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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · OCTOBER 2010

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# Concentration-Dependent Hole Mobility and Recombination Coefficient in Bulk Heterojunctions Determined from Transient Absorption Spectroscopy

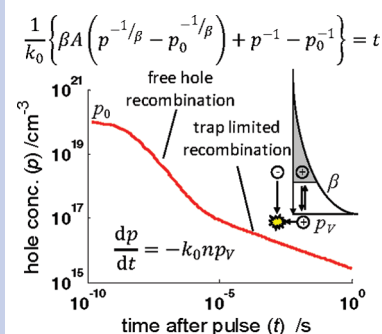
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**ABSTRACT** A simple analytical function, based on the multiple trapping model, is used to describe the bimolecular recombination of charge carriers in a bulk heterojunction (BHJ) film in the presence of an exponential energetic tail of localized hole “trap” states. The function is used to fit charge carrier decay data from an unannealed P3HT/PCBM film measured by transient absorption. The analysis assumes that only free holes participate in recombination and transport. This implies an effective recombination rate coefficient which varies with the ratio of free to trapped holes. The fit parameters yield a bimolecular recombination constant for free holes with free electrons ( $k_0 = 3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) and information about the distribution of trap states (trap distribution parameter  $\beta = 0.29$ ). Assuming the Langevin recombination limit, the analysis yields a concentration-dependent effective hole mobility saturating at  $\mu_0 \approx 7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This approach should be useful to compare BHJs in a consistent and meaningful manner.

**SECTION** Electron Transport, Optical and Electronic Devices, Hard Matter



Efficient photoinduced charge separation has been widely observed in organic film blends employing materials with different chemical potentials. There are extensive efforts to use such charge photogeneration for the photovoltaic conversion of solar energy.<sup>1</sup> The formation of a bulk heterojunction (BHJ), which is an interpenetrating network of different organic materials where the domain size of each phase is on the nanometre scale, facilitates efficient photoinduced charge separation. This is because the dissociation of photogenerated excitons into charge-carrying polarons (electrons and holes) generally occurs at the interface between the materials, and exciton diffusion lengths are typically only a few nanometers.<sup>2</sup> However, the enhanced charge dissociation achieved within a BHJ relative to that in a standard heterojunction comes at the cost of increased bimolecular recombination (recombination of electron and hole polaron charge carriers) due to the high interfacial area between the phases and the longer charge collection pathways in a photovoltaic device.

Recently, it was shown that bimolecular recombination can severely limit the performance (particularly the open-circuit photovoltage,  $V_{oc}$ ) of BHJ organic solar cells.<sup>3</sup> The work also indicated that the mobility of charge carriers was dependent on the concentration of separated charge in the device.<sup>4</sup> This is thought to be related to trapping of charge carriers in localized electronic states within the band gap of bulk organic materials.<sup>5</sup> Numerical simulations based on trapping/detrapping events using an exponential distribution of trap states

have proven very successful in describing bimolecular recombination in BHJs, where recombination events are limited by the transport of charge carriers through a trap-rich medium.<sup>6</sup>

To understand and optimize the function of devices based on organic materials, it is important to have a set of characterization tools enabling fundamental material parameters to be derived. In addition to the bimolecular recombination coefficient, which is related to the morphology of the material, the charge carrier mobility ( $\mu$ ) is currently a parameter of great interest in organic electronic materials. For example, not only are high  $\mu$  values required for the efficient collection of charge in polymer photovoltaics, but hole mobility limits the frequency response of organic transistors.<sup>7</sup>

There are many approaches available to measure  $\mu$ , each with inherent difficulties and limitations. For example, time-of-flight (TOF), field-effect transistors (FET) measurements, and space-charge-limited conduction (SCLC) are measured on devices and will thus include effects of processes that occur at the electrode interfaces.<sup>8,9</sup> On the other hand, flash photolysis (FP) and pulse radiolysis (PR) transient microwave conductivity (TRMC) probe bulk samples that do not include electrodes.<sup>8,9</sup> Sample morphology has been shown to greatly influence the charge carrier mobility, and this results in a

Received Date: August 18, 2010

Accepted Date: October 6, 2010

Published on Web Date: October 11, 2010

high sensitivity to the preparation methods needed for different measurements,<sup>10</sup> as well as to regioregularity<sup>11</sup> and crystalline orientation.<sup>12</sup> Different measurement techniques also result in significant variation of device charge concentration. Both modeling and experiments have clearly shown that the mobility depends on temperature and charge density.<sup>3,5,6,8,13–24</sup> Despite this, a single value for the mobility is often reported, without relevant information about the above parameters. Thus, comparing literature values is difficult.

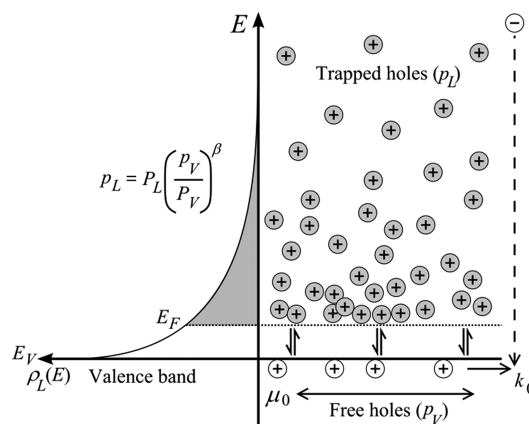
This Letter presents an analytical expression which can be easily fit to transient absorption spectroscopy (TAS) measurements of charge carrier concentration in BHJ films. The expression is based on a multiple trapping model of charge carriers in the material. The multiple trapping model has been successfully applied to other systems such as dye-sensitized solar cells and mesoporous water splitting electrodes.<sup>13,25,26</sup> Recently, Tachiya and Seki have derived analytical expressions that describes the decay of charge carriers in a BHJ controlled by the relative rates of trapping, detrapping, and recombination of holes.<sup>27</sup> Using a simpler approach, we derive an expression from the multiple trapping model that allows the bimolecular recombination coefficient, the hole mobility, and information about the distribution of trap states to be determined from TAS data. These parameters are useful for understanding the behavior of a particular organic BHJ blend on a more fundamental level than is typically achieved by most other mobility measurements. We demonstrate the applicability of the technique on a widely studied BHJ, a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). Our approach should prove useful for the future optimization and development of organic devices, particularly when complemented with photoelectrical measurements.<sup>28</sup>

The TAS measurements considered here involve monitoring the change in optical absorbance ( $\Delta OD$ ) of a BHJ film on glass following a short femtosecond laser pulse at time  $t = 0$ . The  $\Delta OD$  corresponds to the change in the excited charge concentration in the film. Our method is only valid for TAS signals in which charge separation has already been completed.

The multiple trapping model, schematically depicted in Figure 1, considers the total concentration of holes ( $p$ ) separated into a conducting population in the material's "valence band" or HOMO level (with concentration  $p_V$ ) and a population localized in traps (with concentration  $p_L$ ) so that  $p = p_V + p_L$ . In the context of a multiple trapping model, the population of holes in the valence band can be thought of as holes in transit (or hopping) between trapping states. We assume that the distribution of trap states is exponential, as has been observed experimentally<sup>19,29</sup> such that the concentration of trapped holes is related to the Fermi energy ( $E_F$ ) in the material by

$$p_L = P_L e^{\beta(E_V - E_F)/k_B T} \quad (1)$$

where  $P_L$  is the total number of available trap states,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $E_V$  is the valence band edge. The temperature-dependent parameter  $\beta$  describes the width of the trap distribution and is often



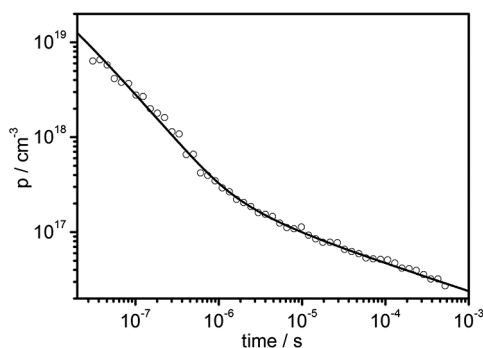
**Figure 1.** Schematic describing how the distributions of trapped and free holes are in quasi-equilibrium and only free holes can move and recombine with electrons.

expressed in terms of a characteristic temperature,  $T_0$ , so that  $\beta = T/T_0$ .<sup>6,8,13</sup> Note that other work suggests that the distribution of trapping states may have a Gaussian distribution (for example, ref 30).

We also assume the quasi-static approximation, which states that trapped holes are in instantaneous local equilibrium with conducting holes, that is, the trapping/detrapping dynamics are fast relative to other processes.<sup>13,31</sup> This approximation allows analysis of the system to be greatly simplified as trapping rates do not need to be explicitly considered. The convergence of transient absorption decays at longer times from different initial charge concentrations suggests that the approximation is valid for sufficiently high starting concentrations.<sup>6,17</sup> Additionally, we assume that trapped holes are immobilized and cannot recombine (neglecting contributions from tunnelling). Thus, only the valence band holes can recombine with electrons in the fullerene phase; these electrons are considered to be effectively free. For PPV/PCBM blends, the electron mobility in the PCBM phase was observed to be much greater than the hole mobility in the polymer phase.<sup>32</sup> Thus, here, we assume that the relative population of free to trapped holes is the factor that dominates the transport and recombination kinetics. The analysis could also be modified to describe kinetics limited by electron trapping. These assumptions together lead to the following expression for the bimolecular recombination rate

$$\frac{dp}{dt} = -k_0 n p_V \quad (2)$$

where  $k_0$  is the trap-free bimolecular recombination rate constant and  $n$  is the total population of electrons. Solving eq 2 for  $p(t)$  will allow for a TAS decay trace to be described because  $\Delta OD \propto p$  (and/or  $n$ ). To derive an analytic solution to eq 2, we first assume that Boltzmann statistics give a reasonable description of the concentration of conducting holes ( $p_V = P_V \exp[(E_V - E_F)/k_B T]$ ). Second, we assume that the majority of the holes in the film are normally localized ( $p_L > p_V$ ), which leads to the approximation that the localized fraction can be estimated from the total concentration of holes ( $p_L \approx p$ ). These approximations, together with charge



**Figure 2.** The decay of holes in a 1:1 P3HT/PCBM unannealed film following pulsed laser excitation measured by transient absorption spectroscopy probing the P3HT polaron absorption at 980 nm (circles). The solid black line shows fit of eq 3 to the data, where  $\beta = 0.29$ ,  $k_0 = 3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ,  $A = 4 \times 10^{42} \text{ cm}^{[5-(3/\beta)]}$ , and  $p_0 \approx 10^{19} \text{ cm}^{-3}$ . The value for  $p_0$  is not well-determined due to time resolution limitations of the experimental setup.

neutrality, allow for an analytic solution of eq 2, yielding an expression relating  $p$  to  $t$  when an initial population of holes,  $p_0$ , was formed after the laser pulse at  $t = 0$  (see the Supporting Information for a complete derivation)

$$\frac{1}{k_0} \{ \beta A (p^{-1/\beta} - p_0^{-1/\beta}) + p^{-1} - p_0^{-1} \} = t \quad (3)$$

Here,  $A$  is a constant related to the distribution and concentration of available trap states,  $A = P_L^{(1/\beta)}/P_V$ . The simplifications made in deriving this expression are assessed and shown to give a reasonable approximation to a more complete analysis in the Supporting Information. Rearranging eq 3 to express the total population of holes,  $p$ , as a function of time,  $p(t)$ , is impossible, but fitting of the analytic expression to data is straightforward nonetheless. Instead of fitting  $p(t)$  versus  $t$ , fitting is performed on the other axis, that is, fitting  $t(p)$  versus  $p$ .

To test the model, TAS measurements were performed as described previously on a nonannealed, spin-cast, 1:1 mixture of P3HT and PCBM.<sup>17</sup> A nonannealed device is suitable for our analysis because the phase domain sizes are very small. Recombination dynamics should then be more similar to that of a bipolar (or homogeneous) medium.<sup>19</sup> Figure 2 shows an example of a TAS decay where the change in absorbance has been converted to hole concentration according to  $p = N_A \Delta \text{OD} / (\epsilon_M d)$ , where  $N_A$  is Avogadro's number,  $d = 100 \text{ nm}$  is the film thickness, and  $\epsilon_M = 2 \times 10^4 \text{ M cm}^{-1}$  is the estimated molar extinction coefficient.<sup>3,17</sup> Plotted on a log–log scale, the decay indicates two clear slopes which can be interpreted in terms of the multiple trapping model. At early times, a slope of  $-1$  is evident and can be attributed to bimolecular recombination of a large population of free holes in the valence band with electrons, as we have discussed previously.<sup>17</sup> At later times ( $t > 10^{-6} \text{ s}$ ), as the total concentration of holes diminishes, the slope of the decay is reduced corresponding to a regime where hole recombination is trap-limited. Figure 2 also shows the least-squares fit of eq 3 to the data, which yielded the parameters shown in the caption where  $\beta = 0.29$  and  $k_0 = 3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Measurements with higher temporal resolution at early times would

also enable a value for the initial concentration of separated holes ( $p_0$ ) to be determined from the fit (see Figure S3 in the Supporting Information). Note that varying the energy of the initial laser pulse yields different  $p_0$  values, as has been seen previously for both unannealed MDMO-PPV/PCBM and P3HT/PCBM systems.<sup>6,17</sup> The initially different charge concentrations approximately converge to the trap-limited regime after sufficient time. The exception is at very low laser pulse energies, where the hole population is insufficient to completely thermalize within the deepest traps on a time scale faster than recombination (i.e., the quasi-static approximation is no longer valid).

As mentioned above, the properties of organic semiconductors are very sensitive to the preparation procedure and impurity. With this in mind, we briefly compare the fitting parameters with observations in the literature. The trap distribution parameter  $\beta$  corresponds to a characteristic temperature of  $T_0 = 1028 \text{ K}$ , which is comparable to previous findings<sup>8</sup> and suggests a characteristic trap depth ( $k_B T_0$ ) of around 90 meV, in agreement with activation energy observed for transport under an electric field in P3HT.<sup>16</sup> This gives some confidence that the simple analytical model can be used to derive reasonable estimates of the trapping characteristics of polymers and BHJ blends.

Furthermore, the fitted parameters can be used to make an estimate of the charge concentration dependence of both recombination and mobility. From the derivation of eq 3 given in the Supporting Information, we see that an effective recombination rate constant can be written as a function of the total hole concentration according to

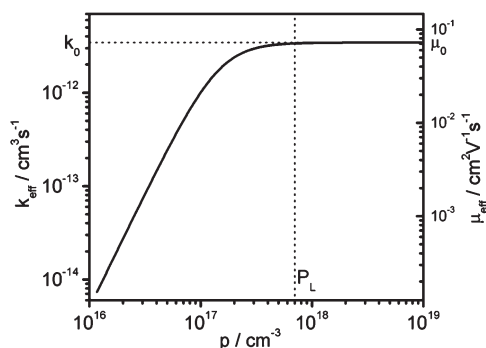
$$k_{\text{eff}}(p) = \frac{k_0}{\left(1 + \frac{p_L}{p_V}\right)} = \frac{k_0}{(1 + A p^{[1-(1/\beta)]})} \quad (4)$$

In the same way, the effective hole mobility,  $\mu_{\text{eff}}$ , can be described using the trap-free hole mobility,  $\mu_0$ , and the fraction of trapped and free holes.<sup>5,22</sup> Thus, the effective hole mobility is described by  $\mu_{\text{eff}} = (\mu_0/k_0)k_{\text{eff}}$ . If there is negligible phase separation (such as in a nonannealed sample), we can describe recombination in the blend as Langevin in character.<sup>33</sup> In that case, the ratio  $\mu_0/k_0$  can be estimated from the Debye equation,<sup>34</sup> which leads to

$$\mu_{\text{eff}}(p) = \frac{k_{\text{eff}}(p) \epsilon \epsilon_0}{eB} \quad (5)$$

where  $\epsilon$  is the dielectric constant (the relative permittivity at the low-frequency limit) of the blend,  $\epsilon_0$  is the permittivity of free space, and  $e$  is the charge on an electron. In eq 5, we have also introduced a parameter,  $B$ , which accounts for nanomorphology and other factors influencing the probability of recombination such as nonzero separation at the point of recombination.<sup>35,36</sup> Comparing actual mobility values to eq 5 is a means for determining values for  $B$  in blend materials.<sup>19</sup> Such studies have shown that a nonannealed blend is close to the Langevin limit ( $B = 1$ ) because the phase domain sizes are very small.<sup>19</sup> Equation 5 assumes that the mobility of the holes limits recombination so that the electron mobility in the Debye equation can be neglected.<sup>3,17</sup> Thus, both the effective





**Figure 3.** The effective bimolecular recombination rate constant,  $k_{\text{eff}}$ , and the calculated minimum effective hole mobility,  $\mu_{\text{eff}}$ , as a function of hole carrier concentration calculated with eqs 4 and 5 using the fitting parameters from the TAS data in Figure 2 for an unannealed P3HT/PCBM film. A dielectric constant of  $\epsilon = 3.8$  was used.

bimolecular recombination rate constant and minimum effective hole mobility are charge-density-dependent, as shown in Figure 3.

Thus, from a TAS measurement on a nonannealed BHJ of P3HT and PCBM, the maximum saturated hole mobility for nonannealed P3HT is estimated to be  $\mu_0 = 7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This value is comparable to the values of  $4.4 \times 10^{-2}$  and  $2 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  reported for the trap-free mobility of holes in P3HT derived from FET<sup>9</sup> and TOF<sup>18</sup> experiments, respectively. In general, reported hole mobilities for P3HT ranges between  $2 \times 10^{-1}$  and  $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , whether measured by FET,<sup>12,16,21,37</sup> TOF,<sup>10,18,25</sup> SCLC,<sup>7</sup> or pulse radiolysis TRMC.<sup>8,9</sup> The trap distribution parameter observed here is consistent with that observed in P3HT/PCBM devices; however, the hole mobilities here are higher due to observation at higher charge concentrations.<sup>4</sup> As Figure 3 illustrates, it is important to report the charge density for the measurement as this clearly influences the effective mobility.  $P_L$  cannot be uniquely determined by our data because  $P_L$  and  $P_V$  are covariant in expression for  $A$ . However, the total concentration of available trap states can be roughly estimated from Figure 3 to be  $10^{17}$ – $10^{18} \text{ cm}^{-3}$ , in agreement with previous studies of this combination of materials.<sup>17</sup> For example, this leads to a value of  $P_V \approx 10^{19} \text{ cm}^{-3}$  for the number of available valence band states (if  $P_L \approx 7 \times 10^{17} \text{ cm}^{-3}$ ). In a previous study of a MDMO-PPV/PCBM BHJ, it was found that  $P_L$  was on the order of  $1 \times 10^{17}$ .<sup>6</sup>

We now briefly consider the limitations of the model and validity of some of the critical approximations. The assumption that concentrations of conducting and trapped charges can be described by Boltzmann statistics and by eq 1 is shown to be reasonable in the Supporting Information, section SII. The approximation  $p \approx p_L$  introduced during the derivation of eq 3 is not valid at short times when  $p_0 > P_L$ . In section SIII of the Supporting Information, we show that, despite this, eq 3 gives a good approximation to the decay when compared to a numerical solution of eq 2 with the quasi-static assumption. We see that the concentration of holes given by eq 3 for the example shown in Figure 2 is up to 26% less than the numerical solution at times corresponding to  $p_V \approx p_L$ . At shorter and longer times, the approximation gives good

agreement with the numerical solution. Other examples are also shown in the Supporting Information. These indicate that the approximate model presented here is likely to give meaningful values as long as it is fitted to data spanning a sufficiently large time range. Lastly, if the rate of hole trapping ( $k_t$ ) and detrapping is not fast relative to recombination (i.e., the quasi-static approximation is not valid), then Tachiya and Seki have found an analytical solution for the case where  $k_0 = k_t$  using a version of the multiple trapping model which requires a trapping rate constant but does not require the assumption of a concentration of conducting valence states.<sup>27</sup> They also present a solution for the quasi-static case; this is similar to ours at times when recombination is trap-limited if we assume that  $P_V = \text{constant}/k_t$ .

In summary, we have presented a simple analytical function based on the multiple trapping model that can fit TAS data to yield information about the bimolecular recombination constant, the effective hole mobility, and the trap distribution of BHJ films. The method was demonstrated using an unannealed P3HT/PCBM blend and gave values consistent with those of previous observations using other techniques. The success of the multiple trapping model in explaining the materials behavior indicates the importance of quoting mobility or recombination constants in terms of the total charge concentration in the cell. We hope our approach will prove to be a useful tool for analyzing and comparing the many possible material systems in a consistent and meaningful manner.

**SUPPORTING INFORMATION AVAILABLE** Details of the derivation of eq 3 are presented in section SI, and assessment of the approximations and assumptions used is presented in sections SII and SIII. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**ACKNOWLEDGMENT** We are grateful to the EPSRC and BP Solar for funding. M.P.E. is grateful to the Knut and Alice Wallenberg foundation for funding. We are very grateful to Tracey Clarke and Fiona Jamieson for measurements, to Brian O'Regan for his helpful discussions, and to Thomas Kirchatz for his critical reading of the manuscript.

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