therefore, the SN considered as the most active photostabilizer, followed by SP, SI, SB, SC and SN which is the least active. Just like carbonyl, hydroxyl compounds are also produced during photodegradation of PS. Scheme 1 explain the carbonyl and hydroxyl groups result from the photodegradation of PS in the presence of oxygen. Therefore, hydroxyl index could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Fig. 2.

### 3.1. Variation of PVC molecular weight during photolysis in the presence of 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole

Analysis of the relative changes in viscosity average molecular weight ( $\bar{M}_v$ ), has been shown to provide a versatile test for random chain scission. Fig. 3 shows the plot of  $\bar{M}_v$  versus irradiation time for PS film with and without 0.5% (wt/wt) of the selected additives, with absorbed light intensity of  $1.052 \times 10^{-8}$  ein.  $\text{dm}^{-3} \text{s}^{-1}$ .  $\bar{M}_v$  is measured using Eq. (3) with benzene as a solvent at 25 °C.

It is worth mentioning that traces of the films with additives are not soluble in chloroform indicating that cross-linking or branching in the PS chain does occur during the course of photolysis (Mori et al., 1977). For better support of this view, the number of average chain scission (average number cut per single chain) ( $S$ ) (Shyichuk and White, 2000) was calculated using the following equation:

$$S = \frac{\bar{M}_{v,0}}{\bar{M}_{v,t}} - 1 \quad (7)$$

where  $\bar{M}_{v,0}$  and  $\bar{M}_{v,t}$  are viscosity average molecular weight at initial (o) and  $t$  irradiation time, respectively.

The plot of  $S$  versus time is shown in Fig. 4. The curve indicates an increase in the degree of branching such as that might arise from cross-linking occurrence. It is observed that insoluble material was formed during irradiation which provided an additional evidences 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  $\alpha$  is given as:

$$\alpha = \frac{m \cdot s}{\bar{M}_v} \quad (8)$$

where  $m$  is the initial molecular weight.

The plot of  $\alpha$  as a function of irradiation time is shown in Fig. 5.

The values of  $\alpha$  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 PS. In the initial stages of photodegradation of PS, the value of  $\alpha$  increases rapidly with time, these indicators indicate a random breaking of bonds in the polymer chain.

Another way of degradation reaction characterization is the measurement of the quantum yield of the chain scission ( $\Phi_{cs}$ ). The quantum yield for chain scission was calculated for PS films with and without 0.5% (wt/wt) of additive mentioned above using the relation (4). The  $\Phi_{cs}$  values for complexes are tabulated in Table 1.

The  $\Phi_{cs}$  values for PS films in the presence of additive are less than that of additive free PS (blank), which increases in the order:

SN, SC, SB, SI, SP and PS

### 3.2. Suggested mechanisms of photostabilization of PVC by 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole

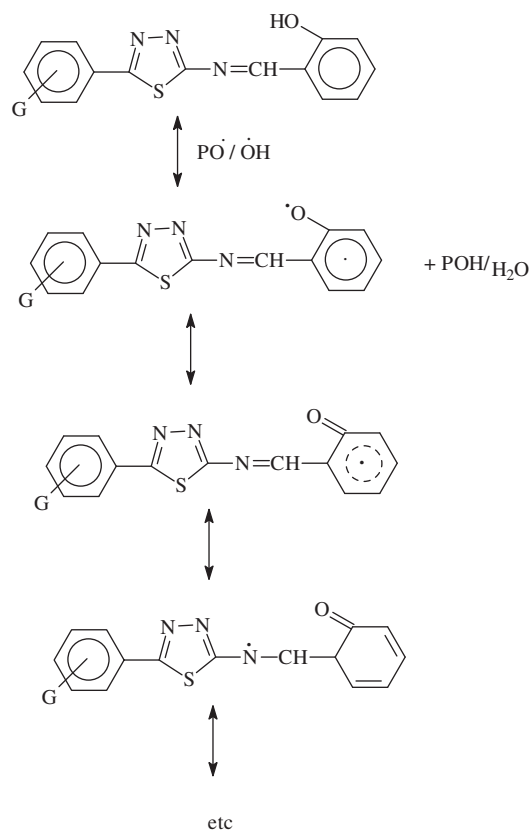
Through the overall results obtained, the efficiency of metal thiadiazole derived Schiff base complexes as photostabilizers for PVC films can be arranged according to the change in the carbonyl and polyene concentration as a reference for the comparison as shown in Figs. 1–5:

SN > SC > SB > SI > SP

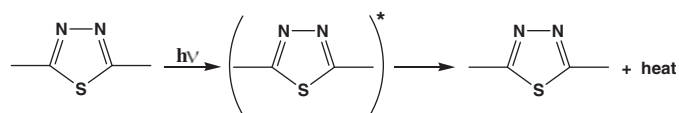
Schiff base stabilizes PS by different mechanisms, such as UV absorber, screener or by radical scavenger. These stabilizers provide very good long-term stability and are usually referred to these mechanisms.

The most probable mechanism involved in a photostabilization is the change energy of absorbed photon to the intermolecular proton transfer. This reaction may occur by two proposed cycles Schemes 2 and 3, the first passes by intersystem crossing (ICS) process to the excited triplet state, while the second is referred to internal conversion (IC) process to the ground state (Yousif et al., 2007, 2009).

Other mechanism explains the use of this compound as photostabilizer is by charge separated species which could be



**Scheme 5** The suggested mechanism of photostabilization of PS by SE, SN, SE and SP compounds as radical scavenger.



**Scheme 6** Suggested mechanism of photostabilization of 1,3,4-thiadiazole as UV absorber.

form of the excited state such a structure would allow dissipation of energy through rotation on increased vibration about the central bond as shown in [Scheme 4](#).

The hydroxyl group of the additive might act as a radical scavenger for the photostabilization process. Therefore, this Schiff bases, besides acting as UV absorber they may also act as radical scavenger additives ([Rasheed et al., 2009](#)) ([Scheme 5](#)).

The rings of 1,3,4-thiadiazole play a role in the mechanism of the stabilizer process by acting as UV absorber ([Yousif et al., 2007, 2009](#)). The UV light absorption by these additives containing 1,3,4-thiadiazole dissipates the UV energy to harmless heat energy ([Scheme 6](#)).

These additives stabilize the PS films through UV absorption or screening, peroxide decomposer and radical scavenger mechanisms. The 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were found to be the most efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using SN complexes as commercial stabilizers for PS.

#### 4. Conclusions

In the work described in this paper, the photostabilization of PS films using 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds were studied. These additives behave successfully as photostabilizers for PS films. The additives take the following order in photostabilization activity according to their decrease in carbonyl and hydroxyl indices for PS films:

SN > SC > SB > SI > SP

These additives stabilize the PS films through UV absorption or screening, peroxide decomposer and radical scavenger mechanisms. The SN compound was found to be the most efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds as commercial stabilizers for PS.

#### Acknowledgments

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