
Proceedings of the 12th International Symposium UFPS, Vilnius, Lithuania 2004

Slowup of Bimolecular Recombination in Organic Polymer Solar Cells

J.-M. NUNZI^a, G. JUŠKA^{b,*}, F. JEAN^a AND K. ARLAUSKAS^b

^aEquipe de Recherche Technologique Cellules Solaires Photovoltaïques Plastiques
Université d'Angers 2, boulevard Lavoisier, 49045 Angers, France

^bDepartment of Solid State Electronics, Vilnius University
Sauletekio 9, build. 3, 01513 Vilnius, Lithuania

For the retrieval of best polymers for effective organic solar cells as testing parameter we have used the coefficient of bimolecular recombination (B). The B measurement demonstrated that in pure MEH-PPV layers its value is close to the value of Langevin recombination coefficient (B_L), while in case of perylene/MEH-PPV junction layers the ratio $B/B_L \cong 0.013$, and in blends of MEH-PPV with PCBM $B/B_L < 0.01$.

PACS numbers: 72.80.Le, 72.20.Jv

1. Introduction

Recently, due to probable low-cost and technological simplicity, the interest in organic polymer solar cells (OSC) has grown up. However, in layers of organic polymers the charge carrier mobility μ , which is prevailed by hopping, is low ($\leq 10^{-4}$ cm²/(V s)). To obtain the energy conversion coefficient, and, herewith, current density, comparable with ones of crystalline solar cells (SC), the density of photogenerated pairs must be very high. On the other hand, the low charge carrier mobility of organic polymers is caused by short, comparing to Coulomb radius, hopping distance. The latter, in turn, causes decreased photogeneration quantum efficiency (Onsager-type) and bimolecular recombination (Langevin-type). The Langevin recombination is predetermined by probability for electron and hole to meet in coordinate space, and the coefficient of recombination $B_L = e(\mu_n + \mu_p)/\varepsilon\varepsilon_0$, where the symbols have their standard meaning [1, 2]. Recently at least two possibilities have been known, how to reduce bimolecular recombination by creating separate paths for electrons and holes. The first of them is

*corresponding author; e-mail: gytis.juska@ff.vu.lt

based on the formation of hetero-junction of electron and hole transporting materials [3, 4]. Created by light, the excitons are destructed at the junction interface, and so created electrons and holes diffuse in different transporting materials. In organic polymers the typical diffusion length does not exceed $0.1 \mu\text{m}$. Thus, the thickness of OSC is limited, and, herewith, the amount of absorbed light is limited as well. The second possibility is based on usage of blends of electron and hole transporting materials [1].

The aim of this work is to compare the features of ultrafast bimolecular recombination (described by coefficient B) in pure poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV), perylene/MEH-PPV junction structure and [6,6]-phenyl C60 butyric acid methyl ester (PCBM)/MEH-PPV blend and to select the optimal structure for solar cells. The magnitude of B/B_L ratio was chosen as a testing parameter.

2. Method

In Ref. [5] the more detailed description of estimation of B using time-of-flight (TOF) method is given. The method is based on measurement of amount of extracted charge from the reservoir created by short pulse of high intensity light (L). When the amount of photogenerated charge in the reservoir is higher than CU (here C is the geometric capacitance of sandwich-type sample, U is the voltage applied onto sample's electrodes), the electric field (F) inside of reservoir is screened quickly. The extraction of charge carriers thins thickness of reservoir d_L , and the reservoir vanishes at the extraction time t_e . In case of thick layer ($d \gg d_L$) the magnitude of extraction current is limited by space charge, while in case of thin layer ($d \cong d_L$) it is limited by resistance of electrodes or/and loading resistor. When $L \rightarrow \infty$, the amount of extracted charge ($Q_e(L)$) saturates Q_s [4]:

$$Q_s = \int_0^{t_e} j(t)dt = \frac{ed_L S}{Bt_e} \quad \text{or} \quad \frac{B}{B_L} = \frac{CU t_{tr} d_L}{Q_s t_e d}. \quad (1)$$

When $B = B_L$ and if $d \gg d_L$, $Q_s = CU$ [6]. In case of monomolecular recombination $t_e \sim \ln L$, while when recombination is absent $t_e \sim L$. Thus, the measurements of $Q_e(L)$ and $t_e(L)$ allow us to estimate the type of recombination, and evaluate B .

3. Experiment and results

The sandwich-type layers have been formed by deposition of perylene on glass substrate covered by ITO with following coating by MEH-PPV. The MEH-PPV/PCBM blends of various ratios where coated on glass substrates covered by ITO. The semi-transparent Al or Au electrode was deposited on the top of structures.

The measurements have been provided by conventional TOF method. The standard ND:YAG laser (pulses of light $h\nu = 2.3$ eV, halfwidth 25 ps, and intensity 1 mJ/cm²) has been used and the electric signals has been recorded by Tektronix TDS3032 oscilloscope.

Q_e has been estimated by integrating transients of photocurrent, and t_e from these transients as $t_e = [t_{1/2}(L \rightarrow \infty) - t_{1/2}(L \rightarrow 0)]$ (here $t_{1/2}(L)$ is halfwidth of photocurrent transient at given intensity of light). The typical transients of TOF photocurrent are demonstrated in Fig. 1 and $\mu_p = 1.3 \times 10^{-6}$ cm²/(V s) ($F = 10^5$ V/cm) mobility (field) of holes has been evaluated.

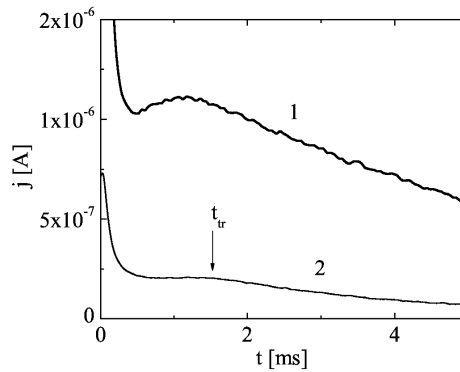


Fig. 1. Photocurrent transients of perylene/MEH-PPV junction structure at high (1) and low (2) intensity of exciting pulse of light L .

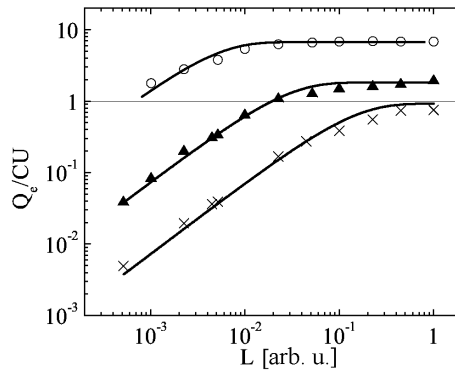


Fig. 2. Extracted charge dependences on intensity of exciting pulse of light L (\times — pure MEH-PPV, solid triangle — perylene/MEH-PPV junction, \circ — blend of MEH-PPV/PCBM).

The investigation result of pure MEH-PPV was that $Q_s = CU$ (see Fig. 2), therefore $B \cong B_L = 6.9 \times 10^{-13}$ cm³/s, as it was expected in case of single organic polymer [7].

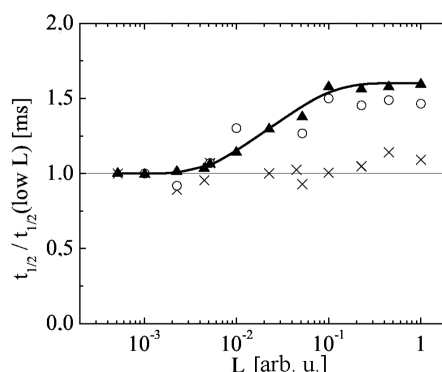


Fig. 3. Dependences of halfwidth of photocurrent transient on intensity of exciting pulse of light L (\times — pure MEH-PPV, solid triangle — perylene/MEH-PPV junction, \circ — blend of MEH-PPV/PCBM).

In perylene/MEH-PPV ($d_L = 0.1 \mu\text{m}$, $d = 2.7 \mu\text{m}$) layer the extraction current has been estimated to be limited by space charge. The tendency to saturation of $Q_e(L)$ and $t_e(L)$ with intensity of light is clearly seen in Figs. 2 and 3. In this case $B = 0.013B_L = 1.3 \times 10^{-12} \text{ cm}^3/\text{s}$, which causes that the mobility of electrons in perylene is much higher than holes in MEH-PPV ($\mu_n = 2.4 \times 10^{-4} \text{ cm}^2/(\text{V s})$).

From investigation results of MEH-PPV/PCBM blends it follows that Q_s much exceeds CU , and the value $B = 6 \times 10^{-10} \text{ cm}^3/\text{s} < 0.01B_L$ was estimated. It shows that the mobility of electrons in blends is even higher, but we could not estimate it, because of high dispersivity of transport.

Acknowledgments

This work was partly supported by joint Lithuania-France research project “Gilibert” (“FONEPC”) and by Lithuanian VMSF Grant No.T-68/04.

References

- [1] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Funct. Mater.* **11**, 15 (2001).
- [2] M. Pope, C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press, New York 1999.
- [3] J.-M. Nunzi, *C.R. Physique* **3**, 523 (2002).
- [4] N. Nekrašas, G. Sliaužys, G. Juška, K. Arlauskas, J. Stuchlik, J. Kočka, *Acta Phys. Pol. A* **107**, 373 (2005).
- [5] G. Juška, M. Viliūnas, K. Arlauskas, J. Kočka, *Phys. Rev. B* **51**, 16668 (1995).
- [6] G. Juška, *Lithuanian J. Phys.* **29**, 600 (1989).
- [7] H. Bässler, *Polym. Adv. Technol.* **9**, 402 (1998).