

New Stabilizers for Polystyrene Based on 2-Thioacetic Acid Benzothiazol Complexes

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ABSTRACT: The photostabilization of polystyrene (PS) films by 2-thioacetic acid benzothiazol with Sn(II), Cd(II), Ni(II), Zn(II), and Cu(II) complexes was investigated. The PS films containing complexes of concentration 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 viscosimetric average molecular weight of PS with irradiation time were also tracked (using benzene as a solvent). The quantum yield of the chain scission (Φ_{cs}) of these complexes in PS films was evaluated and found to range

between 3.60×10^{-6} and 7.78×10^{-6} . The results obtained showed that the rate of photostabilization of PS in the presence of the additive is in the following trend: $Ni(L)_2 > Cu(L)_2 > Zn(L)_2 > Cd(L)_2 > Sn(L)_2$. 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 additive mechanisms were suggested. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1922–1927, 2012

Key words: PS; photostabilizer; UV light; quantum yield

INTRODUCTION

Polystyrene (PS) is one of the most attractive polymer materials used in the fields of chemistry, biological and medical sciences, and food industry because of its excellent chemical and physical properties such as transparent, nontoxic, low adsorption toward large biomolecules and small drug molecules, modestly resist to acidic and alkaline solutions and organic solvents, easy to be shaped into various vessels, and cost effective. In the chemical and bioanalytical laboratories, PS dishes and substrates are frequently used for cell culturing, immunoassay, and various biosensors with the fast development of the micrototal analysis systems.^{1–3} One of the important uses of PS is in the manufacture of cover signal lamps of some automobiles. PS is subjected to the irradiation of sunlight on outdoor exposure.⁴ It is well known that all commonly used plastics degrade under the influence of sunlight and that is why the photostability of polymers is one of their most important properties. As a possible way to solve the

problem of polymer stabilization, a number of different stabilizers have been successfully used.^{5,6} 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.⁷

The photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of stabilizer: (1) light screeners, (2) UV absorbers, (3) excited-state quenchers, (4) peroxide decomposers, and (5) free radical scavengers; of these, it is generally believed that excited-state quenchers, peroxide decomposers, and free radical scavengers are the most effective.

The synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research. A number of ligands including polydentate amines, crown ethers, phosphines, bipyridines, and naphthyridines have been bound mainly with polystyrene divinylbenzene copolymers. These studies are mostly concerned with ion binding and catalytic aspects. Very little information exist as to whether and to what extent such metal ion

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complexation can influence the properties of the macromolecule.^{8,9}

The photochemical activity and the protection of PS films by the UV absorbers including Ni(II) chelate complexes have been studied.⁹ The current work is aimed to develop an approach for our ongoing research on the photostabilization of PS. The photostabilization of PS was studied using 2-thioacetic benzothiazole complexes.

EXPERIMENTAL

Materials

The following complexes were all prepared by the method described by Yousif et al.¹⁰

Synthesis of 2-thioacetic acid benzothiazole

A mixture of 2-mercapto benzothiazole (0.1 mol) and chloroacetic acid (0.1 mol) in the presence of KOH as a basic media was refluxed for 3 h to give 2-thioacetic benzothiazole. The white yellow precipitate formed was filtered and crystallized from ethanol to give the final product.

Preparation of complexes

Addition of ethanol solution of the suitable metal salt (nickel acetate tetrahydrate, tin chloride, copper acetate, cadmium acetate dihydrate, and zinc acetate dihydrate) to an ethanol solution of 2-thioacetic acid benzothiazole in 2 : 1 (ligand : metal) molar ratios was carried out. After reflux for half an hour, crystalline colored precipitates were formed at room temperature. The rustling solids were filtered off, washed with distilled water, and dried and recrystallized from ethanol and dried at 50°C.

Bis(2-thioacetic acid benzothiazol) tin(II) Sn(L)₂

Bis(2-thioacetic acid benzothiazol)

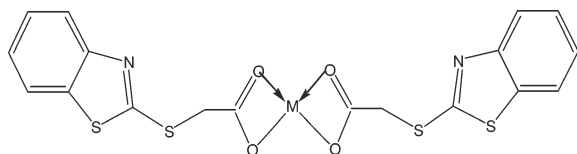
cadmium(II) Cd(L)₂

Bis(2-thioacetic acid benzothiazol) nickel(II) Ni(L)₂

Bis(2-thioacetic acid benzothiazol) zinc(II) Zn(L)₂.

Bis(2-thioacetic acid benzothiazol) copper(II)

Cu(L)₂



Where M = Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II).

Experimental techniques

Films preparation

Commercial PS supplied by Petkim Company (Turkey) (viscosity-average molecular weight = 24,000 g mol⁻¹, melt at 200°C) was reprecipitated from chloroform solution by alcohol for several times and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of PS solution (5 g/100 mL) in chloroform were used to prepare polymer films (3 cm × 3 cm) with 40 μm thickness (measured by a micrometer (Chicago) type 2610 A; Germany). The prepared complexes (0.5% concentrations) were added to the films starting at 0 concentrations (blank). The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual chloroform solvent, film samples were further dried at room temperature for 3 h under vacuum-reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-Panel Company.

Irradiation experiments

Accelerated testing technique. Accelerated weatherometer Q.U.V. tester (Q-Panel Company) was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (of the type fluorescent ultraviolet lights) with 40 W each. These lamps are of the type UV-B 313 giving spectrum range between 290 and 360 nm with a maximum at a wavelength of 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on 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.

Photodegradation measuring methods

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⁻¹ using FTIR 8300 Shimadzu spectrophotometer. The position of carbonyl absorption is specified at 1720 cm⁻¹ and the hydroxyl group at 3450 cm⁻¹.¹¹ The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl and hydroxyl peaks. Then, carbonyl (*I*_{CO}) and hydroxyl (*I*_{OH}) indices were calculated by comparison of the FTIR absorption peak at 1720 and 3450 cm⁻¹ with reference peak at 1450 cm⁻¹, respectively. This method is called band index method that includes¹²

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

where A_s is the absorbance of peak under study; A_r is 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 baseline (A Top Peak – A Baseline) is calculated using the Baseline method.¹¹

Determination of average molecular weight (\overline{M}_v) using viscometry method. The viscosity property was used to determine the average molecular weight of polymer, using the Mark-Houwink relation.¹²

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

where $[\eta]$ is the intrinsic viscosity; K and α are the constants depending on the polymer–solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. The solutions were prepared 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 (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_0}, \quad (3)$$

where η_{re} is the relative viscosity.

$$\eta_{sp} = \eta_{re} - 1. \quad (4)$$

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

$$[\eta] = \left(\sqrt{2}/c\right) \left(\eta_{sp} - \ln \eta_{re}\right)^{1/2}, \quad (5)$$

where c is the concentration of polymer solution (g/100 mL).

By applying eq. (5), the molecular weight of degraded 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:

$$[\eta] = 4.17 \times 10^{-4} M_v^{0.6}, \quad (6)$$

The quantum yield of main chain scission (ϕ_{cs})¹³ was calculated from viscosity measurement using the following relation:

$$\phi_{cs} = (CA/\overline{M}_{v,0}) \left[\left([\eta_0]/[\eta] \right)^{1/\alpha} - 1 \right] / I_0 t \quad (7)$$

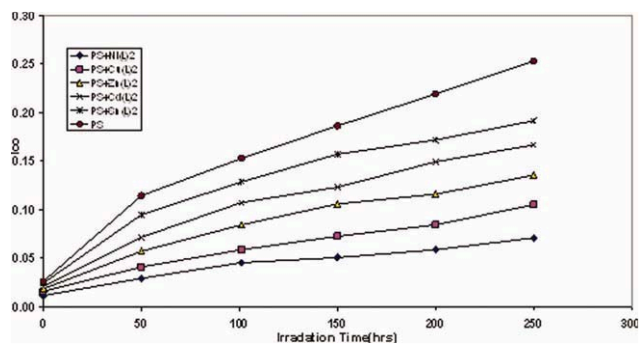


Figure 1 The relationship between the carbonyl index and irradiation time for PS films (40 μm thickness) containing different additives. The concentration of additives is fixed at 0.5% by weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

RESULTS AND DISCUSSION

The 2-thioacetic acid benzothiazol complexes with Sn(II), Cd(II), Ni(II), Zn(II), and Cu(II) were used as additives for the photostabilization of PS films. 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 $\lambda = 313$ nm led to a clear change in the FTIR spectrum. The appearance of bands in 1720 cm^{-1} was attributed to the formation of carbonyl groups related to aliphatic ketone. The hydroxyl band that appeared at 3450 cm^{-1} was annotated to the hydroxyl group.¹⁴ 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. However, in Figure 1, the I_{co} of Sn(L)₂, Cd(L)₂, Zn(L)₂, Cu(L)₂, and Ni(L)₂ showed lower growth rate with irradiation time with respect to the PS control film without additives. Because the growth of carbonyl index with irradiation time is lower than PS control, as seen in Figure 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 Ni(L)₂ is the most active photostabilizer, followed by Cu(L)₂, Zn(L)₂, Cd(L)₂, and Sn(L)₂, which is the least active. Just like carbonyl, hydroxyl

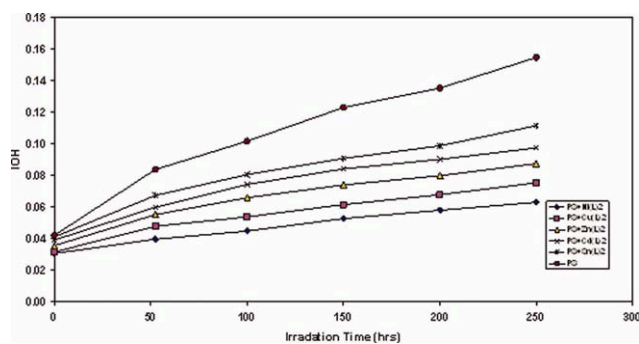


Figure 2 The relationship between the hydroxyl index and irradiation time for PS films (40 μm thickness) containing different additives. The concentration of additives is fixed at 0.5% by weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compounds are also produced during photodegradation of PS. Therefore, hydroxyl index (I_{OH}) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure 2.

Variation of PS molecular weight during photolysis in the presence of 2-thioacetic acid benzothiazol complexes

The analysis of relative changes in viscosity-average molecular weight (\bar{M}_v) has been shown to provide a versatile test for random chain scission. Figure 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 $1.052 \times 10^{-8} \text{ ein dm}^{-3} \text{ s}^{-1}$. (\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 crosslinking or branching in the PS chain does occur during the course of photolysis.¹⁵ For better support of this view, the number of average chain

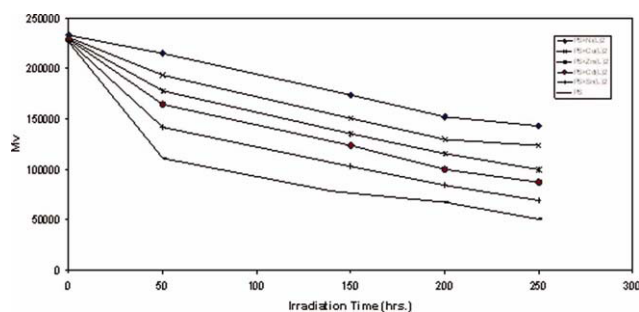


Figure 3 Changes in the viscosity-average molecular weight during irradiation of PS films (40 μm) (control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

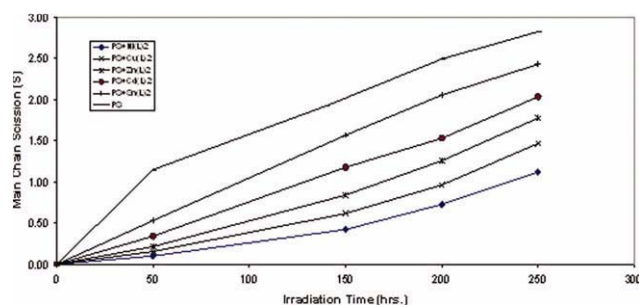


Figure 4 Changes in the main chain scission (S) during irradiation of PS films (40 μm; control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

scission (S ; average number cut per single chain)¹⁶ was calculated using the following relation:

$$S = (\bar{M}_{v,o} / \bar{M}_{v,t}) - 1 \tag{8}$$

where ($\bar{M}_{v,o}$) and ($\bar{M}_{v,t}$) are viscosity-average molecular weight at initial (o) and at irradiation time (t), respectively. The plot of S versus time is shown in Figure 4. The curve indicates an increase in the degree of branching such as that might arise from crosslinking occurrence. It is observed that insoluble material was formed during irradiation, which provided an additional evidence to the idea that crosslinking does occur.

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

$$\alpha = \frac{m \cdot s}{\bar{M}_v}, \tag{9}$$

where m is the initial molecular weight.

The plot of α as a function of irradiation time is shown in Figure 5.

The values of α of the irradiated samples are higher when additives are absent and lower in the

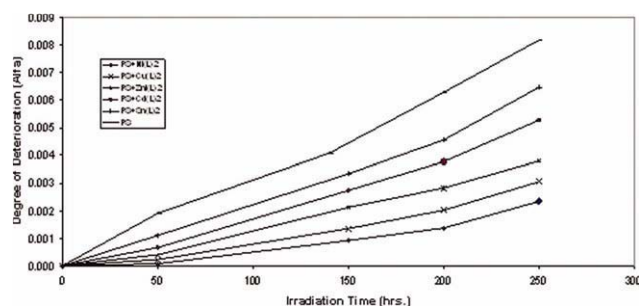


Figure 5 Changes in the degree of deterioration (α) during irradiation of PS films (40 μm) (control) and with 0.5 wt % of additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Quantum Yield (Φ_{cs}) for the Chain Scission for PS Films
(40 μm) Thickness With and Without 0.5 (wt/wt)
Additive After 250-h Irradiation Time

Additive (0.5 wt %)	Quantum yield of main chain scission (Φ_{cs})
PS+Sn(L) ₂	3.20 E -06
PS+Cd(L) ₂	4.09 E -06
PS+Ni(L) ₂	5.67 E -06
PS+Zn(L) ₂	6.14 E -06
PS+Cu(L) ₂	7.78 E -06
PS (control)	9.56 E -05

presence of additives when compared with the corresponding values of the additive-free PS. In the initial stages of photodegradation of PS, the value of α increases rapidly with time; these indicators indicate a random breaking of bonds in the polymer chain.

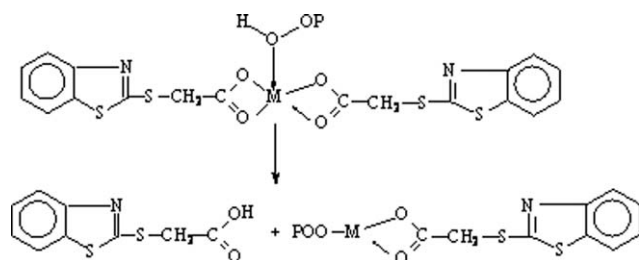
On the other hand, the degradation reaction characterization is measurement of the quantum yield of the chain scission (Φ_{cs}). The quantum yield for chain scission was calculated for PS films with and without 0.5% (wt/wt) of additive mentioned above using relation (5). The Φ_{cs} values for complexes are tabulated in Table I.

The Φ_{cs} values for PS films in the presence of additive are less than that of additive-free PS (blank), which increase in the following order: Ni(L)₂ > Cu(L)₂ > Zn(L)₂ > Cd(L)₂ > Sn(L)₂ > PS.

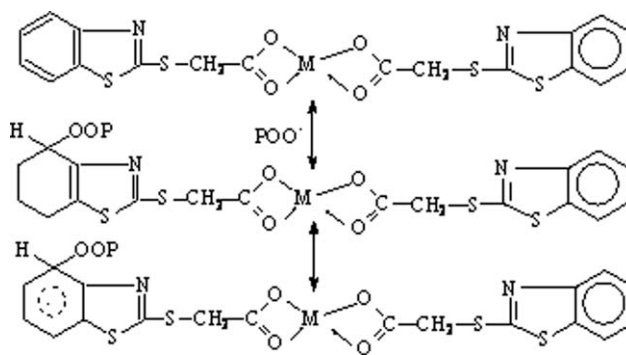
Suggested mechanisms of photostabilization of PS by 2-thioacetic acid benzothiazol complexes

Depending on the overall results obtained, the efficiency of 2-thioacetic acid benzothiazol complexes as stabilizer for PS films can be arranged according to the change in the carbonyl and hydroxyl concentration as a reference for comparison (as shown in Figures 1–5) as follows: Ni(L)₂ > Cu(L)₂ > Zn(L)₂ > Cd(L)₂ > Sn(L)₂.

Metal chelate complexes are generally known as photostabilizers for PS through both peroxide decomposer and excited-state quencher. Therefore, it is expected that these complexes act as peroxide



Scheme 1 Suggested mechanism of photostabilization of complexes as peroxide decomposer.



Scheme 2 Suggested mechanism of photostabilization of carboxylate complexes as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.

decomposer through the proposed mechanism (Scheme 1).¹⁷

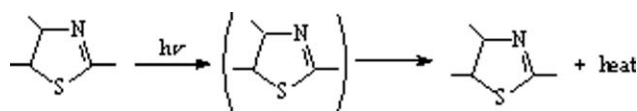
These metal chelate complexes also function as radical scavengers through energy transfer and by forming unreactive charge transfer complexes between the metal chelate and the excited state of the chromophore (POO) and stabilize through resonating structures¹⁸ as shown in Scheme 2.

The ring of benzothiazol in this compound plays an important role in the mechanism of stabilizing process by acting as UV absorber.¹⁹ The UV light absorption by these additives containing benzothiazol dissipates the UV energy to harmless heat energy (Scheme 3). This mechanism is in agreement with that reported by Adil et al.²⁰

CONCLUSIONS

In this work, the photostabilization of PS films using 2-thioacetic acid benzothiazol complexes was studied. These additives behave as successful 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: Ni(L)₂ > Cu(L)₂ > Zn(L)₂ > Cd(L)₂ > Sn(L)₂.

These additives stabilize the PS films through UV absorption or screening, peroxide decomposer, and radical scavenger mechanisms. The nickel complexes were found to be the more efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using Ni(II) complexes as commercial stabilizers for PS.



Scheme 3 Suggested mechanism of photostabilization of benzothiazole as UV absorber.

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