

Electrical Properties of Iodine - Doped 4-4'- Diaminodiphenyl Sulphone Terminated Poly (P-Aminobenzaldoxime) Thin Films. (PABD-DDS): I₂

Wael A. S. Abdul Ghafor¹, Waleed A. Hussain² and Maha A. Abdul Hassan¹

¹ Polymer Research Centre,

² Physics Dept. Coll. of Education, Basrah University.

ISSN -1817 -2695

((Received 4/9/2005, Accepted 4/2/2009))

Abstract:

Current-Voltage characteristics of Iodine-doped 4-4' Diaminodiphenyl Sulphone terminated Poly (P-Aminobenzaldoxime) (PABD-DDS):I₂ thin films in metal / polymer /metal structure have been investigated. Measurements have been carried out at temperature range 305-373K to determine the conduction mechanism. It was found that charge transfer complexes conduction mechanism is a dominant one throughout the temperature range studied. The average values of drift mobility and trapped carrier density estimated from these characteristics have been found strongly effected by the presence of impurities. The dependence of current and activation energy on the iodine concentration were explained on the basis of charge transfer interaction type between impurities and polymer structure.

Key words: Conduction mechanism, Conductivity, Semiconductive polymer, Iodine doping, Charge transfer complex

Introduction:

Polymer coatings have been widely used in electrical applications because of their numerous excellent properties such as toughness, flexibility, high resistance to an abrasion, high electrical insulation and good moisture and chemical resistance. Polymers coating have shown optical properties, which are highly promising for opto-electronics applications [1-5]. It is well known that polymers based on carbon atoms backbones have intrinsically conducting unless it modified chemically [6]. Even those formed from polyacetylene (CH)_x which have highest conductivity among untreated polymers, must be modified chemically to be designate electrically conductive. Identifying their conduction mechanism still up now considered as a complex process because of the influence of several parameters in the polymer characteristics. Polymer materials have different characteristics. Conduction can be made by forming charge transfer complexes with either donor or acceptor electrons [7]. The effect of methyl substituent and different legend environments on several properties of the orthometalated charge transfer complexes are examined by varying the donor acceptor properties

[8]. Change transfer doping with alkali metals can lead to a classical approach to n-type electron-rich carbon materials [9, 10]. On the other hand it was observed that doping material not only enhanced the electrical conductivity but also developed the stability to the environment as in polyacetylene. Although few studies on the effect of impurities such as iodine on the polymers conductivity are available, detailed investigations effect of various electrical parameters such as carrier mobility, activation energy. Trap concentrations ...etc have been rarely reported. This report can be considered as preliminary results because of the exact nature of the interaction between iodine and the polymer chain is not yet well understood.

Various mechanism such as space charge limited current, tunneling, Richardson-Schottky, Poole-Frenkel effect and thermal ionization of traps and impurities which are applied on inorganic system have been invoked by different workers [11-16]. Signification evidence has been pointed to predict specific mechanism. Tunneling effect occurs only in thin films and that electrode-limited or bulk-limited mechanism was corresponding to the Richardson-Schottky or Poole-Frenkel mechanism

at high temperature and high fields whereas space charge limited current depend on applied voltage, thickness and the temperature of the film [17].

Previous study [18] was carried out on 4-4'-diamino sulphone diphenyl terminated poly [p-Aminobenzaldehyde] in the temperature rang (306-

373) K concluded that, hopping conduction is an expected mechanism which explained the electron mobility between the trap states. This paper is an extension to the above study, the effect of iodine doping on the electrical properties of (PABD-DDS).

Experimental Details:

The polymer was synthesized by condensation reaction of poly (P-amino benzaldehyde) and 4-4'-diamino diphenyl sulphone. The interaction details and chemical analysis of the product polymer were thoroughly discussed else where [19]. Doping with iodine was carried out from solution phase. Films of thickness around 20 μm were grown by a solution slow evaporation technique .The concentration of iodine was varied from 2 to 16 weight percent. Sample in the structure Al /polymer/ Al has been prepared by vacuum deposition aluminum electrodes with cross-section area 1cm^2 .The (current-voltage) characteristic were studied by[LEYBOLD-HERAEUS I-measuring amplifier D(Germany)]

at different temperatures . The current in the quasi steady state was recorded 3 minutes after application of the voltage.The pure and doped films resistivities, were measured in the sandwich configuration as a function of temperature ranging from (305-373) K with a uniform heating rate. The variation of current was measured point by point as a function of the applied voltage and the temperature.

Doping can also be carried out with different methods; such that mixing dilute solution of the two component solution or by bubbling gas through the polymer solution which called (vapor phase doping).

Results and Discussion:

Determination conducting mechanism of material based on analyzing the experimental results can be taken from measuring (current-voltage) and (conductivity- temperature) characteristics can be controlled and easily programmed to reach the mostly expected results. There is a little to say unless other investigations are considered, which support the true results such as study the effect of electrodes materials ..etc. Figure (1) shows the (current-voltage) characteristics of pure and Iodine-doped (PABD-DDS) films measured at room temperature. It was seen that each curve has one distinct region that referred to ascertain conduction, which is ohmic. The current was increased with increasing Iodine concentration. There is a plenty of evidence over the past decade emphasize that the electron mobility along the polymer chain can be increased by doping with oxidizing or reducing agents [18]. Iodine dopant that acts as oxidized agent produces a free positive charges on to the chain. In order to study the effect of Iodine on the activation energy, the current in pure as well as doped films was monitored with voltages at different temperatures as shown in figures (2 and 3) for 2 and 4% concentration respectively as example.The conductivity of the pure polymer at 305K was found to be of the order 5×10^{-11} S/m, the

conductivity was also increased with increasing temperature as shown in figure (4).The conductivity was also increased at any particular temperature with increasing iodine impurity. Rastogi and Hoppra [20] and Rao et al [21] have also recorded similar characteristics due to doping polyvinyl chloride and polyvinyl formal respectively with Iodine. Figure (4) also, shows the temperature dependence of the conductivity for different Iodine concentration, the plots of σ versus $10^3/T$ (K^{-1}) were used to calculate the activation energy. Indeed, undoped, (PABD-DDS) as well as doped one with electron acceptors has possess semiconducting property because its conductivity increases as the temperature increased [21], moreover the activation value has a positive temperature coefficient of electrical conductivity in this temperature region [23].

The experimental results show, that, the activation energy was strongly depended on Iodine concentration and have found to be decreased with increasing Iodine concentration in the polymer as shown in figure (5). Iodine molecules may be resided in different sites such as amorphous/crystalline boundaries aeries, ends of the polymeric chain or even substitutionally in the polymeric chains. It has been reported earlier by Abdul Ghafor and et al [24], that studying high field

conduction in pure, [Benzidine terminated poly (P-amino benzaldoxime)], films were governed mainly by hopping charges between the electronic states. On the other hand the effect of Iodine on the conduction behavior of PVF (polyvinylidene fluoride) films were related to formation charge transfer complex involving the polymer molecules and Iodine[25], Rao and et al [26] have suggested that iodine impurities in the polyvinyl formal may be held between the polymer chains by weak static electroforces formed between Iodine molecules and hydrogen atoms and explained the decrease in the activation energy due to the increased in the crystallinity of the polymer matrix due to the

electrostatic interaction between iodine atoms and molecular chains. Optical analysis can be made to confirm our explanation. Absorption band edge of charge transfer appears at 465 nm as shown in figure (6) and has a red shift by increasing doping concentration. It can be concluded from the above results, that doping with Iodine results to increase electrical conductivity of (PABD-DDS) polymer. The polymer shows appositive thermal coefficient of conductivity and its activation energy decrease with increasing doping concentration. Absorption peak at visible region related to the Iodine molecules which are suggested to form charge transfer complexes with the polymer chains.

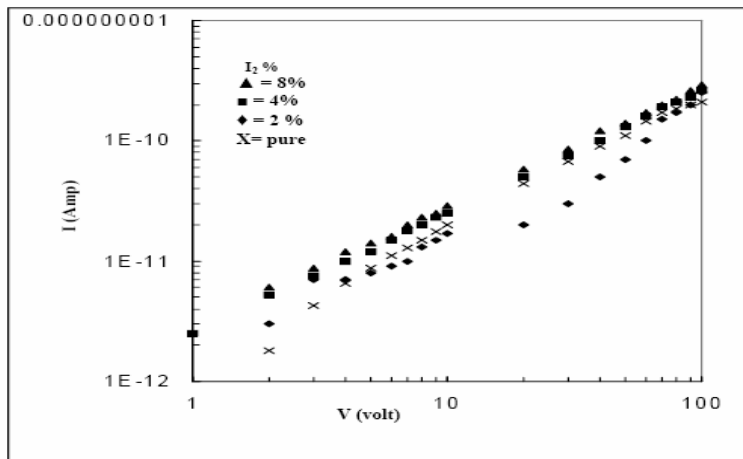


Fig (1): (Current-Voltage) Characteristic of Iodine-doped [PABD-DDS] films of thickness 150 μm at room temperature curve (\blacklozenge , \blacksquare , \blacktriangle) correspond to films doped with iodine concentration (2,4,8%) respectively. Curve x for pure film

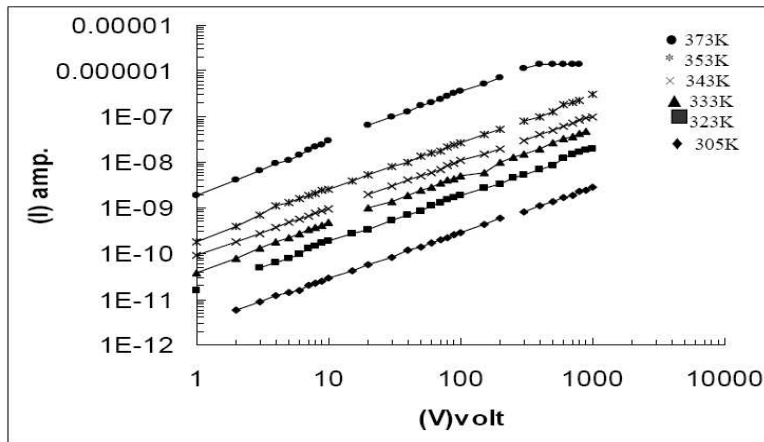


Fig (2): (Current-Voltage) characteristics of 2% iodine-doped [PABD-DDS] measured at different temperatures.

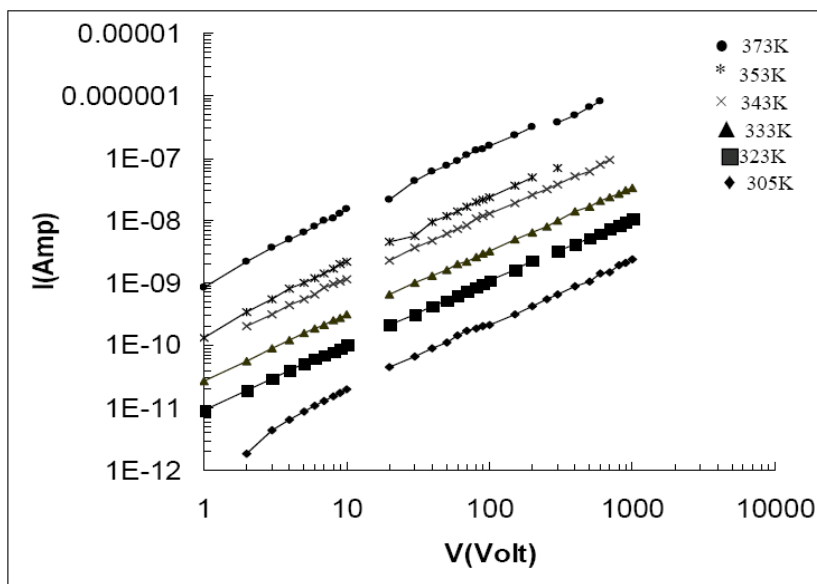
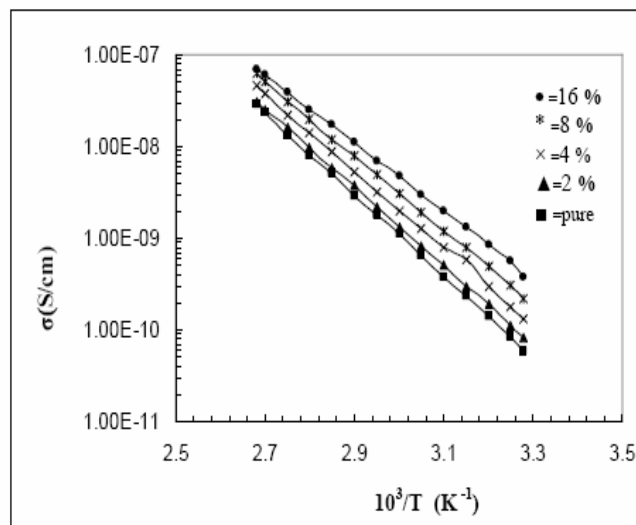
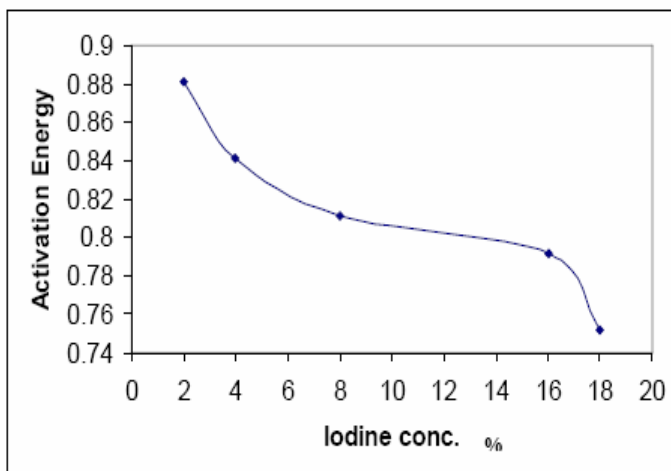


Fig (3): (Current-Voltage) characteristics of 4 % Iodine-doped [DDS-PABD] measured at different temperatures.



Fig(4): Plots of $\log(\sigma)$ versus $10^3/T$ for different iodine concentration (0.0,2,4,8,16)% by weight respectively. Curve ■ is for pure one.



Fig(5): The variation of activation energy with iodine concentration.

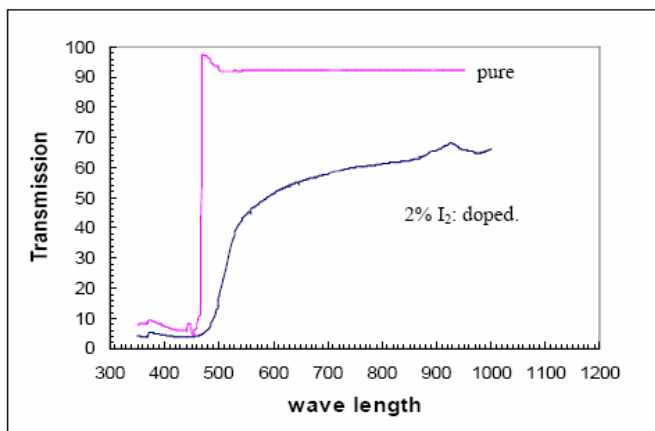


Fig (6) : The transmission % spectra of pure and 2% iodine doped film measured at room temperature (wave length in nm).

References:

1. C. Ionescu- Zanetti, A. Mechler,, S.A. Carter, and R, Lal; *Advanced Materials*, 16(5) p 385. (2004).
2. J. M. Leger, S. A. Carter, B. Ruhstaller, H. G. Nothofer, U. Scherf, H. Tillman, H. H. Horhold; *Physical Reviw B*.6805(5) p 4209. (2003).
3. Y. K. Nakazawa, S. A. Carter, H.G. Nothofer; and U.Scherf; *Applied Physics Letters*, 80)20 p3832-3834. (2002).
4. J. D. Scott, J. C. Brock, J. R. Salem, S. Rammos, L. Bozano, and S. A. Carter; *Synthetic Metals*, 111 p289-293 . (2000).
5. B. Ruhstaller, J.C. Scott, P.J. Brock, U. Scherf, and S. A. Carter; *Chem. Phys. Lett.*317 p238-44. (2000)
6. T. A. Skoithiem, Edt, 'Handbook of conducting polymers' Vol 1, Marcel, Dekker Inc. P. 489 . (1986).
7. Same ref 6. P. 48.
8. R. R. Das, C. L. lee, and J. J. Kim; *Mat. Res. Soc. Symp. Proc.* 708, BB3.39.1. (2002).

9. R. S. Lee, H. J. Kim, and J. E. Fischer; and R. E. Smalley; Nature ,P388. (1997).
10. M. Bockrath, J. Hone, A.Zettl, P. L. Mc Euen, A. G. Rinzler, and R.E. Smally, Phys. Rev .B61, P10606. (2000).
11. R. Bahri, and H. P. Singh; Thin Solid Films, 69, p 281. (1980).
12. E. Staryaga, and J. Swiatek; Thin Solid Films 56, p 281. (1980).
13. T. V. Rao, and K. L. Chopra; Phys.Status Solidi (a) 53, p43 (1979).
14. J. Chutia, and K. Barua, Thin Solid Films, 55, p 387. (1978).
15. S. D Phadke, K. Sathianadan , and R. N. Karekar, Thin Solid Films, 51 , L9. (1978).
16. V. K. Jain, C. L. Gupta, and R. K. Jain; Indian J. Pure Appl. phys 16, p 625.(1978).
17. H. Stubb, E. Punkka, and J. Paloheim; Materials Science and Engineering 10 , p 85-140. (1993).
18. M. Opallo; Materials Scince, 20, 1, , p 7-14. (2002).
19. W.A.S. Abdul Ghafor, W. A. Hussain, A. M. Haddad, and G. A.Adam, Basrah J. Science 18 , p131-144. (2000).
20. A. C. Rastogi, and K. L. C. Hopra; Thin Solid Films, 26 , p61. (1975).
21. V. N. Rao, T. S. Rao, and N. N. Das; J.Phys. Chem. Solids, 47, p 33. (1986).
22. Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, M. Sekerci, Y. Balci, and I. Aksoy; Synth. Met, 107, p191. (1999).
23. Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, S. Saydam, M. Sekerci, and F. S. Boydag; Synth. Met, ,138. (2001).
24. W. A. S Abdul Ghafor, and A. M.Haddad; Basrah J.Science, 15, p129-139. (1997).
25. S. Chand, S. Radhakrish ran, and P. C. Mehen dru; J. phys. D: Appl phys. 15, P. 2449. (1982).
26. T. V. Rao, and K. L. Chapra; Physics Status Solidi (a) 53, P. 43. (1979).

Iodine- doped 4-4- diaminodiphenyl Sulphone Terminated Poly (P- Aminobenzaldoxime)

وائل عبد السلام عبدالغفور¹ وليد علي حسين² مها عبد علي عبدالحسن¹
¹مركز ابحاث البوليمر
²قسم الفيزياء- كلية التربية - جامعة البصرة - البصرة - العراق

المستخلص

تمت دراسة ميزات (الفولتية- التيار) لرقائق البوليمر

Iodine- doped 4-4- diaminodiphenyl Sulphone Terminated Poly (P- Aminobenzaldoxime)

مركبه بهئية معدن/ بوليمر/ معدن، لتعين الية التوصيل اجريت القياسات في مدى درجات الحرارة (305 -373) كلفن. وجد ان الية التوصيل المتحكمة في هذا المدى من درجات الحرارة هي انتقال معقدات الشحنة. كما وجد ان معدل قيمة التخركية وكثافة الحاملات المقتنصة التي تم تخمينها من خلال الخصائص تعتمد بشدة على وجود الشوائب. وان اعتماد التيار وطاقة التنشيط على تركيز اليود تم تفسيرها على اساس انواع تفاعلات انتقال الشحنة بين الشوائب وتركيب البوليمر.