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Hanan Ibrahiem
Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq,
hanan.ibrahiem@nahrainuniv.edu.iq

Emad Yousif
Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq,
emad.yousif@nahrainuniv.edu.iq

Gamal A. El-Hiti
Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia, gelhiti@ksu.edu.sa

Mohammed H. Al-Mashhadani
Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq,
mohammed.mashhadani@nahrainuniv.edu.iq

Dina S. Ahmed
Department of Chemical Industries, Institute of Technology-Baghdad, Middle Technical University, Baghdad, Iraq, dina_saadi@mtu.edu.iq

See next page for additional authors

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RESEARCH ARTICLE

Impact of Ultraviolet Radiation on the Aging Properties of PVC Films Doped by Tin(IV) Complexes

Hanan Ibrahiem [1], Emad Yousif [1,*], Gamal A. El-Hiti [2], Mohammed H. Al-Mashhadani [1], Dina S. Ahmed [3], Muna Bufaroosha [4]

[1] Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
[2] Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia
[3] Department of Chemical Industries, Institute of Technology-Baghdad, Middle Technical University, Baghdad, Iraq
[4] Department of Chemistry, College of Science, United Arab Emirates University, Al-Ain, United Arab Emirates

ABSTRACT

Using ^{1}H-, ^{13}C-, and ^{119}Sn-nuclear magnetic resonance (NMR) spectroscopies in addition to Fourier transform infrared spectroscopy (FTIR) for structural identification, we synthesized and studied three tin complexes of Ibuprofen in this study. To improve poly(vinyl chloride) (PVC)'s photo-stability, the produced complexes were mixed one at a time. FTIR techniques were employed to evaluate their effectiveness, and the results indicated the formation of new groups inside the polymer structure following exposure to ultraviolet radiation. We also investigated the weight loss of the polymer under irradiation and calculated the average molecular weight by comparing the viscosity before and after exposure. Additionally, a variety of methods were used to investigate the surface morphology of PVC before and after radiation. After irradiation, PVC treated with Ibuprofen tin complexes showed less cracks and spots and a smoother surface than untreated PVC, according to optical and scanning electron microscopy (SEM) data. The modified polymers showed increased resistance to photodegradation and had lower roughness factor, weight reduction, surface damages, and small fragments generated compared to the blank PVC. This shows that the Ibuprofen tin compounds that were produced may work extremely well as photo-stabilizers for PVC. Complex 1 performed better than the other stabilizers, which can be due to its large conjugation system.

Keywords: Ibuprofen tin complexes, optical microscope, PVC photostability, SEM, surface morphology

Introduction

PVC is utilized extensively in transportation, construction, and other industries due to its high rigidity, flame retardancy, chemical resistance, and affordability. PVC has fewer applications due to its weak photostability, even with these benefits. PVC quickly experiences autocatalytic dehydrochlorination in the presence of sunshine when used outside, resulting in the creation of conjugated polyene sequences and material discoloration. [1,2] The mechanical qualities of PVC deteriorate as a result of these chemical changes. In order to improve PVC's anti-aging qualities, a number of additives are used, including radical scavengers, absorbers, excited-state quenchers, and UV light screening agents. [3–5] Furthermore, it has been demonstrated that adding inorganic fillers as light shield agents enhances PVC's anti-aging properties. [6,7] The nature of the polymer has a significant impact on how different polymers interact with one another.

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* Corresponding author.
E-mail addresses: hanan.ibrahiem@nahrainuniv.edu.iq (H. Ibrahiem), emad.yousif@nahrainuniv.edu.iq (E. Yousif), gelhiti@ksu.edu.sa (G. A. El-Hiti), mohammed.mashhadani@nahrainuniv.edu.iq (M. H. Al-Mashhadani), dina_saadi@mtu.edu.iq (D. S. Ahmed), muna.bufaroosha@uaeu.ac.ae (M. Bufaroosha).

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When it comes to char yields, weight loss rate, and onset temperature, various plastic categories exhibit distinct behaviors. While the breakdown of other polymers is a single-step process, the decomposition of PVC can be split into two stages: the dehydrochlorination stage and the breakdown of the intermediate from the dehydrochlorination stage.[8] The decomposition of combinations becomes more complex due to the varied behaviors of polymers. The degree of phase dispersion or the polymer's miscibility has a significant impact on how various polymers interact with one another.[9] As a result, the melting process can cause homogenous mixes to develop when heated. While interactions take place in the phase boundaries of a heterogeneous blend, inhomogeneous samples, the degradation products of each polymer are in direct contact with each other, resulting in a higher combined influence on thermal degradation.[10] One polymer's breakdown products can either stabilize or destabilize the blend's other polymers.[11] The polymers' molecular weight was lowered by random scission, depolymerization, intramolecular transfer reaction, and intermolecular transfer reaction, among other degradation reactions.[12]

This paper provides a detailed account of the synthesis of Ibuprofen tin complexes and offers a comprehensive evaluation of their efficacy as photostabilizers for polyvinyl chloride (PVC). Ibuprofen tin complexes are postulated to serve as effective ultraviolet (UV) absorbers. The rationale behind their application as photo-stabilizers lies in their capacity to absorb UV light, thereby shielding PVC from the deleterious effects of UV-induced decomposition. The significance of this project extends beyond mere material stabilization; it holds substantial environmental promise by potentially mitigating plastic usage, a critical factor contributing to the escalating harm inflicted upon the marine ecosystem. As these ibuprofen tin complexes demonstrate their potential to enhance the UV resistance of PVC, this research aligns with the broader goal of fostering sustainable practices and addressing environmental concerns associated with plastic waste.

Materials and methods

Chemicals and reagents were sourced from Sigma-Aldrich and employed without additional purification. Polyvinyl chloride (PVC) with an average molecular weight (MV $\approx$ 169,000) was obtained from Petkim Petrokimya. The identification of synthesized molecules involved the use of various techniques. The FTIR spectrophotometer (8300 Shimadzu, Kyoto, Japan) was employed for initial characterization. Subsequently, 1H-NMR and ^{13}C-NMR spectra (recorded in DMSO-d6 with TMS) were acquired using a Bruker DRX300 NMR spectrometer, and Varian INOVA and Bruker DRX spectrometers were utilized for data collection, including ^{119}Sn NMR (107 MHz). UV exposure of PVC films was conducted using an accelerated weather meter from Q-Panel Company. NMR samples, consisting of 20 mg of substance dissolved in 2 mL of Dimethyl sulfoxide (DMSO) at room temperature, were prepared and analyzed with 400 MHz ^{1}H and ^{13}C-NMR and 107 MHz ^{119}Sn-NMR. Samples were exposed to radiation at ambient temperature, with a maximum wavelength of 365 nm. Furthermore, the Ostwald U-Tube Viscometer method was utilized to measure viscosity in order to determine the molecular weight of the polymer. TESCAN MIRA3 LMU EDS was used to examine the morphology of PVC film surfaces, using an accelerating voltage of 10 kV.

Synthesis of Ph_2SnL_2 Complex (1)

An appropriate quantity of Ph_2SnCl_2 (0.34 g; 1.0 mmol) and Ibuprofen (0.412 g; 2.0 mmol) were combined, and the mixture was stirred for six hours in boiling methanol (30 mL). After bringing the combination down to ambient temperature and filtering it to extract the crude product, methanol (15 mL) was added to recrystallize the crud product to obtain the intended chemical (complex **1**).

Synthesis of Bu_3SnL and Me_3SnL Complex (2 and 3)

In boiling methanol (30 mL), an appropriate amount of Ibuprofen (0.206 g; 1.0 mmol) was combined with either 0.19 g; 1.0 mmol) or 0.33 g; 1.0 mmol) of Me_3SnL. The mixture was then stirred for eight hours. The resulting mixture was then allowed to reach room temperature before being filtered, and methanol (15 mL) was added to recrystallize the crud product to obtain the intended molecules (complex **2** and **3**).

Making PVC films

To get a homogeneous mixture, PVC (5.0 g) in tetrahydrofuran (THF; 100 mL) was agitated for two hours at room temperature with 0.5 weight percent of the complexes. Subsequently, it was put onto the glass plates to create uniform films 40 μm thick. A vacuum was used to dry each manufactured film in order to eliminate any remaining solvent that may have affected the measurements.

Applying the weight loss method to examine PVC photodegradation

By estimating the weight loss of the polymer throughout the irradiation duration in the presence of the stabilizers, the photo-stability of PVC was also investigated. Eq. (1) was thus used to compute weight loss.

$$\text{Weight loss } (\%) = \frac{W_0 - W_t}{W_0} \times 100 \quad (1)$$

At which W0 denotes the PVC weight prior to irradiation and Wt denotes the weight following radiation. [13]

Applying FTIR methodology to examine PVC photodegradation

The photodegradation of polymer films was also investigated using the FTIR approach, which tracked the emergence and expansion of alkene and carbonyl C=O groups. [14] Applying Eq. (2), the functional group index (Is) for the groups C=O and C=C was ascertained.

$$I_s = \frac{A_s}{A_r} \quad (2)$$

At which Ar is the standard peak absorbance and As is the absorbance of the functional group.

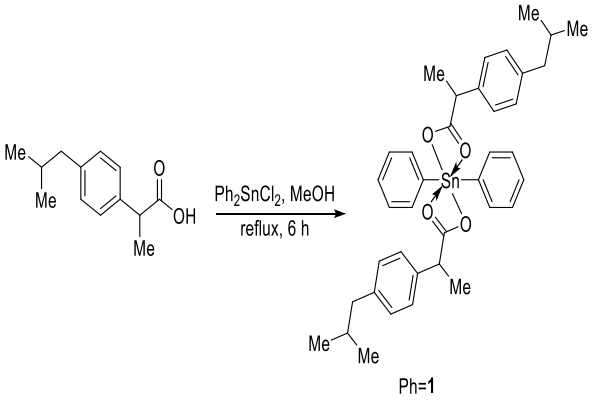
Determining PVC's average Molecular Weight (MV)

Eq. (3) was used to quantify the intrinsic viscosity [η] of the polymer solution and the MV of PVC following irradiation. The Mark-Houwink equation is the name given to this formula. [15]

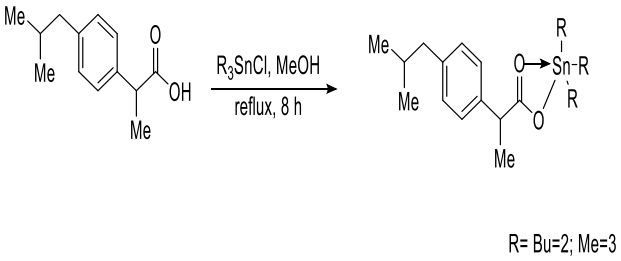
$$[\eta] = 1.63 \times 10^{-2}\, M_v^{0.766} \quad (3)$$

Results and discussion

The synthesis of three distinct organotin(IV) complexes, namely Ph_2SnL_2, Bu_3SnL, and Me_3SnL, was achieved through the amalgamation of di- and tri-organotin chlorides with ibuprofen, employing a ligand (L). This synthetic process was conducted under reflux conditions, spanning 6–8 hours, utilizing methanol as the solvent (refer to Schemes 1 and 2 for a graphical representation of the synthesis). Notably, the choice of ibuprofen as a component contributes to the enhanced stability of the resulting tin compounds, ensuring a high level of purity. [16] Comprehensive data pertaining to these synthesized complexes are meticulously presented in Table 1 for further reference and analysis see Schemes 1 and 2.



Scheme 1. Preparation of complex 1.



Scheme 2. Preparation of complexes 2 and 3.

Table 1. Physical properties of Ibuprofen tin complexes.

Complex	Code	Color	Melting point°C	Yield%
Ph_2SnL_2	1	White	208–210	72
Bu_3SnL	2	White	198–200	65
Me_3SnL	3	White	192–194	75

Characterization of Ibuprofen and its complexes by FTIR spectroscopy

The free ligand, ibuprofen, usually shows up as a band at 1700–1750 cm^{-1} corresponding to the C=O stretching vibration and a significant carboxylic acid broad peak in the region of 3200–3500 cm^{-1}, which belongs to OH groups, in the FTIR spectra study. This peak is also influenced by the carboxylic acid's hydroxyl (OH) group. The spectra of Ph_2SnL_2, Bu3SnL, and Me3SnL exhibit significant alterations upon complexation with di- or tri-organotin chlorides in methanol under reflux conditions.

Regarding Ph_2SnL_2, the carboxylic acid peak undergoes a noteworthy alteration. The OH stretching band, which is normally located between 3200 and 3500 cm^{-1}, disappearing is a crucial indicator of coordination through the carboxylic acid group. The C=O stretching vibration changes or shifts, frequently

showing up at a wavenumber that is marginally different from the free ligands, indicating that the carboxylate is involved in the complex formation. There could be further peaks that show up in the lower frequency ranges (500–1500 cm^{-1}), which are associated with vibrations of the metal-ligand.

In a similar vein, Bu_3SnL's FTIR spectrum shows alterations indicative of the ligand-tributyltin coordination. The OH group clearly vanishes, typically followed by changes in the C=O peak. There are new peaks that occur, such as those between 2800 and 2900 cm^{-1}, which belong to the CH of aliphatic groups and show the development of metal-ligand connections. To detect these modifications, a comparison with the ligand spectrum is essential.

The trimethyltin combination Me3SnL should exhibit similar OH peak disappearance and changes in the C=O stretching band, according to the FTIR analysis. The carboxylic acid group's involvement in complexation is amply demonstrated by the absence of the OH group and any changes in the C=O peak location. Further spectrum alterations could reveal the type of interactions between the metal and the ligand.

A comprehensive analysis of the modifications brought about by metal coordination is possible by contrasting these complexes with the free ligand's FTIR spectrum. Coordinating through the carboxylic acid group is supported by the removal of the OH group in all complexes and changes in the C=O peak. Any distinct characteristics or changes in the complexes' spectra can shed light on the particular interactions that occur between certain organotin species and the ligand.

Characterization of Ibuprofen and its complexes by NMR spectroscopies

Nuclear Magnetic Resonance (NMR) spectroscopy was used to characterize the three organotin(IV) complexes, Ph_2SnL_2, Bu_3SnL, and Me_3SnL, which were synthesized utilizing ibuprofen as a ligand (L) and di- or tri-organotin chlorides under reflux conditions in methanol solvent. The proton signals of the organotin complexes and the ligand Ibuprofen were seen in the ^{1}H-NMR spectra, which made it possible to determine the chemical shifts and coupling patterns. The coordination modes were determined with the help of the ^{13}C-NMR spectra, which revealed details on the carbon habitats in the complexes and the ligand. Additionally, validating the formation of organotin(IV) complexes and evaluating the tin coordination conditions required the use of ^{119}Sn-NMR spectroscopy. These NMR techniques were crucial in clarifying the structures and validating the effective synthesis of these organotin complexes, offering important insights into their coordination chemistry and chemical characteristics.

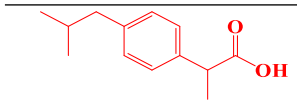
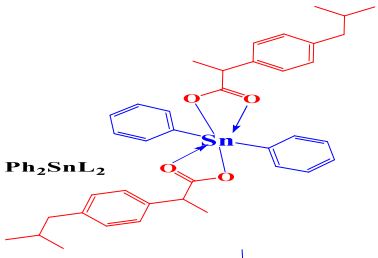
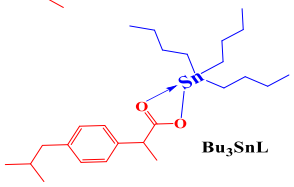
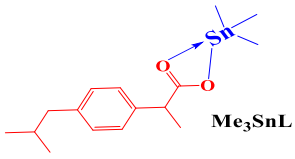
Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

The ^{1}H NMR spectrum of Ibuprofen, the ligand used in the synthesis of organotin(IV) complexes, reveals important information about its structural characteristics. First, the presence of a free hydroxyl moiety is shown by a sharp singlet at 10.50 ppm, which corresponds to the hydroxyl group (OH). As we get into the aromatic area, the two doublets at 7.38 ppm and 7.19 ppm with an 8.0 Hz coupling constant (J) represent the molecule's aromatic protons (Ar). The existence of these peaks confirms the integrity of the aromatic ring in ibuprofen. Furthermore, the proton next to the carbonyl group (CH next to carbonyl) corresponds to a quartet at 3.73 ppm with a coupling constant (J) of 11.0 Hz. This peak demonstrates the carbonyl functionality of the ligand. A multiplet at 2.51 ppm is visible in the spectrum upon closer examination, and it is thought to be caused by protons in the methylene group (CH_2) next to the aromatic ring. It is important to note, though, that this peak appears to overlap with signals from dimethyl sulfoxide (DMSO). This could be the result of insufficient solvent suppression during the NMR acquisition, or it could be the result of solvent contaminants.

In addition, a multiplet at 2.07 ppm in the spectrum indicates a proton (CH) sandwiched between two methyl groups. This peak aligns with Ibuprofen's predicted structure. Ultimately, the presence of these methyl substituents is confirmed by two doublets at 1.51 ppm and 1.02 ppm with coupling constants of 8.0 Hz, which reflect the methyl groups (CH_3) in the ligand. The hydroxyl group, aromatic protons, carbonyl adjacent protons, methylene group, methine group, and methyl groups are among the distinctive peaks in the ^{1}H NMR spectra of Ibuprofen that correlate to its structural constituents. When creating organotin(IV) complexes, this spectrum is an invaluable tool for verifying the identification and purity of the ligand. The effective coordination of the ligand with the organotin species would be indicated by any alterations or shifts in these peaks during complex formation. The data from the ^{1}H-NMR spectra of the produced ligand and complexes were compiled in Table 2.

The structure and bonding interactions of the diphenyltin complex, Ph_2SnL_2, where two molecules of the ligand Ibuprofen are coordinated to the tin core, are shown by the ^{1}H-NMR spectrum.

Table 2. ^{1}H-NMR spectral data for ligand and metal complexes.

Compound	^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm, J in Hz)
 **Ibuprofen (L)**	10.50 (s, 1H, OH), 7.38 (d, J = 8.0 Hz, 2H, Ar), 7.19 (d, J = 8.0 Hz, 2H, Ar), 3.73 (q, J = 11.0 Hz, 1H, CH next to carbonyl), 2.51 (m, 2H, CH_2 next to Ar, overlapped with DMSO), 2.07 (m, 1H, CH, next to two methyl), 1.51 (d, J = 8.0 Hz, 3H, CH_3), 1.02 (d, J = 8.0 Hz, 6H, $2CH_3$).
 **Ph_2SnL_2**	7.52-7.39 (m, 10H, 2Ar ring linked to Sn), 7.31 (d, J = 8.0 Hz, 4H for two Aromatic of Ibuprofen linked to Sn), 7.21 (d, J = 8.0 Hz, 4H for two Aromatic of Ibuprofen linked to Sn), 3.56 (q, J = 11.0 Hz, 2H, 2CH next to carbonyl), 2.51 (m, 4H, $2CH_2$ next to Ar, overlapped with DMSO), 2.08 (m, 2H, 2CH, next to two methyl), 1.54 (d, J = 8.0 Hz, 6H, $2CH_3$), 1.04 (d, J = 8.0 Hz, 12H, $4CH_3$).
 **Bu_3SnL**	7.41 (d, J = 8.5 Hz, 2H, Ar), 7.18 (d, J = 8.5 Hz, 2H, Ar), 3.71 (q, J = 10.0 Hz, 1H, CH next to carbonyl), 2.51 (m, 2H, CH_2 next to Ar, overlapped with DMSO), 2.08 (m, 1H, CH, next to two methyl), 1.65 (t, J = 12.0 Hz, 6H, $3CH_3$ of butyl next to Sn), 1.51 (d, J = 8.0 Hz, 3H, CH_3 of Ibuprofen), 1.32 (m, 12H, $6CH_2$ of butyl linked to Sn), 1.03 (d, J = 8.0 Hz, 6H, $2CH_3$ of Ibuprofen), 0.96 (t, J = 10.0 Hz, 9H, $3CH_3$ terminal of butyl linked to Sn).
 **Me_3SnL**	7.46 (d, J = 8.6 Hz, 2H, Ar), 7.17 (d, J = 8.6 Hz, 2H, Ar), 3.68 (q, J = 10.0 Hz, 1H, CH next to carbonyl), 2.51 (m, 2H, CH_2 next to Ar, overlapped with DMSO), 2.06 (m, 1H, CH, next to two methyl), 1.51 (d, J = 8.0 Hz, 3H, CH_3 of Ibuprofen), 1.37 (s, 9H, $3CH_3$ next to Sn), 1.02 (d, J = 8.0 Hz, 6H, $2CH_3$ of Ibuprofen).

A multiplet between 7.52 ppm and 7.39 ppm, containing ten protons (m, 10H) in the aromatic area of the spectrum, corresponds to the aromatic protons from the two phenyl rings directly related to the tin atom (two aromatic rings linked to Sn). These peaks attest to the phenyl groups' existence and bonding to the tin core. Furthermore, two doublets with a coupling constant (J) of 8.0 Hz at 7.31 ppm and 7.21 ppm show the aromatic protons (4H) of the ligand Ibuprofen that is directly bonded to tin. These peaks support the coordination of the Ibuprofen ligands to the tin atom. The diphenyltin complex Ph_2SnL_2's ^{1}H-NMR spectra no longer show the OH signal, indicating that coordination took place via Ibuprofen's carboxylic group. The free hydroxyl functionality of Ibuprofen is lost when its carboxylic acid group couples with the tin atom. This chemical shift further supports the complex formation via this particular binding contact and offers compelling evidence that the coordination site does, in fact, involve the carboxylic group.

As we move into the aliphatic region of the spectrum, we can see additional evidence of the carbonyl functionality in the ligand and its coordination with tin. A quartet at 3.56 ppm with a coupling constant (J) of 11.0 Hz corresponds to the protons (2H) next to the carbonyl group (2CH next to carbonyl). A multiplet at 2.51 ppm, resembling the spectrum of the Ibuprofen ligand, reveals the protons (4H) in the methylene groups ($2CH_2$) next to the aromatic rings. However, as was already indicated, this signal seems to overlap with DMSO, which could indicate insufficient suppression of the solvent during the NMR test or possible contaminants in the solvent. Moreover, a multiplet at 2.08 ppm is compatible with the structure of the ligand and represents the protons (2H) positioned between two methyl groups (2CH). Ultimately, the presence of these methyl substituents is confirmed by two doublets at 1.54 ppm and 1.04 ppm with coupling constants of 8.0 Hz, which reflect the methyl groups (6H) in the ligand. In general, the diphenyltin complex Ph_2SnL_2's ^{1}H-NMR spectrum offers strong proof that two Ibuprofen ligands are coordinated with the tin core. The successful creation of the organotin complex and the resulting illumination of its molecular structure and bonding interactions is demonstrated by the observed chemical shifts and coupling patterns, which align with the anticipated structural features.

An important source of information about the structural properties of the complex is the ^{1}H-NMR spectrum of the tributyltin complex Bu_3SnL, in which one molecule of the ligand Ibuprofen is coupled to the tin center through its carboxylic group. The aromatic protons (2H each) from the ligand's Ibuprofen moiety

(Ar) are represented by two doublets in the aromatic region of the spectrum at 7.41 ppm and 7.18 ppm with a coupling constant (J) of 8.5 Hz. This suggests that the coordination to tin did not significantly alter the chemical shifts of these protons.

The presence of the carboxylic functionality in the ligand and its coordination with tin are confirmed by a quartet at 3.71 ppm with a coupling constant (J) of 10.0 Hz, which corresponds to the proton (1H) next to the carbonyl group (CH next to carbonyl). Protons (2H) at the methylene group (CH_2) next to the aromatic ring are indicated by a multiplet at 2.51 ppm, albeit there is considerable overlap with DMSO. This could be because of solvent contaminants or insufficient solvent suppression during the NMR test. In addition, the spectrum shows a multiplet at 2.08 ppm, which is compatible with the structure of the ligand and represents a proton (1H) positioned between two methyl groups (CH).

Signals associated with the butyl groups of the tributyltin moiety are also visible in the spectrum. The protons (6H) from the butyl groups that are next to the tin core are represented by a triplet at 1.65 ppm ($J = 12.0$ Hz). Furthermore, a multiplet at 1.32 ppm is indicative of the protons (12H) in the butyl chains that are connected to the tin atom. Ultimately, a triplet at 0.96 ppm ($J = 10.0$ Hz) indicates how the butyl chains' terminal methyl groups (9H) are coordinated with tin. The predicted structural components and the coordination mode are confirmed by the ^{1}H-NMR spectra of the tributyltin complex Bu3SnL, where coordination occurs through the carboxylic group of Ibuprofen. The chemical shifts and coupling patterns observed in the spectrum align with the structure of the ligand and the coordination of a single Ibuprofen molecule to the tin center, providing insights into the molecular makeup and bonding interactions of the complex. An essential source of information about the structural properties of the trimethyltin complex, Me_3SnL, is the ^{1}H-NMR spectrum. In this complex, one molecule of the ligand Ibuprofen is coupled to the tin center through its carboxylic group. Two doublets with a coupling constant (J) of 8.6 Hz at 7.46 ppm and 7.17 ppm in the aromatic part of the spectrum represent the aromatic protons (2H each) from the Ibuprofen moiety (Ar). These peaks reveal that the coordination to tin had no discernible impact on the chemical shifts of these aromatic protons.

The presence of the carboxylic functionality in the ligand and its coordination with tin are confirmed by a quartet at 3.68 ppm with a coupling constant (J) of 10.0 Hz, which corresponds to the proton (1H) next to the carbonyl group (CH next to carbonyl). Protons (2H) in the methylene group (CH_2) next to the aromatic ring are indicated by a multiplet at 2.51 ppm; nevertheless, there seems to be some overlap with DMSO, which may be the result of solvent contaminants or insufficient solvent suppression during the NMR experiment. In addition, the spectrum shows a multiplet at 2.06 ppm, which is compatible with the structure of the ligand and represents a proton (1H) positioned between two methyl groups (CH).

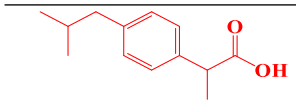
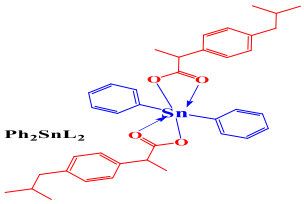
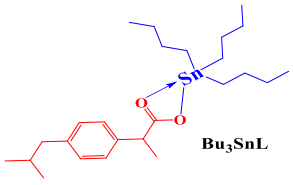
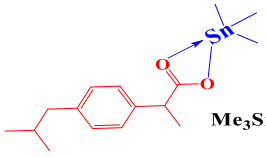
Signals pertaining to the trimethyltin moiety's methyl groups are also visible in the spectrum. Next to the tin core, the methyl protons (9H) are represented by a singlet at 1.37 ppm. Furthermore, the methyl groups (3H each) of the Ibuprofen ligand are represented by a doublet at 1.51 ppm with a coupling constant (J) of 8.0 Hz and a doublet at 1.02 ppm with the same coupling constant, showing that these methyl groups are still present in the coordinated complex. Overall, the trimethyltin complex Me_3SnL's ^{1}H NMR spectra, which show that coordination occurs through Ibuprofen's carboxylic group, validate the predicted structural components and reveal the coordination mode. The molecular makeup and bonding interactions of the complex are clarified by the spectrum's chemical shifts and coupling patterns, which are compatible with the ligand's structure and the coordination of one Ibuprofen molecule to the tin center Table 2.

Characterization by proton nuclear magnetic resonance (^{13}C-NMR) spectroscopy

Understanding the structural characteristics and behavior of chemical compounds requires a fundamental understanding of chemistry, which includes characterization. One effective analytical method used for this is ^{13}C-NMR spectroscopy. Here, we will investigate the use of ^{13}C-NMR spectroscopy to characterize the structural features of the molecules that were previously mentioned: the trimethyltin complex (Me_3SnL), the tributyltin complex (Bu_3SnL), and the diphenyltin complex (Ph_2SnL_2). These molecules are all coordinated with the ligand Ibuprofen. ^{13}C-NMR spectroscopy sheds light on the coordination modes, bonding interactions, and general molecular structures of these compounds by providing necessary information on their carbon surroundings.

The Ibuprofen ligand's ^{13}C-NMR spectra offer essential information about the carbon habitats inside the molecule, enabling the study of its structural characteristics. The spectrum shows several unique peaks, each of which corresponds to a different carbon atom in the ibuprofen molecule. The carbon atom in the carboxylic acid group (COOH), which is a typical chemical shift for carbonyl carbon atoms, is responsible for the peak at 181.20 ppm. This peak attests

Table 3. ^{13}C-NMR spectral data for ligand and metal complexes.

Compound	^{13}C-NMR (100 MHz: DMSO-d_6, δ, ppm, J in Hz)
 **Ibuprofen (L)**	181.20, 141.63, 141.37, 132.66, 132.03, 47.61, 47.49, 29.38, 23.93, 19.05.
 Ph_2SnL_2	179.50, 152.10, 141.22, 140.94, 134.04, 131.63, 131.42, (130.62, 130,59 two peaks overlapped) 47.76, 46.39, 28.28, 22.83, 18.59.
 Bu_3SnL	176.11, 142.22, 141.94, 132.63, 131.62, 48.76, 47.39, 30.21, 29.28, 25.95, 23.83, 19.59, 15.67, 12.40.
 Me_3SnL	173.58, 142.22, 141.94, 132.63, 131.62, 48.76, 47.39, 29.28, 23.83, 19.59, 3.61.

to the presence of Ibuprofen's carboxylic acid functionality, a crucial structural component of the drug. Ibuprofen's aromatic ring (Ar) has two strong peaks at 141.63 ppm and 141.37 ppm that correlate to its carbon atoms. These carbon atoms' near chemical shifts demonstrate the ring's aromatic character and their existence attests to the ligand's aromatic moiety's integrity. The presence of the aromatic structure is further supported by the peaks at 132.66 ppm and 132.03 ppm, which are also linked to the carbon atoms inside the aromatic ring. These peaks provide more proof of the aromatic nature of the ligand.

Moving on to the aliphatic portion of the spectrum, the aliphatic carbons next to the carbonyl group (CH next to carbonyl) are responsible for the peaks at 47.61 ppm and 47.49 ppm. These peaks attest to the presence of carbon atoms next to the ligand's carbonyl functionality. The peaks at 29.38 ppm, 23.93 ppm, and 19.05 ppm are associated with the aliphatic carbon atoms present in the ligand's structure. These peaks represent the various carbon environments within the aliphatic chains of the Ibuprofen molecule, as shown in Table 3.

The diphenyltin complex Ph_2SnL_2's ^{13}C-NMR spectra provide crucial insights into the complex's structural properties and the way the Ibuprofen ligand coordinates with the tin center. The spectrum shows several unique peaks, each of which corresponds to a different carbon atom in the complex. The carbon atom in the carbonyl group (C=O) of the coordinated Ibuprofen ligand is responsible for the peak at 179.50 ppm. This peak signifies the ligand's carboxylic acid functionality, which is essential for the coordination with the tin core.

Two noticeable peaks at 152.10 ppm and 141.22 ppm represent the carbon atoms in the coordinated Ibuprofen's aromatic ring (Ar). The fact that these carbon atoms' chemical shifts indicate that the ring is aromatic proves that the tin coordination did not substantially change the ligand's aromatic structure. The carbon atoms within the aromatic ring are also linked to the peaks at 140.94 ppm, 134.04 ppm, 131.63 ppm, and 131.42 ppm, indicating the existence of the aromatic moiety in the complex. The peaks at 130.62 ppm and 130.59 ppm, in particular, seem to overlap, suggesting that these carbon environments are adjacent to one another or that there may be structural symmetry.

Close to the aliphatic area of the spectrum, where the peaks at 47.76 ppm and 46.39 ppm indicate the presence of carbon atoms close to the carbonyl functionality in the ligand. These peaks are assigned to the aliphatic carbons next to the carbonyl group (CH next to carbonyl). Peaks at 28.28 ppm, 22.83 ppm, and 18.59 ppm correspond to the aliphatic carbon atoms found in the structure of the ligand.

These peaks show the different carbon environments found in the aliphatic chains of the ligand Ibuprofen. The diphenyltin complex Ph_2SnL_2's ^{13}C-NMR spectra show that the ligand and tin center are coordinated, in addition to confirming the presence of the anticipated structural elements in ibuprofen. The ligand's structural integrity is generally preserved by the coordination process, as indicated by the chemical shifts of the carbon atoms in its aromatic and aliphatic regions. This information sheds light on the complex's molecular makeup and bonding interactions.

The structure of the tributyltin complex, Bu_3SnL, and the manner in which the ligand, Ibuprofen, is attached to the tin atom are both disclosed by the ^{13}C-NMR spectrum. Different peaks in the spectrum indicate the locations of the carbon atoms inside the complex. We may learn about the carbon atom in the carboxylic acid portion of Ibuprofen from the peak at 176.11 ppm. This peak serves as evidence that the carboxylic acid of ibuprofen is attached to the atom of tin, which is crucial for the formation of the complex. The aromatic ring of ibuprofen contains two prominent peaks that reveal the carbon atoms at 142.22 ppm and 141.94 ppm. This indicates that even after connecting to the tin, the ring is still present. The hypothesis that the ring is still intact in the complex is supported by the peaks at 132.63 ppm and 131.62 ppm, which are likewise associated with the ring.

The carbon atoms close to the carbonyl group in Ibuprofen are visible when we look at the peaks at 48.76 ppm and 47.39 ppm in the non-aromatic portion of the spectrum. This demonstrates that the tin atom and the carbonyl group are still attached. The remaining peaks at various ppm levels correspond to carbon atoms found in the remaining three butyl groups of Ibuprofen's structure, indicating that the complex preserves Ibuprofen's overall structure. Briefly, the ^{13}C-NMR spectra of Bu_3SnL show that the carboxylic acid, aromatic ring, and carbonyl group of ibuprofen are still present and linked to tin in the complex. This aids in our comprehension of the complex's structure and the ligand's bonding process with the tin atom.

An understanding of the structural properties of the complex and the nature of the coordination can be gained from the ^{13}C-NMR spectra of the trimethyltin complex, Me_3SnL, in which one molecule of the ligand Ibuprofen is coupled to the tin center through its carboxylic group.

Different peaks are seen in the spectrum, each of which corresponds to a different carbon atom in the complex. The carbon atom in the carboxylic acid group (COOH) of the coordinated Ibuprofen ligand is indicated by the peak at 173.58 ppm. This peak attests to the ligand's coordination with the tin center and the existence of the carboxylic acid functionality, which is essential for the formation of complexes. There are two prominent peaks at 142.22 ppm and 141.94 ppm, which are the carbon atoms of the coordinated ibuprofen's aromatic ring (Ar). These chemical changes support the maintenance of the ligand's aromatic structure inside the complex by indicating that the ring's aromatic character does not alter upon coordination with tin. Further proof of the presence and integrity of the aromatic moiety in the compound can be seen in the peaks at 132.63 ppm and 131.62 ppm, which are also linked to the carbon atoms inside the aromatic ring.

As we move into the aliphatic portion of the spectrum, the peaks at 48.76 ppm and 47.39 ppm are ascribed to the aliphatic carbons in the Ibuprofen ligand that are near the carbonyl group (CH next to carbonyl). These peaks provide evidence that the carbon atoms in the complex that are close to the carbonyl functionality are still attached to the tin atom. The aliphatic carbon atoms inside the ligand's structure are represented by peaks at 29.28 ppm, 23.83 ppm, and 19.59 ppm, which show the different carbon environments within the aliphatic chains of Ibuprofen. Finally, there is a noticeable peak at 3.61 ppm that is probably related to the carbon atom of the trimethyltin moiety. This peak is crucial since it shows that the tin atom is present in the complex. The trimethyltin complex Me_3SnL's ^{13}C-NMR spectra offer strong proof that the complex retains the carboxylic acid, aromatic ring, and carbonyl functionalities of the Ibuprofen ligand. The structural integrity of the ligand is maintained during coordination with tin due to the chemical shifts of carbon atoms in both the aromatic and aliphatic regions. These shifts provide information on the molecular makeup and bonding interactions within the complex.

Characterization by 119-Tin nuclear magnetic resonance (^{119}Sn-NMR) spectroscopy

Using ^{119}Sn-NMR spectroscopy to characterize the above-synthesized complexes is an essential analytical method that sheds light on the coordination environment and structural characteristics of the tin atoms inside these organotin(IV) complexes. Three significant aspects of these complexes are reflected in the reported chemical shifts for Ph_2SnL_2 (−205.29 ppm), Bu_3SnL (−234.30 ppm), and Me_3SnL (−273.73 ppm). The chemical shifts of tin atoms in the ^{119}Sn-NMR spectra are very sensitive to their bonding interactions and coordination environment. The nature of the coordination around the tin atom, which can vary from being tightly bound to the ligand to being comparatively sheltered by the surrounding

atoms, is indicated by the observed chemical shifts for these complexes.

First, Ph_2SnL_2 shows a chemical shift of −205.29 ppm, indicating a tin atom that is moderately protected. In this complex, a coordination environment that partially shields the tin atom from the external magnetic field may result from the coordination of two phenyl groups from diphenyltin to the Ibuprofen ligand. This data is in line with the idea that the aromatic rings play a role in the ligand-tin center coordination process.

Compared to Ph_2SnL_2, Bu_3SnL exhibits a chemical shift of −234.30 ppm, indicating a distinct coordination environment. A more substantial shielding effect on the tin atom is suggested by the more downfield (lower ppm) shift. Because of the larger size of the butyl groups in the tributyltin complex, there is likely more steric hindrance, which creates a unique coordination environment around the tin atom.

Lastly, among the three complexes, the tin atom suffers the most significant shielding effect for Me_3SnL, which has a chemical shift of −273.73 ppm. The chemical shift in the trimethyltin complex indicates a coordination environment where the tin atom is effectively insulated from the external magnetic field due to its relatively tiny methyl groups. The compact structure of the methyl groups may be the cause of this coordinating environment. Regarding the coordination environment and bonding interactions of the tin atoms in these organotin(IV) complexes, ^{119}Sn-NMR spectroscopy offers important information. The chemical changes that have been observed (−205.29 ppm for Ph_2SnL_2, −234.30 ppm for Bu_3SnL, and −273.73 ppm for Me_3SnL) suggest that there are differences in the coordination environments. These differences are probably caused by the kind and size of organic groups that are affixed to the tin center. This spectroscopic method makes a substantial contribution to the thorough characterization of these complexes and facilitates comprehension of their structural characteristics.

Utilizing weight loss to examine the photo-stability of PVC films

Exposure of PVC to light, heat, and humidity leads to autocatalytic dehydrochlorination. The elimination of HCl causes drastic changes in both the mechanical and physical properties of PVC. For example, the formation of unsaturated small fragments, a decrease in molecular weight, and a weight loss of PVC was observed as a result of cross-linking and chain scission due to its photoirradiation. [17,18] Therefore, we determined the weight loss of PVC caused by photoirradiation to assess the role played by complexes **1–3** (0.5% by weight) in stabilizing the polymeric chains. Eq. (1) was used to calculate the PVC weight loss (%) and plotted against the time of irradiation (every 50 h); Fig. 1. The use of low concentrations (0.5% by weight) of additives has been influential not only in reducing the photodegradation of PVC but also does not lead to a change in color or physical properties of the polymeric films. [19] Fig. 1, shows that the weight loss was highest for the blank PVC in which no additives were used. It was clear that the use of complexes **1–3** led to a decrease in weight loss compared with the blank film. The weight loss (%) was fast and sharp at the beginning of the irradiation (first 50 h) and continued to increase with the time of irradiation.The additives with the highest aromatic content (i.e., complexes **1**) were more efficient as PVC photostabilizer compared with ones containing aliphatic substituents (i.e., complexes **2** and **3**).

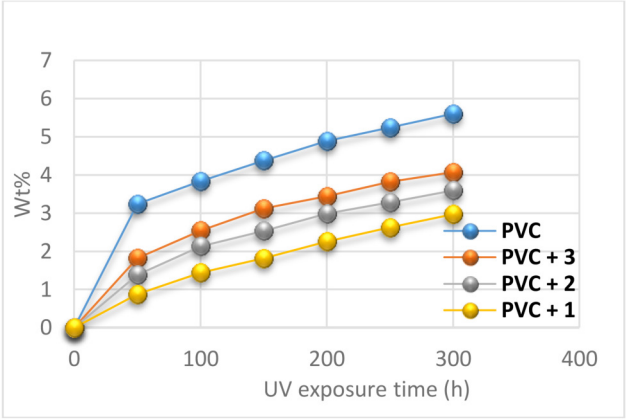


Fig. 1. Change in weight loss (%) of PVC films.

FTIR spectrophotometry

Radiation in an environment of oxygen, or PVC photooxidation, produces radical species, such as carbon and chloride radicals. These free radicals cause PVC to degrade destructively and produce volatile byproducts like HCl. [20,21] It led to the production of PVC residues with C=O (such as ketones and chloroketones) and C=C (unsaturated chains) groups.

The technique of FTIR spectroscopy was employed to evaluate the influence of sunlight on PVC. As the irradiation process went on, the bands that corresponded to the vibrations of the C=O (1714 cm^{-1}) and C=C (1618 cm^{-1}) groups were seen to form and increase. The increase in the intensity of these functional groups was measured against a peak that is unaffected by the process, the C-H bond (1328 cm^{-1}), as a reference. [22,23] The FTIR spectra of the PVC blank Fig. 2 demonstrates the alterations in the C=O and

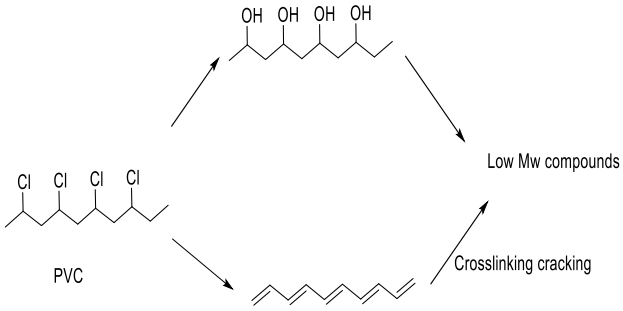


Fig. 2. PVC decomposition pathway.

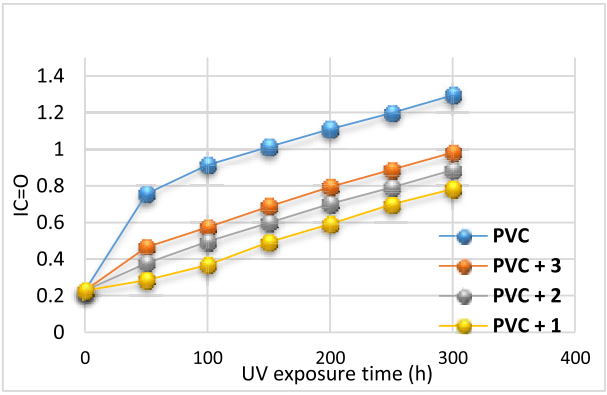


Fig. 3. Changes in the $I_{C=O}$ index for PVC films.

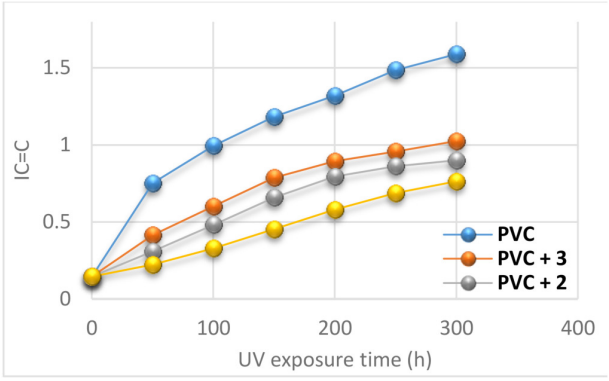


Fig. 4. Changes in the $I_{C=C}$ index for PVC films.

C=C vibration bands' intensities brought about by radiation.

After radiation, Eq. (2) was used to compute the $I_{C=O}$ and $I_{C=C}$, which were then plotted against the radiation period Figs. 3 and 4. As the radiation treatment carried on, the $I_{C=O}$ and $I_{C=C}$ rose; the changes were most significant for the blank PVC. When comparing the PVC blends with complexes **1–3** to the blank film, the increases in the $I_{C=O}$ and $I_{C=C}$ were less.[24] The films with the most strongly aromatic additives (i.e., complexes 1) had the lowest $I_{C=O}$ and $I_{C=C}$.

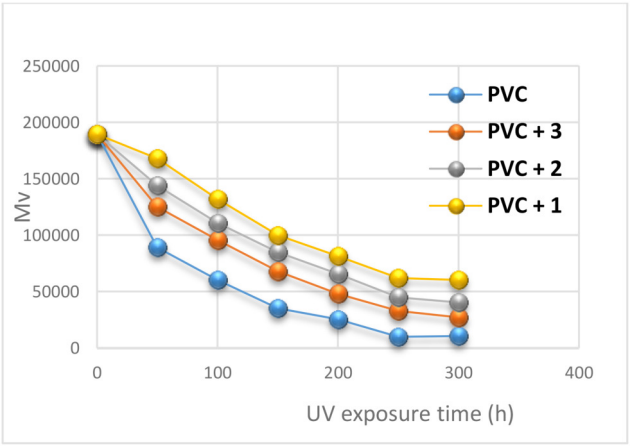


Fig. 5. Changes in the Mv for PVC films.

Average Molecular Weight (Mv)

PVC is photoirradiated, which results in the loss of tiny polymeric fragments and a drop in Mv. The polymeric chains' chain scission and cross-linking are the primary causes of the PVC's MV declines. Since the intrinsic viscosity [η] is greatly influenced by Mv, a decrease in it is anticipated for the PVC film solution that has been exposed to radiation.[25] The PVC films that had been exposed to radiation at various intervals were dissolved in THF, and their viscosities were measured in order to evaluate the impact of the radiation on the MV. Eq. (2) was used to obtain the Mv, which was then plotted versus the radiation exposure time (50–300 hours); Fig. 5. A few insoluble residues were observed, suggesting that PVC underwent branching and cross-linking during the irradiation process. With an increase in irradiation duration, the Mv fell both rapidly and gradually. Without fail, every complex lowers the Mv reduces. Complexes **1–3** produced a high degree of stability and significantly decreased the depression of the Mv of PVC. Complex **1** proved to be the most successful when compared to the other PVC photostabilizers.

Surface analysis

Various forms of microscopy were employed to examine the imperfections and harm that occurred on the surface of the PVC that had been exposed to radiation.[26] The non-irradiated films have uniform, smooth, and regular surfaces in theory Fig. 6. In comparison to the blends comprising additives **1–3**, the damages and abnormalities that formed on the surface of the irradiated blank PVC were more visible, as seen by the optical microscope photographs Fig. 7. It was evident that PVC was somewhat shielded from photodegradation by the ibuprofen–tin complexes.

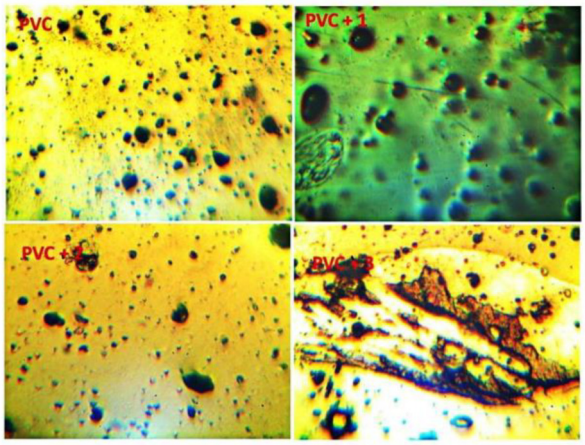


Fig. 6. Microscope images of non-irradiated PVC films.

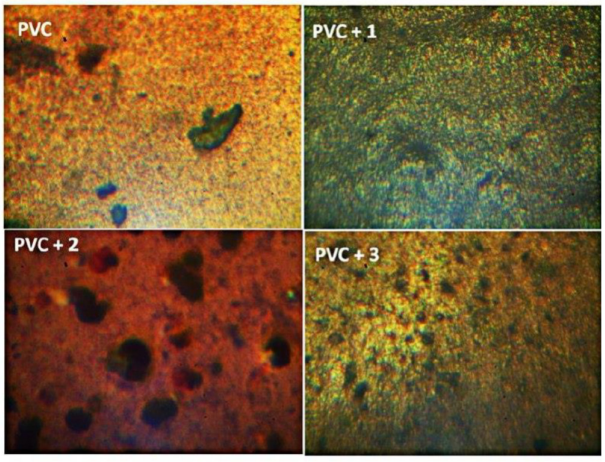


Fig. 7. Microscope images of irradiated PVC films.

The scanning electron microscope (SEM) images Fig. 8 showed that the surface of the blank PVC was severely damaged after irradiation. Fewer damages were seen within the surface of the PVC blends containing ibuprofen–tin complexes and, in particular, additive 1.[27]

The force microscope (AFM) images Fig. 9 showed rough surfaces for the PVC films after irradiation. The surface of the irradiated film (blank) showed a high degree of roughness and irregularities compared with the blends containing complexes **1–5**. The roughness factor (Rq) was 381.8, 41.3, 52.3, and 57.6 for the irradiated blank PVC and those blended with complexes **1**, **2,** and **3**, respectively.[28]

Photostabilization mechanisms

When PVC films are exposed to radiation, the di- and tri-organotin(IV) complexes function as photostabilizers. The sequence of the three organotin

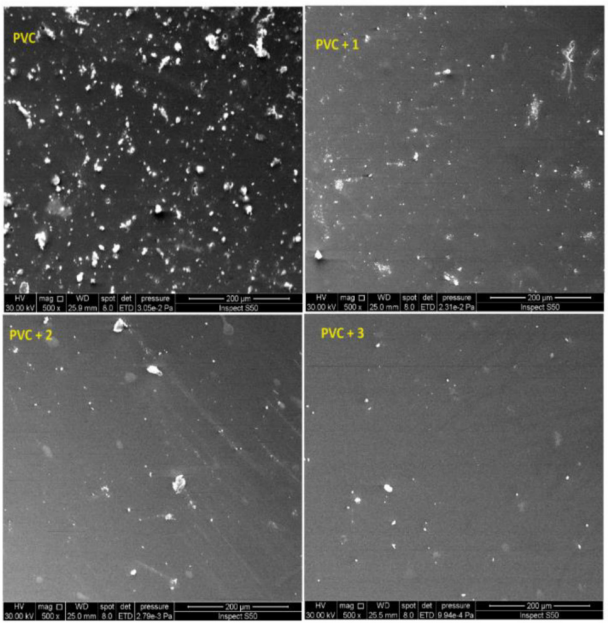


Fig. 8. SEM images of irradiated PVC films.

complexes' efficiency is 1 > 2 > 3, and they were created to lessen PVC photodegradation. These chemicals can stabilize PVC films through a variety of methods. Due to its potent Lewis acidity, tin can function as a highly effective HCl scavenger Fig. 10. The oxygen atoms of the carboxylate group can displace the chlorine atom within the polymer backbone by the tin(IV) ion. When utilized as secondary stabilizers, these stabilizers produce good long-term photostabilization of PVC.[29,30]

The complexes may function as peroxide breaks down to lessen PVC's photodegradation. PVC undergoes photo-oxidation, which generates radicals that react with oxygen to form POOH. Accordingly, peroxides like hydroperoxides may be broken down by tin complexes Fig. 11.

As seen in Fig. 12, this kind of stabilizer can stop PVC from photodegrading by acting as a scavenger of free radicals. These additives have the potential to form a compound with an excited chromophore. Additionally, because of the photo-stabilizer conjugation system that absorbs the UV, these photo-stabilizers may absorb ultraviolet light directly before it reaches the PVC and disperse this energy to lower levels where it does not damage the chemical structure of the polymer chains.

Conclusion

As photo-stabilizers for the PVC, three organotin complexes, designated 1–3, were created by reacting di– and tri-organotin chlorides with ibuprofen.

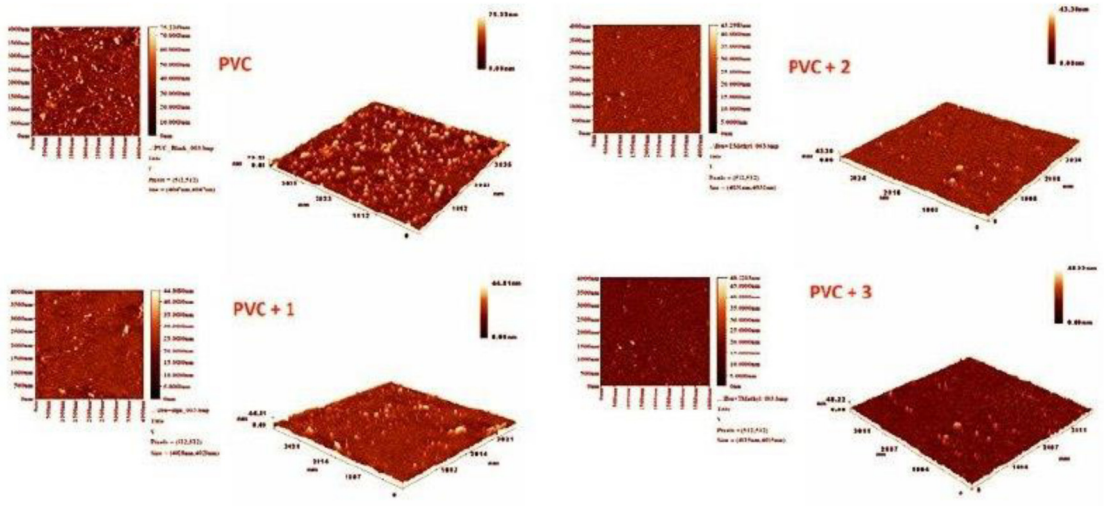


Fig. 9. AFM images of irradiated PVC films.

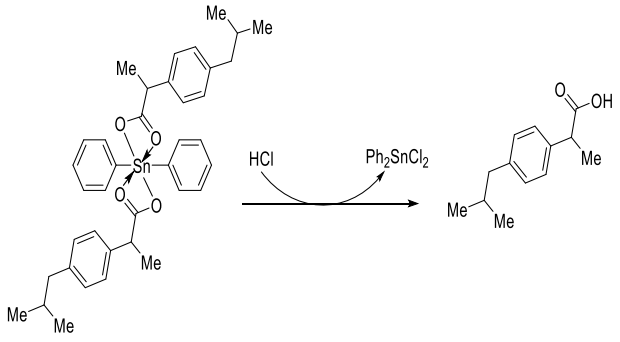


Fig. 10. Organotin complexes act as hydrochloride scavengers.

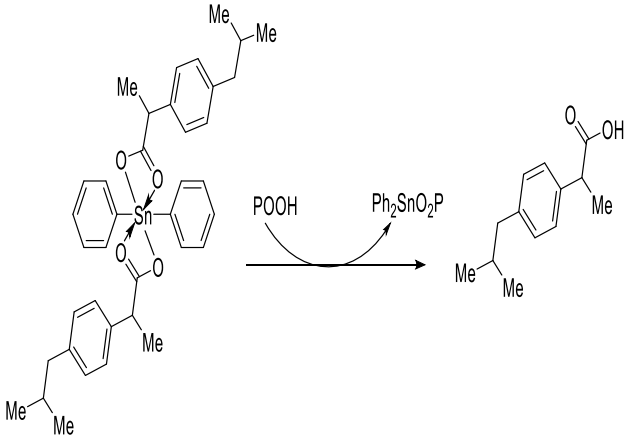


Fig. 11. Organotin complexes as peroxide decomposers.

Through a variety of analytical techniques, these additives demonstrated their effectiveness in reducing the photodegradation of PVC films. These techniques demonstrated a noteworthy decrease in the photodegradation of PVC films. They tracked the growth of specific functional groups, namely carbonyl

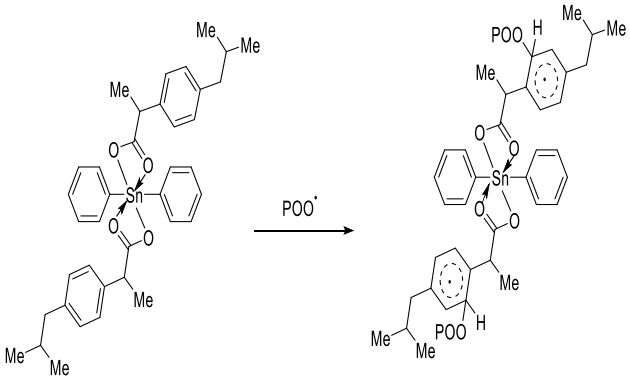


Fig. 12. The function of photostabilizers as radical scavengers.

($I_{C=O}$) and polyene ($I_{C=C}$), during the 300-hour irradiation period, the percentage of weight loss, and surface modifications of PVC films with and without additives. PVC film stabilization is achieved by organotin(IV) complexes through a range of mechanisms, such as primary stabilizers, HCl scavengers, and peroxide decomposers. The modified polymers showed reduced surface damage, low roughness factor, and lower decrease in weight, consistent with less formation of short-chain fragments compared to the nonmodified PVC. The influence of photostabilization on PVC was as follows: **1** > **2** > **3** > PVC (blank). Based on many processes, the Ph_2SnL complex proved to be the most successful as a photostabilizer for PVC films.

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Authors' declaration

- Conflicts of Interest: None.
- We hereby confirm that all the figures and tables in the manuscript are ours. Furthermore, any figures and images, that are not ours, have been included with the necessary permission for republication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at Al-Nahrain University.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.

Authors' contribution statement

H. I. and E. Y. designed the study. G. A. E. and M. H. A. performed the experiments and expressed and purified all proteins. D. S. A. analyzed the data. M. B. wrote the paper with input from all authors.

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تأثير الأشعة فوق البنفسجية على عوامل التعرية لافلام متعدد(كلوريد الفينيل) المشوبة بمعقدات القصدير (IV)

حنان إبراهيم[1], عماد يوسف[1], جمال الهيتي[2], محمد المشهداني[1], دينا سعدي احمد[3] ,منى بوفروشه[4]

[1]قسم الكيمياء ،كلية العلوم، جامعة النهرين، بغداد ،العراق.
[2]قسم البصريات، كلية العلوم الطبية التطبيقية، جامعة الملك سعود، الرياض, المملكة العربية السعودية.
[3]قسم الصناعات الكيمياوية، معهد تكنولوجيا-بغداد، الجامعة التقنية الوسطى، بغداد، العراق.
[4]قسم الكيمياء، كلية العلوم، جامعة الإمارات العربية المتحدة، العين، الإمارات العربية المتحدة.

الخلاصة

باستخدام مطيافية الرنين المغناطيسي النووي (بروتون, كاربون, قصدير) بالإضافة إلى مطيافية الأشعة تحت الحمراء (FTIR) لتشخيص المعقدات، تم تحضير ودراسة ثلاث من معقدات القصديرمن الإيبوبروفين. لتحسين الثبات الضوئي لمتعدد(كلوريد الفينيل) (PVC)، تم خلط هذه المعقدات مع متعدد(كلوريد الفينيل). وتم استخدام مطيافية الأشعة تحت الحمراء لتقييم فعاليتها. تمت دراسة فقدان وزن البوليمر بعد التشعيع ومتوسط الوزن الجزيئي من خلال مقارنة اللزوجة قبل التعرض وبعده. بالإضافة إلى ذلك، تمت دراسة مورفولوجيا سطح متعدد(كلوريد الفينيل) قبل وبعد التشعيع. بعد التشعيع، أظهرت افلام متعدد(كلوريد الفينيل) المشوب بمعقدات القصدير- الإيبوبروفين شقوقًا وبقعًا أقل وسطحًا أكثر سلاسة من افلام متعدد(كلوريد الفينيل) غير المشوب، وفقًا للنتائج المستحصلة من المجهر الضوئي والمجهر الإلكتروني الماسح (SEM). أظهرت البوليمرات المحورة مقاومة متزايدة للتحلل الضوئي وكان لها عامل خشونة أقل، وانخفاض في الوزن، وأضرار في السطح، مقارنة بفلم متعدد(كلوريد الفينيل) غير المشوب. وهذا يدل على أن معقدات القصدير- الإيبوبروفين التي تم تحضيرها هي مثبتات ضوئية لمتعدد(كلوريد الفينيل). حيث ان المعقد 1 هو أفضل من المثبتات الضوئية الأخرى.

الكلمات المفتاحية: معقدات القصدير-الإيبوبروفين, المجهر الضوئي, الثبات الضوئي لمتعدد(كلوريد الفينيل), المجهر الالكتروني الماسح, مورفولوجيا السطح.