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Features of Charge Carrier Concentration and Mobility in π-Conjugated Polymers

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Summary: We show the possibilities of experimental investigation of charge carrier mobility and concentration features by extraction methods of equilibrium, photoexcited and injected charge carriers in π-conjugated polymers, where, due to relatively high conductivity, the classic time-of-flight method is inappropriate.

Keywords: charge carrier extraction; conjugated polymers; hole concentration; hole mobility; thin films

Introduction

π-Conjugated polymers are used extensively in light-emitting, field-effect and other molecular electronic devices. The relatively low charge carrier mobility of these polymers causes that the conventional time-of-flight (TOF) method is used for investigation of charge carrier transport features. However, this method can be applied if Eq.1 is fulfilled

$$t_{\mathrm{tr}} = \frac{d^2}{\mu U} << \tau_\sigma = \varepsilon\varepsilon_0 / \sigma \tag{1}$$

where μ is charge carrier mobility, t_{tr} is duration of charge carrier drift through the interelectrode distance d, U is voltage applied on sample electrodes, τ_σ is dielectric relaxation time, ε is dielectric permittivity, and σ is the bulk conductivity of sample. The latter condition means that in the bulk of sample the amount of equilibrium charge (ep_0d) must be less than the amount of charge on sample electrode ($\varepsilon\varepsilon_0U/d$). In opposite case, after voltage has been applied on sample electrodes, the amount of equilibrium charge is sufficient that the electric field inside of sample, during a time shorter than the charge carrier transit time, will be redistributed. In relatively high-conductivity polymers, the condition that $t_{\mathrm{tr}} << \tau_\sigma$ can be achieved by reducing thickness of samples, i.e. by measuring thin layers. However, in such a case, the absorption depth of even UV light is comparable to the

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thickness of sample. Thus, the bulk charge carrier photogeneration prevails. Moreover, the high capacitance of thin layers causes that only the integral mode of TOF photocurrent transients may be used for investigations. Compared with the current mode in the case of surface charge carrier photogeneration, the shape of photocurrent transient of integral TOF mode is not so expressive, causing very often erroneous interpretation.

In this paper we would like to demonstrate the possibilities of investigation of π-conjugated polymers using charge carrier extraction by the linearly increasing voltage (CELIV) method, for which condition (1) is not necessary, and to discuss errors, which may appear using TOF method for investigation of charge carrier mobility when this condition is ignored.

Polymers and equipment

The π-conjugated polymers used were: poly(*p*-phenylenevinylene) (PPV), regioregular poly(3-hexylthiophene) (RRPHT), regiorandom poly(3-hexylthiophene) (RRaPHT), regioregular poly(3-octylthiophene) (RRPOT; Sigma Aldrich), regioregular poly(3-dodecylthiophene) (RRPDDT), and regioregular poly(3-alkylthiophene) (RRPAT). All layers have been prepared by spin coating or solution casting. The polymer was dissolved in chloroform in a concentration of 10 mg/ml. The solutions were filtered through a 0.20 μm filter before the solution was cast onto pre-patterned ITO-covered glass substrates (Planar International). Finally a 30-nm (semitransparent) aluminium top electrode was evaporated under a pressure of 1 Pa. The films were made in air, but stored and measured in a closed-cycle cryostat (Oxford CCC1104) under vacuum to make temperature measurements possible.

The experimental setup for the CELIV measurement was made up; a variable pulse generator (Stanford DS345) and a memory oscilloscope (Tektronix TDS680B) were used to record the extraction currents. The only restriction imposed by the experimental setup is that at least one contact of the sample should be (partially) blocking. The voltage rise speed, A, used in these experiments, ranged between 10 and 10^6 V/s. For the TOF measurements, a nitrogen laser (Oriel), with a pulse width of 7 ns, energy 3.55 eV and energy per pulse of 500 μJ was used together with the pulse generator and a delay function generator (Stanford DG 535) to ensure a proper delay time between voltage and light pulses. TOF was measured with 50 Ω input impedance on the oscilloscope.

Extraction of equilibrium charge carriers

The linearly increasing voltage pulse applied on sandwich-type sample electrodes, one of which is blocking, raises a current transient, the shape of which is presented in Fig. 1.

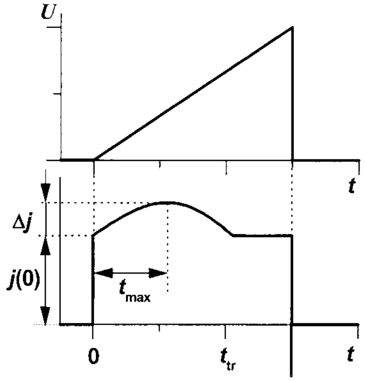

Fig. 1. Schematic view of CELIV method.

From the very initial step of this current $j(0)$, the interelectrode distance d or the dielectric permittivity $\varepsilon\varepsilon_0$ may be estimated:

$$\frac{\varepsilon\varepsilon_0}{d} = \frac{j(0)}{A}. \tag{2}$$

From $t_{\max}$ and Δj, the drift mobility is calculated

$$\mu = \frac{2d^2}{3At_{\max}^2}, \quad \text{when } \Delta j \leq j(0), \text{ i.e. } t_{tr} \leq \tau_\sigma, \tag{3}$$

$$\mu = \frac{\tau_\sigma d^2}{At_{\max}^3}, \quad \text{when } \Delta j \gg j(0), \text{ i.e. } t_{tr} \gg \tau_\sigma. \tag{4}$$

The bulk conductivity can be estimated as

$$\sigma = \frac{3\varepsilon\varepsilon_0}{2t_{\max}} \cdot \frac{\Delta j}{j(0)}, \tag{5}$$

and, from calculated μ and σ, the equilibrium charge carrier density p_0 can be found.[1] The shortage of this method is that the above mentioned parameters are measured in electric field varying in time. However, due to the fact that major extraction of charge carriers occurs at $t_{\max}$, the estimated parameters will correspond to the values when electric field is $F = A\ t_{\max} /$

d. In Fig. 2, typical μ, σ, p_0 dependences on A show that charge carrier concentration is independent of A and thus on electric field. The p_0 dependences on temperature demonstrate a similar result (Fig. 3). Hence, the mobility dependence on temperature causes activation characteristic of conductivity.

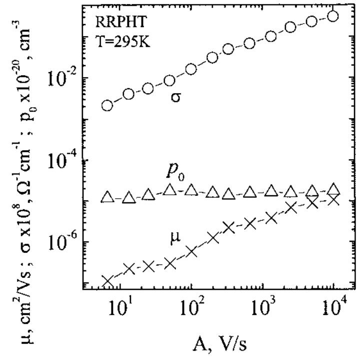

Fig. 2. Dependences of σ, μ, and p_0 on A.

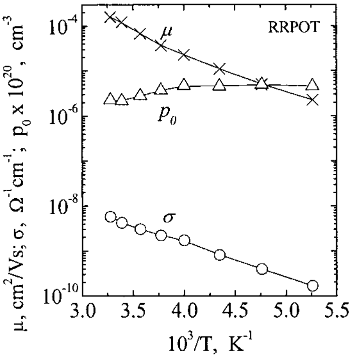

Fig. 3. Dependences of σ, μ, and p_0 on T.

The numerical modelling results in the case of Gaussian distribution of localised states demonstrated regularities of CELIV parameters, which allow, from experimentally measured $\Delta j \sim A^{\beta}$ and $t_{\max} \sim A^{\gamma}$ power-law dependences, to evaluate the nature of mobility dependence on electric field.[2] If $\mu(F)$ is caused by stochastic transport, then $(\beta - \gamma) = 1$ and $(\beta + \gamma) < 0$ must be valid (see Fig. 4).

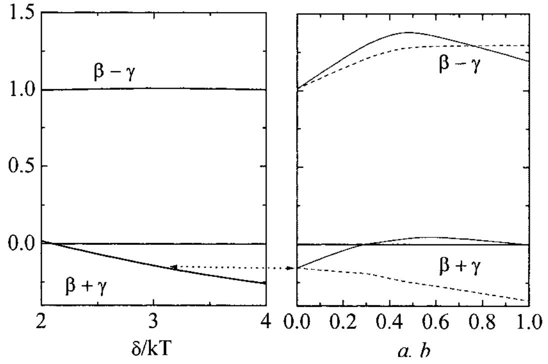

Fig. 4. Numerical modelling of $(\beta + \gamma)$ and $(\beta - \gamma)$ as a function of dispersion parameter δ/kT and of Pool-Frenkel parameters a for mobility (dashed line) and b for retrapping time (full line) using $\delta/kT = 3$.

If micromobility (μ_0) depends on electric field according to the Poole-Frenkel law ($\mu_0 \sim \exp(a\sqrt{F})$) typical of organic polymers then $(\beta - \gamma) > 1$, $(\beta + \gamma) < 1$ and decreases when a increases. Experimentally, a increases when the temperature is decreasing.

When the retrapping probability from localised states depends on electric field in a similar way ($\tau_R^{-1} \sim \exp(b\sqrt{F})$), then $(\beta - \gamma) > 1$ and $(\beta + \gamma)$ increases with b. Experimental investigation results of PPV, RRPHT, RRPOT gave that $(\beta - \gamma) > 1$ and $(\beta + \gamma) > 0$, which demonstrates that the mobility and, herewith, conductivity dependence on electric field is caused by electric field-induced release from the localised states.[2,3]

For low A, i.e. under a weak electric field condition, $\Delta j > j(0)$ has been obtained for a majority of π-conjugated polymers. The latter condition means that $\tau_\sigma << t_{tr}$, hence, the main necessary TOF condition is not fulfilled. According to Ref. [4], when the voltage on sample electrodes, $U < U_c = ep_0 d^2/2\varepsilon\varepsilon_0$ (U_c is critical voltage corresponding to the condition $t_{tr} = 2\tau_\sigma$), after equilibrium charge carrier extraction from the depletion depth $l < d$, the drift of charge through the depletion region is obtained and the current is

$$j(t) = Q_0\sqrt{\frac{2}{t_{tr}\tau_\sigma}} \cdot \exp\left(-\frac{t}{\tau_\sigma}\right). \qquad (6)$$

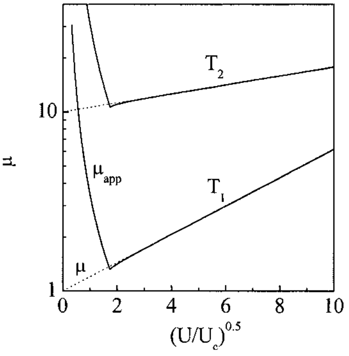

Fig. 5. Comparison of the calculated electric field dependences of the apparent TOF mobility (full line) and true mobility (dotted line) for different temperatures ($T_2 > T_1$). The calculations include the Poole-Frenkel type field-dependent mobility but no diffusion or trapping.

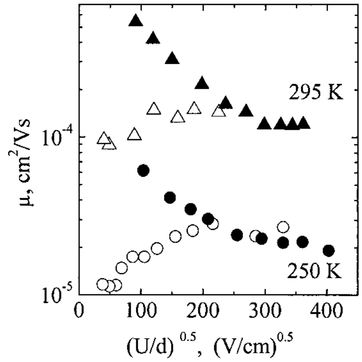

Fig. 6. Electric field dependence of drift mobility in RRPOT measured using TOF (solid dots) and CELIV (open dots) at 295 K and 250 K.

In $\log j \sim \log t$ plot the shape of $j(t)$ transient looks similar to the dispersion-type small charge drift transient. However, the apparent transit time through depletion region is independent of voltage on electrodes, and the calculation using this transit time gives erroneous mobility values, $\mu_{\mathrm{app}} = 2U_c/U\ln 2$ (see Fig. 5). In Fig. 6, the mobility dependences on electric field, measured using TOF and CELIV (of the same RRPOT layer), are presented, demonstrating that the apparent mobility (estimated by TOF) decrease with electric field is caused by electric field redistribution due to extraction of equilibrium charge carriers. Since the equilibrium charge carrier concentration is independent of temperature, the value of critical voltage is independent of temperature too, as it is seen in Fig. 6. To evaluate the critical electric field from the conductivity values, it is obvious that not only in RRPOT, but also in PPV, RRPAT [5-8], the measured mobility decrease with electric field is erroneous.

Extraction of photoexcited charge carriers

In CELIV measurement, illumination of sample by continuous light of bulk absorption induces extraction of photoexcited charge carriers (photo-CELIV), similarly to equilibrium charge extraction. More wide-ranging possibilities may be obtained if the pulse of linearly increasing voltage is applied delayed by some time t_d after sample has been illuminated by short pulse of light. From the CELIV and photo-CELIV current transients, the dependences of charge carrier mobility and concentration on delay time can be investigated. A schematic view of the photo-CELIV method is shown in Fig. 7.

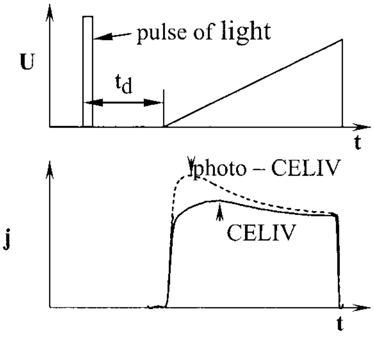

Fig. 7. Schematic view of photo-CELIV.

Experimentally measured hyperbolic mobility (Fig. 8) and photoexcited charge carrier concentration (Fig. 9) dependences on t_d indicate the dispersive character of transport. The drift mobility decrease with increasing t_d may be caused by charge carrier trapping to deeper localised states in the case of dispersive transport. Another reason for such dependence may be the drift mobility dependence on t_d caused by charge carrier density, which decreases when t_d increases. The tentative experimental results point to the latter case. From concentration dependence on t_d (see Fig. 9), the time $\tau_{1/2}$ has been estimated, which corresponds to the time period when the initial amount of photoexcited charge carriers decreases by half. Different $\tau_{1/2}$ values have been obtained for different polymers: 10^{-5} s for RRPOT, and 10^{-2} s for RRPDDT. The increasing of $\tau_{1/2}$ when decreasing temperature indicates the trapping influence on recombination.

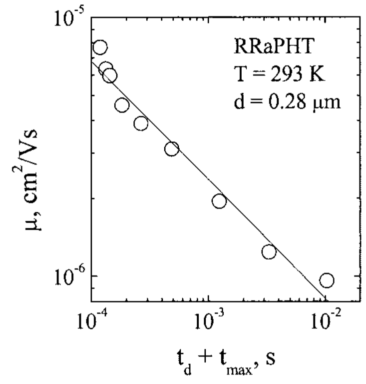

Fig. 8. Dependence of photoexcited charge carrier mobility on delay time.

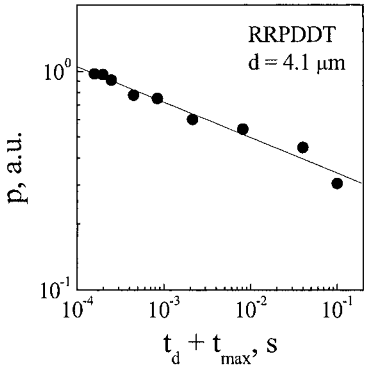

Fig. 9. Dependence of photoexcited charge carrier concentration on delay time.

Extraction of injected charge carriers

In Fig.10, a schematic view of current when the saw-type voltage is applied on the sample electrodes (injection-CELIV) is shown. In the beginning the increasing voltage (region I) in the charge carrier extraction direction is applied, and the capacitance current transient is obtained only. When the decreasing voltage changes its polarity (region III), the charge carrier injection begins. After the voltage changes direction again (region IV), the extraction of injected charge carriers is clearly seen. The dependences of amounts of injected Q_i and extracted Q_e charge carriers on voltage for constant triangle pulse duration are shown in Fig. 11.

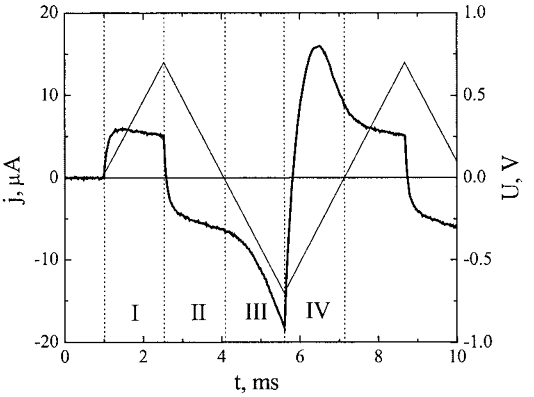

Fig. 10. Schematic view of injection-CELIV. Current transient – bold line. Voltage – thin line.

These results are compared with charge Q_0 of geometric capacitance of sample. The two experimental results indicate that the space charge limited current condition is fulfilled. First result is that the Q_i depends linearly on voltage, and the second is that in region IV, after the voltage changes direction while polarity remains the same, the current changes its sign (Fig. 10). The equality $Q_i = Q_e$ shows that charge carrier lifetime is longer than duration of extracting pulse t_p (see Fig. 11), and, during injection, charge collects at the blocking electrode. For $t_p >> t_{tr}$, $Q_e/Q_0 = t_p/3t_{tr}$ is valid, and thus the charge carrier mobility can be evaluated.

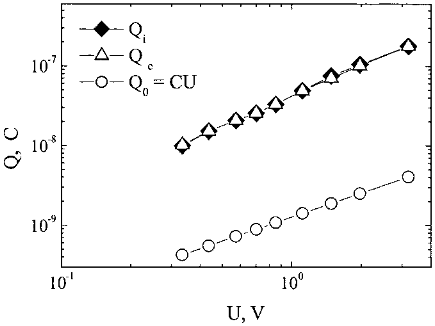

Fig. 11. Dependences of injected (Q_i), extracted (Q_c) charge, and charge of geometric capacitance (Q_0) on triangle-pulse voltage U.

Conclusions

In this paper the possibilities of investigation of features of equilibrium and photoexcited charge carrier transport in π-conjugated polymers of relatively high conductivity, using CELIV methods, have been demonstrated. The following experimental results have been obtained:

- The conductivity dependences on temperature and electric field are caused by drift mobility;
- The dependence of drift mobility on electric field is caused by electric-field release of charge carriers from trapping states;
- In low-electric-field region measured by TOF, a decrease in apparent mobility with increasing electric field is caused by the electric field redistribution;
- A decrease in drift mobility and concentration of photoexcited charge carriers when delay time after photoexcitation increases has been observed, pointing to the influence of trapping in energetically distributed localised states;
- The charge carrier transit time together with the mobility can be evaluated investigating the extraction of injected charge in low-conductivity and not photosensitive materials.

Acknowledgments

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