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Studies on Dark and Photoconductivity of MEH-PPV:C_{60} Thin Films

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1. Introduction

Since the last decade conducting polymers like the poly[2-methoxy, 5-(2'-ehtylhexyl-oxy) -p-phenylene vinylene] (MEH-PPV) have attracted enormous attention due to their wide application prospects in devices such as LEDs and Photovoltaic Cells[1,2]. Photoinduced electron transfer from the excited state of the MEH-PPV onto C_{60} has been reported to be very rapid with a charge transfer rate ($> 10^{12}$ sec^{-1}) due to formation of neutral donor (D) and acceptor (A) complex leading to efficient charge separation as required in applications like thin film heterojunction diodes and photovoltaic cells[2]. To understand the electron injection into the C_{60} we present here our preliminary results of dark and photoconductivity studies of MEH-PPV:C_{60} thin films for various ratios (by weight) of MEH-PPV: C_{60}.

2. Experimental

Thin Films of MEH-PPV:C_{60} mixture in ratios of 1:1, 1:2 and 1:3 by weight in chloroform were prepared by rod spreading technique onto finely cleaned glass plates to a thickness of approximately 200 nm. Prior to thin film deposition, Al strips of 0.5 μm thickness were coated as contact materials at the edges so as to achieve the device area ≅ 0.1cm^2 by vacuum sublimation at 6.65 mPa pressure. The dark and photoconductivities were studied in the temperature range from −115℃ to 200℃ in a vacuum of 10^{-5} torr. The temperatures were monitored from −115 ℃ to 200 ℃ and the measurements were performed such that the system remains in equilibrium at each temperature for both heating and cooling cycles. A 300W white daylight lamp was used for illumination at a fixed intensity of 155 mW/cm^2 for all measurements under illumination. Samples were covered and kept in vacuum of 1.33mPa immediately after deposition of the thin films. The dark and photo conductivity results of MEH-PPV:C_{60} thin films are compared with bare MEH-PPV thin film. The activation energies are calculated using the Arrhenus plots [σ vs. 1000/T] of the MEH-PPV: C_{60} thin film.

3. Results and Discussion

It is found from Fig.1 and Fig.2 that with the increase of C_{60} concentration, the activation energy tends to decrease for both dark and photoconductivity plots indicating that presence of C_{60} in MEH-PPV facilitates ultrafast charge transfer. The charge separation is stabilized by carrier delocalization. The electron transfer is found to occur from the photoexcited broad π (valence) band to π*(conduction) band of the semiconducting polymer, MEH-PPV[3]. The photoexcitation of the conducting polymer with photon energies greater than π–π* gap the electron transfer is a very rapid process with the charge transfer occurring in the time range of 10^{-12} s. The C_{60} induces the electron transfer from the π* band to the conduction band of the C_{60} thereby increasing the photoconductive response of the composite film. Apart from this the recombination of electron and hole is inhibited by the spatial separation of the electron on MEH-PPV and the hole on the C_{60} respectively, thus the life time of the charge carriers is enhanced appreciably leading to lower activation energy. Table I and Table II show the decreasing trend in activation energies with increase in C_{60} concentration in the MEH-PPV thin films. Further experiments are in progress.

Table I: Activation Energy as a function of MEHPPV:C_{60} ratio from Dark Conductivity plots.

Sl. No.	MEH-PPV:C_{60}	Activation Energy (eV)
1.	1:0	0.67
2.	1:1	0.47
3.	1:2	0.38
4.	1:3	0.35

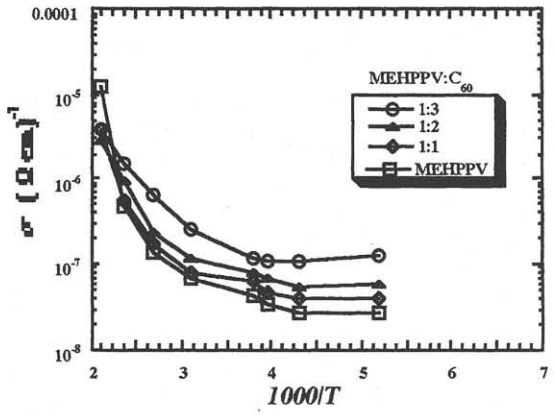

Fig.1 Dark Conductivity measurements: Plots of σ vs. $1000/T$ for thin films of MEHPPV:C_{60}

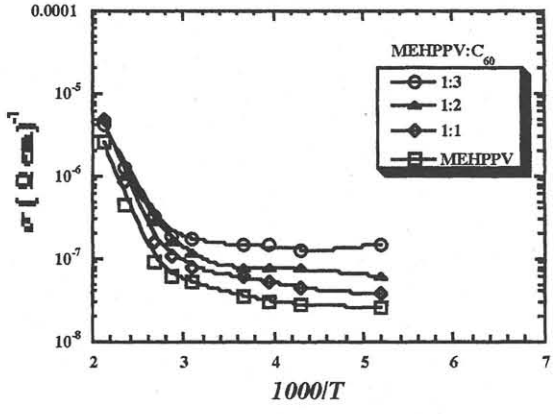

Fig.2. Photoconductivity measurements: Plots of σ vs. $1000/T$ for thin films of MEHPPV:C_{60}

Table II: Activation Energy as a function of MEH-PPV:C_{60} ratio from Photoconductivity plots.

. Sl. No.	MEH-PPV:C_{60}	Activation Energy (eV)
1.	1:0	0.43
2.	1:1	0.42
3.	1:2	0.35
4.	1:3	0.33

3. Conclusions

We have successfully deposited MEH-PPV-C_{60} thin films by low cost road spreading method using the solution of the MEH-PPV-C_{60} mixture in chloroform. The miscibility of C_{60} in MEH-PPV is also found to be high with no formation of any individual clusters in the solution. The solution is stable for long duration and the films are stable with no change in color.

It is found that the presence of C_{60} in the polymer matrix enhances both the dark and photoconductivities of the thin films due to rapid charge transfer from the π^* to the conduction band of C_{60} at a very fast rate ($>10^{12}$ sec^{-1}) thereby reducing the activation energy for conduction for both the dark and photoconduction. The lower activation energy justifies the fact that the C_{60} inhibits the recombination of the conducting charges in the polymer lattice. Due to amorphous nature of the MEH-PPV polymer the glass transition temperature is quite low about T_g=65℃ [5]. During the heating and cooling cycles of the MEHPPV-C_{60} thin film above T_g the thin film is found to experience self annealing thereby making the polymer chains to move freely to enhance the packing of the polymer due removal of the frozen-in defects and thereby reducing the free volume or pores left after evaporating the loosely bound solvent molecules once we exceed the temperature above T_g. Thus the enhanced interface between C_{60} molecules and MEH-PPV molecules makes the effective area for electron injection large there increasing the dark and photoconductivity and thus decreasing the activation energy of the charge carriers. Apart from this, during the heating cycle of the films, there is a slight diffusion of the contact Al atoms into the polymer thereby creating an interactive layer of C-Al bond. This removes the exciton quenching near the interface thereby reducing the activation energy barrier as seen from Table I and Table II.

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