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Preparation of Poly(3HT - Co - TH) - PMMA Polymer Blend Films and Study Their Optical Properties

Imad Al - Deen Hussein Ali Al - Saidi, Hussein Falih Hussein, and Numan Sleem Hashim

Department of Physics, College of Education for Pure Sciences, University of Basrah, Basrah, Iraq

al_saidi_imad@yahoo.com

***Abstract** - Poly(3HT - Co - Th) - PMMA polymer blend films at different percentage weight ratios of the copolymer poly(3HT - Co - Th) were prepared using the casting method. Their optical properties were studied. The copolymer poly(3HT - Co - Th) was prepared using the addition method, where thiophene was added to 3 - hexylthiophene in the presence of $FeCl_3$ at room temperature. Then, the polymer blend poly(3HT - Co - Th) - PMMA was prepared by the addition of the prepared copolymer to the poly(methylmethacrylate) (PMMA) polymer. The optical absorbance (A) and transmittance (T) spectra of the prepared polymer blend films were measured over the wavelength range 300 - 800 nm for different weight ratios of the copolymer poly(3HT- Co - Th) using a UV - Visible double - beam spectrophotometer. The optical parameters of the poly(3HT- Co - Th) - PMMA polymer blend films, the real part (ε_r) and the imaginary part of the dielectric constant (ε), and the optical energy bandgap (E_g) were determined.*

The obtained results indicate that the prepared polymer blend poly (3HT- Co - Th) - PMMA films promise practical applications in photonic and optoelectronic devices.

Keywords - *Thiophene, Copolymer, Polymer Blend Films, Optical Properties, Optical Energy Band Gap.*

I. INTRODUCTION

Optical materials are playing an increasingly important role in the technological evolution of optical and photonic applications. The development of new optical materials has received much interest because of their possible applications as nonlinear optical materials for various optical devices [1 - 6]. Many different polymeric materials can be considered as good optical materials for these applications. Such materials are attractive due to their potential applications in a number of optical and photonic devices including, optical switches, optical power limiter, solar cells, optical sensors, light-emitting diodes (LED's), and optoelectronic devices [3, 4, 7 - 12]. The study of techniques to alter how incident light (or laser beam) interacts with optical materials has become an important element in advancing various applications. Understanding the properties of optical materials, such as polymeric materials, when interacting with incident light (or laser beam) has been of vital importance in developing optical, photonic, and electronic devices [13 - 16]. Thiophene is one of the conjugate polymers with several advantages: high solubility in organic solvents, environmental stability, and high electrical conductivity [17 - 20]. For the present study, the addition of the thiophene to the 3 - hexylthiophene was used to create a new copolymer, that is poly(3HT - Co - Th). The polymer blend poly(3HT - Co - Th) - PMMA was then prepared by the addition of the prepared copolymer to the poly(methylmethacrylate) (PMMA) polymer. Film samples of this polymer blend, using the casting method, were prepared. It is found that these prepared film samples exhibit significant absorption over the range of the visible region of the electromagnetic spectrum. Such new prepared polymer films can be used for different optical and electric practical applications.

In the present paper, the poly(3HT - Co - Th) - PMMA polymer blend films were prepared, and their optical properties were studied. The optical parameters of these prepared polymer films, including the real (ε_r) and the imaginary (ε_i) parts of the dielectric constant (ε), and the optical energy bandgap (E_g) were determined for different weight ratios of the copolymer poly(3HT- Co - Th). The effect of the copolymer poly(3HT- Co - Th) weight ratios on these optical parameters' values was also studied.

II. MATERIALS AND EXPERIMENTAL METHODS

The addition polymerization method was used to prepare the copolymer poly(3HT - Co - Th). The two monomers, 3 - hexylthiophene (3HT) and thiophene (Th), were supplied by the Aman International Industrial Company, India. Two different weight ratios of the 3 - hexylthiophene (3HT) and the thiophene (Th) monomers were chosen for the preparation of the copolymer poly (3HT- Co - Th). These two weight ratios are shown in Table.1. It is found that the mixture of the monomers 3HT and Th with the weight ratio, 3HT: Th = 9:1, show better solubility and dissolution in the chloroform solvent compared to that of the mixture of these monomers with the weight ratio, 3HT: Th = 8:2. Therefore, the weight ratio 3HT: Th = 9:1 was chosen to prepare the polymer blend poly(3HT - Co - Th) - PMMA. The poly(3HT - Co - Th) - PMMA polymer blend films were prepared by dissolving 4 gm of PMMA polymer in 10 ml of Chloroform solution. The produced solution was stirred for four hours until the polymer completely dissolved. Then, different percentage weight ratios of the copolymer poly(3HT - Co - Th), 0.033 %, 0.040 %, 0.046 %, 0.053 %, and 0.060 % were added to the PMMA solution. The solutions of these percentage weight ratios were stirred until the two polymers mixed, and homogeneous solutions were formed. Proper quantities of the produced solutions with different weight ratios of the copolymer poly(3HT - Co - Th) were cast on glass slides of 1 mm thickness and left to dry progressively, and hard polymer films were obtained. The average thickness of these polymer films was around 1 mm.

TABLE 1: The weight ratios of the monomers 3HT and the Th used to prepare the copolymer poly(3HT- Co - Th).

Weight ratio	Percentage Weight of Th (%)	Percentage Weight of 3HT (%)
9: 1	10	90
8: 2	20	80

The absorbance (A) and the transmittance (T) spectra of the prepared polymer film samples were measured by using Cecil UV - Vis double - beam spectrophotometer (Model CE -7500) of the wavelength range 190 - 1100 nm.

III. RESULTS AND DISCUSSION

The absorbance (A) and the transmittance (T) spectra of the poly(3HT - Co - Th) - PMMA polymer blend films at different weight ratios were recorded over the wavelength range 300 nm - 800 nm using the UV-Vis double - beam spectrophotometer. Representative examples of the spectra of the absorbance and the transmittance are shown in Figs. 1 and 2, respectively. Fig. 1 shows that all the highest absorbance peaks are located around a wavelength of 466 nm. The absorbance values at the highest peaks are in the range of 0.05 - 0.34 (Arb. Units) for the weight ratio range 0.033% - 0.060% of the copolymer poly(3HT - Co - Th). The highest transmittance values of the poly(3HT- Co - Th) - PMMA polymer blend film samples are in the range of 55 % - 90 % for the weight ratio range 0.033% - 0.060% of the copolymer poly(3HT- Co - Th), as shown in Fig. 2. It is observed that the values of the absorbance (A) and transmittance (T) are significantly dependent on the weight ratio of the copolymer poly(3HT - Co - Th). As seen in Figs. 1 and 2, the value of absorbance (A) is increased as the weight ratio percentage of the copolymer poly(3HT - Co - Th) increases, while the value of transmittance (T) is decreased as the weight ratio percentage of the copolymer poly(3HT - Co - Th) increases.

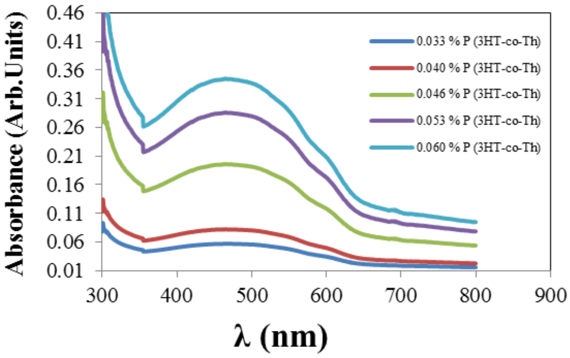

Fig.1: UV- Visible absorbance spectra of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

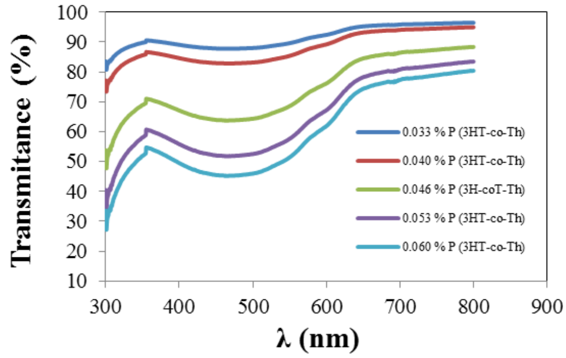

Fig. 2: UV - Visible transmittance spectra of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

The linear absorption coefficient (α) of an optical medium (or a film sample) of thickness t is usually described by the Lembert - Beer law as [21]:

$$I = I_0 \, e^{-\alpha t} \qquad (1)$$

where I_0 is the incident light intensity and I is the transmitted light intensity. The absorbance (A) of the medium sample is defined by: $A = I_0 / I$, and, thus, Eq. (1) can be written as follows [21, 22]:

$$A = e^{\alpha t} \qquad (2)$$

or it takes the form:

$$\alpha = 2.303 \frac{A}{t} \qquad (3)$$

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

$$R = 1- (T\, e^{\alpha t})^{1/2} \qquad (4)$$

where T is the transmittance of the film sample and is defined by $T = I / I_0$.

The extinction coefficient (k) of the film sample is related to the absorption coefficient (α) according to the following relation [23]:

$$k = \frac{\alpha \lambda}{4 \pi} \qquad (5)$$

where λ is the wavelength of the incident light.

The refractive index (n) of the film sample is given by the following relation [24]:

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

The complex dielectric constant (ε) of the film sample is given by the following relation [23, 26]:

$$\varepsilon = \varepsilon_r + i\,\varepsilon_i \qquad (7)$$

where ε_r and ε_i are the real and the imaginary parts of the dielectric constant (ε), respectively, and are given by the following relations:

$$\varepsilon_r = n^2 + k^2 \qquad (8)$$

and

$$\varepsilon_i = 2\,n\,k \qquad (9)$$

The real (ε_r) and the imaginary (ε_i) parts of the dielectric constant (ε) of the polymer blend film were determined for different weight ratios of the copolymer poly(3HT - Co - Th) using Eqs. (8) and (9) with Eqs. (2) - (6). Figs. 3 and 4 show, respectively, the relations between ε_r and ε_i, and the incident photon energy (hν), for the polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th). It is noticed that the values of the real dielectric constant (ε_r) are significantly greater than that of the imaginary dielectric constant (ε_i). It is seen that the values of ε_r and ε_i are increased with increasing the weight ratio of the copolymer poly(3HT - Co - Th). The highest values of the ε_r and ε_i are approximately 5.8 and 14.8×10^{-5}, respectively, around the incident photon energy hν = 2.6 eV for the film sample with the weight ratio of 0.060 % of the copolymer poly(3HT - Co - Th).

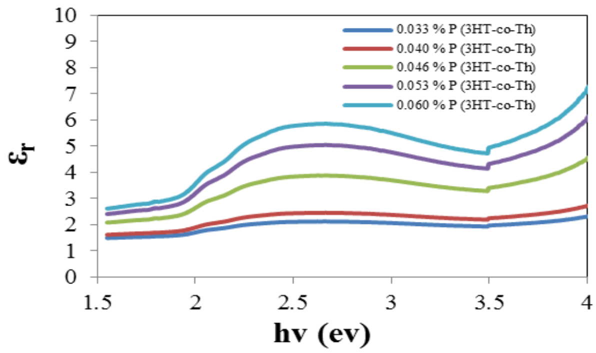

Fig. 3: The real dielectric constant (ε_r) of the poly(3HT - Co - Th) - PMMA polymer blend film as a function of the incident photon energy (hν) for different weight ratios of the copolymer poly(3HT - Co - Th).

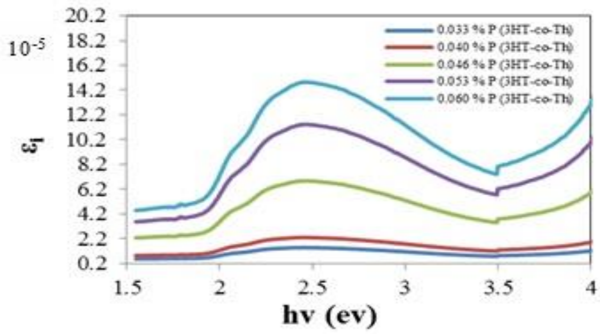

Fig. 4: The imaginary dielectric constant (ε_i) of the poly(3HT - Co - Th) - PMMA polymer blend film as a function of the incident photon energy (hν) for different weight ratios of the copolymer poly(3HT - Co - Th).

The optical energy bandgap (E_g) is an important optical parameter that characterizes the optical material. It is related to the absorption coefficient (α) and the incident photon energy (hν) according to the following relation [21, 24, 27]:

$$(\alpha h \nu)^m = C\,(h\nu - E_g) \qquad (10)$$

where h is the Planck's constant, ν is the frequency of incident photons, C is a constant, its value depends on the transition probability, and m is an index, its value depends on the type of the electronic transition [27], and m is an index, its value depends on the type of the electronic transition. The results showed that the transition is the indirect allowed transition. Therefore, we have taken m = 1/2 in Eq. 4 to calculate the value of E_g. The values of the optical energy band gap E_g of the poly(3HT- Co - Th) - PMMA polymer blend films were calculated from the intersection of the extrapolated linear part of the plot of $(\alpha h \nu)^{1/2}$ versus the incident photon energy (hν), as shown in Fig. 5. The estimated values of E_g for the poly(3HT - Co - Th) - PMMA polymer blend film for different weight ratios of the copolymer poly(3HT - Co - Th) are given in Table 2. It is seen that the value of the pure PMMA polymer film is equal to 4.73 eV. In the presence of the copolymer poly(3HT - Co - Th), the optical energy band gap of the pure PMMA polymer film is significantly modified, and its value decreased with increasing the weight ratio of the copolymer poly(3HT - Co - Th).

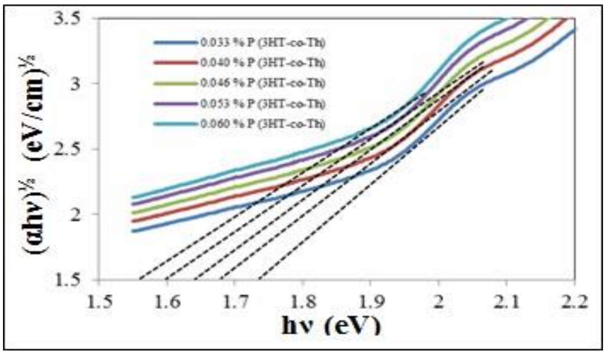

Fig. 5: Plot of $(\alpha h \nu)^{1/2}$ against the incident photon energy (h ν) of the poly(3HT - Co - Th) - PMMA polymer blend film for different weight ratios of the copolymer poly(3HT - Co - Th).

TABLE 2: The estimated values of the optical energy bandgap (E_g) of the poly(3HT - Co - Th) - PMMA polymer Blend film for different weight ratios of the copolymer poly(3HT - Co - Th).

Sample	The optical energy bandgap (E_g) (eV)
PMMA	4.73
0.033 % poly(3HT - Co - Th)	1.74
0.040 % poly(3HT - Co - Th)	1.68
0.046 % poly(3HT - Co - Th)	1.64
0.053 % poly(3HT - Co - Th)	1.60
0.060 % poly(3HT - Co - Th)	1.56

IV. CONCLUSIONS

In the present paper, the copolymer poly(3HT - Co - Th) was prepared using the addition polymerization method. The blend polymer poly(3HT - Co - Th) - PMMA was prepared by adding the copolymer poly(3HT - Co - Th) to the pure PMMA polymer. The casting method was used to prepare the polymer blend films used for the measurements of the optical properties of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th). The results obtained indicated that the addition of the copolymer poly(3HT - Co - Th) to the PMMA polymer could be lead to a significant improvement in the optical properties of the PMMA. It is observed that the optical parameters of the prepared polymer film samples that are measured in the present paper, the absorbance (A), the transmittance (T), the real dielectric constant (ε_r), the imaginary dielectric constant (ε_i), and the optical energy bandgap (E_g), showed significant changes with changing the percentage weight ratio of the copolymer poly(3HT - Co - Th). The obtained results suggest that the prepared poly(3HT - Co - Th) - PMMA polymer blend films with tunable optical and electrical properties can be potential materials for use in the fields of the optical biosensor, solar cell, optoelectronics, and photonic devices.

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