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Ministry of Higher Education
and Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry



NEW PHOTOSTABILIZERS FOR POLY(VINYL CHLORIDE) BASED ON SOME METAL COMPLEXES OF 2-(6- METHOXYNAPHTHALEN-2-YL)PROPANOATE

A Thesis

**Submitted to the College of Science Al-Nahrain University as a
Partial Fulfillment of the Requirements for the Degree of M. Sc. in
Chemistry**

By:

Husam Ekrrayem Salman

(B.Sc. 2009)

Supervised by:

Assist. Prof. Dr. Emad A. Yousif & Lecturer Dr. Jawad K. Shneine

Supervisor certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the Degree of Master of Science in Chemistry.

Assistant Prof.

Dr. Emad A. Yousif

Lecturer

Dr. Jawad K. Shneine

In view of the available recommendation, we forward this thesis for debate by the Examining Committee.

Assistant Prof.

Dr. Hilal S. Wahab

Head of Department Chemistry

College of Science

Al-Nahrain University

Examining Committee Certification

We, the examining committee, certify that we read this thesis and have examined the student (**Husam Ekrayyem Salman**), in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science in Chemistry.

Chairman

Signature:

Name: Prof. Dr. Basima M. Sarhan

Date: /11/2012

Member

Signature:

Name: Assist. Prof.

Dr. Hadi M. A. Abood

Date: /11/2012

Member

Signature:

Name: Assist. Prof.

Dr. Khaleel K. Abd

Date: /11/2012

Supervisor

Signature:

Name: Assist. Prof.

Dr. Emad A. Yousif

Date: /11/2012

Supervisor

Signature:

Name: Lecturer

Dr. Jawad K. Shneine

Date: /11/2012

Approved for the College Committee of Graduate Studies

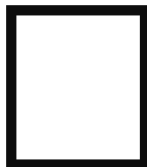
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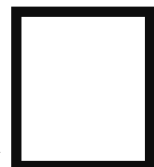
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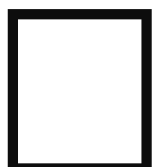
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Abstract

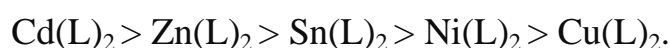
The preparation of Bis[2-(6-methoxynaphthalen-2-yl)propanoate] chelate complexes with nickel(II), copper(II), zinc(II), cadmium(II) and tin(II) were described in this thesis.

Infrared, ultraviolet–visible, spectrophotometric techniques, magnetic susceptibility, atomic absorption, conductivity measurements and melting point were used to characterize the free ligand and the above chelate complexes. All these complexes were found to act as stabilizer in PVC films.

The light of wavelength (313 nm) with intensity of ($1.052 \times 10^{-8} \text{ ein.dm}^{-3} \cdot \text{S}^{-1}$) was used for irradiation of polymer films at room temperature. The rate of photodegradation and photostabilization of PVC film (thickness 30 μm) were monitored by measuring the carbonyl, polyene, hydroxyl and chlorine indices (I_{co} , I_{po} , I_{oH} and I_{cl}) values as a function of irradiation time and ultraviolet–visible spectrophotometry using 0.5% wt/wt concentration of stabilizer.

It was found that the carbonyl index (I_{co}), polyene index (I_{po}) and hydroxyl index (I_{oH}) values increased with irradiation time, while the chlorine index (I_{cl}) values decreased with irradiation time, and this increase depend on the type of additives (free ligand and complexes).

The following trend was obtained for the photostabilization effect of PVC film in presence of these additives:



According to the experimental results obtained several mechanisms were suggested depending on the structure of the additives. Among these mechanisms, HCl scavenging, UV absorption, peroxide decomposer and radical scavenger for photostabilizer additives.

The mode of chain scission was also investigated by measuring the variation of average viscosity molecular weight with irradiation time for PVC films with and without additives. It was found that the values of the variation of average viscosity molecular weight decreased with increasing irradiation time.

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Abbreviation list

Full meaning used in this thesis	Abbreviation
Poly (vinyl chloride)	PVC
Poly ethylene	PE
Vinyl chloride monomer	VCM
N,N-Dimethyl formamide	DMF
Sensitizer molecule	S
Polymer molecule	P
Tetrahydrofuran	THF
Di methyl sulphoxide	DMSO
Index of the group under study	I _s
Absorbance of peak under study	A _s
Absorbance of reference peak	A _r
Bis[2-(6-methoxynaphthalen-2-yl)propanoate] nickel (II)	Ni(L) ₂
Bis[2-(6-methoxynaphthalen-2-yl)propanoate] copper (II)	Cu(L) ₂
Bis[2-(6-methoxynaphthalen-2-yl)propanoate] zinc (II)	Zn(L) ₂
Bis[2-(6-methoxynaphthalen-2-yl)propanoate] cadmium (II)	Cd(L) ₂
Bis[2-(6-methoxynaphthalen-2-yl)propanoate] tin (II)	Sn(L) ₂
Potassium-2-(6-methoxynaphthalen-2-yl)propanoate	L
Hindered amine light stabilizer	HALS
Fourier Transform Infrared spectroscopy	FTIR
Ultraviolet-Visible spectroscopy	UV
Temperature in kelvin	T
Gram susceptibility	X _g
Correction factor	D
Molar susceptibility	X _M
Magnetic Moment	μ
Average molecular weight	(\bar{M}_v)
intrinsic viscosity	η
Relative viscosity	η _{re}
Specific viscosity	η _{sp}
Quantum yield of main chain scission	φ _{cs}
Incident intensity	I _o
Irradiation time in second	t
Concentration	C

Chapter One

1- Introduction

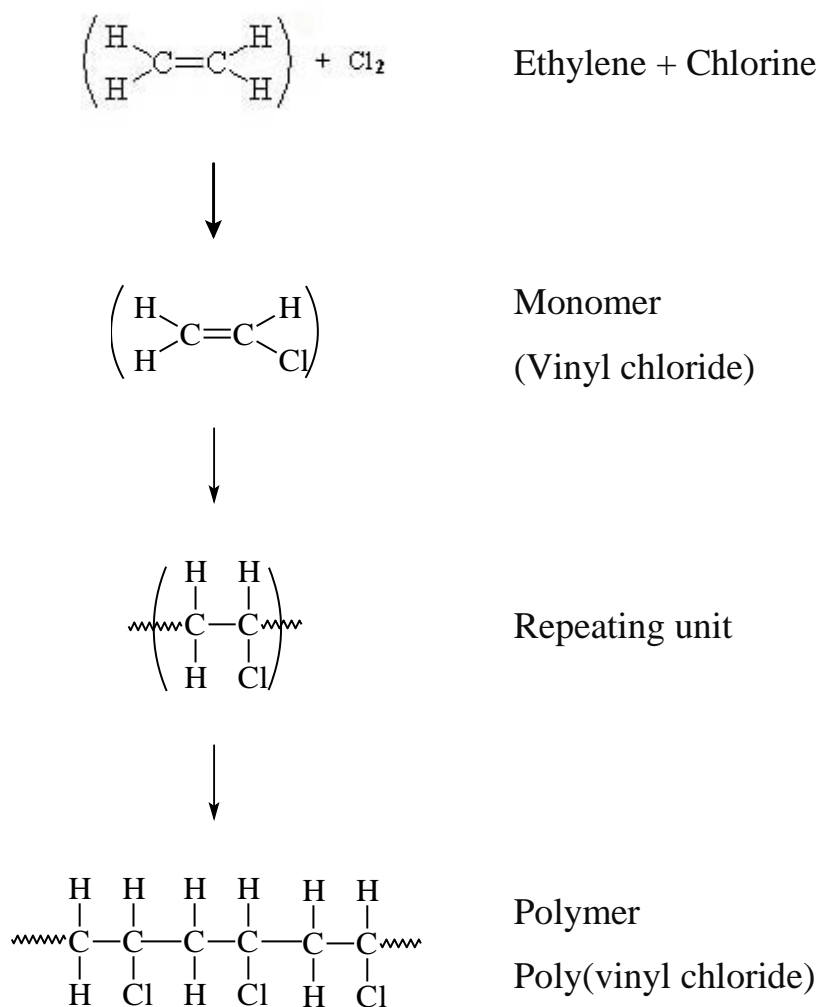
1-1- The origin of poly(vinyl chloride) and its subsequent development

Vinyl chloride monomer and its polymers occupy a unique place in the history of plastics. Arriving early in technology of synthetic resins, they have not been displaced by new polymers. On the contrary, they have become increasingly important⁽¹⁾.

Vinyl chloride had its beginning in the laboratory of the French chemist Regnault⁽²⁾ in 1835, he produced vinyl chloride by mixing ethylene dichloride with an alcoholic solution of potassium hydroxide. The material remained laboratory curiosity, however, until Ostromislensky⁽³⁾, investigated vinyl chloride chemistry in 1912.

The first world war resulted in heavy demands on German's chemical industry. Because of rubber shortage, German chemists again investigated Regnault's work, and in 1918 Klatte and Rollet⁽⁴⁾, developed the first practical method of polymerizing vinyl chloride. The polymer was called poly(vinyl chloride), which is abbreviated as PVC, and it has good physical and chemical properties, abrasion resistance and good strength properties. The major market of PVC is its use in the outdoor applications such as building and construction industry⁽⁵⁾, but the main problem is that PVC is sensitive to the weathering, UV irradiation and presence of oxygen and humidity induces changes in mechanical properties and colour⁽⁶⁾.

This polymer is produced by addition polymerization of the monomer vinyl chloride⁽⁷⁾, (Scheme 1-1)



Scheme (1-1): Preparation of vinyl chloride and poly(vinyl chloride).

Poly(vinyl chloride) (PVC) is a linear-chain polymer with bulky chloride side-groups which prevent crystalline regions occurring normally. PVC is hard and rigid material at room temperature⁽⁸⁾. Straight poly(vinyl chloride) is colorless rigid material. It has relatively high density and low softening point⁽⁹⁾. The presence of the chlorine atom causes an increase in the inter chain attraction, hence an increase in the hardness and stiffness of the polymer is recognized. PVC is also a polar polymer because of C-Cl dipole. These properties make PVC polymers as good candidate in the application involving high frequencies because high dielectric constant and high power factor values higher than polyethylene owing to the polar carbon-chlorine bond⁽⁸⁾.

Poly(vinyl chloride) has very limited solubility. The most effective solvents are those which appear to be capable of some form of interaction with the polymer. It has been suggested that poly(vinyl chloride) is a weak proton donor and effective solvents are proton acceptor⁽⁹⁾. Thus the PVC polymer is soluble at room temperature in oxygen-containing solvents such as ethers (dioxane, tetrahydrofuran), ketones (cyclohexanone, methyl isobutyl ketone) and nitro compounds such as nitrobenzene⁽¹⁰⁾.

1-2- Poly(vinyl chloride) (PVC)

Poly(vinyl chloride), better known by its abbreviation PVC, is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide⁽¹¹⁾.

Thermoplastics from poly(vinyl chloride) (PVC) have a considerable commercial importance in industry and in every day life, they are successfully replacing some natural raw materials due to their particular properties which offer a combination of easy modification in thermoplastic processing, rigidity, compatibility with a large number of other products, resistance to corrosion and low cost technology⁽¹²⁾.

The low cost and the good performance of poly(vinyl chloride) products have increased the utilization of this polymer in building, mainly in exterior applications, such as window profiles, cladding structure and siding⁽¹¹⁾. However; plastics are very susceptible towards solar ultraviolet radiation, so when it is exposed to long term outdoor environment, it undergoes more or less a rapid degradation resulting in discoloration, cracking of surface, stiffing and ultimately loss or decrease in their useful mechanical engineering properties⁽¹³⁾. The extent of outdoor service life of synthetic polymers (plastics) or naturally occurring polymers are limited by their structures, the type and amount of additives and the magnitude of UVB rays absorbed, also the temperature and humidity may further reduce use life⁽¹⁴⁾.

All materials are subjected to weathering. New materials such as high polymers placed in different weathering conditions must be evaluated for lifetime performance. Organic polymeric materials (mainly synthetic plastics) are widely used in various industrial fields and the needs for these materials are increasing. Following a continuous and continuing upward trend, the high polymers now occupy second place behind steel in the scale of most important groups of materials. It is said that their amount used in industrial field can become 50 % of total materials, including metals and ceramics, in the 21st century⁽¹⁵⁾. Plastics can be protected from thermal and photodegradation by using suitable additives (stabilizers), leading to a complex material whose behavior and properties are quite different from the PVC resin by itself⁽¹⁶⁾. These stabilizers designed to prohibit or slow down the degradation process in order to prolong the use life of the plastic⁽¹⁷⁾.

1-3- Types of polymer degradation

Degradation refers to a chemical changes in polymers that result in undesirable changes in the values of in-use properties of materials accompanied by lowering molecular weight⁽¹⁸⁾. It diminishes the life time of industrial product for plastic and engineering polymers. In other side, solid plastic waste is considered to be among the main sources of environmental pollution that have a direct effect on living organisms, so in the last years intensive research has been carried out in order to produce photo and biodegradable polymers that can enhance degradation at a low molecular products that could be easily removed by environment. Therefore a number of researches in this direction were achieved⁽¹⁹⁻²²⁾. Generally, many factors are responsible in causing photodegradation of polymeric materials, they are divided into two categories:

- I) Internal impurities, which contain chromophoric groups; which are introduced into macromolecules during polymerization processing and storage; they include:

- a- Hydroperoxide.
 - b- Carbonyl.
 - c- Unsaturated bonds (C=C).
 - d- Catalyst residue.
 - e- Charge–transfer (CT) complexes with oxygen.
- II) External impurities, which may contain chromophoric groups, are:
- a- Traces of solvents, catalyst, etc.
 - b- Compounds from polluted urban atmosphere and smog, e.g. polynuclear hydrocarbons such as naphthalene and anthracene in polypropylene and polybutadiene.
 - c- Additives (Pigments, dyes, thermal stabilizers, antioxidant, photostabilizers, etc.).
 - d- Traces of metals and metal oxides from processing equipment and containers, such as Fe, Ni or Cr.

There are many different modes of polymer degradation⁽²³⁾. These are very similar since they all involve chemical reactions that result in bond scission. These modes are⁽²³⁾:

I) Chemical degradation:

Chemical degradation refers, in its sense, exclusively to processes, which are induced under the influence of chemical reagent (e.g. acids, bases, solvents reactive gases, etc.).

II) Thermal degradation:

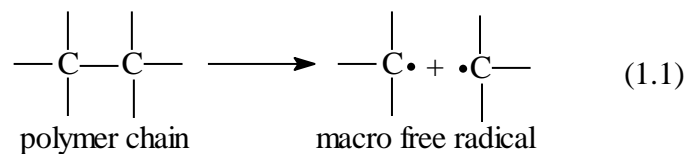
Thermal degradation refers to the case where the polymer, at elevated temperatures, starts to undergo chemical changes without the simultaneous involvement of another compound.

III) Biodegradation:

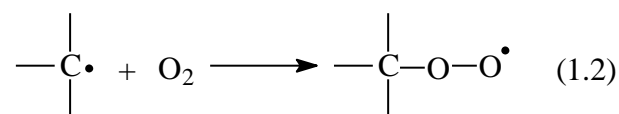
Biologically initiated degradation is strongly related to chemical degradation as far as microbial attack is concerned. Microorganisms produce variety of enzymes which are capable of reaction with natural and synthetic polymers.

IV) Mechanical degradation:

This generally, refers to macroscopic effects brought about under the influence of shear forces. These forces result in the formation of macro free radicals as follows:



Such free radicals can recombine in the absence of oxygen, but in the presence of oxygen peroxy radicals may be formed, which leads to the degradation of polymeric chains.



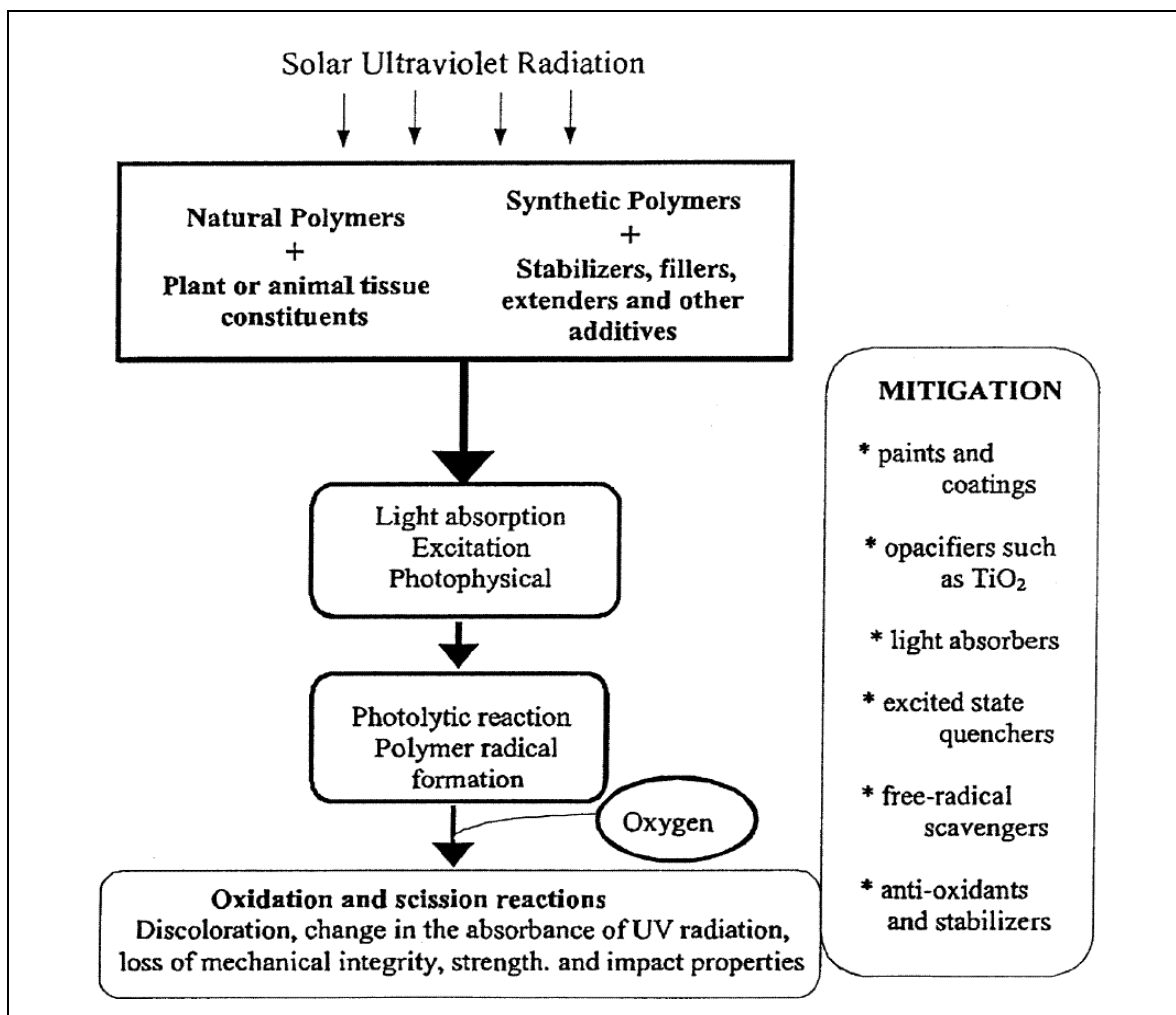
V) Photodegradation :

Light induced polymer degradation, or photodegradation, include the physical and chemical changes caused by irradiation of polymers with ultraviolet or visible light. In order to be effective, light must be absorbed by the substrate (polymeric system). Thus, the existence of chromophoric groups in the macromolecules is a prerequisite for the initiation of any photochemical reaction. Generally, photochemically important chromophores absorb in the UV range .

The importance of photodegradation of polymers derives, therefore, from the fact that the UV portion of the solar radiation can be absorbed by various polymeric

materials. Photodegradation may occur in the absence of oxygen (chain breaking or cross-linking) and the presence of oxygen (photo-oxidative) degradation.

In most polymers the photo-oxidative degradation mechanism is induced by UV radiation and other catalyst (or both of them) and can be accelerated at elevated temperatures. Scheme (1-2) shows the basic steps involved in photodamage and illustrates the various strategies commonly used to mitigate light-induced degradation of polymers.



Scheme (1-2): Schematic diagram of the various stages of light-induced damage in polymers and its mitigation⁽²⁴⁾.

1-4- Polymer weathering

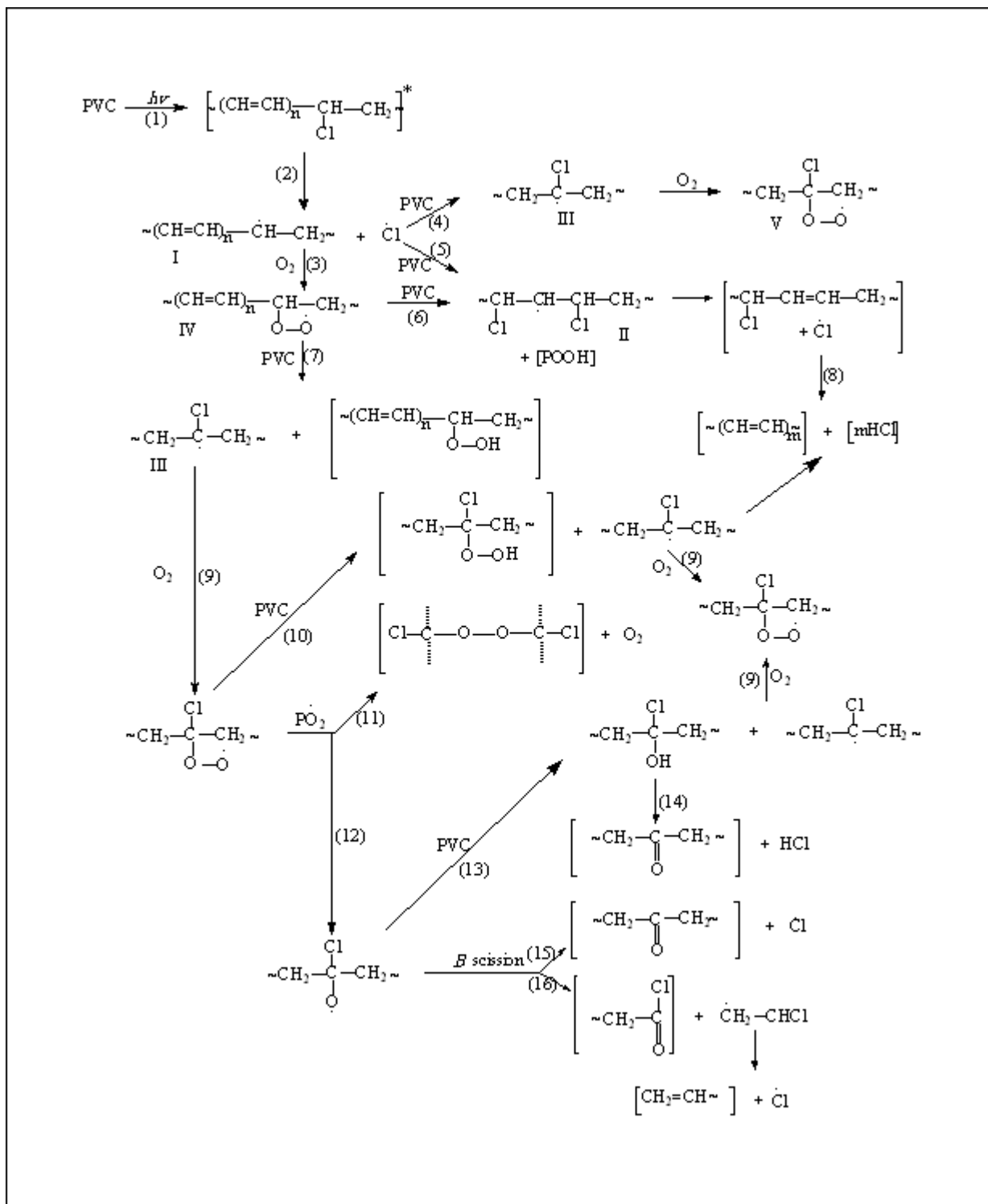
Low degrees of chain scissioning of the large macromolecules, which have the highest probability for chain scissioning, are sufficient to cause severe losses in the materials physical properties. As the polymer industry evolved, considerable effort was expanded to understand, at a molecular level, the degradation of polymers during weathering, and means were found to retard it⁽²⁵⁾.

Degradation of polymeric materials occurs in a wide variety of environments and severe conditions, and very often limits the service lifetime. It occurs as the result of environment-dependent chemical or physical attack, often caused by a combination of degradation agents, and may involve several chemical and mechanical mechanisms⁽²⁶⁾. Degradation of high polymers can be considered to be an irreversible change in some properties that is detrimental to their usefulness. Although polymer properties can be slightly affected during their processing, storage, and transportation, the most significant degradation occurs during exposure to the environment. Parameters used for polymer processing are relatively severe, but they are applied for a short duration and usually involve the action of oxygen and water⁽²⁷⁾.

1-5- Mechanism of photo-oxidative degradation of poly(vinyl chloride)

A natural weathering that has great effect is produced by oxygen and light radiation, referred to technically as photo-oxidation. Materials subjected to oxygen are degraded much faster in the presence of radiation than in its absence and vice versa. The low diffusion coefficient of oxygen in engineering polymers (such as polyolefins, polyamides, and polycarbonate) results in a gradation of oxidation from the surface to the bulk⁽²⁸⁾. The photo-oxidation and thermal degradation of polyolefins has been the subject of extensive studies ever since their commercial introduction. Resistance to oxidation increases with increasing density of the

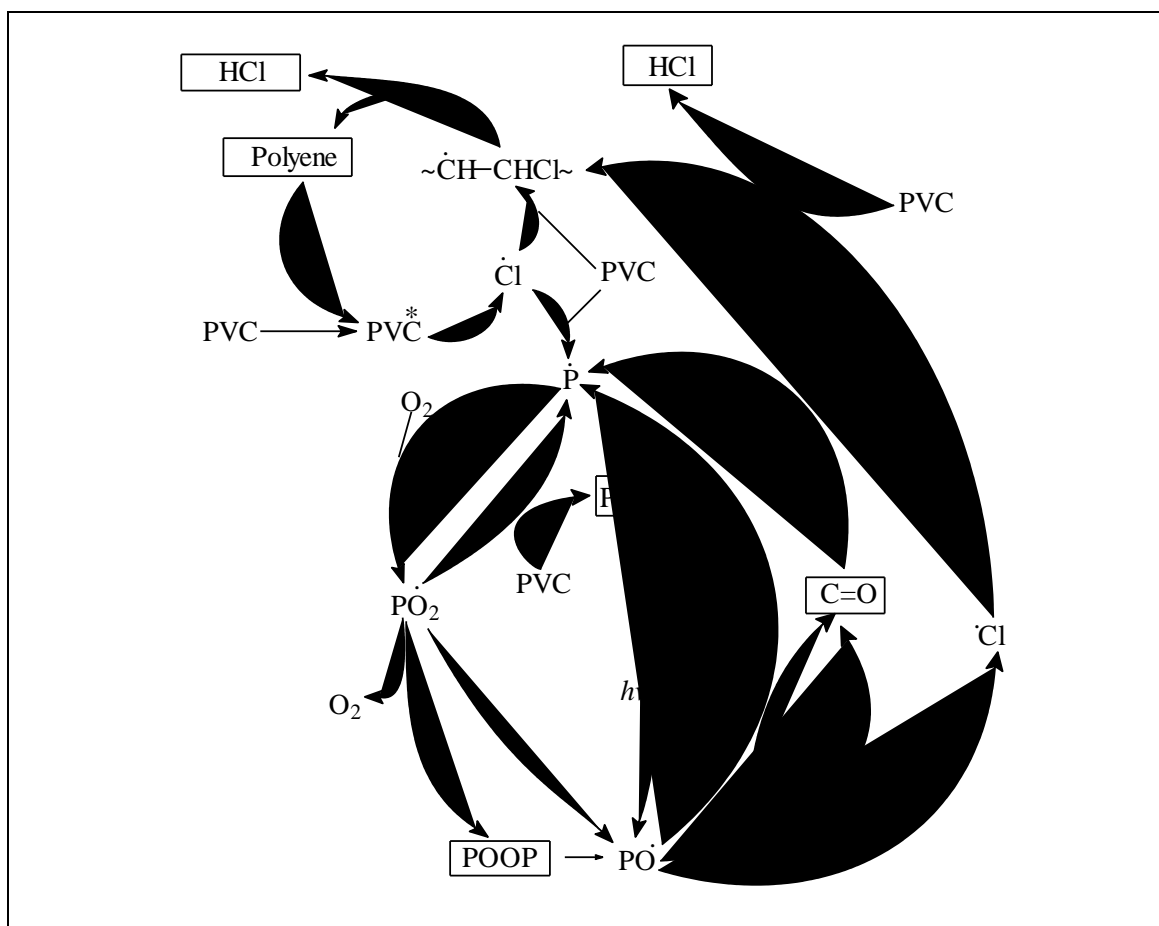
polyolefins because a less branched polymer has a diminished permeability to gases and smaller number of tertiary carbon atoms in the macromolecule (which constitute sensitive points of attack)⁽²⁹⁾. When exposed to natural weathering, PVC deteriorates and becomes increasingly colored and brittle, with a steady decrease in mechanical properties such as tensile strength, elasticity, and impact resistance. Owing to its large outdoor application, PVC has to be protected against photodegradation⁽²⁹⁾. The main factors influencing degradation of PVC products include oxygen, humidity, light, mechanical stress, aggressive media, and ionizing radiation; all are accelerated by increasing temperature⁽³⁰⁾. In the presence of the UV radiation, oxygen seems to attack the PVC chains randomly or on sites that are not involved in the mechanism of thermal degradation⁽³¹⁾. Flexible (plasticized) PVC weathering resistance is determined substantially by the plasticizer; its oxidative stability is generally the deciding property. Each component (stabilizer, UV absorber, pigment, colorant, processing additives, and plasticizer) of the PVC compound possesses its own weathering stability, but it is the interaction of all the components that determines the utility of the material⁽³²⁾. The mechanism of photo-oxidation is explained by reaction Scheme (1-3).



Scheme (1-3): Reaction scheme of the photogradation of PVC in the presence of O₂⁽³³⁾.

The overall mechanism now suggested for the photo-oxidation of PVC to account for the main primary products can be summarized by the reaction scheme shown in Scheme (1-4) where P[•] represents radical $\sim(\text{CH}=\text{CH})_n\text{-}\underset{\text{Cl}}{\text{C}}\text{-CH}_2\text{-}$ or $\sim\text{CH}_2\text{-}$

$\sim\text{CCl-CH}_2\sim$. The two major chain process which develop simultaneously are clearly apparent⁽³³⁾.



Scheme (1-4): Photooxidation reaction scheme of PVC⁽³³⁾.

1-6- Photostabilization mechanisms in polymers

The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics. Polymer photostabilization continues to be rapidly advancing area of scientific and technological interest. An overview of photodegradation shows that in the absence of strong UV absorption by a polymer, even small amounts of impurities or chromophores are sufficient to induce photo-oxidative degradation. Inhibition or at least retardation of the reaction responsible for degradation is a necessity for a successful UV stabilization⁽³⁴⁾.

Practice shows that when the polymer contains a photostabilizer, the oxidation rate is much reduced. Stabilizers reduce but do not completely prevent oxidation, so it can be expected that some reactions will take place in the interior of a stabilized polymer. Any consideration of polymer stabilization has to take in account some basic parameters of the additives such as diffusion, solubility, and volatility. It is generally accepted that an efficient additive should be well soluble in the polymer, whereas views on the importance of the mobility or diffusiveness of additives are not as firmly established⁽³⁵⁾. The protection mechanism of UV absorbers is based essentially on absorption of the harmful UV radiation and its dissipation in a way that does not lead to photosensitization, e.g. dissipation as heat. In addition to having a very high absorption themselves, these chemicals must be very light stable, because otherwise they would be consumed too fast in nonstabilizing reaction. An important disadvantage of UV absorbers is the fact that they need a certain absorption depth to provide good protection of a polymer⁽³⁶⁾. From the view point of photostability, polymers can be grouped as follows:

I) Highly photostable polymers are commonly used without any photostabilizer added, e.g., poly(tetrafluoroethylene) and poly(methylmethacrylate), and have an outdoor life of many years.

II) Moderately photostable polymers can be used outdoors without any photostabilizer, e.g., poly(ethyleneterephthalate), polycarbonate, poly(vinyl fluoride), and poly(vinylidene fluoride), and have life of a few years.

III) Poorly photostable polymers need extensive photostabilization for outdoor use, e.g., polyolefins, poly(vinyl chloride) (PVC), polystyrene (PS), aliphatic and aromatic polyamides, polyurethanes, diene rubbers, and polymeric coatings, and have an outdoor lifetime of less than a year when compounded without any photostabilizer added⁽³⁷⁾.

An acceptable classification of UV stabilizers groups these additives as follows: UV screeners (absorbers or pigments), excited state deactivators (quencher), hydroperoxide decomposer, and radical scavengers⁽³⁶⁾.

1-6-1- Ultraviolet stabilizers

Additives to plastics and other polymer materials which prevent the photodegradation or photo cross-linking caused by ultraviolet light, present in sunlight and various kinds of artificial light sources.

A number of books and reviews⁽³⁷⁻⁴¹⁾, discuss photostabilization mechanism and photostabilizer properties.

The amount of an absorber required to provide economical protection in a plastic is governed by several factors such as:

- (i) Thickness of the plastics.
- (ii) Tolerance of color.
- (iii) Effect of high concentration of absorber in plastics.
- (iv) Compatibility of the absorber in the plastics.

Ultraviolet stabilizers can be classified according to their mechanisms of action in the photostabilization process into:

- (i) UV absorber and light screeners.
- (ii) Quenchers (Deactivate excited states singlet and / or triplet).
- (iii) Hydroperoxide decomposers.
- (iv) Radical scavengers.
- (v) Singlet oxygen, ($^1\text{O}_2$), quenchers.

Ultraviolet stabilizers that are available commercially can be classified by chemical structure into⁽⁴²⁾:

- (i) Pigments.
- (ii) Metal xanthates.
- (iii) Chelates.
- (iv) Salicylates.
- (v) Salicylanilides.
- (vi) Hydroxy phenyl benzotriazoles.
- (vii) Hydroxy benzophenones.

1-6-2- Mechanism of UV absorbing and light screening

1-6-2-1: Mechanism of UV absorber

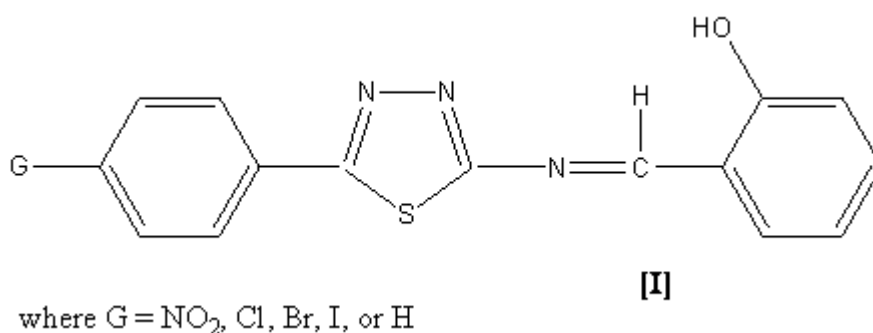
Plastics and organic coatings used outdoors are exposed to ultraviolet (UV) radiation in the range of 295 to 400 nm which is often the primary cause of their degradation and weathering. UV absorbers (UVAs) commonly are used in these applications to prevent UV radiation from reaching the bulk of the polymer or from penetrating the coating and reaching a UV-sensitive substrate. Early in the development of UVAs, it was recognized that they did not perform perfectly and could be depleted during exposure. Indeed, as early as 1961, Hirt, Searle, and Schmitt wrote⁽⁴³⁾:

“The protective absorbers are not everlasting; they do photodecompose, but at a much slower rate than the materials which they are designed to protect. The photodecomposition was found to be dependent on a number of factors including the substrate in which the absorber is dispersed and the wavelength of irradiation.”

Meyer and Geurhurt reported, for the first time in 1945⁽⁴⁴⁾, the use of UV absorber in a polymer. They found that the outdoor life of cellulose acetate film was greatly prolonged by adding phenyl salicylate (Salol).

After that, resorcinol monobenzoate, a much more effective absorber, was introduced in 1951, for stabilization of polypropylene (PP), but Salol continued to be the only important commercial stabilizer for several years⁽⁴⁵⁾.

Yousif et al.⁽¹⁶⁾ improved the photostabilization of PVC films in the presence of Schiff base 2N-Salicylidene-5-(Substituted)-1,3,4-thiadiazole compounds as photostabilizers for PVC films. These compounds (Schiff base) stabilize PVC by different mechanisms such as UV absorbers, screener or by radical scavenger with structure (I), and having a high performance and efficiency for protection the polymer against photodegradation.



1-6-2-2: Light screeners

Light screeners reduce the amount of UV radiation reaching the chromophore groups in polymers either by (a) reflecting and/or scattering the radiation, or (b) by absorbing the radiation. These light screeners can be sub divided into⁽⁴⁶⁾:

1. Pigments:

Pigments are insoluble inorganic or mineral and organic compounds of complex structure, which used as additives, are incorporated into polymers, coating, inks, etc. for:

- (i) Cost reduction.
- (ii) Reinforcement.
- (iii) Hardening.
- (iv) Improving slip and skid resistance.

(v) Colour effect.

(vi) Storage stability.

A pigment as a light screener should be:

(i) Light stable for long term performance without fading.

(ii) Heat stable to withstand polymer processing conditions.

(iii) Migration resistant.

(iv) Low cost and non-toxic.

Light-absorbing properties, photochemical behavior and nature of pigment fading determine the practical application of pigments in polymer^(47,48).

The chemical nature of a pigment is also very important. For example iron oxide (Fe_2O_3) protects polyolefins but rapidly catalyses the decomposition of polyvinyl chloride on exposure to UV radiation. The influence of pigments in polymer photostability is not completely understood. If an absorbing pigment is introduced into a polymer, it act as an inner screen for photo products. If these products are not photooxidized, they accumulate in the polymer matrix. Since pigments act as highly absorbing additives, photooxidative phenomena will be limited mainly to the surface of samples.

2. Carbon black:

Carbon black contains different functional groups such as carbonyl, hydroxyl, quinone, ether, etc.

Carbon black absorbs UV radiation more efficiently than conventional colour pigments, and they are most efficient light stabilizers for polymers⁽⁴⁹⁾, such as polyethylene.

Their high efficiency as light stabilizers is probably due to their ability to act as inner filters for UV radiation, free radical scavengers, because many of the

carbon blacks contain stable free radicals⁽⁵⁰⁾, and quenchers of singlet and triplet states of polymers. The effectiveness of carbon blacks is dependent upon⁽⁵¹⁾ the type of carbon black, the particle size and the degree of dispersion in the polymer phase. Figure (1-1) shows a model of carbon black with different functional groups such as carbonyl, hydroxyl and quinone.

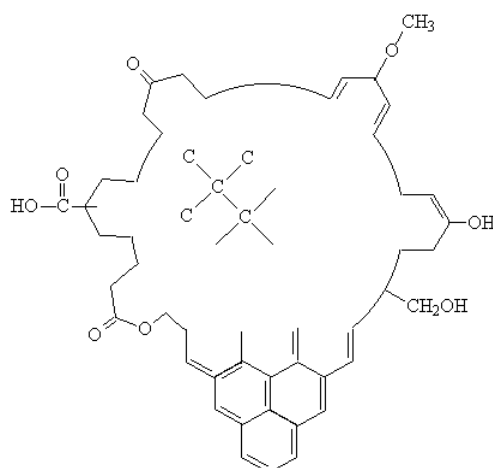


Figure (1-1): Carbon black model illustrating possible functional groups.

1-6-3- Quenchers

Quenchers deactivate excited states (singlet and/or triplet) of chromophoric groups in polymers before bond scission can occur by two mechanisms^(52,53).

1. Energy transfer process.
2. Chemical and/or physical deactivation.

The quenching process is successful only if the quencher molecule is within quenching distance of the excited (singlet and/or triplet) of the chromophoric group within the latter's life time. High diffusion constants in a polymer matrix, (i.e.) good mobility of quencher and/or excited chromophoric group and long lifetime of excited chromophoric group, may therefore enlarge the apparent action sphere of the quencher.

In the solid state, transfer of energy occurs by resonance or dipole-dipole interactions. The photooxidative degradation is promoted by the electronically excited oxygen molecule (singlet oxygen ¹O₂) formed in polymers. The [¹O₂] can also

be generated in polymers by energy transfer from electronically excited carbonyl group to dissolved molecular oxygen⁽⁵⁴⁾. The quenching of [¹O₂] is also necessary for effective stabilization. Nickel chelates have been proven to be very effective quenchers for excited state of [¹O₂]⁽⁵⁵⁾.

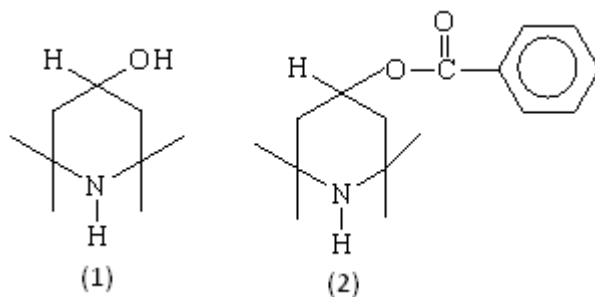
1-6-4- Free radical scavengers

Free radical scavenging in initiation, propagation and branching steps of oxidative degradation of polymers is, together with deactivation of peroxidic species, the principal stabilization mode. Different approaches to free radical scavenging are dictated by differences in the chemical character of C- and O-centered radicals.

There is a rather limited choice of compound acting as scavengers of free radicals and satisfying requirements for commercially applicable stabilizers. Moreover, scavenging of free radicals has to compete with two other reactions (i.e.) self reaction of free radicals and reaction with oxygen.

1-6-5- Hindered amine stabilizer (HAS)

Hindered amine light stabilizer (HALS) belong to a new group of products developed during the nineties of the last century on the industrial scale. They are presently used in plastics formulations intended for outdoor use (0.05–2.0 wt.% level)⁽⁵⁶⁾, such as (4-hydroxy-2,2,6,6-tetramethyl piperidine (1) and 4-Benzoyloxy-2,2,6,6-tetramethyl piperidine, (sanol 774)^(57,58), (2).



The mechanism of (HALS) activity includes scavenging of R^\bullet , ROO^\bullet and deactivation of hydroperoxides (ROOH) and peracids, which are based on a complex of chemical transformations. Nitroxide the key intermediate formed from (HALS), is prone to scavenge alkyls and forms alkylhydroxylamines⁽⁵⁷⁾.

1-7- Enhanced (Sensitized) photodegradation of polymers

Synthetic and semisynthetic polymer materials were originally developed for their durability and resistance to all forms of degradation including biodegradation. Special performance characteristics are achieved through the control in item of their molecular weight and functionality during the processing and under items operative conditions. However, the above quoted features that make the polymeric materials so convenient and useful to the human life, have contributed to create a serious plastic waste, burden, and spreading of plastic litter which make environmental contamination⁽⁵⁸⁾.

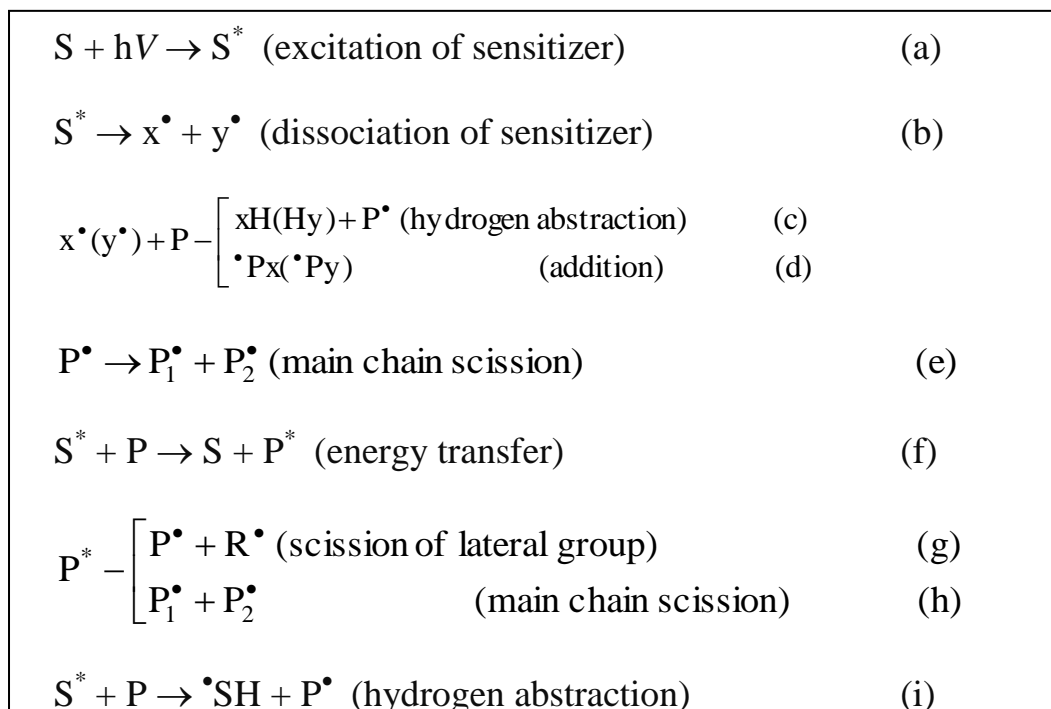
Consequently, photosensitized degradation of polymers is considered as a means of elevating the solid waste problem as far as polymeric materials are concerned. The problem of degradable plastic can be solved by the application of specially designed photodegradable polymers⁽⁵⁹⁾.

Present attempts to develop plastics with reduced outdoor stability are based on^(60,61):

- (i) Synthesis of polymers with light-sensitive groups e.g., aliphatic ketone groups located predominantly in the main chain or pendant groups.
- (ii) Application of photoinitiator (or photosensitizer) which, added to polymers or plastics, photoinitiates (or photosensitize) their degradation^(62,63). Such photodegradable plastics, under sun irradiation, lose their physical and mechanical properties, become brittle, and are finally broken down into small particles by natural erosion, rain, wind, etc., they eventually, form powder which

passes into the soil where it is attacked by microorganisms and lastly re-enters the biocycle.

By the addition of sensitizers, one may distinguish between several types of interaction between sensitizer and macromolecule as illustrated by the following Scheme (1-5):

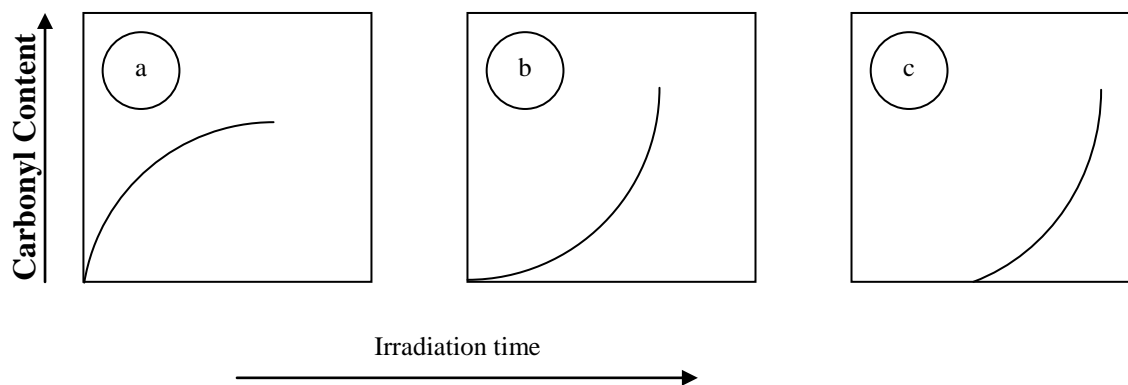


Scheme (1-5): Sensitized photodegradation⁽⁶³⁾.

According to S = sensitizer molecule, P = polymer molecule (i) in scheme (1-5), the macro radical generated reacted with oxygen thus starting the photo-oxidation of the polymer. So one may distinguish between the two types of sensitization mechanisms in the presence of oxygen⁽⁶³⁾:

- a. Oxygen molecules are involve intrinsically in the sensitization process.
- b. Reaction intermediates are generated via an interaction of macromolecules with excited sensitizer molecules or other reactive species formed during the decay of the excited state (radicals). These intermediates react with oxygen, thus the route of the degradation mechanism is changed due to the presence of oxygen.

From the phenomenological point of view, three kinds of oxidative behavior can be observed, according to the classification of Amin and Scott⁽⁶⁴⁾, as shown in Scheme (1-6), these are:



Scheme (1-6): Schematic representation of sensitized photo-oxidation of polymers⁽⁶⁴⁾.

- a. The polymer is initially rapidly oxidized, the initial rate increases with increasing sensitizer concentration. At longer irradiation time, the oxidation is auto-retarded. Benzophenone and its derivatives are typical examples of this kind of sensitizers.
- b. The oxidation may be auto-accelerated by the sensitizer e.g. Transition metal complexes, such as Fe(III) acetylacetonates.
- c. An initial induction period exists which increases with increasing sensitizer concentration, e.g. metal complexes of 2-hydroxy acetophenone (oxime)⁽⁴⁴⁾.

1-8- Photostabilization of poly(vinyl chloride)

The degradation of PVC at elevated UV light required in thermoplastic processing is an intrinsic characteristic of the polymer and consists of dehydrochlorination, auto-oxidation, mechano-chemical chain scission, crosslinking and condensation reactions. This degradation must be controlled by the addition of

stabilizers. The stabilizer must prevent the dehydrochlorination reaction that is the primary process in degradation. There are two ways the stabilizer can act⁽⁶⁵⁾:

- By reacting with allylic chlorides. This process should be faster than the chain propagation itself, requiring a very active nucleophile. However, the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer. To be effective, the stabilizer must be associated by complex formation with polymer chlorine atoms, which means it should have a lewis acid character⁽⁶⁶⁾.

This association should take place in regions where the polymer molecules have maximum mobility; in other words, where the conformation of the polymer can favor the degradation processes.

- Once the degradation starts, it is very fast and can be stopped only if the stabilizer is already associated with the chlorine atom that becomes allylic. These regions are the surfaces of the primary particles of PVC, where the stabilizer molecules are associated with the chlorine atoms. The exceptional effectiveness of such stabilizers at very low concentrations is explained by their entropically favorable position for stopping degradation^(66,67). In general, these stabilizers, because of their effectiveness, prevent the formation of bonds and maintain very good early color in the polymer. These stabilizers are called primary stabilizers⁽⁶⁷⁾.
- Scavenging the hydrogen chloride generated by degradation is another way to stop the process as the HCl is a catalyst for the chain propagation reaction and the initiation step.

However, the diffusion of HCl is quite slow because HCl is associated with the double bond where it was generated. When HCl diffuses away from the reaction center, degradation reaction stops. The stabilizer should scavenge HCl with high effectiveness to avoid its catalytic effect in chain initiation that starts another dehydrochlorination chain. This type of stabilizer cannot prevent the

dehydrochlorination in its early stages. PVC discolors and the initial color is not maintained. However, by scavenging HCl, this type of stabilizer avoids the autocatalytic degradation and consequently, overall degradation is much slower. These stabilizers provide very good long-term stability and are usually referred to as secondary stabilizers⁽⁶⁸⁾.

To have good stabilization of PVC with good early color and long-term stability, the two types of stabilizer should be combined appropriately for each particular PVC formulation. Stabilization is complicated by the fact that primary stabilizers become strong Lewis acids by reacting with the HCl that catalyzes the initiation and propagation of PVC degradation. To avoid this, secondary stabilizers should react efficiently with HCl to protect the primary stabilizers⁽⁶⁸⁾.

The alkyltin derivatives mono and dimethyl-butyl and octyltin, alkyl thioglycolates, mercaptopropionates and alkyl maleates, all these compounds react with HCl to form the corresponding tin chloride. These compounds consequently function as secondary stabilizers⁽⁶⁹⁾.

Metal carboxylates stabilize PVC by either mechanism, depending on the metal. Strongly basic carboxylates combined with metals such as K, Ca, or Ba, which have little or no Lewis acidity are mostly HCl scavengers. Metals such as Zn, Cu, Ni and Cd, which are stronger Lewis acids and form covalent carboxylates, not only scavenge HCl, but also substitute carboxylate for the allylic chlorine atoms⁽⁷⁰⁾.

Trialkyl phosphites scavenge HCl by an Arbuzov reaction⁽⁷¹⁾ and form dialkyl phosphites. They react also with allylic chlorides, but this process plays a secondary role⁽⁷¹⁾.

Kwei et al.⁽⁷²⁾ reported that UV photolysis of PVC in THF solution in the presence of copper salicylate and copper phthalocyanine gave good stabilizer different from the PVC by itself.

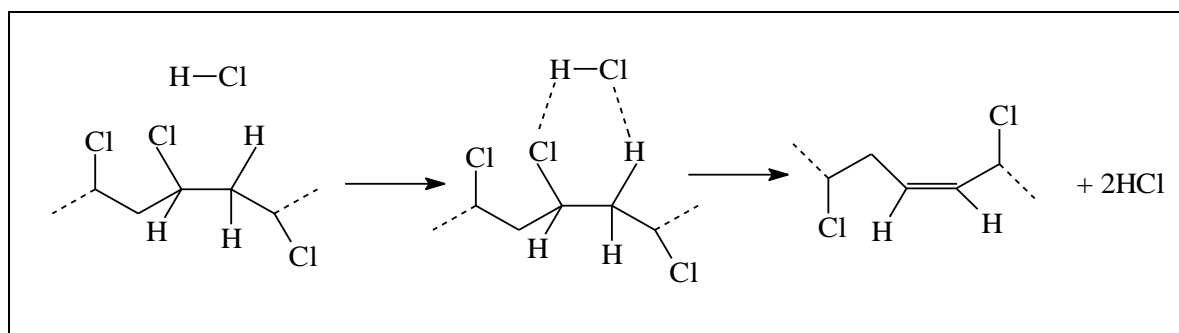
The light stability of PVC plates has been substantially increased by protecting their surface with a UV-cured acrylic clearcoat containing both a UV absorber and HALS radical scavenger. To ensure a long-lasting adhesion, the coating was photochemically grafted onto the PVC substrate. The coated PVC sample remained transparent, non colored and glossy upon accelerated QUV-B weathering for a long time. An additional advantage of this method of photostabilization is to improve some of the surface properties of the coated polymer, such as its resistance to solvents, abrasion and scratching. The method was also successfully used to recover highly photodegraded PVC and make it even more weathering resistant than the original polymer⁽⁶⁹⁻⁷⁴⁾.

When PVC is processed at UV, it is degraded by dehydrochlorination, chain scission, and crosslinking of macromolecules. Free hydrogen chloride (HCl) evolves and discoloration of the resin occurs along with important changes in physical and chemical properties⁽⁷⁵⁾.

The evolution of HCl takes place by elimination from the polymer backbone; discoloration results from the formation of conjugated polyene sequences of double bonds. Subsequent reactions of highly reactive conjugated polyenes crosslink or cleave the polymer chain.

In the degradation of solid PVC, the degradation rate increases with time, indicating an autocatalytic process. Hydrogen chloride formed in the degradation increases both the degradation rate and the mean number of double bonds in the polyene sequence, and consequently plays an essential catalytic role in PVC degradation⁽⁷⁶⁾.

Six-center transition state in the catalytic presence of HCl Scheme (1-7) structural irregularities such as allylic chlorine atoms eliminate chlorines in the chain.

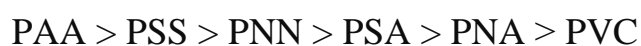


Scheme (1-7): Suggested mechanism of autocatalytic process in presence of hydrogen chloride formed⁽⁷⁶⁾.

Many studies of modification of PVC have been conducted. These studies are mostly concerned with modify poly(vinyl chloride) by introducing aromatic and heterocyclic moieties through displacement reaction. However, aromatic and heterocyclic polymers are more photostable than aliphatic polymers.

Their photostability can be explained by the stability of aromatic and heterocyclic rings due to resonance by the great strength of bonds connecting the rings and also by the high ability to remove the harmful UV light in many ways such as, screening of radiation, absorption of radiation and intersystem crossing. Recently Yousif et al.⁽⁷⁷⁾ studied the new photostabilizers for poly(vinyl chloride) based on some diorganotin(IV) complexes and they found that the modified polymer is more stable than the PVC without modification.

Yousif and Hameed studied⁽⁷⁸⁾ the photostability of some modified poly(vinyl chloride) containing pendant benzothiazole and benzimidazole ring by mixing 2-amino benzothiazole with poly(vinyl chloride) (PAA), 2-mercapto benzothiazole with poly(vinyl chloride) (PSS), 2-Amino benzimidazole with poly(vinyl chloride) (PNN), 2-amino benzothiazole and 2-mercapto benzothiazole with poly(vinyl chloride) (PSA), 2-amino benzimidazole and 2-amino benzothiazol with poly(vinyl chloride) (PNA). They reported that the photostability following the order:



1-9- Aim of the present work

This work was designed to reach the following targets:

- Introduction of new photostablizing materials with good and high compatibility with PVC.
- Shedding more light on the mechanism of photostablization of PVC by organic and organometallic compounds. This process will lead to better understanding of the photostabilization process of polymers in general and PVC in specific.

To achieve these targets, the study includes the use of 2-(6-methoxynaphthalen-2-yl)propanoate metal complexes as photostabilizers of PVC.

These materials might possess the properties of HCl scavenging, UV absorption, peroxide decomposer and radical scavenger, which lead for photostablization of PVC.

Chapter Two

2- Experimental Part

2-1- Chemicals

All of the reagents and starting materials used in the present work are of reagent grade and were used without further purifications unless otherwise noted.

Compound	Supplied from
2-(6-methoxynaphthalen-2-yl)propanoic acid	BDH
Potassium hydroxide	BDH
Tetrahydrofuran	BDH
Nickel (II) acetate tetrahydrate	BDH
Tin (II) chloride	Fluka
Copper (II) acetate	BDH
Cadmium (II) acetate dihydrate	M&B
Zinc (II) acetate dihydrate	Fluka
Ethanol	Fluka
Dimethyl sulfoxide	BDH
N,N-Dimethyl formamide	BDH

2-2- Techniques

2-2-1- Melting point

Melting points were recorded on a hot stage Gallen Kamp melting point apparatus and were uncorrected in Al-Nahrain University, Department of Chemistry.

2-2-2- Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra in the range (4000-400) cm^{-1} cut were recorded as KBr disc on FT-IR.8300 Shimadzu Spectrophotometer in Al-Nahrain University, Department of Chemistry.

2-2-3- Ultraviolet-Visible Spectroscopy (UV-Vis)

The UV-visible spectra were measured using Shimadzu UV-vis. 160 A-Ultraviolet Spectrophotometer in the range (200-1000) nm in Al-Nahrain University, Department of Chemistry.

2-2-4- Magnetic susceptibility measurements

The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Bruke Magnet B.M.6 (England) in Al-Nahrain University, Department of Chemistry.

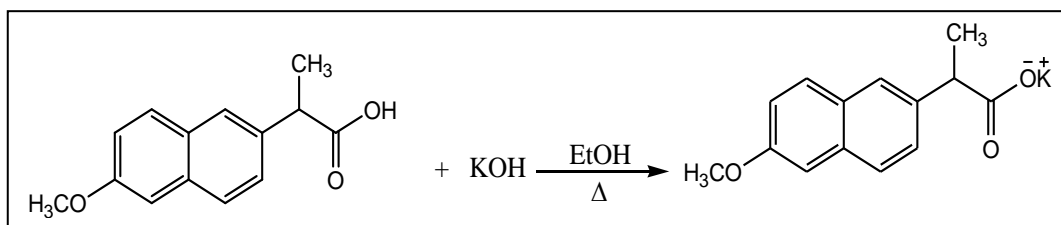
2-2-5- Conductivity measurements

The molar conductivity measurements were obtained using WTW 740 (Germany) in Al-Nahrain University, Department of Chemistry.

2-3- Synthesis of materials

2-3-1- Synthesis of Potassium-2-(6-methoxynaphthalen-2-yl)propanoate

A mixture of 2-(6-methoxynaphthalen-2-yl)propanoic acid (0.1 mole) (0.5 g) and (0.1 mole) (0.12 g) of KOH (to make the medium alkaline) dissolved in (10 ml) ethanol and then refluxed for three hours and then add excess of KOH to give Potassium-2-(6-methoxynaphthalen-2-yl)propanoate. The yellow precipitate which formed was filtered and recrystallized from ethanol to give the final product. The steps of the synthesis of Potassium-2-(6-methoxynaphthalen-2-yl)propanoate can be shown in reaction (2-1).



Reaction (2-1): preparation of ligand salt.

2-3-2- Preparation of complexes⁽⁷⁹⁾

Addition of ethanol solution (5 ml) of the suitable metal salt (Nickel (II) acetate tetrahydrate $[\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}]$ (0.25 g), Tin (II) chloride $[\text{SnCl}_2]$ (0.38 g), Copper (II) acetate $[\text{Cu}(\text{CH}_3\text{CO}_2)_2]$ (0.3 g), Cadmium (II) acetate dihydrate $[\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$ (0.5 g) and Zinc (II) acetate dihydrate $[\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$ (0.5 g) to an ethanol solution (5 ml) of potassium-2-(6-methoxynaphthalen-2-yl)propanoate (0.7 g) in 2:1 (ligand : metal) molar ratio were carried out. After reflux for half an hour, crystalline colored precipitates formed at room temperature. The resulting precipitates were filtered off, washed with ether, dried and recrystallized from ethanol and dried at 50 °C. The steps of the synthesis of complexes can be shown in reaction (3-1).

2-4- Photodegradation measuring methods

2-4-1- Films preparation

A solution of poly(vinyl chloride) or modified poly(vinyl chloride) (5g/100ml) in tetrahydrofuran (THF) was used to prepare (30 μm) thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hours.

2-4-2- Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Philips, Germany), was used for irradiation of PVC films. These lamps are of the type (UV-B 313) giving wavelength range between (290 to 360 nm) and the maximum wavelength light intensity is at

(313 nm). The polymer film samples were fixed parallel to each other and the lamp of the UV incident radiation is vertically incident on the samples. The distance between the polymer films and the source was 25 cm. The irradiation samples were changed place from time to time to insure homogeneous intensity of incident radiation on all the samples.

2-4-3- Measuring the photodegradation rate of PVC films using infrared spectrophotometry

The photodegradation of PVC film samples were followed by monitoring by FT-IR spectra in the range (4000-400) cm^{-1} . The position of hydroxyl, carbonyl and polyene absorption is specified by the bands at (3460 cm^{-1}), (1770 cm^{-1}) and (1629 cm^{-1}) for the calculation of hydroxyl, carbonyl and polyene indices respectively. The photodegradation during different irradiation times were followed by observing changes in hydroxyl, carbonyl and polyene bands. The hydroxyl (I_{OH}), carbonyl (I_{CO}) and polyene (I_{PO}) indices were calculated by comparison of the FT-IR absorption band at (3460 cm^{-1}), (1770 cm^{-1}) and (1629 cm^{-1}) with reference band at (1328 cm^{-1}), respectively. This method is called band index method⁽⁸⁰⁾ which includes:

$$I_s = \frac{A_s}{A_r}$$

A_s = Absorbance of peak under study.

A_r = Absorbance of reference peak.

I_s = Index of the group under study.

Actual absorbance, the difference between the absorbance of base line and top peak ($A_{\text{Top Peak}} - A_{\text{Base Line}}$), is calculated using the Base Line method⁽¹⁶⁾.

2-4-4- Measuring the photodegradation rate of polymer films using Ultraviolet-visible spectrophotometer⁽⁷⁹⁾

The ultraviolet-visible spectrophotometer type (Shimadzu Uv-vis. 160) was used to measure the changes in the Uv-visible spectrum during the irradiation time for each compound at the maximum absorption band (λ_{\max}).

The absorption spectrum was measured in the range of (200-400 nm) and the (λ_{\max}) at each absorption was also recorded at different irradiation times. The infinite irradiation time was considered and the infinite absorption (A_{∞}) was assumed to be after the infinite irradiation time.

The first order equation was used to determine the photodegradation rate constant for modified polymer (K_d):

$$\ln(a-x) = \ln a - K_d t \dots\dots\dots(2-1)$$

Where a, represent the stabilizer concentration before irradiation and x, represent the change in stabilizer concentration after irradiation time (t).

If A_0 represent the absorption intensity of the polymer film containing stabilizer before irradiation, and A_t represent the absorption intensity after (t) time of irradiation, then:

$$a = A_0 - A_{\infty}$$

$$x = A_0 - A_t$$

$$a - x = A_0 - A_{\infty} - A_0 + A_t = A_t - A_{\infty} \dots\dots\dots (2-2)$$

Then equation (2-1) becomes

$$\ln (A_t - A_{\infty}) = \ln(A_0 - A_{\infty}) - K_d t \dots\dots\dots (2-3)$$

Thus a plot of $\ln (A_t - A_{\infty})$ versus irradiation time (t) gives straight line with a slope equal to (K_d) which indicates that photodecomposition of the modified polymers is first order.

2-4-4- Determination of viscosity average molecular weight (\overline{M}_v) using viscometry method

The viscosity property was used to determine the molecular weight of polymer, using the Mark-Houwink relation⁽⁸¹⁾.

$$[\eta]=K\overline{M}_v^\alpha \dots\dots\dots(2-4)$$

$[\eta]$ =is the intrinsic viscosity.

$K, \alpha =$ are constants dependent upon the polymer-solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (gm/100ml) and the flow times of polymer solution and pure solvent are t and t_0 respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_0} \dots\dots\dots(2-5)$$

η_{re} = Relative viscosity .

$$\eta_{sp} = \eta_{re} - 1 \dots\dots\dots(2-6)$$

The single–point measurements were converted to intrinsic viscosities by the relation (2-7)⁽⁸²⁾.

$$[\eta]=\frac{\sqrt{2}}{c} (\eta_{sp} - \ln\eta_{re})^{1/2} \dots\dots\dots (2-7)$$

C = Concentration of polymer solution (gm/100ml).

Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution. The following equation was used⁽¹⁶⁾;

$$[\eta]=1.38 \times 10^{-4} M_w^{0.77} \dots\dots\dots (2-8)$$

Equation (2-8) was used to calculate (\bar{M}_v) for PVC without additives before irradiation, and equation (2-7) used to measure (\bar{M}_v) of polymers with additives after irradiation.

The quantum yield of main chain scission (Φ_{cs}) was calculated from viscosity measurement using the following relation⁽⁸²⁾.

$$\Phi_{cs} = (CN_A/\bar{M}_{v,0}) \left[([\eta_0]/[\eta])^{1/\alpha} - 1 \right] / I_0 t \dots \dots \dots (2-9)$$

Where:

C = concentration.

N_A = Avogadro's number.

$(\bar{M}_{v,0})$ = the initial viscosity – average molecular weight.

$[\eta_0]$ = Intrinsic viscosity of polymer before irradiation.

$[\eta]$ = Intrinsic viscosity of polymer after irradiation.

α = Exponent in the relation: $[\eta] = KM^\alpha$.

I_0 = Incident intensity.

t = Irradiation time in second.

Chapter Three

3- Results and Discussion

3-1- Synthesis and identification of potassium-2-(6-methoxynaphthalen-2-yl)propanoate and its complexes

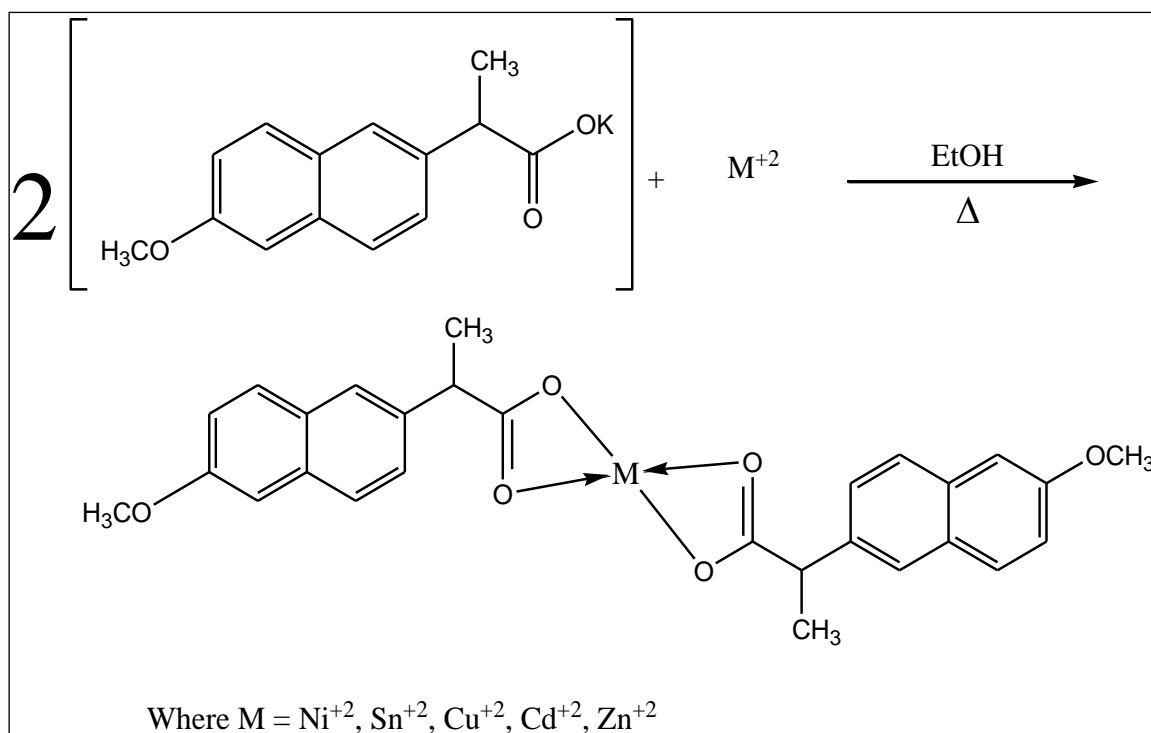
3-1-1- Infra-Red Spectroscopy

The synthetic route for the preparation of potassium-2-(6-methoxynaphthalen-2-yl)propanoate is outlined in chapter two. This ligand was prepared by the reaction of (0.1 mol) (0.5 g) of 2-(6-methoxynaphthalen-2-yl)propanoic acid with (0.1 mol) (0.12 g) of potassium hydroxide (KOH).

Table (3-1) shows the physical data for the ligand and the prepared complexes. The data of metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

Table (3-1): Physical data for preparation ligand and the complexes

Compound	Molecular Weight g/mol	Melting point °C	M found (calc.) %
KL	268	228-229	-
Ni(L) ₂	516	76-78	10.28 (11.36)
Cu(L) ₂	521	>205	9.72 (12.18)
Zn(L) ₂	523	105-107	11.14 (12.49)
Cd(L) ₂	570	178-180	21.45 (19.70)
Sn(L) ₂	576	144-145	21.23 (20.58)



Reaction (3-1): preparation of complexes

The reaction between this ligand with Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) salts gave different types of complexes.

The FTIR spectrum, Figure (3-1) of this ligand shows a characteristic stretching absorption bands at 3342 cm^{-1} , 1600 cm^{-1} , 1452 cm^{-1} , 1028 cm^{-1} , 1570 cm^{-1} , and 1309 cm^{-1} assigned to hydroxyl group, $\nu(\text{COO})$ asym., $\nu(\text{COO})$ sym., $\nu(\text{OCH}_3)$, $\nu(\text{C}=\text{C})$ of the aromatic ring and $\nu(\text{C}-\text{H})$ bending of ($-\text{CH}_3$) respectively⁽⁸³⁾. The (COO) stretching vibrations are important to predict the bonding mode of the ligand. The values of $\Delta\nu$ [$\Delta\nu = \nu \text{ asym.}(\text{COO}) - \nu \text{ sym.}(\text{COO})$] can be divided into three groups; (a) In compounds where $\Delta\nu (\text{COO}) > 350 \text{ cm}^{-1}$, the carboxylate group binds in a monodentate fashion. However, other very weak intra- and intermolecular interactions cannot be excluded. (b) When $\Delta\nu (\text{COO}) < 200 \text{ cm}^{-1}$, the carboxylate groups of these compounds can be considered to be bidentate. (c) In compounds where $\Delta\nu (\text{COO}) > 200 \text{ cm}^{-1}$ and $< 350 \text{ cm}^{-1}$ an intermediate state between monodentate and bidentate (anisobidentate) occurs⁽⁸³⁾. It has also been

suggested that the $\Delta\nu$ (COO) value in the chelating mode is less than the $\Delta\nu$ (COO) in a bridging mode. Stretching of metal-oxygen bands of the complexes appeared in low frequency region (480-432) cm^{-1} (83). The IR data of the ligand and complexes are shown in Table (3-2), Figures (3-1) to (3-6).

Table (3-2): Characteristic absorption bands of potassium-2-(6-methoxynaphthalen-2-yl)propanoate and its complexes

Compound	ν (COO) asymetrical cm^{-1}	ν (COO) symetrica l cm^{-1}	$\Delta\nu = [\nu$ asym.(COO) – ν sym.(COO)]	ν (M-O) cm^{-1}
L	1600	1452	148	-
Ni(L) ₂	1568	1409	159	435
Cu(L) ₂	1587	1404	183	474
Zn(L) ₂	1600	1454	146	476
Cd(L) ₂	1545	1392	153	432
Sn(L) ₂	1606	1460	146	480

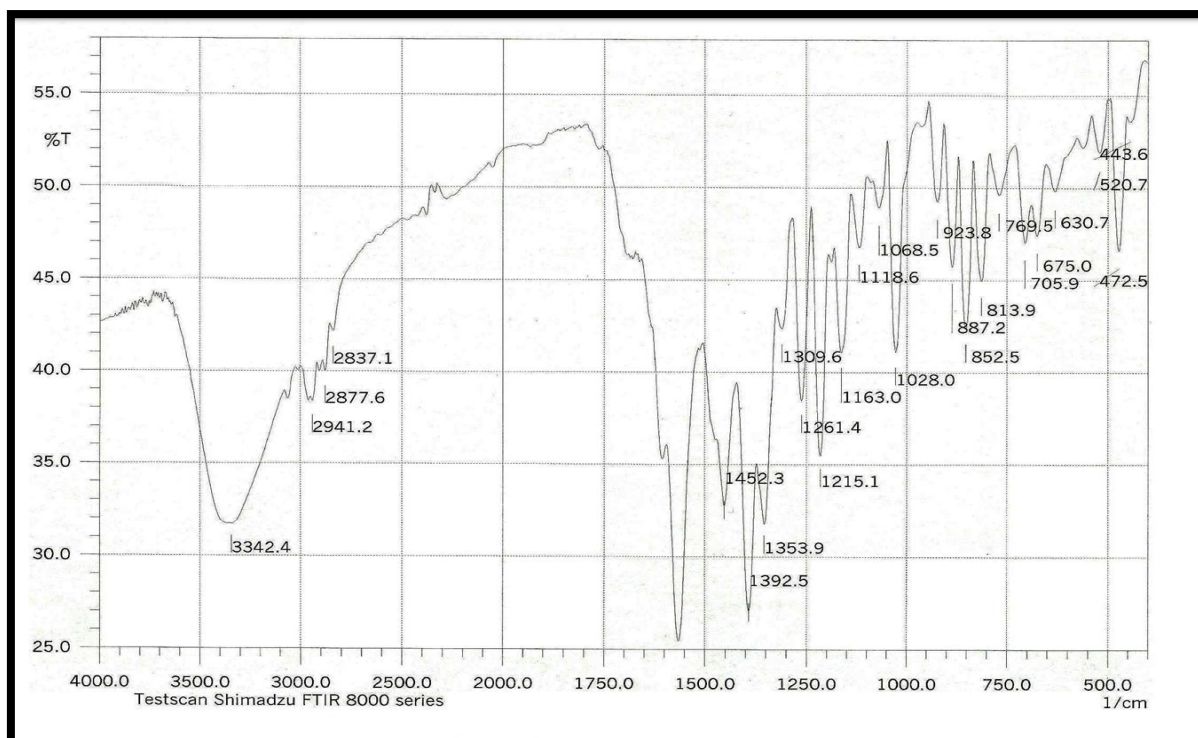


Figure (3-1): FTIR spectrum of potassium-2-(6-methoxynaphthalen-2-yl)propanoate

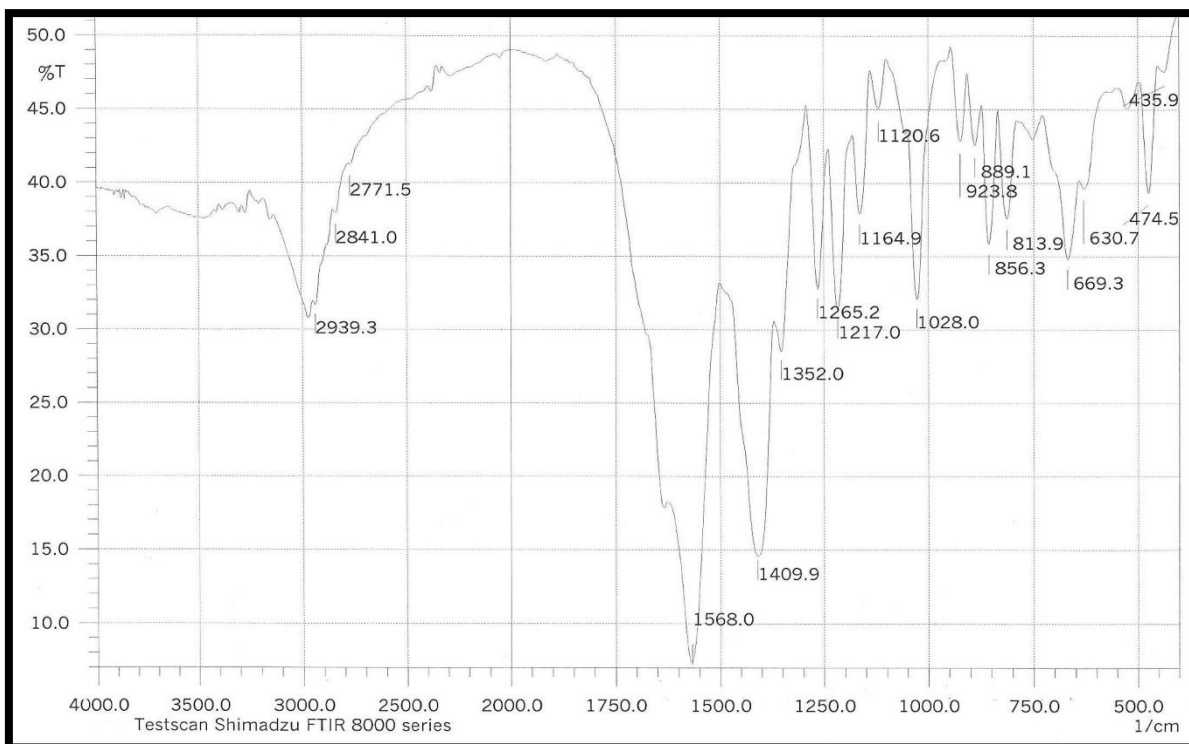


Figure (3-2): FTIR spectrum of Ni(L)₂

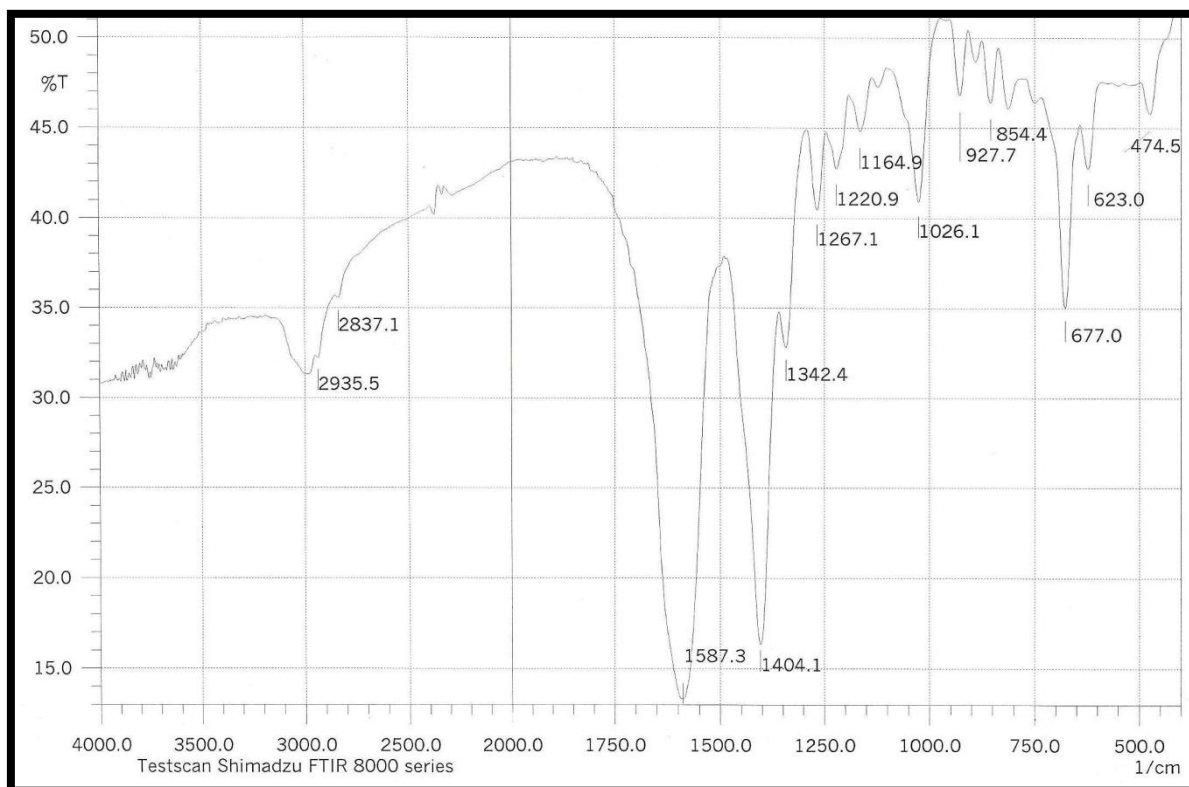


Figure (3-3): FTIR spectrum of Cu(L)₂

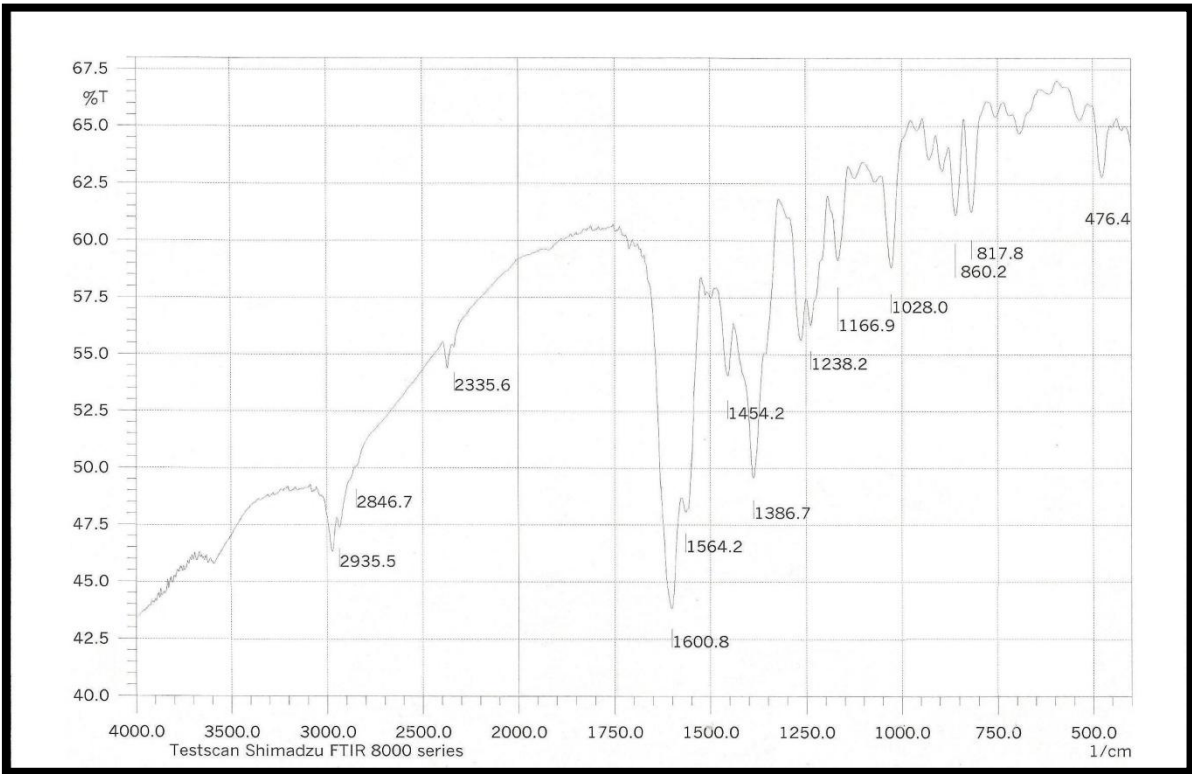


Figure (3-4): FTIR spectrum of Zn(L)₂

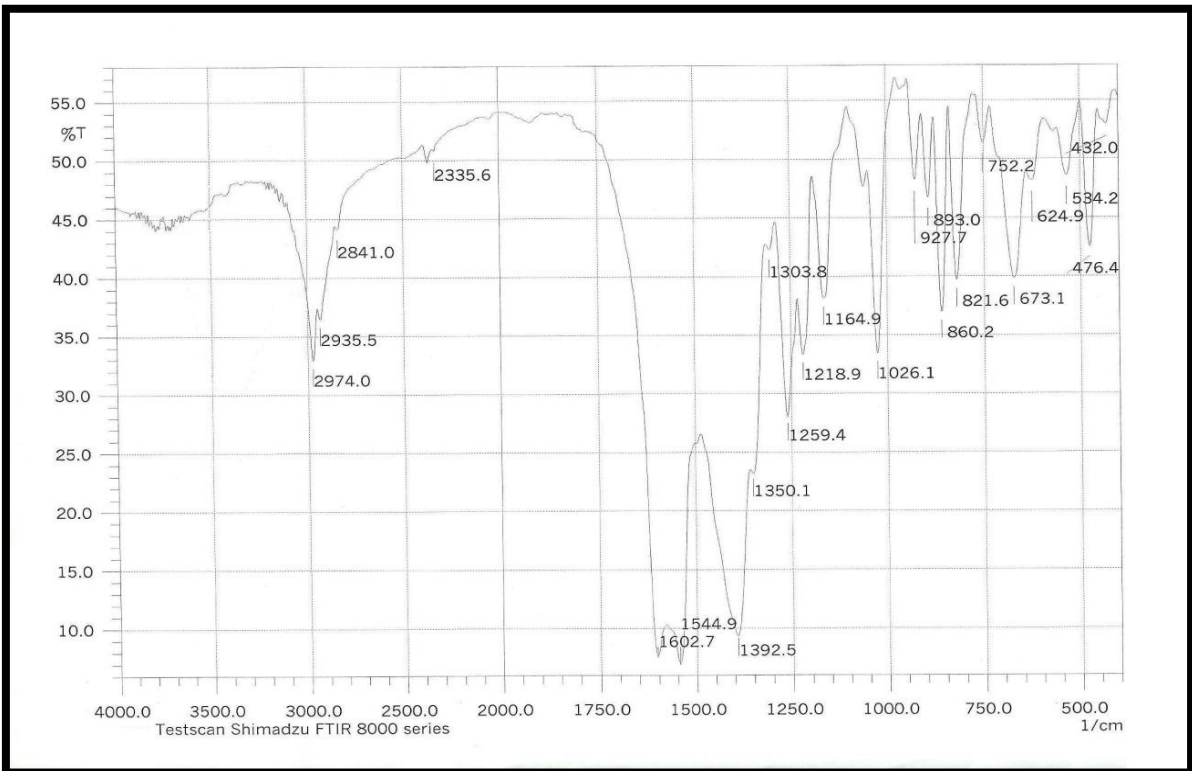


Figure (3-5): FTIR spectrum of Cd(L)₂

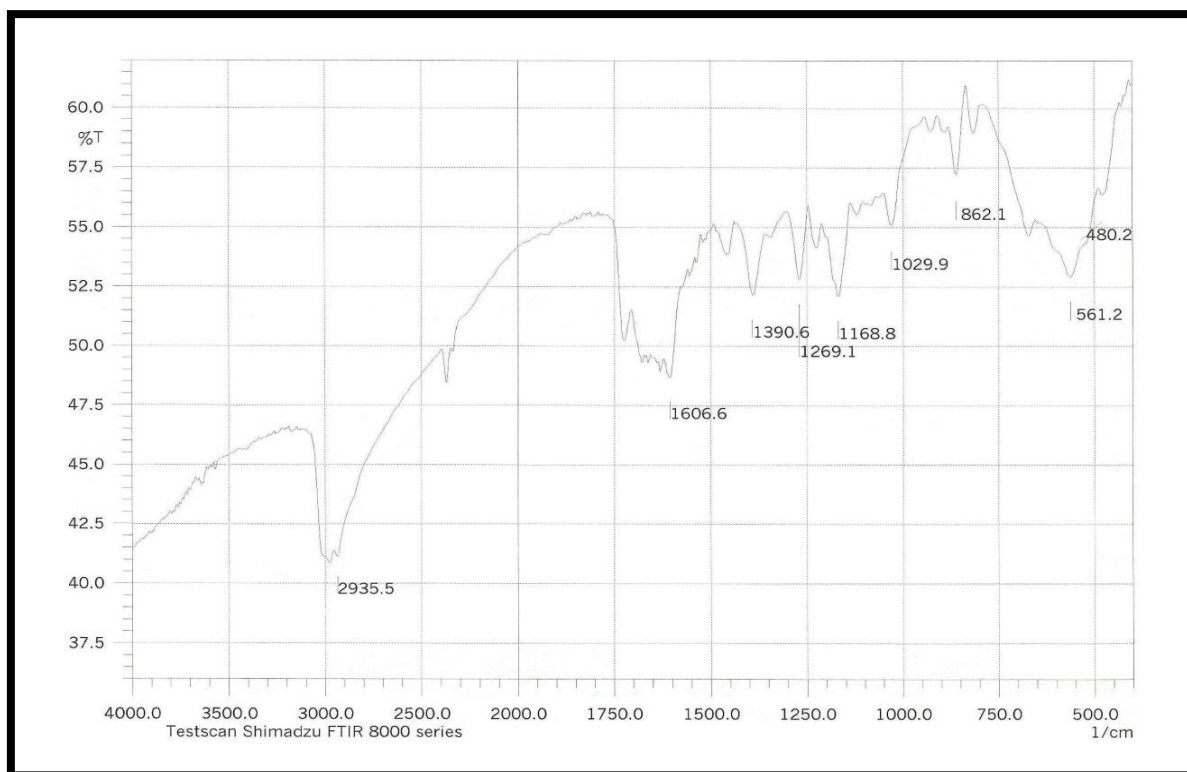


Figure (3-6): FTIR spectrum of Sn(L)₂

3-1-2- Ultraviolet-Visible Spectroscopy

The ultraviolet visible electronic spectrum of the potassium-2-(6-methoxynaphthalen-2-yl)propanoate (L) (10^{-3} M) in DMSO solvent is recorded and shown in Figure (3-7), a bands at the wavelength (274, 324 and 336 nm) this transitions attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition⁽⁸⁴⁾.

The electronic spectra of 2-(6-methoxynaphthalen-2-yl)propanoate complexes show, as expected, different absorptions from that of the free ligand. In the complexes these bands were shifted to different wavelength than the corresponding bands in the ligand as shown in Table (3-3), which appears in the wavelength range between 261 to 335 nm.

The ligand field electronic transitions between the metal d orbitals appear in Ni(II) and Cu(II) bands located in the visible region⁽⁸⁵⁾ at 430 nm for Ni(L)₂ assigned to the transition ${}^3T_1(F) \rightarrow {}^3T_1(P)$ and 709 nm for Cu(L)₂ assigned to the transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ⁽⁸⁴⁾.

The other complexes were diamagnetic as expected for d¹⁰ ions, so that no (d-d) transition can be expected in the visible region.

Table (3-3): Electronic spectra for potassium-2-(6-methoxynaphthalen-2-yl)propanoate and its complexes in DMSO solvent

Compound	Color	Absorption Bands (nm)	Assigned Transition
L	Yellow	274	$\pi \rightarrow \pi^*$
		324	$\pi \rightarrow \pi^*$
		336	$n \rightarrow \pi^*$
Ni(L) ₂	Pale green	261	$\pi \rightarrow \pi^*$
		325	$n \rightarrow \pi^*$
		430	${}^3T_1(F) \rightarrow {}^3T_1(P)$
Cu(L) ₂	Green	264	$\pi \rightarrow \pi^*$
		333	$n \rightarrow \pi^*$
		709	${}^2B_{1g} \rightarrow {}^2A_{1g}$
Zn(L) ₂	White	274	$\pi \rightarrow \pi^*$
		322	$\pi \rightarrow \pi^*$
		335	$n \rightarrow \pi^*$
Cd(L) ₂	White	275	$\pi \rightarrow \pi^*$
		299	$\pi \rightarrow \pi^*$
		335	$n \rightarrow \pi^*$
Sn(L) ₂	White	284	$\pi \rightarrow \pi^*$
		302	$n \rightarrow \pi^*$

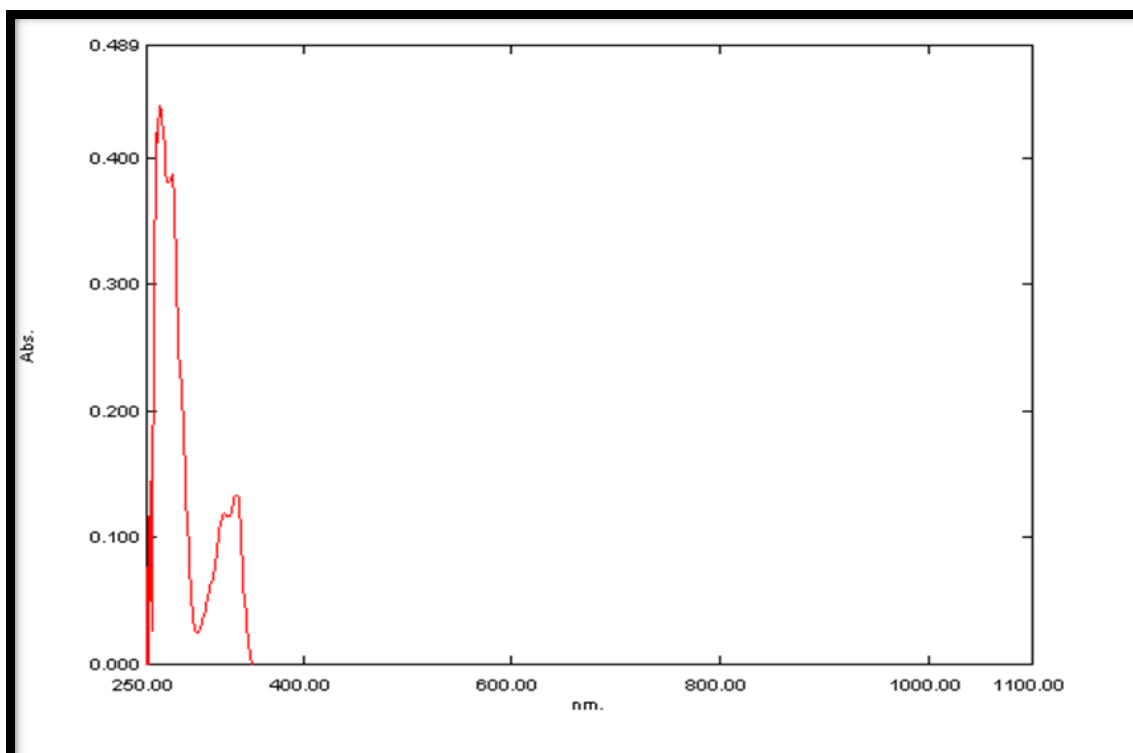


Figure (3-7): The ultraviolet visible spectrum for the ligand (L) in DMSO solvent.

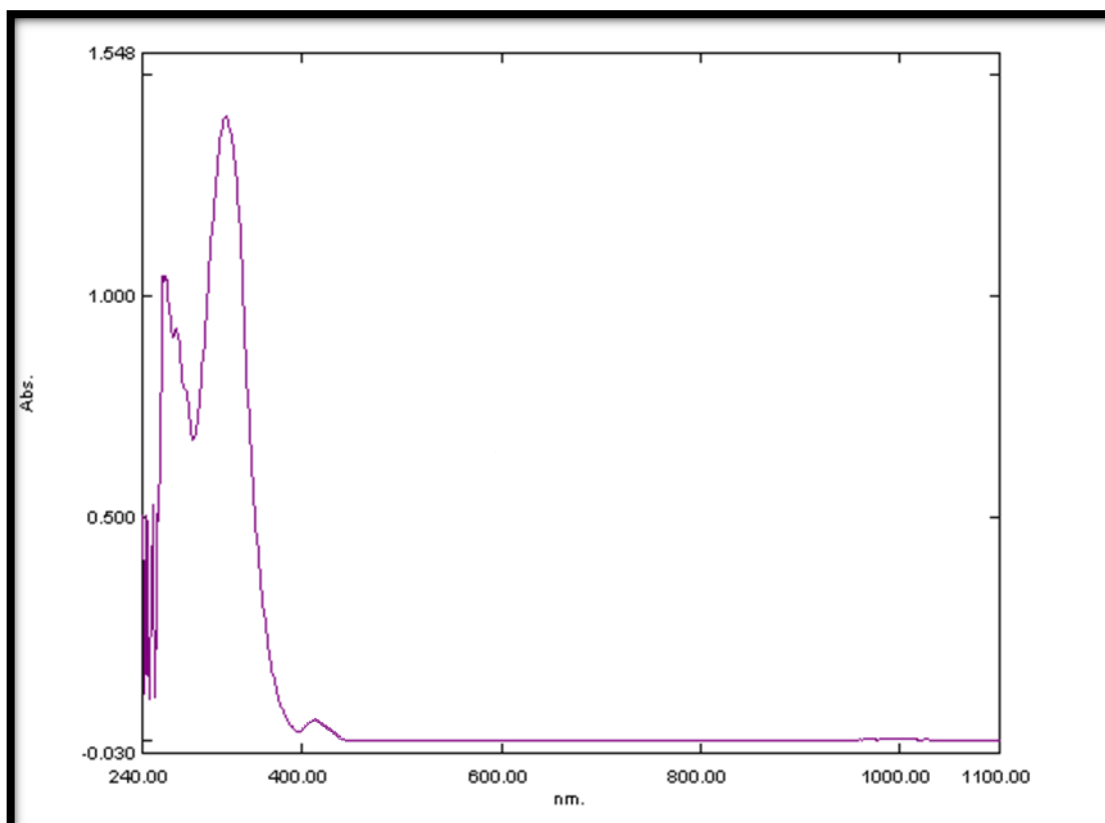


Figure (3-8): The ultraviolet visible spectrum for Ni(L)₂ in DMSO solvent.

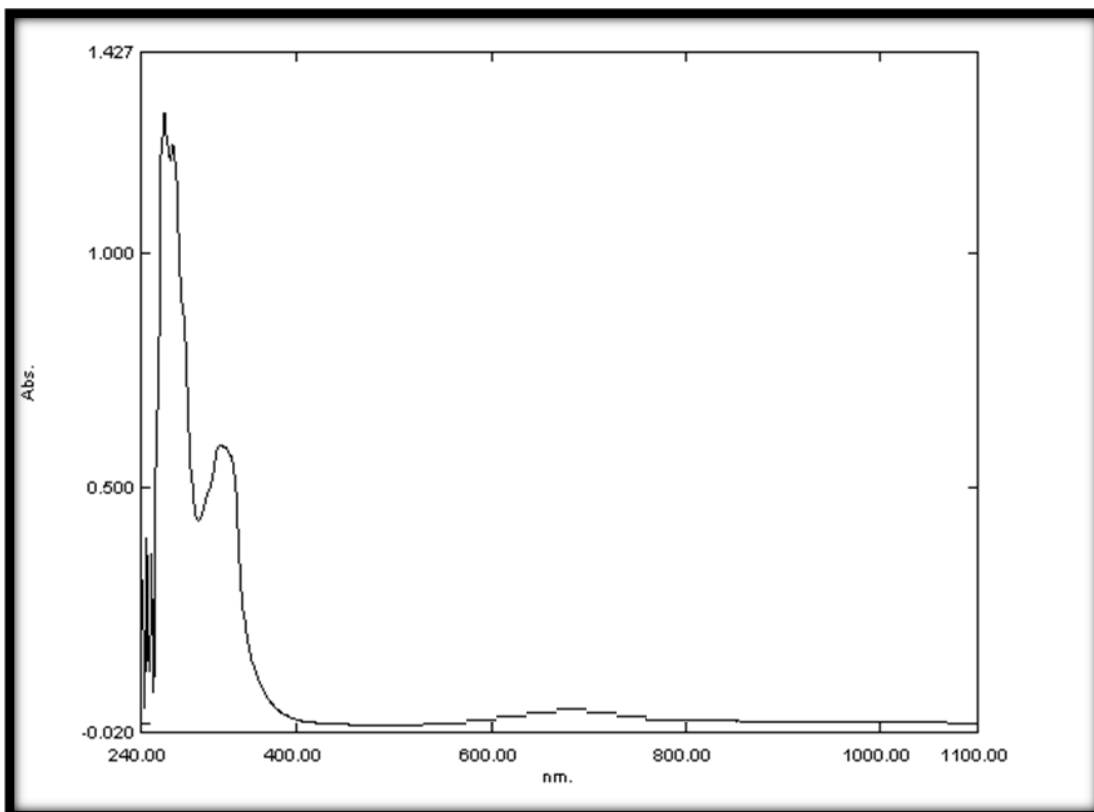


Figure (3-9): The ultraviolet visible spectrum for Cu(L)₂ in DMSO solvent.

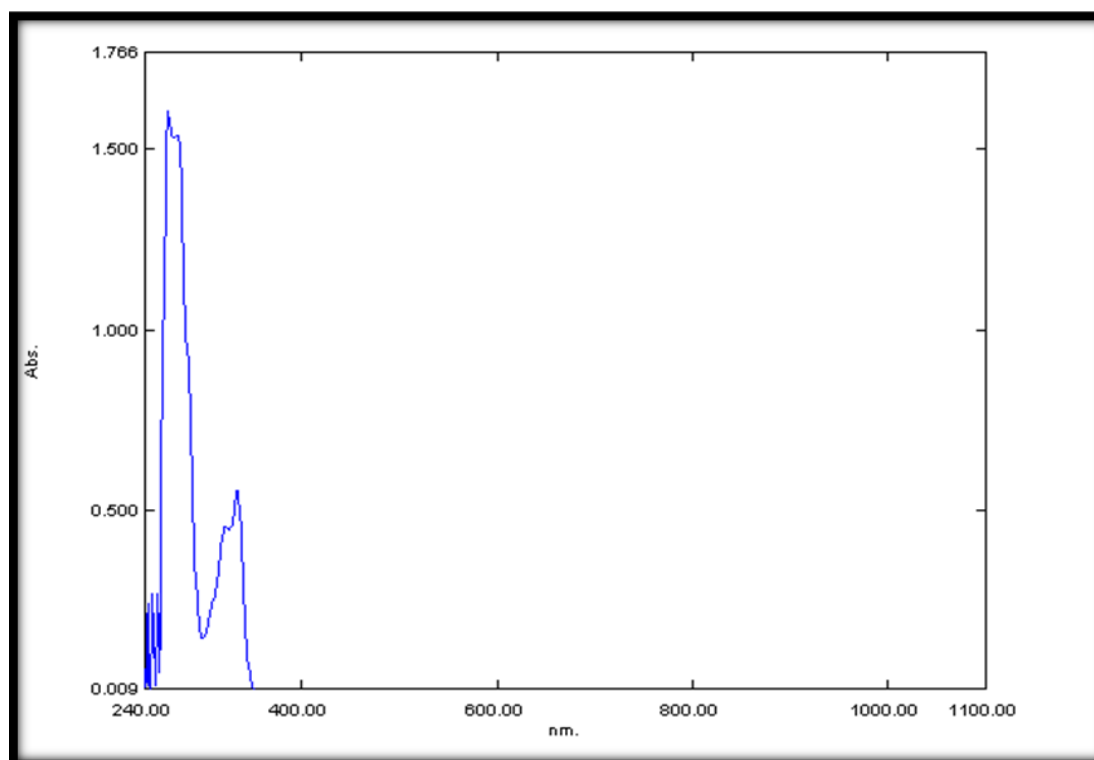


Figure (3-10): The ultraviolet visible spectrum for Zn(L)₂ in DMSO solvent.

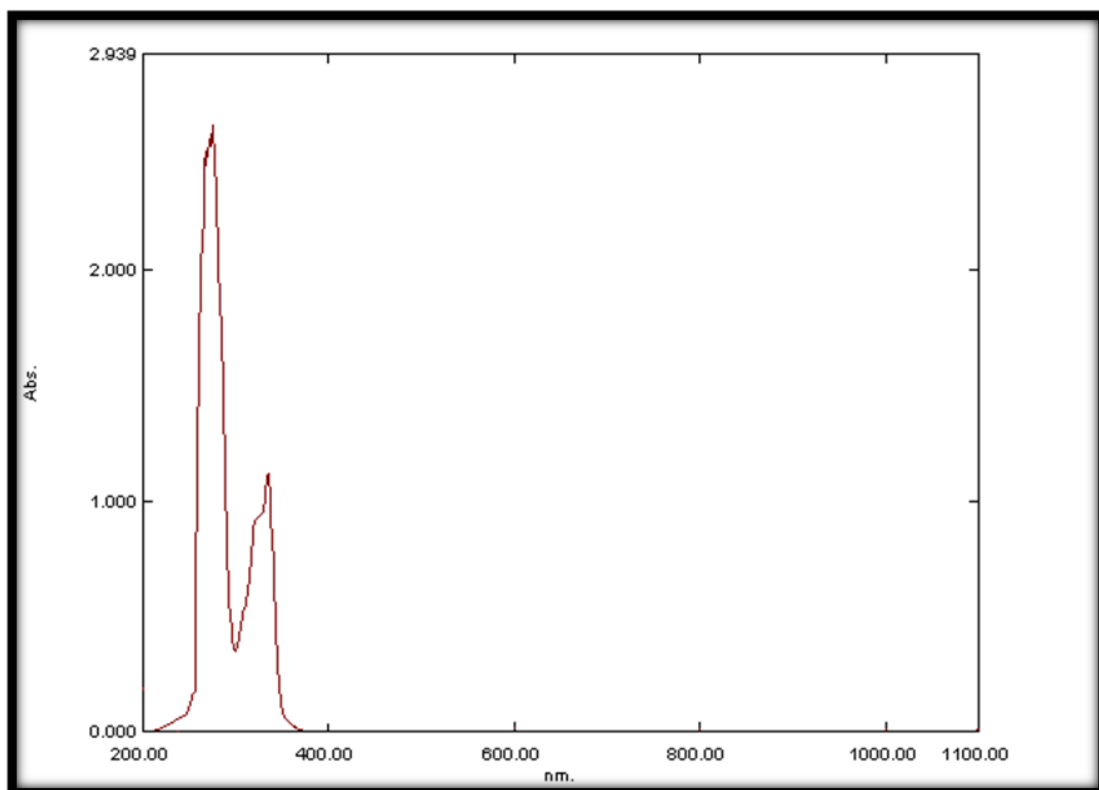


Figure (3-11): The ultraviolet visible spectrum for Cd(L)₂ in DMSO solvent.

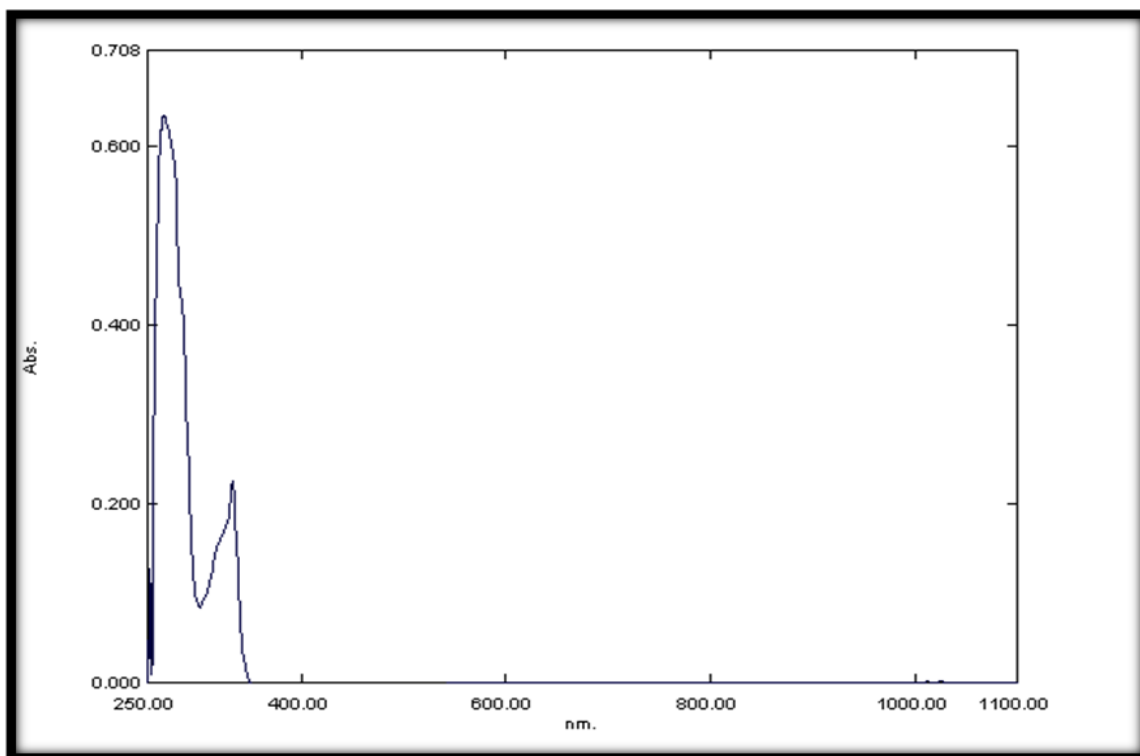


Figure (3-12): The ultraviolet visible spectrum for Sn(L)₂ in DMSO solvent.

3-1-3- Magnetic susceptibility and conductivity measurements

The experimental magnetic moment for each metal complexes is listed in Table (3-4).

Magnetic measurements are widely used in studying transition metal complexes⁽⁸⁴⁾. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbitals in the outer shell of this elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex.

The resultant magnetic moment of an ion is due to both orbital and spin motions⁽⁸⁶⁾. The magnetic moment is given by the following equation:

$$\mu_{s+L} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M}$$

μ = Magnetic moment.

S = Spin quantum number.

L = Orbital quantum number.

$$\text{B.M} = 9.27 \times 10^{-24} \text{ J.T}^{-1}$$

Although detailed determination of the electronic structure requires consideration of the orbital moment, for most complexes of the first transition series the spin-only moment is sufficient, as any orbital contribution is small⁽⁸⁷⁾.

$$\mu_s = \sqrt{4S(S+1)} \text{ B.M.}$$

Or

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.}$$

$$S = n(1/2)$$

n = Number of unpaired electrons.

The value of magnetic susceptibility of the prepared complexes at (25 °C) temperature is calculated using the following equation:

$$\mu_{\text{eff}} = 2.83 \sqrt{X_A \cdot T} \quad \text{B.M}$$

Where : $X_A = X_m + D$

$X_m = X_g \cdot \text{Mwt.}$

Mwt = Molecular weight of complex.

X_g = Mass susceptibility.

D = Pascal's constant.

X_m = Molar susceptibility which was corrected from diamagnetic.

μ_{eff} = Effective magnetic moment.

T = Temperature in Kelvin (°C +273).

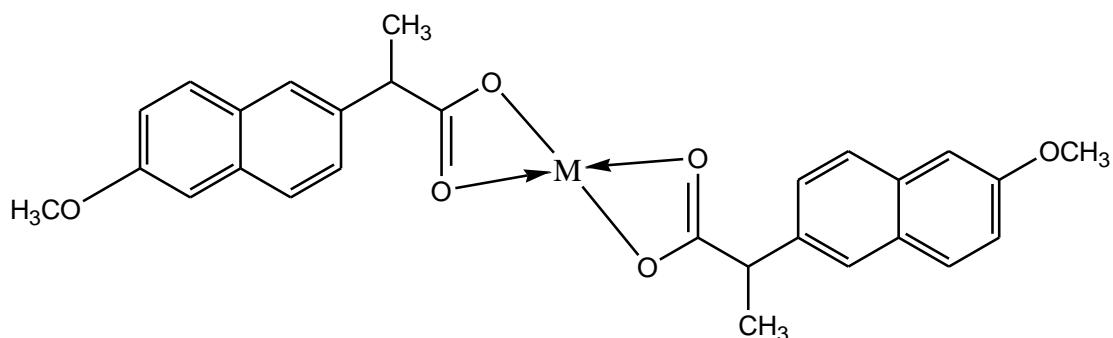
The magnetic moment for Ni(II) complex is approximately 2.91 B.M., this value refers to tetrahedral structure. While the value of Cu(II) complex is approximately 1.53 B.M. led to suggest the square planar structure⁽⁸⁴⁾.

Molar conductivity measurement in DMF solvent at 25 °C showed that all the complexes were non-electrolyt as shown in Table (3-4).

Table (3-4): Magnetic Moment, Conductivity measurements for potassium-2-(6-methoxynaphthalen-2-yl)propanoate and its complexes in DMF solvent

Symbol	Name	Conductivity $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	Magnetic Moment (B.M.)	Suggested Structure
L	Potassium-2-(6-methoxynaphthalen-2-yl)propanoate	-	-	-
Ni(L)₂	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] nickel(II)	13	2.91	Tetrahedral
Cu(L)₂	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] copper(II)	15	1.53	Square Planner
Zn(L)₂	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] zinc(II)	11	0.00	Tetrahedral
Cd(L)₂	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] cadmium(II)	10	0.00	Tetrahedral
Sn(L)₂	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] tin(II)	14	0.00	Squar pyramidal

On the basis of the preceding discussion, the structures of the complexes may be suggested as follows:



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

3-2- Ultra-violet spectral studies of photodecomposition of 2-(6-methoxynaphthalen-2-yl)propanoate complexes in PVC films

The photooxidative degradation and photodehydrochlorination process of PVC have been discussed in a number of reviews^(88,89). The PVC contains only C-C, C-H and C-Cl bonds, therefore it is not expected to absorb light of wavelength longer than (190-220 nm)⁽⁹⁰⁾.

The fact that free radicals are formed after irradiation at longer wavelengths (220-370 nm) indicates that some kinds of chromophores must be present in a polymer⁽⁹⁰⁾. The light and heat instability of PVC must be caused by structural abnormalities that are present to varying extents in different types of commercially available polymer samples, such as unsaturated end groups and oxidized structures such as hydroperoxide groups⁽⁹¹⁾ and carbonyl groups⁽⁹²⁾.

The carbonyl groups generated during the photo-oxidation process of PVC, extend the PVC film absorption to longer wavelengths⁽⁹³⁾. These groups absorb light when they irradiated with light of wavelength between (200-700 nm) and activated to the singlet and triplet excited states which enhances various successive photo-oxidation reactions⁽⁹³⁾.

It is generally accepted that photodegradation⁽⁹⁴⁾ and photothermal degradation⁽⁹⁵⁾ occur with discoloration of the polymer due to the polyene formation. The change in ultraviolet-visible spectrum of PVC after irradiation indicates the formation of hydroperoxide, carbonyl and polyene groups⁽⁹⁵⁾.

It is generally accepted that carbonyl and polyene groups formed during UV irradiation of PVC, is most probable and are responsible for the yellow coloration of the polymer⁽⁹⁶⁾.

The physical properties of additives and polymers play a very important role in determining the additives efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of additive (photostabilizer, antioxidant, thermal stabilizer.... etc.) must be evenly distributed which requires that it be compatible with the polymer matrix⁽⁹⁷⁾. The additives used in this study were chosen to be completely soluble in polymer solvent (THF).

The photodecomposition rate constant (K_d) was calculated. The (K_d) values were computed using the UV spectra changes of PVC films. Figure (3-13) shows the change in UV spectra with irradiation time for $Cd(L)_2$ in PVC film at ($\lambda = 313$ nm). We can indicate from this figure that during the aging process, the concentration of the double bonds are increased correspondingly.

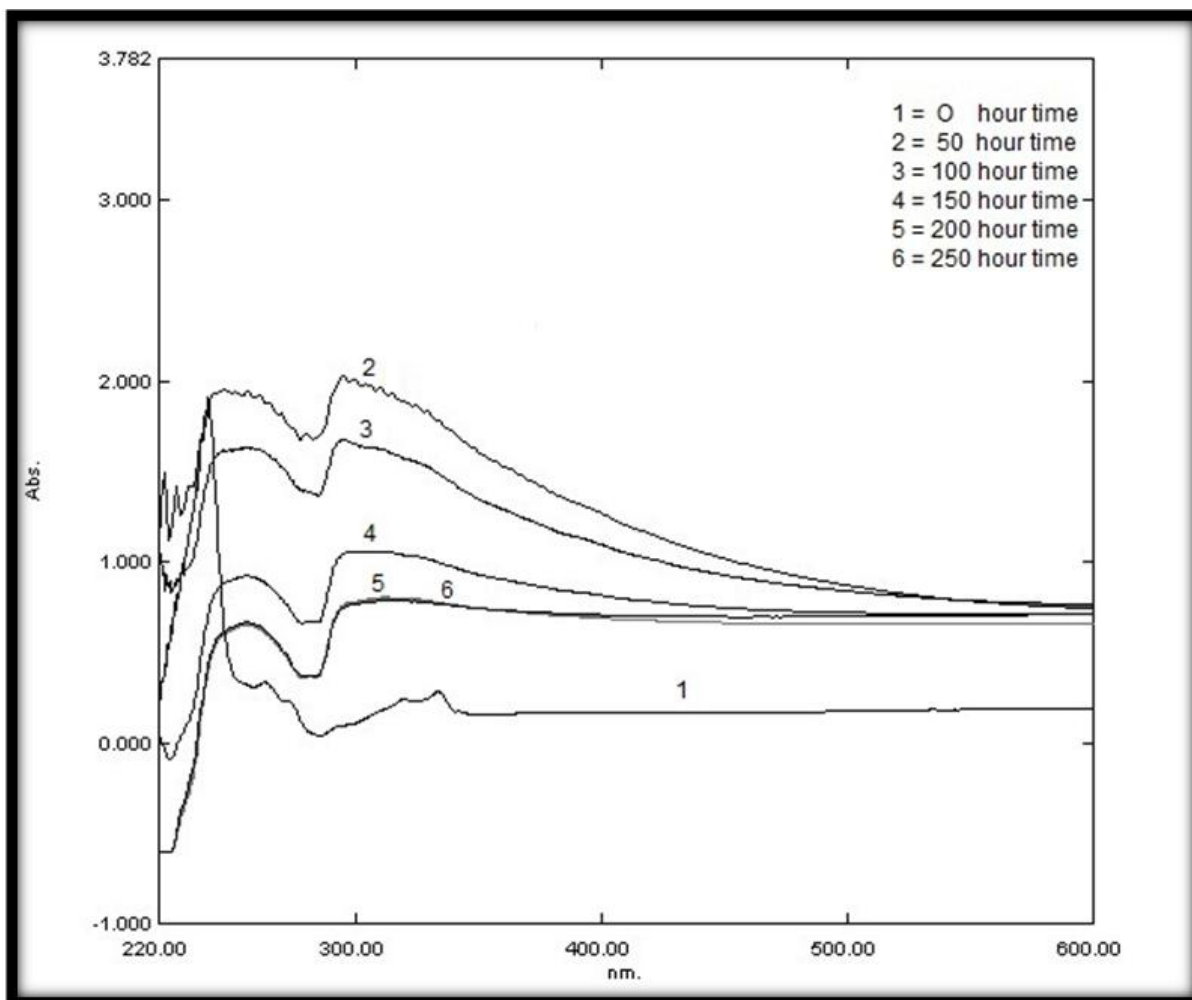


Figure (3-13): UV-Vis spectra of PVC + additive [Cd(L)₂] at different irradiation times.

The plot of irradiation time versus $\ln (A_t - A_\infty)$, gives straight line that indicates primarily a first order reaction. The slope equal to the decomposition rate constant (k_d).

Figure (3-14) shows the variation of $\ln (A_t - A_\infty)$ with irradiation time for PVC films with and without additives.

Table (3-5): Variation of $\ln (A_t - A_\infty)$ with irradiation time of PVC films thickness (30 μm) containing 0.5% of additives

Irradiation time (sec.)	PVC	Cu(L) ₂	Ni(L) ₂	Sn(L) ₂	Zn(L) ₂	Cd(L) ₂
0	0.62	0.55	0.49	0.37	0.23	0.100
180000	0.62	0.52	0.47	0.39	0.22	0.090
360000	0.56	0.49	0.43	0.33	0.23	0.095
540000	0.51	0.46	0.40	0.28	0.25	0.099
720000	0.50	0.45	0.41	0.29	0.19	0.060
900000	0.47	0.40	0.39	0.27	0.18	0.050

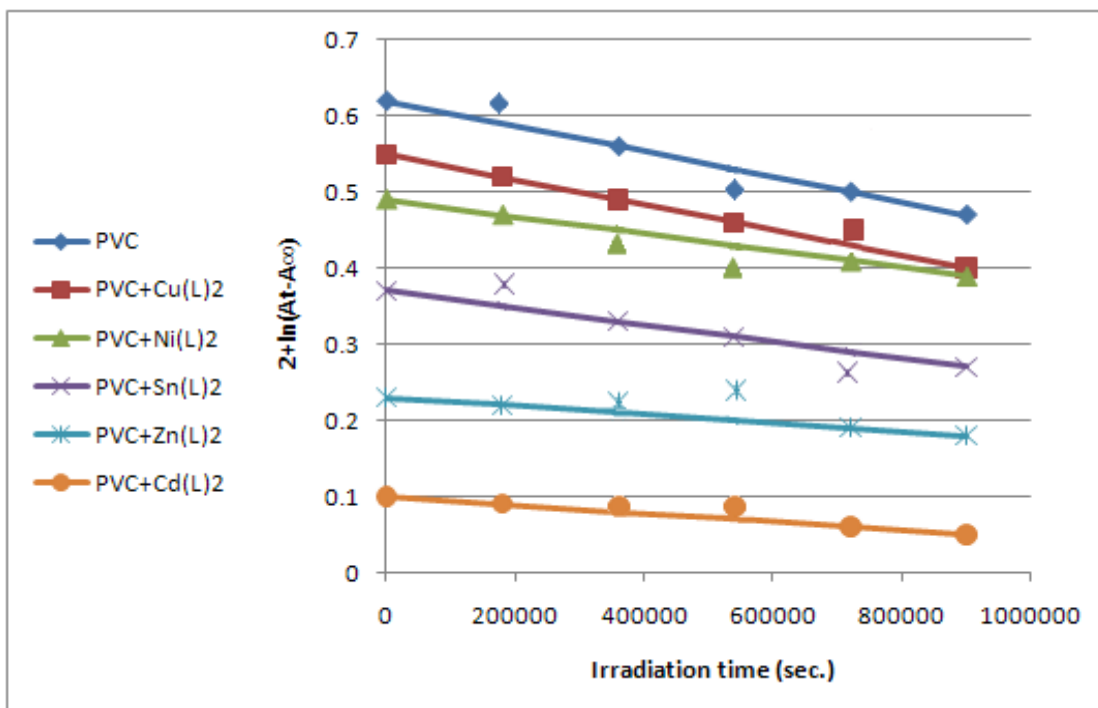


Figure (3-14): Variation of natural logarithm of $\ln (A_t - A_\infty)$ with irradiation time of additives in PVC film thickness (30 μm).

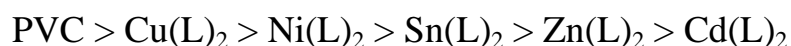
The values of the first order rate constant of all the modified polymers films (k_d) calculated by the same way and shown in Table (3-6).

Table (3-6): Photodecomposition rate constant (K_d) of PVC films thickness (30 μ m) containing 0.5 % of additives

Polymers	$K_d \cdot 10^{-3} (S^{-1})$
Cd(L) ₂	2.91
Zn(L) ₂	3.49
Sn(L) ₂	6.73
Ni(L) ₂	7.58
Cu(L) ₂	9.11
PVC	11.05

The photostabilizers always possess low K_d values, which mean that these modified polymers are stable towards UV light.

One could notice that K_d values are sensitive to the type of additives in PVC films, which decrease in the following order:



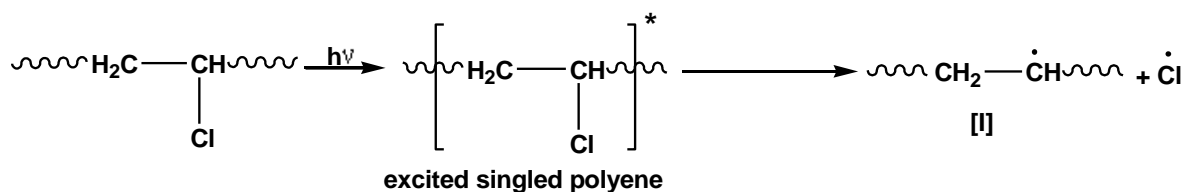
and this might point out to increase the photostability of these additives in this term.

3-3- Photostabilization of PVC films by Bis[2-(6-methoxynaphthalen-2-yl)propanoate] complexes

The new complexes modified polymers Cu(L)₂, Zn(L)₂, Ni(L)₂, Cd(L)₂ and Sn(L)₂ were used as photostabilized PVC as additive comparing with PVC films.

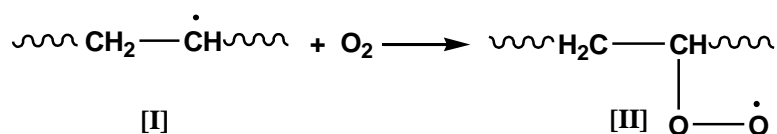
In order to study the photochemical activity of these modified polymers for the photostabilization of films, the carbonyl, polyene, hydroxyl and chlorine indices were monitored with irradiation time using IR spectroscopy. The formation of carbonyl group (C=O), polyene group (C=C)_n and hydroxyl group (O-H) during photolysis of PVC film could be illustrated by the following mechanism.

When PVC is photolysed in the presence of (O₂), the primary photochemical processes occur (the excited singlet polyenes).



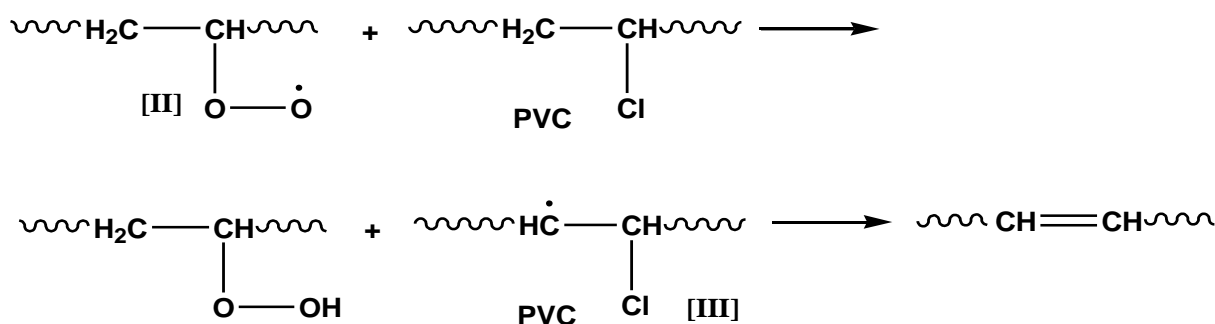
Those excited states will thus disappear by the different routes including the allylic (C-Cl) bond cleavage with formation of (Cl \cdot) radical and polyenyl radical [I].

The polyenyl radical [I] which bears no (Cl) atom in the α -position is very likely to be scavenged by (O₂) to give peroxy radical [II]

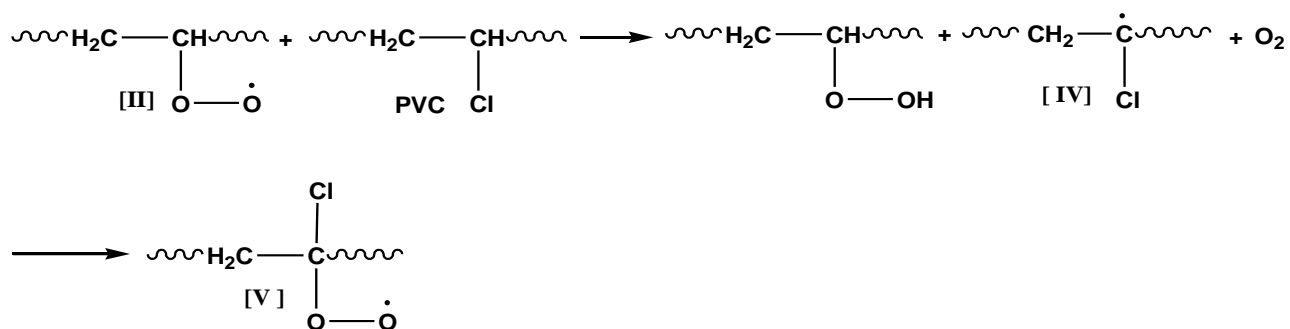


Rate constant measurement on related model compounds suggest that peroxy radical [II] react with the (-CH₂-) and (CH-Cl) groups on PVC at rates that are comparable⁽²³⁾.

The attack on (CH₂) group yield radical [III].

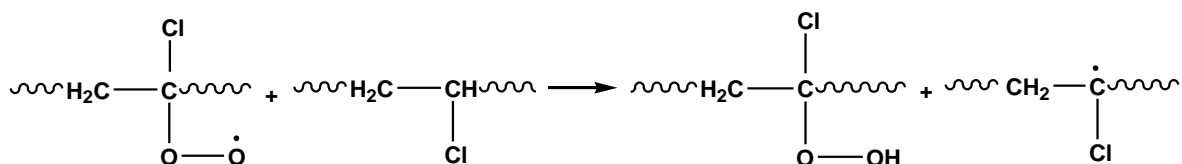


This radical contributes to the chain-dehydrochlorination of PVC. The attack of peroxy radical [II] on the (-CH-Cl) group yield radical [IV] which possesses no labile β -chlorine and is likely to react with (O₂) to give a γ -chloroalkyl peroxy radical [V].

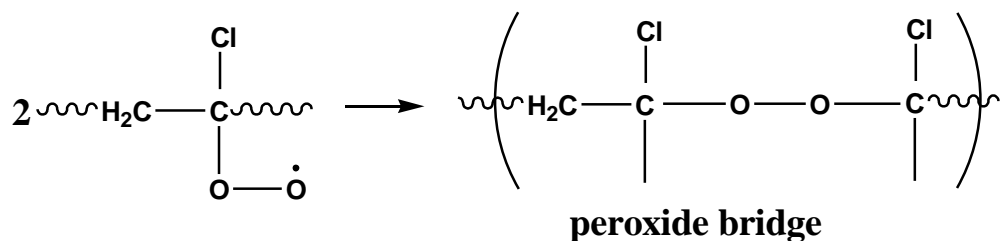


The main oxidation products of PVC are expected to result primarily from the various reactions of this radical [V], there are two major routes of the fade (disappearances) of the γ -chloroalkyl peroxy radical.

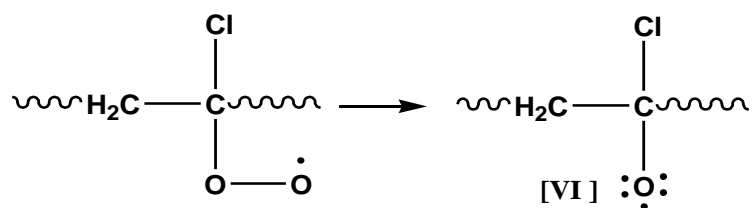
The hydrogen abstraction from PVC with the formation of hydroperoxide groups.



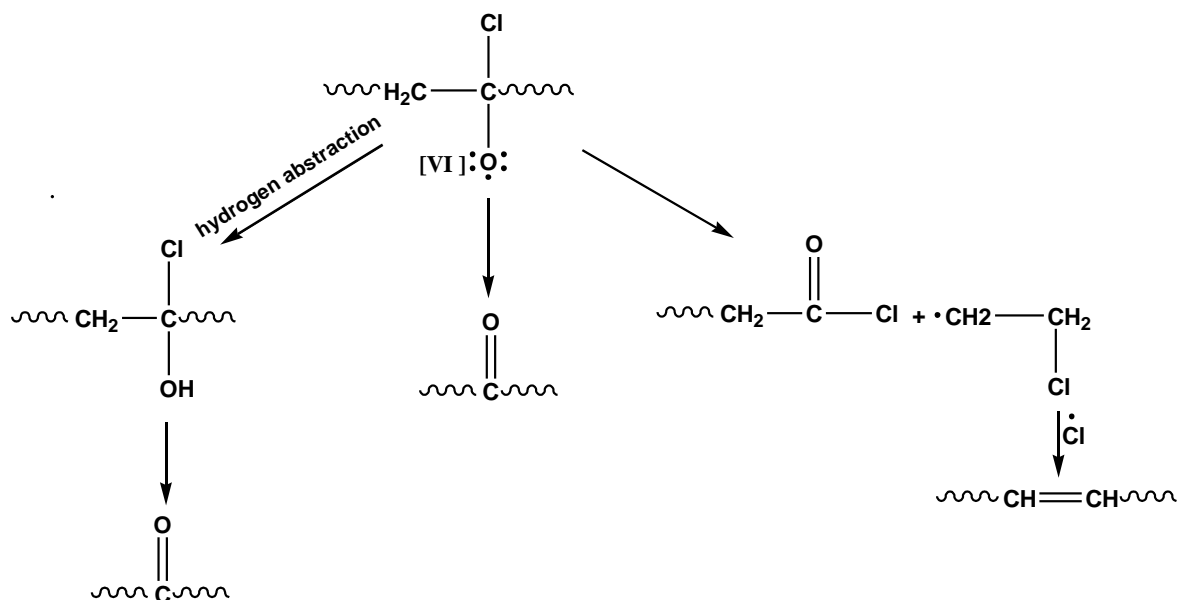
The bimolecular interaction, the later leads to the formation of either a peroxide bridge (termination reaction),



or the formation of alkoxy radicals[VI].



The most usual reaction of alkoxy radicals [VI] is the hydrogen abstraction. The unstable α -chloroalcohol formed by reaction of alkoxy radical with PVC will rapidly decompose into the corresponding ketone.



Tertiary alkoxy radicals are also proved to be stabilized by β -scission which may involve either (C-Cl) bond cleavage to form ketone and/or (C-C) bond cleavage to form polyene. The irradiation of PVC films with light of wavelength, $\lambda = 313$ nm lead to a clear change in their FTIR spectrum, as shown in Figures (3-15) and (3-16). Appearance of bands at 1770 cm^{-1} attributed to the formation of carbonyl group, which is related to chloro ketone and aliphatic ketone, together with formation of a band at 1629 cm^{-1} related to polyene group⁽⁹⁸⁾. The hydroxyl band appeared at 3460 cm^{-1} is related to alcohol functions⁽⁹⁸⁾.

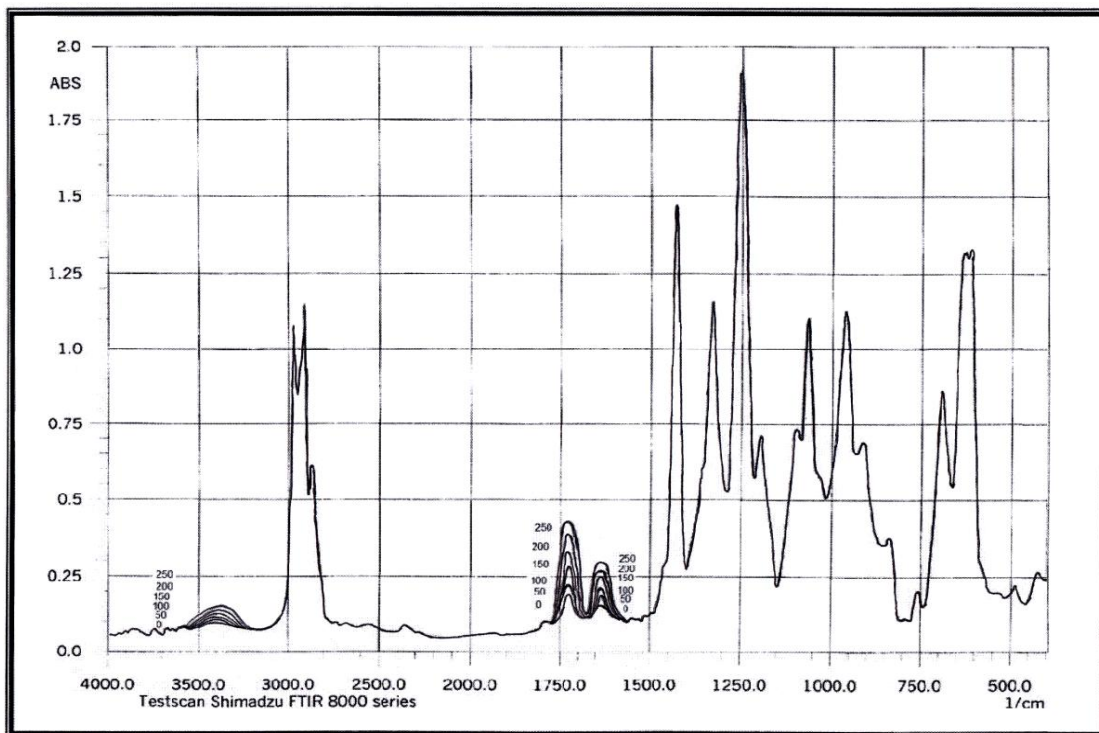


Figure (3-15): FTIR spectrum of [PVC+Sn(L)₂] at different irradiation time.

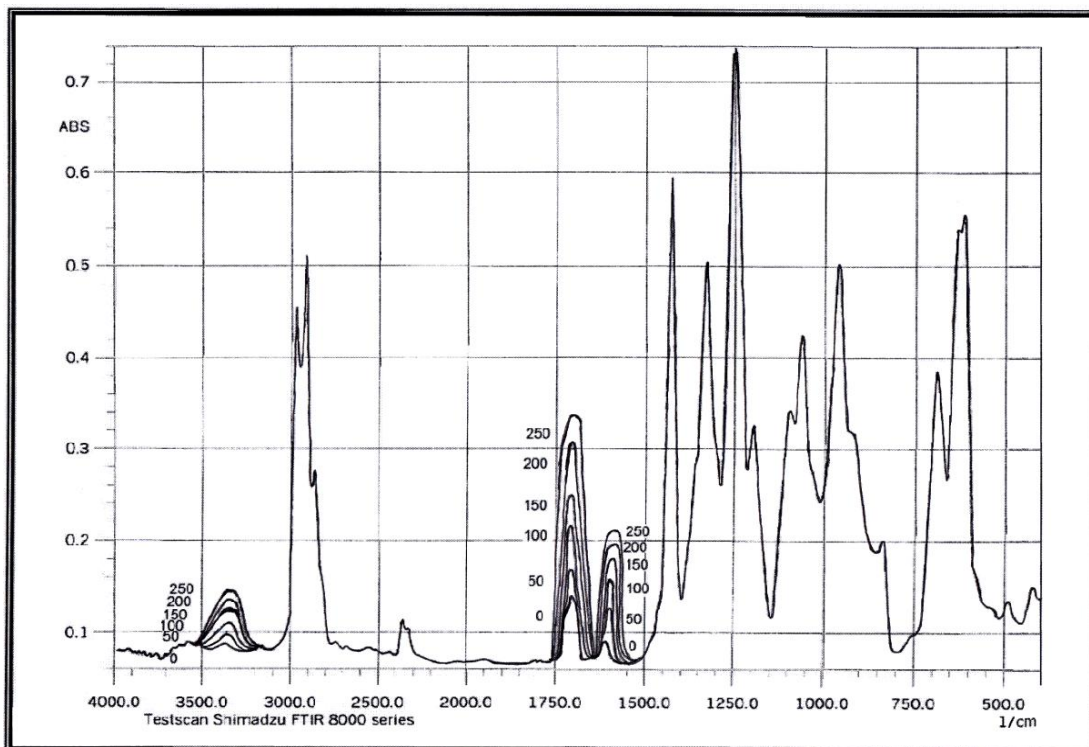


Figure (3-16): FTIR spectrum of [PVC+Cu(L)₂] film at different irradiation time.

The absorption of the polyene, carbonyl, hydroxyl and chlorine groups are used to follow the extend of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{CO}), polyene index (I_{PO}), hydroxyl index (I_{OH}) and chlorine index (I_{Cl}).

Therefore, one should expect that the growth of carbonyl index is a measure to the extent of degradation. As seen from Figure (3-17) that the PVC in presence of the additives $Cu(L)_2$, $Zn(L)_2$, $Ni(L)_2$, $Cd(L)_2$ and $Sn(L)_2$ show lower growth rate of carbonyl index with irradiation time with respect to unmodified PVC film (blank). These modified polymers might be considered as photostabilized with respect to the PVC polymer.

Table (3-7): Increasing in the carbonyl index (I_{CO}) with irradiation time of PVC films thickness (30 μ m) containing 0.5% of additives

Irradiation time (hours)	PVC	$Cu(L)_2$	$Ni(L)_2$	$Sn(L)_2$	$Zn(L)_2$	$Cd(L)_2$
0	0.111	0.073	0.056	0.041	0.038	0.009
50	0.326	0.200	0.171	0.146	0.141	0.090
100	0.610	0.390	0.311	0.278	0.235	0.178
150	0.996	0.589	0.463	0.361	0.312	0.270
200	1.380	0.765	0.652	0.575	0.511	0.402
250	1.622	1.093	0.886	0.699	0.584	0.461

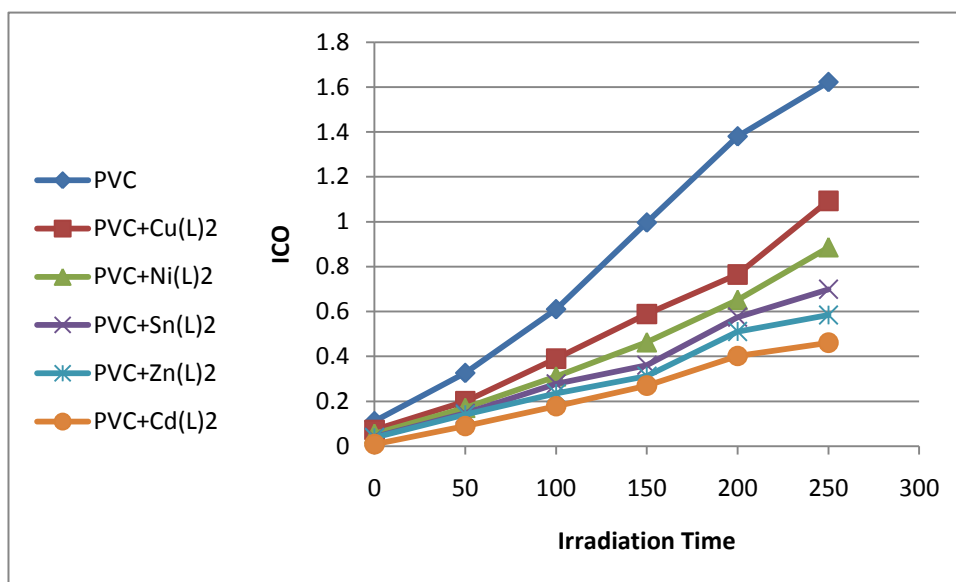


Figure (3-17): The relationship between the carbonyl index and irradiation time for PVC and modified PVC films.

The good photostabilizer show a longer induction period. Therefore, from Figure (3-17) the Cd(L)₂ is the most active photostabilizer, followed by Zn(L)₂, Sn(L)₂, Ni(L)₂ and then Cu(L)₂ which is less active. As it was mentioned before that polyene compounds are produced during photodegradation of PVC. Therefore, polyene index (I_{PO}) was monitored with irradiation time. The same trend obtained as carbonyl index, Figure (3-18).

Table (3-8): Increasing in the polyene index (I_{PO}) with irradiation time of PVC films thickness (30µm) containing 0.5 % of additives

Irradiation time (hours)	PVC	Cu(L) ₂	Ni(L) ₂	Sn(L) ₂	Zn(L) ₂	Cd(L) ₂
0	0.231	0.21	0.139	0.145	0.173	0.093
50	0.323	0.289	0.222	0.182	0.154	0.123
100	0.552	0.465	0.339	0.274	0.199	0.147
150	0.731	0.587	0.510	0.456	0.296	0.240
200	0.968	0.810	0.697	0.585	0.348	0.283
250	1.269	1.011	0.912	0.760	0.512	0.312

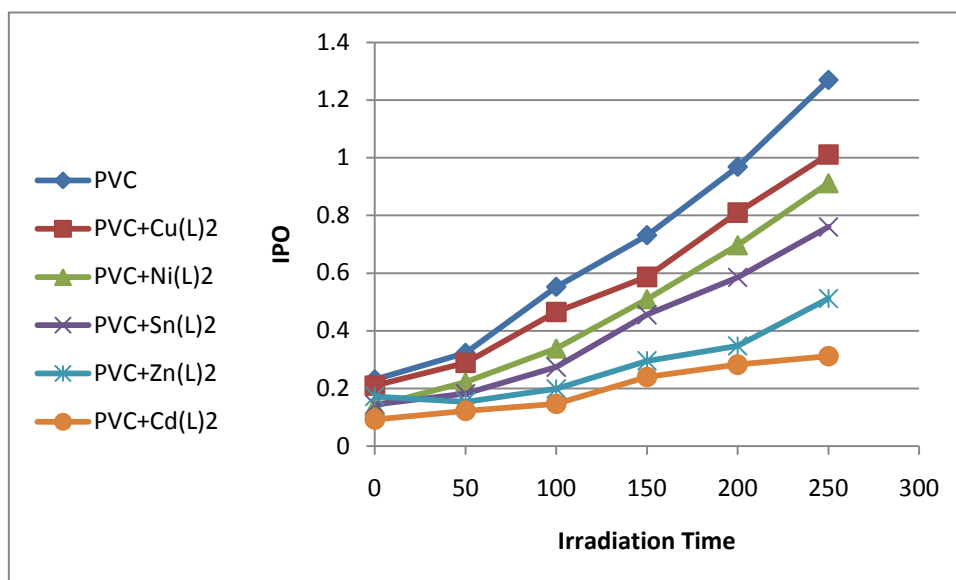


Figure (3-18): The relationship between the polyene index and irradiation time for PVC and modified PVC films.

Hydroxyl functions are produced during photodegradation of PVC. Therefore, hydroxyl index (I_{OH}) was monitored with irradiation time for PVC and with additive $Ni(L)_2$, $Cu(L)_2$, $Zn(L)_2$, $Cd(L)_2$ and $Sn(L)_2$ polymers.

From Figure (3-19) the $Cd(L)_2$, $Zn(L)_2$, $Sn(L)_2$, $Ni(L)_2$ and $Cu(L)_2$ show lower growth rate of hydroxyl index with irradiation time with respect to PVC film without modification.

Table (3-9): Increasing in the hydroxyl index (I_{OH}) with irradiation time of PVC films thickness (30 μ m) containing 0.5 % of additives

Irradiation time (hours)	PVC	$Cu(L)_2$	$Ni(L)_2$	$Sn(L)_2$	$Zn(L)_2$	$Cd(L)_2$
0	0.048	0.028	0.023	0.018	0.014	0.012
50	0.130	0.083	0.071	0.062	0.059	0.039
100	0.239	0.152	0.131	0.110	0.103	0.077
150	0.300	0.249	0.200	0.157	0.136	0.112
200	0.436	0.366	0.305	0.244	0.223	0.200
250	0.586	0.533	0.502	0.419	0.312	0.251

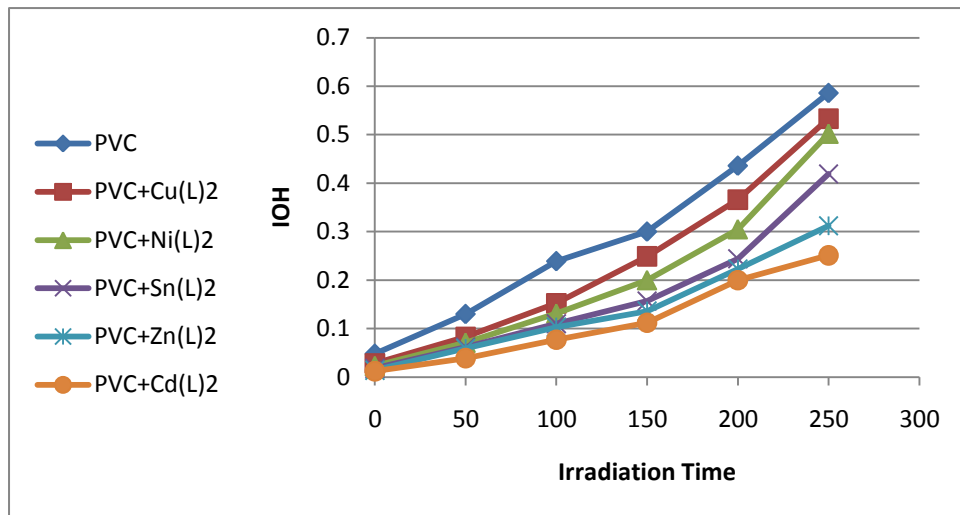


Figure (3-19): The relationship between the hydroxyle index and irradiation time for PVC and modified PVC films.

Photooxidation is initiated by the abstraction of labile atoms by the radical impurities formed in primary processes, especially hydrogen and chlorine atoms neighboring unsaturated bonds are susceptible to break off.

The chlorine index (I_{Cl}) was induced to study the process of photodegradation of PVC with different irradiation time. The chlorine index (I_{Cl}) was monitored with irradiation time for PVC with and without additives. By the FTIR spectra, the intensities of (C-Cl) bands at ($600-700\text{ cm}^{-1}$) gradually decreased, which is additional evidence of the elimination of HCl from PVC under UV irradiation⁽⁹⁹⁾. Figure (3-20) show the decreasing in the growth rate of chlorine index with irradiation time with respect to PVC film without additives (blank).

The good photostabilizer shows longer induction period. Therefore, $Cd(L)_2$ is the most active photostabilizer, followed by $Zn(L)_2$, $Sn(L)_2$, $Ni(L)_2$ and then $Cu(L)_2$ which is less active.

Table (3-10): Decreasing in the chlorine index (I_{Cl}) with irradiation time of PVC films thickness (30 μ m) containing 0.5 % of additives

Irradiation time (hours)	PVC	Cu(L) ₂	Ni(L) ₂	Sn(L) ₂	Zn(L) ₂	Cd(L) ₂
0	1.122	1.179	1.211	1.237	1.292	1.323
50	1.066	1.105	1.135	1.182	1.266	1.291
100	0.873	0.954	1.048	1.119	1.232	1.273
150	0.663	0.737	0.893	1.073	1.201	1.254
200	0.430	0.563	0.737	0.950	1.087	1.222
250	0.211	0.402	0.622	0.723	0.853	1.075

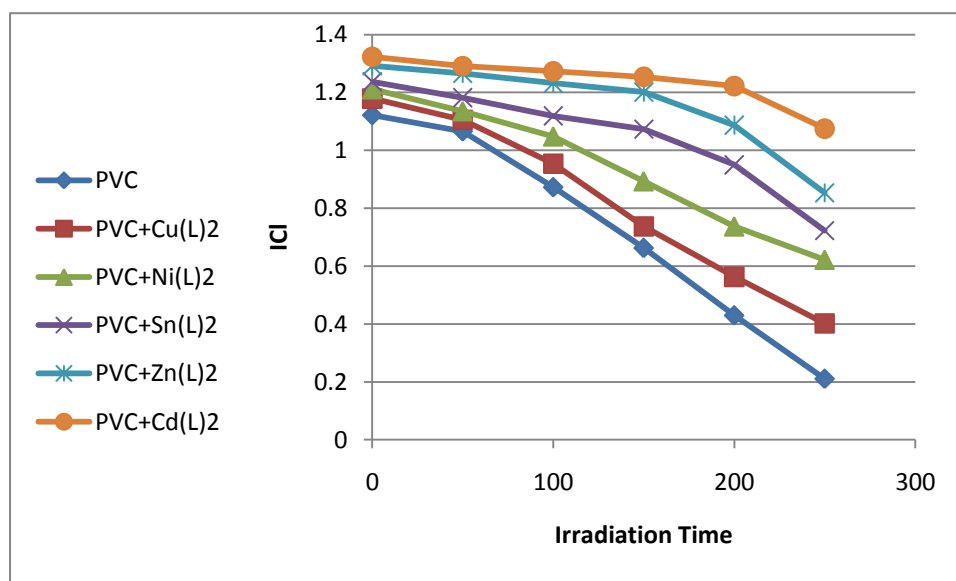


Figure (3-20): The relationship between the chlorine index and irradiation time for PVC and modified PVC films.

Photodegradation of Polymer films has a great effect on the rate of oxidation process. It can effect in light absorption and oxygen diffusion.

The role of oxygen in the photodecomposition of PVC is complex. It has been found that oxygen:

- I- Decreases the energy of activation⁽¹⁰⁰⁾.
- II- Accelerates the rate of dehydrochlorination reaction⁽¹⁰¹⁾.
- III- Causes bleaching by attacking the polyene structure and shortening the length of conjugation⁽¹⁰²⁾.
- IV- Promotes chain scission and crosslinking⁽¹⁰³⁾.

Generally, photo-oxidation rate decreases with increasing film thickness⁽¹⁰⁴⁾, since the oxygen diffusion rate for a given quantity of polymer is proportional to the surface area, and decreases with increasing film thickness. Therefore, in the present work, the photodegradation of PVC films was studied in thickness (30 μ m).

The physical properties of modified polymers play an important role in determining the modification efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of photostabilizer additive must be evenly distributed which requires that it must be compatible with the polymer matrix⁽⁹⁷⁾.

3-4- Variation of PVC molecular weight during photolysis

An analysis of the relative change in viscosity average molecular weight (\bar{M}_v), described by Scott⁽¹⁰⁵⁾ has been shown to provide a versatile test for random chain scission. Figure (3-21) shows the plot of (\bar{M}_v) versus irradiation time for modified PVC films and PVC film (blank). (\bar{M}_v) is measured using equation (2-4) and THF as a solvent at 25 °C.

Table (3-11): Variation of \bar{M}_v with irradiation time of PVC films thickness (30 μ m) containing 0.5 % of additives

Irradiation Time (hours)	M_v PVC	M_v Cu(L) ₂	M_v Ni(L) ₂	M_v Sn(L) ₂	M_v Zn(L) ₂	M_v Cd(L) ₂
0	62157	62157	62157	62157	62157	62157
50	32145	52660	55812	58532	60908	61501
100	29723	45359	48473	51793	54112	54955
150	26615	39398	41123	44501	46291	47068
200	20261	33256	35020	37685	40734	42725
250	17758	29668	32367	36959	38287	39081

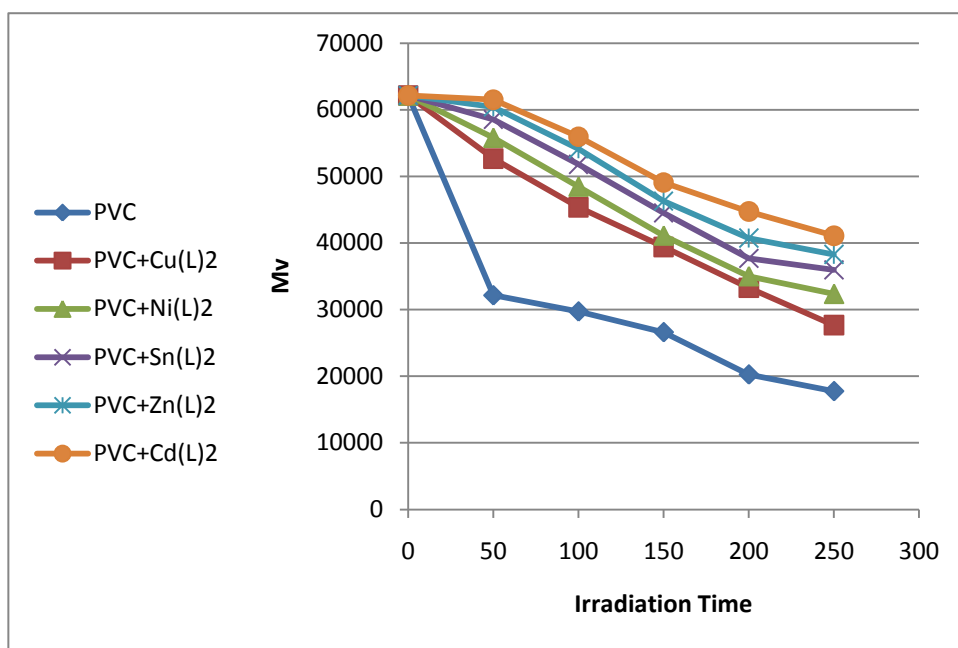


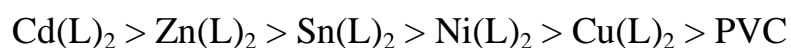
Figure (3-21): Changes in the viscosity average molecular weight (\bar{M}_v) during irradiation for PVC and modified PVC films.

It is worth mentioning that traces of the PVC films with additives are not soluble in THF indicating that cross-linking or branching in the PVC chain does occur during the course of photolysis⁽⁹¹⁾.

The plots indicate a rapid decrease in (\overline{M}_v) initially then it slows down, suggesting that the initial rapid drop in (\overline{M}_v) is due to the main chain scission at various locations that distributed along the polymer chain. The photodegradation becomes slower and bond scission may be random.

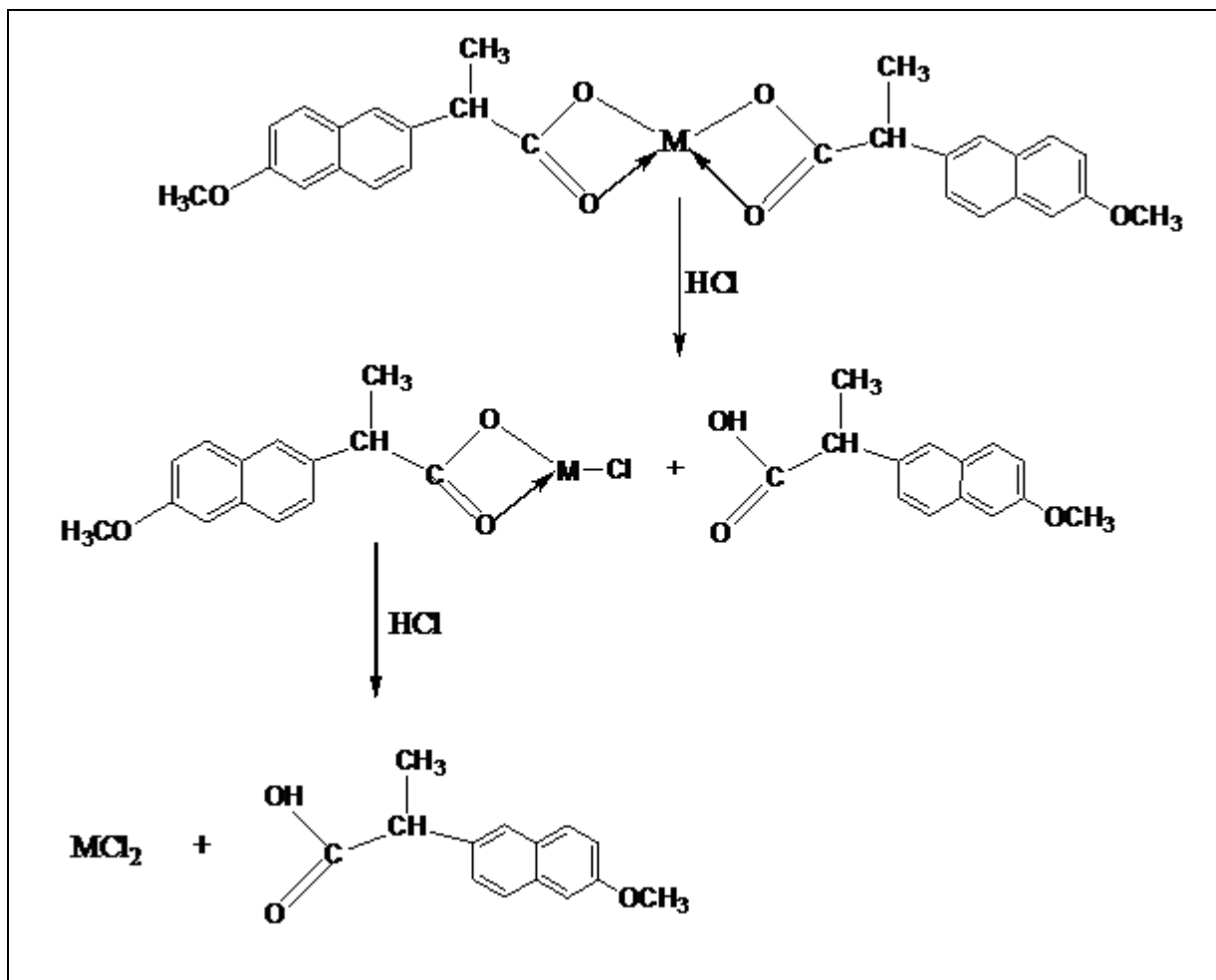
3-5- Suggested mechanisms of photostabilization of PVC by the Bis[2-(6-methoxynaphthalen-2-yl)propanoate] complexes

Through the overall results obtained, the efficiency of Bis[2-(6-methoxynaphthalen-2-yl)propanoate] complexes as stabilizers for PVC films can be arranged according to the change in the carbonyl, polyene, hydroxyl and chlorine concentration as a reference for comparison as shown in Figure (3-17), (3-18), (3-19) and (3-20).



Metal carboxylates stabilize PVC by mechanisms, depending on the metal, metals such as Cd, Zn, Sn, Ni and Cu which are stronger lewis acids and form covalent carboxylates, not only scavenge HCl, but also substitute carboxylate for the allylic chlorine atoms⁽¹⁰⁶⁾.

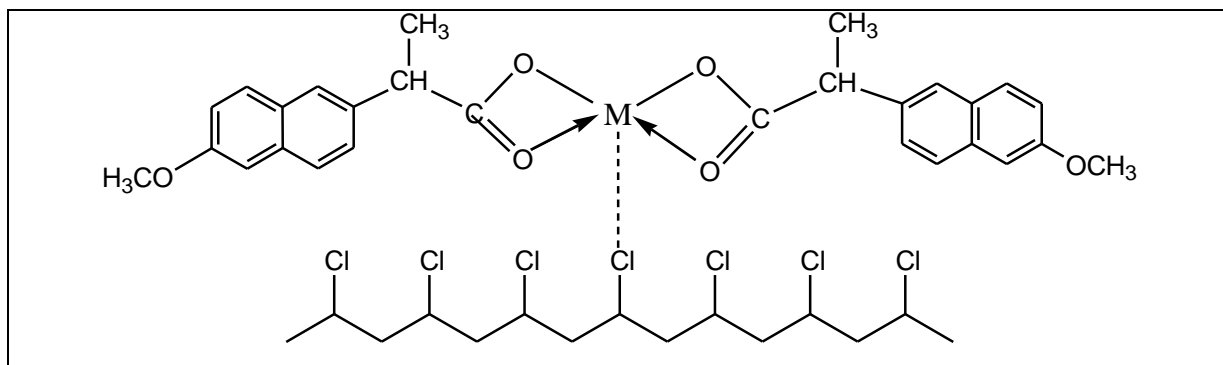
These stabilizers provide very good long-term stability and are usually referred to as secondary stabilizers, Scheme (3-2).



Scheme (3-2): Suggested mechanism of photostabilization of M(L)_2 complexes as HCl scavengers.

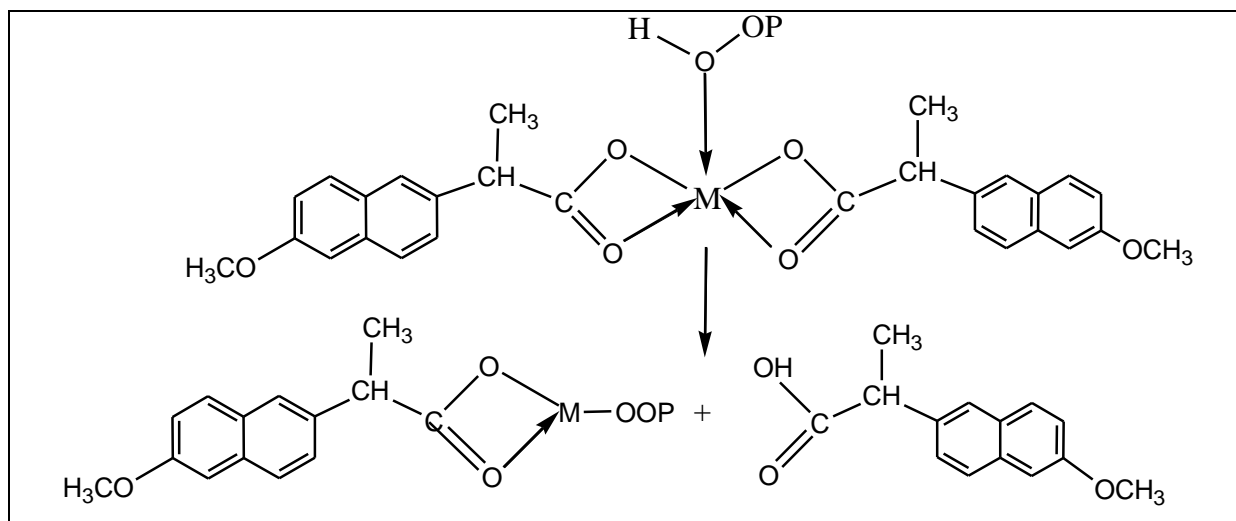
IR spectroscopy has shown that metals carboxylates associate with PVC molecules at the surface of primary particles⁽¹⁰⁶⁾ and are consequently, very effective in the substitution of allylic chlorine. In this mechanism the stabilizer classified as primary stabilizers.

It has been postulated that metals stabilizers associate with chlorine atoms at the surface of PVC primary particles which explains their high efficiency in PVC stabilization⁽¹⁰⁷⁾, Scheme (3-3).



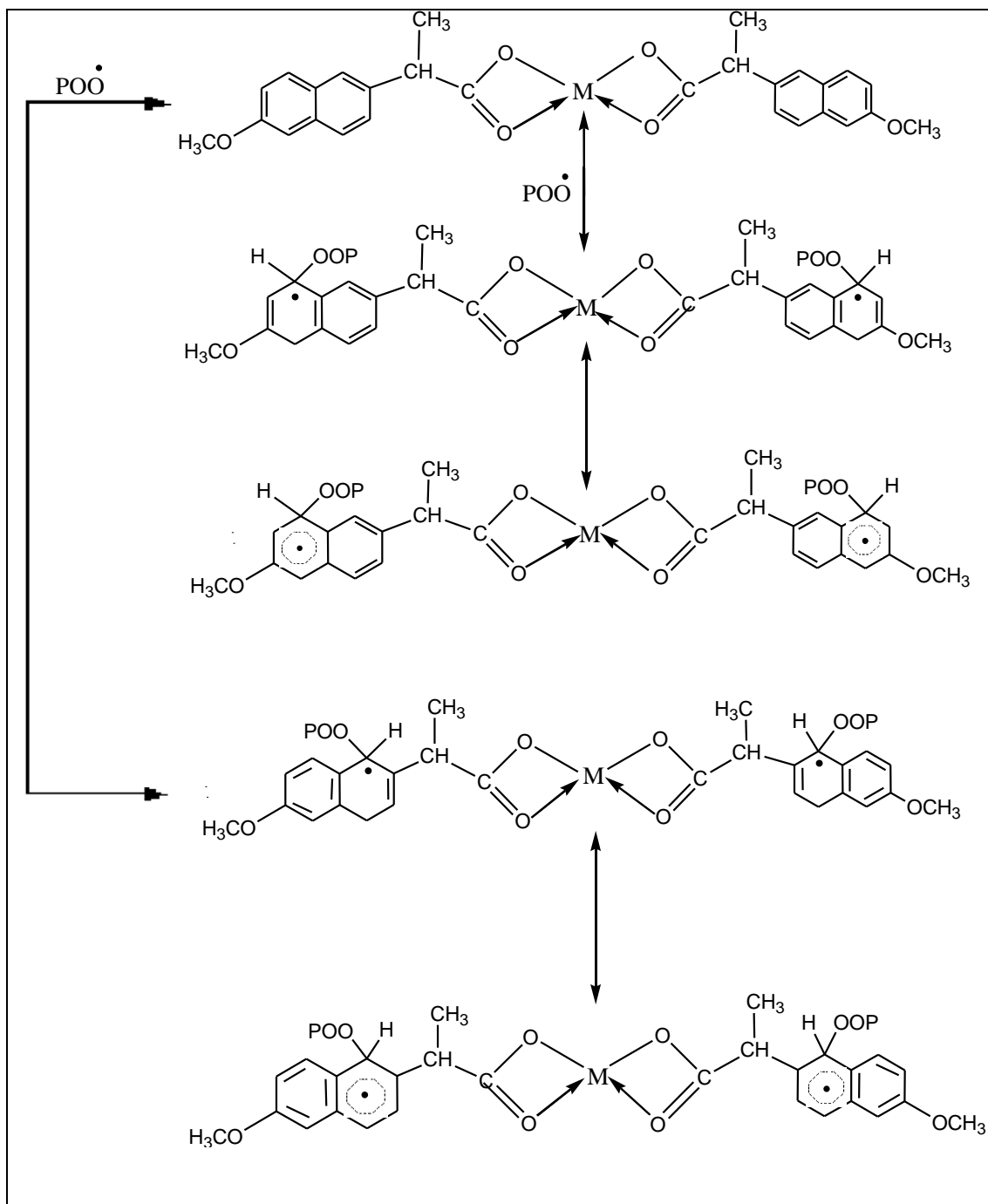
Scheme (3-3): Suggested mechanism of photostabilization of $M(L)_2$ complexes as primary stabilizers .

Metal chelate complexes generally known as photostabilizers for polyolefins⁽¹⁰⁸⁾ through both peroxide decomposer and excited state quencher. Therefore, it is expected that these complexes act as peroxide decomposer through the following proposed mechanism, Scheme (3-4).



Scheme (3-4): Suggested mechanism of photostabilization of $M(L)_2$ complexes as peroxide decomposer.

These metal chelate complexes also function as radical scavengers through energy transfer and by forming unreactive charge transfer complexes between the metal chelate and excited state of the chromophore (POO^*) and stabilize through resonating structures as shown in Scheme (3-5).



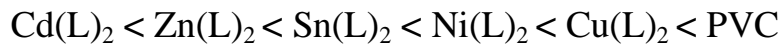
Scheme (3-5): Suggested mechanism of photostabilization of carboxylates complexes as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.

Another way of degradation reaction characterization is the measurements of the quantum yield of the chain scission (Φ_{cs}). The quantum yield for chain scission was calculated⁽¹⁰⁹⁾ for PVC films of modified polymers by using the relation (2-9). The Φ_{cs} values for these polymers are tabulated in Table (3-12).

Table (3-12): Quantum yield (Φ_{cs}) for the chain scission for PVC films (30 μ m) thickness with and without additives after 250 hrs. irradiation time

Additive	quantum yield of main chain scission (Φ_{cs})
Cd(L) ₂	1.28E-07
Zn(L) ₂	1.46E-07
Sn(L) ₂	1.35E-07
Ni(L) ₂	2.88E-07
Cu(L) ₂	3.71E-07
PVC	5.14E-05

The Φ_{cs} values for modified PVC films are less than that of unmodified PVC (blank), which increase in the order:



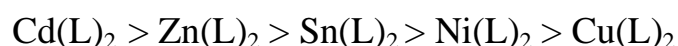
The explanation of low values of Φ_{cs} is due to that, in large molecule of PVC the energy is absorbed at one site, and then the electronic excitation is distributed over many bonds so that the probability of a single bond breaking is small, or the absorbed energy is dissipated by non reactive processes.⁽¹¹⁰⁾

It is well established that the quantum yield (Φ_{cs}) increases with increasing temperatures⁽¹¹¹⁾ around the glass transition temperature, (T_g) of the amorphous polymer, and around the melting temperature of crystalline polymers. In the study presented in this work, the photolysis of PVC film is carried out at a temperature (25–40 °C) well below the glass transition temperature (T_g of PVC = 80 °C). Therefore, the Φ_{cs} dependency on temperature is not expected to be observed.

3-6- Conclusions

In the work described in this thesis, the photostabilization of poly(vinyl chloride) (PVC) films by using Bis[2-(6-methoxynaphthalen-2-yl)propanoate] complexes were studied.

These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl, polyene, hydroxyl and chlorine indices (I_{CO} , I_{PO} , I_{OH} and I_{Cl}) for PVC films.



These additives stabilize the PVC films through HCl scavenging, UV absorption or screening, peroxide decomposer and radical scavenger mechanisms.

The cadmium complexes were found to be the more efficient in photostabilization process according to the photostability and mechanism mentioned above. This support the idea of using cadmium complexes as commercial stabilizer for PVC.

3-7- Suggestions for future work

From the obtained results and discussion, one might suggest the following experiments as further ideas to extend the work already discussed in this thesis:

1. Studying the photo-activity of the additives in other polymers such as PS, LDPE, HDPE and comparing the activity of these additive in photostabilization of PVC.
2. Comparing the efficiency of the synthesized additives with some commercial stabilizers, and following the photostability of PVC. Using outdoor weathering condition, might be good extensions of this work in photostabilization of PVC.

3. Further study of combination of these additives in photostabilization of PVC is needed to investigate the synergism and antagonism phenomenon, for the mixture of two type of additives.
4. Following the effect of additives by other physical and mechanical properties. The photostabilization of PVC film of this additive might also followed by measuring the physical and mechanical properties after irradiation.

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الخلاصة

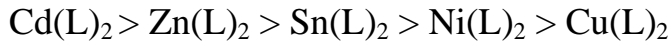
تم خلال هذا البحث تحضير وتشخيص معقدات مع ثنائي [2-(6-ميثوكسي نفتالين-2-وايل)بروبانويت] مع كل من النيكل (II)، النحاس (II)، الخارصين (II)، الكاديوم (II) و القصدير (II) ودراسة تأثيرها في التجزئة والتثبيت الضوئي لبولي (كلوريد الفانيل) (PVC).

حيث شخّصت جميع هذه المركبات من خلال مطيافية الأشعة تحت الحمراء (FTIR) والأشعة فوق البنفسجية والمرئية (UV-Vis.) بالإضافة إلى قياس الحساسية المغناطيسية والامتصاص الذري وقياسات التوصيلية الكهربائية وبعض الخصائص الفيزيائية الأخرى.

تم متابعة سرعة التجزئة والتثبيت الضوئي للرقائق البوليمرية بسمك (30) مايكرومتر والحاوية على المضافات المحضرة وبنسبة (0.5 %) مع زمن التشعيع بقياس قيم معامل الكربونيل والبولين والهيدروكسيل ومعامل الكلور (I_{CO} , I_{PO} , I_{OH} , I_{Cl}). استخدم في تشعيع الرقائق البوليمرية ضوء بطول موجي (313nm) وشدة ($1.05 \times 10^{-8} \text{ ein. dm}^{-3} \cdot \text{S}^{-1}$) وبدرجة حرارة الغرفة.

وجد ان قيم معامل الكربونيل والبولين والهيدروكسيل (I_{CO} , I_{PO} , I_{OH}) تزداد مع زيادة زمن التشعيع، بينما قيم معامل الكلور (I_{Cl}) تقل مع زيادة زمن التشعيع.

من خلال قيم معامل الكربونيل والبولين والهيدروكسيل النامية مع زمن التشعيع، وجد أن المضافات المحضرة تسلك كمثباتات للتجزئة الضوئية، والتي أخذت الترتيب التالي :



ومن خلال النتائج العملية المستحصلة اقترحت بعض الميكانيكيات اعتماداً على الصيغة التركيبية للمادة المضافة، لذلك فهي قانصات HCl، ممتصات الأشعة فوق البنفسجية، مجزئات البيروكسيد وقانصات الجذور الحرة.

وتم خلال البحث دراسة قطع السلسلة البوليمرية وقيم من توج الكم وذلك بقياس مقدار التغير في متوسط اللزوجة للوزن الجزيئي مع زمن التشعيع، فوجد ان مقدار التغير في متوسط اللزوجة للوزن الجزيئي يقل بزيادة زمن التشعيع.



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين / كلية العلوم
قسم الكيمياء

مثبتات ضوئية جديدة لبولي (كلوريد الفانيل) بأستخدام بعض أيونات العناصر لمعقدات 2-(6-ميثوكسي نفتالين-2-وايل)بروبانويت

رسالة مقدمة الى
كلية العلوم-جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير في الكيمياء

من قبل

حسام اكريم سلمان

بأشراف:

الأستاذ المساعد الدكتور عماد عبد الحسين يوسف

و

المدرس الدكتور جواد كاظم شنين