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IASET

A STUDY OF EFFECT OF COPPER(II)-COMPLEX(CU-BHBH) ON THE PHOTODEGRADATION OF POLYSTYRENE FILMS

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ABSTRACT

This study included photodegradation of polystyrene films after exposing them to light using Schiff's base of Copper-complex. The films were made by mixing with the polymer solution at different weight percentages in the range (0.025%-0.4%) with thickness of (70±5 μm). The specimens were irradiated for different times at wavelength (365nm) at 40˚C. The photodegradation of the prepared films with and without additives were followed by FT-IR technique for evaluating both ICO and IOH. Ultraviolet-visible (UV-Vis) was used to calculate the rate of degradation. The results indicated that the synthesized complex has induced the degradation which increases as the concentration of the additives increase which coincides with the resulted Kd increments which followed in presence and without of 0.05% of the added Copper-complex by measuring both the number average molecular weight and the degree of decomposition, besides the chain mean scission (S) and the degradation degree (α). it was found that in the presence of the metal complex led to decrement in the molecular weight (M.W) and chain scission which fit with other researchers.

KEYWORDS: Schiff's Base, Polystyrene, Photodegradation, Copper (II)-Complex

INTRODUCTION

In recent years there is a great interest in the photo-oxidative degradation of polymeric materials; because macromolecules have increasingly wide spread commercial applications. Polymeric materials, synthetic, semi-synthetic and natural are photodegradable when exposed to the environment [1,2]; all commercial organic polymers degrade in air when exposed to sun light as the energy of sun light is sufficient to cause the breakdown of polymeric bonds. Moreover, degradation is due to the action of short-wavelength (UV) rays (λ-290nm) present in solar spectrum. Thus the life of thermoplastics for outdoor applications becomes limited due to weathering [3-5]. The photodegradation of polystyrene and its analogous has been reviewed [6-8] and was a subject of many scientific publications [9-14]. Increased photodegradation of polystyrene rates at wavelengths >280 nm require that ketone or other carbonyl groups be introduced in to the molecule by copolymerization or grafting. Photo-oxidative degradation of polystyrene is accelerated by the presence of compounds which become activated by Sunlight such as metal salts and transition metal complexes [15-17] which catalyze the decomposition. It is well known that trace amounts off metallic impurities or additives present in polymer play an important role in photodegradation of the substrates (18-20). In this study a new type of transition metal tetradentate Schiff's base 1,3-bis(2-hydroxybenzyl-idene)hydrazine has been used as (UV) photo inducer for polystyrene degradation.

EXPERIMENTAL SECTION

All chemicals used for the preparation of the titled compounds were of reagent grade quality. Some of the solvent was distilled before use. The ligand and complex were prepared with a procedure similar to that reported in the literature [21,22].

Synthesis of Ligand (L)

Salicylaldazine was synthesized by stirring a solution of salicylaldehyde (2.44g, 2.0mmol) with hydrazine (0.5g, 1mmol, 80%) at (25ml) of ethanol. The yellowish powder produced was filtered off and washed with ethanol. Its m.p. was of 210˚C.

Preparation of Complex (L-M)

Complex was obtained by dissolving 1.5 mol of the appropriable metal salt ($CuCl_2.2H_2O$) in ethanol and dissolving 0.5 mol of ligand in ethanol as well, and then the PH was raised to 8 by adding 10% w/v of NaOH solution. Different intensely colored precipitate was obtained which was then filtered, washed with an excess of absolute ethanol. Its m.p. was of m.p. 228˚C. Scheme (1) shows synthesis of ligand and L-M.

(L)

(L-M)
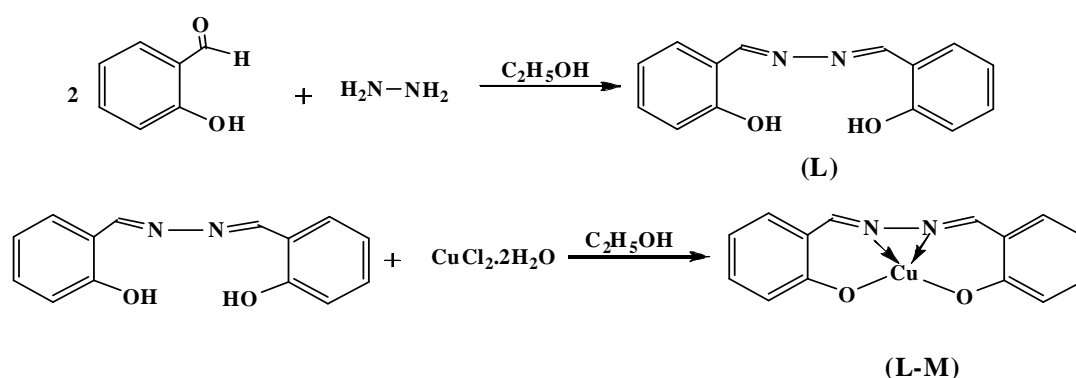
Scheme 1

Purification of Polystyrene

Commercial polystyrene (PS) supplied by Turkish company was freed from additives by reprecipitation three times from chloroform solution in ethanol. The purified polymer was dried under reduced pressure at room temperature for 24 hours.

Films Preparation

Different concentration of polystyrene solution (g/ml) in chloroform was used to prepare (70±5 μm) thickness of polymer films, measured by a micrometer type (Q. panel, company, USA) with and without complex prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual chloroform solvent, film samples were further dried at room temperature for five hours under reduced pressure.

Irradiation of Samples (Accelerated Testing Technique)

Accelerated weather meter (locally assembled) was used for the irradiation of polymer films. It contains lamp type (Fluorescent Ultraviolet Light) 18 watt (Japan). There is lamp of the type (UV-A 365) giving the maximum wavelength of (365nm). The polymer film samples were fixed vertically and parallel to the lamp to ensure that UV incident radiation is vertically incident on the samples, the irradiated samples were changed with respect to their from time to time to fulfill that the intensity of light incident on all sample is of uniform intensity.

RESULTS AND DISCUSSIONS

The photodegradation is an important way to reduce the problem of environmental pollution caused by the wastes of polymeric materials (plastics) to obtain compounds of lower molecular weights, which decomposed by micro organisms [23], knowing that the exposure of polystyrene molecule to high-energy light UV lead to a polymeric molecule interaction with photons of light producing carbonyl, hydroxyl and hydroperoxides as a result of the decomposition of the polymer. Previous researches [15,16] were used aliphatic and aromatic complexes to increase the rate of photo-oxidative chips of polystyrene, at this study a complex (CU-BHBH) was used to achieve this purpose different weight percentages, ranged between (0.025-0.4%). Polymeric films were irradiated lonely and with the complex by ultraviolet (UV) under atmospheric oxygen for periods of different time, which range (20-320hrs.), respectively as table 1 indicates.

UV-Visible

The process of photodegradation of polystyrene chips at different concentrations of the complex (CU-BHBH) were studied by the spectrum of UV-Vis, When exposing films of polystyrene to UV radiation for a periods of time that leads to the transformation of chips color to yellowish color. That change indicates the photolysis of the polymer. For calculating the rate of decomposition (K_d) that carried out by recording absorption spectrum of the UV and during the process of at different times of irradiation. It has been observed that the absorption spectrum for these chips varies from time of irradiation as in (Figure 1) shows where one could notice the change in the absorption spectrum of the polymer before and after irradiation process of photodegradation.

Table 1: Absorbance Values of the Polystyrene with Thickness (70±5 μm) Containing Different Concentrations of the Complex (Cu-L) and Calculated at a of 300 nm Spectrum Measurements of UV-Vis with Time

| Irradiation Time (hr)	Absorbance					
Concentration %	0.0	20	40	80	160	320
PS	0.150	0.313	0.560	0.779	0.979	1.025
PS + 0.025% CuL	0.256	0.578	0.704	0.852	1.166	1.318
PS + 0.050% CuL	0.307	0.669	0.797	1.262	1.344	1.494
PS + 0.100% CuL	0.329	0.748	0.865	1.318	1.423	1.560
PS + 0.200% CuL	0.344	0.861	0.968	1.456	1.609	1.730
PS + 0.400% CuL	0.356	0.936	1.208	1.538	1.745	1.970

The rate of changing in the absorption spectrum with respect to time of irradiation depends on the concentration of the complex additive which increases with increasing concentration of the complex due to increase the active substance (figure 2-6). For the purpose of calculating the rate constant for photolysis of polymeric chips in the presence of complex additive, this achieved by drawing the relationship between the time of irradiation and the logarithm of absorption in (A_∞-A_t) (figure 7-11) and the slope was a straight line, which shows that the interaction light of this complex was of the first class which was the determinant of the constant rate of photolysis (K_d) in different concentrations previously determined and under the same conditions table 2, which shows that the values of (K_d) be sensitive to concentrations of the additive where increases their values in accordance with corresponding previous studies [15], this confirms that the additive accelerates the process of interaction between the polymer and light.
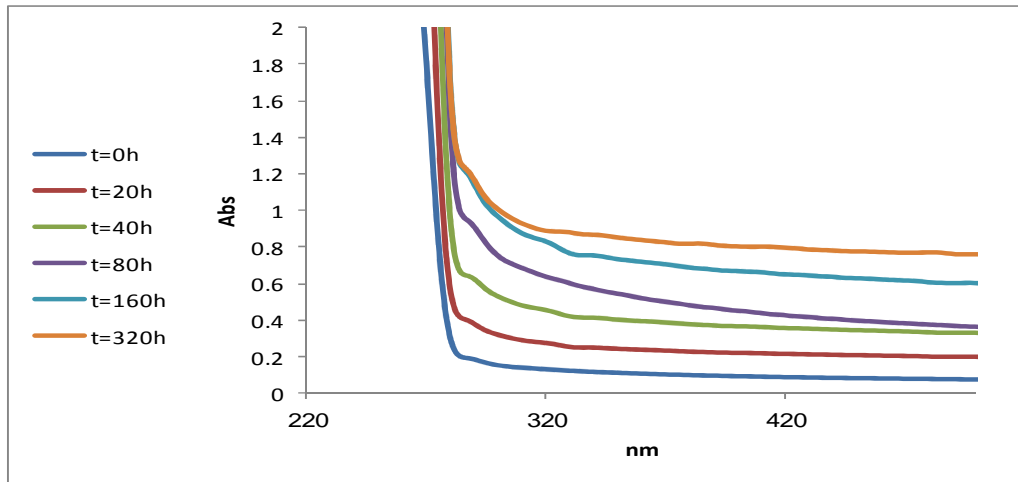
Figure 1: Change in the Spectrum of UV-Vis for Pure Polystyrene with Thickness (70±5 µm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm
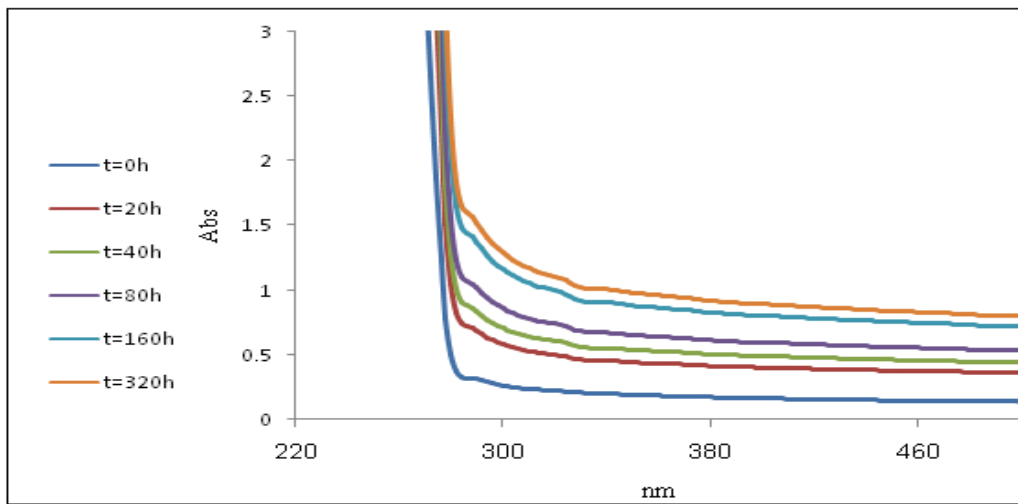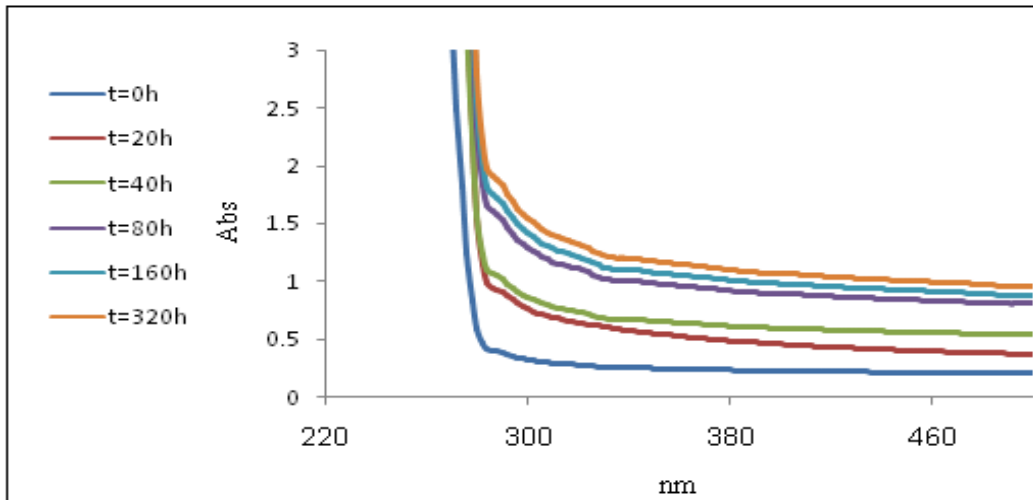

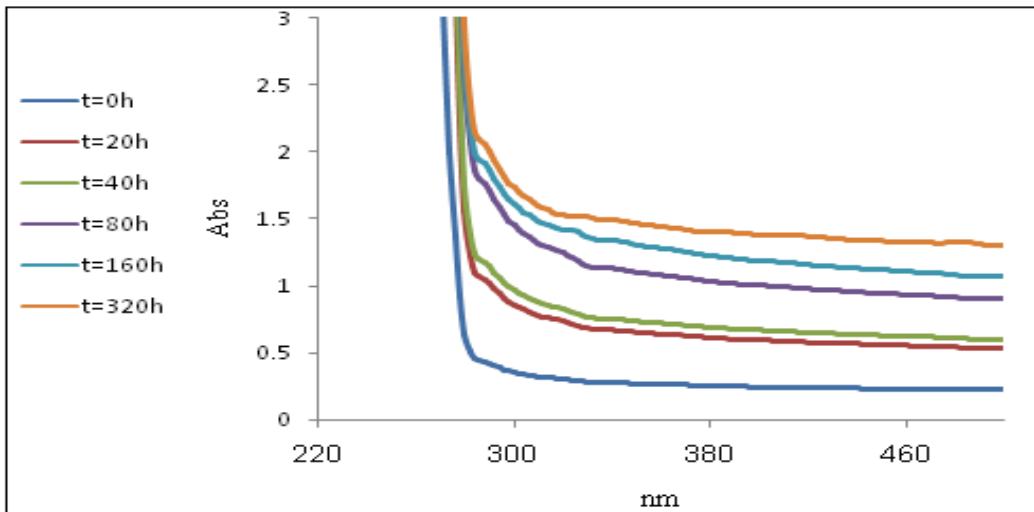**Figure 2: Change in the Spectrum of UV-Vis for Polystyrene Containing Concentration (0.025%) of the Complex (Cu-L) with Thickness (70±5 µm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm**
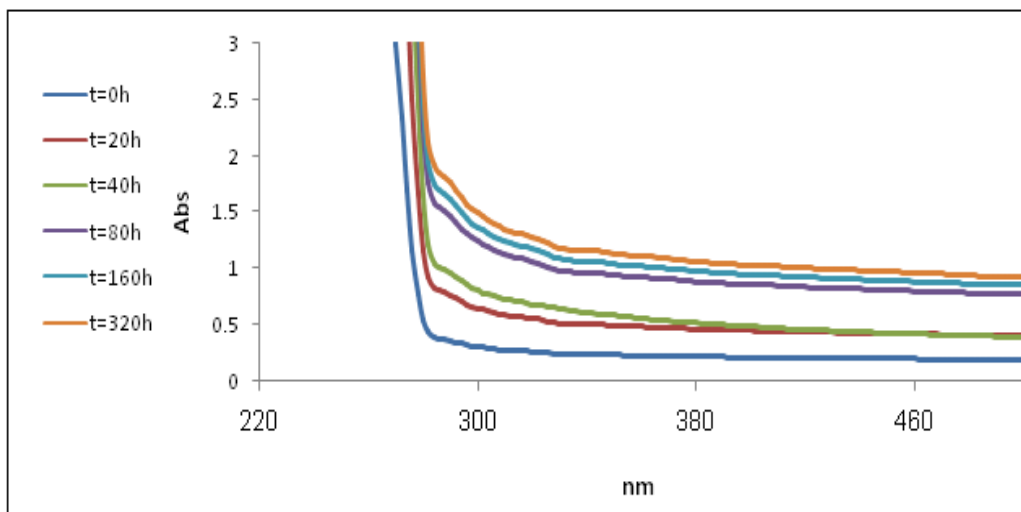
Figure 3: Change in the Spectrum of UV-Vis for Polystyrene Containing Concentration (0.05%) of the Complex (Cu) with Thickness (70±5 µm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm

Figure 4: Change in the Spectrum of UV-Vis for Polystyrene Containing Concentration (0.1%) of the Complex (Cu-L) with Thickness (70±5 μm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm

Figure 5: Change in the Spectrum of UV-Vis for Polystyrene Containing Concentration (0.2%) of the Complex (Cu-L) with Thickness (70±5 μm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm
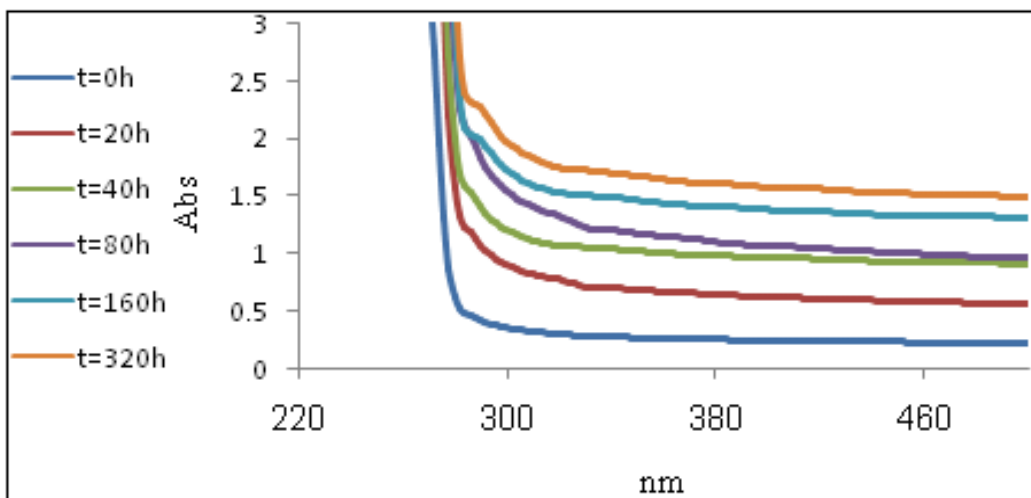

Figure 6: Change in the Spectrum of UV-Vis for Polystyrene Containing Concentration (0.4%) of the Complex (Cu-L) with Thickness (70±5 μm) at Different Times of Irradiation and Calculated at a Wavelength of 300 nm
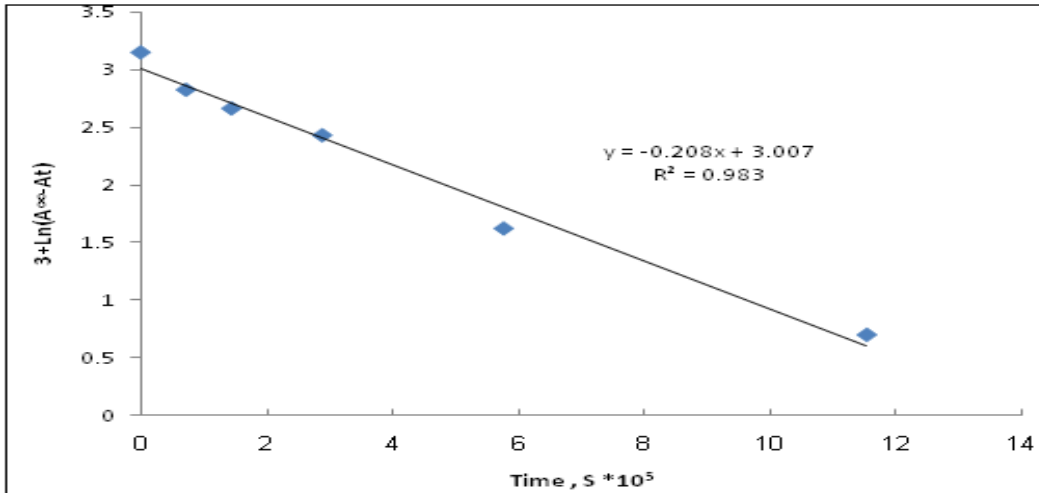
Figure 7: The Relationship between the Logarithm of Polystyrene Films Containing of Complex (Cu-L) with Thickness (70±5 μm) and Concentration (0.025%) with Irradiation Time
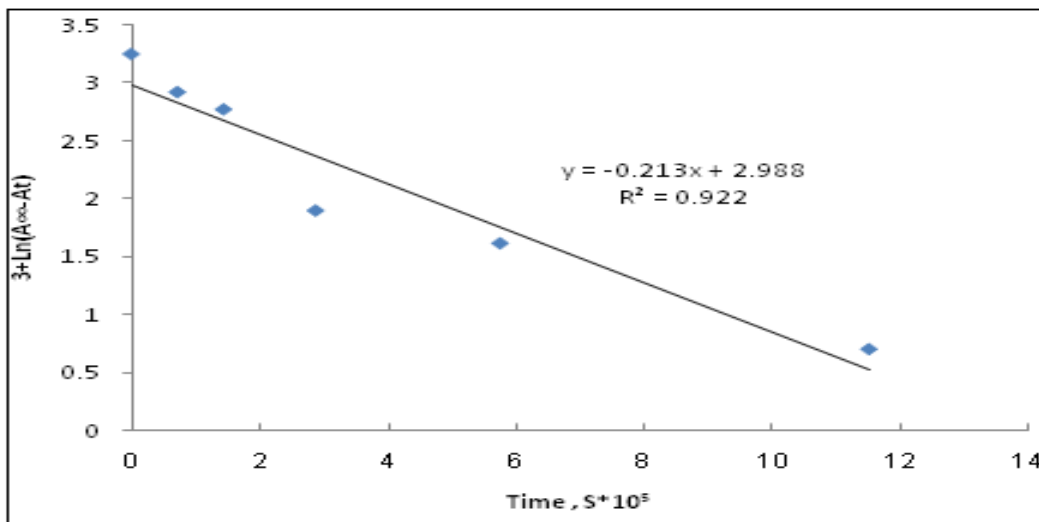

Figure 8: The Relationship between the Logarithm of Polystyrene Films Containing of Complex (Cu-L) with Thickness (70±5 μm) and Concentration (0.05%) with Irradiation Time
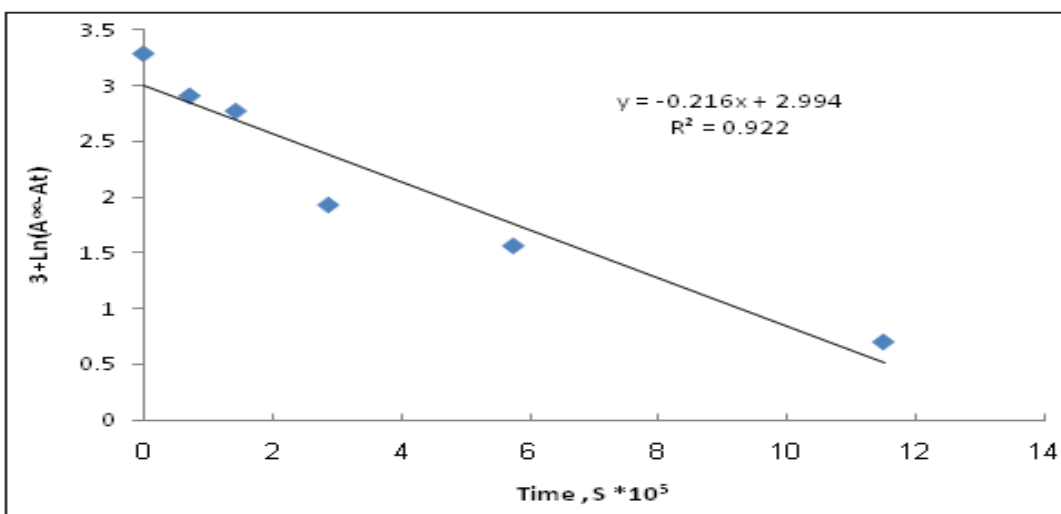

Figure 9: The Relationship between the Logarithm of Polystyrene Films Containing of Complex (Cu-L) with Thickness (70±5 μm) and Concentration (0.1%) with Irradiation Time

Figure 10: The Relationship between the Logarithm of Polystyrene Films Containing of Complex (Cu-L) with Thickness (70±5 μm) and Concentration (0.2%) with Irradiation Time
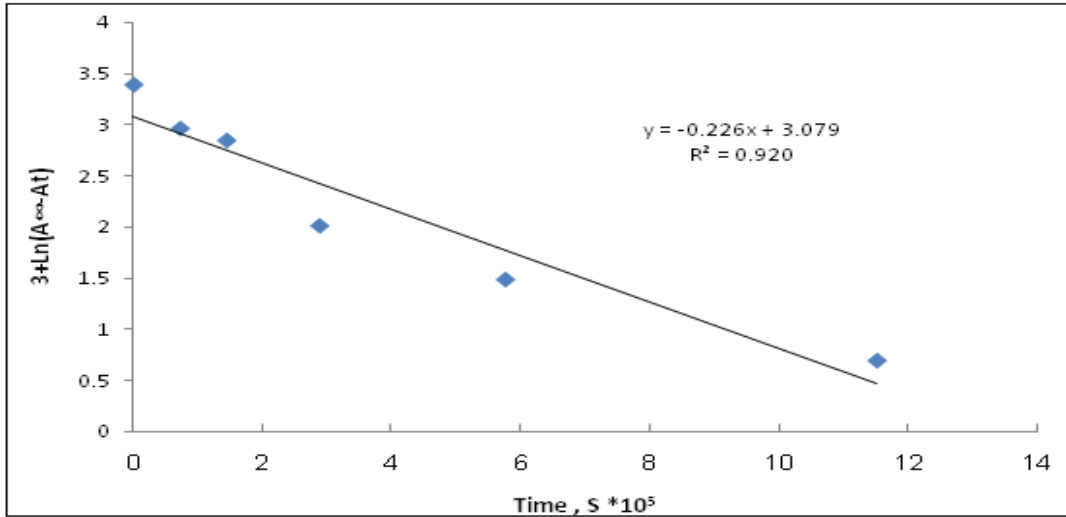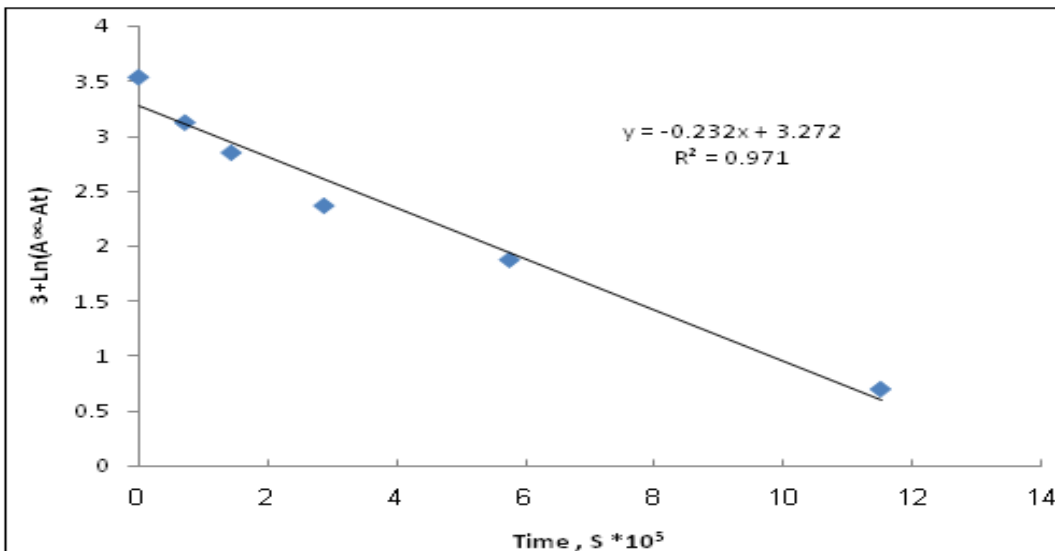

Figure 11: The Relationship between the Logarithm of Polystyrene Films Containing of Complex (Cu-L) with Thickness (70±5 μm) and Concentration (0.4%) with Irradiation Time

Table 2: Values Constants of Rate Decomposition K_d of the Complex (Cu-L) in Polystyrene Chips

$K_d(Sec)^{-1}X10^{-4}$	Concentrations
2.087	0.025
2.139	0.05
2.161	0.1
2.267	0.2
2.321	0.4

IR Spectra

The exposure to pure polystyrene to high-energy rays of wavelength (365nm) that leads to obvious changes in the spectrum of infrared (IR) [24] which gave two broad bands, the first band of carbonyl group (C=O) appears at (1600-1700cm^{-1}), which increases with irradiation time [25]. This band presence with very few values before the start of the process of irradiation for chips due to stress of thermal oxidative through the manufacturing process (figure 12).

The second band of hydroxyl and hydroperoxide polymer appears at range (3180-3600 cm^{-1}), where increases the value of the absorbance with the increase of the concentration of the complex (figure 13). Therefore the value of the coefficient growth of absorption of hydroxyl group (I_{OH}) and of carbonyl group (I_{CO}) are higher in the case of high concentrations of the additive (tables 3,4) and (figure 14,15), which were calculated by use the base-line method [26], this results correspond with the values calculated from the decomposition constant values (highest value K_d). Also, calculations showed an average molecular weight by viscometry method of polymeric chips before and after addition, that this average decrease with increase the time of irradiation and the concentration of the complex additive compared with that of the reference due to the fragmentation of chains of polymeric chains (tables 5, 6) and appears (figure 16) that the decrease at viscous molecular weight be fast at the beginning of irradiation and then slow down and that leads to break weak bonds [27].
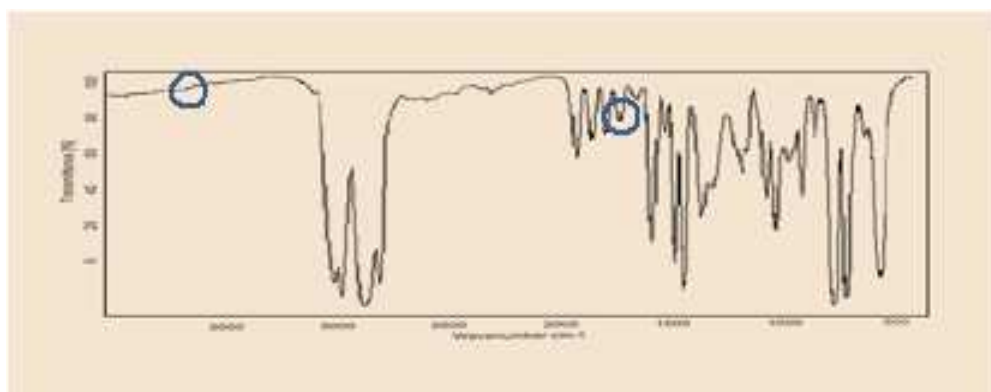

Figure 12: Infrared Spectrum of Pure Polystyrene Film with Thickness (70±5 µm) before Irradiation
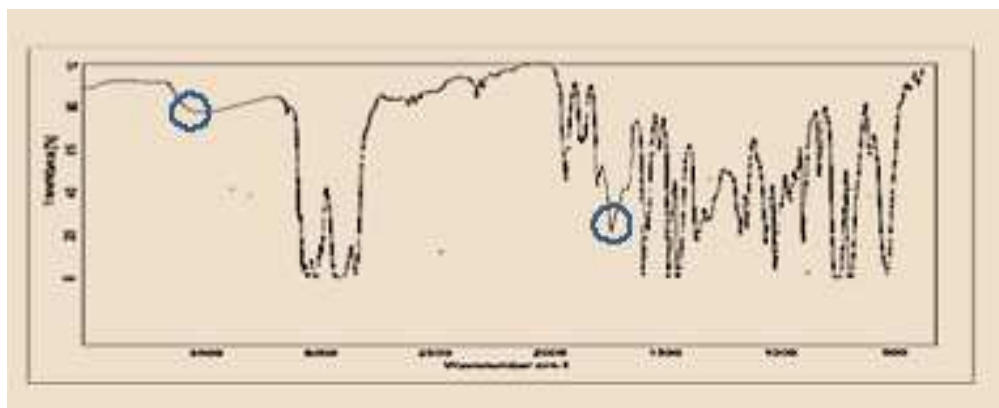

Figure 13: Infrared Spectrum of Polystyrene Film with Thickness (70±5 μm) Containing Concentration (0.1%) of the Complex (Cu-L) and the Time of Irradiation (160 Hours)

Table 3: Coefficient Values Carbonyl (I_{CO}) with Irradiation Time for Complex (Cu-L)

| Percentage by Weight for Additives W%	Irradiation Time (hr.)				
	0.0	40	80	160	320
PS	0.157	0.354	0.620	0.803	1.125
PS + 0.025	0.170	0.518	0.865	1.187	1.266
PS + 0.05	0.175	0.650	0.976	1.296	1.387
PS + 0.1	0.179	0.774	1.203	1.501	1.565
PS + 0.2	0.186	0.861	1.350	1.557	1.614
PS + 0.4	0.193	0.989	1.480	1.618	1.663

Table 4: Coefficient Values Hydroxyl (I_{OH}) with the Irradiation Time of the Complex (Cu-L)

Percentage by Weight for Additives W%	Irradiation Time (hr.)				
	0.0	40	80	160	320
PS	0.000	0.106	0.156	0.256	0.312
PS + 0.025	0.000	0.202	0.291	0.330	0.417
PS + 0.05	0.000	0.237	0.354	0.403	0.462
PS + 0.1	0.000	0.280	0.399	0.448	0.550
PS + 0.2	0.000	0.357	0.470	0.534	0.613
PS + 0.4	0.000	0.421	0.565	0.625	0.679

The average viscous molecular weight (figure 17) is proportional to the square of the molecular weight with time. The results showed that the bonds between the polymer chains were random along the polymeric chain and confirmed by the linear relationship of the average cut the chain and the degree of degradation with time (figure 18, 19), respectively [28], which shows that the values of (S) and (α) of chips supported by complex additive are higher than for chips the pure of polystyrene. These results gave perspective for using of complex as a good catalyst for photodegradation of plastic materials to accelerate the decomposition to reduce the environmental pollution.
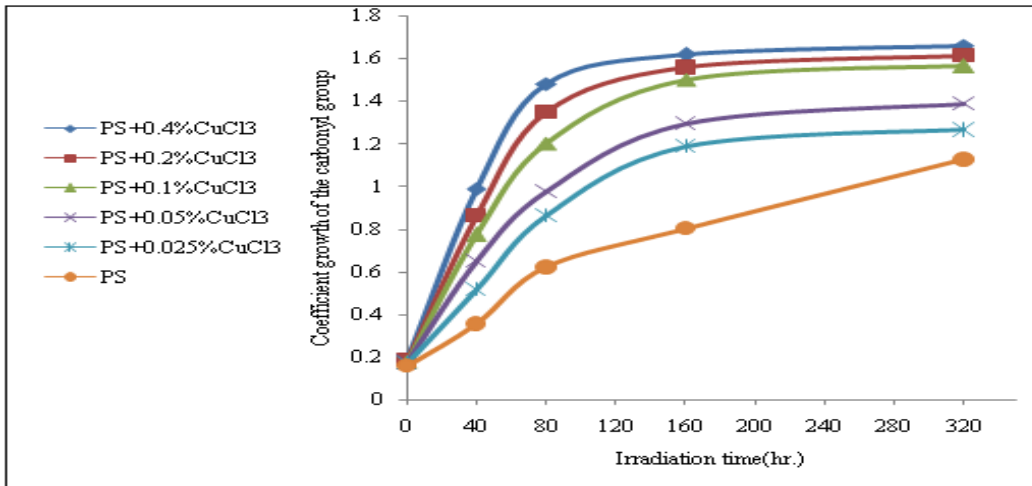
Figure 14: The Relationship between the Absorption Coefficient of the Carbonyl and Irradiation Time of the Results Listed in the Table (3)
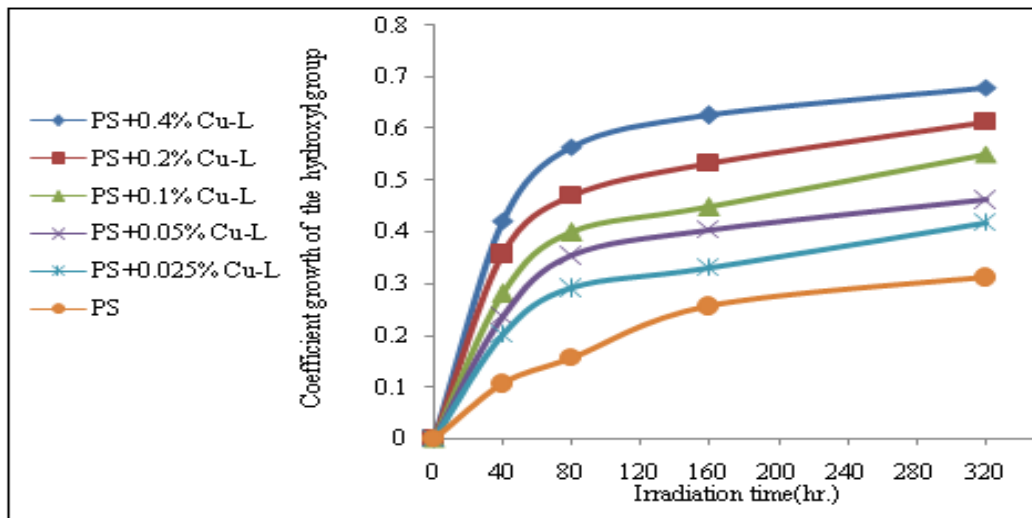

Figure 15: The Relationship between the Absorption Coefficient of Hydroxyl and Irradiation Time of the Results Listed in the Table (4)

Table 5: Values Calculated from Measuring of the Viscous Molecular Weight for Pure Polystyrene

Irradiation Time (hr.)	$\overline{Mv} \times 10^6$	$\overline{(Mv)}^2 X 10^{11}$	$\dfrac{dMv}{dt} = \dfrac{M_{vo} - M_{vt}}{t}$	The Degree of Polymerization (P)	$\dfrac{1}{P} X 10^{-4}$	The Degree of Degradation $\alpha \times 10^{-4}$	Average Cut Series (S)
0.0	1.085	11.772	∞	10417.666	0.959	0.0	0.0
20	0.863	7.447	3.083	8286.125	1.206	0.247	0.257
40	0.724	5.241	2.506	6951.512	1.438	0.479	0.499
80	0.651	4.238	1.506	6250.600	1.599	0.640	0.666
160	0.585	3.422	0.868	5616.898	1.780	0.821	0.855
320	0.457	2.088	0.545	4387.902	2.278	1.319	1.374

Table 6: Values Calculated from Measuring of the Viscous Molecular Weight for Polystyrene with Complex (Cu-L)

Irradiation Time (hr.)	$\overline{Mv} \times 10^6$	$\overline{(Mv)}^2 X 10^{11}$	$\dfrac{dMv}{dt} = \dfrac{M_{vo} - M_{vt}}{t}$	The Degree of Polymerization (P)	$\dfrac{1}{P} X 10^{-4}$	The Degree of Degradation $\alpha \times 10^{-4}$	Average Cut Series (S)
0.0	1.085	11.772	∞	10417.666	0.959	0.0	0.0
20	0.714	5.097	5.152	6855.496	1.458	0.499	0.520
40	0.637	4.057	3.111	6116.178	1.635	0.676	0.704
80	0.575	3.306	1.770	5520.883	1.811	0.852	0.887
160	0.502	2.520	1.012	4819.971	2.074	1.115	1.162
320	0.354	1.253	0.634	3398.943	2.942	1.983	2.066
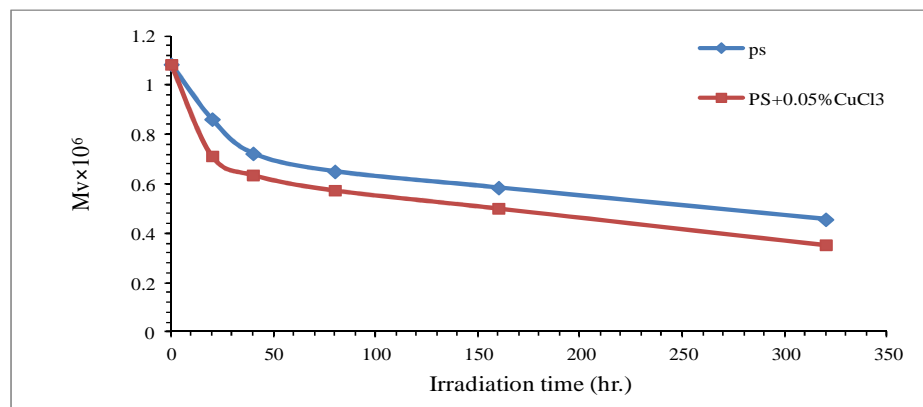
Figure 16: Relationship between Average Viscous Molecular Weight with Irradiation Time for Polystyrene with Thickness (70±5 μm) Presence and Absence of Concentration (0.05%) of the Complex (Cu-L)
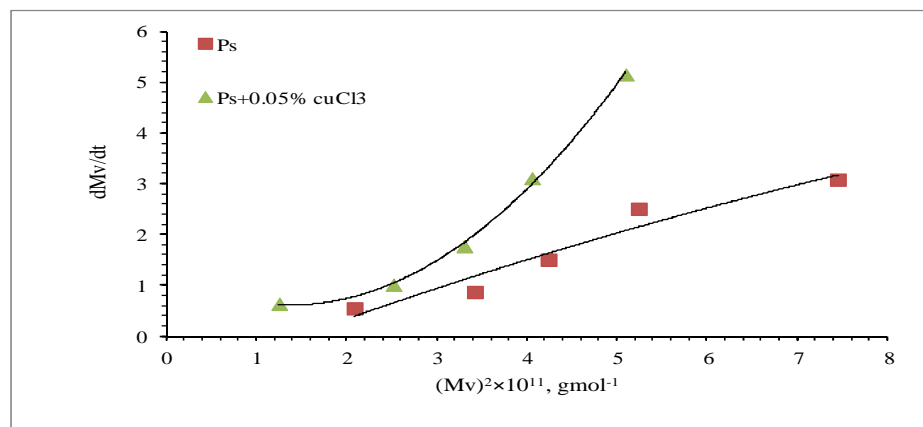
Figure 17: Relationship between Decreases of the Average of Molecular Weight (dMv/dt) and the of Viscous Molecular Weight for Polystyrene with Thickness (70±5 μm) Presence and Absence of Concentration (0.05%) of the Complex (Cu-L)
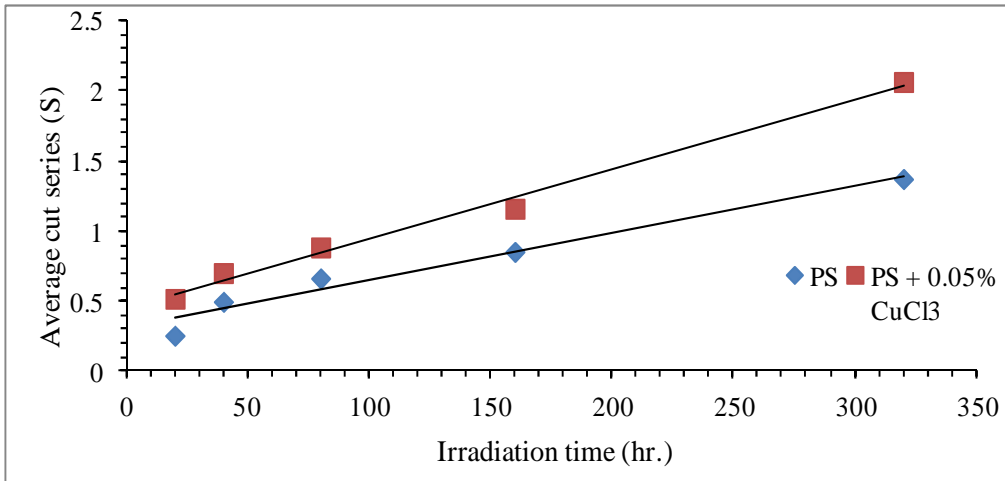
Figure 18: Relationship between Average Cut Series (S) with Irradiation Time for Polystyrene with Thickness (70±5 μm) Presence and Absence of Concentration (0.05%) of the Complex (Cu-L)
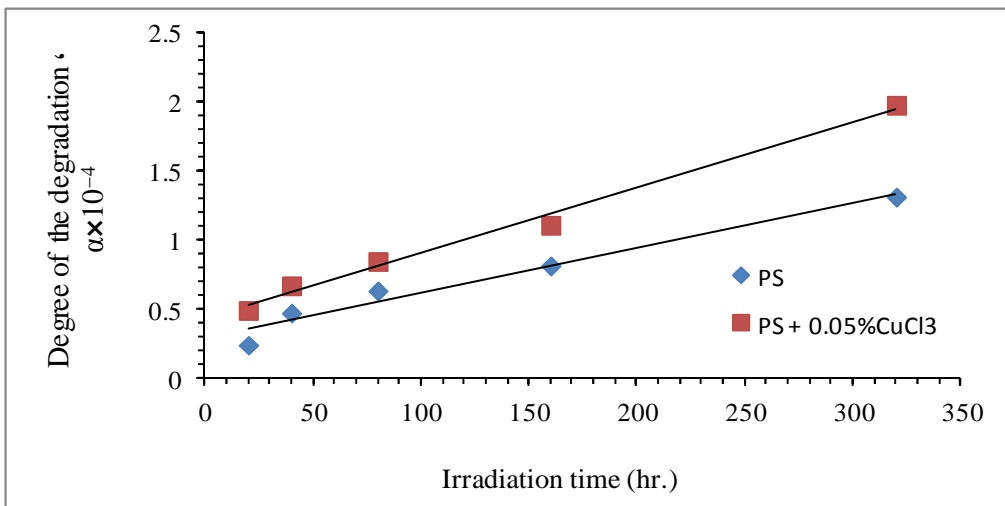

Figure 19: Relationship between Degree of Degradation (P) with Irradiation Time for Polystyrene with Thickness (70±5 μm) Presence and Absence of Concentration (0.05%) of the Complex (Cu-L)

CONCLUSIONS

- Addition of complex of copper ion (Cu II) increased of the photodegradation due to absorption of ultraviolet (UV), where the complex containing of chromophors increasing photo-oxidation under atmospheric oxygen via formed free radicals.

- Effect of the time factor, it was found that the rate of degradation increasing with exposing irradiation period at (320 hrs.).

- Study the effect of the different concentrations of the complexes in the degradation, it was found that the rate of degradation of polymer increases with increasing concentration for each complex.

- The results and calculations for average viscous molecular weight ($\overline{Mv}$), average numerical cut the chain (S) and the degree of degradation (α), confirmed increasing of photodegradation via photo-oxidation.

REFERENCES

1. Grassie, N.; Scott, G; *Cambridge University Press, London*, **1985**.

2. Trozzolo, A. M; *(W.Hawkins), Wiley Interscience Publishers*, **1971**, 159.

3. Sivaram, S.; Singh R. P.; *Adv. Polym. Sci.*, **1991**, 101,169.

4. Gugumus, F.; (G.Scott,ed.), *Elsevier, Amsterdam,* **1990**, 169-210.

5. Rabek, J. F.; Ranby, B.; *John Wiley, NewYork*, **1975**.

6. Ranby, B.; Rabek, J. F.; (Garner, D. P.; Stahl, G. A.; eds.), *ACS.Symp. ACS Washington, D. C. Ser.*, **1981**, 229, 291.

7. Geuskens, G.; David, C.; *(G.Geuskens, ed.), Halsted Press, NewYork*, **1975**, 113.

8. Weir, N. A.; *(N,Grassie, ed.), Applied Science Publishers, Ltd., London*, **1982**, 4, 143.

9. Cozzens, R. F. ; Manitz, W. B. ; Fox, R. B. ; *J. Chem. Phys.* **1968**, 48, 581.

10. Geuskens, G.; *(N,Grassie, ed.), Applied Science Publishers, Ltd., London*, **1981**, 3, 207.

11. Kovacevic, V.; Bravar, M.; Hace, D.; *Polym. Photochem.,* **1984**, 4, 393.

12. Kubica, J.; Waligora, B.; *Eur. Polym. J.,* **1977**, 13, 325.

13. Ranby, B.; Lucki, J.; *Pure Appl Chem.,* **1980**, 52, 295.

14. Wolinski, L.; Witkowski, K.; Turzynski, Z.; *Makromol. Chem.*, **1984**, 185, 75, 725.

15. Hameed, K. A.; Samar, A. A.; *J. of Anbar for Pure Science*, **2013**, 7, 1.

16. Tarik, A. A.; Hameed, K. A.; Ahmed M. M.; *J. of Anbar for Pure Science*, **2007**, 1, 2.

17. Duha, A. A.; *Master thesis, Iraq*, **2000**.

18. Chandra, R.; Singh, B. P. Singh, S.; Handa, S. P.; *polymer Sci.*, **1981**, 22, 523.

19. Kato, Y.; Carlesson, D. J.; Wiles, M. J.; *Appl. Polym Sci.*, **1969**, 13, 1447.

20. Pohs, J. E.; *suppl.*, **1984**, 654.

21. Jain M. P.; Kumar, S.; *Talanta*, **1977**, 24, 149.

22. Emmanuel, C.O.;, Emmanuel chukwuemeka okafor, *Talanta*, **1978**, 25, 241-242.

23. Pospisil, J. D.; *Polymer Composites. Makroleculare Chemie,* **1994**, 216, 55.

24. Kuzina, S. I.; Mikhailovm, A. I.; *Eur Polymer. J.*, **1998**, 34, 1157.

25. Lucki, J.; Ranby, B.; *J. Poly. Deg. Stab.*, **1979**, 1, 1, 22.

26. Alliwi, S. M.; Al-Ani, R. R.; Awad, D. A.; *Iraqi J. Polymers*, **2001**, 5, 107.

27. Jellinek, H. H.; *Amsterdam, Oxford*, N. Y., **1978**, 198.

28. Chandra, R.; Handa, S. P.; *J. Appl. Polymer. Sci.*, **1982**, 1945, 27, 78.