



## Original Article

# Synthesis and Characterization of Schiff Bases Derived from 3-(4-methoxyphenyl) Acrylic Acid and 3-(Benzo[d][1,3]dioxol-5-yl) Acrylic Acid

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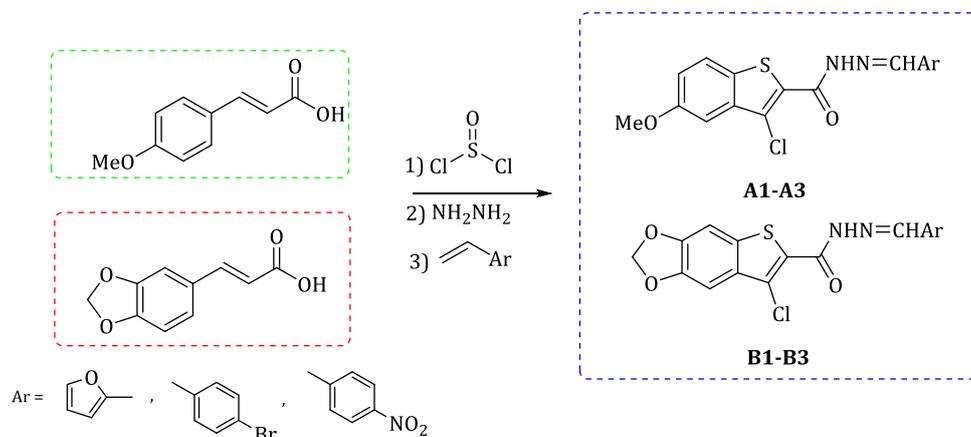
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## ABSTRACT

Two kind of Schiff bases (A1-A3) and (B1-B3) containing a benzothiazole moiety have been synthesized, description by (FT-IR and <sup>1</sup>HNMR, <sup>13</sup>CNMR) and used as photo stabilizers for poly (styrene-co-butadiene) at low concentrations. The first type (A1-A3) was created by reacting 4-methoxy cinnamic acid with thionylchloride to produce 3-Chloro-1-benzothiophene-2-carbonyl-chloride and after that, it was reacted with hydrazine to give 3-chloro-6-methoxybenzo[b]thiophene-2-carbohydrazide (A). In contrast, the Schiff bases compounds (B1-B3) were synthesized by reacting 3,4-(methyenedioxy) cinnamic acid with thionyl chloride to produce 7-chlorothieno [2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbonyl chloride, and then it was reacted with hydrazine to produce 7-chlorothieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide (B). Several methods were used to evaluate the effectiveness of Schiff bases as photo stabilizers on poly (styrene-co-butadiene). For instance, the changes in infrared and ultraviolet spectra, chain scission, molecular weight, and quantum yield upon exposure to the UV light were observed. All of the additives applied significantly slowed down photo-degradation of poly (styrene-co-butadiene).

## GRAPHICAL ABSTRACT



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## Introduction

The UV radiation, which makes up around 5% of solar radiation, is considered one of the key factors in the polymers' degradation. The minimal wave-length regarding ultra-violet radiation which reaches the surface of the earth is 290 nm, since some of radiation is filtered via ozone layer and other atmosphere elements. The particular groups of a polymer that absorb radiation experience an increase in the electronic excitation leading to molecular scission and loss of characteristics. Thus, understanding photo-degradation becomes crucial as polymer materials are used in more practical applications [1, 2]. Commercially, it is crucial for additives to be incorporated into polymeric materials. Likewise, the additives utilized should be harmless, inexpensive, non-volatile, colorless, and compatible with polymeric materials [3]. To slow down photo degradation, non-biodegradable polymers like PS could be combined with various additives like stabilizers, plasticizers, and colorants [4,5]. These additives primarily serve as flame retardants, antioxidants, quenchers, UV stabilizers, quenchers, radical scavengers, and antistatic agents [6-9]. Metal complexes [10-16], heterocycles [17,18], and aromatics [19-21] are the most often utilized additives for stabilizing PS against photo degradation. Lately, when exposed to the UV irradiation, Schiff bases can function as effective poly (vinyl chloride) photo stabilizer [22]. Those Schiff bases might be added to PS to increase its resistance to photo-degradation. They served as the UV absorbers and stabilizers. However, because they may emit in a specified range, Schiff bases make ideal candidates for the photo-voltaic solar cell, sensor, and OLED applications [16,17]. Recently, we reported on a few simple Schiff bases as luminescent coating types with one chromophore providing white luminescence [18]. In addition, understanding the excited state and how it relates to molecule structure or molecular aggregation could aid in defining the optical characteristics of organic materials [22-24].

In this study, as part of the investigation about the photo-stabilization regarding polymeric materials, we indicate the effective utilization of

the highly aromatic Schiff bases at low concentrations as photo-stabilizers to reduce photo-degradation of poly (styrene-co-butadiene) films in the case of exposure to the ultraviolet irradiation for prolonged period (420 hours).

## Materials and Methods

All the chemical and solvents were provided from Sigma-Aldrich and Fluka (*N,N*-Dimethylformamide (DMF), chloroform, benzene, toluene, hexane, pyridine, glacial acetic acid, absolute ethanol, 1,4-dioxane, 4-methoxy cCinnamic acid, 3,4-(methyenedioxy) cinnamic acid, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, furfural, thionyl chloride and hydrazine hydrate). The apparatus is SMP30 melting points equipment, melting points were measured in open capillary tubes and were not adjusted. At Dept. of Chemistry, College of Sciences, University of Mustansiriyah, FT-IR were recorded with the use of a SHIMADZU FT-IR8400S spectrophotometer. By using DMSO-*d*<sub>6</sub> as the solvent and tetra-methylsilane (TMS) as internal standard, 400 MHz HNMR spectra utilized a Bruker BiospinGmb H model ultra-shield. A mix of n-hexane and ethyl acetate (3: 2) was used as the eluent in a staining jar at the Gazi Osman Pasha (GOP) University in Turkey's TOKAT Center, and the progress of all reactions and purity checks were monitored by thin layer chromatography (TLC) (Table 1).

### *Chloro-1-benzo-thiophene-2-carbonyl-chloride (C1) synthesis*

Toluene (40 ml), SOCl<sub>2</sub> (18.14 mL, 0.25 mol), and 4-methoxycinnamic acid (8.9 g, 0.05 mol) were mixed for 1 hour at room temperature. Following the cautious addition of 0.4 ml of pyridine, the reaction mix was refluxed for 72 hours. The resultant residue was filtered to become crystallized as yellow, suspended in dry hexane (200 mL) [25], and its physical attributes are described in Table 2.

### *Synthesis 7-chlorothiemo [2',3':4,5] benzo[1,2-d][1,3]dioxole-6-carbonyl chloride(C2)*

Toluene (40 mL), SOCl<sub>2</sub> (18.14 mL, 0.25 mol), and 3,4-(methyenedioxy) cinnamic acid (9.61 g, 0.05 mol) were mixed for an hour at room temperature.

Following the cautious addition of 0.4 ml of pyridine, the reaction mix was refluxed for 72 hours. The resultant residue was filtered to become crystallized as yellow, suspended in dry hexane (200 mL) [25], and its physical attributes are described in Table 2.

**Table 1:** Symbols, names and structures of synthesized compounds

Symbols of Compounds	Compound structure	Compound name
A		3-chloro-6-methoxy-benzo[b]thiophene-2-carbohydrazide
A1		3-chloro-N'-(furan-2-ylmethylene)-6-methoxybenzo[b]thiophene-2-carbohydrazide
A2		N'-(4-bromobenzylidene)-3-chloro-6-methoxybenzo[b]thiophene-2-carbohydrazide
A3		3-chloro-6-methoxy-N'-(4-nitrobenzylidene)benzo[b]thiophene-2-carbohydrazide
B		7-chlorothieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide
B1		7-chloro-N'-(furan-2-ylmethylene)thieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide:
B2		N'-(4-bromobenzylidene)-7-chlorothieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide
B3		7-chloro-N'-(4-nitrobenzylidene)thieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide

*Method for Synthesis of hydrazineno compounds [A] and [B][26]*

Immediately after preparing the compound, it was mixed by compound [C1] or [C2] (0.005 mol) in 1,4-dioxane (30mL) and hydrazine hydrate 80% (25 ml, 15.37 gm, and 0.48 mol) was added

dropwise. In addition, the mixture was refluxed for 4 hours (by using chromatography thin layer (TLC) where the reaction was monitored and the hot mixture was poured over the ice water and was kept overnight, and then it was filtered to award the precipitated and the solid precipitate

recrystallized from ethanol to obtain the compound (A) and (B) [26]. Table 2 indicates the physical properties.

#### Synthesis of the Schiff bases compounds

(15 ml) of absolute ethanol was used to dissolve substituted aldehyde compounds (0.001 mol). A few drops of catalytic glacial acetic acid were added to the solution to acidify it. (0.001 mol) from [A] or [B] dissolved in (15 ml) ethanol was

added after the mix was stirred at the temperature of the room for 5 minutes. In addition, this mix was heated under reflux for approximately six to eight hours, and thin-layer chromatography (TLC) was used to monitor the process. The mix was allowed to cool after the reaction, and the formed precipitate was filtered through filter paper, dried, and after that re-crystallized with the use of DMF [27]. The physical parameters are provided in Table 2.

**Table 2:** Physical properties of synthesized compounds

Symbols	Chemical Formula	Yield (%)	M.P. (°C)	Color	Recrystallization Solvent
A	C <sub>10</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub> S (256.70)	51	190-192	White Yellow	Ethanol
A1	C <sub>15</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>3</sub> S (334.77)	65	206-208	pale yellow	DMF
A2	C <sub>17</sub> H <sub>12</sub> BrClN <sub>2</sub> O <sub>2</sub> S (423.71)	80	225-227	White yellow	DMF
A3	C <sub>17</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>4</sub> S (389.81)	85	215-217	Bright yellow	DMF
B	C <sub>10</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>3</sub> (270.69)	55	277-279	Greenish Yellow	Ethanol
B1	C <sub>15</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>4</sub> (348.76)	70	279-280	Pale yellow	DMF
B2	C <sub>17</sub> H <sub>10</sub> BrClN <sub>2</sub> O <sub>3</sub> S (437.69)	83	264-266	Yellow	DMF
B3	C <sub>17</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>5</sub> S (403.79)	67	275-277	Deep yellow	DMF

#### Films preparation

To guarantee complete homogeneity, a mixture of Schiff bases (A1-A3) and (B1-B3) (0.1 %) in tetrahydrofuran (THF) was added at a concentration of (0.50%) weight of poly (styrene-co-butadiene). To better understand how additives affect photo-stabilization of polymeric materials, different films were made. After 17.5 days of the UV irradiation, the films were examined for changes in the bands of the absorption noted at 1645 (C=C), 1724 (C=O), and 3400cm<sup>-1</sup> (OH). The variations in the intensities of these functional groups were put to comparison with the peak emerged at 1330 cm<sup>-1</sup> and was attributable to the CH<sub>2</sub> bonds in the polymer backbone. The IR spectra were used to calculate the indices of the C=C (I<sub>C=C</sub>), C=O (I<sub>C=O</sub>), and OH (I<sub>OH</sub>) groups. Compared with the films containing additives, the variations in I<sub>C=C</sub>, I<sub>C=O</sub>, and I<sub>OH</sub> were quite high for blank poly(styrene-co-butadiene) films. An Ostwald U-tube viscometer was used to calculate the intrinsic viscosity of polymer solution. The flow times of polymer solution and pure solvent were t and t<sub>0</sub>, respectively. The polymer solution was produced by dissolving it in a solvent, and then the viscosity was determined.

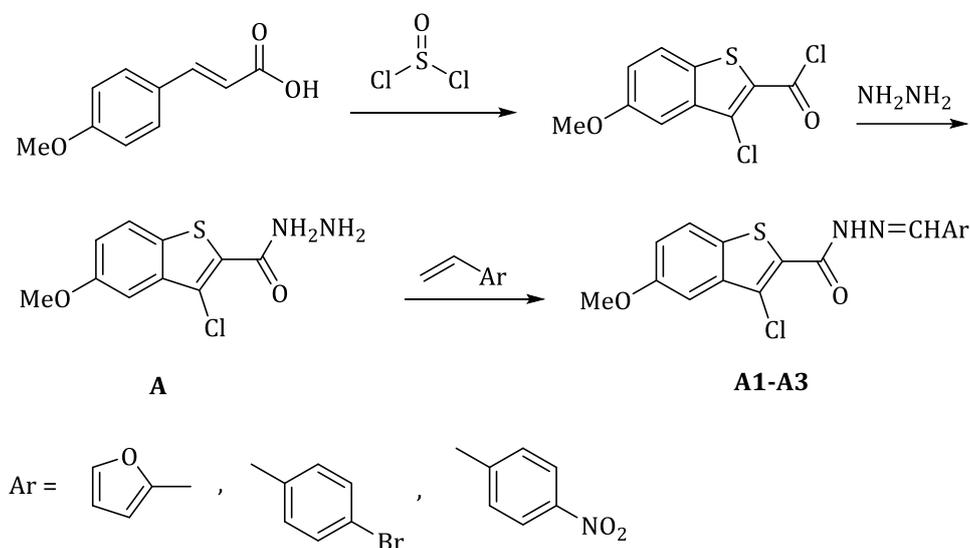
## Results and discussion

#### Synthesis of Schiff Bases (A1-A3) and (B1-B3)

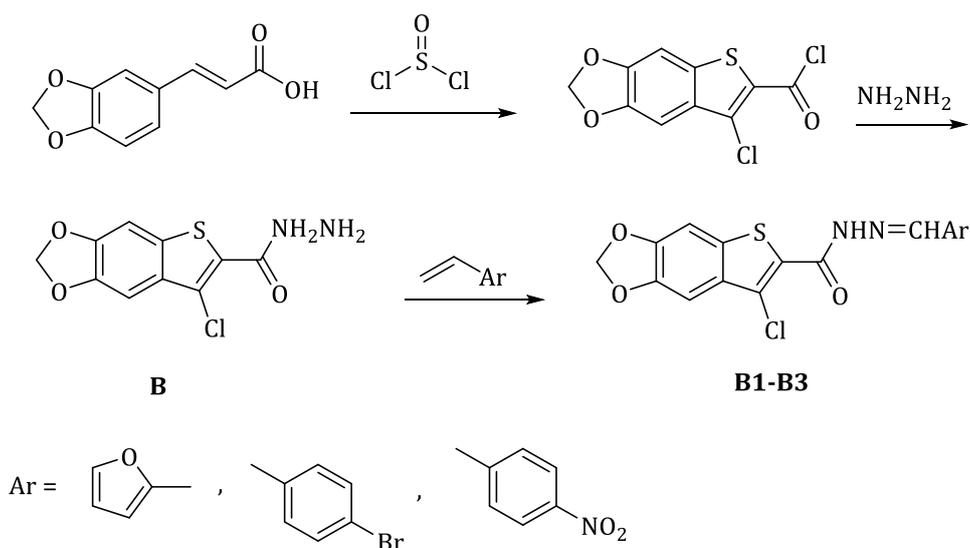
The Schiff bases compounds (A1-A3) were synthesized from reacting of 4-methoxycinnamic acid with thionyl chloride to produce 3-Chloro-1-benzothiophene-2-carbonyl-chloride, and then reacted with hydrazine to produce 3-chloro-6-methoxybenzo[b]thiophene-2-carbohydrazide (A), while the Schiff bases compounds (B1-B3) were synthesized from the reaction of 3,4(methyenedioxy) cinnamic acid with thionyl chloride to produce 7-chlorothieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbonyl chloride, and then reacted with hydrazine to produce 7-chlorothieno[2',3':4,5]benzo[1,2-d][1,3]dioxole-6-carbohydrazide (B). Schiff bases (A1-A3) and (B1-B3) were obtained depending on a procedure from literature [27]. In addition, reaction of an equal molar mix of 3-chloro-6-methoxybenzo[b]thiophene-2-carbohydrazide (A), or 7-chlorothieno [2',3':4,5] benzo[1,2-d][1,3] dioxole-6-carbohydrazide (B), and a number of the compounds of the carbonyl was conducted in anhydrous ethanol in an acidic medium (i.e.

glacial acetic acid) under reflux for 6 to 8 hours gave crude products. Crystallization of the crude product by using ethanol or DMF revealed pure Schiff bases (A1-A3) and (B1-B3) in 65–85%

yields, respectively, as demonstrated in Schemes (1 and 2). The Schiff bases' colors were ranged from white or greenish-yellow to yellow.



**Scheme 1:** The synthesized compounds (A) and its derivatives (A1-A3)



**Scheme 2:** The synthesized compounds (B) and its derivatives (B1-B3)

Compounds (A) and (B) and all Schiff bases were described via FT-IR, <sup>1</sup>HNMR, and <sup>13</sup>CNMR. The FT-IR of compounds (A) indicated stretching bands asymmetrical and symmetrical (NH<sub>2</sub>) at 3437, 3365 cm<sup>-1</sup>, band at 3324 cm<sup>-1</sup> for (NH), 3068 cm<sup>-1</sup> for (CH arom.), 2893-2992 cm<sup>-1</sup> for (CH aliph.), 1663 cm<sup>-1</sup> for (C=O), 1625 cm<sup>-1</sup> for (NH bending), 1601 cm<sup>-1</sup> for (C=C), cm<sup>-1</sup> for C-O and cm<sup>-1</sup> for C-Cl. FT-IR of compounds (B) illustrated the stretching

bands asymmetrical and symmetrical (NH<sub>2</sub>) at 3359, 3317 cm<sup>-1</sup>, band at 3299 cm<sup>-1</sup> for (NH), 3075 cm<sup>-1</sup> for (CH arom.), 2915-2968 cm<sup>-1</sup> for (CH aliph.), 1617 cm<sup>-1</sup> for (C=O), 1503 cm<sup>-1</sup> for (C=C), 1256 cm<sup>-1</sup> for C-O and 879 cm<sup>-1</sup> for C-Cl, FT-IR of all Schiff bases revealed the disappearance of stretching bands asymmetrical and symmetrical (NH<sub>2</sub>). The rest of the bands were presented in Table3.

**Table 3:** Characteristic vibrational bands in (cm<sup>-1</sup>) of prepared Schiff bases

Compound No.	NH	CH <sub>arom.</sub>	CH <sub>aliph.</sub>	C=O	C=C	C-Br	NO <sub>2</sub>
A1	3363	3080	2925,2995	1650	1609	-	-
A2	3320	3160	2840,2939	1655	1601	1057	-
A3	3364	3163	2844,2935	1656	1602	-	1515 (asym.), 1338 (sym.)
B1	3310	3169	2904,3000	1653	1587	-	-
B2	3305	3166	2855,2915	1656	1609	1034	-
B3	2990	3169	2853,2919	1656	1597	-	1521 (asym.), 1340 (sym.)

**Table 4:** The <sup>1</sup>H-NMR and <sup>13</sup>CNMR spectrum of compounds [A1, A2, A3, B1, B2, and B3]

Compounds	<sup>1</sup> HNMR spectrum	<sup>13</sup> CNMR spectrum
[A1]	Signals at $\delta=3.34$ ppm (s, 3H, and OCH <sub>3</sub> ), $\delta=6.62-7.88$ (m, 6H, and Ar-H), 10.30 ppm (s, 1 H, and N=CH), and $\delta=11.79$ ppm (s, 1H, and NH).	Signals at $\delta=56.2$ ppm (OCH <sub>3</sub> ), $\delta=106.78, 109, 114.2, 146, 148.45, 149.57$ ppm (C aromatic), $\delta=163.82$ ppm (CH=N), and $\delta=172.54$ ppm (C=O),
[A2]	Signals at $\delta=3.89$ ppm (s, 3H, and OCH <sub>3</sub> ), $\delta=7.17-8.36$ (m, 7H, and Ar-H), 8.88 ppm (s, 1H, and N=CH), and $\delta=10.52$ ppm (s, 1H, and NH).	Signals at $\delta=56.27$ ppm (OCH <sub>3</sub> ), $\delta=105.95, 117.02, 124.06, 129.61, 132.40, 133.73, 139.44,$ and $148.39$ ppm (C aromatic), $\delta=160$ ppm (CH=N), and $\delta=168.47$ ppm (C=O).
[A3]	Signals at $\delta=3.89$ ppm (s, 3H, and OCH <sub>3</sub> ), $\delta=7.19-8.36$ (m, 7H, and Ar-H), 8.80 ppm (s, 1H, and N=CH), and $\delta=10.16$ ppm (s, 1 H, and NH).	Signals at $\delta=64.27$ ppm (OCH <sub>3</sub> ), $\delta=109.11, 117.93, 121.09, 132.17, 148,$ and $149.75$ ppm (C aromatic), $\delta=163$ ppm (CH=N), and $\delta=172.74$ ppm (C=O).
[B1]	Signals at $\delta=6.16$ ppm (s, 3H, and OCH <sub>2</sub> O), $\delta=6.62-7.88$ (m, 5H, and Ar-H), 8.30 ppm (s, 1H, N=CH), and $\delta=10.31$ ppm (s, 1H, and NH).	Signals at $\delta=102.2$ ppm (OCH <sub>2</sub> O), $\delta=112.77, 114, 117.89, 124.20, 129.5, 129.50, 132.17, 140.148.83, 148.45,$ and $149.56$ ppm (C aromatic), $\delta=163.82$ ppm (CH=N), $\delta=166.79$ ppm (C=O),
[B2]	Signals at $\delta=3.24$ ppm (s, 3H, and OCH <sub>2</sub> O), $\delta=6.08-8.71$ (m, 5H, and Ar-H), 8.71 ppm (s, 1H, and N=CH) and $\delta=10.47$ ppm (s, 1H, and NH).	Signals at $\delta=102.38$ ppm (OCH <sub>2</sub> O), $\delta=110.33, 117.90, 124.03, 125.45, 129.61, 130.67, 132.40, 132.48, 133.73, 140.35,$ and $149.64$ ppm (C aromatic), $\delta=161.18$ ppm (CH=N), $\delta=167.53$ ppm (C=O).
[B3]	Signals at $\delta=6.2$ ppm (s, 3H, and OCH <sub>3</sub> ), $\delta=7.28-8.48$ (m, 7H, Ar-H), $\delta=8.87$ ppm (s, 1H, and N=CH) and 10.31 ppm (s, 1H, and NH).	Signals at $\delta=102$ ppm (OCH <sub>2</sub> O), $\delta=107.99, 114.43, 117.93, 124.59, 136.77, 140.72, 148.45,$ and $149.74$ ppm (C aromatic), $\delta=163.81$ ppm (CH=N), $\delta=170.05$ ppm (C=O).

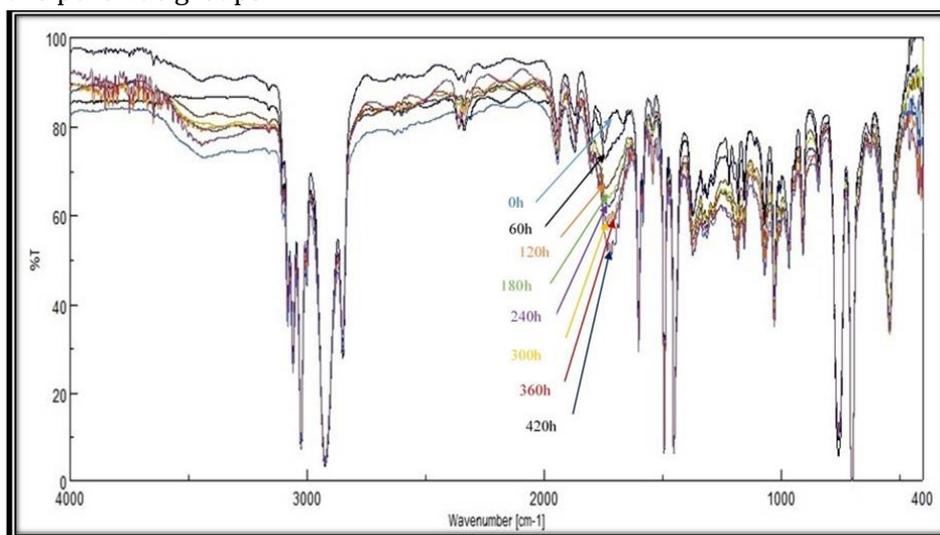
*Study of photo-degradation of poly (styrene-co-butadiene) by Fourier Transform Infrared (FTIR) Spectroscopy*

The UV absorption was thought to be the catalyst for the initiation of PSB's photo-oxidative

degradation. Various internal chromophoric impurities, included the followings [28, 29]:

1) Styrene and butadiene monomer was polymerized by the reaction of oxygen with PSB developing radicals, resulting in the formation of peroxide groups.

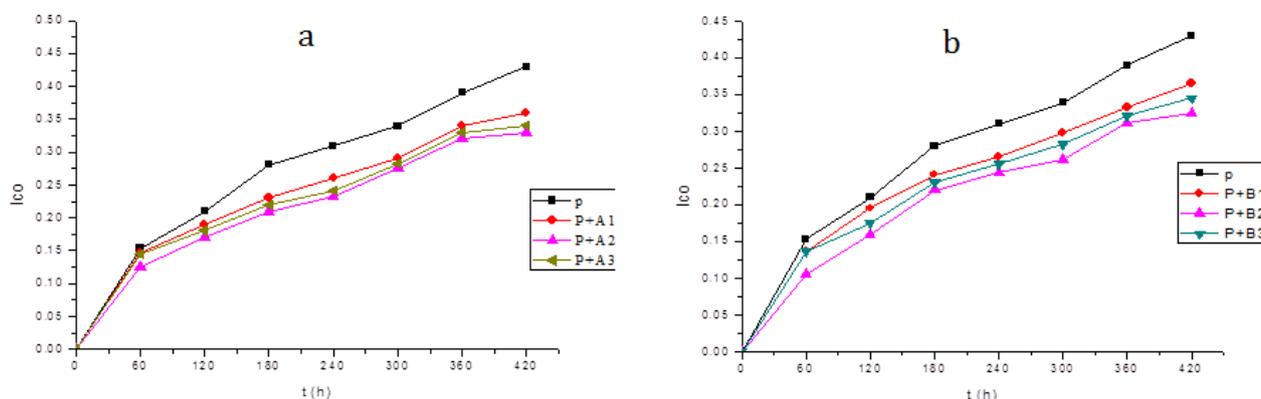
2) At PSB chain's end, pendant acetophenone groups were created by the photo- or thermal-reaction of hydro peroxide groups.



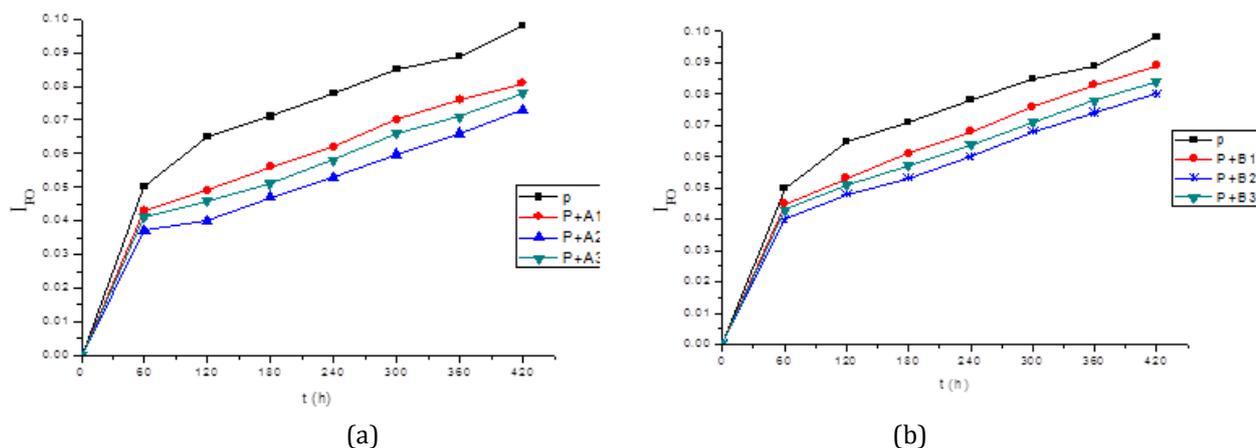
**Figure 1:** FT-IR spectrum of PSB (control) 30  $\mu\text{m}$  thickness under the UV degraded irradiation time (0-420) hours

It is acknowledged that carbonyl produced throughout the UV irradiation of polymers is most likely what causes the polymer's yellow color [29]. The ability of polymer film to absorb longer wavelengths is increased by the carbonyl, hydroxyl, and C=C groups produced throughout the photo-oxidation process of the polymer [30], as displayed in Figure (1). In the case when such groups are exposed to light with a wave-length of between 200 and 700 nm, they absorb light and become excited to the singlet and triplet states, which promotes a number of subsequent photo-oxidation reactions [31]. Figures (2-6) illustrate the relations between ( $I_{CO}$ ), ( $I_{PO}$ ), and ( $I_{OH}$ ) with

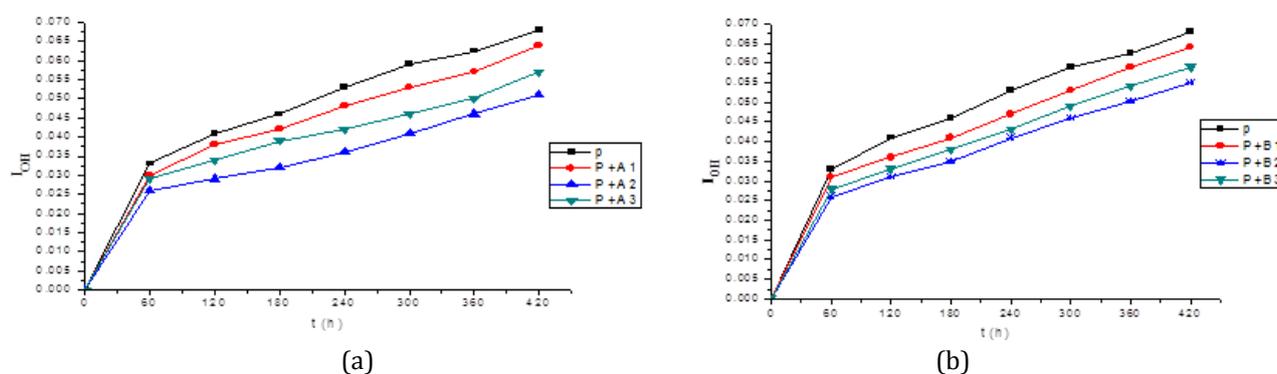
time of irradiation for the PSB films (30  $\mu\text{m}$ ) thickness containing 0.1 % from additives [B2, B1, and B3] and [A2, A1, and A3]. The additives performance in photo-stabilizing or photodegrading polymers depends heavily on the physical features of both the polymers and the additives. For instance, any form of additive (antioxidant, photo-stabilizer, thermal stabilizer, and so on) needs to be compatible with the polymer matrix to be evenly distributed [32]. The employed additives in this work were all completely soluble in the polymer solvent (chloroform)..



**Figure 2:** Correlation between ( $I_{CO}$ ) with irradiation time for (a) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (A1- A3), and (b) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (B1-B3)



**Figure 3:** Correlation between ( $I_{p0}$ ) with irradiation time for (a) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (A1-A3), and (b) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (B1- B3)



**Figure 4:** Correlation between ( $I_{0H}$ ) with irradiation time for (a) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (A1- A3), and (b) PSB films (30  $\mu\text{m}$ ) thickness that contains 0.1% from the additives (B1- B3)

It was noted that the additives utilized in the current study undergo photolysis and photodecomposition. This led to the calculation of

the photo decomposition rate constant ( $K_d$ ), as indicated in Table 5.

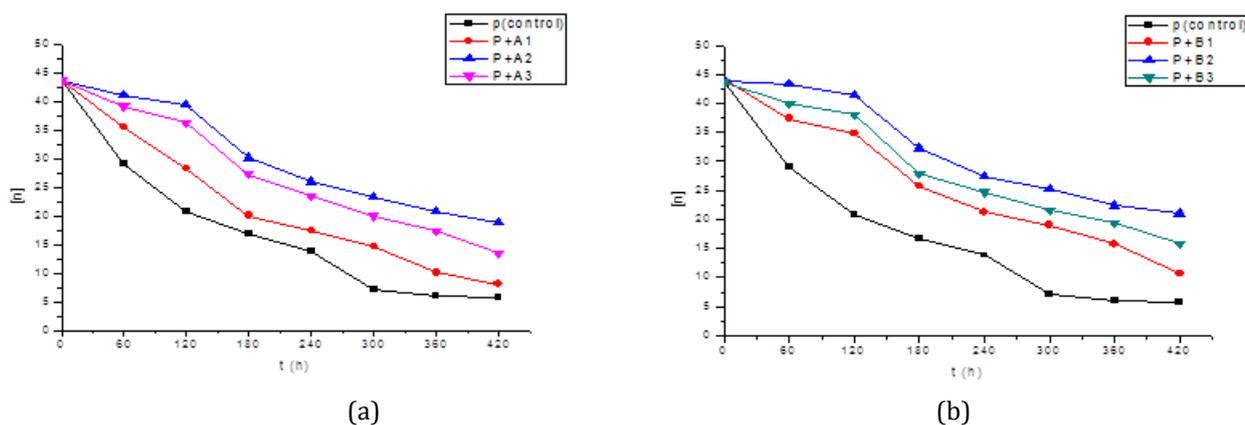
**Table 5:** Photo-decomposition rate constant ( $K_d$ ) of PSB films thickness (30  $\mu\text{m}$ ) that contains 0.1%w/w of additives

Compounds	$K_d$ ( $\text{sec}^{-1}$ )
PSB(blank)	$-1.07489 \times 10^{-6}$
PSB+A1	$-1.36174 \times 10^{-6}$
PSB+A2	$-7.68355 \times 10^{-7}$
PSB+A3	$-7.53612 \times 10^{-7}$
PSB+B1	$-7.22903 \times 10^{-7}$
PSB+B2	$-7.71917 \times 10^{-7}$
PSB+B3	$-8.09529 \times 10^{-7}$

Photo-stabilizers consistently have low ( $K_d$ ) values, indicating the fact that they are stable to the UV light [33]. It is clear that ( $K_d$ ) values vary depending on the additives used in PSB films, and they act in the following order:  
 PSB (control) > (A1)> (B1) > (A3) > (A2) > (B2) > (B3)

*Study the Photo-degradation of poly (styrene-co-butadiene) by viscosity*

Figure (2) depicts the plot of ( $\eta$ ) vs. irradiation time for PSB films with and without 0.1 % (w/w) of additives (A1-3) after measuring intrinsic viscosity ( $\eta$ ) of polymer solution (B1-3).



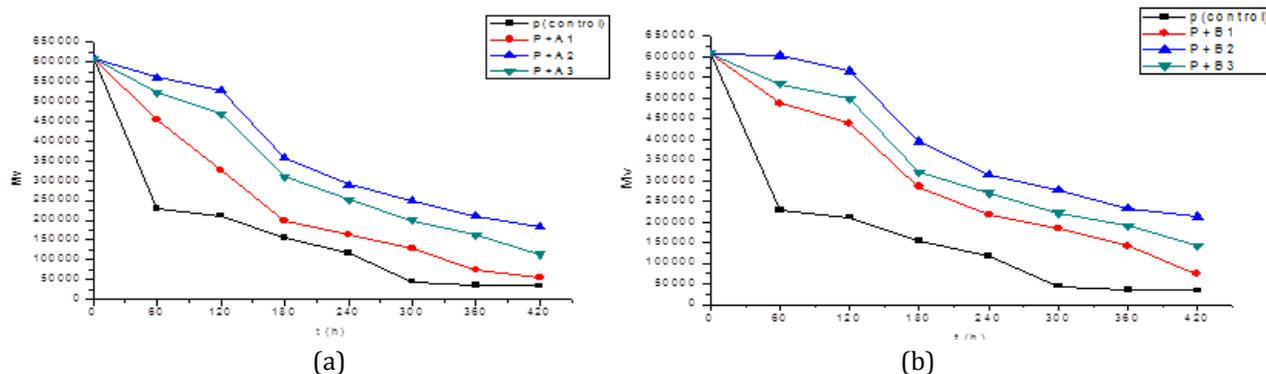
**Figure 5:** Plot of ( $\eta$ ) vs. the time of irradiation for (a) PSB films with and without 0.1% (w/w) of additives (A1-3), and (b) PSB films with and without 0.1% (w/w) of additives (B1-3)

The intrinsic viscosity ( $\eta$ ) of copolymer (PSB) without additive is less compared with that of copolymer (PSB) with the additive.

The analysis of relative changes in the viscosity average molecular weight ( $M_v$ ) described by Scott [33] indicated to present test for the random chain scission. Figure (4) illustrates ( $M_v$ ) plot vs. the time of irradiation for PSB films with and without 0.1% (w/w) of the additives (A1-3) and (B1-3) with the absorbed intensity of the light of  $6.2 \times 10^{-9}$  ( $\text{Ein Dm}^{-3}\text{S}^{-1}$ ). Through the viscosity measurement of the solution, the measurement of molecular weight is obtainable. The viscosity approaches are quite popular due to the fact that they are

experimentally simple [34]. Then, ( $M_v$ ) was measured Benzene was used as a solvent at  $25^\circ\text{C}$ , the plot indicated the ( $M_v$ ) rapid decrease initially and after that, it decreased gradually suggesting it as a result of the main chain scission at various locations along the polymer chain.

The poly (styrene-co-butadiene) degradation resulted in a decrease in the viscosity because degraded poly (styrene-co-butadiene) became of a low molecular weight compared with the undegraded polymer due to the fact that degraded polymer undergoes the chain scission decreasing molecular weight's value [35].



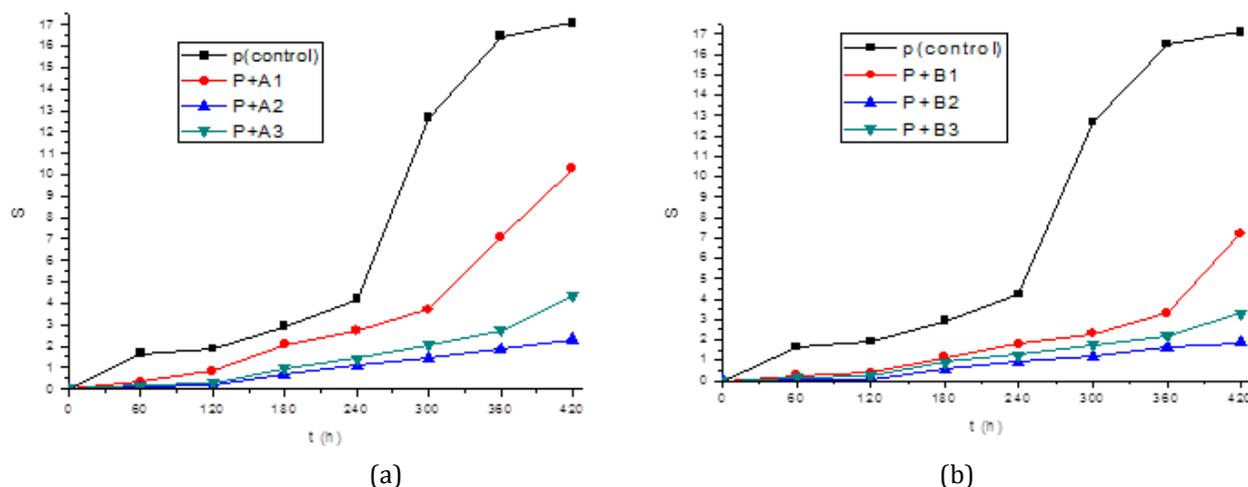
**Figure 6:** Changes in  $M_v$  for (a) poly (styrene-co-butadiene) with and without Schiff bases (A1, A2, and A3), and (b) poly (styrene-co-butadiene) with and without Schiff bases (B1, B2, and B3)

There was an inverse correlation between the number of average chain scission ( $S$ ) and  $M_v$  which can be noticed by Equation (1) [36]. The  $S$  value is dependent upon  $M_v$  that has been measured at initial (0) and final times ( $t$ ) of the irradiation:

$$S = M_{v,0} / M_{v,t} - 1 \quad (1)$$

Which is why it was expected that the  $S$  value has the ability of proving the branching and cross-linking degree within polymeric chains due to the PSB photo-degradation [37]. Figure 7 illustrates a curve indicating the increase of the branching degree so that it could arise from the cross-linking occurrence. It was noticed that insoluble material was created throughout the irradiation which

provided more additional evidences concerning the cross-linking occurrence.

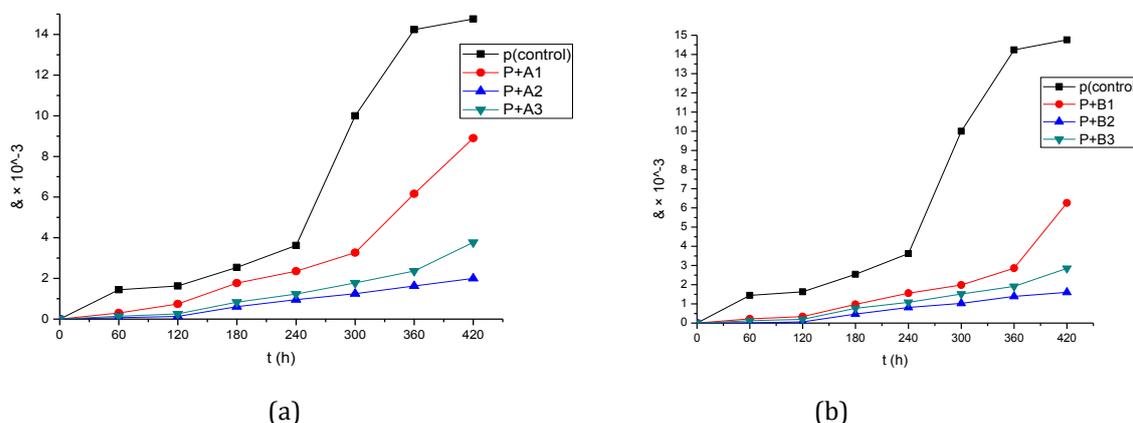


**Figure 7:** Changes in S for (a) poly (styrene-co-butadiene) with and without Schiff bases (A1-A3), and (b) poly (styrene-co-butadiene) with and without Schiff bases (B1-B3)

In addition, there was also an inverse correlation between deterioration degree ( $\alpha$ ) and  $M_v$ , which has been expressed by Equation (2) where m represents initial molecular weight of poly(styrene-co-butadiene). Thus, the  $\alpha$  value could provide an indication for breaking the weak bonds distributed randomly within polymer backbone [28][38]:

$$\alpha = m.S/M_v \quad (2)$$

As seen in Figure 8, the  $\alpha$  values of irradiated samples are higher without additives and lower with additives compared with corresponding values of additive free poly(styrene-co-butadiene). In initial photo-degradation stages of the poly(styrene-co-butadiene), the  $\alpha$  value is rapidly increased with the time; and it was considered as an indication of random bond breaking in polymer chain [39]



**Figure 8:** Changes in  $\alpha$  for (a) poly (styrene-co-butadiene) with and without additives (A1-A3), and (b) poly (styrene-co-butadiene) with and without Schiff bases (B1-B3)

The degree of poly(styrene-co-butadiene) photo-degradation may be measured from chain scission ( $\Phi_{cs}$ ) quantum yield. Equation (3) was used to calculate  $\Phi_{cs}$  for the PSB films following the irradiation and listed in Table (6). The  $\Phi_{cs}$  values were impacted by the value of concentration (C), Avogadro's number (A),  $M_{v,0}$ , irradiation time (t) in sec., and incident intensity ( $I_0$ ):

$$\Phi_{cs} = (CA/M_{v,0})([\eta_0]/[\eta])1\alpha/-1/I_0t \quad (3)$$

The  $\Phi_{cs}$  values for poly (styrene-co-butadiene) films in the presence of some additives are less than the PSB (*i.e.* blank) which are increased in the following order:

PSB (control) > A1 > (A3) > (A2)

PSB (control) > B1 > (B3) > (B2)

The explanation of low  $\Phi_{cs}$  values is because in the large poly (styrene-co-butadiene) molecule,

energy undergoes the absorption at 1 site, and after that, electronic excitation undergoes the distribution over several bonds so that likelihood

of one bond breaking is small, or absorbed energy undergoes the dissipation by the non-reactive procedures [40].

**Table 6:** Quantum Yield ( $\Phi_{cs}$ ) for chain scission for the PSB films (30  $\mu\text{m}$  thick) with and with no 0.1% (w\w) additives A(1-3) after 420 hours of irradiation time

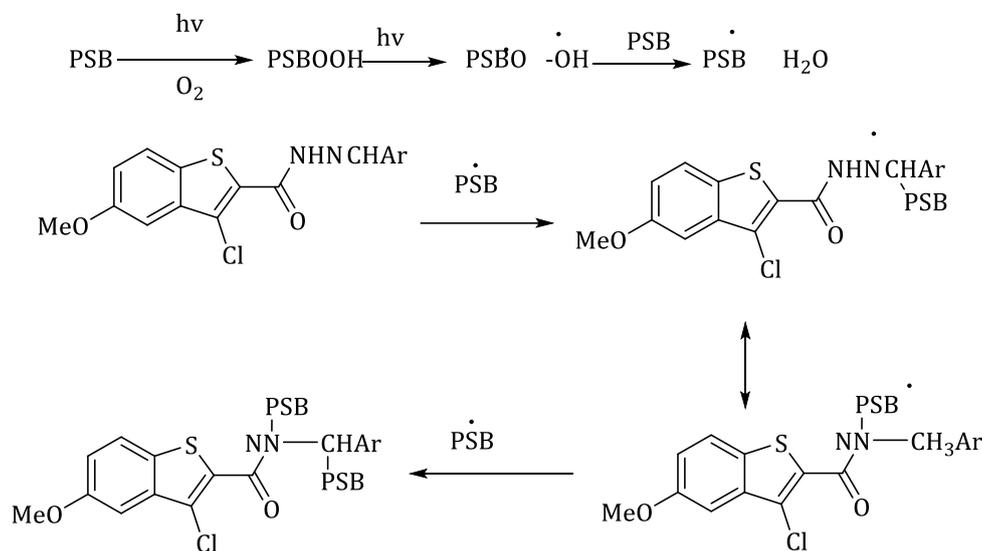
Compounds	$\Phi_{cs}$
PSB(blank)	$2.685 \times 10^{16}$
PSB+A1	$1.3 \times 10^{16}$
PSB+A2	$3.7 \times 10^{15}$
PSB+A3	$6.56 \times 10^{15}$
PSB+B1	$1.39 \times 10^{16}$
PSB+B2	$7.022 \times 10^{15}$
PSB+B3	$9.997 \times 10^{15}$

*The PSB suggested photo-stabilization mechanisms by the Schiff bases (A1-A3) and (B1-B3)*

The action of Schiff base additives as a photo-stabilizer in the PSB films could be a result of the ultraviolet absorption by those additives and the dissipation of this energy into the harmless heat. The Schiff base results in the PSB stabilization through various mechanisms like the UV absorber and screener by the radical scavenger. Schiff bases A1, B1, A2, B2, A3, and B3 play the role of good photo-stabilizers and protected PSB films from the

photo-decomposition in the case of the exposure to the ultra-violet light for long period. Schiff bases resulted in the reduction of photo-degradation and the chain cross-linking levels of the PSB. They are effective due to the fact that they include aromatic rings, azomethine bonds, and heteroatoms [41].

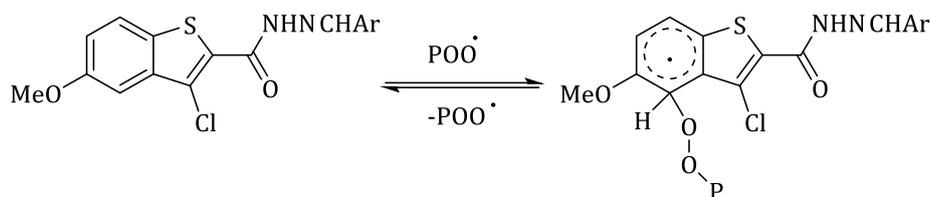
PSB photo-oxidation results in generating radicals of the polymeric chain that may be stabilized via forming stable complexes with the Schiff bases B (1-3) and A (1-3), as depicted in Scheme 3.



**Scheme 3:** Proposed PSB photo-stabilization mechanism by Schiff bases form stable complexes that include the PSB radicals

In addition, Schiff bases A1, A2, A3, B1, B2, and B3 play the role of the radical scavengers and have the ability of destroying the high-energy oxygenated species (*i.e.* the chromophores) like

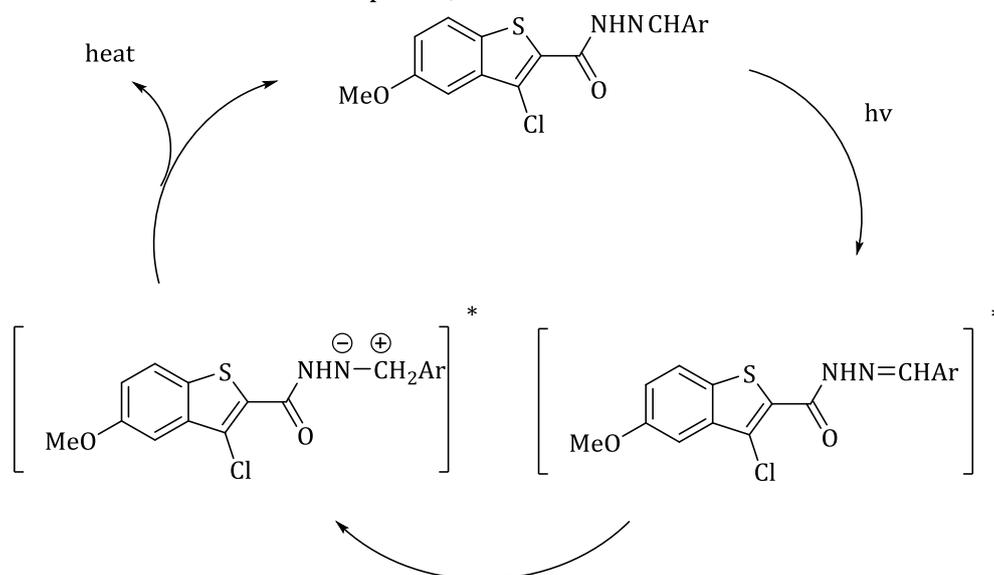
the peroxide radicals (POO). Schiff bases produce complexes with the peroxide radicals with high stability as a result of the resonance within aromatic rings, as displayed in Scheme 4.



**Scheme 4:** Proposed mechanism of PSB photo-stabilization by the Schiff bases as the radical scavenger

The linkage of the azomethine (CH=N) within Schiff base structure has a significant impact on the photo-stabilization of the polymer [42, 43]. The bond CH=N provides the Schiff bases with acting ability as ultraviolet absorbers [44] which is why mechanism utilization of this compound, as

photo-stabilizer, is through the charge separated species that might be in an excited state form. This structure would be allowing energy dissipation via the rotation on the increased vibration about central bond, which can be observed in Scheme 5.



**Scheme 5:** The proposed mechanism of PSB photo-stabilization with the Schiff bases compounds as the UV absorber

## Conclusion

Six Schiff bases (A1, A2, A3, B1, B2, and B3) contained benzothiophene ring systems. Structures elucidated by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR. The Schiff bases were utilized with success at the low concentration levels, as effective poly (styrene-co-butadiene) photo-stabilizers. The additives containing the ring of the thiophene has been found as the most effective ones. These additives behave successfully as photo-stabilizer for PSB films. They take the following order in photo-stabilization activity according to their decrease in carbonyl ( $I_{CO}$ ), hydroxyl ( $I_{OH}$ ), polyene ( $I_{PO}$ ), and the weight loss for PSB films  
 PSB (control) > (PSB+A1) > (PSB+A3) > (PSB+A2)  
 PSB (control) > (PSB+B1) > (PSB+B3) > (PSB+B2)

This type of the additive could play the role of a sufficient radical scavenger and absorber of the UV radiation, as a result of its high aromatic content and the presence of azomethine group, respectively.

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## Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

## Conflict of Interest

The author declared that they have no conflict of interest.

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