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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF POLY (3HT - Co - Th) - PMMA POLYMER BLEND FILMS

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.

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Abstract

Poly(3 - Hexylthiophene - Co - Thiophene) copolymer was prepared by applying the addition polymerization method. Then, the copolymer was added to the poly(methyl methacrylate) (PMMA) polymer to produce the poly(3HT - Co - Th) - PMMA polymer blend. In order to characterize the optical properties of the prepared polymer blend, poly(3HT - Co - Th) - PMMA polymer blend films were prepared at different percentage weight ratios of the copolymer using the casting method. The surface structure of the prepared copolymer was analyzed by using the Fourier transform infrared (FT - IR) spectroscopy as well as the atomic force microscopy (AFM) technique. The optical absorbance (A) and the transmittance (T) spectra of the prepared films were measured by using the UV-Vis spectrophotometer in the wavelength range 300 nm - 800 nm. These optical spectra were used to determine the main optical parameters of the polymer blend films. Results indicated that the prepared poly(3HT - Co - Th) - PMMA polymer blend films can be promising candidates for photonic and optoelectronic applications.

Introduction

Thiopheneis a based polymer material can be used for different applications in the photonic and optoelectronic devices such as, light emitting diodes (LED's), solar cells, optical sensors, optical switching, and optical power limiting [1 - 12]. Thiophene is one of the conjugated polymers that have distinguished advantages such as high solubility in common solvents, environmental stability, good light absorption, and high electrical conductivity [4, 13 - 16]. Polymeric materials have unique properties that make these materials useful for the optical and electrical applications [17 - 23]. Poly(methyl methacrylate) (PMMA) is an important one of these polymeric materials [9, 24]. In this investigation, PMMA polymer was chosen as the suitable material added to the copolymer poly(3HT - Co - Th) to obtain a new blend polymer poly(3HT - Co - Th) - PMMA, which can be used for various optical and electrical applications.The prepared polymer exhibits high absorption over the visible region of the electromagnetic spectrum. Addition of the copolymer poly(3HT - Co - Th) to the polymer PMMA can lead to significant modifications in the optical and electrical properties of the polymer PMMA. The modifications of the optical and electrical properties of the polymer PMMA can also be done by doping the polymer with a suitable organic dye [25 - 27].

Corresponding Author:- Imad Al - Deen Hussein Ali Al - Saidi
Address**:-** Department of Physics, College of Education for Pure Sciences, University of Basrah, Basrah, Iraq.

In the present investigation, the poly(3HT - Co - Th) - PMMA polymer blend films were prepared at different weight ratios of the copolymer poly(3HT - Co - Th), that formed from the monomers thiophene (Th) and 3 - hexylthiophene (3 - HT) by the addition polymerization method. The main optical parameters of the prepared films were determined and the effect of the weight ratios of the copolymer poly(3HT - Co - Th) on the structure and the optical properties of the polymer blend films was also investigated.

Experimental Details

Preparation of the Copolymer Poly(3HT - Co - Th)

The molecular weights of the monomers, thiophene (Th) and 3 - hexylthiophene (3 - HT), used in this investigation, are 84.14 gm / mol and 168.30 gm / mol, respectively, and their chemical structures are shown in Fig. 1. These two monomers were obtained from Aman International Industrial Company.

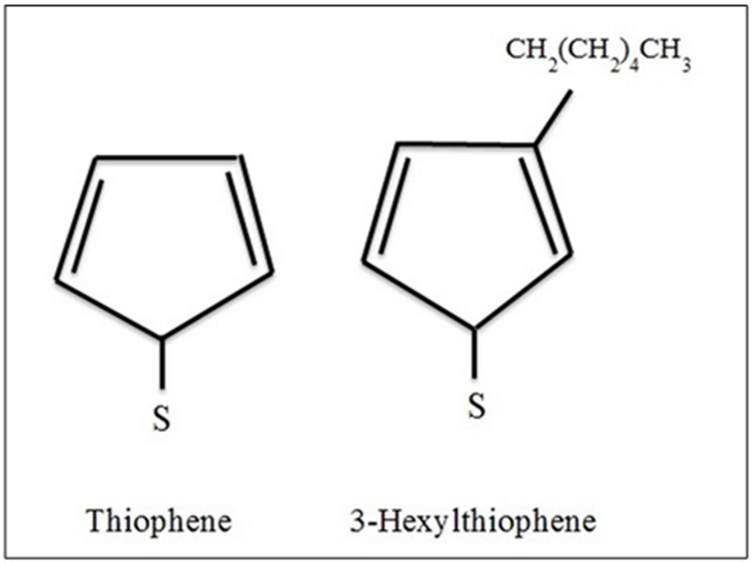

Fig. 1:- The Chemical structures of the thiophene and the 3 - hexylthiophene.

Addition polymerization method was used to prepare the copolymer poly(3HT - Co - Th). 2 gm of $FeCl_3$, was used as catalyst, added to 12 ml of chloroform ($CHCl_3$) and the mixture was stirred using a magnetic stirrer for 15 minutes. Different weight ratios of the monomers, 3 - HT and Th, were mixed together and then by the drop-wise method added to the $FeCl_3$ mixture. The resulting mixture was stirred for 24 hours. The crude polymer precipitate was filtered using PTFE membrane filter of thickness 1 μm and then washed with the ethanol, the methanol, and the acetone to get rid the traces of the catalyst. The obtained dark brown powder was dried under vacuum at a temperature of 70 ^oC for 6 hours. Two weight ratios, 9:1 and 8:2 of 3HT:Th were chosen for the preparation of the copolymer poly(3HT - Co - Th). It is found that the two monomers of the weight ratio 3HT:Th = 9:1 are easy to dissolve in the chloroform solvent compare to the two monomers of the weight ratio 3HT:Th = 8:2. Therefore, the weight ratio 3HT:Th = 9:1 was used for the preparation of the polymer blend poly(3HT - Co - Th) - PMMA.

Preparation of the Polymer Blend Films

The poly(3HT - Co - Th) - PMMA polymer blend films at different weight ratios of the copolymer poly(3HT - Co - Th) were prepared using the casting method. 4 gm of PMMA polymer was dissolved in 10 ml of chloroform and the produced solution was stirred for 3 hours until the PMMA polymer completely dissolved. Then, different percentage 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. Five solutions with different percentage ratios were obtained. These solutions were stirred until the two polymers mixed together and homogeneous solutions were formed. The solutions of the different weight ratios of the copolymer poly(3HT - Co - Th) were cast on glass slides of 1 mm thickness and left to dry and hard polymer films were obtained. The average thickness of these polymer films was around 1 mm.
The surface structure of the prepared copolymer was analyzed by using the Fourier transform infrared (FT - IR) and the atomic force microscopy (AFM) techniques.

Results and Discussion

FT - IR Analysis of the Prepared Copolymer Poly(3HT - Co - Th)

Characteristic FT - IR absorption spectrum of the copolymer poly(3HT - Co - Th) is shown in Fig. 2. The band at 2925 cm^{-1} in the spectrum is corresponding to the C = C - H stretching, the band at 1645 cm^{-1} is attributed to the C = C characteristic peak, and the absorption band at 1309 cm^{-1} corresponds to the C - C stretching. The peak located at ≈ 721 cm^{-1} is belonging to the C - S poly(3HT - Co - Th) stretching .

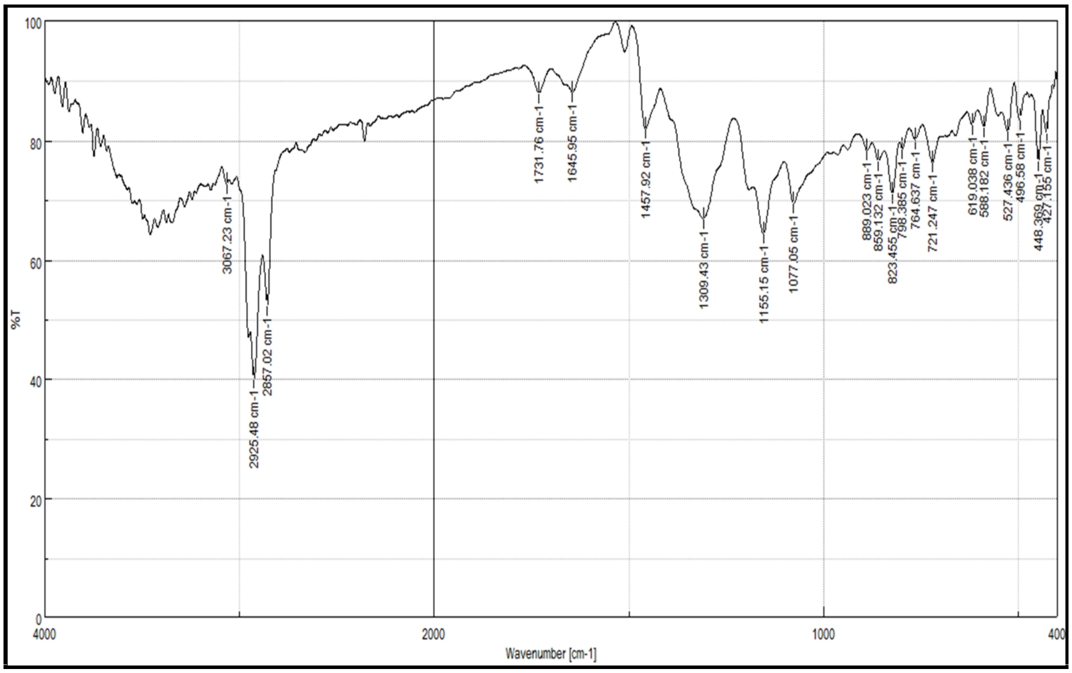

Fig. 2:- FT - IR absorption spectrum of the copolymer poly(3HT - Co - Th).

AFM Analysis of the Poly(3HT - Co - Th) - PMMA Polymer Blend Films

Fig. 3 shows the two and three dimensions AFM images of the surface morphology of the poly(3HT - Co - Th) - PMMA polymer blend film for three weight ratios of the copolymer poly(3HT - Co - Th), 0.033 % , 0.046 % , and 0.060 %. It is revealed, from the AFM analysis, that the prepared poly(3HT - Co - Th) - PMMA polymer blend films have semi-crystalline structures. The structure parameters of the prepared polymer blend film are significantly affected by the change of the percentage ratio of the copolymer poly(3HT - Co - Th). The values of the root mean square roughness (RMS) of the poly(3HT - Co - Th) - PMMA polymer blend film surface are; 15.20 nm, 6.71 nm, and 11.60 nm at the percentage values, 0.033 %, 0.046 %, and 0.060 %, of the copolymer poly(3HT - Co - Th), respectively.The corresponding values of the roughness average (R_a) are; 13.20 nm, 5.57 nm, and 10.10 nm. It is clearly noticed that the surface roughness average of the prepared polymer blend film decreased when the percentage ratio of the copolymer poly(3HT - Co - Th) increased from 0.033 % to 0.046 %, and then starts to increase as the percentage ratio increased to 0.060 %. The corresponding values of the polymer film maximum height (R_{max}) are; 52.7 nm, 30.5 nm, and 40.3 nm. It is found that the values of the grain number of the prepared polymer blend film at the three percentage values, 0.033 %, 0.046 %, and 0.060 %, of the copolymer poly(3HT - Co - Th) are; 444, 703, and 432, respectively. In addition, the average diameter (size) of the grain is changed with the change in the percentage value of the copolymer poly(3HT - Co - Th), and its values are, 101 nm, 80.20 nm, and 71.22 nm, for the three percentage values of the copolymer.

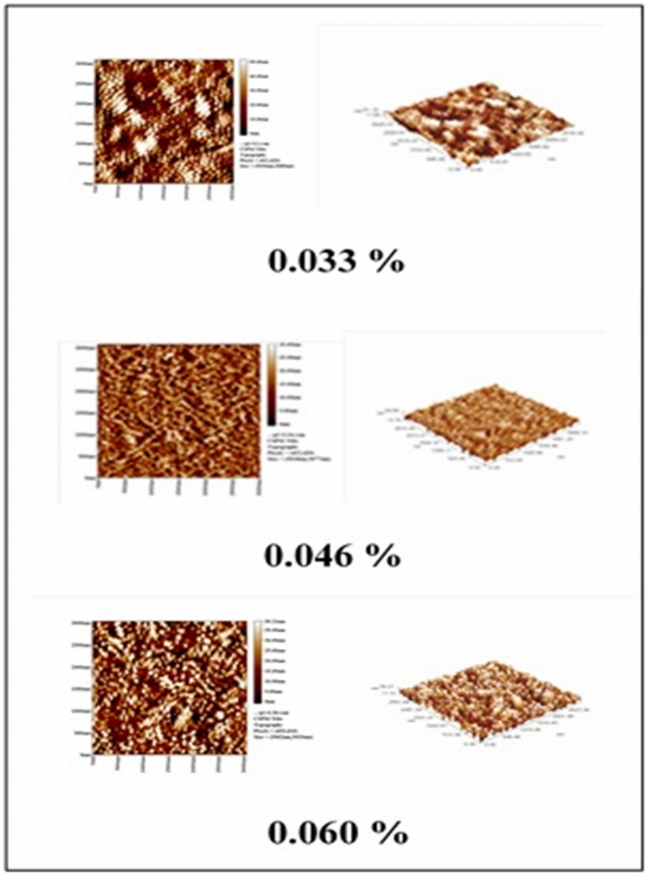

Fig. 3:- Two and three dimensions images of the surface morphology of the poly(3HT - Co - Th) - PMMA polymer blend film, measured by the atomic force microscopy (AFM), for different percentage ratios of the copolymer poly(3HT - Co - Th).

Optical Properties of the Poly(3HT - Co - Th) - PMMA Polymer Blend Films

The absorbance (A) and the transmittance (T) spectra of the poly(3HT - Co - Th) - PMMA polymer blend films at different weight ratios of the copolymer poly(3HT - Co - Th) were measured over the wavelength range 300 nm - 800 nm using Cecil Ultraviolet - Visible (UV - Vis) double - beam spectrophotometer (Model CE - 7500, England). Typical spectra of the absorbance and the transmittance of the poly(3HT - Co - Th) - PMMA polymer blend film are shown in Figs. 4 and 5, respectively. Fig. 4 shows that all the highest absorbance peaks are located around the wavelength 466 nm. The values of absorbance are in the range of 0.05 - 0.34 (Arb. Units) when the weight ratios are in the range 0.033 % - 0.060 % of the copolymer poly(3HT - Co - Th). The highest value of the transmittance is 90 % for the film sample with the percentage ratio 0.033 % of the copolymer poly(3HT - Co - Th). While, the lowest transmittance value of the poly(3HT - Co - Th) - PMMA polymer blend film is 55 % for the sample with the percentage ratio 0.060 % of the copolymer poly(3HT - Co - Th), as seen in Fig. 5. It can be deduced, from the results, that the values of the absorbance and the transmittance of the prepared polymer blend films are significantly depend on the weight ratio of the copolymer poly(3HT - Co - Th). The value of the absorbance of the prepared polymer film increased when the weight ratio of the copolymer poly(3HT - Co - Th) increased, while, the polymer film transmittance value decreased when the weight ratio of the copolymer poly(3HT - Co - Th) increased.

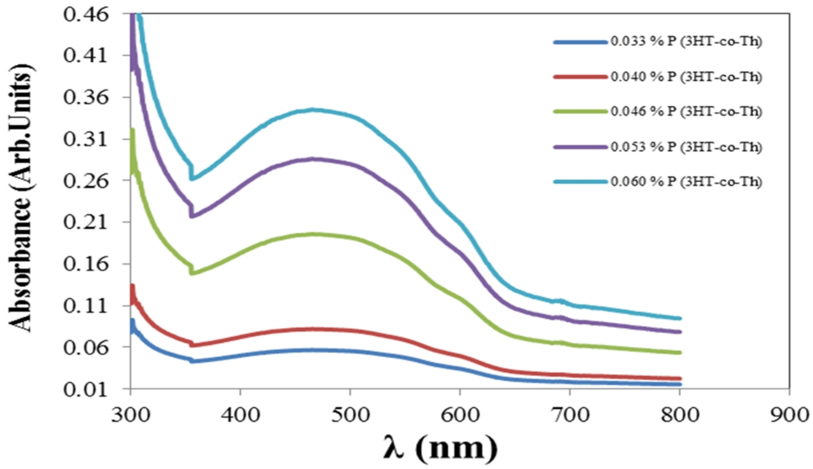

Fig. 4:- UV - Visible absorbance spectra of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

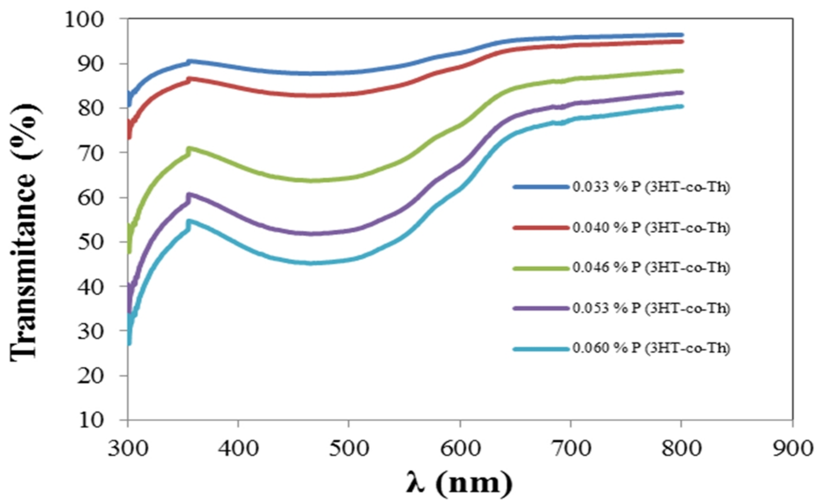

Fig. 5:- UV - Visible transmittance spectra of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

The optical conductivity (σ_{opt}) of the material is given by the following relation [28]:

$$\sigma_{opt} = \frac{\alpha\, n\, c}{4\pi} \qquad (1)$$

where n is the refractive index of the material and c is the velocity of light.

The absorption coefficient (α) of polymer film of thickness t can be given by the following relation [29, 30]:

$$\alpha = 2.303\ \frac{A}{t} \qquad (2)$$

where the absorbance (A) is determined from the spectrum of the absorbance.

The electrical conductivity (σ_{elect}) of the polymer film is related to its optical conductivity (σ_{opt}) according to the following relation [28]:

$$\sigma_{elect} = \frac{2\,\lambda\,\sigma_{opt}}{\alpha} \quad (3)$$

where λ is the wavelength of the incident photon.

Eqs. (1) - (3) were used to determine σ_{opt} and σ_{elect} of the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th). The variations of σ_{opt} and σ_{elect} with incident photon energy (hν) are shown in Figs. 6 and 7, respectively, for different weight ratios of the copolymer poly(3HT - Co - Th). The evaluated highest peak values of σ_{opt} are within the range (0.30 - 4.60) × 10^{10} (sec^{-1}), at the incident photon energy of 2.66 eV. While the values of σ_{elect} are within the range (3.5 - 5.92) × 10^{5} (S / cm), at the incident photon energy of 2.25 eV, over the percentage range 0.033 % - 0.060 % of the copolymer poly(3HT - Co - Th). It is seen that the value of σ_{elect} is high at the low photon energies and decreases with increasing the incident photon energy (hν).

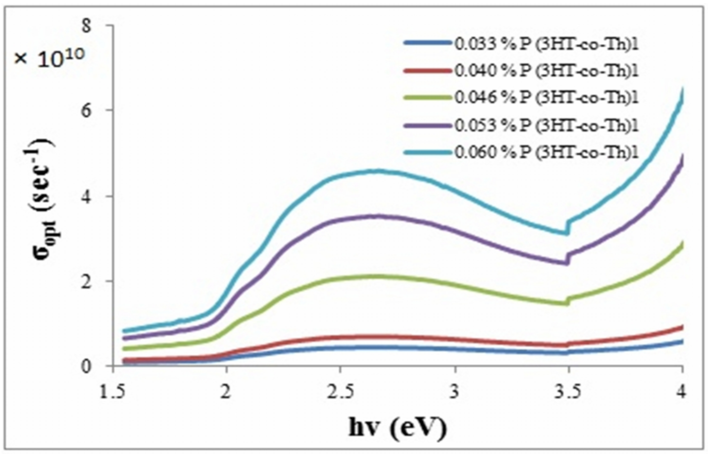

Fig. 6:- The variation of the optical conductivity (σ_{opt}) with the incident photon energy (hν) for the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

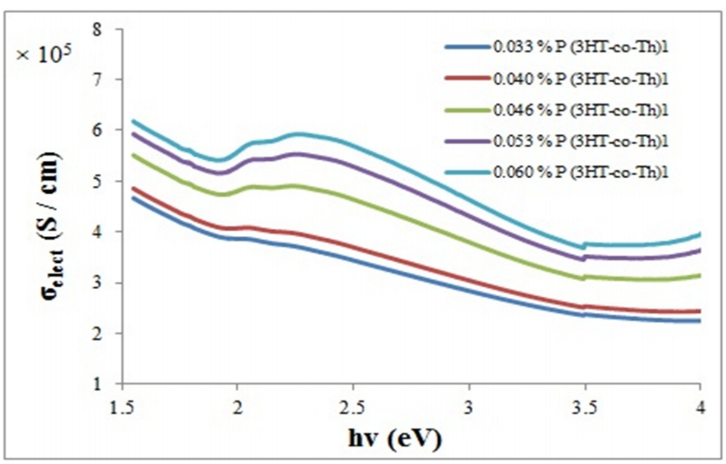

Fig. 7:- The variation of the electrical conductivity (σ_{elect}) with the incident photon energy (hν) for the poly(3HT - Co - Th) - PMMA polymer blend film at different weight ratios of the copolymer poly(3HT - Co - Th).

Conclusions

In the present investigation, the blend polymer poly(3HT- Co - Th) - PMMA was prepared by the addition of the prepared copolymer poly(3HT - Co - Th) to the pure PMMA polymer. The casting method was used for the preparation of the polymer blend films that used for the characterization of the poly(3HT - Co - Th) - PMMA polymer blend films and the measurements of their optical properties. The obtained results indicate that the addition of the copolymer poly(3HT- Co - Th) to the polymer PMMA can lead to considerable improvement in the optical properties of the polymer PMMA. The prepared films exhibited significant changes in their structures and optical properties with changing the weight ratio of the added copolymer poly(3HT - Co - Th).

The obtained results suggest that the prepared poly(3HT - Co - Th) - PMMA polymer blend films are suitable for the applications in the photonic and optoelectronic devices.

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