Suitable Definition of Drift Mobility

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Measurement of the drift mobility defined as the proportionality constant of the mean velocity (v) to the electric field strength (E) is necessary for understanding of carrier transport. However, it is difficult to obtain v from the time-of-flight transients. Thus the velocity obtained from the transit time has been analyzed instead of the mean velocity. The most common measurement of the mobility (μ_{k_ex}) is obtained from the time derived from the intersection of the asymptotes to the plateau and tail of the transients. Because the long tail of photocurrent transients for molecularly doped polymers indicates anomalous dispersion of carrier transit times, the difference between v/E and μ_{k_ex} is not negligible. Recently, a theoretical photocurrent transients equation (PTE) has been introduced. Fitting of the PTE to nondispersive transients gives the values of v and the diffusion coefficient (D) simultaneously. In this article, using the PTE, both the mobility (μ_{k_cal}), obtained from a kink in the photocurrent transient, and the tail-broadening parameter (W_{cal}) were derived as functions of v, D and sample thickness. We have tried to explain the anomalous behavior of μ_{k_ex} and the tail-broadening parameter (W_{ex}) in order to verify the PTE. The dependences of μ_{k_ex} and W_{cal} on the electric field and the sample thickness satisfactory agreed with those of μ_{k_ex} and W_{ex}. These verify the PTE and suggest that fitting of the PTE to photocurrent transients is suitable way to obtain the drift mobility.

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Introduction

Molecularly doped polymers (MDPs), in which guest charge transport molecules are dispersed in the host polymer matrix, are widely used for a photoconductor,[1–3] photorefractive devices,[4,5] organic electroluminescent devices,[6] and the synapse bond devices.[7] The fundamental processes of these devices involve carrier transport phenomena. Carrier transport also plays an important role in carrier injection.[8] Hence, an understanding of the carrier transport mechanism is a matter of great significance for science and technology.

Carrier transport has been evaluated by several methods.[9] The most common method is measurement of the photocurrent transients by time-of-flight (TOF).[1–3] In this measurement, the displacement current when a carrier packet moves in a sample is measured. Therefore the number of arrived carriers cannot be simply detected, and a detailed analysis of the photocurrent transients is necessary to obtain the drift mobility.[1,3] However, in the conventional method, the drift mobility μ_{k_ex} is derived from the time t_0 defined by intersection of the asymptotes to the plateau and tail of the transient. The tail of the current does not decrease linearly. Hence, t_0 shows variation that originates in the choice of the tangent line. Therefore, μ_{k_ex} contains ambiguity. In addition to this, the velocity obtained from t_0 is not the mean velocity. This situation is an obstacle to understanding the carrier transport mechanism.

Recently, a method of obtaining both the velocity (v) and the diffusion coefficient (D) from the photocurrent transient has been developed.[10,11] In Refs. 10 and 11, the theoretical photocurrent transients equation (PTE) was proposed. It was based on the fact that a carrier packet drifts at a constant velocity and spreads by diffusion. The top electrode is assumed to act as a reflecting and partially absorbing wall and the counter electrode is assumed to act as an absorbing wall. By fitting the PTE to a photocurrent transient, v and D can be obtained simultaneously. The obtained velocity is independent of thickness and shows no negative field dependence in a low electric field. Thus the fitting method is a suitable way to obtain the mobility.[12] However, the method of obtaining the mobility by the fitting of the PTE to photocurrent transients has not been widely used yet. The reasons for this are (1) the traditional method is fairly straightforward and (2) this fitting method has not been generally verified.

In this article, we have tried to explain the anomalous behavior of μ_{k_ex} and the tail-broadening parameter[13] (W_{ex}) using the PTE. In the following section, the different definitions of the drift mobilities are reviewed. Then, μ_{k_cal} and W_{cal} as functions of v, D and L that derived from the PTE are reviewed, where μ_{k_cal} is the mobility obtained from a kink in the photocurrent transients and W_{cal} is the tail-broadening parameter. Finally, the dependences of μ_{k_cal} and W_{cal} on the electric field, the temperature, and the thickness are analyzed and discussed.

Definitions of Drift Mobilities[1–3]

As shown in Fig. 1, typical non-dispersive transients for MDPs have an initial spike, a plateau of variable duration, and a long tail. The initial spike has been explained as the results of trapping at sites with waiting

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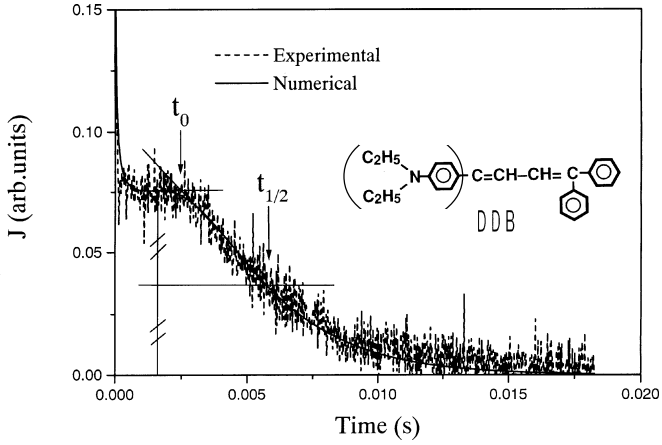

Figure 1. Time-of-flight photocurrent transient signal and some definitions of the transit time. The broken line is the experimentally measured photocurrent, and the solid line is the current obtained by calculating Eq. 1 using the parameters obtained by fitting. The inset shows a structural molecular formula for charge transporting molecule, DDB.

times that are comparable to the transit time,[3] the thermalization of the carrier packet within the density of states (DOS),[3] or forward diffusion of carriers at the illuminated surface.[10,11] The plateau region indicates the displacement of a carrier packet at constant velocity and diffusion.[3] The long tail shows the breakdown of Einstein's relationship relating the mobility and the diffusion coefficient.[3]

By analyzing the shape of the photocurrent transients, we can obtain a few kinds of mobilities in accordance with different definitions of the transit times. Pautmeier and co-workers have shown the Monte Carlo simulation results[14] for mobilities derived from transit times:

(a) the time t_0 defined by the intersection of the asymptotes to the plateau and tail of the transient,
(b) the time $t_{1/2}$ for the photocurrent to decay to one-half its value at t_0, and
(c) the ensemble average arrival time.

The logarithm of the mobility from method (a) shows proportionality with the square root of the electric field. On the other hand, the logarithms of the mobilities from methods (b) and (c) are proportional to the square root of the field in only high electric field regions. However, the experimental results that differ from the above-mentioned simulation results have been reported.[1,3]

The time t_0 corresponds to the time when the current begins to decrease rapidly. Because the carrier packet is generated as a sheet, the time t_0 is approximately the arrival time of the earliest carriers at the counter electrode. The earliest carrier is thought to be transported by a combination of drift and forward diffusion.[10,11] At the time t_0, the sum of the drift length and the diffusion length representing the earliest carriers is equal to the sample thickness. Because the diffusion length is proportional to $t^{0.5}$, the contribution of the diffusion length increases with decreasing the sample thickness. Actually, the μ_{k_ex} has sometimes shown thickness dependence.[1,3]

The experimental procedure for measuring of the average velocity using the PTE is expressed as follows.[10,11]

$$J(t) = -\frac{en_0}{2L}\sqrt{\frac{D}{\pi t}}\left[\exp\left\{-\frac{(L-vt)^2}{4Dt}\right\} - \exp\left\{-\frac{v^2t^2}{4Dt}\right\}\right] + \frac{en_0 v}{2L}\left[\mathrm{erf}\left(\frac{vt}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{L-vt}{2\sqrt{Dt}}\right)\right], \quad (1)$$

where n_0 is the number of holes, L is the thickness of the MDP, and erf(x) is the error function. The fitting of Eq. 1 to the transients gives the values of D, v, and n_0. The mobility μ_a and the transit time t_a obtained by fitting are written as $\mu_a \equiv v/E$ and $t_a \equiv L/v$.

As illustrated in Fig. 1 with a solid line, Eq. 1 was successfully fitted to experimental photocurrent transients whose shapes were non-dispersive over a temperature range from 260 K to 330 K and over electric field range from 1 to 3.6 MV/cm. The sample used in this measurement was DDB doped bisphenol-A-polycarbonate with a ratio of 0.26 in molar units, where DDB is a charge transporting molecules shown in Fig. 1 as an inset.

The mobility of an MDP depends on electric field and temperature, as well as on the structure of donor and acceptor functionality. These dependences have been described by the disorder formalism.[15] The disorder formalism was developed by Bässler,[15] and was verified by Borsenberger and co-workers.[1,3] According to Refs. 10 through 12, the dependence of μ_a on electric field and temperature is also described in Eq. 2:

$$\mu(T,E) = \mu_0 \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right]\exp\left[C\left\{\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right\}\sqrt{E}\right], \quad (2)$$

where σ is the width of the DOS, Σ is a parameter that describes the degree of positional disorder, μ_0 is the prefactor mobility, and C is an empirical constant, typically 2.9×10^{-4} (cm/V)$^{1/2}$. The values of D also show a similar dependence on temperature and electric field as[10,11]

$$D(T,E) = D_0 \exp\left[-\left(\frac{T_1}{T}\right)^2\right]\exp\left[C_D\left\{\left(\frac{T_1}{T}\right)^2 - \Delta\right\}\sqrt{E}\right], \quad (3)$$

where D_0, T_1, Δ, and C_D are constants. The parameters of a DDB doped bisphenol-A-polycarbonate with a ratio of 0.26 in molar units are $\mu_0 = 1.10 \times 10^{-2}$cm^2/Vs, $\sigma = 0.115$ eV, $\Sigma = 2.89$, $C = 2.90 \times 10^{-4}$ (cm/V)$^{1/2}$, $D_0 = 6.30 \times 10^{-2}$ cm/s, $T_1 = 896$ K, $\Delta = 6.26$, and $C_D = 1.35 \times 10^{-3}$ (cm/V)$^{1/2}$. To deduce the values of μ_{k_cal} and W_{cal}, the parameters in Eqs. 2 and 3 will be used in a later section.

Expressions for μ_{k_cal} and W_{cal} as Functions of v, D and L

In this section, both μ_{k_cal} and W_{cal} as functions of v, D and L derived by using the PTE are reviewed.[16] First, the definition of the time t_0 must be derived. In graphical way, the time t_0 is derived from the intersection of the asymptotes to the plateau and tail of the transients. However, the tail of the TOF current does not decrease linearly. Hence the choice of the tangent line of the tail has variation and t_0 contains ambiguity. The definition of t_{0_cal} as the intersection between the tangent line at

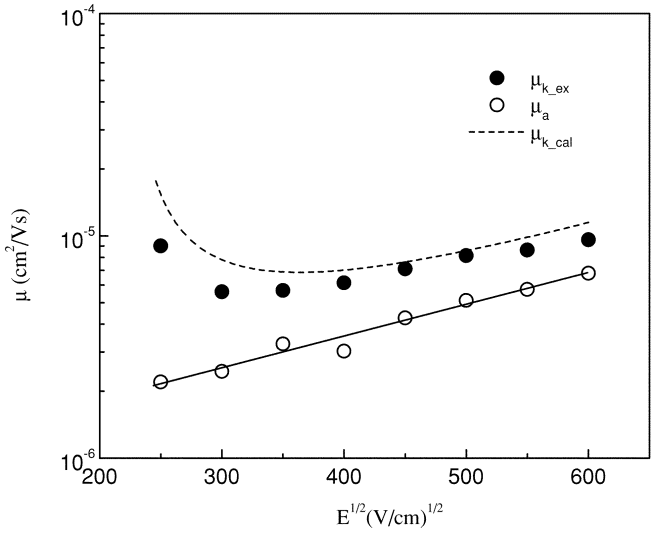

Figure. 2. Dependence of μ of the DDB-doped polymer on the square root of the applied electric field. The solid circles show μ_{k_ex} at T = 285 K. The μ_a is shown by the open circles and the solid line. The values of μ_{k_cal} shown as the dashed line are calculated from Eq. 4.

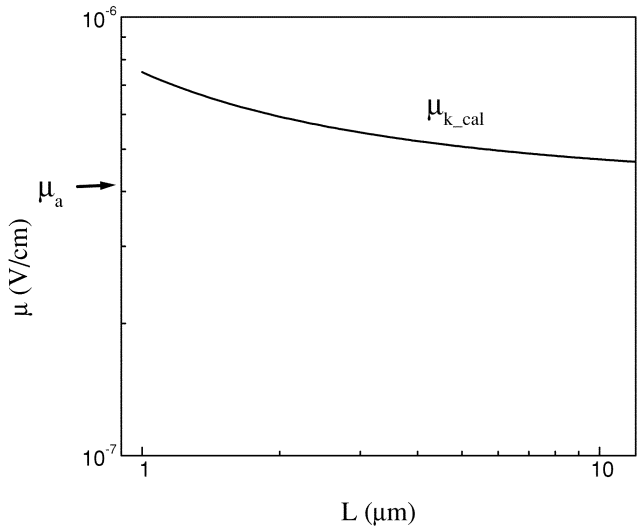

Figure 3. Dependence of μ_{k_cal} on sample thickness at T = 303 K and $E = 2.5 \times 10^5$ V/cm. The μ_a is shown by the arrow.

plateau and the tangent line at t_a is reasonable. In this case, t_{0_cal} is expressed as a function of v, D, and L:

$$t_{0\_cal} = \frac{L}{v} \cdot \frac{\left(1 - \sqrt{\frac{\pi D}{Lv}} - \frac{3D}{2Lv}\right)}{\left(1 - \frac{D}{2Lv}\right)}. \tag{4}$$

The expression of $t_{1/2\_cal}$ for the photocurrent to decay to one-half its value at plateau[16] was found to be

$$t_{1/2\_cal} = \frac{L}{v}\left(1 - \frac{D}{Lv}\right). \tag{5}$$

The tail-broadening parameter W is defined[13] as

$$W = \frac{t_{1/2} - t_0}{t_{1/2}}. \tag{6}$$

The parameter W as the function of D, v, and L is obtained by inserting Eqs. 4 and 5 into Eq. 6 as

$$W_{cal} = \frac{\frac{1}{2}\left(\frac{D}{Lv}\right)^2 + \sqrt{\frac{\pi D}{Lv}}}{\left(1 - \frac{D}{Lv}\right)\left(1 - \frac{D}{2Lv}\right)}. \tag{7}$$

In the case of $Lv >> D$, we obtain from Eq. 7:

$$W_E = \sqrt{\frac{\pi D}{vL}}. \tag{8}$$

If Einstein's relationship relating mobility and diffusion holds, Eq. 8 reduces to

$$W_E = \sqrt{\frac{\pi kT}{eLE}}. \tag{9}$$

Previous reports[17,18] have shown anomalous behaviors of W_{ex} that were not similar to those of W_E. The dependence of W_{cal} on E, T, and L is discussed in a later section.

Comparison of Mobility Behaviors

Let us compare behaviors of mobilities: μ_a, μ_{k_ex}, and μ_{k_cal}. The graphical analysis of TOF transients gives μ_{k_ex} and the PTE analysis give v (= $\mu_a E$) and D. The μ_{k_cal} can be expressed as a function of E, L, and T by substituting Eqs. 2 and 3 with the above-mentioned parameters of DDB-doped polymer.

The dependences of μ_{k_ex}, μ_{k_cal} and μ_a on the square root of the electric field is shown in Fig. 2, where $L = 7.6 \times 10^{-4}$ cm and T = 285 K. The logarithm of μ_{k_ex} is shown as solid circles which is larger than μ_a, shown as open circles. The difference between μ_{k_ex} and μ_a increases as the electric field decreases. The field dependence of μ_{k_cal} shown as the dashed line is similar to that of μ_{k_ex}, thus t_0 can be approximated by Eq. 4. The negative field dependence of μ_k at low electric field originates in a large diffusion coefficient of MDPs.[10,11] The time t_0 that gives μ_{k_ex} is close to the arrival time of the earliest carriers at the counter electrode. The carrier packet spreads with time by diffusion, thus the arrival time of the earliest carriers is shorter than the transit time t_a. If the applied electric field is small, the carriers will spend a long time to transit the layer. Under this condition, the difference between t_0 and t_a is large. Therefore the ratio of μ_k to μ_a is large.

The slope of μ_{k_ex} approaches that of μ_a in the high electric field region. This suggests that the disorder formalism parameters σ and Σ obtained from μ_{k_ex} in the high electric field region show small deviation from those obtained from μ_a.

Figure 3 shows the thickness dependence of the mobility where T = 300 K and $E = 2.5 \times 10^4$ V/cm. The logarithm of μ_{k_cal} shows thickness dependence and is different

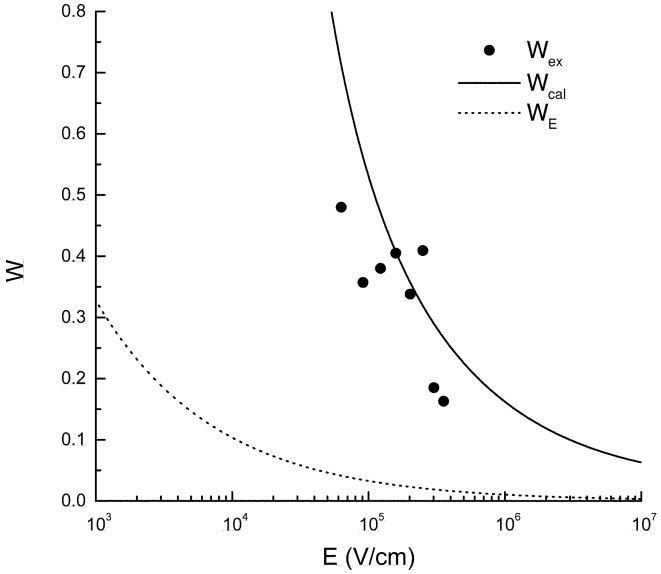

Figure 4. W versus E. The solid circles show W_{ex} of DDB-doped polymer at $T = 303$ K and $L = 7.6 \times 10^{-4}$ cm. The field dependence of W_{cal} of DDB-doped polymer shown by the solid line is similar to that of W_{ex}. The dashed line shows W_E.

from log μ_a shown by the arrow. The difference between μ_a and μ_{k_cal} is particularly marked when the sample is thin. This dependence agreed adequately with those of μ_{k_ex} in many studies.[1,3] These unexpected behaviors are not due to the experimental error but due to the fact that t_{0_cal} is a function of E and L as shown in Eqs. 2, 3, and 4. To discuss the dependence of μ_{k_cal} as an actual characteristic value of a substance, the thickness of the sample should be sufficiently large in this system.

Behavior of the Tail-broadening Parameter W

Borsenberger and co-workers have experimentally and numerically described the dependence of W_{ex} on various parameters in detail.[17,18] The anomalous dependence of W_{ex} on the electric field, the temperature, and the thickness has been reproduced by their detailed Monte Carlo simulations. In this section, the values of W_{cal} are calculated by substituting experimentally obtained values of v and D into Eq. 7 in the same way with μ_{k_cal}. As a result, the reproduction of W_{ex} by W_{cal} has been achieved as follows.

Figure 4 shows the electric field dependence of W_{cal} as the solid line. It agrees adequately with the W_{ex}, which is indicated by solid circles. In this case, the W decrease monotonously with the electric field. The W sometimes increases with the electric field. This dependence is reproduced with different values of v and D.

The W_{ex} also shows the temperature dependence as solid circles in Fig. 5 as well as W_{cal} as solid line. The temperature dependence of W_{cal} is similar to that of W_{ex}.

We also analyze Borsenberger and Bässler's data by the PTE. Figure 5 in Ref. 18 indicates that W depends on the temperature and is independent of the concentration of the charge transporting molecule when the electric field and the sample thickness are constant. The substitution of the data of this figure into Eq. 7 gives D/v at $E = 2.0 \times 10^5$ V/cm and $L = 10.0$ μm. The obtained values of D/v are used for the calculation of W_{cal} as functions of L, shown in Fig. 6 in Ref. 18. Figure 6 shows the thickness dependence of W_{cal} as a solid line with that of W_{ex} re-plotted from Ref. 18 as symbols. The dependence of W_{cal} is similar to that of W_{ex} except for the thin thickness region. When the sample is thin, the plateau of TOF transients disappear because the earliest carriers arrive at the counter electrode immediately. In this case, the comparison between W_{ex} and W_{cal} is meaningless.

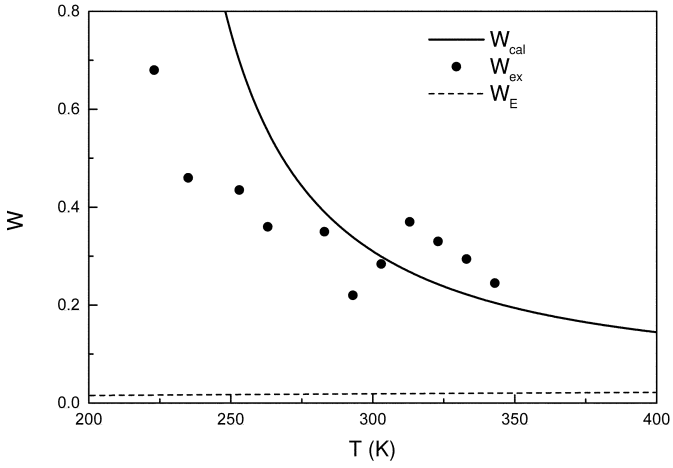

Figure 5. W versus temperature. The solid circles show W_{ex} obtained at $E = 3.0 \times 10^5$ V/cm and $L = 7.6 \times 10^{-4}$ cm. The solid line is W_{cal}. The dashed line shows W_E.

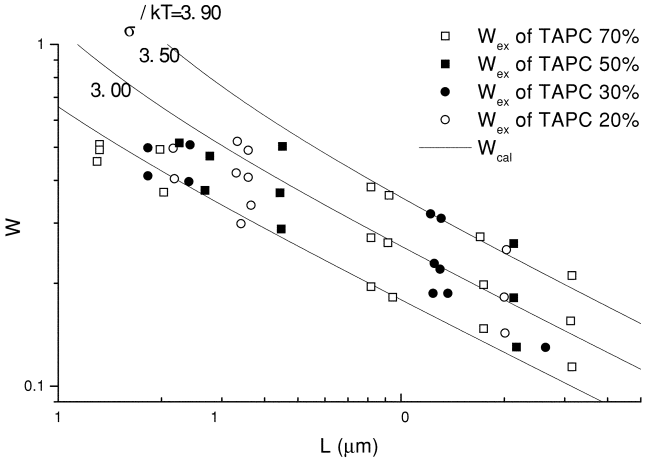

Figure 6. The thickness dependence of W_{ex} of TAPC-doped polystyrene, parameteric in T where TAPC is 1,1-bis(di-4-tolylaminophenyl)cyclohexane. The data of W_{ex} are re-plotted of Fig. 6 in Ref. 18. The field was 2.0×10^5 V/cm. The temperature dependence of W_{ex} at $E = 2.0 \times 10^5$ V/cm and $L = 10$ μm was also shown in Ref. 18. The substitution of the data into Eq. 7 gives D/v at $E = 2.0 \times 10^5$ V/cm and $L = 10$ μm. The obtained values are used for the calculation of W_{cal} dependence on L shown by the solid line. The dependence of W_{cal} is similar to that of W_{ex}.

In Figs. 4 and 5, W_E of Eq. 9 is shown as the dashed line. Figure 4 shows monotonous decrease in W_E over all the electric field region; however, such behavior of W_E has not yet been reported. The W_E is proportional to $T^{0.5}$. Figure 5 shows W_{ex} is not proportional to $T^{0.5}$. These results are a reminder that Einstein's relationship does not hold in the MDPs.

Because the values of μ_{k_cal} agreed adequately with those of μ_{k_ex}, μ_a is a suitable definition of the drift mobility. The values of W_{cal} are similar to those of W_{ex} in Figs. 4, 5 and 6. Hence the expressions of t_0 (Eq. 4) and $t_{1/2}$ (Eq. 5) as functions of v, D and L are suitable, and

the values of v and D that substituted into Eqs. 4 and 5 describes well the carrier transport of the MDPs. These results verify the description of charge transport in MDPs by the PTE.

Summary

The mobility (μ_{k_cal}) obtained from a kink in the photocurrent transient and the tail-broadening parameter (W_{cal}) as functions of v, D and L have been derived from the PTE based on the fact that a carrier packet drifts at a constant velocity and is spread by diffusion. The dependence of μ_{k_cal} and W_{cal} on electric field, temperature, and sample thickness have been investigated by substituting the experimentally obtained v, and D. The dependences of μ_{k_cal} and W_{cal} agreed adequately with those of μ_{k_ex} and W_{ex}. Our analysis also shows if the sample is sufficiently thick and the electric field is sufficiently high, the deviation of μ_k from μ_a calculated from v is small for purposes of interpreting the dependences of the mobility in terms of the disorder formalism. These results suggest that the PTE describe the photocurrent transients in MDPs adequately, and the analysis by the PTE is suitable for measuring the carrier transport in MDPs. ▲

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