Al-Nahrain University
College of Science
Department of Chemistry

SYNTHESIS AND PHOTOSTABILITY STUDY OF SOME MODIFIED POLY(VINYL CHLORIDE) CONTAINING PENDANT BENZOTHIAZOLE AND BENZIMIDOZOLE RING

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

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March 2007 **Safar 1428**

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We, examining committee, certify that we have read this thesis and examined the student in its content, and that in our opinion it is adequate with standing as a thesis for the **Degree of M. Sc. in Chemistry**.

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Date:	**Date:**

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Date:

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيم

الْحَمْدُ لِلَّهِ الَّذِي هَدَانَا لِهَذَا وَمَا كُنَّا لِنَهْتَدِيَ

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صدق الله العظيم

سورة الأعراف الآية(٤٣)

الإهداء

أهدي ثمرة عملي...إلى مصباح طريقي...

أمي وأبي

إلى كل من كانوا سندي...

إخوتي

إلى كل من بذل جهدا" لمساعدتي ...

هديل

Abbreviation list

Abbreviation	Full meaning used in this thesis
PVC	Poly (vinyl chloride)
PE	polyethylene
EPDM	Ethylene-propylene-diene monomer.
ISC	Intersystem crossing
IC	Internal conversion
HALS	Hindered amine light stabilizer
S	Sensitizer molecule
P	Polymer molecule
THF	tetrahydrofuran
Q.U.V.	Accelerated testing technique
I_s	Index of the group under study
A_S	Absorbance of peak under
A_r	Absorbance of reference peak
$(\overline{M}_v)$	Average molecular weight
η	intrinsic viscosity
η_{re}	Relative viscosity

η_{sp}	*Specific viscosity*
C	*Concentration of polymer solution*
α	*degree of deterioration*
ϕ_{cs}	*quantum yield of main chain scission*
I_o	*Incident intensity*
t	*Irradiation time in second*
S	*Main chain scission*
Pt	*average* ***of*** *polymerization*

Acknowledegments

The honor is mine to express my sincere thanks and gratitude to my supervisors ***Dr. Ayad S. Hameed and Dr. Emad A. Yousif*** *for their guidance and sustain efforts throughout this work.*

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2007

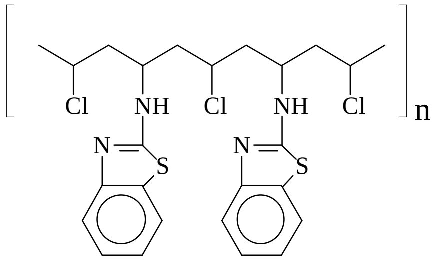
Abstract

The present work consist of two parts:-

Part one:-synthesis and characterization

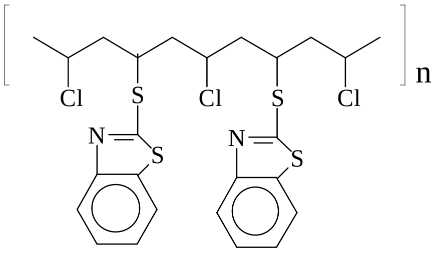
Five modified PVC polymers containing benzothiazole and benzimidazole as bending groups in the repeating units were synthesized in this work according to the following:

1-PAA: Reaction of PVC with 2-amino benzothiazole in THF solvent afforded the following modified polymer (PAA)



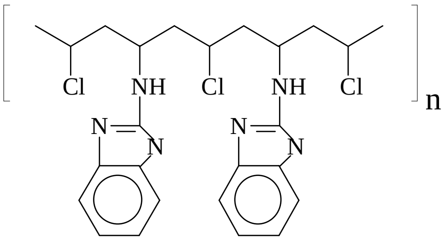
PAA

2-PSS: Treatment of PVC with 2-mercapto benzothiazole in THF solvent under basic condition furnishes the following modified polymer (PSS)



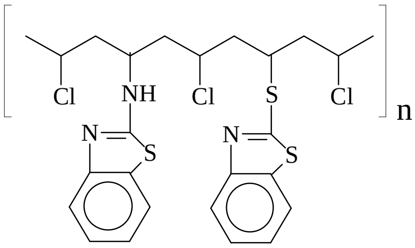
PSS

3-PNN: The modified PVC polymer (PNN) was prepared by the reaction of PVC with 2-amino benzimidazole



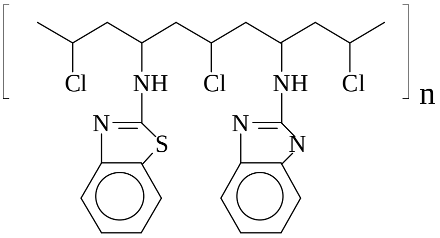
PNN

4-PSA: Reaction of PVC polymer with a mixture of equall amount of 2-amino and 2-mercapto benzothiazole yields the following modified PVC polymer (PSA)



PSA

5-PNA: The PVC polymer when treated with a mixture of equivalent quantities of 2-amino benzothiazole and 2-amino benzimidazole afforded the following modified PVC polymer(PNA)



PNA

Structures of all these modified polymers have been confirmed by spectral (IR,UV) analysis. The results indicated the presence of benzothiazole and benzimidazole rings in the polymeric chain.

Part two:-Photostability study

The influence of introducing benzothiazole and benzimidazole as a pending groups into the repeating unit of PVC has been studied on the bases of photostability measurements. The photostability of modified polymers were studied by monitoring the carbonyl Index (I_{CO}), polyene index (I_{po}) and poly hydroxyl index (I_{OH}), all results obtained indicated that PAA, PSS, PNN, PSA and PNA gave lower growth rate of I_{CO}, I_{PO} and I_{OH} with irradiation time with respect to unmodified PVC film (control) . The following trends of photostability are obtained

PAA>PSS>PNN>PSA>PNA

According to the experimental results several reaction mechanisms were proposed depending on the presence of benzothiazole and benzimidazole moieties in the polymer chain.

The kinetic of photodegradation of modified PVC was also investigated and showed the usual kinetic behavior in degradation process, since the linear relation between square root of carbonyl index $(I_{CO})^{1/2}$ and irradiation time was obtained. The mode of chain scission was also investigated by measuring the variation of average viscosity molecular weight with irradiation time for modified PVC. The degree of deterioration (α) and the average number of chain scission (S) values were also calculated.

Contents

Chapter One: Introduction

Chapter Two: Experimental

Chapter Three: Results & Discussion

Arabic Abstract

Chapter One

Introduction

1-1- Poly(vinyl chloride)

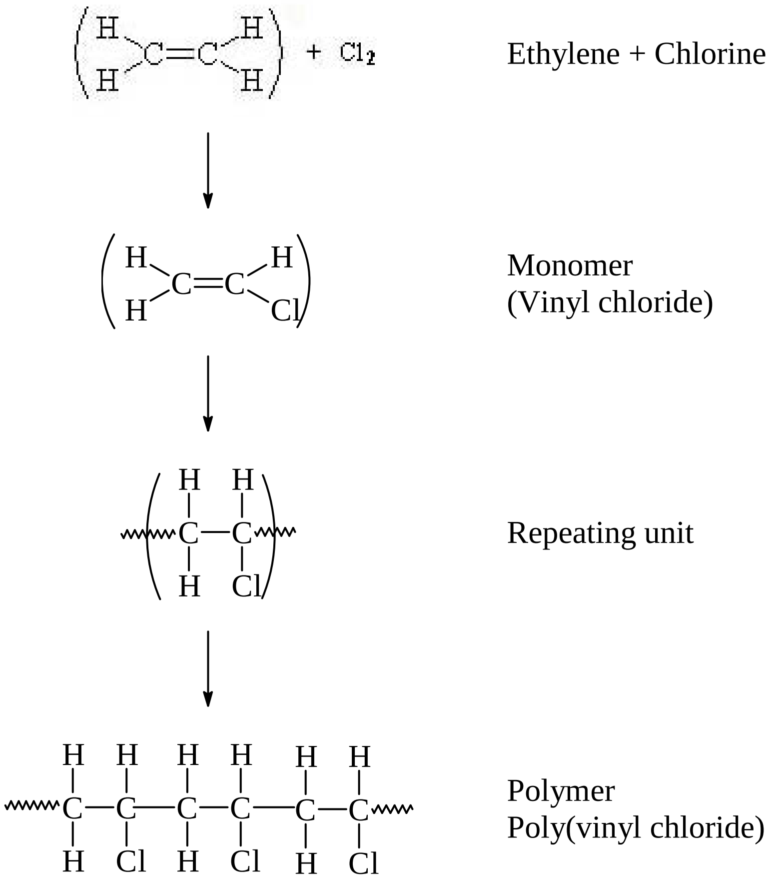
Vinyl chloride monomer and its polymers occupy a unique place in the history of plastics. Arriving early in technology of synthetic resins, they have not been displaced by new polymers. To the contrary, they have become increasingly important(1).

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 found awide acceptance as substitute for rubber as well as building materials .

In the United Kingdom PVC was not produced on commercial scale until the out break of second world war(1).

This polymer is produced by addition polymerization of the monomer vinyl chloride(5), (Scheme 1-1)



Scheme(1-1) Preparation of 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(6).

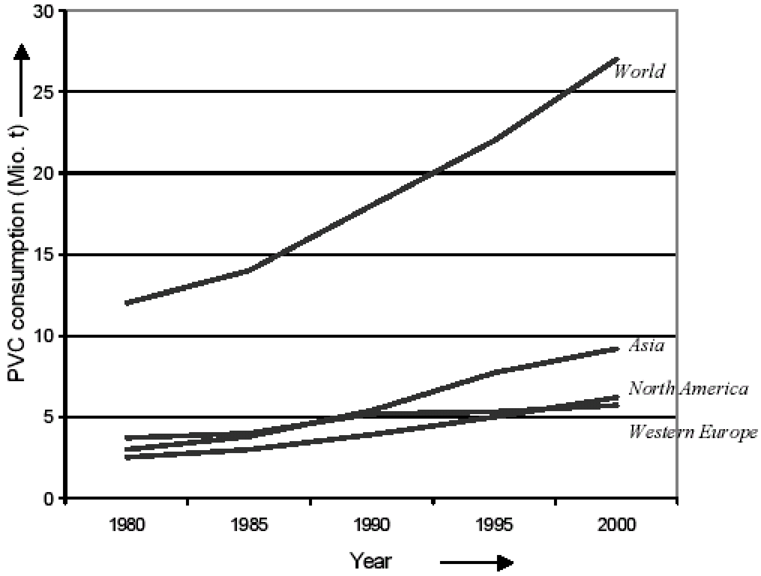
Straight poly (vinyl chloride) is colorless rigid material. It has relatively high density and low softening point(7).

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(6).

Poly (vinyl chloride) has very limited solubility. The most effective solvents are those which appear to be capable of some form of interaction with polymer. It has been suggested that poly (vinyl chloride) is a week proton donor and effective solvents are proton accepter(7). Thus the PVC polymer is soluble at room temperature in oxygen-containing solvents such as ethers e. g. dioxane, tetrahydrofuran; ketones e. g. cyclohexanone, methyl isobutyl ketone and nitro compounds, e. g. nitrobenzene(8).

1-2-The Economic and Technical Importance of Poly(vinyl chloride) Stabilizers

Poly(vinyl chloride) (PVC) was one of the first thermoplastics developed. It has become worldwide a very important bulk plastic over its almost 70 year history. PVC world consumption and in different geographic areas through the years 1980- 2000 are shown in Scheme (1.2)



Scheme (1.2) PVC consumption from 1980 to 2000(9).

The projected consumption of PVC in the near future (1998–2010) is much higher in the developing world and in countries in transition. Estimated demand for Asia alone is more than that for the USA, Canada and the European Community combined(10).

PVC – including the various copolymers of vinyl chloride and chlorinated PVC – is expected to remain important among thermoplastics because of its compatibility with a large number of other products (e. g., plasticizers, impact modifiers), in contrast to other plastics. Because PVC's mechanical properties can be adjusted over a wide range, yielding everything from rigid to flexible end products, there are many different processing methods and applications for PVC. The toxicological problems which at one time were major obstacles in the manufacture and processing of PVC were solved satisfactorily many years ago(11-14).

1-3-Definitions and Historical Aspects of Photodegradation of polymers

A wide variety of synthetic and naturally occurring high polymers absorb solar ultraviolet radiation and undergo photolytic, photo-oxidative, and thermo-oxidative reactions that result in the degradation of the material(15-17). The degradation suffered by these materials may range from mere surface discoloration; affecting the aesthetic appeal of a product, to extensive loss of mechanical properties; which severely limits their performance. The deleterious effects of solar UV-B radiation in particular, on wood, paper, biopolymers and polymers (plastics and rubber), are well known. The phenomenon is of special interest to the building industry, which relies on polymer building products that are routinely exposed to sunlight during use. Most of the common polymers used in such applications contain photostabilizers to reduce photodamage and to ensure acceptable lifetimes under outdoor exposure conditions. The use of plastics in building applications is popular in the developing world because of the low cost and the ease of use of plastic components compared to the conventional metal, glass, mortar, wood and other materials. Plastics are used in other products such as outdoor furniture, fishing gear and marine craft, which are also routinely used outdoors. Table (1-1) illustrates the diversity of products that fall into this category. A large body of research literature on polymers deals directly with the issue of increasing the useful lifetimes of such products under routine outdoor exposure conditions(10,18-20).

Solar radiation reaching Earth's surface is characterized by wavelengths from approximately 295 up to 2500 nm . The solar radiation classified as UV-B (280-315nm) having energy of 426-380 KJ mol^{-1} ; fortunately, the higher-energetic part of UV-B; 280-295 nm is filtered off by the stratosphere and does not reach the Earth's surface, UV-A (315-400 nm, having energy between 389 and 300 KJ mol^{-1} and are less harmful for organic materials than UV-B, visible (400-760 nm); and infrared (760-2500 nm)(21).

Photo-oxidation of organic materials is a major cause of irreversible deterioration for a large number of substances. It is responsible not only for the loss of physical properties of plastics, rubbers, fibers, and other polymeric substrates, but also for rancidity of foodstuffs. Deterioration of hydrocarbon lubricating oils, as well as biological aging and is also implicated in some diseases.(22)

Aging of natural rubber was noted long before. Hoffman in 1861 drow attention to the role of oxygen in the deterioration of organic materials(23). Practical solutions were sought to overcome the problem of loss of properties with aging. Animal foodstuff were preserved by smoking, this process almost certainly results in the absorption of phenolic materials by the fatty components of the food. Similarly, additives were selected to prolong the life span of natural rubber. By the early years of the last century, considerable progress was made toward finding practical solution to combat the problem of oxidation and property deterioration, and a number of chemical compounds including phenols, quinones and amines were patented and offered as remedies(24-26).

Barnard et al.(27,28) : at the British Rubber Producers Research Association, developed a free radical chain reaction mechanism to explain the autoxidation of rubber which was later extended to other polymers and hydrocarbon compounds of technological importance(29).

Table (1-1) Plastics materials routinely exposed to solar UV radiation(10).

Building applications	Plastic window and door frames, siding, mobile-home skirting, gutters and downspouts, conduits, cable covering, flooring, outdoor furniture. Exterior fascia and soffit [rigid PVC formulations] Membrane roofing, geomembranes, weather-stripping [plasticized PVC, EPDM rubber, other rubbers] Glazing, covers for lighting fixtures [polycarbonate and acrylics] Varnishes and coatings used to protect surfaces. Highway marking paints. Resins used in the repair of monuments
Agricultural applications	Irrigation hoses, pipes, netting [PE and PVC]. Tanks for storage of water [Unsaturated polyester, and PE] Mulch films and greenhouse films [PE and PVC]
Transportation	Automobile tires [rubber]. Plastics used in automobile, aircraft, and marine vessel construction [composite]
Other	Fishing nets, sails, outdoor temporary housing, outdoor furniture, fibers and textiles
Biopolymers	Wool, human hair, wood, chitinaceous materials
PE, polyethylene; PP, polypropylene; PVC, poly(vinyl chloride); EPDM, ethylene-propylene-diene monomer.	

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, and

  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.), and

  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(30). These are very similar since they all involve chemical reactions that result in bond scission. These modes are(30):

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:

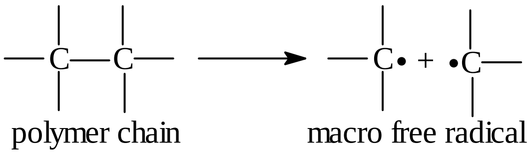
Thermal degradation refers to the case where the polymer, at elevated temperatures, starts to undergo chemical changes without the simultaneous involvement of another compound.

III) Biodegradation:

Biologically initiated degradation also 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.

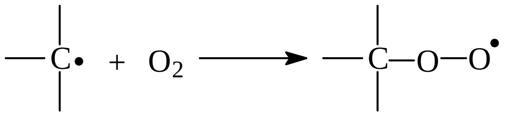
IV) Mechanical degradation:

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:



$$-\mathrm{C}-\mathrm{C}- \longrightarrow -\mathrm{C}\bullet + \bullet\mathrm{C}- \quad (1.1)$$

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.



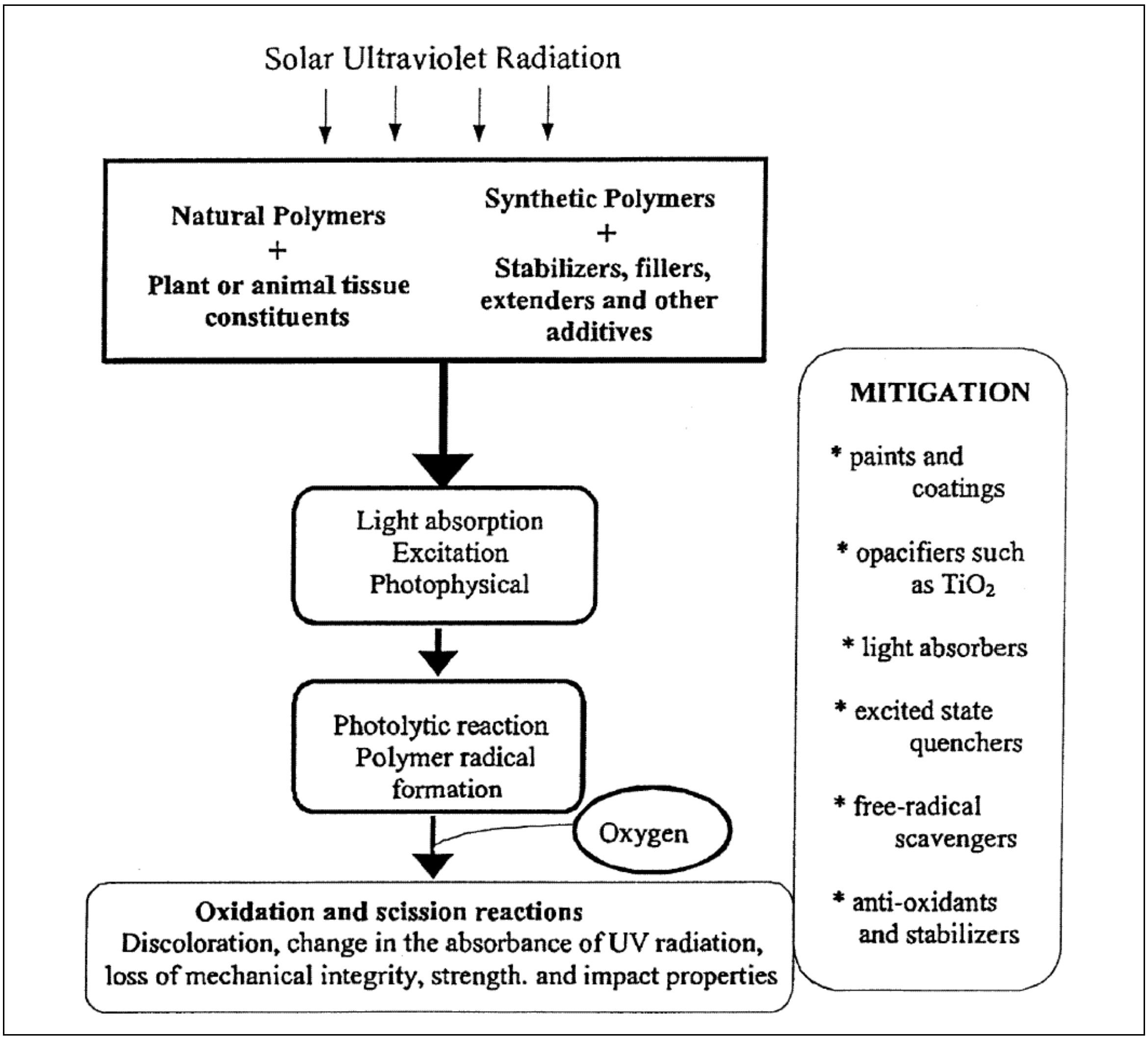
$$-\mathrm{C}\bullet + O_2 \longrightarrow -\mathrm{C}-\mathrm{O}-\mathrm{O}^{\bullet} \quad (1.2)$$

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 (1.3) shows the basic steps involved in photodamage and illustrates the various strategies commonly used to mitigate light-induced degradation of polymers.

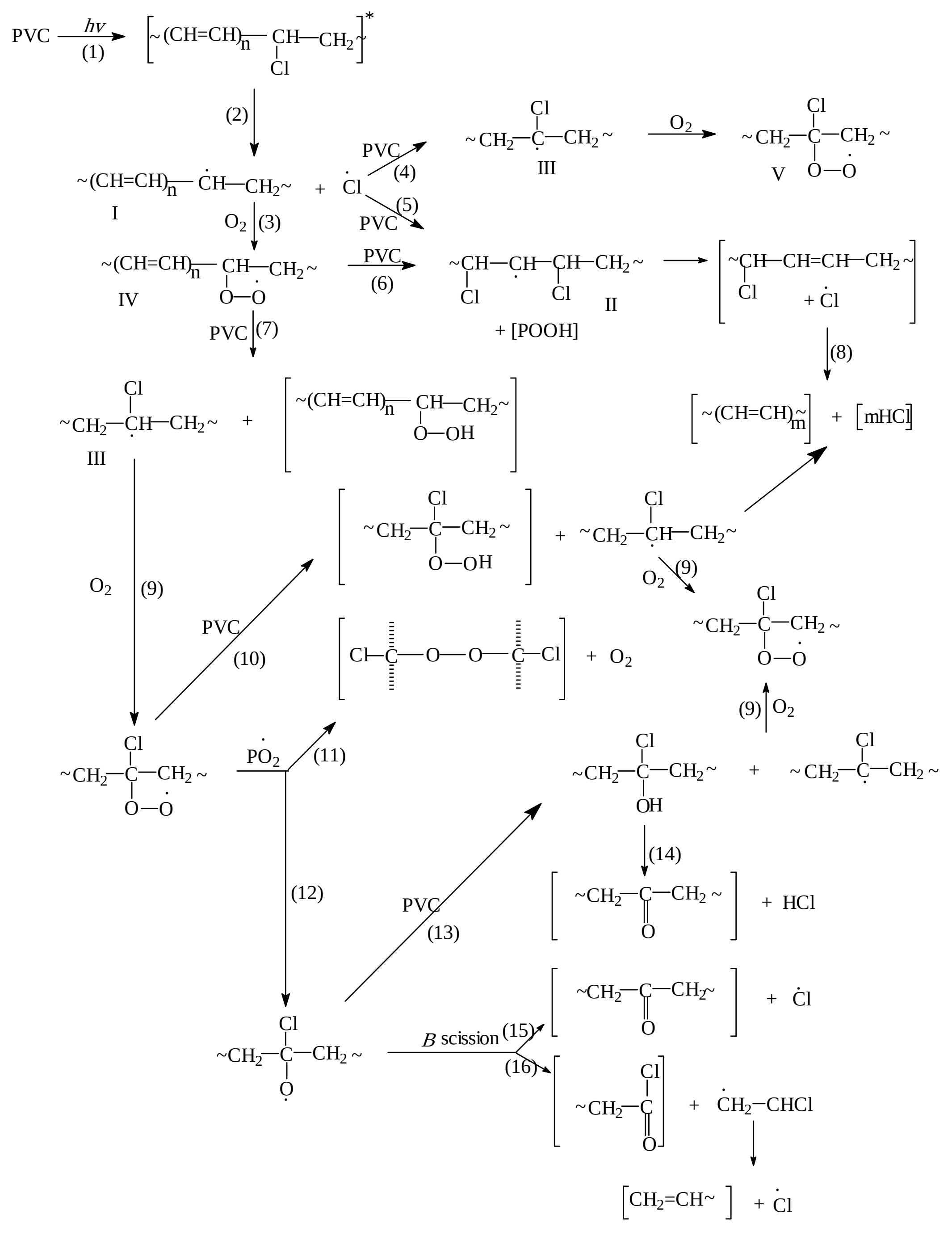


Scheme (1.3) Schematic diagram of the various stages of light-induced damage in polymers and its mitigation(19).

1-4-Mechanism of photo oxidative degradation of Poly(vinyl chloride)

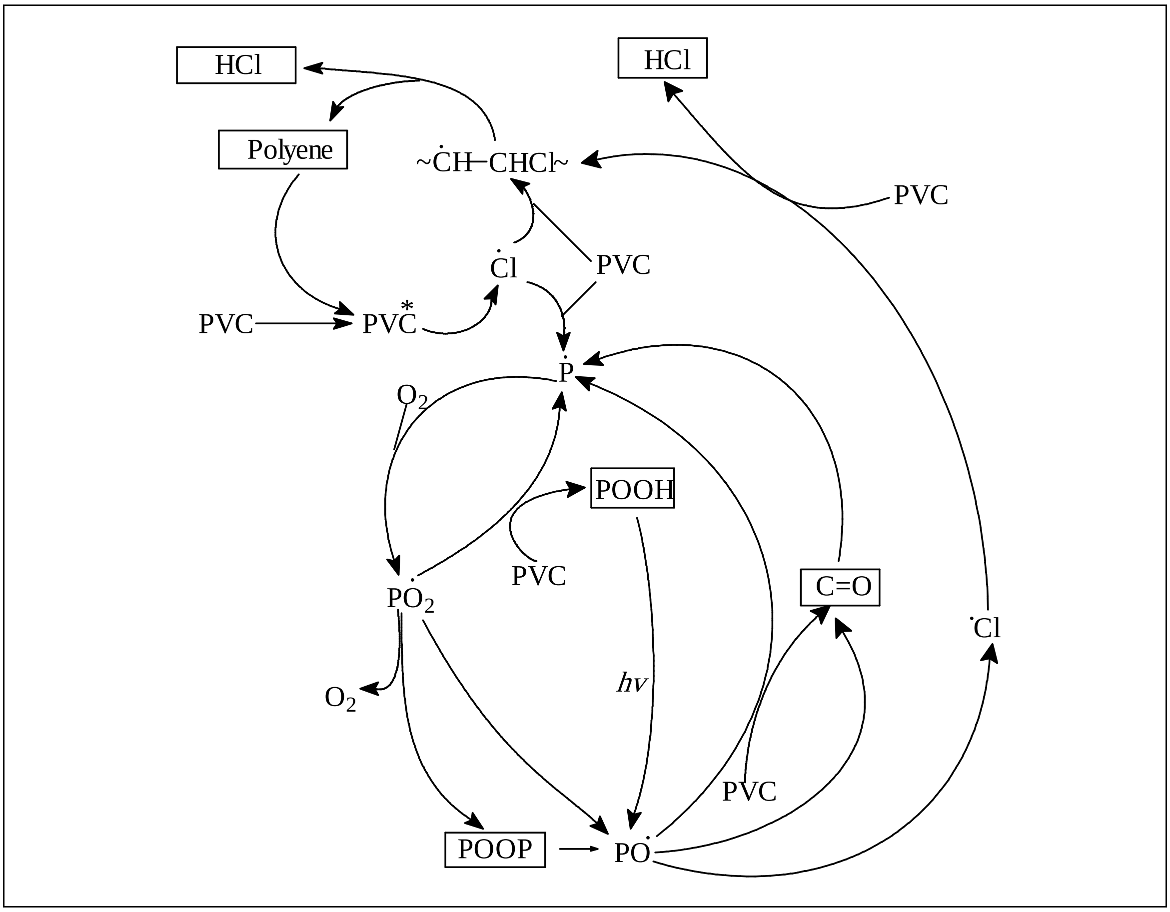
Ultra violet radiations are known to have deleterious effects on most industrial polymers inducing chemical modification and scission of polymer chain, which ultimately lead to an undesirable loss of the mechanical and surface properties of the irradiated material. The extent of this degradation depends primarily on the presence of photosensitive chromophores both in polymer chain, either as structural unit or defects, and in the impurities, which always contaminate processed polymeric materials.

In the case of PVC, a dehydrochlorination chain reaction develops rather rapidly upon exposure to sunlight, thus requiring efficient stabilization if the polymer is to be used for outdoor application. In spite of numerous investigations(31-36) the reason for high photosensitivity of PVC are still the subject of much speculation since the monomer unit itself contains no chromophore absorbing in the solar emission range. The degradation is generally conceded to start from the defect in the polymer chain but their precise nature remains controversial(37); hydroperoxides, aromatic carbonyl groups, olefinic bonds, metal salts, chain peroxide linkages and irregularities, can be responsible for the photo-initiation of free radical oxidation of PVC. The mechanism of photooxidation is explained by reaction Scheme (1-4).



Scheme (1.4) Reaction scheme of the photodgradation of PVC in the presence of O_2(38).

The overall mechanism now suggested for the photooxidation of PVC to account for the main primary products can be summarized by the reaction scheme shown on Scheme (1.5) where $P^{\cdot}$ represents radical $\sim(CH=CH)_n-{}^{\cdot}CH-CH_2\sim$ or $\sim CH_2-{}^{\cdot}CCl-CH_2\sim$. The two major chain process which develop simultaneously are clearly apparent(38).



Scheme (1.5) Photooxidation reaction Scheme of PVC(38).

1-5-Photostabilization mechanisms in polymers

The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics.

1-5-1-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(39-43), 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, ($^1O_2$), quenchers.

Ultraviolet stabilizers that are available commercially can be classified by chemical structure into(44):

(i) Pigments.

(ii) Metal xanthates.

(iii) Chelates.

(iv) Salicylates.

(v) Salicylanilides.

(vi) Hydroxy phenyl benzotriazoles.

(vii) Hydroxy benzophenones.

1-5-2-Mechanism of UV absorbing and light screening

1-5-2-A: Mechanism of UV absorber

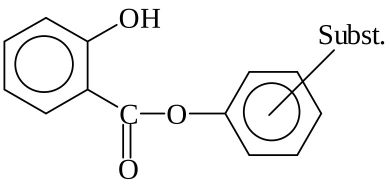
Plastics and organic coatings used outdoors are exposed to ultraviolet (UV) radiation in the range of 295 to 400 nm which is often the primary cause of their degradation and weathering. UV absorbers (UVAs) commonly are used in these applications to prevent UV radiation from reaching the bulk of the polymer 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:(45)

"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."

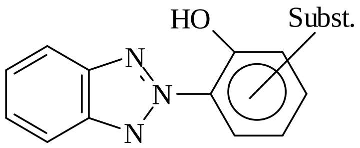
Meyer and Geurhurt reported, for the first time in 1945(46), the use of UV absorber in a polymer. They found that the outdoor life of cellulose acetate film was greatly prolonged by adding phenyl salicylate (Salol).

After that, resorcinol monobenzoate, a much more effective absorber, was introduced in 1951(47), for stabilization of polypropylene (PP), but Salol continued to be the only important commercial stabilizer for several years.

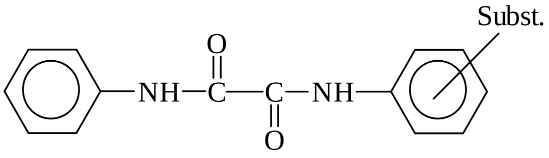
Jan Pospisil(21) reported that certain phenolic and non-phenolic UV absorbers with structures (1), (2), (3) and (4) respectively, having high performance and inherent photostability in the 300-400nm. region are used for protection of polymer against photodegradation.



(1)



(2)



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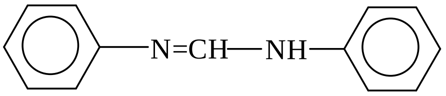


(4)

Hydroxy benzophenones and hydroxyphenyl benzotriazoles are the most extensively studied UV absorber(48).

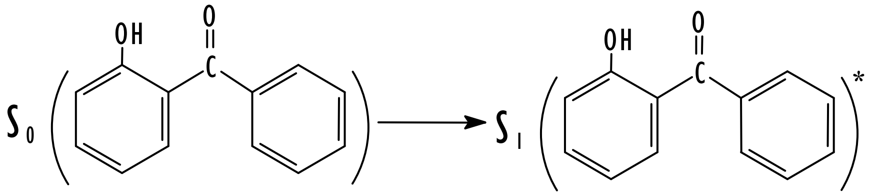
Generally, after photons are absorbed by the chromophores, molecules rise to the higher excited states, by spin inversion of singlet states. The singlet states may change to triplet state by intersystem crossing (ISC) or return to lower excited state by internal conversion (IC) (these are radiationless processes). Excited states have the ability to lose the excitation energy by some radiation processes such as (Floursence, phosphorescence) or by energy transfer to another molecule.

Concerning the energy transformation in hydroxy benzophenones, it has been shown with 2-hydroxy benzophenone(48,49), that on exposure to light, it is transformed into enol form which turns back into its initial form on losing thermal energy to the medium. On the basis of spectroscopic data, it is concluded that the energy transformation involves exclusively fast radiationless transition.

The photostabilizing mechanism of *O*-hydroxy benzophenone has been the subject of many investigations(50).

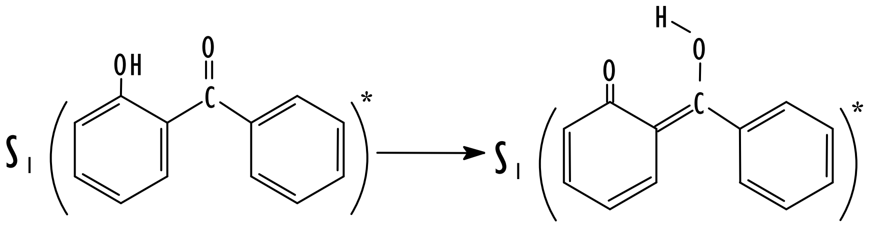
The most probable mechanism involved is the change of energy of absorbed photon to intramolecular proton transfer during which a quinone structure is formed.

O-hydroxyphenone molecule in the ground state (S_0) absorb a photon as is excited to the singlet state (S_1)



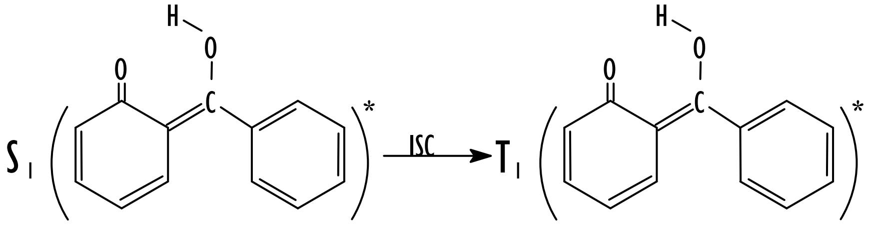
(I-3)

In this excited singlet state (S_1) the proton of a hydroxyl group is transferred to the carbonyl group, during which quinone structure is formed:



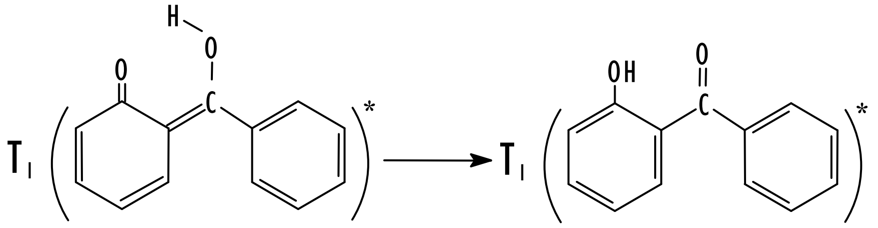
(I- 4)

The excited singlet sate (S_1) of quinone structure transfer by intersystem crossing (ISC) process to the excited triplet state (T_1).



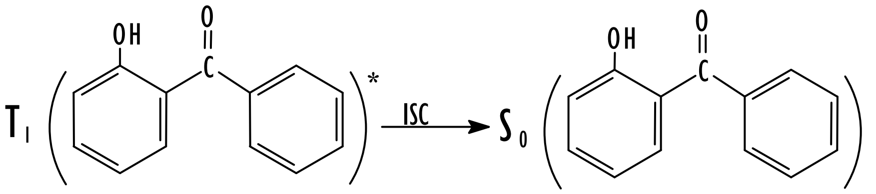
(I-5)

Since in the excited triplet state (T_1), the stable structure is the ketone structure,



(1-6)

The intersystem crossing (ISC) process leads the excited triplet sate (T_1) of ketone structure directly to the ground state (S_0):



(1-7)

Olson and Schroeter(51), have shown that urethane and silylated derivatives of hydroxybenzophenones are effective photostabilizers, but can not photostabilize polymers by the mechanism of intramolecular proton transfer. These compounds can act as(52-60).

(i) Light screeners.

(ii) Excited state quenchers of chromophoric groups present in polymers.

(iii) Free radical scavengers.

(iv) Hydroperoxide decomposers.

1-5-2-B: 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(52):

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(61,62).

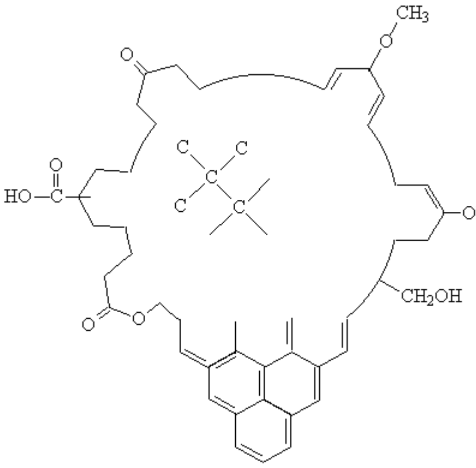
The chemical nature of a pigment is also very important. For example iron oxide protects polyolefins but rapidly catalyses the decomposition of polyvinyl chloride on exposure to UV radiation. The influence of pigments in polymer photostability is not completely understood. If an absorbing pigment is 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(63), 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(64), and quenchers of singlet and triplet states of polymers. The effectiveness of carbon blacks is dependent upon(65) the type of carbon black, the particle size and the degree of dispersion in the polymer phase. Scheme (1.6) shows a model of carbon black with different functional groups such as carbonyl, hydroxyl and quinone .



Scheme (1.6) Carbon black model illustrating possible functional groups.

1-5-3-Quenchers

Quenchers deactivate excited states (singlet and/or triplet) of chromophoric groups in polymers before bond scission can occur by two mechanisms(66.67).

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 life time 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 $^1O_2$) formed in polymers. The [$^1O_2$] can also be generated in polymers by energy transfer from electronically excited carbonyl group to dissolved molecular oxygen(68). The quenching of [$^1O_2$] is also necessary for effective stabilization. Nickel chelates have been proven to be very effective quenchers for excited state of [$^1O_2$](69).

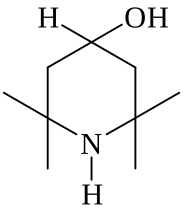
1-5-4-Free radical scavengers

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.

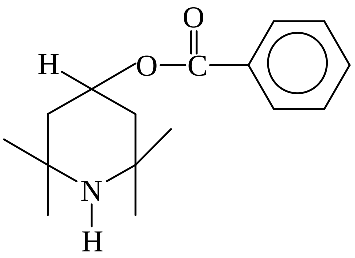
There is a rather limited choice of compound acting as scavengers of free radicals and satisfying requirements for commercially applicable stabilizers. Moreover, scavenging of free radicals has to compete with two other reactions (i.e.) self reaction of free radicals and reaction with oxygen.

1-5-5-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)(70), such as (4-hydroxy –2,2,6,6-tetramethyl piperidine (5) and 4-Benzoyloxy-2,2,6,6-tetramethyl piperidine, (sanol 774)(71,72), (6)



(5)



(6)

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 Oalkylhydroxylamines(71).

1-6-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(72).

Consequently, photosensitized degradation of polymers is considered as a means of alleviating 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(73).

Present attempts to develop plastics with reduced outdoor stability are based on(74,75):

(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(76,77). 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 reenters 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 (1-7):

$$S + hV \rightarrow S^{*} \quad \text{(excitation of sensitizer)} \qquad \text{(a)}$$

$$S^{*} \rightarrow x^{\bullet} + y^{\bullet} \quad \text{(dissociation of sensitizer)} \qquad \text{(b)}$$

$$x^{\bullet}(y^{\bullet}) + P - \left[\begin{array}{ll} xH(Hy) + P^{\bullet} \ \text{(hydrogen abstraction)} & \text{(c)} \\ {}^{\bullet}Px({}^{\bullet}Py) \qquad \text{(addition)} & \text{(d)} \end{array} \right.$$

$$P^{\bullet} \rightarrow P_1^{\bullet} + P_2^{\bullet} \ \text{(main chain scission)} \qquad \text{(e)}$$

$$S^{*} + P \rightarrow S + P^{*} \quad \text{(energy transfer)} \qquad \text{(f)}$$

$$P^{*} - \left[\begin{array}{ll} P^{\bullet} + R^{\bullet} \ \text{(scission of lateral group)} & \text{(g)} \\ P_1^{\bullet} + P_2^{\bullet} \qquad \text{(main chain scission)} & \text{(h)} \end{array} \right.$$

$$S^{*} + P \rightarrow {}^{\bullet}SH + P^{\bullet} \quad \text{(hydrogen abstraction)} \qquad \text{(i)}$$

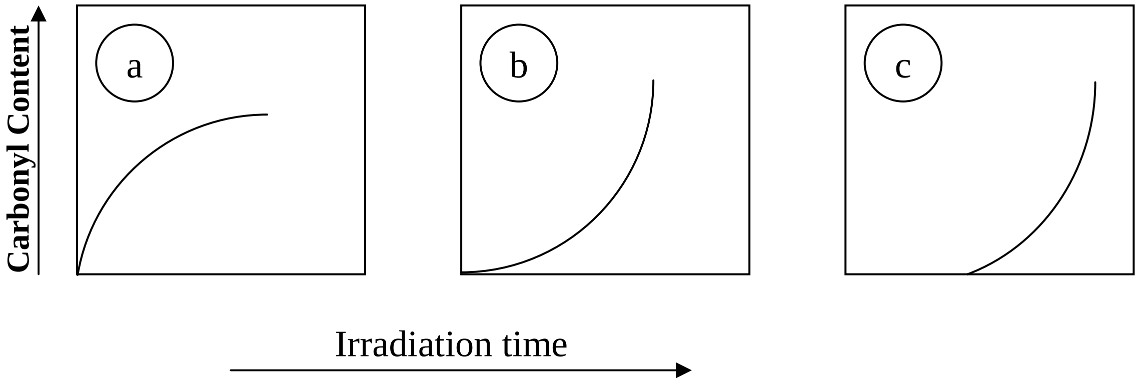
Scheme (1-7): Sensitized photodegradation(77).

According to S = sensitizer molecule, P = polymer molecule (i) in Scheme (1-7), 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(77):

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(78). As shown in Scheme (1-8),these are:



Scheme (1-8): Schematic representation of sensitized photo-oxidation of polymers(78).

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) a cetylacetonates.

c. An initial induction period exists which increases with increasing sensitizer concentration, e.g. metal complexes of 2-hydroxy

acetophenone oxime.

1-7-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(79):

- 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(80).

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(80,81).

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(81).

- 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(82).

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(82).

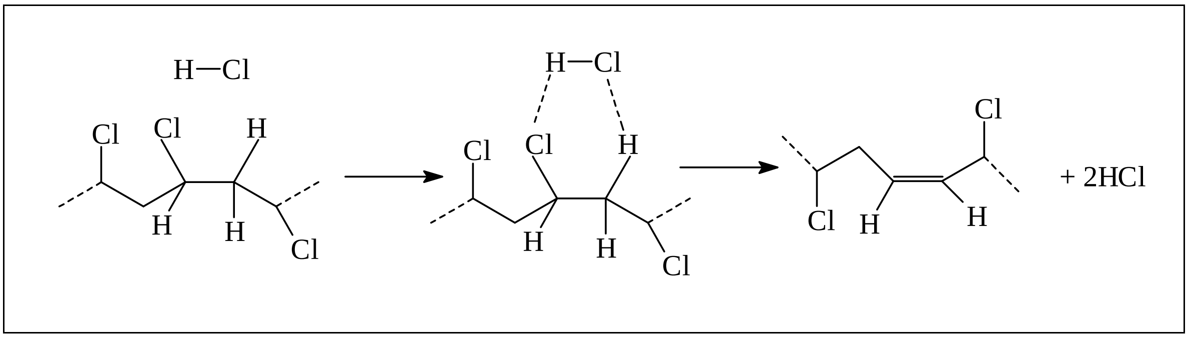
The light stability of PVC plates has been substantially increased by protecting their surface with a UV-cured acrylic clearcoat containing both a UV absorber and HALS radical scavenger. To ensure a long-lasting adhesion, the coating was photochemically grafted onto the PVC substrate. The coated PVC 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(83-88).

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(89).

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(90).

Six-center transition state in the catalytic presence of HCl Scheme (1-9) Structural irregularities such as allylic chlorine atoms eliminate chlorines in the chain.



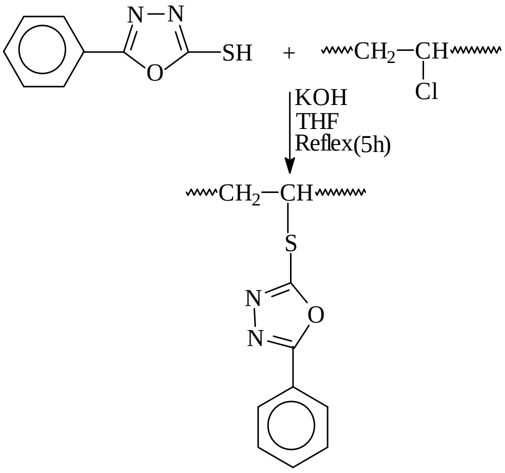
Scheme (1-9) Suggested mechanism of autocatalytic process in presence of Hydrogen Chloride formed(90).

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, intersystem crossing.

Recently Aliwi et al.(91) synthesized new modified PVC by the reaction of PVC with 2-mercapto-5-phenyl 1,3,4-oxadiazole in THF solvent (Scheme1.10) and they found that the new polymer is more stable than the PVC without modification



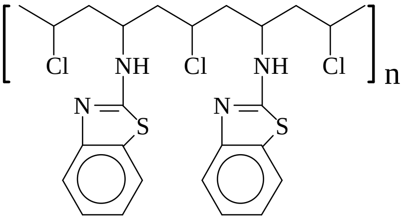
Reaction of PVC with 2-mercapto-5-phenyl 1,3,4- oxadiazole

Yousif and Hameed studied(92) the photostability of reacted poly(vinyl chloride) with 2-amino-5-(phenyl)-1,3,4-thiadiazole(LI), 2-amino-5-(p-nitro phenyl)-1,3,4-thiadiazole(LII), 2-mercapto-5-phenyl 1,3,4-oxadiazole(LIII) and 2-mercapto-5-(p-hydroxy phenyl) 1,3,4-oxadiazole(LIV) All results obtained showed that the rate of photodegradation of PVC-L films, 30 micrometer in thickness followes the trend:

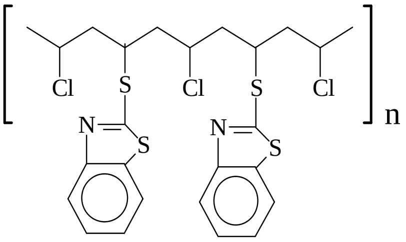
PVC> PVC-LIII> PVC-LIV> PVC-LI > PVC-LII

Aim of the work

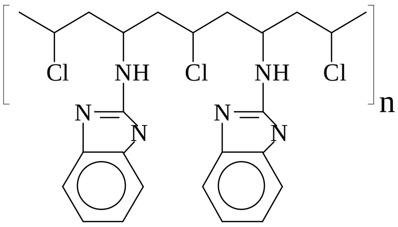
Synthesis of PVC polymer bonded to heterocyclic units is the field of our research . A number of heterocyclic units including 1,3,4 – oxadiazole , 1,3,4 – thiadiazole,porphyrine,bipyridine have been bound with PVC , In this study we attempt to modify poly (vinyl chloride), PVC by introducing benzimidazole and benzothiazole in the backbone of the PVC chain through chlorine displacement reaction , and we hope that such modification may showes interesting changes in overall thermal stability and interesting changes in over all properties of PVC such us , photostability , optical property , dielectric properties relative to un modified PVC, according to these finding , it was planned to frame a macromolecules which combine these two heterocyclic units for their characterization and photostability toward uv light .The synthesized (PVC-heterocyclic units) polymers having the following structural formula.



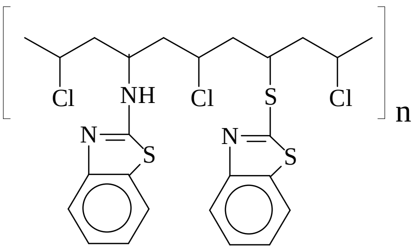
PAA



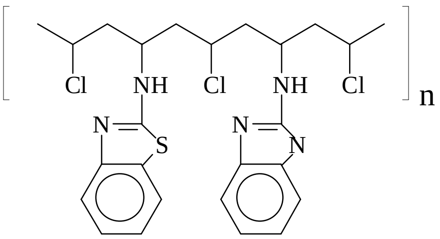
PSS



PNN



PSA



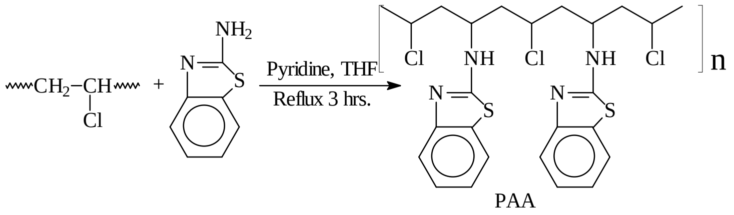
PNA

Chapter Three

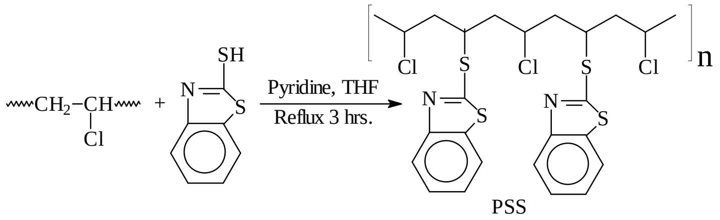
Results and Discussion

3-1-Synthesis of PVC bound benzothiazole and benzimidazole ring system

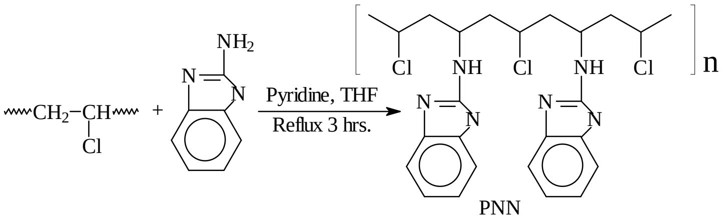
Polymers with an aromatic and heterocyclic rings have been drawing the attention of researchers more due to their importance in many aspects of interest, among these polymers are modified poly(vinyl chloride) (PVC). poly(vinyl chloride) are modified by introducing aromatic and heterocyclic moieties through halogen displacement reaction mainly by S_{N2} mechanism, modified PVC polymers have developed over the past decade into a fast growing industrial application field. They have also attracted attention because of their importance as catenation ligands. Also, the thermal stabilities of (PVC-aromatic).Polymers are comparable better than unmodified PVC. In addition, most of them showed improved changes in electro physical properties, especially in dielectric properties. In continuation of our earlier studies on the synthesis of modified PVC, we undertook in this research the synthesis of some new modified PVC containing heterocyclic systems viz., benzothiazole and benzimidazole (polymers prepared), with a view to finding out the effect of introducing these moieties on physical and chemical properties of PVC. Equations (3-1 to 3-5) present the formation of polymers prepared.



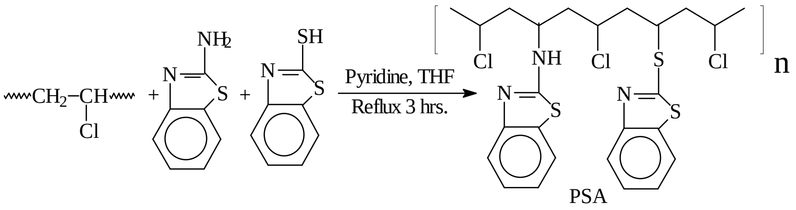
3-1



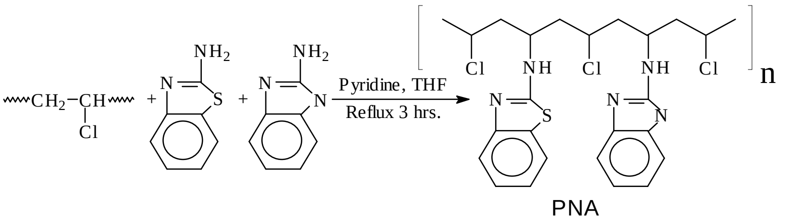
3-2



3-3

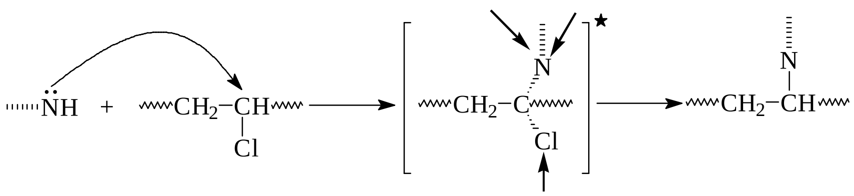


3-4



3-5

The reaction was initiated by the nucleophilic attack of (S,N) atoms on the carbon carrying chlorine atom in the polymeric chain followed by departure of chloride anion as a good leaving group.



3-2-Characterization of modiefied polymers

3-2-1- Infra-red Spectroscopy

The structure of the present polymers was confirmed by Infra-red spectroscopy. The most common bands are tabulated in Table (3-1),beside the typical i.r absorption bands , each of the present polymers showed other band characteristic of its own structure, Figures (3-1)-(3-6) showed the following features , a medium to strong band at about (630) cm^{-1} which could be attributed to (C-Cl) , the appearance of a medium band at about (1550) cm^{-1} indicated that the end groups of these polymers are C=C double band , the bands at around (2900) cm^{-1} which was assigned to the typical aliphatic (C-H) stretching vibration was also observed, moreover , these polymers exhibited significant bands in the region at (3050 for *v*(C-H aromatic) , 1635 for *v*(C=N) and at 750 for (C-H bending of *O*-disubstituted benzene) that clearly indicated the presence of the benzothiazole and benzimidazole nucleus in the backbone of PVC chain.

Table (3-1) Characteristic absorpation bands of polymers.

Polymer Symbol	IR Spectral Data (cm^{-1})	Assignment
PAA	3274	N-H stretching
	3058	C-H stretching of benzene ring
	2923	C-H stretching of $-CH_2-$
	1635	C=N stretching of thiazole ring
	1531	C=C stretching of end of PVC chain
	1438	C-H bending of $-CH_2-$
	1303	C-H bending of $-CH_3$
	763	C-H bending of ortho disubstituted benzene ring
	628	C-Cl stretching

PSS	3025	C-H stretching of benzene ring
	2900	C-H stretching of $–CH_2$-
	1630	C=N stretching of thiazole ring
	1589	C=C stretching of end of PVC chain
	1434	C-H bending of $–CH_2$-
	1350	C-H bending of $–CH_3$
	655	C-Cl stretching
PNN	3375	N-H streching
	3070	C-H streching of benzen ring
	2931	C-H stretching of $–CH_2$-
	1646	C=N stretching (being broad)
	1569	C=C stretching of end of PVC chain
	1458	C-H bending of $–CH_2$-
	1319	C-H bending of $–CH_3$
	732	C-H bending of ortho disubstituted benzene ring
	621	C-Cl stretching
PSA	3200	N-H stretching (being broad)
	3078	C-H stretching of benzene ring
	2896	C-H stretching of $–CH_2$-
	1616	C=N stretching (being broad)
	1531	C=C stretching of end of PVC chain
	748	C-H bending of ortho disubstituted benzene ring
	651	C-Cl stretching
PNA	3270	C-H stretching of benzene ring
	2931	C-H stretching of $–CH_2$-
	1643	C=N stretching of imidizole ring
	1539	C=C stretching of end of PVC chain
	1450	C-H bending of $–CH_2$-
	1328	C-H bending of $–CH_3$
	750	C-H bending of ortho disubstituted benzene ring
	628	C-Cl stretching
		N-Hstretching(being broad)
PVC	2970,2910,2860	C-H streching of $–CH_2$ and –CH-
	1429	C-H bending of $–CH_2$-
	615.2	C-Cl stretching

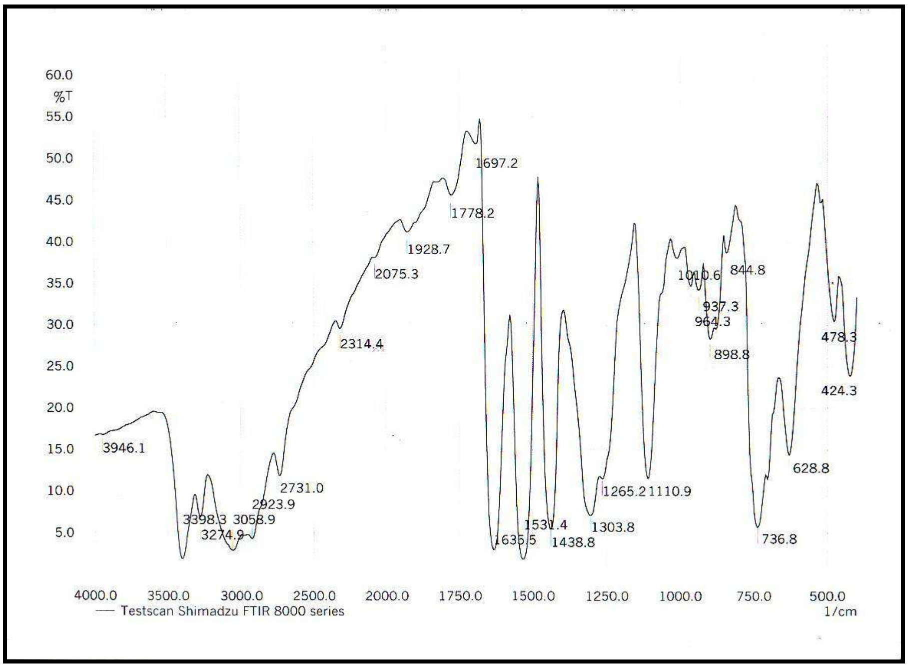


Figure (3-1) FTIR spectrum for PAA

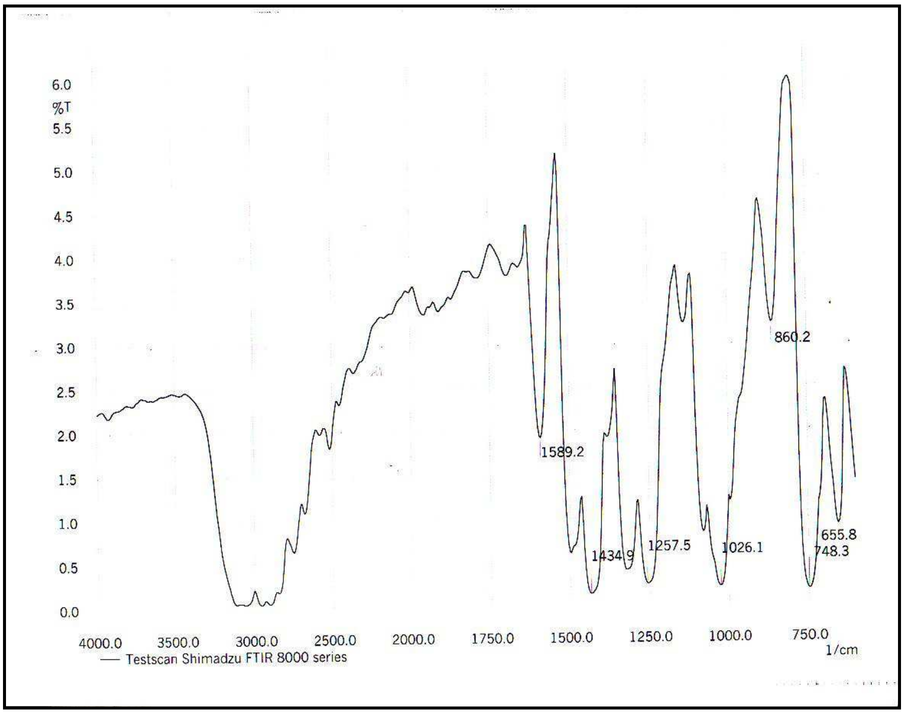


Figure (3-2) FTIR spectrum for PSS

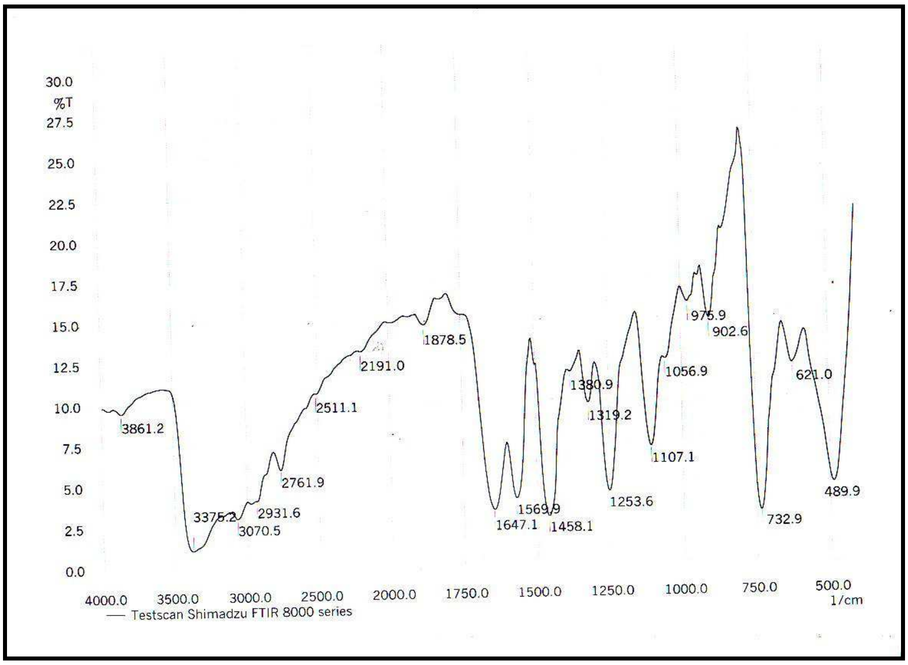


Figure (3-3) FTIR spectrum for PNN

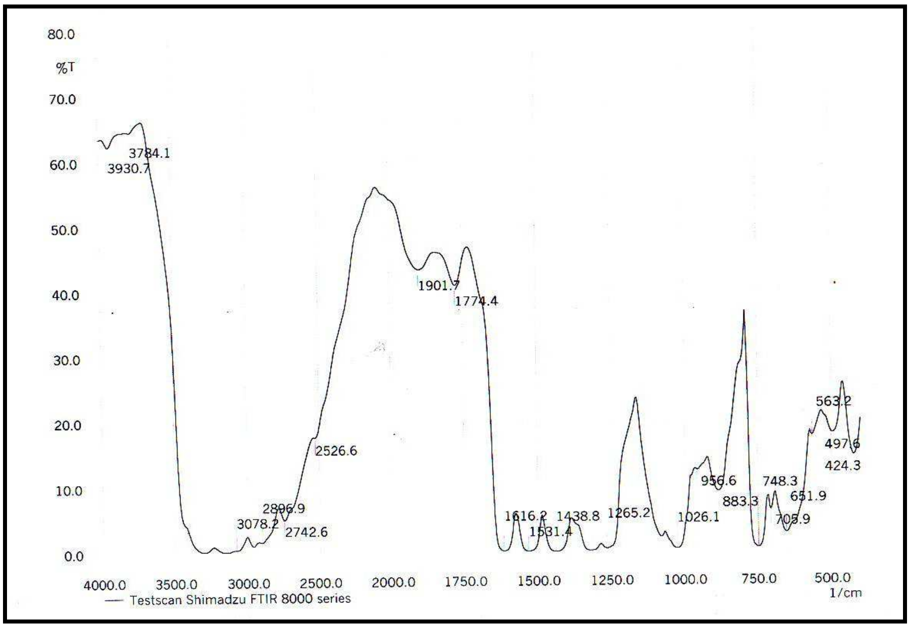


Figure (3-4) FTIR spectrum for PSA

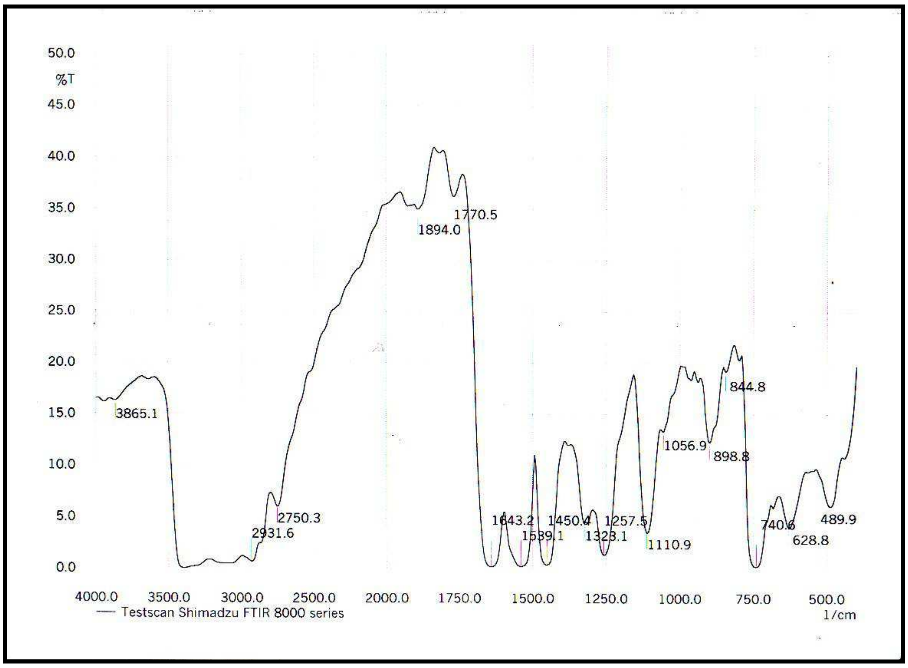


Figure (3-5) FTIR spectrum for PNA

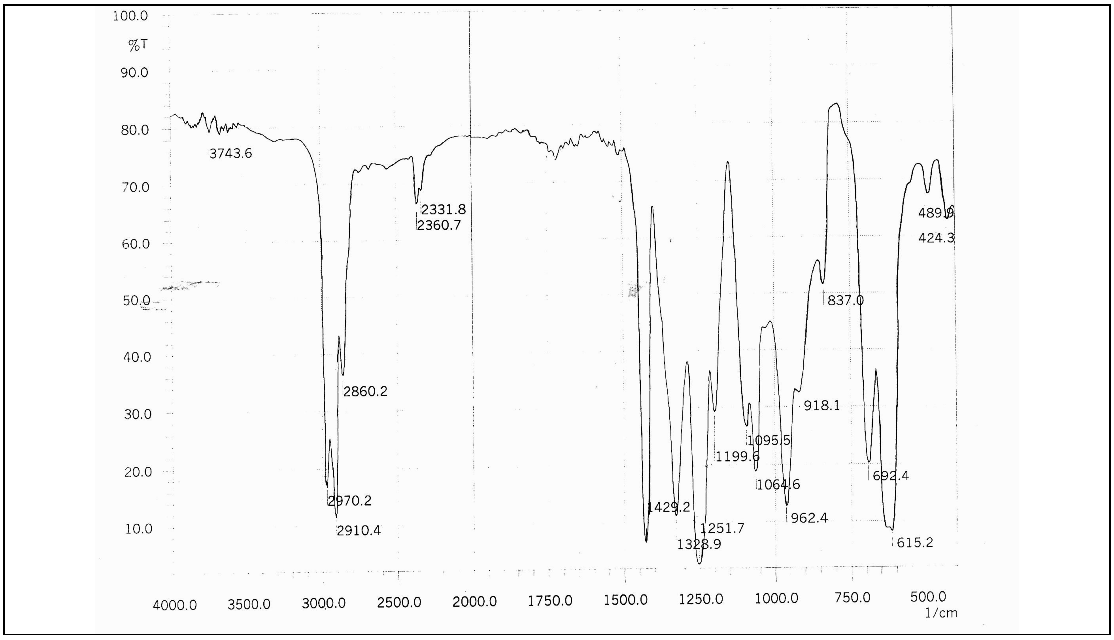


Figure (3-6) FTIR spectrum for PVC

3-2-2- Ultraviolet-visible Spectroscopy

The ultraviolet-visible spectrophotometry technique is used to characterize the polymers in tetrahydrofuran (THF) as a solvent.The ultraviolet visible electronic spectra of the modified polymers, (Figures (3-7) to (3-12)) showed an absorption bands could be attributed to the $\pi \rightarrow \pi^*$ electronic transitions, These transitions are assigned in relevance to the structures of polymers . As shown in Table (3-2).The increase of the absorbance in the uv-vis range for samples containing modified PVC can be explaned by the formation of conjugation double bonds (band corresponding to the $\pi \rightarrow \pi^*$ transition) in these modified polymers resulting from introducing an aromatic benzothiazole and benzimidazole rings. Thus, shifting the absorbance to longer wavelengths (i.e the bathochromic effect) is good evidence that modification were formed in our PVC .moreover, the broading in the bands (fig (3-7)-fig (3-12)) caused by the presence of other chromophores such as (C=N ,etc) which absorb in the above region and this overlapping bands make the interpretation of the results difficult.

Table (3-2) Electronic spectra of polymers in THF solvent.

Compound	Color	Absorption Bands(nm.)
PAA	White	234
		262
		293
PSS	Yellow	230
		324
PNN	Brown	224
		276
		281
PSA	Brown	226
		265
PNA	Brown	234
		249
		270
PVC	Colorless	219
		254

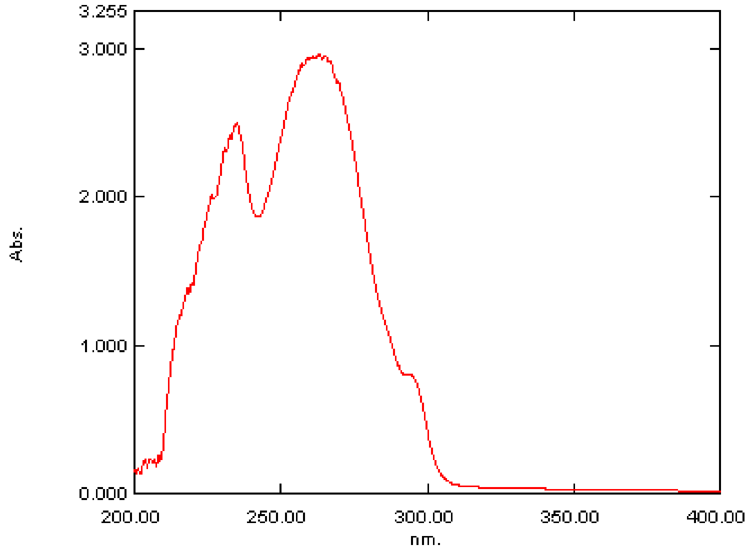


Figure (3-7): The ultraviolet visible spectrum for (PAA) in THF solvent.

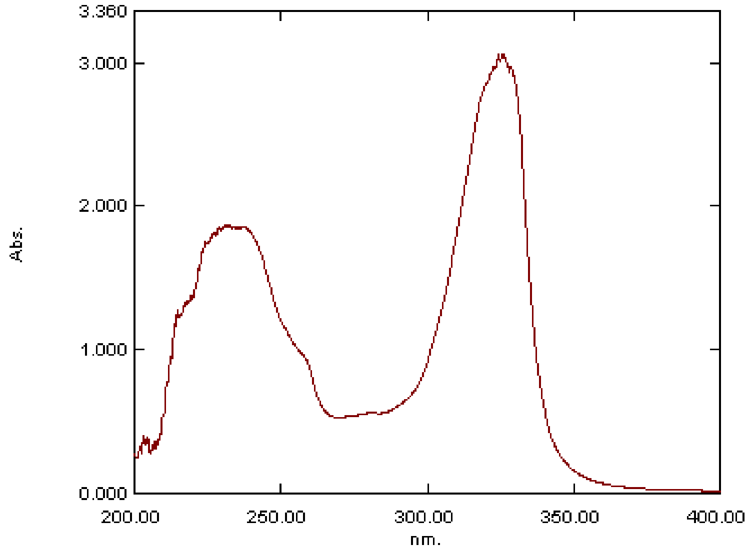


Figure (3-8): The ultraviolet visible spectrum for (PSS) in THF solvent.

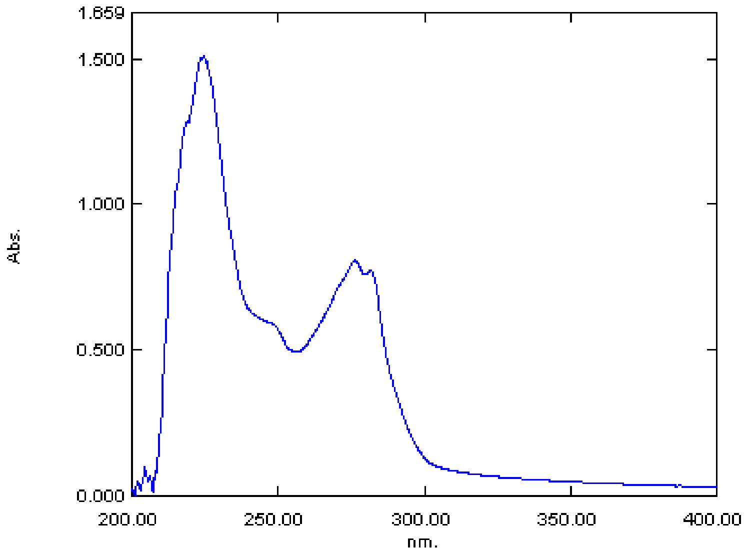


Figure (3-9): The ultraviolet visible spectrum for (PNN) in THF solvent.

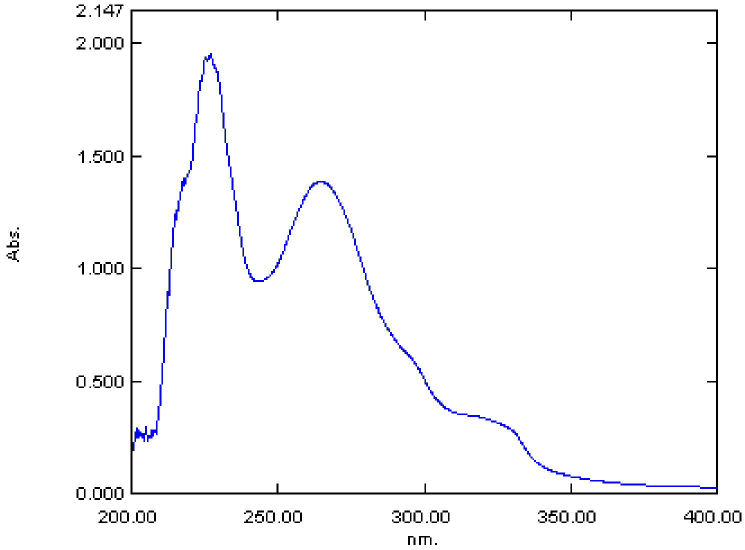


Figure (3-10): The ultraviolet visible spectrum for (PSA) in THF solvent.

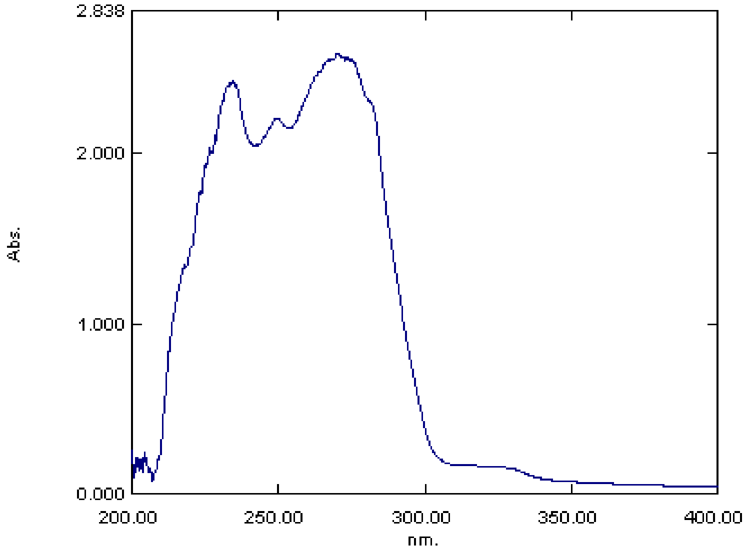


Figure (3-11): The ultraviolet visible spectrum for (PNA) in THF solvent.

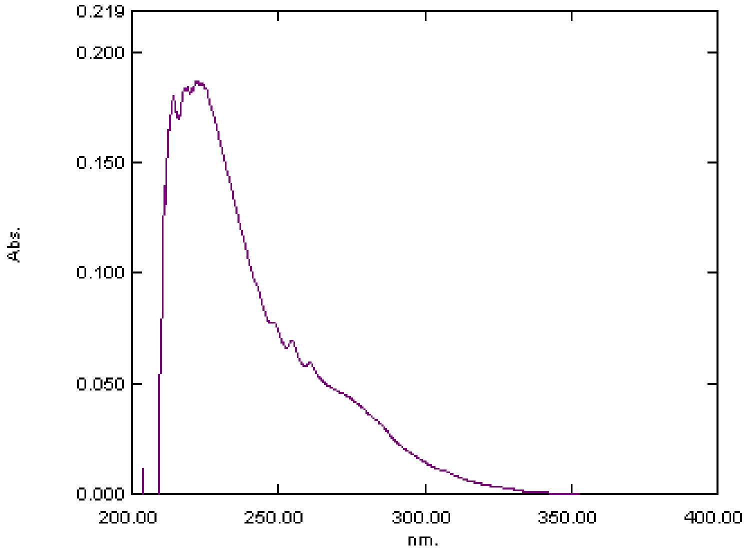


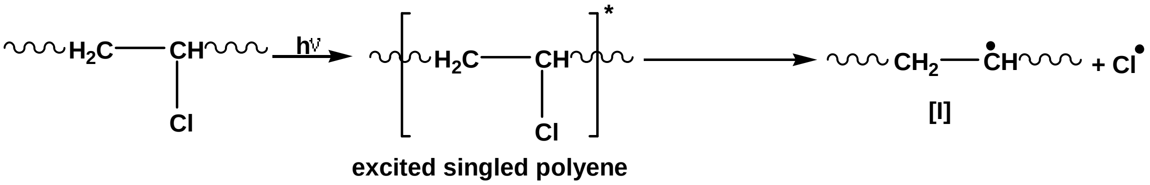
Figure (3-12): The ultraviolet visible spectrum for (PVC) in THF solvent.

3.3 Photostabilization of modified PVC films

The new modified polymers PAA, PSS, PNN, PSA and PNA. were used as photostablized modified PVC comparing with PVC films(control).

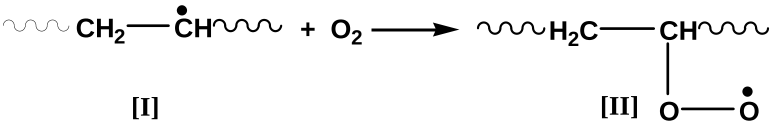
In order to study the photochemical activity of these modified polymers for the photostabilization of films, the carbonyl, polyene and hydroxyl indices were monitored with irradiation time using IR spectroscopy. The formation of carbonyl group (C=O) and polyene $(C=C)_n$ and (O-H) during photolysis of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

When PVC is photolysed in the presence of (O_2), the primary photochemical processes occur (the excited singlet polyenes).



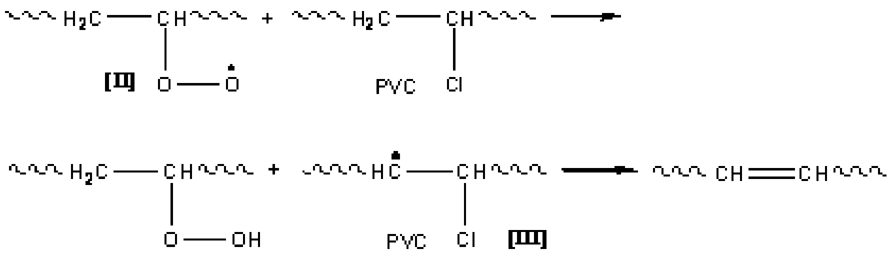
Those excited states will thus disappear by the different routes including the allylic (C-Cl) bond cleavage with formation of $(Cl^{\cdot})$ radical and polyene radical[I].

The polyenyl radical [I] which bears no (Cl) atom in the α-position is very likely to be scavenged by (O_2) to give peroxy radical [II]

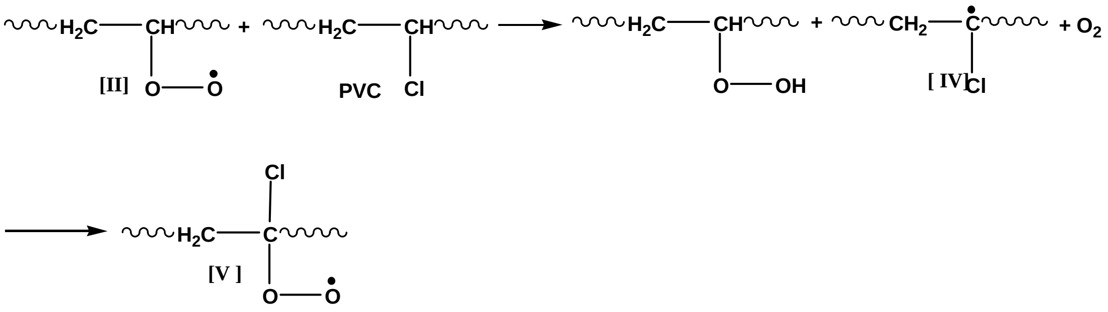


Rate constant measurement on related model compounds suggest that peroxy radical [II] react with the $(-CH_2-)$ and (CH-Cl) groups on PVC at rates that are comparable(30).

The attack on (CH_2) group yields radical [III].

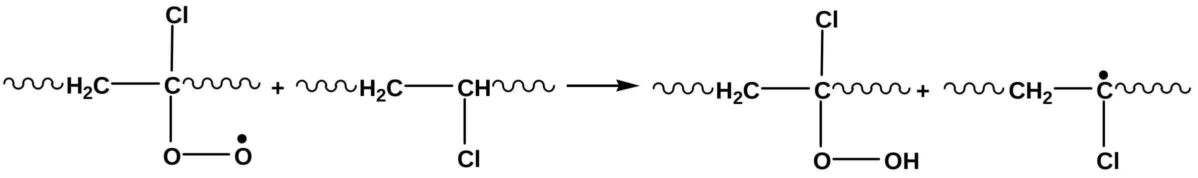


This radical contributes to the chain-dehydrochlorination of PVC. The attack of II on the (-CH-Cl) group yield radical [IV] which possesses no labile β-chlorine and is likely to react with (O_2) to give a γ-chloroalkyl peroxy radical [V].

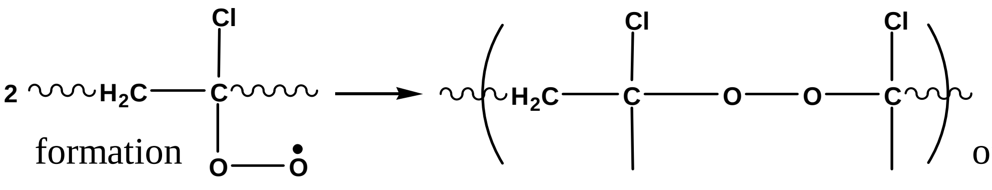


The main oxidation products of PVC are expected to result primary from the various reactions of this radical[V], there are two major routes of the fate (disappearances) of the γ-chloroalkyl peroxy radical.

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

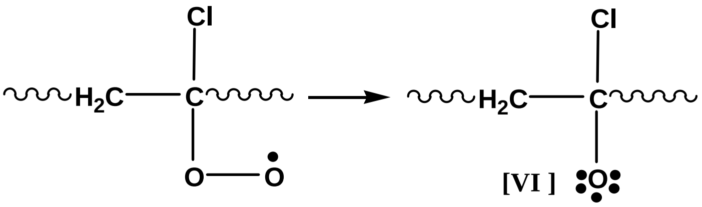


The bimolecular interaction, the later leads to the formation of either a peroxide bridge (termination reaction), or the formation of alkoxy

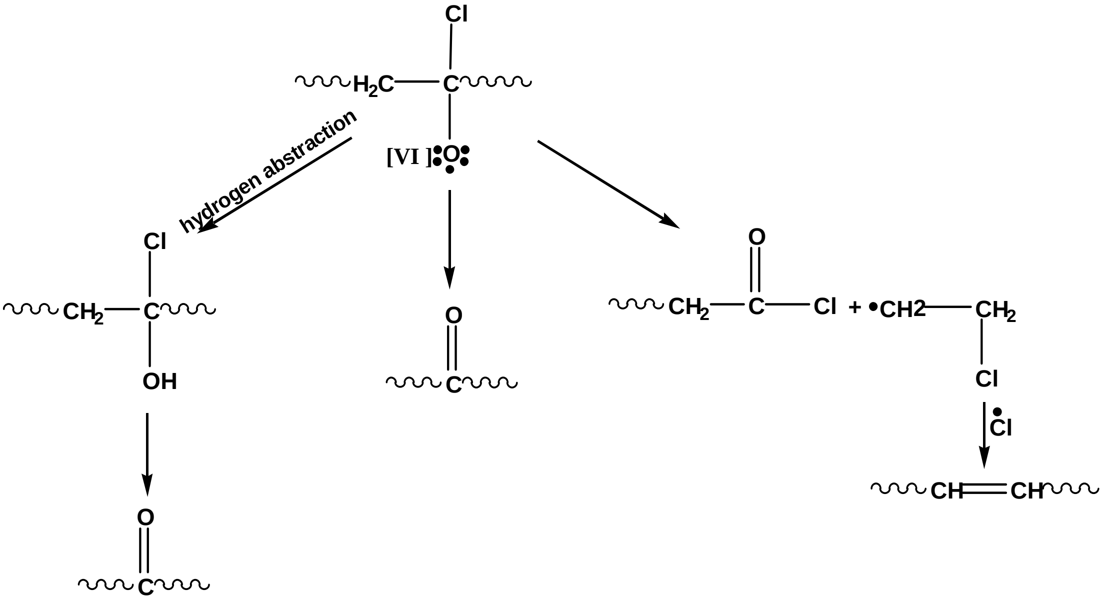


peroxide bridge

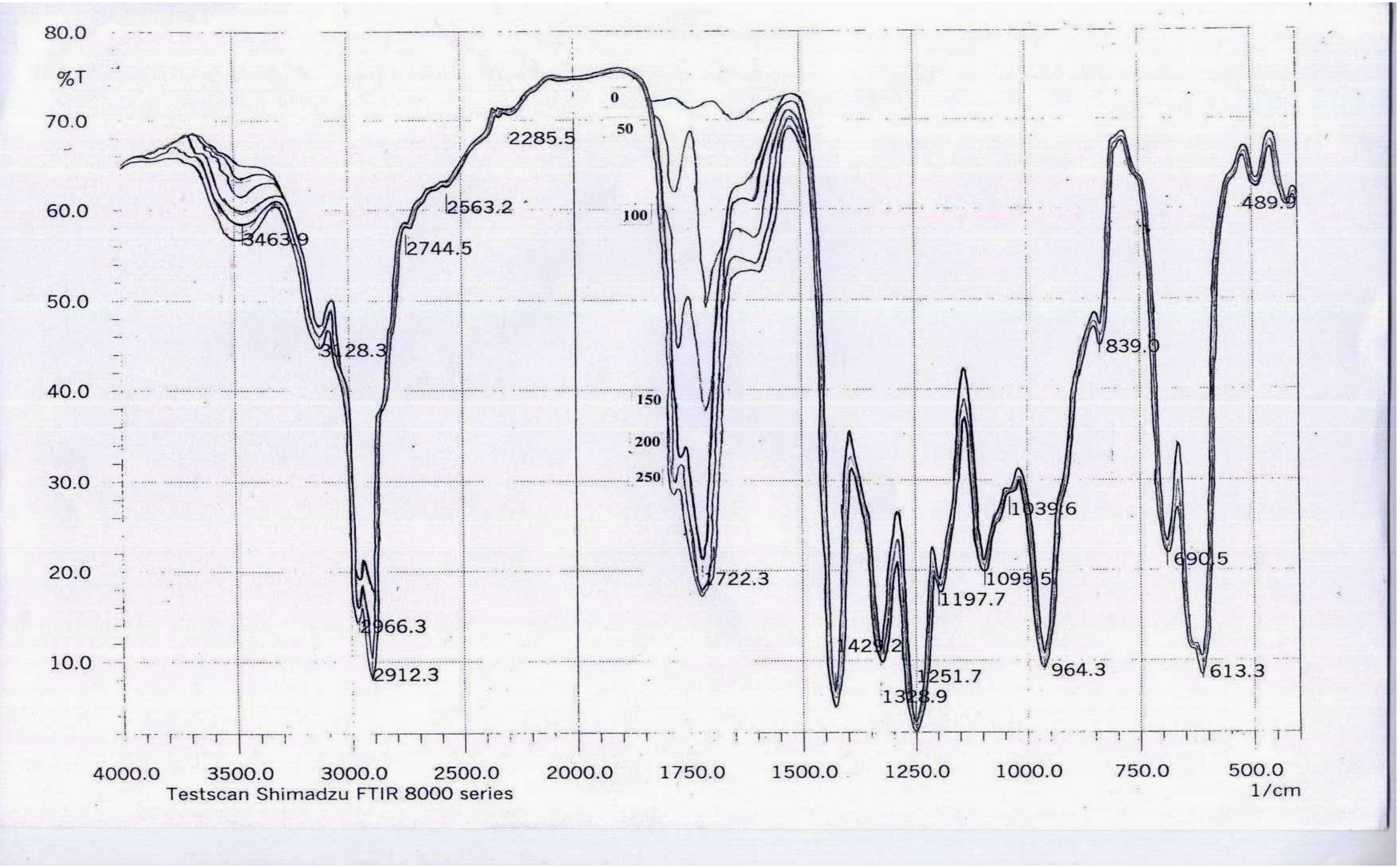
radicals[VI].



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 or/and (C-C) bond cleavage to form polyene . The irradiation of PVC films with light of wavelength,λ = 313nm lead to a clear change in their FTIR spectrum, as shown in Figure (3-13). Appearance of bands at 1772 cm^{-1} and 1722 cm^{-1} respectively, attributed to the formation of carbonyl group, the first is related to chloro ketone with the second one is due to aliphatic ketone, together with formation of a band at 1604 cm^{-1} related to polyene group(97). The hydroxyl band appeared at 3500 cm^{-1} is realated to alcohol functions(97).



Figure(3-13):change in IRspectrum of PVCfilm (30μm) thickness atdifferent irradation time (numbers in spectra are irradiation time in hours.

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

Therefore, one should expect that the growth of carbonyl index is a measure to the extent of degradation. As seen from Figure (3-14) that the modified polymers PAA, PSS, PNN, PSA and PNA show lower growth rate of carbonyl index with irradiation time with respect to unmodified PVC film (control). these modiefied polymers might be considered as photostabilized with respect to the PVC polymer.

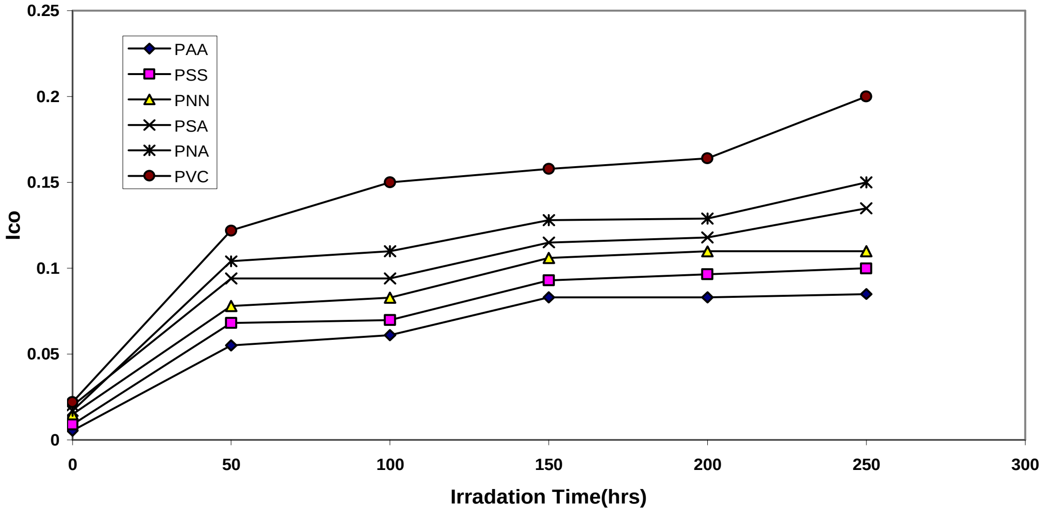


Figure (3-14): The relationship between the carbonyl index and irradiation time for PVC and modified PVC films (30 μm) thickness.

The good photostabilizer show a longer induction period. Therefore, from Figure (3-14), the PAA is the most active photostabilizer, followed by PSS, PNN, PSA and then PNA which is less active.As it was mentioned before polyene compounds are produced during photodegradation of PVC. Therefore, polyene index (I_{PO}) was monitored with irradiation time. The same trend obtaind as carbonyl index.

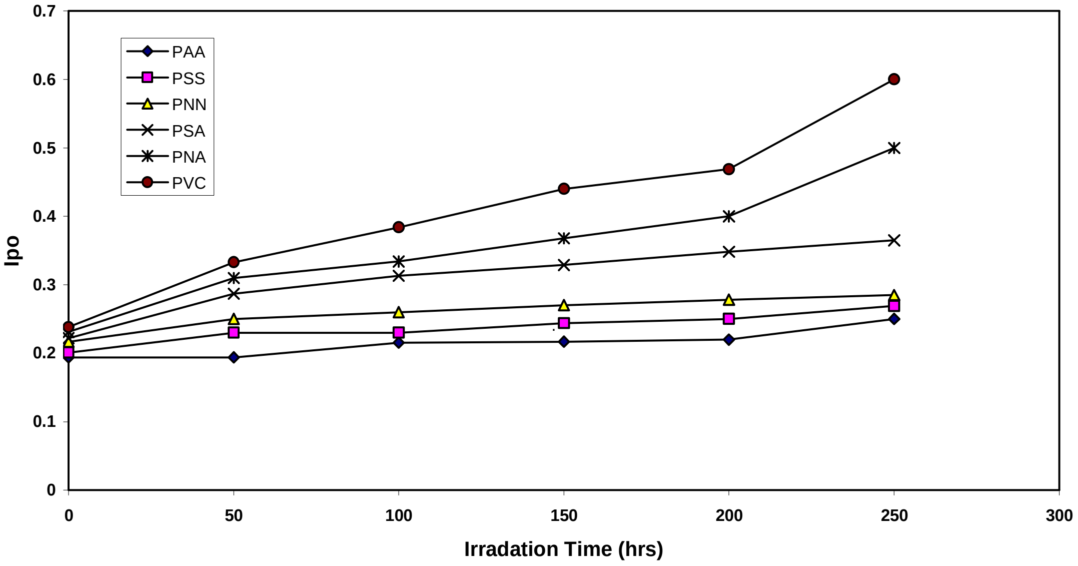


Figure (3-15): The relationship between the polyene index and irradiation time for PVC and modified PVC films (30 μm) thickness.

Hydroxyl functions are produced during photodegradation of PVC. Therefore, hydroxyl index (I_{OH}) was monitored with irradiation time for unmodified pvc and modified pvc (PAA,PSS,PNN,PSA,PNA) polymers. From Figure (3-16) the PAA, PSS, PNN, PSA and PNA show lower growth rate of hydroxy index with irradiation time with respect to PVC film without modification (control).

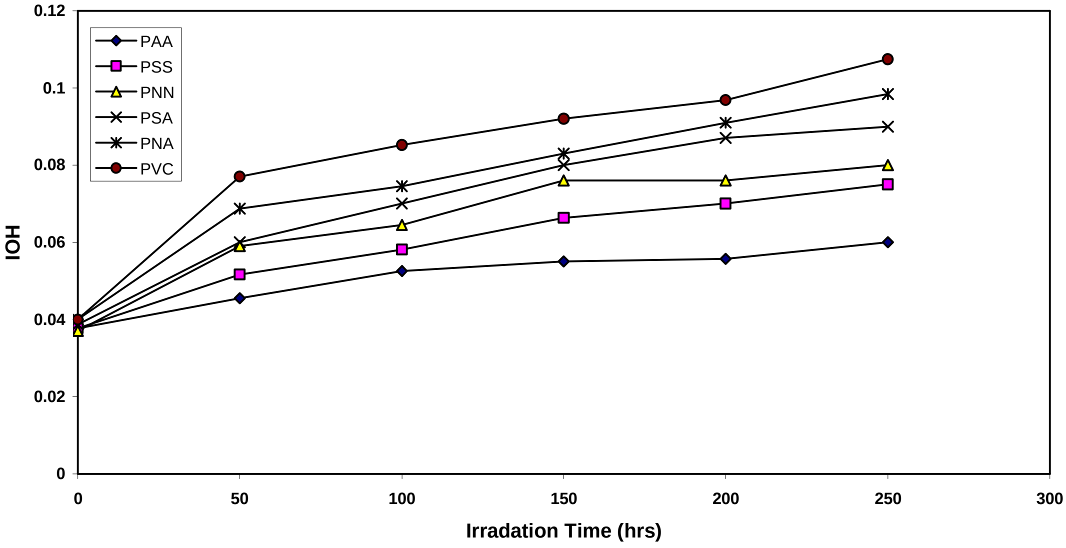
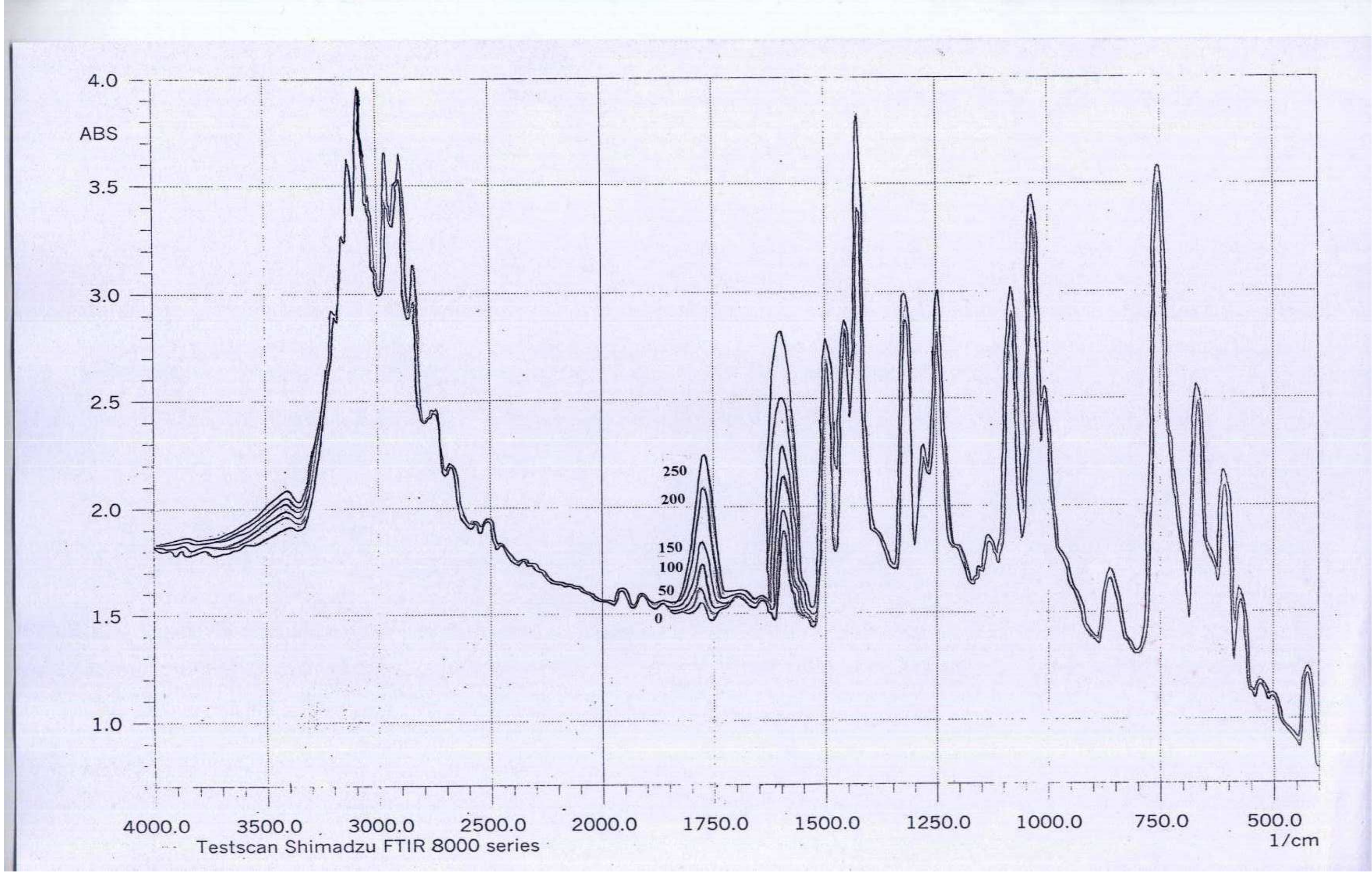


Figure (3-16): The relationship between the hydroxyle index and irradiation time for PVC and modified PVC films (30 μm) thickness.



Figure(3-17):change in FTIR spectrume of Pss film (30μm) thickness at different irradation time

Table (3-3) Increase in the carbonyl index (I_{co}) with irradiation for all PVC film (30μm) in thickness.

time	PAA	PSS	PNN	PSA	PNA	PVC
0	0.0053	0.0089	0.015	0.02	0.017	0.022
50	0.055	0.068	0.0781	0.094	0.104	0.122
100	0.061	0.0697	0.0828	0.094	0.11	0.15
150	0.083	0.0929	0.106	0.115	0.128	0.158
200	0.083	0.0965	0.1098	0.118	0.129	0.164
250	0.085	0.1	0.11	0.135	0.15	0.2

Table (3-4) Increase in the polyene index (I_{PO}) with irradiation for all PVC film (30μm) in thickness.

time	PAA	PSS	PNN	PSA	PNA	PVC
0	0.194	0.201	0.217	0.222	0.231	0.238
50	0.194	0.23	0.25	0.287	0.31	0.333
100	0.2154	0.23	0.26	0.313	0.334	0.384
150	0.217	0.244	0.27	0.329	0.368	0.44
200	0.22	0.25	0.278	0.348	0.4	0.469
250	0.25	0.269	0.285	0.365	0.5	0.6

Table (3-5) Increase in the hydroxyl index (I_{OH}) with irradiation for all PVC film (30μm) in thickness.

time	PAA	PSS	PNN	PSA	PNA	PVC
0	0.0377	0.0377	0.037	0.0387	0.04	0.04
50	0.0455	0.0516	0.059	0.06	0.0687	0.077
100	0.0525	0.0581	0.0645	0.07	0.0745	0.0852
150	0.055	0.0663	0.076	0.08	0.083	0.092
200	0.0557	0.07	0.076	0.087	0.091	0.0968
250	0.06	0.075	0.08	0.09	0.0984	0.1074

Polymer film has a great effect on the rate of oxidative photodegradation 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(98).

II- Accelerates the rate of dehydrochlorination reaction(99).

III- Causes bleaching by attacking the polyene structure and shortening the length of conjugation(100).

IV- Promotes chain scission and crosslinking(101).

Generally, photo-oxidation rate decreases with increasing film thickness(102), 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 (30μm)

The physical properties of modified polymers play a very important role in determining the modification efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of additive photostabilizer must be evenly distributed which requires that it be compatible with the polymer matrix(48).

3-2-4-Kinetics of PVC photo-oxidation

It is well known(103) that the photo-oxidation of polymers for example PVC, involves free radical chain reactions as shown below:

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \qquad ....(3\text{-}1)$$

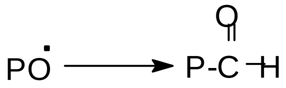
$$PO_2^{\bullet} + PH \xrightarrow{kd} POOH + P^{\bullet} ....(3-2)$$

Reaction (3-2) is considered as the rate determining step of photodegradation.(104)

Every hydroperoxide molecule produced subsequently undergoes photolysis to give an alkoxy radical, which both provides a new initiating radical in the system and at the same time produces carbonyl compounds.

$$\mathrm{POOH} \xrightarrow{h\nu} \mathrm{P\dot{O}} + \mathrm{\dot{O}H} \qquad (3\text{-}3)$$

$$\mathrm{PO^{\bullet}} + \mathrm{P^{-}H} \xrightarrow{ki} \mathrm{POH} + {}^{\bullet}\mathrm{P^{-}} \qquad (3\text{-}4)$$



$$\mathrm{P\dot{O}} \longrightarrow \mathrm{P\text{-}\overset{O}{\overset{\|}{C}}\text{-}H} \qquad (3\text{-}5)$$

Since Norrish type I photolysis products are the major end products of the photo-oxidation, it seems likely that this process (3-2) makes a major and possibly a dominant contribution to the production of free radicals in the second stage of photo-oxidation:

$$\mathrm{P'COOP} \xrightarrow[\text{Norrish type I}]{h\nu} \mathrm{P'CO_2} + \mathrm{\dot{P}''} \qquad (3\text{-}6)$$

$$\mathrm{P'CO_2^{\bullet}} + \mathrm{PH} \xrightarrow{Kif} \mathrm{P^{\bullet}} + \text{hydroperoxide} \qquad (3\text{-}7)$$

$\mathrm{P^{\bullet}}$

PH = polymer molecule.

Termination is likely to be by normal disproportionation of alkylperoxy radicals:

$$2\mathrm{PO_2^{\bullet}} \xrightarrow{kt} \text{stable product} \qquad (3\text{-}8)$$

Thus, the rate of initiation reactions (3-2) and (3-3) is given by (I) (I_{CO}) is the carbonyl index.

$$R_i = K_{if}\,(I_{CO})\,[PH] \;\ldots\ldots\ldots\ldots\text{(i)}$$

The rate of degradation is expressed by equation (ii)

$R_d = K_d\,[PO^{\bullet}]\,[PH]$ …………(ii)

The rate of termination is expressed by equation (iii)

$R_t = K_t\,[PO^{\bullet}_2]^2$ ……………(iii)

Under steady state conditions:

Rate of termination (R_t) = Rate of initiation (R_i)

$K_t\,[PO^{\bullet}_2]^2 = K_{if}\,(I_{CO})\,[PH]$

$$[PO_2^{\bullet}] = \left(\frac{K_{if}}{K_t}(I_{CO})[PH]\right)^{1/2} \text{.................(iv)}$$

Substitute (iv) in (ii) give :

$$R_d = K_d\left(\frac{K_{if}}{K_t}\right)^{1/2}[PH]^{3/2}(I_{CO})^{1/2} \text{..................(v)}$$

$$R_d = K_c(I_{CO})^{1/2} \text{..(vi)}$$

Where $K_C = Kd\left(\frac{K_{if}}{K_t}\right)^{1/2}[PH]^{3/2}$

Since

$$R_d = \frac{d(I_{CO})^{1/2}}{dt} = K_t(I_{CO})^{1/2} \text{.......................(vii)}$$

Hence, $t = K_C(I_{CO})^{1/2} + \text{constant}$ ....(viii)

In attempt to verify the applicability of equation (viii) in the present system, the square root of carbonyl index is plotted with irradiation time for PVC control, PAA, PSS, PNN, PSA and PNA Figure (3-18). In all cases, the straight line obtained from this plot indicate that the above system mechanism for the photooxidative degradation of modified and unmodified PVC is in agreement with experimental data obtained.

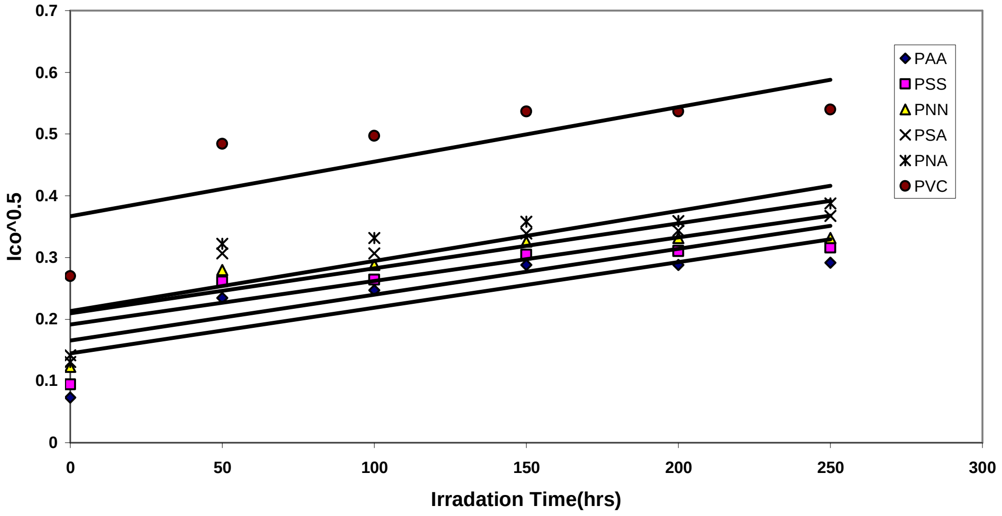


Figure (3-18): The carbonyl group formation in UV irradiated PVC (control) and modiefied polymers.

Kc values might be calculated from the plots shown in Figure (3-18), and it was found that K_c for each species were: PAA (0.007), PSS (0.0073), PNN(0.0077), PSA (0.0079), PNA(0.00.81) and PVC(0.0092).

Thus: Kc PAA< Kc PSS < Kc PNN < Kc PSA
< Kc PNA < Kc PVC.

3-2-5-Variation of PVC molecular weight during photolysis

An analysis of the relative change in viscosity average molecular weight $(\overline{M}v)$, described by Scott$^{(105)}$ has been shown to provide a versatile test for random chain scission. Figure (3-19) shows the plot of $(\overline{M}v)$versus irradiation time for modified PVC films and PVC film, with absorbed light intensity of $1.43*10^{-8}$ ein. dm^{-3}. s^{-1} . $(\overline{M}v)$ is measured using equation (2-8) and THF as a solvent at 25 ^{o}C .

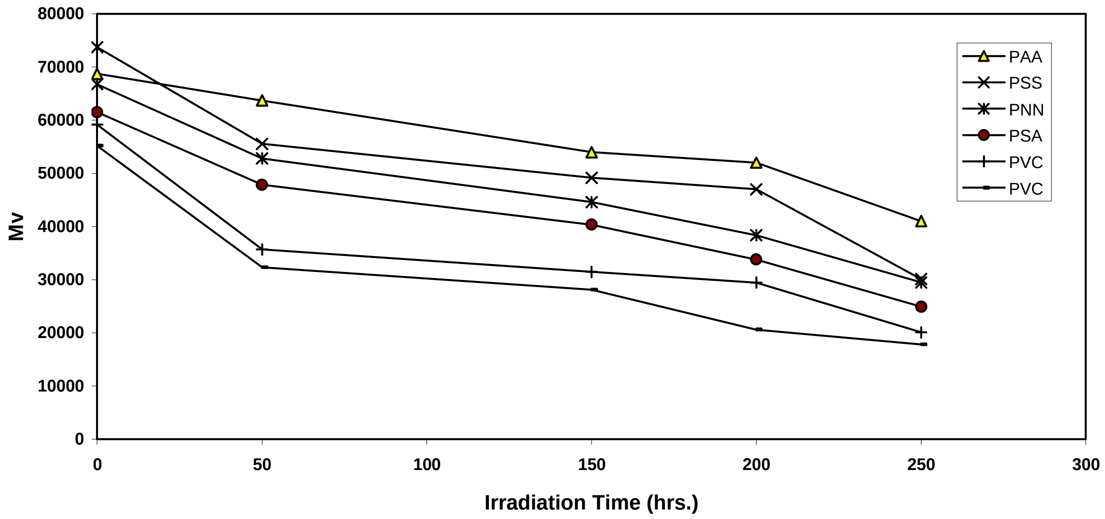


Figure (3-19): Changes in the viscosity average molecular weight $(\overline{M}v)$ during irradiation of PVC films (30 μm) (control) and modified PVC

It is worth mentioning that traces of the 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(106).

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. If the scission of bond is random, the rate of decrease in $(\overline{M}v)$ should be proportional to the square of the viscosity – average molecular weight (107) at that irradiation time. Therefore, in order to clarify the type of bond scission the rate in the decrease of $(\overline{M}v)$ with time, the value of $(\frac{d\overline{M}_v}{dt})$ was calculated using the relation (3-9).

$$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t} \quad \text{..............................}(3-9)$$

Where $\overline{M}_{v,o}$ and $\overline{M}_{v,t}$ are viscosity average molecular weight at (zero) and (t) irradiation time respectively.

The plots Figure (3-20), shows $\frac{d\overline{M}_v}{dt}$ against $(\overline{M}_v)^2$, which were found to be not linear. The plots show that the weak bond links is randomly distributed along the polymer chains.

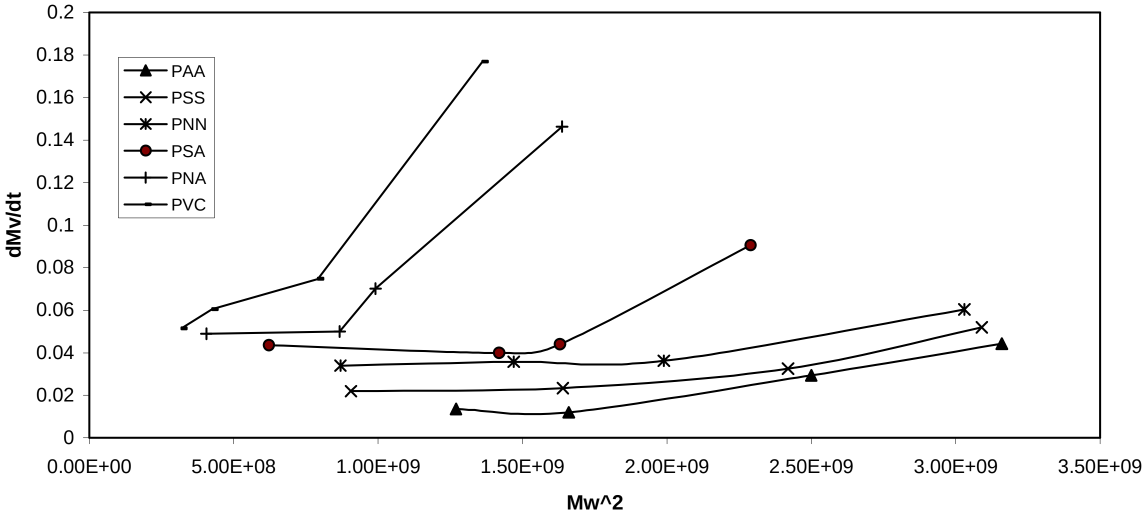


Figure: (3-20): Rate variation of molecular weight change $(d\overline{M}v/dt)$ **during irradiation of PVC films (30 μm) (control) and modified PVC films**

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

$$\alpha = \frac{m}{\overline{Mv}_0} \qquad (3-10)$$

Where m and Mv_0 are the molecular weights of irradiation time, respectively.

The plot of α as a function of irradiation time is shown in Figure (3-21). The curves indicate that the degradation is taking place by the random breaking of one type of bond.

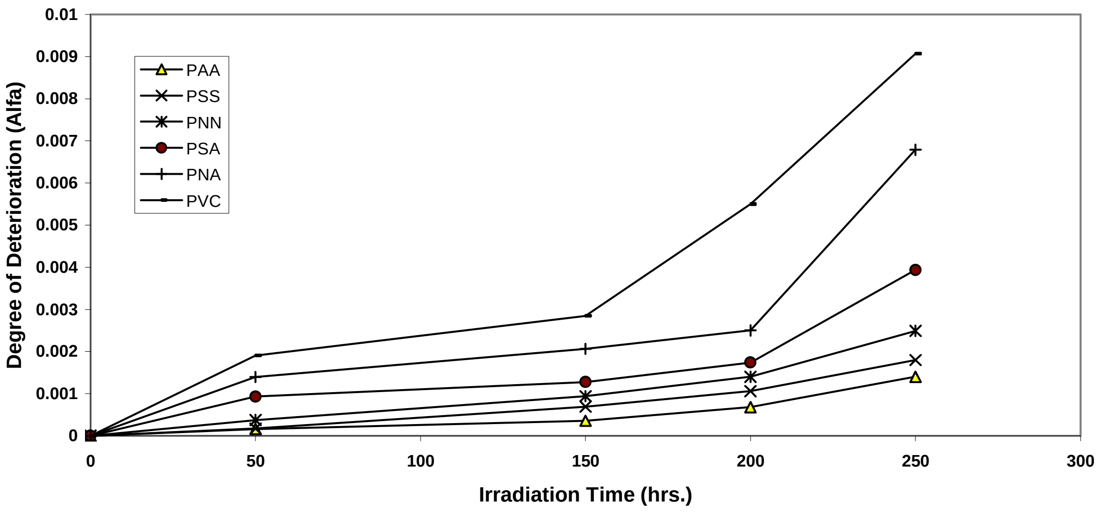


Figure (3-21): Changes in the degree of deterioration (α) during irradiation of PVC films (30μm) (control) and modified PVC films

The values of α of the irradiated samples are higher without presence of additives and lower in presence of additives compared to the corresponding values of the additive free PVC. In the initial stages of photodegradation of PVC, the values of α increases rapidly with time, which indicates a random breaking of bonds in the polymer chain.(108)

For more support of this view, the number average chain scission (average number cut per single chain) (S) was calculated using the relation (3-11):

$$S = \frac{\overline{M}_{v,o}}{\overline{M}_{v,t}} - 1 \qquad (3-11)$$

Where $\overline{M}_{v,o}$ and $\overline{M}_{v,t}$ are viscosity average molecular weight at (zero) and (t) irradiation time respectively.

The plot of S versus time is shown in Figure (3-22). The curve indicates an increase in the degree of branching such as might arise from cross-linking occurrence.

It is observed that, insoluble material was formed during irradiation, an extra evidence to the idea that cross-linking dose occur.

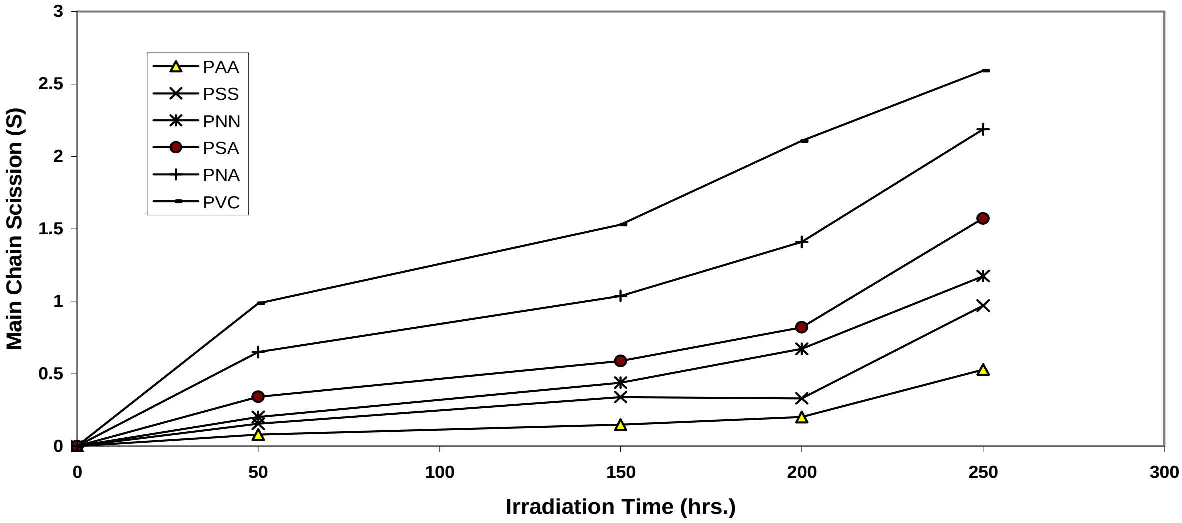


Figure (3-22): Changes in the number average chains during irradiation of PVC films (30μm) (control) and modified PVC films

The plot of 1/Pt versus irradiation time is adopted by Awad$^{(109)}$ to characterize degradation reaction of polymer as shown in Figure (3-23). The curve indicates that increase in the inverse of number average degree of polymerization with irradiation time

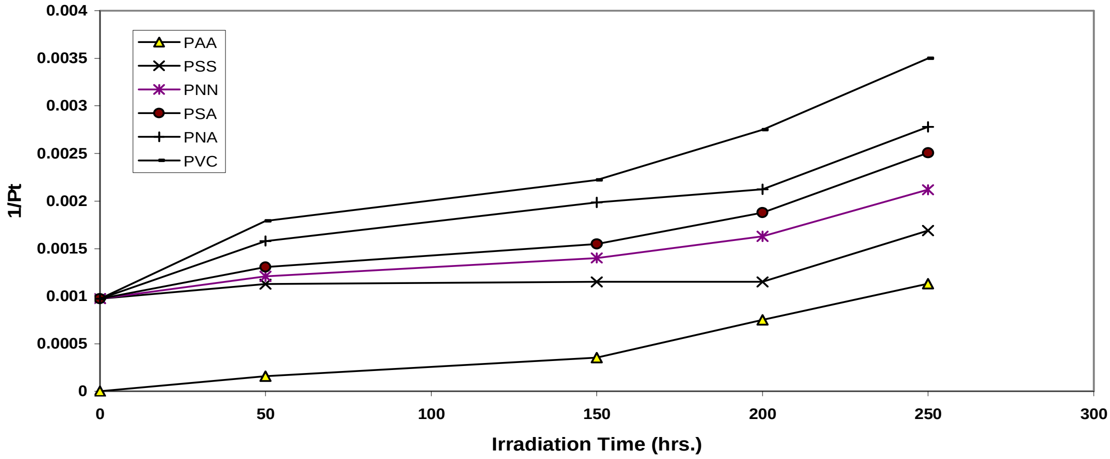


Figure (3-23): Changes in thereciprocal of number average of polymerization (1/Pt) during313 nm during irradiation of PVC films (30μm) (control) and modified PVC films

Table (3-6): the values which calculate from average molecular weight

1-PAA

Radiation time	$\mathbf{X10^{-4}}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\|p_t x10^4$	S	$\alpha X10^3$
0.0	6.87	∞	1026.69	9.7	0	0
50	6.37	0.0136	6329.11	1.58	0.08	0.15
150	5.4	0.012	2832.86	3.53	0.15	0.353
200	5.2	0.029	1333.33	7.5	0.2	0.68
250	4.1	0.044	884.95	11.3	0.53	1.4

2-PSS

Radiation time	$\mathbf{X10^{-4}}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\|p_t x10^4$	S	$\alpha X10^3$
0.0	7.37	∞	1026.69	9.7	0	0
50	5.555	0.022	888.88	11.25	0.15	0.17
150	4.92	0.023	869.56	11.5	0.34	0.69
200	4.70	0.032	869.56	11.5	0.33	1.06
250	3.0	0.052	591.71	16.9	0.97	1.80

3-PNN

Radiation time	**X10**$^{-4}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\vert p_t x10^4$	S	$\alpha X10^3$
0.0	6.68	∞	1026.69	9.7	0	0
50	5.28	0.034	826.45	12.1	0.20	0.37
150	4.45	0.035	713.27	14.02	0.43	0.94
200	3.836	0.036	613.87	16.29	0.67	1.40
250	2.949	0.06	471.92	21.19	1.17	2.48

4-PSA

Radiation time	**X10**$^{-4}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\vert p_t x10^4$	S	$\alpha X10^3$
0.0	6.15	∞	1026.69	9.7	0	0
50	4.78	0.043	765.69	13.06	0.34	0.93
150	4.03	0.040	645.99	15.48	0.59	1.28
200	2.38	0.044	531.91	18.80	0.82	1.74
250	2.49	0.090	399.04	25.06	1.57	2.94

5-PNA

Radiation time	$\mathbf{X10^{-4}}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\vert p_t x10^4$	S	$\alpha X10^3$
0.0	5.92	∞	1026.69	9.7	0	0
50	3.56	0.049	632.91	15.8	0.65	1.39
150	3.15	0.050	503.52	19.86	1.04	2.06
200	2.94	0.070	471.69	21.2	1,41	2.50
250	2.01	0.014	359.71	27.8	2.19	6.78

6-PVC

Radiation time	$\mathbf{X10^{-4}}\,\overline{M}v$	$\frac{d\overline{M}_r}{dt} = \frac{\overline{M}_{v,o} - \overline{M}_{v,t}}{t}$	P_t	$1\vert p_t x10^4$	S	$\alpha X10^3$
0.0	5.52	∞	1026.69	9.7	0	0
50	3.23	0.051	558.66	17.9	0.98	1.9
150	2.8	0.06	450.45	22.2	1.53	2.84
200	2.06	0.074	363.63	27.5	2.11	5.5
250	1.78	0.177	285.71	35.0	2.59	9.07

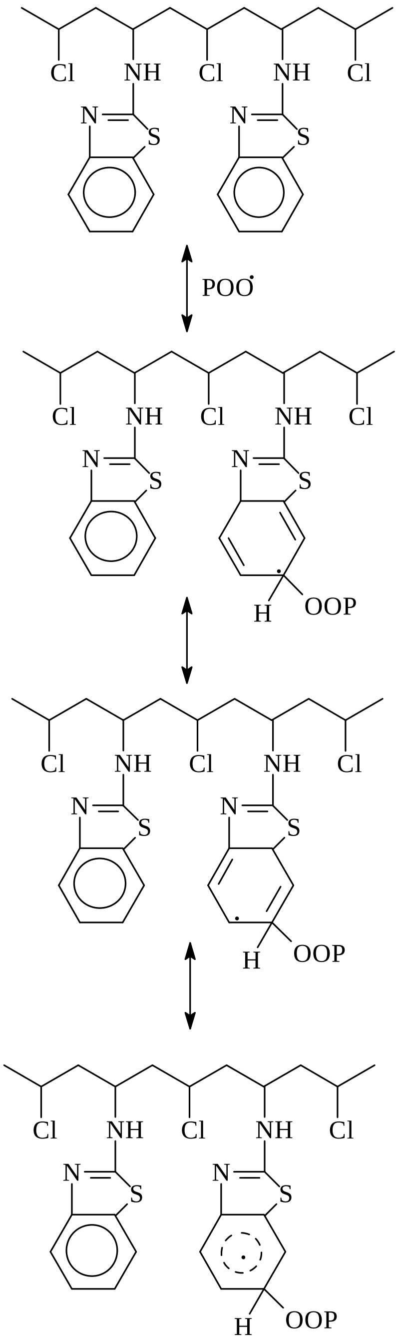
3-4-Suggested mechanisms of photostabilization of PVC by modifaction

Through the overall results obtained, the efficiency of modified polymers PVC films can be arranged according to the change in the carbonyl, polyene and hydroxyl Indexes as a reference for comparison as shown in Figure (3 -14), (3-15) and (3 -16).

PAA > PSS > PNN > PSA > PNA

1-The reaction between PVC and hetrocyclic units reduce the number of HCl in this polymer which led to decrese the probability of labraition Cl from PVC chain.

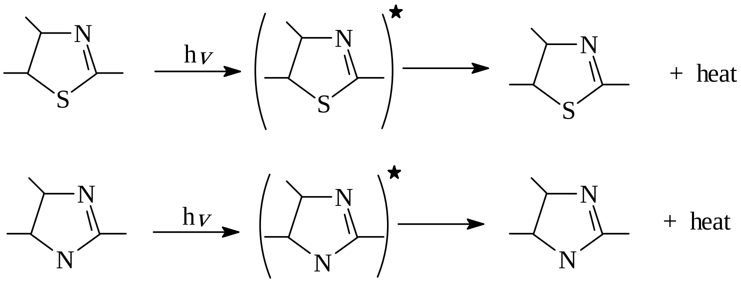
2-These polymers also function as radical scavengers through energy transfer and by forming unreactive charge transfer complexes between the modified polymers and excited state of the chromophore ($POO^{\cdot}$) and stabilize through resonating structures as shown in Scheme (3-1)



Scheme (3-1): Suggested mechanism of photostabilization of PAA as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.

3- The benzothiazole and benzimidazole rings in these modified polymers plays a role in the mechanism of the stabilizer process by acting as UV absorber.

The UV light absorption by these polymers containing these heterocylic units dissipates the UV energy to harmless heat energy Scheme (3-2). Further more, this ring play a role in resonating structures conjugation of radical in peroxide decomposer Scheme (3-1), which support these rings as photostabilizer(91).



Scheme (3-2): Suggested mechanism of photostabilization of modified polymers as UV absorber.

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(110) for PVC films of modified polymers the relation (2-13). The Φ_{cs} values for these polymers are tabulated in Table (3-6).

Table (3-6): Quantum yield (Φcs) for the chain scission for PVC and modified PVC films films (30μm) thickness after 250 hrs. irradiation time.

Additive (0.5%wt)	quantum yield of main chain scission (Φ_{cs})
PAA	1.11E-07
PSS	1.36E-07
PNN	1.39E-07
PSA	1.59E-07
PNA	2.82E-07
PVC	5.12E-05

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

$$\xrightarrow{\textbf{PAA, PSS, PNN, PSA, PNA, and PVC}}$$

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.(111)

It is well established that the quantum yield ($\Phi_{cs.}$) increases with increasing temperatures(112) around the glass transition temperature, (Tg) 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 blow the glass transition temperature (Tg of PVC = 80 °C). Therefore, the Φ_{cs} dependency on temperature is not expected to be observed.

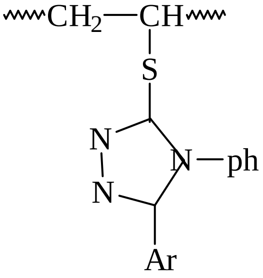
Conclusions

We prepared five modified polymers by the covalent modification of commercial PVC with benzothiazole and benzimidazole binding units.The modified polymers differ in their susceptibility to photooxidative degradation from that unmodified PVC. The photostability effects of these heterocyclic moities was indicated on the basis of carbonyl, polyene and hydroxyl indexes.The results obtained demonstrates that all the modified polymers are good photostabilizer rather than unmodified PVC.

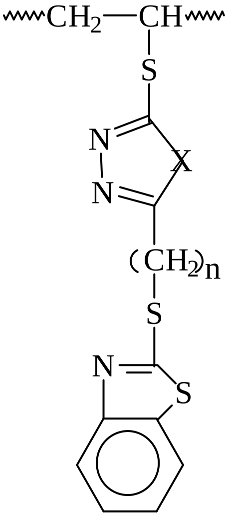
Suggestion for further work

We hope to continue our extensive program directed towards the synthesis of new poly (vinyl chloride) polymers bound heterocyclic systems ,therefore, the following work will be done in the near future.

1- A variety of new pvc-bound 1,2,4 –triazole unite having the following structural will be synthesized.

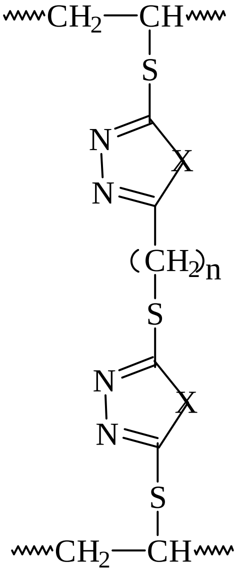


2- Synthesis of new pvc-bound bis heterocyclic having the following structural formula.



X = O, S, and NH

3- Synthesizing cross linked pvc-bound 1,3,4, -oxadiazole 1,3,4, -thiadiazole and 1,2,4, -triazole with the following structural formula.



X = O, S, and NH

4- Studying the photostability and optical properties of the above three series.

5-complexation of the our synthesized polymers and the above three series with several transition-metal ions.

6-Applying the integral intensity method of the methyl plus methylene plus methane complex band (CH_3+CH_2+CH)at 2650-3040 cm for monitoring the degradation process.

Chapter two

Experimental

2.1 Chemicals:

All of the reagent and starting materials used in the present work are of reagent grade and are used without purification unless otherwise noted.

Compound	Supplied from
2-Amino benzothiazole	BDH
2- mercapto benzothiazole	BDH
2-Amino benzimidazole	BDH
Diethyl ether	BDH
Ethanol 95%	BDH
Pyridine(purified by refluxing over KOH)	Fluka
Tetrahydrofuran (THF)	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.

2-2-2- Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectra in the range (4000-400) cm^{-1} cut were recorded as KBr disc on FTIR.8300 Shimadzu Spectrophotometer.

2-2-3- Ultraviolet-visible spectroscopy (UV)

The uv-visible spectra were measured using Shimadzu Uv-vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm.

2-2-4- Sofftening point

Sofftening points were determined using thermal microscope (Kofler-method), Reichert thermovar.

2-3-Purification of Poly(vinyl chloride)(93)

Commercial poly(vinyl chloride) (PVC) supplied from Petkim company (Turkey) was purified from additives by re-precipitation from tetrahydrofuran (THF) solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for (24) hours.

2-4-Preparation of modified polymers

(in this experimentals we can not determine no. of mole of PVC because it not found molecular weight constant for that we use weight and fixed it)

2-4-1-Preparation of modified polymer (PAA)

2-amino benzothiazole (1.67mmole) was added to (0.125g) poly (vinyl chloride) and three drops of pyridine in (25 mL) tetrahydrofuran (THF) was also added . A white prcipitate was formed after refluxing the mixture for three hours the modified polymer (PAA) was filtered,washed with redistilled water,ethanol,ether and dried under vaccum.

2-4-2-Preparation of modified polymer (PSS)

2- mercapto benzothiazole (1.49mmole) was added to (0.125g) poly(vinyl chloride) and three drops of pyridine in (25 mL) tetrahydrofuran (THF) was also added . A yellow prcipitate was formed after refluxing the mixture for three hours, the modified polymer (PSS) was filtered,washed with redistilled water,ethanol,ether and dried under vaccum.

2-4-3-Preparation of modified polymer (PNN)

2-Amino benzimidazole (1.87mmole) was added to (0.125g) poly(vinyl chloride) and three drops of pyridine in (25 mL) tetrahydrofuran (THF) . A brown prcipitat was formed after refluxing the mixture for three hours the modified polymer (PNN) was filtered, washed with redistilled water, ethanol, ether and dried under vaccum.

2-4-4- Preparation of modified polymer (PSA)

A solution of mixture of (0.83mmole) 2-amino benzothiazole and (0.75mmole) of 2-mercapto benzothiazole and three drops of pyridine in (25 mL) tetrahydrofuran (THF) was added to (0.125g) poly(vinyl chloride) .A brown prcipitat was formed after refluxing the mixture for three hours, the modified polymer (PSA) was filtered, washed with redistilled water, ethanol, ether and dried under vaccum.

2-4-4- Preparation of modified polymer (PNA)

A solution of mixture of (0.94mmole) 2-amino benzimidazole and (0.83mmole) 2-amino benzothiazol and three drops of pyridine in (25 mL) tetrahydrofuran (THF) was added to (0.125g) poly(vinyl chloride). A brown prcipitate was formed after refluxing the mixture for three hours, the modified polymer (PNA) was filtered, washed with redistilled water, than ethanol, ether and dried under vaccum.

The physical prpoerties of prepared modified polymers are listed in Table (2-1)

Table (2-1) The Sofftening point of the prepared polymers.

N0	Name	Color	Sofftening point (^{0}C)
1	**PAA**	White	92-95
2	**PSS**	Yellow	103-106
3	**PNN**	Brown	161-167
4	**PSA**	Brown	141-146
5	**PNA**	Brown	130-138
6	**PVC**	Colorless	200-205

2-5- photodegradation measuring methods

2-5-1- Films Preparation

Asolution of Poly(vinyl chloride) solution 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. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure.

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2.5.2- 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 spectrum range between (290 to 360 nm) and the maximum wavelength light intensity is at (313nm).

The polymer film samples vertically fixed and parallel to the lamps to be sure that UV incident radiation is vertically incident on the samples. The irradiation samples are changed places from time to time to be sure that the intensity of light incident on all samples is equal.

2.5.3- Measuring the photodegradation rate of PVC films using infrared spectrophotometery:

The photodegradation of PVC film samples were followed by monitering of FTIR spectra in the range (4000-400) cm^{-1} The spectra were recorded using FTIR 8300 Shimadzu Spectrophotometer.

The position of carbonyl absorption is specified by the bands at (1722 cm^{-1}) and (1602 cm^{-1})(22) for the calculation carbonyl and polyene indices respectively. The photodegradation during different irradiation times were followed by observing changes in carbonyl and polyene bands. Then carbonyl (Ico) and polyene (Ipo) indices were calculated by comparision of the FT-IR absorption band at (1722 cm^{-1}) and (1602 cm^{-1}) with reference band at (1328 cm^{-1}), respectively. This method is called band index method(22) which includes:

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

As = Absorbance of peak under study.

Ar = Absorbance of reference peak.

Is = Index of the group under study.

Actual absorbance, the difference between the absorbance of base line and top peak (A Top Peak – A Base Line), is calculated using the Base Line method(94).

2-5-4-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(95).

$$[\eta]=K\overline{M}_v^{\alpha}...............(2-8)$$

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

K, α = 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_o respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re}=\frac{t}{t_o}....................(2-9)$$

η_{re} = Relative viscosity .

$$\eta_{sp}=\eta_{re}-1\ \ ....(2\text{-}10)$$

The single – point measurements were converted to intrinsic viscosities by the relation (2-11).(94)

$$[\eta]=\left(\sqrt{2}/c\right)\left(\eta_{sp}-\ln\eta_{re}\right)^{1/2}.....................(2-11)$$

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 equations were used(96);

$$[\eta]==1.38*10^{-4}Mw^{0.77}------------(2\text{-}12\ )$$

Equations (2-12) were used to calculate $(\overline{M}_v)$ for PVC without additives before irradiation, and equation (2-11) used to measure $(\overline{M}_v)$ of polymers with additives after irradiation.

The quantum yield of main chain scission (ϕ_{cs}) was calculated from viscosity measurement using the following relation$^{(94)}$.

$$\phi_{cs} = (CN_A/\overline{M}_{v,o})\left[\left([\eta_o]/[\eta]\right)^{1/\alpha} - 1\right]/I_o t \text{...............}(2-13)$$

Where:

C = concentration.

N_A = Avogadro’s number.

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

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

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

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

I_o = Incident intensity.

t = Irradiation time in second.

References

1. E. C. Leonaed, “Vinyl and Diene Monomer”, New York (1971).
2. V. Regnault, *Ann. Chem. Phys., 2(1835)538.*
3. I. Ostromislensky, *Chem. Zentr., 1(1980)23.*
4. F. Klatte and A. Rollet, *Chem. Astr.,12(1918)231.*
5. G. S. Misra, Introductor Polymer Chemistry, New York (1993).
6. J. Kernsears and J. R. Darby, “The Technology of Plasticizers” New York (1982).
7. J. V Koleste and L. H. Warimam, “Poly(Vinyl chloride)” London (1969).
8. R. Mogorkiswicz, “Engineering Properties of Thermoplastic” London (1970).
9. P. Coghlan “A Discussion of Some the Scientific Issues Concerning the Use of PVC”., CSIRO Molecular Science, Australian National University (2000).
10. A. L. Andrady, S.H. Hamid, X.Hu and A. Torikai, *J. Photochem. Photobiol., B, 46(1998)96.*
11. R. Baloglu and M. Fisch, *Polym. Deg. Stab., 45(1994)30.*
12. M. H. Al-Malack, S. Y. Sheikheldin, N. M. Fayad, and N. Khaja, *Water, Air and Soil Pollution, 120(2000)195.*
13. M. H. Al-Malack, *J. Hazardous Materials, B, 82(2001)363.*
14. M. H. Al-Malack and S. Y. Sheikheldin, *Water. Res., 35(2001) 3283.*
15. T. Ayako and H. Hirose, *Polymer Deg. Stab., 63(1999)441.*
16. G. Scott, *Polymer Deg. Stab., 68(2000)1.*

17. L. Valkoa, E. Kleinb, P. Kovarikb and P. Simonb, Eur. *Polym. J., 37(2001)1123.*

18. A. L. Andrady, *Adv. Polym. Sci., 128(1997)49.*

19. A. Torkai, T. Kobatake and F. Okisaki, *J. Appl. Sci., 67(1998)1293.*

20. J. Sampers, *Polymer Deg. Stab., 67(2002)455.*

21. J. Pospisil and S. Nespurek, *Prog. Polym. Sci., 25(2000)1261.*

22. N. Grassie and G. Scott, “Polymer Degradation and Stabilization”, Cambridge University Press, London, (1985).

23. B.Mohamad, M.SC.Thesis, Al-Mustansiria Univesity,(2003).

24. U. S. Patent, 99(1870)935.

25. U. S. Patent, 680(1901)387.

26. German Patent, 221(1908)310.

27. E.A.Yousif, Ph.D.thesis, Al-Nahrain University,(2004).

28. L. Bateman and G. Gee, *Proc. Roy. Soc., 376(1948) 9.*

29. A. M. Trozzolo in “Stabilization Against Oxidative Photodegradation”, (W. Hawkins), Wiley Interscience Publishers, P.159, (1971).

30. W. Schnabel, polymer Degradation: Principle and Practical Applications. Hanser Int., München. Chap. 14, (1981).

31. L. P. Real and J. L. Gardette, *Polym. Testing, 20(2001)779.*

32. C. Ratnam, M. Nasir, A. Baharin and K. Zhang, *Eur. Polym. J. 37(2001)1667.*

33. L. Real and J. Gardette, *Polym. Testing, 20(2001)1943.*

34. A. Valet, *Progr. Org. Caat., 35(1999)223.*

35. U. Gesenhues and J. Hocken, *J. Vinyl. Tech., 6(2000)80.*

36. C. Decker and K. Zahouily, *Polym. Degrad. Stab., 64(1999)293.*

37. W. H. Gibb and J. R. McCallum, *Eur. Polym. J.,10(1974)529.*

38. C. Decker, *Eur. Polym. J.,20(1984)149.*

39. J. Kresta, Polymer Additives, Plenum Press, New York, (1984).

40. W. Hawkins, Polymer Degradation and Stabilization, Springer Verlag, Berlin, (1984).

41. W. Schnabel, “Development in polymer Degradation”, (Allen; N.S., ed), Vol. 2, Applied Science Publishers, Ltd.), London, P. 237, (1982).

42. J. E., Guillet, *Pure Appl. Chem., 36(1973)127.*

43. Z. Osawa, “Degradation and Stabilization of polymers”, (Jellinek, H.H.G., ed.), Elsevier, Amsterdam (1983).

44. K. Santos, P. Suarez and J. Rubim, *Poly. Deg. Sta., 90(2005)34.*

45. R. Hirt, N. Searle and R. Schmitl, “Ultraviolet Degradation of Plastics and The use of Protective Ultraviolet absorbers”, SPE Transaction (1961).

46. L. W. Meyer and W. M. Geuhart, *Ind. Eng. Chem.,37(1945)232.*

47. W. M. Geurhard, R. O. Hill and M. H. Broyles, U.S. Pat., 571(1951)703.

48. F. Gugumus, in “Development in Polymer Stabilization-1”, (G. Scott, ed.), Applied Science Publishers Ltd., London, P. 261, (1979).

49. N. S. Allen, *Polym. Photochem., 3(1983)167.*

50. E. Collell, *J. Amer. Chem. Soc., 90(1968)6550.*

51. D. R. Olson and S.H. Schroeter., *J. Appli. Poly. Sci., 22(1978)2165.*

52. B. Dindar and S. Icli, *J. Photochem. Photobio. A: Chem.,140(2001)263.*

53. M. Senna, H. Hamid and M. Hussein, *Nuclear Instr. Methods Phys. Res. Section B, 187(2002)48.*

54. O. Birer, S. Suzer, V. Sevil and O. Cuven, *J. Molec. Structure, 482(1999)515.*

55. O. Birer and S. Suzer, *Polymer, 42(2001)1833.*

56. J. Pospisil, W. Habicher, H. Zweifel, J. Pilar, S. Nespurek and O. Piringer, *Polymer and Polymer Composites, 10(2002)37.*

57. G. Start., *Polym. Degr. Stab., 67(2002)83.*

58. U. Gesenhues, *Polym. Degr. Stab., 68(2000)185.*

59. R. Benavides, B. Castillo and G. Arias, *Polym. Degr. Stab., 73(2001)417.*

60. C. Ratnam and K. Zaman, *Polym. Deg. Stab.,65(1999)481. Stab.,65(1999)99.*

61. N. Allen, and J. Mckellar, “Photochemistry of Dyed and Pigmented polymers”, Applied Science Publishers, Ltd. London, (1980).

62. P.P., Klemchuk, *Polym. Photochem., 1(1983)3.*

63. F.H. Winslow, W. Matreyek and A.M. Trozzolo, *Amer. Chem. Soc. Polymer. Prepr., 10(1969)1271.*

64. M. Szwarc, *J. Polym. Sci., 19(1956)589.*

65. F. R. Williams, M.W. Jordan, and E.M. Dannerberg, *J. Appl. Polym. Sci., 9(1965)861.*

66. D. M. Wiles, *Pure Appli. Chem., 50(1978)291.*

67. D. M. Wiles, and D. J. Carlsson, *Polym. Degrad. Stabil., 3(1980)61.*

68. M. Heskins and J.E. Guillet, *Macromolecules, 1(1968)97.*

69. R. G. Schmitt and R.C. Hirt, *J.A.ppl. Polym. Sci., 7(1963)1565.*

70. L. Bucsiova, S. Chemela and P. Hrdiovic, *Polym. Deg. Stab.,71(2001)135.*

71. R. Bagheri, K.B. Chakraborty and G. Scott, *Polym. Degrad. Stabil., 4(1982)1.*

72. J. Sedlar, J. Marchal and J. Petrui, *J. Polym. Photochem., 2(1982)175.*

73. UNIDO, Internali and (Center for science and High Technology, TRIESTE, ITALY. Internal Workshop on Environmentally Degradable *Plastics. October 4-8, (1999).*

74. L. Alexandra and J. E. Guillet, *J. Polym. Sci., A1, 13(1975)483.*

75. K. Sugita, T. Klip and J.E. Guillet, *J. Polym. Sci., 14(1976)1901*

76. S. L. Fitton, R.N. Howard and G.R. Williamson, *Brit. Polym. J., 2(1970)217.*

77. G. Scott, *Plast. Rubb. Text., 1(1970)361.*

78. M.U. Amin and G. Scott., *Eur. Polym. J., 10(1974)1019.*

79. T. Hjertberg and M. Sovick “Degradation and Stabilization of PVC, Own, E. D.,(Ed.), (1984).

80. R. Bacaloglu and M. Fisch, Polym. Deg. Stab., 45(1994)30.

81. R. Bacaloglu and O. Pradova, *Makromole Chem., 187(1986)221.*

82. M. Fisch and R. Bacaloglu, *J.Vinyl Addit. Technol., 5(1999)205.*

83. C. Decker and K. Zahouily, *J. Polym.Sci, 36(1998)2571.*

84. S. Lakshmi and A. Jayakrishnan, *Polymer, 39(1998)151.*

85. D. Feldman, D. Banu. *J. Appl. Polym. Sci. 9(1997)1731.*

86. D. Fray, *Plast. Rubber. Compos.,28(1999)327.*

87. M. M. Hirschler, *Prog. Rubber Plast. Technol.,10(1994)154.*

88. R. Weber and J. Vreeburg, *Pur. Appl. Chem., 708(1996)1713.*

89. J. Fauvarque, *Pur. Appl. Chem., 68(1996)1713.*

90. D. Cadogan, *Plast. Rubber. Compos.,28(1999)476.*

91. S. M. Aliwi, E. A. Yousif and A. M. Otaiwi, *J. Al-Nahrain Univirsty, 49(8)2005.*

92. E. A. Yousif and A. S. Hameed, Accepted *J. Al-Nahrain Univ.(2006).*

93. J. F. Rabek, G. Canbak and B. Ranby, *J. Appl. Polym. Sci., 31(1977)2211.*

94. R. Fox and T. Price, *J. Appl. Polym. Sci, 3(1965)2303.*

95. R. Houwink*, J. Prakt. Chem.,157(1940)15.*

96. J. Koleske and L. Wartman, “Poly(Vinyl Chloride), Macdonald Technical & Scientific, London(1969).

97. C. Decker and M. Balandier*, Eur. Polym. J., 18(1982)1085.*

98. G. Palma and M. Carenza*, J. Appl. Polym. Sci., 14(1970)1737.*

99. M. Balandier and C. Decker, *Eur. Polym. J., 14(1978)995.*

100. D. Braun and R. Bender, *Eur. Polym. J., 22(1969)269.*

101. C. Decker and M. Balandier*, Polym. Photochem., 1(1981)221.*

102. F. Winslow, M. Hellman, W. Matrayek and S. Stills, *Polym. Eng. Sci., 6(1966)237.*

103. F. Mori, M. Koyama and Y. Oki*, Angew. Makromol. Chem., 75(1979)113.*

104. C. Chew, L. Gan and G. Scoot, *Eur. Polym. J., 13(1977)361.*

105. G. Scott, in “Polymers and Ecological Problems”, (J.E. Guillet, ed.), Plenum press, New York, P. 27, (1973).

106. W. Gibb and J. MacCallum*, Eur. Polym. J., 10(1974)529.*

107. R. Chandra and S. Hanada, *Polym. Degrad. Stabi., 37(1992)73.*

108. A. Taha, Ph. D. Thesis, Al-Mustansiryha Unvirsty, (2002).

109. D. Awad, M. Sc. Thesis, Al-Mustansiryha Unvirsty, (2000).

110. J. F. Rabek and B. Ranby, Photodegradation, photo-oxidation and Photostabilization of Polymers, John Wiley, New York, (1975).

111. R. Chandra and S. Hanada, *J. Appli. Polym. Sci., 27(1982)1945.*

112. H. Jellinek, Aspects of Degradation and Stabilization of polyolefines, Elsevier, Amsterdam, (1978).

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اسم الرسالة:

تحضير ودراسة الثباتية الضوئية لبعض بوليمرات (كلوريد الفاينل) المحورة والمحتوية على حلقة البنزوثايزول والبنزاميدازول المتدلية

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تحضير ودراسه الثباتيه الضوئيه لبعض بوليمرات (كلوريد الفاينل) المحورة والمحتوية على حلقة البنزوثايازول والبنزإميدازول المتدلية

رسالة مقدمة إلى
كلية العلوم–جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير في الكيمياء

من قبل

هديل صلاح منصور

صفر ١٤٢٨ آذار ٢٠٠٧

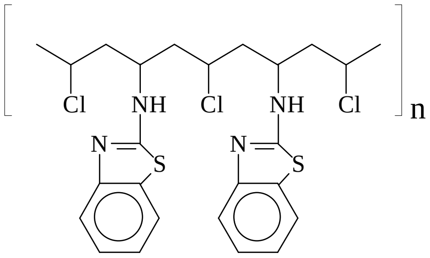
الخلاصة:-

يتضمن البحث المقدم من جزئين:-

الجزء الأول:-

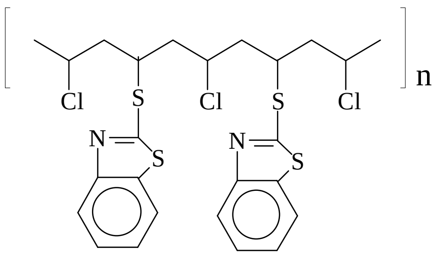
لقد تم في هذا البحث تحضير متعدد (كلوريد الفانيل) المحتوي على بنزوثايزول و بنزاميدازول كمثبتات ضوئية تبعا" للخطوات التالية:-

اولاً:- تم تحضير بوليمر (PAA) الناتج من مزج ٢- أمينو بنزوثايزول مع بولي (كلوريد الفانيل)



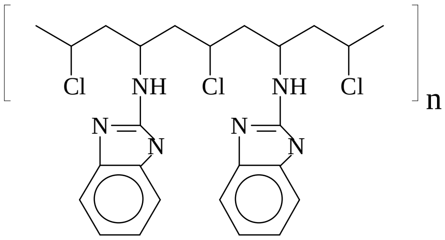
PAA

ثانياً:- تم تحضير بوليمر (PSS) الناتج من معاملة بولي (كلوريد الفانيل) مع ٢- مركبتو بنزوثايزول في ظروف قاعدية



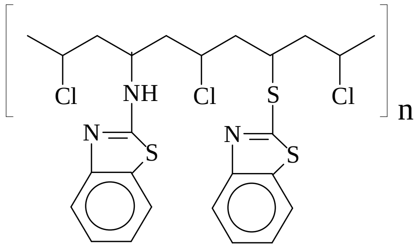
PSS

ثالثاً:- تم تحضير بوليمر (PNN) الناتج من تفاعل بولي كلوريد الفانيل مع ٢-أمينو بنزإميدايزول



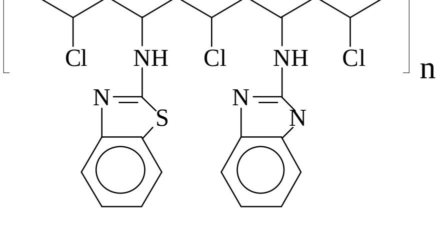
PNN

رابعاً:- تم تحضير بوليمر (PSA) الناتج من تفاعل بولي (كلوريد الفانيل) مع مزيج من كميات متساوية من ٢- أمينو و ٢- مركبتو بنزوثايزول



PSA

خامساً:- تم تحضير بوليمر (PNA) والناتج من معاملة بولي (كلوريد الفانيل) مع مزيج من كميات متساوية من ٢- أمينو بنزوثايزول و ٢- أمينو بنزإميدايزول



PNA

خلال هذا الجزء تم تشخيص جميع صيغ البوليمرات الناتجه من مزج حلقات بنزوثايزول وبنزإميدايزول مع رقائق بولي(كلوريد الفانيل) بأستعمال مطيافية الأشعة تحت الحمراء (FT–IR) والأشعة فوق البنفسجية(UV)

الجزء الثاني:الثباتية الضوئية:-

لقد تبين في هذا البحث إن حلقات البنزوثايزول وبنزإميدازول المضافة إلى بوليمر (كلوريد الفانيل) وتعدد الاواصر المزدوجة هي أساس لقياس الثباتية الضوئية حيث تمت دراسة الثباتية الضوئية لرقائق البوليمر من خلال متابعة قيم معامل امتصاص الكاربونيل والبولين والهيدروكسيل(I_{CO},I_{PO},I_{OH}) ومن خلال قيم معامل الكاربونيل والبولين والهيدروكسيل النامية مع زمن التشعيع وجد إن البوليمرات المحضرة تسلك كمثبتات ضوئية والتي أخذت الترتيب الأتي:

PAA>PSS>PNN>PSA>PNA

ومن خلال النتائج العملية المستحصله اقترحت بعض الميكانيكيات إعتمادا" على وجود حلقات بنزوثايزول وبنزإميدايزول في السلسلة البوليمرية.

ومن خلال تحديد حركة التجزئه الضوئية لبوليمرات (كلوريد الفانيل) المحورة وبرسم العلاقه بين مربع الجذر لمعامل الكاربونيل مع زمن التشعيع وجد إن العلاقه تكون خطيه وهي العملية الطبيعية المتوقعه.

وتمت دراسة قطع السلسلة البوليمرية وقيم منتوج الكم وذلك بقياس التغير في المتوسط اللزوجي للوزن الجزئي مع زمن التشعيع ،كما تم حساب درجة التجزئه (α) والمعدل العددي لقطع السلسلة(S).