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Viscoelastic, Spectroscopic and Microscopic Study of the Photo Irradiation Effect on the Stability of PVC in the Presence of Sulfamethoxazole Schiff's Bases

Emad Yousif^{1,*}, Gamal A. El-Hiti^{2,*}, Zainab Hussain³ and Ali Altaie⁴

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- ¹ Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq
- ² Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia
- ³ Department of Chemistry, College of Science, Misan University, Misan 62001, Iraq; zalaa4842@gmail.com
- ⁴ Department of Chemistry, College of Science for Women, Baghdad University, Baghdad 64021, Iraq; altaiealisalman@gmail.com
- * Correspondence: emadayousif@gmail.com (E.Y.); gelhiti@ksu.edu.sa (G.A.E.-H.); Tel.: +966-11469-3778 (G.A.E.-H.); Fax: +966-11469-3536 (G.A.E.-H.)

Abstract: The photostabilization of poly(vinyl chloride) (PVC) films having five Schiff's bases derived from sulphamethoxazole has been investigated. The casting method was used to produce PVC films containing sulphamethoxazoles (0.5% by weight), in tetrahydrofuran. The photostabilization activities of five additives were determined by monitoring the hydroxyl, polyene and carbonyl indices with irradiation time. In addition, the quantum yield of the chain scission (Φ cs) and the changes in viscosity average molecular weight of PVC films containing Schiff's bases were evaluated with irradiation time. The rate of photostabilization for PVC films in the presence of five Schiff's base additives was found to be the highest in the case of 2-hydroxybenzylidene derivative and the lowest in the unsubstituted benzylidene derivative. Several mechanisms have been suggested to explain the photostabilization of PVC in the presence of Schiff's bases that mainly act as UV absorbers and radical scavengers for photostabilizers.

Keywords: photostabilizer; photochemistry; UV-Vis spectroscopy; PVC; sulphamethoxazoles; UV absorber

1. Introduction

Photodegradation of polymeric materials take place when exposed to ultraviolet (UV) radiation. Ultraviolet absorbers (UVAs) are chemicals that can absorb ultraviolet radiation and reduce their damaging effects. Such chemicals can act as ultraviolet stabilizers and can be added to various polymeric materials. Various ultraviolet light stabilizers are known and have been used in various interesting materials such as cosmetics, plastics and films [1]. Photochemical degradation can take place as a result of chemical reaction, or photochemical degradation, which could be initiated through the energy from UV solar radiation. Antioxidant materials are known as heat and light stabilizers that can be added to plastics to avoid its deterioration [1].

The photo-crosslinking and photodegradation of polymers caused by the sun and artificial ultraviolet can be prevented by the use of UV-stabilizers. Many ultraviolet light stabilizers incorporate inorganic and organic (aromatic and heterocyclic) moieties. The most common inorganic UV-stabilizers contain chromic, titanium, iron and chrome oxides as well as carbon black. The uneven distribution of such additives within polymeric materials leads to reduction of their incompatibility within the polymer matrix. As a result, inorganic UV-stabilizers are not very common

for industrial applications since their concentration within the polymer matrix is low [2]. Organic UV-stabilizers usually have low molecular weights such as the ones containing phenyl benzoate, hydroxybenzophenone, benzotriazoles and fluorescent moieties. A number of problems such as volatility, incompatibility, solvent extraction and migration could be obtained as a result of the addition of organic UV-stabilizers to polymeric materials (plastic) that might lead to polymeric materials strong diminution. The use of reactive UV-stabilizers [3] with compatible side chains, for example, could overcome some of the limitations associated with the use of UV-stabilizers [4]. The UV-resistance within the polymeric materials could be increased by the use of high molecular weight UV-stabilizers. The compatibility between high molecular weight UV-stabilizers and polymer matrices are essential [5]. It is highly important to stabilize synthetic polymers to reduce or prevent the damaging effect that can be caused by heat, light and air. Therefore, it is essential to consider photostabilization of polymers that involves various photochemical reactions within polymer chains during the irradiation process.

A number of UV-stabilizers are known in which the mode of action is highly dependent on the direct UV absorption, radical scavengers, peroxide decomposers, excited state quenchers and light screeners, for example [6–15]. Recently, we have reported the use of various additives to increase photostabilizing efficiency and photochemical stability of polymeric materials [16–19] as part of our interest in the synthesis of polymeric materials with interesting applications [20–22]. In this paper, we report the successful use of Schiff's bases derived from sulphamethoxazole as UV-stabilizers in the photostabilization of polyvinyl chloride (PVC).

2. Experimental Section

2.1. General

The Fourier transform Infrared (FT-IR) spectra were recorded on FTIR-8300 Shimadzu Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) within the frequency range of 400–4000 cm⁻¹. The ultraviolet-visible (UV-Vis) spectra were recorded on Shimadzu UV-Vis 160A-Ultraviolet Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) within the range of 200–1100 nm. The surface morphology images of PVC films were recorded on the Meiji Techno Microscope (New York Microscope Company, New York, NY, USA).

2.2. Synthesis of Schiff's Bases 1–5

Several Schiff's bases 1-5 (Table 1 and Figure 1) having sulphamethaxazole moiety were synthesized based on a literature procedure [23] from reactions of sulphamethoxazole and aromatic namely 2-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, aldehydes, 3-nitrobenzaldehyde, 4-bromobenzaldehyde and benzaldehyde, in ethanol in the presence of few drops of glacial acetic acid as a catalyst under reflux condition for 12 h. The mixture was left to cool down and the solid produced was filtered, washed ethanol and recrystallized from 4-(2-hydroxybenzylideneamino)-N-(5-methylisoxazol-3-yl)benzene ethanol to give sulfonamide 4-(4-(dimethylamino)benzylideneamino)-N-(5-methylisoxazol-3-yl)benzene (1), sulfonamide (2), *N*-(5-methylisoxazol-3-yl)-4-(3-nitrobenzylideneamino)benzene sulfonamide (3), 4-(4-bromobenzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide (4) and 4-(benzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide (5). The structures of Schiff's bases 1-5 were confirmed by various spectroscopic techniques and their data were found to be consistent with those previously published [23].

Compound	Name
1	4-(2-Hydroxybenzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide
2	4-(4-(Dimethylamino)benzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide
3	N-(5-Methylisoxazol-3-yl)-4-(3-nitrobenzylideneamino)benzene sulfonamide
4	4-(4-Bromobenzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide
5	4-(Benzylideneamino)-N-(5-methylisoxazol-3-yl)benzene sulfonamide

Table 1. Structure of Schiff's bases 1–5 used as additives along with poly(vinyl chloride) (PVC).



Figure 1. Structure of compounds 1-5.

2.3. Film Preparation

The commercial PVC was precipitated from its tetrahydrofuran solution by the addition of ethanol in a dropwise manner. The solid obtained was collected by filtration and dried under reduced pressure for 24 h at room temperature. The PVC polymeric films (30 µm thickness) were prepared by the use of a Digital Vernier Caliper 2610A micrometer (Vogel GmbH, Kevelaer, Germany) in which a fixed PVC concentration, as a solution in tetrahydrofuran (5 g/100 mL), was used. The PVC polymeric films were mixed with the synthesized Schiff's bases 1–5 (0.5% by weight). In addition, a PVC sample was used as a blank without addition of any of Schiff's bases. To maintain the high optical quality and to limit the turbidity of the mixture, the hygrometry during casting and the rate of solvent evaporation should be controlled. The film transmission should be high (>80%) within the near-UV range. The evaporation technique was used to produce the films for 24 h at room temperature. The tetrahydrofuran residues were removed by drying PVC at room temperature for 3 h. Fixation of the PVC films were carried out by the use of aluminum plate stands (0.6 mm in thickness) that have been supplied by the Q-Panel Company (Homestead, FL, USA) [13].

2.4. Accelerated Testing Technique

The polymeric PVC films were irritated in air by the use of accelerated weather-meter QUV tester (Q-Panel Company; Homestead, FL, USA) at $6.02 \times 10^{-9} \text{ ein} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ light absorption intensity. The accelerated weathering tester has a stainless steel plate with two holes in the front side and a third at the back. There is a UV-B fluorescent ultraviolet lamp (40 W), in each side, giving a spectrum at 290–360 nm range in which maximum wavelength is 313 nm. To insure that the UV incident radiation is perpendicular on the samples, the PVC polymeric films were fixed vertically and parallel to the lamps. Samples were rotated from time to time to ensure that the intensity of incident light is the same on all samples [24].

2.5. Photodegradation Measuring Methods

2.5.1. Measuring the Photodegradation Rate of PVC Polymeric Films Using Infrared Spectrophotometry

An FTIR 8300 Shimadzu Spectrophotometer (Shimadzu, Tokyo, Japan) was used to follow-up the progress of PVC polymeric films photodegradation within the 400–4000 cm⁻¹ range. The carbonyl, polyene and hydroxyl groups' absorptions took place at 1724, 1631 and 3400 cm⁻¹, respectively. The changes in carbonyl, polyene and hydroxyl absorption peaks indicated the photodegradation

progress at various irradiation times. The comparison between the FTIR absorption peaks at 1724, 1631 and 3400 cm⁻¹ and the reference peak (1328 cm⁻¹) allows the calculation of carbonyl (I_{co}), polyene (I_{po}) and hydroxyl (I_{OH}) indices [25]. Such a method is known as the band index method, as presented in Equation (1).

$$Is = As/Ar \tag{1}$$

where Is = the index of group under study, As = the absorbance of peak under study and Ar = the absorbance of reference peak. The actual absorbance, the difference between the absorbance of top peak and base line (a top peak–a baseline), can be calculated by the use of baseline method [25].

2.5.2. Measuring the Photodegradation by Weight Loss

The calculation of weight loss percentage of the photodegraded PVC films in the presence and absence of Schiff's base additives allows the determination of the stabilizing effectiveness, as shown in Equation (2) [26].

Weight loss % =
$$[(W_1 - W_2)/W_1] \times 100$$
 (2)

where W_1 = the weight of PVC sample before irradiation and W_2 = the weight of the PVC sample after irradiation.

2.5.3. Measuring the Photodegradation by Morphology Study

A laboratory microscope (New York Microscope Company, New York, NY, USA) was used to study the surface morphology (top surface) of PVC polymer films after and before irritation in which an irradiation time of 250 h was used.

2.5.4. Determination of Viscosity Average Molecular Weight by Using Viscometry

Viscosity is a simple and widespread method to calculate the average molecular weight of polymeric materials [27]. The average molecular weight is proportional to the viscosity of polymeric material solution. Equation (3), the Mark–Houwink relation, is used to calculate the relative molecular weight.

$$[\eta] = K \overline{M}_{\rm V}^{\alpha} \tag{3}$$

where $[\eta]$ = the intrinsic viscosity, \overline{M}_V = average molecular weight of polymeric material, α and K = constants which depend on the polymer-solvent system at a particular temperature. Ostwald U-tube viscometer was used to measure the intrinsic viscosity of a PVC polymeric solution (g/100 mL).

The relative viscosity (η_{re}) and specific viscosity (η_{sp}) for polymeric solution (g/100 mL) can be calculated by the use of Equations (4) and (5), respectively.

$$\eta_{re} = \frac{t}{t_0} \tag{4}$$

$$\eta_{\rm sp} = \eta_{\rm re} - 1 \tag{5}$$

where t = the flow time for PVC polymeric solution and t_0 = the flow time for pure solvent.

1

The single-point measurements were converted to intrinsic viscosities by the use of Equation (6).

$$[\eta] = \left(\sqrt{2}/C\right) \left(\eta_{\rm sp} - In\eta_{\rm re}\right)^{\frac{1}{2}} \tag{6}$$

where C = the PVC polymeric concentration in solution (g/100 mL).

Molecular weights of PVC polymeric materials in tetrahydrofuran as a solvent, in the presence and absence of Schiff's base additives, can be calculated from intrinsic viscosities. Equation (7) was used to calculate the quantum yield of main chain scission (Φ_{CS}) from viscosity measurement.

$$\Phi_{CS} = \left(CA/\overline{M}_{V,O}\right) \left[\left(\left[\eta_{o}\right]/\left[\eta\right]\right)^{\frac{1}{\alpha}} - 1\right]/I_{o}t$$
(7)

where *C* = the concentration, *A* = Avogadro's number, $\overline{M}_{V,O}$ = the initial viscosity–average molecular weight, I_o = incident intensity, t = the irradiation time in second, $[\eta_o]$ = intrinsic viscosity of PVC polymeric films before irradiation, $[\eta]$ = intrinsic viscosity of PVC polymeric films after irradiation and α = constant.

3. Results and Discussion

3.1. Photochemical Study of the PVC Films by FTIR Spectroscopy

Schiff's bases 1-5 were used as additives for the photostabilization of PVC films. Previous studies showed that the most effective concentration of additives was 0.5% by weight [16,17]. Therefore, Schiff's bases 1-5 were used at a concentration of 0.5% by weight for the photostabilization of PVC polymeric films. Exposing the PVC films to light over various radiation times leads to clear changes in their FTIR spectra (Figure 2). The two absorption bands appeared at 1770 and 1724 cm^{-1} were attributed to the carbonyl groups formation, chloroketone and aliphatic ketone, respectively. The bands that have appeared 1631 and 3400 cm^{-1} were attributed to the formation of C=C bond conjugated to a carbonyl group and hydroxyl groups of the hydroperoxide and alcohol, respectively (Scheme 1). The figures for the absorption bands in question are in agreement with the recently published work [16]. However, the work reported by Gardette et al. in 1989 [28] have attributed the absorption bands resonated at 1785 and 1745 cm⁻¹ for the carbonyl groups of acid chloride and α, α' -dichloroketone, respectively in which hydroperoxides, chloroketones, acid chlorides, carboxylic acids were the main products from photooxidation of PVC. The indices for the carbonyl (I_{CO}), polyene (IPO) and hydroxyl (IOH) groups were monitored along with irritation time by the use of FTIR spectrophotometry to study the activities of Schiff's bases 1-5 as additives for PVC films' photostabilization [29]. The relationships between the irradiation time and indices for the carbonyl (I_{CO}) , polyene (I_{PO}) and hydroxyl (I_{OH}) for photostabilization of PVC films in the presence of Schiff's bases 1-5 as additives are represented in Figures 3-5. Figures 3-5 clearly indicated that compounds 1-5 have a lower growth rate with irradiation time compared to PVC in the absence of any additives (blank) [30]. Therefore, such additives can be considered as photostabilizers for PVC polymeric films in which compound 1 was found to be the most efficient photostabilizer among the ones used in this study, followed by 2, 3, 4 and 5.



(a) before irradiation

Figure 2. Cont.



Figure 2. The FTIR spectra for PVC films (30- μ m thickness) with Schiff's base **1** (0.5% by weight) as additive before (**a**) and after (**b**) irradiation.



Scheme 1. Some possible products from the photooxidation of PVC films.



Figure 3. The relationship between the irradiation time (h) and carbonyl index (I_{CO}) for PVC films (30 µm thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.



Figure 4. The relationship between the irradiation time (h) and polyene index (I_{PO}) for PVC films (30 µm thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.



Figure 5. The relationship between the irradiation time (h) and hydroxyl index (I_{OH}) for PVC films (30 µm thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.

3.2. Determination of the Stabilizing Efficiency by Weight Loss Method

The calculation of weight loss percentage of the photodegraded PVC films, by the use of Equation (2), allows measurement of the stabilizing effectiveness. Weight loss occurs due to formation volatile and low molecular weight by-products that resulted from photodegradation of PVC on exposure to light. The weight loss of PVC films increased as degradation time increases [31]. Figure 6 shows the relationship between the weight loss percentages as a function of irradiation time. The results obtained showed that Schiff's bases 1–5 have a significant stabilization effect against photodegradation of PVC films in which compound 1 was the most effective among the others.



Figure 6. The relationship between the irradiation time (h) and weight loss (%) for PVC films (30 μ m thickness) with Schiff's bases **1–5** (0.5% by weight) as additives.

3.3. Surface Morphology for Poly(vinyl chloride) Films

The morphological study of the surface of polymers has many advantages. For example, it gives a clear picture about the surface irregularity, defects and the crystalline case [32]. In addition, it allows monitoring the changes within the surface of the polymeric material as a result of photodecomposition or stabilization of polymers when exposed to ultraviolet radiation in which decomposition process can occur as chain scission [33]. The surface morphology images of the non-irradiated PVC films in the presence and absence of Schiff's base additives are shown in Figure 7. It is clear that the PVC film surface was smooth in which no white spots were detected.



Figure 7. Microscope images for the non-irradiated PVC films (30 μ m thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.

The PVC films were irritated for 250 h and the morphology images have been recorded (Figure 8). It is clear that the blank PVC film, irritated for 250 h, was full of white spots and grooves as a result of photodegradation of polymeric materials due to elimination of HCl. In addition, the morphological image of irritated PVC (blank) showed cracks within its surface and color changes [34]. However, in other cases where Schiff's base additives were used, the surface was almost smooth and fewer white spots exist indicating efficient stabilization effects. Clearly, Schiff's base additives 1–5, and in particular compound 1, reduce the photodegradation of PVC film through inhabitation of dehydrochlorination.



Figure 8. Microscope images for the irradiated (250 h) PVC films (30 μ m thickness) with Schiff's bases **1–5** (0.5% by weight) as additives.

3.4. Variation of Poly(Vinyl Chloride) Molecular Weight during Photolysis

The analysis of the relative changes in viscosity average molecular weight (M_V) provides an important test for random chain scission. Figure 9 shows the relationship between the irradiation time and changes in \overline{M}_V for PVC polymeric films in the presence of Schiff's base additives (0.5% by weight) at $6.02 \times 10^{-9} \text{ ein} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ light absorption intensity. The average molecular weight (\overline{M}_V) was measured at room temperature in tetrahydrofuran. Traces of insoluble PVC films were observed in the presence of Schiff's base additives, which is an indication that cross-linking or some degree of PVC branching have taken place during the photolysis process [35].



Figure 9. The relationship between the irradiation time (h) and viscosity average molecular weight $(\overline{M}_{\rm V}; \text{ g/mol})$ for PVC films (30 µm thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.

The number of average chain scission (S) was calculated by the use of Equation (9) [36].

$$S = \overline{M}_{V,O} / \overline{M}_{V,t} - 1 \tag{8}$$

where $\overline{M}_{V,O}$ = the viscosity average molecular weight at the initial time (0), $\overline{M}_{V,t}$ = the viscosity average molecular weight at *t* irradiation time. Figure 10 shows the relationship between the irradiation time and changes in the number of average chain scissions (S) and clearly indicated a degree of cross-linking and branching.



Figure 10. The relationship between the irradiation time (h) and main chain scission (S) for PVC films (30 μ m thickness) with Schiff's bases 1–5 (0.5% by weight) as additives.

In the initial stages of photodegradation, randomly distributed weak bonds can be broken quickly [37]. The degree of deterioration (α) was calculated by the use of Equation (10).

$$\alpha = m.S/\overline{M}_V \tag{9}$$

where m = the initial molecular weight. Figure 11 shows the relationship between the irradiation time and degree of deterioration (α). Clearly, the α values for the irradiated PVC samples with Schiff's base additives were lower compared to the case where no additive (blank) was used. The α values were found to be increased rapidly with irradiation time in the initial stages of photodegradation of PVC films, which could be due to a random polymeric chain bonds breaking.



Figure 11. The relationship between the irradiation time (h) and degree of deterioration (α) for PVC films (30 µm thickness) with Schiff's bases **1–5** (0.5% by weight) as additives.

The quantum yield of the chain scission (Φ_{cs}) can provide further evidence for the PVC photodegradation reaction [18]. The Φ_{cs} values for PVC films in the presence of additives were calculated by the use of Equation (7) and the values are reported in Table 2.

Table 2. Quantum Yield (Φ_{cs}) for the chain scission for PVC films (30 µm thickness) in the presence and absence of additives (0.5% by weight) after irradiation (250 h).

Additive (0.5 <i>wt</i> %)	Quantum Yield of Main Chain Scission (Φ_{cs})
PVC (blank)	$6.3 imes 10^{-05}$
PVC + compound 1	$5.4 imes 10^{-09}$
PVC + compound 2	$8.4 imes 10^{-09}$
PVC + compound 3	$1.3 imes 10^{-08}$
PVC + compound 4	$1.7 imes 10^{-08}$
PVC + compound 5	$3.1 imes 10^{-08}$

From Table 2, it was clear that the Φ_{cs} values in the presence of additives were smaller than that for the PVC additive free (blank). The reason for the Φ_{cs} low values could be due to the fact that the energy was absorbed at one site and the electronic excitation was distributed over a large number of bonds within PVC macromolecules. As a result, the possibility to break a single bond becomes low or energy absorption can be dissipated by non-reactive processes [38].

3.5. Suggested Mechanisms for the Photostabilization of PVC Films in the Presence of Schiff's Bases 1-5

The efficiency of Schiff's bases 1–5 as photostabilizers for PVC films was found to follow the order 1 > 2 > 3 > 4 > 5 based on the changes in the hydroxyl, carbonyl and polyene concentration. The Schiff's bases 1–5 can stabilize PVC films through various mechanisms including energy transfer from the polymers excited chains to the additives, cross-linking between PVC polymeric chains and additives' UV absorption [16,39–42]. The stabilization of PVC films could take place as a result of the direct absorption of UV radiation by the Schiff's bases 1–5 in which energy can be dissipated as a heat (Scheme 2). Similarly, it is believed that the isoxazole ring itself could stabilize the PVC through direct absorption of UV radiation, but the substituents on the imine bond clearly had the predominant stabilization effect.



Scheme 2. Possible photostabilization of PVC through direct absorption of UV radiation by Schiff's base additives **1–5**.

The interaction between the PVC polymeric chains and Schiff's base additives has been suggested to be dependent on the coordination between the heteroatoms within Schiff's bases, and, in particular, the nitrogen of imine bonds, and the polarized carbon-chlorine bonds within the PVC polymeric chains [16]. It is believed that strong interactions between PVC polymeric chains and Schiff's bases could lead to an effective energy transfer. Therefore, the attraction between PVC chains and Schiff's bases 1–5, as a result of the polarities of oxygen atoms within isoxazole ring, nitrogen of imine bonds and PVC carbon-chlorine bonds has been suggested to stabilize the polymeric materials through dissipation of the energy from the PVC excited state by energy transfer (Scheme 3). However, there is no experimental evidence to support such speculation.



Scheme 3. Possible photostabilization of PVC films through interaction between Schiff's base additives **1–5** and PVC films.

Since the performance of Schiff's bases tested is different, it is likely that the nature of substitution on the phenyl ring had an effect on the level of PVC films' stabilization. Compound **1** was found to be the most effective additive towards stabilization of the PVC films. Such effect could be due to the presence of hydroxyl groups on the phenyl ring attached to the imine bond. It was reported that the stabilization of PVC films in the presence of Schiff' base compounds could be explained through a proton transfer for the singlet excited state (S¹) of the additive followed by internal conversion (IC), proton transfer and then dissipation of energy as a heat [42]. In addition, it was reported that stabilization of PVC can take place through intersystem conversion (ISC) of the S¹ state of the additive to the triplet excited state (T¹) followed by a proton transfer and then conversion to the ground state (S⁰) in which energy was dissipated as heat [42]. Therefore, photostabilization of PVC films through a proton transfer and intersystem crossing (ISC) in the presence of Schiff's base **1** was suggested in Scheme **4**.



Scheme 4. Possible photostabilization of PVC films through a proton transfer and intersystem crossing (ISC) in the presence of Schiff's base **1**.

Finally, the hydroxyl group in Schiff's base **1** could act as radical scavenger in the PVC photostabilization process (Scheme 5).



Scheme 5. Possible photostabilization of PVC films through a radical scavenger in the presence of Schiff's base **1**.

4. Conclusions

Schiff's bases containing sulfamethoxazole moiety have been proven to act as photostabilizers for the photostabilization of poly(vinyl chloride). The order of photostabilization activity was 1 > 2 > 3 > 4 > 5, based on decreases in carbonyl, polyene and hydroxyl indices as well as the weight loss for PVC films. 4-(2-Hydroxybenzylideneamino)-*N*-(5-methylisoxazol-3-yl)benzene sulfonamide (1) was found to be the most efficient Schiff's base in the photostabilization process of PVC mainly due to the presence of hydroxyl group as well as sulfamethoxazole moiety. Various mechanisms were suggested to explain the photostabilization of PVC in which Schiff's bases act as photostabilizers through dissipation of the energy as heat, electrostatic attraction between the PVC and additives and direct absorption of UV radiation.

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