

SYNTHESIS AND PHOTOCHEMICAL STUDY OF POLY(VINYL CHLORIDE) - 1,3,4-OXADIAZOLE AND 1,3,4-THIADIAZOLE

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Abstract

Poly(vinyl chloride) (PVC) has been reacted with 2-amino-5-(phenyl)-1,3,4-thiadiazole(L_I), 2-amino-5-(*p*-nitro phenyl)-1,3,4-thiadiazole(L_{II}), 2-mercapto-5-phenyl 1,3,4-oxadiazole(L_{III}) and 2-mercapto-5-(*p*-hydroxy phenyl) 1,3,4-oxadiazole(L_{IV}) in THF to form the modified PVC, which has been characterized by spectroscopic methods.

The photostabilization of PVC-L films compounds was investigated, the photostabilization activity of these compounds were determined by monitoring the carbonyl and polyene indices with irradiation time.

All results obtained show that the rate of photodegradation of PVC-L films, 30 micrometer in thickness following the trends:



According to the experimental results obtained, mechanism were suggested depending on the structure of the PVC-L compounds.

Introduction

Synthesis of polymer-bound chelating ligands and the selective chelation of specific metal ions is a field of active research⁽¹⁾. A number of ligands including polydentate amines, crown ethers, phosphines and bipyridines have been bound with mainly polystyrene divinylbenzene copolymers⁽²⁻⁶⁾. These studies are mostly concerned with ion-binding and catalytic⁽⁷⁾ aspects. Very little information appears to exist as to whether, and to what extent, such organic compounds can influence the properties of the macromolecule. Recently, scientists were able to modify⁽⁸⁻¹⁰⁾ PVC by introduction aromatic and heterocyclic moieties through halogen displacement reaction. PVC, thus modified, showed improved overall photochemical stability. The facial chlorine displacement from PVC indicated the possibility on easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes. In view of any information on PVC in this line, we undertook the synthesis of 2-amino-5-

(phenyl)-1,3,4-thiadiazole(L_I), 2-amino-5-(*p*-nitro phenyl)-1,3,4-thiadiazole(L_{II}), 2-mercapto-5-phenyl

1,3,4-oxadiazole(L_{III}) and 2-mercapto-5-(*p*-hydroxy phenyl) 1,3,4-oxadiazole(L_{IV}). This article will describe the synthetic procedure adopted and the photostability of these polymers towards UV light.

Experimental

1-Purification of Poly(vinyl chloride)⁽¹¹⁾

Commercial Poly(vinyl chloride) (PVC) supplied from Petkim company (Turkey) was freed 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.

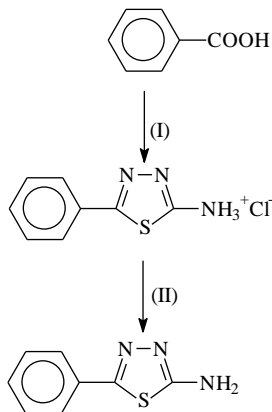
2-Synthesis of materials

2-1-Synthesis of 2-amino-5-(phenyl)-1,3,4-thiadiazole(L_I)⁽¹²⁾

Mixture of benzoic acid (0.01mole), thiosemicarbazide (0.01mole), phosphorus oxychloride (5 ml) was refluxed gently for (3) hours. After cooling, water was added (50 ml). The mixture was refluxed for (4) hours and filtered. The filtrate was neutralized with

potassium hydroxide. The precipitate was filtered and washed with distilled water and crystallized from (ethanol-water) to give the desired product.

The stepwise synthesis of this compound shown in Scheme (1).

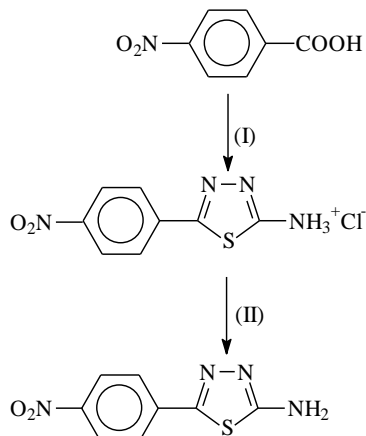


Scheme (1) Reagents and conditions:
(I) thiosemicarbazide, POCl₃, EtOH, reflux 3 hrs . (II) KOH .

2-2-Synthesis of 2-amino-5-(*p*-nitro phenyl)-1,3,4-thiadiazole(L_{II})⁽¹²⁾

Mixture of *p*-nitro benzoic acid (0.01mole), thiosemicarbazide (0.01mole), phosphorus oxychloride (5 ml) was refluxed gently for (3) hours. After cooling, water was added (50 ml). The mixture was refluxed for (4) hours and filtered. The filtrate was neutralized with potassium hydroxide. The precipitate was filtered and washed with distilled water and crystallized from (ethanol-water) to give the desired product.

The stepwise synthesis of this compound shown in Scheme (2).

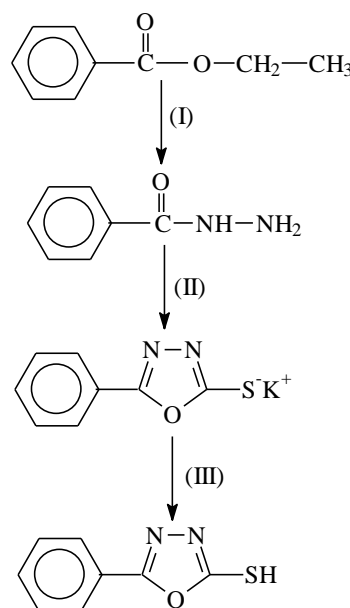


Scheme (2) Reagents and conditions:
(I) thiosemicarbazide, POCl₃, EtOH, reflux 3 hrs . (II) KOH

2-3-Synthesis of 2-mercapto-5-phenyl 1,3,4-oxadiazole(L_{III})⁽¹²⁾

A mixture of ethyl benzoate (0.1 mole) and hydrazine hydrate (0.1 mole) was refluxed for two hours, ethanol (50 ml) was added and refluxed for (5) hours. The precipitate benzoyl hydrazine which separated on cooling was filtered and washed with cold methanol. To a solution of benzoyl hydrazine (0.02 mole) in ethanol (100ml) at (0°C) were added carbon disulfide (0.04mol) and potassium hydroxide (0.02 mole) the mixture was refluxed for (7) hours .the solvent was evaporated and the residue dissolved in water and acidified with dilute hydrochloric acid. The precipitate was filtered and crystallized from (ethanol-water) to give 2-mercapto-5-phenyl 1,3,4-oxadiazole.

The steps of the synthesis of 2-mercapto-5-phenyl 1,3,4-oxadiazole can be shown in Scheme (3).



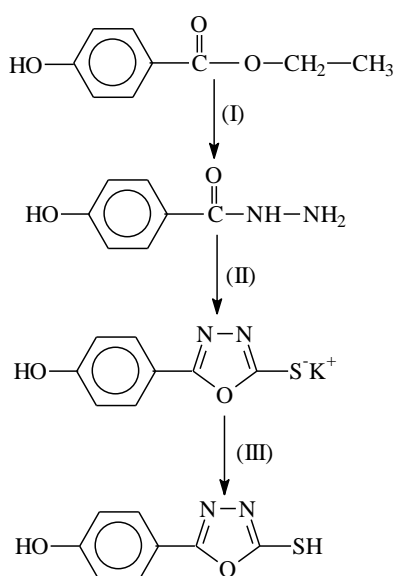
Scheme (3) Reagents and conditions.
(I) NH₂NH₂, EtOH, reflux, 7 hr. (II) CS₂, KOH, reflux 5 hrs. (III) HCl.

2-4-Synthesis of 2-mercapto-5-(*p*-hydroxy phenyl) 1,3,4-oxadiazole(L_{IV})⁽¹²⁾

A mixture of *p*-hydroxy ethyl benzoate (0.1 mole) and hydrazine hydrate (0.1 mole) was refluxed for two hours, ethanol (50 ml) was added and refluxed for (5) hours. The precipitate benzoyl hydrazine which separated on cooling was filtered and washed with cold

methanol. To a solution of benzoyl hydrazine (0.02 mole) in ethanol (100 ml) at (0°C) was added carbon disulfide (0.04 mol) and potassium hydroxide (0.02 mole) the mixture was refluxed for (7) hours .the solvent was evaporated and the residue dissolved in water and acidified with dilute hydrochloric acid. The precipitate was filtered and crystallized from (ethanol-water) to give 2-mercapto-5-phenyl 1,3,4-oxadiazole.

The steps of the synthesis of 2-mercapto-5-(*p*-hydroxy phenyl) 1,3,4-oxadiazole can be shown in Scheme (4).



Scheme (4) Reagents and conditions.
(I) NH_2NH_2 , EtOH, reflux, 7 hr. (II) CS_2 , KOH, reflux 5 hrs. (III) HCl.

2-5-Synthesis of PVC-Ligands compounds⁽¹³⁾

A mixture of 0.1 gram of PVC dissolved in THF and (0.05 mole) from appropriate prepared ligand was refluxed for three hours. The precipitated modified polymer separated by evaporated the solvent. The color prepared polymer are found in Table (1)

Table (1)
Physical data of the prepared polymer.

Symbol	Color	m.p. °C
PVC-L _I	White	212-214
PVC-L _{II}	Yellow	143 d
PVC-L _{III}	Yellow	255 d
PVC-L _{IV}	Brown	266 d

Experimental Techniques

Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains stainless steel plate, which has two holes in the front side and another one behind. Each side contains lamps type (Fluorescent Ultraviolet Lights) 40 watt each. 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 sample is equal.

Photodegradation measuring methods Measuring the photodegradation rate of polymer films using infrared spectrophotometry

The photodegradation of polymer film samples were followed by monitoring 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, the bands at 1722 cm^{-1} and (1602 cm^{-1})⁽¹⁴⁾ for the calculation carbonyl and polyene indices respectively.

The photodegradation during different irradiation times were followed by observing changes in carbonyl and polyene peaks. Then carbonyl (I_{co}) and polyene (I_{po}) indices were

calculated by comparison of the FTIR absorption peak at 1722 cm^{-1} and 1602 cm^{-1} with reference peak at 1328 cm^{-1} , respectively. This method is called band index method⁽¹⁵⁾ which includes:

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

A_s = Absorbance of peak under study.

A_r = Absorbance of reference peak.

I_s = Index of the group under study.

Actual absorbance, the difference between the absorbance of base line and top peak (A Top Peak – A Base Line), is calculated using the Base Line method⁽⁸⁾.

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR) spectra in the range $(4000-400)\text{ cm}^{-1}$ cut were recorded as Potassium Bromide disc on FTIR.8300 Shimadzu Spectrophotometer.

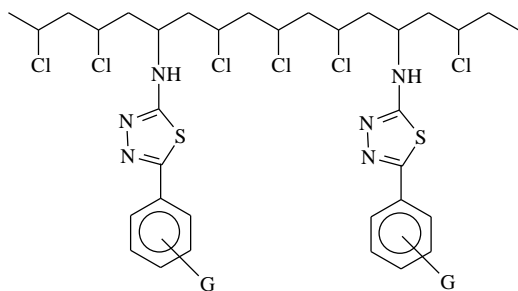
The (PVC-L_I and PVC-L_{II}) spectra show bands due to -N-H, C=N, mono and para di-substituted benzene ring at $(3278-3300)\text{ cm}^{-1}$ $(1627-1595)\text{ cm}^{-1}$ and $(968-852)\text{ cm}^{-1}$ respectively.

These absorption which was shown in Table (2) are in agreement with the tentative structure of the polymers (PVC-L_I) and (PVC-L_{II}). The infrared spectra of (PVC-L_{III}) and (PVC-L_{IV}) show bands at $(2293-2862)\text{ cm}^{-1}$, $(1610-1640)\text{ cm}^{-1}$ and $(1247-1080)\text{ cm}^{-1}$ which may be assigned to C-H aliphatic absorption, C=N and (ν asymm. and sym. of C-O-C(ether linkage), vibrations respectively, also analysis of the spectra of these two modified polymers shows that the appearance of absorption band of C-H aliphatic of PVC and the disappearance of ν S-H at 2700 cm^{-1} is good evidence for occurring the modification.

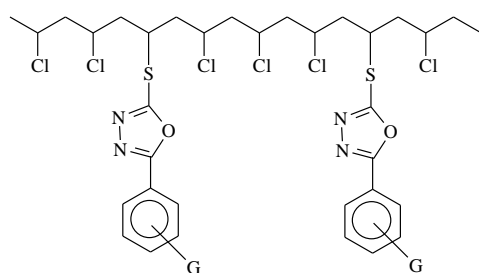
Table (2)
IR spectra of PVC-L compounds

Compound	IR (cm^{-1})	Assignments
PVC	2900	C-H
	609	C-Cl
PVC-L _I	3278	N-H
	3055	C-H (aromatic)
	2862	C-H (aliphatic)
	1627	C=N
	612	C-Cl
PVC-L _{II}	3300	N-H
	2858	C-H (aliphatic)
	1595	C=N
	1517	Asym. NO ₂ (N-O)
	1342	Sym. NO ₂ (N-O)
PVC-L _{III}	684	C-Cl
	2923,2826	C-H
	1647	C=N
	615	C-Cl
	1249	Asym. (C-O-C)
	1087	Sym. (C-O-C)
PVC-L _{IV}	3253	O-H
	1600	C=N
	1304	Asym. (C-O-C)
	1074	Sym. (C-O-C)
	835	C-H(aromatic) bends out of plane

On the basis of the preceding discussion, the structure of the ligands and complexes may be suggested as in the following Schemes.



Scheme (5) where G= -H or -NO₂



Scheme (6) where G= -H or -OH

Results and Discussion

2-amino-5-(phenyl)-1,3,4-thiadiazole(L_I), 2-amino-5-(*p*-nitro phenyl)-1,3,4-thiadiazole(L_{II}), 2-mercapto-5-phenyl 1,3,4-oxadiazole(L_{III}) and 2-mercapto-5-(*p*-hydroxy phenyl) 1,3,4-oxadiazole(L_{IV}) were used as photostabilizer.

In order to study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry.

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

Therefore, one should expect that the growth of carbonyl index is a measure to the extent of degradation. As seen from Figure (2) that the presence of PVC-L_I, PVC-L_{II}, PVC-L_{III} and PVC-L_{IV} show lower growth rate of carbonyl index with

irradiation time with respect to PVC film without additives (control).

As shown in Figure (1), the growth of carbonyl index with irradiation time is lower than PVC control. So, these additives might be considered as photostabilizers of PVC polymer.

The efficient photostabilizer show a longer induction period. Therefore, from Figure (1), the PVC-L_{II} is the most active photostabilizer, followed by PVC-L_I PVC-L_{IV} and PVC-L_{III}, 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 and the presence and absence of these additives. Results are shown in Figure (2).

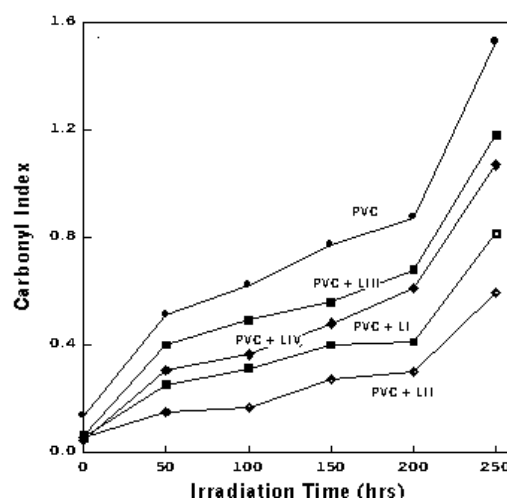


Figure (1): The relationship between the carbonyl index and irradiation time for PVC films (30 μ m) thickness containing different additives, concentration of additives are fixed at 0.5% by wight.

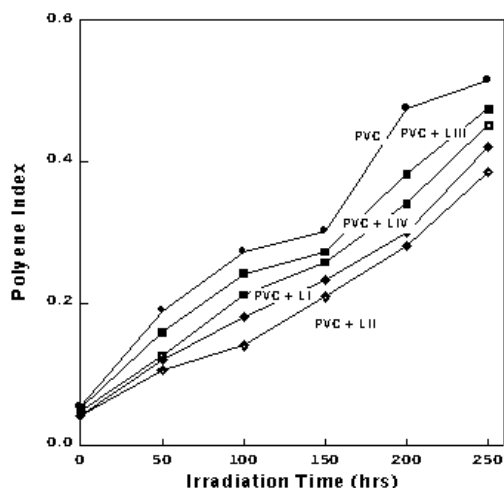
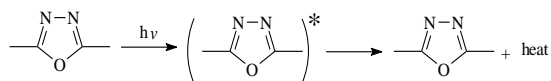


Figure (2): The relationship between the polyene index and irradiation time for PVC films (30 μm) thickness containing different additives, concentration of additives are fixed at 0.5% by weight.

Organic compounds generally known as photostabilizers for poly olefins⁽¹⁷⁾ The 1,3,4-oxadiazole and 1,3,4-thiadiazole rings in this compounds play a role in the mechanism of the stabilizer process by acting as UV absorber.

The UV light absorption by these additives containing these ring dissipates the UV energy to harmless heat energy Scheme (1).



Scheme (7): Suggested mechanism of photostabilization of 1, 3, 4 oxadiazole compounds as UV absorber.

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