

Article - Engineering, Technology and Techniques

# Synthesis and Characterization of New Modified Poly(vinyl chloride) Polymers and Study of their Photodegradation under Irradiation with Ultra-Violet Radiation

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## HIGHLIGHTS

- The Photostability of modified PVC polymer was investigated under irradiation with UV radiation.

**Abstract:** The present work describes synthesis and characterization of new modified Poly (vinyl chloride) polymer containing amino and mercapto - derivatives as pendent groups in the repeating units. This is performed via reacting of heterocyclic compound contain thiol and amine groups with PVC in tetrahydrofuran as solvent. The structure of modified PVC polymer was characterized by IR and <sup>1</sup>H-NMR. The Photostability of modified PVC polymer was investigated under irradiation with ultra violet radiation from mercury vapor lamp 150 watt. The photostability effects of this heterocyclic compound depends on the basicity of carbonyl, alkene and hydroxyl indexes. The obtained results showed that the photostability of modified PVC polymer was decreased with increasing of irradiation time and with elevation of reaction temperature as well as in case of increasing of period of illumination.

**Keywords:** Modified PVC; Photodegradation; irradiation; photostability; illumination.

## INTRODUCTION

Various techniques can be used to prepare polymers like cationic, anionic and radical polymerization. Different methods of characterization used for the determination of structure–property relationships, thermal, mechanical, and structural properties can be investigated. Recently, different polymers were used in various applications like construction, electronic, automotive, pharmaceutical industries, and cosmetic due to their properties [1-3]. Poly (vinyl chloride) (PVC) is a very important polymer due to its excellent properties,

relatively low cost, good performance and complete safe issues in concerning with its usage [4,5]. These properties make it used more widely in outdoor applications such as doors, windows, cladding, drainpipes, electrical insulation, and cling film. PVC polymer is polar due to presence of C-Cl bond and this bond make polymer a linear chain, rigid and prevent crystalline region normally [6,7].

PVC polymer is one of the most important polymers due to its versatility and excellent physicochemical properties. PVC is employed in a wide range of fields [8-10]. This type of polymer has been subjected to numerous reactions, mainly dehydrochlorination [11] and nucleophilic substitutions [12], degradation [13], grafting and cross-linking [14]. Poly (vinyl chloride) has little solubility and soluble only in solvents containing oxygen atom like ethers, dioxane, tetrahydrofuran and ketones [15]. Moreover, exposing PVC for a long time to ultraviolet (UV) radiation, resulted undesirable changes in their physical and chemical properties. Therefore, the researchers were interested into stabilizing PVC against irradiation to reduce the photodegradation rate [16-18].

Many researchers investigated the effect of absorption radiation and especially UV radiation on the behavior of PVC. So as to find a better understanding and control to prevent or at least minimize the extent of the degradation processes. In spite of the useful information obtained by using the more recent techniques available, it must be acknowledged that the reasons which make PVC so susceptible to UV light are still not fully elucidated [19, 20].

This chapter is an attempt to clarify and take stock of the current situation. Particular emphasis will be laid on the various aspects of the major photochemical processes involved, especially with regard to the nature of the initiating chromospheres and the effect of such important factors as the intensity and wavelength of the incident light, the irradiation temperature and the presence of oxygen. The mechanism of the photodegradation and photooxidation of PVC will be discussed based on some recent quantum yield results [21, 22].

The current study involves synthesis and characterization of new modified Poly (vinyl chloride) polymer containing amino and mercapto -derivatives as pendent groups in the repeating units. Stability of the prepared polymer against ultra violet radiation will be investigated under illumination with UV light. In addition, this factor will be investigated under elevation in reaction temperature.

## MATERIAL AND METHODS

All the starting materials that were used in this study were purchased from Sigma Aldrich and EMD Company. Melting points were determined on a Gallenkamp MFB-600-Melting point Stuart apparatus, FT-IR spectra were recorded on a Bruker spectrometer. <sup>1</sup>H-NMR analysis was recorded on a Bruker AC 400 NMR spectrometer, operating at 400 MHz for <sup>1</sup>H-NMR and 100 MHz for <sup>13</sup>C-NMR. All chemical shifts ( $\delta$ ) are reported in ppm relative to tetramethylsilane (TMS) as reference ( $\delta=0.0$  ppm). UV/VIS double beam Spectrophotometer PG CECIL- CE7200 Instruments.

### Synthesis of compound [1]:

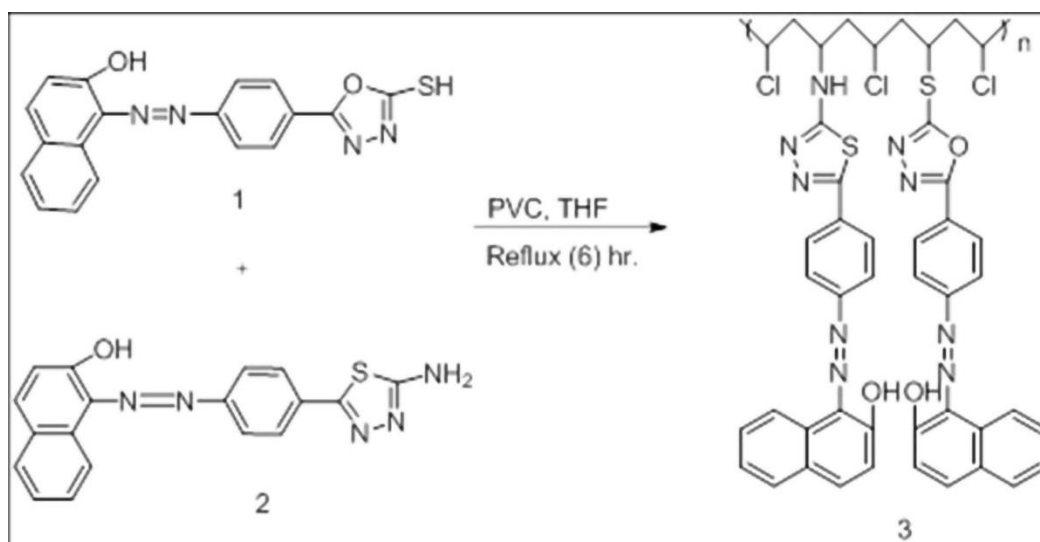
Compound (1) was prepared according to previous work [23, 24].

### Synthesis of compound [2]:

(0.001 mole, 2.92 g) Of 4-((2-hydroxynaphthalen-1-yl) diazenyl) benzoic acid and (0.001 mole, 0.911 g) thiosemicarbazide were dissolved in (8 mL) POCl<sub>3</sub>, then was refluxed for (4) hours, after that (20mL) distil water was added and refluxed for (4) hours. Then filtered and recrystallized by ethanol afforded compound (2): molecular formula: C<sub>18</sub>H<sub>13</sub>N<sub>5</sub>OS, color: brown, in yield: 87%, m.p. = 197-199 °C. IR ( $\nu = \text{cm}^{-1}$ ): 3399 (O-H), 3286, 3148 (NH<sub>2</sub>), 3062 (C-HAr.), 1617 (C=N), 1603 (C=C, Ar.), 1564 (N=N). <sup>1</sup>H-NMR ( $\delta$ , ppm): 5.667 (s, H, OH), 6.764-8.464 (m, 10H, Ar-H). <sup>13</sup>C-NMR ( $\delta$ , ppm): 117.329 (C, Ar-C), 121.724-155.5 (C, Ar-C), 165.5 (C, C-OH), 166.692 (C, N-C-S), 175.920 (C, C-S).

### Synthesis of PVC polymer derivative [3]:

PVC (0.15 g.) was dissolved in (16 mL) of THF and (0.001 mol.) of compounds (0.40 g) 1,2,4-thiadiazole derivative (1), and (0.35 g.) 1,3,4-oxadiazole derivative (2) respectively. Pyridine (6) drops was added to the above solution, then it was refluxed for (6) hours. The obtained solution was filtered and washed with distilled water for several times to yield compound (3), color: pale pink, m.p. >200 °C, IR ( $\nu = \text{cm}^{-1}$ ): 3390.29 (C-H, Ar.), 2953.88-2848.17 (C-H, alph.), 1764.85 (C=N.), 1712.68 (C=C, Ar.), 1603.76 (N=N), 988 (C-O-C). <sup>1</sup>H-NMR ( $\delta$ , ppm, DMSO-*d*<sub>6</sub>): 0.5-5.783 (H, CH, CH<sub>2</sub>) for PVC, 7.023-7.962 (C, Ar-C) (Scheme 1).



**Scheme 1.** Synthesis route of compound [3]

### Photo degradation of the prepared modified oxa+thia / PVC polymer

Photodegradation of oxa+thia/PVC polymer was performed by irradiation of polymer solution in benzene with UV light from mercury vapor lamp 150 watt (TQ150Z2, Karl Kolb Company). The used modified polymer concentrations were (0.02, 0.04 and 0.06 g./100 mL). Irradiation was initiated by flushing radiation for a period of six hours for each case at different temperatures under normal atmospheric conditions. Photo degradation of the used polymer derivatives was carried out at three different temperatures 25, 30 and 35 °C. Upon irradiation and periodically each one-hour, samples were withdrawn and each of density and time flow for each of solvent and the solutions were measured using picnometer flask and Ostwald viscometer respectively. Upon finding densities for each of solvent and solutions for each case. Then viscosity and relative viscosities can be calculated as follows for each case [25].

$$\eta/\eta_0 = t_x d / t_0 \times d_0 \quad (1)$$

Whereas  $\eta$ ,  $t$  and  $d$  are the viscosity, time flow and density of the polymer solutions.  $\eta_0$ ,  $t_0$  and  $d_0$  are that for the used solvent. Specific viscosity ( $\eta_{\text{specific}}$ ) calculated with respect to the relative viscosity ( $\eta_{\text{relative}}$ ) as follows:

$$\eta_{\text{relative}} = \eta_{\text{solution}} / \eta_{\text{H}_2\text{O}} \quad (2)$$

$$\eta_{\text{specific}} = \eta_{\text{relative}} - 1 \quad (3)$$

The intrinsic viscosity ( $[\eta]$ ) can be calculated by plotting  $\eta_{\text{specific}}/c$  concentration on Y-axis versus concentration on X-axis and the obtained intersection would equal to intrinsic viscosity  $[\eta]$ . From the obtained intrinsic viscosity, molecular weight can be calculated from the following relation:

$$[\eta] = kM^\alpha \quad (4)$$

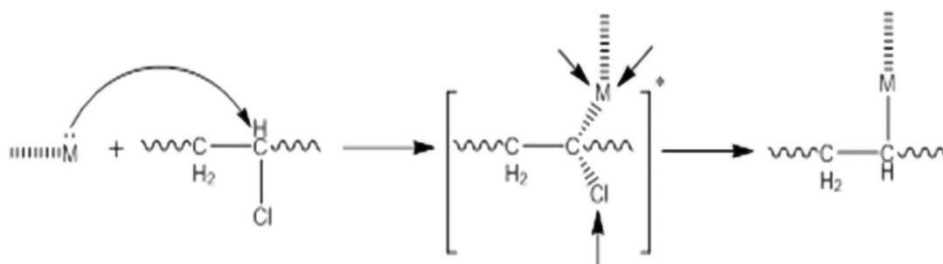
Whereas  $k$  and  $\alpha$  are constants for each solvent (for benzene  $k = 0.49 \times 10^{-4}$ ;  $\alpha = 0.76$ ).

## RESULTS AND DISCUSSION

### Characterization of Compound [3]:

In this part, synthesis of new modified PVC polymer containing thiadiazole derivative and oxadiazole derivative was performed to find out the effect of introducing these moieties on physical and chemical properties of modified and unmodified PVC polymers. The reaction was initiated by the nucleophilic attack of sulfur and nitrogen atoms on the carbon carrying chlorine atom in the polymeric chain followed by departure of chloride anion as a good leaving group (Scheme 2). The I.R spectrum of compound (3) exhibited absorption bands of C-H<sub>aliph.</sub> at (2915.79, and 2848.32)  $\text{cm}^{-1}$  and disappearance absorption bands at (3399.76, and

3286.29)  $\text{cm}^{-1}$  of  $\text{NH}_2$  group and absorption bands at (3256.84, 3187.25)  $\text{cm}^{-1}$  of S-H group.  $^1\text{H-NMR}$  spectrum of this compound showed signals at 1.3-3.5 for aliphatic hydrogen of poly vinyl chloride and disappearance signal at of hydrogen of thiol group.



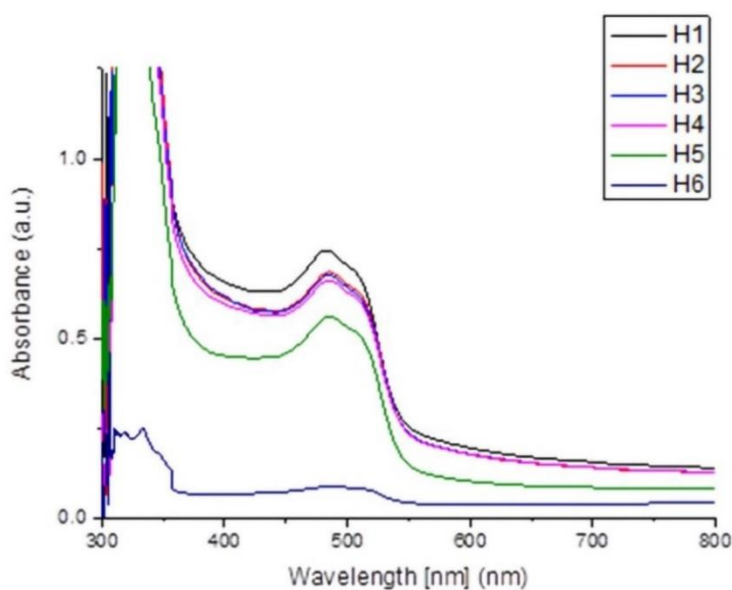
**Scheme 2.** Proposed mechanism of synthesis compound [3]

### Photodegradation of oxa+thia/PVC under Irradiation at 25 °C

#### UV-Visible spectra for Photodegradation of oxa+thia/PVC under irradiation at 25 °C

The photodegradation of oxa+thia/PVC polymer under irradiation with UV radiation was investigated by irradiation with UV light at 25 °C and the photodegradation of this polymer was followed via recording each of FTIR spectrum, and UV-visible spectrum for each irradiated sample. In addition to that, change in molecular weight of the polymer (oxa+thia/PVC) under irradiation condition was followed from measuring of the viscosity of the irradiated sample over a period of irradiation [26]. From the obtained results, it was found that, degradation of the modified polymer was developed increasingly with increase of irradiation time from one to six hours. This probably due to the role of UV radiation in breaking of linkers which are connecting chains of the polymer together as UV radiation possess a sufficient energy that is comparable to the bonds energies that are present in the polymeric chains. Photodegradation of oxa+thia/PVC was followed with UV-Visible spectroscopy as shown in Figure1. From these spectra, there were a reduction in the intensity of absorption peak with development of irradiation time. This confirm occurrence of degradation in polymeric chains upon absorption of UV radiation under reaction conditions [27].

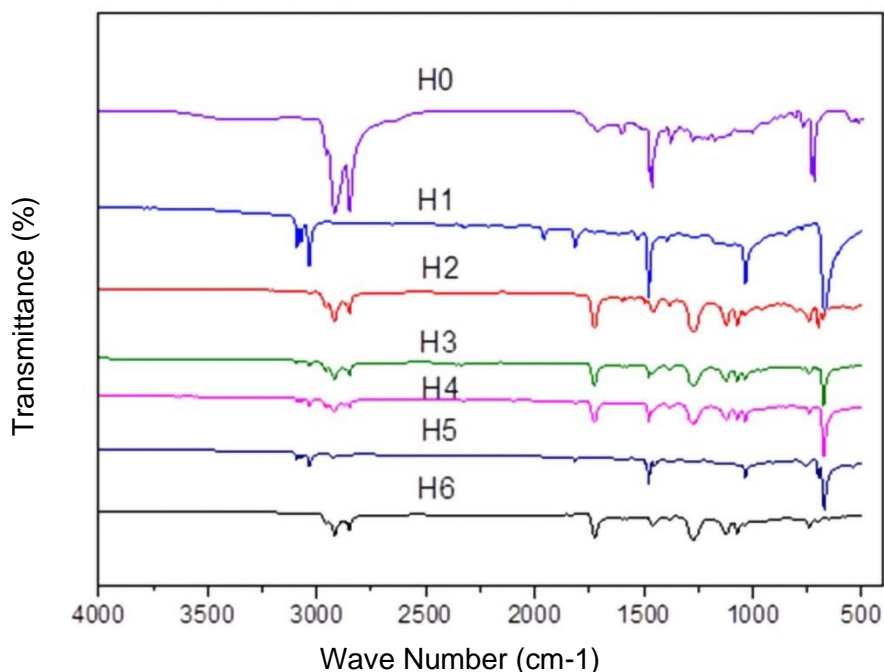
In general, different types of polymers undergo chemical and physical changes due to breaking of some bonds within the structure of the polymer, when these polymers are exposed for a long time of exposure to the radiation under normal atmospheric conditions [27]. The extent of these changes are mainly dependent on the presence of light absorbing chromospheres within the structure of the investigated polymer. In this context, polymer containing aromatic or carbonyl groups in their structure as a backbone or branched units are likely to absorb the radiation in UV and visible region and hence it becomes photosensitive materials [28].



**Figure 1.** UV-visible spectra for photodegradation of oxa+thia/PVC at 25 °C

### FTIR spectra for photodegradation of oxa+thia/PVC under Irradiation at 25°C

Photodegradation of oxa+thia/PVC under illumination with UV radiation was confirmed using FTIR spectroscopy and the obtained spectra are shown in Figure 2. From these spectra, it can be seen that, there were changes in absorption peaks of oxa+thia/PVC with irradiation time progress. This arises due to the fragmentation in polymer chains due to breaking of some bonds in the polymeric chains because of absorption of UV radiation, which confirms photodegradation of the polymer upon irradiation, and absorption of the energy from the UV photons [26-28].

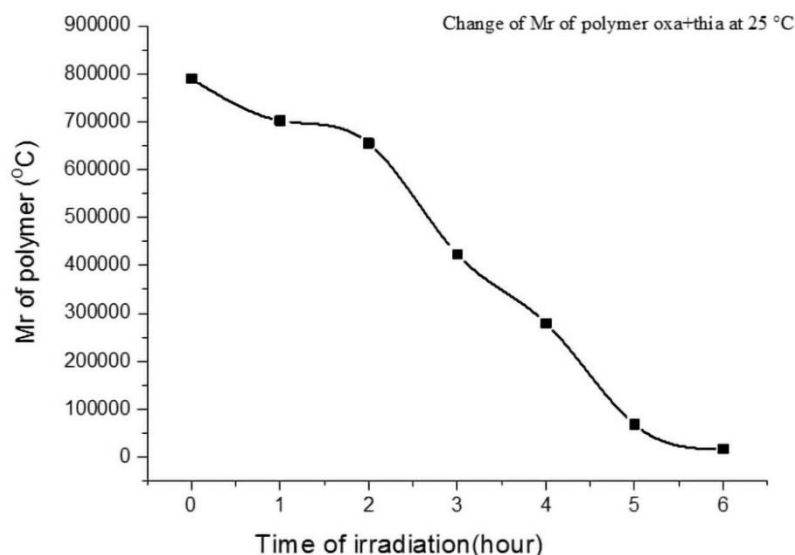


**Figure 2.** FTIR spectra for oxa+ thia/PVC polymer at different times of irradiation at 25 °C.

### Change in Mr of the polymer of oxa+thia/PVC under Irradiation at 25 °C

Changes in Mr of oxa+thia/PVC upon irradiation with UV light was followed by calculating Mr at a period of one hour up to six hours at 25 °C. The obtained Mr. before irradiation was 805634 Dalton (gm./mol.). Molecular weight periodically was calculated from viscosity measurements.

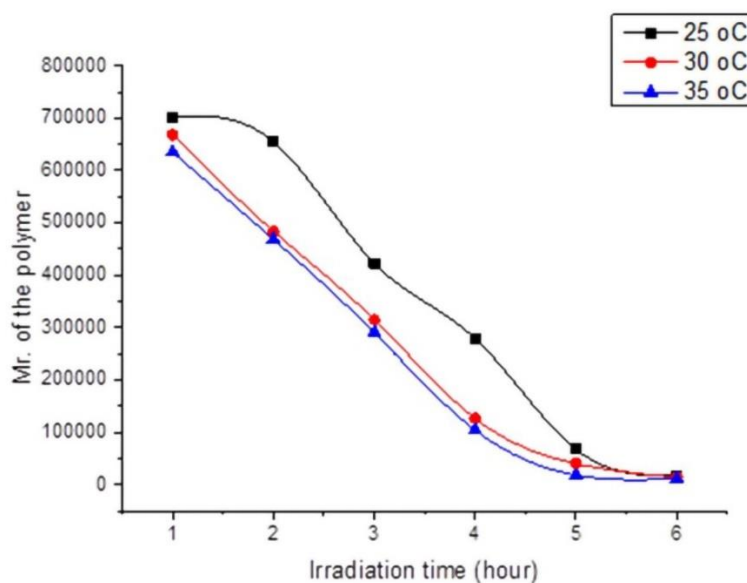
From these results, it can be seen that there was reduction in Mr of the polymer with development of irradiation time. This observation can be attributed to the effect of UV radiation in breaking of some bonds that are linked among polymeric chains (Figure 3). The result of this process is the producing of smaller polymeric chains with lower densities which leads to formation of chains with lower molecular weight with increasing of irradiation time [26-28].



**Figure 3.** Photodegradation of oxa+thia/PVC polymer under irradiation with UV light at 25°C.

### Effect of temperature on photodegradation of oxa+thia/PVC

To study effect of temperature on photodegradation of oxa+thia/PVC a series of experiment were performed applying identical reaction conditions with variation only in reaction temperature. These reactions were carried out at three different temperature, 25, 30 and 35 °C. The obtained results are presented in Figure 4. From the obtained results, it can be seen that, Mr. of the polymer was reduced continuously with development of irradiation time for all cases [24-28]. On the other hand; Mr. of the polymer was reduced with elevation of reaction temperature at the same period from one to six hours. Increasing reduction in Mr. for the polymer under irradiation with elevation in temperature can be attributed to the contribution of thermal energy in enhancement of diffusion in solution as well as to contribution of thermal energy in breaking some bonds which connecting polymeric chains. It is well known that, the thermal energy is directly proportional with temperature (thermal energy =  $kT$ , whereas  $k$ , is the Boltzmann constant and  $T$  is the temperature in Kelvin scale). This synergetic effect of reaction temperature with energy of UV light can lead to enhance of bonds breaking and fragmentation of polymeric chains into smaller molecular weight chains with the development of reaction period [29-31]. This would lead to reduce relative molecular weight of the polymer.



**Figure 4.** The effect of irradiation time and temperature on Mr. of oxa+thia/pvc fragmentation at 25, 30, and 35 °C.

## CONCLUSIONS

New modified Poly (vinyl chloride) polymer containing amino and mercapto -derivatives as pendent groups in the repeating units was synthesized. Thiol and amine groups enhance PVC structure and the structure of new modified polymer was approved using different techniques. From the obtained results in this study, it was found that the photostability of oxa+thia/PVC polymer under irradiation with UV radiation was reduced with development of irradiation time and with elevation in reaction temperature.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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