Study of Optical Properties of Bromophenol Blue Dye Doped P3OT– PMMA Polymer Blend Films

Imad Al - Deen Hussein Ali Al - Saidi, Hussein Falih Hussein, Arafat Hady Kareem

***Abstract*— The optical properties of the undoped Poly(3 - octylthiophene) (P3OT) – Poly(methyl methacrylate) (PMMA) polymer blend film and the Bromophenol blue (BPhB) dye – doped P3OT – PMMA polymer blend films were studied. The undoped polymer film and the dye - doped polymer films at different dye concentrations were prepared using casting method. The optical absorbance and transmittance spectra were measured in the wavelength range 300 – 1100 nm for different dye concentrations using UV – Visible double – beam spectrophotometer. These optical spectra were used to characterize the optical properties of the prepared polymer films. The essential optical parameters of the BPhB dye – doped polymer blend film, such as, reflectance (R), absorption coefficient (α), extinction coefficient (k), refractive index (n), optical and electrical conductivities (σ_{opt} and σ_{elect}), and optical energy band gap (E_g), were determined. The effect of the dye concentration on these parameters was investigated. The results reveal the suitability of the BPhB dye – doped P3OT – PMMA polymer blend films for optical and photonic devices applications.**

***Index Terms*— Optical properties, Bromophenol Blue dye, Dye - doped polymer blend films, Optical parameters, Optical energy band gap.**

I. INTRODUCTION

Organic dye – doped polymers of significant optical and electrical properties have received great interest in the linear and nonlinear optics due to their practical applications such as, optical switching, optical limiting, signal processing, solar cells, optical sensors, light emitting diodes (LED's), and optoelectronic devices [1-13]. Optical characterization of these dye – doped polymers are considerably important to obtain knowledge concerning their optical parameters such as, absorption coefficient, refractive index, extinction coefficient, optical and electrical conductivities, and energy band gap. The study of these parameters is quite essential to examine the suitability of the optical materials for the device applications.

The dye – doped polymeric materials with suitable optical properties can be considered as promising candidates for some optical and photonic devices [14, 15]. The optical and electrical properties of many polymeric materials can be modified and improved by doping them with suitable dyes in the forms of dye – doped polymer films. Such films could be used for practical applications [16 - 18]. Among the various polymers, Poly(3 - octylthiophene) (P3OT) and Poly(methyl methacrylate) (PMMA) polymers have received special considerations . P3OT polymer and its derivatives have good optical and chemical stabilities under the environmental conditions and large absorption in the visible region of the electromagnetic spectrum [19]. These features make P3OT interesting polymeric material for applications of the solar cells and optical and chemical sensors. PMMA polymer is recognized as an optical material, it has significant properties, it is a transparent material for the visible light, has good thermal and environmental stabilities, flexible and ease of fabrication, as well as it has a relatively low cost [12, 20].

In this paper, we present the effect of doped Bromophenol blue (BPhB) dye on the optical properties of the P3OT – PMMA polymer blends. The dye – doped polymer films were prepared using the well - known casting method. The optical properties of the prepared polymer film samples were investigated for different dye concentrations and the essential optical parameters were determined.

II. THEORETICAL

The intensity of the transmitted light beam through the sample medium of a thickness t is given by the Lambert-Beer law [21]:

$$I = I_0 \exp(-\alpha t) \tag{1}$$

where I_0 is the intensity of the incident light beam and α is the linear absorption coefficient of the sample medium.

The absorbance (A) of the sample medium is expressed by the relation [21, 22]:

$$A = \log_{10}\left(\frac{I_0}{I}\right) \tag{2}$$

From Eqs. (1) and (2), we can write the absorption coefficient (α) of the sample medium as follows:

$$\alpha = 2.303\,\frac{A}{t} \tag{3}$$

The extinction coefficient (k) of the sample medium is given by the relation [23]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

where λ is the wavelength of the incident light beam.

The reflectance (R) of the sample medium can be determined from the following relation [23 - 25]:

$$R = 1 - (T e^{\alpha t})^{1/2} \tag{5}$$

Imad Al - Deen Hussein Ali Al – Saidi, Hussein Falih Hussein, Arafat Hady Kareem, Department of Physics, College of Education for Pure Sciences, University of Basrah, Basrah, Iraq.

where $T = I / I_0$ is the transmittance of the sample medium.

The linear refractive index (n) of the sample medium is related to both the extinction coefficient (k), and the reflectance (R) according to the following relation [24]:

$$n = \left[\frac{1+R}{1-R}\right] + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2} \quad (6)$$

The optical conductivity of the sample medium is given by the following relation [23]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad (7)$$

where c is the velocity of light.

The electrical conductivity (σ_{elect}) of the sample medium is related to its optical conductivity (σ_{opt}) according to the following relation [23]:

$$\sigma_{elect} = \frac{2\lambda \sigma_{opt}}{\alpha} \quad (8)$$

The relation between the optical energy band gap (E_g), the absorption coefficient (α), and the incident photon energy ($h\nu$) is given by the Tauc's relation [26]:

$$(\alpha h\nu)^m = C(h\nu - E_g) \quad (9)$$

where C is a constant, h is the Planck's constant, ν is the frequency of the incident photons, and m is an index, its value depends on the electronic transition responsible for the absorption. m = 1/2, 3/2, 2, or 3 for, indirect allowed, indirect forbidden, direct allowed, direct forbidden, transitions, respectively. In the present work, it is found that the mechanism of the measured absorption spectra of the prepared samples is the indirect allowed transition, therefore, we have taken m = 1/2 for the calculation of the values of E_g; using Eq. (9).

III. MATERIALS AND EXPERIMENTAL DETAILS

Bromophenol Blue (BPhB) dye was chosen for the present study and it was purchased from Sigma - Aldrich. The molecular formula of the BPhB dye is $C_{19}H_{10}Br_4O_5S$ and its molecular weight is 670 g / mole. The chemical structure of BPhB dye is shown in Fig. 1. The molecular formula of the P3OT polymer is $(C_{12}H_{18}S)_n$ and its molecular weight is 70000 g / mole, while the molecular formula of the PMMA polymer is $(C_5O_2H_8)_n$ and its molecular weight is 84000 g / mole. The samples of undoped polymer film and the BPhB dye – doped polymer blend films were prepared using casting method. A required weight (6 g) of PMMA polymer was dissolved in 10 ml solvent of chloroform and then the mixture was stirred at room temperature using a magnetic stirrer until the polymer completely dissolved. A certain quantity (0.02 %) of P3OT polymer was added to the PMMA solution and then, by using the magnetic stirrer, the mixture was stirred to obtain a homogenous solution. Suitable quantities of the prepared solution were cast on thin glass slides and left until dried at room temperature.

The BPhB dye – doped polymer blend films were prepared as follows: Firstly, a certain of BPhB dye powder was dissolved in the solvent of chloroform to obtain solution in certain concentration, then this solution was diluted by the chloroform solvent and samples of solutions with different dye concentrations were obtained (0.20, 0.25, 0.30 mM). Secondly, a certain quantity from the prepared P3OT – PMMA mixture solution was added to each one of the three prepared dye solutions. These solutions were stirred using the magnetic stirrer, and homogenous solutions were obtained. Then, proper quantities of these final solutions were cast on thin glass slides and kept to dry at room temperature. Dye - doped polymer film samples with different concentrations (0.20, 0.25, 0.30 mM)) and an average thickness of 0.9 mm were obtained. The prepared film samples were examined and found, they are uniform and optically clear.

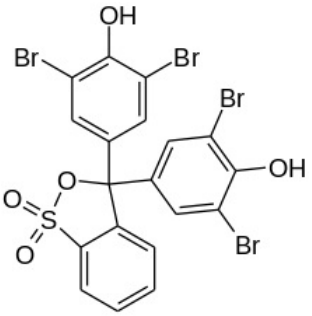

Fig. 1. Chemical structure of Bromophenol Blue dye.

IV. RESULTS AND DISCUSION

The absorbance (A) and the transmittance (T) of the undoped (free of BPhB dye) polymer film and the BPhB dye – doped polymer blend films at different dye concentrations were recorded over the wavelength range 300 nm – 900 nm using UV-Vis double – beam spectrophotometer. The spectra of the absorbance and the transmittance are shown in Fig. 2 and Fig. 3, respectively. It is clearly seen that the peak of the absorbance curve for the undoped polymer film sample is lower than the absorbance peaks of the dye – doped polymer film samples. The value of the absorbance at the peak of the spectral curve of the undoped polymer film sample is ≈ 18 %. This value is increased for the samples doped with the BPhB dye and the highest value (at the peak of the absorbance curve) is 34 % for the sample with the dye concentration of 0.30 mM.

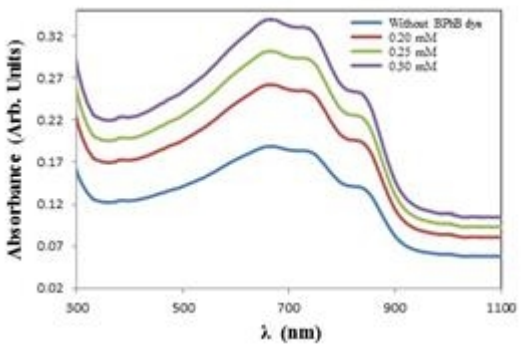

Fig. 2. UV- Visible absorbance spectra of P3OT – PMMA polymer film. (i) Without Bromophenol Blue (BPhB) dye. (j - l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

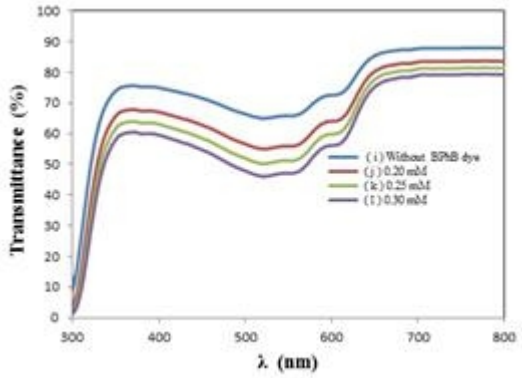

Fig. 3. UV- Visible transmittance spectra of P3OT – PMMA polymer film. (i) Without Bromophenol Blue (BPhB) dye. (j - l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

As seen in Fig. 2, that all the peaks are located at the wavelength 640 nm and the value of the absorbance is increased as the dye concentration increases. Fig. 3 shows the transmittance of the undoped polymer film sample and the dye – doped polymer film samples. In Fig. 3, the highest value of the transmittance for the undoped sample is 86 %, while the highest value of the transmittance for the sample with BPhB dye concentration of 0.30 mM is 76 % , at the wavelength 660 nm, and this value starts to decrease as the dye concentration increases.

The reflectance (R) of the undoped polymer film sample and the BPhB dye – doped polymer blend film samples at different dye concentrations was calculated using Eq. (5) and the obtained values of R were plotted as a function of the wavelength (λ), as shown in Fig. (4). It is clearly noticed that the highest value of the reflectance (R) of the polymer sample of free of BPhB dye is ≈ 12 % , and this value starts to increase as the dye concentration increases for the dye – dope polymer film sample. The highest value of R is 19.5 % at λ = 525 nm for the sample with dye concentration of 0.30 mM.

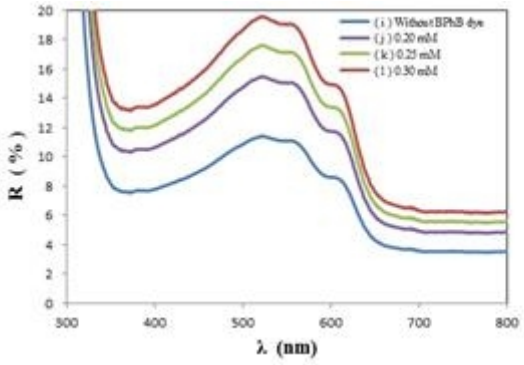

Fig. 4. UV- Visible reflectance spectra of P3OT – PMMA polymer film. (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

The absorption coefficient (α) of the undoped polymer film sample and the BPhB dye – doped polymer blend film samples at different dye concentrations was calculated using Eq. (3) and the obtained values were plotted as a function of the incident photon energy (h ν), as shown in Fig. 5. The highest value (the peak value) of α for the undoped polymer film sample is 5 cm^{-1} at the incident photon energy of 2.4 eV. This value is significantly increased when the polymer blend film sample doped with the BPhB dye. The value of α is a dye concentration dependent, this value increases when the dye concentration increases. The highest value of α (as seen in Fig. 5) is 9 cm^{-1} at the incident photon energy of 2.4 eV, for the sample with the dye concentration of 0.30 mM.

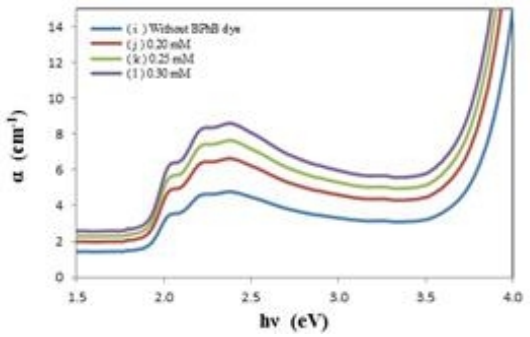

Fig. 5. The absorption coefficient (α) of the P3OT – PMMA polymer film as a function of the incident photon energy (h ν). (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

The extinction coefficient (k) of the undoped polymer film sample and the BPhB dye – doped polymer blend film samples at different dye concentrations was calculated using Eq.(4). Fig. 6 illustrates the relation between the extinction coefficient (k) and the incident photon energy (h ν), for the undoped polymer film sample and the dye - doped polymer samples at different dye concentrations. The peak value of k for the undoped polymer film sample is 2.1×10^{-5} at h ν = 2.2 eV, while the peak value of the BPhB dye – doped polymer blend film sample at dye concentration of 0.30 mM is 3.7×10^{-5} at the same value of the incident photon energy (h ν = 2.2 eV). It is clearly seen that the curve of the extinction coefficient (k) exhibits behavior is similar to that of the absorption coefficient (α), this is due the corporate relation between the extinction coefficient (k) and the absorption coefficient (α).

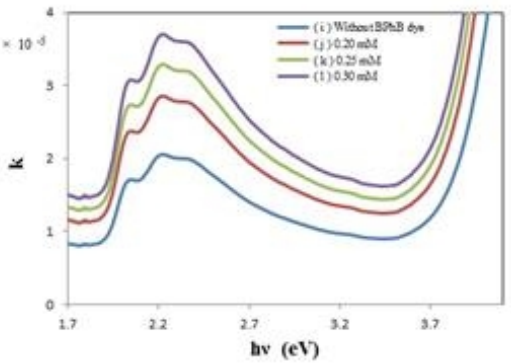

Fig. 6. The extinction coefficient (k) of the P3OT–PMMA polymer film as a function of the incident photon energy (h ν). (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

The values of the refractive index (n) of the undoped polymer film sample and the BPhB dye – doped polymer blend film samples at different dye concentrations were

calculated using Eq.(6). Fig. 7 illustrates the relation between the refractive index (n) and the incident photon energy (h ν), for the undoped polymer film sample and the dye-doped polymer samples at different dye concentrations. It is obvious that the values of the refractive index (n) of the dye - doped polymer samples are larger than the value of refractive index (n) for the undoped polymer film sample. The highest value of the refractive index (n) for the dye - doped polymer sample with the dye concentration of 0.30 mM is 2.4 at h ν = 2.4 eV, while the peak value of n for the undoped polymer film sample is 1.9, at the same value of the incident photon energy.

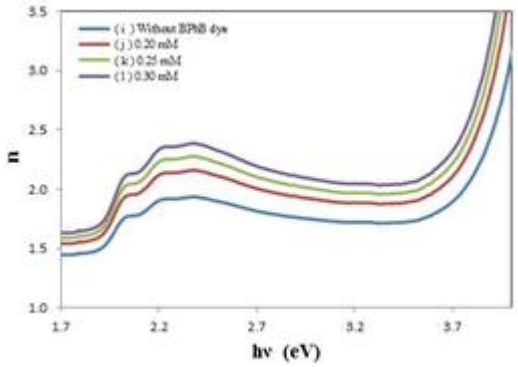

Fig. 7. The refractive index (n) of the P3OT – PMMA polymer film as a function of the incident photon energy (h ν). (i) Without Bromophenol Blue (BPhB) dye.. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

The values of the optical and electrical conductivities, σ_{opt} and σ_{elect} of the undoped polymer film sample and the BPhB dye – doped polymer blend film samples at different dye concentrations were calculated using Eqs. (7) and (8), respectively. The variations of σ_{opt} and σ_{elect} with the incident photon energy are shown in Fig. 8 and Fig. 9, respectively, for different dye concentrations. For the BPhB dye – doped polymer blend film samples, the evaluated value of σ_{opt} at the highest peak is 5×10^{10} (sec) $^{-1}$, while the value of σ_{elect} at the highest peak is 6.3×10^{5} (S . cm $^{-1}$) , at the dye concentration of 0.30 mM. The corresponding values for the undoped P3OT - PMMA polymer films are $\sigma_{opt} = 2.2 \times 10^{10}$ (sec) $^{-1}$ and $\sigma_{elect} = 5.1 \times 10^{5}$ (S . cm $^{-1}$). It can be seen that the value of σ_{elect} is high at the low photon energies and decreases with increasing the incident photon energy (h ν).

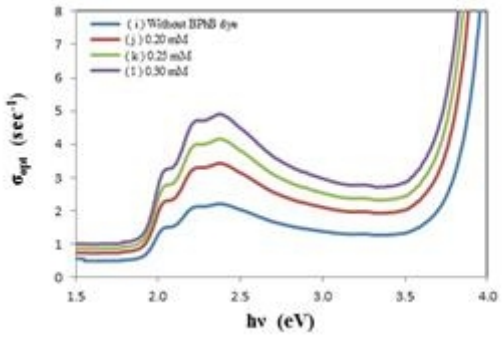

Fig . 8. The optical conductivity (σ_{opt}) of the P3OT – PMMA polymer film as a function of the incident photon energy (h ν). (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

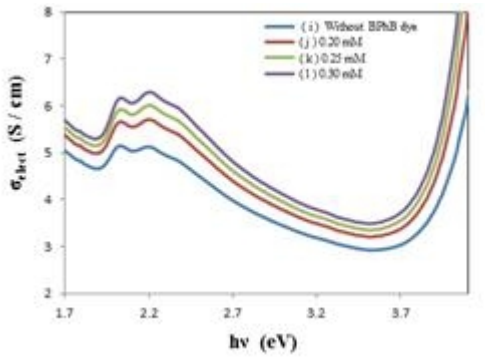

Fig . 9. The electrical conductivity (σ_{elect}) of the P3OT - PMMA polymer film as a function of the incident photon energy (h ν). (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

Using Eq. (9), $(\alpha h \nu)^{1/2}$ was plotted as a function of the incident photon energy (h ν), as shown in Fig. 10. The estimated values of the optical energy band gap (Eg) of the undoped P3OT - PMMA polymer blend film andthe BPhB dye - doped polymer blend films were obtained from the intercept of the extrapolated linear part of the plot of $(\alpha h \nu)^{1/2}$ versus the incident photon energy (h ν) with h ν – axis (where α h ν = 0), as shown in Fig. 10 for the undoped P3OT – PMMA polymer film and the BPhB dye - doped polymer films, at different dye concentrations. The estimated values of Eg are summarized in Table 1. It is seen in this table that the value of Eg for the undoped P3OT - PMMA polymer film is 1.8 eV, and this value decreased when the P3OT – PMMA polymer doped with BPhB dye. This value is also affected by the change in the dye concentration, where the obtained values of Eg are 1.73, 1.68, and 1.62 eV for the dye concentration, 0.20, 0.25, and 0.30 mM, respectively.

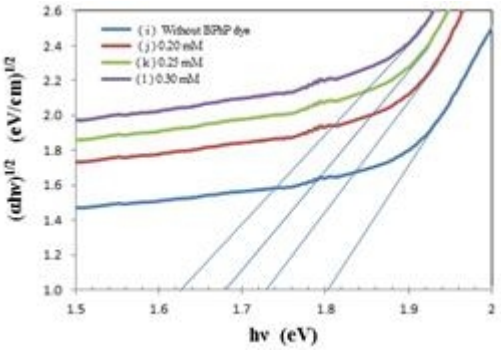

Fig. 10. Plot of $(\alpha h \nu)^{1/2}$ versus the incident photon energy (h ν) for the P3OT – PMMA polymer film. (i) Without Bromophenol Blue (BPhB) dye. (j – l) With Bromophenol Blue (BPhB) dye at different concentrations; 0.20 , 0.25 , and 0.30 mM , respectively.

Table 1. The estimated values of the optical energy band gap (E_g) of the undoped P3OT – PMMA polymer film and the BPhB dye - doped polymer films at different dye concentrations.

Sample	Optical energy band gap (E_g) (eV)
Undoped polymer	1.800
(BPhB) 0.20 mM	1.730
(BPhB) 0.25 mM	1.680
(BPhB) 0.30 mM	1.622

V. CONCLUSIONS

The optical properties of Poly(3 - octylthiophene) (P3OT) – Poly(methyl methacrylate) (PMMA) polymer blend film and Bromophenol Blue (BPhB) Poly(3- octylthiophene) (P3OT) – Poly(methyl methacrylate) (PMMA) polymer blend films were studied. These materials were selected because they have potential device applications. The results indicated that the values of the absorption, the extinction coefficients, the refractive index, and the optical and the electrical conductivities of the P3OT – PMMA polymer increased when it is doped with Bromophenol Blue (BPhB) dye and the values of these essential parameters are also increased with increasing the dye concentration. It is found that the optical energy band gap of the P3OT – PMMA polymer blend exhibited appreciably reduction when the polymer doped with BPhB dye. It was observed that the increase in the dye concentration can lead to a significant reduction in the energy band gap due to BPhB dye particles increasing. Results indicated that the BPhB dye - doped P3OT – PMMA polymer blend film is a promising candidate for optical and electrical device applications.

REFERENCES

[1] F. Z. Henari and S. Cassidy, "Nonlinear Optical Properties and All - Optical Switching of Congo Red in Solution", *Optik*, 123, 711 – 714, 2013.
[2] I. Al-D. H. Al-Saidi, and S. Al-D. Abdulkareem, "Nonlinear Optical Properties and Optical Power Limiting of Leishman Dye Using Z- Scan Technique", *J. Mater. Sci.: Mater. Electron*., 20, 2713 – 2718, 2015.
[3] Imad Al - Deen Hussein A. Al - Saidi and Saif Al – Deen Abdulkareem, "Study of Nonlinear Optical Properties and Optical Power Limiting of Leishman Dye Using Z-Scan Technique", *Indian J. Phys*., 89, 1199 – 1203, 2015.
[4] Imad Al - Deen Hussein A. Al - Saidi and Saif Al – Deen Abdulkareem, "Nonlinear Optical Properties and Optical Power Limiting Effect of Giemsa Dye Polymer Films", *Opt. Laser Technol*., 82, 150 – 156, 2016.
[5] J. M. Hales, S. Barlow, H. Kim, S. Mukhopadhyay, J. - L. Bredas, J. W. Perry, and S. R. Marder, "Design of Organic Chromophores for All - Optical Signal Processing Applications", *Chem. Mater*., 26, 549 – 560, 2014.
[6] M. Fitra, I. Daut, N. Gomesh, M. Irwanto, and Y.M. Irwan, "Dye Sola Cell using Syzigium Oleina Organic Dye", *Energy Procedia*, 36, 341 – 348, 2013.
[7] A. Sacco, M. Gerosa, S. Bianco, et. al., "Dye-Sensitized Solar Cell for a Solar Concentrator System", *Solar Energy*, 125, 307 – 313, 2016.
[8] W. Hou, Y. Xiao, G. Han, and J. Yu Lin, "The Applications of Polymers in Solar Cells: A Review", *Polymers*, 11, 143, 2019.
[9] G. Harsanyi, Polymer Films in Sensor Applications: Technology, Materials, Devices and their Applications (Technomic Publishing Company Inc., Pennsylvania, USA, 1995).
[10] F. S. Chien, C. R. Wang, Y. L. Chain and R. J. Wu, "Fast Response Ozone Sensors with ZnO Nanorods Grown by Chemical Vapor Deposition", Sens. Actuators B: Chemical, 1 4 4 , 120 – 125, 2010.
[11] S. C. Lo and P. L. Burn, "Development of Dendrimers: Macromolecules for Use in Organic Light-Emitting Diode and Solar Cells", *Chemical. Reviews*, 107, 1097 – 1116, 2007.
[12] S.-L Yeh, C.-Y. Zhu, and S.-W. Kuo, "Transparent Heat – Resistant PMMA Copolymers for Pacing Light-Emitting Diode Materials", *Polymers*, 7, 1379 - 1388, 2015.
[13] O. Ostroverkhova, (Ed.), Handbook of Organic Materials for Optical and Opto-electronic Devices: Properties and Applications (Woodhead Publishing Ltd., UK, 2013).
[14] H. S. Nalwa, (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices (Academic Press, New York, 2001).
[15] M. Cada, "Nonlinear optical devices", *Opt. Pur. Y Apl.*, 38, 1 – 11, 2005.
[16] L. H. Sperling, Introduction to Physical Polymer Science, (John Wiley and Sons, Inc., Hoboken, 2006).
[17] H. Frey and H. R. Khan, (Eds.), Handbook of Thin Film Technology (Springer-Verlag,Berlin, Germany, 2015).
[18] C. Fleischmann, M. Lievenbrück, and H. Ritter, "Polymers and Dyes: Developments and Applications", *Polymers*, 7, 717 – 746, 2015.
[19] K.-Y. Jen, G. G. Miller and R. L. Elsenbaumer, "Highly Conducting, Soluble, and Environmentally-Stable Poly (3 - alkylthiophenes)". *J. Chem. Soc. Chem. Commun*., 5, 1346 – 1347, 1986.
[20] U. Ali, K. Juhanni Bt, A. Karim, and N. A. Buang, "A Review of the Properties and Applications of Poly (methyl methacrylate) (PMMA)", *J. Polymer Review* 55, 678 -705, 2015.
[21] N. F. Mott and A. E. Davis, Electronic Process in Non-Crystalline Materials, 2 Edn, (University Press, Oxford, UK, 1979).
[22] D. E. Gray, American Institute of Physics Handbook, 3 Edn., (McGrow Hill Book Co., New York, USA, 1982).
[23] J. I. Pankove, Optical Processes in Semiconductors, (Prentice Hall, New York, USA, 1971).
[24] T.S. Moss, Optical Properties of Semiconductors, (Academic Press, New York, USA, 1974).
[25] I. Eckertova, Physics of Tthin Films, 2 Edn., (Plenum Press, New York, USA, 1986).
[26] J. Tauc, Amorphous and Liquid Semiconductors, Vol. 159, (Plenum Press, New York, 1974).

Prof. Dr. Imad Al - Deen Hussein Ali Al – Saidi, received his B. Sc. degree in Physics from Department of Physics, College of Science, Al – Mustanseriah University, in 1975, M. Sc. degree in Nuclear Physics from Department of Physics, College of Science, Baghdad University, in 1978, and Ph. D. degree in Molecular Physics / Laser Physics from Department of Physics, Faculty of Science, Heriot – Watt University, United Kingdom, in 1987. Fields of interest include, laser physics, molecular physics, molecular and laser spectroscopy, linear and nonlinear optics, optical power limiting, thin films, dye - doped polymers films, instabilities and chaos in the dynamical systems, solar cells, optical and gas sensors, and neutron activation analysis.

Prof. Dr. Hussain Falih Hussain received his B. Sc. and M. Sc. Degrees in Physics, in 1991 and 2000, respectively, and his Ph. D. degree in Polymer Physics, in 2011, from the Department of Physics, College of Education for Pure Sciences, University of Basrah. His research interests in polymer physics, solar cells, and gas sensors.

Arafat Hady Kareem received his B. Sc. and M. Sc. degrees in Physics from Department of Physics, College of Education for Pure Sciences, University of Basrah, in 1995 and 2012, respectively, He is currently working toward his Ph. D. degree in Applied Physics at Department of Physics. His current research interests include linear and nonlinear optics, laser physics, polymer physics, and gas sensors.