Negative Mobility Dependence on Electric Field in Poly(3-alkylthiophene)s

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We have measured dependencies of conductivity and carrier mobility on the temperature and applied electric field in the samples of regioregular poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) by the Charge Extraction by Linearly Increasing Voltage (CELIV) method. The samples were produced by the drop-casting and spin-coating methods on the Indium-Tin-Oxide substrate and provided with Al contact at the top. We had observed the "negative" mobility dependence at low electric fields, i.e., the mobility used to decrease with increasing electric field. To our knowledge this is the first time, when such behaviour was confirmed by the CELIV method in P3OT samples, though it was reported earlier by the Time-of-Flight (TOF) in other disordered materials.
Keywords: polythiophenes, conductivity, carrier mobility, CELIV.

INTRODUCTION

In organic device development and engineering carrier transport properties are of primary importance as they are directly related with key material parameters giving device efficiency and functionality. Charge carrier mobility is the main factor limiting carrier transport in disordered polymer materials. It can be manipulated not only by material structure engineering, but, in particular material, also by electric field and temperature. Therefore the investigation of mobility behaviour is not only important, but the challenging task as well. First of all this is because of very low mobility values which are by many orders of magnitude less than in crystalline inorganic semiconductors. Therefore measurement of such low values inevitably causes uncertainties, related not only to the transport character itself, e.g., if it is dispersive or not, but to the experimental procedure as well. The classical Time-of-Flight (TOF) mobility measurement method [1] was many times proved to have sensitivity problems in dispersive materials. Moreover it faces the fundamental limitations in high conductivity materials, originating from the requirement that the dielectric relaxation time τ_σ must be longer than the carrier transit time t_{tr}. Only if this condition is fulfilled electric field in a sample remains constant over the sample thickness (otherwise it can be redistributed by equilibrium charge carriers in time intervals shorter that t_{tr}), and carrier number does not decrease during their transit through the sample because of recombination. It was demonstrated in [2] that ignoring this fundamental limitation may cause an erroneous overestimation of the mobility values measured by TOF. The recently proposed Charge Extraction by Linearly Increasing Voltage (CELIV) method [3, 4] was argued to be free of these limitations, and is therefore much better suitable for the investigation of the high conductivity materials, in which enough carriers exist to create a measurable current upon extraction. Moreover CELIV enables simultaneous evalua-

tion of the concentration of majority equilibrium charge carriers [5]. If there aren't enough charge carriers to be extracted, they can be generated by light pulses prior to the application of the extracting voltage pulses. This modification was called Photo-CELIV [6]. On the other hand, if high resistivity material is insensitive to light, carriers can be injected in the dark electrically by a rectangular voltage pulse. This mobility measurement modification was called Dark Injection Space-Charge-Limited-Current (DI SPLC) transient method [7]. Also mobility can be evaluated from the I-V measurements in the space-charge-limited-current case [7] or extracted from the transfer characteristics of a field effect transistors (FET) [8, 9].

If experimental possibilities allow one to compare mobility behaviour measured by different methods, usually results coincide within errors. So, e.g., in [10] mobility behaviour in spiro-MeOTAD was compared by I-V, DI SCLC and TOF methods, and a nice coincidence was obtained. In contrast, in [2] authors have investigated regioregular poly(3-octylthiophene) (RR-P3OT) by TOF and CELIV, and clear differences were found in the mobility behaviour by both methods. TOF indicated the so-called "negative" mobility dependence on applied low electric field strength, i.e., the mobility used to decrease with increasing electric field. Meanwhile CELIV gave the usual mobility increase by increasing field. Therefore a conclusion was drawn that the "negative" dependence, instead of being material property, can be caused by experimental errors, i.e., neglect of the limitations of TOF. The "negative" dependence was observed in regioregular P3HT by TOF in [11] and attributed to the significant spatial disorder of material. In [12] comparative study of regioregular P3HT was performed by CELIV and TOF, and this time both results confirmed the "negative" behaviour.

Therefore such "negative" mobility dependence still appears to be ambiguous, because it was confirmed by CELIV in only one type of material, namely, regioregular P3HT purchased from Rieke Metals, Inc. and H. C. Starck GmbH [12]. The samples were prepared by the doctor-

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blade technique. Therefore in this investigation we test by the CELIV method both regioregular P3HT and regioregular P3OT purchased from different supplier and prepared by different method.

SAMPLES AND EXPERIMENT

Samples of the regioregular poly(3-hexylthiophene) (P3HT) and regioregular poly(3-octylthiophene) (P3OT) samples were investigated by the Charge Extraction by Linearly Increasing Voltage (CELIV) method. The polymer structures are presented in Fig. 1. The materials were purchased from Aldrich and were used without further purification. The samples were produced from chloroform solution (3 wt % – 6 wt %), by the drop-casting and spin-coating methods on the glass plate, coated by Indium-Tin-Oxide (ITO). The Al contact was evaporated at the top in high vacuum. The thicknesses of the samples ranged from 620 nm to ≥ 1 μm.
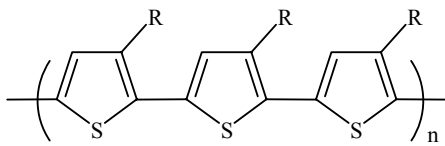
Fig. 1. Structures of the investigated polymers: regio-regular poly(3-hexylthiophene) ($R = C_6H_{13}$) and regioregular poly(3-octylthiophene) ($R = C_8H_{17}$)

The principles of the original CELIV method are given in Refs. [3, 4]. In CELIV, a carrier extraction from the sample is assured by applying a triangular voltage pulse with a constant increase rate. To extract carriers at least one of the contacts should be blocking and voltage of the reverse polarity should be applied. The obtained CELIV traces, as, e.g., presented in Fig. 2, demonstrate characteristic maxima, when the electric field in the sample becomes strong enough to extract most of the carriers. From these traces mobility was calculated as [3, 4]:

$$\mu = \frac{2d^2}{3At_{max}^2 \left[1 + 0.36 \frac{\Delta j}{j(0)}\right]}, \quad (1)$$

and sample conductivity could be found as:

$$\sigma = \frac{3\varepsilon\varepsilon_0 \Delta j}{2t_{max} j(0)}. \quad (2)$$

Here A is the voltage increase rate, t_{max} is the time elapsed after the application of the pulse, when characteristic maximum is observed, d is the sample thickness, $j(0)$ is the plateau value corresponding to the capacitive displacement current of the sample and Δj is the height of the current spike. In Eq. (1) the electric field re-distribution effect during charge extraction is taken into account. This makes mobility measurements in conductive samples with relatively high carrier concentrations reliable.

RESULTS AND DISCUSSION

In Fig. 2 examples of the CELIV traces are presented in the P3HT sample prepared by the drop-casting method. Clear differences are seen at different experiment temperatures in Figs. 2, a, and 2, b). At higher temperature
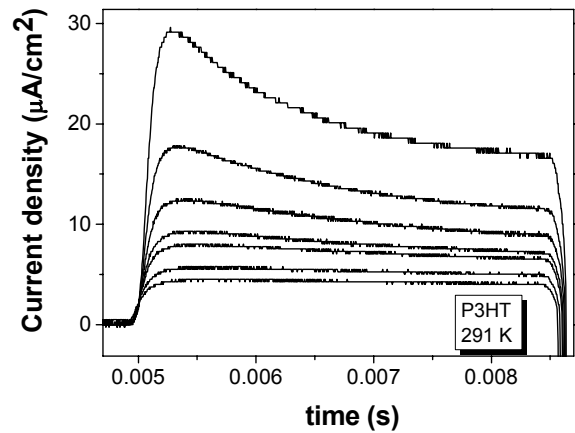
a
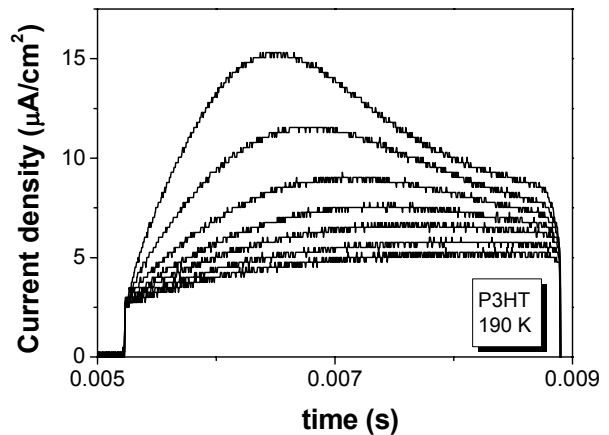
b

Fig. 2. Examples of the CELIV traces observed at different voltage increase rates in the P3HT sample prepared by the drop-casting method. The presented oscillogrammes were obtained at different temperatures: a – 291 K, b – 190 K

the maximum position t_{max} does not move with increasing voltage increase rates A. Therefore, according to Eq. (1), mobility should decrease. In contrast, at 190 K a clear shift of the maxima towards shorter times is observed with the increasing voltage growth rate. The calculated mobility dependencies on the electric field strength at different temperatures are presented in Fig. 3. Similar dependencies were obtained for the P3OT samples, indepeending on the polymer deposition technique (Fig. 4). To our knowledge this is the first time, when the "negative" mobility behaviour was confirmed by the CELIV method in P3OT, though in P3HT it was observed earlier [12]. By TOF similar effect was experimentally confirmed many times in different disordered materials as, e.g., molecularly doped polymers, molecular glasses, etc. It is necessary to note that we had confirmed such behaviour by changing voltage increase rate not only by varying the voltage pulse height and keeping a pulse duration constant, but also by varying the pulse duration and keeping its height constant.

By interpreting experimental results usually the problem arises that no theory adequately explains various transport phenomena in polymers, particularly the electric field and temperature dependencies of drift mobility [13 – 18]. The most frequently used approaches refer to hopping transport character in disordered organic solids and are

based either on a modified Poole-Frenkel (PF) model [14] or a Gaussian disorder model (GDM) [19]. The latter was later extended to include correlation effects [20 – 22]. In the Poole-Frenkel (PF) model the mobility can be described as a field and temperature assisted detrapping process of a carrier from the Coulomb potential of a charged trap. The mobility is given by [14]:

$$\mu = \mu_0 \exp\left[-\frac{E_0 - \alpha F^{1/2}}{kT_{eff}}\right] \quad (3)$$

with

$$1/T_{eff} = 1/T - 1/T_R , \quad (4)$$

where F is an electric field strength, E_0 is an activation energy of the carrier transport at zero electric field, and T_R is the empirical reference temperature at which mobility is supposed to be known. Nevertheless this model, though being able to describe both mobility increase with electric field strength as well as its decrease, does not provide any physical clues about the nature of the processes.
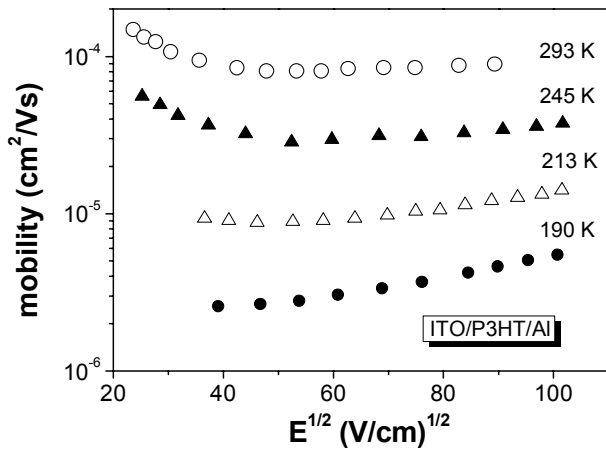
Fig. 3. Mobility dependencies on the applied electric field strength in the P3HT sample prepared by the drop-casting method at different temperatures as indicated on the Figure
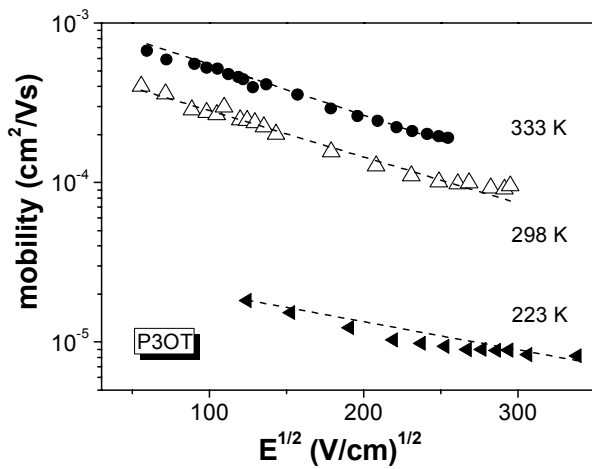
Fig. 4. Mobility dependencies on the applied electric field strength in the P3OT sample at different temperatures as indicated on the Figure. The dashed lines represent fitting curves calculated according to the Gaussian disorder model (Eq. 5)

In the GDM model charge transport in disordered organic conductors is supposed to proceed by means of hopping in a Gaussian site-energy distribution. This density of states (DOS) reflects the energetic spread in the charge transporting levels of chain segments due to fluctuation in conjugation lengths and structural disorder. Within the Gaussian disorder model the mobility is given by [19]:

$$\mu(F,T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp\left\{C\left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]\sqrt{F}\right\}. \quad (5)$$

This equation was derived from Monte-Carlo simulations of the hopping processes of charge carriers in a material with energetic (σ) and positional disorder (Σ) described be Gaussian distribution functions. μ_∞ is the high temperature limit of the mobility and C is a specific parameter that is obtained from the simulations as $C = 2.9 \times 10^{-4}$ (cm/V)$^{1/2}$. In this case a difference between the mobility decrease and increase with electric field, as implied by Eq. (5), can be attributed to the change of the influence of energetic and positional disorder. Mathematically the "negative" dependence can be observed when the spatial disorder parameter Σ becomes greater than the energetic disorder parameter σ/kT. The underlying physics can be understood by taking into account the random hopping nature of the transport. One can suppose that at low electric fields carriers, jumping over the random network of the energetically unfavourable states, might be able to find energetically more expedient route when they are not forced to jump in a direction determined by the external electric field. In material with the great spatial disorder such possibility could diminish with increasing electric field strength, when carriers are forced to make difficult jumps only along the electric field lines. Thus, at lower field values, mobility will decrease. When the field increases significantly, it "energizes" jumps even over the energetically separated states, leading to the mobility growth. The similar explanation was originally proposed to explain negative differential hopping conductivity in doped inorganic semiconductors [23 – 25].

Behaviours approximated by both these empirical equations has been observed in many materials. Experimentally, the main difference between both models is the temperature dependence. A consequence of hopping in a Gaussian DOS is the non-Arrhenius behaviour of the mobility [19]. Nevertheless within the limited temperature range it is practically impossible to discriminate between both dependencies. Furthermore, the simulations of the GDM reproduced the $\ln(\mu) \sim \sqrt{F}$ dependence only in a narrow field range at high fields (10^8 V/m) [18]. Apart from that, both models require many parameters that can be used to fit the experimental data, depending on the preferred model. This causes that actually both approaches can be applied to fit experimental results, basing on the chosen physical mechanism, that in many cases is not known *a priori* [26]. Therefore there are rare examples where a clear distinction between the two models has been possible [27]. Nevertheless the GDM model clearer distinguishes between the different types of mobility behaviour. Therefore it was used to fit the experimental data of P3OT, presented in Fig. 4. We have used the same

fitting parameters for all curves in Fig. 4, just the temperature was varied. The following fitting values were obtained: $\mu_\infty = 2.20 \times 10^{-2}$ cm²/Vs, $\Sigma = 5$, $C = 4.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.074$ eV. Meanwhile to fit the "negative" mobility part in P3HT sample in Fig. 3 these values were as follows $\mu_\infty = 5.30 \times 10^{-3}$ cm²/Vs, $\Sigma = 9.5$, $C = 6.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.058$ eV. They are very similar to that reported in, e.g., [12], except the relatively high value of Σ. As this parameter just merely qualitatively describes the spatial disorder, this might be an indication of the higher inhomogeneity of the P3HT sample as compared to the P3OT sample. The difference between the energetic disorder parameters σ in both samples should be pointed out too. This value is higher in the P3OT sample, probably relating to the longer side chains (C$_8$H$_{17}$) in this material as compared to P3HT (C$_6$H$_{13}$). We had also fitted the growing mobility dependence of the last sample by both models: GDM and PF. The GDM model gave the following fitting values: $\mu_\infty = 1.00 \times 10^{-3}$ cm²/Vs, $\Sigma = 0.5$, $C = 5.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.061$ eV. Reasonably the value of Σ was significantly lower in this case, indicating the prevailing influence of the energetic disorder at higher electric fields. Decrease of the fitting parameter μ_∞ reflects the obvious fact that the intersection of the approximation of "negative" mobility part with y-axis at zero electric field will always lay higher than that of the similar approximation of "normal" part. Meanwhile the values of σ coincide nice within the range of experimental errors. The best fit according to the PF model was obtained with the following parameters: $\mu_0 = 2.70 \times 10^{-3}$ cm²/Vs, $E_0 = 0.165$ eV, $T_r = 700$ K, $\alpha = 2.50 \times 10^{-4}$ eV(cm/V)$^{1/2}$. The last value coincides well with the experimental result of [11] and with the theoretical evaluation presented in [28].

We had also investigated temperature dependencies of mobility and conductivity in both materials as it is presented in Fig. 5 as an example. Characteristically, in all samples relative changes of mobility and conductivity are the same within the range of experimental errors as it can be seen from this Figure. This evidences that conductivity grows due to the thermally activated mobility, and not due to the change of carrier number, as it could be expected in case of their thermal generation. From the obtained results it is impossible to determine which of the discussed mobility models can be applied, because both mobility representations *versus* reciprocal temperature (inset of Fig. 5) and its squared values do not deviate much from the straight lines. Thus, to compare also the effective activation energy values E_0 given by the PF model, we had calculated it from the slopes of mobility dependencies on reciprocal temperature in both materials. In P3HT this effective activation energy was similar to that already evaluated above, *i.e.*, it ranged from about 0.14 eV to 0.17 eV, and in P3OT samples we found values of about (0.24 – 0.26) eV. Such difference qualitatively coincides with the inequality of the values of the energetic disorder parameters σ also reported above.

Nevertheless the "negative" dependence was observed only in the drop-casted P3HT sample. In a spin coated one we have just obtained the usual mobility increase with electric field as it presented in Fig. 6. The evaluated PF mobility model parameters were as follows: $\mu_0 = 5.00 \times 10^{-3}$

cm²/Vs, $E_0 = 0.21$ eV, $T_r = 600$ K, $\alpha = 4.00 \times 10^{-4}$ eV(cm/V)$^{1/2}$. The fitting parameters of the GDM model were the following: $\mu_\infty = 3.00 \times 10^{-3}$ cm²/Vs, $\Sigma = 0.5$, $C = 9.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.071$ eV. Both these sets indicate the higher effective activation energy value in the PF model and the bigger energetic disorder in the GDM model. It can be assumed that namely this higher energetic values mask appearance of the effects associated with spatial disorder. Indeed, by the spin-coating more homogeneous samples could be produced than by drop casting. This is in agreement with the conclusion derived also in [11, 12].
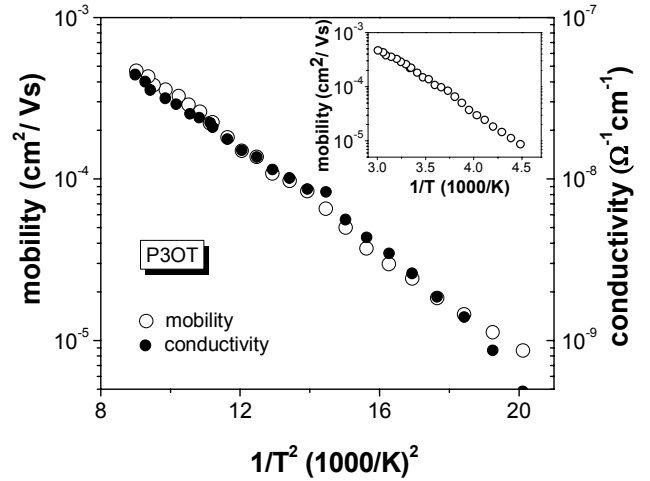

Fig. 5. Dependencies of the mobility and conductivity on temperature in the P3OT sample in different scaling
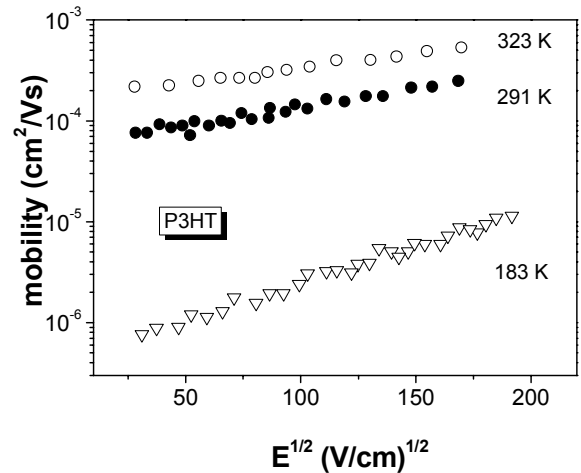

Fig. 6. Mobility dependencies on the applied electric field strength in the P3HT sample prepared by the spin-coating method at different temperatures as indicated on the Figure

SUMMARY AND CONCLUSIONS

We have investigated carrier mobility behaviour depending on the temperature and applied electric field strength in the regioregular poly(3-hexylthiophene) (P3HT) and regioregular poly(3-octylthiophene) (P3OT) samples by the Charge Extraction by Linearly Increasing Voltage (CELIV) method. The samples were produced by the drop-casting and spin-coating methods on the glass substrate, coated by Indium-Tin-Oxide (ITO). Aluminium contacts were evaporated on the top.

We had observed the "negative" mobility dependence at low electric fields in P3OT samples produced both by the the drop-casting and spin coating, and P3HT samples produced by the drop-casting, i.e., in these samples the mobility used to increase with decreasing electric field strength. To our knowledge this is the first time, when such behaviour was confirmed by the CELIV method in P3OT polymer, though it was reported many times by the Time-of-Flight (TOF) method in different disordered materials. Data were analysed within the Poole-Frenkel and Gaussian disorder models. Within the framework of the latter model the "negative" mobility dependence was explained by the relatively high spatial disorder of materials. On the other hand, both models pointed out the higher effective thermal activation energy and the higher energetic disorder of the P3OT samples as compared to P3HT. This could be due to the longer side chains of P3OT polymer. In the P3HT samples produced by the spin-coating, the "negative" mobility behaviour was not observed. The possible reason of different behaviour of the P3HT samples prepared in different ways it might be that by the drop casting more inhomogeneous samples are produced, as compared to the spin coating method.

Acknowledgments

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