

Optical properties modification of polystyrene films by 2N-salicylidene-5-(p-nitro phenyl)-1,3,4-thiadiazole complexes

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Abstract

The present study focused on modification of the optical properties of polystyrene (PS) films with 2N-salicylidene-5-(p-nitro phenyl)-1,3,4-thiadiazole (SN) complexes. The polystyrene films were cast from chloroform solvent with the thickness of 30 micrometer. The polystyrene films composites with 0.5% by weight of this additive. The optical data were analyzed and interpreted in term of electronic transition. According to energy gap data the conductivity of polymer with and without additives were obtained.

Introduction

Optical properties of polymers constitute an important aspects in study of electronic transition and possibility of their application as optical filters, cover in solar collection, selection surfaces and green house⁽¹⁾.

The information about the electronic structure of crystalline and amorphous semiconductors has been mostly accumulated from the studies of optical properties in wide frequency range. The significance of amorphous semiconductors is in its energy gap⁽¹⁾.

The simplest definition of the optical gap is the minimum energy difference between lowest minimum of conduction band and the highest maximum of valance band⁽²⁾.

The main two types of optical transitions are direct and indirect transition, both involve the interaction of an electromagnetic wave with the electron in the valance band with may cross the forbidden gap to the conduction band⁽³⁾.

Indirect transition is possible only by phonon-assisted transition. The value and shape of the mobility gap in the amorphous semiconductors depend on the preparation conditions such as substrate temperature, annealing temperature, degree of impurity and defect of the material. Any variation in such parameters lead to a shift in the absorption edge towards higher or lower energy⁽⁴⁾.

The absorption coefficient is defined by⁽⁵⁾ This can be determined from the normal incidence transmission through plane-parallel plate of thickness (d). Interference and multiple reflections are neglected. The reflectance(R) and transmittance (T) are related by equation (1):-

$$T = B(1 - R)^2 \exp(-\alpha d) \dots (1)$$

Where B is a constant, this equation can be rewritten in equation (2):-

$$\alpha d = 2.303A - \ln[B(1-R)^2] \dots (2)$$

A is the optical absorbance, (A = -log T).

The long wavelength tail of absorbance spectrum is attributed to background absorption which in turn refers to the term $\ln[B(1-R)^2]$ in equation (1). So the absorption coefficient $\alpha(\omega)$ in term of absorbance become :-

$$\alpha(\omega) = \frac{2.303}{d} A \dots (3)$$

For direct band- to - band transition, the energy dependence of absorption coefficient is of the form:

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^2}{h\nu} \dots (4)$$

Where (hν) is the photon energy and (Eg) is the energy gap, (r) is constant depending on the type of the electronic transition, R takes the value (1/2) for allowed direct transition and (3/2) for forbidden direct transition and the absorption coefficient ($\alpha \geq 10^3 \text{ cm}^{-1}$). The energy dependence absorption coefficient is of the form:-

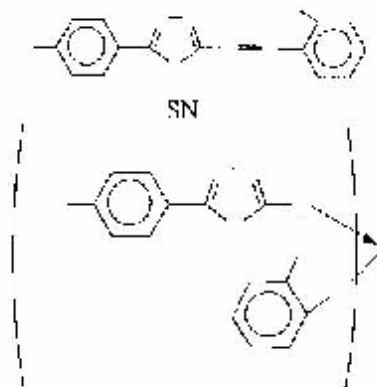
$$\alpha = \frac{\alpha_0 (h\nu - E_g - E_p)^r}{h\nu} \dots (5)$$

where (Eg) is the minimum energy gap, (E_p) is the phonon energy, (+) absorbed (-) limited, (r) take the value of 2 for allowed indirect transition and 3 for forbidden indirect transition, indirect transition occurs for ($\alpha < 10^3$).

Polymers, in general, are transparent and colorless the existence of conductive additive raising the transition wavelength into visible region and the optimized lighter structure is very useful in some specific advanced technology such as electrochromic displays [5]. Optical switching and rechargeable batteries⁽⁶⁾.

Experimental

2N-salicylidene-5-(*p*-nitro phenyl)-1,3,4-thiadiazole(SN), Bis[2N-salicylidene-5-(*p*-nitro phenyl)-1,3,4-thiadiazole] tin(II) Sn(SN)₂, Bis[2N-salicylidene-5-(*p*-nitro phenyl)-1,3,4-thiadiazole] nickel(II) Ni(SN)₂, Bis[2N-salicylidene-5-(*p*-nitro phenyl)-1,3,4-thiadiazole] copper(II) Cu(SN)₂ and Tris[2N-salicylidene-5-(*p*-nitro phenyl)-1,3,4-thiadiazole iron(II) Fe(SN)₃ were prepared by the method described by Yousif⁽⁷⁾.



Where M = Sn(II), Ni(II) and Cu(II)

Purification of Polystyrene⁽⁸⁾:

Commercial Polystyrene (PS) with average number molecular weight (2×10^5) determined by viscometric technique⁽⁹⁾ was freed from additives by re-precipitation twice from chloroform solution in ethanol. The purified was dried under reduced pressure at room temperature for 24 hours.

Techniques: -

Films Preparation: -

Different concentrations of polystyrene solutions in chloroform was used to prepare 30 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany) with out and with 0.5% of the metal complexes prepared. The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual chloroform solvent, film samples were further dried at room temperature for three hours

under reduced pressure. The optical absorbance (A) of the sample were measured as a function of wavelength (λ) ranged from 200 to 900 nm by using Shimadzu UV-vis 160A-Ultraviolet-spectrophotometer and all measurements were performed at room temperature.

Results and Discussion

The relation between $(nh\nu)^{1/2}$ and $(nh\nu)^{-2}$ versus photon energy for the undoped PS sample (Control) is shown in Figures (1,2) for allowed and forbidden transition.

Figures (1,2) show single absorption peaks and this is confirm that pure PS (Control) has no any electronic transition in the visible region.

For doped samples, two distinct absorption peaks, shown in Figures (3,4) could be attributed to the formation of polarons and bipolarons in the doped films^(10,11). The evidence of Polaron formation is made that the reaction in band to band transition due to shifting the band density of state toward the energy gap. This observation is not similar to the doping in conventional semiconductors when the band to band absorption strength does not affected by the formation of dopant state in the energy gap⁽¹²⁾.

The effect of the %weight metal complexes addition on the values of activation energies 1 and 2 with photon energies is also investigated and the result are shown in Table (1,2)

Table (1). Allowed indirect transition and assisting phonons energies

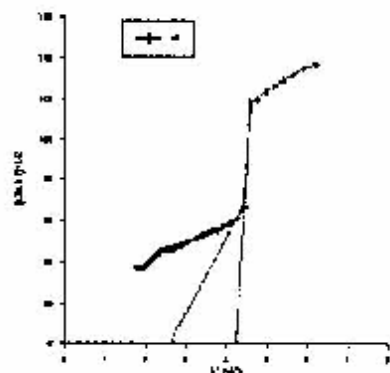
Samples	Eg1 (eV)	Ep1 (eV)	Eg2 (eV)	Ep2 (eV)
PS	-	-	4.2	2.5
PS+0.5%SN	2.4	0.1	4.2	2.45
PS+0.5%Sn(SN) ₂	1.8	1.3	4.3	1.5
PS+0.5%Fe(SN) ₂	1.5	0.7	4.35	1.45
PS+0.5%Cu(SN) ₂	2.2	1.6	4.375	1.175
PS+0.5%Ni(SN) ₂	2.3	1.3	4.4	1

Table (1) Indirect allowed and forbidden energy band gaps and assisting phonons energies for PS, PS-SN and PS L. Mⁿ composites

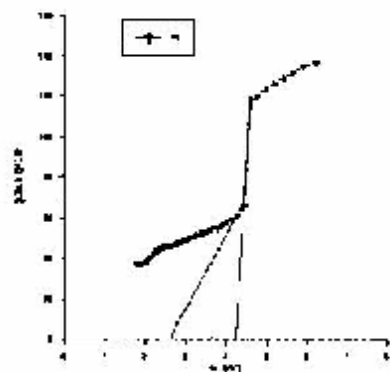
Table (2). Forbidden indirect transition and assisting phonons energies

Samples	Eg1 (eV)	Ep1 (eV)	Eg2 (eV)	Ep2 (eV)
PS	-	-	4.2	2.5
PS+0.5%SN	2.1	0.2	4	2.4
PS+0.5%Fe(SN) ₂	1.8	1	4.375	2.175
PS+0.5%Sn(SN) ₂	1	0.8	4.2	2
PS+0.5%Cu(SN) ₂	1.6	1.2	4.3	1.85
PS+0.5%Ni(SN) ₂	2	1.2	4.3	1.5

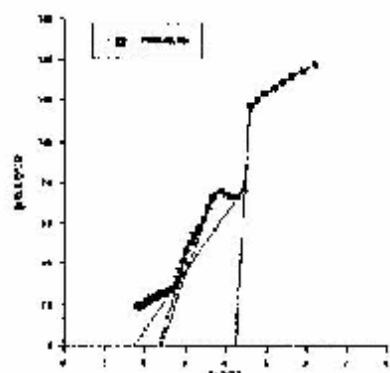
The results presented in Figures (1) indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from valance band to bonding bipolaron band. The second band represents the transition from valance band to anti-bonding bipolaron band, which is in a good agreement with results, are obtained by Bredas et al.^{7,33}



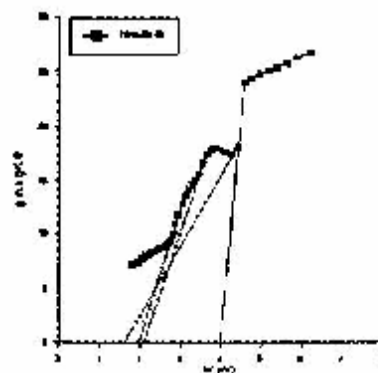
Figure(1) Allowed indirect transition $(\alpha hw)^{12}$ Vs. Energy for PS



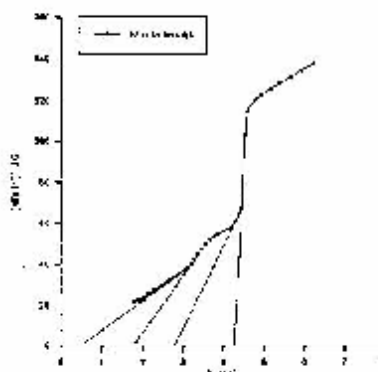
Figure(2) Forbidden indirect transition $(\alpha hw)^{13}$ Vs. Energy for PS



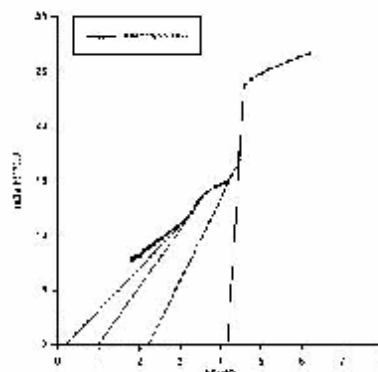
Figure(3) Allowed indirect transition $(\alpha hw)^{12}$ Vs. Energy for PS+0.5%SN



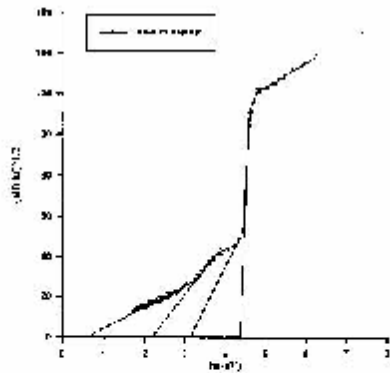
Figure(4) Forbidden indirect transition $(\alpha hw)^{13}$ Vs. Energy for PS+0.5%SN



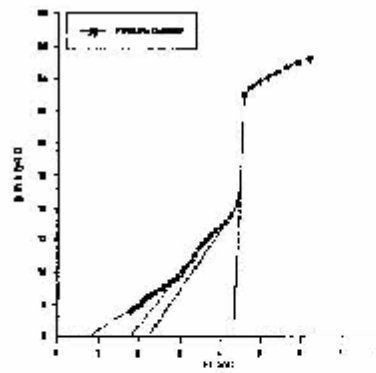
Figure(5) Allowed indirect transition $(\alpha hw)^{12}$ Vs. Energy for PS+0.5%Sn(SN)₂



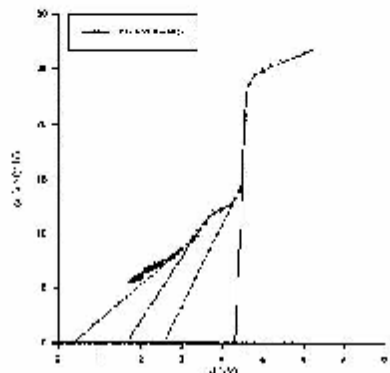
Figure(6) Forbidden indirect transition $(\alpha hw)^{13}$ Vs. Energy PS+0.5%Sn(SN)₃



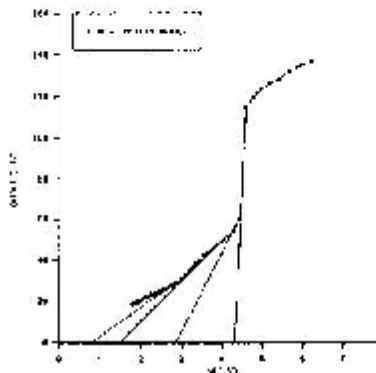
Figure(7) Allowed indirect transition $(\alpha h\nu)^{22}$ Vs. Energy for PS-0.5%Fe(SN)₂.



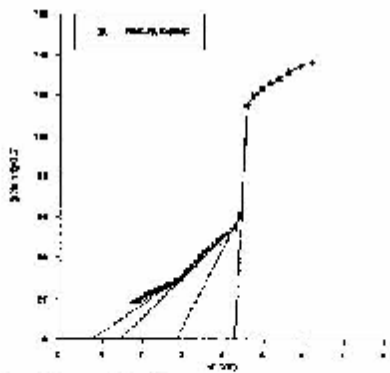
Figure(10) Forbidden indirect transition $(\alpha h\nu)^{13}$ Vs. Energy for PS+0.5%Cu(SN)₂.



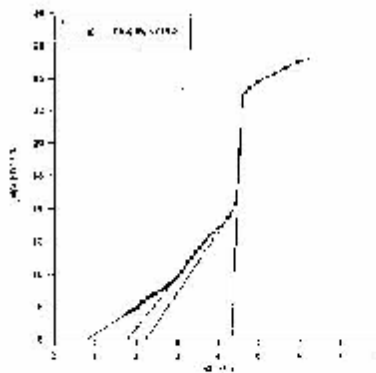
Figure(8) Forbidden indirect transition $(\alpha h\nu)^{12}$ Vs. Energy for PS10.5%Fe(SN)₂.



Figure(11) Allowed indirect transition $(\alpha h\nu)^{12}$ Vs. Energy for PS-0.5%Ni(SN)₂.



Figure(9) Allowed indirect transition $(\alpha h\nu)^{12}$ Vs. Energy for PS10.5%Cu(SN)₂.



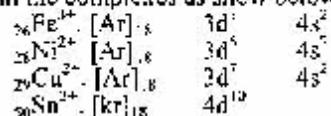
Figure(12) Forbidden indirect transition $(\alpha h\nu)^{13}$ Vs. Energy for PS+0.5%Ni(SN)₂.

Conductivity measurement⁽¹⁶⁾ of PS with and without additive can be obtained by adopting the data of energy gap. (see Table (1) and Figures from (1 to 12)).

The conductivity measurement for PS in the presence of additive increase in the following order
 PS, PS+0.5%Sn, PS-0.5%Sn(SN)₂,
 PS10.5%Fe(SN)₂, PS-0.5%Cu(SN)₂, and
 PS10.5%Ni(SN)₂



The trend obtained might be attributed to the nature of the complexes and the electron configuration of the metal ion in the complexes as show below:



Therefore the coordination ability of square planer (Cu^{II}) and tetrahedral (Ni^{II}) with PS chain is more than that in (Fe^{II}) and (Sn^{II}) because they have unsaturated coordination place in orbital d.

References

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