STUDY ON ELECTRICAL PROPERTIES OF CONJUGATED POLYMERS

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ABSTRACT

The idea of doping was first conceived with regard to organic, small-molecule compounds. Evaporation at a high temperature may be used to build very thin films consisting of these very tiny molecules. After then, a dopant molecule comes from a different source and is coevaporated with the host. By proceeding in this manner, a uniform dispersion of the doping throughout the host may be accomplished. Conjugated polymers, on the other hand, are deposited via a technique using a solution. It is difficult to process thin films from a solution that contains a dopant since doing so quickly leads to charge transfer and aggregation already present in the solution, which in turn makes processing such films impossible. As a result, in this work, we have examined the optical as well as the electronic characteristics of conducting polymers. Additionally, it has been shown how the optical and electronic properties have been altered as a result of charge transfer that has happened as a result of doping. The optical and electrical characteristics of conjugated polymers were discussed in this article. In addition, the charge transport models that are used to explain the hole and electron transport process are a part of the electrical characteristics that are given for conjugated polymers. The impact of doping on both the optical and electrical characteristics of the material was also investigated in this work.

KEYWORDS: *optical, polymers*

INTRODUCTION:

The phrase "organic metals" refers to polymers that have a reasonably high electrical conductivity and are considered to be relatively recent additions to the scientific lexicon. The advent of these materials occurred in the late 1970s, at the same time that they began to dominate the scientific community and subsequently the commercial sector. Because such materials lie at the heart of organic electronics, their impact is difficult to overstate because their significance cannot be overstated. They were used in biosensors, electrochemical transistors, photovoltaics, touch screens, solar cells, supercapacitors, and a variety of other applications.

In their most fundamental form, organic metals may be understood as conducting polymers. It's possible that using the words "conductivity" and "polymers" in the same sentence will leave you scratching your head, given that the vast majority of plastics are excellent insulators. However, in 1977 Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa conducted a series of studies that proved a considerable conductivity of polyacetylene thin films. The oxidation of polyacetylene with chlorine, bromine, and iodine resulted in a conductivity value of 105 S/cm. This is 109 times more than the conductivity value of typical polymer materials. The conductivity of silver and copper, which is equivalent to 108 S/cm, may be compared to this number to illustrate its applicability. Unfortunately, the initial materials that were examined revealed undesirable qualities such as instability when exposed to air humidity and water solubility, which precluded an industrial use from being possible. This remained the case until the latter half of the 1980s, when the Bayer corporation received a patent on poly(3,4-ethylenedioxythiophene), also known as PEDOT, which represented a major advance in the field of organic electronics.

It is common knowledge that conjugated polymers, also known as CPs, are the most promising contender in the area of organic semiconductors because to the ease with which they can be processed, the colour tenability, and other factors. The devices that are based on structure CPs are comprised of a very basic structure. This structure consists of an emissive polymer that is positioned between a cathode with a low work function and an anode with a high work function. Due to the fact that the majority of CPs exhibit trap-limited electron transport, polymer LED devices are hole dominated systems. This leads to the degradation of the polymer diode. It is thus vital to accomplish balanced electron and hole transport in order to construct a polymer-based LED device that operates at a high level of efficiency. We have included the idea of doping so that we may reach an equilibrium in the amount of electrons and holes that are transported. The idea of doping was first conceived with regard to organic, small-molecule compounds. Evaporation at a high temperature may be used to build very thin films consisting of these very tiny molecules. After then, a dopant molecule comes from a different source and is coevaporated with the host. By proceeding in this manner, a uniform dispersion of the doping throughout the host may be accomplished. Conjugated polymers, on the other hand, are deposited via a technique using a solution. It is difficult to process thin films from a solution that contains a dopant since doing so quickly leads to charge transfer and aggregation already present in the solution, which in turn makes processing such films impossible. Therefore, in this research, we have discussed the optical as well as the electronic characteristics of conducting polymers. Additionally, it has been shown how the optical and electronic properties have been altered as a result of charge transfer that has happened as a result of doping.

OBJECTIVE

1. To study on Electrical Properties of Conjugated Polymers
2. To study on Optical Properties of Conjugated Polymers

Optical Properties of Conjugated Polymers

Optical Absorption: The formation of excited state molecules. In a small molecule that has an isolated double bond, the absorption of a photon with an energy that is higher than the energy gap (E_g) between the two orbitals can cause a pi electron to be promoted from a lower energy state to a higher energy state. This occurs when the photon has an energy that is greater than the energy gap. On the other hand, an identical molecule that contains conjugated double bonds would have a highest occupied molecular orbital (HOMO)

with a higher energy level and a lowest unoccupied molecular orbital (LUMO) with a lower energy level. Because the orbital interactions caused the energy gap to diminish, a photon with a lower energy may now promote a pi electron from HOMO to LUMO. As a consequence, the energy gap Eg in conjugated polymers can be even smaller than it was before.

Relaxation of excited states is what optical emission is all about. An exciton is an electron-hole pair that is electrostatically bonded and is produced when a semiconducting polymer absorbs a photon with sufficient energy (hv). This promotion of an electron from the HOMO to the LUMO level results in the production of excitons. This species in an aroused condition is able to move from one site to another until it deactivates by some mechanism and returns to its normal state. The process of luminescence is considered to be one of the most valuable deactivation processes in conjugated polymers (light emission). Luminescence may be broken down into two distinct subtypes: fluorescence and phosphorescence. These distinctions are made according to the spins of the electrons that are engaged in radiative transitions, as illustrated in Figure 1.

Phosphorescence is the name given to the process of light emission that occurs when electrons in excited states have the same spin as electrons in the ground state orbitals that correspond to those excited states. The term "fluorescence" refers to the emission that occurs when the excited electron has the opposite spin as the electron that resides in the ground orbital that corresponds to it. Phosphorescence is the process that occurs when an electron moves from a triplet excited state in which the electron spins are unpaired to a singlet ground state in which the electron spins are coupled. This transition is explicitly prohibited by the selection rule of quantum mechanics, and it happens at a rate that is substantially slower than fluorescence, which involves a transition that is permitted between a singlet excited state and a singlet ground state. A state energy diagram or a Jablonski diagram, such as the one shown in Figure 1, may be used to explain the many additional photophysical processes that take place in electronic excited states. S0 stands for the singlet ground state, while S1 and S2 stand for the first and second excited states, respectively. The singlet ground state is abbreviated. T1 is the symbol used to designate the first triplet excited state. Each of these levels of electrical energy has its own unique vibrational energy, denoted by the notation v = 0, 1, 2, and so on. The normal progression of an electron from S0 to S1 or S2 after the absorption of an intense photon is as follows: In most cases, stimulated electronic systems quickly relax via an internal conversion to the S1 level with the lowest vibration. The singlet exciton has ample time to travel substantial distances inside a conjugated polymer when it is in this excited state (S1,] = 0, 1, 2, etc.). This state is denoted by the notation S1. After some time, the excited electron will fall back to its ground state, which will then be followed by fluorescence. These radiative transitions are designated as (0, 0), (0, 1), (0, 2), and so on. Fluorescence is caused by electronic transitions moving from the lowest vibrational level (v= 0) of S1 to the vibrational level (v = 0, 1, 2) of the electronic ground state (S0).

Conjugated polymers' electrical properties may be broken down as follows:

Because conjugated polymers are highly disordered systems, the idea of band conduction via the movement of free electrons or holes is no longer used to explain the transport mechanisms that occur in these materials. Charge carriers are required to bounce from location to location across the expansive energy environment in order to participate in transportation. The hopping probability between occupied i to unoccupied j states depends upon energy difference Δij between the two states i and j and relative distance between corresponding two states Rij. The probability of hopping transition is given by

$$\nu_{hop} \alpha \exp\left\{-2\gamma a \frac{R_{ij}}{a}\right\}. \qquad (1)$$

This makes it possible by electric field term. Now the temperature dependence of mobility is given by

$$\mu = \mu_0 \exp\left\{-\left(\frac{T_0}{T}\right)^\gamma\right\}. \qquad (2)$$

γ represents the field enhancement factor which reflects the fact that upon increasing temperature conductivity arises with increase in available states.

Hole Transport in Conjugated Polymers. The gadget is made up of a single sheet of polymer that is placed between two electrodes so that researchers may study the mobility of holes (one hole injecting contact and one electron blocking contact). In this investigation, gold is used as an electron blocking contact material. The current in polymer-based hole only (HO) diodes is typically space charge limited (SCL), and Child's law is used to define the current density.

$$J = \frac{9}{8}\mu_p \varepsilon_r \varepsilon_0 \frac{V^2}{L^3}, \qquad (3)$$

where $\varepsilon_0 \varepsilon_r$ is the permittivity of the material, L is the film thickness, and μp is zero-field hole mobility which obeys the following temperature and field dependence, the thing that will be discussed in the next section.

Models of charge transport may be used to describe the movement of holes in conjugated polymers. Because of chemical flaws, kinks, twists, and eventually conjugation breakdowns, conjugated polymeric systems are not flawless systems. These faults may occur in the system. Therefore, band-to-band transfer is not viable at this time, and the hopping process is responsible for governing charge movement. In inorganic semiconductors, it might be difficult to see how charge moves through the material. There is not one standard method currently available, and several different models have been developed to characterise the mobility. The mobility is shown to be dependent on the amount of charge carriers present, the electric field, and the temperature in the majority of the models. Only a select few of the models that are relevant to our work are outlined below.

1. The Relationship Between the Field and Temperature and How It Affects Hole Mobility SCL currents are able to provide a good description of hole transport in conjugated polymers when applied at lower fields initially. However, when the field strength is increased, the current density will often exhibit strange behaviour owing to an increase in the hole mobility. This indicates that carrier mobility improves in the presence of an electric field, and this phenomenon has been adequately described within a model of space charge limited conduction (SCLC), which takes into consideration a stretched exponential field dependency of mobility.

$$J = q\mu_p(0,T)\,p(x)\,E(x),$$

$$p(x) = \frac{\varepsilon\varepsilon_0}{q}\frac{dE(x)}{dx},$$

$$\mu_p(E,T) = \mu_p(0,T)\exp\left(\gamma\sqrt{E}\right), \tag{4}$$

$$\text{where } \mu_p(0,T) = \mu_{p_0}\exp\left(-\frac{\Delta_0}{K_BT}\right),$$

where μ_{p_0} is the electric field and temperature independent hole mobility, Δ_0 is the zero-field activation energy, K_B is Boltzmann's constant, T is the temperature of the sample, and γ is field enhancement factor. Equation (4) is used to describe the charge transport in a variety of semiconducting polymers; however it lacks theoretical justification.

2. The Gaussian Disorder Model and the Correlated Disorder Model. Bassler proposed that the energy level (LUMO ¨ and HOMO) of the polymer can be approximated using a Gaussian distribution. Under this Gaussian distribution approximation, the density of states (DOS) is given by

$$\text{DOS}_{\text{Gaussian}} = \frac{N}{\sqrt{2\pi}\sigma_{\text{DOS}}}\exp\left(-\frac{E^2}{2\sigma_{\text{DOS}}^2}\right), \tag{5}$$

where N is the total density of states, σ_{DOS} is the width of the Gaussian density of states, and E is measured relative to the center of the DOS.

The GDM model describes the carrier transport as a biased random walk among the hopping sites with Gaussian distributed random site energies. GDM predicted T and F dependence of charge carrier mobility to be

$$\mu(F,T) = \mu_0\exp\left[-\left(\frac{2\sigma}{3k_BT}\right)^2\right]$$

$$\cdot\exp\left[C_0\left\{\left(\frac{\sigma}{k_BT}\right)^2 - \Sigma^2\right\}\sqrt{E}\right], \tag{6}$$

where σ and Σ are energetic disorder and positional disorder are the two types of disorder, whereas C_0 is the constant. The PF-like field dependency of mobility was, however, only recreated by the GDM model across a rather limited range of electric field strengths. As a result of this, some have come to the conclusion that UGDM does not accurately depict disorder behaviour in disorder molecular organic systems. Recent calculations and simulations have shown that the existence of long range energy correlation gives rise to mobility similar to that of Poole Frenkel (PF) across a considerably greater field range. This was verified by the fact that this phenomenon occurred. This disparity in field dependence between GDM and the experimental results was resolved by Gartstein and Conwell when they introduced a correlation between the energies of spatially close sites using an empirical relation. This allowed them to account for the differences between the two sets of data. This spatial correlation of energies that is included in the correlated Gaussian disorder model (CGDM) can be justified as arising from long range energy correlation from the charge dipole interaction or correlation in thermal fluctuation in molecular geometries. Both of these correlations can be found in molecular geometries.

$$\mu(F,T) = \mu_0 \exp\left[-\left(\frac{3\sigma}{5k_BT}\right)^2\right]$$

$$\cdot \exp\left[C_0\left\{\left(\frac{\sigma}{k_BT}\right)^{3/2} - \Gamma^2\right\}\sqrt{\frac{eaE}{\sigma}}\right], \qquad (7)$$

where $C0$ and Γ are the parameters of the model, Γ characterizes the geometrical disorder, and a is the intersite hopping distance. Poplavskyy and Nelson explained the hole transport in the organic small molecule material $2,2',7,7'$ -tetrakis-(N,N-di-4-methoxyphenylamino)- $9,9'$ -spirobifluorene(methoxy-spiro) using GDM. In the recent study, Redecker et al. also described the hole transport behavior using GDM in blue and white polymers.

3. Pasveer's Model. In addition, researchers have come to the conclusion that an other significant element, known as carrier density, which also had an effect on carrier mobility was significantly underestimated. If we disregard the effect that the carrier density has on the density of states in these polymers, both the hopping distance and the breadth of the density of states will be underestimated as a result. As a result, Pasveer et al. suggested an enhanced version of the Gaussian disorder model that takes into account density dependent mobility in conjunction with electric field and temperature (EGDM). In this model, they attempted to account for the mobility dependency on the electric field and the charge carrier density, both of which are taken into account by the field and density enhancement functions:

$$\mu_p(T,p) = \mu_0 \exp\left[\frac{1}{2}\left(\hat{\sigma}^2 - \hat{\sigma}\right)\left(2pa^3\right)^\delta\right],$$

$$\text{where } \mu_0 = \frac{a^2\nu_0 e}{\sigma},$$

$$\mu_p(T,p,E) \approx \mu_p(T,p)\, f(T,E),$$

$$\delta = 2\frac{\ln\left(\hat{\sigma}^2 - \hat{\sigma}\right) - \ln(\ln 4)}{\hat{\sigma}^2}, \qquad (8)$$

$$f(T,E) = \exp\left\{0.44\left(\hat{\sigma}^{3/2} - 0.22\right)\right.$$

$$\left.\cdot\left[\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right]\right\},$$

$$\text{where } \hat{\sigma} = \sigma/K_BT.$$

The fact that EGDM takes into account both the density and the field dependency of the mobility is one of its most appealing features. In addition to this, it only needs three factors, all of which are temperature independent, which makes the process of fitting experimental data much simpler. There are a number of reports that may be used in conjunction with this model to provide a description of the charge transport in materials of this sort. Zhang et al. documented the hole transport in poly[(9,9-di-n-octylfluorenyl2,7-diyl)-alt-(benzo[2, 1, 3]thiadiazol-4,8-diyl)] (F8BT) by constructing an ohmic hole contact on F8BT by employing the high work function anode MoO3 as the hole injection contact. This allowed for the hole transport to occur.

In the Case of Conjugated Polymers, Doping

The incorporation of p-type materials into conjugated polymers has been accomplished by the process of improved hole injection into the matrix, which was then followed by the alteration of the interfaces. Doping of a p-type dopant, tetrafluorotetracyanoquinodimethane (F4-TCNQ), with conjugated polymers with a broad range of the HOMO levels was investigated in a case study that was published by Nollau et al. As a consequence of doping, they were able to demonstrate that the bulk conductivity as well as the hole current both rise by many orders of magnitude while simultaneously reducing the turn-on voltage.

The researchers Zhang et al. from the University of Groningen in the Netherlands looked at an alternative method to study the impact of doping in organic semiconductors. Doping the materials will result in a simultaneous increase in carrier concentration and carrier mobility, which will cause the conductivity of the materials to rise. This is because the conductivity of any material is the product of the carrier mobility and the number of charge carriers in the material. In semiconducting materials, the transfer of carriers often takes place by a process known as hopping between the GDOS. Therefore, if we disregard the effect that carrier density has on the density of states in these polymers, we will end up with an inaccurate assessment of both the hopping distance and the breadth of the density of states. As a result, they suggested using a mobility model that was reliant on density in conjunction with electric field dependency and temperature dependence.

They have addressed many situations of regulated p-type and n-type doping of poly[2-methoxy-5-(2-ethylhexyloxy)- 1,4-phenylenevinylene] (MEH-PPV) deposited from solution [29]. The p- and n-type dopants that they used were tetrafluorotetracyanoquinodimethane (F4-TCNQ) and bis(pentamethylcyclopent They have shown that aggregation can be avoided and doped films may be deposited with a regulated carrier density by selecting appropriate dopant solvents and changing the polarity of the solution. This was accomplished by choosing acceptable dopant solvents.

It has been discovered that the electron transport in conducting polymers is characterised by exponential distribution of traps, and as a consequence, hole current is no longer equal to electron current. As a consequence of this, it has been found that the electron transport in MEH-PPV becomes comparable to hole transport when the traps are deactivated. In this particular experiment, the n-type dopant DMC was introduced into the MEH-PPV compound. They were able to achieve this by filling the traps with electrons from the DMC donor, which resulted in a trap-free space-charge limited electron current in the MEH-PPV. Doping resulted in a significant increase in charge transport for both p-type and n-type materials, and Zhang et al. demonstrated that in MEH-PPV, the mobility of free electrons is comparable to that of holes.

Zhang and Blom have published their findings on the doping-induced changes to the electrical characteristics. They looked at the electron and hole transport in the F8BT material. They started by studying hole transport after they resolved the injection barrier by using MoO3 as a hole injection contact. This allowed them to study hole transport. In addition, they conducted research on the electron transport in F8BT and discovered that it was hindered by traps. Subsequently, the n-type doping of DMC was able to deactivate these traps.

Recent research on the electron transport properties of tris(8-hydroxyquinolinato)aluminum (Alq3) that is doped with cesium carbonate (Cs2CO3) have been described [30]. By using an electron injection layer

composed of cs2co3, they establish an ohmic contact with the Alq3. In addition to this, they looked into the impact that doping Cs2CO3 had; they found that it led to an increase in conductivity as well as mobility.

CONCLUSION

Within the scope of this research project, we aimed to conduct a comprehensive evaluation of the optical and electrical features of CPs. We have examined the impact that dopant has on the optical and electrical characteristics of CPs and discussed our findings. This work, in essence, sheds appropriate light on the optoelectronic characteristics of conducting polymers, which enables us to utilise it with a better knowledge for the creation of polymer-based polymer light emitting diodes. [Citation needed] (PLED).

REFERENCES

1. C. K. Chiang, C. R. Fincher Jr., Y. W. Park et al., "Electrical conductivity in doped polyacetylene," Physical Review Letters, vol. 39, no. 17, pp. 1098–1101, 1977.

2. M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, "Controlled doping of phthalocyanine layers by cosublimation with acceptor molecules: a systematic Seebeck and conductivity study," Applied Physics Letters, vol. 73, no. 22, pp. 3202–3204, 1998.

3. W. Gao and A. Kahn, "Controlled p-doping of zinc phthalocyanine by coevaporation with tetrafluorotetracyanoquinodimethane: a direct and inverse photoemission study," Applied Physics Letters, vol. 79, no. 24, pp. 4040–4042, 2001.

4. M. Yan, L. Rothberg, B. R. Hsieh, and R. R. Alfano, "Exciton formation and decay dynamics in electroluminescent polymers observed by subpicosecond stimulated emission," Physical Review B, vol. 49, no. 14, pp. 9419–9422, 1994.

5. M. Pollak and I. Riess, "A percolation treatment of high-field hopping transport," Journal of Physics C: Solid State Physics, vol. 9, no. 12, article 2339, 1976.

6. L. Li, G. Meller, and H. Ksina, "Temperature and fielddependence of hopping conduction in organic semiconductors," Microelectronics Journal, vol. 38, no. 1, pp. 47–51, 2007.

7. V. L. Malevich, "On the high-frequency electric field effect on the two-phonon hopping transport," Physica Status Solidi B, vol. 163, no. 2, pp. K101–K105, 1991.

8. H. C. F. Martens, P. W. M. Blom, and H. F. M. Schoo, "Comparative study of hole transport in poly(p-phenylene vinylene) derivatives," Physical Review B, vol. 61, no. 11, pp. 7489–7493, 2000.

9. M. A. Lampert and P. Mark, Current Injection in Solids, Academic Press, New York, NY, USA, 1970.

10. P. W. M. Blom and M. C. J. M. Vissenberg, "Charge transport in poly(p-phenylene vinylene) light-emitting diodes," Materials Science and Engineering R: Reports, vol. 27, no. 3-4, pp. 53–94, 2000.

11. D. H. Dunlap, P. E. Parris, and V. M. Kenkre, "Charge-dipole model for the universal field dependence of mobilities in molecularly doped polymers," Physical Review Letters, vol. 77, no. 3, pp. 542–545, 1996.

12. S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, "Essential role of correlations in governing charge transport in disordered organic materials," Physical Review Letters, vol. 81, no. 20, pp. 4472–4475, 1998.

13. Yu. N. Gartstein and E. M. Conwell, "High-field hopping mobility in molecular systems with spatially correlated energetic disorder," Chemical Physics Letters, vol. 245, no. 4-5, pp. 351–358, 1995.

14. D. Poplavskyy and J. Nelson, "Nondispersive hole transport in amorphous films of methoxy-spirofluorene-arylamine organic compound," Journal of Applied Physics, vol. 39, no. 1, article 341, 2003.