



(RESEARCH ARTICLE)



Synthesis of heterocyclic ring (1,2,4-triazole) as polystyrene photo stabilizer

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Abstract

New heterocyclic compounds contain triazole ring (play very important role in photostabilization as UV absorber) synthesized by reaction between the di Schiff base (compound 3) with aromatic alkyl halide (Benzyl bromide) and shows there activity as photostabilizer for polystyrene through exposure to the UV-Light (300 hours). Finally Infrared spectroscopy, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and instrumental methods were used to characterize products and their structures.

Keywords: Triazole; Photostability; Heterocyclic compounds; Schiff base; Synthesis

1. Introduction

Heterocyclic chemistry is a detached branch of organic chemistry with a lengthy history and successful future. Heterocyclic chemistry now brings reagents and synthetic process of its own to the production of pharmaceuticals [1], insecticides [2], as well as connected fields like polymers [3], dyes [4, 5], and material sciences [6]. 1,2,4-triazoles and its derivatives are heterocyclic compounds involve five-membered ring includes two atoms of carbon and three atom of nitrogen [7]. They are UV absorbers and play an essential role in photostabilization [8, 9]. The photostabilization method entails the use of chemicals (preferably with a heterocyclic ring) and their application to polystyrene (PS) (one of the most valuable assets of the modern plastic manufacture, owing to its premium physical features and low cost, it used in a wide range of applications, including electronics, construction, home, and medical equipment, as well as disposable food services.) [10]. When PS is exposed to natural sunshine, it undergoes oxidative destruction [11]. Unmodified polymers are brittle and sensible to variables and environmental conditions, make it occasionally unusable matter [12]. The numerous uses due to it scheappriceo discover us trial polymer. Polymer modification has gotten more attention since it gives the modified material specific qualities such improved thermal stability, multiphase physical sensations, compatibility, impact reaction, elasticity, and rigidity [13].

2. Instruments

Melting temperatures were measured by using (FALC melting point device). Fourier-transform infrared spectroscopy were measured by using instrument BRUKER (FT.IR), KBr disc $^1\text{H NMR}$, $^{13}\text{C NMR}$, Microscope, SEM, and AFM.

3. Chemicals

Chemicals were analar or pure grade, and solvents were dried and purified

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3.1. Synthesis

3.1.1. Synthetic pathway of 4-hydroxybenzohydrazide (1).

4-hydroxy methyl benzoate (0.03 mol, 5 g) added to 25ml ethanol to reflux for 4 hours in a round bottom flask with hydrazine hydrate (0.10 mol, 5 ml). The precipitate formed filtered, dried and then washed by ethanol [14].

3.1.2. Synthetic pathway of 4-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl)phenol (2).

4-hydroxybenzohydrazide (0.03 mol, 4.8g) was added to solution contain dissolved potassium hydroxide (0.05 mol, 3 g) in (25 mL) of absolute ethanol. Mixture was cooled in ice bath with stirring. Add to this mixture (0.19 mole, 11.5 mL) carbon disulfide in small amounts with constant stirring. Overnight, at room temperature, the reaction mixture was left to stir constantly. The potassium-2-(4-hydroxybenzoyl) hydrazinecarbodithioate formed and reacted with hydrazine hydrate (0.14 mol, 7 ml) with reflux for 8 hours. The mixture color changed to green along with liberation of H₂S (tasted by paper covered with lead acetate) and a homogenous solution resulted. By addition cool water (20 ml) and acidification with concentrated HCl, a white solid was precipitated, filtered, ethanol-washed and left to dry [14].

3.1.3. Synthesis pathway of 4,4'-(((1,4-phenylenebis(methaneylylidene)) bis (azaneylylidene)) bis(5-mercapto-4H-1,2,4-triazole-4,3-diy))diphenol (3).

compound (2) (2 mol, 0.5 g) with terphthaldehyde (1 mol, 0.3 g) were mixed in (10 ml) DMF and glacial acetic acid (three drops), then mixed solution was refluxed for about 10 hours. Then Precipitate filtered, dried and washed by ethanol [15].

3.1.4. Synthesis pathway of 1,1'- (1,4-phenylene) bis (N- (3-(4-(benzyloxy) phenyl) -5-(benzylthio)-4H-1,2,4-triazol-4-yl)methanimine)(4).

Dissolve (1mol. 0.1g) of compound (3) in 10 ml of acetone with 2 drops of DMF and (2mol. 0.04g) of K₂CO₃ in a round bottom flask. Benzyl bromide (4mol. 0.2g) was added after dissolving (4). The mixed solution was stirred overnight before being placed into ice water, filtered, and the precipitate allowed to dry before proceeding to the next stage [16]. As shown in scheme 1

3.1.5. preparation of modified films.

After dissolving (0.005g) of product (4) in 10 ml chloroform with 2 drops of DMSO, add (0.5g) of polystyrene to the round bottom flask and stir for more than 3 hours, pour into the glasses sink and let for 24 hours to evaporate all chloroform by using the evaporation technique [17].

4. Results and discussion

1, 2, 3, and 4 compounds are synthesized in Scheme 1. The physical properties as well as FT-IR spectrum data are listed in the tables below.

Table 1 Physical feature of [2, 3, 4] Compounds

No.	Chemical Formula	Molecula Weight (g/Mol)	Color	Melting Point (C°)	Yield (%)
2	C ₈ H ₈ N ₄ OS	208.24	White	240-242	94
3	C ₂₄ H ₁₈ N ₈ O ₂ S ₂	514.58	Light yellow	Over300	79
4	C ₅₂ H ₄₂ N ₈ O ₂ S ₂	875.08	Yellow	228-230	35

Scheme 1 shows the general synthesis procedure for (2, 3, and 4) compounds. And, as shown by FT-IR device values, the appearance of (1522-1591) cm⁻¹ due to the (C=N) group of the triazole ring, along with two other characteristic stretching vibration bands at (3309 and 3269) cm⁻¹ belonging to the (NH₂) group, that disappeared completely when Schiff base formed due to the formation of C=N at cm⁻¹ (1652). Table 2 shows the FT-IR typical spectra for compounds [2], [3], and [4].

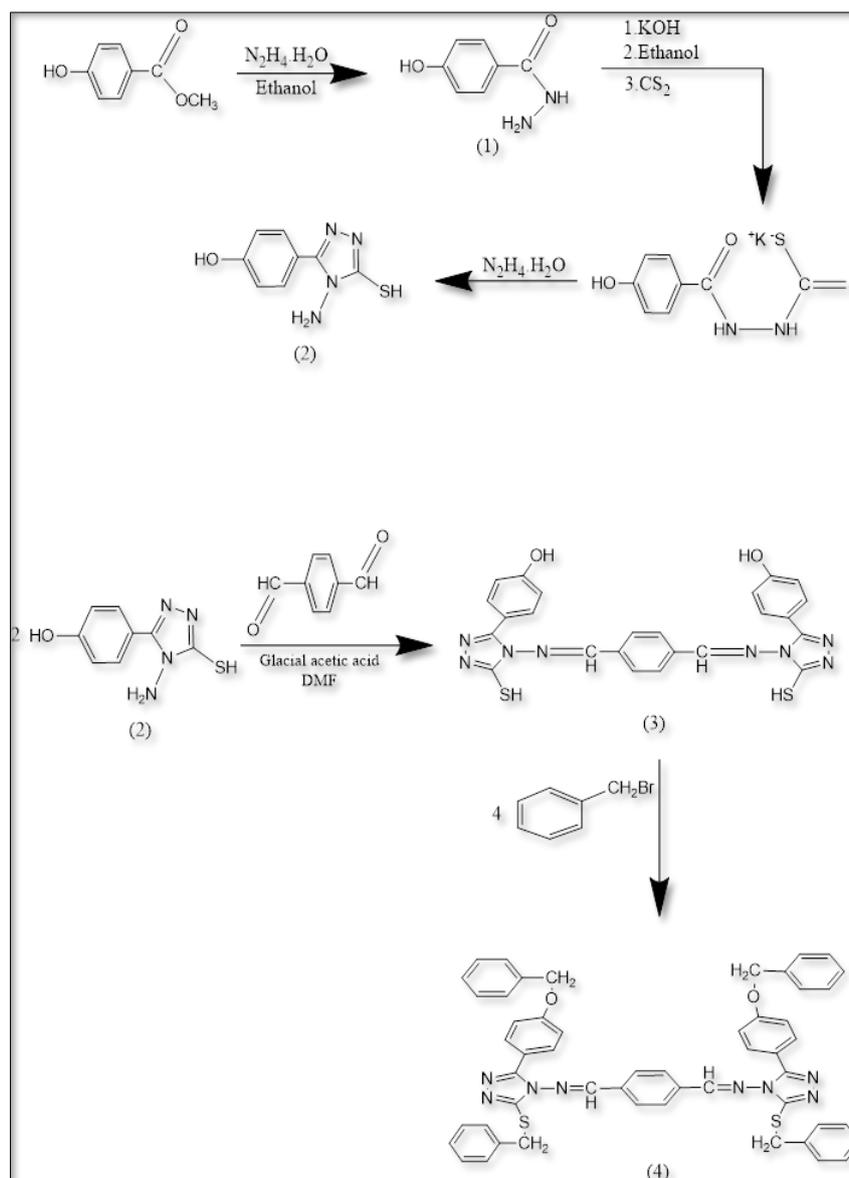


Figure 1 General synthetic pathway of (1, 2, 3, and 4) compounds

Table 2 FT-IR Spectral data of [2, 3, 4] compounds

No.	Frequency numbers (cm^{-1})
2	(1522 cm^{-1}) for C=N of triazole ring. stretching (3309 cm^{-1} and 3269 cm^{-1}) for symmetric and asymmetric NH_2 and (653 cm^{-1} , 2799 cm^{-1}) for C-S and S-H group respectively Figure 2
3	(3215 cm^{-1}) for O-H group, (3073 cm^{-1}) for C-H aromatic, (2926 cm^{-1} and 2801 cm^{-1}) for C-H aliphatic, (1652 cm^{-1} , 1591 cm^{-1}) for C=N exocyclic and endocyclic respectively. Beside to disappearance of (3309 cm^{-1} and 3269 cm^{-1}) for symmetric and asymmetric NH_2 . Figure 3
4	(3032 cm^{-1}) for C-H aromatic, (2950 cm^{-1} and 2860 cm^{-1}) for C-H aliphatic, (1623 cm^{-1} , 1555 cm^{-1}) for exocyclic and endocyclic C=N and (837 cm^{-1}) for p-position, (673 cm^{-1}) for C-S and (1058 cm^{-1}) for C-O. Figure 4

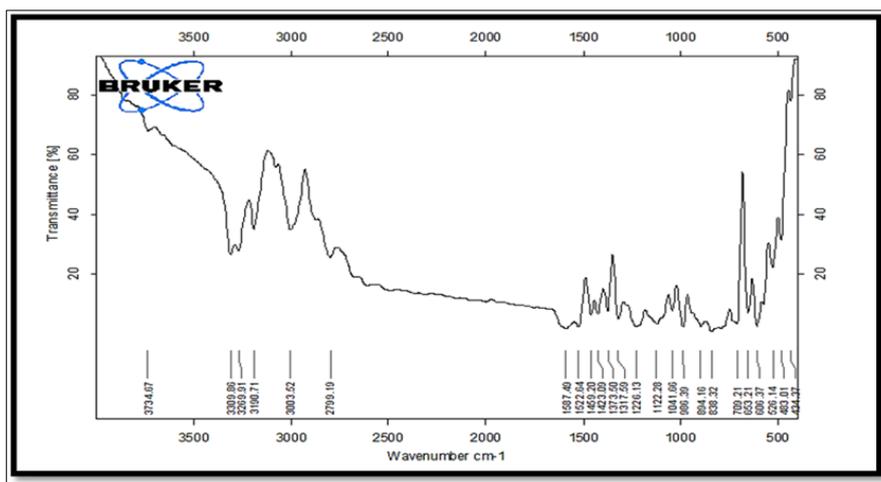


Figure 2 FT-IR of compound 2

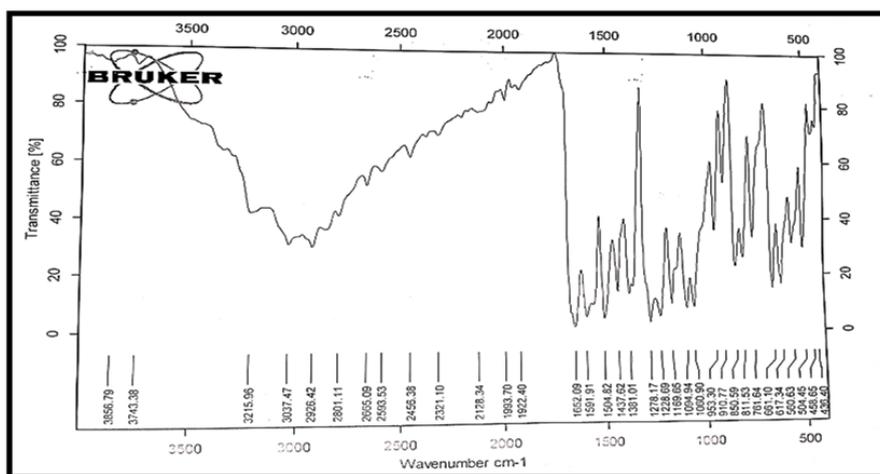


Figure 3 FT-IR of compound 3

5. Characterization on polystyrene

5.1. Using weight loss method

The formation of free radical moieties during photooxidation of polystyrene causes cross-linking of the polymeric chains. To find out how effective complex (4) is as stabilizer, the weight loss was estimated using equation [1] after the polystyrene was irradiated for 300 hours.

$$\text{Weight loss \%} = [(W1 - W2) / W1] 100 \% \dots\dots [1]$$

Table 4 Measurement of weight loss for polystyrene with additives

Additives	Irradiation time (hours)						
	0	50	100	150	200	250	300
polystyrene	0	0.831	0.869	1.025	1.284	1.37	1.549
PS + 4	0	0.582	0.593	0.642	0.658	0.764	0.839

The graph between weight loss and irradiation time show that polystyrene with additive more effective than polystyrene alone.

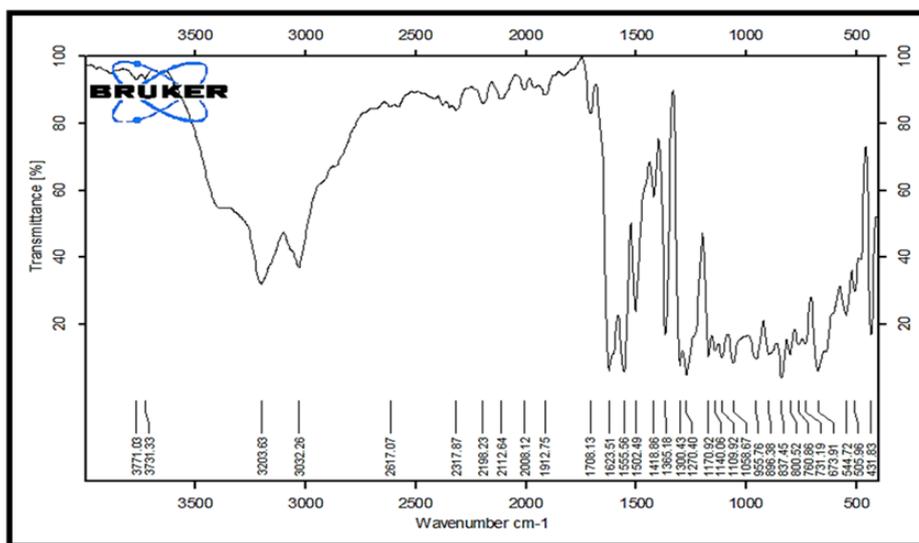


Figure 4 FT-IR of compound 4

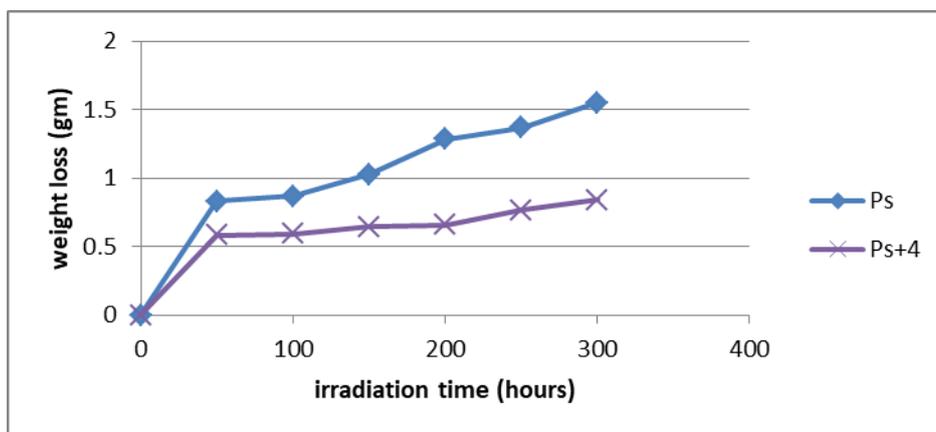


Figure 5 Weight loss vs. irradiation time of polystyrene with (4) compound

5.2. By Light Microscope, AFM, SEM, and EDX

To obtain a clear image of the surface of polystyrene films, light microscopes, atomic force microscopes, and scanning electron microscopes (SEM) are all used. Additional information about the chemical component found in polystyrene film can also be obtained using EDX. When polystyrene was irradiated, it generated cracks, roughness, and a change in color due to photo-degradation, which caused polystyrene bonds to break, as shown in the photographs below. The surface appeared softer and had fewer cracks after adding (4) compound to the polymer. Figure 6, 7, 8, 9.

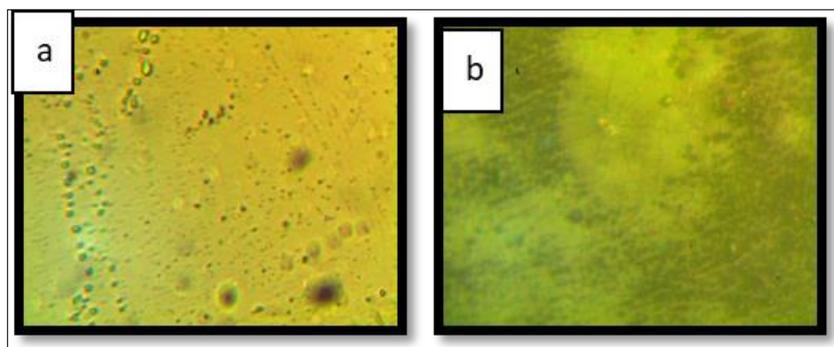


Figure 6 Light Microscope image of (a) polystyrene (b) PS + 4

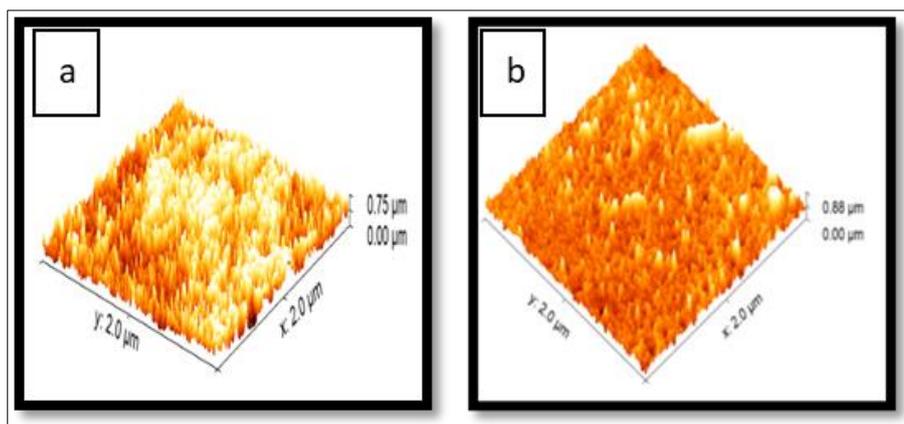


Figure 7 AFM image of (a) polystyrene (b) PS+ 4

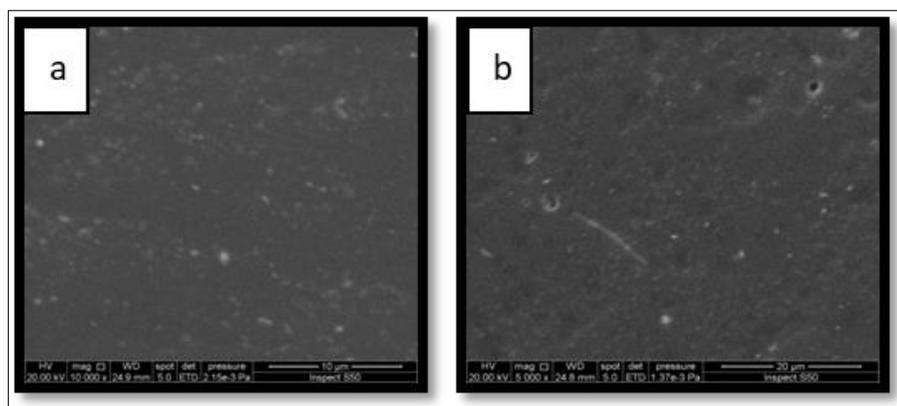


Figure 8 SEM image of (a) polystyrene (b) PS+ 4

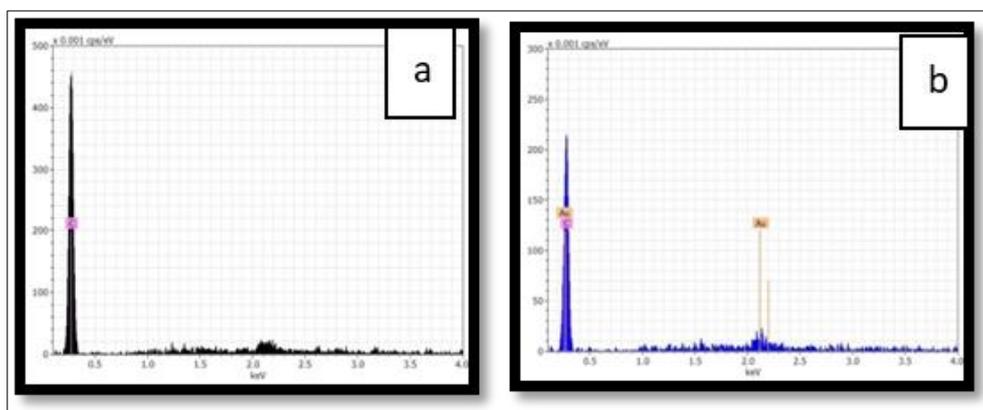


Figure 9 EDX of (a) polystyrene (b) PS +4

6. Conclusion

From synthesized compounds and their characterization by (Infra-red, hydrogen and carbon nuclear magnetic resonance) spectrum data and applied on polystyrene film and from Microscope, AFM, SEM, and EDX conclude the

polymer with (4) compound efficient more than polymer without additives that ensure the (4) compound can be used as photostabilizer of polystyrene.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] KJ. Saunders Chapman & Hall, London & New York. 1988.
- [2] JW Nicholson. (Royal Society of Chemistry Paperbacks.
- [3] Cleiton M.da Silva ,Daniel L.da Silva , Luzia V.Modolo Advanced Research Journal.Cairo University . 2011.
- [4] Przybylski P, Huczynski A, Pyta K, Brzezinski B, Bartl F. Biological properties of schiff bases and azo derivatives of phenols. *Curr Org Chem.* 2009; 13(2): 124–48.
- [5] Bringmann G, Dreyer M, Faber JH, Dalsgaard PW, Staerk D, Jaroszewski JW, et al. Ancistrotananzanine C and related 5,10- and 7,30-coupled naphthylisoquinoline alkaloids from *Ancistrocladus tanzaniensis*. *J Nat Prod.* 2004; 67(5): 743–8.
- [6] de Souza AO, Galetti FCS, Silva CL, Bicalho B, Parma MM, Fonseca SF, et al. Antimycobacterial and cytotoxicity activity of synthetic and natural compounds. *Quim Nova.* 2007; 30(7): 1563–6.
- [7] Ashish Asrondkar, Vrushali Patil, Shantanu Pande, A.S.Bobade, AS Chowdhary. *IOSR. Journal of Applied Chemistry (IOSR-JAC).* 2013; 2278-5736(6): 16-19.
- [8] Yousif E, Al-Amiery AA, Kadhum A, Kadhum AAH, Mohamad AB. Photostabilizing efficiency of PVC in the presence of Schiff bases as photostabilizers. *Molecules.* 2015; 20(11): 19886-19899.
- [9] Mark JE. *Physical Properties of Polymers Handbook* Springer, New York. 2007.
- [10] Manzi-Nshuti C, Chen D, Su S, Wilkie CA. Structure–property relationships of new polystyrene nanocomposites prepared from initiator-containing layered double hydroxides of zinc aluminum and magnesium aluminum. *Polymer degradation and stability.* 2009; 94(8): 1290-1297.
- [11] Marek A, Kapralkova L, Schmidt P, Pflieger J, Humlicek J, Popisil J, Pilar J. *Polym. Degrad. Stabil.* 2006; 91: 444–458.
- [12] Hassan A, Sivaneswaran K. Processability study of abs impact modified PVC-U Composites - Effect of Rice Husk Ash (RHA) fillers and coupling agents. *J. Techno.* 2005; 42: 67–74.
- [13] Yousif E, Abdallah M, Hashim H, Salih N, Salimon J, Mudhaffar B, Win Y. Optical properties of pure and modified poly (vinyl chloride). *Inte. J. Ind. Chem.* 2013; 4: 1–8.
- [14] Abdul Hameed A, Hassan F. Synthesis, Characterization and Antioxidant Activity of Some 4-Amino-5-phenyl-4H-1,2,4- triazole-3-thiol Derivatives, *Int. J. App. Sci. Tech.* 2014; 4 (2): 202-211.
- [15] Arun K, Gupta, Sumeet P, Arpit P, Sanjay J. Synthesis of some 4-Amino-5-(substituted-phenyl)-4H-[1, 2, 4] triazole-3-thiol derivatives and Antifungal activity. *Int. J. of Pharm. & Life Sci.* 2012; 3(7): 0976-7126.
- [16] Usha R, Kalpattu KB. Claisen rearrangement of meta-substituted aryl propargyl ethers in poly (ethylene glycol). *Heterocycles.* 1984; 22: 1351–1357.
- [17] Rabek J, Canback G, Lucky J, Ranby B. Studies on the Photooxidation Mechanism of Polymers. IV effect of Ultraviolet Light (2537 Å) on Solid PVC Particles Suspended in Different Liquids. *J Polym Sci.* 1976; 14: 1447-1462.