

# Synthesis of New Modified PVC and their Photostability Study

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## Abstract

Reaction of PVC with carbothioimide, thiadiazole and triazole derivative in THF solution give a new polymers which were soluble in THF, DMF, DMSO, Three modified PVC polymer were synthesized through reaction of compounds (1-4) with PVC in THF solvent. The Photo stability of the prepared modified polymer was investigated. The modified polymers differ in their susceptibility to photo oxidation degradation from that unmodified PVC. The photostability effects of these heterocyclic moieties were monitored on the basis of carbonyl, polyene and hydroxyl indexes. The obtained results demonstrate that all modified polymers are more photostabilized, rather than unmodified PVC. All the structure of these compounds [1-4] and P1,P2,P3 were confirmed by FT-IR, UV/Vis spectroscopy, mass spectrum for compound [2] and <sup>1</sup>H-NMR for compound [4].

**Key word:** PVC, Photostability.

## 1. Introduction

Poly vinyl chloride (PVC) is one of the most important polymers due to its valuable properties, the growth of the PVC production is due to the steady expansion of its application fields<sup>[1]</sup>. Owing to limited solubility and low heat resistance of PVC, processing and production of materials based on the effective of the additives (stabilizers and plasticizers). The presence of the C-Cl bond facile obtaining wide range of polymeric materials and articles with a new set of valuable service properties<sup>[1]</sup>. By chemical modification reactions of PVC with appropriate compounds anew polymers with improved physical properties can be obtained<sup>[2,3]</sup>. Since Poly (vinyl

chloride) has very limited solubility as mentioned before hence the most effective solvents are those which appear to be capable to form interaction with polymer. It has been suggested that poly (vinyl chloride) is a weak proton donor and effective solvents are proton acceptor<sup>[4]</sup>. Thus the PVC polymer is soluble at room temperature in oxygen-containing solvents such as ethers e. g. dioxane, tetrahydrofuran; ketones e. g. cyclohexanone, and nitro compounds, e.g. nitrobenzene<sup>[5]</sup>. In this view we undertook the synthesis of polyvinyl chloride with or contain bearing heterocyclic moieties, and study the photostability of the produced polymers.

## 2. Experimentals

### 2.1. Materials and Instruments

All chemical were of reagent grade (supplied by either BDH or Aldrich) and used as received without further purification. The FTIR spectra in the range (4000-400) cm<sup>-1</sup> cut were recorded as KBr disc on FT-IR.84005 Shimadzu Spectrophotometer. The UV-vis spectra were measured in THF using (Hitachi U-2000) Ultra-violet spectrophotometer in the range (200-800) nm. The <sup>1</sup>H-NMR spectrum was obtained using a Bruker 300MHz NMR spectrophotometer with (TMS) as the internal reference and d<sup>6</sup>-DMSO as a solvent.

### 2.2. Preparation of organic compounds.

#### 2.2.1. Preparation of 2-(4- methoxy benzoyl) thiosemicarbazide<sup>[6,6a]</sup> (1).

To a stirring solution of thiosemicarbazide (0.91g, 0.01mol) in dry pyridine 20 mL, at (-5) C°, a solution of 4-methoxy benzoyl chloride<sup>[7]</sup> (1.7g, 0.01mol) in dry benzene 20 mL was added dropwise. The stirring was continued for one hour at -5 C° and then overnight at room temperature. The solvent was evaporated. Water 50mL was added to the residue. The precipitate was filtered and recrystallized from ethanol to give product (1). The physical properties of compound (1), yield 80%, deep yellow, m.p. (227-228)°C, FT-IR (KBr): 3088 cm<sup>-1</sup> v (C-H aro.), (3473,3288) cm<sup>-1</sup> v (N-H), 1182 cm<sup>-1</sup> v (C=S), 2955 cm<sup>-1</sup> v (C-H) aliphatic, 1671 cm<sup>-1</sup> v (C=O), (1533,1600) cm<sup>-1</sup> v (C=C). UV THF λ<sub>max</sub> nm: 243,299,335.

#### 2.2.2. Preparation of 5-(4-methoxy phenyl)-4H-1,2,4-triazole-3-thiol<sup>[8,6a]</sup> (2)

A stirring solution of compound (1) (2.25g, 0.01mol) and 20 mL 4% aqueous sodium hydroxide solution was refluxed for 4 hours. Then, the mixture was filtered and the filtrate was acidified with dilute hydrochloric acid. The precipitate was filtered and washed several times with water and recrystallized from ethanol to give product [2]. The physical properties of compound [2] yield 75%, paint yellow, m.p. (260-263) °C, FT-IR (KBr): 1612 v(C=N) 3241 v (N-H), 1224 v (C=S), 2682 v (S-H), 1523, 1600 v (C=C), 3001 v (C-H aro.), 2918 v(C-H aliph.). UV THF λ<sub>max</sub> nm: 253,289,323.

#### 2.2.3. Preparation of 5-(4- methoxy phenyl)-1H-1,2,4-triazole-3yl-thio acetic acid<sup>[6a]</sup> (3)

To a stirring mixture of chloro acetic acid (0.945g, 0.01mol) and 10% aqueous sodium hydroxide 10 mL, a solution of compound (2) (2.07g,0.01mol) in 10% aqueous solution of sodium hydroxide 10 mL was added and the mixture was refluxed for three hours. After cooling, the solution was acidified with concentrated hydrochloric acid. The Precipitate was filtered and recrystallized from ethanol to give product (3). The physical properties of compound (3), yield 80%, yellow color, m.p. (201-202) °C, FT-IR (KBr): 1678 cm<sup>-1</sup> v(C=O), (3400-3200) cm<sup>-1</sup> v (O-H abroad), 3125 cm<sup>-1</sup> v (C-H aro.), (2837-2933) cm<sup>-1</sup> v (C-H aliph.), (1525, 1600) cm<sup>-1</sup> v (C=C), 773 cm<sup>-1</sup> v (S-C). UV THF λ<sub>max</sub> nm: 248,294,334.

#### 2.2.4. Preparation of 5-[(p- methoxy phenyl)-3-(2-amino)-1,3,4-thiadiazol-5-yl-thiomethyl] 1,2,4-triazole <sup>[6a]</sup> (4)

A mixture of compound (3) (2.65g, 0.01mol), thiosemicarbazide (0.91g, 0.01 mol), and phosphorus oxychloride 10 mL was refluxed gently for (48) hours. The mixture was cooled and water 50 mL was added with stirring. The precipitate was filtered, washed with hot water and recrystallized from and 50% DMF to give product [4]. The physical properties of compound (4), yield 60%, yellow color, m.p. (143-145) °C, FT-IR (KBr): 1630 cm<sup>-1</sup> ν(C=N), (3380-3240) cm<sup>-1</sup> ν(N-H), 3072 cm<sup>-1</sup> ν(C-H aro.), (2869-2974) cm<sup>-1</sup> ν(C-H aliph.), (1521, 1600) cm<sup>-1</sup> ν(C=C), 762 cm<sup>-1</sup> ν(S-C). UV THF λ<sub>max</sub> nm: 248, 294, 334.

#### 2.3. Purification of Poly(vinyl chloride) <sup>[9]</sup>

Commercial poly(vinyl chloride) (PVC) supplied from Petkim company (Turkey) was purified by re-precipitation three times from tetrahydrofuran (THF) solution with methanol. The purified polymer was dried under reduced pressure at room temperature for (24) hours before used

#### 2.4. Preparation of modified polymers

The appropriate compounds of [1 or 2 or 4] (0.04 mmole) was added to a mixture (0.25g) poly(vinyl chloride) and three drops of pyridine in (25mL) tetrahydrofuran (THF) The mixture was refluxed for (5hr.). And the product polymers were filtered, washed with redistilled water, ethanol and ether then dried under vacuum. The physical property of compound (P1): color brown, FT-IR (KBr): 3176 cm<sup>-1</sup> ν(NH), 1569 cm<sup>-1</sup> ν(C=N) (2944-2888) cm<sup>-1</sup> ν(C-H alp.), 621 cm<sup>-1</sup> ν(C-Cl) 3080 cm<sup>-1</sup> ν(C-H arom.) 1390 cm<sup>-1</sup> ν(C=S), 1525 cm<sup>-1</sup> ν(C=C), 1678 cm<sup>-1</sup> ν(C=O) UV THF λ<sub>max</sub> nm: 225, 272, 281, 318. The physical property of compound (P2): color yellow. FT-IR (KBr): 3180 cm<sup>-1</sup> ν(NH), 1582 cm<sup>-1</sup> ν(C=N), 757 cm<sup>-1</sup> ν(S-C), (2927-2896) cm<sup>-1</sup> ν(C-H aliph.), 3090 cm<sup>-1</sup> ν(C-H aro.) 640 cm<sup>-1</sup> ν(C-Cl) 1535 cm<sup>-1</sup> ν(C=C). UV THF λ<sub>max</sub> nm: 280, 226, 265, 323. The physical properties of compound (P3): yellow color. FT-IR (KBr): 3185 cm<sup>-1</sup> ν(NH), 1593 cm<sup>-1</sup> ν(C=N), 744 cm<sup>-1</sup> ν(S-C), (2928-2890) cm<sup>-1</sup> ν(C-H aliph.) 3080 cm<sup>-1</sup> ν(C-H arom.) 650 cm<sup>-1</sup> ν(C-Cl), (1540, 1600) cm<sup>-1</sup> ν(C=C). UV THF λ<sub>max</sub> nm: 208, 244, 334.

### 3. Experimental Techniques

#### 3.1. Accelerated testing technique

Accelerated weather meter Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymer 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 λ between (290 to 360 nm) and the maximum wavelength light intensity is at (313nm). The polymers film, samples were vertically fixed and parallel to the lamps to be sure that UV incident

radiation is vertically incident on the samples. The irradiated samples are changed places from time to time to be sure that the intensity of incident light on all samples is equal.

#### 3.2. Photo degradation measuring methods

Measuring the photo degradation rate of polymer films was performed by infrared spectrophotometry. The photo degradation of polymer film samples were followed by monitoring of FTIR spectra in the range (4000-400) cm<sup>-1</sup> the spectra were recorded using FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified, the bands at 1722 cm<sup>-1</sup> and (1602 cm<sup>-1</sup>) <sup>[12]</sup> for the calculation carbonyl and polyene indices, respectively. The photo degradation during different irradiation times were followed by observing changes in carbonyl and polyene peaks. Then carbonyl (I<sub>co</sub>) and polyene (I<sub>po</sub>) and hydroxyl(I<sub>OH</sub>) indices were calculated by comparison of the FTIR absorption peak at 1722 cm<sup>-1</sup> and 1602 cm<sup>-1</sup> with reference peak at 1328 cm<sup>-1</sup>, respectively. This method is called band index method <sup>[10]</sup> which includes:

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

A<sub>s</sub> = Absorbance of peak under study.

A<sub>r</sub> = Absorbance of reference peak.

I<sub>s</sub> = Index of the group under study.

The actual absorbance, the difference between the absorbance of base line and top peak (A Base Line-A Top Peak), is calculated using the Base Line method <sup>[11]</sup>. Three determination of viscosity average molecular weight (M<sub>v</sub>) using viscometry method.

The viscosity property was used to determine the molecular weight of polymer, using the Mark-Houwink relation <sup>[12]</sup>.

$$[\eta] = K (\overline{M}_v)^{\alpha'} \dots\dots\dots 1$$

[η] = Is the intrinsic viscosity.

K, α = are constants dependent upon the polymer-solvent system at a particular temperature <sup>[13]</sup>.

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 (1gm/100ml) and the flow times of polymer solution and pure solvent are t and t<sub>0</sub>, respectively. Specific viscosity (η<sub>sp</sub>) was calculated as follows.

The relative viscosity (η<sub>rel</sub>) which is given by the ratio of the flow time for the solution (t) to the flow time of the pure solvent (t<sub>0</sub>), is calculated from equation (2)

$$\eta_{rel} = \frac{t}{t_0} \dots\dots\dots 2$$

η<sub>re</sub> = Relative viscosity .

The specific viscosity (η<sub>sp</sub>), which is the relative increment in viscosity of the solution over the viscosity of pure solvent, is calculated from equation (3)

$$\eta_{sp} = \eta_{rel} - 1 \quad \dots\dots\dots 3$$

The single-point measurements were converted to intrinsic viscosities by the relation [4],<sup>[14]</sup>

$$[\eta] = \left[ \left( \sqrt{2} / C \right) (\eta_{sp} - \ln \eta_{rel}) \right]^{1/2} \quad \dots\dots\dots 4$$

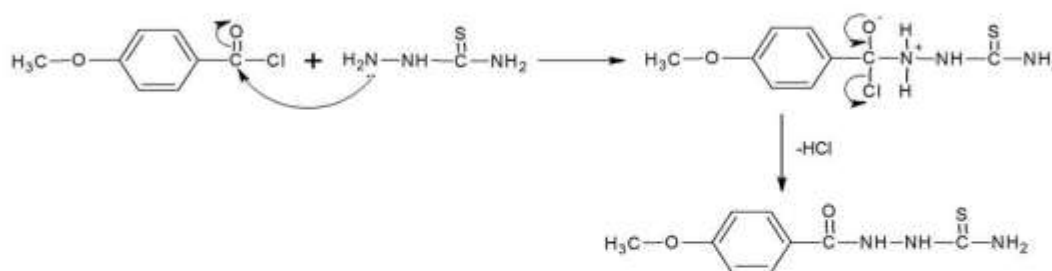
C = concentration of polymer solution in 1g/100 ml.

Molecular weight of PVC with and without modification was calculated from intrinsic viscosities measured in THF solution<sup>[15]</sup>.

#### 4. Results and Discussion

##### 4.1. Identification of organic compounds

Compound [1] was synthesized from the reaction of 4- methoxy benzoyl chloride and thiosemicarbazide . The suggested mechanism of this reaction can be outlined as shown in scheme (1)<sup>[16]</sup>.

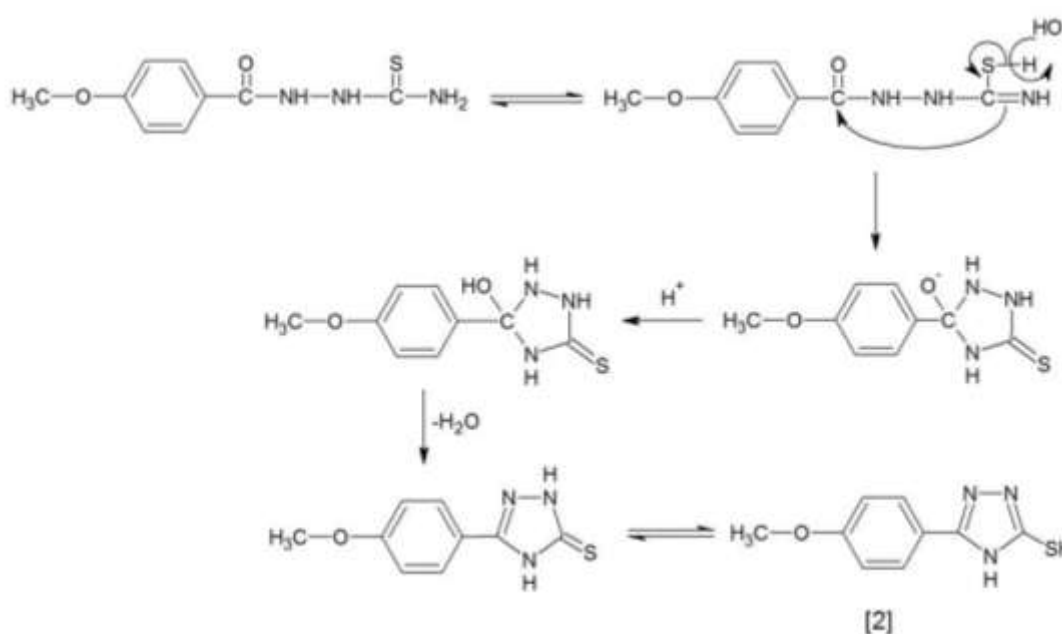


Scheme (1)

The reaction is initiated by nucleophilic attack of the most nucleophilic nitrogen of thiosemicarbazide on the carbonyl carbon of the acid chloride in a nucleophilic substitution reaction .The structural assignments of compound [1] was based on melting point( 227-228°C) and their spectral (FTIR and UV) spectroscopy. The FTIR spectrum of compound [1], figure (1), indicate significant bands in the region (3288, 3188, 1671) cm<sup>-1</sup> due to NH stretching vibrations of NH<sub>2</sub>, CONH group Respectively. The spectrum also show stretching band at 1182 cm<sup>-1</sup> due

to C=S<sup>[17,18]</sup>. UV spectrum of compound [1] was obtained in THF [C(M) = 1x10<sup>-4</sup>]. The electronic spectrum of this compound exhibited the characteristic bands due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions at ( $\lambda_{max}$  nm: 243,299,335.) figure (5).

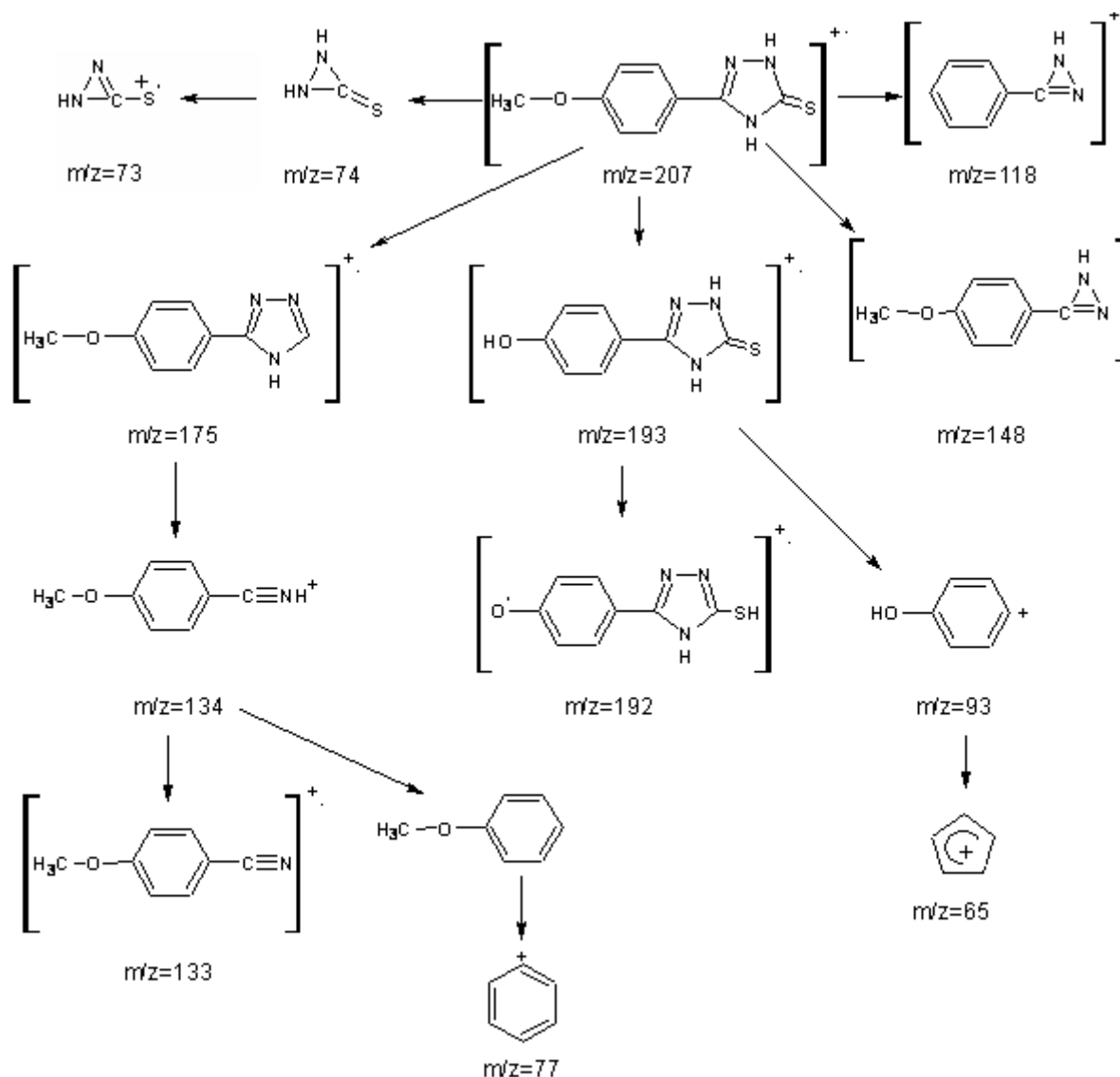
To synthesize the corresponding triazole compound [2], cyclization of carboxylic acid thiosemicarbazide derivative [1] in the presence of (4%) aqueous sodium hydroxide has been employed, the mechanism for this reaction may be outlined as follows, scheme (2)<sup>[19]</sup>.



Scheme (2)

This compound was characterized by FTIR, UV and mass spectroscopy. The FTIR spectrum of compound [2] figure (2), indicate the disappearance of absorption band due to  $\nu$  C=O (amide) stretching of compound [2] together with appearance of a stretching band at  $1612\text{ cm}^{-1}$  which is assigned to  $\nu$  C=N band of triazole moiety. It also shows stretching bands at  $1224\text{ cm}^{-1}$  and  $2682\text{ cm}^{-1}$  due to  $\nu$  C=S and  $\nu$  S-H respectively, which confirmed the tautomerism between thion and thiol forms <sup>[19-21]</sup>. UV spectrum of compound [2] was obtained in THF the electronic spectrum of this compound exhibited the

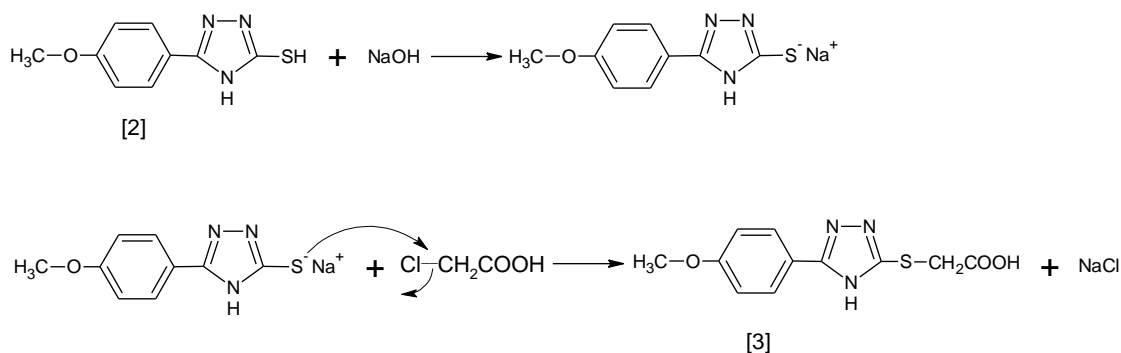
characteristic bands due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions figure (6). The mass spectrum of compound (2) at ( $\lambda_{\text{max}}$  nm: 253,289,323.) figure (9), shows the molecular ion at  $m/z=207$  which corresponds to the molecular weight of the structure assigned to this compound. The mass spectrum ions of 1,2,4-triazole ring shows a loss of HCN from the triazole ring giving the radical cation at  $m/z=148$ . The radical cation at  $m/z=133$  was also visualized in the spectrum which is good evidence to formation of the 1,2,4-triazole ring. The other fragmentation of compound [2] was shown in scheme (3).



### Scheme (3)

The reaction between compound [2] and  $\alpha$ -chloroacetic acid is a typical of the nucleophilic substitution reaction of the thiotriazole<sup>[22]</sup>, where the

$\alpha$ -halogroup could be replaced easily in this reaction with high yield product <sup>[23]</sup>. The mechanism of this reaction could be outlined as follows, scheme [4].

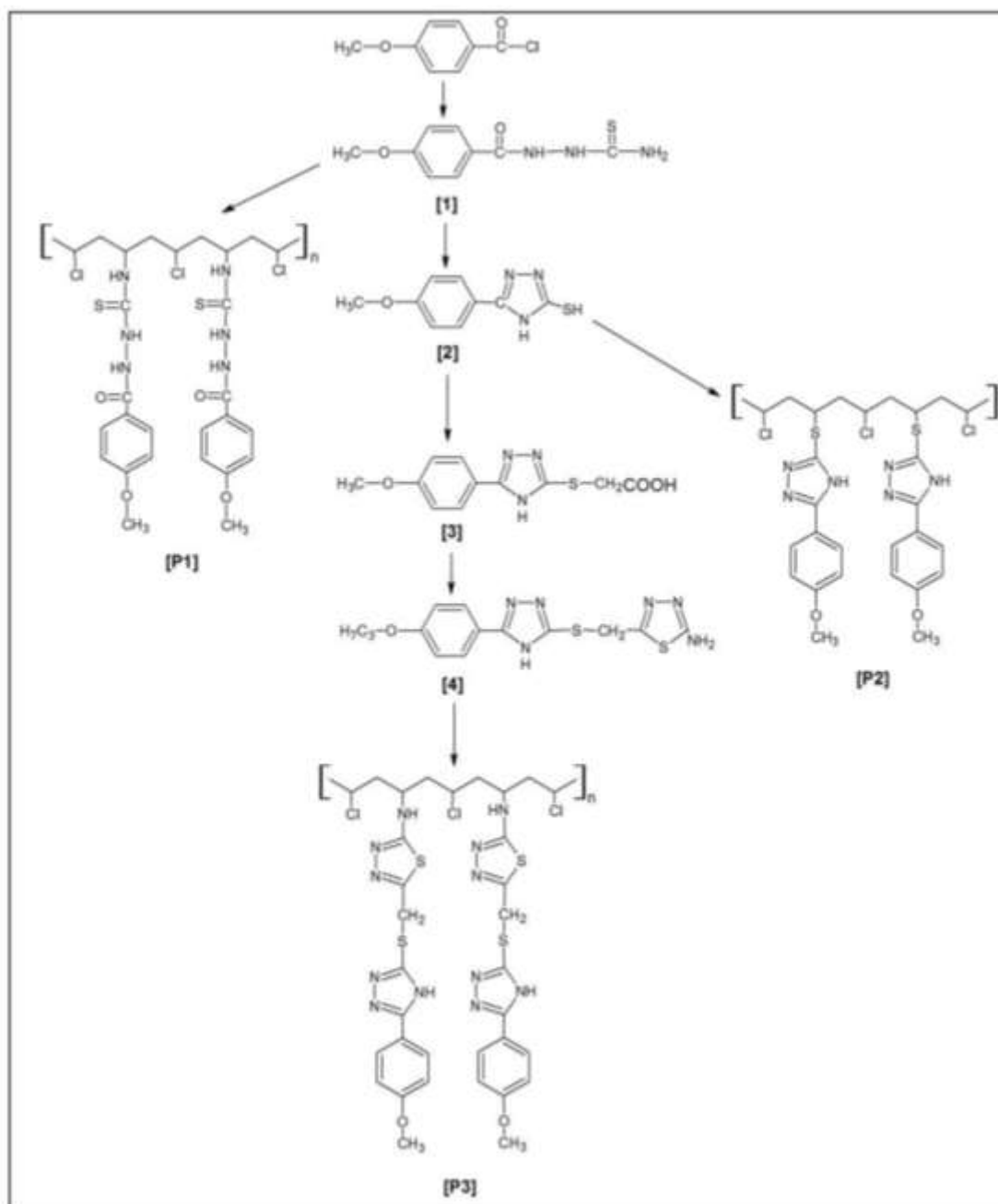


Scheme (4)

Compound [3] was identified by FTIR and UV spectroscopy. The FTIR spectrum of compound [3] figure (4) indicate abroad band between (3203-2787)  $\text{cm}^{-1}$  due to the carboxylic moiety<sup>[17]</sup>, and band at 1673  $\text{cm}^{-1}$  assignable to C=O stretching, the spectrum also shows bands at (3933)  $\text{cm}^{-1}$  and (2933-2837)  $\text{cm}^{-1}$  due to OH and aliphatic C-H stretching. Compound [4] was prepared by refluxing compound [3] and thiosemicarbazide in  $\text{POCl}_3$ . The FTIR spectrum of compound [4], figure (4), indicate the disappearance of the broad bands due to  $\nu$  O-H and C=O stretching of compound [3] together with the appearance of two peaks in the region (3100-3380)  $\text{cm}^{-1}$  which could be attributed to asymmetric and symmetric stretching vibrations of  $\text{NH}_2$  group and two further peaks, one at 1614  $\text{cm}^{-1}$  due to C=N stretching for triazole ring and the second peak at 1630  $\text{cm}^{-1}$  due to C=N stretching for thiadiazole ring. <sup>1</sup>HNMR spectrum of compound [4] figure (10) exhibit the following characteristic chemical shifts (DMSO as a solvent) a doublet consides on each other at  $\delta$  (6.95-8.12) which could be attributed to the four protons of the benzene ring. The spectrum also show sharp signal at  $\delta$  4.02 for two protons of methylene group (S-CH<sub>2</sub>) and the other singlet peak at  $\delta$  3.88 were also appear could be assigned to the three protons of the methoxy group. A peak at  $\delta$  4.62 was shown in spectrum which could be assigned to the proton of (N-H) triazole moiety while a weak broad peak at  $\delta$  6.15 for two protons of amine group

(NH<sub>2</sub>). (The signal at  $\delta$  2.5 is due to the solvent DMSO).

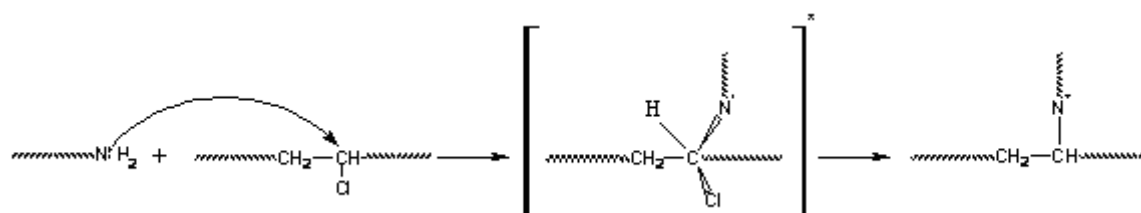
Poly(vinyl chloride) (PVC) is a polymer of great commercial importance, and it has a variety of applications ranging from containers for blood or urine to .cable insulation and packaging materials<sup>[24]</sup>. One of the most important obstacles for PVC application is its low thermal and photostability against sunlight, thus, modification of PVC have intensively been examined in the literature. For instance, it has been shown by our group that the degradation rate of modified PVC by heterocyclic are lower than unmodified PVC i.e, this modification potentially have "stabilizing effect on the PVC. The covalent modification of PVC through introduction of heterocyclic units such as (1,3,4-oxadiazole, 1,3,4-thiadiazole, benzothiazole, benzoxazole, benzimidazole)<sup>[23]</sup> to the polymer main chain can be achieved by nucleophilic substitution reaction of chlorine atoms. Mercapto and amino heterocyclic compounds have been shown to be appropriate modification reagents for this strategy. In this research, synthesis of new functional polymeric material by modifying of the commercially available polymer (PVC), through introducing 1,3,4-thiadiazole and 1,2,4-triazole [Modified PVC polymers (PI, P2 and P3) were prepared by the reaction of compounds (1,2 and 4) with equivalent moles of PVC in THF]. The synthetic details of the applied strategy for this modification of PVC are shown in scheme (5)

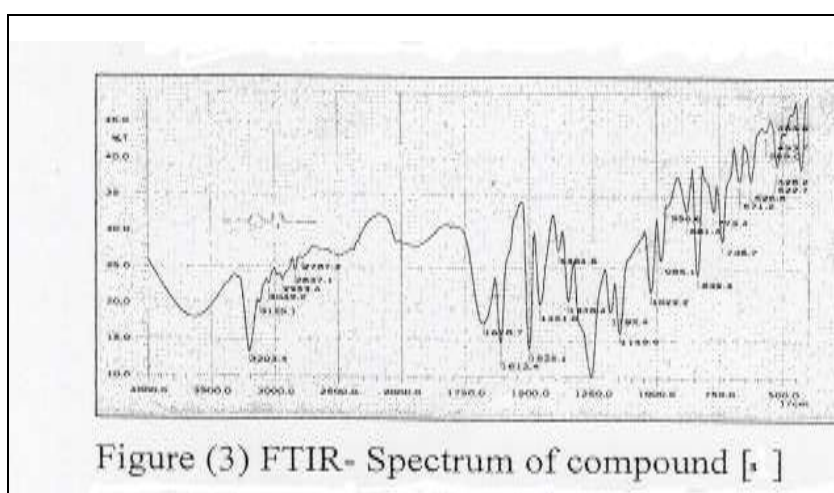
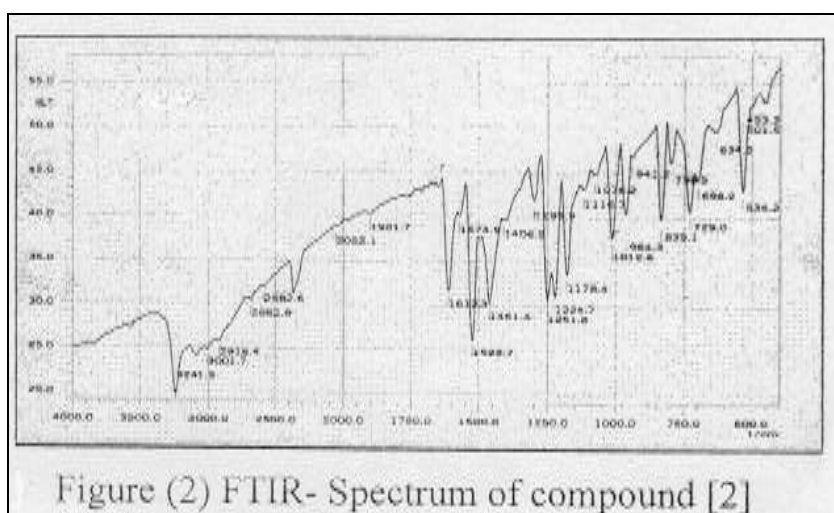
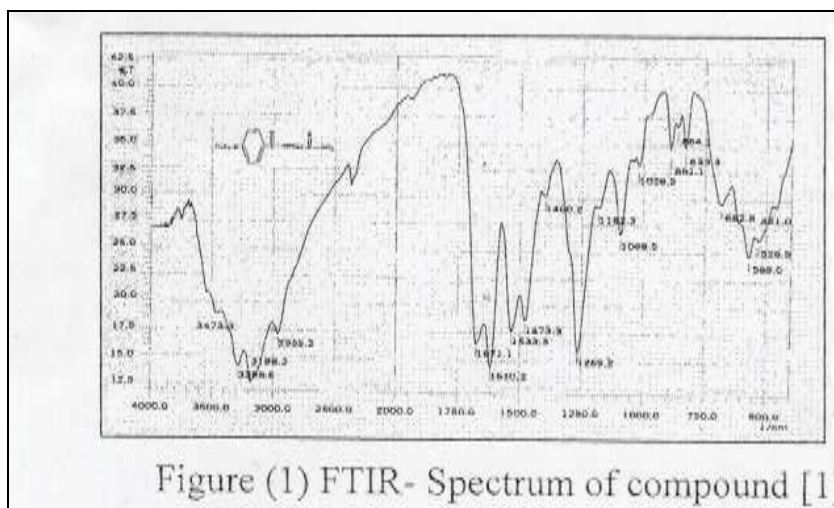


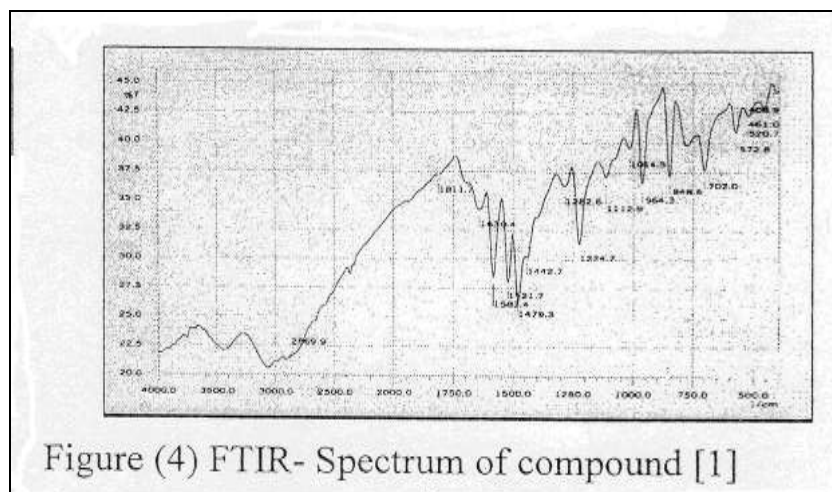
Scheme (5)

The reaction was initiated by the nucleophilic attack of (N) atom on the carbon carrying chlorine atom of

PVC in the polymeric chain followed by departure of chloride anion as a good leaving group.

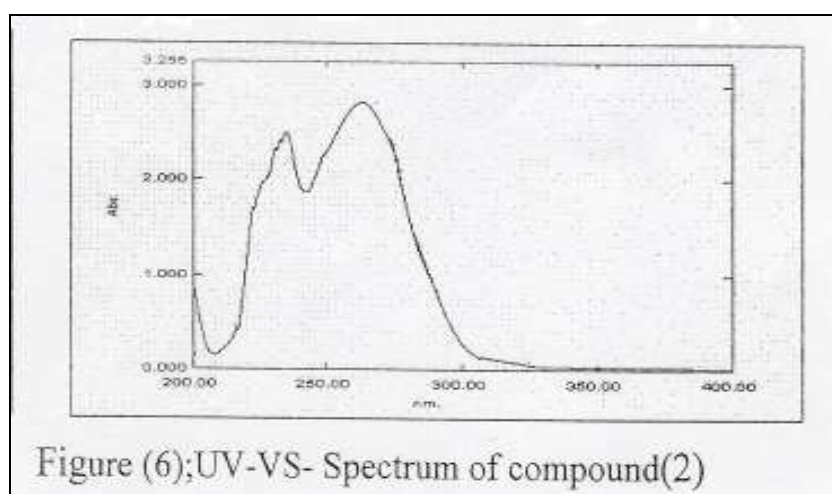
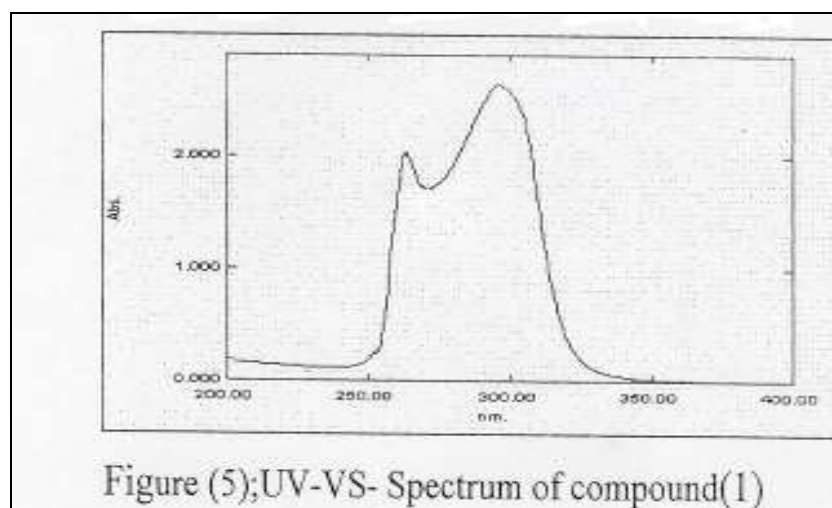


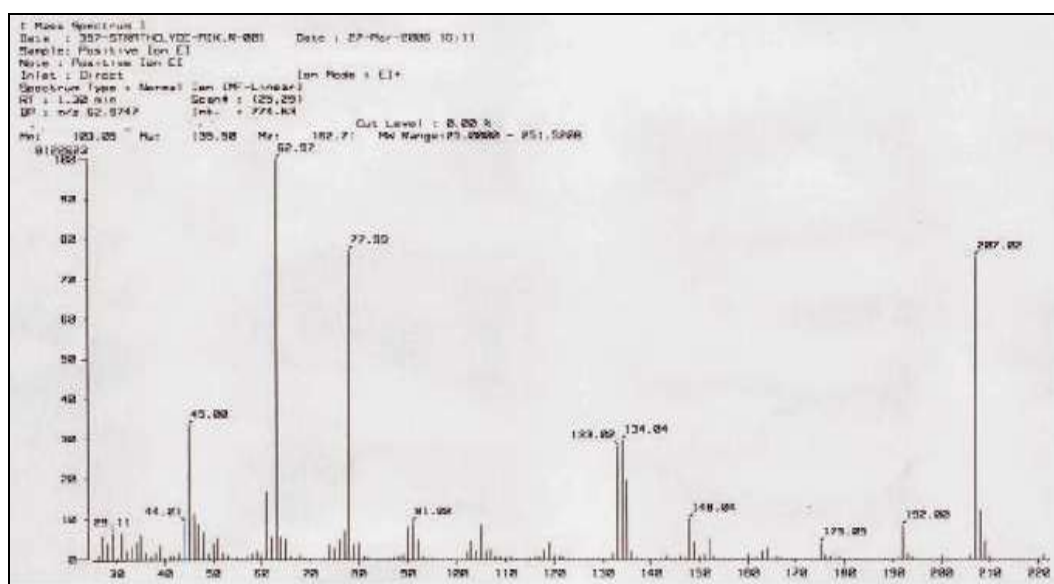
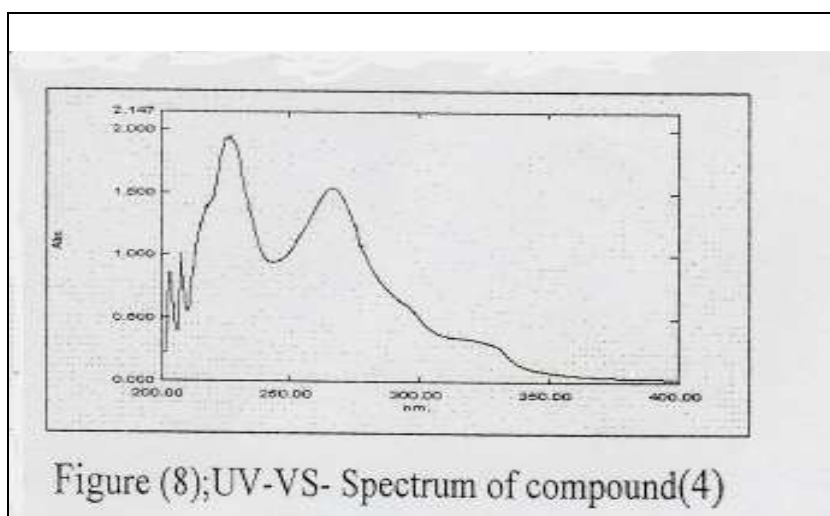
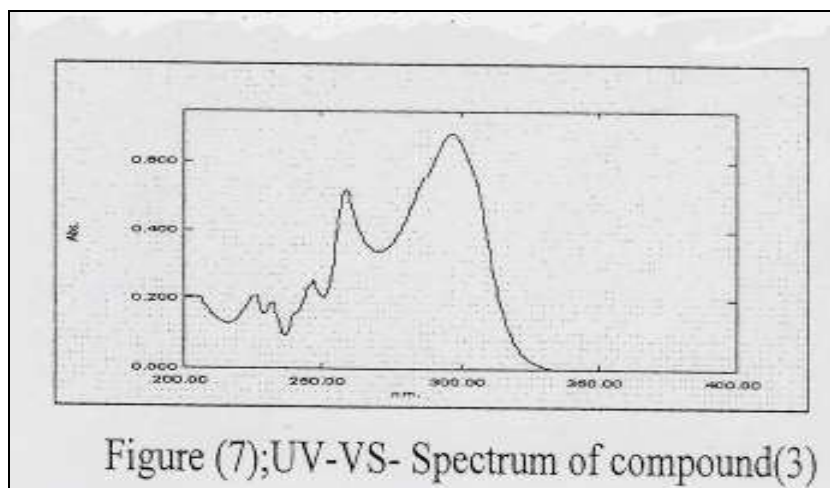


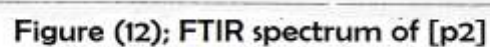


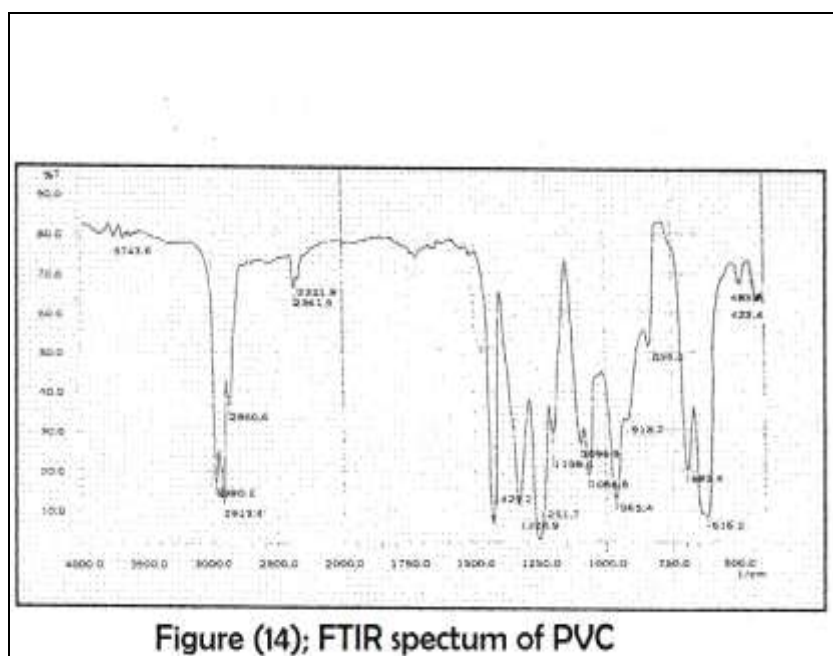
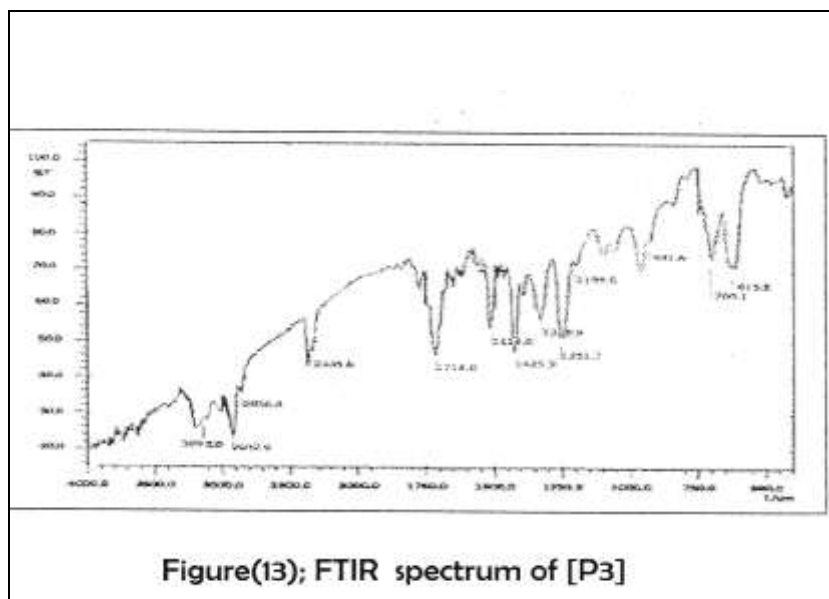
The structure of the modified polymers was established on the basis of its FTIR and UV-Vis spectroscopy, each of the present polymers showed other bands characteristic of its own structure. The

successful modification of PVC with benzylsemicarbazide, triazole ring as pendent groups and thiadiazole ring and can be demonstrated by FTIR spectroscopy, as shown in Figure {(11-14)},









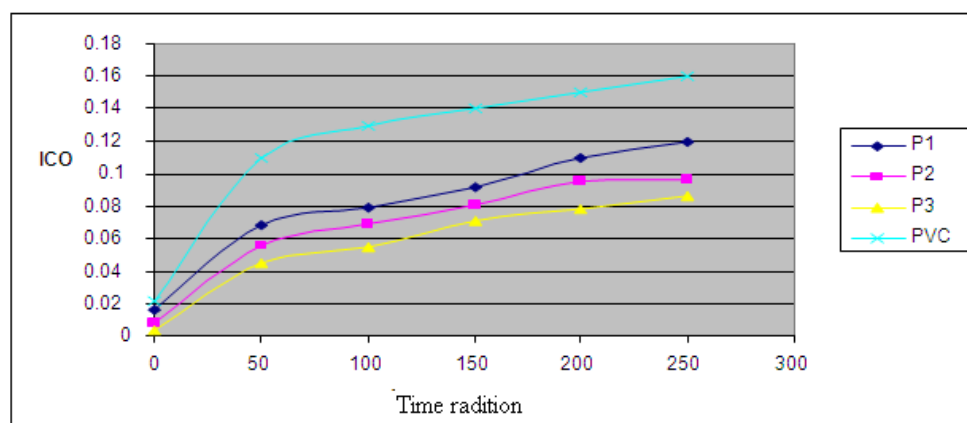
### 5. Photostabilization of modified PVC films

The new modified polymers PI, P2 and P3 were used as photostabilized PVC. In order to study the photochemical activity of these a modified compound for the photostabilization of PVC films, the carbonyl and polyene were monitored with irradiation using IR spectrophotometry. The irradiation of both PVC and modified polymer films, with light of wavelength,  $\lambda = 313\text{nm}$  leads to a dramatic change in their FTIR spectrum, as shown in FTIR spectrum Figure (2) the appearance of bands at  $1772\text{ cm}^{-1}$  were attributed to the formation of carbonyl group, which is related to chloro ketone and aliphatic ketone, together with the appearance of a band at  $1615\text{ cm}^{-1}$  related to polyene group<sup>[25]</sup>, while the hydroxyl band appeared at  $3250$

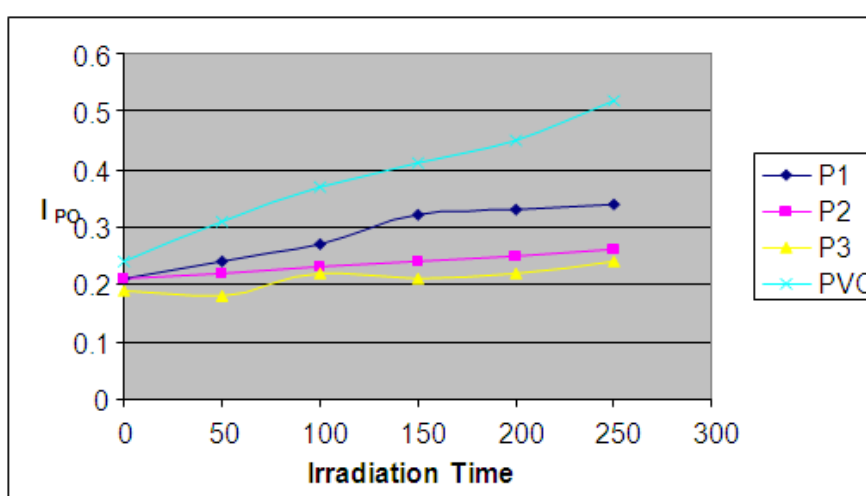
$\text{cm}^{-1}$  is related to alcohol functions<sup>[26,27]</sup>. The absorption of the polyene, carbonyl and hydroxyl groups is used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index ( $I_{\text{CO}}$ ), polyene index ( $I_{\text{PO}}$ ), and hydroxyl index ( $I_{\text{OH}}$ ). Therefore, one should expect that the growth of carbonyl index is a measure of extent degradation. As seen from Figure (4) that the modified polymers, P3 show lower growth rate of carbonyl index with irradiation time with respect to unmodified PVC film (control). These modified polymers might be considered as photo stabilized with respect to the PVC polymer figures (15-17) and Tables (1-3).

**Table1: Increase in the carbonyl index ( $I_{co}$ ) with irradiation time (minutes) for all polymeric films.**

Time	PI	P2	P3	PVC
0	0.016	0.008	0.004	0.022
50	0.068	0.056	0.045	0.11
100	0.079	0.069	0.055	0.13
150	0.092	0.081	0.071	0.14
200	0.11	0.095	0.078	0.15
250	0.12	0.096	0.086	0.16

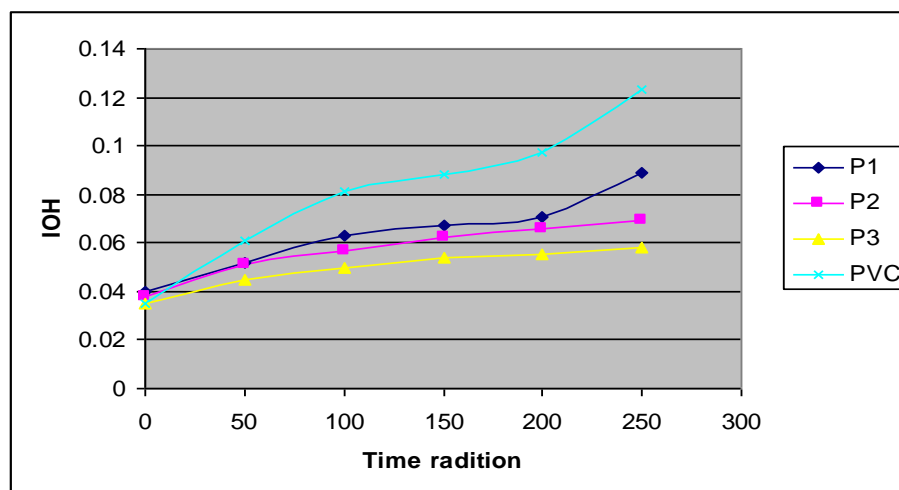
**Figure 15: The relationship between the carbonyl index and irradiation time for PVC and modified PVC films.****Table2: Increase in the polyene index ( $I_{pp}$ ) with irradiation time (minutes) for all polymeric films**

Time	PI	P2	P3	PVC
0	0.21	0.21	0.19	0.24
50	0.24	0.22	0.18	0.31
100	0.27	0.23	0.22	0.37
150	0.32	0.24	0.21	0.41
200	0.33	0.25	0.22	0.45
250	0.34	0.26	0.24	0.52

**Figure16: The relationship between the polyene index and irradiation time for PVC and modified PVC films**

**Table3: Increase in the hydroxyl index ( $I_{OH}$ ) with irradiation time (minutes) for all polymeric films**

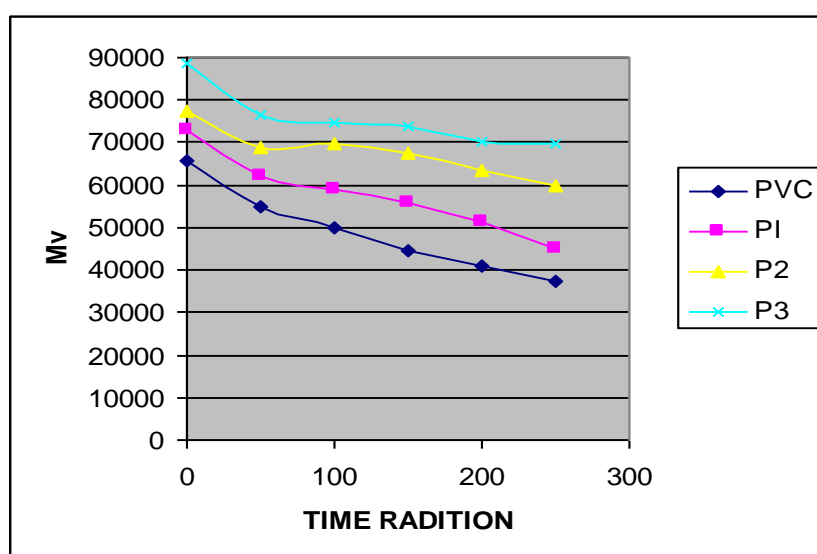
Time	PI	P2	P3	PVC
0	0.0397	0.0377	0.035	0.035
50	0.052	0.051	0.0447	0.061
100	0.063	0.057	0.05	0.081
150	0.067	0.062	0.054	0.088
200	0.071	0.066	0.055	0.097
250	0.089	0.069	0.058	0.123

**Figure 17: The relationship between the hydroxyl index and irradiation time for PVC and modified PVC films.**

### 5. Variation the molecular weight of PVC films during photolysis.

More information about the course of oxidative photo degradation of PVC films stabilized is provided by the results of the change in viscosity average molecular weight ( $M_v$ ). The viscometric

measurements during the photolysis was carried out for PVC and modified polymers PI, P2 and P3 films ( $40\mu\text{m}$ ) thickness at different irradiation times by using THF as a solvent at  $25^\circ\text{C}$ . The relative change in viscosity average molecular weight  $M_v$ , is shown in figure (18).

**Figure 18: The changes in the viscosity average molecular weight ( $\overline{M}_v$ ) during irradiation of PVC films ( $40\mu\text{m}$ ) (control) and modified PVC**

It is worth mentioning that traces of the films with a modified are not soluble in THF indicating that cross-linking or branching in the PVC chain dose occurs during the course of photolysis<sup>[28]</sup>.

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

For randomly distributed weak bond links ,which break rapidly in the initial stages of photo degradation ,the degree of deterioration  $\alpha$  is given as;-

$$\alpha = 1/P_0 - 1/P_t \dots\dots\dots 5$$

Where  $P_0$  and  $P_t$  are degree of polymerization at zero and t time

The plot b as a function of irradiation time is shown in figure (19) .The curves indicate that degradation is taking place by the random breaking of one type of band.

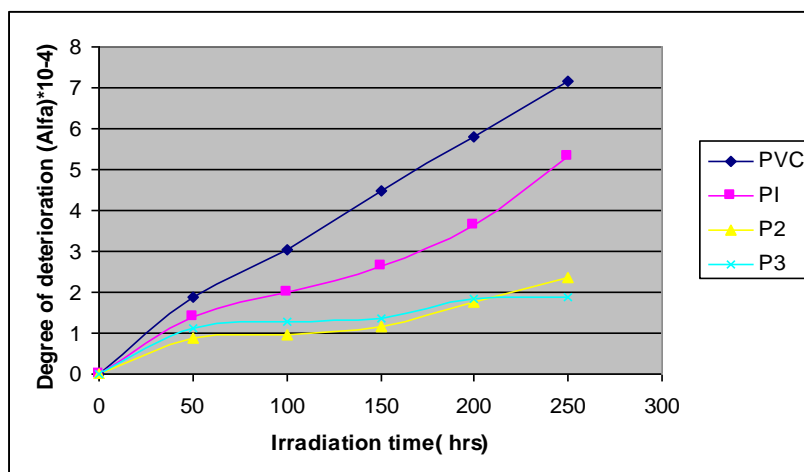


Figure 19: Changes in the number average chains during irradiation of PVC films (control) and modified PVC films.

The values of ( $\alpha$ ) of the irradiated samples are higher without modification and lower in modified compounds compared to the corresponding values of the additive free PVC

In the initial stages of photo degradation of PVC, the values of ( $\alpha$ ) increase rapidly with time, which indicates a random breaking of bonds in the polymer chain.

For more support of this view, the number average chain scission (average number cut per single chain) (S) was calculated using the relation (6):

$$S = \alpha P_0 \dots\dots\dots 6$$

( $\alpha$ ) the degree of deterioration,  $P_0$  is degree of polymerization at zero, the plot of (S) versus time is shown in figure ( 20 ).The curves an increase in the degree of branching such as that might arise from cross – linking occurrence.

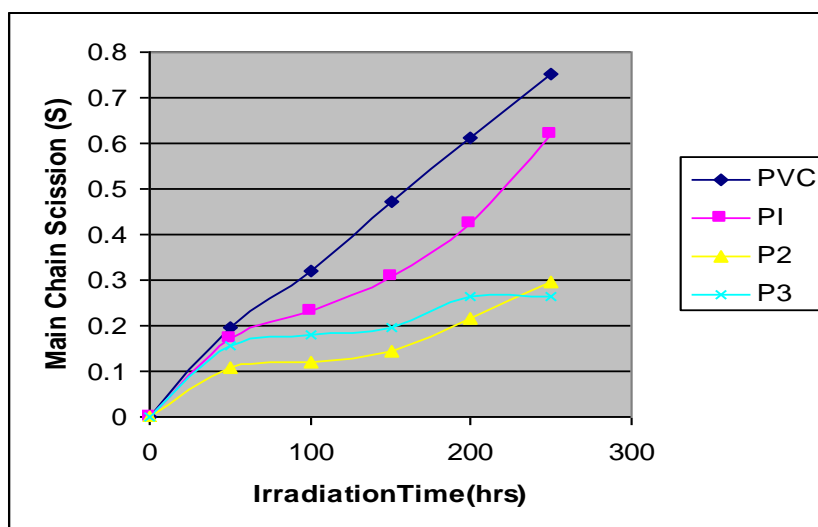


Figure (20): Changes in the number average chains (S) during irradiation of PVC (control) and modified PVC films (40 $\mu$ m)

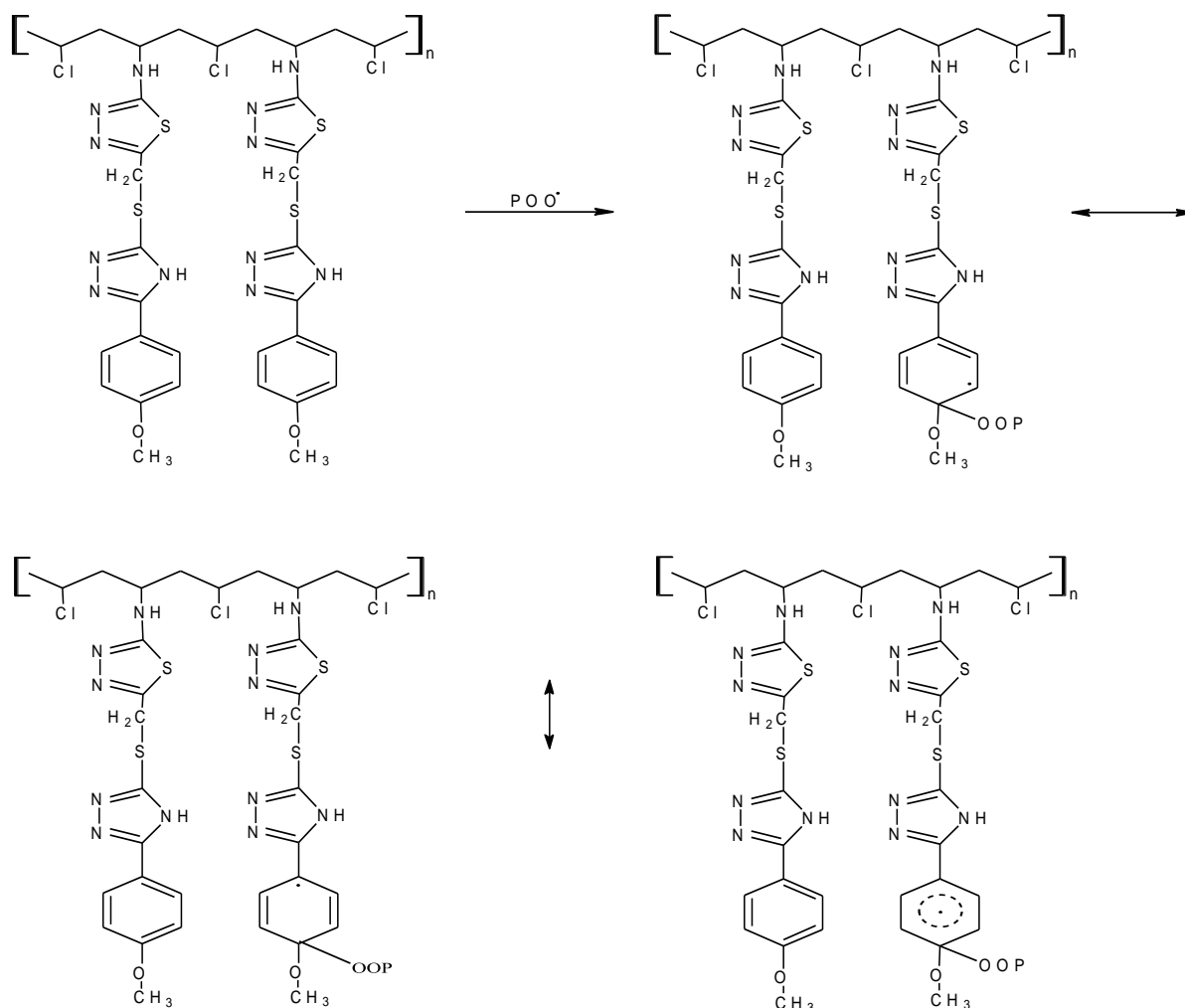
It is observed that, insoluble material was formed during irradiation, which means that extra evidence to the idea that cross-linking dose occur during the process .

#### 6. Suggested mechanisms of photostabilization of modified polymer.

Through the overall results obtained, the efficiency of the PVC modified polymers films can be arranged according to the change in the carbonyl, polyene and hydroxyl indexes as a reference for comparison as shown in Figures (5-7).

#### P3>P2>P1>PVC

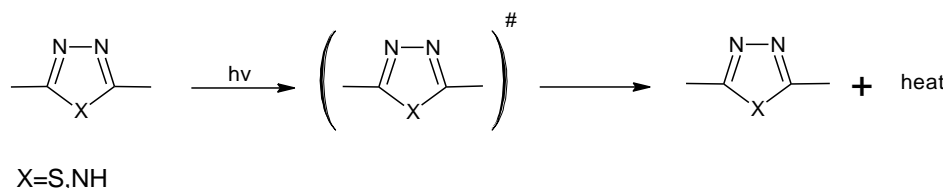
The reactions between PVC and heterocyclic units reduce the number of HCl in this polymer which led to decrease the probability of liberation Cl from PVC chain. These polymers also acts radical scavengers through energy transfer and by forming charge transfer complexes between the modified polymers and excited state of the un reactive chromophore (POO) and stabilize through resonating structures as shown in scheme (6). This mechanism is correct to all benzene rings in all polymers.



**Scheme 6: Suggested mechanism of photostabilization of PI as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.**

The rings of 1,3,4-thiadiazole or 1,2,4-triazole play a role in the mechanism as stabilizer to the modified polymers containing 1,3,4- process by acting as UV

absorber. The UV light absorption by thiadiazole and triazole will dissipates the UV energy to harmless heat energy, scheme (7).



**Scheme 7: Suggested mechanism of photo stabilization of 1,3,4-thiadiazole, and 1,2,4-triazole as UV absorber<sup>[29]</sup>**

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## تحضير ودراسة الاستقرار الضوئية لبعض بوليمرات البولي كلوريد الفاينيل المحوره

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### الملخص

ان تفاعل PVC مع الكاربونثايوايمايد ، الثايدايازول ومشتق تريازول في محلول THF يعطي بوليمرات جديدة قابلة للذوبان في مذيب THF,DMSO,DMF . ثلاثة بوليمرات محورة للـ PVC قد حضرت من خلال تفاعل المركبات (٤،١) مع PVC ذائبة في مذيب THF. الثباتية الضوئية للبوليمرات المحورة قد تحققت. تختلف البوليمرات المحورة في تأثيرها بالاكسدة الضوئية مقارنة بالـ PVC لوحده. تأثيرات الثباتية الضوئية هذه ترجع الى تأثير وجود حلقتي الثايدايازول والتريازول وقد تم تقييمه من خلال قياس المحتوى الهيدروكسيلي، للكاربونيل، والبوليتين. تبين النتائج المكتسبة بأن كل البوليمرات المحورة اعطت صورا اكثر استقرارا بدلاً من الـ PVC غير المحور. جميع المركبات المحضرة قد شخصت بأطياف الـ UV و FT-IR ودرجات الإنصهار و قد شخص المركب [٤] بطيف <sup>1</sup>H-NMR في حين شخص المركب [٢] بطيف الكتلة.