



Physicochemical Studies of Polymeric Matrix containing Phenolic Dye

Samar Mabrouk¹, Dalia M. Ayad¹, Amr Mohamed Abdelghany², Ehab Abdel-Latif^{1*}

¹ Chemistry Department, Faculty of Science, Mansoura University, 35516 Mansoura, Egypt

² Spectroscopy Department, Physics Division, National Research Centre, 33 Elbehouth St., Dokki, 12311 Giza, Egypt

* Correspondence to: ehabattia00@gmx.net

Received: 9/9/2021
Accepted: 14/9/2021

Abstract: The synthesis of our targeted phenolic azo dye **6** was initiated by diazotization of 4-aminoacetophenone (**1**) and diazocoupled with resorcinol (**3**) to furnish the corresponding the product, 4-(acetylphenylazo)-resorcinol (**4**). Condensation of **4** with thiosemicarbazide afforded the corresponding thiosemicarbazone **5**, which underwent Hantzsch type reaction upon reaction with 4-chlorophenacyl chloride to yield the corresponding thiazolyl-phenylazo-resorcinol dye **6**. Polymeric matrix of poly vinyl alcohol was doped with minor concentration of the synthesized dye and their effects on the physical properties was studied including structural and optical properties .

keywords: Phenolic Dye; PVA; FTIR; HUMO-LUMO; UV/Vis.

1. Introduction

A dispersed dye is described as water-insoluble dye substantially containing, for example, cellulose acetate for one or more hydrophobic fibres and usually applied by fine aqueous dispersion. The dispersed dyes are mainly used to dye both chemical fibres (di- and triacetates) and synthetic fibres such as polyester and polyamides. Disperse dyes are compounds of small molecular size that do not contain solubilizing groups (-SO₃H, -SO₃Na, -COOH, -COONa), but have polar substituents such as -OH, -CH₂OH. They have a small but still substantial solubility in water because of their small size [1-3]. Disperse dyes came into existence two or three years after the introduction of (secondary) cellulose acetate rayon by the British Celanese Company in 1920 and first they were known as acetate dyes. None of the existing dyes then in use for natural fibers was suitable. About 1923 the suitable dyes for acetate fibers were generally accepted to have basic properties and a simple molecular structure, though it seemed like they would have poor water solubility. Yet the problem of insufficient solubility is still occurring. The discovery of the disperse technique solved this problem. Holland Ellis of British Celanese Ltd., succeeded in producing the aqueous suspension (dispersion) of a number of water insoluble azo

dyes by dispersing them in sulpho-ricinoleic acid [4,5]. A groundbreaking approach to the issue of synthetic fibre coloration was the production of dispersed dyes, which are dyes insoluble in water and applied from aqueous dispersion. The dispersed dyes are essentially insoluble in water and were prepared to be applied by grinding them into microscopic fine particles of a few microns in order in the presence of dispersing agents and then by drying the resulting suspension. By diffusion into the fibers from lower dye bath concentrations, the resulting easily dispersible solid can stain the more hydrophobic acetate fibers. The production of dispersed dyes resulted in an upsurge in new chemistry, leading to new intermediates that were unsuitable for water-soluble dyestuff synthesis. It was necessary to rethink the structural features influencing the properties of dyeing and fastness; it was necessary to invent smaller and more lightweight dye molecules that would cover the entire colour spectrum gamut.

2. Experimental Work

2.1. Synthesis of 4-(acetylphenylazo)-resorcinol (**4**):

The title azo dye **4** has been prepared from 4-aminoacetophenone and resorcinol according

to the experimental technique that described in the literature [6-8].

2.2. Synthesis of 2-(1-(4-((2,4-dihydroxyphenyl)azo)phenyl)ethylidene)hydrazine-1-carbothioamide (5):

The title azo dye **5** has been prepared by condensation of 4-(acetylphenylazo)-resorcinol (**4**) with thiosemicarbazide according to the literature procedure [6-8].

2.3. Synthesis of 4-((E)-4-((E)-1-(2-(4-(4-chlorophenyl)thiazol-2-yl)hydrazono)ethyl)phenyl)azo)resorcinol (6):

A 100 mL round bottomed flask was charged with thiosemicarbazone **5** (0.99 g, 3 mmol), ethanol (30 mL) and 0.5 mL triethylamine. 4-Chlorophenacyl chloride (0.57 g, 3 mmol) was added to the flask and then the reactions components was refluxed with stirring for four hours. The solid that formed upon cooling was separated by filtration and dried.

Reddish brown solid, m.p. = 288-290°C, yield = 72%. IR (KBr): broad centered at 3348 (O-H and N-H), 2935 (saturated C-H). ¹H NMR (DMSO-*d*₆): 2.28 (s, 3H, CH₃), 6.58 (s, 1H, Ar-H), 6.76 (d, *J* = 8.50 Hz, 1H, Ar-H), 7.08 (s, 1H, thiazole-H5), 7.41 (d, *J* = 8.50 Hz, 1H, Ar-H), 7.61 (d, 2H, *J* = 9.00 Hz, Ar-H), 7.84 (d, 2H, *J* = 9.00 Hz), 7.98 (d, 2H, *J* = 9.00 Hz, Ar-H), 8.16 (d, 2H, *J* = 9.00 Hz, Ar-H), 9.75 (s, 1H, OH), 9.97 (s, 1H, OH), 11.83 ppm (s, 1H, C=N-NH). Analysis calculated for C₂₃H₁₈ClN₅O₂S (463.94): C, 59.54; H, 3.91; N, 15.10%. Found: C, 59.28; H, 3.96; N, 15.21%.

2.4. Thin composite films preparation and characterization.

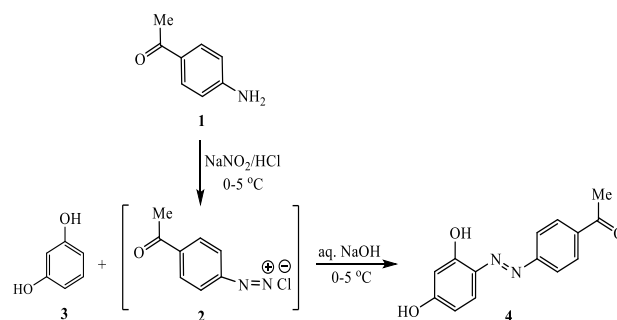
The main material used in this study is Polyvinyl alcohol (PVA), The fine white powder odourless of PVA [Mw=14,000 gmol⁻¹, Cham Lan] and synthesized phenolic dye. Pre-calculated amount of polymeric matrix was dissolved separately in a 50 ml DMSO at room temperature (25 °C) strongly stirred. Weight per volume of the studied phenolic dye was also dissolved and mixed with PVA solution. XRD applied by PANalytical X-Pert adopting CuK α radiation using 30 kV operating potential within the Bragg's angle extended from 5-80°. FT-IR absorption spectra were determined by apply the single beam Fourier transform infrared spectroscopy (Nicolet iS10,

ThermoFisher Scientific) recorded within the spectral region of 4000-400 cm⁻¹ to detect functional group of studied samples. UV/Vis. electronic spectral data were recorded in the wavelength region 200-1000 nm using spectrophotometer (Jasco V570).

3. Results and discussion

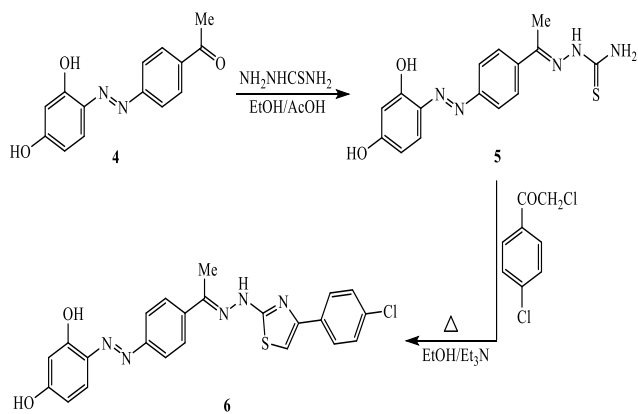
3.1. Synthesis of thiazolyl-phenylazo-resorcinol dye 6

The synthetic route for the target phenolic azo dye of the type **6** is outlined in Schemes 1 and 2. Firstly, 4-aminoacetophenone (**1**) was diazotized via treatment with the in situ prepared nitrous acid (NaNO₂ and HCl) and then diazocoupled with resorcinol (**3**) in sodium hydroxide solution to produce the corresponding the coupling product, 4-(acetylphenylazo)-resorcinol (**4**) [6-8] (Scheme1).



Scheme (1)

Condensation of 4-(acetylphenylazo)-resorcinol (**4**) with thiosemicarbazide was carried out by refluxing in ethanol and drops of acetic acid to afford the corresponding thiosemicarbazone **5** [6-8], which underwent Hantzsch type reaction upon heating with 4-chlorophenacyl chloride in ethanol and triethylamine yielded the corresponding thiazolyl-phenylazo-resorcinol dye **6** (Scheme 2). The chemical structure of phenolic azo dye **6** is supported by the compatible elemental and spectroscopic analyses. The IR spectrum recorded a broad absorption near 3348 cm⁻¹ for the O-H and N-H groups. The ¹H NMR spectrum displayed singlet for three protons at 2.28 ppm (CH₃), singlet for one proton at 7.08 ppm (thiazole-H5), and three singlet signals at 9.75, 9.97 and 11.83 ppm for the protons of two hydroxyl protons and NH proton, respectively. The aromatic protons resonated as singlet and doublet signals in the region from 6.58 to 8.16 ppm as described in the experimental section.



Scheme (2)

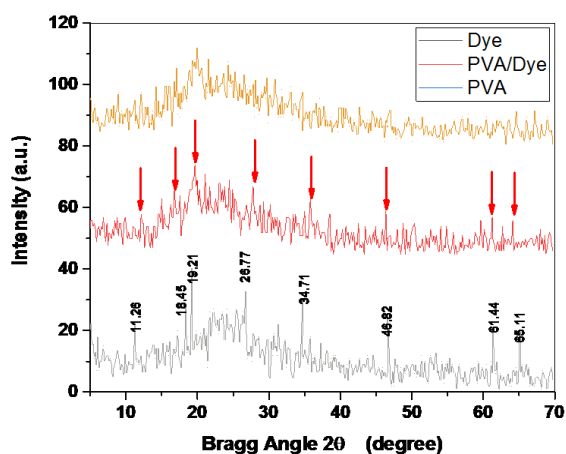


Figure (1): XRD pattern of the synthesized phenolic dye pulverized powder PVA, and PVA doped phenolic dye.

3.2. X-ray diffraction (XRD)

X-ray diffraction analysis technique can be considered as a powerful tool that employed to investigate the internal structural arrangement of studied material indicating if it is crystalline or amorphous depending on structural arrangement.

Figure (1) reveals the XRD pattern of the synthesized drug pulverized powder of 4-((*E*)-(4-((*E*)-1-(2-(4-(4-chlorophenyl)thiazol-2-yl)hydrazono)ethyl)phenyl)azo) resorcinol, PVA, and PVA doped phenolic dye. Obtained data plotted as Bragg angle 2θ versus intensity reveals a sharp diffraction peaks located at about 11.26, 18.45, 19.21, 26.77, 34.71, 46.82, 61.44, and 65.11° pointed to the crystalline nature of the synthesized Phenolic dye. PVA polymeric matrix previously reported by several authors [9-12] and characterized by halo centered at about 20° related to the semi-crystalline nature of the matrix. The interaction between PVA matrix and phenolic dye was approved through the appearance of specific

sharp band located at the same position of that of corresponding phenolic dye superimposed over the amorphous pattern.

3.3. UV Visible electronic spectral data

Spectra associated with molecules that absorb energy within the Ultraviolet and/or visible region to excite n-electrons from bonding or non-bonding states to higher anti-bonding orbitals can be used to estimate information about the electronic transitions of studied material in different states. Other physical parameters also can be drawn from such spectral data including the difference between higher and lower occupied molecular states (HUMO-LOMO) and optical energy gap [13,14].

Figure (2) shows the UV/Vis. electronic transition of the studied phenolic dye using dimethyl sulfoxide (DMSO) as a solvent and reference material. Obtained spectra shows strong charge transfer band located at 245 nm attributed to $n \rightarrow \pi^*$ transition with a kink at their descending lobe at about 300 nm with a broad peak originally located at about 425 nm attributed to the electron transition with the drug structure result in the pale yellow color of the dye. In addition, the optical energy gap can be calculated using the wavelength λ_{edge} in the intersection of fundamental absorption edge with x-axis using the formula; $E_g = h c / \lambda_{\text{edge}}$. Such information can be approved using that obtained from optimized 2D and 3D structural units in combination with HUMO-LUMO data

shown in Figure (3).

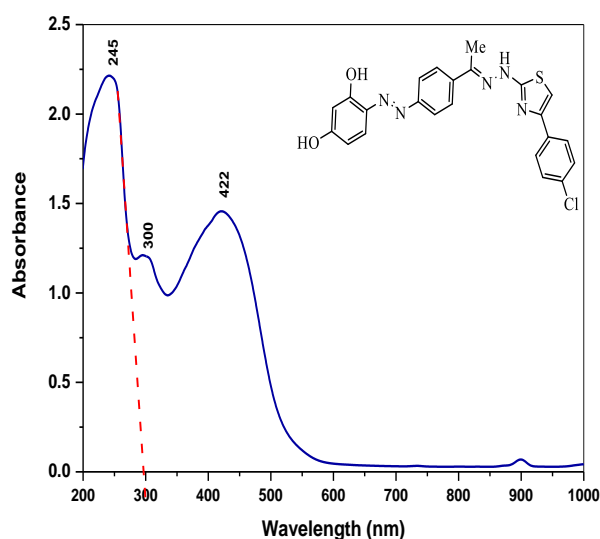


Figure (2): UV/Vis. electronic transition of the studied phenolic dye

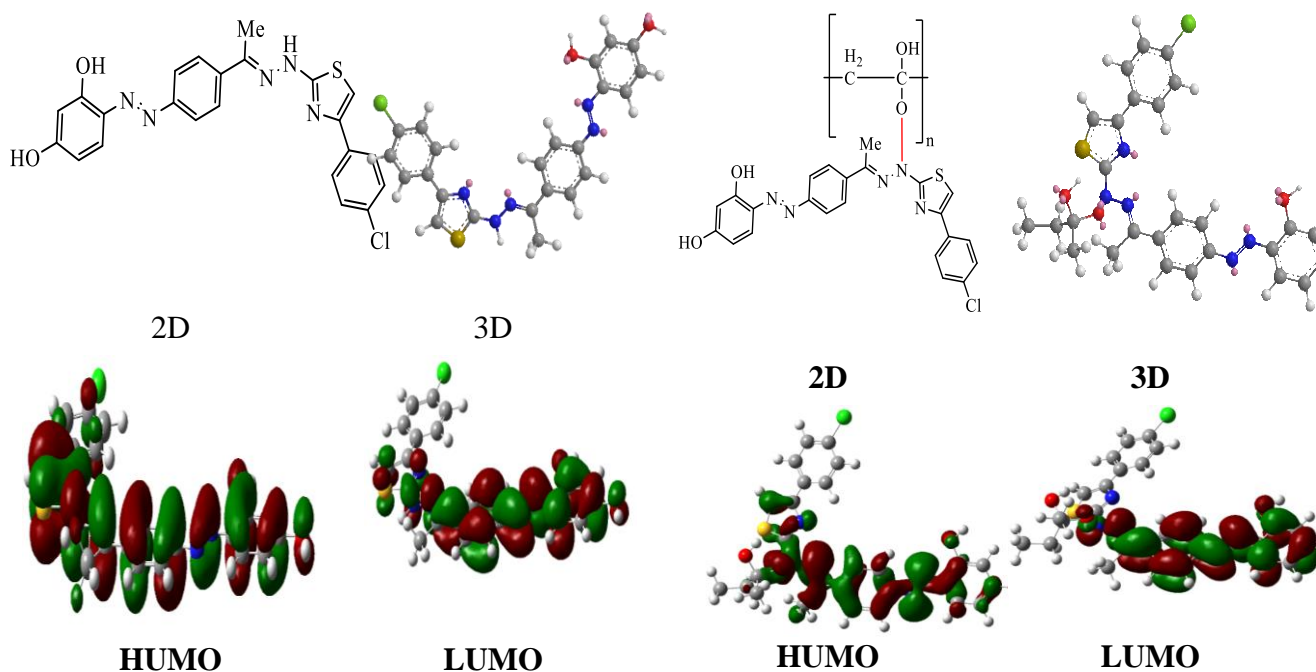


Figure (3): optimized 2D and 3D structural units of phenolic dye in combination with their HUMO-LUMO energies

Figure (4) shows the UV/Vis. electronic transition of the studied PVA and PVA/phenolic dye thin composite films using air as a reference material. Obtained spectra shows strong charge transfer band located at 245 nm attributed to $n \rightarrow \pi^*$ transition with an additional kink at their descending lobe at about 300 nm with a broad peak originally located at about 425 nm attributed for the presence of dye within the polymeric matrix [15,16]. Energy gap, HUMO-LUMO were also calculated as shown in Figure (5).

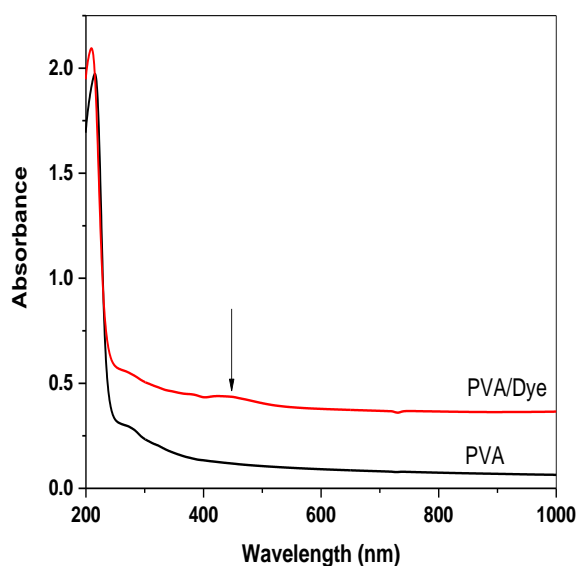


Figure (4): UV/Vis. electronic transition of the studied PVA an PVA/phenolic dye composite thin film

Figure (5): optimized 2D and 3D structural units of PVA/phenolic dye in combination with their HUMO-LUMO energies

Conclusion

The targeted thiazolyl-phenylazo-resorcinol dye **6** was synthesized through coupling of diazotized 4-aminoacetophenone with resorcinol followed by condensation of the product with thiosemicarbazide and finally Hantzsch-type cyclization the produced thiosemicarbazone by 4-chlorophenacyl chloride. Minor concentrations of the synthesized thiazolyl-phenylazo-resorcinol dye was applied on polymeric matrix of poly vinyl alcohol to study their effects on the physical, structural and optical properties.

4. References

1. Choi, T. S., Shimizu, Y., Shirai, H., & Hamada, K. (2000). Solubilization of disperse dyes in cationic gemini surfactant micelles. *Dyes and Pigments*, **45**(2), 145-152.
2. Perry, J. M., Kanasaki, Y. N., Karadakov, P. B., & Shimizu, S. (2021). Mechanism of dye solubilization and de-aggregation by urea. *Dyes and Pigments*, 109530.
3. Benkhaya, S., M'rabet, S., & El Harfi, A. (2020). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications*, **115**, 107891.
4. H. Ellis (1923) (British Celanese Ltd.), B.P., 219 349.

5. Kalivel, P. (2021). Treatment of Textile Dyeing Waste Water Using TiO₂/Zn Electrode by Spray Pyrolysis in Electrocoagulation Process. In *Dyes and Pigments*. IntechOpen.
6. Hudari, F. F., de Almeida, L. C., da Silva, B. F., & Zanoni, M. V. B. (2014). Voltammetric sensor for simultaneous determination of p-phenylenediamine and resorcinol in permanent hair dyeing and tap water by composite carbon nanotubes/chitosan modified electrode. *Microchemical Journal*, **116**, 261-268.
7. da Silva, A. R. L., dos Santos, A. J., & Martínez-Huitle, C. A. (2018). Electrochemical measurements and theoretical studies for understanding the behavior of catechol, resorcinol and hydroquinone on the boron doped diamond surface. *RSC advances*, **8**(7), 3483-3492.
8. Gaffer, H. E. & Althagafi, I. I. (2020). Synthesis of new azobenzene dyes clubbed with thiazolidinone moiety and their applications. *Pigment & Resin Technology*, **49**, 207–214.
9. Abdelghany, A. M., Menazea, A. A., & Ismail, A. M. (2019). Synthesis, characterization and antimicrobial activity of Chitosan/Polyvinyl Alcohol blend doped with Hibiscus Sabdariffa L. extract. *Journal of Molecular Structure*, **1197**, 603-609.
10. Abdelghany, A. M., Ayaad, D. M., & Mahmoud, S. M. (2020). Antibacterial and energy gap correlation of PVA/SA biofilms doped with selenium nanoparticles. *Biointerface Res. Appl. Chem*, **10**, 6236-6244.
11. Badawi, A., Alharthi, S. S., Assaedi, H., Alharbi, A. N., & Althobaiti, M. G. (2021) Cd0. 9Co0. 1S nanostructures concentration study on the structural and optical properties of SWCNTs/PVA blend. *Chemical Physics Letters*, **775**, 138701.
12. Nayak, S. M., Anjum, R., Husain, J., Dattu, H., Afrooze, A., & Rahika, G. (2021). PVA-ZNO nanocomposites thin films for sensing devices. *Ferroelectrics*, **577**(1), 221-228.
13. Abdelghany, A. M., Youssif, M. I., Abdelrazek, E. M., & Rashad, D. S. (2021). ICMMS-2: Computational DFT Study of Gold Containing PVP/PEO/Gold Organometallic Polymer Nanocomposites. *Egyptian Journal of Chemistry*, **64**(3), 7-8.
14. Mamone, M., Bura, T., Brassard, S., Soligo, E., He, K., Li, Y., & Leclerc, M. (2020). Optimized synthesis of fluorinated dithienyl-diketopyrrolopyrroles and new copolymers obtained via direct heteroarylation polymerization. *Materials Chemistry Frontiers*, **4**(7), 2040-2046.
15. Bouzidi, A., Jilani, W., Yahia, I. S., Zahran, H. Y., & Assiri, M. A. (2020). Optical analysis and UV-blocking filter of cadmium iodide-doped polyvinyl alcohol polymeric composite films: synthesis and dielectric properties. *Journal of Inorganic and Organometallic Polymers and Materials*, **30**(10), 3940-3952.
16. Brza, M. A., Aziz, S. B., Anuar, H., Ali, F., Dannoun, E. M., Mohammed, S. J., & Al-Zangana, S. (2020). Tea from the drinking to the synthesis of metal complexes and fabrication of PVA based polymer composites with controlled optical band gap. *Scientific reports*, **10**(1), 1-17.