



Diorganotin (IV) Complexes Aid Switch to Protect the Photodecomposition of PVC in Outdoor Buildings

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Abstract

Three organotin (IV) complexes with different R-groups were used as additives for PVC. The photo-degradation rate constant of poly (vinyl chloride) upon irradiation with an ultraviolet light were investigated in the presence of Organotin(IV) complexes as photo stabilizers. Poly (vinyl chloride) photo-degradation rate constant was lower for the films containing Organotin (IV) complexes ($5.6-1.5 \times 10^{-3} \text{ sec}^{-1}$) compared to the blank film ($9.0 \times 10^{-3} \text{ sec}^{-1}$).

Keywords: Organotin(IV), Photo stabilizers, UV irradiation, Poly(vinyl chloride), Photo degradation rate constant (k_d).

Introduction

Organotin (IV) compounds have gained significant interest in both the chemical and pharmaceutical industry. Tin (IV) form stable complexes with a unique structure and physicochemical properties that are used in organic synthesis as heat stabilizers and catalysts, in drug development as biologically active agents, and in other areas [1, 3]. One of the most importance points is using organotin compounds as Poly(vinyl chloride) photo stabilizers [4, 5]. Poly (vinyl chloride) is second just to polyethylene among the five sorts of general plastic materials, which was broadly utilized in industries including architecture, electronic, chemical engineering, packaging, transportation, etc. [6].

Monetarily accessible PVC has different auxiliary deformities because of the nearness of photosensitive chromophores, for example, allylic chlorine because of irregular unsaturation, tertiary fortified chloride, and contaminations inside the PVC polymeric chains can prompt photo degradation. Furthermore, the steric hindrance inside the monomeric units, i.e., the tacticity, could impact the corruption procedure [7]. In this manner, the assessment of the adjustments in the PVC properties under administration

conditions is significant so as to discover approaches to improve the solidness of PVC containing items [8, 9]. The photo stability of PVC polymeric materials to UV light (300-400 nm) has been examined [10, 12]. Different added substances at low concentration have been utilized to restrain the photo degradation. Besides organotin additives, there are organics [13], Schiff bases [14, 17], and others [18, 19]. As our interest of polymeric materials [20-23], we started researching the physical properties of PVC films containing organotin complexes as photo stabilizers with respect to UV light for significant lot (300 h). The photograph of photodecomposition rate consistent (k_d) was determined of PVC films.

Experimental

Synthesis of Organotin(IV) Complexes 1-3

Three organotin (IV) complexes, **1-3**, were synthesized as reported [24] from the reaction of naproxen and diorganotin (IV) chloride salts. The reaction of an equimolar mixture of naproxen (two mole equivalents) and dibutyltin (IV) chloride or diphenyltin (IV) chloride or dimethyltin (IV) chloride in methanol under reflux for 8 h gave the

corresponding *bis* (naproxen) diorganotin (IV) complex 1-3 respectively as in Figure 1. The structures and characterizations of Sn (IV) complexes have been confirmed by the

elemental analyses and various spectroscopic data and were in agreement with the ones reported [24].

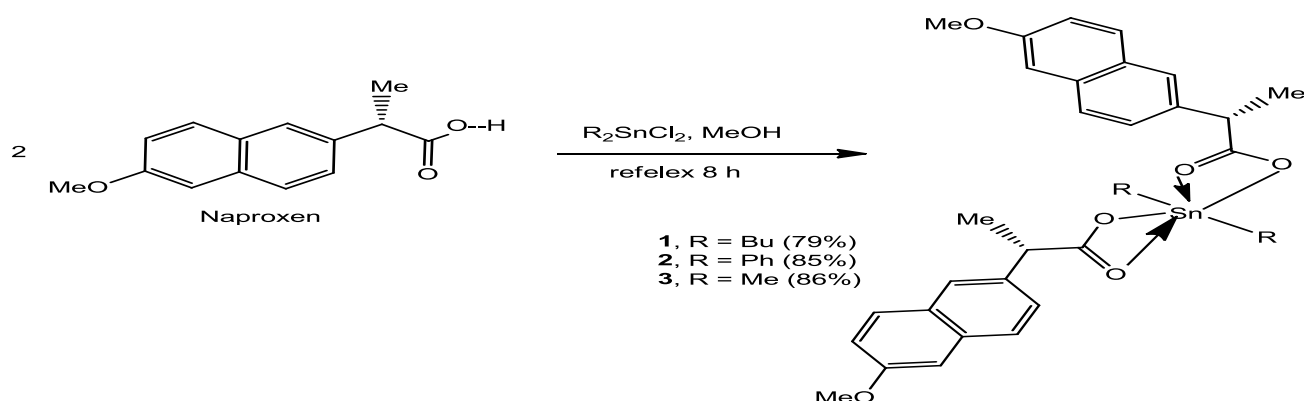


Fig. 1: Synthesis of diorganotin(IV) complexes 1-3

Films Preparation

PVC in tetrahydrofuran (5 g/100 mL) was re-precipitated with ethanol and dried for 24 h at 20°C under reduced pressure. The organotin complexes (0.5% by weight) were mixed with PVC at room temperature and were fixed using aluminum plate stands (Q-Panel Company, Homestead, FL, USA) [25, 27]. The thickness of PVC films (40 μm thickness) was measured using a Digital Caliper Vernier (Kevelaer, Germany).

Accelerated Testing Technique

Irradiation (290-360 nm; $\lambda_{\text{max}} = 313 \text{ nm}$) of PVC films was carried out using a standard procedure with an accelerated weather-meter QUV tester for 300 h.

Photodegradation Rate (k_d) of PVC Films using UV Spectrophotometer

A Shimadzu UV-Vis 160A-Ultraviolet Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) was used to measure the changes in the UV-visible spectra of PVC films during irradiation ($\lambda_{\text{max}} = 313 \text{ nm}$) [28]. The photodecomposition rate constant (k_d) of PVC films were calculated using Equations:

$$(a - x) = \ln a - k_d t \quad (1)$$

$$a - x = A_0 - A_\infty - A_0 + A_t = A_t - A_\infty \quad (2)$$

$$(A_t - A_\infty) = (A_0 - A_\infty) - k_d t \quad (3)$$

Where, $a = A_0 - A_\infty$; $x = A_0 - A_t$

a = concentration of PVC before irradiation; x = change in PVC concentration at time t during irradiation; A_0 = the absorption intensity of the PVC at t_0 , A_∞ = the absorption intensity at t_∞ and A_t = the absorption intensity after irradiation time t .

The plot of $(A_t - A_\infty)$ versus irradiation time (t) gives straight line in which the slope equals to k_d . The photodecomposition of PVC follows a first order kinetics [29].

Results and Discussion

The effect of organotin (IV) complexes on the PVC films photodecomposition was investigated. The PVC films (40 μm thickness) containing organotin (IV) complexes (0.5% by weight) were irradiated with a UV light ($\lambda_{\text{max}} = 313 \text{ nm}$) for 300 h. The irradiation led to a clear change in PVC films and decomposition took place. The plot of $\ln(A_t - A_\infty)$ against irradiation time (t) gave a straight line. The graphs showed first order kinetics in which the slope equaled the decomposition rate constant (k_d) for PVC films.

Figure (2) shows the change in $\ln(A_t - A_\infty)$ against irradiation time (t) for PVC films in the absence any additives. Figures 2-5 show the changes in the $\ln(A_t - A_\infty)$ against irradiation time for PVC films containing organotin (IV) additives (0.5% by weight) as stabilizers of PVC films on irradiation with light. Table 1 showed the photodecomposition rate constant (k_d) values of PVC films containing organotin(IV) complexes along with that of PVC (blank).

Table 1: Photodecomposition rate constant (k_d) of PVC films on UV irradiation (300 hrs.)

Film	k_d (sec ⁻¹)
PVC (control)	9.0×10^{-3}
PVC + 1	5.6×10^{-3}
PVC + 2	2.2×10^{-3}
PVC + 3	1.5×10^{-3}

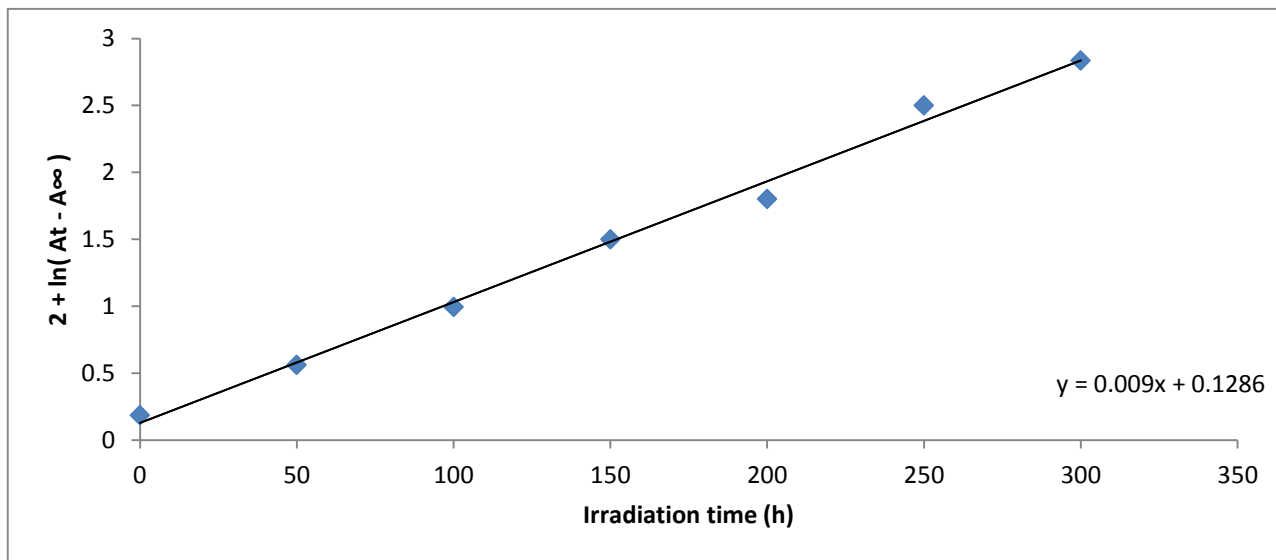


Fig. 2: Changes in ($A_t - A_\infty$) of PVC film (Control) against irradiation time

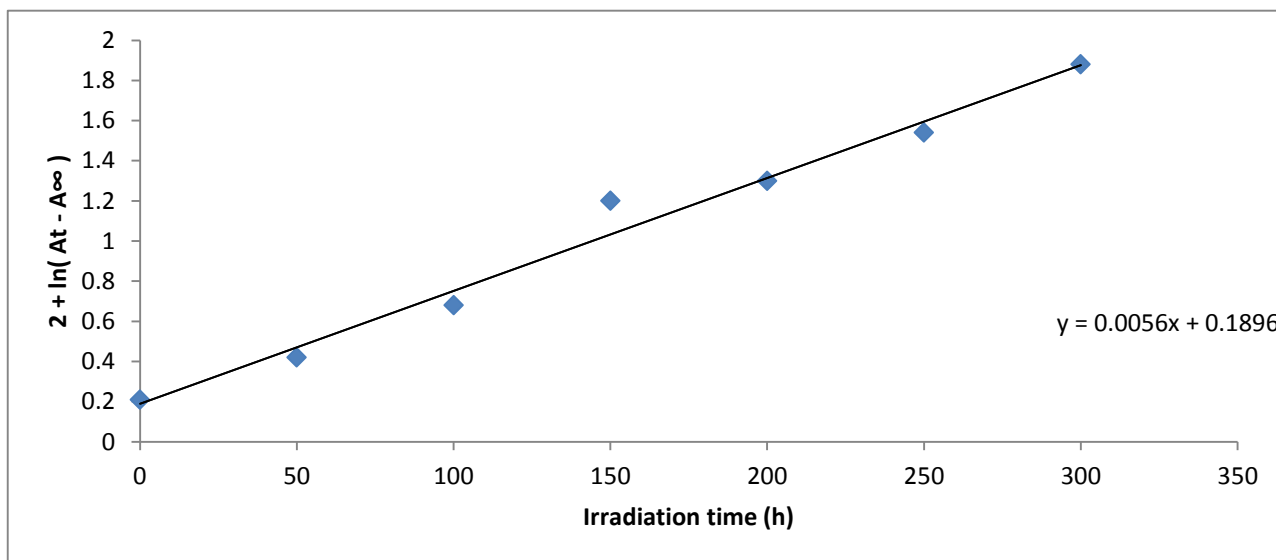


Fig. 3: Changes in ($A_t - A_\infty$) of PVC+1 film against irradiation time

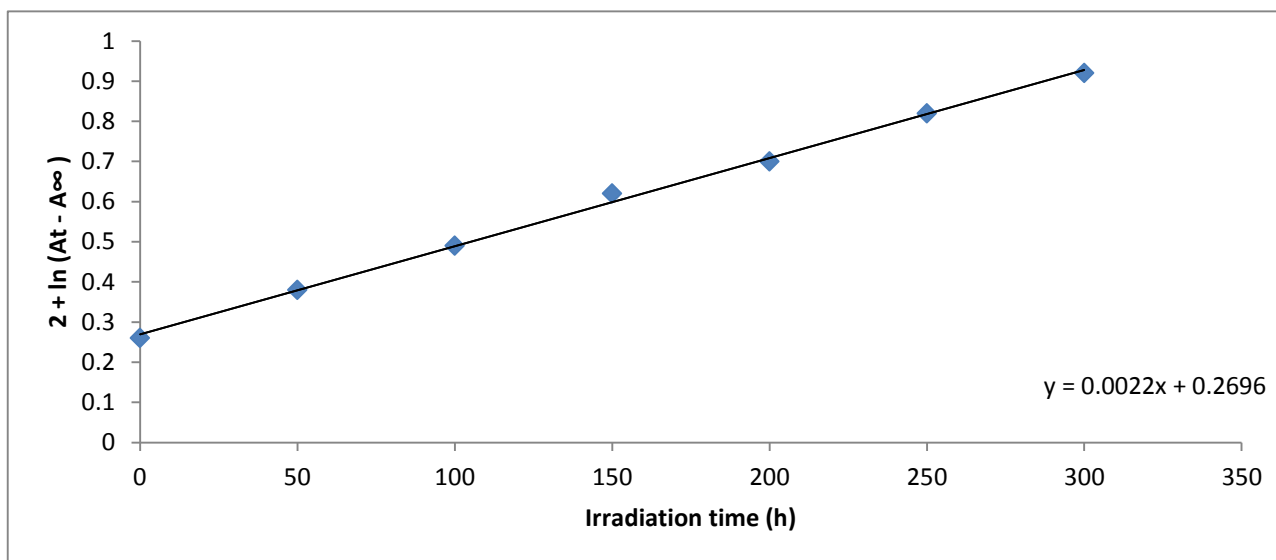


Fig. 4: Changes in ($A_t - A_\infty$) of PVC+2 film against irradiation time

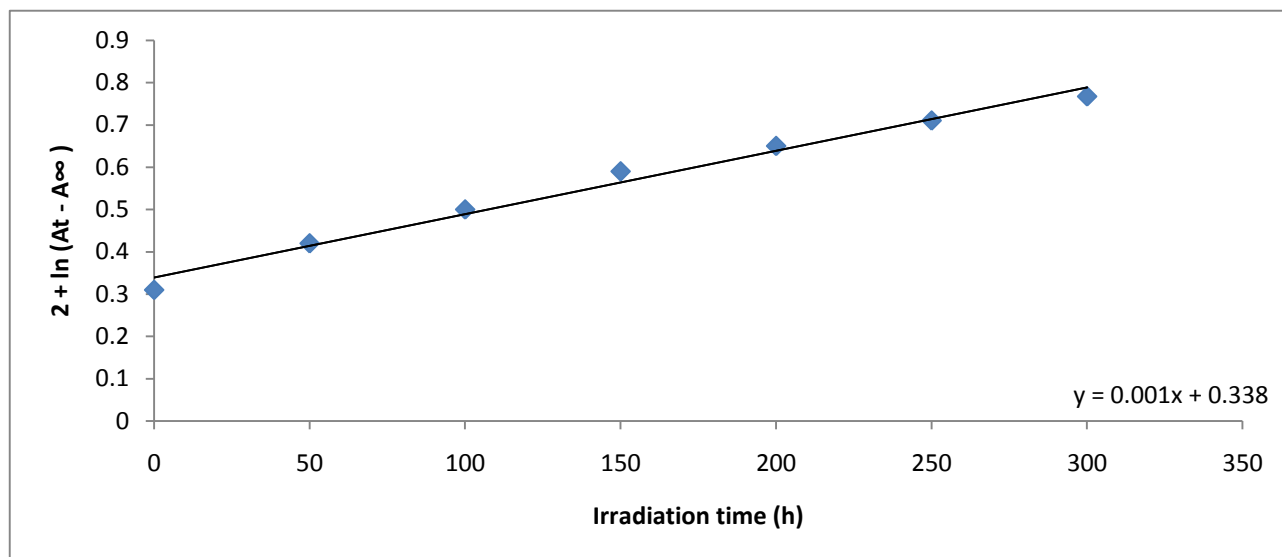


Fig. 5: Changes in $(A_t - A_\infty)$ of PVC + 3 film against irradiation time

It's clearly from Table 1 and Figures 2-5; that the rate constant (k_d) values are sensitive to presence of organotin (IV) complexes. The PVC photodecomposition rate constant for PVC films were high ($9.0 \times 10^{-3} \text{ sec}^{-1}$) in the absence of any additives. The rate constant was decreased significantly when organotin (IV) complexes were used as additives. The photo stabilization of PVC in the presence of organotin (IV) complexes follow the order of $1 < 2 < 3$. The complex 3 was the most efficient than the other complexes in photo stabilization of PVC films. Obviously, organotin (IV) complexes have acted as photo stabilizers for the photo stabilization of PVC films. The most efficient photo stabilizer always have low (k_d) value and that means

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these organotin (IV) complexes are stable towards UV light.

Conclusions

The photodecomposition rate constants for PVC films containing organotin (IV) complexes have been reduced significantly compared to the PVC in the absence of any additives. The photodecomposition rate constant for PVC films containing organotin (IV) was ($5.6-1.5 \times 10^{-3} \text{ sec}^{-1}$) compared to ($9.0 \times 10^{-3} \text{ sec}^{-1}$) for the blank PVC film. Dimethyltin (IV) complex was the most effective complex towards the photo stabilization of PVC. Such complex can be used as a PVC photo stabilizer for long term protection from sunlight and/or UV radiation.

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