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Negative mobility dependence in polythiophenes P3OT and P3HT evidenced by the charge extraction by linearly increasing voltage method*

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Abstract. We investigated mobility in the regioregular poly(3-octylthiophene) (RR-P3OT) and regioregular poly(3-hexylthiophene) (RR-P3HT) by the Charge Extraction by Linearly Increasing Voltage method (CELIV). The samples were produced by the drop-casting and spin-coating methods on the Indium-Tin-Oxide substrate and provided with Al contacts. In both materials we had observed the "negative" mobility dependence at low electric fields, i.e., the mobility used to decrease with increasing electric field (in P3HT, this was only observed here in the drop-casted sample). Such behaviour was never observed by CELIV in P3OT before. Data were analysed within the Poole-Frenkel and Gaussian disorder models. The higher energetic disorder parameters were obtained in P3OT as compared to P3HT. This could be related to the longer side-chains of P3OT. We had demonstrated that in both materials with increasing temperature conductivity grows due to the thermally activated mobility.

PACS. 72.80.Le Polymers; organic compounds (including organic semiconductors) – 81.40.Rs Electrical and magnetic properties (related to treatment conditions)

1 Introduction

In organic electronics carrier transport properties are of primary importance as they are directly related with macroscopic material parameters determining device functionality. Carrier mobility is the main factor limiting charge transport in highly disordered polymers. Low mobilities require different experimental approaches than in crystalline inorganic semiconductors and inevitably cause uncertainties, related not only to the transport itself but to the experimental procedure as well. The classical Time-of-Flight (TOF) method [1], though informative and straightforward, has sensitivity problems in dispersive materials. It also faces the fundamental limitations in conductive materials, originating from the requirement that the dielectric relaxation time τ_σ must exceed the carrier transit time t_{tr} in order to assure the constant electric field over the sample and to retain carrier number unchanged during their transit. Disregard of this requirement may cause an overestimation of the mobility measured by TOF [2]. The recent Charge Extraction by Linearly Increasing Voltage (CELIV) method was argued to be free of these limitations and better suitable for the conductive materials [3,4]. Moreover CELIV enables simultaneous evaluation of the concentration of majority equilibrium carriers [5]. If there aren't enough carriers to be extracted, they can be generated by light pulses in Photo-CELIV [6]. On the other hand, if high resistivity material is insensitive to light, carriers can be injected by a rectangular voltage pulse using the Dark Injection Space-Charge-Limited-Current (DI SPLC) transient method [7]. Mobility can also be evaluated from the I–V measurements in the SPLC case [7] or extracted from the transfer characteristics of FETs [8,9].

If mobility can be evaluated by different methods, one expects obtaining coinciding results, as, e.g., in [10], where mobility in spiro-MeOTAD was compared by I–V, DI SCLC and TOF. In contrast, in [2] clear discrepancies were found in P3OT by TOF and CELIV. TOF indicated the so-called "negative" mobility dependence at low electric fields, i.e., the mobility used to decrease with increasing field. Meanwhile CELIV gave the usual mobility growth. Therefore a conclusion was drawn that the "negative" dependence, instead of being material property, can be caused by neglect of the limitations of TOF. Conversely, the "negative" dependence was observed in P3HT by TOF in [11] and attributed to the spatial

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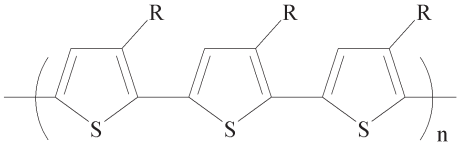

Fig. 1. Structures of poly(3-hexylthiophene) (R = C_6H_{13}) and poly(3-octylthiophene) (R = C_8H_{17}).

disorder of material. In [12] a comparative study of P3HT was performed by CELIV and TOF, and both methods confirmed the "negative" behaviour.

Therefore such "negative" mobility dependence still appears to be ambiguous, because it was confirmed by CELIV in only one material, RR-P3HT, from Rieke Metals, Inc. and H. C. Starck GmbH [12]. The samples were prepared by the doctor-blade technique. Therefore in this investigation we test by the CELIV method both RR-P3HT and RR-P3OT purchased from different supplier (Aldrich) and prepared by different methods.

2 Samples and experiment

Samples of RR-P3OT and RR-P3HT (Fig. 1) were investigated by the CELIV method. The materials were purchased from Aldrich and were used without further purification. The samples with thicknesses from 620 nm up to $\geqslant 1$ μm were produced by the drop-casting and spin-coating methods on the Indium-Tin-Oxide (ITO) substrate. The Al contacts were evaporated on the top.

The mobility and conductivity can be found from the maximum position $t_{\max}$ of the CELIV signal [3,4]:

$$\mu = \frac{2d^2}{3At_{\max}^2\left[1+0.36\frac{\Delta j}{j(0)}\right]}, \quad \sigma = \frac{3\varepsilon\varepsilon_0\Delta j}{2t_{\max}j(0)}. \qquad (1)$$

Here A is the voltage growth rate, d is the sample thickness, $j(0)$ is the capacitive displacement current and Δj is the height of the current spike. The voltage growth rate was varied from about 70 V/s up to 10000 V/s depending on the sample and experimental conditions either by changing pulse amplitude at the fixed width and by changing pulse duration at the fixed amplitude. Both methods gave coinciding results for all investigated samples. The precise maximum positions were determined by differentiating the current kinetic curves. The values of $j(0)$ were found experimentally at higher voltage growth rates where only sharp "rectangular" jumps caused by the capacitive displacement current could be seen. In this way experimental errors could be kept below 10 to 20 per cent (i.e., comparable to the dimensions of the data points on the plots).

3 Results and discussion

In Figure 2 examples of the CELIV traces are presented in the P3HT sample prepared by the drop-casting. At

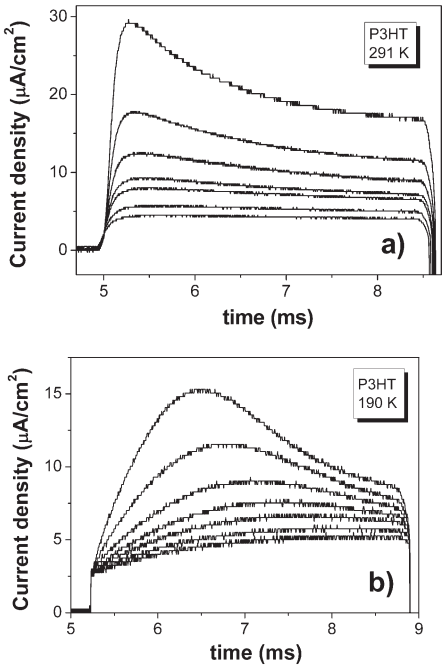

Fig. 2. Examples of the CELIV traces measured at different voltage increase rate in the P3HT sample prepared by the drop-casting at different temperatures: (a) 291 K, (b) 190 K.

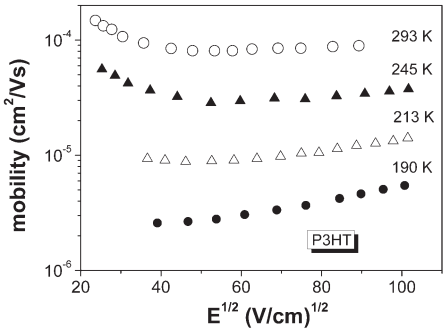

Fig. 3. Mobility dependencies on the applied electric field at different temperatures in the P3HT sample prepared by the drop-casting method.

the room temperature the maximum position $t_{\max}$ does not move with increasing A, indicating decreasing mobility (see Eq. (1)). In contrast, at 190 K the maximum shifts towards shorter times with the increasing voltage growth rate. The mobility dependencies on the electric field for P3HT and P3OT are presented in Figures 3, 4. To our knowledge this is the first time, when the "negative" mobility behaviour was confirmed by CELIV in P3OT, though in P3HT it was observed before [12]. By TOF similar effect was demonstrated many times in different disordered materials, e.g., molecularly doped polymers, molecular glasses, etc.

Characteristically, no theory adequately explains various transport phenomena in polymers, particularly the electric field and temperature dependencies of mobility. The most frequently used approaches refer to hopping transport character and are based either on a

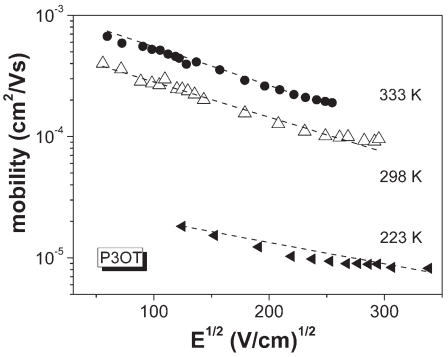

Fig. 4. Mobility dependencies on the applied electric field in the P3OT sample at different temperatures. The dashed lines represent fitting according to GDM.

Poole-Frenkel (PF) model [13] or a Gaussian disorder model (GDM) [14]. The latter was later extended to include correlation effects [15–17]. In the 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 [13]:

$$\mu = \mu_0 \exp\left[-\frac{E_0 - \alpha F^{1/2}}{kT_{eff}}\right] \quad \text{with} \quad 1/T_{eff} = 1/T - 1/T_R, \tag{2}$$

here F is an electric field, E_0 is an activation energy of the carrier transport at zero field, and T_R is the empirical reference temperature at which mobility is supposed to be known. This model, though being able to describe both mobility increase and decrease with electric field, does not provide any physical clues about the nature of the processes.

In GDM transport is supposed to proceed by means of hopping in a Gaussian site-energy distribution, caused by fluctuation in conjugation lengths and structural disorder [14]:

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

Equation (3) was derived from Monte-Carlo simulations of the hopping processes in a material with energetic (σ) and positional disorder (Σ). μ_∞ is the high temperature limit of the mobility and C is a parameter obtained from the simulations: $C = 2.9 \times 10^{-4}$ (cm/V)$^{1/2}$. In GDM the "negative" dependence takes place when the spatial disorder parameter Σ exceeds the energetic disorder parameter σ/kT. 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 routes when they are not forced to jump in a direction of the external field. If the spatial disorder is big such possibility could diminish with increasing field, when carriers are forced to make difficult jumps along the electric field lines. Thus, mobility will decrease. When the field increases significantly, it "energizes" jumps even over the energetically separated states, resulting in mobility growth. Previously in a similar manner the negative differential hopping conductivity in doped inorganic semiconductors was explained [18–20].

Experimentally, the main difference between both models is their temperature dependence. Nevertheless within the limited temperature range it is practically impossible to discriminate between both dependencies. Furthermore, the simulations of GDM reproduced the $\ln(\mu) \sim \sqrt{F}$ dependence only in a narrow field range at high fields (10^8 V/m) [21]. Moreover, as both approaches require many fitting parameters, they can be applied to fit experimental data, basing on the physical mechanism that in many cases is not known a priori [22]. Therefore there are rare examples where a clear distinction between the two models has been possible [23]. Nevertheless GDM clearer points up the underlying physics, therefore it was used to fit the data of P3OT in Figure 4. We had varied just the temperature, keeping other parameters unchanged: $\mu_\infty = 2.20 \times 10^{-2}$ cm^2/Vs, $\Sigma = 5$, $C = 4.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.074$ eV. To fit the "negative" part in P3HT (Fig. 3) these values were as follows $\mu_\infty = 5.30 \times 10^{-3}$ cm^2/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. This might be an indicator of the higher inhomogeneity of the P3HT sample as compared to the P3OT sample. The energetic disorder parameter σ is higher in P3OT, probably relating to the longer side chains (C_8H_{17}) in this material as compared to P3HT (C_6H_{13}). Fitting by GDM of the growing part in Figure 3, where mobility increases with increasing electric field, resulted in the following values: $\mu_\infty = 1.00 \times 10^{-3}$ cm^2/Vs, $\Sigma = 0.5$, $C = 5.00 \times 10^{-4}$ (cm/V)$^{1/2}$, $\sigma = 0.061$ eV. Reasonably the value of Σ was lower in this case, indicating the prevailing influence of the energetic disorder at higher fields. Decrease of the parameter μ_∞ reflects the obvious fact that the intersection of the approximation of the "negative" mobility part with y-axis at zero electric field will always lay higher than that of the similar approximation of the "normal" part. Meanwhile σ values coincide nicely within experimental errors. The best fit of the PF model was obtained with the following parameters: $\mu_0 = 2.70 \times 10^{-3}$ cm^2/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 in [24].

We had also investigated temperature dependencies of mobility and conductivity in both materials (Fig. 5). Characteristically, in all samples relative changes of mobility and conductivity are the same within the range of errors. This evidences that conductivity grows due to the thermally activated mobility, and not due to the change of carrier number, as it would be in case of their thermal generation. It is impossible to determine which mobility model can be applied, because both mobility plots versus $1/T$ (inset of Fig. 5) and $1/T^2$ do not deviate much from the straight lines. Thus, we had calculated also the effective activation energy values E_0 in the PF model. In

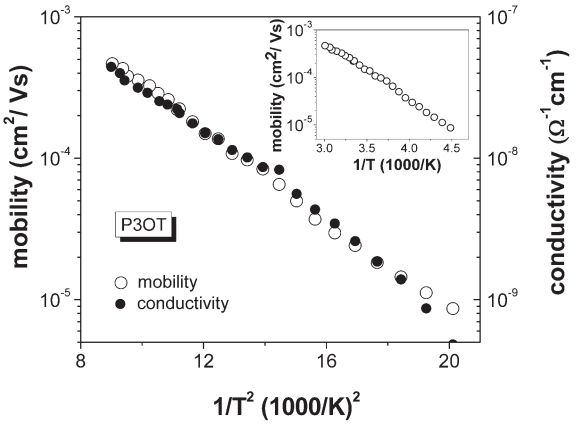

Fig. 5. Dependencies of the mobility and conductivity on temperature in the P3OT sample measured at 2×10^4 V/cm field strength.

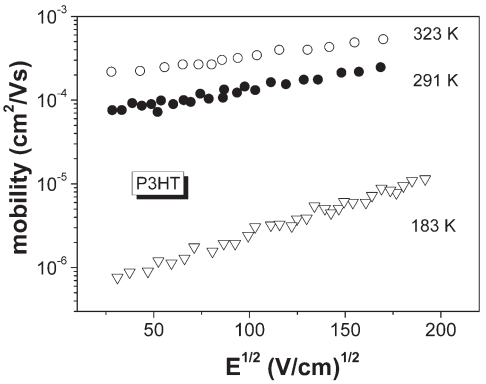

Fig. 6. Mobility dependencies on the applied electric field at different temperatures in the P3HT sample prepared by the spin-coating method.

P3HT E_0 was similar to that presented above: it ranged from 0.14 to 0.17 eV; in P3OT it was about 0.24–0.26 eV. These values qualitatively reflect difference of the energetic disorder parameters σ reported above.

The "negative" dependence was observed only in the drop-casted P3HT sample. In the spin coated one we have obtained the usual mobility growth (Fig. 6). The evaluated PF model parameters were as follows: $\mu_0 = 5.00 \times 10^{-3}$ cm^2/Vs, $E_0 = 0.21$ eV, $T_r = 600$ K, $\alpha = 4.00 \times 10^{-4}$ eV(cm/V)$^{1/2}$. The GDM parameters were the following: $\mu_\infty = 3.00 \times 10^{-3}$ cm^2/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 GDM. It can be assumed that namely the higher energetic disorder masks appearance of the spatial disorder effects. Indeed, by the spin-coating more homogeneous samples could be produced than by the drop casting. This is in agreement with the conclusion derived also in [11,12].

4 Summary and conclusions

We have investigated dependencies of the mobility and conductivity on the applied electric field and temperature in the RR-P3OT and RR-P3HT by the CELIV method. The samples were produced by the drop-casting and spin-coating methods on the ITO substrates and provided with Al contacts.

At low electric fields we had observed the "negative" mobility dependence in P3OT samples and P3HT samples produced by the drop-casting, i.e., in these samples the mobility used to increase with decreasing electric field. Though such behaviour was observed many times by TOF in different disordered materials, to our knowledge, it was not reported by the CELIV method in P3OT before. The Poole-Frenkel and Gaussian disorder models were applied for the analysis. Within the framework of the Gaussian disorder model the "negative" mobility dependence was explained by the relatively high spatial disorder of materials. On the other hand, the higher effective thermal activation energy and the higher energetic disorder of P3OT as compared to P3HT were pointed out by both models. This could be due to the longer side chains of P3OT. 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 might be the better homogeneity of the samples produced by the spin coating as compared to the drop casting method.

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