Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yang, Ke , Wang, Yanping , Jain, Aloke , Samulson, Lynne and Kumar, Jayant(2007) 'Determination of Electron and Hole Mobility of Regioregular Poly(3-hexylthiophene) by the Time of Flight Method', Journal of Macromolecular Science, Part A, 44: 12, 1261 — 1264

To link to this Article: DOI: 10.1080/10601320701606711

URL: http://dx.doi.org/10.1080/10601320701606711

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 1261–1264

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701606711

Determination of Electron and Hole Mobility of Regioregular Poly(3-hexylthiophene) by the Time of Flight Method

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Time of flight method (TOF) is used to measure the electron and hole mobility of a spin coated regioregular poly(3-hexylthiophene) (P3HT) film. We find that both electron and hole have the same mobility (about $3.8 \sim 3.9 \times 10^{-4}$ cm^2/Vs) at an applied field of 120 kV/cm. It is demonstrated in this paper that the electron-hole recombination process may prevent the electron transport in the material due to the fact that the carrier recombination time is much shorter than the transit time.

Keywords: time of flight; electron and hole mobility; poly(3-hexylthiophene)

1 Introduction

Organic materials have broad application in electronic and optoelectronic devices such as field effect transistors (FET) (1), light emitting diodes (LED) (2), and solar cells (3–5). One of the widely used hole transporting materials is regioregular poly(3-hexylthiophene) (P3HT). Through its Head-to-Tail coupling between adjacent rings, the polymer chains self-order to form microcrystalline regions of π stacked lamella with strong interchain interactions (6), which significantly improves the mobility over the disordered amorphous polythiophene, i.e. regiorandom poly(3-hexylthiophene) (7). The time of flight (TOF) method is an established method to characterize carrier mobility in materials (7–15). In the P3HT, usually the hole is the majority charge carrier and the electron is the minority charge carrier. The hole mobility of the regioregular P3HT has been measured by the TOF method, (7–11) as well as fabrication of field effect transistors (16, 17) and carrier extraction by a linearly increasing voltage (CELIV) (9, 18). For the electron mobility of the regioregular P3HT, it is generally believed that electrons are strongly trapped in P3HT, and that the electron mobility is almost zero since it is immobile. Only one paper reports the measurement of electron mobility of the regioregular P3HT by TOF method using the bias +Al/P3HT/ITO− and pulsed illumination through the ITO electrode (8). However, there are no analyses in that paper on why the electron mobility is measurable under these experimental conditions. In this paper, we propose that the electron-hole recombination process may interfere with the observation of the electron transit time in TOF, and therefore, the hole concentration in P3HT should be significantly reduced in order to observe the electron transit time. The analyses of the experimental conditions for measuring electron mobility of P3HT are provided, which can also be applied to TOF measurements of other materials where the electron-hole recombination process may prevent the measurement of the minority carrier mobility.

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2 Electron-Hole Recombination Effect

The electron-hole recombination process may significantly hinder the TOF experiment, since the photo-generated electrons (or holes) may recombine with existing holes (or electrons) inside the material before they reach the counter electrode. In these cases, the obtained TOF transit time is not the time for the photo-generated carriers passing through the sample, but the average lifetime of these carriers. Therefore, in TOF measurements, one needs to make sure that the lifetime of the photo-generated carriers is longer than their TOF transit time.

The carrier lifetime can be estimated from the Langevin theory (19) under the condition that the mean free path of the carriers is less than the radius of capture, which is generally valid for organic solids with room temperature mobility less than 1 cm^2/Vs. The bimolecular rate constant γ_{eh} for free electron-hole recombination is given by:

$$\gamma_{eh} = e\mu_T/(\varepsilon\varepsilon_0), \tag{1}$$

where e is the electron charge, $\mu_T = \mu_e + \mu_h$ is the sum of the electron and hole mobility, ε is the dielectric constant of the medium, ε_0 is the vacuum permittivity.

Therefore, the recombination rate for electron is γ_{eh} n_h, where n_h is the hole concentration, and the electron recombination lifetime τ_e is given by:

$$\tau_e = 1/(\gamma_{eh}\ n_h). \tag{2}$$

The above equations can be used to estimate the electron lifetime in regioregular P3HT. Using $\mu_e = \mu_h = 3.8 \times 10^{-4}$ cm^2/Vs (see later part of this paper), and $\varepsilon = 3.2$ (20, 21), we obtain the bimolecular rate constant for free electron-hole recombination in the P3HT $\gamma_{eh} = 4.3 \times 10^{-10}$ cm^3/s. The hole concentration of the regioregular P3HT in the case of hole injecting contact is estimated to be $n_h \approx 10^{15} \sim 10^{17}$ cm^{-3} (16). The electron lifetime in the regioregular P3HT is thus estimated to be $\tau_e \approx 2.3 \sim 0.023$ μs, which is shorter than the usual TOF transit time. Therefore, to obtain the electron mobility of the P3HT through TOF experiment, the hole concentration should be reduced in order to extend the electron lifetime.

To reduce the hole concentration in order to measure the electron mobility, hole injection into P3HT should be blocked and a hole depletion region with width comparable to P3HT film thickness needs to be created. The work function of the hole exit contact should be less than or equal to the ionization energy (also called HOMO, the highest occupied molecular orbit) of the P3HT in order to prevent hole accumulation at the hole exit interface.

3 Experimental

Regioregular P3HT was purchased from Aldrich Chemical Company and used as received. The P3HT film was spin-coated from concentrated chloroform solution onto ITO substrate. The film thickness was determined to be 3.5 μm by the Dektak IIA surface profile measuring system made by the Sloan Technology. A semi-transparent aluminum film was thermally evaporated on top of the P3HT film. The applied bias for both electron and hole mobility measurements was +Al/P3HT/ITO−, with pulsed light illumination on ITO side for electron mobility measurement and on Al side for hole mobility measurement. The pulsed light illumination was at 532 nm, provided by a frequency-doubled YAG laser. A constant bias of 20∼50 V was applied to the sample during the measurement. A digitizing oscilloscope HP 54510B was used to measure the photo current transients. Each data set was averaged over 128 photo current transients generated by light pulses. The TOF measurement was performed at room temperature, in vacuum (10^{-2} Torr).

Since the work function for Al is 4.3 eV, and the ionization energy for P3HT is 4.8 eV, the bias +Al/P3HT/ITO− will block hole injection from Al side into the P3HT due to the potential barrier (0.5 eV). It also creates a hole depletion region inside the P3HT with width comparable to the thickness of the P3HT film when the external voltage is applied, since the Al/P3HT interface is a reverse biased Schottky barrier for holes. There is no hole accumulation in P3HT/ITO interface, since the work function of ITO is 4.8 eV, same as the ionization energy of the P3HT. Therefore, this configuration significantly reduces the hole concentration inside the P3HT and extends the electron lifetime, making it possible to measure the electron transit time and to obtain the electron mobility through the TOF method. For hole mobility measurement, the bias +Al/P3HT/ITO− will reduce the space charge (hole) buildup and increase the accuracy of the measurement.

The experimental configuration with the bias −Al/P3HT/ITO+ and pulsed light illumination on the Al side cannot give the electron transit time, since holes are injected from ITO side and the photo generated electrons recombine with holes before they reach the counter electrode.

4 Results and Discussions

Figures 1 and 2 are typical averaged photocurrent transients of electrons and holes. The transit time is determined by the intersection of the two tangential lines for the plateau and for the tail of the photocurrent transients in the Log-Log plot. For all data in this paper, the slopes of the tangential lines before the transit time are less than 1 and the slopes of the tangential lines after the transit time are larger than 1. The plateaus are not evident in the linear plots as seen in the insets in Figures 1 and 2. They are only evident in the Log-Log plots. The mobility of the material is calculated from the following equation with consideration of the different work functions of the contacts:

$$\mu = \frac{L^2}{V\ Tr}, \tag{3}$$

where μ is the mobility, L is the thickness of the film, Tr is the transit time. V is the internal potential difference of the material, which equals to the applied voltage plus 0.5 volt (the difference of the work function of Aluminum and ITO divided by the electron charge) (19).

The field dependence for the electron and hole mobility at root temperature is shown in Figures 3 and 4, respectively. They can be fitted to the equation:

$$\mu = \mu_0 \exp\left(\alpha E^{1/2}\right) \tag{4}$$

with negative field dependence, i.e. $\alpha < 0$ for both electron and hole mobility, where μ_0 is the zero field mobility. The Bässler's model (22) could be used to explain the negative field dependence. In that model, α is expressed as

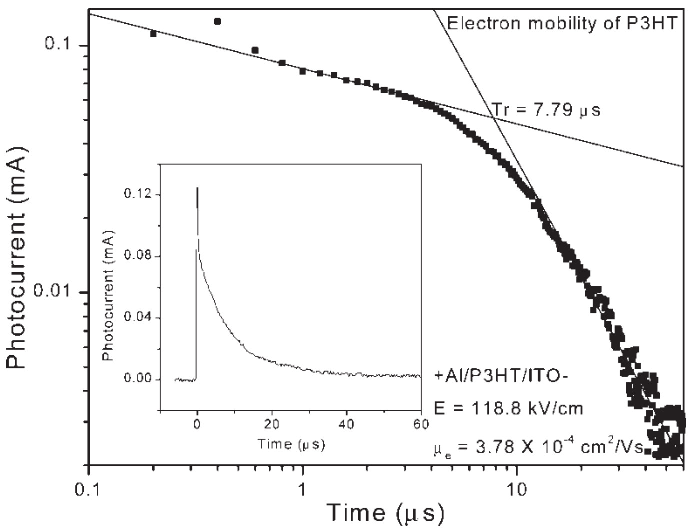

Fig. 1. A typical electron photocurrent transient in TOF measurement. The intersection of the tangential lines in the Log-Log plot determines the electron transit time and the electron mobility. The inset is the linear plot of the same photocurrent transient.

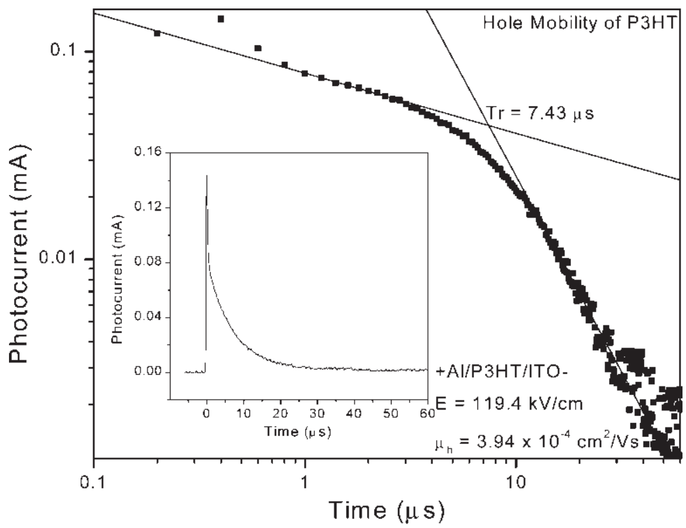

Fig. 2. A typical hole photocurrent transient in TOF measurement. The intersection of the tangential lines in the Log-Log plot determines the hole transit time and the hole mobility. The inset is the linear plot of the same photocurrent transient.

$C[(\sigma/kT)^2-\Sigma^2]$, where C is a positive constant, σ is the distribution width of the free energy of transport sites, Σ is the position disorder parameter. Their combination could give $\alpha < 0$ at certain temperatures. However, it should be noted that at higher electric fields, the negative field dependence and the mobility fits in Figures 3 and 4 may not be valid (7–11).

The experiments indicate that the electron mobility of P3HT could be obtained in TOF measurement after reducing hole concentration. Electrons in P3HT are not trapped in deep traps, but have the mobility as good as that of the holes. To make use of the electron transport property, one needs to reduce hole concentration to extend the electron lifetime. For example, the P3HT could be used as an electron transport layer in optoelectronic devices when one electron injecting contact and one hole blocking contact are used. The electron injecting contact should have work function smaller than or equal to the electron affinity of the P3HT, i.e. 2.9 eV. P3HT could also be used to make light emitting diode by injecting electrons into the material and making use of the electron-hole recombination effect. By using an electron injecting contact as the source and a hole blocking contact as the drain, one can make an electron-transporting field effect transistor out of the P3HT and also measure the electron field effect mobility.

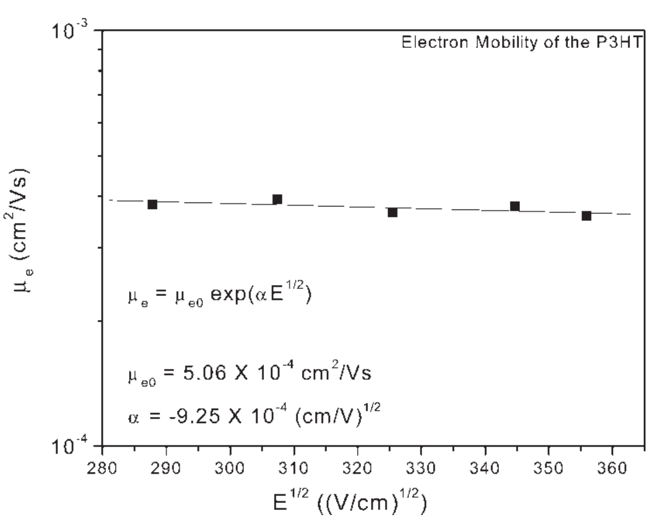

Fig. 3. The field dependence of the electron mobility.

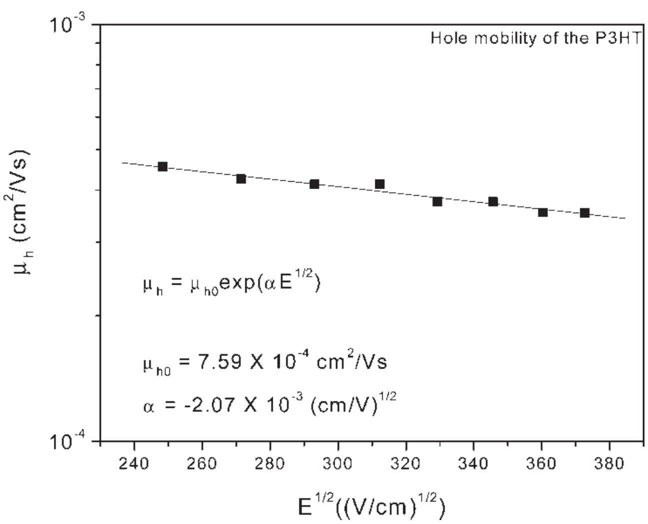

Fig. 4. The field dependence of the hole mobility.

5 Conclusions

Electron-hole recombination prevents the observation of electron transport and hinders the TOF measurement of the electron transit time in P3HT when a hole-injecting contact is used as the counter electrode. Hole blocking contact should be used as the counter electrode to reduce the hole concentration and extend the electron life time and to enable accurate measurement of the electron transit time and the mobility. Both electron and hole mobility of P3HT were measured using hole blocking contact. Their mobility are the same, about $3.8 \sim 3.9 \times 10^{-4}\ \mathrm{cm^2/Vs}$ at the field about 120 kV/cm.

6 Acknowledgements

Partial funding from ONR and NSF is gratefully acknowledged. This paper is sincerely dedicated to the late Professor Sukant K. Tripathy.

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