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Synthesis and Application of Levofloxacin–Tin Complexes as New Photostabilizers for Polyvinyl Chloride

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Abstract: Polyvinyl chloride (PVC) is a synthetic polymer with a wide range of applications with impact on our daily life. It can undergo photodegradation with toxic products that are hazardous to both human health and the environment. In addition, photodegradation shortens the useful lifetime of the material. Elongation of the effective lifespan of PVC is, therefore, a salient area of research. Recently, a lot of attention has been directed toward the design, preparation, and usage of new additives that are capable of reducing the photodecomposition of PVC. This work investigates the synthesis of new levofloxacin-tin complexes and their potential exploitation against the photodecomposition of PVC. Several levofloxacin-tin complexes have been synthesized, in high yields, by a simple procedure and characterized. The potential use of the additives as photostabilizers for PVC has been investigated through the determination of weight loss, molecular weight depression, formation of fragments containing carbonyl and alkene groups, and surface morphology of irradiated PVC films. The results show that the new additives are effective in reducing the photodegradation of PVC. The new levofloxacin-tin complexes act as absorbers of ultraviolet light and quenchers of highly reactive species such as free radicals produced during photodegradation. They are more effective photostabilizers compared with organotin complexes previously reported. The complexes containing aromatic substituents were more effective than those counterparts having aliphatic residues.

Keywords: levofloxacin–tin complexes; polyvinyl chloride; photodecomposition; weight loss; molecular weight depression; surface morphology

1. Introduction

Plastics are invaluable materials and consequently are produced on a massive scale to meet ever-increasing demand [1]. Plastics display an assortment of chemical and physical properties which make them suitable for a variety of applications [2–4]. They are strong, light, water-resistant as well as resistant to microorganisms. They can also be produced cost-effectively in different shapes and forms. Thus, the application of plastics ranges from a replacement for paper in packaging to steel and wood in construction. Polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrene, and polyethylene terephthalate represent ca. 90% of the total plastics demand [5]. Plastics generally undergo degradation under ultraviolet (UV) radiation or if exposed to oxygen at high temperature [6]. The degradation due to UV absorption, for example, alters both the physical and mechanical properties of the polymeric materials leading to color changes, cracks, and deformation [7]. For a long duration of utility, therefore, it is desirable for plastics to be manufactured in a way that reduces the photooxidation and photodegradation processes [8].

PVC is a common polymeric material that is inexpensive to manufacture and has increasing global demand. PVC is utilized heavily in the building sector, office supplies, furniture, toys, packaging, medical devices, tubing, films, and sheets [9,10]. However, PVC
is generally hazardous to the health of humans and the environment. Therefore, PVC should be recycled and reutilized. Flotation is a useful method to treat solid particles and is widely used for the efficient recovery of minerals, solid waste, and heavy metals in water [11–13]. In addition, like many plastics, PVC suffers from photodegradation when exposed to UV light, sunlight, and high temperatures [14,15]. Photodegradation leads to undesirable alteration of its chemical and physical properties [16]. Examples of the changes include mass loss, elimination of volatile products, and generation of fragments of low molecular weight [17–21]. To hinder these changes and improve its photostability, PVC is mixed with additives during manufacture.

Ideally, only low concentrations of the additives are required, and they should cause no changes to the physical properties of PVC. They should also be inexpensive to produce, non-volatile, non-toxic, and environmentally friendly [22]. PVC additives are largely UV light absorbers, free radical scavengers, heat stabilizers, energy quenchers, flame retardants, and smoke suppressors [23]. Commercial additives include bis(2-ethylhexyl) phthalate, tris(di-tert-butylphenyl)phosphite, tetrachlorobiphenyl (Figure 1), and metal (e.g., barium and zinc)-containing materials [24,25]. Toxicity to humans or the requirement for co-stabilizers, however, are disadvantages of these additives [26,27]. The design, generation, and utilization of new additives are still imperative [6]. In the recent past, organotin complexes, polyphosphates, Schiff bases (Figure 1), and many other materials have been investigated as additives for the protection of PVC against photodegradation [6,28–31].

Figure 1. A selection of examples of PVC additives.

Organotin compounds possess an interesting range of properties and their uses have included various medicinal applications [32–34]. In addition, they have been used as stabilizers for polymers, agrochemicals, wood preservatives, catalysts, disinfectants, and biocides [35]. It is therefore unsurprising that the synthesis of new organotin complexes has attracted the attention of researchers in both academia and industry. Organotin compounds have also been investigated as PVC stabilizers [36]. The current work involves the synthesis of new levofloxacin-tin complexes and their role in the stabilization of PVC against irradiation. Levofloxacin is chiral and a very stable solid with a high melting point which has also been used as an antibiotic [37]. It is aromatic and contains a high content of heteroatoms (34.6%; O, N, and F) and thus the tin complexes were expected to act as good stabilizers by inhibition of the photodecomposition of PVC.
2. Materials and Methods

2.1. General

Chemicals and reagents were sourced from Merck (Gillingham, UK). PVC (Mv = ca. 180,000) was acquired from Petkim Petrokimya (Istanbul, Turkey). The elemental content (%) was measured on a Shimadzu AA-6880 spectrophotometer (Tokyo, Japan). The FTIR spectra were obtained using an FTIR-Shimadzu 8300 spectrophotometer (Tokyo, Japan). The $^1$H (400 MHz) and $^{119}$Sn NMR (149 MHz) spectra were recorded in deuterated dimethyl sulfoxide (DMSO-$d_6$) on Bruker BioSpin GmbH spectrometer (Zürich, Switzerland). A Q-Panel tester (Homestead, FL, USA) was used to irradiate the PVC films (UV light, $\lambda_{\text{max}} = 365$ nm; light intensity = $6.2 \times 10^{-9}$ Einstein dm$^{-3}$ s$^{-1}$) at 25 $^\circ$C. The tester has two fluorescent lamps (UV light; UV-B 365, 40 watts) on the sides. The films were placed parallel vertically at a distance of 10 cm from the light UV source and, to ensure uniform irradiation from all sides, the films were rotated from time to time. The viscosity measurements were performed on an Ostwald U-Tube viscometer (Ambala, India). Investigation of the surface morphology of the irradiated films was carried out using a Meiji Techno Microscope (Tokyo, Japan), an FEI Inspect S50 microscope (Brno, Czech Republic), and a Veeco instrument (Plainview, NY, USA).

2.2. Synthesis of Tin Complexes 1 and 2

A mixture of levofloxacin (361.4 mg, 1.0 mmol) and triphenyltin chloride (Ph$_3$SnCl; 1.0 mmol, 385.5 mg) or tributyltin chloride (Bu$_3$SnCl; 1.0 mmol, 325.5 mg) in methanol (MeOH; 30 mL) was heated under reflux for 6 h (Scheme 1). An off-white solid was collected by filtration on cooling, washed with MeOH (2 x 10 mL), and dried under reduced pressure to give complex 1 or 2 in 79 or 81% yield, respectively (Table 1).

![Scheme 1. Synthesis of tin complexes 1 and 2.](image)

Table 1. Melting point, yield, and microanalyses of complexes 1–5.

| Complex | M.P. (°C) | Yield (%) | C       | H       | N       | Sn        |
|---------|-----------|-----------|---------|---------|---------|-----------|
| 1       | 110–113   | 79        | 60.78 (60.87) | 4.96 (4.82) | 5.91 (5.92) | 16.69 (16.71) |
| 2       | 128–130   | 81        | 55.31 (55.40) | 7.17 (7.13) | 6.45 (6.46) | 18.22 (18.25) |
| 3       | 222–225   | 85        | 57.90 (58.02) | 5.06 (4.87) | 8.44 (8.46) | 11.92 (11.95) |
| 4       | 194–196   | 83        | 55.30 (55.42) | 6.12 (5.92) | 8.79 (8.81) | 12.42 (12.45) |
| 5       | 175–178   | 78        | 52.37 (52.49) | 5.12 (5.10) | 9.64 (9.67) | 13.62 (13.65) |

2.3. Synthesis of Tin Complexes 3–5

A mixture of levofloxacin (722.8 mg, 2.0 mmol) and diphenyltin dichloride (Ph$_2$SnCl$_2$; 1.0 mmol, 343.8 mg), dibutyltin dichloride (Bu$_2$SnCl$_2$; 1.0 mmol, 303.8 mg), or dimethyltin dichloride (Me$_2$SnCl$_2$; 1.0 mmol, 219.7 mg) in methanol (MeOH; 40 mL) was heated under reflux for 8 h (Scheme 2). On cooling, the off-white solid obtained was removed, washed with MeOH (2 x 15 mL), and dried to give complexes 3–5 in yields of 78–85% (Table 1).
2.4. PVC Films Preparation

PVC (5 g) was mixed with the tin complexes 1–5 (25 mg) in THF (100 mL) and stirred for 2 h. The resulting homogeneous mixture was poured onto a glass plate containing 15 holes of the thickness of ca. 40 µm. The plate was left to dry at 25 °C for 24 h and the films produced were dried in a vacuum oven at 40 °C for 8 h to ensure the removal of any traces of THF.

2.5. Determination of the Weight Loss of PVC

The PVC films were weighed prior to (W₀) and following (Wₜ) irradiation for a different duration (t). The PVC weight loss (%) due to irradiation was calculated using Equation (1) [38].

\[
\text{Weight loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100
\]  

2.6. Determination of the Average Molecular Weight (Mᵥ) of PVC

The PVC films after irradiation were dissolved in THF and their intrinsic viscosity, [η], was measured. Equation (2), the Mark–Houwink equation [39], was used to determine the Mᵥ of irradiated films.

\[
[\eta] = 1.63 \times 10^{-2} M_0^{0.766}
\]

2.7. FTIR Spectrophotometry of PVC

Small polymeric fragments containing carbonyl (C=O) and alkene (C=C) moieties are generated on the photodegradation of PVC. This process involved is mainly dehydrochlorination, the elimination of hydrochloride (HCl) from the PVC chains [40,41]. The FTIR spectra were recorded after different irradiation times of PVC. The intensities of the C=O (1714 cm⁻¹) and C=C (1618 cm⁻¹) absorption bands were monitored and compared to a reference peak (C–H bonds; 1328 cm⁻¹). The absorbances of the functional group (Aₛ; A_C=O or A_C=C) and the reference peak (Aᵣ; A_C–H) were used to calculate the functional group index (Iₛ; I_C=O or I_C=C) using Equation (3) [42].

\[
I_s = \frac{A_s}{A_r}
\]

3. Results and Discussion

3.1. Synthesis of Tin Complexes 1–5

Levofloxacin-tin complexes 1–5 were synthesized (Schemes 1 and 2) as off-white solids in good yields (Table 1). The reaction of levofloxacin and trisubstituted tin chlorides in a 1:1 molar ratio gave the respective complexes 1 and 2 (Scheme 1), while the reaction of
levofloxacin and disubstituted tin chlorides in a 2:1 molar ratio gave the corresponding complexes 3–5 (Scheme 2).

The FTIR data for complexes 1–5 indicated the disappearance of the OH absorption band that appears at 3443 cm\(^{-1}\) for levofloxacin. It was clear that the carboxylic proton has been eliminated on complexation with tin to produce 1–5. Indeed, the FTIR spectra of 1–5 showed new absorption bands at the 540–571 cm\(^{-1}\) and 450–495 cm\(^{-1}\) regions assigned to the Sn–C, and Sn–O bonds, respectively (Table 2). The carbonyl group (C=O) appeared as a strong absorption band in the 1614–1618 cm\(^{-1}\) region. The carboxylate (COO\(^-\)) group in complexes 1–5 appeared as two absorption bands at 1707–1714 cm\(^{-1}\) and 1383–1399 cm\(^{-1}\) corresponding to asymmetric (\(\nu_{\text{asym}}\)) and symmetric (\(\nu_{\text{sym}}\)) vibrations, respectively. The differences (\(\Delta\nu\)) between the \(\nu_{\text{asym}}\) and \(\nu_{\text{sym}}\) were 310–331 cm\(^{-1}\) (Table 2) indicating bidentate asymmetry [43].

Table 2. The FTIR absorption bands for complexes 1–5.

| Complex | C=O \(\nu\) cm\(^{-1}\) | COO \(\nu\) cm\(^{-1}\) | C=O \(\Delta\nu\) cm\(^{-1}\) | Sn–C \(\nu\) cm\(^{-1}\) | Sn–O \(\nu\) cm\(^{-1}\) |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1       | 1618            | 1714            | 1386            | 328             | 1588            |
| 2       | 1617            | 1718            | 1399            | 315             | 1575            |
| 3       | 1614            | 1714            | 1383            | 311             | 1581            |
| 4       | 1618            | 1707            | 1395            | 312             | 1586            |
| 5       | 1617            | 1707            | 1397            | 310             | 1587            |

The \(^1\)H NMR data for 1–5 did not show the presence of the carboxylic proton which appears at 15.21 ppm in the spectrum of levofloxacin. This provided further evidence that the complexation had taken place in which the carboxylic proton was replaced by the tin atom. The \(^1\)H NMR spectra of 1–5 are consistent with the presence of the protons from levofloxacin and substituent groups (phenyl, butyl, and methyl) attached to the tin atom (Table 3). The \(^119\)Sn NMR spectra showed distinctive singlet signals between −170.6 and −502.8 ppm (Table 3). Clearly, the tin atom has coordinated with levofloxacin to produce complexes 1–5. The chemical shifts indicated that complexes 1 and 2 have a coordination number of five while it is six for 3–5 [44–46].

Table 3. \(^1\)H and \(^119\)Sn NMR spectral data for 1–5.

| Complex | NMR (DMSO-\(d_6\), \(\delta\) ppm), and \(J\) (Hz) | \(^1\)H | \(^119\)Sn |
|---------|-----------------------------------|-----|-------|
| 1       | 9.13 (s, 1H, Ar), 7.95 (d, \(J = 12.0\) Hz, 1H, Ar), 7.57–7.32 (m, 15H, 3 Ph), 4.95 (m, 1H, CH), 4.58 (dd, \(J = 4.0\) & \(12.0\) Hz, 1H, 1H of CH\(_2\)), 4.37 dd, \(J = 4.0\) & \(12.0\) Hz, 1H, 1H of CH\(_2\)), 3.31 (m, 4H, CH\(_2\)CH\(_2\)), 2.45 (br, 4H, CH\(_2\)CH\(_2\)), 2.28 (s, 3H, Me), 1.45 (d, \(J = 7.0\) Hz, 3H, Me) | −170.6 | |
| 2       | 9.05 (s, 1H, Ar), 7.62 (d, \(J = 12.0\) Hz, 1H, Ar), 5.00 (m, 1H, CH), 4.65 (dd, \(J = 4.1\) & \(12.0\) Hz, 1H, 1H of CH\(_2\)), 4.43 dd, \(J = 4.1\) & \(12.0\) Hz, 1H, 1H of CH\(_2\)), 3.43 (m, 4H, CH\(_2\)CH\(_2\)), 2.78 (br, 4H, CH\(_2\)CH\(_2\)), 2.50 (s, 3H, Me), 1.74 (m, 6H, 3 CH\(_2\)), 1.62 (m, 6H, 3 CH\(_2\)), 1.39 (d, \(J = 7.0\) Hz, 3H, Me), 1.15 (m, 6H, 3 CH\(_2\)), 0.95 (t, \(J = 7.1\) Hz, 9H, 3 Me) | −175.9 | |
| 3       | 8.94 (s, 2H, Ar), 7.92 (d, \(J = 12.0\) Hz, 2H, Ar), 7.54–7.32 (m, 10H, 2 Ph), 5.02 (m, 2H, CH), 4.60 (dd, \(J = 4.0\) & \(12.0\) Hz, 2H, 1H of 2 CH\(_2\)), 4.40 (dd, \(J = 4.0\) & \(12.0\) Hz, 1H of 2 CH\(_2\)), 3.38 (m, 8H, 2 CH\(_2\)CH\(_2\)), 2.75 (br, 8H, 2 CH\(_2\)CH\(_2\)), 2.42 (s, 6H, 2 Me), 1.46 (d, \(J = 7.1\) Hz, 6H, 2 Me) | −502.8 | |
| 4       | 9.01 (s, 2H, Ar), 7.52 (d, \(J = 12.0\) Hz, 2H, Ar), 4.92 (m, 2H, 2 CH), 4.54 (dd, \(J = 4.0\) & \(12.0\) Hz, 2H, 1H of 2 CH\(_2\)), 4.40 dd, \(J = 4.1\) & \(12.0\) Hz, 2H, 1H of 2 CH\(_2\)), 3.44 (m, 8H, 2 CH\(_2\)CH\(_2\)), 2.75 (br, 8H, 2 CH\(_2\)CH\(_2\)), 2.51 (s, 6H, 2 Me), 1.60 (m, 4H, 2 CH\(_2\)), 1.52 (m, 4H, 2 CH\(_2\)), 1.36 (d, \(J = 7.0\) Hz, 6H, Me), 1.20 (m, 4H, 2 CH\(_2\)), 0.83 (t, \(J = 7.2\) Hz, 6H, 2 Me) | −313.5 | |
| 5       | 9.00 (s, 2H, Ar), 7.51 (d, \(J = 12.1\) Hz, 2H, Ar), 4.94 (m, 2H, 2 CH), 4.58 (dd, \(J = 4.0\) & \(12.2\) Hz, 2H, 1H of 2 CH\(_2\)), 4.40 (dd, \(J = 4.0\) & \(12.2\) Hz, 2H, 1H of 2 CH\(_2\)), 3.43 (m, 8H, 2 CH\(_2\)CH\(_2\)), 2.72 (br, 8H, 2 CH\(_2\)CH\(_2\)), 2.48 (s, 6H, 2 Me), 1.45 (d, \(J = 7.0\) Hz, 6H, 2 Me), 0.89 (s, 6H, 2 Me) | −227.3 | |
3.2. Weight Loss on Irradiation

Autocatalytic dehydrochlorination of PVC occurs when it is exposed to light, heat, and humidity. The discharge of HCl from PVC causes significant changes to its mechanical and physical properties. Thus, cross-linking and chain scission due to photoirradiation can lead to the formation of unsaturated small fragments, a decrease in molecular weight, and a loss in weight [38,47]. To assess the role played by complexes 1–5 (0.5% by weight) in stabilization, therefore, the weight loss of PVC on photoirradiation was determined. Equation (1) was used to calculate the percentage weight loss (%) and plotted against the time of irradiation (at 50 h intervals, Figure 2). Notably, the low concentration (0.5% by weight) of additives used is effective in reducing photodegradation of PVC without changing the color or physical properties of the films [48]. Figure 2 showed that the loss in weight was highest for the blank film with no additives. Clearly, the use of complexes 1–5 led to a decrease in weight loss relative to the blank film. The percentage weight loss was sharpest at the beginning of the irradiation (first 50 h) and continues steadily with irradiation. The percentage weight loss (%) after 50 h of irradiation was 0.26, 0.01, 0.06, 0.03, 0.09, and 0.12 for the blank PVC film, and those containing complexes 1, 2, 3, 4, 5, respectively. After the irradiation period (300 h), the corresponding percentage of weight losses (%) were 0.53, 0.21, 0.30, 0.26, 0.35, and 0.39 for the blank PVC film, and those containing complexes 1, 2, 3, 4, 5, respectively. Complexes 1 and 3, the additives with the highest aromatic content, were more efficient at PVC photostabilization compared with those containing aliphatic substituents (i.e., complexes 2, 4, and 5). The order of photostabilization of PVC was 1 > 3 > 2 > 4 > 5.

![Figure 2. Percentage weight loss of PVC films as a function of irradiation time.](image)

3.3. Average Molecular Weight (Mv) on Irradiation

Photoirradiation of PVC leads to the generation of smaller polymeric fragments with a subsequent decrease in Mv. The processes leading to the decrease in Mv of PVC include cross-linking and chain scission of the polymeric chains. The intrinsic viscosity [n] of a solution of the polymer is very sensitive to Mv and, therefore, it would be expected to drop for the irradiated PVC films [39,49]. In order to assess this, the PVC films were dissolved in THF following different irradiation times, and their viscosities were determined. Equation (2) was used to calculate the Mv values which were plotted against the duration of irradiation (50–300 h; Figure 3). Some insoluble residues were observed, indicating that branching and cross-linking of PVC have taken place during the irradiation process. In general, the values of Mv decreased steadily with irradiation time. All complexes 1–5 reduced the decreases in Mv relative to the blank film with complex 1 being the most effective. Hence, the reduction in the Mv of the blank PVC film after 100 h of irradiation...
was 58% whereas it was only 5% when 1 was used. After 300 h of irradiation, the reduction in Mv was 96% for the blank PVC film and 55% for the blend containing complex 1.

**Figure 3.** A plot of average molecular weight against irradiation time for PVC films.

### 3.4. FTIR Spectrophotometry on Irradiation

PVC photooxidation occurs on photoirradiation in the presence of oxygen with the formation of radical species (e.g., chloride and carbon radicals). The radicals cause destructive degradation of PVC with the ejection of volatile products such as HCl [50]. This results in PVC residues containing C=O (e.g., ketones and chloroketones) and C=C (unsaturated chains) groups (Figure 4) [47,51]. These groups are amenable to investigation by FTIR.

**Figure 4.** Photooxidation of PVC. *: Excited state.
The appearance and growth of the vibration bands corresponding to the C=O (1714 cm\(^{-1}\)) and C=C (1618 cm\(^{-1}\)) groups were monitored during the irradiation process. The increase in the intensity of the bands due to these functional groups was compared to a reference peak (C–H bond; 1328 cm\(^{-1}\)) that does not change significantly during the process [42]. The FTIR spectra for the PVC film without additives (Figure 5) show the changes that took place in the intensities of both C=O and C=C vibration bands as a result of irradiation.

![FTIR spectra of blank PVC file](image)

**Figure 5.** FTIR spectra of blank PVC file (a): before irradiation and (b): after irradiation.

Following irradiation, Equation (3) was used to calculate the values of \(I_{\text{C=O}}\) and \(I_{\text{C=C}}\) which were plotted against the duration of irradiation (Figures 6 and 7). The values of \(I_{\text{C=O}}\) and \(I_{\text{C=C}}\) increased with irradiation time and the changes were highest for the blank PVC film. The increases in the \(I_{\text{C=O}}\) and \(I_{\text{C=C}}\) were lower for the PVC blends with complexes 1-5 when compared to the blank film. The lowest \(I_{\text{C=O}}\) and \(I_{\text{C=C}}\) were observed for the films with the highly aromatic complexes 1 and 3. So, the \(I_{\text{C=O}}\) values after 300 h of irradiation were 0.98, 0.53, 0.66, 0.62, 0.72, and 0.79 for the blank PVC film, and those containing complexes 1, 2, 3, 4, 5, respectively. The corresponding \(I_{\text{C=C}}\) values at the end of irradiation were 0.93, 0.53, 0.66, 0.62, 0.70, and 0.77, respectively.
3.5. Surface Analysis on Irradiation

Changes in the surface of irradiated PVC film can be probed definitively using different types of microscopies [52,53]. Fundamentally, the surface of the nonirradiated film should be regular, homogenous, and smooth [28]. The optical microscopy images (Figure 8) showed that the damage and irregularities that appeared on the surface of the blank PVC film after irradiation were more apparent than for the blends containing additives 1–5. Accordingly, the levofloxacin–metal complexes provided protection for PVC film against photodegradation on exposure to UV.

Scanning electron microscope (SEM) imaging (Figure 9) revealed significant damage on the surface of the blank PVC film after irradiation. The effect was less on the surfaces of the PVC blends containing the levofloxacin–tin complexes, particularly additives 1 and 3.
Figure 8. Microscope images of irradiated PVC films.

Figure 9. SEM images of irradiated PVC films.
The atomic force microscope (AFM) images (Figures 10 and 11) showed rough PVC film surfaces after irradiation. The blank irradiated film had the highest degree of roughness and irregularities in comparison to the blends containing complexes 1–5. The roughness factors (Rq) were 483.0, 31.3, 42.6, 38.8, 48.3, and 55.1 for the irradiated blank film and those blended with complexes 1, 2, 3, 4, and 5, respectively. Notably, blending with complex 1 led to a 15.4-fold improvement in the Rq of the PVC film. The utilization of levofloxacin tin complexes as PVC additives led to greater improvement in Rq than the other reported organotin complexes [54–60] apart from those containing a high content of aromaticity and heteroatoms (Table 4) [61–63].

![AFM images](image)

**Figure 10.** AFM images of blank PVC film: (a): before irradiation and (b): after irradiation.

**Table 4.** Reduction in the Rq (by fold) of PVC using organotin complexes.

| Organic Unit in Tin Complex                  | Rq Reduction (Fold) | Reference |
|---------------------------------------------|---------------------|-----------|
| Levofloxacin                                | 15.4                | [this work] |
| Naproxen                                    | 5.2                 | [54]      |
| Carvedilol                                  | 6.4                 | [55]      |
| Furosemide                                  | 6.6                 | [56]      |
| Valsartan                                   | 7.4                 | [57]      |
| Telmisartan                                 | 9.4                 | [58]      |
| Trimethoprim                                | 11.3                | [59]      |
| Norfloxacin                                 | 12.9                | [60]      |
| Ciprofloxacin                               | 16.6                | [61]      |
| 4-(Benzylideneamino)benzenesulfonamide      | 18.4                | [62]      |
| 4-Methoxybenzoic acid                       | 21.2                | [63]      |

### 3.6. Photostabilization Mechanisms

On photoirradiation of PVC, highly reactive species containing radicals are formed [38,64]. UV absorbers soak up the energy from the light and release it slowly over time in a harmless form [65]. Levofloxacin–tin complexes stabilize PVC in a number of ways, including acting as absorbers of UV light and radical scavengers. Additionally, the tin atom in the additives (e.g., complex 1) is highly acidic and capable of eliminating the HCl released during irradiation (Scheme 3). Hydroperoxides (PO₂H) also cause photooxidative degradation of PVC [66]. Levofloxacin-containing additives (e.g., complex 1) function as hydroperoxide decomposers (Scheme 3). Finally, the polarized bonds within both the PVC and levofloxacin interact with each other to stabilize the blends.
**Figure 11.** AFM images of irradiated PVC films (a): PVC/1 (b): PVC/2, (c): PVC/3, (d): PVC/4, and (e): PVC/5.
Scheme 3. Role played by complex 1 in stabilizing polyvinyl chloride.

4. Conclusions

Several new levofloxacin-tin complexes were produced in high yields using an efficient procedure. The levofloxacin-tin complexes were mixed with polyvinyl chloride and their role as photostabilizers was investigated. The additives reduced the damage caused to polyvinyl chloride polymeric chains due to irradiation. The new additives reduce the formation of degraded fragments and irregularities within the surfaces of polyvinyl chloride films. In addition, they decrease the reduction in molecular weight and mass loss. Levofloxacin-tin complexes are absorbers of ultraviolet light and quenchers of radicals, peroxides, and hydrogen chloride produced during photodegradation. The newly synthesized are more effective as photostabilizers than many organotin complexes that have been reported. The additives containing a higher content of aromaticity were more effective than those containing aliphatic substituents. Using the complexes as additives is therefore a promising route to augmentation of the useful lifetime of PVC, noting that their environmental impact is yet to be assessed.

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References
1. Geyer, R.; Jambeck, J.R.; Law, K.L. Production, use, and fate of all plastics ever made. Sci. Adv. 2017, 3, e1700782. [CrossRef] [PubMed]
2. Neuba, L.D.M.; Junio, R.F.P.; Ribeiro, M.P.; Souza, A.T.; Lima, E.D.S.; Filho, F.D.C.G.; Figueiredo, A.B.-H.D.S.; Braga, F.D.O.; De Azevedo, A.R.G.; Monteiro, S.N. Promising mechanical, thermal, and ballistic properties of novel epoxy composites reinforced with Cyperus malaccensis sedge fiber. Polymers 2020, 12, 1776. [CrossRef] [PubMed]
3. Zhang, Y.; Yu, X.; Cheng, Z. Research on the application of synthetic polymer materials in contemporary public art. Polymers 2022, 14, 1208. [CrossRef] [PubMed]
35. Davies, A.G. Organotin Chemistry, 2nd ed.; Wiley-VCH: Weinheim, Germany; John Wiley: Chichester, UK, 2004.
36. Arks, E.; Balköse, D. Thermal stabilisation of poly(vinyl chloride) by organotin compounds. Polym. Degrad. Stab. 2005, 88, 46–51. [CrossRef]
37. Croom, K.F.; Goa, K.L. Levofloxacin: A review of its use in the treatment of bacterial infections in the United States. Drugs 2003, 63, 2769–2802. [CrossRef]
38. Pospíšil, J.; Nešpurek, S. Photostabilization of coatings. Mechanisms and performance. Prog. Polym. Sci. 2000, 25, 1261–1335. [CrossRef]
39. Pepperl, G. Molecular weight distribution of commercial PVC. J. Vinyl Addit. Technol. 2000, 6, 88–92. [CrossRef]
40. Karayildirim, T.; Yamik, J.; Yüksel, M.; Saglam, M.; Haussmann, M. Degradation of PVC containing mixtures in the presence of HCl fixators. J. Polym. Environ. 2005, 13, 365–379. [CrossRef]
41. Nief, O.A. Photostabilization of polyvinyl chloride by some new thiadiazole derivatives. Eur. J. Chem. 2015, 6, 242–247. [CrossRef]
42. Gaumet, S.; Gardette, J.-L. Photo-oxidation of poly(vinyl chloride): Part 2—A comparative study of the carbonylated products in photo-chemical and thermal oxidations. Polym. Degrad. Stab. 1991, 33, 17–34. [CrossRef]
43. Alcock, N.W.; Culver, J.; Roe, S.M. Secondary bonding. Part 15. Influence of lone pairs on coordination: Comparison of diphenyl-tin (IV) and –tellurium (IV) carboxylates and dithiocarbamates. J. Chem. Soc. Dalton Trans. 1992, 9, 1477–1484. [CrossRef]
44. Pejchal, V.; Holeček, J.; Nadvorník, M.; Lyska, A. 13C and 119Sn NMR spectra of some mono-n-butyltin (IV) compounds. Collect. Czechoslov. Chem. Commun. 1995, 60, 1492–1501. [CrossRef]
45. Shahid, K.; Ali, S.; Shahzadi, S.; Badshah, A.; Khan, K.M.; Maharvi, G.M. Organotin (IV) complexes of aniline derivatives. I. Synthesis, spectral and antibacterial studies of di- and triorganotin (IV) derivatives of 4-bromomaleamic acid. Synth. React. Inorg. Met. Chem. 2003, 33, 1221–1235. [CrossRef]
46. Rehman, W.; Baloch, M.K.; Badshah, A.; Ali, S. Synthesis and characterization of biologically potent di-organotin (IV) complexes of mono-methyl glutarate. J. Chin. Chem. Soc. 2005, 52, 231–236. [CrossRef]
47. Chaochanchaikul, K.; Rosarppat, V.; Sombatsompop, N. Photodegradation profiles of PVC compound and wood/PVC composites under UV weathering. Express Polym. Lett. 2013, 7, 146–160. [CrossRef]
48. Balakit, A.A.; Ahmed, A.; El-Hiti, G.A.; Smith, K.; Yousif, E. Synthesis of new thiophene derivatives and their use as photostabilizers for rigid poly(vinyl chloride). Int. J. Polym. Sci. 2015, 2015, 510390. [CrossRef]
49. Skillcorn, D.E.; Perkins, G.G.A.; Slark, A.; Dawkins, J.V. Molecular weight and solution viscosity characterization of PVC. J. Vinyl Addit. Technol. 1993, 15, 105–108. [CrossRef]
50. Gardette, J.L.; Gaumet, S.; Lemaire, J. Photooxidation of poly(vinyl chloride). I. A reexamination of the mechanism. Macromolecules 1989, 22, 2576–2581. [CrossRef]
51. Pi, H.; Xiong, Y.; Guo, S. The kinetic studies of elimination of HCl during thermal decomposition of PVC in the presence of transition metal oxides. Polym. Plast. Technol. Eng. 2005, 44, 275–288. [CrossRef]
52. See, C.H.; O’Haver, J. Atomic force microscopy characterization of ultrathin polystyrene films formed by admicellar polymerization on silica disks. J. Appl. Polym. Sci. 2003, 89, 36–46. [CrossRef]
53. Nikafshar, S.; Zabihi, O.; Ahmadi, M.; Mirmohseni, A.; Taseidifar, M.; Naebe, M. The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber. Materials 2017, 10, 180. [CrossRef]
54. Hadi, A.G.; Yousif, E.; El-Hiti, G.A.; Ahmed, D.S.; Jawad, K.; Alotaibi, M.H.; Hashim, H. Long-term effect of ultraviolet irradiation on poly(vinyl chloride) films containing naproxen diorganotin(IV) complexes. Polymers 2019, 24, 2396. [CrossRef]
55. Mousa, O.G.; El-Hiti, G.A.; Baashen, M.A.; Bufaroosha, M.; Ahmed, A.; Ahmed, A.A.; Ahmed, D.S.; Yousif, E. Synthesis of carvedilol-organotin complexes and their effects on reducing photodegradation of poly(vinyl chloride). Polymers 2021, 13, 500. [CrossRef] [PubMed]
56. Ali, M.M.; El-Hiti, G.A.; Yousif, E. Photostabilizing efficiency of poly(vinyl chloride) in the presence of organotin(IV) complexes as photostabilizers. Molecules 2016, 21, 1151. [CrossRef] [PubMed]
57. Mohammed, A.; El-Hiti, G.A.; Yousif, E.; Ahmed, A.A.; Ahmed, D.S.; Alotaibi, M.H. Protection of poly(vinyl chloride) films against photodegradation using various valsartan tin complexes. Polymers 2020, 12, 969. [CrossRef] [PubMed]
58. Hadi, A.G.; Jawad, K.; El-Hiti, G.A.; Alotaibi, M.H.; Ahmed, A.A.; Ahmed, D.S.; Yousif, E. Photostabilization of poly(vinyl chloride) by organotin(IV) compounds against photodegradation. Molecules 2019, 24, 3557. [CrossRef] [PubMed]
59. Yaseen, A.A.; Yousif, E.; Al-Tikrity, E.T.B.; El-Hiti, G.A.; Kariuki, B.M.; Ahmed, D.S.; Bufaroosha, M. FTIR, weight, and surface morphology of poly(vinyl chloride) doped with tin complexes containing aromatic and heterocyclic moieties. Polymers 2021, 13, 3264. [CrossRef]
60. Fadhil, M.; Yousif, E.; Ahmed, D.S.; Mohammed, A.; Hashim, H.; Ahmed, A.; Kariuki, B.M.; El-Hiti, G.A. Synthesis of new norfloxacin–tin complexes to mitigate the effect of ultraviolet-visible irradiation in polyvinyl chloride films. Polymers 2022, 14, 2812. [CrossRef]
61. Ghazi, D.; El-Hiti, G.A.; Yousif, E.; Ahmed, D.S.; Alotaibi, M.H. The effect of ultraviolet irradiation on the physicochemical properties of poly(vinyl chloride) films containing organotin(IV) complexes as photostabilizers. Molecules 2018, 23, 254. [CrossRef]
62. Ghani, H.; Yousif, E.; Ahmed, D.S.; Kariuki, B.M.; El-Hiti, G.A. Tin complexes of 4-(benzylideneamino)benzenesulfonamide: Synthesis, structure elucidation and their efficiency as PVC photostabilizers. Polymers 2021, 13, 2434. [CrossRef]
63. Hadi, A.G.; Baqir, S.J.; Ahmed, D.S.; El-Hiti, G.A.; Hashim, H.; Ahmed, A.; Kariuki, B.M.; Yousif, E. Substituted organotin complexes of 4-methoxybenzoic acid for reduction of poly(vinyl chloride) photodegradation. Polymers 2021, 13, 3946. [CrossRef]
64. Scott, G. Mechanism of Polymer Degradation and Stabilization; Elsevier: New York, NY, USA, 1990.
65. Larché, J.F.; Bussière, P.O.; Therias, S.; Gardette, J.L. Photooxidation of polymers: Relating material properties to chemical changes. Polym. Degrad. Stab. 2012, 97, 25–34. [CrossRef]
66. Pospíšil, J.; Klemchuk, P.P. Oxidation Inhibition in Organic Materials; CRC Press: Boca Raton, FL, USA, 1989; Volume 1, pp. 48–49.