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Transport study of a novel polyfluorene/poly(p-phenylenevinylene) copolymer by various mobility models

Lin Ke · Ronald Cai Cheng Han · Chellappan Vijila · Soo Jin Chua

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Abstract The polyfluorene/poly(p-phenylenevinylene) copolymer based hole-only devices are fabricated and the current–voltage characteristics are measured as a function of temperature. The hole current is fitted well with space-charge limited and field-dependent mobility model, which provides a direct measurement of the hole mobility μ as a function of electric field E and temperature. The mobility is fitted with existing Gill's model, Gaussian disorder model, correlated Gaussian disorder model and Brownian motion model. Energy hopping time and activation energy are obtained from Brownian motion model. Microscopic transport parameters are derived and a consistent picture of the influence of the molecular structure of the polymer on the charge transport is depicted. For the polyfluorene/poly(p-phenylenevinylene) copolymer, although with a high degree of irregularity in structure and larger energetic disorder, the two bulky structure favors charge delocalization and remove defect sites, results in a higher mobility. The results suggest space-charge limited and field-dependent mobility model combine with various mobility model, include Brownian motion model, is a useful technique to study charge transport in thin films with thicknesses close to those used in real devices.

L. Ke (✉) · C. Vijila · S. J. Chua
Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore
e-mail: karen-kl@imre.a-star.edu.sg

R. C. C. Han · S. J. Chua (✉)
Center of Optoelectronics, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore
e-mail: elecsj@nus.edu.sg

Introduction

Conjugated polymers have become important because of their clear possibilities for display applications. A great deal of work has been done on polymer light-emitting diodes (PLEDs) for commercial applications [1, 2]. In order for the technological applications to develop to their full potential it is essential to have a thorough understanding of the photophysics of these materials and the factors which affect it. The photophysics of the excited state is determined by the electronic structure of the polymer which is intimately linked to the conformation of the polymer [3]. As conjugated polymers have tremendous scope for structural disorder, it is important to understand the conformation of a polymer in order to understand both the optical and electronic properties. Among the factors that determine the photophysics of the materials and devices, the charge-carrier mobilities are significant in two particular respects. The first is in relation to the charge balance factor for injection and transport of electrons and holes to the recombination zone. This is a critical parameter in controlling quantum efficiency [4]. The second concerns the attainment of the high brightness required for passive matrix addressed displays and application in transistor. High charge-carrier mobilities are needed [5]. Additionally, high mobilities are essential for the construction of electrically pumped laser diodes, an area which has recently attracted significant interest [6, 7].

A commonly used method for studying charge transport in organic materials is the time-of-flight (TOF) technique [8]. However it has high requirement on the sample preparing and measurement technique. Generally for solution-processable materials, this is performed on a thick sample of a few micrometers thickness to ensure that the optical density of the sample is sufficient for the photoexcited carriers to be generated within a small percentage of the device thickness. For solution processable materials, this usually entails preparation of a drop-cast film in order to achieve the desired thickness. Hence, the charge transport measurements are made on films that are different from the spin-coated films commonly used to make LEDs.

In this letter, we report the mobility and structure parameters of a novel polyfluorene/poly(p-phenylenevinylene) copolymer. The observation of space-charge limited current of the copolymer device enables us to obtain the charge carrier mobility directly from the *J–V* characteristics in both the low- and high-field regime. The structure parameters are derived by various existed mobility models and newly developed Brownian Walk model [9]. The results are compared with the results we obtain from TOF technique. It is shown that the space charge limited conduction (SCLC) method is a useful technique to study charge transport in thin films with thicknesses close to those used in real devices [10, 11].

Experiment

The devices under investigation consist of double polymer layers which are sandwiched between two electrodes on top of a glass substrate. ITO-coated glass with a sheet resistance of 20 Ω/square is used as a substrate for OLED device fabrication. The routine cleaning procedure includes sonication in acetone, methanol and de-ionize water followed by oxygen plasma treatment. A 20 nm Poly (styrene sulfonate)-doped poly (3,4-ethylene dioxythiophene) (PEDOT) and 100 nm thick polyfluorene/poly(p-phenylenevinylene) copolymer was spin coated on top of a patterned indium-tin-oxide (ITO). The chemical structure of polyfluorene/poly(p-phenylenevinylene) copolymer is shown in Fig. 1 inset. As a top electrode a 300 nm Ag is evaporated. In such a hole-only device the work functions of the anode is close to the valence band of the conjugated polymer while the electron injection has a big barrier which preventing electron injection from the negatively biased electrode. The device is then encapsulated with epoxy and UV cured. The current density versus voltage (*J–V)* measurement is performed by putting the devices inside the Weiss WK1-180 climate test chamber.

Results

Figure 1 scattered data show the dependence of the current density with voltage *(J–V)* characteristic of polyfluorene/poly(p-phenylenevinylene) copolymer-based devices [8]. The temperature is from 234.5 K to 353 K. The current density depends strongly on both the applied bias voltage and the temperature. For the low voltage range, *J–V* characteristic could be understood by considering the trap-free space-charge-limited-current (SCLC) for a single carrier given by $J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$, where L is the thickness of the polymer, *V* the applied bias and that $\varepsilon_r = 3$ and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m (permittivity of free space). In Fig. 1, the conventional SCLC model simulation results are shown as dotted lines. At higher electrical field, it is observed that the current density *J* is larger than expected from above calculation. At high electrical field E, the *J–V* dependencies of organic devices can be fitted accurately

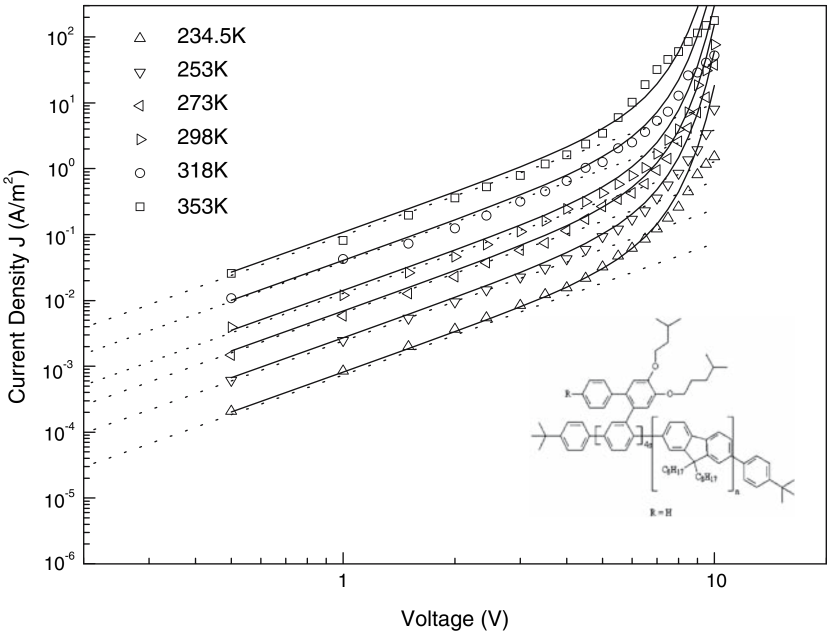

Fig. 1 Current density *J* versus voltage *V* of ITO/ polyfluorene/poly(p-phenylenevinylene) copolymer /Ag hole-only device with thickness 100 nm for various temperatures. At low fields the predicted *J–V* characteristics according to the conventional SCLC model shown as dotted lines. The inset shows the chemical structure of polyfluorene/poly(p-phenylenevinylene) copolymer

within a trap-free space-charge-limited-current (SCLC) model and taking into account a stretched exponential field dependence of the mobility: $\mu = (\mu_0 e^{-\Delta/kT})e^{\gamma\sqrt{E}}$, where Δ is the activation energy, *k* the Boltzmann's constant, μ_0 is zero-field mobility, and γ describing the ''field activation'' of the mobility [9]. This empirical dependence of the mobility on the applied electrical field appears generic for a large class of disordered organic semiconductors such as molecularly doped polymers, pendant group polymers, conjugated polymers and organic glasses etc [10]. The calculated *J–V* characteristics as predicted by a SCLC model using the field dependent mobility are plotted as solid lines in Fig. 1. It shows that the combination of field dependent mobility and space charge effects provides a consistent description for the voltage dependence of the current in our hole only devices.

Figure 2 shows the Arrhenius plot of the zero-field mobility μ_0 as a function of temperature 1000/T and the coefficient γ as a function of 1000/T. The solid lines are the fitting curves with Gill's model and the parameters obtained are $B \approx 2.54 \times 10^{-5}$ eV(V/m)$^{-1/2}$, $T_0 = 730$ K and zero field mobility $\mu_{0,\mathrm{Gill}} \approx 2.15 \times 10^{-9}$ m^2/Vs, are comparable to what was obtained previously in other PPV-derivative hole-only derivative hole-only device [12] suggesting that similar hopping conduction occurs in conjugated polymer as well. This agreement demonstrates that our method of determining the carrier mobility directly from the *J–V* measurements is able to yield equivalent information on the mobility as obtained by TOF experiments.

The experimental data is fitted with Gaussian Disorder Model (GDM) model. Figure 2 also shows the Arrhenius plot of the zero-field mobility μ_0 as a function of temperature 1000/T^2. Figure 3 shows the Arrhenius plot of the coefficient γ as a function of temperature 1000/T^2. The parameters obtained from GDM model are $\sigma_{\mathrm{GDM}} \approx 0.136$ eV, $C_0 \approx 2.9 \times 10^{-6}$ (m/V)^{½}, $\mu_{0,\mathrm{GDM}} \approx 2.12 \times 10^{-9}$ m^2/Vs. The value of the constant C obtained is in excellent agreement with the published value 16. The experimental data is fitted with Correlated Disorder Model (CDM). Figure 3 also shows the Arrhenius plot of the coefficient γ as a function of temperature 1000/T$^{1.5}$. The parameters obtained from CDM are $\sigma_{\mathrm{CDM}} \approx 0.138$ eV, $a \approx 0.85$ nm, $\mu_0 \approx 2.07 \times 10^{-9}$ m^2/Vs. The experimental data is fitted with Brownian Motion Model [9].

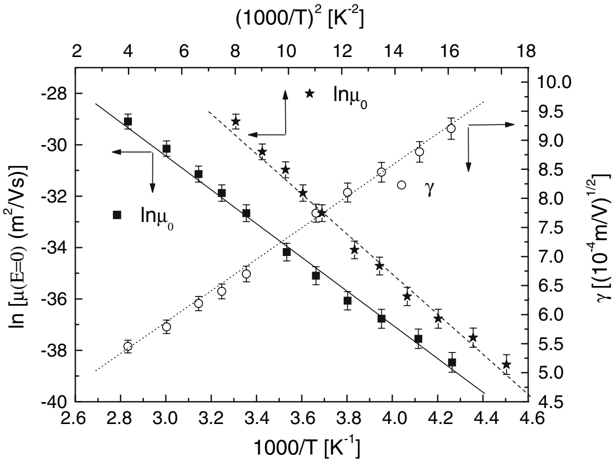

Fig. 2 Arrhenius plot of the zero-field mobility $\mu(E = 0)$ against 1000/T and (1000/T)^2 and Plot of γ (which described the field dependence of the mobility) as a function of 1000/T for polyfluorene/poly(p-phenylenevinylene) copolymer

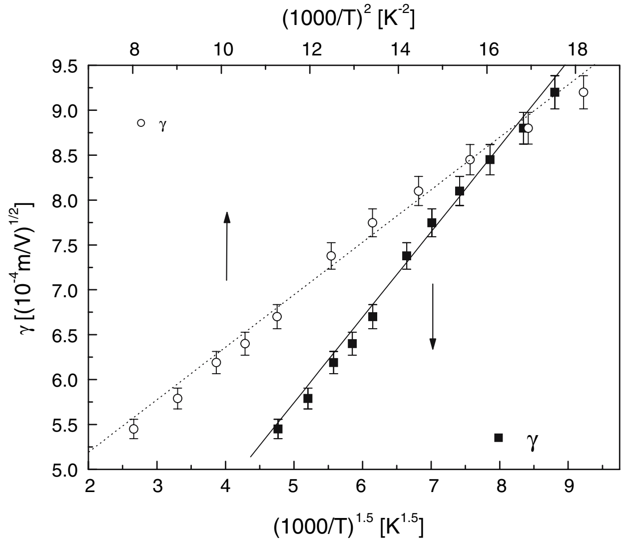

Fig. 3 Plot of coefficient γ against (1000/T)^2 and (1000/T)$^{1.5}$

$$\mu = \tanh\left(\frac{\beta\sqrt{E}}{kT}\right)\frac{qd^2}{\tau_0\beta\sqrt{E}}\exp\left(\frac{\beta\sqrt{E}-\Delta}{kT}\right),$$

where τ_0 characterizes the intersite hopping time in the limit of infinite temperature. The duration per hop, τ is assumed to be thermally activated with an activation energy Δ, therefore, $\tau = \tau_0 \exp\left(\frac{\Delta-\beta\sqrt{E}}{kT}\right)$. Distance transverse per hop assumes to be *d*. β is a parameter to characterize the inner potential barrier. This mode is derived based on hopping conduction between localized states using the concept in Brownian motion. The hopping time τ and the activation energy Δ are obtained from the fitting procedure. The parameters obtained from fitting with Brownian Motion Model are: $\Delta_{\mathrm{PPV}} \approx 0.57$ eV, By assuming T = 298 K (room temperature), $\tau_0 \approx 1.3 \times 10^{-14}$ s, $d = 0.79$ nm.

The TOF experiment involves photogeneration of a packet of charge carriers by illumination of a sample sandwiched between two electrodes. The drift of the carriers under an external bias to the collecting electrode results in a time-dependent current that is monitored across an external load resistor. The transit time t_T, for the arrival of carriers, is related to the carrier mobility μ via the

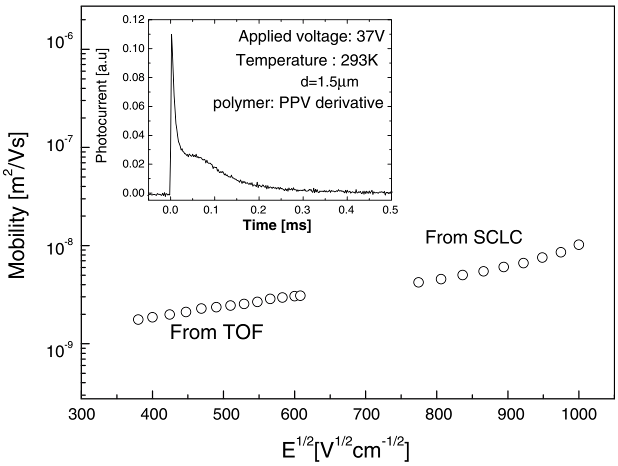

Fig. 4 The mobility μ deduced from the TOF transit times as a function of electrical field in low electrical field and the hole mobility derived from SCLC method in higher electric field. The inset picture shows the TOF results

relation $\mu = d/t_T E$ where d is the film thickness and E the external bias field. Figure 4 inset plots shows the TOF curves. The initial current spike is followed first by a very clear constant current plateau extending from 1 ms to 4 ms. This corresponds to non-dispersive hole transport with a time-independent drift velocity. The subsequent drop in the current is caused by the holes reaching the ITO electrode at which they are discharged. Carrier transit time t_T are readily identified and were enumerated at each of a range of different bias fields from the intersection point of the asymptotes to the double-logarithmic current versus time plots. Figure 4 shows the mobility μ_p deduced from these transit times, plotted as a function of electrical field. The hole mobility derived from TOF is found to lie in the range 2.1×10^{-9} m^2/Vs (E = 370 V/cm) to 3×10^{-9} m^2/Vs (E = 630 V/cm), and shows only a weak field dependence. The hole mobility derived from SCLC method in higher electric field is also plotted together. It shows that the mobility obtained by two methods in low and high E field respectively can be aligned and the values are agreed well with each other. It was shown that the SCLC method can be an alternative technique to study charge transport in highly dispersive organic materials. It was demonstrated that the advantages over the TOF method in that it can be used in thin films that are representative of real devices.

Discussion

Table 1 summarized the parameters derived from above mentioned different models. Polyfluorene/poly(p-phenylenevinylene) is a copolymer of polyfluorine (PF) and phenyl-substituted PPV derivative with two long bulky structures. Compared structure disorder parameter C_0 of copolymer of 2.9×10^{-6} $(m/V)^{½}$ while the rigid polyflourine is 2.1×10^{-6} $(m/V)^{½}$. The larger structure disorder generally means larger intersite distance of the materials. This is clearly shown in the results that intersite distance of 0.85 nm for copolymer compared with rigid of PF of 0.4 nm [13, 14]. Compare with the pure PF, side bulky structure copolymer has lower degree of regularity and larger structure disorder.

Table 1 Summary of parameters obtained by various mobility models for polyfluorene/poly(p-phenylenevinylene) copolymer

Models	Fitting results	
Gill's Model	$B(V/m)^{-1/2}$	2.54×10^{-5}
	T_0(K)	730
	$\mu_{0,\mathrm{Gill}}$ [m^2/Vs]	2.15×10^{-9}
GDM	C_0 $(m/V)^{½}$	2.9×10^{-6}
	σ [eV]	0.136
	$\mu_{0,\mathrm{GDM}}$ [m^2/Vs]	2.12×10^{-9}
CDM	a [nm]	0.85
	σ [eV]	0.138
	$\mu_{0,\mathrm{CDM}}$ [m^2/Vs]	2.07×10^{-9}
Brownian Walk Model	Δ [eV]	0.57
	τ_0 [s]	1.3×10^{-14} s

The energetic disorder σ could be related to the configuration or the arrangement of the monomers in the polymer. The presence of two longer side bulky chains results in an increased configuration freedom for copolymer. As such, this result in an un-orderly packing of the monomers in copolymer, which leads to a larger energetic spread between the electronic levels of the individual chain segment thus giving rise to a higher energetic disorder of σ 0.138 eV. In rigid of PF, the presence of a short sidegroup coupled with a long sidegroup increases the number of possible monomer packing configurations. The decreased configuration freedom results in a less disordered packing of the monomers hence leading to a lower energetic spread over the electronic levels of the individual chain segment thus a lower energetic disorder of 0.085 eV is expected [15].

Although the copolymer has larger structure disorder and energetic disorder compared with the PF, the copolymer has a higher zero field of mobility value around 2.15×10^{-9} m^2/Vs. This also can be explained from copolymer chain conformation. The presence of defects in the polymerization could have a dramatic effect. In the PF, there exist defects due to the partially conjugated polymers which form like decreased transport sites, thus the mobility will decrease. However, in the copolymer, the site defects are removed, thus the mobility will increase, and the yield efficiency will increase too.

In most polymer-based devices, the current that can be transported through the active polymer is limited by the slow hopping of carriers between chains. Once the carriers do recombine, the resulting electroluminescence is easily quenched by rapid interchain exciton migration to a low energy defect or trap site. A very fast hopping is derived by Brownian walk model for copolymer. Short hopping time of 1.3×10^{-14} s is obtained. This is due to the fact that the copolymer has many short spectroscopic units 2–3 monomers as well as a large conformational disorder, on which the hopping will be very efficient due to good spectral overlap. A recent study suggests that the PF has a flexible chain with conjugation lengths of 6–8 monomers and a slower 1 ps hopping time than the copolymer studied here [14]. The disorder we found for PF is much smaller, resulting in a wormlike conformational structure, leading to a more linear arrangement of the spectroscopic units which results in a longer excitation transfer distance for a single hop.

Activation energy can be derived by Brownian walk model which is normally estimated only by empirically equation [12, 14]. The temperature dependence of Δ (in eV) can be described by the following empirical equation: $\Delta = 0.0031 \times T - 0.08$. $\tau_{0,}$ is the average hopping time between adjacent sites within the chain, and distance the excitation travels before it is trapped can be calculated. These parameters are important in describing the energy migration along the backbone/energy transfer between polymer chains and the main technique we use to examine the dynamics of energy transfer is time-resolved stimulated emission anisotropy which is again another high requirement experiment tool. All the above fitting results provide new insights for characterization and optimizing the use of conjugated polymers in optoelectronic applicaitons.

In summary, the polyfluorene/poly(p-phenylenevinylene) copolymer is studied. The mobility are obtained by various temperature *J*–*V* curves and fitted with traditional Gill's model and GDM and CDM model. Useful parameters molecular structure and charge transfer properties of the polymer are derived. Activation energy and average hopping time are also derived from Brownian motion model which has been formulated based on one dimension hopping conduction between localized states. The derivation results are compared with TOF results to investigate the effects that the copolymer's conformation structure on performance. For the polyfluorene/poly(p-phenylenevinylene) copolymer, although with a high degree of irregularity in structure and larger energetic disorder, the two bulky structure favors charge delocalization and remove defect sites, thus provide copolymer a higher mobility. A shorter hopping time derived is another proof of the increased mobility in copolymer. The study demonstrated that the SCLC method combine with various model fitting, include Brownian motion model, is still a useful technique to study charge transport in thin films with thicknesses close to those used in real devices.

Conclusions

The current–voltage characteristics of a novel polyfluorene/poly(p-phenylenevinylene) copolymer based hole-only devices are measured as a function of temperature. The hole current is fitted well with space-charge limited and field-dependent mobility model, which provides a consistent picture of the influence of the molecular structure of the polymer on the charge transport. Energy hopping time and activation energy are obtained from Brownian motion model, which are difficult to measured using traditional characterization technique. The results suggest that space-charge limited combine with various mobility models, include Brownian motion model, is still a useful technique to study charge transport in thin films with thicknesses close to those used in real devices. For our novel polyfluorene/poly(p-phenylenevinylene) copolymer, although a high degree of irregularity in structure, the two bulky structure favors charge delocalization and remove defect sites, thus provide copolymer a higher mobility. A shorter hopping time derived from Brownian motion model is another proof of the increased mobility in copolymer.

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