*Macromol. Symp.* **2004**, *212,* 415-420

# Dispersive and Non-Dispersive Hole Transport in Fluorene-Arylamine Copolymers

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**Summary:** Hole transport in two fluorene-arylenediamine copolymers is studied by means of time-of-flight (ToF) and space-charge-limited dark-injection (SCL DI) transient current methods. Non-dispersive and dispersive hole transport is observed for a range of sample thicknesses, applied electric fields and temperatures.

**Keywords:** charge transport; conjugated polymers; polyfluorene; space-charge limited transient current; time-of-flight

## Introduction

Poly(9,9-dioctylfluorene) (PFO) and its copolymers are considered to be some of the most promising materials for use in polymeric light-emitting diodes (PLEDs). Recently a new family of PFO copolymers, dioctylfluorene-arylenediamine conjugated polymers, was developed [1]. These materials, which show high hole mobilities reaching $\mu \sim 10^{-3}$ cm$^2$/Vs combined with low ionisation potentials (~5.0-5.3 eV), have a good potential for applications in PLEDs. Here we present a comparative study of charge transport in two representative polymers (see Fig. 1), poly(9,9-dioctylfluorene-*co-N,N'*-bis(4-butylphenyl)-*N,N'*-diphenyl-1,4-phenylenediamine) (PFB) and poly(9,9-dioctylfluorene-*co-N,N'*-bis(4-butylphenyl)-*N,N'*-diphenylbenzidine) (BFB), which exhibit non-dispersive and dispersive time-of-flight mobilities, respectively [1]. In this work, time-of-flight (ToF) and space-charge-limited dark-injection (SCL DI) transient current methods [2] are used to study the hole mobilities in a range of sample thicknesses, applied electric fields and temperatures. It is shown that the SCL DI method is a useful technique to study charge transport in thin films with thicknesses close to those used in real devices.

## Experimental

The samples were prepared by spin-coating a polymer solution in toluene onto an ITO-coated glass substrate (for ToF measurements) or onto poly[(ethylenedioxy)thiophene]/poly(styrenesulfonic acid) (PEDOT:PSS)-pre-coated ITO

DOI: 10.1002/masy.200450851

substrates (for SCL DI measurements). The Al, Au or Ag top electrodes were thermally evaporated through a shadow mask at a typical pressure of $10^{-6}$ mbar. A frequency-tripled ($\lambda = 355$ nm) Nd:YAG laser provided short light pulses ($\tau = 6$ ns) for the ToF measurements. The samples were housed in an Oxford Instruments cryostat and were kept under helium atmosphere. An HP 8114A pulse generator was used for SCL DI measurements. Both ToF and DI transients were detected with a Tektronix digitising oscilloscope.

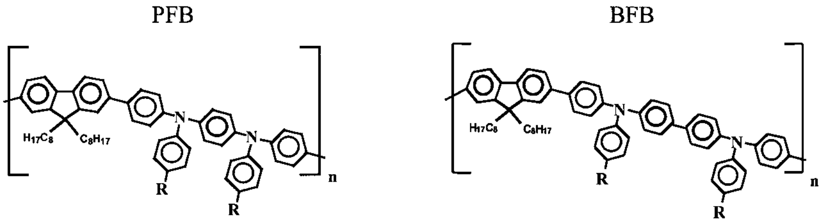

Figure 1. Chemical structures of the copolymers used (R = $n$-$C_4H_9$).

## Non-Dispersive Hole Transport in PFB

Figure 2 shows typical ToF (a) and SCL DI (b) hole transients in PFB films. It is clear from the ToF transient that the hole transport is non-dispersive (see also [1]), i.e., a distinct current plateau is observed in ToF transients that allows to easily determine the transit time. The DI transient, shown in Fig. 2b, has a characteristic shape with a maximum, as expected for a trap-free insulator with a perfectly injecting (ohmic) contact. The position of the maximum $t_{DI}$ is related to the space-charge-free transit time $t_{tr}$ and, correspondingly, the mobility $\mu$ via [2]

$$t_{DI} = 0.786 \cdot t_{tr} = 0.786 \cdot d/(\mu E), \qquad (1)$$

where $d$ and $E$ are the thickness and applied electric field, respectively.

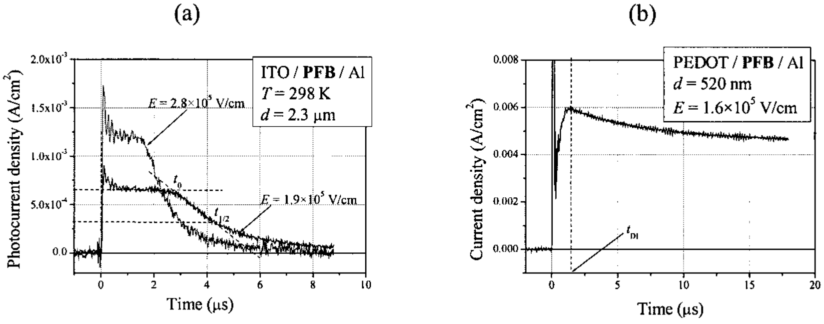

Figure 2. Typical ToF (a) and SCL DI (b) transients in PFB films at room temperature.

The appearance of the SCL maximum also indicates that PEDOT:PSS provides an ohmic contact to PFB. This result is expected from the ionisation potentials of these materials: $I_p$ = 5.2 eV for PEDOT [3] and 5.09 eV for PFB [1].

Figure 3a shows the variation of hole mobilities, determined from the transit time $t_0$ (as shown in Fig. 2a), as a function of temperature and electric field. We used the Gaussian disorder model (GDM), developed by Bässler and coworkers [4], to analyse the data presented here. The results of this analysis, compared to those for the "building blocks" of PFB, namely homopolymer PFO and small molecule TPD, are shown in Table 1. According to this table, introduction of the arylenediamine blocks into the homopolymer PFO results in a reduced energetic disorder $\sigma$, but, on the other hand, the mobility prefactor $\mu_0$ is reduced as well.

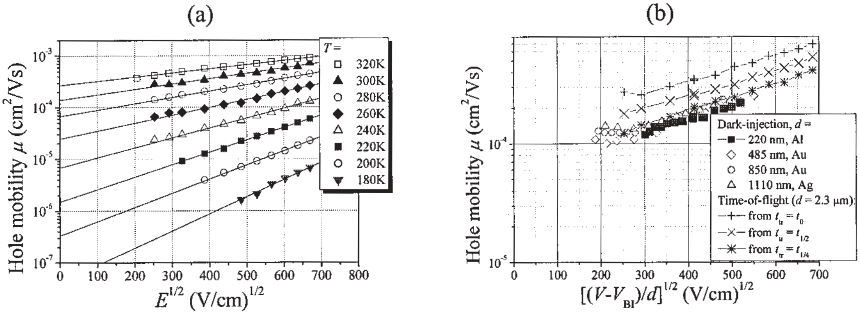

Figure 3. (a) ToF hole mobilities at different temperatures and electric fields and (b) comparison of ToF mobilities with SCL DI mobilities at different sample thicknesses at room temperature in the Poole-Frenkel representation in copolymer PFB.

Table 1. Parameters of the GDM for PFB, compared with those for the homopolymer PFO and triarylamine molecule TPD.

| **Material** | $\mu_0$ **(cm²/Vs)** | $\sigma$ **(eV)** | $\Sigma$ | $C_0$ **(cm/V)$^{1/2}$** |
|---|---|---|---|---|
| PFB | 0.016 | 0.085 | 1.8 | $3\cdot10^{-4}$ |
| PFO [5] | 0.049 | 0.103 | 2.7 | $2.5\cdot10^{-4}$ |
| TPD [6] | 0.08 | 0.077 | 2.3 | $3.7\cdot10^{-4}$ |

Figure 3b presents the comparison of the ToF mobilities with those obtained by the SCL DI method. It is seen that the best agreement is obtained when ToF mobility is calculated using the transit time $t_{1/4}$, i.e. the time at which the photocurrent drops to a quarter of its plateau value (see also Fig. 2a). SCL DI measurements also show that the mobility is independent of sample thickness down to ~200 nm implying that ToF mobilities, measured on thick (~1 μm or more) samples can be used to predict hole mobilities in the thin (~200 nm) samples, which are required for many applications.

## Dispersive Hole Transport in BFB

Figure 4a shows a typical ToF hole transient in a 1.3-μm-thick film of BFB coated on an ITO substrate. It is clear that the hole transport in this material is highly dispersive (see also [1]), as the ToF transient exhibits only a weak inflection point, which we assign to the transit time $t_{tr}$ [5,6]. Figure 4b shows a typical dark-injection transient measured on a sample of the same thickness but with an injecting PEDOT electrode. The ionisation potential of BFB ($I_p$ = 5.26 eV) well matches that of PEDOT ($I_p$ = 5.2 eV), therefore an ohmic contact for hole injection might be expected in such a structure. The observed current transient does not, however, have the characteristic maximum expected from the theoretical predictions for a trap-free insulator [2], and observed in the non-dispersive polymer PFB discussed above. However, a pronounced inflection point in log $I$ - log $t$ presentation is observed. The position of the inflection point scales with the applied voltage and we assign it to the SCL DI transit time $t_{DI}$, defined in Eq. (1). Hole mobilities calculated from the ToF data agree well with those calculated from these SCL DI data using Eq. (1), measured on samples with $d$ = 1.3 μm.

As the thickness of the sample decreases, the experimentally observed SCL DI transients show more distinct features as shown in Fig. 5, where typical transients at the same electric field are compared for samples of different thicknesses. Here the shape of the transient changes from that with an inflection point ($d$ = 700 nm and also 1.3 μm; see Fig. 4b) to that with a clear maximum ($d$ = 420 and 290 nm). A similar effect is observed with respect to the applied electric field: as the electric field increases, the transit time feature (an inflection point or a maximum) becomes more pronounced.

Such changes of the shape of the SCL DI transients can be well understood assuming the presence of a significant number of traps in the material. As it was shown earlier by Many and Rakavy [7], introduction of traps in a perfect insulator leads to a gradual disappearance of the current maximum in a SCL DI transient as the characteristic trapping time $\tau$ becomes comparable with or smaller than the SCL transit time of carriers $t_{DI}$. As the thickness of the sample decreases, the transit time decreases while the characteristic trapping time remains the same, leading effectively to less trapping. Also, as the electric field grows, the Fermi level rises filling deep traps and reducing the effectiveness of trapping. This results in the same effect, i.e., the transit time feature in the transient becomes more pronounced.

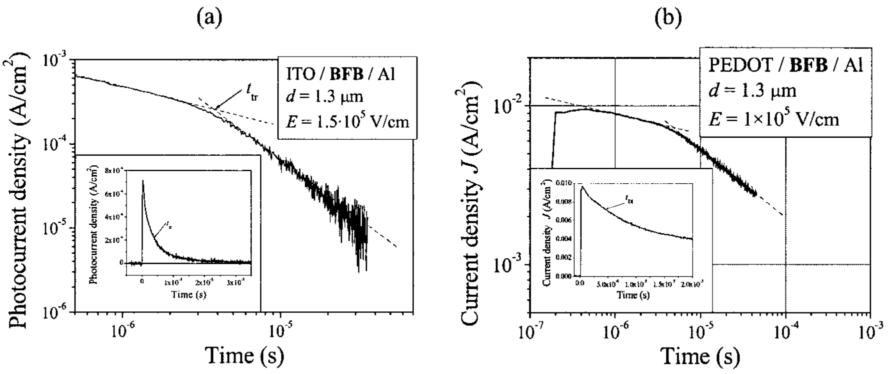

Figure 4. (a) Typical ToF transient and (b) typical dark-injection transient in 1.3 μm thick BFB samples at room temperature.

It has to be noted, however, that the quantitative analysis of the charge mobility is not straightforward in the presence of the strong trapping observed in BFB. Equation (1) that relates the position of the DI peak to the mobility was derived assuming no trapping and therefore should be applied with caution to materials with strong trapping.

Numerical modelling of charge transport in the presence of space-charge in a disordered distribution of energy states with a distribution of trap levels is needed and is currently under way.

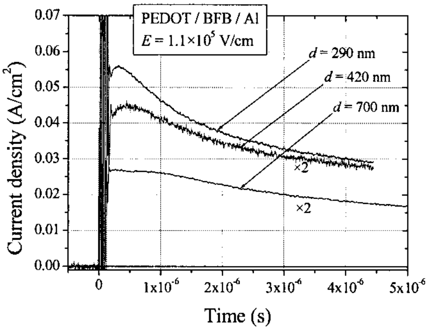

Figure 5. Typical SCL DI transients in BFB samples of different thicknesses at room temperature.

## Summary

Hole transport in fluorene-arylenediamine copolymers PFB and BFB was studied by ToF and SCL DI techniques. The Gaussian disorder formalism was succesfully applied to mobility-field-temperature data in PFB yielding hopping transport parameters for this material. It was shown that the hole mobility in PFB measured by the SCL DI method agrees well with that obtained by the ToF method and is independent of sample thickness down to thicknesses of at least 200 nm.

It was shown for BFB that the SCL DI method can be an alternative technique to study charge transport in highly dispersive organic materials. It was demonstrated that the influence of trapping in such experiments becomes less important as the thickness of the sample decreases or the electric field increases.

It is clear that the SCL DI method has advantages over the ToF method in that it can be used in thin films that are representative of real devices; it is also less sensitive to trapping for highly dispersive materials, especially in thin films. The problem could be to find suitable ohmic contacts with which to undertake the experiments.

## Acknowledgements

We thank Mark Bernius, Jim O'Brien and Mike Inbasekaran of the Dow Chemical Company for providing the polyfluorenes that we have studied. We also thank the Dow Chemical Company (Polymer Semiconductors) and the UK Engineering and Physical Sciences Research Council for financial support (grants GR/N 34772 and GR/M 45115).

[1] M. Redecker, D. D. C. Bradley, M. Inbasekaran, W. W. Wu, E. P. Woo, *Adv. Mater.* **1999**, 11, 241.
[2] M. A. Lampert, P. Mark, *Current Injection in Solids*, Academic Press, New York 1970, p. 116-121.
[3] T. M. Brown *et al, Appl. Phys. Lett.* **1999**, 75, 1679.
[4] H. Bässler, *Phys. Status Solidi (B)* **1993**, 175, 15.
[5] D. Poplavskyy, T. Kreouzis, A. J. Campbell, J. Nelson, D. D. C. Bradley, *Mater. Res. Soc. Symp. Proc.* **2002**, 725, P.1.4.1-11.
[6] M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.* **1984**, 88, 4707; H. H. Fong, K. C. Lun, S. K. Fo, *Chem. Phys. Lett.* **2002**, 353, 407.
[7] A. Many and G. Rakavy, *Phys. Rev.* **1962**, 126, 1980.