Langevin recombination and space-charge-perturbed current transients in regiorandom poly(3-hexylthiophene)

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(Received 3 June 2004; revised manuscript received 14 October 2004; published 15 March 2005)

We have studied photogenerated charge carrier transport and recombination in thick films of regiorandom poly(3-hexylthiophene) by using the current mode time-of-flight technique. We measured the extracted charge as a function of light intensity and applied voltage, and found that for $\alpha d \gg 1$ it saturates at a value that can be stored on the contacts $Q_e = CU_0$ as expected for diffusion controlled bimolecular recombination, i.e., Langevin recombination. As a consequence we can only measure space charge perturbed current transients. We measured a field-dependent hole mobility of the order of 10^{-5} cm^2/V s, which extrapolated to zero field determines the Langevin bimolecular recombination coefficient 4×10^{-12} cm^3/s.

DOI: 10.1103/PhysRevB.71.125205 PACS number(s): 73.50.Gr, 73.50.Pz, 73.61.Ph

I. INTRODUCTION

Time-of-flight (TOF) is a commonly used method when studying charge carrier transport properties of low conductivity and low mobility materials such as disordered organic materials and π-conjugated polymers (PCPs).[1] In TOF measurements the sandwich-type sample is illuminated from one side with a very short laser pulse creating a sheet of charge carriers drifting through the sample. The carriers are extracted at the opposite electrode and the current transients allow us to determine transport properties of the photogenerated charge carriers.

The main reason for disorder in PCPs is fluctuations in the segment lengths of the π-bonded polymer (the so-called effective conjugation length) and/or lattice polarization energy.[2] As a consequence of disorder charge carriers will relax[3] within the inhomogeneously broadened Gaussian distribution of localized states towards the statistically defined transport level[4] and reach dynamic equilibrium. If dynamic equilibrium is not reached before the carriers have been extracted, then the carrier transients will be featureless[5,6] and the transients will depend on the measurement conditions. On the other hand, if dynamic equilibrium is achieved the carrier transients will typically show a clear plateau with a drop in the current level as the carriers reach the opposite electrode from which the charge carrier transit time t_{tr} is estimated[7] and the mobility can be calculated using $\mu = d^2/t_{\mathrm{tr}}U_0$, where d is the thickness of the film and U_0 is the applied voltage. Hence, in order to obtain true material specific parameters it is important for the charge carriers to reach dynamic equilibrium. This can be achieved by having a thick enough films (several μm) so that the relaxation time is (much) smaller than the transit time, by using materials with a narrow disorder distribution[7] or by selectively injecting carriers into the occupational DOS using tunable charge carrier generation layers.[8,9]

Transport properties are also affected by recombination of charge carriers. In low mobility materials such as PCPs diffusion controlled bimolecular recombination, or the so-called Langevin recombination is dominating.[10] In Langevin recombination, when oppositely charged carriers are within the so-called Coulomb radius $r_c = e^2/4\pi\epsilon\epsilon_0 kT$ (where e is the electron charge, ϵ is relative dielectric permitivitty, ϵ_0 is absolute permitivitty, k is Boltzmann's constant, and T is the temperature), the charge carriers are attracted to each other by their mutual Coulomb field. Since the hopping distance in low mobility materials is usually much smaller than r_c, as is the case when the charge carrier mobility $\mu \leqslant 1$ cm^2/V s, the carriers will have a lower probability to escape recombination. The carriers will eventually find each other and recombine either radiatively or nonradiatively. The magnitude of Langevin bimolecular recombination coefficient can then be calculated using the following relation:

$$\beta_L = \frac{e(\mu_p + \mu_n)}{\epsilon\epsilon_0}, \tag{1}$$

where $\mu_p(\mu_n)$ is the mobility of holes (electrons). This is also indeed what has been found in the literature.[11,12] If one type of carriers is much faster than the other (usually holes for PCPs), then Langevin recombination coefficient will be determined by the faster carriers.

In pristine PCPs the intrinsic photogeneration yield is on the order of $10^{-4}-10^{-2}$, due to the high exciton binding energy.[13,14] The efficiency strongly depends on electric field and photon energy, but independent on temperature. For strongly absorbed light and high light intensities the electric field is immediately screened in the region $d_L = \ln(L_0'+1)/\alpha$,[15] where α is the absorption coefficient at the laser wavelength[16] and $L_0' = eL_0 d/\epsilon\epsilon_0 U_0$ is the number of photogenerated charge carriers normalized to the number of charge carriers stored on the contacts where L_0 is the surface density of photogenerated charge carriers. In this region charge carrier recombination occur until the remaining charge carriers in the reservoir are extracted within the characteristic extraction time t_e which can be

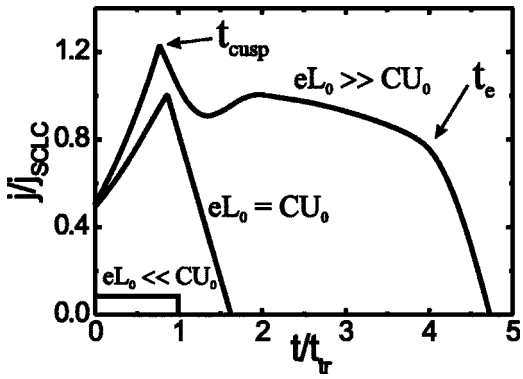

FIG. 1. Schematic current transients (j-TOF) as a function of light intensity with no carrier recombination.

longer than the transit time t_{tr} when the (bimolecular) lifetime of the charge carriers is longer than the transit time (see Fig. 1).

In current mode TOF (j-TOF), i.e., when $t_{\mathrm{tr}} \ll \tau_{\mathrm{RC}}$, where τ_{RC} is the time constant of the measurement setup, having surface photogeneration ($\alpha d \gg 1$) and neglecting the carrier recombination we can work in three different regimes depending on the amount of photogenerated charge carriers, namely, small-charge-current (SCC) (when $L_0' \ll 1$), space-charge-perturbed-current (SCPC) ($L_0' \approx 1$) or space-charge-limited-current mode (SCLC) ($L_0' \gg 1$), see Fig. 1. To the best of our knowledge, there are no reports on SCLC transients of photogenerated charge carriers in PCPs. In this paper we present experimental data on the effect of Langevin recombination on TOF transients in a model system for PCPs, namely, regiorandom poly(3-hexylthiophene) (RRaPHT). We show that at high light intensities Langevin recombination causes limitation on the maximum charge that can be extracted from the sample leading to the fact that only space charge perturbed current transients can be observed. Furthermore, we present analytical as well as numerical calculations to extract the bimolecular recombination coefficient, and show that it is in good agreement with what is expected from Langevin recombination. The obtained results show that if Langevin recombination is present, then it might eventually set an upper limit on the efficiency of photovoltaic cells.

II. THEORY

In general, the charge carrier extraction mechanism in high light intensity (SCLC) TOF is as follows. The external electric field in the photogenerated charge carrier reservoir is screened within a very short time $t_s \ll t_{\mathrm{tr}}$.[16] The charge carriers, extracted from the reservoir causes a decrease of the reservoir thickness d_L, whereas, the field still remains zero in the reservoir. The diffusion controlled charge carrier bimolecular recombination will therefore be independent on extraction and we can simplify the decay kinetics in the reservoir as

$$\frac{dp}{dt} = -\beta pn = -\beta p^2. \tag{2}$$

This equation has the solution $p(x,t) = \{[p(0,0)\exp(-\alpha x)]^{-1} + \beta t\}^{-1}$, where $p(0,0) = \alpha L_0/e$ is the initial hole concentration.

The total number of photogenerated carriers N_0 equals to the sum of recombined (RC) carriers N_{rec} extracted carriers N_{ext}, and carriers left in the reservoir at any given time N_{res}: $N_0 = N_{\mathrm{rec}}(t) + N_{\mathrm{ext}}(t) + N_{\mathrm{res}}(t)$. We define a time t_e such that $N_{\mathrm{res}}(t_e) = 0$. By using charge carrier conservation together with the solution for bimolecular recombination we therefore arrive at

$$\int_0^d p(x,t_e)dx = \frac{1}{e}\int_0^\infty j_e dt, \tag{3a}$$

$$\frac{e}{\alpha\beta t_e}\ln\left(\frac{1+(\beta\alpha L_0 t_e/e)}{1+[\beta\alpha L_0 t_e \exp(-\alpha d)/e]}\right) = \int_0^\infty j_e dt, \tag{3b}$$

where j_e is the extraction current density. For $\alpha d \gg 1$ Eq. (3b) simplifies to

$$\frac{ed_L}{\beta t_e} = \int_0^\infty j_e dt = Q_e/S, \tag{4}$$

where S is the contact area. This equation can also be written as

$$\frac{t_e}{t_{\mathrm{tr}}} = \frac{\beta_L}{\beta}\frac{CU_0}{Q_e}\frac{d_L}{d}. \tag{5}$$

This relation is *independent* of the RC time constant of the TOF measurement setup.

It has been previously shown by Juška *et al.*[17,18] that when $\alpha d \gg 1$ and $\beta = \beta_L$, then the extracted charge saturates at high intensities as

$$Q_e' = 1 - \exp(-L_0'), \tag{6}$$

where Q_e' is the extracted charge normalized to the charge stored on the contacts ($Q_e' = Q_e/CU_0$). A physical reason for the extracted charge saturation to CU_0 in the SCLC TOF regime, when $\beta = \beta_L$ is that carrier transit time is equal to the dielectric relaxation time $\tau_\sigma = \epsilon\epsilon_0/\sigma$ and charge carrier bimolecular lifetime τ_β. In the case of $\alpha d \to \infty$ the extracted charge is $Q_e = CU_0$, and our numerical calculations show that for real conditions ($\alpha d > 1$), the extracted charge only fractionally exceeds CU_0. Equation (5) shows that if the charge carrier recombination is of Langevin type ($\beta = \beta_L$), then the extracted charge is equal to the charge stored on the contacts $Q_e = CU_0$ and the ratio between the extraction time and transit time is equal to the ratio between the photogeneration region and sample thickness ($t_e/t_{\mathrm{tr}} = d_L/d$). Equation (5) can also be used to determine the ratio (β_L/β), when the extraction time t_e is seen.

To further describe the current transients and extracted charge we calculate the current transients numerically by solving the set of Poisson, current and kinetic equations.[19] To simplify the model, the following assumptions are

made: (i) at time $t=0$ the electric field F is homogeneous throughout the sample and the voltage on the electrodes is constant during the whole transient, (ii) there are no thermally generated carriers, i.e., we study an insulating photoconductor, (iii) only holes can move through the sample, and, finally, (iv) there is no monomolecular recombination, trapping or diffusion.

III. EXPERIMENT

As the model system for low mobility materials we use regiorandom poly(3-hexylthiophene) (RRaPHT). RRaPHT, obtained form Sigma Aldrich, handled and stored in N_2 environment, was dissolved in water free chloroform with typical concentrations of 1–20 mg/ml. The solutions were filtered through a 0.2-μm filter before spin coating or solution casting on top of prepatterned ITO-covered glass substrates (Planar International). Finally a 30 nm (semitransparent) aluminum top electrode, with typical dimensions 4–12 mm^2 was evaporated on top of the polymer under vacuum below 10^{-6} mbar. The samples were made in dry N_2 atmosphere and annealed for 10 h at 100 °C in vacuum. The measurements were carrier out in a closed-cycle cryostat (Oxford CCC1104). The abovementioned procedures leads to nondispersive current transients in RRaPHT, whereas, after sample exposure to air, transients become dispersive and the conductivity rises due to extrinsic effects.

We use the standard current mode time-of-flight (j-TOF), i.e., the RC time constant is much smaller than the charge-carrier transit time $\tau_{RC} \ll t_{tr}$. For the photogeneration of charge carriers, we used a 6 ns Quantel Nd:YAG laser operating at the second harmonic (532 nm) and third harmonic (355 nm) generation. For thick films ($d=8$ μm) $\alpha d=35$, allowing us to treat the charge carriers as being surface generated. To get the highest possible charge carrier densities the samples were illuminated through the ITO side.

The photogenerated charge carrier surface density can be estimated using the equation $L_0=N_{abs}\eta_{ch}/S$, where N_{abs} is the number of photons absorbed in the sample: $N_{abs}=E\lambda[1-\exp(-\alpha d)](1-R)/hc$, with λ and E is the wavelength and laser light energy per pulse, respectively, h Planck's constant, R the reflection coefficient from the sample, η_{ch} the quantum efficiency for charge generation, and c the speed of light. We use the measured field-dependent quantum efficiency η_{ch} for charge generation in similar samples.[20] The current transients are normalized to the SCLC value (without the factor 9/8) $j_{SCLC}=\epsilon\epsilon_0\mu U_0^2/d^3$. We use $\mu=\mu_p$, since the electron mobility was measured to be at least a few orders of magnitude lower than a hole mobility.

IV. RESULTS AND DISCUSSION

In Fig. 2(a) we show experimental TOF transients in an 8-μm-thick RRaPHT film as a function of light intensity and in Fig. 2(b) the numerically calculated TOF transients for Langevin recombination as a function of normalized number of photogenerated charge carriers L_0'. The parameters used in the calculations are the same as in the measurements, namely, $d=8$ μm, $C=2.3\times10^{-11}$ F, $R'=RC/t_{tr}$

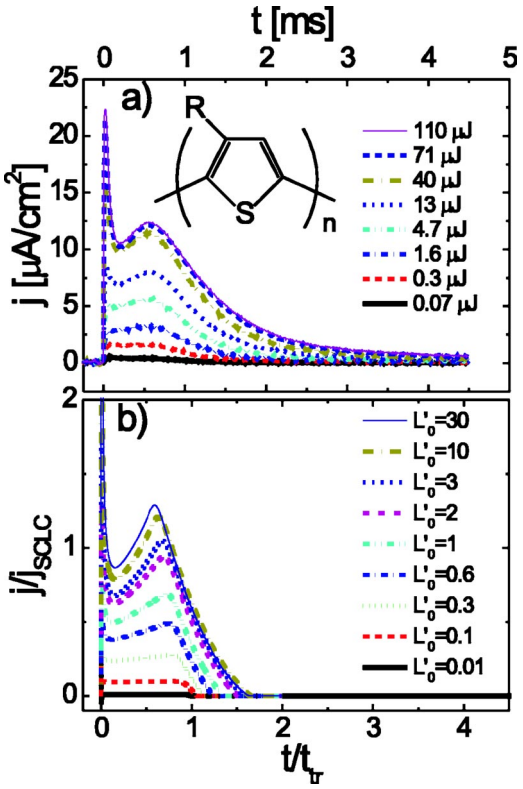

FIG. 2. (Color online) Current transients as a function of light intensity. In (a) the experimentally measured 8-μm-thick RRaPHT film with applied electric field of 100 kV/cm and in (b) the numerically calculated transients with the intensity given in normalized units (see text). The parameters in (b) were chosen to correspond the experimentally measured values, namely, $R'=0.004$, $\alpha d=35$, $\beta'=1$. The inset in (a) shows the structure of RRaPHT.

$=R\epsilon\epsilon_0\mu U_0 S/d^3=0.004$, $\alpha d=35$, and $\beta'=\beta/\beta_L=1$. At low light intensities, the transients show a well-developed plateau, expected for nondispersive small charge current mode transients. At intermediate light intensities, we see the development of a cusp, and at high light intensities, the transients saturate as a function of light intensity and show a well-developed SCPC cusp. Both experimentally measured and theoretically calculated transients for Langevin recombination case resemble each other almost perfectly except for the tail in the experimentally measured transients which can be attributed to the charge trapping, neglected in the numerical calculations.

As can be seen in Fig. 2 the transit time of holes at high light intensities shifts to shorter times than the t_{SCC}^{tr} as predicted by SCLC theory.[21] It is also seen that the initial current spike, related with very fast screening of electric field, rises with intensity. We emphasize, that even for the highest light intensities in the SCLC mode, the saturated TOF transients show only SCPC-like behavior.

For better understanding of the charge transport and recombination in the sample, we calculated numerically TOF transients for various β/β_L ratios, which are presented in Fig. 3. It shows TOF transient dependence on the bimolecular recombination rate for high light intensities. For

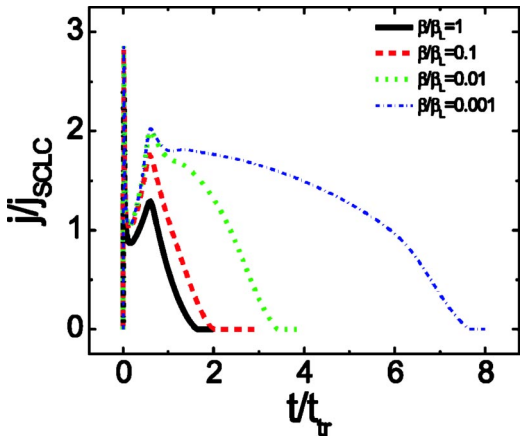

FIG. 3. (Color online) Numerically calculated current transients for various β/β_L ratios. The parameters used in calculations are $R'=0.004$, $\alpha d=35$ with the normalized number of photogenerated charge carriers $L_0'=30$. Please note the similarities to Fig. 1 which shows transients without recombination.

$\beta/\beta_L=1$, the extracted charge is $Q_e=CU_0$. For fast bimolecular recombination ($\beta/\beta_L=1$) the transients show SCPC behavior, with the extraction time being shorter than the carrier transit time. When the recombination rate is slower than Langevin rate ($\beta/\beta_L<1$), the extraction time exceeds the transit time and the characteristic extraction time t_e appears in the transients. The numerically calculated transient for ($\beta/\beta_L=1$) resemble the experimentally measured.

By integrating the current transients from Figs. 2(a) and 2(b) over time we get the extracted charge that has been transported through the sample. Figure 4 shows the experimentally measured and numerically calculated extracted charge as a function of number of photogenerated charge carriers. Almost a perfect match between the experimentally measured and theoretically calculated extracted charge can be seen. The numerically calculated points can be fitted very well using Eq. (6). As predicted by Eq. (6), the extracted

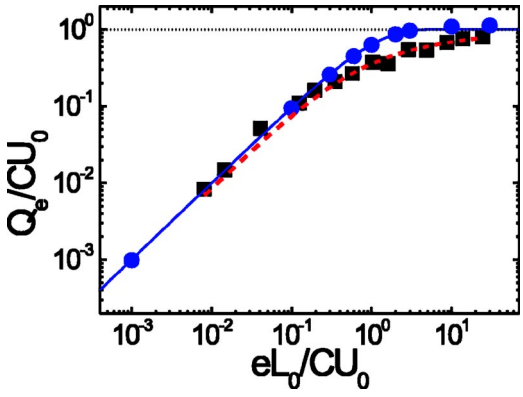

FIG. 4. (Color online) Normalized extracted charge as a function of normalized number of photogenerated charge carriers. The squares are the experimentally measured values, circles are the calculated data, using the full numerical model, while the full line is the fit, using Eq. (6). The dashed line is calculated including exciton bimolecular annihilation (see text). The dotted line shows when the extracted charge equals CU_0.

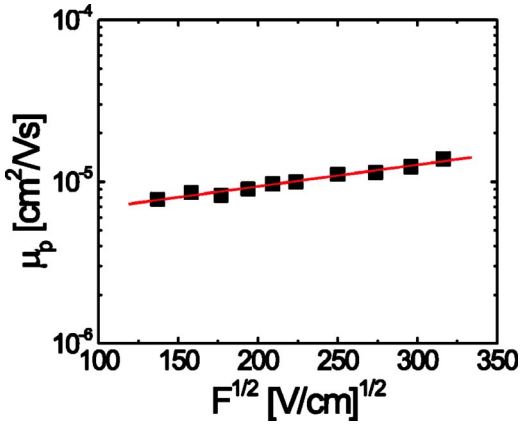

FIG. 5. (Color online) Experimentally measured hole mobility as a function of electric field for RRaPHT.

photogenerated charge follows a linear dependence at low intensities and saturates to CU_0 at high light intensities, proving the diffusion controlled bimolecular recombination of charge carriers in RRaPHT.

A deviation of the experimentally measured collected charge from the numerically calculated is observed (see Fig. 4) and it can be attributed to (a) monomolecular carrier recombination, (b) exciton diffusion to the bulk of the sample, (c) nonlinear dependence of charge carrier generation related to bimolecular exciton-exciton annihilation, and (d) extracted charge will not saturate because d_L increases as a function of light intensity, however the increase is very slow. In Fig. 4 we fit the experimentally measured points assuming nonlinear charge carrier generation, which is a direct outcome of exciton-exciton (bimolecular) annihilation.[22,23] The fitting corresponds very well to measured values with an exciton-exciton bimolecular recombination coefficient $\beta_{\mathrm{exc}}=1.23\times10^{-10}$ cm^3/s, exciton to charge carrier decay rate[22] $\gamma=1.71\times10^5$ /s, and quantum efficiency[20] for charge carrier generation $\eta_{\mathrm{ch}}=2\times10^{-4}$. These values were calculated taking the exciton lifetime $\tau_{\mathrm{exc}}=10^{-9}$ s. The concentration of excitons at which the bimolecular recombination starts to dominate is $n_{\mathrm{exc}}=8\times10^{18}$ cm^{-3}. This corresponds to a laser pulse intensity of 50 μJ/cm^2, which is similar to what has been observed in transient absorption spectroscopy.[23]

The hole mobility, calculated from the experimentally measured SCPC transients as a function of electric field, is shown in Fig. 5. To estimate the SCPC transit time we used $t_{\mathrm{tr}}^{\mathrm{SCPC}}=0.8\times t_{\mathrm{tr}}^{\mathrm{SCC}}$.[21] However, we note that the prefactor expected for pure SCPC transients are 0.8, but in photo-SCLC transients it depends on light intensity.[24] This is due to the decrease of the effective sample thickness when increasing light intensity $d_{\mathrm{eff}}=d-d_L=d-[\ln(L_0'+1)/\alpha]$. Therefore the charge carriers have to travel a shorter distance and the transit time becomes shorter. Because the charge carriers are recombining in the charge reservoir where the electric field is zero, then by extrapolating the field dependent hole mobility to zero field $\mu(F=0)=6.5\times10^{-6}$ cm^2/V s we calculate a bimolecular recombination coefficient $\beta_L=4\times10^{-12}$ cm^3/s. The reservoir extraction time t_e can be calculated from Eq. (5). When $\beta_L=\beta$, the extracted charge $Q_e=CU_0$ and for the

transients shown in Fig. 2 ($L_0'=30$ and electric field $F=100$ kV/cm) we get the relation $d_L/d=t_e/t_{\mathrm{tr}}=0.1$ giving $t_e=5.3\times10^{-5}$ s.

V. CONCLUSIONS

In summary we have shown the effect of diffusion controlled bimolecular recombination on *j*-TOF transients in a model system for low mobility π-conjugated polymers. We show that Langevin-type diffusion controlled bimolecular recombination causes fast recombination, where the maximum extracted charge for films with $\alpha d \gg 1$ is $Q_e=CU_0$. Therefore we can only observe SCPC type transients. The bimolecular recombination coefficient found to be 4×10^{-12} cm^3/s at room temperature.

ACKNOWLEDGMENTS

We are grateful to Planar International for the ITO substrates. Partial financial support from the Academy of Finland through Projects Nos. 50575, 203317 and the Lithuanian State Science and Studies Foundation through Project No. T-68/04 is acknowledged.

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