Enhanced electrical and optical properties of iodine doped LDPE films

K Sreelatha and P Predeep
Laboratory for Unconventional Electronics & Photonics, Department of Physics, National Institute Technology, Calicut, Kerala, India 673 601
Condensed Matter Physics Laboratory, Department of Physics, Sree Narayana College, Kollam, Kerala, India

E-mail: ppredeep@gmail.com

Abstract. In this study, an attempt has been made to dope Low Density Polyethylene (LDPE) with iodine and to study the effect of iodine doping on the optical band gap of LDPE films. The DC conductivity measurements and UV/Vis spectral studies are employed to characterize the samples. Iodine treatment induces colour change in the polymer film which supports the interaction between iodine molecules and polyethylene chains. I$_2$ molecule links the polymer chains electronically and provides conducting pathways by forming DA complexes. The absorption band of complex films has extended to the visible and near infrared region of the spectrum. Further there are discernible shifts found in the energy gap and band edge towards lower energies on doping with iodine. This is essentially due to the formation of strong DA complexes upon iodine doping which improves the conducting behaviour.

1. Introduction
Organic electronics or plastic electronics is a relatively new field of research that involves challenges regarding electronic devices made with carbon-based materials, such as (semi)conducting polymers and other organic materials. Conducting plastics are the best choice to be employed in the fabrication of electronic devices as they possess the electronic properties of a semiconductor and the specific properties of plastics such as light weight, high mechanical strength and flexibility. Another important motivation for the interest in organic (semi)conductors is its easy processability and expected low cost of the end product. The developments in memory materials, optoelectronic devices and applications focused to biomedicine are also emerging as progressing areas. There are many potential applications including, light emitting devices, nonlinear optical devices, photovoltaic devices, plastic field-effect transistors, and electro-magnetic shielding. The ability of the polymer to form thin film from solution allows them to be deposited on many kinds of substrates, providing opportunities [1] for many novel applications.

Low Density Polyethylene (LDPE) with its proven advantages of plastic flexibility and transparency has all the potential to find applications ranging from consumer electronics to optoelectronics, microelectronics and a host of new photonic applications. LDPE has short and long
branches of polyethylene [2] made of covalently bonded carbon atoms with hydrogen or methyl (CH$_3$) groups in a planar zigzag chain. Owing to the branched nature, LDPE has a reduced percentage of crystallinity and this increases the dependence of electrical behaviour on the non-crystalline and interfacial regions. Even though LDPE is chemically unreactive at room temperature it is slowly attacked by strong oxidizing agents such as halogens. Electrical conductivity can be enhanced by doping the polymer with oxidizing or reducing agents. A suitable dopant improves [3, 4] the charge carrier mobility of the polymer. It is known that iodine molecule possess acceptor properties and high electron affinity and it captures electron from the polymer macromolecule, forming donor/acceptor (DA) complexes with LDPE chains which improves the conducting behaviour of the polymer.

In this study, an attempt has been made to dope LDPE with iodine molecule and to study the effect of iodine doping on the optical band gap of LDPE films. UV/Vis spectral studies are employed to characterize the samples. The DC conductivity measurements of the doped films are made by the four probe techniques.

2. Experimental

2.1. Materials
Low Density Polyethylene films of thickness 0.03 mm were purchased from Good Fellow materials; U. K. Iodine (Merck) of analytical grade was purchased from local suppliers and used as received.

2.2. Sample preparation
Thin films of LDPE and iodine crystals are placed in a sealed tube for several days. Iodine is introduced through diffusion of iodine vapour into the PE chains. After this the samples are uncovered and stayed in air for time long enough to remove excess iodine from the surfaces of the samples.

2.3. Characterization
The DC conductivity measurements of the doped films are made by the four probe techniques using the Keithly 6514 Electrometer and Keithly 2000 DMM. The UV-Visible absorption spectra of the samples are recorded at room temperature on Cary 5000 at a scan rate of 600 nm per minute in the wavelength range 300-900 nm. From this data, the optical band gap is determined.

3. Result and discussion

3.1. DC Conductivity
Iodine treatment changes transparent LDPE films to purple and then to black shade with the increase in the doping period. The colour change supports the interaction between iodine molecules and polyethylene chains. Iodine exists in the form of neutral I$_2$ or as molecular aggregates I$_n$ in the amorphous regions of the polymer [5-8]. I$_2$ molecule links the polymer chains electronically and reduces the inter chain barrier to charge transfer thereby increasing conduction. The electron transferred to the I$_2$ molecule moves either as stable iodide ion [5] or is transferred again to another polymer molecule with the iodine acting as a transfer agent [8, 9]. Thus iodine provides conducting pathways through the non-crystalline regions interconnecting the crystallites by forming DA complexes at appropriate sites on the chains. Further electrons captured by iodine pass through iodine states to reach electron vacancy (EV) sites on adjacent PE chains where recombination can occur to maintain conduction [5]. As the time of exposure to iodine is increased the colour, conductivity and iodine content in the film also increases. The conductivity of the doped films reached a maximum value of about 3.5 x 10$^{-5}$ Scm$^{-1}$.
The current-voltage characteristic of LDPE iodine films measured at room temperature is shown in figure 1. The conduction observed in these films shows a practically linear plot indicating the Ohmic characteristics of the charge transfer complexes.

\[ \alpha h\theta = A(h\theta - E_g)^n \]  

(1)

Here \( \alpha \) is the absorption coefficient, \( h\theta \) the photon energy, \( A \) is a constant and the index \( n \) is the distribution of the density of states which assumes values \( 1/2, 3/2, 2 \) and \( 3 \) depending on the nature of
the electronic transition responsible for the absorption. $n = 1/2$ corresponds to the direct allowed transition energy gap.

The direct band gap is determined from plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) as shown in figure 3. The intercept of these curves on the photon energy axis gives the direct bandgap. For pure LDPE films the direct bandgap lies at 3.65 eV while for doped films, the value decreases to 2.25 eV. The reduction in the band gap due to iodine doping indicates the incorporation of iodine into the polymer chain and, thereby, extending the density of states more into the visible and near IR region of the electromagnetic spectrum as compared to that of the undoped case.

4. Conclusion

Electrical and optical properties of the LDPE-iodine film depend on exposure time and iodine concentration. Energy gap shifts to lower energies on doping with iodine thus increasing the capability of polymers to conduct. In LDPE, iodine exists as neutral iodine in between the polymer chains, acts as electron transfer agents, links the polymer chains electronically and reduces the inter chain barrier to charge transfer thereby increasing conduction.

5. References

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