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The Mobility and Decay Kinetics of Charge Carriers in Pulse-Ionized Microcrystalline PCBM Powder

By Matthijs P. de Haas, John M. Warman,* Thomas D. Anthopoulos, and Dago M. de Leeuw

The mobility and decay kinetics of charge carriers produced by nanosecond pulsed ionization of a microcrystalline powder sample of phenyl- C_{61} -butyric acid methyl ester (PCBM) have been investigated by time-resolved microwave conductivity. The sum of the electron and hole trap-free mobilities within crystallites is between 0.04 and 0.3 cm² V⁻¹ s⁻¹ at room temperature with an activation energy of 0.066 eV. The decay of the conductivity, which takes place over a timescale of milliseconds at room temperature, is controlled mainly by charge-carrier trapping with an activation energy of 0.53 eV. An upper limit of 1×10^{-18} m³ s⁻¹ is estimated for the rate coefficient of charge recombination, which is more than four orders of magnitude lower than expected for diffusion-controlled recombination, indicating PCBM to be an “indirect bandgap” semiconductor.

1. Introduction

The high electron affinity of C_{60} has made this moiety an extremely popular candidate as the acceptor component in all-organic, bulk heterojunction photovoltaic cells. This application of buckminsterfullerene was initially demonstrated by measurements on blends of unsubstituted C_{60} with conjugated polymers.^[1–4] More recently, the most commonly used C_{60} derivative in such devices has been the methyl ester of phenyl- C_{61} -butyric acid (PCBM) which, because of its high solubility in organic solvents, can be readily purified and film-cast using conventional techniques.^[5] The efficiency of solar cells based on admixtures of PCBM with, among others, conjugated polymeric materials has been found to depend strongly on mixture composition.^[6–10] A factor which undoubtedly plays an important role in this sensitivity is the tendency for PCBM to phase separate into microcrystalline aggregates at high PCBM contents.^[6–14] The use of a pure polycrystalline film of PCBM as the electron transport layer in field-effect transistors (FETs) has also been investigated.^[15–18] Because of these potential practical applications there is considerable interest at present in the electronic properties of solid PCBM, particularly in its micro- or polycrystalline form.

In the work presented here we have used pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) to investigate the mobility and decay kinetics of charge carriers formed in a microcrystalline powder sample of PCBM. In this method

the sample is weakly ionized with a nanosecond pulse of high-energy radiation resulting in the formation of a uniform concentration of charge carriers on the order of micromolar (ca. 10^{21} m⁻³). The transient change in conductivity of the sample is monitored in an electrodeless way, from nanoseconds to milliseconds after the pulse, as the change in the microwave dielectric loss of the sample. Because of the ultrahigh frequency (ca. 30 GHz) and low field strength (< 100 V cm⁻¹) of the probing microwaves, the random diffusional motion of the charge carriers within the crystallites is only slightly perturbed. From such PR-TRMC transients information can be obtained on the trap-free mobility of charge carriers, and on the kinetics of charge-carrier trapping and/or recombination. The results obtained are compared with previous PR-TRMC measurements on a powder sample of unsubstituted C_{60} ,^[19] and with measurements on polycrystalline films of PCBM using DC techniques.^[15–18,20–22]

2. Results and Discussion

PR-TRMC transients obtained on single-shot pulsed ionization of a bulk (ca. 250 mm³) sample of microcrystalline PCBM powder are shown in Figure 1. For the 2 ns pulse used the initial concentration of charge-carrier pairs formed within the solid was ca. 4×10^{21} m⁻³ ($7 \mu\text{mol L}^{-1}$), equivalent to the ionization of approximately four PCBM molecules per million. Since the dimensions of the individual microcrystals lie within the 1 to 10 μm range, the number of ionization events per crystallite is several thousand at least.

PR-TRMC transients are characterized by an end-of-pulse magnitude, from which the trap-free charge-carrier mobility can be estimated, and an eventual after-pulse decay of the conductivity, which provides information on the kinetics of charge-carrier trapping and/or recombination. These aspects of the results are discussed separately below.

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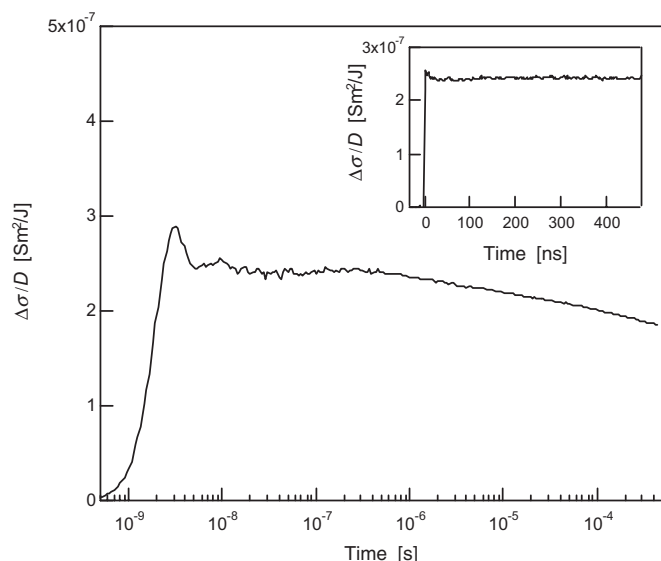


Figure 1. The dose (D)-normalized conductivity (σ) of PCBM powder on ionization at 22 °C with a single 2 ns pulse of 3 MeV electrons, displayed on a logarithmic timescale in the main figure and on a linear timescale, over the first 500 ns after the pulse, in the inset.

2.1. The End-of-Pulse Conductivity

Because of the similarity between the sample dimensions and the ca. 1 cm wavelength of the K_a -band (26–42 GHz) microwaves used, the magnitude of the TRMC signal is frequency dependent, as shown in Figure 2. The sinusoidal form of the dependence is determined by the relative dielectric constant,

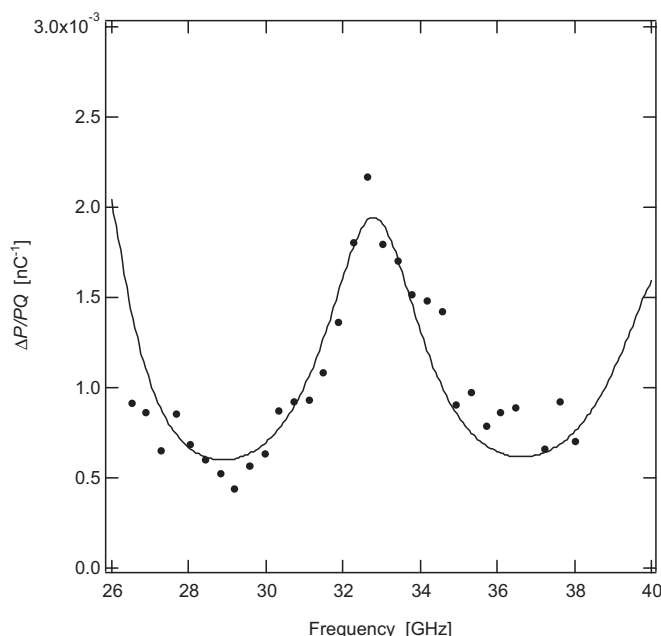


Figure 2. The frequency dependence of the radiation-induced change in microwave power (ΔP) reflected by the sample at room temperature monitored at 10 ns after a 2 ns pulse (points). Full line: the calculated, best-fit to the frequency dependence using a dielectric constant in solid PCBM of 4.1.

ϵ_r , and the (known) dimensions of the sample. From the calculated fit to the frequency dependence, shown as the full line in the figure, the value of ϵ_r for PCBM (taking into account the packing fraction of the solid) is 4.1. This is close to the value of 3.9 reported for a thin film of PCBM,^[20] and is within the range of 4.0 to 4.5 found for unsubstituted C₆₀.^[23]

From the fit of the calculated curve to the absolute magnitude of the experimental data, the value of the radiation-induced conductivity, $\Delta\sigma$ [S m^{-1}], can be determined.^[24,25] The end-of-pulse conductivity corresponding to the transients shown in Figure 1 is 2.8 mS m^{-1} . The conductivity is usually presented as the dose-normalized parameter $\Delta\sigma/D$ [$\text{S m}^2 \text{J}^{-1}$] with D [J m^{-3}] the energy per unit volume deposited in the sample during the pulse. Of interest in what follows is the value of $\Delta\sigma/D$ at the end of the pulse, that is, prior to any significant post-pulse decay. At room temperature $[\Delta\sigma/D]_{\text{eop}}$ was determined to be $2.5 \times 10^{-7} \text{ S m}^2 \text{J}^{-1}$, independent of the concentration of carriers produced in the pulse over the range from 1×10^{21} to $4 \times 10^{22} \text{ m}^{-3}$ (pulse length varied from 0.5 to 20 ns).

2.2. The Charge-Carrier Mobility at Room Temperature

The dose-normalized end-of-pulse conductivity is related to the sum of the mobilities of the positive and negative charge carriers formed, $\Sigma\mu = \mu(+) + \mu(-)$, by^[26]

$$[\Delta\sigma/D]_{\text{eop}} = W_p \Sigma\mu / E_p \quad (1)$$

In Equation 1, E_p is the average energy deposited (in electron volts) per initial ionization event. For high-energy radiation E_p can be estimated with reasonable accuracy ($\pm 20\%$) using the Alig formula:^[27]

$$E_p \approx 2.7 E_1 + 0.5 \quad (2)$$

In Equation 2, E_1 is the ionization potential (for molecular materials) or the bandgap (for semiconductor materials). For PCBM we take a value of $E_1 = 6.1 \text{ eV}$,^[6,28] which gives $E_p \approx 17 \text{ eV}$.

The parameter W_p in Equation 1 is the probability that initially formed electron–hole pairs survive to the end of the pulse; that is, they do not undergo sub-nanosecond (geminate) charge recombination. Since W_p has a maximum value of unity, a minimum value of the mobility sum can be derived from the end-of-pulse conductivity:

$$\Sigma\mu_{\text{min}} = E_p [\Delta\sigma/D]_{\text{eop}} \quad (3)$$

The value of $\Sigma\mu_{\text{min}}$, determined using Equation 3 on the basis of the above value of $[\Delta\sigma/D]_{\text{eop}} = 2.5 \times 10^{-7} \text{ S m}^2 \text{J}^{-1}$ with $E_p = 17 \text{ eV}$, is $0.043 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. We emphasize that this is the minimum value for the sum of the electron and hole mobilities since the individual values cannot be separately determined using the present technique.

Time-of-flight (TOF) measurements of mobilities in single crystals of PCBM have not, as yet, proven possible. Estimates of the electron mobility within ca. 100 nm thick polycrystalline films of

PCBM have, however, been made on the basis of current-density-voltage (J - V) characteristics within the space-charge-limited current (SCLC) regime. The initial estimate of $0.002 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by Mihailetchi et al.^[20] has recently been superseded by a higher estimate in the range 0.008 to $0.033 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, reported by Tuladhar et al.^[21] Mobility values determined from the transfer characteristics of field-effect transistor devices using a polycrystalline PCBM film as the transport layer have also displayed a tendency to increase with time, from $0.0045 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[15] to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[16,17] to the most recent values in the range 0.05 – $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[18] In a recent flash-photolysis TRMC (FP-TRMC) study of PCBM/polyphenylenevinylene (PPV) blends, the electron mobility within microcrystalline PCBM aggregates was estimated to be $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[10] The most recent mobility values determined using different techniques are seen to be similar in magnitude, or even higher, than the $\Sigma\mu_{\text{min}}$ value of $0.043 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ determined in the present work.

Of relevance at this point are mobility determinations reported previously for unsubstituted C_{60} . Identical PR-TRMC measurements to those reported here were performed some time ago on a powder sample of C_{60} .^[19] From the value of $[\Delta\sigma/D]_{\text{eop}} = 1.7 \times 10^{-6} \text{ S m}^2 \text{ J}^{-1}$, $\Sigma\mu_{\text{min}}$ is calculated to be $0.29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ using $E_p = 17 \text{ eV}$. This is almost an order of magnitude higher than the mobility found for PCBM in the present work, indicating peripheral substitution to have a negative influence on charge transport.

Importantly, TOF measurements on single crystals of C_{60} (ca. $100 \mu\text{m}$) have been carried out. In one report, on crystals grown from a CS_2 solution, both electrons and holes were found to have mobilities at room temperature of $(1.1 \pm 0.1) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[29] In another, on crystals formed by sublimation of pure C_{60} , values of (0.5 ± 0.2) and $(1.7 \pm 0.2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained for the electron- and hole-charge-carrier mobilities, respectively.^[30] We conclude that the mobility sum in bulk crystalline C_{60} must be close to $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and that both electrons and holes contribute significantly to this overall value of $\Sigma\mu$. This latter conclusion has been substantiated for PCBM in a FET study,^[17] and in a TOF study of a blend of PCBM (33 wt %) in polystyrene (PS).^[21] We should point out that a value two orders of magnitude smaller than the TOF value for $\Sigma\mu$ for C_{60} was estimated from a photoconductivity study of a sub-micrometer thin film using the Auston microstripline-switch technique.^[31]

The fact that the $\Sigma\mu_{\text{min}}$ determined from PR-TRMC measurements on a C_{60} powder is a factor of seven lower than the value of $\Sigma\mu$ determined from the TOF measurements on single crystals could be due to two factors. Firstly, the effective mobility of charge carriers confined within the microcrystallites of a powder sample could be lower than in a bulk single crystal as a result of backscattering at the crystal surface. A rough estimate of the surface-scattering time, t_{ss} , for a charge carrier of mobility μ within a microcrystallite of dimension d can be obtained from the relationship

$$t_{\text{ss}} \approx (d/2)^2 / 6\mu(k_B T/e) \quad (4)$$

with $k_B T/e$ the characteristic thermal energy in eV (ca. 0.025 eV at room temperature), where k_B is the Boltzmann constant, T is

temperature and e is the electronic charge. For d between 1 and $10 \mu\text{m}$ (a typical range for precipitated powders), t_{ss} varies from ca. 20 ns to $2 \mu\text{s}$ for a charge-carrier mobility in the bulk of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These scattering times are orders of magnitude longer than the reciprocal radian frequency of 5 ps of the microwaves used to probe the material. We conclude that surface scattering is unlikely to be the underlying explanation for the fact that $\Sigma\mu_{\text{min}}$ for C_{60} powder is considerably lower than the value of $\Sigma\mu$ determined from the TOF measurements.

A second possible reason for the difference is that the survival probability, W_p , is in fact considerably smaller than the value of unity used to calculate $\Sigma\mu_{\text{min}}$, that is, a large fraction of the initially formed electron-hole pairs could have undergone sub-nanosecond, geminate recombination within the pulse. The small initial spike in the PR-TRMC transients shown in Figures 1 and 3 may be a remnant of such rapidly decaying geminate ion pairs. A value of W_p of 0.15 would be required to explain the difference. If a similar value of W_p were to be applicable for the present PCBM sample, then the "true" value of $\Sigma\mu$ within the microcrystallites of this material would be calculated to be ca. $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. We conclude therefore that the room-temperature mobility sum of the charge carriers within the crystalline regions of PCBM lies within the range of 0.04 to $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is in agreement with the results given above of the most recent DC measurements on polycrystalline films and the FP-TRMC estimate determined for a blend containing PCBM aggregates.

2.3. The Mobility Temperature Dependence

PR-TRMC transients have been measured over the temperature range from -80°C to 170°C and examples are shown in Figure 3. The end-of-pulse conductivity is seen to increase considerably with increasing temperature. Since the pair-formation energy, E_p , should be temperature independent, we attribute this to a temperature-activated increase in the charge mobility.

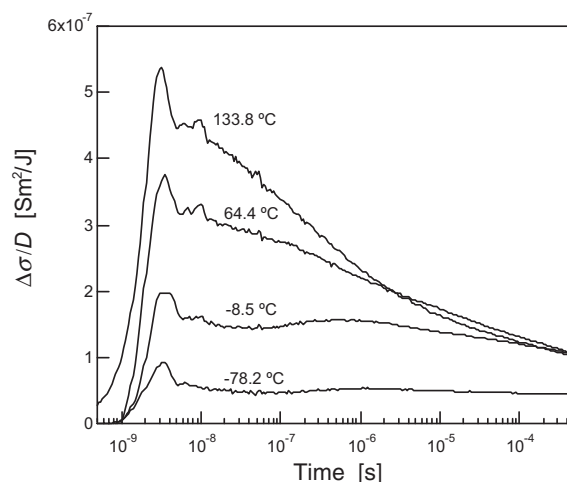


Figure 3. The transient dose-normalized conductivity of PCBM powder on ionization with a single 2 ns pulse at the temperatures shown.

The values of $\Sigma\mu_{\min}$ derived from $[\Delta\sigma/D]_{\text{cop}}$ are listed in Table 1 and are plotted in an Arrhenius fashion against the reciprocal temperature in Figure 4.

Table 1. The temperature dependence of the minimum mobility sum, $\Sigma\mu_{\min}$, and the half-life of the conductivity decay, $\tau_{1/2}$, together with the hopping frequency and hopping time, ν_j and τ_j , derived from $\Sigma\mu_{\min}$.

T [°C]	1000/T [K ⁻¹]	$\Sigma\mu_{\min}$ [cm ² V ⁻¹ s ⁻¹]	ν_j [ps ⁻¹]	τ_j [ps]	$\tau_{1/2}$ [μs]
-78.2	5.13	0.011	0.11	9.26	>1000
-49.8	4.48	0.018	0.20	4.90	>1000
-8.5	3.78	0.031	0.42	2.40	>1000
22.5	3.38	0.043	0.65	1.55	400
64.4	2.96	0.061	1.05	0.96	30
102.0	2.66	0.078	1.49	0.67	5.0
133.8	2.46	0.089	1.85	0.54	1.2
169.4	2.26	0.094	2.12	0.47	0.40

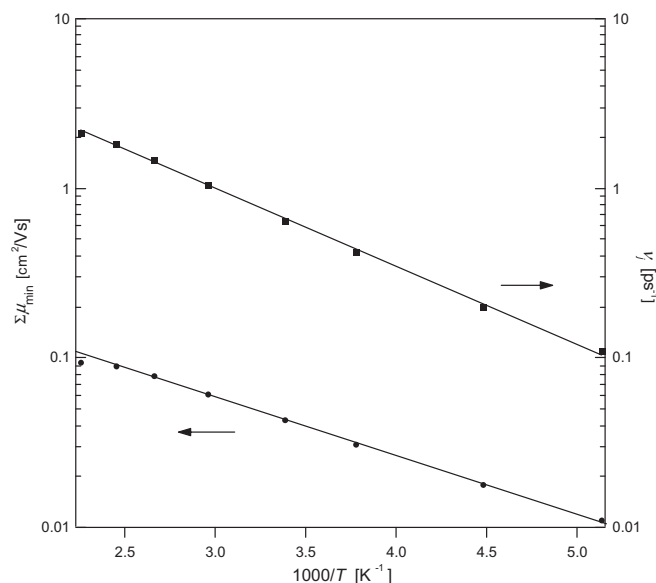


Figure 4. Arrhenius type plots of the temperature dependence of the mobility, $\Sigma\mu_{\min}$ (circles), and the hopping frequency, ν_j (squares).

A reasonably good linear dependence is found from which an activation energy of 0.066 eV is determined with an extrapolated value of $\Sigma\mu_{\min}$ of 0.62 cm² V⁻¹ s⁻¹ at 1/T=0. The activation energy is somewhat larger than the value of 0.046 eV found in the PR-TRMC study of unsubstituted C₆₀ powder.^[19] In the most recent FET study of PCBM,^[18] a somewhat higher activation energy of ca. 0.10 eV was found for the electron mobility.

If charge-carrier motion is a random 3D diffusion process that involves electron transfer over an average distance d_j , then the electron-transfer or hopping frequency $\nu_j = 6D/d_j^2$ with D the diffusion coefficient. Substituting for $D = \mu k_B T/e$ gives,

$$\nu_j = 6\mu(k_B T/e)/d_j^2 \quad (5)$$

The hopping frequency is a more fundamentally relevant parameter than the mobility particularly when discussing the temperature dependence of charge transport. Assuming that electron transfer occurs between nearest-neighbor PCBM moieties, we have calculated the values of ν_j corresponding to the measured values of $\Sigma\mu_{\min}$ using a value of $d_j = 1.0$ nm, as measured crystallographically.^[32] The values are listed together with the hopping times, $\tau_j = 1/\nu_j$, in Table 1 and are plotted as a function of the reciprocal temperature in Figure 4. From the straight line drawn through the points, an activation energy of 0.091 eV is obtained with an extrapolated value of $\nu_j = 2.6 \times 10^{13}$ s⁻¹ at 1/T=0, corresponding to a hopping time limit of 39 fs.

If the electron and hole do in fact have similar mobilities, as suggested by the TOF measurements on C₆₀ single crystals,^[29,30] TOF measurements on a PCBM/PS blend,^[21] and FET measurements on a PCBM film,^[17] then individual hopping times that are a factor of approximately two longer than the above value would be derived. On the other hand, if the survival probability parameter, W_p , is considerably less than unity as suggested above, higher mobilities and hence even shorter hopping times would be calculated.

A further consequence of W_p being considerably less than unity is that this parameter may also be temperature dependent. Since the Onsager distance decreases with increasing temperature, W_p would be expected to gradually increase for a constant thermalization distance and dielectric constant. If this effect were to be taken into account, activation energies somewhat smaller than those based on the temperature dependence of $\Sigma\mu_{\min}$ would be obtained. The values of 0.066 eV for the mobility and 0.091 eV for the hopping frequency given above may therefore be taken to be upper limits.

2.4. The After-Pulse Decay

The most dramatic difference between the results reported previously for an unsubstituted-C₆₀ powder sample and those for the present sample of PCBM is the orders of magnitude longer lifetime of the mobile carriers in the latter. Whereas the transient conductivity at room temperature decayed within a few tens of nanoseconds in the case of C₆₀,^[19] for PCBM a large fraction of the mobile carriers still survives even on a timescale of milliseconds. This difference can most probably be attributed to the much higher solubility of PCBM in organic solvents, which allows it to be subjected to more rigorous purification procedures.

As can be seen in the inset of Figure 1, the conductivity of PCBM remains almost constant over the first few hundred nanoseconds after the pulse at room temperature. In the logarithmic time representation, evidence of even a slight, after-pulse growth in the conductivity can be discerned. This behavior becomes more apparent at subambient temperatures, as shown by the lowest temperature transients in Figure 3. We have carried out rigorous tests of the response of the detection equipment to check whether this effect is an instrumental artifact but this appears not to be the case. A possible explanation

of the observed growth is that the material contains a small amount of less well-ordered, amorphous regions from which charge carriers diffuse relatively slowly to higher mobility, crystalline regions. We emphasize that this effect results in at most only a 20 % after-pulse increase in the conductivity.

At all temperatures the conductivity ultimately decays. Below room temperature this occurs on a timescale of milliseconds or longer, that is, beyond the upper time window of the detection system. As can be seen in Figure 3, above room temperature the decay, which is highly dispersive, becomes increasingly rapid. Since the kinetics could not be described in terms of a time-independent first- or second-order rate coefficient, a phenomenological measure of the timescale of the decay has been taken to be the time for the conductivity to decrease to 50 % of its end-of-pulse value, denoted $\tau_{1/2}$. The values of the half-life are listed in Table 1.

The temperature dependence of the decay is much more dramatic than that found for the mobility with $\tau_{1/2}$ decreasing by three orders of magnitude in going from room temperature to 169 °C. The $\tau_{1/2}$ values are plotted in an Arrhenius fashion in Figure 5, and, as can be seen, a good linear dependence is obeyed. The corresponding activation energy of the decay rate ($1/\tau_{1/2}$) is found to be 0.53 eV.

The question arises as to whether the decay of the conductivity results from recombination or trapping of the mobile charge carriers. As pointed out in a previous section, several thousand ionization events will occur within a micrometer-sized particle even for the shortest pulses used in the present work. If diffusional recombination between electrons and holes within a

crystallite occurs with a rate coefficient k_r , the first half-life of the conductivity resulting from this process should be given by:

$$\tau_r = 1/k_r N_{\text{eop}} \quad (6)$$

The rate of decay of the conductivity would then be expected to increase with increasing concentration of charge carriers (N_{eop}) formed in the pulse. However, on increasing the concentration from 1×10^{21} to $20 \times 10^{21} \text{ m}^{-3}$ (0.5 to 10 ns pulses, respectively), no significant change in the decay kinetics was found. A slight increase in the decay rate was, however, observed on further increasing the concentration to $40 \times 10^{21} \text{ m}^{-3}$ (20 ns pulse). We conclude that for pulses of 10 ns or less, charge-carrier trapping is the dominant mode of removal of the mobile carriers, and that the large activation energy found is associated with this trapping process.

From the half-life of 400 μs at room temperature for a 2 ns pulse ($N_{\text{eop}} = 4 \times 10^{21} \text{ m}^{-3}$), we can estimate an upper limit to the value of k_r of ca. $1 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$. For a diffusion-controlled recombination process, the rate coefficient is given by the Debye expression (ϵ_0 : permittivity of a vacuum):

$$k_D = \sum \mu e / \epsilon_0 \epsilon_r \quad (7)$$

For $\epsilon_r = 4.1$ and $\sum \mu$ within the range of 0.04 to $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, k_D ranges from 1.8×10^{-14} to $1.3 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$.

Recombination in crystalline PCBM occurs therefore with a rate coefficient that is four orders of magnitude or more lower than that expected for a diffusion-controlled reaction. The very low efficiency of charge recombination is probably a result of the fact that the transition from the lowest, S_1 , excitonic state of the C_{60} moiety to the ground, S_0 , state is symmetry forbidden.^[33] In solid-state terminology, PCBM is an “indirect band-gap” semiconductor.

The consequences of this can be looked at in a more general way by substituting for $\Delta\sigma_{\text{eop}} = eN_{\text{eop}}\sum\mu$ in Equations 6 and 7, which leads to an expression for the half-life of the conductivity that would be expected if recombination did occur via a diffusion-controlled process.

$$\tau_{1/2}(D) = \epsilon_0 \epsilon_r / \Delta\sigma_{\text{eop}} \quad (8)$$

For the transients shown in Figure 1, $\Delta\sigma_{\text{eop}}$ equals 2.8 mS m^{-1} , which results in a predicted half-life on the basis of Equation 8 of only 13 ns. This is five orders of magnitude shorter than the half-life value of approximately one millisecond actually found!

It is of interest to compare the present conductivity decay kinetics for PCBM with those found using the PR-TRMC technique for pure, solid PPV derivatives^[26,34] and poly(3-hexylthiophene) (P3HT),^[35] both compounds that are commonly used in PCBM/polymer blends for photovoltaic applications. In both cases the temporal decay was found to be well-described by a stretched-exponential expression. For the same dose conditions, the decays for the polymeric materials at room temperature were much more rapid than for PCBM with first half-lives on the order of a microsecond or less, that is, three orders

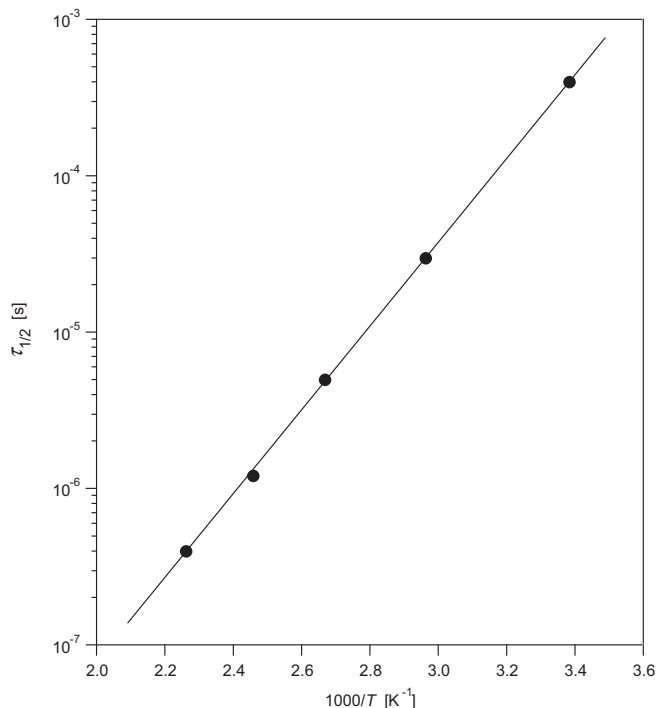


Figure 5. Arrhenius type plot of the temperature dependence of the first half-life, $\tau_{1/2}$, of the transient conductivity.

of magnitude or more faster. Much slower charge-carrier decays have been found in the PCBM blends with these polymers.^[36–39] This has been attributed to spacial localization and trapping in separate electron- and hole-affinic domains within these heterogeneous materials. Recently, however, evidence has been provided for both electron and hole transport occurring via the PCBM component for high PCBM contents.^[21] If that is the case, the ultraslow recombination of holes and electrons observed in the present work could be of relevance to the performance of photovoltaic devices.

The nature of the trapping process that is mainly responsible for the decay of the conductivity in the present material remains unknown. However, the high activation energy found suggests that it may involve a chemical reaction with PCBM moieties. Of possible relevance to this is the finding that on returning to room temperature after the heating trajectory, the half-life of the transient conductivity was considerably shorter than found initially for the pristine material. This was surprising in view of the fact that no phase transitions or weight-loss of the material has been found in differential scanning calorimetry or thermogravimetric studies for temperatures below 250 °C; considerably higher than the highest temperature of 169 °C to which the present sample was exposed. Since trapping and/or chemical degradation of the material may be associated with the presence of oxygen, subsequent experiments have been carried out in which the sample could be rigorously evacuated.^[40] The results will be presented in a subsequent publication.

3. Conclusions

Based on a pulse-radiolysis time-resolved microwave conductivity study of microcrystalline PCBM powder we reach the following conclusions: a) the sum of the electron and hole trap-free mobilities within the micrometer-sized crystallites, $\Sigma\mu$, lies within the range of 0.04 to 0.3 cm² V⁻¹ s⁻¹ with a corresponding hopping frequency, ν_j , in the range of 0.6 to 4.5 ps⁻¹. b) The upper limits to the activation energies of $\Sigma\mu$ and ν_j are 0.066 eV and 0.091 eV, respectively. c) At room temperature the radiation-induced conductivity decays over a timescale of milliseconds. d) For initial charge-carrier concentrations of ca. 10²² m⁻³ or less, the ultimate decay of the conductivity is controlled by trapping of the mobile carriers with an activation energy of 0.53 eV. e) An upper limit to the rate coefficient of charge recombination of 1 × 10⁻¹⁸ m³ s⁻¹ is estimated, which is more than four orders of magnitude lower than expected for diffusion-controlled charge recombination. f) A small (< 20 %) fraction of the material is less well ordered (possibly amorphous), which results in a slight initial growth in the conductivity within the first microsecond after the pulse as charges diffuse to higher mobility crystalline regions. g) Evidence is found for degradation of the material after exposure to high temperatures. The latter finding is relevant to the application of PCBM in device structures since high-temperature annealing is frequently used to “improve” device performance. This aspect is discussed more fully in a separate publication.^[40]

4. Experimental

The methyl ester of phenyl-C₆₁-butyric acid (PCBM), supplied by Nano-C (“PCBM-01”, > 99.5 %, lot nr G-11-05-04), was used without further purification. Investigation by X-ray diffraction and polarization microscopy showed the powder to consist mainly of crystallites with dimensions of several micrometers. Differential scanning calorimetry and thermogravimetric measurements indicated no structural reorganization or significant weight loss to occur below 250 °C.

The powder was compressed into a cavity consisting of a 14 mm length of K_a-band waveguide (3.55 mm × 7.1 mm rectangular cross section) closed at one end with a metal plate. From the measured weight and length (ca. 10 mm) of the sample, the packing fraction of the solid was determined to be 0.51 based on a density of 1.65 g cm⁻³ [19,23]. The powder pellet was irradiated with a single nanosecond-duration pulse of 3 MeV electrons from a Van de Graaff accelerator. The energy deposited per unit volume in the solid, D , was 1.44 Q kJ m⁻³ with Q the beam charge in the pulse in nC. For the most frequently used pulse, 2 ns (ca. 8 nC), the initial concentration of charge-carrier pairs formed, based on a pair formation energy, E_p , of 17 eV, is ca. 4 × 10²¹ m⁻³ (7 μmol L⁻¹) corresponding to four ionization events per million PCBM molecules. Since a 1 μm diameter particle has a volume of ca. 10⁻¹⁸ m³, the number of ionization events within each microcrystallite of the present powder will be at least several thousand.

Any transient change in the conductivity of the sample was monitored with nanosecond time resolution as a decrease in the microwave power, $-\Delta P/P$, reflected by the cavity. Single-shot transients could be monitored using either a linear time base digitizer with a 1 ns rise time over the first few hundred nanoseconds after the pulse, or a pseudo-logarithmic time base digitizer from 10 ns to 1 ms. The microwave frequency could be varied over the range 26 to 38 GHz. Several single-shot transients could be averaged to improve the signal-to-noise ratio if necessary. The data-reduction procedures have been described in detail in previous publications [24–26].

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