

# Negative electric field dependence of charge carrier drift mobility in conjugated, semiconducting polymers

Attila J. Mozer<sup>\*</sup>, Niyazi Serdar Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstr. 69, A-4040 Linz, Austria

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## Abstract

The temperature and electric field dependence of the hole mobility in regioregular poly(3-hexylthiophene) (P3HT) is studied by time-of-flight (TOF) technique. It is observed that above  $\sim 250$  K the slope of the electric field dependence of mobility becomes negative. Such phenomenon has been reported previously for a variety of amorphous charge transport materials, but not clearly observed in conjugated semiconducting polymers. The temperature and electric field dependence of mobility is analyzed both in the framework of Gill's phenomenological data analysis and disorder formalism. The occurrence of negative field dependence in the measured regioregular P3HT samples is attributed to the small energetic ( $\sigma = 70$  meV), but large spatial disorder ( $\Sigma = 3.4$ ).

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## 1. Introduction

The occasionally observed negative electric field ( $E$ ) dependence of charge carrier mobility ( $\mu$ ) is a fascinating feature of hopping charge transport in disordered organic solids [1]. Earlier studies showed that in molecularly doped polymers [2], particularly at low concentration of the dopant molecules [3], the typical  $\log \mu \propto \beta E^{1/2}$  field dependence of the mobility vanishes at a certain temperature  $T_0$ , and  $\beta$  becomes negative at higher temperatures ( $T > T_0$ ). The phenomenological analysis of Gill [4] describes the occurrence of such phenomena according to the following equation:

$$\mu(T, E) = \mu_0 \exp \left[ - (\Delta - \beta E^{1/2}) / k_B T_{\text{eff}} \right], \quad (1)$$

where  $T_{\text{eff}}^{-1} = T^{-1} - T_0^{-1}$ ,  $T$  (K) is the temperature,  $\Delta$  (eV) is the zero field activation energy,  $\beta$  ( $\text{eV}(\text{V cm}^{-1})^{-1/2}$ ) is the Poole–Frenkel coefficient,  $T_0$  is the temperature at which the Arrhenius plots of mobility at various electric fields intercept,  $\mu_0$  is the mobility at  $T_0$ ,  $k_B$  is the Boltzmann constant. Although the Gill formula predicts negative field dependence of mobility above  $T_0$ , it does

not discuss the underlying physical nature of it, nor attributes any physical meaning to parameter  $T_0$ .

The disorder formalism suggested by Bäessler [5] became widely accepted to describe the basic features of charge transport in various amorphous organic materials, such as molecularly doped polymers [3,6], molecular glasses [7] and conjugated polymers [8,9]. One of the key features of the model is that it can account for mobilities that decrease with increasing electric field. The model rests on the notion that due to the disordered nature of amorphous molecular solids, both the energy and the intersite distance of charge transport sites are subject to a statistical distribution. The following functional form of the temperature and electric field dependence of mobility was proposed based on Monte Carlo simulations of a hopping system in a Gaussian distribution of density of states using the master equation of Miller–Abrahams [10] type for the elementary hopping rate:

$$\mu(T, E) = \mu_0 \exp \left[ - \frac{2}{3} \hat{\sigma}^2 \right] \exp \left[ - C(\hat{\sigma}^2 - \Sigma^2) E^{1/2} \right], \quad (2)$$

where  $\hat{\sigma} = \sigma / (k_B T)$  and  $\Sigma$  are parameters characterizing energetic disorder and positional disorder,  $\sigma$  (eV) is the width of the Gaussian density of states,  $\mu_0$  ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )

<sup>\*</sup> Corresponding author. Fax: +43-732-2468-8770.

E-mail address: [attila.mozer@jku.at](mailto:attila.mozer@jku.at) (A.J. Mozer).

is a prefactor mobility in the energetic disorder-free system,  $E$  ( $\text{V cm}^{-1}$ ) is the electric field, and  $C$  is a fit parameter. A charge carrier between hops accelerated by the external electric field gains electrostatic energy equals to  $eEa$  ( $a$  is the intersite distance,  $e$  is the elementary charge), which lowers the activation energy for forward jumps, and gives rise to the typical  $\log \mu \propto \beta E^{1/2}$ ,  $\beta > 0$  electric field dependence. Simulations showed that positional disorder influences the electric field dependence of the mobility in an opposing way [1,11]. According to Eq. (2), the slope of the field dependence becomes negative, when the spatial disorder parameter  $\Sigma$  exceeds the energetic disorder parameter  $\sigma/k_B T$ . A physical explanation, similar to what was originally suggested to describe negative differential hopping conductivity in impurity inorganic semiconductors [12,13], was also provided. In a hopping system with large spatial distribution, faster routes as well as dead-ends are created for the carriers executing their random walk. At higher fields, the faster routes whose direction is not aligned with the direction of the external electric field are diminished; therefore, the carrier is forced to make the difficult jumps resulting in decreasing mobility with increasing electric field [14]. Typical values of  $\sigma$  and  $\Sigma$  in molecularly doped polymers in which negative field dependence of mobility has been observed was  $\sigma = 0.1$  eV,  $\Sigma = 5$ , and the transition temperature  $T_0$  was around or above room temperature [3,15]. A recent study on molecular glasses [16], in which charge transport is studied in the pristine charge transporting molecules without any binding matrix, has shown that if  $\sigma$  is sufficiently low ( $\sigma = 59$  meV), negative field dependence of mobility may be observed even though  $\Sigma$  is not particularly high ( $\Sigma = 2.4$ ).

Charge transport in conjugated, semiconducting polymers have been the subject of intensive research due their application in novel opto-electronic devices such as polymer light emitting diodes [17], polymer field effect transistors [18], photovoltaic devices [19], etc. The observed charge transport properties are often described within the framework of disorder formalism, and lately a modified model taking into account correlated disorder [20] has been introduced. It is often observed that the distribution in the length of the conjugated segments caused by kinks or chemical defects increases disorder in conjugated polymers as compared to their oligomeric counterparts or other small molecules [21]. Representative values of  $\sigma$  determined in conjugated polymers are 80–100 meV [9,22] and the extrapolated values of  $T_0$  are well above room temperature, for e.g., 1200 K in a polyphenylenevinylene-ether [22], 600 K in poly(dialkoxy *p*-phenylene vinylene) (PPV) [23] and 465 K in poly(1,4-phenylene-1,2-diphenoxyphenyl vinylene) (DPOP-PPV) [24], at which the conjugated polymer either undergoes morphological changes or degrades. Therefore, the occurrence of negative field

dependence in conjugated polymers was not clearly observed up to date.

In this Letter, we report the temperature and electric field dependence of the mobility in a film of chemically purified, highly regioregular poly(3-hexylthiophene). We have found that the field dependence of the mobility vanishes at  $T_0 \sim 250$  K, and becomes negative at higher temperatures. The rather low transition temperature  $T_0$  is attributed to the small energetic disorder ( $\sigma = 70$  meV) but high positional disorder parameter ( $\Sigma = 3.4$ ) of the measured regioregular poly(3-hexylthiophene) samples. In addition, the small value of  $\sigma$  provides the opportunity to determine charge carrier mobility as low as 100 K, extending the temperature dependence studies to lower temperatures, where the predictions of existing theoretical models are discriminating. Temperature dependence of the measured time-of-flight (TOF) mobility can be approximated with the predictions of both Gill's model ( $\log \mu \propto 1/T$ ) and disorder formalism ( $\log \mu (E = 0) \propto 1/T^2$ ) at high temperatures ( $>160$  K), however, deviations at lower temperatures ( $<160$  K) from both models are observed.

## 2. Experimental

Regioregular poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals, Inc., and was further purified according to [25]. The 4.6  $\mu\text{m}$  thick P3HT films were prepared by the doctor blade technique from 6 wt% chloroform solution onto structured ITO-coated glass substrates (substrate temperature 40 °C). On top, semitransparent Al was evaporated as cathode in a vacuum better than  $10^{-5}$  mbar (Al layer thickness 40 nm). The samples were reverse biased (ITO as a negative and Al as a positive terminal), and illuminated from the Al side using the second harmonic (532 nm) of a Nd:YAG pulsed laser with 3 ns pulse durations. The photogenerated charges drifted through the sample under the external electric field applied by a voltage supply, and were recorded by a digitizing oscilloscope using a low noise current amplifier. The devices were kept under the applied bias between the light pulses to ensure extraction of all the photogenerated carriers between the measurements. The transients were recorded in either a single-shot mode or averaging several transients (at lower temperatures) in order to increase signal to noise ratio. The repetition rate of the light pulses was 0.8 Hz. The transit time of charge carriers was defined as the meeting point of the asymptotes of the two linear regimes in the logarithm photocurrent versus logarithm time plots [1]. The incoming light intensity was adjusted by optical density filters that total number of photogenerated charges was less than 10% of the total capacitor charge. In addition, the intensity dependence of the photocurrent transients was checked at several

temperatures by decreasing the incoming light intensity, and no variation of the transit times was observed. The TOF mobility was calculated as  $\mu = d^2/(V \times t_{tr})$ , where  $\mu$  ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) is the mobility,  $d$  (cm) is the film thickness,  $V$  (V) is the applied potential, and  $t_{tr}$  (s) is the transit time of charge carriers. The temperature dependence measurements were performed using a temperature controlled liquid nitrogen cooled cryostat (Oxford Optistat DN-V, ITC 503 temperature controller, precision  $\pm 0.1$  K). The thickness of the films was determined using a Tencor Instruments Alphastep Semiconductor Profiler.

### 3. Results and discussion

The electric field dependence of hole mobility in regioregular P3HT is illustrated in Fig. 1 parametric in temperature. At all temperatures, the mobility follows the  $\log \mu \propto \beta E^{1/2}$  relationship. It is clearly seen that coefficient  $\beta$  of the field dependence of mobility vanishes around  $\sim 250$  K, and becomes negative at higher temperatures. Although earlier reports on TOF mobility in P3HT showed mobilities that increase at lower electric fields [26,27], later it was argued that the apparent increase of mobility was due to the short dielectric relaxation time in the samples measured, resulting in a redistribution of the electric field before the majority of charge carriers exit the sample (transit time  $>$  dielectric relaxation time) [28]. It was shown that under these conditions the mobility is overestimated, and the alternative method of charge carrier extraction by linearly increasing voltage (CELIV) [29] can be used. The behavior shown on Fig. 1 is significantly different what was reported in [25,26]. Above 250 K, the log mobility decreases with constant slope at all electric fields. In addition, the CELIV curves showed no extraction of

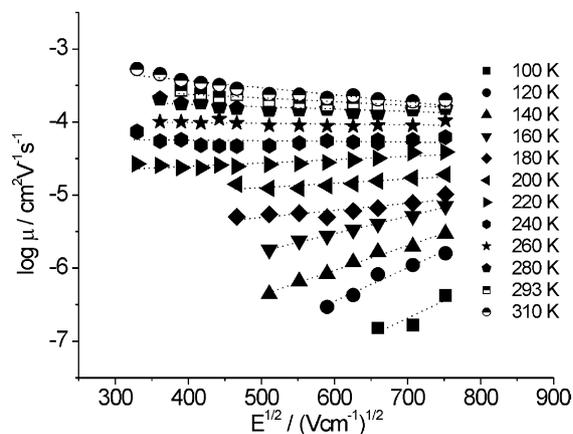


Fig. 1. Electric field dependence of the hole mobility in regioregular P3HT at various temperatures determined by time-of-flight technique. The lines represent linear fits of the data.

equilibrium charge carriers indicating low conductivity of our samples (estimated dielectric relaxation time is  $> 10^{-3}$  s at room temperature).

Fig. 2a, b compares the photocurrent transients recorded at various applied voltages at 310 and 160 K, respectively. The transit time decreases as the applied voltage is increased at both temperatures, however, the decrease in transit times is more pronounced at low temperatures. At 310 K, the mean velocity of the charge carriers defined as  $v = d/t_{tr}$  does not increase proportionally as the electric field is increasing resulting in the observed negative field dependence of mobility ( $\mu = v/E$ ).

In Fig. 3, the logarithm of mobility is plotted versus the inverse temperature at various applied voltages. The temperature dependence is well approximated with a linear relationship, however, deviation from the straight-line behavior at lower temperatures is observed. The Arrhenius plots of mobility intercept at  $T_0 \sim 250$  K, following the prediction of Eq. (1). The effective activation energy of mobility ( $E_{act} = \Delta - \beta_{PF} E^{1/2} (1000k_B)^{-1}$ ) was calculated from the slope of the temperature dependence at each electric field, and plotted versus squared electric field in the inset of Fig. 3. A linear relationship is found, and the zero field activation energy  $\Delta = 0.29$  eV and  $\beta = 2.9 \times 10^{-4} \text{ eV}(\text{V cm}^{-1})^{-1/2}$  is calculated. The calcu-

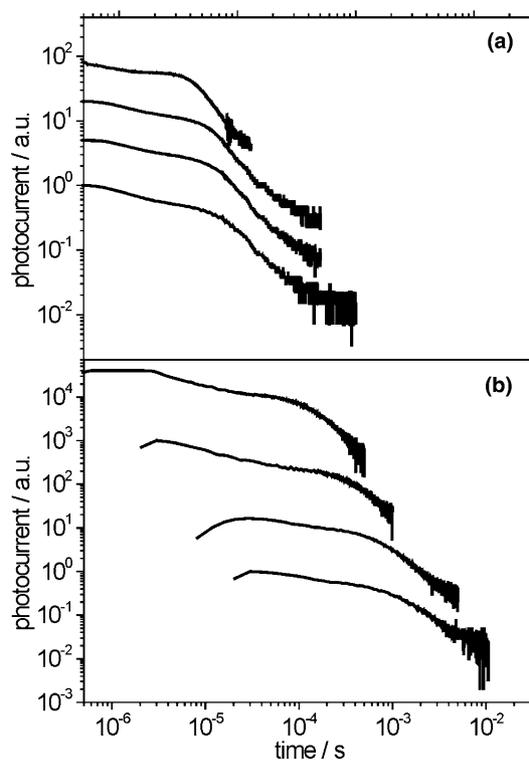


Fig. 2. Time-of-flight photocurrent transients recorded at (a): 310 K, and (b): 160 K at applied voltages (from bottom to top) of 100, 140, 180, and 260 V. The photocurrent transients are scaled for better comparison.

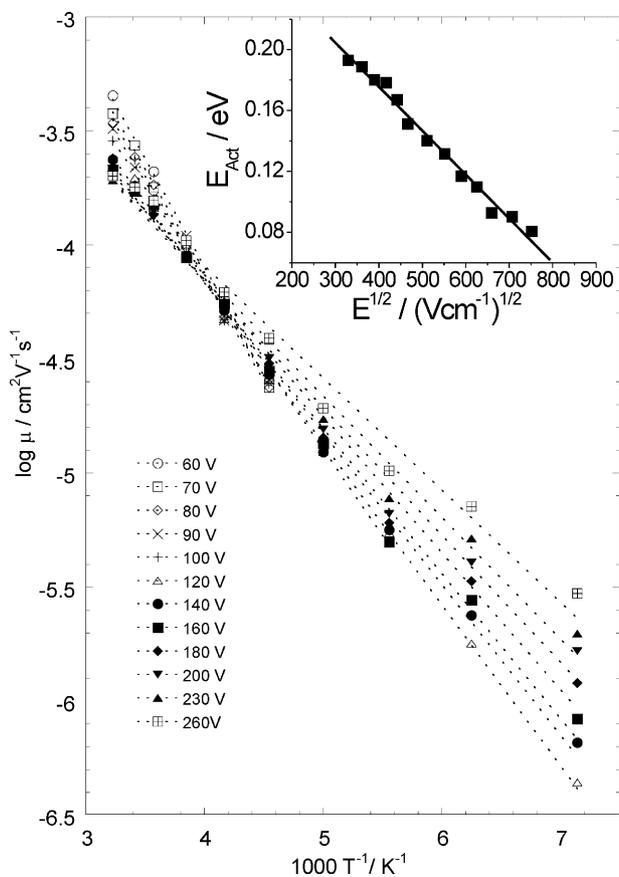


Fig. 3. Arrhenius plots of logarithm mobility at various applied voltages. (Inset) Plot of the apparent activation energy versus the squared electric field. Lines represent linear fits of the data.

lated  $\beta$  value compares well with the theoretically calculated one ( $\beta = 4 \times 10^{-4} \text{ eV}(\text{V cm}^{-1})^{-1/2}$ ) [22].

The logarithm of mobility extrapolated to zero electric field (ordinate intercept in Fig. 1) is plotted against the squared inverse temperature in Fig. 4. The relationship is approximated with a linear relationship according to Eq. (2), but again, deviation from the straight-line behavior at lower temperatures is observed.

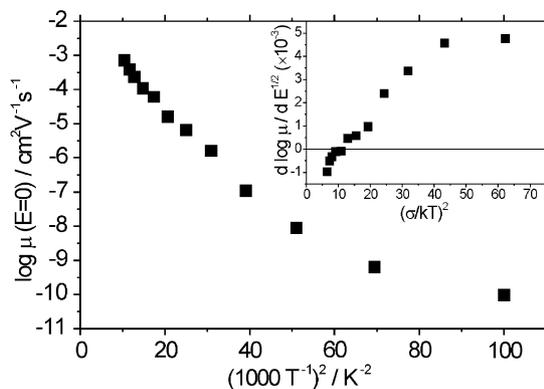


Fig. 4. Logarithm of zero field mobility values versus  $(1000/T)^2$ . (Inset) The slope of the field dependence of the logarithm mobility determined from Fig. 1 versus  $(\sigma/kT)^2$ , calculated using  $\sigma = 0.070 \text{ eV}$ .

Such deviation has been attributed to the time dependence of the energy relaxation process of the photo-generated charges [22]. It was argued that at a critical temperature  $T_c$ , the time required to reach quasi-equilibrium for the packet of carriers exceeds the transit time, and a transition from non-dispersive to dispersive transport occurs [22,30]. The microscopic transport parameters of Eq. (2) was extracted from slope of the logarithm of zero field mobility versus  $1/T^2$  plot at the higher temperature range (310–160 K), and  $\sigma_1 = 70 \text{ meV}$  and  $\mu_0 = 0.011 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was calculated. Using these values,  $T_c = 170 \text{ K}$  is calculated according to the following equation [1]:

$$\left(\frac{\sigma}{kT_c}\right)^2 = 44.8 + 6.7 \log d, \quad (3)$$

where  $d$  is a parameter related to the thickness in cm units. Since the temperature dependence of Eq. (2) holds valid only when the charge carriers reached quasi-equilibrium, deviations from the  $\log \mu$  versus  $1/T^2$  dependence below the non-dispersive to dispersive transition temperature ( $T_c$ ) is expected. The occurrence of non-dispersive to dispersive transition is also manifested in the change of the shape of the photocurrent transient: below  $T_c$  the recorded photocurrent transients are rather dispersive, meanwhile at higher temperatures they typically feature a short plateau indicative of non-dispersive transport (see Fig. 2a, b).

The slope of the field dependence ( $d \log \mu / d E^{1/2}$ ) against the energetic disorder parameter  $(\sigma/k_B T)^2$  is plotted in the inset of Fig. 4. The slope is decreasing continuously with increasing temperature, crosses 0 at  $(\sigma/k_B T)^2 = 11.6$  ( $T = 239 \text{ K}$ ), and becomes negative at high temperatures. Using  $\sigma = 70 \text{ meV}$ , the value of spatial disorder parameter  $\Sigma = 3.4$ , and the constant  $C = 1.53 \times 10^{-4} (\text{cm V}^{-2})^{1/2}$  was calculated in the same higher temperature region (310–160 K). The small value of  $\sigma = 70 \text{ meV}$  together with large  $\Sigma = 3.4$  is held responsible for the negative field dependence of mobility, which is in accordance with previous observations in disordered organic solids.

The large value of spatial disorder may be related to the complex morphology of the several micrometer thick P3HT films prepared by the doctor blade technique. Initial results show that the films are semicrystalline, in which ordered regions are embedded in an amorphous matrix. In such cases, one expects that the mobility in the ordered regions is higher due to the better interchain electronic coupling creating favorable paths as compared to the amorphous regions [31]. The photogenerated charge carriers at higher temperatures but low electric fields can reach the opposite electrode by following such favorable paths (diffusion), however, at high electric fields, paths whose direction is not aligned with the direction of external electric field will be

diminished resulting in lower drift mobility. A more detailed study, including the effect of morphology of the films on the TOF mobility studies will be published.

#### 4. Conclusions

Negative field dependence of mobility was clearly observed in a purified, highly regioregular conjugated polymer poly(3-hexylthiophene). The unusually low transition temperature  $T_0$ , is attributed to the small energetic but large spatial disorder. The data is analyzed within a framework of Gill's formula as well as the disorder formalism, and reasonable agreement is obtained for both models at higher temperatures. Deviations from the prediction of both theoretical models are observed at lower temperatures, which may be attributed to the transition from non-dispersive to dispersive nature of the transport at lower temperatures.

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